

The variation is very slight, as the plot is drawn on a scale by which one division represents about 0.06 per cent. of the values obtained. The two equations obtained are more nearly concordant when we take into consideration that the average of the specific gravities of the samples is about 1.0360. This would raise the calculated value 0.000003 on the scale, or a little more than one half of a division. We, therefore, have adopted as the most probable values what happens to be the mean. Our conclusion, then, is that within the concentrations expressed by the specific gravity factors, 1.035 and 1.045, we can calculate the absolute specific gravity influence of any acid hydrolyzed starch solution by the equation, $\Sigma = 0.004023 - 0.000001329(195 - [\alpha]_D)$, when the specific rotatory power (obtained by the factor 0.00386) is known. These values within the limits of concentration given are correct to less than two-tenths per cent. of their values. For commercial glucoses, the factor 0.00393, taken as a constant, is sufficiently exact for most determinations.

While this equation will now enable us to determine the exact amount of carbohydrate in solution when the specific gravity has been previously corrected for the influence of other dissolved material, the simpler computation based on the factor 0.00386 will doubtless continue in use as more convenient for those calculations where proportion of carbohydrates is alone desired.

We have also under investigation the action of heat on commercial glucoses when samples are boiled down to candies, as well as the study of certain disturbing influences on the determination of cupric reducing powers of glucoses. The results are not yet complete enough for publication.

A FURTHER COMMUNICATION ON THE ESTIMATION OF PHOSPHORIC ACID BY TITRATION OF THE AMMONIUM PHOSPHOMOLYBDATE PRECIPITATE WITH STANDARD ALKALI.

BY B. W. KILGORE.

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DURING the past four years the writer has done a great deal of work on this method,¹ and the results obtained in this laboratory for the past two years, at least, by five analysts,

¹ Bul. 43 and 47, pp. 68-104 and 62-83, Chem. Div., U. S. Department of Agriculture; Bul. 119, North Carolina Experiment Station; and this Journal, 16 and 17, Nos. 11 and 12.

warrant us in considering it thoroughly accurate and reliable. More recently the method has been extensively and successfully employed in experiment station and other laboratories. Some chemists, however, have not been able to get uniformly good results with it. These appear to be mostly those who have worked the method but little, while the difficulty with others seems to be due to a misunderstanding as to how the method should be carried out.

At the last meeting of the Association of Official Agricultural Chemists, two main objections were brought against its adoption as an official method at that time. One was that it had not been tried upon a sufficient variety of fertilizers and fertilizer materials used in the trade to show that it would give as good results on all of them as it had upon those it had been worked upon, when in the hands of those who had worked the method to any extent.

The other objection was that brought out in the paper¹ of Mr. T. S. Gladding. Mr. Gladding had made twenty-two comparative tests of the volumetric method with the official gravimetric method and his gravimetric method on a microcosmic salt and various fertilizers with closely agreeing results in all cases. He then turned over a set of precipitates to an assistant to filter and wash free of acids, according to the method. It was found that the precipitates could not be freed from acid; and upon closer examination it was observed that the water was dissolving the precipitate.

The experiments, the results of which follow in the table, were planned to throw light upon, and if possible to settle, these two questions.

¹ Bul. 49, Chem. Div., U. S. Department of Agriculture, p. 75.

COMPARATIVE PHOSPHORIC ACID RESULTS ON VARIOUS FERTILIZER MATERIALS BY GRAVIMETRIC AND VOLUMETRIC METHODS.

