

Extractive Photometric Simultaneous Determination of Copper(II) and Gold(III) with Syn-Phenyl-alpha-Pyridyl Ketoxime : Analysis of Gold-plating Bath

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A spectrophotometric method is developed for the simultaneous estimation of gold and copper in alloys or plating bath. Syn-phenyl-alpha-pyridyl ketoxime forms complexes with gold(III) and copper(II) at pH 9, which are extractable in chloroform. A method based on the measurements of absorbances at 455 and 550 nm is presented. The composition of an unknown mixture of these elements or the plating bath solution can be determined by solving the following simultaneous equations.

$$\begin{aligned} [\text{Au}] \times 10^4 &= 1.164 \times A_{455} - 1.727 \times A_{550} \\ [\text{Cu}] \times 10^4 &= 4.657 \times A_{550} - 0.270 \times A_{455} \end{aligned}$$

The interference due to CN^- , pyridine, thiourea etc. in the determination of the composition of the plating bath can be eliminated by using formaldehyde. The standard deviation of the method is $\pm 0.71\%$ for Au and $\pm 0.63\%$ for Cu.

SEVERAL formulae of the plating baths for electro-deposition of red to pink gold-copper alloys are reported in "Canning Hand-book on electroplating" and in other literature on electroplating¹⁻⁵. A cyanide bath containing 10 parts of gold and 6 parts of copper, thiourea, pyridine and ammonium sulphate gives a glossy pink deposit of 18 carat gold¹. A deposit of 80% gold is obtained from 4 parts of gold and 5 parts of copper present in a bath containing cyanide, EDTA, tartar emetic and phosphate at pH 5.3². A bath containing gold and copper in 1 : 2 proportion and also cyanide and sulphite gives a thick bright alloy coating at pH 7.3³. Whereas a bath containing sulphites, ethylenediamine, acetates, borax and arsenic or antimony as a brightner are recommended for deposition of gold-copper alloy containing 67 to 96% gold⁴. Co-deposition of gold, copper and silver gives range of shades of red to rose. It is stated that "the colour of the rose gilding will vary with the temperature and voltage as well as with the proportions of gold, copper and silver in the bath. No quantities can be given because conception of what is a 'rose colour' differs"⁵. The successful control on quality of the deposit and also the composition and colour depend on the maintenance of the composition of the bath and other conditions such as current density, pH etc. Hence the determination of the composition of the plating bath is analytically important problem of an industrial significance.

The literature survey indicated that the copper content can be found out polarographically⁶, potentiometrically with salicylaldoxime⁷, complexometrically with EDTA using murexide as an indicator^{8,9}, colorimetrically with EDTA at 740 nm¹⁰ or volumetrically with thiosulphate¹¹. The gold content of the bath can be out by polarographic method¹² assay as

metallic gold^{13,15,20}, amalgam formation of gold and further colorimetric method^{14,24} spectrophotometrically at 239 nm¹⁶, atomic absorption analysis^{17,21,22} and titrimetry²³. Gold can also be determined in cyanide waste^{25,26} and jewellery by using ring oven technique²⁷.

The literature procedures for determination of both copper and gold are with sodium diethyldithiocarbamate²⁹ and stannous chloride method³⁰. Grassby, Gill and Bradford recommended wet ashing, followed by precipitation of gold by hydrogen peroxide and colorimetric determination of copper with bis-cyclohexanone oxalyldihydrazone or polarographically¹⁸. Becka and Tischer recommended titrimetric methods consisting of use of chlorine, EDTA, glycine, HCl, addition of KI and titration of gold at 60° with thiosulphate and of sulphocyanide, hydrochloric acid, KI and titration with thiosulphate¹⁹. This paper describes a spectrophotometric method by using syn-phenyl-alpha-pyridyl ketoxime (HPPK). The selection of HPPK is based on the fact that both gold and copper form complexes at pH 9.0 which are extractable in chloroform and that their absorbances are additive. The method is quick requiring less time than the conventional methods.

Experimental

The spectral measurements over the visible region were done on a Carl Zeiss Spectrophotometer Spekol with 10.01 mm matched pair of glass cuvettes. For measurements of pH values of the solutions a Philips pH meter PR-9405 L was used with Philips PV-9014 combination electrode. The pH meter was standardized by using phthalate and borax buffers.

