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Application of Oxazolone Azo Dye Modified Alumina as New Sorbent for Separation of Palladium from Anodic Slime and Wastewater Samples

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ABSTRACT

In the present work, a new kind of alumina-based adsorbent with high selectivity and stability and efficient adsorption was prepared. Alumina was coated with an oxazolone azo dye, 2-(4-{2-[4-(dimethylamino) phenyl]-1-diazenyl}phenyl)-4-[1-phenyl methylidene]-5(4H)-oxazolone, and then used for preconcentration of trace amounts of palladium. The analytical procedure involved the complex formation of Pd with oxazolone azo dye as a chelating agent in buffer media of pH 5. The stability of sorbent was excellent and adsorption capacity did not change significantly after 100 consecutive uses of 50.0 mg of modified alumina. Under the optimum conditions, the preconcentration factor of the method was 150. The linearity was maintained in the concentration range of 0.33 ng mL^{-1} to 8.0 mg mL^{-1} in the original solution. For 2.0 µg mL^{-1} of Pd, the relative standard deviation 1.4% and detection limit 0.25 ng mL^{-1} was obtained. The proposed method was successfully applied to the determination of trace amounts of palladium in the anodic slime and wastewater samples.

KEYWORDS: Modified Alumina; Oxazolone Azo Dye; Palladium; Wastewater.

1. INTRODUCTION

The importance of palladium has grown in recent years due to its increasing use in the production of dental and medical devices, jewelry, and catalytic converters. Although the benefits of car catalysts are indisputable, the emission of Pd into the environment is largely associated with the production and recycling of catalytic converters in the metal finishing industry as well as the operation of vehicle catalysts [1]. Due to its electrical conductivity and durability, Pd(II) is widely used in electronic industry for production of multi-layer ceramic (chip) capacitors, conductive tracks in hybrid integrated circuits, plating connectors and lead frames, and jewelry [2-3].

Owing to the co-existence of various heavy metal ions in industrial effluents or other water resources, selective separation of metal ions attracts much attention in both industries and researches. Selective adsorption of an ion on suitable solid sorbent possessing selectivity is inherently attractive to remove metal ions from dilute aqueous solution. Palladium analysis requires analytical methods of high sensitivity, selectivity and the control of interference effects. The most widely used methods for the determination of Pd in various samples including dispersive liquid-liquid extraction [1, 4, 5], cloud point extraction [6-8], coprecipitation [9-10], ion exchange [11] and solid phase extraction [12-14]. Solid phase extraction (SPE) has known as a powerful tool for separation and enrichment of various inorganic and organic analytes. SPE has several advantages over other techniques, including stability and reusability of the solid phase, high preconcentration factors, ease of separation and enrichment under dynamic conditions, no need for organic solvents, which may be toxic and minimal costs due to low consumption of reagents [15].

Among various support materials, alumina is an extensively used support for various solid phase extractors because of its numerous advantages, as it does not swell and has good mechanical strength, small solubility and stability in a broad pH range [16]. Immobilization of organic compounds on the surface of the solid support is usually aimed at modifying the surface with certain target functional groups for a higher selectivity of the extraction. The selectivity of the modified solid phases to ward certain metal ions is attributed to several well-known factors, such as the size of the organic compound used to modify the sorbent, the activity of the loaded surface groups and the type of the interaction of functional group [17]. In this work, an oxazolone azo dye, 2-(4-{2-[4-(dimethylamino) phenyl]-1-diazenyl} phenyl)-4-[1-phenyl methylidene]-5(4H)-oxazolone (Fig. 1), was coated onto alumina and was then used as a new sorbent for preconcentration and separation of palladium. Conditions for effective adsorption of trace levels of palladium were optimized. Application of the proposed method was examined for analysis of the various samples such as anodic slime, water and wastewater.

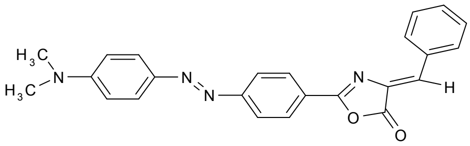

Fig. 1. 2-(4-{2-[4-(dimethylamino)phenyl]-1-diazenyl} phenyl)-4-[1-phenyl methylidene]-5(4H)-oxazolone

2. EXPERIMENTAL

2.1. Apparatus and Reagents

An atomic absorption spectrometer model Sens AA (Dandenong, Victoria, Australia, http://www.gbcaustralia.com) equipped with deuterium lamp background corrector was used for determination of palladium in air-acetylene flame. The instrumental settings of the spectrometer were as follows: wavelength, 244.8 nm; slit width of 0.2 nm; lamp current, 5 mA; acetylene flow 3.5 L min^{-1} and air flow 1.5 L min^{-1}. A mechanical shaker KS 130 basic (Deutschland, Germany, www.ika.net) having speed control and timer was used for preparation of the sorbent. Funnels-tipped glass tube (5×100 mm) equipped with stopcock were used as column for the preconcentration purposes. The bed height the adsorbent in the column was approximately 10 mm. A 691 Metrohm pH meter (Herisau, Switzerland, http://www. metrohm.com) was employed for pH measurements.

