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Comparison of different calibration techniques of laser induced breakdown spectroscopy in bakery products: on NaCl measurement

Gonca Bilge¹, Kemal Efe Eseller^{2*} , Halil Berberoglu³, Banu Sezer⁴, Ugur Tamer⁵ and Ismail Hakki Boyaci⁴

Abstract

Laser induced breakdown spectroscopy (LIBS) is a rapid optical spectroscopy technique for elemental determination, which has been used for quantitative analysis in many fields. However, the calibration involving atomic emission intensity and sample concentration, is still a challenge due to physical-chemical matrix effect of samples and fluctuations of experimental parameters. To overcome these problems, various chemometric data analysis techniques have been combined with LIBS technique. In this study, LIBS was used to show its potential as a routine analysis for Na measurements in bakery products. A series of standard bread samples containing various concentrations of NaCl (0.025%–3.5%) was prepared to compare different calibration techniques. Standard calibration curve (SCC), artificial neural network (ANN) and partial least square (PLS) techniques were used as calibration strategies. Among them, PLS was found to be more efficient for predicting the Na concentrations in bakery products with an increase in coefficient of determination value from 0.961 to 0.999 for standard bread samples and from 0.788 to 0.943 for commercial products.

Keywords: Laser induced breakdown spectroscopy, Artificial neural network, Partial least square, Bakery products, Sodium

Introduction

Laser induced breakdown spectroscopy (LIBS) is an atomic emission spectroscopy technique in which laser beam excites and intensively heats the surface of sample. Excited sample is taken to a gaseous plasma state and dissociated to all molecules and fine particles, which produces a characteristic plasma light. Intensity of this plasma light is associated with concentration of the elements in the sample. LIBS has many advantages as it allows for rapid, real-time and in situ field analysis without the need for sample preparation [1–10]. Moreover, its application has expanded to the fields such as

metallurgy, mining, environmental analysis and pharmacology [11–14].

Intensity of LIBS signal is influenced by various factors including laser energy, detection time window, distance between lens and chemical and physical matrix [15]. Chemical matrix effect is the most important one since the molecular and chemical composition of the sample is directly related with chemical matrix, and it perturbs the LIBS plasma [16]. Minor elements in the sample structure can cause matrix effects and interactions on the major element spectral lines. Furthermore, LIBS signal intensity is influenced by atmospheric composition, and occurred plasma products are interacted with sample surface. To overcome matrix effect, many approaches have been developed. Traditionally, spectral peak intensity or peak area is analyzed through LIBS data versus

* Correspondence: efe.eseller@atilim.edu.tr

²Department of Electrical and Electronics Engineering, Atilim University, 06836 Ankara, Turkey

Full list of author information is available at the end of the article

concentration of samples for quantitative analyses, which is the standard calibration curve method (SCC) [17]. Chemometric techniques are being used more widely in order to enhance analytical performance of LIBS [18]. Recent works have shown that multivariate analysis such as partial least square (PLS) and artificial neural network (ANN) give promising results for quantitative analysis [19–22]. These advanced techniques reduce the complexity of spectra and enable valuable information. In LIBS analysis, many fluctuating experimental parameters decrease the relation between elemental composition and LIBS intensity [23]. ANN provide a mathematical model from input data and gives information about unknown samples processing like a human neural network. It simulates the human intelligence for objective learning. ANN has been used for identification of polymers by LIBS [24] analysis of LIBS data for three chromium doped soils [25], and quantification of element in soils and rocks [26]. The other most commonly used chemometric method is PLS. It is a pattern recognition technique which can analyze bunch of spectral lines instead of a single specific line intensity as in standard calibration curve method. As a consequence, combination of chemometric methods and LIBS technique have given promising results for quantitative studies.

Na is an essential element for human diet. However, if consumed excessively, it may cause some health problems such as high blood pressure [27], strokes and coronary heart diseases [28]. Thus, sodium levels in food should be controlled. In a human diet, 70–75% of the total sodium chloride (NaCl) intake is obtained from processed foods, out of which cereal and cereal products constitute approximately 30% [29]. Therefore, NaCl content in bread, the most consumed food all over the world, should be lowered and adhered to Codex Alimentarius. Na content can be controlled by using standard methods such as flame atomic absorption spectrometry (AAS), titration and potentiometry [30, 31]. These methods are time consuming and complex due to their sample preparation process and their inconvenience for in situ and point detection analyses. Therefore, new, rapid and practical techniques are required.

