

# Spectrophotometric determination of the platinum metals

## IX.\* Highly sensitive extraction determination of rhodium with 4-(2-pyridylazo)resorcinol in the presence of micellar hexadecylpyridinium bromide

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The effect of the presence of the cationic tenside hexadecylpyridinium bromide on the formation of the coloured product of the reaction of Rh(III) with 4-(2-pyridylazo)resorcinol is described. The micelle-solubilized ion-associate has been used in a highly sensitive extraction-spectrophotometric determination of Rh(III) ( $\epsilon(520\text{ nm}) = 18\text{ m}^2\text{ mmol}^{-1}$  for the extract,  $S(\text{Rh(III)}) = 55\text{ ng cm}^{-2}$ , the range of determination of Rh(III) 0.08 to  $1.00\text{ }\mu\text{g cm}^{-3}$ ) and the effect of interfering ions has been evaluated.

Описано влияние катионного тензида бромистого гексадецил-пиридиния на образование окрашенного продукта в реакции Rh(III) с 4-(2-пиридилазо)резорцином. Солюбилизированный в виде мицелл ионный ассоциат был использован в высокочувствительном экстракционно-спектрофотометрическом определении Rh(III) ( $\epsilon(520\text{ nm}) = 18\text{ м}^2\text{ ммоль}^{-1}$  для экстракта,  $S(\text{Rh(III)}) = 55\text{ нг см}^{-2}$ , интервал определения Rh(III) от 0,08 до  $1,00\text{ мкг см}^{-3}$ ) и оценено влияние мешающих ионов.

Tensides have been used to advantage as a third component of coloured systems in determination of metals at low concentrations with chromogenic reagents. The favourable effect of tensides on the metal—dye complexes, manifested in an improvement in the characteristics of the spectrophotometric determination of the metal (a shift in the  $\lambda_{\text{max}}$  value, an increase in the sensitivity of the reaction, a change in the pH of the medium or in the reaction rate), has been commonly explained by the formation of ion-associates of the charged metal—dye chelates with the tensides.

The present work studies the effect of the tensides on the reaction of rhodium with the azo-dye 4-(2-pyridylazo)resorcinol, PAR. According to *Shriwastava, Garg, and Dey* [1] PAR reacts with Rh(III) on heating the mixture on a water bath, with the formation of a red chelate with a composition of

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\* For Part VIII see *Chem. Papers* 39, 83 (1985).

$x(\text{Rh}):x(\text{PAR}) = 1:2$  that can be used for the determination of rhodium ( $\text{pH} = 4.0$ ,  $\lambda_{\text{max}} = 510 \text{ nm}$ , molar absorption coefficient  $\varepsilon = 0.7 \text{ m}^2 \text{ mmol}^{-1}$ ).

In the presence of the tenside hexadecylpyridinium bromide (CPB), the formation of a red ion-associate has been confirmed that is solubilized by the tenside micelles and can be extracted into chloroform. The reaction can then be employed for a highly sensitive determination of rhodium. The value  $\varepsilon(520 \text{ nm}) = 18 \text{ m}^2 \text{ mmol}^{-1}$  for the extract is more than 25 times higher than that for the chelate in an aqueous medium without the tensides.

## Experimental

### *Apparatus*

The spectrophotometric measurements were carried out on a Unicam SP 800 instrument (Pye—Unicam, Cambridge), using cuvettes of 1.00 cm i.d. The pH of solutions was measured using an Acidimeter EK instrument (Druopta, Prague) with a glass and a saturated calomel electrode. The pH-meter was calibrated using standard buffers. The reaction at an elevated temperature ( $\theta = 100^\circ\text{C}$ ) was studied using a U 10 thermostat (Medingen, GDR).

### *Solutions and reagents*

0.1 M stock solution of rhodium was prepared by dissolving  $\text{RhCl}_3 \cdot 4\text{H}_2\text{O}$  (Safina, Vestec) in distilled water. The rhodium content in this solution was determined gravimetrically [2], as  $\text{Co}(\text{NH}_3)_6 \cdot \text{Rh}(\text{NO}_3)_6$ .

0.001 M stock solution of PAR was prepared by dissolving the substance (Chemapol, Prague) in distilled water. It has been found that this solution of PAR is only stable for 10 h when stored in the light and at laboratory temperature.

0.01 M stock solution of CPB was prepared by dissolving the substance (Lachema, Brno), purified by recrystallization from 30 % ethanol, in 20 % methanol and diluting with distilled water. Further, 0.01 M stock solutions of the following tensides were used: Septonex (Slovakofarma, Hlohovec), hexadecyltrimethylammonium bromide (Lachema, Brno), Zephiramin (Fluka, Buchs, Switzerland), sodium dodecylsulfate (Zdravotnické zásobování, Říčany, Czechoslovakia).

The test solution pH was adjusted with buffers prepared from 0.2 M- $\text{CH}_3\text{COOH}$  and 0.2 M- $\text{CH}_3\text{COONa}$ . The ionic strength was adjusted by adding 3 M- $\text{NaCl}$ .

