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Ultra-trace Determination of Palladium(II) by Spectrophotometric Flow Injection Analysis

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In this work, a simple, selective and rapid flow injection method of analysis (FIA) is developed for ultra-trace determination of palladium. The method is based on the catalytic effect of palladium on the oxidation of naphthol green B by periodate. Naphthol green B undergoes an oxidation reaction with metaperiodate in acidic medium to form a colorless product at a very slow rate. It was found that this reaction can be quickly done at the presence of trace amount of Pd^{2+} . The reaction was monitored spectrophotometrically by measuring the difference between absorbance of naphtholgreen B of solutions with and without Pd^{2+} at the $\lambda_{\text{max}} = 721 \text{ nm}$. The reagents and manifold variables, which have influences on the sensitivity, were investigated and the optimum conditions were established. Under these conditions, the influences of some important species on the determination of Pd^{2+} by flow system were examined and most of them did not show any interference effect on the flow injection determination. It is obvious that under the optimized conditions absorbance signal was linearly dependent on Pd^{2+} concentrations in the ranges of 2.0-90.0 ng ml^{-1} with a detection limit of 0.9 ng ml^{-1} ($S/N = 3$) and a sample rate of 35 ± 5 samples/h. The proposed method has been successfully applied for the analysis of ultra-trace amounts of Pd^{2+} in human serum and water samples.

Keywords: Palladium(II), Flow injection analysis, Spectrophotometry, Naphthol green B

INTRODUCTION

Noble metals, particularly palladium, find an extensive use in the electrical industry as contacts in telephone relays and printed circuits, as grids for electronic tubes and electrodes for high quality spark plugs. Palladium affects the environment to an increasing degree as a new pollutant, especially by the technical use of catalysts containing active palladium metal [1]. Catalytic converters containing platinum group metals (PGMs) have been used for the treatment of pollutants in exhaust gases from motor vehicles. Palladium, rhodium and platinum are the PGMs mostly used for this purpose. While these automotive catalysts enable 90% of the three major gaseous pollutants, namely carbon monoxide, unburned hydrocarbons and

nitrogen oxides, to be transformed into harmless products. They present the disadvantage of releasing fine particulate matter or dusts (resulting from the abrasion or deterioration of the catalyst through combined mechanical and thermal effects) containing PGMs into the environment. Therefore, the metals have accumulated along motorways, in vegetation and on soil surfaces and concerns have arisen with respect to the health risks generated by the possible inhalation of dusts and contamination through food and water [2,3]. Palladium has been used in different areas of science and technology, including agents, brazing alloys, petroleum, electrical industries and catalytic chemical reactions [4-6]. The metal may enter the environment and interact with complexing materials, such as humic substances [7]. Palladium has no biological role, and all palladium compounds should be regarded as highly toxic and carcinogenic. Palladium chloride is toxic, harmful if

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swallowed, inhaled or absorbed through the skin, However palladium chloride was formerly prescribed as a treatment for tuberculosis at the rate of 0.065 g per day (approximately 1 mg kg⁻¹) without too many bad side effects [8]. Because of increasing applications of pd²⁺ and toxicity of its compounds to mammals, fish and higher plants [9]. Therefore, the determination of palladium is interesting in environmental analysis. For the trace determination of palladium in environmental samples, highly sensitive and selective techniques including electrothermal atomic absorption spectrometry (ETAAS) [3] inductively coupled plasma-atomic emission spectrometry (ICP-AES) [10]. Neutron activation analysis (NAA) [11] inductively coupled plasma-mass spectrometry (ICP-MS) [2], total reflection X-ray fluorescence (TXRF) spectrometry [13] flame atomic absorption spectrometric (FAAS) [14-17], kinetic spectrophotometric [18,19] electrochemistry [20-22] and spectrophotometry [23-25] have been used. The first two techniques can be applied to environmental samples only in combination with the separation/preconcentration procedures. The direct application of spectrometric techniques to the detection of metals in complex matrices samples is limited by numerous interferences and also the most of these methods are expensive. The flow injection (FI) method is a very useful technique for the rapid and reproducible determination of many samples. Moreover, FI technique can make reproducible timing analysis, eliminate sample pretreatment and minimize solvent and reagent consumption. The influence of variables is studied, and the developed procedure is employed for the determination of palladium in real samples with satisfactory results.

