Near infrared sensing of a heterogeneous agricultural fluid product

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Introduction

Composition analysis by near infrared (NIR) spectrometry usually uses models based on statistical methods, which include calibration and validation procedures. These models are based on optical principles, in which the homogeneous nature of the sample is a basic assumption. Therefore, the application of a homogenising treatment to the samples is recommended for the calibration procedure. Naturally, agricultural fluid products are heterogeneous and, in some cases of on-line sensing, it is impossible to fulfill the requirement for homogeneity and some precautions are needed.

Several models have been published describing the NIR absorption behaviour of mixtures and solutions, including the Beer–Lambert law (see Burns and Ciurczak),[1] through Kubelka–Munk (K–M) equation,[2] the Mie equation (see Burns and Ciurczak)[1] and Hecht.[3,4] According to Willams and Norris,[5] some models have been found to be impractical for NIR spectroscopy, while the solution or calculation of others is usually very complicated. A discrete model of light propagation through a medium was suggested by Bull,[6] to evaluate the effect of the size of the particles in mixture; it used a similar approach to that of K–M models, in which two main directions are defined: out of the light source and back to it. Bull[6] solved the case of the homogeneous layers by means of series. In order to evaluate the effect of the heterogeneous distribution of the ingredient of the sample, an alternative treatment to the discrete approach should be used. Fresh, raw cow's milk is an important agricultural fluid product, both in its natural form and as a raw material for the dairy and food industries. The feasibility of NIR models to determine the fat content of homogenous samples of fresh, raw cow's milk was discussed by Schmilovitch *et al*.[7] Treatment of the heterogeneous fresh raw milk is needed and the means to do this is one of the main objectives of the present research. The objective of this research was to evaluate the effect of the heterogeneous distribution of the ingredient concentration on the intrepretation of NIR measurements by means a spectroscopic model.

Method

At the present stage, the research is concerned with a sample with no voids and having constant temperature. A discrete, modified model approach is used with computer simulation, NIR experiments and measurements of the sample heterogeneity.

Several experiments were conducted in order to establish the data and parameters needed for modelling and simulating the effects of a heterogeneous cross-section on NIR measurements. The flow-chart in Figure 1 illustrates the experiments and the method for including their results in the implementation of the model and the simulations. A Quantum 1200 (LTI, MD, Rockville, USA) spectrometer was used, with a grating which covered the range of 600–1200 nm with a silicon detector.

Modelling

On the basis of the discrete approach, a modified model was developed to describe the radiation passing through layers of the sample. In order to solve such a model, a step-wise iteration procedure should be used in such a manner that each step advances the process through one layer. For iteration *j* in layer *i,* there is radiation from layer *i* in the direction from the light source $T_{j,i}$ and reflected radiation $R_{j,i}$, back to the light source. $T_{j,i}$ comprises the unabsorbed part of $T_{j-1,i-1}$ which arrived from layer $i - 1$ in the previous step j–1 and the reflected part of $R_{j-1,i-1}$, which arrived from layer $i + 1$ in the pevious step $j - 1$.
Thus we have:

$$R_{j,i} = T_{j-1,i-1} \cdot \mu_i + R_{j-1,i+1} \cdot (1 - \mu_i) \cdot \sigma_i$$
$$T_{j,i} = R_{j-1,i+1} \cdot \mu_i + T_{j-1,i-1} \cdot (1 - \mu_i) \cdot \sigma_i$$

where σ_i is the layer absorbency and the μ_i layer specular reflectance.

