

SPECTROPHOTOMETRIC STUDY OF THE INTERACTION OF PLATINUM(IV) WITH NEW DERIVATIVES OF AZOLIDONES

Oleksandr Tymoshuk¹, Lesia Oleksiv^{1, ✉}, Petro Rydchuk¹, Taras Chaban²,
Svitlana Tymoshuk¹, Vasyl Matiychuk¹

<https://doi.org/10.23939/chcht14.02.139>

Abstract. The interaction of Pt(IV) ions with the new derivatives of azolidones by spectrophotometric method was investigated. The spectrophotometric method for the determination of Pt(IV) using 5-hydroxyimino-4-imino-1,3-thiazolidine-2-one at pH 5.0 in acetate buffer medium was elaborated. The proposed method was tested by determination of Pt(IV) in model solutions and metallic alloy.

Keywords: spectrophotometry, platinum(IV), azolidones, complex.

1. Introduction

Platinum and its alloys attract considerable attention due to valuable physical, chemical and mechanical properties. Platinum and its compounds have wide practical application in various industries, including: chemical, jewelry, metallurgical, pharmaceutical, medical, electro- and radioengineering, and others [1, 2]. If platinum is added to alloy its catalytic properties are improved. Alloys of platinum with cobalt are characterized by strong ferromagnetic properties [3]. Platinum catalysts are also widely used in the automotive industry [4]. Therefore, it is important to control the content of platinum in industrial and natural objects, which requires the development of new simple and reliable methods for this metal determination as the main component or admixture in various materials.

Different highly sensitive methods are used for the platinum determination, in particular: atomic absorption spectroscopy, inductively coupled plasma mass spectrometry, neutron activation analysis, and others [4]. However, the use of these methods is limited by the high cost of the equipment and most of them require prior separation and concentration to avoid matrix interference and increase sensitivity. Therefore, spectrophotometric methods, which provide high sensitivity due to the

application of specific and sensitive organic reagents, are often used as an alternative. It is known from literature that rhodanine derivatives are among the reagents for platinum determination [1, 5-8]. Some examples of these reagents used for the determination of platinum are given in Table 1.

Most of the reactions are long-lasting and the interaction takes place in a strongly acidic medium. Also, these techniques are not suitable for objects with low content of platinum and a significant siliceous matrix (ceramic silicate catalysts, silicate ores, field transistors, etc.). Conducting an analysis according to the proposed methods is either impossible or involves considerable difficulty in sample preparation. Therefore, the aim of our work was to develop simple, sensitive, selective, expressive and accessible methods for platinum determination using the new organic reagents that would be suitable for the analysis of such objects in non-acidic media (in order to carry out the determination in the presence of silicate ions, REM and other interfering ions without prior separation). In our previous work we demonstrated an important role of azoheterocycles in organic [9-12] and analytical chemistry [13-24]. In particular the new spectrophotometric methods, with good analytical characteristics, for the determination of Pd(II), Rh(III), Ir(IV), Ru(IV), Cu(II), Zn(II), Cd(II), Hg(II), and Ni(II) by using azolidone derivatives were developed [13-25].

Therefore, in our work, we have investigated the interaction of Pt(IV) ions with the new analytical reagents that are analogs of rhodanine and belong to the class of azolidones – 4-[2-(3-methyl-5-oxo-1-phenyl-1,5-dihydro-4*H*-pyrazol-4-ylidene)-hydrazino]-benzenesulfonate sodium (PHBS), 5-hydroxyimino-4-imino-1,3-thiazolidin-2-one (HITO) and 4-[*N*-(4-imino-2-oxo-thiazolidin-5-ylidene)-hydrazino]-benzenesulfonic acid (ITHBA), which were previously investigated as reagents for other platinum metals (Pd(II), Rh(III), Ir(IV), and Ru(IV)) [13-15, 17]. The research is of considerable relevance since a significant number of azolidone derivatives and their complexes with platinum metals are potential anti-cancer agents [26].

¹ Ivan Franko National University of Lviv,
6, Kyryla and Mefodiya St., 79005 Lviv, Ukraine

² Danylo Halytsky Lviv National Medical University,
69, Pekarska St., 79010 Lviv, Ukraine

✉ L_lozynska@ukr.net

© Tymoshuk O., Oleksiv L., Rydchuk P., Chaban T., Tymoshuk S.,
Matiychuk V., 2020

Table 1

Use of rhodanine derivatives for spectrophotometric determination of platinum

Reagent	Metal	Conditions	Ref.
Sulfochlorophenolazorhodanine	Pt(IV)	3M HCl, 4 h, $\lambda=500$ nm; 2M HCl + 2M H ₃ PO ₄ , ascorbic acid, 4 h, $\lambda=500$ nm	[1], [5], [6]
Sulfochlorophenolazorhodanine	Pt(II)	3M HCl + ascorbic acid, 20 h (293 K), $\lambda=500$ nm; 2M HCl + 2M H ₃ PO ₄ + ascorbic acid, 4 h (293 K), $\lambda=500$ nm	[1], [5], [7]
Sulfochlorophenolazothiopro-piorhodanine (tyrodine)	Pt(II)	7.6M H ₃ PO ₄ , 3 h, $\lambda=510$ nm	[6], [7]
Sulfochlorophenolazothiopro-piorhodanine (tyrodine)	Pt(IV)	7.6M H ₃ PO ₄ + ascorbic acid 3-4 h, $\lambda=510$ nm	[1]
<i>m</i> -Sulfobenzeneazorhodanine	Pt(IV)	2M H ₃ PO ₄ , 15 min (353 K), $\lambda=520$ nm	[5], [8]

