

Comparison of Different Calibration Techniques by Laser Induced Breakdown Spectroscopy in Bakery Products

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4

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27 **ABSTRACT**

28

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

42

43 **Keywords:** Laser induced breakdown spectroscopy; Artificial neural network; Partial least
44 square; Bakery products; Sodium.

45 **1. Introduction**

46

47 Laser induced breakdown spectroscopy (LIBS) is an atomic emission spectroscopy
48 technique in which laser beam excites and intensively heats the surface of sample. Excited
49 sample is taken to a gaseous plasma state and dissociated to all molecules and fine particles,
50 which produces a characteristic plasma light. Intensity of this plasma light is associated with
51 concentration of the elements in the sample. LIBS has many advantages as it allows for rapid,
52 real-time and in situ field analysis without the need for sample preparation [1-10]. Moreover,
53 its application has expanded to the fields such as metallurgy, mining, environmental analysis
54 and pharmacology [11-14].

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

63 through LIBS data versus concentration of samples for quantitative analyses, which is the
64 standard calibration curve method (SCC) [17]. Chemometric techniques are being used more
65 widely in order to enhance analytical performance of LIBS [18]. Recent works have shown that
66 multivariate analysis such as partial least square (PLS) and artificial neural network (ANN)
67 give promising results for quantitative analysis [19-21]. These advanced techniques reduce the
68 complexity of spectra and enable valuable information. In LIBS analysis, many fluctuating
69 experimental parameters decrease the relation between elemental composition and LIBS
70 intensity [22]. ANN provide a mathematical model from input data and gives information about
71 unknown samples processing like a human neural network. It simulates the human intelligence
72 for objective learning. ANN has been used for identification of polymers by LIBS [23] analysis
73 of LIBS data for three chromium doped soils [24], and quantification of element in soils and
74 rocks [25]. The other most commonly used chemometric method is PLS. It is a pattern
75 recognition technique which can analyze bunch of spectral lines instead of a single specific line
76 intensity as in standard calibration curve method. As a consequence, combination of
77 chemometric methods and LIBS technique have given promising results for quantitative
78 studies.

79 Na is an essential element for human diet. However, if consumed excessively, it may cause
80 some health problems such as high blood pressure [26], strokes and coronary heart diseases
81 [27]. Thus, sodium levels in food should be controlled. In a human diet, 70-75% of the total
82 sodium chloride (NaCl) intake is obtained from processed foods, out of which cereal and cereal
83 products constitute approximately 30% [28]. Therefore, NaCl content in bread, the most
84 consumed food all over the world, should be lowered and adhered to Codex Alimentarius. Na
85 content can be controlled by using standard methods such as flame atomic absorption
86 spectrometry (AAS), titration and potentiometry [29-30]. These methods are time consuming

87 and complex due to their sample preparation process and their inconvenience for in situ and
88 point detection analyses. Therefore, new, rapid and practical techniques are required.

89 Quantitative analysis of bakery products has been analyzed by standard calibration curve
90 [31]. For the present study, we performed a measurement of Na concentrations in bakery
91 products by LIBS and conducted a direct comparison between standard calibration curve, ANN
92 and PLS in terms of prediction accuracy and prediction precision. Combination of LIBS
93 technique and PLS model is a promising method to perform routine analysis for Na
94 measurements in bakery products.

