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Fast spark discharge-laser-induced breakdown spectroscopy method for rice botanic origin determination

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ABSTRACT

A simple, fast, and efficient spark discharge-laser-induced breakdown spectroscopy (SD-LIBS) method was developed for determining rice botanic origin using predictive modeling based on support vector machine (SVM). Seventy-two samples from four rice varieties (Guri, Irga 424, Puitá, and Taim) were analyzed by SD-LIBS. Spectral lines of C, Ca, Fe, Mg, N and Na were selected as input variables for prediction model fitting. The SVM algorithm parameters were optimized using a central composite design (CCD) to find the better classification performance. The optimum model for discriminating rice samples according to their botanical variety was obtained using $C = 5.25$ and $\gamma = 0.119$. This model achieved 96.4% of correct predictions in test samples and showed sensitivities and specificities per class within the range of 92–100%. The developed method is robust and eco-friendly for rice botanic identification since its prediction results are consistent and reproducible and its application does not generate chemical waste.

1. Introduction

Quality and safety of food crops are essential for protecting the consumers. Rice is one of the most worldwide consumed cereals since it is an important source of carbohydrates, proteins, vitamins and minerals and its production cost is relatively low (Gupta, 2015; Promchan, Günther, Siripinyanond, & Shiowatana, 2016; Zhu et al., 2018). The quality of rice mainly depends on its harvest, seed type, processing, geographical origin, and botanical variety. Nowadays the high demand for quality products has resulted in a large number of rice genotypes. According to the requirements of international trade, the variety labeling must be controlled for protecting the authenticity of rice (Gupta, 2015; Luo et al., 2019). In this context, the identification of botanical origin of the rice grains is crucial for research related to this crop.Rice authenticity analysis is a challenging due to the similarity in grain composition and chemical properties. A huge number of proposals employing different analytical techniques have been carried for this purpose. Rice varieties harvested from several countries have been accurately differentiated by hyperspectral imaging (Wang et al., 2015), Raman spectroscopy (Zhu et al., 2018), genomic DNA extraction (Becerra, Paredes, Gutiérrez, & Rojo, 2015; Brondani, Borba, Rangel, & Brondani, 2006; Chuang, Lur, Hwu, & Chang, 2011), chemical tests (Tiwari, Rastogi, Chandrakar, Sarawgi, & Verulkar, 2013), and digital image analysis based on color and morphological features (Gupta, 2015; Zhao-yan, Fang, Yi-bin, & Xiu-qin, 2005). The above methods related to chemical analysis require the use of reagents and generate chemical residues after analysis, increasing the cost per analysis. In addition, chemical methods involve extensive sample handling, increasing the analysis time and the risk of introducing errors. In contrast, methods using Raman spectroscopy and images (digital or hyperspectral) are fast and clean methods, however they are unable to generate results correlated to mineral chemical composition of samples. According to previous studies the genotype significantly affects the mineral content in rice (Itani, Tamaki, Arai, & Horino, 2002; Meng, Wei, & Yang, 2005). Therefore, there is still a lack of a fast and clean method, capable of providing an accurate classification of rice genotypes based on their mineral composition.

Laser-induced breakdown spectroscopy (LIBS) is an emission spectroscopy technique able to perform multielemental analysis. A LIBS measure is accomplished from a laser pulse, which promotes a

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microsampling, vaporization of sampled portion, breakdown and ionization of sample compounds. From ionization processes a plasma with temperatures reaching 10,000 K is produced. The plasma temperature causes atomization/ionization and excitation of sample elements. Upon returning to the lower energy state, excited species emit electromagnetic radiation at characteristics wavelengths allowing the identification of the specie. Additionally, the intensities of radiation can be correlated to the concentration of the species in the sample (Miziolek, Palleschi, & Schechter, 2006). Some LIBS system can show low analytical sensitivity, but this inconvenience has been overcome by coupling devices for signal enhancement (Bol'shakov, Mao, & Russo, 2017; Li et al., 2018; Sobral & Robledo-martinez, 2016), like spark discharge (SD) (Vieira et al., 2018; Pérez-rodríguez et al., 2019).

