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# Spectrophotometric Determination of Ru(IV) Using 5-Hydroxyimino-4-imino-1,3-thiazolidin-2-one as a Novel Analytical Reagent

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#### Abstract

The interaction of Ru(IV) ions with a novel analytical reagent – 5-hydroxyimino-4-imino-1,3-thiazolidin-2-one, by spectrophotometric method was investigated. The complex is formed at pH 5.0 in acetate buffer medium after heating in the boiling water bath (~371 K) for 25 min. The complex has maximum absorption at 350 nm and is stable for 24 h. Beer's law is valid over the concentration range of 0.5–6.1  $\mu g$  mL<sup>-1</sup> for Ru(IV). The molar absorptivity at  $\lambda$  = 350 nm is 6.21 ×  $10^3$  L mol<sup>-1</sup> cm<sup>-1</sup>. The limit of detection of this method is 0.2  $\mu g$  mL<sup>-1</sup>. The interfering effect of various cations and anions on the spectrophotometric determination of the Ru(IV) were investigated. The proposed method was successfully applied to the determination of Ru(IV) in alloys.

Keywords: Spectrophotometry; ruthenium(IV); 5-hydroxyimino-4-imino-1,3-thiazolidin-2-one.

#### 1. Introduction

Ruthenium and its compounds are widely used in various fields: as a catalyst in chemical, petroleum, and pharmaceutical industries, in electrical contacts, resistors, as electrode materials for supercapacitors, and it improves the corrosion properties of alloys, etc.<sup>1-3</sup> There is a need to develop sensitive, simple and inexpensive methods for the quantitative determination of ruthenium in different samples. For the determination of ruthenium, different analytical techniques such as: voltammetry, atomic absorption spectrometry, high performance liquid-chromatography, thin-layer chromatography, inductively coupled plasma atomic emission, inductively coupled plasma mass spectroscopy are used.<sup>3</sup> But spectrophotometric methods have been widely used thanks to their simplicity, versatility and cheapness.<sup>3-12</sup>

For spectrophotometric determination of ruthenium, S and N containing organic compounds are widely

used.<sup>3–6,8–12</sup> Azolidones belong to such compounds. This class of organic compounds was discovered in the middle of the 20<sup>th</sup> century.<sup>13</sup> These compounds exhibit different biological activity, in particular hypoglycemic, antimicrobial, fungicidal, antiviral, antiinflammatory, and antitumor.<sup>14–16</sup>

In our previous studies, the physicochemical properties of the new reagents: 5-hydroxyimino-4-imino-1,3-thiazolidin-2-one (HITO), 4-[*N*'-(4-imino-2-oxo-thiazolidin-5-ylidene)-hydrazino]-benzenesulfonic acid and 1-(5-benzylthiazol-2-yl)azonaphthalen-2-ol, which belong to the class of azolidones, and the interaction of Pd(II), Rh(III), Pt(IV), Ir(IV), Cu(II), Zn(II), Cd(II), Ni(II), and Hg(II) ions with these reagents were investigated 17-28 and the methods of their determination with good metrological characteristics were proposed. 18-25,27,28 Therefore in this paper, we investigated the interaction of ruthenium(IV) ions with 5-hydroxyimino-4-imino-1,3-thiazolidin-2-one.

#### 2. Experimental

#### 2. 1. Apparatus

A ULAB 108-UV computerized spectrophotometer equipped with 1.0 cm quartz cells was used for absorbance measurements. Absorption spectra were obtained in the wavelength range of 240–600 nm with the step of 2 nm using distilled water as a blank.

The pH measurements and adjustments were performed using pH-meter model pH-150 M equipped with a combination glass electrode.

Voltammetric measurements were carried out using oscillopolarograph CLA-03 and computerized polarographic setup equipped with linear potential scan in three-electrode cell (indicator electrode – dropping mercury electrode, reference electrode – saturated calomel electrode and auxiliary electrode – platinum).

Spectrometer Bruker Avance (400 MHz) was used for registration <sup>1</sup>H NMR spectra of compounds dissolved in DMSO-d<sub>6</sub>, internal reference of TMS.

#### 2. 2. Reagents

All chemicals used in the research were analytically pure and all aqueous solutions were prepared using distilled water.

