

The complexometric determination of thorium (IV) indirect, using tartaric acid as masking agent

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Introduction :

Thorium is widely distributed in nature though in small proportions. The commercial source of the mineral is monazite sands. Thorium and alloys have been used as reducing agents and thorium as a contact catalyst and also in propagation of incandescent mantles^{1,2}.

Thorium is normally determined by direct EDTA titration³, particularly in presence of other metal ions at pH 2-3. Thorium⁴ is used for the detection and photometric determination of thorium in dilute hydrochloric acid medium. Ions like U^{VI} , Fe^{III} , Ti^{IV} , Zr^{IV} , Sn^{IV} and sulfate interfere and the ions of lanthanides. Al^{III} and U^{VI} do not interfere in the determination with thorium. Arsenazo (III)^{5,6} reacts with thorium ions even in 4-10 N hydrochloric acid at which the ions of most other elements do not react with this reagent. 8-Quinolinol^{7,8} precipitates Th^{IV} quantitatively, even from dilute acetic acid solution at pH 3.7-4.0. This provides the condition for the separation of thorium from Ce^{IV} . Yellow $Th(C_9H_6OH)_4$ precipitates at room temperature. Xylenol orange⁹ reacts with thorium(IV) (molar ratio 1 : 1) at pH 2.7-3.3 to form a compound with absorption maximum at 570 nm. Potentiometric titration of the Th-EDTA complex using a mercury chloride³ is not convenient, as the procedure requires maintenance of ideal conditions. Gravimetric determinations of thorium as sebacate³ and subsequent ignition to the oxide, ThO_2 permits the separation by a single precipitation of thorium from relatively large amounts of the lanthanides (La, Pr, Nd, Sm) and completely specific for thorium and procedures for the gravimetric determination of the element usually describe a sequence of repetitive precipitations involving at least two different reagents. Thorium is also determined by indirect complexometric determination using 5-sulphosalicylic acid¹⁰, spectrophotometrically using arsenazo(III)¹¹, X-ray spectrometrically¹² using trioctylphosphine oxide, toluate ionophores¹³ and by laser-induced breakdown spectrometry¹⁴.

The present method describes tartaric acid as an indirect masking reagent for the Th-EDTA complex at pH 2-3 under ordinary conditions.

Experimental :

All the reagents used were of analytical reagent grade or chemically pure grade. Thorium nitrate solution was prepared by dissolving a known amount of thorium nitrate in distilled water and standardized by the sebacate method (gravimetry)³. The titrant bismuth nitrate solution (0.02 M) was prepared in distilled water and standardized by the oxydide³ method. EDTA solution (0.02 M) was prepared using its disodium salt of EDTA 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 potassium nitrate crystals (1 : 100).

Procedure :

To an aliquot of solution containing 9.36 mg to 46.8 mg of thorium(IV), an excess of 0.02 M EDTA solution was added and diluted and then xylenol orange indicator was added. The surplus EDTA was titrated against bismuth nitrate solution at pH 2-3 to the sharp color change of the indicator. To this solution, an excess of 10% tartaric acid solution was added, The contents burnmixed well and the EDTA relested was titrated with standard bismuth nitrate solution. The second titre value corresponds to the thorium(IV) present.

Results and discussion :

The absolute formation constant $\log K_{Th}$ of the thorium-EDTA complex is reported to be 22.63^{15} , yielding a log conditional stability constant of 8.21 at pH 2. Thorium(IV) forms a stable $Th(C_4H_2O_6). 9H_2O^{16}$ complex with tartaric acid. The tartaric acid in excess is able to displace EDTA quantitatively from the Th-EDTA complex at room temperature. An excess of the reagent has no adverse effect and the absence of any precipitate in the reaction mixture favours sharp end points. The amount of 10% tartaric acid solution required to decompose the Th-EDTA complex completely was established by adding different volumes of tartaric acid to the solution containing 18.72 mg of Th^{IV} in the form of th- EDTA complex determining the amount of Th^{IV} recovered. It was found that about 8.0 ± 0.05 ml of 10% tartaric acid was required.

Accuracy and precision :

The determination of thorium(IV) in thorium nitrate solution shows that accurate and reproducible results are obtainable with an acceptable relative error $\pm 0.21\%$ and standard deviations < 0.06 mg. On comparing the computed value of the students' 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.

Effect of foreign ions :

Interference by foreign ions in the determination of thorium(IV) by the method proposed was studied with aliquots containing 18.72 mg of thorium (IV) . The presence of the following ions did not interfere within the concentration range studied : 75 mg Zn^{II} , Co^{II} , Ni^{II} , Pb^{II} , Hg^{II} , Cu^{II} , Bi^{II} , Tl^{III} ; 10 mg of Pd^{II} , Mn^{II} ; 100 mg of Fe^{III} ; 50 mg of Cr^{III} , U^{VI} , Ce^{III} ; 200 mg of acetate, borate, phosphate and 250 mg of nitrate and chloride.

Analysis of Th^{IV} in alloy and alloy compositions :

Alloy sample Mag-Thor (HK31A) and artificial mixtures corresponding to the metal ions containing Mg, Zr, Zn and Mn with thorium were prepared and analysed, by the proposed method. Good recoveries were obtained.

Conclusions :

A new method for the determination of thorium(IV) using a masking technique is reported. The method is simple and rapid as it does not require heating, adjustments of pH and also does not require standardization of EDTA. The reagent, tartaric acid is

readily available. The reagent does not form any precipitate either with bismuth, the titrant or with thorium, the metal ion to be determined under the experimental conditions. 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 thorium in its alloy and alloy composition.

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