Application of the reaction system methylene blue B–$(NH_4)_2S_2O_8$ for the kinetic spectrophotometric determination of palladium in citric buffer media

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Abstract

A new, simple, rapid, sensitive and selective kinetic spectrophotometric method for Pd(II) traces determination was elaborated in this paper. It is based on the catalytic effect of palladium ions upon the oxidation of methylene blue B (MBB) by $(NH_4)_2S_2O_8$ (APS) in citric buffer (BUF) solution. At the working temperature of 25 °C and the wavelength of 662.4 nm, the optimal conditions for palladium determination were found. *RSD* value was found to be 2.6 to 4.9% for the investigated concentration range of Pd(II). Limit of detection (*LD*) was found to be 2.0 ng cm^{-3} Pd(II), and limit of quantification (*LQ*) is 6.9 ng cm^{-3} Pd(II). Only the presence of Pb^{2+}, Hg^{2+} and Sn^{2+} in the reaction mixture interferes the determination of palladium by this method, while Au^{3+} and Ag^{+} have the catalytic effect upon the reaction rate. By this method, it is possible to determine the Pd(II) traces in the concentration range of 3.3×10^{-8} to 1.0×10^{-6} g cm^{-3}. The method was confirmed by determination of Pd(II) traces in alloy PtRhG as well as in the powder of Pt. The obtained results were compared to those obtained by ICP-OES method and good agreement of results was found.

Keywords: Pd(II) determination, catalyst, kinetic spectrophotometric method.

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Palladium is well known as the catalyst of different heterogenic reactions, as well as the catalyst or the inhibitor of homogeneous reactions in solution. Pd(II) has ability to form complexes with a great number of substances, so the spectrophotometric measurements are very often applied for palladium determination. Among many methods with spectrophotometric detection, there are also some kinetic spectrophotometric methods for palladium determination. Some of them are based on its catalytic effect upon the reduction of organic dyes by sodium hypophosphite [1–3]. In those reactions, in the presence of palladium, the nascent hydrogen is forming as the additional reductor. Palladium also catalyzes some reactions of oxidation in solution. So, the kinetic method was published for determination of Pd(II) as the catalyst of the oxidation of purpurine by hydrogen peroxide in carbonate buffer [4]. Also, the catalyzed oxidation of pyrogallol red by the same oxidant, at pH 9.7 and by measuring the decrease of absorbance at 540 nm, was reported [5]. This method was applied for Pd(II) determination in catalytic material. Two kinetic methods, based on the inhibitory effect of palladium upon the reaction of oxidation in solution, were reported, too [6,7]. The kinetic method was published at the end of the last century for palladium determination in mixture with platinum and gold [8]. The method was confirmed in ores analysis. Recently, in 2008, the interesting and sensitive kinetic method was reported for Pd(II) determination in synthetic and waste water samples, based on its catalytic effect on the resazurine sulfide reaction [9]. The decrease of absorbance at 602 nm, over a fixed time, is proportional to the concentration of Pd(II) in the range of 10.0 to 160.0 ng cm^{-3}.

Many other methods with spectrophotometric determination were published during last 30 years [10–43], for palladium determination in catalysts, Pd-charcoal, synthetic mixtures and palladium alloys [11–14,34], metallurgical samples [17], palladium asbestos and B complex ampoules [19,40], real and synthetic waste waters [29,42], anodic slime, road sediment, ores [21,43], estuarine sediment CRM 277 [38], dental alloy Ortop, type 4 and Pt–Pd wire [27], environmental samples, plating effluents, etc. The group of authors published interesting methods, one in 2000 and the

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other in 2001, for Pd(II) determination in airborne particulate matter, hydrogenation and automobile exhaust, gas converter catalysts by stopped-flow injection and liquid–liquid extraction-spectrophotometry [32,36]. Also, Pd(II) was determined as complex after collection on the resin Amberlite XAD-7 and elution [21,27], after solid-liquid extraction at 90 °C [28], etc.

Palladium was determined in different samples by AAS [44–46] and AES [47], as well as by electrophoresis [48], ICP-MS [49], fluorescent quenching analysis, and some other analytical methods.

Comparing with the other methods, the main goal of our investigation was to develop new, sensitive, rapid and easy to perform kinetic method for spectrophotometric determination of palladium by using common and available chemicals. In addition, we wanted to check the method on the real samples in order to confirm its possibilities for further applications. Although there are more sensitive methods for Pd(II) traces determination than the proposed one, for example some AAS and ICP-MS methods, the results of our work, like quick performance at room temperature, good reproducibility of experimental results, satisfied selectivity of the method, low limit of detection and quantification using cheap equipment and substances, recommend our new kinetic spectrophotometric method for many different potential Pd(II) determinations in solution.

