Implementation of Non Destructive FTNIR Method for Quick Estimation of Peanut Quality Based on FFA and Peroxide Value

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Abstract

The possibility of rapid estimation of moisture, protein, fat, free fatty acid (FFA), and peroxide value (PV) content in peanut kernel was studied by Fourier transform near-infrared spectroscopy (FTNIR) in the diffuse reflectance mode along with chemometric technic. The moisture, fat and protein of fresh and damaged seeds of peanuts ranging from 3 to 9 %, 45 to 57 % and 23 to 27 % respectively, were used for the calibration model building based on partial least squares (PLS) regression. The peanut samples had major peaks at wavenumbers 53.0853, 4954.98, 4464.03, 4070.85, 74.75.63, 8230.21, and 6178.13 in per cm. First and second derivate mathematical preprocessing was also applied in order to eliminate multiple baselines for different chemical quality parameters of peanut. The FFA had the lowest value of calibration and validation errors (0.579 and 0.738) followed by the protein (0.736 and 0.765). The quality of peanut seeds with lowest root mean square error of cross validation of 0.76 and maximum correlation coefficient (R^2) of 96.8 was obtained. The comprehensive results signify that FT-NIR spectroscopy can be used for rapid, non-destructive quantification of quality parameters in peanuts.

Highlights

- Peanut quality detection was done by Fourier transform near-infrared spectroscopy
- Rapid estimation of moisture, protein, fat, FFA, and PV in peanut was done by FTNIR
- The method gave lowest RMSE of 0.76 in cross validation and maximum R^2 of 96.8
- Peanut fresh/spoiled samples prediction had a low predictive error of 0.05-1.83

Introduction

Peanut is one of the major source of edible oil and protein content available for human consumption and is consumed worldwide. The freshness and quality of peanut are the major concerns in the food markets as in storage, it is most likely to undergo either surface contamination or a change in internal quality in terms of oil and flavor by gaining moisture and oxygen from the atmosphere. A peanut is considered to be of good quality if it have a moisture content in range of 5–7 %, protein (25–30 %), and an oil content (45–55 %) (Bilal et al. 2020; Raigar and Mishra 2016). Moreover, peanuts are rich in fiber, folate, vitamin E, magnesium and phenolic compounds which is beneficial for human health (Mora-Escobedo et al. 2015). The nutritional and sensory acceptability of peanut is mostly dependent on moisture and oil content (Free fatty acid, Peroxide value). In addition, peanuts may gain excess oxygen content which leads to rancid flavor while if they gain excess moisture, it will promote microbial growth on the surface of the peanut which thereby change the color of the peanuts. The majority of physico-chemical AOAC methods for determination of quality characteristics of peanut are time consuming, slow and fatal (Mishra et al. 2018). Thus, there is a missing piece or pieces in the research literature that has not yet been explored regarding a technique that somewhat allows rapid testing of peanut quality.

Some of non-destructive and rapid testing methods are rapidly popularized in the current food scenario out of which the Fourier transform near infrared spectroscopy (FTNIR) is an advanced instrumental method, which may be used for the rapid determination of nutrients and characterization of food products. FTNIR offers many unique benefits such as non-destructive nature, economical, environment friendly, shorter time intake, and no additional sample preparation. Chemometric approaches (partial least square) are commonly used to analyze the data obtained from FTNIR for correlations of the models (Srivastava et al. 2018b; Nturambirwe et al. 2019).

Latest research has set out the adaptability and potentiality of FTNIR for analysis of the physical and chemical properties of several food samples. Srivastava et al. (2018 b) studied the quality of the rice grain and differentiated the infested rice with good quality rice grain. Moreover, the determination of quality change during the storage of the rice due to insect was also reported in the study. The rapid method for analysis of phytic acid was done for the green gram seeds (Pande and Mishra 2015). Several studies showed the analytical capacity of FTNIR was excellent for essential and nonessential amino acids, fatty acids, and microbial contaminations in cereals and oilseeds (Mishra et al. 2018; Carvalho et al. 2019; Lopes et al. 2020).

Although, FTNIR spectroscopy intermodal with multivariate analysis has been employed to measure the composition in cereals, oilseeds and legumes in term of their moisture, protein and, oil content etc. The intimate relationship between spectroscopic measurement and physical/microbial impurities as surface contamination, and quality of peanut seeds still a research issue. Also, the study attempt on the application of Fourier transform near-infrared spectroscopy (FTNIR) for discrimination of peanut kernel quality characteristics namely infested kernel, surface impurities etc. for peanut with an incrementally rise in storage days. Thus, the objective

of this study was to evaluate the chemical and nutritional quality characteristic of peanut samples by using the FTNIR spectroscopy technique with multivariate partial least squares analysis regression (PLSR).

