



Cite this: DOI: 10.1039/c4ay01160k

Redox behavior and adsorptive cathodic stripping voltammetric determination of nanomolar levels of palladium using a novel Schiff base reagent containing a squaric acid moiety

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The redox behavior of a palladium(II)-3,4-bis(2-hydroxyphenyl-imino) cyclobut-1-en-1,2-diol complex at Pt, Au and hanging mercury drop electrodes (HMDE) was studied for developing a low cost and precise method for determination of Pd concentration in road dust and other environmental samples. Hence, a controlled adsorptive accumulation of this complex on HMDE provided the basis for adsorptive cathodic stripping voltammetric (AdCSV) measurements of palladium at nanomolar levels at pH 9–10 and at -0.64 V vs. the Ag/AgCl reference electrode. The calibration plot was obtained in the range of 1.87×10^{-9} to 3.05×10^{-7} M (0.2 to $32.5 \mu\text{g L}^{-1}$) Pd. The limit of detection was found to be 4.70×10^{-10} M ($0.05 \mu\text{g L}^{-1}$), with a relative standard deviation (RSD) of $\pm 2.1\%$ ($n = 5$) at $2.0 \mu\text{g L}^{-1}$ Pd level. Common anions and cations did not interfere in the determination of Pd concentration. The method was applied to the determination of the concentration of Pd in pure authentic samples, roadside dust and water samples. The method offers a simple system coupled with good reproducibility, accuracy, ruggedness and cost effectiveness.

Received 15th May 2014
Accepted 26th June 2014

DOI: 10.1039/c4ay01160k

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1. Introduction

Platinum-group elements (PGEs) have low crustal abundance ($\approx 1 \text{ ng g}^{-1}$). In the earth's crust, Pd usually occurs in its native form associated with one or more of the other PGEs as well as with Cr, Au, Fe, Ni, and Cu.¹ In different areas of science and technology, Pd has been used in brazing alloys, petroleum, electrical industries, catalytic chemical reactions and in converters in motor vehicles.² Concentrations of Pd in fresh water, salt water, soil, sewage sludge and in ambient air levels in urban areas where Pd catalysts are used generally range from 0.4 to 22 ng L^{-1} ; 19 to 70 pg L^{-1} ; <0.7 to $47 \mu\text{g kg}^{-1}$; 18 to $260 \mu\text{g kg}^{-1}$ and below 110 pg m^{-3} ,³ respectively. Drinking water usually contains $<24 \text{ ng L}^{-1}$ Pd; this metal is found in urine of adults in the concentration range of 0.006 to $<0.3 \mu\text{g L}^{-1}$, while the average dietary intake of Pd for humans appears to be up to $2 \mu\text{g}$ per day.³ Thus, the development of analytical techniques for analysis of PGEs including Pd is growing because of their applications in medicine, micromechanics and chemical

engineering. Because of Pd toxicity,⁴ the frequency at which even trace levels of this metal are being monitored in surface waters, soil surfaces, plants and particulate matter has been rapidly increasing. The low level of Pd together with the high concentration of interfering matrix components often requires a preconcentration step combined with a matrix separation.⁵ Hence, it is necessary to develop a method to accurately and precisely determine the concentration of Pd in samples with very low analyte content, such as in airborne particulate matter, various water samples and urine.

A series of analytical methods, *e.g.*, flame atomic absorption spectrometry (FAAS), graphite furnace-AAS, electrothermal AAS, AAS, inductively coupled plasma-optical emission spectroscopy (ICP-OES), ICP-mass spectrometry (MS) and electrospray ionization mass spectrometry (ESI-MS), have been reported for analysis of trace levels of Pd.^{4–18} The high costs of the instruments, complexity, preconcentration step and the need of some degree of expertise for their proper operation are the main disadvantages of these techniques. Thus, recent years have seen an upsurge of interest in the development of low-cost, easy-to-operate, highly sensitive and reliable methods for routine analysis of Pd, which is of prime importance.

Numerous adsorptive cathodic stripping voltammetry (AdCSV) methods have been reported for sensitive Pd concentration determination.^{19–29} To the best of our knowledge, the Schiff base 3,4-bis(2-hydroxyphenylimino)cyclobut-1-en-1,2-diol

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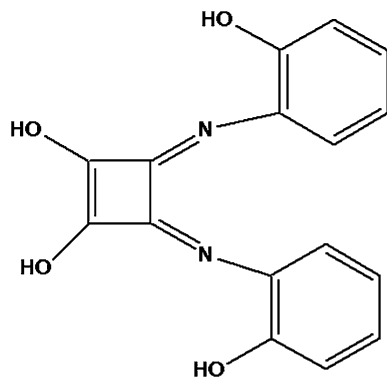


Fig. 1 Chemical structure of 3,4-bis(2-hydroxyphenylimino)cyclobut-1-en-1,2-diol Schiff base.

(SQ-OH) (Fig. 1) has so far not been used as a chelating agent for voltammetric and/or spectrometric determination of Pd and other platinum-group elements. Thus, this article is focused on: (i) studying the redox behavior of Pd with the SQ-OH; (ii) developing a low-cost and precise AdCSV method for Pd analysis; (iii) studying the interference by other metal ions and organic contaminants; and finally (iv) applying the proposed method to determine the concentration of Pd in various environmental samples. The developed method compares favorably with many spectrometric and electroanalytical methods in terms of better selectivity, precision, linear dynamic range (LDR), limit of detection (LOD), ease of use and less interference.

