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Analytical Methods

Analysis of bakery products by laser-induced breakdown spectroscopy

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ABSTRACT

In this study, we focused on the detection of Na in bakery products by using laser-induced breakdown spectroscopy (LIBS) as a quick and simple method. LIBS experiments were performed to examine the Na at 589 nm to quantify NaCl. A series of standard bread sample pellets containing various concentrations of NaCl (0.025–3.5%) were used to construct the calibration curves and to determine the detection limits of the measurements. Calibration graphs were drawn to indicate functions of NaCl and Na concentrations, which showed good linearity in the range of 0.025–3.5% NaCl and 0.01–1.4% Na concentrations with correlation coefficients (R^2) values greater than 0.98 and 0.96. The obtained detection limits for NaCl and Na were 175 and 69 ppm, respectively. Performed experimental studies showed that LIBS is a convenient method for commercial bakery products to quantify NaCl concentrations as a rapid and in situ technique.

1. Introduction

70–75% of the total sodium chloride (NaCl) intake in the human diet is obtained from processed foods (James, Ralph, & Sanchez Castillo, 1987), out of which cereal and cereal products constitute approximately 30% (FSAI, 2005). Hence, reducing the NaCl content in bakery products could decrease the overall NaCl intake in human diet. Since a large number of deaths related to excessive salt intake are due to the consumption of bread with high NaCl contents, this quantity must be reduced (He & MacGregor, 2007). Moreover, studies have shown that excessive dietary Na intake increases blood pressure (Elliott et al., 1996) and may cause strokes (Xie, Sasaki, Joossens, & Kesteloot, 1992) and coronary heart diseases (Tuomilehto et al., 2001). However, many bakers are reluctant to reduce the salt content in bread because it may lead to insufficient dough strength and undesirable sensory profiles. NaCl is an important ingredient in bakery products as it contributes to the dough-making process by regulating the fermentation rate, strengthening the dough and adding to the taste of the bread (Salovaara, 1982).

In addition, NaCl is a quality control indicator in bakery products. The NaCl level in foods should adhere to Codex Alimentarius standards. Therefore, NaCl detection is critical in bakery products. Several methods are used to determine the NaCl content in bakery products. Some of these methods are based on the presence of Na ions, whereas others are based on that of Cl ions (Plácido et al., 2012). The potentiometric method, which utilizes ion selective Na or Cl electrodes, is most widely used to determine the amount of salt in food products. Other commonly used methods include titration to determine Cl levels and flame atomic absorption spectrometry to determine Na content (Capuano et al., 2013; Smith & Haider, 2014). These methods are time consuming, and their application procedures are difficult. They also require sample preparation, which makes them unsuitable for in situ and point detection analyses. Therefore, laser-induced breakdown spectroscopy (LIBS) has emerged as a valuable tool for quick and in situ analyses (Choi, Lee, & Yoh, 2013; Singh et al., 2008).

LIBS is an optical emission spectroscopy technique based on laser-produced plasma, in which a laser beam excites and intensively heats a small volume of the sample. The heated sample is taken to a gaseous plasma state and is broken down into atoms, which produces a characteristic light. This light is analyzed spectrally; and through calibration, the intensity of the spectra indicates the concentration of the elements in the sample (St-Onge et al., 2004).

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Most materials, such as solids, liquids and gases, can be analyzed quantitatively and qualitatively by using LIBS (Miziolek, Palleschi, & Schechter, 2006; Pandhija & Rai, 2008, 2009; Rai & Rai, 2008; Singh, Rai, & Rai, 2009). This technology has many advantages including quick and real-time analysis through in situ field operations without the need for sample preparation (Pandhija, Rai, Rai, & Thakur, 2010). Moreover, its application has expanded to the fields such as metallurgy, mining, environmental analysis and pharmacology (Radziemski, 1994; Rusak, Castle, Smith, & Winefordner, 1997; Sneddon & Lee, 1999; St-Onge, Kwong, Sabsabi, & Vadas, 2002; Tognoni, Palleschi, Corsi, & Cristoforetti, 2002). However, there are few LIBS applications in food technology, some of which are in food safety applications such as detection of pesticides in powdered spinach and rice pellets (Kim, Kwak, Choi, & Park, 2012) and identification of *Escherichia coli* O157:H7 and *Salmonella enterica* in foods and on surfaces (Multari, Cremers, Dupre, & Gustafson, 2013). Other food applications include the examination of quality properties in foods, such as the determination of macro and micronutrients in sugarcane leaves (Nunes et al., 2010), and direct determination of trace elements in starch-based flours (Cho et al., 2001).

In this study, detection of Na in bakery products is conducted by using a simple and inexpensive LIBS system for quantifying NaCl concentration to demonstrate the applicability of LIBS for the analysis of NaCl in bakery products. To this end, standard bread samples are chosen as the model system. In addition, commercial bakery products (crackers, biscuits and different types of breads) are included in this study. Further, titration and atomic absorption spectroscopy methods were used to confirm NaCl and Na concentrations in the samples.

