

Spectrophotometric Determination of Nickel (II) with Diphenylcarbazone and Triton X-100

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Summary. The chromogenic reaction of nickel (II) with diphenylcarbazone (DPC) in the absence and presence of nonionic surfactant, Triton X-100 was studied at pH 8.6 using phosphate-borax buffer medium. The molar absorptivities of both binary and sensitized complexes were 3.71×10^4 and 9.15×10^4 $\text{l.mol}^{-1}.\text{cm}^{-1}$ at 553 nm and adhered to Beer's law in the concentration ranges 0.03-1.17 and 0.03-1.00 mg/l of nickel (II), respectively. The molar compositions of the aqueous and sensitized complexes were 1:2 (nickel-DPC). Potassium fluoride and ammonium thiocyanate were used to mask the interfering ions. The method was used for the determination of nickel in River Nile water, cooling water, industrial wastewater, oils and steel alloys.

Introduction

Many different organic compounds have been used as a spectrophotometric reagents for the determination of nickel (II) in aqueous solutions.⁽¹⁻⁵⁾ Addition of some surfactants and protective colloids to nickel (II) complexes have been used to enhance their spectral intensity.⁽⁶⁻¹¹⁾

Experimental

Apparatus

All absorbance measurements were conducted on SHIMADZU UV-VIS-NIR scanning spectrophotometer using 1 cm matched quartz cells. A Crison Digit Model 501 ion analyzer equipped with glass-calomel electrode was used for pH measurements and pH adjustment, respectively.

Reagents

All chemicals used in the proposed method were of analytical grade. Aqueous solutions were prepared with bi-distilled water. Standard nickel (II) stock solution of 1×10^{-2} M was prepared by dissolving 0.6572 g of nickel sulphate hexahydrate in water containing 1.0 ml of concentrated sulphuric acid, and dilute the solution to 250 ml with water. Diphenylcarbazone (DPC) reagent solution of 1×10^{-2} M was prepared by dissolving 1.2013 g of DPC in ethanol and diluting to 500 ml with ethanol. Triton X-100 was prepared as 5% v/v stock solution. Borax-phosphate buffer was prepared by adjusting the pH of 5×10^{-2} M borax solution with 0.1 M potassium hydrogen phosphate to the desired pH value.

General Procedure

The following procedure was used for the determination of Ni (II)-DPC complexes. To an aliquot of the sample containing 0.75-25.0 μg of nickel (II), add 1.5 ml of 1×10^{-2} M DPC reagent, 2.5 ml of ethanol and 1.25 ml of 2% v/v Triton X-100 in case of micellar medium. The volume is completed to the mark in a 25-ml volumetric flask with phosphate-borax buffer solution of pH 8.6. The absorbance is measured at 553 nm against a reagent blank after mixing directly for aqueous complex and after 25 minutes in case of sensitized complex. The calibration graph was prepared using the same procedure.

Results and Discussion

Effect of pH

A study of the effect of pH on nickel (II)-DPC complexes in the absence and presence of Triton-X 100 has been examined in the pH range 6.5-9.5. Maximum and constant absorbances of the complexes were obtained in the pH range 8.2-9.0. Hence, all the studies were carried out in phosphate-borax buffer solution of pH 8.6.

Effect of surfactants and protective colloids

In an attempt to enhance the absorbance of the binary complex nickel (II)-DPC. Some surfactants and protective colloids were tested. The utilized surfactants were of

the cationic, CTAB, CPB, CPC and Zephiramine; nonionic, Triton X-100, Emulsifier S, Tween 20, Tween 40, Tween 60 and Tween 80; anionic, SAS, SDBS, and SLS types. Moreover, the protective colloids were Arabic gum, PVA, PVP and Gelatin. The concentrations of these surfactants were greater than their critical micelle concentration whereas, protective colloids used as 0.2% w/v in the final solution. Maximum enhancement of the complex absorbance was obtained in the presence of nonionic surfactant Triton X-100. Therefore, Triton X-100 was used for further studies.

Spectral characteristics

The absorption spectra of nickel-DPC complexes in the absence and presence of Triton X-100 and their reagent blank are shown in Fig.1. Both two complexes and their reagent blank demonstrate maximum absorption at 553 and 492 nm, respectively.

Effect of DPC concentration

The effect of reagent concentration on the absorbance of the nickel complexes was studied at optimum conditions. The reagent concentration was varied between 4×10^{-5} M and 2.4×10^{-3} M throughout the study. Maximum colour was developed using a reagent concentration equal or higher than 1×10^{-2} M and 1.2×10^{-2} M, respectively for aqueous and sensitized nickel (II) complexes.

Choice of solvent

It was found that ethanol is the best solvent for dissolving DPC reagent. The study revealed that, the binary and sensitized complexes were exerted maximum absorbance in the presence of ethanol up to 20% and 25%, respectively. However, 10% ethanol content was used in the proposed procedure for the two complexes.

