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Utility of cloud-point preconcentration and spectrophotometry for determination of trace amounts of palladium(II) and their analytical applications

Alaa S. Amin *

Chemistry Department, Faculty of Science, Benha University, Benha, Egypt

Abstract A cloud-point preconcentration process using micelle of the cationic surfactant cetyltrimethylammonium bromide to extract Pd(II) from aqueous solutions was investigated. The method is based on the color reaction of palladium with 4-(2-benzothiazolylazo)2,2′-biphenyldiol in the presence of potassium chloride at pH 3.85 phosphate buffer media and micelle-mediated extraction of complex. The optimal extraction and reaction conditions (e.g., reagent concentration, surfactant concentration, and the effect of time and temperature) were studied and the analytical characteristics of the method (e.g., detection and quantification limits, linear range, preconcentration and improvement factors) were obtained. Linearity was obeyed in the range of 2.0–240 ng mL^{-1} of Pd(II) ion and the detection limit of the method was 0.6 ng mL^{-1}. The relative standard deviation (RSD) and relative error for six replicate measurements of 150 ng mL^{-1} Pd(II) were 1.05% and 1.36%, respectively. The interference effect of anions and cations was also tested. The method was applied to the determination of Pd(II) in water, spiked water, synthetic alloys and in Pd–charcoal, plating effluents, catalyst and soil samples.

* Address: Faculty of Community, Department of Medical Science, Umm Al-Qura University, Makkah, Saudi Arabia.
  E-mail address: asamin2005@hotmail.com

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1. Introduction

Interest in the development of analytical techniques for determination of the noble metals is growing as a result of their applications in chemical engineering, micromechanics and medicine. Palladium has been used in different areas of science and technology, including agents, brazing alloys, petroleum, electrical industries and catalytic chemical reactions (Kezler and Iberts, 1983; Machida et al., 1987; Ensafi and Keyvanfard, 2002). The metal may enter the environment and interact with complexing materials, such as humic substances (Hees et al., 1998). Palladium has no biological role, and all palladium compounds should be regarded as highly toxic and

carcinogenic. Thus, because of its increasing use, on the one hand, and the toxicity of Pd(II) compounds to mammals, fish and higher plants, on the other hand (Lee, 1980), the determination of palladium is interesting in environmental analysis.

Palladium has extensive use in alloys, catalysts and in low voltage electrical contacts. It is an efficient catalyst that is widely used for hydrogenation and dehydrogenation reactions. The palladium content of earth crust is 0.01–0.02 µg mL^{-1} owing to corrosion resistance nature and it exists in various natural minerals, soil and rocks. Palladium and its alloys have wide range of application in both the chemical industries and instrument making. It is used in jewellery, dentistry applications, fine instruments, such as watches and some surgical tools for the purification of hydrogen gas (Bruzzoniti et al., 2003). The direct determination of palladium in various environmental samples with different instrumental methods is not possible to decrease the concentration levels of trace amounts in different environmental samples. The Azo dyes with the heterocyclic diazo-component form colored complexes with many metal ions in solution (Savvin et al., 2000; Lazaro et al., 1998; Morozko and Ivanov, 1995; Ivanov, 1982). Several analytical techniques have reported for the determination of trace elements in natural water like ICP-AES, ICP-MS, ETAAS, GFAAS, NAA, CE which are very expensive and in addition to that direct determination of trace metal ions by following methods is not sufficiently sensitive. So many spectrophotometric methods have been developed for the determination of palladium (More and Sawant, 1994; Dakshinamoorthy et al., 1994; Chhakkar and Kakkar, 1994; Zhu and Yang, 1993; Jha and Mishra, 1993; Fuli et al., 1993; Sakuraba and Oguma, 1994; Mathew and Khopkar, 1997). To overcome the above drawbacks it requires previously separation and preconcentration technique which is subsequent determination with spectrophotometric techniques.

