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Multiparametric analysis of cheese using single spectrum of laser-induced breakdown spectroscopy

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ABSTRACT

The potential of using laser-induced breakdown spectroscopy (LIBS) for prediction of chemical quality/control parameters in a cheese matrix was investigated. Traditional methods are usually time-consuming and require complex pre-treatments, the use of toxic chemicals and laboratories and personnel equipped with these analytical skills. In this study, 11 different chemical analyses commonly performed on cheese samples were conducted using traditional methods on 82 full-fat, white pickled and ripened cheese samples. Additionally, these parameters of interest were correlated with multi-elemental spectra of LIBS using partial least squares regression. The results obtained for moisture, dry matter, salt, total ash, total protein, pH, fat, acidity, water soluble nitrogen, trichloroacetic acid soluble nitrogen, and phosphotungstic acid soluble nitrogen (R^2_{cal} = 0.964, 0.959, 0.970, 0.973, 0.952, 0.971, 0.733, 0.762, 0.714, 0.633, and 0.707, respectively) indicated that LIBS could be used as an alternative or complementary method in quality control of cheese.

1. Introduction

Cheese is a worldwide consumed fermented dairy product (Tong et al., 2017), and it exhibits differences in its chemical composition depending on where the milk is collected, the season, processing, ripening level and so on. As part of the dairy industry, manufacturers are always under pressure to deliver consistently high quality cheese to the market. Quality attributes such as fat, sodium and nutrient content, which are regulated by governmental agencies, have high importance for both manufacturers and consumers (Berges & Casellas, 2009). In addition, pH of cheese is also vital for manufacturers and is widely used as one of the chemical process control parameters along with other significant parameters such as the ratio of salt, moisture, dry matter, and fat in the dry matter for production (Kraggerud, 2011). Therefore, much more resources should be allocated in the production process to increase and maintain its quality.

Achieving constant production of a high quality product can only be accomplished by means of frequent monitoring and quality control analyses. Rapid and reliable analyses of cheese samples are critical to all manufacturers and consumers as well as for brand reputation. However, frequent monitoring of quality control parameters of cheese is currently not feasible, especially for dairy farms involved in the production of cheese. The analyses performed on dairy farms are usually simple tests carried out only on the received raw milk. These tests can be grouped as physical and chemical tests (pH, alcohol test, titratable acidity, freezing point and density) and microbiological tests (methylene blue dye reduction, total aerobic plate count, total spore count and heat resistant spore count, total counting of psychotropic aerobes) (TetraPak, 2014). Therefore, modern analytical techniques used for determination of the quality parameters in a fast and cheap manner without any need of skilled people, chemicals and consumables are always under further investigation.

Chemical compositional analysis of cheese generally comprises the measurement of moisture, dry matter, total ash, fat, salt, total protein and acidity, all of which are conducted by following the methods of International Dairy Federation (IDF), Association of Official Analytical Chemists (AOAC) and International Organisation for Standardisation (ISO). Each parameter has its own significance and approach for analysis. Moisture and total solids are determined

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using the gravimetric method (AOAC, 2005c,f; IDF, 2004a), which is important in terms of legal and economic aspects and for labelling. For example, water is an inexpensive filler and dry matter is a determining parameter in the price of foods (Bradley et al., 1992). Furthermore, protein and fat values of milk is expressed in dry matter for comparison of milk. Total protein content of cheese samples is calculated from the total nitrogen content according to Kjeldahl method (AOAC, 2005a; IDF, 2001). Total ash refers to the total mineral content which is also determined gravimetrically (AOAC, 2005e). The fat in cheese affects the texture, flavour, mouthfeel and consistency (Bylund, 2003), and it can be measured either by using Schmid–Bondzynski–Ratzlaff (SBR) technique or Gerber method (AOAC, 2005d; IDF, 2004b), whereas salt content needs to be measured using a Mohr titration method (AOAC, 2005g; IDF, 2006). Titratable acidity is determined by titration (AOAC, 2005b), and pH is measured potentiometrically (Fox, Guinee, Cogan, & McSweeney, 2000). In cheese making, measurement of pH is extremely important to control fermentation/acid production, and hence the final quality.