Due to its analytical advantages such as providing quick analyzes, dispensing or requiring minimal sample pretreatment and not using chemical supplies for analysis, the LIBS technique has been extensively applied for qualitative and quantitative analysis in various fields of the science including industrial (Noll, Fricke-Begemann, Connemann, Meinhardt, & Sturm, 2018; Sun et al., 2018), agricultural (Andrade & Pereira-filho, 2016; Sezer, Bilge, Sanal, Koksel, & Boyaci, 2017), biomedical (Busser, Moncayo, Coll, Sancey, & Motto-ros, 2018; Rehse, Salimnia, & Miziolek, 2012) and environmental researches (Butler, Cairns, Cook, Davidson, & Mertz-kraus, 2018; Zorov, Popov, Zaytsev, & Labutin, 2015). More recently it has gained special attention for cereal monitoring and control (Peng, He, Jiang, et al., 2019; Peng, He, Zhao, et al., 2019; Yang, Zhu et al., 2018).

The multielemental LIBS spectrum contains a large volume of sample information and the extraction of important spectral characteristics for the analytical purpose, as well as the simultaneous use of these characteristics with their respective weights, depends on the development of multivariate methods. In this context, chemometrics has effectively contributed to the development of LIBS methods. Some methods have been reported for rice analysis. Luo et al. (2019) adopted LIBS combined with multilayer perceptron neural network (MLP) for rapid identification of rice species. Other authors employed LIBS for successfully classification of rice samples according to its geographic origin by using principal component analysis (PCA) coupled to support vector machine (SVM) (Yang, Zhou, et al., 2018; Yang, Zhu et al., 2018) and extreme gradient boosting (XGBoost) together with k-nearest neighbor (k-NN) (Pérez-rodríguez et al., 2019). These methods suggest the LIBS potential for rice classification issue. However, the great challenge of each application is to extract the relevant information from the LIBS spectra according to the intended purpose and the choice of appropriate algorithm to process such information and generate the classification model.

Considering the above, the present work focuses on the development of a SD-LIBS-based method for rapid determination of rice botanic origin using SVM. Aiming to build an optimal classifier, a central composite design (CCD) was used to successfully fit the algorithm performance parameters.

2. Material and methods

2.1. LIBS instrumentation

A LIBS system coupled to a spark discharge (SD) device for sensitivity improvement, previously described by Vieira et al. (2018), was used in this work. The LIBS system consisted of a Q-switched laser Nd:YAG (Quantel, Big Sky Ultra 50, USA) emitting pulses at 1064 nm and operating at its maximum power energy (50 mJ) with a pulse duration of 20 ns, ablation laser fluence of ~ 70 J cm^{-2} and spot diameter about 300 μm. The plasma emission was collected at an angle of 45° in relation to the laser beam by using an optical fiber bundle and conducted to four spectrometers, Ocean Optics (LIBS HR2000+, USA). The spectrometers provided an optical resolution of 0.1 nm FWHM (full width at half maximum) and cover the spectral range from 200 to 600 nm. The Q-switched delay was set to 1 μs and the fix spectrometer integration time was 1 ms. The OOLIBS software (Ocean Optics, USA) was used to control the instrument and data acquisition.

Each sample were placed in sampling chamber which included a sample holder controlled by a joystick able to move the sample in the "x-y" directions and a video camera for monitoring the laser pulses on sample. All spectra were acquired by setting an output voltage of 4.5 kV.

2.2. Rice samples

Rice samples from four genotypes of Oryza Sativa L. species were obtained from different agricultural cooperatives of Corrientes province (Argentina). The samples were randomly selected by the cooperatives and, a set containing fifteen samples from Guri genotype, twenty-two from Irga 424, twenty from Puitá and fifteen from Taim was constituted. All 72 samples acquired come from the 2017 harvest.

2.3. Sample preparation and analysis

Considering the concentration of minerals differs in the different fractions of the grain (Lu, Tian, Liao, Zhang, Yang, Labavitch, & Chen, 2013) and aiming to measure the total content of minerals with adequate precision, the rice samples were individually homogenized by cryogenic grinding using a cryogenic mill from Spex 6750 (Metuchen, NJ, USA). 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. A mechanical press (Solab SL – 10/15, Piracicaba, Brazil) was used to prepare two pellets of each sample. The pellets with 12 mm in diameter and 2 mm thick were prepared by applying 10 tons of pressure to about 250 mg of powdered samples. The pellets were analyzed by LIBS spreading twenty laser pulses on each side of the pellet in different locations, moving the sampler in the x-y directions for each pulse. Thereby forty spectra were obtained from each prepared pellet resulting in 80 spectra per rice sample.

