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Analytical Chemistry

COMPLEXOMETRIC DETERMINATION OF SOME TRIVALENT METAL IONS INDIVIDUALLY OR IN MIXTURE OR IN ORES USING PYRIDINOL AZO DYES AS VISUAL INDICATORS

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In the present study, complexometric determinations of some trivalent metals, viz., Sc(III), Ga(III), In(III), Fe(III) and Cr(III) individually or when present together in a mixture, have been carried out using pyridinol-azo-dyes AHP-4S, DHP-4S and CPD-4S as visual indicators and that of Al(III) in bauxite samples using AHP-4S. At the end point, the colour change (orange to magenta) is instantaneous and sharp. Interferences due to diverse ions have also been studied in detail.

Keywords : Complexometric Determinations; Fe(III), Cr(III), Al(III), Sc(III), Co(III), Ir(III) and Al(III) in Ores

INTRODUCTION

ONLY very few selective and sensitive methods are known for the estimation of trivalent metal ions complexometrically (Flaschka & Schwarzenbach, 1968). In this communication, the azo dyes 1-(2′-amino-3′-hydroxy-4′-pyridylazo) benzene-4-sulphonic acid (AHP-4S), 1-(2′,3′-dihydroxy-4′-pyridylazo), benzene-4-sulphonic acid (DHP-4S) and 1-(5′-chloro-2′,3′-dihydroxy-4′-pyridylazo), benzene-4-sulphonic acid (CPD-4S) (Gupta *et al.*, 1977, 1978, 1979) have been used as indicators for the indirect complexometric determination of Al(III), Sc(III), Ga(III), In(III), Fe(III), and Cr(III) individually or in a mixture using Cu(II) solution for back titration. The liability of Al-EDTA complex has been utilized in complexometric determination of Al(III) using only AHP-4S as indicator.

EXPERIMENTAL

Reagents

Scandium (III) solution was prepared by dissolving Sc_2O_3 in hot HCl, gallium (III) by dissolving gallium metal in hot $HClO_4$, indium(III) by dissolving the metal in hot HNO_3, chromium(III) by dissolving anhydrous $CrCl_3$ in hot HCl, iron(III), aluminium(III) annd copper(II) solutions were prepared from $(NH_4)_2SO_4 . Fe_2(SO_4)_3 . 24H_2O$, $K_2SO_4 . Al_2(SO_4)_3 . 24H_2O$ and $CuSO_4 . 5H_2O$ in double distilled water followed by addition of few drops of dilute H_2SO_4. The reagent solutions and all other standard solutions of metal ions were prepared as described in earlier work (Gupta *et al.*, 1977, 1978, 1979).

Recommended Procedure

To a suitable aliquot containing 0.045–6.000mg of Sc(III) or 0.070–6.970mg of

Ga(III) or 0.115–17.220mg of In(III) or 0.110–16.800mg of Fe(III) or 0.052–6.240mg of Cr(III) or 0.027–3.240mg of Al(III) in 20 ml, add excess of EDTA. In the determination of Cr(III) boil for 5–10 minutes so that complexation is complete. In the determination of Ga(III) add 5ml alcohol. To this, add 5 ml of CH_3COONa/CH_3COOH buffer of *p*H 5.2 and titrate the excess of EDTA between temperature 20–80°C with Cu(II) solution (1×10^{-2}M) using 2–3 drops of 0.25 per cent AHP-4S indicator solution or add 5 ml of NH_4Cl/NH_4OH buffer of *p*H 10.0 and titrate as above using 2–3 drops of 0.25 per cent DHP-4S or CPD-4S solution. Colour change at the end point is orange to magenta.

