

## Determination of the mineral composition of Brazilian rice and evaluation using chemometric techniques

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Douglas G. da Silva,<sup>ab</sup> Ieda S. Scarmínio,<sup>bc</sup> Daniela S. Anunciação,<sup>ab</sup>  
Anderson S. Souza,<sup>ab</sup> Erik G. P. da Silva<sup>d</sup> and Sergio L. C. Ferreira<sup>\*ab</sup>

The mineral composition of Brazilian rice samples was determined and the data obtained were evaluated using principal component analysis (PCA) and hierarchical cluster analysis (HCA). Nineteen commercial rice samples were analyzed, six being brown, seven parboiled and six white. The elements were determined employing inductively coupled plasma optical emission spectrometry (ICP OES), and the accuracy was confirmed using a certified reference material of rice flour. The PCA showed the formation of three clusters: a group with the brown rice samples, other with the parboiled rice samples and another of the white rice samples. PCA also showed that the brown rice samples are richer in minerals than the white and parboiled rice samples. Calcium, sodium, zinc and manganese in white rice samples are higher than in parboiled rice samples, while the parboiled rice has higher contents of iron, magnesium, strontium, potassium and phosphorus. HCA also demonstrated formation of three major groups, confirming the results obtained by PCA. Application of HCA in the subgroups of rice samples clearly showed separation of rice brands and also separation between the raw and cooked samples. The mineral composition in the rice samples analyzed agrees with data reported by other authors. This paper revealed that the mineral compositions for white, brown and parboiled rice are significantly different.

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### 1 Introduction

Rice is a grain used to feed more than half human world population. Like all plants, the mineral composition of rice depends crucially on the chemical nature of the soil, use of fertilizers and herbicides, irrigation water and other factors. Since this is a food of great importance in the human diet, the nutritional assessment of rice provides data relevant to nutritionists and doctors.<sup>1–4</sup> Falahi *et al.* determined Fe, Zn, Ca, Cu, Pb and Cd in ninety-nine polished white rice samples grown in Iran.<sup>5</sup> Another paper quantified nutrients and toxic elements in rice samples consumed in Thailand.<sup>6</sup> A study characterized using a chemometric technique the rice consumed in Valencia City, Spain.<sup>7</sup> A work evaluated the mineral composition of rice consumed in Pakistan.<sup>8</sup> Antoine *et al.* determined the content of toxic and essential elements of brown and white rice consumed in Jamaica.<sup>9</sup> Other papers have also been published involving the determination of toxic elements such as mercury<sup>10,11</sup> and cadmium in rice.<sup>12</sup>

Principal component analysis (PCA) and hierarchical cluster analysis (HCA) are chemometric techniques of multivariate analysis that allow graphical visualization of analytical data, even when the number of samples and variables is large, examining the presence or absence of natural groupings between samples.<sup>13</sup> PCA reduces the dimensionality of the original dataset, preserving the greatest amount of information. This reduction occurs by means of establishing new orthogonal to each other variables, termed principal components (PCs).<sup>11</sup> HCA can group the samples into classes, based on the similarity of the participants of the same class and differences between members of different classes. The graph obtained is called a dendrogram.<sup>11</sup> PCA and HCA are techniques that complement each other and they have been employed for evaluation of results of data analysis.<sup>14–20</sup>

The present paper determined and compared the mineral compositions of brown, parboiled and white rice samples consumed in Salvador City, Brazil. The effect of cooking on the mineral content was also investigated. All the data obtained were evaluated using the multivariate analysis techniques PCA and HCA.