All reagents were of analytical grade. Deionized and distilled water was used in all experiments. The stock solution 1000.0 µg mL^{-1} of Pd (II) was prepared by dissolving 0.1660 g $PdCl_2$ (99.999%, Aldrich, Milwaukee, USA) in 2 M HCl (37.0%, Merck, Darmstad, Germany), and diluting to 100.0 mL with distilled water. The standard working solutions were diluted daily prior to use. The ligand oxazolone azo dye was synthesized and purified as reported in the literature [18]. A 0.1% (w/v) solution of the synthetic ligand was prepared by dissolving 0.10 g of oxazolone azo dye in ~5 mL of acetone and DMSO and diluting to 100.0 mL with mixture of two solvents. Buffer solution was prepared from 0.1 mol L^{-1} dipotassium hydrogen phosphate (Aldrich, Milwaukee, USA) for pH ~5. A solution of thiourea 1.0 mol L^{-1} was prepared by dissolving 7.680 g of thiourea (99.0-101%, Merck, Darmstad, Germany), in distilled water and diluting to 100.0 mL with distilled water. Al_2O_3 (0.063-0.2 mm or 70-230 mesh ASTM) (Merck, Darmstad, Germany) was used as sorbent.

2.2. Preparation of the alumina coated with oxazolone azo dye

About 6 g of the alumina was added to 50.0 mL of the solution containing 0.1% oxazolone azo dye in a stoppered pyrex glass flask, and the mixture was shaken on mechanical shaker at room temperature for about a night. The reagent coated alumina was filtered through a cellulose membrane filter (Millipore) of 0.45 µm pore size, washed with distilled water tree times and dried at room temperature for 24 h.

The modified alumina was confirmed by IR analysis (Fig. 2). Comparison of the IR spectrum of bare alumina with modified alumina, many new peaks appeared in the spectrum. The infrared spectrum of the ligand showed strong absorption band at 1788 cm^{-1} which was assigned υ (C=O) vibration. The strong band observed at 1652 cm^{-1} in the spectrum was owing to the υ (C=N). The bands observed at 2924, 1600, and 1547cm^{-1} were assigned to υ (C-H), υ (C=C, Ar) and υ (C=C, vinyl) vibrations respectively. The bare adsorbent (Fig. 2, (a)) showed the characteristic peaks at 3481–2800, 1635 and 1000–400cm^{-1} that are mainly owing to the alumina matrix.

However, the IR-spectrum of modified alumina adsorbent with ligand is dominated by the peaks corresponding to the alumina matrix and some of the strong band corresponding to ligand, for example at 1788, 1652, 1600 and 1548 owing to υ(C=O), υ(C=N), υ(C=C, Ar) and υ(C=C, vinyl) respectively (Fig. 2, (b)). Consequently, the above experimental results suggest that alumina is successfully modified by the oxazolone azo dye ligand.

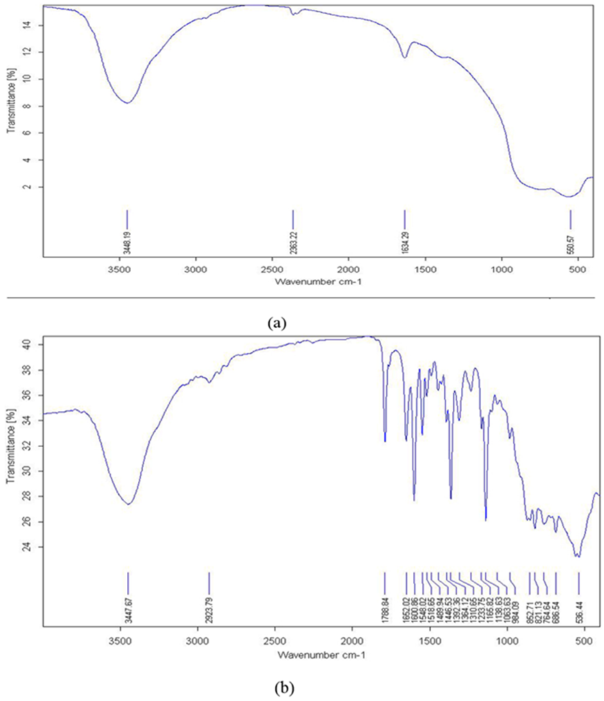

Fig. 2. FT-IR spectra: (a) bare alumina, (b) modified alumina.