LIBS has been used in several applications such as milk, bakery products, tea, vegetable oils, water, cereals, flour, potatoes, palm date and different types of meat [32]. Food supplements have been investigated to identify spectral signatures of minerals (Ca, Mg, C, P, Zn, Fe, Cu, and Cr) [33]. Quantitative analysis of NaCl in bakery products has been analyzed by standard calibration curve [34, 35]. For the present study, we performed a measurement of Na concentrations in bakery products by LIBS and conducted a direct comparison between standard calibration curve, ANN and PLS in terms of prediction accuracy and prediction precision.

Combination of LIBS technique and PLS model is a promising method to perform routine analysis for Na measurements in bakery products. In this paper, three calibration methods (SCC, ANN, PLS) have been compared in bakery food applications for the first time.

Experimental

LIBS experimental setup

LIBS spectra were recorded using a Quantel-Big Sky Nd:YAG-laser (Bozeman, MT, USA), HR2000 Ocean optics Spectrograph (Dunedin, FL, USA) and Stanford Research System Delay Generator SRS DG535 (Cleveland, OH, USA). Figure 1 shows the experimental setup. The excitation source was Q-switched Nd:YAG laser (Quantel, Centurion), operating at 532 nm with maximum energy of 18 mJ per pulse and approximately 9 ns (FWHM) pulse duration. Laser repetition rate is adjustable in the range of 1–100 Hz, but the experiment is performed at 1 Hz. The beam diameter at the exit was 3 mm with 5 mrad divergence. A 50 mm focal length lens was used to focus the beam size on to the pellet surface. Emitted plasma was collected with a pickup lens in 50 mm diameter and aligned at approximately 90 degree with respect to laser beam and then coupled to the fiber tip of the spectrometer. The distance between the pickup lens and the focal point of the laser beam is approximately 15 cm. In this work, HR2000 (Ocean Optics) spectrometer was used as the detection system with a resolution of approximately 0.5 nm in the 200–1100 nm range. 588.6 nm Na line was detected by gating the spectrometer 0.5 μ s after the laser pulse and with a 20 μ s gate width. All measurements were performed under ambient conditions and exposed to atmosphere. Samples were measured by the LIBS technique in triplicate, scanning five different locations and four excitations per location.

Sample preparation

Bread flour and bread additive yeast were purchased from a local market. Nitric acid (HNO₃) and NaCl were purchased from Sigma Aldrich (Steinheim, Germany). Standard bread samples were prepared in accordance with American Association of Cereal Chemists (AACC) Optimized Straight-Dough Bread-Baking Method No. 10–10.03 [33]. Twelve standard bread samples were produced by using this method at various salt concentrations ranged between 0.025 and 3.5%. The bread dough, comprising 100 g flour, 0.2 g bread additive, 25 ml of 8% yeast solution, 25 ml salt solution at various concentrations and 10 ml water, was kneaded by hand for 15 min. Dough pieces were rounded and incubated for 30 min during the first fermentation. 30 min later, the dough was punched and incubated for another 30 min during the second fermentation. After that, the dough was formed, placed into tins for the final fermentation and

