VOLUMETRIC ESTIMATION OF VANADIUM IN PRESENCE OF SMALL AMOUNTS OF CHROMIUM, WITH SPECIAL REFERENCE TO THE ANALYSIS OF ROCKS AND ORES.[1]

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OUTLINE AND LIMITATIONS OF THE METHOD.

WHEN chromium and vanadium occur together and the former has been estimated colorimetrically as detailed in the preceding paper,[2] the vanadium can in many instances be at once estimated without separating from the chromium by the well-known method of titration with potassium permanganate in sulphuric acid solution after reduction by sulphurous acid and expulsion of all excess of the latter.

The application of the method is subject to one limitation—the chromium must not be present above a certain moderate amount. This limitation is due to the considerable amount of permanganate required to produce a clear transition tint when titrating in a hot solution, as is necessary with vanadium. In a cold solution of chromic sulphate much less permanganate is needed to produce the peculiar blackish tint without a shade of green, which affords a sure indication of excess of permanganate, but in a hot and especially a boiling solution the oxidation of the chromium[3] itself takes place so rapidly that a very large excess of the reagent may be added before a pronounced end-reaction is obtained. Nevertheless, as will be shown, quite satisfactory determinations of as little as one or two milligrams of vanadium pentoxide can be made in presence of as much as thirty milligrams of chromic oxide.

Inasmuch as chromium is almost never a prominent constituent of the clays, coals, iron ores, and rocks in which vanadium has been thus far reported, the method promises to be of great advantage in rock and ore analysis, where these elements probably frequently occur together, generally with phosphorus and sometimes arsenic. It is not directly applicable in

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[1] Read before the Washington Section, April 14, 1898.

[2] This Journal, 20, 454.

[3] Storer, through Gmelin-Kraut, 2, [2] 290.

presence of molybdenum, and arsenic must first be removed by hydrogen sulphide if present.

TESTING THE METHOD.

A solution of sodium vanadate was prepared by fusing 0.937 gram of pure vanadium pentoxide with sodium carbonate and diluting to one liter. Each cubic centimeter contained 0.000937 gram vanadium pentoxide. Of this, sufficient amounts were mixed with varying volumes of a standard solution of potassium chromate. After in some cases determining chromium colorimetrically, sulphuric acid was added, sulphur dioxide gas[1] introduced for a few moments, and the excess of the latter expelled by boiling in a rapid current of carbon dioxide, without which its complete expulsion is difficult. When cooled to from 70°–80° C. the titration was made with very dilute solution of permanganate corresponding to about one milligram vanadium pentoxide to the cubic centimeter as calculated from its equivalent in iron. By repeating the reduction and boiling, any number of check-tests can be rapidly made in the same solution. The solutions ranged in bulk from 50 to 200 cc. according to the amounts of chromium added.

With the larger chromium contents the differences in the quantity of permanganate used, according as titration was effected at practically boiling temperature or a somewhat reduced one, were very apparent. In one case at nearly boiling heat, ten milligrams of chromic oxide were largely oxidized to chromium trioxide, as shown by the change of color from dark green to yellow. Even at 70°–80° with this amount of chromium the results for vanadium will be too high unless the precaution is taken to ascertain the needed correction by adding permanganate to an equal bulk of hot chromic sulphate solution containing approximately the same amount of chromium. When this is done, however, the results are satisfactory even when as much as thirty milligrams of chromic oxide are present and only one or two milligrams of vanadium pentoxide.

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[1] The direct use of a solution of sulphur dioxide or of an alkaline sulphite is inadmissible unless these have been freshly prepared, since after a lapse of time they contain other oxidizable bodies than sulphurous acid or a sulphite. The sulphur dioxide is best obtained as wanted by heating a flask containing a solution of sulphur dioxide, or of a sulphite to which sulphuric acid has been added.

Doubtless the modified iodometric method of T. Fischer[1] will in general give sharper results where chromium is present in considerable amount, and if so it should be preferred to titration by permanganate. But its use involves the preparation of a standard thiosulphate instead of the ever-ready permanganate solution, and the manipulations are more time-consuming. The object has been in the present case to reach satisfactory results with the greatest expedition, and when chromium is not present in considerable amount this is accomplished.

The following tables contain the results of a considerable number of tests, those in Table II being tabulated separately in order to show the degree of accuracy attainable with a large excess of chromium by applying the correction above mentioned and also the amount of this correction.

TABLE I.

