ON THE COLORIMETRIC DETERMINATION OF SMALL QUANTITIES OF PHOSPHORIC ACID AND OF SILICA.

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IN some of the field work of this bureau the analysis of drainage waters and of water extracts of soil is required daily. For this purpose the usual gravimetric processes are deemed impracticable on account of the time required, and it has been necessary to use more rapid volumetric, colorimetric, and photometric methods.

The writer suggested, and in the spring and early summer of the past year made an examination of, some known rapid colorimetric methods for the determination of phosphoric acid and of silica in these soil solutions. Incidentally, as the presence of iron in considerable amounts introduces errors in the determination of phosphoric acid, the rapid methods for the detection and estimation of minute quantities of iron have received some attention. As these latter methods have been thoroughly worked out and are quite well known, but passing reference need be made to them here.

For the estimation of phosphoric acid, the method described by Lepiere[1] and later studied in more detail by Woodman and Cayvan[2] promised to be the most rapid and to present the fewest difficulties in its manipulation.

For the adaptation of this method to the analysis of soil solutions, the influence of other compounds, both organic and inorganic, must be eliminated or determined. It was found that turbidity, organic matter where it produced a colored solution, ammonia salts in large amounts, iron salts in small amounts, dissolved silica and filter-paper introduce errors which are not negligible.

REMOVAL OF SUSPENDED MATTER.

Turbidity may be removed by filtering through a Chamberland filter, which of course removes some of the phosphoric acid from the first runnings (see Table VIII). It may also be quite largely, sometimes completely, removed by evaporation to dryness

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[1] *Bull. Soc. Chim.*, **15**, 1213 (1896).

[2] This Journal, **23**, 96.

and filtering; or it may be corrected for by matching the standard phosphomolybdate solution against the turbid solution and subtracting this reading from the final readings. None of these procedures is perfectly satisfactory, but nothing better has yet been devised. All have been used here, according to the difficulties presented. Where filtration will remove all suspended matter, this procedure is to be preferred, but as this cannot always be accomplished, the Chamberland filter or evaporation must be resorted to.

In the work about to be described the reagents were prepared as directed by Woodman and Cayvan[1] and were free from interfering substances. The same lot was used throughout the work, and all work was done at from 18°-22° C., the standard and the unknown solution being of course at sensibly the same temperature.

REMOVING ORGANIC MATTER.

Organic matter which colors the solution at all must be removed or it must be corrected for as above described, before reliable readings can be made. To accomplish this, two methods were tried: treatment with aqua regia, and ignition with magnesium nitrate. Several treatments with aqua regia were required to insure the destruction of all organic matter, after which the solutions were carried to dryness, taken up with water and 2 cc. nitric acid and compared in a reflecting colorimeter. The following readings were obtained:

TABLE I.

	Amount P_2O_5 added.	Amount P_2O_5 recovered.		Amount P_2O_5 added.	Amount P_2O_5 recovered.
	Parts per million.			Parts per million.	
1	1.0	1.0	4	5.0	4.3
2	2.0	1.1	5	7.0	6.1
3	3.5	2.4	6	9.0	7.1

We see that there is considerable loss of phosphoric acid from this concentrated aqua regia solution, a fact previously pointed out by Woodman and Cayvan.

Other phosphate solutions were then treated with magnesium nitrate free from silica, evaporated to dryness with nitric acid, and ignited in a porcelain dish until all carbon was burned off. The residue was then taken up with water and nitric acid, and compared with the standard solution.

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[1] *Loc. cit.*

TABLE II.

	Amount P_2O_5 added. Parts per million.	Amount P_2O_5 recovered. Parts per million.
1	1.0	1.0
2	2 0	1.8
3	4.0	3.7
4	6.0	5.9
5	8.0	7.9
6	9.0	9.2
7	10.0	9.9
8	3.0	2.7
9	1.0	1.0
10	5.0	5.2
11	10.0	10.0
	Average loss,	0.06

The loss here is quite small, being as a rule within the limit of error of the reading. From these experiments it appears that the organic matter may be satisfactorily removed without loss of sensible amounts of phosphoric acid by ignition with magnesium nitrate and subsequent evaporation with nitric acid.[1] It may be said, however, that when the color due to organic matter is not greater than 0.2 to 0.3 part per million, it is hardly worth while to remove the organic matter, as a correction may be made for it by reading the color due to organic matter against the standard, and correcting the final reading by the reading thus obtained.

