

one stand; there is no danger from explosion due to flame; a steady, continuous source of heat, not affected by draughts or other external influences, is secured. The lamp socket is easily held in position by means of a clamp; the heat is instantly available, and quickly removed. Using this source of heat (ether) extractions are carried on continuously through the night, no attention being required after first regulating the flow of condensed solvent.

E. O. THOMAS.

THE BUREAU OF STANDARDS' ANALYZED SAMPLES.

It will be of interest to those of our readers who are not already informed to know that the Bureau of Standards is prepared to supply analyzed samples (150 grams each) of standard irons and steels, at the following rates:

Single samples of 150 grams, each sample.....	\$2.00
In lots of three to nine samples, each sample.....	1.67
In lots of ten to nineteen samples, each sample....	1.50
In lots of twenty samples or more, each sample....	1.25

Orders for samples should be accompanied by a remittance.

The list follows:

Cast Iron C with medium Si, P, Mn.
 Cast Iron D with high Si, P, Mn.
 Bessemer Steels with approximately 0.1, 0.2 and 0.4% C.
 Basic Open Hearth Steels with 0.1, 0.2, 0.4, 0.6, 0.8 and 1% C.
 Acid Open Hearth Steels with 0.1 and 0.2% C.

Cast Iron B is exhausted but will be replaced in time.

Bessemer bars with 0.6 and 0.8 per cent. C and acid open hearth bars with 0.4, 0.6, 0.8 and 1 per cent. C are on hand, but the process of preparing samples is very slow and it may be a year before the last of them is ready for distribution.

The preparation of special steel standards is under consideration.

It may be added that the Bureau is also prepared to distribute to applicants samples of an analyzed argillaceous limestone¹ suitable for the manufacture of Portland cement.

Samples of cane sugar of known calorific value for the standardization of calorimeters are also furnished by the Bureau. It is hoped to furnish in time a variety of materials for calorimetry, and also a very pure sugar for the standardization of polarimeters.

Announcement will be made in these columns whenever any standard samples are ready for distribution.

The Bureau also calibrates volumetric apparatus, for a small charge, provided the pieces have identification marks and conform in other respects to the Bureau's requirements. Circular No. 9, which may be had upon request, gives information in regard to these points.

W. F. HILLEBRAND.

REPORT OF THE COMMITTEE ON THE ANALYSIS OF PHOSPHATE ROCK.

The first report of the committee appointed by the National Fertilizer Association on the analysis of phosphate rock has just been issued. The committee which was appointed early in the year by the Association consisted of Messrs. C. F. Hagedorn, C. H. Dempwolf, Jr., and F. B.

¹ *Jour. Am. Chem. Soc.*, 28, 229.

Carpenter, all well-known chemists connected with large fertilizer interests. The essential features of the report, with the exception of the names of the analysts, follow:

To the Members of the National Fertilizer Association:

The discrepancies between the results of chemists in the analysis of phosphate rock have often been the cause of disputes between buyer and seller, sometimes resulting in costly litigation, and usually ending in a feeling of diminished confidence by the manufacturer for his chemist. While it is true that there are limits to the accuracy of analytical methods, we believed that the great variations were due mainly to the use of different methods or to various modifications of the same method. It was, therefore, considered to be of great importance that some work be done on this subject, and it was the object of this investigation to examine the various analytical methods for phosphate rock, which are now in use, with a view to the adoption by our Association of methods which will yield uniform results.

Four sets of samples of the following kinds of phosphate rock were prepared: Tennessee Brown, Tennessee Blue, South Carolina and Florida. These were distributed among the chemists of our Association and the commercial chemists who make a specialty of fertilizer analyses. Each chemist was instructed to determine moisture, phosphoric acid (also calculated to calcium phosphate) and iron and aluminum oxides, using the routine method of his laboratory and to return a complete report of the results, together with a copy of his methods.

Thirty-one reports were received, which we have classified according to methods, giving in each case a brief outline of the method. Below each table we have also noted the important modifications of these methods.

MOISTURE.

We include in this table the essential points in the method in each case; viz., the size of sample, time of drying and temperature of oven.