EXPERIMENTAL

Apparatus

Spectrophotometric measurements were performed on UV–Vis spectrophotometer Shimadzu UV–Vis 1650 PC (Shimadzu, Japan). ICP-OES measurements were performed on ICP-OES, model ICAP 65000 Duo (Thermo Scientific, UK). The cylindrical cells were thermostated at 25.00±0.02°C using thermo circulating bath (Julabo MP-5A). The pH measurements were performed using a Hach H260G pH-meter with a non-glass pH probe PH77SS (Hach, USA).

Reagents and chemicals

Analytical grade reagents, provided by Merck, Germany, unless indicated otherwise and ultrapure water (18.2 MΩ, water purification system Thermo Fisher Scientific Smart2Pure Standard) were utilized for solutions preparation. Adequate polyethylene vessels were used for storage of the solutions. Citric buffer solutions were prepared by mixing $NaC_6H_5O_7$ and NaOH or HCl solution (0.1 mol dm^{-3}) according the rule and their pH values were checked using a pH-meter. A stock Pd(II) solution (1×10^{-4} g cm^{-3}) was prepared by dissolving the exactly measured dry $PdCl_2$ in HCl solution (0.01 mol dm^{-3}). The concentration of the stock solution was checked gravimetrically. The methylene blue B solution was prepared by dissolving the exactly measured substance in deionised water. All the polyethylene containers and the glassware were washed by diluted hydrochloric acid (1:1), solution of potassium hydroxide in ethanol and then repeatedly well rinsed by tap, distilled and deionised water. All concentrations described here are the initial concentrations in the reaction mixture at time zero after mixing. Each kinetic result is the average of five determinations.

Procedure

In order to obtain good mechanical and thermal stability, the instruments were run for ten minutes before the first measurement. Selected volumes of reactants and deionized water were poured separately in the reaction mixture vessel with four compartments (Budarin vessel) up to a predeterminated total volume of 10 cm^3. The solution of Pd(II) was measured into one leg of the Budarin vessel for catalytic reaction and the same volume of deionized water was measured for non-catalytic reaction. After thermostating for 10 min, the reagents were mixed and simultaneously the stopwatch was turned on. To properly rinsed spectrophotometer cell with a path length of 10 cm, the solution was immediately added and absorbance was measured every 15 s, starting from the 45th s of reaction, up to 10 min of the reaction. Spectrophotometric measurements were performed at the wave length of 662.4 nm, and at working temperature of 25±0.02 °C.

The reaction was tested by examination the influence of each component of the reaction mixture upon the reaction rate of catalytic and non-catalytic reaction. The concentration of each component was changing consecutively, while the concentrations of other components, as well as the working temperature, were kept constant.

RESULTS AND DISCUSSION

While the reaction proceeds, the initial blue color of the solution fades and a colorless reaction product is formed. Neither the exact mechanism of reaction nor the chemical nature of the products was of major interest in the investigation. The spectrophotometric measurements were performed at the wavelength of absorption maximum of methylene blue B (662.4 nm) in citric buffer media (Fig. 1). The logarithm of absorbance-time curves is linear during the first 5–10 min of reaction for different Pd(II) concentrations, so all kinetic results were treated by the integral variant of the tangent method [50]. The rate of reaction was obtained using the slope of the kinetic curves of the absorbance-time plot.

Hence, the influence of the pH value of the selected citric buffer solutions on the rate of both the catalytic and non-catalytic reaction was examined in the pH interval of about 1.0 to about 2.0 (Fig. 2). The value of 1.6 was selected as the most appropriate one, because it provides very well difference of reaction rates of the catalytic and non-catalytic reaction and good reproducibility of absorbance measurements in the absorbance area of the least error for spectrophotometric measurements (the area of absorbance values from about 0.1 to about 1.0), for both reactions. The same principles were used for optimal conditions selection in all further investigations. The citric buffer pH 1.6 was used in subsequent examinations.