### 2 Experimental

#### 2.1 Instrumentation

The determination of the chemical elements was performed using a Varian model Vista PRO Inductively Coupled Plasma

<sup>a</sup>Instituto de Química, Universidade Federal da Bahia, CEP 40170-290, Salvador, BA, Brazil. E-mail: slcf@ufba.br; Fax: +55-71-32355166; Tel: +55-71-32355166

<sup>b</sup>Instituto Nacional de Ciência e Tecnologia, INCT, de Energia e Ambiente, Universidade Federal da Bahia, 40170-290 Salvador, BA, Brazil

<sup>c</sup>Departamento de Química, Laboratório de Quimiometria em Ciências Naturais, Universidade Estadual de Londrina, 86051-980 Londrina, PR, Brazil

<sup>d</sup>Departamento de Ciências Exatas & Tecnologia, Universidade Estadual Santa Cruz, Ilhéus, BA, Brazil

Optical Emission Spectrometer (Mulgrave, Australia) with axial viewing and a Charge Coupled Device (CCD) detector. A Sturman-Master chamber and a V-Groove nebulizer were also utilized. The instrumental conditions of the spectrometer established during the analyses were: power (1.3 kW), plasma gas flow (15.0 L min<sup>-1</sup>), auxiliary gas flow (1.5 L min<sup>-1</sup>) and nebulizer gas flow (0.8 L min<sup>-1</sup>).

The elements and the analytical wavelengths used for quantification were as follows: Ca II (317.933 nm), K II (766.491 nm), Mg II (285.213 nm), Na I (589.592 nm), P I (213.613 nm), Fe II (238.204 nm), Mn II (259.372 nm), Sr II (421.552 nm) and Zn II (202.548 nm).

The accuracy of the analytical technique was confirmed using a certified reference material of rice flour furnished by National Institute of Standard and Technology. The results obtained in this experiment are shown in Table 1.

## 2.2 Chemicals and reagents

The decontamination of the glass apparatus was performed using 10% v/v nitric acid solution for 12 h prior to use. All solutions were prepared employing ultra pure water (18.2 MΩ cm) from a Milli-Q system (Millipore, MA, USA) and the chemical reagents were of analytical grade, from Merck (Darmstadt, Germany). Standard stock solutions for all elements with a concentration of 1000 mg L<sup>-1</sup> were used to prepare working standard solutions by diluting each of these solutions with 1% (v/v) nitric acid.

## 2.3 Samples

Nineteen commercial rice samples were acquired from supermarkets in March, 2011 from Salvador City, Bahia State, Brazil, six being brown rice samples, seven parboiled rice samples and six white rice samples. These were dried at room temperature in a desiccator containing anhydrous calcium chloride for 72 hours. Afterward, all these samples were stored in plastic flasks.

The cooking of the samples was performed in a conventional microwave oven. The residual water from this process was discarded and the cooked rice was analyzed.

## 2.4 Sample preparation using a digester block<sup>21,22</sup>

In digestion tubes were deposited rice samples (2.0 g) and 3 mL concentrated nitric acid (Merck) and 3 mL of 30% (v/v) hydrogen peroxide (Merck) were added for complete digestion

of the samples. The tubes were put in a TECNAL model TE 040/25 block digester and cold finger condensers, which were cooled *via* refrigerated water attached to the tubes. The mixtures were heated for three hours. Then, the residues were diluted to 10 mL with ultra pure water. All the samples were digested in triplicate.

## 2.5 Software

Principal Component Analysis and Hierarchical Cluster Analysis calculations were carried out using the Statistica 6.0<sup>23</sup> software. Ward's linkage method was used for the hierarchical cluster analysis.<sup>24</sup>

# 3 Results and discussions

## 3.1 Determination of the mineral composition of Brazilian rice

The experimental work involved initially the analysis of nineteen raw rice samples in triplicate. Afterward, all these samples were cooked in triplicate and also analyzed. Thus, a total of 114 experiments were performed for the determination of Ca, Mg, Na, P, Fe, Mn, Sr and Zn in raw and cooked rice samples.

