

Spectrophotometric determination of platinum metals. IV.* Determination of rhodium and platinum with Chromazurol S in the presence of cation-active tensides

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The interaction of Chromazurol S with Rh(III) and Pt(IV) was investigated in the presence of cetylpyridinium or 1-(ethoxycarbonyl)pentadecyltrimethylammonium bromide. A new spectrophotometric method for the determination of the two metals has been developed on this basis.

Было изучено взаимодействие Хромазуrola S с Rh(III) и Pt(IV) и бромидами цетилпиридиния и 1-(этоксикарбонил)пентадецилтриметил-аммония. На этом основании разработан новый спектрофотометрический метод определения этих двух металлов.

The use of ternary systems involving a metal, a dye, and a cation-active tenside for photometric determination of the platinum metals has been recently studied [1—6], using metallochromic indicators of the triphenylmethane type and tetraalkylammonium or pyridine type cation-active tensides. In the framework of a systematic study of the use of some of these dyes (Chromazurol S, Eriochromocyanine R, Xylenol Orange [7]; Pyrocatechol Violet, Pyrogallol Red, and Bromopyrogallol Red [8]) in these systems, the reaction of Rh(III) and Pt(IV) with Chromazurol S was investigated in the presence of cetylpyridinium bromide (CPB) or 1-(ethoxycarbonyl)pentadecyltrimethylammonium bromide (CPTB) and a method for the spectrophotometric determination of the two metals was developed. The determination of Rh(III) was applied to the analysis of a rhodium alloy with platinum [9], after preliminary separation of platinum.

Chromazurol S (CAS) was used by *Saxena* and *Dey* [10] for a photometric determination of Rh(III), using the binary complex with $\lambda_{\max} = 570$ nm. The reaction of Pt(IV) with CAS has not yet been described in the literature.

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Experimental

Apparatus and chemicals

Spectrophotometric measurements were performed on an SP 800 instrument (Unicam, Cambridge) and a Spekol instrument (Zeiss, Jena) using 1.00 cm cuvettes. The acidity of solutions was measured with a glass and a saturated calomel electrode on an Acidimeter EK instrument (Druopta, Prague).

A 10^{-1} M stock solution of rhodium was prepared by dissolving 2.8140 g $\text{RhCl}_3 \cdot 4\text{H}_2\text{O}$ (Safina, Vestec) in 100 ml of distilled water. The rhodium content in this solution was determined gravimetrically [11] as $[\text{Co}(\text{NH}_3)_6][\text{Rh}(\text{NO}_2)_6]$ after precipitation with $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$. A 10^{-3} M stock solution of platinum was prepared by dissolving 0.0444 g $(\text{NH}_4)_2\text{PtCl}_6$ (Johnson and Matthey, London) in distilled water acidified with at least 0.3 ml of 0.1 M-HCl [12] and diluting with distilled water to 100 ml. The platinum content in the solution was checked gravimetrically, precipitating the platinum with benzylphenyl-dimethylammonium chloride [11].

A 10^{-3} M stock solution of Chromazurol S was prepared by dissolving 0.1512 g of the substance (Merck, Darmstadt) in 250 ml of distilled water. A 5×10^{-3} M stock solution of cetylpyridinium bromide was prepared by dissolving 0.4805 g of the substance (Lachema, Brno) in 250 ml of 20% methanol [13]. A 5×10^{-3} M stock solution of 1-(ethoxycarbonyl)pentadecyltrimethylammonium bromide was prepared by dissolving 0.5280 g of the substance (Spofa, Prague) in 250 ml of distilled water.

Required pH values of the solutions were maintained by buffers containing 0.2 M acetic acid and 0.2 M sodium acetate. For the study of the effect of other ions, 10^{-1} M solutions of these ions were prepared and were further diluted as required; solutions of the platinum metals were prepared with 10^{-3} M concentration. The ionic strength of solutions was maintained by adding 1 M- NaNO_3 or 2 M- KNO_3 .

