

## Spectrophotometric method for palladium determination using 5-hydroxyimino-4-imino-1,3-thiazolidin-2-one and application to the analysis of intermetallides

Lesya LOZYNSKA<sup>1\*</sup>, Oleksandr TYMOSHUK<sup>1</sup>, Petro RYDCHUK<sup>1</sup>

<sup>1</sup> Department of Analytical Chemistry, Faculty of Chemistry, Ivan Franko National University of Lviv, Kyryla i Mefodiya St. 6, 79005 Lviv, Ukraine

\* Corresponding author. Tel.: +380-32-2394048; e-mail: l\_lozynska@ukr.net

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This work describes the application of a new, simple and rapid spectrophotometric method to the determination of palladium in the intermetallides  $\text{Yb}_{40}\text{Pd}_{38}\text{Sn}_{22}$  and  $\text{Yb}_{40}\text{Pd}_{40}\text{Ga}_{20}$ . The method is based on the interaction of palladium(II) ions with 5-hydroxyimino-4-imino-1,3-thiazolidin-2-one at  $\text{pH} = 5.0$ , in a medium of acetate buffer and sodium chloride. The range of the determined concentrations of palladium is  $6.0 \cdot 10^{-6}$ - $6.0 \cdot 10^{-5}$  M.

Intermetallides / Palladium(II) / Spectrophotometry / 5-hydroxyimino-4-imino-1,3-thiazolidin-2-one

### Introduction

Palladium-containing materials possess valuable chemical and physical properties. Consequently, they play an important role in different industries. Palladium and its alloys have a wide range of applications, both in chemical industry and in instrumentation. They also have widespread use in dental and medical devices and the manufacture of jewelry. Palladium and palladium-based alloys can store hydrogen isotopes at moderate temperatures and pressures [1]. In the last few years, palladium has been used as one of the components of a three-component catalyst for automobile exhaust fumes [2]. Palladium-based alloys are widely used in dentistry [3,4]. The evaluation of the palladium content in intermetallides obtained after fusion and other samples is an important task and requires the development of new methods for reliable determination in a wide range of concentrations.

One of the common methods for the determination of palladium is spectrophotometry, the main advantages of which are simplicity, accessibility and rapidity. There exist many spectrophotometric methods for the determination of palladium, using organic or inorganic reagents, but they have some limitations [5,6]. Therefore, the search for new accessible, selective and sensitive reagents, which would make it possible to determine the palladium content also in complex objects, is an important task.

Among the large number of known reagents, azolidons and their derivatives, which contain functional groups with electron donor atoms S, N, O [7], have attracted special interest. Rodanine, which belongs to the class of azolidons, and its derivatives are successfully used in analytical practice as reagents for the determination of noble and heavy metals [8-14].

We used a new organic reagent, 5-hydroxyimino-4-imino-1,3-thiazolidin-2-one (HITO), for the spectrophotometric determination of palladium. It was found that HITO forms a new compound with Pd(II) ions [15,16], a sufficiently stable complex with the components in the ratio 1:1. The optimal conditions for the formation of this compound and some of its spectrophotometric characteristics are reported in Table 1. This method is simple and rapid. The intensity of the analytical signal used in the spectrophotometric determination of palladium(II) with HITO depends linearly on the concentration of metal ion in solution. The metrological characteristics of the developed method are presented in Table 2 ( $n$  = number of parallel experiments,  $P$  = confidence probability). The method of spectrophotometric determination of palladium(II) using 5-hydroxyimino-4-imino-1,3-thiazolidin-2-one is characterized by good sensitivity and can be used in a wide concentration range of the metal. We have now applied this method to the determination of palladium in two alloys of composition  $\text{Yb}_{40}\text{Pd}_{38}\text{Sn}_{22}$  and  $\text{Yb}_{20}\text{Pd}_2\text{Ga}_{78}$ .

**Table 1** Spectrophotometric characteristics of compound of Pd(II) with HITO.

$\lambda_{\text{opt}}$ , nm	$pH_{\text{opt}}$	$\epsilon_{\lambda}$ , L·mol <sup>-1</sup> ·cm <sup>-1</sup>	Me:L	lg $\beta$	$t_{\text{heat}}$ , min
350	5.0	$5.9 \cdot 10^3$	1:1	6.0	10

**Table 2** Metrological characteristics of the spectrophotometric determination of palladium(II) with HITO ( $C_{\text{HITO}} = 8.0 \cdot 10^{-5}$  M;  $C_{\text{NaCl}} = 0.1$  M;  $C_{\text{CH}_3\text{COONa}} = 0.32$  M;  $pH = 5.0$ ;  $l = 1.0$  cm;  $\lambda = 350$  nm;  $n = 5$ ;  $P = 0.95$ ).

