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Short Communication

Modification of Glassy Carbon Electrode by (E)-2-(Mercapto-phenylamino-methylene)-3-oxo-N-p-tolyl-butanamide for the Determination of Ultra – Trace Levels of Palladium by Adsorptive Stripping Voltammetry

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The present work provides a simple, fast, and inexpensive analytical method for determination of trace palladium (II) using adsorptive stripping voltammetry technique and modified glassy carbon electrode (GCE) as a working electrode. (E)-2-(Mercapto-phenylamino-methylene)-3-oxo-N-p-tolyl-butanamide (MPMPB) was adsorbed on the GC surface to increase the method selectivity and sensitivity by the palladium coordination with this ligand. The proposed method provided extremely low detection limit of palladium (0.002 ng mL^{-1}), whereas, the linearity was in the range of 0.02 – 0.13 ng mL^{-1}. The systematical study of the interferences of some electroactive species was carried out, and the results showed the high selectivity of the method. The concentration of palladium in some real samples was successfully determined, and the results of proposed procedure were compared with the measurements taken from a standard analytical method (ICP – MS).

Keywords: Cathodic Adsorptive Stripping Voltammetry, Palladium, Trace analysis, Electroanalysis, Determination.

1. INTRODUCTION

More progress was made over the last few decades in the field of electroanalytical methods development for the determination of analytes at ultra-trace concentrations levels. Adsorptive Stripping Voltammetry (ASV) is considered one of the most sensitive methods for monitoring analytes concentrations at picomolar levels, therefore, such methods are appropriate for the determination of metals in a variety of environmental, industrial and clinic samples [1 – 12]. Recently, palladium is used in different fields of science and technology such as petrochemical industries, complexing agents, brazing alloys, and catalytic chemical reactions. However, palladium has no any role in biological processes, and all of its compounds are classified as highly carcinogenic and toxic substances. Because of its increasing use, toxic palladium compounds can be transmitted into living organisms causing harmful effects to human, animal and plant [13–16]. Thus, monitoring ultra – trace concentrations of this element in environmental samples becomes very important. However, the matrix complexity and extremely low concentration levels of palladium in environmental samples (ng g^{-1}) make the direct determination of this element in such samples difficult task. Therefore, the separation and preconcentration methods must be combined with detection techniques to remove sample interferences and raise the palladium concentration [17–21]. Liquid – liquid extraction is widely employed for the determination of palladium in variety of samples [22 –24], however, this method suffers from emulsion formation, low sensitivity and the use of large volumes of toxic organic solvents. As an alternative, other extraction and preconcentration methods were used like cloud point extraction [25], solid phase extraction [26–28], homogeneous liquid – liquid extraction [29, 30], single – drop microextraction [31, 32], and dispersive liquid – liquid microextraction [33 – 38]. However, such methods are sometimes time – consuming and expensive. Stripping voltammetric techniques whether adsorptive differential pulse anodic stripping voltammetry (DP-ASV) or adsorptive differential pulse cathodic stripping voltammetry (DP-CSV) have excellent analytical characteristics such as speed, high sensitivity, and the possibility of simultaneous analysis of mixtures. However, the metal ions are effectively adsorbed on the working electrode surface only when they are converted into complexes using suitable ligands, here, a high signal – to – noise ratio is generated. Therefore, the main aim of the present work is to modify GCE by MPMPB, for the first time , and used the modified electrode for the direct determination of palladium in some environmental samples without the need for using UV-digestion as a continuation of our previous works in this area [6].

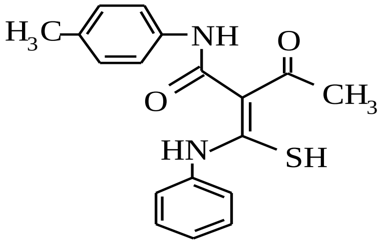

Figure 1. The structure of MPMPB

2. EXPERIMENTAL

2.1. Apparatus

The potentiostat used in voltammeter experiments is PAR Princeton, (NJ, USA) model 273 which is controlled by the software version 4.30 and model 270/250. Three – electrode cell containing Ag/AgCl electrode saturated with potassium chloride solution as a reference electrode, a platinum wire as a counter electrode, and modified GC as a working electrode was employed for performing all voltammetric measurements. A magnetic stirrer model KIKA Labortechinik made in Germany was employed for mass transport with the help of teflon – coated bar. pH measurements were carried out by VWR scientific products (model 2000, USA).

