



Determination of Palladium in Water by FAAS after Preconcentration and Separation with the Modified Barium-Strontium Titanate Powder by Dithizone

DONG ZHANG* and PING YU

School of Environmental and Chemical Engineering, Shen yang Ligong University, Shenyang 110159, P.R. China

*Corresponding author: Tel/Fax :+ 86 24 24680345; E-mail: sylgxdong@sina.com

(Received: 14 April 2011;

Accepted: 25 November 2011)

AJC-10747

A new method of preconcentration and separation with the modified barium-strontium titanate powder by dithizone (dithizone-BST) combined with flame atomic absorption spectrometry (FAAS) was proposed for the determination of trace palladium. The optimum experimental parameters for the adsorption and preconcentration of Pd(II), such as pH value of medium, contact time, eluent and coexisting ion, have been investigated. Moreover, the thermodynamics and kinetics of the adsorption were studied. The results showed that the Pd(II) could be quantitatively retained by the dithizone-BST in the pH range of 2 using hydrochloric acid, the adsorption time was 15 min and capability of adsorption was 21.135 mg g⁻¹. The adsorption behaviour followed a Langmuir adsorption isotherm and a pseudo-second-order kinetic model, the adsorption was an endothermic and spontaneous physical process. The Pd(II) adsorbed on the dithizone-BST could be completely eluted by using ethylenediamine and sodium hydroxide mixture. The detection limit of this method for Pd(II) was 0.22 µg/L and the enrichment factor was 100. The method has been applied to the determination of trace amounts of Pd(II) in water with satisfactory results.

Key Words: Palladium(II), FAAS, Solid phase extraction, Dithizone, Barium-strontium titanate.

INTRODUCTION

Palladium is a noble metal of economic importance due to its extensive use in metallurgy, various chemical syntheses, medicinal devices, electronics applications, production of multi-layer ceramic capacitors. In recent years, with the rapid development of automobile manufacturing, one of the most important applications of palladium is the production of catalytic converters for car engines^{1,2}. At present, determining the presence of Pd(II) in water is typically accomplished by atomic absorption spectrometry (AAS) and inductively coupled plasma atomic emission spectrometry (ICP)³⁻⁵. However, it is difficult to determine extremely low concentrations of the palladium in complex matrices by these methods without enrichment and separation procedures. Therefore, due to the effect of matrix and low concentrations of Pd(II), an enrichment and separation procedure prior to detection is required. The widely used techniques for the separation and preconcentration include solvent extraction⁶⁻⁸, co-precipitation⁹, ion-exchange⁵ and solid phase extraction (SPE)^{10,11}, etc. In these techniques, solid phase extraction techniques have become increasingly popular compared with the classical pre-separation and enrichment methods because of their high enrichment factor, rapid phase separation, low cost and lower organic solvent consumption, as well as the ability to combine

with different detection techniques in on-line or off-line mode. The main solid-phase extraction sorbents are chelating resin^{12,13}, modified silica^{14,15}, active carbon¹⁶ and carbon nanotubes¹⁷, etc.

In present study, the modified barium-strontium titanate powder by dithizone (dithizone-BST) has been used in the adsorption of lead and cadmium with satisfied results^{18,19}. But the dithizone-BST use in solid-phase extraction of Pd(II) in the water has not been studied. In this work, dithizone-BST was used as an solid phase extraction agent to preconcentration and separation of palladium in water.

EXPERIMENTAL

A WYX-9003A atomic absorption spectrometer (Shenyang Yi Tong Analytical Instrument Co. Ltd.) equipped with hollow cathode lamps for palladium, was used for palladium determination. The measurements were done in air-acetylene flame and the operation conditions of the palladium were as follows: wavelength is 244.8 nm, spectral band width is 0.2 nm, lamp current is 5.0 mA, burner height is 8.0 mm, acetylene gas consumption is 8000 mL min⁻¹ and air flow consumption is 900 mL min⁻¹. All pH measurements were made with a PHS-3C model digital pH meter (Shanghai REX Instrument Factory, Shanghai, China) equipped with a combined pH electrode. A

constant temperature bath shaker (Jintan Experiment Instrument Factory, Jiangsu China) was used to shaking for adsorption and elution.

