



Original Research Article

Evaluation of total and bioaccessible concentration of minerals in creole beans



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ABSTRACT

The present study evaluated the total and bioaccessible concentrations of minerals in raw and cooked Creole beans. An analytical methodology was optimized, which involved several steps from sample preparation, accuracy study, data treatment, and instrumental analysis – using a microwave-induced plasma optical emission spectrometer (MIP OES). The present study provides information about the total concentration of the metals Ba, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Pb, Zn and the bioaccessible fraction of metals Ba, Cu, Fe, Mn, Pb and Zn in three different types of creole beans. The elements that presented a greater quantity on all beans, both raw and cooked, were K and Mg. K varied from 12,600 to 13,300 mg/kg for the raw beans and 4590–10300 mg/kg for the cooked beans. Mg varied between 1620 and 1980 mg/kg for the raw beans and 670–1040 mg/kg for the cooked beans. The BRS Expedito type showed a higher concentration of K and Mg on raw and cooked beans. However, when the bioaccessibility study was carried out among the elements listed above, the most bioaccessible were Cu and Zn. Cu presented a bioaccessible fraction percentage between 52.6–59.2% for raw beans and 38.5–61.2% for cooked beans. Zn presented a bioaccessible fraction percentage between 45.6–50.6% for raw beans and 43%–63.5% for cooked beans. The results found on this study indicate that, possibly, the water and the cooking process significantly influences the mineral content. Also, studying mineral concentration on cooked beans is more nutritionally important than characterizing the raw grain, as beans are a type of food mostly consumed on its cooked form.

1. Introduction

Vegetables are the main type of food on the diet of developing countries and play a significant role in human nutrition. Among these vegetables, common beans (*Phaseolus vulgaris* L.) are the most consumed by the population and constitute a complex mixture of nutrients. Common beans present bioactive compounds, and are rich in vitamins (thiamine, riboflavin, vitamin K, vitamin B6) and minerals (iron, zinc, manganese, copper, magnesium, calcium, phosphorus and potassium).

The human body needs an appropriate amount of minerals for proper functioning, since they are fundamental for many enzymatic reactions, and are also applied on the synthesis of nutrients and on physiological

processes (Carvalho et al., 2012; Ribeiro et al., 2012; Galán et al., 2013). Minerals cannot be synthesized by the human body itself, so they must be ingested through food. An example of food that has a considerable concentration of minerals in its constitution are the beans. Beans present beneficial health effects, for they act on the prevention and/or reduction of chronic non-communicable diseases risk, such as cardiovascular diseases, obesity, diabetes *mellitus* and cancer (Mesquita et al., 2007; Afonso, 2010; Hayat et al., 2014; Nyau, 2014).

However, beans, like any other vegetable, are grown directly in the soil, so it deserves attention on determining essential and potentially toxic elements, since these elements are accumulated in the soil, originated mainly from smoke, rain, municipal and industrial waste and from

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the use of fertilizers. Therefore, some plants absorb many elements that can be incorporated into the grains, bringing risks to human health (Pereira et al., 2018). Regarding these elements, some of them are considered essential for human life, including oxygen (O), carbon (C), hydrogen (H), nitrogen (N), calcium (Ca), phosphorus (P), sulfur (S), potassium (K), sodium (Na), chlorine (Cl), magnesium (Mg), iron (Fe), copper (Cu), cobalt (Co), manganese (Mn), molybdenum (Mo), iodine (I), zinc (Zn), among others. There are also some elements considered potentially toxic, such as barium (Ba), cadmium (Cd), chromium (Cr), lead (Pb) and lithium (Li). Their toxicity will depend on the continued exposure of organisms to high concentrations of these elements (Lasat, 2002; Marsola et al., 2005; Turkmen et al., 2009).

During preparation, threshing and cooking are common steps on domestic bean processing. Some minerals are believed to leach into the water used for cooking or for immersion; however, it is not yet clear whether this is inferable to all minerals or to what extent it happens. In addition, the influence of storage or peeling steps on the degree of leaching is still an open question (Oghbaei and Prakash, 2016).

The total concentration of elements present on our food do not provide information on the fraction that may be bioaccessible to the human body, that is, what is being released from the food matrix into the gastrointestinal tract (Jacob et al., 2012; Minekus et al., 2014; Pereira et al., 2018; Souza et al., 2019). Concerning food intake, we can highlight two different processes: the bioavailability, which is the amount that an active substance is absorbed in the small intestine, and the bioaccessibility, which is the amount that a food constituent present in the human intestine, after it is released from the food matrix and becomes available to be absorbed through the intestine (Holst and Williamson, 2008; Shim et al., 2009; Tagliazucchi et al., 2010). The bioaccessible fraction is influenced by the chemical forms of the elements, by the behavior of species and organometallic complexes in the gastrointestinal tract and by interactions with the food matrix (Khouzam et al., 2011).

Therefore, assessing the total and bioaccessible concentration is very important since there is no evidence that the total content of an element on a certain food is a good indication of its real nutritional value; or to what extent the amount of potentially toxic elements present on any type of food can really be released into the human organism (Paredes, 2017). There is no report in the literature about minerals' concentration on Creole beans, about the bioaccessibility of these minerals and about the changes that cooking the beans will (or will not) cause on the concentration and bioaccessibility of these minerals. Thus, the objective of this study was to evaluate the total and bioaccessible concentrations of minerals in raw and cooked beans. For this end, we have optimized an analytical methodology, which involved several steps from sample preparation, accuracy study, data treatment, and instrumental analysis, in which case the microwave-induced plasma optical emission spectrometer (MIP OES) was used.

2. Materials and methods

2.1. Samples

Common bean grains of black tegument (*Phaseolus vulgaris* L.), – the Creole seeds group BRS Expedito, TB02–19 and TB02–23, were obtained from the Brazilian Agricultural Research Corporation (Embrapa) – Station Clima Temperado. A commercial sample of common black tegument beans was also used to optimize the method, as there was no more amount of the Creole samples available. The samples were stored in transparent polyethylene bags with a thickness of 80 µm and stored at 16 ± 1 °C, for a maximum period of 365 days, until the analyses were carried out. For each Creole bean cultivar (BRS Expedito, TB02–19 and TB02–23), the analyses were performed in triplicate, that is, a cultivar was prepared three times for later quantification of the triplicates, thus obtaining an average for the results.

