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Polyaminoanthraquinone Modified Electrodes as Electroanalytical Sensors

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Poly 1-amino-9,10-anthraquinone, PAAQ, films were prepared by the electropolymerization of 1-amino-9,10-anthraquinone, AAQ, on platinum substrates. The polymerization process was carried out in both nonaqueous (Acetonitrile containing 0.1 mole L^{-1} $LiClO_4$ as supporting electrolyte) or aqueous (6.0 mol L^{-1} H_2SO_4) media. The electropolymerization process is fast and economic. The prepared films are stable and have been used as sensors for the electroanalytical determination of p-aminophenol, ascorbic acid, dopamine, hydroquinone, catechol, pyrogallol, cerium chloride and epinephrine. The determination is based on the cyclovoltammogramic method. The cyclic voltammetry was always carried out under the same conditions, where a scan rate of 100 mV s^{-1} in the specified potential range for each electrolyte at room temperature were used. A range of concentration between 0.01 to $1.0x10^{-4}$ mol L^{-1} analyte was perfectly determined. The determination process is based on the oxidation peak currents of the analyte in the cyclic voltammogram obtained by the PAAQ modified electrode. A calibration curve was drawn for each analyte from which any unknown concentration in the specified range of measurements could be accurately obtained from the value of the peak current.

Keywords: Cyclic voltammetry, Electroanalytical determination, Poly 1-amino-9, 10-anthraquinone, p-aminophenol, ascorbic acid, dopamine

1. INTRODUCTION

The concept of modified electrodes is certainly one of the exciting developments of the last three decades. The underlying motivations for electrode surface modifications stem from the desire for improved electrocatalysis and freedom from surface fouling effects. Alternatively, electrodes can be modified to prevent undesirable reactions from competing kinetically with the desired electrode process [1, 2]. The most widely adapted scheme for electrocatalysis is to use soluble or surface-immobilized electron transfer mediators, so that oxidation or reduction of the desired substrate occurs at a potential nearer to its expected thermodynamic potential. However, this scheme can only be useful

if the formal potentials of mediator catalyst and substrate are similar. In other words, electron exchange via redox mediators is limited by the redox potential of the mediator, which generally provides only a very narrow useful potential window. Polymer films modified electrodes have wide applications in the fields of chemical sensors and biosensors [3-5]. Such modified films can significantly improve the electrocatalytic properties of substrates, decrease the overpotential, increase the reaction rate and improve the stability and reproducibility of the electrode response in the area of electroanalysis [6, 7]. Electropolymerization is a convenient method for immobilizing polymers on various conductive substrates because the deposition can be controlled by adjusting the electrochemical parameters and the process is located at the electrode surfaces. Thus, the thickness, permeation and charge transport characteristics of the modified polymeric films can be well defined [8-10].

Phenolic compounds are a class of polluting chemicals which when absorbed through the skin and mucous membranes can cause damage to the lungs, liver, kidney and genitor urinary tract in animals and human [11]. Approximately 165 phenols are known to have toxic effects on plants and animals [12]. Thus, there is a continuously increasing demand for selective and sensitive detection of phenols and its derivatives, since these toxic compounds are present in the waste waters of a large number of industries, including those for coal conversion, wood preservation dyes, petroleum refining, resins and plastics [13]. So far, a great deal of methods have been established for the determination of these compounds, including liquid chromatography [14], synchronous fluorescence [15], chemiluminescence [16], spectrophotometry [17], gas chromatography/mass spectrometry [18], pH based-flow injection analysis [19], electrochemical methods [20, 21], etc. However, some of these mentioned methods are noneconomic and of low sensitivity. Electrochemically deposited polymer-modified electrodes are stable and show reproducible results with high sensitivity [22]. They were used, recently to determine the concentration of phenolic compounds in variety of samples [23-25].

Catecholamines, including dopamine and epinephrine are important hormones and neurotransmitters that play an important role in the regulation of physiological processes in living systems [26, 27]. Extreme abnormalities of catecholamine levels in biological fluids are symptoms of several diseases such as Parkinsonism and its drugs are also used to treat anaphylactic shock, bronchial asthma and organic heart disease [28]. The electrochemical behavior of epinephrine and dopamine at poly taurine modified glassy carbon electrodes exhibited enhanced sensitivity and excellent electrochemical discrimination to dopamine and epinephrine [29]. Other polymer modified electrodes were conducted, very recently, to follow this issue [30-33].