95

96 **2. EXPERIMENTAL**

97 **2.1. LIBS experimental setup**

98

99 LIBS spectra were recorded using a Quantel-Big Sky Nd:YAG-laser (Bozeman, MT,
100 USA), HR2000 Ocean optics Spectrograph (Dunedin, FL, USA) and Stanford Research System
101 Delay Generator SRS DG535 (Cleveland, OH, USA). Fig. 1 shows the experimental setup. The
102 excitation source was Q-switched Nd:YAG laser (Quantel, Centurion), operating at 532 nm
103 with maximum energy of 18 mJ per pulse and approximately 9 ns (FWHM) pulse duration.
104 Laser repetition rate is adjustable in the range of 1-100 Hz, but the experiment is performed at
105 1 Hz. The beam diameter at the exit was 3 mm with 5 mrad divergence. A 50 mm focal length
106 lens was used to focus the beam having about 10-micron spot size on to the pellet surface.
107 Emitted plasma was collected with a pickup lens in 50 mm diameter and aligned at
108 approximately 90 degree with respect to laser beam and then coupled to the fiber tip of the
109 spectrometer. The distance between the pickup lens and the focal point of the laser beam is
110 approximately 15 cm. In this work, HR2000 (Ocean Optics) spectrometer was used as the
111 detection system with a resolution of approximately 0.5 nm in the 200-1100 nm range. 588.6

112 nm Na line was detected by gating the spectrometer 0.5 μ s after the laser pulse and with a 20
113 μ s gate width. All measurements were performed under ambient conditions and exposed to
114 atmosphere. Samples were measured by the LIBS technique in triplicate, scanning five different
115 locations and four excitations per location.

116

117 **2.2. Sample preparation**

118

119 Bread flour and bread additive yeast were purchased from a local market. Nitric acid
120 (HNO₃) and NaCl were purchased from Sigma Aldrich (Steinheim, Germany). Standard bread
121 samples were prepared in accordance with American Association of Cereal Chemists (AACC)
122 Optimized Straight-Dough Bread-Baking Method No. 10-10.03 [32]. Twelve standard bread
123 samples were produced by using this method at various salt concentrations ranged between
124 0.025 and 3.5%. The bread dough, comprising 100 g flour, 0.2 g bread additive, 25 ml of 8%
125 yeast solution, 25 ml salt solution at various concentrations and 10 ml water, was kneaded by
126 hand for 15 min. Dough pieces were rounded and incubated for 30 min during the first
127 fermentation. 30 min later, the dough was punched and incubated for another 30 min during the
128 second fermentation. After that, the dough was formed, placed into tins for the final
129 fermentation and incubated for 55 min at 30 °C. Subsequently, the bread was baked for 30 min
130 at 210 °C, taken out of the oven and cooled. Following this process, bread samples were dried
131 at 105 °C for 2 h and cooled in a desiccator to be used for the LIBS measurements. Then, 400
132 mg of dried powdered bread samples were shaped into a pellet under 10 t of pressure using a
133 pellet press machine.

134 **2.3. Na detection in bakery products by atomic absorption spectroscopy**

135

136 Na content of standard bread samples and commercial samples were analyzed by atomic
137 absorption spectroscopy (reference method for Na measurements). Samples were prepared
138 based on the EPA Method 3051A through microwave-assisted digestion for atomic absorption
139 spectroscopy measurements [33]. At the beginning, 0.3 g of the dried sample and 10 ml
140 concentrated HNO₃ were placed in a fluorocarbon polymer vessel. The samples were extracted
141 by heating with a laboratory microwave unit. Next, the vessel was sealed and heated in the
142 microwave unit. After cooling, the vessel contents were filtered with Whatman No. 1 filter
143 paper and diluted in 100 ml of deionized water. The atomic absorption spectra for Na were
144 recorded with the ATI-UNICAM 939 AA Spectrometer (Cambridge, UK) at 588.599 nm.

