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Extraction and Assessment on Non-Catalytic and Catalytic Wij's Method of Iodine Value Measurement of some Extracted Oils of Different Groundnut Varieties Grown in India

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ABSTRACT

Present research examines the comparison between catalytic or accelerated method with original or non-catalytic Wijs method for IV analysis.In the present work, Fast method is used for the measurement of Iodine value (IV), wherein mercuric acetate is directly used in the powder form. The method only requires to add the catalyst mercuric acetate in the process of determination without changing the operational steps of the Wijs method. Compared with the Wijs method in which it will take at least 30 minutes to finish it, the fast determination method can make the determination reaction finished in 3 minutes. The iodine value of extracted oils of different groundnut seeds varieties such as Rajasthan Nagori RD 1:10(RRD1:10), G10 Gujarat(G10G), Shivpuri(Sv),Rajasthan Gugeri(Rg),TMV-2,G2-52, Karad-9(Kd-9) and T-64 were determined by regular Wijs method for 30 minutes whereas when we apply catalytic Wijs method with use of 2 mg, 5 mg and 10 mg of mercuric acetate to perform as catalyst then it is reducing the time of analysis to 3 minutes. The analytical results showed that there was no great difference between the two methods with the relative error less than 0.2%. When catalyst is used the different values obtained for standard deviations are 0.17 for 2mg, 0.33for 5mg and 0.27 for 10 mg whereas 0.26 for non-catalyst addition and 0.2 for oil content. The resultsobtained in the present work shows Rg, Kd-9 and T-64 has more % difference in IV in case of 2mg catalyst.

KEYWORDS: *IV (Iodine Value), Wijs method, mercuric acetate, groundnut seed extracted oils*

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1. INTRODUCTION

The pea nut, often called as "The King of Oilseeds", is botanically known as Arachis hypogaea and belongs to family Leguminosae, which is also called Fabacae. The pea nuts differ in the quantity as well the quality of oil. These differences in the pea nut oil may be due to several factors *i.e.* genotype, the level of maturity of the seed, season and geographical area of production[4].India is the largest producer of groundnut in the world. Around 88% of the groundnut area and production in India is concentrated in five states: Andhra Pradesh, Gujarat, Karnataka, Tamil Nadu, and Maharashtra. Nearly 83% of the total area is under rainy-season groundnut and the other 17% is cultivated during the post rainy season. During 1995-98, groundnut was grown in India over 7.47 Mha with a total production of 8.02 Mt [5].India possesses varying climatic conditions results in cultivation of a wide range oil bearing crops trees and nuts. Peanuts make an important contribution to the diet in many countries. Peanut seeds are a good source of protein, lipid and fatty acids for human nutrition [16]**.** The oil content of groundnut differs in quantity, the relative proportion of fatty acids, geographical location, seasons and growing conditions [2]**. Barku et al., 2012** have reported changes on the chemical composition as a result of processing. However, little information on the effect of traditional processing on peanuts quality was reported. The chemical properties of oils are amongst the most important properties that determine the quality and help to describe the present condition of oils. Its constitute one of the essential components of balanced diet as good source of energy. The study indicated that Peanut oil, may have a higher shelf life, nutritional value and industrial applications. Vegetable oil had made an important contribution to the diet in many countries [3].

Iodine value is important parameter of different vegetable oils is the amount of unsaturation of the constituent fatty acids. This has been measured by the iodine value (IV), which is currently determined by the Wijs method. Various methods are available to determine the IV of fats and oils, such as that of Hanus and Hubl, Hofmann and Green, Rosenmundand Kuhnhenn and margosches method. The IV of vegetable oils can provide very useful information in other scientific fields. Although many methods have been developed, the Wijs method is the most widely used as a standard methodin food analysis laboratories. Major drawbacks of that method include the use of dangerous iodinetrichloride (Wijs reagent) and the time-consuming asduration of the reaction is as long as 30-60 minutes and procedures for reagent preparation and chemical analysis. Numerous efforts have been made to reduce the time by use of accelerators as mercuric acetate. In this paper mercuric acetate is used as a catalyst/accelerator to achieve a