No.	Chromic oxide. Milligrams.	Vanadium pentoxide. Milligrams.	Vanadium pentoxide found. Milligrams.	Error. Milligram.
1	1	9.37	9.22	—0.15
2	1	0.94	1.04	+0.10
			0.98	+0.04
3	1.5	5.25	5.49	+0.24
			5.43	+0.19
4	2	5.62	5.5	—0.12
			5.5	—0,12
5	3	4.68	4.78	+0.10
			4.78	+0.10
			4.83	+0.15
6	3	5.62	5.58	—0.04
			5.58	—0.04
7	3.5	18.74	18.89	+0.15
			18.97	+0.23
8	6	5.6	6.1	+0.50
9	6	4.68	4.78	+0.10
10	6	5.62	5.58	—0.04
11	10	5.62	5.58	—0.04
12	10	23.52	23.81	+0.29
			23.71	+0.19
13	10	46.85	46.98	+0.13
			47.20	+0.35
14	25	23.52	23.65	+0.13
			23.75	+0.23
15	87.5	23.52	23.71	+0.19

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[1] Inaugural Dissertation, Rostock, 1894, p. 33.

TABLE II.

Showing application of degree of correction for larger amounts of chromium, obtained by adding potassium permanganate to an equal bulk of solution containing a like amount of chromic sulphate.

No.	Chromic oxide. Milligrams.	Vanadium pentoxide. Milligrams.	Vanadium pentoxide found. Uncorr.	Vanadium pentoxide found. Corrected.	Error. Milligram.	Volume of solution.
16	20	0.94	1.59	0.99	+0.05	50–100 cc.
17	20	1.87	2.69	2.09	+0.22	"
			2.39	1.79	−0.08	
			2.59	1.99	+0.12	
18	20	18.74	19.4	18.73	−0.01	"
			19.3	18.63	−0.11	
			19.3	18.63	−0.11	
19	30	1.87	2.99	2.14	+0.27	About 100 cc.
			2.79	1.94	+0.07	
			2.79	1.94	+0.07	
			2.69	1.84	−0.03	
			2.69	1.84	−0.03	
20	30	1.87	2.69	1.79	−0.08	200 cc.
			2.89	2.09	+0.22	
			2.89	2.09	+0.22	
			2.79	1.89	+0.12	
21	62	46.85	48.60	47.60	+0.75	200 cc.

In spite of the fact that the correction in most of the trials of this last table represents a large proportion of the permanganate used, the results must be considered satisfactory in view of the small amount of vanadium present, and they show that the method in competent hands after a little experience affords trustworthy figures.

TESTING THE METHOD ON ROCKS AND ORES.

The following table shows its availability for rocks and ores. Known amounts of both chromium and vanadium were added to an iron ore and to a silicate, both free from arsenic, which were then fused with sodium carbonate and nitrate and further treated as follows: After extracting with water and reducing manganese by alcohol, the silica and alumina were mostly removed by nearly neutralizing with nitric acid and evaporating to near dryness. The washed precipitate was ignited and treated with hydrofluoric and sulphuric acids, the residue fused with sodium carbonate, since it frequently contains a little chromium, and again nearly neutralized, etc. To the combined and slightly alkaline filtrates was added mercurous nitrate, the precipitate of phosphate, vanadate, chromate, and carbonate was ignited in platinum, fused with a little sodium carbonate, leached with water, and filtered into a small graduated flask. After colorimetric determination of the chromium, sulphuric acid was added, both chromium and vanadium were reduced by sulphur dioxide gas, and the titration carried out as described.

TABLE III.

No.	Chromic oxide. Milligrams.	Vanadium pentoxide. Milligrams.	Vanadium pentoxide found. Milligrams.	Vanadium pentoxide. Error. Milligram.
22 (Five grams iron ore)	7	6.76	6.81	+0.05
			6.48	—0.28
			6.43	—0.33
			6.37	—0.37
23 (Five grams iron ore)	3	3	3.08	+0.08
			3.13	+0.13
			3.03	+0.03
			3.08	+0.08
24 (Two grams silicate)	1.6	1.87	1.86	—0.01
			1.97	+0.10
			2.07	+0.20
			1.86	—0.01

These and other experiments show that by taking not over five grams of ore or rock, vanadium, if present to the extent of 0.01 or 0.02 per cent., can be readily estimated by exercising reasonable care in all the operations. Absolute confirmation of its presence can be easily obtained by evaporating and igniting the solution to remove excess of sulphuric acid, taking up with a few drops of dilute nitric acid, and adding to the solution in a test-tube a drop or two of hydrogen peroxide. In this way positive or negative assurance as to the presence of vanadium, is given when the result of titration alone might be uncertain. Addition of ether at the same time affords a simultaneous test for chromium by its blue color, and this might perhaps be made use of, if necessary, to remove all, or the greater part of the chromium from the titration of the vanadium, since the oxidation product of the latter does not dissolve in the ether.

It is even possible that the dark brown color produced by hydrogen peroxide might be utilized for an exact colorimetric method for estimating vanadium.

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