

Determination of Vanadium in Rocks, Minerals, Ores, etc. with Benzohydroxamic Acid

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Manuscript received 4 February 1972; revised 13 December 1972; accepted 26 December 1972

A rapid, accurate and precise method for the colorimetric estimation of vanadium in geological materials based on the colour reaction of vanadate with benzohydroxamic acid in aqueous-ethanol medium at pH 2.5 have been described. A procedure based on the extraction of the coloured complex by methyl isobutyl ketone at pH 2.0 which permits the spectrophotometric determination of vanadium present in various types of rocks, minerals and ores in ppm level have also been described.

DAS GUPTA and Singh¹ have studied the colour reaction of vanadium and benzohydroxamic acid (BHA) in aqueous ethanol medium. The colour produced by vanadium-BHA is extractable by oxygenated organic solvent like hexanol-1, ethyl acetate and other higher alcohols². The extraction procedure has been applied in the estimation of vanadium in steel, alloys and petroleum products,^{3,4} in biological materials⁵ and uranium materials.⁶

As the versatile analytical procedure for the estimation of minor and trace quantities of vanadium in geological materials are not abundant,^{2,7} the necessity for a rapid but accurate method for the estimation of vanadium in those materials has long been felt. An investigation on the various conditions for the colour reaction of vanadium with BHA has been undertaken with a view to develop a simple, rapid, accurate and precise colorimetric procedure suitable for the estimation of vanadium in various types of rocks, minerals, ores, etc. The results of this investigation have been reported in this communication.

Experimental

Apparatus :

(1) Spectrophotometer (Unicam SP 500) (2) pH meter (Beckman Zeromatic II with expanded scale).

Reagents and Chemicals :

1. Benzohydroxamic acid solution : 1% (w/v) : Purified 1 gm. of benzohydroxamic acid (Dr. Theodor Schuchart, Germany) was dissolved in 100 ml of absolute alcohol (G.R., E.Merck).

2. Buffer solution (pH 2.5) : 19 gm. of monochloroacetic acid was dissolved in 50 ml of water. 25 ml of this solution was neutralised with 2N NaOH solution. The remaining monochloroacetic acid solution was then added to the neutralised solution. The pH of the solution was checked and adjusted if necessary to pH 2.5 in a pH meter.

3. Standard vanadium solution : A stock solution of vanadium (0.5 mg/ml) was prepared from ammonium vanadate (A.R., B.D.H.). Dilute solution of vanadium (0.01 mg/ml) was prepared from the stock solution.

All other chemicals and reagents used are of either G.R. or A.R. variety.

Procedure : Fuse 0.5 gm of the sample with about 3 gm. of Na₂CO₃ in a platinum crucible for about an hour. Cool the melt, remove the cake and transfer to a 250 ml beaker. Add 25 ml of water, crush the cake with a glass rod till it is completely disintegrated. Digest on a hot plate for an hour, filter and wash the residue five times with 10 ml portions of hot 1% Na₂CO₃ solution. Acidify with 4N H₂SO₄ (about 15 ml.). Warm and stir thoroughly to drive out CO₂. If much chromium is present add 5 ml of H₂O₂ (100 vol.) and make the solution alkaline with caustic soda. Boil to decompose the H₂O₂ completely. Acidify with 4N H₂SO₄. Cool, transfer the solution to a 100 ml volumetric flask and make up the volume with distilled water.

Determination of vanadium in aqueous-ethanol : Pipette out 20 ml or a suitable aliquot of the solution containing not more than 0.2 mg of vanadium in 50 ml volumetric flask. Add 2 ml of buffer solution of pH 2.5. Check the pH of the solution by a pH meter and adjust it to pH 2.5. Add 1 ml of benzohydroxamic acid solution and 20 ml absolute alcohol. Shake to mix the solution and then make up the volume upto the mark with distilled water. Measure the O.D. by spectrophotometer at 450 nm in a suitable size of the cell against reagent blank. Convert the O.D. to the amount of vanadium with the aid of a calibration curve prepared following the aforesaid procedure.

