The results, by the official method, of 13 and 14*d*, and 21 and 22*e* are very singular and inexplicable to us. These four (*d* and *e*, each in duplicate) were weighed out at one sitting and dried in a bath, heated by boiling water, which was in action constantly from morning till night for days before and after this particular lot was dried (alone). The weights came to a standstill and the percentages in one case agreed closely, yet the figures are something like half the true values, They are given here merely as a matter of record. although we were unable to find a cause for the queer conduct.

To show the time required for extraction, four determinations of fat are given in Table III.

TABLE III.—EXTRACTION OF FAT.

No.	Quantity taken. Grams.	Periods of extraction. Minutes.	Change in weight of sample. Per cent.	Fat. Per cent.
47	1.6494	30	−84.92	
		20	— 0.05	
		15	— 0.02	84.99
48	1.6116	20	−88.18	
		30	— 0.61	
		15	— 0.00	88.79
49	1.6312	45	−84.02	
		15	— 0.05	84.07
50	1.4076	45	−82.23	
		15	— 0.04	82.27

The method is applicable to various other substances, the proper gas being aspirated through the apparatus, and the pressure reduced if this is desirable. With finely ground material, a layer of asbestos should cover the bottom of the crucible and a plug of cotton placed in the inner end of the outlet tube, to insure against loss.

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[CONTRIBUTION FROM THE FOOD LABORATORY OF THE BUREAU OF CHEMISTRY, U. S. DEPARTMENT OF AGRICULTURE, NO. 1. SENT BY H. W. WILEY.]

A COMPARISON OF THE HALOGEN ABSORPTION OF OILS BY THE HÜBL, WIJS, HANUS, AND McILHINEY METHODS.

BY L. M. TOLMAN.

Received May 26, 1904.

THE Hübl method for determining the iodine absorption of oils and fats is the official method, but it has several faults which affect its accuracy. First, the solution rapidly loses strength if made up as the official method directs, and in a week or so is unfit for use; second, it is so slow in its reaction with some of the oils, such as linseed, that a serious error is brought about by the change in strength in the solution during the reaction. Wijs[1] shows how great this error might be, and the following table shows how much difference the time of titrating the blank makes in the iodine number.

TABLE I.—IODINE NUMBER OF LINSEED OIL BY THE HÜBL METHOD.

Time of absorption. Hours.	Blank titrated at beginning.	Blank titrated at end.
2	173.74	.....
7	177.65	170.39
24	181.89	163.16

These figures show a decrease in the iodine number after seven hours, if the blank is titrated at the end of the determination. Wijs considers that the true iodine number in this case lies between 173.7 and 181.89. This change in strength can be greatly lessened by using purified absolute alcohol, but even under these conditions the solution soon becomes so weak that it is of no further use.

Another objection to the Hübl method is that practically each analyst employs a modification of his own, especially, as regards the time necessary for the solution to remain in contact with the oil; and, as is well known, very different results are obtained in this way on the same oils, which results have been collected as data obtained by the Hübl method. The following directions from various authorities as to the time needed for the Hübl test show how varied is the practice in this regard. Allen[2] recommends two hours. Our official method requires three hours. Lewkowitsch[3] recommends four hours. Wijs[4] showed that with linseed oil seven hours was necessary, and it is a very common practice among analysts to allow from eighteen to twenty-four hours. These different practices can not fail to bring about diverse results.

In order to determine which of these methods would be the most satisfactory, the following work was undertaken.

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[1] *Chem. Rev. Fett u. Hartz-Ind.*, **6**, 6 (1889).

[2] "Commercial Organic Analysis," Vol. II, Part I, p. 64.

[3] "Chemical Analysis of Oils, Fats, and Waxes," 1899, p. 173.

[4] *Chem. Rev. Fett u. Hartz-Ind.*, **6**, 7 (1899).

THE WIJS SOLUTION.

Wijs[1] directs that there be an excess of 70 per cent. of the iodine added in the determination in order to insure complete and rapid absorption, but the results on linseed oil given in Table II indicate that such a large excess is unnecessary. In each of the determinations 0.1500 gram of linseed oil was used and the solution was allowed to stand thirty minutes in contact with the oil.

TABLE II.—IODINE ABSORPTION OF LINSEED OIL WITH VARYING EXCESS.

