

Spectrophotometric Determination of Nickel in Nickel-Aluminium Alloy and Palladium in Palladium-Barium Sulphate Using 6-Methyl-2-Pyridinecarboxaldehyde-4-Phenylsemicarbazone as a Complexing Reagent

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Summary: A new spectrophotometric reagent 6-methyl-2-pyridinecarboxaldehyde-4-phenylsemicarbazone has been synthesised and its colour reactions with cadmium(II), cobalt(II), cobalt(III), copper(II), nickel(II), palladium(II) and zinc(II) is studied spectrophotometrically. Their molar absorptivities for metal chelates are observed in range of $1.2-6.7 \times 10^4$ L.mole⁻¹ cm⁻¹. Reaction time, solution stability and solvent extraction from aqueous to organic phase have been examined. The complexes are easily extractable in chloroform. Each of the complex obeys the Beer's law. The method is applied for the determination of nickel in nickel-aluminium alloy and palladium in palladium-barium sulphate.

Introduction

Semicarbazones and thiosemicarbazones have attracted some interests as anti-tuberculosis agent and their metal chelates are active against certain type of tumour [1,2]. They have been also studied extensively as analytical reagents and some of useful applications have been reported for the determination of metal ions using spectrophotometer [3-6]. A number of semicarbazones have been reported as spectrophotometric reagents [7-11] for cobalt(II), nickel(II), copper(II), cadmium(II), zinc(II) and mercury(II) [12], cobalt and iron(II) [13], aluminium and zinc [14], copper [15] and iron(III) [16,17]. They have also been used as indicators in complexonitric titrations [11,12]. Reagent pyridine-2-carboxaldehyde semicarbazone [7] has been used as spectrophotometric reagent for copper(II), nickel(II) and cobalt(II) with maximum absorbances within 345-350 nm. Incorporation of phenyl group in thiosemicarbazide has been reported to have positive effect on the sensitivity of the colour reactions towards metal ions [18]. Addition of methyl group adjacent to donor nitrogen atom in

the pyridyl ring is also reported to enhance its basic properties [19]. It is therefore in the present work 6-methyl-2-pyridinecarboxaldehyde-4-phenyl-semicarbazone (MPPSC) has been prepared by the condensation of 4-phenylsemicarbazide and 6-methyl-2-pyridine carboxaldehyde and its reactions towards metal ions have been studied spectrophotometrically.

Results and Discussion

The reagent was easily prepared by simple condensation of 6-methyl-2-pyridinecarboxaldehyde and 4-phenylsemicarbazide. The product was obtained in good yield (90% theoretical). The mass spectrum indicates a prominent molecular ion peak M^+ at m/z 254 (25%). The fragment peaks are observed at m/z 162(35%) and 134 (100%) due to loss of C_6H_5NH- and $C=O$ respectively. This is followed by the loss of N_2 to obtain a peak at m/z 106(50%) corresponding to $[CH_3C_5H_3N-CH_2]^+$ fragments.

The IR of the reagent indicates bands as could be expected from its structure (Fig. 1) including prominent bands due to NH vibrations (3388 and 3210 cm^{-1}) and $\text{C}=\text{O}$ (1705 cm^{-1}).

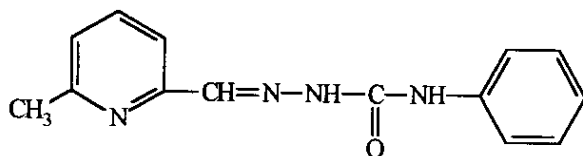


Fig. 1: Structural diagram of reagent.

