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Spectrophotometric determination of Ni(II), Co(II) and Cu(II) by using 7-(14-nitrophenylazo)-8-hydroxyquinoline-5-sulfonic acid in micellar media

Anupreet Kaur[a] and Usha Gupta[a]

Punjabi University, Science and Art Faculty, Department of Chemistry, Patiala, Punjab, India

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ABSTRACT

A direct method has been developed for the spectrophotometeric determination of Ni(II), Co(II) and Cu(II) using 7-(14-nitrophenylazo)-8-hydroxyquinoline-5-sulfonic acid (p-NIAZOXS) as a complexing reagent in the micellar media. Beer's law was obeyed over the range from 0.24-1.46µg/mL for Ni (II), 0.29-1.3 µg/mL for Co(II) and 0.22-1.36µg/mL for Cu(II). Sandell's sensitivity and Molar absorptivity have been found to be 0.0037µg/cm^2 and 2x10^4 Lmol^{-1}cm^{-1} for Ni(II), 0.0024µg/cm^2 and 2.54x10^4 Lmol^{-1}cm^{-1} for Co(II), and 0.0034µg/cm^2 and 2.2 x10^4 Lmol^{-1}cm^{-1}for Cu(II). Each metal complex was stable for more than 24 hrs under optimized conditions. The effect of various diverse ions have been studied and above method has been applied for the determination of Ni(II), Co(II) and Cu(II) in environmental, food samples and water samples. The developed method has been found to be quite simple, rapid, sensitive and reproducible results were obtained. The precision (RSD<1.5%) and the accuracy obtained were satisfactory.

Keywords: 7-(14-nitrophenylazo)-8-hydroxyquinoline-5-sulphonic acid (p-NIAZOXS).

INTRODUCTION

Important positive and negative roles of trace heavy metal ions in human health are known. Lots of studies have been performed for the determination of trace metal ions in various media including some body tissues and fluids, natural waters etc. Also the investigation of trace heavy metal contents in food samples including honey, vinegar, lemon juice, sour cream, yogurt, buttermilk, chocolate, cocoa, honey, molasses and other food samples are an important part of analytical chemistry [1-4]. Metals like Ni(II), Co(II) and Cu(II) play important role in physiology of our body because they are the essential constituents of some enzymes like urease, nickel super oxide dismutase (NiSoD) coenzymes, vitamin $B_{12,}$ tryosinase and galactose oxidase but their toxic effects on human health and environment are not unknown because they are totally

nondegradable, which means they are virtually indestructible in the environment. Cobalt is an important element, not only for industry but also for biological systems. It is present in vitamin B12 and is an essential micro nutrient for all living systems. However, in larger amounts it is toxic and causes pulmonary disorders, dermatitis, nausea and vomiting. Copper ingestion by humans causes nausea, vomiting, abdominal pain, metallic taste, and diarrhea. The most serious harmful health effects from exposure to nickel, such as chronic bronchitis, reduced lung function, and cancer of the lung and nasal sinus, have occurred in people who have breathed dust containing certain nickel compounds while working in nickel refineries or nickel-processing plants. So, they are receiving increasing attention in pollution and nutritional studies. Various analytical methods for the determination of these metal ions have been reported. Solvent extraction, high performance liquid chromatographic, flame photometry, atomic absorption spectrometry, polarography, plasma emission and neutron activation analysis[5-7]. Some of these are very sensitive, but require costly instrumentation.

But, spectrophotometric methods for determination of metals have a lot of merits such as simplicity, economical, little contamination and convenient to use. Introduction of surfactants added another plume to the cap of spectrophotometric methods. Use of micellar media is important as they solubilize the metal complexes, enhance the absorption intensity and improve the detection limit. Micellar media also avoids the use of toxic organic solvents