Titrations in Presence of Diverse Ions

Interferences due to a large number of foreign ions have been studied by taking 0.450mg of Sc(III) or 0.697mg of Ga(III) or 1.150mg of In(III) or 1.120mg of Fe(III) or 0.520mg of Cr(III) or 0.270mg of Al(III) and following the recommended procedure. The anions like SO_4^{2-}, ClO_4^-, NO_3^-, NO_2^-, BrO_3^-, PO_4^{3-}, SO_3^{2-}, citrate, tartrate, F′, Cl′, Br′, I′, CNS^- did not interfere even in large amounts ($\sim$ 5000 ppm). The other anions like $C_2O_4^{2-}$, BO_3^{3-}, thiourea could be tolerated in smaller amounts ($\sim$ 1000 ppm). Metal ions which have been masked in large amounts ($\sim$ 5000 ppm) by anions are given in parentheses Hg^{2+} (I′), Ag^+ (I′), Ti^{4+} (F^-) and metal ions which are masked in small amounts ($\sim$ 1000 ppm) are Ge^{4+}(F′), Pb^{2+}(I′), Sn^{2+}(F′). Many other metal ions could be masked or tolerated. Bivalent metal ions Zn^{2+}, Ni^{2+}, Cd^{2+} etc.) which form strong complexes with EDTA or give colour reaction with pyridinol azo dyes interfere seriously. Cyanide was found to interfere seriously in all the cases.

A. Estimation of Chromium(III) in Presence of other Trivalent Metal Ions : As Cr(III) does not form complex with EDTA in the cold, the modified procedure for the analysis of the mixture containing Cr(III) is used as follows :

To an aliquot of the solution containing chromium(III) and other trivalent metal ions excess of EDTA was added and titrated with Cu(II) using AHP-4S indicator following the recommended procedure. The EDTA consumed is equivalent to the amount of trivalent metal ion, other than chromium(III). Another equal aliquot was added to it excess of EDTA, boiled for 5–10 minutes and cooled. Titrate with copper(II) as above. This EDTA consumed is equivalent to the total amount of chromium (III) and other trivalent metal. The difference gives the amount of chromium(III).

B. Procedure for the Aluminium(III) in Presence of Other Trivalent Metal Ions : To an aliquot of the mixture excess of EDTA was added, heated for 5–10 minutes, cooled and titrated with copper(II) using AHP-4S indicator following the recommended procedure, till the colour change from orange to magenta is obtained. The EDTA consumed is equivalent to the total amount of metals present. Now to this titrated solution sodium fluoride was added and boiled for 5 minutes. While boiling, the colour of the solution changes from magenta to orange as the Al(III)-EDTA complex breaks, aluminium fluoride is formed and free EDTA is liberated. The solution was further cooled and the liberated EDTA was titrated with Cu(II)

as above. This additional amount of Cu(II) is equivalent to the amount of Al(III) present in the sample. The difference gives the amount of other trivalent metal present.

Determination of Aluminium in Bauxite Samples

Pre-analysed bauxite samples were analysed by the procedure given below :

About one gram of the bauxite sample pre-dried at 100–110°C was weighed and transferred to 400 ml Corning beaker. 25 ml of concentrated HCl + HNO_3 mixture (10 : 15) was added. The mixture was stirred and heated on a sand bath till all the nitrous fumes dissappear. Add 20 ml 1 : 1 H_2SO_4 and continue further digestion. The fuming was continued till all the nitrates or chlorides were destroyed. The beaker was cooled, 100 ml of doubly distilled water was added and the mixture was digested on a water bath for about half-an-hour and filtered through Whatman No. 40 filter paper. Then the mixture is washed with 3 to 5 per cent H_2SO_4. The filtrate is preserved and the residue was transferred together with filter paper to a platinum crucible. It was dried, incinerated and then ignited till no trace of carbon is left. The residue was further fused with fusion mixture and after cooling extract with 10 per cent H_2SO_4. The extract is mixed with earlier extract and made up to a total volume of 250 ml and the aluminium content was determined by following the procedure B. The results of the study (average of six estimations for each sample) are shown in Table I.

TABLE I

Analysis of bauxite samples for aluminium contents

No. of sample	Al_2O_3 % present	Al_2O_3 % found	Error %
1	48.25	48.10	0.31
2	55.00	54.88	0.18
3	47.05	47.15	0.21
4	48.80	48.60	0.40

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