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Short-wave near-infrared spectroscopy analysis of major compounds in milk powder and wavelength assignment

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ABSTRACT

In this study, short-wave near-infrared (NIR) spectroscopy at 800–1050 nm region was investigated for the analysis of main compounds in milk powder. Through quantitative analysis, the feasibility is further demonstrated for the simultaneous measurement of fat, proteins and carbohydrate in milk powder. Two models, partial least-squares and least-squares support vector machine, were compared and utilized for regression coefficients and loading weights. The affect of standard normal variate spectral pretreatment to model performance was evaluated. Based on the resulted coefficients and loading weights, interesting wavelength regions of nutrition in milk powder are screened and the assignment of all specific wavelengths is firstly proposed in the details associated with chemical base. Instead of the whole short-wave NIR spectral data, these assigned wavelengths which can be reliably exploited were used for the content determination. Compared with other spectroscopy technique, assigned short-wave NIR spectral wavelengths did a good work. Determination coefficients for prediction are 0.981, 0.984, and 0.982, respectively for three components. The proposed wavelength assignment in the short-wave NIR region could be used for the component contents determination of milk powder, and could be as a guidance to interpret the spectra of milk powder.

1. Introduction

Short-wave near-infrared (NIR) spectroscopy technique is promising for the fast and nondestructive analysis of biological materials. As its high transmittance ability in the region of 700–1100 nm, the short-wave NIR spectra are being applied to construct excellent detectors for the nondestructive component determination in biological materials. The short-wave NIR region allows NIR energy to penetrate more deeply into a sample with much less heating effect than the long-wave NIR region (1100–2500 nm). Single-beam data can be reliably exploited in the short-wave NIR region to reduce measurement time [1] and the effects that arise from the water vibration in long-wave NIR region can be diminished [2]. Moreover, compared with other spectroscopy technique, short-wave NIR spectra can be obtained using inexpensive fiber optics, it can be measured with inexpensive light sources (tungsten lamps) and detectors (silicon diode array) [3], and it can be designed to be an inexpensive handheld instrument. Sasic and Ozaki used short-wave NIR to quantitative analysis of fat, protein, and lactose in raw milk by partial least-squares regression and wavelength assignment [4]. He et al. studied the measurement of sugar content of yogurt using short-wave NIR [5]. Subedi et al. investigated the mango eating quality at harvest using short-wave NIR [6].

Contents of main components are one of the important factors for the quality of milk powder. Chemical composition analyses are routinely performed for the inspection of

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main components in commercial milk powder, e.g. fats, proteins, and carbohydrates. However, most currently available chemical techniques for these analyses are time consuming, destructive and costly. A rapid, non-destructive, reliable and less expensive method is highly desirable in the milk powder industry. NIR spectroscopy is a feasible way for the components determination of the milk powder based on the NIR spectra [7–10]. Almost all the NIR experiments of milk powder were made for the long-wave NIR regions. Nutritional parameters in infant formulas powdered milk were also evaluated by Raman spectroscopy [11]. However, although with advantages over other spectroscopy technique, the study of quantitative and qualitative analysis of milk powder based on short-wave NIR spectra was less investigated. Moreover, there are a few investigations on the wavelength assignment in this region. The above mentioned reports were executed for the content determination based on the whole spectral data. Few reports were done for the content determination based on the assigned wavelengths. The wavelength assignment could be as a guidance to interpret the spectra of milk powder. If the performance based on wavelength assigned short-wave NIR spectra could be close to or higher than other common spectroscopy technologies, with its advantages of high transmittance ability and single-beam data reliable measurement, wavelength assigned short-wave NIR spectra can develop inexpensive on-line sensors and instruments for nondestructive determination and noninvasive diagnosed of the nutrition content in milk powder.

