



On-line Preconcentration of Pd(II) Using Polyamine Silica Gel Filled Mini Column for Flame Atomic Absorption Spectrometric Determination

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Abstract In this study, a novel method for determination of Pd(II) ions at trace level was developed using on-line preconcentration onto polyamine group bonded silica (PA-SG) with flame atomic absorption spectrometric determination. Pd(II) uptake dynamics of PA-SG was studied batchwise by investigating acidity and chloride concentration of aqueous phase, contact time and initial concentration of Pd(II) ions. The Pd(II) adsorption capacity of PA-SG was found to be 158.7 mg g⁻¹ from aqueous phase containing 0.1 M HCl. The on-line preconcentration procedure of Pd(II) was optimized with main analytical parameters including sample and eluent flow rate, eluent type and volume and matrix ions. The optimum eluent type and flow rate of sample and eluent were found to be 1.0% thiourea in 1.0 mol L⁻¹ HCl and 7.5 mL min⁻¹, respectively. The preconcentration factor and sampling frequency were calculated to be 23.9 and 20 h⁻¹, respectively. The calibration graph was linear over the range 10–200 µg L⁻¹. The limits of detection (3σ) and quantification (10σ) values were computed to be 3 µg L⁻¹ and 10 µg L⁻¹, respectively. The RSD, % was found to be 4.6% for five measurement of 25 µg L⁻¹ of Pd(II) ions. The accuracy of the developed method was successfully checked by determination of Pd(II) level of certified reference material platinum ore (SARM 7B). The proposed method was successfully applied for Pd(II) determination in various

environmental water samples such as river, lake, sea and tap water, and spent auto catalyst.

Keywords On-line preconcentration · Solid phase extraction · Flame atomic absorption spectrometry · Chelating resin · Flow injection · Silica gel · Modification · Polyamine · Pentaethylenehexamine

Introduction

In recent years, platinum group elements (PGE) have been widely used in the pharmaceutical industry, especially in many cancer drugs and in the automotive industry due to new applications in catalyst production (Muzikar et al. 2006). Among the precious metals, especially palladium, finds wide utilize in the electrical industry for contacts in the telephone relay and in the electrodes circuits for electronic tubing and high quality buzzers. Palladium is released as a major pollutant in the environment, in particular by the use of catalysts containing active palladium metal (Jamali et al. 2007). The release of the palladium ions has been found to increase contamination levels of soil, plant and road sediments near highways (Muzikar et al. 2006).

The development of analytical methods for accurate and precise determination of Pd(II) ions are important both in monitoring the environmental impacts, quality control at industrial products and in the development of procedure for the recovery of palladium ions from waste materials (Nakajima et al. 2009; Zhou et al. 2014a, b). Several sensitive and selective techniques for determination of palladium ions involving as flame atomic absorption spectrometry (FAAS) (Hassanien 2009), inductively coupled plasma optic emission spectrometry (ICP-OES)

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(Niemelä et al. 2012), inductively coupled plasma mass spectrometry (ICP-MS) (Krishna et al. 2009), inductively coupled plasma atomic emission spectrometry (ICP-AES) (Zheng et al. 2007), instrumental neutron activation analysis (INAA) (Avino et al. 2011), cyclic voltammetry (SV) (Velmurugan et al. 2017), X-ray fluorescence spectrometry (Messerschmidt et al. 2000) have been used.

Determination of Pd(II) ions at low concentration in the samples containing high matrix ions makes its direct determination difficult due to interferences from matrix ions and/or insufficient detection limit of the instrument. Therefore, preconcentration and separation procedure before the measurement step is required for determination of Pd(II) ions in environmental samples (Bruzzoniti et al. 2003). Up to now, many different techniques such as coprecipitation (Soylak and Tuzen 2008), solvent extraction (Kondo et al. 2015), liquid–liquid extraction (LLE) (Anthemidis et al. 2001), ion exchange (Schoeman et al. 2017), solid phase extraction (SPE) (Sharma et al. 2012), electrodeposition (Booth et al. 2017), and cloud point extraction (CPE) (Tavakoli et al. 2008) have been used for separation and preconcentration of the Pd(II) ions.

Among the above-mentioned methods, the solid phase extraction method is most often used due to its high preconcentration factor (PF), low cost, low solvent consumption, high recovery, fast phase separation and suitability with different on-line or off-line detection/determination techniques. Many sorbents such as activated carbon (Tavakkoli et al. 2014), modified alumina (Golshaei et al. 2015), multiwalled carbon nanotube (Ghaedi et al. 2013), Amberlite XAD resins (Kovalev et al. 2000), polystyrene-based sorbent (Saitoh et al. 2005), modified silica gel (Mladenova et al. 2012) and polymeric resins (Godlewska-Żyłkiewicz et al. 2012) have been used as a sorbent for off-line solid phase extraction of Pd(II) ions. The main disadvantage of off-line SPE is that it requires a large amount of sample and long time. The on-line SPE methods eliminate these problems and provide advantages such as decrease of sample and eluent consumption, accuracy and precision of analytical results reduction of contamination from laboratory environment due to closed system and enable a fast operation (Nakajima et al. 2009). However, the on-line SPE method is not free from problems. The sorbents used in this method should have a fast metal uptake ability from solution containing high matrix ions and the adsorbed metal ions onto sorbent should be eluted quickly and easily. For this purpose, synthesis of novel sorbents having these properties and its applications to on-line solid phase extraction has been focused in recent years (Antonio et al. 2016; Bosch Ojeda et al. 2007; Zolfonoun and Yousefi 2016; Jia et al. 2016; Rojas et al. 2006;

Rossi et al. 2017; Tarley et al. 2017a, b; Sivrikaya et al. 2016; Karadaş and Kara 2013; Karadaş et al. 2013).