The stock solution of Ru(IV) ([ $RuCl_6$ ]<sup>2-</sup>) was prepared by sintering the exact mass of pure metallic ruthenium (99.99%) with the oxidizing mixture of NaOH and NaNO<sub>3</sub> (3:1) in a corundum crucible at 900 K (45–60 min). The obtained fusion was dissolved in 3.0 mol  $L^{-1}$  HCl. The form of Ru(IV) in the obtained stock solution was identified by the comparison of its absorption spectra with the ones described in the literature.<sup>29</sup> Because of the possible losses during sintering, the obtained solution of Ru(IV) was additionally standardized using iodometric titration.<sup>3,5</sup> Working solutions of Ru(IV) were prepared by suitable dilution of the stock solution with 1.0 mol  $L^{-1}$  hydrochloric acid.

The stock solution of 5-hydroxyimino-4-imino-1,3-thiazolidin-2-one was prepared by the dissolution of an exact mass of the reagent in ethanol (96% v/v). Working solution of HITO was prepared by dilution the stock solution with water. Synthesis of HITO was carried out according to the methodology given in the literature,<sup>30</sup> the only difference was the use of 10% HCl instead of 5%, that increased the practical yield of the reagent: 5.8 g (50 mmol) 4-iminothiazolidine-2-one in 10% HCl was placed in a 100 mL round-bottomed flask with a mechanical stirrer and was cooled to 273 K. Then the solution of 10.5 g sodium nitrite in 20 mL of water was added dropwise by stirring for 3 h and the resulting mixture was left for 12 h at room temperature. The precipitate was filtered, washed with water and acetone, and dried at 60 °C. The yield was 70%. The melting point is 477-480 K. After that the HITO was recrystallized from the ethanol.  $^{1}$ H NMR (400 MHz, DMSO-d<sub>6</sub>;  $\delta$ , ppm): 8.98 s (H, NH), 9.34 s (H, NH), 13.10 s (H, OH). The purity of HITO was determined chromatographically with a mass spectrometric detection and it was 100%.

The solutions of CH<sub>3</sub>COONa and NaOH were prepared by dissolving of appropriate amount of CH<sub>3</sub>COONa and NaOH in water. The solutions of HCl and CH<sub>3</sub>COOH were obtained by dilution of concentrated HCl and CH<sub>3</sub>COOH with water. The universal buffer solutions (UBS) were prepared by mixing H<sub>3</sub>PO<sub>4</sub>, H<sub>3</sub>BO<sub>3</sub> and CH<sub>3</sub>COOH.<sup>31</sup>

#### 2. 3. Procedure

#### Spectral and protolytic characteristics of the HITO

In a series of 25.0 mL calibrated flask the volumes of HITO ( $8.0 \times 10^{-3}$  mol L<sup>-1</sup>), NaCl (2.0 mol L<sup>-1</sup>), UBS (1.5 mol L<sup>-1</sup>) and distilled water ( $\sim 15$  mL) were added. Then pH was adjusted in the acceptable range of 2.0-12.0 by NaOH (4.0 mol L<sup>-1</sup>) and distilled water was added up to the mark. For pH 1.0 the solution was prepared in a similar way, but without adding the UBS and pH was adjusted by HCl (6.0 mol L<sup>-1</sup>). Then the absorption spectra were measured against the distilled water.

### Recommended procedure for determination of Ru(IV) by using HITO

An aliquot of the solution that contained 12.5–152.5 µg of Ru(IV) was transferred into a 25.0 mL volumetric flask. To this solution 0.125 mL of  $8.0 \times 10^{-3}$  mol L<sup>-1</sup> HITO, 1.25 mL of 2.0 mol L<sup>-1</sup> NaCl, 2.0 mL of 4.0 mol L<sup>-1</sup> CH<sub>3</sub>COONa, and distilled water (~15 mL) were added. Then the pH (pH 5.0) was adjusted by means of CH<sub>3</sub>COOH or CH<sub>3</sub>COONa solutions and distilled water was added to complete the volume. After that the solutions were heated in the boiling water bath (~371 K) for 25 min and cooled to room temperature (~293–295 K). The absorbance was measured at 350 nm against a reagent blank, prepared in the same way but without the addition of Ru(IV).

#### Determination of ruthenium in the alloys

The  $Ce_{45}Ru_{25}Ga_{20}$  and  $TbRuGa_5$  alloys were prepared by art melting of pure components (not less than 99.9%) under an argon atmosphere. Then the alloys were annealed in evacuated quartz ampoules at 870 K for 720 h.<sup>32</sup>