2. Experimental methods

2.1. Reagents

Silver nitrate ($AgNO_3$), potassium chromate (K_2CrO_4), nitric acid (HNO_3) and NaCl were purchased from Sigma Aldrich (Steinheim, Germany). Bread flour and bread additive yeast were purchased from a local market. Standard bread samples were produced according to American Association of Cereal Chemists (AACC) Optimized Straight-Dough Bread-Baking Method No. 10–10.03 (AACCI, 2010). Twelve standard bread samples were produced by 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 mixed by hand for 15 min. Dough pieces were rounded and incubated for 30 min during the first fermentation. After 30 min, the dough was punched and incubated for 30 min during the second fermentation. Then, the dough was formed, placed into tins for the final fermentation and 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.

2.2. LIBS instrumentation

LIBS spectra were recorded using a Quantel-Big Sky Nd:YAG-laser (Bozeman, MT, USA), HR 2000 Oceanoptics Spectrograph (Dunedin, FL, USA) and Stanford Research System Delay Generator SRS DG535 (Cleveland, OH, USA). The experimental setup was presented in Fig. 1. The laser was operated at a fundamental wavelength of 532 nm and used for sample ablation. It was then run in the Q-switched mode at a repetition rate of 1 Hz. External gated detection was performed at 0.5 µs gate delay and 20 µs gate width. Spectrograph was externally triggered from the laser at every pulse with the delay generator. The laser energy was adjusted at 14 mJ/pulse. Samples were measured by the LIBS technique by

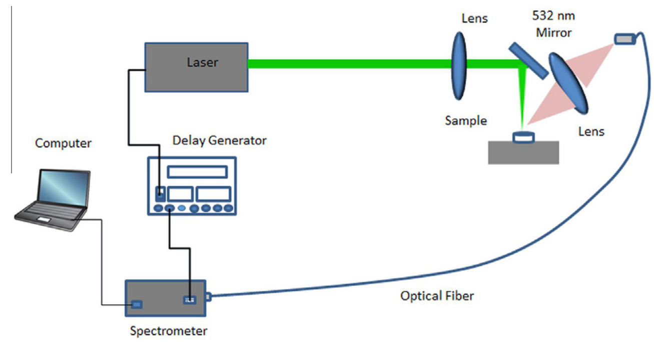

Fig. 1. Experimental setup of laser-induced breakdown spectroscopy (LIBS).

scanning five different locations and four excitations per location. LIBS experiments were performed in order to examine the Na content at 589 nm in bakery products to quantify NaCl, which was necessary to obtain calibration curves. This was achieved by preparing standard bread samples with various known concentrations of NaCl ranged between 0.025% and 3.5%. For the LIBS measurements, bread samples were dried at 105 °C for 2 h and cooled in a desiccator. Then, 400 mg of dried powdered bread samples were formed as a pellet under 10 tons of pressure using a pellet press machine. Samples were measured by using LIBS technique in triplicate, scanning five different locations and five excitations per location. The calibration curves for the Na line at 589 nm were obtained by plotting its intensity versus NaCl and Na concentrations in each sample.

2.3. NaCl detection in bakery products via titration (Mohr method)

NaCl content of standard bread samples and commercial samples were measured by Mohr method (reference method for NaCl measurements), which is a conventional method for NaCl detection in bakery samples (Serna-Saldivar, 2012). It is based on the determination of chloride ion concentration by titration with $AgNO_3$. In this method, samples were dried at 105 °C for 2 h, and 10 g of the dried samples were balanced into a conical flask. Following this process, hot water was added to the flask, and the flask was shaken thoroughly. The solution was sealed in a 250 ml conical flask using filter paper. Then, the conical flask was washed with hot water, which was poured onto the filter paper. As a result, salt on the filter paper was passed to the flask. After the solution in the flask was cooled, it was filled with deionized water till the level reached the 100 ml volume line. Because the reaction is better in alkaline media, a NaOH solution was used to make the solution alkaline. K_2CrO_4 (2–3 drops) was added, and the solution was titrated with $AgNO_3$. When all chloride ions were precipitated, the titration was terminated. Then, additional $AgNO_3$ ions reacted with the chromate ions of the K_2CrO_4, forming a red–brown precipitate of silver chromate (Serna-Saldivar, 2012). The percentage of NaCl in the samples was calculated according to the following equation:

$$\mathrm{NaCl}\% = \frac{\text{Titre value} \times \text{Normality of } AgNO_3 \times 0.0584 \times 100}{\text{Weight of sample}} \times 2.5 \quad (1)$$

2.4. Na detection in bakery products by atomic absorption spectroscopy

Na content of standard bread samples and commercial samples were measured using atomic absorption spectroscopy (the reference method for Na measurements). Samples were prepared according to the EPA Method 3051A by microwave-assisted