145

146 **2.4. Data analysis**

147

148 Data analyses were performed by SCC, PLS and ANN. Calibration and validation results
149 were obtained and compared with each other. Performances of the models were evaluated
150 according to coefficient of determination (R^2), relative error of prediction (REP), and relative
151 standard deviation (RSD). After that, LIBS spectra of commercial products were analyzed to
152 examine the matrix effect. To compare the 3 methods, REP values were used to evaluate the
153 prediction accuracy.

$$154 \quad REP(\%) = \frac{100}{N_v} \sum_{i=1}^{N_v} \left| \frac{\hat{c}_i - c_i}{c_i} \right| \quad (1)$$

155

156 N_v =number of validation spectra

157 c_i =true concentration

158 \hat{c}_i =predicted concentration

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

160

161
$$RSD(\%) = \frac{100}{N_{conc}} \sum_{k=1}^{N_{conc}} \frac{\sigma_{C_k}}{C_k} \quad \text{with} \quad \sigma_{C_k}^2 = \sum_{i=1}^{\rho} \frac{(\hat{c}_{ik} - c_k)^2}{\rho - 1} \quad (2)$$

162

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

164 ρ =number of spectra per concentration

165 σ =Standard deviation

166

167 We first presented the quantitative results of LIBS data according to standard calibration
168 method which is based on the measurement of Na atomic emission at 588.599 nm in standard
169 bread samples. In this method, instrumental noise was subtracted from spectra. Then,
170 background normalization was applied according to 575.522 nm where there is no atomic
171 emission spectral line. Scanning five different locations and four excitations per location, we
172 analyzed the samples by the LIBS technique in triplicate, for each sample (pellet) 20 shots were
173 accumulated. The calibration curves for the Na line at 588.599 nm were obtained by plotting
174 its intensity (peak height) versus the Na concentrations in each sample. 26 data (each of them
175 includes 20 spectra) for calibration, 13 data for prediction of SCC method were used. Following
176 that, LIBS spectra of commercial products were analyzed via SCC method, and the results were
177 compared with measured Na concentrations by AAS.

178 In this study we used two different multivariate analysis methods. One of them is PLS in
179 which we used the same data set as in previous work. Data of LIBS spectra ranged between
180 538.424 nm and 800.881 nm were used instead of whole spectrum because the most quantitative
181 data could be obtained from this region. LIBS data matrix was obtained by analyzing the spectra
182 of 39 standard bread samples (26 samples for calibration, 13 samples for the validation) for
183 PLS analysis. Data analysis was performed using PLS with Stand-alone Chemometrics

184 Software (Version Solo 6.5 for Windows 7, Eigenvector Research Inc., Wenatchee, WA, USA).
185 Data matrix of selected LIBS data and concentration was embedded into the software as
186 calibration data, and PLS algorithm was performed using different components between 1-15.
187 Mean center was applied as pre-processing to calibration input data. Prediction ability of
188 obtained model was determined with the validation data set. Selection of latent variable's
189 number related to the difference between cumulative variance and the prediction ability is very
190 important. While cumulative variance increases with the latent variable number - which is 11
191 for this study-, prediction ability does not increase after obtaining the model. For this reason, it
192 is important to find optimum approach between cumulative variance and prediction ability. In
193 the PLS model, predictability was determined by calculating the root mean square error of
194 calibration (RMSEC) and root mean square error of prediction (RMSEP) for the validation [34].
195 Minimum RMSEC and RMSEP values were selected for PLS model. After that, Na
196 concentrations in commercial products were analyzed by PLS, and results were compared with
197 results of AAS.

198

$$199 \quad RMSEC = \sqrt{\frac{\sum_{i=1}^m (actual - calculated)^2}{M - 1}}$$

200

$$201 \quad RMSEP = \sqrt{\frac{\sum_{i=1}^n (actual - calculated)^2}{N}}$$

202

203 M: number of samples used in calibration data set

204 N: number of samples used in prediction data set

205

206 The other applied multivariate method is ANN. The same experimental data were used for
207 quantitative analysis with The Neural Network Toolbox, MATLAB® Release 14 (The
208 Mathworks, Natick, MA). The independent variable is the LIBS spectra between 538.424 nm
209 and 800.881 nm, and dependent variable is the Na concentrations. Similar to the PLS method,
210 26 data set was used for calibration, 13 data set was used for validation of the trained network.
211 We used the neural network functions of training for calibration and transfer functions of logsig
212 and purelin for validation. Then, the number of nodes in hidden layer was optimized between
213 1-10, and it was found that seven hidden nodes showed the best performance.