The data obtained in these 114 analyses were evaluated using PCA. The nine elements were established as columns and the rice samples as rows. The evaluation was performed on auto-scaled data because of different orders of magnitude in the element concentrations. The loadings of the original variables for the first principal component (PC1) are: calcium (-0.7249); magnesium (-0.8599); sodium (-0.7407); phosphor (-0.8261); iron (-0.9164); manganese (-0.8525); strontium (-0.8775) and zinc (-0.7820) and they represent 68.11% of the total variance. The second principal component (PC2) accounts for 19.79% of the total variance. This way, the first two principal components can model the data because they describe 87.89% of the total variance. Fig. 1 presents the PC1 × PC2 biplot resulting from the application of PCA. In this plot, the scaling procedure of PC analysis ensures that the lengths of the vectors representing variables and those of the sample vectors are on the same scale.

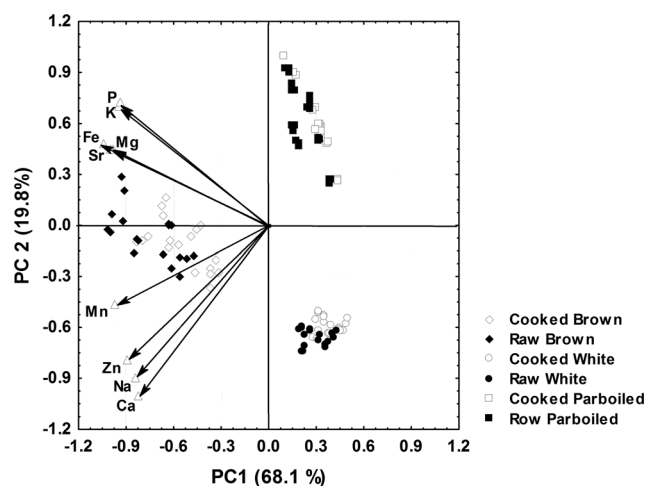


Fig. 1 Biplot of the first principal component (PC1) versus the second principal component (PC2) for the 114 analyses.

Table 1 Accuracy of the analytical method

Element	Certified value	Results found
Calcium (%)	0.0116 ± 0.0006	0.0118 ± 0.0006
Potassium (%)	0.126 ± 0.004	0.1280 ± 0.0008
Magnesium (%)	0.0554 ± 0.0005	0.056 ± 0.002
Sodium (%)	6.81 ± 0.97	6.60 ± 0.80
Phosphor (%)	0.154 ± 0.009	0.153 ± 0.008
Iron (mg kg <sup>-1</sup> )	7.5 ± 0.4	7.4 ± 0.9
Manganese (mg kg <sup>-1</sup> )	19.8 ± 0.6	20.0 ± 1.6
Zinc (mg kg <sup>-1</sup> )	19.8 ± 0.8	19.4 ± 0.5

As can be seen, three clusters for the analyzed samples are formed: a group with the brown rice samples, other with the parboiled rice samples and another with the white rice samples. A slight separation between raw and cooked samples can be also observed. Since the first PC has large negative loadings for the nine elements determined, the brown rice samples with lower scores are expected to have high concentrations of these elements. Variables located close to each other in a biplot are interpreted as being similar in behavior. Inspection of the plots for P and K indicates they are more highly correlated with each other than they are with Mn. That is, P and K belong to the same vector whereas Mg and Sr are in the same vector with Fe. PCA also showed that the brown rice samples are richer in minerals than the white and parboiled rice samples. Calcium, sodium, zinc and manganese in the white rice samples are higher than in the parboiled rice samples, while the parboiled rice has higher contents of iron, magnesium, strontium, potassium and phosphor, Fig. 1.

The same data obtained with the 114 analyses were also evaluated by HCA, and the results are shown in Fig. 2. In this dendrogram can be observed also the formation of three groups that are: parboiled rice samples, brown rice samples and white rice samples, it was confirming the results previously found with the PCA.

