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Assessing mineral profiles for rice flour fraud detection by principal component analysis based data fusion

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A R T I C L E I N F O

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A B S T R A C T

The present work proposes to detect adulteration in rice flour using mineral profiles. Eighty-seven flour samples from two rice kinds (Indica and Japonica) plus thirty adulterated flour samples were analyzed by ICP OES. After obtaining the quantitative elemental fingerprint of the samples, PCA and LDA were applied. Binary and multiclass associations were considered to assess rice flour authenticity through fraud identification. Models based on element predictors showed accuracies ranging from 72 to 88% to distinguish adulterated and unadulterated samples. The fusion of the mineral features with the principal components (PCs) obtained from PCA provided classification rates of 100% in training samples, and 91–100% in test samples. The proposed method proved to be a useful tool for quality control in the rice industry since a perfect success rate was achieved for rice flour fraud detection.

1. Introduction

Food adulteration and fraud have increased on a global scale due to the growing demand for food. These illegal practices, consisting of reducing the food quality by intentional or unintentional substitution of food with inferior foreign particles or removing vital components from original food, represent a potential threat to food safety, which can lead to serious public health risks (Bansal, Singh, Mangal, Mangal, & Kumar, 2017; Hong et al., 2017; Tibola, Alves, Dossa, & In, 2018). In this sense, authenticity and traceability measurements have become important issues in food testing for ensuring its safety and quality, as well as consumer protection.

Cereal grains, flour, and their derived products form a part of the staple diet for most of the world population. Natural cereal flours are rich in essential minerals, vitamins, fibers, carbohydrates, fats, oils, and protein, making them high nutritional value sources. Thus, a wide variety of cereal flour based products is available in the market (Ambrose & Cho, 2014). Rice flour, in particular, has been largely used as raw material in the food industry for manufacturing various processed products such as cake, cookie, noodle, muffin, supplement bars, bread, beverage, vinegar (Gujral & Rosell, 2004; Kim, 2013; Murakami, Kuramochi, Koda, Nishio, & Nishioka, 2016; Sasaki, Kohyama, Miyashita, & Okunishi, 2014), among others. It is especially popular for preparing gluten-free foods, which are suitable for celiac patients (López, Pereira, & Junqueir, 2004; Thiranusornkij, Thamnarathip, Chandrachai, Kuakpetoon, & Adisakwattana, 2018). The high commercial demand for this type of products has been exploited for financial gain through food adulteration. Therefore, the quality of rice flour as raw material must be verified through food authentication testing and adulteration detection in order to ensure consumer protection against fraudulent activities.

Several methods have been developed for the determination of adulteration (Anami, Malvade, & Palaiah, 2019; Timsorn, Lorjaroenphon, & Wongchoosuk, 2017), illegal additives (Xu, Yan, Cai, & Yu, 2013), and fraud of geographical origin (Chung, Kim, Lee, & Kim, 2015; Liu et al., 2019), genotypes (Nakamura & Ohtsubo, 2010; Sampaio, Castanho, Almeida, Oliveira, & Brites, 2020), and quality types (Teye, Amuah, McGrath, & Elliott, 2019) in rice flour and grains. The analytical techniques most commonly used for these purposes are near-infrared (NIR) spectroscopy (Sampaio et al., 2020; Teye et al., 2019; Xu et al., 2013), inductively coupled plasma optical emission spectrometry (ICP OES) (Chung et al., 2015; Kelly et al., 2002),

