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Review

On-line application of near infrared (NIR) spectroscopy in food production

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ABSTRACT

Near infrared (NIR) spectroscopy represents an emerging analytical technique, which is enjoying increasing popularity in the food processing industry due to its low running costs, and since it does not require sample preparation. Moreover, it is a non-destructive, environmental friendly, rapid technique capable for on-line application. Therefore, this technique is predestined for implementation as an analytical tool in industrial processing. The different fields of application of NIR spectroscopy reported in the present review highlight its enormous versatility. Quantitative analyses of chemical constituents using this methodology are widespread. Moreover, a wide range of qualitative determinations, e.g. for authenticity control, sample discrimination, the assessment of sensory, rheological or technological properties, and physical attributes have been reported. Both animal- and plant-derived foodstuffs have been evaluated in this context. Highly diverse matrices such as intact solid samples, free-flowing solids, pasty, and fluid samples can by analysed by NIR spectroscopy. Sophisticated conditions for the application in industrial scale comprise among others measurements on moving conveyor belts, in continuous flows in tubes, and monitoring of fermentation processes. For such purposes, different construction designs of NIR spectrometers for hyperspectral imaging, portable devices, fibre optical and direct contact probes as well as tube integrated probes measuring through windows, and automated sample cell loading have been developed. In the present review, emphasis was put on studies dealing with on-line application of NIR spectroscopy for industrial processes in the food industry, which were categorised according to their application conditions into semi-industrial scale and industrial scale.

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1. Introduction

Increasing demand on quality assurance in food production requires sophisticated analytical methods for objective quality control. Traditional analytical methods are, however, labour-intensive, time-consuming, and expensive. Vibrational techniques, such as near infrared (NIR) spectroscopy, offer a straightforward, rapid, and cost effective alternative. Since NIR spectroscopy allows measurements without prior sample preparation, in- and on-line applications are feasible. Therefore, this technique meets the requirements of industrial applications for continuous quality control and process monitoring. However, as being based on indirect measurements, yielding highly convoluted and broad spectra, virtually impossible to interpret with the unaided eye, NIR spectroscopy requires calibration with mathematical and statistical tools (chemometrics) to extract analytical information from the corresponding spectra (Blanco & Villarroya, 2002; Huang, Yu, Xu, & Ying, 2008; Siesler, 2008).

The present work is intended to be a helpful and easy to understand introduction to vibrational spectroscopy, particularly NIR spectroscopy, rather than an in-depth description of its fundamental basics. Therefore, although being the undoubted basis, physical and mathematical considerations or mathematical terms have been avoided wherever possible. Besides comprehensively reviewing on-line applications, our intention has been to provide an end user friendly guide to NIR spectroscopy shedding light on the principles of this powerful analytical technique.

In particular, we made the experience that on-line applications

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of NIR spectroscopy have been claimed as the overall aim of numerous studies. However, in numerous cases, a closer look reveals that on-line application has not been performed at all in the corresponding studies, which is not made unambiguously clear. Besides the laboratory bench-top applications, there are applications under industrial conditions or at least close to industrial conditions, e.g. dealing with moving samples. Reports in scientific publications of applications under real practical conditions in the industry or close/comparable to that are fairly rare. Therefore, we reviewed recent publications of NIR spectroscopy for food production and categorised them into laboratory applications, which were taken into account in the historical context and as an overview only; semi-industrial scale, meaning conditions close to industrial processes, e.g. on a moving conveyor belt or in a pilot scale production facility; and industrial scale applications, performed under industrial conditions or very close to industrial process conditions.

2. Fundamentals of vibrational spectroscopy

Optical radiation covers the wavelength range of 100 nm–1000 μm of the electromagnetic spectrum. It is subdivided into the ultraviolet (UV) region from 100 to 380 nm, the visible (VIS) light ranging from 380 to 780 nm, and the infrared (IR) radiation of wavelengths above 780 nm. Within the IR region, the near infrared (NIR) region covers wavelengths from 780 nm up to 2.5 μm, mid infrared (MIR) covers the region from 2.5 to 25 μm, and far infrared (FIR) the adjoining region up to 1000 μm. Due to different physical processes, characteristic emission and absorption spectra are observed providing valuable information on individual substances and the composition of complex mixtures. Electronic transitions being highly energetic cause absorbance in the UV or VIS range (Herold, Kawano, Sumpf, Tillmann, & Walsh, 2009). As an example, peptide bonds and conjugated double bonds absorb energy in the UV region. Molecules exhibiting a large number (at least 5 or 6) of conjugated double bonds such as carotenoids, chlorophylls, and anthocyanins cause absorption in the VIS region and may, thus, be used for colour evaluation (Dufour, 2009). Vibrational transitions, being characterised by lower energy values compared to electronic transitions, are reflected in the NIR and MIR region. Low-energy rotational transitions affect the MIR and FIR range (Herold et al., 2009). The most predominant absorption bands in NIR spectra of biological samples originate from overtones and combinations of fundamental vibrations of C–H, N–H, O–H and S–H bond in organic molecules observed in MIR range (Blanco & Villarroya, 2002; Sandorfy, Buchet, & Lachenal, 2007). Unfortunately, water highly absorbs NIR radiation. Since being the major chemical constituent of fruits and vegetables, the NIR spectrum of plant-derived samples is dominated by water (Cozzolino, Cynkar, Shah, & Smith, 2011b). MIR spectroscopy yields sharp absorption peaks for individual chemical bonds under certain chemical conditions enabling the identification of organic compounds. However, due to the high absorbance of MIR radiation by biological material, penetration depth is low, thus only allowing superficial measurements in micrometre ranges. In contrast, absorptivity of overtones and combinations in NIR spectroscopy is much weaker than the fundamentals in MIR spectroscopy, usually by a factor of 10–100, thus allowing higher penetration depths. This is crucial for applications measuring inhomogeneous biological material (Herold et al., 2009; Sandorfy et al., 2007). Unfortunately, NIR bands are usually broad and severely overlapped resulting in strong multicollinearity. Therefore, assignment of NIR bands is frequently difficult (Ozaki, Morita, & Du, 2007) making NIR spectra less valuable for compound identification purposes. Moreover, Beer's Law, relating the concentration of a substance to the absorption of light, and

therefore allowing quantitation, only applies to transparent media where scattering can be excluded. However, in turbid media, such as in biological tissues, interaction of light with the sample proves to be highly complex invalidating Beer's Law. Besides Fresnel reflectance on sample interfaces, light that enters the sample can be scattered backward (diffuse reflectance), or forward (diffuse transmission). Moreover, absorbance may occur directly or after some scattering events (Friebel et al., 2009). As a benefit, in addition to being a fingerprint of the chemical composition, NIR spectra comprise information of the physical properties of the investigated sample (Siesler, 2008). Finally, multivariate statistics, involving either non-linear techniques such as support vector machines and neural networks, or linear techniques such as multiple linear regression (MLR) and partial least squares (PLS) regression need to be applied in order to extract analytical information from the spectra (Herold et al., 2009) (see Section 2.5).

2.1. Instruments

Nearly all modern MIR spectrometers are Fourier transform (FT) based instruments with different interferometer designs. In contrast, monochromator/detector principles in scanning NIR spectroscopy are variable. Besides different spectrometer types with moving parts, like grating instruments and FT spectrometers with Michelson or polarisation interferometers, fast-scanning instruments without moving parts such as diode-array, acousto-optic tunable filters (AOTF), and light-emitting diode (LED) systems are available (Lin, Rasco, Cavinato, & Al-Holy, 2009; Siesler, 2008). A typical NIR spectrometer consists of a radiation source, a wavelength selection device (e.g. a monochromator), a sample holder, a photoelectric detector for the measurement of the intensity of the detected light and conversion into electrical signals, and a computer system for spectral data acquisition and processing (Lin et al., 2009). Different optical geometries are available for NIR spectroscopy. Predominant sample presentation modes being distinguished are "transmission", "reflection", "transflection", and "interaction" (Herold et al., 2009; Tsuchikawa, 2007). According to the reflection and transmission optical geometry used, light attenuation by the sample, relative to the reference, is referred to as reflectance (R) and transmittance (T), respectively. Most studies use log 1/T or log 1/R values for performing chemometric analyses (Herold et al., 2009).

2.2. Data pre-treatment

The principal aim of spectra pre-treatment is the transformation of the data in such a manner that Beer's Law, stating the linear correlation of absorbance and analyte concentration, can be applied (Rinnan, Nørgaard, et al., 2009). However, NIR spectra are frequently characterised by unfavourable spectral variations and baseline shifts originating for instance from light scattering in solid or opaque liquid samples, variations in temperature, density, and particle size of samples, and spectral noise of the spectrometer. Therefore, pre-treatment methods like noise reduction, baseline correction, resolution enhancement, as well as centering and normalisation are commonly applied. For noise reduction, moving-average and the Savitzky–Golay method are most common for smoothing; alternatively, wavelet transform is applied. Baseline correction may be performed by derivative methods, Multiplicative Scatter Correction (MSC), Orthogonal Signal Correction (OSC), and standard normal variate (SNV). Overlapped and hidden bands in NIR spectra can be resolved by resolution enhancement methods derivation, difference spectra, mean centering, and Fourier self-deconvolution. Mean centering can be regarded as a difference spectrum between individual spectra and an averaged spectrum, adjusting the data set by the reposition of the centroid of the data to

the origin of the coordinate system. Normalisation adjusts the data set by equalisation of the magnitude of each sample (Ozaki et al., 2007; Rinnan, Berg, & Engelsen, 2009).

2.3. Chemometrics for multivariate calibration and data analysis

Chemometrics denotes the application of statistical and mathematical methods to extract information from chemical and physical data. Two of the most important and widely used chemometric methodologies are multivariate calibration and multivariate classification. Multivariate calibration aims at finding quantitative relationships between two sets of measurement data. This may be spectra recorded by rapid NIR spectroscopy and the results determined by conventional techniques, thus requiring tedious and costly laboratory analyses. The calibration model obtained may be applied to accurately predict the desired parameters in unknown samples using the rapid method, therefore replacing the conventional method (Heise & Winzen, 2002; Næs, Isaksson, Fearn, & Davies, 2002). Moreover, cluster analyses and discriminant analyses are applied as multivariate classifications for qualitative determinations. Cluster analyses may group data without any predefined class structure. Discriminant analyses classify unknown samples into groups (Ballabio & Todeschini, 2009; Næs et al., 2002).

2.4. Selection of calibration samples

The quality of the calibration equation may strongly depend on the number of calibration samples used for quantitative and qualitative analyses. The predictive value of the equation obtained is generally increased with the number of samples used for calibration. Moreover, sample selection proves to be a crucial step of the calibration procedure. In order to obtain a calibration model satisfyingly predicting desired target parameters in unknown samples by means of NIR spectroscopy, calibration samples and samples to be predicted need to be part of the same population. Calibration samples should be representative for the population to be predicted with a variation as large as possible, but limited to the region of interest. The entire natural range of spectral and reference value variability should be covered. Moreover, the samples should be evenly distributed within the range. For agricultural commodities, the sample set should be sufficiently variable with respect to variety, production area, production year, and maturity stage to meet the aforementioned requirements (Kawano, 2002; Næs et al., 2002; Williams, 2008). Several chemometric algorithms are available for the efficient selection of calibration samples fulfilling these criteria. Among them, the Kennard–Stone algorithm is the most widely used (Blanco Romía & Alcalà Bernàrdez, 2009).