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

219

220 **3. RESULTS AND DISCUSSION**

221

222 For the calibration study, a total of 780 spectra (20 spectra for each pellet, 3 pellet for each
223 sample, 13 standard bread sample) and for commercial products a total of 360 spectra (20
224 spectra for each pellet, 3 pellet for each sample, 13 standard bread sample) were recorded by
225 LIBS. Fig.2. illustrates the LIBS spectra of different amount of NaCl containing standard bread
226 samples. The peak at 588.599 nm belongs to Na and peak at 769 nm belongs to K according to
227 NIST atomic data base [35]. Fig.2 shows that as the intensity of Na band at 588.599 nm
228 increases, the NaCl levels in breads rises, as well.

229 Calibration models were developed according to three different methods, which are SCC,
230 ANN and PLS for quantitative treatments attained from a calibrated data set (standard bread

231 samples). Then, prediction ability of the regression of obtained model was evaluated via
232 validation data set (standard bread samples, excluding the calibration data set, were treated as
233 unknown) to test the accuracy and precision of calibration model. After that, Na concentrations
234 of commercial products were predicted and compared with results of standard method AAS.
235 This treatment is found to be useful for evaluating the matrix effect and the potential of LIBS
236 in commercial samples.

237 The traditional way to obtain calibration curve is using reference samples which contain
238 constant concentrations of major element and varying concentrations of target element. For this
239 purpose, standard bread samples were prepared at different salt concentrations and analyzed via
240 LIBS. Standard calibration curve of Na was obtained by plotting its intensity at 588.599 nm
241 versus the measured Na concentrations (Fig.3(a)). Each point in calibration curve demonstrates
242 the average value of 3 pellet samples, and each pellet contains accumulation of 20 laser shut.
243 RSD, REP values and the other results were summarized for this calibration strategy in Table1.

244 PLS calibration was performed using the same standard bread samples with known NaCl
245 concentrations. The spectral interval of 538.424 nm to 800.881 nm was chosen because most
246 of the atomic emission lines are in this region. For enhancing the performance of PLS method,
247 mean center was applied as pre-processing to calibration input data. Formed PLS calibration
248 model and validation data set are presented in Fig.3(c). Low RMSEC (0.01835) value and high
249 coefficient of determination was chosen to develop the calibration model. Low RMSEC
250 (0.01835) and RMSEP (0.10925) values were chosen for validation. The high coefficient of
251 determination values, $R^2 = 0.999$ for calibration and $R^2=0.991$ for validation were observed
252 (Fig.3(c)). RSD and REP values of PLS is presented in Table1.

253 In addition to the PLS method, ANN was also used for Na quantification in standard bread
254 samples. Same calibration and validation data set were used for ANN model. The networks that
255 had maximum R^2 values between predicted and actual data were selected as the best trained

256 network. Then, the best-trained network was used for prediction of Na content in standard
257 breads with ANN. The predicted calibration and validation data sets were compared with
258 experimental data sets and high correlations were obtained for Na concentrations (Fig.3 (b)).
259 High coefficient of determination values, ($R^2=0.987$) and ($R^2=0.964$), were observed for
260 calibration and validation data sets, respectively. REP and RSD values of ANN model is
261 presented in Table1.

262 When the PLS method was compared with standard calibration curve and ANN methods
263 according to Table1, the PLS method gave the best results with R^2 values of 0.999 for
264 calibration and 0.991 for validation. Furthermore, PLS has shown an excellent potential with
265 high prediction precision and prediction accuracy compared to other methods.

