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

THE DETERMINATION OF PHOSPHATES IN POTABLE WATERS.

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THE estimation of phosphates is a part of the sanitary examination of waters which has been somewhat neglected in the past, doubtless because the ordinary methods of determination are quite tedious and because the exact significance to be attributed to the presence and amount of phosphates is a question still in abeyance. There can be no question, however, in consideration of the probable decomposition and oxidation of the organic phosphorus compounds in animal excretions, that an excessive amount of phosphates in a water, unless otherwise accounted for, is an indication of pollution. If then the amount could be estimated by a method sufficiently simple and rapid, enough data might readily be gathered to render the determination of much greater value than at present. Especially would this be true in comparing several waters from the same locality.

Repeated trials of methods which have been proposed have shown that there is none which is perfectly satisfactory for accurate and rapid work. The extremely small quantities of phosphate found even in polluted waters would seem to preclude the use of gravimetric methods. Such methods, however, have been used. Hehner,[1] and also Harvey,[2] concentrate a large quantity of the water and determine the phosphate gravimetrically as ammonium phosphomolybdate. All gravimetric methods are objectionable on account of the time required. Furthermore, not being very delicate, they necessitate considerable concentration, which, as will be shown later, almost invariably occasions a loss of phosphate. Phipson[3] precipitates the phosphate from a large volume of water by means of alum and an excess of ammonia, making the final precipitation with ammonium molybdate. The process is a long one and experiments with a more delicate method showed that the precipitation of the phosphate is not complete.

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[1] *Analyst*, 4, 23; and 5, 135.

[2] *Ibid.*, (1880), 197.

[3] *Chem. News*, 56, 251.

On the whole, the colorimetric methods seem best adapted for the determination. Several such methods have been proposed, based on the color given to dilute phosphate solutions by ammonium molybdate in the presence of nitric acid. Lepierre[1] evaporates a liter of water, dehydrates the silica by repeated evaporations with nitric acid, ignites strongly, and filters. The phosphate in the filtrate is estimated colorimetrically by ammonium molybdate. Jolles and Neurath[2] use potassium molybdate instead of the ammonium salt, and Jolles[3] has applied the method to the determination of phosphoric acid in water, removing the silica from the residue obtained by the evaporation of a liter of water by ignition at 130° C. These methods are open to the same objections as the gravimetric methods, namely that by requiring the evaporation of large quantities of water they introduce serious liability to error and are too tedious to be of general use. Furthermore, the temperature at which the residue should be ignited to remove silica is a matter of importance, especially when dealing with small amounts. In view of these considerations it was deemed advisable to make a critical study of the colorimetric methods.

APPARATUS AND REAGENTS.

Ammonium Molybdate.—50 grams of the pure neutral salt were dissolved in a liter of distilled water.

Nitric Acid (sp. gr. 1.07).—Approximately one part of acid (sp. gr. 1.42) to five parts of water.

Standard Phosphate Solution.—0.5324 gram of pure crystallized sodium phosphate ($Na_2HPO_4.12H_2O$) was dissolved in freshly distilled water, 100 cc. of nitric acid (1.07) added, and the whole diluted to 1 liter. This solution is diluted to make the standards. One cc. = 0.0001 gram P_2O_5. The solution keeps without change for several months if preserved in well-stoppered bottles of hard glass; after a longer time it becomes slightly stronger, owing to the silica dissolved from the glass.

Standard Silica Solution.—About 5 grams of precipitated and washed silica were dissolved in an excess of sodium hydroxide made from metallic sodium. The solution was made faintly acid

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

[2] *Monatshefte*, **19**, 5 (1898).

Archiv. f. Hygiene, **34**, 22 (1899).

with nitric acid, diluted to a definite volume, and the silica determined in an aliquot part. The standard solution was made by diluting this strong solution until 1 cc. = 0.001 gram SiO_2.

It was found that sodium or potassium molybdate offered no particular advantages over the ammonium salt. The color obtained was no more intense and was distinctly greener, which made the reading of the standards much more difficult. It was found also that for a given amount of the phosphate solution the depth of color and the rapidity with which it developed depended to a certain extent upon the quantity of reagents used. The best results were obtained by the use of 4 cc. of the ammonium molybdate solution and 2 cc. of the nitric acid.

