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To cite this article: Lu Wang, Da-Wen Sun, Hongbin Pu & Jun-Hu Cheng (2017) Quality analysis, classification, and authentication of liquid foods by near-infrared spectroscopy: A review of recent research developments, Critical Reviews in Food Science and Nutrition, 57:7, 1524-1538, DOI: 10.1080/10408398.2015.1115954

To link to this article: <https://doi.org/10.1080/10408398.2015.1115954>



Accepted author version posted online: 08 Jan 2016.
Published online: 08 Jan 2016.



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Quality analysis, classification, and authentication of liquid foods by near-infrared spectroscopy: A review of recent research developments

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ABSTRACT

Nowadays, near-infrared spectroscopy (NIR) has become one of the most efficient and advanced techniques for analysis of food products. Many relevant researches have been conducted in this regard. However, no reviews about the applications of NIR for liquid food analysis are reported. Therefore, this review summarizes the recent research developments of NIR technology in the field of liquid foods, focusing on the detection of quality attributes of various liquid foods, including alcoholic beverages (red wines, rice wines, and beer), nonalcoholic beverages (juice, fruit vinegars, coffee beverages, and cola beverages), dairy products (milk and yogurt), and oils (vegetable, camellia, peanut, and virgin olive oils and frying oil). In addition, the classification and authentication detection of adulteration are also covered. It is hoped that the current paper can serve as a reference source for the future liquid food analysis by NIR techniques.

KEYWORDS

Near infrared spectroscopy; liquid food; food quality; classification; adulteration; beverages; milk; oil

Introduction

Liquid foods, such as beverages (alcoholic beverages and nonalcoholic beverages), milk, and oil, play an important role in human diet. With the development of modern society and economy, liquid food products have become an indispensable part of people's daily diet. Therefore, much attention has been paid to detect the quality and safety of liquid foods. Nevertheless, the quality and nutritional values are still the main concern of liquid foods because of their various raw materials, and some liquid foods (such as milk) are very perishable. Therefore besides the need of processing techniques such as drying (Cui, Sun, Chen, & Sun, 2008; Sun & Woods, 1994), cooling (McDonald & Sun, 2001; Sun, 1997; Wang & Sun, 2004; Zheng & Sun, 2004) and freezing (Kiani, Zhang, Delgado, & Sun 2011) to maintain their quality, there are also needs for novel and rapid methods to analyze and classify their quality, as highly variable liquid foods exist in the market. In addition, classification of liquid foods is very important; for example, alcoholic beverages are usually with different age and origins, and different dairy products and oils are from different raw materials. Adulteration is another main concern in the production and trade of liquid foods, which requires appropriate detection and analytical tools during production and marketing. There have been many traditional methods available for analyzing liquid foods such as high performance liquid chromatography (HPLC), gas chromatography (GC), wet chemical methods, and sensory analysis. For example, HPLC is commonly used to

discriminate wine age with chemical features, including pigment composition (Woodcock et al., 2008) and flavonoids (Finn et al., 2006). Besides, chromatography is also widely used to verify the authenticity of liquid foods (Van Leeuwen et al., 2014). However, these traditional methods are time-consuming and cannot be applied for online applications. Therefore, new and non-destructive methods should be adopted (Wu and Sun, 2013a; 2013b; 2013c; Wang et al., 2002; Jackman et al., 2009; Barbin et al., 2012; Kamruzzaman et al., 2012; Kamruzzaman et al., 2013; ElMasry et al., 2012; ElMasry, Barbin et al., 2012; Feng et al., 2012; Liu et al., 2014; Barbin et al., 2013; Feng and Sun, 2013; Feng, ElMasry et al., 2013b).

Near infrared (NIR) spectroscopy is based on the absorption of electromagnetic radiation in the region of 400–2500 nm. NIR radiation interacting with samples can be absorbed, transmitted, or reflected, which can be captured by utilizing different measurement modes of NIR equipment. NIR spectra comprise broad bands associated with the combinations of vibration modes (O–H, N–H, and C–H) and overtones of molecular vibrations. Therefore, quality attributes of samples can be assessed through the analysis of their NIR spectrum (Qiao et al., 2015). NIR can also be used to accurately and steadily monitor and assess quality changes of raw materials and final products with simple sample preparation (Zhu et al., 2013). Moreover, through the analysis of quality attributes, classification and authentication of liquid foods can be analyzed.

Based on the NIR spectroscopy analysis, the NIR spectra are normally related to the actual concentration of relevant components in the sample matrix through multivariate statistical procedures (e.g. principal component analysis (PCA) (Magwaza et al., 2012) and partial least squares (PLS)) (Lorente et al., 2012). With fast developments in chemometrics, NIR techniques have become more and more widely applied on the quality analysis of liquid foods, such as alcohols (Ghasemi-Varnamkhasti and Forina, 2014), soluble solid contents (SSC) (Wu et al., 2010), fat, proteins, lactose (Kawasaki et al., 2008), and acid value (AV), viscosity (Yavari et al., 2009), trace elements, amino acid, volatile, aroma, phenolic compounds, and typical minerals (Dugo et al., 2005; Yu et al., 2007b; Meng et al., 2015). In addition, some published papers about using NIR spectroscopy to classify the geographical origin of wines (Liu et al., 2008a; Saurina, 2010) and oil (Galtier et al., 2007), and the classification of varieties (Cozzolino et al., 2012; He et al., 2007) are also reported. Furthermore, several studies have also explored the feasibility of NIR spectroscopy to verify adulteration in wines (Pontes et al., 2006; Cozzolino et al., 2012), milk (Zhang et al., 2014), and oil (Galtier et al., 2007).

Recently, some reviews showed the application of NIR spectroscopy for on/in-line monitoring of foods and beverages quality (Wang et al., 2007; Huang et al., 2008). Weeranantaphan et al. (2011) and Liu et al. (2013) reviewed the application of NIR spectroscopy for analyzing meat and fish quality. However, no review on the applications of NIR spectroscopy in liquid food analysis is available. Therefore, in this review, recent

developments of NIR spectroscopy on quality analysis, classification, and authentication of liquid foods (including beverage, milk, and oil) are discussed.

Applications for beverages analysis

Beverages mainly are of two types: alcoholic beverages and nonalcoholic beverages. Continuous and detailed controls are needed to ensure the quality, classification, and authenticity of beverages. For many years, NIR spectroscopy has been widely used for rapid analysis of alcoholic (Table 1) and nonalcoholic (Table 2) beverages.

Alcoholic beverages

Alcoholic beverages mainly consist of wine, Chinese rice wine (a kind of sweet and golden wine made mainly from glutinous rice and wheat), and beer. It is essential to analyze the composition of wine since this can reflect the overall quality, which influences its taste and popularity. The main quality analyses of wine by NIR spectroscopy are alcohols, pH, SSC, trace metals, and some other quality attributes (including anthocyanin, pigmented polymers, sugars, and phenolic and titratable acidity) (Liu et al., 2009; Di Egidio et al., 2010). Some researches on classifying geographic origin, grape variety, and maturity of alcoholic beverage by NIR spectroscopy are also reported (Reid et al., 2006). In addition, NIR spectroscopy has been used for the authentication of age, distilled alcoholic beverage, origin,

Table 1. Applications of NIR spectroscopy in alcoholic beverage quality analysis.