reduction in the reaction time.The official methods for determination of iodine value (IV) involve the reaction of double bonds in oils with halogenating reagent (Wijs solution) over 30 min followed by iodometric titration of the liberated iodine obtained through reaction of excess Wijs reagent with potassium iodide with sodium thiosulphate solution using starch as an indicator. Wijs method is generally adopted for the measurement of iodine value **[1,6]**.Generally Wijs method is used for measurement of iodine value and this method has a drawback that duration of the reaction is as long as 30-60 minutes. and involves following reactions:

$$ICl + KI \longrightarrow KCl + I_2$$

$$I_2 + 2\ Na_2S_2O_3 \longrightarrow 2\ NaI + Na_2S_4O_6$$

1.1. Related work

Shin-ichiKikuno et al (1975) investigated the methods of quick determination of iodine value especially for the oil in the hydrogenation process and have found after all the Wijs method could be appropriate by only shortening the reaction time to three minutes for the oils of iodine value less than about 100. It also studied the effect of catalyst, temperature, time and I/CL ratio during the determination of iodine value [12].Hashemy et al (1977) studied the IV of 121 samples of butter as well as some common oils and fats by applying both the standard and rapid Wij's and Hanus methods. In the rapid method a 2.5% of mercuric acetate in acetic acid was used. The results obtained are close and comparable for 1 min Wij's and 3 min Hanus methods as compared with 30 min reaction time of standard procedures [8].

According to the united state patent (1981) when the magnesium acetate or sodium acetate is used in the form of a solution in glacial acetic acid, preferably having a concentration of 3-5 wt. %. In this method; the reaction time of a sample with the Wij's solution is as short as short as about 3 minutes. Then, the iodine value is measured in the same manner as in the Wijs method. Since the analysis time is thus remarkably shortened [14].Lihua et al (1999) investigated a fast method for determining the IV of oils and fats using mercuric acetate without changing the operational steps of the Hanus method and reduced time from 30 minutes to 3 minutes. The experimental result indicates that fast method gives a variation coefficient is 0.31 % [9].

A Spectrophotometric analytical system was also proposed by Thomaidis *et al.* for determination of olive oil IV. The method involves the absorbance measurement at 392 nm of unreacted Hanus solution, i.e. IBr in glacial acetic acid. In addition to instrumental analysis, potentiometric titration was proposed as an alternative approach for analysis of biodiesel from palm oil. Wijs method is, however, lengthy or time consuming for regular quality control purposes as it requires around 30-60 minutes for the reaction of oils with the Wijs solution. Spectroscopic techniques, e.g. FTIR, FT-NIR etc., have also been proposed for fast and non-destructive IV analysis of oils. However, the method involves enormous mathematical calculations, and requires sophisticated instrument which is not normally available in general quality assurance (QA) laboratory of refining of hydrogenation plant. In addition, the FTIR method necessitates the standardization of oils or fatty acids used for construction of calibration graph by using the time consuming official methods [13].

OndrejHendl et al (2001) studied a rapid method for determining the IV, of vegetable oils was developed. The method was based on using derivative FTIR measurements. The infrared derivative spectrum of pure vegetable oils was measured between 4000-400cm-1 and the heights of the derivative spectrum for functional grp band maxima were determined. The pure vegetable oils as samples were used throughout this study. The method was used for the determination of IV of 12 edible vegetable oils as well as castor and linseed oils. Oils with IV ranging from 10- 190 were tested and found to give satisfactory values. Results were obtained with good precision and accuracy, typically exhibiting 5% relative standard deviation[10].