The listed parameters control the production process and final quality as well as nutritional value, legal obligations, labelling requirements and such. However, the above mentioned official methods have certain disadvantages such as requiring lengthy and complex sample preparation, the use of hazardous chemicals and laboratories and personnel equipped with these analytical skills. Additionally, handling each analysis individually requires much more time and amount of sample; therefore, the cost needed to complete all the analyses will increase. All these points indicate that the traditional methods used today are not sufficient to produce economical and simple solutions to keep up with the increasing demands of analyses. All things considered, it would be beneficial for the cheese industry to have an alternative/complementary method that is direct, rapid, in-situ, robust, and acceptably accurate and sensitive to be implemented in routine analyses of chemical quality control parameters throughout the production and in the final products.

Recently, spectroscopic methods including near infrared spectroscopy (Karoui et al., 2006a; Wittrup & Nørgaard, 1998), Fourier transform mid-infrared-attenuated total reflection (McQueen, Wilson, Kinnunen, & Jensen, 1995), mid-infrared transmittance spectroscopy (Margolies & Barbano, 2018), fluorescence spectroscopy (Loudiyi et al., 2018), low-resolution and high-resolution nuclear magnetic resonance (Gianferri, Maioli, Delfini, & Brosio, 2007; Lamanna, Piscioneri, Romanelli, & Sharma, 2008) combined with chemometric methods have been shown to be effective for determination of different combination of chemical quality parameters in various cheese samples. However, to the best of our knowledge, laser-induced breakdown spectroscopy (LIBS) has not been utilised in a study to determine multiple quality parameters in cheese samples from a single spectrum.

LIBS is a rapid and multi elemental analysis technique in which a laser creates plasma by focusing the beam through the lens on the sample surface and causes the molecules of the samples to breakdown into atoms. After that a rapid energy deposition that creates vapour from a very small amount of sample occurs. Then, an ultrasonic shockwave with high temperature micro plasma occurs, and this plasma expands into space and loses its energy. At the final relaxation stage, atoms emit a characteristic light that is detected by a spectrometer (Multari, Cremers, Dupre, & Gustafson, 2013; Pace, D'Angelo, Bertuccelli, & Bertuccelli, 2006). The application field of LIBS is very wide including metallurgy, soil, mining, forensic and environmental analyses (Lennard, El-Deftar, & Robertson, 2015; Rusak, Castle, Smith, & Winefordner, 1997; Shirvani-Mahdavi & Shafiee, 2016; St-Onge, Kwong, Sabsabi, & Vadas, 2002; Tognoni, Palleschi, Corsi, & Cristoforetti, 2002). Currently, there is an increasing trend of using LIBS in food analyses due to its certain advantages such as speed, relative experimental ease, spatial resolution, sensitivity, no/minimum sample preparation, no hazardous chemical use, and applicability in solids, liquids and gases. There are preliminary studies about food quality measurement by using LIBS such as calculating salt content in bakery products, ash and total protein in cereal samples (Bilge, Boyacı, Eseller, Tamer, & Çakır, 2015; Bilge et al., 2016; Sezer, Bilge, & Boyaci, 2016). However, these food items have entirely different chemical composition and structure, and they are the first studies in the field. In the literature, there are also a few different studies in which cheese is used as a sample matrix, but the aim of those studies was not to determine the chemical quality of samples. For example, Liu, Gigant, Baudelet, and Richardson (2012) used cheese samples to determine the effect of the moisture on LIBS signal. In that study, cheese was used due to its high moisture content as a sample type.

The aim of this study was to evaluate the potential of LIBS along with multivariate analysis as a practical method for determination of chemical quality control parameters including moisture, dry matter, total ash, total protein, salt, pH, fat, and acidity, which were referred to as primary parameters in this study and water soluble nitrogen (W-SN), trichloroacetic acid soluble nitrogen (TCA-SN), and phosphotungstic acid soluble nitrogen (PTA-SN), which were called secondary parameters. For this purpose, Ezine Cheese was used as model cheese matrix. The new method is expected to provide a simultaneous and multi-parametric analysis of cheese for quality control analyses to be carried out by the food industry and government agencies.

