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SPECTRAL AND PHYSICO-CHEMICAL ANALYSIS OF VEGETABLE OILS

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ABSTRACT

Physico-chemical properties of vegetable oils such as sunflower, groundnut and rice bran oil were studied. In this research paper physico-chemical characteristics such as, color, refractive index, specific gravity, acid value, iodine value, saponification value of the given oil samples was determined using different methods.Spectral analysis of these oils was also carried by FTIR spectroscopy. FTIR experiment was performed on three different oils on Perkin Elmer instrument.

Keywords – Spectral analysis, physico-chemical properties, Vegetable Oils.

INTRODUCTION

Dietary fats and oils are important substances that play a key role in maintaining good health .In the Indianculinary culture use of edible oils plays an integral role in cooking for human consumption cooking oils can be categorized into three groups .Ghee ,coconut oil and palm kernel oils are the major sources of saturated fats .Linseed ,soybean corn and sunflower oil are rich in linoleic acid and linolenic acids PUFA and Canola ,mustard ,rice bran olive and ground nut oil and rich in oleic acid MUFA .Edible vegetable oils are foodstuffs which are composed primarily of glycerides of fatty acids being obtained only from vegetable sources. Quality and purity are two of the most important parameters in the analysis of the edible oils and have been the subject of several researchers studies (1).Oil characterization is the basis for further nutritional and food technological investigations such as adulteration detection . There are several methods suggested to detect the adulteration of sunflower .Most of them are based on physical and chemical constant including determination of theIodine value saponification value, density, UV absorbance and refractive index .Oils are known to decompose over time producing unpleasant taste and odor.This is called rancidity .It is caused by the presence of free fatty acids and by atmospheric oxidation .Therefore a number of parameters have been used to characterize the identity and edibility of vegetable oils .

To investigate the physicochemical properties of oils such as sunflower oil groundnut oil and rice branoil we purchase from local market.In this research paper physicochemical characteristics such as color,refractive index,specific gravity,acid value,peroxide value of the

given oil sample was determined using different methods.The color of sample is determined with computerized Lovi bond colorscan, for Refractive Index Abbe Refractometer,Specific Gravity by RD bottle and acid value by BIS method[4].Methyl Ester of fatty acid was prepared by saponification and esterification and determined by Gas liquid chromatography.

The application of FTIR technique expanded in food research and particularly has become apowerful analytical tool in the study of edible oils and fats. It is a rapid,non –destructive technique with minimum sample preparation necessary .It allows the qualitative determination of organic compounds as the characteristic vibrational mode of each molecular group causes the appearance of bands in the infrared spectrum at a specific frequency ,which is further influenced by the surrounding functional groups .Infrared spectroscopy also referred to as mid infrared spectroscopy, has a wavelength range of 4000-400 cm^{-1} .Mid infrared spectra has been used to characterize edible oils and fats.It provides an absorption spectrum of energy level transitions caused by molecular vibrations and rotations, which provide information regarding molecular functional groups (2). They differentiate in the intensity and the exact frequency at which the maximum absorbance of the bands appears , according to the composition of the sample. According to the nature and composition of the oilsample exact position of the band has been observed when the proportion of fatty acids changed. (3)

MATERIALS AND METODS

Sunflower (RBD) Oil

Refined, bleached and deodorized sunflower oil (trade name "Sundrop") manufactured by M/S I.T.C. Agro-tech. Limited, Secundrabad India was purchased from the local market and was used in the experiments.

Groundnut (RBD) Oil

Refined, bleached, and deodorized groundnut oil (trade name "Dalda") manufactured by Brooke Bond Lipton India Limited, Calcutta India was purchased from local market and was used for blending purpose with RBD sunflower oil.

Rice bran (RBD) Oil

Botanical name - Oryza sativa bran oil is also called healthy oil inAsian Countries .

Ricela group of Companies is today “world’s largest producer” and India’s “Highest explorer” of refined rice bran oil established in the year 1992, with the sole objective of producing and promoting rice bran oil as “ world healthiest cooking oil “. It is used for blending purpose with sunflower oil and groundnut oil, was procured from local markets.