For comparing the colors the ordinary Nessler tubes were used at first, but it was found that if tubes of too small diameter were used the colors were not easily read; if of too large diameter the delicacy of the reaction is considerably decreased. The tubes which have been found most satisfactory have a capacity of 100 cc. They are of hard, white glass, about 2.5 cm. in diameter and 24 cm. long to the 100 cc. mark. The color is a rather difficult one to read closely and for very accurate readings probably some form of colorimeter could be used to advantage. For any but the most refined work, however, it will be found amply sufficient to compare the tubes by a north light against a reflecting white surface, such as a pure white unglazed porcelain tile supported at an angle of about 40°. This procedure was followed in all this work, and was found most practical where a number of tubes are to be compared rapidly.

Using no greater precautions than those just described, the delicacy of the test is considerable. If care is taken to choose two tubes, identical in all respects, it is possible to detect 0.002 cc. of the standard phosphate solution in 50 cc. of water. If the tubes are heated to 60° C. 0.001 cc. can be read. The delicacy of the reaction is therefore sufficient to show the presence of 1 part of phosphate as P_2O_5 in 500,000,000 parts of water. On the other hand, comparatively large quantities of phosphate may be present in 50 cc. of water, without causing precipitation or turbidity on the addition of the reagents except after standing a considerable time. On account of the difficulty in matching the more intense colors no higher standard than 10 cc. of the standard solution in 50 cc. of water is ever used, and it has been determined by direct experiment that a standard as high as this will not become turbid at room temperature for twelve or fifteen hours. The color of the phosphate standard is an additive property; it makes no difference, apparently, whether the higher standards are made up directly or by the addition of more of the standard solution to the lower standards.

The question of the permanency of the phosphate standards was one of the first ones investigated. Lepierre, in the article previously cited, stated that the phosphate standards can be preserved for several months without change. Careful comparison of a number of standards from day to day, however, showed that this was not strictly true. The change in some of the higher standards while slight was still distinctly noticeable when carefully observed, and in others, especially the lower ones, the color faded so much in two or three days that the standards were rendered useless. Nor was any other substance found giving the right color which was suitable for the preparation of permanent standards. The most satisfactory was a dilute solution of picric acid, which gave a yellowish green color very similar to the phosphate color. But it was found impossible to keep even these standards in glass tubes since the solvent action on the alkali of the glass was sufficient to form a slight amount of the alkali picrate, which has a more intense color than the picric acid itself; hence, the standards slowly increased in color. The attempt was therefore abandoned and fresh phosphate standards were used for all comparisons.

STUDY OF THE PHOSPHATE REACTION.

For a given volume of water and a definite amount of reagents the depth of the phosphate color is a function of two factors; namely, the amount of phosphate present and the temperature. To determine the exact effect of the latter for the conditions employed in this work, readings of various phosphate standards were made at different temperatures. Differing amounts of the standard solution were diluted to 50 cc., and, after the addition of the reagents, were heated gradually in a water-bath from 20° to 60° C. Readings were taken every 5°. If the reagents are added after heating, the colors are not so clear. The heating was not carried beyond 60° because above this temperature the standards become cloudy and the higher standards tend to precipitate. The maximum color is given between 90° and 100°, but the tendency to precipitation renders the reading at this temperature impracticable. The most satisfactory colors are obtained at 20°–30°, practically at room temperature. A variation of a few degrees causes only a slight error. The results are given in the following table :