0.05-0.1 g of the sample of alloy were dissolved in 10 mL of HCl + HNO<sub>3</sub> (1:1) mix. The obtained solution was evaporated to wet salts and dissolved in 50.0 mL of  $3.0 \text{ mol L}^{-1}$  HCl solution. If the alloy dissolved incompletely sintering of the new sample with oxidative mixture of NaOH and NaNO<sub>3</sub> (1:3) was carried out. The obtained solution was dissolved in HCl of  $3.0 \text{ mol L}^{-1}$  and the content of the beaker was quantitatively transferred into a 250.0 mL volumetric flask and diluted to the mark with distilled water. If necessary, the solution with lower concentration of ruthenium was prepared by dilution of stock solution with  $1.0 \text{ mol L}^{-1}$  hydrochloric acid. For ruthe-

nium determination, the aliquots of alloys (0.5–1.0 mL) were analyzed as described previously in "Recommended procedure for determination of Ru(IV) by using HITO". The content of ruthenium was calculated using the method of a normal calibration curve. Voltammetric determination of ruthenium(IV) ions using pyrocatechol violet at pH 4.0 (polarizing range of -0.5 to -1.5 V and the potential sweep rate of 0.5 V s<sup>-1</sup>) was used as the reference method.<sup>33</sup>

#### 3. Results and Discussion

# 3. 1. Spectral and Protolytic Characteristics of HITO in Water Medium

The new analytical reagent, 5-hydroxyimino-4-imino-1,3-thiazolidin-2-one (Fig. 1), is a sand color powder, which is poorly soluble in water (0.05 g  $\rm L^{-1}$ ), but soluble in ethanol, methanol, n-propanol, isoamyl alcohol, ethylene glycol, glycerol, dimethylformamide and dimethylsulfoxide.

Previous research of the spectral characteristics of HITO<sup>18–22</sup> has shown that its absorbance spectra depend on pH (Fig. 2). At pH 1.0–6.0 HITO has a maximum at the wavelength of 264 nm, pH 7.0–267 nm and at pH 8.0–12.0 two absorption bands:  $\lambda = 278$  nm,  $\lambda = 330$  nm. Beer's law is applicable at 256 nm (pH 5.0) over a wide concentration range (Fig. 3). The molar absorptivity at  $\lambda = 256$  nm is  $1.60 \times 10^4$  L mol<sup>-1</sup> cm<sup>-1</sup> and at  $\lambda = 278$  nm –  $1.24 \times 10^4$  L mol<sup>-1</sup> cm<sup>-1</sup>,  $\lambda = 330$  nm –  $1.02 \times 10^4$  L mol<sup>-1</sup> cm<sup>-1</sup>. The acid dissociation constant of HITO was found (p $K_a = 7.1$ ). This indicates that HITO is a weak acid.

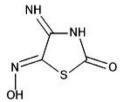
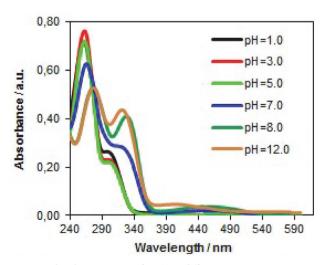


Fig 1. Structural formula of the HITO.



 $\textbf{Fig 2.} \ \textbf{Absorbance spectra of HITO at different pH}.$ 

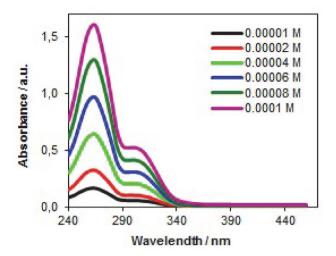


Fig 3. Absorbance spectra of HITO of different molar concentration.

The experimental results show that the absorbance spectra of HITO change over time in the range of pH 6.0–12.0. The influence of oxygen on the shape of absorption spectra of HITO over time at pH 8.0 and pH 9.0 was checked and it was found that oxygen does not affect the shape of absorption spectra. Therefore, we consider that changes in absorbance spectra of a reagent in the range of pH 6.0–12.0 are related to the hydrolysis of the imino group, which lasts for 60 min (Scheme 1). This process is irreversible, since after acidification of solutions to pH 2.0 spectrum of the reagent did not coincide with the spectrum of HITO in acidic media.

**Scheme 1.** Hydrolysis of 5-hydroxyimino-4-imino-1,3-thiazoli-din-2-one.

#### 3. 2. Interaction of Ru(IV) Ions with HITO

HITO forms with Ru(IV) ions a complex compound of sandy color in weakly acidic medium, just like with Pd(II), Pt(IV), Rh(III), and Ir(IV)<sup>18–22</sup>. The absorbance spectra of the reagent itself and Ru(IV)-HITO complex are shown in Fig. 4. According to Fig. 4, the maximum difference in absorbance of the HITO and complex compound is at 350 nm. Thus all futher absorbance measurements were carried out at 350 nm wavelength against reagent blank (where the absorbance of the reagent is negligible).