The volatility of phosphoric acid upon evaporation of these water solutions is at first sight rather startling to analysts, and while there is not the slightest doubt that it does take place from solutions of phosphoric acid[2] and from disodium phosphate solutions, there appears to be no reason to think that it occurs from solutions containing sufficient bases to form the normal phosphates. In no case has the writer obtained a loss from solutions of this character. As phosphates dissociate readily, it seems possible that water extracts of soils may contain occasionally some free phosphoric acid or acid phosphates from which phosphoric acid is partly volatilized upon evaporation. That this does not take place in the presence of a large excess of base, even from acid solutions, is shown positively by the experiments with magnesium nitrate.

INFLUENCE OF THE PRESENCE OF OTHER SALTS.

Ammonia salts in considerable quantities decrease slightly the intensity of the color reaction. Ammonium nitrate added to the unknown solution at the rate of 0.04 gram per 50 cc. gave readings on 4 parts per million of standard of only 3 parts, which increased a little on standing, but the solution soon precipitated.

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[1] Subsequent work has confirmed these results in every instance.

[2] It seems possible that this apparent loss may be due to the formation of pyrophosphoric acid.—EDITOR.

Ammonium chloride does not give a water-white solution always —has a tendency to be slightly opaque, and it also prevents the full development of the color. The figures obtained are given in the table.

TABLE III.—EFFECT OF AMMONIUM SALTS.

Parts per million NH_4NO_3.	Parts per million P_2O_5 added to NH_4NO_3 solution.	=	Parts per million P_2O_5 without NH_4NO_3.	Solution with NH_4NO_3 commenced to precipitate.
4000	1.0	=	0.7	not in 5 min.
4000	4.0	=	2.0	nearly as dark but precipitated too rapidly to be sure.
4000	4.0	=	3.0	nearly as dark but precipitated too rapidly to be sure.
800	4.0	=	3.3	precipitated in 50 min.
800	4.0	=	3.7	" " 75 "

Calcium nitrate, barium chloride, potassium nitrate, and aluminum sulphate, separately and together, were added to solutions at the rate of 0.25 gram of each salt to 50 cc. of solution. None of these except the aluminum sulphate affected the readings more than 0.1 part per million, or within the limit of error of readings. Aluminum sulphate in this quantity gave a dark, opaque solution which could not be matched satisfactorily against the standard.

It was found that iron salts in considerable quantities exerted a marked influence not only on the color of the solution itself, in the first instance, an influence which it was found could be corrected for by reading against the standard, but there is also a reaction between the iron salt and the molybdate, a reaction which appears to bear a relation to the amount of iron present, and which possibly may be used for the estimation of the iron in solution. As iron is present in many soil extracts, the reaction of iron with the molybdate solution required careful study in order to determine the amounts and conditions which would vitiate the phosphate readings. The results of the investigation of this point are given in Table IV. Unless otherwise stated, the two solutions were identical in all particulars except that one contained iron in the amounts given in the table. The iron salt was made from pure wire, the solution of which was evaporated to dryness several times to remove traces of silica and hydrochloric acid.

TABLE IV.—COLOR PRODUCED BY IRON SALTS WITH MOLYBDATE SOLUTION.

Preliminary Series.

Parts per million of Fe in solution.	Parts per million P_2O_5 to equal color of Fe solution before molybdate was added.	Parts per million P_2O_5 to equal color of Fe solution after molybdate was added to Fe solution.	Parts per million of P_2O_5 to equal color produced by adding 1 part per million P_2O_5 to Fe solution containing molybdate.
4000	3.0	6.5	...
2000	..	3.0	...
2000	0.6	2.5	...
2000	..	4.0	1.05
2000	..	3.1	0.95
2000	..	3.0	1.10
400	2.2	3.2	...
200	0.8	1.6	1.10
80	0.2	0.8	1.00
40	0.1	0.3	1.00
40	0.1	0.5	...
40	0.1	0.5	1.00
		Final Series.	
100	0.1	0.75 0.75 0.80	
50	0.0	0.40 0.40 0.50	
20	0.0	0.10 0.10	
10	0.0	0.00 0.00	
8	0.0	0.00 0.00	
4	0.0	0.00 0.00	
2	0.0	0.00 0.00	

