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 spectrophotometrically[4] 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-metrically[5] at $25° \pm 0.5°$ and $\mu = 0.1M$ (NaClO$_4$) in aq. dioxane.

The reagent has intramolecular hydrogen-bonded *trans*-structure as revealed by electronic and IR studies[6]. Other compounds having the same functional group are also assigned a similar structure based on NMR[7] and IR data after ^{15}N labelling[8].

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$_4$.5H$_2$O 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

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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 ions[1-7] 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

TABLE 1 — PHYSICO-CHEMICAL CHARACTERISTICS OF THE COMPLEXES

Characteristics	Ru-PAP	Rh-PAP	Pd-PAP
pH range	4·7-6·1	4·0-8·0	3·0-7·0
Colour	Reddish	Green	Green
λ_{max} (nm)	615	580, 625	610, 665
Range for Beer's law (ppm)	0-3·03	0-4·12	0-13·80
Sensitivity of metal, $\mu g/cm^2$ (Sandell's definition)	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
ϵ_{max}	20500 at 615 nm	23000 at 580 nm 21500 at 625 nm	6500 at 610 nm 8150 at 665 nm
Optimum range for accurate determination (ppm)	0·8-3·0	0·5-4·0	2·0-11·75
Quantity of PAP required for complete complexation	15 times	10 times	4 times
Composition (M:L)	1:2	1:2	1:2
Effect of time and temperature for full complexation	40 min on boiling water-bath and quite stable	Formed in cold, stable even on heating	Formed in cold, dissociates after 15 min but chloroform extract is quite stable
Amount of acetate buffer of appropriate pH added for 10 ml of the solution	3·0 ml	2·0 ml	2·0 ml
Mean absorbance value	0·412	0·215	0·815
Standard deviation	0·001	0·002	0·004

PAP reacts with Ru(III), Rh(III) and Pd(II) in cold to give coloured complexes. This fact has been made the basis for the spectrophotometric determination of Ru(III), Rh(III) and Pd(II) in presence of large number of metal ions.

The absorption characteristics together with various other physico-chemical constants for the three complexes are summarized in Table 1.

A stock solution ($1 \times 10^{-3}M$) of PAP was prepared in 95% (v/v) methanol and subsequent dilutions were done with methanol.

The stock solution of Ru(III), Rh(III) and Pd(II) ($1 \times 10^{-2}M$) were prepared by dissolving AR grade samples (Johnson Matthey, London) in concentrated hydrochloric acid and were standardized gravimetrically using appropriate methods. The subsequent dilutions were done with double distilled water maintaining requisite acidity of the solutions. All other reagents used were of AR quality.

Determination of Ru(III) — To an aliquot containing 8 to 30 μg of Ru(III) were added 1 ml of 0·03% PAP in methanol and 3 ml of acetate buffer of pH 5·5. The contents were heated for 50 min on boiling water-bath. On cooling the red coloured complex was extracted with 10 ml of freshly distilled chloroform. The extinction of the complex was measured at 615 nm versus chloroform blanks.

Determination of Pd(II) or Rh(III) — To an aliquot containing 5 to 40 μg of Rh(III) or 20 to 115 μg of Pd(II) were added 1 ml of 0·03% and 1 ml of 0·015% PAP in methanol for Rh(III) and Pd(II) respectively. pH were adjusted between 4·0-8·0 for Rh(III) and between 3·0 and 7·0 for Pd(II) using acetate buffers. The greenish complexes were extracted with 10 ml portions in chloroform. The extinctions were measured versus blanks at 625 and 665 nm respectively.

To study the effect of foreign ions, a series of solutions containing fixed amount of Ru(III) (2·02 ppm) or Rh(III) (1·03 ppm) or Pd(II) (10·64 ppm) were prepared in presence of number of foreign ions and the amount of metal ion determined by follow-ing the recommended procedures. The limits of tolerance for various diverse ions in ppm, in the estimation of Ru(III), Rh(III) and Pd(II) are given below:

In the estimation of Ru(III), sulphate and chloride (1000 each); bromide, iodide, fluoride, nitrate, sulphite, iodate, nitrite, calcium, barium, strontium (500 each); lead, bismuth, silver and aluminium (4 each); lanthanum (100), arsenic, auric and zirconium (5 each); thorium, chromium (50 each); platinum, mercury (10 each) do not interfere. EDTA, citrate, tartrate, and oxalate prevent the formation of complex, while thiosulphate, thiourea, thiocyanate, phosphate and borate interfere seriously. Cu(II), U(VI), Fe(II), Fe(III), Co(II), Os-(VIII), Ni(II), Cd(II), Zn(II), Pd(II), Rh(III), Ir(III), V(V) and Mn(II) interfere as they also form coloured complexes at room temperature.

