

TITLE: Near infrared spectroscopy—advanced analytical tool in wheat breeding, trade, and processing

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REVIEW PAPER

Near Infrared Spectroscopy—Advanced Analytical Tool in Wheat Breeding, Trade, and Processing

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Abstract Due to its suitability to be processed in wide range of final products, wheat has an upmost significance among all cereals. The global wheat marketing are becoming increasingly demanding with regard to all aspects of wheat quality. To fulfil these demands, each link in wheat production chain—breeding, trade, and processing should be supported by objective and reliable quality assessment tool such as the near infrared spectroscopy (NIRS) technique. The aim of this paper is to summarize the recent advances in the applications of NIRS technique for wheat quality control applicable in wheat breeding, trade, and processing. Although heavily intertwined, each link is characterized by specific NIRS applications, with ultimate aim —the production of consumer-appealing and safe final products.

Keywords Near infrared spectroscopy · Wheat · Composition · End-use quality · Safety · Functionality

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Introduction

Product quality improvement and the rationalization of production in many branches of industry require a permanent quality control of intermediate and finished products and continuous monitoring of technological processes. Different techniques of vibrational spectroscopy (mid- and near infrared and Raman) have proved its applicability for above-mentioned purposes, where the near infrared spectroscopy (NIRS) appeared to be particularly useful due to the numerous advantages it provides. The application of the NIRS technique significantly reduces the test time and costs and does not require the use of chemicals and sample preparation, making it superior over traditional chemical analytical methods, especially in industrial quality control and process monitoring applications (Cen and He 2007; McClure 2007; Siesler 2008). The prerequisite for the use of the NIRS method is an appropriate calibration model developed to relate the compound (or property) of interest to the sample's spectral data. NIRS calibration model development is a very demanding task due to the complex composition of analyzed samples which result in severe overlapping of interfering bands representing the component(s) (or properties) of interest. Due to the significant overlapping of NIR bands, the NIR spectral region for many years was mainly used for fundamental research in chemistry and physics and had no analytical application. The initial application of the NIRS technique in routine analysis is related to the determination of moisture and protein in cereals, in the '60s (Massie and Norris 1965). Since then, the permanent development of the NIRS devices, chemometrics techniques, and computer technology has contributed to the development of the NIRS technique that is currently used for testing a wide range of foodstuffs (Workman 2008). The NIR analytical technique has developed to such an extent that nowadays it uses different spectral ranges, different ways of recording and processing of spectra, different sample presentations, and various statistical methods used for calibration model development (Osborne and Fearn 1986; Baeten and Dardenne 2002; Murray 2004; Pojić 2010).

Over the past decade, the NIRS measurements have been extended from determination of the certain constituents present in the sample to the determination of functional properties of samples. In this sense, the functional properties are defined as the ability of a commodity to manifest the

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properties in accordance with intended purposes. Since the functionality of the commodity is strongly affected by its physico-chemical properties which do not manifest characteristics absorption in NIR spectral region, the use of NIRS to predict functionality is based on the relationship between physico-chemical properties and certain constituent having absorptions in NIR region (protein, oil, starch etc.) (Williams 2007).

The objective of this paper is to give an overview of current and most important applications of the NIRS technique in wheat technology.

The Specificity of NIRS Methodology

Principles of NIRS

NIRS is a spectroscopic technique that measures the absorption of NIR radiation (from about 800 to 2,500 nm) by the sample. Detection of absorbed NIR radiation by the sample is conducted by measurement of transmittance, reflectance, interactance, and/or transflectance, where the suitable acquisition mode is dependent on the sample type and the constituent and/or property being analyzed. *Transmittance* mode involves the measurement of radiation that passes through a sample, whilst *reflectance* mode involves the measurement of radiation reflected from the sample surface. In *transflectance* measurement, the radiation is transmitted through the sample, reflected from a diffusely reflecting plate and then again transmitted back through the sample. *Interactance* mode involves illumination and detection at laterally separated points on the sample's surface (Osborne 2000).

When sample is exposed to NIR radiation, the energy of chemical bonds involving hydrogen (CH, NH, OH, SH) is changed. Due to very complex composition of the analyzed samples, different organic bonds involving hydrogen absorb the NIR radiation. As a result, the molecular overtone and combination bands seen in the NIR spectral region are very broad, overlapped, and difficult to assign to specific chemical components (Fig. 1). Consequently, the useful spectral information can only be extracted by applying modern chemometrics methods in the calibration development process resulting in calibration model that enables the practical application of NIRS. In this regard, the calibration model defines the relationship between the obtained spectral data and the content of the compound or property of interest obtained by selected reference method. Being an indirect method, the performance of the NIRS method is highly dependent on the quality of the reference method used for basis in calibration development process. Therefore, the validation process should be as much comprehensive as possible to demonstrate all the necessary characteristics of the NIRS method for its fitness-for purpose, where accuracy is the characteristics of most concern (Pojić 2006). The accuracy of the NIRS models is commonly described by the coefficient of determination (R^2), standard error of calibration (SEC), standard error of cross validation, and/or standard error of prediction (SEP). Moreover, as being an indirect method, standard error of reference laboratory method (SEL) has a great importance for interpretation of predictive ability of developed NIRS models, by expressing the ratio of SECV vs. SEL and/or SEP vs. SEL (Hruschka 2001).

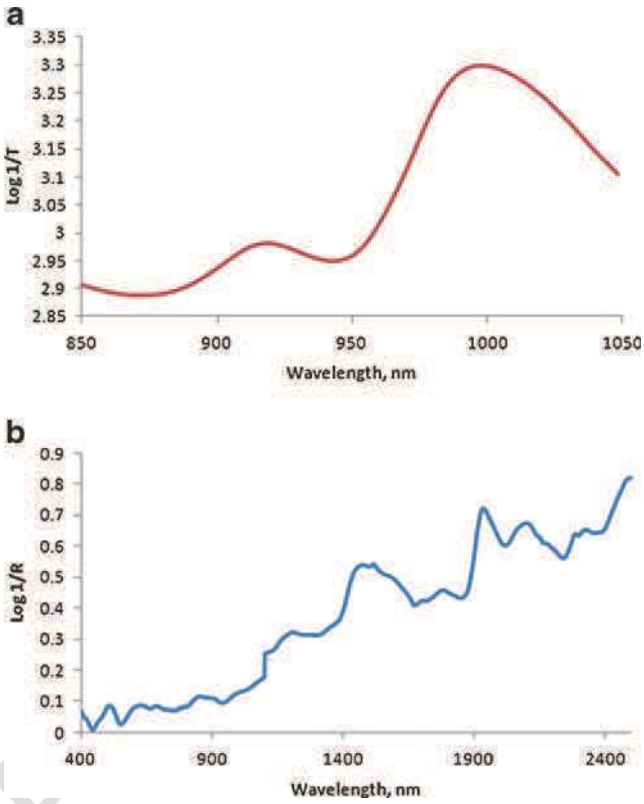


Fig. 1 NIR transmittance (850–1,050 nm) (**a**) and NIR reflectance spectrum of wheat flour (1,100–2,500 nm) (**b**)

Chemometric Methods in NIRS

Due to the above-mentioned complexity of NIR spectrum, NIRS analysis requires extraction of relevant information from many variables which is achieved by application of chemometrics which involve the utilization of mathematics, statistics, and computational techniques to NIR spectral data. When applied to NIRS, chemometric techniques could be roughly divided into techniques used for spectral data preprocessing and multivariate techniques used in calibration model development (Pasquini 2003; Lin and Ying 2009; Agelet and Hurburgh 2010).

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Chemometric Techniques for Spectral Data Pre-processing

Spectral data pre-processing commonly precedes the calibration model development stage in order to reduce the spectral interferences and to emphasize the spectral effects related to the sample composition of functional properties. In general, spectral data pre-processing techniques can be divided into two different categories depending on the goal of correction: (1) *normalization methods* that are used for the correction of the baseline shifts and curvilinearity and for multiplicative interference as a result of scattering and (2) *differention methods* that are used for correction of peak overlapping and signal enhancement from the chemical information and constant or linear baseline drift (Zeaiter et al. 2005; Ozaki et al. 2007; Wang and Paliwal 2007).

Most commonly used spectral normalization methods comprise the standard normal variate (SNV) transformation, robust normal variate (RNV) transformation, de-trend method (D), and multiplicative scatter correction (MSC). Savitzky and Golay (SG) and Fourier transform (FT) algorithms are commonly used for data smoothing and differentiation.

The selection of certain pre-processing is not defined by general rule and is usually guided by experience requiring a trial-error process. The selection of adequate pre-processing technique is dependent on the type of NIR signal (i.e., transmittance, reflectance), sample characteristics, instrument design, and ultimate aim (calibration or discrimination). In general, the application of pre-processing techniques enhance the predictive ability of a future calibration model, except in the case when pre-processing excessively smoothes the signal which may adversely influences the model predicting ability.

Multivariate Techniques Used in Calibration Model Development

In general, multivariate techniques used in calibration model development process could be classified as *qualitative* (1) and *quantitative methods* (2). Qualitative methods could be classified as:

- Exploratory data analysis (principal component analysis (PCA), factor analysis (FA)),
- Unsupervised pattern recognition analysis (cluster analysis),
- Supervised classification analysis (linear discriminant analysis (LDA), quadratic discriminant analysis (QDA), categorical regression, K-nearest neighbours analysis (KNN), artificial neural networks (ANN)) and
- High-dimensional classification analysis (soft independent modeling of class analogy (SIMCA), regularized discriminant analysis (RDA), penalized discriminant analysis (PDA)) (Wang and Paliwal 2007).

Relatively new chemometric techique introduced for classification purposes is extended canonical variates analysis (ECVA), which enables finding multivariate directions that separates groups and simultaneously classifying these, as well as provides separation of several groups along one direction (Nørgaard et al. 2006).

It should be noted that classification techniques could be used for calibration population definition and calibration sample set structuring as previously described by Shenk and Westerhaus (1991a, b). Sample selection on the basis of their spectral characteristics proved to be practical method allowing the elimination of the samples with extreme spectra as well as spectrally similar samples. The statistics commonly used for sample selection comprised the Global Mahalanobis distance (GH) indicating the extent to which the spectra of a sample is different from the average spectra of all samples within the calibration set, and Neighborhood Mahalanobis distance (NH) which indicates the extent to which the spectra of a sample is similar to the spectra of neighboring samples within the calibration set. Widely accepted limit for GH is 3.0, while for NH, it is 0.60 for the spectral interval 1,100–2,500 nm or 0.20 for spectral interval 850–1,050 nm. Hence, the benefits from sample selection are twofold: the sample set is efficiently structured and the substantial savings in wet laboratory analysis are enabled without losing the predictive ability of the NIRS model (Shenk and Westerhaus 1991b; Shenk et al. 2008).

