

Extractive Spectrophotometry of Palladium(II) and Ruthenium(III) with Phenanthraquinone Monothiosemicarbazone

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A procedure is described for the extractive spectrophotometric determination of palladium and ruthenium with phenanthraquinone monothiosemicarbazone. Palladium forms a 1:2 complex which is soluble in chloroform and has an absorption maximum at 600 nm when extracted from 1M acetic acid solution. Ruthenium forms a 1:2 complex which is soluble in chloroform and has an absorption maximum at 660 nm when extracted from 2M acetic acid solution. Both complexes are stable and conform to Beer's Lambert law. The molar absorptivity (and Sandell's sensitivity) for palladium and ruthenium are 2.2×10^4 l. mole⁻¹ cm⁻¹ (0.04 µg/cm²) and 4.74×10^4 l. mole⁻¹ cm⁻¹ (0.02 µg/cm²) respectively. The proposed method is suitable for detection and determination of palladium and ruthenium in the presence of associated metal ions. The results of the analysis of synthetic mixtures are reported.

PHENANTHRAQUINONE monothiosemicarbazone (PQMT) has been used for the spectrophotometric determination of traces of copper in ferrous and nonferrous alloys¹. Extension of this study revealed that PQMT could be used for the extractive spectrophotometric determination of palladium(II) and ruthenium(III).

Experimental

Apparatus and reagents: A Zeiss spectrophotometer (Jena) with 1 cm silica cell was used for the absorbance measurements. The stock solutions of palladium ($1 \times 10^{-2} M$) and ruthenium ($1.68 \times 10^{-2} M$) were prepared by dissolving analytical grade palladium chloride and ruthenium trichloride (Johnson Matthey, London) and standardized by known methods. The solutions of lower concentration were prepared by appropriate dilution of the stock solutions.

Phenanthraquinone monothiosemicarbazone (PQMT) was synthesized by the reported method² and 0.01% (w/v) or 0.06% solution in dimethyl formamide (DMF) was used for palladium and ruthenium estimations respectively. All other chemicals were of analytical grade.

Procedure: A 10 ml aliquot of solution containing 25 to 180 µg of palladium, 2 ml of 0.01% PQMT in DMF and acetic acid (1M) is taken and extracted for 15 sec with two 5 ml portions of chloroform. The organic phase is separated, dried with anhydrous sodium sulphate and the absorbance is measured at 600 nm against the reagent blank prepared in the same manner. Similarly, 10 ml aliquot of solution containing 10 to 150 µg of ruthenium, 4 ml of 0.06% PQMT in DMF and acetic acid (2M) is taken. The mixture is heated for 10 min in a boiling water bath, cooled and extracted for 15 sec

with two 5 ml portions of chloroform. The chloroform layer is separated, dried with anhydrous sodium sulphate and the absorbance of the green coloured complex is measured at 660 nm against the reagent blank prepared analogously. The palladium and ruthenium contents are computed from the calibration graph.

Results and Discussion

The extraction behaviour of palladium and ruthenium from various acidic media is shown in Table 1. Pd-PQMT complex quantitatively extracts into chloroform from 1-3 M acetic acid, hydrochloric acid and perchloric acid solutions. Ru-PQMT complex, however, extracts from 2-3 M acetic acid, 1-3 M hydrochloric acid and 1-2 M

TABLE 1—EXTRACTION OF PALLADIUM(II) AND RUTHENIUM(III) COMPLEXES AS A FUNCTION OF ACIDITY

Acid		%Extraction		Distribution ratio D	
		Pd	Ru	Pd	Ru
CH ₃ COOH	0.25M	87.7	80.0	7.10	4.0
	0.50M	95.0	87.5	19.23	7.0
	1.00M	100	92.3	∞	13.0
	2-3M	100	100	∞	∞
	4.00M	82.7	81.7	4.8	5.6
HCl	0.5M	80.0	85.6	4.0	6.0
	1-3M	100	100	∞	∞
	4.0M	83.4	88.9	5.0	8.1
HClO ₄	0.5M	76.0	83.4	3.1	5.0
	1-2M	100	100	∞	∞
	3.0M	100	96.4	∞	26.7
H ₂ SO ₄	4.0M	92.0	90.0	11.5	9.0
	0.5M	52.4	40.0	1.1	0.67
	1.0M	56.0	45.2	1.27	0.83
	2-3M	60.0	37.3	1.5	0.60
HNO ₃	0.5M	80.1	15.3	0.4	0.19
	1.0M	88.2	20.0	0.61	0.25
	2-3M	84.0	17.0	0.50	0.20

perchloric acid solutions. Nitric acid and sulphuric acid media are unsuitable for extraction of both palladium and ruthenium. The extraction period for quantitative extraction of both Pd and Ru is only 15 sec. The extracted palladium and ruthenium complexes absorb at 600 and 660 nm respectively (Fig. 1) and adheres to Beer's law over the concentration range of 25 to 180 μg of Pd and 10-150 μg of Ru/10 ml of organic phase. The molar absorptivity and Sandell's sensitivity for Pd-PQMT complex is 2.2×10^3 l. mole⁻¹ cm⁻¹ and 0.04 $\mu\text{g}/\text{cm}^2$ respectively. For Ru-PQMT complex, the molar absorptivity and Sandell's sensitivity is found to be 4.74×10^3 l. mole⁻¹ cm⁻¹ and 0.02 $\mu\text{g}/\text{cm}^2$ respectively. The colour of the complexes is stable for 24 hr. 2 ml of 0.01% PQMT solution and 4 ml of 0.06% PQMT solution in DMF is enough for quantitative extraction of Pd and Ru respectively. Excess of reagent had no adverse effect on the intensity of the colour.

