Quantitative Analysis of Tapioca Starch using FT-IR Spectroscopy and Partial Least Squares

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ABSTRACT

In the modern competitive world, agriculture sectors and food processing industries need new tools and technologies for the classification of raw materials based on its ingredients presence (Protein, Carbohydrate, Sugar, Fat, Fiber, Vitamin, and Minerals etc.) and to be used for suitable application process based on its ingredients. In order to ensure the final product quality in food processing industry, it is essential to identify and feed the high quality raw materials for higher end applications and Segregate low grade materials for lower end applications.

Tapioca is the important crop in the world after wheat, rice, mice, potato and barely. It has lot of applications in pharmaceuticals, food industries, paper industries and textile industries. It is essential to ensure the quality of tapioca and segregate it based on its constituent for different applications to make the industrial final product as competitive.

Currently in industries, Tapioca starch constituent identified by means of traditional wet chemical methods, as per Indian Standard testing procedure IS4706 (Part-II)-1978. These methods are time-consuming, costly, require skilled operators and would not suitable for rapid identification check at the reception of raw materials. This paper focus on extraction of the ingredients in tapioca using Fourier Transform Infra Red spectroscopy (FTIR) with Chemo metric analysis.

Tapioca starch ingredients were found out from FT-IR Spectrum by identifying the corresponding functional group peak absorption value with FTIR Standards. Calibration model for determination of concentration was built separately using Partial Least Square (PLS). The conventional wet chemical methods results from the observed industrial data were compared with proposed work according to root mean square error of prediction (RMSEP) value. The RMSEP for the ingredients in tapioca was found as 0.003924%for protein, 0.3557% for water, 0.00392% for ash and 2.3162 for starch. This method was suitable for predicting the concentration of the ingredients present in tapioca with high precision. These results can be further used for classification of tapioca towards various industrial needs.

General Terms

Quantitative Analysis, Multivariate Techniques

Keywords

Fourier Transform Infrared Red (FT-IR) Spectroscopy, Partial Least Squares (PLS), Tapioca Starch, Beer-Lambert's law, Near Infrared (NIR), Root Mean Square Error of Prediction (RMSEP).

1. INTRODUCTION

Tapioca is a starch extracted from cassava roots. Tapioca accumulates food in its roots. After growing leaves and other green parts, it starts to produce carbohydrate. The ability to produce and accumulate starch depends on the variety, the age at which it is harvested, the amount of rainfall and other factors. Tapioca is a stable food in some regions and is used worldwide as a thickening agent, mainly in foods. The variety of dishes made from tapioca roots increases the cultivation of this plant in world wide. Application of tapioca starch in pharmaceutical and food industries is increased nowadays. So it is essential to test the quality of tapioca starch and segregate it based on its constituent for different applications to make the industrial final product as competitive.

Identification of raw materials is a requirement of the good manufacturing practices, with the aim of ensuring product safety, raw material traceability and consistent quality. Starches can be identified by means of traditional wet chemical methods [1]. These methods are time consuming, money consuming and they require skilled operators. These methods are not adequate for the rapid identification check to be performed in the food industry at the reception of raw materials or just before their use in production. Various alternative methods such as NIR Spectroscopy [7,8], FT-IR spectroscopy[4,6,11], FT-NIR spectroscopy[13,14], nuclear magnetic resonance, X-ray fluorescence, or X-ray diffraction spectroscopy have already been successfully evaluated for the identification and the characterization of some selected raw materials. Applying new powerful chemo metric tools along with FT-IR spectroscopy has proved to be a promising technology for the identification of modified starches [2, 4].This study aimed at evaluating the potential of FT-IR spectroscopy to identify starches in industry environment.

