QUALITY EVALUATION OF FRYING OIL AND CHICKEN NUGGETS USING VISIBLE/NEAR-INFRARED HYPER-SPECTRAL ANALYSIS

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ABSTRACT

The application of visible/near-infrared hyper-spectral analysis to monitor the quality of frying oil and fried breaded chicken nuggets was investigated.

Partial least squares (PLS) calibration models were developed to predict the acid value, total polar components and viscosity of heated oils with different ratios of hydrogenation. Coefficient of determination (R^2) and root mean square error (RMSE) were calculated to assess the performance of each model. Results of the study demonstrated good prediction ability of the calibration models for the quality parameters with R^2 values of over 0.92.

The second study was based on developing calibration models for prediction of moisture and fat contents of fried breaded chicken nuggets with different levels of moisture and fat contents. Performing the same procedure for evaluation of the PLS calibration models, results of the study demonstrated that moisture and fat contents of fried breaded chicken nuggets could be predicted with R^2 values of 0.92.

RÉSUMÉ

L'application de l'analyse hyper-spectrale du 'visible/infra-rouge proche' pour le contrôle de la qualité des huiles de friture et de pépites panées frites de poulet a été étudiée.

Des modèles des moindres carrés partiels (MCP) de calibration ont été développés pour prévoir l'indice d'acidité et la viscosité des huiles de chauffage (à différent rapport d'hydrogénation) ainsi que la prédiction de tous les composants polaires. Afin d'évaluer la performance de chaque modèle, les coefficients de détermination (R^2) et les erreurs de la racine carrée moyenne (ERCM) ont été calculés. Pour tous les paramètres de qualité, les résultats ont démontré que les modèles de calibrations utilisées ont de bonnes capacités de prédiction. Les valeurs de R^2 obtenus pour ces models étaient supérieures ou égale à 0.92.

La deuxième étape de l'étude à été basée au développement de modèles de calibrations pour la prédiction de l'humidité et des teneurs en graisse des pépites panées frites de poulet ayant des niveaux d'humidité et de teneurs en graisse différents. En utilisant le même procédé d'évaluation des modèles de calibration MCP, les résultats de l'étude ont démontrés que l'humidité et les teneurs en graisse des pépites panées frites de poulet pourraient aussi être prédit avec les valeurs R^2 ≥ 0.92.

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To my parents,

CONTRIBUTION OF AUTHORS

This thesis consists of two manuscripts, both of which I am the primary author. The manuscripts were co-authored with Dr. Ning Wang, my thesis supervisor, Dr. Michael Ngadi, my thesis co-supervisor, and Dr. Shiv Prasher. Dr. N. Wang and Dr. M. Ngadi had direct advisory input and solutions to the concepts, designs, and result analysis during my thesis research work. The thesis was also reviewed by Dr. N. Wang and Dr. M. Ngadi.

Chapters 4 and 5 were presented at the 2004 and 2005 Annual Conferences of The American Society of Agricultural Engineers (ASAE). The manuscript of Chapter 4 was submitted for publication on E-Journal of CIGR in 2004 and is currently under revision. Chapter 5 will be submitted for publication on a scientific publication in food engineering area in 2005.

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NOMENCLATURE

A	The *m* by *p* matrix of absorbance values
A	Contact surface area between food and oil
AOAC	Association of Official Analytical Chemists
AOCS	American Oil Chemists' Society
AV	Acid value
b	Path-length of light
C	The *m* by *n* matrix of concentration values
c	Concentration of the absorbing material
db	dry basis
DC	Direct current
DSC	Differential scanning calorimetry
E_A	The matrix of residual spectra
Ea	The matrix of errors in absorbance
E_c	The matrix of concentration errors
F	The *f* by *p* matrix of eigenvectors
F_a	The *f* by *p* matrix of spectral eigenvectors
F_c	The *f* by *n* matrix of concentration eigenvectors
FFA	Free Fatty Acid
FOV	Field of view
FT-IR	Fourier Transform infrared
FTIR-ATR	Fourier Transform infrared attenuated total reflectance
FT-NIR	Fourier Transform near infrared
h	convective heat transfer coefficient
IR	Infrared
MAXR	Maximum R^2
MID-IR	Middle infrared
MLR	Multiple linear regression

PC	Personal computer
PCA	Principal Component Analysis
PLS	Partial Least Squares
PRESS	Prediction Residual Error Sum of Squares
PUFA	Polyunsaturated fatty acid
PV	Peroxide value
Q	Heat energy
R^2	Determination coefficient
RMSE	Root Mean Square Error
S	*m* by *f* matrix of scores
SEC	Standard error of calibration
SEV	Standard error of validation
SLDA	Stepwise linear discriminant analysis
TPC	Total polar components
U	The *m* by *f* matrix of concentration scores
UHT	Ultra high temperature
VI	Viscosity
VIS/NIRS	Visible/near infrared spectroscopy
ΔT	Temperature difference

Greek

$A(\lambda)$	Absorbance at wavelength λ
γ	Shear rate
$\varepsilon(\lambda)$	molar absorption coefficient at wavelength λ
λ	wavelength (nm)
μ	Viscosity
σ	Shear stress

I. GENERAL INTRODUCTION

Visible/near-infrared spectroscopy (VIS/NIRS) along with chemometric multivariate analysis is among the most powerful techniques for quantitative analysis of foods because of abundantly valuable chemical and structural information that are contained in the NIR spectrum of a food substance. The bands in this region of spectrum mainly consist of overtones and combinations of fundamental vibrations of functional groups in the mid-infrared (MID-IR or IR) region which appear as broad overlapping bands in NIR region. This brought a lot of uncertainty of assigning bands to specific functional groups until in the last decade, advances in modern multivariate algorithms enabled the extraction of a lot of valuable information about chemical composition of food substances.

The extension of the spectral range of spectroscopy equipments to visible range (VIS/NIR equipments) made it also possible to measure different pigments (McCaig et al., 1992; Williams and Sobering, 1993). This was done by measuring reflectance values at specific wavelengths corresponding to the pigment (McCaig, 2002).

VIS/NIR reflectance spectroscopy has shown a lot of advantages over traditional chemical methods. It is a non-destructive fast method with high precision that requires minimum or no sample preparation. It allows the elimination of hazardous reagents required in chemical wet methods and no waste is produced during the analysis. It is a multi-analytical technique that has the potential to measure different components of foods simultaneously. However, VIS/NIRS is highly dependent on time-consuming calibration procedures including complex data treatments (Buning-Pfaue, 2003). But once the instrument is calibrated, simultaneous measurements can be done in few minutes.

In the past few years, NIRS has been widely used in the analysis and quality assessment of fats and oils. Successful applications of NIRS for determination of *trans* content, peroxide value (PV), iodine value and degree of unsaturation, and Free Fatty Acid (FFA) content of oils have been reported in the literature (Li et al., 2000a; Li et al., 2000b; Van de Voort et al., 1994; Moh et al., 1999; Yildiz et al., 2002, Cozzolino, 2005). In studying the application of NIRS in frying oil analysis, Engelsen (1997) reported that NIRS could be a good general-purpose technique for evaluating frying oil deterioration, with high accuracy in prediction of FFA and viscosity. However, lack of spectral information from secondary oxidation products was reported.

As a powerful technique, VIS/NIR reflectance spectroscopy has also been applied in quantitative analysis of food major components such as water, fat, proteins and carbohydrates. The basis of the quantitative analysis is to relate the changes in the VIS/NIR response of a food substance to the concentration changes of the corresponding component. Successful applications of VIS/NIRS for determination of moisture and fat contents of a variety of food products have been reported in the literature (Cozzolino, 2005; Miralbes, 2003; Togersen et al., 2003; Wold and Isaksson 1997; Mitsumoto et al., 1991).

In frying industry, one of the largest industries in food preparation, traditional chemical and physical tests performed for evaluation of frying oil quality and fried product quality involve tedious and time-consuming procedures, some of which requiring the use of hazardous reagents and solvents. Moreover, they are not amenable for on-line measurements.

Quality characteristics of fried foods are determined by measuring related properties such as moisture and fat/oil contents. Frying oil quality has an intimate influence on the amount of oil absorption which consequently alters the organoleptic and nutritional characteristics of the food being fried. Thermal degradation of frying oil at high frying temperatures (hydrolysis, oxidation and polymerization) and formation of high molecular weight polar compounds lead to an increase in the viscosity of oil and as a result, an increase in the amount of oil absorption (Orthoefer and Cooper, 1996). Therefore, in order to maintain good quality of the product, it is necessary to monitor the changes in the frying oil quality.

A lot of research has been conducted to develop advanced techniques of oil quality evaluation such as differential scanning calorimetric, chemosensory and ultrasonic systems, and Fourier Transform Infrared (FT-IR) spectroscopy to replace traditional methods (Tan and Man, 1999; Benedito et al., 2002; Innawong et al., 2004a; Innawong et al., 2004b).

However, current literature lacks enough exploration on the possibility of applying the VIS/NIRS in determination of frying oil main quality indicators including oil chemical index of quality, total polar components (TPC). Also no investigation has been reported on the application of NIRS on moisture and fat analysis of fried foods.

The development of rapid VIS/NIRS analytical techniques for determination of quality parameters of both frying oil, including TPC, and fried foods (moisture and fat contents) will address this need. Also selection of wavelengths of most variation in the spectra for calibration model development will lead to a successful design of a fast and reliable on-line technique to replace chemical methods.

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II. GENERAL OBJECTIVES

This study had the general objective of developing VIS/NIRS calibration models for quantitative evaluation of quality parameters of frying oil and fried breaded chicken nuggets. The specific objectives were:

1. To establish VIS/NIR-based calibration models to predict the acid value, total polar components and viscosity of different mixture of hydrogenated and non-hydrogenated oils that have gone through heating cycles.
2. To select the best wavelength regions for prediction of the heated oil quality parameters.
3. To establish VIS/NIR-based calibration models for prediction of moisture and fat contents of fried breaded chicken nuggets.
4. To select the best wavelength regions for prediction of moisture and fat contents of fried breaded chicken nuggets.
5. To test and validate the performance of each calibration model on prediction of the mentioned quality parameters.

III. GENERAL LITERATURE REVIEW

3.1 DEEP FAT FRYING

Deep-fat frying involves immersion of food in hot oil for a period of time. It is a popular food preparation technique in both industry and restaurants for being fast and convenient.

Frying temperature is usually above the boiling point of water, between 165 to 185°C (Gunstone, 2004). Heat is transferred to the food through the oil as the heat transfer medium. This leads to the moisture outflow from the food and oil absorption from the frying medium in replacement of the evacuated water.

Frying process involves physical, chemical and sensory changes in the food being fried. The rapid dehydration of the surface develops the crispy texture of the crust. Formation of the crust, fat absorption, development of flavors and surface color are the unique attributes of fried foods that are highly favored by consumers.

3.1.1 Heat transfer

Heat needs to be transferred from the oil to the food for frying to begin. This mainly occurs in convection mode and can be expressed by the Newton's law:

$$Q = hA(\Delta T) \qquad (3.1)$$

Where Q is the amount of heat energy transferred, h is the convective heat transfer coefficient, A is the contact surface area between the food and the oil, and ΔT is the temperature difference between the oil and food.

Some of the heat transferred to the surface of the food is then transferred within the food, to cook the interior part, by conduction under unsteady state conditions (Singh, 1995). The rate of conductive heat transfer depends on the thermal properties of the food including thermal conductivity, thermal diffusivity, specific heat and density. These properties are subjected to change during frying (Buhri and Singh, 1994).

3.1.2 Mass transfer

Moisture loss from the food and oil uptake into the food are the major mass transfer processes during frying. Rapid dehydration of the exterior surface of the food causes an outward migration of water from the interior portion of the food. Evaporation of water from the food surface removes off the heat from the surrounding oil and prevents excessive dehydration and burning of the surface (Blumenthal, 1991). Migration of water from the food leaves open pores through which the oil is absorbed by capillarity as a replacement process. The amount of oil uptake by the food is affected by different parameters such as the food being fried, frying conditions including time and temperature and the type and chemistry of the frying oil (Blumenthal, 1996)

The rate of mass transfer during frying is affected by frying conditions such as frying time and temperature. Gamble et al. (1987) described the mechanism of moisture loss as a transfer phenomenon taking place due to the diffusion gradient between the dry surface and wet core of the food. They reported that both moisture loss and fat uptake were closely correlated to the square root of frying time. Similar relationship between moisture loss and frying time was reported in potato slice frying (Rice and Gamble, 1989).

Bauman and Escher (1995) reported that moisture loss occurred faster at higher temperatures during deep-fat frying of potato chips. Ni and Datta (1999) also found that moisture content decreased as the oil temperature increased. Krokida et al. (2001) found that moisture content of French fries was lower when fried at higher temperatures and for a fixed temperature, moisture content decreased by time. Pedreschi and Moyano (2005) reported that higher frying temperature resulted in lower oil uptake in fried potato slices. Budzaki and Seruga (2005) reported that moisture loss and fat uptake became more intense at higher temperatures during deep-fat frying of Krostula dough. The oil content was reported higher when fried at 190±1°C than when fried at 160±1°C for the same frying time and the moisture loss rate increased as temperature increased. The authors also concluded that both moisture loss and fat uptake could be described by an empirical first-order kinetic model.

3.2 FRYING OIL

Frying oil provides an effective medium of heat transfer from the heat source to the food during deep-fat frying process (Orthoefer et al., 1996).

Repeated use of oil at elevated temperatures in the presence of moisture and air causes thermal degradation of oil. This includes oil hydrolysis, oxidation and polymerization (Clark and Serbia, 1991). The quality of frying oil has an intimate contribution to the quality of fried food (Blumenthal, 1991). Degradation of oil during frying leads to changes in the quality of the food being fried. Therefore, understanding the oil chemistry and its changes during frying is necessary to optimize the frying process and to maintain the fried food quality.

3.2.1 Oil chemistry

Fats and oils mainly consist of triacylglyceride (more than 95%) (Gunstone, 2004) which is composed of three fatty acids esterified to a glycerol molecule (Figure 3.1).

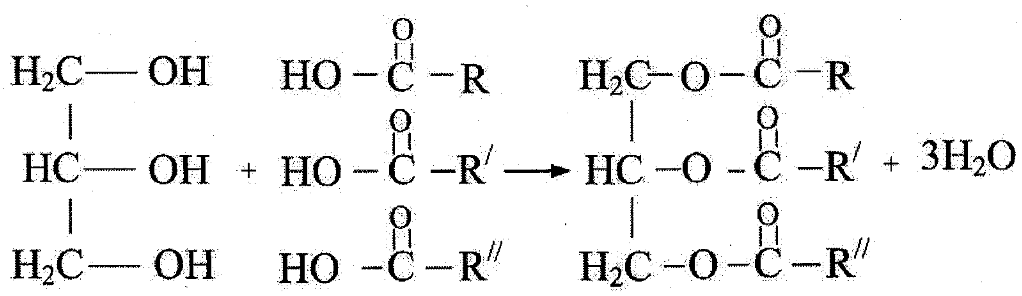

Figure 3.1 Formation of triacylglyceride from esterification of one glycerol molecule with three fatty acids.

Fatty acid is a long hydrocarbon chain with a carboxyl group at one end. Most animal and vegetable fats and oils contain fatty acids with 14 to 22 carbon atoms in their hydrocarbon chain. Properties of fats and oils depend on the type of their individual fatty acids and their level of unsaturation. Fatty acids with no double bond in their hydrocarbon chain are called saturated fatty acids. Those containing one or more double bonds are called monounsaturated and polyunsaturated fatty acids (PUFA), respectively. Saturated fatty acids have higher melting point and therefore are solid at room temperature. Fatty acids with more double bonds stay liquid at room temperature. Oils containing more unsaturation in their structure (vegetable oils) are less stable and more likely to undergo degradation.

Double bonds can be sited at different places in an unsaturated fatty acid. The position of double bonds has greater role in determining the stability of fatty acid rather than the number of them. Fatty acid molecules with closer double bonds are more unstable (Stockwell, 1988).

