THE COLORIMETRIC ESTIMATION OF SMALL AMOUNTS OF CHROMIUM, WITH SPECIAL REFERENCE TO THE ANALYSIS OF ROCKS AND ORES.[1]

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INTRODUCTION.

HAVING occasion to analyze a number of highly titaniferous magnetites containing chromium, phosphorus, and vanadium, it became a serious problem to effect satisfactory separations of all these bodies in a form fit for separate determinations. The method of T. Fischer[2]—digestion of the precipitated lead salts with a strong solution of potassium carbonate—appears to offer the long-needed satisfactory quantitative separation of arsenic, phosphorus, chromium, tungsten, and molybdenum from vanadium, the normal lead meta-vanadate remaining quite unattacked, according to the author, while the other lead salts are wholly decomposed, but the applicability of this method to the separation of the minute amounts often found in rocks and ores has not been tested. The time required is considerable, hence it was desirable to devise a more rapid way for determining both chromium and vanadium without resorting to this separation. That this object has been measurably achieved, with certain limitations as to vanadium, the work thus far done seems to indicate. The present paper will deal only with the rapid estimation of chromium either in absence or presence of any or all of the elements above mentioned.

In view of the high coloring power of the chromates, it is surprising that this property does not seem to have been made the basis for a quantitative method for the estimation of chromium. A search through some of the more important textbooks has revealed no reference to such a method, and I am unaware that one has even been suggested. Yet the results attainable by colorimetric comparisons of dilute alkaline solutions of unknown strength with those of a known standard, leave little to be desired in point of quantitative accuracy.

As with colorimetric methods in general this one gives better results with small than with large percentages of chromium, yet it can be applied in the latter cases with very fairly satisfactory

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[1] Read before the Washington Section, March 10, 1898.

[2] Inaugural Dissertation, Rostock, 1894.

results by making a larger number of consecutive comparisons with the same solution.

OUTLINE OF METHOD.

The chromium is brought into a measured volume of solution as monochromate rendered alkaline by sodium carbonate, and the whole or a portion of this solution is then compared with a definite amount of a somewhat stronger standard likewise made alkaline with sodium carbonate. The latter is diluted with water till both seem to be exactly alike in color, when a simple calculation gives the amount of chromium sought. The actual comparison takes little time and any number of repetitions can be made if desired in order to secure greater accuracy from the mean of a large number of observations. The preparation of the solution to be tested offers nothing novel, but certain precautions have to be observed therein as well as in the color comparisons which will be touched upon later.

TESTING OF METHOD BY COMPARISON OF STANDARD SOLUTIONS.

Two standard solutions were prepared by dissolving 0.25525 and 0.5105 gram potassium chromate in one liter of water made alkaline by a little sodium carbonate, each cubic centimeter then corresponding respectively to one-tenth and two-tenths milligram chromic oxide, in which latter form chromium is usually reported in rocks and ores. Definite amounts of one of the standards were then diluted with varying amounts of water in a tall, square glass vessel with exactly parallel sides. Into an exact duplicate of this vessel five or more cc. of the standard were introduced from a burette and diluted with water from another burette till exact agreement seemed to be reached on looking through the glasses horizontally.

In the following tables are recorded all observations without regard to the sequence in which they were made. No greater pains were taken to get exact agreement of color than are ordinarily observed in our routine titanium estimations, which are carried out in a precisely similar manner, so that the results may be taken to represent every-day work without extreme precautions. In only two cases can the observations be considered really bad, *viz.*, the third comparison of No. 6 and the first of No. 16.

TABLE I.

Ten cc. standard represent one milligram chromic oxide.

