Analyse du lait à la ferme par spectroscopie infrarouge (IR-TF ou FTIR) : un outil de gestion de la qualité

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No de projet : IA216684 **Durée :** 04/2016 – 04/2018

FAITS SAILLANTS

The overall objective of this project is the development of a new prototype for on-site analysis of milk quality at the dairy farm using infrared spectroscopic-based milk analysis methods. The project is proceeded through four main stages. **(1)** ***Assembly of three prototypes for on-farm FTIR milk analysis and optimization of sample handling and spectral acquisition conditions:*** for the assembly of a prototype, different combinations of infrared (IR) spectrometers and sample introduction methods were evaluated. The spectrometers evaluated included Fourier transform infrared (FTIR) spectrometers from different vendors as well as a filter-based IR spectrometer that employs a linear variable filter (LVF) coupled with a line array detector. In addition, three types of sample handling accessories were evaluated. ***(2) Calibration of the prototype analyzers for the quantitative determination of milk composition:*** Raw-milk samples provided by Valacta (an accredited milk analysis laboratory) together with their certificates of analysis. These samples were employed to calibrate the prototype analyzer for the prediction of fat, protein, and lactose content. The calibration models for the prediction of fat and protein content yielded very strong correlations between the predicted values and the reference values provided by Valacta. ***(3) Laboratory testing of prototype on-farm milk analyzers:*** Prototypes 1 and 2 developed in this project were moved to Valacta for testing. Analysis of the spectra of incoming raw-milk samples collected in parallel with Valacta's FTIR analysis for validation and refinement of the calibration models ***(4) On-farm testing of prototype milk analyzers:*** Two dairy farm with 75 cows whose milk is sampled regularly and taken to Valacta for analysis participated in the final validation studies. The analytical results from the prototype milk analyser were in very good agreement with the results provided by Valacta.

OBJECTIF(S) ET MÉTHODOLOGIE

The objective of this research is to develop a prototype for a miniaturized on-site milk analyzer that employs the infrared (IR) technology, since it is the basis for the current official method for milk analysis. The investigative method relies on scanning producer raw milk samples by several IR spectrometers and sample introduction methods. Portable Fourier transform infrared (FTIR) and handheld linear variable array (LVF) infrared spectrometers were selected for this study. The sampling method employed to acquire the infrared spectra included an infrared liquid transmission cell with calcium fluoride windows and attenuated total reflectance (ATR) accessory, whereby the milk sample is poured on to the ATR surface. In addition, different approaches were investigated to homogenize milk and to pump milk through the transmission cell. Partial least squares (PLS) regression was used for developing calibration models for the major milk components (i.e. fat, protein and lactose), urea and beta-hydroxybutyrate (BHB), and leave-one-out approach was used for cross validation of the calibration models.

RÉSULTATS SIGNIFICATIFS POUR L'INDUSTRIE

1- Portable FTIR spectrometers are superior to LVF spectrometers for on-site milk analysis (Table 1).

2- Transmission cells with calcium fluoride windows are superior to ATR measurement for on-site milk analysis (Table 1).
3- Controlling the temperature of the transmission cell did not improve the prediction accuracy of the calibration models of the major milk components.
4- Ultrasonication is an effective method for milk homogenization. Raw milk can be adequately homogenized by applying 3000 joules of ultrasonication energy for ~120s to a 5 mL milk sample containing ~4.5% fat. In addition, ultrasonication will degas the milk sample and generate heat to raise the temperature of the milk to ~ 48°C (Figure 1).
5- The flow rate of milk in to the infrared transmission cell must be adjusted to ~2 mL/min to avoid fat and protein depositions in the cell and to avoid formation of bubbles in the milk stream and to achieve a durable milk flow.
6- The use of a syringe to pull the milk in the IR cell was found to be efficient compared to the use of mechanical pumps.
7- The following table summarizes the prediction capability of the calibration models that were developed using different combinations of spectrometers and sample introduction methods

Table 1 Evaluation of the performance of different portable milk analyzers porotypes developed during the course of this project