Quantitative multivariate techniques that proved their potential for wide range of NIRS applications are multiple linear regression (MLR), principal component regression (PCR), and partial least squares (PLS), which has appeared to be the most preferred technique. The utilization of listed techniques is based on the assumption that the compound or property of interest and absorbance are linearly related. However, instrumental factors and/or the physico-chemical nature of the sample could cause non-linearity between the spectral data and sample composition or property requiring non-linear calibration methods, where the artificial neural networks (ANN) has the most dominant importance (Blanco and Villarroya 2002; Agelet and Hurburgh 2010). Support vector machine (SVM), as a relatively new chemometrics technique, is also used for non-linear modelling (Wang and Paliwal 2007).

NIRS Instruments

Each NIRS instrument is designed to contain sample compartment, light source, wavelength selection system and detector, where the technology used for wavelength selection determines the classification of the modern NIRS instruments, distinguished as:

- Filter instruments (interference filter instruments and acousto-optic tunable filter instruments (AOTF)),

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– Diode-based instruments,
– Dispersive instruments and
– Interferometric (Fourier Transform) instruments (Pasquini 2003; Wang and Paliwal 2007; Agelet and Hurburgh 2010).

The first phase of the application of the NIRS technique was designated by the usage of simple interference filter instruments with 3 to more than 20 filters, representing the absorptions of the most popular applications, such as protein, moisture, and oil in cereals. Nowadays, in the light of recent research innovations, filter instruments might be considered as obsolete technology, but they are very useful for narrow and very specific purposes, especially for on-line and in-field applications (Osborne 2000; Pasquini 2003; Wang and Paliwal 2007; Agelet and Hurburgh 2010).

AOTF instruments due to their mechanical simplicity with no moving parts, high scan speed over a wide range of NIR spectral region, and wavelength stability could be a justified choice for different on-line applications.

Diode-based instruments, covering the spectral range of 400–1,700 nm, are suitable for specific in-field applications due to its low-cost, portable size, high power efficiency, high sample throughput and long lifetime (Osborne 2000; Pasquini 2003; Wang and Paliwal 2007; Agelet and Hurburgh 2010).

Dispersive instruments, based on diffraction gratings or grating monochromators, are most commonly used NIRS instruments in wheat quality control, used in visible and NIR spectral region. They are typically available as commercial stand-alone bench type instruments suitable for measuring the intensity of transmission of NIR radiation from the spectral range 850–1,050 nm or measuring the intensity of diffuse reflection of NIR radiation from the spectral range 1,000–1,400 nm. For research and development purposes, requiring wider spectral ranges, stand-alone bench type instruments are available for spectral ranges 400–2,500, 400–1,700, 1,100–2,500, and/or 1,000–2,600 nm.

Although dispersive NIR instruments have sufficient throughput for most laboratory applications, lower price and very low noise, over the last 10 years, Fourier-Transform NIR instruments (FT-NIR) have been more and more used in wheat quality control (Manley et al. 2002; Armstrong et al. 2006; Foca et al. 2011). However, FT-NIR instrument for prediction of selected quality parameters of wheat flour was firstly used by Sorvaniemi et al. (1993). FT-NIR instruments offer higher signal-to-noise ratios, high wavelength accuracy, faster spectral acquisition and higher resolutions compared to grating monochromator instruments (Armstrong et al. 2006; Osborne 2006).

The selection of appropriate NIRS instruments primarily depends on the purpose of application—research or commercial applications. Research applications require high versatility in terms of broad spectral range, high spectral resolution, and different sample presentation modes. However, the selection of proper commercial instrument should be guided by type of samples being analyzed, working environment, and the level of expected accuracy (Wang and Paliwal 2007; Agelet and Hurburgh 2010).

Application of NIRS in Wheat Quality Control

Due to its role in human nutrition and its flexibility to be processed in wide range of final products (e.g. bread, pastry, cookies, pasta), wheat has an upmost significance among all cereals. Production of each type of wheat-based final product requires specific end-use quality which represents the combination of physical, chemical, and rheological properties (Pasha et al. 2010). Labor-intensive and time-consuming nature of conventional methods for determination of wheat properties have stimulated the rapid development of the NIRS method in wheat quality control. The NIRS technique for wheat quality control can be applied in two different ways: as an analytical method for accurate and rapid determination of composition as being applied in trade and as a screening method as being applied in wheat breeding and processing (Williams 2007, 2008). In the first stage of commercial application of the NIRS technique during the 1970s, it was predominantly applicable for prediction of protein, moisture, and oil content in cereals while in the second stage during the 1980s was predominantly related to the prediction of more complex constituents such as complex carbohydrates. The third stage of NIRS application in wheat technology is related to the prediction of its end-use properties, while the final stage of NIRS application is related to the prediction of functional and safety quality indicators. Due to the fact that the overall quality of wheat is dependent on its composition, functionality, and safety, all of them have an equal importance in wheat breeding, trade, and processing (Fig. 2) (Williams 2007, 2008).

A number of reports on the potential of NIRS to be used as an analytical tool in wheat quality determination are available in the literature which involves either classification or calibration. In this regard, it should be noted that the ultimate goal of the application of the NIRS technique is not solely the best estimates of the reference values, but a discrimination of the samples according to their spectral properties reflecting their functionality (Christy and Kvalheim 2007; Miralbés 2008). The application of NIRS technique for classification purposes is based on fact that samples with different spectral responses are different in physical and/or chemical properties. Differences in the spectral responses are a consequence of genetics, growing conditions, and seasons. Reported NIRS applications for classification purposes are summarized in Table 1. The first application of the NIRS technique for classification purposes was for identification of wheat varieties suitable for bread baking (Bertrand et al.

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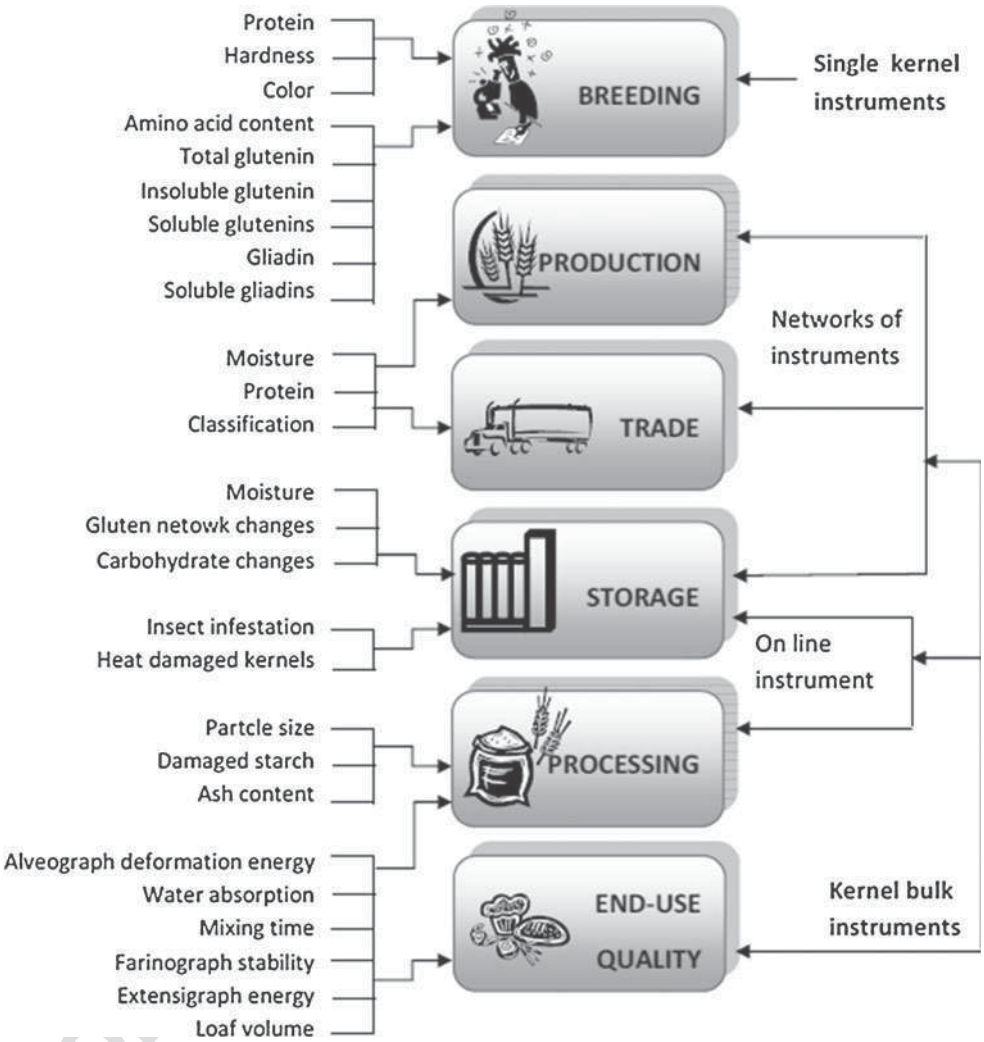


Fig. 2 The relationship between different NIRS applications in wheat quality control

1985). Soon after, several classification applications for wheat were reported. Delwiche and Norris (1993) reported successful classification of ground samples of hard red winter (HRW) and hard red spring (HRS) wheat. Neural network classification of wheat classes was reported by Chen et al. (1995) and Song et al. (1995). Song et al. (1995) used the spectral range 850–1,050 nm in transmittance mode, while Chen et al. (1995) used NIR diffuse reflectance spectra in the spectral range 1,100–2,500 nm. Chen et al. (1995) indicated that the spectral information in the long NIR wavelength region of ground grain was more useful for differentiation of wheat classes than that in the short NIR wavelength region, while Song et al. (1995) proposed spectral range from 899 to 1,049 nm for rapid classification without losing accuracy. Delwiche and Massie (1996) reported successful classification of individual kernels of wheat classes by PLS or MLR models which was based on the color (551–750 nm) and intrinsic properties (1,120–2,476 nm), where its accuracy were dependent on the spectral region and the number of wheat classes included into a model. Dowell (2000) as well as Wang et al. (2002) reported the successful application of NIRS for classification of vitreous and non-vitreous wheat kernels suggesting that the scattering effects, grain hardness, and differences in starch and protein content between vitreous and non-vitreous kernels contributed the more to the classification of vitreous and non-vitreous kernels. Cocchi et al. (2005) and Foca et al. (2009) demonstrated the successful NIRS application for distinction of bread wheats and flours of different baking quality. Miralbés (2008) demonstrated discrimination of European wheat varieties originated from two growing regions—Spain and France. Another application of the NIRS technique for classification purposes was reported by Dowell et al. (2009a) which was related to the selecting and sorting waxy wheat kernels by using an automated single kernel NIR sorting system. It was indicated that wavelengths 985, 1,130, 1,210, 1,310 and 1,432 nm were the most important for the waxiness classification. Delwiche et al. (2011a) also reported the utilization of the NIRS technique to be used for differentiation of the starch waxy genotypes with accuracy 90–100 %. It was suggested that the spectral differentiation of waxy and non-waxy samples was enabled due to the lipid–amylose complex which reduces with waxiness, physical differences

