[CONTRIBUTIONS FROM THE LABORATORIES OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY.]

THE SIGNIFICANCE OF PHOSPHATES IN NATURAL WATERS.

BY A. G. WOODMAN.

Received April 14, 1902.

THE determination of phosphates in a drinking-water is a matter which has not received the attention from water analysts that has been given to the estimation of various other constituents. Any one who looks through the literature cannot help noticing how few are the published results of quantitative estimations of the phosphate content of natural waters, apart from mineral waters. Yet this determination, by reason of the conversion of organic phosphorus compounds into phosphates through the processes of decay, is one which might reasonably be expected to throw considerable light on the question of the pollution of natural waters by objectionable material.

The reasons for this dearth of published data are not far to seek. To be of value the amount of phosphate must be known within rather narrow limits. Qualitative tests are not sufficient. The mere presence of phosphates is by no means definite or even confirmatory evidence of organic pollution. Rocks and minerals containing phosphates are found nearly everywhere and traces, at times even considerable quantities, may be dissolved, especially by waters rich in carbonic acid. This, however, does not constitute a serious objection to the utility of the determination. The same is true of many, if not most, of the constituents upon which reliance is placed in judging of the quality of a water. Unpolluted waters often contain notable amounts of nitrates and chlorides and a true judgment can be rendered only after comparison with samples from adjacent but unpolluted sources.

The chief reason, however, has been the lack of an accurate and simple method, sufficiently delicate, and of enough data to work out a standard for comparison. It is even declared, with some authority, that the determination is entirely worthless. Wanklyn says of it:[1] "Much nonsense has been talked about phosphates in drinking-water; and the fact has been overlooked that, except as

[1] "Water Analysis," p. 109 (1891).

infinitesimal traces, they cannot exist along with carbonate of lime in a clear water." And at a later date Thresh remarks:[1] "The difficulty of detecting phosphates, when silica is also present, as is usually the case, the still greater difficulty of estimating the quantity, and the very doubtful value of the information when obtained, has caused most chemists to ignore their presence. Traces may be found in wholesome waters, and their absence affords no proof that a water is free from pollution, hence the determination is useless."

That, in spite of Wanklyn's statement to the contrary, appreciable quantities of phosphates may exist in natural waters along with carbonate of lime, has been shown by Hehner.[2] It is pointed out that, theoretically, from the established solubility of calcium phosphate a water may contain 36.6 parts of phosphorus pentoxide per million; and that water saturated with carbon dioxide, a condition which frequently does exist, may hold in solution as much as 67.5 parts of phosphorus pentoxide in a million, which is quite as large an amount as is the case with several of the mineral constituents usually determined. In an actual case cited the amount of phosphate found was 5.5 parts phosphorus pentoxide per million, and Harvey[3] found 14.7 parts in a well water from the chalk formation.

The second objection, the lack of a simple and accurate process of estimation, is no longer valid since the former gravimetric methods, which were tedious and introduced the liability to serious error in concentrating large volumes of water, have been replaced by colorimetric methods. The colorimetric processes, which are based in general upon the reaction with alkali molybdates, as proposed in 1880 by J. West-Knights[4] and later improved by Lepierre[5] and by Jolles and Neurath,[6] have been critically studied in this laboratory[7] and the method finally adopted seems to solve the problem in a satisfactory manner. The method as applied to colorless waters, for which it is best suited, may, for convenience, be briefly repeated here.

[1] "Water Supplies," p. 170 (1896).
[2] *Analyst*, **5**, 135 (1880).
[3] *Ibid.*, p. 197.
[4] *Ibid.*, **5**, 197 (1880).
[5] *Bull. Soc. Chim.*, **15**, 1213 (1896).
[6] *Monatsh. Chem.*, **19**, 5 (1898).
[7] Woodman and Cayvan: This Journal, **23**, 96 (1901).

Fifty cc. of the water and 3 cc. of nitric acid (sp. gr. 1.07) are evaporated to dryness in a 3-inch porcelain dish on a water-bath. The residue is heated in an oven for two hours at the temperature of boiling water. The dry residue is then treated with 50 cc. of cold distilled water, added in several portions, and poured into the comparison tube. It is not necessary to filter the solution. Four cc. of ammonium molybdate (50 grams per liter) and 2 cc. of nitric acid are added, the contents of the tube mixed, and the color compared, after three minutes, with standards made by diluting varying quantities of the standard phosphate solution (1 cc. = 0.0001 gram phosphorus pentoxide) to 50 cc., and adding the reagents as above. A blank should always be made on the distilled water used for dilution, especially if it has stood for any length of time in glass vessels.