2.2. Reagents and solutions

All chemicals used in the present work were highly purified and employed without further purification. A suitable weight of palladium nitrate (Merck, BDH, Germany) required for preparation of 1000 µg mL^{-1} of Pd(II) ion was dissolved in deionized water and the volume was then completed to 100 mL, the obtained solution was titrated complexometrically by EDTA [39]. MPMPB ligand (Fig.1) at concentration level of $1x10^{-4}$ mol L^{-1} was prepared by dissolving the required weight in 50 mL of ethanol (50%) [40].

2.3- Synthesis of ligand (MPMPB)

(E)-2-(Mercapto-phenylamino-methylene)-3-oxo-N-p-tolyl-butanamide (MPMPB) were synthesized as follows: a cold suspension of potassium hydroxide 0.01 mole in DMF 30 mL was added the acetoacetanilide 0.01mole, followed by phenyl isothiocyanate 0.01 mole. The mixture was stirred for 5 h at room temperature. The reaction mixture was poured into ice-cold water and acidified by dilute HCl 10% v/v. The solid product formed was filtered off, washed with distilled water, dried and crystallized from ethanol to give compound characterized by elemental analysis, IR, thermal analysis and UV-Visible spectrum [41 -43].

2.4. Electrode modification.

GCE was modified by immersing in MPMPB ligand solution ($1 x10^{-4}$ mol L^{-1}) for 20 seconds. After the adsorption of ligand on the electrode surface, the modified GCE becomes ready for measurements.

2.4. The use of modified GCE for Pd(II) determination by using Square Wave Cathodic Adsorptive Stripping Voltammetry (The recommended SW–CASV procedure).

The modified glassy carbon electrode was immersed an electrochemical cell containing 15 mL of Britton – Robinson buffer (0.10 mol L^{-1} , pH 8), the mixture was stirred by a magnetic stirrer, and nitrogen gas was passed though the cell for 10 min before obtaining background square wave voltammogram. The stirring was stopped, and the background square wave voltammogram was recorded from 0 to – 0.6 V against reference Ag/AgCl electrode after the equilibration time of 15 second. To draw the calibration curve, 30 µL of standard Pd (II) solutions at concentration levels from 2×10^{-10} to 2×10^{-9} mol L^{-1} were added to supporting electrolyte in three electrode cell, all solutions were stirred at 400 rpm at open circuit conditions, and SWV was recorded in negative potential. The real water samples used in the present work were filtered using a suitable membrane filter to remove suspended materials, and aliquots of samples (30µL) were treated according to the recommended SW–CASV procedure. It should be noted that in each measurement, renewed surface of MPMPB – glassy carbon electrode was used. The optimized operational conditions of the recommended SW–CASV procedure is shown in Table.1.

Table 1. The optimum operational parameters selected to the determination of Pd(II) by SW- CASV at GCE.

Parameter	Selected value
Accumulation potential	0.0 V
Final potential	-0.6 V
Modulation time	10 S.
Frequency	50 HZ
Scan increment	2 mV
Accumulation time	165 s
pH	8.00
Buffer type	0.1M Britton- Robinson universal buffer

3. RESULTS AND DISSCUSION

3.1. Characterization of (MPMPB) Ligand.

3.1.1. Microchemical analysis.

The results of analysis C.H.N.S of the solid ligand (E)-2-(Mercapto-phenylamino-methylene)-3-oxo-N-p-tolyl-butanamide (MPMPB) are illustrates in Table 2.