The present work describes a novel on-line preconcentration method using polyamine silica gel coupled with FAAS for determination of Pd(II) ions in environmental samples, spent auto catalyst and certified reference material platinum ore. The Pd(II) adsorption performance of the sorbent was investigated and then on-line preconcentration method was optimized by studying effective factors such as sample and eluent flow rate, eluent type and volume and matrix ions and then, the analytical figures of merit of the developed method was computed.

Experimental

Instrumentation

The measurement of the Pd(II) level in the samples was carried out by a Shimadzu AA6701F flame atomic absorption spectrometer (FAAS) (Shimadzu Corporation, Kyoto, Japan). The FAAS operating conditions were adjusted to optimal condition according to user manual book to obtain the best sensitivity for Pd(II). Air/acetylene flame with acetylene flow rate of 1.8 mL min^{-1} , slit width of 0.5 nm, lamp current of 10 mA, wavelength of 244.8 nm and deuterium background correction were used. The signals were measured as peak height. The pH values were monitored with a Schott Model CG 840 pH meter (Schott AG, Mainz, Germany) equipped with a combined pH electrode. The Heidolph RZR 2020 model mechanical stirrer (Heidolph Instruments GmbH & Co. KG, Schwabach, Germany) and IKA MSH Basic model heated magnetic stirrer (IKA Werke GmbH, Staufen, Germany) were used at synthesis of PA-SG. IKA 4000i model orbital shaker (IKA Werke GmbH, Staufen, Germany) was used for the batch adsorption experiments.

In on-line preconcentration system, to forward the sample solution through mini column to FAAS, a peristaltic pump (Ismatec, Cole-Parmer GmbH, Wertheim, Germany) having four channels was used. 3-stop tubings of Tygon[®] were fixed to the peristaltic pump. The peristaltic pump was connected with polyethylene tubings to 2 two-way valves and then to glass mini column (0.4 mm i.d., 6.0 cm long) (Omnifit, Cambridge, UK). Outlet of the column was connected to FAAS. The valve have a loop can be changeable at a desired volume of eluent. The schematic diagram of the on-line preconcentration system is shown in Fig. 1.

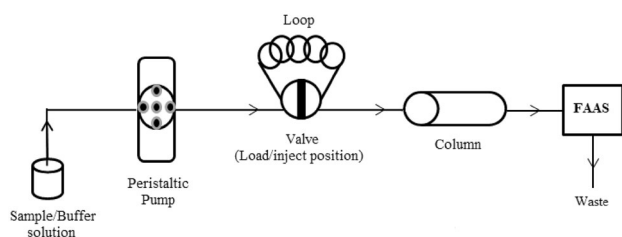


Fig. 1 The schematic diagram of on-line pre-concentration system

Chemicals and Solutions

The chemicals used in this study were of analytical reagent grade. Distilled-deionized water with a chemical resistivity of 18 MΩ.cm was used in all analyses. Distilled water was prepared from tap water using Nüve ND 12 water distiller apparatus (Nüve A.Ş., Ankara, Turkey). Deionized water was prepared from the distilled water using Milli-Q® integral water purification system (Millipore, Bedford, MA, USA). The working and standard solutions were prepared by daily stepwise dilution of spectroscopic grade Pd(II) standard solution (1000 mg L⁻¹ Pd(II), Merck KGaA, Darmstadt, Germany). Silica gel, 3-chloropropyl-trimethoxysilane, triethylamine (Merck KGaA, Darmstadt, Germany), pentaethylenhexamine (Fluka, Steinheim, Germany), were used without any purification. The acidity of Pd(II) solutions were determined by adding dilute HCl, HNO₃ or NaOH solution (Merck KGaA, Darmstadt, Germany) and controlled with pH meter. The platinum ore SARM 7B from The South African Bureau of Standards, which certified reference material was used for testing accuracy of the proposed method. Synthesis and characterization of silica gel modified by covalent attachment of polyamine group was given in the previous study (Sivrikaya et al. 2014). Proposed structure of polyamine silica gel is illustrated in Fig. 2. The content of pentaethylenhexamine on the modified silica gel was found to be 0.53 mmol g⁻¹ (Sivrikaya et al. 2014).