<table>
<tr><th>Spectrometer</th><th>Sample Introduction Method</th><th>Milk</th><th>Component</th><th>Corr. Coeff. r</th><th>RMSEP%</th></tr>
<tr><td rowspan="6">IRsphinx – LVF IR Spectrometer</td><td rowspan="6">ATR</td><td rowspan="3">Producer raw milk</td><td>Lactose</td><td>0.97403</td><td>0.0662</td></tr>
<tr><td>Protein</td><td>0.85969</td><td>0.254</td></tr>
<tr><td>Fat</td><td>0.39419</td><td>0.459</td></tr>
<tr><td rowspan="3">Sonicated producer raw milk</td><td>Lactose</td><td>0.98020</td><td>0.0694</td></tr>
<tr><td>Protein</td><td>0.96030</td><td>0.164</td></tr>
<tr><td>Fat</td><td>0.80816</td><td>0.592</td></tr>
<tr><td rowspan="4">Agilent FTIR Excalibur 3000</td><td rowspan="4">ATR</td><td rowspan="3">Producer raw milk</td><td>Lactose</td><td>0.95926</td><td>0.0975</td></tr>
<tr><td>Protein</td><td>0.98485</td><td>0.106</td></tr>
<tr><td>Fat</td><td>0.84779</td><td>0.390</td></tr>
<tr><td>Sonicated producer raw milk</td><td>Fat</td><td>0.63533</td><td>0.427</td></tr>
<tr><td rowspan="3">Prototype 1 FTIR Bomem MB150</td><td rowspan="3">Temperature controlled transmission cell</td><td rowspan="3">Sonicated producer raw milk</td><td>Lactose</td><td>0.39196</td><td>0.228</td></tr>
<tr><td>Protein</td><td>0.93841</td><td>0.168</td></tr>
<tr><td>Fat</td><td>0.96440</td><td>0.153</td></tr>
<tr><td rowspan="3">Prototype 2 Agilent Cary 630 Portable FTIR</td><td rowspan="3">Transmission cell</td><td rowspan="3">Sonicated producer raw milk</td><td>Lactose</td><td>0.70404</td><td>0.178</td></tr>
<tr><td>Protein</td><td>0.97594</td><td>0.108</td></tr>
<tr><td>Fat</td><td>0.96008</td><td>0.169</td></tr>
<tr><td rowspan="9">Prototype 3 Bruker Alpah Portable FTIR</td><td rowspan="9">Transmission cell</td><td rowspan="3">Valacta milk calibration set – industrial homogenization</td><td>Lactose</td><td>0.96845</td><td>0.019</td></tr>
<tr><td>Protein</td><td>0.92949</td><td>0.037</td></tr>
<tr><td>Fat</td><td>0.99992</td><td>0.025</td></tr>
<tr><td rowspan="3">Valacta raw milk calibration set - sonicated</td><td>Lactose</td><td>0.81272</td><td>0.036</td></tr>
<tr><td>Protein</td><td>0.96985</td><td>0.065</td></tr>
<tr><td>Fat</td><td>0.99996</td><td>0.012</td></tr>
<tr><td rowspan="3">Sonicated producer raw milk</td><td>Lactose</td><td>0.95029</td><td>0.0793</td></tr>
<tr><td>Protein</td><td>0.96521</td><td>0.0746</td></tr>
<tr><td>Fat</td><td>0.99496</td><td>0.0585</td></tr>
</table>

Environ une page, y compris tableaux, graphiques ou illustrations en autant que possible, et la section suivante « APPLICATIONS POSSIBLES POUR L'INDUSTRIE ».

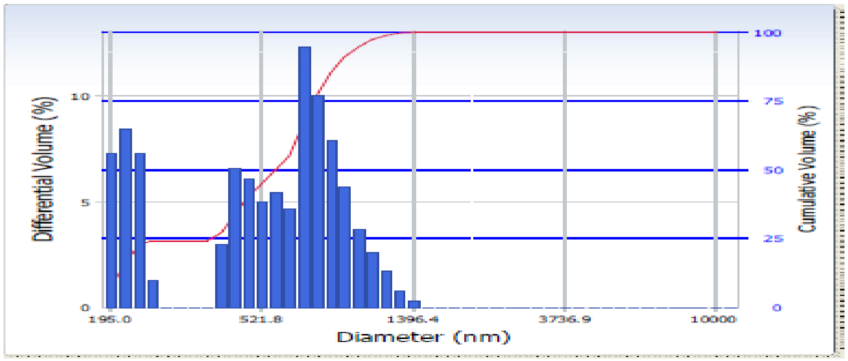

Figure 1 The particle size distribution of milk after homogenization by ultrasonication treatment