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inductively plasma coupled mass spectrometry (ICP-MS) (Ariyama, Shinozaki, & Kawasaki, 2012; Cheajesadagul, Arnaudguilhem, Shiowatana, Siripinyanond, & Szpunar, 2013; Maione, Batista, Campiglia, Barbosa, & Barbosa, 2016), and DNA isolation protocol (Becerra, Paredes, Gutiérrez, & Rojo, 2015; Chuang, Lur, Hwu, & Chang, 2011; Nakamura & Ohtsubo, 2010; Vemireddy, Satyavathi, Siddiq, & Nagaraju, 2015). Although the methods using NIR are fast, non-destructive, and easy to apply, and methods applying genomic DNA extraction are quite sensitive and selective, they are not capable of generating results related to sample mineral chemical composition. In this regard, multi-elemental fingerprint techniques play an important role since the quality of rice depends on its mineral content (Itani, Tamaki, Arai, & Horino, 2002; Meng, Wei, & Yang, 2005). Comparing the aforementioned atomic emission spectroscopies, ICP OES is a relatively inexpensive technique, which has proven to be a reliable analytical tool for quick and precise determination of trace elements in complex matrices (Donati, Amais, & Williams, 2017; Novaes et al., 2016).

Multielemental data are increasingly assisted by chemometrics for solving rice authentication issues. Searching for ways of obtaining more and better information, researchers have begun using data fusion approaches which have proven to be useful alternatives to increasing the reliability of modeling of foodstuff specifications compared to the use of independent original sources of information. This trend has emerged for improving the synergy among the input features coming from analytical techniques in order to obtain better classification or prediction results (Borràs et al., 2015).

The aim of the present work was to evaluate the mineral profiles obtained by ICP OES for detecting fraud in rice flour samples using data fusion based on principal component analysis (PCA). For this purpose, linear discriminant analysis (LDA) was applied to distinguish between pure and adulterated samples according to their element content. Later, the modeling performance was significantly improved by fusing measured mineral concentrations with the principal components (PCs) obtained from PCA.

2. Experimental

2.1. Chemicals and standard solutions

HNO_3 69% (w/v) and H_2O_2 30% (w/v) reagent grade were purchased from Merck (Darmstadt, Germany). Ultrapure water (18.2 MΩ cm at 25 °C) obtained from a Milli-Q Plus Water purification system (Millipore Corp., Molsheim, France) was used to prepare all standard and working solutions. Calibration solutions were prepared from adequate dilutions of a TraceCERT® CRM multi-element standard solution acquired from Sigma-Aldrich (St. Louis, MO, USA). A SRM rice flour (NIST® SRM 1568b) acquired from Sigma-Aldrich (St. Louis, MO, USA) was used to assess the proposed method accuracy. Argon (99.998% purity) supplied by Praxair (Córdoba, Argentina) was employed as plasmogen and carrier gas.

2.2. Sample collection and preparation

Eighty-seven brown rice samples from two subspecies (Indica and Japonica) of Oryza Sativa L. species, harvested in 2017, were obtained from different agricultural cooperatives of the Corrientes province (Argentina). In this work, Indica samples were considered high-quality rice, while Japonica samples were considered inferior-quality rice, according to the morphological characteristics and the preference level of the Argentine population.

A cryogenic mill from Spex 6750 (Metuchen, NJ, USA) was used to make rice grains into flour, and then the resulting powdered samples were passed through a 60-mesh (0.3 mm aperture) sieve. The set grinding program consisted of 2.0 min for pre-freezing, 2.0 min for grinding and 3.0 min for freezing between the two milling steps. The adulterated samples were prepared by fortifying Indica rice flour with Japonica rice flour at concentrations of 25% (w/w), 50% (w/w), and 75% (w/w). Thus, the entire rice flour sample set consisted of 51 pure Indica, 36 pure Japonica, plus 30 adulterated, which resulted in a total of 117 samples.

An Ethos One (Milestone, Chicago, USA) microwave oven was used for the decomposition of the samples. Around 250 mg of dry flour were placed in closed digestion vessels, and 5 mL HNO_3 (65%, v/v), and 2 mL H_2O_2 (30%, v/v) were added later. The digestion procedure was completed following a three-stage temperature program: first stage: 25–200 °C for 10 min, second stage: 200 °C for 15 min, and third stage: 200–110 °C for 10 min, followed by ventilation until the digested solutions reached room temperature. Finally, the digested samples were diluted to 25 mL with deionized water and prepared for analysis by ICP OES. Blank solutions were prepared in the same way. Each flour sample was digested and analyzed in triplicate.