Table 2. Microchemical analysis data of ligand (MPMPB)

Compound	Colour	M.wt	C % Calc. (found)	H% Calc. (found)	N% Calc. (found)	S% Calc. (found)
$C_{18}H_{18}N_2O_2S$	Cotton yellowish	326.42	66.23 (66.21)	5.56 (5.54)	8.58 (8.56	9.82 (9.80)

3.1.2. Infrared spectra of (MPMPB)

The infrared spectrum of the ligand *(MPMPB)* is shown in Fig. (2). The strong absorption band which appears in the range 3246-3181 cm^{-1} can be assignment to the stretching vibration of (NH) group .The appearance of two bands in the range 1677, 1617 cm^{-1} corresponds to the stretching vibrations of two carbonyl groups (C=O).

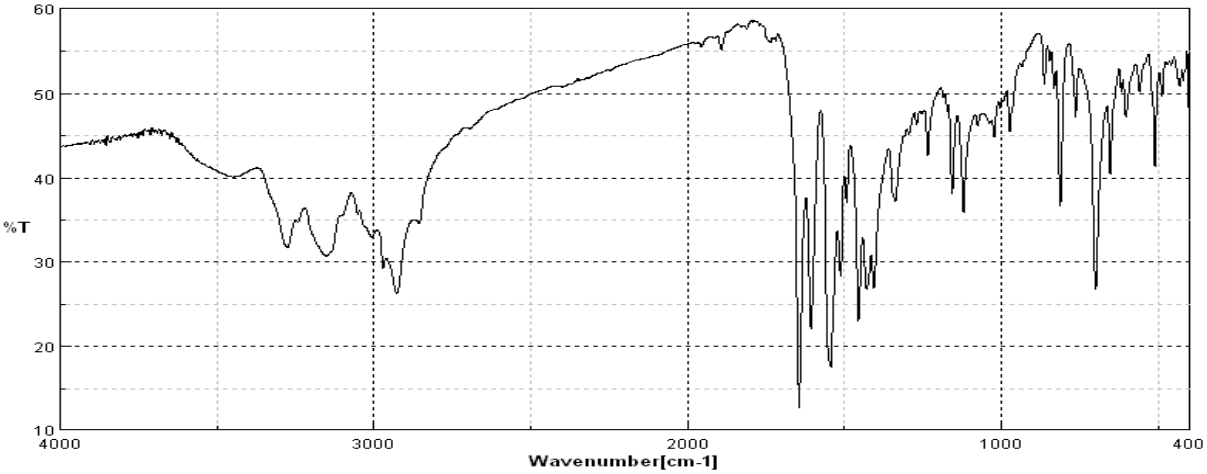

Figure 2. Infraread spectra of Ligand (MPMPB).

2.1.3. Thermal Analysis of (MPMPB)

(MPMPB) undergoes gradual thermal decomposition, the obtained TG curve in Fig. (3), shows that the ligand decomposes completely at 730°C with mass loss in two consecutive steps. The first step in the range 150 - 275°C corresponds to loss amounted to 33.1%, which may be attributed to the removal of the non-coordinated part of ligand. The second step of a mass loss 66.9%, in the temperature range 310-730°C, correspounds to the decomposition of the coordinated part of the ligand 2-(Mercapto-phenylamino) methylene)-3-oxobutanal.

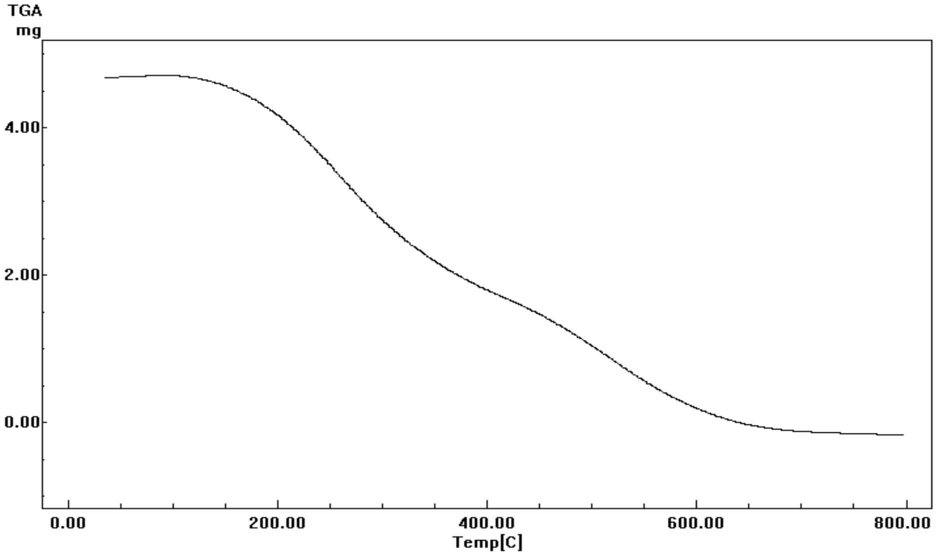

Figure 3. Thermogravimetric analysis curve of (MPMPB).

