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 evening, June 5. In the absence of the President, Mr. Otto Hehner took the chair.

The minutes of the previous meeting were read and confirmed.

The following gentlemen were proposed for election: As members—Robert William Atkinson, B.Sc. (London), F.I.C., Consulting Analyst, 44, London Square, Cardiff; J. Walter Leather, Ph.D., F.I.C., Government Agricultural Chemist, India, Dehra Dun, N.W.P., India. As associates—Herbert Burgess, assistant to Professor Graham; and T. H. P. Heriot, assistant to Mr. R. H. Harland.

Mr. Mitchell read the following paper:

A NEW THERMAL METHOD FOR THE EXAMINATION OF OILS.

BY OTTO HEHNER, F.I.C., AND C. A. MITCHELL, B.A., A.I.C.

ONE of the earliest quantitative methods used in the examination of fats and oils is that of Maumené, in which the rise of temperature due to the interaction of oil and sulphuric acid is measured. Although practically very useful data can be obtained by the method, especially when employed in the more refined form introduced by Thomson and Ballantyne and others, yet it appears unlikely to afford any exact insight into the constitution of any particular oil, the rise of temperature being due to a great variety of causes. Thus the sulphuric acid causes hydrolysis of the glyceride, oxidation and sulphonation of the fatty acids, besides sulphonation of the glycerine, the oxidation not stopping short at any well-defined point, but often proceeding to the complete disruption of the molecule.

It is certain that the amount of heat evolved stands in some form of close relation to the degree of unsaturation of the fatty acid, for generally an oil consisting mainly of olein shows a less rise of temperature than a semi-drying oil containing linolein, and this, again, than drying oils containing a glyceride of linolenic acid. As the degree of unsaturation is now more or less accurately measurable by the iodine absorption, it follows broadly that the higher the iodine absorption the higher the Maumené figure. That this is the case when different specimens of the same oil are examined by the same observer is illustrated by the following table.

G. F. Tennille (*Jour. Amer. Chem. Soc.*, 1895, pp. 33-41; *Abts. Analyst*, 1895, p. 63) gives the Hübl and Maumené figures for nine samples of lard. When the

Maumené figure is multiplied by the factor 1.748, a number corresponding fairly closely with the Hübl figure is obtained :

Maumené Figure.				Hübl No.		Calculated I. No.	
1.	30.5	...	...	54.5	...	53.31	
2.	31.8	...	...	55.6	...	55.59	
3.	34.8	...	...	58.6	...	60.73	
4.	30.0	...	...	53.7	...	52.44	
5.	31.5	...	...	55.4	...	55.06	
6.	31.7	...	...	56.1	...	55.41	
7.	25.5	...	...	47.7	...	44.57	
8.	31.5	...	...	51.7	...	55.06	
9.	29.5	...	...	52.0	...	51.57	

Similarly from eleven olive-oil analyses published by Lengfeld and Paparelli (*Rev. Inter. des Falsifications*, v., 1892, p. 98; *Abst. Jour. Soc. Chem. Ind.*), the Maumené number multiplied by 2.1837 also gives an approximation to the iodine number :

Maumené Figure.				Hübl No.		Calculated I. No.	
1.	37	...	...	80.80	...	80.80	
2.	35	...	...	77.28	...	76.53	
3.	39.5	...	...	87.35	...	86.26	
4.	37.5	...	...	83.35	...	81.99	
5.	41	...	...	88.68	...	89.53	
6.	38	...	...	81.45	...	83.08	
7.	36	...	...	79.50	...	78.61	
8.	34.5	...	...	79.53	...	75.44	
9.	33.5	...	...	78.42	...	73.26	
10.	36.5	...	...	85.44	...	79.71	

The samples are all stated to be undoubtedly pure Californian oils.

It will be seen that while the factor for the lards is 1.748, for the olive-oils it is 2.1837. Whether this is due to difference in manipulation or strength of acid, or whether the more unsaturated olive-oil evolves proportionately less heat than the lards, it is impossible to say from these figures.