2.2. Reagents

The reagents used for this study were of analytical grade and all solutions were prepared using deionized water, which was obtained from a glass distillation system, model MA078/5 (Marconi, Piracicaba, Brazil) and, later, deionized passing through a column, model CS1800 Evolution (Permutation, Curitiba, Brazil). The analyte multi-elemental solution was prepared from stock solution N° 6 for ICP (Sigma-Aldrich, Taufkirchen, Germany) containing 100 mg L⁻¹ of each analyte. The HNO₃ (Vetec, Rio de Janeiro, Brazil) used in the sample preparation stage and the HCl (Qhemis, Jundiaí, Brazil) were distilled twice, below the boiling point, in quartz distillers, model MA-075 (Marconi, Piracicaba, Brazil). For this stage, H₂O₂ 30 % (v/v) was also used (Synth, Diadema, Brazil).

In the chemical steam generation, solutions of NaBH₄ 0.5 % (m/v) stabilized in NaOH 0.5 % (m/v) and HCl 2.0 % (w/v) were used (Qhemis, Jundiaí, Brazil). For bioaccessibility studies, the following reagents were used: α-Amylase from *Aspergillus oryzae*, pepsin, bile and pancreatin (Sigma, St. Louis, USA); CaCl₂(H₂O)₂ (Vetec, Rio de Janeiro, Brazil), NaOH (Vetec, Rio de Janeiro, Brazil), KCl (Merck, Darmstadt, Germany), NaCl (Merck, Kenilworth, USA), NaHCO₃ (Synth, Diadema, Brazil), MgCl₂(H₂O)₆ (Sigma, St. Louis, USA), (NH₄)₂CO₃ (Synth, Diadema, Brazil), HCl (Qhemis, Jundiaí, Brazil) and KH₂PO₄ (Sigma-Aldrich, St. Louis, USA).

All the used materials and glassware were washed with water and detergent and then were immersed for 48 h in 10 % HNO₃ (v/v) (Vetec, Rio de Janeiro, Brazil). Subsequently, they were rinsed with deionized water and dried at room temperature.

2.3. Instrumentation

For elemental determination, an optical emission spectrometer with microwave-induced plasma (MIP OES) model Agilent 4200 (Agilent Technologies, Melbourne, Australia) equipped with a OneNeb nebulizer and a *Multimode Sample Introduction System* (MSIS, “multimode”) nebulizer chamber was used. The nitrogen used for plasma generation is extracted from atmospheric air using a model 4107 nitrogen generator (Agilent Technologies, Melbourne, Australia). The measurements were performed with a pump speed of 15 rpm, 15-second sample aspiration time, 15-second stabilization time and 3-second reading time. For acid decomposition and bioaccessibility studies, the samples of raw beans were milled using a laboratory mill model Lab Mill 3100 (Perten, São Paulo, Brazil) and then homogenized in a vortex mixer (Kasvi, São Caetano, Brazil). For cooked beans, the cooking time for each sample was previously performed using the methodology described by Mattson (1946), commonly used for beans. All containers and utensils used in the bean cooking process were previously decontaminated for 48 h in 10 % HNO₃ (v/v). Deionized water was used for cooking and all procedures were carried out avoiding any contamination and interference in the samples. After that, the samples were cooked during the pre-established time with deionized water. Cooked bean samples (bean peel, bean paste and remaining cooking broth) were macerated and homogenized in porcelain pistle. For the acid decomposition, a digestive block model MA-4025 (Marconi, Piracicaba, Brazil) was used. A reflux system was attached to each digester tube, as described by Oreste et al. (2013), with water recirculation at 15 °C, maintained on refrigeration by a unit model Q MA083 (Marconi, Piracicaba, Brazil).

To determine the bioaccessible fraction, a pH meter model PHS-3B (PHtec, Santa Barbara d'Oeste, Brazil), a Dubnoff bath with agitation and heating to 37 °C model Q226M2 (Quimis, Diadema, Brazil) and a maximum speed centrifuge model 5804 (Eppendorf, Hamburg, Germany) were used for the sample preparation.

2.4. Optimization of the sample preparation method

To enable the determination of the total concentration, a study for

the sample preparation was carried out. The decomposition tests varied depending on the amount of bean sample, time and temperature of the digester block, in addition to the variation of the HNO₃ concentration. Therefore, masses from 250 to 1000 mg; periods ranging from 2 to 4 h; temperatures of 150 and 200 °C; and HNO₃ concentration of 65, 50, 40 and 30 % v/v were used. After defining the best conditions, the sample masses were weighed, in triplicate, directly into the decomposition tubes and 5 mL of HNO₃ was added, with varied concentrations. The reflux system was attached to the tube and the samples were placed in a digester block under heating, varying the temperatures and the decomposition time in accordance with HNO₃ concentration. At the end of each period, the solutions were removed from the block and cooled for subsequent addition of 1 mL of H₂O₂, returning to the block again for another 1 h. Afterwards, the sample solutions obtained were cooled and transferred to polypropylene (PP) flasks and increased to 50 mL with deionized water.

For each altered condition on the decomposition study, the determination of the dissolved solids content and the acidity content resulting from the final solution were evaluated (IAL - Instituto Adolfo Lutz, 2008). These determinations are important since the MIP OES manufacturer recommends that the solutions introduced in the equipment have a maximum of 3% dissolved solids and 5% acidity, in order to preserve the optical parts of the equipment (Agilent Technologies, 2016; Sampaio et al., 2020). And so, we sought to optimize a methodology for preparing bean samples that would be suitable for analysis using this technique, avoiding subsequent dilutions after preparation, which could compromise the detection limits of the method, and prevent the determination of microconstituents. The condition that presented the lowest percentage of acidity and soluble solids, which was the condition chosen for the decomposition of the bean samples and consequently for the multi-elementary determination by MIP OES was the 1000 mg sample mass, with a period of 4 h-digestion at a temperature of 200 °C, and the use of diluted nitric acid (40 % v/v) for the decomposition. For the cooked beans, the moisture content was analyzed in order to weigh the sample mass corresponding to a 1000 mg mass of the raw beans.