Spectrophotometric methods play a prominent role, as they involve less cost and they are rapid and sensitive. The organized molecular assemblies such as micelles are used in spectroscopic measurements due to their possible effects on the systems of interest. In the field of metal ion complex, at a concentration above critical micelle concentration (cmc) micelles .form a complex with advantageous properties, such as hyperchromic and bathochromic shifts, that can modify the sensitivity of the method by affecting the interferences and matrix effects[8]. The ability of micellar systems to solublize slightly soluble or even insoluble complexes has been used to enhance the analytical merit of given methods. Most organic solvents that are used as extraction solvents can be classified as toxic and environmental pollutants, and some have been listed as carcinogenic by the US Environmental Protection Agency (EPA). Application of micellar systems avoids the solvent extraction step which is necessary following the formation of slightly soluble complexes in the absence of micelles. So, there is need to develop a simple, sensitive and selective method for determination of these metal ions in various samples. In the present work, 7-(14-nitrophenylazo)-8-hydroxyquinoline-5-sulfonic acid used as chromogenic complexing reagent for spectrophotometric determination of Ni(II), Co(II) and Cu(II) in micellar media which form water insoluble complex and can be solublised in micellar media. The method has been found to be simple, rapid and sensitive for the determination these metal ions.

MATERIALS AND METHODS

2.1. Reagents

All the reagents used were of analytical grade (unless otherwise stated). Doubly distilled water was used throughout the present study.

2.2. Preparation of 7-(14-nitrophenylazo)-8-hydroxyquinoline-5-sulfonic acid

The reagent was conveniently prepared by coupling 8-hydroxyquinoline-5-sulphonic acid with an equivalent quantity of p-nitrodiazobenzene chloride in alkaline solution. An amount of 0.02

moles of p-nitroaniline and 5 mL of concentrated hydrochloric acid were dissolved in 25 mL of water, cooled to 5 °C, and diazotised with 0.02 moles of sodium nitrite dissolved in 5 mL of water. After 20 min the diazonium solution was slowly added to a solution of 0.02 moles of 8-hydroxyquinoline-5-sulphonic acid containing 5 g of sodium carbonate and 50 mL of water also cooled to 5°C. After two hours, hydrochloric acid (1:4) was added until the solution was slightly acidic (pH 3-5).

The 7-(14-nitrophenylazo)-8-hydroxyquinoline-5-sulfonic acid (p-NIAZOXS) separated as a dark red precipitate which was filtered off, washed with water, dissolved in diluted sodium hydroxide and re-precipitated with hydrochloric acid. The precipitate was washed with deionized water to eliminate the free acid until a negative chloride reaction with $AgNO_3$ was obtained. Then it was dried at 105°C overnight.

IR data: (υ cm^{-1}) Aromatic-CH stretch: 3699.92, 3622.76; OH stretch: 3377.77; NO_2 stretch: 1344.55; Aromatic C=C stretch: 1593.40, 1500; -CH in plane bending: 1090, 1030.90, 1009.93; -C-N stretch: 900.4; Aromatic C=C bending out of plane: 500.17, 460.79, 420.14

2.3. Apparatus

A shimadzu 1700 UV-Vis spectrophotometer equipped with 1.0 cm quartz cell and a digital century pH meter Cp 901 were used for absorbance and pH measurements respectively.

2.4. Metal ion solutions

Stock solutions of Ni (II), Co (II) and Cu (II) metal ions were prepared from their salts in doubly distilled water and standardized. Working solutions were prepared from standard solutions by their appropriate dilution as and when required.

2.5. General Procedure

To an aliquot of metal ion solution containing 0.2 µg of Ni (II), 0.2 µg for Co (II), and 0.2 Cu (II) taken separately was added 2mL of (0.1%) p-NIAZOXS reagent solution and pH (3-7.4) was adjusted by using 1mL of acetic acid- sodium acetate buffer and (8-9.2) pH by using ammonia/ammonium chloride. The complexes formed were solublised by adding 5.0mL of appropriate surfactant and diluted upto 10mL in a standard flask. The absorbance of the resulting solutions was measured at λ_{max} 518 nm for Ni (II), 520 nm for Co (II), and 516.5 nm for Cu (II) against reagent blank prepared under similar conditions. The complexes were stable for more than 24hrs. in all the three cases. The results of determination are in the Table 1. The characteristic absorption spectra are shown.