That the same factor does not hold good for different oils, although analysed by one observer, is evident from the carefully determined figures of De Negri and Fabris (*Zeit. Anal. Chem.*, 1894, 547-574); the relation between the Maumené and Hübl figures calculated from the mean data of 203 samples of olive-oil is as 1 to 2.314. Applying this factor to other oils also analysed by De Negri and Fabris, we obtain the following figures :

Maumené Figure.				Hübl No.		Calculated I. No.	
Olive-oil (203 samples)	...	35	...	81	...	81	
Earthnut	...	49	...	95 - 95.4	...	113.4	
Hazelnut	...	35- 36	...	86.2- 86.8	...	81- 83.3	
Almond	...	51- 52	...	93 - 95.4	...	118- 120	
Rape	...	92- 95	...	108 -108.8	...	213- 220	
Hempseed	...	95- 96	...	157.5	...	220- 222	
Maize	...	86	...	111.2-112.6	...	199	
Cotton seed	...	50- 53	...	106.9-110	...	115.7-122.6	
Linseed	...	122-126	...	158.7-159.78	...	282 -291.5	

It is obvious from these numbers that there is nothing like constant relation between the Hübl and Maumené numbers in the above cases.

Even when the specific temperature reaction as proposed by Thomson and Ballantyne, whereby differences in the strength of the sulphuric acid used are compensated, is taken as the basis of calculation, no one factor can be found equally applicable to various kinds of oils.

C. Fawsitt (*Journ. Soc. Chem. Ind.*, 1888, p. 552) has also attempted to utilize the heat evolved by sulphur chloride (S_2Cl_2). The reaction in this case is probably less complicated than in the case of sulphuric acid, but is still too involved to allow of definite conclusions being drawn from the thermic data. Thus, S_2Cl_2 evolves some heat with stearic acid and with glycerin, and, what is still a greater objection, the reaction is not instantaneous, but takes considerable time for its completion. With drying-oils more heat is certainly evolved than with non-drying ones, but there appears to be no definite relation.

The action of bromine upon unsaturated fatty bodies is instantaneous, and is attended with considerable evolution of heat. It is complete and quantitative, as was lately shown by one of us (*ANALYST*, xx., p. 49). It is not complicated to any extent by secondary reactions; the amount of hydrobromic acid formed measures the substitution, and is very small in most cases. The measurement of the heat evolved promised to supply much more definite data than in the case of H_2SO_4 and S_2Cl_2 .

As the action of bromine upon some of the oils is very violent, it was found necessary to moderate it by the introduction of a diluent, such as chloroform or glacial acetic acid. Owing to its higher boiling-point, the latter has the advantage of allowing of a wider range of rise in temperature, but necessitates the use of the free fatty acids, which without great precaution readily become oxidized. We have satisfied ourselves that there is no heat evolved with either of these bodies. Originally we carried out the reaction in an ordinary test-tube packed with cotton-wool into a beaker, using one gramme of the oil or fatty acid dissolved in 10 c.c. of chloroform and 1 c.c. of bromine. In our later experiments, the results of which we give below, we made use of a vacuum-jacketed test-tube such as is used by Professor Dewar in his experiments on liquid air. From such tubes there is practically no loss of heat through the glass, the only way of escape being from the surface exposed to the outer air. This is, however, a matter of no moment, as the reaction is, as before mentioned, an instantaneous one. As compared with the rise of temperature obtained by the use of an ordinary test-tube, the vacuum-jacketed tube gives results about two degrees higher under the conditions mentioned above as to quantity of substance and solvent used. We believe that the vacuum-jacketed tube might be usefully employed in other calorimetric estimations. Of course, it would be possible to calculate, by making allowance for the heat-capacity of the glass, and the specific heats of the solvent, oil, bromine, and bromination products, the exact amount of heat evolved; but for analytical purposes the observed rise of temperature is fully sufficient. The thermometer used was a standard thermometer divided into fifths of a degree centigrade. As the bromine must be exactly measured, a 1 c.c. pipette was used, connected at the upper end with a narrow tube filled with caustic lime, and having an asbestos plug at each end. The bromine, oil, and solvent were all brought to the same initial temperature.

The following are some of the figures obtained, the calculated iodine number being the rise in temperature multiplied by 5.5.