The accuracy of the method was first assessed through the decomposition of two tomatoes leaves CRMs (CRM-Agro FT_012016) and an infant formula (NIST Infant Formula 1846), separately, and using the same conditions optimized for the beans sample. Afterwards, a new acidic decomposition was performed, mixing the CRMs with the beans sample. For this, they were weighed together with the beans (500 mg of each) for subsequent acid decomposition. The calculation for recovery percentage is presented in Eq. 1:

$$\% \text{ Rec} = \text{DV/RV} \times 100 \quad (1)$$

Where:

DV = detected value for CRM mix plus bean sample

RV = reference value for CRM mix plus bean sample. Obtained through the results of the CRM under the conditions of the method and correlated with the heavy mass (500 mg).

2.5. Bioaccessible fraction

For bioaccessibility studies, the *in vitro* digestion process was used, adapted from Minekus et al. (2014). The method simulates the human digestive process that occurs in the mouth, stomach, and intestine, using simulated digestion fluids (saliva, gastric and intestinal juice). Approximately 5 g of each sample of raw and cooked beans were put in PP flasks and were weighed. On the first step, 10 mL of synthetic saliva and 1 mL of 7.5 mmol L⁻¹ CaCl₂ were added directly to the samples, the pH of the solution was adjusted to 7 with the addition of 1 mol L⁻¹ NaOH and subsequently sent to the Dubnoff bath (Ethik Technology, Vargem Grande, Brazil) with heating at 37 °C and agitation for 10 min. On the second stage, 9.1 mL of synthetic gastric juice, 700 µL of 2 mmol L⁻¹ CaCl₂ and 1 mol L⁻¹ HCl were added to adjust the pH of the solution to 3,

and again sent to the Dubnoff bath (Ethik Technology, Vargem Grande, Brazil) with heating at 37 °C and stirring for 2 h. On the third stage, 18.5 mL of intestinal juice, 1.35 mL of 9 mmol L⁻¹ CaCl₂ and 1 mol L⁻¹ NaOH were added to adjust the pH to 7, and the solutions were bathed at 37 °C with stirring for another 2 h. Then, the solutions were placed in an ice bath for 20 min to inactivate the enzymes and later centrifuged for 10 min at 11,200 g to separate the bioaccessible fraction (supernatant), which was used to determine the analytes by MIP OES. The solid part, on the other hand, was subjected to a new acidic decomposition, as already described, to assess the accuracy of bioaccessibility through a mass balance, being already reported in the literature by Souza et al. (2019). The bioaccessible mineral quantities were determined using the *in vitro* bioaccessibility test. The bioaccessibility was calculated using Eq. 2:

$$\% \text{ B} = [\text{TB}]/[\text{T}] \times 100 \quad (2)$$

Where:

[TB]: element concentration obtained by the bioaccessibility test *in vitro*;

[T]: total concentration of the element in the food obtained by total digestion.

2.6. Statistics

The results of the total concentration of minerals were subjected to ANOVA analysis of variance with the comparison of means through the Tukey test at a significance level of 5% comparing all the cultivars within the same treatment (raw and cooked). And the results of the total concentration of raw and cooked minerals for each cultivar separately were subjected to ANOVA analysis of variance using the Student's t - test at a 5% significance level.

3. Results and discussion

3.1. Variation of sample mass

To evaluate the influence of the sample mass used for decomposition concerning acidity and dissolved solids, masses between 250 and 1000 mg were weighed and subjected to acid decomposition at temperatures of 150 and 200 °C for 3 h. The results obtained are shown in Fig. 1 (A and B), respectively. According to the graphics below, it was possible to observe that larger masses causes a decrease on the acidity content, not exceeding 5.0 % (v/v). The dissolved solids content did not increase significantly, remaining below 3% (w/v) even in larger masses. The same was observed on the work of Sampaio et al. (2020), which used a mass variation and correlated it with the acidity and carbon content for sugar samples. Thus, the sample mass chosen was 1000 mg, since greater masses favors obtaining better detection limits for the proposed method.

3.2. Effect of HNO₃ concentration and decomposition time

One of the main factors for choosing the best decomposition conditions is acidity, so we tested different concentrations of HNO₃ (50, 40 and 30 %) for the decomposition of a 1000 mg of sample. The results obtained for acidity and total dissolved solids are shown in Fig. 2.

It was possible to observe that with HNO₃ in 30 %, the acidity content was low, but there was no complete decomposition, resulting on solid particles and on higher dissolved solids content. In 40 %, there was a decrease in solids dissolved on the final solution and the acidity was approximately 3% (v/v). When the HNO₃ concentration was increased to 50 %, an increase in acidity was observed, but there was a decrease on the dissolved solids content. Thus, the condition chosen for decomposition and that remained with a clearer solution and a lower acidity content was the concentration of HNO₃ in 40 % (v/v). Although the decompositions were being carried out with a fixed period of 3 h, to assess whether a longer or shorter decomposition time would have a

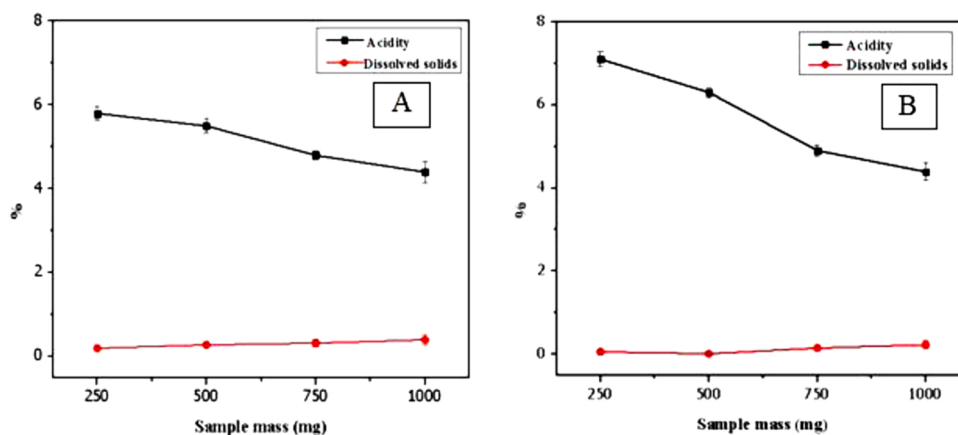


Fig. 1. Effect of the variation of the beans mass during the acid decomposition under fixed conditions: 5.0 mL of HNO₃ (65 % v/v); 3 h at 150 °C (A) and 200 °C (B); final volume of 50 mL.

