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Analysis of water in food by near infrared spectroscopy

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Abstract

The analysis of water by near infrared spectroscopy (NIRS) was the first successful application of this rapid technology which has been developed over the past 30 years into a routine method for many agricultural commodities and food constituents. Nowadays, NIRS technology offers many advantages because its rapidity allows more frequent measurements at all stages from purchase of raw materials and ingredients to the control of the finished products. NIRS-methods are well suited to in-line use. Nevertheless the two dominant and broad peaks, near to 1440 and 1930 nm in nearly every NIR spectrum due to water, are responsible for some typical complications in this analysis. Effects of hydrogen bonding and sample temperature are found to affect the reliability of NIRS results.

Keywords: Near infrared spectroscopy; Analysis of water; Method development; Applications; Hydrogen bonds; Sample temperature

1. Introduction

1.1. Advantages and disadvantages of NIR spectroscopy

NIR spectroscopy offers a number of important advantages over traditional chemical methods. It is a physical, non-destructive method, requiring minimal or no sample preparation and its precision can be high. In contrast with traditional chemical analysis, no reagents are required and no wastes are produced. It is a multi-analytical technique: several determinations can be made simultaneously. The method offers the possibility of measuring physical and chemical properties. Once calibrated, the NIR spectrometer is simple to operate. NIR instruments have a very high signal to noise ratio which is typically 10000:1.

The chief disadvantages are the dependence on time-consuming and laborious calibration procedures and the complexity in the choice of data treatment. Much work has to be done on the generation of the NIRS method development which is necessary for each group of food. The greatest disadvantage is probably the weak sensitivity to minor constituents.The sensitivity limit is about 0.1% for most constituents (Iwamoto & Kawano, 1992). Another limitation may be the transfer of calibrations due to optical differences between instruments (Givens, De Boever, & Deaville, 1997).

1.2. Principles of NIRS, method development and the performance of NIRS methods

Near infrared light is defined as the wavelength region from 730 to 2300 nm, lying between the visible light and the infrared light.The NIR reflecting spectra are characterized by overtone and combination bands of fundamental vibrations occurring in the mid infrared.

That means broad and overlapping bands less suited to structural studies and microanalysis. All organic bonds have absorption bands in the NIR region, whereas minerals may only be detected in organic complexes and chelates or indirectly by their effect on hydrogen bonds. As the overtones and combination bands are much weaker than the fundamental absorption bands, NIR spectroscopy allows the analysis of samples up to several millimeters in thickness.

The first step is to perform a calibration experiment which is crucial in quantitative NIR spectroscopy. This involves collecting a set of reference or calibration samples, which should contain all chemical and physical variations to be expected in the unknown samples, which will be determined or "predicted" later. The purpose of this calibration experiment is to establish a multiple linear regression between the NIR spectra data and the chemical parameters of the analysed sample set.

PCA ("Principal Component Analysis") reduces the large multivariate data of the original spectra to a limited number of independent factors. These principal components (PCs) express the main variations of the

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spectra and serve as regressors while decreasing systematic variation in the regression step.

PLS algorithms (“Partial Least Squares”) are generally used to set up the multivariate model and are based on two data sets (of the same objects), the chemical values and the spectra. The purpose of PLS regression is to establish a model that allows the analysis of a unknown sample. That means that one can get a prediction of the required results of chemical parameters based on the NIR spectrum of the unknown sample (e.g. Shenk, Workman, & Westerhaus, 1992).

1.3. Raw data pretreatment; method performance

Raw data often need, prior to analysis, to be mathematically preprocessed to remove defects observed in the spectra. The derivative computation is used for removal of baseline shifting and for resolution of overlapping peaks. The first and the second derivatives are the most commonly used. The multiplicative scatter correction is another spectral transformation that focuses on particle size effects. The correction consists of an additive and multiplicative term for each sample, relative to a defined reference spectrum.

Several statistical criteria are used to describe the performance of NIRS-methods. This means that the values of these statistical criteria are used to decide whether the developed method is acceptable for predicting the required chemical parameters of the unknown samples: The “Standard Error of Calibration” (SEC) and the “Standard Error of Prediction” (SEP) are estimations of calibration and validation procedures (Büning-Pfaue, Hartmann, Kehraus, & Urban, 1998; Büning-Pfaue, Hartmann, Harder, Kehraus, & Urban, 1998; Mark, 1992; Shenk et al, 1992; Workman, 1992).