2.3. Determination of elemental content

The mineral composition of rice flour samples was determined using an iCAP 6000 Series (Thermo Fisher Scientific, England) inductively coupled plasma optical emission spectroscopy, equipped with a Cetac ASX-520 (Thermo Fisher Scientific, England) autosampler. The ICP OES operating conditions were: 1.2 kW RF Power, 10 L min^{-1} plasma gas flow rate, 0.6 L min^{-1} auxiliary gas flow rate, 0.45 L min^{-1} nebulizer gas flow rate, 0.5 mL min^{-1} sample flow rate, with concentric nebulizer and cyclonic spray chamber. The lines that exhibited low interference and high analytical signal were selected. The wavelengths selected were as follows: Al 396.152 nm, Ba 233.527 nm, Ca 373.690 nm, Cu 324.754 nm, K 769.897 nm, Mg 285.213 nm, Na 589.592 nm, P 213.618 nm, S 182.562 nm, and Zn 213.857 nm.

2.4. Chemometric analysis

2.4.1. Data matrix and preprocessing

The original data based on mineral profiles were transformed into a matrix format X (117 × 10), in which the columns corresponded to the 10 elemental variables measured by ICP OES, and the rows, to the 117 pure (Indica and Japonica) and adulterated flour samples. Prior to classification modeling, the data matrix was autoscaled to equalize the variability ranges in prediction results since variables were measured at different concentration scales.

2.4.2. Exploratory analysis and classification modeling

Principal component analysis (PCA) was applied to visualize the natural distribution of samples in a reduced dimensional space. The calculation of the PCs also allowed to verify the existence of relationships among the variables in a multidimensional space (Bro & Smilde, 2014).

The detection of rice flour adulteration was made by discriminating unadulterated (pure) and adulterated samples. Several classifiers based on binary and multiclass combinations were fitted to reach this goal. All sample groups evaluated were chosen according to the two rice flour kinds analyzed. The predictive modeling of rice flour was carried out by linear discriminant analysis (LDA). LDA is a supervised learning algorithm used to discriminate groups of samples by maximizing the variance among groups and minimizing the variance within each group (Moncayo, Manzoor, & Caceres, 2015).

Each sample set to be evaluated was randomly divided into two subgroups (calibration and validation) in order to build the classifiers. The calibration set corresponded to 70% of the total samples, and the validation set contained the remaining 30%. In order to keep the group distributions matching to the original matrix, the splitting up into subgroups was performed in a stratified manner. The calibration set was used to create classifiers, while the validation set served to test the built models.

Table 1
Figures of merit for the ICP OES method and precisions and recoveries obtained for rice flour analysis.

Element	Standard calibration curve			LOD	LOQ	Precision (RSD %)		Recovery (%)[a]		Certified value
	Slope	Intercept	r^2	(mg kg^{-1})	(mg kg^{-1})	Intra-day[a]	Inter-day[b]	Spiked samples	SRM	(mg kg^{-1})
Al	1145.1	45.2	0.9994	0.100	0.334	6.2	10.8	102.7	107.3	4.21 ± 0.34
Ba	518.9	−117.6	0.9985	0.105	0.350	5.3	7.4	95.1		
Ca	1960.7	1147.2	0.9999	0.083	0.277	2.6	5.9	90.4	93.5	118.4 ± 3.1
Cu	5022.4	−2810.5	0.9984	0.336	1.121	7.5	9.2	107.2	97.6	2.35 ± 0.16
K	511.6	255.2	0.9998	0.075	0.251	4.1	7.5	101.5	110.3	1282 ± 11
Mg	1932.9	440.5	0.9999	0.053	0.178	3.2	8.1	89.1	87.5	559 ± 10
Na	30.75	−19.72	0.9997	0.075	0.250	7.1	11.6	96.5	104.7	6.74 ± 0.19
P	14.67	26.70	0.9993	0.117	0.391	5.0	5.7	103.0	92.1	1530 ± 40
S	3.010	6.292	0.9997	0.090	0.301	4.7	10.3	98.1	105.4	1200 ± 10
Zn	14.13	13.25	0.9963	0.334	1.114	1.8	2.5	105.2	90.6	19.42 ± 0.26

[a] Average of three determinations (n = 3).
[b] Average of nine determinations (n = 9).