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t1.1 **Table 1** An overview of selected NIRS applications for classification purposes

t1.2 Application	Acquisition mode	Spectral range	Type of sample	Preprocessing	Chemometrics technique	Classification performance	Reference
t1.3 Baking quality	Reflectance	1,100–2,500	Intact grain	n/a	PCA, MDA	87 %	Bertrand et al. (1985)
t1.4 Classification of wheat classes	Reflectance	1,100–2,500	Ground meal	n/a	PCA, DA	75–95 %	Delwiche and Norris (1993)
t1.5 Classification of wheat classes	Reflectance	1,100–2,500	Ground meal	Log 1/R, 2nd der.	ANN	95.1–97.0 %	Chen et al. (1995)
t1.6 Classification of wheat classes	Transmittance	850–1,050	Intact kernels	2nd der.	ANN	97–100 %	Song et al. (1995)
t1.7 t1.8 Classification of wheat classes	Relectance	537–993 1,100–2,500	Intact kernel	Log 1/R	PLS, MLR	65–99 %	Delwiche and Massie (1996)
t1.9 Vitreousness	Reflectance	400–1,700	Intact kernel	Log 1/R	PLS	73–100 %	Dowell (2000)
t1.10 Vitreousness	Reflectance	400–1,700	Intact kernel	Log 1/R	PLS	91.1–100 %	Wang et al. (2002)
t1.11 Baking quality	Reflectance	400–2,500	Flour	Log 1/R, SNV 1st, 2nd der.	SIMCA	0–100 %	Cocchi et al. (2005)
t1.12 Wheat varieties	Reflectance	400–2,500	Intact kernel	WMSC, 2nd der.	PCA, DA, PLS	94–99.5 %	Miralbés (2008)
t1.13 Baking quality	Reflectance	400–2,500	Flour	n/a	SIMCA	89–100 %	Foca et al. (2009)
t1.14 Waxy wheat kernels	Reflectance	900–1,700	Intact kernels	n/a	PLS	71–97.6 %	Dowell et al. (2009a)
t1.15 Starch waxiness	Reflectance	400–2,500	Intact kernels, ground meal	1st, 2nd der.	PCA, LDA	90–100 %	Delwiche et al. (2011a)

PCA Principal component analysis; *MDA* multiple discriminant analysis; *DA* discriminant analysis; *ANN* artificial neural network; *PLS* partial least square; *MLR* multiple linear regression; *SIMCA* soft independent modeling of class analogy; *LDA* linear discriminant analysis; *WMSC* weighted multiplicative scatter correction; *1st der.* first derivative; *2nd der.* second derivative

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in endosperm that affect light scatter, or changes in starch crystallinity. The classification models reported utilizing either PCA or ANN, where ANN models proved to perform better than PCA with Mahalanobis distance classifier. It should be noted that application of the NIRS technique for classification purposes is characterized by high complexity due to the fact that NIR spectral features reflect different aspects of wheat quality, where the contribution of certain relevant constituent and/or property can often be low or hidden. Moreover, NIR spectral classification offers new, challenging options in identifying functional properties in breeding, single seed sorting, process control, and in food formulation and production (Jespersen and Munck 2009).

NIRS in Wheat Breeding

End-use quality of wheat has always been an issue of a great concern for wheat breeders. End-use quality of wheat is determined on the basis of milling yield, kernel texture, empirical rheological parameters, while the parameters obtained by test baking and pasta preparation (loaf volume, product appearance etc.) are considered as the ultimate indicators of end-use quality of wheat (Mastilović et al. 2010). Due to insufficient quantities of sample available in the early stages of breeding process, a reliable and comprehensive evaluation of wheat functionality is disabled. Moreover, this problem is further aggravated by the need to assess the quality of huge number of lines. Therefore, the potential of the NIRS technique as being applied as an assistant tool in breeding programs is firstly recognized among the cereal breeders. Its importance among cereal breeders has been further increased due to its ability to predict real differences in quality among breeding materials and its non-destructive nature (Osborne 2006). However, commercially available NIR instruments designed to be used for measuring wheat bulk samples proved to be inapplicable in cereal breeding programs due to the quantity of the sample required. Starting from this problem, modifications of standard measuring cells as well as development of new micro-cells has been introduced and a single seed sample accessories has been designed to be embedded into conventional bulk NIRS grain analyzer to enable single kernel analysis (Nielsen et al. 2003). Furthermore, NIR single kernel characterization system has been developed enabling its further applications for breeding purposes (Delwiche 1995, 1998; Delwiche and Hruschka 2000; Shadow and Carrasco 2000; Maghirang and Dowell 2003; Bramble et al. 2006; Dowell et al. 2006a; Wesley et al. 2008; Dowell et al. 2009b). Although the data on wheat quality obtained for the individual kernels are not sufficiently significant compared to data obtained for bulk samples, it was demonstrated that the accuracy of single kernel instruments were equivalent to its bulk counterpart. The most common single kernel NIR applications reported so far are related to the prediction of protein content (Delwiche 1995; Delwiche and Hruschka 2000; Pasikatan and Dowell 2004; Bramble et al. 2006), wheat grain hardness

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(Maghirang and Dowell 2003; Delwiche et al. 2006), as well as color classification of wheat of different classes (Dowell 1998; Wang et al. 1999). Moreover, the development of more complex applications such as wheat protein composition, which relate directly to end-use quality, was found to be particularly important for cereal breeding purposes (Wesley et al. 2008). Differences in the functionality of proteins are associated with differences in the amino acid composition, the position of these amino acids in the protein molecules, and the composition of storage proteins (glutenins and gliadins). First attempt to predict the amino acid composition in wheat by NIRS was made by Rubenthaler and Bruinsma (1978) who demonstrated the possibility to determine lysine concentration by modeling the ratio lysine/crude protein for several small wheat populations (R^2=0.72–0.96). Later research of Williams et al. (1984) indicated that second derivative of the log 1/R of ground wheat samples was the most effective in prediction of lysine, threonine, tryptophan, and methionine content to achieve the acceptable accuracy for screening purposes in cereal breeding programs. Almost 20 years later, Fontaine et al. (2002) demonstrated the NIRS application for fast and accurate prediction of methionine (SECV=0.009; R^2=0.91), cystine (SECV=0.012; R^2=0.92), lysine (SECV=0.015; R^2=0.91), threonine (SECV=0.010; R^2=0.97), tryptophan (SECV=0.008; R^2=0.84), arginine (SECV=0.027; R^2=0.90), isoleucine (SECV=0.012; R^2=0.97), leucine (SECV=0.018; R^2=0.98), and valine (SECV=0.019; R^2=0.94) contents in wheat and other cereals.

One of the first attempts to develop NIRS calibration model for prediction of wheat storage protein composition was made by Delwiche et al. (1998). It was possible due to the fact that the main fractions of gluten—glutenin and gliadin, exhibit some differences in their NIR spectra which enable them to be determined in mixtures with starch (Wesley et al. 1999). Total glutenin, insoluble glutenin, and gliadin contents can also be measured in whole wheat kernel by NIR against HPLC as a reference method (Delwiche et al. 1998; Seabourn et al. 1998; Wesley et al. 1999; 2001; Bhandari et al. 2000; Millar 2003; Dowell et al. 2006b). An overview of the NIRS applications for prediction of wheat storage protein composition is given in Table 2. The results of Wesley et al. (1999) indicated that robust calibrations for gliadin and glutenin content can be developed using both curve-fitting and PLS calibration techniques. Millar (2003) reported very comprehensive research on the development of prediction models for high- (HMW) and low-molecular weight (LMW) glutenins and gliadins in whole wheat, ground wheat, and flour samples, comprising the use of discrete wavelengths typical of filter instruments as well as the visible and NIR spectral range. The models developed for the whole wheat samples were characterized by poorer predictive ability in comparison to those developed for the flour and ground wheat samples. Also, the models developed by using a filter instrument approach were of unacceptably poor predictive ability in comparison to those developed for the whole visible and NIR spectral range. Moreover, Millar (2003) also tested the possibility of the development the robust calibration models on the basis of typical methods of two countries, UK and France, indicating improved potential of such models for general use. Liu et al. (2009) indicated that the protein bands around 1,980, 2,040, 2,200, 2,260, and 2,350 nm could be associated with gluten proteins that influence the end-use quality of wheat flour. By summarizing the listed studies concerning the prediction of gliadin and glutenin content, the NIRS method could be designated with sufficient accuracy when applied for screening purposes in breeding programs with small standard error of cross validation and with coefficient of determination higher than 0.80. Also, works of (Dowell et al. 2006b) showed that efficiency of NIRS calibration models for prediction of soluble glutenins and gliadins were dependent on the used NIR spectral range, form of samples (flour, kernel) and wheat variety, being more efficient when the model was developed for hard red winter wheat than for hard red spring wheat (Table 2). Although some authors has recommended the use of instrument with a monochromator in reflectance mode over the range of 2,000 to 2,300 nm (Wesley et al. 2001), it has been proven that use of instruments in transmittance mode with narrower spectral range below 2,000 nm could also be applicable for this application (Dowell et al. 2006b; Scholz et al. 2007).

