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Comparative Study between Modified and Standard Wijs Method for Measurement of Iodine Value of Different Edible Vegetable Oils and Fats Using Accelerator

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***Abstract*: In this paper, a modified method for determining the iodine value of oil and fat is reported. The method only requires adding the catalyst mercuric acetate in the process of determination without changing the operational steps of the Wijs method and compared with the standard AOAC Wijs method in which reaction of a sample with the Wijs solution is as long as 30-60 minutes. The fast determination method can make the determination reaction finished in 3 minutes. Where in 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 different vegetable oils such as refined palmolein oil (Rpm1, Palm gold-Active) Sesame oil (Se ,Tilsonna) ,Refined ricebran oil (Rrb, King's), Refined sunflower oil (Rsf, Swaad), refined sunflower (Sf1) (Sweekar), refined sunflower (Sf2) (Sundrop), refined sunflower(Sf3) (Gemini) and refined groundnut (Gn) (RRprimio) 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 0.05 to 0.99 for 2mg, 0.18 to 1.35 for 5mg and 0.17 to 0.8 for 10 mg whereas 0.07 to 0.82 for non-catalyst addition. The results obtained in this present work are more % difference in IV of refined groundnut oil (Rgn).**

***Keywords*: IV (Iodine Value), Mercuric acetate, Vegetable oils, Wijs method.**

1. Introduction

Vegetable oils are extracted from seeds, such as soy, cotton, corn, and sunflower. They are characterized by high concentrations of triglycerides and lower amounts of mono and diglycerides, free fatty acids, tocopherols, proteins, sterols, and vitamins [1]. Triglycerides with a high number of unsaturations predominate in most of the vegetable oils (e.g. soy, cotton, corn, and sunflower oils), which makes them more susceptible to oxidation. Some refined oils, such as those extracted from sunflower, canola, and soybean are essentially intended for food preparation [13]. Iodine value is proportional to the degree of unsaturation of the product and indicates its oxidative stability. The official method for biodiesel and vegetable oils (EN 14111) is based on titration of the excess of a halogen reagent with a sodium thiosulfate solution. It is time-consuming, requires a large reagent amount (e.g. 25 mL of Wijs reagent) and consequently generates a significant waste volume [14].

The 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 [1,2]and involves following reactions:

$$ICl + KI \longrightarrow KCl + I_2$$
$$I_2 + 2\ Na_2S_2O_3 \longrightarrow 2\ NaI + Na_2S_4O_6$$

AOAC Wijs method is used for measurement of iodine value and this method has a drawback that duration of the reaction of a sample with the Wijs solution is as long as 30-60 minutes. To achieve a reduction in the reaction time, there has been known a rapid measurement method wherein mercuric acetate is used as a catalyst. In this paper mercuric acetate is used as a catalyst/accelerator to achieve a reduction in the reaction time.

2. Literature Review

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 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 [3].

S. mukherjee studied, investigated and developed a rapid method for the estimation of unsaturation of fats and oils by use of an aqueous solution of sodium hypochlorous acid reagent as

an absorption reagent with a reaction time of 4 to 5 minutes was recommend, the estimations are more rapid or all drying or non-drying group oils give accurate results within the specified time [4].

Shin-ichiKikuno et al 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 [5].

Hashemy et al 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 [6]. A fast method was studied and investigated by Li hua et al 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 % [7]. A new method for the determining the IV of oil and fat was only requires adding 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%. This method was investigated by Zhongguo-ging (2004) [8]. Yang Li,Ji Dong-bing et al 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 [9].

The recently spectroscopic techniques, e.g. FTIR, FT-NIR etc., have been proposed for fast and non-destructive analysis of oils for iodine value. However, the method involves much mathematic calculations, and uses sophisticated instrument which is not normally available in general laboratory. In addition, the methods required the standardization of oils or fatty acids used for construction of calibration graph by using the time consuming official methods.

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 [10].

A rapid method for determining the IV, of vegetable oils was studied and developed by Ondrej Hendl et al (2001). 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 [11].

Objective of the study 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.