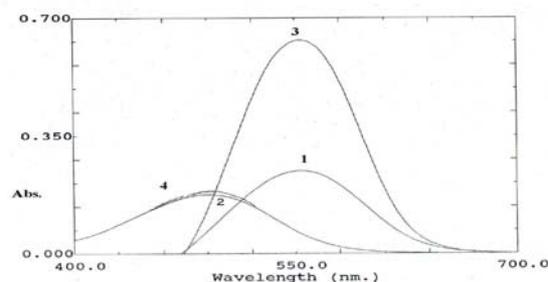


Fig.1. Absorption spectra of Ni-DPC complexes in the absence and presence of Triton X-100 and their reagent blank. Curve 1, shows the binary complex; curve 2, reagent blank, Curve 3, sensitized complex; curve 4, reagent blank.

Effect of Triton X-100 concentration

A study of the effect of Triton X-100 concentration on the determination of the nickel (II)-DPC complex was carried out using variable concentrations of Triton X-100 ranging between 0.004 and 0.04% v/v. The results revealed that, the sensitization of the binary complex was in the presence of $\geq 0.04\%$ v/v Triton X-100. Therefore, 1.25 ml of 2% v/v Triton X-100 was used in the proposed method.

Time required for color development

The formation and stability of the nickel (II)-DPC complexes with respect to time were investigated using the optimum experimental conditions of determination. The study showed that, the maximum absorbance has been takes place immediately in aqueous complex, whereas, the color development of the sensitized complex requires 15 minutes after mixing. The order of addition of the reagent and surfactant has no effect on the stability of the formed complex.

Calibration graphs and statistical analysis of data

The nickel (II)-DPC complexes obeyed Beer's law in the concentration ranges 0.03-1.17 and 0.03-1.00 mg/l of nickel (II) in the absence and presence of Triton X-100, respectively. The values of the molar absorptivities as determined by a least squares method for eighteen results each were 3.71×10^4 and $9.15 \times 10^4 \text{ l.mol}^{-1}.\text{cm}^{-1}$ at 553 nm for both nickel (II)-DPC complexes. Sandell's sensitivity index of the complexes values was 1.58 and 0.64 ng.cm^{-2} , respectively.

Composition of the complexes

The binary and sensitized complexes of nickel with DPC have been studied by the molar ratio and continuous variation methods. The study confirmed the formation of 1:2 (Ni-DPC) complex in the absence and presence of Triton X-100. The stability constants were carried out at constant ionic strength using KNO_3 . The determined values of the stability constant (β) were 2.4×10^9 and 6.1×10^9 for both aqueous and sensitized complexes, respectively using continuous variation method.

Effect of diverse ions

A systematic study of the foreign ions in the determination of nickel (II) has been made under the experimental conditions. Presented data in Table 1, show the

amounts of the ions that do not interfere and the tolerance limit was taken the amount that cause $\pm 2\%$ error in the absorbance value. However, several metal ions including Fe (II & III), Sn (II & IV), Cr (III & IV), Cu (II), Cd (II), Zn (II), malonate and EDTA were seriously interfered. On the other hand, some masking agents were used to increase the selectivity of the method. Potassium fluoride was used to mask Fe (II & III), Sn (II & IV) and Cr (III & VI) ions, whereas, ammonium thiocyanate was used to mask Cu (II), Cd (II) and Zn (II) ions.

Table 1. Effect of foreign ions on the determination of nickel (II), $[\text{Ni}^{2+}]$, 8×10^{-6} M; [DPC], 3×10^{-4} M; 10% ethanol; [Triton X-100], 0.1% v/v; pH 8.6.

Ion added	Tolerance limit [ion]/ $[\text{Ni}^{2+}]$
Li^+ , K^+ , Na^+ , CO_3^{2-} , SO_4^{2-} , $\text{S}_2\text{O}_3^{2-}$, H_2O_2 , $\text{NH}_2\text{OH.HCl}$, formate, phosphate and ascorbic acid.	> 10000
NH_4^+ , Ca^{2+} , Mg^{2+} , Ba^{2+} , Sr^{2+} , F^- , NO_2^- , Cl^- , NO_3^- , ClO_4^- , ethanolamine, DEA, TEA and acetyl acetone.	> 5000
Co^{2+} , Cu^{2+b} , Mn^{2+} , Hg^{2+} , Fe (II)^a , Fe (III)^a , Sn (II)^a , Sn (IV)^a , Cr (III)^a , Cr (VI)^a , Br^- , CN^- , SCN^- , oxalate, citrate and tartrate.	> 1000
Be^{2+} , Al^{3+} , Bi^{3+} , As (III), Sc (III), Zr (IV), Ti (IV), V (IV), Mo (VI), U (VI), W (VI), I^- , succinate and thiourea.	> 500
Pb^{2+} , Cd^{2+b} and Zn^{2+b} .	> 100

Masking agents:

- a. 0.5 ml of 0.1 M potassium fluoride b. 1.0 ml of 10^{-2} M ammonium thiocyanate

Application of the method

The developed method has been successfully applied for the determination of nickel (II) in water, alloys and petroleum oil samples. The analyzed water samples were collected from River Nile, cooling water in some power stations in Egypt and

industrial wastewater of different plants whereas, oil samples from crude oil of different companies in Egypt. On the other hand, the samples of steel alloys were certified. The results obtained were in good agreement with atomic absorption spectrometric method.

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