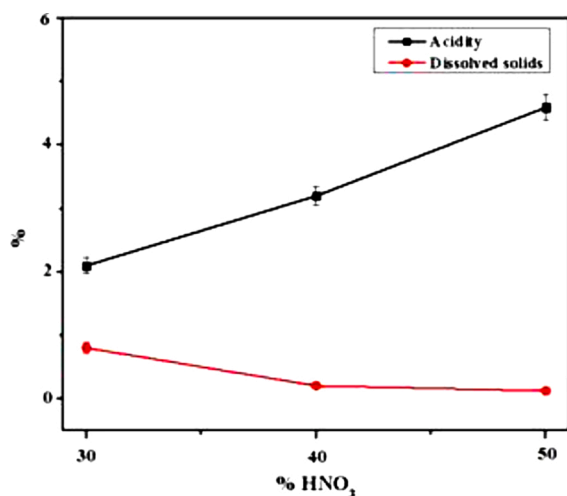


Fig. 2. Effect of the variation of the concentration of HNO₃ 30, 40 and 50 % (v/v) for the decomposition. Parameters fixed: 1000 mg of sample; 3 h at 200 °C; final volume of 50 mL.

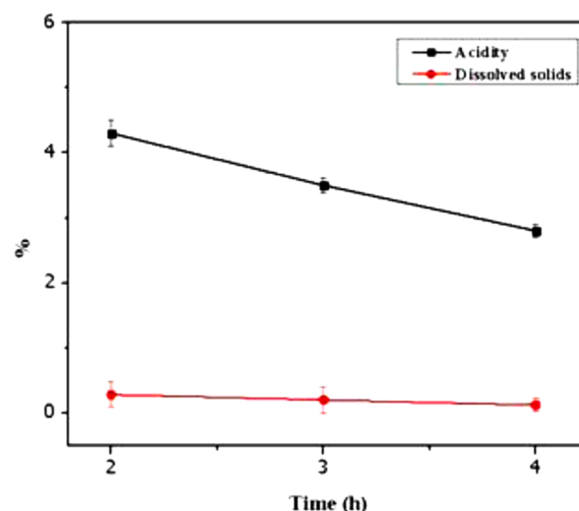


Fig. 3. Effect of the variation of the time of decomposition. Parameters fixed: 1000 mg of sample; 5 mL of HNO₃ 40 % (v/v); temperature at 200 °C; final volume of 50 mL.

difference, the periods of 2, 3 and 4 h were also tested in relation to the content of dissolved solids and acidity. The results obtained are shown in Fig. 3.

According to the results presented in Fig. 3, it was observed that the period of time influences the decomposition of the samples and mainly the acidity content. Thus, the decomposition time was fixed at 4 h. The same result was also observed in the work of Sampaio et al. (2020): they came to the conclusion that 4 h was also enough to decompose sugar samples in the digester block, obtaining a lower acidity content.

After all the presented parameters, we found that the best conditions of decomposition were for a mass of 1000 mg; 5 mL 40 % (v/v) HNO₃; and 200 °C for 4 h. Followed by the addition of 1 mL of H₂O₂ for an extra hour. At the end, the solution was increased with deionized water to a volume of 50 mL.

3.3. Figures of merit

To verify the veracity and precision of the results obtained through acid decomposition, analyte addition tests were carried out in three different concentrations on the bean samples, obtaining recoveries ranging from 81 to 113 %, and the relative standard deviations (RSDs) were less than 10 %. The added concentrations were on the linear range of analytical curves obtained by MIP OES (Table 1).

Furthermore, the accuracy of the proposed method was also assessed

by decomposing the tomato leaves CRMs (CRM-Agro FT_012016) and the infant formula CRM (NIST Infant Formula 1846). The results for these two materials are shown in Table 2. It is possible to see that good recoveries between 84 and 119 % were obtained. Afterwards, the digestion of a mixture of these two CRMs with the beans sample was also evaluated, as described on item 2.4. For the calculation of the recovery percentage, the detected values (DV) of the CRM plus the beans and the reference value (RV) for each element in this mixture were considered. Thus, average recoveries between 81 and 113 % were obtained for all elements, as shown in Table 3.

3.4. Total analyte concentration

The elements studied were Ba, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Pb and Zn; and the total amount of the elements studied were obtained for raw and cooked beans. Table 4 shows the results of total mineral concentrations for raw and cooked beans.

In raw beans, for the elements Co, Cr, Li and Mo, the concentrations were below the detection limits of the method LD(m). The most abundant element in raw beans is K, which varied from 12,600 to 13,300 mg/kg and showed no difference between the samples ($P \leq 0.05$). Common beans with a high concentration of K are a suitable alternative for people who practice intense physical activity and, therefore, require higher

Table 1

Measured concentrations of analytes by MIP OES after different additions in beans. Values in mg kg⁻¹ (n = 3).

