FT-NIR Method to Determine Moisture in Gluten Free Rice Based Pasta during Drying

Navneet Singh Deora, Aastha Deswal, H. N. Mishra

Abstract—Pasta is one of the most widely consumed food products around the world. Rapid determination of the moisture content in pasta will assist food processors to provide online quality control of pasta during large scale production. Rapid Fourier transform near-infrared method (FT-NIR) was developed for determining moisture content in pasta. A calibration set of 150 samples, a validation set of 30 samples and a prediction set of 25 samples of pasta were used. The diffuse reflection spectra of different types of pastas were measured by FT-NIR analyzer in the 4,000-12,000cm^{-1} spectral range. Calibration and validation sets were designed for the conception and evaluation of the method adequacy in the range of moisture content 10 to 15 percent (w.b) of the pasta. The prediction models based on partial least squares (PLS) regression, were developed in the near-infrared. Conventional criteria such as the R^2, the root mean square errors of cross validation (RMSECV), root mean square errors of estimation (RMSEE) as well as the number of PLS factors were considered for the selection of three pre-processing (vector normalization, minimum-maximum normalization and multiplicative scatter correction) methods. Spectra of pasta sample were treated with different mathematic pre-treatments before being used to build models between the spectral information and moisture content. The moisture content in pasta predicted by FT-NIR methods had very good correlation with their values determined via traditional methods ($R^2 = 0.983$), which clearly indicated that FT-NIR methods could be used as an effective tool for rapid determination of moisture content in pasta. The best calibration model was developed with min-max normalization (MMN) spectral pre-processing ($R^2 = 0.9775$). The MMN pre-processing method was found most suitable and the maximum coefficient of determination (R^2) value of 0.9875 was obtained for the calibration model developed.

Keywords—FT-NIR, Pasta, moisture determination.

I. INTRODUCTION

THE ability to quantify moisture in real-time is critical for optimizing the operation of production dryers. This can be of paramount importance in case of pasta dryers in the food industries since ruining one batch of product can be very costly [1]. The goal in any drying process is to reach optimum product moisture using the least amount of energy in the quickest amount of time without sacrificing product quality. If pasta is over-dried it might not be suitable for sale, energy would have been wasted in the drying process, and the throughput of the dryer would not have been optimized [2].

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If product is under-dried it creates operational inefficiency since the dryer will need to be stopped and restarted several times in order to sample for moisture verification. Also, high-moisture product could cause product stability issues during long term storage of pasta and consumer acceptance. Additionally, drying is a process which requires high energy input because of the high latent heat of water evaporation and relatively low energy efficiency of industrial dryers. Very high moisture content in the final product can attracts mold, bacteria, and insects, all of which can result in shelf life issues or cooking quality deterioration. Of course only a careful control of the process conditions coupled to a deep knowledge of the material properties, may avoid those undesired effects, while still maintaining high production rates.

Near infrared (NIR) reflectance spectroscopy is a high-precision, fast, accurate, easy and non-destructive technique that can be used as a replacement of time-consuming methods [3]-[5]. NIR radiation covers the range of the electromagnetic spectrum between 800 and 2,500nm (4,000-12,000cm^{-1}) [6]. Among the various methods available for determination of moisture content in food materials, standard gravimetric method is one among the most accurate ones [7]. But, it is time consuming and a destructive method. The same sample cannot be reused for any other purpose. Additionally, convectional drying methods like gravimetric does not lead to any kind of process understanding so entire batches can simply be thrown out without understanding the root cause of failure. In such case, near infrared reflectance spectroscopy can be used as a replacement for time-consuming methods [5], [8]. NIR spectroscopy is also well suited to online use. Once calibrated, an NIR spectrometer may be operated with minimal training [9]. NIR region contains information concerning the relative proportions of bands, which varies according to the structural components of the organic molecules [10]. The change depends on the chemical composition of the product, as well as on its light scattering properties, which are related to the microstructure.