Reagent : The reagent syn-phenyl-alpha-pyridyl ketoxime (HPPK) was synthesized from 2-Benzoyl pyridine²⁸. An ethanolic solution (1%) (i. e. $1.515 \times 10^{-2} M$) was used.

For Correspondence

Standard Cu(II) solution, containing 100 γ /ml. Cu was prepared by dissolving 100 mg of A. R. copper wire in 1 ml concentrated nitric acid and evaporating almost to dryness and then with 1 ml concentrated sulphuric acid to give white fumes. It was then made upto 100 ml and was standardized by sodium diethyl-dithiocarbamate²⁹.

Pure gold metal (63.28 mg) was dissolved in aqua regia (3 ml A. R. HCl+1 ml A. R. HNO₃), was boiled to decompose all nitric acid and the resultant gold chloride was diluted to 100 ml. It was then standardized by stannous chloride method³⁰.

pH values of the solutions were adjusted by using 1 M sodium carbonate.

Redistilled chloroform (BDH) and glass distilled conductivity water were used throughout.

Procedure Dilute the plating bath 100 fold and transfer an aliquot of the solution containing 100 μ g Au and 60 μ g Cu in a beaker, to which add 2 ml formaldehyde (AR. BDH). Warm and then cool the solution. Add 10 ml water and 2 ml HPPK and adjust the pH to 9 with sodium carbonate. Transfer this solution to a 100 ml separatory funnel. Carry out extraction with chloroform as given earlier. Measure the absorbance of the lower organic layer of chloroform at 550 nm and 455 nm. Calculate the concentrations of gold and copper from the appropriate simultaneous equations.

Results and Discussion

The absorption spectra of the chloroform extracts of gold and copper complexes of HPPK at pH 9.0 are given in Fig. 1. The reagent does not absorb in the visible region. The spectroscopic properties of the complexes are summarized in Table 1.

TABLE 1—SPECTROSCOPIC PROPERTIES OF THE COMPLEXES

HPPK Complex of	λ_{max}	Wavelength chosen for measurement	ϵ_{550}	ϵ_{455}^a	Solubility
Au (III)	455	455	544	9397	Two extractions in chloroform are sufficient to extract the complexes completely.
Cu (II)	475	550	2349	3485	

Analysis of a binary alloy : For the analysis of a gold-copper alloy, dissolve a weighed quantity of an alloy in aqua regia and further boil with conc. hydrochloric acid and evaporate to dryness on a steam bath and dissolve in water. If silver is present, filter off as chloride and wash with water. Make the filtrate and washings upto the mark in a volumetric flask.

Dilute an aliquot containing upto 80 μ g of gold and 60 μ g of Cu with 10 ml of water and adjust the pH to 9. Transfer it then to a separatory funnel. Add 3 ml of reagent and 3 ml chloroform and extract. Use one more portion of 3 ml. chloroform for complete extraction of the complexes and finally make it upto the mark in 10 ml volumetric flask. Measure the absorbance of the solution at 550 nm and 455 nm. Find out the concentrations of gold and copper from the appropriate simultaneous equations. If the silver is present in an alloy, determine its percentage by difference.

Analysis of plating bath :

Preparation of plating bath solution : Plating bath contains 10 parts Au as Au(CN)₃, 6 parts Cu as potassium cuprocyanate, 5 parts thiourea, 2 parts pyridine and 20 g/l. (NH₄)₂SO₄¹. It gives pink coloured alloy deposit on a piece of silver foil.

Analysis : The plating bath can be analysed at any stage to check the gold and copper content by using the procedure given below.

