

# THE ANALYST.

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## PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS.

THE monthly meeting of the Society was held at the Chemical Society's Rooms, Burlington House, on Wednesday, February 6th, the President (Dr. Stevenson) occupying the chair.

The minutes of the previous meeting were read and confirmed.

Mr. D. J. O'Mahony, F.C.S., Public Analyst for the city of Cork and for the county of Cork, was proposed for election as a member of the Society.

Mr. Hehner then read the following paper :

### ON THE DETERMINATION OF THE BROMINE ABSORPTION OF FATS GRAVIMETRICALLY.

BY OTTO HEHNER.

It is not the writer's intention to add another to the already numerous modifications of processes intended for ascertaining the haloid absorption of unsaturated fatty compounds. The Hübl process, evolved from the bromine absorption process first described by Allen (*Pharmaceutical Journal*, September 25, 1880), and which is substantially the same as that used by Mills and Snodgrass (*Soc. Chem. Ind.*, 1884, No. 64), and Mills and Akitt (*Soc. Chem. Ind.*, 1884), is however, after all, merely a conventional one, and only gives concordant results when worked under exactly comparative conditions, from which, as laid down by Hübl, it is not desirable to depart. The process certainly does not measure the iodine absorption of any oil, but probably the iodochloro-absorption. From iodine solution, without the addition of mercuric chloride, as used by Gantter (*Zeitsch. f. Anal. Chem.*, 1893, p. 81), Dieterich, and others, oils take a far smaller percentage of iodine than corresponds to the Hübl number; and the proportion of mercuric chloride used has an immense influence upon the result. The present contribution is, therefore, merely intended as a study, and not as a proposed method, although I believe that in some cases it may be found both convenient, and that it may afford another factor in judging of the constitution of an oil.

The instability of the Hübl solution is a great drawback to its use. When many determinations are made this is not a matter of much moment, but when only occasional determinations are to be carried out the solution must always be freshly prepared and standardized; this gives an amount of trouble out of proportion to the result aimed at, and has the further disadvantage that freshly made solutions are apt to give capricious results.

In such cases a gravimetric method is always to be preferred to a volumetric one; the former has the additional advantage that the products of the reaction are obtained in such a form that their physical properties can be afterwards investigated, a matter, which, unfortunately, has been entirely neglected with the haloid addition products of oils, although promising valuable information.

If to an oil bromine is added, without the intervention of a solvent, combination takes place immediately; the reaction is, however, in many cases rather violent. By diluting with a suitable solvent, preferably chloroform or carbon tetrachloride, the action, though moderated, is equally complete.

A varying amount of hydrobromic acid is at the same time formed, and this is attributed by Mills to the presence of water in the materials; but is far more likely due to the formation of substitution compounds, besides the additive compounds. That this is so appears to me to be proved by some experiments which (following McIlhiney) I have made: Bromine added to chloroform containing some water produces no acid whatever, for when potassium iodide is added to such a mixture after a little time and in sufficient amount to convert the whole of the free bromine into a corresponding amount of iodine, and after the latter has been acted upon by an excess of hyposulphite solution, the resulting solution is perfectly neutral to phenolphthalein. This more or less roundabout method is necessary for testing, because iodine plus a hyposulphite yields tetrathionate and iodide without alteration of the reaction, while free bromine oxidizes the hyposulphite into sulphate, free sulphuric acid and free hydrobromic acid. The amount of free acid formed when bromine acts upon oil gives a measure for the amount of substitution. P. C. McIlhiney (*Jour. Am. Chem. Soc.*, 1894, p. 275; *ANALYST*, 1894, p. 141) has utilised in the manner previously employed and described by Allen (*Com. Org. Analysis*, ii., 383) the determination of the free acid formed as a measure of the substitution as distinguished from the addition. I have obtained the following figures: A sample of pure olive oil, treated with bromine, yielded 1.5 per cent. of free hydrobromic acid, another sample 2.7 per cent., castor oil 2.7 per cent., butter-fat 0.9 per cent., but a sample of boiled linseed oil 8.87 per cent. My figures, as far as they go, corroborate those found by McIlhiney, with the exception that he finds that no free acid is formed by the action of bromine upon boiled linseed oil. I know nothing about the origin of the sample tested by myself, and it is quite possible that it might contain either rosin or some other adulterant.