2. Materials and methods

2.1. Cheese samples and their preparation

In this study, 82 full-fat, ripened commercial Ezine cheese samples, which are offered for sale in dairy farms and markets in Canakkale region of Turkey, were used. According to geographical registration certificate issued by Turkish Patent Institute in 2006, Ezine cheese is a type of white cheese that is produced using combinations of milk from goats, sheep and cows fed with the natural vegetation and water resources in certain areas specified in the registration certificate. Ezine cheese must contain minimum of 40% goats' milk, between 45 and 55% sheep's milk and the maximum of 15% cows' milk in its mixture (Delice, Guneser, & Yuceer, 2013; Yuceer et al., 2009). Ezine cheese, which is ripened in brine solutions and produced according to white cheese standards differs from other cheeses due to the absence of a starter culture in its production, sourcing the milk from certain locations and the use of blends of goat, sheep and cow milk and sea salt in its production. Ezine cheese production is made in the dairy farms in the region.

Cheese samples were purchased from 31 different manufacturers in vacuum packed blocks of at least 500 g. The samples that were obtained from the same manufacturer and were produced in different seasons were also included to increase the number of samples for this study. Cheese samples were taken to our laboratory and stored at 4 ± 1 °C until further analysis. Approximately 1 cm of the outside of the cheese block was cut and discarded due to possible drying and concentration differences before starting the analyses. Subsequently, the samples were crushed and mixed in lab-type mortars and transferred to locked plastic storage bags. pH and titration acidity analyses were performed immediately. The rest of the cheese samples were stored at −18 °C until all the reference methods and LIBS analyses were conducted.

2.2. Reference methods

The protein content of the samples was calculated using Kjeldahl method through the conversion factor as 6.38 (ISO, 2003). The amount of water-soluble nitrogenous substances in cheese samples was determined using the Micro-Kjeldahl method (Kuchroo & Fox, 1982). The amount of nitrogen dissolved in 12% TCA-SN and 5% PTA-SN were prepared according to the method specified by Polychroniadou, Michaelidou, and Paschaloudis (1999) and Jarrett, Aston, and Dulley (1982), respectively. The Gerber method was used to determine the fat content in cheese (ISO, 2009). Salt analysis in cheese was carried out according to the Mohr method (AOAC, 2000a). Gravimetric method was used to determine the moisture and dry matter of cheese (ISO, 2008). Dry ashing method was used to determine the total ash in cheese samples (AOAC, 2000b). To measure the pH of the samples, 20 g of the shredded cheese sample was weighed and homogenised with an Ultra Turrax (ESGE, Model EM2, Geneva, Switzerland) after adding 40 mL of purified water. The pH value of this prepared mixture was measured with a digital pH meter (Sartorius, PB-11, Göttingen, Germany). Then, the mixture used for the pH measurement was filtered through glass wool to a volume of 500 mL; 25 mL of this prepared filtrate was taken and 3 drops of phenolphthalein was added dropwise and titrated with 0.1 N sodium hydroxide until a pink colour was formed (Bradley et al., 1992). The titratable acidity level of the cheese sample was calculated in terms of lactic acid percentage.

2.3. LIBS setup

LIBS experiments were carried out using a Nd:YAG laser (Litron Nano SG, Warwickshire, UK), which emits a laser pulse at 1064 nm. The spectra of the samples were recorded using a 5-channel spectrometer (Applied Spectra, Fremont, CA, USA) that records the spectrum between 186 and 900 nm. The experimental setup of LIBS system is illustrated in Fig. 1: (i) laser head, (ii) laser power supply and controller, (iii) spectrometer; (iv) fibre optic cable, (v) plano convex collection lenses (F = 6 cm), (vi) plano convex focusing lens (F = 10 cm), (vii) Nd:YAG mirror, (viii) computer, (ix) sample holder. The laser was operated at 8 Hz repetition rate, 50 mJ pulse^{-1} energy, 650 ns gate delay, and 1.05 ms integration time. An optical path was designed to focus the laser beam on the sample surface using the plano convex lens (F = 10 cm). After plasma formation, the emitted light was collected through a collection system that consisted of two different 2 inch-diameter plano convex lenses with a focal length of 6 cm, and directed to the spectrometer with a fibre optic cable. The samples were scanned at 10 different regions and 10 shots per region. Each sample was analysed in duplicate. All experimental parameters were kept constant for different cheese parameters of interest.