Zhongguo-ging (2004) investigated a new method for the determining the IV of oil and fat was only requires to add catalyst mercuric acetate in the process of determination without changing the operational procedure of Hanus method to reduce the reaction time of 30 minutes to 4 minutes. The experimental results indicate that the relative error is lower than 0.5 % and coefficient of variation is lower than 0.2% [17].According to Yang Li,Ji Dong-bing et al (2014) investigated the improved determination method was tested by adding Wijs reagent and 10 ml 3% magnesium acetate solution as catalyst reacting for 13 min., Acc. The result showed that there was no great difference between 2 methods with relative error less than 2%. It indicated that catalyst magnesium acetate had no adverse effect on accuracy of determination results [15].

Objective of thestudy is to develop a method by which time of the Wijs method can be reduced by use of mercuric acetate as a catalyst/accelerator. Research work aims at establishment of rapid, reliable and economical method for determination of IV of vegetable oils and examines the comparison between catalytic or accelerated method with original or non-catalytic AOAC Wijs method for IV analysis.

2. Material and methods

2.1. Procurement of Materials

The groundnut varieties of different places such asRajasthan Nagori RD 1:10(RRD1:10), G10 Gujarat(G10G), Shivpuri(Sv),Rajasthan Gugeri(Rg),TMV-2,G2-52, Karad-9(Kd-9) and T-64 have been collected and purchased from the Jalgaon oil mill association, Jalgaon and carried out extraction of oil, these extracted oil usedin the present study for the determination of Iodine value(IV) analysis. All the chemicals and reagents used in present experimental methodology are analytical grades.

2.2. Extraction of oil of collected seeds

The groundnut oil seed were purchased from local market. The groundnut seeds were separated from shaft by hand picking method .The seeds were freed of the dirt were collected into a separate pre cleaned beaker .from each sample 500 g were crushed and weighed using commercial grinder and fed to a soxhlet extractor and hexane was used as the extraction solvent, equipped with thimble and fitted with a 2 L round bottomed flask .The extraction was carried out for a period of 8 hours. At the end of the extraction period, the solvent was recovered by using a rotary evaporator and residual oil was dried at 75^0C for one hour. The extract was transferred to desiccators and then stored in air tight container until needed for further analysis [11**].**

The amount of oil extracted was determined using the following equation

Oil content (%) = weight of oil extracted / weight of seed x100

2.3. Methods

2.3.1. Experimental Methodology

The iodine value determination methods are all similar in principle, involving the treatment of a solution of the fat or oil in a suitable solvent with a solution containing a free halogen, for a definite length of time; then the conversion of the excess halogen to iodine by treatment with potassium iodide, followed by titration with thiosulphate in the usual way. In the present work, an attempt has been made to reduce the time of the Wijs method by use of mercuric acetate as a catalyst/accelerator. It provides a rapid method for the measurement of iodine value, wherein mercuric acetate is directly used in the powder form. The methodology includes addition of Wijs solution to a sample in an ordinary manner and then a powder form of the catalyst is added.

The iodine value for a sample is determined in three set of experiments with 2 mg, 5 mg and 10 mg of mercuric acetate as a catalyst. The sample is allowed to react with the Wijs solution for reaction time about 3 minutes and then the iodine value is measured in the same manner as in the Wijs method.

2.3.2. Experimental procedure for determination of IV is according to Wijs method [7,8].

The only variation is the use of mercuric acetate as a catalyst to reduce the analysis time. To a 500ml conical flask with glass topper was weighed accurately an appropriate quantity of the dry oil/fat as per expected value (0.2-0.22mg),to which 25ml of carbon tetrachloride have been added and agitated for proper mixing. To this was added 25 ml Wijs reagent and mercuric acetate. The sample was evaluated in three set of experiments with 2 mg, 5mg, and 10 mg of mercuric acetate as catalyst. The flask was fitted with glass stopper wetted with KI solution, swirled for proper mixing and kept in a dark for about 3 minutes for reaction. The test was also performed in absence of mercuric acetate where it was kept in darks for 30 minutes. Simultaneously a blank test was also performed. At the end of reaction, to the flask was added 15 ml KI solution followed by 100 ml freshly boiled and cooled water with rinsing of the stopper. Liberated iodine was titrated with standardised sodium thiosulphate solution (0.1N) using starch as indicator until the blue colour formed disappears after through shaking. The iodine value was determined as follows:

Iodine value = 12.69* (B-S)* Normality of $Na_2S_2O_3$ /Weight of Sample taken

Table 1.1 reports the iodine value of extracted different oils determined by regular Wijs method and by the catalytic Wijs method with use of 2 mg, 5 mg and 10 mg mercuric acetate.