The “Bias” corresponds to the average difference between measured and predicted values. If the Bias values are negligible, the SEP value can be equated with the standard deviation and therefore, in the case of a statistical certainty of 0.95, the maximum error range can be specified as ±2 SEP called either the “error of top of ranges” or the “maximum error range“ (Büning-Pfaue & Kehraus, 2001).

The coefficients of multiple determination (R^2_{cal} and R^2_{val}) allow one to determine the amount of variation in the data which is adequately modelled by the calibration equation as a total fraction of 1.0. The “Standard Error of Cross Validation” (SECV) is another important term to check a multivariate model; its value is calculated in the same way as the SEP.

2. The status of water in food and its influence on the NIR spectrum

Water is a strong absorber in the infrared (IR), including the NIR region spectrum, and near infrared spectra of samples with high water contents (>80%) are strongly dominated by the signature from water.

In food such as milk, sliced potato and pear flesh, tofu and meat, where the water contents reach about 70–90%, the absorption bands appear at nearly similar wavelengths to those of pure water. In addition, these food samples show the strongest absorption in the band near 1400–1410 nm, which is also observed in pure water samples. On the other hand, dry foods, such as soybeans, wheat and rice flours, have a different pattern from waterery foods. In particular, the band associated with free water seems to disappear in dry food except for a trace of absorption detectable in soybean flour near 1430 nm.

In order to confirm an assigment for this band, changes in spectra of sliced pear flesh were measured during a process of dehydration. It was shown that the sharp absorption band at 1406 nm decreased in intensity, together with the process of dehydration. Then a new absorption band at 1430 nm was initiated, detectable as a shoulder when the flesh was dehydrated below 45% water content.

Fig. 1 shows the raw NIR spectrum of potato in the region of 1100–2500 nm.

Strong near infrared absorption bands of water near 1400–1440 nm and 1900 to 1950 nm have often been applied to a quantitative analysis of water content in foods. But there are changes in the absorption band at the 1400 nm region and they are caused by the state of water in food.

The spectrum looks simple, but in reality it is very complicated. The importance of the NIR spectrum of water stems from the fact that frequencies and intensities of bands due to water alter with changes in the strength of hydrogen bonds and hydration. Besides free water molecules, there are other water molecules with one and two OH-groups engaged in hydrogen bonds. These hydrogen bonds influence the NIR absorption.

Following the assignment of Luck (1974), the spectrum consists of four main maxima located at c. 970 nm, c. 1190 nm, c. 1450 nm and c. 1940 nm due to the second overtone of the OH stretching band ($3\nu_{1,3}$), the combination of the first overtone of the O–H stretching and the OH-bending band ($2\nu_{1,3}+\nu_2$), first overtone of the OH-stretching band ($2\nu_{1,3}$) and combination of the OH-stretching band and the O-H bending band ($2\nu_{1,3}+\nu_2$), respectively.

Water associates strongly with ions, organic monomers and polymers by hydrogen bonds; therefore, water absorption bands in the near infrared spectrum are influenced by effects of solutes in water. There are shifts of absorption to lower or higher wavelengths and these shifts seem to be in relation to the hydration potential of respective solutes. This corroborates the fact that the near infrared spectrum is easily affected by conditions surrounding water molecules. The hydrogen bonds are

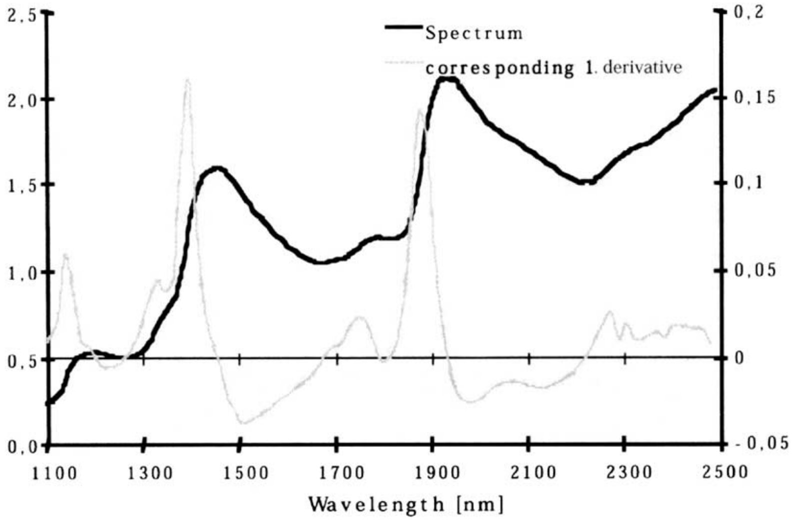

Fig. 1. NIR spectrum of a watery food (potato) with the two broad absorption bands (water) and the corresponding derivative.