In FT-NIR technique among different multivariate calibration tools partial least-squares (PLS) method can be used in food industry by extracting features from spectra [11] to relate the changes in spectral data with the changes in the sample [12]. The information extracted can be condensed in the latent variables or factors, which are used in the calibration and prediction steps [13]. PLS makes use of the information of the NIR spectrum and the established analyte values associated with the spectrum. The developed equation applied to unknown samples and the analyte is determined [11].

The present study was carried out with the objective of developing a rapid method for detection of moisture content in dried pasta using FT-NIR spectroscopy. In commercial pasta production, we can use this method to determine the end point in drying of pasta rapidly without destroying the sample and also to check the same during packaging and storage.

II. MATERIAL AND METHODS

A. Sample Preparation

Distilled water was added to commercial durum semolina and to achieve desired level of hydration with 32% wb moisture content [14]. The wetted blends were mixed at high speed in a Hobart mixer for 4 min and placed in a mixing chamber and extruded through a ribbon die to form flat pasta with 1.5mm thickness [15]. Extruded pasta was dried in a laboratory dryer using low temperature (40°C) [16]. The samples of dried pasta were obtained at various stages of drying such that final moisture content in the pasta is in the range of 10-15% wb. Dry pasta samples with different moisture content were ground carefully to avoid heating of the pasta then they were sieved using a mesh size of less than 315μm to ensure appropriate particle size distribution. Samples of dry pasta with varying concentration of moisture were prepared by proper mixing of distilled water. The moisture content of pasta was determined by standard gravimetric method by placing 5–10g of samples in an oven at $102 \pm 2°C$ for 24h. The loss in weight was noted down, and moisture content was calculated based on the initial weight. Ground pasta samples were kept in airtight bags until use.

In order to meet the general requirements on the number of calibration samples for NIR-based studies, the guidance of the ISO standard on the use of NIR on food samples was regarded [17] that call for at least 130 samples. Accordingly, 150 pasta samples were investigated with respect to moisture content. The number of samples, data of reference measurements and corresponding NIR spectra were taken into account the development of the calibration model. Triplicate measurements were taken for each sample and the average values were taken for calibration of spectra.

B. Spectral Measurement

FT-NIR MPA™ spectrometer (Bruker optics, Germany) combined with Opus 5.5 software was used for analysis of pasta samples by generating spectrum for each sample in the spectral region 4,000 to 12,000cm^{-1}. This spectrometer with an integrated Michelson interferometer [3] utilized the Fourier transform and had distinct advantages compared to dispersive spectrometers (Fig. 1). A Michelson interferometer, the simplest form of an interferometer, consists of two mutually perpendicular plane mirrors, one of which moves along its axis at a common velocity, and a beam splitter. The beam splitter partially reflects the source energy to the fixed mirror and reflects the remaining energy to the moving mirror. The beams reflected from the mirror are combined by the beam splitter and directed to the detector.
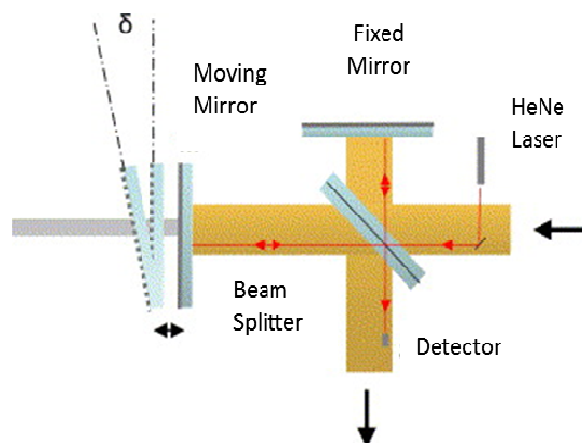

Fig. 1 Schematic Diagram of Standard Michelson interferometer [27]

The spectra generated over a range of wave numbers from 12,000 to 4,000cm^{-1} were interpreted based on the overtones of different functional groups in the product. Resolution of this spectrophotometer is 1.7536cm^{-1} with a maximum value of 2cm^{-1}, and scan time was 5s at the maximum. The background measurement was done initially by using reference spectra (empty sample bottle) before loading the sample's spectra. The spectra were measured in diffused reflectance mode by keeping 8-10g of sample in small sample bottle. For each sample, three spectra were recorded at three different points by rotating the sample bottle at 120 0. The average of these three spectra was taken for analysis. All the measurements were carried out under controlled room condition (temperature 24 ± 2^0C, RH 35 ± 2 percent).