A modified barium-strontium titanate powder by dithizone (dithizone-BST) was prepared in our laboratory as described elsewhere^{18,19}. A stock solution (1 g L^{-1}) of Pd(II) was prepared by dissolving 1.666 g of palladium dichloride (Sinopharm Chemical Reagent Co., Ltd., China) in 5 mL of aqua regia and dilution to 100 mL with distilled water. Working standard solutions were prepared from the stock solution daily. Hydrochloric acid and sodium hydroxide (all from Sinopharm Chemical Reagent Co. Ltd., China) were used to adjust pH of the sample solutions. Ethylenediamine (100 g L^{-1}) and sodium hydroxide (20 g L^{-1}) mixture.

A quantity of Pd(II) solution was placed into a 50 mL calibrated colourimetric cylinder with plug. The pH was adjusted to 2 with hydrochloric acid or sodium hydroxide solution. After diluting to the mark with water of pH 2, 0.1 g of dithizone-BST was added. Covered with a plug, the colourimetric cylinder was shaken for 15 min in the constant temperature bath shaker. Filtrated using filter, then the concentration of Pd(II) in filtrate was determined by flame atomic absorption spectrometry and adsorption capacity was calculated. Then the adsorbent was washed with water of pH 2 to remove any unadsorbed Pd(II), the adsorbed Pd(II) was eluted with 5 mL of ethylenediamine (100 g L^{-1}) and sodium hydroxide (20 g L^{-1}) mixture by shaking for 5 min. The concentrations of the Pd(II) in the eluents was determined by flame atomic absorption spectrometry and the recovery was calculated.

RESULTS AND DISCUSSION

Effect of pH on the adsorption: One of the most important parameters affecting the adsorption procedure is the pH. Because the pH values of the medium governing the complexation of dithizone with Pd(II). In order to study the effect of pH on the adsorption, the pH was adjusted in the ranges of 1-9 using hydrochloric acid or sodium hydroxide solution and then the adsorption procedure described was applied. The results are shown in the Fig.1. The adsorption percentage of Pd(II) at the pH ranges of 1 to 3 was 100 %. In this work, pH 2 was selected as the optimal condition.

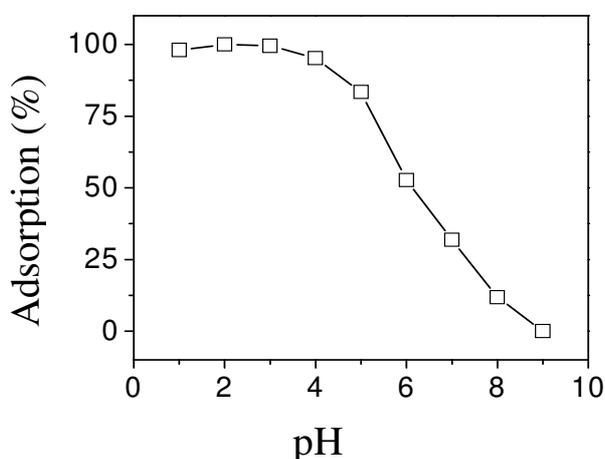


Fig. 1. Effect of pH on the adsorption

Effect of temperature and contact time: In order to study the influence of temperature and shaking time on the adsorption of Pd(II) onto dithizone-BST, the adsorption capacities were determined at different temperature and contact time, respectively. The results are showed in Fig. 2. It is seen that temperature and contact time had a great influence on the adsorption equilibrium time and the amount adsorbed. With the increase of temperature, the equilibrium adsorption capacities were increasing and the needed time to adsorption equilibrium was shortened. At 293 K, the adsorption needed 10 min to reach equilibrium. When the temperature was up to 313 K, the time was only 5 min.

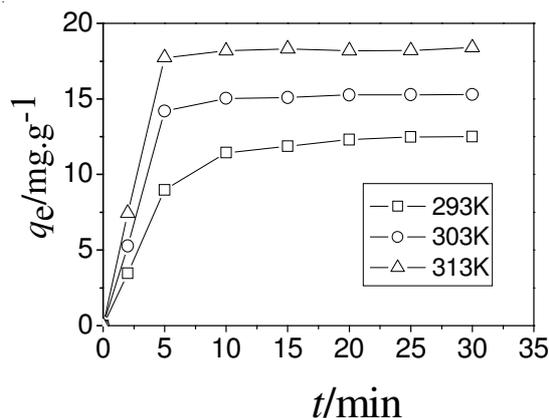


Fig. 2. Effect of contact time on Pd(II) adsorption at various temperatures

Adsorption isotherms and thermodynamic studies: Pd(II) adsorption isotherm data starting at different initial concentrations were investigated following the models of Langmuir and Freundlich.