EXPERIMENTAL

Reagents and Solutions

Doubly distilled water and analytical reagent grade chemicals were used during all of the experimental studies. Naphthol green B solution 4.6 × 10⁻⁴ M was prepared by dissolving 0.0400 g of the compound (Merck) in water and solution was diluted to the mark in a 100-ml volumetric flask. Metaperiodate stock solution 0.010 M was prepared by dissolving 0.5750 g of potassium metaperiodate (Merck) in water and diluting to 250 ml in a 250-ml volumetric

flask. Standard stock pd²⁺ solution (100.0 µg ml⁻¹) was prepared by dissolving 0.0250 g Pd(NO₃)₂·2H₂O in 0.50 M HNO₃ and diluting to 100-ml volumetric flask. Working solutions were prepared daily by appropriate dilution with water. Stock solution (1000 µg ml⁻¹) of interfering ions was prepared by dissolving appropriate amounts and suitable salts in water, hydrochloric acid, or sodium hydroxide solution. All glassware were cleaned with detergent solution, rinsed with tap water, soaked in dilute HNO₃ solution (2% V/V), rinsed with water and dried.

Flow Injection Analysis

Figure 1 shows the schematic diagram of the flow system. Silicon rubber tube with inner 0.8 mm i.d. was used for delivering of the solutions. The 8-channel peristaltic pump (ismatec, MCP process, IP 65) was fitted for pumping solutions. A mixed solution of naphtholgreen B, metaperiodate and buffer solution as a carrier stream was delivered through silicon rubber tubing (at 35 °C). The thermostatic water bath (Gallen Kamp Griffin, BGL 240 V) was used at a given temperature of 35 ± 0.1 °C. The standard solution of palladium was injected into a carrier stream with a sample injector (Rhodyne, model 9125). A UV-Vis spectrophotometer (2501 CECIL) equipped with a flow through cell with 10 mm path length connected to recorder was used for monitoring the variation in the absorbance spectrum. The reaction was monitored spectrophotometrically by measuring the difference between absorbance of naphtholgreen B of solutions with and without pd²⁺, at λ_{max} = 721 nm. ΔA (analytical signal) is difference between absorbance of solution in presence of pd²⁺ (peak height) and absence of pd²⁺ (base line) in this system.

Determination of Palladium(II) in Human Serum

Mineralization of 2.0 ml of the samples was carried out for 1.0 h at 100 °C with the addition of 4 ml of concentrated nitric acid [26]. Then samples were analyzed directly after neutralization with sodium hydroxide solution and diluted with doubly distilled water to a suitable volume.

RESULTS AND DISCUSSION

Naphtholgreen B (Fig. 2) undergoes an oxidation

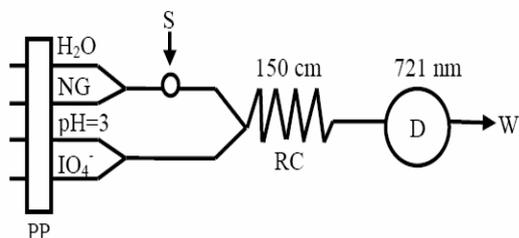


Fig. 1. Schematic diagram of the flow system. (flow rate of 42 ml h^{-1} for each channel, sample loop volume of $200 \mu\text{l}$, reaction coil length of 150 cm , absorbance wavelengths: $\lambda_{\text{max}} = 721 \text{ nm}$); S, injection valve; RC, reaction coil; temperature, $35 \text{ }^\circ\text{C}$; D, spectrophotometer; PP, peristaltic pump.