Wijs solution. cc.	Value in N/10 iodine. cc.	Amount of iodine absorbed in N/10 iodine. cc.	Iodine number.	Excess of iodine. Per cent.
25	61.28	23.16	193.4	62
20	49.35	23.13	193.7	53
15	37.08	23.13	193.7	37

These figures show that with an excess of only 37 per cent. the same results were obtained in thirty minutes as with an excess of 62 per cent. Linseed oil was used on account of its high iodine number and because it takes longer to obtain complete absorption with it than with oils of a lower iodine value. This smaller excess effects a great saving in solution and makes titrations more rapid. This smaller excess does not greatly affect the speed of reaction, as is shown in Table III.

TABLE III.—EFFECT OF EXCESS OF THE WIJS SOLUTION ON SPEED OF REACTION.

	Iodine numbers.	
Time. Minutes.	Excess of iodine, 62 per cent.	Excess of iodine, 37 per cent.
1	191.1	189.0
5	191.9	191.2
10	191.1	191.4
15	191.7	191.4
30	192.3	191.4
60	193.1	....

These results show that the reaction between the Wijs reagent and the oil is very rapid, even with only 37 per cent. excess.

Table IV shows that when the determinations are made in the light the iodine number seems to increase up to a definite point where it remains constant for a short time, then gradually in-

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[1] *Ztschr. für Nahrungs und Genus.*, **5**, 499 (1902).

creases up to four hours with no tendency to remain constant. In the dark the iodine number remained constant from one to two hours.

TABLE IV.—IODINE NUMBER OF LINSEED OIL BY THE WIJS SOLUTION.

Time. Minutes.	Iodine numbers. In light.	Iodine numbers. In dark.
1	192.4	186.1
10	193.1	192.6
30	193.1	192.9
60	194.1	193.5
120	194.7	193.4
240	195.7	....

TABLE V.—EFFECT OF TIME AND LIGHT ON THE WIJS AND THE HANUS SOLUTION.

Time.	Iodine numbers. In light.	Iodine numbers. In dark.
Wijs.		
30 minutes	191.9	192.1
5 hours	194.0	193.0
Hanus.		
30 minutes	189.1	189.2
5 hours	191.9	192.1

It will be noticed from these results that on the Wijs solution, standing thirty minutes, the light has no effect; the same may be said of the Hanus. In the five-hour test two effects are noted in the Wijs, namely, there is a very slight increase in the iodine number over the figures obtained in thirty minutes, and the results obtained in the light are slightly greater than those obtained in the dark. With the Hanus solution there is a slight increase in five hours over thirty minutes, but no difference in light or dark. This would indicate that it is not necessary to stand either the Wijs or Hanus solution in a dark cupboard when thirty minutes are allowed for the reaction.

This increase of absorption on long standing is probably due to secondary reactions as is shown in the results with iodine chloride in carbon tetrachloride given in Table VI. Upon standing longer than thirty minutes, substitution takes place and longer standing shows a remarkable, though gradual, change in the results.

TABLE VI.—IODINE NUMBER BY IODINE CHLORIDE IN CARBON TETRACHLORIDE.

Time. Hours.	Total.	Addition.	Substitution.
5	210.8	184.9	12.9 in light
5	204.8	190.9	6.9 in dark
1	198.6	194.2	2.2 in light
½	195.2	194.6	0.80 in light

These figures show that the addition apparently decreases with time after one hour, with a gradual increase in the total amount of iodine entering into combination. This indicates that with iodine chloride in carbon tetrachloride, standing longer than thirty minutes is no advantage and longer than one hour gives entirely unreliable figures. It seems probable that the same thing will be shown with iodine chloride in acetic acid, although to a much less extent, and that long standing gives untrue results. With iodine bromide in carbon tetrachloride the secondary reactions are much weaker, but the gradual increase up to eighteen hours standing with the Hanus solution is doubtless due to the same cause. This indicates that there is a maximum as well as a minimum time which should be allowed for the reaction, and for the Wijs solution this limit is between fifteeen minutes and one hour, the advantage being with the shorter time rather than the longer, thirty minutes being satisfactory for either solution.

THE HANUS SOLUTION.

Hanus[1] also advises an excess of 70 per cent. in order to insure complete absorption, and the results given in Table VII show that nearly this large excess is necessary to obtain complete absorption on linseed oil in thirty minutes.

TABLE VII.—IODINE NUMBER OF LINSEED OIL WITH VARYING EXCESS OF IODINE.

The Wijs solution. cc.	Value in N/10 iodine. cc.	Amount of iodine absorbed in N/10 iodine. cc.	Iodine number.	Excess of iodine. Per cent.
25	54.76	23.26	196.3	57
20	44.08	22.73	191.9	48
15	33.06	21.86	184.5	34

These figures, if compared with Table II, show how much slower in reaction the Hanus solution is than the Wijs, and how much greater excess is needed to produce the same results. Table VIII also brings out the slowness of the Hanus solution as compared with the Wijs.

