

**KINETIC DETERMINATION OF Pd(II)
BASED ON THE OXIDATION OF METHYLENE BLUE B BY
AMMONIUM PERSULFATE IN THE PRESENCE OF Au(III)**

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Abstract. *A kinetic method is described for Pd(II) determination, based on its catalytic effect on the reaction of oxidation of methylene blue B by ammonium persulfate in the presence of Au(III). The probable relative error was determined for the concentration interval of $2.2 \cdot 10^{-7}$ to $10.0 \cdot 10^{-7}$ g/cm³ Pd(II). In ranges between 2.4 %, for the concentration of $7.8 \cdot 10^{-7}$ g/cm³ Pd(II), and 6.0%, for the concentration of $2.2 \cdot 10^{-7}$ g/cm³ Pd(II). Appropriate kinetic equation was formulated and the sensitivity of $3.3 \cdot 10^{-8}$ g/cm³ Pd(II) was limited. Also, the effect of different ions upon the reaction rate was tested. The method was verified by Pd(II) determination in the alloy PtRhG, by both kinetic and ICP-AES method.*

Key words: *kinetic method, Pd(II) determination*

INTRODUCTION

Pd(II) is well known catalyst in many homogeneous reactions. There are two groups of kinetic methods for Pd(II) determination: the methods based on the reduction of different organic compounds and the methods based on the oxidation of organic substrates.

Sanchez-Pedreno et al. developed methods of organic compounds reduction by hypophosphite. Using toluidine-blue [1], phenosafranine [2] and pyronine [3], Pd(II) was determined with sensitivity of 0.08-0.5 µg/cm³. With the same reductor, using erio-glucine and phenol-red as substrates, Dutt and Mottola determined 0.1 µg/cm³ and 0.003 µg/cm³ Pd(II), respectively [4].

Yugoslavian authors developed methods of oxidation by hydrogen peroxide as the oxidant. Vajgand et al. determined Pd(II) as the catalyst of 1-amino-2-naphthol-4-sulfonic acid oxidation, with sensitivity of 4 ng/cm³ [5]. Pecev, Igov and Miletić developed kinetic methods using carmine acid [6] and indigo carmine [7] as the substrates, and reached the

sensitivity of $0.2 \mu\text{g}/\text{cm}^3$ and $0.4 \mu\text{g}/\text{cm}^3$ Pd(II), respectively. Miletić and Mitić determined Pd(II) on the basis of its catalytic effect on the purine oxidation in the carbonate buffer with sensitivity of $5.0 \cdot 10^{-8} \text{ g}/\text{cm}^3$ [8]. On the basis of their method for kinetic determination of Au(III) [9], which was found to be catalysed by Pd(II), Igov, Rančić et al. developed the method, presented in this work, for Pd(II) determination, using the same reaction system: methylene blue B (MBB) as reductor, ammonium persulfate (APS) as oxidant and Au(III) as the catalyst.

EXPERIMENTAL

Apparatus

Spectrophotometric measurements were performed on a Perkin-Elmer Lambda 15 UV-VIS spectrophotometer, at a wavelength $\lambda = 662.4 \text{ nm}$. A cylindrical cuvette with an optical path length of 10 cm was used. A pH-meter Radimeter PHM 29 b with combined electrode GK 2311 C was used to monitor the pH. Water thermostating bath Sutjeska, type 10, was used for the working temperature of $T = 25.0 \pm 0.1^\circ\text{C}$ regulation.

ICP-AES measurements were performed on atomic-emission spectrometer Applied Research Laboratory, model 3410+ at a wavelength $\lambda = 340.458 \text{ nm}$.

Reagents

All solutions were prepared from p.a. grade reagents (from Merck) using deionized water as a solvent and were kept in polyethylene vessels. A stock solution of Pd(II) ($1.0 \cdot 10^{-4} \text{ g}/\text{cm}^3$) was prepared by weighing out a required amount of PdCl₂. The exact concentration of Pd(II) in the stock solution was determined volumetrically [10]. The MBB and APS solutions were prepared by dissolving the exactly measured dry substances in deionized water. Buffer solutions were prepared by mixing appropriate volumes of $0.1 \text{ mol}/\text{dm}^3$ sodium citrate and $0.1 \text{ mol}/\text{dm}^3$ HCl solutions. The Au(III) stock solution ($4.0 \cdot 10^{-3} \text{ g}/\text{cm}^3$) was prepared by dissolving 1 g H(AuCl₄)·4H₂O in the adequate volume of deionized water. The concentration of solution was verified electrogravimetrically [10] and then the working solution of asking concentration was prepared by deionized water.

Procedure

Adequate volumes of the reagents and deionized water were pipetted out into four separate compartments of Budarin vessel [11] to the total volume of 9 cm^3 and thermostated 10 minutes for all kinetic measurements. Afterwards, the reagents were mixed and the chronometer was turned on. The reaction mixture was then transferred to the spectrophotometric cuvette. Absorbance was measured every 30 seconds during the first five minutes from the onset of the reaction.

