INDIRECT COMPLEXOMETRIC DETERMINATION OF CADMIUM (II) USING CITRIC ACID AS A MASKING AGENT

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INTRODUCTION

Cadmium is a rare element, 67th element in the order of abundance, a few deposits of CdS, CdO and basic carbonates exists on earth's surface. Because cadmium is more volatile and more readily oxidized than zinc, CdO is deposited with zinc dusts in the flues of zinc producing retorts. Cadmium is used for alkali Ni/Cd storage batteries used both in diesel locomotives and also as the 'nicad' rechargeable 'dry batteries' used in radios and electrical appliances.

Various alloys of cadmium are commercially significant. Solder with the composition Cd 40 %, Zn 60 %, can be used with aluminium. An alloy of Bi 50 %, Pb 26.7 %, Sn 13.3 %, and Cd 10 % has a melting point of only 70^0 c. Cadmium is highly toxic to a wide variety of living organisms, including man[1-3]. Inhalation of cadmium rapidly affects the respiratory tract and caters kidneys. After long exposure to small amounts, cadmium may become concentrated in the gonads.

The principal methods of quantitative analysis for cadmium are (a) titrimetric, by using EDTA at pH 10 with eriochrome black-T as indicator[4] and at pH 4.5 using xylenol orange as indicator[5] ; (b) gravimetric methods involve precipitation of cadmium as CdS and by using B-naphthoquinoline and weighing as $(C_{13}H_9NH_2)$ CdI_4 complex which is formed from acid solution.

In the potentiometric titration of cadmium, copper can also be simultaneously determined[6] using glass electrodes. In another complexometric method, cadmium was determined in the presence of zinc in homogenous water ofganic solvent medium using ethylxanthate[7] , cadmium was determined in the presence of zinc (II) using EGTA and antipyralazo (III) indicator[8], at pH 13. Ni^{II}, Co^{II}, Co^{III}, Al^{III} and Fe^{III} ions interfered. Determination of cadmium using 1, 10-phenanthroline as a selective releasing agent[9] is convenient, but Cu^{II}, Hg^{II}, Co^{II}, Zn^{II}, Ti^{III} and Ni^{II} interfere severely.

The present method uses citric acid as an indirect masking reagent for Cd-EDTA complex at pH 5-6 under ordinary conditions.

EXPERIMENTAL

All the reagents used were of analytical reagent grade or chemically pure grade. Cadmium (II) acetate solution (0.02 *M*) was prepared by dissolving a known amount of cadmium (II) acetate in distilled water and standardized by the oxine method**.** The titrant lead nitrate solution (0.02 *M*) was prepared in distilled water and standrdized by chromate 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. A 1 % solution of citric acid was prepared in double distilled water. Xylenol organe indicator was made by mixing it with ground potassium nitrate crystals (1 : 100).

PROCEDURE

To an aliquot of a stock solution containing 4.24-21.20 mg of cadmium, a known volume of EDTA solution in excess of Cd^{II} present is added and diluted to about 80 cm^3. To this solution, hexamethylene tetramine (10 ± 4 g) is added to adjust the pH to 5.0-6.0, the surplus EDTA is titrated with lead nitrate solution to the sharp colour change from yellow to red using xylenol orange indicator. To this solution an excess of 1 % citric acid is added and the EDTA released is titrated with standard lead nitrate solution as before. The second titre value is equivalent to cadmium (II) present.

RESULTS AND DISCUSSION

The formation constant log β of the Cd^{II}-EDTA complex is reported to be 16.4 yielding a log conditional stability constant at pH 5.0 of 10.0 Cadmium (II) in the form of Cd^{II}-EDTA complex with citric acid with log β value 11.3. Experiments show that cadmium (II) forms a stable water soluble complex at pH 5.0-6.0.

The amount of 1 % citric acid solution required to decompose the Cd^{II} -EDTA complex completely was established by adding different volumes to solution containing 8.48 mg of cadmium (II) in the form of cadmium (II) recovered; about 10 ml of 1 % citric acid was required.

Accuracy and precision

The determination of cadmium(II) acetate solution was performed at different concentrations of cadmium(II) using the above reagent. Accurate and reproducible results are obtained with a permissible relative error of ± 0.47 % and standard deviations ≤0.05 mg. On comparing the computed value of sludent 't' (2.776 for 5 % level of significance) with tabulated values, it can be observed that in most of the cases there is no significance difference between the reference values and the values obtained by the proposed method.

Effect of foreign ions

Interference by foreign ions in the determination of Cd^{II} by the method proposed was studied with aliquots containing using 8.48 mg of cadmium. The presence of following ions did not interfere within the concentration ranges studied. 20 mg of Ag^{I}, Cu^{II}, 25 mg of Al^{III}, Ce^{III}, La^{III}, Fe^{III}, Bi^{III}, Cr^{III}, In^{III}, Y^{III}, Au^{III}, Zr^{IV}, Sn^{IV}, F^- 200 mg of Cl^-, 250 mg of Br^-, BO_3^{3-} and 50 mg of Tl^{I}. Severe interference occured from Hg^{II}, Ti^{II}. The stability constant of interfering ion Hg^{II} with citric acid is 10.99, Ti^{III} is not available in the literature. Interference can be obviated using secondary masking agent. Hg^{II} can be masked using potassium bromide, Ti^{II} can be masked by using sodium sulfite.

APPLICAIONS

Analysis of cadmium(II) in complexes

A number of cadmium(II) complexes with sulfur donor ligands were prepared by conventional method and their purity was checked by the elemental analysis. About 0.1-0.2 g of the complex was decomposed using concentrated nitric acid and heated to near dryness. The residue were dissolved in distilled water and made up to 100 ml in a standard flask. Aliquots of 20 ml used for the determination of cadmium by the proposed method.

Analysis of cadmium(II) in alloys and alloy compositions

Cadmium forms solid alloys with silver, aluminium, lead, platinum and titanium. The pure alloy samples containing metals like aluminium, lithium, maganesium, zinc and titanium were taken and heated with concentrated nitric acid and the oxides of nitrogen are expelled with the use of concentrated sulphuric acid until the evolution of brown fumes ceases. The residue was extracted with distilled water and made upto 100 ml in a standard flask. Aliquots of 5-10 ml were used for the titration by the recommended procedure. Good results were obtained.

CONCLUSIONS

The method proposed has following notable features

I. The reagent citric acid does not form any precipitate either with cadmium(II), the metal ion to be determined or with lead nitrate, the titrant under experimental conditions. This facilitates a sharp end point.

II. The method works well a 4.24-21.20 mg of cadmium(II).

III. Citric acid is easily available and cheap.

IV. The method does not require heating or cooling before or during titration.

V. The lack of affect of diverse ions on the accuracy and precision of the method indicates that the method be suitable for determination of cadmium in its alloy and alloy compositions.

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