STUDIES IN THE SEPARATION AND ESTIMATION OF TITANIUM USING VANILLIN AS AN ANALYTICAL REAGENT

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Introduction

The growing importance of titanium in the manufacture of alloys, refractory materials, paints, pigments and a variety of organo-metallic compounds and its use in ultrasonic transmitters, rectifiers and as catalyst has created the need for the development of improved and refined methods for its purification and estimation.

Thornton,[8] Welcher[9] and recently, Kolthoff and Elving[5] have reviewed the analytical chemistry of titanium. Among the many reagents that have been suggested for the gravimetric determination of titanium and its separation from other metals, oxine and its derivatives, tannin, cupferron, thioglycolic acid, sulpho-salicylic acid, *p*-hydroxy phenyl arsonic acid and guanidine carbonate have been reported to be useful. Most of these, however, suffer from some limitations. Oxine does not always give a quantitative separation[1] and sulpho-salicylic acid is only useful for its separation from iron and aluminium. Guanidine carbonate can be used for the precipitation of titanium in the presence of aluminium, chromium, tungstate, molybdate and uranyl ions only while thioglycolic acid is useful for the separation of iron from titanium. In the case of cupferron, vanadium, tungsten, cerium, thorium, iron, copper and zirconium interfere and in tannin method, uranium interferes.

Recently, Majumdar and Bag[6] have proposed chelidonic acid for the determination of titanium and zirconium and their separation from each other as well as many other metals. The present authors[3] have used di-ammonium-5, 5′-indigo disulphonate for the determination of zirconium and its separation from titanium. The present investigation deals with the determination of titanium and its separation from copper (II), nickel (II), iron (III), zirconium (IV), vanadium (V), molybdenum (VI), tungsten (VI), uranium

(VI) and trivalent rare-earths using 4-hydroxy-3-methoxy benzaldehyde (vanillin).

Vanillin has previously been used[9] for the detection of iron (III), chlorine and hydrochloric acid. Helmekoski[2] has studied the chelate-forming reactions of vanillin with molybdenum (VI), tungsten (VI), vanadium (V), tin (IV) and bismuth (III). Sommer[7] has studied its reaction with titanium (IV) in non-aqueous medium. The present authors have used it earlier[4] for the gravimetric determination of thorium and cerium (IV) and their separation from each other as well as from uranium (VI) and trivalent rare-earths. It has now been found that when an aqueous or alcoholic solution of vanillin is added to titanium solution at pH 3·5–6·5, an insoluble yellow titanium-vanillin complex is immediately formed and on ignition the complex gives TiO_2 which can be weighed.

EXPERIMENTAL

An aqueous 1·0% solution of vanillin (E. Merck) was used as precipitant. The metallic salts used were either of B.D.H. (Analar) or E. Merck (Pro Analysi) grade. Dilute hydrochloric acid, ammonium acetate and ammonium hydroxide solutions were used for the adjustment of pH. The pH measurements were made with a Beckman pH meter Model H2 using suitable glass electrode.

Determination of Titanium with Vanillin

To an aliquot portion of titanium solution (containing about 2 mg. of TiO_2 per ml.), an excess of 1·0% aqueous solution of vanillin at 40°–50° C. is added and the pH of the solution adjusted to 3·5–6·5. The yellow titanium-vanillin complex so precipitated is digested on a water-bath for 5 to 10 minutes, cooled, filtered through Whatman No. 40 filter-paper, washed with water, dried and ignited to titanium oxide. Determination of titanium by this method is shown in Table I.

Effect of pH on the Formation of Titanium-Vanillin Complex

The effect of pH on the formation of titanium complex with vanillin was studied at pH 1·0–6·5 using dilute solutions of ammonium acetate, ammonium hydroxide and hydrochloric acid for pH adjustment. Though the precipitation of titanium-vanillin complex begins at pH 2·5, it is complete only above pH 3·5 (Table II).

Determination of Titanium in Presence of Iron (III) and Zirconium (IV)

Vanillin forms with iron (III) a stable water-soluble red complex at pH 1·5–4·5 and a brick red precipitate at higher pH. Zirconium (IV) forms

TABLE I

Determination of titanium

Sl. No.	Weight of TiO_2 taken (oxine method) (mg.)	Weight of TiO_2 found (vanillin method) (mg.)
1	39·10	39·10
2	19·55	19·55
3	19·52	19·55
4	9·80	9·75
5	3·90	3·90

TABLE II

Weight of TiO_2 taken (oxine method) = 19·55 mg.

pH	2·0	2·5	3·0	3·5	4·0	5·0	6·5
Weight of TiO_2 found (Vanillin method) (mg.) ..	15·30	19·25	19·55	19·55	19·55	19·55	

no insoluble complex up to pH 4·5. The determination of titanium in the presence of varying amounts of iron (III), or/and zirconium (IV) has thus been carried out between pH 3·5 and 4·0 following the same procedure as in the case of titanium alone. The results obtained are given in Table III.

Determination of Titanium in Presence of Other Cations

Since vanillin does not form any insoluble complex at pH 3·5–6·5 with copper (II), nickel (II), zinc (II), manganese (II), cobalt (II), chromium (III), vanadium (V), molybdenum (VI), tungsten (VI), uranium (VI) and trivalent rare-earths, titanium has been separated from about ten times the quantity of these ions and determined without any modification of the method described for titanium alone.

Thorium, cerium (IV), aluminium, citrate, tartrate and oxalate ions even when present in minute quantities have been found to interfere in the above estimation.

TABLE III

Determination of titanium in presence of iron (III) and zirconium (IV)

Sample No.	Weight of TiO_2 taken (mg.)	Weight of iron (III) added as Fe_2O_3 (mg.)	Weight of Zr (IV) added as ZrO_2 (mg.)	Weight of TiO_2 found (mg.)
1	39·10	22·4	..	39·10
2	39·10	..	20·75	39·05
3	39·10	..	41·50	39·10
4	19·55	44·8	..	19·55
5	19·55	224·0	..	19·55
6	19·55	..	41·50	19·55
7	19·55	44·8	41·50	19·50
8	39·10	44·8	41·50	39·10

SUMMARY

4-Hydroxy-3-methoxy benzaldehyde (vanillin) precipitates titanium quantitatively between pH 3·5 and 6·5. The precipitate on ignition gives TiO_2 which can be weighed. Titanium can be readily separated and estimated gravimetrically in the presence of chromium (III), cobalt (II), copper (II), iron (III), manganese (II), molybdenum (VI), nickel (II), tungsten (VI), uranium (VI), vanadium (V), zinc (II), zirconium (IV), and trivalent rare-earths.

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