The reagent reacts with cadmium(II), cobalt(II), cobalt(III), copper(II), nickel(II), palladium(II) and zinc(II) to develop coloured solutions in neutral to slightly basic media immediately, except palladium(II) which develops maximum colour within 30 min. (Table-1). The complexes are easily extractable in chloroform. The coloured solutions of copper(II), nickel(II), palladium(II) and zinc(II) complexes are stable for more than 24 hours. Cobalt(II) and bismuth(III) complexes, when extracted in chloroform indicated solution stability for two hours. The effect of pH on the colour reaction results into colour development within 4-10, but colour of cadmium(II), nickel(II), palladium(II) and zinc(II) develops maximally at pH 9, cobalt(II) and cobalt(III) at pH 8.5 and copper(II) at pH 7 (Fig. 2). Cobalt(III) shows highest molar absorptivity of $6.7 \times 10^4\text{ L. mole}^{-1}\text{ cm}^{-1}$ in chloroform (Table-1). The Beer's law for cobalt(II), cobalt(III), nickel(II) and zinc(II) was observed at final concentration of 0.1 - $1.3\text{ }\mu\text{g/mL}$, while for cadmium(II), copper(II) and palladium(II) was obeyed with 0.4 - $3.6\text{ }\mu\text{g/mL}$. The validity of calibration curves was tested by analyses of test solutions and relative % error was found within ± 0 - 1.5% .

In order to determine the composition of metal chelates, the molar ratio of the reagent MPPSc with respect to metal ion was varied within $0.5:1$, $1:1$, $2:1$, $3:1$ and $4:1$ v/v and procedure was followed as A. The absorbances were measured at their respective wavelengths of maximum absorbance against reagent blank, prepared separately, following the same procedure for each of the different composition, except addition of metal ion was omitted. The graphs were plotted by recording the change in absorbances against

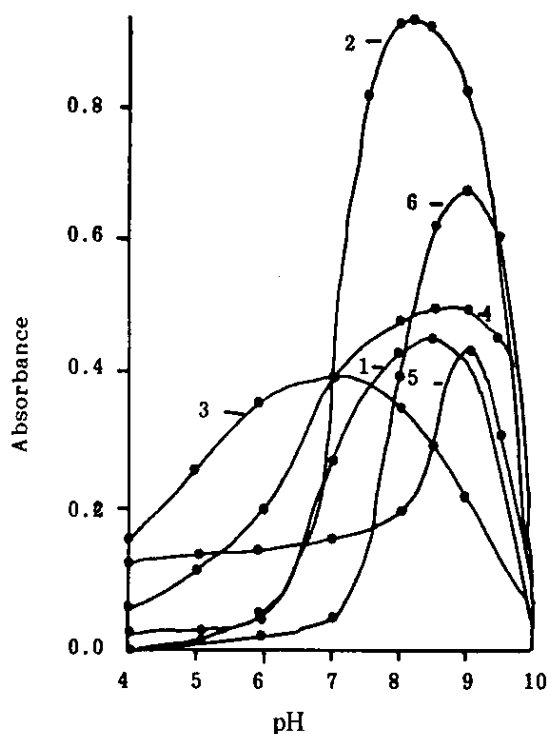


Fig. 2: Effect of pH on the absorbance of (1) cobalt(II), (2) cobalt(III), (3) copper(II), (4) nickel(II), (5) palladium(II) and (6) zinc(II) complexes: Solvent: methanol-water, concentration $1,2,3,6 = 1\text{ }\mu\text{g/mL}$. $4 = 0.5\text{ }\mu\text{g/mL}$ and $5 = 2\text{ }\mu\text{g/mL}$.

different ligand: metal ratios. It was observed that the absorbances of nickel(II) and palladium(II) reach maximum at ligand: metal ratio $2:1$ and remain constant at higher reagent concentration.

The presence of 10 ppm of tartrate, citrate, phosphate, beryllium, magnesium, barium, calcium, manganese, sodium, potassium and 2 ppm of iron, lead, oxovanadium, platinum, gold did not interfere to the determination of 2 ppm of nickel or palladium. But cadmium, bismuth, copper and zinc introduced a positive error in determination of nickel and palladium when absorbance was measured at 380 nm and 357 nm respectively. However the palladium(II) also shows an absorption band at 470 nm ($\epsilon = 4950\text{ L. mole}^{-1}\text{ cm}^{-1}$) at pH 9, which is not observed in cadmium(II), cobalt(II), cobalt(III), copper(II), nickel(II) and zinc(II) (Fig. 3). Thus, their interfering effect could

