Separation and preconcentration of palladium using modified multi-walled carbon nanotubes without chelating agent

Chun-Gang Yuan · Yan Zhang · Shuping Wang · Ailing Chang

Abstract A solid phase extraction procedure is presented for the separation and preconcentraton of trace levels of Pd (II) ion by using oxidized multiwalled carbon nanotubes (MWCNTs). Experimental parameters (pH, type of eluent, sample volume and flow rate of sample solutions) were studied in detail. The Pd(II) adsorbed on the MWCNTs was eluted with 3.0 M nitric acid and then determined by flame atomic absorption spectrometry. The effects of potentially interfering ions on the recovery of Pd(II) were also examined. Under optimized conditions, the method provides a preconcentration factor of 165, has a linear range from 1.0 ng mL^{-1} to 200 ng mL^{-1} of Pd(II), a detection limit of 0.3 ng mL^{-1}, and a relative standard deviation 5.3% at 50 ng mL^{-1} of Pd(II). The method was validated by the extraction and determination of Pd(II) in water, fly ash, and road dust samples.

Keywords Carbon nanotubes · Separation and preconcentration · Palladium

Introduction

It has been reported that palladium affects the environment to an increasing degree as a new pollutant for its wide application in many fields including petroleum, electrical industries and catalytic chemical reactions [1], especially the usage as an effective catalyte for the fuel control of automobiles. Considering the dramatic increasing demand of automobiles consumption in recent years around the world, the level of Pd (II) in our environment will be definitely elevated. The potential toxic effects of palladium have also been recognized already. Exposure to certain level of palladium compounds can cause asthma, allergy and other serious health problems [2]. So, it is of special interest in environmental analysis and very important for public health to develop new separation and preconcentration method for detection of palladium in real samples [3, 4].

There were various techniques such as atomic absorption spectrometry (AAS), inductively coupled plasma optical emission spectrometry (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS) used for the determination of palladium [5–8, 13]. Even the instrumental methods mentioned above were with high sensitivity and selectivity, separation and preconcentration were always necessary because of the complex compositions of the complex matrix [9]. Low concentrations of Pd in environmental samples always caused much more interference during the determination of palladium [10]. To solve this problem and minimize the interference caused by the complex matrix, many separation and preconcentration methodologies had been developed and applied prior to detection by the instruments. The methods included solid phase extraction (SPE) [4–10, 13], dispersive liquid-liquid microextraction (DLLME) [3, 11, 14], and even the most recently developed liquid-liquid micro-extraction technology-solidified floating organic drop micro-extraction (SFODME) [12]. Due to its simplicity, low cost and contaminant free [15], solid phase extraction was most preferentially used for preconcentration of Pd compared with other separation and preconcentration methods [8, 13, 16–20].

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Many kinds of adsorbents were used as extraction phase for Pd which included chelating resin [7, 17], nanoparticles of gamma-alumina [16], dithiocarbamate-coated fullerene C60 [5], modified silica [4, 9, 10], nanometric titanium dioxide [18], carbon nanofibers [20], modified organo nanoclay [21] and so on [13, 19, 22–25]. An attractive tendency in the field of solid phase extraction is to find the new sorbent materials with expressive performance, such like high chemical resistance, selectivity, large surface area, and high sorption capacity [26]. Because of their unique properties and strong adsorption ability, carbon nanotubes (CNTs) were widely studied for preconcentration of analytes in analytical chemistry recently. Zhou et al. [27, 28] preconcentrated atrazine, simazine, nicosulfuron, thifensulfuron-methyl and metsulfuron-methyl in environmental water samples using carbon nanotubes. Liang et al. [29–31] applied carbon nanotubes to separation and preconcentration of various metals in water samples in their several papers. Katsumata et al. [32] developed a method for preconcentration of diazinon by using multiwalled carbon nanotubes (MWCNTs) as an adsorbent. Cai and Niu [33–35] successfully extracted sulfonylurea herbicides, chlorophenols, and other organic pollutants from aqueous samples. Although a lot of researches were carried out for preconcentration of metals ions from water samples using carbon nanotubes [36–39], there was no report about the separation and preconcentration of Pd(II) in geological and environmental samples by carbon nanotubes. It is interesting and necessary to examine the analytical potential of MWCNTs for sensitive detection of Pd. In addition, palladium is not only a pollutant. It is one of noble metals and getting scarce in future. So, its preconcentration is also of interest and useful for recycle of such precious metal.