In the testing of the effect of foreign ions, 0.1 M solutions of these ions were used and were diluted as required. Only the solutions of the platinum metals were prepared with a concentration of  $1 \text{ mmol dm}^{-3}$ .

All the chemicals used were of anal. grade purity.

### *Procedure*

In a  $25 \text{ cm}^3$  volumetric flask,  $2.5 \text{ cm}^3$  of a freshly prepared 0.001 M PAR solution,  $10 \text{ cm}^3$  of the 0.2 M acetate buffer of  $\text{pH} = 5.2$ ,  $4.2 \text{ cm}^3$  of 3 M- $\text{NaCl}$  and  $2.5 \text{ cm}^3$  of

0.01 M CPB solution are added. The solution is mixed and the sample containing 2.0 to 25.0  $\mu\text{g}$  Rh(III) is added. The reaction mixture is diluted with distilled water and heated for 2 h on a boiling water bath. After cooling and dilution to the final volume, the solution is extracted for 4 min into 10  $\text{cm}^3$  of  $\text{CHCl}_3$ . The system is allowed to stand for 10 min, the phases are separated and after 20 min, within which the solution becomes clear, the absorbance of the extract is measured at  $\lambda = 520 \text{ nm}$  against the blank.

## Results

It has been found [3] that the presence of a cationic tenside in an aqueous mixture of Rh and PAR leads to a pronounced hyperchromic and a small bathochromic shift in the spectra ( $\Delta\lambda_{\text{max}} \approx 10 \text{ nm}$ ), a shift of the formation of the red product toward a less acidic region ( $\Delta\text{pH} \approx 1$ ) and to an increase in the reaction rate.

Therefore, the effect of tensides on the reaction of rhodium with PAR in an acetate buffer was studied in greater detail. Cationic tensides (Zephiramin, hexadecylpyridinium bromide — CPB, Septonex, hexadecyltrimethylammonium bromide — CTMAB), anionic ones (sodium dodecylsulfate — SDS), and nonionic tenside (Triton X-100) were used. The largest effect on the spectra of the chelate Rh—PAR ( $\text{pH} = 5.1$ ,  $c(\text{Rh}) = 12 \mu\text{mol dm}^{-3}$ ,  $c(\text{PAR}) = 0.1 \text{ mmol dm}^{-3}$ , the time of heating the mixture on a boiling water bath 45 min,  $c_T > \text{cmc}$ , where cmc is the critical micelle concentration of the tenside,  $c_T$  is the tenside concentration) has been found for CPB among the cationic tensides; anionic and nonionic tensides do not affect the spectra and the reaction conditions. Tetramethyl- and tetraethylammonium bromide also exert no effect.

Thus CPB was further used and formed an associate with  $\lambda_{\text{max}}$  at 515 nm; the difference curve has then  $\lambda_{\text{max}} = 520 \text{ nm}$ . The effect of the experimental conditions was examined at the  $\lambda_{\text{max}}$  value of the difference curve: it has been found that the formation of the coloured product in an acetate buffer of pH 5.1 to 5.6 and a low ionic strength ( $I = 5 \text{ mmol dm}^{-3}$ , adjusted with NaCl) is complete within 45 min of heating on a boiling water bath (in the absence of the tenside this time increases up to 90 min) [1]. However, if  $c(\text{NaCl}) = 0.5 \text{ mol dm}^{-3}$  at the same pH range, the mixture must be heated for more than 100 min to attain complete colouration and the product is then stable for at least 2 h.

Under these conditions ( $\text{pH} = 5.2$ ,  $c(\text{NaCl}) = 0.5 \text{ mol dm}^{-3}$ , heating for 120 min on a boiling water bath), the  $c(\text{PAR})$  value must be at least  $0.1 \text{ mmol dm}^{-3}$ . The dependence of the product absorbance on  $c_T$  has indicated that the tenside concentration in the aqueous mixture must be greater than  $0.9 \text{ mmol dm}^{-3}$ . It is known from the literature [4] that cmc for CPB equals  $0.8 \text{ mmol dm}^{-3}$  and decreases to about  $0.2 \text{ mmol dm}^{-3}$  in the presence of NaCl.

Hence a decisive role of micelles of the tenside can be assumed in the formation of the coloured product.

Chloroform has been used for the extraction of the micellar product Rh—PAR—CPB and the extract spectra are given in Fig. 1. It can be seen that the ion-associate PAR—CPB is also extracted into chloroform [5] and exhibits  $\lambda_{\max} = 395 \text{ nm}$  under the present conditions. The extract Rh—PAR—CPB has  $\lambda_{\max}$  values for both the normal and the difference curve that are identical with those in aqueous solution, *i.e.* 515 nm and 520 nm, respectively. From the dependence of the extract absorbance on the time of extraction it follows that the minimum time of extraction is 2 min, the absorbance begins to decrease after extraction longer than 8 min. The efficiency of a single extraction amounted to 86.7%. The reagent ratio identical with that in aqueous solution,  $x(\text{Rh}):x(\text{PAR}) = 1:2$ , has been found from the Job plots for the extract of the coloured micellar product obtained under the optimal conditions (pH of the aqueous solution 5.2, 0.2 M acetate buffer,  $c(\text{Rh} + \text{PAR}) = 0.1 \text{ mmol dm}^{-3}$ ,  $c_{\text{T}} = 1 \text{ mmol dm}^{-3}$ ,  $c(\text{NaCl}) = 0.5 \text{ mol dm}^{-3}$ , heating for 120 min on a boiling water bath,  $\lambda = 500 \text{ nm}$ , 520 nm, and 550 nm).

