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Maria Markiewicz-Keszycka

Maria Piedad Casado-Gavalda

Xavier Cama-Moncunill

See next page for additional authors

Authors

Maria Markiewicz-Keszycka, Maria Piedad Casado-Gavalda, Xavier Cama-Moncunill, Raquel Cama-Moncunill, Yash Dixit, Patrick J. Cullen, and Carl Sullivan

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Analytical Methods

Laser-induced breakdown spectroscopy (LIBS) for rapid analysis of ash, potassium and magnesium in gluten free flours

Maria Markiewicz-Keszycka[a], Maria P. Casado-Gavalda[a,*], Xavier Cama-Moncunill[a], Raquel Cama-Moncunill[a], Yash Dixit[a], Patrick J. Cullen[a,b], Carl Sullivan[a]

[a] School of Food Science and Environmental Health, Dublin Institute of Technology, Cathal Brugha St., Dublin 1, Ireland
[b] Department of Chemical and Environmental Engineering, University of Nottingham, UK

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ABSTRACT

Gluten free (GF) diets are prone to mineral deficiency, thus effective monitoring of the elemental composition of GF products is important to ensure a balanced micronutrient diet. The objective of this study was to test the potential of laser-induced breakdown spectroscopy (LIBS) analysis combined with chemometrics for at-line monitoring of ash, potassium and magnesium content of GF flours: tapioca, potato, maize, buckwheat, brown rice and a GF flour mixture. Concentrations of ash, potassium and magnesium were determined with reference methods and LIBS. PCA analysis was performed and presented the potential for discrimination of the six GF flours. For the quantification analysis PLSR models were developed; R^2cal were 0.99 for magnesium and potassium and 0.97 for ash. The study revealed that LIBS combined with chemometrics is a convenient method to quantify concentrations of ash, potassium and magnesium and present the potential to classify different types of flours.

1. Introduction

The global market for gluten free (GF) products has significantly increased during the last decade and it is estimated to reach USD 7.59 billion by 2020 (MarketsandMarkets™, 2014). The main reason for this trend is an increasing progress in the diagnosis of coeliac disease, non-coeliac gluten/wheat sensitivity and health awareness of consumers (Gobbetti, Pontonio, Filannino, Giuseppe, & De Angelis, 2017). However, numerous studies report that people on GF diets are often exposed to nutritional imbalances including low magnesium intake (Gobbetti et al., 2017). In order to improve nutritional quality of GF breads, pastas, breakfast cereals and baked goods, GF flour mixtures can be fortified with raw materials rich in minerals and mineral premixes (Naqash, Gani, Gani, & Masoodi, 2017; Rybicka & Gliszczyńska-Świgło, 2017). The monitoring of elemental content of raw materials provides valuable information for food technologists and ensures food quality.

Ash analysis allows the determination of the inorganic matter in flour samples. Ash content affects the hygroscopicity and colour of baked products and is commonly performed by combustion of the sample at high temperatures in a muffled furnace. Residues remaining after ignition consist of inorganic constituents such as macro and microelements. This approach requires a considerable amount of time to obtain results and is not suitable for in-situ analysis. In terms of specific mineral composition, the food industry also rely on expensive, labour-intensive and time-consuming laboratory methods.

Laser-induced breakdown spectroscopy (LIBS) is an optical emission spectroscopy technique that is fast, chemical-free and multi-elemental. A laser pulse is applied to the sample and is absorbed by the surface. A small amount of material is ablated, producing a plasma plume which consists of atoms, ions and free electrons. The cooling plasma emits light, which is collected by a spectrometer and the corresponding spectrum is recorded. The spectrum obtained provides information about the elemental composition of the target material (Rakovský, Čermák, Musset, & Veis, 2014).

Minerals such as potassium and magnesium play a key role in the prevention of cardiovascular diseases related to high sodium intake (Singh, Kumar, Awasthi, Singh, & Rai, 2016). The World Health Organization (WHO) recommends a daily sodium intake of less than 2 g and potassium of more than 3.5 g (World Health Organization, 2012a; World Health Organization, 2012b). A ratio of Na to K below 1 in the diet helps to reduce blood pressure and the risk of cardiovascular diseases. Heart health is also supported by adequate magnesium intake, which prevents atherogenesis and inappropriate clotting (Rosanoff, 2013). A diet based on processed food and refined grains can lead to an imbalance of these essential elements resulting in combined K-Mg deficiency which is increasingly common (Zheltova et al., 2017).

* Corresponding author.
E-mail address: maria.casado@dit.ie (M.P. Casado-Gavalda).

