

# Spectrophotometric Determination of Rhodium(III) and Palladium(III) with Difurfurylthiocarbohydrazone, a Sensitive as well as Selective Reagent

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A very few organic thio ligands<sup>1</sup> (mostly thiocarbohydrazone<sup>2</sup>) are suitable for the spectrophotometric determination of rhodium and palladium in traces and in presence of various noble and base metals. In the present communication, difurfurylthiocarbohydrazone (DFTCH) has been utilised as a sensitive and selective reagent for both Rh<sup>III</sup> and Pd<sup>II</sup> in the presence of various base and Pt-metals.

## Results and Discussion

The absorption spectra of Rh<sup>III</sup>-DFTCH (1.4 µg ml<sup>-1</sup> in EtOAc) and Pd<sup>II</sup>-DFTCH (1.2 µg ml<sup>-1</sup> in EtOAc) complexes reveal  $\lambda_{\text{max}}$  for both the complexes at 377 nm while that of the reagent at 330 nm. Palladium formed complex at room temperature while the rhodium complex was formed on heating (boiling water-bath) for 15–20 min. The constant absorbance value of Rh<sup>III</sup>-DFTCH complex was obtained in the pH range 5.6–6.7 and that of the Pd<sup>II</sup>-DFTCH complex in the range 4.0–6.0. Both the complexes were stable for more than 24 h. The composition of the complexes, viz. Rh(C<sub>11</sub>H<sub>9</sub>N<sub>4</sub>O<sub>2</sub>S)<sub>3</sub> and Pd(C<sub>11</sub>H<sub>9</sub>N<sub>4</sub>O<sub>2</sub>S)<sub>2</sub>, were established using mole-ratio<sup>3</sup> and slope-ratio<sup>4</sup> methods. Ethyl acetate was taken as the working solvent. Behaviour of different solvents (isobutyl methyl ketone, 1,2-dichloroethane, chloroform, benzene, carbon tetrachloride and ethyl acetate) towards extraction of the complexes at 24° revealed ethyl acetate to be the proper working solvent. Beer's law is obeyed for both the Pd<sup>II</sup> and Rh<sup>III</sup> complexes at 377 nm over the concentration range 0.48–2.4 and 0.34–1.44 ppm respectively. The physical parameters of the complexes are as follows : for Pd<sup>II</sup>-DFTCH, molar absorptivity  $4.48 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ , Sandell's sensitivity<sup>5</sup> 0.0024 µg cm<sup>-2</sup>, relative mean error 0.4631%, standard deviation 0.1757 and coefficient of variation 0.7396%; for Rh<sup>III</sup>-DFTCH the corresponding values are  $6.1 \times 10^4$ , 0.0017, 0.6482, 0.1402 and 0.7905.

In determining the effect of diverse ions, 24 µg of Pd and 18 µg of Rh were mixed separately with desired amount of the foreign ion in question and determined according to the recommended procedures, and the results of tolerance limits (i.e. concentration of the diverse ions causing an error less than  $\pm 2\%$ ) are as follows : Cd<sup>II</sup>, Zn<sup>II</sup> (2.5 mg each); Cr<sup>III</sup>, Fe<sup>III</sup>, Co<sup>II</sup>, W<sup>VI</sup> (2.0 mg each); Ti<sup>IV</sup>, V<sup>V</sup>, Mn<sup>II</sup>, Ni<sup>II</sup>, Cu<sup>II</sup>, Pb<sup>II</sup>, Bi<sup>III</sup>, Au<sup>III</sup>, Mo<sup>VI</sup>, U<sup>VI</sup> (1.0 mg each) are tolerated for the estimation of Rh<sup>III</sup> as well as Pd<sup>II</sup>. Further, Ir<sup>III</sup> (1.0 mg), Os<sup>VI</sup> (0.5 mg), Ru<sup>III</sup> (0.6 mg), Rh<sup>III</sup> (0.12