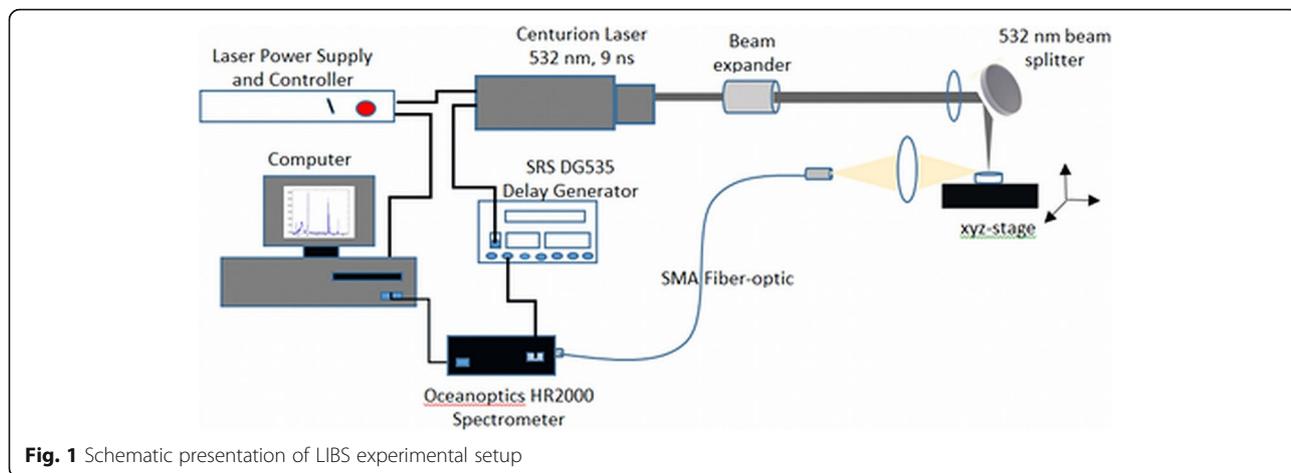


Fig. 1 Schematic presentation of LIBS experimental setup

incubated for 55 min at 30 °C. Subsequently, the bread was baked for 30 min at 210 °C, taken out of the oven and cooled. Following this process,, bread samples were dried at 105 °C for 2 h and cooled in a desiccator to be used for the LIBS measurements. Then, 400 mg of dried powdered bread samples were shaped into a pellet under 10 t of pressure using a pellet press machine.

Na detection in bakery products by atomic absorption spectroscopy

Na content of standard bread samples and commercial samples were analyzed by atomic absorption spectroscopy (reference method for Na measurements). Samples were prepared based on the EPA Method 3051A through microwave-assisted digestion for atomic absorption spectroscopy measurements [36]. At the beginning, 0.3 g of the dried sample and 10 ml concentrated HNO3 were placed in a fluorocarbon polymer vessel. The samples were extracted by heating with a laboratory microwave unit. Next, the vessel was sealed and heated in the microwave unit. After cooling, the vessel contents were filtered with Whatman No. 1 filter paper and diluted in 100 ml of deionized water. The atomic absorption spectra for Na were recorded with the ATI-UNICAM 939 AA Spectrometer (Cambridge, UK) at 588.599 nm.

Data analysis

Data analyses were performed by SCC, PLS and ANN. Calibration and validation results were obtained and compared with each other. Performances of the models were evaluated according to coefficient of determination (R²), relative error of prediction (REP), and relative standard deviation (RSD). After that, LIBS spectra of commercial products were analyzed to examine the matrix effect. To compare the 3 methods, REP values were used to evaluate the prediction accuracy.

$$REP(\%) = \frac{100}{N_v} \sum_{i=1}^{N_v} \left| \frac{\hat{c}_i - c_i}{c_i} \right| \tag{1}$$

N_v = number of validation spectra.

c_i = true concentration.

ĉ_i = predicted concentration.

In addition, we used RSD as a prediction precision indicator.

$$RSD(\%) = \frac{100}{N_{conc}} \sum_{k=1}^{N_{conc}} \frac{\sigma_{c_k}}{C_k} \dots \text{with } \sigma_{C_k^2} = \sum_{i=1}^{\rho} \frac{(\hat{c}_{ik} - c_k)^2}{\rho - 1} \tag{2}$$

N_{conc} = number of different concentrations in the validation set.

ρ = number of spectra per concentration.

σ = Standard deviation.

We first presented the quantitative results of LIBS data according to standard calibration method which is based on the measurement of Na atomic emission at 588.599 nm in standard bread samples. In this method, instrumental noise was subtracted from spectra. Then, background normalization was applied according to 575.522 nm where there is no atomic emission spectral line. Scanning five different locations and four excitations per location, we analyzed the samples by the LIBS technique in triplicate, for each sample (pellet) 20 shuts were accumulated. The calibration curves for the Na line at 588.599 nm were obtained by plotting its intensity (peak height) versus the Na concentrations in each sample. Twenty-six data (each of them includes 20 spectra) for calibration, 13 data for prediction of SCC method were used. Following that, LIBS spectra of commercial products were analyzed via SCC method, and the

results were compared with measured Na concentrations by AAS.