2.4. Partial least square regression analysis

In this study, a multivariate method was required due to the presence of large amount of data available in LIBS spectrum. Accordingly, multivariate data analyses (PLS_Toolbox, Version 7.2, Eigenvector Research Inc., Wenatchee, WA, USA) were performed on the LIBS data. In this study, PLS was used for modelling of moisture, dry matter, total ash, total protein, salt, pH, fat, acidity and W-SN, TCA-SN and PTA-SN as a function of LIBS spectra. Using the software, PLSR calibration model for each parameter was developed and further validated by using external validation set. PLSR data were randomly divided into calibration data (n = 42) sets and external validation data set (n = 40). Root mean square error of calibration (RMSEC) and root mean square error of prediction (RMSEP) values referring to uncertainty of the calibration and validation and coefficient of determination (R^2) values were calculated. Also, relative error of prediction (REP), relative error of standard deviation (RSD), limit of detection (LOD) and limit of quantitation (LOQ) values were calculated as shown in Eqs. (1–4) (Gondal, Seddigi, Nasr, & Gondal, 2010; Yang, 2009):

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

where Nv = number of validation spectra, ci = true concentration, ĉi = predicted concentration;

$$RSD(\%) = \frac{100}{N_{conc}}\sum_{k=1}^{N_{conc}}\frac{\sigma_{c_k}}{c_k} with\ {\sigma_{c_k}}^2 = \sum_{i=1}^{p}\frac{(c_{ik} - c_k)^2}{p-1} \quad (2)$$

where N_{conc} = number of different concentrations in the validation set, ρ = number of spectra per concentration, σ = standard deviation;

$$LOD = 3.3 \times \frac{S.D.}{S.} \quad (3)$$

$$LOQ = 10 \times \frac{S.D.}{S.} \quad (4)$$

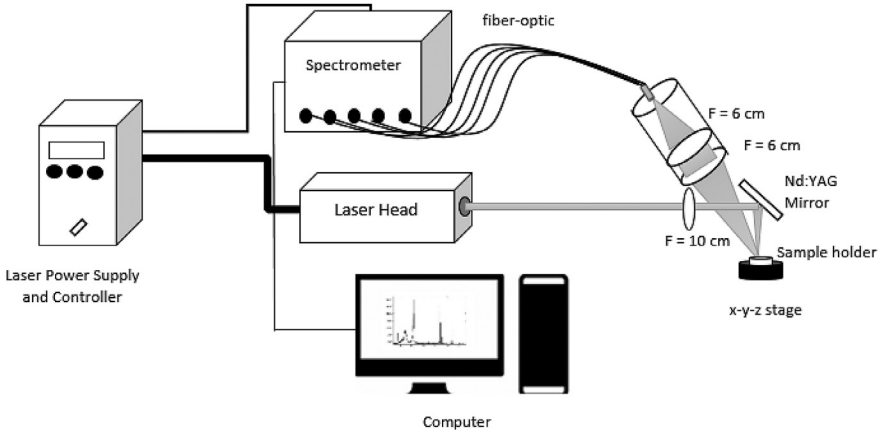

Fig. 1. Schematic presentation of experimental LIBS setup.

where S.D. = standard deviation of the predicted values, S = slope of the calibration curve.

3. Results and discussion

In this study, 82 different traditional Ezine cheese samples were used to develop PLSR models for moisture, dry matter, total protein, total ash, salt, pH, fat, acidity, W-SN, TCA-SN and PTA-SN. In the LIBS analysis, high power laser source was focused on the sample surface to produce laser induced plasma followed by emission of light. Emission lines of the elements were analysed quantitatively depending on the intensity of the peaks. Fig. 2 displays the full spectrum of four cheese samples with different compositions. Also, the most prominent lines found in the LIBS spectra are also listed in Table 1 according to the National Institute of Standard Technology (NIST) Atomic Spectral Database (NIST, 2017). As can be seen in Fig. 2, LIBS spectra of the cheese samples have revealed the presence of several elements that represent both organic (C, H, O) and inorganic (Fe, Mg, Ca, Na, K, P) structures. In Fig. 2, major spectral changes are highlighted. Certain spectral differences were noted depending on the intensity between 240 and 250 nm, 270–300 nm, 350–400 nm, 580–590 nm, 640–660 nm, 740–750 nm, and 780–800 nm; which represent C, Mg, Cn band and Ca, Na, H, N and O, respectively.