Linearity, M	Calibration equation, $C_{\text{Pd}}$ , M	$C_{\text{min}}$ , M	$C_{\text{lim}}$ , M	Correlation coefficient, $R$
$6.0 \cdot 10^{-6}$ - $6.0 \cdot 10^{-5}$	$\Delta A_{350} = 0.012 + 6260C_{\text{Pd}}$	$2.1 \cdot 10^{-6}$	$6.3 \cdot 10^{-6}$	0.998

## Experimental

All the aqueous solutions used in the research were prepared using distilled water. All the chemicals were of analytical grade.

A stock solution of Pd(II) was prepared by dissolving metallic palladium (99.999 %) in a mixture of concentrated HNO<sub>3</sub> and HCl (1:3). Standard Pd(II) solutions were prepared by dissolving an aliquot of palladium(II) stock solution in 1.0 M HCl.

A solution of 5-hydroxyimino-4-imino-1,3-thiazolidin-2-one was prepared by dissolving the accurate weight of the reagent in 96 % v/v ethanol.

Solutions of CH<sub>3</sub>COONa, NaCl and NaOH were prepared by dissolving appropriate amounts of CH<sub>3</sub>COONa, NaCl and NaOH in water. The solution of HCl was prepared by dilution of concentrated HCl.

Absorption spectra were recorded using a 108 UV/ULAB spectrophotometer and a 1 cm quartz cell. All of the absorbance measurements were performed at ~20 °C.

The *pH* measurements were carried out with a pH-meter, model pH-150 M, equipped with a combination glass electrode (Gomelsky Plant of Measuring Devices, Belarus).

Voltammetric investigations were carried out using a CLA-03 oscillograph with a digital setup, equipped with a computer and a three-electrode thermostated cell (electrode-indicator, cathode – a drop mercury electrode; reference electrode, anode – a mercury chloride (saturated calomel) electrode; auxiliary electrode – platinum) using linear potential sweep. Dissolved oxygen was removed from the investigated solutions by passing argon for 15 min.

Activation of the solutions was performed by thermal treatment in a boiling water bath.

## Results and discussion

The method of spectrophotometric determination of palladium using 5-hydroxyimino-4-imino-1,3-thiazolidin-2-one was applied to the analysis of the ternary intermetallic systems Yb<sub>40</sub>Pd<sub>38</sub>Sn<sub>22</sub> ( $\omega_{\text{Pd}} = 29.8$  % (w/w)) and Yb<sub>40</sub>Pd<sub>40</sub>Ga<sub>20</sub> ( $\omega_{\text{Pd}} = 33.9$  % (w/w)). Before using the technique to

determine palladium in real samples, including intermetallics, it was necessary to investigate the selectivity of the method. Therefore the influence of the most common related ions and some masking agents was investigated. The results of this study are shown in Table 3. As seen from this table, the developed method is characterized by good selectivity, since even when present in large amounts, alkaline-earth metals, Ni(II), Co(II), Pb(II), Cd(II), Zn(II), and other ions that are often included in palladium-containing objects, do not interfere. The selectivity relative to Cu(II) and Fe(III) ions (from 5-fold to 40-fold excess) could be improved by using one of the following masking agents: EDTA, Citr<sup>3-</sup>, Tart<sup>2-</sup>, PO<sub>4</sub><sup>3-</sup>. It was also possible to increase the selectivity in regard to ruthenium(IV), using EDTA ( $C_{\text{Pd(II)}}:C_{\text{Ru(IV)}} = 1:1$ ). Ga(III), Sn(II) and Yb(III) ions, in the amounts contained in the studied intermetallics, do not interfere with the determination of palladium.

### Dissolution of the intermetallic samples

The alloys were dissolved in a mixture of concentrated HCl and HNO<sub>3</sub> (3:1) under heating. To obtain solutions of the analytes, 0.1-0.2 g of the intermetallic alloy were dissolved in 10-20 ml of a mixture of the above-mentioned acids. The mixture was boiled in a beaker in a sand bath for 1-2 hours. The dry residue was dissolved in a 2.5 M HCl solution and transferred into a 100.0 ml volumetric flask.

### Determination of palladium in intermetallics

For the analysis, aliquots of 0.2-0.3 ml were taken. The palladium content was evaluated using the method of normal calibration curve, by means of an appropriate analytical procedure of determination. The duration of an analysis without preliminary sample preparation was approximately 1 hour.

