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Extractive Spectrophotometric Determination of Micro Amounts of Nickel(II) Using Benzildithiosemicarbazone

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Nickel(II) reacts with benzildithiosemicarbazone in aqueous dimethyl formamide solution in ammonium chloride ammonium hydroxide buffer of pH 9.0 giving yellowish orange precipitate. The 1 : 1 complex in chloroform has a maximum absorption at 410 nm and is stable for 48 h. Beer's law is obeyed in the range 0.1–1.6 μg/ml of nickel(II). The effect of various foreign ions is also studied. The method is applied for the estimation of micro amounts of nickel(II) in nichrome wire and steel samples and the results are compared with atomic absorption spectrophotometric method.

INTRODUCTION

Various chromophoric reagents have been reported in literature for the extractive spectrophotometric analysis of nickel(II) in recent years. Though, thiosemicarbazones are considered to be good extracting agents for the photometric determination of metals, only a few of these[1–6] are used in extractive spectrophotometric determination of nickel(II). The above methods for nickel(II) are either less sensitive or less selective. Hence, the authors tried to use benzildithiosemicarbazone (BDT) for the extractive spectrophotometric determination of nickel(II). BDT forms a yellowish orange precipitate at pH 9.0 with nickel(II) under specific conditions. This prompted them to study the versatility and use of BDT as an analytical reagent for the extractive spectrophotometric determination of nickel(II).

EXPERIMENTAL

Absorbance measurements are made on recording spectrophotometer (model Shimadzu UV-240), supplied by Shimadzun Corporation, Japan. Comparison of the results is made on Hitachi, model 170–30 atomic absorption/flame spectrophotometer, manufactured by Hitachi Ltd., Tokyo, Japan. A digital pH-meter model LI-120 (Elico) is used for measuring the pH of solutions.

Benzildithiosemicarbazone is prepared by the method reported by Reddy *et al.*[7] Stock solutions of 0.1 M BDT in 40% v/v dimethyl formamide and 0.01 M nickel(II) in double distilled water are used for the studies. The stock solution is then standardised by gravimetry using dimethylglyoxime[8]. Further dilutions are made by using double distilled water. All other chemicals are of AR grade. 1 mg/mL solutions of various interfering radicals are prepared using double distilled water.

Procedure

An aliquot of a mixture containing 10 μg of nickel(II), 4.0 mL of ammonium chloride-ammonium hydroxide buffer (pH 9.0), 2.0 mL of 0.8516×10^{-3} M BDT solution and 1.0 mL of 0.1 M lithium nitrate (salting out agent) are transferred into a 25 mL separating funnel. The contents are shaken twice with 5.0 mL of choloroform each time for 30 seconds. The organic layers are collected and dried with anhydrous sodium sulphate. The absorbance of the yellowish-orange complex (Ni-BDT) is measured at 410 nm against the reagent blank. Nickel content is computed from calibration graph.

RESULTS AND DISCUSSION

Nickel(II) reacts with BDT in ammonium chloride-ammonium hydroxide buffer of pH 9.0 and gives a yellowish-orange precipitate. The complex is extractable into chloroform. It has maximum absorption at 410 nm and is stable for 48 h. The conditions for effective extraction are established by studying the effects of various factors such as pH, solvent, reagent concentration and salting out agent, in order to develop a sensitive and rapid extractive spectrophotometric method for the determination of nickel(II) in microgram levels.

Absorption spectra: The spectrum of the complex is recorded over the wavelength range 300–500 nm against reagent blank. The complex has maximum absorption at 410 nm and the reagent has maximum absorption at 320 nm. The reagent has minimum absorbance at the maximum absorbance of the complex and is not interfering in the determination. Hence further absorbance measurements of the complex are made at 410 nm.

Effect of pH: The effect of pH on the extraction of Ni-BDT complex into the organic phase has been studied to find out the suitable pH that can be maintained in this determination. A plot between pH and absorbance shows that the extraction of the complex into organic phase increases as the pH increases from 2.0 and remains constant from 8.0 to 10.0. Again it decreases from pH 10.0 onwards. Hence, ammonium chloride–ammonium hydroxide buffer is used for further studies, considering 9.0 as optimum pH.

Choice of solvent: n-Amyl alcohol, isoamyl alcohol, n-butanol, benzene, carbon tetrachloride, chloroform, chlorobenzene, cyclohexane, cyclohexanol, MIBK, nitrobenzene and n-propyl acetate solvents are employed to extract Ni-BDT complex. Of all the solvents tried, choloroform is found to extract the complex effectively. Hence chloroform is chosen for further investigations.

Effect of reagent concentration: The effect of reagent concentration is studied by measuring absorbances at 410 nm containing different concentrations of the reagent solutions. The study reveals that a minimum of 10-fold excess of the reagent is essential for complete complexation. Hence, a tenfold molar excess of the reagent is chosen for all further studies.

Effect of salting out agent: A few salts are tried as salting out agents to increase the extraction efficiency in a single step. Of these, 1.0 mL of 0.1 M lithium nitrate is found to extract Ni-BDT complex completely into chloroform in a single step. The aqueous phase is tested using dimethylglyoxime method disclosing that no nickel is present in it.