I operate as follows in order to obtain the bromo-compounds in a state fitted for weighing: A small, wide-mouthed fat flask is carefully weighed, and from 1 to 3 grammes of the fat to be tested introduced into it. These are dissolved in a few c.c. of chloroform, and then pure bromine is added, drop by drop, until the bromine is decidedly in excess. Both the chloroform and bromine must be previously tested in a blank experiment, to make sure that they contain no appreciable residue. The flask is then heated on the water-bath till most of the bromine is driven off; a little more chloroform is added, and the mixture again heated, the chloroform vapour helping to drive out the excess of bromine. The addition of chloroform may once more be repeated. The flask and its contents are then placed in an air-bath regulated for about 125° C., and kept there until their weight is constant; this takes

several hours. A little acrolein and hydrobromic acid escape during the drying, and the residue in some cases darkens slightly; in others a clear yellow heavy bromo-oil is obtained. Drying at 100° C. does not lead to satisfactory results.

The following are some of the results, as compared with the Hübl figures, upon the same samples. For comparison, by multiplying with 1·587, I calculate the gain in weight of the oil into iodine:

Substance.	Iodine by Hübl.		Iodine corresponding to Bromine gravimetrically.	
Olive oil ...	...	80·3	...	81·5
„ ...	...	80·2	...	79·9
„ ...	...	80·6	...	80·7
Lard ...	...	65·7	...	64·4
„ ...	...	„	...	64·6
„ ...	...	63·2	...	64·1
„ ...	...	60·1	...	61·4
Maize oil ...	...	122·0	...	123·2
Butter-fat ...	...	34·0	...	34·3
Mutton-fatty acids ...	...	48·1	...	47·8
Castor oil ...	...	83·0	...	69·5
Boiled linseed oil ...	...	132·5	...	159·5
Almond oil, fatty acids	...	—	...	102·3

In the case of the almond oil the Hübl figure was not determined, but calculating upon 95·5 per cent. of fatty acids in almond oil, the figure 102·3 for the fatty acids corresponds to 97·7, which is that given by the Hübl method for pure almond oil.

It will be seen that in most cases the iodine figure calculated from the gravimetric bromine absorption is in satisfactory approximation to the Hübl number, considering that that number is liable to variations of from 1 to 2 per cent., even in duplicate analyses (Amthor and Zink, *Zeitsch. Anal. Chem.*, 1892, p. 536). But in the case of castor oil the bromine process, as used by myself, gives a substantially lower result than the Hübl method; while in that of the sample of boiled linseed oil the reverse is the case. Whatever the explanation of this may be, and without desiring to generalize upon such scanty data, it is remarkable that in both those cases, where the oils contained more oxygen than ordinary oils do, the figures are substantially different. This difference may be worthy of further investigation. W. Fahrion (*Chem. Zeit.*, 1892, xvi., p. 1472) has already shown that the behaviour of castor oil towards Hübl solution is anomalous.

The numbers obtained by Mills, in concert with his two collaborators, in a few corresponding cases (*loc. cit.*), may be usefully cited here. I have calculated Mills's bromine figures into their iodine equivalents (80 Br : 127 I):

Substance.	Mills's Figure, as Iodine.		Average Hübl Number.	
Almond oil ...	...	85·3	...	96—99
Maize oil ...	...	118·1	...	119
Olive oil ...	...	95·2	...	82—85
„ ...	...	85·7	...	„
Castor oil ...	...	92·6	...	83—84
Butter-fat ...	...	44·3	...	26—38
Lard ...	...	59·2	...	50—67
Linseed oil ...	...	120·7	...	148—183
„ (boiled)	...	162·6	...	—

Thus the Mills figures in almost every case agree very indifferently with the Hübl numbers. Curiously enough, Mills found a higher bromine number for castor oil than corresponds to the Hübl number; while for boiled linseed oil he finds actually a higher absorption than that of fresh linseed oil, when the contrary might be expected.

I would point out another curious fact, namely, that while unsaturated fats take up from an iodine solution, without the intervention of mercuric chloride, some iodine, showing that some iodo-addition compound is formed, it is not possible to obtain any gravimetric iodine addition number by acting upon such oils with iodine and drying the product. The iodine gradually volatilizes from the product, the weight of which decreases till it is not more, but sometimes even less, than that of the fat originally taken. The mass at first becomes green, then darkens much, almost chars at 125° C., and its melting-point rises considerably, solid fatty acids being formed. This is well known to be the case at very high temperatures, Wilde and Reichler (*Bull. Soc. Chem.*, 1889, No. 1, p. 295) having shown that oleic acid, heated with 1 per cent. of iodine to 270—280° C., yields about 70 per cent. of stearic acid. From my experiments it is obvious that this reaction takes place at much lower temperatures than these.