Table-1: Quantitative spectrophotometric data of colour reaction with metal ions

Metal ion	Solvent	pH of maximum colour development	λ_{max} nm	ϵ -L-mole ⁻¹ x10 ³	Solution stability
Cu(II)	Methanol-water	7	388	25.4	> 24 hr
	Chloroform		398	27.5	> 24 hr
Co(II)	Methanol-water	8.5	373	45.3	> 2hr
	Chloroform		388	56.0	> 2 hr
Co(III)	Chloroform	8.25	388	67.2	> 2 hr
Ni(II)	Methanol-water	9	380	55.3	> 24 hr
	Chloroform		394	63.4	> 24 hr
Zn(II)	Methanol-water	9	380	41.3	> 1 hr
	Chloroform		395	37.3	> 24 hr
Pd(II)	Methanol-water	9	357	27.5	> 24 hr
			470	4.95	
Cd(II)	Methanol-water	9	383	48.2	> 12 hr

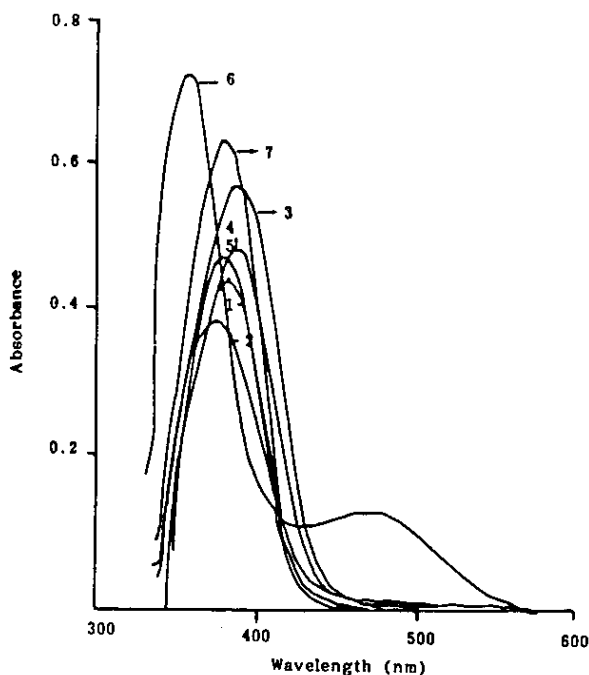


Fig. 3: Absorption spectra of (1) cadmium(II), (2) cobalt(II), (3) cobalt(III), (4) copper(II), (5) nickel(II), (6) palladium(II) and (7) zinc(II) complexes of MPPSC. Solvent: Methanol water, except (3) in chloroform. Concentrations: 2,3 and 5=0.5 $\mu\text{g/mL}$; 1 and 7=1 $\mu\text{g/mL}$; 4=1.2 $\mu\text{g/mL}$ and 6=1.4 $\mu\text{g/mL}$.

be eliminated by measuring the palladium absorbance at 470 nm, but with some loss in sensitivity.

Addition of phenyl group in semicarbazide and methyl group adjacent to donor nitrogen in pyridyl ring in ligand pyridine-2-carboxaldehyde-semicarbazone to form MPPSc proved useful with bathochromatic shift of wave-length of maximum absorbance of copper, nickel and cobalt within 373-398 nm with enhancement in colour reaction toward metal ion as compared 2-pyridinecarboxaldehyde-semicarbazone [7].

Finally, the spectrophotometric method was applied for the analysis of nickel contents in nickel-aluminium alloy and palladium in palladium barium sulphate. The nickel contents in nickel-aluminium alloy was found 50.6% with coefficient of variation (C.V) 0.5% (Expected 50%) and palladium in palladium-barium sulphate was found 4.95% with C.V. 0.2% (Expected 5%).

Experimental

Preparation of 6-methyl-2-pyridinecarboxaldehyde-4-phenyl-semicarbazone (MPPSC)

4-phenylsemicarbazide (1.247 g) dissolved in ethanol-water (1:1) (40 ml) was added to 6-methyl-2-pyridinecarboxaldehyde (1 g) in ethanol (20 ml). Glacial acetic acid (0.2 ml) was added and the mixture was refluxed for 30 minutes. The mixture was kept at 5°C overnight. The white crystalline material obtained was recrystallized from ethanol m.p. 222°C. Calculated values for $\text{C}_{14}\text{H}_{24}\text{N}_4\text{O}$ required % C=66.141, H=5.549, N=22.047 were found C=66.472, H=5.43, N=22.268.

