effectiveness carried through the mixing and baking operations and retained in the finished piece.

Peroxide formation occurring in a fat contained in a test piece such as a soda cracker, when subjected to the oven test offers an interesting field of investigation. Since the peroxide content cannot be determined directly on the piece, it is necessary to devise a simple and rapid method of extracting the fat without altering its peroxide characteristics. S t a n d a r d extraction methods are time consuming and involve procedures which are apt to change the peroxide content of the fat as it existed in the baked piece. We have been working with the usual solvent mixture of acetic acid and chloroform used for the peroxide determination. Our procedure involves grinding the test piece finely, taking a sample weight dependent on the fat content, warm-

ing it gently and extracting with successive portions of the solvent mixture, which are decanted through a fast flowing filter. The peroxide number is determined directly on the combined extracts. By this method a determination can be carried to completion within a few minutes. The fat content of the test piece is accurately determined by the usual extraction procedure, and the proper correction applied to the peroxide figure obtained.

The weight of sample taken and the amount of the chloroform-acetic acid mixture used for extraction seem to exert some slight effect on the peroxide value found. Moisture in excess of that ordinarily present during the peroxide determination must also be avoided. However, these variables including any slight incompleteness of the extraction do not appear to be sufficiently great to render the method unsatisfactory

for following peroxide formation of fats in baked pieces. If further work substantiates this indication, it should be helpful in studying the relative keeping quality of shortenings before and after the usual mixing and baking practices have been applied.

Aside from its limitations the oven test is subject to the same errors inherent in all accelerated stability procedures. These errors for the most part are largely a matter of technique and generally exert their influence as pro-oxidative factors tending to produce stability data below the true keeping quality of the product under examination. By adopting the simple practical procedure outlined in the foregoing remarks and careful attention to cleaning of the apparatus, reproduceable results and reasonable checks between laboratories are possible.

THE IODINE VALUE OF TUNG OIL
A Modified Wijs Method Giving Constant Values With Varying Excess, Time and Temperature.
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IN comparing the merits of analytical methods it is well to keep in mind just what we expect the method to do.

From the practical angle we expect such a method to be as simple as possible. At the same time it must give constant results. These results should be as independent as possible from secondary factors, such as temperature, time, etc.

From the scientific standpoint we expect it to give the true theoretical values. The Iodine Value of an oil, for instance, should indicate either the true degree of total unsaturation or with some oils, a partial unsaturation point. For instance, in the case of tung oil there is the true total Iodine Value of around 230 (3) (4) (5). Also, two true partial Iodine Values are possible, one around 90 and one around 160, corresponding to the points where one and two of the three double bonds of the elaeo stearati, respectively, have added iodine.

In many cases we will find that a method that gives a true theoretical value will also be the one that gives the most consistent results and is least influenced by secondary factors. The most accurate method from the scientific standpoint will therefore almost always be the most practical one—provided, of course, that it is simple to operate.

The Iodine values of many oils, as determined with the present methods, are such true constants, and are therefore not influenced by minor variations in temperature, time or excess reagent.

With tung oil the situation has unfortunately been different. The value found by the Wijs method in its various customary forms does not agree with either one of the theoretical true values—it is too high for the true partial ⅔ value of 160 and on the other hand, much lower than the true total value of around 230.

It should, therefore, not surprise us that this Iodine Value is a function of excess iodine, of time and of temperature. Instead of dealing with a true constant in this case, as we do, for instance, in the case of cottonseed oil, we are really dealing with an arbitrarily chosen section of a variable function.

This has been known for some time and the iodine value of tung oil has been the subject of a number of investigations. An admirably accurate and comprehensive study of the dependence of the iodine value of tung oil on the excess of reagent, on time, and on temperature was published in 1935 by the Chinese investigators, Ho, Wan and Wen (1). From the quantitative relationship which they derived it is apparent that with the ordinary

method no constant value is obtained. In order to overcome the inconsistency of the results they suggest recalculating the determined value to certain standard conditions. However, such standard conditions are purely arbitrary, i.e., they do not correspond to any true constant of the sample.