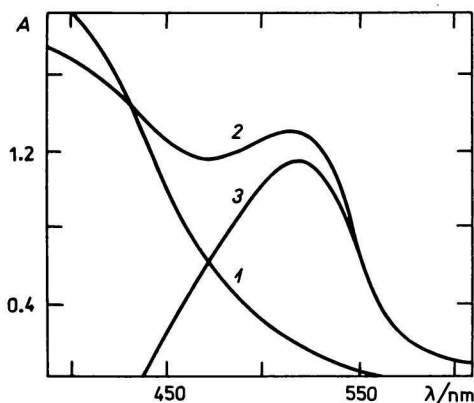


Fig. 1. Absorption spectra of the extract of Rh—PAR—CPB.

pH = 5.2,  $c(\text{Rh}) = 10 \mu\text{mol dm}^{-3}$ ,  
 $c(\text{PAR}) = 0.1 \text{ mmol dm}^{-3}$ ,  
 $c(\text{CPB}) = 1 \text{ mmol dm}^{-3}$ , heated for 2 h on a boiling water bath, extracted for 2 min into  $10 \text{ cm}^3$  of  $\text{CHCl}_3$ ; measured against  $\text{CHCl}_3$ .

1. PAR—CPB; 2. Rh—PAR—CPB;  
 3. difference between 2 and 1.

The extraction procedure has been utilized in the development of a method for the determination of Rh(III):  $\varepsilon(520 \text{ nm}) = 18 \text{ m}^2 \text{ mmol}^{-1}$  for the extract. The calibration curve was found to be linear from  $\varrho(\text{Rh(III)}) = 0.08\text{—}1.00 \mu\text{g cm}^{-3}$ , Sandell sensitivity  $S(\text{Rh(III)}) = 55 \text{ ng cm}^{-2}$ .

The effects of interfering ions that have been selected according to their possible presence in practical rhodium samples and measured under the optimal conditions of the extraction determination of Rh(III) are listed in Table 1.

It can be seen that the presence of a suitable tenside has a beneficial effect on the reactions of metals with chromogenic reagents. In this case it has been confirmed that anionic chelates [1], here  $\text{RhL}_2^-$  (where  $\text{PAR} = \text{H}_2\text{L}$ ), are only

Table 1

The effect of ions on the extraction determination of Rh(III)

M	Salt used	$x(\text{M}) : x(\text{Rh})$ ratio <sup>a</sup>
Ag(I)	AgNO <sub>3</sub>	no interference
Co(II)	CoCl <sub>2</sub> · 6H <sub>2</sub> O	always interfere
Ni(II)	NiCl <sub>2</sub> · 6H <sub>2</sub> O	10 : 1
Zn(II)	Zn(NO <sub>3</sub> ) <sub>2</sub> · 6H <sub>2</sub> O	5 : 1
Cu(II)	CuSO <sub>4</sub> · 5H <sub>2</sub> O	5 : 1
Cr(III)	Cr(NO <sub>3</sub> ) <sub>3</sub> · 9H <sub>2</sub> O	always interfere
Fe(III)	Fe(NO <sub>3</sub> ) <sub>3</sub> · 9H <sub>2</sub> O	5 : 1
Ru(III)	(NH <sub>4</sub> ) <sub>2</sub> Ru(H <sub>2</sub> O)Cl <sub>5</sub>	5 : 1
Pd(II)	PdCl <sub>2</sub>	always interfere
Os(IV)	(NH <sub>4</sub> ) <sub>2</sub> OsCl <sub>6</sub>	5 : 1
Ir(IV)	(NH <sub>4</sub> ) <sub>2</sub> IrCl <sub>6</sub>	10 : 1
Pt(IV)	H <sub>2</sub> PtCl <sub>6</sub>	10 : 1

a) The ratio of the molar concentration of the elements,  $x(\text{M}) : x(\text{Rh})$ , at which the foreign ion interferes in the determination of rhodium (the ratios  $x(\text{M}) : x(\text{Rh}) = 1 : 10, 1 : 1, 5 : 1, 10 : 1$ , and  $100 : 1$  were evaluated).

affected by tensides with the opposite charge on their hydrophilic part, here cationic tensides. It can be assumed that the ion-associate produced has the composition  $\{\text{CP}^+ \cdot \text{RhL}_2^-\}_0$ , where  $\text{CP}^+$  is the tenside cation. As it has been found that  $c_T > \text{cmc}$  is required for the formation of the product, it can be considered that another condition of the formation of the product is the presence of tenside micelles that solubilize the product. This is also supported by the fact that tetraalkylammonium ions that cannot form micelles (they have not the tenside character) exert no effect on the spectra of the anionic chelate  $\text{RhL}_2^-$ .

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