	No. 1 Tenn. Analyst. brown.	No. 2 Tenn. blue.	No. 3 Fla. pebble.	No. 4 S. C. S. C.	Weight, grams.	Time, hours.	Tempera- ture C.
1	1.26	0.68	0.80	0.48	2	5	100
2	0.89	0.39	0.40	0.20	1	5	100
3	0.79	0.25	0.27	0.06	2	5	100
4	0.69	0.33	0.28	0.13	2	5	100
5	0.99	0.45	0.47	0.26	5	C.W.	100
6	0.92	0.43	0.48	0.30	5	5	100
7	1.06	0.45	0.54	0.27	2	5	100
8	1.10	0.50	0.45	0.25	2	5	100
9	1.14	0.52	0.66	0.34	5	5	105
10	1.09	0.42	0.46	0.20	2	4	100
11	1.16	0.55	0.66	0.38	10	5	100
12	1.14	0.55	0.66	0.55	2	2	100
13	1.22	0.54	0.62	0.34	20	12	100
14	0.93	0.38	0.52	0.26
15	1.37	0.72	0.87	0.50	10	C.W.	100-05
16	1.00	0.35	0.59	0.28	5	5	100
17	1.30	0.70	0.80	0.40	10 & 5	3	100
18	1.40	0.60	0.80	0.60	10 & 5	3	100
19	1.09	0.49	0.52	0.28	5	4	100
20	1.15	0.48	0.49	0.32	1	5	100
21	1.09	0.51	0.63	0.27	10	C.W.	105-10
22	1.06	0.53	0.63	0.40	5	5	100
23	0.57 ¹	0.35	0.27	0.17	5	5	105-10
24	1.07	0.48	0.52	0.27	5	5	105
25	1.20	0.48	0.60	0.40	...	5	100
26	1.20	0.50	0.60	0.30	2	3	105
27	1.12	0.46	0.56	0.31	5	5	100

¹ Omitted from average.

	No. 1 Tenn.	No. 2 Tenn.	No. 3 Fla.	No. 4 S. C.	Weight, grams.	Time, hours.	Tempera- ture C.
Analyst. brown.	blue.	pebble.					
28	0.95	0.27	0.43	0.14	5	105
29	0.36 ¹	0.35	0.35	0.23	2	5	100
30	1.02	0.46	0.52	0.27	5	5	100
31	1.50	0.73	0.84	0.48	5	C.W.	105
32	1.09	0.37	0.52	0.24	2	2	100
Average	1.10	0.48	0.56	0.31			
Max'm	1.50	0.73	0.87	0.60			
Min'm	0.69	0.25	0.27	0.06			
Diff.	0.81	0.48	0.60	0.54			

The wide variations found in the above table are without doubt due to differences in manipulation, as the samples were very carefully prepared, and were as nearly uniform as it is possible to make them. The temperature of the oven and the manner of cooling before weighing have a great influence on the moisture result. There are water ovens which do not furnish a temperature of 100° C. even with the water boiling and the control of an air bath is always more or less imperfect. If the moisture determinations are made either on watch glasses, using one watch glass as a cover while cooling, or in shallow aluminum, or glass weighing dishes provided with a tightly fitting stopper, so that the sample can be stoppered while cooling and weighing, and if the temperature of the oven is fully 100° we believe that the results would agree much more closely.

PHOSPHORIC ACID.

Official Gravimetric Method.—This method is too well known to require an outline. It is described in Wiley's "Principles and Practice of Agricultural Analysis," Vol. 2, page 16. The figures in this and the following tables refer to the percentage of P_2O_5 on the wet basis.

Analyst.	No. 1.	No. 2.	No. 3.	No. 4.
1	31.32	27.27	31.50	26.43
2	31.41	27.32	31.06	26.60
3	31.67	27.35	31.37	26.73
4	31.49	27.44	31.33	26.77
5 ²	31.83	27.82	31.32	27.08
6	31.88	27.74	31.40	26.90
7	31.96	27.52	31.46	26.72
8	31.47	27.23	31.34	26.48
9	32.01	28.03	31.80	26.81
10	31.50	28.13	32.13	27.20
11	32.20	27.51	31.33	26.89
12 ³	31.08	26.95	30.94	26.52
13 ⁴	30.91	26.72	30.59 ¹	26.01
14	31.18	27.24	31.00	26.46
15	31.61	27.10	31.00	26.20
16	31.84	27.05	31.92	27.31
17	31.79	27.10	31.77	27.24
18 ⁵	31.72	27.47	31.18	26.71
19	31.29	27.05	31.31	26.53
Average	31.59	27.37	31.40	26.71
Maximum	32.20	28.13	32.13	27.31
Minimum	30.91	26.72	30.94	26.01
Difference	1.29	1.41	1.19	1.30

¹ Omitted from average.