Amounts phosphate added.	25°.	30°.	35°.	40°.	45°.	50°.	55°.	60°.
6 cc·········	6.2	7.2	7.7	8.2	8.7	9.6	...	10.2
	6.2	7.2	7.8	8.3	8.7	10.2	10.4	10.7
	6.2	7.7	8.2	9.0	9.2	9.7	10.4	10.3
Average	6.2	7.3	7.6	8.5	9.0	9.8	10.4	10.5
5 cc·········	5.1	5.9	6.6	7.3	7.8	8.0	8.6	9.6
	5.1	5.3	6.1	7.2	7.9	8.4	8.6	9.4
	5.1	5.2	6.3	7.1	8.0	8.3	8.7	8.9
	5.1	5.6	6.6	7.0	7.8	8.5	8.6	9.2
Average	5.1	5.5	6.4	7.2	7.9	8.3	8.6	9.2
4 cc·········	4.1	4.7	5.1	5.4	6.4	6.6	6.9	7.1
	4.1	4.8	5.1	5.5	6.4	6.5	6.8	7.3
	4.1	4.8	5.1	5.5	6.4	6.6	7.0	7.4
Average	4.1	4.7	5.1	5.5	6.4	6.6	6.9	7.2
3 cc·········	3.1	3.4	3.9	4.5	5.1	5.7	5.8	6.2
	3.4	3.7	4.4	4.7	5.2	5.3	5.7	5.9
	3.2	3.7	3.9	4.3	4.9	5.4	5.5	6.2
Average	3.2	3.6	4.1	4.5	5.1	5.5	5.7	6.1
2 cc·········	2.2	2.5	2.7	2.9	3.1	3.4	3.6	3.9
	2.2	2.5	2.8	3.1	3.2	3.4	3.7	3.9
	2.4	2.6	2.9	3.0	3.3	3.4	3.5	3.9
Average	2.2	2.5	2.8	3.0	3.2	3.4	3.6	3.9
1 cc·········	1.1	1.2	1.4	1.5	1.5	1.7	1.9	1.9
	1.1	1.2	1.3	1.4	1.5	1.7	1.8	1.8
	1.1	1.2	1.4	1.5	1.5	1.5	1.7	2.0
Average	1.1	1.2	1.4	1.4	1.5	1.6	1.8	1.9
0.7 cc······	0.75	0.80	0.85	0.95	1.1	1.2	1.25	1.27
	0.75	0.80	0.85	0.90	1.05	1.15	1.25	1.28
	0.75	0.80	0.83	0.95	1.05	1.15	1.20	1.25
Average	0.75	0.80	0.85	0.93	1.05	1.17	1.22	1.26

Amounts phosphate added.	25°.	30°.	35°.	40°.	45°.	50°.	55°.	60°.
0.5 cc......	0.60	0.65	0.70	0.80	0.90	0.95	1.05	1.10
	0.60	0.60	0.65	0.75	0.85	0.90	0.95	0.95
	0.60	0.65	0.70	0.75	0.85	0.85	0.95	0.95
Average	0.60	0.65	0.70	0.77	0.87	0.90	0.98	1.01
0.4 cc......	0.45	0.50	0.55	0.65	0.70	0.75	0.80	0.80
	0.45	0.55	0.55	0.57	0.60	0.65	0.70	0.70
	0.45	0.55	0.55	0.58	0.65	0.67	0.70	0.70
Average	0.45	0.53	0.55	0.60	0.65	0.68	0.72	0.72
0.3 cc......	0.33	0.36	0.39	0.44	0.48	0.58	0.63	0.68
	0.33	0.36	0.39	0.45	0.50	0.55	0.60	0.65
	0.33	0.36	0.39	0.44	0.54	0.58	0.60	0.65
Average	0.33	0.36	0.39	0.44	0.51	0.57	0.61	0.66
0.2 cc......	0.23	0.27	0.31	0.32	0.34	0.37	0.38	0.39
	0.23	0.27	0.30	0.33	0.33	0.36	0.38	0.39
	0.23	0.27	0.30	0.33	0.34	0.37	0.38	0.39
Average	0.23	0.27	0.30	0.33	0.34	0.37	0.38	0.39
0.1 cc......	0.11	0.13	0.14	0.16	0.17	0.18	0.19	0.20
	0.12	0.13	0.14	0.16	0.17	0.18	0.19	0.20
Average	0.11	0.13	0.14	0.16	0.17	0.18	0.19	0.20

Some of the results are shown graphically in Fig. 1, in which readings have been taken as ordinates and temperatures as abscissas. The curves show slight irregularities, due to the difficulty of reading exactly. The increase in color with increased temperature is considerable, double in the higher standards. All of the standards on cooling go back to less than their original color. No case of precipitation occurred, although some of the highest standards were too turbid to be read easily.