Cloud-point preconcentration (CPP), based on the clouding phenomena of surfactants, has become more and more attractive. CPP offers many advantages over traditional liquid–liquid extraction (Li and Hung, 2003). For charged micelles, the phenomenon rarely occurs, presumably because electrostatic repulsion prevents phase separation in most cases. In the presence of salt, long-tailed cationic surfactants can self-assemble in aqueous solution into long, flexible wormlike micelles, thus rendering the solution viscoelastic (Rehage and Hoffmann, 1991; Hoffmann, 1994). High concentrations of salt cause cationic surfactant solutions to separate into immiscible surfactant-rich and surfactant-poor phases (Vassiliades, 1970). This phenomenon, originally termed coacervation, has been investigated since the 1940s and was first observed for mixtures of the cationic surfactant Hyamine 1622 with salts such as potassium thiocyanate (KSCN) and potassium chloride (KCl) (Booij, 1949; Cohen et al., 1954). The phase separation is typically of the upper consolute type, i.e., it occurs on cooling below a characteristic temperature Tc, which, in turn, increases with salt content. Some separation and preconcentration cloud-point extraction procedures have been developed for various chemical species prior to their determination by different methods (Silva et al., 2006; Bezerra et al., 2005; Suvardhan et al., 2007; Sun et al., 2006; Afkhami et al., 2006, 2007; Madrakian et al., 2007).

In the present study, a novel reagent 4-(2-benzo-thiazolylazo)2,2′-biphenyldiol (BTABD) was synthesized for the cloud point preconcentration of palladium from various environmental samples. The method was based on the complexation of palladium with BTABD in the presence of cetyltrimethyl-ammonium bromide (CTAB) at pH 3.85 using with suitable buffer (phosphate buffer). Optimum experimental conditions were investigated with respect to a standard solution of the same matrix, in order to examine the possibility to obtaining the maximum extraction efficiency with minor sample treatment and minimal experimental conditions. This is an alternative method to the solid phase extraction and column techniques for the analysis of metal ions in various samples of environmental importance.

2. Experimental

2.1. Apparatus

A Perkin–Elmer Lambda 12 UV/Vis spectrometer was used for recording absorbance spectra with 0.5-cm quartz cell. An Orion research model 601 A/digital ionalyzer pH meter was used for checking the pH of solutions. A water bath with good temperature control and a centrifuge with 25-mL calibrated centrifuge tubes (Superior, Germany) were used to accelerate the phase separation process.

2.2. Reagents

Standard stock solution of palladium(II) chloride (0.01 mol L^{-1}) was prepared by dissolving 0.17740 g of PdCl$_2$ in 100 mL of water acidified with 0.5 mL of concentrated hydrochloric acid. The resulting solution was standardized by EDTA method (Merck, 1982). Working solutions were obtained by suitable dilution of the stock solution with deionized-distilled water. The surfactant, cetyltrimethyl-ammonium bromide (CTAB) (obtained from Sigma company) was used without further purification.

BTABD was synthesized according to the method described previously (Amin, 2000). Stock solutions of 5.0×10^{-4} mol L^{-1} BTABD were prepared by dissolving an appropriate weight of pure reagent in least amount of ethanol (15 mL) and then diluted to the mark in a 100-mL calibrated flask with ethanol. The solutions of different pH 2.75–10.63 phosphate buffer were prepared as described early (Britton, 1952). N,N-Dimethylformamide (DMF) solvent and potassium chloride salt were purchased from Merck.

2.3. General procedure

An aliquot of palladium(II) standard solution was transferred to a 25 mL centrifuge tube, 3.0 mL of the 5.0×10^{-4} mol L^{-1} BTABD solution and 7.5 mL buffer solution of pH 3.85 were added. This was followed by the addition of 4.0 mL of 2.5×10^{-3} mol L^{-1} surfactant CTAB solution and 2.5 mL of 0.4 mol L^{-1} of KCl solution. The solution was taken up to the mark with bidistilled water and warmed at water bath of $45 \pm 2.0\ °C$ and allowed to stand for 5.0 min. Separation of the aqueous and surfactant-rich phase was accomplished by centrifugation for 10 min at 4000 rpm. Then, the aqueous phase could be separated by inverting the tube. The surfactant-rich phase of this procedure was dissolved and diluted to 0.5 mL with the DMF and transferred into a 0.5-cm quartz cell. The absorbance of the solution was measured at 679 nm.