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The aim of this work was to assess the feasibility of LIBS to determine ash, potassium and magnesium content in GF flours. A model was built using different types of GF flours namely buckwheat, brown rice, potato, tapioca and maize. Based on this model, concentrations of ash, potassium and magnesium were predicted in the above mentioned flours as well as in a validation sample not included in the calibration model – a GF flour blend. LIBS, an emerging Process Analytical Technology (PAT), has already been successfully utilized for the evaluation of elemental composition of food materials such as milk, meat and wheat flour (Andersen, Frydenvang, Henckel, & Rinnan, 2016; Bilge, Sezer, et al., 2016; Bilge, Velioglu, Sezer, Eseller, & Boyaci, 2016; Bilge et al., 2016a, 2016b; Cama-Moncunill et al., 2017; Casado-Gavalda et al., 2017; Zheng, Shi, Wang, & Liu, 2015). However, to the authors' knowledge no studies on GF flours have been performed.

2. Material and methods

2.1. Flour samples

A total of 6 different types of flours were used in this study: buckwheat, brown rice, potato, tapioca, maize and a commercially available GF flour blend which is a mixture of the previous five flours. Three batches of each type of GF flours were obtained and each batch was analysed in triplicate. Thus a total of 54 samples were analysed ($n = 6 \times 3 \times 3 = 54$). All flours were purchased from local shops in Dublin, Ireland.

2.2. Reference analyses

2.2.1. Dry matter and ash content

Dry matter and ash analyses were performed according to 925.10 and 923.03 AOAC official methods, respectively. For dry matter analysis, 2 g of the sample were dried in an oven at 130 °C until constant mass was obtained (usually 2–3 h). For ash analysis, 2 g of the sample were incinerated in a muffle furnace at 580 °C until stable weight was achieved (usually overnight).

2.2.2. Atomic absorption spectroscopy

Potassium and magnesium content of all flours were determined using atomic absorption spectroscopy (AAS) (Varian 55B AA, Agilent Technologies, United States). Samples were prepared in triplicate according to the 985.35 AOAC standard method with minor modifications. First, approximately 2 g of sample were placed in a crucible and charred on a hot plate. Then samples were moved to a muffle furnace at 580 °C until light grey/white ash resulted. After combustion, 1 M nitric acid (CAS 7697-37-2, Sigma Aldrich, Inc.) was added to the cold ashes and heated up on a hotplate until all ash was dissolved. A further dilution with 1 M nitric acid was performed to maintain Mg and K concentration within the AAS optimum measuring range (0–1 ppm for magnesium and 0–2 ppm for potassium). An air-acetylene type flame was used for AAS analysis. To avoid interferences in air-acetylene, magnesium content was determined in the presence of lanthanum chloride solution. In addition, caesium chloride was added to suppress ionisation of potassium in the air-acetylene flame. The metal specific hallow cathode lamps with an operating current of 4 mA (for magnesium) and 5 mA (for potassium) were used as radiation sources at a wavelength of 285.2 nm for magnesium and 769.9 nm for potassium. Calibration curves were performed using five standard solutions, which were prepared by serial dilutions of a commercial AAS standard of potassium (96665, Fluka Analytical) and magnesium (42992, Fluka Analytical) in 1 M nitric acid.

2.3. LIBS analysis

2.3.1. Sample preparation

Approximately 400 mg of flour, per sample, was placed into a 13-mm diameter stainless steel die and pelletised using an applied load of 10 tons for 3 min with a hydraulic press (GS01160, Specac Ltd., Orpington, United Kingdom). All samples were prepared in triplicates obtaining a total of 54 sample pellets.

2.3.2. LIBS setup and spectra acquisition

The schematic LIBS system setup used in this study is presented elsewhere (Cama-Moncunill et al., 2017). LIBS spectra were recorded by a LIBSCAN-150 system (Applied Photonics, UK). The system used a Q-switched Nd:YAG laser operating at its fundamental wavelength ($\lambda = 1064$ nm) (ultra Quantel laser, 601 Haggerty Lane Bozeman, Mt, USA), generating pulses each of 5 ns duration with a pulse energy of 150 mJ at a repetition rate of 1 Hz. The laser was coupled with a set of six fibre-optic compact optical spectrometers (Avantes, AvaSpec, Netherlands), which covered the spectral range of 185–904 nm. The full width at half maximum (FWHM) ranged from 0.06 nm for the deep ultraviolet (UV) range to 0.18 nm for the visible near infrared (Vis-NIR) range. Light was collected by an array of 6 plasma light collection optics located in the laser head for the different wavelength regions. Additionally, the system was fitted with a miniature CCD camera enabling the observation of the size and shape of the craters generated by laser ablation. The pellet samples were placed in a sample chamber fitted with a motorized computer controlled X-Y-Z translation stage (XYZ-750, Applied Photonics Limited, Skipton North Yorkshire, United Kingdom). The best quality spectra were obtained at a constant optimum focal length of 76 mm. Samples were measured directly in air.