Bromide, fluoride, sulphate, nitrate, iodate, calcium, strontium (500 each), mercury, iridium, ruthenium, gold, aluminium, tin, silver, titanium (6 each); chromium, thorium (50 each); lanthanum (100), manganese, gallium, bismuth, arsenic (3 each) do not interfere in the estimation of Rh(III). Serious interferences are caused by thiocyanate, iodide, thiourea, thiosulphate, phosphate, citrate, tartrate. Fe(II, III), Pd(II), Cu(II), Co(II), Cd(II), Zn(II), Ni(II), Mn(II), V(V) and U(VI) interfere due to the formation of coloured complexes. The interferences due to iron (100), aluminium (15) have been avoided using fluoride as masking agent. The interference due to mercury and lead were avoided by keeping chloroform extract for about an hour, during which mercury and lead complexes dissociate completely.

Bromide, nitrate, phosphate, calcium, barium strontium (500 each); fluoride, lanthanum (200 each); sulphate, chloride (1000 each); tartrate (40) oxalate (10), mercury (20), aluminium (10), lead, bismuth (50), tin, magnesium, platinum(IV), gold (10 each); silver, ruthenium, osmium, iridium (5 each); uranium (1·5), zinc (1·5), nickel (1·0), cadmium (1·5), manganese (1·5) do not interfere. Interferences due

to 2 ppm each of Rh(III), V(V), and Fe(III) were avoided by using tartrate (20 ppm) as masking agent. Still large amounts of iron and aluminium could be tolerated in presence of fluoride ions. For removing interferences due to zinc, cadmium and nickel, the initial pH 5·5 was raised to 8·0 and after extraction with chloroform the pH of the aqueous phase brought again to 5·5 by adding acetic acid followed by acetate buffer of pH 5·5. Added 1 ml of 0·03% PAP again. The solution was heated on a water-bath for 50 min, cooled and extracted with 10 ml portions of freshly distilled chloroform and the extinction measured at 615 nm against chloroform blanks.

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Potentiometric Estimation of Potassium Octacyanomolybdate(IV)

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Potentiometric estimation of potassium octacyanomolybdate(IV) in hydrochloric acid medium in the presence of iodine monochloride using potassium iodate as titrant is described. The method affords satisfactory and reproducible results in 6 to 7M HCl.

VERY few methods are available in literature on the estimation of octacyanomolybdates. The utility of Mn(VII), Ce(IV), Cr(VI) and Mn(III) compounds in potentiometric determination of potassium octacyanomolybdate(IV) in sulphuric acid medium have been investigated[1]. Applicability of halogen containing oxidants in the estimation of potassium octacyanomolybdate(IV) has not been explored as yet. Moreover at present no method is available for estimation of potassium octacyanomolybdate(IV) in hydrochloric acid medium. This communication deals with the potentiometric estimation of potassium octacyanomolybdate(IV) with potassium iodate in hydrochloric acid medium using iodine monochloride method.

Potassium octacyanomolybdate(IV) was synthesized by the recommended method[2] and its solution was prepared and standardized as reported earlier[3]. Iodine monochloride was prepared by the usual method[4]. The standard solution of potassium iodate
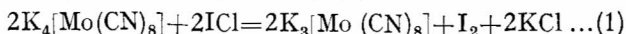
Potassium octacyano-molybdate(IV) (mmole)		Error %
Taken	Found	
0·0951	0·0950	−0·10
0·1237	0·1230	−0·57
0·1521	0·1510	−0·72
0·1807	0·1790	−0·94
0·2610	0·2580	−1·16
0·3420	0·3380	−1·16
0·5140	0·5180	+0·79
0·4285	0·4340	+1·30

was prepared by the recommended method[5]. The e.m.f. measurments were carried out on a OSAWA vernier potentiometer in conjunction with a spot galvanometer. A bright platinum foil was used as indicator electrode. A saturated calomel electrode served as reference electrode.

An aliquot of potassium octacyanomolybdate(IV) solution was placed in a titration cell and 6 ml of iodine monochloride solution was added. The requisite amount of conc. hydrochloric acid was added to the mixture so as to make the overall acidity 6M in a final volume of 50 ml. The reaction mixture was cooled and titrated potentiometrically with potassium iodate solution. The end point was located using analytical (derivative) method. The results are given in Table 1. It has been observed that an overall acidity of 6-7M with respect to HCl gives satisfactory and reproducible results. Erratic results are obtained if the acidity is less or more than 6-7M. In 2M HCl no inflection is observed.

In the present case, iodine monochloride is the real oxidant. Iodine monochloride oxidizes potassium octacyanomolybdate(IV) to octacyanomolybdate(V) according to Eq. (1).

$$2K_4[Mo(CN)_8]+2ICl=2K_3[Mo(CN)_8]+I_2+2KCl \dots(1)$$

The iodine liberated from iodine monochloride in amounts equivalent to that of octacyanomolybdate(IV) is oxidized by potassium iodate to iodine monochloride in concentrated hydrochloric acid medium.

The results are low below 5·5M HCl probably because of incomplete reaction (1) and air oxidation of octacyanomolybdate(IV). The over consumption of iodate above 7·5M HCl is perhaps due to partial decomposition of octacyanomolybdate(V) to an oxidizable Mo(V) species.

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