TABLE VIII.—IODINE NUMBERS BY HANUS SOLUTION IN VARYING TIMES.

Time. Minutes.	Iodine No. 1. In light.	Iodine No. 2. In light.	Iodine No. 3. In dark.	Iodine No. 4. In dark.	Iodine No. 4. In light.
1	164.8	164.6	166.9	....	....
5	178.9	....	....	....	....

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[1] *Ztschr. für Nahrungs und Genus.*, 4, 913 (1901).

TABLE VIII.—(*Continued*).

Time. Minutes.	Iodine No. 1. In light.	Iodine No. 2. In light.	Iodine No. 3. In dark.	Iodine No. 4. In dark.	Iodine No. 4. In light.
10	181.3	182.2	187.7	....	....
15	184.6	186.7	....	....	....
30	185.6	187.5	191.0	189.2	189.1
Hours.					
1	185.6	187.5	191.3	....	....
2	....	188.5	191.0	....	....
4	....	189.5	....	....	....
5	....	...	....	192.1	191.9
18	....	193.3	....	....	....

These results on samples of linseed oil by different analysts show that it takes thirty minutes by the Hanus solution to reach the constant stage which is reached by the Wijs in ten minutes. The absorption is constant from thirty minutes to one hour and then begins the gradual rise, as was the case with the Wijs, and the same explanation is suggested. The Hanus is less affected by light than the other solutions.

BROMINE SOLUTION AND CARBON TETRACHLORIDE AS A SOLVENT IN THE WIJS AND HANUS METHODS.

In connection with the work of testing the Hanus and Wijs solutions, it was thought well to test the bromine solution proposed by McIlhiney and also the substitution of carbon tetrachloride as a solvent, for acetic acid, in the Hanus and Wijs methods. The advantage of this solvent is that it is neutral and permits of an estimation of the substitution which takes place in the reaction between the oil and the halogen. It was thought that if a change was to be made in our present method and any information of added value could be obtained by the use of a solvent of this nature, it would be well to adopt at this time the best method obtainable.

Solutions of iodine chloride, iodine bromide, and bromine in carbon tetrachloride were prepared, using the same strength as in the Wijs and Hanus methods and approximately N/3 bromine, as directed by McIlhiney. A solution in carbon tetrachloride of linseed oil of known purity was prepared and used in most of the experiments. The actual amount of oil used in each test was affected to a very slight degree by changes in temperature. As a rule, a fresh solution was made up for each set of tests and only very slight variations were found in the iodine numbers obtained by the Wijs and Hanus solutions in acetic acid at any time. In each determination 0.1500 gram of oil was used, which made it possible to regulate the excess of reagent and other conditions very exactly.

With these solutions several questions were to be decided:

1. How do the results obtained compare with those given by other solutions, especially the Hübl?

2. How long a time is required to obtain maximum figures?

3. Does water affect the amount of substitution?

4. How does light affect the reaction between oil and the halogen?

5. Does the age of the solution affect the results?

In the following results all figures are calculated to iodine for the sake of comparison.

The bromine solution will be considered first, the figures being given in Table IX.

Table IX gives a comparison of the values obtained by the different methods on a sample of oil giving a Hübl number of 180. The solutions were all freshly prepared and chemically pure carbon tetrachloride, perfectly dry, was used in making them up. The results obtained show a very satisfactory agreement. The substitution figures are very small in all the solutions and appeared only after long standing in the Wijs and bromine solutions, being largest with the Wijs. The maximum addition figure was not reached with any of the solutions in less than one hour, as is shown in Table IX. The results with the bromine solution were so different from those obtained on the same oil with other bromine solutions that the cause was sought with considerable interest. The relative speed of these solutions is about the same as with acetic acid as the solvent, as might be expected. The Wijs reagent is by far the most active, as shown in the other cases.

First a little water was added to the solution of oil in carbon tetrachloride; then the fresh bromine solution was added and allowed to stand in the light for one hour and no substitution was shown, but when the water was added to the oil solution in carbon tetrachloride and thoroughly shaken so that the water was taken up by the carbon tetrachloride, the following results were obtained, the other conditions being the same:

TABLE IX.—IODINE NUMBERS OBTAINED BY THREE DIFFERENT METHODS.