To improve reproducibility of the results the laser beam was fired at 100 locations for the same sample/pellet in a 10×10 grid pattern and moved by a step size of 0.70 mm. To obtain the best signal-to-noise ratio, each spectrum was the result of 3 accumulations per location. To avoid the detection of strong bremsstrahlung, the continuum plasma emission was analysed at a gate delay time of 1.27 μs and 1.1 ms integration time.

2.4. Chemometrics and data analysis

Chemometric analysis were performed using R (R Core Team, 2016). For principal component analysis (PCA) and partial least square regression (PLSR) modelling the 'pls' package and other in-house functions were used (Mevik, Wehrens, & Liland, 2016). Pre-processing of the LIBS spectral data included correction of non-linearities and signals' variations caused by potential matrix effects. Firstly, one hundred spectra acquired for each pellet were averaged to obtain one spectrum per pellet. Before applying PCA and PLSR modelling to the averaged spectra, data were baseline corrected.

The main idea of PCA is to reduce the dimensionality of the dataset consisting of a large number of interrelated variables, while retaining as much of the variation present in the data set as possible (Reinholds, Bartkevics, Silvis, van Ruth, & Esslinger, 2015). PCA was applied on the entire 54 sample data set. In the present study PCA illustrates the potential for an unsupervised classification by dividing the samples into clusters based on the variance of their corresponding LIBS spectra.

In order to obtain quantitative results, the PLSR technique was employed. PLSR models the relationship between two data sets. It is a predictive two-block regression method based on estimated latent variables and is applied to the simultaneous analysis of the two data sets; X (spectra) and Y (reference analysis) (Miquel Becker, Christensen, Frederiksen, & Haugaard, 2003). In the present study, the dataset was divided into a training set (30 spectra based on two batches of five flours, in triplicate; GF flour blend was omitted in this set) which was employed to develop the calibration model, and a validation set (24 spectra based on one batch of five flours, in triplicate and three batches in triplicate of the GF flour blend). Cross-validation was conducted using the leave-one-out method. The accuracy of the model was evaluated by the coefficients of determination and the values of root mean square error for calibration (RMSEC), validation (RMSEP) and cross-

Table 1
Results of reference analysis (dry matter) for ash, K and Mg contents of gluten free flours samples (n = 3).

Sample name	Ash (%)			Potassium (mg/g)			Magnesium (mg/g)		
	Batch 1	Batch 2	Batch 3	Batch 1	Batch 2	Batch 3	Batch 1	Batch 2	Batch 3
Buckwheat flour	1.68 ± 0.02	1.66 ± 0.04	1.64 ± 0.02	4.67 ± 0.02	4.62 ± 0.07	4.55 ± 0.05	2.08 ± 0.02	2.08 ± 0.03	2.08 ± 0.02
Brown rice flour	1.28 ± 0.01	1.23 ± 0.04	1.27 ± 0.01	5.52 ± 0.01	5.35 ± 0.03	5.45 ± 0.06	2.44 ± 0.01	2.13 ± 0.02	2.44 ± 0.02
Potato flour	0.23 ± 0.01	0.24 ± 0.02	0.25 ± 0.00	0.15 ± 0.00	0.14 ± 0.00	0.15 ± 0.00	0.09 ± 0.00	0.09 ± 0.00	0.09 ± 0.00
Tapioca flour	0.17 ± 0.02	0.16 ± 0.01	0.16 ± 0.01	0.22 ± 0.01	0.23 ± 0.02	0.22 ± 0.02	0.04 ± 0.00	0.03 ± 0.00	0.04 ± 0.01
Maize flour	0.07 ± 0.01	0.06 ± 0.01	0.08 ± 0.00	0.06 ± 0.03	0.05 ± 0.02	0.08 ± 0.04	0.03 ± 0.00	0.04 ± 0.01	0.07 ± 0.02
Gluten free flour blend	0.37 ± 0.02	0.38 ± 0.00	0.36 ± 0.02	1.93 ± 0.05	1.91 ± 0.01	1.92 ± 0.03	0.41 ± 0.07	0.50 ± 0.01	0.51 ± 0.01

validation (RMSECV).

3. Results and discussion

3.1. Ash and mineral composition

In the available literature, there are few reports describing the elemental profile of buckwheat flour, brown rice flour, commercially available gluten free flour mixtures and gluten free starches such as maize, potato and tapioca. The results of reference analysis obtained in this study for the different types of GF flours are presented in Table 1.