All chemicals employed were of anal. grade.

Results

The effect of a tenside on the reaction of rhodium with Chromazurol S was studied with CPB. It was found that the presence of a cation-active tenside causes a bathochromic shift from 550 to 640 nm and a substantial increase in the reaction sensitivity. The spectra are given in Fig. 1. The ternary system is formed at pH 3.6–4.4, in contrast to the binary complex [10], after heating the mixture for 30 min on a boiling water bath. The coloured system formed (Table 1) is stable for at least 4 h.

Although the formation of a binary Pt(IV)—CAS complex has not been confirmed, in the presence of a cation-active tenside, CPB or CPTB, a coloured system is formed with a maximum on the difference curve at 640–650 nm. The effect of CPB and CPTB is similar, only the experimental conditions differ somewhat (Table 1). The ternary system is not formed at laboratory temperature

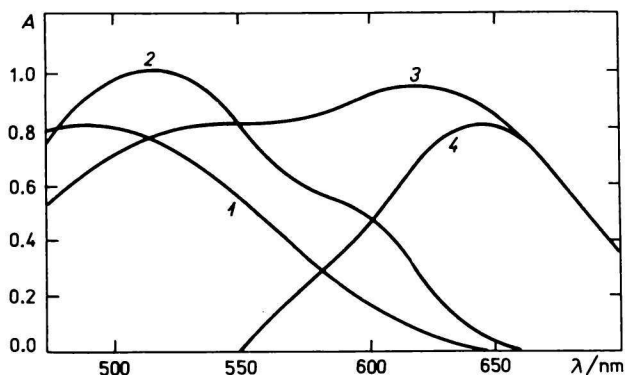


Fig. 1. Absorption spectra of the Rh(III)—CAS—CPB system.
 1. CAS; 2. CAS—CPB; 3. Rh(III)—CAS—CPB; 4. difference 3—2.
 $c_{\text{Rh}} = 1.2 \times 10^{-5} \text{ M}$; $c_{\text{CAS}} = 8 \times 10^{-5} \text{ M}$; $c_{\text{CPB}} = 4 \times 10^{-4} \text{ M}$; pH 3.8; $I = 0.1$.
 The mixture was heated for 30 min on a boiling water bath.
 The measurement was carried out against water.

Table 1

Optimum conditions for the formation of the metal—CAS—tenside ternary complex

Metal	Tenside	pH	I^a	Time of heating min	c_{tenside} 10^4 M	c_{CAS} 10^4 M
Rh(III)	CPB	3.8	0.1	30	4.0	0.8
Pt(IV)	CPB	4.5	0.1	40	5.0	1.0
Pt(IV)	CPTB	3.5	0.1	100	5.0	1.0

a) The I value was adjusted with KNO_3 or NaNO_3 .

and the mixture must be heated on a boiling water bath for at least 30 min (CPB) or 100 min (CPTB) to obtain a very stable coloured system the absorbance of which does not change for at least 6 days. As it was found that both the ternary system and the "blank", *i.e.* the CAS—tenside solution under the same conditions, are strongly affected by strong electrolytes, a constant ionic strength value ($I = 0.1 \text{ M}$) was maintained by adding KNO_3 or NaNO_3 . The effect of strong electrolytes was followed for both tensides and it was found that it is most marked in evaluation of the optimum tenside amount. In the absence of strong electrolytes the colour of the system is stable only in a narrow range of tenside concentration, whereas in the presence of 0.1 M-KNO_3 the colour is stable with 2×10^{-4} to $6 \times 10^{-4} \text{ M}$ tenside.