The blank solution was submitted to the same procedure with Pd(II).

2.4. Determination of palladium in spiked and natural water samples

The extraction efficiency was studied using spiked water samples for the recovery of palladium. Doubly distilled water was spiked with known amounts of metal standards (30, 60 and 90 ng mL^{-1}) and allowed to stand over night. The concentration of palladium in spiked water samples was determined. The natural water samples were filtered through a 0.45 μm pore size membrane filter to remove suspended particulate matter and then stored at 4 °C in the dark. The final solution was determined by following the above general procedure.

2.5. Determination of palladium in catalyst

For the catalyst, 0.1 g of sample was weighed accurately into a Teflon high-pressure microwave acid digestion bomb (Fei Yue, Analytical Instrument Factory, Shanghai, China) and 3.0 mL of concentrated nitric acid, 2.0 mL of hydrochloric acid and 5.0 mL of 30% hydrogen peroxide were added. The bombs were sealed tightly and then positioned on the carousel of the microwave oven (Model WL 5001, 1000 W, Fei Yue Analytical Instrument Factory, Shanghai, China). The system was operated at full power for 10 min. The digest was evaporated to near dryness. The residue was dissolved with 10 mL 10% hydrochloric acid, and then transferred into a 50 mL calibrated flask and diluted to volume with 10% hydrochloric acid. Then 5.0 mL of 10% citric acid was added to mask the nickel and cobalt. The palladium content was analyzed according to the general procedure. The recovery of palladium was carried out using the added 1.0 μg of palladium in sample, and a standard method using flame atomic absorption spectrometry as described in (Dong et al., 2004) was used as a reference method.

2.6. Determination of palladium in soil samples

A soil sample (5.0 g) was weighed into a 250 mL Teflon high-pressure microwave acid-digestion bomb (Fei Yue Analytical Instrument Factory, Shanghai, China) and 50 mL of aqua regia were added. The bomb was sealed tightly and then positioned in the carousel of a microwave oven (Model WL 5001, 1000 W, Fei Yue Analytical Instrument Factory, Shanghai, China). The system was operated at full 826 Yang et al. power for 30 min. The digested material was evaporated to incipient dryness. Then, 50 mL of 5.0% hydrochloric acid was added and heated close to boiling to leach the residue. After cooling, the residue was filtered and the undissolved residue was washed two times with 5.0% hydrochloric acid. The filtrates were quantitatively collected in a 200 mL volumetric flask and the palladium content was analyzed according to the general procedure.

3. Results and discussion

BTABD is often used as a chromgenic reagent for the determination of niobium(V) (Amin, 2000). The addition of surfactant-active substances improves the selectivity and sensitivity of Nb(V) determinations due to the batho- and hyperchromic effects that can be observed.

Complex of Pd(II) with BTABD in the presence of CTAB in aqueous media has a maximum absorbance at 673 nm. The solution was turbid by addition of the chloride ion. Therefore, the ternary complex of Pd(II)–BTAHQ–CTAB can be extracted by CPP method. The absorption spectrum of the ternary complex in surfactant-rich phase shows a maximum absorbance at 679 nm (Fig. 1). After separation of surfactant-rich phase, the absorbance was measured at 679 nm against a reagent blank as the reference.

3.1. Optimization of the system

To take full advantage of the procedure, the reagent and surfactant concentrations and reaction conditions must be optimized. Various experimental parameters were studied in order to achieve optimum conditions. These parameters were optimized by setting all parameters to be constant and optimizing one each time.

The effect of pH on the absorbance at a constant concentration of complex in surfactant-rich phase was investigated in the range of 2.75–10.63. The absorbance of the Pd(II)–BTABD–CTAB system at 679 nm in surfactant-rich phase was studied against the reagent blank. The absorbance was nearly constant in the pH range of 3.6–4.0. Therefore, pH 3.85 was selected as optimal (Fig. 2). Moreover, the amount of pH 3.85 was studied to select the optimum volume. A 6.0–9.0 mL of pH 3.85 gave the highest absorbance value. Therefore 7.5 mL of pH 3.85 per 25 mL was selected for all further studies.