The fact that tung oil has a true partial iodine value at around 160 has first been observed by van Loon (2) who noticed a break in a curve obtained by plotting a series of 2½ hour Wijs numbers against the weight of sample used in their determination.

A similar break at 160 is apparent in curves which were obtained by calculating back from some of the data given by Ho, Wan and Wen and similarly plotting the iodine numbers against the sample weights per 25 ml. of Wijs solution. Two such curves, corresponding to two different temperatures, are shown on Fig No. 1.

Translated into physical chemistry these curves show that two distinct reactions of different mechanisms are taking place. This agrees with the observation made about ten years ago by Gelber and Boeseken (3) that 2 out of the 3 double bonds in eleostearic acid will add iodine instantly, whereas the third double bond is attacked more slowly.
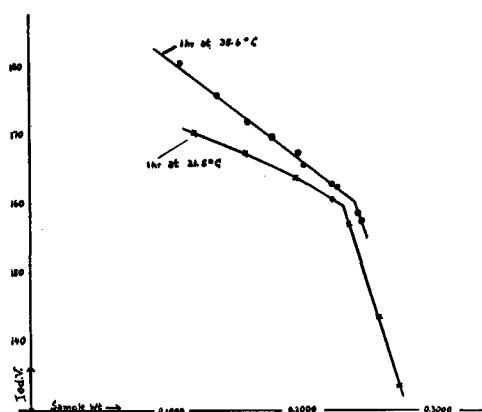
FIGURE 1

If the mechanisms of these two steps in the reaction are different —as the curves seem to indicate— it must be possible to find experimental conditions which will favor the completion of the first step before the second one has had an opportunity to begin. If this can be done, we will then have a method to determine the true partial iodine value of the tungoil, rather than— as we do now—to determine any one of the many possible points on these curves. The iodine value of tung oil will then be a true constant, which is not affected by secondary variations of excess, time or temperature.

Inspection of the curves indicates in what direction the conditions must be changed in order to realize this end. We notice that on the right, where larger samples were used, the values lie below 160. The excess of reagent was evidently not large enough to complete the first step.

On the left side the iodine values are higher than the partial saturation point of 160. Here the first step has been completed and the second step has taken place to a varying degree. We note that this left branch is more nearly horizontal in the curve for the lower temperature. It seems, therefore, that by lowering the temperature the addition of iodine to the third double bond can be restrained.

The effect of the time factor is parallel to that of the temperature, the Chinese investigators having shown that a 10 degree drop in temperature in this left region corresponds to doubling the time of reaction.

We must therefore reduce both time and temperature to a minimum in order to avoid the occurrence of the second reaction and at the same time apply enough excess of Wijs

solution or use small enough samples of oil to ensure completion of the first part of the reaction. If we then plot the determined values against sample weights, we should get a curve which will differ from these (Fig. 1) in that the left hand branch should be horizontal.

T h r e e determinations with varying s a m p l e weights were run for 10 minutes in a thermostat at 10° C. Both the iodine bottle and the Wijs solution were brought to this temperature beforehand. Under these conditions there is still some dependence on excess. If plotted, the desired horizontal is not yet obtained, though we have come closer to it. (Fig. 2).

SERIES A—Temp. 10° C.—Time 10 min.

Sample Wt. in grams (for 25 ml Wijs sol.)	Iod. Val.
0.1060	164.0
0.1508	162.5
0.1818	161.3

Three further tests at 10° C. which were titrated after only 2 minutes gave almost identical iodine numbers, though the weight of the sample used varied almost 50%.

SERIES B—Temp. 10° C.—Time 2 min..

Sample Wt. in grams (for 25 ml Wijs sol.)	Iod. Val.
0.1125	160.7
0.1384	161.2
0.1609	160.5

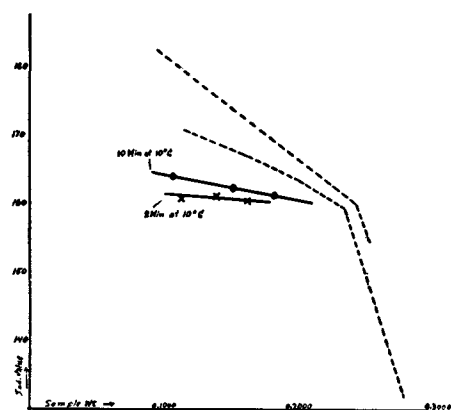The three points almost form a horizontal line. (Fig. 2.)