2.5. Calibration techniques

Particularly NIR spectroscopy is characterised by the lack of selective wavelengths directly correlated with distinct sample properties. A wide range of different chemical and physical attributes of complex samples have an impact on NIR spectra resulting in overlapped bands. Thus, univariate calibration based on least square regressions (LSR) is inappropriate, since a direct relationship of the property to be predicted and the measured signal is required. To overcome this problem, multiple or all spectral predictor variables (e.g. wavelengths) are used for establishing multivariate calibrations. The standard multiple linear regression (MLR), based on the least squares (LS) criterion, represents the simplest way of performing an inverse multivariate calibration. Spectral measurements commonly suffer from high linear relations between variables, the so-called multicollinearity problem. Methods based on MLR with few carefully selected variables may be applicable.

However, standard regression techniques based on LS estimation are commonly unsuitable for calibration since they yield very unstable and unreliable regression coefficients and predictions due to multicollinearity. The multicollinearity problem may be solved by deriving few orthogonal (uncorrelated) linear combinations (components or factors) from spectral variables rather than using original data for establishing regression equations. The variables are compressed by discarding irrelevant and unstable parts, i.e. redundancy and noise, while most of the meaningful information is retained. Consequently, more stable and reliable regression equations and predictions are obtained. Principal component regression (PCR) and partial least squares (PLS) regression are most frequently applied data compression techniques that construct new variables (Blanco Romía & Alcalà Bernàrdez, 2009; Martens & Næs, 1989; Næs et al., 2002). PCR comprises principal component analysis (PCA) of the spectral variables for data compression and subsequent least squares regression between selected principal components (PC) and the corresponding reference values (Blanco Romía & Alcalà Bernàrdez, 2009; Mark, 2008). The PLS regression (PLSR) algorithm using the information of both the spectroscopic variables and the respective parameter variables of the analysed samples is the main difference between PLSR and PCR. Data are compressed by directly relating spectral and parameter variances instead of using selected, most dominant PCs. The resulting linear combinations of the variables used for calibration are referred to as latent variables, factors or components. These contain the entire spectral information and are more directly related to spectral variability than the PC. Balancing of the spectral and parameter information reduces the impact of large but irrelevant spectral variance to the calibration model. Hence, the objective is to ensure that the first few latent variables contain as much information of predictive value as possible (Blanco Romía & Alcalà Bernàrdez, 2009; Günzler & Gremlich, 2003; Martens & Næs, 1989).

The optimal number of factors, latent variables or components should be selected to minimise the error of the prediction model. An insufficient number of factors does not cover all relevant information, leading to underfitted, suboptimal calibration models. Using too many factors goes along with redundancies and noise of the spectral variability within the calibration equation. Therefore, the model becomes overfitted, being strongly data dependent with poor prediction results for new samples. Smaller numbers of factors together with approximately the same prediction error are therefore favourable. The optimum number of factors is commonly determined by prediction testing, using a test set or cross-validation (Blanco Romía & Alcalà Bernàrdez, 2009; Næs et al., 2002) (see also Section 2.7).

The aforementioned linear calibration techniques frequently perform well. However, in some cases, non-linear methods are required in order to obtain satisfactory calibration models. Important methods for solving extrinsic non-linearity problems are based on mathematical pre-treatment by applying transformation techniques. Another common way is the addition of extra variables, obtained from the original spectral variables. Subsequently, linear calibration techniques are applicable. To overcome intrinsic non-linearities of the data, the application of non-linear regression methods, such as local regression methods (e.g. locally weighted regression (LWR)) or neural networks, are required (Blanco Romía & Alcalà Bernàrdez, 2009; Cozzolino et al., 2011b; Næs et al., 2002; Pérez-Marín, Garrido-Varo, & Guerrero, 2007).

Already during calibration, it is crucial for a realistic assessment of the prediction performance that the entire sample set is divided into a calibration set for building the calibration and a separate validation set that is not included into the calibration. Otherwise, the prediction performance will be overoptimistic. The most realistic way is the prediction of an independent test set of a vintage,

field etc. not contained in the calibration set.

2.6. Validation

Following the computation of calibration equations, its prediction performance for unknown samples needs to be evaluated. This is of particular importance for the selection between alternative calibration methods and for the decision how many factors are to be used in the calibration. The root mean square error (RMSE) is an important criterion, which is indicated in the same units as the original measurements. RMSE values should be as low as possible to obtain acceptable calibration equations (Næs et al., 2002).

2.6.1. RMSEC
Root mean square error of calibration (RMSEC) is an empirical estimate of prediction error of the reference values within the calibration set. The calibration equation is tested directly on the calibration data, thus being an internal validation. Therefore, it is essentially an estimate of the model error rather than of the prediction error. The error may be highly underestimated and, therefore, estimated prediction ability may be highly overoptimistic. The term designates the square root of the mean square for residuals. In this equation, the residual for each sample is equal to the reference value (y_i) for all samples within the calibration set subtracted from the value predicted by NIR ($\widehat{y}_i$) divided by the number of samples (n) or the degrees of freedom ($n - A - 1$, where A accounts for the number of factors used in the model) (Eq. (1)) (Blanco Romía & Alcalà Bernàrdez, 2009; Næs et al., 2002; Workman, Jr., 2008).

$$RMSEC = \sqrt{\frac{\sum_{i=1}^{n} (\widehat{y}_i - y_i)^2}{n - A - 1}} \tag{1}$$

2.6.2. RMSECV
The root mean square error of cross-validation (RMSECV) is based on calibration data only. For leave-one-out full-cross-validation, samples are successively deleted from the calibration set. Alternatively, segments of the sample set may be selected for deletion. Subsequently, the calibration equation is developed using the remaining samples. Calibration performance is tested by predicting the deleted sample or samples and comparing the predicted values with the reference values. The selected sample or sample set segment is reintroduced into the calibration set, and the next sample or segment is deleted. The procedure is continued until all samples have been deleted once. RMSECV is calculated from the difference of the reference values (y_i) and the respective predicted value ($\widehat{y}_i$) divided by the number of samples (n) (Eq. (2)). RMSECV can be regarded as an estimate of the RMSEP (see 2.6.3) since the only difference represents the manner how samples are chosen for validation; therefore, being a less independent internal validation (Næs et al., 2002; Workman, Jr., 2008).

$$RMSECV = \sqrt{\frac{\sum_{i=1}^{n} (\widehat{y}_i - y_i)^2}{n}} \tag{2}$$

2.6.3. RMSEP
Root mean square error of prediction (RMSEP) is an estimate of the variation of the reference and predicted values of an independent validation set not contained in the calibration set. Prediction testing is based on splitting the total data set into two subsets, one of which is used for calibration and the other for validation only. RMSEP is calculated as the square root of the mean square for

residuals for a number of n_{val} samples in the validation set, where the residual equals predicted ($\widehat{y}_i$) minus reference (y_i) values *for* samples outside the calibration set (Eq. (2)). The removal of samples for validation at the expense of the calibration set poses a major disadvantage of this approach. Therefore, these samples cannot contribute to obtain enhanced regression coefficients allowing better prediction. Moreover, it is of particular importance to cover the relevant range of test samples best possible since calibration equations will exhibit varying properties for different test sets. Hence, validation meeting this prerequisite may yield a much more reliable estimate of the prediction error than internal validations (Blanco Romía & Alcalà Bernàrdez, 2009; Næs et al., 2002; Workman, Jr., 2008). If samples for the test set are part of the entire sample set also used for calibration, they are not independent in a strict sense. Therefore, real independent validation requires a truly independent test set, e.g. originating from a different season or field, to be predicted (Herold et al., 2009).

$$RMSEP = \sqrt{\frac{\sum_{i=1}^{n_{val}} (\widehat{y}_i - y_i)^2}{n_{val}}} \tag{3}$$

2.6.4. Bias
The Bias represents the systematic error being the average difference between the predicted ($\widehat{y}_i$) and reference values (y_i) of the respective number of n samples (Eq. (3)) (Herold et al., 2009; Martens & Næs, 1989; Workman, Jr., 2008).

$$Bias = \sum_{i=1}^{n} \frac{(\widehat{y}_i - y_i)}{n} \tag{4}$$

2.6.5. Bias-corrected standard errors
The standard error of prediction (SEP) represents a further common performance gauge often used for instance in NIR spectroscopy. It is defined as the standard deviation of the predicted residuals, which can be interpreted as the average difference between the predicted ($\widehat{y}_i$) and the reference values (y_i) describing the variance ascribable to random unexplained error in the prediction set (Eq. (5)) (Næs et al., 2002; Workman, Jr., 2008).

$$SEP = \sqrt{\frac{\sum_{i=1}^{n_{val}} (\widehat{y}_i - y_i - Bias)^2}{n_{val} - 1}} \tag{5}$$

The standard error of calibration (SEC) and standard error of cross-validation (SECV) can be derived from the Bias-corrected equations of RMSEC and RMSECV in an analogous manner, respectively.

SEP, SEC and SECV are related with RMSEP, RMSEC and RMSECV as shown in Eq. (4). Equality is not absolutely exact since for SEP defined as standard deviation, $n_{val}-1$ is used as denominator, whereas n_{val} is used for RMSEP (Martens & Næs, 1989; Næs et al., 2002).

$$RMSEP^2 \text{ or } RMSEC^2 \text{ or } RMSECV^2 \approx SEP^2 \text{ or } SEC^2 \text{ or } SECV^2$$
$$+ Bias^2 \tag{6}$$

2.6.6. Coefficient of determination (R^2)
The coefficient of determination (R^2) provides information on

the goodness of fit of a model. Values ranging from 0 to 1.0 can be attained, with 0 indicating no correlation and 1.0 revealing perfect linear relationship of predicted and reference values, respectively. Therefore, this statistical evaluation allows the determination of the degree of variation in the data that is adequately modelled by the calibration. Values of R^2 multiplied with 100% indicate the percentage of variation within the data modelled by the calibration equation. R^2 values as close as possible to 1.0 are desired for calibrations. The general notation for R^2 is given in Eq. (5) with reference values y_i, predicted values $\hat{y}_i$, and the mean value of the reference values $\overline{y}$ (Herold et al., 2009; Workman, Jr., 2008).

$$R^2 = \frac{\sum_{i=1}^{n} (\hat{y}_i - \overline{y})^2}{\sum_{i=1}^{n} (y_i - \overline{y})^2} \tag{7}$$

Plotting reference values y_i against predicted values $\hat{y}_i$ may be as well valuable for assessing calibration model performance. Good calibrations will result in a straight line close to the bisecting line between the x- and y-axes. Moreover, the obtained plot can be used for the identification of regions exhibiting different levels of prediction accuracy (Næs et al., 2002).

2.6.7. RPD

The ratio of prediction to deviation (RPD) is another useful statistics commonly used for the interpretation of calibrations and is defined as the ratio of the standard deviation (SD) of the reference values to RMSEP or RMSECV (Eq. (6)). Higher values indicate a better prediction ability standardised to the SD (Cozzolino et al., 2011b; Herold et al., 2009; Nicolaï et al., 2007).

$$RPD = \frac{SD}{RMSEP \ \ or \ \ RMSECV} \tag{8}$$

2.7. Selection of the number of factors

The selection of the optimal number of factors, latent variables or components to be used in the calibration model is another crucial topic with regard to all data compression techniques. Too few factors do not comprise all relevant information of the spectral data for establishing a reliable model. Therefore, this underfitting effect yields suboptimal calibration models. On the other hand, using too many factors goes along with redundancies and noise of the spectral variability within the calibration equation. Hence, the model becomes overfitted and will be very data dependent, and prediction results will be poor. The overfitting effect is of lower relevance with higher numbers of samples. Parameter estimates, and thus, the predictions are getting more precise the more samples are involved (Blanco Romía & Alcalà Bernàrdez, 2009; Günzler & Gremlich, 2003; Næs et al., 2002).