Chemicals Used

All the chemicals used for analytical work were of AR grade obtained from M/S Qualigens Fine Chemicals Mumbai, India.

Determination of Physico-chemical Characteristics

Physico-chemical characteristics of experimental oil samples were determined by using the following procedures.

Color

The of the sample was determined with"Computerized Lovibond Colourscan" manufacture by "The Tintometer Ltd, Salsburg U.K." by using AOCS Tintometer scale.

It is a computer-based system for the color analysis of the oil samples. Prior to measurement, the oil samples were melted and filtered through a filter paper to remove any impurities and the last traces of the moisture. The size of color scanning quartz cell was 1.0 cm. The cell was filled with clear, filtered sample and placed in position inside the optics module of the colorscanner. After feeding the requisite data the results were directly obtained on the computer screen. During the color scanning of the samples, the observer angle was fixed at 2° and illuminated at D65 (6500K). The color of the samples was reported directly using following relationship.

Color reading in (1cm) cell = (aY+5bR) or (a Y + 10 bR)

where

a= The sum of total of the various yellow (y) slices used and

b= The sum total of the various red (R) slides used.

Refractive Index

Abbe refractometer[4] was used to determine the refractive index of samples.

The prism of the refractometer was cleaned by the acetone and dried. The temperature of the refractometer was adjusted to 30 ± 1°C. A few drops of the sample was placed on the lower prism and the prism was closed, tightened firmly with the screw-head and allowed to stand for one or two minutes. Thereafter the instrument was adjusted to obtain the most distinct reading possible.

Whenever required, the temperature correction was made using the following formula

$$R = R' + K(T'-T)$$

Where

R= The reading of the refractometer reduced to the specified temperature, T°C

R'= The reading at $T'^{0}C$

K = Constant 0.000385 for oils

T' = The temperature at which the reading R' is taken

T = The specified temperature

Specific Gravity

Specific gravity of the original samples was determined against water at 30 °C using a specific gravity bottle of 10 ml capacity following method (4).

Perfectly dried specific gravity bottle was taken and filled with water. The stopper was inserted to exclude the extra water. After wiping the bottle dry it was weighed accurately on Dhona 200D electrical balance. After weighing with water, replaced the water from bottle

and dried and filled with oil sample as above and weighed accurately. The specific gravity was calculated as follows

$$\text{Specific gravity (at 30°C)} = \frac{\text{weight of oil}}{\text{weight of the water}}$$

Further this was corrected to 30°C by the following factor

Specific gravity at TC/T°C s'+ 0.00041 (T1-T)

Where

S = Specific gravity at T /T°C

T = Temperature at which the specific gravity was determined

and

T = Standard temperature, 30°C

Acid Value

The acid value of the recorded samples was determined by method (4). Accurately weighed sample of oil (2 to 3 g) was mixed with neutral ethyl alcohol, warmed, and titrated against standard sodium hydroxide solution using phenolphthalein as indicator. The acid value was calculated using the following relationship.

$$\text{Acid value} = \frac{56.1 \times N \times V}{W}$$

where

N = Normality of aqueous sodium hydroxide solution

W = Weight in gms of the sample

and

V = Volume in ml of sodium hydroxide solution consumed

Iodine Value

Iodine values of the samples were obtained by using method. The oil sample (0.2-0.3 g) was weighed accurately into the 500 ml Iodine value flask and 25 ml of carbon tetrachloride was added to dissolve the contents. Then 25 ml of Wijs solution (iodine monochloride in glacial acetic acid) was added and glass stopper was replaced afterwetting it with potassium iodide solution (freshly prepared by dissolving 10 g potassium iodide, free from potassium iodate, in 90 ml water). The flask was swirled and was allowed to stand in dark for 45 minutes. Thereafter the flask was taken out and 15 ml of potassium iodide solution was added followed by addition of 100 ml distilled water rinsing the stopper also. The iodine, which liberated, was titrated against standard sodium thiosulphate solution until the color of solution was straw yellow. At this stage 1 ml of starch solution (1%) was added to flask and titration was confirmed until the blue color formed on addition of starch

disappeared after through shaking with the stopper on. A blank determination was also made simultaneously under similar conditions and the iodine value of the relationship. sample was calculated using the following

$$\text{Iodine value} = \frac{12.69 \times (B-S)\ N}{W}$$

Where

B = Volume in ml of standard thiosulphate solution used in blank determination.