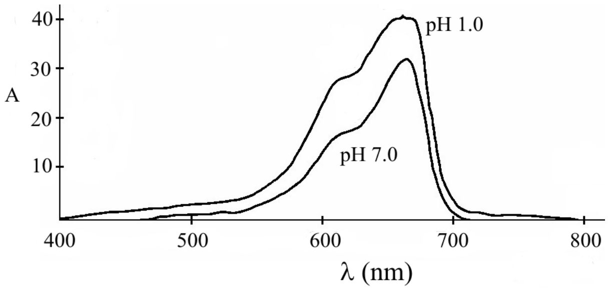

Fig. 1. Absorption spectra of MBB in citric buffer. Initial conditions: MBB 7.15×10^{-6}mol dm^{-3}; 25±0.02 °C.

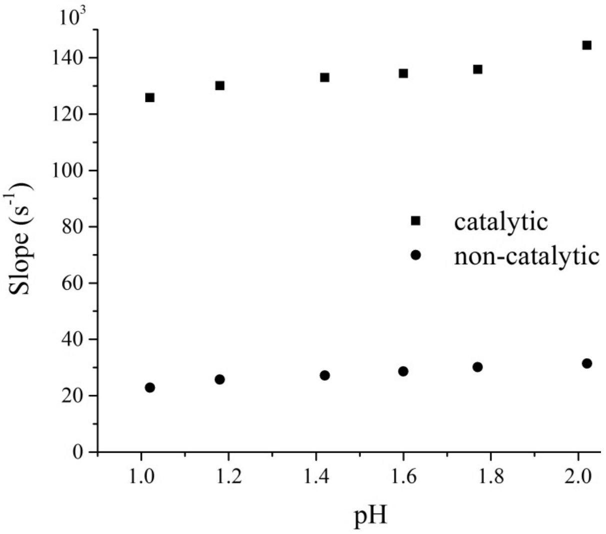

Fig. 2. Dependence of the reaction rate on pH. Initial conditions: MBB 4.4×10^{-6} mol dm^{-3}; APS 20.8×10^{-2} mol dm^{-3}; BUF 8.3×10^{-3} mol dm^{-3}; Pd(II) 1.0 μg cm^{-3}; 25±0.02 °C.

The rate of the non-catalytic reaction shows first order dependence on the buffer concentration, while the catalytic reaction rate shows complex dependence (Fig. 3) within the range of 2.8×10^{-3} to 9.7×10^{-3} mol dm^{-3}, and a concentration of 8.3×10^{-3} mol dm^{-3} was selected as the optimal concentration of citric buffer for further measurements.

The dependence of the rate of the catalytic and non-catalytic reaction on the reductor concentration was monitored within the concentration range of about 4.4×10^{-6} to about 11.0×10^{-6} mol dm^{-3} MBB. Within this interval, both the catalytic and non-catalytic reaction rate shows a first order dependence of the MBB concentration (Fig. 4). As optimal, a concentration of 4.4·10^{-6}mol dm^{-3} MBB was selected.

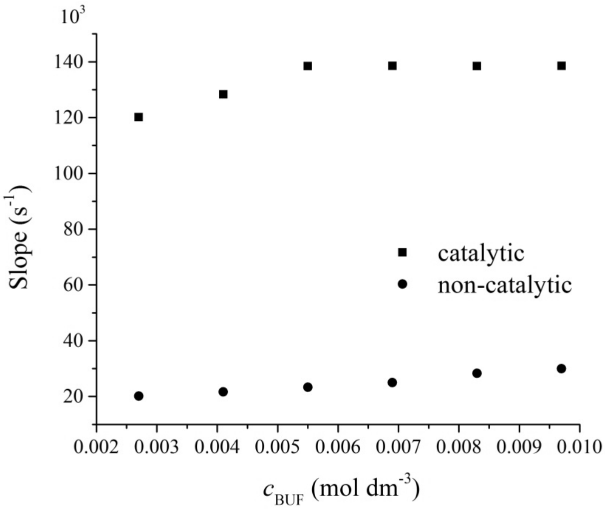

Fig. 3. Dependence of the reaction rate on the BUF concentration. Initial conditions: pH 1.6; MBB 4.4×10^{-6} mol dm^{-3}; APS 20.8×10^{-2} mol dm^{-3}; Pd(II) 1.0 μg cm^{-3}; 25±0.02 °C.

