DOES VANADIUM INTERFERE WITH THE DETERMINATION OF PHOSPHORUS IN SOILS WHEN THE PHOSPHORUS IS WEIGHED AS MAGNESIUM PYROPHOSPHATE ?¹

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In a recent paper, Robinson (8) gives the results of the following experiment: "Solutions containing 0.0050 gm. V_2O_5 and 0.00864 gm. P_2O_5 were treated with magnesia mixture in the usual manner and allowed to stand 6 hours; 0.0088 gm. P_2O_5 was found. When the precipitation for the same amounts had stood 17 hours there was apparently 0.0145 gm. P_2O_5 . From these experiments it appears that with the small amounts of vanadium and phosphorous occurring in soils a satisfactory separation can be made with magnesia mixture, *provided the precipitate does not stand more than 3 to 4 hours.*"² Robinson does not suggest it,

² Our italics.

but the fact remains that this statement of his calls into question practically all of the determinations of phosphoric acid that have been made on either rocks or soils. Washington (9, p. 165) states that the magnesia precipitate should stand for 12 hours. Hilgard (3) recommends that the precipitate stand 24 hours before filtering. The Halle Experiment Station (10) allows 48 hours for the complete separation of the precipitate.

This list might be continued almost indefinitely, for at least 50 per cent of the texts on quantitative analysis specify that it is desirable that the precipitate stand "over night" and, even in those texts which state that 3 to 4 hours' standing causes complete precipitation, there is no hint that a longer standing may produce erroneous results.

Inasmuch as vanadium is probably present in most soils (7) and rocks (4) in amounts which in some instances equal or even exceed the phosphorous content, it was deemed advisable to see if Robinson's conclusion as to the possible contamination of the magnesium pyrophosphate by vanadium was actually justifiable.

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A contamination of the magnesium precipitate by vanadium would occur only providing the vanadium was precipitated both by the molybdate and by the magnesia mixture. It is well established that vanadium is precipitated by ammonium molybdate only in the presence of phosphoric acid, and that *complete* precipitation of the vanadium requires a large excess of phosphorous. Cain and Hostetter (1, p. 254) state that 10 mg. of phosphorous is necessary for the complete precipitation of 1 mg. of vanadium.

It would seem, therefore, that in a soil analysis a separation of phosphorous and vanadium would be made, to a large extent at least, in the molybdate precipitation, and that sufficient quantities of vanadium would not remain to contaminate seriously the magnesia precipitate, even if all of the remaining vanadium should be precipitated by the magnesia mixture. On this latter point, Robinson's experiment furnishes the only available data that we have been able to find.

We have, therefore, investigated the behavior of vanadium when added directly to a phosphate solution and precipitated by magnesia mixture as well as when added to soil extracts and precipitated by ammonium molybdate followed by the usual magnesia precipitation.

EXPERIMENTAL

Precipitation of a mixed solution of phosphate and vanadate by magnesia mixture

It will be noted in Robinson's experiment that at the end of 6 hours the P_2O_5 recovered was but 0.00014 gm. in excess of that added, while at the end of 17 hours it was 0.00586 gm. in excess, or slightly more than would be produced by the complete precipitation of the added vanadium. Such a differential rate of precipitation is certainly unusual, and if *complete* precipitation of vanadium occurs in 17 hours it should take more than a single determination to show that only a mere trace is precipitated in 6 hours.

It was suggested to us that a possible explanation of the vanadium precipitation might be found in the well known fact that a high concentration of ammonium salts causes ammonium meta-vanadate to precipitate from solution. We have, therefore, tested the behavior of a mixture of sodium phosphate and ammonium meta-vanadate when treated with magnesia mixture in the presence of varying concentrations of ammonium hydroxide. The volume of the solution in which the precipitation was made was, in each instance, 100 c.c. The data are shown in Table I.

It will be observed that an increase in the weight of the magnesium precipitate was obtained only when the concentration of the ammonia exceeded 20 per cent by volume. In all instances where vanadium was added, the magnesium pyrophosphate was more or less colored, ranging

from light yellow to almost orange. However, the amount of color present did not correspond accurately to increases in weight.