Prediction testing is commonly used for determining the optimum number of factors for calibration. Plotting the RMSEP versus the number of factors may be highly valuable for determining the number of components to be used. Principally, the smallest RMSEP value is desirable if a clear-cut optimum is observed. Fewer factors may prevent overfitting and result in more stable calibrations for predicting unknown samples. Therefore, smaller numbers of factors going along with approximately the same prediction error are favourable. In the absence of a clear minimum RMSEP, the optimum number of components can be chosen by selecting the number of factors resulting in an RMSEP not being significantly lower than for the subsequent factors of the model. In the case of an insufficient number of samples available for a test set comprising samples not used to construct the model, a cross-validation procedure can be used to select the optimal number of factors based on RMSECV (Blanco Romía & Alcalà Bernàrdez, 2009; Næs et al., 2002). Leave-one-out cross-validation and cross-validation by splitting the data into segments (typically 5—10) can be used to evaluate the optimum number of factors for all but one sample/segment, and to evaluate the models on the omitted sample/segment. However, this procedure tends to select models with higher variances, leading to overfitting and overoptimistic prediction performance (Filzmoser, Liebmann, & Varmuza, 2009; Krstajic, Buturovic, Leahy, & Thomas, 2014). To overcome this, selection and assessment of predictive models by repeated cross-validation and nested cross-validation may be applied (Krstajic et al., 2014). Repeated double cross-validation represents a strategy for optimising the complexity of regression models and for a realistic estimation of prediction errors for unknown samples. This strategy is used for repeated splits of the data into test sets and calibration sets as well as for estimation of the optimum number of components and is qualified for small data sets (Filzmoser et al., 2009).

2.8. Outlier detection

Outliers are samples not fitting in the model. An outlier is characterised by anomalous spectral data or a high residual between the predicted value and reference value. Removal of outliers may apparently improve the model performance; however, useful variance from the model may be removed, leading to poorer predictions of new sample sets. Therefore, outliers should only be removed for good reasons, when their origin and the causes for their unreasonable behaviour is clear. To be precise, for practical purposes in routine commercial analysis, there can be no outliers since every sample must be tested. Hence, the removal of outliers may lead to the loss of a valuable source of information for the prediction of unusual samples or under unexpected measurement conditions (Herold et al., 2009; Williams, 2007).

Plots of the Hotelling's T^2 and Q (sum of squares of residuals), and leverage statistics can be used for evaluating the calibration for the presence of outliers. The Q statistic is applied to assess conformity of each sample to the model. The difference between the original data and the data reconstructed on the basis of the calibrated model is determined. Hence, large Q values indicate samples not well covered by the model. Hotelling's T^2 statistic, based on the sum of normalised squared scores, determines the variation in each sample within the model. The leverage accounts for the sample distance from the centre of the model. Both large values of Hotelling's T^2 and leverage indicate a sample that has large influence on the model. Hotelling's T^2 and leverages are always correlated despite having different scales (Ballabio & Consonni, 2013). Extrapolated calibration models may be indicated by a high value in the T^2 plot but not in the Q plot. A high value in Q and not T^2 may be caused by a variability in the recorded signal that is not considered in the model (Kradjel & Lee, 2008).

3. Overview of the application of NIR spectroscopy in the food industry

The light of the NIR region was discovered by Herschel in the year 1800 (Herschel, 1800; McClure, 2003). The agricultural food sector was the first adopting NIR spectroscopy as an analytical technique. Until the early applications of NIR spectroscopy reported in the 1950s, it was not believed that it comprises any analytical value (Blanco & Villarroya, 2002). NIR spectroscopy was first applied extensively to grains and seeds in the 1960s and 1970s (Cooper, 1983). This application was substantially developed by K. H. Norris at the Beltsville Laboratories of the United States Department of Agriculture (Davies & Grant, 1987) starting in 1962

with the determination of moisture contents of various types of seeds (including grains, oilseeds and edible beans). Applying this method, water in methanol extracts was determined (Hart, Norris, & Golumbie, 1962). Thus, this method was based on indirect measurements. Additionally, NIR spectroscopy aiming at the assessment of fruit and vegetable quality was one of the earliest applications (Davies & Grant, 1987). Further early applications in the agricultural sector have been reviewed elsewhere (McClure, 2003). Potential applications in food analysis have attracted a great deal of attention, due to the availability and applicability of various calibration methods together with the development of modern computer science since the 1980s (Cen & He, 2007).

Davies and Grant (1987) surveyed the application of NIR spectroscopy for the analysis of various food constituents (e.g. fat, sugars, protein, and moisture) in various matrices (e.g. fruits and vegetables, meat, and milk), covering reports which were mainly published in the first half of the 1980s. In 1990, Williams and Stevenson (1990) reviewed a broad spectrum of applications of NIR reflectance analysis in the food industry, including first applications to specific raw materials and food products. In the same period, several applications in the food and agricultural sector were also reviewed by Martin (1992). More recently, Cen and He (2007) gave an overview of the versatile application of NIR reflectance spectroscopy for assessing food quality. The comprehensive review of Woodcock, O'Donnell, and Downey (2008) covers numerous reports of the application of NIR spectroscopy to the area of food and beverage quality ranging from 1997 to 2008. The authors concluded that all the reviewed applications of NIR spectroscopy, often in combination with chemometric analyses, may play a valuable role in food industry.

Besides the aforementioned general reviews of NIR spectroscopy application in the food sector, reviews of more specialised applications have been recently published and will be briefly summarised below.

The application of NIR reflectance spectroscopy to predict meat and meat quality was reviewed by Prieto, Roehe, Lavín, Batten, and Andrés (2009) covering publications between 1997 and 2008. In summary, NIR was considered useful for the determination of chemical constituents and to categorise meat into quality classes. However, the potential for estimating technological and sensory attributes was limited, presumably due to the heterogeneity of the meat samples and their preparation, the low precision of the reference methods, and the subjectivity of the test panel members.

The application of NIR spectroscopy to the analysis of muscle food (meat and fish) in the period of 2005–2010 has been extensively reviewed by Weeranantanaphan, Downey, Allen, and Sun (2011). It was concluded that these studies may contribute to the development of modern processes serving modern industrial and consumer needs and trends. However, some reluctance with regard to the adoption and application of NIR technology despite its advantages was noted in the food industry. This may be attributed to the dependency on reference analytical methods which may cause difficulties, particularly with empirical analytical methods commonly used by food processing industry. Application of infrared spectroscopy (including NIR spectroscopy) was also reviewed elsewhere for meat and meat products (Gangidi & Proctor, 2009), and for fish and related products (Uddin & Okazaki, 2009).

Fagan, Castillo, O'Callaghan, Payne, and O'Donnell (2009) reviewed the application of infrared spectroscopy to milk and dairy products.

Karoui et al. (2009) covered the application of infrared spectroscopy to eggs and egg products. Compared to other food commodities, only few applications have been reported; mainly the determination of egg freshness and the quantitation of the main components protein and fat in liquid and dried egg products was reported.

A detailed overview of the measurement of fruit and vegetable quality by means of NIR spectroscopy was given by Nicolaï et al. (2007). Multi- and hyperspectral imaging applications have also been used and yielded promising results with regard to the determination of texture attributes and fruit maturity. The application of IR spectroscopy both in the NIR and the MIR region have been taken into consideration for fruit and vegetables by Schulz and Baranska (2009). Furthermore, Huang, Rasco, and Cavinato (2009) focused on the analysis of fruit juices also in both spectral ranges.

Recently, the application of NIR spectroscopy for analysing the quality of citrus fruits was reviewed (Magwaza et al., 2012). NIR spectroscopy was regarded as the most advanced technique among non-destructive quality assessment methods with respect to instrumentation, application, accessories, and available chemometric software.

Cozzolino (2009) highlighted the applicability of NIR spectroscopy for the qualitative and quantitative analysis of natural plant products. Among these, food products, which have not been systematically considered in previous reviews, were reviewed. An overview of the current practice in NIR spectroscopy for cereals and cereal products was given by Jespersen and Munck (2009). Furthermore, wine and beer analysis was the focus of infrared spectroscopic investigations (Cozzolino & Dambergs, 2009). Successful discrimination of wines according to their geographical origin and varieties by means of NIR/VIS spectroscopy has been demonstrated by several authors (Bauer et al., 2008; Cozzolino & Dambergs, 2010; Cozzolino, Cynkar, Shah, & Smith, 2011a).

4. On-line application of NIR spectroscopy in the food industry

For on-line measurements, the essential prerequisite represents the suitability of the spectrometer construction for process integration. The device needs to be compact enough for that purpose and remote control via Ethernet or fibre-optic probes can be advantageous. Depending on the application conditions, the device needs to be explosion-proof, water-proof, and easy to clean. Moreover, it should withstand harsh process environment, such as high or low temperatures, vibrations, dust, and humidity. Hence, the instrumentation has to be robust with few moving parts and a high degree of thermal stability. Materials having direct contact must be food-safe and inert under the potentially chemically challenging conditions (e.g. high chloride concentrations). Rapid analyses in real-time are required in combination with fast data processing, analysis, and storage. It is in the nature of things of on-line measurements that sample preparation is impossible. Therefore, measurements have to be conducted with intact samples in that form they occur in the process. Despite the rough environment for the spectrometers, collecting representative and reliable spectra under industrial conditions remains challenging due to temperature fluctuations, moving samples, sample presentation, and the inhomogeneity of intact samples. For practical usability, the spectrometers require to be quick and easy to maintain with minimal disruption of the production process. Finally, ease of use with no special knowledge required during routine operation is highly desirable. A range of spectrometers designed for on-line process implementation is commercially available. Examples can be taken from the literature cited in Section 5, where commercial systems are used in most applications.

According to the realisation of process implementation, off-line, at-line, on-line, and in-line measurements can be distinguished, their definitions most commonly used being as follows (Callis, Illman, & Kowalski, 1987; Dickens, 2010; Koch, 1999):

- off-line: analysis of samples discontinuously sampled in a remote or centralised laboratory
- at-line: usage of a dedicated instrument installed in close proximity to the process line with the possibility of sample conditioning
- on-line: investigation not directly in the production flow/process line but with recirculation loop (by-pass) or an automated sampling system integrated in the process stream to present and condition samples to the analysis instrument
- in-line: investigation of samples with a direct interface of the instrument to the production flow/process line (*in situ*).

Besides these definitions, in practice, the terms in-line and on-line are apparently used interchangeably or both terms are used as umbrella term, respectively. In the present work, on-line is used as umbrella term. For publications cited, the term of the original article is used.

4.1. General information, early applications, and reviews

The application of NIR spectroscopy for process control was already taken into account in 1983. General principles were discussed, and a 7-filter instrument specifically designed for on-line real time process control application was introduced (Cooper, 1983). Prior to 1980, process control based on NIR spectroscopy has not been commonly reported (Workman, Jr., 1993). Subsequently, besides other constituents, ethanol contents were measured accurately and precisely in beer (Halsey, 1985). The laboratory application was suggested to be extended to in-line process control in breweries for fermentation monitoring and the control of dilution after high gravity brewing, respectively. Davies and Grant (1987) stated that "on-line methods of using NIR analysis are being developed and this is expected to be one of the most important applications for the future use of NIR in the food industry". Instruments were reported to be available from several companies; however, going along with a lack of published information.