Batch Adsorption Studies

The adsorption dynamics of Pd(II) ions on PA-SG were investigated with a batch adsorption method. The effects of solution acidity and chloride concentration, Pd(II) initial concentration and contact time on the adsorption of Pd(II) ions were investigated. The solutions containing 50 mL Pd(II) ions at different concentrations (50 or 100 mg L⁻¹) were shaken with 50 mg of PA-SG at ambient temperature for various times using the orbital shaker. Then, mixture

was filtered off and the concentrations of Pd(II) ions remaining in the solution was determined by FAAS, and the amounts of Pd(II) adsorbed onto PA-SG were computed by Eq. (1).

$$q_e = \frac{(C_o - C_e) \cdot V}{m}, \quad (1)$$

where q_e is amount of Pd(II) adsorbed on PA-SG (mg g⁻¹); C_o is initial Pd(II) concentration (mg L⁻¹); C_e is concentration of Pd(II) remained in the solution (mg L⁻¹); V is volume of Pd(II) solution (L); m is amount of PA-SG (g) (Karaçetin et al. 2014).

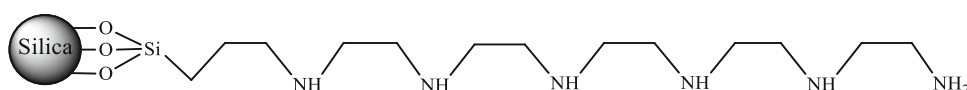
On-line Preconcentration Procedure

The mini column was filled about 120 mg of PA-SG and then preconditioned at desired acidic condition using appropriate acid solution (by 0.1 M HCl in optimal condition) for 30 s at 5 mL min⁻¹ flow rate. The sample was passed at 5 or 7.5 mL min⁻¹ for 60 s. The eluent was filled to the loop. The column was washed with 0.1 M HCl solution for 20 s to eliminate the matrix ions. After sample loading and cleaning, the valve was shifted to the inject position and the eluent was passed through the column at 7.5 mL min⁻¹ flow rate. The eluate containing Pd(II) was reached directly into the FAAS and the observed peak height was recorded. After this cycle, the column was cleaned with 0.1 M HCl solution for 45 s and the system was ready for the next operation. All experiments were carried out three times and the average of the results was submitted in this study.

Sample Preparation

Spent auto catalyst from local auto service from Sakarya, Turkey was carefully grinded using agate mortar. The certified platinum ore SARM 7B and spent auto catalyst was digested using concentrated HCl–HNO₃ solutions according to literature. Briefly, 2.00 g of the CRM or catalyst was mixed with 40 mL of reverse aqua regia and the suspension was evaporated to dryness. Then, 20 mL of 1/1 (v/v) concentrated HCl–HNO₃ solution was added over the residue. After evaporation to dryness; 30 mL of 10% HCl solution was added to the beaker and the suspension was filtered off and the filtrate was completed to 100 mL. After adjustment of the pH of the sample to 1.0, the developed on-line SPE procedure was performed for the determination of Pd(II) level in the samples (Sivrikaya et al. 2011; Imamoglu et al. 2005).

Fig. 2 Proposed structure of polyamine silica gel



The proposed method was also employed for determination of the Pd(II) levels in some environmental water samples such as Sakarya River, laboratory tap water, Sapanca lake and Marmara seawater. The water samples were immediately acidified with HNO₃ to a pH of 2.0 and then filtered using 0.45 μm cellulose acetate membranes. After spiking of 0.1 M chloride in the final samples, the developed method was used for the determination of Pd(II) level in the samples. Spiking and recovery test was also carried out to test accuracy of the developed method.

Results and Discussion

Optimization of Sample Solution Acidity and Chloride Concentration for Pd(II) Uptake

In order to study the effect of solution acidity on the Pd(II) adsorption by PA-SG, the HNO₃ level was changed between 0.025 and 5.0 M in 50 mL of Pd(II) solutions containing 50 or 100 mg L⁻¹ Pd(II) and 0.1 M chloride. Then, 50 mg of PA-SG was added to these Pd(II) solutions. After their shaking for 240 min, the concentration of Pd(II) ions remaining in the filtrate was measured by FAAS. The changes in adsorption of Pd(II) ions with the acidity of the solutions are shown in Fig. 3. Pd(II) adsorption is found to be increased by increasing of HNO₃ concentration in the solution from 0.025 to 0.1 M. Further increasing of the solution acidity decreases the adsorption of Pd(II) and does not even lead to Pd(II) adsorption in the solution containing 5.0 M HNO₃. On the other hand, it is known that adsorption of polyamine with other metal ions [Fe(III), Cu(II), Ni(II), etc.] also occurs at lower nitric acid concentrations than < 0.01 M (or pH 2 and above) (Fan et al. 2012; Radi et al. 2013; Wang et al. 2014). The adsorption of Pd(II) at lower HNO₃ level than < 0.025 M was not investigated to eliminate adsorption of these metals. For this reason, it was