3.2.2 Hydrogenation of oils

Hydrogenation is a chemical reaction in processing oils and is defined as addition of hydrogen to the double bonds contained in a triacylglyceride structure. The aim of hydrogenation is to convert a liquid oil to a semi-solid (partial hydrogenation) or solid fat (full hydrogenation) and to increase the oxidative stability of frying oil. The basic hydrogenation reaction is shown in Figure 3.2.

$$\text{-CH=CH-} + H_2 \longrightarrow \text{-CH}_2\text{-CH}_2\text{-}$$

Figure 3.2 Basic hydrogenation reaction on an unsaturated carbon-carbon double bond.

The operation is usually catalyzed by nickel which is suspended in the oil during hydrogenation and filtered out at the end of the process from the oil (Hastert, 1996). When the three components of the reaction, oil, hydrogen and the catalyst, are brought together in the reactor, the reaction takes place on the surface of the catalyst where oil and hydrogen get into close contact. Temperature, agitation degree, gas (hydrogen) pressure and the amount of the catalyst are the main operation variables that affect the results of hydrogenation (O'Brien, 1998).

Hydrogenation is a very complex reaction due to isomerisation reactions during which some of double bonds are isomerised either to new positions usually to lower energy state (O'Brien, 1998) or from *cis* to *trans* isomers with higher melting points. This means that during hydrogenation, double bonds are either saturated by hydrogen or isomerised. The positional isomerisation of double bonds usually does not affect the melting point of the triacylglyceride (Dijkstra, 2002) while formation of *trans* isomers increases the melting point, allowing the oil to stay solid at lower temperatures. Formation of *trans* double bonds during hydrogenation has recently become a limiting issue in using hydrogenated oil for frying purposes due to health concerns.

3.2.3 Types of frying oil

Animal fats were primarily used as frying oil until 1986. Due to nutritional concerns, the food industry tends to use blends of vegetable and animal oils as well as partially hydrogenated vegetable oils (Moreira et al., 1999).

All variety of fats and oils including vegetable oils, hydrogenated vegetable oils, animal oils and margarines and shortenings are used for frying. However, not all frying fats and oils can be used for all purposes (Blumenthal, 1996). Selection of a suitable frying oil must be based on the process of interest, food being fried, storage and shelf life of the finished product and the cost (Podmore, 2002). A good frying oil should be low in free fatty acids (FFA), saturated and *trans* unsaturated acids and high in *cis* monounsaturated acids for nutritional reasons. Unsaturated fats are more likely to undergo oxidative degradation. Therefore, despite the nutritional value of essential polyunsaturated fatty acids, frying oil should be low in polyunsaturation to have higher oxidative stability.

The vegetable oils that are usually used for frying include soybean, cottonseed, corn, peanut, palm, olive, canola, safflower and sunflower oil. Olive oil, canola oil and peanut oil are the most widely used oils with high level of unsaturation. Canola oil and sunflower oil are usually partly hydrogenated to have higher stability during frying. Palm oil is also suitable for frying due to the high level of natural antioxidants in its composition (Moreira et al., 1999).

3.2.4 Oil degradation during frying

Complex physical and chemical changes occur during deep-fat frying leading to thermal and oxidative decomposition. The break down of oil is mainly caused by hydrolysis, oxidation and polymerization reactions that take place at high frying temperatures in the presence of oxygen and moisture which lead to physical and chemical changes in oil. Physical changes are mainly increased viscosity and foaming, color changes and decreased smoke-point. Main chemical changes are increased FFA, polar components and high molecular weight products as well as decreased levels of unsaturation, flavor quality and nutritive value (Warner, 1998). Heat (frying temperature), as a process factor affecting the oil degradation rate, accelerates the formation of FFA and polymerization reaction (Gebhardt, 1996).

Formation of volatile and non-volatile products during oil decomposition affects the functional and nutritional properties of the oil and consequently as of the food being fried. Volatile degradation products are mainly responsible for flavor development in oil and fried food.

3.2.4.1 Hydrolysis

The major chemical decomposition of the oil during frying is hydrolysis. The fatty acids are hydrolyzed off the triacylglyceride structure in the presence of moisture from the food at frying temperatures. As a result, FFA, monoglycerides, diglycerides, and glycerol are formed which will speed up the degradation of the remaining triacylglycerides by allowing greater emulsification of water from the food into the oil. However, most of the FFA produced during frying are volatilized and removed from the oil (Perkins, 1996).

3.2.4.2 Oxidation

In oxidation reactions, carbon atoms next to the double bonds in the triacylgliceride structure are oxidized by the oxygen in the air resulting in the break down of the hydrocarbon chain. This leads to the formation of volatile compounds such as short chain fatty acids, hydroperoxides, conjugated dienoic acids, aldehydes, ketones, alcohols, and other compounds that contribute to off-flavors in the oil. Hydroperoxides are unstable at high frying temperatures and decompose immediately (Perkins, 1996) to secondary oxidation products (alcohols, aldehydes and ketones) (Moh et al., 1999). Oils with higher degrees of unsaturation are more reactive with oxygen and therefore more unstable during the frying process (Gebhardt, 1996). Trace metals such as copper and iron speed up the oxidation reactions (Stevenson et al., 1984) particularly at high frying temperatures by catalising the decomposition of hydroperoxides into secondary oxidation peroxides. These metals should never be used in the frying equipment.

3.2.4.3 Polymerization

A third type of oil degradation process during frying, is the formation of cyclic monomers, dimers and polymers through polymerization. This will lead to changes in physical properties of frying oil such as color, viscosity, density and solidification characteristics. Gutierrez and Dobarganes (1988) indicated that the increase in the density and viscosity of frying oil is due to polymerization reactions. As polymerization continues, the varnish formed by the fat deposites on the metal surface of the fryer (Stauffer, 1996) decreasing its heat conductivity. Polymeric constituents are foam stabilizers and make the fat foam when the food is being fried. However, polymerization is of less importance as the other two degradation processes render the oil discardable long before polymerization affects it.

3.2.5 Quality assessment of frying oil

The quality of frying oil has an intimate effect on the quality of the fried food (Innawong et al., 2004b). Various quality attributes are used to evaluate the quality of frying oil, such as FFA content, peroxide value, color and viscosity measurements, as traditional methods, as well as total polar components, oxidized fatty acids and conjugated diens contents, as standardized methods (Orthoefer and Cooper, 1996). Common parametres that are mainly measured as indicators of frying oil degradation level are discussed in the following sections.

3.2.5.1 Total Polar Components (TPC)

Deterioration of oil during frying is usually followed by an increase in the polariy of the oil (Innawong et al., 2004b). The level of polar components is a good indicator of frying oil quality. TPC includes all newly formed compunds that have higher polarity such as oxidized triglycerides, polymerized triacylglycerides, diacylglycerides and fatty acids (Dobarganes et al., 2000). According to the AOCS official method Cd 20-91, polar components are determined by column chromatography (AOCS, 1989). The polar fraction of used frying oil is absorbed in the silica gel column and the non-polar fraction is eluted from the column by elution solvent. TPC is then determined by calculating the difference between the weight of the sample added to the column and that of the eluted non-polar fraction. TPC percentage is considered as the chemical index of oil degradation by measuring cumulative degradation products in the frying oil (Blumenthal, 1996). According to some regulations for discarding the used oil, the frying oil should be discarded when the level of TPC is 25-27% (Xu, 2003).

3.2.5.2 Free Fatty Acid (FFA)

Free fatty acids are developed during frying from both hydrolysis and oxidation reactions (Orthoefer and Cooper, 1996). The percentage of FFA usually increases with frying time and is used frequently as an indicator of the used frying oil quality. FFA is determined according to AOCS alkaline titration method Ca 5a-40 with a difficult to distinguish end point for highly dark oils. The result is usually reported as percent oleic acid. It can also be expressed in terms of acid value by multiplying the FFA% (percent oleic acid) by 1.99 (AOCS, 1989). Acid value is reported in milligrams of alkaline per gram of sample. In commercial practice the oil is usually discarded when the FFA level reaches to 1% (Tseng et al., 1996).

3.2.5.3 Peroxide Value (PV)

Peroxides are unstable products that are produced from the oxidation reactions in oil. However, there are limitations in using PV as a standard method for assessing frying oils. Peroxides are immediately destroyed at frying temperatures and decomposed to secondary oxidation products. The test itself is also very sensitive to sample temperatures (Blumenthal, 1996). Peroxide value can be determined using official AOCS iodometric method Cd 8-53 which determines all substances that oxidize potassium iodide (KI) under the test conditions and expresses the PV in terms of milliequivalents of peroxide per 1,000 grams of sample (AOCS, 1989).

3.2.5.4 Viscosity

Formation of high molecular weight compounds (dimmers and polymers) from the polymerization reactions during frying, leads to an increase in the viscosity of frying oil. Therefore, it can be considered as an indicator of the degradation level of the used oil (Tseng et al., 1996).

Vegetable oils are considered as Newtonian fluids. For a Newtonian fluid, the relationship between shear rate and shear stress is constant and equal to the viscosity (Moreira et al., 1999). This relationship is expressed by the following equation:

$$\sigma = \mu\gamma \qquad (3.2)$$

Where, σ is the shear stress, γ is the shear rate and μ is the viscosity.

Viscosity can simply be measured by various types of viscometers but since it highly depends on the temperature, a standardized temperature must be used for measurements (Orthoefer and Cooper, 1996). Viscosity is reported in Pascal seconds (Pa.s).

3.2.6 Advanced methods of frying oil quality evaluation

Traditional chemical methods for evaluation of frying oil quality involve tedious and time-consuming procedures of measuring the relevant parameters along with application of hazardous solvents. Recently, a lot of researches have been conducted to develop simplified and faster techniques to replace the traditional methods.

Tan and Man (1999) developed a differential scanning calorimetric (DSC) method to determine TPC in heated oils. Using a stepwise multiple linear regression analysis, DSC thermogram parameters were found to be highly correlated with the TPC of the heated oils with calibration R^2 values of over 0.97. Validation of calibration resulted R^2 values of over 0.95.

Benedito et al. (2002) studied an ultrasonic assessment of olive oil quality during frying by correlating the ultrasonic measurements to quality parameters. Viscosity was found to be highly correlated with velocity and attenuation with R^2 values of 0.99 and 0.96. It was also observed that due to the relation between TPC and viscosity changes, this method could be used to determine TPC. However, this method is highly sensitive to temperature changes.

Innawong et al. (2004a) studied the application of a chemosensory system to determine the frying oil quality and to differentiate among good, marginal and unacceptable oils. R^2 values of 0.87 to 0.96 were found between the quality parameters of oils and the sensor signals. The system was also capable of differentiating frying oils with different qualities. Innawong et al. (2004b) investigated the potentials of Fourier Transform Infrared (FT-IR) attenuated total reflectance to determine the frying oil quality. They found high correlations between the FT-IR spectral data and FFA (R^2 of 0.90-0.97) and PV (R^2 of 0.90 to 0.97). It was also found that using the whole spectral range of 4000-850cm^{-1}, principal component analysis (PCA) calibration could clearly identify between acceptable, marginal and unacceptable frying oils.

Visible/Near-infrared spectroscopy (VIS/NIRS) has been of vast amount of investigation on its application in fats and oils analysis as will be discussed in section 3.4.2.3. VIS/NIRS has the distinctively valuable advantage of no sample preparation requirement, over most other techniques. It was reported as a good general-purpose technique for evaluation of frying oil deterioration (Engelsen, 1997). It proved to have good accuracy on prediction of viscosity and FFA. But lack of spectral information from secondary oxidation products was reported. Current literature lacks enough exploration on the possibility of applying the VIS/NIRS in determination of heated oils quality by predicting the oil chemical index of quality (TPC) along with other relevant parameters.

The development of a multi-analytical VIS/NIRS technique for simultaneous prediction of major oil quality parameters including TPC will address this need. Also selection of wavelengths of most variation in the spectra will lead to the design of a simplified on-line instrument for frying oil quality evaluation with lower cost.

3.3 BREADED FRIED FOOD PRODUCTS

Among various types of fried food products, breaded foods are increasingly favored by consumers due to their unique textural properties such as a porous crispy crust and more desirable color and flavor. There is a wide variety of breaded food products available in the market. These include breaded chicken nuggets, fish and sea food, meat, vegetables and fruits. Breaded chicken nuggets are one of the most popular fried products.

Breading is defined as a dry mixture of flour, starch and seasonings with a coarse nature that is applied to moistened foods prior to cooking (Suderman, 1983). Breading comprises up to 30% of the weight of the food. The starch content of the breading provides a base for crust formation especially in foods with low starch content such as meats and vegetables. The breading layer functions as a barrier to reduce moisture loss from the food and consequently to reduce the oil absorption (Rao and Delaney, 1995). Breading also improves desirability of the food by enhancing the appearance of the fried product and resulting in a deep golden color upon frying. It also functions as a carrier of spices and seasonings that enhance the taste.

3.3.1 Quality properties of breaded fried foods

The main quality parameters in fried foods are sensory (appearance, flavor and texture) and nutrition parameters. These quality characteristics are determined by measuring related properties of the product such as moisture and fat contents, color, flavor and texture (Moreira et al. 1999). Moisture and fat contents are considered to be important parameters in fried food quality determination (Altunakar, 2004). Factors affecting the rate of moisture loss and fat uptake during frying are discussed in section 3.1.2.

Moisture content has a distinctive influence on the texture desirability of the fried food. Therefore, minimizing the moisture loss from the food during frying is important to maintain the fried food quality. Moisture content also has an influence on the amount of fat absorbed by the food because the oil is absorbed as a replacement to the moisture loss from the food.

Fat content is very important in fried food quality considering both textural and health concerns. A product with high oil content is oily and tasteless while a product with very low fat content has a hard and unpleasant texture (Moreira et al., 1999). Reduced-fat foods are now being increasingly demanded by consumers due to health concerns.

Moisture and fat contents of fried foods are currently measured according to traditional methods of oven drying and solvent extraction, respectively (Baumann and Eschert, 1995; Tseng et al., 1996; Altunakar et al., 2004; Baik and Mittal, 2005). Official methods mainly used are AOAC method 950.46 (oven drying) for moisture determination and AOAC method 991.39 (solvent extraction) for fat determination (AOAC, 2000). These methods involve long and tedious procedures and are destructive.

VIS/NIRS offers important advantages of being a fast and non-destructive multi-analytical technique as well as eliminating the use of hazardous solvents involved in wet chemical methods. Several studies have been undertaken on VIS/NIRS analysis of moisture and fat contents of food products as will be discussed in sections 3.4.2.1 and 3.4.2.2. However, no report was found on the application of this method on moisture and fat analysis of breaded fried foods.

Investigation of applications of VIS/NIRS technique and development of a calibration model for determination of these quality parameters can lead to a successful design of a fast on-line quality assessment technique for breaded fried foods.

3.3.2 Moisture loss and fat uptake in breaded food products during frying

As described before, moisture migration from the core to the surface of the food is done by creating voids in the food structure. In breaded fried foods such as chicken nuggets, the coating around the food provides a protective barrier that retains the moisture by enforcing the food structure against the formation of pathways for water towards the surface. This consequently results in reduced amount of fat uptake to this type of products. Ahmed et al. (1997) stated that the oil content of deep-fat fried snacks decreased with increased starch content.

Rayner et al. (2000) studied the effect of soy protein coating on the amount of fat uptake during deep-fat frying of different foods (donuts, potato disks, French fries). They reported that the fat content of coated donuts was reduced 55% on dry basis compared with uncoated donuts.

The amount of moisture loss and oil uptake in breaded foods depends on the porosity and density of the coating around the food (Suderman, 1993). The rates of both flows (moisture loss and fat uptake) are higher in foods coated with porous breading rather than those coated with dense breading. According to Suderman (1993), the coating around the food becomes more permeable to oil absorption with frying time. As the frying time passes, the oil absorption starts while the moisture outflow to the surface decreases.

Altunakar et al. (2004) studied the effect of different starch types on quality attributes of deep-fat fried chicken nuggets. They found that the highest porosity and oil content was obtained in samples containing corn starch in their coating formula. Pregelatinized tapioca starch in the coating yielded fried products with the highest moisture and lowest oil contents.

