

Online analysis of dairy products with FT-NIR spectroscopy

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Introduction

Today, near infrared (NIR) spectroscopy is widely established for analysis of dairy products, at-line as well as in the laboratory, and has reduced the amount of wet chemical analysis required. In the recent years a lot of dairy companies merged and the production of dairy products was concentrated on less but bigger facilities. The high output of modern production plants may become very critical. A lot of money can be wasted in a short period of time if a process came out of control or specification. Here NIR is a suitable tool for fast analysis and process control, offering financial benefit due to avoiding bad products and increasing yield.

The most difficult task for implementing a on-line dairy NIR solution is the sampling. Two in-line applications using a process Fourier transform (FT)-NIR spectrometer are described in the following. The moisture and salt analysis in salted butter and the analysis of fat, moisture and protein in whole milk powder.

For salted butter it is important to maximise the moisture content without going out of specification, and to stay as close as possible to the target salt concentration, thus increasing yield. This application applies to salted butter although unsalted has been tested with similar results.

For milk powder, parameters like fat, protein and moisture are crucial to determine as they effect the product quality and consistency and give an insight on how to adjust further manufacturing steps like drying processes and milk standardization.

Experimental

Salted butter

A Bruker Matrix-F FT-NIR spectrometer system with optical multiplexer operating in the 10000–4000 cm⁻¹ (1000–2500 nm) region was installed with a single reflectance probe inserted downstream from the butter churn (Figure 1 left). A sampling valve was located in close proximity to the probe so a representative scanned sample could be obtained. A starter calibration was developed and used to maximize the range of moisture values in the samples collected for analysis and subsequent calibration development. Samples for calibration were taken over a four-week period and were either analysed immediately after collection or refrigerated for later analysis depending on availability of resources.

Validation followed for a similar time during which the calibration model was evaluated for reproducibility and repeatability and updated as required in “calibration maintenance” mode. Reference moisture tests were performed using the Kohman method and salt estimations were performed using the Mohr titration method. The Kohman method is a simple gravimetric method which involves weighing a sample of butter (about 10 g) in an metal container, heating it on a hot

plate to evaporate the moisture and re-weighing. The moisture is expressed as a percentage of the total weight. The Mohr titration method involves titrating silver nitrate against salt with potassium dichromate as an indicator.

Milk powder

Again a Bruker Matrix-F system was installed with a single reflectance probe inserted into an automatic sampler under standalone PLC control (Figure 1 right). The sampler uses a pneumatic ram to take sub samples into a pipe (spool) in which the probe is located. The scanned sample is then returned to the process or diverted and collected for reference analysis. The advantage of using a sampler is that it is possible to collect the exact sample for reference analysis that had been scanned by the analyser.

Samples for calibration were taken over a four-week period and were analysed immediately after collection using the methods listed below. Validation followed for a similar period during which the calibration model was evaluated for reproducibility and updated if required in “calibration maintenance” mode.

The moisture concentration was determined using the Karl Fischer titration method. The fat analysis was determined using the Rosse–Gottlieb gravimetric reference method. The protein concentration was determined using the Dumas combustion technique on a Leco instrument.



Figure 1. left: butter spool with probe in situ; right: automatic powder sampler for milk powder.

Results

Figure 2 shows examples of a butter and milk powder spectrum (resolution 8 cm^{-1}). The OH group absorbances are clearly visible especially in the butter spectrum at around the 7000 and 5200

cm^{-1} regions with the H–O–H combination band at 5250 cm^{-1} being the most dominant. Salt correlations are obtained by an apparent shift in the moisture peak. Fat (C–H) shows a strong absorbance (combination band) around 4400 cm^{-1} and 5800 cm^{-1} . In the milk powder spectrum protein (N–H) shows a broad absorbance (combination band) at 4800 cm^{-1} .