For improving modeling performance, data fusion based on PCA was also carried out. This strategy allowed for the increase of the number of input variables by merging the elemental data measured with the principal components (PCs) obtained from PCA.

2.4.3. Metrics and software

The performance of the fitted models was evaluated by measuring the accuracy (ratio between all correct predictions and total number of examined cases), sensitivity (correct positive predictions divided by the number of positive cases), and specificity (correct negative predictions divided by the number of negative cases). R-project software version 3.6.3 (R Core Team, 2020) was used for chemometric data analysis.

3. Results and discussion

3.1. Analytical performance parameters

The figures of merit of the method developed to determine the mineral composition of rice flour samples are summarized in Table 1. Good linear relationships were obtained from the calibration curves built considering five different concentration levels (in triplicate) in the selected range for each element. The regression equation parameters (slope and intercept) were determined by least squares linear regression analysis, and coefficients of determination (r^2) higher than 0.9963 were obtained. The sensitivity of the proposed method was evaluated through the limits of detection (LOD) and quantification (LOQ), which were calculated as 3 and 10 times, respectively, the standard deviation of measurements of 10 blank solutions, divided by the slope of the calibration curve, according to the AOAC guidelines (AOAC, 2016). The LODs were from 53 to 336 μg kg^{-1} and LOQs ranged from 178 to 1121 μg kg^{-1}. These results demonstrate the consistency of the developed method in terms of linearity and sensitivity.

Recovery and precision were assessed by randomly fortifying selected rice flour samples with known concentrations (10 and 100 μg kg^{-1}) from a multi-element standard solution. The analyses were performed over a period of three days. In addition, a standard reference material (SRM 1568b – Rice Flour) was analyzed in triplicate. The variability of the measurement was expressed as the relative standard deviation (% RSD). The intra-day and inter-day precisions for the elements analyzed ranged from 1.8 to 7.5% and 2.5 to 11.6%, respectively. The average recoveries obtained from the fortified samples were from 89.1 to 107.2%. Furthermore, the replicate analysis of SRM 1568b showed overall accuracies in the range of 87.5–110.3%, with RSD values less than 12.2% (Table 1). These values showed good agreement compared to certified values. According to AOAC (2016), all results were within the acceptable criteria for intermediate precision (≤15% RSD) and recovery (80–110%). These findings indicate that proposed method performance was satisfactory and contributed to get reliable results. Besides, the major components of the rice flour analyzed did not interfere significantly in the determination of the elements after an adequate digestion procedure, evidencing the absence of matrix effects.

3.2. Mineral content

Element profiles were determined in 117 rice flour samples by proposed ICP OES method. The samples were classified into three groups: Indica rice flour (51), Japonica rice flour (36) and adulterated flour (30) samples. Fig. 1 shows the averages of element concentrations obtained for each analyzed flour type, and the overall averages were also presented.

According to the results obtained, the overall content decreased in the following order: P > K > Mg > S > Na > Ca > Ba > Zn > Al > Cu. P and K were clearly the most abundant elements, with values within the ranges 3191–3314 and 2529–2635 mg kg^{-1}, respectively, while trace elements were Al and Cu, with values ranging from 4.57 to 6.12 and 2.30 to 2.40 mg kg^{-1}, respectively. Indica samples showed the highest mineral concentrations, except for Ba and Ca elements. The values found in adulterated samples were mostly intermediate between the Indica and Japonica classes, associated with lower dispersion values than the latter, clearly being made by different ratios of both rice flour types. Considering the different element concentration ranges, small differences were observed for Mg, Ba, and Al, while Cu values were not significantly different for evaluated flour groups. Cu, Ca, and S concentrations were similar to those reported in powder rice samples (Promchan, Günther, Siripinyanond, & Shiowatana, 2016). Chung and collaborators (Chung et al., 2015) also observed similar contents for K and Mg and higher values for Al and Zn from brown rice grains. The concentrations of Ba, Na, and P were greater than those found in processed rice from Brazil (Runge, Heringer, Ribeiro, & Biazati, 2019) and Thailand (Promchan et al., 2016), respectively.