Early applications of NIR spectroscopy to on/in-line food process have been demonstrated by Scotter (1990). Parameters such as original gravity, alcohol content, protein, fat, moisture, and carbohydrates contents were evaluated in the course of physicochemical characterisation of beer, wine, and liquor from wet corn milling, dry milk powder, flour, pre-crushed sunflower seed, fish product, and butter.

In 1991, Grevesmuehl, Kradjel, and Kellner (1991) presented a commercial NIR analyser optimised for closed loop control in industrial production. Applications in the food industry comprise the analysis of both liquid and solid samples. Such applications may be found in e.g. the sugar processing industry for the determination of Brix values in raw, thin and thick juice as well as in brewing, allowing to control an on-line blending station for continuously adding water to high gravity beer. Solid sample analyses comprise the measurement of moisture and protein in flour; fat, moisture, and protein in milk powder processing; the analysis of fat in cream cheese as well as fat and protein in meat.

A review of process NIR spectroscopy, including on-line applications in the food industry, in a period of 1980–1994 was published by Workman, Jr. (1993). On-line applications reviewed in this work comprised the continuous control of fermentation processes for the production of lactic acid, the on-line classification of poultry carcasses into three classes with regard to disease conditions, process control in a beet sugar factory, and in a flourmill. Bellon, Vigneau, and Sévila (1994) stated on-line NIR spectroscopy in the food industry to be of high quality; however, on-line applications were reported to be novel.

As an example, NIR spectrometers have been demonstrated to be applicable for on-line measurements of moisture, fat, and protein in two types of cheese at pilot plant and full production scale (Hoyer, 1997).

Recent applications of NIR spectroscopy for on-line and in-line monitoring of food and beverage quality have been extensively reviewed by (Huang et al., 2008). These applications were divided into different product categories. For meat analysis (beef and pork), predominant constituents, such as fat, water, and protein, were mainly taken into consideration. Fruit and vegetables have been mainly analysed with regard to their major components such as sugar and acidity, and defects like internal browning. The quantitation of moisture, protein, dry matter, starch as well as structural analyses of gluten and protein are of particular relevance for grain and grain products. In dairy industry, on-line NIR measurements may be applied for the determination of major milk constituents, such as fat, protein, and lactose, and for process control in cheese making and monitoring of yogurt and filmjölk fermentations. Furthermore, quality parameters as well as adulteration of oils have also been monitored spectroscopically. Moisture determination in dried salted coalfish is an example for on-line application of NIR spectroscopy in fishery. Beverage industry has also been reported as a potential user of on-line monitoring via NIR spectroscopy, such as in wine fermentation, the assessment of continuous processing of juices with regard to soluble solids and the detection of adulteration of apple juice. Further applications comprise on-line viscosity and conductivity measurements in frozen sorbet, the monitoring of colour and composition during the extrusion of corn flour, and the monitoring of kinetics of dough proofing and bread staling. According to the authors, NIR spectroscopy is widely accepted as one of the most promising on/in-line process control techniques for non-destructive, reliable and accurate monitoring of chemical and physical parameters upon food processing.

Bock and Connelly (2008) studied innovative uses of NIR spectroscopy in food processing. Among others, on-line applications of NIR spectroscopy were reported, namely meat grading applications for the evaluation of *longissimus* beef steak tenderness or the classification of beef samples as tender, intermediate, and tough. Dairy applications covered in this review article comprise in-line NIR measurements to monitor continuous curd setting processes, to predict curd-cutting time, and an on-line sensor to monitor yogurt production. In cereal technology, investigations via on-line sensors to determine optimal dough composition, and mixing time or to monitor dough mixing and development with a fibre optic interactance probe were reported. It was concluded that NIR spectroscopy showed great advantages in process monitoring applications. However, these conclusions were limited due to the need of further large-scale on-line studies in food industry to verify reliability and accuracy under typical process conditions.

Another general overview of on-line measurements by means of NIR spectroscopy in food engineering can be found in the review of Lee (2007).

Besides numerous other applications of NIR spectroscopy to predict meat and meat quality, Prieto et al. (2009) also took on-line applications in industrial processing into consideration. First applications were the on-line estimation of fat, moisture and protein contents in small ground beef samples on a conveyor. Further applications to determine the chemical composition of moving beef and pork samples on a conveyor belt or the outlet of a meat grinder have also been reported. Moreover, the application of a fibre optic probe to assess chemical, technological and sensory attributes in intact carcasses was reviewed. In conclusion, NIR spectroscopy technique proved to be able to simultaneously predict various meat quality attributes on-line under the conditions of industrial processing.

Berzaghi and Riovanto (2010) also reported on-line applications

of NIR spectroscopy during meat processing in a grinder and an industrial mixer. Moreover, application in milk and dairy industry were presented, namely on-line evaluation of milk quality upon milking, on-line monitoring of rennet-induced milk coagulation, and curd synaeresis. Additional examples in dairy industry were given by Giangiacomo and Cattaneo (2007) describing the determination of fat in milk and cheese or moisture in butter and cheese, the monitoring of continuous butter production, the control of milk spray-drying, and the evaluation of protein denaturation upon thermal treatment of whey.

In their review of non-destructive measurement of fruit and vegetable quality by means of NIR spectroscopy Nicolaï et al. (2007) pointed out that most applications have been demonstrated under laboratory environment and static conditions. Only few publications of notable exceptions of on-line implementation for measuring intact fruits (e.g. apples, citrus fruits and stone fruits) have been cited. Commercially available NIR sensors from different manufacturers applicable in grading lines are now available from various suppliers. However, lacking availability of scientific evidence of the accuracy of these systems is considered a major drawback.

The particular scope of the use of NIR spectroscopy in olive oil industry was covered by Armenta, Moros, Garrigues, and Guardia (2010). In this context, on-line monitoring of acidity value, bitter taste and fatty acid composition, total levels of carotenoids and chlorophylls upon processing of virgin olive oils in olive mills were considered. Additionally, on-line determination of moisture and fat contents was reported by different authors. It was concluded that most studies have only been conducted on laboratory scale and only few were applied under real process conditions in olive mills. Consequently, to gain more profound knowledge of the applicability of NIR spectroscopy under process conditions, close collaboration between research facilities and industrial processors is urgently needed.

Aït Kaddour and Cuq (2011b) reviewed studies on NIR spectroscopy for monitoring wheat product processing. According to the authors, NIR spectroscopy may provide valuable information on the changes of chemical and physicochemical properties of food during processing and has been mainly performed as an in-line monitoring tool for bread dough mixing. The monitoring of dough proofing, flour agglomeration processes, pasta extrusion and lamination processes, thermal treatment and product storage are further applications specified in this review article. NIR spectroscopy was concluded to be suitable for in-line monitoring of wheat processing. Additionally, Aït Kaddour and Cuq (2011a) focused on the use of dynamic NIR spectroscopy to monitor bread dough mixing, mainly as an in-line method. NIR spectroscopy appeared to be able to provide information relevant to calculate reaction rate constants of the process, thus allowing to monitor chemical and physical changes in dough structure during mixing.

Monitoring and control by means of NIR spectroscopy in fermentation processes comprise among others the quantitative determination of glucose, lactic acid, and biomass in real time in lactic acid fermentation processes, the determination of main constituents in fermentation broths of an L-glutamic acid fermentation process, and the quantitation of glucose formed upon enzymatic starch saccharification (Yano, 2007).

Practical implementations of on-line NIR based technologies in cane sugar factories to improve performance has been taken into account by O'Shea, Staunton, and Slupecki (2011). Commercial applications are used to establish innovative strategies for quality, remuneration and process control purposes. Different configurations for the analysis of cane, sugar, and bagasse where developed allowing the determination of parameters such as fibre content, ash, dry matter, polarisation, and Brix values. For this purpose, the

sampling head may be mounted over sugar conveyer belts, thus allowing continuous monitoring. This system was found to be able to determine conventional sugar parameters such as polarisation, moisture, ash, colour, and reducing sugars but also polyphenol content, mineral contents, and antioxidant capacity.

5. Specific on-line applications

An overview of recent on-line application of NIR spectroscopy in different areas in the food industry is presented in Tables 1 and 2. Differentiation was made between applications on laboratory scale, for which an on-line application was only discussed or taken into consideration, semi-industrial pilot scale applications with on-line measurements and applications performed under industrial conditions or conditions close to those. Spectroscopic evaluation in the visible (VIS) range of the electromagnetic spectrum was often included in addition to the NIR region, indicating that the VIS range frequently contains relevant information for the calibration. Multi- and hyperspectral imaging technology is an emerging and promising tool for process analysis and control (ElMasry & Sun, 2010; Gowen, O'Donnell, Cullen, Downey, & Frias, 2007). The applicability of this technique for monitoring and analysing food products on moving conveyor belts or in continuous processes appears particularly promising (Weeranantanaphan et al., 2011). This is also documented by the numerous recent publications considering on-line applications of NIR imaging technology.

5.1. Laboratory applications

An evidence for the relevance of on-line applications of NIR spectroscopy may be found in the aforementioned reviews and the original papers cited therein. Moreover, there is now also an increasing desire for the application of on-line NIR spectroscopy in foodstuff analysis. Even if conducted as preliminary or feasibility studies under laboratory conditions, on-line process control and quality prediction by means of NIR spectroscopy has often been taken into account and expressed as overall aim. Generally, authors came to the conclusion that NIR spectroscopy presents a promising and feasible method for on-line application. Most studies were conducted with the commodities of fruit and vegetables, meat and meat products, as well as milk and dairy products. Prediction of chemical constituents (e.g. moisture, total soluble solid content (TSS), protein, fat, and ergosterol), technological quality parameters (e.g. water holding capacity), physical parameters (e.g. firmness, weight, and size), and classification or ranking of samples were taken into consideration (Collell, Gou, Picouet, Arnau, & Comaposada, 2010; Flores, Sánchez, Pérez-Marín, Guerrero, & Garrido-Varo, 2009; Morales-Sillero et al., 2011; Porep, Erdmann, Körzendörfer, Kammerer, & Carle, 2014; Prevolnik, Čandek-Potokar, & Škorjanc, 2010).

5.2. Semi-industrial scale

On-line implementation of NIR spectroscopy under conditions close to industrial processes, for example on a moving conveyor belt or in a pilot scale production facility, recently evaluated are summarised in Table 1. A broad spectrum of commodities in the area of plant as well as of animal foodstuffs was studied. Some examples will be reviewed in more detail in the following.

A study considering fresh pork quality prediction using on-line NIR/VIS reflectance spectroscopy (350–1100 nm) was conducted by Liao, Fan, and Cheng (2010). For this purpose, intact slices of *longissimus dorsi* muscles were scanned under simulated on-line conditions. Spectra were derived from the cut surface on a conveyor belt using a prototype system. The spectral range was

Table 1
Semi-industrial on-line applications of NIR spectroscopy in the food sector.