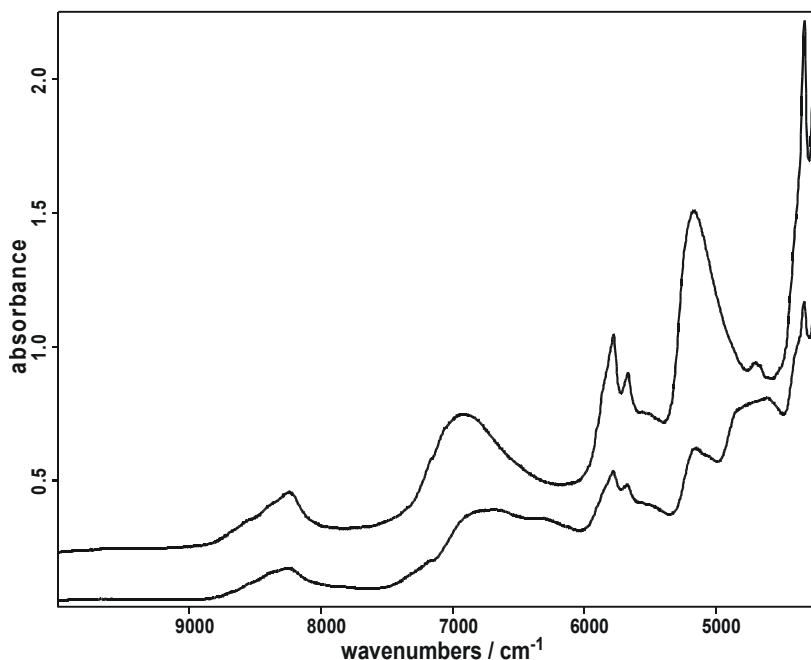


Figure 2. NIR spectra of butter (top, shifted for better overview) and milk powder (bottom).

Salted butter

Butter samples were acquired and calibrations developed for moisture (171 samples, range 15.2 to 16.2%) and salt (64 samples, range 1.15 to 1.5%). The calibrations were calculated and optimized using full cross validation leading to root mean square error of cross-validation (*RMSECV*) 0.06% for moisture and 0.03% for salt. In Figure 3 the NIR predictions are plotted against the reference values.

The calibrations were then validated by obtaining on-line predictions for 32 samples. The root mean square error of prediction (*RMSEP*) was 0.07% for moisture and 0.05% for salt.

Milk powder

Around 150 samples were acquired and calibrations developed for moisture (range 2.1 to 3.4%), fat (25.8 to 30.2%) and protein (range 23.3 to 26.0%). For the calibration optimization a test set of 139 samples was used. The calibration and validation results are very close: moisture *RMSEE* 0.06%, *RMSEP* 0.08%; fat *RMSEE* 0.11%, *RMSEP* 0.14% and protein *RMSEE* 0.17%, *RMSEP* 0.17%. In Figure 4 the validation results are shown as NIR prediction vs reference values.

In both cases the validation errors are very close to the reproducibility targets and laboratory errors of standard methods.

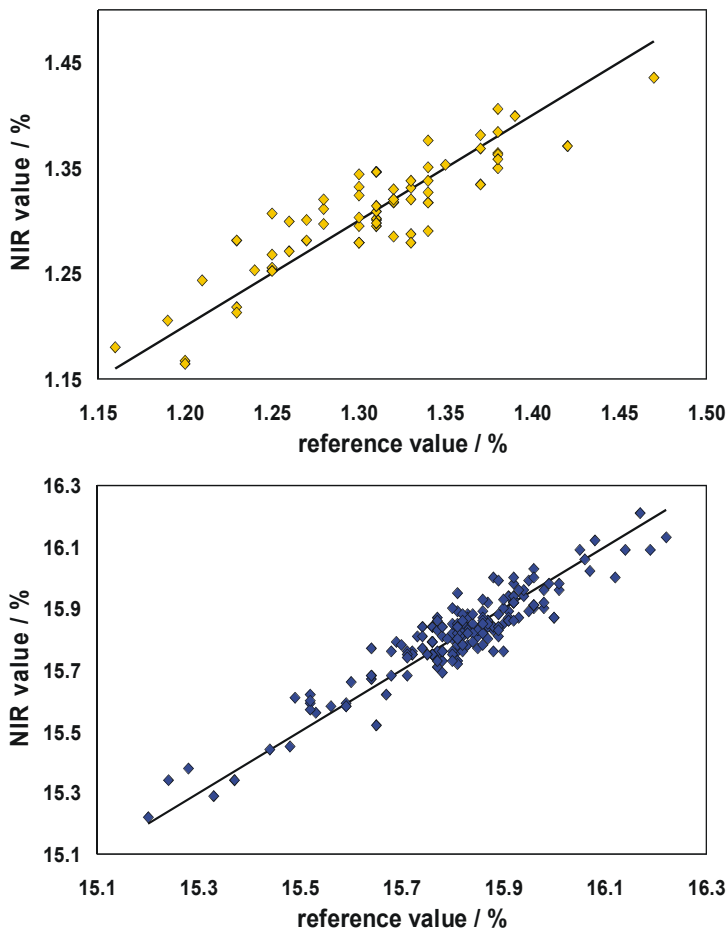


Figure 3. Calibration results (full cross-validation) for salt (top) and moisture (bottom) in salted butter.