RESULTS AND DISCUSSION

3.1. Effect of surfactant

Various surfactants such as Tween-20, Tween-80, TritonX-100, Cetyltrimethyl ammonium bromide (CTAB), Cetylpyridinium bromide (CPB), Sodium dodecyl sulfate (SDS) and Brij-35 were tried. Best results were obtained with Tween-20 for Ni (II), TritonX-100 for Co (II) and Cu(II). The dosage of Tween-20, TritonX-100 (1%v/v) were in range of 3.0-8.0mL. So, 5.0 mL of the respective surfactant were recommended for further studies. The results are given in Table1.

3.2. Effect of pH

Effect of pH was studied by the general procedure and it was found that absorbance was maximum in the pH range of 7.0-10.0 for Ni(II), Co (II) and Cu (II). The results are given in Table1.

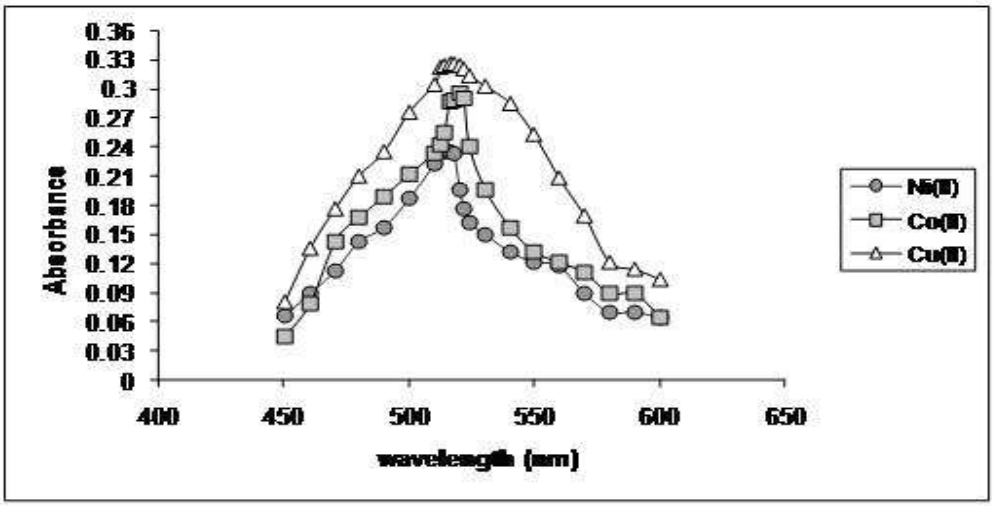

Figure 1. Absorption spectra
(a) Nickel-p-NIAZOXS in the presence of Tween-20 surfactant at (518nm)
(b) Cobalt-p-NIAZOXS in the presence of TritonX-100 surfactant at (520nm)
(c) Copper- p-NIAZOXS in the presence of Brij-35 surfactant at (516.5nm)

3.3. Interferences

The effects of diverse ions on the determination of these metal ions were studied in detail. The criterion for interference was an absorbance value varying by more than ±5% from the expected value for Ni(II), Co(II), and Cu(II). To test the effect of diverse ions, 16.14 µg Ni(II), 15.10 µg Co(II), and 42.0 µg Cu(II) were taken in the presence of various foreign ions. Each of these metal ions could be determined without any interference in the presence of 50 fold excess of the following cations: Cd(II), Al(III), Cr(III), Mg(II), Mn(II), Zn(II), Pb(II), Hg(III), Ag(I), Au(III),Pt(IV), Se(IV),Te(IV) and Ba(II). Amongst the anions examined (amounts in mg, given in parentheses), the following anions did not interfere: oxalate (80), tartrate (100), cyanate (100), nitrate (90), nitrite (90), acetate (100), sulphate (70), thiocyanate (20), metabisulphate (30), citrate (90), bromide (70), fluoride (95) and chloride (95). Thiourea, sodium thiosulphate and EDTA interfere strongly in the determination of Ni (II)/ Co (II) / Cu (II). Among the three, Cu (II) and Co (II) can be masked by sodium thiosulphate and EDTA respectively. Co (II) can be determined in the presence of Ni (II) by converting. Ni (II)-p-NIAZOXS complex into Ni-ammine complex by adding excess of ammonia as Co (II)-p-NIAZOXS complex remained unaffected. Ni (II) could be determined in the presence of Cu (II)/Co (II) by adding 5mL of 2% sodium thiosulphate. Interference of iron (100 fold in excess) in the determination of these metal ions could be removed by adding 2.0 mL of 5% sodium fluoride solution. Interference due to Pd (II) in the determination of these metal ions could be removed by pre-extraction into chloroform at pH 2.5.