In this study we used two different multivariate analysis methods. One of them is PLS in which we used the same data set as in previous work [34]. Data of LIBS spectra ranged between 538.424 nm and 800.881 nm were used instead of whole spectrum because the most quantitative data could be obtained from this region. LIBS data matrix was obtained by analyzing the spectra of 39 standard bread samples (26 samples for calibration, 13 samples for the validation) for PLS analysis. Data analysis was performed using PLS with Stand-alone Chemometrics Software (Version Solo 6.5 for Windows 7, Eigenvector Research Inc., Wenatchee, WA, USA). Data matrix of selected LIBS data and concentration was embedded into the software as calibration data, and PLS algorithm was performed using different components between 1 and 15. Mean center was applied as pre-processing to calibration input data. Prediction ability of obtained model was determined with the validation data set. Selection of latent variable's number related to the difference between cumulative variance and the prediction ability is very important. While cumulative variance increases with the latent variable number - which is 11 for this study-, prediction ability does not increase after obtaining the model. For this reason, it is important to find optimum approach between cumulative variance and prediction ability. In the PLS model, predictability was determined by calculating the root mean square error of calibration (RMSEC) and root mean square error of prediction (RMSEP) for the validation [37]. Minimum RMSEC and RMSEP values were selected for PLS model. After that, Na concentrations in commercial products were analyzed by PLS, and results were compared with results of AAS.

$$RMSEC = \sqrt{\frac{\sum_{i=1}^m (actual - calculated)^2}{M-1}}$$

$$RMSEP = \sqrt{\frac{\sum_{i=1}^n (actual - calculated)^2}{N}}$$

M: number of samples used in calibration data set.

N: number of samples used in prediction data set.

The other applied multivariate method is ANN. The same experimental data were used for quantitative analysis with The Neural Network Toolbox, MATLAB® Release 14 (The Mathworks, Natick, MA). The independent variable is the LIBS spectra between 538.424 nm and 800.881 nm, and dependent variable is the Na concentrations. Similar to the PLS method, 26

data set was used for calibration, 13 data set was used for validation of the trained network. We used the neural network functions of training for calibration and transfer functions of logsig and purelin for validation. Then, the number of nodes in hidden layer was optimized between 1 and 10, and it was found that seven hidden nodes showed the best performance.

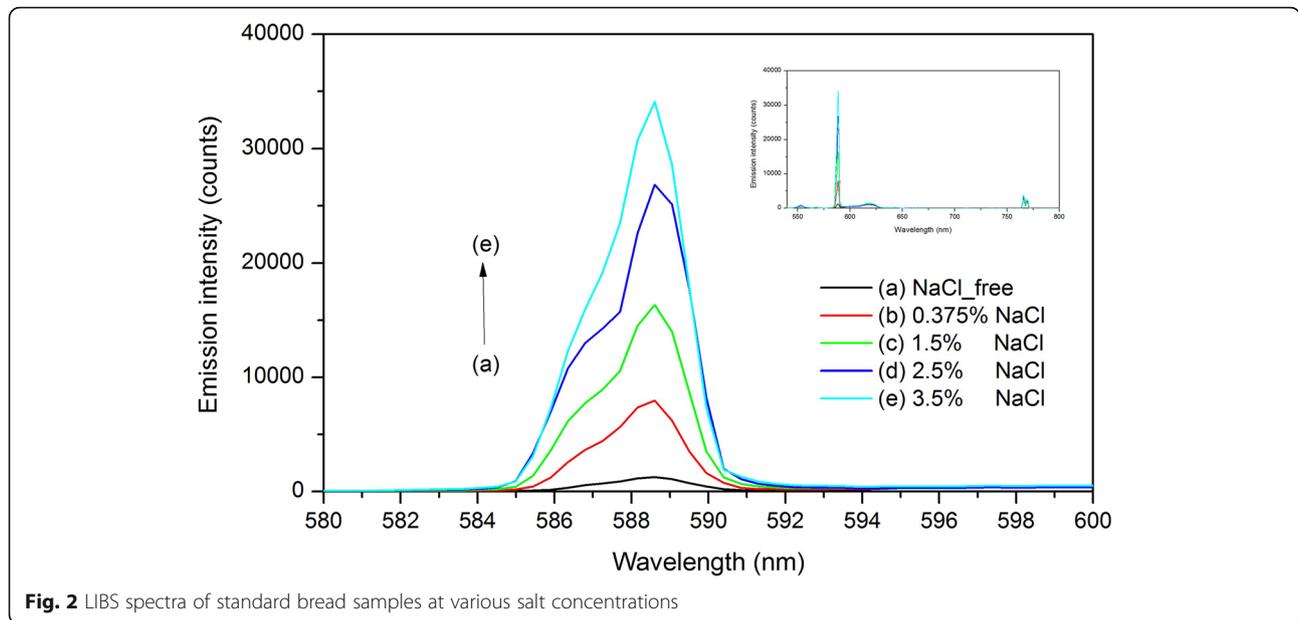
The coefficient of determination (R^2) value was considered for evaluating of the prediction capability of the method and choosing the network. Estimation value of ANN was determined by comparing the actual values and predicted values. After that, Na concentrations in commercial products were analyzed by ANN, and the results were compared with results of AAS.