Quality attribute	Data analysis method	Accuracy	References
Alcohols	PLS LDA		Zeaiter et al., 2006 Di Egidio et al., 2010
pH	SVM, PLS SVM, PLS PLS	$R_{val} = 0.915$ $R_{val} = 0.872$ $r = 0.94$	Yu et al., 2009 Yu et al., 2009 Liu et al., 2007
PLS	$r = 0.93$	Ye et al., 2014	
SSC	PLS PLS, MLR, SVM	$r = 0.95$ $r = 0.9762, 0.9818$	Liu et al., 2007 Liu et al., 2009
PLS	$r = 0.91$	Ye et al., 2014	
Total acidity	PLS	$r = 0.98$	Ye et al., 2014
Total ester	PLS	$r = 0.92$	Ye et al., 2014
Trace metal	PLS	$R_{cal} = 0.958, 0.885$ $R_{val} = 0.861, 0.7$ $R_{val}^2 = 0.90, 0.86, 0.89$	Yu et al., 2007a
Ca, Fe, K	PLS		Cozzolino et al., 2008b
Anthocyanin			Cozzolino et al., 2004
Pigmented polymers	PCA, DPLS, LDA		Cozzolino et al., 2006
Sugars	PCA, LDA	87%	Di Egidio et al., 2010
Phenolic compounds	PCA, LDA PLS PCR, PLS	100% $r = 0.93-0.94$	Di Egidio et al., 2010 Cozzolino, 2015
Titratable acidity	LS-SVM, PLS	$R_{val} = 0.888$	Martelo-Vidal and Vázquez, 2014
Quality scores	PLS	$r = 0.61$	Yu et al., 2009
Age	DA LS-SVM, PCA, RBF	94.4%	Cozzolino et al., 2008b Yu et al., 2006b Yu et al., 2008
Geographical origins	PLS, DA, KNN, LDA, Step LDA PLS-DA, LDA DA, DPLS PLS SLDA, PLS-DA 86, 67, 67, 87.5% LDA	82, 100, 71% 100, 84.7, 72, 85% 97.2, 100% 97.5, 80, 70.5%	Ghasemi-Varnamkhasti and Forina, 2014 Liu et al., 2006 Shen et al., 2012 Yu et al., 2007b Liu et al., 2008
Varieties	PCA, SIMCA KNN	98.96% 100%	Wu et al., 2015 Pontes et al., 2006
Adulteration	PCA, SIMCA I-SVM	69% 100% 90%	Ghasemi-Varnamkhasti and Forina, 2014 Pontes et al., 2006 Chen et al., 2014

Table 2. Applications of NIR spectroscopy in nonalcoholic beverage quality analysis.

Quality attribute	Data analysis method	Accuracy	References
SSC	PLS	$r = 0.98$	Cen et al., 2006
	iPLS, siPLS, biPLS, MLR	$r_p^2 = 0.979$	Wu et al., 2010
pH	PLS	$r = 0.85$	Shao and He, 2007
	PLS, SVM	$r = 0.959$	Liu and He, 2007
	PLS	$r = 0.96$	Cen et al., 2006
	iPLS, siPLS, biPLS, MLR	$r_p^2 = 0.951$	Wu et al., 2010
	PLS	$r = 0.92$	Shao and He, 2007
Organic acids	PLS, SVM, LS-SVM	$r = 0.9987, 0.9996$	Liu et al., 2011
	PLS, SVM	$r = 0.961, 0.975$	Liu and He, 2008
	PLS, LS-SVM	$r = 0.973$	Liu and He, 2007
	PLS	$r = 0.944, 0.93$	Cen et al., 2006
	PLS, SVM, LS-SVM	$r = 0.9997, 0.9985$	Liu et al., 2011
Glucose, fructose, sucrose	PLS	$R^2 = 0.9931$	Xie et al., 2009
Sugar	LS-SVM	$r = 0.9939$	Wang et al., 2008
Sensory attributes	PLS	$r = 0.84, 0.87, 0.93, 0.91, 0.88, 0.91$	Ribeiro et al., 2011
Varieties	PCA, LDA	86, 80%	Cozzolino et al., 2012
	PLS-DA		
	PLS-DA, LS-SVM	$R^2 = 0.992$	Liu et al., 2008

and alcohol concentration (Costa et al., 2004; Pontes et al., 2006).

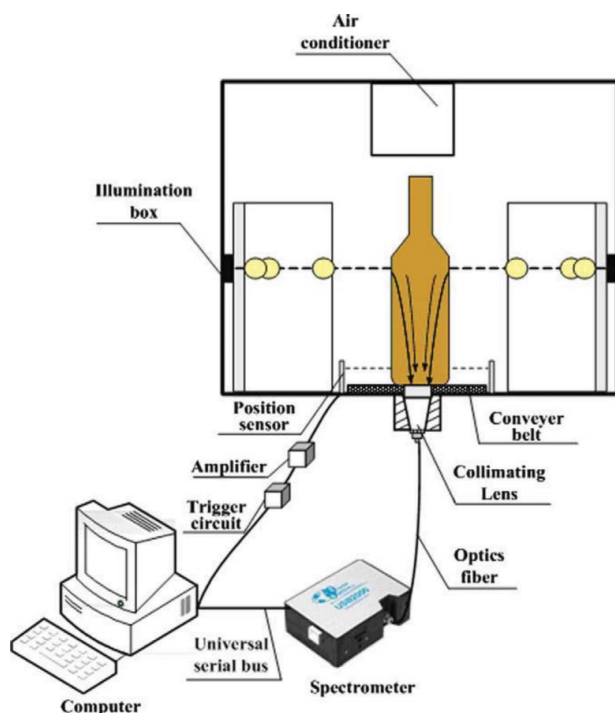
Quality analysis of alcoholic beverages by NIR spectroscopy

There have been many researches on the determination of chemical composition of wine, with evaluation of alcohol content being one of the main targets, as alcohol content

contributes to consumer's acceptance and willingness to pay. The results in previous studies (Zeaiter et al., 2006; Yu et al., 2009; Di Egidio et al., 2010) showed that NIR spectroscopy is an appropriate method to measure alcohols in wine. Zeaiter et al. (2006) applied NIR spectroscopy to monitor the alcohol content during wine fermentation. Calibration model was developed by the PLS regression (PLSR) method, and dynamic orthogonal projection (DOP) was used to correct prediction model, and the robustness of calibration and prediction results was improved with the combination of PLS and DOP methods. In another study conducted by Yu et al. (2009), alcohol in rice wine was analyzed by the NIR spectroscopy system (Fig. 1) with least squares support vector machines (LS-SVM) method. LS-SVM presented better performance than PLS regression. Recently, Di Egidio et al. (2010) evaluated alcohols (ethanol and glycerol) based on NIR spectra by FT-NIR. PCA, stepwise de-correlation of variables algorithm (SELECT), linear discriminant analysis (LDA), and PLS regression were used to pretreat spectral data, select features, predict the fermentation stage during all phases, and simultaneously predict ethanol.

During wine fermentation and final products, pH is an important property that makes a major contribution to the quality of wine. pH influences the acidity, anthocyanin formation, and maturation process as well as complicates biochemical changes during fermentation (Morata et al., 2006; Sun et al., 2006), and it is thus important to evaluate pH value due to consumers' increasing awareness of potential health risks. Several researchers (Liu et al., 2007; Yu et al., 2009, 2014) have investigated the feasibility of using NIR spectroscopy for pH detection to satisfy this demand. Liu et al. (2007) determined the pH values of rice wines using NIR transmission spectroscopy combined with a hybrid chemometric method of PLS. Adequate wavelengths for pH prediction were proposed based on x -loading weights and regression coefficients. The study showed that NIR spectroscopy possessed relatively high reliability in the prediction of pH with the correlation coefficient (r) of 0.94, standard error of prediction (SEP) = 0.02, and root mean square error of prediction (RMSEP) = 0.02. The calibration accuracy and robustness are needed to be improved, and further applications in rice wine fermentation are needed to be developed. Recently, Yu et al. (2009) used the same NIR spectroscopy system (Fig. 1) and the same LS-SVM method with alcohols to determine pH in rice wine. The results showed that LS-SVM presented better performance with higher correlation coefficients for validation (R_{val}) of 0.915, 0.888, and 0.872 for alcohol content, titratable acidity, and pH, respectively, than PLS regression.