Sample	Sample presentation	Acquisition mode	Regression method[a]	Spectral range (range used)	Spectral pre-treatment[b]	Attributes [unit] (measurement ranges)	Calibration performance[c]	Ref.
Meat/meat products								
Fresh pork, *Longissimus dorsi*	Intact slices, conveyor belt	Reflectance	PLS	350–1100 nm (450–910 nm)	MC + DWT + Deriv.+MSC	Intramuscular fat [%] (2.45–3.57)	R^2_{cal} = 0.852; RMSEC = 0.074; R^2_{val} = 0.767; RMSEP = 0.087	Liao et al. (2010)
						Protein [%] (19.07–23.32)	R^2_{cal} = 0.821; RMSEC = 0.469; R^2_{val} = 0.757; RMSEP = 0.405	
						Water [%] (64.65–74.12)	R^2_{cal} = 0.832; RMSEC = 0.762; R^2_{val} = 0.794; RMSEP = 0.776	
						pH value [ ] (5.03–6.14)	R^2_{cal} = 0.865; RMSEC = 0.093; R^2_{val} = 0.824; RMSEP = 0.104	
						Shear force value [N] (9.70–34.79)	R^2_{cal} = 0.723; RMSEC = 0.229; R^2_{val} = 0.278; RMSEP = 0.360	
Fresh pork, *Longissimus dorsi*	Intact slices, conveyor belt	Reflectance	PLS	350–1100 nm (450–910 nm)	DWT + Deriv.	pH value [ ] (5.03–6.14)	R_{cal} = 0.908; RMSEC = 0.100; RMSECV = 0.139; R_{val} = 0.906; RMSEP = 0.125	Liao et al. (2012)
Pork sausages	Intact, in drying tunnel	Reflectance	PLS	n.a.[d]	n.a.	Water activity (a_w) [ ]	RMSEP = 0.007	Stawczyk, Muñoz, Collell, and Comaposada (2009)
Iberian pig	Intact carcasses	Reflectance	PLS2-DA	1600–2400 nm (1600–2208 nm)	None	Classification into feeding regimes	60.6–93.9% correct	Zamora-Rojas, Pérez-Marín, Pedro-Sanz, Guerrero-Ginel, and Garrido-Varo (2012)
Seafood								
Cod (*Gadus morhua*) fillets	Intact, conveyor belt	Interactance imaging	None (PCA)	400–1000 nm (487, 557, 606, 646 nm)	SNV, SG	Differentiating between fresh and frozen–thawed	96–100%	Sivertsen et al. (2011)
		Interactance imaging	PLS	400–1000 nm (487, 606, 646, 980 nm)	None	Freshness [days on ice] (0–13)	R = 0.93; RMSECV = 1.64	
Fish fillets	Intact, conveyor belt	Interactance imaging	PLS	460–1040 nm (760–1040 nm)	n.a.	Water [%] (56.45–85.41)	R_{cal} = 0.94; RMSEC = 2.45; RMSECV = 2.73	ElMasry and Wold (2008)
						Fat [%] (0.12–22.92)	R_{cal} = 0.91; RMSEC = 2.70; RMSECV = 2.99	
Super-chilled salmon fillets	Intact, conveyor belt	Interactance imaging	PLS	760–1040 nm	AVG, SNV	Ice fraction [%] (0–30)	R^2_{CV} = 0.98; RMSECV = 2.06	Ottestad, Høy, Stevik, and Wold (2009)
						Fat [%] (7.9–31.2)	R^2_{CV} = 0.94; RMSECV = 2.30	
Salmon fillets	Intact, conveyor belt	Interactance imaging	PLS	760–1040 nm	AVG, SNV	Fat [%] (3.81–29.64)	R^2_{CV} = 0.958; RMSECV = 2.00	Segtnan, Høy, Lundby, Narum, and Wold (2009)

Table 1 (continued)

Sample	Sample presentation	Acquisition mode	Regression method[a]	Spectral range (range used)	Spectral pre-treatment[b]	Attributes [unit] (measurement ranges)	Calibration performance[c]	Ref.
Milk/dairy products								
Coagulating milk	In cheese vat	Reflectance	PCA + NLR	1000–2500 nm (1000–1850 nm)	n.a.	Coagulating process, automatic cutting time determination	$R^2 > 0.99$	Lyndgaard et al. (2012)
Curd	Through a glass window installed in the cheese vat wall	Reflectance	PLS (+JK)	189–1100 nm	n.a.	Moisture [g/100 g] (75.5–91.3)	$R_{cal} = 0.86$–0.93; SEP = 0.97–1.7	Mateo et al. (2010)
Curd		Reflectance	PLS	980 nm + additional parameters		Moisture [g/100 g] (75.5–91.3)	$R_{cal} = 0.96$/0.98; SEP = 0.77/0.9	
Whey		Reflectance	PLS (+JK)	189–1100 nm		Solids [g/100 g] (7.07–4.18)	$R_{cal} = 0.71$–0.83; SEP = 0.11–0.30	
Curd, whey	In cheese vat	Reflectance	PLS + JK	300–1100 nm	None	Whey fat [%] (0.448–1.482)	$R_{CV} = 0.95$; RMSECV = 0.061	Fagan et al. (2009)
						Curd moisture [%] (52.3–83.2)	$R_{CV} = 0.89$; RMSECV = 3.187	
Fruit/vegetables								
Potatoes	Pulped, conical container	Reflectance	PLS2	400–2500 nm	MSC	Starch [%] (18.0–23.4) Coagulating protein [%] (0.69–1.95)	RMSECV = 0.4 RMSECV = 0.16	Brunt et al. (2010)
Apples (Golden Delicious)	Intact, sample cups on conveyor	Reflectance imaging	MLR	680, 880, 905, 940 nm	n.a.	Magness–Taylor firmness [N] (25.1–81.5)	$R_{cal} = 0.87$; SEC = 6.78; $R_{val} = 0.86$; SEP = 6.86	Lu and Peng (2007)
Apples (Red Delicious)						Magness–Taylor firmness [N] (~21–99)	$R_{cal} = 0.87$; SEC = 7.49; $R_{val} = 0.86$; SEP = 7.24	
Pears	Intact, manual on tray conveyor	Transmittance	GA-PLS	200–1100 nm (533–930 nm)	n.a.	Sugar [°Brix] (~7.5–14.5)	$R^2_{cal} = 0.915$; RMSEC = 0.348; $R^2_{val} = 0.878$; RMSEP = 0.457	Xu, Qi, Sun, Fu, and Ying (2012)
			GA-SPA-MLR				$R^2_{cal} = 0.893$; RMSEC = 0.392; $R^2_{val} = 0.880$; RMSEP = 0.459	
Apples (Red Delicious)	Intact, in motion	Transmittance	PLS	550–1050 nm	Deriv.	Mouldy core detection	100% > 30% level of decay; 92% healthy	Shenderey et al. (2010)
Potato chips	Intact, black plastic box on conveyor belt	Interactance imaging	PLS	760–1040 nm	SNV + AVG	Fat [%] (26.7–49.3)	$R_{CV} = 0.99$; RMSECV = 0.99	Pedreschi et al. (2010)
		Interactance imaging		760–1040 nm		Dry matter [%] (82.9–98.6)	$R_{CV} = 0.97$; RMSECV = 0.86	
		Reflectance/interactance imaging		460–740 nm + 760–1040 nm		Acrylamide [µg/kg] (40–1770)	$R_{CV} = 0.83$; RMSECV = 266	
Watermelons	Intact, conveyor belt	Transmittance	MC-UVE-SMLR	687–920 nm (200–1110 nm)	BOC	SSC [°Brix] (7.47–9.37)	$R_{cal} = 0.77$; RMSEC = 0.29; $R_{val} = 0.66$; RMSEP = 0.39	Jie et al. (2014)
Olives	Intact, conveyor belt	Reflectance	PLS	380–1690 nm	Deriv., MSC, SNV	Free acidity [% oleic acid] (0.09–26.06)	RMSEC = 2.16–2.53; $R^2_{val} = 0.41$–0.74; RMSEP = 2.53–4.67	Salguero-Chaparro et al. (2013)
						Moisture [%] (31.42–74.55)		

Product	Sample	Mode	Method	Wavelength	Preprocessing	Parameter	Results	Reference
						Oil content [%] (5.11–30.34)	RMSEC = 2.02–2.95; R^2_{val} = 0.76–0.88; RMSEP = 2.98–5.48	
Olives	Intact, conveyor belt	Reflectance	PLS	380–1690 nm	SNV, DT, SG	Fat content [g/kg] (51.1–303.4)	RMSEC = 2.05–2.34; R^2_{val} = 0.52–0.79; RMSEP = 2.16–4.09 RMSEC = 1.88[e]; R^2_{val} = 0.86; RMSEP = 2.02[e]	Salguero-Chaparro and Peña-Rodríguez (2014)
			LS-SVM			Free acidity [g/kg oleic acid] (0.9–212.0)	RMSEC = 2.07[e]; R^2_{val} = 0.73; RMSEP = 2.41[e]	
			LS-SVM			Moisture [g/kg] (314.2–745.5)	RMSEC = 2.31[e]; R^2_{val} = 0.91; RMSEP = 2.89[e]	
Grain/grain products								
Batter	Direct contact in mixer	Reflectance	None (PCA, 2D COS)	1000–2500 nm (1000–2325 nm)	Smoothing, +SG	Monitor batter mixing (water content 51.8, 54.4, 56.7 g/100 g)	Successful for 51.8, 54.4 g/100 g	Aït Kaddour, Morel, and Cuq (2008)
Extruded semolina pasta	Directly after extrusion process	Reflectance	PLS	308–1704 nm (354–1675 nm)	None	Moisture [kg/kg] (0.314–0.744)	R^2_{cal} = 0.964; RMSEC = 0.021; R^2_{CV} = 0.956; RMSECV = 0.024	Temmerman et al. (2007)
Wheat, rye, triticale	Whole grains, conveyor belt	Reflectance	PLS	960–1690 nm	MC + EMSC + SG	Fermentable substance [%] (62.12–75.47)	R^2_{cal} = 0.635; RMSEC = 1.12; RMSEP = 1.21	Pohl and Senn (2011)
						Ethanol yield [L/100 kg] (37.70–47.65)	R^2_{cal} = 0.718; RMSEC = 0.60; RMSEP = 0.67	
Wheat	Whole grains, conveyor belt	Reflectance	PLS-DA, SVM	1100–2400 nm	n.a.	Ergot bodies (0–14) Ergot 0–10,000 mg/kg	R^2_{val} ≥ 0.99 R^2_{val} ≥ 0.99	Vermeulen, Fernández Pierna, Egmond, Dardenne, and Baeten (2012)
Brown rice	Automatic load into sample cell (conditions like in grain elevators)	Transmittance	PLS	840–1048 nm	MC + MSC	Protein [%] (5.8–10.1)	R^2_{val} = 0.95–0.97; SEP = 0.16–0.19	Li et al. (2013)
						Moisture [%] (10.9–31.1)	R^2_{val} = 0.99 → 0.99; SEP = 0.19–0.53	
Milled rice						Protein [%] (5.8–10.1)	R^2_{val} = 0.97–0.99; SEP = 0.09–0.16	
						Moisture [%] (11.0–18.4)	R^2_{val} = 0.98–0.99; SEP = 0.11–0.30	
Wheat						Protein [%] (7.4–18.0)	R^2_{val} = 0.92–0.97; SEP = 0.31–0.56	
						Moisture [%] (8.0–41.8)	R^2_{val} = 0.99–>0.99; SEP = 0.34–0.79	
Durum wheat semolina wet agglomeration	Directly in the mixer bowl	Reflectance	None (PCA)	1000–2500 nm	SG	Different water supply conditions and water addition levels	Qualitative description of physical and chemical variations	Mandato, Taliani, Aït-Kaddour, Ruiz, and Cuq (2013)
Other								
Rice wine	In brown glass bottle, conveyor belt	Transflectance	PLS	350–1200 nm	n.a.	Alcohol [% (v/v)] (17.09–18.64)	R_{val} = 0.889; RMSEP = 0.187%	Yu et al. (2009)
			LS-SVM				R_{val} = 0.915; RMSEP = 0.168	
			PLS			Titratable acidity [g/L] (3.78–4.89)	R_{val} = 0.843; RMSEP = 0.176	
			LS-SVM				R_{val} = 0.888; RMSEP = 0.146	

Table 1 (*continued*)

Sample	Sample presentation	Acquisition mode	Regression method[a]	Spectral range (range used)	Spectral pre-treatment[b]	Attributes [unit] (measurement ranges)	Calibration performance[c]	Ref.
			PLS			pH value [ ] (4.2–4.41)	R_{val} = 0.833; RMSEP = 0.037;	
			LS-SVM				R_{val} = 0.872; RMSEP = 0.033	

[a] Abbreviations: PLS, partial least squares; GA, genetic algorithm; MLR, multilinear regression; SPA, successive projection algorithm; MC-UVE, Monte-Carlo uninformative variable elimination; SMLR, stepwise MLR; LS-SVM, least squares support vector machine; DA, discriminant analysis; SVM, support vector machines; JK, jack-knifing; PCA, principal component analysis; 2D COS, generalised two-dimensional correlation spectroscopy; NLR, non-linear regression.