	Test solution.		Comparison standard.						
No.	Standard. cc.	Diluted with water. cc.	cc.	H_2O added. cc.	Contents as chromic oxide. Milligrams.	Chromic oxide found. Milligrams.	Chromic oxide present. Milligrams.	Error. Milligram.	Chromic oxide. Per cent. found.
1	10[1]	90[1]	5	44.00	0.5	0.98	1	—0.02	98.0
2	20[2]	80[2]	5	21.00	0.5	1.92	2	—0.08	96.0
3	40	60	10	14.60	1.0	4.06	4	+0.06	101.5
4	40	60	9.7	14.25	0.97	4.05	4	+0.05	101.2
			10	13.95	1.0	4.17	4	+0.17	104.4
			10	14.30	1.0	4.11	4	+0.11	102.9
			10	14.20	1.0	4.13	4	+0.13	103.3
5	40	60	10	14.65	1.0	4.05	4	+0.05	101.4
			10	15.65	1.0	3.90	4	—0.10	97.5
6	40	60	10	15.25	1.0	3.96	4	—0.04	99.0
			10	14.30	1.0	4.11	4	+0.11	102.9
			10	13.15	1.0	4.32	4	+0.32	108.0
			10	14.75	1.0	4.04	4	+0.04	101.0
			20	29.50	2.0	4.04	4	+0.04	101.0
7	50	50	10	9.75	1.0	5.06	5	+0.06	101.2
8	50	50	10	10.00	1.0	5.00	5	0.00	100.0
9	60	40	10	7.20	1.0	5.81	6	—0.19	96.7
10	75	25	20	6.65	2.0	7.505	7.5	+0.005	100.1
			20	6.60	2.0	7.519	7.5	+0.019	100.2
			10	3.15	1.0	7.605	7.5	+0.105	101.4
			15	4.70	1.5	7.610	7.5	+0.11	101.5
11	10	10	10	10.15	1.0	0.992	1	—0.008	99.2
			20	19.75	2.0	1.006	1	+0.006	100.6
12	10	11	10	10.60	1.0	1.02	1	+0.02	102.0
13	14.2	26.9	10	18.60	1.0	1.43	1.42	+0.01	100.7
			20	35.70	2.0	1.47	1.42	+0.05	103.5
14	15	24.35	10	16.55	1.0	1.48	1.5	—0.02	98.7
15	16	20	10	13.30	1.0	1.54	1.6	—0.06	96.2
			20	24.30	2.0	1.63	1.6	+0.03	101.9
16	31.9	20.6	10.5	8.10	1.05	2.96	3.19	—0.23	92.8
			20.5	14.20	2.05	3.10	3.19	—0.09	97.2
17	62.05	22.3	20	7.00	2.0	6.25	6.205	+0.45	100.7
			40	12.00	4.0	6.49	6.205	+0.285	104.6

Mean percentage found, 100.5.

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[1] Color in this dilution too faint.

[2] Limit of dilution for clear distinction of color in a thickness of three and three-tenths cm.

TABLE II.

Varying amounts of standard No. 2 (1 cc. = 0.2 mg. Cr_2O_3) diluted till of the same concentration as standard No. 1.

	Standard.						
No.	cc.	Water added. cc.	Contents as chromic oxide. Milligrams.	Chromic oxide found per 100 cc. Milligrams.	Chromic oxide present in 100 cc. Milligrams.	Error. Milligram.	Chromic oxide. Per cent. found.
18	5	5.2	1	9.80	10	—0.2	98.0
19	10	9.95	2	10.02	10	+0.02	100.2
20	15	15.8	3	9.74	10	—0.26	97.4
21	20	20.0	4	10.00	10	0.00	100.0
22	30	29.5	5	10.08	10	+0.08	100.8

Mean 99.3 Grand mean 100.36.

The first table and the grand mean show an apparent personal tendency toward slightly high results, though it is possible that this is due to a slight difference in the internal dimensions of the two glasses, the same one always having been used for the standard solution. If this is so, a long series of tests with glasses reversed should give a general mean slightly below 100.

TESTING THE METHOD ON ORES AND ROCKS.

In order to prove the value of the method in rock analysis, varying amounts of the standard solution were evaporated in a large crucible with five grams of an iron ore carrying phosphorus and vanadium, and fused with twenty grams of sodium carbonate and three grams sodium nitrate. The aqueous extract, after reduction of manganese by methyl or ethyl alcohol, was nearly neutralized by nitric acid and evaporated to secure approximate separation of silica and alumina. As a precautionary measure, since a little chromium is usually carried down, the precipitate was ignited, silica was removed by hydrofluoric and sulphuric acids, the residue was fused with sodium carbonate, and alumina again separated as before. To the combined filtrate was added mercurous nitrate and the slightly washed copious precipitate of phosphate, chromate, vanadate and carbonate of mercury was ignited with the paper in a platinum crucible, which can be done without much fear of loss or of injury to the crucible. The residue was then fused with a little sodium carbonate, extracted with water, filtered into a graduated flask and made up to 50 or 100 cc., according to the intensity of the color, and compared with the standard. A similar operation was carried out with a silicate rock. Table III shows the results.

TABLE III.