Changes in wine quality, including taste, color, flavor, and odor, are caused by the sediment of SSC during the process of fermentation and storage. The sediment of SSC is a sequential phenomenon that starts immediately after fermentation. The traditional method to measure the SSC of wine is by titration, which is time-consuming and costly. NIR spectroscopy provides fast and non-destructive measurements and can be potentially used for real-time detection. It has been reported that SSC serves as a parameter to control wine fermentation (Liu et al., 2007, 2009; Ye et al., 2014). Liu et al. (2007) determined SSC of rice wines using NIR transmission spectroscopy combined with a hybrid chemometric method of PLS. Adequate wavelengths

**Figure 1.** NIR spectroscopic system for wine composition prediction (Yu et al., 2009).

for SSC prediction were proposed based on x -loading weights and regression coefficients. The r , SEP, and RMSEP values were 0.95, 0.16, and 0.17, respectively, for SSC. Two years later, Liu et al. (2009) determined the SSC value for beer using NIR spectroscopy combined with chemometric methods (including successive projections algorithm (SPA), regression coefficient analysis (RCA), and independent component analysis (ICA)). They also developed three calibration models (PLS, multiple linear regression (MLR), and LS-SVM models) using three effective wavelength (EW) selection methods. It was shown that the most accurate and fastest method for the determination of SSC of beer was the SPA-LS-SVM model.

Trace metal is another important parameter that indicates wine quality. Cozzolino et al. (2008a) measured white and red Australian wines by NIR and determined the concentrations of six elements (potassium (K), sodium (Na), magnesium (Mg), calcium (Ca), iron (Fe), and copper (Cu)). The calibration models were developed using the PLSR method and the pre-processing method of standard normal variate (SNV). However, the results showed that NIR spectroscopy was not suitable for quantitative routine use in an analytical laboratory. In addition, Yu et al. (2007b) developed PLSR models with NIR spectra to predict potassium and magnesium contents quantitatively with the correlation coefficient of calibration (R_{cal}) of 0.958 and 0.885 and the correlation coefficient of validation (R_{val}) of 0.861 and 0.700, respectively.

Except the main quality attributes, some researches focused on predicting anthocyanin (Cozzolino et al., 2004), pigmented polymers (Cozzolino et al., 2006), titratable acidity (Yu et al., 2009), quality scores (Cozzolino et al., 2008b), and sugars and phenolic contents (Cozzolino, 2015; Di Egidio et al., 2010; Martelo-Vidal and Vázquez, 2014). Francis et al. (2005) recognized the correlation between wine color density and quality scores and confirmed the relation between the color of red wine with grape-derived anthocyanin, including anthocyanin-derived pigments, malvidin-3-glucoside (M3G), and phenolic compounds formed during fermentation and aging (Eglinton et al., 2004; Herderich and Smith, 2005). Cozzolino et al. (2004) quantitatively predicted the above three anthocyanins (including sugars, alcohols, and phenolic compounds) by NIR spectroscopy, and Eglinton et al. (2004) monitored the time course of both phenolic formation and degradation of anthocyanin to identify essential parameters for anthocyanin stability. Although there have been many researches about predicting fermentation products and chemical compounds by NIR, there have been just a few studies about the spectra loadings/scores during wine fermentation (Uturbia et al., 2004). Cozzolino et al. (2004) monitored changes in phenolic compounds in red wine fermentation by combining NIR spectroscopy and multivariate analysis (PCA, LDA, and discriminant partial least squares analysis (DPLS)). They also used PCA to demonstrate consistent progressive spectral changes in the process of fermentation, and used LDA to classify samples in terms of particular time points in fermentation regardless of variety or vintage. The connection between the spectra and scores/loadings showed that NIR spectroscopy could be used to qualitatively detect changes during red wine fermentation. Di Egidio et al. (2010) collected NIR spectra by Fourier

transform-near infrared spectroscopy (FT-NIR) to evaluate sugars (glucose and fructose) and phenolic compounds (phenolic, anthocyanin, and flavonoid). PCA, SELECT, LDA, and PLS regression were used to pre-treat spectral data, select features, predict the fermentation stage during all phases, and simultaneously predict glycerol, sugar, and phenolic compounds, respectively. Moreover, NIR spectroscopy could be used to quantify phenolic compounds in fermentation process and classify wine samples in different fermentation steps. The result showed that spectroscopic methods were effective to control the quality of wine and provide online information during the whole fermentation process. Cozzolino et al. (2008a) assessed sensory properties of commercial Australian red wine using NIR spectroscopic data. The red wine samples were graded by sensory panels, and PLSR models were developed between Vis-NIR spectra (400–2500 nm) and overall quality scores with $r = 0.61$ and $SEP = 0.81$.

Classification of alcoholic beverages by NIR spectroscopy

Wine has many varieties because of different geographical origins, which are related to quality and flavor of wine. The quality of wine can affect its commercial value, thus it is necessary to classify different geographical origins (Reid et al., 2006). There have been some researches about discrimination of different rice wines with different geographical origins. Wu et al. (2015) demonstrated the feasibility of ultraviolet (UV) spectroscopy combined with chemometric data analysis as an effective method to classify Chinese rice wines from four geographical origins (“Zhejiang,” “Jiangsu,” “Shanghai,” and “Fujian”) in China. Seven mathematical pre-treatments and three model development methods were applied to compare the performance of multivariate classification models, and the results showed that the SNV-LDA models achieved better performances with 98.96% classification rate. Shen et al. (2012) also discriminated Chinese rice wine from three geographical origins (“Fujian,” “non-Shaoxing,” and “Shaoxing”) using NIR spectroscopy combined with chemometrics. PCA, discriminant analysis (DA), and DPLS were used to develop discriminant models using pre-processed spectral data. The calibration and validation results by DA and DPLS methods indicated that NIR combined with chemometrics was a useful method to distinguish Shaoxing wines from non-Shaoxing and Fujian wines. Yu et al. (2007a) also discriminated Chinese rice wine of different geographical origins (Shaoxing and Jiashan, China). The qualitative analysis was developed by PLSR models and the best prediction performance of calibration models of the two geographical origins was in the wavelength range of 1300–1650 nm. In terms of red wine classification with different geographical origins, Liu et al. (2006) used multivariate analysis, including PCA, LDA, and partial least squares discriminant analysis (PLS-DA) to classify the geographical origin of commercial *Tempranillo* wines from Spain and Australia with NIR spectroscopy, and showed that the correct classification rate was higher than 80% between the two different geographical origins. The study regarded the NIR method as a qualitative method, although the precision of the classification models was limited by many factors (including the number of samples used to build calibration models, similarity in climate, and soil characteristics). Another research about classifying geographical

origins was made by Liu et al. (2008a), who classified Riesling wines from four different countries (Australia, New Zealand, France, and Germany) by NIR spectra combined with PCA, PLS-DA, and step-wise linear discriminant analysis (SLDA) based on PCA scores. The validation models were developed by full cross validation (leave-one-out). The results showed that the PLS-DA calibration models with correct classification of 97.5, 86, and 80% were achieved for Australian, New Zealand, and European Riesling wines, respectively.

