Study of the Kaufmann Method For Determining Iodine Numbers[1]

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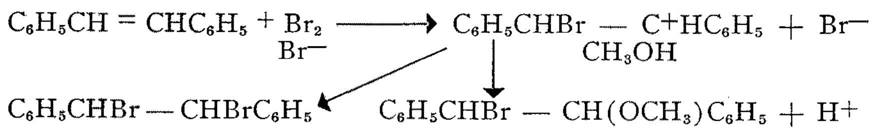
Abstract

A study has been made of the effect of heat, light, time of reaction, and size of sample on iodine numbers obtained by the Kaufmann method. The iodine numbers of several oils have been determined by this method and compared with those found by other well-known methods. The formation of acid by the reaction between the Kaufmann reagent and a number of oils, has been investigated.

INTRODUCTION

SINCE a knowledge of the degree of unsaturation in oils and fats is of considerable importance, many methods have been suggested for determining this property by halogenation. In connection with the analytical work of the U. S. Regional Soybean Industrial Products Laboratory it was considered desirable to investigate these various methods to find the one best suited for use with soybean oil from the standpoint of convenience, accuracy, and information obtained. Of the more recent methods proposed, that of Kaufmann (4) seemed to offer the greatest usefulness because the solution used can be prepared with ease, is free from noxious vapors and odors, and is comparatively stable. Several recent investigations (1, 3) have been most favorable to the Kaufmann iodine number method.

Since Kaufmann's reagent, prepared by adding bromine to absolute methanol saturated with sodium bromide, is neutral, the possibility of measuring the extent of substitution by determining the acid formed during bromination, was considered. It was found, however, that the reaction resulting in a monomethoxy-monobromo derivative instead of the dibromide produces a quantity of acid which overshadows that which may be formed by substitution. Meinel (7), who studied this reaction of bromine in methyl alcohol with ethylenic bonds, postulated a reaction involving the addition of methyl hypobromite. He studied in some detail the effects of groups adjacent to the double bond on the extent of this reaction. Bartlett and Tarbell (2) in a careful study of the kinetics of the reaction showed that the addition of methyl hypobromite does not occur and that the mechanism shown below, with stilbene as an example, is more probable.



$$\begin{tikzcd} C_6H_5CH = CHC_6H_5 + Br_2 \arrow[r] & C_6H_5CHBr - C^+HC_6H_5 + Br^- \arrow[dl, "Br^-"'] \arrow[d, "CH_3OH"] \\ C_6H_5CHBr - CHBrC_6H_5 & C_6H_5CHBr - CH(OCH_3)C_6H_5 + H^+ \end{tikzcd}$$

The work herein reported comprises a study of the various factors involved in determining the iodine number of soybean oil by the Kaufmann method. In addition, the iodine numbers obtained by the Kaufmann method are compared with those found by other widely accepted methods, such as the Wijs, Hanus, and Rosenmund-Kuhnhenn.

EXPERIMENTS AND DISCUSSION

The time of reaction, temperature, light, and excess of reagents are of primary importance in halogen addition to a double bond. Table I illustrates the effects of the first two factors on the iodine number of a solvent-extracted soybean oil, determined by the Kaufmann method.

Individual analyses are given to show the precision attained. In this table it may be noted that the duplicate figures for two hours at 24° differ by 0.6 of a unit. This represents the extreme spread of six determinations made on different days. For the longer reaction times at the higher temperature the blanks became unsatisfactory and the figures were found to be unreliable, probably because of loss of bromine by vaporization or reaction with the alcohol. At room temperatures, however, the reagent may be pipetted with ease. From the standpoint of precision, reasonable variations of time and temperature exert little influence on the iodine number as found by the Kaufmann method. A few experiments showed that for a two-hour reaction time diffuse daylight had no effect on the course of the reaction.

Kaufmann prescribes definite limits to the size of sample, depending on the iodine number of the oil. The necessity for this limitation is shown in Table II which presents the iodine numbers of soybean oil and clarified butterfat. If sufficient time is allowed, the excess reagent becomes relatively unimportant, but for a reasonable time of reaction, such as two hours, the large excess (about 300 percent) specified by Kaufmann must be used. Kaufmann's assertion that a reaction time of one-half hour was sufficient for oils of low iodine number could not be confirmed for butterfat having an iodine number between 33 and 34.

From the data of Table II it appears that when about 300 percent excess reagent and a two-hour reaction time are used, the Kaufmann method gives reproducible figures for iodine number.