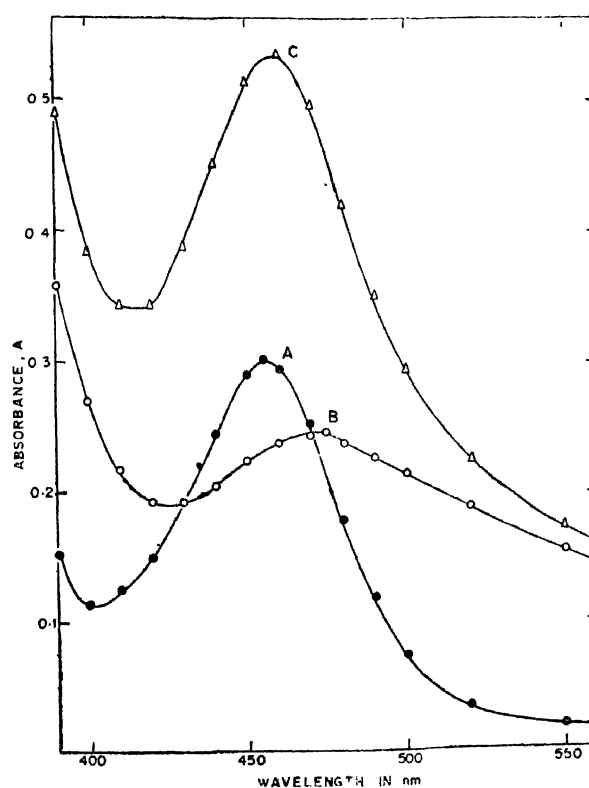


Fig. 1. Absorption spectra of (A) —●—●—●—●— gold complex $3.214 \times 10^{-5} M$ (B) ○—○—○—○— copper complex $7.874 \times 10^{-5} M$ and (C) △—△—△— mixture of gold and copper complexes. (chloroform extracts)

As the complexes can be extracted in chloroform at pH 9.0 quantitatively and as the absorbances are additive, the relation

$$A_{455} = \epsilon_{455}^{Au} [Au] + \epsilon_{455}^{Cu} [Cu]$$

$$A_{550} = \epsilon_{550}^{Au} [Au] + \epsilon_{550}^{Cu} [Cu]$$

can be used to develop simultaneous equations

$$[Au] \times 10^4 = 1.164 \times A_{455} - 1.727 \times A_{550}$$

$$[Cu] \times 10^4 = 4.657 \times A_{550} - 0.270 \times A_{455}$$

which can be used to get the composition of the alloy or the plating bath solution. Table 2 summarizes the results of analyses of several synthetic mixtures.

dehyde reacts with cyanide to give formaldehyde cyanohydrin and its decomposition products.³¹

Tables 3 and 4 summarizes the results of the alloys and plating bath solution.

Interferences : Platinum metals, nickel, cobalt or iron must be absent, as these elements seriously interfere. Sulphites and several organic constituents of the plating bath interfere but these can be eliminated by decomposition prior to extraction.

TABLE 2—ANALYSES OF SYNTHETIC MIXTURES

Sample	Quantity taken		Quantity found		Relative standard deviation, %	
	Au(III) × 10 ⁻⁵ M	Cu(II) × 10 ⁻⁵ M	Au(III) × 10 ⁻⁵ M	Cu(II) × 10 ⁻⁵ M	Au	Cu
1.	3.21	1.65	3.19	1.65	-0.71	+0.63
2.	3.21	6.60	3.20	6.58	-0.13	+0.03
3.	2.41	3.30	2.40	3.28	-0.07	-0.45
4.	3.21	4.95	3.20	5.00	-0.25	+0.03
5.	0.80	6.60	0.81	6.54	+0.59	-0.54
6.	4.02	6.60	4.02	6.54	+0.29	-0.51

TABLE 3—ANALYSES OF Au+Cu ALLOYS

Sample	Composition of the Alloys.	Wt. of the Sample in mg.	Expected		Found		%			
			mg	Au %	mg	Cu %	mg	%		
A	70% Au 30% Cu	12.50	8.75	70.00	3.75	30.00	8.58	68.64	3.68	29.44
B	60% Au 40% Cu	10.75	6.45	60.00	4.30	40.00	6.39	59.44	4.25	39.54
C	55% Au 45% Cu	8.24	4.53	55.00	3.71	45.00	4.40	53.43	3.61	43.78
D	50% Au 50% Cu	6.70	3.35	50.00	3.35	50.00	3.23	48.21	3.30	49.26

TABLE 4—ANALYSIS OF A PLATING BATH

Plating Bath	Volume of the Plating Bath Solution	Quantity expected		Quantity Found	
		Au	Cu	Au	Cu
Plating Bath prepared according to ref. 1.	1.0 ml.	100.00 μg	60.00 μg	98.92 μg	59.23 μg

Analyses were carried out in triplicate for each mixture and the standard deviation of the above set of observations is ±0.71 for Au(III) and ±0.63 for Cu(II).

The plating bath contains CN, pyridine and thiourea. The interference due to these, can be removed by using formaldehyde. Gold and copper ions are released from their cyanide complexes when formal-

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