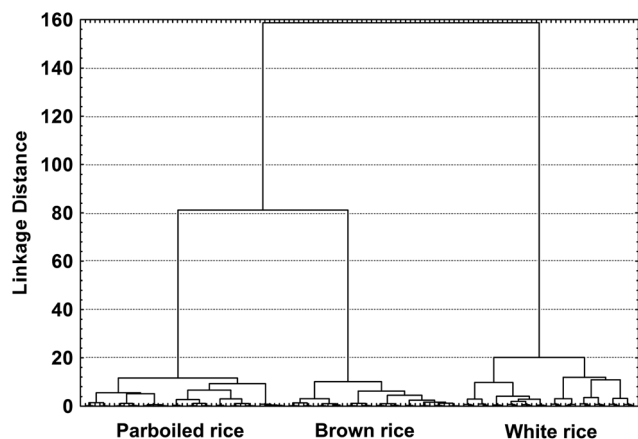


Fig. 2 Ward's linkage cluster dendrogram for the 114 raw (R) and cooked (C) rice samples analyzed.

### 3.2 Effect of cooking on the mineral composition of rice samples

Application of PCA to the subgroups of rice samples clearly showed the separation between the raw and cooked samples, Fig. 3a–c. To confirm these results paired comparison analysis was used. This analysis is useful to eliminate the influence of factors that are not of direct interest, for example, the difference in origins of the rice. The number of principal components was chosen from a scree plot. We used the score values of PC1 and PC2 for raw and cooked samples to estimate the distribution of a point on the  $t$  distribution and compare it with the value tabulated for each subgroup. The  $t$ -value with 17 degrees of freedom for brown rice and white rice is  $t_{17,95\%} = 2.11$ , while the  $t$ -value with 20 degrees of freedom for parboiled rice is  $t_{20,95\%} = 2.09$ , all at the confidence level of 95%. For brown rice the values calculated for PC1 and PC2 were  $\hat{t}_{PC1} = 25.46$  and  $\hat{t}_{PC2} = 11.59$ ; for white rice,  $\hat{t}_{PC1} = 19.38$  and  $\hat{t}_{PC2} = 4.3$ , and for parboiled rice  $\hat{t}_{PC1} = 5.93$  and  $\hat{t}_{PC2} = 5.03$ . As these values are greater than  $t_{17,95\%}$  and  $t_{20,95\%}$ , it can be concluded that there is indeed a systematic difference between the chemical composition of raw rice and cooked rice.

A comparison of the two treatments was used to prove a statistically significant difference between the raw and cooked rice as well as to determine which ions undergo modification upon cooking. Table 2 shows the differences between the averages for cooked and raw rice with their respective confidence intervals at the 95% confidence level. Since those intervals for Ca, K, Mg, Na, P and Fe ions do not include zero, it can be concluded that the contents of these metals are reduced while cooking, unlike the Mn, Sr and Zn ions where most of the intervals contain zero. These results are consistent with the PCA for white, brown and parboiled rice, Fig. 3, where the variables with the highest absolute values of the loadings are Ca, Na, Fe, Mg and K.

The data obtained by analysis of the 36 samples of raw and cooked white rice were evaluated by HCA; six different brands of white rice were used in the experiment. Considering: (RW) – for raw white rice and (CW) – for cooked white rice, the result of this evaluation as the dendrogram (Fig. 4) shows clustering for the six brands of rice, and also it can be seen the separation

