



An overview of the use of infrared spectroscopy and chemometrics in authenticity and traceability of cereals



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ABSTRACT

Although both near infrared (NIR) spectroscopy and mid infrared (MIR) spectroscopy combined with multivariate data analysis (MVA) have been extensively used to measure chemical composition (e.g. protein, moisture, oil) in a wide number of grains few reports can be found on the use of this methods for varietal discrimination and traceability of cereals. In this overview applications of NIR spectroscopy and MIR spectroscopy combined with multivariate data methods such as principal component analysis (PCA), partial least squares discriminant analysis (PLS-DA), linear discriminant analysis (LDA) to aid on the authentication and traceability of cereals are discussed.

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1. Introduction

Cereal grains are among the most important of the foods we grow. A large proportion of cereal grains is milled and marketed as flour: this is then used to produce bread, cakes, biscuits and many other commodities (Schwartz & Whistler, 2009; Xie et al., 2005). Starch is the major component of cereal grains, and changes in its biophysical and biochemical properties such as amylose, water uptake, amylopectin, viscosity; will have an effect on its end use properties (e.g. bread, malt, beer, polymers) (Schwartz & Whistler, 2009; Xie et al., 2005). The starch stored in the seeds and tubers of various agricultural crops including maize, wheat, rice, barley, potato and cassava provides the main source of energy in the human diet (Schwartz & Whistler, 2009).

In the developed world, starch is also utilized in the production of food (bread) and beverages (beer, whisky), as well as the manufacturing of adhesives, cosmetics, detergents, paper and textiles (Schwartz & Whistler, 2009). Starch is also currently being used in the production of biodegradable packing materials and the development of biodegradable plastics is becoming an increasingly attractive alternative to petroleum-based products (Schwartz & Whistler, 2009; Wiley, Tanner, & Chandler, 2009). Expansion of dietary and industrial uses of starch is creating an increased demand for starch in the market place. With the advancements in genetic engineering and modern breeding technologies, it is now possible to modify starch biosynthesis in different plant species (Schwartz & Whistler, 2009; Shanon et al., 2009).

Current chemical and physical methods used in research and by the industry to determine composition and monitor quality issues in cereals are slow, destructive, and some are based on empirical relationships. The lack of simple, reliable and non-destructive methods for the determination of chemical composition in agricultural products has been one of the main obstacles for the development of rapid quality control in both the food industry and commercial trade. Conventional methods of analysis for quality control involve time consuming, laborious, costly procedures and chemical reagents (Cozzolino, 2009, 2012; Karoui, Downey, & Blecker, 2010; Weeranantanaphan et al., 2011; Williams, 2010). During recent years, the combination of novel instrumentation and chemometric techniques has resulted in the development of rapid methods relating multivariate data, such as near infrared (NIR) and mid infrared (MIR) spectra of samples, to the concentration of specific chemical constituents (Cozzolino, 2009, 2012; Karoui et al., 2010; Weeranantanaphan et al., 2011).

Infrared radiation is the region of the electromagnetic spectrum between the visible and the microwave wavelengths. The nominal range of wavelengths for near-infrared (NIR) is between 750 and 2500 nm (13,400 to 4000 cm^{-1}), while for the mid-infrared (MIR), the spectral range is from 2500 to 25,000 nm (4000 to 400 cm^{-1}) (Subramanian & Rodrigez-Saona, 2009). Solid, liquid or gaseous samples can absorb some of the incoming infrared radiation at specific wavelengths resulting in a 'fingerprint' or spectrum (Cozzolino, 2011; Smyth & Cozzolino, 2011, 2013; Subramanian & Rodrigez-Saona, 2009). Spectral 'signatures' in the MIR result from the fundamental stretching, bending, and rotating vibrations of the sample molecules, while NIR spectra result from complex overtone and high frequency combinations at the shorter wavelengths. Although NIR intensities are 10–1000 times lower than for the MIR

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range, and the peaks concomitantly smaller, highly sensitive spectrometers can be built through several means including the use of efficient detectors and brighter light sources (Cozzolino, 2009, 2011; Subramanian & Rodriguez-Saona, 2009). This allows concentrated bulk or even aqueous materials to be scanned and analyzed quickly and easily. Spectral peaks in the MIR frequencies are often sharper and better resolved than in the NIR, all the higher overtones (1st through 6th) of the O–H, N–H, C–H, and S–H bands from the MIR region are still observed in the NIR region, although much more weak than the fundamental frequencies in the MIR (Subramanian & Rodriguez-Saona, 2009). In addition to the existence of combination bands (e.g. C–O stretch and N–H bend in protein), gives rise to a crowded NIR spectrum with strongly overlapping bands. A major disadvantage of this characteristic overlap and complexity in NIR spectra has been the difficulty of quantification and interpretation of data from NIR spectra. On the other hand, the broad overlapping bands can diminish the need for using a large number of wavelengths in calibration and analysis routines (Cozzolino, 2011; Smyth & Cozzolino, 2011, 2013; Subramanian & Rodriguez-Saona, 2009).

Worldwide interest in food quality and methods of production has increased significantly in recent decades, due in part to changes in eating habits, consumer behavior, and the increased industrialization and globalization of food supply chains. Demand for high levels of quality and safety agriculture and food production requires high standards in quality assurance and process control; satisfying this demand in turn requires appropriate analytical tools for analysis both during and after production (Cozzolino, 2009, 2012; Karoui et al., 2010; Weeranantanaphan et al., 2011). Desirable features of such tools include speed, ease-of-use, minimal or no sample preparation, and the avoidance of sample destruction. These features are characteristic of a range of spectroscopic methods including MIR spectroscopy and NIR spectroscopy (Karoui et al., 2010; McClure, 2004; Weeranantanaphan et al., 2011).