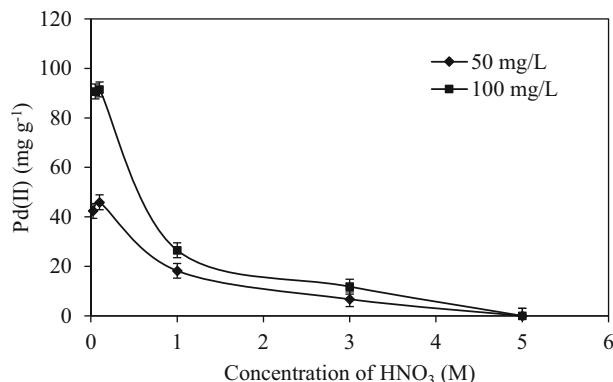


Fig. 3 Effect of solution acidity on the adsorption of Pd(II) ions with PA-SG ($n = 3$)

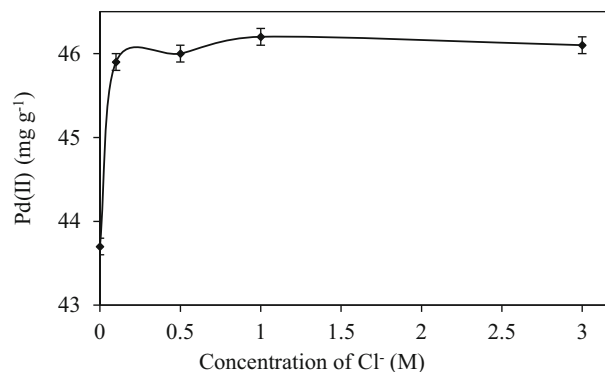


Fig. 4 Effect of concentration of chloride ions using on-line preconcentration method ($n = 3$)

decided that the acidity of the sample solution for the efficient adsorption of Pd(II) ions was 0.1 M HNO₃ containing solutions.

The effect of chloride concentration on the Pd(II) uptake of PA-SG was examined batchwise. For this purpose, chloride concentrations ranging from 0.0 to 3.0 M were added to Pd(II) solution (50 mL) in 0.1 M HNO₃. Then, 50 mg of PA-SG was suspended with the solutions and shaken for 360 min. The change of Pd(II) adsorption by the chloride concentration is shown in the Fig. 4. Increasing of chloride concentration from 0.0 to 0.1 M caused an about 5% increase in adsorption of Pd(II) and further increase in chloride level not caused positive or negative effect on the adsorption. Therefore, to obtain the most efficient Pd(II) adsorption with PA-SG, optimal chloride level of Pd(II) solutions were found to be 0.1 M. On the other hand, Pd(II) adsorption ability of PA-SG from solution containing 3.0 M chloride also suggests that the interaction between Pd(II) and polyamine silica gel is mainly due to formation of the chelating complex. However, since the presence of chloride ions enhances the adsorption, the ion exchange mechanism also contributes to Pd(II) adsorption.

Effect of Contact Time and Kinetics of Pd(II) Ions on PA-SG

The effect of contact time on the Pd(II) uptake of PA-SG was examined batchwise. To investigate the adsorption kinetic of Pd(II) ions and to find the equilibrium time, 20 mg of PA-SG was added to 200 mg L⁻¹ Pd(II) solutions (50 mL) containing 0.1 M chloride ions and stirred at ambient temperature for various times ranged from 5 to 600 min. The adsorption of Pd(II) ions on PA-SG by contact time is shown in Fig. 5. The adsorption of Pd(II) was rapidly increased in first 30 min and then, the adsorption was increased slowly until reach the equilibrium conditions at 360 min. Even if the Pd(II) adsorption on PA-

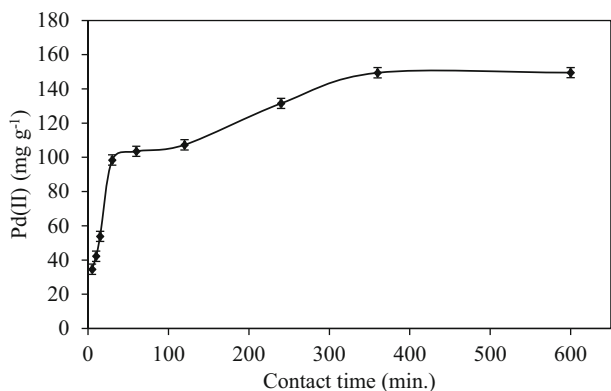


Fig. 5 Effect of contact time on the adsorption of Pd(II) ions on PA-SG ($n = 3$)

SG seems to be long, the PA-SG can adsorb 34.60 mg Pd(II) ions in the first 5 min. This capacity is quite sufficient for uptake trace level of Pd(II) from solution and so, PA-SG can be reliably used for on-line preconcentration Pd(II) ions.

The adsorption of Pd (II) ions on PA-SG was applied to two different kinetic models that pseudo first order and pseudo second model.

Pseudo first order kinetic model equation can be given by Eq. (2) by:

$$\ln(q_e - q_t) = \ln q_e - k_1 t, \tag{2}$$

where q_e (mg g^{-1}) and q_t (mg g^{-1}) show amount of Pd(II) adsorbed on PA-SG at equilibrium and at time t and k_1 (min^{-1}) is pseudo first order rate constant. A plot of $\ln(q_e - q_t)$ versus t is a straight line, where q_e and k_1 are calculated from intercept and gradient of the line, respectively (Lagergren 1898).