No.	Chromic oxide added. Milligrams.	Chromic oxide found. Milligrams.
I. Five grams iron ore	7.03	7.18
	...	7.20
	...	7.25
	...	7.21
II. Five grams iron ore	2.99	3.08
	...	3.13
III. Two grams silicate	1.6	1.53
	...	1.57
	...	1.59

When the percentage of chromic oxide in an ore or mineral is more than about two-tenths per cent. and vanadium has not also to be estimated, much time may be spared by at once taking the color of the original extract from the sodium carbonate fusion, after insuring complete reduction and removal of manganese, and perhaps concentrating. But if the chromium is much less than this amount, and especially if several grams of powder have been operated on, it becomes difficult or impossible to obtain a filtrate of sufficiently small bulk to show a decided color. Therefore, in such cases, and when vanadium is likewise to be estimated, it is necessary to precipitate as above with mercurous nitrate in order to eventually have a small bulk of sufficiently colored solution. Even then, for very minute amounts, it is necessary to use Nessler tubes exactly as in ammonia estimations.

If niter has been used in the fusion and the crucible has been attacked by it, a yellow color of the filtrate may be due to dissolved platinum, but neither the proportion of niter nor the temperature of the blast should ever be high enough to permit the crucible to be attacked.

THE COLORIMETRIC APPARATUS AND ITS USE.

The glasses employed were of approximately square section, about twelve cm. high and three and three-tenths cm. inside measurement, with exactly parallel sides, and of course as nearly alike as they could be obtained. One pair of opposite sides of each should be blackened. With glasses of the thickness mentioned it is generally advisable to use from five to ten cc. of standard at a time and to so regulate the strength of the solution to be tested that it shall contain more than two milligrams chromic oxide in 100 cc. which is about the limit of distinct visibility in a thickness of three and three-tenths cm.

In order to exclude the effect of side light in this and other similar methods (titanium for instance), it is very convenient to have a simple light box that can be easily held in one hand, about thirty-five cm. long and thirteen to fourteen cm. square, painted black inside and out and with one end closed by a piece of ground glass, the other open. For a space equal to the width of the glasses the cover is removed at the top next the glass end, to permit of the insertion of the glasses, side by side, in such a way that no light shall penetrate around their sides or between them. A stiffly sliding, black, cardboard shutter is movable up and down immediately back of the glasses, so that all light can be cut off except that which comes through the liquid.

Precautions of this kind are necessary if accurate results are to be counted on. Except for mere traces this simple combination of glasses and darkened box ensures greater accuracy and rapidity of work than Nessler tubes and is preferable likewise, so far as my own experience goes, to expensive instruments like the colorimeter of Soleil–Duboscq, etc. The glasses should, of course, have exactly parallel sides and equal diameters, though they may perhaps be made with advantage rather narrow in one direction to permit of using smaller bulks of liquid.

In making the color comparisons the box is best held close to a window, so as to get a full strong light. The condition of the light seems to make an appreciable difference in the accuracy of the comparisons, all of which were made by daylight.

ACCURACY OF RESULTS.

Especially for comparatively and very small amounts of chromium the method gives exact results, better than can ordinarily be hoped for from any gravimetric method, considering the fact that as a rule other substances are present which it is extremely difficult to remove completely.

A few comparisons between colorimetric and gravimetric determinations of chromium in a few rocks are here given to show the order of agreement, the former having been made several months and even years after the latter.

Gravimetric. Per cent.	Colorimetric. Per cent.
trace	0.018
0.05	0.051
0.14	0.12
0.08	0.083
trace	0.013
none	0.0086
none	0.0067

The outcome was somewhat of a surprise, for it was scarcely to be expected that the long and laborious gravimetric separations should have resulted so well as they are shown to have done. It should be mentioned that for the gravimetric tests but one or two grams at most were used, which accounts for the reported absence of chromium in two instances, this report being based on the lack of color in the aqueous extract of the alkaline fusion after removal of manganese.

No experiments have been made with high percentages, but the tables give with certainty the degree of accuracy even then attainable. Whether the chromic oxide to be estimated is one-tenth per cent. or one hundred per cent., the percentage result is the same provided the dilution is alike in each case. For instance, if 99.5 per cent. is found in a total solution of 100 cc. containing 0.01 gram chromic oxide, the same percentage holds if the total volume were ten liters holding one gram chromic oxide.

It is probably inadvisable to increase the strength of the standard much above that of No. 2 above, containing two-tenths milligram chromic oxide in form of potassium chromate to the cubic centimeter.

No tests have been made with other alkaline solutions than sodium carbonate, in order to ascertain if there is a difference in the color intensities for like dilution, nor is it probably important to do so.

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