2. Experimental

2.1. Reagents and materials

Analytical reagent-grade chemicals were used as received. The reagent 3,4-bis(2-hydroxyphenylimino)cyclobut-1-en-1,2-diol was prepared from the condensation of squaric acid with *o*-aminophenol in a molar ratio of 1 : 2 as reported.³⁰ A series of Britton–Robinson (BR) buffers (pH 2–11.9) was prepared from a mixture of acetic (0.08 M), phosphoric (0.08 M), and boric (0.08 M) acids after adjusting the pH to the desired pH value with NaOH (0.02 M), and these buffers were used as supporting electrolytes. A BDH stock solution (1000 mg L⁻¹) of palladium(II) was used for the preparation of more diluted solutions in de-ionized water. A stock solution (1.2 × 10⁻³ mol L⁻¹) of SQ-OH was prepared in methanol, stored in a refrigerator, and employed within a week. Concentrated HF, HCl and HNO₃ acids (Merck, Darmstadt, Germany) were used for the digestion of the certified reference materials (CRM) *IAEA-soil-7* and the geological standard sample (GBW07291). The influence of diverse ions commonly found together with palladium, *e.g.* ions of Al, Cu, Cr, Fe and Mg (1000 mg L⁻¹), was investigated. All glassware and electrochemical cells were pre-cleaned by soaking in HNO₃ (10% v/v), washed with de-ionized water and dried before use.

2.2. Apparatus

Adsorptive differential pulse cathodic stripping voltammetric (AdCSV) and cyclic voltammetry (CV) measurements were

Table 1 ICP-MS operational conditions for palladium determination

Parameter	
ICP RF power (W)	1100
Nebulizer gas flow (L min ⁻¹)	0.94
Plasma gas (Ar) flow rate (L min ⁻¹)	15
Auxiliary gas (Ar) flow rate (L min ⁻¹)	1.2
Lens voltage (V)	0.9
Analog stage voltage (V)	-1750.0
Pulse stage voltage	800
Quadrupole rod offset std	0.0
Discriminator threshold	22
Cell path voltage std (V)	-13
Cell rod offset (V)	-18.0
Atomic mass (am)	52.9407
Sample flow rate, mL	093

performed on a Metrohm 746 VA trace analyzer and 747 VA stand, using a three-compartment voltammetric cell (10 mL) composed of HMDE (0.38 mm²), Pt wire (BAS model MW-1032) and Ag/AgCl, (3 M KCl) as working, counter and reference electrodes, respectively. A Perkin Elmer ICP-MS Sciex model Elan DRC II (California, CT, USA) was used as a reference material for method validation and palladium concentration determination at the operational parameters (Table 1). A Perkin-Elmer (model Lambda 25, USA) spectrophotometer with a 10 mm (path width) quartz cell was used for recording the UV-Visible spectra (190–1100 nm) and absorbance measurements. De-ionized water was obtained from a Milli-Q Plus system (Millipore, Bedford, MA, USA) and was used for preparation of the standard solutions. A Jenway pH meter (Model, 3505, UK) and a microwave system (Mars model, 907500, USA) were used respectively for pH measurements and sample digestion of the certified reference material.

2.3. Recommended AdCSV procedure

An accurate volume (10 mL) of the B–R buffer at pH 9–10 was transferred to the electrochemical cell, and a stream of pure N₂ gas was passed through the test solution for 15 min before recording the voltammogram. The scan was initiated in the negative direction of the applied potential from 0.0 V to -1.5 V vs. the Ag/AgCl reference electrode. After recording the voltammogram, an accurate volume (10.0 μL) of the SQ-OH reagent (5.1 × 10⁻⁶ mol L⁻¹) was added. The solution was purged with N₂ gas for 5 min. Stirring was then stopped and, after 10 s quiescence time, the voltammogram was recorded again. Unless otherwise stated, the background voltammogram of the supporting electrolyte and the blank solution was recorded at pH 9–10 under the optimum operational parameters of deposition potential (-0.2 V), accumulation time (300 s), starting potential (0.0 V), scan rate of 100 mV s⁻¹ and pulse amplitude of 60 mV of chelated Pd at the surface of the Hg drop of the HMDE. After recording the voltammogram of the blank solution, an accurate volume (10–100 μL) of Pd solution (1.2 × 10⁻⁶ mol L⁻¹) was added and the solution was purged with N₂ gas for 5 min. Stirring was then stopped and, after 10 s quiescence time, the

scan was initiated in the negative direction of applied potential from 0.0 V to -1.5 V vs. the Ag/AgCl electrode. The voltammograms were finally recorded again as described, under the same operational parameters.

2.4. Applications

2.4.1. Analysis of certified reference materials. Accurately weighed amounts ($0.13\text{--}0.15 \pm 0.01$ g) of the CRM sample (*IAEA-soil-7*) were placed in Teflon beakers (50.0 mL) containing HF (5 mol L^{-1} , 7.0 mL), concentrated HCl (2.0 mL), and concentrated HNO_3 (5.0 mL). Various amounts of standard Pd^{2+} were added to the samples at room temperature³⁰ to confirm the correctness of the method. The reaction mixture was heated at $100\text{--}150$ °C for 1 h. After NO_2 fumes had ceased, the reaction mixture was evaporated almost to dryness and re-dissolved in concentrated HNO_3 (5.0 mL). The process was repeated three times and the mixture was again evaporated to dryness. The solid residue was re-dissolved in dilute HNO_3 (5.0 mL, 1.0 mol L^{-1}) and the mixture was filtered through Whatman 41 filter paper, transferred to a volumetric flask (25.0 mL), and deionized water was added to the solution until the flask was filled to the mark. An accurate volume of the digested sample was adjusted to pH 9–10 (5.0 mL) and a few drops of NaOH (1.0 mol L^{-1}) and B–R buffer (4–5 mL) at pH 9–10 were added to adjust the solution pH. The solution was transferred to the volumetric cell and the AdCSVs were recorded by applying a negative potential scan from 0.0 to -1.5 V vs. the Ag/AgCl electrode at the optimum conditions. The peak current at ~ -0.64 V was measured and used for constructing a linear standard addition plot and the Pd content in the CRM sample was determined.