The presence of less than 20 parts of iron (Fe) per million of solution introduces no appreciable error in the determination, while as much as 50 parts per million vitiate the phosphate results, unless the amount of iron present is known and its reading subtracted from the total reading. As soil extracts seldom contain more than 0.1 to 5 parts per million of iron, further study of the influence of iron has been temporarily discontinued, but it is hoped to devote more attention to this point later. It is of course necessary, where the presence of considerable iron is indicated, to assure one's self that not more than 20 parts per million are present before the reading can be accepted as representing phosphoric acid alone. This is quite readily ascertained by adding potassium sulphocyanide or ferrocyanide to the acidulated extract and matching the developed color against an iron standard.[1]

EFFECT OF VARYING THE AMOUNT OF NITRIC ACID PRESENT.

Woodman and Cayvan[2] found that the depth of color and the rapidity with which it developed depended to a certain extent on the amount of reagents present in the solution, and further state that the best results were obtained with 4 cc. of ammonium molybdate solution (50 grams of the salt per liter) and 2 cc. of nitric acid (sp. gr. 1.07) per 50 cc. of the solution to be examined.

It appeared advisable to make an experimental study of these points in order to obtain data on the allowable variations in amounts of added reagents. To this end solutions containing different amounts of nitric acid and also different amounts of standard phosphate solution were compared with solutions containing 2 cc. of nitric acid and 4 cc. of molybdate. The results follow:

TABLE V.—EFFECT OF VARYING THE QUANTITY OF NITRIC ACID ADDED.

HNO_3 + Cc.	Na_2HPO_4 + Cc.	Molybdate = Cc.	Na_2HPO_4 + Cc.	HNO_3 + Cc.	Molybdate. Cc.
1	1	4	0.83	2	4
2	1	4	1.04	2	4
3	1	4	1.10	2	4
4	1	4	1.15	2	4
5	1	4	1.24	2	4
6	1	4	0.98	2	4
7	1	4	0.97	2	4
8	1	4	0.88	2	4
10	1	4	0.84	2	4

The intensity of the color is sharply and regularly affected by the amount of nitric acid present, and it is of particular interest to note that there is a maximum point at which the color is most intense: with less acid or with more acid present the intensity of color is considerably reduced and it is evident that to obtain strictly comparable results the standard and the solution to be read must contain, in a given volume, sensibly the same amount of acid.

Possibly these results are also of interest in throwing light on the precipitation of ammonium phosphomolybdate and may ex-

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[1] Sutton's "Volumetric Analysis," eighth edition, p. 245.

[2] *Loc. cit.*

plain the results sometimes obtained. It is a well-known fact that the color of the precipitate varies with the amount of acid present from a light lemon-yellow to a deep orange, and the speed with which the precipitate is formed also varies with the amount of nitric acid present. Under the best conditions this precipitation takes place rapidly and is complete; the supernatant fluid is practically as colorless as water, even when it contains a considerable amount of iron salt. On the other hand, under some other condition the precipitate forms slowly, is "muddy," filters and washes slowly, and shows a decided tendency to run through the filter, while the filtrate generally has a decided color, due apparently to the ammonium phosphomolybdate still in solution.

The above results show that the presence of 5 cc. of nitric acid (sp. gr. 1.07) per 50 cc. of solution gives the most intense color, and this amount has been adopted for this work. Whether or not this relation gives the optimum condition for the precipitation of ammonium phosphomolybdate, remains to be investigated.

EFFECT OF VARYING THE QUANTITY OF MOLYBDATE.

The effect of varying the quantity of molybdate was studied in the same way. The standard and the solution to be read were identical in all particulars except that in the standard the amount of molybdate present in 50 cc. was always 4 cc., while in the other solution the amount of molybdate varied.

TABLE VI.—EFFECT OF VARYING THE QUANTITY OF MOLYBDATE ADDED.

Molybdate +	Na_2HPO_4 +	HNO_3 =	Na_2HPO_4 +	molybdate +	HNO_3.
Cc.	Cc.	Cc.	Cc.	Cc.	Cc.
2	1	5	0.85	4	5
4	1	5	1.00	4	5
6	1	5	1.15	4	5
8	1	5	0.97	4	5
12	1	5	0.96	4	5

The results show considerable differences due to varying the amount of molybdate. These differences are not as great nor is the maximum point as well defined as with different amounts of nitric acid, and there seems to be no reason for changing the amount of molybdate adopted by Woodman and Cayvan as giving the most satisfactory results.