relatively weak and, therefore, the light absorbance energy will be very sensitive to ion strength, gelatinisation, swelling and the presence of other ions and molecules.

Different models describing water structure may be divided into two main classes: mixtures and continuum models (Nemethy, 1974). The former indicates an equilibrium mixture of discrete species, differing according to their numbers of hydrogen bonds. The latter suggests almost completely hydrogen-bonded molecules in a continuous network where distortion of the H-bonds results in a continuous distribution of the H-bond distances, angles and energies.

Maeda, Ozaki, Tanaka, Hayashi, and Kojima (1995) tried to discriminate between a number of commercial natural mineral waters using NIR spectroscopy and principal component analysis (PCA). In order to obtain fundamental knowledge about the development of micro analysis for constituents in water, the discrimination of three varieties of commercial natural water, ultra pure water and deionised water, was attempted using near infrared spectroscopy. Although the compositional differences between the commercial mineral waters are very small, NIR spectroscopy can probably discriminate between them because the spectrum of water is very sensitive to changes in hydration (Tanaka, Shibata, Hayashi, & Kojima, 1995).

The smaller absorption of water with no hydrogen bonds makes it possible to differentiate molecular species by numbers of hydrogen bonds in the molecule. In other words, by use of the NIR bands of water, one can investigate the hydrogen bonds and hydration of water in water itself, in aqueous solutions, different polymers and different soluble monomers as food constituents. Therefore, it is possible to determine the concentrations of ions from spectral changes in the water bands induced by the hydration of ions. Moreover, the NIR spectra of water can be employed to determine various physical and chemical properties of water.

3. Influence of sample temperature on NIR absorption

It is well known that the NIR spectrum of water is sensitive to temperature. Fig. 2 illustrates the influence of temperature on the spectral data of the watery meat sample between 710–1080 nm. The second derivative spectra of beef longissimus muscles are compared and the samples were maintained at 5, 10, 15 and 20 °C (Mitsumoto, Ozawa, & Mitsuhashi, 2000).

Spectral differences between 5 and 10 °C were very small. However, the spectral differences between 10 and 15 °C or between 15 and 20 °C were large, although

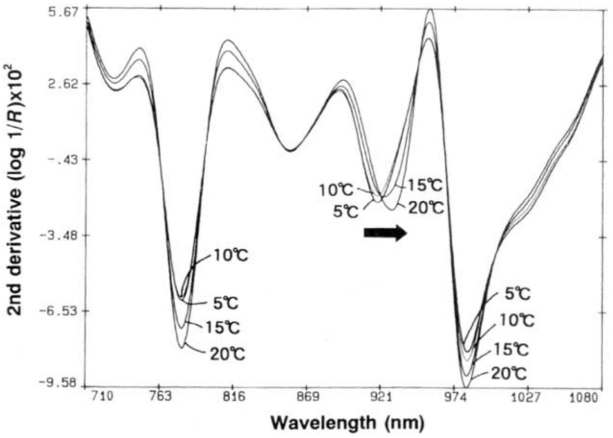

Fig. 2. Second derivative spectra of beef *longissimus* muscles, samples maintained at 5, 10, 15 and 20 °C (Mitsumoto et al., 2000).

other authors reported that temperature had no influence on the shift of absorption bands in the second derivative spectrum, e.g. the position of the three absorption bands was independent of the temperature.

These large spectral variations of the water NIR absorption spectrum induced by temperature are interpreted in the literature as being due to changes of the hydrogen-bonded water structure. Indeed, all water molecules undergo random motion, making or breaking the hydrogen bond. This is the main reason for changes in NIR-spectra affected by the temperature. Many attempts have been made to investigate the influence of food sample temperature on the estimation of the status of water using near infrared spectroscopy (Iwamoto, Uozumi, & Nishinani, 1986).