Materials And Methods

2.1 Sample Preparation

Fresh and good quality peanut samples were procured from the local market of Kharagpur, West Bengal, India. A total of 50 samples were collected which were categorized as: fresh, mature, damaged, fungus infected, roasted, partially roasted, long time stored, and rancid peanuts respectively. Every sample was analyzed in triplicates ($n = 150$) to minimize the error percentage along with the same confidence level.

2.2 Peanut quality assessment by standard methods

Determination of important physical and chemical peanut quality parameters of fresh as well as different type of peanut samples were measured by using standard AOAC (2000) laboratorial protocols. The moisture content was analyzed by hot air oven dry method (AOAC, 2000). Protein content was determined by Kjeldahl method, fat content by SOX THERM apparatus. The peroxide value (PV) and Free Fatty acid (FFA) value were analyzed by using the standard laboratory protocols.

2.3 FTNIR Method Development

Fourier transform near-infrared (MPA™, Bruker, Germany) instrument composed of quartz beam splitter, PbS sensor, and an interferometer. The FTNIR was connected to a software (Opus 5.5) to investigate the peanut samples individually based on distinctive spectrum for each sample. The spectra was generated in diffused reflectance mode of each peanut sample in wave numbers from 12,000 to 4000 cm^{-1} due to diverse functional group distinguished in the kernel of peanut. Approximately 100 grams of peanut kernels was tightly packed in a Duroplan™ cup (Germany) which was placed on a rotating wheel assembly with a test holder. While taking each spectrum of the sample, the speed of scanner was calibrated to 10 kHz, and a mean of 94 outputs was taken (Srivastava et al. 2019). An empty cup was used to record the background spectrum, and to accomplish the co-linearity in the sample spectrum; the background spectrum was kept active for minimum 24 hrs. The data obtained from standard AOAC method was inserted into the Bruker FT-NIR system to create a spectral library for the development of rapid, nondestructive method for quality evaluation of peanut.

2.4 Spectra Pretreatment

The obtained spectra of whole peanut kernel might also have unrelated information, so in these situations, spectral pretreatment is employed to eliminate or minimize the variability of spectra. Thus, pretreatment help in developing more simple and robust models. So, the study used vector normalization, first derivative, straight line subtraction, and multiplicative scatter correction techniques (Srivastava et al. 2018a).

2.5 Model Calibration and Validation

About 80% of the peanut samples were used for the calibration purpose and rest for the validation. The afforested model was then used to predict the validation group peanut samples. The standard deviation (SD), relative standard deviation (RSD), and the ratio of SD of validation data to standard error (residual predictive deviation: RPD), root mean square error of estimation (RMSEE), root mean square error of cross validation (RMSECV), and coefficient of determination (R^2) were evaluated for the accuracy of the developed models. The spectra of one test sample was removed, and a PLS model was generated with the left spectra of the test set. The residue was again determined with the same model, and the procedure was rerun till every test set sample was utilized for the model prediction. The execution of the PLS-calibration model was evaluated by cross validation of the calibrated peanut samples. The models calibrated were co-related with the spectra values in opposition to the concentration of each peanut quality parameters (moisture, fat, protein, FFA, and PV Values) evaluated by the standard AOAC (2000) method. The PLS is based on highlighting the features which give highest change in both the data sets (reference and spectral). Thus, PLS accounts variability in terms of new axis known as PLS factors. The final effectiveness of PLS model was signified by the RMSEE, RMSECV (cross-validation), and R^2 .

Results And Discussion

3.1 Statistical description and correlation analysis

A considerable quantity of sample collection and concoct is prudence to explicate the deviations which may arise due to higher degree and complexity in the chemical and nutritional quality of peanut samples (Srivastava et al. 2018b). A total of 150 peanut samples were observed for the change in moisture, FFA, PV value, fat and protein content.

3.2 Elucidation of FTNIR Spectral Attributes for quality of peanut

The overall spectrum range of 12500 to 4000 per cm was noticed after complete scanning of the different peanut samples. Figure 1 shows spectra of different peanut samples with major peaks at wavenumbers 53.0853, 4954.98, 4464.03, 4070.85, 74.75.63, 8230.21, and 6178.13 in per cm. First and second derivate mathematical preprocessing was also applied in order to eliminate multiple baseline for different chemical quality parameters of peanut. Interpretation of spectral characteristics is of importance for the identification of the information region, which shall help in the model development via FTNIR analysis (Srivastava et al. 2018 a,b). The fresh peanut samples are represented by pink line spectra, partial roasted by red line spectra, roasted by yellow line spectra, mature by black line spectra, long time stored by light green line spectra, rancid by violet line spectra, fungus infested by light blue line spectra, and damaged by dark blue line spectra respectively (Fig. 1).