The method as outlined has been used on a number of waters from various sources which have been examined from time to time and the results, together with the figures for the other important determinations usually made are given in the accompanying tables. For convenience they are divided roughly into three classes: waters which may fairly be considered unpolluted; samples of doubtful purity; waters plainly polluted. This classification is based on the amounts of the other constituents rather than on the quantity of phosphate in order to determine the valuation and limits of the latter. Table IV gives the results of analysis of several samples from the same general source, showing the correspondence of the various constituents under varying conditions. The results are given in all cases in parts per million.

On examining the results it will be observed that the amount of phosphate shows considerable variations for a given class of waters, which might indeed well be expected when we take into consideration the readiness with which it is absorbed or precipitated. It has been found too, that it seems to be more or less dependent upon the amount of iron, an instance of which will be found in No. 20 of Table III; a part of the phosphate has been removed, no doubt, by sedimentation as ferric phosphate.

In Table I samples 2 and 3 had been standing in the collecting bottles for some time before being analyzed, which would have a tendency to make the results too high. Sample 9 is interesting by comparison with a sample from the same source (III, 8) taken

TABLE I.—UNPOLLUTED WATERS.

No.	Locality.	Residue.	Free ammonia.	Albuminoid ammonia.	Nitrites.	Nitrates.	Chlorine.	Hardness.	Phosphorus pentoxide.	Remarks.
1	Southboro, Mass	....	0.008	0.060	0.000	0.000	1.8	11.1	0.90	Spring in the woods.
2	Newburyport, Mass....	50.0	0.002	0.024	0.001	0.400	9.2	....	2.7	City supply—driven wells.
3	Belmont, Mass	....	0.006	0.008	0.001	0.500	3.29	....	1.7	Spring.
4	Lowell, Mass.....	102.0	0.012	0.046	0.000	0.400	2.7	....	0.54	City supply.
5	Winsted, Conn.....	31.5	0.017	0.020	0.000	0.000	4.2	....	0.44	Spring—no contamination.
6	Poughkeepsie, N. Y...	....	0.003	0.010	0.002	1.250	5.8	....	0.4	Purified water.
7	Dublin, N. H.....	....	0.006	0.016	0.000	0.000	1.6	8.0	0.08	
8	Dublin, N. H.....	....	0.008	0.006	0.000	0.080	0.8	9.0	0.14	
9	Jamaica Pond, Mass...	....	0.014	0.406	0.000	0.000	8.0	....	0.20	Heavy growth of organisms —*Oscillatoria prolifica.*
10	Marion, Mass	....	0.004	0.120	0.000	0.600	94.0	....	0.70	Near salt water.
11	Marion, Mass	....	0.002	0.002	0.008	0.400	11.2	30.9	0.80	Artesian well.
12	Marion, Mass	....	0.000	0.024	0.000	0.150	12.0	55.0	0.14	Milky with clay.
13	Bedford, Mass	....	0.002	0.008	0.000	0.100	3.0	38.0	0.80	
14	Essex, Mass	....	0.018	0.070	0.001	0.350	7.0	21.0	0.0	Cistern, unpolluted.
15	Essex, Mass	85.0	....	0.096	....	0.560	10.5	....	0.54	Spring near tide-water.

TABLE II.—DOUBTFUL WATERS.

No.	Locality.	Residue.	Free ammonia.	Albuminoid ammonia.	Nitrites.	Nitrates.	Chlorine.	Hardness.	Phosphorus pentoxide.	Remarks.
1	Canton, Mass.....	....	0.002	0.032	....	1.600	40.0	....	0.4	
2	Canton, Mass.....	61.0	0.005	0.024	0.000	1.600	7.2	....	1.6	
3	Winsted, Conn.....	200.0	0.240	0.070	0.019	4.900	25.4	....	0.26	
4	Cambridge, Mass.....	116.0	0.004	0.032	0.000	3.000	8.24	....	1.8	
5	Essex, Mass.....	214.0	0.000	0.052	0.002	4.500	16.0	...	3.0	Pump and watering trough near road.
6	Canaan, N. H.....	....	0.086	0.154	0.015	2.500	4.0	....	1.6	
7	Canaan, N. H.....	....	0.012	0.068	0.000	2.000	4.0	....	1.6	
8	Bedford, Mass.....	72.5	0.000	0.012	0.003	1.100	4.4	26.0	0.80	Milky with clay.
9	Jamaica Plain, Mass....	109.5	0.032	0.002	0.000	2.000	12.0	47.0	0.60	On hill—few houses near.
10	Boxford, Mass.....	....	0.000	0.032	0.000	0.900	6.0	61.0	1.2	Well near road.
11	Boxford, Mass.....	....	0.000	0.024	0.000	1.900	2.5	20.0	1.8	Well at foot of hill.
12	Hopkinton, Mass.....	. ..	0.004	0.000	0.000	0.450	4.8	....	2.2	
13	Essex, Mass.....	....	0.014	0.092	0.000	0.560	....	41.6	1.4	Well in pasture.
14	Mattapoisett, Mass.....	....	0.004	0.026	0.016	1.850	19.0	41.6	0.4	
15	Wenham, Mass.....	188.0	0.008	0.106	0.030	0.500	10.8	....	1.7	

TABLE III.—POLLUTED WATERS.