3.4 VISIBLE/NEAR-INFRARED SPECTRAL ANALYSIS OF FOODS

3.4.1 General introduction

3.4.1.1 History

The investigation of characteristics of Near-Infrared (NIR) region of the electromagnetic spectrum dates back to 1800, when William Herschel found that his thermometer registered temperatures even beyond the red portion of the visible spectrum. The importance of hydrogen bonds in producing NIR absorption was found in 1881 (Abney and Festing, 1881). The assignment of NIR spectral bands of organic compounds to specific functional groups was introduced between 1922 to 1929 (Ellis, 1929). The first NIR instruments especially for on-line measurements were introduced to market in the mid 1960s. One of the earliest on-line applications was the development of instruments for on-line analysis of flour in 1980s (Osborne, 1986; Osborne et al., 1989). Instruments with extended spectral range including the visible range (VIS/NIR) became available about 15 years ago (McCaig, 2002). This allowed for the measurement of different pigments by measuring the absorbance (reflectance) at specific wavelengths associated with the pigments (McCaig et al., 1992; Williams and Sobering, 1993). Recent advances in VIS/NIRS have enabled its applications in predicting the composition of foods. With the development of mathematical multivariate data analysis methods and the availability of high speed microprocessors, a lot of valuable information can be extracted from the VIS/NIR spectra of foods in a fast and accurate fashion.

3.4.1.2 Theory of near infrared spectroscopy

The infrared region of the electromagnetic spectrum lies from 700 to 10^6 nm which is divided into three regions, near infrared (NIR), middle infrared (mid-IR or generally referred as IR), and far infrared. Smaller wavelengths have higher energy levels. Table 3.2 shows the division and characteristic transactions of the infrared regions.

Table 3.1 Division and characteristics of infrared region (Osborne, 1993)

Region	Characteristic transactions	Wavelength range (nm)
Near infrared (NIR)	Overtones combinations	700-2500
Mid-infrared (IR)	Fundamental vibrations	$2500\text{-}5\times10^{4}$
Far infrared	Rotations	$5\times10^{4}\text{-}10^{6}$

All atoms and molecules prefer to stay in their lowest energy state which is called “ground state”. If a molecule absorbs radiation energy, it changes to an excited state and creates an absorption spectrum. The absorption of IR radiation by the covalent bonds of a molecule causes them to vibrate by stretching and bending. To cause a molecule to vibrate, an IR radiation ray should have the same frequency as the vibration frequency of that molecule.

Different kinds of bonds in a molecule exhibit different absorption bands or characteristic absorption in IR region where the fundamental vibrations occur. Each of these vibrations then raises overtones and combination bands that are observed in the NIR region of the spectrum. Knowledge of IR absorption wavelength bands for each functional group is therefore necessary to be able to locate the corresponding bands in the NIR region. The position of fundamental bands in IR region is very well defined (Bellamy, 1975). The approximation of the position of overtones can be simply done by dividing the wavelength of the fundamental vibration by 2, 3 and 4 for the first, second and third overtones (Wetzel, 1983). Strong bonds containing light atoms, specially hydrogen (the lightest atom), show their absorption bands in NIR region which mainly arise from overtones and combinations of fundamental vibration of the hydrogenic bond. These bands are broad compared with detailed structure observed in mid-IR region, since the extensive overlapping bands make it difficult to assign a band to specific groups for qualitative and quantitative purposes. However, sophisticated multivariate chemometric algorithms, which mathematically correlate spectral changes to the changes of a specific functional group, have become a powerful analytical technique.

Overtones and combination bands in NIR region are much weaker than the fundamental absorption bands. This brings the advantage of analyzing much thicker samples comparing with difficult sample preparation in IR spectroscopy. Nowadays, VIS/NIRS with the advantages of simpler and cheaper instrumentation, very less or no sample preparation requirements and easy sample handling along with the possibility of eliminating the use of hazardous solvents used in reference chemical methods is emerging as a potential tool for rapid and non-destructive quantitative analysis.

3.4.2 VIS/NIR quantitative analysis of foods

As mentioned before, near-infrared spectra of major components of food (water, proteins, carbohydrates and lipids) contain the overtones and combinations of these molecules' fundamental vibrations, particularly those involving hydrogen (Osborne, 1993), in mid-IR region. These components leave spectral fingerprints in both visible and near infrared regions that can be used for quantitative analysis of food components. Quantitative analyses are conducted by correlating changes in the VIS/NIR spectral response to changes in the concentration of the corresponding component.

3.4.2.1 Determination of water content of foods by NIRS

Pure water is documented to have five spectral bands at 1940, 1450, 1190, 970 and 760 nm at 20°C (Curcio and Petty, 1951). The bands at 1450, 970 and 760 nm are the first, second and third overtones of O-H stretching, respectively and the bands at 1940 nm and 1190 nm are combination bands of O-H stretching and bending. All these bands may be shifted due to changes in temperature and variations in hydrogen bonding when water is in a food matrix (Osborne, 1993). Also the presence of other molecules with O-H group can influence NIR absorption. Strong absorption bands of water at 1400-1450 nm and 1900-1950 nm have mainly been used for quantitative analysis of water in foods (Bunin-Pfaue, 2003).

Leroy et al. (2003) observed bands of water at 980, 1450 and 1950nm in beef *Longissimus thoracis* cuts. Alomar et al. (2003) observed that absorption bands at wavelengths of 964, 1440 and 1960 were associated to water molecules while investigating chemical analysis of bovine meat by NIR reflectance spectroscopy. Mitsumoto et al. (1991) obtained a high multiple correlation coefficient (R^2) of 0.94 and standard error of calibration (SEC) of 1.41 for water content of beef cuts with the reflectance spectral data in NIR region by developing a multiple linear regression model. Wavelengths of 1388, 1760, 2156 and 2322 nm were selected for moisture determination. Wold and Isaksson (1997) reported that moisture content of whole Atlantic salmon could be predicted with R^2 of 0.86 and SEC of 0.98% from cross validation using NIR diffuse spectroscopy. Miralbes (2003) developed partial least squares (PLS) calibration models for prediction of chemical composition of wheat by NIR transmittance spectroscopy. Moisture content of wheat could be predicted with R^2 of 0.99 for calibration set and SEC of 0.11. Validation of the calibration model resulted R^2 of 0.99 and standard error of validation (SEV) of 0.14. Moisture content of fish oils was determined by near-infrared spectroscopy using PLS regression with R^2 of 0.94 and SEC of 0.03 from cross validation and R^2 of 0.80 and SEV of 0.05 from prediction of validation set (Cozzolino, 2005).

3.4.2.2 Determination of fat/oil content of foods by NIRS

The NIR absorption bands of fats are mainly observed due to CH_2 chain of fatty acid structure. The first overtones of CH_2 are observed at 1734 and 1765 nm, while the second overtone occurs at 1200 nm and the stretch-bend combinations at 2310 and 2345 nm in the NIR spectrum (Osborne, 1993).

Mitsumoto et al. (1991) obtained a R^2 of 0.96 and SEC of 1.34 for fat content of beef cuts with the reflectance spectral data in NIR region by developing a multiple linear regression model. Wavelengths of 1350, 1534, 1978 and 2292 nm were selected for fat determination. Clark and Short (1994) studied uncooked ground beef with fat contents of 0.34-58.7%. The SEC and R^2 of calibration were reported to range between 1.62-2.38% and 0.96-0.98, respectively. The SEV and R^2 of prediction of the validation set ranged between 1.92-2.65% and 0.90-0.95, respectively. Isaksson et al. (1996) reported the R^2 value of 0.96 for prediction of fat content of ground beef (with fat content of 6% to 22%), using an on-line NIR system. Wold and Isaksson (1997) reported that fat content of whole Atlantic salmon could be predicted with R^2 of 0.87 and SEC of 1.12% from cross validation of calibration set using NIR diffuse spectroscopy. Misra et al. (2000) developed a multiple linear relationship (MLR) calibration model for determination of oil content of groundnuts. Wavelengths of 918, 928, 940, 950, 968, 975, 985, 998, 1010, 1023, 1037 and 1045 nm were used in the calibration model. Oil content was predicted with SEC of 3.54 and R^2 of 0.82 for calibration and SEV of 5.82 and R^2 of 0.86 for prediction of validation set. Leroy et al. (2003) observed bands of fat at 1200 and 1800 nm while investigating the use of NIRS for evaluation of technological and organoleptic parameters of beef *Longissimus thoracis.* Alomar et al. (2003) studied the application of near infrared reflectance spectroscopy for chemical analysis of bovine meat. Wavelengths of 928, 1760 and 2310 nm were associated to fat content. The fat content was reported to be predicted with R^2 of 0.82 and SEC of 0.44% from cross validation.

3.4.2.3 Chemical analysis of fats/oils by NIRS

Several studies have been conducted to associate the spectral bands found in the NIR region to corresponding functional groups of fat and oil constituents. NIRS has been used as a fast and reliable technique to monitor the oxidation levels in oils, to determine composition of fats and oil such as FFA and *trans* fatty acids and to evaluate the quality of oils.

Van de Voort et al. (1994) found that absorption bands between 3600 and 3400 cm^{-1} were due to an -OO-H stretching vibration and related to hydroperoxide moieties. Therefore the approximation of the overtones of these bands were at 1417-1500 nm for the first overtone and 954-1011 nm for the second overtone of the -OO-H stretching band.

Moh et al. (1999) determined PV in thermally oxidized crude palm oil by NIRS. They developed a PLS calibration model for predicting the PV based on the spectral region of 1350-1480 nm with the single-point baseline at 1514 nm. The model performed with the SEC of 0.156 and R^2 of 0.994 for the PV range of 2.17-10.28 meq/kg. Validation of the model with independent set of samples resulted the SEV of 0.17 with R^2 of 0.996.

Yildiz et al. (2002) developed PLS calibration models to predict the PV of soybean and corn oil. Validation of the model showed that for samples with the PV range of 0-20 meq/kg, a correlation coefficient of 0.99 was obtained between the reference method values and NIR predicted values with SEV of 0.72meq/kg. They found that the main changes in spectra occurred at 2068 nm as the oxidation level increased which were associated with the formation of hydroperoxides.

Fatty acid composition is considered as a very important nutritional index of fats and oils. Holman and Edmondson (1956) assigned the absorption bands at 1690, 2150 and 2190 nm to C-H bonds in cis-unsaturated fatty acids. Later, Sato et al. (1991) found that in the NIR spectra of fats and oils, the bands of *cis*-unsaturation and the carbon chain length of fatty acids appear around 1600-1800 nm. Using this region Sato et al. (1998) reported that, NIR method could estimate the ratio of linoleic acid composition in seeds of *Brassica napus* with R^2 of 0.85.

Man and Moh (1998) developed NIRS calibration models in the range of 1850-2050 nm for determination of FFA in crude palm oil and its fractions. Most variations were found to be at 1882, 2010 and 2040 nm. FFA could be predicted with calibration R^2 values over 0.97 and validation R^2 values over 0.94.

In a study of application of NIRS for estimation of fatty acid composition in oil, Sato (2002) reported that the absorption band in the region of 1600-1800 nm was shifted to shorter wavelengths when the degree of unsaturation increased and it was shifted to higher wavelengths when the carbon chain length increased.

Cozzolino et al. (2005) developed PLS calibration models for prediction of FFA content of fish oils with NIRS. FFA was determined with R^2 of 0.96 and SEC of 0.59 from cross validation and R^2 of 0.98 and SEV of 0.5 from prediction of validation set.

Li et al. (2000a) developed a PLS calibration model to determine *trans* contents of edible fats and oils using Fourier Transform near-infrared (FT-NIR) spectroscopy. They found that the optimal spectral regions for *trans* determination were 8975-7189 cm^{-1}, 5238-5056 cm^{-1} and 4779-4564 cm^{-1}, with single-point baselines at 7575, 5247 and 4800 cm^{-1}. *Trans* content of the unknown samples was predicted with the accuracy of about ±1.1 %.

Mailer (2004) developed PLS calibration models using the spectral range from 400 to 2250 nm to determine quality parameters in olive oil and reported very high accuracy for prediction of major components. Major fatty acids, oleic and linoleic acids, could be predicted with R^2 of 0.99 and 1.00. FFA and chlorophyll contents were predicted accurately with R^2 of 0.97 and 0.98, respectively.

3.4.3 VIS/NIR qualitative and discriminant analysis of foods

A large number of applications of NIRS are related to quality assessment and discriminant analysis of foods. Discrimination is done based on spectral properties of samples that belong to one of several distinct groups (Indahl et al., 1999).

Kleynen et al. (2003) applied discriminant analysis for sorting the 'Jonagold' apples using a multi-spectral vision system. Wavelengths of 450, 500, 750 and 800 nm were found to be the most efficient wavebands for apple sorting.

Uddin and Okazaki (2004) studied the application of NIRS for classification of fresh and frozen-thawed fish. Spectral data collection was done on meat juices and Principal Component Analysis (PCA) and Multiple Linear Regressions (MLR) algorithms were used for discriminant analysis. It was found that the fresh and frozen-thawed fish could be discriminated with 100% accuracy.

Two different types of bread wheat flours could be classified, according to their NIR spectra, into different quality categories using a wavelet-based feature selection/classification algorithm (Cocchi et al., 2005).

NIRS has also been used for discriminant analysis of fats and oils. Li et al. (2000b) developed PLS calibration models for discrimination between four oil types using a FT-NIR spectrometer. All four types of oils could be differentiated clearly from each other. Results of the validation test also demonstrated that the developed calibration model could clearly identify validation oil samples.

Hourant et al. (2000) built a model based on stepwise linear discriminant analysis (SLDA) to classify different types of oils and fats according to their sources. Spectral information within the regions of 1700-1800 nm and 2100-2400 nm were used for discrimination. Validation of the model with a test set demonstrated that 90% of samples could be clearly classified.

3.4.4 Mathematical modeling for NIRS analysis

3.4.4.1 General principle

NIRS quantitative method, as a secondary method of analysis, requires calibration with a set of samples of known composition (training set) to establish a correlation between the spectral information and the variation in the composition of interest. Various algorithms can be employed to develop such calibration models such as Beer's law as a simple basis for calibration and more sophisticated multivariate mathematical algorithms such as PLS and PCA.

3.4.4.2 Beer's law

The basis of quantitative analysis in absorption spectroscopy is the Beer's law, which states that the intensity of the absorption at a particular wavelength of the electromagnetic radiation is proportional to the concentration of the absorbing material and the path-length of the electromagnetic radiation through the sample. It defines a simple linear relationship between the absorbance intensity and the concentration of the component of interest. This can be shown as:

$$A(\lambda) = \varepsilon(\lambda)bc \qquad (3.3)$$

Where $A(\lambda)$ is the absorbance at wavelength λ, $\varepsilon(\lambda)$ is the molar absorption coefficient at this wavelength, b is the path-length and c is the concentration of the absorbing material. Determination of $\varepsilon(\lambda)$ can be done by measuring the absorbance of a calibration standard with known concentration of the component of interest. This coefficient for a given component at a selected wavelength is a constant. However Beer's law has limitations when concentration of more than one component varies as it does not include the contribution of more than one component to $A(\lambda)$ and can not model the interactions between components. Therefore, a variety of advanced multivariate calibration methods have been developed for the analysis of multi-component materials (Sedman, 2000) such as PLS and PCA. Multivariate techniques basically solve a series of equations by using many measurements for each sample for one calibration value and have the advantage of including more of the available spectral data.

3.4.4.3 Principal component analysis (PCA)

Principal component analysis is a multivariate spectral decomposition technique that breaks down the spectral data into its most variations. Assuming that the main variation in the calibration set spectra is due to the changes in the concentration of the components of the sample, a set of "variation spectra" are calculated that represent changes in the absorbance at all the wavelengths of the spectra and relate to the concentration of the components in a sample. This data are then used to build the calibration model instead of the raw spectral data. The original calibration spectra can be reconstructed using "variation spectra" or eigenvectors (loading vectors, principal components or factors). This is done by multiplying each eigenvector by a different scaling constant and summing the results together along with the mean spectrum until matching the original spectrum. The spectral residual is referred to the difference between the reconstructed spectrum and the original one. The scaling constants are known as scores. PCA scores represent the largest variations that are common among the entire calibration standard spectra. Scores are then regressed against the component concentration data (Thermo Galactic, 2003).

In PCA, the training data is therefore reduced to two matrices of eigenvectors (spectra) and scores (weighting values for calibration spectra). Therefore with m number of calibration training samples, p number of wavelengths used in calibration and f number of eigenvectors:

$$A = SF+E_A \qquad (3.4)$$

Here, A is the *m* by *p* matrix of absorbance values, S is the *m* by *f* matrix of scores for all the spectra, F is the *f* by *p* matrix of eigenvectors and E_A is the matrix of residual spectra.

