

TABLE 1 — ANALYTICAL AND CONDUCTANCE DATA FOR THE LIGAND AND ITS COMPLEXES

Compound	Molar conductance in EtOH (ohm ⁻¹ cm ² mole ⁻¹)	Calc. (%)			Found (%)		
		M	C	H	M	C	H
C ₁₃ H ₁₁ NOS*	—	—	68.12	4.80	—	67.82	4.69
H[Pd(C ₁₃ H ₁₀ NOS)Cl ₂] [†]	82 [‡]	26.17	38.38	2.70	26.00	37.96	2.62
[Pd(C ₁₃ H ₁₀ NOS) ₂]	0.0	18.91	55.47	3.55	18.60	55.32	3.27
[Hg(C ₁₃ H ₁₀ NOS) ₂]	0.0	30.55	47.51	3.04	30.23	47.21	2.92
[Hg(C ₁₃ H ₁₀ NOS)]	0.0	46.80	36.39	2.33	46.39	36.08	2.30
[Ag(C ₁₃ H ₁₀ NOS)]	0.0	32.11	46.44	2.97	32.00	46.06	2.88

*[S: Calc. 13.97. Found: 14.06%]. †[Cl: Calc.: 17.22. Found: 17.10%]. ‡In nitromethane.

respectively as revealed by amperometric titrations. The titrations were carried out at the plateau of the polarogram of Pd(II) chloride (−0.44 V). In the case of 1:1 Hg(I) and Ag(I) complexes and 1:2 Hg(II) complex the titrations were carried out at the plateau of the polarogram of the ligand (−0.55 V). These stoichiometries were confirmed by conductometric titrations.

Procedure for the determination — 50 ml of 1M KCl or KNO₃ were added to a known volume of standard metal ion solution and the volume made up to 100 ml by adding doubly distilled water. An aliquot (20 ml) of this solution was transferred to a polarographic cell and deaerated by bubbling pure nitrogen gas. A potential of −0.44 V in the determination of Pd(II) and −0.55 V in the determination of other metals (vs SCE) was applied, using dme as an indicator electrode. Measured volumes of the reagent solution were added and after each addition, the solution was stirred by bubbling nitrogen gas and the current was measured after an interval of a few seconds.

12-/21.3 ppm of Pd(II), 60-/100 ppm of Hg(II), 120-/200 ppm of Hg(I) and 50-/108 ppm of Ag(I) can be determined with an accuracy of ±0.5%.

Interference by the presence of external ions was studied by taking an aliquot of the metal ion solution, adding 5-10-fold excess of the foreign ion and carrying out the titrations as described above. Li(I), Na(I), K(I), Rb(I), Tl(I), Mg(II), Ca(II), Sr(II), Ba(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Pb(II), Cd(II), Mn(II), Sn(II), UO₂(II), Al(III), Cr(III), Fe(III), Tl(III), As(III), Sb(III), Bi(III), In(III), Ga(III), La(III), Ir(III), Au(III), Sn(IV), Th(IV), Zr(IV), Ce(IV), Pt(IV), Mo(VI), W(VI) do not interfere while even the traces of Ru(III) and Rh(III) interfere.

However, Pd(II), Hg(I and II) and Ag(I) interfere in each other's estimation.

Preparation of the solid complexes and their IR studies — 1:2 (metal-ligand) complexes of Hg(II) and Pd(II) and 1:1 complexes of Hg(I), Ag(I) and Pd(II) were prepared by mixing the calculated amounts of reactants containing a little excess of the latter. The precipitates were filtered, washed several times with distilled water and then dried *in vacuo* over anhydrous H₂SO₄. The separation and washings of the suspended precipitates of 1:1 Pd(II) complex were carried out by centrifuging.

The silver complex was not photosensitive. The analytical and conductance data of the complexes are given in Table 1. All the complexes, except the 1:1 Pd(II) complex, are non-electrolytes in ethanol.

The νOH band observed at 3240 cm⁻¹ in the IR spectrum of the ligand disappeared in the spectra of the palladium complexes while a very weak band at 2590 cm⁻¹ in the spectrum of the ligand due to νSH disappeared in the spectra Hg(II), Hg(I) and Ag(I) complexes. There was a shift in the position of ν—C=N— band from 1580 cm⁻¹ in the ligand to 1560 cm⁻¹ in the spectra of Pd(II) and Hg(II) complexes. This indicates the coordination of Pd(II) through oxygen and nitrogen and of Hg(II) through sulphur and nitrogen.

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N-Phenyl-N-(2-benzothiazolylazo)hydroxylamine as an Analytical Reagent for Pd(II), Cu(II) & Ni(II)

S. K. MUKERJI & N. C. SOGANI

Chemistry Department, University of Rajasthan, Jaipur

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N-Phenyl-N-(2-benzothiazolylazo)hydroxylamine has been successfully used as an analytical reagent for the gravimetric determination of Pd(II), Cu(II), and Ni(II). The solid complexes of the general formula, (C₁₃H₉N₂SO)₂M, have been isolated at pH 2.5-3.0 for Pd(II) and Cu(II) and at pH 4.5-5.5 for Ni(II). The stability constants of chelates have also been determined pH-metrically in aq. dioxane.