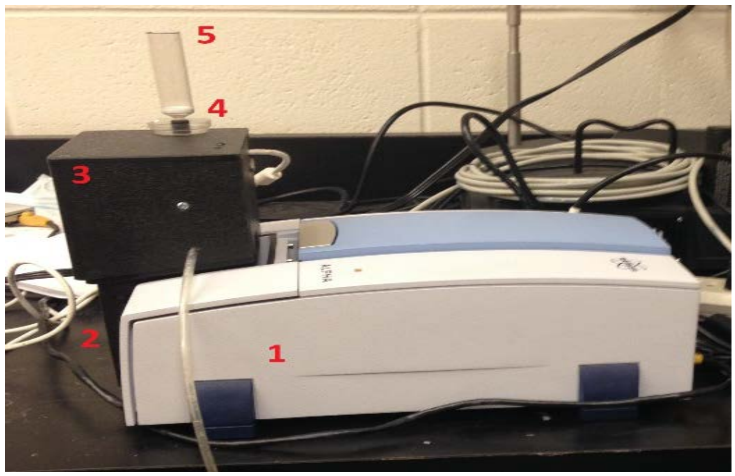

Figure 2 Prototype 3: 1. Alpha II FTIR portable spectrometer, 2. Transmission cell with calcium fluoride windows and ~50 µm pathlength, 3. Pumping head, 4. 25 µm filter, 5. Milk Inlet

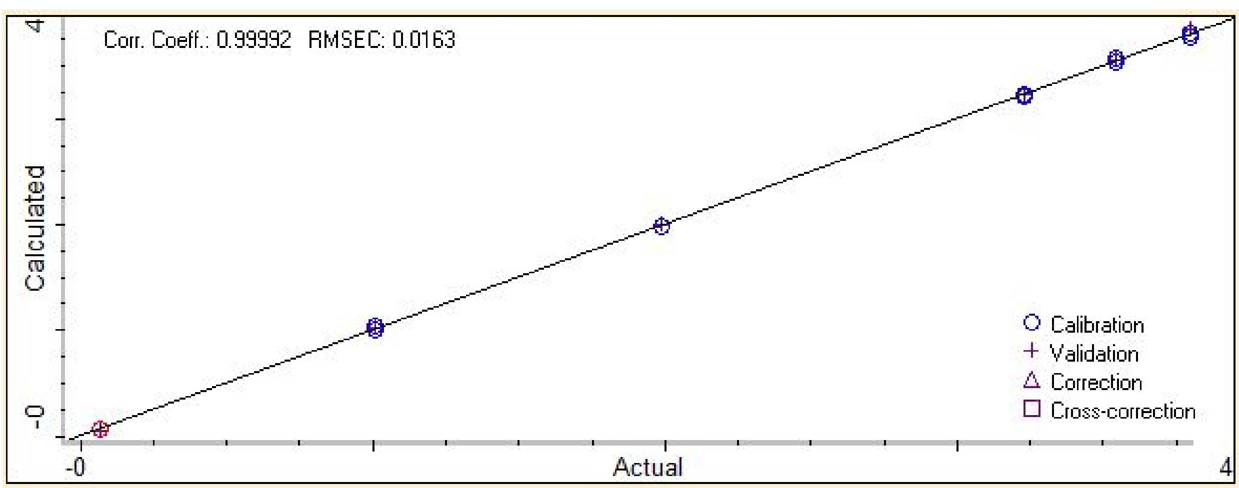

Figure 3 Prototype 3: PLS calibration curve for milk fat developed using Valacta's industrially homogenized milk official calibration kit

