PHOTOMETRIC DETERMINATION OF IRON.

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THE present investigation was undertaken for the purpose of ascertaining whether the photometric method was applicable to colored precipitates.

Solutions of iron of various degrees of dilution were prepared and their strength accurately determined gravimetrically. The iron was precipitated with potassium ferrocyanide. Ferric nitrate, sulphate and chloride were found to give practically the same results. In all the solutions nitric acid was present, though never more than to the extent of 1 per cent. This was in order to insure that the iron was in the ferric condition.

As in the previous investigations,[1] a common candle was used with the simple photometric cylinder. The more accurate instrument suggested by Professor D. D. Jackson[2] was not at our command. The work was carried on in the diffused light of the laboratory, but the cylinder was protected by the hand and body against any glare of light from the windows.

Preliminary tests with the solid ferrocyanide showed that constant readings could not be obtained. The reading was found to be a function of the amount of the ferrocyanide added. This is because the ferric ferrocyanide precipitate is soluble in an excess both of the iron and ferrocyanide solutions. We therefore made a 5 per cent. solution of the potassium ferrocyanide and used it from a burette. On adding this drop by drop to a ferric solution, there first appears a blue color, then a coarse precipitate which presently breaks up into a fine state of division and finally dissolves. The greatest opacity and therefore the lowest photometric reading occurs just when the precipitate begins to break up. This point is reached when the amount of ferrocyanide bears to that of the iron present about the proportion of its molecular weight to the atomic weight of iron; or when the ferrocyanide is a little in excess of the amount necessary to convert the iron into Prussian blue. For example, a solution which contained 0.0054 gram of iron required 0.7 cc. of the 5 per cent. ferrocyanide solution, or 0.035 gram

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[1] This Journal, **18**, 661.

[2] *Ibid.*, **23**, 799.

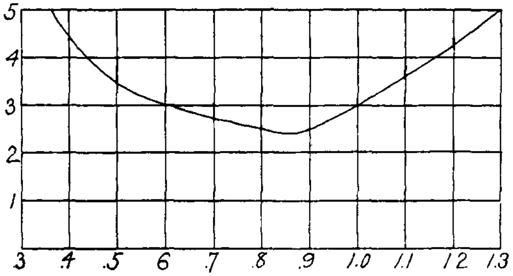
potassium ferrocyanide. These numbers are in the proportion of 54 to 350 or 56 (atomic weight of iron) to 366 (molecular weight of potassium ferrocyanide 368).

It was found that at the point of maximum opacity, or where the reading had a minimum value, constant conditions and constant readings could be obtained. The following method was then adopted: The solution whose strength was to be determined was placed in a lipped beaker in quantity sufficient to fill the photometer to the required height, and the ferrocyanide added, drop by drop, until the precipitate just appeared. The solution was thoroughly mixed by pouring back and forth, and the reading taken. Another drop of the ferrocyanide was added and another reading taken (which should be lower than the first one). This process was continued until a minimum was obtained and the readings began to rise again. The lowest reading was the one adopted.

With a little practice only four or five readings are necessary to find the minimum, which is the easier to detect because the opacity near the minimum remains nearly the same for two or three readings.

An example and diagram will illustrate the peculiar action under consideration.

	cc.	cc.	cc.	cc.	cc.	cc.	cc.	cc.	cc.
Ferrocyanide used....	0.4	0.5	0.6	0.7	0.8	0.9	1.0	1.1	1.2
	cm.	cm.	cm.	cm.	cm.	cm.	cm.	cm.	cm.
Photometer readings..	4.4	3.6	3.0	2.7	2.5	2.5	3.0	3.7	4.3



It appears that the ascending arm of the curve is nearly a straight line and rises at an angle a little higher than that of the descending arm.

A series of determinations was made and each was tested by numerous readings. In the first column of the table which follows is given the number of the solution; in the second its real strength in per cent. of iron or grams in 100 cc.; in the third is the photometric reading; in the fourth is the product of the reading and strength; in the fifth is the strength computed from the first equation determined below; in the sixth the difference between the computed and real strength; in the seventh the strength as computed from the second equation; and in the eighth the difference between this and the real strength.

No.	Strength. y = per cent. Fe.	Reading. x.	xy.	$y = \frac{0.03027}{x-0.28}$.	Difference.	$y = \frac{0.02955}{x-0.375}$.	Difference.
1	0.01153	2.9	0.03344	0.01155	0.00002	0.01170	0.00017
2	0.00864	3.8	0.03283	0.00859	0.00005	0.00863	0.00001
3	0.00757	4.3	0.03255	0.00753	0.00004	0.00754	0.00003
4	0.00692	4.7	0.03252	0.00685	0.00007	0.00683	0.00009
5	0.00606	5.3	0.03212	0.00603	0.00003	0.00600	0.00006
6	0.00528	6.0	0.03168	0.00529	0.00001	0.00525	0.00003
7	0.00470	6.7	0.03149	0.00471	0.00001	0.00467	0.00003
8	0.00422	7.4	0.03123	0.00425	0.00003	0.00421	0.00001
9	0.00379	8.1	0.03070	0.00387	0.00008	0.00383	0.00004
10	0.00352	8.7	0.03062	0.00359	0.00007	0.00355	0.00003
11	0.00313	9.7	0.03036	0.00321	0.00008	0.00317	0.00004

Assuming the equation of the hyperbola $xy + by = a$ in which x represents the photometric reading and y the strength of the solution, and forming the observation and normal equations and solving for the constants we obtain the equation

$$y = \frac{0.03027}{x - 0.28}.$$

Twenty-two sets of observations, including readings from 1.7 cm. to 10.7 cm., were used in the computation of this equation and its efficiency may be judged by the numbers in the first column of differences in the table above.