Pseudo second order kinetic model is given by the following Eq. (3):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{3}$$

where k_2 ($\text{g mg}^{-1} \text{min}^{-1}$) is second order rate constant. A plot of t/q_t versus t gives a straight line, and q_e and k_2 are calculated from gradient and intercept of the line, respectively (Ho and McKay 1998).

Pseudo first order and pseudo second order kinetic models constants for Pd(II) adsorption by PA-SG are given

in Table 1. The calculated q_e values ($q_{e \text{ cal}}$) for the pseudo first and second order kinetic models are close to the experimental q_e values ($q_{e \text{ exp}}$). However, when the correlation coefficients of the two kinetic models are compared, it is seen that the correlation coefficient of the pseudo second order kinetic model is closer to unity. Hence, Pd(II) adsorption onto PA-SG is more compatible with pseudo second order kinetic model.

Pd(II) Adsorption Isotherms

The Langmuir and Freundlich isotherms have been successfully applied to identification of Pd(II) adsorption data (Langmuir 1918; Freundlich 1906). The Langmuir and Freundlich isotherms are expressed by the following Eqs. (4 and 5), respectively:

$$q_e = \frac{q_{\text{max}} K_L C_e}{1 + K_L C_e} \tag{4}$$

$$q_e = K_F C_e^{1/n} \tag{5}$$

where K_L and q_{max} are Langmuir constants related to free energy or adsorption enthalpy (L mg^{-1}) and maximum monolayer adsorption capacity (mg g^{-1}), respectively, and Freundlich coefficients n and K_F are related to adsorption intensity and adsorption capacity, respectively (Ghasemi and Asadpour 2007; Moazezi and Moosavian 2016). The curves of Langmuir and Freundlich isotherms are shown in Fig. 6 and isotherm coefficients of both models are given in Table 2.

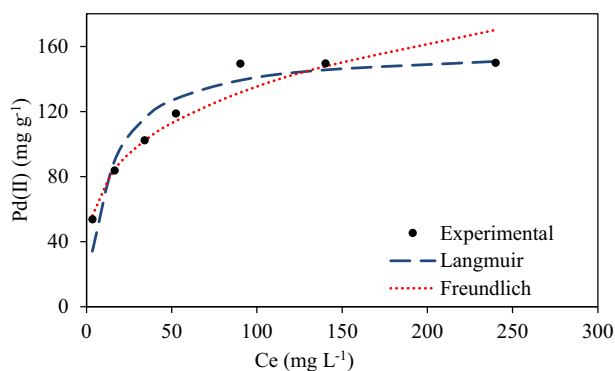


Fig. 6 Experimental, Langmuir and Freundlich isotherm graphs for adsorption of Pd(II) ions

Table 1 Parameters of pseudo first order and pseudo second order kinetic models for Pd(II) adsorption by PA-SG

$q_{e \text{ exp}}$ (mg g^{-1})	Pseudo first order			% Recovery	Pseudo second order			% Recovery
	$q_{e \text{ cal}}$ (mg g^{-1})	$k_1 \times 10^2$ (min^{-1})	r^2		$q_{e \text{ cal}}$ (mg g^{-1})	$k_2 \times 10^4$ ($\text{g mg}^{-1} \text{min}^{-1}$)	r^2	
149.5	145.4	1.6	0.8354	97.2	156.3	2.2	0.9960	104.5

Table 2 Constants of Langmuir and Freundlich isotherms

Langmuir constants			Freundlich constants		
q_{\max} (mg g ⁻¹)	$K_L \times 10^2$ (L mg ⁻¹)	r^2	K_F	n	r^2
158.7	7.9	0.9960	40.4	3.8	0.9599

Considering the correlation coefficients of Langmuir and Freundlich isotherms for the adsorption of Pd(II) ions with PA-SG, it is seen that the correlation coefficient of Langmuir isotherm is higher than Freundlich isotherm and closer to unity. Furthermore, the maximum adsorption capacity experimentally found was more accurately estimated by the Langmuir isotherm. Therefore, it was concluded that adsorption of Pd(II) ions with PA-SG is more compatible with Langmuir isotherm equation.

The maximum Pd(II) adsorption capacities of different adsorbents are listed in Table 3 for comparison. Although higher capacity sorbents than the Pd(II) adsorption capacity of PA-SG were reported in the literature, PA-SG can also be listed among the high Pd(II) adsorption capacity sorbents and this capacity is enough for the on-line preconcentration of trace level of Pd(II) ions.