In order to study the effect of temperature on the spectrum, Iwamoto, Kawano, and Abe (1995) designed a sample cell which can control the sample temperature in the range from −140 to 80 °C. The second derivative of the spectra of water thus obtained showed three distinct peaks in the 1350–1700 nm region; they were assigned to three different molecular species of water, e.g. free water molecules (SO), molecules with one group engaging in a hydrogen bond (S1) and molecules with two OH groups participating in hydrogen bonds (S2). As the sample temperature increases, the peak due to SO increases, while those due to S1 and S2 decrease.

Of course, the main purpose of the water research in NIRS is not the prediction of the temperature of water but the analysis of the temperature-dependent spectral changes of water as one constituent in a complex mixture such as food. Abe, Kusuma, Kawano, and Iwamoto (1995) applied a curve-fitting technique to analyse the fine structure of the NIR spectrum of water. The absorption band near 970 nm was decomposed into five components which were assigned to five different species of water, differing in the number of hydrogen bonds in which they were involved, from zero (CO) to four (C4). The band intensities of CO, C1 and C2 species increase with temperature, while those of C3 and C4 decrease. Based on calculation of the average number and energy of hydrogen bonds from the fraction of each component and their heat capacity (constant pressure), the melting and the vapourizing enthalpy of water were estimated to be 7.8 and 44 kJ mol^{-1}, respectively.

Maeda et al. (1995) also investigated the NIR spectra of water. Their study aimed at providing new insight into temperature-dependent spectral variations in the NIR region of water: the absorption band near 6900 cm^{-1} consists of at least five component spectra. Each component spectrum may be ascribed to the water species with no, one, two, three or four hydrogen bonds. It has been found that the number of species with no hydrogen bonds increase largely with temperature, while those with more than two hydrogen bonds decrease.

4. Repeatability file for minimizing unwanted effects caused by water in food

Water often creates difficulties in the use of near infrared (NIR) spectroscopy calibrations when unforeseen hydration and dehydration processes occur during sample handling. This is especially true for NIR spectroscopy routine analysis of freshly harvested samples when the calibration in use is based on samples with equilibrated moisture content.

The repeatability (rep) file serves to minimize the influence of such unwanted effect on the results of NIR spectroscopy calibrations (Infrasoft International, 1996; Tillmann & Paul, 1998; Westerhaus, 1990). A rep file contains only spectra of the same, fixed samples, measured repeatedly under different conditions. The variation in the spectra of any of the respective single samples relates to the changing conditions at the time of measurement (e.g. temperature, residual moisture content or compacting of the sample). Therefore, the repeatability file includes differences of spectra, representing, e.g., the day-to-day variation in operation environment, variation among standardized instruments, or large differences in sample temperature to be minimized by the calibration procedure.

During calibration development, this file is added to the calculations so that wavelength regions are neglected which are markedly affected by the change in sample conditions. The goal of the repeatability file is to make the calibration equation insensitive to changes in temperature and instruments, but not to reduce the accuracy of the calibration; changes in temperature affect the sample and the instrument.

In general, a repeatability file is always helpful for minimizing systematic differences among instruments and minimizing the effects of sample temperature on variation in routine analysis. Temperature is the major factor, resulting in unwanted variation in analysis repeatability across instruments after standardization.

The repeatability file was originally proposed to account for temperature variations between instruments in a network set up. Now it has been used successfully to improve calibrations used in a network. Tillmann and Paul (1998) demonstrated the benefits of using a repeatability file for NIRS calibration development and the advantage of using a repeatability file is illustrated by their results comparing validation with moist and dry samples. The results are exemplarily illustrated in Table 1 by comparing the alternative to the exclusion of the water-sensitive bands from the calibration.