These experiments would indicate that, even if all of the vanadium of soils were present in the ammonium phospho-molybdate precipitate, a contamination of the pyrophosphate precipitate would not normally take place, inasmuch as the concentration of ammonia in the solution should not exceed 20 per cent by volume. There is a possibility, however, that

TABLE I

THE WEIGHTS OF MAGNESIUM PYROPHOSPHATE OBTAINED BY PRECIPITATING PHOSPHORIC ACID WITH MAGNESIA MIXTURE IN THE PRESENCE OF DIFFERENT AMOUNTS OF AMMONIUM META-VANADATE AND VARYING CONCENTRATIONS OF AMMONIA, THE PRECIPITATE IN ALL CASES STANDING 20 HOURS

P ₂ O ₅ Taken gm.	V ₂ O ₅ Taken gm.	Mg ₂ P ₂ O ₇ Found gm.	Mg ₂ P ₂ O ₇ Found gm.	Mg ₂ P ₂ O ₇ Found gm.
		10% ¹ NH ₄ OH	20% ¹ NH ₄ OH	30% ¹ NH ₄ OH
0.0032	None	0.0049	0.0051	0.0050
0.0032	None	0.0050	0.0048	0.0051
0.0032	0.0014	0.0050	0.0049	0.0055
0.0032	0.0014	0.0050	0.0052	0.0061
0.0032	0.0028	0.0050	0.0050	0.0058
0.0032	0.0028	0.0050	0.0051	0.0066
0.0032	0.0042	0.0051		
0.0032	0.0042	0.0051		

¹ Per cent by volume of concentrated ammonia.

the vanadium might be precipitated from solution by some conditions which did not occur in our experiments, and we have, therefore, tested the effect of vanadium on the determination of the phosphorous contained in a soil solution.

The effect of vanadium on the determination of soil phosphorous

A standard solution of ammonium meta-vanadate was prepared and added in different amounts to a soil solution prepared by a 5-day digestion of a soil with 1.115 specific gravity hydrochloric acid and subsequent procedure as for Solution "A" in Hilgard's (3) manual. The hydrochloric acid solution after the addition of the vanadium was evaporated with nitric acid to change chlorides into nitrates, taken up with dilute nitric acid and the phosphoric acid precipitated with ammonium molybdate and ammonium nitrate in the usual manner. In all cases the molybdate precipitate was left in a warm place over night. The influence of the vanadium could be readily observed, since where vanadium was added the precipitate was colored more or less deeply orange. The magnesium ammonium phosphate was precipitated as usual, in an ammonia concentration of 15 to 18 per cent by volume, and after standing for 3 hours was filtered off and weighed. The filtrates were then allowed to stand 24 hours longer in order to determine how much V₂O₅ would be precipi-

tated between 3 hours and 27 hours. According to Robinson's data, all of the vanadium precipitated by the ammonium phospho-molybdate should have appeared here. Table II shows the results obtained.

TABLE II
RESULTS SHOWING THE EFFECT OF VANADIUM UPON THE DETERMINATION OF
SOIL PHOSPHOROUS, MAGNESIUM PRECIPITATE REMOVED AFTER 3 HOURS

P_2O_5 Taken gm.	V_2O_5 Added gm.	$Mg_3P_2O_7$, 3 hrs. gm.	P_2O_5 , 3 hrs. gm.	$Mg_3P_2O_7$ in filtrate, 3 to 27 hrs. gm.
None	0.0028	None	None	0.0001
None	0.0028	0.0002		0.0002
0.0026	None	0.0044	0.0028	0.0001
0.0026	None	0.0041	0.0026	None
0.0026	None	0.0043	0.0027	0.0001
0.0026	0.0014	0.0037	0.0024	
0.0026	0.0014	0.0041	0.0026	
0.0026	0.0028	0.0037	0.0024	0.0001
0.0026	0.0028	0.0039	0.0025	0.0002
0.0026	0.0056	0.0039	0.0025	0.0002
0.0026	0.0056	0.0040	0.0026	0.0003

It will be noted that the added vanadium has in no way interfered with the determination of phosphorous and that the vanadium was not precipitated from the filtrate after filtering off the magnesium ammonium phosphate.