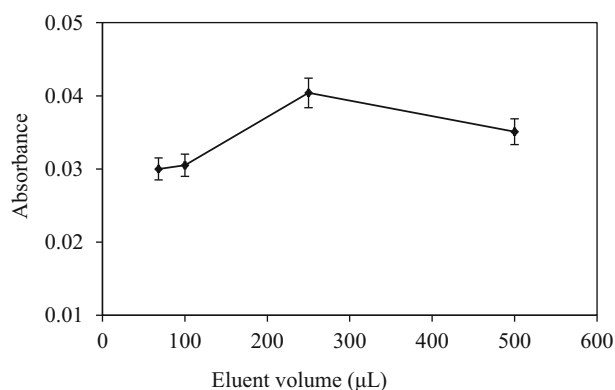
Optimization of the On-line Preconcentration Procedure

Optimization of the Eluent

To determine the most efficient eluent for Pd(II) ions from the PA-SG, solutions of thiourea in HCl were tested as eluent. For this purpose, Pd(II) solution was passed through the column at a flow rate of 5 mL min⁻¹ and adsorbed Pd(II) ions eluted with different thiourea in HCl solution at a flow rate of 5 mL min⁻¹. The results in Table 4 demonstrated that the absorbance was the best when 1.0 and 3.0% thiourea in 1.0 M HCl was used as eluent. 1.0% thiourea in 1.0 M HCl solution was selected as the optimal eluent due to contain fewer dissolved matter.

Table 4 The effect of different eluent concentration using the on-line preconcentration system (mean \pm standard deviation, $n = 3$)

Eluent	Absorbance
Thiourea, 3% in 1 M HCl	0.0378 \pm 0.0015
Thiourea, 3% in 0.1 M HCl	0.0378 \pm 0.0006
Thiourea, 1% in 1 M HCl	0.0378 \pm 0.0005
Thiourea, 1% in 0.1 M HCl	0.0362 \pm 0.0010

**Fig. 7** Effect of eluent volume on the on-line preconcentration system ($n = 3$)

Different eluent volumes (68–500 μL) were tested to optimize the on-line preconcentration system. For this purpose, the sample solution was passed through the column at a flow rate of 5 mL min⁻¹ for 1 min and then, retained Pd(II) ions on PA-SG were eluted at a flow rate of 7.5 mL min⁻¹. The results in Fig. 7 show that full elution of adsorbed Pd(II) on the PA-SG is not achieved when 68 μL of the eluent volume is used. Full elution was done by 250 μL volume of the eluent. Therefore, 250 μL of the eluent volume was optimized in this study.

Effect of eluent was studied at flow rates in the range from 2.5 to 7.5 mL min⁻¹ using 250 μL of 1% thiourea in 1 M HCl and the highest absorbance was obtained at

Table 3 Comparison with other sorbents of Pd(II) adsorption capacities in the literature

Adsorbent	Adsorption capacity (mg g ⁻¹)	References
L-lysine modified crosslinked chitosan resin	109.47	(Fujiwara et al. 2007)
Mesoporous carbon, CMK-3	63.85	(Zalupski et al. 2014)
3'-Nitro-4-amino azobenzene modified chitosan	29.33	(Wang et al. 2011)
N-aminoguanidine immobilized persimmon tannin	213.90	(Gurung et al. 2013)
Graphene oxide	80.78	(Liu et al. 2013)
1,3,5-Triazine-pentaethylenhexamine polymer	517.20	(Saymet et al. 2015)
Ethylenediamine modified magnetic chitosan nanoparticle	138.00	(Zhou et al. 2010)
The Indian almond tannin	41.86	(Ramakul et al. 2012)
Polyamine silica gel	158.7	This study

7.5 mL min⁻¹. So, the 7.5 mL min⁻¹ was selected as the optimum eluent flow rate.

Optimization of the Sample Flow Rate and Volume

The flow rate of the sample solution determines the contact time between the analytes and the sorbent in the on-line preconcentration procedures. Hence, sorbents should have fast kinetics of sorption of analytes for success of on-line preconcentration method. High flow rate of both sample and elution solutions are preferred in on-line preconcentration systems. The sampling frequency increases by high flow rate of sample solutions. The low flow rate of eluent solution causes to peak expansion.

The sample solution (5 mL) containing 0.1 mg L⁻¹ Pd(II) was passed through the mini column at various flow rates ranged from 2.5 to 7.5 mL min⁻¹. It was found that there was no change in the absorbance by the increasing of sample flow rate. Therefore, the highest flow rate of 7.5 mL min⁻¹ was chosen as the optimum sample flow rate.

Different volumes of sample solutions in 0.1 M HCl containing same amount of Pd(II) (0.5 µg) were passed through the mini column and then, adsorbed Pd(II) ions were eluted using 250 µL of % 1 thiourea in 0.1 M HCl at flow rate of 7.5 mL min⁻¹. The Pd(II) absorbances were not decreased up to 30 mL of sample volume. So, it can be concluded that the method can reliably be used up to 30 mL sample volume when the concentration of Pd(II) is low to achieve high PF or to obtain smaller LOD values.