Besides the functionality determined by the condition of protein–proteinase complex of wheat grain, the functionality of wheat depends on the condition of carbohydrate complex as well. Changes in the functionality of starches are associated with differences in the amylose to amylopectin ratio (Delwiche et al. 1998; Williams 2007). Hence, flour paste viscosity and the quality of pasta and noodle products are highly influenced by the carbohydrate composition of the grain, in particular amylose and amylopectin fractions (Epstein et al. 2002). The NIR spectra of amylose and amylopectin are very similar due to the fact that they consist of the same glucose unit. Therefore, very little progress has been made in estimating the quality of carbohydrate components in wheat (Epstein et al. 2002), whereas several authors have reported on the application of NIR to the measurement of amylose in rice (Villareal et al. 1994; Delwiche et al. 1995; Delwiche et al. 1996; Shimizu et al. 1998; Bao et al. 2001). However, certain progress towards the estimation of condition of carbohydrate complex was made by Wesley and Blakeney (2001) who investigated starch gelatinization in starch–protein–water mixtures by means of dynamic NIRS. Their results indicated that wavelength of 1,160 nm was associated with the bonding of water molecules in the mixture, e.g., with the gelatinization of the starch granules. The changes in the absorbance at 1,160 nm also provided information on the interactions

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t2.1 **Table 2** An overview of the NIRS applications for prediction of wheat storage protein composition

t2.2	Application	Acquisition mode	Spectral range, nm	Type of sample	Chemometrics		Calibration performance			Reference
t2.3					Preprocessing	Modeling	R^2	SECV	SEP	
t2.4	Gliadin content	Reflectance	1,100–2,500	Flour	MSC	PLS	0.93	n/a	n/a	Delwiche et al. (1998)
t2.5		Reflectance	1,100–2,500	Intact grain, flour	n/a	n/a	0.76–0.79	n/a	n/a	Seabourn et al. (1998)
t2.6		Reflectance	400–2,500	Flour	2nd der.	PLS	0.84	n/a	n/a	Wesley et al. (1999)
t2.7		Reflectance	400–2,500	Flour	SNV+D, 2nd der.	MPLS	0.78	0.43	n/a	Wesley et al. (2001)
t2.8		Reflectance	400–2,500	Ground meal, flour	SNV+D, 1st der., 2nd der.	MPLS	0.72–0.83	0.42–1.69	n/a	Millar (2003)
t2.9		Reflectance	400–2,500	Intact grain	SNV+D 1st der., 2nd der.	MPLS	0.42–0.72	0.60–1.88	n/a	Millar (2003)
t2.10	Soluble gliadins content	Transmittance	850–1,050	Intact grain/flour	1st der.	PLS	0.89/0.89	0.64/0.64	n/a	(Dowell et al. 2006b)
t2.11		Reflectance	835–2,502	Intact grain/flour	1st der.	PLS	0.85/0.84	0.76/0.77	n/a	Dowell et al. (2006b)
t2.12		Reflectance	950–1,650	Intact grain/flour	1st der.	PLS	0.88/0.88	0.65/0.67	n/a	Dowell et al. (2006b)
t2.13		Reflectance	400–2,500	Intact grain/flour	1st der.	PLS	0.86/0.86	1.72/0.71	n/a	Dowell et al. (2006b)
t2.14	Glutenin content	Reflectance	1,100–2,500	Flour	MSC	PLS	0.91	n/a	n/a	Delwiche et al. (1998)
t2.15		Reflectance	400–2,500	Flour	2nd der.	PLS	0.70	n/a	n/a	Wesley et al. (1999)
t2.16		Reflectance	400–2,500	Intact grain	MSC, 1st der.	MPLS	0.74	1.07	n/a	Bhandari et al. (2000)
t2.17		Reflectance	400–2,500	Flour	SNV+D, 2nd der.	MPLS	0.83	0.38	n/a	Wesley et al. (2001)
t2.18		Transmittance	850–1,050	Intact grain/flour	1st der.	PLS	0.93/0.93	0.59/0.62	n/a	Dowell et al. (2006b)
t2.19		Reflectance	835–2,502	Intact grain/flour	1st der.	PLS	0.89/0.91	0.76/0.68	n/a	Dowell et al. (2006b)
t2.20		Reflectance	950–1,650	Intact grain/flour	1st der.	PLS	0.81/0.95	1.02/0.53	n/a	Dowell et al. (2006b)
t2.21		Reflectance	400–2,500	Intact grain/flour	1st der.	PLS	0.92/0.96	0.64/0.48	n/a	Dowell et al. (2006b)
t2.22	Soluble glutenins content	Transmittance	850–1,050	Intact grain/flour	1st der.	PLS	0.77/0.78	0.40/0.39	n/a	Dowell et al. (2006b)
t2.23		Reflectance	835–2,502	Intact grain/flour	1st der.	PLS	0.75/0.75	0.42/0.41	n/a	Dowell et al. (2006b)
t2.24		Reflectance	950–1,650	Intact grain/flour	1st der.	PLS	0.61/0.79	0.51/0.38	n/a	Dowell et al. (2006b)
t2.25		Reflectance	400–2,500	Intact grain/flour	1st der.	PLS	0.75–0.78	0.39–0.42	n/a	Dowell et al. (2006b)
t2.26	Insoluble glutenins content	Transmittance	850–1,050	Intact grain/flour	1st der.	PLS	0.85/0.83	0.65/0.68	n/a	Dowell et al. (2006b)
t2.27		Reflectance	835–2,502	Whole grain/ flour	1st der.	PLS	0.85/0.82	0.64/0.71	n/a	Dowell et al. (2006b)
t2.28		Reflectance	950–1,650	Whole grain/ flour	1st der.	PLS	0.84/0.86	0.67/0.63	n/a	Dowell et al. (2006b)
t2.29		Reflectance	400–2,500	Intact grain/flour	1st der.	PLS	0.84/0.86	0.66/0.63	n/a	Dowell et al. (2006b)
t2.30	HMW glutenins	Reflectance	400–2,500	Intact grain	MSC, 1st der.	MPLS	0.88	0.60	n/a	Bhandari et al. (2000)
t2.31		Reflectance	400–2,500	Ground meal, flour	SNV+D, 1st der., 2nd der.	MPLS	0.74–0.79	0.92–1.02	n/a	Millar (2003)
t2.32		Reflectance	400–2,500	Intact grain	SNV+D, 1st der., 2nd der.	MPLS	0.48	1.27	n/a	Millar (2003)

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t2.33 **Table 2** (continued)

Application	Acquisition mode	Spectral range, nm	Type of sample	Chemometrics		Calibration performance			Reference
t2.34				Preprocessing	Modeling	R^2	SECV	SEP	
t2.35 LMW glutenins	Reflectance	400–2,500	Ground meal, flour	SNV+D, 1st der., 2nd der.	MPLS	0.64–0.65	1.17–1.18	n/a	Millar (2003)
t2.36	Reflectance	400–2,500	Intact grain	SNV+D, 1st der., 2nd der.	MPLS	0.23	1.32	n/a	Millar (2003)

PLS partial least square; *MPLS* modified partial least square; *MSC* multiplicative scatter correction; *SNV* standard normal variate; *D* detrend; *1st der.* first derivative; *2nd der.* second derivative; R^2 coefficient of determination (R^2 values≥0.70 shown in bold font); *SECV* standard error of cross validation; *SEP* standard error of prediction; *n/a* data not available

among protein, starch, and water during heating (Wesley and Blakeney 2001).

Crosbie et al. (2007) demonstrated the promising results in developing calibration models for determination of flour swelling volume used in screening wheat breeding lines for starch quality intended for noodle production (R^2=0.56–0.86; SEP=0.77–1.65).

Increasing consumer demand for wide range of safe and nutritious food products has set up new demands for cereal breeders. The concern for enhanced nutritional quality has been brought into focus together with agronomic performance and processing quality of newly breed lines. Hence, the improvement of the content of phytochemicals and other bioactive compounds in cereals is getting more and more important. However, very limited research work has been reported dealing with the application of NIRS technique for assessment of phytochemicals and other bioactive compounds in rice and corn, whereas no results has been reported for wheat either for classification or calibration purposes, assuming that it could be one of the challenges for future NIRS applications (Brenna and Berardo 2004; Zhang et al. 2008; Ward et al. 2008; McGoverin et al. 2010).

NIRS in Wheat Trade

As previously stated, the first stage of commercial application of the NIRS technique was predominantly related to the adding value to cereal crops and associated with the prediction of certain constituent in cereals (protein, moisture, oil, starch, cellulose). One of the oldest and most important applications of NIRS in food and agriculture sector is for the measurement of protein content in grains, especially in wheat (Williams 2007). Measuring protein content in wheat has been a successful application of NIRS due to strong and broad absorption by the N–H bonds in the NIR spectral region despite the substantial differences in the nature of NIRS and traditional chemical methods for protein content determination (Williams 1987). Therefore, works that demonstrate the potential of NIR methods for determination of protein are numerous (Williams 1979; Williams et al. 1985; Williams and Sobering 1993; Cozzolino et al. 2006; Mutlu et al. 2011). The very first official commercial application of NIRS in 1975 is associated with the Canadian Grain Commission and change from wheat protein-marketing system based on the Kjeldahl method to the system based on NIRS method. Although different countries established their own systems for classifying their wheat on the basis of different parameters of end-use quality, wheat grading systems is commonly based on the basis of protein content (Váradi et al. 1999; Hulasare et al. 2003; Williams 2007). Nevertheless, the system of official inspection of certain countries requires identification of wheat classes which is related to the classification applications of NIRS.

Assurance of Confidence in NIRS Results

The application of the NIRS technique has been facing a bad publicity as a "black box" technique over a years, but the development of global ANN NIRS calibrations has significantly improved the reputation of this technique. The global calibrations concept has significantly facilitated the wheat quality control in trade due to the fact that they are capable to analyze from 90 % to 95 % of all samples of a product of interest. Global calibrations are developed to be used for broad range of samples originated from different locations and production years with acceptable accuracy (Shenk et al. 2008). Nevertheless, the acceptance of the NIRS method by the AACC, AOAC, ICC, and ISO confirmed its applicability for routine use (Váradi et al. 1999). Before its adoption as an official analytical method, special attention had to be paid to the regulatory requirements for analytical procedures especially due to the fact that the NIRS technique heavily relies on the use of chemometrics calibration and statistical analysis of data (Mark et al. 2002). For this reason, it is of upmost importance to verify the characteristics of the NIRS method to demonstrate its fitness for intended purpose (Mark et al. 2002; Pojić et al., 2006, 2008, 2009). In order to demonstrate the analytical capability of the NIRS

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technique for its application in grain trade, accuracy and precision (e.g., reproducibility) are the characteristics of upmost importance. The importance of accuracy is so high due to the fact that premiums of 1.30–1.50$ are paid for increments of 0.1 % in protein content per ton. Unlike precision, accuracy can be easily achieved by adjustment of calibration model. Precision of the NIRS method is affected by the instrument and calibration used and the environmental conditions in which the measurements are performed (Büchmann et al. 2001). Apart from those characteristics, transferability of calibrations among different instruments is also very important especially in the case when single organization handles several instruments. The establishment of NIRS networks worldwide facilitate monitoring the performance of a large number of NIRS instruments and determination of the wheat value as well (Büchman 1996; Büchmann et al. 2001).

NIRS Networks

In order to provide independent measurements of required quality which are internationally equivalent, as well as to fully utilize the advantages of NIRS technology and keep the simplicity of the NIRS operation and maintenance, the measurement and technical infrastructures has been set up worldwide comprising the networks of NIRS instruments for measurements of protein content in wheat (Büchman 1996; Büchmann et al. 2001; Büning-Pfaue 2003; Majcen and Taylor 2004; Tseng et al. 2004; Pojić and Mastilović 2005; Pojić et al. 2008). NIRS network comprises from two up to several hundred even thousands of NIRS instruments (slave units) standardized to a central (master) unit. The main goal of a NIRS network is to ensure the transferability of calibrations between instruments and to achieve the same level of accuracy for each individual instrument in the network regardless of operator or location. This is achieved by the standardization procedure that has to be conducted at least once a year in order to achieve the optimal performance of the slave instruments. After standardization, the systematic instrument-to-instrument variation is virtually eliminated, while the random variation between the slave instruments and the master unit is small and not influenced by the standardization (Büchmann and Runfors 1995). The main advantages of the NIRS networks are ensuring reliability and uniformity in grain quality control as well as simplified procedures in calibration monitoring and upgrading. The performance of NIR networks is generally tested in different ring trials commonly organized by the manufacturers of the NIRS instrument included in the network. On the basis of several ring tests, it has been proved that the results of the reference methods agree well with the results of the NIRS method for several constituents within the scope of the network. Moreover, the NIRS method has proved the superior reproducibility over the reference methods (Büning-Pfaue 2003; Möller 2009, 2011).