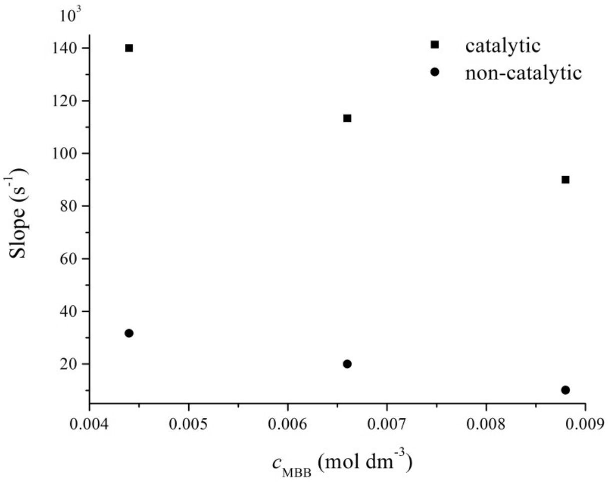

Fig. 4. Dependence of the reaction rate on the MBB concentration. Initial conditions: pH 1.6; APS 20.8×10^{-2} mol dm^{-3}; BUF 8.3×10^{-3} mol dm^{-3}; Pd(II) 1.0 μg cm^{-3}; 25±0.02 °C.

At last, the influence of the concentration of the oxidant was tested (Fig. 5). Inside the investigated concentration range of $(NH_4)_2S_2O_8$ of about 8.3×10^{-2} to about 25.0×10^{-2} mol dm^{-3}, both the catalytic and non--catalytic reaction rate shows a first order dependence of the oxidant concentration. APS concentration of 25.0×10^{-2} mol dm^{-3} was selected as the adequate for further work because it provides the best difference of reaction rates of the catalytic and non-catalytic reaction.

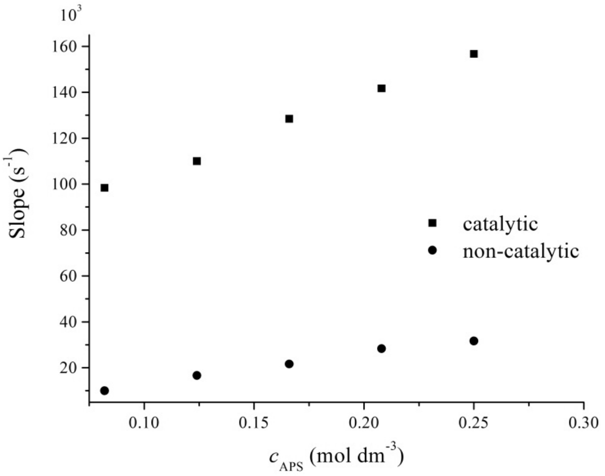

Fig.5. Dependence of the reaction rate on the APS concentration. Initial conditions: pH 1.6; MBB 4.4×10^{-6} mol dm^{-3}; BUF 8.3×10^{-3} mol dm^{-3}; Pd(II) 1.0 µg cm^{-3}; 25±0.02 °C.

Hence, the optimal conditions were found to be: pH 1.6, c_{BUF} =8.3×10^{-3}mol dm^{-3}, c_{MBB} = 4.4×10^{-6} mol dm^{-3}, c_{APS} = 25.0×10^{-2} mol dm^{-3}.

Under the optimal conditions, the dependence of catalytic reaction rate on the Pd(II) concentration was observed at three temperatures: 23±0.02, 25±0.02 and 27±0.02 °C(Fig. 6). The linear dependence of calibration curves falls within the range of 3.3×10^{-8} to 1.0×10^{-6} g cm^{-3} Pd(II).

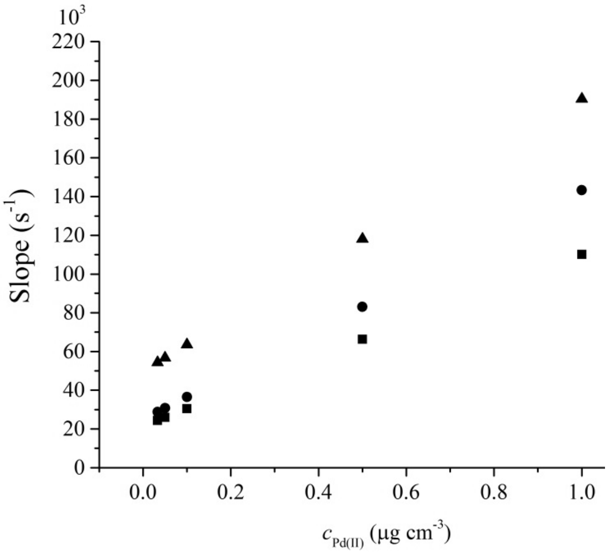

Fig.6. Dependence of the reaction rate on the Pd(II) concentration. Initial conditions: pH 1.6; MBB 4.4×10^{-6} mol dm^{-3}; BUF 8.3×10^{-3} mol dm^{-3}; APS 20.8×10^{-2} mol dm^{-3}; 1 – 23±0.02, 2 – 25±0.02, 3 – 27±0.02 °C.