3.3. Predictive modeling of rice flour

3.3.1. Exploratory data analysis

Before any chemometric processing, mineral profiles were autoscaled to provide an equal contribution of variables in prediction results. To describe the associations and patterns of the set of input measures, PCA was applied to data matrix made up of concentrations of 10 elements from 117 rice flour samples. The extracted first two PCs explained 47.7% of total variance (Fig. 2), so that the 100% variability of the data was represented by the first fifteen PCs. In addition, an absence of correlations between the input variables was detected by calculating the corresponding PCs.

From the score plot (PC2 vs. PC1) projected in Fig. 2, a tendency to

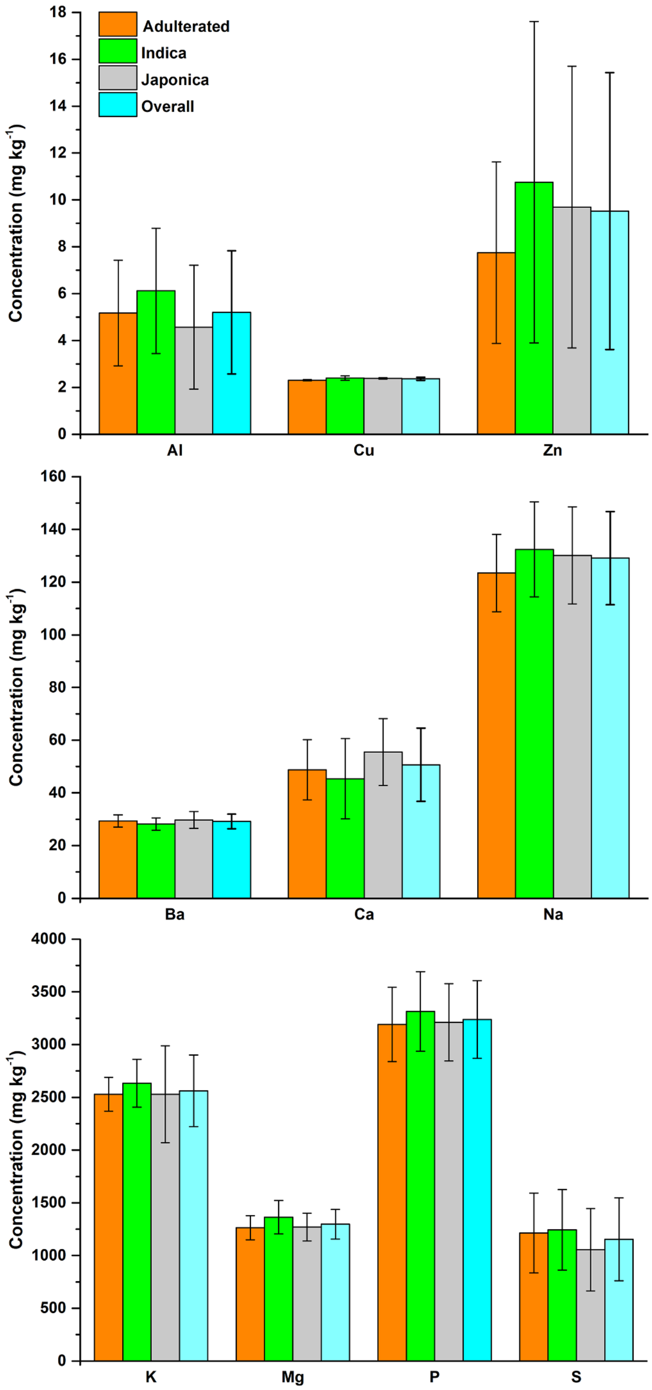

Fig. 1. Mineral compositions found in rice flour samples. Error bars represent the standard deviations of measurements.

differentiate pure flour samples is noted. Samples from Japonica rice flour were grouped in the negative values of PC2, while samples from Indica rice flour exhibited mostly positive scores on PC2. However, adulterated samples were scattered throughout the space from score plot, probably because these samples were constituted by different proportions of both rice types. The results indicate that both the discrimination of rice flour subspecies and the detection of adulterated samples can be accomplished by applying a supervised pattern recognition method like LDA.