3.2. Explanation of voltammetric behavior and suggestion of possible mechanism of working electrode reaction.

One of the methodologies used to increase the sensitivity and selectivity of voltammetric determination of palladium (II) is the treatment of working electrode surface by an appropriate ligand, hence, the MPMPB molecule was physically adsorbed on GCE surface; therefore, this bidentate ligand can coordinate with the palladium (II) ion to form a surface complex [39]. The electrochemical behavior of palladium (II) ion (2×10^{-6} mol L^{-1}) on modified GCE surface was studied by cyclic voltammetry (CV) in 0.1 mol L^{-1} of universal buffer over the potential range of 0.0 to $\mathbf{-0.6}$ V. Cyclic voltammograms were recorded before and after the addition of palladium (II) ion, however, the voltammograms have had the same waves in both cases. These waves are corresponding to reduction of keto or Imine group, therefore, these groups were not shared in the coordination with Pd (II) ion. On the other hand, the [Pd^{++}-MPMPB] species accumulated on GCE surface provided a large catalytic – adsorptive current peak at $\mathbf{E_{max} = -0.18\ V}$ due to a two – electron reduction of keto or imino groups present in MPMPB and conversion of Pd(II) to Pd(I). Therefore, the whole mechanism consists of two steps as follows:

Preconcentration step:

$Pd^{++}{}_{(solution)}$ + MPMPB $_{(adsorbed)}$ → [Pd^{++}-MPMPB] $_{(adsorbed)}$ …………………… (1)

Reduction step:

[Pd^{++}- MPMPB] $_{(adsorbed)}$ + e^- → [Pd+ - MPMPB] $_{(adsorbed)}$ ……… …………….. (2)

Depending on the fact which states that Pd (II) has the coordination number of 6, the chemical formula of the complex formed between Pd (II) and MPMPB ligand should have four water molecules if Pd (II) ion is bonded to two active sites of the ligand as shown in Fig.4.

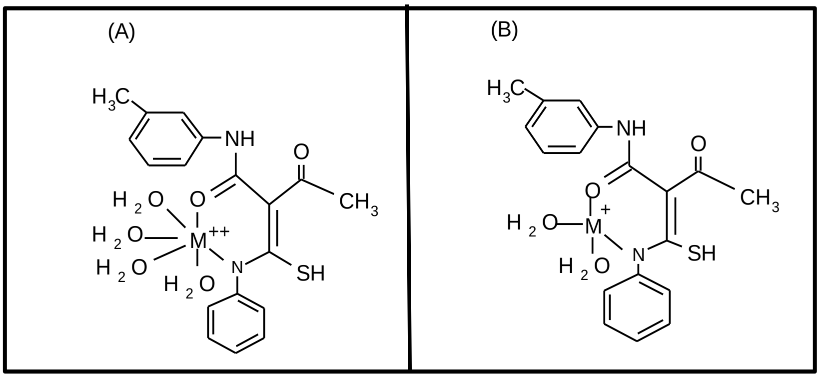

Figure 4. The proposed molecular structures of (A) Pd^{++} - MPMPB and (B) Pd^{+}- MPMPB complexes.