Conclusion

In this study it was shown that on-line FT-NIR spectroscopy can be successfully implemented in dairy production processes. Especially in times of merging companies and high throughput plants fast methods are necessary to avoid products out of specification. Besides the speed of a spectroscopic method, the high amount of spectral information is an advantage of NIR. From one measurement the determination of important parameters like moisture, fat and protein can be readily performed. The performance figures and results of the used FT-NIR systems are equalling at least any on line technique currently available and are very comparable to laboratory methods.

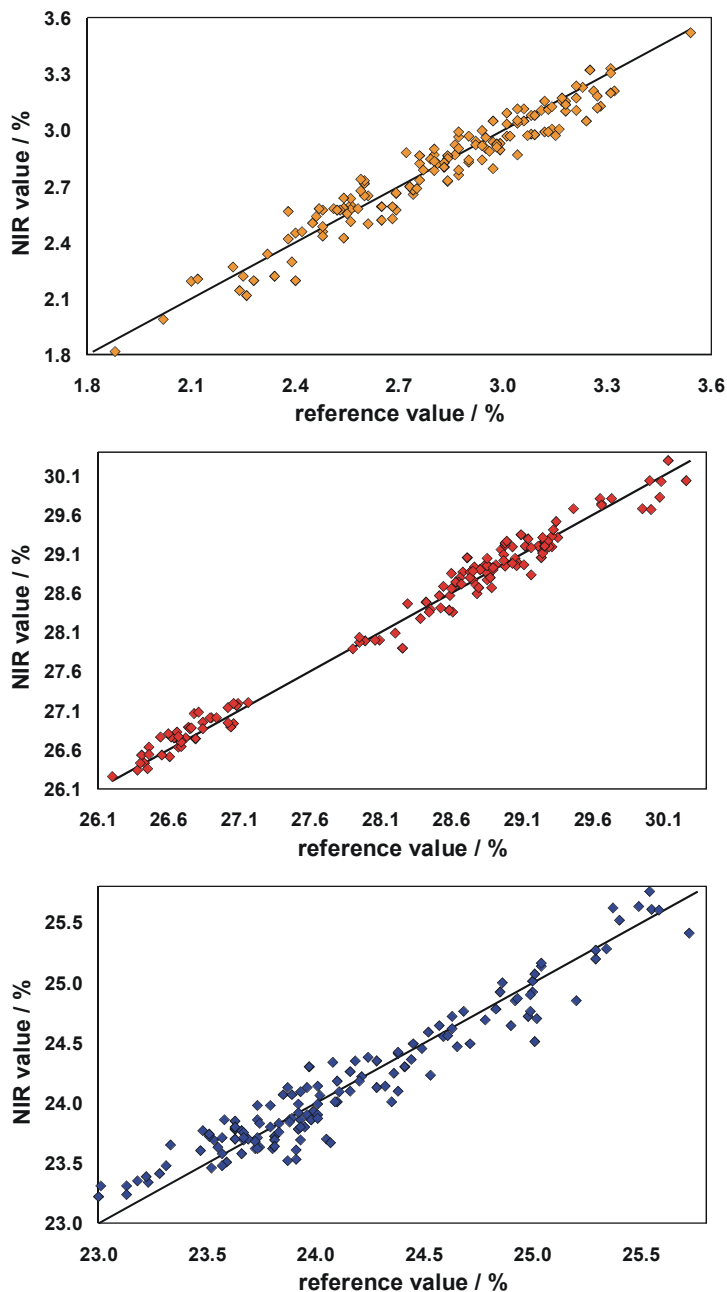


Figure 4. Validation results (test set validation) for moisture (top) and fat and protein (bottom) of milk powder.