PLS calculations were carried out to determine oil content (%) and other constituents in rapeseed. Table 1 shows the resulting performance values of dry and moist samples but only for the constituent oil. Two different possibilities of rep file and wavelength-elimination (to

Table 1
Test of "Repeatability File" (R 1 and R 2) by equilibrated validation statistics (prediction of the oil content in rapeseed) compared to the alternative by exclusion of both sensitive water bands (wavelength elimination 1 and 2) from calibration; A: dry samples, B: moist samples (Tillmann & Paul, 1998, modified)

A			
Version:	SEP	BIAS	RSQ
Control	0.76	0.8	0.5
wavel. elimination 1	0.83	0.8	0.94
wavel. elimination 2	0.85	0.14	0,93
Rep. File R 1	0.72	0.1	0.95
Rep. File R 2	0.77	0.21	0.95
B			
Control	3.01	0.47	0.11
wavel. elimination 1	1.72	1.04	0.36
wavel. elimination 2	1.74	1.17	0.38
Rep. File R 1	1.21	0.31	0.42
Rep. File R 2	0.98	0.27	0.59

exclude the sensitive water bands) were calculated. The control was established with a rep file using all wavelengths. The expected consequences were decreased SEP- and Bias values for the rep file calibrations compared to the alternative by exclusion of the sensitive water bands; the same applies to all other constituents in rapeseed. This demonstrates the sensitivity of these calibrations to moisture in the samples and the advantage of using a repeatability file for improving the performance values for all constituents by 50% or more. Otherwise, there is no influence on repeatability file testing of dry samples. Therefore, calibration and validation of dry samples with the exclusion of wavelength segments or the use of the repeatability file has nearly no influence in the performance of this NIRS method. This is in accordance with experiences with many other samples. The repeatability file was originally proposed to account for temperature variations between instruments in a network set up. Now it has been used successfully to improve calibrations used in a network. The advantage of using a repeatability file, compared to the exclusion of certain absorption bands is that it is not necessary to determine where the absorption bands of interfering substances occur in the NIR region. This could be especially interesting for other problems, such as sensitivity to salinity, temperature or pH value. Furthermore, the calibration process seems to be able to use an important wavelength in the water band when using a repeatability file. Excluding this region in the calibration process led to worse results. Therefore, the use of a repeatability file is a superior alternative to exclusion of the water bands from calibration, to reduce the sensitivity of the calibrations to moisture variations in the samples.

5. Applications of NIRS methods for determining water content

The determination of water content was the first application of NIR spectroscopy in the analysis of food. Calibrations have been developed for estimating the water content of a wide range of foods, including grain, snacks, bread, sweets, cheese and milk powder. Many of these calibrations used the 1949 nm wavelength region as the primary measurement, this being a combination NIR absorption band for water, involving OH-stretch and OH-bond vibrations (Givens et al., 1997).

However, a number of applications have been reported which use NIR to determine water content in high moisture food, solid or semi-solid food. They can be analysed directly by using cuvettes or, e.g., optical probes.

Nowadays, analysis of intact samples is possible by using a large moving sample cell (Shenk et al., 1992). The introduction of fibre optics contributed to an enormous expansion of NIR spectroscopy for remote measurements, for example, for products which are difficult to handle, such as fruits, vegetables, meat and fish. The miniaturization of spectrometers also makes them a powerful analytical tool where robust systems in hostile enviroments are required.

5.1. Meat grinding

Fig. 3 gives a schematic overview of an on-line analysis system, which determines the chemical composition of meat during the grinding of industrial scale batches of ground beef and pork (a: grinding machine; b: NIR-Sensor; c: NIR spectrometer; d: ground meat). This NIR analysis of meat allows rapid assessment of several parameters simultanously, e.g. water, fat and protein contents (Togersen, Nilsen, & Hildrum, 2000).

5.2. Liquid samples

For a long time NIR technology was considered to be problematic for liquid samples.

However, in recent years several NIR techniques for liquid samples have been reported. These techniques can be divided into the following three groups:

off-line technique: for example, transmittance measurement in cuvettes/sample cups and dry extract spectroscopy by infrared reflectometry technique, both performed in the laboratory.
at-line technique: direct transmittance and transflectance measurements with fibre optics, performed at the production line.
on/in-line techniques: direct reflectrometry, transmittance or transflectance measurements with fibre optics, performed on or in the production line.