	The Wijs method.				The Hanus method.				Bromine method (in light).		
		Carbon tetrachloride.				Carbon tetrachloride.					
Time. Minutes.	Acetic acid.	Total.	Addition.	Substitution.	Acetic acid.	Total.	Addition.	Substitution.	Total.	Addition.	Substitution.
1	186.1	....	....	....	166.9	164.0	164.0	0.0	156.3	156.3	0.0
2	....	192.8	192.8	0.0	....	....	....	..	....	....	..
10	192.6	193.6	193.6	0.0	187.7	182.5	182.5	0.0	....	....	..
15	....	....	....	..	....	....	....	..	....	....	..
30	192.9	195.2	194.6	0.80	191.1	188.6	188.6	0.0	193.2	193.2	0.0
60	193.5	198.6	194.2	2.20	191.3	189.7	189.7	0.0	197.0	197.0	0.0
120	193.4	....	....	..	191.0	....	....	..	196.7	194.2	1.27

TABLE X.—BROMINE ABSORPTION WITH SOLUTION OF OIL IN ONE HOUR.

Oil solution.	Total.	Addition.	Substitution.	Condition.
Wet	217.6	163.9	26.87	Light
"	166.0	166.0	0.0	Dark
Dry	197.4	197.4	0.0	Light
"	166.7	166.7	0.0	Dark

These figures show conclusively that with the bromine solution moisture and light affect most remarkably the reaction between the oil and the bromine. The fact that a little water added to the solution did not affect the results can be explained on the ground that no mixture of the water with the carbon tetrachloride solution of the oil had taken place. When the water was mixed with the solution and the flask was in the light a substitution of 26.87 was obtained, but when the flask was set in the dark there was no substitution. The addition figures in both cases are practically the same, but do not agree with the addition figures obtained on the dry oil in the light.

This brings us to the conclusion that the bromine solution does not substitute in the light in the absence of moisture, or at least only very slightly; that it does not substitute in the dark even in presence of moisture, and also does not add to the same extent as it does in the light; that the bromine solution in the light and in the presence of moisture and oil forms hydrobromic acid, the amount formed being dependent almost entirely on the time of contact between the oil and the bromine. The blanks of the solutions showed no formation of acid at all. As the solutions of bromine previously used had always given considerable substitution, fresh solutions of bromine, iodine chloride, and iodine bromide in carbon tetrachloride were placed in glass-stoppered flasks and used from day to day to see what effect the age of the solution had on the amount of substitution. The results are shown in Table XI.

Table XI shows how much variation there is in the results by the bromine solution when the same solution has been used. The only varying factors are the amount of light due to weather conditions and the amount of moisture which may be absorbed by the carbon tetrachloride solution of bromine. The absorption of moisture seems to be the only explanation of the great change which takes place on standing The titer of the bromine solution remains practically constant, showing only a very slight change.

TABLE XI.—EFFECT OF AGE OF SOLUTION ON IODINE NUMBERS AND AMOUNT OF SUBSTITUTION.

(In light one hour.)

Age of solution. Days.	Bromine.			Iodine chloride in carbon tetrachloride.			Iodine bromide in carbon tetrachloride.		
	Total.	Addition.	Substitution.	Total.	Addition.	Substitution.	Total.	Addition.	Substitution.
Fresh	197.0	197.0	0.0	198.4	194.2	2.20	189.7	189.7	0.0
2	....	....	..	199.2	194.4	2.40	190.0	190.0	0.0
4	195.7	191.2	2.32	197.9	193.2	2.33	190.3	190.3	0.0
6	200.6	189.9	5.41	200.4	198.7	0.86	192.3	192.3	0.0
9	196.2	194.5	0.86	....	....	...	....	.....	..
10	....	....	...	200.6	193.8	3.44	190.0	188.1	0.86
13	219.1	162.9	28.16	....	....	...	....	....	..
(In dark one hour.)									
13	166.7	166.7	0.0	....	....	...	....	....	..
10	....	....	..	200.4	194.1	3.18	191.1	189.1	0.94

That the amount of light may affect the results by the bromine solution to a great extent was shown by the following experiments:

The bromine solution in contact with the oil was exposed to direct sunlight for two minutes and a duplicate was kept in the dark two minutes. The total absorption in the first case was 204.7, addition 166.1, substitution 19.30; in the second case the total was 179.7, addition 165.2, substitution 7.29. On the Wijs and Hanus solutions age has very little effect, and it makes no difference whether the reaction takes place in the dark or light as to the amount of substitution or addition when only thirty minutes are allowed for the reaction; if five hours are allowed, as shown in Table VI, light greatly increases substitution.