One way analysis of variance (ANOVA) was performed on the ash, K and Mg content for the three batches of all gluten free flours under examination. No significant differences were found in the ash content between the batches of all examined flours. The K levels were not significantly different between the batches of buckwheat, potato, tapioca, maize and GF flour ($P > .05$). However, batches of brown rice flour showed significant differences for K level ($P < .001$). Similar no significant differences in Mg content were observed between batches of buckwheat, potato, tapioca and GF flour ($P > .05$). However, with regard to brown rice flour and maize the differences between batches of maize and rice were significant at $p < .05$ and $p < .0001$ respectively. The Tukey's Honest Significant Difference (HSD) test revealed the differences between the second batch of brown rice flour and batches 1 and 3 for both K and Mg; in case of maize batch 1 and 3 differed significantly ($p < .05$) in Mg content, however no differences were found between batches 2–1 and 3–2. The detailed results of the Tukey's HSD test can be found in the supplementary material (Tables S1 and S2).

In our experiment the highest content of ash (1.66%) was found in buckwheat flour, which was similar to that reported by Bonafaccia, Marocchini, and Kreft (2003). Torbica, Hadnadev, and Dapčević Hadnadev (2012) and Costantini et al. (2014) reported higher concentration of ash in buckwheat flour, above 2%. Results obtained in this study confirm that buckwheat flour is a good source of potassium and magnesium, and contains high amounts of these elements. High concentrations of these elements in buckwheat flour were also reported by Rybicka and Gliszczyńska-Świgło (2017) who reported potassium and magnesium contents of 4.11 and 1.57 mg/g respectively. Hager, Wolter, Jacob, Zannini, and Arendt (2012) also found similar amounts of potassium and magnesium in buckwheat. Moreover, data found in the literature indicate that GF flours, especially buckwheat flour are naturally low in sodium and rich in potassium, thus the Na to K ratio is favourable from a nutritional point of view (Rybicka & Gliszczyńska-Świgło, 2017).

The mineral content of rice depends on where the plant was grown and the rice variety (Davis et al., 2017). Brown rice is a whole grain rice which unlike white rice contains the hull, bran layer and cereal germ. These parts of the rice grain contain most of the nutritional components such as minerals and vitamins (Mir, Bosco, & Shah, 2017).

The calculated ash content of the brown rice flour reported in this study is similar to that found by Deepa, Singh, and Naidu (2008), however Zubair, Anwar, Ali, and Iqbal (2012) found a higher concentration of 1.9% in brown basmati rice. Moreover, the obtained results indicate that rice flour has the most abundant potassium and magnesium content among the examined GF flours although one batch of the brown rice flour samples had significantly lower concentration of potassium and magnesium than the two other batches. K and Mg concentration for rice flour recorded, in the present study, was higher than that found by Oko and Ugwu (2011). The most similar potassium concentration in brown rice was obtained by Deepa et al. (2008) and Zubair et al. (2012) who compared different rice varieties and found K concentration between 2.38 and 3.04 mg/g.

The most commonly used GF starches are refined from maize, tapioca, white rice and potato. Their main role is to provide structure and texture to GF products (Witczak, Ziobro, Juszczak, & Korus, 2016). The results of our study obtained for tapioca, potato and maize indicate that these flours are low in ash content with the lowest value noted for maize. Potassium content is the highest for tapioca, followed by potato and maize. The obtained results indicate that potato flour has the most abundant magnesium content among these refined starch flours.

3.2. LIBS qualitative evaluation of GF flours

Fig.1 shows the baseline corrected LIBS spectra of the different GF flours in the wavelength range from 185 to 904 nm. The baseline correction method, also known as detrending, utilizes individual spectra and standardizes spectral variations caused by random shifting in the continuum emission background due to matrix effects (Santos et al., 2012). The presented spectra are an average of 3 samples (3 replicates each; 9 spectra). Buckwheat and brown rice flours contain the highest ash content and consequently have the most intense emission lines corresponding to the various elements. As observed in Fig.1 these spectral lines can be seen in other types of flours, however with decreasing ash content these emission lines are less intense.

Buckwheat and brown rice flour spectra allowed for the isolation of 46 spectral lines. The identification of these lines was performed with reference to the NIST (US, National Institute of Standards and Technology) database (Kramida, Ralchenko, Reader, & Team, 2016). Ten different emitters belonging to three groups of atomic or molecular species were identified. The first group consists of mineral elements such as magnesium, calcium, potassium, sodium and rubidium; the second group represents organic elements: carbon, hydrogen, oxygen and nitrogen; and the third group is the molecular bond of CN. However, it needs to be stressed that CN, H, N and O lines can originate both from the sample and from the surrounding air (Abdel-Salam, Al Sharnoubi, & Harith, 2013). A visual comparison of the emission lines showed high similarity for potato and tapioca samples. This can be attributed to the similar chemical composition of these flours.