² We quote an interesting paragraph from the methods of Wiley and Hoffman, "We believe that many rock solutions contain silica in a fine condition which passes through the single paper used by most analysts and believe it advisable to filter all rock solutions through at least three papers of the S & S No. 597 grade before measuring off the aliquot. With some samples we have used six papers in order to obtain a clear solution."

³ Yellow ppt. formed in the cold and digested for 30 minutes at 60–65° C.

⁴ Yellow ppt. is washed six times with 2 per cent. HNO_3 (50 cc. each time), Magnesium ammon. phosphate is burned for one hour in muffle furnace and for fifteen minutes in blast-lamp.

⁵ Sulphuric acid with about 4 g. mercuric oxide is used as the solvent.

To some extent the variations here may be due to departure from the official method but probably most largely to differences in details not included in the description of this method. Six different factors for converting magnesium pyrophosphate to P_2O_5 were reported. The factors were as follows: 0.6375, 0.63757, 0.6376, 0.638, 0.63965, 0.6397, the theoretically correct factor being 0.63757, although 0.6376 is close enough.

Volumetric Method, sometimes called Pemberton's Method.—The solution of the yellow precipitate in standard potassium hydrate and titration by a standard acid solution is its chief feature. An outline of this method may be found in Bureau of Chemistry, Bulletin No. 107, page 4.

Analyst.	No. 1.	No. 2.	No. 3.	No. 4.
1	31.58	27.53	31.29	26.53
2	31.65	27.47	31.19	26.50
3	32.20	28.25	31.85	27.75
4	32.10	27.90	31.86	27.26
5	31.40	27.40	31.55	26.50
6	31.88	28.33	31.78	27.36
7	31.50	27.10	31.30	26.45
8	31.00	26.90	30.88	26.18
9	31.99	27.20	31.83	27.43
10	31.39	27.30	31.00	26.39
Average	31.67	27.54	31.45	26.83
Maximum	32.20	28.33	31.86	27.75
Minimum	31.00	26.90	30.88	26.18
Difference	1.20	1.43	0.98	1.57

Citrate Method.—Based upon the power of alkaline ammonium citrate to hold in solution the salts of iron aluminum, and calcium, thus permitting the direct precipitation of phosphoric acid as ammonium magnesium phosphate. Described fully in Wiley's "Principles and Practice of Agricultural Analysis," Vol. 2, page 57.

Analyst.	No. 1.	No. 2.	No. 3.	No. 4.
1	31.35	27.01	31.36	26.57
2	32.42 ¹	27.44	32.03	26.98
3	31.33	27.59	32.07	26.91
4	33.34 ¹	28.41 ¹	31.86	26.82
5	33.50 ¹	29.30 ¹	31.70	27.00
Average	31.34	27.35	31.80	26.86
Maximum	31.35	27.59	32.07	27.00
Minimum	31.33	27.01	31.36	26.57
Difference	0.02	0.58	0.71	0.43

Gladding Method.—In this method the ammonium phosphomolybdate is dried and weighed, the percentage of P_2O_5 being calculated from this weight.

Analyst.	No. 1.	No. 2.	No. 3.	No. 4.
1	31.53	27.25	31.35	26.43
2	31.54	27.43	31.08	26.31
Average	31.54	27.34	31.22	26.37
Difference	0.01	0.18	0.27	0.12

IRON AND ALUMINUM OXIDES.

Smith or Modified Von Grueber Method.—The rock is dissolved in hydrochloric acid and the iron is determined by titrating a portion of this solution with potassium permanganate. A second portion of the original solution is added to an excess of strong KOH solution, which while precipitating the iron retains the aluminum in solution as potassium aluminate. From this solution the aluminum is separated as phosphate by the addition of HCl and ammonia.

¹ Omitted from average.