Table 1.1 IV Analysis of IV of extracted groundnut oils by non-catalytic and catalytic Wijs method with reaction time of 30 and 3 min

Sr. No.	Groundnut variety	% oil Content	Expected IV	Use no catalyst	Use the catalyst			% Difference between catalytic and non-catalytic Method		
				Reaction time						
				30 min.	3 min					
					(2mg)	(5mg)	(10mg)	(2mg)	(5mg)	(10mg)
1	RRD1:10	44.29	85-99	91.45	85.65	87.28	89.12	6.34	4.56	2.55
2	G10G	44.95		91.8	86.52	88.40	90.25	5.75	3.7	1.69
3	Sv	40.81		92.59	87.16	89.49	90.99	5.86	3.55	1.73
4	Rg	43.85		91.90	85.98	87.60	89.66	6.44	4.68	2.44
5	TMV-2	44.19		92.16	87.06	89.47	90.91	5.53	2.92	1.36
6	G2-52	44.9		92.58	87.36	90.06	91.45	5.64	2.72	1.22
7	Kd-9	39.81		92.61	86.78	89.66	90.20	6.30	3.19	2.6
8	T-64	36.78		92.44	86.72	88.66	90.24	6.19	4.09	2.38
9	Total	339.58	--	737.53	693.23	710.62	722.82	48.05	29.41	15.97
10	Mean	42.45		92.19	86.65	88.83	90.35	6.01	3.68	2.0
11	Sd	0.2		0.26	0.17	0.33	0.21	0.1	0.14	0.1
12	CV	0.47		0.28	0.2	0.37	0.23	1.66	2.88	5
13	SEM	0.12		0.15	0.1	0.19	0.12	0.06	0.06	0.06

IV-Iodine value, SD-standard deviation, CV-coefficient of variance, SEM-standard error mean

3. Statistical Analysis:

The data obtained from the experimental measurements and accuracy of different parameters for different varieties of Groundnut seeds have been analysed and the Statistical parameter like standard deviation, coefficient of variance and standard mean error were calculated for % oil content and iodine value using 2mg,5mg and 10 mg of mercuric acetate for 30 and 3 minutes.All the experiment was carried out in triplicateand the results are presented as the mean ± SD, CV, ± SEM. Accuracy and descriptive Statistics of different groundnut varieties from different parts of India as shown in figure 1to3.

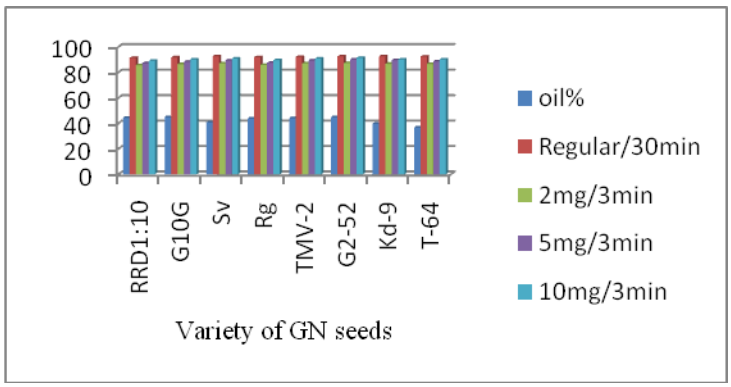

Figure1 Shows comparison of IV between reaction time of 30min and 3min using 2mg, 5mg and 10mg mercuric acetate catalyst

