

ON HUBL'S IODINE METHOD FOR OIL ANALYSIS.

BY AUGUSTUS H. GILL AND WALTER O. ADAMS.

Received November 29, 1899.

THIS method, as is well known, depends upon the fact that the unsaturated glycerides in the oils form addition products with iodine: it has the disadvantage that substitution products—the amount varying with the time of action and strength of the solution—are formed as well. If their formation could be prevented the test would be much increased in value and it was to ascertain if this were possible that this investigation was undertaken.

As ordinarily prepared, the solution contains mercuric chloride and iodine in alcohol: by their interaction mercuric chloride and iodine chloride are formed¹ and it is supposed that the latter is the active agent.

$\text{HgCl}_2 + \text{I}_2 = \text{HgClI} + \text{ICl}$. Ephraim¹ and also Wijs² have shown that practically the usual iodine numbers are obtained when a solution of iodine chloride in alcohol is employed. Schweitzer and Lungwitz³ found that mercuric bromide caused a larger iodine number than the chloride: "that manganese bromide, cadmium, nickel and cobalt chlorides cause practically no addition⁴ and that the latter gives the highest true iodine addition figure." As with mercuric chloride, there is no reason why mercuric bromide might not similarly form iodine bromide and this be the active agent.

These metallic salts may play another part in the reaction besides the formation of iodine chloride, that of carriers of halogen, similar to that played by mercury in the Kjeldahl process when dissolving the substance in sulphuric acid. That some such agent is necessary, is shown by the results of Gantter,⁵ who found that a solution of iodine in carbon tetrachloride acts very slowly upon the oil and that the results are irregular,— a result which the authors can substantiate, both with oils and oleic acid.

The substance selected as a carrier in the following experiments

¹ *Ztschr. angew. Chem.*, 284 (1895).

² *Ber. d. chem. Ges.*, 31, 750.

³ *J. Soc. Chem. Ind.*, 14, 1031.

⁴ It would seem as if this should be "substitution."—Author.

⁵ *Ztschr. anal. Chem.*, 32, 181.

was mercuric iodide, and as it is more soluble in methyl than ethyl alcohol the former was employed: that used was free from acetone and anhydrous, being distilled from quicklime. Thirty grams of mercuric iodide and 25 grams of sublimed iodine were dissolved in a liter of methyl alcohol; of this solution 30 cc. were employed for each test and the customary procedure followed. Oleic acid and various oils were used to test the efficacy of this solution; the oleic acid was the purest obtainable, and gave no test for stearic acid.

The results are given in the accompanying table:

AMOUNT OF IODINE ABSORBED BY VARIOUS ACIDS AND OILS.

A. Acids.

Substance.	Time. Hrs.	Hübl.	Iodide.	
Stearic Acid.	4	8.99	7.25	
		8.70	6.97	
		8.82	6.93	
Average.		8.84	7.05	
Oleic Acid.	4	101.0	91.31	89.19
		100.9	89.64	89.39
		103.5	90.93	90.54
Average.		101.7	90.2	
	3	—	89.10	89.23
	20	99.38 ¹		97.88 ¹
98.41			97.50	
98.37			97.65	
	25	—		98.02
				97.70
				97.88

B. Oils.

Substance.	Time. Hrs.	Hübl.	Iodide.
Olive.	4	82	78.9 79.0 79.3
Cottonseed.	4	107	91.6 91.2 92.9
Prime lard.	4	74	72.4 71.6 71.5
Neatsfoot.	4	59	55.8 56.0 55.6

It will be noticed in the case of stearic acid, which should have no iodine absorption, that the substitution, while not

¹ As is evident, considerable substitution has taken place here: this when corrected for gave the theoretical value, 90. This is at variance with the observation of Schweitzer and Lungwitz, *loc. cit.*, 1034.

entirely avoided, is materially lessened by about 20 per cent. With oleic acid, the numbers obtained by the iodide process average but 0.2 per cent. higher than the theoretical, 90 per cent., which is the closest agreement, so far as known, obtained by any process; they are 11 points lower than those obtained by the usual Hübl process. A slight substitution did occur as shown by the hydriodic acid liberated. This was increased by lengthening the time of action of the solution, as seen from the 20- and 25-hour tests; the 3-hour test was conducted to determine if the substitution could not be eliminated by a shorter time. It was found that it did take place, indicating apparently that substitution and addition occur simultaneously: a small amount of substitution was found in the case of the oils as well as with oleic acid.

Attention was called in the early part of this paper to the fact that alcoholic solutions of iodine caused a low and variable addition of halogen to oleic acid; this is more particularly the case if carbon tetrachloride be used as a solvent; chloroform seems to increase this addition very materially. With the former, 66.74, 67.32, and 65.46 per cent. of iodine were added to oleic acid, whereas with the latter, 89.02, 83.66, and 85.86 per cent. were added.

As the solution used contained no halogen but iodine, thus excluding the formation of halides of iodine, and no water, excluding the liberation of oxygen, it would seem that we had here a method which, while as ready of application as the original Hübl, possessed the additional advantage of giving the true iodine figure.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY,
BOSTON, November, 1899.

THE IODOMETRIC DETERMINATION OF SMALL QUANTITIES OF CARBON MONOXIDE.

BY LEONARD P. KINNICUTT AND GEORGE R. SANFORD.

Received November 2, 1899.

IN a previous paper¹ one of us mentioned that there might be more danger to be apprehended from the continuous breathing of air containing very small amounts of water gas, such as

¹ *Municipal Engineer*. 17, 71.