In order to ensure the smooth network operation, the necessary procedures and tasks have been defined and divided between different organizations. The network structure usually comprises the reference laboratory, which analyzes check samples and monitors the performance of the calibrations used, the Administrative center, which handles database maintenance and communication between instruments and the Calibration Centre, which develops new calibrations and makes recommendations about calibration adjustments. The central network authority—Network board, makes decisions about network organization and calibration changes. The first near infrared transmission network was set up Denmark in 1991 comprising 40 NIRS instruments Infratec 1221 and 1229 Grain Analysers (FOSS Tecator AB) using calibration model developed on the basis of partial least squares regression technique (PLSR). Shortly after, similar PLSR-based networks was established throughout Europe, North America, and Australia comprising more than 3,000 of instruments. Although their existence significantly improved grain quality control, some drawbacks were evident, primarily related to the PLS nature of the calibration models. Namely, different PLS models presented in different networks were developed on the basis of different reference methods at different laboratories which were not a good basis for international crop trade. Moreover, the PLS models were not stable over time, while plots of NIRS predicted vs. reference results tended to be curvilinear. In order to avoid the listed drawbacks, the use of ANN regression technique was proposed in NIRS calibration development by Büchman (1996) and soon after was commercially used in Sweden by the Swedish Agrolab NIT network (Agronet). Since 1997, the spread of use of ANN calibrations in the NIRS networks has been evident worldwide offering improved performance over PLS models. This improved performance is related to the lower values of standard error of predictions, better accuracy (especially at extremely high moisture levels), better transferability between the instruments in the network, and better stability over time in comparison to those obtained with the PLS models. Global ANN calibrations with data from Europe, North America, and Australia were introduced in 1999. Since then, continuous improvements in hardware, software, and calibration models have been apparent (Majcen and Taylor 2004). The best support of the importance of NIRS network could be the research of Casada and O'Brien (2003) who demonstrated the significance of standardization and maintenance procedures employed by FGIS for their NIRS instruments for protein determination. They have shown that variations in the NIRS protein content measurements during storage were subjected more to variation between instruments than to the other variables, suggesting the importance of

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consistency between instruments included in the wheat marketing system.

NIRS in Wheat Processing

An issue of major concern in wheat processing is prompt availability of information on wheat and flour quality in order to enable the process optimization and production of products of consistent quality. These aspirations have been initiated the adoption of the NIRS method in each segment of wheat processing: storage, milling, and baking. Since wheat quality means different things, depending on the place in wheat processing chain, the applications of the NIRS method in wheat processing is characterized by wide diversity.

NIRS in Wheat Storage

The role of NIRS application in wheat storage is twofold. Firstly, its role at the receival point at silos for determination of relevant wheat quality characteristics that will enable reliable segregation of grain according to quality is invaluable. Secondly, its role to detect quality changes in stored grain is also of high importance (Gergely and Salgó 2003, 2005, 2007; Cassells et al. 2007).

NIRS Monitoring of Post-harvest Maturation Gergely and Salgó (2003, 2005, 2007) showed that NIR spectroscopy was effective in monitoring the biochemical processes during post-harvest wheat maturation. Firstly, they analyzed the post-harvest maturation processes in wheat kernel with special respect to changes in moisture content and natural hydration/dehydration processes. The changes in three water absorption bands (1890–1,920, 1,400–1,420, and 1,150–1,165 nm) indicated that the different transitions of water molecules could be sensitively followed in different NIR spectra regions (Gergely and Salgó 2003). Secondly, the amount and variation in content of different carbohydrates during maturation was analyzed. The characteristic changes in three carbohydrate absorption bands (1,585–1,595, 2,270–2,280, and 2,325–2,335 nm) were identified and concluded that the starch accumulation and synthesis/decomposition of water-soluble carbohydrates during post-harvest maturation could be followed by monitoring these three regions of NIR spectra. Thirdly, they also confirmed the potential of NIRS as being applied to monitor the amount and changes of different proteins during post-harvest maturation. It was found that the accumulation of proteins and gluten network formation could be followed by monitoring the two regions of NIR spectra (2,055–2,065 and 2,175–2,180 nm). Cassells et al. (2007) also confirmed the ability of NIRS to indicate the changes occurred during storage, confirming that observed changes in the wheat grain happened solely due to changes in the grain, but not due to the different performance of the NIR instruments.

NIR Monitoring of Stored-grain Hygiene The detection of stored-grain insect infestation is also a good practice in storage technology (Pojić and Janić Hajnal 2011). Among the others available techniques for detection of insects in stored grains, NIRS have proved its usefulness for such application (Neethirajan et al. 2007). One of the first attempts to detect the external and internal insect infestation in wheat by NIRS in reflectance mode was reported by Ridgway and Chambers (1996) who observed large spectral differences between sound kernels and kernels internally infested with grain weevil. The discrimination of the sound and infested kernels was based on second derivative spectra exhibiting the differences in chemical composition and physical structure between the sound and infested kernels. In that case, the recognition of both external and internal infestation was enabled due to the detection of insect protein and/or chitin and moisture (Ridgway and Chambers 1996). Soon after, Ghaedian and Wehling (1997) also discriminated the sound and weevil-larva-infested kernels by means of NIRS and PCA within the spectral range 1,100–2,500 nm. Ridgway and Chambers (1998) highlighted the utilization of NIRS at certain wavelengths for detection of insects infested kernels due to different appearances of sound and infested kernels. It was found that wavelengths of 1,202 and 1,300 nm was useful for differentiation the insect from the wheat kernels. Ridgway et al. (1999) chose near infrared region 700–1,100 nm to detect kernel infestation by grain weevil. They developed two-wavelength classification models, either on the basis of 982 and 1,014 nm or 972 and 1,032 nm, which proved to correctly classify over 96 % of samples. The origins for the spectral differences between sound and infested kernels could have been subjected to decrease in starch content or increase in kernel moisture content which were related with kernel infestation. Further work of Baker et al. (1999) confirmed the NIRS potential in detection of insect infested kernels by developing PLS model for classification of uninfested vs. infested kernels (R^2= 0.90; SECV=0.15). Maghirang et al. (2003) demonstrated the potential of NIRS to be used for classification of sound kernels and kernels that contained live or dead rice weevils in different growth stages with accuracy 63–94 %. By selecting calibration sample set of wheat kernels containing either live or dead insects, the findings of Maghirang et al. (2003) suggested how calibration sample sets can be handled and indicated that immediate sample processing in calibration development is not necessary. One of the latest reports in the field was given by Dowell et al. (2010) who measured insect infestation of wheat kernels using single kernel NIR system (15.7–96.9 % correctly classified kernels) and NIR laser array technology (8.8–95.3 % correctly

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classified kernels). The obtained results indicated that performance of a NIR laser array system to predict insect traits is similar to a commercial NIR system.

Another NIRS application related with the monitoring of kernel quality was reported by Wang et al. (2001) who demonstrated the utilization of the NIRS technique for assessment of heat-damaged wheat kernels. This application was based on the existing of the spectral differences between undamaged and heat-damaged wheat kernels. Developed PLS and two-wavelength models (985/1,050; 1,550/1,575 nm) were of good performance with classification accuracy of 100 % and >97 %, respectively.

NIRS in Wheat Milling

NIRS has been extensively adopted in milling industry to test wheat as starting raw material, and flour as final product (Osborne 2000). Milling properties of wheat are determined on the basis of direct (semolina and flour extraction yields) and indirect quality indicators (virtuousness and grain hardness). The starting point for the development of NIRS application for prediction of milling quality of wheat was based on the fact that milling properties are affected by the physico-mechanical properties of wheat endosperm. Also, the fact that the procedure for assessment of milling properties is time-consuming, expensive, and not standardized additionally contributed to the development of indirect methodology for prediction of milling properties of wheat (Blažek et al. 2005).

Indirect Milling Properties The applicability of the NIRS technique for determination of wheat hardness is related to its potential to distinguish between the strength of adhesion between starch granules and protein matrix being different for hard and soft wheat. Consequently, hard wheat is characterized by higher absorbance values in comparison to soft wheat (Maghirang and Dowell 2003; Greffeuille et al. 2006). Also, soft and hard wheat exhibit different milling behavior so that the ground material of hard wheat is characterized by larger particle size in comparison to that of soft wheat which causes the spectral baseline shift, used for measuring hardness by NIRS, being larger for hard wheat (Kawano 2002). The numerous studies dealing with the measurements of kernel hardness by NIRS technique are available in the literature, proving that hardness can be measured in both meal and whole grain, either in reflectance (800–2,500 nm) or in transmittance mode (800–1,050 nm) (Osborne 2006, 2007). One of the first attempts to determine wheat hardness by NIRS is attributed to Williams (1979), who suggested separate NIRS model development for hard and soft wheat in order to achieve the best accuracy. Also, the better accuracy of the model developed for hard wheat was demonstrated, due to the stronger interference of starch with protein for soft wheat. Performance of the NIRS technique in the transmittance mode as being applied for prediction of grain hardness was demonstrated by Williams (1991) (R^2=0.90–0.92; SEP=3.37–3.47). Soon after, moisture and protein content and growing season were identified as factors affecting the measurement of the NIR hardness index (Brown et al. 1993; Windham et al. 1993). Consequently, an algorithm for correction of the NIR hardness index due to the differences in moisture content was proposed, providing measurements of NIRS hardness independent of moisture content (Windham et al. 1993). Maghirang and Dowell (2003) indicated better performance of PLS calibration model developed for visible and NIR spectral range (R^2=0.91; SECV=7.57) over the model developed for NIR spectra alone (R^2=0.88; SECV=8.67), where the wavelengths associated with protein, starch, and color (650 to 700 nm, 1,100, 1,200, 1,380, 1,450 and 1,670 nm) contributed the most to the hardness prediction of whole wheat kernel. Simultaneously, the attempts for single-kernel calibration model development for hardness index were made, which resulted in models of unsatisfactory accuracy (R^2= 0.40–0.49; SECV=20.94–22.68) (Maghirang and Dowell 2003). Fact that no international standard reference method for wheat hardness was not recognized, the NIRS method for measurement of Hardness Index was adopted by the AACC (Osborne 2007; AACC 2000). Determination of wheat hardness according to AACC method 39-70A is based on the measuring reflectance at 1,680 and 2,230 nm of the ground wheat. At the wavelength of 1,680 nm, the absorbance (log 1/R) is not affected by major constituents present in the sample, but only by particle size. In this regard, the wavelength of 1,680 nm has been called the reference wavelength for baseline correction in quantitative NIRS analysis (Kawano 2002). Compared with other methods for kernel hardness determination which are predominantly two-dimensional, NIRS hardness measurement is considered as a three-dimensional measurement that recognizes size and shape, which therefore make a more comprehensive principle for measuring wheat hardness index (Williams 2008). Manley et al. (2002) for the first time demonstrated the utilization of the Fourier transform NIRS technique for determination of kernel hardness in whole wheat flour (R^2=0.42; SEP=2.13). Armstrong et al. (2006) confirmed that the FT-NIRS technique could be used for measuring hardness in whole grain with acceptable calibration performance (R^2=0.83; SECV=11.46).