Considering the case of $n - 2$ layers with m iterations the "readings" T (Transmittance) and R (Reflectance), in layers $i = n$ and $i = 1$, respectively, observed by sensors placed outside the sample medium, are obtained as the sum of these layers. The factors μ_i and σ_i could be calculated from the Beer–Lambert equation of reflectance and transmittance, assuming that each layer is homogeneous. This enables us to evaluate different states of heterogeneity, by controlling the factors μ_i and σ_i. In the case of a linear distribution of ingredient concentration:

$$C = C_0 + K \cdot X$$

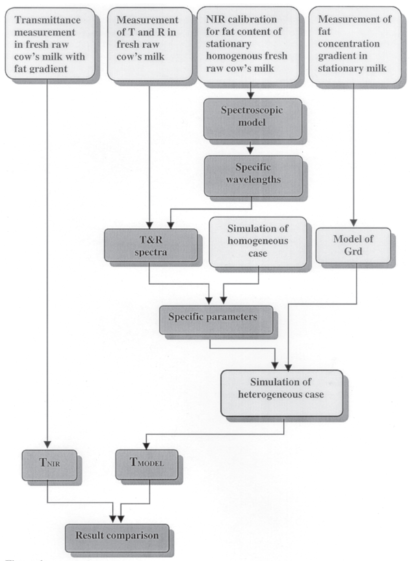

Figure 1. Flow-chart of the research method.

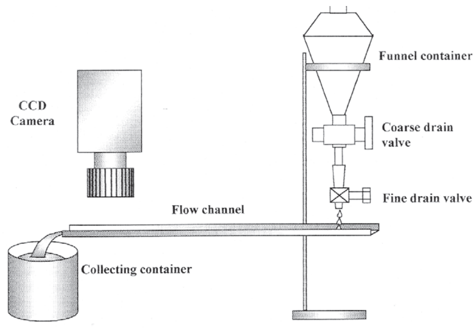

Figure 2. Schematic description of the system for video imaging of milk containing coloured fat.

where C is the ingredient concentration, X is the cross-section path, and K represents the heterogeneity, with $K = 0$ when the material is homogeneous then:

$$\sigma_i = 10^{-\varepsilon \cdot C_i \cdot dx}$$

where ε is the molar absorbency, c_i the concentration and dx the layer pathlength.

A computer simulation, using Matlab 5.0 software, was programmed to implement this model. With this simulation, the number of iterations (m) needed to stabilise "readings" T and R and the number of layers (n) and the valid range of the non-dimensional parameters were evaluated.

Experimental

Preliminary evaluation of fat distribution in fresh, raw cow's milk flowing through a rectangular tube

The objective of this experiment was to evaluate whether one should be concerned about a heterogeneous distribution in a real case of on-line measurement. A special technique was developed to colour the fat globules in fresh, raw cow's milk. A toner (Sudan Red 7B) was diluted in alcohol and added to high-fat concentration milk, where it was absorbed by the membranes of the fat globules.

This fat milk was produced from fresh, raw milk using spill fractionation. The red fat coloured globules were extracted by means of a slow centrifuge and added to skimmed milk (produced by spill fractionation), resulting in pink milk of which the saturation of the red colour represented the fat concentration. In a preliminary test the milk with coloured fat was held stationary in a vertical tube for one hour, where the upper layer of the milk column turned reddish and the lower layer turned white with the red saturation representing the fat concentration. The milk was then made to flow through a rectangular channel (15 mm wide) by means of the system shown in Figure 2. An RGB CCD video camera (JVC TK1270E) with to an IVP150 frame grabber (Bargold, Haifa, Israel) was used to digitise the frame to a 510 by 510 pixels by three-colour image, with a resolution of 0.15 mm per pixel, and images of laminar steady flow were obtained. Analysis of these images, according to gray-scale magnitude (an example is presented in Figure 3), indicated the distribution of fat concentration across the cross-section and demonstrates the importance of taking heterogeneous conditions into account.

Measurement of related transmittance *(T)* and reflectance *(R)* in fresh, raw cow milk

Five samples of fresh raw milk (not homogenised or pasteurised) were measured. The same conditions of light source energy, darkness in the sampling compartment, detector and sensor gain were maintained for both T and R. The results comprised associated spectra of R and T, which were used later for evaluating specific parameters for the non-dimensional model. The optical configuration of the experiment is illustrated schematically in Figures 4(a) and 4(b).