3.3. The optimization of the recommended SW–CASV procedure.

The electrochemical behavior of complex formed between Pd(II) ion and MPMPB as a function of the stripping peak current (I_p) was examined using different supporting electrolytes e.g. KCl, $NaNO_3$, $NaClO_4$, acetate buffer, phosphate buffer and Britton – Robinson (B – R) buffer. The height and the shape of current peak should be taking into consideration when choosing type of buffer. However, the universal buffer **(**Britton – Robinson**)** provided the best height and shape of current peak. Thus, the pH influence of universal buffer on square wave stripping voltammetry for the determination of Pd (II) ions at concentration level of 2×10^{-6} mol L^{-1} equivalent to 212.8 ng mL^{-1} was investigated in pH rang 3 – 12 and using 0.1 mol L^{-1} of buffer. The stripping peak current of Pd^{++} – MPMPB complex was small at pH = 4, however, the current dramatically increased at pH = 8. Over than pH =8, the cathodic potential of Pd^{++} – MPMPB complex was shifted to less positive values. Therefore, the supporting electrolyte pH was adjusted at 8 using 0.1 mol L^{-1} of universal buffer (see Fig.5, and Fig. 6).

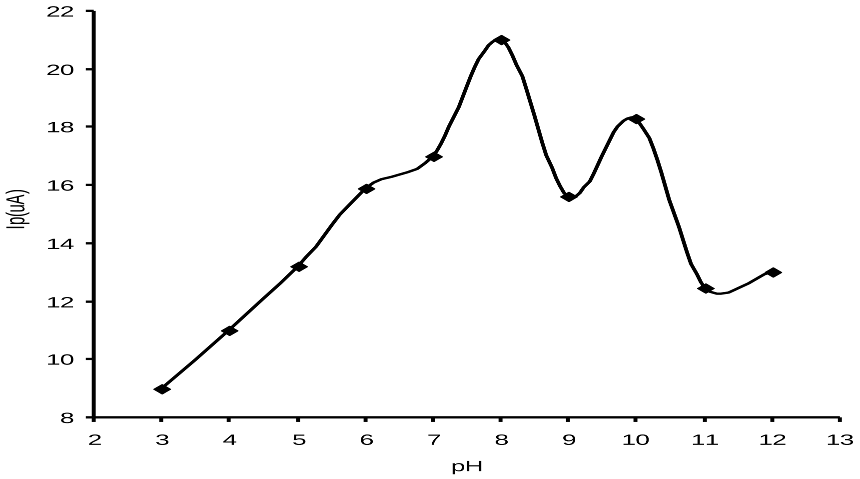

Figure 5. The plot of I_p versus (B – R) buffer pH in the presence of 212.8 ng mL^{-1} of Pd(II) ion at (0)V accumulation potential and 15s accumulation time .

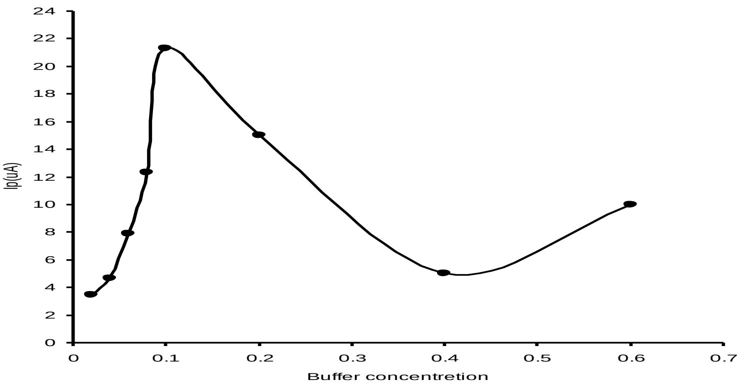

Figure 6. The plot of I_p versus (B – R) buffer concentration in the presence 212.8 ng mL^{-1} of Pd(II) at pH = 8.0, 0 V accumulation potential and 15 s accumulation time.

The relationship between accumulation potential and I_p when determination of 212.8 ng mL^{-1} of Pd (II) ion was studied in the potential range of + 0.2 to – 0.6 V at pH= 8.00. I_p increased in the range of + 0.2 to – 0.1 V, however, the maximum value of I_p was at 0.00 V as demonstrated in Fig.7. Therefore, this value was used in the subsequent work. The relationship between accumulation time and I_p was linear in the range of 0.0 to 165 s as shown in Fig. 8 when immersing the electrode in an aqueous solution containing 212.8 ng mL^{-1} of Pd(II) ions.

