Indian Journal of Chemistry
Vol. 28A, April 1989, pp. 342-343

Extractive spectrophotometric determination of cobalt using xanthates

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Received 3 March 1988; revised 25 June 1988; accepted 8 August 1988

The 1:3 (metal-ligand) complexes of cobalt with various xanthates are extractable into chloroform and show linear response upto 5 ppm of cobalt when the absorbance is measured at 355 nm. The molar absorptivities and Sandell's sensitivities of the complexes are in the ranges $(0.98\text{-}1.65)\times 10^4$ l mol^{-1}cm^{-1} and 0.006-0.004 μg Co/cm^2 respectively.

A literature survey revealed that xanthates have been widely used as analytical reagents[1-4]. Cobalt(II) has been reported to interfere in the spectrophotometric determination of nickel and palladium with xanthates[1,2]. In the present note the behaviour of alkali xanthates towards cobalt(II) has been investigated. The optimum conditions for extraction of the metal have been established. The xanthates used are potassium ethyl, propyl, butyl, benzyl and isoamyl xanthates.

Experimental

A Shimadzu PR1 model spectrophotometer fitted with optically matched quartz cells of 10 mm path length was used for absorbance measurements and a ECL 5651 digital *p*H meter was used to measure the acidity of the aqueous solution.

A stock solution of Co(II) was prepared from cobalt nitrate (BDH) in distilled water followed by standardisation with EDTA. Solutions of diverse ions were prepared from their corresponding salts. Various xanthates were prepared in the laboratory[5] and their aqueous solutions (0.5%) were used for extraction. Chloroform and other solvents were distilled before use.

General procedure

To an aliquot containing upto 50 μg of cobalt, was added 0.2 ml of the aqueous xanthates solution. The volume of the mixture was made to 10 ml and 2 *M* with respect to HCl. The complexation was instantaneous. The aqueous phase was then equilibrated with 10 ml of chloroform for 1 min. The separated organic layer was poured over anhydrous sodium sulphate to remove any retained water droplets. Finally the absorbance of the chloroform extract was measured at 355 nm against a blank. The amount of cobalt extracted, was computed from a calibration curve.

Results and discussion

The spectra of cobalt complexes in chloroform show absorption maxima at 355 nm in all the cases. The reagent blanks showed insignificant absorbances from 320 nm onwards. All analytical measurements were carried out at 355 nm. Steady and maximum absorbance was found to be achieved when the extractions were carried out from $6\text{-}1\times 10^{-8}\,M$ hydrochloric acid medium. In all the other cases the remaining aqueous phases, after a single extraction, were free of cobalt as tested by an independent method.

The system obeys Beer's law upto 5 ppm of cobalt when measured at 355 nm. The molar absorptivities of the complexes, based on cobalt content, are in the range $(0.98\text{-}1.65)\times 10^4$ l mol^{-1}cm^{-1} and Sandell's sensitivities in the range 0.006-0.004 μg Co/cm^2. It was noted that 0.1 ml of 0.5% aqueous xanthate solutions were sufficient to extract 30 μg of cobalt in a single operation. To test the interferences, 0.2 ml of the reagent solution was used, as the added diverse ions might consume a part of it.

The pattern of the absorption spectra of the complexes, as extracted from $6\text{-}1\times 10^{-10}\,M$ HCl, remained unchanged. This indicated the formation of only one complex species in all the respective xanthates. The composition of the cobalt complexes with various xanthates was found from the slope of Log D versus Log [ligand] to be 1:3 (metal-ligand). The colour of the organic extracts was stable for at least 24 hr.

Some other solvents like carbon tetrachloride, benzene, butyl alcohol and ethyl acetate were also tested as extracting solvents, but these offered no special advantages over chloroform.

Interferences

Behaviour of various xanthates towards the extraction of cobalt is almost similar as seen from the interference studies. To test the effect of foreign ions, cobalt was determined by the recommended procedure in presence of the respective foreign ions. Extractions were carried out from 2 *M* hydrochloric acid medium to avoid some unwanted interferences. Anion was considered to interfere if the recovery of cobalt differed by more than ± 3% from the actual amount taken. Average of three determinations was taken in each case. Cobalt (30 μg) could be determined without any interference in presence of 200-fold excess of the following ions: Al(III), Be(II), Cd(II), Ca(II), Ba(II), Sr(II), Ce(III), Cr(III), Fe(II), Th(IV), U(VI), La(III), V(V), Pb(II), Mg(II), Mn(II), Hg(II), Mo(VI), Pt(IV), Rh(III), Pd(II), Zn(II), and Zr(IV). Nickel(II) interfered. The system tolerated 500-fold excess of the following ions: EDTA, thiosulphate, bromide, iodide, fluoride, phosphate, ascorbate, oxalate, citrate, tartrate, acetate, borate and phthalate. In absence of the real samples, the method has been tested on a number of synthetic mixtures.

The precision and accuracy of the proposed method was tested by analysing solutions containing a known amount of cobalt following the general procedure using potassium isoamyl xanthate. The average of six determinations of 30 μg cobalt was found to be 29.66 μg with the relative mean deviation of ± 3.74%.

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