The adequate equations of calibration curves for 23±0.02 (Eq. (1)), 25±0.02 (Eq. (2)), and 27±0.02 °C (Eq. (3)), were calculated as follows:

$$\text{Slope} = (0.00896\pm0.00001)c + (0.02146\pm0.00012) \quad (1)$$

$$\text{Slope} = (0.01163\pm0.00002)c + (0.02492\pm0.00013) \quad (2)$$

$$\text{Slope} = (0.01367\pm0.00002)c + (0.04982\pm0.00010) \quad (3)$$

where c is Pd(II) concentration,·10^{-7} g cm^{-3}.

The accuracy and precision of the method were checked for three different Pd(II) concentrations within the range of the calibration curve. Five repeated measurements were performed for each concentration. Satisfactory results were obtained. For Pd(II) concentrations of 2.2×10^{-7}, 7.8×10^{-7} and 10.0×10^{-7} g cm^{-3}, *RSD* values were found to be 4.9, 3.1 and 2.6%, respectively.

The selectivity of the method was established by interference studies: selected ions were separately added in the reaction mixture. The tolerance limit was estimated as the concentration of the added ion that gives up to a 3% relative error in the determination of palladium. Cations were added as chlorides or nitrates and anions were added as sodium or potassium salts. Each ion was added in six known concentration ratios (0.01:1, 0.1:1, 1:1, 10:1, 100:1 and 1000:1) against the constant Pd(II) concentration of 1.0 µg cm^{-3}. The measurements were performed at 25±0.02 °C, and about 30 most frequently used cations and anions were tested (Na^+,Ag^+, Ca^{2+}, Sr^{2+}, Ba^{2+}, Mg^{2+}, Zn^{2+}, Cu^{2+}, Pb^{2+}, Ni^{2+}, Co^{2+}, Hg^{2+}, Sn^{2+}, Bi^{3+}, Fe^{3+},Al^{3+}, As^{3+}, Sb^{3+}, Au^{3+}, acetates, tartarates, oxalates, molybdates, wolframates, Br^-, I^-, NO_3^-, SO_4^{2-}, CO_3^{2-} and PO_4^{3-}). The results presented in Table 1 reveal that proposed methods for palladium determination have a very good selectivity.

Only the presence of Pb^{2+}, in the ratio 1:1, and $Hg^{2+}$and Sn^{2+}, in the ratio 0.1:1 against the palladium concentration, interferes with the determination of palladium. The presence of Au^{3+}, in the ratio 1:1, and Ag^+, in the ratio 100:1, catalyzes the determination of palladium by proposed method. The ions that interfere determination of palladium can be easily removed by standard analytical methods like masking, precipitation, etc., depending of different samples nature.

By application of spectrophotometric technique, at the wavelength of 662.4 nm, a limit of quantification (*LQ*) of 6.9 ng cm^{-3} Pd(II), was reached, and the limit of detection (*LD*) of 2.0 ng cm^{-3} Pd(II), was obtained. *LQ* was defined as the ratio signal:noise = 10:1 and *LD* was defined as signal 3:1 against the blank.

The method was successfully applied to Pd(II) determination in alloy PtRhG and Pt powder. Prepared solutions, containing traces of palladium, were analyzed by application of both, the presented kinetic method on the 662.4 nm and ICP-OES method on the 340.458 nm. As presented in Table 2, there is a good agreement of results.

Table 1. Selected results of interference studies for palladium determination. Initial conditions: pH 1.6; MBB 4.4×10^{-6} mol dm^{-3}; BUF 8.3×10^{-3} mol dm^{-3}; APS 25.0×10^{-2} mol dm^{-3}; Pd(II) 1.0 µg cm^{-3}; 25±0.02 °C