2.3. General procedure

Funnel-tipped glass tube (ten columns, 10 cm long and 0.5 cm in diameter) equipped to stopcock was used as the column for preconcentration purposes. A small amount of glass wool was placed in the end of the columns to prevent loss of the sorbent during sample loading. Then, the columns were packed with 50 mg of the alumina coated with oxazolone azo dye and conditioned with a buffer solution at pH~5. The bed height the adsorbent in the column was approximately 10 mm. An aliquot of the sample solution containing Pd(II) (0.25-40.00 µg) was taken in a 50 mL beaker and to it was added 2 mL buffer solution with pH 5. The total volume of the solution was made up to about 30 mL with distilled water. It was then passed through the column containing 50 mg of the sorbent with flow rate of 3 mL min^{-1}. The flow rate of solution was controlled by using a stopcock in end of the column. The retained palladium was eluted from the solid phase with 2.5 mL of 3.0 mol L^{-1} HCl and then 2.5 mL of thiourea 1.0 mol L^{-1}. This solution was aspirated into an air-acetylene flame for the determination of Pd by FAAS. Calibration curve for the determination of palladium was prepared according to the proposed procedure under the optimum conditions.

2.4. Analysis of real samples

The water different samples were obtained from a spring (Rigan, Bam, Iran), tap water (Kerman, Iran), mineral water Plour (Mazanderan Mineral water industries company) and the wastewater from a Barez rubber manufacturing firm (Kerman, Iran). The water samples were collected in cleaned polyethylene bottles and filtered through a cellulose membrane filter (Millipore) of 0.45 µm pore size. A volume 100.0 mL of water samples was transferred to a beaker, and pH was adjusted to 5 by addition of the buffer solution. Then the proposed procedure was applied to these samples. The levels of palladium in the samples were determined by flame atomic absorption spectrometry.

The anodic slime samples were obtained from Sarcheshmeh copper complex (Rafsanjan, Iran). Digestion of anodic slime samples were carried out by the follow method: The anodic slime samples were dried at 110 C for 2 h. A 0.5 g amount of the slime was decomposed with 10-15 mL of aqua regia and the solution was evaporated to dryness. The process was repeated twice. 10-15 mL of a mixture containing 0.4 M NaBr, 0.01 M KSCN and 0.05 M HNO_3 was added to the residue. The suspension was filtered through a filter paper, and the insoluble part was washed with the NaBr-KSCN-HNO_3 mixture. The filtrate and washing (final volume ≤100.0 mL) in the receiving vessel were passed through the column and the palladium was determined with proposed method.

3. RESULTS AND DISSCUTIONS

The preliminary experiments showed that the bare alumina can adsorb a lot of metal ions, but, adsorption was not selective and the recoveries were incomplete. By immobilization of the ligand oxazolone azo dye on the alumina, only, Pd can be adsorbed in the specified pH. On the other hand, the coating of alumina with the ligand increases the adsorption capacity for Pd. In order to achieve the best performance, the separation/preconcentration procedure was optimized for various analytical parameters, such as pH of the sample, the flow rate of eluent and sample solution, amount of the adsorbent, volume and type of the eluent solution, volume of the buffer and volume of the sample solution. Various ions interference effects were also investigated.

3.1. Effect of pH

Since the pH of the aqueous solutions is an important analytical factor in solid phase extraction studies of metal ions [19], the influence of pH on the recovery of Pd ions was examined in the pH range of 2-9 by using the diluted solution HNO_3 and NaOH or the proper buffers. As can be seen from Fig. 3, Pd (II) ions were recovered at pH range of 4-6. pH 5 was selected for further study and was kept at 5 using potassium dihydrogen phosphate buffer solution.