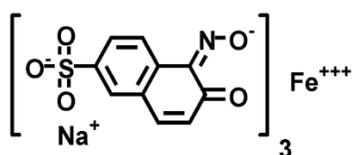


Fig. 2. Naphtholgreen B structure.

reaction with metaperiodate in acidic medium to produce a colorless solution with very slow reaction rate. Its absorption maximum is 721 nm in this solution. It was found that this reaction rate is sharply increased at the present of trace amount of pd^{2+} . This reaction is followed spectrophotometrically by controlling absorbance change of the reagent at 721 nm by a flow injection method. To have high analytical signal, the effect of reagent concentrations and manifold variables on the analytical signal was studied.

Effect of Chemical Variables

The influence of pH, metaperiodate concentration, naphtholgreen B concentration on the peak height was studied to find the optimum conditions.

The effect of pH on the peak height was studied in the range of $1.0\text{--}6.0$ (Fig. 3). The results show that the peak height increases with pH up to 3.0 and decreases at higher pH values. This phenomenon is due to the fact that, in $\text{pH} < 3.0$, naphthol green B is protonated and thus the rate of reaction decreases. On the other hand, at higher pH values

($\text{pH} > 3.0$), the ability of periodate to oxidize naphthol green B decreased. Therefore, a pH of 3.0 (buffer acetate, 0.2 M) was selected as the optimum pH value.

The influence of naphthol green B concentrations on the peak height was studied in the concentration range of $0.23 \times 10^{-5}\text{--}4.6 \times 10^{-5} \text{ M}$ (Fig. 4). The results show that the peak height increases with increasing naphthol green B concentration up to $1.38 \times 10^{-5} \text{ M}$ and decreases at higher concentrations. This may be due to the aggregation of the dye at higher concentrations [27]. Therefore, a naphthol green B concentration of $1.38 \times 10^{-5} \text{ M}$ was selected for further study.

The effect of the metaperiodate concentration on the peak height was studied for the range of $0.1 \times 10^{-4}\text{--}8.0 \times 10^{-4} \text{ M}$ (Fig. 5). Peak height increases with increasing metaperiodate concentration up to $5.0 \times 10^{-4} \text{ M}$ and decreases at higher concentrations. This behavior at higher concentrations may be due to increase the reaction rate of dye and periodate in blank solution (in the absence of pd^{2+} ion) compared to situation that pd^{2+} is present in the solution. Therefore, a final concentration of $5.0 \times 10^{-4} \text{ M}$ of metaperiodate was selected as the optimum concentration.

Effect of Manifold Variables

Influence of variables such as reaction coil, injected volume, flow rate and temperature on the peak height was studied. The peak height depends on the residence time of the sample in the system that is affected by the flow rate and reaction coil length.

The results during the investigation of the effect of reaction coil length in the range of $30\text{--}180 \text{ cm}$ shows that by increasing the reaction coil length up to 150 cm , the sensitivity increases (Fig. 6). At shorter distances, there is not enough time for reagents to be mixed and above this reactor length, increased dispersion will decrease the peak height.

The effect of flow rate was tested under optimum conditions in the range of $10\text{--}60 \text{ ml h}^{-1}$ (Fig. 7). The results show that the best pump flow rate (the maximum peak height and minimum dispersion) will be obtained in 42 ml h^{-1} for each channel. At lower flow rates the dispersion will be high whereas at greater flow rates the reaction may be incomplete.