D. Calibration and Validation of Developed Model

The pasta samples prepared with different levels of moisture were used for developing a model. Thirty samples were prepared for the calibration, and cross-validation method was used for validation of the developed partial least squares (PLS) model. In cross validation, the spectrum of one sample of the calibration set is deleted from this set, and a PLS model is built with the remaining spectra of the calibration set. The left out sample is predicted with this model, and the procedure is repeated with leaving out each of the samples of the calibration set. This method is followed in this study.

Spectra of samples with known value of moisture content were collected in triplicate as described above, and the average of these three was used for multivariate analysis. These acquired spectra were then used to determine a calibration function by using the PLS regression model. The method of PLS regression bears some relation to principal component analysis; instead of finding the hyperplanes of maximum variance, it finds a linear model describing some predicted variables in terms of other observable variables. It is used to find the fundamental relations between two matrices (X and Y), i.e., a latent variable approach to modeling the covariance structures in these two spaces. A PLS model will try to find the multidimensional direction in the X space that

explains the maximum multidimensional variance direction in the Y space. PLS is particularly suited when the matrix of predictors has more variables than observations. The calibration model was developed and validated through cross-validation technique. Data pre-processing is an important stage in performing calibration. By pre-processing the data, a good correlation between the spectral data and the concentration values can be ensured.

In this study, vector normalization, Min-max normalization and multiple scatter correlation pre-processing methods were used. In vector normalization, the spectrum will be normalized by first calculating the average intensity value and subsequent subtraction of this value from the spectrum. Then, the sum of the squared intensities is calculated, and the spectrum is divided by the square root of this sum. In min-max normalization method spectrum first subtracts a linear offset and then sets the Y-maximum to a value of 2 by multiplication with a constant. Then it is used similar to the vector normalization. Multiplicative scatter correction performs a linear transformation of each spectrum for it to best match the average spectrum of the whole set. This method is often used for spectra measured in diffuse reflection. The performance of the final PLS model was evaluated in terms of root mean square error of cross-validation (RMSECV), in case of cross-validation, and the coefficient of determination (r^2). The RMSECV is calculated as follows (1);

$$RMSEV = \sqrt{\frac{\sum_{i=1}^{n}(y_{ai}-y_{pi})^2}{n}} \qquad (1)$$

where, n is the number of samples in the calibration set, y_{ai} is the reference measurement result for the sample i, and y_{pi} is the estimated result for sample i when the model is constructed with the sample i removed. The number of PLS factors included in the model is chosen according to the lowest RMSECV. This procedure is repeated for each of the pre-processed spectra. Coefficient of determination between the NIR predictive and the reference measurement value are calculated as follows in (2), where $\hat{y}_i$ is the estimated result of the model for sample i, and $\bar{y}$ is the mean of the reference results for all samples in the calibration set.

$$r^2 = 1 - \sqrt{\frac{\sum_{i=1}^{n}(\hat{y}_i-y_i)^2}{\sum_{i=1}^{n}(y_i-\bar{y})^2}} \qquad (2)$$

E. Validation Using Fresh Samples

Moisture content of pasta samples (other than the set used for calibration) were determined using the predicted model, standard gravimetric method, and by an infrared digital moisture analyzer (AND MX-50 model) in order to verify the accuracy of the developed method. Triplicate measurements were taken by each method for the same sample, and results were analyzed statistically.