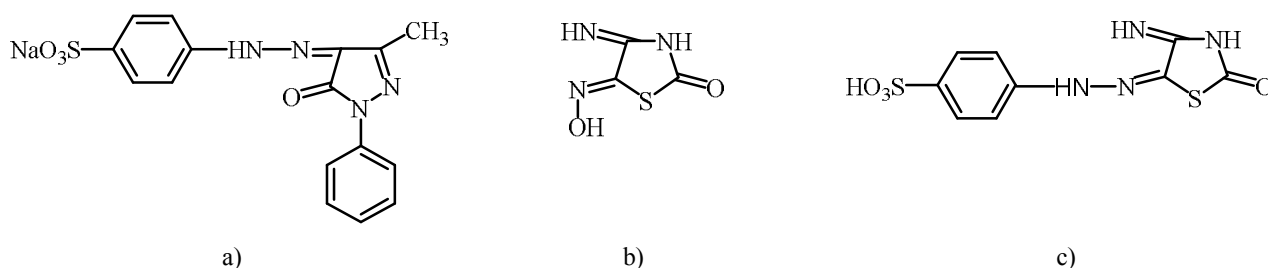


Fig. 1. Structural formulas of PHBS (a), HITO (b) and ITHBA (c)

PHBS is an orange powder, well soluble in water; HITO is a crystalline sand-colored powder, poorly soluble in water ($0.05 \text{ g}\cdot\text{l}^{-1}$), but well soluble in a number of organic solvents: ethanol, methanol, *n*-propanol, isoamyl alcohol, ethylene glycol, glycerol, dimethylformamide, and dimethyl sulfoxide. ITHBA is a yellow powder, well soluble in water. Structural formulas of these reagents are shown in Fig. 1.

2. Experimental

2.1. Reagents

A stock solution of Pt(IV) was prepared by dissolving the metallic platinum (99.999%) in a mixture of concentrated nitric and hydrochloric acids (1:3) by heating on a sand bath. The standard working solution of Pt(IV) was prepared by diluting an aliquot of platinum(IV) stock solution in $1.0 \text{ mol}\cdot\text{l}^{-1}$ HCl.

The stock solutions of 4-[2-(3-methyl-5-oxo-1-phenyl-1,5-dihydro-4*H*-pyrazol-4-ylidene)-hydrazino]-benzenesulfonate sodium and 4-[*N*-(4-imino-2-oxo-thiazolidin-5-ylidene)-hydrazino]-benzenesulfonic acid were prepared by dissolving the appropriate amounts of pre-purified reagents in distilled water.

A stock solution of 5-hydroxyimino-4-imino-1,3-thiazolidin-2-one was prepared by dissolving the appropriate amount of pre-purified reagent in 96% v/v ethanol.

Solutions of NaCl, CH₃COONa, NaOH, and other solutions of sodium salts (an anionic effect of which was investigated) were prepared by dissolving the respective salts in distilled water. The solutions of HCl and CH₃COOH were prepared by dilution of the corresponding concentrated acids. The standard solutions of different metals (which were used during the study of the selectivity) were prepared by dissolving the exact mass of the corresponding metal in hydrochloric or nitric acids, their mixture, or their salts in distilled water or in dilute HCl or HNO₃. The solution of Ru(IV) was prepared by sintering of metal with the oxidizing mixture NaNO₃ + NaOH (1:3) with further dissolving the fusion in $3.0 \text{ mol}\cdot\text{l}^{-1}$ HCl. The solutions of Ir(IV) and Rh(III) were prepared by sintering corresponding metal with the oxidizing mixture NaNO₃ + NaOH (1:3) and BaO₂ with further dissolving the fusion in $3.0 \text{ mol}\cdot\text{l}^{-1}$ of hydrochloric acid.

2.2. Equipment

Spectrophotometric measurements were performed using ULAB 108UV computerized spectrophotometer and 1.0 cm quartz cells.

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

The pH-meter model pH-150 M equipped with a combination glass electrode was used for pH measurements.

