The Determination of the Iodine values of Fats and Oils by Winkler's Bromate Method.

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Of the various methods and modifications that have been proposed from time to time for the determination of the Iodine values of fats and oils, Hubl's and Wijs' are the only two which have found more or less general application.

As early as 1854 Knop proposed the use of potassium bromate and hydrobromic acid for the determination of Iodine values and lately again Tolle (*J. Pharm. Chem*, 1905, *21*, 111 and 183) and Mossier (*Phan. Zeit.*, 1907) have proposed the use of Bromine from one source or another for the determination of the degree of unsaturation of fats. Mossler uses a mixture of potassium bromate and bromide acidified with dilute sulphuric acid and determines the unused bromine by adding excess of stannous chloride and titrating with decinormal iodine solution. Winkler (1909) has modified Mossler's process and estimates the excess of bromine by adding potassium iodide and titrating the liberated iodine by the aid of standard tMosulphate solution.

W. Vaubel (*Zeit. Angew. Chem.*, 1910, *23*, 2078) and J. Kilmont (*Arch. Pharm.*, 1912, *250*, 561) have used Winkler's modification of Mossler's method with different concentrations of bromate solution and different quantities of bromide.

Winkler uses a nearly decinormal solution of bromate, namely 2·784 per litre, together with two to three times the quantity of bromide theoretically necessary (20 - 30 grams) and acidiies the mixture with 10 per cent. hydrochloric acid.

The advantages claimed by Winkler are that the bromate solution is readily prepared by weighing the requisite amount of the solid and that it is quite stable and can be kept for long periods without deterioration.

According to Lewkowitsch (Chem. Tech. and Analysis of Oils, Fats and Waxes 1913, vol. 1. 394) the addition of bromine is not to be recommended as substitution as well as

addition of bromine occurs and the numbers obtained are thus too high. (Compare Mills J. *Soc. Chem. Ind.*, 1883, 435 ; 1884, 366, McIlhiney ibid 1894, 668).

Weiser and Donath (*Zeit, untersuch. Nahr. Genuss.*, 1914, *28*, 65 ; for abstr. cf. *J. Soc. Chem. Ind.*, 1914, 53, 873) haye made experiments in order to compare the results obtained by Winkler's process in the ease of various oils, animal fats and some pure fatty acids with the numbers obtained by using Hubl's, Wijs' and Waller's methods.

They find that Winkler's method gives values which agree better with Hubl's results than with Wijs'. As a rule the latter are too high. They strongly recommend the Winkler method because the time required is less, the method is cheap and is very easy to work. They recommend using about 50 per cent. excess of bromine and give the following quantities of oil or fat to be used in different cases :— for oils with an iodine value below 100 0·2 to 0·5 gram, for oils with an iodine value between 100 and 150 0·15 to 0·20 gram and oils with a value about 1 50 0·1 to 013 gram.

The tabular statement of results given by Weiser and Donath show that during the first 10 minutes addition of bromine is nearly complete and the values obtained for 10, 30, 60 or 120 minutes are much the same. For oils with low iodine values 30 minutes contact with the bromine solution is recommended, but for oils with high iodine values (above 100) 60 minutes is advisable and for linseed oil a period of 2 hours is recommended and for certain fish oils even 4 hours are essential.

The following numbers are given for certain unsaturated fatty acids.

	Value Obtained.	Calculated value.
Erucic ...	72·0 ...	75
Elaidic ...	87·5 ...	90
Oleic ...	94·0 ...	90
llicinoleic ...	87·2 ...	85
Undecylenic ...	137·0 ...	137·8

It is well known that the Hubl and Wijs methods do not give satisfactory results for unsaturated acids containing an ethylene linking in the $\alpha\beta$ -position with respect to the carboxylic group. As, however, such acids or esters are not met with in common fats and oils the question is of little importance in connection with the iodine values of natural fats and oils.

Weiser and Donath claim that the Winkler method gives quite good results with such acids as crotonic, tiglic and cinnamic, all of which contain an $\alpha\beta$ ethylene linking. The numbers actually given are :—

	Value obtained by the Bromate method.	Theoretical value.	Value obtained by Wijs method.
Crotonic	... 291	... 295	... 45
Tiglic	... 253	... 253·7	... 6·2
Cinnamic	170	174·4	54

They state, however, that the bromate method does not yield satisfactory results with dibasic acids such as itaconic, aconitic and maleic. This is not surprising as it is well known that two or more carboxyl groups adjacent io an ethylene linking tend to inhibit the addition of bromine at the linking. (Compare Hugo Bauer, *Ber.*, 1904, *87*, 3317).

Experimental.

As a number of iodine values had to be determined in these Laboratories we. decided to test the Winkler method and to compare the results with those obtained by the Hubl and Wijs methods.

Table 1 gives the results obtained in the ordinary way in diffused daylight.

A suitable weight of the fat or oil was taken dissolved in 10 c.c. of pure carbon tetrachloride and the solution mixed with 50 c.c. of a standard bromate-bromide solution and after the addition of 10 c.c. of 10 % hydrochloric acid the mixture was well shaken, kept for a given length of time and the excess of bromine determined by adding 10 c.c. of 10 per cent. potassium iodide solution and titration with standard thiosulphate using soluble starch as indicator. The standard bromate-bromide solution was prepared by dissolving 2·784 grams of potassium bromate and 25 grams of potassium bromide in water and making up to a litre. In all earlier experiments this solution was standardised by means of thiosulphate after the addition of acid and potassium iodide, but this was found to be unnecessary as the bromate is usually quite pare.

