	Palm kernel oil.	Cocoa-nut oil.	Cocoa-nut oil, butter and other fats.
Soda solution used	25.0 c.c.	30	25
Sulphuric acid solution used in titrating back	0.6 c.c.	0.3	13.3
Soda solution used in neutralising volatile acids	15.4 c.c.	20.7	11.7
Equivalent found in blank analyses (to be deducted, ...)	0.6 c.c.	0.4	0.3
Equivalent of volatile acids ...	14.8 c.c.	20.3	11.4
Silver nitrate solution	24 c.c.	24	16
N/10 sodium chloride solution added to 175 c.c. of filtrate ...	21 c.c.	21	14
Excess of sodium chloride found in solution	10.4 c.c.	14.1	0.6
The silver salt precipitated	11.9 c.c.	16.1	7.5
Equivalent of volatile acids ..	14.8 c.c.	20.3	11.4
„ insoluble salts	11.9 c.c.	16.1	7.5
„ soluble salts	2.9 c.c.	4.2	3.9

Butter fat figure, obtained by deducting one-quarter of the cocoa fat figure from the soluble equivalent.
 $3.9 - (\frac{1}{4} \times 7.2) = 2.1$.

Cocoa fat figure, obtained by deducting one-seventh of butter fat figure from the insoluble equivalent.
 $7.5 - (\frac{1}{7} \times 2.1) = 7.2$.

Analyses of margarine. (Composition unknown.)

Insol.	Sol.	Cocoa fat figure.	Butter fat figure.	Cocoa fat.	Butter fat.
7.5	3.9	7.2	2.1	c: 40%	c: 7.5%
8.4	2.2	8.4	—	c: 50%	—
16.9	3.9	16.9	—	c: 100%	—
12.6	3.0	12.6	—	c: 80%	—
4.2	3.2	3.9	2.2	c: 25%	c: 8%

Analyses of fat and fat mixtures. (Composition known.)

Insol.	Sol.	Cocoa fat figure.	Butter fat figure.	Cocoa fat.	Butter fat.
4.2	26.1	—	20.1	—	c: 100%
15.3	3.6	15.3	—	c: 100%	—
14.8	5.8	14.4	2.2	c: 90%	c: 8%
13.7	6.7	13.1	3.4	c: 80%	c: 13%

The result obtained varies from the actual composition within 2 per cent.

Analyses of margarine. (Composition unknown.)

Insol.	Sol.	Cocoa fat figure.	Butter fat figure.	Cocoa fat.	Butter fat.
8.9	2.3	8.9	—	c: 55%	—
11.2	2.8	11.2	—	c: 70%	—
4.7	1.6	4.7	—	c: 30%	—
14.4	3.6	14.4	—	c: 90%	—
9.6	2.3	9.6	—	c: 60%	—
4.2	3.3	3.9	2.3	c: 25%	c: 8%
4.8	1.4	4.8	—	c: 30%	—
10.1	2.0	10.1	—	c: 65%	—
8.6	4.4	8.2	2.3	c: 50%	c: 8%
13.7	3.7	13.7	—	c: 85%	—
6.0	4.6	6.6	2.9	c: 40%	c: 10%
0.4	0.5	—	—	—	—

DISCUSSION.

THE CHAIRMAN said the apparatus and method of analysis were certainly very elegant, and the underlying principle was sound. There would be in the first instance the usual objection to any new apparatus which was especially difficult to overcome in a case like butter, where millions of analyses had been made by the established Reichert process. The method of clearing the

filtrate by adding sodium nitrate was a great advantage; but how the result would compare with the so-called adopted figures and the limits within which they varied, could not be solved by one operator alone. Every butter analyst ought to try and compare this method with the results of the standard method. The apparent advantage was that in the case of cocoanut oil and palm kernel oil, the volatile soluble and volatile insoluble acids seemed to stand in the definite proportions of 4 to 16, and 3 to 12. That might be so for silver salts; but by using this method they lost at once the very distinct difference between the cocoanut oil and the palm kernel oil, namely, the difference in the Reichert-Meißl values and in the titration numbers of the insoluble volatile acids. As Mr. Blichfeldt pointed out, his method did not attempt to differentiate between palm kernel oil and cocoanut oil; but this was becoming every day more and more important.

