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Multivariate near-infrared and Raman spectroscopic quantifications of the crystallinity of lactose in whey permeate powder

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Abstract

The use of near-infrared (NIR) and Fourier transform Raman spectroscopy for quantification of crystalline lactose content in whey permeate powder was investigated using chemometric methods. Sample sets consisting of binary mixtures of crystalline (50.0–98.0%) and amorphous lactose and process whey permeate samples with different amounts of crystalline lactose (75.0–95.5%) added were analyzed. The best results for quantification of crystallinity were obtained by partial least squares (PLS) regression on NIR data in five selected intervals in the range 1100–2498 nm. Data analysis on the total sample set of 35 samples yielded a prediction error (root mean square error of cross validation) of 0.627%. The corresponding result for Raman spectroscopy in the range 3500–100 cm^{-1} was 1.62%. Interval-PLS regression was used for the selection of relevant spectral intervals as well as for improving the spectral interpretation. Alternating regression was used to show that the amorphous lactose preparation contained only a negligible amount of crystalline lactose.

Keywords: Lactose; Crystal; Amorphous; iPLS; biPLS; Alternating regression; Whey permeate powder; NIR; Raman

1. Introduction

Lactose is used in many industrial products, especially in foods and pharmaceuticals, and lactose monohydrate (Beevers & Hansen, 1971) is the main component in whey permeate powder with a typical content of 80–95% (w/w). Whey permeate powder is used as an ingredient in spreads, instant drinks, bakery products and desserts. In whey permeate, lactose exists predominantly in the crystalline form, but whey permeate also contains some amorphous lactose (approximately 10%). Amorphous lactose in the glassy state is often undesirable in some food and pharmaceutical products, because it is meta stable which can lead to caking due to water adsorption followed by crystallization (Ross, 1997).

The demand for consistent and improved quality of food products requires development of instrumental methods for rapid determination of quality parameters. Currently, a great deal of interest is focused on the application of spectroscopic techniques such as near-infrared (NIR) and Raman that enable non-destructive at-/on-line monitoring in the food and pharmaceutical industries. Both NIR and Raman spectroscopies measure molecular vibrations and they, in contrast to mid-infrared (MIR) radiation, can be transmitted through quartz-based optical fibers, enabling simple and flexible sampling at the process line. Previous studies have shown that NIR spectroscopy has great potential as an

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analytical technique for the determination of homogeneity of powder blends (Scotter, 1990; Wargo & Drennen, 1996; Muzzio, Robinson, Wightman, & Brone, 1997; Luner, Majuru, Seyer, & Kemper, 2000; El-Hagrasy, Morris, D'Amico, Lodder, & Drennen, 2003) and quantification of lactose content (Kaffa, Norris, Kulscár & Draskovits, 1982; Baer, Frank, Loewenstein, & Birth, 1983; Buckton, Yonemochi, Hammond, & Moffat, 1998; Laporte & Paquin, 1999; Lane & Buckton, 2000; Tarkosova & Copikova, 2000; Hogan & Buckton, 2001) in various food systems. NIR studies (Buckton et al., 1998; Lane & Buckton, 2000; Hogan & Buckton, 2001) carried out on binary model systems were shown to yield high correlation with the crystallinity of lactose, which appears promising for the application of NIR for studying lactose crystallinity in complex food ingredients and products.

While a few on-line applications of Raman spectroscopy have been implemented in non-food industries, Raman spectroscopy has not yet been adopted by the food industry to the same extent (Li-Chan, 1996). Like NIR spectroscopy, Raman spectroscopy can be used with quartz fiber optic probes. In contrast to NIR and IR, water is relatively inactive in Raman spectroscopy, which is potentially an advantage in food applications and may provide good possibilities for remote sampling and direct application in production lines. A few reports using Raman spectroscopy on carbohydrates (Góral & Zichy, 1990; Engelsen & Nørgaard, 1996; Kacuráková & Mathlouthi, 1996; Söderholm, Roos, Meinander, & Hotokka, 1999; Söderholm, Roos, Meinander, & Steinby, 2000) and powders (Pellow-Jarman, Hendra, & Lehnert, 1996; De Paepe, Dyke, Hendra, & Langkilde, 1997; Taylor & Zografi, 1998) have been published, but the technical developments within Raman instrumentation and fiber optic probes continue to increase the number of potential applications. In one study, Raman spectroscopy was used to determine the crystallinity of dry powder samples of different starch materials (Bulkin, Kwak, & Dea, 1987).

The aim of the present study is to investigate and compare the suitability of NIR and Fourier Transform (FT)-Raman spectroscopy for quantification of the amount of crystalline lactose in a predominantly crystalline lactose whey powder. A sample set containing four subsets, including one two-component system of amorphous and crystalline lactose and three standard addition sets of different whey permeate powders were analyzed by NIR and FT-Raman spectroscopy. Predictive models allowing the calculation of the percentage (w/w) of crystalline lactose from measured NIR and Raman spectra were developed using multivariate partial least squares (PLS) regression and alternating regression models.

2. Materials and methods

2.1. Preparation of amorphous lactose

Amorphous lactose was produced by freeze-drying a 30% (w/w) solution of α-lactose monohydrate (Sigma-Aldrich, St. Louis, MO, USA) using a CD8 (Heto-Holten, Allerød, Denmark) freeze dryer. The primary dry of the freeze drying process was set to 1.5 hPa for 2 h at −10 °C, 10 h at 20 °C and 12 h at 25 °C. The yield of amorphous lactose was collected under vacuum in small glass bottles and stored at –20 °C. The amorphous lactose was ground using a mortar and pestle immediately before it was mixed (30 min) with crystalline lactose. The whole procedure was carried out as rapidly as possible in order to minimize the uptake of atmospheric moisture. As judged from analysis of both the NIR and Raman spectra of duplicates, no problems were encountered that could be attributed to the mixing procedure, i.e. the spectral differences between duplicates were minor compared with the overall changes between different samples.

2.2. Sample sets—overview

Four subsets, BM, WP1, WP2, and WP3, of homogenized samples were produced. Sample set BM contained binary mixtures of crystalline α-lactose monohydrate and amorphous lactose. The other three sample sets (WP1, WP2 and WP3) were based on whey permeate powder process samples (delivered by Arla Foods, Viby J, Denmark) with different amounts of crystalline lactose added.

2.3. Two-component sample set (BM)

The two-component sample set (BM) contained mixtures of crystalline α-lactose monohydrate and freeze-dried amorphous lactose with concentrations of crystalline α-lactose monohydrate ranging from 50% to 98% (w/w). The BM sample set comprised 16 samples with crystalline lactose concentrations: 50%, 60%, 70%, 72%, 74%, 80%, 82%, 84%, 86%, 88%, 90%, 92%, 94%, 95%, 96%, and 98%. All samples were mixed in 60 mL plastic bottles (Nalgene, Rochester, NY, USA) for one hour using a rolling mill developed by the Chemistry Department (The Royal Veterinary and Agricultural University, Frederiksberg, Denmark). Pure samples of amorphous lactose (0% crystalline lactose) and crystalline lactose (100%) were also measured.

2.4. Whey permeate powder sample sets

The three process products of whey permeate powder (WP1, WP2 and WP3) were Variolac 830, 836 and 950, respectively. WP1 and WP2 were pre-crystallized