Fig. 2 shows a comparison of K and Mg emission lines of the different types of flours. It shows that an increased level of K and Mg concentration leads to an increased emission intensity. As previously mentioned, the reference analysis revealed that one batch of rice flour had a lower concentration of potassium and magnesium compared to the rice samples from the two other batches. It can be seen from Fig. 2 (B) that the intensity of the magnesium lines for this sample are very close to the intensities of the magnesium lines of the buckwheat

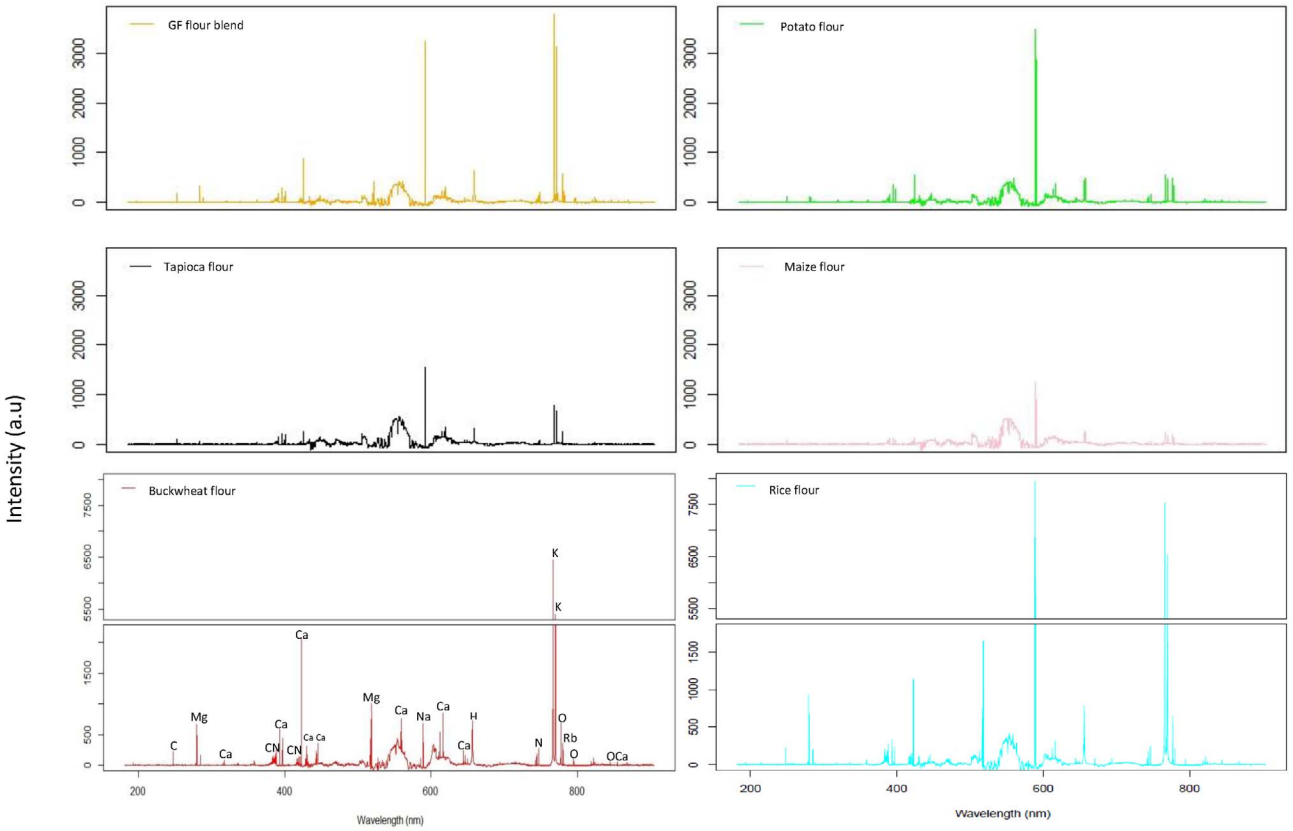

Fig. 1. Mean LIBS spectra of different gluten free flours.