Effect of BTABD concentration on the extraction and determination of Pd(II) was investigated in the range of 1.0–10×10^{-5} mol L^{-1}. The sensitivity of the method increased by increasing BTABD concentration up to 6.0×10^{-5} mol L^{-1} and decreased at higher concentrations. It was expected that increasing BTABD causes an increase in the absorbance of complex, because increasing in BTABD concentration caused an increase in concentration of the complex. At concentrations higher than 7.0×10^{-5} mol L^{-1}, the concentration of uncomplexed BTABD in surfactant-rich phase increases significantly.
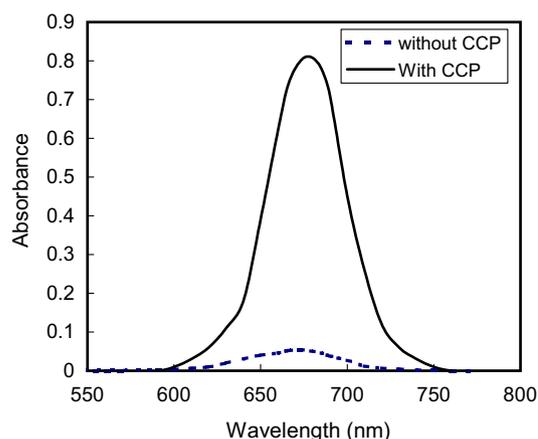

Figure 1 Absorption spectra for 150 and 1500 ng mL^{-1} Pd(II) complexed with 6×10^{-5} mol L^{-1} BATBD with CPP and without CPP, respectively.
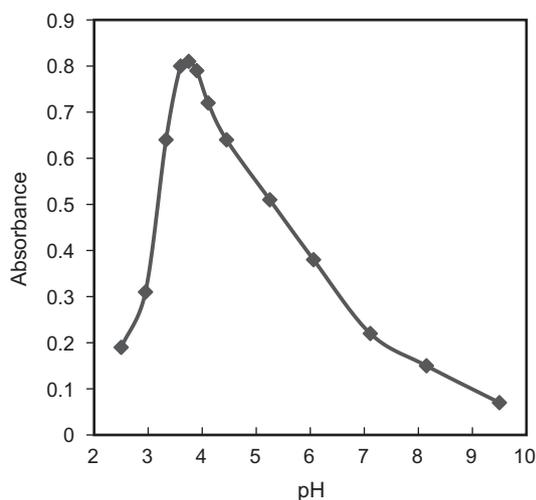
Figure 2 Effect of phosphate buffer solution on the complexation of 150 ng mL^{-1} Pd(II) using 6×10^{-5} mol L^{-1} BTABD after CCP.

Therefore, most probably decrease of absorbance change at concentrations higher than 7.0×10^{-5} mol L^{-1} is due to this fact that the free BTABD competes with the complexes in extraction to surfactant-rich phase. A concentration of 6.0×10^{-5} mol L^{-1} of BTABD was selected as the optimum.