S = Volume in ml of standard sodium thiosulphate solution

N = Normality of the solution of sodium thiosulphate and

W = Weight of the sample (in gm)

Peroxide Value

Peroxide value of RBD sunflower oil, RBD groundnut oil and samplegrown during deep-fat frying of Potato chips were determinedby using method[4]. The oil sample (5.00+ 0.05 g) was weighed accurately in to a glass stoppered conical flask of 250 ml of capacity and then 30 ml acetic acid chloroform solution was added. The flask was swirled to completely dissolve the sample and then 0.5 ml of saturated potassium iodide solution was added. The solution was allowed to stand exactly one minute with occasional shaking and then 30 ml of distilled water was added. Thereafter the contents of the flask were titrated with 0.1 N sodium thiosulphate solution with constant and vigorous shaking. The titration was continued up to the almost disappearance of yellow color. The end point was determined by using starch indication and judged with disappearance of blue color. A blank determination was also made simultaneously under similar condition and peroxide value as milli equivalent per 1000 grams of sample was calculated using following relationship.

$$\text{Peroxide value} = \frac{(S-B) \times N \times 1000}{W}$$

Where

S = Volume in ml of sodium thiosulphate solution used up by the sample.

B = Volume in ml of the sodium thiosulphate solution used up in the blank determination.

N = Normality of sodium thiosulphate solution and

W = Weight of g of the sample.

Fatty Acid Composition

Methyl esters of RBD sunflower, RBD groundnut oil was prepared and by gas - liquid chromatography.

Preparation of Methyl Esters (FAME)

Saponification and esterification process are used to prepare the methyl esters of the oil samples (5). About 10 gm of oil were refluxed with 50 ml of alcoholic potassium hydroxide (78%) in ethanol, w/v) for 3 hrs. After that the content were transferred in separatory funnel with addition of 50 ml of cold distilled water. Their content of the unsaponifiable were extracted out twice with 50 ml aliquots of petroleum ether. The soap solutions were acidified with requisite amount of 2N sulphuric acid to obtain free fatty acids. The free fatty acids were extracted with 5 x 10 ml portions of diethyl ether. The combined ether extracts of each sample were dried using anhydrous sodium sulphate and filtered. The fatty acid of the samples was recovered by distilling of the ether under moderate vacuum from dried extracts.

The fatty acids recovered from the samples were esterified by refluxing 4 h, with 5 volume of acidified methanol (100 ml methanol containing 1 ml concentrated sulphuric acid). The esterified contents of the flask were transferred into separating funnels with equal volume ofdistilled water. The methyl esters were extracted with 5 x 10 ml portion of diethyl ether. The combined ether extracts of each sample were washed thrice first with 50 ml aliquots of 10% sodium bicarbonate solution and then with 50 ml of aliquots of distilled water. Anhydrous sodium sulphate is used to dry the ether extracts and then filtered. The methyl esters of the fatty acids of the samples were recovered by distilling off the ether under moderate vacuum from the dried extracts. The recovered extracts were dissolved in diethyl ether in desired quantity and subjected in gas liquid chromatograph by micro syringe for determination of their fatty acid composition.

