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DETERMINATION OF PHOSPHATES IN NATURAL WATERS.

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THE potability of water is impaired by the presence of decaying organic matter. In this process of decay one of the numerous changes produced is the conversion of organic phosphorus compounds into phosphates. But the presence of phosphates does not necessarily indicate a source of contamination, because they may also be present as a result of waters charged with carbonic acid percolating through the rocks and minerals. Particularly in the case of streams and shallow wells the water may contain a large amount of phosphates derived from the fertilizers being used on the adjacent farms. Even the early investigators held that potable waters might contain a large amount of phosphates. In the case of unpolluted waters containing notable quantities of chlorides and nitrates, they are only condemned in the presence of other contaminating ingredients, so, as an additional source of evidence in aiding us in the interpretation of the analysis of drinking-waters, Woodman and Cayvan[1] have called attention to the desirability of phosphate determinations.

Many methods have been suggested for the determination of phosphates in the presence of silica, but until very recently no satisfactory procedure has been devised. Schreiner[2] presented a colorimetric method by means of which both the silica and phosphates can be very accurately determined when present in small amounts. This method is based on the fact that the silicomolybdate gives different depths of color by varying the conditions of treatment, while the intensity of color, due to phosphomolybdates, is the same under these conditions. If the ammonium molybdate and nitric acid are added one hour apart, the color of the silicomolybdate is half as great as the color produced by adding them simultaneously; that is, 50 cc. of a solution of silica are placed in a flat-bottomed tube and 5 cc. of nitric acid (sp. gr. 1.07) and 4 cc. ammonium molybdate are added and this compared with a standard phosphate solution prepared by adding the same quantities of the reagents and reading after twenty minutes; this is designated the "*a*" reading. If another 50 cc. of the silica solution are taken and 4 cc. of ammonium molybdate are added, and at the end of one hour 5 cc. of nitric acid (sp. gr. 1.07) added and in twenty minutes compared with the standard, we have what is designated the "*b*" reading. In the case where there is no phosphate present the ratio of the "*a*" reading to the "*b*" reading is 2 : 1. If phosphates are present, the difference between the "*a*" and "*b*" readings represent just one-half of the silica coloration and twice this difference subtracted from the "*a*" reading gives the value of the color due to the phosphates.

That 5 cc. is the amount of nitric acid (sp. gr. 1.07) that gives the greatest intensity of color was also ascertained by us before Schreiner's paper came to our notice. In order to test the accuracy of his method and the factor for the determination of silica a

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[1] This Journal, **25**, 1056 (1903).

[2] *Ibid.*, **23**, 96 (1901); **24**, 735 (1902).

silicate solution was prepared by dissolving sodium silicate in water, acidifying with nitric acid and standardizing by determining the silica by volatilizing with hydrofluoric acid. The solution was then diluted until 1 cc. contained 0.1 mg. of SiO_2. Then known amounts of this solution were taken and diluted to 75 cc., and, after adding the reagents, compared with a standard which contained 0.01 mg. of P_2O_5 per 1 cc. From the following table it is evident that for all practical purposes the relation of the "*a*" to the "*b*" readings is 2 : 1 and that the reading for SiO_2 with a P_2O_5 standard is equal to twice the actual value in SiO_2. The heading of the columns are self-explanatory.

TABLE I.

SiO_2 added. Mg.	Readings. "*a*"	"*b*."	Ratio of readings. "*a*"/"*b*."
0.2	41	20	2.05
0.4	82	40	2.05
0.6	122	61	2.00
0.8	162	82	1.98
1.0	198	98	2.02

This method has recently been shown[1] to be applicable to the determination of phosphates in soil and plant extracts. In natural waters, however, as Schreiner himself has pointed out,[2] the phosphates are frequently very low in comparison with the silica and in the application of this method to the determination of phosphates in drinking-waters, relatively a very considerable error may result. In order to ascertain the maximum and minimum amounts of silica in the several types of water in the State of Illinois some 5,000 or 6,000 analyses by the Illinois State Water Survey[3] were carefully examined.