In the first step of the quantitative study, the direct relation between LIBS spectra and the reference results namely moisture, dry matter, total protein, total ash, salt and pH were investigated. According to the data in the literature, H and O elements in LIBS spectrum signifies the moisture content of the samples (Liu et al., 2012). Due to the relationship with moisture, dry matter can also be correlated to the LIBS spectrum. Also, the intensity of Na element was the calculation basis of the salt content (Bilge et al., 2015). On the other hand, N element in the spectrum was related to the total protein content (Sezer et al., 2016). According to the previous studies, total ash (Bilge et al., 2016) and pH (Harhira et al., 2016) values could also be correlated to the LIBS spectrum. Based on this information, six different major parameters were directly correlated to a single LIBS spectrum. PLSR calibration (n = 42) and validation (n = 40) graphs are presented in Fig. 3. The calibration and validation models were constructed by choosing high coefficient of determination values. The PLSR results of the first six

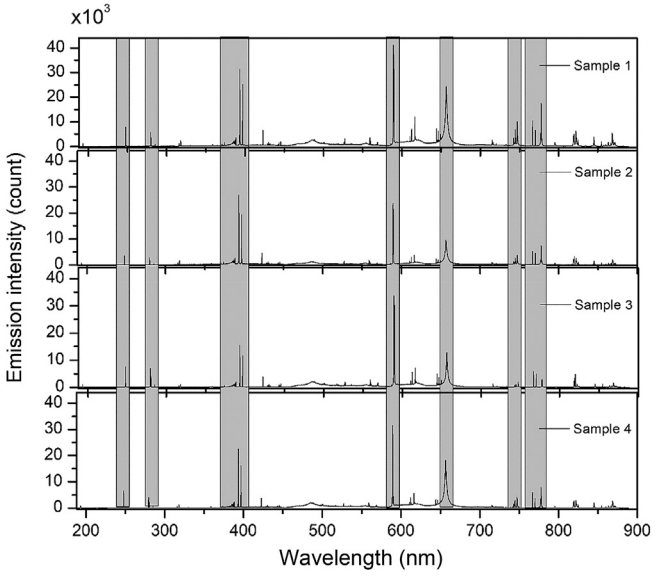

Fig. 2. LIBS spectra of different Ezine cheese samples.

Table 1
Most prominent line assignment from various elements in the 188–900 nm spectral region.

Emission lines (nm)	Possible elements
247.859	C I (247.860)
279.500	Mg I (279.553)
280.204	Zn I (280.200)
393.360	Ca II (393.366), Ca I (393.529)
396.821	Ca II (396.8469)
422.700	Ca I (422.672), Ca II (422.815)
443.548	Ca I (443.569)
445.517	Ca I (445.478)
516.600	Fe I (516.748), Mg I (516.732)
589.245	Na I (588.995)
589.806	Na I (588.995)
716.065	Ca I (714.815), Fe I (714.814)
742.758	N I (742.360)
744.545	N I (744.229)
747.212	N I (746.831)
766.783	K I (766.489)
770.107	K I (769.8965)
777.541	O I (777.569)
819.221	Na I (819.482)
821.922	Mg I (821.3034)

chemical parameters are summarised in Table 2. Additionally, low RMSEC and RMSEP values were obtained from the developed calibration and validation models, respectively. For the evaluation of the system precision and sensitivity, RSD and REP values were calculated and shown in Table 2.