2.4.2. Analysis of palladium in samples of road dust. Homogenized samples of road dust were collected from the surface of the roadside dust of the busy streets of Jeddah City, from heavy and light traffic locations. The method of Narin *et al.*³¹ was applied for the digestion of trace metal ions from the road dust samples in the presence of various known Pd concentrations. Accurately weighed amounts ($0.13\text{--}0.15 \pm 0.01$ g) of the road dust sample were placed in Teflon beakers (25.0 mL) containing HF (5 mol L^{-1} , 7.0 mL), concentrated HCl (2.0 mL) and concentrated HNO_3 (5.0 mL), and various standard amounts of Pd^{2+} were added to the samples at room temperature.³¹ The samples were dried at 110 °C for 2 h, ground through a 200-mesh sieve and homogenized for analysis. Accurately weighed amounts (0.13 to 0.16 g) of the roadside soil samples were digested in concentrated HCl– HNO_3 (3 : 1 w/v) in a conical flask (100 mL) and refluxed for 4 h. Each sample solution was centrifuged, filtered through a $0.45 \mu\text{m}$ membrane filter, transferred to the measuring flask (25.0 mL) and filled to the mark with HNO_3 (0.5 mol L^{-1}). The solution was adjusted to pH 10, transferred to the cell and AdCSVs were recorded from 0.0 to -1.5 V vs. the Ag/AgCl electrode at various additions of standard Pd solutions. The peak current at ~ -0.64 V was measured and the change in peak current was used for constructing a linear plot of standard addition against a reagent blank.

2.4.3. Analysis of total palladium in water samples. A Red Sea water sample (100.0 mL) was collected from the coastal area

of North Jeddah city, Saudi Arabia. Tap water samples in the laboratory, after allowing the water to flow for 5 min, were also collected. Water samples were filtered through a $0.45 \mu\text{m}$ cellulose acetate membrane filter and subjected to UV digestion at 254 nm in the presence of HCl (10% v/v) for 5 h. Palladium was then analyzed following the recommended AdCSV procedure. The Pd content was also determined by the standard ICP-MS at the recommended instrumental parameters for comparison.

3. Results and discussion

3.1. Electronic spectra of the reagent SQ-OH and its Pd^{2+} chelate

The reaction of the reagent SQ-OH with Pd(II) in aqueous solution revealed that the reaction is pH dependent. Detailed study of the pH revealed formation of a stable brown-colored complex species of Pd–SQ-OH at pH 9–10. At this pH, the reaction was fast, as indicated from the development of an intensely colored complex species in a very short period of time. An electronic spectrum of Pd(II)–SQ-OH complex showed four absorption peaks at $\lambda_{\text{max}} = 269, 294, 340$ and 388 nm (Fig. 2) with molar absorptivities of $3.71 \times 10^4, 3.41 \times 10^4, 2.91 \times 10^4$, and $2.55 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$, respectively. The spectrum of the free Schiff base showed three peaks at $\lambda_{\text{max}} 275, 310$ and 389 nm with molar absorptivities of $\epsilon = 1.40 \times 10^4, 1.14 \times 10^4$ and $1.48 \times 10^2 \text{ L mol}^{-1} \text{ cm}^{-1}$, respectively. The color change and the observed bathochromic shift of λ_{max} of the reagent to a longer wavelength upon addition of Pd^{2+} confirmed formation of the Pd–Schiff base complex. The ratio of Pd(II) to SQ-OH in the complex was determined by continuous variation methods.³² Formation of a 1 : 2 molar ratio of Pd to SQ-OH was achieved, confirming formation of a complex with the formula $[\text{Pd}(\text{SQ-OH})_2]$. The complex was stable over 3 h, as noticed from the constancy of its absorbance at λ_{max} . The complex was crystallized from ethanol as brown crystals and it decomposed at 280 °C. The structure of the complex $[\text{Pd}(\text{C}_{24}\text{H}_{22}\text{N}_4\text{O}_4)]$ was also confirmed from its elemental analysis: analytical found: C = 54.42, H = 3.42, N = 7.67 and Pd = 15.54%; calculated: C = 55.14, H = 3.16, N = 11.74, S = 8.01 and Pd = 15.28%.

3.2. Redox behaviour of Pd(II)–SQ-OH complex

A detailed AdCSV investigation of the SQ-OH reagent in the absence and presence of Pd^{2+} ions at various pH values was carried out. Representative AdCSVs at various pH values are shown in Fig. 3. At pH < 6.5, no cathodic peaks were noticed, suggesting no Pd ion complex was formed and/or that any Pd complex species formed with the SQ-OH Schiff base was unstable. Poor adsorption of the reduced species, formation of hydrogen at the surface of the HMDE and the instability of the electrogenerated species may also account for this observation.³³ The Schiff base may also be reduced at a more negative potential than the allowed potential window of the HMDE.

In the pH range 6.5 to 7, two well-defined cathodic peaks at -0.04 V and -0.20 V vs. the Ag/AgCl electrode were observed and were safely assigned to the adsorption and/or formation of

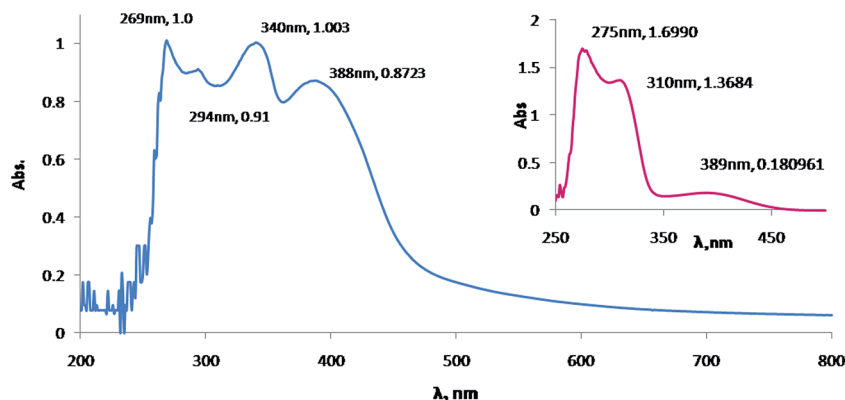


Fig. 2 Electronic spectra of the Schiff base SQ-OH and its Pd(SQ-OH)₂ complex in DMF. Palladium = 3.0×10^{-6} mol L⁻¹ and [SQ-OH] = 1.0×10^{-5} M.