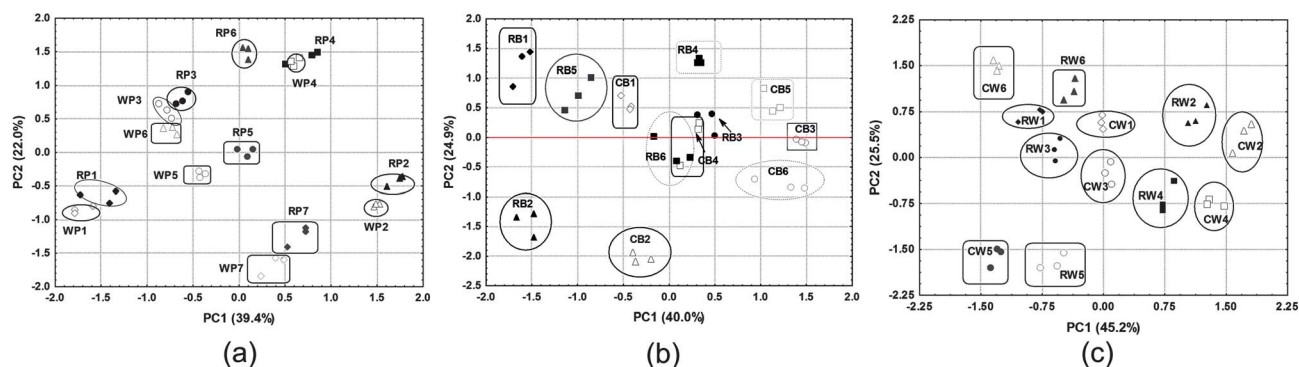
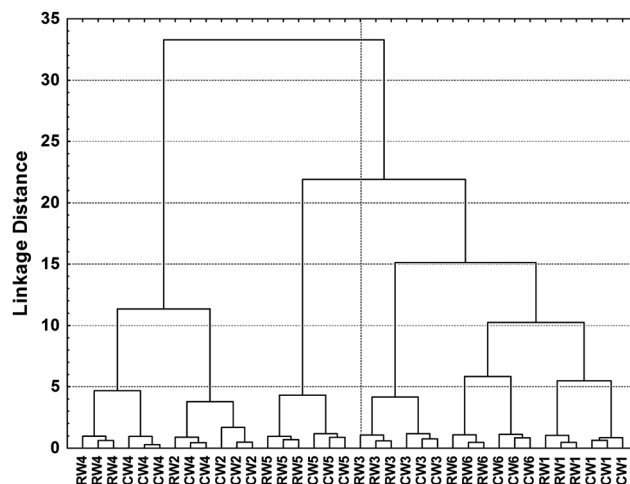


Fig. 3 Score plots of the first two principal components for the three sets (a) raw (RP) and cooked (CP) parboiled rice; (b) raw (RB) and cooked (CB) brown rice and (c) raw (RW) and cooked (CW) white rice.

**Table 2** Comparison of the differences between the averages for cooked and raw rices with their respective confidence intervals