In the literature, homogeneity, complexity, particle size, composition and surface condition of the sample as well as the reproducibility of the laser shots are reported to be the major parameters affecting RSD values, which was reported in the range of 1–10% (Hussain & Gondal, 2013). The first six analytical parameters revealed that there is a high coefficient of determination range between 0.972 and 0.986 for calibration and between 0.952 and 0.973 in test validation sets, with a latent variable 3 and 4. In this study, cheese samples in the validation data set have moisture, dry matter, protein, ash, salt and pH values in the range of 44.6–53.1%, 44.9–55.1%, 34.9–42.2%, 6.2–11.6%, 4.7–9.8% and 4.5–5.2, respectively. According to the parameters considered as standards for cheese production (moisture, dry matter, total protein, total ash, salt, pH), it can be seen that a successful correlation between LIBS spectra and the reference measured values were achieved. Furthermore, it takes long hours and requires much more effort to obtain these six parameters by using conventional analysis techniques. However, LIBS can accomplish this with high accuracy and precision from a single spectrum within seconds.

In the second step, fat, acidity, W-SN, TCA-SN and PTA-SN values, which are referred to as secondary parameters in this study, were investigated with regards to the LIBS spectra. Surprisingly, correlation was found between these values and LIBS spectra although they did not contain any direct elemental relationship. The coefficient of determination values were not as high as the values in the first six parameters, but the data implied that there were reasonable correlations among them. Secondary analytical parameters showed that there was a coefficient of determination ranged between 0.761 and 0.829 for calibration and between 0.633 and 0.762 in test set validation, with a latent variable 5 and 6. In this study, cheese samples in the validation data set have fat, acidity, W-SN, TCA-SN and PTA-SN values in the range of 44.6–59.9%, 0.94–1.71%, 0.09–0.2%, 0.05–0.12% and 0.0004–0.02%, respectively. The PLSR results for secondary parameters are given in Table 3.

It may give the impression that the calculated models do not predict values accurately enough to consider them as good models. W-SN, TCA-SN and PTASN are soluble nitrogen (SN) fractions, and