3.3.2. Discrimination of unadulterated rice flour samples

LDA was carried out to develop classification models using mineral compositions. To evaluate the discrimination of unadulterated rice flour samples (pure Indica and Japonica), the sample set was randomly divided into 61 samples for calibration and 26 samples for validation. Fig. 3A shows a projection of the samples in the space defined by the first two discriminant functions (DF). DF2 exhibited that the Indica sample scores were mostly associated with negative values, while the Japonica ones were so with positive ones. Consequently, this scatter plot revealed two distinct clusters, evidencing a good separation of high-quality (Indica) and inferior-quality (Japonica) rice flour samples.

Fig. 3B illustrates the confusion matrix obtained for this model, summarizing the success rate and the percentage of predicted true and false negatives and positives. The misclassification rates were less than 12%. Additionally, relevant information about sensitivity (true positive rate) and specificity (true negative rate) can be obtained from this graph. The model provided a sensitivity of 93% and specificity of 80%. These parameters are fundamental to assess the robustness of the classification protocol. The pure rice flour samples were correctly classified with an overall accuracy of 88%.

3.3.3. Adulteration detection

Binary and multiclass classifications were carried out to evaluate the detection of rice flour adulteration. For fitting the classifiers, each sample set to be evaluated was split up into calibration and validation subsets. Table 2 presents the results obtained for classification of the three groups of samples evaluated. The overall prediction accuracies ranged from 72 to 85%, indicating good success rates. The discrimination of adulterated and unadulterated (Indica and Japonica) samples from binary associations showed sensitivities and specificities in the ranges 50–63% and 80–100%, respectively. The better fitted model achieved the following correct predictions per class: 93% for Indica, 89% for Japonica and 78% for adulterated rice flour samples (Table 2). These results indicate that Indica class can be differentiated from remaining classes with a high success rate. In addition, the Japonica and Adulterated flours can be discriminated against each other with 100% sensitivity and specificity, respectively.

3.3.4. Data fusion based on PCA

Considering that the predictive capability of the LDA algorithm can be improved by increasing the number of input variables (Hastie, Tibshirani, & Friedman, 2008), the mineral profiles measured were fused to the principal components (PCs) obtained from PCA. The optimal number of PCs was selected when 100% of the total variance was explained. The fused matrix here was composed of 117 rows corresponding to the rice flour samples and 25 columns which consisted of 10 element concentrations plus 15 optimized PCs. To build the classifiers, the original sample set was again trained and validated.

Table 3 summarizes the classification results obtained for the models based on data fusion. The overall correct predictions in training samples were 100% for all cases, while, in test samples, they ranged from 91 to 100%. PCA based data fusion enabled to distinguish among high-quality rice and inferior-quality rice flours and to identify adulterated flour samples with a perfect success rate. Despite having used a low-level data fusion, implementing this strategy was effective in improving classification modeling performance, proving that the process of integrating multiple data of the same object can be more informative and productive than the simple visualization of the original sources independently (Borràs et al., 2015), which shows this tools great advantage.

A comparison of the main methods reported for the determination of adulteration in rice flour and grains with the proposed method was carried out (Table SM1, Supplementary Material). As can be seen, several analytical techniques and chemometric algorithms have been used for this purpose. The extraction of relevant features from specific properties provided by the different employed analytical techniques has been frequently applied to evaluate rice authenticity. Tools of this type have been quite useful for improving classification performance of the pattern recognition algorithms. Several authors have used PCA to select

