Food Chemistry 212 (2016) 183–188

Contents lists available at ScienceDirect

Food Chemistry

journal homepage: www.elsevier.com/locate/foodchem

Analytical Methods

Determination of whey adulteration in milk powder by using laser induced breakdown spectroscopy

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ARTICLE INFO

Article history:
Received 6 March 2015
Received in revised form 16 May 2016
Accepted 26 May 2016
Available online 27 May 2016

Keywords:
Whey adulteration
Milk powder
Laser induced breakdown spectroscopy (LIBS)
Mineral composition
Chemometrics

ABSTRACT

A rapid and *in situ* method has been developed to detect and quantify adulterated milk powder through adding whey powder by using laser induced breakdown spectroscopy (LIBS). The methodology is based on elemental composition differences between milk and whey products. Milk powder, sweet and acid whey powders were produced as standard samples, and milk powder was adulterated with whey powders. Based on LIBS spectra of standard samples and commercial products, species was identified using principle component analysis (PCA) method, and discrimination rate of milk and whey powders was found as 80.5%. Calibration curves were obtained with partial least squares regression (PLS). Correlation coefficient (R^2) and limit of detection (LOD) values were 0.981 and 1.55% for adulteration with sweet whey powder, and 0.985 and 0.55% for adulteration with acid whey powder, respectively. The results were found to be consistent with the data from inductively coupled plasma – mass spectrometer (ICP-MS) method.

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1. Introduction

Dairy products have high nutritional value and are widely consumed food groups for public nutrition, and dairy ingredients are also widely used in food industry. Therefore, they are one of the most commonly adulterated products due to their great economic importance (Cattaneo & Holroyd, 2013; De La Fuente & Juarez, 2005). Some adulteration techniques can be listed as adding water to milk, admixtures of the milks from different species, fat replacement, and cheese whey addition (De La Fuente & Juarez, 2005). Addition of cheese whey to milk or whey solids to dairy products is one of the most frequently applied adulteration method (De La Fuente & Juarez, 2005; Oancea, 2009). Whey is a low cost by-product of cheese making process. Addition of whey to milk or addition of whey powder to milk powder which is used in many product formulations may not cause a health hazard, but has economic, nutritional and legal implications. Hence, adulterations of dairy products are a major concern of both consumers and food manufacturers. Several methods have been developed to detect milk adulteration with whey. These methods can be categorized into two main groups, one of which is based on compositional differences between sweet/acid whey and milk through determination of the ratio of casein and whey protein by using derivative spectroscopy (Miralles, Bartolomé, Amigo, & Ramos, 2000), electrophoretic analysis (De Souza, Arruda, Brandao, & Siqueira, 2000) and polarography (Mrowetz & Klostermeyer, 1976). The principal of the other method is based on detection of caseinomacropeptide (CMP), which is a glycomacropeptide (GMP) and a specific compound of cheese making process. Therefore, GMP is a good chemical marker to detect milk adulteration with whey (Ferreira & Oliveira, 2003). When milk is treated with chymosin, k-casein is hydrolyzed into two peptides during cheese making process; one of them is para-k-casein which is incorporated in cheese curd, and the other one is solubilize GMP in whey (Brody, 2000). Thus existence of this peptide confirms adulteration in milk with whey (Neelima, Sharma, Rajput, & Mann, 2013). In order to detect GMP quantitatively, colorimetry (Fukuda, Roig, & Prata, 2004), reversed phase high performance liquid chromatography (HPLC) (Elgar et al., 2000), cation exchange chromatography (Léonil & Mollé, 1991), coupled to mass spectrometry (Mollé & Léonil, 2005), cellulose acetate electrophoresis (Nakano, Ikawa, & Ozimek, 2007), capillary zone electrophoresis (Cherkaoui, Doumenc, Tachon, Neeser, & Veuthey, 1997), polyacrylamide gel

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http://dx.doi.org/10.1016/j.foodchem.2016.05.169
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electrophoresis sodium dodecyl sulfate (SDS-PAGE) (Galindo-Amaya, Valbuena-Colmenares, & Rojas-Villarroel, 2006), immunochemical assays, ELISA (Chávez et al., 2012) have been developed. However, these methods are not suitable for routine analysis because they require a long analysis time and expensive equipment and materials. The recent advances in infrared spectroscopy have made it possible to analyze milk adulteration with whey by using infrared spectroscopy and chemometric analysis (Santos, Pereira-Filho, & Rodriguez-Saona, 2013), mid-infrared spectroscopy (MIR) and multivariate calibration method (Aparecida de Carvalho et al., 2015).