Results and discussion

For the calibration study, a total of 780 spectra (20 spectra for each pellet, 3 pellet for each sample, 13 standard bread sample) and for commercial products a total of 360 spectra (20 spectra for each pellet, 3 pellet for each sample, 13 standard bread sample) were recorded by LIBS. Figure 2. illustrates the LIBS spectra of different amount of NaCl containing standard bread samples. The peak at 588.599 nm belongs to Na and peak at 769.900 nm belongs to K according to NIST atomic data base [38]. Figure 2 shows that as the intensity of Na band at 588.599 nm increases, the NaCl levels in breads rises, as well.

Calibration models were developed according to three different methods, which are SCC, ANN and PLS for quantitative treatments attained from a calibrated data set (standard bread samples). Then, prediction ability of the regression of obtained model was evaluated via validation data set (standard bread samples, excluding the calibration data set, were treated as unknown) to test the accuracy and precision of calibration model. After that, Na concentrations of commercial products were predicted and compared with results of standard method AAS. This treatment is found to be useful for evaluating the matrix effect and the potential of LIBS in commercial samples.

The traditional way to obtain calibration curve is using reference samples which contain constant concentrations of major element and varying concentrations of target element. For this purpose, standard bread samples were prepared at different salt concentrations and analyzed via LIBS. Standard calibration curve of Na was obtained by plotting its intensity at 588.599 nm versus the measured Na concentrations (Fig. 3a). Each point in calibration curve demonstrates the average value of 3 pellet samples, and each pellet contains accumulation of 20 laser shut. RSD, REP values and the other results were summarized for this calibration strategy in Table 1.



PLS calibration was performed using the same standard bread samples with known NaCl concentrations. The spectral interval of 538.424 nm to 800.881 nm was chosen because most of the atomic emission lines are in this region. For enhancing the performance of PLS method, mean center was applied as pre-processing to calibration input data. Formed PLS calibration model and validation data set are presented in Fig. 3c. Low RMSEC (0.01835) value and high coefficient of determination was chosen to develop the calibration model. Low RMSEC (0.01835) and RMSEP (0.10925) values were chosen for validation. The high coefficient of determination values, $R^2 = 0.999$ for calibration and $R^2 = 0.991$ for validation were observed (Fig. 3c). RSD and REP values of PLS is presented in Table 1.

In addition to the PLS method, ANN was also used for Na quantification in standard bread samples. Same

calibration and validation data set were used for ANN model. The networks that had maximum R^2 values between predicted and actual data were selected as the best trained network. Then, the best-trained network was used for prediction of Na content in standard breads with ANN. The predicted calibration and validation data sets were compared with experimental data sets and high correlations were obtained for Na concentrations (Fig. 3b). High coefficient of determination values, ($R^2 = 0.987$) and ($R^2 = 0.964$), were observed for calibration and validation data sets, respectively. REP and RSD values of ANN model is presented in Table 1.

When the PLS method was compared with standard calibration curve and ANN methods according to Table 1, the PLS method gave the best results with R^2 values of 0.999 for calibration and 0.991 for validation. Furthermore, PLS has shown an excellent potential with high