Direct Milling Properties The possibility of the NIRS technique to be used for monitoring of milling process in terms of gap control of first-break rolls was initially demonstrated by Pasikatan et al. (2001). This application was enabled due to spectral variations caused by differences in particle size. PLS models developed against cumulative mass of size

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fraction as the reference value was characterized by successful predictive ability for prediction of size fraction of first-break ground wheat with particles ≤400 μm. Promising standard errors of performance and coefficients of determination initiated extended research on the utilization the NIRS technique as a granulation sensor. Therefore, the first attempt to develop granulation models for hard red winter (HRW) resulted in models for four different size ranges >1,041 μm (R^2=0.93; SECV=3.25; SEP=3.25), >375 μm (R^2=0.88; SECV=1.26; SEP=1.28), >240 μm (R^2=0.84; SECV=0.59; SEP=0.42), and >136 μm (R^2=0.73; SECV=0.36; SEP=0.68), being of improved performance compared to initial models. Second attempt to develop granulation models for soft red winter wheat (SRW) resulted in models of lower predictive ability for finest size fraction (>1,041 μm (R^2=0.95; SECV=2.48; SEP=3.53); >375 μm (R^2=0.95; SECV=1.30; SEP=1.83); 240 μm (R^2=0.90; SECV=0.86; SEP=1.38) and >136 μm (R^2=0.58; SECV=0.42; SEP=1.30) in comparison to those developed for HRW. The better performance of granulation models for HRW wheat for finest size fraction in comparison to those for SRW wheat was achieved due to narrower particle size distribution and better sieving properties (Pasikatan et al. 2002; Pasikatan et al. 2003).

The first contribution to the investigation of applicability of the NIRS method for prediction of direct milling properties of wheat was made by Blažek et al. (2005). NIRS coupled with MPLS/PLS and ANN chemometric technique was used for development of models for direct milling properties prediction (semolina extraction rate, flour extraction rate, semolina extractability and Mohse yield). However, the statistical indicators of models' predictive ability were dependent on the chemometrics technique applied, poor (R^2 <0.60) and inconclusive, except for the semolina extractability modeled by ANN (R^2=0.98, SECV=0.81).

Flour Quality The degree of mechanically damaged starch incurred during flour milling is an important indicator of flour quality. Osborne and Douglas (1981) firstly demonstrated the possibility of use of NIRS to predict the degree of starch damage in flour. The calibration obtained using log (1/*R*) data at 1,442, 1,580, 2,060, and 2,258 nm, associated with overtones and combinations of vibration frequencies of free and hydrogen-bonded O–H bonds in starch, resulted in acceptable model predicting ability (R^2=0.90; SEP=4.2). Later work of Finney et al. (1988) confirmed the applicability of the NIRS technique with discrete wavelengths to be used for estimation of damaged starch (R^2=0.93). Morgan and Williams (1995) broaden the research on the NIRS starch damage to the whole NIR spectral region (1,100–2,500 nm) indicating the superiority of NIRS over traditional wet-chemistry methods (R^2=0.92; SEP=3.00). Miralbés (2004) demonstrated the potential of NIRS in the transmittance mode throughout the spectral region 850–1,050 nm to be used for prediction of starch damage in monitoring the milling process (R^2=0.92; SECV=1.25; SEP=1.63).

Determination of ash content by NIRS is particularly useful for process control in the wheat milling industry to monitor the consistency of milling and the compliance with flour specifications and legal regulations. On the other hand, ash content determines the purity of the flour and is commonly used for the control of the milling process (Miralbés 2004). Although inorganic substances do not absorb energy in the NIR spectral region, some authors demonstrated that the NIRS method can be used for reliable prediction of the ash content in different food matrixes (Clark et al. 1987; Deaville and Flinn 2000; Armstrong et al. 2006; Dowell et al. 2006b; Mentink et al. 2006; Osborne 2007; Pojić et al. 2010). Since ash content cannot be directly measured by NIRS, it is assumed that it is predicted by correlation with the total amount of organic compounds and water present, because of the large number of wavelengths used in the process of calibration development that give significant information (Garnsworthy et al. 2000; Osborne 2007; Frankhuizen 2008; AACC 2000). Another assumption which explains why the NIRS determination of flour ash is possible is high correlation between flour ash and fiber contents. Hence, the NIRS models for ash prediction could be associated with bran cellulose present in the flour, rather than with the mineral content themselves (Williams, et al. 1981). The successful NIRS application for determination of flour ash content was reported by Miralbés (2004) (R^2= 0.98; SECV=0.021; SEP=0.024) and Armstrong et al. (2006) (R^2=0.97; SECV=0.03). Eventually, the NIRS method for flour ash determination has been included among the approved methods of the American Association of Cereal Chemists (AACC 2000). Nonetheless, the developed calibration models was characterized by better precision in comparison to the standard method for ash determination due to the numerous sources of uncertainties associated with the reference method for ash measurement (Miralbés 2003; Pojić 2010).

The end-use quality of flour is dependent on the amount and the quality of the gluten proteins and on the interactions between the biochemical constituents present in flour. The development of the calibration models for the parameters of the end-use quality of wheat/flour is based on the correlation between each of these quality parameters and protein content which is easily modelled by NIR (Delwiche et al. 1998). However, this statement could be ambiguous due to NIR sensitivity to both protein content and quality (Wesley et al. 2001). The reported applications of NIRS for determination of end-use quality of wheat/flour are summarized in Table 3. First attempt in the research of potential of NIR spectroscopy to determine the end-use properties of wheat was made by

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Rubenthaler and Pomeranz (1987) which resulted in prediction models for water absorption, mixing time and loaf volume, where the model for prediction of water absorption was characterized by the highest correlation with the log 1/*R* spectral data (Rubenthaler and Pomeranz 1987). The following work presented by Williams et al. (1988) was more comprehensive in terms of diversity of NIRS modeled rheological parameters. It showed the potential of NIRS to predict Farinograph stability, Extensograph energy, and Alveograph deformation energy with acceptable accuracy (Table 3). Further research reported by Pawlinsky and Williams (1998), Hrušková et al. (2001), Hrušková and Šmejda (2003), Miralbés (2003,2004), (Dowell et al. 2006a, b), Vázquez et al. (2007), Jirsa et al. (2008) were carried out by using analyzers of higher generation—scanning monochromators (Table 3). The reported results were inconclusive due to the fact that developed models for prediction of different rheological properties were of variable efficiency. The efficiency of prediction of functional properties of wheat were affected by the form of the samples used (whole grain, ground grain, or flour) as well as by the by the composition of the sample sets which were insufficiently variable with respect to producing year due to the fact that seasonal conditions influence the degree to which protein content is related to functional properties of wheat (Pawlinsky and Williams 1998). Moreover, the calibration accuracy for prediction of rheological properties is limited by the inherent variability of the reference rheological methods. The latest reports on the possibility of NIRS method to be used for prediction of certain rheological parameters were given by Mutlu et al. (2011) and Arazuri et al. (2012) (Table 3). Although different in the form of samples used for scanning (flour and whole grain), chemometrics technique used for modelling (ANN and PLS) and spectral range (400–2,500 and 570–1,850 nm), these works confirmed the potential of NIRS to be used for prediction of functional properties.

NIRS in at- and on-line Process Monitoring Rationalization and optimization of production, and obtaining products of high and consistent quality require the application of contemporary methods for production monitoring, where at-line or on-line NIRS instrumentation are irreplaceable. At-line NIRS analyzers are commonly placed within the production area, and require available personnel to operate the device. In contrast, on-line analyses are embedded within the production process where measurements, sample handling, and sample preparation are automatically controlled not requiring available operator (Pram Nielsen et al. 2001; Ghosh and Rodgers 2008). NIR on-line samplers were firstly developed to predict the protein content of flour, but nowadays the diversity of on-line NIRS application has considerably advanced due to the development of new on-line probe accessories and introduction of new chemometric procedures (Osborne 2007; Siesler 2008).

In wheat processing, whole grain on-line NIR analysis enable analysis of grain as it is conveyed in a transport system by illuminating the sample in a flow by NIR radiation, which interacts with the sample, resulting in measuring the reflected or transmitted radiation. Hence, the continuous monitoring the composition of wheat blends and monitoring of tempering process is enabled within 3–15 s at the rate of 20 t/h. In the milling plants, on-line NIR analysis could be applied for monitoring the quality of incoming wheat and for on-line prediction of flour moisture, protein, and ash contents of flour mill streams and final flour. Moreover, on-line NIRS analysis could be employed in the process of flour standardization to monitor flour blending, flour fortification, and/or flour improvement before delivery (Gradenecker 2003; Osborne 2007; Williams 2007).

When developing models for on-line applications, special attention should be paid for calibration sample selection. They must cover the whole range of constituents of interest and also must include a comprehensive variability of other components present in the sample matrix, including physical variables (e.g., particle size). On-line purposes commonly require the simpler calibration model developed by means MLR on the basis of a few selected wavelengths, PLS, and/or PCA on the basis of spectral regions. Generally, a more complicated calibration models may provide higher accuracy for the current sample set, but their long-term reliability or tolerance to variability is questionable. Also, in NIRS on-line applications, the possible strategy is to develop the initial calibration model useful in finding not included variability (Lee 2007).

NIRS in Wheat Safety Monitoring

In the last decade, the increased attention in cereal marketing has being paid to cereal safety in terms of the presence of toxic substances such as residues of pesticides, fumigants, herbicides, heavy metals, and mycotoxins. However, residues of pesticides, fumigants, herbicides, and heavy metals cannot be estimated by NIRS with sufficient accuracy and precision for industrial use. Nonetheless, calibrations for the prediction of deoxynivalenol (DON) have been reported besides the claims that DON does not possess spectral bands in the NIR spectral region (Dowell et al. 1999). However, developed DON models were not capable of detecting mycotoxins contamination at accepted levels for human food (<2.0 ppm) due to too high SEP values. In contrast, higher acceptance limits for feed in terms of the mycotoxins content (≤5 ppm), enabled more reliable application of the NIRS technique within the feed industry (Williams 2007).