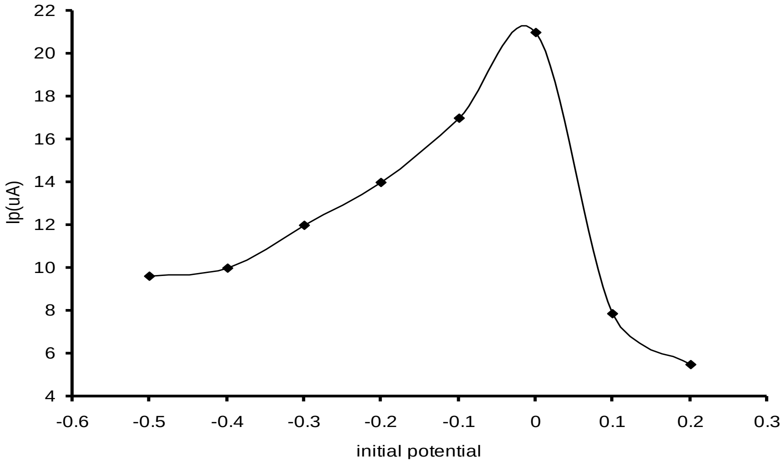

Figure 7. The plot of I_p against different initial potentials (V) in the presence of (212.8 ng mL^{-1}) of Pd(II) ion at (pH = 8.0).

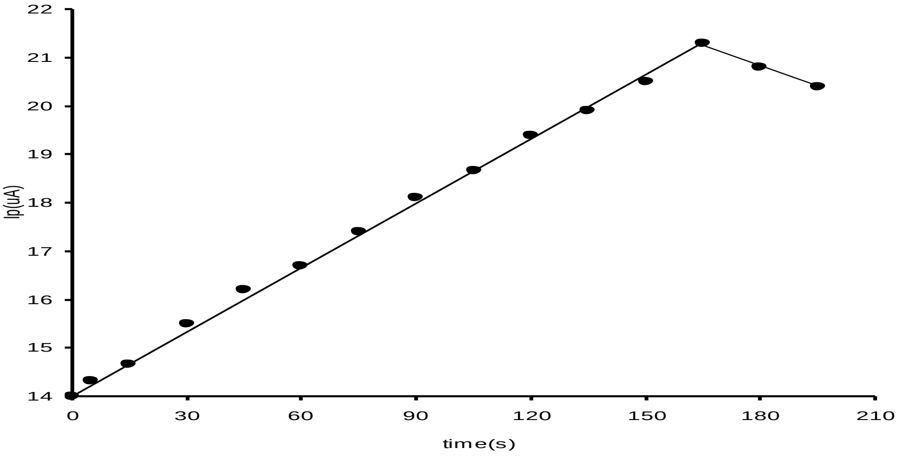

Figure 8. The relationship between I_p and accumulation time.

3.4. The evaluation of analytical performance of the proposed method.

Under the optimized experimental conditions, the linear dynamic range of developed procedure was 0.021 – 0.13 ng mL^{-1} (200 – 2000 pM). The limit of detection computed using the equations reported in [6] was 0.002 ng mL^{-1} with relative standard deviation and correlation coefficient of ± 0.01%, and 0.9986, respectively. Fig.7 shows the change of I_p recorded at – 0.185 V of different concentrations of Pd(II) ions , whereas, Fig.8 demonstrates the calibration plot of the developed method. The high sensitivity of our method is observed when comparison with previously published methods as shown in Table.3.

Table 3. The comparison of the proposed electrode with previously reported electrodes

Ref.	Electrode	Detection Limit of Pd(II)	Method
This work	Glassy Carbon Electrode	0.002 ng mL^{-1}	Adsorptive Stripping voltammetry
44	hanging mercury drop electrode	10 ng/L	Adsorptive Stripping voltammetry
45	Renewable bismuth bulk annular band working electrode (RBiABE)	0.12 μg L^{-1}	differential pulse adsorptive stripping voltammetry
46	(Hg(Ag)FE) Amalgam- Silver electrode	0.15 μg L^{-1}	Adsorptive Stripping Voltammetric
47	static mercury drop electrode (SMDE	0.05 μg L^{-1}	Adsorptive Stripping voltammetry
48	glassy carbon electrode modified with a bismuth film	0.12 μg L^{-1}	Adsorptive Stripping Voltammetry
49	Carbon Paste Electrode (CPE)	0.05 μg L^{-1}	Adsorptive Stripping voltammetry
50	un-modified screen printed carbon electrode	1.32μM	Adsorptive Stripping voltammetry
51	hanging mercury drop electrode (HMDE)	0.029 ng/mL	Adsorptive Stripping voltammetry

