

ployed in the computations and the specific refractivities calculated from them, together with the factors given above.

TABLE III.

	N.	D obs.	D calc.	K obs.	K calc. ²	K ³ .
SiO ₂ { Quartz.....	1.5472 ¹	2.652 ¹	2.3	0.11961 ¹	0.1380	0.1220
Trydymite..	1.4830 ¹	2.318 ¹		0.12319 ¹	0.1240	
Fused Quartz	1.4590 ¹	2.213 ¹		0.12354 ¹	0.1188	
CaO.....	1.8320 ¹	3.316 ¹	4.1	0.13266 ¹	0.1073	0.1210

SUMMARY.

1. A series of soda lime glasses have been made and their refractive indices measured.

2. The existence of a double silicate of the type $2\text{Na}_2\text{O} \cdot 3\text{CaO} \cdot x\text{SiO}_2$, which is doubtless the double metasilicate, described by Kultaschew and Wallace, has been made evident.

3. The specific refractivities of these glasses, computed with the aid of the calculated densities, are additive from pure sodium silicate up to the composition in which the molecular proportion of soda to lime is 2 : 3.

4. Factors have been derived by means of which the specific refractivity of soda lime glasses may be calculated. These are for the formula of Lorentz and Lorenz: SiO_2 , 1.220; CaO , 1.210; Na_2O , 0.1302.

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A NEW METHOD FOR THE DETERMINATION OF VANADIUM.

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The following method for the determination of vanadium in steel depends upon the selective oxidation of ferrous sulfate in the presence of vanadyl sulfate by means of manganese dioxide. The vanadyl sulfate is then titrated by adding an excess of permanganate, the excess permanganate being titrated by sodium arsenite.

This differential oxidizing action apparently contradicts the results of J. R. Cain,⁴ who found that both iron and vanadium are oxidized, but the reasons for this discrepancy are shown in the note which follows on page 256.

The manganese dioxide should be sufficiently fine to pass through a 200-mesh sieve, and yet should settle in a beaker of water in 30 seconds.

The process in detail is as follows: In a 500 cc. flask a two-gram sample of the steel or iron is dissolved in a mixture of 30 cc. of water and 12 cc. concentrated H_2SO_4 with application of heat. Then one cc. of HNO_3 (sp. gr. 1.42) is added cautiously to oxidize the iron and the solution is boiled for a few minutes to remove the nitrous fumes. Then the solution is diluted with 30 cc. of water and a strong solution of KMnO_4 is added to completely oxidize all carbon, etc., and the solution is boiled. If the per-

manganate or the resulting MnO_2 should disappear, not enough permanganate has been used, and more should be added. Now ferrous sulfate is added to reduce the MnO_2 , HMnO_4 , H_2CrO_4 , and H_3VO_4 , etc., and the solution is again boiled to remove any possible nitrous fumes. Then pure distilled water is added to make the volume about 250 cc., $N/10$ KMnO_4 added until the solution is pink, and the solution cooled to tap water temperature. Ferrous sulfate solution is added until all reducible compounds including chromic and vanadic acids are reduced. Only enough ferrous sulfate should be added to be certain that there is a decided excess present. A solution, one cc. of which equals about 0.01 gram of iron, is the one used. Now about one gram of C. P. MnO_2 is added and the solution shaken vigorously. After two minutes a drop is tested with ferricyanide on a white plate to see if the iron is completely oxidized. It generally takes from four to six minutes. At the end of each minute the solution is tested for ferrous iron until none is present and the shaking is continued for about one-half minute longer. It should be noted that a bluish color will always be obtained in the presence of vanadyl sulfate after the test drop has stood for a few seconds. The end should be taken when the test does not show blue immediately. The blue color which forms after a few seconds, even when there is no ferrous iron present, is due to the reduction of ferri- to ferrocyanide by the vanadyl sulfate. One can become familiar with this end by adding a drop of ferric sulfate containing vanadyl sulfate to a drop of ferricyanide on a white plate.

The MnO_2 oxidizes the ferrous sulfate to ferric sulfate, but does not oxidize the vanadyl sulfate $[\text{V}_2\text{O}_5(\text{SO}_4)_2]$. Then the MnO_2 is filtered off on an asbestos mat, using suction. From a burette a standard solution of KMnO_4 is added until a pink tinge is present in the solution, and one cc. more is added, and after one minute the excess permanganate is titrated with Na_3AsO_3 solution. The end point is very sharp. If at this point the operator is not satisfied with this titration, the excess arsenite may be oxidized with KMnO_4 , ferrous sulfate again added, then oxidized with MnO_2 as before, and the titration repeated, thus giving a check on the titration. A blank determination must be run on a vanadium-free steel, and the result deducted. The blank generally amounts to about 0.00075 gram V. The time required is about one-half hour and the results are very satisfactory. In fact the accuracy is about that of a phosphorus determination.

The vanadium steel standard furnished by the Bureau of Standards was analyzed by the above method. The result of the Bureau chemists is 0.0143 per cent. V and the average of the cooperating chemists is 0.15 per cent. V. The writer obtains the following results, the average being 0.143 per cent.:

0.140	0.138
0.147	0.147
0.143	0.143

To further test the method, two-gram samples of

¹ Larsen, *loc. cit.*

² Using Lorentz and Lorenz formula and "D calc."

