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Analytical note

Ash analysis of flour sample by using laser-*i*nduced breakdown spectroscopy

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ABSTRACT

Ash content is a measure of total mineral content in flour. It is also an important quality parameter in terms of nutritional labeling as well as processing properties of various cereal products. However, laboratory analysis takes a long time (5–6 h) and results in considerable waste of energy. Therefore, the aim of the study was to develop a new method for ash analysis in wheat flour by using laser induced breakdown spectroscopy (LIBS). LIBS is a multi-elemental, quick and simple spectroscopic method. Unlike basic ash analysis method, it has the potential to analyze a sample in a considerably short time. In the study, wheat flours with different ash contents were analyzed using LIBS and the spectra were evaluated with partial least squares (PLS) method. The results were correlated with the ones taken from standard ash analysis method. Calibration graph showed good linearity with the ash content between 0.48 and 1.39%, and 0.992 coefficient of determination (R^2). Limit of detection for ash analysis was calculated as 0.026%. The results indicated that LIBS is a promising and reliable method with high sensitivity for routine ash analysis in flour samples.

1. Introduction

The inorganic part of the food that remains after burning at high temperatures is called ash. Ash content represents the mineral content of the food and consists of major elements such as Na, K, Ca and Mg, and trace elements such as Fe, Zn, Cu. Although the average ash content of various food groups varies from 0.1% to 2.5% on wet weight basis, it plays an important role in food matrix [1]. Ash content affects the rheological properties and baking quality and determines nutritional quality of foods [2]. It is widely used as an index, especially for refinement of foods such as wheat flour. Ash content is a good indicator to understand the discrimination of bran and germ from the wheat kernel during flour milling. This is because bran has approximately twenty times higher ash content than endosperm. Furthermore, minerals in powder foods are responsible for increasing hygroscopicity indirectly through water-mineral bonds and indirectly mineral-carbohydrate interactions [2].

In order to determine the total mineral content of wheat flour, ash content is measured. In the basic ash method, well-mixed flour sample is placed in a muffle furnace at 550 °C for soft wheat flours or 575–590 °C for hard wheat flours. Sample is incinerated until light gray ash or constant weight is obtained. After cooling, the sample is weighed and ash content is calculated on dry basis [4]. This procedure is time consuming (5–6 h) and causes energy waste. Hence, alternative processes are needed for the ash analysis.

Ashing is also the first step of elemental analysis with atomic absorption spectroscopy and inductively coupled mass spectroscopy. Recent studies have focused on laser induced breakdown spectroscopy (LIBS) as a new, rapid and in-situ elemental analysis technique [5,6] in which plasma is created by means of focusing the laser through the lens on the sample surface. Due to the high temperature, sample is vaporized, excited and characteristic plasma light is formed. The obtained light is collected with fiber optics and directed into the spectrometer, and spectral signals are produced. These signals are related with chemical compositions of the sample [7]. Usually for optimal results, LIBS does require at least minimal sample preparation step, especially for powdered samples and is a rapid and in-situ method, which makes it distinct from atomic absorption spectrometer (AAS) and inductively coupled plasma-mass spectrometer (ICP-MS). The application field of LIBS has been expanding gradually, including studies on metallurgy, mining, environmental analysis and pharmacology [8–10]. However, there are only a few studies on food applications such as analysis of rice powder, unpolished-rice flour and starch [11] and Ca in breakfast cereals [12], Na and NaCl analysis in bakery products [13]. LIBS is also used for ash

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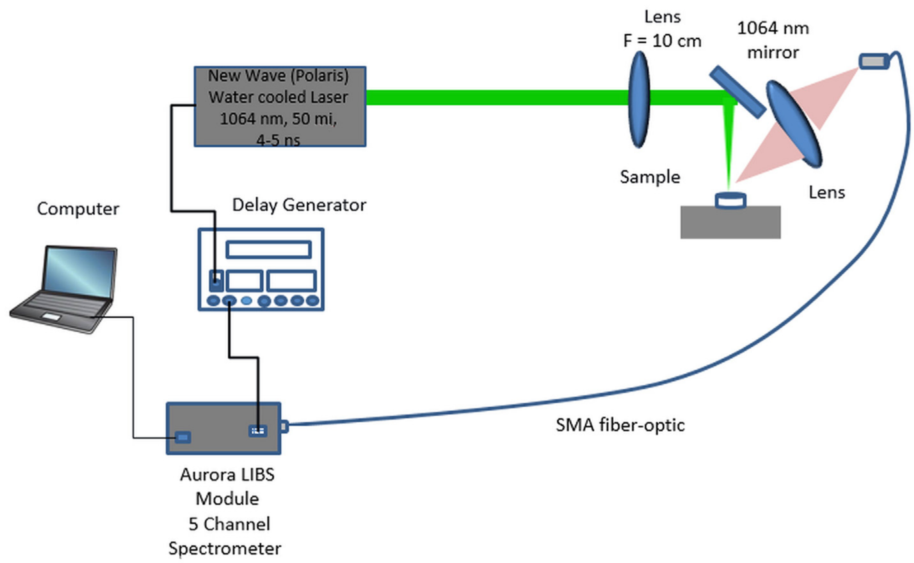