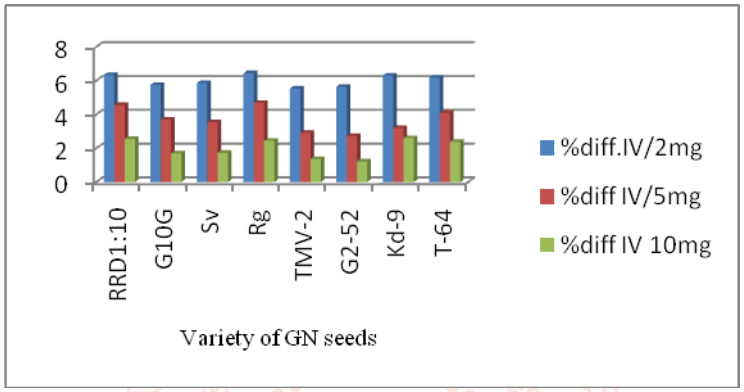

Figure 2 Shows comparison between % difference in catalytic and non catalytic IV in 3min using 2,5 and 10mg of mercuric acetate

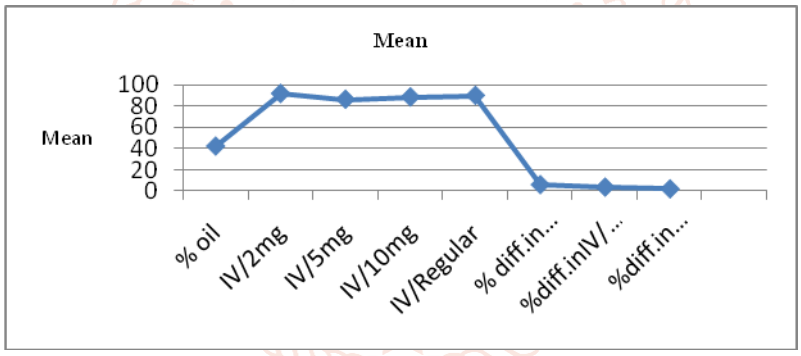

Figure 3 Accuracy of % oil content and IV for different varieties of Groundnut seed extracted oils

4. Results and discussions

It is observed that with increase in the quantity of catalyst reduces the difference in iodine value obtained by regular Wijs method and modified Wijs method. Comparatively more difference is noted in case iodine value by Wijs method and modified Wijs method for Rg,Kd-9andT-64, wherein the allowed time of 3 minutes is not sufficient for reaction between iodine monochloride and Rg,Kd-9andT-64 in case of 2mg catalyst. This has however reduced with the increase of catalyst quantity. Higher time of reaction may favour the reduction in difference in values of IV by regular Wijs method and modified Wijs method. It is apparent from the **Table 1.1** that the iodine value for oil/fat obtained by the Wijs method and by the experimental method (modified Wijs method) is not significantly different. Also results obtained by use of mercuric acetate lies within the expected range, as per Food safety and standards act 2006 and Food product and Standards regulation 2011 [column (a) of Table] [8**]** , of iodine value for respective oil/fat. The presence of catalyst has facilitated the increased reaction rate with reduction in time of analysis. The obtained value of IV for all studied samples by modified Wijs method represents the success of mercuric acetate to perform as catalyst in reducing the time of analysis to 3 minutes. Moreover, as all the reported values are average of three readings, has demonstrated the reproducibility of the analysis data.

5. Conclusion

It is apparent that IV obtained in 3 minutes with catalyst are slightly less than those obtained after 30 minutes without catalyst. Based on the analytical results of this study ,all the IV found that there is no significant difference between the IV obtained by this catalytic method and standard AOAC method. Thus as a result catalytic Wijs method can be adopted as online quality control technique for rapid analysis during hydrogenation of oils and fats. The use of 10 mg of mercuric acetate gives least variation in the values obtained for all the studied oil samples.

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