³ Factors used in computing specific refractivities.

⁴ THIS JOURNAL, 3, 476 (1911).

vanadium-free steel with the addition of ferro-vanadium containing 0.00684 gram of vanadium were analyzed. The results were 0.00680 and 0.00690 gram V. Another sample with 0.0342 gram V was analyzed, and 0.03432 gram V was found.

To test the effect of chromium on the method, the Bureau of Standards' sample above mentioned was analyzed with the addition of 0.100 gram Cr. The results were 0.143 per cent. and 0.143 per cent. V, showing that chromium has no effect on the vanadium results. Scores of other determinations have been made, proving the accuracy of the method.

The KMnO_4 solution used equals 0.001 gram iron per cc., and the arsenite solution has the same strength. This makes the KMnO_4 equal 0.000917 gram vanadium per cc. The arsenite solution is made by dissolving about 2.25 grams As_2O_3 in Na_2CO_3 solution and diluting to 2,000 cc.

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A RAPID METHOD FOR THE DETERMINATION OF VANADIUM IN STEELS, ORES, ETC., BASED ON ITS QUANTITATIVE INCLUSION BY THE PHOSPHOMOLYBDATE PRECIPITATE.

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I. INTRODUCTION.

The fact that vanadium is carried down with ammonium phosphomolybdate when the latter is precipitated in solutions of the former has long been known. Likewise, the fact that the precipitate so obtained has different properties from the normal phosphomolybdate has been mentioned by several authors. The orange to brick-red color of this vanadium-bearing precipitate is quite different from the color of the normal ammonium phosphomolybdate, called from its color the "yellow precipitate." Brearley and Ibbotson¹ mention the increased solubility in dilute nitric acid of the vanadium-bearing precipitate over the normal precipitate, and give some conditions to lessen precipitation of vanadium with phosphorus in steel analysis. The phenomenon has usually been studied with regard to the determination of phosphorus in the presence of vanadium, since the precipitation of vanadium with ammonium phosphomolybdate interferes with an exact determination of phosphorus by the ordinary methods. Especially is this true in steel analysis. The possibility of easily separating vanadium from iron by this method has, we believe, never been studied before. The present research was undertaken in order to decide whether or not vanadium could be completely precipitated with phosphoric acid, and, if so, to learn if it could be determined quantitatively.

2. PRELIMINARY CONDITIONS FOR PRECIPITATING THE VANADIUM.

The necessary ratio of phosphoric acid to vanadic acid for complete precipitation of the latter was in-

vestigated qualitatively by following the change in color of the phosphomolybdate precipitated with increasing additions of phosphoric acid. A nitric acid solution of a vanadium-free steel was prepared; to this was added a known amount of vanadium from a carefully standardized ammonium vanadate solution. To equal volumes of the steel solution so prepared were added gradually increasing volumes of a roughly standardized sodium phosphate solution, and the phosphoric acid was precipitated by the molybdate reagent, observing the conditions for this precipitation usually given in texts on steel analysis. With small amounts of phosphoric acid the precipitate was of a deep orange color, which became progressively lighter as the phosphorus increased, finally approaching the color of the normal or vanadium-free phosphomolybdate when relatively very large amounts of phosphoric acid were added. The filtrates were treated by precipitating a further small amount of phosphoric acid, and judging by the color of the precipitate whether or not precipitation was complete the first time. The color of the precipitate proved to be a very delicate qualitative criterion, and very soon it was possible in this manner to fix with fair accuracy the ratio of phosphoric acid to vanadic acid in order to carry down all the vanadium with one precipitation. As methods for the quantitative determination of the vanadium were developed this ratio was determined with greater accuracy. The mechanism of the precipitation and the question of this ratio are subjects that will be described in more detail in another paper. It is sufficient for the present purpose to say there is a co-precipitation of vanadium under the above general conditions, which can be controlled accurately enough to make the precipitation uniformly quantitative. The conditions will be detailed later.

Other questions affecting the probable accuracy of the determination were (1) the solubility of the vanadium-bearing precipitate in the usual washing solutions, and (2) the optimum temperature for precipitation. As to the solubility of the precipitate, it was soon found that the presence of vanadium caused marked changes in the solubility of ammonium phosphomolybdate. It was noticed that when the precipitate dissolved to any extent in the washing solutions these were strongly colored, usually having a straw or orange tint. It was thus possible to decide this question qualitatively, and Table I gives some of the results obtained. It will be seen that acid ammonium sulfate and ammonium nitrate solutions are best adapted for washing the yellow precipitate. Incidentally, the marked solubility in dilute solutions of potassium nitrate and of nitric acid is of interest, for these are the wash solutions recommended by some authorities for use when determining phosphorus in steel. It is evident that such use may occasion errors in the phosphorus determination if vanadium is present in appreciable amount. It seems probable that the solubilities vary considerably with the proportion of vanadium present in the precipitates.

¹ "The Analysis of Steel Works Materials," 1902, p. 165.