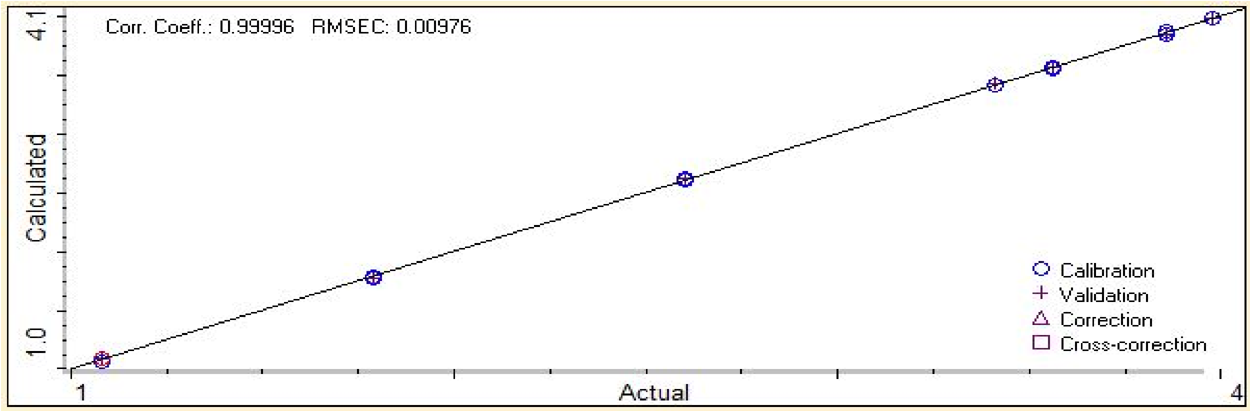

Figure 4 Prototype 3: PLS calibration curve for milk fat developed using Valacta's sonicated raw milk official calibration kit

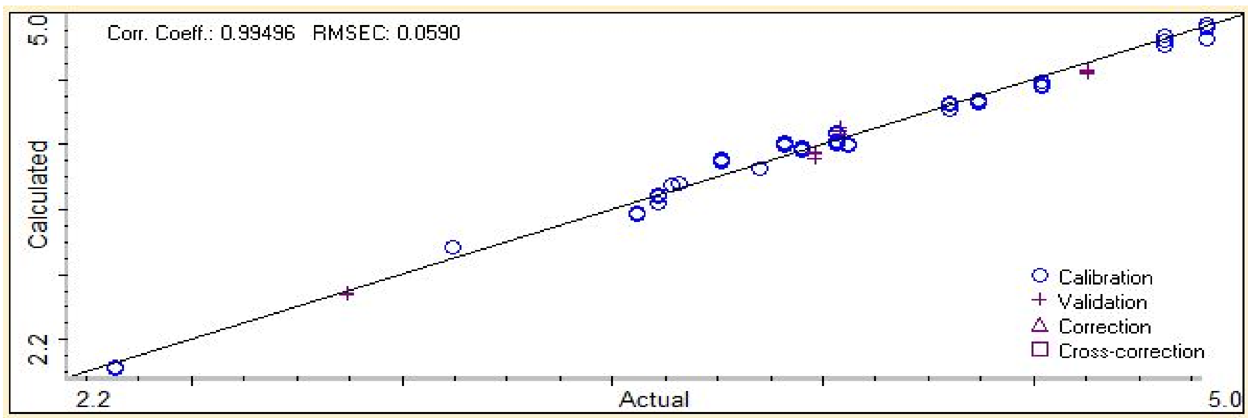

Figure 5 Prototype 3: PLS calibration curve for milk fat developed using sonicated producer raw milk