The expression of the Langmuir model²⁰ is:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \quad (1)$$

where, q_e is the equilibrium metal ion concentration on the adsorbent (mg g^{-1}), C_e is the equilibrium metal ion concentration in solution (mg L^{-1}), q_m is the monolayer capacity of the adsorbent (mg g^{-1}) and K_L is the Langmuir adsorption constant (L mg^{-1}).

The logarithmic expression of the Freundlich equation is²⁰:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (2)$$

where, q_e is the equilibrium metal ion concentration on the adsorbent (mg g^{-1}), C_e is the equilibrium metal ion concentration in solution (mg L^{-1}) and K_F (L mg^{-1}) and n are the Freundlich constants for adsorption capacity and adsorption intensity, respectively.

The adsorption isotherms are shown in Fig. 3. The values of q_m , K_L , K_F and $1/n$ and the correlation coefficients (r) for Langmuir and Freundlich are given in Table-1.

The values of the correlation coefficients (r) demonstrate almost perfect agreement between the experimental data and the Langmuir model. This indicate that the adsorption of Pd(II) by the dithizone-BST was monolayer-type. The values of the Langmuir constant, K_L , increased as temperature increased,

indicating that the adsorption capacity and intensity of adsorption are enhanced at higher temperatures.

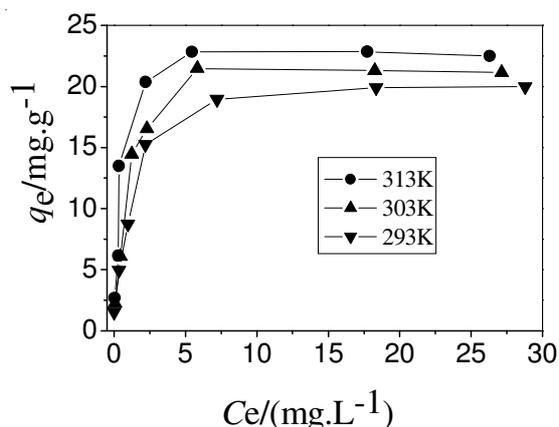


Fig. 3. Adsorption isotherms

TABLE-1
LANGMUIR AND FREUNDLICH CONSTANTS
FOR THE ADSORPTION OF Pd(II)

T/K	Langmuir			Freundlich		
	q_m	K_L	r^2	n	K_F	r^2
293	21.135	5.058	0.9970	2.15	6.042	0.4345
303	21.519	5.457	0.9991	2.535	7.124	0.464
313	21.927	5.947	0.9973	2.309	7.287	0.5293

Thermodynamic parameters such as adsorption enthalpy (ΔH), Gibbs free energy (ΔG) and entropy (ΔS) for the adsorption process can be calculated from the van't Hoff equation and Gibbs-Helmholtz equation²⁰:

$$\ln C_e = -\ln K_0 + \frac{\Delta H}{RT} \quad (3)$$

$$\Delta G = -RT \ln C_e \quad (4)$$

$$\Delta S = \frac{\Delta H - \Delta G}{T} \quad (5)$$

where, R is the ideal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), T is temperature (K), K_0 is constant and C_e is the solution concentration at equilibrium. The slope of the plots of $\ln C_e$ versus $1/T$ used to determine ΔH , ΔG and ΔS were obtained from eqns. 4 and 5 respectively. The results are listed in Table-2.

TABLE-2
ISOSTERIC ENTHALPY CHANGES, GIBBS FREE ENERGY
CHANGES AND ENTROPY CHANGES OF ADSORPTION

Temperature (K)	$\Delta H(\text{kJ mol}^{-1})$	$\Delta G(\text{kJ mol}^{-1})$	$\Delta S(\text{J mol}^{-1} \text{ K}^{-1})$
293		-5.24	40.846
303	6.734	-6.01	41.696
313		-6.39	43.292

In fact, the positive value of ΔH for the processes further confirms the endothermic nature of the process; the free energy, ΔG , is negative and decreases as temperature rises. This suggests the adsorption process is spontaneous and the spontaneity increases as temperature increases. The positive entropy of adsorption reflects the process was entropy drive.

Kinetics modeling: In order to quantify the extent of uptake in adsorption kinetics, two simple kinetic models were

tested. First-order rate equation²⁰ based on solid capacity is generally expressed as:

$$\ln(q_e - q_t) = \ln q_e - K_1 t \quad (6)$$

where, K_1 (min^{-1}) is the equilibrium rate constant of the first-order adsorption and q_e and q_t (mg g^{-1}) are the amounts of Pd(II) adsorbed at equilibrium at any time t.