The FTNIR spectra originated was normally distinctive for every peanut samples. The higher absorbance spectra specified the damaged (1.3 AU), fungus infested (0.92 AU), and rancid (0.73 AU) peanut samples while the lower absorbance spectra specified the fresh (0.31 AU), partial roasted (0.34 AU), and roasted (0.48 AU) peanut samples. The mature (0.56 AU) and longtime stored (0.69 AU) peanut samples lied in the midway of the two (higher/lower) absorbance spectra (Srivastava et al. 2018 a, c). The water combination (OH stretch. + OH bend) absorbance band due to moisture content of the peanut sample was found at 5212 cm^{-1} . The absorbance band range $5180\text{ to }5150\text{ cm}^{-1}$ revealed the symmetrical stretching and bending of -OH group, while the asymmetrical stretching was found at $7270\text{ to }7220\text{ cm}^{-1}$ (Mishra et al. 2018). The bound -OH functional group of first and second overtones lied in the range of $6927\text{ to }6380\text{ cm}^{-1}$ and $9408\text{ to }9359\text{ cm}^{-1}$ respectively. The N-H stretching and N-H bend of the amide group for the protein content of the peanut were noticed at $5552\text{ and }4843\text{ cm}^{-1}$ respectively. The spectral band at 5239 cm^{-1} and 4954 cm^{-1} was due to the carboxylic acids in the second and first overtone stretch which corresponds to the FFA content of the peanut (Adewale et al. 2014). The peroxide bonds were observed at $4070, 4273, \text{ and } 5308\text{ cm}^{-1}$ due to R-O-R stretch.

3.3 PLS Model for Quality Characteristics of peanut

The Beer's law holds a specific application in the empirical regression as a correlation accord between peanut category and the spectral signatures of it. The PLSR was employed for the quantification and characterization of the peanut samples by integrating the spectral characteristics in the OPUS-QUANT 5.5 software tool of the instrument (Srivastava et al. 2018 a, Chen et al. 2014). The moisture content, protein, fat, FFA and PV values gave good performance and high correlation for the calibration and validation values in the different peanut samples. The linear regression graphs of calibration (a) and cross validation (b) for the moisture content, protein, fat, FFA, and PV value are shown in Figs. 2–6 respectively. The fitting accuracy along with PLS factors, R^2 , RMSECV, and RMSEE of the calibration and cross validation for the moisture content, fat, protein, FFA and PV values in the peanut samples is represented in the Table 1.

The accuracy and suitability of a model is signified through its preprocessing treatment selection with high R^2 and minimum RMSECV, RMSEE values for the validation and calibration data set respectively. The rank in the regression graphs called as the PLS factors is based on the number of correct factors chosen to establish variation between the different peanut samples and the spectrum bands of them. The FFA had the lowest value of calibration and validation errors (0.579 and 0.738) followed by the protein (0.736 and 0.765), moisture content (0.69 and 0.90), PV value (0.84 and 1.36), and fat content (1.44 and 2.22) respectively.

A PLS factor of 5 for FFA, and moisture content signified that these variables were used for validating the model (Szegedi et al. 2011; Srivastava et al. 2018 a, c). A higher R^2 with lower calibration and validation errors with 1 PLS factor for protein was observed to be in accordance with studies appraising proteins of other oilseeds (Velasco and Becker 1998). Thus, the higher value of R^2 at minimum value of the RMSEE show the accuracy and precision of the FTNIR model developed. The model developed found to be in line with the previously developed model for rapeseed and soybean (Ferreira et al. 2014). These findings highlight the usefulness of FTNIR in detecting the multiple components in a peanut seed in a non-destructive way and found to be helpful in determining the quality of peanut.

Table 1

Different statistical values during validation and calibration for various response variables utilizing different spectral preprocessing techniques in FT-NIR models development.

Response variables	Wavelength bandwidth	Spectral preprocessing (Mathematical)	PLS factor	Validation		Calibration	
				RMSECV ^x	R ²	RMSEE ^y	R ²
Moisture content	9565.5-3488.2	First derivative	5	0.90	83.24	0.691	91.87
Fat	9565.5-3488.2	First derivative	7	2.22	82.82	1.43	93.89
Protein	9565.5-3488.2	First derivative	1	0.765	96.6	0.736	97.04
FFA	12378.9-3594.8	Second derivative	5	0.738	95.97	0.579	97.96
PV %	12378.9-3594.8	Second derivative	7	1.36	85.06	0.845	95.68
^x Root mean square error of cross validation							
^y Root mean square error of estimation							