The presence of mycotoxins is always associated with fungal infestation either with field *Fusarium* species or storage fungi, such as *Aspergillus* and *Penicillium* species.

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t3.1 **Table 3** An overview of NIRS applications for prediction of selected rheological properties of wheat and flour

t3.2 Application	Acquisition mode	Spectral range, nm	Type of sample	Chemometrics		Calibration performance			Reference
t3.3				Pre-processing	Modeling	R^2	SECV	SEP	
t3.4 Farinograph absorption	Reflectance	1,100–2,400	Flour	Log 1/R	MLR	0.81	n/a	n/a	Rubenthaler and Pomeranz (1987)
t3.5	Reflectance	1,100–2,500	Flour	Log 1/R, 1st, 2nd der.	n/a	n/a	n/a	0.65	Williams et al. (1988)
t3.6	Reflectance	400–2,500	Intact grain	Log 1/R	PLS	0.85–0.91	n/a	1.42–1.74	Pawlinsky and Williams (1998)
t3.7	Reflectance	400–2,500	Flour	SNV, 1st der.	PLS	0.52	2.5	3.4	Hrušková et al. (2001)
t3.8	Transmittance	850–1,050	Flour	SNV+D, 1st der.	MPLS	0.98	0.35	0.46	Miralbés (2004)
t3.9	Transmittance	850–1,050	Intact grain/ flour	1st der.	PLS	0.65/0.69	1.35/1.26	n/a	Dowell et al. (2006b)
t3.10	Reflectance	835–2,502	Intact grain/ flour	1st der.	PLS	0.65/0.63	1.35/1.40	n/a	Dowell et al. (2006b)
t3.11	Reflectance	950–1,650	Intact grain/ flour	1st der.	PLS	0.66/0.67	1.32/1.32	n/a	Dowell et al. (2006b)
t3.12	Reflectance	400–2,500	Intact grain, Flour	1st der.	PLS	0.76/0.63	1.12/1.37	n/a	Dowell et al. (2006b)
t3.13	Reflectance	400–2,500	Flour	n/a	ANN	0.83	n/a	n/a	Mutlu et al. (2011)
t3.14 Farinograph stability	Reflectance	1,100–2,500	Flour	Log 1/R, 1st, 2nd der.	n/a	n/a	n/a	3.3	Williams et al. (1988)
t3.15	Reflectance	400–2,500	Intact grain	Log 1/R	PLS	0.46–0.80	n/a	1.9–3.87	Pawlinsky and Williams (1998)
t3.16	Reflectance	400–2,500	Flour	SNV, 1st der.	PLS	0.31	3.4	4.7	Hrušková et al. (2001)
t3.17	Transmittance	850–1,050	Intact grain/ flour	1st der.	PLS	0.30/0.06	3.50/3.99	n/a	Dowell et al. (2006b)
t3.18	Reflectance	835–2,502	Intact grain/ flour	1st der.	PLS	0.16/0.13	3.76/4.15	n/a	Dowell et al. (2006b)
t3.19	Reflectance	950–1,650	Intact grain/ flour	1st der.	PLS	0.15/0.15	3.92/3.90	n/a	Dowell et al. (2006b)
t3.20	Reflectance	400–2,500	Intact grain/ flour	1st der.	PLS	0.06/0.06	4.03/3.97	n/a	Dowell et al. (2006b)
t3.21 Extensograph extensibility	Reflectance	Flour	400–2,500	SNV, 1st der.	PLS	0.26	21	27.1	Hrušková et al. (2001)
t3.22 Extensigraph area	Reflectance	Flour	1,100–2,500	Log 1/R, 1st, 2nd der.	n/a	n/a	n/a	29	Williams et al. (1988)
t3.23	Reflectance	Flour	400–2,500	SNV, 1st der.	PLS	0.49	28.3	45.6	Hrušková et al. (2001)
t3.24 Extensigraph resistance	Reflectance	Intact grain	400–2,500	Log 1/R	PLS	0.41–0.76	n/a	25.4–123	Pawlinsky and Williams (1998)
t3.25	Reflectance	Flour	400–2,500	SNV, 1st der.	PLS	0.46	79.1	102.8	Hrušková et al. (2001)
t3.26 Alveograph deformation energy (W)	Reflectance	Flour	1,100–2,500	Log 1/R, 1st, 2nd der.	n/a	n/a	n/a	17	Williams et al. (1988)
t3.27	Reflectance	Flour	400–2,500	SNV, 1st der.	PLS	0.10	31.61	33	Hrušková and Šmejda (2003)
t3.28	Transmittance	Intact grain	850–1,050	SNV+D, 1st der.	MPLS	0.81–0.93	4.7–18.73	6.10–24	Miralbés (2003)
t3.29	Transmittance	Flour	850–1,050	SNV+D	MPLS	0.92	16.5	21.5	Miralbés (2004)
t3.30	Transmittance	Intact grain/ flour	850–1,050	1st der.	PLS	0.69/0.70	43.63/45.63	n/a	Dowell et al. (2006b)
t3.31	Reflectance	Intact grain/ flour	835–2,502	1st der.	PLS	0.66/0.70	48.60/45.69	n/a	Dowell et al. (2006b)
t3.32	Reflectance	Intact grain/ flour	950–1,650	1st der.	PLS	0.69/0.70	46.02/45.54	n/a	Dowell et al. (2006b)
t3.33	Reflectance	Intact grain/ flour	400–2,500	1st der.	PLS	0.70/0.75	45.72/41.68	n/a	Dowell et al. (2006b)
t3.34	Reflectance	Intact grain, ground meal, flour	400–2,500	SNV+D, 1st, 2nd, 3rd der.	MPLS	0.40–0.51	n/a	58.2–64.7	Vázquez et al. (2007)
t3.35	Reflectance	Flour	400–2,500	SNV, 1st der.	PLS	0.58–0.65	29.7–34.4	21.0–24.5	Jirsa et al. (2008)
t3.36	Reflectance	Flour	400–2,500	SNV, 1st der.	MPLS	0.67–0.83	27.9–33.8	32.0–44.5	Jirsa et al. (2008)
t3.37	Reflectance	Intact grain	570–1,850	log 1/R, 1st, 2nd der.	PLS	0.79–0.86	11.53–15.55	13.07–16.1	Arazuri et al. (2012)
	Reflectance	400–2,500	Flour	SNV, 1st der.	PLS	0.24	20.23	21.72	Hrušková and Šmejda (2003)

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t3.40 **Table 3** (continued)

t3.41 Application	Acquisition mode	Spectral range, nm	Type of sample	Chemometrics		Calibration performance			Reference
				Pre-processing	Modeling	R^2	SECV	SEP	
t3.38 Alveograph resistance to extension (P)	Transmittance	850–1,050	Intact grain	SNV+D, 1st der.	MPLS	0.79–0.85	3.7–5.43	4.8–6.7	Miralbés (2003)
t3.40	Transmittance	850–1,050	Flour	SNV+D	MPLS	0.86	4.67	6.07	Miralbés (2004)
t3.41	Transmittance	850–1,050	Intact grain, Flour	1st der.	PLS	0.11–0.20	13.81–14.54	n/a	Dowell et al. (2006b)
t3.42	Reflectance	835–2,502	Intact grain/ flour	1st der.	PLS	0.05/0.04	15.20/15.06	n/a	Dowell et al. (2006b)
t3.43	Reflectance	950–1,650	Intact grain/ flour	1st der.	PLS	0.23/0.07	13.74/14.66	n/a	Dowell et al. (2006b)
t3.44	Reflectance	400–2,500	Intact grain/ flour	1st der.	PLS	0.26/0.24	13.34/13.72	n/a	Dowell et al. (2006b)
t3.45	Reflectance	400–2,500	Intact grain, ground meal, flour	SNV+D, 1st, 2nd, 3rd der.	MPLS	0.30–0.50	n/a	18.3–23.7	Vázquez et al. (2007)
t3.46	Reflectance	400–2,500	Flour	SNV, 1st der.	PLS	0.82–0.87	16.2–19.7	21.0	Jirsa et al. (2008)
t3.47	Reflectance	400–2,500	Flour	SNV, 1st der.	MPLS	0.85–0.93	14.0–18.9	22.6–28.4	Jirsa et al. (2008)
t3.48	Reflectance	400–2,500	Flour	n/a	ANN	0.95	n/a	n/a	Mutlu et al. (2011)
t3.49	Reflectance	570–1,850	Intact grain	log 1/R, 1st, 2nd der.	PLS	0.49–0.77	3.98–6.18	4.87–6.74	Arazuri et al. (2012)
t3.50 Alveograph extensibility (L)	Reflectance	400–2,500	Flour	SNV, 1st der.	PLS	0.10	12.06	12.92	Hrušková and Šmejda (2003)
t3.51	Transmittance	850–1,050	Intact grain/ flour	1st der.	PLS	0.69/0.71	17.44/16.83	n/a	Dowell et al. (2006b)
t3.52	Reflectance	835–2,502	Intact grain/ flour	1st der.	PLS	0.65/0.72	18.47/16.55	n/a	Dowell et al. (2006b)
t3.53	Reflectance	950–1,650	Intact grain/ flour	1st der.	PLS	0.70/0.71	17.33/16.50	n/a	Dowell et al. (2006b)
t3.54	Reflectance	400–2,500	Intact grain/ flour	1st der.	PLS	0.69/0.71	17.45/16.91	n/a	Dowell et al. (2006b)
t3.55	Reflectance	400–2,500	Flour	n/a	ANN	0.36	n/a	n/a	Mutlu et al. (2011)
t3.56	Reflectance	570–1,850	Intact grain	log 1/R, 1st, 2nd der.	PLS	0.81–0.92	5.89–17.94	8.05–12.81	Arazuri et al. (2012)

PLS partial least square; *MPLS* modified partial least square; *MSC* multiplicative scatter correction; *SNV* standard normal variate; *D* Detrend; *1st der.* first derivative; *2nd der.* second derivative; R^2 coefficient of determination (R^2 values≥0.70 shown in bold font); *SECV* standard error of cross validation; *SEP* standard error of prediction; *n/a* data not available