MUKERJI in a comparative study of the efficacy of various hydroxamic acids for the determination of metal ions, established the superiority of the title reagent¹ over N-phenyl-N-(phenylazo)-hydroxylamine and its analogues^{2,3}. The analytical

utility of the reagent for Cu(II) is described in this note. However, Pd(II) and Ni(II) were also determined by a similar procedure. The pK_a value of the reagent was determined spectrophotometrically⁴ and was found to be 11.36 ± 0.02 at 414 nm and 25°. The precipitated metal chelates have the formula $(C_{13}H_9N_4SO)_2M$, where $M = Pd(II)$, $Cu(II)$ or $Ni(II)$. The stability constants of the chelates of Cu(II), Pd(II) and Ni(II) have also been determined pH -metrically⁵ at $25^\circ \pm 0.5^\circ$ and $\mu = 0.1M$ ($NaClO_4$) in aq. dioxane.

The reagent has intramolecular hydrogen-bonded *trans*-structure as revealed by electronic and IR studies⁶. Other compounds having the same functional group are also assigned a similar structure based on NMR⁷ and IR data after ¹⁵N labelling⁸.

The solutions of metal ions, carbonate-free sodium hydroxide and buffer solutions were prepared by dissolving weighed amounts of AR grade salts, and standardized by conventional methods wherever necessary. Dioxane was purified by the conventional procedure. pH was measured on a Cambridge Bench type pH -meter.

Estimation of Cu(II) — A solution of $CuSO_4 \cdot 5H_2O$ containing 20 mg of the metal was diluted to about 150 ml, and 4 ml of 10% (w/v) sodium potassium tartrate added to it to stabilize the complex followed by 2.5 ml of 1N HCl to bring the pH between 2.5 and 3. To this solution which might also contain varying quantities of foreign ions, a 1% (w/v) ethanolic solution of the reagent was added in excess (25%). The copper complex separated out as a light-violet precipitate. It was digested, filtered, washed and dried to a constant weight at 120° to 125°.

Several determinations were made using varying amounts of the reagent under different pH conditions. Completion of the precipitation was tested both gravimetrically and by spot tests on the filtrate. The removal of excess of reagent by complete hydrolysis was indicated by the formation of a bluish-black colour on adding a drop of NaOH solution, whereas incomplete hydrolysis was indicated by a greenish-yellow colour.

It has been found that 10-30 mg of Cu(II) can be determined accurately using this reagent in the presence of eight-fold excess of Cd(II), Hg(II) and Al(III) five-fold excess of Co(II), Ni(II) and Zn(II), four-fold excess of Ti(IV), Fe(II), Fe(III), Sn(II), Bi(III) and Sb(III), and three-fold excess of Ce(IV), Mn(II) and Zr(II).

Pd(II) forms a chocolate coloured complex between pH 2.5 and 3.0 whereas Ni(II) forms a deep

yellow granular complex between pH 4.5 and 5.5. Alkali and alkaline earth metals, Pb(II), Rh(II), Ir(III), Pt(IV), Tl(IV) and La(III) did not yield a more deeply coloured precipitate with the reagent.

The metal chelates formed by the reagent are more intensely coloured, thermally stable, have more favourable conversion factors and greater stability constants (Table 1) than those of *N*-phenyl-*N*-(phenylazo)hydroxylamine. The presence of a heterocyclic benzothiazole ring may be attributed to the intensification of colours of the chelates and to a better coordinating tendency. In reproducibility of the results and specificity this reagent is superior to all other reagents used for determining Cu(II) and Pd(II).

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Solvent Extraction & Spectrophotometric Determination of Ru(III), Rh(III) & Pd(II) using 1-(2'-Pyridylazo)-2-phenanthrol

B. S. GARG & R. P. SINGH

Department of Chemistry, University of Delhi
Delhi 110007

and

A. K. RISHI

Department of Chemistry, A.R.S.D. College
New Delhi 110021

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1-(2'-Pyridylazo)-2-phenanthrol (PAP) forms chloroform soluble coloured complexes with Ru(III), Rh(III) and Pd(II) with λ_{max} 615; 580, 625; and 610, 665 nm respectively. The extinctions of the complexes remain maximum and constant in the pH range 4.7-6.1; 4.0-8.0; 3.0-7.0 for Ru(III)-PAP; Rh(III)-PAP and Pd(II)-PAP complexes respectively. The sensitivities of the colour reactions are 0.0049 at 615 nm; 0.0044 at 580 nm, 0.0048 at 625 nm; 0.016 at 610 nm, 0.013 at 665 nm respectively. A modification of the method enhances the selectivity for the determination of Ru(III).

THE use of 1-(2'-pyridylazo)-2-phenanthrol (PAP) as a good chromogenic reagent for transition metal ions¹⁻⁷ has been earlier determined by us.

TABLE 1 — STABILITY CONSTANTS (AT $\mu = 0.1M$) AND CONVERSION FACTOR OF METAL COMPLEXES

Metal	With $C_{12}H_{11}N_3O$		With $C_{13}H_{10}N_4OS$	
	Conversion factor	$\log K_1K_2$	Conversion factor	$\log K_1K_2$
Pd(II)	0.2009	22.66	0.1651	22.92
Cu(II)	0.1303	22.31	0.1055	22.63
Ni(II)	0.1215	17.50	0.0984	17.88