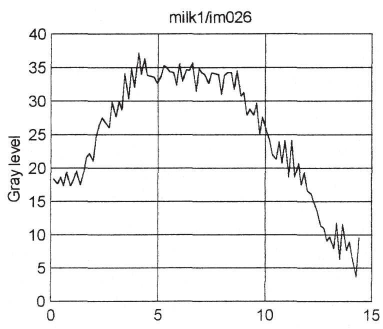

Figure 3. Example of results of image analysis according to grey-scale level.

Calibration of fat content in fresh, raw cow's milk

In order to establish the ability of NIR to measure the fat content of fresh, raw cow's milk under on-line conditions, by using the

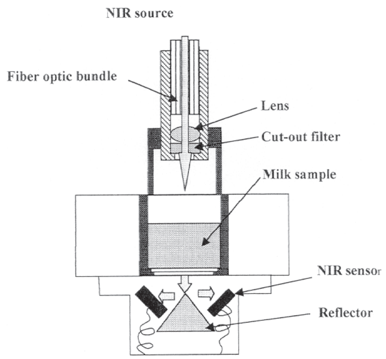

Figure 4(a). Optical configuration of the transmittance measurement experiment.

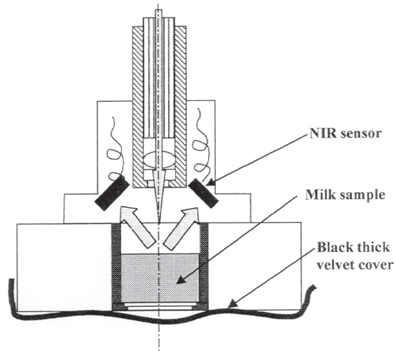

Figure 4(b). The optical configuration of the reflectance measurement experiment.

NIR range (600–1200 nm), 120 samples were examined. The optical configuration is illustrated in Figure 4(a); the path length was 10 mm. One hundred and twenty samples of fresh, raw cow's milk were scanned by the NIR spectrometer a short time after milking. Parallel samples were tested for fat concentration by the routine procedure by means of a Milcoscan instrument (Foss, Sweden). Models were obtained for this data by means of the Spectra Metrix software (LTI, USA, 1989).

Measurement of fat gradient in fresh, raw cow's milk

Fractions of fresh, raw cow's milk samples were collected by means of a specially developed device illustrated in Figure 5. Three fractions (the upper, middle and lower layers) were designated, to represent the fat concentration gradient in each of the eight measuring tubes, which were drained at 15 min intervals. Milk samples were held under static conditions at room temperature (23°C). Natural floatation of fat globules in the sample created a certain gradient. The samples from a 90 mL cylindrical column were collected into test tubes and later tested for fat content by means of a Milcoscan instrument (Foss, Sweden). An example of the change in fat concentration in the three layers plotted

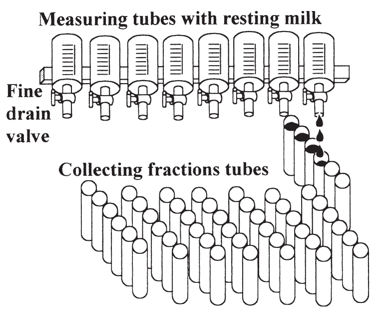

Figure 5. Schematic view of the system used for collecting fractionated fresh, raw cow's milk samples.

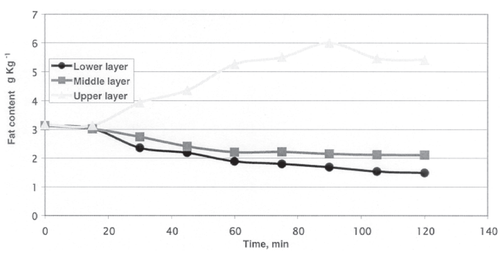

Figure 6. The time variations of fat concentration in three layers of resting samples of fresh, raw cow's milk.