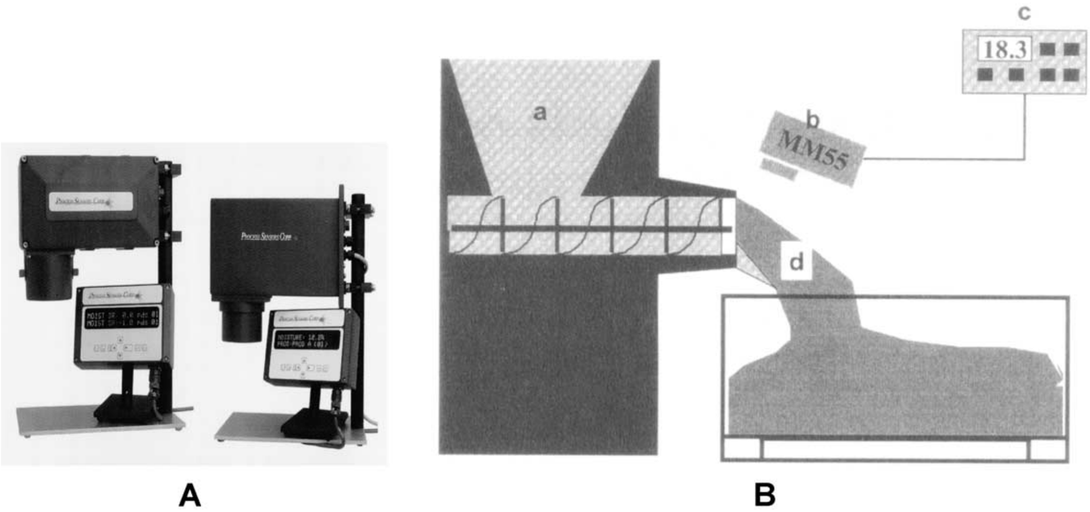

Fig. 3. NIR process sensors operating as single discrete gauges or as sensors (A) in a multi point network; NIR on-line analysis of the chemical composition of meat during grinding on industrial scale batches (B) (Togersen et al., 2000; modified).

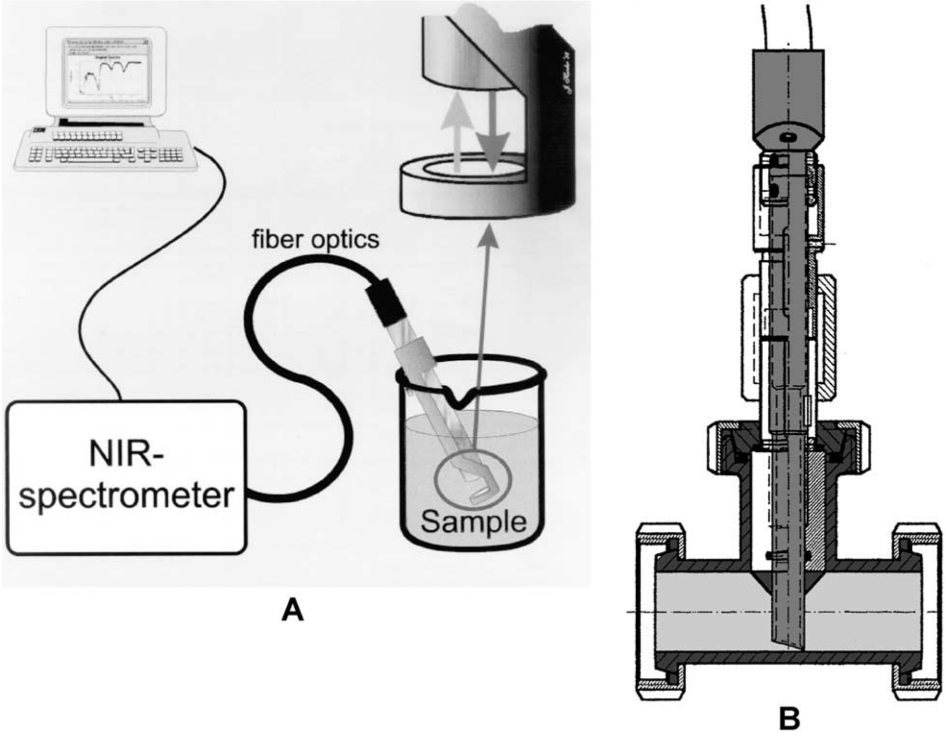

Fig. 4. NIR (water) measurement for liquid samples, transflectance (A) and reflectance optic probe (B).

Fig. 4 illustrates the transflectance measurement technique with fibre optics and the in-line measurement by direct reflectometry technique.

The advantage of on/in-line measurements are obvious, involving time, cost and effort savings. The typical disadvantage of the use of fibre optics is loss of precision. Improvements of equipment and data processing methods can reduce this problem significantly.