Fig. 1. LIBS experimental setup.

analysis in herbaceous materials [14] and elemental analysis of plant materials such as *Cannabis* plant material [15] and *Ocimum* L. species [16].

The study is focused on development of a new method for ash analysis in wheat flour by using LIBS. The aim was to develop a relatively rapid, practical and economical method compared to the conventional ones. For this purpose, wheat flours with different ash contents were analyzed with LIBS, and the spectra were evaluated using chemometric methods. The results of LIBS were compared with the results of basic ash method, and mineral matter composition of wheat flour was investigated with AAS method.

2. Experimental

2.1. Sample preparation

Wheat flour samples with different ash contents were obtained from Ankara Metropolitan Municipality Bakery Plant (Ankara Halk Ekmek Fab. Ankara, Turkey). Milled flour samples at different fineness were used randomly. The flour samples were dried in a drying cabined at 105 °C for 2 h. For LIBS analysis, three pellets were prepared from each flour sample (400 mg) with a pellet forming press under 10 tons of force. The diameter and height of pellet is 13 mm and 2 mm, respectively. Sixty-nine different flour samples with different ash contents were analyzed to obtain data for the calibration graph. Furthermore, 16 flour samples were analyzed for the validation of LIBS method.

2.2. Ash analysis

3–5 g of flour samples were weighted into ashing dishes. Then the samples were placed in a muffle furnace at 550 °C for soft wheat flours or 575–590 °C for hard wheat flours. They were incinerated until light gray ash or constant weight was obtained. After cooling, the samples were weighted, and ash contents were calculated on dry basis (Eq. (1)) [4].

$$\%\text{Ash} = \frac{\text{dry weight of residue}}{\text{sample weight}} \times 100 \quad (1)$$

2.3. LIBS instrumentation

LIBS spectra were recorded using a Polaris New Wave 50 mJ 1064 nm Nd:YAG laser (Fremont, CA USA) and Applied Spectra 5 channel Aurora LIBS spectrometer (Fremont, CA USA). Fig. 1 shows the experimental setup of the LIBS system. The laser was operated at a fundamental wavelength of 1064 nm and used for sample ablation. It was operated in the Q-switched mode at a repetition rate of 4 Hz, 300 ns gate delay and 1.05 ms integration time. The laser energy was 38 mJ/pulse. Pelleted samples were scanned with laser at 7 different regions for each pellet, and 15 shots were performed from each region.

2.4. Data analysis

To evaluate the multi elemental spectrum and reduce the matrix effect of flour samples, flours with different ash contents were analyzed using PLS application in the program (Version7.5.2 for Windows 7, Eigenvector ResearchInc., Wenatchee, WA, USA). In this study, 69 different flours with various ash contents were used for calibration data set; and 16 different flours with various ash contents were used for validation data set. Orthogonal signal correction (OSC), standard normal

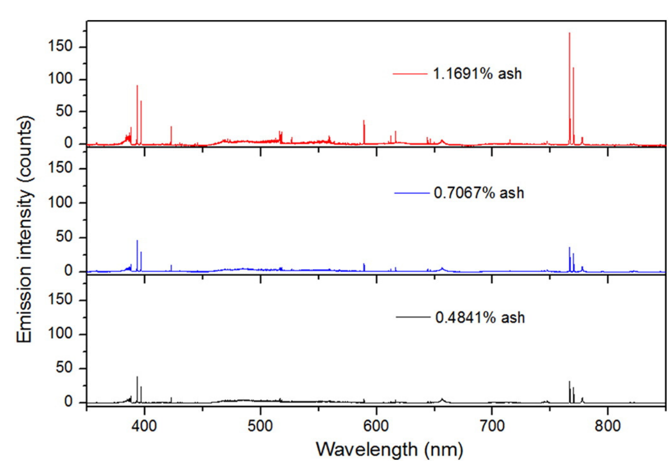

Fig. 2. LIBS spectra of flour samples with different ash content.