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Standardization of milk mid-infrared spectra from a European dairy network

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ABSTRACT

The goal of this study was to find a procedure to standardize dairy milk mid-infrared spectra from different Fourier transform mid-infrared spectrophotometers (different brands or models) inside a European dairy network to create new farm-management indicators (e.g., fertility, health, feed, environmental impact) based on milk infrared spectra. This step is necessary to create common spectral databases, allowing the building of statistical tools, to be used by all instruments of the network. The method used was piecewise direct standardization (PDS), which matches slave-instrument spectra on master-instrument spectra. To evaluate the possibility of using common equations on different instruments, the PDS method was tested on a set of milk samples measured on each machine, and an equation predicting fat content of milk is applied on all. Regressions were performed between master and slaves fat predictions, before and after PDS. Bias and root mean square error between predictions were decreased after PDS, respectively, from 0.3781 to 0.0000 and from 0.4609 to 0.0156 (g of fat/100 mL of milk). The stability over time of these results was confirmed by an application of the coefficients created by PDS 1 mo later on the slave spectra. These preliminary results showed that the PDS method permits a reduction of the inherent spectral variability between instruments, allowing the merging of Fourier transform mid-infrared milk spectra from different instruments into a common database, the creation of new types of dairy-farm-management indicators, and the use of these common calibrations for all Fourier transform mid-infrared instruments of the European dairy network.

Key words: Fourier transform mid-infrared spectrometry, standardization, dairy milk, piecewise direct standardization

INTRODUCTION

This work is the first step of a project aiming to develop innovative farm-management web applications based on the use of Fourier transform mid-infrared (**FT-MIR**) spectrometry analysis of milk to enable a sustainable and profitable management of the milk production. Fourier transform mid-infrared spectrometry is the worldwide method of choice for composition and quality controls during routine liquid milk testing. It allows a fast, nondestructive quantification of milk chemical properties to avoid reference methods, which are usually tedious, expensive, and time consuming. In 1961, a patent application for a FT-MIR method determining fat, protein, and lactose in milk was introduced (Goulden, 1964). The first apparatus, an IRMA (Infrared Milk Analyzer, Grubb Parsons, Newcastle upon Tyne, UK) using a monochromator, was based on the principle of measuring direct absorption of the infrared energy at specific frequencies by carbonyl groups in the ester linkages of the fat molecules, by peptide linkages between amino acids of protein molecules, and by the O-H groups in lactose molecules. A second generation of infrared instrumentation has adopted the change from wavenumber selection by diffraction grating to optical filters (Grappin and Jeunet, 1976) and was largely used by Central milk laboratory testing, where both tank milk and individual-cow samples were tested. Fourier transform mid-infrared supplies complementary chemical information and allows a high throughput with high sensitivity in a short response time from a very small quantity of sample (Ghosh and Jayas, 2009). In 1993 the first purpose-built FT-MIR instrument based on the Fourier transform infrared (FT-MIR) technology was marketed (Anadis MI-200; Asselain et al., 1996). With the introduction of the FT-MIR, new applications have been developed because of the use of the full spectrum of the sample. In this way, FT-MIR has been applied for the determination of more and more milk components such as proteins composition (Bonfatti et al., 2011), minerals (Soyeurt et al., 2009), ketone bodies (van Knegsel et al., 2010), lactoferrin (Soyeurt et al., 2007), and fatty acid profile (Rutten et al., 2009; Soyeurt et al., 2011). Then recent studies were performed using these milk components predicted by FT-MIR to

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predict physiological indicators of the animal (Friggens et al., 2007; Mohammed et al., 2011).