Effect of CTAB concentration on the extraction and determination of Pd(II) was investigated in the range of 1.0–8.0×10^{-4} mol L^{-1}. The amount of the absorbance for sample increased by increasing CTAB concentration up to 4.0×10^{-4} mol L^{-1} and decreased at higher concentrations. The blank signal also increased by increasing CTAB concentration. This is due to more extraction of BTAHQ by increasing CTAB concentration, but the difference between the sample and blank signals (ΔA) increased by increasing CTAB concentration up to 4.0×10^{-4} mol L^{-1} and decreased at higher concentrations (Fig. 3). Therefore, 4.0×10^{-4} mol L^{-1} CTAB was chosen as the optimum.
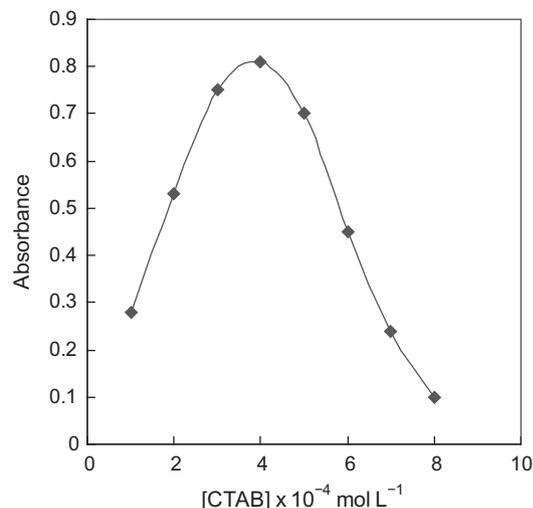
Figure 3 Effect of 10^{-4} mol L^{-1} CTAB on the complexation of 150 ng mL^{-1} Pd(II) using 6×10^{-5} mol L^{-1} BTABD after CCP.

Addition of salt can cause cationic surfactant solutions to separate into immiscible surfactant-rich and surfactant-poor phases. Several inorganic salts including NaCl, NaF, KNO$_3$, KCl, KBr and KI were tested and KCl was found as the best. Therefore, chloride was added to induce micelle growth and extraction of complex. The effect of chloride concentration was studied in the range of 0.01–0.08 mol L^{-1}. Addition of 0.04 mol L^{-1} chloride sufficed for maximum extraction of the complex and the signal decreased at higher concentrations. A concentration of 0.04 mol L^{-1} chloride was selected for further works.

The temperature affected the complexation and CPP procedure. The results indicated that complexation was completed at 45 ± 2.0 °C which was selected for further studies. Furthermore, the effect of time on the reaction and also on the CPP procedure was investigated. The results showed that complexation reaction was completed in 5.0 min. Also a 10 min centrifugation at 4000 rpm was found to be enough for successful CPP.

Because the surfactant-rich phase was precipitate, different solvents were tried so as to select the one producing the optimal results regarding sensitivity. Among methanol, ethanol, DMF, acetone and acetonitrile, DMF gave the best results due to high sensitivity and low overlapping of spectra of components. Therefore, DMF was chosen in order to have appropriate amount of sample for transferring and measurement of the absorbance of the sample and also a suitable preconcentration factor. Therefore, a preconcentration factor of 50 was archived using the proposed method.

3.2. Stoichiometric ratio

The nature of the complex was established at the optimum conditions described above using the molar ratio and continuous variation methods. The plot of absorbance versus the molar ratio of BTABD to Pd(II), obtained by varying the BTABD concentration, showed inflection at molar ratio 2.0, indicating presence of two BTABD molecules in the formed complex. Moreover, the Job method showed a ratio of BTABD to Pd(II) = 2.0. Consequently, the results indicated that the stoichiometric ratio was (2:1) [BTABD:Pd(II)]. The conditional formation constant (log K), calculated using Harvey and Manning equation applying the data obtained from the above two methods, was found to be 4.08, whereas the true constant was 4.00.

For ion associate complexes of Pd–R–CTAB, the stoichiometric ratio as obtained from molar ratio indicated the formation of 1:2 for [Pd(R)$_2$]:CTAB; so we conjectured that an ion association complex [Pd(R)$_2$]$^{2-}$[CTAB]$_2^{2+}$ is formed in the system. The structure of which is probably as follows:

$$Pd(II) + 2R \rightleftarrows [Pd - R_2]^{2-}$$
$$[Pd - R_2]^{2-} + 2[CTAB]^+ \rightleftarrows \{[Pd - R_2]^{2-}[CTAB]_2^{2+}\}$$
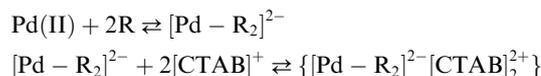
3.3. Selectivity

The effect of different cations and anions on the determination of 150 ng mL^{-1} Pd(II) by the proposed method was studied. An ion was considered to be an interference when it caused a variation greater than ± 5.0% in the absorbance of the sample. For the determination of 150 ng mL^{-1} Pd(II) by this

procedure, the foreign ions can be tolerated at the levels given in Table 1. BTABD forms stable complexes with various metal ions, including transition metal ions. Most of the cations and anions examined do not interfere with the extraction and determination of Pd(II). The results showed that Ni(II) and Co(II) have low tolerance limits. However, Ni(II) and Co(II) can be masked with citric acid. The tolerance limits reaches 0.25 mg for Co(II) and 0.15 mg for Ni(II) when masked with citric acid.