FIGURE 2

We are obviously in, or very close to, the desired region of constancy.

Let us consider the experimental side of this determination. The regular Wijs solution has been used. The sample weights were taken a little smaller than in the usual procedure but still large enough to obtain accurate weigh-

ings on a standard analytical balance. The time of contact was cut from 1 hour to 2 minutes. In order to work at the lower temperature a thermostat, set for 10° C., was required.

Instead of working at lower temperatures, a possibility seemed to exist to obtain a similar effect; i.e., to slow down the second reaction by working at lower concentrations. In order to determine if the total concentration will influence the iodine value three Wijs numbers were carried out in the standard fashion at room temperature for 1 hour, but with varying quantities of chloroform.

In experiment No. 2, Series C, we have just twice the total volume and in No. 3 four times the total volume or $\frac{1}{4}$th of the usual concentration. An individual blank was run for each concentration.

SERIES C—Temp. 25° C.—Time 1 hour—
Sample Wt. constant

	No. 1	No. 2	No. 3
Chloroform, ml ..	10	45	115
Total Volume, ml	35	70	140
Iodine Value	169.1	166.7	165.2

Actually, the resulting iodine numbers do depend on the concentration and a comparison of these figures with the equations of Ho, Wan and Wen shows that the decrease obtained by cutting the concentration to $\frac{1}{2}$ roughly corresponds to lowering the temperatures by about 8-10° C. However, we discarded this procedure because it was thought impractical to use such large quantities of a fairly expensive solvent for a method primarily intended to serve the industrial laboratory.

Instead we proceeded in another direction to overcome the necessity of using a thermostat. The bottles containing the samples in solution were placed in a beaker filled with cracked ice and water. The Wijs solution itself was left at room temperature and run into the chilled bottle under continuous swirling. It was determined that in this way the actual temperature of the reacting mixture was about 4 to 5° C. during the addition of Wijs solution and $\frac{1}{2}$ to 1° after 2 minutes. provided that an Erlenmeyer flask or similar thinwalled glassware was used and provided this flask was swirled gently in the ice bath for one minute before running in the reagent and during all the two minutes' reaction period.

On first sight this does not seem to be a very accurate way of controlling temperature. However,

here we are aided by the fact that this partial iodine value of tung oil now is a true constant and not an arbitrarily chosen point from a functional curve. Thus, we are bound to get a good check even if the temperature varies a few degrees one way or the other. This is true for variations in any other secondary factor as well. Let us look at some further series. One ot them—Series E-H—was run with varying sample weights; i.e., with varying excess of reagent, and the other two—Series G, Series K —with very gross variations in the time factor.

SERIES E & H—Time 2-2½ min.
Sample Wt. in grams

(for 25 ml Wijs sol.)	Iod. Val.
0.0740	161.6
0.0932	161.7
0.1191	161.5
0.1212	160.9
0.1372	160.9
0.1486	159.9
0.1493	159.7
0.1596	159.5

SERIES G—Sample Wt. = 0.0930 g
(for 25 ml Wijs sol.)

Time	Iod. Val.
1½ min.	161.3
2½ min.	161.7
10 min.	163.2

SERIES K—Sample Wt. = 0.1165 g
(for 25 ml Wijs sol.)

Time	Iod. Val.
2½ min.	160.2
5 min.	161.4
10 min.	162.7

In Series E and H we see that a radical variation in sample weight of over 100% only introduces an error of 2 points between the two extremes. It is well to keep in mind at this point that with the generally adopted Wijs method the error with such a variation in sample weight of 100% would be 8 to 12 points, depending on the temperature used. This is to say that the error which is introduced by unavoidable variations in the weight of sample will now be only from 1/4 to 1/6 of that which it was with the standard method. At the same time the analyst will have the result in one hour's time less than with the old method. All this at no greater cost than that of a beaker of cracked ice.