In Table II, the maximum and minimum amounts of SiO_2 expressed in parts per million, are given for the various types of water designated at the head of the columns.

TABLE II.

	River.	Spring.	Deep well.	Shallow well.
Maximum	11.3	65.3	64.2	51.8
Minimum	5.0	2.3	1.8	4.0

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[1] This Journal, **26**, 808 (1904).

[2] *Ibid.*, **25**, 1061 (1903).

[3] Chemical Survey of the Waters of Illinois. Report for years 1897-1902, by A. W. Palmer.

From the data available it appears that the P_2O_5 content ranges between 0.5 and 5.0 parts per million and it is very evident that the silica is in large excess of the phosphates.

It occurred to us that since Schreiner's method gives such good results when the P_2O_5 and SiO_2 are approximately equal or the P_2O_5 in excess, *that if we were to add a quantity of* P_2O_5 *sufficient to bring the* P_2O_5 *content of the water up approximately to that of the* SiO_2, *or in excess of it, that the original amount of* P_2O_5, *and incidentally the* SiO_2, *could be readily and very accurately determined.*

In order to test this a series of solutions was prepared containing known quantities of P_2O_5,[1] varying from 0.01 to 0.5 mg. of P_2O_5 and 0.2 mg. of SiO_2 in 75 cc. of the solution. A second series containing the same quantities of P_2O_5, but with 0.4 mg. of SiO_2 was also prepared. These solutions were then treated with a definite quantity of P_2O_5, the reagents added, and the "*a*" and "*b*" readings taken by means of a standard P_2O_5 solution. It was found that a quantity of P_2O_5, equal to 0.4 mg. or more, would give good results when added to the above concentrations of P_2O_5 and SiO_2, but less than 0.4 mg. proved to be much less satisfactory. So it was concluded to add 0.5 mg. of P_2O_5 to the various concentrations and determine the amounts of P_2O_5 and SiO_2 actually introduced into the solutions by carrying out the method as described by Schreiner.

In Table III are given the experimental data for various concentrations of P_2O_5 and SiO_2, to which 0.5 mg. P_2O_5 were added and the solution diluted to 75 cc. In the first two columns are given the P_2O_5 and SiO_2 content of the solutions in milligrams, while in the next two are the "*a*" and "*b*" readings. In the next three columns are the values of the readings which represent the amount of P_2O_5 added to solutions (0.5 mg.), the original amount of P_2O_5 and of SiO_2 present, while in the last two columns are the original amounts of P_2O_5 and SiO_2, calculated from the "*a*" and "*b*" readings and expressed in milligrams per 75 cc. of solution.

From a comparison of the original content of the solutions, as given in the first two columns of the table and the found values

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[1] A standard solution of Na_2HPO_4 was prepared by dissolving 2 grams of the substance in 1 liter of water and standardizing by the magnesium ammonium phosphate and also by the ammonium phosphomolybdate methods. The solution was then diluted so that 1 cc. contained 0.1 mg. of P_2O_5. This solution was used for preparing our phosphate solutions and also for the preparation of the standards.

TABLE III.—ADDITION OF KNOWN AMOUNT (0.5 MG.) OF P_2O_5 TO SOLUTIONS OF SiO_2 AND P_2O_5.