The influence of sample volume on the peak height in

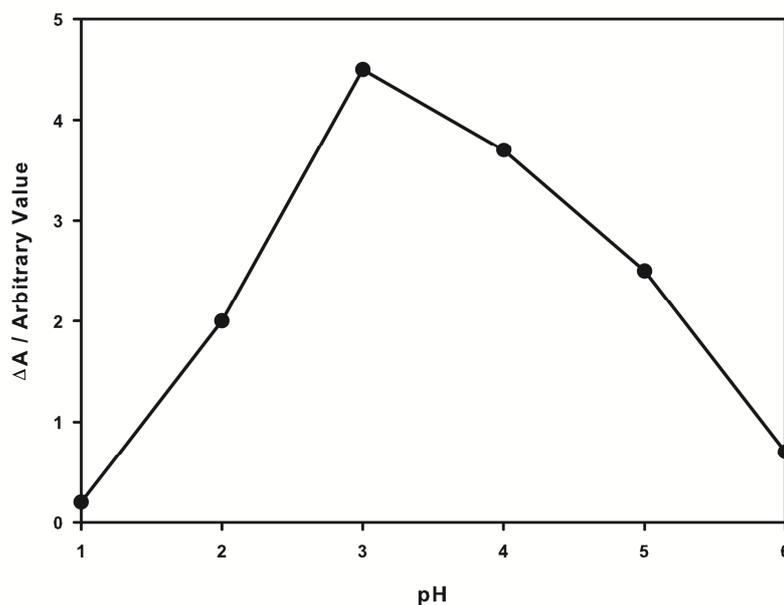


Fig. 3. Effect of pH on the sensitivity. Conditions: 4.6×10^{-5} M naphthol green B, 1×10^{-2} M metaperiodate, 20.0 ng ml^{-1} palladium, temperature of $30 \text{ }^\circ\text{C}$, sample loop volume of $150 \text{ } \mu\text{l}$, flow rate of 34 ml h^{-1} for each channel, reaction coil length of 150 cm .

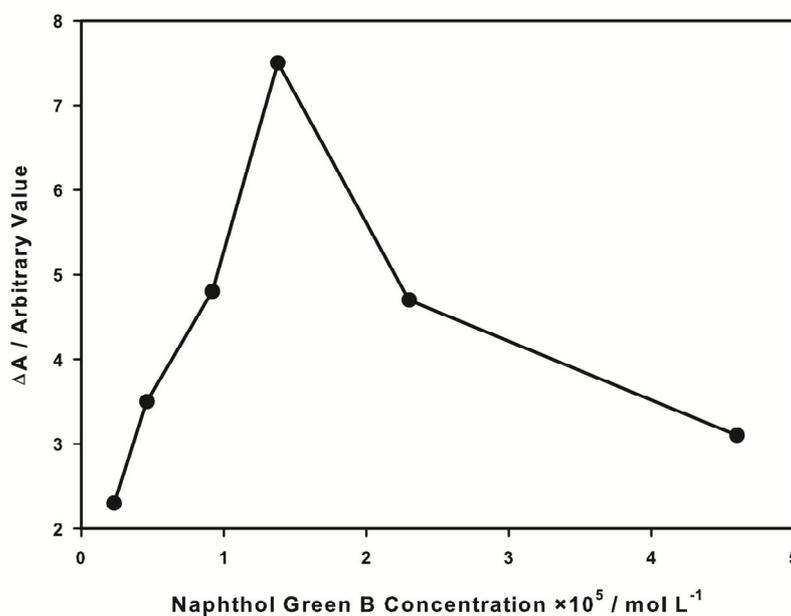


Fig. 4. Effect of naphthol green B on the sensitivity. Conditions: $\text{pH} = 3$, 1×10^{-2} M metaperiodate, 20.0 ng ml^{-1} palladium, temperature of $30 \text{ }^\circ\text{C}$, sample loop volume of $150 \text{ } \mu\text{l}$, flow rate of 34 ml h^{-1} for each channel, reaction coil length of 150 cm .