From the foregoing results it appears reasonably certain that in order to obtain reliable and comparable results the standard and the unknown solution must always contain the same quantities of nitric acid and of molybdate and be at the same temperature.

Should different workers use different amounts of reagent, their results could not be strictly comparable.

EFFECT OF FILTER-PAPER.

In the experiments on the removal of silica and also in some of those on the loss of phosphoric acid on evaporation of the solution, it was observed that the readings were higher than they should have been. As all the work was done in platinum dishes the only point where other material could get in was where the solutions were filtered to remove silica. In order to determine if anything is taken up from the filter, solutions of various strength were passed through 7 cm. S. & S. No. 590 paper with the following results:

Parts per million before filtering.	Parts per million after filtering.	Gain, parts per million.
1	1.16	0.16
1	1.14	0.14
2	2.12	0.12
2	2.17	0.17
5	5.01	0.01
5.5	5.50	0.00

The filters were washed until filtrates had a volume of 50 cc. each. The results indicate that in passing through the filter these nitric acid solutions of phosphates have taken up silica, phosphoric acid or organic matter equal to an average reading of 0.15 part per million in four cases, while in two experiments there is no apparent gain. It seems probable that in these latter cases the amount taken up from the paper, is masked by incomplete removal of the phosphoric acid from the paper, in the volume of wash-water used. Beyond a doubt filtration introduces a plus error, which may only be apparent in very dilute solutions. Results given in this paper have been corrected in accordance with the above data.

REMOVAL OF SILICA.

As it is necessary to remove silica from the solution before reading, it was thought that this might be most expeditiously and certainly accomplished by treatment with hydrofluoric acid.

Repeated trials, however, showed that this is not true. While the silica was completely removed finally, it was found that it was necessary to remove all hydrofluoric acid before standardizing, as the smallest quantity of fluorides prevented completely the development of the color. As at least three evaporations with nitric acid were required to accomplish the removal of hydrofluoric acid, the standard procedure of evaporation with nitric acid and drying at 100° for two hours was returned to.

The writer's experience confirms the statement of Woodman and Cayvan that a single evaporation removes completely the silica from the solution in those cases where lime and magnesia salts are absent, but where lime and magnesia salts are present in considerable quantities, the amount of silica remaining in solution after one evaporation and filtration is too great to be neglected.

For the study of these points a solution of sodium silicate was prepared which, by gravimetric analysis, gave from first evaporation and filtration, 266 parts per million SiO_2; second evaporation and filtration, 2 parts per million SiO_2; third evaporation and filtration, 0 part per million SiO_2; total, 268 parts per million SiO_2.

The filtrate from the third evaporation contained no silica by the colorimetric method. 250 cc. of this silicate solution were transferred and made up to 1 liter, with the view of obtaining a solution containing about as much dissolved silica as is found in many soil extracts.

By calculation from the above determinations this contained 67 parts SiO_2 per million; first evaporation and filtration removed 63 parts SiO_2 per million; second evaporation and filtration removed 2 parts SiO_2 per million; total recovered, 65 parts SiO_2 per million.

By the colorimetric method the solution contained 65 parts SiO_2 per million.

The filtrate from the first evaporation contained, colorimetrically, less than 0.05 part per million, average of four determinations. The filtrate from the second evaporation contained, colorimetrically, less than 0.1 part per million. The filtrate from the third evaporation contained, colorimetrically, less than 0.1 part per million.

In order to determine the effect of the presence of lime and magnesia salts, a solution containing 25 mg. of calcium nitrate and 25 mg. of magnesia was added to portions of silicate solution and silica determined colorimetrically as well as gravimetrically.

Gravimetrically obtained: First evaporation and filtration removed 63 parts SiO_2 per million; second evaporation and filtration removed 5 parts SiO_2 per million; total, 68.

Colorimetrically obtained: 67 parts SiO_2 per million; calculated, 67 parts SiO_2 per million.

Filtrate from the first evaporation gave, colorimetrically, 1.42 parts SiO_2 per million. Filtrate from the second evaporation gave, colorimetrically, 0.1 part SiO_2 per million. Filtrate from the third evaporation gave, colorimetrically, less than 0.1 part SiO_2 per million.

From these results it appears that in the absence of lime and magnesia salts the silica left in most soil solutions after one evaporation may be neglected, but in the presence of these salts two evaporations are necessary.