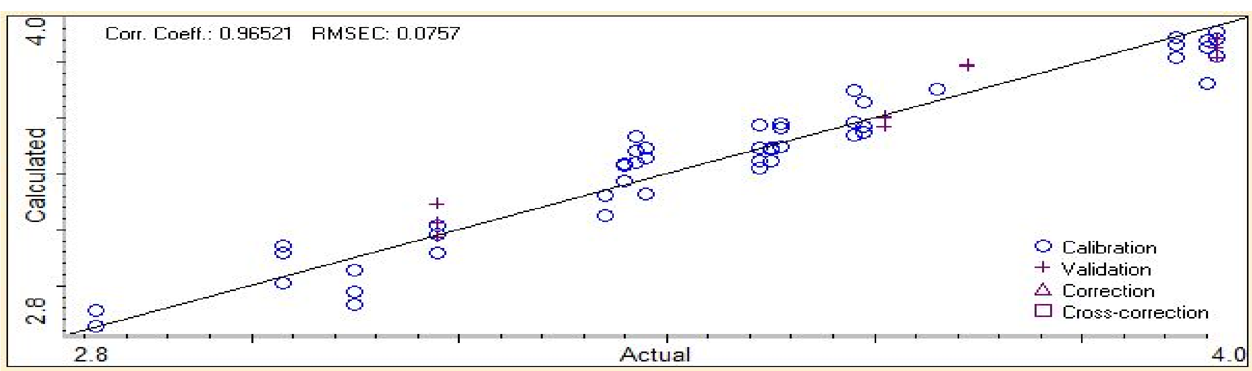

Figure 6 Prototype 3: PLS calibration curve for milk protein developed using sonicated producer raw milk

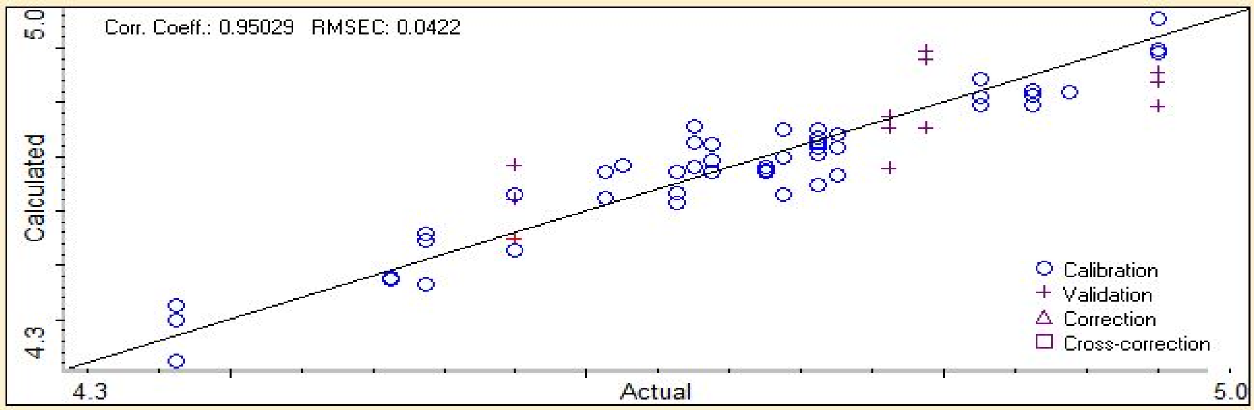

Figure 7 *Prototype 3: PLS calibration curve for milk lactose developed using sonicated producer raw milk*