[b] Abbreviations: MSC, multiplicative scatter correction; Deriv., derivative; SNV, standard normal variate; BOC, baseline offset correction; DT, detrend; SG, Savitzky–Golay derivative; MC, mean centering; EMSC, extended MSC; DWT, discrete wavelet transform.

[c] Abbreviations: R, correlation coefficient; R_{cal}, correlation coefficient of calibration; R_{val}, correlation coefficient of validation; R^2, coefficient of determination; R_{cv}, correlation coefficient of cross-validation; R^2_{val}, coefficient of determination of validation; R^2_{cv}, coefficient of determination of cross-validation; SEC, standard error of calibration; SEP, standard error of prediction; RMSEC, root mean square error of calibration; RMSEP, root mean square error of prediction; RMSECV, root mean square error of cross-validation. Errors are in the same unit as defined by the attribute, R and R^2 are dimensionless.

[d] n.a., not available.

[e] Assumingly in % (w/w).

narrowed to 450–910 nm for calibration with PLS regressions. Discrete wavelet transform was applied to de-noise the spectra. First derivative and multiplicative scatter correction (MSC) were used for data pre-treatment. Quality attributes were investigated with variable performance. According to the authors, calibration models for shear force value were poor; in contrast, models for intramuscular fat, protein and moisture content prediction can be used for rough estimations, and prediction of pH value should be a reliable and rapid alternative to pH probe measurements under on-line processing conditions.

Liao, Fan, and Cheng (2012) aimed at improving the prediction of pH value in fresh pork meat with apparently the same data as used by Liao et al. (2010). Spectra where de-noised in the same way as in the previous study, and the first derivative was used for further evaluation. In contrast to the previous publication, MSC was not reported, and three samples with comparatively high standard deviations were eliminated. The model performance was only slightly impaired when removing 85% of the variables by the application of uninformative variable elimination to provide a simpler and more cost effective calibration model.

NIR/VIS spectroscopy has also been assessed for differentiating fresh and frozen-thawed cod fillets and for evaluating the freshness of cod as days stored on ice (Sivertsen, Kimiya, & Heia, 2011). An interactance hyperspectral imaging spectrometer was used for on-line analyses under industrial conditions revealing that fresh and frozen-thawed fillets can be clearly discriminated. Determination of freshness as days on ice had an accuracy of 1.6 days. The results showed that changes during cold storage and freezing-thawing process could be mostly deduced from the visible range of the spectra, whereupon haemoglobin and myoglobin oxidation was assumed to be responsible for these changes.

The study of Mateo et al. (2010) focused inter alia on the evaluation of on-line NIR spectroscopy for monitoring key synaeresis indices during cheese manufacture. The study was conducted under semi-industrial scale conditions in an 11 L cheese vat. Measurements were realised using an on-line NIR/VIS sensor through a glass window installed in the cheese vat wall. The reflected light was transmitted to the detector via a fibre optic cable. Different optical sensing techniques with single wavelength measurement at 980 nm and alternatively using a broad wavelength spectrum (189–1100 nm) were assessed. The experimental design comprised variation of technological (e.g. curd stirring speed) and compositional (e.g. milk fat) parameters. Different models for predicting curd moisture content were based on single wavelength measurements alone or in conjunction with compositional and technological parameters and on spectra over a broad wavelength range. For predicting whey solids, only the latter technique proved to be successful. PLS with cross-validation or with jack-knifing was carried out for calibration in all experiments. It was concluded that optical-based sensing technologies provide the opportunity to predict key synaeresis metrics on an industrial scale. However, additional studies are required prior to application of this technology in commercial cheese manufacture.

Cutting time determination representing an eminent technological parameter in dairy production was investigated by real-time monitoring of milk coagulation by means of in-line NIR spectroscopy. Measurements were performed via a fibre-connected reflectance probe in a cheese vat in a wavelength range of 1000–2500 nm. Spectral information was supposed to be used for automatic cutting time determination. For this purpose, two different kinetic models were developed for the entire coagulation process and for the individual phases of the coagulation. With an R^2 > 0.99 both models performed very well rendering the results potentially useful for continuous optimisation and control of the cutting point in cheese production (Lyndgaard, Engelsen, & Berg,

Table 2
Industrial on-line applications of NIR spectroscopy in the food sector.

Sample	Sample presentation	Acquisition mode	Regression method[a]	Spectral range (range used)	Spectral pre-treatment[b]	Attributes [unit] (measurement ranges)	Calibration performance[c]	Ref.
Meat/meat products								
Inhomogeneous pork trimmings	Intact, conveyor belt in plastic box	Interactance imaging	PLS	760–1040 nm	EMSC	Fat [%] (1.5–63.7)	R_{cal} = 0.985; RMSECV = 1.90; RMSEP = 3.4/2.82	O'Farrell et al. (2010)
Beef, *M. longissimus thoracis*	Intact, manual around the surface	Reflectance	PLS	350–1800 nm	None	L* value [ ] (31.49–53.93)	R^2_{cal} = 0.86; SEC = 0.88; R^2_{CV} = 0.83; SECV = 0.96	Prieto et al. (2009)
					None	a* value [ ] (16.71–28.89)	R^2_{cal} = 0.86; SEC = 0.71; R^2_{CV} = 0.71; SECV = 0.95	
					None	b* value [ ] (3.40–15.40)	R^2_{cal} = 0.91; SEC = 0.52; R^2_{CV} = 0.84; SECV = 0.69	
					None	Cooking loss [%] (16.26–29.84)	R^2_{cal} = 0.35; SEC = 2.13; R^2_{CV} = 0.23; SECV = 2.35	
					MSC, Deriv.	Volodkevitsch shear force [N] (16.95–98.33)	R^2_{cal} = 0.37; SEC = 11.12; R^2_{CV} = 0.21; SECV = 12.70	
					MSC, Deriv.	Slice shear force (3 days post mortem) [N] (89.28–385.75)	R^2_{cal} = 0.54; SEC = 46.49; R^2_{CV} = 0.31; SECV = 55.76	
					None	Slice shear force (14 days post mortem) [N] (61.43–273.28)	R^2_{cal} = 0.31; SEC = 26.97; R^2_{CV} = 0.23; SECV = 28.49	
					MSC, Deriv.	Tenderness [ ] (3.00–6.70)	R^2_{cal} = 0.28; SEC = 0.56; R^2_{CV} = 0.16; SECV = 0.60	
					MSC, Deriv.	Juiciness [ ] (3.80–5.90)	R^2_{cal} = 0.21; SEC = 0.39; R^2_{CV} = 0.13; SECV = 0.41	
					Deriv.	Flavour [ ] (2.57–5.70)	R^2_{cal} = 0.59; SEC = 0.34; R^2_{CV} = 0.40; SECV = 0.42	
					Deriv.	Abnormal flavour [ ] (2.00–6.70)	R^2_{cal} = 0.22; SEC = 0.35; R^2_{CV} = 0.13; SECV = 0.37	
					None	Overall liking [ ]	R^2_{cal} = 0.25; SEC = 0.37; R^2_{CV} = 0.20; SECV = 0.38	
Beef, Aberdeen Angus (*M. longissimus thoracis*)	Intact, manual around the surface	Reflectance	PLS	350–1800 nm (1100–1800 nm)	Deriv., MSC	Individual fatty acids [mg/100 g] (0.9–9.4 to 346–2152)	R^2_{cal} = 0.19–0.70; SEC = 0.3–298; SECV = 0.4–381	Prieto et al. (2011)
					Deriv., MSC	Groups of fatty acids [mg/100 g] (34–67 to 415–2638)	R^2_{cal} = 0.16–0.73; SEC = 6.6–824; SECV = 8.1–1029	
Beef (Limousin) (*M. longissimus thoracis*)						Individual fatty acids [mg/100 g] (0.7–9.3 to 194–1978)	R^2_{cal} = 0.12–0.76; SEC = 0.4–185; SECV = 0.5–192	
						Groups of fatty acids [mg/100 g] (27–65 to 238–2376)	R^2_{cal} = 0.12–0.75; SEC = 0.4–458; SECV = 9.0–477	
Beef (*longissimus lumborum*)	Intact, manual scan	Reflectance	PLS	400–2500 nm (400–1500 nm)	n.a.[d]	Slice shear force [kg] (9.87–39.87)	Successful sorting tough from tender	Rust et al. (2008)
Beef trimmings	Intact single trimmings, conveyor belt	Interactance imaging	PLS	750–1050 nm	SNV	Fat [%] (2.1–82.7)	R_{cal} = 0.98; RMSECV = 3.0; R_{val} = 0.84; RMSEP = 8.7	Wold et al. (2011)
	Intact small batches, conveyor belt					Fat [%] (8.2–31.0)	R_{val} = 0.99; RMSEP = 1.34	
Beef carcasses	Intact, manual to M. longissimus dorsi	Reflectance	PLS	350–2500 nm (450–1850 nm)	EMSC, OSC	Classification of pH of carcasses as normal (<5.8) and high (≥5.8)	>90% correct	Reis and Rosenvold (2014)
Beef carcasses	Intact, manual to M. gracilis	Reflectance	PLS	350–1800 nm (400–1800 nm)	SNV + DT, MSC	pH [ ] (5.34–5.63/5.43–5.68)	R^2_{CV} = 0.52/0.06; SECV = 0.04/0.04	Marchi (2013)
						L* value [ ] (30.80–41.31/30.17–44.38)	R^2_{CV} = 0.41/0.53; SECV = 1.67/1.93	
						a* value [ ] (7.04–16.72/9.48–17.90)	R^2_{CV} = 0.58/0.31; SECV = 1.33/1.54	
						b* value [ ] (10.44–18.89/10.28–17.94)	R^2_{CV} = 0.57/0.17; SECV = 0.96/1.25	
						Cooking loss [%] (23.16–33.48/32.61–41.30)	R^2_{CV} = 0.31/0.01; SECV = 1.79/1.47	
						Warner–Bratzler shear force [N] (19.96–48.50/26.17–61.20)	R^2_{CV} = 0.13/0.08; SECV = 6.51/6.98	
Dry-cured ham slices	Intact	Interactance imaging	PLS	760–1040 nm (820–1040 nm)	SNV	Water [%] (40.84–60.89)	R^2_{cal} = 0.956; RMSEC = 1.03; RMSEP = 1.34	Gou et al. (2013)
						Fat [%] (3.66–19.70)	R^2_{cal} = 0.921; RMSEC = 1.36; RMSEP = 1.36	

(continued on next page)

Table 2 (*continued*)