Several of the methods previously proposed for the determination of phosphates involve the concentration of the water, followed by heating at various temperatures. Preliminary experiments had shown the liability to loss during such procedure, and the point was further investigated. One liter of water, containing 5 cc. of phosphate solution and 2 cc. of nitric acid, was evaporated to dryness ; a loss of 16 per cent. of the phosphate occurred. Phosphate standards made up in a volume of 50 cc., with varying amounts of nitric acid, were evaporated to dryness and some of them heated in an air-bath at 100° for periods varying from

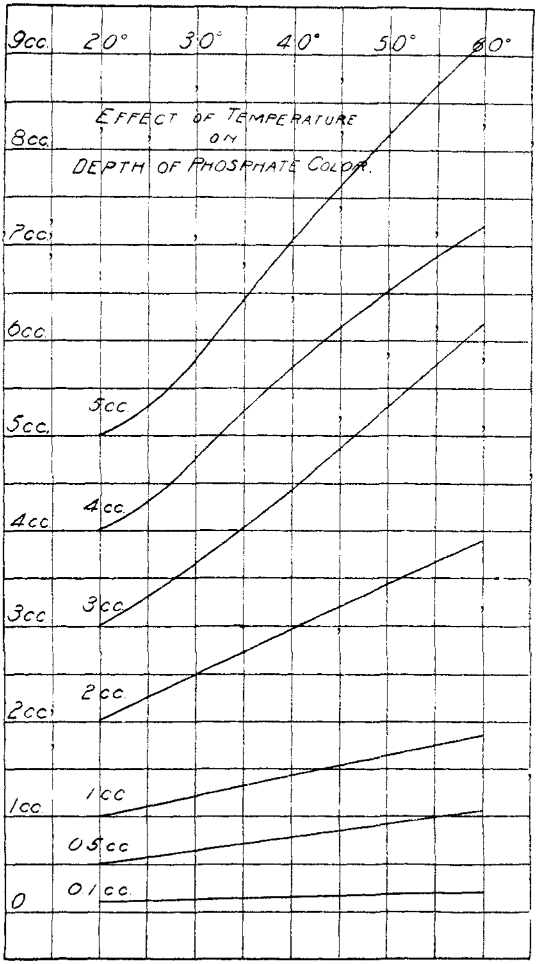

Fig. 1.

fifteen minutes to two hours. A loss of phosphate always occurred whether done in platinum or porcelain dishes. Other standards were evaporated and heated at 135° C., still others were ignited over a free flame ; a loss was found in all cases. An idea of the magnitude of the loss may be gained from the following figures :

Evaporated without Nitric Acid and Heated One Hour at 100°.

	In porcelain dishes.						In platinum dishes.					
Amount added	0.1	0.2	0.5	1.0	2.0	5.0	0.1	0.2	0.5	1.0	2.0	5.0
" found	0.1	0.18	0.45	0.75	1.8	4.9	0.07	0.12	0.4	0.85	1.8	4.9

Evaporated as Above but Heated One Hour at 135°.

	In porcelain dishes.						In platinum dishes.					
Amount added	0.1	0.2	0.5	1.0	2.0	5.0	0.1	0.2	0.5	1.0	2.0	5.0
" found	0.0	0.0	0.0	1.0	1.5	4.0	0.0	0.0	0.1	0.6	1.3	2.7

In all cases where nitric acid was used and the residue was heated at 100°, the loss on a 2 cc. standard was from 0.02 to 0.22 cc. greater the more acid used. Where the ignition was made over a free flame the loss varied from 25 to 50 per cent., highest in the low standards. Without the addition of nitric acid the loss on evaporation was very irregular. In the presence of a definite quantity of acid the loss was more nearly constant. Without going into great detail it may be said that it was apparent that the loss was due to some change taking place while the solution is dilute and hot. The total loss occurs usually during the concentration of the solution to one-half its volume.

THE EFFECT OF SILICA.

The properties of dilute solutions of ammonium silicomolybdate were also studied since silica is the principal substance which interferes with the phosphate test.