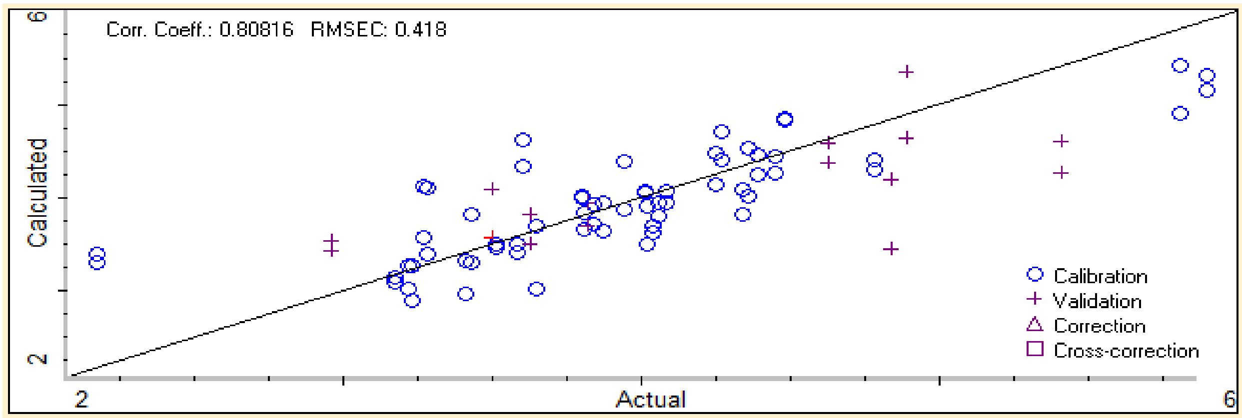

Figure 8 ATR-LVF: PLS calibration curve for milk fat developed using sonicated producer raw milk

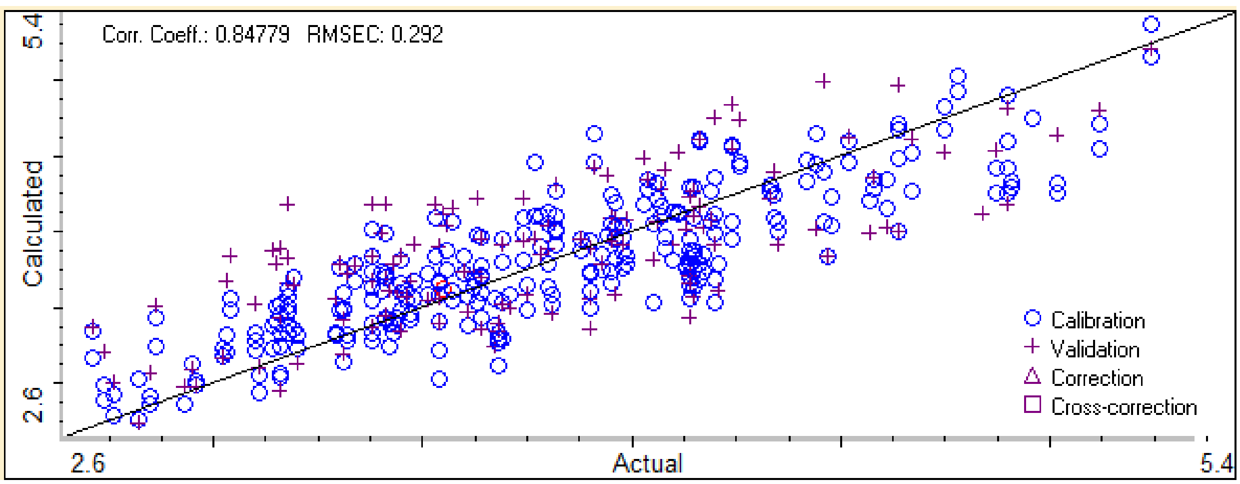

Figure 9 ATR-FTIR: PLS calibration curve for milk fat developed using producer raw milk

