

tained by the hydroxide-peroxide method but the manipulation is less convenient. The nitric acid method as used gave low results.

In the determination of phosphorus practically identical results were obtained whether the material was oxidized by combustion in oxygen, by heating with carbonate and nitrate, or by boiling with sulphuric acid and ammonium nitrate. For the analysis of food materials and physiological products the last-mentioned method will probably be found most convenient, especially in laboratories where the Kjeldahl method for nitrogen is largely used.

In analyzing animal and vegetable materials there is very much greater danger of loss by volatilization of sulphur than of phosphorus.

The writer desires to express his indebtedness to Prof. W. O. Atwater of Wesleyan University, who encouraged this work in many ways and in whose laboratory a large part of it was done, and to Mr. Emil Osterberg who assisted with many of the determinations.

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FURTHER NOTES ON THE BROMINE ABSORPTION OF OILS.

BY PARKER C. MCILHINEY.

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IN TWO papers published in the *Journal* of this Society,¹ the writer submitted a method of examining fats and oils in which the substance to be examined was acted upon by bromine dissolved in carbon tetrachloride. The most important advantage claimed for the method was that if the oil or fat contains substances with which bromine reacts to form substitution products, the fact will be made known by the production of a certain amount of hydrobromic acid which is determined in one part of the process. The ordinary animal and vegetable oils and fats, such as olive oil, lard, cottonseed oil, linseed oil, etc., which are practically pure glycerides, absorb almost the whole of the bromine which disappears during its action upon them by direct addition, that is to say, the bromine unites with pairs of carbon atoms which had previously been connected by double or triple bonds, and consequently but

¹ Vol. 16, 275, and 21, 1084.

little hydrobromic acid is produced by the reaction. The analytical process gives, for each test made, two figures, one showing the bromine absorbed by direct addition and the other the amount which has substituted hydrogen.

The most frequent adulterants of fatty oils are petroleum and rosin, both of which are relatively cheap. Both of these react with bromine to produce hydrobromic acid, and thereby give very distinct indications of their presence in other oils. An extended application of the process has not resulted in any modifications except in one instance, when we have to deal with a substance which is partly organic and partly inorganic. This condition occurs in boiled linseed oil and more particularly in driers. The oxides of lead and of manganese which are natural constituents of these substances, and also the lime which is sometimes present, neutralize, as might be expected, a part or the whole of the hydrobromic acid, which may be formed by the reaction of bromine with such an adulterant as rosin or petroleum. Consequently when metallic compounds are present it is not safe to assume that an oil is free from rosin simply because its bromine substitution figure is low. If there is any considerable amount of rosin the small amount of lead and manganese present in boiled oil will not obscure the indications, especially as not only is the substitution figure of rosin very high (75 or thereabouts as compared with 3 for linseed oil), but its addition figure is very low, only about 5 as against 105 for linseed oil. On account of the small proportion of driers usually added, it may easily happen, however, that a sample of boiled oil which contains a drier partly composed of rosin or of mineral oil may give bromine figures which are not at all suspicious. If the oil is adulterated with rosin or with mineral oil in larger amounts, 5 per cent. or more, such as would naturally be added if the purpose was to cheapen the product, the lowering of the addition figure will be sufficiently marked to attract attention even if mineral bases are present in sufficiently large amounts to entirely neutralize the hydrobromic acid, and the occurrence of so much mineral base is not likely.

It may be remarked that the iodine figure of rosin is about 0.8 of that of linseed oil, and that the adulteration with rosin may be quite serious without any marked lowering of the Hübl figure.

In the case of the analysis of driers used in making boiled oil, the same remarks apply, but in a much greater degree.

To sum up the matter we may say that the introduction into an oil of mineral bases, such as lime and the oxides of lead and of manganese, decreases the bromine substitution figure given by the oil, and this reduction must be taken account of in the analysis of boiled linseed oil and of driers.

It may be of interest to give some account of the effect of varying conditions upon the results obtained by the process. First with regard to the time required for the contact. A number of experiments have been made to ascertain how long a time is required for the reaction to be completed. It appears, as a result of the experiments, that as far as the reaction of bromine and the pure glycerides is concerned, the reaction goes on to completion in a very short time, probably one minute or less, even in the case of oils absorbing most halogen, such as linseed oil. This appears to be true, generally, providing the absorption is entirely by addition. If part or all of the absorption of halogen is by substitution, the amount absorbed varies, as it is natural to expect that it would, with the time of contact between halogen and the substance. Lewkowitsch¹ takes exception to the author's conclusion that on account of the great variation in the results caused by differences in the time occupied by the experiments, the iodine figure of rosin is of little value as a "constant". He calls attention to the fact that the Hübl figure varies with the time of contact in the case of other substances than rosin. In reply it may be said that in the case of unsaturated glycerides the importance of the time factor is insignificant as compared with its importance when the halogen absorption is mostly by substitution. The writer still feels that the iodine figure of rosin is hardly definite enough to entitle it to recognition as a "constant".

A number of experiments were made to compare the rapidity with which bromine in carbon tetrachloride solution acts upon such a material as common rosin, with the rapidity of the action of Hübl's solution on the same material.

