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CHELATOMETRIC DETERMINATION OF RHODIUM(III) USING WATER-ETHANOL SOLUTIONS

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An EDTA back-titration of rhodium(III) has been proposed taking advantage of rapid chelation in water-ethanol solutions. The optimum amount of rhodium was 0.5 - 10 mg and the standard deviation was 0.76%. The method is applicable to the analysis of some rhodium(III) complexes.

Although a rapid and accurate method of determination of rhodium was eagerly requested in the study of platinum metal complex chemistry1), no reliable procedure of titration involving EDTA chelatometry has been published yet2). This is probably due to the extreme inertness of the chloro complexes of rhodium(III) in aqueous solution3). The authors have found that the addition of ethanol results in remarkable enhancement of the rate of chelation of EDTA with rhodium(III), and applied this observation to the back-titration of rhodium(III) as described below.

A stock solution of rhodium(III) chloride (0.01 mol dm^{-3}) was prepared by dissolving rhodium(III) chloride trihydrate, from Wako Chemicals Co. or Koso Chemicals Co., in water slightly acidified with hydrochloric acid. The concentration of rhodium was standardized by gravimetric method weighing as metallic rhodium4). The emission spectroscopic (Shimadzu QF-60) and flame photometric analysis (Shimadzu AA-640-12) revealed that both rhodium salts were pure enough for this titrimetric study. The EDTA solution (0.01 mol dm^{-3}) was standardized against 0.01 mol dm^{-3} copper(II) solution. Other chemicals were all of guaranteed quality and ethanol was purified by distillation.

A sample solution containing 0.5 - 10 mg of rhodium(III) was transferred

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into a 300 ml glass-joint Erlenmeyer flask attached with a condenser. To this was added about double the molar quantity of EDTA. The mixture was diluted with water to ca. 50 ml and the pH of the solution adjusted to 1 - 5 with dilute sodium hydroxide or hydrochloric acid. Ethanol (25 ml) was added and the mixture was heated gently for 30 min (ca. 83°C). The condenser was rinsed with water and removed. To the solution was added 5 ml of 1 mol dm^{-3} acetate buffer (pH 5.0), and, while warm, the excess EDTA was titrated with 0.01 mol dm^{-3} copper(II) solution using PAN or Cu-PAN as an indicator. The data are shown in Table 1. The results are quite satisfactory in the range of 0.5 - 10 mg of rhodium, the standard deviation being 0.76%.

Table 1. EDTA Titration of Rhodium(III) using Water-ethanol Solutions

Rh(III) taken mg	Rh(III) found mg	Rh(III) taken mg	Rh(III) found mg
0.5026	0.49_4	5.040	5.04
	0.50_5		5.03
	0.50_5		5.04
	Av. 0.50_1		Av. 5.04
2.011	2.01	10.08	10.11
	2.01		10.09
	2.02		10.11
	Av. 2.01		Av. 10.10

Since the procedure is based on the back-titration, metal ions which react with EDTA interfere. Furthermore, some common anions were found to interfere with the titration as shown in Table 2. Therefore, rhodium must be separated from these interfering ions prior to the titration.

Addition of ethanol enhances the rate of chelation of EDTA to rhodium(III) resulting in quantitative stoichiometry of the reaction. Change in the electronic spectra during the heating is shown in Fig. 1. In the presence of ethanol, $[Rh(Hedta)(H_2O)]$ is rapidly formed via $[RhCl(Hedta)]^-$ 5). Similar titration procedure without addition of ethanol gave positive errors of ca. 5%, which may be due to an incomplete complexation of rhodium.

Table 2. Effect of Diverse Anions

Anions	Salts used	Tolerance limit (mole ratio to Rh)
SO_4^{2-}	Na_2SO_4	10
NO_3^-	$NaNO_3$	1
Cl^-	NaCl	500
CH_3COO^-	$CH_3COOH-CH_3COONa$	10
PO_4^{3-}	$KH_2PO_4-Na_2HPO_4$	7

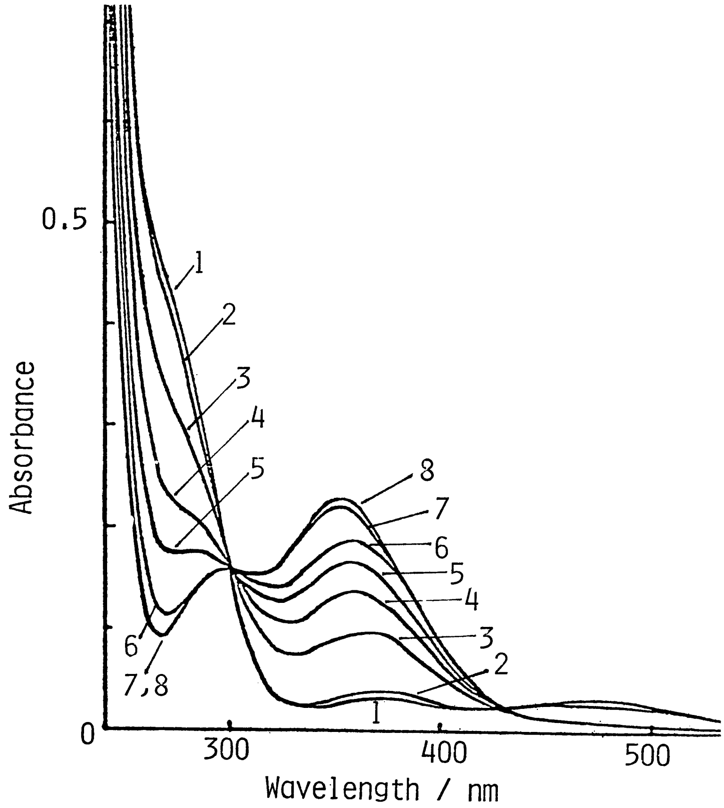

Fig. 1. Change in electronic spectra of rhodium(III)-EDTA system in water-ethanol solution at 82.5°C.

[Rh(III)]: 7.00×10^{-4} mol dm^{-3}

[EDTA]: 1.44×10^{-3} mol dm^{-3}

[EtOH]: 33%(v/v)

Heating time (min):

1: 0, 2: 8, 3: 16, 4: 18,

5: 20, 6: 22, 7: 45, 8: 60.

The proposed method was applied to the analyses of $[RhCl(NH_3)_5]Cl_2$ and $[Rh(Hedta)(H_2O)]$. A definite amount (ca. 20 mg) of either complex was decomposed by the fusion with $K_2S_2O_7$ (1 - 2 g), and dissolved in water. A modified hydrolytic method[4)] was used in the subsequent procedure. The solution was boiled, mixed with 1 ml of 10% $NaBrO_3$ and the pH of the solution was adjusted to 6 - 7 by adding 10% Na_2CO_3. Rhodium(III) hydroxide was precipitated by continued boiling, filtered off with Toyo No.5C filter paper, washed with a small amount of water, and dissolved in a hot HCl solution (1-3 mol dm^{-3}). The solution was dried up carefully on a water bath and the residue dissolved in water was submitted to the proposed titrimetric procedure. The results are satisfactory as seen in Table 3.

Table 3. Analyses of Rhodium(III) Complexes

	Complex taken mg	Rh calcd mg	Rh found mg
$[RhCl(NH_3)_5]Cl_2$	18.525	6.47	6.40
	29.731	10.4	10.2
$[Rh(Hedta)(H_2O)]$	19.293	4.70	4.71
	16.858	4.11	4.12

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