Mass spectrum indicates M^+ at m/z (rel. intensity) 254 (25) and fragment peaks at m/z 162(35), 134 (100), 106 (50).

IR in KBr in cm^{-1} (rel.intensity) indicates bands at 3388(s), 3210(m) for NH, 1705 (vs) for C=O, 1600(s), 1590(vs), 1540(vs), 1500(m) for C=C and C=N, 1380(s) for CH_3 .

A. Analytical procedure

Metal ion solution (1-2 mL) containing (0-50 μg) was transferred to a volumetric flask (10 ml) and was added reagent solution (1 mL; 0.2% w/v in methanol) and appropriate buffer solution (2 mL). The volume was adjusted to mark with

methanol. The absorption spectrum was recorded in visible region within 700-350 nm against reagent blank in the same solvent system.

B. Solvent extraction procedure

Solution (1-2 mL) containing metal ions (0-50 µg) was transferred to separating funnel and reagent solution (1 mL; 0.2% w/v in methanol) and appropriate buffer solution (2 mL) were added. To this chloroform (5 mL) added was mixed well. The layers were allowed to separate and organic layer was collected in 10 mL volumetric flask. The extraction was repeated with chloroform (3 mL). The final volume was adjusted with chloroform.

The solutions containing (1 mg/mL) of metal ions were prepared from CdCl₂.H₂O, (CH₂COO)₂Co.4H₂O, CuSO₄.5H₂O, NiSO₄.6H₂O, PdCl₂ and Zn(CH₂COO)₂.2H₂O.

The buffer solutions at unit internals within pH range 1-10 were prepared from hydrochloric acid (0.1M), sodium chloride (1M), sodium acetate (1M), acetic acid (1M), sodium bicarbonate (1M), sodium carbonate (saturated), ammonium chloride (1M) and ammonia (37%).

The variation in absorbance with pH was investigated by adding 2 mL of different buffer solutions in pH range 1-10 by following procedure A. The absorption spectrum of the solutions were recorded after making up the volume to the mark and after lapse of different time to evaluate the solution stability of the complex.

6-methyl-2-pyridinecarboxaldehyde (Aldrich) and 4-phenylsemicarbazide (Fluka) were used. Elemental microanalysis and mass spectrum of the reagent were recorded at HEJ Research Institute of Chemistry, University of Karachi. Spectrophotometric studies were carried out on Hitachi 220 Spectrophotometer. IR in KBr was recorded on Perkin Elmer 1430 Infrared spectrophotometer.

Determination of Nickel in Nickel-Aluminium Alloy

Rany nickel (0.2508 g) (Fluka) was added hydrochloric acid (10 ml) (37%) and nitric acid (5 mL) (65%). The contents were heated gently to

near dryness and more hydrochloric acid (5 mL) was added and contents were again heated to dryness. The residue was dissolved in water and volume was adjusted to 100 mL. The solution 0.5 ml was further diluted to 50 mL. The solution (0.5 mL) was taken and procedure A was followed.

Determination of Palladium in Palladium Barium Sulphate

Palladium-barium sulphate (0.1 g) (Sigma Chemical Company) was transferred to a beaker and nitric acid 5 mL (65%) and hydrochloric acid 10 ml (37%) was added. The mixture was heated gently on hot plate to 2-3 mL. The residue was dissolved in water, filtered and volume was made up to 50 mL. The solution (0.5 mL) was taken and ascorbic acid (1 mL, 1% w/v in water) was added and procedure A was followed. The absorbance spectrum was recorded after 30 min.

Conclusion

The potential of the new reagent (MPPSC) has been investigated for the spectrophotometric determination of metal ions. The reagent is selective for palladium. The method has been applied for the determination of palladium and nickel with C.V. within ± 0.5%.

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