In this presented paper, MWCNTs was investigated as an adsorbent for the preconcentration of trace Pd in fly ash, road dust and water samples. MWCNTs were packed into one SPE mini-column after modified and oxidized by concentrated nitric acid. The experimental conditions for quantitative recovery, separation and preconcentration of palladium were optimized.

Experimental

Instruments

The detection and analysis was carried out using a Shimadzu AA-6800 atomic absorption spectrometer (Kyoto, Japan, http://www.shimadzu.com/) equipped with a flame burner. All measurements were carried out in an air/acetylene flame. Other operational parameters for Pd detection including lamp currents, wavelength and flow rate of gas were those recommended by the manufacturer. A pH meter with glass-electrode was employed for measuring pH values in the aqueous samples. A flow-injection system (Beijing Titan Instruments Co. Ltd, Beijing, China, http://www.bjtitanco.com/) was employed to introduce solution through the packed SPE column.

Reagents and solutions

De-ionized water was used for all dilutions throughout the work. All chemicals were of analytical grade or better without further purification. The tubes and glassware used in the experiment were soaked in (15%, v/v and 50%, v/v) HNO_3 solutions overnight and rinsed at least three times with deionized water before use to minimize the contamination caused by metals from containers. Palladium standard solution was prepared daily by appropriate dilution of 1,000 mg L^{-1} palladium stock solution (General Research Institute for Nonferrous Metals, Beijing, China, http://www.grinm.com/). Multi-wall carbon nanotubes (MWCNTs) were supplied by Shenzhen Nanotech Port Co. Ltd (Shenzhen, China, http://www.nanotubes.com.cn/) with purity >95% and diameter ranging from 60 to 100 nm.

Modification of MWCNTs, preparation of the column and preconcentration procedure

The MWCNTs used in our study was oxidized with concentrated nitric acid in order to create binding sites to Pd(II). 2.0 g of MWCNTs was suspended in 50 mL concentrated nitric acid and the mixture was refluxed with stirring for 2 h. The solid was then filtered and washed by deionized water. The oxidized MWCNTs was dried at 105 °C for 4 h. After being ground gently, the modified MWCNTs was ready for use.

Three hundred milligrams of MWCNTs was loaded into an empty SPE column (6 mL) equipped with two porous frits at up side and bottom. Before use, the column was cleaned and preconditioned with water and solution at desired pH. The packed column was cleaned and regenerated by 6.0 M HNO_3 for further use after each experiment. The standard solution or samples were pumped through the packed SPE column by a flow-injection system. Pd(II) in solution was adsorbed onto the SPE column. Then, the column was eluted by 3.0 M HNO_3. Pd(II) in elution was determined by FAAS.

Application to water and geological samples

The geological standard reference material (GBW07342) was purchased from Institute of Geophysical and Geochemical Prospecting, Langfang, China. The road dust

samples were collected from the road sites having dense traffic in Baoding city. The fly ash samples were collected from one power plant in north of China.

The water samples analyzed in our experiment were collected in the city where the authors accommodated and filtered through a 0.45 μm membrane filter.

The ore, road dust, fly ash samples were roasted at 600 °C for 1 h. After cooling they were grounded, passed through an 80 mesh sieve and then homogenized, respectively. A 2.0 g specimen of each sample was weighed into a 100 mL beaker. 10 mL of aqua regia was added to the beaker and the mixture was heated to moist residue. Then, another 10 mL of aqua regia was added again to the residue and the mixture was evaporated to nearly dryness. The insoluble part was filtered through a filter paper and washed with 1.0 M HNO_3. The filtered solution was then diluted to 100 mL in a marked flask with water. The pH value for each sample was adjusted to the desired pH by 1.0 M NaOH before extraction. 50 mL of the diluted digested sample solution was subjected to the recommended procedure.