Analyst.	No. 1.	No. 2.	No. 3.	No. 4.
1	7.56	3.27	2.66	4.54
2	7.12	3.39	2.48	4.17
3	7.56	3.60	2.49	4.59
4	7.43	3.52	2.56	4.67
5	7.09	3.07	2.67	3.91
6 ²	7.76	8.43 ¹	2.81	5.21 ¹
7	7.65	3.62	2.55	4.60
8	7.31	3.27	2.47	4.23
9	7.54	3.16	2.47	4.80
10	7.53	3.49	2.81	4.40
11	6.94	3.22	2.28	3.93
12	5.60 ¹	4.12	2.56	3.95
Average	7.41	3.43	2.57	4.34
Maximum	7.76	4.12	2.81	4.80
Minimum	6.94	3.07	2.28	3.91
Difference	0.82	1.05	0.53	0.89

Gladding Method.—In this method the separation of the alumina by means of a KOH solution is somewhat similar to that of the Smith method. The precipitation of the aluminum phosphate, however, is made by a neutral solution of ammonium acetate as in the acetate method. The iron is determined by titration with a standard solution of potassium bichromate.³

Analyst.	No. 1.	No. 2.	No. 3.	No. 4.
1	7.35	2.42	2.42	4.10
2	7.17	3.06	2.46	4.36
3	7.36	4.84 ¹	2.41	2.61 ¹
4	7.63	4.37	2.36	4.54
Average	7.38	3.28	2.41	4.33
Maximum	7.63	4.37	2.46	4.54
Minimum	7.17	2.42	2.36	4.10
Difference	0.46	1.95	0.10	0.44

Acetate Method.—The HCl solution of the rock is nearly neutralized with ammonia, after which are added a few centimeters of ammonium acetate and heated to 70° C., which completely precipitates the iron and aluminum phosphates. This is dissolved in HCl and reprecipitated in the same manner. One-half of the combined weight of phosphates is usually taken to represent the Al₂O₃ and Fe₂O₃.

Analyst.	No. 1.	No. 2.	No. 3.	No. 4.
1	7.49	3.58	2.51	4.30
2	7.02	2.73	2.19	4.10
3	8.76	3.92	3.31	5.20
4	7.85	8.56	2.85	4.49
5	6.95	2.90	2.19	4.08
Average	7.33	3.28	2.43	4.24
Maximum	7.85	3.92	2.85	4.49
Minimum	6.95	2.73	2.19	4.08
Difference	0.90	1.19	0.66	0.41

Glaser Method.—In this method the lime is first removed by converting into calcium sulphate by means of sulphuric acid in the presence of strong alcohol. After filtering, a portion of the solution is evaporated to expel alcohol, diluted and heated to boiling. Ammonia, added until alkaline precipitates the iron and aluminum as phosphates.

Analyst.	No. 1.	No. 2.	No. 3.	No. 4.
1	6.72	3.60	2.59	4.07
2	6.20	3.06	2.13	3.20
3 ¹	8.32	6.16 ¹	2.71	4.26
4	7.33	3.75	2.40	4.27
5 ⁴	6.20	6.50 ¹	2.30	3.00 ¹

¹ Omitted from average.

² Five g. rock are treated in a platinum crucible with 4 cc. H₂SO₄ and 20 cc. HF. This is evaporated to dryness on a steam bath and fused with Na₂CO₃. Fusion dissolved in dil. hydrochloric acid and water.

³ Ref. J. Am. Chem. Soc., 18, 721.

⁴ Solvent: Aqua regia.

Analyst.	No. 1.	No. 2.	No. 3.	No. 4.
Average	6.97	3.47	2.43	3.95
Maximum	8.32	3.75	2.71	4.26
Minimum	6.20	3.06	2.13	3.20
Difference	2.12	0.69	0.58	1.06

Jones Variation of Glaser Method.—This is practically the same as the Glaser method, except that about ½ the quantity of sulphuric acid and 1½ times the amount of alcohol are used.

Analyst.	No. 1.	No. 2.	No. 3.	No. 4.
1 ²	7.37	8.37 ¹	2.63	4.43
2 ²	7.82	8.00 ¹	2.12	4.64
Average	7.59		2.37	4.53
Difference	0.45		0.51	0.21

Wyatt's Method.—The phosphates of iron and aluminum are precipitated from a portion of the original solution by making slightly alkaline with ammonia and then acid with acetic acid. The ppt. is filtered, dissolved, and reprecipitated in the same way.

