nitrate and gently warmed. A marked precipitate of metallic silver was formed, this proving the presence of formic acid in corn oil. This acid was reported by Rokitiansky, but its occurrence has not been confirmed by any later observer.

The soluble acids thus far determined in corn oil are therefore summarized as follows :

| Name of acid. | Formula. | Name of analyst. |
|---|---|---|
| Formic | $CH_2O_2$ | Rokitiansky |
| Acetic | $C_2H_4O_2$ | Vulté and Gibson |
| Caproic[1] | $C_6H_{12}O_2$ | Rokitiansky |
| Caprylic[1] | $C_8H_{16}O_2$ | Rokitiansky |
| Capric[1] | $C_{10}H_{20}O_2$ | Rokitiansky |

Scientific knowledge as to the properties of the various fatty acids is at present so scanty and fragmentary and the lack of any connected scheme for their analysis is so absolute that the complete investigation of any oil presents almost insurmountable difficulties. Further examination of corn oil is needed in order to establish or disprove the presence of caproic, caprylic, capric, and ricinoleic acids and also to determine the relative percentages of the various acids with accuracy. The present investigation adds to the known constituents of the oil, acetic, hypogaeic, and arachidic acids, and confirms the presence of formic acid, which was up to this time considered doubtful.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE NORTH CAROLINA DEPARTMENT OF AGRICULTURE.]

# KILGORE'S MODIFICATION OF THE VOLUMETRIC METHOD OF ESTIMATING PHOSPHORIC ACID.[2]

BY C. B. WILLIAMS.

Received November 12, 1900.

IN the laboratories of fertilizer control stations and other institutions where a large number of determinations of phosphoric acid are required to be made quickly and accurately each year, it has been recognized for some time as almost imperative that some method shorter than the "gravimetric" should be devised. In 1894 Mr. Kilgore, then reporter on phosphoric acid for the Association of Official Agricultural Chemists, realizing this

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[1] Probable only.

[2] Read before the November meeting of the North Carolina Section of the American Chemical Society.

urgent demand, was the first to take up systematically the task by first thoroughly investigating himself and then submitting, as reporter, to the test of the Association the modified volumetric method. In his report he gave credit to Mr. Henry Pemberton who had, the previous year, published the description of a method based on this principle and which had been used very satisfactorily by a number of chemists. With this latter method, Mr. Kilgore had obtained fairly good but not uniformly good results.

After considerable experimentation as regards precipitant, precipitation, and filtration, he proposed a modification of this method, stating he had found that the modification gave him more satisfactory results with fertilizers. Since then each successive year has witnessed a still further modification until now we have a method that is used in a large number of laboratories in America with very gratifying results both in point of accuracy and rapidity.

The writer was, during the past spring, enabled to precipitate by shaking, wash and titrate thirty phosphoric acid samples daily with great facility by the modified volumetric method.

The reagents used are the same as those prescribed for the volumetric method by the Association of Official Agricultural Chemists except that the strengths of the standard solutions of potassium hydroxide[1] and nitric acid are made up so that 1 cc. of each will represent 0.5 milligram of phosphoric acid, this being one-half the strength given in the Association method.

The method as carried out is as follows :

Totals are brought in solution in the usual way by boiling in a 200 cc. flask, on a sand-bath, 2 grams fertilizer with 30 cc. concentrated nitric acid and 10 cc. concentrated hydrochloric acid to about 8 or 10 cc. concentration, except in fertilizers containing much iron and alumina, in which instance 30 cc. concentrated hydrochloric acid alone is first added and boiled for about thirty or forty minutes ; then, after slightly cooling, 30 cc. concentrated nitric acid is added and the boiling continued until the excess of hydrochloric acid is removed. After cooling make up to volume and filter out aliquot portions or allow to stand several hours before

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[1] The standard potassium hydroxide is freed from carbon dioxide by first dissolving it in 95 per cent. alcohol, letting settle and then filtering off by reverse filtration the supernatant solution free from the insoluble potassium carbonate. This method is much quicker and simpler than the barium hydroxide method.

measuring out. This latter is done in order that the supernatant liquid may become perfectly clear so it can be measured out with a pipette without filtration.

Twenty cc. of solution corresponding to 0.2 gram fertilizer (except in samples containing over 20 per cent. of phosphoric acid, when 10 cc. is used) are measured into a 500 cc. Erlenmeyer flask, the inside diameter of whose neck measures about 40 mm., and to it is added 10 to 12 grams of ammonium nitrate and 50 cc. of distilled water. Neutralize the excess of acid with ammonia. When the contents have cooled, 30 cc. of recently filtered molybdic solution are added and the flask, after securely stoppering with a rubber stopper, is placed in a Wagner shaking machine which is revolved by a hot air motor and here shaken for thirty minutes. The shaking machine is maintained at 45 to 55 revolutions per minute, as this velocity has been found to give the maximum agitating efficiency. Remove the flask from the shaking machine and filter and wash by suction on a filter prepared as follows :

Through the rubber stopper in a 16-ounce pressure bottle of Erlenmeyer form is passed the small end of a carbon filter; in the bottom of this is a perforated porcelain plate or disk to which is rigidly fastened a No. 19 copper wire, about 25 cm. long, that projects downwards into the pressure bottle. The disk is covered with a thin layer of asbestos.

