

Evaluation of determination of iodine value of extracted groundnut seed oils by using mercuric acetate as accelerator

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Abstract: In the present research work, 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. In this paper, use of mercuric acetate as catalyst and the absorption reaction time has been reduced to 3 min. It is the purpose of this paper to present a modified method for estimation of unsaturation of oils. A modified method is used for the measurement of iodine value, wherein mercuric acetate is directly used in the powder form. An attempt has been made to reduce the time of the Wijs method by use of mercuric acetate as a catalyst/accelerator. The iodine value of extracted oils of different groundnut seeds varieties of Gujarat such as GG-11, TG-17, GG-2, J-11, as TRG-4 (Trg-4), TAG-24 (Tg-24), G-20 (G-20) and swaraj-44 (Swj-44) 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. When catalyst is used the different values obtained for coefficient of variations are 0.28 for 2mg, 0.37 for 5mg and 0.32 for 10 mg whereas 0.23 for non-catalyst addition. The results obtained in the present work shows Swj-44 and Trg-4 have more % difference in IV in case of 2mg catalyst.

Keywords: Groundnut seeds, oil extraction, IV (Iodine Value), Wijs method mercuric acetate

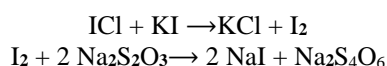
1. Introduction

Groundnut, (*Arachis hypogaea* L.) also known as peanut or earthnut is a native to a region in eastern South America [19]. Groundnut/peanut (*Arachis hypogaea*) is a legume which is widely grown as a food crop. The genus *Arachis*, a member of the family Leguminosae, is among the major oil seeds in the world. China, India and USA are the main producers of groundnuts to the rest of the world [6]. Groundnut is now grown worldwide in the tropical and temperate zones primarily as an oil seed crop [4]. The oil content of groundnut differs in quantity, the relative proportion of fatty acids, geographical location, seasons and growing conditions [1]. Vegetable oils are in high demand due to diseases associated with fat from animal origin. The groundnut cake has several uses in feed and infant food formulations [3].

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. The processors of oil and fat are in need of a quick determination method of iodine value of oils and fats especially in case of checking the degree of unsaturation of them in the hydrogenation process. Wijs method has a drawback that duration of the reaction is as long as 30-60 minutes. In this paper mercuric acetate is used as a catalyst/accelerator to achieve a reduction in the reaction time. Present research examines the comparison between accelerated using mercuric acetate improved method with original AOAC Wijs method for IV analysis.

The aim of this research study is to develop a method by which time 3 and 30 minutes of the Wijs method can be reduced by use of mercuric acetate as a catalyst/accelerator.

The official methods for determination of iodine value (IV) involve the reaction of double bonds in oils with halogenating reagent (Hanus or 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 [2,7] and involves following reactions:



IV of fats and oils can be determined by different methods like Wijs, Hanus, Hubl, Hofmann and Green and Rosenmund-Kuhnhenh methods. In this regard many methods have been developed but the Wijs method is the most widely used. Hoffman and Green used mercuric acetate as a catalyst in the Wijs method to obtain complete iodine absorption in three minutes [10]. Benhen and Klee modified the Rosenmund-Kuhnhenh Method so that only one minute reaction time was required [5].

According to Jmrat et al, various methods and modifications that have been proposed on time to time for the determination of the Iodine values of fats and oils, Hubl's and Wijs' are the only two methods which have found more or less general application

[8]. Hoffman and Green used mercuric acetate as a catalyst in the Wijs method to obtain complete iodine absorption in three minutes [10]. Benhen and Klee modified the Rosenmund-Kuhnenn Method so that only one minute reaction time was required [5]. A rapid method for the estimation of unsaturation of fats and oils was investigated and developed by Mukherjee, use of an aqueous solution of sodium hypochlorous acid reagent as an absorption reagent with a reaction time of 4 to 5 minutes was recommended, the estimations are more rapid or all drying or non drying group oils give accurate results within the specified time [13]. 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. This method was investigated by Shin-ichikikuno and co-researchers in 1975 [16]. 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 Wijs 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 Wijs and 3 min Hanus methods as compared with 30 min reaction time of standard procedures [9].

According to the United States 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 Wijs solution is 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 [18]. 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 % [12].

Ondrej Hendl 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 4000-400 cm⁻¹ and the heights of the derivative spectrum for functional group 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. [14]. 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 [17]. 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% [21]. 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 [20].

2. Material and methods

2.1 Procurement of Materials

The different groundnut seed variety of Gujarat such as GG-11, TG-17, GG-2, J-11, TRG-4 (Trg-4), TAG-24 (Tg-24), G-20 (G-20) and Swaraj-44 (Swj-44) have been collected and purchased from the Jalgaon oil mill association, Jalgaon and carried out extraction of oil, these extracted oil used in 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°C for one hour. The extract was transferred to desiccators and then stored in air tight container until needed for further analysis [15].