3.4 Comparative evaluation of FT-NIR and chemical analysis

The developed FTNIR procedure was validated by computing the RPD which is the standard deviation (SD) of the reference set with the standard error of prediction. Generally, RPD 2.5-3.0 (coarse) and 3.1–4.9 (fine) indicate the separating of the samples. A RPD value of 5.0–8.0 are suitable for quality and process analysis, and a RPD more than 8.0 is relevant for broad applications (Williams 2001; Ferreira et al. 2014). The maximum RPD value were noticed in FTNIR method for FFA (41.27), moisture content (34.92), and PV (29.49) indicating good definiteness and model performance in prediction of the concerned value. More RPD variability for different peanut sample was due to the composition of peanut for different process parameters. The efficacy of the developed FT-NIR method for quality testing i.e. moisture content, fat, protein, FFA and PV value of peanut were verified with the chemical testing of unknown (3 set of different peanut samples) samples of peanut. In this validation, the FTNIR spectra of 2 sets of peanut (fresh and spoiled) were taken and was taken for determination of its moisture content, protein, fat, PV value and FFA content by using the standard chemical methods. Both the chemical and FTNIR predicted findings were compared with paired sample t-test by using the statistically tool (SPSS, 22.0) and the results are shown in Table 2. There was no statistical significant differences in the means of FTNIR and laboratory standard methods. Thus, it signifies that the application of the FTNIR method developed over the analytical ones can save time as well as cost for the determination of peanut quality before it is further processed and it also leave no chemical residues as in the laboratory standard methods.

Table 2

Different quality parameters of fresh and spoiled peanut samples obtained through rapid FTNIR method and lab analytical methods

Sample	Parameter	FTNIR						Analytical methods					
		Avg	SD	RSD	RPD	Error (%)	Accuracy (%)	Avg	SD	RSD	RPD	Error (%)	Accuracy (%)
Fresh peanut	Moisture	6.27	0.03	0.46	34.92	0.00	100.00	6.19	0.07	1.20	13.48	0.01	99.99
	Fat	45.43	0.31	0.68	0.99	0.31	99.69	46.03	0.22	0.47	0.25	0.86	99.14
	Protein	26.37	1.43	5.41	14.91	0.10	99.90	26.17	0.93	3.55	19.87	0.05	99.95
	PV %	0.26	0.03	13.04	29.49	0.00	100.00	0.25	0.01	4.49	87.71	0.00	100.00
	FFA	1.80	0.02	1.35	41.27	0.00	100.00	1.76	0.04	2.14	26.54	0.00	100.00
Spoiled peanut	Moisture	14.89	0.74	4.95	1.36	0.54	99.46	14.62	0.43	2.93	2.33	0.18	99.82
	Fat	40.65	0.95	2.34	0.20	4.72	95.28	40.85	0.59	1.45	0.32	1.83	98.17
	Protein	24.66	2.17	8.81	2.41	0.90	99.10	23.66	1.35	5.71	3.84	0.35	99.65
	PV %	15.75	0.67	4.27	1.49	0.45	99.55	15.70	0.64	4.07	1.56	0.41	99.59
	FFA	9.48	0.11	1.18	8.96	0.01	99.99	9.34	0.11	1.14	9.40	0.01	99.99
tcal = 0.029; tcrl = 2.31; α = 0.05													

Conclusion

The applicability of FT-NIR spectroscopy for the rapid detection of quality of peanut has been studied. From the results, the prediction competencies for peanut quality parameter model indicate the FTNIR method significantly fitted. The intuitive FTNIR method can pave a way forward for the unknown sample spectra detection with the reference spectra of peanuts already stored in the spectral library of the FTNIR. Thus, any unknown sample can be identified easily within seconds. Analysis of unknown peanut samples (fresh and spoiled) was predicted precisely with a low predictive error range of 0.05-1.83, which further validated the accuracy of the method developed using FTNIR. These rapid nondestructive FTNIR methods can be employed for the identification and differentiation between the fresh and spoiled peanuts samples in near future. This developed technique has an opportunity for further improvement in the grading of the peanut samples at an initial stage during the quality check and thereby food industries can be easily benefitted from it as it would save both time and effort as the spoiled peanut sample can be easily detected in initial screening via FTNIR.

Declarations

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Author's contribution: All authors contributed to the study conception and design. HNM and SS contributed to technical and conceptual content. RKR and SS contributed to the technical writing of the paper. Material preparation, data collection and analysis were performed by SS and RKR. All authors read and approved the final manuscript.

Compliance with Ethical Standards: This article does not contain any studies with human participants or animals performed by any of the authors.

Conflict of Interest: The authors declare that they have no conflict of interest.

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Figures

Figure 1

Spectra of different peanut samples

b)

Figure 2

Linear regression chart for moisture a) calibration and, b) cross validation in peanuts

a)

b)

Figure 3

Linear regression chart for protein a) calibration and, b) cross validation in peanuts

a)

b)

Figure 4

Linear regression chart for fat a) calibration and, b) cross validation in peanuts

a)

b)

Figure 5

Linear regression chart for FFA a) calibration and, b) cross validation in peanuts

a)

b

Figure 6

Linear regression chart for PV value a) calibration and, b) cross validation in peanuts