Since it is of interest to compare the Kaufmann iodine numbers with those found by other methods in current use, Table III has been prepared to show iodine numbers found by several methods on a wide variety of oils, ranging from 8.4 to 202. Each figure is an average of duplicate determinations. The procedure of the American Oil Chemists' Society was followed for the Wijs method. The Hanus method as adopted by the Association of Official Agricultural Chemists was used. A solution of iodine monochloride in carbon tetrachloride was made and used as described by Marshall (6). The directions of Rosenmund and Kuhnhenn (8) were followed in preparing 0.1 N pyridine sulfate dibromide solution in acetic acid. A solution of the latter reagent was also made up 0.2 N, a strength comparable with that used in the

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[2] A cooperative organization participated in by the Bureaus of Chemistry and Soils and Plant Industry of the U. S. Department of Agriculture, and the Agricultural Experiment Stations of the North Central States of Illinois, Indiana, Iowa, Kansas, Michigan, Minnesota, Missouri, Nebraska, North Dakota, Ohio, South Dakota, and Wisconsin.

other methods. The precision obtained with the Wijs, Hanus, and 0.1 N Rosenmund-Kuhnhenn reagents was equal to or better than that shown in Table I for the Kaufmann method. The Marshall reagent and the stronger Rosenmund-Kuhnhenn solution gave figures which varied more widely. Consequently, only a few determinations were made with these reagents.

It is evident from Table III that the Kaufmann, Wijs, and Hanus methods agree fairly well except for oiticica, menhaden, and tung oils. The Rosenmund-Kuhnhenn determinations also agree for oils of low iodine number but are appreciably different for oils having iodine numbers above 100. The use of a stronger reagent for the Rosenmund-Kuhnhenn method does not materially affect the results obtained. The higher Wijs iodine number for menhaden oil is in agreement with data from a similar study (5). The presence of licanic and elaeostearic glycerides in oiticica and tung oils, respectively, offers difficulties in determining the iodine number. The usual procedures endeavor to measure the halogen required for saturation of two of the three double bonds. It is generally known that this result is not attained by the methods here examined and that the Hanus method in particular gives results much too high. The precision of the Wijs and Kaufmann methods is less for the tung and oiticica oils than for the others, and in order to obtain reproducible results conditions must be duplicated within narrow limits, a fact previously noted in the method of the American Oil Chemists' Society.

In this paper the term "acidity number" is used to indicate the number of centigrams of iodine equivalent to the acid liberated per gram of oil during the iodine number determination. This acidity number is obtained by the usual iodometric acid titration. Potassium iodate added to the iodine number reaction mixture reacts with the excess potassium iodide present and liberates iodine equivalent to the acid available. In Table IV high acidity numbers are found for castor and oiticica oils with the Marshall reagent and for oiticica and tung oils with the Kaufmann reagent. The castor and oiticica oils contain hydroxy and keto groups, respectively, which may be the cause of increased substitution

TABLE I.
EFFECT OF TIME AND TEMPERATURE ON THE KAUFMANN IODINE NUMBER OF SOYBEAN OIL

Temperature	Iodine number when reaction time was —				
	½ hour	1 hour	2 hours	24 hours	48 hours
°C					
9 ± 1°	131.4	131.3	132.0	132.9	132.8
	131.3	131.6	132.3	133.0	133.0
24 ± 1°	131.1		132.3	132.2	132.5
	131.9		132.9	132.5	132.5
40 ± 1°	131.4	132.8	132.7	131.8	131.5
	131.9	133.0	132.8	132.2 [1]	131.3 [1]

[1] The blanks for the samples standing for long periods at the higher temperature were so much lower than the blanks at room temperature that the iodine numbers so obtained cannot be considered entirely satisfactory.

TABLE II.
RELATION OF SIZE OF SAMPLE AND REACTION TIME TO THE KAUFMANN IODINE NUMBER

SOYBEAN OIL

Size of sample	½ hour		2 hours		24 hours	
	Iodine No.	Excess reagent	Iodine No.	Excess reagent	Iodine No.	Excess reagent
		Percent		Percent		Percent
Standard[1]	131.9	364	132.3	355	132.5	339
	131.1	369	132.9	368	132.2	372
Twice standard	123.6	152	131.1	137	132.1	132
	122.8	148	131.4	131	132.6	125
Thrice standard			126.6	59	132.1	52
			126.3	64	132.3	55
BUTTERFAT						
Standard[1]	33.1	370	33.5	362	33.8	351
	33.2	363	33.6	355	34.1	351
Twice standard	30.9	153	32.9	131	33.7	119
	29.7	166	32.9	132	33.8	125
Thrice standard			31.1	71	33.6	53
			32.0	61	33.6	48