266 To make comparison, Na concentrations in commercial samples such as biscuits, crackers
267 and some kinds of breads were also analyzed with AAS. Comparative results between AAS and
268 LIBS for commercial products analyzed with SCC, ANN and PLS models were presented in
269 Fig.4(a), (b), (c) and RSD, REP values were summarized in Table2. SCC is the most commonly
270 applied method for quantitative analyses because of its simplicity. However, this method is only
271 useful if the standard sample's matrix resembles to the real sample's matrix [36]. Hence, this
272 situation makes it more difficult to obtain the calibration set. Also in commercial products, PLS
273 gave the best results with high prediction ability compared to other methods. Low RMSEC
274 (0.29861) and RMSEP (0.13893) values were chosen for validation of commercial products.
275 PLS model increased the R^2 value from 0.788 to 0.943 for commercial products. When the
276 standard calibration curve for standard bread samples is considered, it is clear that the relation
277 between Na concentration and LIBS signal is linear. This tendency explains why PLS gave
278 better results than ANN, which is more convenient for nonlinear models. Principal of ANN
279 model is based on receiving a series of input data evaluated by each neuron; therefore, data are
280 weighted dynamically. It compares the weighted sum of its inputs to a given threshold value

281 and performs the nonlinear function to calculate the output [18]. On the other hand, the overall
282 performance of PLS are quite satisfactory with a high prediction accuracy and precision
283 compared to other methods. High RSD values can be explained with fluctuating of LIBS
284 experimental parameters such as changing plasma conditions and spectral interference. These
285 problems can be overcome by obtaining high numbers of shots for each sample. Prediction
286 ability of PLS model is more satisfactory for validation data of standard bread samples than
287 validation data of commercial products. This is due to matrix differences between standard
288 bread samples and commercial products. Application field of PLS has expanded to biomedical,
289 pharmaceutical, social science and other fields [37-39], and it has recently shown great potential
290 in LIBS applications [40].

291 Combining LIBS and PLS methods to measure Na concentrations gave acceptable results
292 for also commercial products because the PLS as a multivariate analysis is more accurate,
293 robust and reliable compared to SCC method. Limit of detection (LOD) was calculated as
294 0.0279%, and limit of quantification (LOQ) was calculated as 0.0930% for PLS. In some
295 studies, authors obtained lower detection limits, as low as 5 ppm [41] and even 0.1 ppb by using
296 dual-pulse and crossed-beam Nd:YAG lasers for Na on a water film [42]. However, our LOD
297 and LOQ values are quite low for food products, which makes this method convenient for
298 measurement of Na even in dietary food.

299

300 **4. CONCLUSION**

301

302 Na is an important ingredient in food products both for its potential to cause health problems
303 such as heart diseases and stroke, and for its usage as a quality control parameter influencing
304 taste, yeast activity, strength of the gluten network, and gas retention [43]. Thus, Na levels in
305 food should be controlled in accordance with the recommendations. Measurement of Na in

306 breads can be performed by titration, AAS and potentiometric methods. These regulatory
307 methods are time consuming and require sample preparation. In contrast, LIBS can be a rapid
308 and valuable tool for Na measurement in bakery products.

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

317

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319

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322

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327 and B.S., System optical design and data processing has been done by K.E.E and H.B.. I.H.B
328 and U.T. performed the validation of theoretical framework which this research based on,
329 polished the text and brought the manuscript into its final form.

330

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450

451 **Figure Captions**

452

453 **Fig.1.** Schematic presentation of LIBS experimental setup.

454

455 **Fig.2.** LIBS spectra of standard bread samples at various salt concentrations.

456 **Fig.3.** Calibration and validation plots developed with SCC (a), ANN (b), PLS (c) data analysis
457 techniques.