Before the ICP-AES measurements, the solutions were prepared by dissolving 0.1 g of alloy powder into 12 cm^3 of aqua regia during the heating. Solutions were afterwards vaporized on the small volume and filled up to the predetermined volume [12].

RESULTS AND DISCUSSION

During the course of the reaction the initially blue color of the reaction mixture fades away while colorless reaction product is being formed. The logarithm of absorbance versus the reaction time shows a linear dependence within the first three minutes (in some experiments within the whole investigated time interval). Therefore, the integral variant of the tangent method [13] was applied for kinetic analysis.

By changing the concentration of the reagents one at the time: pH (Fig. 1), the concentration of methylene blue B, [MBB], (Fig. 2), and the concentration of ammonium persulfate, [APS], (Fig. 3), while the concentrations of all other components are kept constant, and by applying the integral variant of the tangent method for kinetic analysis, the following rate expressions for the catalyzed (1) and noncatalyzed (2) reactions were derived:

$$-d[\text{MBB}]/dt = k_1 \cdot [\text{MBB}] \cdot [\text{APS}] [\text{Pd(II)}] \quad (1)$$

and

$$-d[\text{MBB}]/dt = k_0 \cdot [\text{MBB}] \cdot [\text{APS}] \quad (2)$$

Here, k_1 and k_0 are the rate constants of the catalyzed and uncatalyzed reaction, respectively.

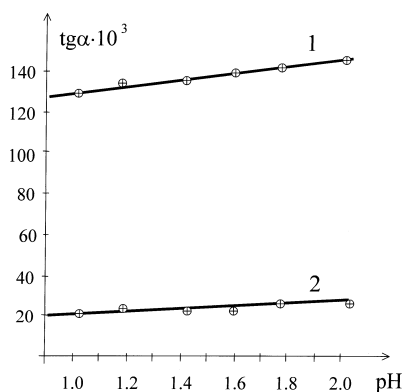


Fig. 1. Dependence of $\text{tg}\alpha$ on pH value of citric buffer for catalytic (1) and noncatalytic (2) reactions.

Initial conditions:
 $[\text{MBB}] = 4.4 \cdot 10^{-6} \text{ mol/dm}^3$;
 $[\text{APS}] = 20.8 \cdot 10^{-2} \text{ mol/dm}^3$;
 $[\text{Au(III)}] = 5.6 \cdot 10^{-8} \text{ g/cm}^3$;
 $[\text{Pd(II)}] = 1 \mu\text{g/cm}^3$; $T = 25.0 \pm 0.1^\circ\text{C}$.

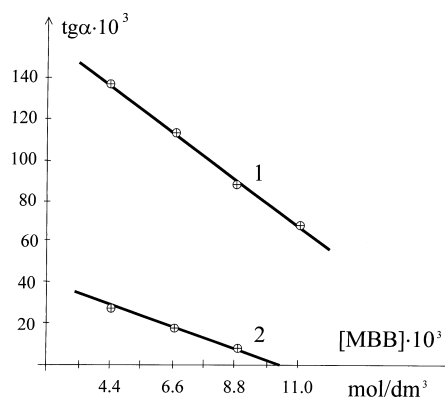


Fig. 2. Dependence of $\text{tg}\alpha$ on MBB concentration for catalytic (1) and noncatalytic (2) reactions.

Initial conditions:
 $[\text{APS}] = 20.8 \cdot 10^{-2} \text{ mol/dm}^3$;
 $[\text{Au(III)}] = 5.6 \cdot 10^{-8} \text{ g/cm}^3$;
 $[\text{Pd(II)}] = 1 \mu\text{g/cm}^3$; $T = 25.0 \pm 0.1^\circ\text{C}$;
 $\text{pH} = 1.6$.

Optimal conditions for Pd(II) determination were found to be: $\text{pH} = 1.6$; $[\text{MBB}] = 4.4 \cdot 10^{-6} \text{ mol/dm}^3$; $[\text{APS}] = 2.5 \cdot 10^{-1} \text{ mol/dm}^3$ and $[\text{Au(III)}] = 5.6 \cdot 10^{-8} \text{ g/cm}^3$.

The calibration curve was constructed (Fig. 4) and the calibration curve equation (3) was calculated:

$$\text{tg}\alpha = 0.0116 \cdot c + 0.0249 \quad (3)$$

where c is $\text{Pd(II)} \cdot 10^7 \text{ g/cm}^3$ concentration.

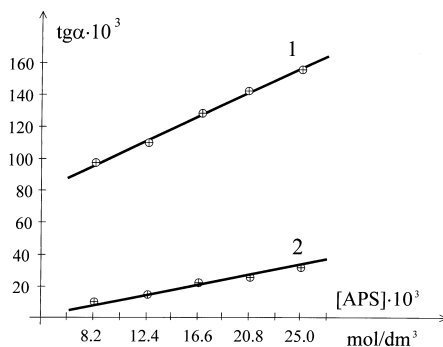


Fig. 3. Dependence of $\text{tg}\alpha$ on APS concentration for catalytic (1) and noncatalytic (2) reactions.