2. MATERIALS AND METHOD

Fig 1 shows the functional block diagram of the proposed work. It consists of light source, interferometer and detector. The sample was placed between interferometer and detector. Ceramic is used to produce infrared light source which fall on the sample, produces corresponding interferrogram in the detector. This interferrogram obtained from the spectroscopy was Fourier transformed and the resultant spectrum was analyzed using chemometric Technique.
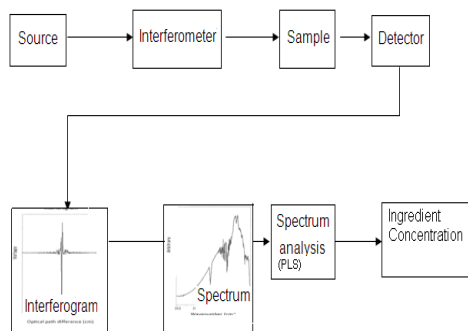
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Fig 1: Block Diagram of Proposed Method

2.1 Wet Chemical methods

Industries are using traditional chemical methods to determine the constituents of tapioca starch. Ingredients of tapioca starch were determined for 20 samples using wet chemical methods and listed in Table 2. These experiments were done at SPAC tapioca industry, Poonachi, Erode District.

2.2 FT-IR spectroscopy

2.2.1 Working principle of spectroscopy

When infrared radiation passes through a material, some intensity passes through without interacting with the molecules, while the remainder interacts with molecules and is absorbed. The proportion of absorbed intensity over the total intensity that enters the material is in direct relation to the concentration of absorbing molecules. This is the principle of Beer-Lambert's law [4]. It describes the absorption of infrared radiation by molecules by means of a simple equation:

$$A_\lambda = c_\lambda \times b \times \varepsilon$$

Where

A_λ - Measured Absorbance at a specific wavelength

ε_λ - Absorption Coefficient of the material at that wavelength

b - Path length through the sample

c - Concentration of the absorbing material

Beer-Lambert's law: $A_\lambda = c_\lambda \times k$

By measuring the absorbance of an unknown sample at the appropriate wavelength, one can predict the concentration of the sample using the following equation:

$$\text{Unknown concentration } c_\chi = \frac{A_\lambda}{k_\lambda}$$

The shimadzu IR affinity-1 make FT-IR spectroscopy was used for obtaining the starch spectrum. It employ ceramic light source with DLATGS detector. These spectrum were obtained at VIT university, Vellore.

2.2.2 Sample Preparation

Tapioca starch sample were taken from SPAC tapioca Pvt Ltd, Poonachi. Sample was prepared using pellet method. In this method, a few milligrams of the starch sample were mixed with approximately 0.5-g of potassium bromide. The mixture was subjected to pressure of 20 psi to make it as pellet of 13 mm size. The pellet was placed between interferometer and detector in the sample holder of the spectroscope.
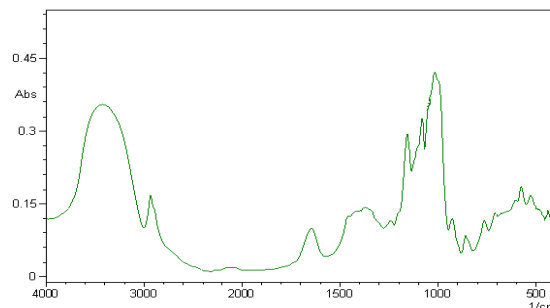

Fig2: FT-IR Spectrum of Tapioca Starch

2.2.3 Acquired FT-IR Spectra

The sample is placed in the FT-IR spectroscopy. Infra red light source generates wavelength from 4000 to 400 cm^{-1} 32 times per sample with a resolution of 4. Infrared spectrum was Fourier transformed and recorded in the absorption mode. Fig 2 shows the Interferogram obtained from FT-IR spectroscopy between wave number and absorption. IR solution software is employed for getting the spectrum.

2.2.4 Peak Detection

As per Beer's law the amount of absorption is directly proportional to the amount of constituent present in the starch. Fig 3 shows the peak values of the tapioca starch spectrum corresponding to the absorption values. Here the peak values were determined using local maxima concept. The local maximum of a function is a value that greater than all values that are near it.
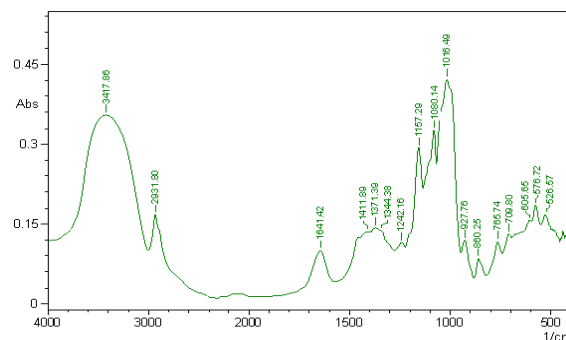