The amount of oil extracted was determined using the following equation

$$\text{Oil content (\%)} = \frac{\text{weight of oil extracted}}{\text{weight of seed}} \times 100$$

2.3 Methods

2.3.1 Experimental Methodology

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 to 3 min. 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 method only requires adding the catalyst mercuric acetate in the process of determination without changing the operational steps of the Wijs method. To a 500ml conical flask with glass topper was weighed accurately an appropriate quantity of the dry oil/fat as per expected iodine 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. After completion 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 (blank and sample) was titrated with 0.1N sodium thiosulphate to reach pale yellow end point, nearly 2ml starch indicator was added to the flask and continue titrating the blue colour just disappears after through shaking (Usually colourless end point). The iodine value was determined as follows:

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

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				(2mg)	(5mg)	(10mg)
				30 min.	3 min					
1	GG-11	43.9	85-99	92.88	86.56	88.35	90.12	6.38	4.72	2.97
2	TG-17	44.84	85-99	92.16	86.88	88.76	91.0	5.73	3.69	1.26
3	GG-2	42.48	85-99	91.89	86.72	88.46	90.76	5.63	3.73	1.23
4	J-11	44.2	85-99	92.47	86.92	89.38	91.34	6.0	3.34	1.22
5	Trg-4	42.19	85-99	92.12	86.78	88.46	90.02	6.51	3.97	2.28
6	Tag-24	43.9	85-99	91.32	85.66	88.88	90.85	6.2	3.81	1.61
7	G-20	41.81	85-99	91.07	85.50	87.84	89.36	6.12	3.55	1.88
8	Swj-44	40.78	85-99	92.79	86.91	88.60	90.33	6.34	3.44	2.09
9	Total	344.1	--	736.7	691.93	708.73	723.78	48.91	30.25	14.54
10	Mean	43.01	--	92.09	86.49	88.59	90.47	6.11	3.78	1.82
11	SD	0.28	--	0.26	0.32	0.28	0.21	0.3	0.2	0.2
12	CV	0.65	--	0.28	0.37	0.32	0.23	4.91	5.29	11.05
13	SEM	0.16	--	0.15	0.18	0.16	0.12	0.17	0.12	0.12

*Average values of three measurements, σ -standard deviation, CV-coefficient of variation, SEM-Standard mean error

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 triplicate and 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.

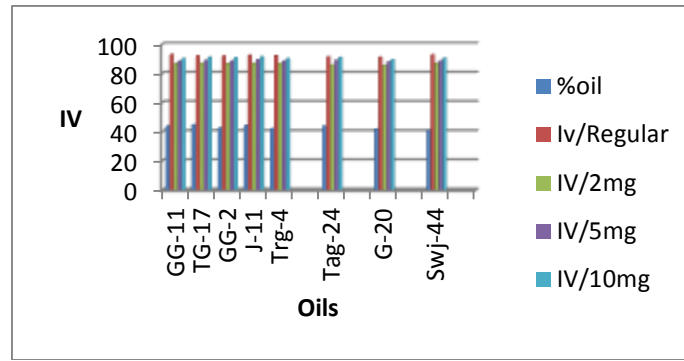


Figure1: Shows comparison of IV between reaction time of 30min and 3min using 2mg,5mg and 10 mg mercuric acetate catalyst

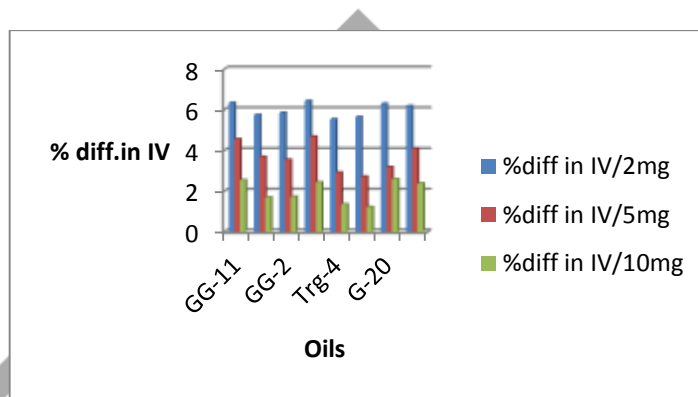


Figure 2: Shows comparison between % difference in catalytic and non catalytic IV in 3 min using 2,5 and 10mg of mercuric acetate

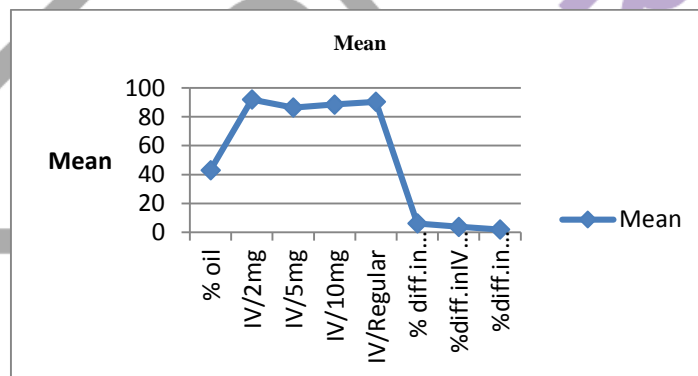


Figure 3 Accuracy of % oil content and IV for different varieties of Groundnut seed extracted oils

4. Results and discussions

The presence of catalyst has facilitated the increased reaction rate with reduction in time of analysis. 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 Swj-44 and Trg-4, wherein the allowed time of 3 minutes is not sufficient for reaction between iodine monochloride and Swj-44 and J-11 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. The **Table 1.1** shows that the iodine value for oil/fat obtained by the Wijs method and by the experimental method (modified Wijs method) is not significantly different. The 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 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

This present work introduces significant reduction in the analysis time, measurement accuracy and reproducibility of data for the determination of non-catalytic and catalytic IV analysis. A modified method for determining the iodine value of oil and fat in 3min(Catalytic) and 30 minutes (Non-catalytic) is reported in this paper. The experimental results compared with the Wijs method, It is found that there is no significant difference between the IV obtained by this catalytic method and standard AOAC method. The experiment indicates that the relative deviation is lower than 0.28% for standard AOAC wijs method and for modified method gives a variation coefficient in between 0.23 to 0.37%. 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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