

Development of Modified Method of Measurement of Iodine Value of Extracted Oils of Different Groundnut Varieties by using Mercuric Acetate as Accelerator

Dr Shashikant Pardeshi
Food Analyst
DPHL, Jalgaon, India

Abstract

In the present work, a new modified method is used for the measurement of iodine value, wherein mercuric acetate as catalyst is directly used in the powder form in the process of determination without changing the operational steps of the Wijs standard method. The analytical results obtained with this standard method compared with those from modified Wijs method. The modified determination method can make the determination reaction finished in 3 minutes. 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 such as RS-1(Rs-1),TAG-3a(Tg-3a),TAG-51(Tg-51),K-6(K-6), Uf70-130, K-1, K-3 and Rsb-103-87 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 0.31 for 2mg, 0.34for 5mg and 0.34for 10 mg whereas 0.25 for non-catalyst addition. The results obtained in the present work shows Tg-51and Tg-3a have more % difference in IV in case of 2mg. The standards mean error in the range of 0.16-0.18.

Keywords: Groundnut Seed, Oil Extraction, IV (Iodine Value), WIJS Method, Mercuric Acetate

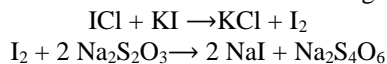
I. INTRODUCTION

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^[17]. The oil content of groundnut differs in quantity, the relative proportion of fatty acids, geographical location, seasons and growing conditions. 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^[1]. 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].

The characterisation of fats and oils is dictated by some distinct physical and chemical parameters like texture, density refractive index, specific gravity, iodine value, colour, essential content, unsaponifiable composition, acid value, Free fatty acid content, peroxide value ,P-anisidine value and BTT etc are dependent on the source of oil; geographic, climatic, and agronomic variables of growth of the oil helps to determine its conformity as safe and standard edible oil by which the purity check of extracted oil can be done. Thus one must assess quantitatively the influence of these variables on characteristics of oils and fats; in present case on characteristics of extracted oil of different varieties of groundnut seeds using 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^[2,5]. 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 mercuric acetate is used as a catalyst/accelerator to achieve a reduction in the reaction time. The 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.

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 [2,5] and involves following reactions:



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 mercuric acetate is used as a catalyst/accelerator to achieve a reduction in the reaction time.

A. Literature Review

Hoffman and Green used mercuric acetate as a catalyst in the Wijs method to obtain complete iodine absorption in three minutes [7]. Benhen and Klee modified the Rosenmund-Kuhnhehn Method so that only one minute reaction time was required [4]. A rapid method investigated and developed for the estimation of unsaturation of fats and oils by use of an aqueous solution of sodium hypochlorous acid reagent as a 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 [10].

The researcher was 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 [13]. The IV of 121 samples of butter as well as some common oils and fats was studied 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 [7].

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 Wijs 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]. A fast method investigated 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 new method investigated 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% [18]. The improved determination method was investigated and tested by adding Wijs reagent and 10 ml 3% magnesium acetate solution as catalyst reacting for 13 min., 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 [17].

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 [14].

The rapid method for determining the IV, of vegetable oils was studied and 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 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 [11].

II. MATERIAL AND METHODS

A. Procurement of Materials

The groundnut variety of different places such as RS-1(Rs-1), TAG-3a(Tg-3a), TAG-51(Tg-51), K-6(K-6), Uf70-130, K-1, K-3 and Rsb-103-87 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.

B. 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^[12].

The amount of oil extracted was determined using the following equation

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

C. 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 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 is according to Wijs method ^[5,6].

The only variation is the use of mercuric acetate as a catalyst to reduce the analysis time. To a 500ml conical flask with glass stopper 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 (0.0998 N) using starch as indicator until the blue colour formed disappears after through shaking. The iodine value was determined as follows:

$$\text{Iodine value} = 12.69 * (B-S) * \text{Normality of Na}_2\text{S}_2\text{O}_3 / \text{Weight of Sample taken}$$