Fig3: FT-IR Spectrum of Tapioca Starch with peak detection

2.2.5 FT-IR Standard comparison

The resulting spectrum represents the molecular absorption, creating a molecular fingerprint of the sample. Like a fingerprint no two unique molecular structures produce the same infrared spectrum. This makes infrared spectroscopy useful for several types of analysis [1].

The mid-infrared spectrum (4000–400 cm^{-1}) is approximately divided into four regions. The nature of a group frequency is determined by the region in which it is located. The regions

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are generalized as follows: the X–H stretching region (4000–2500 cm^{-1}), the triple-bond region (2500–2000 cm^{-1}), the double-bond region (2000–1500 cm^{-1}) and the fingerprint region (1500–600 cm^{-1}).The fundamental vibrations in the 4000–2500 cm^{-1} region are generally due to O–H, C–H and N–H stretching. O–H stretching produces a broad band that occurs in the range 3700–3600 cm^{-1}. From the literature review, N–H stretching is usually observed between 3400 and 3300 cm^{-1}. This absorption is generally much sharper than O–H stretching and therefore be differentiated. C–H stretching bands from aliphatic compounds occur in the range 3000–2850 cm^{-1}. If the C–H bond is adjacent to a double bond or aromatic ring, the C–H stretching wave number increases and absorbs between 3100 and 3000 cm^{-1} [12].

The principal bands in the 2000 – 1500 cm^{-1} region are due to C=C and C=O stretching. Carbonyl stretching is one of the easiest absorptions to recognize in an infrared spectrum. It is usually the most intense band in the spectrum and depending on the type of C=O bond, occurs in the 1830–1650 cm^{-1} region. The metal carbonyls absorb above 2000 cm^{-1}. C=C stretching is much weaker and occurs at around 1650 cm^{-1}, but this band is often absent for symmetry or dipole moment reasons. C=N stretching also occurs in this region and is usually stronger.

2.2.6 Ingredient Analysis

Tapioca starch ingredients were found out by corresponding functional group peak absorption value with FTIR Standards using local maxima concept. These peak absorption values and corresponding functional groups were listed in Table 1.The FT-IR spectrum of tapioca starch sample was further analyzed to find out the concentration of the ingredients using PLS algorithm.

Table 1 Peak Absorption Value

S.No	Wave number in 1/cm	Absorption Value	Functional Group Identified
1	526.566768	0.168397	Bromide
2	576.715984	0.186171	Bromide
3	605.65	0.156648	Bromide
4	709.804288	0.131525	Pyridines
5	765.739952	0.117585	Pyrrole
6	860.251936	0.085807	Arenes
7	927.760496	0.120024	Alkenes
8	1016.486032	0.422543	Carboxyclic acids
9	1080.13696	0.325271	Carboxyclic acids
10	1157.2896	0.293624	Carboxyclic acids
11	1242.157504	0.115895	Carboxyclic acids
12	1344.385	0.133467	Alkanes
13	1371.388176	0.142547	Alkanes
14	1411.892	0.125237	Alkenes
15	1641.422416	0.100281	Alkynes
16	2931.80032	0.168339	Carboxyclic acids
17	3417.861952	0.355421	Amines

3. QUANTITATIVE ANALYSIS

3.1 Partial Least Square Algorithm

The Quantitative analysis was carried out by means of partial least squares [6]. The calibration model for constituent determination between the spectral data and the experimental data was built using PLS. X_{PLS} is the input data for PLS modeling, where each row represents spectrum data from tapioca starch and Y vector represents the experimental values of the concentration obtained from the SPAC industries through wet chemical methods. By partial least squares analysis, the wave numbers corresponding to peak values were used to develop the calibration model. Table 2 shows the training, testing data and the predicted output.

