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Technical note: At-line prediction of mineral composition of fresh cheeses using near-infrared technologies

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ABSTRACT

Milk and dairy products are important sources of macro- and trace elements for human health. However, fresh cheeses usually have a lower mineral content than other cheeses, and this makes mineral prediction more difficult. Although mineral prediction in several food matrices using infrared spectroscopy has been reported in the literature, very little information is available for cheeses. The present study was aimed at developing near-infrared reflectance (NIR, 866–2,530 nm) and transmittance (NIT, 850–1,050 nm) spectroscopy models to predict the major mineral content of fresh cheeses. We analyzed samples of mozzarella (n = 130) and Stracchino (n = 118) using reference methods and NIR and NIT spectroscopy. We developed prediction models using partial least squares regression analysis, and subjected them to cross- and external validation. Average Na content was 0.15 and 0.22 g/100 g for mozzarella and Stracchino, respectively. The NIR and NIT spectroscopy performed similarly, with few exceptions. Nevertheless, none of the prediction models was accurate enough to replace the current reference analysis. The most accurate prediction model was for the Na content of mozzarella cheese using NIT spectroscopy (coefficient of determination of external validation = 0.75). We obtained the same accuracy of prediction for P in Stracchino cheese with both NIR and NIT spectroscopy. Our results confirmed that mineral content is difficult to predict using NIT and NIR spectroscopy.
Key words: mozzarella cheese, Stracchino cheese, mineral, sodium

Technical Note

Milk and dairy products are important sources of macro- and trace elements for human health. It has been estimated that milk and dairy products provide the greatest dietary amounts of Ca and P, at 59 and 27% of human daily intake, respectively (Lombardi-Boccia et al., 2003). They also provide about 7% of the daily intake of Na, 9% of K, and 11% of Mg (Lombardi-Boccia et al., 2003). Calcium and P are essential for the health of bones and teeth (Bonjour et al., 2009), but Na has been implicated in hypertension and cardiovascular disease (Matthews and Strong, 2005; Aburto et al., 2013). The European Food Safety Authority and the World Health Organization have recommended a daily Na intake of less than 2.4 g, and mandatory labeling regulations require that "salt" (defined as Na × 2.5) be listed on product labels [Regulation (EU) No 1169/2011)] to help consumers in their purchasing decisions. Consequently, cheese producers may need to develop at-line tools to facilitate the determination of mineral content in cheese manufacturing, comply with labeling requirements, and add more detailed health claims to their products.

Infrared spectroscopy offers a rapid, objective, and nondestructive analysis of the sample at a much lower cost than common reference laboratory methods. Spectra collection can be performed using infrared technologies in reflectance or transmittance mode, but differences in accuracy have been reported for cheese. Moisture has been more accurately predicted in transmittance mode, but sensory and rheological attributes have been more accurately predicted in reflectance mode (Woodcock et al., 2008). To our knowledge, only a few studies have developed prediction models for the mineral composition of cheese using infrared spectroscopy in reflectance mode; Karoui et al. (2006a) used mid-infrared spectroscopy in transmittance mode to predict the NaCl content of Emmentaler cheese, and Manuelian et al. (2017b) used transmittance mode to predict the content of several minerals in cheese. The aims of the present study were to (1) develop near-infrared reflectance (**NIR**) and near-infrared transmittance (**NIT**) spectroscopy models to predict the major mineral composition of fresh cheeses, and (2) compare

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the effectiveness of these 2 infrared approaches in predicting the mineral content of cheese.

We collected a total of 130 mozzarella and 118 Stracchino samples from April to September 2016 in a large commercial Italian cheesemaking factory (Granarolo S.p.A, Bologna, Italy). Both fresh cheese varieties were made with pasteurized partially skimmed cow's milk. Mozzarella cheese production involved heating the milk to 33 to 39°C. Then, microbial rennet, a commercial culture starter and, if needed, citric acid (to correct milk acidity), were added to the milk, which was kept at 32 to 33°C. After milk coagulation and setting, the curd was broken with a metallic tool called a *spino*. Part of the whey was drained, and the curd was left to acidify in the remaining whey until it reached a pH of 5.3 to 5.4 and the cheesemaker determined it to be mature by a spinning test. The mature curd was completely drained, comminuted, and forwarded to the stretching machine. After complete spinning, the plasticized curd was shaped into spherical shapes and put into hardening and brining vats to develop its peculiar thin skin. Finally, the pieces of mozzarella were packaged in plastic bags in a light microfiltered brine. For Stracchino, milk was heated to 37 to 38°C and pumped into a cheese vat, where calf rennet, a commercial culture starter, and organic acid (to correct milk acidity) were added. After coagulation the curd was roughly cut, left for a rest period, and then separated from the whey. To reduce pH and drain excess whey, the curd was distributed into plastic rectangular molds and stewed for 5 h at 23 to 30°C. The mature curd was then placed in refrigerated brine for 4 to 5 d at 4°C before ripening.