2.3. Procedure for Determination of Pt(IV) using HITO

An aliquot of the test solution containing Pt(IV) within $(7.0 \cdot 10^{-6})$ – $(8.0 \cdot 10^{-5})$ mol·l⁻¹ in the final volume, 0.25 ml of $8.0 \cdot 10^{-3}$ mol·l⁻¹ etanolic solution of 5-hydroxyimino-4-imino-1,3-thiazolidine-2-one, 1.25 ml of 2.0 mol·l⁻¹ solution of sodium chloride, 2.0 ml of 4.0 mol·l⁻¹ sodium acetate solution, and distilled water (~15 ml) were added in a volumetric 25.0 ml flask. The acidity of the solution obtained was checked at pH-meter, the pH value was adjusted to 5.0 by acetate acid or sodium acetate and distilled water was added to complete the volume. Measurement of the absorbance of the investigated solution was carried out after 60 min of heating of solutions in a boiling water bath (~371 K) and cooling to room temperature (~291–296 K) at the wavelength $\lambda = 350$ nm on a spectrophotometer using cuvettes with $l = 1.0$ cm against blank solution.

2.4. Procedure for Determination of Pt(IV) in the Alloy

Alloys weighing about 0.07 g were dissolved in 10–20 ml of concentrated chloride and nitric acid (3:1). The mixture was boiled in a sand bath for several hours. The solution was quantitatively transferred into a 50.0 ml volumetric flask and brought to the mark with 2.5M HCl. The working solution was prepared by diluting stock solution 10 times with 1.0 mol·l⁻¹ HCl. For the analysis aliquots of 1.0–2.0 ml were taken. The determination of

Pt(IV) in the alloy was carried out according to the procedure described in Subsection 2.3. The concentration of Pt(IV) was found using the pre-built calibration curve or comparison method.

3. Results and Discussion

3.1. Investigation of Pt(IV) Interaction with PHBS, HITO and ITHBA

Our previous researches of the spectral and protolytic characteristics of the PHBS, HITO and ITHBA [13, 15, 16] shown that these reagents are characterized by high values of molar absorption coefficients, which are in the range of $(1.02 \cdot 10^4)$ – $(2.53 \cdot 10^4)$ l·mol⁻¹·cm⁻¹. The greatest values were found for ITHBA and PHBS ($2.53 \cdot 10^4$ l·mol⁻¹·cm⁻¹ and $2.50 \cdot 10^4$ l·mol⁻¹·cm⁻¹, respectively) at 382 and 390 nm. Concentration constants of acidity were determined: for HITO $pK_a = 7.1$ and for ITHBA $pK_a = 10.0$. The investigated azolidones do not form tautomers in the concentration range from 10^{-5} to 10^{-4} mol·l⁻¹. It was found that HITO is unstable with time in the range of pH = 6.0–12.0, and ITHBA is unstable within pH = 10.0–12.0.

It was investigated that in the presence of Pt(IV) ions, the absorption spectra of PHBS in the pH range of 1.0–12.0 are characterized by some increase in absorption maximum at $\lambda = 250$ nm, but no changes occur in the visible region of the spectrum of the reagent itself. A similar situation was observed during the interaction of Pt(IV) with ITHBA, which means that using PHBS or ITHBA for spectrophotometric determination of platinum is inappropriate (Fig. 2).

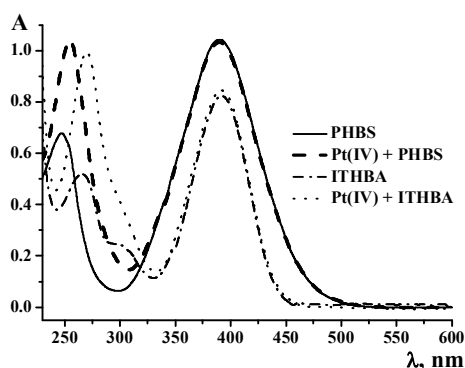


Fig. 2. Absorption spectra of PHBS, ITHBA and Pt(IV) with the reagents (PHBS: $C_{\text{Pt(IV)}} = 2.0 \cdot 10^{-5}$ mol·l⁻¹; $C_{\text{PHBS}} = 4.0 \cdot 10^{-5}$ mol·l⁻¹; $C_{\text{NaCl}} = 0.1$ mol·l⁻¹; pH = 5.0; $l = 1.0$ cm; ITHBA: $C_{\text{Pt(IV)}} = 2.0 \cdot 10^{-5}$ mol·l⁻¹; $C_{\text{ITHBA}} = 4.0 \cdot 10^{-5}$ mol·l⁻¹; $C_{\text{NaCl}} = 0.1$ mol·l⁻¹; pH = 8.0; $l = 1.0$ cm)

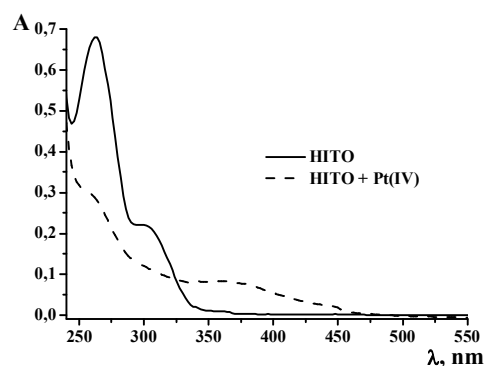


Fig. 3. Absorption spectra of HITO and complex Pt(IV) with HITO ($C_{\text{Pt(IV)}} = 2.0 \cdot 10^{-5}$ mol·l⁻¹; $C_{\text{HITO}} = 4.0 \cdot 10^{-5}$ mol·l⁻¹; $C_{\text{NaCl}} = 0.1$ mol·l⁻¹; pH = 5.0; $l = 1.0$ cm)

HITO interacts with Pt(IV) ions to form a complex [18, 19]. The electronic absorption spectra of the resulting complex and reagent are shown in Fig. 3.

