

Spectrophotometric Determination of Palladium(II) & Copper(II) with *p*-Anisaldehyde Thiosemicarbazone: Analysis of Alloys & Minerals

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Received 7 December 1982; revised and accepted 5 April 1983

p-Anisaldehyde thiosemicarbazone is proposed as a new reagent for the spectrophotometric determination of Pd(II) and Cu(II). The reagent forms a 1:1 yellow coloured complex with Pd(II) (pH 2.9-4.3) and 1:2 orange yellow coloured complex with Cu(II) (0.1-0.6 *M* NaOH) instantaneously at room temperature. The Pd(II)-PAT and Cu(II)-PAT complexes exhibit maximum absorbances at 366-375 nm and 398-406 nm respectively. Beer's law is obeyed over the range 0.06-3.3 ppm of Pd(II) and 0.1-10 ppm of Cu(II). Sandell's sensitivity is determined to be 4.9 ng cm⁻² for Pd(II) and 10.4 ng cm⁻² for Cu(II). The efficacy of the proposed methods is demonstrated by the analysis of alloys and mineral.

In our earlier paper¹, *p*-anisaldehyde thiosemicarbazone (PAT) was proposed for the spectrophotometric determination of nickel(II). The efficacy of PAT as a sensitive reagent for the spectrophotometric determination of palladium(II) and copper(II) has now been investigated and the results are reported in this note.

Materials and Methods

All the chemicals used were of AR grade. Palladium chloride (Johnson Matthey Chemicals) was dissolved in 0.1 *M* hydrochloric acid and this stock solution standardised gravimetrically by the dimethylglyoxime method². Cupric chloride (AR) was dissolved in distilled water and this stock solution standardised gravimetrically by the thiocyanate method³. A 0.3% solution of PAT was prepared in 90% ethanol (v/v). Solutions of diverse ions of suitable concentrations were prepared using analytical grade reagents. Walpole buffers of pH values ranging from 0.65-5.2 were prepared by mixing 1 *M* hydrochloric acid and 1 *M* sodium acetate solutions.

Beckman spectrophotometer model DB with 1 cm silica cells was used for absorbance measurements. pH of the solutions were measured (vs SCE) with a pH meter model L1-10 (M/s Electronic and Industrial Instruments, Hyderabad).

Determination of palladium(II) or copper(II)—To aliquots of stock solutions containing 1.5-82.5 µg of palladium(II) or 0.25-250 µg of copper(II) were added 5 ml of hydrochloric acid-sodium acetate buffer (pH 3.95), 5 ml of ethanol for palladium(II) or 1.5 ml of 5 *M* sodium hydroxide + 7.5 ml of ethanol for copper(II) and 5 ml of 0.3% PAT solution, and diluted to 25 ml with doubly distilled water, mixed well and the

absorbances were measured at 370 nm for palladium(II) solutions and at 402 nm for copper(II) solutions against the corresponding reagent blank. The amount of palladium(II) or copper(II) was then deduced from the calibration graph.

Determination of copper in brass, bronze and copper-nickel alloy—Copper alloy (approximately 0.1 g) was treated with conc. nitric acid (3 ml) and the mixture heated gently. After the alloy had dissolved, excess HNO₃ was destroyed by adding conc. HCl (6 ml) in 2 ml portions and evaporating to dryness after each addition of HCl. The residue was dissolved in doubly distilled water and the volume made upto 500 ml with doubly distilled water. Suitable aliquots of this solution were used for reaction with PAT as described in the procedure for the determination of copper(II). The absorbance was measured at 402 nm and the copper concentration was read from the calibration graph. The results are given in Table 3.

Results and Discussion

PAT forms an yellow coloured complex with palladium(II) in hydrochloric acid, sulphuric acid or acetic acid or Walpole buffer medium and an orange yellow coloured complex with copper(II) in the alkaline medium, instantaneously at room temperature (27°C). However, Pd(II)-PAT complex is stable only in Walpole buffer medium for a period of 45 min, while Cu(II)-PAT complex is stable only in alkaline medium for a period of 1 hr. Hence the determination of Pd(II) and Cu(II) are recommended only in Walpole buffer and alkaline medium respectively. The spectral characteristics of palladium(II)-PAT and copper(II)-PAT complexes are summarised in Table 1. The effective ethanolic concentration is found to be 32-72%

(v/v) for Pd(II)-PAT complex and 40-72% (v/v) for Cu(II)-PAT complex. Below these ranges, turbidity is obtained and above 72% ethanol maximum absorbance is not obtained. For the purposes of

determination of Pd(II) and Cu(II), 40% and 50% ethanolic media have been selected. Excess PAT (61-fold for Pd and 9-fold for Cu) is needed for the full development of the colour intensity. There is no appreciable change in the absorbance of the two complexes if the order of addition of the reagents is varied. Errors are in general about $\pm 2\%$.

Job's method of continuous variation⁴ and mole ratio⁵ method indicated 1:1 and 1:2 stoichiometries for Pd(II)-PAT and Cu(II)-PAT complexes, the apparent stability constants (log K) being 5.7 and 5.62 respectively. The cationic nature of the complexes was indicated by ion-exchange experiment on Dowex 50W- $\times 8$ cation exchanges resin. The colours of the complexes were retained by resin and the eluents were colourless. Reverse was found to be true with an anion exchange resin.