THE COLORIMETRIC DETERMINATION OF SILICA.

In their study of the effect of silica on the development of color, Woodman and Cayvan[1] found that while some color was developed instantly, it did not reach the maximum intensity in less than from one and one-half to two and one-half hours, and their results further show that the color due to the formation of the ammonium silico-molybdate is about one-tenth that produced by an equivalent amount of ammonium phosphomolybdate. This reaction apparently was used first by Jolles and Neurath[2] for the determination of silica in waters. For our determination of silica a solution of sodium silicate was prepared and the silica determined gravimetrically. Portions of this solution were compared with the standard phosphate solution under identical conditions as to temperature, nitric acid, molybdate solution, and volume. The data obtained are given in the following table:

TABLE VII.—READINGS OF SiO_2 IN TERMS OF P_2O_5.

Preliminary Series.

Mg SiO_2 in solution read.	Mg. P_2O_5 required to equal color produced by SiO_2.	1 mg. SiO_2 equals mg. P_2O_5.
0.10	0.19	1.90
0.10	0.175	1.75
0.20	0.35	1.75
0.20	0.37	1.85
0.30	0.51	1.70
0.30	0.57	1.90

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[1] *Loc. cit.*

[2] *Ztschr. angew. Chem.* (1898), p. 315.

TABLE VII—(*Continued*).

Mg. SiO_2 in solution read.	Mg P_2O_5 required to equal color produced by SiO_2.	1 mg. SiO_2 equals mg. P_2O_5.
0.50	0.92	1.84
0.51	0.90	1.78
0.70	1.35	1.93
0.70	1.28	1.83
1.00	1.80	1.80
	Average,	1.82
	Final Series.	
0.068	0.1265	1.86
0.136	0.2464	1.81
0.204	0.3741	1.83
0.272	0.4785	1.78
0.340	0.5907	1.73
	Average,	1.80

The table shows that the intensity of color produced by the silica is on an average 1.8 times that produced by an equivalent amount of phosphoric acid. That is, the phosphate readings divided by 1.8 or multiplied by 0.55 equals SiO_2.[1] It will be seen from the final results, in which most reliance is placed—as they were obtained after considerable experience with the method—that there is a gradual decrease in this factor with increasing quantities of silica. The time required for the full development of the color was much shorter than found by Woodman and Cayvan, apparently reaching the maximum in less than twenty minutes, after which time it remained stationary for some time and then slowly faded.

On the basis of this work the procedure which I have adopted for the determination of silica and phosphoric acid in soil solutions is as follows:

The water or extract is tested for iron by adding potassium ferrocyanide to the acidified solution. The absence of interfering amounts of iron having been shown, a measured volume of the water or soil extract is freed from suspended matter by filtration or by passing through a Chamberland filter (reject the first 100 cc. that passes) or by evaporating to dryness and filtration, or in some cases where the water is but slightly turbid the turbidity or color is corrected for by determining its amount in terms of the

[1] These results differ greatly from those given by Woodman and Cayvan, but so far no time has been available for further study of this point.

standard, the reading thus obtained being afterwards subtracted from the final readings. Add to the clear extract 5 cc. of nitric acid (sp. gr. 1.07) and 4 cc. of molybdate solution. Place in the camera, allow ten to thirty minutes for development of color and compare with a standard phosphate solution, which may conveniently contain 10 parts per million of phosphorus pentoxide and be contained in a sliding tube connected by rubber tubing with a side neck tube graduated in cubic centimeters within the camera. (The color of the standard is not affected by the rubber tube during one working day, but the standard should be made fresh each day.) The readings thus obtained (several should be made and the average taken) minus the reading for turbidity, when calculated to a volume of 100 cc., equals $P_2O_5 + SiO_2$ in parts per million of solution.

Another measured portion of the water or extract is evaporated to dryness twice with a filtration between the evaporations in a porcelain or platinum dish with 3 cc. nitric acid (sp. gr. 1.07) plus a little magnesium nitrate,[1] heated two hours in a water oven, 5 cc. nitric acid (sp. gr. 1.07) added, filtered, washed to about 45 cc., placed in a camera and compared. If colored, the reading is noted, and is finally subtracted from the total reading. Add 4 cc. of ammonium molybdate and thoroughly mix. Place in the camera and compare after two to five minutes. The corrected reading calculated to volume of 100 cc. is P_2O_5 in parts per million of solution. This reading subtracted from the $SiO_2 + P_2O_5$ reading and the difference multiplied by 0.55 gives the silica.