3.1.1. The optimal conditions of the Pt(IV)–HITO complex formation

In the presence of Pt(IV) ions the maximum of HITO at 264 nm decreases and a shoulder of absorption in the wavelengths range of 325–450 nm is observed. The maximum difference in absorption of the reagent and the Pt(IV)–HITO complex is observed at 350 nm (Fig. 3), therefore, all further studies were conducted at this wavelength. The complex compound Pt(IV)–HITO is formed in wide limits of the medium acidity, and the maximum yield is observed at pH = 5.0–6.0 (Fig. 4). However, since HITO is unstable in the range of pH = 6.0–12.0, no research was conducted for the effect of pH on the formation of the Pt(IV) complex from HITO within these limits of the acidity of the medium.

The impact of the nature of the anions and the ionic strength on the interaction of Pt(IV) with HITO in the presence of various sodium salts was studied. Anions (Cl⁻,

NO₃⁻, SO₄²⁻, ClO₄⁻, CH₃COO⁻) practically do not effect the formation of the Pt(IV)–HITO complex. To create a constant ionic strength and stable pH the acetate buffer solution (0.32M) and sodium chloride (0.1M) were used as the reaction medium.

The complex formation of Pt(IV) with HITO occurs quite slowly at room temperature (~291–295 K). Since the kinetic inertness of the halide complexes of platinum metals can be overcome by heating, in the case of HITO, the formation of a colored complex compound Pt(IV) with HITO was studied under heating in a boiling water bath (~371 K, Fig. 5). Maximum values of absorbance for Pt(IV)–HITO compound without heating are achieved after 24 h, and when heated in a boiling water bath – after 60 min. Therefore, further research was carried out after 60 min of heating of solutions in a boiling water bath. The values of absorbance of the solution of complex obtained after heating remain stable for 8–10 h.

The ratio of components in the complex compound of Pt(IV) with HITO was determined by methods of continuous variations and mole-ratio (Figs. 6 and 7).

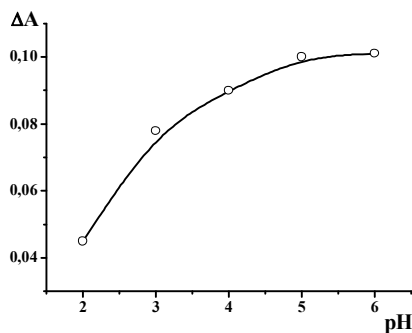


Fig. 4. Effect of pH on the Pt(IV)–HITO complex formation ($C_{\text{Pt(IV)}} = 2.0 \cdot 10^{-5} \text{ mol} \cdot \text{l}^{-1}$; $C_{\text{HITO}} = 4.0 \cdot 10^{-5} \text{ mol} \cdot \text{l}^{-1}$; $C_{\text{NaCl}} = 0.1 \text{ mol} \cdot \text{l}^{-1}$; pH = 5.0; $l = 1.0 \text{ cm}$; $\lambda = 350 \text{ nm}$)

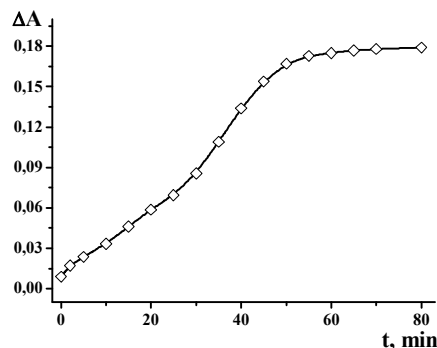


Fig. 5. Effect of heating time on the Pt(IV)–HITO complex formation ($C_{\text{Pt(IV)}} = 2.0 \cdot 10^{-5} \text{ mol} \cdot \text{l}^{-1}$; $C_{\text{HITO}} = 4.0 \cdot 10^{-5} \text{ mol} \cdot \text{l}^{-1}$; $C_{\text{NaCl}} = 0.1 \text{ mol} \cdot \text{l}^{-1}$; $C_{\text{CH}_3\text{COOH} + \text{CH}_3\text{COONa}} = 0.32 \text{ mol} \cdot \text{l}^{-1}$; pH = 5.0; $l = 1.0 \text{ cm}$; $\lambda = 350 \text{ nm}$)

