

described under the first method in which the ether was used, I obtained a good yield of cyanacetic acid without difficulty.

The reactions between nitriles and both fatty and aromatic acids will be more fully developed in this laboratory.

ORGANIC LABORATORY, SCHOOL OF MINES,
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THE DETERMINATION OF PHOSPHORIC ACID.

BY S. W. JOHNSON.
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THE papers on determination of phosphorus in steel by Messrs. Dudley and Pease, by Mr. Handy, and by Messrs. Doolittle and Eavenson, remind me of some work done at my instigation in the years 1880, 1889, and 1890, and published in the Annual Reports of the Connecticut Agricultural Experiment Station for those years.

In 1880, Mr. (now Professor) H. L. Wells, demonstrated that the citrate method for determining phosphoric acid may give good results under certain conditions, but that the results are correct because of a compensation of errors, the ammonium magnesium phosphate not carrying down quite all the phosphorus but containing enough impurities to counterbalance that loss. Over ninety determinations were made, many of them in duplicate, on forty different substances (fertilizers), after a large number of preliminary trials had indicated the effect of varying the several conditions which might influence the results. In most cases the percentages of phosphoric acid found in duplicate agreed well together and also agreed fairly with those given by the molybdate method. In a few cases, however, considerable discrepancies appeared and it was evident that further study was needful before the citrate method could be fully trusted for fertilizer work.

In 1889, in conjunction with Dr. T. B. Osborne, investigation of the citrate method was resumed. The German agricultural chemists were beginning to use it and J. H. Vogel had published details of procedure. We found that Vogel's process gave results too low and not closely agreeing with the molybdate method. By using more and stronger magnesium mixture and a larger quantity of concentrated ammonia, we overcame this discrepancy, and in sixty-seven determinations on bone-dust superphosphates, cotton-hull ashes, cotton-seed meal, tankage,

bone char, phosphatic guano, and phosphate rock, we found that but three citrate determinations differed from those by molybdate, by more than 0.3 per cent., and but four others by more than 0.2 per cent. The greatest discrepancy between the two methods was 0.41 per cent., while the average difference was 0.09 per cent. In thirty cases the citrate method averaged 0.117 per cent. more, in thirty-three cases 0.079 per cent. less, than the molybdate method. These percentages were reckoned on 0.4 gram of substance containing from 0.5 to 31.5 per cent. of P_2O_5 . The determinations were not made with unusual care, but were turned off rapidly as a part of the routine work of the station.

The citrate method was found to give unsatisfactory results where iron and alumina were present in considerable quantity, as in case of "Grand Cayman's Rock," "Thomas Gilchrist Slag," and "Keystone Phosphate." A series of trials under varied conditions was made in 1889 with the hope to ascertain the cause of the discrepancies but without success.

Some analyses of the ignited precipitate obtained by the citrate method may be quoted here :

COMPOSITION OF IGNITED "CITRATE PRECIPITATES."

	Bone.	Super-phosphate.	Grand Cayman's phosphate.	South Carolina rock.	Bolivian guano.	Dis-solved bone black.
Carbon.....	0.41	0.19	0.44	0.15	0.48	0.27
Silica	0.12	0.40	0.10	0.24	0.19
Calcium oxide.....	2.59	2.13	2.05	3.21	3.95	2.05
Magnesium pyrophosphate	95.49	96.07	95.66	95.77	94.98	97.83
Ferric and aluminum phosphate.....	0.71	0.35	0.31
Loss	1.51	1.49	0.74	0.42	0.35
	100.00	100.00	100.00	100.00	100.00	100.65

The loss probably consisted in part, of magnesia and in part also of pyrophosphoric acid. It is seen that the ignited precipitates contained from two to four per cent. of lime, that iron and alumina entered into the precipitate in small quantity when these elements were abundant in the original substance, and that where there was little or no loss, the recovered phosphoric acid amounted to from 95 to 97.8 per cent. of the precipitate.