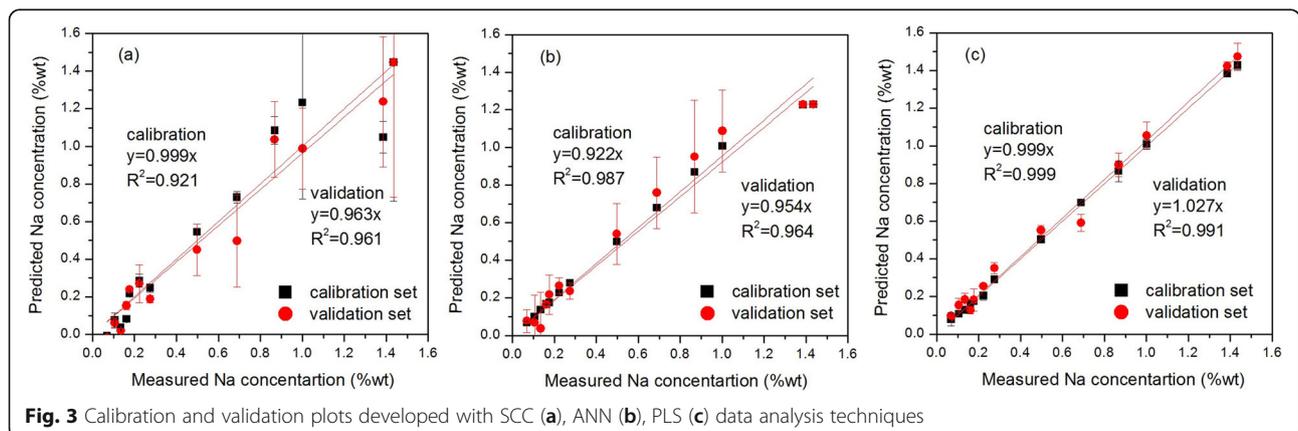


Table 1 Prediction of Na concentrations in standard bread samples with SCC, ANN and PLS

	SCC	ANN	PLS
R ² for calibration	0.921	0.987	0.999
R ² for validation	0.961	0.964	0.991
REP	28.92%	36.29%	19.42%
RSD	26.31%	25.31%	11.23%

prediction precision and prediction accuracy compared to other methods.

To make comparison, Na concentrations in commercial samples such as biscuits, crackers and some kinds of breads were also analyzed with AAS. Comparative results between AAS and LIBS for commercial products analyzed with SCC, ANN and PLS models were presented in Fig. 4a, b, c and RSD, REP values were summarized in Table 2. SCC is the most commonly applied method for quantitative analyses because of its simplicity. However, this method is only useful if the standard sample’s matrix resembles to the real sample’s matrix (<http://physics.nist.gov/PhysRefData/ASD/index.html>).

In addition experimental uncertainties may effect calibration curve. Low detection capabilities and matrix effects are negative factors for LIBS in SCC. Specific reference materials are preferred to obtain better calibration curves. However due to difficulties in obtaining proper reference materials, efficiency of SCC method is limited. Hence, this situation makes it more difficult to obtain the calibration set. Also in commercial products, PLS gave the best results with high prediction ability compared to other methods. Low RMSEC (0.29861) and RMSEP (0.13893) values were chosen for validation of commercial products. PLS model increased the R² value from 0.788 to 0.943 for commercial products. When the standard calibration curve for standard bread samples is considered, it is clear that the relation between Na

Table 2 Prediction of Na concentration in commercial products with SCC, ANN and PLS

	SCC	ANN	PLS
R ² for commercial products	0.788	0.426	0.943
RSD for commercial products	9.54%	17.07%	15.68%

concentration and LIBS signal is linear. PLS generates new principal components based on response of measured concentration data. Linear regression of the new principal components help to control the variation response variable [39]. Hence PLS yields precise calibration. This tendency explains why PLS gave better results than ANN, which is more convenient for nonlinear models. Principal of ANN model is based on receiving a series of input data evaluated by each neuron; therefore, data are weighted dynamically. It compares the weighted sum of its inputs to a given threshold value and performs the nonlinear function to calculate the output [18]. On the other hand, the overall performance of PLS are quite satisfactory with a high prediction accuracy and precision compared to other methods. High RSD values can be explained with fluctuating of LIBS experimental parameters such as changing plasma conditions and spectral interference. These problems can be overcome by obtaining high numbers of shuts for each sample. Prediction ability of PLS model is more satisfactory for validation data of standard bread samples than validation data of commercial products. This is due to matrix differences between standard bread samples and commercial products. Application field of PLS has expanded to biomedical, pharmaceutical, social science and other fields [39–42], and it has recently shown great potential in LIBS applications [43].