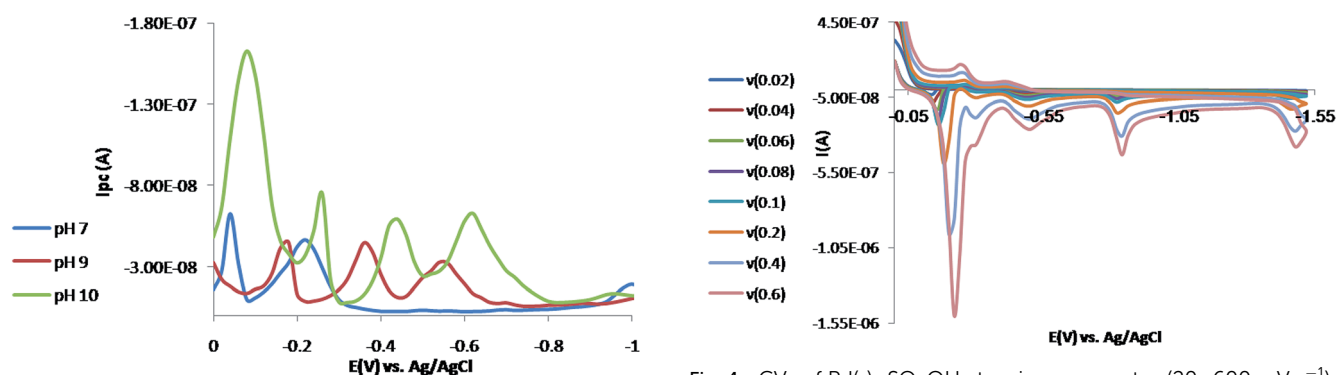


Fig. 3 AdCSVs of palladium(II)-SQ-OH complex species in B-R buffers at the HMDE vs. the Ag/AgCl electrode. Palladium = 3.0×10^{-6} mol L⁻¹, [SQ-OH] = 1.0×10^{-5} M; scan rate = 100 mV s^{-1} and pulse amplitude of 50 mV.

the Hg-SQ-OH salt and reduction of the azomethine,³⁴ respectively. At pH 8–9, two peaks at -0.18 and -0.35 V and a new peak at -0.56 V were observed and attributed to reduction of the hydroxyl group of the Schiff base and the involvement of protons on the reduction steps.³³ Between pH values of 9 and 11, four well-defined peaks at -0.1 , -0.27 , -0.45 and -0.64 V were observed at more negative potentials compared to the peaks observed at pH < 9 (Fig. 3). At pH 11, the cathodic peak potentials shifted to more negative values indicating prior protonation in the region of the azomethine, leading to a decrease in the electron density on the electroactive functional group and facilitating the acceptance of an electron during the reduction step. Reduction of the two azomethines *via* direct exchange of 4 electrons in four successive one-electron/one-proton steps may have also occurred.^{33,35} The plot of the change of the cathodic peak potential at -0.56 V *vs.* pH is linear and best fits the following regression equation:

$$E_{p,c} = -0.124 \text{ pH} + 0.661, (R^2 = 0.9787) \quad (1)$$

The data suggest that B-R buffer with a pH value between 9 and 10 should be used in the development of a low-cost AdCSV method for determining the concentration of Pd.

Fig. 4 CVs of Pd(II)-SQ-OH at various scan rates (20–600 mV s⁻¹) at pH 10 at the HMDE vs. the Ag/AgCl electrode.

Cyclic voltammograms (CV) of the Pd(II)-SQ-OH complex in the potential range of 0.0 to -1.5 V at the HMDE in B-R buffer of pH 9–10 were recorded at various scan rates (ν). Representative CVs are shown in Fig. 4. At a scan rate in the range 20–600 mV s⁻¹, the CV showed four well-defined cathodic peaks at -0.16 , -0.48 , -0.82 and -1.46 V. On the reverse scan, two anodic peaks at -0.26 and -0.42 V with potential separation ($\Delta E_p > 100$ mV) were observed, suggesting the irreversible nature of the reduction steps. The peak potentials were shifted to more negative values upon increasing the scan rate, confirming the irreversible nature of the reduction.

The plots of $E_{p,c}$ of the first and second cathodic peaks at -0.16 , -0.48 V *vs.* $\log \nu$ are linear (Fig. 5), with slope values proportional to αn_α , where n_α is the number of electron transfers involved in the reduction steps and α is the corresponding charge-transfer coefficient of the adsorbed Pd species. These results added further support to the irreversible nature of the reduction process.^{35–37} The values of n_α and α of the adsorbed Pd species were calculated from the slope of the linear plots of $E_{p,c}$ *vs.* $\log \nu$ (Fig. 5) using the following equation:

$$\Delta E_{p,c} / \Delta \log(\nu) = -29.58 / \alpha n_\alpha \quad (2)$$

The number of electrons (n_α) transferred in the rate-determining step was found to be equal to 2 and the value of α was in

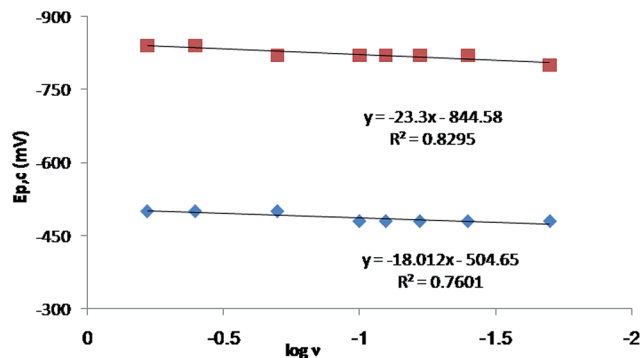


Fig. 5 Plots of the first (◆) and second (■) cathodic peak potentials vs. $\log(v)$ of the CVs of Pd-SQ-OH complex at the HMDE at pH 10 vs. the Ag/AgCl electrode.

the range 0.89 ± 0.05 indicating the irreversible nature of the cathodic process at the surface of the HMDE. The value is somewhat close to the theoretical value (1.0) expected for an adsorption process at HMDE.^{36,37} In the CV, the irreversible nature of the electrode processes was also confirmed from the progressive shift of the $E_{p,c}$ to more negative values on rising the sweep rate.