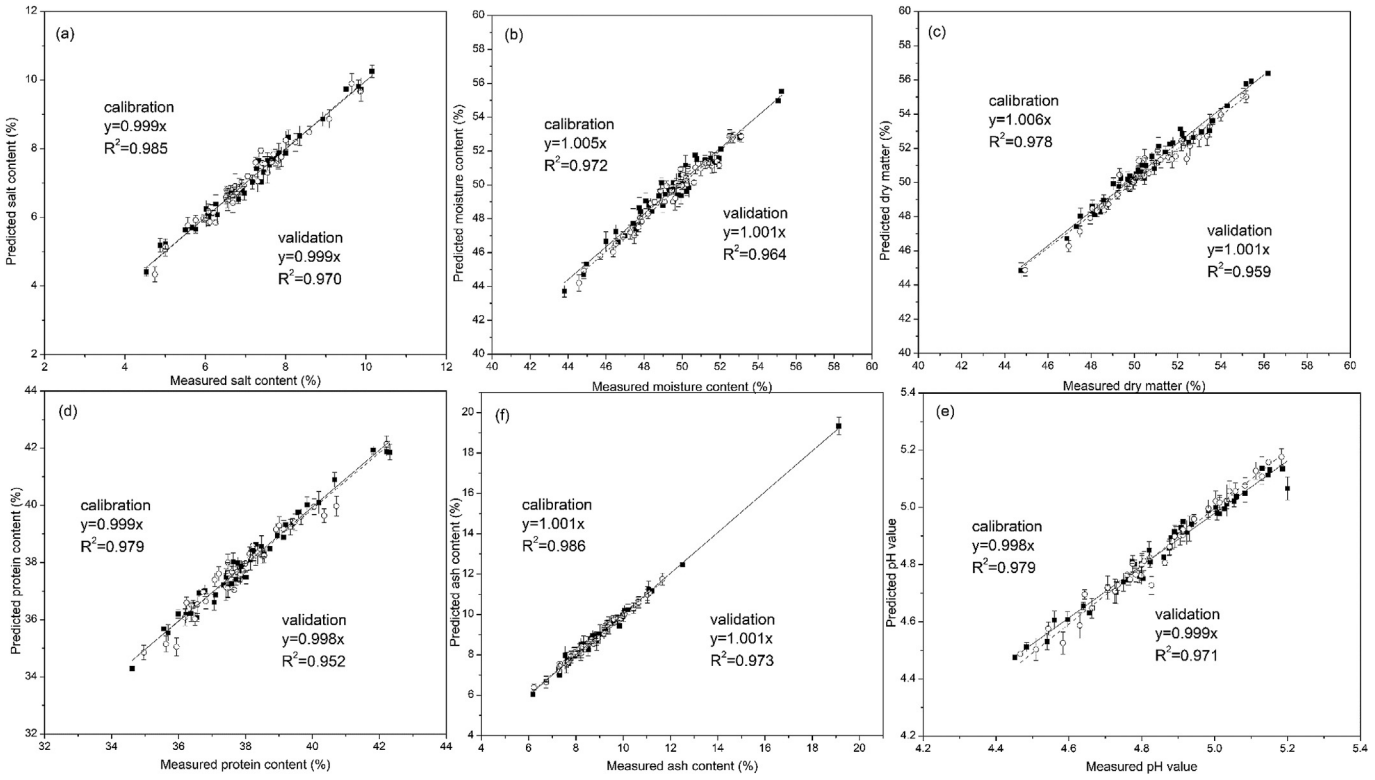

Fig. 3. Calibration (fx1) and validation (fx2) plots of the primary chemical parameters of the cheese samples: salt (a), moisture (b), dry matter (c), total protein (d), total ash (e), pH (f).

Table 2
Statistical PLSR results of the primary chemical parameters (moisture, dry matter, total ash, total protein, salt and pH).

Parameter	Salt (%)	Moisture (%)	Dry matter (%)	Protein (%)	pH	Ash (%)
Pre-processing	1st derivative, normalise	Mean centre, 1st derivative	Normalise, OSC	OSC, mean centre	Normalise, mean centre	OSC
R^2 calibration	0.985	0.972	0.978	0.979	0.979	0.986
R^2 validation	0.970	0.964	0.959	0.952	0.971	0.973
LOD (%)	0.61	1.01	1.34	0.86	0.01	0.11
LOQ (%)	2.03	3.38	4.48	2.85	0.03	0.31
RSD (%)	3.08	2.01	1.98	1.80	1.48	1.91
REP (%)	3.75	3.87	3.78	5.00	3.29	2.95
RMSEC	0.22	2.36	1.23	0.38	0.04	1.37
RMSEP	0.79	5.84	4.74	2.92	0.15	1.44
Latent variable	4	4	3	4	4	3

Table 3
Statistical PLSR results of the secondary chemical parameters (fat, acidity, W-SN, TCA-SN, PTA-SN).

Parameter	Fat measurement (%)	Acidity (%)	W-SN (%)	TCA-SN (%)	PTA-SN (%)
Pre-processing	2nd derivative, OSC	2nd derivative, OSC, mean centre	1st derivative, OSC	1st derivative, mean centre	OSC, normalise, 1st derivative
R^2 calibration	0.829	0.817	0.761	0.780	0.813
R^2 validation	0.733	0.762	0.714	0.633	0.707
LOD (%)	2.50	0.11	1.0	0.7	0.2
LOQ (%)	8.34	0.38	3.0	2.2	0.7
RSD (%)	3.51	3.53	5.46	10.44	11.35
REP (%)	8.71	7.54	9.82	12.03	11.95
RMSEC	1.83	0.04	2.0	0.9	0.1
RMSEP	5.36	0.20	4.0	2.0	0.4
Latent variable	5	5	5	6	6

ripening of cheese process enhances the SN content, which is related with nitrogen element. On the other hand, with the ripening of cheese, pH, titratable acidity and free volatile free acids increase. Therefore, there is a linear correlation between pH and secondary parameters such as SN fractions and acidity (Abdel Baky, Elf Ak, Rabie, & El Neshewy, 1982). Although, there is no specific emission peak, which can be recognised in the LIBS spectra related to these secondary parameters, this relation can be explained with the positive results of LIBS. In future studies, what exactly causes this secondary relation can be further investigated. Also, more data with higher variability can be included to improve the calibration and validation.

