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# DETERMINATION OF THE HEAT OF BROMINATION IN OILS.[1]

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THE qualitative value of the degree of heat produced in mixing oils with sulphuric acid, is pointed out in Bulletin No. 13, Part IV, pages 475 *et seq.* In that bulletin a great number of examples are given, showing the different behavior of different fats and oils when treated according to the method first proposed by Maumené with sulphuric acid under standard conditions. It is evident that in a process of this kind the actual rise of temperature observed is dependent upon many varying conditions, such as the initial temperature, strength of sulphuric acid, relative proportions of sulphuric acid and oil employed, perfectness of insulation and other data depending on the analytical system itself. The data obtained under standard conditions, however, are extremely valuable in discriminating between fats of different characters. For instance, the rise of temperature produced by a given weight of butter fat is only about one-fourth of that produced by an equal weight of cotton oil under the same conditions. In the bulletin mentioned above, formulas are also given whereby some quantitative idea may be obtained of the relative proportions of the two constituents in a mixed oil. The fact that the natural glycerides contain unsaturated radicals capable of combining with the halogens has long been recognized, and Hübl, as is well known, has based a quantitative method of great value upon the ability of glycerides to absorb iodine. Chlorine and bromine are also absorbed with equal or greater avidity, and attempts have been made to establish quantitative methods in which these halogens take the place of iodine in the Hübl process.

Hehner and Mitchell[2] propose an innovation upon the general principles of the Hübl method in which the degree of chemical action is not measured by the residue of the halogen left unabsorbed, but by the degree of heat produced by the chemical reaction which takes place. They have not made any attempt

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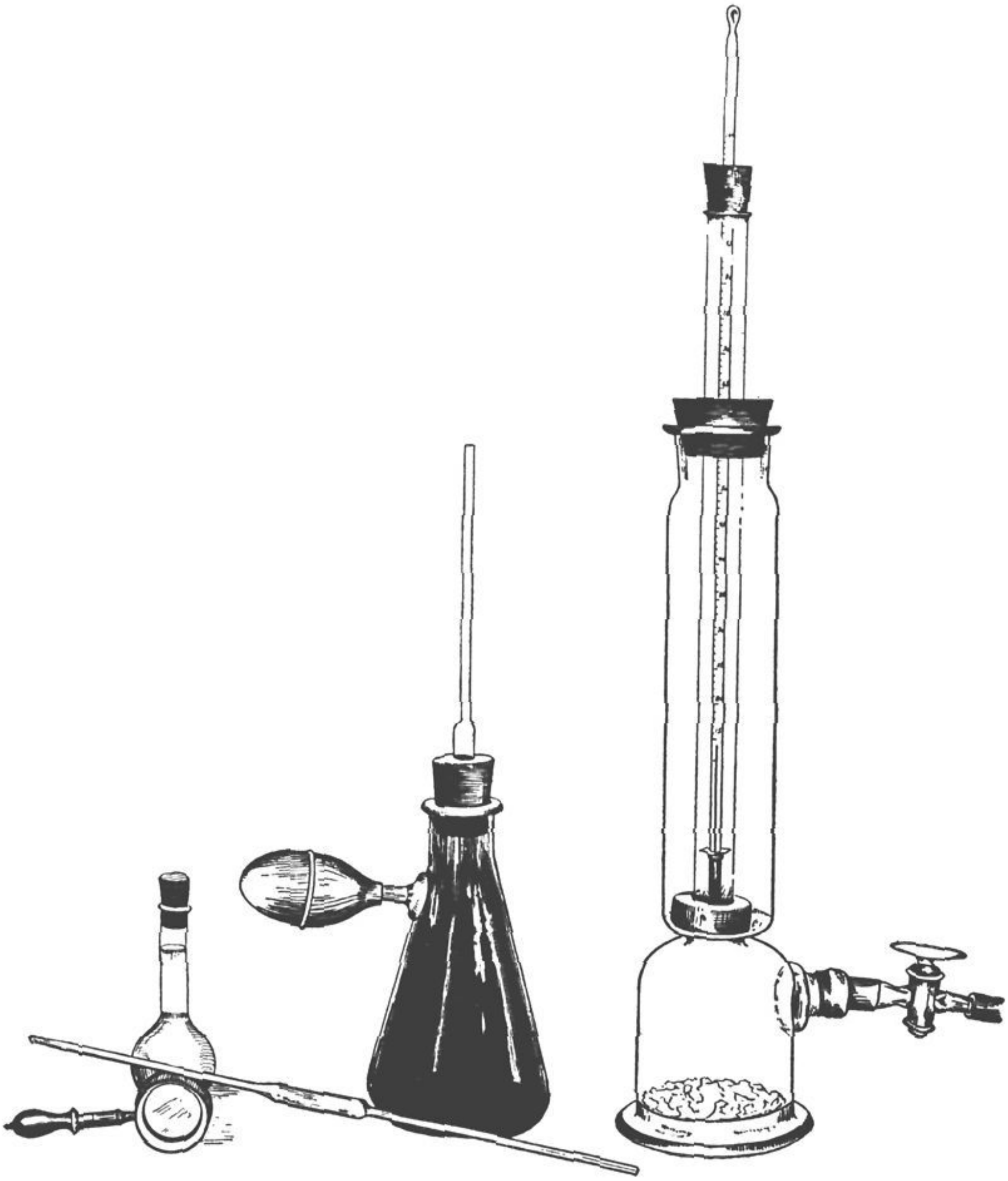
[1] Read at the Cleveland Meeting, December 31, 1895.