The current functions ($i_{p,c}/\nu^{1/2}$) at -0.50 V and -0.82 V vs. Ag/AgCl increased upon raising the scan rate. Thus, the reduction process of the Pd(II)-SQ-OH favors chemical reaction of the EE type mechanism^{36,37} and the product of the reduction process also undergoes a very rapid follow-up chemical reaction.³⁷ The plot of $i_{p,c}$ vs. $\nu^{1/2}$ is linear, indicating that the reduction process is a diffusion-controlled electrochemical process.³⁷ The surface coverages (Γ) of Pd-SQ-OH at the HMDE, Pt and Au working electrodes were also determined at various scan rates.^{35,37} The $i_{p,c}$ at -0.64 V is related to the surface concentration of the electroactive species by the equation:

$$i_{p,c} = n^2 F^2 A \Gamma \nu / 4RT \quad (3)$$

where n = number of electrons involved in the electrode reaction, A is the geometric surface area of the working electrode (HMDE, Pt or Au), Γ (mol cm^{-2}) is the surface coverage and other symbols have their usual meaning.³⁷ The Γ values were calculated from the slopes of the linear plots of $i_{p,c}$ vs. scan rate. Assuming $n = 2$, the Γ values were found to be 4.2×10^{-10} , 4.19×10^{-11} and 3.08×10^{-10} mol cm^{-2} at the HMDE, Au and Pt electrodes, respectively. The value of Γ at the HMDE suggests that this electrode should be used in the development of an AdCSV method for analysis of Pd in environmental samples. The cathodic peak at the HMDE was also well defined, sharp, and symmetric.

3.3. Analytical parameters

The redox behaviour of palladium(II)-SQ-OH chelate, the sensitivity of the developed $i_{p,c}$ at -0.64 V and at pH 10, and the high surface coverage of Pd at the HMDE suggests that the Schiff base SQ-OH should be used for developing a low-cost and convenient AdCSV method to determine Pd concentrations.

Thus, the effect of pH (2.5–11) on peak current at -0.64 V was studied. Maximum $i_{p,c}$ was achieved at pH 11. The SQ-OH reagent is most likely dissociated easily at $\text{pH} > 9$ and participated in complex formation with Pd^{2+} . However, in a solution of pH 9–10 (Fig. 6) the observed cathodic peak at -0.64 V was well resolved and reproducible. Thus, in the subsequent work, a solution of pH 9–10 was adopted as a convenient supporting electrolyte in the following experiments.

The AdCSV peak current intensity depends on the accumulation potential ($E_{acc.}$) (0.0 to -0.8 V) in B-R buffer at pH 9–10 during the preconcentration step. Thus, the effect of accumulation potential on the $i_{p,c}$ at -0.64 V vs. the Ag/AgCl electrode was studied (Fig. 7). The $i_{p,c}$ was strongly influenced by the preconcentration potential and maximum $i_{p,c}$ was achieved at $E_{acc.} = -0.2$ V. The AdCSVs also showed that at $E_{acc.} = -0.2$ V, the $E_{p,c}$ at -0.64 V was much more developed, symmetric and sharp. Hence, an adsorption potential of Pd(II) was favoured at an accumulation potential of -0.2 V. At a potential more negative than -0.2 V, the $i_{p,c}$ decreased gradually and levelled off (Fig. 7). The accumulation potential of Pd(II)-SQ-OH could bear a negative charge at the employed pH. Thus, an accumulation potential of -0.2 V was chosen for subsequent

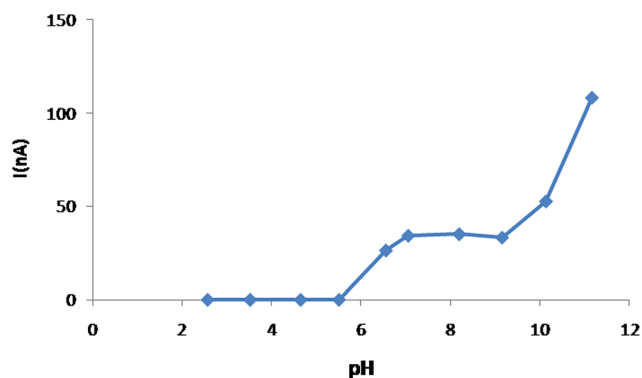


Fig. 6 Plot of pH vs. $i_{p,c}$ at -0.64 V. $[\text{SQ-OH}] = 5.1 \times 10^{-6}$ M; $[\text{Pd}^{\text{II}}] = 1 \times 10^{-6}$ mol L^{-1} ; deposition potential = -0.4 V; deposition time = 180 s; pulse amplitude = 0.05 V and at 100 mV s^{-1} scan rate.