Sample	Sample presentation	Acquisition mode	Regression method[a]	Spectral range (range used)	Spectral pre-treatment[b]	Attributes [unit] (measurement ranges)	Calibration performance[c]	Ref.
						Salt [%] (1.99–10.20)	R^2_{cal} = 0.912; RMSE = 0.54; RMSEP = 0.71	
Lamb (M. longissimus lumborum)	Intact, manual scan	Reflectance	GA-PLS	350–2500 nm (400–2450 nm)	SG + Deriv.	Individual fatty acids [mg/100 g] (3.24–10.87 to 264–1570)	R^2_{CV} = 0.35–0.74; RMSECV = 1.56–126.49; R^2_{val} = 0.32–0.73; RMESP = 1.57–128.31	Pullanagari, Yule, and Agnew (2015)
						fatty acid groups [mg/100 g] (190.8–547.2 to 385.39–2065)	R^2_{CV} = 0.61–0.71; RMSECV = 28.09–191.23; R^2_{val} = 0.60–0.67; RMESP = 27.86–192.21	
						intramuscular fat content [%] (2.78–18.56)	R^2_{CV} = 0.71; RMSECV = 1.55; R^2_{val} = 0.69; RMESP = 1.60	
Seafood								
Crabs (*Cancer pagurus*)	Living, conveyor belt	Interactance imaging	PLS	760–1040 nm	SNV	Amount of edible meat (quality index) [ ] (11.4–42.3)	R_{cal} = 0.96; RMSEP = 2.58	Wold et al. (2010)
Milk/dairy products								
Raw milk	Bypassed continuous flow in milking robot system	Interactance	PLS	600–1050 nm	None	Fat [%] (0.94–7.39)	R^2_{cal} = 0.96; SEC = 0.24; R^2_{val} = 0.95; SEP = 0.25	Kawasaki et al. (2008)
						Lactose [%] (2.06–5.06)	R^2_{cal} = 0.82; SEC = 0.28; R^2_{val} = 0.83; SEP = 0.26	
						Protein [%] (2.77–4.38)	R^2_{cal} = 0.78; SEC = 0.15; R^2_{val} = 0.72; SEP = 0.15	
						SCC [log SCC/mL] (3.78–5.88)	R^2_{cal} = 0.64; SEC = 0.33; R^2_{val} = 0.68; SEP = 0.28	
						Milk urea nitrogen [mg/dL] (10.41–15,73)	R^2_{cal} = 0.31; SEC = 1.68; R^2_{val} = 0.53; SEP = 1.50	
Raw milk	Tube of milking place at farms	Reflectance	PLS	851–1649 nm	Normalisation	Fat [%] (0.4–14.8)	R^2_{cal} = 0.99; SEC = 0.13–0.19; R^2_{val} = 0.99; RMSEP = 0.16–0.20	Melfsen et al. (2013)
						Protein [%] (2.3–4.2)	R^2_{cal} = 0.89–0.99; SEC = 0.04–0.10; R^2_{val} = 0.74–0.98; RMSEP = 0.05–0.18	
						Lactose [%] (3.5–5.3)	R^2_{cal} = 0.53–0.95; SEC = 0.05–0.15; R^2_{val} = 0.18–0.95; RMSEP = 0.05–0.18	
Milk powder	Grab sampler	n.a.	n.a.	1100–2500 nm (1100–2200 nm)	n.a.	Moisture [%]	SEP = 0.07–0.09	Holroyd et al. (2013)
	Fibre optics probe					Moisture [%]	SEP = 0.09–0.14	
Buttermilk powder	Part of product stream in a chute			n.a.		Moisture [%]	SEP = 0.17	
Skim milk powder						Moisture [%]	SEP = 0.13	
Whole milk powder	Pneumatic ram			1000–2500 nm		Moisture [%]	SEP = 0.08	
						Fat [%]	SEP = 0.11–0.14	
						Protein [%]	SEP = 0.17	
	Fibre optic probe	Reflectance				Moisture [%]	SEP = 0.03	
						Fat [%]	SEP = 0.07	
Fruit/vegetables								
Grapes	Crushed, in a bypass pipe at wineries	Reflectance	PLS	400–1800 nm (450–850 nm + 1050–1650 nm)	None	Relative density (1.0623–1.1084)	RMSEC = 0.0024–0.0051; R^2_{val} = 0.130–0.775; RMSEP = 0.0028–0.0043	Porep et al. (2015)
						Fructose [g/kg] (52.0–129.8)	RMSEC = 3.3–7.0; R^2_{val} = 0.050–0.732; RMSEP = 3.5–6.9	
						Glucose [g/kg] (50.1–127.5)	RMSEC = 3.4–7.8; R^2_{val} = 0.296–0.747; RMSEP = 3.7–7.3	
						Glycerol [g/kg] (0.00–3.76)	RMSEC = 0.17–0.42; R^2_{val} = 0.056–0.698; RMSEP = 0.13–0.39	
						Gluconic acid [g/kg] (0.00–3.77)	RMSEC = 0.08–0.41; R^2_{val} = 0.089–0.777; RMSEP = 0.07–0.51	
						Acetic acid [g/kg] (0.00–1.15)	RMSEC = 0.06–0.14; R^2_{val} = 0.001–0.574; RMSEP = 0.05–0.12	

Table 2 (*continued*)

Sample	Sample presentation	Acquisition mode	Regression method[a]	Spectral range (range used)	Spectral pre-treatment[b]	Attributes [unit] (measurement ranges)	Calibration performance[c]	Ref.
						Titratable acidity [g/kg] (3.6–14.1)	RMSEC = 0.6–1.2; R^2_{val} = 0.486–0.862; RMSEP = 0.5–1.1	
						pH value (2.75–4.12)	RMSEC = 0.09–0.17; R^2_{val} = 0.229–0.787; RMSEP = 0.08–0.15	
						Tartaric acid [g/kg] (4.1–9.4)	RMSEC = 0.4–0.7; R^2_{val} = 0.179–0.626; RMSEP = 0.4–0.7	
						Malic acid [g/kg] (1.5–14.9)	RMSEC = 0.6–1.3; R^2_{val} = 0.372–0.877; RMSEP = 0.4–1.4	
Grapes	Crushed, in a bypass pipe at wineries	Reflectance	PLS	400–1800 nm (450–850 nm + 1050–1650 nm)	None	Ergosterol [mg/kg] (0.07–49.24)	R^2_{cal} = 0.808–0.862; RMSEC = 0.48–4.17; R^2_{val} = 0.700–0.750; RMSEP = 0.60–3.66	Porep et al. (2015)
Grain/grain products								
Wheat	Exit auger of combine harvester	Reflectance	PLS	600–1100 nm	n.a.	Protein [g/kg] (80–145)	R^2_{val} = 0.94; SEP = 3.1	Long et al. (2008)
						Protein [%]	SEP = 0.03	

[a] Abbreviations: PLS, partial least squares; GA, genetic algorithm.

[b] Abbreviations: MSC, multiplicative scatter correction; Deriv., derivation; SNV, standard normal variate; DT, detrend; SG, Savitzky–Golay derivative; EMSC, extended MSC; OSC, orthogonal signal correction.

[c] Abbreviations: R_{cal}, correlation coefficient of calibration; R_{val}, correlation coefficient of validation; R^2_{cal}, coefficient of determination of calibration; R^2_{val}, coefficient of determination of validation; R^2_{CV}, coefficient of determination of cross-validation; SEC, standard error of calibration; SEP, standard error of prediction; SECV, standard error of cross-validation; RMSEC, root mean square error of calibration; RMSEP, root mean square error of prediction; RMSECV, root mean square error of cross-validation. Errors are in the same unit as defined by the attribute, R and R^2 are dimensionless.

[d] n.a., not available.

2012).

Melons were assessed for their soluble solids contents by NIR/VIS transmittance spectroscopy in a spectral range of 687–920 nm. For this purpose, on-line measurements were conducted by means of a prototype system with sample presentation in trays moving on a conveyor belt (0.3 m/s). According to the authors, a calibration model based on Monte-Carlo uninformative variable elimination (MC-UVE) combined with stepwise multiple linear regressions (SMLR) and baseline offset correction (BOC) spectra pre-processing yielded optimal results (Jie, Xie, Rao, & Ying, 2014).

Intact olives were also assessed by NIR/VIS reflectance spectroscopy (380–1690 nm) in a semi-industrial scale process line on a conveyor belt. Depending on spectra pre-processing and validation strategies, predictive performance achieved varied. Consequently, real time quality and compositional analysis of olives for olive oil production upon their reception at the olive mill was a future aim (Salguero-Chaparro, Baeten, Fernández-Pierna, & Peña-Rodríguez, 2013).

An automated semi-industrial system with an in-line NIR reflectance spectrometer for the chemical characterisation of potatoes was developed by Brunt, Smits, and Holthuis (2010). Measurement of NIR spectra (400–2500 nm) was conducted with an optical fibre connected probe in a conical container equipped with a stirring device measuring pulped potato samples. A PLS (partial least squares) calibration model for starch and coagulating protein concentration revealed promising results. According to the authors, the first test of the automated NIR in-line analysis system was successful. It provided calibration models indicating a high potential for the development of good models for the determination of a range of different constituents of potatoes.

Potato chips were monitored on-line for fat, dry matter and acrylamide contents using NIR interactance imaging with an NIR/VIS scanner (Pedreschi, Segtnan, & Knutsen, 2010). Sixty potato chips samples were produced in different frying runs, spectra were collected and used together with reference values to construct a PLS regression model. Measurements were conducted in black plastic boxes on a conveyor belt. Two wavelength ranges were used, comprising the VIS range (460–740 nm) where measurements were performed in pure reflectance mode and the NIR range (760–1040 nm) applying the interactance mode. Model performance of fat and dry matter content appeared to be very good. Inclusion of the VIS region into the models did not show any benefit for their prediction. The optimal model for acrylamide content included both spectral regions, however, compared to the aforementioned models revealed poorer performance, but still indicating the suitability of this model for on-line screening and classification purposes.

Moisture and protein contents, being important quality attributes, were determined in rice and wheat samples by means of NIR spectroscopy (840–1048 nm). For this purpose, the sample cell was automatically loaded and transmittance spectra were recorded. Calibration models comprising previous harvesting periods were validated by using sample sets of the respective subsequent year. Best validation statistics achieved were a coefficient of determination of validation (R^2_{val}) of > 0.99 and a standard error of prediction (SEP) of 0.19% for moisture content in brown rice; R^2_{val} = 0.99 and SEP = 0.09% for protein content in milled rice; R^2_{val} > 0.99 and SEP = 0.34% for moisture content in wheat; and R^2_{val} = 0.97 and SEP = 0.31% for protein content in wheat, respectively. The technique applied in this study was reported to be implemented in industrial practice in grain elevators (Li, Kawamura, Fujita, & Fujikawa, 2013).

NIR reflectance spectroscopy was also investigated with regard to its potential to monitor moisture contents in extruded semolina pasta. Samples were scanned in-line directly after the extrusion process, showing good performance. Therefore, in-line NIR spectroscopy may replace conventional destructive drying methods for moisture content determination (Temmerman, Saeys, Nicolaï, &

Ramon, 2007).

5.3. Industrial scale

In this category, studies performed under industrial conditions or very close to industrial process conditions are considered (Table 2). For example, probes have been installed into tubes for monitoring fluid samples, above conveyor belts for solid goods or spectra have been recorded manually under industrial conditions. Most applications were reported for meat products.