III. RESULTS AND DISCUSSION

Fig. 2 depicts the characteristic absorption spectra of the calibration data set. Spectra are comparable to those reported by various authors [18], [19]. It can be examined from Fig. 2, that the water absorption bands were around 5,155 and 7,000cm^{-1}corresponding to O–H stretching and O–H deformation. The most intensive band in the spectrum belongs to the vibration of the second overtone of the carbonyl group (5,784cm^{-1}followed by the C–H stretch and C–H deformation vibration (6,912cm^{-1}), the -CH2 (5,528cm^{-1}), and the –CH3 overtone (5,808cm^{-1}). The vibration of the carbonyl group, –CH and –CH2 vibrations, are caused by the constituents such as protein and some aroma compounds. The NIR region contains bands that often overlap, making it difficult to extract spectral parameters of the individual bands. However, Chemometrics have provided a way of overcoming these problems through development of empirical models. These models aim to relate the relationship between multiple spectral intensities from many calibration samples to the known analytes in these samples. For the purpose of quantitative analysis mathematical transformations are of paramount importance. In previously reported studies, it was shown that multivariate calibration by partial least-squares (PLS) regression can extract relevant information for quantitative determinations despite the lack of distinct peaks [20].
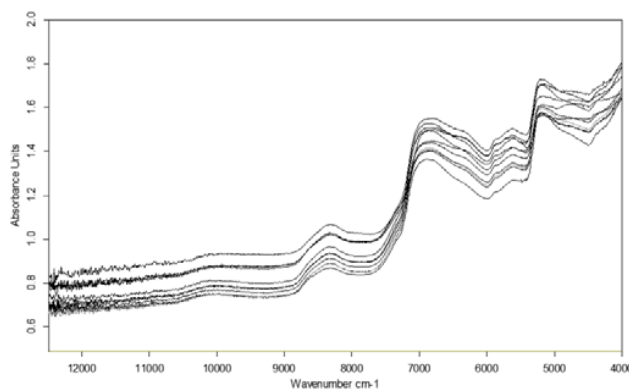

Fig. 2 FT-NIR absorption spectra of calibration data set

In the application of PLS algorithm, it is generally known that the spectral pre-processing methods and the number of PLS factors are critical parameters [21]-[22]. The optimum number of factors is determined by the lowest RMSECV and highest value for r^2 [23]. Corresponding to each PLS factor for determining moisture content with different spectral pre-processing methods, values of RMSECV and r^2 values were calculated. As seen from Figs. 3 and 4 among the different pre-processing method used, min-max normalization was found out to be superior to others. The best methods were judged on the basis of maximum and minimum value of r2 and RMSECV respectively. It can be seen from the figure that the value of RMSECV decreases precipitously with initial factors; however, it progressively decreases as PLS factor increases. This model needs five PLS factors. In this application, min-max normalization seems to perform better than other pre-processes.
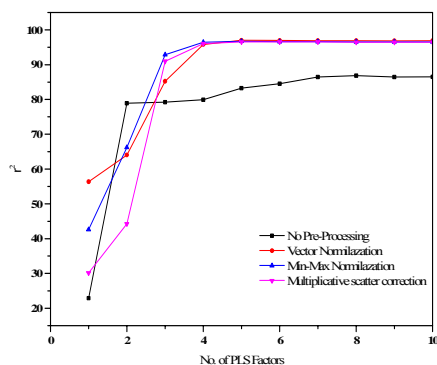
Fig. 3 Relation between r^2 and PLS factors for the various pre-processing Methods
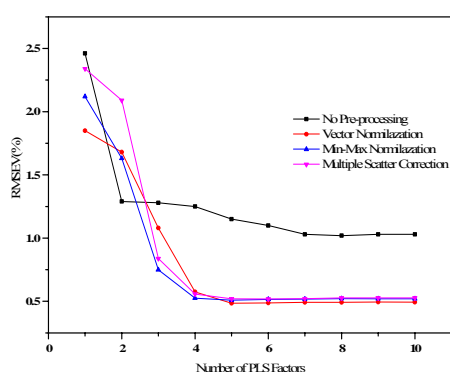

Fig. 4 Relation between RMSECV and PLS factors for various pre-processing Methods