Authentication of alcoholic beverages by NIR spectroscopy

Besides wine analysis, NIR spectroscopy was also used to verify the adulteration of alcoholic beverages.

Chinese liquor is one of the famous distilled spirits, and liquor authentication is becoming more and more important for the market. Chen et al. (2014) classified and verified the adulteration of liquors by using NIR spectroscopy and chemometric classification. Costa et al. (2004) developed the NIR spectroscopy system to verify the adulteration of distilled alcoholic beverages and classify different beverages, and Saiz-Abajo et al. (2004) used NIR spectroscopy to classify wine vinegar and alcohol vinegar in north Spain with calibration and prediction classification rates of 85.7% and 100%, respectively. In addition, Pontes et al. (2006) classified and verified adulteration of distilled alcoholic beverages (vodka, rum, brandy, and cachas) using NIR spectra and chemometric methods (PCA and soft independent modeling of class analogy (SIMCA)). The above studies proved that NIR spectroscopy is effective in verifying adulteration with small number of wine samples and high sampling throughput without need for prior treatment and reagents.

The quality of wine is also related to age. Therefore, adulterating young wine into aged wine is a common fraudulent practice in the wine market. However, few reports about classifying wine with different marked ages using NIR spectroscopy are available. Ghasemi-Varnamkhasti and Forina (2014) demonstrated that aged beers could be discriminated and classified by NIR coupled with multivariate computational tools.

Yu et al. (2006a) used NIR spectroscopy to discriminate Chinese rice wine with different marked ages (1, 3, and 5 years) based on discriminant analysis of raw and second derivative spectra, where the calibration result of raw spectra was better. Later, Yu et al. (2008) used NIR combined with LS-SVM to discriminate rice wine age and predict enological parameters, and showed that LS-SVM was better than traditional PLS regression in determining alcohol content, pH, and titratable acidity. Moreover, LS-SVM gave better results than discriminant analysis regarding discrimination of rice wine age. Therefore, the study indicated that LS-SVM was a fast and reliable quantitative and qualitative method to estimate the age of rice wine.

Nonalcoholic beverages

Nonalcoholic beverages are the beverages without any alcoholic composition, which include juice, fruit vinegar, coffee, and cola beverages. There are different kinds of fruit juices in the market. Many fruits not only have a high economic value but are also good resources to make juice and wine (Li and He, 2006). Some researches applying NIR spectroscopy to measure SSC,

pH, acids, and other quality attributes juice are reported (Cen et al., 2006; Cen et al., 2007; Fang et al., 2007; Xie et al., 2009; Wu et al., 2010). On the other hand, fruit vinegar is a kind of healthy and popular beverage all over the world. Fruit vinegars are made mainly from different kinds of fruits (apple, lemon, and peach), and their residuals are by modern processing techniques and traditional fermentation. Fruit vinegars are rich in organic acids (acetic, formic, tartaric, lactic, and malic acids), amino acids, mineral, and vitamins. The internal qualities of fruit vinegars are related to different varieties of fruits. NIR spectroscopy has been applied in discriminating the aging storage of vinegar (Casale et al., 2006) and the varieties of fruit vinegars (Liu et al., 2008b), predicting the chemical constituents during storage (Saiz-Abajo et al., 2006), reducing sugars (Fu et al., 2005), and organic acids of plum vinegar (Liu and He, 2009). Another popular nonalcoholic beverage is coffee, quality of which is influenced by the chemical composition of roasted or green (unroasted) beans and the production system. NIR spectroscopy has been used to analyze coffee such as quantifying caffeine (Esteban-Diez et al., 2007), total sugar (Morgano et al., 2007), chlorogenic acid, trigonelline (Davrieux et al., 2004), and defining the roasting degree of coffee beans (Alessandrini et al., 2008) as well as evaluating the quality of espresso beverages, predicting after taste, bitterness, acidity, and body in Arabica and Robusta coffee (Esteban-Diez et al., 2004). Some studies applying NIR spectroscopy to measure the components of drinking cola (Liu et al., 2008b, 2011) have also been reported.

Quality analysis of nonalcoholic beverages by NIR spectroscopy

Soluble solid contents, pH, and carbonation are important quality properties of nonalcoholic beverages (including fruit juice, vinegar, and soft drinks) which affect the quality and consumer's appreciation. Cen et al. (2006) used NIR spectroscopy to detect SSC in orange juices by PLSR methods with different preprocessing methods (wavelet package transform (WPT), SNV, and Savitzky-Golay first derivative (S. Golay 1st-Der)). The results showed that PLS regression with SNV was the best method ($r = 0.98$, SEP = 0.68, and RMSEP = 0.73). Cen et al. (2006) used regression coefficients to propose the "fingerprint," which represented features of orange juice and reflected sensitivity toward some elements at a certain band. Wu et al. (2010) compared several wavelength selection algorithms, and quantitatively determined SSC in grape juice with NIR spectra. Uninformative variable elimination (UVE) (the coefficients of determination for prediction set (r_p^2) = 0.979, and the residual predictive deviation (RPD) = 6.971) did better than interval partial least squares (iPLS), synergy interval partial least squares (siPLS), and backward interval partial least squares (biPLS). The overall results demonstrated that UVE-SPA was powerful for efficient variables selection in SSC analyses. There have been some researches about determining SSC in bayberry juice. Shao and He (2007) determined the internal quality of bayberry juice and established the relationship between SSC parameters and NIR spectral with multivariate calibration methods of PLS. At the same time, they analyzed the sensitive wavelengths corresponding to the SSC of bayberry juices or some element at a certain band. The research results showed

that the best model for predicting SSC of bayberry juice (95.9%) was developed with spectral data (absorbance ($\log 1/R$)) in the wavelengths of 970–990 nm.

The acidity (including citric and tartaric acids) in fruit juice is shown by pH and is related to variations in color and taste of fruit juice. Cen et al. (2006) used NIR spectroscopy to detect not only SSC but also pH in orange juices by PLS regression with the same preprocessing methods as SSC. The results showed that the highest accuracy was achieved by PLS regression with SNV ($r = 0.96$, SEP = 0.06, and RMSEP = 0.06). Cen et al. (2007) also detected two kinds of organic acids (citric and tartaric acids) in orange juice with NIR spectroscopy, and r and RMSEP in the best models for citric and tartaric acids were 0.944 and 0.596, and 0.930 and 0.013, respectively. The results showed that the NIR spectroscopy technique was able to rapidly and reliably detect citric and tartaric acids in orange juice. Wu et al. (2010) also determined pH in grape juice while comparing several wavelength selection algorithms. Similar to the determination result of SSC, UVE-SPA was the best method to analyze pH ($r_p^2 = 0.979$ and RPD = 6.971). Shao and He (2007) determined the pH of bayberry juice using NIR spectra with PLS and analyzed the sensitive wavelengths corresponding to pH or some element at a certain band with regression coefficients by PLS. The best model for predicting acidity (pH) of bayberry juice was developed with spectral data setting as the logarithms of reflectance reciprocal (absorbance ($\log 1/R$)) in the wavelengths of 910–925 nm. Liu et al. (2008b, 2011) simultaneously measured the acetic, formic, and tartaric acids and pH of different fruit (apple, lemon, and peach) vinegars by NIR spectroscopy combined with LS-SVM. PLS models were developed with different preprocessing methods, and the performance of LS-SVM models was compared with three different kinds of inputs, including wavelet transform (WT), latent variables (LV) by explained variance, and effective wavelength by regression coefficients, x -loading weights, modeling power, and ICA. The LS-SVM models were developed with a two-step grid search technique and RBF kernel function. Smoothing way of Savitzky-Golay and SNV were used as preprocessing methods. The results indicated that LS-SVM models ($r = 0.9987$) were better than PLS models ($r = 0.961$) to predict organic acids, and EW-LS-SVM models ($r = 0.9996$) was better than LV-LS-SVM models ($r = 0.975$) to predict pH in different fruit vinegars.

