

ON THE DETERMINATION OF THE IODINE VALUE.

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(Read at the Meeting, June 7, 1899.)

It is not my intention to add a new modification to those that have been published since the appearance of Hübl's classical paper on the determination of the iodine values of fats and oils; but as the theory of Hübl's process has at last reached a satisfactory solution, chiefly through the papers published by Wijs, I thought it might be useful to summarize the present position of this question.

The papers of Wijs have been fully abstracted in this journal, and I need therefore only refer to them (ANALYST, 1898, xxiii., 238, 240). They corroborate Ephraim's experiments (ANALYST, 1895, xx., 176) that ICl is added on to the unsaturated carbon atoms. It is true that Wijs assumes that the active agent in the Hübl solution is IOH; yet, as this leads to a somewhat artificial explanation of the chemistry of the process, inasmuch as some postulates demanded thereby are not borne out by experiment, it will be sufficient for practical purposes, as leading to the same analytical result, to adopt the explanation that ICl is absorbed by each pair of doubly-linked carbon atoms. Wijs proposed at first to use a solution of ICl in 95 per cent. acetic acid, but he has more recently replaced this by a solution of ICl in glacial acetic acid, as he must have found, like myself, that the former solution does not possess the stability he claimed for it. This is proved by the following figures, obtained in my laboratory by Dr. Peck:

EFFECT OF TIME ON WIJS' IODINE SOLUTION.

Time.	Solution of $I_2 + Cl_2$ in 95 per cent. Acetic Acid.	Solution of $I_2 + Cl_2$ in 99 per cent. Acetic Acid.	Solution of $ICl_3 + I_2$ in 99 per cent. Acetic Acid.
Grammes of I, 1 c.c. of the solution is equal to:			
Original value ...	0.02682	0.02550	0.0259
After 16 hours ...	0.02642	—	—
After 40 hours ...	0.02625	—	—
After 64 hours ...	0.02581	—	—
After 2 months ...	—	0.02554	0.0258
After 3 months ...	0.01997	—	—
After 5 months ..	0.01911	—	—

The solution of ICl in glacial acetic acid is infinitely superior to the original Hübl solution as regards stability; furthermore, as it can be prepared rapidly, and as the time in testing is very much shortened, the process must be considered a very valuable one, all the more so as Wijs' maintains that his iodine values are probably the most nearly correct. As I have been using the Hübl solution for a number of years, and have determined the iodine constants for a great number of fats and oils by means of this method, it seemed to me necessary to ascertain whether all these iodine numbers could still be regarded as correct, especially so as Wijs had shown in one of his publications (*ANALYST*, 1898, xxiii, 241) that the iodine numbers obtained by his method for ten different oils were invariably higher by several units than those recorded by Hübl's process. Special stress has been laid on the fact that Wijs obtained for a sample of allyl alcohol the iodine value of 436.8 after ten minutes, whereas the Hübl solution gave him 425 after twenty hours' standing, whilst I had published a few years ago the iodine values of 349 to 376.* Since I calculated from some experiments given in Wijs' first paper the iodine value of 392, and, furthermore, since determinations made with different samples of allyl alcohol have no decisive value, I considered it necessary to examine, conjointly with Wijs, one and the same sample, although it is easy to see that allyl alcohol is not a specially suitable substance to decide the questions at issue.

Wijs was good enough to send me a sample of allyl alcohol which gave him by his method the iodine number 429. The experiments carried out in my laboratory by Dr. Peck gave the following results:

IODINE VALUES OF ALLYL ALCOHOL.			
WIJS' METHOD.		HÜBL METHOD.	
Solution $\text{ICl}_3 + \text{I}_2$.	Solution $\text{I}_2 + \text{Cl}_2$.	Solution two to three days' old.	
419.09 } 419.09 }	420.09	{ 421.27 421.27 421.87 422.17	

I add some experiments also made by Dr. Peck on pure elaidic acid, M.P., $44.5^\circ \text{C}.$:

IODINE VALUE OF ELAIDIC ACID.			
WIJS' METHOD.		HÜBL METHOD.	
Solution $\text{ICl}_3 + \text{I}_2$.	Solution $\text{I}_2 + \text{Cl}_2$.	Solution two to three days' old.	
88.66 	88.96 	88.24	
88.93 	88.89 	—	
— 	89.98† 	89.01†	
— 	89.98† 	89.01†	

These experiments, as also a further number of determinations made with cotton-seed stearin, prove conclusively that iodine determinations made with Hübl solution lead to correct results, provided that the Hübl method is applied in a proper

* This sample cannot have been pure, it must have contained some moisture.

† In these experiments the substance was made up to a known volume in the solvent, and aliquot parts of this were used in the test.

manner. This method has been described fully by me elsewhere, and I need not therefore refer to it here at any length. My conclusion that both methods yield practically identical results has since been fully corroborated by Wijs himself, who has shown the reason why different results were obtained by different observers when working with Hübl solution, although individual observers working under exactly the same conditions obtained identical results. He has also proved experimentally that the time during which the Hübl solution is allowed to act must not be chosen arbitrarily, and that it makes a considerable difference whether the blank test is done at the commencement or at the finish of the actual test; and he has further shown that the Hübl solution must have been allowed to stand one day before use, in order to attain a certain degree of stability, if I may so term it, and that this solution should not be allowed to act any longer than six or seven hours on the fat under examination. If these rules are adhered to, both solutions yield identical results.

In conclusion, I wish to tender my best thanks to Dr. E. L. Peck for his valuable assistance in the preparation of this paper.

DISCUSSION.

The CHAIRMAN (Mr. ALLEN) said that he had met with glacial acetic acid which contained a considerable proportion of sulphurous acid. It was purified almost entirely by partially freezing it, and allowing the unfrozen portion to drain off. Obviously the presence of such an impurity in the acetic acid would very greatly reduce the figure obtained in the original iodine titration.

Dr. LEWKOWITSCH said that, as has been done already by Wijs, great stress must be laid upon the importance of testing the glacial acetic acid, and ascertaining that it had no reducing effect upon permanganate.