Effect of Matrix Ions

To examine the effects of the matrix ions for the determination of Pd(II) ions at the on-line preconcentration system, various heavy metal ions and some major cations and anions were spiked to 0.1 mg L⁻¹ Pd(II) solutions. Then, the solutions were passed through the mini column

Table 6 Experimental parameters of the developed on-line preconcentration method for Pd(II) ions

Conditioning solution	0.1 M HCl
Conditioning flow rate	5 mL min ⁻¹
Conditioning flow time	30 s
Sample flow rate	5 or 7.5 mL min ⁻¹
Sample flow time	60 s
Washing rate	5 mL min ⁻¹
Washing time	20 s
Eluent type	% 1 thiourea in 0.1 M HCl
Eluent volume	250 µL
Eluent flow rate	7.5 mL min ⁻¹

for 1 min at a flow rate of 7.5 mL min⁻¹, and the elution was done using 250 µL of %1 thiourea in 0.1 M HCl at a flow rate of 7.5 mL min⁻¹. The concentrations of matrix ions given in Table 5 caused a relative error of less than 5% in the on-line determinations of Pd(II). So, the developed on-line preconcentration technique for Pd(II) can reliably be used for the determination of Pd(II) levels in real samples containing similar matrix ions.

Analytical Figures of Merit

Experimental parameters of the developed on-line preconcentration method for Pd(II) ions are listed in Table 6 and the analytical figures of merit of the method containing calibration curve equation, linear range, limit of detection (LOD), limit of quantification (LOQ), and preconcentration factor is listed in Table 7.

The LOD of 3 µg L⁻¹ and LOQ of 10 µg L⁻¹ were described as $3\sigma/m$ and $10\sigma/m$, respectively, where σ is the standard deviation of ten replicates of blank signal and m is the slope of the calibration curve after preconcentration system. The relative standard deviation (RSD) for the

Table 5 Effect of matrix ions on on-line preconcentration of Pd(II) ions

Matrix ions	Added as	Concentration (mg L ⁻¹)	Absorbance	% Changes of absorbance
Cu ²⁺	Cu(NO ₃) ₂	40	0.0643	+ 2.0
Fe ³⁺	Fe(NO ₃) ₃	40	0.0615	- 2.5
Ni ²⁺	Ni(NO ₃) ₂	40	0.0653	+ 3.7
Cd ²⁺	Cd(NO ₃) ₂	40	0.0665	+ 1.4
Cr ³⁺	Cr(NO ₃) ₃	40	0.0626	- 0.6
K ⁺	KNO ₃	1000	0.0622	- 1.1
Na ⁺	NaNO ₃	20,000	0.0604	- 4.2
Ca ²⁺	Ca(NO ₃) ₂	1000	0.0625	- 0.8
Mg ²⁺	MgCl ₂	1000	0.0611	- 3.1
SO ₄ ²⁻	Na ₂ SO ₄	1000	0.0618	- 1.8
PO ₄ ³⁻	KH ₂ PO ₄	1000	0.0602	- 4.5
Cl ⁻	NaCl	20,000	0.0620	- 1.5

Table 7 Analytical characteristics of Pd(II) ions by on-line preconcentration system

Parameter	Analytical features
Linear range ($\mu\text{g L}^{-1}$)	10–200
On-line calibration equation (c in $\mu\text{g/L}$)	$A = 6 \times 10^{-4}c - 3 \times 10^{-4}$
Direct aspiration equation (c in mg/L)	$A = 2.5 \times 10^{-2}c + 4 \times 10^{-4}$
Preconcentration factor	23.9
Correlation coefficient	0.9916
LOD ($\mu\text{g L}^{-1}$) (3σ , $n = 10$)	3.0
LOQ ($\mu\text{g L}^{-1}$) (10σ , $n = 10$)	10.0
RSD (%)	4.6
Sampling frequency (h^{-1})	20

$25 \mu\text{g L}^{-1}$ of Pd(II) was 4.6% at five replicate measurements. Additionally, RSD was calculated from the real samples analysis results of CRM platinum ore SARM 7B and was found to be 5.7% ($n = 3$). The calibration curve was linear in the range of 10–200 $\mu\text{g L}^{-1}$. The preconcentration factor of 23.9 was obtained from the ratio of calibration curves slopes obtained with the on-line preconcentration and direct aspiration. The sampling frequency of the on-line preconcentration method was calculated to be 20 h^{-1} which showing the rapidity of the developed method.

Accuracy of the On-line Preconcentration Method

To test the accuracy of the proposed method, the proposed method was applied to the certified reference material platinum ore SARM 7B for the determination of Pd level. The obtained results in Table 8 show that the found Pd level by the developed on-line preconcentration method was determined with a relative error of -8.4% . Student's test (t test) at 95% confidence level was performed to examine the compliance of obtained value and the certified reference value. It was found that the t_{exp} (experimental value) value of 2.81 was lower than t_{crit} (critical value) of 4.30. Therefore, there is no significant difference between the obtained and the certified values at 95% confidence level.

Determination of Pd(II) Level in Various Samples

This developed method was successfully applied to the determination of Pd(II) levels in spent auto catalyst and water samples. To check the accuracy of the method, different amounts Pd(II) ions were spiked to these water

Table 8 Determination Pd level in certified reference material (SARM-7B) by the developed on-line preconcentration method (mean \pm standard deviation, $n = 3$)

Sample	Obtained value ($\mu\text{g g}^{-1}$)	Certified value ($\mu\text{g g}^{-1}$)
SARM-7B	1.41 ± 0.08	1.54 ± 0.032

samples and recoveries were computed after measuring of Pd(II) levels by on-line preconcentration system coupled with FAAS. The found Pd(II) concentrations in environmental water samples, spiked and recovery values of Pd(II) are presented in the Table 9. The level of Pd(II) was found to be below LOD level of the method. The recoveries of Pd(II) ions from spiked samples are in the range of 98.0–108% showing the method can be used successfully for Pd(II) determination in environmental samples in the presence of different matrices. Application of the method to solid material for the determination of Pd(II) level was also carried out using spent auto catalyst sample. The Pd(II) concentration in the spent auto catalyst was found to be $3530 \pm 70 \mu\text{g/g}$. The found level of Pd(II) in spent auto catalyst is similar to the results in the literature (Saçmacı et al. 2013).