These results would indicate that in the light with a dry solution, bromine will give the same addition numbers as the Wijs and Hanus solutions, but in the dark it does not give addition values which have any relation to those given in the light. The presence of moisture and light gives results of no value at all. If the determinations are made with dry reagents in the dark, comparative results can be obtained, but these results can not be compared with figures given by any other methods. From this work it is concluded that the bromine solution is exceedingly unreliable, being affected by conditions hard to control, that the solutions of iodine chloride and iodine bromide in carbon tetrachloride are much less affected by these conditions and give much more satisfactory results which are comparable with those obtained by the same reagents in acetic acid, but that these solutions are affected to a greater or less degree by the presence of moisture and for ordinary work would not be satisfactory substitutes for the Hübl method. The following results on moist solutions of oil show that the iodine chloride and iodine bromide solutions are not affected by the presence of light or moisture in thirty minutes.

TABLE XII.—EFFECT OF LIGHT AND MOISTURE ON IODINE NUMBERS WITH IODINE CHLORIDE AND IODINE BROMIDE SOLUTIONS.

Solution.	Total.	Addition.	Substitution.	Conditions.
ICl in CCl_4 ..	200.9	192.4	4.25	In light 30 minutes.
" ...	200.9	192.4	4.25	In dark 30 minutes.
IBr in CCl_4 ...	191.2	187.7	1.75	In light 30 minutes.
" ...	191.2	187.7	1.75	In dark 30 minutes.

The chief use of any solution of this kind is in the detection of such substances as rosin oil and similar products, as the reaction between the oil and halogen is chiefly by substitution, and a solution which gives varied results would be unsatisfactory. The following results on rosin oil show that the Wijs reagent in carbon tetrachloride is as active as the bromine, and on account of its other advantages would be a much more satisfactory solution to be used for this determination.

TABLE XIII.—IODINE NUMBERS OF ROSIN OIL IN THIRTY MINUTES.

Solution.	Total.	Addition.	Substitution.
ICl in CCl_4	257.0	5.46	125.7
IBr in CCl_4	190.8	24.50	83.8
Br	257.0	5.46	125.7

The iodine bromide reacts very slowly and gives quite different results from the other solution, while iodine chloride and bromine give the same results, so that the iodine chloride would be the most satisfactory solution for this work. But it does not appear that any of these solutions can be satisfactorily substituted for the Wijs, Hanus, or Hübl in the ordinary work, as they give results not comparing well with present data, require many special precautions, and vary in their reaction with age.

Carbon tetrachloride, which had been recovered by distilling and drying with calcium chloride and then redistilling, acted much the same as carbon tetrachloride, which had been shaken up with water, giving large substitution values. We were not able to prepare a recovered product so that it would give the results obtained with Kahlbaum's chemically pure, dry carbon tetrachloride.

As a result of this work the following conclusions are offered:

(1) That much better results are obtained by the Wijs and Hanus solutions than by the Hübl.

(2) That the Hanus solution gives results much more closely agreeing with the existing data and is easier to prepare, but an excess of 60 to 70 per cent. is necessary to obtain quick action.

(3) That the Wijs solution is more rapid in its action, and an excess of 35 per cent. is sufficient, effecting a large saving in reagents and time of titrating, but it gives higher results.

(4) That thirty minutes is sufficient time for the action of either the Hanus or Wijs solution.

(5) That acetic acid is a better solvent for the work than carbon tetrachloride.

(6) That the bromine solution or iodine chloride or iodine bromide in carbon tetrachloride are not satisfactory for ordinary work.

(7) That iodine chloride in carbon tetrachloride is the most satisfactory solution, if determination of substitution is to be made.

(8) That both the iodine chloride and iodine bromide, being much less volatile than the bromine, there is much less danger of loss in that way with the former reagents.

The author wishes to acknowledge the assistance of Mr. Albert F. Seeker, of this laboratory, who repeated a large amount of the analytical work as a check on the results.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY, WASHINGTON AGRICULTURAL COLLEGE AND SCHOOL OF SCIENCE.]

ON THE REACTION OF LARD FROM COTTONSEED MEAL-FED HOGS, WITH HALPHEN'S REAGENT.

BY ELTON FULMER.

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IN December, 1902, we published[1] some results obtained by the application of Halphen's test to samples of lard rendered from the fat of hogs which had been fed with a ration containing

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[1] This Journal, 24, 1148-1155 (1902).