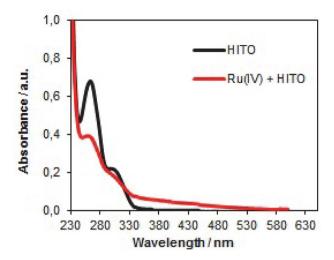


Fig 4. Absorbance spectra of reagent and complex Ru(IV) with HITO

The effect of pH on the absorbance of Ru(IV)-HITO complex compound was investigated over the range 1.0–7.0 in order to find the optimum conditions (Fig. 5). The optimum pH range for complex formation lies between pH 4.5–5.5. So, further investigations were carried out at pH 5.0.

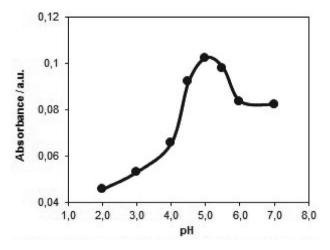
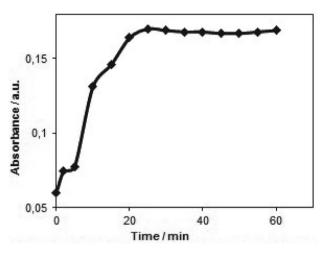


Fig 5. Effect of acidity on the maximum yield of  $\operatorname{Ru}(\operatorname{IV})$  with HITO colored complex.

The investigation of the influence of ionic strength on the maximum yield of the complex is necessary for the study of optimal conditions for complexation. Therefore, the influence of the concentration and nature of anions of sodium salts (NaCl, NaNO<sub>3</sub>, NaClO<sub>4</sub>, Na<sub>2</sub>SO<sub>4</sub>, CH<sub>3</sub>COONa) was investigated. The yield of the complex practically does not depend on the nature of anion. The SO<sub>4</sub><sup>2-</sup> and NO<sub>3</sub><sup>-</sup> ions practically do not affect the yield of complex, ClO<sub>4</sub><sup>-</sup> – in large surpluses slightly decreases the yield of the complex. The yield of the complex insignificantly increases in

the presence of Cl<sup>-</sup> and CH<sub>3</sub>COO<sup>-</sup> ions. Therefore, NaCl and CH<sub>3</sub>COONa were chosen as a reaction medium.

The interaction of Ru(IV) ions with HITO at room temperature ( $\sim$ 291–296 K) occurs very slowly. So the possibility of accelerating this process by heating the system in the boiling water bath ( $\sim$ 371 K) was investigated (Fig. 6). The results show the maximum yield of the complex is observed after heating for 25 min in the boiling water bath ( $\sim$ 371 K). The rapid formation of the Ru(IV)-HITO complex during heating can be related to reduction of the kinetic inertness of the [RuCl<sub>6</sub>]<sup>2-</sup> complex. The Ru(IV)-HITO complex is stable for 24 h.



**Fig 6.** Effect of heating time on the maximum yield of Ru(IV) with HITO colored complex.

The composition of the complex was determined by the mole-ratio method and the method of continuous variations (Fig. 7). The results of both methods agree and show that the molar ratio of Ru(IV) to HITO is 1:1. It was found that a 1.5–2-fold molar excess of the reagent is suffi-

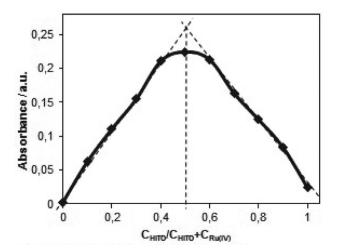


Fig 7. The method of continuous variations.

$$\begin{array}{c} HN \\ NH \\ S \\ OH \end{array} + [RuCl_{\theta}]^{2-} + H_3O^+ \longrightarrow CI \\ OH \\ OH \\ \end{array} + 2HCI + H_2O$$

**Scheme 2.** The proposed scheme of Ru-HITO complex formation.

cient to obtain maximum absorbances of the Ru(IV)-HI-TO complex. The formal stability constant is  $5.1 \times 10^6$ .

Based on the experimental results obtained from the study of the interaction of Ru(IV) ions with HITO and the data given in the literature,<sup>34,35</sup> it can be assumed that the complex formation most probably takes place as shown in Scheme 2.

Under the optimum conditions a calibration graph for Ru(IV) was obtained. The Beer's law is obeyed in the range from 0.5 to 6.1  $\mu g\ mL^{-1}$  for ruthenium(IV). The molar absorptivity is  $6.21\times 10^3\ L\ mol^{-1}\ cm^{-1}$ . The metrological characteristics of spectrophotometric determination of ruthenium(IV) with HITO are given in Table 1.

