

and have given very satisfactory results. The skeletons of small animals may be thus examined in relief, and the actual position of objects embedded in solid material discovered. It is conceivable that by the use of a fluorescent screen, and two cathodes placed some distance apart in the Crookes tube, these cathodes receiving discharges alternately, and thus producing two separate displaced sources of Röntgen rays, two stereoscopic fluorescent images may be produced on the screen. If, now, shutters or diaphragms are placed between the screen and the eyes, opened and closed synchronously with the discharges, and alternately with respect to each other, the image will be seen on the screen stereoscopically. In this way, by a rapid examination, the true space relations of embedded objects may be noted.

CHEMICAL SECTION.

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DR. HARRY F. KELLER, President, in the chair.

A SOURCE OF ERROR IN THE DETERMINATION OF PHOSPHORIC ACID BY THE CITRATE METHOD.

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The citrate method of phosphoric acid determination has been highly recommended for the analysis of superphosphates, basic slag and mineral phosphates by so many chemists of renown that its applicability can hardly be doubted—at least, not to agricultural analysis. Still, some analysts assert that this method has failed to show satisfactory results in their hands, especially on mineral phosphates.

A great number of tests made during the last year have led me to believe that this failure, in many cases, is due chiefly to a delay of the filtration of the ammonium-magnesium precipitate. In making a series of comparative tests, I did not, for a long time, encounter any serious difference

between the citrate and molybdate methods, until once I was compelled, in the analysis of a sample of South Carolina phosphate, to let the ammonium-magnesium precipitate stand over night; while, in all previous cases, excepting some tests on citrate-insoluble phosphoric acid, the filtration had been executed either immediately after the precipitation, or not any later than about three hours thereafter.

The results obtained on this sample were: citrate method, 29.60 per cent.; molybdate method, 28.32 per cent. The test was repeated by the citrate method, with the result 28.48 per cent. As in this latter test the filtration of the ammonium-magnesium precipitate had been executed immediately after the precipitation, I suspected that the high result of the first test had been caused by the delay of the filtration. To ascertain the correctness of this suspicion, several other tests were made, and the fact was thereby established that results obtained by filtration, immediately, or only a short time after precipitation, agree very well with the molybdate method; while those obtained by filtration, after about fifteen hours, are entirely too high. A close observation during those tests showed that the filtrate from the magnesium precipitate, when obtained at once after precipitation, remained perfectly clear for about four hours, after which time a slight turbidity appeared, which increased more and more until, after standing over night, a small precipitate of silica and aluminum and iron oxide had formed. In all filtrates from precipitates which had stood over night, no after-precipitation could be observed.

Of the numerous tests made, the following show the most remarkable figures :

Acidified South Carolina Rock :

	<i>Per Cent.</i>
Molybdate method	16.00
Citrate method (filtration after two hours)	15.92
Citrate method (filtration after fifteen hours)	16.96

Florida Phosphate :

	<i>Per Cent.</i>
Molybdate method	32.16
Citrate method (filtration immediately after precipitation)	32.32
Citrate method (filtration after fifteen hours)	33.92

It has been claimed that, by using concentrated sulphuric acid as a solvent, not only a large amount of calcium oxide, but of aluminum oxide, also, is precipitated. Hoping to at least reduce the error, I treated some samples with 50 cubic centimeters of concentrated sulphuric acid, boiling for thirty minutes, but failed to get any other results than those obtained by the use of hydrochloric and nitric acids.

In the determination of the citrate-insoluble phosphoric acid of acidified mineral phosphates, the danger of getting high results by a delay of the filtration is not so great, as a considerable amount of silica, iron and aluminum oxides is removed by the action of the neutral citrate of ammonium solution at 65° C.; yet, on some samples, results become entirely too high.

From my experience in the citrate method, I have come to the conclusion that the general direction to filter the magnesium precipitate, either right after precipitation or at any later time, holds good only for the determination of the water-soluble phosphoric acid of superphosphates and the insoluble phosphoric acid of animal phosphates, such as bone-meal, and bone-black. In the determination of the insoluble phosphoric acid of mineral phosphates, their superphosphates, and all mixtures containing the same, the filtration of the magnesium precipitate must take place either immediately after the precipitation, or not any later than three hours afterwards, if a contamination by silica and aluminum and iron oxides shall be avoided. With this precaution, however, excellent results can be obtained by the citrate method, provided an appropriate amount of citrate of ammonium solution is used.

According to my experience, the best results are obtained by using 0.4 grams of substance and 75 cubic centimeters of citrate solution in the determination of total phosphoric acid. For the citrate-insoluble phosphoric acid, 0.4 grams of substance and 40 cubic centimeters of citrate solution have proved, in my hands, to give the most satisfactory results.