Samples	Ca	K	Mg	Na	P	Fe	Mn	Sr	Zn
Brown rice	-76.10 ± 23.00	-607.60 ± 136.80	-121.00 ± 24.95	-97.00 ± 17.70	-430.30 ± 87.73	-1.03 ± 0.74	-0.24 ± 4.23	-0.03 ± 0.15	0.33 ± 2.15
	-77.20 ± 8.40	-398.10 ± 34.97	-126.90 ± 15.40	-121.30 ± 15.97	-395.60 ± 152.70	-1.00 ± 1.10	-0.97 ± 1.90	-0.16 ± 0.27	-1.00 ± 1.60
	-71.70 ± 18.52	-457.60 ± 40.67	-65.00 ± 28.09	-68.80 ± 26.48	-307.10 ± 103.20	-0.52 ± 0.26	-1.26 ± 2.44	-0.24 ± 0.22	0.32 ± 1.79
	-82.10 ± 18.83	-640.50 ± 202.16	-188.00 ± 50.02	-94.40 ± 19.70	-340.00 ± 31.28	-1.31 ± 0.68	-3.48 ± 4.59	-0.02 ± 0.24	-0.003 ± 2.46
	-46.30 ± 17.44	-478.90 ± 168.89	-98.50 ± 16.77	-78.90 ± 30.97	-356.1 ± 22.44	-0.82 ± 0.28	-3.57 ± 1.68	0.12 ± 0.20	0.33 ± 1.80
	-78.43 ± 20.33	-405.80 ± 216.42	-78.5 ± 16.04	-80.3 ± 14.22	-578.63 ± 376.28	-0.92 ± 0.13	-3.55 ± 3.67	-0.09 ± 0.22	0.88 ± 0.89
White rice	-43.80 ± 1.62	-202.13 ± 67.85	-27.40 ± 15.31	-51.1 ± 14.77	-128.8 ± 12.23	-0.31 ± 0.22	-2.32 ± 0.91	0.0 ± 0.02	-1.01 ± 0.98
	-28.10 ± 6.89	-152.77 ± 30.68	-23.13 ± 9.03	-60.3 ± 12.43	-70.3 ± 16.32	-0.24 ± 0.20	-0.87 ± 0.59	-0.003 ± 0.01	-0.48 ± 1.95
	-44.30 ± 7.00	-197.10 ± 47.19	-27.40 ± 8.20	-36.80 ± 13.46	-109.00 ± 26.98	0.11 ± 0.23	-0.59 ± 0.73	0.00 ± 0.04	-0.01 ± 1.70
	-25.80 ± 9.92	-144.40 ± 9.60	-14.07 ± 5.96	-56.90 ± 8.36	-103.80 ± 13.84	-0.22 ± 0.19	-0.72 ± 1.26	0.007 ± 0.05	-2.00 ± 0.93
	-43.90 ± 5.81	-201.00 ± 28.30	-11.17 ± 10.62	-42.70 ± 16.42	-73.00 ± 15.60	-0.35 ± 0.28	-0.80 ± 1.63	-0.003 ± 0.03	-1.34 ± 1.45
	-46.10 ± 11.74	-212.40 ± 27.50	-26.70 ± 6.33	-63.30 ± 12.84	-147.50 ± 18.76	-0.42 ± 0.31	-0.17 ± 0.97	-0.02 ± 0.05	-1.68 ± 1.45
Parboiled Rice	-8.5 ± 7.61	89.63 ± 223.94	-22.1 ± 13.20	-6.43 ± 14.00	-128.13 ± 104.93	-0.13 ± 0.55	-0.96 ± 0.43	-0.06 ± 0.23	-0.017 ± 1.06
	-14.50 ± 4.29	-26.60 ± 80.82	-12.83 ± 19.35	-6.00 ± 7.34	-151.00 ± 22.06	-0.22 ± 0.41	-0.73 ± 0.44	-0.01 ± 0.06	-0.58 ± 0.45
	-7.90 ± 3.53	-232.00 ± 91.6	2.63 ± 17.33	-2.30 ± 8.36	-240.77 ± 37.51	0.45 ± 0.19	-0.18 ± 0.53	0.003 ± 0.06	-0.01 ± 0.69
	-8.3 ± 5.45	107.47 ± 132.58	-19.3 ± 23.4	1.63 ± 3.41	-292.00 ± 61.25	-0.40 ± 0.58	-0.04 ± 0.46	0.05 ± 0.05	-1.00 ± 0.48
	-11.8 ± 2.97	-334.57 ± 33.33	-23.10 ± 10.57	4.87 ± 5.77	-202.70 ± 65.10	-0.82 ± 0.50	0.20 ± 0.27	-0.02 ± 0.04	-0.017 ± 0.58
	-7.1 ± 4.11	-143.70 ± 36.98	-15.63 ± 16.97	-3.00 ± 6.63	-398.80 ± 16.31	-0.29 ± 0.67	-0.47 ± 0.50	-0.70 ± 0.03	-0.01 ± 1.35
-12.60 ± 8.89	-25.87 ± 91.63	5.63 ± 17.47	-9.63 ± 13.99	-254.9 ± 45.90	-0.31 ± 0.22	-0.36 ± 0.52	-0.05 ± 0.06	1.99 ± 0.99	

**Fig. 4** Ward's linkage cluster dendrogram for the 36 raw (R) and cooked (C) white rice samples.

between raw and cooked samples for the same brand of rice. The results achieved for brown rice and polished rice were similar to those found for white rice.

The results obtained with PCA demonstrated that the mineral compositions of brown rice, white rice and parboiled rice are different. In addition, HCA (Fig. 4) also showed that raw rice samples are different than the cooked rice samples.

Considering these results, the mineral content was determined according to the type of rice, and also the condition of raw and cooked rice. The average content and ranges of concentration for the elements are shown in Tables 3 and 4, for raw and cooked rice, respectively.

