Potential estimation of minerals content in cow milk using mid-infrared spectrometry

H. Soyeurt[1]*, D. Bruwier*[1]*, P. Dardenne*[2]*, J.-M. Romnee*[2] *& N. Gengler*[1,3]

[1]*Gembloux Agricultural University, Animal Science, B-5030 Gembloux, Belgium*
[2]*Walloon Agricultural Research Center, Quality Department, B-5030 Gembloux, Belgium*
[3]*National Fund for Scientific Research, B-1000 Brussels, Belgium*

Summary

Mineral contents in milk influence the human and animal health. The variation of sodium (Na) could also be a good indicator of mastitis and are related to the milk fever. A low intake of calcium (Ca) promotes the osteoporosis in human. Consequently, knowing regularly the mineral contents in milk could be interesting. Unfortunately, the common chemical analyses used to measure the concentrations of mineral in milk are expensive. The aim of this study was to develop some calibration equations to predict the contents of mineral directly in bovine milk using mid-infrared (MIR) spectrometry. Using a principal components approach, 70 samples were chosen based on their spectral variability from the 1 609 collected milk samples. A total of 14 samples were considered as outliers. So, 57 samples were analyzed by inductively coupled plasma atomic emission spectrometry (ICP-AES) to estimate the reference concentrations of minerals. Based on these values and the corresponding spectra, 3 calibration equations were built permitting to predict the contents of Ca, Na and phosphorus (P). To assess the accuracy of the developed equations, a full cross-validation was applied. In the same way, the RPD ratio corresponding to the ratio of the standard deviation to the standard error of cross-validation was estimated. The best accuracy was observed for the calibration equations estimating the contents of Ca (R^2cv=0.82, RPD=2.35) and P (R^2cv=0.77, RPD=2.06). In conclusion, the MIR spectrometry seemed to be a good alternative method to predict the contents of Ca and P in bovine milk.

Key words: Calcium, Sodium, Phosphorus, Cow milk, Mid-infrared.

Introduction

The contents of mineral are important for the human and animal health. The contents of calcium (Ca) are related to the osteoporosis in human (Nordin, 1997). The variation in the content of sodium (Na) in milk is related to the milk fever (El-Amrousi and Hofmann, 1970), alkalosis (Nicpon and Hejlasz, 1985) and could be a good indicator of mastistis (Waldner *et al*., 2001).

In Belgium, some recent dairy products are enriched in Ca to prevent the osteoporosis due to a low intake of this mineral per day. This process of production requires regular analyses of milk to quantify the contents of Ca. In the same way, if we want to detect the presence of mastitis, it is essential to realize also a regular check of the mineral contents in bovine milk. However, the common chemical analyses [e.g., inductively coupled plasma atomic emission spectrometry (ICP-AES)] are expensive.

Mid-infrared (MIR) is an electromagnetic radiation located from 1 000 to 5 000 cm^{-1}. The fundamental absorptions of molecular vibrations occurred in this region confer a high sensitivity to the chemical environment (Belton, 1997). This method is also fast and cheap. Finally, this method has already used by many milk laboratories to measure the content of major milk components as the percentages of fat, protein, urea or lactose. This last advantage is the most interesting if we want to implement largely and routinely the measures of minerals in milk.

The aim of this study was to develop the calibration equations for the measurement of Ca, Na and phosphorus (P) directly in bovine milk using MIR spectrometry.

Material and method

A total of 1 609 milk samples were collected twice during one year (Mars 2005 - May 2006) from 475 cows in 8 herds. These cows belonged to 6 dairy breeds: dual purpose Belgian Blue, Holstein Friesian, Jersey, Montbeliarde, Normande, and non-Holstein Meuse-Rhine-Yssel type Red and White. According to the ICAR rules, milk sample contained 50% of morning milk and 50% of evening milk. One part of these samples was analyzed by MIR spectrometry (Foss MilkoScan FT6000) at the Walloon milk committee (Battice, Belgium) and the generated spectra files were recorded. The second part of these samples was conserved at -26°C waiting the reference chemical analysis. This large number of samples covered a large variation of milk composition.

Seventy samples were used for the calibration procedure. They were chosen from their spectral variability using a principal component approach. The mineral contents were measured 6 times using ICP-AES without previous mineralization of milk. Nine samples showed a bad conservation and were not analyzed and 4 were considered as outliers from PCA results. The final data set contained 57 milk samples. From the reference concentrations of mineral obtained by ICP-AES and the corresponding spectral data, 3 calibration equations were built by partial least squares regressions using a specific program for multivariate calibration (WINISI III, <*www.winisi.com*>). No previous pre-treatment was used on spectral data. To assess the accuracy of the developed calibration equations, a full cross-validation was used. Different statistical parameters were estimated: the standard error of calibration (SEC), the calibration coefficient of determination (R^2c), the standard error of cross-validation (SECV), and the cross-validation coefficient of determination (R^2cv). The RPD ratio corresponding to the ratio of the standard deviation to SECV were also estimated to assess the accuracy of the developed equations.

Results and discussion

Table 1 shows the descriptive statistics of the 57 analyzed milk samples as well as the statistical parameters estimated for the developed equations. If the RPD value is superior to 2, the result given by the calibration equation can be considered as a good indicator of the studied trait. The RPD value was superior to 2 for the calibration equations, which predicted the contents of Ca and P in bovine milk.

Table 1. Descriptive statistics.

mg/l of milk	No.	Mean	SD	SEC	R^2c	SECV	R^2cv	RPD
Na	57	431.39	102.10	41.11	0.84	57.31	0.69	1.78
Ca	57	1 251.58	157.44	48.87	0.90	66.98	0.82	2.35
P	57	1 071.02	107.03	29.42	0.92	51.87	0.77	2.06

Guéguen and Pointillart (2000) indicated that 65% of Ca is bonded to the casein. Consequently, the prediction of Ca by MIR spectrometry could not give more information than a correlation between the protein content and the Ca. So, the correlations between the known milk components such as the percentages of fat, protein, urea and lactose in milk and the predicted mineral contents were calculated to assess the pertinence of this prediction of minerals by MIR spectrometry. The correlation between the protein percentage and the Ca content equal to 0.21 was largely inferior to the correlation estimated from the calibration (0.95) (Rc) and the correlation estimated from the cross-validation (0.90) (Rcv). The other estimated correlations were also inferior to Rc and Rcv. The same observations can be done for P. However, the content of Na seems to be better predicted based on the correlation between the percentage of lactose and Na. So, this calibration seems to be not really interesting for a potential use.

Table 2. Correlations between the mineral contents measured by ICP-AES and the known milk components.

	Ca	P	% fat	% protein	% lactose	Urea
Na (mg/l of milk)	-0.25	-0.08	-0.49	0.33	-0.76	0.46
Ca (mg/l of milk)		0.58	0.52	0.21	0.19	-0.37
P (mg/l of milk)			0.38	0.56	-0.02	0.14
%fat (g/dl of milk)				0.29	-0.41	0.39
%protein (g/dl of milk)					0.19	-0.12
%lactose (g/dl of milk)						-0.33

Conclusions

Even if the developed calibration equations need the addition of more analyzed samples, the MIR spectrometry seems to be a fast method to predict the contents of minerals directly on milk samples. The calibration equations, which predicted the contents of Ca and P, showed the best accuracy. The implementation of these equations in milk laboratories could offer interesting industrial (e.g., nutritional quality) and management applications (e.g., animal selection).

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