Mr. E. GRANT HOOPER agreed with the Chairman that the silver salts really promised to be useful in the way of effecting a separation of the soluble fatty acids. He asked if the author having effected such a separation had decomposed the silver salts and determined the refractions of the two classes of acids.

Mr. E. R. BORROR said that if figures were obtained for butters giving abnormally high and low values respectively, then the probable delicacy of the process would be a mere matter of calculation. Had the author made experiments with cocoanut "stearine" or palm kernel "stearine"? These would contain less soluble and insoluble volatile acids, and probably also in different ratios, which might considerably alter the figures. As these products were largely on the market they should not be lost sight of. The chief use of this method seemed to be to find if margarine contained more than the legal limit of 10 per cent. of butter fat.

Mr. BLICHFELDT, in reply, said they had not yet tried to determine refraction of the different acids, but they intended to do so; and that was certainly the next question to be settled. Of course the soluble silver salts from butter fat varied in the same way as the Reichert-Meißl and Polenske values. His calculation was based entirely on the ratio, and it seemed to be more constant. If a butter had a low Reichert-Meißl figure, say, down to 25, the insoluble would come down as well in many cases. If in cocoa fat the ratio of 1 to 4 was altered to 1 to 5, which they had never found, the figure would come down to 1.8, instead of 2.1. He believed cocoanut stearine was not much used in England, and he had had no opportunity of analysing it. It would raise the melting point in the margarine; but the manufacturer seemed to have other ways of doing that, which were less expensive, so that it was not generally used.

Nottingham Section.

Meeting held at Nottingham, on Wednesday, May 18th, 1910.

MR. S. J. PENTECOST IN THE CHAIR.

THE DETERMINATION OF PHOSPHORIC ACID BY MEANS OF STANDARD SILVER NITRATE.

BY JOHN M. WILKIE, B.SC., A.I.C.

Considering the facility with which phosphoric acid can be determined by means of a standard silver solution, it is somewhat remarkable that the method has not received more attention. Perrot (this J., 1888, 311) precipitated silver phosphate in presence of acetic acid and determined the residual silver after filtration with standard sodium chloride. Clark (this J., 1888, 311) investigated Perrot's method with the idea of making it available for the analysis of commercial phosphates. After adding excess of silver he nearly neutralised the acid solution, leaving it but faintly acid to litmus. The precipitated silver phosphate

was then filtered, washed with hot water, dissolved in hot dilute nitric acid, and the silver determined by Volhard's method. Holleman (this J., 1894, 763, 843) converted phosphoric acid or an alkali phosphate to the dialkali salt by means of caustic soda, and precipitated the silver phosphate in presence of sodium acetate. The residual silver was then determined by Volhard's method in an aliquot part of the filtrate. In my previous paper (this J., 1909, 68) I stated that the results obtained by me when using Holleman's method were in all cases slightly high. Since that time Liebermann (Analyst, 1909, 361) has somewhat modified the Holleman method; he adds a considerable amount of nitric acid to the phosphoric acid solution, adds excess of normal silver nitrate and then ammonia until litmus paper shows an amphoteric reaction, and finally determines residual silver after filtration by Volhard's method. Of course it is obvious that any successful method must be founded on Holleman's lines, as filtration and washing are to be deprecated for several reasons. It might be here mentioned that Baxter & Jones (Chem. News, 1910, 1,161), in connection with a determination of the atomic weight of phosphorus, have recently investigated the constancy of composition of the precipitate obtained when disodium phosphate and silver nitrate interact. They find the silver phosphate thus obtained is of constant composition, a rather important point in connection with the use of silver nitrate for the determination of phosphoric acid.