Beer's law obedience: The absorbances of various solutions containing different amounts of nickel(II) are measured at 410 nm against reagent blank under the above established optimum conditions of study. From the graph it is observed that a linear plot passing through the origin obeys Beer's law in the range 0.1–1.6 μg/mL of nickel(II). The Ringbom plot[9] has a sigmoid shape with a linear segment at intermediate absorptance values from 0.32–0.67 and concentration values from 0.325 to 0.80 μg/mL. The molar absorptivity and Sandell's sensitivity[10] of the method are 3.617×10^4 lit mol^{-1} cm^{-1} and 0.00162 μg cm^{-2} respectively. The standard deviation is 0.0014 μg/mL, the relative standard deviation is 0.45% and the standard error is 0.00047.

Composition of the complex and instability constant: The composition of the complex is established to be 1 : 1 :: Ni(II) : BDT by Job's method[11] by studying the absorbances of various solutions containing varying volumes of equimolar (1.7032×10^{-4} M) solutions of Ni(II) and BDT at 410 nm against reagent blank. The composition of the complex is verified by molar ratio[12] and Asmus'[13] methods at 410 nm and is found to be in good agreement with Job's method. The instability constant values calculated from Asmus' method and Edmond and Birnbaum's method[14] are 5.6818×10^{-4} and 5.6850×10^{-4} respectively at room temperature.

Effect of foreign ions: Various foreign inons are examined for their effect on the extraction of 1.0 μg/mL of nickel (II). The tolerance limit is set at a change of absorbance of ± 0.02 at 410 nm.

Cations like As(III), As(V), Mg(II), Mo(VI) and W(VI) do not interfere even when present in fifty fold excess. Bi(III), Hg(II), Mn(II), Th(IV), U(VI) and Zr(II) do not have any effect up to twentyfive fold excess. Fe(III) and V(V) can be tolerated upto tenfold excess only. Ag(I) Cd(II), Co(II), Cu(II), Pb(II) and Zn(II) interfere seriously.

Anions like fluoride, chloride, bromide, tartarate, thiocyanate, thiosulphate and thiourea do not interfere even when present in fiftyfold excess. Oxalate, phosphate and pyrophosphate interfere seriously. EDTA masks Ni(II) completely.

The interference of Cu(II) and Co(II) can be eliminated by using 1.0 mL of 2% thiosulphate as a masking agent. The interference of Pb(II), Zn(II) and Cd(II) is masked with 1.0 mL of 2% thiocyanate solution. Fe(III) is masked with 1.0 mL of 1% citrate solution.

The method developed is applied for the determination of nickel (II) in nichrome wire and steel samples (BCS No. 462 and BCS No. 463) and the data is shown in Tables-1 and 2. The results obtained are compared with atomic absorption spectrophotometric method.

TABLE-1
ESTIMATION OF NICKEL IN NICHROME WIRE
Certified composition Fe = 15%, Cr = 15%, Ni = 60%

S.No.	Amount of Ni found %		Difference
	BDT method	AAS method	
1.	58.720	58.435 0	—
2.	58.940	58.6200	—
3.	59.104	58.9860	—
4.	59.120	59.0860	—
Average	58.971	58.7817	0.1893

TABLE-2
ESTIMATION OF NICKEL IN CHROMIUM STEEL

S. No	Amount of Ni found, %		Difference
	BDT Method	AAS Method	
a. BCS No. 462: Mn = 0.74%, Cr = 12.35%, Ni = 12.53%, Fe = 73.77%			
1.	12.520	12.5000	—
2.	12.550	12.5100	—
3.	12.53 0	12.5400	—
4.	12.500	12.5400	—
Average	12.525	12.5225	0.0025
b. BCS No. 463: Mn = 0.77%, Cr = 18.3%, Ni = 9.65%, Fe = 70.65%			
1.	9.600	9.62	—
2.	9.640	9.65	—
3.	9.610	9.63	—
4.	9.650	9.62	—
Average	9.625	9.63	0.005

TABLE-3
COMPARISON OF BDT WITH OTHER THIOSEMICARBAZONES FOR NICKEL(II)

Reagent	λ_{max} (nm)	pH	Molar absorptivity lit. mol^{-1} cm^{-1}	Solvent	Ref.
2,4-dihydroxy acetophenone thiosemicarbazone	385	7.5	8.2×10^3	n-butanol	3
Quinoline-2-aldehyde thiosemicarbazone	460	—	1.58×10^4	Chloroform	4
Dipyridylglyoxal dithiosemicarbazone	410	5.2	1.17×10^4	Chloroform	5
Benzildithiosemicarbazone	410	9.0	3.617×10^4	Chloroform	Present method

Conclusions

The proposed method is compared with the previously reported thiosemicarbazones[3–5] (Table-3). It is evident that BDT is the most sensitive thiosemicarbazone for the extractive spectrophotometric determination of nickel(II). Further the selectiviity of the method is improved by using proper masking agents.

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