3.4. Analytical characteristics

Table 2 summarizes the analytical characteristics of the optimized method, including regression equation, linear range and limit of detection, reproducibility, and preconcentration and improvement factors. The limit of detection (IUPAC, 1978), defined as $C_L = 3S_B/m$ (where C_L, S_B, and m are the limit of detection, standard deviation of the blank and slope of the calibration graph, respectively), was 0.6 ng mL^{-1}. Because the amount of Pd(II) in 25 mL of sample solution is measured after preconcentration in a final volume of 0.5 mL DMF, the solution is concentrated by a factor of 50. The improvement factor, defined as the ratio of the slope of the calibration graph for the CPP method to that of the calibration graph in micellar media without preconcentration, was 150.

The relative standard deviation (RSD) and relative error for six replicate measurements of 100 ng mL^{-1} of Pd(II) was 1.44% and 1.81% and for 150 ng mL^{-1} was 1.05% and 1.36%, respectively.

The sensitivity expressed as molar absorptivity of the proposed method is compared with those of published spectrophotometric methods (Table 3). Although the SPS method depending on the complexation with a chromogenic reagent disodium 1-nitroso-2-hydroxynaphthalene-3,6-disulphonate (Nitroso R salt) gave a higher sensitivity (8.77×10^5 L mol^{-1} cm^{-1}) (Bilba et al., 2004), compared with the proposed method, it suffered from higher values of detection and quantification limits, in addition to a wider range of determination. The higher sensitivity of the proposed method is notable, greater even than that of the SPE (Yang et al., 2006) that used 2-(2-Quinolylazo)-5-diethylaminobenzoic acid. Also, the proposed method is more sensitive than the other method that is based on spectrophotometry (Table 3).

3.5. Analytical applications

Aiming to demonstrate the usefulness of the proposed system a set of samples comprising several water samples was analyzed.

Table 2 Analytical features of the proposed method.

Parameters	CPP method	Before CPP
Amount of DMF	0.5	–
pH	3.85	3.85
Optimum [BTABD]	6×10^{-5}	6×10^{-5}
Reaction time (min)	5.0	5.0
Stirring time (min)	10	–
Beer's range (ng L^{-1})	2.0–240	300–40,000
Ringbom range (ng L^{-1})	5.0–225	750–38,500
Molar absorptivity (L mol^{-1} cm^{-1})	5.75×10^5	3.83×10^3
Sandell sensitivity (ng cm^{-2})	0.0182	27.8
Regression equation		
Slope (μg L^{-1})	5.4	0.036
Intercept	0.004	−0.014
Correlation coefficient (r)	0.9996	0.9988
RSD[a] (%)	1.05	1.85
Detection limits (ng L^{-1})	0.6	90
Quantification limits (ng L^{-1})	0.19	297
Preconcentration factor	50	–
Improvement factor	150	–

The system was run using the optimized parameters summarized in Table 2. The results of sample are shown in Table 4. Accuracy was assessed by comparing results with these obtained using FAAS. Applying the paired t-test and f-value (Miller and Miller, 2005) no significant difference at 95% confidence level was observed.

The proposed method was successfully applied to the determination of Pd(II) ion in spiked water samples. The results are shown in Table 5. The recoveries are close to 100% and indicate that the proposed method was helpful for the determination of Pd(II) in the real samples. Palladium is determined in certain synthetic mixtures corresponding to its alloys and in activated charcoal by using this method. The values are determined in good agreement with certified values as shown in Table 6.

