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Selective Complexmetric Determination of Titanum (IV) by Using 5-Sulphosalicylic Acid as Releasing Agent

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ABSTRACT
A complexometric method for the determination of titanium in the presence of other metal ions based on the selective masking ability of 5-sulphosalicylic acid towards titanium is described. Titanium (IV) present in a given sample solution is complexed with a known excess of EDTA and surplus EDTA is titrated against zinc sulphate solution at pH 5-6 using xylenol orange as the indicator. A known excess of 10% solution of 5-sulphosalicylic acid is then added. The mixture is then shaken well and the EDTA released from Ti-EDTA complex is titrated against the standard zinc sulphate solution. Reproducible and accurate results are obtained for 0.96 – 28.75 mg of titanium (IV) with relative error ± 0.17% and standard deviations ≤ 0.02 mg. The interference of various ions is studied. This method was applied to the determination of titanium (IV) in its alloys.

KEYWORDS: Titanium determination, Complexometry, 5-Sulphosalicylic acid, Releasing agent.

1. INTRODUCTION

Titanium is the ninth abundant metal in the earth crust. It is often encountered in the +4 oxidation state with d^0 configuration. The metal has a low density, good strength, is easily fabricated and has excellent corrosion resistance. Important titanium minerals are rutile, brookite, anatase, illmenite and titanite. The purest titanium is obtained by van Arkel and de Boer [1]. The methods used for the determination titanium include stripping voltammetry [2] inductively coupled plasma atomic emission spectrometry [3] gravimetry, spectrophotometry [4-6]. Most of these methods are disadvantages in terms of cost and need extreme care during the operation. Complexometry gives simple and rapid method for the determination of titanium. Sodium fluoride can be used for the release of titanium from Ti(IV)-EDTA complex [7]. But there is severe interference from aluminium. Titanium is determined by indirect complexometric determination using malic acid [8], Lactic acid [9], ascorbic acid [9], sodium potassium tartarate [10].

The present method describes 5-sulphosalicylic acid as a selective releasing agent for the Ti(IV)-EDTA complex at pH 5-6 under ordinary conditions.

2. EXPERIMENTAL

2.1. Materials

All reagents used were of analytical or chemically pure grade. Zinc Sulphate solution (0.02 M) was prepared in distilled water and standardized by quinalidate [11] method. EDTA (0.02 M) solution was prepared by dissolving the disodium salt of the compound in distilled water. Titanium sulphate solution was prepared from potassium tianyl oxalate [12] and standardized using cupferron [13] gravimetrically. 10% solution of 5-sulphosalicylic acid is prepared in distilled water. Solutions of various metal ions were prepared by dissolving calculated amounts of metal nitrate in distilled water. Xylenol orange indicator was made by mixing it with ground potassium nitrate crystals (1:100).

2.2. Method

To an aliquot of the solution containing 0.96 – 28.75 mg of titanium (IV), excess of 0.02 M EDTA was added and adjusted the pH 2-3 using ammonium hydroxide. The surplus EDTA was titrated against zinc sulphate solution at pH 5-6 (hexamine) to the sharp colour change of xylenol orange indicator. To this solution an excess of 10% sulphosalicyclic acid was added, the contents were mixed well and the EDTA released was titrated with standard zinc sulphate solution. The second titre value corresponds to the Titanium (IV) present.

1ml 0.02 M zinc sulphate = 0.96 mg of Ti(IV)

2.3. Analysis of titanium alloys

A known weight of the alloy was carefully decomposed with aqua-regia by evaporation to near dryness.

The residue was then cooled, dissolved in and made up to a known volume using 2N sulphuric acid. Aliquots of this solution were used for estimation as per proposed procedure.