A comparison of the results given in Table I shows that in each case examined, with the exception of acids containing an $\alpha\beta$ ethylene linking the iodine value as determined by Winkler's method in diffused daylight tends to increase with the time

during which the unsaturated substance is left in contact with the bromine solution. This is almost undoubtedly due to bromine substitution as the values obtained after 30 minutes or more are much higher than the theoretical. In this table the values obtained by using Hubl's and Wij's methods are also given for purposes of comparison. The values given indicate that the Wijs numbers are usually higher than the Hubl numbers, as already found by previous investigators.

The results obtained by Winkler's method and tabulated in Table I cannot be regarded as highly satisfactory and we carried out further experiments in order to ascertain whether more concordant results could not be obtained by working in the absence of light. Table II gives the results obtained.

THESE RESULTS INDICATE

I. That with ordinary fats and oils the, iodine value does not show the same tendency to increase with the time as was noticed when the experiments were conducted in diffused daylight. This is probably due to the fact that bromine substitution takes place much more slowly in the absence of light. It is thus essential to work in the absence of light in order to obtain reliable results with ordinary oils and fats.

II. That acids such as crotonic and cinnamic (from storax) with α p ethylene linkings give correct iodine values even after 30 minutes if light is excluded.

III. That esters of acids containing α P ethylene linkings give abnormally low values. This is somewhat remarkable as the experiments of Sudborough and Thomas (J. C. S, *Trans.*, 1910, *97*, 715 and 2450) indicate that in the dark the velocity of addition of bromine to cinnamic acid is of much the same order of magnitude as when an ester is substituted for the acid.

The values obtained with the esters of cinnamic; acid were not at all concordant but even after four hours iodine values varying between 30 and 40 were obtained. There appears to be very little difference as regards the rate of addition of bromine between the methyl and ethyl esters of cinnamic acid. On the other hand it is found that methyl crotonate combines with bromine more readily than the ethyl ester.

The cause of the variability in the results found 1ms not been discovered. We tried experiments in which a finely divided solid was added to the mixture. Substances such as Kieselgühr, finely divided silica and glass wool appear to have no

effect on the rate of absorption. On the other hand finely powdered bone charcoal produces a considerable increase in the rate of addition of bromine. For example the addition of ·024 grams of bone charcoal to nearly 0·1 gram of ethyl cinnamate raises the iodine value from mean value 18·6 to about 121 and of ethyl crotonate from 24·5 to 170·3.

As the general results of our experiments we conclude that Winkler's method is the most convenient and gives reliable results for ordinary fats and oils if the addition takes place in the absence of light.

Weiser and Donath make no reference to the influence of light and it is highly probable that they worked in the dark.

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TABLE I.

Method.	Time in minutes.	Oleic acid. 90.0	Brassidic acid. 75.1	Crotonic acid. 295.1	Methyl crotonate. 253.8	Ethyl crotonate. 222.6	Storax cinnamic acid. 171.5	Cinnamic acid. synthetic.	Methyl cinnamate. 156.6	Ethyl cinnamate. 144.2	Castor oil. 83-90	Groundnut oil. 83-100	Olive oil. 79-88
Winkler Bromate Bromide method.	10	96.7	77.0				70.17; 77.7	From 67·6 to 77.8		36.8; 40.5	77.9	83.1	83.6
	20	98.8	77.6										
	30			296.0		26.9; 38 0	179; 179			115.8; 102.0	86.3	92·6; 94.1	85.4
	40	103.4	80.3								86.8		
	60	108.0	81.4	298.0			178; 180 174; 180	175.7; 174.6		152·6 158·0		97.7	87.1
	120				131.8; 148.1	118.8; 134.9.			155.6; 158.0.	148.8; 145.7.	88.15		93.9
Hubl's method.		94.2; 94·3	71.5; 71.4								86·3; 86·1.	91·6 90.3	80.6; 80.7
Wijs' method		95.9; 95·6	73.5; 72.9								85.2; 85.1 85.3	94.5 93.9	82.8; 82.8

TABLE II.

Method.	Time in minutes.	Brassidic acid. 75.1	Cinnamic acid. synthetic. 171.5	Methyl cinnamate. 156 6	Ethyl cinnamate. 144.2	Crotonic acid. 295.1	Methyl crotonate. 253.84	Ethyl crotonate. 222.6	Castor oil. 83-90	Ground nut oil. 83-100	Olive oil. 79-88	Linseed oil.
Winkler Bromate Bromide	20	73.9										
	30		80.6 ; 78.66	13.5	From 10·9 to 31·5	295·0	49·1 ; 46·37	15·7 ; 18·1	84·2	91·6	82·0	170.5
	60	74.0	118.8; 126.0	From 9·5 to 12·6	From 9·3 to 32·2	295.0 ; 295·0.	52·5 to 71·5	25·8 ; 22·9	85·0 ; 85·0	91·8	82·6	176.6 ; 176.6.
	120	74.9		From 13·1 to 42·8.	From 13·7 to 30·2.	295·0	From 78·6 to 97·4	37·6 ; 39·3 39·2 ; 34·3	85·5	91·9 ; 92·0	82·8	180.0
	240	75.7		From 27·4 to 39·4	From 24·0 to 40·0.	295·0	123·3; 116·6	50·6 ; 55·4 55·7.	86·3	92·4	82·5 ; 82·9.	179.8
Hubl's		71.5 ; 71.4							86·3 ; 86·1	91·6 ; 90·3	80·6 ; 80·7	178·3 ; 178·7.
Wij's		73 5 ; 72.9 ;							85·2 ; 85·1 85·3	94·5 ; 93·9.	82·8 ; 82·8	