Analyst.	No. 1.	No. 2.	No. 3.	No. 4.
1 ³	7.27	2.20	2.27	4.10
2	6.22	3.30	2.54	2.94
3 ²	6.20	7.42 ¹	2.43	5.00
Average	6.56	2.75	2.41	4.01
Maximum	7.27	3.30	2.54	5.00
Minimum	6.20	2.20	2.27	2.94
Difference	1.07	1.10	0.27	2.06

COMPARISON OF AVERAGES.

Method.	No. 1.	No. 2.	No. 3.	No. 4.
Smith	7.41	3.43	2.57	4.34
Gladding	7.38	3.28	2.41	4.33
Acetate	7.33	3.28	2.43	4.24
Glaser	6.97	3.47	2.43	3.95
Jones Mod. of Glaser	7.59	2.37	4.53
Wyatt	6.56	2.75	2.41	4.01

EFFECT OF DIFFERENT SOLVENTS IN THE DETERMINATION OF IRON AND ALUMINA.

We have received from Messrs. L. P. Brown and Company, Nashville, Tenn., an interesting comparison showing the effect of different solvents in the determination of iron and alumina, which we give in the following table:

Sample.	Solvent	Fe ₂ O ₃ and Al ₂ O ₃		
		Fe ₂ O ₃ .	Al ₂ O ₃ .	Al ₂ O ₃ .
No. 1	100 cc. HCl (1:1)	3.40	4.16	7.56
Tenn. Brown	50 cc. HCl conc.	3.51	3.51	7.02
10 g.	30 cc. HCl conc. and 20 cc. HNO ₃ conc.	3.74	3.73	7.47
No. 2	100 cc. HCl (1:1)	1.31	2.29	3.60
Tenn. Blue	50 cc. HCl conc.	1.52	1.49	3.01
10 g.	30 cc. HCl conc. and 20 cc. HNO ₃ conc.	6.38	1.47	7.85
No. 3	100 cc. HCl (1:1)	1.10	1.39	2.49
Fla. Pebble	50 cc. HCl conc.	1.26	1.40	2.66
10 g.	30 cc. HCl conc. and 20 cc. HNO ₃ conc.	1.58	1.47	3.05
No. 4	100 cc. HCl (1:1)	3.11	1.48	4.59
So. Car.	50 cc. HCl conc.	3.20	1.39	4.59
10 g.	30 cc. HCl conc. and 20 cc. HNO ₃ conc.	3.52	1.43	4.95

Note especially the effect of aqua regia on No. 2 sample and that in all cases the addition of HNO₃ seems to increase the Fe₂O₃. This is due to the presence of pyritic iron which remains undecomposed when hydrochloric acid is used. The effect of aqua regia as a solvent can also be seen in several of the tables under iron and alumina, especially in the case of No. 2, or Tennessee blue rock.

¹ Omitted from average.

² Solvent: Aqua regia.

³ Aqua regia used as solvent for Nos. 1, 3 and 4. HCl (1:1) used on No. 2.

This is one of the most important questions to be decided and for the present we recommend the use of hydrochloric acid (1:1) as a solvent in the determination of iron and alumina.

In some experiments conducted by Dr. F. B. Carpenter, of the Virginia-Carolina Chemical Company, it was found that the length of time in which the solution is boiled makes a material difference in the results of iron and alumina and for that reason they have adopted a definite amount of acid (1:1) to 2 g. of rock, boiled for one hour on the hot plate.

CONCLUSION.

It should be remembered that our main object is to agree upon uniform methods to be used in settlement analyses. Regarding the reports received as expressions of opinions by the chemists named, it becomes evident in the case of phosphoric acid, which method should be selected. The results of the volumetric and the Gladding methods are excellent, but at this time there are not sufficient reasons for substituting either of these for the present official method.

In the case of the methods for iron and alumina, the results indicate that the methods most generally used are those employing a KOH solution in the separation of the iron from the alumina, *viz.*, the Smith and the Gladding methods. In the other methods, the iron and alumina was determined by weighing the combined phosphates. Of these the acetic and the Glaser methods are the most important, and it is our opinion that some modification of the acetate method could be worked out which would be extremely satisfactory, as it appeals to chemists on account of its simplicity as compared with other methods. The close agreement of the reports on iron and alumina is noticeable, excepting a few results and those in which aqua regia was employed.