3. Material and Methods

A. Procurement of Materials

Vegetable oils such as refined palmolein oil (Rpm1, Palm Gold-Active) Sesame oil (Se, Tilsonna), Refined ricebran oil (Rrb, King's), Refined sunflower oil (Rsf, Swaad), refined sunflower (Sf1) (Sweekar), refined sunflower (Sf2) (Sundrop), refined sunflower(Sf3) (Gemini) and refined groundnut (Gn) (RRprimio) oils have been purchased from the local market and used in the present study for the determination of IV analysis. All these oils were in different forms of packaging while some in poly packs (HDPE), others were in tetra packs, plastic bottles, cans, pet and glass bottles of 1 liter and 5 liters. Since these eight different brands of edible oils were easily available for procurement (Table 1). Most of the brands have mentioned nutritional values, green vegetarian logo and best before 6 to12 months, free from argemone oils on their packs. These different cooking oils are used in the present study for the determination of IV analysis. All the chemicals and reagents used in present experimental methodology are analytical grades.

B. Methods

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

Table 1
Different oils purchased from local market of Jalgaon city

S.no.	Name of oils	Brand	Place of manufacturer company	Product type/expiry*
1	Refined Palmplein oil	Palm gold–Active	Sarda Agro Oil Ltd., H.Office: Satamrai, Goganpahad, R.R.Disst., Hyderabad (A.P); B.Office:S.No.287, Thammavaram Village, Near light house, Kakinada-533005	Best before eight months from packaging. Free from Argemone oil
2	Sesame oil	Tilsonna	Recon Oil Industries Private Ltd., 5 Chunawala Estate, Kondivitta Road, Mumbai-400059	100% natural and pure, double filtred
3	Refined Ricebran oil	King'S	Adani wilmer limited (unit II)VIII, Dhrup, Tal-Mundra, Dist. Kutch Gujarat	Physically refined,100% pure ,Retains maximum oryzanol, contains natural antioxidants
4	Refined sunflower oil	Swaad	Adani wilmer limited (unit II)VIII, Dhrup, Tal-Mundra, Dist. Kutch Gujarat	free from argemone oils, contains permitted antioxidants and OMG-3, essential PUMA
5	Refined sunflower oil	Sweekar	Marico ltd, A.P organics Pvt Ltd, Vill - Maanwala Saron Road, Dhuri -148024(Punjab)	Low absorb oil, free from argemone oils, contains permitted antioxidants (TBHQ),antifoaming agents
6	Refined sunflower oil	Sundrop	Agrotech foods limited, Premier soya oil limited, Industrial area, Jhotwara-302012	Free from Argemone oil, Contains permitted antioxidants (TBHQ), Nutrition Facts (Approximate composition per 20g): Calories180, Saturates-12%, Mono & Poly Saturates88%, Added Vitamin A-534 I.U., Added Vitamin D-116 I.U. vitamin-E-10 I.U.
7	Refined sunflower oil	Gemini	Cargill India private limited, VIII- Bhimsar, Kutch, Gujarat-148024	Free from Argemone oil, Nutrition Facts (Approximate composition per 100g): Calories884, Saturates-10.1%, MUS 45.4%, PUS 40.1%.
8	Refined groundnut oil	RR Primio	Elite Tradex Pvt, A-8, Supa- Parner, MIDC, Dist. - Ahmednagar - 414301	Nutritional Facts: MUFA-54%, PUFA-29%, SFA7%, Calories/10g-88

Table 2
IV Analysis of IV of vegetable oils by non-catalytic and catalytic Wijs method with reaction time of 30 and 3 min

S. No.	Oil/ fats Code	Expected IV	Use the catalyst			Use no catalyst	% Difference between catalytic and non-catalytic Method		
			Reaction time						
			3 min			30 min			
			2mg	5mg	10mg				
		(a)	(b)	(c)	(d)	(e)	2mg	5mg	10mg
1	Rpm	54-62	54.02	55.17	56.26	58.15	7.10	5.12	3.25
2	Se	103-120	102.51	103.95	105.76	108.26	5.31	3.98	2.31
3	Rrb	103-128	105.81	108.66	110.76	114.66	7.72	5.23	3.40
4	Rsf	100-145	114.33	117.48	120.24	124.48	8.15	5.62	3.41
5	Sf1	100-145	125.76	126.63	128.34	129.03	3.0	2.18	2.04
6	Sf2	100-145	124.58	125.66	127.76	128.17	6.52	5.21	3.56
7	Sf3	100-145	123.88	125.48	127.44	128.46	3.83	3.43	2.06
8	Gn	85-99	85.12	87.34	90.68	91.87	6.53	5.56	4.94