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Since the present concentrations of the mycotoxins, expressed in parts per million, cannot be directly detected, the use of the NIRS technique for approximate predictions of mycotoxins has been based on the identification of fungi-damaged kernels. In this regard, the detection of mycotoxins by NIRS is enabled due to chemical and optical properties occurred as a result of fungal contamination, so the capability of the NIRS to predict mycotoxin content is attributed to the identification of small changes in the texture of infected kernel and the way of reflectance and/or transmittance of the radiant energy by the infected kernels (Pettersson and Åberg 2003; Williams 2004). Consequently, the reported wavelengths from visible spectral region associated with detection of fungal and mycotoxin contamination are due to color changes of infected cereal grains (Fernández-Ibañez et al. 2009). The overview of wavelengths associated with detection of mycotoxin in cereals, predominantly in wheat, is given in Table 4. First attempt to enable NIRS measurements for the estimation of DON and ergosterol in single kernels of highly infected wheat was made by Dowell et al. (1999). It was demonstrated that spectral interval of 500–1,700 nm could be utilized for single-kernel spectral analysis, where wavelengths associated with O–H (750, 950, 1,400 nm), C–H (1,200, 1,400, and 1,650 nm), and N–H (1,050 and 1,500 nm) overtones contributed the more to the classification model. Pettersson and Åberg (2003) demonstrated the possibility to develop a PLS regression model for prediction of DON in wheat kernels by NIRS in transmittance mode (670–1,100 nm) just above the maximal limits for wheat flour proposed by EU (R^2=0.984; SECV=381 μg/kg) (Pettersson and Åberg 2003). Williams (2004) demonstrated the utilization of NIRS technique both in transmittance (700–1,098 nm) and reflectance (400–2,500 nm) mode as being applied for prediction of *Fusarium*-damaged kernels and DON contamination. By observing the NIR spectra of whole wheat samples with high DON contamination and free of DON, a strong band around 778 nm was found. However, the obtained results for both Fusarium-damaged kernels (R^2=0.62–0.69;

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t4.1 **Table 4** Summary of wavelengths associated with detection of mycotoxin and fungal contamination in cereals

t4.2 Application	Spectral range	Wavelength, nm	Type of cereal	Reference
t4.3 FDK/DON	400–1,700	750, 950, 1,050, 1,200, 1,400, 1,500, 1,650	Wheat	Dowell et al. (1999)
t4.4 FDK	940–1,700	1,182, 1,242	Wheat	Delwiche (2003)
t4.5 DON	700–1,098	778	Wheat	Williams (2004)
t4.6 FDK	1,000–1,700	1,200	Wheat	Delwiche and Hareland (2004)
t4.7 DON	Interference filters	675, 1,480	Wheat	Delwiche (2005)
t4.8 FDK	940–1,700	500, 550, 750, 1,152, 1,248, 1,476	Wheat	Delwiche and Gaines (2005)
t4.9 FDK	350–2,500	1,204, 1,365, 1,700	Wheat	Peiris et al. (2009)
t4.10 DON	350–2,500	1,408, 1,904, 1,919	Wheat	Peiris et al. (2009)
t4.11 FDK	950–1,650	1,160–1,220 and 1,395–1,440	Wheat	Peiris et al. (2010)
t4.12 FB1	600–1,050	650, 710, 935, 990	Corn	Dowell et al. (2002)
t4.13 FB1	550–1,700	590, 995, 1,200, 1,410	Corn	Dowell et al. (2002)
t4.14 Total fungal infection	400–2,500	1,430, 1,470, 1,820, 2,140, 2,180	Corn	Berardo et al. (2005)
t4.15 FB1	400–2,500	1,190, 1,954–2,378	Corn	Berardo et al. (2005)
t4.16 AFB1	400–2,500	480–600, 870–1,200	Corn, barley	Fernández-Ibañez et al. (2009)

FDK Fusarium damaged kernels; *DON* deoxynivalenol; *FB1* fumonisin B1; *AFB1* aflatoxin B1

SEP=1.11–1.27 %) and DON (R^2=0.64–0.72; SEP=1.14–1.36 ppm) were not sufficiently accurate for official food quality control, in contrast to their application in feed industry (Williams 2004). Delwiche (2003) by means of NIRS diode array spectrometer (940 to 1,700 nm) demonstrated that two-wavelength model (1,182 and 1,242 nm) could be accurately applied for classification of *Fusarium*- and other mold-damaged kernels, provided it is applied for precisely aligned kernels using a combination of kernel mass. These findings highlighted that utilization of the NIRS technique for classification of *Fusarium*-damaged kernels does not require the spectral data from a broad wavelength region (1,000–1,700 nm). Further research of Delwiche and Hareland (2004) additionally demonstrated the potential of NIRS to be used for classification of *Fusarium*-damaged kernels revealing that wavelength around 1,200 nm was very effective for discrimination of sound and *Fusarium*-damaged kernels. Also, it was indicated that most effective classification was achieved when single kernel NIR reflectance is combined with kernel mass. The promising results of previous studied initiated the design of NIRS-based optical sorting devices for reduction of *Fusarium*-damaged kernels and deoxynivalenol (Delwiche 2005; Delwiche and Gaines 2005). First attempt revealed NIR wavelength regions important for design of monochromatic and bichromatic high-speed sorters for reduction of *Fusarium*-damaged kernels. In this regard, the best two-wavelength models was of 500 and 550 nm for the visible region alone (94 % accuracy), 1,152 and 1,248 nm for the NIR region alone (97 %), and 750 and 1,476 nm for the hybrid region (86 %) (Delwiche and Gaines 2005). Second attempt revealed the efficiency of two-wavelength model (675 and 1,480 nm) for the reduction of DON concentration of *Fusarium*-infected soft red winter wheat. It was found that one-pass sorting decrease the DON concentration to 51 % of the original concentration, while successive passes additionally decrease the original concentration of DON (Delwiche 2005). Due to the existence of certain relation between mycotoxin and ergosterol (fungal-specific lipid) concentrations, reports dealing with determination of ergosterol by NIRS are also important (Lindell 2011). Although performed for barley samples, study of Börjesson et al. (2007) proved that prediction of ergosterol could be performed either in reflectance or transmittance mode. Despite using different wavelength regions 850–1,050 and 400–2,500 nm, the quite similar results were obtained.

The utilization of the FT-NIR technique for the determination of DON in durum and common wheat at levels far below the DON maximum permitted EU limits for unprocessed wheat was reported by De Girolamo et al. (2009) (R^2=0.71–0.83; RMSECV=470–555 μg/kg; RMSEP=306–379 μg/kg). The discrimination between high and low DON contaminated samples was carried out by qualitative models developed on the basis of discriminant analysis for and by semi-quantitative models developed on the basis of PLS regression models.

The work of Peiris et al. (2009) contributed to the progress in application of the NIRS technique for prediction of DON and *Fusarium*-damaged kernels. The potential of NIRS for prediction of *Fusarium*-damaged kernels on the basis of DON levels was demonstrated. For this purpose, the examination of NIR spectra of DON and NIR spectra of single kernels with and without of DON was performed. DON absorption bands were found at 1,408, 1,904 and 1,919 nm. Moreover, the differences in spectral responses between *Fusarium*-damaged and sound kernels were noticeable at 1,204, 1,365, and 1,700 nm and could be associated with the differences in main structural kernel compounds (protein, starch, lipids). Shifts in absorption peaks between *Fusarium*-damaged and sound kernels noticeable in spectral intervals 1,425–1,440 and 1,915–1,930 nm might have been

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attributed to DON. Further research of Peiris et al. (2010) demonstrated the potential of automated single kernel NIRS method for identification of *Fusarium*-damaged kernels and prediction of DON. The achieved classification accuracy of sound and *Fusarium*-damaged kernels was 98.9–99.9 %, while DON calibration performance was characterized by R^2=0.87 and SEP=60.8 ppm. The spectral differences between NIR spectra of *Fusarium*-damaged and sound kernels were indicated, with distinct differences in spectral regions 1,160–1,220 nm and 1,395–1,440 nm, associated with carbohydrates, lipids, proteins, and DON levels. These findings were in accordance with the previous research of Peiris et al. (2009) which showed an NIR absorption peak of DON at ≈1,410 nm. Further studies should be undertaken aiming at lower DON detection limits and lower SEP values.

Although beyond the scope of this review, it should be noted that recent research conducted by means of NIR hyperspectral imaging indicated that the capability of NIRS for approximate predictions of mycotoxins could be also attributed to the presence of chitin and ergosterol in *Fusarium*-damaged kernels (Delwiche et al. 2011).

Despite the fact that wheat is one of the most consumed cereal worldwide and the fact that mycotoxins are carcinogenic, mutagenic, hepatotoxic, and immunosuppressive toxins, reports on determination of other types of mycotoxins (e.g., aflatoxin, fumonisin) in wheat and wheat-based products by either NIRS of FT-NIRS are limited in the relevant academic literature (Fernández-Ibañez et al. 2009). However, the certain number of reports is available related to detecting aflatoxin in corn and barley (Pearson et al. 2001; Dowell et al. 2002; Berardo et al. 2005; Fernández-Ibañez et al. 2009). Therefore, one of the future perspectives in NIRS application for determination of wheat safety should encompass this segment of development (Table 4).

NIRS in Wheat Functionality Monitoring

Extensive studies on dietary and health issues of cereals have initiated the research on feasibility of the NIRS technique as being applied in prediction of its functional properties from the nutrition standpoint. The applicability of the NIRS technique for determination of fiber content in cereals and cereal products has already been demonstrated. However, a small number of studies have addressed the applicability of NIRS to predict total dietary fiber and its constituents, soluble and insoluble fiber, in unprocessed cereals in relation to the studies dealing with determination of fiber contents in cereals products (Kays et al. 1999). One of the most recent successful applications of the NIRS technique has been related to the development of calibration models to predict the total arabinoxylan and water-extractable arabinoxylan content in cereals including wheat. The initially developed calibration models reported by Shewry et al. (2012) were transferable between different types of NIR instrumentation. The authors indicated the need to increase the robustness of the calibrations by broadening the calibration sets to encompass higher variability (Shewry et al. 2012).

Conclusion

The NIRS technique provides a rapid, non-destructive, environmental friendly, and accurate analysis of the sample composition, its functional properties, and safety. Due to the listed advantages, it represents a suitable tool for the routine use in a wide range of laboratory and industry applications. Having demonstrated the potential of the NIRS technique for prediction of certain constituents and/or functional properties of wheat and wheat-based products that do not exhibit absorption in the NIR spectral range, it can be stated that the NIRS technique is characterized by high R&D potential. In this regard, the future perspectives of the NIRS technique in wheat technology should equally comprise each aspect of NIRS technique: instrumentation, chemometrics, and applications. The NIRS instrumentation evolves in terms of development of hyphenated instruments, NIR imaging and portable NIR spectrometers. More versatile instruments in terms of design of sampling accessories and different acquisition modes should be provided with the minimal changes in the instrument operational configuration. The complexity of high dimensional and nonlinear measured data has imposed the need for new chemometric techniques, while the assessment of phytochemicals and other bioactive and toxic hazardous compounds in wheat represents one of the challenges for future NIRS applications. To facilitate the spectral data management obtained by versatility of available NIRS instruments, it is of upmost importance to allow unrestricted access, data import, export and conversion to different commercially available chemometrics software packages.

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