

Selective & Simultaneous Determinations of Cu(II) & Pd(II) with 3-(*o*-Carboxyphenyl)-1-phenyltriazeno N-Oxide & Cu(II) Determination in Ore & Alloys

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Cu(II) and Pd(II) can be quantitatively precipitated at pH 2.0-8.0 and the complexes can be directly weighed as $\text{Cu}(\text{C}_{13}\text{H}_9\text{N}_3\text{O}_3)_2\text{H}_2\text{O}$, $\text{Pd}(\text{C}_{13}\text{H}_9\text{N}_3\text{O}_3)_2\text{H}_2\text{O}$ and $\text{Pd}(\text{C}_{13}\text{H}_9\text{N}_3\text{O}_3)\text{NH}_3$ after drying at 115-20°. The methods are simple, rapid and selective. Interferences of most of the ions could be removed simply by control of pH or by using fluoride or tartrate as a masking agent.

ALTHOUGH there are numerous methods for the gravimetric determination of Cu(II), any suitable method which can determine the metal in the presence of all other ions, is wanting. Methods using thiocyanate and other reagents¹, usually suffer from interferences by some of the common ions.

Dimethylglyoxime² is widely applied for the determination of Pd(II) but the reagent has the following limitations: (i) slight solubility, (ii) the acidic (0.25*N*) solution at which the determination is carried out and (iii) the interferences of Ni(II), platinum and nitrates. Other more soluble nioximes¹ also need the absence of Ni(II).

Bidentate hydroxytriazeno³ precipitates both Cu(II) and Pd(II) quantitatively but has to be used within a narrow pH range of 2.0-3.0, with only slight excess reagent and in the absence of V(IV,V), Ag(I) and Os(IV).

As an improvement over the hydroxytriazeno, tridentate 1-(*o*-carboxyphenyl)-3-hydroxy-3-phenyltriazeno was prepared and used for analytical purposes³⁻⁵. Since the hydroxytriazenes have been shown to exist predominantly in the N-oxide form⁶ (IR), the triazeno, in a recent work⁷, has been renamed as 3-(*o*-carboxyphenyl)-1-phenyltriazeno N-oxide.

In the present paper, the above reagent has been found to be highly selective for simultaneous determination of Cu(II) and Pd(II) in their binary mixtures and in the presence of almost all other ions at a wide pH range of 2.0-8.0. This reagent has been successfully utilized for the determination of Cu(II) in ore and alloys.

Materials and Methods

The reagent was prepared as described earlier³. A 1% (w/v) solution of the reagent in 95% ethyl alcohol was used for the precipitation of the complexes.

A standard solution of Cu(II) sulphate was prepared by dissolving electrolytically pure copper in nitric acid. Palladium(II) chloride solution was prepared by dissolving the salt in boiling water

containing a few drops of hydrochloric acid. It was standardized with dimethylglyoxime.

Solutions of niobium and tantalum were prepared from their specpure oxides (Johnson-Matthey) by fusing with potassium bisulphate and dissolving the cooled clear melts in 5% tartaric acid solution and standardizing by hydroxide method. A solution of Ti(IV) was prepared from potassium tetraxy oxalate while that of Mo(VI) from ammonium molybdate. Titanium was estimated with the present reagent³ and Mo(VI) by the oxime method. Solutions of other cations were prepared from their analytical grade nitrate, chloride or sulphate salts and their strengths determined by usual procedures.

General procedure—An aliquot of Cu(II) or Pd(II) solution containing 5-15 mg of Cu(II) or Pd(II) was diluted to 150 ml with distilled water. Reagent solution containing approximately twice the amount required by stoichiometry was added with stirring (6-8 and 4-6 ml solutions per 10 mg of Cu and Pd respectively), the pH adjusted to 2.0-8.0 and the solution digested on a water-bath for 20 min until coagulation of the complex. The precipitate was filtered hot in a weighed sintered glass crucible [porosity-3 with Cu(II) complex and porosity-4 with that of Pd(II)], washed with wash liquid comprising of 200 ml boiling water, 5-6 drops conc. ammonia solution and 500 mg solid ammonium chloride and finally with distilled water. The precipitate was dried at 115-20° and weighed.

Determination of Cu(II) and Pd(II) in their binary mixture—Since thiocyanate has no masking effect on Cu(II) at any pH between 2.0 and 8.0 and on Pd(II) at pH 7.0-8.0 but masks Pd(II) completely within pH 2.0-6.5, the two metal ions have been estimated from a mixture, separating first Cu(II) complex using excess of the masking agent at any pH between 2.0 and 6.5 and then Pd(II) complex at pH 7.0-8.0.