No.	Locality.	Residue.	Free ammonia.	Albuminoid ammonia.	Nitrites.	Nitrates.	Chlorine.	Hardness.	Phosphorus pentoxide.	Remarks.
1	Newburyport, Mass...	322.5	0.026	0.090	0.008	42.5	57.1	....	3.6	
2	Beverly, Mass.....	227.0	....	0.028	0.001	16.000	20.1	....	3.8	
3	Everett, Mass.....	....	0.008	0.018	0.004	19.000	26.1	....	6.8	Spring water sold in city.
4	Essex, Mass.....	....	0.010	0.050	0.010	10.000	36.7	....	8.6	Town pump.
5	Framingham, Mass...	691.0	0.930	0.080	0.010	50.000	72.2	....	3.8	Well in barnyard.
6	Newburyport, Mass...	88.0	0.010	0.016	0.000	7.000	20.4	....	1.8	Driven well.
7	Canton, Mass.....	...	0.000	0.034	0.000	11.000	46.1	....	3.8	
8	Jamaica Pond, Mass...	67.5	0.010	0.134	0.003	0.220	8.4	....	3.7	Pond practically free from *Oscillatoria*.
9	Essex, Mass	200.0	0.000	0.036	0.000	2.250	32.5	....	8.0	Well near the house.
10	Poughkeepsie, N. Y...	20.6	0.013	0.150	0.006	1.750	5.2	....	1.4	Brook contaminated by sewage effluent.
11	Poughkeepsie, N. Y...	21.3	0.029	0.140	0.011	0.600	11.3	....	3.8	Brook contaminated by sewage effluent.
12	Poughkeepsie, N. Y...	....	0.004	0.046	0.010	6.500	25.1	....	9.0	Brook contaminated by sewage effluent.
13	Bedford, Mass.....	203.0	0.004	0.108	0.000	5.500	6.7	57.0	1.4	
14	Canaan, N. H.....	....	0.006	0.112	0.002	15.000	32.0	110.0	4.0	
15	Long Island, N. Y....	836.0	0.006	0.036	0.003	34.000	80.0	400.0	3.2	Artesian well.
16	Newport, R. I.....	142.0	0.008	0.026	0.001	3.750	16.0	46.0	2.0	
17	Annisquam, Mass.....	....	0.014	0.006	0.000	2.250	35.0	38.0	2.4	
18	W. Falmouth, Mass...	....	0.084	0.100	0.010	4.500	38.0	43.0	2.4	
19	Essex, Mass.....	....	0.014	0.054	0.002	8.330	41.0	104.5	13.3	Well—large henyard on slope above.
20	Natick, Mass.....	....	0.120	0.080	0.022	16.600	47.8	....	2.6	Sewage effluent—high in iron.

TABLE III.—POLLUTED WATERS (*Continued*).

