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Spectrophotometric Determination of Ni(II) with 2-Acetyl Thiophene Thiocyanate

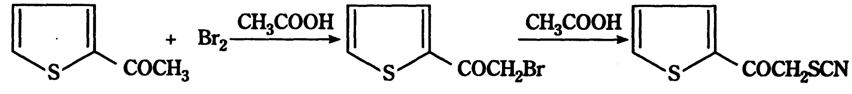
R.S. LOKHANDE*, A.B. CHAUDHARY and S. NIRUPA
Department of Chemistry, Mumbai University, Vidyanagri, Kalina, Mumbai-400 098, India

2-Acetyl thiophene thiocyanate (ATT) was synthesized and its characterization was carried out using IR, NMR and elemental analysis. The development of a new method is proposed for the extraction and spectrophotometric determination of Ni(II) at microgram level. The reagent forms a complex with Ni(II) and was extracted in ethyl acetate at pH 10.4 having absorption maxima at 500 nm. Beer's law is obeyed over the range of 2–100 μ/mL of Ni(II). The molar absorptivity is 0.12×10^4 L mol^{-1} cm^{-2} and Sandell sensitivity 0.048 μg cm^{-2}. The stoichiometric ratio of the complex was found to be 1 : 2. Interference of the diverse cations and anions has been studied. The method has been applied to commercial and synthetic samples.

Key words: Spectrophotometry, determination, nickel(II), 2-acetyl thiophene thiocyanate.

INTRODUCTION

There are many organic ligands synthesized and its complex behaviour with transition metals has been studied with a separation technique like solvent extraction. The reagents such as oximes[1–5], hydroxytriazenes[6–8], DTPA[9], azo compounds[10, 11], semicarbazones and thiosemicarbazones[12–15] are used for spectrophotometric determination of transition metal ions. There is very little work done for exploring the possibility of thiocyanate as an extracting reagent. There is some work using salts of thiocyanate for extraction of metals. The reagent was prepared by brominating 2-acetyl thiophene and then reacting the brominated derivative with KSCN taking solvent as DMSO. The yellow coloured 2-acetyl thiophene thiocyanate (ATT) has the m.p. 97°C. The characterization of the product was carried out with the help of IR which shows stretching of (C=O) at 1640 and stretching of SCN at 2020, NMR in $CDCl_3$ which shows δ 4.5 (2H, s, —CH_2—); δ 7.0–7.33 (1H, t, H_4); δ 7.66–8.0 (2H, m, H_3 and H_5) and elemental analysis recorded was C, 45.88; H, 5.88; N, 16.33%. All the other chemicals used were of analytical reagent grade.



2-Acetyl thiophene

2-Acetyl thiophene thiocyanate

EXPERIMENTAL

The stock solution of nickel sulfate was prepared by dissolving equivalent 100 mg in 100 mL and was diluted, utilized for further studies. A 2% ATT solution in methanol was prepared and was used for further studies. Absorbance and pH measurements were carried out on a Shimadzu UV visible 2100 spectrophotometer with 1 cm quartz cells and a control dynamic digital pH meter with combined glass electrode respectively.

Procedure: Extraction experiments were carried out by shaking the appropriate organic and aqueous solution at an O/A phase ratio of 1 for 10 min. The distribution studies[16] were carried out at 25°C, in various organic solvents and it was found that ethyl acetate showed maximum extraction of the Ni-ATT complex. The measured amount of Ni(II) was taken in a 50 mL beaker and to this 2 mL of ATT was added and stirred for 2 min. The pale yellow coloured complex formed was extracted twice with 5 mL of ethyl acetate in a 10 mL volumetric flask. The combined extract was diluted to 10 mL if required and its absorbance was measured at 500 nm against the reagent blank solution prepared under the same conditions using the same quantity of the reagent.

RESULTS AND DISCUSSION

The extraction of (100 μg) was carried out at various pH (from 2 to 12) keeping the organic to aqueous volume ratio 1 : 1. The extraction was found to be quantitative at pH 10.4. The influence of shaking time for the extraction of Ni(II) was studied for 30–120 sec. The quantitative extraction of Ni(II) was achieved after 40 sec with ATT. With further increase in shaking time, the percentage extraction remained quantitative. The stability of the complex was studied as a function of time and it was found that the complex was stable for 72 h.