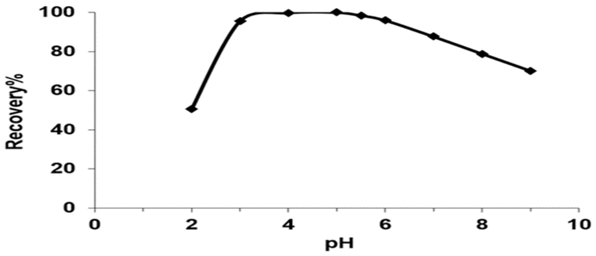

Fig. 3. Effect of pH on the recovery of Pd after preconcentration with the proposed method.

3.2. Effect of type and concentration of eluent

Desorption of the retained Pd (II) from the column was tested using various eluting agents. Since the complex of the Pd (II) with oxazolone azo dye is stable, many of the reagents could not elute Pd (II) from the column, completely. As can be seen from Table 1, the maximum recoveries have been obtained by using 2.5 mL of 3 mol L^{-1} HCl and then 2.5 mL of 1 mol L^{-1} thiourea (final volume 5.0 mL). Therefore, in all the experiments 2.5 mL of 3 mol L^{-1} HCl and then 2.5 mL of 1 mol L^{-1} thiourea was used for desorption of Pd.

Table 1. Effect of elution solutions on the recovery of palladium.

Solution	Recovery(%) [a]
5.0 mL of 3 M HCl	75.5 ± 1.5
5.0 mL of 5 M HNO_3	31.0 ± 0.6
5.0 mL of 0.5 M thiourea	26.8 ± 0.3
5.0 mL of 1 M thiourea	62.4± 0.3
3.0 mL 3 M HNO_3 and then 2.0 mL 1 M thiourea	59.3± 0.7
3.0 mL 3 M HCl and then 2.0 mL 0.5 M thiourea	78.9± 1.1
2.5 mL 1 M thiourea and then 2.5 mL 3 M HCl	96.2 ± 1.7
2.5 mL 3 M HCl and then 2.5 mL 1 M thiourea	100.0 ± 1.3

Conditions: Pd, 10.0 µg; pH ~5; buffer, 2 mL; flow rate, 3 mL min^{-1}; sorbent, 50 mg.

Instrumental settings: Current of Pd hollow cathode lamp 5 mA; absorption line Pd 244.8 nm; slit width 0.2 nm; acetylene flow 3.5 L min^{-1} and air flow 1.5 L min^{-1}.

[a] Average of three determinations, ± standard deviation.

3.3. Effect of flow rate of sample and eluent solution

The retention of an element on a sorbent also depends on the flow rate of the sample solution [20]. Thus, the effect of flow rate of the sample and elution solution on the retention and recovery of palladium was investigated under optimum conditions (pH= 5; elution solution 2.5 mL of 1 mol L^{-1} HCl and then 2.5 mL of 1 mol L^{-1} thiourea). The solution containing Pd was passed through the column with the flow rates adjusted in the range 0.5-3 mL min^{-1}. It was observed that, at flow rates greater than 3 mL min^{-1} there was a decrease in the recovery of palladium. The reason for this decrease is probably insufficient contact of the metal ions and the sorbent to reach equilibrium [20]. Therefore, a flow rate of 3 mL min^{-1} was applied for adsorption of Pd in subsequent experiments. Also, for desorption of Pd, flow rate was varied between 0.5-3 mL min^{-1}. The flow rate of 1 mL min^{-1} was adequate for desorption of Pd.

3.4. Effect of amount of the sorbent

The amount of sorbent is another important parameter that affects the recovery. A quantitative retention is not obtained when the amount of sorbent is less [21]. On the other hand, an excess amount of sorbent prevents the elution of the retained chelates by a small amount of eluent quantitatively. For this purpose, different amounts of the sorbent (10-100 mg) were examined. The results showed that quantitative recoveries (>95%) of the metal ion were obtained when the sorbent quantity was equal or greater than 50 mg. 50 mg of the sorbent was selected for further experiments.

3.5. Breakthrough volume

The measurement of breakthrough volume is important in solid phase extraction because breakthrough volume represents the sample volume that can be preconcentrated without loss of analyte during elution of the sample. The volume of the first aqueous phase, containing a fixed amount of the analytes (10.0 µg Pd), was varied in the range of 50.0-1000.0 mL under the optimum conditions, keeping other variables constant, and was passed through column for preconcentration. It was found that recovery was quantitative to 750.0 mL. At sample volumes>750 mL the recoveries decreased gradually with increasing volume of sample solution. Since the elution solution volume was 5.0 mL; preconcentration factor was obtained 150.

