

**SPECTROPHOTOMETRIC STUDY OF THE BINARY SYSTEM
Ru(III)-SOLOCHROM VIOLET RS AND THE DETERMINATION OF
Ru(III)**

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ABSTRACT

A simple and direct spectrophotometric method using solochrom violet RS has been developed for the determination of Ru(III). The molar absorptivity and the Sandell's sensitivity are calculated to be $10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ and $0.0101 \mu\text{g cm}^{-2}$ respectively. The effect of various parameters including time, pH and added reactant volume has been studied. Beer's law is obeyed over the range 0.20- 7.07 $\mu\text{g/mL}$ of Ru(III). The method has been applied for the determination of Ru(III) in various synthetic and real samples.

RESUMO

Um método espectrofotométrico simples e directo, com solocromo violeta RS, foi usado para determinar o Ru(III). A potência de absorção molar e a sensibilidade Sandell são calculadas para ser $10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ e, respectivamente $0,0101 \mu\text{g cm}^{-2}$. O efeito dos variados parâmetros, incluindo o tempo, o pH e o volume de reactivo juntado, foi também estudado. Na série 0,20-7,07 $\mu\text{g/mL}$ de Ru(III) está respeitada a lei de Beer. O método foi aplicado para determinar o Ru(III) em exemplos reais e sintéticos variados

KEYWORDS : spectrophotometric determination, ruthenium, solochrom violet RS

INTRODUCTION

The solochrom violet RS (sodium salt of 2 hydroxynaphthyl-azo-1 phenol-4-sulphonic acid) was used for the spectrophotometric determination of the following ions: Mo(VI)¹, Zr(IV)², Th(IV)³, Cr(III)⁴, Ga(III)⁵, Al(III)⁶, In(III)⁷, U(VI)⁸, Zn(II)⁹, Cd(II)¹⁰, V(V)¹¹, Nb(V)¹², and Bi(III)¹³.

Solochrom violet RS reacts with ruthenium ions in aqueous solution, at room temperature to give a dark-red water soluble complex.

The present work reports the use of the azo compound solochrom violet RS for spectrophotometric determination of Ru(III). The method has been used for determination of Ru(III) in various samples.

EXPERIMENTAL

A Mettler Delta 320 pH-meter and UV-VIS Zeiss Jena spectrophotometer were used for measurement of pH and absorbance. All reagents used were of analytical grade. RuCl_3 acid solution (10^{-3}M) and solochrom violet RS aqueous solution (10^{-3}M) were prepared. Buffer solutions with pH ranging from 1.81 to 11.92 were prepared according to Prideaux's method¹⁴.

The real samples were descomposed using a microwave digestion under pressure Milestone MLS-1200 Mega processor in TMF vessels.

General procedure

Ru(III) chloride was dissolved in 2M HCl and the solution was standardised¹⁵. The reagent solution (6 mL) was added to a known volume of metal ion solution into 25 mL calibrated flasks. The pH was then adjusted to 3.1 with the appropriate buffer. The absorbance was measured at 550 nm against the blank 20 minutes after the mixing.

RESULTS AND DISCUSSION

The reaction between the Ru(III) and the azo compound results in formation of a complex. This complex shows an absorption maxima at 550 nm, whereas the reagent absorbed negligibly at this wavelength (Fig.1).

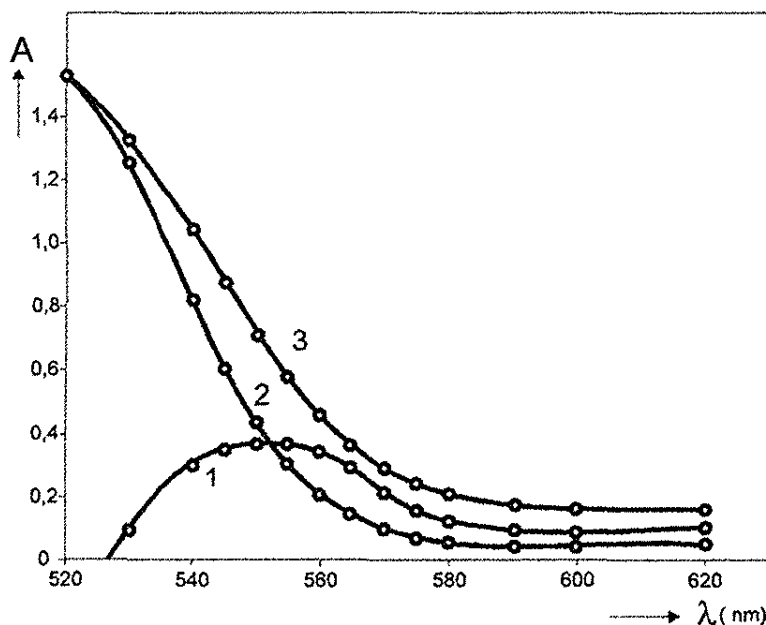


Fig.1. Absorbion spectra of:

1. Ru(III) + solochrom versus solochrom
2. Reactive versus water;
3. Ru(III) + solochrom versus water; ($8 \cdot 10^{-5}\text{M}$ Ru(III)) + $2.4 \cdot 10^{-4}\text{M}$ solochrom; pH=3.1)

The effect of time, reactant, volume and pH on determination of Ru(III) was studied. The optimum time required for development of colour was found to be 5 minutes at room temperature. The effect of concentration of reagent was examined. For 1 mL solution of Ru(III) 10^{-3} M, 3 mL of solochrom violet RS solution 10^{-3} M was sufficient. The absorbance remained practically constant above this value. The formation of the complex was studied over a wide pH range 1.81-11.92 using Prideaux buffer solutions. The results indicate that the absorbance was maximum in the acid domain at pH 3.1 (Fig.2).

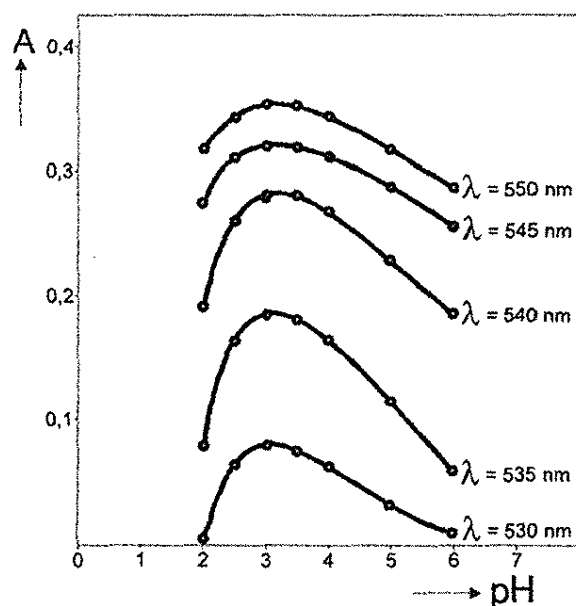
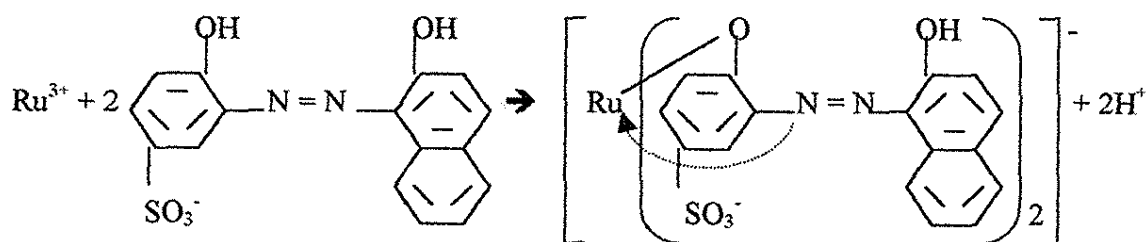


Fig.2. Variation of the absorbance versus pH ($8 \cdot 10^{-5}$ M Ru(III)+2.4 M solochrom).

The composition of the complex Ru(III)-solochrom was established using Job's method of continuous variation and mole ratio method. The mole ratio was found to be 1:1 (Fig.3 and Fig.4).

The reaction between Ru(III) and solochrom violet RS is:



The reactive molar ratio(x) for four nonisomolar series was established and the complex instability constant was calculated using the Job's relation for the 1/2 combination ratio :

$$K = \frac{c^2 p [(p+2)x - 2]^3}{(p-1)^2 (2-3x)}$$

were:

c = the molar concentration of the Ru(III);

p = the ratio of the molar concentration of the reactive and of the Ru(III);

$[B]$ = the molar concentration of the ligand;

x = the reactive molar ratio

The stability constant of the complex ($K_{st}=1/K_{inst}$) is $K_{st}=1.74 \cdot 10^{11}$ and the p_K ($p_K = -\log K_{inst}$) is $p_K = 11.38 \pm 0.01$ for a 95% probability at 25°C temperature and ionic strength $\mu=0.2$.

