An Improved Method of Colorimetric Determination of Vanadium in the Presence of a Relatively Large Amount of Iron

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Introduction

The following is a description of an improved method for the determination of vanadium in the presence of a comparatively large amount of iron, which is originated by Sandell⁽¹⁾ and considered to be the most accurate and most easily manageable one by which chromium and molybdenum are simultaneously determined in silicate rocks. This method proposed by Sandell for the element in silicate rocks is a combination of the reaction with oxine reported by Montequi and Gallego⁽²⁾ and the color reaction of phosphotungstic acid with the element reported by Vinogradov.⁽³⁾ It suffices for the determination of as little as 0.001% of vanadium, 0.001% of chromium and 0.0001% of molybdenum in a sample of only one gram.

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(1) E. B. Sandell, *Ind, Eng, Chem., Anal. Ed.*, **8**, 336 (1936).

(2) R. Montequi and M. Gallego. *Anales soc. espan. fis, quim.*, **32**, 134 (1934).

(3) A. P, Vinograbov, *Compt. rend. acad. sci. U. R. S. S.*, **1931** A, 249.

The outline of this method is as follows: the melt from the carbonate fusion is leached with water and filtered after adding alcohol to reduce the manganate produced. The filtrate, containing chromate, vanadate and molybdate, is diluted conveniently in a measuring flask up to a definite volume, say to 100 ml. For the determination of vanadium, a stable aliquot portion of the solution is taken (usually 10 ml.), neutralized to methyl orange with sulfuric acid and extracted with chloroform after the addition of 2.5% of oxine in 2 *N* acetic acid.

The residue resulting from evaporation of the chloroform extract is fused with sodium carbonate to convert vanadium into sodium vanadate, and the melt then dissolved with water. The solution obtained is colorimetrically determined by the coloration of intense yellow to orange due to the formation of vanadophosphotungstic acid, after treated with sodium tungstate and phosphoric acid in the acid medium.

When the author tried to use this method for the determination of the element in brown coal ash, he occasionally experienced a serious interference from iron. He conducted a number of experiments and succeeded in devising a new method, by which the interference from iron can be avoided and fairly good results are obtainable.

Experiment

The Presence of Ferrous and Ferric Iron in the Aqueous Extract from the Sodium Carbonate Melt.—In Sandell's original report there were instances in which, it was mentiond, ferric iron diminished the color of vanadophosphotungstic acid and made the results low. The amount of iron going into the filtrate from the sodium carbonate melt of an igneous rocks, however, is too small to cause any appreciable error and hence no quantitative data on its interference have been given.

In the analysis of brown coal ash the interference of iron which passed into the extract seriously affected the color reaction. Contrary to the general belief, the amount of iron is considerably large, as shown in Table 1, even when the determination was performed by the approved method, volumetrically or colorimetrically, using a good quantitative filter paper.

Table 1

Iron in the Filtrate

Exp. No.	Ion	Iron in leached solution (1 g. ash used), γ	Remarks
5	Fe^{+++}	275	colorimetrically
	Fe^{++}	469	〃
8	Fe^{+++}	2125	〃
17	Fe^{++}	1252	volumetrically
	Fe^{+++}	6904	〃
51	Fe^{++}	2091	〃
	Fe^{+++}	1308	〃
50	Total Iron	187	colorimetrically

It was found that in 100 ml. of the extract made from the melt of the mixture of sodium carbonate and 1 gram of brown coal ash, n to 0.n mg. of iron was usually present, resulting a serious interference. Yet the use of niter to oxidize iron is undesirable on account of its action on the platinum crucible to develop a yellowish coloration which may be injurious for chromium to be simultaneously determined in the same sample. The presence of iron in the filtrate is presumably due to the peptization of hydrous ferric oxide by silica. In consequence, the greater the content of iron in the sample is, the greater and more serious interference may be expected.