Constituents present.		Readings.		Readings for			Found.	
P_2O_5. Mg.	SiO_2. Mg	"*a*."	"*b*."	0.5 mg. P_2O_5 added.	P_2O_5. original.	SiO_2. original.	P_2O_5. Mg.	SiO_2. Mg.
0.01	0.20	90	71	50	2	38	0.02	0.19
0.05	0.20	95	75	50	5	40	0.05	0.20
0.10	0.20	100	80	50	10	40	0.10	0.20
0.20	0.20	110	91	50	22	38	0.22	0.19
0.50	0.20	138	120	50	52	36	0.52	0.18
0.01	0.40	130	91	50	2	78	0.02	0.39
0.05	0.40	134	95	50	6	78	0.06	0.39
0.10	0.40	140	100	50	10	80	0.10	0.40
0.20	0.40	150	112	50	24	76	0.24	0.38
0.50	0.40	178	138	50	48	80	0.48	0.40

given in the last two, it will be noticed that there is a very fair degree of accuracy except where the content of P_2O_5 is 0.01 mg. (*i. e.*, 0.13 part per million), but in all others the results are really very satisfactory for such small amounts of P_2O_5 (0.67 to 6.7 parts per million). It is apparent that quantities of P_2O_5 as low as 0.05 mg. in 75 cc., *i. e.*, 0.67 part per million, can be very accurately determined by this means.

This method of adding 0.5 mg. of P_2O_5 to each 75 cc. sample of water was employed in the determination of the P_2O_5 in samples of drinking-water sent to the Water Survey for analysis. A number of the results of the sanitary analysis and the P_2O_5 and SiO_2 determinations are given in Table IV, and the values are expressed in parts per million.

In this paper we have called attention to the confirmation of Schreiner's colorimetric method for the determination of phosphates and silica when the proportion of the latter is not excessively great.

We have extended this method to the determination of phosphates in natural waters, where the proportion of silica to phosphate is frequently large, by the addition of a known quantity of P_2O_5 (0.5 mg. per 75 cc. of sample of water) in order to bring the phosphate content up approximately equal to, or in excess of, the silica.

We have determined the P_2O_5 and SiO_2 in a number of samples of polluted and unpolluted waters.

Table IV.

	Number.	Source.	Residue.	Chlorine.	Free NH$_3$.	Albuminoid NH$_3$.	Nitrites.	Nitrates.	P$_2$O$_5$, parts per million.	SiO$_2$, parts per million.
Unpolluted waters.	12,020	93-ft. well	664.8	2.15	0.026	0.052	0.013	0.547	2.34	14.4
	12,014	150-ft. well	386.8	3.40	2.960	0.280	0.000	0.040	2.86	16.0
	12,021	Lake Michigan	330.8	3.10	0.016	0.152	0.002	0.160	2.08	7.1
	12,023	Sulphur Spring	334.8	2.50	0.166	0.099	0.000	0.120	0.78	19.7
	12,025	Iron Spring	320.4	2.30	0.320	0.082	0.005	0.115	1.72	18.9
	12,050	Ice	30.8	2.30	0.840	0.130	0.060	0.074	0.91	0.9
Polluted waters.	12,052	25-ft. well (dug)	397.2	13.5	0.05	0.316	0.080	0.92	7.54	10.4
	12,034	30-ft. well (dug)	4146.6	13.3	0.05	0.056	0.004	6.80	1.04	13.6
	12,033	40-ft. well (dug)	615.2	45.0	0.03	0.134	0.013	25.00	8.58	11.4
	12,047	45-ft. well (dug)	1050.4	68.5	0.016	0.120	0.010	5.00	7.80	3.2
	12,035	50-ft. well (dug)	1004.0	82.0	0.054	0.098	0.009	40.00	7.02	13.8
	12,049	100-ft. well	564.0	64.5	0.004	0.044	0.001	10.40	3.38	14.4
	12,040	Crystal Lake	294.0	3.0	0.072	0.124	0.028	3.73	1.82	4.1
	12,041	Branch Creek, above septic tank	323.6	5.2	0.112	0.168	0.060	3.54	0.52	0.7
	12,042	Septic tank.	647.2	42.0	2.000	0.528	0.500	5.50	8.06	8.4
	12,043	Branch Creek, below septic tank	328.4	7.0	0.188	0.164	0.065	3.94	0.13	0.7

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