**Table 1.** The metrological characteristics of spectrophotometric determination of the Ru(IV) with HITO ( $C(HITO) = 8.0 \times 10^{-4} \, \text{mol L}^{-1}$ ;  $C(CH_3COOH + CH_3COONa) = 0.32 \, \text{mol L}^{-1}$ ;  $C(NaCl) = 0.1 \, \text{mol L}^{-1}$ ; pH = 5.0;  $\lambda$  = 350 nm; l = 1.0 cm; n = 5; P = 0.95)

Characteristic	Value
Limits of Beer's law, $C_{Ru(IV)}$ , $\mu g \text{ mL}^{-1}$	0.5-6.1
Calibration equation, $C_{Ru(IV)}$ , $\mu g mL^{-1}$	$\Delta A = 0.02 + 0.06 \times C$
Limit of detection, $C_{Ru(IV)}$ , $\mu g m L^{-1}$	0.2
Limit of quntification, $C_{Ru(IV)}$ , µg mL <sup>-1</sup>	0.6
Correlation coefficient, R	0.9993

# 3. 3. Effect of Foreign Ions on the Determination of Ru(IV)

The effect of some potentially interfering ions on the determination of ruthenium(IV) was investigated (Table

2). According to the obtained results most metals, which often accompany ruthenium, such as Ni(II), Co(II), Zn(II), Cd(II), Pb(II), Mn(II), REE, and other metals, do not interfere on the determination of Ru(IV). Instead, the technique is characterized by low selectivity concerning the noble metals or Cu(II) and Fe(III). Ag(I) intereferes significantly, even with tolerance limits up to 0.1, which is due to the influence of chloride ions that are in the solution. The presence of many anions, which were investigated, does not interfere (except EDTA) with the determination of Ru(IV). The selectivity to some cations can be increased using masking agents. For example, Cu(II) and Fe(III) were masked with tartrate ions (the tolerance limits reach 2 for Cu(II) and 4 for Fe(III)), citrate ions (the tolerance limits reach 10 for Cu(II) and 15 for Fe(III)) and phosphate ions (the tolerance limits reach 5 for Cu(II) and 10 for Fe(III)).

#### 3. 4. Application of the Method

In order to verify the possibility of the proposed method usage, initially the determination of ruthenium in synthetic samples was carried out. These solutions were prepared by adding known amount of the Ru(IV). The results of analysis Ru(IV) in synthetic mixture are given in Table 3.

The method was also applied to the determination of Ru(IV) in two samples of three-component alloys (Table 4). When ruthenium is added into alloys, mechanical strength increases significantly, while anticorrosion pro-

**Table 2.** Tolerance limits of foreign ions in Ru(IV) spectrophotometric determination using HITO ( $C(HITO) = 8.0 \times 10^{-4} \text{ mol L}^{-1}; C(Ru(IV)) = 2.0 \times 10^{-5} \text{ mol L}^{-1}; C(NaCl) = 0.1 \text{ mol L}^{-1}; C(CH_3COOH + CH_3COONa) = 0.32 \text{ mol L}^{-1}; pH = 5.0; \lambda = 350 \text{ nm}; l = 1.0 \text{ cm})$ 

Ion	$C_{\mathrm{ion}}$ : $C_{\mathrm{Ru(IV)}}$	Ion	$C_{\text{ion}}:C_{\text{Ru(IV)}}$	Ion	$C_{\text{ion}}$ : $C_{\text{Ru(IV)}}$
Pd(II)	0.2	Cu(II)	0.4	Al(III)	30
Ir(IV)	0.15	Pb(II)	100	Ba(II)	>200
Rh(III)	0.15	Cd(II)	100	Mg(II), Ca(II)	>200
Pt(IV)	0.14	Zn(II)	100	$C_2O_4^{2-}$	100
Au(III)	5	Yb(III)	>200	$F^-$	>200
Ag(I)	< 0.1	Tb(III)	>200	$SiO_3^{2-}$	>200
Hg(II)	5	Ho(III)	>200	EDTA	5
Co(II)	50	Gd(III)	>200	Sal-	45
Ni(II)	150	Ga(III)	10	Citr <sup>3-</sup>	>200
Fe(III)	0.6	Ce(IV)	10	Tart <sup>2-</sup>	50
Mn(II)	100	Sn(II)	3	$PO_4^{3-}$	100

Table 3. Determination of Ru(IV) with HITO in synthetic solutions (n = 3; P = 0.95)