Ascorbic acid is a vital component in human diet and is present in both animal and plant kingdoms. It has been used for the prevention and treatment of common cold, mental illness, infertility, cancer and AIDS [34]. Clinical studies have demonstrated that the concentration of ascorbate in biological fluids can be used to assess the amount of oxidative stress in human metabolism [35]. Excessive oxidative stress has been linked to cancer, diabetes mellitus and hepatic disease, and hence there is much interest in the development of reliable methods to quantify ascorbate in biological systems. Taking electrochemical response of ascorbic acid at electropolymerized polymer film coated electrodes as an example, polymer films have been generated, including polyaniline, polypyrrole, polythiophene, poly(alizarin red), poly(malachite green), etc for the oxidation and monitoring of ascorbic acid in biological systems [36, 37]. Most studies are focused on improving the detection limit,

sensitivity, and selectivity. The separation of voltammetric response of ascorbic acid from co-existing materials was always the main concern [9, 31, 38, 39].

Poly (1-amino-9,10-anthraquinone), PAAQ, modified electrodes have the ability to decrease the overpotential and to improve the reversibility of the redox processes of several natural products [40]. The improvement in electrochemical reversibility of a modified electrode leads to sharper current response peaks and prevention of electrode fouling from oxidation products and hence to increased stability of the sensor. Both of these factors are important in obtaining lower detection limits in electroanalytical applications.

In the present paper PAAQ modified electrodes were used for the electroanalytical determination of some biological compounds of technological relevance. In this respect, cyclic voltammetry was mainly employed. Most of the samples used are simulated samples and a some real biological samples have been determined.

2. EXPERIMENTAL

1-Amino-9, 10-anthraquinone (referred to as AAQ herein), Merck, was used as monomer without further purification, HPLC grade acetonitrile (Fischer) was used as received. Sulfuric acid, lithium perchlorate and other chemicals were analytical grade reagents and used as received. The solutions were prepared using triply distilled water.

A standard three electrode all-glass cell was used as the electrochemical cell. The working electrode is a platinum rotating disk of a constant geometrical area of 0.071 cm^2. A silver/silver chloride (Ag/AgCl/3.0 mol L^{-1} KCl) was used as reference electrode and a platinum wire as the counter electrode. Before each experiment the working electrode was polished mechanically with alumina powder down to 1.0 μm diameter, washed with triply distilled water and then rubbed against a smooth cloth. All electrochemical measurements were carried out using an electrochemical work station (IM6d.AMOS system-Zahner Elektrik GmbH & Co.,Kronach, Germany) . The experiments were carried out at room temperature (25 ± 1 ˚C) and the potentials were referred to the silver/silver chloride electrode (E^o= 0.222 V vs. nhe).

PAAQ modified electrodes were prepared from 5.0 x 10^{-3} mol L^{-1} AAQ as monomer and acetonitrile containing 0.1 mol L^{-1} $LiClO_4$ as solvent for that prepared in non-aqueous media by cyclic voltammetry technique for 30 cycles at a scan rate of 100 mV s^{-1} in the potential range from - 0.5 to 1.8 V [41]. The polymer film was also prepared from aqueous medium of 5.0 x 10^{-3} mol L^{-1} AAQ in 6.0 mol L^{-1} sulfuric acid in the potential range between 0.0 and 1.3 V [40]. For the analytical determination of the different compounds, 10.0 x 10^{-3} mol L^{-1} of the compound in 0.1 mol L^{-1} H_2SO_4 solution was used and the cyclic voltammograms were recorded at 100 mV s^{-1} scan rate in the potential range of -0.3 to +1.3 V for modified electrodes prepared from non-aqueous solutions and in the potential range from +0.3 to +0.9 V for those prepared in aqueous medium. For comparison, the same experiments were carried out on bare Pt electrode. To achieve the best reproducibility, each experiment was carried out at least three times and almost identical results were obtained. Analytically pure chemicals and triply distilled water were always used. The values of the oxidation potentials and

anodic peak currents are presented in Tables 1 and 2 for PAAQ prepared in non-aqueous and aqueous media, respectively.