Solutions made up with varying quantities of the standard silica solution gave a color immediately upon adding the reagents. With small and medium amounts of silica the color was slight compared with that developed in an hour ; with high silica standards considerable color developed instantly. It is interesting to note that ammonium molybdate alone with a silica solution made exactly neutral, develops a faint color in an hour, but with a phosphate standard no color appears except in the presence of nitric acid. In twenty-four hours the color due to the silicomolybdate fades appreciably ; it is greener than the color of the phosphomolybdate.

To determine the time necessary for silica standards to attain their maximum color varying standards were mixed with the reagents and 50 cc. of water and compared at definite intervals with fresh phosphate standards. The readings in terms of the standard phosphate solution are given in the following table :

cc. SiO_2 used.	1/2 hour.	1 hour.	1.5 hours.	2.5 hours.	3 hours.	3.5 hours.	4.5 hours.	5 hours.	5.5 hours.	6 hours.	6.5 hours.	7 hours.
0.1	0.03	0.07	0.09	0.03	0.02	0.03	0.02	0.01	0.01	0.01	0.008	0.008
0.7	0.56	0.65	0.67	0.72	0.70	0.67	0.67	0.67	0.66	0.66	0.65	0.65
1.0	0.92	0.96	1.01	1.02	1.07	1.05	1.05	1.04	1.03	1.03	1.02	1.02
3.0	2.75	2.88	2.95	3.01	2.95	2.95	3.10	3.20	3.20	3.25	3.30	3.40
7.0	6.65	6.75	6.95	7.00	7.10	7.20	7.20	7.20	7.25	7.25	7.30	7.35
10.0	9.70	9.95	9.99	9.95	9.95	...	9.95	9.95	9.95	9.95	9.95	9.90

It will be noticed that the lower standards reach a maximum in about two or three hours, and then begin to fade; the medium standards do not seem to reach a maximum even after seven hours.

A number of silica standards, after standing one hour, were heated from 20° to 100° in a water-bath. The color did not change in intensity until 70°–80° was reached, when it began to fade, decreasing up to 100°. The color did not return to its original intensity on cooling slowly to 20°.

Experiments made to determine the conditions under which minute quantities of silica might be rendered entirely insoluble, showed that evaporation with nitric acid and heating at 100° for an hour was insufficient; when the same standards were evaporated and heated at 135° for an hour, recombination took place and some of the silica remained soluble. On heating the residues for *two* hours at 100° instead of one hour, however, no silica remained soluble. The results are shown in the following table: 1, 2, and 5 cc. of the standard silica solution were diluted to 50 cc., 10 drops of nitric acid were added, the solutions evaporated to dryness in porcelain dishes, and heated at different temperatures for two hours. The residue was taken up in cold water and the color read after standing one hour :

Temperature.	Readings.			Per cent. undehydrated SiO_2.		
	1 cc.	2 cc.	5 cc.	1 cc.	2 cc.	5 cc.
60°	0.5	1.2	2.0	50	60	40
80°	0.3	0.7	0.9	30	35	18
100°	0.0	0.0	0.0	00	00	00
135°	0.1	0.4	1.0	10	20	20
150°	0.4	0.5	1.1	40	25	22
190°	0.6	0.8	1.1	60	40	22

These results are shown graphically, using percentages of undehydrated silica as ordinates and temperatures as abscissas, in Fig. 2.