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			% Variation from regular Wijs method		
				Reaction time						
				30 min.	3 min			(2mg)	(5mg)	(10mg)
1	<i>Rs-1</i>	42.59	85-99	92.7	87.54	89.84	91.45	5.57	3.09	1.35
2	<i>Tg-3a</i>	42.49	85-99	91.57	86.28	88.74	90.72	5.78	3.09	0.93
3	<i>Tg-51</i>	41.21	85-99	92.94	87.06	89.71	91.08	6.33	3.48	2.00
4	<i>K-6</i>	40.18	85-99	92.44	87.54	89.71	91.34	5.30	3.33	1.19
5	<i>Uf70-130</i>	42.44	85-99	91.32	87.06	88.80	90.33	4.66	2.76	1.08
6	<i>K-1</i>	40.69	85-99	92.94	88.05	90.59	91.21	5.26	2.53	1.86
7	<i>K-3</i>	41.88	85-99	91.45	86.74	88.94	90.11	5.15	2.74	1.47
8	<i>Rsb-103-87</i>	40.95	85-99	92.68	87.84	89.84	91.57	5.22	3.06	1.20
9	Total	332.43	--	738.04	698.11	716.17	727.81	43.27	24.08	11.08
10	Mean	41.55	--	92.26	87.26	89.52	90.98	5.41	3.01	1.39
11	SD	0.19	--	0.23	0.27	0.3	0.31	0.24	0.18	0.21
12	CV	0.46	--	0.25	0.31	0.34	0.34	4.44	5.98	15.11
13	SEM	0.11	--	0.13	0.16	0.17	0.18	0.14	0.1	0.12

SD-standard deviation, CV-coefficient of variation, SEM-standard error mean

III. 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 figure1to3.

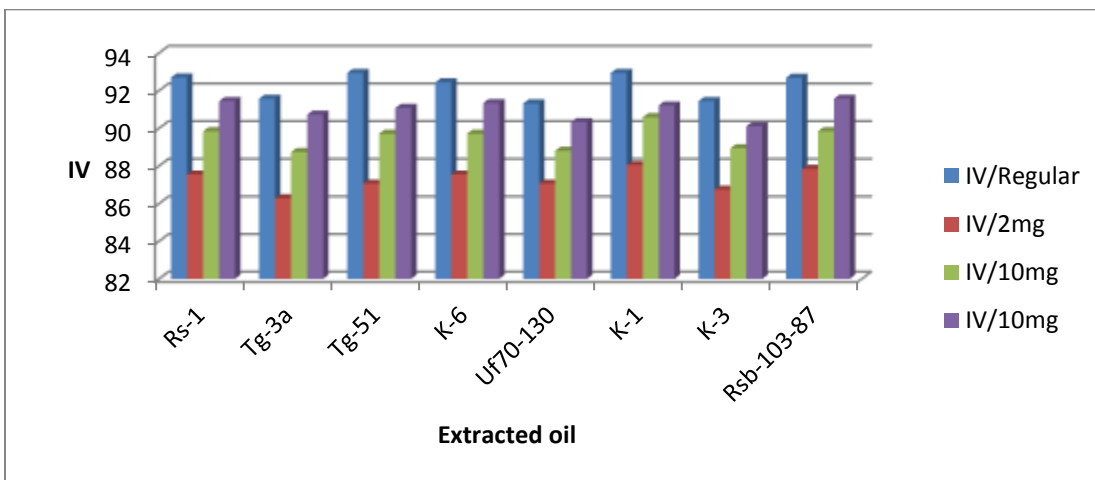


Fig. 1: Shows comparison of IV between reaction time of 30min and 3min using 2mg 5mg and 10 mg mercuric acetate catalyst