3. RESULTS AND DISCUSSION

EDTA reacts with Ti(IV) ion to form an unstable compound [14] which hydrolyses at high pH. Polarograpic studies of Pecsok and Maverick [15] suggested the formation of oxygen containing titanium (IV)-EDTA complex at pH greater than 2. The formation constant (log β) of Ti(IV)-EDTA complex is 17.5 yielding a log conditional stability constant of 12.12 at pH 5.0 [16]. Titanium (IV) forms a stable soluble complex with 5-sulphosalicylic acid with log β value of 42.2 [16]. The 5-sulphosalicylic acid in excess is able to displace EDTA quantitatively from the Ti(IV)-EDTA complex at room temperature.

The amount of reagent required to decompose the Ti(IV)-EDTA complex was established by adding different volumes of 10% 5-sulphosalicylic acid solution to an aliquot of 7.67 mg of Ti(IV) in the form of Ti(IV)-EDTA complex and determining the amount of titanium recovered; about 7±1 mL of 10% 5-sulphosalicylic acid was required. An excess of the reagent has no adverse effect and the absence of any precipitate in the reaction mixture favors sharp end point.

3.1. Accuracy and precision

In order to check the accuracy and precision of the method, determination of titanium in the concentration range 0.96-28.75 mg were carried out under the optimized experimental conditions. The results in Table 1 show that the maximum relative error and the standard deviation of the method are ± 0.17% and ≤ 0.02 mg, respectively. On comparing the computed value of the Student's t test (2.776 for 5% level of significance) with the tabulated value, it can be observed that there is no significant difference between the reference values and the value obtained by the proposed method. From these results, it is reasonable to infer that the proposed method is precise and accurate.

3.2. Effect of foreign ions

Interference by foreign ions in the determination of Ti(IV) using 5-sulphosalicylic acid as a masking agent was studied with aliquots containing 14.38 mg of Ti(IV). The presence of the following ions did not interfere within the concentration range studied: 100 mg of Zn(II), Co(II), Ni(II), Pb(II), acetate, nitrate, sulphate, borate, phosphate; 40 mg of Al(III), Cd(II), Bi(III); 20 mg of Ce(III), Cr(III), Zr(IV), Tl(III), Pd(II). Severe interference occurred from Sn(IV), Th(IV), Fe(III), fluoride and tartarate.

3.3. Applications

In order to explore the practical application of the proposed method, it was extended for the determination of titanium in its alloys like Titanium Beta-CEZ, Ni-Ti shape memory alloy (Shape Memory Applications Inc. California) and Ninitol. The results are in Table 2. Good recoveries were obtained.

Table 1. Determination of titanium (IV) in titanium sulphate solution

Ti(IV) Calculated (mg)	Ti(IV) Found* (mg)	Relative Error (%)	Standard Deviation (mg)	Student's 't' Value**
1.92	1.92	0.00	0.01	0.00
5.75	5.74	-0.17	0.01	1.86
7.67	7.68	+0.13	0.02	1.42
14.38	14.37	-0.07	0.01	2.24
19.17	19.17	0.00	0.01	0.00
23.96	23.97	+0.04	0.01	2.24
28.75	28.76	+0.03	0.01	2.24

* Average of five determinations.

** Student's't' test values for 5% level of Significance =2.776.

CONCLUSIONS

1. A new method for the determination of Titanium (IV) using a masking technique is reported.
2. The method is simple and rapid as it does not require heating and does not require standardization of EDTA.
3. 5-sulphosalcylic acid is readily available.
4. The reagent do not form any precipitate either with zinc sulphate the titrant or with titanium, the metal ion to be determined under the experimental conditions.
5. The lack of effect of foreign ions on the accuracy and precision of the method reveals that the method may be suitable for the determination of titanium in its alloys, mixtures and complexes.

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Table 2. Determination of titanium (IV) in solutions of alloy composition.

Alloy	Composition weight (%)	Ti(IV) Found* (%)	Relative Error (%)	Standard Deviation (%)
Titanium Beta –CEZ Cr + Fe+ Ti	2.00 + 1.00 + 82.00	81.95	-0.06	0.01
Shape memory alloy Ni + Ti	55.00 + 45.00	44.86	-0.31	0.01
Ninitol Ni + Ti	56.00 + 43.80	43.59	-0.48	0.02

* Average of three determinations.

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