Some preliminary work was done to decide under what conditions the determination should be carried out. If the method was to be available for the analysis of commercial phosphates considerable amounts of free nitric acid must of necessity be present, and so the particular alkali and indicator to be used are important points. Liebermann uses litmus as indicator but, while Holleman neutralises with soda, Liebermann employs ammonia. As indicator, phenolphthalein has considerable advantages over litmus; it can be used in the solution, and the end point from colourless to pink is sharp and easy of recognition (compare this J., 1909, 464). Ammonia, while it cannot be used with phenolphthalein, has advantages over soda in that it does not precipitate silver oxide, and a few experiments were made with *N*/10 ammonia, using methyl red as indicator. Non-constant results were obtained, and the dye was precipitated by the silver phosphate, which is not the case with phenolphthalein; even when more dye was added after practically all the silver had been precipitated the end point was difficult to observe. In some of the experiments the neutral solution was filtered directly for the determination of the residual silver; in others varying amounts of acid were added. As the end point was so obscure and the results were not commensurable with the trouble involved, the use of ammonia was not further persisted in. It is here worthy of mention that silver phosphate is very readily soluble in dilute ammonia, thus constituting a grave source of danger.

Holleman's method was then investigated, and with the conditions of working adopted in my previous paper, the high results then obtained were confirmed. Experiments were then undertaken, in which the excess of silver used, the mode of addition of the silver, and the time of standing and the amount of shaking previous to filtration, were all independently varied. In the course of this work, in which a great number of determinations were made, it appeared on many occasions that the problem had been solved. But on further investigation the results obtained were shown to be fortuitous. Ultimately it was found that though silver phosphate was appreciably soluble under the conditions of working adopted, the effect was masked by the compensation due to co-precipitated silver acetate. If the acetate was increased, increasingly high results were obtained. To get over this trouble the silver was added in two moieties, enough was added in the first instance to nearly precipitate all the phosphoric acid, and after vigorous shaking the remainder of the silver was then added. But no better results were obtained in this way. In all these cases, after neutralisation to phenolphthalein had been effected, decinormal sulphuric or nitric acid was added in amount required to give the di- or mono-alkali salt or some intermediate

acidity. Finally, from a consideration of the theoretical aspect of the case, a very small amount of sodium acetate was used, the phosphoric acid solution was just neutralised to phenolphthalein and an amount of decinormal sulphuric or nitric acid was added which bore a simple relation to the amount of acetate added. The sodium acetate has a great value in that it weakens the stronger acid so much that the great bulk of the silver phosphate is precipitated long before the solution is neutral to phenolphthalein, and consequently the end point is much more distinct and more freedom is given as to the particular excess of silver added. In the method as finally worked out this action of the acetate, owing to diminished concentration, is very much weakened, and consequently some other mode of neutralisation was demanded when large quantities of nitric acid were present. Phenolphthalein was added to the phosphoric acid solution, and then strong caustic soda solution cautiously until just pink. The pink tint was then discharged with dilute nitric acid added drop by drop. In the case of solutions containing calcium no special indicator is required, for the precipitated calcium phosphate serves the purpose admirably. In this case the nitric acid was added until the precipitate just dissolved.

Excess of silver nitrate is added to the solution thus prepared, then 10 c.c. of approximately decinormal sodium acetate, and then highly dilute caustic soda (approximately decinormal prepared extemporaneously by diluting the strong solution already referred to) is added with shaking until the solution was just pink, phenolphthalein being the indicator, the final adjustment being made with *N*/10 sodium hydroxide or sulphuric acid. To the solution thus prepared is added 2 c.c. *N*/10 sulphuric acid, and the whole adjusted to volume (150 c.c.) and thoroughly mixed. After filtering the residual silver is determined in an aliquot part (100 c.c.) of the filtrate by Volhard's method.

The results obtained in presence or absence of nitrates (initially added as nitric acid) calcium salts, sulphuric acid, etc., were excellent. The method is rapid and accurate and admirably adapted for the determination of phosphoric acid, alkali or calcium phosphate, but is not available in the presence of appreciable amounts of aluminium or iron. Chloride, if present, must be allowed for. As it is necessary to filter the precipitated silver chloride and determine residual silver in an aliquot part of the filtrate, it is much simpler and just as accurate to add excess of sulphuric acid to the phosphate solution and evaporate on the water bath. After adding nitric acid the determination is made as above. It might be here mentioned that my method of titration of the acetic acid liberated, when phosphoric acid or a soluble phosphate is treated with silver nitrate and sodium acetate, is not affected by co-precipitation of silver acetate.