3.6. Sorption capacity

To determine the amount of analyte retained on the column, for a specific mass of sorbent, several solutions differing in concentrations were made and introduced into the column. Ten milliliters of solutions containing palladium at concentrations in the range of 20.0-200.0 mg L^{-1} were passed through the columns containing exactly 100.0 mg of the sorbent under optimum conditions. The eluting solutions were collected and the presence of the analyte in each of them was tested by FAAS. When Pd was detected in the eluate, the test was stopped and the sorption capacity calculated. The sorption capacity was found to be 15.0 mg Pd^{2+} for 1.0 g sorbent.

3.7. Effect of foreign ions

Various salts and metal ions were added to a solution containing Pd (II) and the general procedure was applied. The tolerance limit was set as the concentration of the ion required to cause ±3% error [22]. The results obtained are given in Table 2. Among the metal ions and salts studied, most did not interfere. Thus, this method is selective and can be used for the determination of Pd in complex samples.

Table 2. Effect of diverse salts and metal ions on the extraction and preconcentration of Pd(II).

Salt or ion	Tolerance limit (mg)
Na_2SO_4 , NaCl	500
$NaHCO_3$, CH_3COONa	250
$Na_2S_2O_3$	200
$K_2Cr_2O_7$	300
NaF	450
$KBrO_3$	50
NaBr	40
KI, $NaNO_2$	50
Cu^{2+}, Zn^{2+}	40
Co^{2+}	30.8
Ni^{2+}	20.5
Cd^{2+}	40.1
Pb^{2+}, Fe^{3+}	20
Hg^{2+}	10.5
Fe^{2+}	20.7
Cr^{3+}	10.25
Au^{3+}	8

Conditions: Pd, 10.0 µg; pH~5; flow rate, 3 mL min^{-1}; sorbent, 50 mg; elution solution, 2.5 mL 3 M HCl and then 2.5 mL 1 M thiourea.

3.8. Reusability and stability of alumina/ oxazolone azo dye

Reusability is one of the key parameters to assess the effectiveness of a sorbent. A series of sorption/desorption experiments were performed to understand the reusability of the synthesized alumina/ oxazolone azo dye. After sorption, the sorbent was treated with 2.5 mL of 3 mol L^{-1} HCl and then 2.5 mL of 1 mol L^{-1} thiourea to desorb palladium and this sorption/desorption procedure was repeated. After each desorption step, the sorbent was washed with doubly distilled water to remove thiourea and condition sorbent. The experiments showed that it can be regenerated over 100 cycles of adsorption-desorption without any significant change in the retention of Pd.

3.9. Analytical performance

The analytical performance of the proposed procedure can be shown for the results of FAAS measurements. Calibration curve for the determination of Pd was prepared according to the proposed procedure under the optimum conditions. The linearity was maintained in the concentration range of 0.05-8.0 μg mL^{-1} in the final solution or 0.33-5.33×10 ng mL^{-1} in the original solution. The equation of the line is A=0.037C+0.0043 with the regression coefficient 0.996 where A is the absorbance and C is concentration of the metal ion (μg mL^{-1}) in the final solution. The limit of detection (LOD) of a method is the lowest analyte concentration that produces a response detectable above the noise level of the system, typically, three times the standard deviation of the blank (n=8) on a sample volume 750.0 mL was found to be was 0.25 and limit of quantitative (LOQ) was 0.83 ng mL^{-1} in the original solution. Eight replicate determinations a mixture of 2.0 μg mL^{-1} of Pd in the final solution, gives a mean absorbance of 0.059 with relative standard deviation (RSD%) of ±1.4%.

3.10. Application to real samples

To assess the capability of the method for real samples with different matrices containing varying amounts of diverse ions, the method was applied to determine palladium in different water and wastewater (rubber manufacturing firm) samples. Also, In order to evaluate the accuracy of the procedure, recovery experiments were also carried out with spiked water samples because of certified reference material for the Pd was not available. According to the results, the concentration of palladium in analyzed water samples was below the LOD of the method. The suitability of the proposed method for the analysis of natural water samples was checked by spiking the samples with 5.0 and 10.0 mL of 2.0 μg mL^{-1} of the analyte ions. Good recoveries were obtained for all analyzed samples (Table 3).

The procedure was also applied to an anodic slime samples that have a more complex matrix than water and wastewater. The anodic slime samples were obtained from Sarcheshmeh copper complex (Rafsanjan, Iran). The correctness of the results was tested by analysis of spiked anodic slime samples. The recovery percentage of palladium ions was evaluated and the results showed that the real samples matrixes did not affect the recovery of palladium. The results are given in Table 4.

