

Ethyl acetic ester retained its color twenty-three hours, then turned colorless.

These results do not agree with the observations of Griggi, that the amyl alcohol solution of perchromic acid is more stable than the solution in ether. The most stable solution is that in ethyl acetic ester. The time of duration given by Griggi, six hours, was evidently found under different circumstances. If the layer of the solvent is allowed to remain upon the aqueous layer the decomposition of the perchromic acid is greatly accelerated. The above experiments were made in this manner. Those of Griggi may, perhaps, have been made under other conditions in this respect.

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**SOME FACTS OBSERVED IN THE DETERMINATION OF
PHOSPHORIC ACID BY THE MOLYBDIC ACID
PROCESS.**

BY RUDOLF DE ROODE.
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THE length of time necessary for the complete precipitation of phosphoric acid seems to be much less than is generally supposed. Portions of the same solution were treated with molybdic solution and allowed to stand at 65° C. for five, ten, fifteen, twenty, thirty, forty, fifty, and sixty minutes, respectively, and two portions stood in a warm place over night. The phosphoric acid determined as usual as magnesium pyrophosphate, showed that the precipitation was complete after standing only five minutes. The weights of magnesium pyrophosphate were as follows:

5 minutes.....	0.0676 gram	} Average 0.0673
10 "	0.0672 "	
15 "	0.0674 "	
20 "	0.0672 "	
30 "	0.0669 "	
40 "	0.0670 "	
50 "	0.0673 "	
60 "	0.0675 "	
12 hours.....	0.0671 "	
24 "	0.0676 "	

By making a determination of phosphoric acid, using twenty-

five cc. of a very dilute sodium phosphate solution and the same quantities of reagents as are used in a regular determination, and then adding twenty-five cc. of this same dilute sodium phosphate solution to a regular determination and using the first determination as a blank which is subtracted from the last, we get a lower result, which would seem to indicate that a regular determination, without the addition of the phosphate solution and subtraction of the blank, gives too high a result.

A dilute sodium phosphate solution (twenty-five cc.) gave, with the same quantities of reagents as ordinarily used,

1.....	0.0158	gram of magnesium pyrophosphate.		
2.....	0.0161	"	"	"
3.....	0.0156	"	"	"
4.....	0.0163	"	"	"
5.....	0.0160	"	"	"
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Average....	0.0160	"	"	"

Twenty-five cc. of an acid phosphate solution, together with twenty-five cc. of the above sodium phosphate solution and the same quantities of reagents gave

	0.0821	gram of magnesium pyrophosphate.		
Blank.....	0.0160	"	"	"
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Difference....	0.0661	"	"	"

The average of the ten results obtained where no blank was subtracted was 0.0673 gram magnesium pyrophosphate, making a difference of 0.0012 gram.

Three of the weighed precipitates of magnesium pyrophosphate, in the series of ten, were redissolved in nitric acid, and reprecipitated with molybdic solution and magnesia mixture, ignited in the same crucibles and weighed. At first the magnesium pyrophosphate weighed :

1	0.0672
2	0.0670
3	0.0671

After solution and reprecipitation :

1	0.0660
2	0.0660
3	0.0659

Again dissolved and reprecipitated as before :

1	0.0659
2	0.0658
3	0.0657

There seems to be no further loss on reprecipitation, and the results, after the second and third precipitation, agree closely with the results obtained by using and subtracting a blank. These results also would indicate that somewhat too high results are obtained by the regular method for phosphoric acid determination.

Another fact along this same line was also observed; *viz.*, that if different quantities of the same phosphate solution are precipitated, the larger quantity gives the lower and more correct result. Thus, twenty-five and fifty cc. of a phosphate solution, precipitated as usual, gave quantities of magnesium pyrophosphate which, when expressed in percentage of P_2O_5 , were :

Twenty-five cc. gave 26.05 per cent. and 26.10 per cent.

Fifty cc. gave 25.96 per cent. and 25.97 per cent.

And another solution in like manner :

Twenty-five cc. gave 36.38 per cent.

Fifty cc. gave 36.18 per cent.

The most plausible explanation of this also seems to be that there is some source of error tending to give too high a result, which is multiplied more the smaller the quantity which is taken, and it would seem desirable, for the sake of accuracy, to employ as large a portion as is convenient.

The foregoing experiments seem to warrant the following conclusions :

1. That our present method for determining phosphoric acid seems to give results which are somewhat too high.
2. That the results obtained by using a large quantity of substance, and obtaining large precipitates, are lower and somewhat more accurate than those obtained where smaller quantities are employed.
3. That somewhat lower and more accurate results are obtained by using a blank made by employing a dilute solution of a phosphate, which is added to each determination. This blank, previously determined, being subtracted from the final result.
4. That accurate results, agreeing with those obtained by the

use of the blank, are obtained by redissolving the magnesium pyrophosphate and reprecipitating.

5. That five minutes digestion at 65° C. seems to be sufficient for the complete precipitation of phosphoric acid by molybdc solution.

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THE ADDITION OF CALCIUM CHLORIDE TO THE SOLUTION OF A FERTILIZER IN THE DETERMINATION OF POTASH.

BY RUDOLF DE ROODE.
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MR. H. A. HUSTON has proposed the addition of a solution of calcium chloride to the solution of a fertilizer in the determination of potash, in order to furnish sufficient calcium to form tricalcium phosphate with all the phosphoric acid present, and thereby permit of the use of platinum dishes in the Lindo-Gladding method. In testing this proposition I find that when sufficient calcium chloride was added to combine with all the phosphoric acid present and then ammonia added in excess and a portion of the solution filtered off, no test for phosphoric acid could be obtained. But, that if in addition to the calcium chloride and ammonia, some ammonium oxalate or carbonate was added, a filtered portion of the solution *did* give a test for phosphoric acid. This is accounted for by the fact that the calcium phosphate, which was precipitated by the ammonia, is changed by the ammonium oxalate or carbonate into calcium oxalate or carbonate and ammonium phosphate, so that the very object for which the calcium chloride was added is defeated by the addition of the ammonium oxalate or carbonate. In order to make the use of calcium chloride effective it is necessary to filter off from the precipitate formed by the calcium chloride and ammonia and then add the ammonium oxalate or carbonate to the filtrate. This necessitates two separate filtrations, and it is doubtful if we have in Mr. Huston's suggestion anything better than, or even so good as in the present alternate method.

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