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

460

461 **Table Captions**

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

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

464

Figures

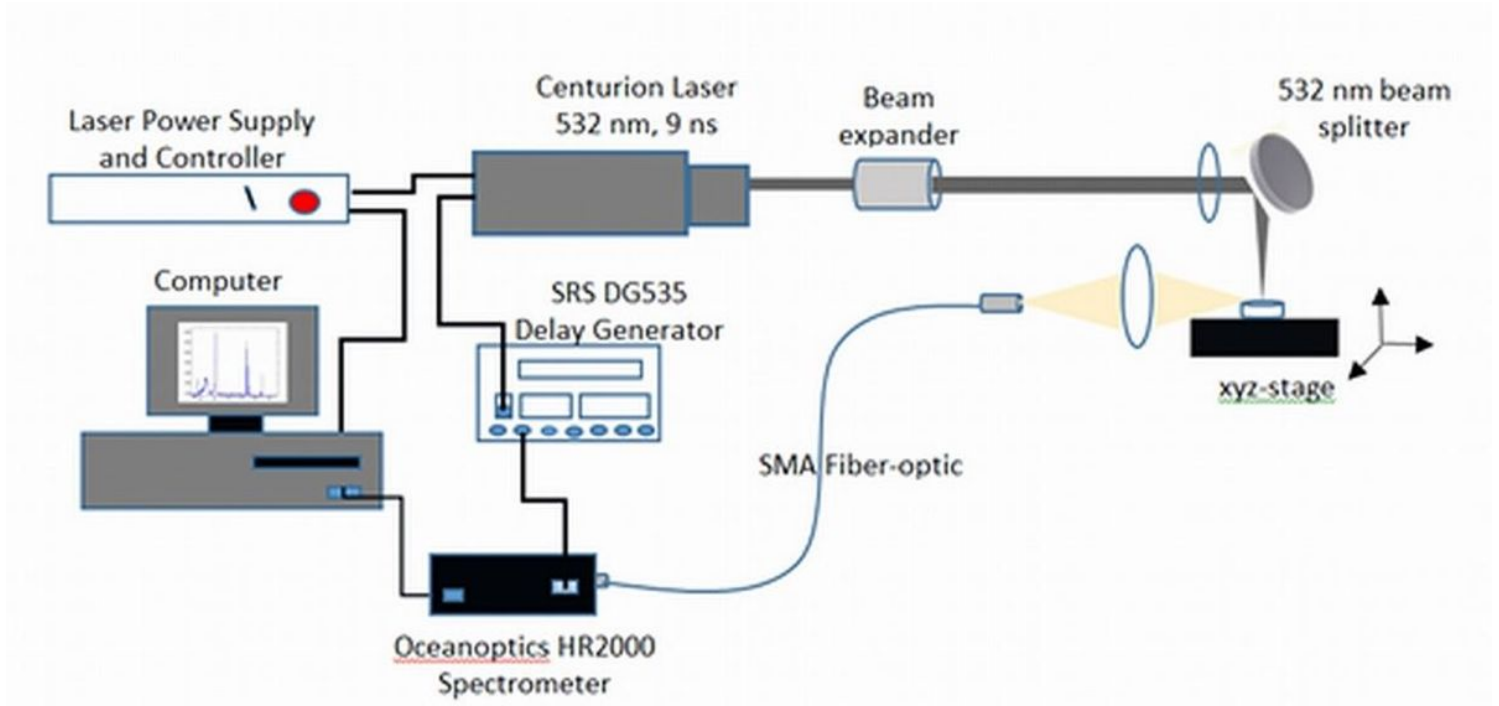


Figure 1

Schematic presentation of LIBS experimental setup.