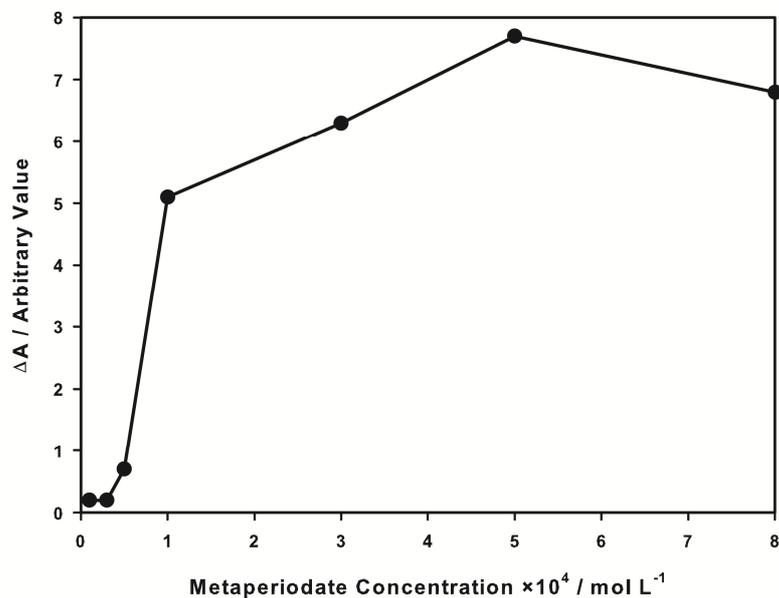


Fig. 5. Effect of metaperiodate on the sensitivity. Conditions: pH = 3, 1.38×10^{-5} M naphthol green B, 20.0 ng ml^{-1} palladium, temperature of $30 \text{ }^\circ\text{C}$, sample loop volume of $150 \text{ }\mu\text{l}$, flow rate of 34 ml h^{-1} for each channel, reaction coil length of 150 cm .

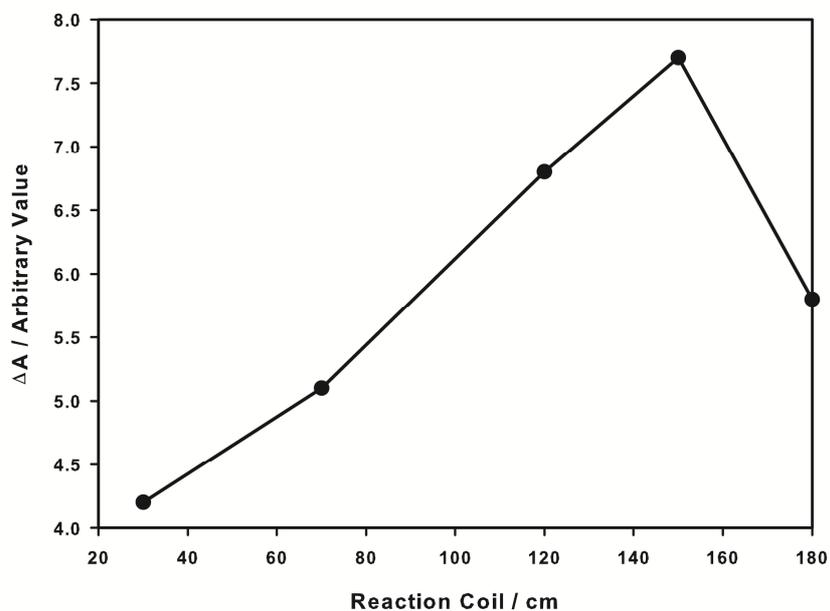


Fig. 6. Effect of reaction coil length on the sensitivity. Conditions: pH = 3, 1.38×10^{-5} M naphthol green B, 5×10^{-4} M metaperiodate, 20.0 ng ml^{-1} palladium, temperature of $30 \text{ }^\circ\text{C}$, sample loop volume of $150 \text{ }\mu\text{l}$, flow rate of 34 ml h^{-1} for each channel.