	Oil or Fat.	Rise of Temperature with Bromine.	Hübl Figure.	Calculated I. No.
1.	Lard	10.6 ...	57.15 ...	58.3
2.	"	10.4 ...	57.13 ...	57.2
3.	"	11.2 ...	63.11 ...	61.6
4.	"	11.2 ...	61.49 ...	61.6
5.	"	11.8 ...	64.69 ...	64.9
6.	"	11.8 ...	63.96 ...	64.9
7.	"	10.2 ...	57.15 ...	56.1
8.	"	10.4 ...	57.8 ...	57.2
9.	"	9.0 ...	50.38 ...	49.5
10.	"	11.0 ...	58.84 ...	60.5
11.	Lard + 10% Cotton-Oil	11.6 ...	64.13 ...	63.8
12.	Lard Fatty Acids ...	10.4 ...	59.6 ...	57.2
13.	"	11.0 ...	59.15 ...	60.5
14.	Mutton Fat (Kidney) ...	8.1 ...	44.48 ...	44.5
15.	" " (Flare) ...	7.6 ...	39.7 ...	41.8
16.	Butter	6.6 ...	37.07 ...	36.3
17.	"	7.0 ...	38.60 ...	38.5
18.	" (Fatty Acids) ...	6.2 ...	36.5 ...	34.1
19.	Almond-Oil	17.6 ...	96.64 ...	96.68
20.	Olive-Oil	15.0 ...	80.76 ...	82.5
21.	Maize-Oil	21.5 ...	122 ...	118.2
22.	Cotton-Oil	19.4 ...	107.13 ...	106.7
23.	Castor-Oil	15.0 ...	83.77 ...	82.5
24.	Linseed-Oil	30.4 ...	160.7 ...	167.2
25.	"	31.3 ...	154.9 ...	172
26.	Rape-Oil	18.4 ...	88.33 ...	101.2
27.	"	17.6 ...	77.2 ...	96.8
28.	Cod-liver-Oil	28 ...	144.03 ...	140
29.	Oil sent as Olive-Oil ...	19 ...	108.5 ...	104.5
30.	" " " ...	19.2 ...	105.7 ...	105.6
31.	" " " ...	18.9 ...	105.7 ...	103.9

It will readily be seen from an examination of the above figures that the factor 5.5 expresses the relation not only of one particular kind of fat, but applies also to most kinds of oils which we have examined, whether the iodine absorption be low or high. Thus, a butter having a Hübl number of 38.6 gives an iodine number, calculated from the temperature rise, of 38.5, whilst almond-oil, with 96.64 Hübl number, gives a calculated number of 96.8. Cotton-seed, with 107.13 Hübl number, shows 106.7 calculated, and cod liver, with 144 Hübl number, calculates to 140.

With the two samples of linseed-oil examined the approximation is not good. Now, since linolic acid appears for each molecule of added bromine to evolve as much heat as does oleic acid, as shown by the figures given by cotton-seed and almond-oil respectively, it is probable, to say the least, that the same holds good for linolenic acid. The difference observed in the case of linseed-oil might, on this assumption, be due to one or both of two causes: either the Hübl number does not fully measure, in the case of highly-drying oils, the unsaturated valency of the molecule, or the samples of linseed-oil tested had undergone more or less oxidation, the oxygen or hydrogen group being replaced by the bromine.

As to the former alternative, it is well known that with highly-drying oils, after three hours' action of the Hübl solution even in considerable excess, the maximum of absorption has by no means been reached, and the Hübl number is, therefore, almost certainly too small in these cases. As to the latter alternative, it has been shown by Ballantyne (*Journ. Soc. Chem. Ind.*, 1891, p. 32) that oils, after having undergone oxidation by exposure to air, show a higher Maumené figure than before. We are inclined to think that our calculated number expresses more accurately the real iodine-combining capacity than does the Hübl figure in these cases.

The two samples of rape-oil examined by us do not show any agreement between the observed and calculated iodine number. We believe the samples to be pure, but the Hübl numbers—viz., 88 and 77—are materially lower than the numbers usually accepted for genuine rape-oil. The calculated numbers, on the other hand, obtained by multiplying the rise in temperature by 5.5 agree very well with the normal numbers of genuine rape-oil. It appears very probable, therefore, that the samples of rape-oil examined had undergone a considerable amount of oxidation, which lowered the Hübl number, but did not affect the bromine absorption; that, in fact, the figure calculated from the heat evolution in this, as in the case of linseed-oil, is the correct iodine-absorption number.

