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Analysis of Vanadium in Vanadiferous Titaniferous Iron Ores

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Abstract

Rapid screening method for the determinations of vanadium as recommended by U.S.G.S. has been verified and made use of in screening the samples. The verification was limited to 0.1% and above. The separation between titanium, iron and vanadium was effected by pouring the hot 0.1 N sodium hydroxide into acid extract. The filtrate has been tested for vanadium. Excellent reproducible results have been obtained, thereby establishing a standard procedure for determining low percentages of vanadium in titaniferrous iron ores.

Introduction

Vanadium and titanium have the ability to form coloured complex with hydrogen peroxide, which creates problems in the estimation of vanadium in titaniferrous magnetites by the relatively very low percentage present in the samples analysed by the authors (up to 0.7%). Of the various colorimetric methods that are in vogue, the U.S.G.S. method of developing colour with stannous chloride and thiocyanate was preferred to sodium tungstate method and followed in screening the samples. The samples which gave more than 0.1% (i.e., more than 1000 ppm) were digested with aquaregia and then fumed with sulphuric acid until copious white fumes were seen coming out, cooled, diluted and filtered. The filtrate was made up to a definite volume. An aliquot of the solution was boiled and added to hot 0.1 N sodium hydroxide and filtered, the filtrate was acidified and hydrogen peroxide was added for the development of colour and compared with standards for vanadium. This procedure was adopted since the concentration of vanadium was less than 1%.

The precipitate was dissolved in sulphuric acid and iron and titanium were estimated by the usual methods. Reproducible were obtained.

These experiments were carried out on vanadium-bearing titaniferous magnetite samples from Masanikere area, Shimoga district, Karnataka State.

Experimental Details

Thiocyanate method: It was observed that when vanadium in 9 M sulphuric was reduced by stannous chloride in the presence of citrate and ethylenediaminetetra acetic acid, the lower valence form ((presumably V (III)) reacted with thiocyanate to form a yellow ether extractable complex.

Reagents: Ethyl ether: Before use shake 100 ml. of ethyl ether with 5 ml. $SnCl_2$ reagent.

E.D.T.A. 2%: Dissolve 2 gm. of sodium salt in 100 ml. water.

Potassium thiocyanate solution 20%: Dissolve 20 gm. pot. thiocyanate in 100 ml. of water. It is necessary to prepare the solution afresh everyday.

Sodium citrate solution 10%: Dissolve 10 gm. sodium citrate in 100 ml. D.M. Water.

Standard vanadium solution 1000 Microgram per ml: Dissolve 1.785 gm. pure vanadium pentoxide (V_2O_5) that has been previously ignited to 500°C in 20 ml. 2.5 M NaOH. Neutralise with 9 M H_2SO_4, add 28 ml. con. H_2SO_4 and dilute to 1 litre with water.

Standard vanadium solution 100 Microgram per ml: Dilute 10 ml. of 1000 Microgram per ml. standard solution to 100 ml. with water.

Stannous chloride Reagent: Dissolve 15 gm. of $SnCl_2$, 2 H_2O in 100 ml. of con. HCl. The reagent should be prepared fresh daily.

Sulphuric acid 9 M: Add Con. H_2SO_4 to an equal volume of water.

Procedure

0.1 gm. of the sample is weighed into a culture tube, 1 ml. 9 M H_2SO_4 is added and heated till the mixture begins to boil vigorously and allowed to cool. 4 ml. of sodium citrate, 2 ml. of E.D.T.A. solution and 3 ml. of $SnCl_2$ reagent are added successively after shaking the tube after each addition. The contents in the tube are cooled and treated with 2 ml. of potassium thiocyanate solution. 2 ml. of ethyl ether is added and the tube is stoppered, the contents are shaken for 20 seconds. The colour intensity is compared with vanadium standards visually. (If a brown scum collects in the ether layer, it is probably due to residual organic matter. This can be overcome by the addition of 1 or 2 ml. water without shaking the test tube. The ether layer will rise into a clear part of the tube and thus separate from the scum).

A modification over the above method for maximum extraction of vanadium present is made by the authors. 0.1 gm. of the sample is weighed into a nickel crucible and mixed with 0.2 gm. of sodium peroxide and fused. The fused mass is extracted with small amount of water (about 5 c.c.) boiled and filtered. The filtrate is acidified with dilute sulphuric acid. The above procedure is followed for the development and measurement of colour from the stage of addition of sodium citrate, E.D.T.A., etc.

Regular method for estimation of V

The samples which gave more than 0.1% (i.e., above 1000 ppm) by the above procedure were taken for regular analysis. One gram of the sample is taken in 250 cc beaker, and decomposed by hydrochloric and nitric acid over a hot plate. Then it is treated with 20 cc. 1 : 1 H_2SO_4 and heated till copious dense white fumes come out. The sample in the beaker is cooled, extracted, filtered, and the filtrate is collected in a 250 cc. volumetric flask. The precipitate is washed with hot water. Then it is ignited in a platinum crucible and hydroflourised. The residue after hydrofluorisation, is fused with pyrosulphate and extracted with water containing 1 : 1 H_2SO_4. This extract is added to the main bulk in 250 cc flask and the volume is made up to the mark.

An aliquot from the main bulk of the sample in 250 cc is taken in a beaker and the acid is nearly neutralised with sodium hydroxide pellets. Then 100 ml. of hot normal solution of NaOH is poured into the neutralised solution. It is then filtered and washed with hot 0.5 N NaOH.

The precipitate is dissolved in hot 1 : 1 H_2SO_4, and the precipitation as described above is repeated to eliminate the interfering elements and filtered. The filtrate is

acidified with 1 : 1 H_2SO_4; the volume of solution is reduced; 3 ml. of 3% hydrogen peroxide is added and the solution is made up to known volume. The absorbance is read at 450 milimicrons against similarly prepared standards. The precipitate is dissolved in hot 1 : 1 H_2SO_4 and the solution is made up to known quantity from which an aliquot can be taken for the determination of iron and titanium.

A series of repetitions have been carried out with different samples and different dilutions and the reproducibility has been verified. The limit of difference which was found to be 0.05% by following the above procedure is presented below:

Sample No.	V % Original Value	V % Repeated Value	Average
1.	0.58	0.60	0.59
2.	0.44	0.48	0.46
3.	0.52	0.48	0.50
4.	0.41	0.40	0.405
5.	0.37	0.35	0.36
6.	0.33	0.30	0.315
7.	0.44	0.41	0.425
8.	0.55	0.52	0.535
9.	0.33	0.32	0.325
10.	0.12	0.10	0.11

The authors tried to extract the sample by the sodium peroxide fusion method. 0.5 gm. of the sample was weighed into a nickel crucible and mixed with 2 gm of sodium peroxide and fused. The fused mass was extracted with water and filtered. The filtrate was reduced to a small volume, acidified with dilute sulphuric acid. 3 ml. of 3% hydrogen peroxide was added and the solution made up to known volume. The absorbance was read at 450 milimicrons against similarly prepared standards. The results were identical to those given in table above.

Conclusions

The rapid method of estimation of vanadium as recommended by U.S.G.S. has been verified and a standard method has been established for determining the percentage of vanadium. This method has an advantage over the known conventional methods, in that, it is accurate, reproducible even in cases where the percentage of vanadium in ores is less than one per cent.

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