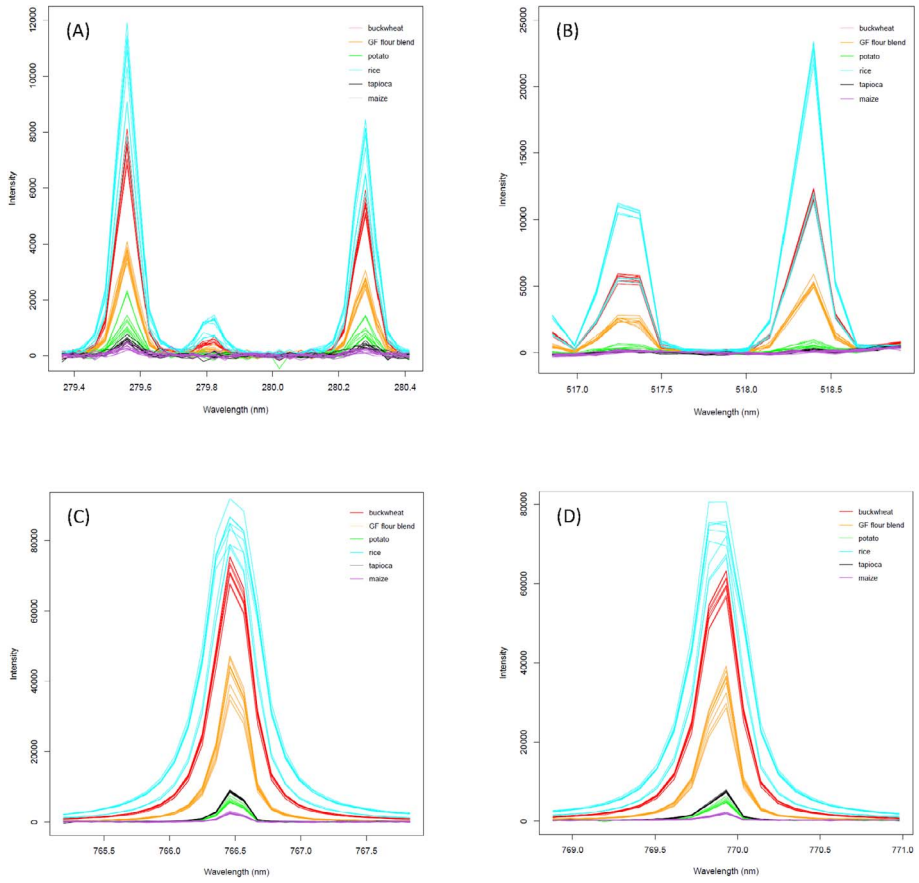

Fig. 2. Comparison between different LIBS spectral intensities of magnesium (A, B) and potassium (C, D) emission lines of six different types of GF flours.

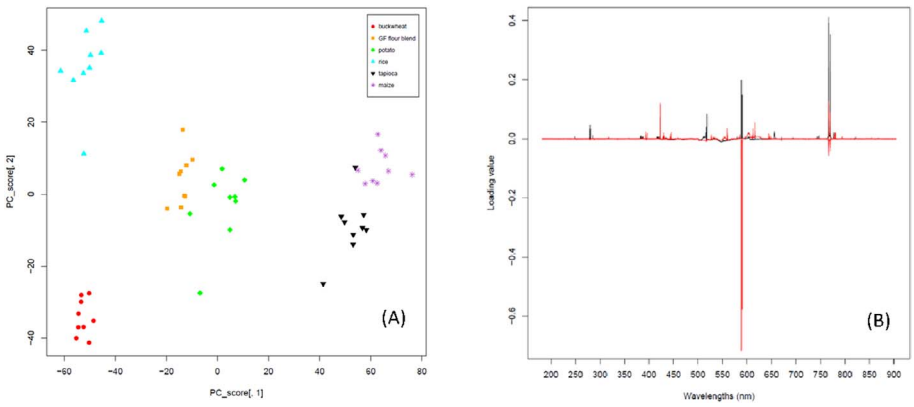

Fig. 3. (A) Score plot for PC1 vs. PC2 of a principal component analysis on LIBS spectra of six different GF flours; (B) Loading plot showing the contribution of each wavelength to the first two PLS factors for ash.

samples. Indeed, the concentration of magnesium in buckwheat flour was very similar to the mentioned rice sample (2.08 and 2.13 mg/g respectively).

Based on the spectra patterns it is possible to classify the samples into groups (Choi, Lee, & Yoh, 2013). In our study, PCA was applied to the entire LIBS spectral data of all samples, presenting a clear visual diagnosis of the different classes of spectra. The resulting score plot is displayed in Fig. 3(A). The PCA results show that the same type of flour with similar spectral patterns cluster together, while different elemental composition causes separation of each flour type.