Added ion	Ion ratio:Pd(II)	Palladium determination, error, %
Na^+	1000	–2.6
K^+	1000	–1.8
Ag^+	100	Catalyzes
Ca^{2+}	1000	+2.1
Sr^{2+}	1000	–1.9
Ba^{2+}	100	+2.7
Mg^{2+}	1000	+2.1
Zn^{2+}	10	–2.9
Cu^{2+}	1	–1.9
Pb^{2+}	1	Interferes
Ni^{2+}	10	+2.8
Co^{2+}	1	+2.6
Hg^{2+}	0.1	Interferes
Sn^{2+}	0.1	Interferes
Bi^{3+}	1	–1.9
Fe^{3+}	10	+1.1
As^{3+}	10	+1.2
Al^{3+}	10	+2.7
Sb^{3+}	1	+1.6
Au^{3+}	1	Catalyzes
Acetates	100	+2.5
Tartarates	100	+2.2
Oxalates	1000	+2.0
Molybdates	1	–2.3
Wolframates	100	–1.9
Br^-	10	+1.1
I^-	10	–2.4
Nitrates	100	+1.8
Sulphates	1000	+1.2
Phosphates	1000	–2.8

Table 2. Pd(II) determination in alloy samples (1,2), and platinum powder samples (3,4). Initial conditions: pH 1.6; MBB 4.4×10^{-6} mol dm^{-3}; BUF 8.3×10^{-3} mol dm^{-3}; APS 25.0×10^{-2} mol dm^{-3}; 25±0.02 °C

Sample	Kinetic determination[a] ×10^7 g cm^{-3}	Recovery, %	Determination by ICP-OES[a] ×10^7 g cm^{-3}	Recovery, %
1	2.84±0.04	96.3	2.99±0.02	99.7
2	2.72±0.06	96.1	2.92±0.02	99.6
3	3.85±0.03	97.1	3.92±0.02	99.7
4	3.97±0.02	97.6	3.95±0.02	99.7

[a] The mean value of five measurements±2*SD*

CONCLUSIONS

The proposed kinetic method for the determination of Pd(II) shows a very good selectivity and provides rapid and easy performance at 25 °C, by using available equipment and cheap chemical substances. The obtained results are precise and reproducible. The *RSD* value was found to be in the range 2.6–4.9% for the investigated concentration range of Pd(II).

On the base of the obtained results, the new spectrophotometric kinetic method is recommendable for the determination of Pd(II) in alloys and metallurgical samples containing traces of palladium, and potentially also in different samples from industrial processes and environment. The results suggest that it could also be a good basis for further investigations in the area of kinetic methods development.

Acknowledgements

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IZVOD

Primena reakcionog sistema metilen plavo B–$(NH_4)_2S_2O_8$ za kinetičko spektrofotometrijsko određivanje paladijuma u citratnom puferu

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U ovom radu je predstavljena nova kinetička spektrofotometrijska metoda za određivanje tragova paladijuma u rastvoru, zasnovana na katalitičkom dejstvu Pd(II) jona na reakciju oksidacije metilen plavog B(MBB) amonijum-persulfatom (APS) u citratnom puferu (BUF). Upotrebom lako dostupne opreme i ralativno jeftinih hemikalija, na temperaturi od 25 °C i talasnoj dužini od 662,4 nm, određeni su optimalni uslovi za odigravanje reakcije i ostvareni precizni i reproduktivni rezultati. *RSD* je u rasponu od 2,6–4,9% za ispitivanu oblast koncentracija Pd(II). Ovom metodom je moguće određivati paladijum u intervalu koncentracija od $3,3\times10^{-8}$ do $1,0\times10^{-6}$ g cm^{-3}. Na osnovu dobijenih rezultata se može zaključiti da nova kinetička metoda pokazuje vrlo dobru selektivnost. Naime, samo prisustvo Pb^{2+}, Hg^{2+}i Sn^{2+} u reakcionoj smeši, ometa određivanje paladijuma ovom metodom, dok ga prisustvo Au^{3+} i Ag^{+} katalizuje. Određena je granica kvantifikacije (*LQ*) od 6,9 ng cm^{-3} Pd(II), kao i granica detekcije (*LD*) od 2,0 ng cm^{-3} Pd(II). *LQ* je definisana kao odnos signal:šum = 10:1 and *LD* kao signal 3:1 u odnosu na slepu probu. Primenom kinetičke i ICP-OES metode, kao referentne, za određivanje paladijuma u uzorcima legure PtRhG i prahu platine i poređenjem dobijenih rezultata, može se zaključiti da je nova kinetička spektrofotometrijska metoda pogodna za određivanje Pd(II) u legurama i metalurškim uzorcima, a potencijalno i u drugim uzorcima iz proizvodnih procesa i životne sredine. Takođe, rezultati ispitivanja ukazuju na to da ona može da bude dobra osnova za dalja istraživanja u oblasti razvoja kinetičkih metoda analize.

Ključne reči: Određivanje Pd(II) • Katalizator • Kinetičko spektrofotometrijska metoda