In this paper, the study was concentrated on the short-wave NIR spectra in the 800–1050 nm region. The feasibility of simultaneous measurement of major components in milk powder was newly investigated using this narrow wavelength, based on the quantitative analysis methods of partial least-squares (PLS) and least-squares support vector machine (LS-SVM). Finally the specific wavelength assignment was newly proposed. Instead of the whole short-wave NIR spectral data, these assigned wavelengths were used for the determination of three main components, fats, proteins and carbohydrates. The regression coefficients and loading weights for each wavelength and component were discussed to obtain the insight into the chemical base for quantitative analysis.

2. Materials and methods

2.1. Sample preparation

A total of 350 milk powder samples were used as the whole data set. Seven brands of 6–12-month infant milk powder were bought from several local super markets. Seven brands include the local brands from the common local brands, high-grade brands, and others from Chinese-foreign joint ventures corporation. Milk powder was stored in an ice filled cooler and transported to the laboratory to be kept at cold temperature ($4 \pm 1\,^{\circ}C$). The whole experiments were made at ambient temperature of 18–20 °C. Each sample was with full of the milk powder in the uniform glass containers (65 mm in diameter, 14 mm in height).

2.2. Spectra measurements

NIR reflectance spectra in the 700–1075 nm region were measured by a handheld FieldSpec Pro FR (325–1075 nm)/A110070, Trademarks of Analytical Spectral Devices, Inc. (Analytical Spectral Devices, Boulder, USA). Considering the 10° field-of-view of the spectral probe, the spectroradiometer was placed at a distance of approximately 150 mm and 45° angle away from the measurement area. As the only illumination, a light source of Lowell pro-lam 14.5 V Bulb/128690 tungsten (Ushio Lighting Inc., Japan) was applied about 300 mm away from the measurement area and 45° of horizon plane. The spectrum of each sample was the average of 30 successive scans. To avoid low signal-to-noise ratio, only the region of wavelengths (800–1050 nm) were employed for the calculations. Absorbance data were stored as log(1/R) (R = reflectance) at 1 nm intervals (250 spectra data points). Then these 30 values were averaged and stored as the absorbance value of this sample. All spectral data were stored in a computer and processed using the RS3 software for Windows (Analytical Spectral Devices, Boulder, USA) designed with a Graphical User Interface.

2.3. Content measurement of main component

Fat content was measured by Röse–Gottlieb method following GB/T 5413.3-1997 (National Standard of China). Protein content was determined by Kjeldahl method as described by GB/T 5413.1-1997 (National Standards of P.R. China) and the factor 6.38 was used to convert the nitrogen values to protein. Carbohydrate content was determined by Lane and Eynor's Method as described by GB/T 5413.5-1997 (National Standards of P.R. China). Content value is the weight per 100 g of milk powder.

2.4. Chemometric analysis

All chemometric analyses were carried out by Unscrambler ver 9.6 (CAMO PROCESS AS, OSLO, Norway) and MATLAB 7.1 (The Math Works, Natick, USA). The free LS-SVM toolbox (LS-SVM v 1.5, Suykens, Leuven, Belgium) was applied with MATLAB to derive all of the LS-SVM models. Four pretreated spectra, namely, first-derivative, second-derivative, standard normal variate (SNV) and multiplicative scatter correction (MSC) spectra led to simplified and more robust models. By calculating first and second derivation, sample-to-sample baseline variations are eliminated and also absorption peaks are enhanced. SNV [12,13] is a mathematical transformation method used to remove slope variation and to correct for scatter effects. MSC [14,15] corrects for difference in light scatter between samples before calibration. Based on total 350 samples, all the regression coefficients, loading weights of three components were automatically determined by software on two chemometric methods, namely, PLS and LS-SVM. In order to investigate the potential of short-wave NIR region for practice application, all the samples were divided into calibration and prediction sets, respectively. Hierarchical cluster analysis was established between samples. It is related to how similar the numerical properties of sample short-wave NIR spectra are. Each sample is linked to the closest sample or group of samples and a characteristic distance is used to describe this