While the majority of studies focused on predicting the major chemical components, some attempts have been made to estimate glucose, fructose, sucrose, sugar, and sensory attributes (Wang et al., 2008; Xie et al., 2009; Ribeiro et al., 2011). Xie et al. (2009) quantitatively and simultaneously determined glucose, fructose, and sucrose in bayberry juice using NIR spectroscopy. They developed the calibration models with PLS regression. In spite of unsatisfactory prediction accuracy of PLS model, the results could be improved by using derivative process with the exception of glucose. Fang et al. (2007) quantitatively analyzed the phenolic compounds of three varieties of bayberry juice. On the other hand, the acidity and sugar content are also very important internal parameters in fruit juice. Fruit vinegar always contains lots of sugar that may cause overweight and health problems. Wang et al. (2008) predicted sugar content in fruit vinegar using the NIR spectroscopy technique

combined with LS-SVM algorithm. They also applied PCA to reduce the dimensionality of the original spectra, selected PCs according to accumulative reliabilities (AR), and built prediction model by LS-SVM. The PCA and LS-SVM models could be applied to fast and accurately determinate sugar contents in fruit vinegar. There have been some studies about bitterness, acidity, and flavor detection. Ribeiro et al. (2011) predicted body, bitterness, acidity, flavor, cleanliness, and the overall quality of Arabica roasted coffee by chemometric analyses of NIR spectral data. PLS was used to construct models, and the ordered predictor selection (OPS) algorithm was applied to select the wavelengths of the regression model. The results showed that proteins and lipids in the roasted beans were related to the attribute of coffee beverage, meanwhile caffeine and chlorogenic acids were related to bitterness, chlorogenic acid to acidity, and caffeine, trigonelline, chlorogenic acid, polysaccharides, sucrose, and protein to flavor, cleanliness, and the overall quality of the roasted coffee beans. At last, a relationship between the sensory attributes of the beverage and the chemical components of coffee beans was established (Ribeiro et al., 2011).

Classification of nonalcoholic beverages by NIR spectroscopy

Classification of nonalcoholic beverages for different varieties is very important. Cozzolino et al. (2012) classified grape juice from commercial Australian Chardonnay and Riesling varieties with PCA, LDA, and PLSDA based on NIR spectra using the leave-one-out validation method. The results showed that the NIR spectroscopy combined with pattern recognition methods could be used to classify grape juice samples of different varieties. Cen et al. (2006) and Li et al. (2007) non-destructively discriminated the varieties of Chinese bayberry in terms of their acidity and sugar content. Liu and He (2007, 2008) and Liu et al. (2008b, 2011) used the same method to predict pH and SSC of cola beverages, measure the component, and classify the varieties of fruit vinegars (apple, peach, lemon, and aloe), respectively. Meanwhile, the results also indicated that it was possible to develop portable and online instruments to classify fruit vinegars during fermentation using effective wavelength.

Applications for dairy analysis

At present there are a variety of dairy products in the market, including cow milk, goat milk, milk powder, and yogurt. Milk is important for social economy with abundant nourishment and occupies a very big part of the global market. Moreover, some dairy products such as yogurt are popular for their higher contents of nutrition, better taste, and easier digestion and assimilation than fresh milk (Sodini et al., 2004). With consumers' growing requirement for food nutrition composition, guaranteeing and improving the quality of milk and dairy products becomes more and more important. It is thus necessary to analyze the varieties of milk and milk products. Fast and accurate NIR reflectance spectroscopy has been widely used to determine milk quality attributes, including protein, fat, lactose, and the fatty acid (FA) composition (Diaz-Carrillo et al., 2004; Soyeurt et al., 2006; Dračková et al., 2008; Coppa et al., 2010; Hsieh et al., 2011; Andueza et al., 2013; Coppa et al., 2014; Núñez-Sánchez et al., 2015). NIR spectroscopy can not only

Table 3. Application of NIR spectroscopy in various milk and dairy products.

Quality attribute	Data analysis method	Accuracy	References
FA	PLS	$R^2 \geq 0.88$	Coppa et al., 2010
	PLS	$r > 0.7$	Andieza et al., 2013
	PLS	$R_{cv}^2 \geq 0.91$, $R_v^2 \geq 0.91$	Núñez-Sánchez et al., 2015
			Coppa et al., 2014
Fat	RBFN	$R^2 = 0.95$	Kawasaki et al., 2008
	PLS	$R^2 = 0.9569$	Hsieh et al., 2011
		$r = 0.951$	Dračková et al., 2008
			Diaz-Carrillo et al., 2004
Protein		$R^2 = 0.83$	Kawasaki et al., 2008
			Diaz-Carrillo et al., 2004
	PLS	$r = 0.92$	Dračková et al., 2008
Lactose		$R^2 = 0.72$	Kawasaki et al., 2008
			Diaz-Carrillo et al., 2004
	PLS	$r = 0.997$	Dračková et al., 2008
Sugar content	PLS	$r = 0.934$	He et al., 2007
	PLS	$r = 0.92$	Shao et al., 2007
Acidity	PLS	$r = 0.91$	Shao et al., 2007
Titratable acidity	PLS	$r = 0.952$	Dračková et al., 2008
pH	PLS	$r = 0.835$	Dračková et al., 2008
SSC		$R^2 = 0.68$	Kawasaki et al., 2008
Total solids	PLS	$r = 0.94$	Dračková et al., 2008
Non-fatty solids	PLS	$r = 0.873$	Dračková et al., 2008
Total casein			Diaz-Carrillo et al., 2004
Casein fractions			Diaz-Carrillo et al., 2004
Freezing point	PLS	$r = 0.935$	Dračková et al., 2008
Density	RBFN	$R^2 = 0.8743$	Hsieh et al., 2011
MUN		$R^2 = 0.53$	Kawasaki et al., 2008
MCP			Cipolat-Gotet et al., 2012
(RCT, k20, a30, a45)			Hsieh et al., 2011
SNF	RBFN	$R^2 = 0.842$	Tsenkova et al., 2006
Disease diagnosis and pathogen identification			
Different types of authentication	BP-A	100%	He et al., 2007;
	IS-kNNI-SVM		Zhang et al., 2014

quantify its component but can also classify the variety of yogurt and analyze authentication with different spectral features (Tsenkova et al., 2006; He et al., 2007). NIR spectroscopy has proved to be a widespread non-destructive method for assessing quality of various milk and dairy products, and quantification of milk fat and unhomogenized milk (Table 3).