Initial conditions:
 $[\text{MBB}] = 4.4 \cdot 10^{-6} \text{ mol/dm}^3$;
 $[\text{Au(III)}] = 5.6 \cdot 10^{-8} \text{ g/cm}^3$;
 $[\text{Pd(II)}] = 1 \mu\text{g/cm}^3$; $T = 25.0 \pm 0.1^\circ\text{C}$;
 $\text{pH} = 1.6$.

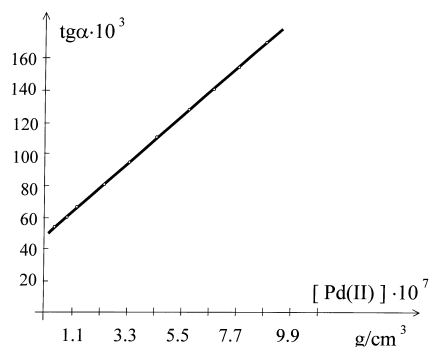


Fig. 4. The calibration curve for Pd(II) determination.

Initial conditions:
 $[\text{MBB}] = 4.4 \cdot 10^{-6} \text{ mol/dm}^3$;
 $[\text{APS}] = 2.5 \cdot 10^{-1} \text{ mol/dm}^3$;
 $[\text{Au(III)}] = 5.6 \cdot 10^{-8} \text{ g/cm}^3$;
 $[\text{Pd(II)}] = 1 \mu\text{g/cm}^3$; $T = 25.0 \pm 0.1^\circ\text{C}$;
 $\text{pH} = 1.6$.

According to the curve, it is possible to determine the Pd(II) concentration in the concentration range from $3.3 \cdot 10^{-8}$ to $1.0 \cdot 10^{-6} \text{ g/cm}^3$ Pd(II).

In order to assess the accuracy and precision of the method, reaction rates were determined for three different Pd(II) concentrations in five replicate determinations (Table 1). The probable relative error varies from 2.4 to 6.0% for the examined concentration range.

Table 1. Accuracy and precision of Pd(II) determination

taken μ $\text{g/cm}^3 \cdot 10^7$	found \bar{x} $\text{g/cm}^3 \cdot 10^7$	n	$S \cdot 10^7$	G %	$[(\bar{x}-\mu)/\mu] \cdot 100$ %
2.2	2.17	5	0.05	6.0	-1.4
7.8	7.92	5	0.07	2.4	+1.5
10.0	10.21	5	0.10	2.6	+2.1

where: \bar{x} -mean value; μ -true value; n-number of determinations; S - standard deviation; G - probable relative error; $[(\bar{x}-\mu)/\mu] \cdot 100$ - accuracy.

The investigation of selectivity examined the influence of some foreign ions in the reaction mixture upon the reaction rate under constant Pd(II) concentration of $1.0 \cdot 10^{-6} \text{ g/cm}^3$ and Au(III) concentration of $5.6 \cdot 10^{-8} \text{ g/cm}^3$. It was found that method shows the relatively good selectivity, because only the presence of Sn(II) and Hg(II) (in the ratio 1:0.1 to the Pd(II) concentration) and Pb(II) (in the ratio 1:1) interferes this reaction. The presence of Au(III) (1:1) and Ag(I) (1:100), catalyses Pd(II) determination by this method.

The method was verified by its application on Pd(II) determination in five samples of

palladium alloy known as PtRhG. The alloy solutions were prepared by the rule and each sample was examined by both kinetic and ICP-AES method in five replications and the received results were compared.

CONCLUSION

By comparing the mean values of five measurements, obtained by kinetic and ICP-AES method for each sample, it was found that the deviation i.e. the probable relative error of results received by kinetic method, towards the results obtained by ICP-AES method, varies from -8.4 to +9.4 %. So, by taking into account the error of the kinetic method, we consider it applicable for this alloy examinations.

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KINETIČKO ODREĐIVANJE P(II) NA OSNOVU OKSIDACIJE METILEN PLAVOG B AMONIJUM PERSULFATOM U PRISUSTVU Au(III)

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Opisana je nova kinetička metoda za određivanje tragova Pd(II) u rastvoru, na osnovu njegovog katalitičkog dejstva na oksidaciju metilen plavog B amonijum persulfatom u citratnom puferu u prisustvu Au(III) u reakcionoj smeši. Na osnovu izvedene kinetičke jednačine za optimalne uslove reakcije, osetljivost metode iznosi $3.3 \cdot 10^{-8} \text{ g/cm}^3 \text{ Pd(II)}$. Relativna greška metode određivana je u intervalu koncentracije od $2.2 \cdot 10^{-7} \text{ g/cm}^3$ do $10.0 \cdot 10^{-7} \text{ g/cm}^3 \text{ Pd(II)}$. Ona se kreće od 2.4 % za koncentraciju od $7.8 \cdot 10^{-7} \text{ g/cm}^3$, do 6.0 % za koncentraciju od $2.2 \cdot 10^{-7} \text{ g/cm}^3 \text{ Pd(II)}$. Metoda je proverena određivanjem Pd(II) u uzorcima legura PtRhG, uz paralelnu primenu ICP-AES metode kao komparativne metode, na iste uzorke.