2.4. Multivariate data analysis

The LIBS spectra were preprocessed for base line correction and peak area integration. These tasks were carried using the Microsoft Excel® (2016). Support vector machine (SVM) classifiers, which are based on constructing a separating maximal margin hyperplane through the training data mapping into a higher dimension space, were evaluated for rice botanical origin prediction. SVM was chosen because it is able to solve nonlinear classification problems establishing linear boundaries among samples groups by using the kernel trick. Kernel function is used to transform the input data into required dimensions, in a more efficient way and with little computational cost (Lantz, 2015).

The SVM parameters were optimized by multivariate analysis using a central composite design (CCD). The parameters needing optimization included the insensitive loss function (γ) and the penalty factor (C). γ controls the amplitude of the kernel function and its choice determines the dimensionality of the feature space; while C controls the trade-off between prediction error minimization on training data and margin maximization (Bona et al., 2017). The modeling from these parameters was evaluated by ten-fold cross-validation. The classification performance of the models obtained was evaluated considering the overall accuracy, which is calculated as the ratio between all correct predictions and total number of examined cases. The maximum accuracy value was considered as the selection criterion. Design matrix and corresponding optimization graph were constructed using Minitab 16 software.

For fitting the classifier from optimized SVM parameters, the samples spectra were again randomly split up into two subsets, a calibration set which corresponded to 75% of the total samples (n = 54), and a validation set containing the remaining 25% (n = 18). In order to keep

the proportion of rice varieties in the new subgroups matching to original matrix, the split up into subgroups was performed in a stratified manner.

The metrics calculated per class included specificity (correct negative predictions divided by the number of negative cases) and sensitivity (correct positive predictions divided by the number of positive cases) (Lantz, 2015). In addition, the Kappa statistic was also calculated. Kappa value is a coefficient of agreement commonly used either for evaluating intra-classifier or inter-classifier reliability, and its measurement takes on greater significance for unbalanced datasets. The calculation of this statistic was detailed by Mchugh (2012). Chemometric data processing was made using R-project software version 3.3.3 (R Core Team, 2017) with caret and chemometric-with-R packages.

3. Results and discussion

The analysis of LIBS spectra from rice samples showed the most of the valuable and high-intensity spectral lines were in following spectral ranges: 247.8 to 343.7, 399.6 to 480.4 and 549.5 to 594.1 nm. After data acquisition, the integrated LIBS spectra were projected on computing platform of R-project software. The software identified collinear variables and peaks with identical areas in the sample groups, which could affect the classification performance. Therefore, the original spectral data was reduced by selecting valuable and high-intensity emission lines as descriptors for the chemometric analysis. The spectral lines assigned to the elements C, Ca, Fe, Mg, N and Na were selected as the input variables for rice varieties predictive modeling. The assignments of these lines were made using the database of the National Institute of Standards and Technology (NIST, 2019). Fig. 1 shows an average spectrum of a rice sample where the selected variables were highlighted. The potential of C, Ca, Fe, Mg, N and Na elements to discriminate rice samples has already been reported by other authors (Luo et al., 2019; Maione, Batista, Campiglia, Barbosa, & Barbosa, 2016; Pérez-rodríguez et al., 2019; Promchan et al., 2016; Yang, Zhou, et al., 2018; Yang, Zhu et al., 2018).

The parameters affecting the SVM classification performance were optimized by multivariate analysis using a CCD (Mason, Gunst, & Hess, 2003). The best conditions for predictive modeling have been established considering the penalty factor (C), and insensitive loss function (γ). The effects of these parameters on the overall accuracy were studied using five levels ($-\sqrt{2}$, –1, 0, +1, and $\sqrt{2}$) to model a second order polynomial. The levels of a CCD are $\sqrt{2}$ coded units distant from the central level (coded as zero level), so all the points lie on a circumference with radius $\sqrt{2}$. The maximum (+1) and minimum (–1) levels for each parameter were defined on the basis of the run tests previously performed, and the values of the levels corresponding to $-\sqrt{2}$, 0, and $\sqrt{2}$ were calculated. Table 1 shows the design matrix with coded and uncoded studied levels of C and γ factors, and the thirteen experiments randomly performed in order to obtain the combination leading to greater accuracy. In addition, Kernel trick was evaluated in order to enable the input data transformation in a linearly separable higher-dimensional feature space (Moncayo, Manzoor, & Caceres, 2015). For this proposal, several functions based on linear, polynomial, gaussian, sigmoid and radial basis function (RBF) kernel, were carried out to test the classification. The use of the latter allowed obtaining the best prediction results in the training samples probably due to its ability to handle multivariate data, and therefore the RBF kernel was set for all the optimization runs.