In the present study, applicability of LIBS for determination of chemical quality control parameters of cheese samples was shown by using Ezine cheese samples as model cheese matrix. Validation study shows that LIBS is an important tool to determine these parameters with great success. In previous studies, different spectroscopic methods such as NIR, MIR, FTIR, NMR have been used to determine the chemical composition of cheese samples. In particular, NIR is one of the most widely used technique with high accuracy and precision in commercial quality assurance (QC) laboratories. It provides more rapid and cost-effective analysis for fat, protein and moisture parameters. However, to the best of our knowledge, LIBS has not been used to determine the multiple chemical quality parameters from a single spectrum in food samples before. Hence, the present study is distinct from the previous ones since it utilises a single LIBS spectrum to determine the moisture, dry matter, total protein, total ash, salt and pH values with high accuracy Also, it provides a rapid and in-situ alternative spectroscopic approach to this field.

When compared with other spectroscopic methods, the proposed methods provide similar accuracy and precision results as can be seen in the values in Table 2. In the literature, multivariate analysis combined NIR spectroscopy showed 6.37% and 5.95% average relative error for fat and protein in ricotta cheese, respectively (Madalozzo, Sauer, & Nagata, 2015). On the other hand, standard error of prediction (SEP) values in moisture and fat are 0.30 and 0.45 for NIR while 0.28 and 0.23 for MIR (Margolies & Barbano, 2018). NIR and MIR spectroscopies were also used for WSN, total nitrogen (TN), non-protein nitrogen (NPN), pH and NaCl parameters. It can be said that LIBS is more promising for NaCl ($R^2 = 0.970$) and pH ($R^2 = 0.971$) measurements compared with NIR ($R^2 = 0.39$ for NaCl, $R^2 = 0.43$ for pH) and MIR ($R^2 = 0.73$ for NaCl, $R^2 = 0.84$ for pH) spectroscopy due to direct analysis in LIBS. Furthermore, WSN validation results showed that 0.77 and 0.80 of R^2 values were found for NIR and MIR, respectively, which resembles LIBS results with 0.71 of validation R^2. On the other hand, NIR is more acceptable for fat analysis than LIBS (Karoui et al., 2006b). Other secondary parameters such as acidity, TCA-SN and PTA-SN have not been studied spectroscopically in the literature. Therefore, LIBS can be a pioneer application for acidity, WSN, TCA-SN and PTA-SN measurements.

Unlike other spectroscopy techniques, LIBS provides direct analysis by measuring H and O elements for moisture and N element for protein. Furthermore, it was demonstrated in the previous studies that LIBS with accurate calibration can also be used in determination of mineral content of the food products, which can also be incorporated to the chemical composition. By this means, LIBS has a major advantage when compared with other spectroscopic methods as it provides both chemical quality and elemental analysis at the same time with minimum sample preparation. While each analysis requires a different chemical analysis procedure in conventional methods, LIBS provides an environmental friendly, rapid and simple single method for multi-parametric analysis. Therefore, it can be a valuable tool for food industry and control laboratories. Also, LIBS has shown that there is an indirect secondary relation between fat, acidity, WSN, TCASN and PTASN values and LIBS spectrum, which should be studied with a controlled sample set rather than real samples to clearly identify the hidden relationship.

4. Conclusion

The present study reveals that LIBS method has an acceptable precision and accuracy to be used in the multi-parameter analysis of Ezine cheese as model cheese matrix. It appears to be a useful method for primary chemical analysis namely moisture, dry matter, total ash, total protein, pH and salt from a single LIBS spectrum. Also, LIBS brings advantages to primary analysis in terms of time, cost and effort. On the other hand, this study indicates that there is a correlation between fat, acidity, WSN, TCASN and PTASN values and LIBS spectra, which has not been previously assessed in the literature. The coefficients of determination values for secondary parameters were not as high as in primary parameters due to the absence of specific emissions, narrow interval given the distribution of the values and secondary relations in the spectra. This correlation opens up a new research topic about LIBS which should be investigated in the further studies to clearly identify the relationship between the measured secondary parameters and LIBS spectra with a controlled set of samples.

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