The proposed method was also applied to determine trace palladium in real samples (Plating effluents, Catalyst and Soils). The results obtained were compared with the FAAS method. The obtained results (Table 7) showed that the recoveries are close to 100% and indicated that the proposed method was helpful for the determination of Pd(II) in these real samples.

4. Conclusion

The proposed procedure gives a simple, very sensitive and low-cost spectrophotometric procedure for determination of Pd(II)

Table 1 Tolerance limits for the determination of 150 ng mL^{-1} of Pd(II) with BTABD (relative error ±5.0%).

Ions added	Tolerance/mg	Ions added	Tolerance/mg
K^+, PO_4^{3-}	25.0	Ti^{4+}, Bi^{3+}, Cr^{6+}	5.0
Al^{3+}, NO_3^-, Cl^-	20.0	Ba^{2+}, $W^{6+, 4+}$	4.0
Na^+, Mg^{2+}, SO_4^{-2}	17.0	Cd^{2+}, Cr^{3+}, Zn^{2+}	3.0
Li^+, borate	15.0	Pb^{2+}, Hg^{2+}, Cu^{2+}	2.0
Ca^{2+}, ClO_4^-, NO_2^-	12.5	Zr^{4+}, Th^{4+}, Sn^{4+}	1.25
Sr^{2+}, IO_3^-, Br^-	10.0	Se^{4+}, Te^{4+}, Pt^{4+}	1.00
$B^{3+} ClO_3^-$, BrO_3^-	8.5	Sb^{3+}, Au^{3+}, Ag^+	0.5
Mn^{2+}, Ce^{4+}, Fe^{3+}	7.0	Co^{2+}	0.25
Mo^{6+}, V^{5+}	6.0	Ni^{2+}	0.15

* Masked with 2.5 mL of 10% citric acid.

Table 3 Comparison of reagents for spectrophotometric determination of palladium.

Reagent	Medium/Solvent	λ_{max} (nm)	ε ($\times 10^4$) L mol^{-1} cm^{-1}	Linear range (μg mL^{-1})	Reference
5-(5-Nitro-2-pyridylazo)-2,4-diaminotoluene	In HCl medium	592	1.9	0–0.9	Yang et al., 1996
o-Hydroxyacetophenone thiosemicarbazone	pH 6.0	370	0.90	0.42–10.6	Murthy and Reddy, 1992
1-(2-Pyridylazo)-2-naphthol	By SLE at 90 °C	678	1.2	0.1–1.8	Gao et al., 1997
2-(5-Nitro-2-pyridylazo)-5-(N-propyl-N-3-sulfopropylamino)-phenol	In weak acidic media	612	10.8	0–2.5	Mori et al., 1999
N-Dodecyl-N′-(sodium-p-aminobenzene-sulfonate)-thiourea	In CTMAB and NaAc–HAc buffer	296	7.41	0–0.5	Ma et al., 2002
Pyridoxal-4-phenyl-3-thiosemicarbazone	In pH 3.0	460	2.20	0.4–6.4	Sarma et al., 2002
2,2′-Dithiodianilline	In pH 3	397	14.7	0.003–0.2	Gholivand and Nozari, 2000
2-(2-Quinolinylazo)-5-diethylamino-benzoic acid	In HCl and CTMAB	625	15.1	0.01–0.6	Huang et al., 2005
2-(2-Quinolylazo)-5-dimethylaminoaniline	In 0.5–2.5 M HCl	600	13.5	0.01–0.7	Si et al., 2005
Benzyloxy benzaldehydethiose micarbazone	In buffer of pH 5.0	477	0.4	5–60	Narayana et al., 2007
2-(2-Quinolylazo)-5-diethylamino-benzoic acid	SPE in (CTAB)	628	14.3	0.01–1.2	Yang et al., 2006
Disodium-1-nitroso-2-hydroxynaphthalene-3,6-disulphonate (Nitroso R salt)	SPS immobilized on Dowex 1 $\times$ 1	510	87.7	15–300 μg L^{-1}	Bilba et al., 2004
BTABD		679	57.44	2.0–240 ng L^{-1}	This work

Table 4 Determination of palladium in natural water samples using cloud point preconcentration.