The two coloured systems were utilized for spectrophotometric determinations of Rh(III) and Pt(IV) with Chromazurol S. The results of the determinations are given in Table 2, containing the sensitivity of the reactions, the wavelengths of the difference curve maxima, λ_{dif} , and the corresponding apparent molar absorption coefficients, ϵ'_{dif} , the metal concentration range over which the Lambert—Beer law

Table 2
Characteristics of the studied systems

System	Sensitivity ^b	λ_{dif} nm	ϵ'_{dif}	Concentration range $\mu\text{g ml}^{-1}$	$s_{x,y}$
Rh—CAS ^a	8.0×10^{-3}	—	—	0.7—7.0	—
Rh—CAS—CPB	1.6×10^{-3}	650	6.2×10^4	0.06—1.5	5×10^{-3}
Pt—CAS—CPB	1.0×10^{-2}	650	1.7×10^4	0.5—5.8	8×10^{-3}
Pt—CAS—CPTB	9.6×10^{-3}	650	2.0×10^4	0.5—6.8	7×10^{-3}

a) See Ref. [10].

b) Sensitivity of the reaction ($\mu\text{g cm}^{-2}$) obtained from the formula, $c A^{-1} 10^{-3}$, where c is the metal concentration ($\mu\text{g ml}^{-1}$) and A is the measured absorbance for $l = 1.00$ cm.

is obeyed, and the assessed standard deviation for the scatter of the points along the regression straight line of the calibration plot, $s_{x,y}$. The data for the Rh—CAS binary system [10] are also given, for the sake of comparison; however, the maximum wavelengths for the ternary systems and the ϵ values are not given, because they cannot be accurately determined from the flat spectra.

The following procedures are recommended for the determinations.

The determination of Rh(III): In a 25 ml volumetric flask, 2.5 ml 1 M-NaNO₃, 5 ml acetate buffer of pH 3.8, 2 ml 10^{-3} M-CAS, 2 ml 5×10^{-3} M-CPB, and a rhodium solution containing 1.5—37 μg Rh(III) are gradually pipetted. The reaction mixture is heated for 30 min on a boiling water bath, cooled to 20—25°C and diluted to 25 ml with distilled water. The absorbance is measured at $\lambda = 650$ nm against the blank solution.

The determination of Pt(IV): a) To a sample solution containing 25—290 μg Pt(IV) are gradually added 5 ml 5×10^{-3} M-CPB, 5 ml 10^{-3} M-CAS, 10 ml acetate buffer of pH 4.5 and 2.5 ml 2 M-KNO₃. The reaction mixture is heated for 40 min on a boiling water bath, cooled to laboratory temperature and diluted with distilled water to 50 ml. The absorbance is measured at 650 nm against the blank solution.

b) The determination of Pt(IV) (25—340 μg Pt) with CPTB is analogous as above (procedure a) with following order of solution addition: KNO₃, CPTB, CAS, and the buffer (pH 3.5). The mixture is heated for 100 min on a boiling water bath.

Interfering ions are surveyed in Table 3, giving the maximum permissible ratios of the interfering ion to the test metal. Ions are considered to interfere when the

Table 3

Survey of interfering ions

Interfering ion	Salt used	Ratio	
		Ion : Rh	Ion : Pt
Os(IV)	$(\text{NH}_4)_2[\text{OsCl}_6]$	interferes	1 : 1
Ir(IV)	$(\text{NH}_4)_2[\text{IrCl}_6]$	1 : 1	1 : 1
Au(III)	$\text{AuCl}_3 \cdot \text{HCl} \cdot 4\text{H}_2\text{O}$	1 : 1	1 : 1
Ag(I)	AgNO_3	1 : 1	1 : 1
Co(II)	$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	100 : 1	100 : 1
Ni(II)	$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	100 : 1	100 : 1
Zn(II)	$\text{ZnSO}_4, \text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	50 : 1	100 : 1
Cl^-	NaCl	200 : 1	10 : 1
CO_3^{2-}	Na_2CO_3	100 : 1	100 : 1
SO_4^{2-}	Na_2SO_4	1000 : 1	1000 : 1
NO_3^-	$\text{KNO}_3, \text{NaNO}_3$	1000 : 1	1000 : 1