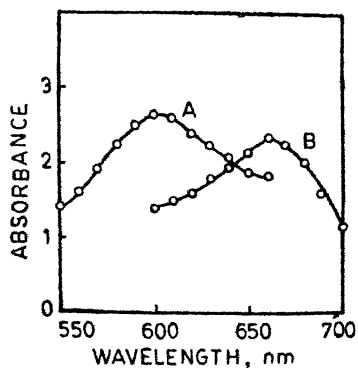


Fig. 1. Absorption spectra of :
(A) Palladium complex and
(B) Ruthenium complex.

The solubility of the palladium and ruthenium complexes was tried in different organic solvents. Results in Table 2 show that the only effective solvents for palladium and ruthenium extractions are chloroform, methyl isobutyl ketone (MIBK), isoamyl alcohol and ethyl acetate.

TABLE 2—EXTRACTION OF Pd-PQMT AND Ru-PQMT COMPLEXES WITH VARIOUS ORGANIC SOLVENTS FROM 2M ACETIC ACID SOLUTION

Solvent	Extraction %	
	Pd	Ru
Carbontetrachloride	0	0
Benzene	52	50
Toluene	48	38
Xylene	45	40
Chloroform	100	100
Isoamyl alcohol	100	100
MIBK	100	100
Ethyl acetate	100	100

Effect of foreign ions : A number of representative ions were tested for their interference in the

determination of palladium (100 μg) and ruthenium (50 μg) by the recommended procedure. The tolerance limit was set at the amount required to cause < 1% error in metal determination. In palladium estimation, ions tolerated are monovalent silver (5 mg), bivalent copper (5 mg), cobalt (5 mg), zinc (5 mg), manganese (5 mg), tin (2 mg), nickel (5 mg), mercury (2.5 mg), trivalent aluminium (2 mg), bismuth (100 μg), chromium (2.5 mg), gold (2 mg), antimony (1 mg), ruthenium (3 mg), rhodium (3 mg), iridium (250 μg), iron (2.5 mg), lanthanum (2 mg), quadrivalent tin (150 μg), platinum (3 mg), thorium (250 μg), selenium (500 μg), tellurium (100 μg), pentavalent vanadium (2 mg), hexavalent uranium (5 mg), chromium (5 mg), osmium (2.5 mg), tartarate (3 mg), citrate (4 mg), ascorbate (5 mg), EDTA (5 mg), phosphate (5 mg), fluoride (5 mg), bromide (5 mg) and chloride (5 mg). Lead (500 μg) requires masking with EDTA. Notable interference is cadmium. Similarly in ruthenium extractions, tolerable ions include Ag (500 μg), Mn (600 μg), Sn (1000 μg), Ni (1500 μg), Pd (100 μg), Pb (1500 μg), Al (2000 μg), Cr (300 μg), Au (500 μg), Sb (600 μg), Rh (300 μg), Ir (200 μg), La (2500 μg), Sn(IV) (500 μg), Pt (1500 μg), Th (100 μg), Se (300 μg), Te (500 μg), V (500 μg), U (500 μg), Os (250 μg), tartarate (1000 μg), citrate (1000 μg), ascorbate (2500 μg), EDTA (1000 μg), phosphate (800 μg), fluoride (5000 μg), bromide (1500 μg) and chloride (2000 μg). Mercury (1000 μg) and Iron (500 μg) require masking with fluoride. 1000 μg of Zn and 300 μg of copper also tolerate if masked with citrate and EDTA respectively. Notable interference in ruthenium determinations are cobalt, cadmium, bismuth and chromium(VI).

Composition of extracted species : The composition of Pd-PQMT and Ru-PQMT complexes were determined by Job's continuous variation method³ and the mole ratio method⁴. Both methods indicate the formation of a 1:2 complex. The dissociation constants, K, of the complexes were found to be 1.38×10^{-3} for Pd and 4.2×10^{-10} for Ru.

TABLE 3—ANALYSIS OF SYNTHETIC MIXTURES*

Composition of mixtures/ μg	Palladium recovered %	Ruthenium recovered %	Relative error %
(1) Pd 100, Pt 1000, Ru 1000	99.0	—	1.0
(2) Pd 100, Co 1000, Ni 1000, Fe 1000	98.5	—	1.5
(3) Pd 100, Ir 100, Au 100, Pt 100	98.0	—	2.0
(4) Ru 50, Os 100, Pd 100, Rh 100	—	98.5	1.5
(5) Ru 50, Au 100, Os 100	—	97.0	3.0
(6) Ru 50, Os 100, Rh 100, Ir 100	—	99.2	0.8

* Triplicate analysis.

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The method is suitable for determination of palladium in presence of Pt, Ru, Rh, Co, Ni, Fe, Ir and Au and that of ruthenium in synthetic mixtures containing Os, Pd, Rh, Au and Ir (Table 3).

The precision of the method is fairly good. The standard deviation for Pd (100 μg) and Ru (50 μg) is 0.003 whereas coefficient of variation is 1.5 and 1.2% respectively.

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