Near infrared spectroscopy with a fiber optic probe for determining the fatty acid profile in raw milk

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Introduction

Milk is a complex beverage and contains many components such as lipids, proteins, carbohydrates and minerals in variable concentrations. The wide variety of milk fatty acids (FA) can be beneficial to human health, especially in the context of the increasing social demands for healthy food. Therefore it is now relevant to accurately estimate milk composition and quality at low cost, and to identify the factors affecting milk variation. This approach is essential for obtaining high quality dairy products.

The study presented here belongs to a broader project which aims at using near infrared (NIR) spectroscopy for daily online measurement within the milking room (*Milkinir* research project, subsidised by the Agricultural Head Office of the Walloon region - DGARNE-DGO3, Belgium). To that purpose, it is essential to propose recording equipment which suits for multiple measurements at several places inside the same area, while preserving a sufficient spectral quality in order to predict a maximum of parameters. The use of fiber optic probes connected to a FT-NIR spectrometer is considered here. The objective of the present study is to evaluate the potential of such a system as an alternative technique to the current methods used for quantification of milk FA composition (mainly based on gas chromatography). The possibility of employing NIR predictive models would hasten the analytical procedure compared to the chemical steps of current reference methods which involve extraction by solvents and derivation of FA before GC analysis.

Materials and Methods

Samples and near infrared spectroscopy

Broad FA variability was ensured by collecting 583 raw cow milk samples from different farms, species and feeding regimes, between August 2008 and June 2009. Individual fresh milk samples were analysed using a FT-NIR Matrix-F (834–2502 nm) from Bruker Optics (Ettlingen, Germany), equipped with a fiber optic probe which measures in transflection mode (IN271P-02, Bruker Optics transflection probe for process control). NIR spectra of the milk samples were collected at 38 ± 1 °C. Each sample was measured in duplicate, and the spectral mean was used for further analysis and calibration models.

Chemometrics

From the total set, 82 samples were selected for calibration using principal component analysis (PCA; Mahalanobis standardised distances between the closest neighbours equal or higher than 0.6). Detailed FA compositions of the 82 selected milk samples were determined by gas chromatography (GC) according to the method of Collomb and Bühler.[1]

Multivatiate analyses were performed in OPUS 6.5 (Bruker Optics, Ettlingen, Germany). Standard normal variate (SNV) correction was applied to the raw data, and spectra were then transformed using a mathematical first order gap derivation (Savitzky-Golay). Predictive equations were developed using modified partial least squares (MPLS) regression with cross-validation (leave one out method).

Results and Discussion

The ratio of standard error of prediction to standard deviation (RPD) provides a basis for standardising the standard error of prediction and should be as high as possible. RPD values of 2.5-3.0 are considered adequate for screening the samples for quality.[2] The statistical models for fat and the studied fatty acids are reported in Table 1. Our results showed better prediction for milk FA in higher concentrations than for the minor constituents. Coppa *et al.*[3] found similar results with NIR spectroscopy of milk powder.

Reference paper as:
H.N. Nguyen, F. Dehareng, M. Hammida, A. Niemöeller and P. Dardenne(2012). Near infrared spectroscopy with fiber optic probe for determinating the fatty acid profile in raw milk, in: Proceedings of the 15th International Conference on Near Infrared Spectroscopy, Edited by M. Manley, C.M. McGoverin, D.B. Thomas and G. Downey, Cape Town, South Africa, pp. 458-460.

Table 1. Statistical models for fat and the FA composition (variability expressed in g.dl^{-1} of milk).

N = 82	Min–Max	SE_C	R^2_C	SE_{CV}	R^2_{CV}	RPD_{CV}
Fat	2.05–5.96	0.05	1.00	0.06	0.99	12.3
C4:0	0.07–0.18	0.01	0.61	0.02	0.48	1.4
C6:0	0.04–0.11	0.01	0.45	0.01	0.39	1.3
C8:0	0.03–0.07	0.01	0.34	0.01	0.27	1.2
C10:0	0.06–0.20	0.02	0.70	0.02	0.45	1.3
C12:0	0.05–0.27	0.02	0.74	0.03	0.50	1.4
C14:0	0.27–0.73	0.05	0.80	0.06	0.71	1.9
C14:1	0.02–0.08	0.01	0.66	0.01	0.56	1.5
C16:0	0.59–2.08	0.11	0.89	0.12	0.86	**2.7**
C16:1	0.03–0.16	0.02	0.72	0.02	0.64	1.7
C17:0	0.01–0.05	<0.01	0.77	<0.01	0.74	2.0
C18:0	0.16–0.71	0.07	0.66	0.07	0.62	1.6
C18:1trans	0.04–0.22	0.03	0.58	0.03	0.51	1.4
C18:1n9	0.25–1.64	0.06	0.95	0.09	0.88	**2.9**
C18:2n6	0.02–0.11	0.01	0.85	0.01	0.69	1.8
C18:3n3	0.01–0.04	<0.01	0.64	<0.01	0.51	1.4
CLA	0.01–0.08	<0.02	0.48	<0.02	0.37	1.3
∑Omega-3	0.01–0.06	<0.01	0.69	<0.01	0.60	1.6
∑Omega-6	0.05–0.16	<0.02	0.77	<0.02	0.65	1.7
SFA	1.57–4.16	0.11	0.97	0.14	0.94	**4.2**
UNSAT	0.48–2.13	0.07	0.96	0.10	0.91	**3.4**
MUFA	0.41–1.81	0.06	0.96	0.08	0.92	**3.5**
PUFA	0.07–0.27	0.02	0.79	0.03	0.69	1.8
SCFA	0.22–0.51	0.04	0.74	0.05	0.52	1.5
MCFA	1.18–3.20	0.16	0.90	0.18	0.88	**2.9**
LCFA	0.59–2.76	0.14	0.91	0.15	0.87	**2.8**