The concentrations found for the elements as shown in Table 3 are in agreement with results achieved by other authors.<sup>5-9</sup>

### 3.3 Evaluation of the mineral composition of the Brazilian rice

The results found as can be seen in Tables 3 and 4 demonstrated that the mineral content of brown rice is always greater than in the white rice and parboiled rice. This can be explained considering that the production of brown rice involves only the removal of the shell that covers the grain in its natural state. For the white rice, the production process of this involves a polishing step of crude rice in order to remove all outer layers, including the pericarp, testa and embryo. This polishing improves the appearance and taste of rice. However, this operation causes a loss of nutritional value for the rice, because some substances of high nutritional value contained in the embryo are removed. This explains the results achieved in this work.

Another evaluation of Table 3 shows that the white rice samples have concentrations of the elements calcium, sodium, zinc and manganese greater than the parboiled rice samples. The explanation for this is that the parboiling process causes diffusion of metals for the outer layers and then they are lost during polishing. The parboiled rice samples have

**Table 3** Mineral composition of raw rice samples (mg kg<sup>-1</sup>)

Element	Brown Rice		White rice		Parboiled rice	
	Average	Concentration range	Average	Concentration range	Average	Concentration range
Ca	470	435–492	335	241–394	128	97–170
K	2967	2342–3472	1106	908–1274	1914	1334–2434
Mg	687	427–1167	155	106–202	326	270–374
Na	552	436–767	355	262–433	82	45–116
P	2364	2103–2947	659	450–910	1575	915–2041
Fe	9.80	7.97–12.41	2.68	1.63–3.67	5.34	4.16–7.72
Mn	24.40	17.32–33.56	10.44	7.72–14.77	5.78	4.15–7.83
Sr	1.37	1.07–2.00	0.20	0.05–0.33	0.69	0.44–0.89
Zn	22.13	19.48–24.37	15.69	13.62–18.12	9.52	6.52–14.05

**Table 4** Mineral composition of cooked rice samples (mg kg<sup>-1</sup>)

Element	Brown Rice		White rice		Parboiled rice	
	Average	Concentration range	Average	Concentration range	Average	Concentration range
Ca	398	386–415	297	215–350	118	93–158
K	2469	1944–2974	921	763–1062	1830	1315–2344
Mg	574	362–959	133	82.8–174.2	313	257–376
Na	461	367–646	303	219–367	79	47–107
P	1962	1781–2517	554	380–763	1339	764–1645
Fe	8.86	7.15–11.38	2.44	1.41–3.25	5.04	3.88–7.59
Mn	22.22	16.35–31.15	9.53	7.45–13.97	5.46	3.79–6.87
Sr	1.30	0.94–1.84	0.20	0.04–0.32	0.60	0.12–0.95
Zn	21.99	19.02–24.04	14.60	13.14–16.78	9.48	6.50–12.06

concentrations of iron, magnesium, strontium, potassium and phosphorus greater than the white rice samples. This has been explained, since the parboiling process causes migration of the soluble minerals of the outer layers to the endosperm of the grain. The evaluation of the data obtained in the sub-groups of rice samples using HCA also revealed that there is a difference in the mineral compositions among the rice brands analyzed in all three sub-groups, although in this paper, only the dendrogram (Fig. 3) for white rice is presented. These differences can be produced by slight differences in rice processing of each brand, or due to their different origins.

In Fig. 3, it is also possible to observe that the raw rice samples have a mineral composition different from the cooked rice samples of the same brand; in this study six samples of different brands were analyzed.

## 4 Conclusions

The PCA and HCA techniques showed that the mineral compositions of brown rice, white rice and parboiled rice samples are different.

The concentrations of calcium, sodium, zinc and manganese in white rice are greater than the parboiled rice, while the parboiled rice has higher contents of iron, magnesium, strontium, potassium and phosphorus.

The PCA and HCA techniques also demonstrated that rice cooking causes a decreased mineral content in this cereal.

The concentrations of calcium, potassium, sodium, magnesium, phosphorus, iron, manganese, strontium and zinc obtained in the brown, white and parboiled rice samples acquired in Salvador City, Brazil are in agreement with data reported by other authors.