Determination of vanadium by extraction with methyl isobutyl ketone : Pipette out 20 ml aliquot in 100 ml beaker. Add 2 ml of buffer solution and adjust the pH to 2.0 by placing it to a pH-meter. Transfer the solution to a separating funnel (100 ml), add 1 ml of benzohydroxamic acid solution and extract the

Presented to the Chemists' Convention, 1971, Bombay.

coloured complex with a pipetted 10 ml portion of methyl isobutyl ketone. Separate out the organic layer and take it in a stoppered test tube containing anhydrous Na₂SO₄. Measure the O.D. of the organic layer in a spectrophotometer at 450 nm against process blank in a suitable size of the cell. The amount of vanadium is calculated from the calibration curve prepared following the procedure of extraction as described above.

The results of the determination of vanadium in ores, minerals and rocks have been recorded in the Tables 1 and 2.

TABLE 1—ESTIMATION OF VANADIUM WITH BHA IN AQUEOUS-ETHANOL MEDIUM

Sample	Major constituents	% V	
		By BHA	By standard procedure ^a
Bauxite	Al ₂ O ₃ , Fe ₂ O ₃ , TiO ₂	0.097	0.100
Bauxite	-Do-	0.195	0.190
Bauxite	-Do-	0.125	0.120
Titaniferous magnetite (composed of magnetite, ilmenite and chromite)	TiO ₂ , FeO, Fe ₂ O ₃ , Cr ₂ O ₃	1.08	1.05

TABLE 2—ESTIMATION OF VANADIUM WITH BHA BY EXTRACTION WITH METHYL ISOBUTYL KETONE

Sample	Type	Source of Sample	ppm V	
			By BHA	Reported value
Rock	Basalt	NANCY ⁹	250	240
Rock	Mica-Fe (biotite)	-Do-	160	160
Rock	Granite (Ga)	-Do-	40	36
Rock	Peridotite	USGS ¹⁰	37	31.2
Iron ore	...	GSI	30	40(*)
Bauxite	...	Do	870	850(*)

(*) By standard procedure^a.

Results and Discussion

As the colour reaction of vanadium is controlled by pH, monochloroacetic acid buffer (pH 2.5) has been found to give satisfactory results. Aqueous-ethanol medium having 40% alcohol has been found to produce a stable colour. It has been further observed that about 3 g. of salt concentration can be easily tolerated in aqueous-ethanol (40%) in 50 ml volume. In the proposed method the common interfering ions like Fe³⁺, Ti⁴⁺, Cu²⁺ etc. are removed during carbonate fusion and subsequent aqueous extraction and Cr²⁺ is reduced to Cr³⁺ by H₂O₂ in solution before the development of the vanadium colour. All the vanadium have been found in aqueous extract after carbonate fusion and the

retention of vanadium by the residue has been found to be negligible (cf. Sandell⁸). The vanadium in aqueous extract is in +5 state, reacts immediately with BHA under the specified condition and the full colour is developed instantaneously which remain stable for more than 24 hr. By this procedure vanadium content from 0.1% to 1% or higher can be estimated with good accuracy. This procedure is particularly suitable for the estimation of vanadium in bauxite, magnetite, ilmenite, chromium bearing minerals, etc. (Table 1).

The vanadium-BHA complex is extractable in organic solvent and in view of the purity, availability, as well as good solvent property and better extraction proficiency the authors have preferred to use methyl isobutyl ketone as an extracting agent instead of alcohols. The extraction has been carried out at pH 2.0 in presence of buffer (monochloroacetic acid) in order to avoid the possible interference from traces of iron. The coloured complex can be extracted by a single extraction which makes the procedure simple and rapid. The method is sensitive, accurate and precise (tables 2 and 3) and can be applied with success for the estimation of vanadium in various types of rocks, minerals and ores where vanadium is present in ppm order.

TABLE 3—PRECISION STUDY

Sample	Average value (% V)	Standard deviation	Coefficient of variation
Rock	0.036	0.0017	4.7
Bauxite	0.087	0.0021	2.4
Bauxite	0.195	0.0026	1.3

Acknowledgement

The authors are grateful to Dr. A. N. Chowdhury, Chief Chemist, Geological Survey of India, for his valuable suggestion and helpful criticism of the work and to the Director General, Geological Survey of India for his kind permission for publishing the paper.

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