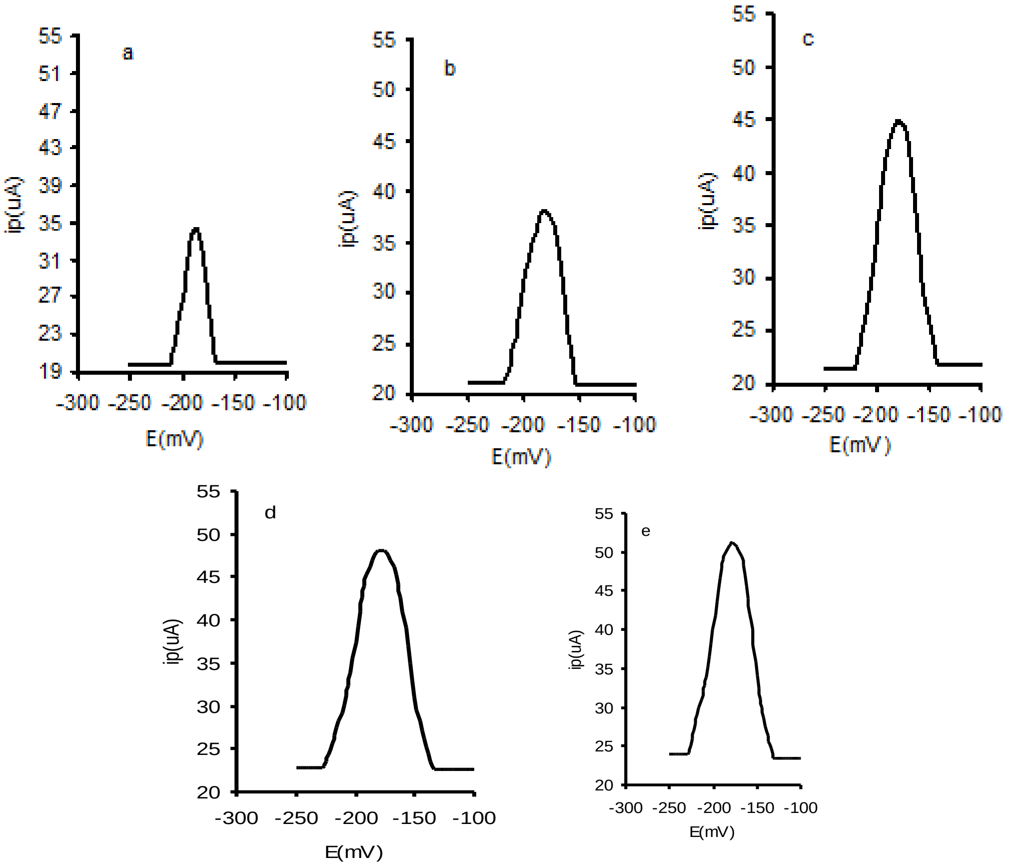

Figure 9. Typical SWCAS voltammograms at different concentrations of Pd(II) ion in presence 0.1M Britton–Robinson buffer (pH= 8.0) and15s accumulation time a):0.02 ng/mL, b):0.04 ng mL^{-1}, c):0.06 ng mL^{-1}, d):0.08 ng mL^{-1}, and e): 0.11 ng mL^{-1}.