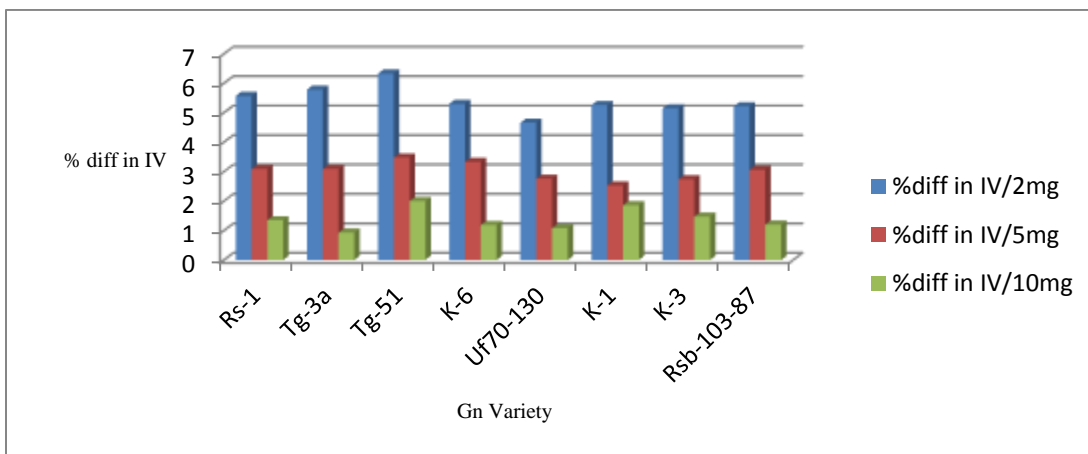


Fig. 2: Shows comparison between % difference in catalytic and non catalytic IV in 3min using 2,5 and 10mg of mercuric acetate

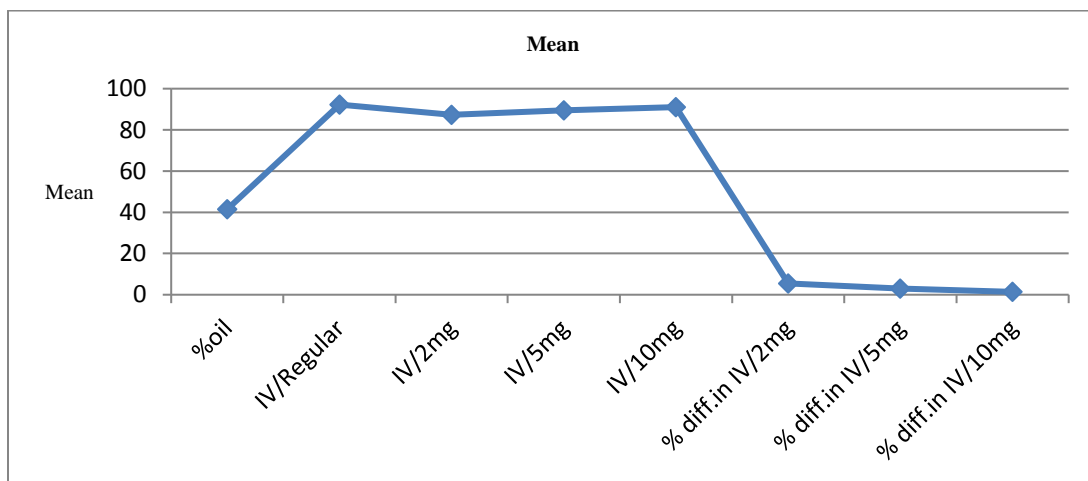


Fig. 3 Accuracy of % oil content and IV for different varieties of Groundnut seed extracted oils

IV. RESULTS AND DISCUSSIONS

The iodine value for oil/fat obtained by the Wijs method and by the experimental method (modified Wijs method) is not significantly different was shown in Table 1.1. 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] ^[6], of iodine value for respective oil/fat. 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. Accordingly use of 10mg of mercuric acetate gives least variation in the values obtained for all the studied oil samples. Comparatively more difference is noted in case iodine value by Wijs method and modified Wijs method for Tg-51 and

Tg-3a in case of 2mg, wherein the allowed time of 3 minutes is not sufficient for reaction between iodine monochloride and Tg-51 and Tg-3a. This has however reduced with the increase of catalyst quantity. 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. Table 1 also shows the accuracy, In case of IV, the standard deviation and coefficient is the range of 0.27-0.31 and 0.31-0.34.

V. CONCLUSION

The analytical results of this study showed that, IV obtained from both standard wijs and modified methods are not significantly different with the relative error 0.34%. The percentage variations obtained from both the methods are more in case of 2mg catalyst while less in case of 10mg catalyst used. Higher time of reaction may favour the reduction in difference in values of IV by regular Wijs method and modified Wijs method. This modified method, possessing good accuracy, significant reduction in the analysis time, measurement accuracy and reliability for the determination of IV in edible oil. Thus as a result catalytic Wijs method can be adopted as online quality control technique for rapid analysis during hydrogenation of oils and fats.