For analysis, each sample (drained from the light brine when necessary) was ground using a MasterChef 8000 robot (Moulinex, Groupe Seb, Milan, Italy) at the cheesemaking factory and split in 2 aliquots. The subsample for chemical analysis was put in an airtight container to preserve product features; transported at 4°C to the laboratory of the Department of Agronomy, Food, Natural Resources, Animals and Environment of the University of Padova (Legnaro, Italy); and analyzed within 24 h of collection. Inductively coupled plasma optical emission spectrometry (ICP-OES; Ciros Vision EOP, Spectro Analytical Instruments GmbH, Kleve, Germany) was used to quantify Ca, Na, P, Mg, and K contents, following the procedure indicated by De Marchi et al. (2017). The subsample for the infrared analysis was directly used to fill a Petri cup (diameter 100 mm, depth 15 mm) and scanned at the cheesemaking factory using 2 infrared instruments, one working in reflectance mode and the other in transmittance. For reflectance mode, each spectrum was an average of 16 sub-spectra recorded at different points by rotating the Petri cup automatically in a Tango Fourier transform NIR spectrometer (Bruker, Billerica, MA) and recorded as $\log_{10}(1/\text{reflectance})$. The Tango spectrometer operated at room temperature, scanning every 4 cm^{-1} from 3,952 to 11,540 cm^{-1}, corresponding to 866 to 2,530 nm. For transmittance mode, each spectrum was an average of 32 sub-spectra recorded at different points by rotating the Petri cup automatically in a FoodScan Dairy Analyzer (Foss Electric A/S, Hillerød, Denmark) and recorded as $\log_{10}(1/\text{transmittance})$. The FoodScan Dairy Analyzer operated at room temperature, scanning every 2 nm from 850 to 1,050 nm. In addition, cheese moisture, fat, and protein contents were indirectly determined at the cheesemaking factory using the FoodScan Dairy Analyzer precalibrated with Foss Artificial Neural Networks Dairy Calibration, as reported by Manuelian et al. (2017a).

Prediction models were carried out using SAS version 9.4 (SAS Institute Inc., Cary, NC). Normality was assessed by visual inspection and by the Shapiro-Wilk test statistic, and $\log_{10}$ transformation was applied to K content of both the mozzarella and Stracchino cheeses to normalize the data. Concentration outliers were defined as values greater than 3 standard deviations from the mean of each mineral. Following this procedure, 3 observations for the P content of mozzarella and 1 observation for the Na content of Stracchino were discarded. Spectral data outliers were assessed using principal component analysis and the Mahalanobis distance, calculated according to Brereton (2015). The plot of the first principal component versus the second (which together explained more than 99% of the total spectral variation) did not point out any obvious spectral outliers. Partial least squares regression analysis (SAS version 9.4; SAS Institute Inc.) was carried out to develop the prediction models, which included the vector of each mineral as a dependent variable and the matrix of transmittance or reflectance as predictors. For each mineral, we split the data set into a calibration set (75% of observations) and a validation set (25% of observations). The calibration set was used to generate the prediction models, and the validation set to externally validate the models and quantify their predictive ability. We repeated this process 4 times for each trait: the first iteration excluded the first of every 4 observations from the calibration set (and therefore included them in the validation set), the second iteration excluded the second observation of every 4, and so on for the third and fourth iterations. One-at-a-time cross-validation was also performed in the calibration set. The mean, standard deviation, and range for each mineral in each iteration were similar for both the calibration and validation sets. We determined the optimal number of model factors as the minimum number of factors needed to achieve the lowest root mean predict-