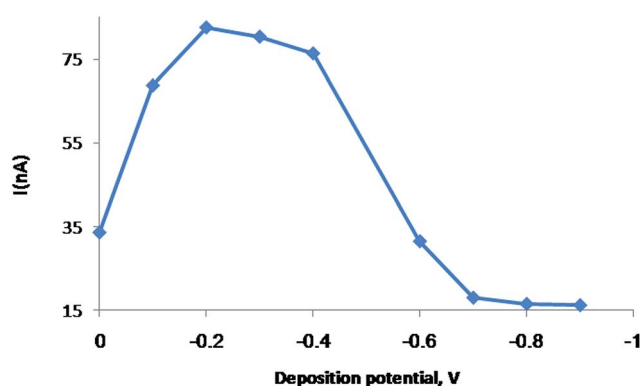
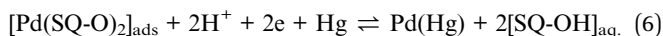
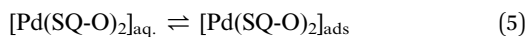
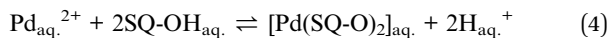


Fig. 7 Effect of deposition potential on $i_{p,c}$ at -0.64 V vs. the Ag/AgCl electrode. Conditions: $\text{pH} = 10$; $[\text{SQ-OH}] = 5.1 \times 10^{-6}$ mol L^{-1} ; $[\text{Pd}^{\text{II}}] = 1.0 \times 10^{-6}$ M; deposition time = 180 s, pulse amplitude = 0.05 V and a scan rate of 100 mV s^{-1} .

experiments, and the overall signal can safely be assigned to the following reactions:



The choice of collection of the analyte is a compromise between surface coverage, sensitivity, the time required for an analysis, and the effect of competitive adsorption. The differential-pulse adsorptive cathodic peak current intensity of Pd(II)-SQ-OH in B-R buffer of pH 9–10 was found to be dependent on the preconcentration time period ($t_{\text{acc.}}$). Thus, the influence of $t_{\text{acc.}}$ (60–420 s) on the $i_{\text{p,c}}$ at -0.64 V was studied at a fixed SQ-OH concentration. The $i_{\text{p,c}}$ current at -0.64 V grew to a limited value upon increasing accumulation time up to 300 s (Fig. 8), suggesting that an equilibrium between the dissolved and adsorbed complex Pd species was reached. Thus, an accumulation time of 300 s was adopted in the subsequent AdCSV experiments of Pd.

The influence of scan rate (20 – 200 mV s^{-1}) on $i_{\text{p,c}}$ at -0.64 V was investigated. The $i_{\text{p,c}}$ increased steadily upon raising the scan rate up to 100 mV s^{-1} . However, the best signal to background current and peak symmetry were achieved at 60 mV s^{-1} . Hence, a scan rate of 60 mV s^{-1} was chosen for the present analytical stripping voltammetry study. The pulse amplitude has a pronounced effect on the AdCSV response of the Pd-SQ-OH species at pH 10. Thus, the peak current intensity of the AdCSV of Pd-SQ-OH in pH 9–10 buffer was studied. The $i_{\text{p,c}}$ was directly proportional to the pulse height up to 90 mV and the $i_{\text{p,c}}$ increased steadily upon increasing the pulse height from 10 – 60 mV. At a pulse amplitude of 70 – 90 mV, the $i_{\text{p,c}}$ increased due to the increase in the capacitive current, however, a sloping background current signal was observed. The strongest peak to background signal for the AdCSV peak current at -0.64 V was observed at 60 mV pulse height. Thus, in the subsequent work, a 60 mV pulse height was selected.

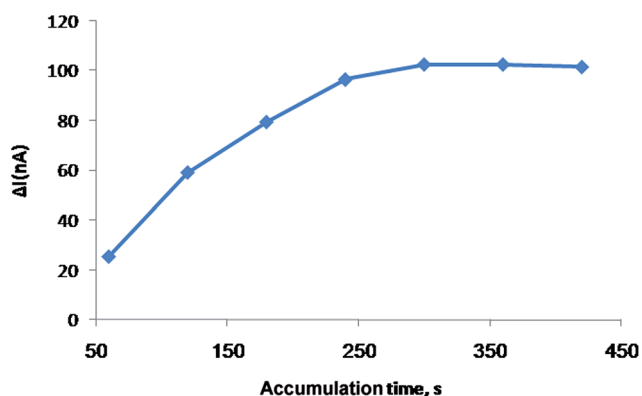


Fig. 8 Plot of deposition time vs. $i_{\text{p,c}}$ at -0.64 V. Conditions: $[\text{SQ-OH}] = 5.1 \times 10^{-6}$ M; $[\text{Pd}^{\text{II}}] = 1.0 \times 10^{-6}$ mol L^{-1} ; deposition potential = -0.2 V; pulse amplitude = 0.05 V and a scan rate of 0.1 V s^{-1} .

The influence of SQ-OH concentration on $i_{\text{p,c}}$ at pH 9–10 was studied. Upon increasing this reagent concentration to 1.0×10^{-6} mol L^{-1} , the $i_{\text{p,c}}$ increased linearly and remained constant up to 5.1×10^{-6} mol L^{-1} (Fig. 9). At SQ-OH $> 5.1 \times 10^{-6}$ mol L^{-1} , the $i_{\text{p,c}}$ leveled off and deteriorated due to competitive adsorption of free reagent. At the breakpoint, the reagent concentration (5.1×10^{-6} mol L^{-1}) was just close to the Pd^{2+} concentration, revealing a $[\text{Pd}(\text{SQ-OH})]$ structure for the adsorbed species. Thus, a concentration of 5.1×10^{-6} mol L^{-1} for SQ-OH was used in subsequent experiments.

3.4. Interference study

Analyses of Pd ions at a concentration of 4.65 μM and in the presence of a relatively high excess concentration of foreign ions Mg^{2+} , Ba^{2+} , Ca^{2+} , Ni^{2+} , Pb^{2+} , Co^{2+} , Cu^{2+} , Zn^{2+} , Al^{3+} , Fe^{3+} , Co^{2+} , Si^{4+} , AsO_2^- , VO_3^- , SbO_2^- and SeO_3^- were carried out, for each of these foreign ions individually, by the developed method. The tolerance limit is defined as the concentration of foreign ion added causing a relative deviation within $\pm 5.0\%$ in the magnitude of the peak current at -0.64 V. Most of these ions did not interfere with the palladium signal. Ca^{2+} and Al^{3+} decreased the stripping current of Pd(II)-SQ-OH, but their interference was masked by adding a few drops of EDTA and NaF, respectively. Fe^{3+} and Si^{4+} increased the stripping current by producing a diffusion-controlled peak-like shoulder on the cathodic side of the Pd(II) peak (-0.64 V). Interference of Fe^{3+} and V^{5+} ions was masked by adding a few drops of triethanolamine. Cobalt(II) at 10-fold excess had no influence on the cathodic peak current.

