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SPECTROPHOTOMETRIC DETERMINATION OF Ni(II) IN INDUSTRIAL SAMPLES AFTER SEPARATION BY ADSORPTION OF ITS 1,4-DIHYDROXYANTHRAQUINONE COMPLEX ON MICROCRYSTALLINE NAPHTHALENE

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Nickel-1,4-dihydroxanthraquinone (DHA) complex formed at pH 8.6 is adsorbed on microcrystalline naphthalene and subsequently dissolved in DMF. Absorbance of the complex at 560 nm is proportional to the concentration of Ni(II) in the range of 0.6–3.0 ppm. Ag(I), Hg(II) and Cd(II) do not interfere in 10-fold concentration but Co(II), Cu(II), Mn(II) and Zn(II) cause serious interference. The method has been successfully applied to determine nickel in hydrogenation catalyst, hydrogenated oils and electroplating bath solutions. Unlike Ni-DMG complex, the absorbance in case of Ni-1,4-DHA need not be recorded immediately as it remains constant with time.

INTRODUCTION

The analysis of nickel in diverse matrices is an important task for the analytical chemists because of the importance of this metal in industry as well as in biological systems[1,2]. Its potential carcinogenecity[3] has added to the need for developing sensitive analytical procedures. Despite limitations, the dimethylglyoxime method is commonly used for the spectrophotometric determinaton of nickel[4,5], though a number or more sensitive methods are known[6–9]. In the present study we report the use of 1,4-dihydroxyanthraquinone (DHA) which has been reported to form a polychelate with Ni(II) in the solid state[10], for the spectrophotometric determination of this metal.

EXPERIMENTAL

Measurement of pH was carried out using ECIL digital (model 5651) pH-meter. UV-VIS spectra were recorded on a Schimadzu SP 260 double beam spectrophotometer. Stock solution (0.01M) of Ni(II) was prepared by dissolving appropriate amount of A.R. grade $NiSO_4.7H_2O$ in acidified distilled water. Working solutions were subsequently made by diluting this stock solution. 0.001M solution of

1,4-DHA was prepared by dissolving the requisite amount in ethanol. Solvents, sodium acetate for pH-measurement and naphthalene used for adsorption were of high grade of purity.

Preparation of Solutions for Absorption Studies

1. To study the effect of varying the pH on the absorbance of the complex, optical density of the solution of the complex at 6.0–8.8 was recorded against DMF as a blank. The solutions were prepared by mixing equal amount of 1×10^{-3} M solutions of the metal and the ligand. The absorbance of corresponding amount of ligand under identical conditions was also measured against the reference.

2. The effect of varying the reagent concentration was studied by keeping the amount of metal ion and all other factors constant. For this purpose equal amount of 1×10^{-3} M Ni(II) solution and increasing amount of equimolar 1,4-DHA solution in ethanol were mixed. In each case pH of the solution was adjusted to 8.6 and the volume made up to 40 ml. Likewise a series of solutions were prepared by taking varying amount of Ni(II) solution and keeping the amount of ligand constant.

3. To study the composition of the complex, Job's method of continuous variations was used. A series of solutions were prepared with different concentration of the metal ion and the ligand keeping the total molarity constant. Adsorption of the complex in each case was carried out on microcrystalline naphthalene[11] produced on adding 2 ml of 20% naphthalene solution in acetone to an aqueous ethanolic solution of the complex. The mixture was shaken for 15 minutes and the contents filtered under suction through a Whatman No. 1 filter paper. Microcrystalline naphthalene carrying adsorbed complex was washed several times with distilled water and finally drained dry. It was then dissolved in 10.0 ml DMF and the spectra recorded against DMF as blank.

4. Sample solutions (except in the case of electroplating-bath sample) were made by refluxing a known amount of the sample with 50 ml of 1 N HCl for *ca.* 2 hrs. The resulting solution was washed with CCl_4 several times to remove the fat and diluting the aqueous layer to 100 ml with distilled water. 1% solution of electroplating-bath sample was directly prepared by dilution.

RESULTS AND DISCUSSION

The Ni-1,4-DHA complex shows an absorption maximum at 560 nm. As the ligand also absorbs at this wavelength, ΔO.D. values were calculated and plotted against the pH of the solution. The ΔO.D. is maximum at pH 8.6 and thus subsequent studies were carried out at this pH.

Effect of 1,4-DHA Concentration on the Absorbance of the System

ΔO.D. values—the difference of absorbance of the complex and the reagent against DMF as blank—of solutions prepared as per (2) above were plotted against the amount of the reagent (Fig. 1). It is found that there is a sharp increase in the ΔO.D. value as the M : L ratio is changed from 1 : 1 to 1 : 5. However, the increase is relatively small till the ratio is 1 : 10, above which no increase is observed. Subsequently, a 10-fold excess of the ligand was maintained during studies.

The ΔO.D. of the solutions of the metal complex each having L : M ratio ≥ 10 and increasing amount of the metal ion was plotted against the concentration of the metal ion. It was found to increase linearly with increase in the amount of the metal ion over concentration range 0.6 to 3.0 ppm.

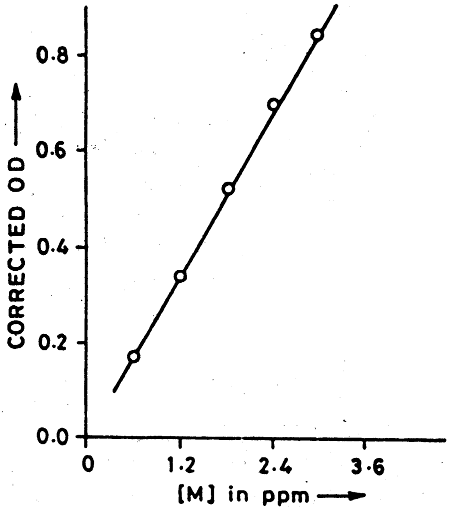

Fig. 1

The composition of nickel-1,4-DHA complex was determined by continuous variations method. The ΔO.D. of the solutions prepared in (3) above was plotted against increasing mole fraction of the metal ion. It shows a maximum at mole fraction 0.5 indicating the formation of a 1 : 1 complex in the solution.

Interference caused by the presence of foreign ions in the photometric determination of nickel using 1,4-dihydroxyanthraquinone was examined by adding the ion to Ni(II) solution before adding the complexone. The complex subsequently formed, after naphthalene adsorption was taken up in DMF and its absorption measured. Cd^{2+}, Hg^{2+} and Ag^{+} do not interfere in 10-fold concentration but Co^{2+}, Zn^{2+}. Cu^{2+} and Mn^{2+} cause serious interference in the determination as the absorption of the nickel-1,4-DHA solution has been found to vary > 1% even when these ions are present in traces.

1,4-Dihydroxyanthraquinone method has been successfully applied to determine nickel in various industrial samples. For this purpose, samples of hydrogenation catalyst (Raney nickel), catalyst waste, hydrogenated oils and electrolyte from nickel electroplating tank have been analysed. The results obtained (in ppm) (average of six estimations) have been compared with dimethylglyoxime-oxidising agent method[12] (given in parenthesis):

Hydrogenation catalyst	269.5 (271.0)
Catalyst waste	69.0 (68.6)

Hydrogenated oil	1.8 (1.7)
Electroplating solution	417.0 (420.0)

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A SEMINAR ON POLLUTION AND ITS CONTROL IN CHEMICAL AND ALLIED INDUSTRIES

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