Materials.	Gravimetric	Volumetric	Washed with	Washed with	Washed with	Amount of so- lution corre- sponding to P ₂ O ₅ substance used in volu- metric method.
	Per cent.	Per cent.	Cc.	three per cent. ammonium ni- trate solution.	three per cent. potassium ni- trate solution.	
1. Cottonseed meal....	2.97	2.97	200	0.2
	...	2.93	500	0.2
	2.96	2.91	500	0.2
2. Tankage	11.62	11.68	200	0.2
	11.67	11.58	500	0.2
	11.60	..	200	...	0.2
	11.45	...	500	...	0.2
3. North Carolina phos- phate	18.27	18.20	200	0.2
	18.27	18.20	500	0.2
	18.18	...	200	...	0.2
	17.88	...	500	...	0.2
4. South Carolina phos- phate	27.98	28.06	200	0.2
	27.98	28.09	500	0.2
	28.04	...	200	...	0.2
	27.74	...	500	...	0.2
5. Pennsylvania phos- phate	18.59	18.59	200	0.2
	18.58	18.56	500	0.2
	18.56	...	200	...	0.2
	18.34	...	500	...	0.2
6. Thomas slag (Amer- ican).....	a16.38	16.05	200	0.2
	a16.43	16.00	500	0.2
	b16.14	15.98	...	200	...	0.2
	c16.04	15.75	...	500	...	0.2
7. Thomas slag (Euro- pean).....	a18.15	17.98	200	0.2
	a18.08	17.97	500	0.2
	c17.90	17.88	...	200	...	0.2
	17.73	...	500	...	0.2
8. Bone meal.....	22.14	22.10	200	0.2
	22.02	22.08	500	0.2
	22.00	...	200	...	0.2
9. Acid phosphate	21.95	...	500	...	0.2
	17.44	17.56	200	0.2
	17.51	500	0.2
	17.51	...	200	...	0.2
....	17.30	...	500	...	0.2	

Materials.	Gravimetric method.	Volumetric method.	Washed with water.	Washed with three per cent. ammonium nitrate solution.	Washed with three per cent. potassium nitrate solution.	Amount of solution corresponding to gms substance used in volumetric method.
10. Mixed fertilizer	10.23	10.40	200	0.2
	10.25	10.35	500	0.2
11. Tennessee phosphate (low grade).....	23.08	23.11	200	0.2
	23.11	500	0.2
12. Tennessee phosphate (high grade).....	35.07	35.00	200	0.1
	34.85	35.00	500	0.1
13. Aluminum phosphate	46.91	47.10	200	0.1
	46.82	47.20	500	0.1
	47.00
14. Florida phosphate..	37.74	37.80	200	0.1
	37.62	37.78	500	0.1
15. Sodium phosphate..	19.97	19.96	200	0.2
	20.07	19.90	500	0.2
	20.03	19.76	200	0.2
	19.97	18.68	500	0.2
	19.82	19.90	...	200	...	0.2
....	19.82	...	500	...	0.2	

Sample No. 6, American Thomas slag, contained a very large amount of iron, while No. 7, European slag, contained considerable iron. "a" were precipitated only once with molybdic solution, and the "white" precipitates were contaminated with iron. "b c" were precipitated twice with molybdic solution to get rid of iron." The "white" precipitates giving results "c c" were free from iron, but "b" still contained a very small amount.

Note.—The solutions used in this work were the same as those given in the description of the method in Bul. 46, Div. Chem., U. S. Department of Agriculture, p. 13.

With reference to the variety of materials, an examination of the publications referred to at bottom of page 703, under reference (1), will show that the method has already been worked upon quite a variety of fertilizer materials and mixed goods, which with the materials investigated in this paper, appears to include nearly all, if not all, the sources of phosphoric acid in the fertilizer trade. Besides these, the large number of results presented to the Association last year by Mr. John P. Street, and

published in the Annual Report of the New Jersey Station,¹ shows that the method gives good results on mixed goods. Mr. Street says: "The materials analyzed included 276 samples of complete fertilizers, of varying composition and origin; and are believed to fairly represent the average goods on the market at the present time. The results secured were extremely satisfactory, the average results by the volumetric method being 10.72 per cent. against 10.70 per cent. by the official method. Of these results, 150 were higher by the volumetric, 113 lower, and thirteen identical with the official method; the greatest variation was 0.16 per cent., and 114 samples varied less than 0.05 per cent.

The results obtained by both the gravimetric and volumetric methods on the samples reported upon in this paper show good agreement, except those on samples 6 and 7, American and European manufactured Thomas slags. The American slag contained a very large amount of iron, and the European one quite a considerable quantity. When the yellow precipitates from these samples were dissolved on the filter with dilute ammonia water considerable iron remained on the filter. The results marked "a" in the table were secured by carrying these through according to the usual custom without reprecipitating to get rid of iron. These "a" results are about 0.40 per cent. higher than the corresponding volumetric ones on the American slag, and considerably higher on the European one. The "white" precipitates giving these high results were seen by color and shown by chemical test to contain iron. A second set of determinations was then made, using the same solutions from which the above results were obtained and precipitating twice with molybdic solution to get rid of iron, when results "c, c and b" were secured. These results show close agreement with the volumetric ones. Result "b" still contained a small amount of iron.