3.11. Comparison with other methods

Comparative data from some papers on solid phase extraction of trace Pd are summarized in Table 5. As can be seen from Table 5, the preconcentration factor of investigated element is superior to most other preconcentration/separation methods except the results reported in the following literature [33]. The sorption capacity and detection limit is also better or comparable with the other methods. The matrix effects with the method were reasonably tolerable. Good recoveries were obtained for the spiked samples, demonstrating that the method can be successfully applied to these samples.

Table 3. Determination of palladium in the water and wastewater samples after preconcentration with the proposed method.

Sample	palladium (ng mL^{-1})		Recovery (%)
	Spiked	Found[a]	
Tap water[b] (Kerman)	0.0	B.L.R.	----
	10.0	10.10±0.15	101.0
	20.0	20.52±0.33	102.6
Spring water[b] (Rigan, Bam)	0.0	0.00	----
	10.0	9.65±0.15	96.5
	20.0	19.37±0.30	96.8
Mineral water[c] (Plour)	0.0	B.R.L.	----
	10.0	10.18±0.21	101.8
	20.0	20.51±0.26	102.5
waste water[d] (Barez)	0.0	12.5±0.15	----
	10.0	21.69±0.15	93.5
	20.0	32.05±0.42	96.4

B.L.R: Below linear range; Sample volume: 100.0 mL
Conditions: pH ~5; flow rate, 3 mL min^{-1}; sorbent, 50 mg; elution solution, 2.5 mL 3 M HCl and then 2.5 mL 1 M thiourea; [a]Average of three determinations, ± S.D.
[b]Kerman, Iran; [c]Mazanderan, Iran
[d]Barez rubber manufacturing firm, Kerman, Iran

Table 4. Recovery palladium from anodic slime samples.

Sample	Palladium (μg g^{-1})		Recovery (%)
	Added	Found[a]	
Anodic slime (S-100)	0.0	40.0±0.7	----
	2.5	42.9±0.9	101.0
	5.0	46.0±1.2	102.5
Anodic slime (S-200)	0.0	85.0±1.6	----
	2.5	88.6±1.2	101.3
	5.0	90.5±1.8	100.6

Sample amount: 500.0 mg
[a]Average of three determinations, ± standard deviation.
Conditions and Instrumental settings: Were the same as Table 1.

4. CONCLUSIONS

Preparation of a new sorbent using alumina and an oxazolone azo dye has been described and shown to be an alternative and efficient route for separation/preconcentration purpose in the determination of palladium in anodic slime and various water and wastewater samples. Preparation of the sorbent is simple, rapid and low cost. The stability of sorbent is excellent and could continuously be used for a long period of time without any appreciable change in its sorption properties towards Pd(II) ions. The new adsorbent showed highly selective adsorption towards Pd(II). Good preconcentration factor was obtained easily by this method. The accuracy of the results was verified by analyzing the spike and various water and wastewater samples. In addition, the new sorbent showed high tolerance to interferences from the matrix ions in various sample. Therefore, proposed method can be applied to various samples having complex matrix such as anodic slime, wastewater.

Table 5. Comparative data from some extraction methods on preconcentration of palladium.

Method	Determination technique	PF	LOD(ng mL^{-1})	RSD%	Sorption capacity(mg g^{-1})	Ref.
SPE	ICP-AES	100	0.2	3.2	5.0	[12]
SPE	FAAS	80	1.0	2.4	----	[24]
CPE	ICP-OES	20.2	0.3	5	----	[24]
SPE	FASS	165	0.3	5.3	15.6	[25]
DLLME	FAAS	45.7	90.0	0.7	----	26]
SPE	ICP-OES	12.9	0.28	4.2	----	[27]
SPE	FAAS	140	0.1	----	2.4	[28]
CPE	FAAS	30	1.6	2.7	----	[7]
CPE	UV-Vis	50	0.6	1.1	----	[8]
SPE	ETASS	----	0.4	3.5	----	[29]
SFODME	FAAS	49.9	0.6	2.0	----	[30]
SPE	FAAS	125	0.54	<4	9.6	[31]
SPE	ETASS	200	0.02	5.2	13.0	[32]
SPE	FAAS	150	0.25	1.4	15.0	This work

PF: Preconcentration Factor, SPE: Solid Phase Extraction; CPE: Cloud Point Extraction; DLLME: Dispersive Liquid-Liquid Microextraction; SFODME: Solidified Floating Organic Drop Micro Extraction.

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