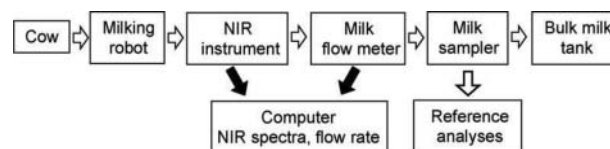
Quality analysis of dairy by NIR spectroscopy

Milk fatty acid is relevant for the overall quality of milk, which is one of the main features for evaluating nutritional quality of milk (Chilliard et al., 2007) and classifying breeding and genetic differences (Arnoult and Soyeurt, 2009). The FA composition of milk draws more and more attention with consumers' increasing demand for healthy and nutritional milk (Ferlay et al., 2006). Núñez-Sánchez et al. (2015) estimated FA contents and predicted indexes of atherogenicity and thrombogenicity with high precision and accuracy by NIR spectra. In the study conducted by Chilliard et al. (2006), a calibration equation for broad-based cow milk was constructed to predict a set of all goat milk samples and the FA composition of goat milk with NIR spectroscopic data. The results demonstrated that it was possible to develop prediction models to aid conformance to new food labeling rules. However, the prediction results for certain fatty acid, especially for those with very low concentrations, were not very accurate and stable. Originally obtained

broad-based calibration equations from cow milk FA composition could predict a goat milk population with a good standardized Mahalanobis distance (H) value, but an increase in unexplained error was observed with goat milk broad-based calibration equations on the same population. Another report on FA prediction using NIR spectroscopy (700–2500 nm) was made by Tsenkova et al. (2006), who found that cow milk from preserved forages and pasture with or without lipid supplements could ensure FA variability. Gas chromatography was used to analyze FA composition in details. However, the accuracy of prediction with low concentrations was lower than with medium-to-high concentrations of individual milk fatty acid. Nevertheless, it was still reliable to predict the content of selected FA composition in liquid milk samples using NIR spectroscopy.

Main constituents (protein, lactose, and fat) of milk have great influences on its quality. Therefore, knowledge of its constituents is essential to analyze the quality of milk. Kawasaki et al. (2005) constructed a NIR spectroscopic sensing system to improve the robustness of calibration models for online measurement of milk quality from two dairy herds. The accuracy was high with calibration and validation models developed from spectral data of the same herd. However, the accuracy of all milk constituents (except fat) obtained from different herds was lower than that of the same herd. The same spectroscopic sensing system and wavelength range from the above research were used by Kawasaki et al. (2008) to obtain NIR spectra (1100–2500 nm) of raw milk in a milking robot system (Fig. 2). Calibration models were developed by PLS regression, and comparison with the reference method was based on standard error of cross validation (SECV). Kawasaki et al. (2008) used PCA and loading of PLS factors to explain the lower SECV obtained with only individual cow's spectral data for calibration. In the two studies, the spectroscopic sensing system (Fig. 3) was used to predict three major milk constituents (fat, protein, and lactose) of unhomogenized milk online. The accuracy and precision of the calibration models were validated, and the results indicated that milk quality and milk form could be improved and managed scientifically with the developed NIR spectroscopic sensing monitoring.

Hsieh et al. (2011) applied radial basis function network (RBFN) to quantify fat, SNF, and the density of the reconstituted raw milk (0, 2, 5, 10, 20, 30, 50, 70, and 100% composition) with visible (Vis) and NIR spectra (400–2500 nm). A response surface method (RSM) was employed to study optimal RBFN parameters (goal error and spread). In the study done by Diaz-Carrillo et al. (2004), NIR calibration models for total protein, total casein, casein fractions (α -, β -, and κ -caseins), fat, and lactose in milk from three Spanish breeds of goats were developed. They also described the spectra of goat's milk, and discussed the contribution of different components.

**Figure 2.** Flow chart of an online NIR spectroscopic sensing system for assessing milk quality in an automatic milking system (Kawasaki et al., 2008).

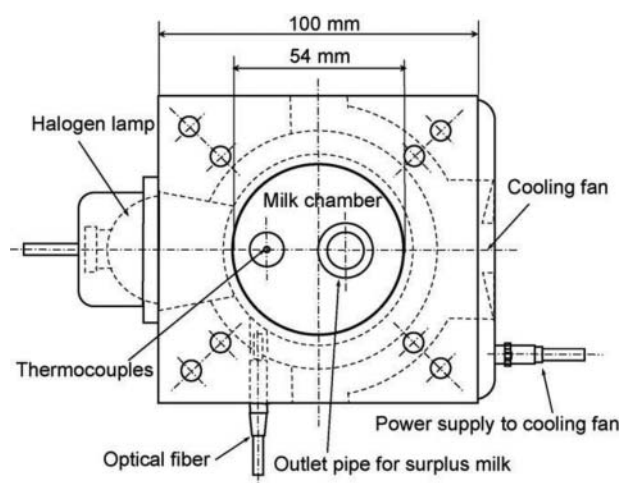


Figure 3. Plane view of NIR spectrum sensor (Kawasaki et al., 2008).

Dračková et al. (2008) showed that FT-NIR was a potentially useful technique for measuring the composition of goat milk (lactose, fat, protein, total solids, non-fatty solid contents, freezing point, titratable acidity, and pH).

In the study conducted by He et al. (2007), sugar content of yogurt was determined by NIR spectroscopy techniques. The model between sugar content measured by sugar content meter and spectral measurement was established based on PLS. The results showed that the NIR spectroscopy technique could be used to predict the sugar content of yogurt. Shao et al. (2007) also analyzed the spectral data with PLS using three different types of preprocessing (Golay smoothing with multiplicative scatter correction (S. Golay smoothing with MSC), S. Golay 1st-Der, and WPT). The logarithms of reflectance reciprocal of absorbance spectral data were used to build the best predicting model with WPT (400–1000 nm). The sensitive wavelengths were proposed based on regression coefficients by PLS. However, the results showed that accurate prediction of the sugar content of yogurt could not be obtained with only one or just a few wavelengths. Therefore, they put forward that maybe it was necessary to use a wider spectrum or even an entire spectrum for sugar content prediction.

Milk quality is connected with not only main constituents (protein, lactose and fat) but also with milk urea nitrogen (MUN), somatic cell count (SCC), physiological condition of cows, and milk coagulation properties (MCP) (Kawasaki et al., 2005, 2008). Optical infrared instruments were used to monitor milk coagulation, curd firming, and syneresis (Fagan et al., 2007; Mateo et al., 2009) and predict MCP (Cipolat-Gotet et al., 2012). The detectors recording absorbance at a single NIR wavelength in the sample during coagulation have replaced the pendulum submerged in milk during lactodynamography (Kubarsepp et al., 2005). Cipolat-Gotet et al. (2012) constructed an NIR spectroscopic sensing system to monitor milk quality in real-time during milking, and the NIR spectra of unhomogenized milk were recorded over a wavelength range of 600–1050 nm. They used a NIR optical device (the optigraph) and a traditional mechanical device (the formagraph) to measure milk coagulation properties. The research revealed that milk coagulation properties, especially curd-firming time and curd firmness average values, have discrepancies between

yielding by the above device. Only the rennet coagulation time was the same using the two methods. At last, it showed that algorithm-constructed mimicking lacto dynamographs were effective to measure milk coagulation properties, especially over the usual test duration of 30 min.

Classification of dairy products by NIR spectroscopy

Near-infrared spectroscopy has been used to fast and non-destructively classify a variety of dairy products. Different yogurts have different flavors, and the main factors influencing the taste of yogurt are acidity (pH values). In a study by He et al. (2007), the relation was established between the varieties of yogurt and reflectance spectra by combining the PCA analysis of spectral data of five typical kinds of yogurt and the back propagation artificial neural network (BP-ANN) technique. The recognition rate was 100% by using BP-ANN with the spectral data pretreated with PCA. Both the time of building and training artificial neural network (ANN) model and the amount of calculation could be cut down largely. It was proved that the model integrating PCA and BP-ANN was an appropriate, rapid, and successful approach for discrimination of different varieties of yogurt.

