SPECTROPHOTOMETRIC DETERMINATION OF ZIRCONIUM IN ZIRCONIUM STEEL

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ABSTRACT

A method for the extraction and spectrophotometric determination of 10–200 ppm of zirconium, based on the red coloured compound formed between promethazine and zirconium-thiocyanate in 1–3.5 M sulphuric acid medium, is described. Various parameters have been standardised. The proposed method is successfully applied for the trace determination of zirconium in zirconium steel.

INTRODUCTION

ZIRCONIUM possesses a combination of physical, chemical and nuclear properties which is unique. The transparency of zirconium to thermal neutrons has found its greatest use as a construction material in nuclear reactors. It is in great demand in making bullet-proof alloy steels. A large number of reagents have been proposed in recent years for the absorptiometric determination of zirconium[1–3]. The most common spectrophotometric method known for the trace determination of zirconium uses thiocyanate as the reagent[1]. This method has now been extended for the estimation of zirconium in the organic extract itself without the need of back extracting into an aqueous phase. The proposed method retains all the usefulness of the earlier one with the added advantage of the enhanced sensitivity and stability.

EXPERIMENTAL

Beckman model DB spectrophotometer with matched 10 mm silica cells was used for absorbance measurements.

A stock solution of zirconium was prepared by dissolving a known weight of zirconium nitrate (AR, BDH) in 2 N nitric acid and diluting the solution to known volume by the addition of doubly-distilled water. The metal content was then determined by EDTA method[4]. The working solutions were prepared by suitable dilution of this standardised stock solution. A 20% aqueous solution of potassium thiocyanate (AR BDH) was prepared. A solution of promethazine (0.05 M) in chloroform was prepared and standardised gravimetrically with 12-tungstosilicic acid[5]. Solutions of diverse ions of suitable concentrations were prepared using AR grade reagents.

Procedure: An aliquot of the stock solution containing 10–200 ppm of zirconium, 4 ml of 10 M sulphuric acid and 5 ml of 20% potassium thiocyanate were taken in a 100 ml separatory funnel and diluted to 20 ml with distilled water. Five ml of 0.05 M promethazine in chloroform was added and the organic phase was equilibrated for 3 min. The red chloroform layer was transferred to a 10 ml volumetric flask. The aqueous layer was extracted twice with 2 ml portions of chloroform. The chloroform extracts were combined in the flask and diluted to the mark with the same solvent. The extract was dried by adding 0.5 g of anhydrous sodium sulphate. The absorbance was measured at 470 nm against a reagent blank prepared under similar conditions.

RESULTS AND DISCUSSION

Promethazine forms a red complex with the binary zirconium thiocyanate complex in 1–3.5 M sulphuric acid solution. The chloroform extract of the ternary complex has an absorption maximum at 466 nm. The reagent blank in chloroform does not show any absorption in the range 400 to 700 nm, thus promoting excellent analytical conditions. To achieve the maximum sensitivity, linearity and reproducibility sufficient reagent must be present during the formation and extraction of a coloured complex. For this purpose, 4–7 ml of 20% potassium thiocyanate, and 3–9 ml of 0.05 M promethazine, are required for the Beer's law range of zirconium.

To find a suitable solvent, extraction of zirconium-thiocyanate-promethazine complex into different organic solvents was investigated. The results indicated that chloroform showed the maximum extraction. The complex was only partly extracted into solvents like benzene, chlorobenzene carbontetrachloride, n-

hexane, toluene and xylene. The chloroform extract of the complex obeyed Beer's law in the range 6–204 ppm of zirconium. To evaluate optimum range and analytical accuracy, the Ringbom's curves were drawn by plotting the percentage transmittance as ordinate and logarithm of the concentration of zirconium as abscissa. The range derived from the maximum slope of the curve is 10–200 ppm of zirconium. The zirconium thiocyanate promethazine complex extracted into chloroform is more stable (14 hr) than zirconium thiocyanate complex (25 min). The molar absorptivity of the ternary complex (1.14×10^3 litre mole^{-1} cm^{-1}) is higher than that of the binary complex (3.2×10^2 litre mole^{-1} cm^{-1}).

The composition of the extractable zirconium-thiocyanate-promethazine complex was studied by Job's method of continuous variations with equimolar solutions. Since three components are involved in the formation and extraction of the complex, two series of experiments were carried out by keeping the concentrations of two components constant and varying the other. Results obtained indicate that the molar ratio of Zr to SCN$^-$ is 1:3 and of Zr to promethazine is 1:1.

Various cations and anions were tested for the possible interference. The results showed that anions like chloride, fluoride, bromide, iodide, nitrate, sulphate, phosphate, acetate, oxalate and citrate do not interfere. The cations that do not interfere are those of alkali metals, alkaline earth metals and lanthanides. The following ions can be tolerated in concentrations hundred times higher than zirconium: Mn(II), Bi(III), Sn(II), Cr(III), Cr(VI), Pb(II), As(III), In(III), Te(IV), Au(III), Pt(IV), Pd(II), Sc(III), Th(IV), La(III). Ten times higher concentration can be tolerated for Co(II), Fe(III), U(VI), Ti(IV), Mo(VI), Ce(IV), Nb(V), Ta(V) and W(VI). Interference was reduced by pre-extracting W(VI), U(VI), Mo(VI), Ce(IV), and Fe(III) from 6 NHCl.

Analysis of zirconium steel

About 0.5 g of the steel sample was weighed into a 250 ml beaker. Hydrochloric acid (20 ml of 6 M) was then added. The solution was gently warmed and cooled. Perchloric acid (7 ml of 72%) was added and the mixture evaporated to copious fumes. The residue was dissolved with 20 ml of distilled water. Iron content of the mixture was then extracted with three 5 ml portions of diethylether[6]. The aqueous solution was boiled, cooled and diluted to 100 ml. A suitable aliquot of this solution was taken in a separatory funnel and the zirconium content was determined by the procedure outlined earlier. Analysis of steel samples gave a result of 0.128% and 0.280% Zr as against the certified values of 0.132% and 0.302%, respectively.

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