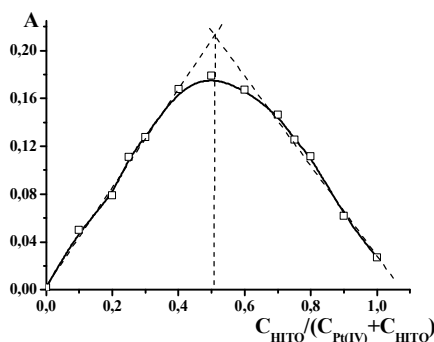


Fig. 6. The continuous variation curve for Pt(IV)–HITO complex ($C_{\text{Pt(IV)+HITO}} = 1.0 \cdot 10^{-4} \text{ mol} \cdot \text{l}^{-1}$; $C_{\text{NaCl}} = 0.1 \text{ mol} \cdot \text{l}^{-1}$; $C_{\text{CH}_3\text{COOH} + \text{CH}_3\text{COONa}} = 0.32 \text{ mol} \cdot \text{l}^{-1}$; pH = 5.0; $l = 1.0 \text{ cm}$; $\lambda = 350 \text{ nm}$; $t_{\text{heat.}} = 60 \text{ min}$ (~371 K))

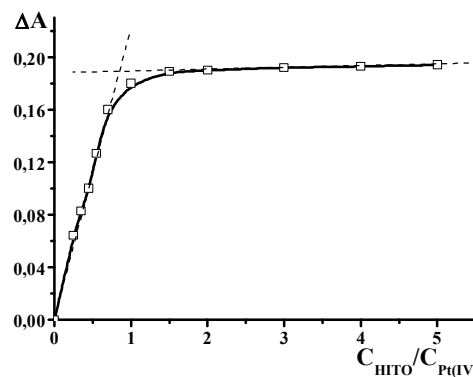


Fig. 7. The mole-ratio method for determination of the composition of the Pt(IV)–HITO complex ($C_{\text{Pt(IV)}} = 5.0 \cdot 10^{-5} \text{ mol} \cdot \text{l}^{-1}$; $C_{\text{NaCl}} = 0.1 \text{ mol} \cdot \text{l}^{-1}$; $C_{\text{CH}_3\text{COOH} + \text{CH}_3\text{COONa}} = 0.32 \text{ mol} \cdot \text{l}^{-1}$; pH = 5.0; $l = 1.0 \text{ cm}$; $\lambda = 350 \text{ nm}$; $t_{\text{heat.}} = 60 \text{ min}$ (~371 K))

As can be seen from Fig. 7, for maximum yield of the complex compound Pt(IV) with HITO 1–1.5-fold excess of the reagent is optimal.

The obtained results indicate the formation of a complex with the ratio of components Pt(IV):HITO=1:1. The value of effective molar absorption coefficient at 350 nm is $5.54 \cdot 10^3 \text{ l} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$. Since the calculation of the stability constant for the platinum complexes is rather complicated due to the long time of the equilibrium processes, it is possible to calculate the complex formal stability constant, equal to $\lg K^f = 5.8$.

3.1.2. Voltammetric investigation of the interaction of Pt(IV) with HITO

In order to confirm the complex formation between ions of Pt(IV) and HITO, a voltammetric method, namely, oscillovoltammetry, was used additionally (Fig. 8).

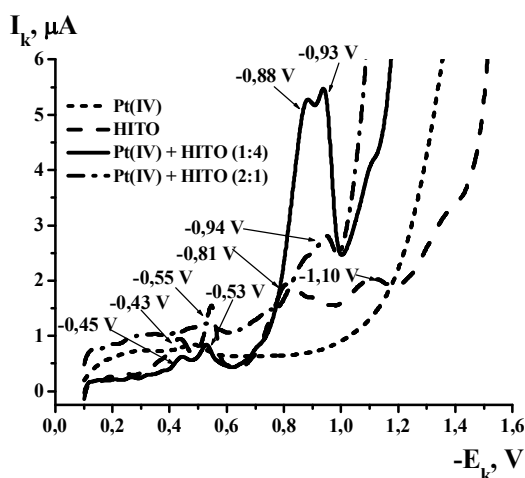


Fig. 8. Voltammograms of reduction Pt(IV) and HITO in the presence and in the absence of Pt(IV) ions ($C_{\text{HITO}} = 8.0 \cdot 10^{-5} \text{ mol} \cdot \text{l}^{-1}$; $C_{\text{NaCl}} = 0.1 \text{ mol} \cdot \text{l}^{-1}$; $C_{\text{CH}_3\text{COOH}} + \text{CH}_3\text{COONa} = 0.32 \text{ mol} \cdot \text{l}^{-1}$; pH = 5.0; $t_{\text{heat}} = 60 \text{ min}$ ($\sim 371 \text{ K}$); $V = 1.0 \text{ V/s}$)

The voltammograms of the reduction of Pt(IV), HITO and the compound Pt(IV)–HITO (Fig. 8) indicate that as a result of the interaction of platinum with HITO a complex is formed. With excess reagent in relation to the

metal, there is a decrease in the reduction peaks of the reagent itself, as well as their displacement. In the presence of HITO the restoration of platinum from the complex is facilitated, and later the ligand itself is reduced on the platinum. In this case, we can talk about the catalysis of the ligand.

3.2. Metrological Characteristics of the Developed Method

It is established that the magnitude of the analytical signal of the complex of Pt(IV) with HITO linearly depends on the concentration of platinum in the solution. Metrological characteristics of the spectrophotometric determination of Pt(IV) with 5-hydroxyimino-4-imino-1,3-thiazolidine-2-one are given in Table 2. The developed method is characterized by wide linear range and is sufficiently sensitive.