The two time series (G and K) show that, as could be expected, there is a very wide time allowance as well. The time may be over-run by 100% without changing the result more than by the usual 1 point of experimental allowance.

In order to show that this method actually gives a value close to the true partial iodine value, corresponding to the ⅔ addition, it was tested on a sample of triply recrystallized alpha elaeostearic acid, melting point 48.5° C.

SERIES N and O—α-elaeostearic acid— m.p. 48.5° C.
Sample Wt. in grams

(for 30 ml. Wijs sol.)	Iod. Va.
0.0821	183.0
0.0951	183.6
0.1221	180.5
Theoretical	182.8

Another oil containing conjugated double bonds which has received considerable attention is the synthetic drying oil which is derived from castor oil by dehydration. Since this dehydrated castor oil, as manufactured by the Woburn Degreasing Co. of New Jersey, contains conjugated double bonds, it was natural to expect that certain precautions had to be taken in the iodine number determination. As in this case the true total iodine value was desired, which should indicate the point of complete saturation rather than of partial saturation of the conjugated double bond system, the possibility of using the Hanus method with this new oil (Isoline) was studied.

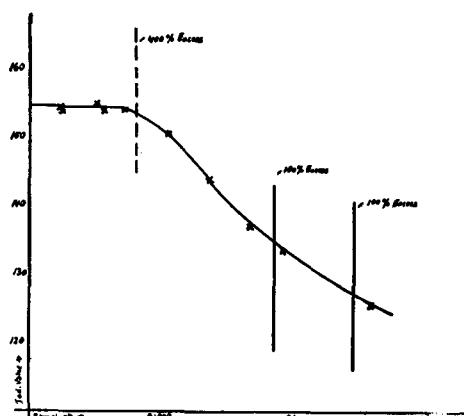The graph (Fig. No. 3) will show that there is a very decided

FIGURE 3

dependence on sample weight; i e.. on excess of Hanus solution. The weight of the sample used is plotted against the iodine number found. The region enclosed in the two vertical lines is that of 100 to 150 per cent excess reagent, as required in the standard method. In this region no constant iodine values are obtained. If the excess employed exceeds 400 per cent, however, which is accomplished by keeping the sample weight below 0.08 grams for 25 ml. of standard Hanus solution, we have perfectly constant iodine values. The iodine number obtained in this constant region, in this case 153, agrees well with that calculated from the drop in acetyl value of the original castor oil from 160 before dehydration to 18 after it has been converted into the dry-

ing oil. The effect of time and temperature, however, has not been eliminated in this case, as it has been in the case of tung oil. Further work is therefore required.

We may conclude that generally in applying a standard method to a new oil, and sometimes to an old one, as in the case of tung oil, we should first ascertain what conditions are necessary to obtain a true chemical constant.

Credit and appreciation is expressed to Dr. K. A. Pelikan for his helpful suggestions.

LITERATURE

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METHOD

Weigh out 0.12 to 0.15 gms. of dry tung oil (*) in an ordinary Erlenmeyer flask (**).

Add 10 ml. of c.p. chloroform and place the flask into a large beaker, half filled with cracked ice, and water, and swirl gently for 1 minute.

Add 25 ml. of Wijs solution, which is prepared according to the A.O.C.S. Specifications. Continue swirling in the ice bath during and after the addition of the reagent (***).

Two minutes (± ½ min.) after completing the addition of Wijs solution, add 10 ml. of 15 per cent KI solution and 40 ml. of distilled water Titrate with 0.1N Na$_2$S$_2$O$_3$ solution, using 1 per cent starch solution as indicator as usual.

The iodine value is expressed as centigrams of equivalent iodine absorbed by 1 gram of oil.

The blank runs may be titrated immediately after the addition of Wijs solution and without the use of the ice bath.

*If this method is employed on pure elaeostearic acid, the sample weight should be 0.10 to 0.13 grams.

**It is not necessary to use glass stoppered iodine flasks because no iodine will be lost by evaporation in the short time of contact required in this method.

***It is not necessary to place the flask in the dark.