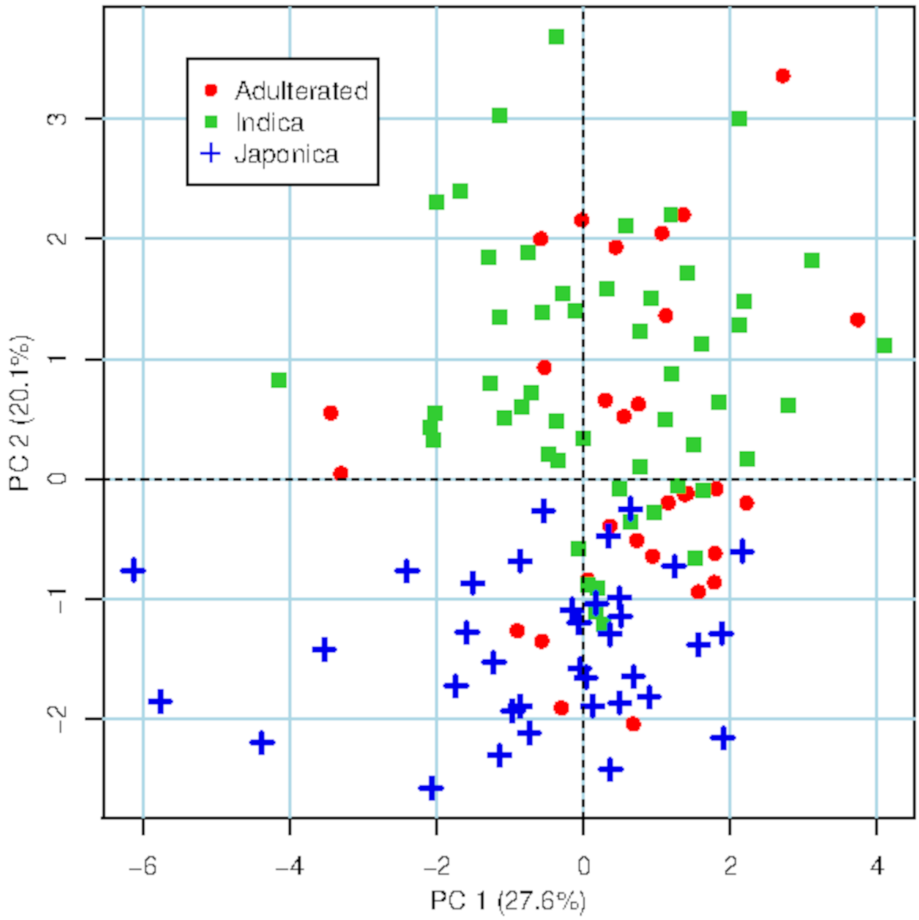

Fig. 2. Projection of scores in the first two principal components (PCs).