Modeling solution	$C_{\mathbf{Ru}}$ : $C_{\mathbf{ion}}$	Added Ru(IV), μg	Found Ru(IV), $x \pm \frac{s \times t_{\alpha}}{\sqrt{n}}, \mu g$	RSD, %	RSD, %	
Ru-Pd-Ni	1:0.1:100	38.0	$39.9 \pm 3.8$	4.0		
Ru-Pt-Co	1:0.1:30	38.0	$39.2 \pm 2.9$	3.1		
Ru-Rh-Zn	1:0.1:50	38.0	$39.6 \pm 1.9$	2.0		

**Table 4.** Determination of ruthenium(IV) in alloys (n = 3; P = 0.95)

Intermetallides		Spectropho	otometry	Voltammetry		
	$\omega_{\scriptscriptstyle Ru}^{\scriptscriptstyle calc}, \%$	$\frac{-\rho_{Ru}}{\omega_{Ru}}\pm\frac{S\times t_{\alpha}}{\sqrt{n}}$ ,%	RSD, %	$\frac{-}{\omega}_{Ru}^{pr}\pm\frac{S\times t_{\alpha}}{\sqrt{n}},\%$	RSD, %	
Ce <sub>45</sub> Ru <sub>25</sub> Ga <sub>20</sub>	23.1	$23.0 \pm 0.9$	1.6	23.2 ± 1.2	2.1	
TbRuGa <sub>5</sub>	16.6	$16.4\pm0.8$	2.0	$16.7 \pm 0.6$	1.4	

perties, conductivity, etc. are improved. For these reasons, it is necessary to control the content of ruthenium in multicomponent systems.

The results are in perfect agreement with the ones

obtained by voltammetric method. According to the data presented in Table 4 and Table 5, the presented method can be applied to real samples with good reproducibility and accuracy.

Table 5. Comparison of the proposed method with other spectrophotometric methods for the determination of ruthenium(IV)

Reagent	Conditions	λ <sub>max</sub> , nm	ε <sub>max</sub> , L mol <sup>-1</sup> cm <sup>-1</sup>	Linear range μg mL <sup>-1</sup>	e, Interfering ions
<i>N,N</i> '-diphenylthiourea <sup>4</sup>	HCl + C <sub>2</sub> H <sub>5</sub> OH, 6 mol L <sup>-1</sup> HCl, 5 min (358 K);	630;	-;	6–18;	-;
	CHCl <sub>3</sub> , 30 min (373 K)	650	_	1.5–7.5	Pt(IV), Fe(II)
Quercetin <sup>7</sup>	0.01-0.1 mol L <sup>-1</sup> HCl, CH <sub>3</sub> OH+ H <sub>2</sub> O (1:1)	291	$5.0 \times 10^{3}$	0.11-30	-
1,10-Phenanthroline <sup>4,8</sup>	pH 6.0, 2 h (373 K)	448	$1.9 \times 10^{4}$	0.1-1.5	Platinoids
2-[(5-Bromo-2-pyridylazo)]- 5-diethylaminophenol and <i>N</i> -hydroxy- <i>N</i> , <i>N</i> <sup>*</sup> -diphenyl- benzamidine <sup>9</sup>	CH <sub>2</sub> Cl <sub>2</sub> , sodium citrate dihydrate, sodium acetate	560	2.99 × 10 <sup>4</sup>	0.2-2.8	Pd(II), Mn(II), Pb(II)
1,4-(2,4-Diphenylthio- semicarbazide) <sup>4</sup>	5.5–6.5 mol L <sup>-1</sup> HCl, CHCl <sub>3</sub> , 10–15 min (373 K)	565	$1.0 \times 10^{4}$	0.5-15.0	Oxidants
<i>p</i> -Nitrosodimethylaniline <sup>4</sup>	pH 4.0, 50 min (323 K)	610	$5.7 \times 10^{4}$	0.3-3.0	Platinoids
Sulphochlorophenolazo- rhodanine <sup>5,10,11</sup>	$2 \text{ mol } L^{-1} \text{ HCl} + 10 \text{ mol } L^{-1} $ CH <sub>3</sub> COOH, 30 min (353 K)	500	$1.6 \times 10^4$	0.5-30	Pt(IV), Rh(III)
Sulphobenzolazophenol- azorodanin <sup>10</sup>	pH 1.0-3.0, surfactants	540	$4.0 \times 10^4$	-	-
Xylenol orange <sup>12</sup>	pH 6.0	575	3.23 × 10 <sup>3</sup>	0.2-2.5	Al(III), V(IV), Cd(II), Cu(II), Ni(II), Zr(IV), Fe(III), Hf(IV), Zn(II), Co(II), Pb(II), Pd, Pt, Rh
5-hydroxyimino-4-imino- 1,3-thiazolidin-2-one	pH 5.0	350	$6.21 \times 10^{3}$	0.5-6.1	Platinoids, Cu(II), Fe(III), Ag(I)

# 3. 5. Comparison with other Spectrophotometric Methods

The proposed method has a better selectivity relative to Ni(II), Co(II), Mn(II), Cd(II), Zn(II), Pb(II), REE, etc. in comparison with other spectrophotometric methods for Ru determination mentioned in Table 5. There is no need to use highly acidic media and organic solvents.