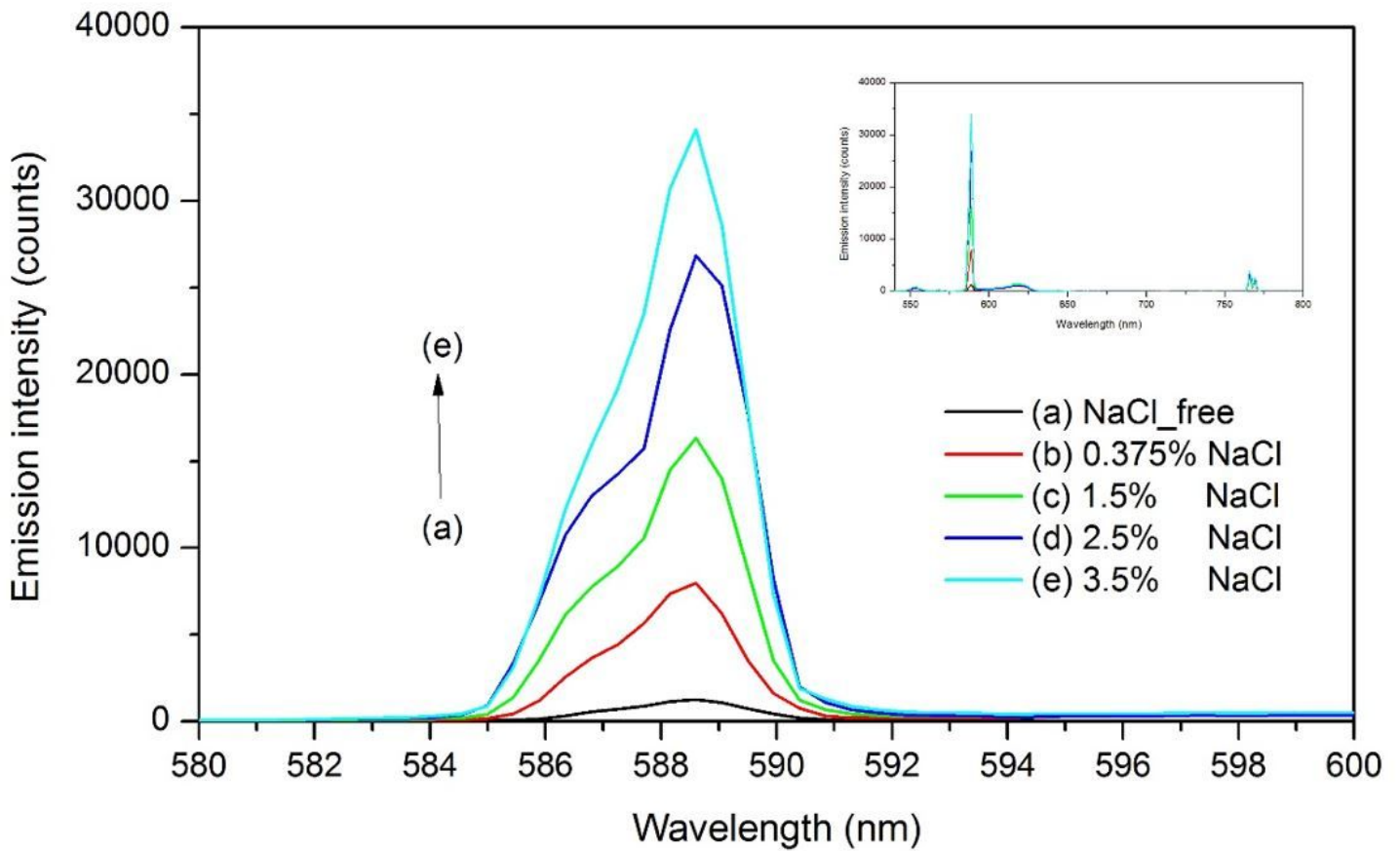


Figure 2

LIBS spectra of standard bread samples at various salt concentrations.