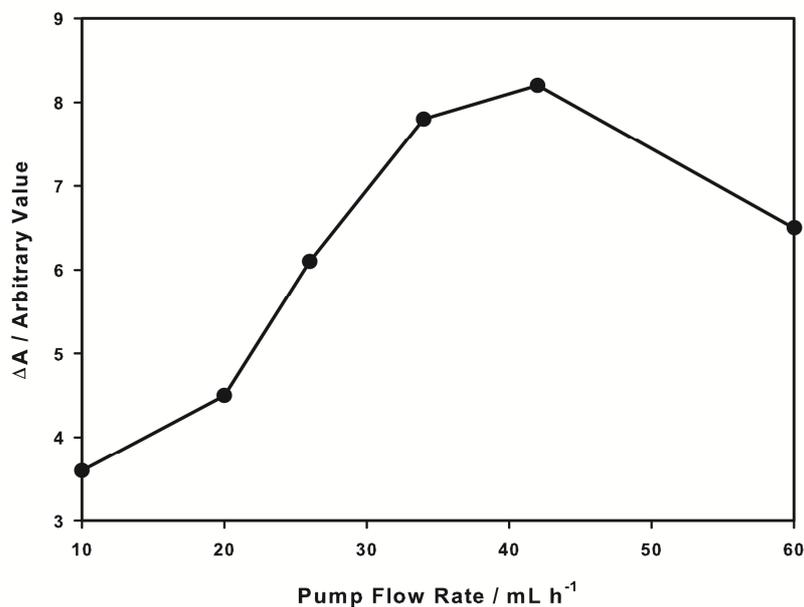


Fig. 7. Effect of pump flow rate on the sensitivity. Conditions: pH = 3, 1.38×10^{-5} M naphthol green B, 5×10^{-4} M metaperiodate, 20.0 ng ml^{-1} palladium, temperature of $35 \text{ }^\circ\text{C}$, sample loop volume of $150 \text{ }\mu\text{l}$, reaction coil length of 150 cm .

Table 1. Effect of Foreign Ions on the Determination of $20 \text{ ng ml}^{-1} \text{ pd}^{2+}$ ^a

Foreign species	Tolerated ratio $W_{\text{species}}/W_{\text{pd}^{2+}}$
Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Ag^+ , Rb^+ , Pb(II) , No(II) , Zn(II) , Cu(II) , Br^- , Cl^- , $\text{C}_2\text{O}_4^{2-}$, $\text{S}_2\text{O}_8^{2-}$, HSO_4^- , ClO_3^- , CO_3^{2-} , NO_3^- , Ni^{2+}	1000
Co^{2+} , Mn^{2+} , Hg^{2+} , Pt^{4+}	500
Os^{8+} , Ru^{3+} , SCN^-	200
I^- , Fe^{2+}	30

^a W is concentration of solution in ng ml^{-1} . $W_{\text{species}}/W_{\text{pd}^{2+}}$ is the amounts of foreign ions in terms of ng ml^{-1} to the amount of pd^{2+} in terms of ng ml^{-1} in solution

the range of $50\text{-}300 \text{ }\mu\text{l}$ was tested under optimum conditions. The results show that the peak height raised by increasing the volume of sample loop volume, but the injection of a large amount of sample results in peak broadening and tailing. Thus, a sample volume of $200 \text{ }\mu\text{l}$

was selected.

The influence of temperature on the peak height was studied for the range of $15\text{-}40 \text{ }^\circ\text{C}$, under above conditions, as previously described. The results show that by increasing temperature up to $35 \text{ }^\circ\text{C}$, peak height increases. So

Table 2. Determination of Pd^{2+} in Real Samples ($n = 3$)^a

Sample	Pd^{2+} added (ng ml^{-1})	Pd^{2+} found (ng ml^{-1})	Recovery (%)
Zayandehroud river water	0.0	-	-
	5.0	4.93 ± 0.07	97.0
	10.0	10.35 ± 0.11	103.5
	15.0	15.47 ± 0.17	103.1
Drinking water	0.0	-	-
	5.0	4.89 ± 0.024	97.8
	7.0	7.21 ± 0.35	103.0
	9.0	9.31 ± 0.041	103.4
Human serum	0.0	-	-
	5.0	5.15 ± 0.11	103.0
	10.0	9.85 ± 0.15	98.5
	20.0	20.55 ± 0.2	102.8

^aNumber of repeating of experiments for calculating standard deviation.

temperature was fixed at 35 °C.