3.5. Analytical performance

Under the optimized conditions of pH 9–10, an accumulation potential of -0.2 V, preconcentration time of 300 s, scan rate of 100 mV s^{-1} , pulse height of -60 mV and SQ-OH concentration of 5.1×10^{-6} M, AdCSV voltammograms at various Pd concentrations were recorded. The results are shown in Fig. 10. The plot of $i_{\text{p,c}}$ at -0.64 V versus Pd^{2+} concentration is linear in the range 1.87×10^{-9} to 3.05×10^{-7} M (0.2 – 32.5 $\mu\text{g L}^{-1}$) Pd and leveled off at higher concentrations because of adsorption saturation.^{32–34} A regression equation of $i_{\text{p,c}}$ (nA) = $1.2215C$ ($\mu\text{g L}^{-1}$) + 2.17 was obtained with a correlation coefficient of 0.9967 .

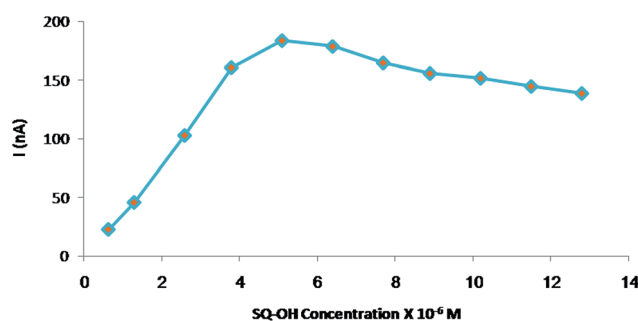


Fig. 9 Plot of SQ-OH concentration vs. $i_{\text{p,c}}$ at -0.64 V. Conditions: pH 9–10; deposition potential -0.2 V; deposition time = 300 s; scan rate = 0.1 V s^{-1} , pulse amplitude = 0.06 V and $[\text{Pd}^{\text{II}}] = 5.1 \times 10^{-6}$ mol L^{-1} .

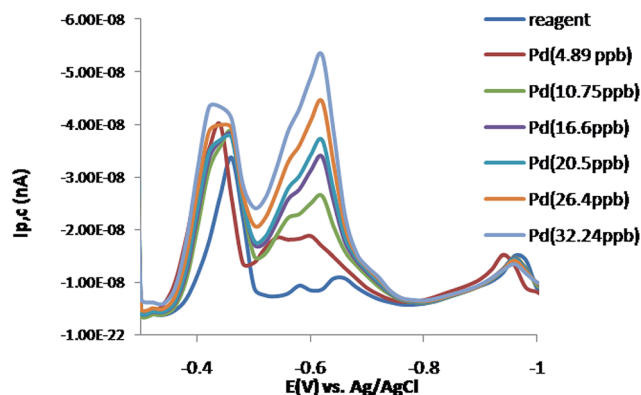


Fig. 10 AdCSV voltammograms of Pd²⁺ over the concentration range 21.87×10^{-9} to 3.05×10^{-7} M (0.2 – $32.5 \mu\text{g L}^{-1}$) at pH 9–10 at the HMDE vs. the Ag/AgCl electrode.

The calculated values of LOD and limit of quantification (LOQ),³⁸ using the formulas $\text{LOD} = 3S_{y/x}/b$ and $\text{LOQ} = 10S/b$ where $S_{y/x}$ is the standard deviation of the y -residual and b is the slope of the calibration plot, were found to be equal to 4.70×10^{-10} M ($0.05 \mu\text{g L}^{-1}$) and 1.55×10^{-9} M ($0.16 \mu\text{g L}^{-1}$), respectively. The analytical features (LOD, LOQ and linear dynamic range) of the developed method compare favorably with those of many spectrometric^{4–18,39–45} and electroanalytical methods.^{19–29,46,47} The developed method provides better LOD and LDR, ease of use and less interference (Table 2). Some of these other methods have shown high LOD and serious interference by halide ions. The LOD of the current method compares favorably with LOD of GFAAS ($0.4 \mu\text{g L}^{-1}$) and FAAS ($1.24 \mu\text{g L}^{-1}$). A value of RSD of $\pm 2.1\%$ ($n = 5$) was achieved at $2.0 \mu\text{g L}^{-1}$ Pd. The LOD of the method is lower than the maximum allowable level of Pd in soil (<0.7 to $47 \mu\text{g kg}^{-1}$) and solid sewage (18 to $260 \mu\text{g kg}^{-1}$) according to the World Health Organization (WHO).^{3,48} The method compares favorably with other reported methods for Pd concentration determination (Table 2). Thus, the developed method shows very good limit of detection, wide linear dynamic range, good precision and

selectivity and these measures are better than and/or comparable with the previously reported methods. Most of the reported methods suffer from the need of technical expertise to carry them out and from the need for costly solvents. Likewise, good preconcentration, simple sample preparation, high selectivity, low LOD and low cost make the developed method suitable for measuring Pd in various environmental samples. The developed method could also be extended for analysis of Pd even at levels $< \text{ng mL}^{-1}$ or ng g^{-1} after preconcentration of Pd from a large sample volume onto a solid sorbent-packed column.⁴⁹

3.6. Analytical applications

The developed AdCSV method was validated by analysis of total Pd in the CRM sample *IAEA-soil-7*. The $i_{p,c}$ at -0.64 V increased linearly as standard Pd was added to the CRM sample. Excellent agreement between the results of the AdCSV and the ICP-MS methods was achieved for Pd analysis (Table 3). The recovery of the AdCSV method was not significant in comparison with the reference ICP-OES method where $t_{\text{critical}} = 2.20 > t_{\text{exp}} = 1.81$ – 1.93 , at a 95% confidence. Thus, the developed AdCSV method was able to effectively analyze palladium in real samples.