#### DISCUSSION.

Mr. Allen said he thoroughly agreed with Mr. Hehner that the reaction occurring in the Hübl method of determining iodine absorptions was far from being understood. He thought the investigation of the products formed in the process would afford new and important information. Thus if, after the titration was finished, chemists would take the trouble to evaporate the chloroform and weigh the residue, the weight of the residue would show whether the product was a chloro-iodo-derivative or an iodo-derivative pure and simple; though he gathered from Mr. Hehner's paper that iodo-compounds prepared in other ways were so unstable as to decompose with facility. The plan employed by McIlhiney of ascertaining the amount of hydrobromic acid formed, and hence deducing the extent to which substitution had occurred, was a method devised by him (Mr. Allen), and found very useful in examining the action of bromine on hydrocarbon oils. He congratulated Mr. Hehner in having hit on so short and easy a method of working, and should await with interest the further development of the process. Although he (Mr. Allen) was the originator of the idea of determining bromine absorptions, or, at least, the first to use and publish a workable process, the employment of the bromine in solution in a menstruum free from water was due to Mills and Snodgrass, whose method of working possessed distinct advantages. It was a remarkable fact that in certain cases the bromine absorption could not be calculated to the corresponding iodine absorption by the factor  $\frac{1.27}{8.0}$ . In 1886, the speaker pointed out the anomaly in the case of the results recorded for almond oil in 1886 (*Journ. Soc. Chem. Ind.*, vol. v., p. 282), and believed in this case some error must have existed in Mills' determination of the bromine absorbed.\* But

\* Mills and Snodgrass found the bromine-absorption of the fatty oil expressed from bitter almonds (from which the commercial oil of almonds is chiefly obtained) to be 26.3, while the oil from sweet almonds absorbed 53.7 per cent. of bromine.—A. H. A.

another curious anomaly exists in the case of linseed oil, which when raw was found by Mills and Snodgrass to take up 76.0 per cent. of bromine (=120.7 per cent. of iodine), whereas boiled linseed oil absorbed 102.4 per cent. of bromine (=162.6 iodine absorption). It was remarkable that a somewhat similar result should have been obtained by Mr. Hehner.

Mr. Richmond said he had had some experience with the Hübl process as applied to butter, and his figures were higher than the usual average. He frequently started the experiment at night, and made the titration the next morning, following in this Archbutt's recommendation. Somewhat higher results were obtained in this way than by allowing two hours for the action of the solution on the oil, the increase sometimes amounting to 4 or 5 per cent. in oils of high iodine absorption. It was very desirable that the process should be so arranged as to avoid such discrepancies if possible. If Mr. Hehner's process gave constant results—as it seemed to promise—it would be in many ways superior to the iodine absorption process.

The President said the paper was an extremely interesting one, especially in the close agreement of the figures, and the facility with which gravimetical measurements of the bromine compounds could be made. He hoped Mr. Hehner would be able to continue his investigations, and emphasized what Mr. Allen had said with regard to the desirability of examining the residues. He thought that the Hübl process might be satisfactorily worked by substituting a compound of iodine and chlorine for mercuric chloride.

Mr. Hehner, in reply, said it was regrettable that the haloid absorption processes had been worked volumetrically in every case; it seemed desirable to him that the products of the reaction should be studied as to their physical and other characters. The nature of the reaction involved in the Hübl process was far from clear; only very few, if any, figures obtained by the action of Hübl solution on pure unsaturated fatty acids had been published—indeed, it seemed exceedingly improbable that any pure unsaturated olein acid had ever been prepared. When the formula of oleic acid was established nothing whatever was known of linoleic and linolenic acids, and the earlier investigators had, indeed, obtained their so-called oleic acid from linseed oil, which was now known to contain hardly any oleic acid at all. The explanation generally accepted as to the action of Hübl reagent was that the free iodine dislodged an equivalent amount of chlorine from the mercuric chloride, mercuric iodide and iodine chloride being formed; but if this were correct, there ought to be a separation of mercuric iodide, and this, as far as he knew, had never been observed. He thought the suggestion of the President as to dispensing with the use of mercury a valuable one, and he would try the use of a solution of iodine chloride instead of the Hübl solution. Mr. Richmond's remarks illustrated what he had said at the beginning of his paper, namely, that the tendency was for every chemist to make his own modification of the Hübl process, and as a consequence different workers often obtained widely divergent results, and this was hardly fair to the Hübl process itself.

Mr. Richmond then read the following three papers :