3. RESULTS AND DISCUSSION

Typical cyclic voltammograms of the electrochemical oxidation of 10.0 x 10^{-3} mol L^{-1} p-aminophenol on both the bare Pt electrode and the PAAQ modified electrode prepared from nonaqueous media are presented in Fig.1. It is clear that the modified electrode has significant response to the oxidation of the p-aminophenol compared to the bare Pt electrode. Beside the remarkable decrease in the overpotential of the oxidation process which is reflected in the lower value of the peak potential, there is a large increase in the peak current corresponding to the oxidation reaction. The electrode was found to be sensitive for the change in the concentration of p-aminophenol, and the anodic peak current increases linearly with the increase of the concentration of the material. This linear relation represents a calibration curve for the determination of unknown p-aminophenol concentration in the specified concentration range (between 2.0 x 10^{-3} and 10.0 x 10^{-3} mol L^{-1}) and is presented as insert in Fig. 1.

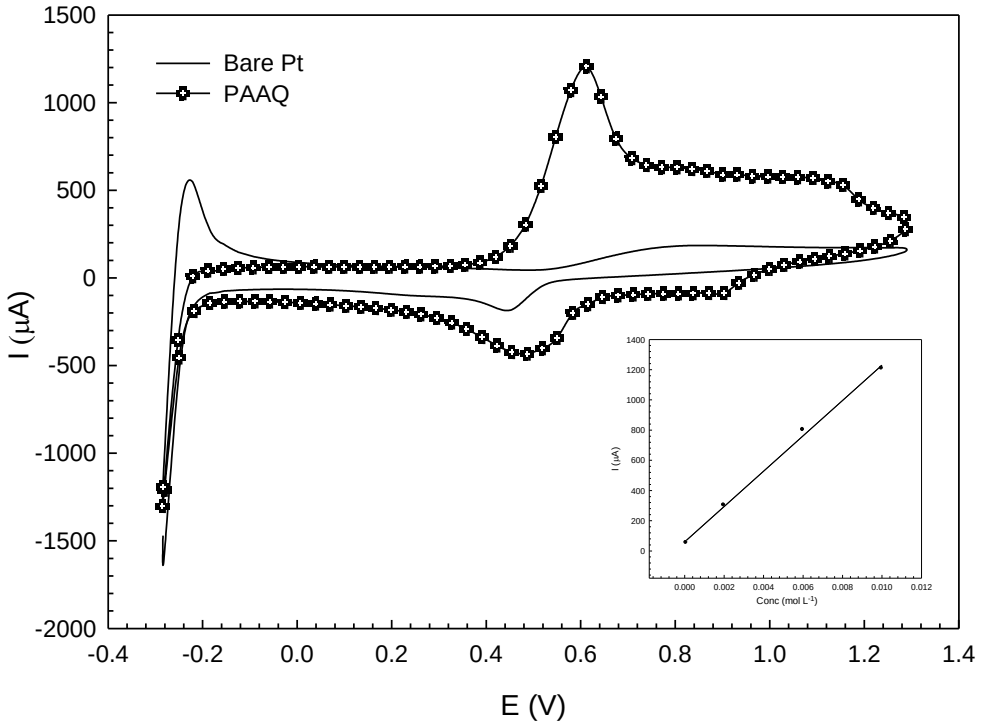

Figure 1. Typical cyclic voltammograms of the electrochemical oxidation of 1.0 x 10^{-2} mol L^{-1} p-aminophenol on both the bare Pt electrode and PAAQ modified electrode prepared from non-aqueous medium recorded at 100 mV s^{-1} scan rate in the potential range between -0.3 and +1.3 V at 25±1 ºC. (insert): Calibration curve for the electroanalytical determination of p-aminophenol on PAAQ modified electrode prepared from non-aqueous media (the concentration was varied between 1.0 x 10^{-5} and 1.0 x 10^{-2} mol L^{-1}).