It appears then that the volumetric method has not only given as good results on all the samples here worked, including the *very high percentages*, as the gravimetric method, but on the samples containing large amounts of iron the results were better. I might state in this connection that we have found the

¹ 17th Annual Report, p. 118.

volumetric method to give very satisfactory results in estimating the phosphoric acid in soils, where a large amount of iron is usually present.¹

Now as to Mr. Gladding's point of telling when the precipitate has been washed sufficiently. It might be stated here also that others have had difficulty at this point and the statement in the method as published in Bulletin 46, Chemical Division, United States Department of Agriculture. p. 14, to wash the precipitate "till no longer acid" is responsible to some extent at least for this trouble.

It is well known that ammonium phosphomolybdate is slightly soluble in water and is an acid salt; and it would therefore be impossible to get a filtrate from washing with water that would be strictly neutral to very delicate indicators, like phenol phthalain. It will be found, however, that when the filtrate is allowed to drop from the neck of the funnel upon delicate litmus paper, that the wash water will be neutral to litmus after 100 to 200 cc. water has passed through. The work here reported and that previously done by us,² together with the work of Street,³ McDonnell, and others, shows that 150 to 250 cc. water, and often less, has been sufficient in all cases to free the precipitates of acid. But as stated by the writer in a previous paper on washing the yellow precipitate, "there is danger, however, of mechanical loss. The precipitate is first washed by decantation with dilute nitric acid and potassium nitrate, and afterwards with water to remove the nitric acid. It is in this after washing, when all the salts have been removed from the precipitate and as much as 600 to 700 cc. of water has been used, the precipitate begins to pass through the filter mechanically and settle to the bottom of the receptacle. We have not, however, found it necessary to wash with more than 300 cc. water."⁴ Perhaps this will explain the difficulty which occurred in Mr. Gladding's laboratory, in that more water was used for washing than was necessary. When these large quantities of water are used the precipitate not only gets through the filter and settles out in

¹ Bul. 47, Chem. Div., U. S. Department of Agriculture, p. 82.

² Bul. 47, Chem. Div., U. S. Department of Agriculture, p. 62.

³ Seventh Annual Report, New Jersey Station, p. 118.

⁴ This Journal, 17, 958.

the filtrate but it dissolves far more readily than when smaller amounts of water are used for washing.

In the light of the experience of the past three years, however, it does not now seem to be necessary to wash with more than 150 to 200 cc. of water, and the smaller of these is not much more, if any, than is used in washing the yellow salt in the gravimetric method.

In the results which precede in the table, I have made an additional test of the washing question by using 200 cc. and 500 cc. of water and the wash solutions, and making the determinations side by side and from the same solutions. The gravimetric results used for comparison were obtained on the same solutions as the volumetric ones. The results show that 200 cc. of water, even with these *very high percentages*, was sufficient in all cases, and that 500 cc. only lowered the results slightly when at all. When 200 cc. of three per cent. ammonium and potassium nitrate solutions were used for washing the results were practically the same as those obtained when the two quantities of water were used, but when they were increased to 500 cc. the results, greatly to my surprise, were much lower. The results were so much of a surprise that quite a number of them were repeated, and while they were not uniform in all cases, they were always low. We had hoped to be able to wash with a very large volume of ammonium nitrate solution without appreciably dissolving the precipitate or causing it to run through the filter. The filtrates from these 500 cc. ammonium and potassium nitrate washes were perfectly clear, but on evaporation the ammonium phosphomolybdate was found to be in solution.

In these determinations three-inch Hirsch funnels, with disks of filter paper covering the bottoms, and right strong suction, were used in filtering. The filtrates were not tested, but other determinations on the same sample by using ordinary funnel and filter paper without pressure showed them to be free of acid, after washing with 150 to 200cc. of water. These results agreed well with those obtained with the pump. All the precipitates were washed twice by decantation with dilute nitric acid and once with potassium or ammonium nitrate solution before washing with water.