mg) and Pt<sup>IV</sup> (0.3 mg) can be tolerated for the estimation of Pd. Again for Rh<sup>III</sup> (18 µg) determination, Os<sup>VI</sup> (0.25 mg), Pd<sup>II</sup> (0.2 mg), Ru<sup>III</sup> (0.45 mg) and Pt<sup>IV</sup> (0.36 mg) caused no error. Fe<sup>II</sup>, Co<sup>II</sup>, Ni<sup>II</sup>, Pb<sup>II</sup>, Cu<sup>II</sup>, Zn<sup>II</sup> and Au<sup>III</sup> were masked with EDTA and Ti<sup>IV</sup> with tartarate; Ru<sup>III</sup>, Pt<sup>IV</sup> and Os<sup>VI</sup> were reduced with hydroxylamine hydrochloride and sulphur dioxide. Interference caused by Pd<sup>II</sup> in the estimation of Rh<sup>III</sup> with DFTCH was avoided by extracting the former at room temperature prior to the estimation. Mercury and Ir<sup>III</sup> interfered in the determination of Rh<sup>III</sup>.

The results of estimation of Pd<sup>II</sup> and Rh<sup>III</sup> in an alloy and synthetic mixtures are shown in Table 1

TABLE 1—ESTIMATION OF Pd AND Rh IN SYNTHETIC MIXTURES AND ALLOY

Sample	Metal found (µg)* with 95% confidence limit		Relative mean error	
	Pd <sup>II</sup>	Rh <sup>III</sup>	Pd <sup>II</sup>	Rh <sup>III</sup>
(a) Synthetic mixtures (µg)				
Ru <sup>III</sup> (144), Pd <sup>II</sup> (48), Pt <sup>IV</sup> (72), Rh <sup>III</sup> (54), Ir <sup>III</sup> (206), Os <sup>VI</sup> (180)	47.69 ± 0.49	—	0.60	—
Os <sup>VI</sup> (180), Pd <sup>II</sup> (72), Ru <sup>III</sup> (184), Pt <sup>IV</sup> (72), Rh <sup>III</sup> (36)	—	36 ± 0.49	—	0.80
Pd <sup>II</sup> (72), Rh <sup>III</sup> (18)	71.88 ± 0.25	18.36 ± 0.45	0.21	1.4
Pd <sup>II</sup> (24), Rh <sup>III</sup> (54)	23.73 ± 0.40	54.45 ± 0.55	1.09	0.34
(b) Alloy (87% Pt <sup>IV</sup> , 13% Rh <sup>III</sup> )				
Pt <sup>IV</sup> (156.4 µg), Rh <sup>III</sup> (23 µg)	—	22.63 ± 0.23	—	0.63

\*Five sets of experiments

## Experimental

A Hitachi U 3210 spectrophotometer with 10 mm quartz cells was used. The pH was measured with a Systronic 331 pH meter. Stock solutions of Pd and Rh were prepared by dissolving their chlorides (Johnson and Mathey; 1 g each) in dilute HCl and standardised respectively by gravimetric<sup>6</sup> and hydrolytic precipitation methods. The stock solutions were suitably diluted with distilled water. Solutions of diverse ions were prepared in distilled water or dilute HCl. The Pt–Rh alloy (Arora Mathey) sample was dissolved in minimum volume of aqua regia and volume of the solution was raised upto 500 ml with distilled water and standardised. Dilute HCl and 10% sodium acetate solutions were used to maintain the acidity of the solution. A  $1 \times 10^{-3} \text{ M}$  difurfurylthiocarbohydrazone solution was prepared in ethanol. All the chemicals used were of A.R. grade.

#### NOTE

**Procedure :** To prepare the reagent, furan-2-aldehyde (9 g) was added dropwise in thiocarbonylhydrazide dissolved in dilute HCl and stirred till the brown mass solidified, which was filtered and crystallised from ethanol.

An aliquot containing known amount of Pd (12–60  $\mu$ g) was diluted to 20 ml with distilled water and its pH was adjusted to 4.0–6.0. Then ethanol (2–3 ml) and the reagent solution (1–2 ml) were added, allowed to stand for 10 min and extracted with ethyl acetate (3  $\times$  5 ml). The ethyl acetate extract was made upto 25 ml, dried and its absorbance measured at 377 nm against the reagent blank.

In case of Rh<sup>III</sup> the pH was adjusted to 5.6–6.7 with HCl and 10% sodium acetate solution. After addition of the reagent solution the mixture was heated over a boiling water-bath for 15–20 min. Subsequent extraction and ab-

sorbance measurements at 377 nm were same as those for Pd<sup>II</sup>.

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