Many studies have showed the differences in mineral composition levels between milk powder and whey products. Although they have the same certain minerals, namely potassium, phosphorus, chloride, calcium and sodium (Cashman, 2006), the amount of these minerals differ in each of them. Mineral and trace element compositions are important for dairy industry in order to detect seasonal and geographical variations of dairy products (Reykdal, Rabieh, Steingrimsdottir, & Gunnlaugsdottir, 2011) and determine whey's area of use as a food ingredient, and to understand their nutritional contribution to foods. Furthermore, it is an indicator of mineral and trace element intake in a geographical region. Today, mineral and trace element compositions of products can be analyzed easily by using inductively coupled plasma mass spectrometer (ICP-MS) (Martino, Sánchez, & Sanz-Medel, 2001; Reykdal et al., 2011).

LIBS, a multi-elemental analysis method used for solids, gaseous and liquids in ppm range, is a rapid and simple procedure not requiring sample preparation step (Díaz Pace, D'Angelo, Bertuccelli, & Bertuccelli, 2006; Hanafi, Omar, & Gamal, 2000). It 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 broken down into atoms, which produces a characteristic radiation of 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). Moreover, its application has expanded to the fields such as metallurgy, mining, environmental analysis and pharmacology (Rusak, Castle, Smith, & Winefordner, 1997; 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 direct determination of trace elements in starch-based flours (Cho et al., 2001), and analysis of mineral composition of milk powder using LIBS (Lei et al., 2011).

The aim of this study was to evaluate the potential of LIBS as a rapid and *in situ* technique for the quantitative and qualitative determination of whey in milk powder. To this end, discrimination of milk and whey powders was performed based on differences of mineral compositions by using LIBS combined with multivariate data analysis techniques such as partial least square (PLS) and principal component analysis (PCA).

2. Experimental methods

2.1. Production of sweet whey, acid whey and milk powders

The raw cow's milk samples from five different reliable sources were obtained from different dairies in Ankara, Turkey. Their creams were separated to obtain skim milk. Some part of the milk was lyophilized to produce skim milk powder and the rest was used to produce sweet or acid whey powder. For this purpose, firstly, raw milk samples were pasteurized at 75 °C for 1 min. In order to obtain the acid whey, yoghurt culture (4%, mixture of *Streptococcus thermophilus, Lactobacillus delbruecki* subsp. *bulgaricus*) was added to milks at 44 °C and incubated for approximately 3 h until pH value reaches 4.5. To obtain sweet whey (rennet whey), fermented calf chymosin (Maxiren, 600 IMCU, DSM Food, Netherland) was added at a sufficient level to coagulate the milk in 30 min at 32 °C. After curd was formed for both methods, serum is separated by centrifugation (5000*g*, 15 min). All liquid samples including skim milk, acid whey, and sweet whey serums are frozen at −20 °C, and they were freeze-dried and grinded until become powdered. In addition to powder production, twelve commercial milk powders, three sweet whey and six demineralized whey powders were also received from six different brands.

2.2. LIBS measurements

For LIBS measurements, 400 mg of milk powder, sweet and acid whey powder samples were formed as a pellet under 10 tone of pressure by using a pellet press machine. Samples were measured in triplicate, by scanning five different locations and five excitations per location with LIBS technique. LIBS spectra were recorded using a Quantel-Big Sky Nd:YAG-laser (Bozeman, MT, USA), HR 4000 Oceanoptics Spectrograph (Dunedin, FL, USA) and Keithley Pulse Generator (Cleveland, OH, USA). The laser was operated at a fundamental wavelength of 532 nm and used for sample ablation. The laser was operated in the Q-switched mode at a repetition rate of 1 Hz, 2 μs gate delay, 30 μs gate width and 1 ms integration time. The laser energy was 18 mJ/pulse. LIBS experiments were performed to examine multi element composition of standard and commercial milk powder and whey products.

For qualitative discrimination of milk products' powders/powder of milk products/milk powder products/, 12 commercial skim milk powders, three commercial sweet whey and six commercial deionized whey powder, five standard skim milk powder, five standard sweet whey powder and five standard acid whey powder were analyzed with LIBS, and the (obtained) spectra was used. For the quantitative study, only the standard samples were used as model samples. The rate of standard sweet and acid whey powders added to standard skim milk powders was 1–40%. The samples were homogenized by mixing, and then the spectra were recorded.

2.3. Detection of milk products powders' elemental composition by ICP-MS

Elemental composition of standard and commercial skim milk powders and whey powders were measured using ICP-MS (as reference method). Samples were prepared according to EPA Method 3051A by microwave-assisted digestion for ICP-MS measurements (EPA Method 3051, 1994). First, 0.3 g of powder and 10 ml concentrated HNO_3 were placed in a fluorocarbon polymer vessel. The samples were extracted by heating with a laboratory microwave unit. Then, 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. ICP-MS spectra were recorded by the Thermo Electron X7 ICP-MS device (Thermo Electron, Winsford, UK).

2.4. Data analysis

Since determination of specific analytes from complex LIBS spectra is considerably difficult, multivariate data analyses were utilized for determination of skim milk powder and whey powders.

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