N : number of samples used to develop the model; SE_C : standard error of calibration; R^2_C : coefficient of determination for calibration; SE_{CV} : standard error of cross-validation; R^2_{CV} : coefficient of determination for cross-validation; RPD_{CV} : residual predictive deviation; SFA : saturated fatty acids; MUFA : monounsaturated fatty acids; PUFA : polyunsaturated fatty acids; UNSAT : unsaturated fatty acids; CLA : conjugated linoleic acid; SCFA : short-chain FA; MCFA : mid-chain FA; LCFA : long-chain FA.

Our prediction models showed good performance (RPD ≥ 2.7) for C16:0, C18:1n9, saturated fatty acids (SFA), unsaturated fatty acids (UNSAT), monounsaturated fatty acids (MUFA), mid-chain FA (MCFA) and long-chain FA (LCFA). Unfortunately, we failed to accurately predict Omega-3/6 fatty acids, conjugated linoleic acid (CLA), polyunsaturated fatty acid (PUFA), short-chain FA (SCFA) and most of the individual FA concentrations. The quality of prediction decreased when FA were present in too low concentrations (i.e. ≤ 0.73 g.dl^{-1} of milk). Linear regression plots of SFA and C4:0 (measured versus predicted values, expressed in g.dl^{-1} of milk) are shown in Figures 1 and 2, respectively.

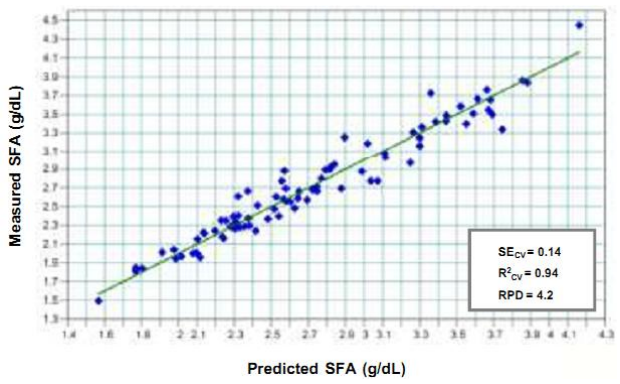

Figure 1. Linear regression plots of measured versus predicted values of SFA.

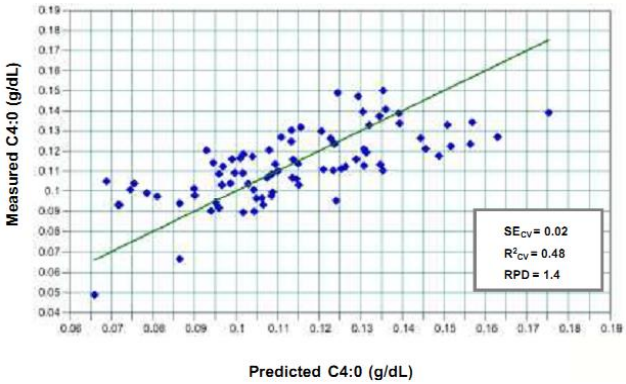

Figure 2. Linear regression plots of measured versus predicted values of C4:0.

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Conclusion

The statistical results showed that a FT-NIR fiber optic probe system can be used to satisfactorily predict fatty acid sums and ratios. For individual milk fatty acids present in low concentrations, it remains valid to use the predicted values as an indicator for batch selection.

Nevertheless, more research should be done by increasing the initial sampling size in order to try to improve the quality of prediction. Moreover, it could be useful to focus on other spectral pretreatment procedures while simultaneously testing other regression methods in an attempt to get more accurate equations to estimate the milk fatty acid profile.

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References

1. M. Collomb and T. Bühler, *Travaux Chimiques en Alimentation et Hygiène* **91**, 306-332 (2000).
2. G. Sinnaeve, P. Dardenne, R. Agneessens and R. Biston, *J. Near Infrared Spectrosc*. **2**, 79-84 (1994).
3. M. Coppa, A. Ferlay, C. Leroux, M. Jestin, Y. Chilliard, B. Martin and D. Andueza, *Int. Dairy J.* **20**(3), 182-189 (2010).

Reference paper as:
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