Authentication of dairy products by NIR spectroscopy

Recently, some reports about unqualified dairy products are available. In order to increase profits, some manufacturers sometimes add some cheap or even harmful materials instead of nutrients in dairy products. Therefore, authentication analysis of dairy products is very important. It has been reported that both raw milk and cow health influence the safety and quality of milk. Milk abnormality is mainly evaluated by the cell count of the main mastitis-causing bacterial pathogens in udder quarter milk as well as by electrical conductivity. NIR spectra of cow's udder quarter milk of individual cows from various farms and at different times of the year were collected in a research (Tsenkova et al., 2006). These multivariate spectra data provided useful information about not only health disorders in cows but also about milk abnormality. The above three features could be measured simultaneously with the developed spectroscopic models. Also Zhang et al. (2014) applied NIR spectra combined with nonlinear pattern recognition methods (improved support vector machine (I-SVM) and improved and simplified K nearest neighbors (IS-KNN)) to discriminate adulterated milks from raw cow milks, and it was demonstrated that the higher the concentration of adulterants, the more accurate were the discrimination results of the NIR pattern recognition models.

Applications for oil analysis

Oils are essential component of diet because of their nutrition and biological properties. There are various oils available in the market, such as vegetable, camellia, peanut, virgin olive oils, and frying oil. Conventional titration analytical methods to measure the contents, oxidation, and adulteration of various oils are expensive, destructive, time-consuming, and laborious. NIR spectroscopy can analyze oils both quantitatively and

Table 4. Applications of NIR spectroscopy in oils.

Quality attribute	Data analysis method	Accuracy	References
AV	PLS-DA	$r = 0.999$	Marquez et al., 2005
	PLS, DPLS	$R^2 = 0.9379$, 96.55%	Rao et al., 2009
	PLS	$R^2 = 0.95$	Yavari et al., 2009
	iPLS, MLR	$r = 0.94$	Pereira et al., 2008
CV	PLS	$R^2 = 0.99$	Ma et al., 2014
	PLS	$r = 0.989$	Wang et al., 2014
IV	PLS	$R^2 = 0.98$	Mba et al., 2014
PV	PLS	$R^2 = 0.9722$	Mba et al., 2014
FA	PLS-DA		Galtier et al., 2007
	PLS		Sundaram et al., 2010
	PLS	$R^2 = 0.709$	Shen et al., 2014
	PLS	$R^2 = 0.87-0.97$	Uncu and Ozen, 2015
Oleic acid, linoleic acid	PLS	$R^2 = 0.9927$	Mba et al., 2014
	PLS, SIMCA	$r = 0.992$	Wang et al., 2006
Viscosity	PLS	$R^2 = 0.91$	Yavari et al., 2009
	iPLS, MLR	$r = 0.96$	Pereira et al., 2008
	PLS	$R^2 = 0.921-0.945$	Shen et al., 2014
TPC	PLS	$R^2 = 0.98$	Yavari et al., 2009
	PLS	$R^2 = 0.790-0.931$	Shen et al., 2014
	PLS	$R^2 = 0.98$	Ma et al., 2014
TPMs, FFAs	FSMLR, PLS	$r = 0.983, 0.943$, 0.999, 0.983	Ng et al., 2007
k225, FAME	PLS-DA	$r = 0.936$, 0.998, 0.992	Marquez et al., 2005
Refractive index	iPLS, MLR	$r = 0.98$	Pereira et al., 2008
Fruit aroma intensity			Sinelli et al., 2010
Oxidative stability	PLS	$R^2 = 0.99$	Uncu and Ozen, 2015
Pigments, phenolic compounds	PLS	$R^2 = 0.98$	Muik et al., 2004
Composition		$R^2 = 0.97$	
Water content		RMSEP = 0.17	
Oil content			
Triacylglycerols	PLS-DA		Galtier et al., 2007
Geographic origins	SRC, LDA, PLS-DA	95.37%	Zhou et al., 2015
Authentication	PLS		Azizian et al., 2015

qualitatively. There have been some studies about the quality analysis (Table 4) of oils by NIR spectroscopy (Ma et al., 2014; Wang et al., 2014; Azizian et al., 2015), such as vegetable (including olive oils) and peanut oils and frying oil detection in terms of geographical classification (Galtier et al., 2007; Casale et al., 2008) and adulteration (Christy et al., 2004; Christy and Ozaki, 2005).

Quality analysis of oils by NIR spectroscopy

In oil processing, oil and fatty acid concentrations of raw materials are the two very important factors because the total oil determines how the materials can be processed into different oil products, and FA content is a quality parameter. NIR has been used to predict fatty acid and oil concentrations of individual peanut kernels (Fox and Cruickshank, 2005; Tillman et al., 2006) while the free fatty acid (FFA) is measured by acid value, which reflects the degree of refining, and the quality and quality change in peanut oil. The present studies of peanut oil using NIR mainly conclude the following two aspects: first, to quantify acid value, and second, to classify the qualified and unqualified peanut oils with acid value. In a study conducted

by Sundaram et al. (2010), the total oil and fatty acid concentration of Virginia and Valencia types of in-shell peanuts were predicted by the NIR reflectance spectroscopy. It was done with sufficient accuracy, which was also rapid for quality control with minimal sample preparation. The calibration set models were developed for predicting total oil and fatty acids by PLS. The RPD values of both types of peanuts (<5) showed that all the calibration models were used for predicting, and the result showed that it might be possible to predict the fatty acid composition accurately for quality control with further analysis of NIR. Furthermore, Rao et al. (2009) applied NIR spectroscopy for quantitative (classifying the unqualified peanut oils; $AV > 3$ mg/g) evaluation of qualified peanut oil ($AV < 3$ mg/g) and for qualitative analysis of acid value of peanut oil by using DPLS. The results revealed that NIR was especially suitable for a larger number of samples. Latter, in the study conducted by Mba et al. (2014), the essential chemical quality parameters (iodine values (IV), FFA, and peroxide values (PV)) of vegetable oil blends (crude palm oil and canola oil) were evaluated by FT-NIR spectroscopy with PLS regression models and spectral processing. In addition, Uncu and Ozen (2015) analyzed some important quality parameters (oxidative stability, pigments, fatty acid, and phenolic composition) of olive oils by FT-NIR spectroscopy with PLSR models.

The quality of oils is also affected by the type of raw material, and the methods of processing, refining, and storage. In order to ensure the quality of oils, the whole producing chain should be controlled appropriately. Zhang et al. (2006) monitored many physical and chemical parameters to control the quality. NIR spectroscopy can rapidly and non-destructively monitor not only the final product but also every stage of the production process. Szlyk et al. (2005) found the precision for the determination of α -tocopherol in edible oils with NIR data and PLS models were higher than the liquid chromatography.

The quality of fried products is critically related to the quality of frying oil. In order to maintain the quality of oil-fried food, monitoring the quality of frying oils is very important. The hydrogenation oil is the most popular oil in the industry. However, the hydrogenation oil may generate fatty acids with high risks to human health. Therefore, hydrogenated oil with lower level of unsaturated oil has become more popular recently. The level of hydrogenation is related to the thermal and oxidative stability of frying oils. Innawong et al. (2004) had differentiated as good, marginal, and unacceptable oils with the FT-IR-attenuated total reflectance spectroscopy (FTIR-ATR). Yavari et al. (2009) quantitatively evaluated quality changes in heated hydrogenated and dehydrogenated oils using Vis-NIR analysis. PLS calibration models were developed in wavelengths of 400–1750 nm for quantitative evaluation of acid value, total polar component (TPC), and viscosity, indicating different quality levels of oils. In summary, Vis-NIR spectroscopy has been proved useful to predict frying oil's quality parameters. The flavor and nutritional value of fried products are related to degradation, and degradation compounds in frying oil can be measured by two important chemical components (total polar materials (TPMs) and FFAs). Both TPMs and FFAs have negative effect on nutrition and flavor (Ng et al., 2007). In addition, Shen et al.