The Action of Iron on the Coloration.—A suitable portion of vanadium standard solution was taken and the following amount of ferric iron added to it. Then vanadium determination was made, the conditions recommended by Sandell being followed. The results are given in Table 2, in which the value was taken soon after the formation of vanadophosphotungstic acid without heating the solution as described below.

Table 2

Interference Due to the Presence of Ferric Iron

Presented (γ as V_2O_3)	Added (γ as Fe)	Found (γ as V_2O_3)	Error,	
25.3	18.9	24.3	− 1.0γ	− 3.9%
46.5	18.9	41.2	− 5.3	−11.4
46.5	37.5	40.8	− 5.7	−12.3
46.5	56.8	36.8	− 9.7	−20.9
70.5	2000	34.5	−36.0	−51.4
131.6	2000	72.5	−59.1	−44.9

It was found that the presence of ferric iron apparently leads to lower result.

Ferric iron as well as vanadium easily react with oxine at the *p*H recommended. Of course the greater part of iron oxiquinolate, extracted together with vanadium, is removed in the second carbonate fusion, though a small part of it might still pass into the water extract solution. The second carbonate fusion of oxiquinolate to convert vanadium to vanadate should therefore be cautiously performed.

The interference caused by ferrous iron was found to be different, however, when it was tested in the same way as ferric iron. Ferrous iron does not react with oxine under the condition described, but it easily reduces vanadate to vanadyl ion which does not react with oxine.(4) Consequently it seriously leads to lower results to such an extent as shown in Table 3.

Table 3

Interference due to the Presence of Ferrous Ion

Presented (γ as V_2O_3)	Added ferric ion (γ as Fe)	Found (γ as V_2O_3)	Eerror,	
45.0	6.8	21.0	−24.0 γ	−53.3%
45.0	13.7	15.0	−30.0	−66.6
45.0	34.0	11.0	−34.0	−77.5
45.0	68.0	9.0	−36.0	−80.0
52.0	0.6	51.0	− 1.0	− 1.9
52.0	1.2	45.0	− 7.0	−13.5
52.0	3.4	48.0	− 4.0	− 7.7
52.0	34.4	19.0	−33.0	−63.5
52.0	68.8	13.0	−39.0	−74.9

It is evident that the interference due to ferrous iron is more serious than that of ferric iron. Next, it was found that the interference, due to ferric iron in the solution with which the color comparison should be made, can be reduced to some extent by heating and keeping it on standing for a while.

The results are the same as given by Wright and Mellon(5) in which 10 mg. of ferric chloride with 0.0025 mg. vanadium change the hue of color in comparison with the standard solution free from iron, but by heating the solution before the comparison is made, the interference can be, to some extent, diminished.

The Oxidation of Vanadium.—It is evident from the above statement that in the presence of ferrous iron, the oxidation to vanadate from vanadyl ion is necessary for securing good results. This is easily accomplished by the addition of just enough potassium permanganate (0.01 *N*) to hot solution, though an excess of it is injurious owing to the destruction of oxine and the darkening the coloration. After the addition of permanganate, cool the solution to room temperature, filter and then follow extraction with oxine as described below. It is evident from Table 4 that the oxidation is useful in these cases.

Table 4

Oxidation of Vanadium with Permanganate

Presented (γ as V_2O_3)	Ion	Found, (γ as V_2O_3)	Error, γ	Remarks
131.6	vanadyl	0	—	not oxidized
		134.9	−3.3	
		128.6	−3.0	
		131.5	−0.1	
70.5	〃	0	—	〃
		69.5	−1.0	
		72.0	−1.5	
		71.0	−0.5	
		67.9	−2.6	
202.1	vanadate and vanadyl	70.5	—	〃
		197.5	−4.8	
		199.3	−2.8	
		202.8	−0.7	
		204.7	−2.6	

The Separation of Iron from Vanadium.—Vanadium and iron react with oxine at the intermediate color of methyl orange (3.1 to 4.4) as the reactive *p*H range of iron with oxine is 2.8 to 11.2 and that of vanadium, from 2.7 to 6.1.(6) Thus iron extracted together with vanadium results in the serious error as shown already, even though only a small part of it might pass again into the water extracted solution through the melt of the second carbonate fusion. With the increase in the amount of iron, the more is the possibility of the interference. Therefore if a considerably large amount of iron is present, preliminary separation is essential. The following procedure has been devised which is based on the fact that only iron reacts with oxine in an alkaline medium.