Thinking that perhaps the vanadium might be precipitated only in the presence of the magnesium ammonium phosphate, the experiment was repeated, the magnesium precipitate being allowed to stand 24 hours. The results are given in Table III.

TABLE III
RESULTS SHOWING THE EFFECT OF VANADIUM UPON THE DETERMINATION OF
SOIL PHOSPHOROUS, MAGNESIUM PRECIPITATE ALLOWED
TO REMAIN 24 HOURS

P_2O_5 Taken gm.	V_2O_5 Added gm.	$Mg_3P_2O_7$, 24 hrs. gm.	P_2O_5 , 24 hrs. gm.
0.0043	None	0.0066	0.0042
0.0043	None	0.0069	0.0044
0.0043	0.0014	0.0067	0.0043
0.0043	0.0014	0.0071	0.0045
0.0043	0.0028	0.0067	0.0043
0.0043	0.0028	0.0067	0.0043

It will be noted that the results are not altered by the added vanadium. The ammonium phospho-molybdate was quite deeply colored in those experiments where vanadium was added, but the tests of the filtrates from the magnesium precipitate showed that the vanadium was still in solution in the ammonia. The ignited precipitates had only a faintly yellow tint and showed only traces of vanadium.

To make our position absolutely sure, however, a third series of experiments was undertaken. In this instance the phosphoric acid was determined not only gravimetrically as pyrophosphate, but the yellow precipitate was also weighed on a Gooch crucible as $(\text{NH}_4)_3\text{PO}_4 \cdot 12 \text{ MoO}_3$ after drying at 160° to 180° to constant weight (5, p. 598), and also determined volumetrically according to the method of J. A. Prescott (6). The results are shown in Table IV.

TABLE IV
RESULTS SHOWING THE EFFECT OF VANADIUM UPON THE DETERMINATION OF
SOIL PHOSPHOROUS BY THREE DIFFERENT METHODS

P_2O_5 Taken gm.	V_2O_5 Taken gm.	P_2O_5 as $\text{Mg}_2\text{P}_2\text{O}_7$ after 24 hrs. gm.	P_2O_5 as Yellow Ppt. Grav. gm.	P_2O_5 Titration of Yellow Ppt. gm.
0.0038	None	0.0039	0.0037	0.0038
0.0038	None	0.0038	0.0036	0.0038
0.0038	None	0.0036		0.0038
0.0038	0.0014	0.0042	0.0036	0.0038
0.0038	0.0014	0.0040	0.0036	0.0037
0.0038	0.0028	0.0037	0.0036	0.0036
0.0038	0.0028	0.0037	0.0036	0.0036

There is no doubt that some vanadium does come down with the yellow precipitate, but that the amount which does precipitate is only a small part of that in solution was demonstrated by qualitative tests on the filtrate from the molybdate precipitation (cf. Cain and Hostetter, Reference 1).

It is equally well demonstrated that when vanadium is present, the precipitation of phosphorous by ammonium molybdate is interfered with and may be incomplete (2). We have purposely limited ourselves to the phosphorous content present in normal soils, using only soil solutions in order to have all of the usual elements present in their usual quantities, and adding vanadium in such quantity as to considerably exceed the maximum amount which would probably be expected in soils.

Possibly our final results represent, to a slight extent, a balancing of errors, but we believe that we have demonstrated that the earlier determinations of phosphoric acid in rocks and soils do not contain appreciable errors due to the presence of vanadium, and that the vanadium present in the soil will not interfere with either the volumetric or the gravimetric determination of phosphorous, even though the magnesia precipitate should stand for 24 hours.

SUMMARY

Robinson suggests that vanadium, if present in a soil or rock, may be precipitated together with the phosphoric acid by ammonium molybdate and may introduce grave errors in the determination of phosphorous as magnesium pyrophosphate if the magnesium precipitate is allowed to

stand more than 3 to 4 hours. This statement is apparently based upon a single determination.

We have made a series of determinations, using soil solutions to which known amounts of vanadium were added, the phosphorous being weighed as pyrophosphate, after standing for 24 hours, and in no instance do we find any appreciable interference by vanadium. The titrametric method for phosphorous is also unaffected by the presence of vanadium in amounts far in excess of the usual soil content.

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