3.4.4.4 Partial least squares (PLS)

Partial least squares is another quantitative spectral decomposition technique that is similar to PCA with the advantage that it performs the decomposition on both spectral and concentration data. This means that when the calibration training spectral data is processed with PLS algorithm, two sets of eigenvectors are generated, a set of spectral loadings representing common variation in spectral data and a set of spectral "weights" representing the changes in spectra due to the differences in concentration. Correspondingly, there will be two sets of scores, one for spectral data and one for concentration data. This means that in PLS the spectra containing higher concentration of the component(s) of interest are weighed more than those with low concentration (Thermo Galactic, 2003).

Therefore for *m* number of calibration training samples, *p* number of wavelengths used in calibration and *f* number of eigenvectors and n number of constituents :

$$A=SF_a+E_a \qquad (3.5)$$

$$C=UF_c+E_c \qquad (3.6)$$

Where, A is the *m* by *p* matrix of absorbance values, S is *m* by *f* matrix of spectral scores, F_a is *f* by *p* matrix of spectral eigenvectors, Ea is matrix of errors in absorbance, C is the *m* by *n* matrix of concentration values, U is the *m* by *f* matrix of concentration scores, F_c is the *f* by *n* matrix of concentration eigenvectors and E_c is the matrix of concentration errors.

Validation of a PLS calibration model is performed by "leave-one-out" cross-validation technique where the same spectra used as training set are predicted back against same model. This means that with *m* number of calibration training samples, the calibration is performed *m*-1 times, predicting the *m*th training sample as an unknown sample (Sedman 2000). The prediction residual error sum of squares (PRESS) is calculated as a function of the squared difference between the predicted and known concentrations from cross validation test and is plotted against the number of factors (Figure 3.3). This plot continues to fall until at some point it starts to flat out. This point can be used as a simple way of determining the best number of factors in PLS calibration models.

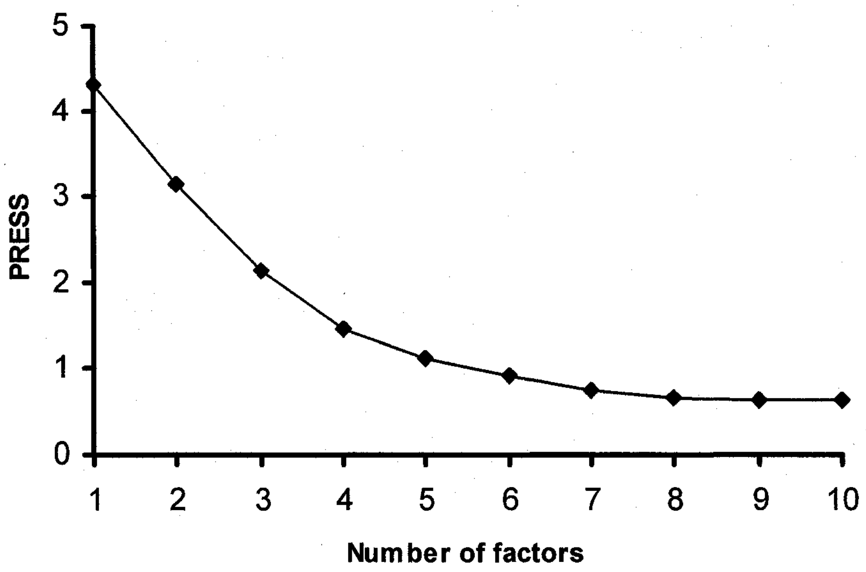

Figure 3.3 A typical PRESS plot from leave-one-out cross validation of a PLS calibration model.

3.4.5 Selection of suitable spectral regions

Factor analysis-based models such as PLS and PCA give the advantage of using a large number of data points by selecting the whole wavelength range of the training set spectra. However, reducing the number of data points by eliminating useless regions can improve the calibration performance and reduce the time for calibration calculations.

Several criteria are used to select suitable spectral regions for calibration. One method is to use "correlation spectrum" for each constituent of interest. Correlation spectrum is created by calculating the correlation between the absorbance/reflectance values at each wavelength with the concentration of the constituent of interest. Moh et al. (1999) used correlation and variance spectra for selection of spectral regions for calibration development to predict PV in thermally oxidized crude palm oil by NIRS.

Another method is to use "linear correlation coefficient" known as "Beta coefficient" in PLS algorithm. The plot of Beta coefficient shows the importance of each wavelength in the calibration model and indicates the regions that are correlated to the concentration of the constituent of interest. It also provides the type of correlation. Positive value of Beta coefficient at a wavelength indicates that an increase in the concentration of the constituent increased the absorbance while a negative value indicates that an increase in the concentration of the constituent decreased the absorbance at that wavelength. Maghirang et al. (2003) used PLS beta coefficient to identify important wavelength bands to detect presence of internal insects in wheat kernels. Perez-Mendoza et al. (2003) used PLS beta coefficient to find important wavelengths used by PLS to classify flours with and without insect fragments.

Other criteria have also been reported by other authors to be used for selection of suitable wavebands. Ventura *et al.* (1998) used the multiple linear regression (MLR) procedure to select the best wavelengths for determination of soluble solids in apple.

Uddin and Okazaki (2004) used MLR procedure to find the wavelengths that had the most contribution to calibration models for classification of fresh and frozen-thawed fish by NIRS.

Miralles *et al.* (2000) used linear regression analysis for selection of suitable wavelengths to determine the ratio of whey protein to total protein in ultra high temperature (UHT) milk.

Goel (2003) used maximum R^2 (MAXR) criterion with PROC REG program of SAS software to choose best models for estimations of various crop biophysical parameters. MAXR criterion finds the best one-variable model, two-variable model, three-variable model and so on which produce highest R^2 values. It begins by finding the best one-variable model. Then a second variable is added to the model that produces the highest increase in the R^2 to build the two-variable model. The best two-variable model is then found by removing one variable in the model and one by one replacement of all other variable not in the model until it produces the highest R^2. This process is called “compare-and-switch”. This procedure continues to build the best three-variable model and four-variable model and so on.

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IV. EVALUATION OF FRYING OIL QUALITY USING VIS/NIR HYPER-SPECTRAL ANALYSIS

4.1 ABSTRACT

Traditional chemical methods of analyzing frying oil quality are time-consuming and not amenable to on-line measurements. The main objective of this study was to evaluate frying oil quality based on visible/near infrared spectral analysis using a hyper-spectroradiometer. The reflectance spectra of the heated oils were collected within the range of 350 to 2500 nm. Acid value, total polar component, and viscosity of oil samples were used as indicators of different quality levels of oil. Partial Least Squares (PLS) calibration models were developed for quantitative evaluations of these parameters. The R^2 and Root Mean Square Error (RMSE) for each prediction were calculated to assess the prediction capability of each calibration model. The study demonstrated that using the established calibration models, quality parameters could be predicted with R^2 values over 0.92.

4.2 INTRODUCTION

Fried food industry is one of the largest industries in North America. Deep fat fried products are popular due to their unique flavor and texture characteristics. During frying, oil is subjected to prolonged periods of heating at high temperatures of about 180°C in the presence of air and water. This leads to a wide range of complex chemical reactions categorized as thermal oxidation, hydrolysis, and polymerization. Undesirable constituents and off-flavors are developed in the frying oil due to these chemical reactions (Innawong et al., 2004a). Also, the build-up of oxidation by-products results in rubbery, formation of hard-to-clean film on the frying surfaces. This diminishes heat transfer rate of frying equipment. Therefore, the quality and stability of the frying oil are critical factors to keep high quality fried products.

The rate of oil degradation during frying is influenced by several factors including the temperature of frying, exposure to air, stability of the oil against oxidation, and the moisture content of the fried food (Orthoefer, 1988). The frying industry is constantly seeking for new frying oils that are stable and impact desired characteristics to fried products. Thermal stability of the frying oil is related to the level of hydrogenation. The oxidative stability of the frying oil will increase with increased degree of hydrogenation. Thus, hydrogenated oils are widely used in the industry. However, during the hydrogenation process *trans* fatty acids are generated which, are associated with increased risk of hazard to human health. This fact has become a major concern for the use of hydrogenated oil in the fried food industry. Recently, as an alternative to hydrogenated frying oil, partially hydrogenated oils with less degree of unsaturation are increasingly adopted.

Degradation of oil during frying is followed by changes in free fatty acid (FFA) level, color, and viscosity, and by an increase in the number of polar molecules as a result of thermal and oxidative breakdown of the hydrocarbon chain in the oil (Innawong et al., 2004b). It is vital that the quality of frying oil is monitored closely in order to maintain appropriate quality of frying oil and fried food. Some food service restaurants evaluate oil quality from subjective parameters such as visual and odor characteristics (Moreira et al., 1999).

Traditional methods for evaluation of thermally degraded oil quality (physical and chemical) such as measurement of total polar compounds (TPC), FFA, carbonyl value, and viscosity, are tedious, time consuming, and not amenable to on-line measurements. Highly increasing consumption of edible oils in deep-fat frying industry entitles the need for rapid, accurate, and cost-effective techniques of oil quality control.

Many studies have been done to investigate potentials of spectroscopic methods to determine quality parameters in edible oils, such as determination of trans content and peroxide value of edible oil using Fourier Transform near-infrared spectroscopy (FT-NIR) (Li et al., 2000a; Li et al., 2000b). Innawong, et al. (2004a) established a method using the whole spectra within the range of

4000-850 cm^{-1} with a FTIR attenuated total reflectance spectroscopy (FTIR-ATR) to differentiate among good, marginal, and unacceptable oils.

Near infrared spectroscopy instruments are widely used for quality control in food industry for their being fast and non-destructive, eliminating the use of hazardous reagents and solvents and offering more flexible sample handling (Li et al., 2000c).

The goal of this study was to investigate the application of visible and near infrared spectroscopy (VIS/NIRS) for quantitative evaluation of quality parameters of different mixtures of hydrogenated and non-hydrogenated oil that have gone through heating cycles. The specific objectives of this study were:

1. To establish calibration models to predict acid value, total polar components (TPC) and viscosity of heated oils.
2. To select the best wavelength regions for prediction of the three quality parameters, and
3. To test and validate the prediction accuracy of the developed calibration models.

4.3 MATERIALS AND METHODS

4.3.1 Oil sample preparation

Hydrogenated and non-hydrogenated canola oils were obtained locally. The hydrogenated and non-hydrogenated oils were blended in the ratios (w/w %) of 0:100 (i.e. non-hydrogenated oil), 40:60 and 80:20 to form three mixtures of oil samples for the study. All the oil samples were heated at 190°C in a domestic fryer on a 9 hrs per day cycle for a total time of 72 hrs. Temperature of the fryer was controlled using a temperature controller (Model 689000-01, Eutech Instrument Pte Ltd., Singapore). Samples of 200 ml were collected at the end of the daily heating cycle and kept at 4°C before they were used for chemical analysis and spectral collection.

4.3.1 Chemical tests

Three major quality parameters of each oil sample, total polar compounds (TPC), acid value, and viscosity, were measured and used as indicators of oil quality.

The TPC of the samples was determined according to the AOCS official method, Cd 20-91, by column chromatography (AOCS, 1989). The efficiency of fractionation was assessed by the thin layer chromatography and results were reported in percentage of polar compounds (m/m).

Acid value of samples was measured according to the AOCS official method, Cd 3a-63, by alkaline titration. The acid value was reported in milligrams of KOH per gram of sample (AOCS, 1989).

Viscosity of samples was measured using a controlled stress/shear rheometer with coaxial concentric cylinder with a built-in peltier plate (Advanced rheometer, AR 2000, TA Instruments Inc., Leatherhead, UK) at 40°C. Viscosity readings were reported in Pa.s.

4.3.3 Spectral collection

Spectral data were collected using a portable hyper-spectroradiometer (FieldSpec® Pro, Analytical Spectral Devices, Boulder, Colorado, USA), which measured reflectance spectra in a wavelength range of 350-2500 nm with a spectral resolution of 3 nm.

During spectral measurement, a petri dish filled with 40 ml oil sample was placed underneath the fiber bundle of the FieldSpec® Pro with a distance of 20 cm. The distance was calculated based on the field of view (FOV) of 18° of the fiber bundle. A DC regulated fiber-optic illuminator (Fiber-Lite PL900-A, Dolan-Jenner Industries Inc, MA, USA) was used as the light source. Two fiber-optic light-guiding branches were mounted on a test frame to guide light to the sample. Figure 4.1 shows the test platform for spectral data collections.

Light reflected from the sample was collected by the fiber-optic bundle and sent to the FieldSpec® Pro for intensity measurement. A white reference panel with approximately 100% reflectance across the entire spectrum was used as a reference standard. At each wavelength reading, a ratio between light intensities from the sample and the white reference was calculated. The View Spec Pro software (Analytical Spectral Devices, Boulder, Colorado, USA) was used for instrument control and computation. All spectra were recorded and stored in a PC. The spectral range of each spectrum was 350-2500 nm. The reflectance was normalized so that the values were within the range of 0 to 1.

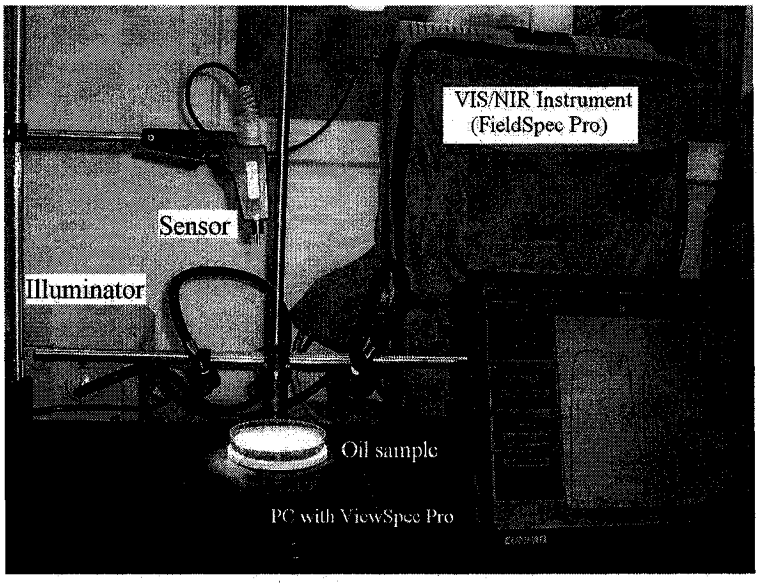

Figure 4.1. Experimental set up for spectral data collection.

4.3.4 Calibration and data analysis

Spectral analysis was conducted using GRAMS/AI 7.02 (Thermo Electron Corp., Salem, NH). All the spectra were truncated to a range of 400-1750 nm to remove the noise bands that were observed within the range of 350-400 nm and 1750-2500 nm. Out of a total number of 54 spectra, 36 were randomly selected to form a training set and were used to develop Partial Least Squares (PLS) calibration models. The remaining 18 spectra formed a validation set to verify the prediction capability of the calibration models.

PLS calibration method was used to decompose the spectra into a set of "variation spectra" that represented changes in reflectance within the spectral range. PLS performs the decomposition on both spectral and targeted parameter(s) simultaneously, so that the calibration models established are related directly to the parameters of interest. In this study, three parameters, acid value, viscosity, and total polar compounds of the oil samples, measured with the chemical analysis, were used as "constituent" data, and the spectra were used as the "spectral" data for training set. These spectra were preprocessed by mean centering and automatic baseline correction (Thermo Galactic, 2003). Mean centering is the process of calculating the average spectrum of the training set spectra and then subtracting the average spectrum from each individual spectrum. Same procedure is performed on the concentration values of each constituent. This enhances the difference between samples in both spectral and constituent data by removing the mean from the data. Automatic baseline correction was chosen to remove the baseline effects from the spectra. The PLS procedure yielded the calibration model, the optimal number of factors used in the calibration model, the significant wavelengths for predicting the constituents, and the predicted constituent for each sample in the training set.