Calibration Graph, Detection Limit, Reproducibility and Accuracy

Under obtained optimized conditions, Pd^{2+} concentration can be determined in the range of 2.0-90 ng ml^{-1} ($n = 7$, $r = 0.99984$). The equation of the calibration graph is ($\Delta A = 0.064 C_{\text{Pd}} + 7.32$), where ΔA is the change in absorbance (maximum peak height with the best baseline) for the sample and C_{Pd} is palladium(II) concentration in ng ml^{-1} . Limit of detection is 0.9 ng ml^{-1} . The relative standard deviation (R.S.D.%) for 6 replicate measurements of 10, 30 and 50 ng ml^{-1} of Pd^{2+} were 2.6, 2.4 and 1.9%, respectively.

Interference study

In this stage the influence of contaminant species presented in various samples on the determination of Pd^{2+} 20 ng ml^{-1} , was investigated. The tolerance limit was defined as the concentration of added ions causing a relative

error less than 3% (Table 1). As the results show the developed method is very selective.

Application of the Method

The proposed method has been successfully applied to determine palladium in the real and synthetic water and human serum samples. The results in Table 2 represent that good recoveries in all samples have been obtained.

Response Characteristics

In Table 3, response characteristics of the proposed method are compared with recently reported methods. In comparison with method of Isotope dilution inductively coupled plasma quadrupole mass spectrometry in connection with a chromatographic separation [11] that homogenized road dust sample used for palladium determination and method of catalytic Spectrophotometric determination [17] that activated charcoal sample used for palladium determination, proposed method is sensitive with

Table 3. Comparison of Determination of pd^{2+} Methods with Proposed Method

Method	DL (ng ml^{-1})	LDR (ng ml^{-1})	Ref.
Electro-thermal atomic absorption spectrometry (ETAAS)	23	-	[3]
Inductively coupled plasma-atomic emission spectrometry (ICP-AES)	15 ng g^{-1}	-	[10]
Neutron activation analysis (NAA)	3.4×10^{-3}	-	[11]
Inductively coupled plasma-mass spectrometry (ICP-MS)	0.075	0.1-87	[12]
Total reflection X-ray fluorescence (TXRF) spectrometry	2.5×10^{-3}	-	[13]
Flame atomic absorption spectrometric (FAAS)	0.6	-	[14]
	1.4	15.0-7000.0	[15]
	1.6	-	[16]
Kinetic spectrophotometric	$90 \text{ [}\mu\text{]g l}^{-1}$	$100 \text{ to } 2000 \text{ [}\mu\text{]g l}^{-1}$	[17]
	4.3	40-200	[18]
Electrochemistry	1.7	71.0-2850.0	[19]
	532	10640.0-319200	[20]
	65	100.0-12000.0	[21]
Spectrophotometry	170.2	532-15960.0	[22]
	0.25	100.0-5000.0	[23]
	0.02	10-1200	[24]
	3.127		[25]
Proposed method	0.1	10-1000	[28]
	0.9	2.0-90.0	In work

a wide linear dynamic range, moreover it has been applied for the determination of pd^{2+} in human serum. Some of sensitive methods in Table 3 have a complex instrumentation and are expensive and some of them use a preconcentration method before the measurement [3,9-11].

CONCLUSIONS

A simple, rapid and selective flow injection inhibition procedure is developed for the determination of pd^{2+} with spectrophotometric detection. This method can be used for

the determination of nanogram amounts of Pd^{2+} with a sample rate of 35 ± 5 samples/h. The main advantages of the method are its simplicity and its large dynamic range which make it possible to determine Pd^{2+} in the real samples with satisfactory results.

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