Solution containing Cu(II) and Pd(II) was diluted with distilled water. To this solid ammonium thiocyanate (1 g) was added and the solution stirred well. Reagent solution was then added in excess

(double of what is needed for the total metal ions) with stirring, the pH adjusted to 2.0-6.5 and digested for about 20-30 min. The precipitate of Cu(II) complex was filtered hot in a G-3 sintered glass crucible, washed first with hot wash liquid and then distilled water, dried at 115-20°C and weighed.

The filtrate containing Pd(II) was quantitatively transferred to a beaker, ammonia solution was added until the pH was raised to 7.0-8.0 and the solution heated on a boiling water-bath for 30 min when a bright yellow complex appeared. The results of the determinations, carried out with different proportions of the metal ions, are shown in Table 1.

Determination of Cu(II) or Pd(II) in presence of Fe(III)—To determine Cu(II) or Pd(II) in the presence of Fe(III), it requires the presence of a large excess of fluoride to mask the Fe(III). Ammonium bifluoride (3 g) was added for every 10-100 mg of Fe(III) present in each estimation.

Aliquots of standard Cu(II) or Pd(II) and Fe(III) were mixed and diluted up to 150 ml with distilled water. To this ammonium bifluoride (3 g) and reagent solution containing approximately twice the amount required by stoichiometry were added when the pH was found to be fixed at about 3.5 where the determination was carried out.

Since the fluoride ion attacks glass in acid medium, the sintered crucibles could not be used directly and in these cases collection and washings were done on a filter paper and then the complexes transferred quantitatively to a beaker, suspended in distilled water, heated to boiling and filtered in a weighed sintered crucible, dried and weighed.

Results and Discussion

Effect of pH and the reagent on the precipitation of Cu(II) and Pd(II)—The metal ions form 1:1 complexes and are quantitatively precipitated with the reagent in the same pH range 2.0-8.0. But below and above this pH range, the results are low due to incomplete precipitation and dissolution of some of the complexes. The Cu(II) complex has the stoichiometry $Cu(C_{13}H_9N_3O_3)H_2O$ at pH 2-8 but Pd(II) forms two distinct complexes in the pH range. Palladium(II) forms a saffron coloured granular precipitate from pH 2.0 to about pH 4.5 having the composition $Pd(C_{13}H_9N_3O_3)H_2O$ which begins to change its colour to yellow on raising the pH with ammonium hydroxide solution and turns to a perfectly bright yellow colour from pH 6.0 to 8.0 corresponding to the composition $Pd(C_{13}H_9N_3O_3)NH_3$. The complexes are insoluble in water and very slightly soluble in the reaction medium at boiling temperatures. The conversion factor for the copper content is 0.1888 and those of palladium are 0.2804 and 0.2811 in the aquo and ammine complexes respectively.

For the precipitation of the complexes only a slight excess (about 25% of the theoretical) of the reagent is found to be optimum. But if desired any excess of the reagent can be used and the excess contaminating reagent can be completely and easily removed from the precipitate by washing with the hot wash liquid. At pH higher than 5.5, the excess

TABLE 1 — DETERMINATION OF Cu(II) AND Pd(II) IN A MIXTURE

Metals taken (mg)		Complexes found (mg)		Metals found (mg)	
Cu(II)	Pd(II)	Cu(II)	Pd(II)	Cu(II)	Pd(II)
10.18	11.56	53.9	41.2	10.17	11.58
30.54	5.78	162.0	20.5	30.59	5.76
5.09	34.68	26.8	123.6	5.06	34.74

reagent remains in solution as the ammonium salt and a simple hot water wash removes the reagent. However, a wash with the wash liquid is recommended in all the cases.

Effect of diverse ions—Solutions containing known amounts of Cu(II) or Pd(II) were precipitated from known amounts of foreign ions with sufficient excess of the reagent in the presence of the complexing agents whenever necessary and determined in the usual way.

250 mg of F^- , tartrate, citrate, 100 mg of AsO_4^{3-} , PO_4^{3-} , BO_3^{3-} , Mg(II), Ca(II), Sr(II), Ba(II) and 50 mg of Pt(IV) and Os(IV) do not interfere. 50 mg of As(III), Sb(III), Bi(III), Be(II), Al(III) and 100 mg of SeO_3^{2-} , TeO_4^{2-} and Sn(II) do not interfere in the presence of tartrate. 50 mg of Cr(III), Mn(II), Co(II), Ni(II), Zn(II), Cd(II), Hg(II), La(II) and 100 mg of Pb(II) and Ag(I) do not form any complex between pH 2.0 and 5.0 and as such, they do not come into interference. 50 mg of Ti(IV), Zr(IV), Hf(IV), V(IV,V), Nb(V), Ta(V), MoO_4^{2-} , WO_4^{2-} , Ce(III, IV) and 100 mg of Th(IV) and $UO_2(II)$ could be masked completely using fluoride ion. There is no interference due to 250 mg of oxalate with Cu(II) at pH 5.0-8.0 and with Pd(II) at pH 2.0-8.0. While determining in the presence of Pb(II) and Ag(I) nitric acid was used instead of hydrochloric acid. Hydrogen peroxide (5 ml, 10 vol.) has no interference. EDTA and CN^- mask both Cu(II) and Pd(II) completely and interfere. The amounts of foreign ions added are not the amounts tolerable.