Analyte	Added	Bean	Rec. (%)	Analyte	Added	Bean	Rec. (%)
Ba	0	5.6 ± 0.1	–	Li	0	< LD (m)	–
	10	15.2 ± 0.5	96		10	9.1 ± 0.2	90
	20	23.9 ± 1.1	91		20	18.1 ± 0.8	90
	30	33.7 ± 1.9	94		30	25.6 ± 0.9	85
Cd	0	< LD(m)	–	Mg	0	2030 ± 42	–
	10	8.1 ± 0.2	81		1510	3260 ± 33	81
	20	16.5 ± 0.9	82		3020	4710 ± 420	89
	30	26.1 ± 1.1	87		4530	5990 ± 150	87
Co	0	0.6 ± 0.1	–	Mn	0	18.4 ± 1.5	–
	10	9.4 ± 0.3	81		10	28.2 ± 0.5	98
	20	18.1 ± 3.6	82		20	34.7 ± 0.6	82
	30	26.9 ± 2.4	87		30	46.3 ± 1.4	93
Cr	0	1.0 ± 0.1	–	Mo	0	0.6 ± 0.1	–
	10	9.3 ± 0.4	82		10	9.8 ± 0.3	92
	20	19.4 ± 1.5	92		20	17.3 ± 0.5	83
	30	34.4 ± 2.8	111		30	32.5 ± 2.5	106
Cu	0	9.1 ± 0.5	–	Pb	0	0.9 ± 0.1	–
	10	20.4 ± 0.5	113		10	9.2 ± 0.2	83
	20	25.6 ± 1.8	82		20	20.1 ± 0.4	96
	30	33.9 ± 2.2	83		30	30.9 ± 0.5	100
Fe	0	77.5 ± 1.7	–	Zn	0	18.8 ± 0.3	–
	50	127 ± 3	99		50	71.4 ± 1.7	105
	75	152 ± 3	99		75	87.1 ± 3.2	91
	100	190 ± 4	112		100	102 ± 6	83
K	0	1370 ± 32	–				
	8750	10,700 ± 230	107				
	17,500	16,700 ± 170	87				
	26,250	25,800 ± 500	93				

concentrations of potassium (Lindinger, 1995). The second most abundant element in raw beans is Mg, which varied between 1.620 and 1.980 mg/kg with BRS Expedito showing a higher concentration and a significant difference ($P \leq 0.05$) from the others.

For the element Ba, the beans presented a concentration between 4.92 and 9.78 mg/kg, with a significant difference ($P \leq 0.05$). For Cd, TB02–23 and TB02–19 beans presented no significant difference ($P \leq 0.05$), whereas for BRS Expedito the concentration was lower than the LD_(m). For Pb, on the beans content, no difference was observed between samples ($P \leq 0.05$) and for both Cd and Pb the content is above the maximum contaminant limit established by RDC No. 42 on 2013 (Anvisa. National Health Surveillance Agency, 2013), – the MERCOSUR Technical Regulation on Maximum Limits of Inorganic Contaminants in

Table 2

Analytical results of the concentrations of Cd, Cu, Fe, K, Mg, Mn, Pb and Zn in certified reference materials. Values in mg kg⁻¹ (n = 3).

Tomato Leaf CRM-Agro FT_012016			
Analyte	CV	VF	Rec. (%)
Cd	26.6 ± 2.1	25.2 ± 0.2	95
Cu	1130 ± 140	1220 ± 86	108
Fe	1120 ± 190	1140 ± 81	102
K	43,300 ± 3800	50,800 ± 500	117
Mg	4110 ± 360	4160 ± 300	101
Mn	470 ± 69	486 ± 37	103
Pb	3.7 ± 0.6	3.9 ± 0.1	108
Zn	37.5 ± 5.0	31.8 ± 0.9	85
NIST Infant Formula 1846			
Cu	5.1 ± 0.3	5.3 ± 0.3	106
Fe	63.1 ± 4.0	71.3 ± 0.5	113
K	7160 ± 380	8530 ± 190	119
Mg	538 ± 29	450 ± 27	84
Zn	60.0 ± 3.2	55.8 ± 1.3	93

CV = certified value; VF = value found; values expressed as averages ± standard deviation; Rec = recovery (%).

Table 3

Analytical results of the concentrations of Cd, Cu, Fe, K, Mg, Mn, Pb and Zn in certified reference materials in the middle of sample of beans. Values in mg kg⁻¹ (n = 3).

CRM Tomato Leaf + Beans					
Analyte	Beans	CRM	RV (CRM + Beans)	DV (CRM + Beans)	Rec. (%)
Cd	< LOD	25.2 ± 0.2	13.7 ± 0.3	12.6 ± 0.1	92
Cu	9.1 ± 0.5	1220 ± 86	591.1 ± 6.6	616 ± 43	104
Fe	77.5 ± 1.7	1140 ± 81	538.4 ± 16.2	610 ± 41	113
K	1370 ± 32	50,800 ± 500	31,100 ± 370	26,100 ± 270	84
Mg	2030 ± 42	4160 ± 300	2780 ± 35	3100 ± 170	112
Mn	18.4 ± 1.5	486 ± 37	245.1 ± 1.6	252 ± 19	103
Pb	0.9 ± 0.1	3.9 ± 0.1	2.5 ± 0.1	2.4 ± 0.1	98
Zn	18.8 ± 0.3	31.8 ± 0.9	31.1 ± 0.3	25.3 ± 0.6	81
CRM Infant Formula + Beans					
Cu	9.1 ± 0.5	5.3 ± 0.3	8.1 ± 0.2	7.2 ± 0.4	89
Fe	77.5 ± 1.7	71.3 ± 0.5	90.6 ± 0.2	74.4 ± 1.1	82
K	1370 ± 32	8530 ± 190	5360 ± 290	4950 ± 110	92
Mg	2030 ± 42	450 ± 27	1260 ± 9	1240 ± 35	98
Zn	18.8 ± 0.3	55.8 ± 1.3	40.8 ± 1.3	37.3 ± 0.8	91

RV = reference value; DV = detected value; values expressed as averages ± standard deviation; Rec = recovery (%).

Food, which states that the maximum limit of elemental concentration for vegetables is 0.1 mg/kg. High concentrations of these elements are unfavorable due to their toxicity. The beans presented concentrations for potentially toxic elements, such as Cd and Pb, requiring bio-accessibility studies to verify whether these concentrations can be released into the body for later absorption, and may or may not present a risk to the human organism (Ferreira et al., 2015; Gong et al., 2016). The presence of potentially toxic metals depends on the characteristics of the soil, such as the organic matter content, the environmental pollution, and the addition of chemicals such as fertilizers, fungicides, insecticides and herbicides in crops (Pereira et al., 2018).

The Cu content of beans varied between 14.2 and 18.8 mg/kg,

Table 4
Total concentration results for raw and cooked beans obtained by MIP OES.