Table 1 presents the values of the stability constants for four nonisomolar solutions series.

Table I
Values of the stability constant

No of the nonisomolar serie	c	p	$[B]$ ligand	x	K_{st}	P_K
1	$5 \cdot 10^{-4}$	2	10^{-3}	0.505	$0.121 \cdot 10^{12}$	11.3837
2	$4 \cdot 10^{-4}$	2.5	10^{-3}	0.450	$0.234 \cdot 10^{12}$	11.3700
3	$2.5 \cdot 10^{-4}$	4	10^{-3}	0.345	$0.101 \cdot 10^{12}$	11.3756
4	$6.66 \cdot 10^{-5}$	10	$6.66 \cdot 10^{-3}$	0.180	$0.241 \cdot 10^{12}$	11.3816

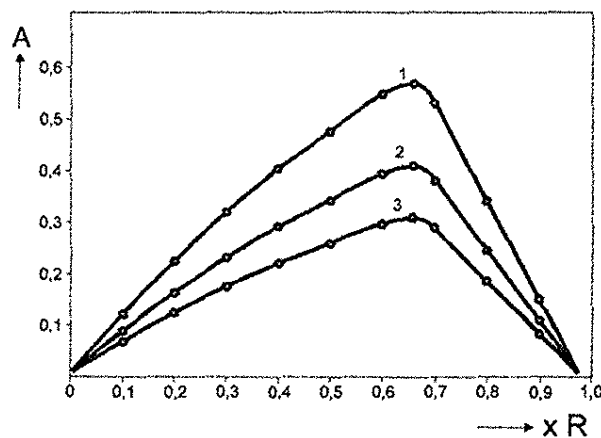


Fig.3. Variation of the absorbance in the isomolar series

1. $1 \times 10^{-3} M$
2. $6.66 \times 10^{-3} M$
3. $5 \times 10^{-4} M$.

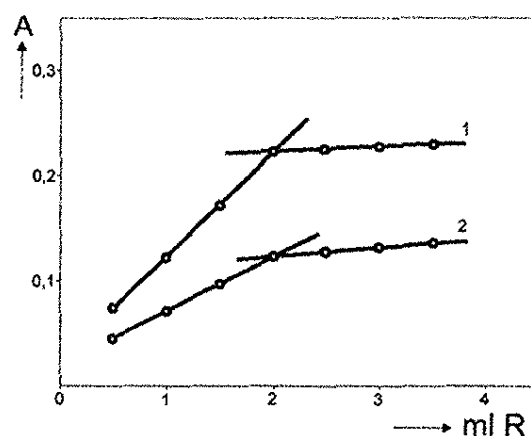


Fig.4. Complex composition determination by molar ratio method

1. $1 \times 10^{-3} M$
2. $5 \times 10^{-4} M$

The charge of the complex ion was determined by the electrophoretic migration method in the presence of a weak solution of potassium nitrate. After 10 minutes the coloured complex ion migrated towards the anode indicating the complex ion to be negatively charged.

Beer's law was obeyed over the concentration range 0.20-7.07 $\mu\text{g Ru(III)/mL}$ (Fig.5). For testing the validity of the method we have statistically interpreted the experimental data through the linear regression method.

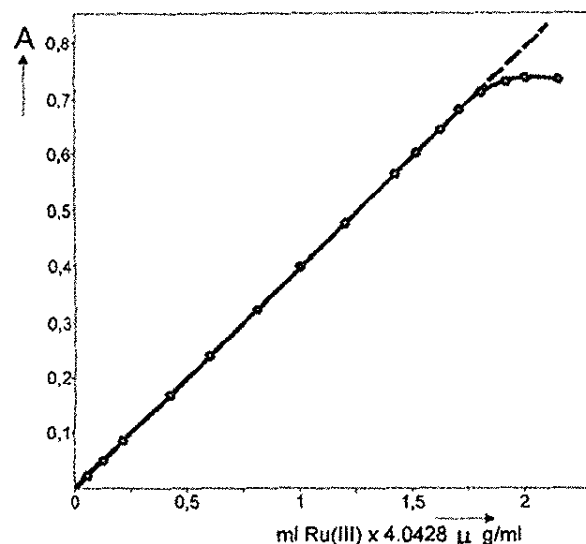


Fig.5. Variation of the absorbance versus Ru(III) concentration ($2 \cdot 10^{-6}\text{M} - 7 \cdot 10^{-5}\text{M}$ Ru(III) + $2.4 \cdot 10^{-5}\text{M}$ solochrom).