Calibration models were established to predict each parameter using the whole range of the spectra. The optimal number of factors for establishing the calibration model was determined by the predicted residual error sum of squares (PRESS). The number of factors with the minimum PRESS value was considered the optimal. Beta coefficients were used to find the significant wavelength ranges (at peak or valley in the PLS Beta Coefficients plot) to predict the constituent of the interest in an oil sample. Eliminating the useless regions, with no or very less contribution to the calibration model, would simplify the performance of the calibration and reduce the time for calibration calculation. Also selected wavelength regions can be used as a basis to design on-line systems with less cost. The terms calibration factors, PRESS, and beta coefficient are described in details in sections 3.4.4.3., 3.4.4.4 and 3.4.5 in literature review. Concentration residuals, the difference between the actual and predicted concentration for samples, were used for outlier detection in a training set. The best calibration model was chosen with the highest R^2 values for the predicted constituents versus actual constituents obtained from cross validation. The Root Mean Square Error (RMSE) for both training and validation set were calculated for each constituent to evaluate prediction performance of the calibration model.

4.4 RESULTS AND DISCUSSIONS

4.4.1 Chemical analysis results

Figures 4.2, 4.3 and 4.4 show changes in acid value, viscosity and TPC%, respectively, during heating for three types of oil samples, namely non-hydrogenated (0:100), 40% hydrogenated (40:60) and 80% hydrogenated (80:20). For fresh oil sample, the average initial (fresh) acid value was 0.1 mg KOH/g fat, whereas the average viscosity and TPC values were about 36 mPa.s and 6%, respectively. The viscosity, TPC and acid values were in the typical range reported for fresh good quality vegetable oils (Danowska-Oziewicz and Karpiska-Tymoszczyk, 2005; Benedito et al. 2002; Goburdhun and Jhurree, 1995). Values of the quality parameters increased with heating time, indicating increased oxidation and polymerization. Quality of the non-hydrogenated oil changed more rapidly, as expected, compared to the oils with higher degrees of hydrogenation. This is attributed to the higher content of unsaturated fatty acids in the non-hydrogenated oil resulting higher oxidation during heating. Based on regulations of most countries, frying oil that has gone through heating cycles should be discarded when its TPC value reaches 25% (Benedito et al., 2002). Results of chemical analysis demonstrated that the 0:100 and 40:60 oils reached the 25% TPC level within the 72h of frying at 190°C used in this study. This would have occurred at even shorter time if the oil was used for frying foods. Therefore, in this study, different levels of oil quality from fresh to discardable stage, were generated. This would justify the applicability of the results of this study for quality determination of oils that have been used for frying foods.

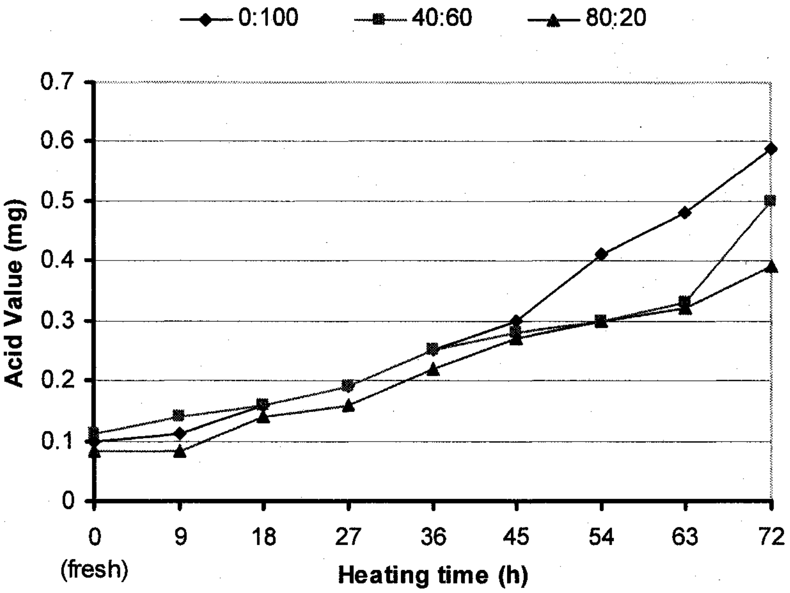

Figure 4.2 Changes in acid values of three types of oil samples with different degrees of hydrogenation during heating.

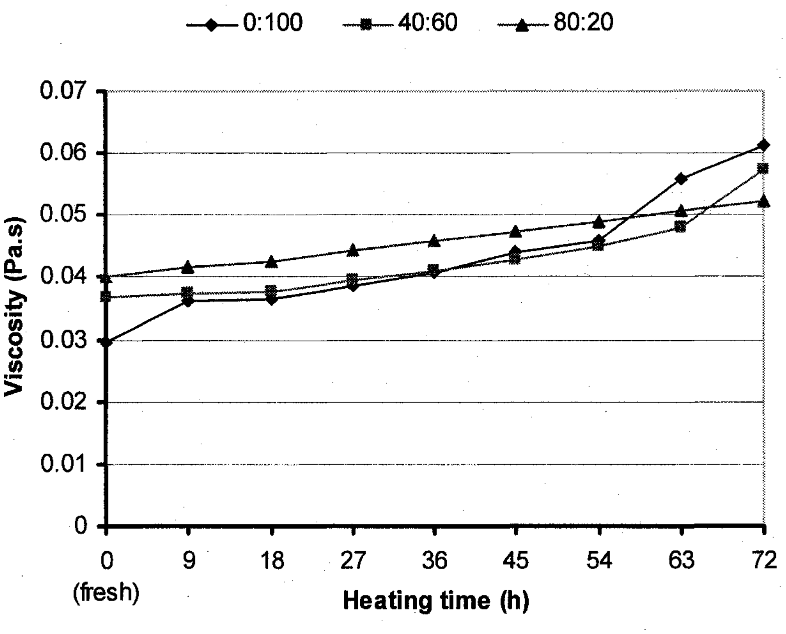

Figure 4.3 Changes in viscosity of three types of oil samples with different degrees of hydrogenation during heating.

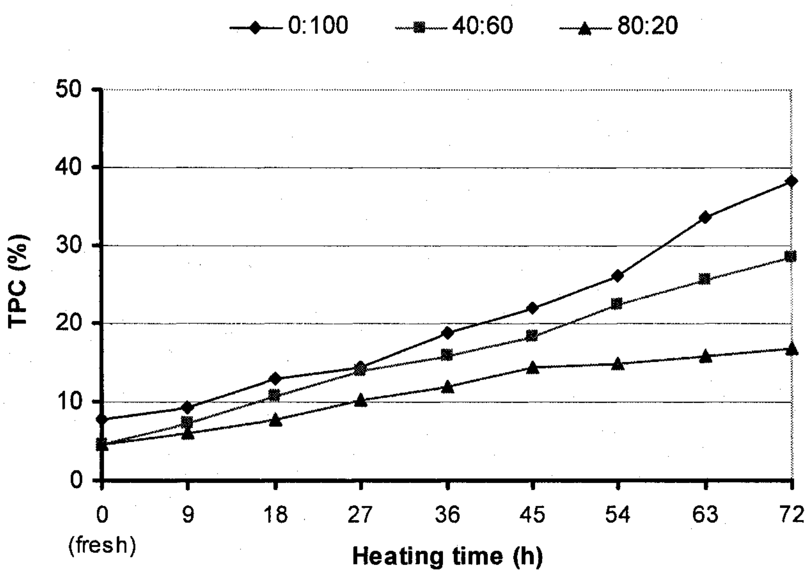

Figure 4.4 Changes in TPC% of three types of oil samples with different degrees of hydrogenation during heating.

4.4.2 VIS/NIR calibration results

Figure 4.5 shows a reflectance spectrum of non-hydrogenated (0:100) canola oil within the range of 400-1750 nm. The differences among the reflectance spectra of three types of oil samples were small and hard to be differentiated visually, except those in visible range (400 – 700 nm) due to color changes of the oil samples during heating.

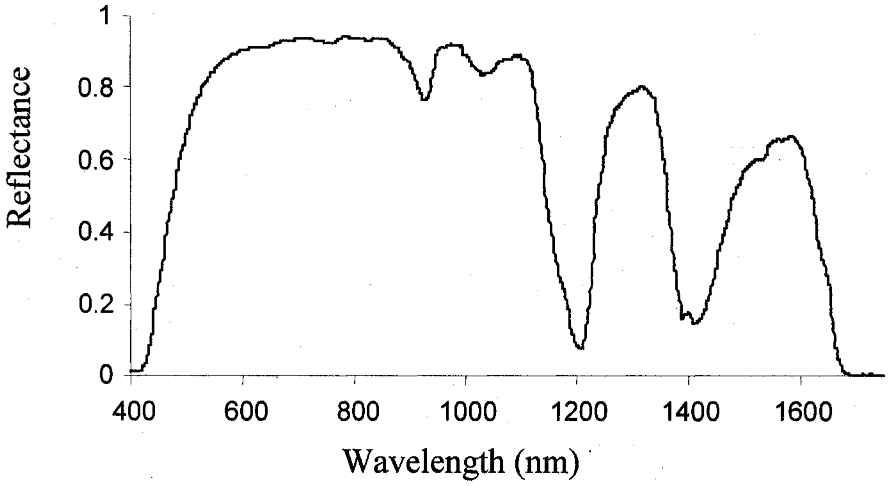

Figure 4.5 A reflectance spectrum of non-hydrogenated (0:100) canola oil within the range of 400-1750 nm

Model 1: Calibration model using the whole spectral range 400-1750 nm.

PLS calibration models were established to predict acid value, viscosity, and TPC with the number of factors of 9, 8, and 8, respectively. Figure 4.6, 4.7 and 4.8 show the PLS cross-validation results of the model. The acid value was predicted with a R^2 of 0.95 for the training set and RMSE of 0.0042 and 0.0111 for the training and validation sets, respectively. The viscosity was predicted with a R^2 of 0.92 for the training set and RMSE of 0.0005 and 0.0007 for the training and validation sets, respectively. The TPC was predicted with a R^2 of 0.98 for the training set and RMSE of 0.308 and 0.755 for the training and validation sets, respectively.

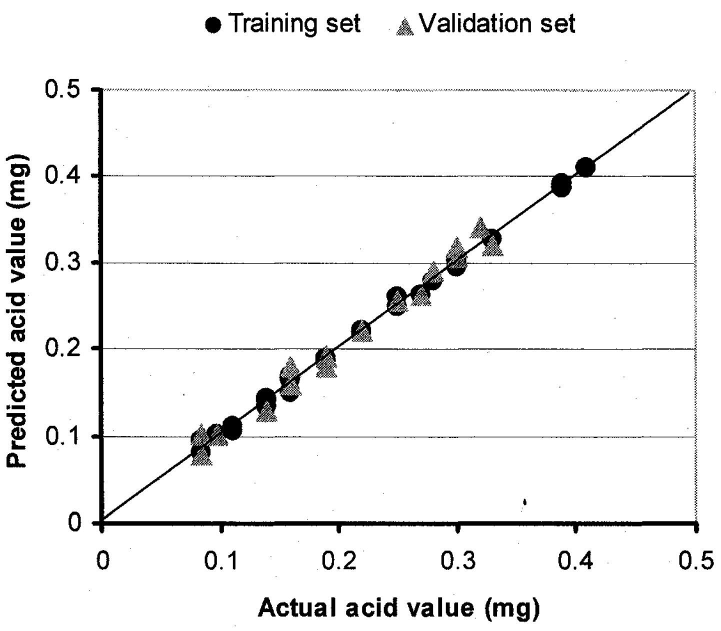

Figure 4.6 Predicted acid value vs. actual acid value, obtained from chemical test, for the training and validation sets.

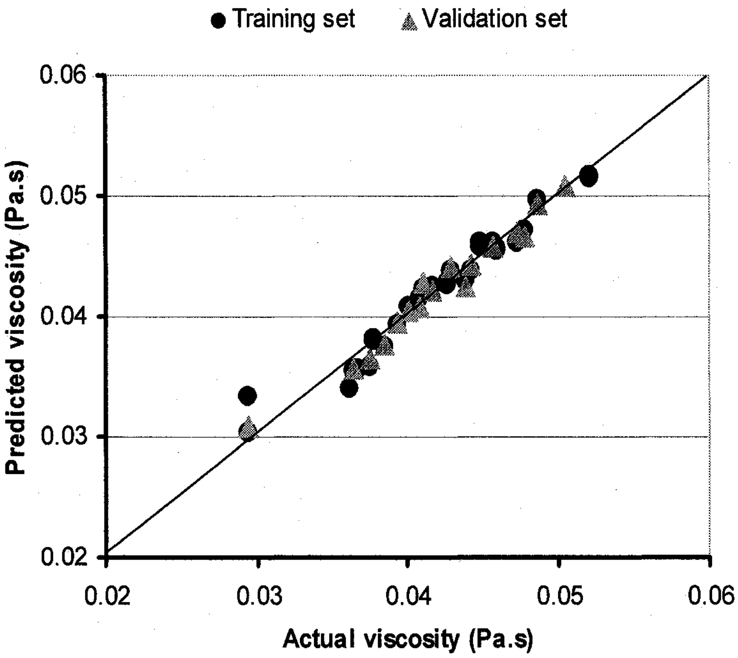

Figure 4.7 Predicted viscosity vs. actual viscosity, obtained from the rheometer, for the training and validation sets.

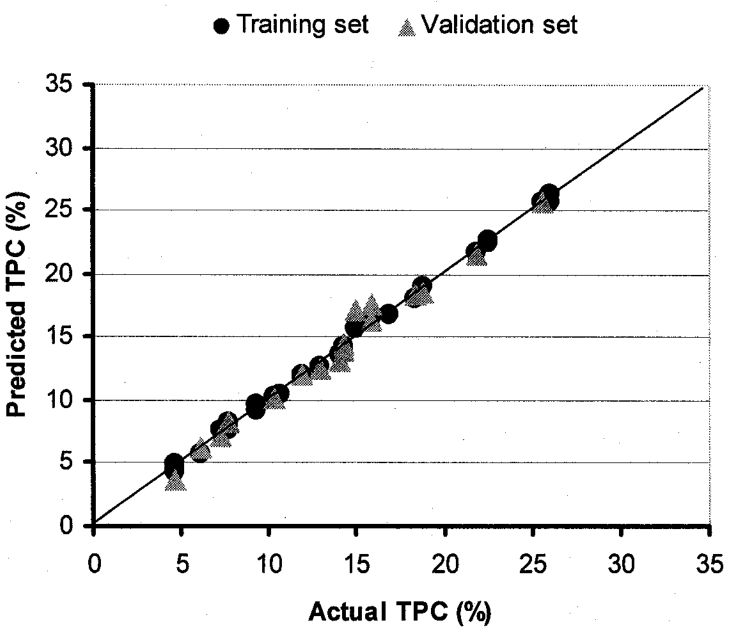

Figure 4.8 Predicted TPC vs. actual TPC, obtained from the chemical test, for the training and validation sets.

Model 2: Calibration models using the feature wavelength ranges

Based on PLS Beta coefficient plot for each constituent, the common spectral regions of the most variations (named, feature wavelength ranges) were found in ranges of 450-550, 850-950, 1140-1180 and 1200-1300 nm.

Variations in the visible region could be due the color changes in oils heated for different times. Lankmary et al. (2004) studied the region of 410-445 nm for classification of two categories of pumpkin seed oil according to their quality, namely accepted and rejected oil. Acceptable oils had higher peaks at 418 nm and lower peaks at 434 compared to rejected oils.

The second overtone of C-H stretching in various chemical groups such as –CH2, –CH3 and HC=CH is observed in the region of 1100-1300 nm (Hourant et al., 2000). The bands around 1180 nm have been assigned to the C-H stretching overtone in HC=CH structure of pure fatty acids containing *cis* double bonds (Sato et al., 1991). The region of 9100-7560 cm^{-1} (about 1098-1322 nm) was reported to contain information about the degree of unsaturation and was used for quantitative determination of Iodine value of edible oils (Li et al., 2000c). Li et al. (2000a) related the region of 8975-7189 cm^{-1} (around 1114-1391 nm) to the *trans* content of edible oils. The bands of C=O also appear at around 900 nm. The observed variations on PLS Beta coefficient plot within the selected wavelength ranges may be explained by the fact that the C=C bounds break down during thermal degradation of oil and *cis* double bonds transform to *trans* double bonds. Oxidation products with C=O group in their structure also form as a result of thermal oxidation.