In view of the results with potassium and ammonium nitrate

solutions it is suggested that one washing by decantation with water take the place of washing with potassium nitrate, following the washing with dilute nitric.

A word may not be out of place here in regard to the titration and end reaction. The greater the amount of yellow precipitate present the more slowly does the phenolphthalein color disappear, but up to twenty per cent. or more, when two-tenths gram of substance is used, the end reaction is quite sharp. For percentages much above twenty I consider one-tenth gram substance better to use, when the end reaction will be found sharp for any percentages one will be called upon to work. To summarize: For percentages below five use four-tenths gram substances (or about); for percentages between five and twenty use two-tenths gram, and above twenty use one-tenth gram.

It will also be found that by adding the indicator after the precipitate has been dissolved in the alkali, that the molybdenum colorations which sometimes interfere with the end reaction will be avoided. This observation was made by Street in his work previously referred to, and my observations corroborate it. Of the results presented in the table, the gravimetric determinations were made by Messrs. W. M. Allen, H. K. Miller, and myself; and the volumetric ones by myself.

The volumetric method was somewhat modified at the last meeting of the Association of Agricultural Chemists, and in such a way as to get around the difficulty of excessive washing spoken of in this paper. I repeat here the method in the form it was recommended that it should be tested in the work of this year:

Dissolve two grams substance in nitric and hydrochloric acids, incinerating beforehand to destroy organic matter if necessary, and make up to volume of 200 cc. For percentages below five use forty cc. of solution, for percentages between five and twenty use twenty cc. (and for percentages above twenty use ten cc.); add five to ten cc. concentrated nitric acid, nearly neutralize with ammonia, heat in the water-bath at 60°-65° C., add fifty cc. freshly filtered molybdic solution for each one-tenth gram phosphorus pentoxide present, and digest in water-bath for ten to fifteen minutes.

Decant the clear liquid on the filter as quickly as possible,

using Hirsch funnel with suction or ordinary funnel and filter paper with or without pressure; wash the precipitate by decantation twice with sixty per cent. nitric acid solution, using about fifty cc. of the solution each time, agitating thoroughly, and allowing the precipitate to completely settle, once with the same amount of three per cent. ammonium or potassium nitrate solution,¹ transfer it to the filter, and wash it five or six times with water, using 150 to 250 cc.² Now wash the filter and contents back into the beaker, add excess of standard alkali, and then a few drops of phenolphthalein, and titrate back with standard nitric acid.

THE ACTION OF NITRIC ACID UPON ALUMINUM AND THE FORMATION OF ALUMINUM NITRATE.

BY THOMAS B. STILLMAN.

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THE bibliography of aluminum, in reference to the action of nitric acid upon the metal, is well worthy of investigation.

The statements are so conflicting, even in the recent literature bearing upon this subject, that direct experimentation was required to demonstrate the solubility of aluminum in nitric acid.

Wöhler³ states: "Aluminium is not attacked by $\text{HNO}_3 + \text{Aq}$ even when concentrated and boiling."⁴

Deville⁵ gives as the result of his experiments that aluminum is not attacked by boiling nitric acid, dilute or concentrated.

Richards⁶ refers to the statement of Deville, but also adds: "In boiling acid solution takes place, but with such slowness that I had to give up this mode of dissolving the metal in my analysis." "By cooling the solution all action ceases."

Buff and Heeren⁷ coincide with Deville, "Aluminium wird weder von verd. noch konz. HNO_3 angegriffen."

Montenartín,⁸ "Aluminium is slowly soluble in 27 per cent.

¹ It is suggested that water be used for this washing by decantation instead of the nitrate solution.

² In our experience 200 cc. of water is sufficient.

³ *Pogg. Ann.*, 2, 223.

⁴ A Dictionary of Chemical Solubilities, by Comey, 1896.

⁵ *Compt. Rend.*, 38, 279.

⁶ Aluminium, its Properties, Metallurgy and Alloys, by J. W. Richards, 1890.

⁷ *Handbuch der anorganische Chemie*, Dammer, 2, 86, 1894.

⁸ *Gazz. Chim. Ital.*, 22, 397.