3.3. Investigation of the Foreign Ions Effect

The effect of various foreign ions, that are often found in platinum-containing objects, on the spectrophotometric determination of Pt(IV) using HITO was researched (Table 3) [18, 19]. The results presented in Table 3 show that the determination of Pt(IV) using HITO is not interfered with the significant excesses of Co(II), Ni(II), Mn(II), Zn(II), Cd(II), Pb(II), Yb(III), Tb(III), Ho(III), Gd(III), Ca(II), Mg(II), and Ba(II). The investigated anions do not interfere with large excesses, therefore some of them were used as masking agents to eliminate the interfering effects of certain cations (Table 4). Due to this, it was possible to increase the selectivity of the developed method for such cations as Ru(IV), Cu(II), Fe(III), and Al(III).

3.4. Application of the Developed Method

The precision and accuracy of the spectrophotometric determination of Pt(IV) with HITO was studied by analyzing the model solutions using the “added-found” method. The results are shown in Table 5.

Table 2

Metrological characteristics of spectrophotometric determination of Pt(IV) with HITO

Linear range, $C_{\text{Pt(IV)}}, \text{mol} \cdot \text{l}^{-1}$	Equation of the calibration curve, $C_{\text{Pt(IV)}}, \text{mol} \cdot \text{l}^{-1}$	Limit of detection, $\text{mol} \cdot \text{l}^{-1}$	Correlation coefficient, R
$7.0 \cdot 10^{-6} - 8.0 \cdot 10^{-5}$	$\Delta A_{350} = (0.014 \pm 0.004) + (5.79 \pm 0.09) \cdot 10^3 \cdot C_{\text{Pt(IV)}}$	$2.4 \cdot 10^{-6}$	0.9995

Notes: $C_{\text{HITO}} = 8.0 \cdot 10^{-5} \text{ mol} \cdot \text{l}^{-1}$; $C_{\text{NaCl}} = 0.1 \text{ mol} \cdot \text{l}^{-1}$; $C_{\text{CH}_3\text{COOH}} + \text{CH}_3\text{COONa} = 0.32 \text{ mol} \cdot \text{l}^{-1}$; pH = 5.0; $l = 1.0 \text{ cm}$; $\lambda = 350 \text{ nm}$; $n = 5$; $P = 0.95$

Table 3

Selectivity of spectrophotometric determination of Pt(IV) with HITO

Ion	$C_{Pt(IV)}:C_{ion}$	Ion	$C_{Pt(IV)}:C_{ion}$	Ion	$C_{Pt(IV)}:C_{ion}$
Pd(II)	1:0.15	Ga(III)	1 : 10	Fe(III)	1 : 0.1
Rh(III)	1:0.1	Sn(II)	1 : 3	Cu(II)	1 : 0.1
Ir(IV)	1 : 0.2	Ce(IV)	1 : 10	Mn(II)	1 : >200
Ru(IV)	1 : 0.25	Al(III)	1 : 8	SiO ₃ ²⁻	1 : >200
Ag(I)	1 : <0.1	Ba(II)	1 : 100	F ⁻	1 : >200
Au(III)	1 : 7	Mg(II), Ca(II)	1 : >200	EDTA	1 : >200
Hg(II)	1 : 10	Pb(II)	1 : 75	PO ₄ ³⁻	1 : >200
Yb(III)	1 : >200	Cd(II)	1 : 75	C ₂ O ₄ ²⁻	1 : >200
Tb(III)	1 : >200	Zn(II)	1 : 100	Citr ³⁻	1 : >200
Ho(III)	1 : >200	Ni(II)	1 : 150	Tart ²⁻	1 : >200
Gd(III)	1 : >200	Co(II)	1 : 50	Sal ⁻	1 : 100

Notes: $C_{Pt(IV)} = 2.0 \cdot 10^{-5} \text{ mol} \cdot \text{l}^{-1}$; $C_{HITO} = 8.0 \cdot 10^{-5} \text{ mol} \cdot \text{l}^{-1}$; $C_{NaCl} = 0.1 \text{ mol} \cdot \text{l}^{-1}$; $C_{CH_3COOH} + CH_3COONa = 0.32 \text{ mol} \cdot \text{l}^{-1}$; pH = 5.0; $l = 1.0 \text{ cm}$; $\lambda = 350 \text{ nm}$

Table 4

Permissible excesses of foreign ions during spectrophotometric determination of Pt(IV) with HITO using masking agents

Ion	Permissible relations $C_{Pt(IV)}:C_{ion}$	Masking agent ($C_{Pt(IV)}:C_{ion}:C_{masking\ agents}$)				
		EDTA	Cit ³⁻	Tart ²⁻	F ⁻	PO ₄ ³⁻
Ru(IV)	1:0.25	1:2:200	–	–	–	–
Cu(II)	1:0.1	1:10:200	1:15:200	1:4:200	–	1:5:200
Fe(III)	1:0.1	1:20:100	1:10:100	1:5:100	1:5:200	1:10:100
Al(III)	1:8	–	–	–	1:30:200	–