Analyte (mg kg ⁻¹)	BRS Expedito		TB02–23		TB02–19	
	Raw	Cooked	Raw	Cooked	Raw	Cooked
Ba	9.8 ± 0.4 ^a	7.0 ± 0.1 ^A	4.9 ± 0.3 ^c	3.5 ± 0.3 ^C	7.6 ± 0.1 ^b	4.3 ± 0.4 ^B
Cd	< LD _(m)	< LD _(m)	0.2 ± 0.0 ^a	< LD _(m)	0.2 ± 0.0 ^a	< LD _(m)
Co	< LD _(m)	2.5 ± 0.2 ^B	< LD _(m)	2.2 ± 0.1 ^B	< LD _(m)	4.3 ± 0.2 ^A
Cr	< LD _(m)	< LD _(m)	< LD _(m)	< LD _(m)	< LD _(m)	< LD _(m)
Cu	18.8 ± 0.3 ^a	4.5 ± 0.1 ^A	14.2 ± 0.5 ^c	2.9 ± 0.3 ^B	17.3 ± 0.7 ^b	3.1 ± 0.3 ^B
Fe	39.3 ± 3.3 ^a	37.1 ± 1.4 ^{Aa/s}	34.4 ± 0.8 ^b	16.9 ± 0.8 ^C	34.9 ± 0.5 ^b	20.1 ± 1.0 ^B
K	13,300 ± 180 ^a	10,300 ± 71 ^A	12,600 ± 320 ^a	4590 ± 260 ^C	12,600 ± 1100 ^a	5060 ± 140 ^B
Li	< LD _(m)	< LD _(m)	< LD _(m)	< LD _(m)	< LD _(m)	< LD _(m)
Mg	1980 ± 18 ^a	1040 ± 77 ^A	1630 ± 51 ^b	670 ± 26 ^C	1620 ± 53 ^b	835 ± 26 ^B
Mn	15.6 ± 0.6 ^a	6.6 ± 0.2 ^A	11.8 ± 0.7 ^b	4.3 ± 0.2 ^C	14.8 ± 0.7 ^a	4.9 ± 0.3 ^B
Mo	< LD _(m)	< LD _(m)	< LD _(m)	< LD _(m)	< LD _(m)	< LD _(m)
Pb	1.2 ± 0.1 ^a	1.4 ± 0.1 ^A	1.1 ± 0.1 ^a	1.2 ± 0.1 ^{Ba/s}	1.0 ± 0.0 ^a	1.2 ± 0.2 ^B
Zn	21.3 ± 0.6 ^b	9.1 ± 0.2 ^B	15.1 ± 0.5 ^c	10.9 ± 0.2 ^B	23.5 ± 1.0 ^a	12.1 ± 0.8 ^A

Simple arithmetic averages ($n = 3$) ± standard deviation with different lowercase letters in the row differ from each other, comparing the raw cultivars and with different uppercase letters in the row differ from each other, comparing the cooked cultivars, by the Tukey test ($p \leq 0.05$). *n/s (not significant) by the *t*-Student test ($p \leq 0.05$) comparing the treatments (raw and cooked) in each cultivar; <LD(m): Values below the detection limit of the method.

showing a significant difference ($P \leq 0.05$), and the BRS Expedito presented a higher concentration. The Fe content of beans varied between 34.4 and 39.3 mg/kg and the BRS Expedito presented a significant difference ($P \leq 0.05$) from other beans. The concentration for Zn varied between 15.1 and 23.5 mg/kg, presenting a significant difference ($P \leq 0.05$) and the TB02–19 beans presented a higher concentration. For the element Mn, the variation was from 11.8–15.6 mg/kg and the TB02–23 beans presented a significant difference ($P \leq 0.05$), presenting the lowest concentration. The Fe and Zn results obtained in this study were lower than those reported by Ramírez-Ojeda et al. (2018) that analyzed the content of minerals and trace elements in vegetables, including beans, and they found 42–49 µg/g for Fe and 21–37 µg/g for Zn in raw beans, whereas the results for Mn on this study are equal to the ones reported by these authors, varying between 11–15 µg / g for raw beans. The Fe and Zn results for raw beans were lower than the ones reported by Viadel et al. (2006a, 2006b, 2009) in their studies with raw beans, which were 66.3 µg/g for iron and 34.5 µg/g for zinc in the cited studies.

It is evident that only for the element Fe, in BRS Expedito, and Pb, in TB02–23, cooking the beans did not provide a significant difference ($P \leq 0.05$) when compared with raw samples. Naozuka and Oliveira. (2015) studied the chemical speciation of iron in different varieties of beans (*Phaseolus vulgaris* L.), studied the cooking effects, and also compared the total concentrations of Fe on raw and cooked grains; and concluded that cooking did not affect the total concentration of Fe in all varieties of beans, which also happened to BRS Expedito.

The cooking process caused a loss in most of the elements, except for the elements Co, K and Pb (on BRS Expedito and TB02–19 samples). The loss of elements during cooking is due to their removal by water. During the cooking process, water molecules enter the interior of the grain matrix, dissolving a portion of the elements present there and carry it out of the grain by leaching. Thus, it is expected the elements content to be lower in cooked grains than in raw grains (Tognon, 2012).

Paredes (2017) evaluated the mineral concentrations on common bean cultivars (*Phaseolus vulgaris* L) before and after cooking and

reported that the elements Zn, Cu, Mn, Ca, Mg and P increase their concentrations when cooking, – these results were also found in the present study for some elements. Meyer et al. (2013) studied raw and cooked beans and presented that the result of cooked cultivars indicated a significant increase ($P < 0.05$) in Mn, Ca and Mg, as well as a decrease in Fe and K ($P < 0.05$) depending on the cultivar evaluated.

The chemical elements they contain (without raw beans) were associated with proteins, fibers and starch grains, are released from these interactions and, therefore, are more susceptible to acid attack during a decomposition, using more likely to be released by the sample matrix, increasing concentration of minerals in cooked beans. When beans are cooked in water, most of their proteins become denatured, natural fibers lose their characteristics and the starch gelatinization process occur. Starch is a carbohydrate made up of long chains in which glucose molecules are linked together to form granules. Starch is not soluble in chilly water, but when it is exposed to a heated water environment (as the environment during cooking), the water starts to penetrate the starch granules and these, in turn, become turgid. As cooking continues, water penetrates the granules and, thus, the starch loses its original structure, generating a viscous dispersion with a consistency of a gel, releasing the elements (Tognon, 2012). Cooking probably also favors the mineral release of some complexes present in beans, such as the phyto-mineral acid complex, which replaced mineral losses due to diffusion in water (Barampama and Simard, 1995). Oliveira et al. (2017) studied the distribution of proteins and metalloproteins in different varieties of beans (*Phaseolus vulgaris* L.) – for common beans, studies showed that, in raw grains, Fe was associated with albumin, globulins and glutelin and, after the process of cooking, Fe was in the albumin and globulin fractions. The authors also comment that heating can result in protein denaturation, so the interactions between proteins and essential elements can be established or lost.