Table 1
Matrix obtained from the central composite design.

Experiment	Levels of coded factors[a]		Levels of uncoded factors[a]	
	C (AU)	γ (AU)	C (AU)	γ (AU)
1	–1	–1	0.50	0.010
2	$-\sqrt{2}$	0	0.45	0.055
3	$+\sqrt{2}$	0	11.97	0.055
4	0	0	5.25	0.055
5	0	0	5.25	0.055
6	0	$+\sqrt{2}$	5.25	0.119
7	+1	+1	10.00	0.100
8	0	0	5.25	0.055
9	+1	–1	10.00	0.010
10	–1	+1	0.50	0.100
11	0	$-\sqrt{2}$	5.25	0.009
12	0	0	5.25	0.055
13	0	0	5.25	0.055

[a] C: penalty factor; γ: insensitive loss function.

The resulting two-dimensional graph of contour curves is shown in Fig. 2. The dark green region represents the maximum overall accuracy and indicates the levels of the parameters to which the prediction in test samples was most successful.

The multiple regression analysis resulted in the following equation:

$$A = 0.2448 + 0.06790 \times C + 5.190 \times \gamma - -0.003450 \times C^2 - -18.54 \times \gamma^2 + 0.07300 \times C \times \gamma$$

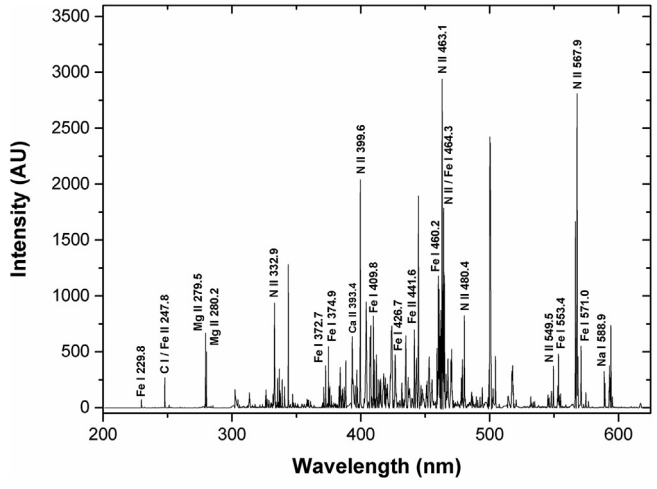

Fig. 1. Average spectra of different rice varieties showing the selected emission lines and corresponding elements used as input variables for sample classification.

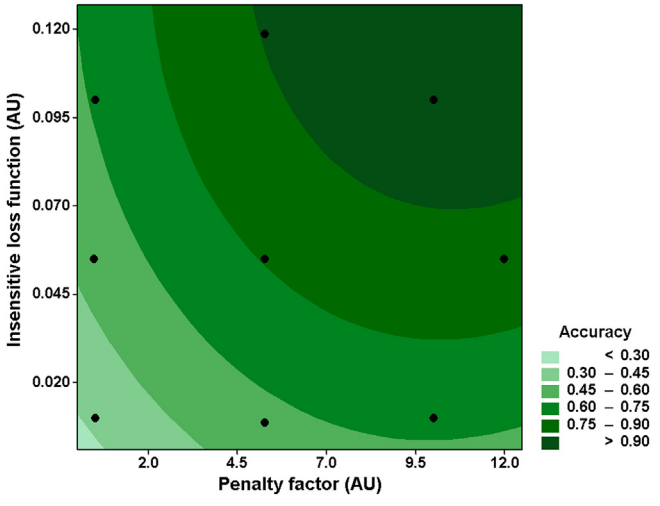

Fig. 2. Central composite design contour curves obtained for the influence of the penalty factor and insensitive loss function parameters on prediction accuracy.

Table 2
Classification metrics obtained from optimized parameters of SVM.