Table 1. Analytical characteristics of 7-(14-nitrophenylazo)-8-hydroxyquinoline-5-sulfonic acid complexes in micellar media.

Characteristics	Ni (II)	Co (II)	Cu (II)
Beer's law range (µg/mL)	0.24-1.46	0.29-1.3	0.22-1.36
Absorption maxima (λ_{max}) (nm)	518	520	516.5
Molar absorptivity ($Lmol^{-1}$ cm^{-1})	2.0×10^4	2.54×10^4	2.2×10^4
Sandell's sensitivity ($\mu g/cm^2$)	0.0037	0.0024	0.0034
pH range	7.0-10.0	7.0-9.2	7.0-10.0
Surfactant used (1%) (5ml)	Tween-20	TritonX-100	TritonX-100
Amount of reagent used (0.1%) (ml)	2.0	2.0	2.0
Relative standard deviation	0.60	0.52	0.81

Applications

Determination of nickel in edible oil

A 0.2-15g of oil sample (vegetable oil) was taken in a beaker and decomposed with concentrated nitric acid. The dried sample was heated in a muffle furnace at 600˚c for 1hrs and then allowed to cool. After the addition of few drops of conc. nitric acid, it was dried and again heated for 1hrs at 700˚c in muffle furnace. The left ash was dissolved in concentrated hydrochloric acid, diluted with double distilled water, and the final volume was made up to 100mL in a standard flask. An aliquot of the resulting solution was taken and determined by the general procedure. The results of the determination are given in Table 2.

Table 2. Determination of Ni(II), Co(II) and Cu(II) in food and pharmaceutical samples(n=5)

Sample	Amount of Metal added (μgml^{-1})	Amount of Metal found (μgml^{-1})	Recovery (%)
Ni(II) (Edible oil)	16.10	22.40	139
Co(II) Cyanocobalamine (Vit B_{12}) Thiaminmononitrate (10.0 mg) Riboflavine (10mg) Nicotinamide (50mg) Pyridoxine hydrochloride (3mg) Calcium pantohenate (16.3 mg) Cyanocobalamine (10.0mg) Ascorbic acid (150mg) Biotin (0.15mg)	20.00	24.19	120
Cu(II) (Milk)	26.80	27.20	101

Determination of cobalt in cyanocobalamine (Vit. B_{12})

Vitamin B_{12} is a first natural product found to contain cobalt. Molecular formula $C_{63}CoN_{14}O_{14}P$ with molecular weight 1355. Tablets of Vit. B_{12} containing cyanocobalamine (50mg) were heated with concentrated nitric acid on a hot plate to convert it into a dried mass. Dissolved the mass in hydrochloric acid and filtered, neutralized the filtrate with ammonia solution. Diluted it further and made upto the mark in a standard flask with double distilled water. Estimation of cobalt was done by general procedure. The results of the determination are given in Table 2.

Determination of copper in milk

500 mL of milk or 5-10g of fly ash or 50mL of wine or beer sample were taken in a beaker and dissolved in concentrated nitric acid and evaporated to dryness. The residue thus obtained was dissolved in distilled water in all cases except milk. Residue of milk was dissolved in hydrochloric acid, filtered and neutralized the filtrate with ammonia solution and then diluted with double distilled water in a standard flask. All samples were standardized by known method, followed by their determination by general procedure. The results of the determination are given in the Table 2.

Table 3. Recovery studies of trace metal ions in baking powder sample

Analytes	Added ($\mu g l^{-1}$)	Found ($\mu g l^{-1}$)	Recovery %
Ni(I)	0.0	3.2	---
	5.0	8.2	100.0
	20.0	23.2	100.0
Co(II)	0.0	0.2	---
	5.0	5.2	100
	20.0	19.2	95.0
Cu(II)	0.0	4.2	---
	5.0	9.0	96
	20.0	25.1	104

Determination of Ni(II), Co(II) and Cu(II) in baking powder

Baking powder and baking soda are used in recipes that contain acidic ingredients (e.g., fruits and maple syrup). These foods are frequently consumed by human. The determination of heavy trace metals in baking powder and baking soda is important for human health. The level of trace

heavy metal ions the food samples including baking soda and powder samples are generally mg/g.