Samples	Palladium found[a] (vg ml^{-1})	
	Present method	FAAS method
Tap water-I[b] (t-and f-test)	26 ± 0.05 (0.87 and 2.67)	25 ± 0.08
Tap water-II[b] (t-and f-test)	22 ± 0.04 (0.56 and 2.13)	22 ± 0.05
River water-I[c] (t-and f-test)	34 ± 0.03 (1.07 and 3.67)	36 ± 0.04
River water-II[c] (t-and f-test)	27 ± 0.04 (1. 15 and 3.84)	26 ± 0.03
Sea water- I[d] (t-and f-test)	61 ± 0.01 (0.62 and 1.83)	58 ± 0.20
Sea water- II[d] (t-and f-test)	45 ± 0.01 (0.92 and 3.16)	46.5 ± 0.01

[a] Mean ± S.D. ($n = 10$).
[b] Collected from Benha, Zagazig, Egypt.
[c] Collected from Shobra, Aswan, Egypt.
[d] Collected from Alexandria, Safaga, Egypt.

Table 5 Recovery of palladium from spiked water samples using CPP technique.

Element	Proposed method (concentration added)					
	30 ng ml^{-1}	60 ng ml^{-1}		90 ng ml^{-1}		
	Found	Recovery (%)[a]	Found	Recovery (%)[a]	Found	Recovery (%)[a]
Palladium	29.8	99.33 ± 0.37	60.2	100.33 ± 0.28	89.8	99.78 ± 0.43
t- and f-test		0.78 and 1.83		0.96 and 2.12		0.86 and 1,98
FAAS (concentration added)						
Palladium	30.5	101.67 ± 0.60	59.3	98.33 ± 0.78	90.8	100.89 ± 0.96

[a] Mean ± S.D. ($n = 6$).

ion that can be applied to real samples. The surfactant has been used for preconcentration of Pd(II) in water, and thus toxic solvent extraction, has been avoided. A comparison between the proposed method with the previously reported methods for CPP and determination of Pd(II) (Table 3) by different spectrophotometric techniques (Yang et al., 1996, 2006; Murthy and Reddy, 1992; Gao et al., 1997; Mori et al., 1999; Ma et al., 2002; Sarma et al., 2002; Gholivand and Nozari,

Table 6 Determination of palladium in some synthetic alloys and in Pd–charcoal.

Sample	Speciality	Found[a] (%), Pd
Alloy 1: Pd 95.4%, Ru 4.6%	High resistance to oxidation and corrosion	94.7 ± 0.7
Alloy 2: Pd 73%, Ag 25%, Ni 2%	Improvement in hardness and in resistance to mechanical wear	73.3 ± 0.2
Alloy 3: Pd 55%, Au 45%	Jewellery alloy	56.2 ± 0.8
Alloy 4: Pd 33%, Au 9%, Co 23%, Ni 35%	Low melting dental alloy	33.6 ± 0.7
Pd charcoal: Pd 11%, C 89%	Hydrogenation and dehydrogenation	10.9 ± 0.5

[a] Average of six determinations.

Table 7 Determination of palladium in the rail sample.

Samples	FAAS method	Found[a]	RSD% ($n = 5$)	Recovery (%) ($n = 5$)
River water	33.5 (ng mL^{-1})	34.0 (ng mL^{-1})	2.5	101.49
Plating effluents	141 (ng mL^{-1})	140 (ng mL^{-1})	2.1	99.29
Catalyst	0.532 (%)	0.535 (%)	1.2	100.56
Soil (Near a highway)	91.5 (ng/g)	91.2 (ng/g)	1.8	99.67
Soil (General)	34.4 (ng/g)	34.1 (ng/g)	3.1	99.13

[a] Average of five determinations.

2000; Huang et al., 2005; Si et al., 2005; Narayana et al., 2007; Bilba et al., 2004) indicates that this method has a lower detection and quantification limits, wider linear range and is a convenient, safe, simple, rapid and inexpensive method for the determination of trace quantities of Pd(II) to real samples.

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