Results and discussion

It was found that Pd(II) in solution could be preconcentrated by oxidized carbon nanotubes without chelating agent in our study. There are various ways including complexing with chelating agent, reduction in valency state and ion exchange process by which metals can be adsorbed on carbon materials from aqueous medium [40]. Because there was no chelating agent used in our experiment, the possible mechanism of adsorption on carbon nanotubes can probably be demonstrated by the reduction in valency state or ion exchange process at the surface of carbon nanotubes. The ability to form coordination complexes and strong interaction between some new carbon materials (such like fullerences) and Pd(II) had been found already [5, 41–43]. In addition, some previous studies also indicated that some of the noble metals including Pd(II) could be reduced to elemental state on the surface of carbon materials [44] and could be easily loaded on carbon materials which were used as Pd/C catalysis widely. All of the above studies indicate that Pd (II) ion may have special affinity with some new carbon materials. This property can probably get Pd(II) retained on the binding sites of oxidized carbon nanotubes more easily than other coexisting ions, which makes the adsorption of Pd(II) more selective. To study the adsorption behaviors of Pd(II) on oxidized MWCNTs and to develop a new method for preconcentration of trace Pd(II) in real samples, the effects of different experimental conditions on the preconcentration and separation of Pd(II) were investigated in our experiment.

Effect of pH

The acidity of solution plays an important role for metal adsorption on carbon nanotubes. In order to totally extract Pd(II) from solution and recover it quantitatively, the effects of pH on the recoveries of Pd(II) on carbon nanotubes were investigated in our experiment. The pH was adjusted by 1.0 M HNO_3 and 1.0 M NaOH. The studied pH range was from 1.0 to 10.0. The recovery of Pd(II) at each pH value was calculated and found to be quantitative at the pH range of 5.0–7.0. The results of the effect of pH on the recovery values are presented in Fig. 1. pH 6.0 was selected as the optimization for the following experiments.
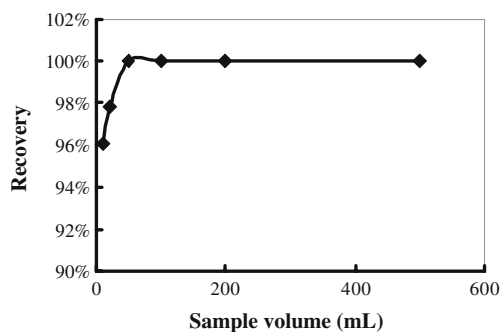
Effect of sample flow rate and volume

The adsorption of metals on carbon nanotubes can be affected by the flow rate of samples. The retention behaviors of Pd(II) can also be related with flow rate. The possible influences of the flow rates of sample solutions were tested in our experiment. The quantitative recoveries were achieved when the flow rates were in the range of 0.5–2.0 mL min^{-1}. However, when the flow rate of the sample was higher than 3.0 mL min^{-1}, the recovery of Pd (II) decreased from more than 95% to less than 87%. Thus, all subsequent experiments were performed at a flow rate of 2.0 mL min^{-1}.

10–500 mL of sample solutions containing 5.0 μg Pd(II) were preconcentrated and eluted according to the established procedure. The results are shown in Fig. 2. It was found that the quantitative recoveries could be obtained for the sample volume up to 500 mL. The recoveries increased with the sample volumes enhanced from 10 mL to 50 mL, and then were kept constant up to 500 mL. When the sample volume was larger than 500 mL, the recoveries decreased slightly. In addition to that, the whole extraction procedure became time-consuming. In our experiment, 500 mL was passed through the column to test the analytical performance, and the absorbed ions were eluted
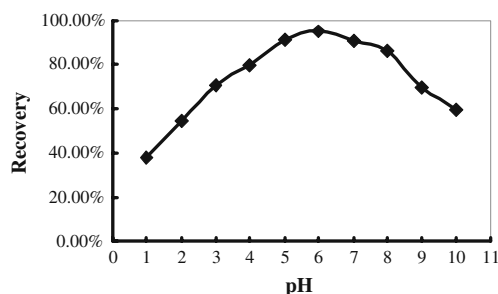
Fig. 1 Adsorption behavior of Pd(II) on MWCNTs under different pH conditions (sample volume 50 mL, flow rate 2.0 mL min^{-1}, elution 3.0 M HNO_3, concentration of Pd(II) 50 ng mL^{-1}, n=3, RSD <7%)