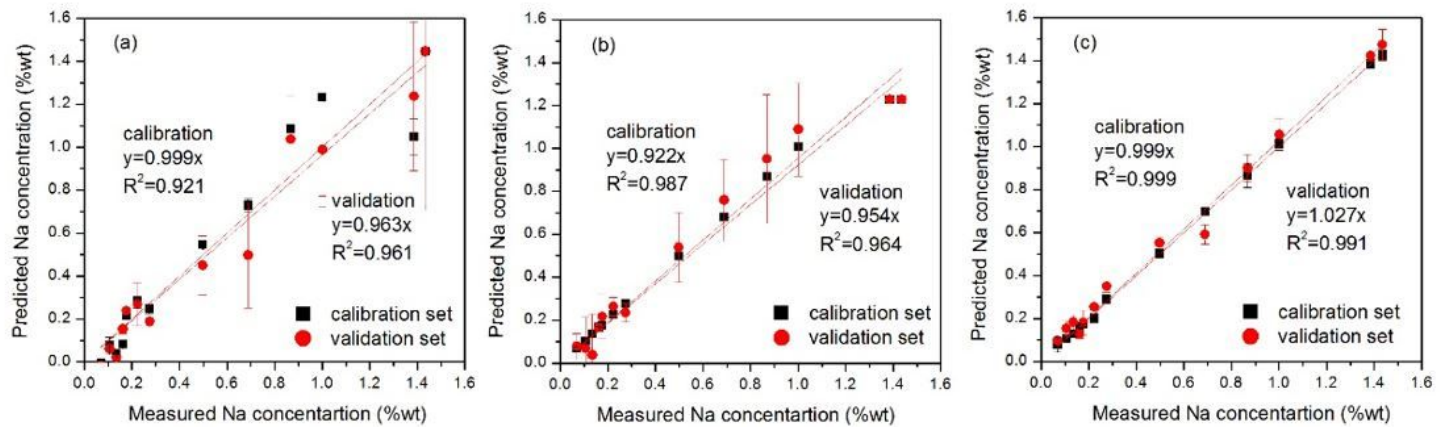


Figure 3

Calibration and validation plots developed with SCC (a), ANN (b), PLS (c) data analysis techniques.

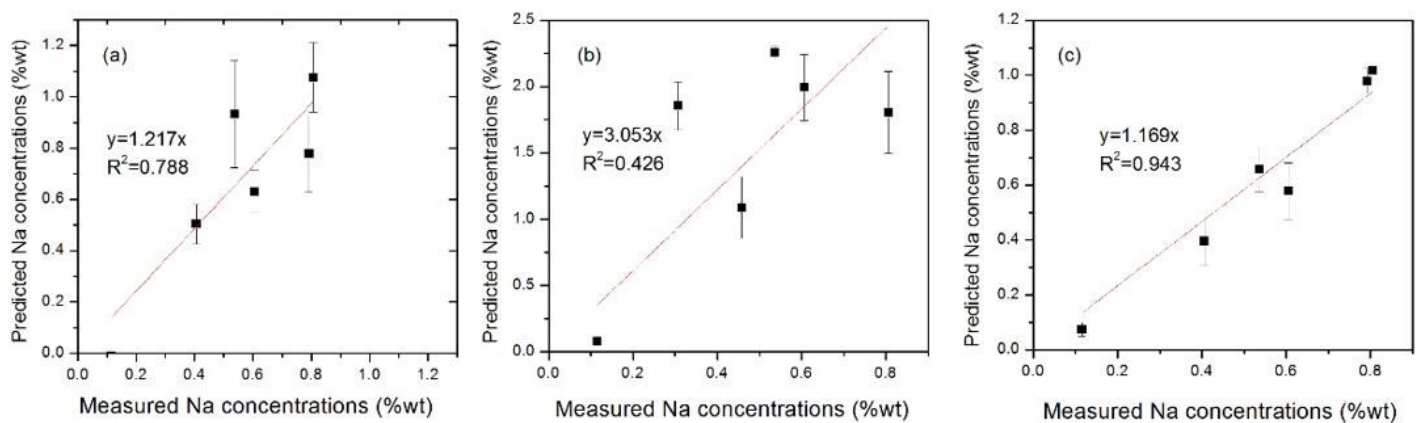


Figure 4

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

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