Notes: $C_{Pt(IV)} = 2.0 \cdot 10^{-5} \text{ mol} \cdot \text{l}^{-1}$; $C_{HITO} = 8.0 \cdot 10^{-5} \text{ mol} \cdot \text{l}^{-1}$; $C_{NaCl} = 0.1 \text{ mol} \cdot \text{l}^{-1}$; $C_{CH_3COOH} + CH_3COONa = 0.32 \text{ mol} \cdot \text{l}^{-1}$; pH = 5.0; $l = 1.0 \text{ cm}$; $\lambda = 350 \text{ nm}$; sign “–” means not investigated

Table 5

Spectrophotometric determination of Pt(IV) with HITO in model solutions

System	$C_{Pt}:C_{ion}$	Added Pt(IV), μg	Found Pt(IV), $\bar{x} \pm \frac{S \cdot t_{\alpha}}{\sqrt{n}}$, μg	S_r , %
Pt-Ru-Co-Ba	1:0.16:30:100	98	98±6	2.6
Pt-Ir-Mn-Cd	1:0.1:100:50		104±10	3.9
Pt-Pd-Ni-Pb	1:0.1:75:50		102±8	3.1

Notes: $C_{HITO} = 8.0 \cdot 10^{-5} \text{ mol} \cdot \text{l}^{-1}$; $C_{NaCl} = 0.1 \text{ mol} \cdot \text{l}^{-1}$; $C_{CH_3COOH} + CH_3COONa = 0.32 \text{ mol} \cdot \text{l}^{-1}$; pH = 5.0; $l = 1.0 \text{ cm}$; $\lambda = 350 \text{ nm}$; $n = 3$; $P = 0.95$

Table 6

The results of the spectrophotometric determination of platinum in intermetallide Yb₂Pt₂Ga using HITO

Method of determination	ω_{Pt}^{calc} , %	$\omega_{Pt}^{real} \pm \frac{S \cdot t_{\alpha}}{\sqrt{n}}$, %	S_r , %
Spectrophotometry	48.4	49.9±3.3	2.7
Voltammetry		47.6±2.4	2.0

Notes: $C_{HITO} = 8.0 \cdot 10^{-5} \text{ mol} \cdot \text{l}^{-1}$; $C_{NaCl} = 0.1 \text{ mol} \cdot \text{l}^{-1}$; $C_{CH_3COOH} + CH_3COONa = 0.32 \text{ mol} \cdot \text{l}^{-1}$; pH = 5.0; $l = 1.0 \text{ cm}$; $\lambda = 350 \text{ nm}$; $n = 3$; $P = 0.95$

The developed method of the spectrophotometric determination of Pt(IV) with 5-hydroxyimino-4-imino-1,3-thiazolidine-2-one was used during the analysis of the intermetallic tricomponent alloy Yb₂Pt₂Ga. Samples of alloy were synthesized on the inorganic chemistry department of Ivan Franko Lviv National University. The correctness of the results of Pt(IV) determination in this alloy was verified using voltammetric method for determining platinum for wave reduction ($E_{1/2} = -0.15$ V) from its complex [PtCl₆]²⁻ [1, 2].

The quantities of ytterbium and gallium contained in the alloy did not interfere with the determination of Pt(IV) with HITO, therefore, there was no masking. The results of Pt(IV) determination in alloy are presented in Table 6.

As can be seen from the table, the obtained results are well correlated with the values determined by voltammetric method and calculated by atomic percent. The relative standard deviation does not exceed the error of the spectrophotometric methods of analysis.

4. Conclusions

It was established that the new derivatives of azolidones PHBS and ITHBA are not suitable for the spectrophotometric determination of Pt(IV) ions. However, HITO interacts with Pt(IV) to form a complex which made it possible to develop a new method for the determination of platinum(IV) ions.

It can be asserted that the developed method based on the reaction of Pt(IV) with 5-hydroxyimino-4-imino-1,3-thiazolidine-2-one is characterized by rather good chemical and analytical characteristics, and also it allows to carry out the determination in less aggressive environments than the known methods. This method can be successfully used for the analysis of platinum in various objects.

References

- [1] Zolotov Yu., Varshal G., Ivanov V.: *Analiticheskaia Khimia Metallov Platinovoi Gruppy: Sbornik Obzornykh Statei*. Editorial URSS, Moskva 2003.
- [2] Ginzburg S., Yezerskaya N., Prokofiev I. *et al.*: *Analiticheskaia Khimia Platinovykh Metallov*. Nauka, Moskva 1972.
- [3] Pedersen A., Ulrikkeholm E., Escudero-Escribano M. *et al.*: *Nano Energy*, 2016, **29**, 249. <https://doi.org/10.1016/j.nanoen.2016.05.026>
- [4] Georgieva M., Andonovski B.: *Anal. Bioanal. Chem.*, 2003, **375**, 836. <https://doi.org/10.1007/s00216-003-1783-7>
- [5] Gur'eva R., Savvin S.: *J. Anal. Chem.*, 2002, **57**, 980. <https://doi.org/10.1023/A:1020917221896>