We recommend that for referee work the Official Gravimetric Method be used for phosphoric acid, and that in the methods now in use for iron and alumina, the solvent be hydrochloric acid (1:1) until the question of the effect of pyritic iron in acidulating can be definitely solved. The methods for iron and alumina will be investigated further with a view to the adoption of one of the methods as standard for our work.

We believe that a strict adherence to uniform details in these methods will yield very much better results and that it is essential for our fertilizer chemists to agree upon these details. We are, therefore, preparing a set of methods to include moisture, the official gravimetric method for phosphoric acid, and the various methods for iron and alumina, which will give complete details as far as possible. These methods will be submitted to all the chemists who previously worked on the samples, with the request that the work be gone over again, following in detail the instructions given. With these additional results at hand, we shall be able to submit a definite proposal concerning the adoption of Association methods.

In the preparation of these methods we shall welcome the suggestions of those interested in this subject.

C. F. HAGEDORN,
C. H. DEMPWOLF, JR.,
F. B. CARPENTER.

A TEST FOR SKIN PULP IN TOMATO CATSUP.

During an investigation of several different brands of tomato catsup for artificial color, a peculiar result was noticed on the addition of lead subacetate. Some catsups became absolutely solid while others formed only a slight flocculent precipitate. It was thought at first that some adulterant was the cause of the large precipitate, but a thorough investigation failed to detect any. Accordingly, tests were made on tomatoes, both green and ripe, fresh from the garden. It was found that whole tomato pulp, after cooking, normally yields a dense white precipitate with lead subacetate while the skins, carefully freed of pulp and boiled with water, yield no precipitate with the same reagent. Tests were then made on commercial pulps of known composition. In every case, whole pulp yielded a dense precipitate. In some samples, supposed to be skin pulps, a certain amount of precipitate was formed, probably due to careless peeling of the original tomatoes, not enough, however, to convey the impression that whole pulp exclusively had been used. The method adopted was as follows: A small quantity of the sample was diluted with three times its volume of water and filtered. The filtrate was treated with a few drops of lead subacetate solution, sp. gr. 1.25. Whole pulp yielded a dense white precipitate, while skin pulp gave only a slight flocculent precipitate. Knowing well the variations possible in the original tomatoes, it is not claimed that any quantitative estimation of the proportion of whole and skin pulp used can be obtained from the volume of the precipitate. However, it is believed that the test furnishes a reliable guide as to the quality of any catsup. The absence of any precipitate is proof of the use of skin pulp.

H. W. COWLES, JR.

THE COMMITTEE ON ANALYSIS OF FATS, SOAPS AND GLYCERINE.

A few weeks before the New Haven meeting of the American Chemical Society (June 30 to July 2, 1908) a subcommittee was appointed by Dr. W. F. Hillebrand, chairman of the Committee on Uniformity in Technical Analysis, for the purpose of developing standard methods for the analysis of fats, soaps and glycerine. The committee thus appointed consists of: W. D. Richardson, chairman; J. W. Loveland, secretary; R. E. Devine, D. Wesson, A. C. Langmuir, B. T. B. Hyde, W. H. Low, and Ernest Twitchell. The first meeting of the committee was held at the Graduates Club, New Haven, Conn. June 30, 1908. It was decided that the scope of the committee for the present be limited to the consideration of the analysis of such materials as are commonly bought and sold. It was further decided that the immediate attention of the committee should be directed toward the analysis of the following products for the constituents named, definitions to be decided upon when necessary: Fats and oils, moisture and volatile matter, free fatty acids, titer, unsaponifiable matter, metallic soaps, gross impurities; Cotton Seed Foots, total fatty acids and resinous matter, moisture; Cotton Seed Black Grease, free fatty acids, moisture, resinous matter, unsaponifiable matter; Cotton Seed Foots Soap, total fatty acids, moisture, combined alkali, free alkali, matter insoluble in alcohol, sodium chloride, unsaponifiable matter; Crude Glycerine, glycerol, organic impurities; Dynamite Glycerine, specific gravity, organic residue, sodium chloride, ash, fatty acids, silver nitrate test; Chemically Pure Glycerine, con-