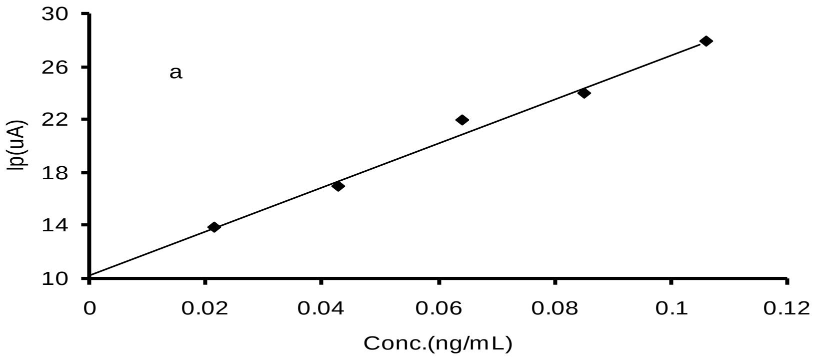

Figure 10. Plot Ip versus concentration of Pd(II) ion at 0.1M Britton– Robinson buffer (pH=8.0) at accumulation Time 60 s .

3.5. The interferences.

The selectivity of the proposed method for the determination of Pd(II) ions in the presence of some common interfering species was systematically investigated. Synthetic solutions containing a fixed amount of Pd(II) ion (212.8 ng mL^{-1}) were spiked with excess amount (at level of 10:1) of interfering species e.g. Glycine, DL- argnine, DL - Valine (amino acids), Ascorbic acid, Urea, Glucose, Fe(III), Pb(II), Na(I) and Cd (II). The results shown in Table. 4 revealed the good selectivity of proposed method.

Table 4. The collected data for of interference on the peak current response of 2×10^{-6} M of Pd(II) metal ion.

No	Interfering substance	Concentration, (mol L^{-1})	Effect**
1	Glycine	$2\times10^{-6} – 2\times10^{-5}$	(14.31) - (–0.48) %
2	DL-argnine	$2\times10^{-6} – 2\times10^{-5}$	25.74 – 62 %
3	DL-valine	$2\times10^{-6} – 2\times10^{-5}$	(46.3) – (-2.89) %
4	Ascorbic acid	$2\times10^{-6} – 2\times10^{-5}$	41.35 – 91.48 %
5	Glucose	$2\times10^{-6} – 2\times10^{-5}$	58.82 – 83.52 %
6	Urea	$2\times10^{-6} – 2\times10^{-5}$	(- 26.03) – (-9.5) %
7	Na(I)	$2\times10^{-6} – 2\times10^{-5}$	(-52.46)–(-26.45) %
8	Fe(III)	$2\times10^{-6} – 2\times10^{-5}$	43.35 – 81.17 %
9	Cd(II)	$2\times10^{-6} – 2\times10^{-5}$	(-52.97)- (-12.81)%
10	Pb(II)	$2\times10^{-6} – 2\times10^{-5}$	4.6 – 35.18%

** Where (-) refers to decrease the current peak.

3.6. Real samples analysis.

Four water samples e.g. tap, sea, river and mineral waters were employed for the evaluation of the proposed SWASV (square wave adsorptive striping voltammetry) method. The efficiency of procedure was tested using recovery percent after adding known concentrations of Pd(II) ions to real samples [52, 53]. The data shown in Table. 4 are analytically accepted where the relative recoveries of palladium were between 86.0 and 99.0%.

Table 4. Determination of Pd (ng/mL) in different water samples

Samples	Spiked Pd^{+2} (ng/mL)	Found [a]	Recovery (%)
Tap water	0.0 5 10	3.03 ± 0. 4 4.73± 0.8 9.65± 1.0	- 94.6 96.5
Sea water	0.0 5 10	3.03 ± 0. 4 4.78± 0.8 9.90± 1.0	- 95.6 99
River water	0 5 10	2.4 ± 0. 2 4.30± 1.1 9.80± 0.6	- 86 98
Mineral water	0 5 10	- 4.79± 1.1 9.85± 0.6	- 95.8 98.5
Synthetic sample	5 10	4.80± 1.1 9.70± 0.6	96 97

[a] Mean ± S.D., n =5

4. CONCLUSION

The electroanalytical method based upon the modified GCE and proposed in the present work may be considered as an excellent alternative approach for the determination of palladium content at ultra – trace concentration levels in group of real samples due to its sufficient selectivity and sensitivity. Our method has been successfully used for the determination of palladium in natural waters with excellent recovery percent.

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