A pseudo-second-order adsorption kinetic rate equation is:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad (7)$$

where, K_2 [$\text{g} (\text{mg min}^{-1})$] is the rate constant of the pseudo-second-order adsorption.

According to the data in Fig. 2, the values of k_1 , k_2 and q_e could be obtained from the intercept and slope of the plot of $[\ln(q_e - q_t)]$ versus t and (t/q_t) versus t, respectively. The results fit the pseudo-second-order plot model better than they fit the first-order rate equation.

The activation energy for Pd(II) adsorption onto the dithizone-BST was calculated by using the logarithmic expression of the Arrhenius equation

$$\ln K_2 = \ln K_0 - \frac{E_a}{R T} \quad (8)$$

here, K_2 is the rate constant of the pseudo-second-order adsorption kinetic rate temperature T(K), K_0 is the frequency factor, R is the ideal gas constant [$8.314 \text{ J} (\text{mol K}^{-1})$] and E_a (kJ mol^{-1}) is the activation energy for the adsorption process. The magnitude of the activation energy can indicate the type of sorption.

The activation energy was obtained from the slope of the plot of $\ln K_2$ values versus $1/T$ using eqn. (9) and was found to be $99.768 \text{ kJ mol}^{-1}$.

$$\ln K_2 = -12000(1/T) + 36.857 \quad (R^2 = 0.981) \quad (9)$$

For adsorption with an activation energy of more than 40 kJ mol^{-1} , the main interaction between the Pd(II) and dithizone is probably coordination bond²⁰.

Choice of eluent and conditions: For choose the proper eluent for desorbing the Pd(II) from dithizone-BST, after the Pd(II) was adsorbed under the optimized adsorption conditions, 5 mL of selected eluent solution such as ethylenediamine, sodium hydroxide, thiourea and ethylenediamine-sodium hydroxide mixture at different concentration were used for elution by shaking 5 min, respectively. The recovery results showed that the best recovery was obtained when ethylenediamine (100 g L^{-1}) and sodium hydroxide (20 g L^{-1}) mixture was used as eluent. And the recovery was up to 98 %. Therefore, ethylenediamine (100 g L^{-1}) and sodium hydroxide (20 g L^{-1}) mixture was chosen. After regeneration, the dithizone-BST was dried and reused 20 times. Its adsorption performance didn't decrease.

Enrichment factor and detection limit: For review the possibility of enrichment low concentrations of Pd(II) from large volumes, $1.0 \mu\text{g}$ of Pd(II) was dissolved in 50, 100, 200, 300, 400 and 500 mL volume of water together, respectively. The amounts recovered are listed in Table-3. It could be seen when the solution volume was 500 mL and the concentration of Pd(II) was $2 \mu\text{g L}^{-1}$, the recovery was above 90 %. The enrichment factor was 100. The detection limit was $0.22 \mu\text{g L}^{-1}$.

TABLE-3
PRECONCENTRATION AND RECOVERY OF PALLADIUM

Volume of the solution (mL)	Quantity in eluent (μg)	Recovery (%)	Enrichment factor
50	0.995	99.5	10
100	1.016	101.6	20
200	0.973	97.3	40
300	0.952	95.2	60
400	0.944	94.4	80
500	0.937	93.7	100

Static adsorption capacity: From the Table-1, at 298 K, the capability of adsorption of dithizone-BST to Pd(II) was 21.135 mg g⁻¹.

Effect of the interfering ions: Different ions were added to solution of 0.2 mg L⁻¹ Pd(II) in the 50 mL volumetric flask. The experimental results showed that recoveries of the Pd(II) remained above 95 % even in the presence of ions in the following concentrations: 1000 mg L⁻¹ for Na⁺, K⁺, NH₄⁺, Cl⁻ and NO₃⁻; 500 mg L⁻¹ for Ca²⁺ and Mg²⁺; 200 mg L⁻¹ for Al³⁺ and PO₄³⁻; 100 mg L⁻¹ for Cr(III), Ag⁺, Co²⁺, Cr(VI) and Cu²⁺; 50 mg L⁻¹ for Zn²⁺ and 1.0 mg L⁻¹ for Pb²⁺, Ni²⁺ and Fe³⁺. As can be seen, the method described separates the Pd(II) from the converter matrix fairly well.