After thoroughly transferring the ammonium phosphomolybdate and washing out the flask onto the asbestos filter, six more washings are given the precipitate. Then remove the stopper from the pressure flask with the small end of the carbon filter still stuck through it and hold upright over the sink and wash the outside free from acid with distilled water. Reverse the carbon filter into the mouth of the flask that originally contained the precipitate, still holding the small stem, and by means of the copper wire that extends beyond the small end of the carbon filter, push out the disk, asbestos and precipitate into the flask ; wash the disk and inside of carbon filter carefully and titrate, using a stirring rod about 30 cm. long to thoroughly agitate during the operation.

In determining insolubles, 40 cc. of solution, corresponding to 0.4 gram fertilizer, are taken. The precipitation, shaking, washing, and titrating are practically the same as with totals, except that little or no water is added in preparing for precipitation. During the past spring 1,000 totals and 1,000 insolubles were made by the above method with not a single incomplete precipitation, the yellow precipitate always coming down in a granular form that was easily filtered and washed.

Distilled water must be used in washing, as the suspended matter in ordinary water, in case it contains any, will not only retard filtration, but will form a compact coating over the precipitate that will greatly increase the difficulty of effecting a solution of the yellow precipitate with standard alkali as well as obscuring the color change of the indicator.

During the past year a large number of comparative results have been obtained in this laboratory on commercial fertilizers offered for sale in the State to test the volumetric method, as described above, with the regular official gravimetric method of the Association. In all instances results were extremely satisfactory.

During the past summer, three samples (two of ground phosphate rock and one of American slag) sent out by the referee on phosphoric acid for the Association of Official Agricultural Chemists, were analyzed with the following results:

| No. | Gravimetric method. | Volumetric method. |
|---|---|---|
| 389[1] | | 13.45 |
| | 13.55 | 13.50 |
| | 13.43 | 13.51 |
| | | 13.50 |
| 390[2] | 17.21 | 16.88 |
| | 17.23 | 16.93 |
| | 17.27 | 16.95 |
| | 17.35 | 16.90 |
| | 17.33 | |
| | 17.27 | |
| 391[1] | 26.01 | 25.90 |
| | 26.10 | 25.80 |
| | 26.11 | 25.85 |
| | 26.02 | 25.88 |

It will be noticed that the gravimetric results on sample No. 390 are perceptibly higher than those determined volumetrically. This is probably due to the presence of iron in the mag-

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[1] Ground phosphate rock.

[2] American slag.

nesium pyrophosphate as a qualitative test, for iron revealed its presence there. As sample No. 391 contains 4.70 per cent. ferric oxide, this may account for the wider variation than in No. 389 between the gravimetric and volumetric results.

RALEIGH, N. C.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF LAFAYETTE COLLEGE.]

# A METHOD FOR PREPARING NORMAL, SEMINORMAL, DECINORMAL, ETC., SULPHURIC ACID OF EXACT STRENGTH.

BY RICHARD K. MEADE.

Received November 10, 1900.

THE principal beauty of the normal system in volumetric analysis is the doing away with calculations. If then it is necessary to use a factor for converting to normal with a solution much of the usefulness of the system is destroyed. Unfortunately with by far the larger number of reagents used in volumetric analysis it is only with the greatest care that such solutions can be made of normal strength. Of the commonly used acid and alkali solutions, only oxalic acid and sodium carbonate can be prepared of exact strength, without first having another standard solution against which to balance a preliminary and then the exact solution. Even then, the latter is frequently too wide of the normal value to be used without a factor. The writer has been for some time preparing normal, seminormal, and more particularly decinormal sulphuric acid of exact strength by the method given below. The solution as prepared by this method needs no checking, except as a safeguard against errors of manipulation on the part of the analyst.

If the electric current is passed through a solution of copper sulphate the salt is decomposed, copper separating upon the cathode and sulphuric acid at the anode. This latter remains in solution and is not decomposed by the current. Hart and Croasdale[1] took advantage of this reaction to standardize alkali solutions. Their results were highly accurate. The writer has frequently made use of this method of standardizing alkali and has obtained results far more satisfactory than by any other method.

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[1] *J. Anal. Chem.*, **4**, 424.