In order to assess the possible analytical applications of the Pd(II)-PAT complex or Cu(II)-PAT complex, the effect of some foreign ions that often

Table 1—Spectral Data for *p*-Anisaldehyde Thiosemicarbazone Complexes of Palladium(II) and Copper(II)

Characteristics	Pd(II)-PAT	Cu(II)-PAT
$\lambda_{\max}$ (nm)	370	402
Optimum (pH/M NaOH)	2.9-4.3	0.1-0.75 M NaOH
Colour	Yellow	Orange Yellow
Beer's law, ppm	0.06-3.3	0.1-10.0
Optimum concentration range on the basis of Beer's law, ppm	0.1-3.0	0.2-9.8
Molar absorptivity (litre mol ⁻¹ cm ⁻¹)	2.16×10^4	6.1×10^3
Sandell's sensitivity, ngcm ⁻²	4.9	10.4
Constant absorbance of the complex in the temperature range (°C)	7-50	5-60

Table 2—Interference of Foreign Ions in the Determination of Palladium and Copper

[Interference studies were carried out for 2 $\mu\text{g/ml}$ or 4 $\mu\text{g/ml}$ of Pd(II) and Cu(II) Mixtures]

Ion added	Tolerance limit ($\mu\text{g/ml}$) for		Ion added	Tolerance limit ($\mu\text{g/ml}$) for	
	Pd(II)	Cu(II)		Pd(II)	Cu(II)
Cu(II)	0.3	—	Au(III)	3	16
Cu(II)	0.5*	—	Au(III)	18†	38‡
Zn(II)	4000	56	Sb(III)	46	280
Ba(II)	4000	15	Sn(II)	146	243
Cd(II)	3200	15	Sn(IV)	201	129
Fe(III)	5	18	Cr(III)	83	102
Co(II)	3400	4	SO ₄ ²⁻	7200	9600
Co(II)	—	26††	NO ₃ ⁻	7200	8400
Ni(II)	1300	84	PO ₄ ³⁻	600	2400
Al(III)	8	56	Thiosulphate	600	840
Al(III)	45†	—	Oxalate	120	4000
As(III)	800	126	Citrate	1700	7200
Pb(II)	3600	200	Tartrate	3200	580
Mn(II)	406	21	EDTA	310	320
Mg(II)	4000	90	F ⁻	680	6400
W(VI)	28	72	Cl ⁻	6800	5800
Mo(VI)	19	180	Br ⁻	6800	9600
Mo(VI)	38†	—	I ⁻	400	720
Ru(III)	2	03	Acetate	1800	9600
Ru(III)	3*	—			
Rh(III)	8	6			
Rh(III)	12†	26†			
Os(VI)	1.5	2			
Os(VI)	20*	11*			
Os(VIII)	18	7			
Os(VIII)	—	33†			
Ir(III)	6	34			
Ir(III)	18†	—			
Pt(IV)	5	13			
Pt(IV)	18*	41†			
Pd(II)	—	10			

*Citrate; †Tartrate; ‡Phosphate; ††Fluoride.

Table 3—Determination of Copper in Its Alloys

Sample (Certified composition, %)	Copper content (ppm)	
	Certified value	Found*
Brass (Cu, 70.03; Zn, 29.97)	2.0	1.98
	4.0	4.05
	6.0	5.95
	8.0	8.06
	10.0	10.10
Bronze (Cu, 89.62; Sn 10.38)	1.0	1.01
	2.0	2.02
	4.0	3.95
	7.0	7.10
	9.0	8.85
Copper-nickel alloy (Cu, 74.85; Ni, 25.15)	3.0	3.00
	4.5	4.44
	6.0	5.95
	7.5	7.55
	9.0	9.00

*Average of five determinations

accompany palladium or copper was examined. For these studies different amounts of ionic species were added to the sample solution containing 50 μg of Pd(II) or 100 μg of Cu(II). The results presented in Table 2 show that many cations and anions do not interfere. Interference from platinum metals and iron can be

reduced by using tartrate, phosphate, fluoride and citrate as masking agents. The amounts of the masking agents added are equal to the tolerance limit indicated in Table 2.

The results in Table 3 show that zinc, tin and nickel in the alloys of copper do not interfere in the determination of copper. The values obtained with PAT compare favourably with the certified values for copper. Since jewellery alloy (95.5% Pd and 4.5% Cu), palladium-gold (50% palladium), steel backed copper-lead automotive bearings (2% Cu, 8% Sn and 90% lead), high tin babbitts (8.5% Cu, 87.5% Sn and 4% Sb) and pewter (3% Cu, 90% Sn and 7% Sb) and the mineral stibiopalladinite (75% Pd and 25% Sb) were not available for analysis, synthetic mixtures containing the metal ions corresponding to the compositions of alloys and the mineral were prepared. The palladium and copper contents were determined following the standard procedure. The results obtained were quite satisfactory.

References

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