[2] Analyst, 20, 146.

to determine the total quantity of heat by calorimetric measurement, but simply estimate the total rise of temperature produced by the reaction. This method I have subjected to a thorough analytical test, and am convinced that it has great value in



analytical operations. On account of the difficulty of executing the method as described by the authors, I have made a number of changes therein which render it not only more accurate, but, especially, more easy of application. The difficulty of handling liquid bromine in quantities of one cc. is evident to every analyst. It is almost impossible to measure and deliver exactly this quantity of liquid bromine into the tube in which the reaction takes place. I have therefore made use of the bromine previously dissolved in chloroform or carbon tetrachloride. I find that one part by volume of bromine in four parts by volume of chloroform makes a solution which is easily kept and easily measured. To avoid any disturbing action of the bromine upon the chloroform, due to the generation of hydrobromic acid, the solution should be kept shielded from the light and only small quantities, such as may be used during the day, made up at a time. Another convenient modification has been introduced in dissolving the fats or oils in chloroform or carbon tetrachloride before beginning the analytical operations. By this means triplicate determinations, or a greater number may be made on the same sample without the trouble and annoyance of weighing each one. Ten grams of the oil or fat are dissolved in chloroform and the volume made up to fifty cc. With this volume nine determinations can easily be made, and it is recommended that at least four be made with every sample.

The apparatus employed is shown in the illustration. The tube holding the reagent and thermometer is about forty centimeters in length and one and a half in internal diameter. It is conveniently held in a drying jar, into which it fits air-tight by means of a rubber stopper. In order to secure the insulation of the inner tube, the air is withdrawn from the drying cylinder through the side tubulure. The solution of bromine and chloroform is placed in a heavy Erlenmeyer flask with a side tubulure near the top, to which is attached a rubber bulb. The flask carries a pipette held in place by a stopper, which by gentle pressure is made air-tight. The thermometer used is graduated in fifths of degrees and it is easily read to tenths by means of a small magnifying glass.

The operation should be conducted in a room which is kept at as nearly as possible constant temperature during the progress of the work.

The solutions having all been prepared, they are placed upon the table with the apparatus and the whole system is allowed to stand until a constant temperature through all parts is reached.

Five cc. of the solution of the fat or oil are placed in the inner tube by means of a pipette, with care to prevent the solution coming in contact with the walls of the tube. The thermometer having been inserted, the bromine solution is forced into the pipette by compressing the rubber bulb with the left hand until the liquid has passed the mark on the stem of the pipette. The top of the pipette is now closed by the forefinger of the right hand, the pressure on the rubber bulb released, the stopper in the Erlenmeyer flask loosened and the bromine in the pipette allowed to flow out until the mark is reached. The bromine solution is transferred to the observation tube and allowed to flow directly into the solution of the fat. It is not important, in this case, to prevent the liquid from touching the sides of the tube as it enters. As soon as the pipette is empty it is withdrawn, replaced in the Erlenmeyer flask and the thermometer at once observed by means of the magnifying glass. The bromination of the fat is practically instantaneous and the mercury in the thermometer will reach its maximum height in about a minute after the pipette delivering the bromine solution is withdrawn. The whole operation of determining the heat of bromination after all the preparations are made can be accomplished within two minutes. When the mercurial column in the thermometer begins to descend, air is admitted into the outer cylinder through the stopcock shown, the tube containing the residue of the reaction is withdrawn by loosening the rubber stopper and its contents emptied. By holding the tube with the mouth down the residual bromine vapor soon escapes and the tube may be cleaned by simply wiping it with a long test-tube cleaner, or may be used again without cleaning after allowing it to stand for half an hour mouth down. Any traces of brominated oil which remain upon the sides of the tube do not unfit it for subsequent use, unless thick enough to obscure the reading of the temperature. By allowing the air thus to re-enter the jacket space the thermometer is soon restored to the normal, and a second determination may be made within half an hour. In this way two determinations an hour can be made with the same system.

In regard to the relation which the rise of temperature, due to bromination, has to the iodine absorption number of a fat, it is stated by Hehner and Mitchell that it is represented by the factor 5.5. It is evident, however, that this factor must be determined separately for every system of apparatus and every solvent employed. Naturally it would be different from the number stated when determined in the manner indicated above. Each analytical system, therefore, must be separately standardized, and the factor thus obtained can be used with considerable certainty for calculating the number representing the iodine absorption.