The solution is made faintly alkaline to phenolphtalein with sodium hydroxide and iron is extracted with chloroform after adding 2.5% of oxine in 2 *N* acetic acid solution (Fraction a). Next the solution is buffered at *p*H 3.8 with 2.5 ml. of sodium citrate(7) and 10 ml. of 0.15 *N* acetic acid, and vanadium is extracted in the same way (Fraction b).

The fraction (a) as well as (b) prepared from the model solution containing the two elements in various concentration were thus tested. Then this method of separation was applied to the analysis of two samples of the brown coal ash (No. 5 and No. 7). Vanadium could not be spectroscopically found in fraction (a) of both samples while iron was detected only in fraction (b) of No. 7. It is hereupon confirmed

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(4) Lundell, Hoffman and Bright, *Ind. Eng. Chem.* **15**, 1064 (1923).

(5) E. R. Wright and M. G. Mellon, *Ind. Eng. Chem., Anal. Ed.*, **9**, 251 (1937).

(6) H. Goto, *J. Chem. Soc. Japan*, **54**, 314 (1935); K. Shiba, *Repts. Tokyo Imp. Ind. Research Lab.*, **27**, 216 (1932).

(7) Dissolve 4.20 g. of citric acid in 40 ml. of 1 *N* sodium hydroxide and dilute to 200 ml. with water.

that practically complete separation was accomplished by this method.

Table 5

Spectroscopic Results Obtained with Model Solution Containing the Two Elements

Sample	Iron (III) (γ as Fe)	Vanadium (γ as V_2O_3)	Spectroscopic results (in oxine extract at pH 10.8)
No. 1	33.3	60	vanadium was not detected
No. 2	25.9	120	
No. 3	18.5	180	

This method of separation is preferably used after oxidation, when a considerable amount of iron is present : e. g., in the determination of vanadium in magnetite sand and other materials abundant in iron.

Procedure.—A preliminary separation of iron from vanadium as mentioned above is recommendable, though this procedure is not always necessary except when the sample is exceedingly rich in iron. The following will be a detailed description of the procedure, though, for practical application, an appropriate abbreviation in the procedure is permissible, depending upon the quality of the sample to be tested.

The water leached solution from the melt of carbonate fusion is made up to a definite volume (say 100 ml.) and an aliquot portion (10 ml.) is taken. Then it is made slightly acid with dilute sulfuric acid and boiled with the addition of potassium permanganate solution just sufficient to oxidize. (Don't add in any excess). After cooling and filtering using a glass filter, it is made slightly alkaline with sodium hydroxide. The compound of iron formed with 2.5% of oxine in 2 N acetic acid is extracted by the chloroform.

Next the solution is buffered at pH 3.8 with 2.5 ml. of sodium citrate and 10 ml. of 0.15 N acetic acid in the order given. Vanadium is then extracted by shaking with 2 ml. of chloroform and 0.1 ml. of 2.5% of oxine in 2 N acetic acid. Repeat the extraction three times in the same way. The last chloroform extract should have a faint yellowish coloration due to the excess of oxine itself. The chloroform extract is drawn off into a platinum crucible, to which 1 ml. of chloroform used to rinse the stem of the funnel is added.