[1] Sample specified by Kaufmann for 25 ml of reagent
0.12 to 0.1 g for oils with iodine number 120 or more
About 0.2 g for oils with iodine number 60 to 120
0.5 to 0.3 g for oils with iodine number 21 to 60
1.0 to 0.5 g for oils with iodine number up to 20

TABLE III.
COMPARISON OF IODINE NUMBERS DETERMINED BY DIFFERENT METHODS

Oil	Iodine numbers determined by —					
	Kaufmann	Wijs	Marshall (ICl in CCl_4)	Hanus	Rosemund-Kuhnhenn 0.1 N	Rosemund-Kuhnhenn 0.2 N
Coconut	8.7	8.7		8.8	8.4	
Butter	33.6	33.9		33.9	33.0	
Lard oil	76.1	77.2		76.9	74.8	
Olive	82.3	83.4		83.5	82.4	
Castor	83.5	83.9	98.5	83.7	83.4	83.2
Peanut	92.8	93.3		92.3	90.1	
Corn	125.9	127.1		125.6	119.5	
Soybean	132.6	134.1	137.0	131.4	125.0	125.0
Oiticica	149.6	144.4	165.5	197.4	136.6	
Tung No. 1[1]	164.4	161.1		216.8	156.5	
Tung No. 2[1]	147.4	151.5	159.8	198.5	145.3	147.6
Linseed	174.2	176.6	182.9	172.7	164.9	166.4
Menhaden	183.0	188.1		183.3	173.9	
Perilla	202.0	203.1		201.0	189.2	
Oleic acid	88.8	88.6		88.6	88.8	

[1] Tung oil No. 1 was a recently purchased commercial oil; No. 2 had been kept for several years in a tightly closed can.

TABLE IV.
IODINE AND ACIDITY NUMBERS DETERMINED BY THE KAUFMANN AND MARSHALL METHODS

Oil	Kaufmann		Marshall	
	Iodine number	Acidity number	Iodine number	Acidity number
Coconut	8.7	.9		
Butterfat	33.6	2.8		
Lard oil	76.1	6.0		
Olive	82.3	6.6		
Castor	83.5	7.6	98.5	23.7
Peanut	92.8	6.8		
Corn	125.9	8.7		
Soybean	132.6	8.5	137.0	2.8
Oiticica	149.6	57.5	165.5	17.3
Tung No. 1	164.4	62.4		
Tung No. 2	147.4	52.2	159.8	8.6
Linseed	174.2	9.9	182.9	4.6
Menhaden	183.0	10.1		
Perilla	202.0	13.4		
Oleic acid	88.8	6.8		
Elaidic acid	89.7	6.0		

TABLE V.
METHOXYL VALUES BEFORE AND AFTER BROMINATION

Oil	Iodine number (Kaufmann)	Acidity number (Kaufmann)	Methoxyl		
			In original oil[1]	In brominated oil	
				Found	Calculated
			Percent	Percent	Percent
Soybean	132.6	8.5	3.0	3.3	2.8
Coconut	8.2	.8	4.0	4.1	4.0
Tung	146.3	50.7	3.1	8.3	9.0

[1] Probably due partially to the formation of isopropyl iodide from glycerol and hydriodic acid.

by the Marshall reagent.

The low figure for the acidity number found for castor oil with the Kaufmann reagent and the agreement between the iodine numbers for this oil determined by the Kaufmann, Wijs, Hanus, and Rosenmund-Kuhnhenn methods indicate that little if any subsitution has occurred with the Kaufmann reagent. For those oils in which conjugated unsaturation does not exist, the small amount of acid found may be the result of substitution of halogen, or addition of methoxyl, or both of these reactions. The high acidity numbers found for oiticica and tung oils might have been predicted on the basis of Meinel's studies indicating the influence of conjugated unsaturation on the addition of methoxyl. Experiments have shown that in the case of oils containing conjugated double bonds at least the major portion of the high acidity numbers found is a result of the reaction with alcohol. Table V presents the results of methoxyl determinations on oils before and after treatment with the Kaufmann reagent. The brominated oil was recovered from the iodine number reaction mixture by first washing the carbon tetrachloride layer with water and then removing the carbon tetrachloride by evaporation. The residue was taken up in ethyl ether, and the resulting solution washed repeatedly with water, after which the ether was removed. The methoxyl was determined in a micro-Zeisel apparatus in the usual way. It is possible to calculate the increase in weight of the original oil caused by the addition of bromine and methoxyl as measured by the iodine and acidity numbers. It is assumed that the methoxyl added during bromination is proportional to the acidity number. If this amount of methoxyl is added to that found in the original oil, the calculated figures for methoxyl are obtained (Table V). The agreement of these figures with those found experimentally is sufficient to support the view that at least the major portion of the acid arises from the addition of methoxyl.