Previous studies have also employed LIBS together with PCA as well as other chemometric methods, including partial least square-discriminant analysis (PLS-DA) and Neural Network (NN) for discrimination and classification purposes. J. Singh and Chandorkar (2016) exploited the feasibility of LIBS and PCA for rapid categorization of different species of cucurbits seeds. The method has been also applied to identify meat species and to detect whey adulteration in milk samples (Bilge, Sezer et al., 2016; Bilge, Velioglu, Sezer, Eseller, & Boyaci, 2016). Kim, Kwak, Choi, and Park (2012) used LIBS in combination with PLS-DA as a discrimination tool for pesticide contaminated rice and spinach. Moncayo, Rosales, Izquierdo-hornillos, Anzano, and Caceres (2016) demonstrated the possibility of using LIBS combined with NN to classify red wine based on its protected designation of origin.

3.3. LIBS quantitative analysis of GF flours

3.3.1. Calibration and validation model

Quantitative analyses were performed by applying the PLSR technique. PLSR is a quantitative regression algorithm which uses several factors containing almost all the information from the spectra to predict an analyte concentration. Thus, in our study the full LIBS spectra were correlated to the content of ash, potassium and magnesium, in the different GF flours.

Firstly, in order to determine the concentration of ash, K and Mg in the samples, three different calibration models were constructed based on the pre-processed spectral data from batch 1 and batch 2 in combination with the different elemental composition ranging from 0.07 to 1.66% for ash, 0.06 to 5.44 mg/g for K and 0.04 to 2.33 mg/g for Mg (Table 1). For further confirmation of our LIBS results, the validation set contained an additional sample with a different concentration than the calibration samples i.e. GF flour blend.

Fig. 4 presents the cross-validation curves for the calibration models as well as the validation curves for ash, K and Mg. The main parameters describing the PLSR models such as RMSEC and RMSECV, as well as RMSEP are given in Table 2. To achieve satisfactory RMSEC scores a small number of PLS factors (2) was required. High R^2_{cal} values and RMSEC values indicate high accuracy of the results (Table 2). After applying cross-validation, the prediction accuracy slightly decreased, however the pattern of cross validation results is highly similar to that obtained for the calibration results. For all analysed samples values of R^2_{cv} were slightly lower than R^2_{cal} and RMSECV higher than RMSEC which indicate that models were not over fitted. These values confirm that despite the differences in chemical and physical properties of the examined samples, the matrix effects did not result in any appreciable scattering of the calibration and validation curves. Thus, the PLSR models displayed good regression quality and high predictive accuracy for both the training and validation samples.

For further evaluation of the PLSR models, loading plots were analysed. Fig. 3(B) shows the PLSR loading plots for the first two components for the ash model, which explained 97% of the total variance. For all three models the first factor was mainly based on the spectral lines of Mg, Ca, Na and K with slight variations in their loadings. All these elements are present in the examined samples and as such their presence in the loading value were expected.

Moreover, the limit of detection (LOD) was determined according to the equation proposed by Allegrini and Olivieri (2014). The LOD values of ash, K and Mg are given in Table 2. Bilge et al. (2016a) also analysed the ash content of wheat flour. The smaller LOD value obtained by these researchers may be due to a more uniform matrix for their samples, higher number of analysed samples and a different calculating method. LOD together with R^2_p values obtained in our study confirm that LIBS has good prediction ability and is a sensitive and reliable tool for analysis of ash, potassium and magnesium in GF flours.

PLSR technique combined with LIBS has been applied to predict elemental composition of different food products. Casado-Gavalda et al. (2017) employed LIBS and the PLSR technique for quantitative analysis of copper content in beef meat spiked with beef liver. Andersen et al. (2016) used PLSR modelling to predict the calcium level in poultry meat. Cama-Moncunill et al. (2017) determined the calcium content in infant formula by applying PLSR to the LIBS spectral data. Bilge et al. (2016a, 2016b) employed LIBS combined with PLSR for the determination of calcium and ash content in wheat flour. Moreover, the presence of organic element lines in the spectra allows LIBS to be used also for organic composition analysis. Sezer, Bilge, and Boyaci (2016) used LIBS for protein analysis in wheat flour and whole meal samples. Similarly, as in this study, the PLSR technique was based on the entire spectra.

4. Conclusion

This work demonstrates the feasibility of LIBS as a rapid process analytical technique for the determination of potassium, magnesium and ash content in different types of gluten free flours. Presented results indicate that LIBS technique might be used for routine analysis in laboratories, offering potential for real-time monitoring of selected