Some determinations by the modified silver method. (I regard as decinormal a phosphoric acid solution containing 1/30 grm. molecule per litre.)

c.c. <i>N</i> /10 H ₃ PO ₄ taken.	c.c. <i>N</i> /10 Ca present.	c.c. <i>N</i> /10 NaCl present.	c.c. <i>N</i> /1 HNO ₃ present.	c.c. <i>N</i> /10 AgNO ₃ added.	c.c. <i>N</i> /10 H ₃ PO ₄ found.
35.11	—	—	15	39.00	35.09 (1)
35.11	30.0	—	30	42.00	35.13 (2)
23.41	0	—	15	26.00	23.46 (3)
23.41	10.0	—	15	26.00	23.42 (4)
23.41	10.0	5.0	15	26.00	23.43 (5)
23.41	0	—	15	28.00	23.43 (6)
23.41	25.0	—	10	26.00	23.39 (7)
11.71	0	—	0	13.00	11.69 (8)
11.71	15	—	10	15.00	11.73 (9)

In exp. (5) HCl was expelled by evaporation with sulphuric acid.

The high result in exp. (3) was obtained when the method had first reached its final form and is given to show the kind of result likely to be obtained by a worker not accustomed to the method.

The only difficulty of the method is due to precipitated silver oxide giving high results and obscuring the end point. If the soda used in the final neutralisation is about decinormal no difficulty is experienced, more especially

If the precipitate be given a few seconds to settle, so that the colour of the supernatant liquid may be observed. If preferred, much stronger soda may be used, provided the precaution is taken to add it drop by drop with constant shaking, but the use of weak soda is recommended. Within limits the determination appears to be independent of the excess of silver used—a minimum excess of 10 per cent. is advisable—with a large excess of silver the difficulty due to precipitation of silver oxide is of course accentuated.

In conclusion, I have to express my indebtedness to Messrs. Boots, Ltd., for the use of their laboratory in which the work was carried out.

NEW METHODS FOR THE ANALYSIS OF COMMERCIAL PHOSPHATES.

BY JOHN M. WILKIE, D.Sc., A.I.C.

For a short account of some of the methods for the determination of phosphoric acid I must refer to my previous communication (this J., 1909, 68). As there mentioned, innumerable modifications of the two chief methods for the determination of phosphoric acid (the ammonium magnesium phosphate and the ammonium molybdate methods) have been suggested from time to time. Quite recently the determination of the ammonium content of these two compounds has again been suggested as a convenient procedure, the ammonia being determined by interaction with a standard hypobromite solution; Brandis (this J., 1910, 455), working on ammonium magnesium phosphate and Artmann (this J., 1910, 455), on ammonium phospho molybdate. In both cases washing of the precipitated phosphoric acid compound is involved. A curious modification of the ammonium molybdate method due to Grete (this J., 1888, 771, and 1909, 1105), in which glue is used, may also be mentioned. Liebermann (Analyst, 1909, 360), has modified Holleman's method by substituting ammonia for soda and employs the method for the determination of phosphoric acid in urine after preliminary precipitation as ammonium magnesium phosphate. The method worked out by me in the paper already referred to depended upon titration of the acetic acid liberated when phosphoric acid or a soluble phosphate was treated with silver nitrate in the presence of sodium acetate. The method of course is strictly an acidimetric one, and though admirably adapted for the determination of phosphates of known constitution, was unsuited for the analysis of commercial phosphates because of two factors—uncertainty as to the constitution of the particular phosphate and as to the presence or absence of other acids. For the present assuming that phosphoric acid and its calcium salts alone are present, dissection is possible if (1) the whole of the undisplaced hydrogen can be determined, (2) the total phosphoric acid can be determined. Consider the simple case of the calcium salt, CaHPO_4 , we have for the non-displaced hydrogen

That is, speaking in terms of c.c. of decinormal solutions of baryta and silver nitrate, the non-displaced hydrogen will be one third of the total phosphoric acid present, and the calcium will be given by difference. In the case of the precipitated calcium phosphate of commerce somewhat more calcium is always present than corresponds to the formula, CaHPO_4 , but this in no wise interferes with the method just outlined, for, still speaking in terms of c.c. $N/10$, the baryta titration will correspond truly to the undisplaced hydrogen and the difference in the baryta and silver titrations will correspond to the total calcium present.