In the context of this research project the FT-MIR spectrum is directly considered as a reflection of the state of the cows, avoiding the step of milk composition, to obtain indicators concerning fertility, health, environment, and feeding among others. Until now, only a few studies have been performed to show the potential of the entire FT-MIR spectra as an indicator of those parameters. Only recent studies have shown that predictions based on direct spectra are much more global, sensitive, and accurate than those based on milk components when they are predicted from FT-MIR. Dehareng et al. (2012) have shown that enteric methane was better predicted when directly working with FT-MIR spectra than the results based on fatty acid predictions. Also recently, the FT-MIR spectrum of milk was shown to be a good indicator of body energy status (McParland et al., 2011), energy intake and efficiency (McParland et al., 2014), and fertility diagnosis (Laine et al., 2013) in dairy cattle.

This innovative approach of using FT-MIR spectroscopy needs the support of important spectral databases associated with reference values for each of the properties to be studied. For this reason, the OptiMIR project was built; it is a European Interreg project involving 6 countries and focuses on the development of prediction tools directly based on FT-MIR spectra. In this work, a large number of commercially available mid-infrared spectrometers (21) from different manufacturers (3) installed in different laboratories (10) located in different countries (3) were used. Because of differences of the instrumental responses between different FT-MIR spectrometers, spectra obtained on one instrument cannot readily be compared with a library acquired on a different instrument. Moreover, the use of calibration models developed on an instrument with FT-MIR spectra obtained on another instrument will usually lead to an increased uncertainty of the prediction model. This is a drawback when recalibrating an instrument or using a historical database. Therefore, spectral corrections adapted to each instrument (standardization procedures) are needed (Rodriguez et al., 2011). One of the most common techniques for instrument standardization is the piecewise direct standardization (**PDS**) proposed by Wang et al. (1991). However, in previous studies it was mainly used with near-infrared spectra (Bouveresse and Massart, 1996) and was not tested for milk spectra. Then, the objective of this work was to demonstrate and validate the use of the PDS to standardize spectra from different models and manufacturers of instruments, by reducing the inherent instrument-to-instrument variability, within the dairy network, such that the milk spectra from all spectrometers (the slaves) can be compared with the milk spectra of a standard instrument (the master). In such a way, it should be possible to create and maintain international databases containing data collected by all the FT-MIR instruments and to relate them to chemical characteristics of the milk (e.g., protein, fat, fatty acids content among others) and to animal physiology (fertility, nutrition, health, and environment).

MATERIALS AND METHODS

Standardization

Standardization samples are measured on a master instrument and on a slave instrument, leading to responses matrices **M** and **S**. The PDS method is based on the fact that the variation of spectroscopic data is limited to small spectral regions. In PDS, the response $\mathbf{m_j}$ measured at wavenumber **j** on the master instrument is related to the wavenumbers located in a small window ($\mathbf{s_j}$) of size **n** around **j** (neighboring) measured on the slave instrument (Figure 1). The window ($\mathbf{s_j}$) was composed by 5 wavenumbers and was the same for all instruments.

$$\mathbf{s_j} = [S_{(j-n)}, \ldots, S_{(j)}, \ldots, S_{(j+n)}]$$

A regression using the principal component regression method is calculated between each spectral response on the master at wavenumber j and the corresponding window s_j on the slave. Vector $\mathbf{b_j}$ is the vector of transformation coefficients for the jth wavenumber, and b_{0j} is the offset term.

$$m_j = \mathbf{s_j b_j} + b_{0j}$$

The **F** matrix contains the $\mathbf{b_j}$ coefficient transformation vectors for all wavenumbers. This way of calculating the $\mathbf{b_j}$ parameter using a moving spectral window leads to a banded diagonal matrix. The $\mathbf{b_0}$ vector contains the offset terms for all wavenumbers. Each time a new sample is measured on the slave instrument, the obtained spectra $\mathbf{S_{new}}$ can be standardize into $(\mathbf{S_{new}})_{\mathbf{std}}$ using **F** and $\mathbf{b_0}$.

$$(\mathbf{S_{new}})_{\mathbf{std}} = \mathbf{S_{new}F} + \mathbf{b_0}$$

The standardization model for every master–slave combination needs to be designed, describing the shift between each slave instrument and the master instrument.