Use of FT-NIR fibre optic probes in on-line monitoring early cheese-making phases

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Introduction

Previous experiences,[1-3] made using a dispersive NIR equipment, showed the suitability of NIRS for monitoring the milk clotting process. In this work, the early cheese-making phases have been monitored using a FT-NIR instrument equipped with transmittance and reflectance probes. On-line process monitoring by using near infrared (NIR) spectroscopy has recently received much attention. The advantages of on/in-line measurements in general involve time, cost and effort savings.[4] The typical disadvantage of the use of fibre optic probes is loss of precision. Improvements on equipment and in data processing methods have reduced this problem significantly.[5-6] The aim of this work was to test the feasibility of NIRS in on-line monitoring milk coagulation process at the pilot scale. Optimisation of spectra processing and comparison of results obtained in transmittance and in diffuse reflectance mode was made.

Materials and methods

Four different substrates were tested: reconstituted skim milk powder, defatted (0.2% fat), partial defatted (1.8% fat), and raw milk (4.0% fat), before and after a heat treatment of 60°C x 15 min.

A 4% v/v calf rennet solution (0.8% v/v in distilled water) was used as clotting agent. The rennet strength was 1: 16000 Soxhlet units (Chr. Hansen, Corsico, Italy). Each coagulation test was made processing about 3000 mL of milk.

Spectra were collected in the full range of wavenumbers from 4000 to 10000 cm-1, every 71 seconds (resolution: 16 cm^{-1}; scanner velocity: 20 kHz; background: 256 scans; sample: 64 scans) for 60 min by using a MATRIX F FT-NIR spectrometer, equipped with trasmittance (1mm path length) and reflectance probes (Bruker Optics S.r.l., Milano, Italy). To minimise the effect of the low signal/noise ratio in transmittance mode, the four different substrates were used as background.

Experiments (8 replicates each) were made at a constant temperature of 35°C.

Visual observation of flock formation was used as reference method.

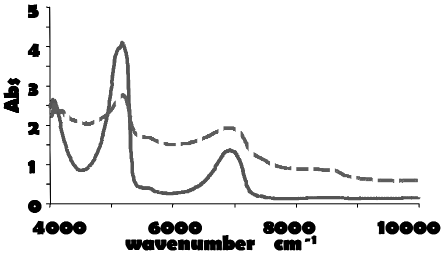
No data pre-treatments were used. Absorbance values at two wavenumbers (6944, 5195 cm-1) were plotted against time to identify potential critical points during the coagulation process on the basis of absorbance behaviour.

Statistics were used in modelling the process using TableCurve 2D software, v.4.00 (AISN Software Inc., USA). Results obtained in transmittance and in diffuse reflectance mode were compared with those obtained by visual observation of flock formation.

Near Infrared Spectroscopy: Proceedings of the 11th International Conference.

Results and discussion

Figure 1 shows an example of FT-NIR spectra of milk coagulation process collected by fibre optic probes in transmittance and in reflectance mode.



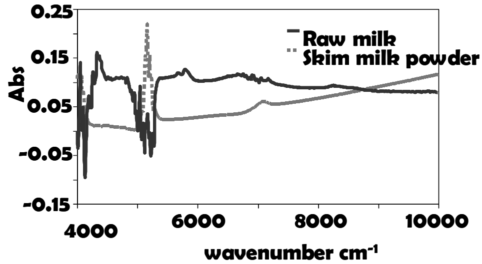


Figure 1. Examples of FT-NIR spectra of milk coagulation process. Transmittance, background air (—),; Reflectance (- - -).

Figure 2. Examples of transmittance FT-NIR spectra using milk as background.

Transmittance

Examples of transmittance spectra obtained using milk as background, are reported in Figure 2.

Spectral data were processed applying the Extra Valcum model (TableCurve software). Three critical points, associated with the "highest acceleration" (max d^2x/dt^2), the "highest speed" (max dx/dt) and the "minimum acceleration" (min d^2x/dt^2) of the coagulation process were identified on spectral curves, as shown in Figure 3. They were found to correspond to the initial clotting time (iCT), the clotting time (CT), and the gelation time (GT) respectively. Best results were obtained processing data collected at 6944 cm^{-1} against time, due to the value of the signal/noise ratio, that was higher than that detected at 5195 cm^{-1}. An example is reported in Figure 4.

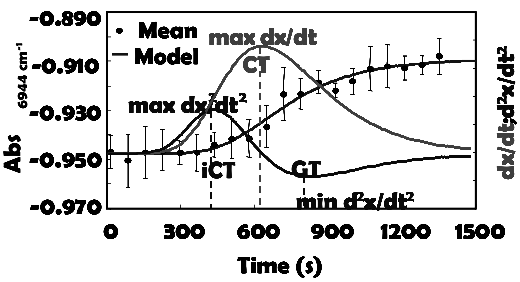


Figure 3. Extra Valcum model

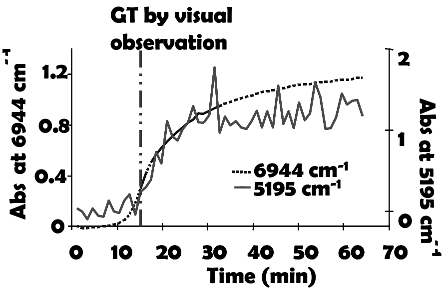


Figure 4. Absorbance behaviour at 6944 and 5195 cm $^{-1}$, during the coagulation process of reconstituted skim milk powder by using a transmittance probe.