A sample of 1.00g was dissolved in a mixture of 500µL concentrated HNO_3 and 20mL of distilled water. The solution was neutralized by using 1.0M NH_3 and then the metal contents of the final solution were determined by spectrophotometry. Results are given in Table 3.

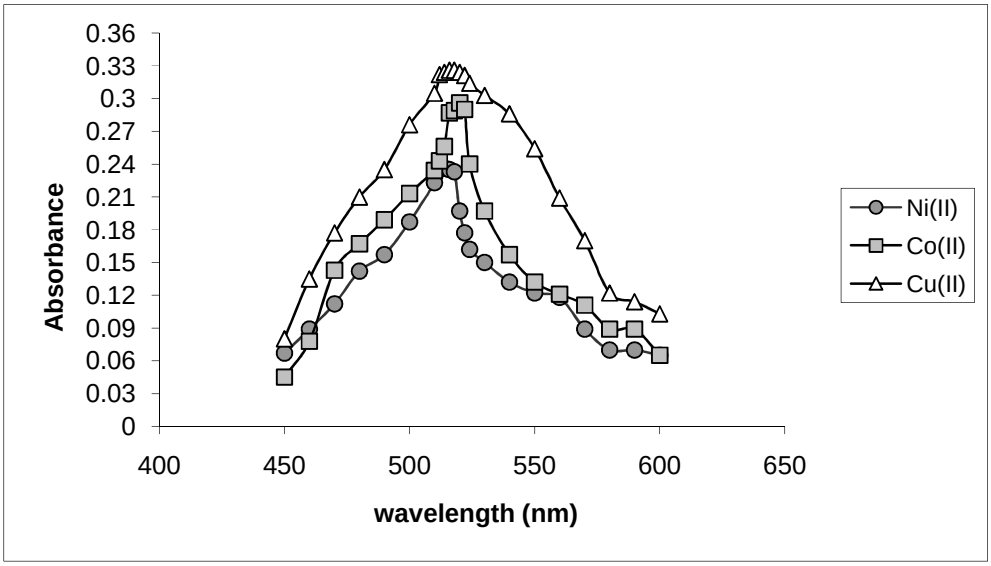

Table 2. Determination of Ni(II), Co(II) and Cu(II) in food and pharmaceutical samples(n=5).

Sample	Amount of Metal added (μgmL^{-1})	Amount of Metal found (μgmL^{-1})	Recovery (%)
Ni(II)	16.10	22.40	139
(Edible oil)			
Co(II)			
Cyanocobalamine (Vit.B_{12})			
Thiaminmononitrate (10.0 mg)			
Riboflavin (10mg)			
Nicotinamide (50mg)	20.00	24.19	120
Pyridoxine hydrochloride (3mg)			
Calcium pantohenate (16.3 mg)			
Cyanocobalamin (10.0mg)			
Ascorbic acid (150mg)			
Biotin (0.15mg)			
Cu(II)	26.80	27.20	101
(Milk)			

Table 3. Recovery studies of trace metal ions in baking powder sample

Analytes	Added (μgL^{-1})	Found (μgL^{-1})	Recovery(%)
Ni(II)	0.0	3.2	---
	5.0	8.2	100.0
	20.0	23.2	100.0
Co(II)	0.0	0.2	---
	5.0	5.2	100
	20.0	19.2	95.0
Cu(II)	0.0	4.2	---
	5.0	9.0	96
	20.0	25.1	104

CONCLUSION

p-NIAZOXS reacts with Ni(II), Co(II) and Cu(II) and forms water insoluble complexes. These complexes were solubilised in the micellar media, thus avoiding the use of costly and toxic organic solvents. Spectrophotometric method has been found to be quite simple, rapid, cheap, less time consuming and gave reproducible results, than most of the other methods, applicable for the determination of these metals in the presence of each other, which makes it an alternative to the existing methods for the determination of these metal ions.

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