REFERENCES

- [1] Asibuo et al (2008),Asibuo J. Y., Akromah. R., Safo-Kantanka O. O., sei, Adu-Dapaah., Hanskofi O.S and Agyeman A., Chemical Composition of Groundnut, *Arachis hypogaea* (L) landraces, *African Journal of Biotechnology*. 7(13), 2203-2208.
- [2] AOAC (2000), Association of official Analytical chemists, 17th edition, Official Method 920.159-Iodine absorption number of oils and Fats/ISI Handbook of food analysis(part XIII)1984,76.
- [3] Barku et al (2012), Barku V. Y., Nyarko, H. D., and Dordunu, P., Studies on the Physicochemical Characteristics, Microbial Load and Storage Stability of Oil from Indian Almond Nut (*TerminaliaCatappal.*), *Food Science and Quality Management*, 8. 9-17.
- [4] Benhem et al (1950), Benhem,G.H.,andKell,L.,An improved method for the determination of iodine number. *Journal of American Oil Chemists Soc.* 27:127-129.
- [5] DGHS (2012), Directorate of General Health Service, Manual of Methods of Test and Analysis for Food(Oil and Fats),Ministry of Health and family welfare, Government of India, New Delhi.31-34.
- [6] FSSA 2006 (2014), Food Safety and Standards Act 2006, Rules 2008, Regulations of food Product and Standards 2011, 8th edition professional book publishers, New Delhi.
- [7] Hashemy et al (1977), S.E.Hashemy-Tonkabony, Rapid iodine value determination using mercuric acetate as accelerator, *journal of American oil chemists society*, 54(6) ,233.
- [8] Hoffman et al (1939), Hoffman,H.D, and Green,C.E..A rapid method for the determination of iodine number, oil and soap,16:236-38.
- [9] LI Hua et al(1999),LI Hua,EniwerArboundrar, AhemeityManlihar.,A fast determination method of IV of oil and Fat, *Journal of Xuzhou Normal University* ,Fine Chemicals,03.
- [10] Mukherjee,S.(1955), A rapid method for estimating unsaturation of Fats and oils by the use of hypochlorous acid reagent. *Journal of American Oil Chemists Soc.* 32,351-353.
- [11] OndrejHendl et al(2001),OndrejHendl,J.A.Howell,J.Lowery,William James., A rapid and simple method for the determination of IV using derivative Fourier transform infrared measurements, *AnalyticachimicaActa*427(1),75-81.
- [12] Pearson(1981),Pearson D., The Chemical Analysis of Food. (8thedition). Longman Group Ltd: 535.
- [13] Shin-ichiKikuno et al (1975),Shin-ichiKikuno,YukinobuMurase,ShoujiMaruzeni and Minoru.,On the Determination of Iodine Value by the Wijs Method, Okamoto.*Journal of Japan Oil Chemists Society*,24(12),876-878.
- [14] Thomaidis et al (2000), Thomaidis N.S.,Georgiou C.A.,Direct parallel flow injection multichannel spectrophotometric determination of iodine value-olive oil, *Ana.chim.Acta*,405,239-245.
- [15] US Patent 4297106 (1981),United States Patent, Rapid method of the measurement of Iodine Value (11)4, 297,106, Makino. (45).
- [16] Yang Li et al(2014),Yang Li, Ji Dong-bingXuedun-hui, ChenRong, Du Hong-ying, Lu Wet-tong., A rapid method for the determination of edible oil iodine value, *Journal of Science and Technology of cereals, oils and Foods*,(02).
- [17] Young et al (1975),Young CT, Worthington KE, Hammons RO, Matloc RS, Waller GR, Morrison RD., Fatty acid composition of Spanish peanut oils as influenced by planting location, soil moisture, conditions, variety and season. *J. Am. Oil Chem. Soc.*, 51:312-315.
- [18] Zhongguo-ging(2004), A rapid method for the determination of iodine number, *Journal of science and Technology of cereals, oils and Foods*,(01).