The NIR predicted results for moisture content in pasta samples using the calibration model is presented in Fig. 5. PLS regression method gave r2 values of 0.9775 for calibration data set and RMSECV value of 0.83 for cross validation. The results of this study clearly demonstrated the capability of FT-NIR for determination of moisture content in the pasta. The predictive abilities of the calibration models were evaluated by the residual predictive deviation (RPD). The RPD is defined as the standard deviation (S.D.) of the population's reference values divided by the standard error in cross validation for the NIRS calibrations [24]. If the error for estimating a constituent (SECV) is large compared to the spread of that compound in all samples (S.D.), a relatively small RPD is calculated, thereby demonstrating that the NIR calibration model is not robust. In contrast, relatively high RPD values indicate models having greater power to predict the chemical composition. Generally, an RPD greater than three could be considered reliable for prediction purpose. also, which was defined as the ratio of the standard deviation of the reference data to the standard error of predicted data for the population tested [25], [26]. RPD value for the present model is 3.5, which is greater than 3 and considered to be desirable for prediction purposes as per [24], [25].
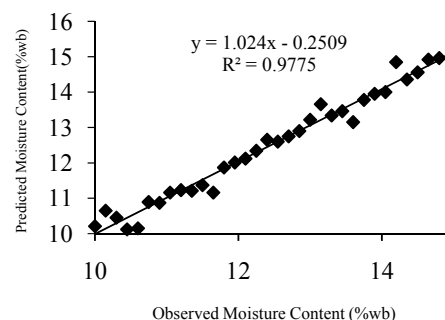

Fig. 5 Linear regression plot of measured versus predicted moisture Content of the calibration data set

The result obtained by the developed method was validated with fresh pasta sample. For cross validating standard gravimetric method and moisture estimation by Moisture analyzer (AND MX-50 model) were used. Moisture content values for each sample was measured in triplicate by the above three methods, and the values obtained were analyzed statistically by single factor ANOVA as shown in Table I.

TABLE I
RESULT OF ANOVA FOR THE MOISTURE CONTENT IN PASTA SAMPLES BY THREE DIFFERENT METHOD

ANOVA: Single factor						
Groups	Avg*	Var.				
Moisture Analyser	5.43	0.06				
FT-NIR method	5.42	0.02				
Gravimetric Method	5.65	0.08				
ANOVA						
Source of Variations	SS	df	MS	F	P-Value	F_{crit}
Between Groups	0.145	2	0.0725	1.21	0.401**	5.14
Within groups	0.357	6	0.0595			
Total	0.502	8				

*(n=3); ** (not significant)

On the basis of F and P-value it can be seen that there is no significant difference between the moisture content values obtained by the above three methods even at 5% level of significance. Thus the new method developed is at par when compared to the standard methods used for moisture determination. Duncan test was also performed using the SPSS 13.0 software. The results of the Duncan test are presented in Table II.

TABLE II
RESULT OF THE DUCAN TEST FOR THE MOISTURE CONTENT DETERMINATION IN THE PASTA

Treatments	Subset	
	1	2
Gravimetric analysis	5.512	
FT-NIR Method	5.604	5.604
Moisture analyser		5.708
Significance(5% level)	0.315*	0.123*

*(n=3); ** (not significant)

The test results showed that there is no significant difference between the values obtained by these three methods at 5% level of significance. This proved that FTNIR spectroscopy is a rapid and efficient tool for detection and quantification of moisture content in green pasta sample

IV. CONCLUSION

This calibration study has demonstrated that the new method developed provides a rapid solution to accurately quantify the moisture content in pasta. The traditional quantitative techniques for moisture analysis require may entail time consuming sample preparation, and are burdened by time delays waiting for results. Alternatively, FT-NIR can analyze moisture content in the pasta without the use of chemicals, providing faster, highly accurate, and reliable results. It also provides short term return on investment by eliminating the cost of consumables, rework, or discarding of product that does not meet specifications. In addition, implementing FT-NIR to replace traditional techniques reduces potential delays waiting for test results needed to make critical production decisions. The speed and accuracy of FT-NIR provides quality data for real-time process improvements, and allows industries to verify that their product specifications are met, thereby maximizing production efficiency and profitability

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