- [6] Gur'eva R., Savvin S.: *Russ. Chem. Rev.*, 1998, **67**, 209. <https://doi.org/10.1070/RC1998v067n03ABEH000375>
- [7] Savvin S., Gur'eva R.: *Talanta*, 1987, **34**, 87. [https://doi.org/10.1016/0039-9140\(87\)80012-7](https://doi.org/10.1016/0039-9140(87)80012-7)
- [8] Gur'eva R., Savvin S.: *Zh. Anal. Khimii*, 1995, **50**, 1150.
- [9] Ostapiuk Yu., Obushak M., Matiychuk *et al.*: *Tetrahedron Lett.*, 2012, **53**, 543. <https://doi.org/10.1016/j.tetlet.2011.11.093>
- [10] Matiichuk V., Potopnyk M., Obushak N.: *Russ. J. Org. Chem.*, 2008, **44**, 1352. <https://doi.org/10.1134/S1070428008090182>
- [11] Gorak Yu., Obushak N., Matiichuk V. *et al.*: *Russ. J. Org. Chem.*, 2009, **45**, 541. <https://doi.org/10.1134/S1070428009040125>
- [12] Zelisko N., Atamanyuk D., Ostapiuk Yu. *et al.*: *Tetrahedron*, 2015, **71**, 9501. <https://doi.org/10.1016/j.tet.2015.10.019>
- [13] Lozynska L., Tymoshuk O.: *Chem. Chem. Technol.*, 2013, **7**, 391. <https://doi.org/10.23939/chcht07.04.391>
- [14] Lozynska L., Tymoshuk O., Vrublevs'ka T.: *Mater. Sci.*, 2015, **50**, 870. <https://doi.org/10.1007/s11003-015-9795-y>
- [15] Lozynska L., Tymoshuk O., Chaban T.: *Acta Chimica Slovenica*, 2015, **62**, 159. <https://doi.org/10.17344/acsi.2014.866>
- [16] Tymoshuk O., Fedyshyn O., Oleksiv L. *et al.*: *Visnyk Lviv Univ. Ser. Chem.*, 2018, **59**, 216. <https://doi.org/10.30970/vch.5901.216>
- [17] Lozynska L., Tymoshuk O.: *Voprosy Khimii i Khimicheskoi Tekhnologii*, 2014, **1**, 80.
- [18] Lozynska L., Tymoshuk O.: *Pat. UA 91160*, Publ. Jun. 25, 2014.
- [19] Lozynska L., Tymoshuk O.: 3rd International Conference of Young Scientists "CCT-2013", Ukraine, Lviv 2013, 166.
- [20] Tupys A., Kalemekiewicz J., Bazel Y. *et al.*: *J. Mol. Struct.*, 2017, **1127**, 722. <https://doi.org/10.1016/j.molstruc.2016.07.119>
- [21] Bazel Y., Tupys A., Ostapiuk Y. *et al.*: *RSC Adv.*, 2018, **8**, 15940. <https://doi.org/10.1039/c8ra02039f>
- [22] Bazel Y., Tupys A., Ostapiuk Y. *et al.*: *J. Mol. Liq.*, 2017, **242**, 471. <https://doi.org/10.1016/j.molliq.2017.07.047>
- [23] Tupys A., Kalemekiewicz J., Ostapiuk Y. *et al.*: *J. Therm. Anal. Calorim.*, 2017, **127**, 2233. <https://doi.org/10.1007/s10973-016-5784-0>
- [24] Fizer M., Sidey V., Tupys A. *et al.*: *J. Mol. Struct.*, 2017, **1149**, 669. <https://doi.org/10.1016/j.molstruc.2017.08.037>
- [25] Tupys A., Tymoshuk O., Rydchuk P.: *Chem. Chem. Technol.*, 2016, **10**, 19. <https://doi.org/10.23939/chcht10.01.019>
- [26] Chaban T., Panchuk R., Klenina O. *et al.*: *Biopolym. Cell*, 2012, **28**, 389. <https://doi.org/10.7124/bc.000075>

Received: September 18, 2018 / Revised: October 12, 2018 / Accepted: December 22, 2018

СПЕКТРОФОТОМЕТРИЧНЕ ДОСЛІДЖЕННЯ ВЗАЄМОДІЇ ПЛАТИНИ(IV) З НОВИМИ ПОХІДНИМИ АЗОЛІДОНІВ

Анотація. Спектрофотометричним методом досліджено взаємодію йонів Pt(IV) з новими похідними азолідонів. Розроблено методику спектрофотометричного визначення платини(IV) за допомогою 5-гідроксимино-4-іміно-1,3-тіазолідин-2-ону за рН 5,0 у середовищі ацетатного буферу. Запропонований метод було апробовано під час визначення Pt(IV) у модельних розчинах та металічному сплаві.

Ключові слова: спектрофотометрія, платина(IV), азолідони, комплекс.