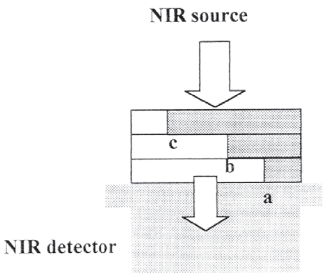

Figure 7. Description of the fractions' "gradient" (Grd) in resting milk sample.

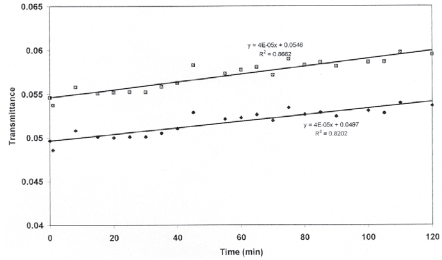

Figure 8. Transmittance of the specific wavelengths of fat (selected by SLR with homogeneous samples).

against time is presented in Figure 6. An expression to represent the fractions, the "gradient" (Grd), can be derived using the first moment of inertia of "concentration area" as follows:

$$\text{Grd} = 1 - (a + 3b + 5b) / [3 \times (a + b + c)]$$

Where a, b and c are the concentration magnitude as shown in Figure 7.

Measurement of NIR transmittance (*T*) in fresh, raw cow's milk samples with fat content gradient

The results of the measurement of fat content gradient in fresh, raw cow's milk, showed that time can represent the gradient, therefore samples were scanned in transmittance mode every 5 min for 120 min (averaging 30 scans each time). Six samples were tested, which had fat concentrations between 2 g Kg^{-1} and 5 g Kg^{-1}. When time or related Grd was used as a variable, a model based on partial least squares regression (PLS) was obtained. Transmittance measurements of wavelengths selected by a single linear regression (SLR) calibration, for fat content concentration in the homogeneous case, are presented in Figure 8. This may be compared with the subsequent simulation model obtained from results from the same case.

Simulation

Simulation of an homogenous case, run by means of the discrete modified model programmed for iteration in Matlab 5.0, produced a representation of the dependence of T_{model} and R_{model} calculation on various combinations of pa-

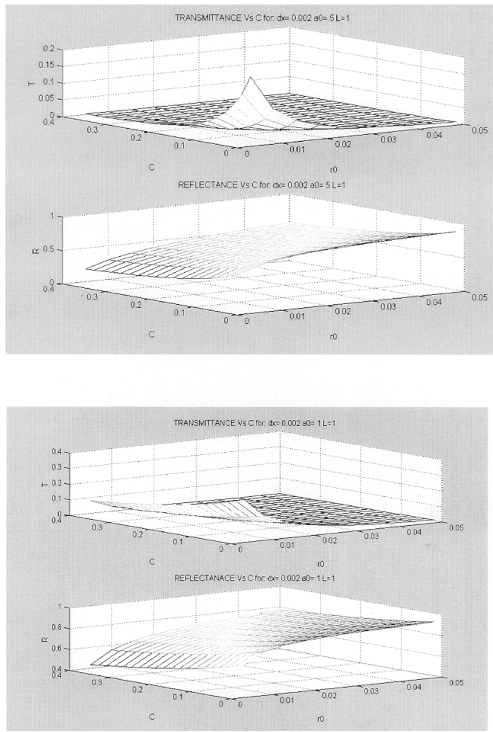

Figure 9. Example of simulation results of a homogeneous case by means of the discrete model T_{model} and R_{model} v. parameters C and r_0 with constant a_0 and dx.

Table 1. SLR model for fat content prediction.