#### 4. Conclusions

This work presents the spectral and protolytic characteristics of the new analytical reagent – HITO and a new spectrophotometric method for the ruthenium(IV) ions determination with this reagent. The developed method is simple, reproducibile, accurate, sufficiently sensitive and selective. It does not require the separation of the matrix and the use of toxic solvents. This method was successfully used for the determination of Ru(IV) in alloys and synthetic mixtures.

#### 5. References

- Q. Li, S. Zheng, Y. Xu, H. Xue, H. Pang, Chem. Eng. J. 2018, 333, 505-518. DOI:10.1016/j.cej.2017.09.170
- L. Wang, T. Liu, Chin. J. Catal. 2018, 39, 327–333.
   DOI:10.1016/S1872-2067(17)62994-2
- M. Balcerzak, Crit. Rev. Anal. Chem. 2002, 32, 181–226.
   DOI:10.1080/10408340290765524
- S. I. Ginzburg, N. A. Yezerskaya, I. V. Prokof'eva, N. V. Fedorenko, V. I. Shlenskaya, N. K. Belsky, *Analiticheskaya Khimiya Platinovykh Metallov*, Nauka, Moscow, Russia, 1972, p. 613.
- Ya. A. Zolotov, G. M. Varshal, V. M. Ivanov, Analiticheskaya Khimiya Metallov Platinovoi Gruppy, Editorial URSS, Moscow, Russia, 2003, p. 592.
- T. D. Avtokratova, Analiticheskaya Khimiya Ruteniya, IAN SSSR, Moscow, Russia, 1972, p. 264.
- M. Balcerzak, M. Kopacz, A. Kosiorek, E. Swiecicka, S. Kus, Anal. Sci. 2004, 20, 1333–1337. DOI:10.2116/analsci.20.1333
- 8. A. V. Bashilov, N. M. Kuzmin, V. K. Runov, *Zh. Anal. Khim.* **1998**, *53*, 738 –743.
- 9. P. Ratre, D. Kumar, Int. J. ChemTech Res. 2014, 6, 236-247.
- R. F. Gur'eva, S. B. Savvin, Usp. Khim. 1998, 67, 236–251.
   DOI:10.1070/RC1998v067n03ABEH000375
- R. F. Gur'eva, S. B. Savvin, Zh. Anal. Khim. 1995, 50, 1150– 1157.
- 12. T. Vrublevs'ka, O. Solovey, O. Volyanyk, Visnyk of the Lviv University. Series Chemistry 2003, 43, 126–129.
- 13. R. S. Lebedev, *Russ. Phys. J.* **2002**, *45*, 822–830. **DOI:**10.1023/A:1021928817028
- D. Kaminskyy, B. Zimenkovsky, R. Lesyk, *Eur. J. Med. Chem.* 2009, 44, 3627–3636. DOI:10.1016/j.ejmech.2009.02.023