Table 3
Accuracy of Iodine value in use of the catalyst and no catalyst

S. No	Oil/ Fats	Use the Catalyst												Use no Catalyst			
		2mg				5mg				10mg							
		IV	σ	CV (%)	SEM	IV	σ	CV (%)	SEM	IV	σ	CV (%)	SEM	IV	σ	CV (%)	SEM
1	Rpm	54.02	0.54	0.99	0.31	55.17	0.75	1.35	0.43	56.26	0.45	0.8	0.26	58.15	0.48	0.82	0.28
2	Se	102.51	0.41	0.39	0.24	103.95	0.58	0.56	0.34	105.76	0.57	0.54	0.33	108.26	0.74	0.69	0.43
3	Rrb	105.81	0.68	0.65	0.39	108.66	0.49	0.45	0.28	110.76	0.59	0.54	0.34	114.66	0.55	0.48	0.32
4	Rsf	114.33	0.44	0.17	0.25	117.48	0.44	0.37	0.25	120.24	0.5	0.41	0.29	124.48	0.77	0.62	0.45
5	Sf1	125.76	0.22	0.17	0.13	126.63	0.37	0.29	0.21	128.34	0.21	0.17	0.12	129.03	0.4	0.31	0.18
6	Sf2	124.58	0.32	0.32	0.18	125.66	0.4	0.38	0.23	127.76	0.32	0.31	0.18	128.17	0.37	0.33	0.19
7	Sf3	123.88	0.35	0.33	0.20	125.48	0.19	0.18	0.11	127.44	0.39	0.36	0.23	128.46	0.14	0.13	0.08
8	Gn	85.12	0.06	0.05	0.03	87.34	0.49	0.45	0.28	90.68	0.48	0.43	0.28	91.87	0.08	0.07	0.04

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

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) Experimental procedure for determination of IV using Wijs method [1,2].

Use of mercuric acetate catalyst, the absorption reaction time has been reduced to 3 min. An appropriate amount of sample was weighed of the dry oil/fat as per expected value (0.2-0.22mg) into a tared Erlenmeyer flask with glass stopper, add 25ml of carbon tetrachloride and flask was swirled to dissolve the sample. To this was added 25 ml Wijs reagent and 2mg, 5mg and 10mg mercuric acetate in powder form. 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 2 reports the iodine value of different vegetable oils determined by regular Wijs method and by the catalytic Wijs method with use of 2 mg, 5 mg and 10 mg mercuric acetate.

4. Statistical Analysis

The data obtained from the experimental measurements and accuracy of IV for different Groundnut seeds oils have been analysed and the Statistical parameter like standard deviation and coefficient of variation were calculated for IV. All the experiment was carried out in triplicate and the results are presented as the mean SD, CV and SEM. Accuracy of descriptive Statistics of different groundnut oils from different parts of India as shown in figure 1 to 5.

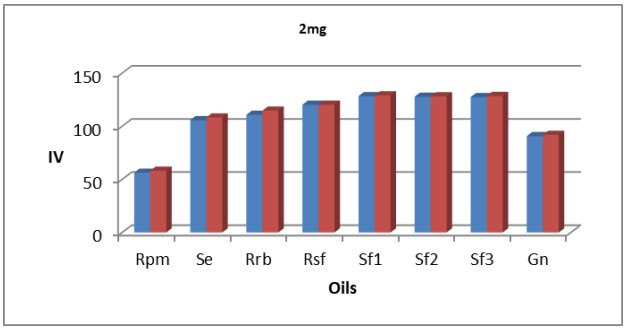

Fig. 1. Comparison of IV between reaction time of 30min and 3min using 2mg mercuric acetate catalyst