Comparison of the On-line Preconcentration Method

Analytical figures of merit of different methods reported in the literature for the on-line preconcentration of Pd(II) ions

Table 9 The determination of palladium in water samples in on-line preconcentration system ($n = 3$)

Sample	Added ($\mu\text{g L}^{-1}$)	Found ($\mu\text{g L}^{-1}$)	Recovery (%)
Sakarya river	–	< LOD	–
	25	27 ± 1	108
	50	51 ± 1	102
Tap water	–	< LOD	–
	25	26 ± 2	104
	50	53 ± 1	106
Sapanca lake	–	< LOD	–
	25	25 ± 1	100
	50	52 ± 2	104
Marmara sea	–	< LOD	–
	25	24 ± 1	98
	50	51 ± 1	102

Table 10 Comparison with other sorbents for the on-line preconcentration of Pd(II) at literature

Column material	Detection method	Detection limit ($\mu\text{g L}^{-1}$)	Preconcentration factor	Application	References
Polyamine metalfix/chelamine resin	FAAS	9.0	20	Synthetic geological samples and certified reference material	(Iglesias et al. 2003)
Silica beads functionalized with diethylenetriamine groups, QuadraSil™ TA	ICP-OES	1.4	12.9	Steam sediment and used auto catalyst certified reference materials	(Nakajima et al. 2009)
Diphenyldiketone-monothiosemicarbazone modified silica gel	AAS	5	335	Tap water and catalytic converter samples	(Sharma et al. 2012)
Dowex-1X8-200	GFAAS	2	8.7	Certified reference materials	(Bosch Ojeda et al. 2007)
Amidinothioureido-silica gel	FAAS	17	–	Metallurgical samples	(Zhang et al. 2002)
Dendrimer-like polyamidoamine immobilized silica	FAAS	3.9	–	Two metallurgical samples	(Wu et al. 2004)
K ⁺ 18-Crown-6	GFAAS	0.016	29	Spiked blood and roadside dust samples	(Limbeck et al. 2004)
Polyaniline (PANI)	ICP-MS ICP-OES	0.0004 0.22	125	Industrial waste water	(Krishna et al. 2009)
Magnetic nanoparticles	GFAAS	0.28	13.9	Certified reference materials and mine samples	(Ye et al. 2014)
Silica gel immobilized thiourea	FAAS	21	15–20	Nickel alloy, an anode slime, an electrolytic solution	(Liu et al. 2000)
Carboxylated pillar[5]arene	FAAS	16.0	16	Certified reference materials and geological samples.	(Zhou et al. 2014a, b)
C60, coated with ammonium pyrrolidinedithiocarbamate (APDC)	ICP-MS	0.044	–	Certified reference materials SARM-7 (platinum ore)	(Leśniewska et al. 2005)
Polyamine silica gel	FAAS	3	23.9	Certified reference material, spent auto catalyst and water samples	This work

are summarized in Table 10. The PF of two methods was reported to be 125 (Krishna et al. 2009) and 335 (Sharma et al. 2012) and the others were in the range of between 8.7 and 29. The PF of the developed method in this study is 23.9 and it could be said that similar PF is obtained with many other studies. The LOD of the on-line preconcentration methods coupled with FAAS is in the range of 3.0 and 16 $\mu\text{g L}^{-1}$ and two instruments (GFAAS and ICP-MS) have a lower LOD values than FAAS. The LOD value of the developed method has the lowest LOD values among the FAAS based methods.

Conclusion

The on-line preconcentration and adsorption of Pd(II) by polyamine attached silica gel was fully investigated for the development novel method for determination of Pd(II) levels. The PA-SG can efficiently uptake Pd(II) ions from solution containing 0.1 M H_3O^+ and Cl^- . The batch adsorption of Pd(II) was reached to equilibrium at 360 min

and PA-SG has Pd(II) uptake capacity of 158.7 mg g^{-1} . The on-line preconcentration of Pd(II) using PA-SG can adsorb and release Pd(II) ions at high flow rate of 7.5 mL min^{-1} . The limit of detection of the method for Pd(II) was 3 $\mu\text{g L}^{-1}$. The required time for the determination of Pd(II) ions by on-line preconcentration system was 3 min and sampling frequency was found to be 20 h^{-1} . The precision and accuracy of this developed method was satisfactory. The method offers many advantages such as simplicity, usability, rapid sample loading, fast elution, and being environmentally friendly and has also very good precision and accuracy for on-line preconcentration of Pd(II) ions.

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