Composition of the complexes—After the precipitation of the metal ions as described in the general procedure, the washed and dried complexes were analysed for metals (copper iodometrically and palladium with dimethylglyoxime) and nitrogen by Duma's method. But neither the carbon nor hydrogen content could be estimated due to the explosive nature of the compounds nor the weight loss due to the coordinated H_2O or NH_3 be known thermogravimetrically for the same reason. The analytical results agree with the compositions given in Table 2.

In support of the above compositions infrared spectra (ν_{max} in cm^{-1}) of the complexes were studied. The sharp ν_{N-H} at 3235 and the broad ν_{O-H} of the carboxyl group at 2970 observed in the pure ligand disappeared in all the complexes and the sharp asymmetric stretch of the carboxyl group at 1680 shifted to lower regions. A broad ν_{O-H} around 3400 and a deformation band at ~ 1600 were observed in

TABLE 2 — ELEMENTAL ANALYSES OF THE COMPLEXES

Complex	Metal (%)		N (%)	
	Calc.	Found	Calc.	Found
Cu(C ₁₃ H ₉ N ₃ O ₃)H ₂ O	18.88	18.95	12.48	12.41
Pd(C ₁₃ H ₉ N ₃ O ₃)H ₂ O	28.04	28.08	11.07	11.13
Pd(C ₁₃ H ₉ N ₃ O ₃)NH ₃	28.11	28.15	14.80	14.68

TABLE 3 — DETERMINATION OF CU IN ORE AND ALLOYS

Samples*	Copper certified (%)	Copper
	(including others)	found (%)
Chalcopyrite	Cu = 31.61	31.72, 31.50
	Fe = 33.59	
White metal No. 8d	Cu = 3.0	3.05, 3.03
	Sn = 86.7	
	Sb = 6.60	
	Pb = 3.26	
H.T. Brass No. 10g	Cu = 60.8	60.82, 60.71
	Zn = 32.0	
	Al = 3.34	
	Mn = 1.36	
Tin bronze	Fe = 1.56	77.85, 77.54
	Cu = 77.69	
	Pb = 6.10	
	Sn = 5.20	
	Zn = 4.5	
German silver	Cu = 62.52	62.38, 62.66
	Ni = 20.35	
	Zn = 16.79	
Monel metal	Cu = 63.8	63.85, 63.95
	Ni = 35.5	
	Fe = 0.65	

*The chalcopyrite ore in the concentrated form, tin bronze, german silver and the Monel metal were kindly supplied by the Metallurgy Department, Jadavpur University, Calcutta 700032; white metal and HT brass were the analysed samples of British Chemical Standard.

both the aquo complexes showing the presence of H₂O molecule. In Pd(II) ammine complex, all the 4 bands usually found in ammine complexes⁸, were observed at ~3200, ~1600, 1300 and 870.

The Cu(II) complex is paramagnetic (1e) and those of Pd(II) diamagnetic but in the absence of any X-ray analysis, no structure could be assigned to them.

Determination of Copper in Chalcopyrite Ore and in White Metal, Brass, Bronze, German Silver and Monel Metal

Chalcopyrite — Accurately weighed ore (1 g) was dissolved in dil. nitric acid and to this was added 3 ml conc. sulphuric acid and heated on a water-bath till the evolution of sulphur dioxide was complete. The content was cooled, filtered in a 250 ml volumetric flask and the volume made up to the mark. An aliquot of 10 ml of this solution was taken and estimated for Cu(II) at pH 3.5 according to the procedure described earlier, adding ammonium bifluoride (3 g) to mask Fe(III) present.

White metal — Accurately weighed alloy (200 mg) was dissolved in dil. nitric acid (10 ml) and heated on a water-bath until the volume was reduced to 2-3 ml. To this 50 ml hot distilled water was added and digested for a few minutes and the white residue of metastannic acid filtered off using a Whatman No. 42 filter paper. To the filtrate was added 10 ml reagent solution (pH was found to be in between 2 and 3) and the copper content estimated according to the general procedure.

Brass, bronze, monel metal and german silver — An accurately weighed amount of the alloy was dissolved in a minimum volume of dilute nitric acid and filtered in a 250 ml volumetric flask, diluted up to the mark and Cu(II) estimated according to the general procedure taking 10 ml aliquot at pH 2.0-5.0.

The results of the determinations in the different samples are recorded in Table 3.

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