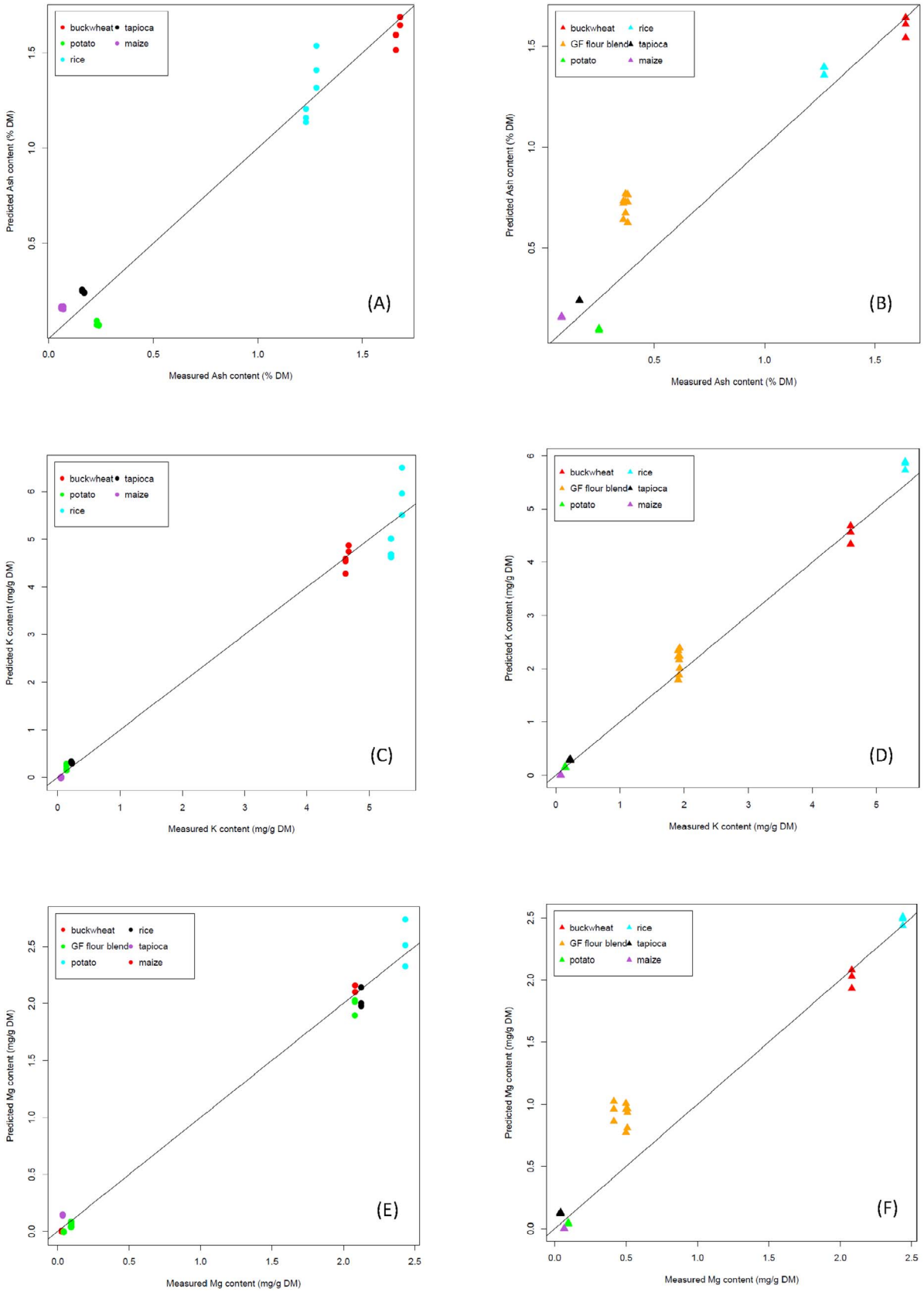

Fig. 4. PLS calibration for cross-validation and validation models of ash (A, B), potassium (C, D) and magnesium (E, F) content in six different types of GF flours.

minerals in industrial plants. Moreover, PCA analysis was performed and presents the ability of LIBS as a discrimination tool. This study also revealed that chemometric approaches such as PLS help dealing with matrix effects allowing the analysis of different raw materials. Further studies to identify other elements and to allow traceability are encouraged. This work demonstrates that LIBS can be a powerful tool for

Table 2
Calibration and prediction performance parameters of PLSR models designed to predict ash, K and Mg in GF flours using LIBS.

Quantified element detected in GF flour	R^2_{cal}	R^2_{cv}	R^2_p	RMSEC	RMSECV	RMSEP	LOD
Ash	0.97	0.97	0.82	0.10%	0.11%	0.22%	0.37%
Potassium	0.99	0.99	0.98	0.24 mg/g	0.29 mg/g	0.23 mg/g	0.85 mg/g
Magnesium	0.99	0.99	0.90	0.08 mg/g	0.10 mg/g	0.29 mg/g	0.29 mg/g

monitoring and improving the safety of food and feed products.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.foodchem.2017.10.063.

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