It is well known that the combination of multivariate data analysis (MVA) with instrumental methods such as NIR spectroscopy and MIR spectroscopy can enhance the information generated in order to increase their use for wide applications including composition measurement, traceability and authenticity (Brereton, 2003; Cozzolino, 2009; Karoui et al., 2010; McClure, 2003; Weeranantanaphan et al., 2011). Therefore, the combinations of MVA with analytical instruments have the ability to determine more than one component at a time and can act as a support to establish links to other sample characteristics (Brereton, 2003; Cozzolino, 2009, 2012; Cozzolino et al., 2012; Karoui et al., 2010; McClure, 2004; Weeranantanaphan et al., 2011). The use of MVA also provides in combination with modern instrumental methods with the ability to detect patterns in a data set and to develop mathematical models to predict or monitor composition and other characteristics such as authenticity and traceability (Brereton, 2003; Cozzolino, 2009, 2012; Cozzolino et al., 2012; Kaddour & Cuq, 2011; Karoui et al., 2010; McClure, 2004; Weeranantanaphan et al., 2011).

Although both NIR spectroscopy and MIR spectroscopy combined with MVA have been extensively used to measure chemical composition in cereals (e.g. protein, moisture, oil) few reports can be found on the use of this methods for varietal discrimination and traceability of cereals. In this overview applications of NIR spectroscopy and MIR spectroscopy combined with multivariate data methods such as principal component analysis (PCA), linear discriminant analysis (LDA) and partial least squares discriminant analysis (PLS-DA) to aid on the authentication and traceability of cereals are discussed.

2. Applications of NIR and MIR

2.1. NIR spectroscopy and varietal classification of wheat, barley, rice and corn

A number of reports on the use of NIR spectroscopy as an analytical tool in wheat quality determination are available in the literature (Miralbés, 2008; Pojić & Mastilović, 2013; Pojić, Mastilović, Pestorić, &

Radusin, 2008). In the NIR literature before 2001 there were few publications that used classification. Recent reports stated that the ultimate goal of the application of the NIR spectroscopy 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 & Kvalheim, 2007; Miralbés, 2008; Pojić & Mastilović, 2013; Pojić et al., 2008). Application of NIR spectroscopy for classification purposes is based on the fact that samples with different spectral responses are different in physical and/or chemical properties (Christy & Kvalheim, 2007; Miralbés, 2008; Pojić & Mastilović, 2013; Pojić et al., 2008). Such differences in the spectral responses are a consequence of genetics, growing conditions, and seasons. The first application of NIR spectroscopy for classification purposes was reported by Bertrand, Robert, and Loisel (1985) for the identification of wheat varieties suitable for bread baking (Bertrand et al., 1985). Delwiche and Norris (1993) reported successful classification of ground samples of hard red winter (HRW) and hard red spring (HRS) wheat. The use of algorithms such as artificial neural network (ANN) classification of wheat classes was also reported (Chen, Delwiche, & Hruschka, 1995; Song et al., 1995).

Delwiche and Massie (1996) reported successful classification of individual kernels of wheat classes using partial least squares regression (PLS) or multiple linear regression (MLR). Dowell (2000) and Wang et al. (2002) reported the successful application of NIR spectroscopy 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, Corbellini, and Foca (2005) and Foca et al. (2009) demonstrated the successful NIR spectroscopy application for distinction of bread wheat and flours of different baking quality.

In Europe, Miralbés (2008) demonstrated discrimination of wheat varieties originated from Spain and France. Another application of the NIR spectroscopy for classification purposes was reported by Dowell et al. (2000) which were related to the selecting and sorting waxy wheat kernels by using an automated single kernel NIR sorting system. In recent years Delwiche, Graybosch, Amand, and Bai (2011) also reported the utilization of the NIR spectroscopy for the differentiation of the starch waxy genotypes with accuracies between 90 and 100%. The combination of NIR spectroscopy and genetic markers were used to classify five wheat varieties sourced from Syria. The author concluded that the combination of NIR with other genetic techniques could be a powerful tool to detect and classify wheat varieties (Saleh, 2012).

Recently the use of NIR hyperspectral spectroscopy was evaluated to classify wheat from Canada (Choudhary, Mahesh, Paliwal, & Jayas, 2009). For classification of Western Canadian wheat classes using wavelet texture features of their hyperspectral images, it was found that the wavelet energy features were more important than the entropy features (Choudhary et al., 2009). The average classification accuracy of the linear discriminant classifier using top 90 features was the highest (99.1%) among all the classifiers tested in this study. It can be concluded that the wavelet texture analysis of near infrared hyperspectral images of bulk wheat kernels is an effective tool for discrimination of wheat classes (Choudhary et al., 2009). Near infrared hyperspectral image analysis has been used to classify individual wheat grains representing 24 different Australian varieties as sound or as being discolored by one of the commercially important black point, field fungi or pink stains (Berman, Connor, & Whitbourn, 2009). The authors have used a training set of 188 grains and a test set of 665 grains. The NIR spectra were smoothed and then standardized by dividing each spectrum by its mean. Penalized discriminant analysis was first used for pixel classification and then a simple rule for grain classification was developed. Overall classification accuracies of 95% were achieved over the 420–2500 nm wavelength range, as well as reduced ranges of 420–1000 nm and 420–700 nm (Berman et al., 2009).

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