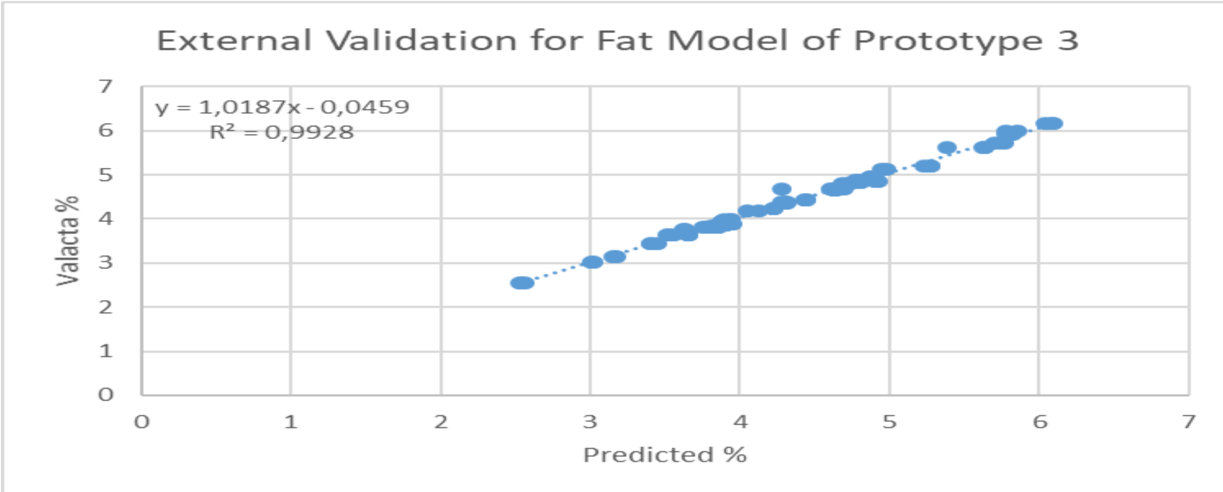

Figure 10 Valacta analysis values versus milk fat predicted values of producer raw milk samples collected from Léothé dairy farm in Saguenay

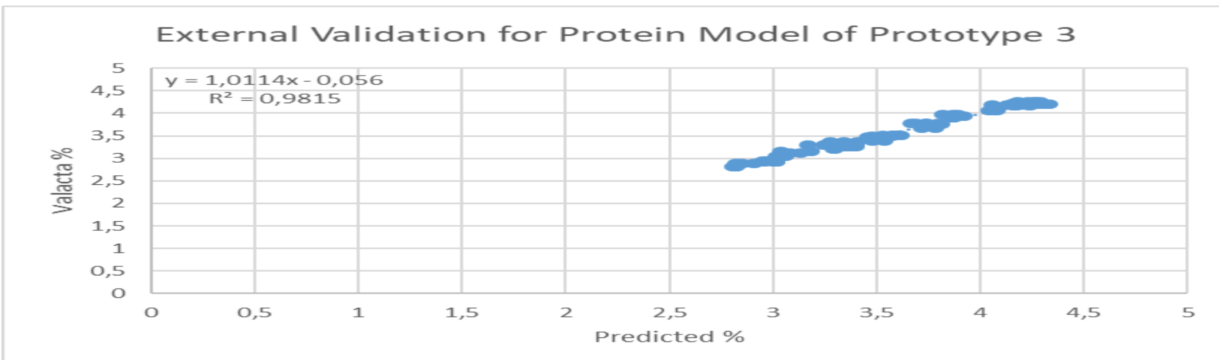

Figure 11 Valacta analysis values versus milk protein predicted values of producer raw milk samples collected from Léothé dairy farm

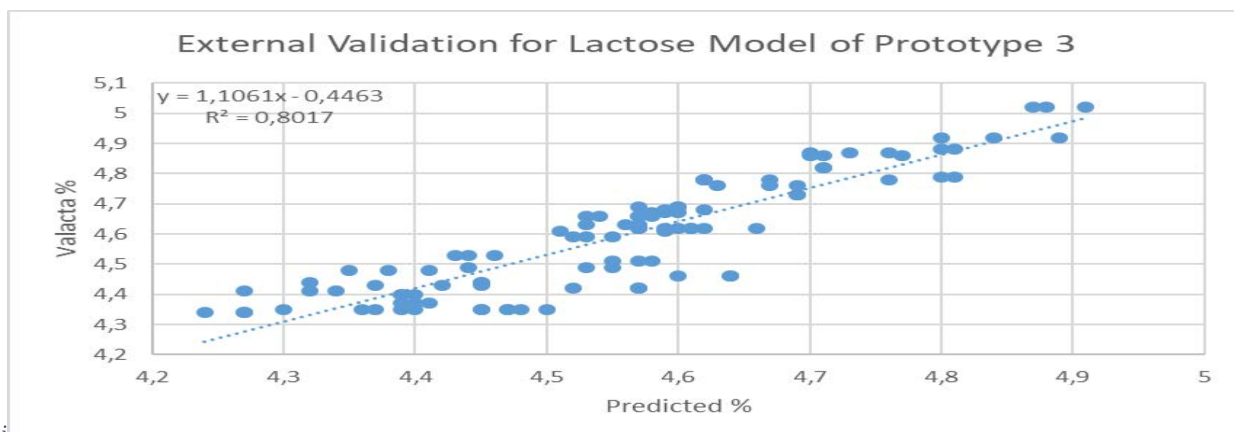

Figure 12 Valacta analysis values versus milk lactose predicted values of producer raw milk samples collected from Léothé farm in Saguenay