Where the original solution is too much colored with organic matter to be accurately corrected for by reading the color thus produced against the standard phosphate solution, it is necessary to evaporate with about 0.1 gram magnesium nitrate[1] and burn off the organic matter. take up with water + 3 nitric acid, evaporate to dryness and heat two hours in the water oven. Add 5 cc. nitric acid and proceed as above. Readings = P_2O_5. In this case silica is not determined.[2]

The results given in the following table have been obtained in the course of the work.

[1] In solutions containing sufficient base to form normal phosphates with all the phosphoric acid, the addition of magnesium nitrate appears to be unnecessary.

[2] Or the organic matter may be destroyed by treating with aqua regia in the presence of sufficient base to prevent loss of phosphoric acid.

TABLE VIII.—DETERMINATION OF $SiO_2 + P_2O_5$ IN MISCELLANEOUS SAMPLES.

	SiO_2 present.	SiO_2 found.	P_2O_5 present.	P_2O_5 found.
	Parts per million.		Parts per million.	
Sodium phosphate solution, No. 1	....	....	49.6	48.5
" " " " 2	....	....	99.1	101.4
Sodium silicate solution	182.0	180.5	...	....
Soil extract, No. 13	....	24.4	....	2.0
" " " 14	....	23.4	....	2.95
" " " 15	....	21.2	....	2.95
" " " 16	....	19.1	....	2.95
" " 1st foot	....	17.9	....	7.3
" " 2nd "	....	8.2	....	1.0
" " 3rd "	....	7.8	....	3.1
" " 4th "	....	11.9	....	1.4
" No. 2806, sandy truck soil	....	2.0	....	10.0
" " 2795, loam soil	....	38.0	....	8.0
" " 3, clay soil	....	30.0	....	8.0
" " 2804, " "	....	28.0	3 grav.	4.0
Sodium phosphate solution, original solution[1]				73.1
" " " first 50 cc. through Chamberland filter				59.1
" " " second 50 cc. " " "				67.6
" " " third 50 " " " "				71.8
" " " left in 50 " in " "				80.3
" " " rinsings of " "				80.3
" " " original solution				80.25
" " " first 50 cc. through Chamberland filter				54.9
" " " second 50 cc. " " "				71.8
" " " third 50 " " " "				84.5
" " " left in 50 " in " "				97.2
" " " rinsings of " "				84.5

In pure solutions the method gives very close readings and very accurate results on dilute solutions. The average error has been well within 0.2 part per million of the solution read where these solutions did not contain more than 10 parts per million and the readings fall below 60 scale divisions on the colorimeter tube. This insignificant error of reading may give rise to larger differences when calculated on the basis of the dry soil. Should the solution to be examined contain more than 10 parts per million, its dilution to this strength and subsequent calculation to the basis of the original solution or to the dry soil may so multiply this error of reading as to render the results valueless. This has been a serious handicap to the method. The use of more concentrated solutions

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[1] Readings made for Professor F. K. King.

is obviously the rational way out of the difficulty. It is also obvious that here we are limited to the use of concentrations from which the phosphomolybdate will not precipitate, within an hour or so. As solutions of greater concentration than 10 parts per million cannot be read closely in 25 mm. tubes, with ordinary light, and as larger tubes were not available, I have not tried greater concentrations in larger tubes, but in several experiments using a strong standard (between 50 and 100 parts per million), in shallow depths in the 25 mm. tubes, it was not found possible to read closer than from 0.5 to 1 part per million. This error of reading, when calculated back to the original solution or to the dry soils, gives as great an error as the closer readings of the more dilute solutions, so this line of study was not carried farther.

In addition to this study conducted with known solutions, the method has also been applied to the soil samples sent out this year by the Association of Official Agricultural Chemists. The results thus obtained are given in the following table, with results obtained by the standard methods for determining phosphoric acid. The average total reading in scale divisions and the corrections on each sample, also in scale divisions, are given in the table. These corrections are for original color of the liquid and for filter-paper.

TABLE IX.—PHOSPHORIC ACID SOLUBLE IN DISTILLED WATER. PARTS PER MILLION OF DRY SOIL. 400 CC. OF SOLUTION USED FOR THE DETERMINATIONS.