Procedure for determining palladium: 0.25 ml of the  $8.0 \cdot 10^{-3}$  M ethanolic solution of HITO and the aliquots of Pd(II) solution, containing  $6.0 \cdot 10^{-6}$ - $6.0 \cdot 10^{-5}$  M of palladium in the final volume, were placed into a beaker. Then 2.0 ml of 4.0 M sodium acetate and 1.25 ml of 2.0 M sodium chloride were added to maintain constant ionic strength. Distilled water was poured to a total volume of ~15-20 ml.

**Table 3** Tolerance ratios of interfering ions during the spectrophotometric determination of Pd(II) in the presence of HITO ( $C_{\text{HITO}} = 8.0 \cdot 10^{-5}$  M;  $C_{\text{Pd(II)}} = 2.0 \cdot 10^{-5}$  M;  $C_{\text{NaCl}} = 0.1$  M;  $C_{\text{CH}_3\text{COONa}} = 0.32$  M;  $pH = 5.0$ ;  $l = 1.0$  cm;  $\lambda = 350$  nm).

Ion	$C_{\text{ion}}:C_{\text{Pd(II)}}$	Ion	$C_{\text{ion}}:C_{\text{Pd(II)}}$	Ion	$C_{\text{ion}}:C_{\text{Pd(II)}}$
Yb(III)	1 : >200	Fe(III)	1 : 0.5	Mg(II)	1 : >200
Sn(II)	1 : 3	Mn(II)	1 : >200	Citr <sup>3-</sup>	1 : >200
Ga(III)	1 : 15	Cu(II)	1 : 0.6	Sal <sup>-</sup>	1 : 100
Ru(IV)	1 : 0.2	Cd(II)	1 : 100	Tart <sup>2-</sup>	1 : >200
Rh(III)	1 : 0.25	Zn(II)	1 : >200	EDTA	1 : >200
Pt(IV)	1 : 1	Pb(II)	1 : 100	F <sup>-</sup>	1 : >200
Ir(IV)	1 : 1	Al(III)	1 : 30	PO <sub>4</sub> <sup>3-</sup>	1 : >200
Ni(II)	1 : 150	Ba(II)	1 : 100	C <sub>2</sub> O <sub>4</sub> <sup>2-</sup>	1 : >200
Co(II)	1 : 50	Ca(II)	1 : >200	SiO <sub>3</sub> <sup>2-</sup>	1 : >200

**Table 4** Results of the determination of palladium in the alloys ( $S_r$  – relative standard uncertainty);  $n = 3$ ,  $P = 0.95$ .

Intermetallide	$\omega_{\text{Pd}}^{\text{calc}}$ , % (w/w)	Spectrophotometry		Voltammetry	
		$\bar{\omega}_{\text{Pd}}^{\text{pr}} \pm \frac{S \cdot t_{\alpha}}{\sqrt{n}}$ , % (w/w)	$S_r$ , %	$\bar{\omega}_{\text{Pd}}^{\text{pr}} \pm \frac{S \cdot t_{\alpha}}{\sqrt{n}}$ , % (w/w)	$S_r$ , %
Yb <sub>40</sub> Pd <sub>38</sub> Sn <sub>22</sub>	29.8	30.6±0.9	1.2	30.2±0.8	1.1
Yb <sub>40</sub> Pd <sub>40</sub> Ga <sub>20</sub>	33.9	34.2±0.7	0.8	34.3±0.6	0.7

Then the  $pH$  value was adjusted ( $pH = 5.0$ ) by adding  $\text{CH}_3\text{COOH}$  or  $\text{CH}_3\text{COONa}$ . After that, the solution was transferred to a volumetric flask of 25.0 ml and adjusted to the mark with distilled water. The solutions were heated in a boiling water bath ( $\sim 98$  °C) for 10 min. After cooling to room temperature ( $\sim 20$  °C), absorbance measurements were carried out against a blank solution at 350 nm in 1.0 cm cuvettes. The results are presented in **Table 4**. It is seen that the results correlate well with the nominal palladium content in the alloys. The values of the relative standard deviations,  $S_r$ , do not exceed the typical values for spectrophotometric analyses. The correctness of the results of the determination of palladium in the intermetallic compounds was checked using the voltammetric method (**Table 4**). Palladium was determined by voltammetry during reduction ( $U = -0.82$  V) of its ammine complex ( $[\text{Pd}(\text{NH}_3)_4]^{2+}$ ) on the dropping mercury electrode [6].

### Conclusions

A new spectrophotometric method for the determination of Pd(II), using HITO, was successfully applied to measure the content of this platinum metal in two intermetallides. The method is characterized by good selectivity and the analysis does not interfere with most concomitant ions. The procedure of determining the palladium content in alloys is simple, rapid, and does not require the use of masking agents, or previous separation of the analyte from other components of the intermetallides. The results

correlate with the nominal content of palladium in the alloys, and were confirmed by voltammetry.

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