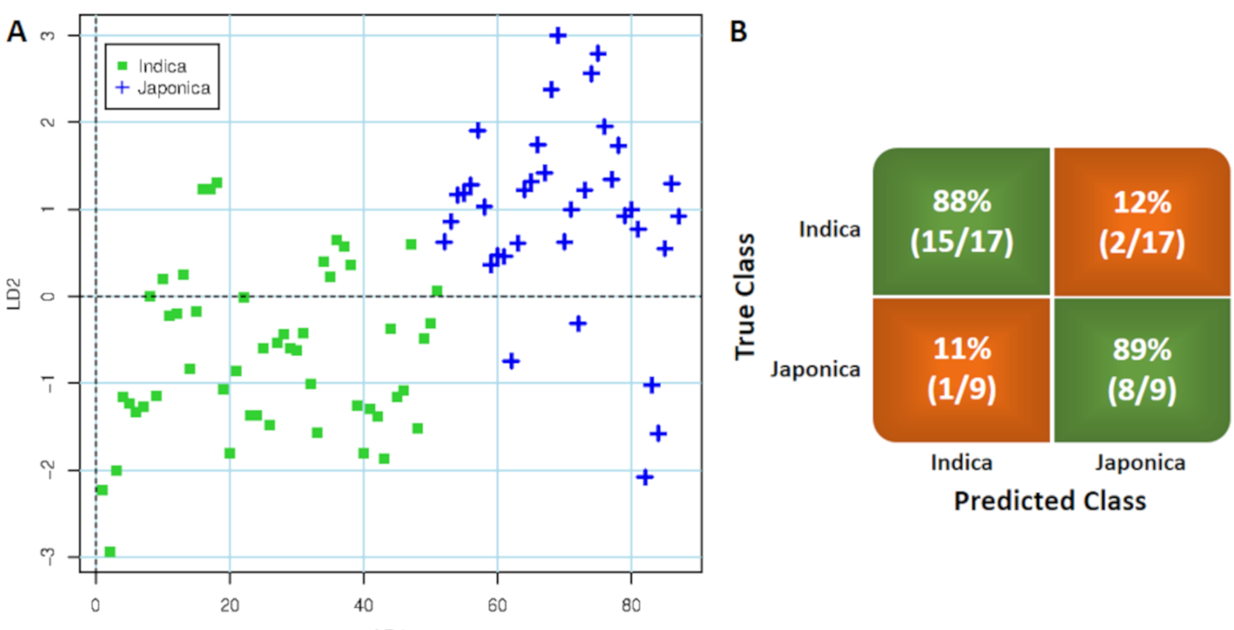

Fig. 3. (A) Scatter plot of the samples in the space DF1 vs DF2 and (B) confusion matrix obtained by analyzing the mineral profiles.

the input variables, however, our proposal takes a novel approach when using the PCs obtained from PCA and the measured mineral variables as descriptors for the chemometric analysis. This data fusion strategy provided a better fitted model than the methods cited in Table SM1 (Supplementary Material). In addition, the performance of developed models ranged from 83.3 to 97.0% in terms of accuracy, while the proposed method showed a perfect classification rate to discriminate adulterated and unadulterated rice flour samples.

Table 2
Classification performance for the rice flour groups evaluated and metrics per class for the best fitted model.

Classes	Number of samples		Accuracy	Sensitivity	Specificity
	Calibration	Validation	(%)	(%)	(%)
Adulterated–Indica	57	24	83	50	100
Adulterated–Japonica	46	20	72	63	80
Adulterated–Indica–Japonica*	83	34	85		
Metrics per class*					
Adulterated	21	9	78	56	100
Indica	35	16	93	90	96
Japonica	25	11	89	100	79

Table 3
Correct classifications obtained by the models based on data fusion.

Classes	Number of samples		Overall accuracy (%)	
	Calibration	Validation	Calibration	Validation
Indica–Japonica	61	26	100	100
Adulterated–Indica	57	24	100	98
Adulterated–Japonica	46	20	100	91
Adulterated–Indica–Japonica	83	34	100	100

4. Conclusions

Mineral profiles were used to detect fraud in rice flour through adulterated sample prediction. The element composition of the flour samples was obtained by ICP OES, and two pattern recognition tools (i.e. PCA and LDA) were successfully applied. The order of abundance for the elements was as follows: P > K > Mg > S > Na > Ca > Ba > Zn > Al > Cu. Most of the elements showed concentrations in agreement with those reported in brown rice samples. The discrimination of the three flour kinds evaluated was achieved by applying LDA algorithm using binary and multiclass associations. Pure and adulterated flour samples were differentiated with overall accuracies in the range 72–88% and specificities ranging from 80 to 100%, using models based on mineral features. The classification performance was improved by merging the principal components (PCs) obtained from PCA with the elemental variables measured, which showed correct predictions greater than 91% in test samples. PCA based data fusion was able to identify adulterated rice flour samples with a perfect success rate. The developed method is trustworthy, easy to apply, and has potential to be used for rice flour quality control in food industry aiming to prevent consumers from financial harm.

CRediT authorship contribution statement

Michael Pérez-Rodríguez: Conceptualization, Investigation, Methodology, Validation, Formal analysis, Visualization, Writing - original draft, Writing - review & editing. **Pamela Maia Dirchwolf:** Formal analysis. **Zenaida Rodríguez-Negrín:** Funding acquisition, Formal analysis, Writing - review & editing. **Roberto Gerardo Pellerano:** Funding acquisition, Supervision, Formal analysis, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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