Model	A_0	A_1	$(nm)_1\lambda$	A_2	$(nm)_2\lambda$
1	16.35	–769.02	1086	329.75	1032
2	17.42	–176.67	908	164.80	944

rameters (Figure 9). The parameters used were c_0—average concentration, r_0—specular reflectance, a_0—absorbence, dx—layer thickness, n—number of layers, m—number of iterations. In these runs, the valid ranges of the parameters were evaluated by comparing the pattern of the results with what was expected according to the Beer–Lambert equations, i.e. logarithmic behaviour of T and R in relation to the concentration. Combining these simulated results with the measurements of T and R in homogeneous fresh, raw cow's milk enabled the related parameters (r_0, a_0 and dx) to be defined. By incorporating these parameters into the programme, a new simulation, representing a heterogeneous case similar to development of a fat gradient in milk, was evaluated. A surface function describing the fat gradient formation in stationary milk was developed. It was based on the superposition of a straight line and an exponential curve, with the integral of the area below the curve kept constant (to represent conservation of mass). The results of this simulation are presented in Figure 10.

Results

Under steady flow conditions, as shown in Figure 3, high fat concentration is found near the side walls and a lower concentration in the middle of the flow channel. The prediction results of the SLR method indicated that T at two wavelengths (λ_1 and λ_2), as presented in Table 1, could be considered for the spectroscopic equation:

$$Fat\ (g\ Kg^{-1}) = A_0 + A_1 \times T_{\lambda 1} + A_2 \times T_{\lambda 2}$$

The standard error of prediction (SEP) of this model was found to be 0.7% for fat content.

The fat concentrations in the various layers of the fresh raw milk standing at room temperature change at a constant rate. This rate could represent the development of the fat concentration gradient. The relationship between this gradient (Grd) and the time was expressed as a linear regression with a correlation factor of $R = 0.92$, indicating that in this case Grd can be evaluated by measuring time.

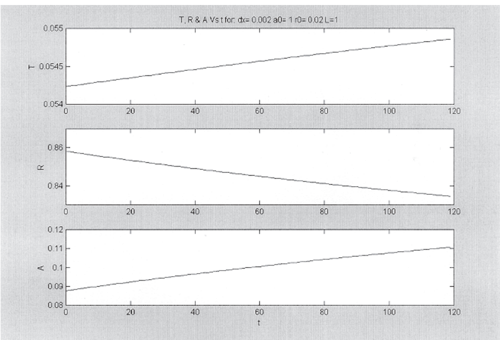

Figure 10. Simulation results of *T* (transmittance), *R* (reflectance) and *A* (absorbence) vs fat gradient.

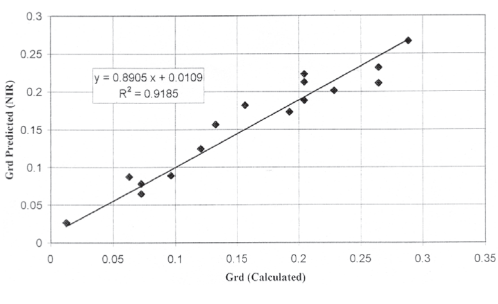

Figure 11. Prediction of Grd. by NIR (by means of PLS with four factors).

Spectral analysis of transmittance v. time or Grd, using a PLS method (calculated with *Spectra Metrix* software, LTI, Rockwell, MD, USA, 1989) confirmed the validity of prediction models, with a representative prediction results, as shown in Figure 11.

Conclusions and discussion

Agricultural fluid products, both flowing and stationary, are likely to be heterogeneous. A modified discrete model describing the propagation of NIR radiation through a heterogeneous medium was developed. The fat concentration gradient of stationary cow's milk samples was determined and the NIR optical parameters of raw fresh milk samples were measured and incorporated in the model. Comparison between the error predicted by the model and the NIR measurements at heterogeneous conditions of fresh, raw cow's milk samples yielded high correlations in their direction and their relative size. These results provide the basis for a technique to evaluate other cases, for example the distribution in fresh, raw cow's milk flowing through a rectangular tube. This technique could be used for the easy evaluation of other cases of NIR radiation measurement through heterogeneous media such as juices and their concentrates, which contain soluble solids.

Acknowledgements

The authors gratefully express their acknowledgement of the assistance of A. Hoffman, H. Egozi and V. Alchanatis in this research and the contribution from the Agricultural Research Organisation, the Volcani Centre, Institute of Agricultural Engineering, Bet Dagan, Israel, No. 733/99.

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