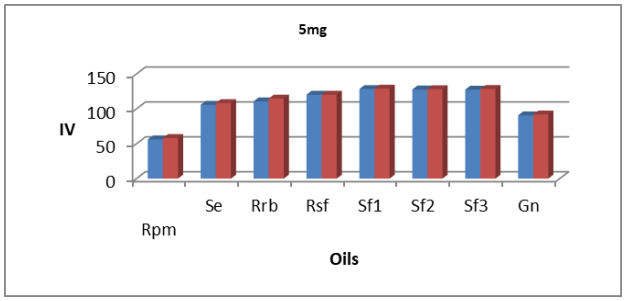

Fig. 2. Comparison of IV between reaction time of 30min and 3min using 5mg mercuric acetate catalyst

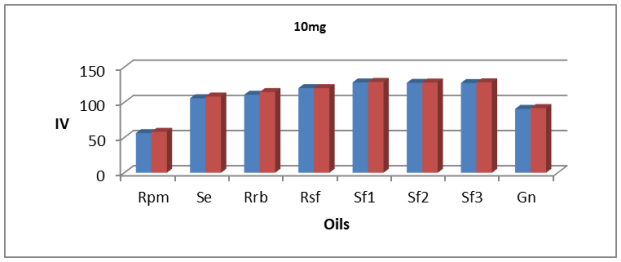

Fig. 3. Comparison of IV between reaction time of 30min and 3min using 10mg mercuric acetate catalyst

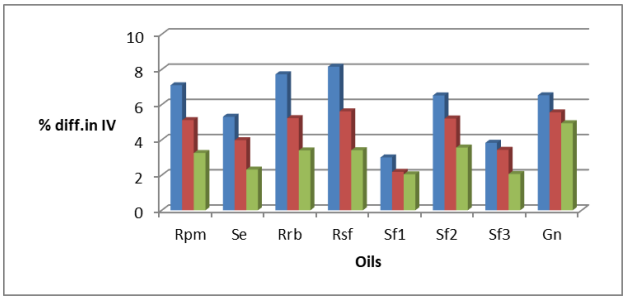

Fig. 4. Comparison between % difference in catalytic and non-catalytic IV in 3min using 2,5 and 10mg of mercuric acetate

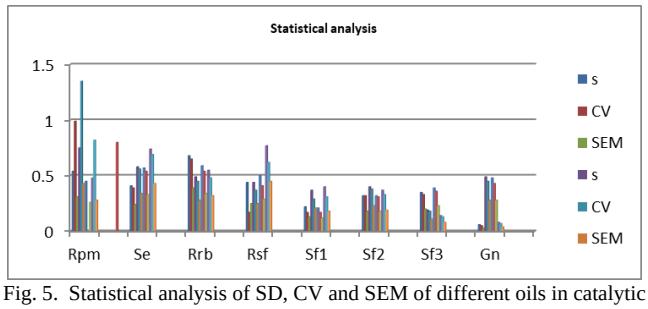

Fig. 5. Statistical analysis of SD, CV and SEM of different oils in catalytic and non-catalytic IV in 3min using 2,5 and 10mg of mercuric acetate

5. Results and Discussions

It is observed that with increase in the quantity of catalyst reduces the difference in iodine value obtained by regular AOAC Wijs method and modified Wijs method. The presence of catalyst has facilitated the increased reaction rate with reduction in time of analysis. Comparatively more difference is noted in case iodine value by AOAC Wijs method and modified Wijs method for Rsf, wherein the allowed time of 3 minutes is not sufficient for reaction between iodine monochloride and Rsf. 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 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. The analytical results of iodine value for oil/fat obtained by the Wijs method and by the experimental method (modified Wijs method) is not significantly different are shown in Table 1. All the experimental values are average of three readings with good reproducibility of results. 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] [12], of iodine value for respective oil/fat. Moreover, as all the reported values are average of three readings, has demonstrated the reproducibility of the analysis data. Table 2 shows the variance of the measured values of the method of setting it to 3 minutes. The coefficient of variation in case of 2mg is 0.05 to 0.99 while in case of 5mg (catalyst addition) 0.18 to 1.35 and in 10 mg, 0.17 to 0.8, even for non-catalyst addition, 0.07 to 0.82.

6. Conclusion

Present research examines the comparison between catalytic or accelerated method with original or non-catalytic AOAC Wijs method for IV analysis. It is found that there is no significant difference between the IV obtained by this catalytic method and standard AOAC method. 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. 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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