The recommended AdCSV method was successfully applied for analysis of Pd in road dust, and the results are in good agreement with the ICP-MS data (Table 3). As can be seen, the added Pd was quantitatively recovered, indicating the validity of

Table 3 Analysis of palladium(II) in the CRMs and roadside dust samples by the developed DP-CSV and ICP-MS methods^a

Sample	Added, $\mu\text{g L}^{-1}$	Found \pm SD, $\mu\text{g L}^{-1}$	Recovery \pm RSD, %
<i>IAEA-soil-7</i> (CRM)	0.0	nd	—
	10.0	9.9 ± 0.10 (10.12 ± 0.13)	99.0 ± 1.01
	20.0	20.6 ± 0.14 (19.6 ± 0.4)	103.0 ± 0.7
Roadside dust	0.0	165.2 ± 2.6 (169.3 ± 2.1)	—
	20.0	189.0 ± 3.7 (192.3 ± 2.5)	102.05 ± 1.99

^a ICP-MS data are given in parentheses.

Table 2 Analytical performance of the developed AdCSV and some of the reported methods^a

Method	LOD, ng mL^{-1}	Linear range, ng mL^{-1}	Reference	Remarks
DLIME coupled FAAS	90.0	100–2000	12	Sensitive, time consuming
Chemosensor	0.029	0.5–12	7	Time consuming
FI-spectrophotometry	0.1	10–10 000	8	2,2-Furyldioxime
USAE-SFODME/FI-FAAS	0.3	1.5–100	5	—
Spectrophotometry	31.95	106.4–1064.0	37	Polyethylenimine
AdCSV, HMDE	0.042	nd	18	DMG
ASV, GCE	169.6	nd	44	—
SWAdSV	0.15	nd	45	DMG
SWAdSV	0.075	nd	22	DMG, HCl
AdCSV	0.05	0.2–32.5	This work	Simple, low coast

^a Abbreviations: AAS = atomic absorption spectrometry, FAAS = flame atomic absorption spectrometry, CPE = carbon paste electrode, DLIME = dispersive liquid–liquid microextraction, USAE-SFODME/FI = ultrasound-assisted emulsification-solidified floating organic drop microextraction, DMG = dimethylglyoxime, USAE-SFODME/FI-FAAS = ultrasound-assisted emulsification-solidified floating organic drop microextraction/flow injection flame atomic absorption spectrometry, FI = flow-injection.

Table 4 Analysis of palladium(II) in various water samples by the developed DP-CSV and ICP-MS methods^a

Sample	Added, $\mu\text{g L}^{-1}$	Found \pm SD, $\mu\text{g L}^{-1}$	Recovery \pm RSD, %
Drinking water	0.0	nd	—
	19.66	18.9 ± 0.13 (19.2 ± 0.3)	96.2 ± 6.98
	39.32	40.2 ± 0.17 (39.7 ± 0.3)	102.15 ± 4.6
	78.65	77.36 ± 0.13 (79.5 ± 0.5)	98.36 ± 1.76
Red Sea water	0.0	0.13 ± 0.05 (0.14 ± 0.01)	—
	19.66	20.21 ± 0.15 (19.8 ± 0.22)	96.2 ± 6.98
	39.32	40.6 ± 0.18 (5.5 ± 0.23)	102.15 ± 4.6

^a ICP-MS data are given in parentheses.

the recommended AdCSV method for analysis of Pd in real samples. The method is as good as the standard method ($t_{\text{critical}} = 2.20 > t_{\text{exp}} = 1.71\text{--}1.83$, 95% confidence level). The proposed method effectively analyzed palladium in real samples.

Analysis of Pd in water samples was carried out by the standard addition method and the results are summarized in Table 4. According to the results in Table 3, the Pd content was below the LOD. The added Pd was quantitatively recovered as can be seen in Table 3. The concentration of Pd²⁺ in a tap water ($0.065 \pm 0.005 \mu\text{g L}^{-1}$) sample was close to the measured value by ICP-MS ($0.07 \pm 0.001 \mu\text{g L}^{-1}$, RSD of $\pm 5.6\%$). Pd recoveries in three consecutive determinations ranged from 96.2 ± 6.98 to 102.2 ± 4.6 and are close to values achieved by ICP-MS (Table 4), confirming the suitability and validity of the present AdCSV method for Pd analysis in real samples. The developed method can be extended for Pd analysis in environmental samples where the analyte content is in its usual ng g^{-1} or ng mL^{-1} range. Such a type of analysis will require an enrichment step prior to AdCSV determination of Pd. This step can be achieved by preconcentration of Pd²⁺ ions from a large sample volume of water onto a polyurethane foam sorbent-packed column⁴⁸ followed by elution with HNO₃ (1.0 mol L^{-1}) and subsequent AdCSV determination.

4. Conclusion

The method developed in the current work was successfully applied for analysis of Pd in pure authentic and real samples. The method can be utilized readily for routine analysis of Pd in water and other matrices since most of the reported methods suffer from many drawbacks such as cost, multiple steps, being time consuming and the need for costly solvents (HPLC). The developed method offers a simple system with good reproducibility, ruggedness and cost effectiveness. The LOD is also lower than the maximum allowable level (MAL) of Pd by the World Health Organization (WHO) in water and favorably compared with the LOD of many spectrochemical (e.g. GFAAS, FAAS and ICP-MS) and electrochemical techniques. The method could also be extended to ultratrace (picomolar) analysis of environmental samples *via* prior on-line preconcentration from large sample volumes onto a polyurethane foam-packed column.

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