No.	Average total scale readings.	Correction in scale readings.	Reading due to P_2O.	P_2O_5 colorimetric.	P_2O_5 volumetric.
2	13.5	1.5	12.0	1.50	1.33
3	10.0	1.5	8.5	1.06	0.64
4	10.0	1.5	7.5	0.94	1.26
5	10.0	3.0	7.0	0.87	0.99
6	48.5	5.5	43.0	5.60	5.10
7	23.0	2.5	20.5	2.56	2.63
8	20.0	3.0	17.0	2.12	1.95

The results given are all that the writer has obtained on soils. No determinations have been rejected.

PRECAUTIONS.

The method is so delicate (one scale division means one-half of one part per million on basis of dry soil when the solution is prepared by treating 1 part of soil with 5 parts of water and taking 50 cc. for the determination), and as has been shown there are so many points at which errors may be introduced, that a final word as to the precautions to be observed in handling it may be given with propriety.

The sodium phosphate ($Na_2HPO_4 + 12H_2O$) from which the standard is made must be practically pure, and be free from silica and iron. It is convenient to make a solution containing 100 parts phosphorus pentoxide per liter, and then dilute this to 10 parts per liter for the reading standard. The greatest care should be used in making this standard as it is here where errors count. Ten cc. of the 100 parts per liter solution should be run into a standardized 100 cc. flask from an accurately graduated burette. Make up to volume at 20°-25° C. with distilled water (free from $SiO_2 + P_2O_5$), add 10 cc. of nitric acid (1.07) and 8 cc. of ammonium molybdate and mix thoroughly. This is the standard with which the unknown solutions are to be compared and it should be made fresh each day.

All reagents including distilled water must be kept in Jena glassware, tested from time to time and made fresh when a mixture of them shows color after standing some time.

As the colorimetric tubes may have a slight color themselves, each should be tested and its reading carefully established. This may be done by filling the tubes with distilled water and reading them with a 1 part per million standard.

The standard and the unknown solution must contain, in equal volumes, equal amounts of reagents and be at sensibly the same temperature.

The solution must contain less than 20 parts per million of iron (Fe).

A correction must be established for each package of filter-paper used. This correction is small, but not to be neglected on S. & S. No. 590 paper.

When the solution contains much lime or magnesia it is best to make two evaporations and filtrations before comparing.

Observing all precautions and making all corrections there is a maximum error of ± 2 scale divisions (each scale division = 1 cc.) in the reading. When the soil solution is made by treating 1 part of soil with 5 parts of water and 50 cc. are taken for the determination. the error on the dry soil is ± 2 parts per million ;

when 100 cc. are taken for the determination the error is ± 1 part per million, so that the working errors may only be neglected when at least 200 cc. of solution are taken for the determination.

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A RAPID METHOD FOR DETERMINING SULPHUR IN COAL AND COKE.

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THE necessity for a rapid method of determining sulphur in fuels, led to the investigation of the action of sodium peroxide on coal. This reaction was suggested by Professor S. W. Parr's paper on his calorimeter as given in this Journal, **22**, 646.

It was found that coal and coke, ignited with a liberal excess of the peroxide, left almost no residue insoluble in a faintly acid solution, and it became a question only of a suitable apparatus. Apparatus was required that would be cheap, in which the charge could be easily ignited, and out of which the melt could be quickly dissolved. For coke, a covered nickel crucible of about 30 cc. capacity answered every purpose; but coal had to be confined in a bomb, as it always burned with explosive violence.

ANALYSIS OF COKE.

700 milligrams of finely powdered coke are intimately mixed with 13 grams of sodium peroxide, in a nickel crucible of about 30 cc. capacity. The peroxide must be finely powdered and dry, and should be weighed rapidly and brushed off the watch-glass with a glass brush. The crucible is covered and a 3-inch fuse is inserted under the edge of the cover and extended well into the mixture. The crucible is then supported on a triangle and placed in about ¾ inch of water; the fuse is ignited, and in three or four minutes, when the mass has cooled sufficiently, the crucible and cover are placed in a small beaker and 30 cc. water added. The mass dissolves completely in about two minutes. After rinsing off the crucible and cover, the solution is made just acid with hydrochloric acid, and filtered through a small filter. The filtrate is boiled and precipitated with barium chloride in the usual way.

The fuses are made by nitrating cotton wicking with a mixture o. 1 part fuming nitric acid (sp. gr. 1.50) and 2 parts concentrated