Fat content in intact inhomogeneous pork trimming was determined on-line by multispectral near-infrared interactance imaging in contactless measurements in large plastic boxes moving on a conveyor belt (O'Farrell, Wold, Høy, Tschudi, & Schulerud, 2010). Wavelengths in a range of 760—1040 nm were covered, and different methods for physical light scattering correction were tested with standard normal variate (SNV) and extended multiplicative signal correction (EMSC). Calibration models were established by applying PLS regression to the data sets. The study aimed at yielding models applicable to individual pixels as well as to averaged spectra obtained from several pixels. Scatter correction with EMSC revealed best results for the calibration set with a root mean square error of cross-validation (RMSECV) of 1.9%. Two industrial trials at an abattoir resulted in a root mean square error of prediction (RMSEP) of 3.4 and 2.82%, respectively. In conclusion, acceptable precision for fat content determination was achieved for on-line NIR measurement of intact inhomogeneous pork trimmings under industrial conditions.

On-line determination of fat content in batches of intact beef trimmings using NIR imaging spectroscopy has been studied by Wold, O'Farrell, Høy, and Tschudi (2011). Interactance measurements were conducted using a commercial NIR imaging scanner mounted over a conveyor belt. Although the system was not directly integrated into a commercial cutting line, the study can be regarded as an application under industrial conditions due to the installation in a beef cutting hall on a running conveyor belt at relevant speed. Calibrations were obtained using PLS regression. Individual trimmings showed low prediction performance due to sample inhomogeneity. Validation with small batches (10—25 kg) resulted in much lower prediction errors. Decreasing RMSEP was observed with increasing batch size leading to values of about 0.6% for 100 kg batches. Thus, it was concluded that the study proved NIR imaging spectroscopy to be a reliable and accurate method for on-line estimation of fat content of batches of beef trimmings.

The following examples of NIR spectroscopy in meat industry can also be considered as on-line applications because studies were performed under industrial conditions at abattoirs. Measurements were conducted manually with fibre-optical probes on static samples in contrast to automated scanning of moving samples on a conveyor belt or in a tube.

Application of NIR/VIS spectroscopy for on-line prediction of physicochemical and sensory properties of beef was assessed by Prieto et al. (2009). Reflectance measurements of M. longissimus thoracis samples were conducted at an abattoir using a fibre optic probe covering a spectral range of 350—1800 nm. Calibration models were obtained applying PLS regression. Prediction ability for colour values was relatively high, whereas cooking loss was predicted with relatively low accuracies. Because of low model performance, it was concluded that instrumental texture measurements cannot adequately be predicted by NIR/VIS spectroscopy. Calibration models obtained for sensory characteristics revealed poor performance, but were still considered useful owing to the subjective reference assessment and the influence of numerous factors on this parameter.

Prieto et al. (2011) evaluated on-line prediction of fatty acid profiles and intramuscular fat content of beef using NIR spectroscopy. Measurements and data analyses were apparently the same as described by Prieto et al. (2009) except reducing the wavelength range to 1100—1800 nm because a broader range did not yield additional information. Samples investigated were M. longissimus thoracis from crossbreed Aberdeen Angus and Limosin cattle. Performance of the calibration models was very different for the prediction of individual and groups of fatty acids. Thus, a specific calibration model for each of the breeds was taken into consideration. In conclusion, the results were regarded promising concerning the potential to accurately predict fatty acid profiles under abattoir conditions with a fast and relatively inexpensive on-line NIR spectroscopic method at an early stage of production.

Moreover, an NIR spectroscopic system was developed for on-line prediction of beef tenderness (Rust et al., 2008). For this purpose, an NIR/VIS spectrometer was applied in reflectance mode covering a wavelength range of 400—2500 nm. Spectra were collected manually with a fibre optic contact probe. The calibration model was developed employing PLS regression. Tenderness, as the dependent variable, was determined measuring slice shear force of longissimus lumborum samples aged for 14 days and after cooking. Parts of the calibration and the entire validation scans were collected in-plant. Model validation resulted in successful sorting of tough from tender carcasses up to 70% certification levels, where significant differences were observed. Removing the top 30% of carcasses sorted as tough by the system, led to 70% of the carcasses that could be categorised as "guaranteed tender". Thus, this in-plant system might be used to sort carcasses for sale to premium markets.

Marchi (2013) also investigated the prediction of beef quality parameters on-line under industrial conditions at two commercial abattoirs. Measurements were performed on the surface of M. gracilis, thus without the need of carcass dissection, using a portable NIR/VIS spectrometer in reflectance mode. Parameters taken into consideration were pH value, colour properties, cooking loss, and Warner—Bratzler shear force determined for M. longissimus thoracis. Predictive performance appeared to be generally low and needs to be improved prior to practical application.

Reis and Rosenvold (2014) aimed at the on-line classification of beef carcasses relying on the pH value of M. longissimus dorsi measured 48 h post mortem. Spectroscopic measurements were conducted manually with split carcasses up to 40 min post mortem in a commercial hot boning abattoir under routine conditions. Established calibration models for predicting pH values two days after slaughtering resulted in correct classification into normal (pH < 5.8) and high (pH ≥ 5.8) in at least 90% of all cases. In this study, animal type specific models (bulls and non-bulls (steers, heifers, and cows) performed better than a global model.

NIR imaging spectroscopy may also be applied for the on-line determination of the edible meat content in live crabs (Cancer pagurus) (Wold, Kermit, & Woll, 2010). Measurements were conducted at high speed with a non-contact NIR interactance imaging system installed above a conveyor belt in a production line. The spectral range applied in this study was 760—1040 nm. PLS regression was used for the calibration. Two different sampling and calibration strategies were assessed. One model was based on the extraction of average NIR spectra from different parts of the crab for calibration and prediction. The second was as well developed from average spectra but predictions were performed pixel-wise within the crab shell. The regression model which performed best was characterised by $R_{cal} = 0.96$ and RMSEP = 2.58. Reference values for the meat content (measured quality index, MQI) were calculated from weight of the meat and size of the crab. The optimal model was reported to be validated for application in industrial scale and

to be used in a crab processing plat.

An on-line application of NIR spectroscopy in dairy industry has been investigated for the quality assessment in an automatic milking system, i.e. for a milking robot (Kawasaki et al., 2008). Spectra in a range of 600—1050 nm were collected in unhomogenised milk in interactance mode. The NIR spectroscope was installed in a bypass with milk flowing continuously through a chamber containing the sensor. PLS regression was used to obtain a calibration model without further spectra pre-treatment. The three major milk constituents fat, lactose, and protein as well as somatic cell count (SCC) and milk urea nitrogen (MUN) were selected as calibration parameters for quality assessment. Owing to the high R^2_{val} values and the relatively low SEP values, it was concluded that sufficient levels of precision and accuracy were achieved. Prediction performance for SCC was considered potentially useful for classifying milk into qualitative groups for the diagnosis of sub-clinical mastitis. Prediction of MUN was poorer than for other milk quality parameters investigated, but might still be used for monitoring the nutritional status of individual cows. According to the authors, this technique may be applied for real-time on-line monitoring during milking using a milking robot with sufficient precision and accuracy, although more detailed investigations are still required.

Furthermore, fat, protein, and lactose contents in raw milk were evaluated by in-line NIR spectroscopic measurements in a spectral range of 851—1649 nm. The device was installed in a milk tube of one milking place on three farms, respectively. The authors emphasised the need to include as much cow, feeding and seasonal variation into the calibration as possible to obtain reliable prediction of unknown samples. Validation statistics for fat, protein and lactose contents were model dependent. Validation using sample sets derived from external farms in combination with calibration sets extended with samples of the farm the validations samples were obtained from, was regarded optimal concerning sample variability of the calibration set and independency of the validation set (Melfsen, Hartung, & Haeussermann, 2013).

Milk powder composition has been predicted by a number of different in- and on-line NIR spectroscopy systems. However, the assessments lack important information such as the applied regression method and validation statistics. Nevertheless, in- and on-line application under industrial conditions was reported. Practically relevant challenges, such as control of the instrument operating temperature, the formation of dusts, and ensuring consistent powder flow, have been reported. In one study, measurements were performed in a range of 1000—2500 nm with fibre optic probes. In conclusion, successful analysis of fat, protein, and moisture contents by FT-NIR was confirmed (Holroyd, Prescott, & McClean, 2013).

NIR spectroscopy may be applied in very early stages of the food production process as exemplified for the determination of grain protein concentration during wheat harvest (Long, Engel, & Siemens, 2008). First experiments were performed in laboratory configuration and on a combine harvester test stand. Finally, the NIR spectrometer was installed on the exit auger of a combine harvester for measuring wheat protein contents in a moving grain stream. Spectra were collected in a wavelength range of 600—1100 nm in diffuse reflectance mode and PLS regression was applied. Correlation of the in-field in-line prediction on the combine harvester and the reference protein concentrations was high, thus demonstrating in-line NIR spectroscopy to provide reliable results of grain protein concentration under field conditions.

Feasibility of on-line assessment for real-time analysis of grape mashes by means of NIR/VIS spectroscopy at production scale upon their reception at wineries has recently been evaluated (Porep, Mattes, Pour Nikfardjam, Kammerer, & Carle, 2015).

Spectrometers were successfully integrated into the reception lines of two wineries during three vintages. In total, the spectra of 1160 samples of commercially delivered grapes were collected. Colour, vintage-, and origin-specific calibrations mostly resulted in better model performance compared to a global model. Variety-specific models appeared to be particularly promising. Models suitable for coarse semi-quantitative predictions of sugar and acid related parameters in combination with grape rot indicators were gathered. In particular, the relatively good performance of acid related parameters compared to available literature data is remarkable. However, predictability of tartaric acid was generally poor. Prediction of grape rot parameters generally suffered from the commonly low contents of these compounds varying within a small range, possibly revealing the limitations of NIR/VIS spectroscopy for this purpose. However, severely affected samples may be detected owing to higher contents, especially if multiple parameters are taken into consideration. Thus, holistic quality assessment of grapes is valid despite of a possibly inaccurate prediction of individual attributes. Hence, even semi-quantitative determinations of the parameters may be used for multifactorial assessment of delivered grape material.

Moreover, NIR/VIS spectroscopy has been applied as a rapid tool for on-line determination of ergosterol under the same industrial conditions (Porep, Mrugala, Pour Nikfardjam, & Carle, 2015). Performance achieved was at least suitable for semi-quantitative measurements of ergosterol in grape mashes upon delivery at wineries, thus enabling the objective detection of conspicuous grape deliveries.

Consequently, on-line implemented NIR/VIS spectrometers were shown to be a promising tool for rapid and objective grape quality assessment in wineries just upon grape reception, thus enabling fair and incentive quality-based pricing. Rejection of spoilt grapes may additionally contribute to improved food safety. Moreover, quality management may be advanced, and further acceptance criterions may be developed. In order to improve their reliability, calibration models need to be further optimised and validated using additional independent data sets from subsequent vintages.

6. Conclusions

The application of NIR spectroscopy in the food sector looks back on a long history. Rapid analyses without the need of sample preparation presents one of the main advantages of this technique. Therefore, this technique bears the prerequisite for real time on-line measurements. However, on-line measurements under industrial conditions remain challenging due to major influences such as temperature fluctuations or moving samples. Furthermore, sample presentation may become a crucial issue for intact samples due to inhomogeneity. Numerous studies claim on-line measurements as their final aim but never perform them, which is often not made unambiguously clear. Therefore, the classification into semi-industrial and industrial applications may help to find practically relevant applications of NIR spectroscopy.

Generally, industrial on-line applications have only rarely been described in scientific publications, although there is a need of further large-scale on-line studies in the food industry to verify reliability and accuracy of NIR spectroscopy under process conditions. However, many of the published studies appear to prove the suitability of NIR spectroscopy as a valuable tool for on-line process control and quality management or at least underline its potential for industrial applications.

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