In the case of superphosphates it is generally sufficient, when the method is applicable, to determine the phosphoric acid by the silver method, since the constitution of the salt is not desired. With the phosphates used in this country this is a very convenient and accurate process, but in the presence of considerable quantities of iron and aluminium the silver method is not available. The methods of analysis here available are somewhat different

from those previously mentioned. Littmann (Chem. News, 1900, 80, 178) neutralised to methyl orange, added sodium citrate and then neutralised to phenolphthalein. Emmerling's well-known method consists in neutralising to methyl orange to give the free phosphoric and sulphuric acids and in titrating the free acid and monocalcium salt by running the superphosphate solution, previously mixed with excess of calcium chloride, into standard soda, using phenolphthalein as indicator. Emmerling (this J., 1888, 343) has also suggested another form of the second titration in which the soda is run into the mixed superphosphate and calcium chloride solutions. This second method of Emmerling's is of more than usual interest, as both Kohn (Analyst, 1908, 376) and Cooksey (Proc. Roy. Soc. of N.S.W., 41, 163) have apparently independently rediscovered the method (cf. Doherty, Analyst, 1908, 273). Emmerling's process is simple and rapid and available in the presence of aluminium and iron.

In the method of this type which I have worked out, I replace the second titration of Emmerling with a determination of the total undisplaced hydrogen in the manner already referred to. Considering a plain aqueous solution of phosphoric acid, we have for the methyl orange titration, $\text{H}_3\text{PO}_4 + \text{NaOH} = \text{NaH}_2\text{PO}_4 + \text{H}_2\text{O}$ (1) and for the undisplaced hydrogen determination,

Of course this method, suitably applied, is available not only for superphosphates, but also for all phosphates. Titration (1) is to be regarded as positive when the original substance is acid—when standard alkali must be added to produce neutrality to methyl orange—and negative when the original substance is alkaline and standard acid must be added to produce neutrality to that indicator. Titration (2) is always positive, but in the case of tribasic calcium phosphate is, of course, zero. Perhaps this becomes more clear if one considers the case of that salt ($\text{Ca}_3\text{P}_2\text{O}_8$) in somewhat greater detail. Under suitable conditions four equivalents of nitric or other acid are required to produce neutrality to methyl orange

Also there is no undisplaced hydrogen in tribasic calcium phosphate that is titration (2) is zero.

As to the conditions under which this second method is available we have to consider two cases, soluble and insoluble phosphates. In the first case taking 26 per cent. superphosphate as a type, 9.309 grms. is shaken with 400 c.c. of water and the total volume made up to 500 c.c. in the usual way. Twenty-five c.c. of the filtrate is transferred to a porcelain dish and titrated in presence of methyl orange until all trace of pink has gone. Let us suppose m c.c. of $N/10$ sodium hydroxide are required. Another 25 c.c. of the filtrate is then transferred to a Jena flask along with 15 c.c. $N/10$ sulphuric acid and boiled a few minutes; after cooling in running water, 30 c.c. of approximately $N/10$ silver nitrate, 30 c.c. of $N/5$ sodium acetate, and a few drops of phenolphthalein are added, and then baryta is run in until a permanent pink tint is produced (cf. this J., 1909, 68). After allowing for the added sulphuric acid, whose function is to prevent precipitation of calcium salts during the boiling to expel carbon dioxide, suppose p c.c. of $N/10$ baryta solution were required. We then have per cent. $\text{Ca}_3\text{P}_2\text{O}_8 = (p-m) 10/6$. In an actual determination on 26 per cent. superphosphate, $p=18.93$; $m=2.5$ giving per cent. = 27.38 (as $\text{Ca}_3\text{P}_2\text{O}_8$).

For the total phosphate content, 9.309 grms. is dissolved by the aid of nitric acid so as to give a total volume of 500 c.c. Portions of 25 c.c. of the filtered solution are treated precisely as above except that a little more silver nitrate is added. The percentage of tri-calcic phosphate is obtained in the same manner.

Of the insoluble phosphates steamed bone meal may be taken as a type. 6.206 grms. is ignited, dissolved by the aid of nitric acid, and after addition of