Table 2 Concentration of Tapioca Constituents from Wet Chemical Method and PLS

S.No	Protein %	Starch %	Moisture %	Ash %	Remarks
1	0.048	99.6	12.5	0.07	Training Data
2	0.052	99.6	13	0.07	
3	0.055	99.5	12.4	0.08	
4	0.053	99.5	12.64	0.09	
5	0.048	99.55	12	0.07	
6	0.049	99.6	12.86	0.09	
7	0.049	99.6	12.76	0.09	
8	0.053	99.5	12.32	0.07	
9	0.049	99.4	13	0.08	
10	0.051	99.6	13	0.08	
11	0.049	99.45	12.3	0.08	
12	0.054	99.7	12.2	0.08	
13	0.061	99.4	12.7	0.08	
14	0.059	99.6	12.7	0.09	
15	0.049	99.6	12.7	0.09	
16	0.054	99.7	12.5	0.07	Testing Data
17	0.055	99.7	12.2	0.07	

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18	0.052	99.4	13	0.08	
19	0.053	99.6	12.8	0.08	
20	0.052	99.5	13	0.09	
21	0.0542	99.960	12.530	0.070	
22	0.0545	100.82	12.450	0.074	Predicted Output
23	0.0517	98.886	12.933	0.080	
24	0.0500	95.957	12.302	0.075	
25	0.0514	96.041	12.437	0.084	

3.1.1 Calibration model

The PLS Calibration model for prediction are

$$X_{PLS} = T*P' + E$$

$$Y = U*Q' + F$$

Training Inputs:

X_{PLS} data matrix of spectrum

Y   data matrix of experimental results

T   is the column of X has the largest square of sum.

U   is the column of Y has the largest square of sum.

E and F Irrelevant variability in X_{PLS} and Y

Training Outputs:

w = X_{PLS}'*u

q = Y'*t

b = u'*t/(t'*t)

p=X_{PLS}'*t/(t'*t)

T   score matrix of X

P   loading matrix of X

U   score matrix of Y

Q   loading matrix of Y

B   matrix of regression coefficient

W   weight matrix of X

Testing:

Using the PLS model, for new X1, Y1 can be predicted as

Y1 = (X1*P)*B*Q'

Where,

X1   testing input

Y1   predicted output of concentration

4. RESULTS AND DISCUSSION

4.1 Model Validation

The performance of the final PLS model was evaluated in terms root mean square error of prediction (RMSEP). RMSEP give the predictive ability of the model for unknown samples. The higher the value of RMSEP leads to poor predictive ability of the model. RMSEP is calculated for the test set which is used for prediction.[13].

The RMSEP is calculated using the following equation:

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

Where,   n - Number of sample in the test set.

y_i - Reference measurement (experimental data),

$\hat{y}_i$ - Estimated result of the model

Table 2 had the predicted concentration values of tapioca starch using PLS. Table 3 shows the RMSEP values for different constituents of tapioca starch.

Table 3 RMSEP values for different Constituent

S.No	Constituent	RMSEP
1	Protein	0.0014
2	Starch	2.3162
3	Moisture	0.3557
4	Ash	0.003924
5	Fiber	0.00447

5. CONCLUSIONS

In the proposed work, Functional groups of tapioca constituent and its concentration were determined using FTIR spectroscopy with chemo metrics techniques within few seconds. When compare to chemical methods currently used in the industries this spectroscopy method encapsulates the advantages: i) reduces time consumption for quality testing, ii) less chemical residue production, iii) cost reduction iv) very important advantage of being a non invasive method.

The calibration model applied for constituent determination of tapioca starch built using partial least square method was accurate in prediction. The RMSEP for the ingredients of tapioca was found as 0.003924%for protein, 0.3557% for water, 0.00392% for ash and 2.3162 for starch. This method was suitable for predicting the concentration of the ingredients present in tapioca with high precision. The RMSEP values were very low in exactly predicting protein, water and ash content. To improve the calibrations, tapioca starch samples with wide range of starch quality parameters can be added in future work. These results can be further used for classification of tapioca towards various industrial needs.

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