Application of the method: The application of the proposed method was carried out surface water and tap water samples. The tap water was collected from our laboratory. The surface water was come from the Hunhe river (Shenyang, China) and filtered through a 0.45 μm membrane filter. The recovery of the analyte line in Table-4. The preconcentration and recovery of palladium(II) is given in Table-3.

TABLE-4
DETERMINATION OF PALLADIUM IN WATER SAMPLES (n=6)

Samples	Found ($\mu\text{g L}^{-1}$)	RSD (%)	Added ($\mu\text{g L}^{-1}$)	Found ($\mu\text{g L}^{-1}$)	Recovery (%)
Tap water	— ^a	—	10	9.43	94.3
Hunhe river water	14.3	2.9	10	24.2	99.0

a. Not detected

The recovery was 94.3-99.0 %, which were excellent for trace analysis. So, the proposed method was demonstrated the

suitability of this sorbent for the selective extraction and determination of trace Pd(II).

Conclusion

According to the research results in this paper, it could be concluded that Pd(II) could be quantitatively retained by the dithizone-BST in the pH of 2.0 using hydrochloric acid, the adsorption time was 15 min and capability of adsorption was 21.135 mg g⁻¹. The adsorption behaviour followed a Langmuir adsorption isotherm and a pseudo-second-order kinetic model, the adsorption was an endothermic and spontaneous physical process. The Pd(II) adsorbed on the dithizone-BST could be completely eluted by using ethylenediamine and sodium hydroxide mixture. The detection limit of this method for palladium was 0.22 $\mu\text{g L}^{-1}$. The proposed method has been applied to the determination of trace amounts of Pd(II) in water with satisfactory results.

REFERENCES

1. S. Tokalioglu, T. Oymak and S. Kartal, *Anal. Chim. Acta*, **511**, 255 (2004).
2. F. Zereini and F. Alt (Eds.), *Palladium Emission in the Environment*, Springer-Verlag, Berlin Heidelberg (2006).
3. A. Limbeck, J. Rendl and H. Puxbaum, *J. Anal. At. Spectrom.*, **18**, 161 (2003).
4. K. Boch, M. Schuster, G. Risse and M. Schwarzer, *Anal. Chim. Acta*, **459**, 257 (2002).
5. P. Kovacheva and R. Djingova, *Anal. Chim. Acta*, **464**, 7 (2002).
6. G.-H. Lee and K.-S. Chung, *Anal. Sci.*, **7**, 1339 (1991).
7. G.H. Faye and W.R. Inman, *Anal. Chem.*, **35**, 985 (1963).
8. J.T. Pyle and W.D. Jacobs, *Anal. Chem.*, **36**, 1796 (1964).
9. M.B. Gómez, M.M. Gómez and M.A. Palacios, *J. Anal. At. Spectrom.*, **18**, 80 (2003).
10. A. Tunçeli and A.R. Türker, *Anal. Sci.*, **16**, 81 (2000).
11. D. Zhang, W.J. Zhang and P. Hou, *Asian J. Chem.*, **23**, 4851 (2011).
12. V.K. Jain, H.C. Mandalia, H.S. Gupte and D.J. Vyas, *Talanta*, **79**, 1331 (2009).
13. S. Tokalioglu, V. Yilmaz, S. Kartal, A. Delibas and C. Soykan, *J. Hazard. Mater.*, **169**, 593 (2009).
14. F.Z. Xie, X.C. Lin, X.P. Wu and Z.H. Xie, *Talanta*, **74**, 836 (2008).
15. L.J. Zhang, X.J. Chang, Y.H. Zhai, Q. He, X.P. Huang, Z. Hu and N. Jiang, *Anal. Chim. Acta*, **629**, 84 (2008).
16. R. Gao, Z. Hu, X.J. Chang, Q. He, L.J. Zhang, Z.F. Tu and J.P. Shi, *J. Hazard. Mater.*, **172**, 324 (2009).
17. A. Duran, M. Tuzen and M. Soylak, *J. Hazard. Mater.*, **169**, 466 (2009).
18. D. Zhang, H.D. Su and H. Gao, *Spectrosc. Spect. Anal.*, **28**, 693 (2008).
19. D. Zhang, H.D. Su, H. Gao and J.C. Liu, *Acta Chim. Sinica*, **65**, 2549 (2007).
20. D. Zhang, C.-I. Zhang and P. Zhou, *J. Hazard. Mater.*, **186**, 971 (2011).