Figure 13 Loading spectrum 1 of the PLS model for BHB developed using spectra collected on prototype 3. Two peaks are

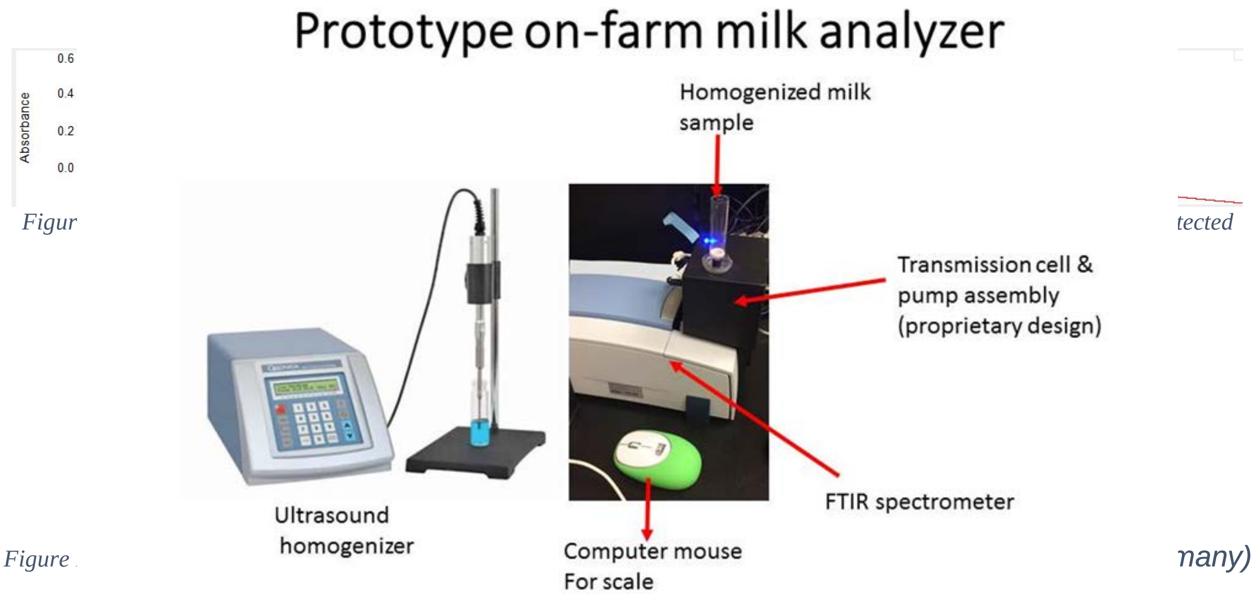

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Figure 16 Prototype on-farm milk analyzer (Prototype 3).

Figure 17 Prototype 3 was externally evaluated at Léothé dairy farm in Saguenay

APPLICATIONS POSSIBLES POUR L'INDUSTRIE ET/OU SUIVI À DONNER

A miniature pumping device could be developed to automate sample introduction into the short pathlength transmission cell and reduce the sample volume required for milk analysis. Reducing the volume of the milk sample will also significantly reduce the time needed to homogenize milk by an ultrasonication probe. Further reduction in homogenization time.

In addition, several modifications can be applied to the current prototype to enhance the accuracy of the spectral chemical information. These modifications include the use of fringeless transmission cell, reducing the pathlength of the cell to 40 µm, applying apodization to the collected milk spectra, hermetically sealing the IR measurement chamber, thermally insulating the spectrometer and increasing the spectral resolution to 8 cm^{-1} instead of 16 cm^{-1}.

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REMERCIEMENTS AUX PARTENAIRES FINANCIERS

Ces travaux ont été réalisés grâce à une aide financière du Programme de soutien à l’innovation en agroalimentaire, un programme issu de l’accord du cadre Cultivons l’avenir conclu entre le ministère de l’Agriculture, des Pêcheries et de l’Alimentation et Agriculture et Agroalimentaire Canada.