We believe that we have established the fact that the heat of bromination, measured as described, affords at the same time the information sought by the Hübl method and that crudely given by the Maumené process. As the whole operation only occupies a minute or so, we think that the method will be found useful in analytical work.

We do not give the factor 5.5 as something absolute. It applies to the particular vacuum-tube used by us and to our precise mode of operation. Each chemist using the method should, by operating upon a sample or two of a non-drying oil with an accurately-determined Hübl number, ascertain the factor for himself.

The conclusions at which we arrive in the foregoing paper may thus be briefly summarized:

1. The Maumené figure stands in some rough relation to the Hübl number, but no definite numerical proportion exists applicable to various oils, as shown by the numbers obtained by various observers.
2. No definite relation appears to exist between the heat evolved by the action of sulphur chloride upon oils and the Hübl number.
3. The rise of temperature observed when bromine acts upon oils stands in proportion to the non-saturation. From such rise the Hübl number can be calculated with very close approach to the numbers obtained by the use of Hübl solution.
4. The accuracy is greater in the case of unoxidized edible fats and oils than in highly-drying oils.
5. The reaction is practically instantaneous.
6. The new method gives at once the Hübl number and what is intended to be given by the Maumené process.

DISCUSSION.

Mr. RICHMOND said he gathered from the authors' remarks upon the Maumené test in the earlier part of the paper that they considered it to be of much less value

than the bromine reaction. He could not agree with the authors in this; in fact, he thought that the two tests were not at all comparable quantitatively. He had been studying the Maumené test for some years, and had come to the conclusion that while a certain part of the rise in temperature might be assigned to the action of the sulphuric acid on the fat, *i.e.*, the hydrolysis of glycerides of the fatty acids, there was a further amount due to the action of the sulphuric acid on the fatty acids, and this latter differed with the various series. Experiments which he had made showed that the rise in temperature resulting from the Maumené reaction varied according to the series to which the fatty acids belonged, and he thought it might be possible to make use of this for estimating the relative proportions of fatty acids of different series present in a sample. In fact, the authors considered the bromine reaction of value, because it gave results equivalent to the iodine absorption, while they condemned the Maumené method because there was no definite relation between it and the iodine absorption. It was on this very ground that he maintained the usefulness of the Maumené reaction as an analytical method; the very fact of its having a different ratio to the iodine absorption in one oil to that in another yielded valuable information not given by the bromine test alone.

Apart from this point, on which he could not agree with the authors, their paper seemed to him of the utmost value, not only because they had devised a rapid and accurate analytical test, but because of the applications of thermo-chemistry to analysis, and their successful attempt, by determining the energy of the reaction, to show the exact nature of the change which was taking place.

Mr. HEHNER said he thought they (the authors) had made it perfectly plain that no attack whatever on the Maumené test had been intended. At the same time it could not be said that the Maumené test had ever been got to give comparable results in the hands of separate observers (although it had been used by many chemists), from causes which one could guess at, but which had never been worked out. The reaction was exceedingly complicated, and the difficulties of working the test were greatly enhanced by the occurrence of side reactions, and by the evolution of sulphur dioxide. On the other hand, the simplicity of the bromine reaction was evident, while its results were obtained in a very short time, and its applicability was increased by the fact that, like the Maumené process, instead of being a volumetric process, it was a simple thermometric method of observation. There was apparently no difference in the amount of heat evolved whether the bromine added were one, two or three molecules, and one might fairly infer from this that the Maumené reaction was also in principle a proportionate one, although Mr. Richmond differed from him in this view. He thought that the method might, in many cases, supply the place of both the Maumené and the Hübl tests, seeing that the indications given by both these tests could be obtained in about one minute with accuracy, but at the same time, as Mr. Mitchell had been careful to point out in reading the paper, it must be taken with a certain amount of caution. With regard to the drying oils in particular, there was something anomalous in the results they had obtained, which pointed to the necessity for further investigation. To edible oils the new method seemed perfectly suited.

Mr. Bevan read the following paper :