Second calibration model was established using the reflectance within the feature wavelength ranges. With the similar procedures of previous calibrations, the cross-validation results for predicting acid value, viscosity, and TPC for three types of oil samples were shown in Figures 4.9, 4.10, and 4.11, respectively. Using the training set, the acid value, viscosity, and TPC were predicted with R^2 of 0.93, 0.93 and 0.92, and RMSE of 0.0190, 0.0011, and 1.403, respectively. The RMSE of the validation sets for the acid value, viscosity, and TPC were 0.0183, 0.0008, and 1.313, respectively.

Table 4.1 lists the calibration models developed and corresponding cross-validation results for predicting three constituents.

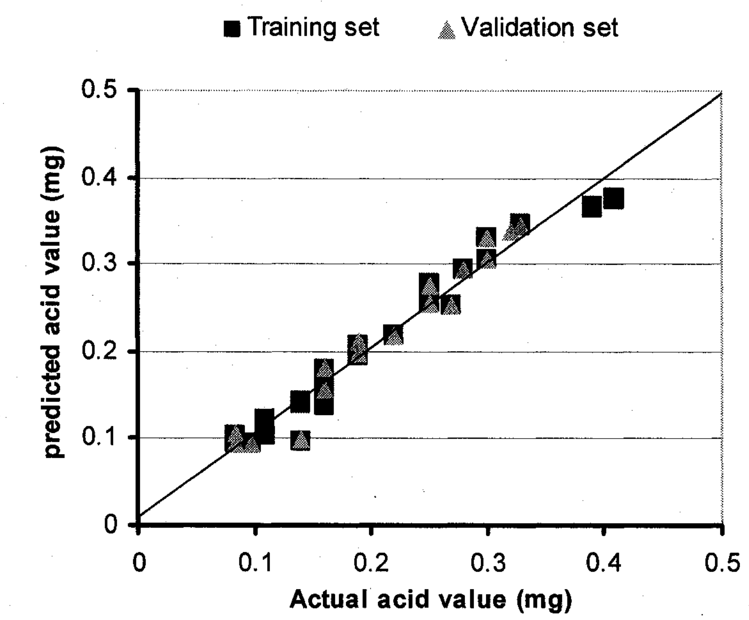

Figure 4.9 Actual acid value obtained from chemical test vs. predicted acid value by the PLS calibration model for training and validation sets within the selected wavelength ranges.

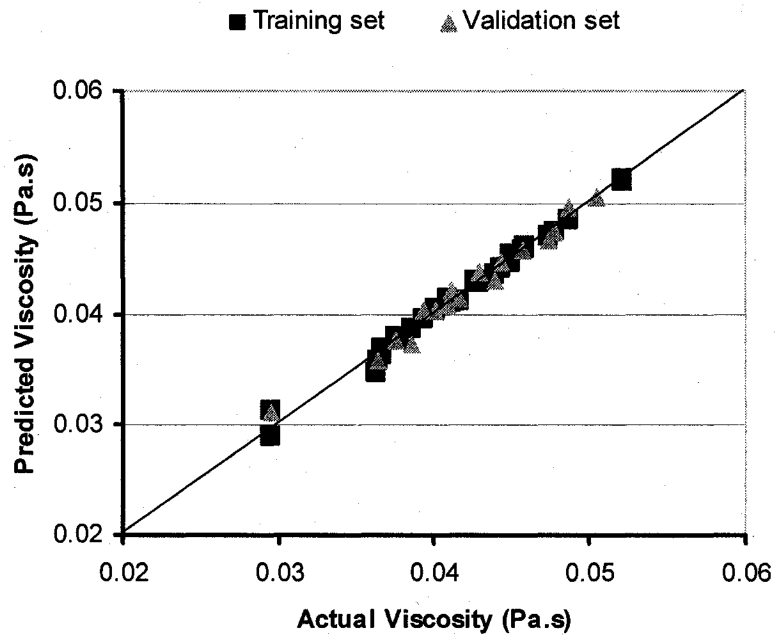

Figure 4.10 Actual viscosity obtained from the rheometer vs. predicted viscosity by the PLS calibration model for training and validation sets within the selected wavelength ranges.

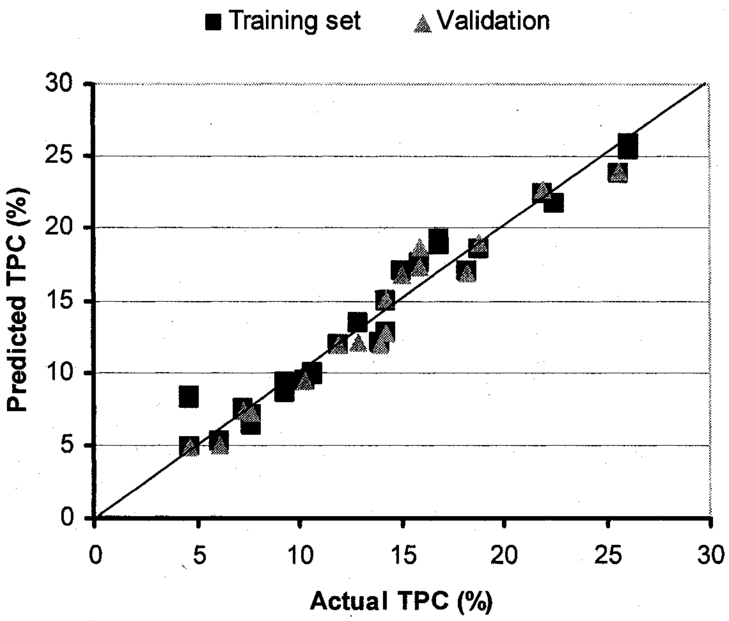

Figure 4.11 Actual TPC obtained from chemical test vs. predicted TPC by the PLS calibration model for training and validation sets within the selected wavelength ranges.

Table 4.1 Summarized results of PLS calibration models

Calibration model	Training set						Validation set			Number of Factors		
	R^2			RMSE			RMSE					
	AV*	VI**	TPC***	AV	VI	TPC	AV	VI	TPC	AV	VI	TPC
Model 1	0.95	0.92	0.98	0.0042	0.0005	0.308	0.0111	0.0007	0.755	9	8	8
Model 2	0.93	0.92	0.92	0.0190	0.0011	1.403	0.0183	0.0008	1.313	4	4	4

* Acid value
** Viscosity
*** Total polar component

4.5 CONCLUSIONS

The results of this study show that the spectral reflectance response of oils in visible and near infrared regions with fine resolution can be used to evaluate the three quality parameters (acid value, TPC, and viscosity) of heated oils.

Developed calibration model using the wavelength range of 400 – 1750 nm could track the changes in three major quality parameters of heated oils with high accuracy. R^2 values obtained from the calibration model were 0.95 for acid value, 0.91 for viscosity and 0.98 for TPC.

Four feature wavelength ranges, 450-550, 850-950, 1140-1180 and 1200-1300 nm, can be used as a basis to design on-line oil quality evaluation system.

VIS/NIR spectroscopy proved to be a useful and fast technique with the capability of simultaneous prediction of heated oil quality parameters. Once the calibration model is developed, the whole analysis can be done in few minutes.

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CONNECTING TEXT

Once the calibration models were developed for quantitative evaluation of frying oil quality indicators, the next step was to investigate the potentials of VIS/NIR reflectance spectroscopy for determination of moisture and fat contents in fried breaded chicken nuggets. In this study, calibration models for prediction of moisture and fat contents of fried breaded chicken nuggets were developed for prediction of the two parameters in both the crust portion and the total chicken nugget sample. The assumption was that due to the relationship between the crust moisture and total moisture content and also between the crust fat content and total fat content, VIS/NIRS calibration models could be developed to predict the total moisture and fat contents based on the readings from the crust portion.

V. PREDICTION OF MOISTURE AND FAT CONTENTS OF BREADED-FRIED CHICKEN NUGGETS USING VIS/NIR HYPER-SPECTRAL ANALYSIS

5.1 ABSTRACT

Moisture and fat contents are two important parameters in quality evaluation of fried chicken nuggets. This study was undertaken to evaluate moisture and fat contents of fried breaded chicken nuggets using VIS/NIR hyper-spectroscopic technique. Breaded nugget samples were fried for different times in hydrogenated canola oil in order to obtain various levels of moisture and fat contents. Reflectance spectra of samples were collected within the range of 400-1750 nm using a spectroradiometer. Partial Least Squares (PLS) calibration models were developed for quantitative evaluation of the two parameters. The R^2 and Root Mean Square Error (RMSE) for each prediction were calculated to assess the prediction capability of the model. R^2 values of 0.92were obtained from cross-validation of calibration for total moisture and fat contents. Validation of the calibration resulted in RMSE of 0.105 for moisture content and 0.017 for fat content predictions.

5.2 INTRODUCTION

Deep-fat frying is considered as one of the most common food preparation operations in the world. Among various types of fried food products, breaded foods are favored by consumers because of their unique textural properties provided by a soft and moist core coated with a crispy crust, along with more desirable color, flavor and nutritive value (Antonova et al. 2003).

During frying, simultaneous heat and mass transfer within and around the food causes various complex physical and chemical changes (Baik and Mittal, 2005). Water is transferred from the food into the frying oil, while the oil is absorbed as a replacement. Due to health concerns and consumers' increasing demands for reduced-fat foods, oil content of fried food has become an important factor in determining quality of fried food. It is also desirable to minimize moisture loss from fried food during frying in order to maintain textural characteristics of the final fried product (Ngadi et al., 1997). It has been reported that the rates of moisture loss and fat uptake depended on the conditions of frying process such as frying temperature and time. Higher frying temperature was found to lead to a faster moisture loss rate (Budzaki and Seruga, 2005). At higher temperatures, a faster crust formation leads to a higher fat absorption for the same frying time (Moreira et al., 1999). However, higher frying temperature may require reduced frying time resulting in lower final fat content of product (Baumann and Escher, 1995). The ratio of food weight and frying oil volume also affects the amount of fat absorption (Moreira et al. 1999). Therefore, in order to optimize the frying process and to improve the quality of fried food, a fast and reliable method for determination of moisture and fat contents of the fried products is needed.

Moisture and fat contents are traditionally measured using the oven drying and solvent extraction methods (AOAC, 2000) with tedious and long procedures. Near-Infrared spectroscopy (NIRS) as an alternative to the time consuming and destructive traditional methods, offers important advantages in food analysis. It is a multi-analytical technique which enables fast and simultaneous measurement of several parameters and has potentials in on-line food analysis. In contrast with chemical methods, NIRS eliminates the use of hazardous solvents and reagents (Buning-Pfaue, 2003). Successful applications of VIS/NIR spectroscopy for analysis of water and fat contents in food have been reported in the past two decades. Togersen et al. (2003) developed an on-line NIR spectroscopic technique for prediction of chemical composition of semi-frozen ground beef such as moisture and fat. Alomar et al. (2003) investigated the prediction ability of NIRS for chemical compositions of raw beef meats. Anderson and Walker (2003) also studied the application of on-line VIS/NIR spectroscopy to determine the fat content in ground beef stream and reported a high accuracy with standard error of prediction (SEP) of 1.00-1.68% for calibration and 2.15-2.28% for validation.

The goal of this study was to develop a rapid VIS/NIR spectroscopic technique to determine moisture and fat contents of fried chicken nuggets. The results can lead to a successful design of an on-line quality assessment technique for chicken nugget products. The specific objectives of this study were:

1. To investigate the potentials of VIS/NIR reflectance spectroscopy for determination of moisture and fat contents in breaded-fried chicken nuggets.
2. To develop calibration models with the highest precision and reliability for determination of moisture and fat contents.
3. To select the best wavelength bands to predict fat and moisture contents, and
4. To test and validate the calibration models' performances on moisture and fat contents prediction.

5.3 MATERIALS AND METHODS

5.3.1 Sample preparation

Frozen breaded chicken nuggets were obtained locally and kept frozen at -18°C until being used. Chicken nuggets with similar size and shape were selected as test samples for the experiment. The average weight of samples was 21.3 g. Frozen chicken nugget samples were thawed at room temperature (22 °C) for 30 mins before frying.

5.3.2 Frying

Chicken nugget samples were deep fried in hydrogenated canola oil using a domestic fryer at 180±2°C. A temperature controller (model 689000-01, Eutech instrument Pte Ltd., Singapore) was connected to the fryer to control the frying temperature. Fresh oil was preheated for 2 h before frying the samples. The chicken nugget samples were deep fried one by one to minimize temperature fluctuation during frying. In order to obtain different levels of moisture and fat contents, the chicken nugget samples were fried for 1, 2, 3 and 6 mins. These frying times were used as the basis for grouping the samples. Twelve samples were collected at each frying time. The fried samples were kept to cool down to room temperature before the spectral reading. Spectral reflectance of all the samples was recorded. Six samples were then randomly selected and grouped for the measurement of moisture and fat contents of the crust part of the chicken nugget namely, crust moisture and crust fat content. The remaining 6 samples were grouped to be used to measure moisture and fat contents of the whole chicken nugget namely, total moisture and total fat content.

5.3.3 Spectral collection

Hyper-spectral reflectance data was acquired using a portable hyper-spectroradiometer (FieldSpec® Pro, Analytical spectral devices, Boulder, Colorado, USA) within a range of 400-1750 nm. Detailed specifications of the instrument were explained in Chapter 4. A fried chicken nugget sample was placed at a fixed distance of 10 cm underneath the detector of the spectroradiometer (Figure 5.1). The distance was determined based on the field of view of the detector (18°C) and the size of the samples. From each sample, three spectral reflectance readings were collected at three different spots of the front side and three other readings from the back side of the sample. Therefore, for each sample, six spectra were collected. Data acquisition process was controlled by the ViewSpec Pro software (Analytical spectral devices, Boulder, Colorado, USA) and the collected spectra were stored for further analysis. Spectral data were grouped based on the frying time, including 36 spectra in each group obtained from six samples. Figure 5.2 shows the procedures of grouping the samples and the corresponding spectra. After spectral data collection, the crust portion of samples assigned for crust moisture and fat analysis was separated for determination of crust moisture and crust fat contents. For the rest of the samples, assigned for total moisture and fat analysis, the whole chicken nugget was used to determine the total moisture and total fat content.