The correlation coefficient, r , having the value 0.9999 indicates a linear dependence of the absorbance on the Ru(III) concentration. The two equations are: $y = 0.0989x + 1 \cdot 10^{-7}$ with the angular coefficient $m_1 = 0.0989$ and $x = 10.1069y + 1.9 \cdot 10^{-6}$ with the angular coefficient $m_2 = 0.09894$. The method proposed for determination of Ru(III) is reproducible and accurate, the relative standard deviation being $\pm 1.1\%$, not affected by systematic errors. The molar absorptivity and the Sandell's sensitivity were calculated to be $10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ and $0.0101 \mu\text{g.cm}^{-2}$ respectively.

Interference studies demonstrated that the colour reaction of Ru(III)-solochrom violet RS is specific. Various cations were added individually to a solution of Ru(III) ($4.04 \mu\text{g/mL}$) and the tolerance limits are as follows: fluoride, chloride, bromide, iodide, acetate, nitrate, sulphate, thiosulphate, carbonate, phosphate and thiourea (Ru(III): anion = 1:200), citrate, oxalate, tartrate, nitrite and EDTA (Ru(III):anion = 1: 100), W(V) and W(IV) until the $\frac{1}{4}$ ratio, Zn(II), Al(III), Ga(III), Tl(I), Tl(III), U(VI), Bi(III), Cr(III), Cd(II), Mo(IV), Zr(IV), Th(IV) at enough great ratios due to the different absorption maxim of the corresponding complexes, Pt(IV), Ir(III), Au(III), Os(VIII), Rh(III), (Ru(III)/cation = 1:12), Co(II) (1:12) and Ni(II) (1:18) are tolerable in the presence of 0.5 ml EDTA solution.

Determination of Ru(III) in synthetic and real samples

The proposed method has been used for determination of Ru(III) both in synthetic mixtures and real samples and the results were statistically evaluated.

The synthetic mixtures had the following percentage composition: (1) Ru(III), 15; Ir(III), 10; Au(III), 10; Pd(IV), 5; Os(VIII), 40; Fe(III), 20; (2) Ru(III), 20; Pt(IV), 30; Co(II), 10; Ni(II), 10; Mo(VI), 20; Ir(III), 10.

Each of mixtures was treated with a mixture of KOH and KNO₃ (8:1.3g) and heated at 800°C for 30 minutes. The cooled melt was leached with water, acidified with concentrated hydrochloric acid (10 mL) and diluted to 100 mL. To an aliquot of the synthetic sample was added solochrom solution (3 mL) and pH was adjusted to 3.1 with the buffer solution; then were added 1% EDTA (0.5 mL) and 5% sodium thiosulphate (2 mL) solutions and ruthenium was spectrophotometrically determined. The determined concentrations (the mean of four determinations) are: 14.92±1.3% (0.53% error) and 19.96±1.1% (0.2% error).

Samples were decomposed using a microwave digestion under pressure processor in TMF vessels. Afterward the solid samples were treated depending on the sample nature either with aqua regia and H₂O₂ 30% or aqua regia, H₂O₂ 30%, HF and H₃BO₃. After digestion the samples were treated as in the case of synthetic mixtures. Ruthenium was determined spectrometrically and by DCP-AES technique, for comparison. The results are presented in Table 2, each analytical procedure being repeated five times.

Table 2. Results obtained for the analysis of two real Ruthenium samples

Sample, mg	New method		Reference method ¹⁶	
	Ru found, %	S _r	Ru found, %	S _r
46	6.54±0.002	0.003	6.70±0.001	0.002
86.5	6.61±0.003	0.002	6.74±0.002	0.001

S_r is the relative standard deviation

CONCLUSIONS

The spectrophotometric study of the binary system Ru(III)-solochrom violet RS leads to the following conclusions:

- the determinations were done in the visible region of the electronic spectrum;
- the complex stability constant is large enough and indicates a satisfactory stability of the complex,
- the present method for the determination of Ru(III) is more sensitive, selective and simple than the earlier known methods¹⁷⁻²¹.

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