No.	Locality.	Residue.	Free ammonia.	Albuminoid ammonia.	Nitrites.	Nitrates.	Chlorine.	Hardness.	Phosphorus pentoxide.	Remarks.
21	Malden, Mass.....	....	0.000	0.016	0.002	7.500	60.8	81.4	7.4	Well surrounded by drains and cesspools.
22	Canton, Mass.....	113.0	0.000	0.038	0.000	3.500	23.5	36.2	5.0	Used only for garden.
23	Newport, R. I.....	....	0.248	0.068	0.500	8.500	83.0	121.1	4.6	Typhoid fever among families using this well.
24	Marblehead, Mass....	360.0	0.000	0.080	0.018	7.500	47.0	140.4	5.6	Surrounded by houses.
25	Marblehead, Mass....	600.0	0.000	0.080	0.008	10.000	56.0	264.5	6.8	Surrounded by houses.
26	Thompson, Conn.....	....	0.000	0.008	0.000	1.850	4.04	42.9	6.6	
27	Thompson, Conn.....	...	0.042	0.046	0.000	2.450	1.04	20.8	3.6	
28	Essex, Mass.....	235.0	0.008	0.040	0.000	3.500	46.6	74.3	4.7	
29	Essex, Mass.....	520.0	0.016	0.088	0 001	5.250	90.6	205.6	7.6	Sink drain within 4 feet of well.
30	Boxford, Mass.....	....	0.002	0.032	0.000	20.000	24.1	132.0	4.8	Well about 50 feet from barn.
31	Dartmouth, Mass.....	....	0.000	0.008	0.000	2.850	8.2	27.3	3.3	
32	Hopkinton, Mass.....	....	0.006	0.004	0.008	7.000	5.9	....	5.4	
33	So. Essex, Mass.....	409.0	0.050	0.078	0.007	7.500	93.8	151.4	4.2	Well between house and barn.
34	So. Essex, Mass.....	290.0	0.116	0.130	0.004	11.200	37.3	180.2	4.9	Well in yard near house.
35	Essex, Mass.....	....	0.000	0.012	0.000	3.050	40.6	60.0	6.0	Spring on slope from cemetery.
36	W. Falmouth, Mass..	169.0	0.000	0.026	0.000	4.500	39.0	45.7	4.0	
37	Stoneham, Mass.....	....	0.082	0.028	0.001	24.000	14.0	125.6	3.2	Spring.cesspool found beside it.
38	Southboro, Mass.....	124.0	0.000	0.000	0.000	3.000	10.0	....	4.0	Well in pasture.
39	Jamaica Plain, Mass..	....	0.010	0.030	0.001	4.250	30.8	114.3	6.6	Well in cellar of house.
40	Jamaica Plain, Mass..	....	0.000	0.028	0.000	4.000	19.2	70.7	4.9	21 feet deep, near house.
41	Jamaica Plain, Mass..	....	0.010	0.024	0.000	4.000	20.2	71.3	4.6	108 feet deep, in barnyard.
42	Cambridge, Mass.....	....	0.034	0.028	0.160	19.000	17.5	126.0	1.3	

TABLE IV.

No.	Locality.	Residue.	Free ammonia.	Albuminoid ammonia.	Nitrites.	Nitrates.	Chlorine.	Hardness.	Phosphorus pentoxide.	Remarks.
1	Sayre, Pa	266.0	0.001	0.018	0.001	1.500	9.7	183.4	2.9	Supply well after pumping out six times.
2	Sayre, Pa	293.0	0.000	0.000	0.000	1.600	12.4	196.6	3.1	Pump in driven well back of station.
3	Sayre, Pa	121.0	0.018	0.042	0.000	0.120	5.0	79.4	0.70	River at "intake."
4	Sayre, Pa	257.0	0.000	0.006	0.001	1.500	9.8	182.8	3.1	Supply well after pumping out nine times.
5	Sayre, Pa	106.0	0.005	0.058	0.000	0.070	4.4	76.8	0.70	House faucet from tap in town.
6	Sayre, Pa	258.0	0.000	0.022	0.001	1.440	9.7	182.8	3.1	Supply well after pumping out three times.

under different conditions, as showing the change in phosphate content through the increase of organic life.

The amount of phosphate and its variation seem to follow the same general line as the other mineral constituents which either accompany the polluting material or are produced by its decay, especially the nitrates and chlorides. It is not, however, so delicate an indicator as these. This correspondence is well shown in the samples in Table IV and also in samples 10 to 12 of Table III, where the increased pollution, as evidenced by the gradual increase in chlorine, is accompanied by increased phosphate.

The results obtained by the colorimetric method would seem to indicate that the limit of 0.5 part of phosphorus pentoxide in a million, as given by Hehner for unpolluted waters, is rather low. A safer amount would be 1.0 part, although the average would doubtless be lower than this.

The highest amount found was 13.3 parts, in sample 19 of Table III. The same rather surprising cases were found as noticed by Hehner in which the amount of phosphate is very much lower than would be expected from the source of the water and the other constituents determined, which may be due to the character of the soil through which the water has percolated. Even with all the drawbacks which are noted there can be no question, in view of the figures given above, that the presence of phosphates in a water in any quantity is significant of pollution, and the determination must be considered as another link (of which we have none too many, anyway) in the chain of circumstantial evidence by which we are often compelled to judge the purity of a water.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY,
BOSTON, MASS., March, 1902.

[CONTRIBUTIONS FROM THE SHEFFIELD LABORATORY OF YALE UNIVERSITY.]

RESEARCHES ON THIOCYANATES AND ISOTHIOCYANATES.

(FIFTH PAPER.)

BY HENRY L. WHEELER AND GEORGE S. JAMIESON.

Received April 14, 1902.

IN this paper we describe a number of exceptions to the rule that the only halogen compounds which undergo any material