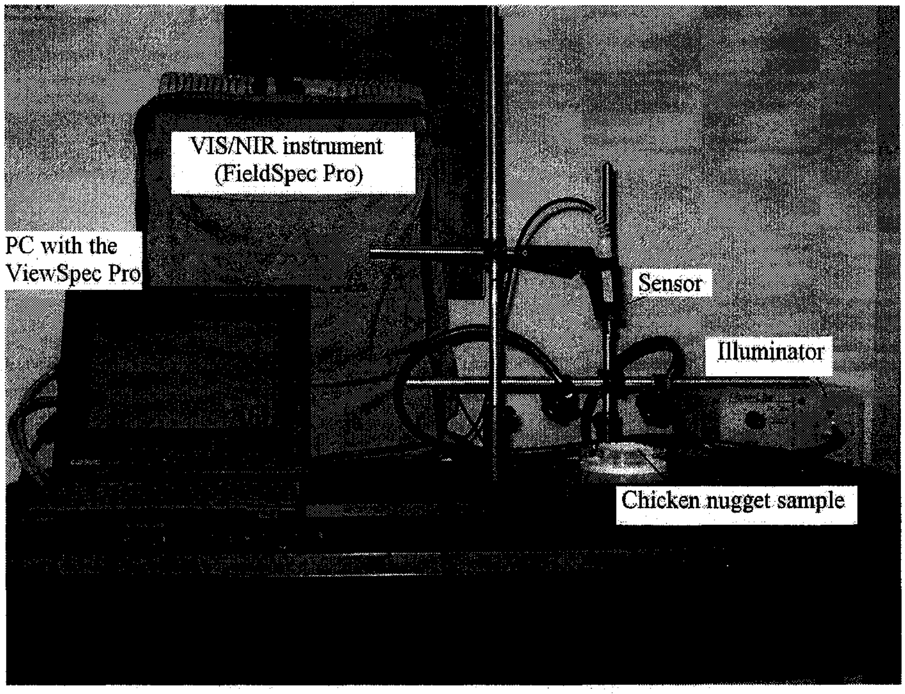
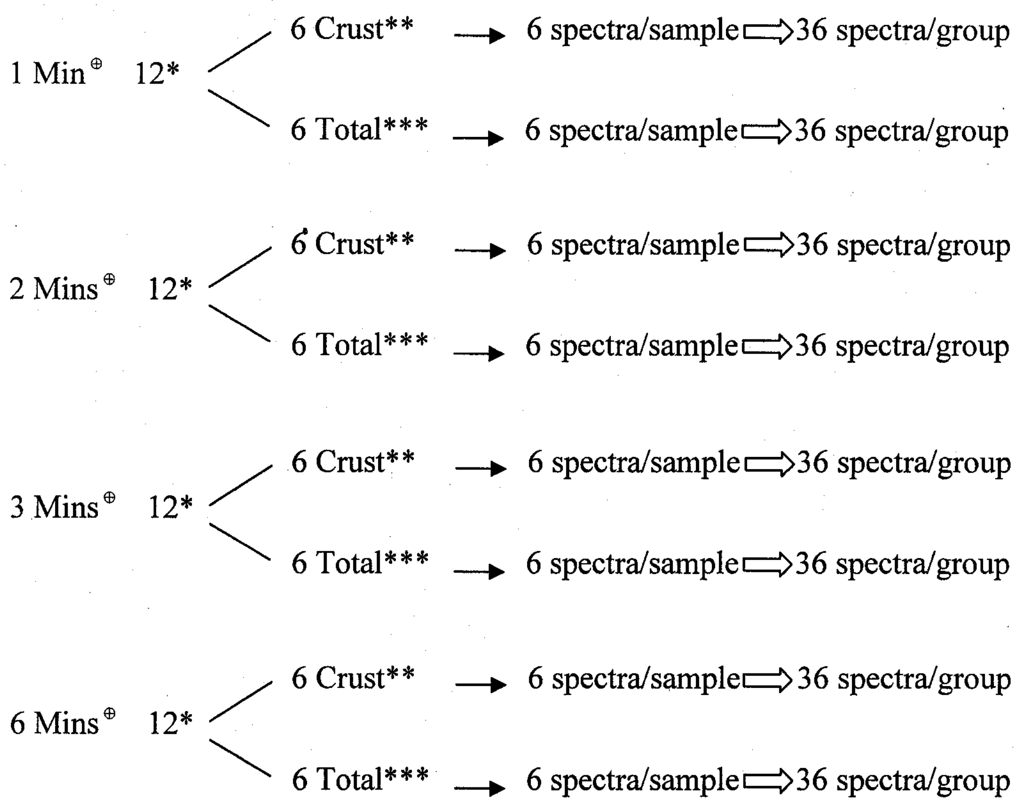


Figure 5.1 Experimental set up for spectral data collections.



⊕ Frying time

* Number of samples fried at each group based on frying time

** Samples for crust moisture and fat analysis

*** Samples for total moisture and fat analysis

Figure 5.2 Procedure of grouping the samples and the corresponding spectra based on the frying time.

5.3.4 Chemical tests

Moisture content: Moisture content was determined using the freeze drying method. Initial mass of fried samples was measured by an electric scale (TR-4102D, Denver Instrument Co., Denver, CO). Drying process was conducted in a freeze dryer (ModulyOD-115, Thermo Savant, Holbrook, NY) at -50°C for 36 h. Final mass of dried samples was measured and moisture content was calculated by difference in weight and reported on dry basis. Dried samples were then kept in a desiccator for further fat analysis.

Fat content: Fat content was determined using AOAC solvent extraction method 991.39 (AOAC, 2000). Portions of 2-5 g of ground sample were weighed with an electronic scale (TR-4102D, Denver Instrument Co., Denver, CO) and placed in a thimble for the instrumental extraction. The fat content of the samples was extracted using a solvent extractor (SER 148, Velp Scientifica, Usmate, Italy) with petroleum ether as the solvent. At the end of the operation, the remaining solvent in the extracted fat was removed in a conventional oven (Isotemp 700, Fisher Scientific, Pittsburg, PA) at 125°C for 30 min. The weight of extracted fat was determined and fat content of samples were calculated by the following formula and reported on dry basis. Fat content on dry basis was calculated as the ratio of the mass of extracted fat and the mass of dried sample.

The mean moisture and fat contents and the standard deviation (SD) in each group of the samples were calculated and the mean values were used for VIS/NIR calibration model development. Results of chemical analyses were reported as average crust moisture and fat and average total moisture and fat.

5.3.5 VIS/NIRS calibration and data analysis

5.3.5.1 Spectral analysis

Spectral analysis was performed using the GRAMS/AI software (ver. 7.02, Thermo Electron Corp., Salem, NH, USA). Four calibration models were developed. Model 1 was developed for crust moisture and fat analysis using full spectral range, while Model 2 was developed for crust analysis using feature wavelength regions. Model 3 was developed for total moisture and fat analysis using full spectral range, while Model 4 was developed for total moisture and fat analysis using feature wavelength regions. To build calibration Models 1 and 2, 30 spectra were randomly selected from the total number of 36 spectra in each group to build the training set. Since there were four groups of samples assigned for crust moisture and fat analysis, a total number of 120 spectra along with their corresponding crust moisture and fat contents were fed to the software for the training set. The remaining 24 spectra was used for validation of calibration model. This procedure was repeated to create training and validation sets for Models 3 and 4.

Partial least-squares (PLS) method was used to establish the calibration models along with mean-centering as the preprocessing and automatic baseline correction. Each calibration model was assessed by a leave-one-out cross validation and the optimal number of factors was determined by the minimum predicted residual error sum of squares (PRESS). Outliers of the training set were detected according to the concentration residuals and eliminated from the training set. Details of PLS multivariate mathematical algorithm are explained in section 3.4.4.4.

Calibration models with highest R^2 from cross validation were chosen as the best model. Root mean square error (RMSE) for the validation set was calculated for each constituent to asses the precision of prediction.

5.3.5.2 PLS feature wavelength selection

For each calibration model, PLS Beta coefficient plots of each constituent (moisture and fat) were used to determine feature wavelength ranges that indicated significant variations in the reflectance spectra. Beta coefficient values are regression coefficients that show the weight of contribution of each wavelength to the calibration model. This could assist in the development of a model which, using selected regions, could predict the moisture and fat contents. Eliminating the regions with no or very less contribution to the calibration model would reduce the time for calibration calculation. Also selected wavelength regions can be used as a basis to design simplified systems with less cost for on-line determination of moisture and fat contents of fried chicken nuggets. For more details about beta coefficient refer to 3.4.5.

5.3.5.3 Multivariate regression analysis for feature wavelength selection

In order to verify the selected feature wavelength ranges from plots of beta coefficient, regression analysis of the spectral data for Models 1 and 3 was performed by the SAS software (V. 8.20, Cary, NC, USA). The reflectance values of each wavelength were used as the independent variable whereas moisture and fat content values were used as dependent variables. The regression analysis was aimed to find feature wavelengths at which the independent variable (reflectance value) contributed to the most variation of each dependent variable (moisture and fat). The PROC REG program was run for the maximum R^2 (MAXR) criterion to determine the best model for prediction of each constituent. The MAXR criterion is explained in details in section 3.4.5.

5.4 RESULTS AND DISCUSSION

5.4.1 Chemical analysis results

Moisture and Fat Contents: The average total moisture content of chicken nugget samples varied from 2.14 to 0.93 g/g (db) when fried for up to 6 mins. The average crust moisture content varied from 0.87 to 0.19 g/g (db) within the same frying time. The average total moisture and average crust moisture content values are listed in table 5.1.

Table 5.1 Mean values of total and crust moisture contents (g/g, db) of the chicken nugget samples

Frying Time (min)	Total Moisture content (g/g, db)	SD (g/g)	Crust Moisture content (g/g, db)	SD (g/g)
0	2.14	0.059	0.87	0.005
1	1.6	0.047	0.56	0.01
2	1.49	0.007	0.48	0.02
3	1.28	0.04	0.42	0.02
6	0.93	0.04	0.19	0.02

The average total moisture content of fried samples was found to be highly correlated with average crust moisture content with R^2 of 0.97.

The average total fat content of fried chicken nugget samples was changed from 0.14 to 0.32 g/g (db) and the average crust fat contents ranged from 0.11 to 0.38 g/g (db) within the 6 min of frying (Table 5.2).

Table 5.2 Mean values of total and crust fat contents (g/g, db) of the chicken nugget samples

Frying Time (min)	Total Fat content db (g/g)	SD (g/g)	Crust Fat content (g/g, db)	SD (g/g)
0	0.14	0.0072	0.11	0.02
1	0.25	0.0137	0.30	0.0044
2	0.30	0.0117	0.35	0.0064
3	0.34	0.0212	0.38	0.0137
6	0.32	0.0213	0.34	0.0165

The total fat contents of the fried samples correlated with crust fat contents (R^2 = 0.91). The range of moisture and fat content values obtained was close to the typical range reported for chicken nuggets (EL-Dirani, 2003; Altunakar, 2004; Li, 2005). The difference between the fat content results of this study and those reported by others might be due to different types of breading, initial moisture and fat contents and type of the oil used. The total moisture content was highly correlated with the total fat content (R^2 = 0.99) within about 3 mins frying. Strong relationship between moisture loss and fat uptake has been reported by several authors on other products (Gamble et al., 1987; Rice and Gamble, 1989; Singh, 1995; Kassama, 2003). However, in this study, this correlation broke down after 3 mins. This was particularly important since it was necessary that the two constituents namely moisture and fat, be treated as independent variables in the NIR calibrations.

5.4.2 VIS/NIR calibration results

Figure 5.3 shows a reflectance spectrum of a chicken nugget sample, fried for 3 mins, within the range of 400-1750 nm.

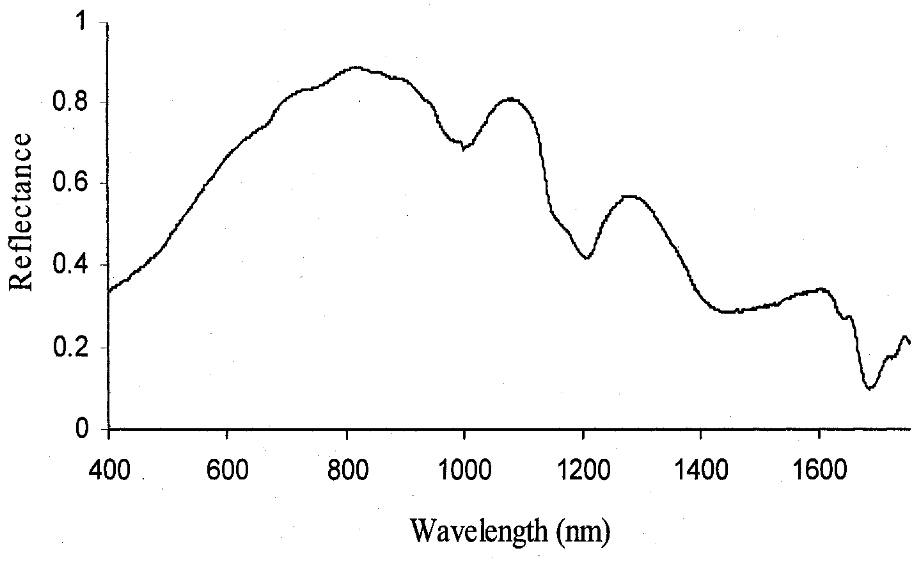


Figure 5.3 A reflectance spectrum of a chicken nugget sample fried for 3 mins.

5.4.2.1 Calibration models for crust moisture and fat prediction

Model 1: Calibration model based on spectral reflectance in the whole range of 400-1750 nm

A PLS calibration model was developed using reflection in the whole wavelength region of 400-1750nm to predict moisture and fat contents of the crust. The optimal number of factors was determined to be 8 and 10 for moisture and fat contents, respectively. Crust moisture content was predicted with R^2=0.95 from cross-validation test and the RMSE value of 0.026 for the prediction of the validation set. Figure 5.4 shows the plot of predicted vs. actual crust moisture content obtained from cross validation of the training set and the validation test.

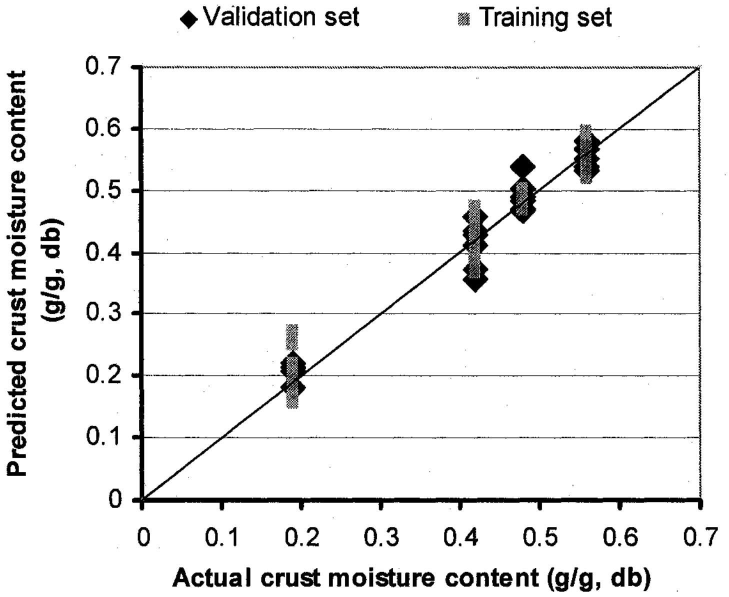


Figure 5.4 Predicted crust moisture content vs. actual crust moisture content, obtained from chemical methods, for the training and validation sets using model 1.

Crust fat content was predicted with R^2=0.94 from cross-validation test and the RMSE value of 0.006 for the prediction of the validation set. Figure 5.5 shows the plot of predicted vs. actual fat content obtained from cross validation of the training set and the validation test.

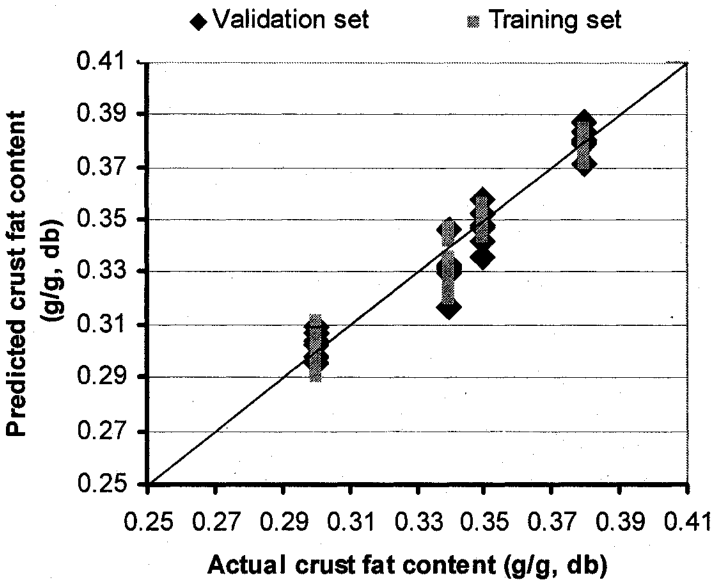


Figure 5.5 Predicted crust fat content vs. actual crust fat content, obtained from chemical methods, for the training and validation sets using model 1.

Model 2: Calibration model based on the spectral reflections in the selected wavelength regions

Common wavelength ranges of the most variation for both constituents (moisture and fat) were determined according to the PLS Beta coefficient plot of the GRAMS/AI (7.02) software. Most variations were found to be within the ranges of 420-450, 550-670, 730-780, 810-1100, 1230-1450 and 1550-1600 nm.