Fig. 2 Adsorption behaviors of Pd(II) with different sample volumes (pH 6.0, flow rate 2.0 mL min^{-1}, elution 3.0 M HNO$_3$, mass of Pd(II) 5.0 μg, n=3, RSD <7%)

Fig. 3 Adsorption capacity of MWCNTs towards Pd(II) (sample volume 100 mL, pH 6.0, flow rate 2.0 mL min^{-1}, elution 3.0 M HNO$_3$, n=3, RSD <7%)

out by 3.0 mL of 3.0 M HNO$_3$. The calculated enrichment factor of our method was 165.

Effect of type, flow rate and volume of elution

Different elution such like HCl, HNO$_3$, 3% thiourea solutions were tried to elute the absorbed Pd(II) on carbon nanotubes. The results are given in Table 1 and indicate that 3.0 M HNO$_3$ was sufficient for quantitative elution. Finally, 3.0 M HNO$_3$ was chosen for further experiments.
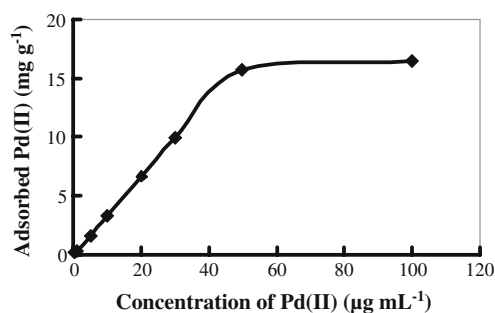
The possible influences of different flow rates of elution (3.0 M HNO$_3$) were also investigated in the range of 0.5– 3.0 mL min^{-1}. The results indicated that when the flow rate of elution was less than 2.0 mL min^{-1}, Pd(II) was quantitatively recovered. However, when the flow rate was higher than 3.0 mL min^{-1}, the recovery decreased dramatically. In our experiment, 0.5 mL min^{-1} was chosen for the best recovery. The volume of elution used was also optimized in our experiment. The results indicated that 3.0 mL of solution was enough for totally elution of Pd(II) from the column.

Adsorption capacity

In order to determine the adsorption capacity of the packed SPE column, 100 mL of solution containing Pd(II) at

different concentrations was loaded. After preconcetration and elution, the recoveries were investigated. The results in Fig. 3 demonstrated that the adsorption capacity of this column for Pd(II) was 15.7 mg g^{-1}.

Effects of coexisting ions

The possible influences of some coexisting ions including cations and anions were tested in our experiment under the optimized conditions. The concentration of Pd (II) in solution was 50 ng mL^{-1}. The results are shown in Table 2. The results showed us that most of coexisting ions in solutions did not affect the preconcentration and elution of Pd(II).

Table 1 Elution of Pd(II) by different solution

Eluent	Recovery (%)
2.0 M HCl	29.1
6.0 M HCl	54.8
0.5 M HNO$_3$	28.6
1.0 M HNO$_3$	40.5
3.0 M HNO$_3$	98.5
6.0 M HNO$_3$	99.1
3% thiourea in 2.0 M HCl	60.2

Table 2 Tolerance of coexisting ions for Pd(II) absorption on MWCNTs

Ions	Concentration (μg mL^{-1})	Recovery (%)
CO_3^{2-}	500	94.9
PO_4^{3-}	500	100.0
Cl^-	500	94.5
Na^+	1,000	90.8
K^+	1,000	92.3
Mg^{2+}	500	85.0
Cu^{2+}	500	90.1
Cd^{2+}	500	91.7
Mn^{2+}	500	86.2
Zn^{2+}	500	95.6
Fe^{2+}	100	86.9
Fe^{3+}	100	83.7
Al^{3+}	100	85.4
Pb^{2+}	50	92.1
Cr^{3+}	50	98.5
Ni^{2+}	50	95.8
Au^{3+}	10	90.3

Table 3 Analytical results of water and digested geological sample solutions (*n*=3)