Variety	Number of samples		Sensitivity(%)	Specificity(%)	Balanced accuracy(%)
	Training	Test			
Guri	11	4	100	100	100
Irga 424	16	6	100	95	97.4
Puitá	15	5	93	100	96.7
Taim	12	3	92	100	95.8
Optimized parameters[a]			C = 5.25; γ = 0.119		
Overall accuracy (%)			96.4		
Kappa value			0.952		

[a] C: penalty factor; γ: insensitive loss function.

Where, A is the response factor corresponding to the overall accuracy, C is the penalty factor, and γ is the insensitive loss function. The adjusted regression coefficient was 93.9%, indicating that the quadratic regression model obtained was able to explain the relationship between the prediction results and the effects of the parameters studied.

Based on the analysis of Fig. 2, it was possible to identify the most suitable region for predicting the rice varieties. The ranges of studied parameters showing the best success rates were 5.25 to 10.0 for penalty factor and 0.055 to 0.119 for insensitive loss function. The optimal classifier was obtained when the parameters $C = 5.25$ and $\gamma = 0.119$ were used, achieving the highest overall accuracy of 96.4%. These optimized values were therefore selected to classify the rice samples according to their botanical variety.

After the optimization of the classifier parameters, it was again trained and validated. Table 2 shows the metrics calculated per class for the best fitted model. The balanced accuracies in prediction of test samples were 100% for Guri, 97.4% for Irga 424, 96.7% for Puitá and 95.8% for Taim samples; and the sensitivities and specificities were in the ranges 92–100% and 95–100%, respectively. Furthermore, this model also showed a kappa value of 0.952 being within the data reliability range of 82–100%, which indicates an almost perfect agreement between the predicted classes and the real classes.

The optimized SVM parameters by two-dimensional response surface analysis allowed improving classification algorithm performance in terms of higher modeling speed, stability and accuracy. Additionally, it favored the computing environment to develop a mathematical model with greater consistency and reproducibility in the prediction results.

4. Conclusions

A new method based on SD-LIBS was developed to authenticate rice samples according to their botanical origin using an optimized SVM model. The predictors for classification were related to C, Ca, Fe, Mg, N and Na elements. A CCD was used to optimize SVM performance. The optimal classifier was built using parameters $C = 5.25$ and $\gamma = 0.119$, which achieved an overall accuracy of 96.4% in test samples. This is the first work describing the chemometric optimization of a SVM model from LIBS profiling to solve rice classification issues. The ability and flexibility of this algorithm for building a generalized rice genotype predictive model have been demonstrated in this work.

The developed method is simpler, faster, and more efficient, compared to other methodologies previously described. Its application could contribute to reduce the number of runs to be undertaken to find a tuned classifier and improving quality of prediction results, and modeling time and computing handling were therefore substantially decreased. Furthermore, the analytical approach addressed here is environmentally safe because it no resulting chemical residues.

CRediT authorship contribution statement

Michael Pérez-Rodríguez: Formal analysis, Writing - original draft, Writing - review & editing. **Pamela Maia Dirchwolf:** Formal analysis. **Tiago Varão Silva:** Formal analysis. **Alan Lima Vieira:** Formal analysis. **José Anchieta Gomes Neto:** Formal analysis, Writing - review & editing. **Roberto Gerardo Pellerano:** Formal analysis, Writing - review & editing. **Edilene Cristina Ferreira:** Formal analysis, Writing - original draft, 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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References

Andrade, D. F., & Pereira-filho, E. R. (2016). Direct determination of contaminants, major and minor nutrients in solid fertilizers using Laser-Induced Breakdown Spectroscopy (LIBS). *Journal of Agricultural and Food Chemistry, 64*, 7890–7898.

Becerra, V., Paredes, M., Gutiérrez, E., & Rojo, C. (2015). Genetic diversity, identification, and certification of Chilean rice varieties using molecular markers. *Chilean Journal of Agricultural Research, 75*, 267–274.

Bol'shakov, A. A., Mao, X., & Russo, R. E. (2017). Spectral emission enhancement by an electric pulse for LIBS and LAMIS. Journal of Analytical Atomic Spectrometry, 32, 657–670.

Bona, E., Marquetti, I., Link, J. V., Makimori, G. Y. F., Arca, V. da C., Lemes, A. L. G., Ferreira, J. M. G., Scholz, M. B. dos S., Valderrama, P., & Poppi, R. J. (2017). Support vector machines in tandem with infrared spectroscopy for geographical classification of green arabica coffee. LWT - Food Science and Technology Journal, 76, 330–336.