SUMMARY

1. The determination of the iodine number of soybean oil by the Kaufmann method is not appreciably affected by moderate changes in temperature and illumination.
2. The excess of reagent is very important and a minimum of 2 hours at room temperature is required.
3. The iodine numbers found by the Kaufmann method differ but little from those found by the Wijs and Hanus methods, except for tung and oiticica oils for which the Hanus method gives values much higher than the Kaufmann and Wijs methods. The Rosenmund-Kuhnhenn method gives results appreciably lower for all oils studied of iodine number above 100.
4. The increased amount of methoxyl in the brominated oil shows that the acid formed during halogenation is not a measure of substitution by the Kaufmann reagent.

BIBLIOGRAPHY

1. Barbour, A. D., Oil and Soap, **11**, 7-9 (1934).
2. Bartlett, P. D., and Tarbell, D. S., J. Am. Chem. Soc. **58**, 466-74 (1936).
3. Godbole, N. N., Ketkar, V. V., Sharma, K. V. J. S., and Kamath, H. R., Fette u. Seifen, **43**, 155 (1936).
4. Kaufmann, H. P., "Studien auf dem Fettgebiet," Verlag Chemie G. m. b. H., Berlin 1935, page 23.
5. Kaufmann, H. P., Ibid., page 29.
6. Marshall, A., J. Soc. Chem. Ind., **19**, 213-5 (1900).
7. Meinel, K., Ann. **510**, 129 (1934); **516**, 231-43 (1935); Ber. **70B**, 429-34 (1937).
8. Rosenmund, K. W., and Kuhnhenn, W., Z. Untersuch. Nahr. u. Genuss., **46**, 154-9 (1923).

A New Liquid Sampler(1)*

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Abstract

In this article, a new sampling device for use in sampling liquids in barrels, drums, tank cars and deeptanks (whether ship or shore) is described. This instrument will not only show immediately the presence of free water or sludge but will permit an accurate measurement of its depth.

HAVING had some difficulties with the various liquid sampling devices on the market, especially when free water is present, we have devised a new sampler which we believe is a valuable instrument for sampling oils, etc. whether in barrels, tank cars or deeptanks.

This device consists of a hollow metal cylinder, 24″ long and $1\frac{15}{16}$″ in diameter, substantially semicircular in cross section, and closed at top and bottom. The interior is divided by metal shelves, making twelve two inch compartments. The flat front is closed by a sliding door, machined to give a perfect leak-proof joint. The device has an extension at the top into which can be added 2 ft. rods to reach the bottom of the container. The slide also has an extension to which 2 ft. rods can be added to open the shutter, thereby operating the sampler with two sets of rods.

It is optional whether to use a set of rods for operating the shutter or to operate it by using a strong piece of twine. The shutter will open by pulling and will close by its own weight. The slide has a metal "stop" attached to the bottom to prevent the shutter from leaving the cylinder, when raised to the top.

The instrument is made of a bronze body, monel slide and steel bar attached to the slide, all chromium plated and therefore can be used in almost any kind of liquid without causing any damage to same.

In sampling a barrel or drum, the container is laid on its side with bung up, the bung removed, and the sampler inserted to the bottom. The slide is then opened, held open a few seconds, closed, and the sampler removed. On opening the shutter, the various sections will be found filled with liquid, the whole forming a representative core of the liquid in the package. If any free water is present it will be found in one or more of the segments, and a direct measurement of the amount of free water can be obtained by counting the number of sections containing only water (each section represents two inches and is equivalent to 1½ oz.) and measuring or estimating the proportions of water and oil in the highest section containing water. As many of these individual samplings can be taken as may be necessary, depending upon whether a 5%, 10%, or 100% sample is being drawn.

In tank cars, the sampler is lowered to the bottom, opened, closed, and removed. This will give a core representing the bottom 24 inches