- R. R. Panchuk, V. V. Chumak, M. R. Fil', D. Ya. Havrylyuk, B.
   S. Zimenkovsky, R. B. Lesyk, R. S. Stoika, *Biopolym. Cell* 2012, 28, 121–128. DOI:10.7124/bc.00003D
- T. I. Chaban, O. V. Klenina, B.S. Zimenkovsky, I.G. Chaban, V. V. Ogurtsov, L. S. Shelepeten, *Pharma Chem.* 2016, 8, 534–542.
- A. Tupys, J. Kalembkiewicz, Y. Ostapiuk, V. Matiichuk, O. Tymoshuk, E. Woźnicka, L. Byczyński, *J. Therm. Anal. Calorim.* 2017, 127, 2233–2242. DOI:10.1007/s10973-016-5784-0
- L. Lozynska, O. Tymoshuk, Chem. Chem. Technol. 2013, 7, 391–395. DOI:10.23939/chcht07.04.391
- L. Lozynska, O. Tymoshuk, In: O.L. Berezko, The Interaction of 5-hydroxyimino-4-imino-1,3-thiazolidin-2-one with Platinum(IV) Ions,3<sup>rd</sup> International Conference of Young Scientists CCT-13, Lviv, Ukraine, 2013, 166.
- 20. L. V. Lozynska, O. S. Tymoshuk, T. I. Chaban, *Metody Obekty Khim. Anal.* **2014**, *9*, 50–54. **DOI:**10.17721/moca.2014.50-54
- 21. L. V. Lozyns'ka, O. S. Tymoshuk, T. Ya. Vrublevs'ka, *Materials Science* **2015**, *6*, 870–876. **DOI**:10.1007/s11003-015-9795-y
- 22. L. V. Lozynska, O. S. Tymoshuk, Voprosy Khimii i Khimicheskoi Tekhnologii, 2014, 1, 80–85.
- L. Lozynska, O. Tymoshuk, T. Chaban, *Acta Chim Slov.* 2015, 62, 159–167. DOI:10.17344/acsi.2014.866
- A. Tupys, O. Tymoshuk, P. Rydchuk, Chem. Chem. Technol. 2016, 10, 19–25. DOI:10.23939/chcht10.01.019
- A. Tupys, J. Kalembkiewicz, Y. Bazel, L. Zapala, M. Dranka,
   Y. Ostapiuk, O. Tymoshuk, E. Woźnicka, *J. Mol. Struct.* 2017,
   1127, 722–733. DOI:10.1016/j.molstruc.2016.07.119
- M. Fizer, V. Sidey, A. Tupys, Y. Ostapiuk, O. Tymoshuk, Y. Bazel, *J. Mol. Struct.* 2017, 1149, 669–682.
   DOI:10.1016/j.molstruc.2017.08.037
- Y. Bazel, A. Tupys, Y. Ostapiuk, O. Tymoshuk, V. Matiychuk, J. Mol. Liq., 2017, 242, 471–477.
   DOI:10.1016/j.molliq.2017.07.047
- 28. Y. Bazel, A. Tupys, Y. Ostapiuk, O. Tymoshuk, J. Imricha, J. Šandrejová, *RSC Adv.*, **2018**, *8*, 15940–15950. **DOI:**10.1039/C8RA02039F
- 29. P. Wehner, J. Hindman, *J. Phys. Chem.* **1952**, *56*, 10–15. **DOI:**10.1021/j150493a003
- I. D. Komaritsa, Chem. Heterocycl. Compd. 1968, 4, 324–325.
   DOI:10.1007/BF00755270
- 31. Yu. Yu. Lur'e, *Spravochnik po analiticheskoi khimii*, Khimiya, Moscow, Russia, 1971, p. 456.
- 32. O. R. Myakush, A. A. Fedorchuk, A. V. Zelinskii, *Neorganicheskiye materialy*, **1998**, 34, 688–691.
- 33. T. Vrublevska, O. Tymoshuk *Voprosy Khimii i Khimicheskoi Tekhnologii*, **2001**, *2*, 9–11.
- 34. R. S. Corrêa, M. M. da Silva, A. E. Graminha, C. S. Meira, J. A. F. dos Santos, D.R.M. Moreira, M. B. P. Soares, G. Von Poelhsitz, E. E. Castellano, C. B. Jr, M. R. Cominetti, A. A. Batista, *J. Inorg. Biochem.* **2016**, *156*, 153–163. **DOI:**10.1016/j.jinorgbio.2015.12.024
- H. Meyer, M. Brenner, S. P. Höfert, T. O. Knedel, P.C. Kunz, A. M. Schmidt, A. Hamacher, M. U. Kassack, C. Janiak, *Dalton Trans.*, 2016, 45, 7605–7615. DOI:10.1039/C5DT04888E

#### **Povzetek**

Raziskali smo interakcijo Ru(IV) ionov z novim analiznim reagentom 5-hydroxyimino-4-imino-1,3-thiazolidin-2-one za uporabo v spektrofotometrični metodi. Kompleks nastane pri pH 5,0 v acetatnem pufru po segrevanju v vreli vodni kopeli (~371 K) 25 min. Kompleks ima maksimum absorpcije pri 350 nm in je stabilen 24 h. Beerov zakon velja v koncentracijskem območju 0,5–6,1  $\mu$ g mL<sup>-1</sup> Ru(IV). Molarna absorptivnost pri  $\lambda$  = 350 nm je 6,21 × 10<sup>3</sup> L mol<sup>-1</sup> cm<sup>-1</sup>. Meja zaznave te metode je 0,2  $\mu$ g mL<sup>-1</sup>. Raziskali smo tudi moteči učinek različnih kationov in anionov na spektrofotometrično določitev Ru(IV). Predlagano metodo smo uspešno uporabili za določitev Ru(IV) v zlitinah.