Effect of reagent concentration: Various volumes of 2% reagent solution were added to the sample solution containing 100 μg of nickel at the respective pH values. The absorbances remained constant when the volume of the reagent solution used was more than 2 mL. Therefore 2 mL of 2% reagent was chosen for the quantitative determination of nickel.

Nature of extracted species: The nature of extracted species was ascertained from the plot of log D *vs.* log R from aqueous media (Fig. 1), where log D is the distribution coefficient of the complex and log R is the concentration of the reagent. The slope of the graph is 1.8173 for ATT. Thus stoichiometry ratio of metal to reagent was found to be 1 : 2 with the reagent.

Beer's law and sensitivity: Calibration graph for nickel(II) was constructed under the optimum conditions. The graph obeys Beer's law in the range of 2–100 μg for nickel. The molar absorptivity and Sandell sensitivity were calculated to be 0.12×10^4 L mol^{-1} cm^{-1} and 0.048 μg cm^{-2}.

Influence of diverse ions on percentage extraction of Ni(II): An interference study showed that large number of cations and anions offer no interference. The tolerance limit was set at the amount of foreign ions required to cause ±1.0% error in the recommended procedure. The presence of various salts of alkali and alkaline earth metals does not show any effect on the absorbance value of Ni : ATT extract. Varying amounts of foreign ions Ca(II) 25 mg, Ba(II)

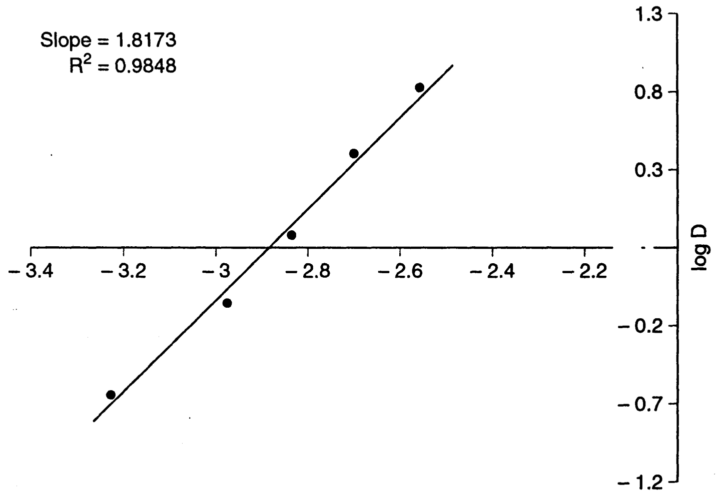


Fig. 1. Stoichiometric ratio of metal to reagent complex of Ni(II) with ATT in ethyl acetate from aqueous media

25 mg, Sr(II) 10 mg, Al(III) 10 mg, Be(II) 10 mg, Pb(II) 25 mg, Mg(II) 10 mg, Hg(II) 10 mg, Bi(III) 25 mg, As(III) 10 mg, V(V) 10 mg, W(VI) 10 mg were added in the fixed amount (500 μg) of nickel(II) to study the interference in the recommended extraction and subsequent determination procedure.

Applications

Various commercial samples and synthetic binary mixtures containing Ni(II) were analysed according to the recommended procedure and the results were compared to those obtained by standard method. The proposed method also facilitates to determine nickel(II) from commercial samples; the results are shown in Table-1.

TABLE-1
SEPARATION OF Ni(II) WITH ATT FROM VARIOUS SYNTHETIC AND COMMERCIAL SAMPLES

S.No.	Sample	Copper found	
		Certified value	Present method
1.	Synthetic mixture		
	(a) Ni(10) Cu(10)	10.0 μg	9.9 μg
	(b) Ni(5) Zn(5)	5.03 μg	5.01 μg
	(c) Ni(5) Zr(5)	4.99 μg	5.01 μg
2.	Hydrogenated oil	0.0013%	0.0012%
3.	Steel	3.04%	3.02%
4.	Brass	0.54%	0.53%

*Average of three determination

Conclusion: The proposed method is found to be competitive as compared to other standard methods. The extraction time required is very little, *i.e.*, only 40 s and the complex is stable for 72 h. The results show good agreement with the standard method. The method is very precise.

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