5.3. Fermentation

Fig. 5 illustrates moisture/water control during fermentation and shows raw NIR spectra of a fermented sample with moisture content changing during the process:

Moisture has a large effect on the reaction rate of fermentation (Suehara et al., 1999).

To promote the fermentation, therefore, it is important to measure the water content of the sample and

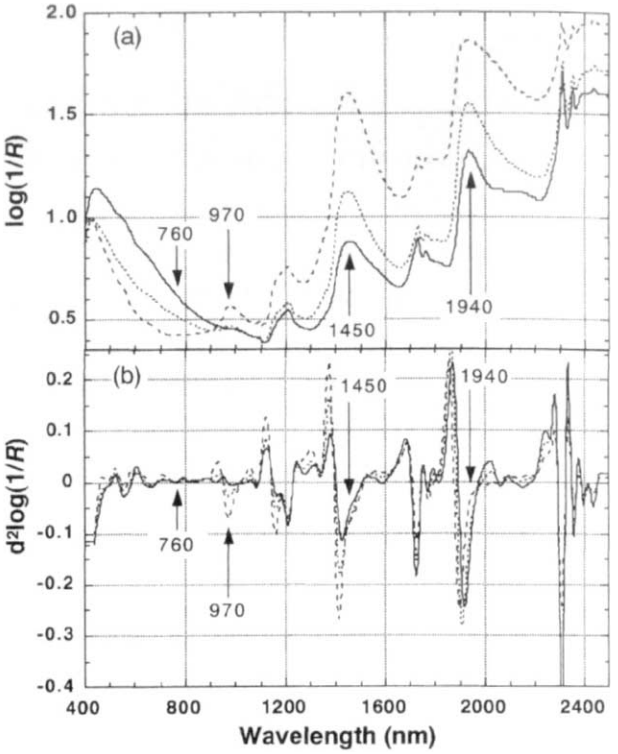

Fig. 5. Moisture/water control during fermentation; NIRS sample measurement (a/b: raw and second derivative spectra) in polyethylene bags (Suehara et al., 1999).

maintain it at a suitable level. This sample reflectance measurement was carried out in polyethylene bags. Raw (a) and second-derivative (b) NIR spectra of fermented samples illustrate the runs from the second day with nearly 70% water to the fifth day with nearly 24.1% water content in the fermented samples.

The baseline of the spectrum shifted upwards while the moisture content increased. The moisture content affected, not only the absorption at the wavelength assigned to water, but also the absorption at all wavelengths measured. The baseline shifting of the spectrum of the fermented sample observed in part A was corrected in the second derivative spectrum, as shown in part B. Therefore, in this case, it is desirable to use the second derivative spectrum for measurement of water content in the fermented sample.

These results suggest that NIR is a useful method for real-time monitoring and control of water content during fermentation. This operational procedure, involved in NIR, is simple and non-destructive, while the time required for measurement is only a few minutes.

5.4. Production of cottage cheese

Fig. 6 illustrates the production and the determination of water in cottage cheese as a very successful in-line measurement of high moisture products (Wüst, Fehrmann, Hoffman, & Rudzik, 1996).