(2014) applied FT-NIR spectroscopy coupled with PLS regression models to rapidly evaluate the levels of FFA, TPC, and viscosity of deep frying oils collected from street vendors. It was demonstrated that FT-IR coupled with PLS regression had better prediction ability for viscosity ($R^2 = 0.921$ – 0.945 , SEP = 0.68–0.71, RPD = 3.54–3.98), and TPC ($R^2 = 0.790$ – 0.931 , SEP = 1.89–2.94, RPD = 2.16–3.55) than for FFA ($R^2 = 0.709$, SEP = 0.14, RPD = 1.83). NIR spectroscopy was also used to measure the two important parameters of degradation products in frying oils. Ng et al. (2007) developed calibration models with both PLS and forward stepwise multiple linear regression (FSMLR). The established models were tested with two independent sets of degraded frying oil samples. It was shown that PLS models gave better results than FSMLR models with wavelengths of 700–1100 nm. Derivative treatments were also used to preprocess the data, but they had limited utility in the longer wavelength (1100–2500 nm).

The quality of oils can be classified in terms of bitterness (k225), oleic–linoleic (MP), and acid value. k225 is a chemical index of oil bitterness. Oleic–linoleic and acid values are estimated based on fatty acids. These are calculated by the percentage of mono-unsaturated and polyunsaturated fatty acids and hydrolytic deterioration. If the values of oleic–linoleic are high, the oils are of high stability. If the acid value value is >2%, the oil sample cannot be consumed directly and need to be refined. There have been some researches based on spectroscopic techniques, including fluorescence spectroscopy (Guimet et al., 2004) and NIR spectroscopy for controlling quality of olive oils (Mailer, 2004), and for quantitatively determining peroxide value and acidity (Lagardere et al., 2004). Marquez et al. (2005) applied optical NIR transmittance spectroscopy for online simultaneous monitoring of acid value, k225, and fatty acid compositions (FAME) in virgin olive oils. NIR spectra were obtained from the usual harvesting time of three olive crops. PLS regression was used to develop models for a rapid and non-pollutant online prediction of all these parameters during processing of virgin olive oils (Fig. 4).

Classification of oils by NIR spectroscopy

Geographical origins and raw materials greatly affect the quality and taste of oil, so it is necessary to classify the variety of oils. There have been many researches distinguishing with NIR spectroscopy oil produce by different geographical origins

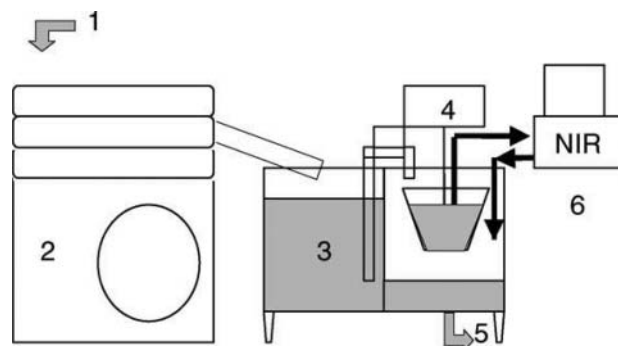


Figure 4. Schematic diagram of localization of sensor NIR in olive oil extraction process (Marquez et al., 2005).

(Bendini et al., 2007; Casale et al., 2008; Galtier et al., 2008; Sinelli et al., 2008). Armenta et al. (2007) classified edible oils of different origins and types by measuring acidity and peroxide index with NIR spectroscopy. Later, Pereira et al. (2008) classified different edible vegetable oils (including corn, soya, canola, and sunflower oils) by measuring the acidity, refractive index, and viscosity simultaneously with NIR spectroscopy. Several wavelengths were selected by using iPLS and SPA, and it was found that a single MLR-SPA model with each parameter (acidity, refractive index, and viscosity) could be used to classify every vegetable oil type. Recently, Sinelli et al. (2010) found that NIR spectroscopy with chemometric strategies was as useful as traditional sensory prediction in classifying different samples of extra virgin olive oil samples on the fruity attribute (average value between 71.6% and 100%). The results showed that the spectroscopic methods could describe the intrinsic quality attributes, including sensory attributes, and draw a complete fingerprint of an oil product.

Authentication of oil by NIR spectroscopy

Oil authenticity is attracting much attention not only for consumers but also for distributors and producers. Adulteration with different vegetable oils has been detected by NIR spectroscopy (Ozdemir and Ozturk, 2007; Sinelli et al., 2010; Zhou et al., 2015). The oil and water contents are emerging areas of authenticity in oil products. Muik et al. (2004) compared NIR and Raman spectrometry to determine the oil and water contents of olive pomace with the same sets for calibration and validation. The results presented that either NIR or Raman spectrometry techniques could accurately detect excessive levels of oil in olive pomace in the extraction process, as well as to estimate water content in olive oils. The biggest advantage was that both spectroscopic techniques could be implemented non-invasively for online monitoring of olive production without any pretreatment. Camellia oil is one of the favorite, nutritional cooking oil with high content of oleic and linoleic acids in Southern China and Southeast Asia. Wang et al. (2006) were able to distinguish pure camellia oil from those adulterated with soybean oil, although the NIR spectral difference between the two was minor. The spectral difference was caused by the difference between oleic acid in camellia oil and linoleic acid in soybean oil. The prediction results from PLS models illustrated that fiber optic diffuse reflectance near infrared spectroscopy (FODR-NIR) could be used to quantitatively classify pure camellia oil and adulteration oils with different levels ($r = 0.992$, RMSEP = 1.78). However, each of the spectral method could only measure a limited quantity of camellia and soybean oils. Another study regarding oil authentication was reported by Galtier et al. (2007), who used NIR spectra to assess the quantity of fatty acids and triacylglycerols, and to authenticate five geographically closely registered designations of origin (RDOs) of French virgin olive oils. The result showed that a considerable improvement in estimating the quality of virgin olive oils by NIR spectroscopy could be achieved in comparison to the traditional chromatography methods. Most recently, Zhou et al. (2015) compared three different modeling methods (sparse representation classification (SRC), LDA, and PLS-DA) to distinguish edible oil (QO) and swill-cooked dirty oil (SO)

by NIR spectroscopy, and the experimental results proved that SRC and NIR spectroscopy had the best ability to distinguish QO and SO with a maximum classification accuracy of 95.37%.

Conclusions

This review mainly introduced recent advances in detecting quality attributes and adulteration of liquid foods. NIR spectroscopy is a powerful technique for predicting essential features of liquids such as beverages, dairy products, and oils. It can simultaneously realize the detection of different quality attributes and classification of different geographical origins. However, there are still some barriers that are to be tackled. First of all, developing low-cost and simple instruments are needed to satisfy the need for online quality monitoring of liquid. Second, in practical applications, some calibration models based on NIR spectroscopy are not always stable and reliable. Hence, it is necessary to choose proper chemometrics to build stable models and develop more accurate and reliable calibration models. In addition, NIR spectrum has a little ability in obtaining the absorption information of minerals, therefore it was difficult to use it for measuring mineral contents sensitively. In order to solve such kind of problems, NIR spectroscopy can be used in combination with other detection techniques such as electronic nose technique, UV light, and X-ray fluorescence spectroscopy.

Funding

The authors were grateful to the Guangdong Province Government (China) for its support through the program of "Leading Talent of Guangdong Province" (Da-Wen Sun). This research was also supported by the National Key Technologies R&D Program (2014BAD08B09), Natural Science Foundation of Guangdong Province (2014A030313244), the International S&T Cooperation Program of China (2015DFA71150), the International S&T Cooperation Program of Guangdong Province (2013B051000010), and the Key Projects of Administration of Ocean and Fisheries of Guangdong Province (A201401C04).

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