Following the Beta coefficient procedure, results of multiple regression procedure of MAXR criterion of SAS analysis indicated that the wavebands of the most variation for moisture determination were 555, 577, 817, 904, 967, 990, 1090, 1398 and 1576 nm, whereas for fat determination were 432, 438, 613, 621, 778, 891, 1044, 1230 and 1390 nm. Variations found in the visible range (400-700 nm) may be due to the color changes of samples fried for different times. Some of the bands found in the NIR region, in this study, were close to what were found in the literature. Bands of pure water are mainly observed at 1940, 1450, 1190, 970 and 760 nm due to O-H stretching overtones and combinations. These bands are subjected to shift in the spectrum of foods due to variations in hydrogen bonding. Bands of fat are mainly observed at 2310, 1765, 1734 and 1200nm in the NIR spectrum. These bands arise from overtones and combinations of CH_2 in fatty acid structure (Osborne et al., 1993). Mitsumoto et al. (1991) observed bands of water at 1388, 1760, 2150 and 2322 nm and bands of fat at 1350, 1534, 1978 and 2294 nm in beef cuts. Misra et al. (2000) used bands of 918, 928, 940, 950, 968, 975, 985, 998, 1010, 1023, 1037 and 1045 for determination of oil content of groundnuts. Alomar et al. (2003) observed bands of water at 964, 1440 and 1960 and bands of fat at 928, 1760 and 2310 nm in Bovine meat. Leroy et al. (2003) observed bands of water at 980, 1450, 1950 nm and bands of fat at 1200 and 1800 nm. .

The results of the MAXR multivariate regression analysis verified the selection of the wavelength regions in Beta coefficient plots since the selected regions covered the peaks found by the MAXR analysis. Validation data set was used to evaluate the prediction accuracy of the MAXR multivariate regression models for both moisture and fat prediction. Moisture and fat contents were predicted with R^2 values of 0.98 and 0.97, respectively.

Model 2 for prediction of crust moisture and fat contents was developed using the selected wavelength regions. Crust moisture and fat contents were predicted with the R^2 values of 0.94 and 0.92 from cross-validation test and the RMSE values of 0.038 and 0.009 for the prediction of the validation set, respectively. Figures 5.6 and 5.7 show the plots of predicted vs. actual crust moisture and fat contents obtained from cross validation of the training set and the validation test respectively.

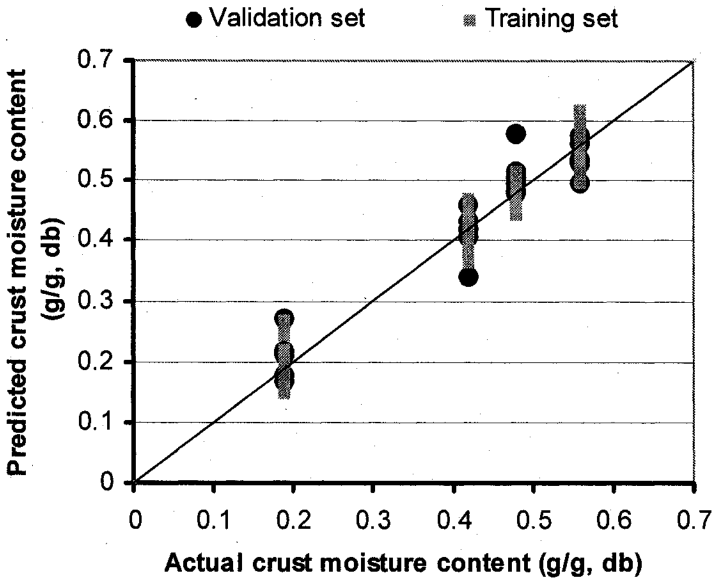


Figure 5.6 Predicted crust moisture content vs. actual crust moisture content, obtained from chemical methods, for the training and validation sets, using model 2.

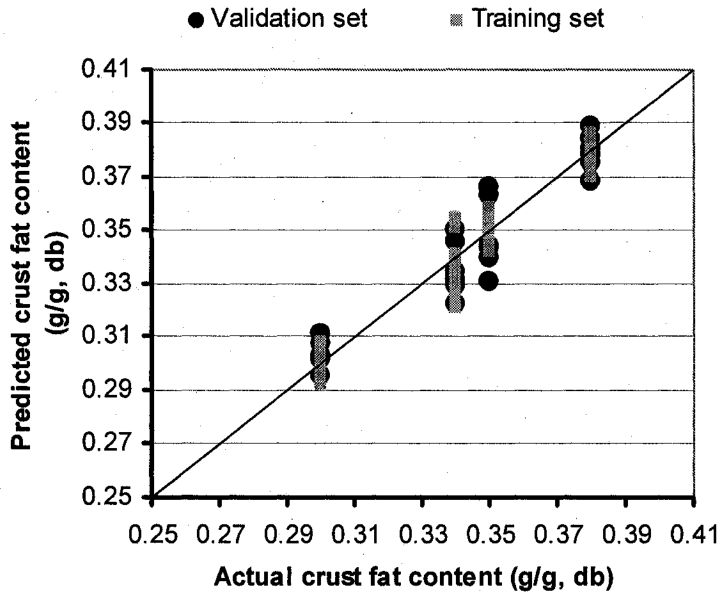


Figure 5.7 Predicted crust fat content vs. actual crust fat content, obtained from chemical methods, for the training and validation sets, using model 2.

5.4.2.2 Calibration models for total moisture and fat prediction

Model 3: Calibration model based on the spectral reflection in the whole range of 400-1750 nm

With the same procedures used for crust moisture and fat prediction calibration models, total moisture and fat contents were predicted both with the R^2 value of 0.94 from cross-validation test and the RMSE values of 0.07 and 0.012 for the prediction of the validation set using the PLS calibration model with the optimum number of factors of 9 for both constituents. Figure 5.8 and 5.9 show the plots of predicted vs. actual total moisture and fat contents obtained from cross validation of the training set and the validation test.

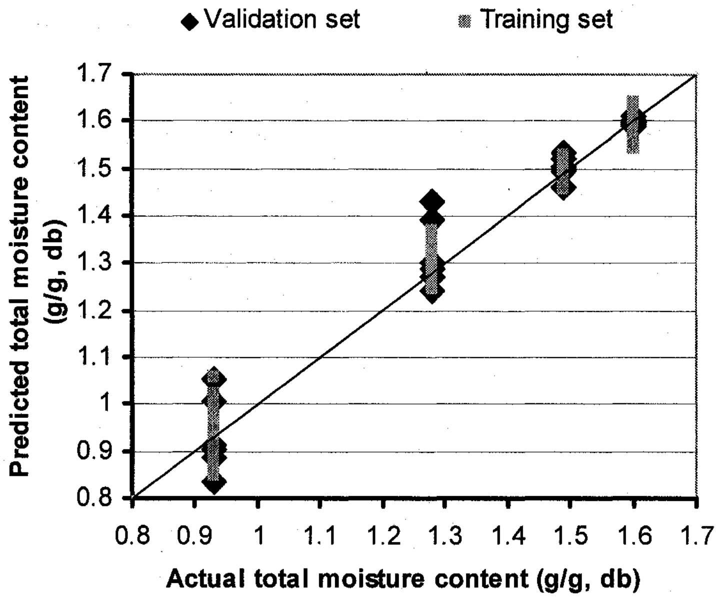


Figure 5.8 Predicted total moisture content vs. actual total moisture content, obtained from chemical methods, for the training and validation sets using model 3.

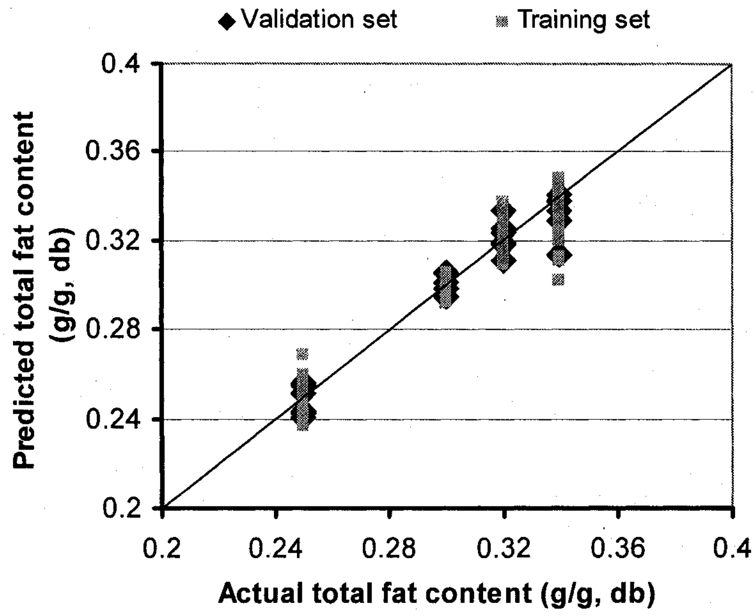


Figure 5.9 Predicted total fat content vs. actual total fat content, obtained from chemical methods, for the training and validation sets using model 3.

Model 4: Calibration model based on the spectral reflection in the selected wavelength regions

With a similar procedure for selection of feature wavelengths as used for crust analysis calibration, the same wavelength ranges were found to show the highest contribution in calibration model 3. The multivariate regression models obtained from the MAXR criterion of SAS analysis were able to predict the moisture and fat contents with R^2 values of 0.96 and 0.94. Using the similar PLS calibration procedures, total moisture and fat contents were predicted with R^2 of 0.92 from cross-validation test and the RMSE values of 0.105 and 0.017 for the prediction of the validation set. Figures 5.10 and 5.11 show the plots of predicted vs. actual total moisture and fat contents obtained from cross validation of the training set and the validation test, respectively.

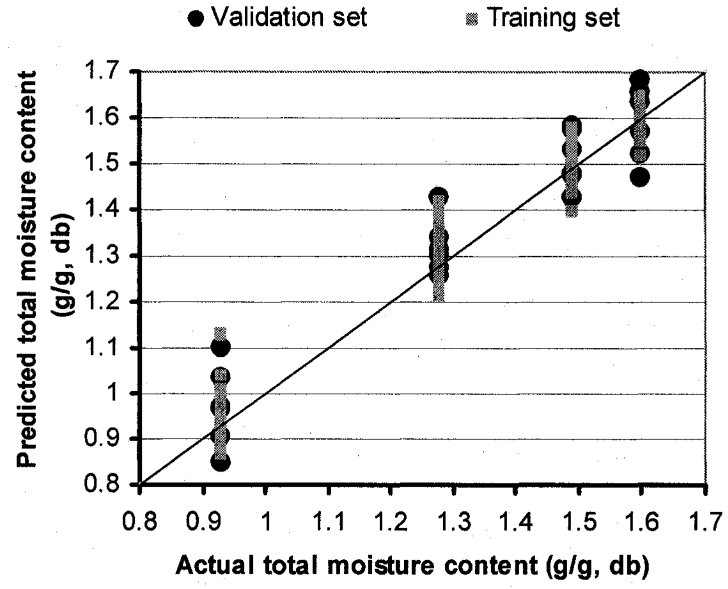


Figure 5.10 Predicted total moisture content vs. actual total moisture content, obtained from chemical methods, for the training and validation sets using model 4.

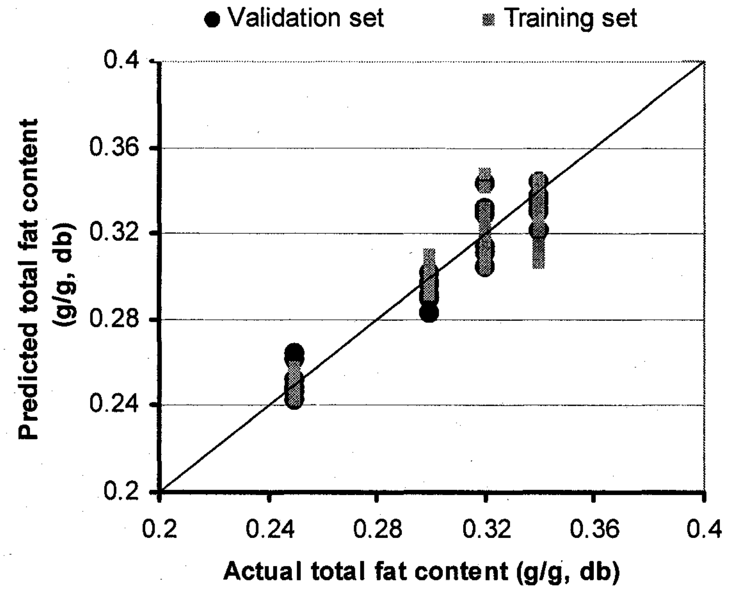


Figure 5.11 Predicted total fat content vs. actual total fat content, obtained from chemical methods, for the training and validation sets using model 4.

Although the spectral information were based on the readings from the surface (crust) of the chicken nugget samples, high correlations were obtained for prediction of total moisture and total fat contents. This could be due to correlation between the total moisture content and crust moisture content (R^2=0.97) and correlation between total fat content and crust fat content (R^2= 0.91) obtained in this study. However, as expected, the validation RMSE values obtained for the total moisture and fat prediction were lower than those obtained for crust moisture and fat prediction. Table 5.3 summarizes the cross-validation and prediction results of the four calibration models developed in this study.

Table 5.3 Summarized results of PLS calibration models

Calibration model	Training set		Validation set		Factors	
	R^2		RMSE			
	Moisture	Fat	Moisture	Fat	Moisture	Fat
Model 1	0.95	0.94	0.026	0.006	8	10
Model 2	0.94	0.92	0.038	0.009	9	9
Model 3	0.94	0.94	0.07	0.012	9	9
Model 4	0.92	0.92	0.105	0.017	9	9

5.5 CONCLUSIONS

Results of this study indicated that the developed calibration models could track the moisture and fat content changes of fried chicken nuggets with the accuracy of R^2 values of 0.92.

Because of the high correlation between the total moisture and crust moisture content and the correlation between total fat and crust fat content, calibration models could be developed to predict the total moisture and fat contents based on the reflectance readings from the crust.

Feature wavelength ranges selected in this study can be used to design on-line systems of quality evaluation of fried chicken nuggets.

VIS/NIR spectral analysis was proved to be a straightforward and fast method without requiring sample preparation and application of hazardous solvents. Once the calibration model is developed, the VIS/NIR instrument is capable of doing the moisture and fat analysis in few minutes.

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VI. GENERAL CONCLUSIONS

The results discussed in this thesis present a demonstration of successful development of rapid quantitative VIS/NIR methods which could monitor the quality parameters of both frying oil and fried chicken nuggets.

VIS/NIR reflectance spectroscopy was found to be able to monitor thermal degradation of frying oils that had gone through heating cycles at frying temperatures. VIS/NIR reflectance responses of heated oils could be used to track the changes in their acid value, total polar components and viscosity upon heating.

Developed calibration models using the wavelength region of 400-1750 nm could predict the three selected oil quality parameters, i.e., acid value, total polar components, and viscosity, with high accuracy. PLS multivariate chemometric algorithm was able to find the spectral regions that were most important in calibration models. The feature wavelength regions of 450-550, 850-950, 1140-1180, and 1200-1300 nm were found to be of most variation in the spectra and contain valuable information that allowed for prediction of the quality parameters. These regions can be used as a basis to design practical oil quality evaluation systems. However, overlapping broad bands in near infrared region brought uncertainty in assigning a band to a specific functional group. Moreover, the complexity of oil degradation products did not allow for assignment of a band to each quality parameter. But using PLS allowed us to develop calibration models with high precision in prediction of these parameters.

In the study of application of VIS/NIRS in prediction of moisture and fat contents of fried breaded chicken nuggets, it was concluded that the developed PLS calibration models could accurately track the changes in the moisture and fat content changes of fried chicken nuggets during frying.

High correlation between the crust moisture and total moisture contents and also between crust fat and total fat contents allowed using the reflectance spectral information from the crust to predict the total moisture and total fat contents.

Feature wavelength ranges of most contribution to the calibration model for prediction of moisture and fat contents were found using PLS. Most variations were observed in the regions of 420-450, 550-670, 730-780, 810-1100, 1230-1450, and 1550-1600 nm which can be used for future design of on-line systems for evaluation of fried chicken nuggets.

In general, VIS/NIR spectroscopy was proved to be a straightforward and practical method of quality evaluation, for both frying oil and fried breaded chicken nuggets, without any sample preparation requirement or application of chemical reagents. This represents a remarkable improvement over traditional methods that are currently available in frying industry.

Based on the results of this study, further research work could be recommended to investigate the potential of VIS/NIRS on discrimination of frying oils based on a) their degree of hydrogenation and b) the degradation level such as among fresh, marginal and discardable oils.

It is also recommended that more investigation be undertaken in correlating the spectral response of fried breaded chicken nuggets with their textural properties such as crispness.