Gas-Liquid Chromatography

Fatty acid composition was determined chromatograph (TREMETRICS 540, USA) having flame with gas ionization detector. The column used for analysis was 3 mm x 2 m stainless steel column packed with 15% DEGS on chromosorb W (80 100 mesh). Chromatographic grade purified nitrogen gas was used as carries. Hydrogen gas of extra high purity was used as the flame ionizationdetector. The flow rate of hydrogen and nitrogen were kept 30 ml/min. The oven and injector temperature were 190°C and 225°C respectively. The methyl ester of fatty acids was dissolved in diethyl ether to a specific concentration (10%) and 0.4 µl of this solution was injected to the gas chromatograph. The percentage of fatty acids were obtained from computerized data processor

Spectral analysis of above-mentioned oils by FTIR Spectroscopy

FTIR experiment was performed on three different oils on Perkin Elmer instrument.Initially dry Nitrogen was purged in samples to keep away from interference with atmospheric carbon dioxide along with water vapors .Approximately ,10UL of oil sample was placed on potassium bromide polished plate .Immediately a uniform thin film was formed on the surface of the potassium bromide plate(6). Consequently, a high resolution spectra was obtained. The sample was scanned at room temperature and collected absorbance frequency data from 4000-600cm^{-1}.

RESULTS AND DISCUSSION

The physical and chemical properties of sunflower, rice bran and groundnut oil were shown in Table 1.

Table 1: Physical and Chemical Properties of Vegetable Oils

PARAMETERS	SUNFLOWER OIL	RICEBRAN OIL	GROUND NUT OIL
Acid value in mg KOH/g	0.16	2.22	.686
Saponification Index (mg / g)	191	184	194
Iodine Index (mg / g)	130	104	84
Specific gravity	.948	.885	.93
Refractive Index at 50℃	1.467	1.46	1.462
Peroxide Value (Meq / kg)	0.46	0.56	2.27
Color	1.0	15.5	13

Acid value of rice bran oil is higher as compared to other vegetable oils. Acid value is an important indicator of vegetable oil quality. Acid Values are used to measure the extent to which glycerides in the oil has been decomposed. The higher the acid value and free acid content the lower is the quality of the oil.

In the present study, saponification value of groundnut oil was higher than other vegetable oil. The Saponification Value is a measure of the average molecular weight of the fatty acids in the oil and it is used to determine the quality and purity of the oil. A higher saponification value indicates a higher concentration of fatty acids, which can affect the taste, aroma and overall quality of the oil. The saponification value can also be used to determine the shelf life and stability of the oil as oil with higher saponification value tend to have a longer shelf life and are more resistant to oxidation.

Iodine Number of groundnut oil is 84 mg/g which is higher compared to other two oils i.e sunflower and rice bran oil. The iodine value is a measurement of the total unsaturation of vegetable oils as well as indicator of their susceptibility to oxidation.

Table 2: Fatty Acid Profile of Vegetable Oil

Mean ± SD			
Types of oil	SFA(%)	MUFA(%)	PUFA(%)
Sunflower oil (n=15)	11.39	52.92	62.69
Groundnut oil (n =7)	19.27	53.77	26.96
Rice bran oil (n=9)	23.63	40.98	14.67

Table 3:Fatty composition of vegetable oil

Fatty Acid	Molecular weight	Group	Sunflower oil	Rice bran oil	Ground nut oil
Palmitic Acid	256	SFA	6.1	15	10
Stearic Acid	284	SFA	5.3	1.9	3.0
Oleic Acid	282	MUFA	21.4	42.5	50.0
Linoleic Acid	280	PUFA	66.4	39.1	30.0

The saturated fatty acid in vegetable oils are palmitic acid and stearic acid, unsaturated fatty acid are oleic acid and linoleic acid. The unsaturated fatty acid are more susceptible to thermal oxidation, hydrolysis and polymerization than saturated acids.

FTIR SPECTRUM ANALYSIS

In this study the molecular functional group of triglycerides linkage (TAG)was confirmed by using FTIR spectroscopy. Spectra analysis by FTIR was carried out by Perkin Elmer Instrument.