In cooked beans, the elements Cd, Cr, Li and Mo presented lower concentrations than the LD_(m). The most abundant elements in cooked beans remained K and Mg. For both elements, beans presented a significant difference ($P \leq 0.05$) and BRS Expedito presented a higher concentration. The Ba element presented concentrations between 3.5 and 7.0 mg/kg, with all beans showing significant differences ($P \leq 0.05$) and BRS Expedito also showing a higher concentration. The Pb element, also as it happened in raw beans, was above the Maximum Contaminant Limit (Anvisa. National Health Surveillance Agenc, 2013). Cooking provided a decrease in the elements Ba and Cd, a positive factor, as these are toxic elements. The Co element presented concentrations between 2.2 and 4.3 mg/kg, with the TB02–19 type showing a significant difference ($P \leq 0.05$) and a higher concentration. For the Cu element, BRS Expedito presented a higher concentration, of 4.5 mg/kg, and a significant difference ($P \leq 0.05$) from the others. The beans presented low concentration for Mn and presented significant difference ($P \leq 0.05$). For the Fe element, the beans presented a significant difference ($P \leq 0.05$) and the concentration was between 16.9 and 37.1 mg/kg, with the highest concentration on BRS Expedito. The concentration for Zn varied between 9.1 and 12.1 mg/kg and the TB02–19 beans presented higher concentration and significant difference ($P \leq 0.05$). The results of Zn for cooked beans found in this study were lower than those found by Ramírez-Cárdenas et al. (2010), that studied the bioavailability of zinc in different beans affected by the type of cultivar and cooking conditions. Inadequate intake of Fe and Zn can cause several health problems. Fe deficiency can lead to morbidity and mortality in children, as well as delay in their cognitive and psychomotor development, and Zn deficiency causes delay in the growth and maturation of neurons, reproductive disorders, mental lethargy, changes in skin and gustatory perceptions (Yang et al., 2007; Tuerk, Fazel, 2009).

3.5. Bioaccessibility of the elements by in vitro gastrointestinal digestion

The bioaccessible concentration of the elements Ba, Cu, Fe, Mn, Pb and Zn was determined in all beans, raw and cooked, and are shown in

Tables 5 and 6. The Li, Cr, Co, Cd and Mo had total concentrations below the LD(m) for all beans, so it was not possible to carry out any determinations on this step. The elements K and Mg were not quantified in the bioaccessible fraction because they are present in high concentrations in the added salts for the gastrointestinal tract simulation. After simulating the three main stages of the digestive system, the supernatant was collected for later determination of the bioaccessible fraction of the analytes.

For the bioaccessibility of raw beans, the elements Cu and Zn were the ones that presented the highest bioaccessible percentages. For Cu and Zn, TB02–23 beans presented a significant difference ($P \leq 0.05$) from other beans concerning the bioaccessible concentration. The Ba element presented a significant difference ($P \leq 0.05$) between the beans for bioaccessible concentration, and the bioaccessible percentage was low, – it should be noted that Ba is a potentially toxic chemical element and its concentration can cause physiological disturbances in the human organism. Pb, a potentially toxic element, presented bioaccessible concentrations below the LD(m). The element Fe, of significant importance, presented low bioaccessibility for all the beans, and for the TB02–23 type, it was below the LD(m). Mn presented good percentages of bioaccessibility, approximately 27 %, and TB02–23 beans presented a significant difference ($P \leq 0.05$) for the bioaccessible concentration.

After cooking, the behavior of the bioaccessible percentage of the elements was different, as shown in Table 6. The elements Cu and Zn remained the two most bioaccessible elements for beans. Cooking provided an increase in the bioaccessible percentage of Cu in TB02–19 and Zn in BRS Expedito and TB02–19 beans. The bioaccessible percentage of Ba, after cooking, presented a decrease from 8 to 16 % on the beans, an important fact, as it is a potentially toxic element to the organism. The bioaccessibility of an element depends not only on the matrix but also on the chemical form of the analyte (Naozuka and Oliveira, 2017).

The percentage of bioaccessible Fe in beans after cooking decreased, between 2.3 and 3.6 %. Meyer et al. (2013) indicated that in common beans grown in Nicaragua, the Fe content was 61–81 mg/kg of which 3–4 % was bioavailable. Galán et al. (2013) observed that Fe bioaccessibility was lower in cooked foods when compared to raw foods – these results resemble those found in this study. Oliveira et al. (2018), that studied the effect of cooking on the bioaccessibility of essential elements in different varieties of beans (*Phaseolus vulgaris* L.), found that Fe was the least accessible element in raw and cooked beans, and the authors still state that the bioaccessibility of Fe to humans from the *Phaseolus* beans is low (1–2 %) and that this decreases after cooking.

For Pb, in raw beans, the concentration was below the LD(m), whereas in cooked beans a concentration between 0.2 to 0.3 mg/kg was observed: a result above the limit allowed by RDC No. 42 of 2013 (Anvisa. National Health Surveillance Agency, 2013). However, even in

Table 5
Bioaccessible concentrations for raw beans.

Analyte (mg kg ⁻¹)	BRS Expedito		TB02–23		TB02–19	
	BC	% BF	BC	% BF	BC	% BF
Ba	3.1 ± 0.1 ^a	32.0	1.3 ± 0.1 ^c	26.2	1.6 ± 0.1 ^b	21.2
Cu	9.9 ± 0.8 ^a	52.6	7.6 ± 0.1 ^b	53.3	10.2 ± 0.1 ^a	59.2
Fe	11.5 ± 0.1 ^a	29.3	< LD(m)	–	2.4 ± 0.1 ^b	6.8
Mn	4.3 ± 0.1 ^a	27.4	3.2 ± 0.3 ^b	27.4	4.1 ± 0.1 ^a	27.8
Pb	< LD(m)	–	< LD(m)	–	< LD(m)	–
Zn	10.8 ± 0.1 ^a	50.6	7.4 ± 0.5 ^b	49.0	10.7 ± 0.2 ^a	45.6

Simple arithmetic averages ($n = 3$) ± standard deviation with different lower-case letters on the line, differ from each other, using the Tukey test ($p \leq 0.05$); BC = bioaccessible concentration; % BF = percentage bioaccessible fraction; <LD(m) = values below the detection limit of the method.