Combining LIBS and PLS methods to measure Na concentrations gave acceptable results for also commercial products because the PLS as a multivariate analysis

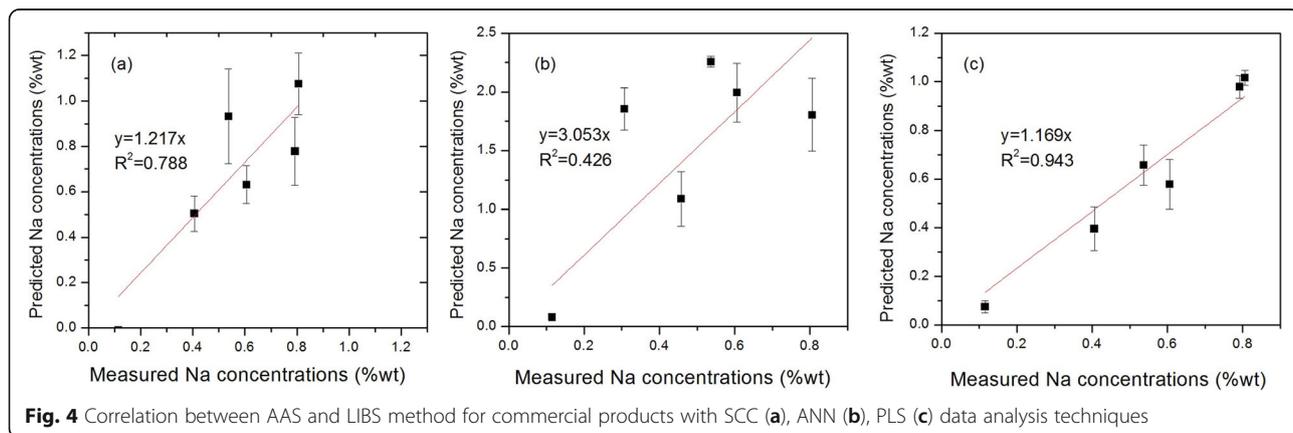


Fig. 4 Correlation between AAS and LIBS method for commercial products with SCC (a), ANN (b), PLS (c) data analysis techniques

is more accurate, robust and reliable compared to SCC method. Limit of detection (LOD) was calculated as 0.0279%, and limit of quantification (LOQ) was calculated as 0.0930% for PLS. In some studies, authors obtained lower detection limits, as low as 5 ppm [44] and even 0.1 ppb by using dual-pulse and crossed-beam Nd:YAG lasers for Na on a water film [45]. However, our LOD and LOQ values are quite low for food products, which makes this method convenient for measurement of Na even in dietary food.

Conclusion

Na is an important ingredient in food products both for its potential to cause health problems such as heart diseases and stroke, and for its usage as a quality control parameter influencing taste, yeast activity, strength of the gluten network, and gas retention [46]. Thus, Na levels in food should be controlled in accordance with the recommendations. Measurement of Na in breads can be performed by titration, AAS and potentiometric methods. These regulatory methods are time consuming and require sample preparation. In contrast, LIBS can be a rapid and valuable tool for Na measurement in bakery products.

A comparative study between the standard calibration curve, ANN and PLS methods was conducted for measurement of NaCl in bakery products. Calibration data set was obtained by preparing the standard bread samples at various salt concentrations. Optimization was performed for each calibration method. According to the calibration results, PLS method gave the best results for validation curves and prediction of commercial samples. Experimental results showed that PLS method enhanced the performance of LIBS for quantitative analysis. Thanks to the PLS method LIBS can be a valuable tool for routine NaCl measurements in bakery products.

Acknowledgements

Furthermore, we gratefully thank Assist. Prof. Dr. Aysel Berkkan for performing atomic absorption spectroscopy analysis.

Authors' contributions

Data Analysis and sample preparation have been performed by GB and BS, System optical design and data processing has been done by KEE and HB. IHB and UT performed the validation of theoretical framework which this research based on, polished the text and brought the manuscript into its final form. The authors read and approved the final manuscript.

Funding

This research received no external funding.

Availability of data and materials

There is no data that needs to be shared.

Declarations

Competing interests

The authors declare no conflict of interest.

Author details

¹Department of Food Engineering, Konya Food and Agriculture University, Meram 42080KonyaTurkey. ²Department of Electrical and Electronics Engineering, Atilim University, 06836 Ankara, Turkey. ³Department of Physics, Ankara Hacı Bayram Veli University, 06900 Polatlı-Ankara, Turkey. ⁴Food Research Center, Hacettepe University, Beytepe, 06800 Ankara, Turkey. ⁵Department of Analytical Chemistry, Faculty of Pharmacy, Gazi University, 06330 Ankara, Turkey.

Received: 18 December 2020 Accepted: 28 June 2021

Published online: 01 September 2021

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