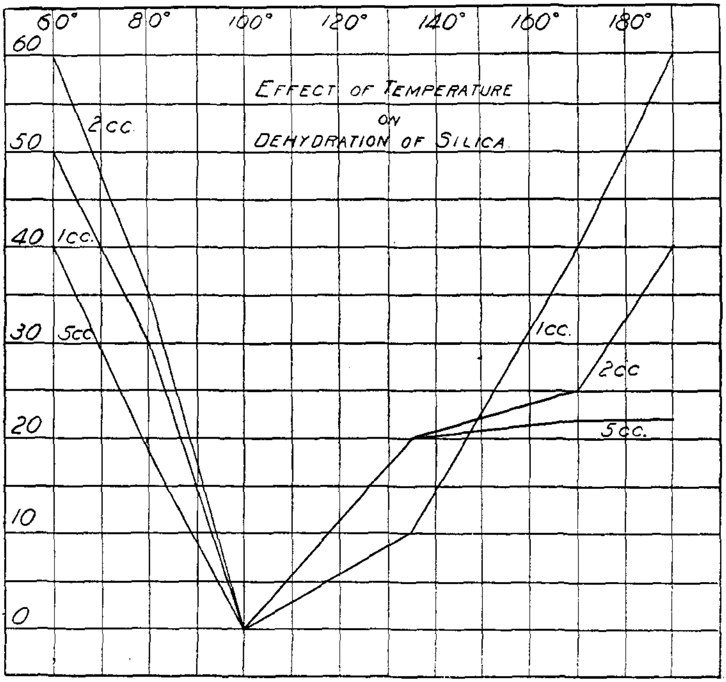

Fig. 2.

OTHER COMPOUNDS WHICH MIGHT INTERFERE.

Since vanadium and titanium resemble phosphorus and silicon quite closely in many of their properties, vanadates and titanates might interfere with the determination of phosphates by a colorimetric method. Titanium is especially liable to occur in the natural waters of regions containing diorites and titanium-bearing ores like ilmenite. The presence of these elements has been observed in natural waters.

Dilute solutions of sodium titanate gave a pale greenish yellow color with ammonium molybdate and nitric acid, but much less intense than the phosphate color. The color did not fade within an hour, but at 20° C. it took twelve minutes for it to appear. By evaporation with nitric acid, and subsequent heating at 100° for two hours, the titanium oxide was rendered completely insoluble.

Ammonium vanadate gave with the ammonium molybdate *alone* a yellow color which was permanent for several hours, but upon the addition of nitric acid this color faded completely in five minutes. Experiments with a standard solution of ammonium vanadate showed that the color given by as much as 0.0003 gram of V_2O_3 in 50 cc. of water fades out entirely in four minutes. Incidentally it was found that 0.000001 gram of V_2O_3 could be detected readily in a volume of 50 cc. It is evident that the small quantities of vanadium which occur in natural waters will not interfere with the determination of phosphates.

COLORIMETRIC ESTIMATION OF PHOSPHATES IN THE PRESENCE OF SILICA.

The previous results had shown the possibility of a method based on the dehydration and elimination of the silica. The conditions must be such that the total phosphate or a definite portion of it shall be left intact and that the silica shall be rendered entirely insoluble. The following method was finally adopted as the one giving the most satisfactory results :

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 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 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 just described will be sufficient for ordinary work. If a more exact determination of the phosphate is required a slight correction should be applied in each case. These corrections were determined by making a number of determinations by the method. The results are shown in the following table. The first two series had 2 cc. of standard silica solution added to each test; the others had only the phosphate.

Phosphate added.	Phosphate found.						Average.	Correction.
0.1	0.07	0.09	0.10	0.10	0.09	0.09	0.09	0.01
0.5	0.46	0.47	0.46	0.45	0.43	0.45	0.45	0.05
0.7	0.63	0.64	0.64	0.65	0.64	0.66	0.65	0.05
1.0	0.85	0.85	0.86	0.86	0.84	0.83	0.85	0.15
3.0	2.55	2.65	2.50	2.50	2.60	3.65	2.60	0.40
5.0	4.55	4.55	4.45	4.45	4.50	4.50	4.50	0.50
7.0	6.65	6.60	6.55	6.55	6.60	6.65	6.60	0.40
10.0	9.60	9.65	9.55	9.60	9.60	9.55	9.60	0.40

Since organic life is present in greater numbers and is more active in surface waters than in ground waters, it is evident that the determination will be of greatest value for the examination of wells. Well waters are usually colorless, and to them the method may be applied directly. It is not yet suitable for colored waters. The determination of phosphates is at present being carried on in this laboratory as a routine determination and the results will be published as soon as sufficient data have accumulated to render a discussion of the entire question of value.

BOSTON, MASS., December 20, 1900.

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EXPERIMENTS ON CHALCOPYRITE.

BY LEONARD P. MORGAN AND EDGAR F. SMITH.

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AT various times experiments have been made in this laboratory looking to the determination of the constitution of certain natural chemical products. Thus, the state of oxidation of the iron in pyrite, marcasite, and arsenopyrite has received