It may be mentioned that it is important not to stir or churn the mixture of the oil and bromine further than is secured by the introduction of the bromine solution itself. By a vigorous churning of the mixture, throwing the warm liquid against the cold sides of the containing tube, I found it possible to reduce the rise of temperature in one instance from 19° to less than 15°. It is evident that much more accurate results could be obtained in all cases by a careful calorimetric measurement of the heat produced by the reaction. For strictly scientific purposes, this is the only rational method of procedure, but the desired end will be served equally well by carefully conducting the process in some such way as indicated above and determining for each system of apparatus employed the factor for calculating the iodine number.

Experience has shown that carbon tetrachloride, by reason of its higher boiling-point and stability, is a more convenient solvent in the preparation of the reagents than chloroform. The rise of temperature obtained, however, with solutions in carbon tetrachlorid, is slightly less than in chloroform. This is not due to a higher specific heat of the carbon tetrachloride, since at 30° the specific heats of the solvents are 0.207 and 0.233 for carbon tetrachloride and chloroform respectively. Either the action of the bromine is more vigorous in the chloroform solution or else the heat due to the bromination of the chloroform and the production of hydrobromic acid is sufficient to account for the difference. In other words, we have here to deal not only with the heat of bromination of the oil, but also with that due to the formation of $CBrCl_3$ and of hydrobromic acid. This is an additional reason for preferring carbon tetrachloride as a solvent. This action is indicated by the following data: One part of bromine and four of chloroform were placed in separate contiguous vessels, in a room subject only to slow changes of temperature, and left at rest for nineteen hours. The temperature of the two liquids at the expiration of this time was exactly 12°. On placing the thermometer in the bromine and pouring the chloroform upon it there was at first a depression of the temperature amounting to seven-tenths of a degree. In a few seconds the temperature began to rise, and at the end of three minutes it had reached 13.3°, showing a rise of over one degree above that of the original solutions.

In the following table the data representing the means of several observations in each instance are given, showing the results of the determination of the heat of bromination of four oils dissolved in the one instance in chloroform and in the other in carbon tetrachloride:

| Name of oil. | Solvents. | Initial temperature. | Final temperature. | Rise of temperature. |
|---|---|---|---|---|
| Olive oil | Chloroform | 22.7° | 42.2° | 19.5° |
| Olive oil | Carbon teteachloride | 15.1 | 33.3 | 18.2 |
| Calycanthus seed oil | Chloroform | 17.2 | 45.9 | 28.7 |
| Calycanthus seed oil | Carbon tetrachloride | 19.3 | 47.0 | 27.7 |
| Salad oil (cotton seed?) | Chloroform | 17.9 | 43.7 | 25.8 |
| Salad oil (cotton seed?) | Carbon tetrachloride | 19.8 | 44.7 | 24.9 |
| Sunflower seed oil | Chloroform | 15.0 | 43.4 | 28.4 |
| Sunflower seed oil | Carbon tetrachloride | 14.0 | 41.6 | 27.6 |

My thanks are due to Mr. E. E. Ewell for assistance in the analytical work.

## DISCUSSION.

*Dr. C. B. Dudley:* The detection of adulterations in commercial oils is a subject that has given us an immense amount of study in the laboratory at Altoona. The commercial results may be easily imagined when it is known that at one time during the past eighteen years lard oil was worth $1.10 a gallon, and cottonseed oil fifty cents a gallon, and that it was no uncommon practice to put into a gallon of lard oil as high as twenty-five per cent. of cottonseed oil. I should state that lard oil is used in making burning oil for hand lanterns and is commonly called signal oil. On this oil depends largely the safety of the running of trains. Cottonseed oil being, as you all know, a semi-drying oil, and does not burn well, hence the seriousness of adulteration may be readily understood. Signal oil mixed with cottonseed oil will go out in from six to eight hours after it is lighted, at least after the first two or three times burning of a wick. The switches must be lighted fourteen hours continuously to insure safety, and the hand lanterns for signalling must be reliable. No small amount of the work done at Altoona has been done in connection with adulterations in oils. We have kept pace with every modification that would enable us to detect adulteration, and have found Maumené's test of very great value, because of its simplicity, its rapidity of application, and the constancy of the results obtained.

There are two serious defects, however, in all the tests that I have ever seen proposed for detecting adulterations in oils. These are: First, none of the proposed methods are based on any characteristic reactions of any given oil so that although we may be able to say that a sample of oil submitted to us is not pure, we are unable to say what other oil it is adulterated with. The second defect is that owing to this lack of characteristic reactions and to the peculiarities of the proposed method, mixtures of various oils can be made, which mixtures will give the same results under the tests as a pure sample of another oil. For example, it is quite easy to make such a mixture of olive and cottonseed oils that the rise in temperature obtained by Maumené's test will be the same as is characteristic of pure lard oil. And the same may be said of the iodine test, etc. So far as our knowledge goes we still lack a means of identifying the characteristic oil that may be present as an adulterant in another, and also we still lack an absolute means of saying positively that a sample of an oil is not a pure one.