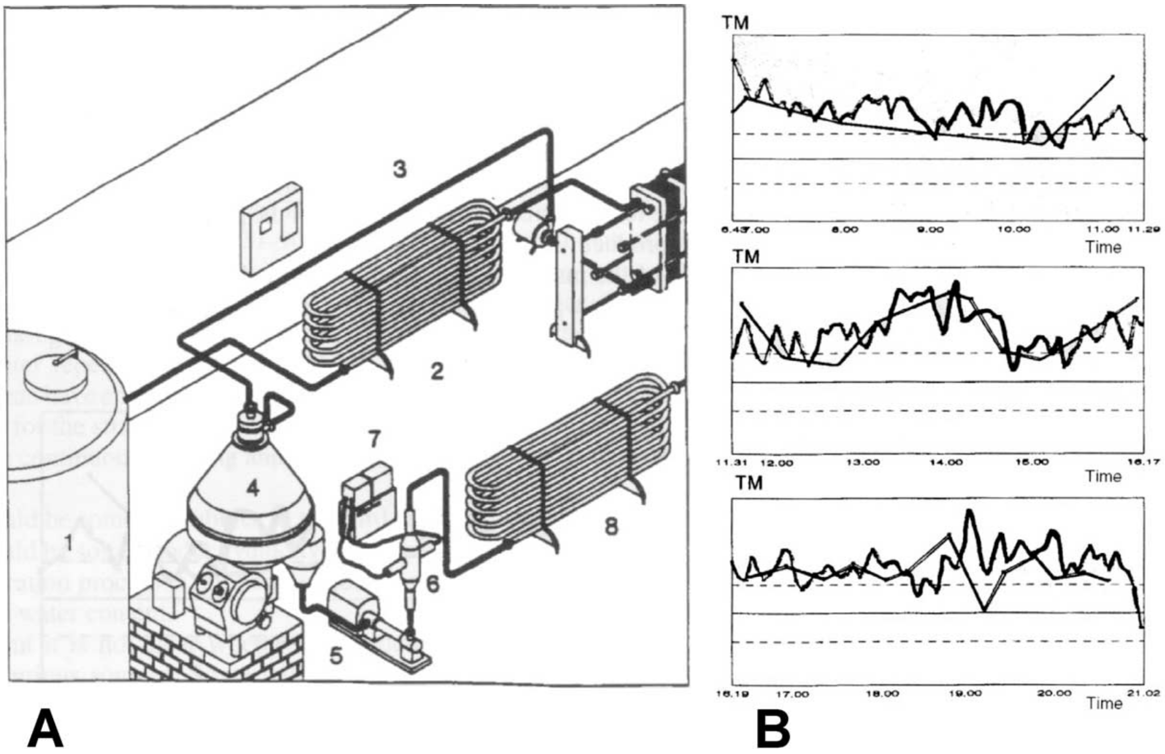

Fig. 6. Determination of water in cottage cheese as an in-line NIRS measurement; production line (A); curves of solid content values (TM; during one production day) predicted by NIRS in comparison to the results of the reference method (B) (Wüst et al., 1996; modified).

The diagram shows the production line for cottage cheese: the milk is coagulated in the tank, pumped through a heater (2) and feeding pipe (3) to the separator (4), where the coagulated milk is separated into whey and curd. A pump brings the curd through the NIR in-line device system (6) which is equipped with a transmission pair of fibres. It was shown that a sample thickness of 8 mm can be measured in transmission mode using the wavelength range from 700 to 1100 nm.

The calibration of the instrument has been problematic due to the transmission device. Taking the spectra in an "off-line" transmission device and comparing with the spectra of the same material in an "in-line" transmission device, the spectra look very different.

After having extracted the optimal conditions for measurement and method development, a calibration was performed by collecting sample spectra and reference values over a period of two months, so that nearly all production variations were included in this calibration. The curves (in the middle) display the results of the solid content (TM) as a function of time over one production day for cottage cheese. The structured curve represents the NIR prediction, where a measurement has been performed every three minutes. The flat line gives the results of the reference method. This means that all differences between NIR prediction and reference value fall within 0.25%. Therefore, the NIR-information about the water content can be returned back to control the separator. In practice this success in quick NIR-in-line-measurement prevents 1000–4000 kg batches having the wrong specification and causing a financial loss.

5.5. Networking of NIRS Instruments; reliable results

A NIRS network may contain from two up to one hundred or more spectrometers. The goal of a NIRS network is to obtain the same analysis for each sample with anyone of the NIR-spectrometers. Method development on a "master" spectrometer must produce the same analysis on the different "host" spectrometers.

Networked NIRS-instruments are used, e.g. by the association of German agricultural experimental and research stations, even for water/dry matter determination in very different samples (e.g. rape seed, grain, forage maize; http://www.vdlufa.de/nirs) This NIRS technique gives cost-effective and homogeneous results. The basic problems in NIR-networking are instrument differences in photometric references, differences in the wavelength scales and differences in the spacing of the recorded wavelengths.

The performance of NIR-networks was tested in different ring tests to show the full potential, even for water determination. The results agreed well with the findings of several ring tests on NIR-methods and their reference methods with other sample constituents: the best repeatability was achieved by the reference methods, while the NIRS methods were in all cases superior in their reproducibility, e.g. reference analyses differed less than NIRS-analyses, when duplicates were run in the same laboratory. However, NIRS-analyses performed by different laboratories were closer to each other than reference analyses of different laboratories.

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