Sample	Measured concentration of Pd in solution samples (ng mL^{-1})[a]	Spiked Pd (ng mL^{-1})	Found (ng mL^{-1})[a]	Recovery (%)[b]	Pd in solid sample (ng g^{-1})[c]
River water	ND	5.0	4.1±1.1	81.1	–
Waste water	2.1±0.6	5.0	6.4±1.2	86.1	–
Fly ash	15.0±1.6	20.0	32.5±6.8	89.9	374.6
Road dust	5.3±1.1	10.0	14.4±2.2	91.2	132.5

[a] Mean ± standard deviation

[b] $100 \times [(\text{found} - \text{measured})/\text{spiked}]$

[c] Calculated content of Pd in the original solid samples

Analytical performance of the method

Under the optimized conditions, 500 mL of sample solution was introduced. The linear range and limit of detection were tested by performing the calibration curve. The correlation coefficient was 0.9935. The regression equation was $A=0.0019 C+0.0038$. The detection limit (DL, 3σ) of the method was found to be 0.3 ng mL^{-1}. The relative standard deviation (RSD) of seven replicate determinations was 5.3%. The results indicated that the established method had good precision and repeatability.

Applications and column reuse

The standard reference material (GBW07342) was analyzed by the recommended procedure in order to validate the method established in our experiment. The content of palladium in the SRM was 1.67±0.13 μg g^{-1}. Using the method developed in our work, palladium content found was 1.56±0.22 μg g^{-1} (*n*=3). The recovery was calculated as 93.7%. The results demonstrated that the obtained values were in good agreement with the certified value. The method was also applied to real environmental samples, such like water, fly ash and road dust. The analytical results were given in Table 3.

The method to regenerate the used column was also studied. It was found that the used column could be regenerated easily by fluxing 10 mL of 6.0 M HNO$_3$ and then 10 mL 2.0 M HCl followed by 10 mL deionized water.

Comparison of MWCNTs method with other methods

Preconcentration and extraction of Pd(II) by the present MWCNTs method was compared with the other extraction methods published in recent years. The results of comparison are shown in Table 4. It can be concluded that the established method has a comparatively low detection limit, high enrichment factor and good linear range.

Table 4 Figures of merits of comparable methods for preconcentration of palladium(II)

Method/reagent used	Detection	LOD[a] (ng mL^{-1})	RSD[b] (%)	Sample/volume (mL)	Analytical range (ng mL^{-1})	Enhancement factor	Ref.
Octadecyl silica membrane disks modified by thioridazine·HCl	FAAS	12	1.2	Industrial samples, water/1,000	–	100	[4]
Dithiocarbamate-coated fullerene C60	GFAAS	0.044	1.5	Road dust/4	–	–	[5]
Amidinothioureido-silica gel	FAAS	17	1.7	Ore samples/4.5	200–4,000	–	[9]
Activated carbon	FAAS	14	<10	Geological samples/200	–	–	[40]
Modified MCM-48 and MCM-41 Silica	FAAS	0.1	<1	Wastewater, soil/1,250	–	400	[45]
Polyamine Metalfix-Chelamine resin-SPE	FAAS	9	3.2	Geological sample, catalyst material/4.7	0.2–2,000	20	[46]
Oxidized MWCNTs	FAAS	0.3	5.3	Water, fly ash, road dust/500	1.0–200	165	This work

[a] Limit of detection

[b] Relative standard deviation

Conclusions

The results indicate that the oxidized MWCNTs has high and selective adsorption capacity towards Pd(II) in aqueous solution. The major merit of the present method over other methods is that Pd(II) can be preconcentrated without chelating agent, which also provides us high enhancement factor. Even the exact chemical mechanism of the selective absorption cannot be fully explained by now, one of the major mechanism for that is probably the strong binding capacity of palladium to carbon. Although the binding sites on oxidized carbon nanotubes such like carboxy groups and hydroxy groups can also bind with other bivalent or trivalent ions, the stronger tendency of palladium towards carbon than other metals probably results in the more selective adsorption. In our study, the column packed with oxidized MWCNTs was used as effective SPE column for Pd(II) separation and preconcentration before flame atomic adsorption spectrometry determination. By separation of Pd (II) from other coexisting ions the interferences which may be caused by complex matrix can be minimized, and the sensitivity of the analytical method can be enhanced greatly as well. This study is also helpful for us to develop new method for palladium recycle from waste or used catalysis.

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