The bromine absorption of a sample of W. G. rosin was determined in four experiments, in one of which the reagent was allowed to act upon the rosin for two minutes, in another for

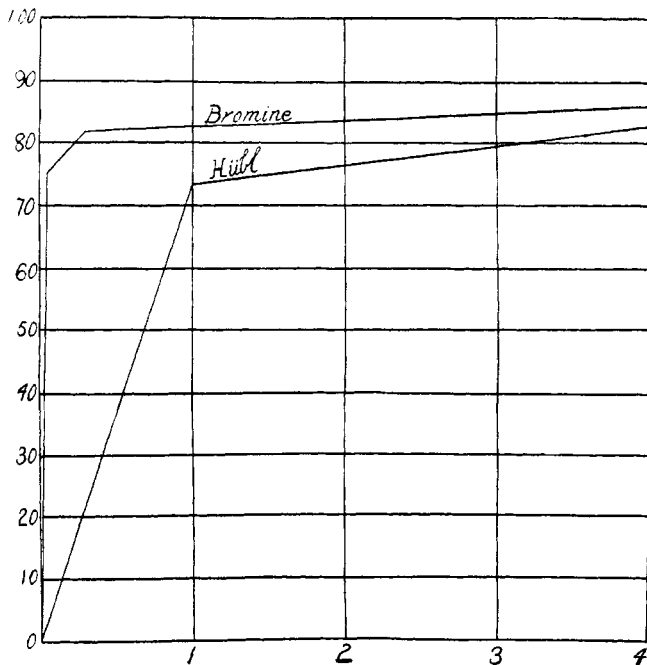
¹ "Oils, Fats, and Waxes," second edition, p. 235.

eighteen minutes, in a third for sixty-nine minutes, and in a fourth for twenty hours; the results were as follows:

Time.	Total bromine absorption. Per cent.
Two minutes.....	160.8
Eighteen minutes.....	174.5
Sixty-nine minutes.....	178.0
Twenty hours.....	213.4

Similar experiments with Hübl's solution of iodine were previously reported by the author.¹ The same sample of rosin was used in both sets of experiments. The results obtained were as follows:

Time.	Total iodine absorption. Per cent.
One hour.....	126.7
Two hours.....	133.1
Four hours.....	142.0
Eight hours.....	144.8
Eighteen hours.....	160.3
Fifty-two hours.....	172.6



COMPARISON OF RAPIDITY OF ACTION OF BROMINE AND OF HÜBL'S SOLUTION UPON ROSIN.

The two sets of experiments are compared graphically in the

¹ This Journal, 16, 56.

figure. The highest absorption found in each case is taken as 100, the lower absorptions being reduced to the same basis and represented in the figure as ordinates. The abscissas represent time in hours. It will readily be seen from the figure that the absorption of bromine is much more nearly complete at the end of a short experiment than that of iodine in the determination of the Hübl figure, and consequently that the bromine absorption of such a material as rosin is a much more definite figure and less affected by the length of the experiment than the Hübl figure is for the same substance, though by no means a "constant."

Rosin may be taken as one of the best examples of the absorption of halogen purely by substitution, the addition figure being very low indeed, though the total absorption is high.

A series of five experiments, made to determine the effect of varying excess of bromine, gave the following results; a sample of pure linseed oil was used for the experiments:

Percentage of excess of bromine.	Total bromine absorption. Per cent.
16.5	92.4
36.4	95.5
42.1	98.3
81.2	101.0
104.3	103.5

It will be seen that an excess of bromine amounting to 100 per cent. or more of that absorbed by the oil is necessary in order that the reaction may speedily go on to completion.

Another series of experiments was made to determine the effects of varying temperature and of the presence or absence of moisture in the oil. The bromine figure of a sample of linseed oil was determined in four ways:

First, in the ordinary way at the room temperature 20° C.

Second, with 10 cc. of water added to each test at the room temperature.

Third, with 10 cc. of water added to each test and the bottles kept immersed in melting ice.

Fourth, with 10 cc. of water added to each test and the bottles heated to 30° C.

The experiments were all carried on at the same time. The shortest test was eighty-eight minutes and the longest one hundred and eighty minutes.

The results obtained were as follows:

	Total bromine absorption.	Bromine addition.	Bromine substitution.
Dry, ordinary condition.....	110.2	104.8	2.7
10 cc. water, ordinary temperature..	108.6	104.0	2.3
10 cc. water, cooled.....	109.8	104.0	2.9
10 cc. water, heated.....	113.2	103.0	5.0

It is noteworthy that the results appear to be but slightly affected by the variations introduced and particularly that the presence of water seems to be without serious effect.

FIXATION OF PHOSPHORIC ACID IN THE SOIL.

By J. T. CRAWLEY.

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It has been known for a long time that when soluble phosphates are applied to the soil, they become fixed by the bases, lime, iron, etc., and are not leached from the soil to any very considerable extent by rain or irrigation waters. By this process water-soluble phosphoric acid is "reverted" or changed to a combination not soluble in water. This is akin to the fixation of potash and ammonia, which are changed into insoluble combinations in the soil.

This is a wise provision of nature and prevents salts and bases in the soil which have been rendered soluble by weathering and other agencies from being washed out and lost from the soil; and it enables the agriculturalist to apply certain forms of soluble fertilizers to growing crops without fear of losing them in the drainage waters. But what becomes of the water-soluble phosphoric acid applied as a fertilizer; is it fixed near the surface, or is it well distributed throughout the soil where the roots of plants can get it?

The following investigation was undertaken for the purpose of determining to what extent water-soluble phosphoric acid is distributed through the soil before it becomes fixed. In certain sections of these islands the cane grows by irrigation; in other sections the rainfall is ample. Where irrigation is practiced the soluble fertilizer is scattered along the cane row, in some cases covered, in other cases not, and followed up within a day or two by irrigation. Three or four inches of water would represent an