Brondani, C., Borba, T. C. O., Rangel, P. H. N., & Brondani, R. P. V. (2006). Determination of genetic variability of traditional varieties of Brazilian rice using microsatellite markers. *Genetics and Molecular Biology, 29*(4), 676–684.

Busser, B., Moncayo, S., Coll, J., Sancey, L., & Motto-ros, V. (2018). Elemental imaging using laser-induced breakdown spectroscopy: A new and promising approach for biological and medical applications. *Coordination Chemistry Reviews, 358*, 70–79.

Butler, O. T., Cairns, W. R. L., Cook, J. M., Davidson, C. M., & Mertz-kraus, R. (2018). Atomic spectrometry update – a review of advances in environmental analysis. *Journal of Analytical Atomic Spectrometry, 33*, 8–56.

Chuang, H., Lur, H., Hwu, K., & Chang, M. (2011). Authentication of domestic Taiwan rice varieties based on fingerprinting analysis of microsatellite DNA markers. *Botanical Studies, 52*, 393–405.

Gupta, J. (2015). Identification and Classification of Rice varieties using Mahalanobis Distance by Computer Vision. *International Journal of Scientific and Research Publications, 5*, 1–6.

Itani, T., Tamaki, M., Arai, E., & Horino, T. (2002). Distribution of amylose, nitrogen, and minerals in rice kernels with various characters. *Journal of Agricultural and Food Chemistry, 50*, 5326–5332.

Lantz, B. (2015). Machinelearning with R (Second Ed.). Birmingham: Packt Publishing Ltd.

Li, Y., Tian, D., Ding, Y., Yang, G., Liu, K., Wang, C., & Han, X. (2018). A review of laser-induced breakdown spectroscopy signal enhancement. *Applied Spectroscopy Reviews, 53*(1), 1–35.

Lu, L., Tian, S., Liao, H., Zhang, J., Yang, X., Labavitch, J. M., & Chen, W. (2013). Analysis of metal element distributions in rice (Oryza sativa L.) seeds and relocation during germination based on X-Ray fluorescence imaging of Zn, Fe, K, Ca, and Mn. PLoS One, 8, e57360.

Luo, Z., Zhang, L., Chen, T., Liu, M., Chen, J., Zhou, H., & Yao, M. (2019). Rapid identification of rice species by laser-induced breakdown spectroscopy combined with pattern recognition. *Applied Optics, 58*, 1631–1638.

Maione, C., Batista, B. L., Campiglia, A. D., Barbosa, F., & Barbosa, R. M. (2016). Classification of geographic origin of rice by data mining and inductively coupled plasma mass spectrometry. *Computers and Electronics in Agriculture Journal, 121*, 101–107.

Mason, R. L., Gunst, R. F., & Hess, J. L. (2003). Statistical design and analysis of experiments. 2nd ed. Hoboken, New Jersey: Wiley.

Mchugh, M. L. (2012). Interrater reliability: The kappa statistic. *Biochemia Medica, 22*, 276–282.

Meng, F., Wei, Y., & Yang, X. (2005). Iron content and bioavailability in rice. *Journal of Trace Elements in Medicine and Biology, 18*, 333–338.

Miziolek, A. W., Palleschi, V., & Schechter, I. (2006). Laser-induced breakdown spectroscopy (LIBS) – Fundamentals and Applications (1st Ed.). New York – USA:

Cambridge University Press.
Moncayo, S., Manzoor, S., & Caceres, J. O. (2015). Chemometrics and Intelligent Laboratory Systems Evaluation of supervised chemometric methods for sample classi fi cation by Laser Induced Breakdown Spectroscopy. *Chemometrics and Intelligent Laboratory Systems, 146*, 354–364.
NIST Atomic Spectra (2019). Accessed from https://physics.nist.gov/PhysRefData/ASD/lines _form.html. *Database*.
Noll, R., Fricke-Begemann, C., Connemann, S., Meinhardt, C., & Sturm, V. (2018). LIBS analyses for industrial applications – an overview of developments from 2014 to 2018. *Journal of Analytical Atomic Spectrometry, 33*, 945–956.
Peng, J., He, Y., Jiang, J., Zhao, Z., Zhou, F., & Liu, F. (2019). High-accuracy and fast determination of chromium content in rice leaves based on collinear dual-pulse laser-induced breakdown spectroscopy and chemometric methods. *Food Chemistry, 295*, 327–333.
Peng, J., He, Y., Zhao, Z., Jiang, J., Zhou, F., & Liu, F. (2019). Fast visualization of distribution of chromium in rice leaves by re-heating dual-pulse laser-induced breakdown spectroscopy and chemometric methods. *Environmental Pollution, 252*, 1125–1132.
Pérez-rodríguez, M., Dirchwolf, P. M., Silva, T. V., Villafañe, R. N., Neto, J. A. G., Pellerano, R. G., & Ferreira, E. C. (2019). Brown rice authenticity evaluation by spark discharge-laser-induced breakdown spectroscopy. *Food Chemistry, 297*, 124960.
Promchan, J., Günther, D., Siripinyanond, A., & Shiowatana, J. (2016). Elemental imaging and classifying rice grains by using laser ablation inductively coupled plasma mass spectrometry and linear discriminant analysis. *Journal of Cereal Science, 71*, 198–203.
R Core Team (2017). R: A language and environment for statistical computing. R Foundation for Statistical Computing. Accessed from https://www.r-project.org/.
Rehse, S. J., Salimnia, H., & Miziolek, A. W. (2012). Laser-induced breakdown spectroscopy (LIBS): An overview of recent progress and future potential for biomedical applications. *Journal of Medical Engineering & Technology, 36*, 77–89.
Sezer, B., Bilge, G., Sanal, T., Koksel, H., & Boyaci, I. H. (2017). A novel method for ash analysis in wheat milling fractions by using laser-induced breakdown spectroscopy. *Journal of Cereal Science, 78*, 33–38.
Sobral, H., & Robledo-martinez, A. (2016). Signal enhancement in laser-induced breakdown spectroscopy using fast square-pulse discharges. *Spectrochimica Acta Part B: Atomic Spectroscopy, 124*, 67–73.
Sun, L., Yu, H., Cong, Z., Lu, H., Cao, B., Zeng, P., ... Li, Y. (2018). Applications of laser-induced breakdown spectroscopy in the aluminum electrolysis industry. *Spectrochimica Acta Part B: Atomic Spectroscopy, 142*, 29–36.
Tiwari, J. K., Rastogi, N. K., Chandrakar, P. K., Sarawgi, A. K., & Verulkar, S. B. (2013). Identification of rice varieties through chemical tests. *Seed Research, 41*, 83–90.
Vieira, A. L., Silva, T. V., de Sousa, F. S. I., Senesi, G. S., Santos, D., Ferreira, E. C., & Neto, J. A. G. (2018). Determinations of phosphorus in fertilizers by spark discharge-assisted laser-induced breakdown spectroscopy. *Microchemical Journal, 139*, 322–326.
Wang, L., Liu, D., Pu, H., Sun, D., Gao, W., & Xiong, Z. (2015). Use of Hyperspectral Imaging to Discriminate the Variety and Quality of Rice. *Food Analytical Methods, 8*, 515–523.
Yang, P., Zhou, R., Zhang, W., Tang, S., Hao, Z., Li, X., ... Zeng, X. (2018). Laser-induced breakdown spectroscopy assisted chemometric methods for rice geographic origin classification. *Applied Optics, 57*, 8297–8302.
Yang, P., Zhu, Y., Yang, X., Li, J., Tang, S., Hao, Z., ... Lu, Y. (2018). Evaluation of sample preparation methods for rice geographic origin classification using laser-induced breakdown spectroscopy. *Journal of Cereal Science, 80*, 111–118.
Zhao-yan, L., Fang, C., Yi-bin, Y., & Xiu-qin, R. (2005). Identification of rice seed varieties using neural network. *Journal of Zhejiang University SCIENCE, 6B*, 1095–1100.
Zhu, L., Sun, J., Wu, G., Wang, Y., Zhang, H., & Wang, L. (2018). Identification of rice varieties and determination of their geographical origin in China using Raman spectroscopy. *Journal of Cereal Science, 82*, 175–182.
Zorov, N. B., Popov, A. M., Zaytsev, S. M., & Labutin, T. A. (2015). Qualitative and quantitative analysis of environmental samples by laser-induced breakdown spectrometry. *Russian Chemical Reviews, 84*, 1021–1050.