In case of Grand Cayman's phosphate rock, duplicate determinations differed as much as 0.3 per cent., and the variations of duplicates of Thomas Slag and Keystone phosphate were even greater. It was also found that by changing the proportions of the reagents and by using on the one hand moderate and on the other vigorous and prolonged agitation, the quantity of phosphoric acid, reckoned from the ignited precipitate, fluctuated, in case of Thomas slag and Keystone phosphate, $2\frac{1}{2}$ and $3\frac{1}{2}$ per cent., respectively although by using large quantities of magnesia mixture and of strong ammonia, accordant and high results were realized.

Thus far we employed the modified rapid molybdate method, precipitating from hot solutions and digesting for one hour at 65° C. Finally in 1890 we found that under this procedure, the molybdate method, though satisfactory in absence of ferric, aluminum, and manganese salts, is, in their presence, little better than the citrate method. In case of Keystone phosphate three determinations by Osborne, using the U. S. "official" method gave figures ranging from 45.25 to 46.68 per cent.!

It was therefore necessary to return to the original Sonnen-schein method and make the precipitations at 40° to 50° C., during six hours. Six determinations thus carried out by Osborne, gave results from 44.67 to 44.86, the average being 44.82 per cent.

Comparative duplicate trials on a carefully made up solution of known composition with $P_2O_5 = 18.93$ per cent.¹ (from crystallized sodium phosphate) $Fe_2O_3 = 20$ per cent., $Al_2O_3 = 4.72$ per cent., and $MnO = 5.09$ per cent. (from sulphates), yielded Osborne, by the original Sonnenschein method, 18.92 and 18.94 per cent., and by the "official" method 19.26 and 19.26 per cent.!

We proved that with relative excess of nitric acid or relative deficiency of molybdic acid, a portion of phosphoric acid may easily fail to be thrown down. We also found that when precipitation is made hot and digestion is conducted at 65° C., ferric iron, and aluminum, if present, are to some extent included in the yellow precipitate and when this is dissolved in the subsequent treatment with ammonia, they pass into the alkaline

¹ Determined in the usual manner as magnesium pyrophosphate.

solution and thence into the ammonium-magnesium phosphate.

To sum up, the citrate method only gives good results by compensation of its errors and under exactly defined conditions which must be empirically determined. A procedure good for calcium phosphates is quite inapplicable to ferric and aluminum phosphates.

Again, the molybdic method, when carried out rapidly at temperatures higher than 50° , or as high as 65° C. in presence of trivalent iron, aluminum, or manganese, gives results too high, and in presence of great excess of nitric acid may give results too low, unless the filtrates from the yellow precipitate are mixed with additional molybdic solution and further digested until no more precipitate can be thrown down.

DOUBLE BROMIDES OF PALLADIUM.

BY EDGAR F. SMITH AND DANIEL L. WALLACE.

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BONSDORFF (*Poggendorff's Annalen der Physik*, [1], N. F., 19, 347) was one of the first chemists to attempt the preparation of double halides of palladium with other metals. Beyond mere mention of the fact that he obtained palladium bromide by the action of a mixture of nitric and hydrobromic acids upon the metal, that the resulting compound apparently combined "mit den Bromiden elektro-positiver Metalle," and that he made double salts of it with the chlorides of potassium, barium, manganese, and zinc, we have not discovered any additional literature relating to the above subject. It does not appear that Bonsdorff analyzed any of the double halides obtained by him.

Desirous of finding a salt or salts of palladium suitable for, but as yet not used in atomic mass determinations of palladium, we took occasion to prepare several double bromides of that metal, hoping to find among them one or more which might be available for the purpose.

Very pure metallic palladium was dissolved in nitro-hydrobromic acid. The residue was moistened with hydrobromic acid and repeatedly evaporated to dryness upon a water-bath. The palladium bromide, reddish-brown in color, was only soluble in water containing hydrobromic acid. Weighed quantities of this