Then to the crucible is again added 0.10 gram of anhydrous sodium carbonate and the solution is gently evaporated on a water bath. A sufficient care must be taken during evaporation because of the tendency of the extract of creeping up the wall of the crucible. Then it is fused thoroughly and warmed after adding a little water to hasten the dissolution of the melt. After cooling, it is filtered through a filter paper treated with 10% of sodium carbonate solution. The solution should be colorless and free from any marked turbidity at this stage.

The following reagents are added in succession to the filtrate, mixing after each addition: 1 ml. of sulfuric acid, 0.1 ml. of 85% of phosphoric acid and 0.2 ml. of 5% of sodium tungstate solution. The solution is gently

Table 6

Reproducibility

Present, γ (as V_2O_3)	Found, γ (as V_2O_3)	Error, γ (as V_2O_3)	Remarks
70.5	72.4	+1.9	ammonium metavanadate
	70.0	−0.5	
	72.6	+2.1	
	67.6	+2.9	
	71.1	+0.6	
131.6	133.0	+1.4	
	132.3	+0.7	
	131.5	−0.1	
	129.5	−2.1	
69.0	67.4	−1.6	1 g. of rock powder (Olivin basalt) was used
(mean value)	70.9	+1.9	
	68.2	−0.8	
	69.7	+0.7	
139.5	138.1	−1.4	vanadium standard solution is added to the water leached solution of the above rock.
	139.0	−0.5	
	138.0	−1.5	
	136.1	−3.4	
	139.8	+0.3	

Table 7

Vanadium Determination in Various Samples

Sample	Sample taken, g.	Found, γ (as V_2O_3)	Content %
Brown coal ash No. 1	1.0583	500	0.047
	1.0583	480	0.046
No. 2	1.0484	108	0.010
	1.0567	115	0.010
No. 3	1.0703	125	0.012
	1.0197	110	0.011
No. 4	1.0069	530	0.053
	1.0069	535	0.053
Olivin basalt	1.5006	72.5	0.0048
	1.5006	68.1	0.0045
Hypeithene dacite obsidian	1.0004	51.5	0.0051
	1.0002	47.2	0.0047
Nepheline basalt	1.0014	37.7	0.0038
	1.0013	40.6	0.0041
	1.0035	41.2	0.0041
Iron sand	0.9540	728	0.076
	1.0005	734	0.073
Leaves of white birch	0.9942	60.5	0.0063
	0.9942	58.4	0.0059

warmed to hasten the formation of vanadophosphotungstic acid. Thus vanadium is determined by using S 43 (434 mμ) filter with Pulfrich photometer.

Results.—A number of experiments were conducted on the reproducibility of this method as shown in Table 6. Preliminary separation of iron from vanadium was not adopted except in a single case, but oxidizing procedure was applied in these cases. Thus the vanadium contents in magnetite sand, rock, leaves and brown coal ash were determined with satisfactory results as shown in Table 7.

Summary

Contrary to the general belief, the author confirmed the presence of iron in the filtrate from the carbonate fusion melt of brown coal ash or rock. The interference leading to lower results due to ferrous iron is more serious than that due to ferric iron as the vanadate ion is reduced to vanadyl when acidified with sulfuric acid. Consequently the oxidizing procedure with potassium permanganate is required to diminish this undesirable effect. If a considerably large amount of iron is present, it is necessary to make a preliminary separation of iron from vanadium in a slightly alkaline medium with oxine and chloroform. Hence the vanadium determination can be carried out following the directions recommended.

The separation method proposed by the author was spectroscopically tested and it was shown that a larger amount of iron can be separated without any trace of vanadium being carried down. However this procedure is not always required and can be eliminated as the quality of the sample to be tested varies.

The interference due to the presence of ferric iron can be reduced to some extent, even when a considerably large amount of iron is present in the solution prepared for the color comparison, by warming it and keeping it on standing for several minutes. Some experiments on the determination of the vanadium content of various samples were also conducted, with the results that the modified method can be used as well with a considerable accuracy.

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