

Extractive photometric method for simultaneous determination of titanium and vanadium in aluminium oxide and aluminium

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A simple, rapid, sensitive and selective spectrophotometric method is proposed for simultaneous determination of vanadium and titanium in aluminium oxide and aluminium with N-Benzylbenzohydroxamic acid (BBHA).

The impurities such as vanadium and titanium from the raw material bauxite pass to some extent into aluminium oxide during the production of alumina by Bayer's Technology¹. These undesirable impurities render aluminium oxide unsuitable for smelting of aluminium by Hall-Heroult Process². Therefore, it is necessary to control vanadium and titanium contents in aluminium oxide. Emission Spectrometer³ and Atomic Emission Spectrometer with inductively coupled plasma⁴ (AES-ICP) are powerful techniques for estimating titanium and vanadium in PPM level but most of them are sophisticated and expensive. Several colorimetric reagents for titanium and vanadium have been prescribed⁵. International Standard Organisation (ISO) and Indian Standard Institute (ISI) suggested two different methods for the determination of titanium and vanadium but these methods have some limitations⁶⁻⁸. N-Benzoylphenyl hydroxylamine (BPHA) and its analogues are widely used reagents for spectrophotometric determination of vanadium⁹⁻¹¹. It is reported that the N-Benzylbenzohydroxamic acid (BBHA) is more selective and sensitive than BPHA¹². A simple, rapid, sensitive and selective method is proposed for simultaneous determination of vanadium and titanium in aluminium oxide and aluminium with N-Benzylbenzohydroxamic acid (BBHA).

Experimental Procedure

Apparatus—Baush and Lomb Spectronic-21 Spectrophotometer.

Reagents and solutions—All the reagents used are of analytical grade. Stock solutions of Ti (IV) and

V(V) are prepared by dissolving potassium titanyle oxalate and ammonium metavanadate in distilled water respectively. The solutions are standardised by standard methods⁵. N-Benzylbenzohydroxamic acid (BBHA) is prepared according to the method described¹³. A 0.1% (w/v) solution of BBHA in alcohol free chloroform is used for extraction work.

Procedure for the preparation of test samples

Aluminium oxide 5 g (± 0.001) of representative aluminium oxide sample¹⁴ is fused by alkaline fusion method¹⁵. The fused mass is extracted with 6N HCl.

Primary aluminium 2.5 g (± 0.001) of the drilled aluminium sample is dissolved and digested with 6N HCl till a clear solution is obtained.

Determination of Vanadium (V)

The whole solution is heated to dryness. Cool, dilute to about 10 ml with water, heat to about 80°C and oxidize the vanadium by addition of 0.1N permanganate solution. After adjusting the acidity to 4.5 M HCl with hydrochloric acid, the solution is transferred to a separating funnel. Add 10 ml of chloroform solution of the reagent and shake vigorously for a minute, separate the colored chloroform layer and collect over anhydrous sodium sulphate in a beaker. Repeat the extraction twice with 4 ml portions of reagent solution in chloroform and mix with the main extract. Transfer the combined extracts to a 25 ml volumetric flask and make-up the volume with chloroform. Measure the absorbance at 510 nm against reagent blank.

Determination of Titanium (IV)

The aqueous phase after removal of vanadium is transferred into a 100 ml beaker, concentrated by evaporation and its acidity is adjusted to 9.0 M HCl. This is then transferred into a separating funnel and the colour is developed and extracted by the procedure as described for vanadium. Yellow colored extract is obtained, the absorbance of which is measured at 380 nm.

Results and Discussion

The reddish violet V(V)-BBHA complex and yellow Ti (IV)-BBHA complex extracted with chloroform from 4.5 M HCl and 9.0 M HCl show maximum absorption at 510 nm and 380 nm respectively. The intensity of the colour is dependent on the acidity but constant over the range 3-7 M HCl for V(V)-BBHA complex and 8-10 M HCl for Ti (V)-BBHA complex.

The volume of aqueous phase may be varied from 10-30 ml without affecting extraction with chloroform and the final absorbance. Chloroform was found to be the most suitable solvent for the extraction.

The absorbance remains constant for atleast a week if the extract is kept in cool dark place. The molar ratio of reagent to vanadium must be atleast 6:1 for full colour development but can be as high as 90:1 without adverse effect on the colour¹². Beer's Law was obeyed over the concentration range of 2-8 ppm of V(V) and Ti (IV). The effective molar absorptivities were found to be 4953 lit. mole⁻¹ cm⁻¹ for V(V) and 6468 lit. mole⁻¹ cm⁻¹ for Ti (IV). The Sandell's

sensitivity were 0.010 µg/cm² and 0.007 µg/cm² for V(V) and Ti (IV) respectively.

Foreign ions which are generally present as major impurities in aluminium oxide and aluminium such as Na⁺, Ca⁺², Zn⁺², Fe⁺³, B⁺³, Ga⁺³, Si⁺⁴ and P⁺⁵ do not interfere.

Results of the simultaneous determination of titanium and vanadium contents in aluminium oxide and aluminium samples are given in Table 1.

Table 1 show that the results obtained from the proposed method compare well with the results of other classical methods. Efficacy of the present method shows that this method has a bright future in aluminium industry.

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Table 1—Simultaneous determination of titanium (IV) and vanadium (V) in aluminium oxide and aluminium

Samples	Sample No.	By proposed method		By AES-ICP		By emission Spectrometer	
		Ti	V	Ti	V	Ti	V
Contents in ppm							
Aluminium Oxide	1	15.49 (±0.023)	14.40 (±0.045)	16.05	15.00	—	—
	2	41.71 (±0.22)	48.88 (±0.050)	42.10	49.20	—	—
	3	22.67 (±0.025)	26.71 (±0.080)	23.10	27.00	—	—
Primary Aluminium	1	17.74 (±0.046)	16.72 (±0.031)	—	—	18.05	17.10
	2	30.14 (±0.099)	22.55 (±0.12)	—	—	31.01	23.30
	3	35.93 (±0.040)	33.38 (±0.039)	—	—	36.30	34.08

- 6 ISO : 1618, *Determination of Vanadium by N-Benzoyl N-Phenylhydroxyl amine in alumina*, (International Organisation for Standardisation, Geneva), (1976).
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