The identification of gelation time (min d^2x/dt^2) by NIRS was comparable with the values obtained by visual observation.

It is worth noting that the correspondence between GT values obtained by using the two methods was satisfactory for all substrates except that when skim milk powder was used (Table 1). In this case the CT (max dx/dt) identified by NIRS was found corresponding to GT obtained by visual observation assay, in agreement with previous results. [1-2]

Bubbles and coats formation into spectral device are the biggest disadvantages of this technique.

Table 1. Determination of parameters related to coagulation process: NIRS indices (transmittance probe) and visual observation of flock formation expressed in seconds.

	NIRS 6944 cm^{-1}			GT by visual observation
	iCT = max d^2x/dt^2	CT = max dx/dt	GT = min d^2x/dt^2	
reconstituted skim milk powder	422	903	1385	914
raw milk (0.2% fat)	740	1365	1991	1954
raw milk (1.8% fat)	465	1121	1776	1635
raw milk (4.0% fat)	133	821	1509	1627
raw milk (0.2% fat) after heat treatment (60°C x 15 min)	688	1207	1726	1596
raw milk (1.8% fat) after heat treatment (60°C x 15 min)	393	996	1599	1594
raw milk (4.0% fat) after heat treatment (60°C x 15 min)	185	1001	1818	1693

Reflectance

Reflectance data needed to be processed using a different algorithm (Asym Sig, TableCurve software), that was able to model the cheese-making process identifying two critical points (CT and GT), as shown in Figures 5-6.

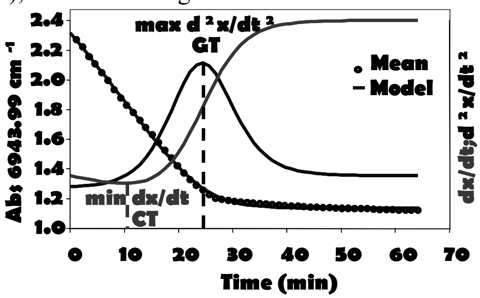


Figure 5. Asym Sig model

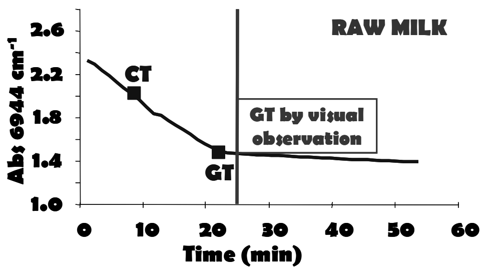


Figure 6. Absorbance behaviour at 6944 cm^{-1}, during the coagulation process of raw milk by using a reflectance probe.

No significant influence on NIR response was found processing absorbance curves of rennet coagulation made with raw and heated (60°C x 15 min) milk.

In general, diffuse reflectance data confirmed the good correspondence between GT interpolated on Asym Sig model (NIR prediction) and GT values obtained by visual observation, as shown in Table 2.

Table 2. Determination of parameters related to coagulation process: NIRS indices (reflectance probe) and visual observation of flock formation expressed in seconds.

	NIRS 6944 cm^{-1}		GT by visual observation
	CT = max dx/dt	GT = max d^2x/dt^2	
reconstituted skim milk powder	881	1246	930
raw milk (0.2% fat)	969	1462	1583
raw milk (1.8% fat)	913	1683	1630
raw milk (4.0% fat)	850	1391	1587
raw milk (0.2% fat) after heat treatment (60°C x 15 min)	1114	1676	1589
raw milk (1.8% fat) after heat treatment (60°C x 15 min)	988	1600	1701
raw milk (4.0% fat) after heat treatment (60°C x 15 min)	458	1233	1488

Also in this case, CT predicted by NIRS showed correspondence with GT detected by visual observation when reconstituted skim milk was used as substrate. Conversely, working on liquid milk, the max d^2x/dt^2 interpolated on Asym Sig model could be identified as GT: it corresponds to the "minimum acceleration" of the coagulation process.

Disadvantage of the geometry used was found to be the position of the probe into vat. Care should be taken that the probe is far from vat faces (walls) and dipped into milk at least for twenty millimetres.

Conclusions

The experimental data proved the feasibility of FT-NIR in on-line monitoring the cheese-making process by using fibre optic probes.

In particular it was verified that:

- the lab model was transferable on raw liquid milk in a pilot scale, by applying corrected or improved algorithms;
- the best signal/noise ratio was obtained at the wavenumber 6944 cm^{-1};
- raw spectral data can be processed without applying mathematical pre-treatments
- fat content did not influence the reliability of NIR response.

References

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