absorbance changes by 5% under the conditions of the determination and for the concentrations $c_{\text{Pt}} = 3.90 \mu\text{g ml}^{-1}$, $c_{\text{Rh}} = 1.48 \mu\text{g ml}^{-1}$. Ions Fe(II) and Fe(III), Ru(III) and Pb(II) interfere even at ion : Pt = 1 : 5 and ion : Rh = 1 : 5 ratios. In the determination of Rh(III), Pt(IV) does not interfere when present at a 1 : 1 ratio, whereas Rh(III) interferes in the determination of Pt(IV) even if present at a Rh : Pt = 1 : 5 ratio.

The above procedures were applied to practical analyses of some materials. Rhodium was successfully determined in its alloy with platinum [9]. The determination of platinum in an Al_2O_3 based catalyst was not successful, because a suitable method for separation of platinum was not found.

The complex composition was verified in the Rh—CAS—CPB ternary system using the Babko method [14], i.e. a triangular method of continuous variations applied to a three-component system ($c_{\text{total}} = 1 \times 10^{-4} \text{ M}$, $\lambda = 650 \text{ nm}$, $I = 0.1 \text{ M}$, pH 3.8, the mixture was heated for 30 min on a boiling water bath). In order to establish the reaction mechanism the number of protons liberated during the complex formation was determined by studying the absorbance of the Rh—CAS—CPB system as a function of pH [15] at the optimum conditions for the ternary complex formation. The former method yielded the ratio Rh : CAS : CPB = 1 : 2 : 2, the latter method indicated liberation of four protons in the formation of the ternary system.

A comparison of the spectra of the aqueous solution of the CAS—CPB binary system and of its extracts into *n*-hexane, chloroform, *n*-butanol, nitromethane has shown that the system is best extracted into solvents with low relative permittivity

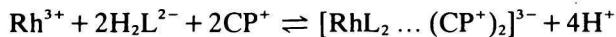
and a nonpolar character, similar to CPTB and Ajatine [16]. In contrast, the Rh—CAS—CPB ternary system formed under the optimum conditions and extracted in the same way attains the highest absorbance values in aqueous media. It follows from these results that CAS—CPB is extracted into solutions of low polarity, whereas Rh—CAS—CPB is charged and there is not extracted.

Conclusion

As shown by the above results, systems metal—CAS—cation-active tenside are suitable for the determination of rhodium and platinum. The colour reactions exhibit a higher contrast and a greater sensitivity than the binary metal—dye complexes. The tenside effect is especially marked with platinum, where it makes possible the formation of a Pt—CAS colour system, which is not formed in the absence of a tenside.

Relatively little attention has been paid to the basis of the reaction among metal, dye, and cation-active tenside; however, it seems that the micellar tenside form is most probably important. The optimum tenside concentrations ensuring the maximum solution colouration in the present systems are in the region of micelle formation. The critical micellar concentrations, c_c , are 7.6×10^{-4} M for CPB [17] and 1.1×10^{-4} M for CPTB [18], at $I = 0.1$ M. This fact is also reflected in the marked effect of the ionic strength of the solution, which is due to the influence of strong electrolytes on the c_c value of the tenside (c_c for CPTB is 7.7×10^{-4} M in the absence of strong electrolytes in the solution [18]).

On the basis of the composition of the Rh—CAS—CPB ternary system found under the optimum formation conditions it can be assumed that ion-associates of CAS with CPB participate in the reaction, *i.e.* $[\text{H}_2\text{L}^{2-} \dots (\text{CP}^+)_2]$. In the presence of CPB the dissociation equilibria of the individual forms of the dye shift to an acidic region and thus dye anion H_2L^{2-} must be considered at the given solution pH. Therefore, the following reaction scheme can be proposed for the formation of the ternary system



This reaction is also in agreement with the negative results obtained in the extraction of the Rh—CAS—CPB ternary complex into nonpolar organic solvents and with the number of protons liberated.

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