The readings below 3 cm. and above 9 cm. were found to be rather uncertain. Rejecting these and some others which seemed to be a little inconsistent with the general series and using only the eleven found in the table, we obtain the equation

$$y = \frac{0.02955}{x - 0.375}.$$

The values computed from this equation are found in the seventh column, and in the eighth column are the differences between these values and the real strengths of the solutions. These differences run a little more regularly than those in the sixth column, but practically one is about as good as the other. They all show that the values computed from either equation are true to the fourth decimal-place of per cent., or to parts in 1,000,000. Using the numbers from 2 to 12 for the probable error of one determination, we find, n being the number of equations, q the number of variables, and v the differences,

$$r = 0.6745\sqrt{\frac{\Sigma v^2}{n - q}} = \sqrt{\frac{0.0000000187}{10 - 2}} = 0.000034,$$

or three parts in 10,000,000.

This method is applicable to all mixed solutions of iron containing no metal which is precipitated with potassium ferrocyanide, such as cobalt, nickel, manganese, etc. In the analysis of phosphates and fertilizers the iron may be determined in the solution made for the determination of phosphorus. It may be necessary to dilute the solution if the iron is present in considerable quantity. The following is an example:

Amount taken: 0.3988 gram phosphate rock, which was dissolved in nitric and hydrochloric acids and made up to 200 cc.

Photometric reading was 6.5 cm., corresponding to 0.00489 per cent. iron. 200 cc. therefore contained 0.00972 gram iron. Of the 0.3988 gram rock, this is 2.45 per cent.

TABLE FOR PHOTOMETRIC DETERMINATION OF IRON.

cm. x.	Per cent. of iron. $y = \frac{0.03027}{x - 0.28}$.	cm. x.	Per cent. of iron. $y = \frac{0.03027}{x - 0.28}$.	cm. x.	Per cent. of iron. $y = \frac{0.03027}{x - 0.28}$.
2.0	0.01759	3.8	0.00859	5.6	0.00569
2.1	0.01663	3.9	0.00836	5.7	0.00558
2.2	0.01576	4.0	0.00814	5.8	0.00548
2.3	0.01499	4.1	0.00792	5.9	0.00539
2.4	0.01428	4.2	0.00775	6.0	0.00528
2.5	0.01363	4.3	0.00753	6.1	0.00520
2.6	0.01305	4.4	0.00732	6.2	0.00511
2.7	0.01251	4.5	0.00717	6.3	0.00503
2.8	0.01201	4.6	0.00701	6.4	0.00495
2.9	0.01155	4.7	0.00685	6.5	0.00487
3.0	0.01113	4.8	0.00670	6.6	0.00479
3.1	0.01073	4.9	0.00655	6.7	0.00472
3.2	0.01036	5.0	0.00641	6.8	0.00464
3.3	0.01002	5.1	0.00628	6.9	0.00457
3.4	0.00970	5.2	0.00615	7.0	0.00450
3.5	0.00940	5.3	0.00603	7.1	0.00444
3.6	0.00910	5.4	0.00591	7.2	0.00437
3.7	0.00885	5.5	0.00579	7.3	0.00431

cm. x.	Per cent. of iron. $y = \frac{0.03027}{x-0.28}$.	cm. x.	Per cent. of iron. $y = \frac{0.03027}{x-0.28}$.	cm. x.	Per cent. of iron. $y = \frac{0.03027}{x-0.28}$.
7.4	0.00425	8.6	0.00363	9.8	0.00318
7.5	0.00419	8.7	0.00359	9.9	0.00314
7.6	0.00414	8.8	0.00355	10.0	0.00311
7.7	0.00408	8.9	0.00351	10.1	0.00308
7.8	0.00402	9.0	0.00347	10.2	0.00305
7.9	0.00397	9.1	0.00343	10.3	0.00302
8.0	0.00392	9.2	0.00339	10.4	0.00299
8.1	0.00387	9.3	0.00335	10.5	0.00296
8.2	0.00382	9.4	0.00331	10 6	0.00293
8.3	0.00377	9.5	0.00328	10.7	0.00290
8.4	0.00372	9.6	0.00324	10.8	0.00288
8.5	0.00368	9.7	0.00321	10.9	0.00285

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ON THE DETERMINATION OF SULPHUR IN COAL.[1]

BY CHARLES W. STODDART.

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THE Committee on Coal Analysis, appointed by the American Chemical Society in 1895, failed to select one standard method for the estimation of sulphur in coal. The following work was undertaken with reference to this fact, and to decide, if possible, which of the many rapid determinations is the most accurate.

COALS EMPLOYED.

The coals used were selected from a large number of samples, and represent a wide range of composition and locality. The following analyses of these coals are arranged in order of hardness, from coke to lignite, with sulphur content as first found by the ordinary Eschka method:

	HH. Per cent.	FF. Per cent.	X. Per cent.	T. Per cent.
Moisture	0.00	1.93	2.22	1.10
Volatile combustible matter	0.70	2.55	3.78	4.87
Ash	10.78	1.97	6.91	16.25
Sulphur	1.03	0.73	0.80	2.02
Carbon	87.49	92.82	86.29	75.76

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[1] Read at the May meeting of the New York Section of the American Chemical Society.