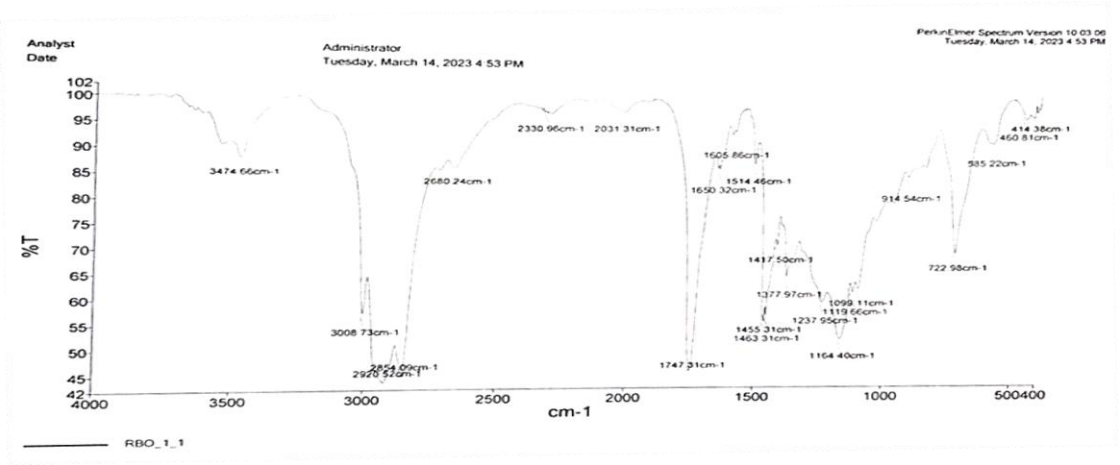

Figure 1 – FTIR of Rice Bran Oil

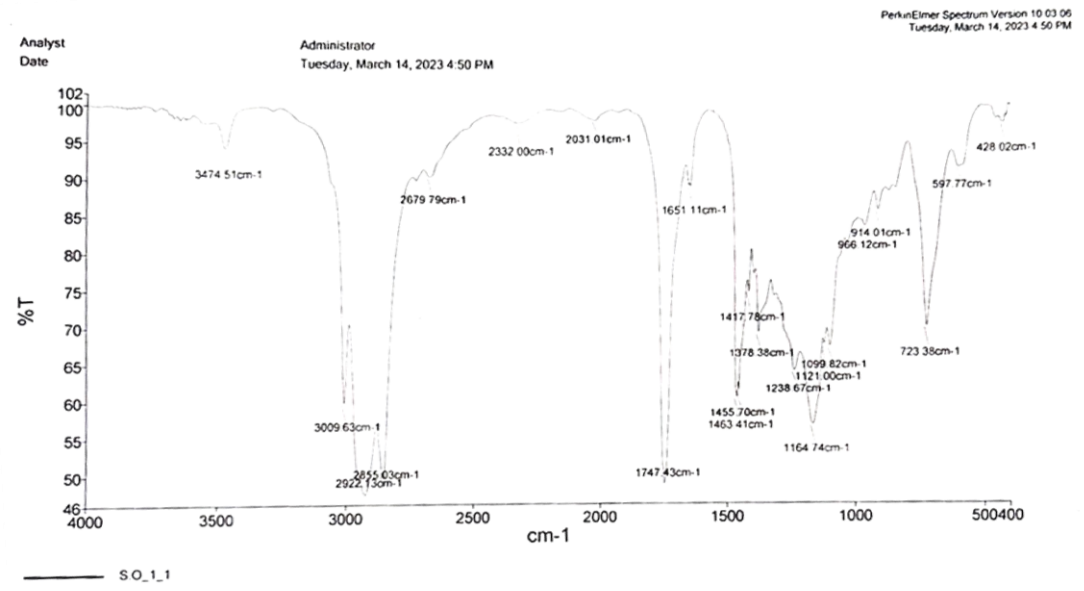

Figure 2 – FTIR of Sunflower Oil

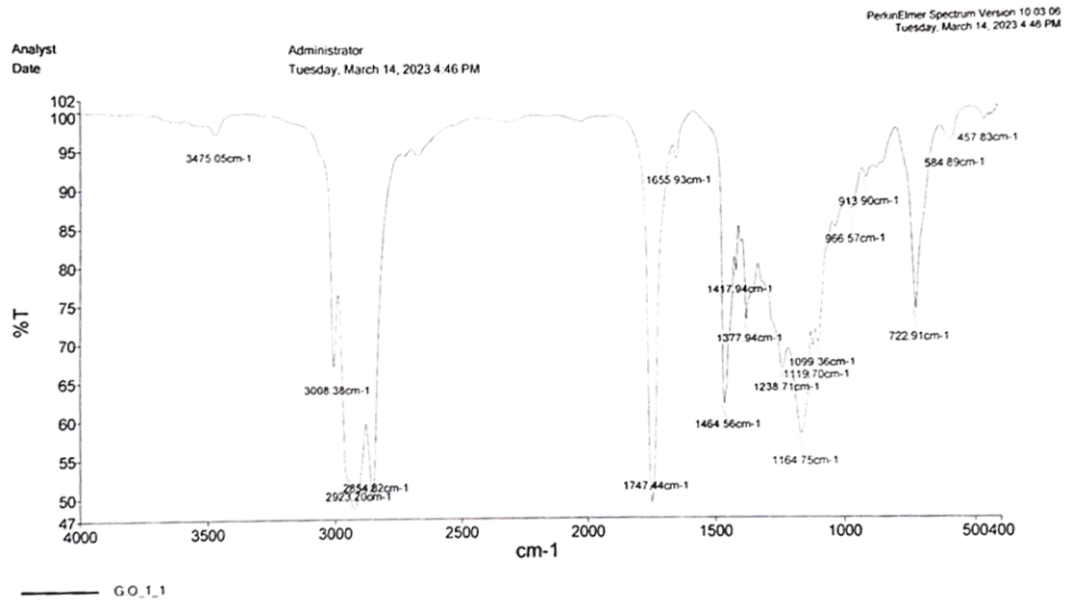

Figure 3 – FTIR of Groundnut Oil

In fig 1-3 represents FTIR spectrum of three oils rice bran oil,sunflower and groundnut oil.All the three oils spectra appeared with similar features. Among the three peaks the high intense vibration frequency band was noticed at 1747.31cm^{-1}, 1747.43cm^{-1} and1747.44cm^{-1}is corresponding to ester carbonyl group of triacyl glyceride group of groundnut ,sunflower and rice bran oils .Association of three carbonyl functional groups is responsible for higher stretching frequency further evident consists of three carbonyl(O=C=O) connectivity.(7)

The important observation (fig 1-3) is stronger absorption for C=O ,whereas for double bond olefin has shown quite low absorbance band typically at 1650.32cm^{-1} ,1651.11cm^{-1}

and1655.93cm^{-1}result of double bond C=C frequency is not interfered with C=O stretching frequency .Unsaturated long chain cis olefinic C-H stretching frequency appeared at 3008.73cm^{-1},3009.63cm^{-1}and 3008.38cm^{-1}. While saturated carbonsymmetrical and asymmetrical stretching observed at 2920.52cm^{-1} ,2922.13cm^{-1} and2923.20cm^{-1}.However,methylene symmetrical bending frequency seen in the range 1455-1164cm^{-1}.

Ester bond of C=O stretching was noted around1164.40cm^{-1},1164.74cm^{-1}and1164.75cm^{-1}.The appearance of broad band in the range 722.98cm^{-1},723.38cm^{-1}and 722.91cm^{-1} is a loop of cis disubstituted is less symmetry than trans conformation .The spectrum also show overtone of a weak bond at3474.66cm^{-1},3474.51cm^{-1}and3475.05cm^{-1}associated with the glyceride ester implies variation in the position as well as absorbance of the bands owing to variation in composition of triglyceride fatty acid structure (8).The FTIR analysis confirms the presence of functional groupsin peanut ,sunflower and rice bran oils . The slight variation of peak values in FTIR result of variation of content between saturated and unsaturated fatty acids. The used methodology is an interesting and quite valuable for the authentication edible oils both in food industry, quality control as well as human health .

CONCLUSION

The acid value of rice bran oil is higher as compared to sunflower and groundnut oil, so rice bran decomposes easily and is inferior in quality. The saponification value of groundnut is higher in comparison to flower and rice bran oil, therefore, rice bran oils have longer shelf life and resistant to oxidation.

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