Table 6
Bioaccessible concentrations in cooked beans.

Analyte (mg kg ⁻¹)	BRS Expedito		TB02–23		TB02–19	
	BC	%BF	BC	%BF	BC	%BF
Ba	0.2 ± 0.0 ^a	2.4	0.2 ± 0.0 ^b	4.3	0.1 ± 0.0 ^c	2.8
Cu	1.7 ± 0.1 ^a	38.5	1.2 ± 0.0 ^b	40.2	1.9 ± 0.1 ^a	61.2
Fe	0.9 ± 0.0 ^a	2.3	0.6 ± 0.0 ^a	3.4	0.7 ± 0.0 ^a	3.6
Mn	< LD(m)	–	< LD(m)	–	0.4 ± 0.0 ^a	8.3
Pb	0.3 ± 0.0 ^a	18.1	0.2 ± 0.0 ^b	13.4	0.3 ± 0.0 ^a	21.5
Zn	5.8 ± 0.2 ^b	63.5	4.6 ± 0.0 ^c	43.0	6.2 ± 0.1 ^a	51.1

Simple arithmetic averages ($n = 3$) ± standard deviation with different lower-case letters on the line, differ from each other, using the Tukey test ($p \leq 0.05$); BC = bioaccessible concentration; % BF = percentage bioaccessible fraction; <LD(m) = values below the detection limit of the method.

cooked beans with a certain concentration of Pb, approximately 80 % of this concentration is not bioaccessible to the organism, that is, the toxicity is lower compared to the total concentration.

The Mn element, which presented about 27 % of bioaccessibility in raw beans, in the cooked beans it presented a decrease, with only TB02–19 beans not presenting itself below the LD(m). The variation of elements content released in the gastrointestinal tract is due to the presence of compounds that can inhibit the absorption of cations and decrease their bioaccessibility, for example, polyphenols, phytates and tannins (Ou et al., 2011; Pereira et al., 2018). Vegetable components, such as fiber and phytic acid, negatively affect the bioaccessibility of certain minerals (Cámara et al., 2005). The presence of these inhibitors could explain the relatively low percentages obtained for most minerals.

According to FAO (FAO/OMS, 2001), the recommended consumption of dried / fresh, cooked vegetables, including beans, is 3 table-spoons per day (average of 80 g). Converting the obtained results in this study for the bioaccessible concentration of cooked beans to mg / 80 g, and correlating it with the daily recommended intake for adults by the Institute of Medicine (2001) which is 14 mg for Fe, 7 mg for Zn, 0.9 mg for Cu and 2.3 mg for Mn, it was possible to observe that beans contribute to part of the intake of these minerals. However, it is evident that it is necessary to consume other vegetables and other types of food combined with beans throughout the day to assist in the supplementing, and it is also important to ingest essential elements that participate in various physiological functions in the body. The maximum allowed value for Ba and Pb is 500 mg and 0.036 mg, respectively (Azevedo and Chasin, 2003; Nielsen and Ladefoged, 2013). Converting the concentrations found for cooked beans to mg / 80 g, it is possible to observe that the bioaccessible concentrations for all elements in all bean cultivars were below the established daily limit, except for Pb. Pb, which is a potentially toxic element, needs further studies to discover the origin of this element in beans, since it can be present on the soil, fertilization, irrigation water, among other factors.

The requirement of Fe for adult males is 8 mg/day and for females is 18 mg/day (Institute of Medicine, 2001). Considering the total amount of Fe in beans, raw beans are more nutritious concerning the presence of Fe, however, considering the bioaccessibility, it is noticed that cooked beans are not the most efficient food regarding the availability of Fe to the body. These results indicate that not all the content of a certain element present in the food is likely to be released from the food matrix during human gastrointestinal digestion, thus making it available (or not) for absorption and consequent use by the body.

4. Conclusion

The study of the concentration of minerals in the cooked beans is more nutritionally important than the characterization of the raw grain, for beans are mostly consumed on its cooked form. The results found in this study indicate that, possibly the water and the cooking process has a considerable influence on the mineral content, and also that the maceration of the beans causes a leaching of minerals. We can observe

that the elements that are present in greater quantity in all beans, both raw and cooked, are K and Mg. However, when the bioaccessibility study was carried out among the elements considered, the most bioaccessible were Cu and Zn. The elements K and Mg were not quantified in the bioaccessible fraction, as they are present in high concentrations in the added salts for simulation of the gastrointestinal tract, thus increasing their concentrations on the solutions, making the determinations unfeasible.

Based on the results presented for the total concentration and for the bioaccessible concentration, it was possible to observe that the BRS Expedito sample presented the highest concentrations for most elements, both on raw and cooked grains. However, this same sample showed the highest total concentrations for Ba and Pb, which are considered to be potentially toxic elements for the human organism. In the bioaccessible concentration, for both raw and cooked beans, there was no greater difference concerning the percentages of the bioaccessible fraction. Thus, it was possible to observe that although the sample may present a great concentration of a certain element, when it is digested by our organism, only part of this concentration is released into the intestinal epithelium for later absorption by the body. Therefore, it is necessary to consume other types of food for later release of these elements, thus meeting the daily needs of the body.

5. CRediT author statement

A. M. Pereira designed the study, interpreted the results and drafted the manuscript.

D. H. Bonemann performed the analysis and interpreted the results.

S. H. Scherdién performed the analysis.

B. P. Ávila drafted the manuscript.

I. F. Antunes is the researcher who works with beans and supported the work.

A. S. Ribeiro guided the work and corrected the manuscript.

M. A. Gualarte guided the work.

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Declaration of Competing Interest

The authors declare no conflict of interest.

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