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## References

- 1 M. M. Zeng, L. X. Zhang, Z. Y. He, F. Qin, X. Y. Tang, X. L. Huang, H. H. Qu and J. Chen, *Anal. Methods*, 2012, **4**, 539.
- 2 P. Alava, T. Van de Wiele, F. Tack and G. Du Laing, *Anal. Methods*, 2012, **4**, 1237.
- 3 M. Tuzen, M. Soylak and L. Elci, *Anal. Chim. Acta*, 2005, **548**, 101.
- 4 M. Tuzen and M. Soylak, *Anal. Chim. Acta*, 2004, **504**, 325.
- 5 E. Falahi, R. Hedaiati and A. R. Ghasvand, *Food Addit. Contam., Part B*, 2010, **3**, 80.

- 6 M. Parengam, K. Judprasong, S. Srianujata, S. Jittinandana, S. Laoharajanaphand and A. Busamongko, *J. Food Compos. Anal.*, 2010, **23**, 340.
- 7 A. Gonzalez, S. Armenta and M. de la Guardia, *Food Chem.*, 2011, **126**, 1254.
- 8 M. Zubair, F. Anwar, S. Ali and T. Iqbal, *Asian J. Chem.*, 2012, **24**, 417–421.
- 9 J. M. R. Antoine, L. A. H. Fung, C. N. Grant, H. T. Dennis and G. C. Lalor, *J. Food Compos. Anal.*, 2012, **26**, 111.
- 10 M. J. da Silva, A. P. S. Paim, M. F. Pimentel, M. L. Cervera and M. de La Guardia, *Anal. Chim. Acta*, 2010, **667**, 43.
- 11 L. O. B. Silva, D. G. da Silva, D. J. Leao, G. D. Matos and S. L. C. Ferreira, *Food Analytical Methods*, 2012, **5**, 1289.
- 12 D. G. da Silva, M. M. Silva, L. O. B. Silva, L. A. Portugal, G. D. Matos and S. L. C. Ferreira, *Anal. Methods*, 2011, **3**, 2495.
- 13 P. R. M. Correia and M. M. C. Ferreira, *Quim. Nova*, 2007, **30**, 481.
- 14 D. S. Anunciacao, D. J. Leao, R. M. de Jesus and S. L. C. Ferreira, *Food Analytical Methods*, 2011, **4**, 286.
- 15 A. A. da Silva, D. De Keukeleire, D. R. Cardoso and D. W. Franco, *Anal. Methods*, 2012, **4**, 642.
- 16 A. M. P. dos Santos, A. C. Oliveira, A. S. Souza, R. M. de Jesus and S. L. C. Ferreira, *Food Analytical Methods*, 2011, **4**, 567.
- 17 Y. N. A. Ni, R. M. Song and S. Kokot, *Anal. Methods*, 2012, **4**, 171.
- 18 M. Hasani and F. Emami, *Anal. Methods*, 2012, **4**, 1339.
- 19 A. Gredilla, J. M. Amigo, S. F. O. de Vallejuelo, A. de Diego, R. Bro and J. M. Madariaga, *Anal. Methods*, 2012, **4**, 676.
- 20 K. H. Low, S. M. Zain and M. R. Abas, *Food Analytical Methods*, 2011, **4**, 276.
- 21 R. M. de Jesus, M. M. S. Junior, G. D. Matos, A. M. P. dos Santos and S. L. C. Ferreira, *J. AOAC Int.*, 2011, **94**, 942.
- 22 S. L. C. Ferreira, L. O. B. Silva, F. A. de Santana, M. M. S. Junior, G. D. Matos and W. N. L. dos Santos, *Microchem. J.*, 2013, **106**, 307.
- 23 *Statistica for Windows*, Statsoft, Inc., Tulsa, OK, USA, 1999.
- 24 A. C. Rencher, *Methods of Multivariate Analysis*, JohnWiley & Sons, Inc. Publication, New York, EUA, 2nd edn, 2002, p. 466.