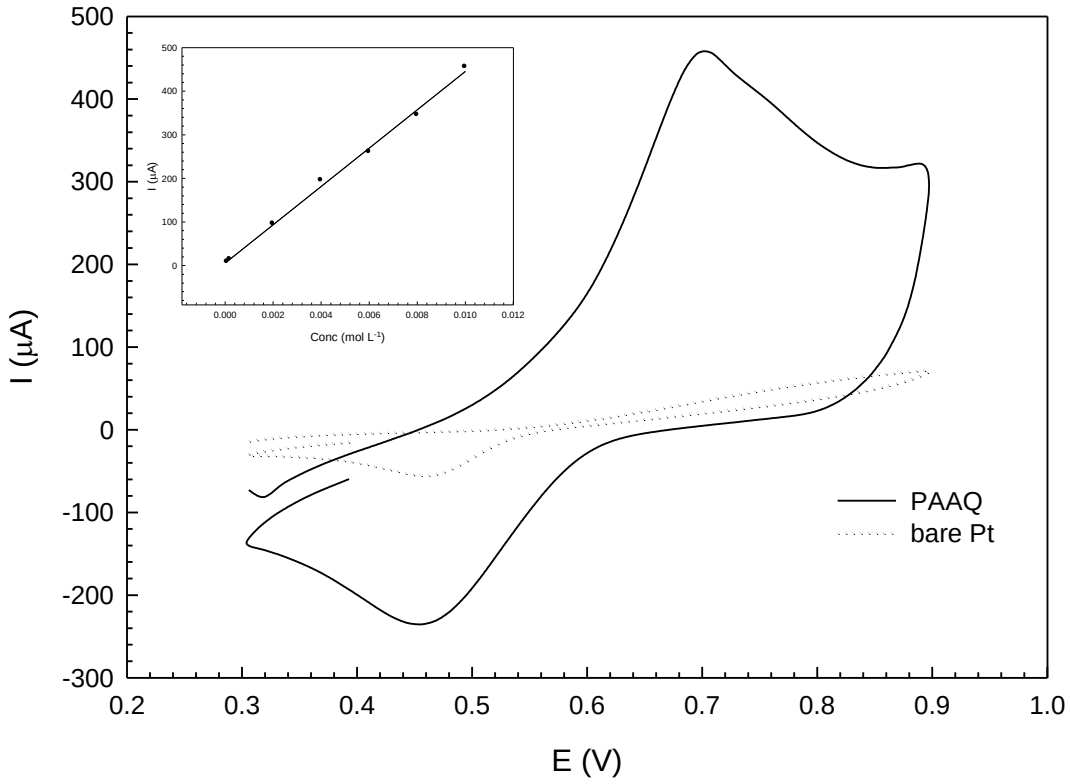

Figure 2. Typical cyclic voltammograms of the electrochemical oxidation of 1.0 x 10^{-2} mol L^{-1} p-aminophenol on both the bare Pt electrode and PAAQ modified electrode prepared from aqueous medium recorded at 100 mV s^{-1} scan rate in the potential range between +0.3 and +0.9 V at 25±1 ºC. (insert): Calibration curve for the electroanalytical determination of p-aminophenol on PAAQ modified electrode prepared from aqueous media (the concentration was varied between 1.0 x 10^{-5} and 1.0 x 10^{-2} mol L^{-1}).

The same experiments have been carried out using PAAQ modified electrode prepared in aqueous media. The response of the modified electrode to p-aminophenol is also clear and the anodic peak current increases with increase of the concentration of p-aminophenol. The only difference is that the peak current is less than one half that measured with the PAAQ prepared in non-aqueous media (cf. Fig. 2). A calibration curve for the determination of p-aminophenol on the PAAQ electrode prepared from aqueous solution is also presented as insert in Fig. 2.

It is very useful and essential to find a simple, accurate, fast and at the same time economic method for the determination of the different above mentioned compounds. The success of the PAAQ modified electrodes for the determination of p-aminophenol presented in Figs. 1 & 2, suggested the use of these electrodes for the determination of ascorbic acid, dopamine, epinephrine, hydroquinone, catechol, pyrogallol and also some cations like cerium III. The quantitative determination of these materials was carried out as described above. The corresponding cyclic voltammograms for these compounds are presented in Fig. 3 (a-g). The calibration curve for each compound was constructed and presented correspondingly in Fig. 4 (a-g). The good linear relation between the peak current and the concentration of the analyte makes this modified electrode very useful for the quantitative determination of these different compounds with high sensitivity, selectivity, and accuracy. As it is

presented in each curve the experiment was also carried out on bare Pt electrode.

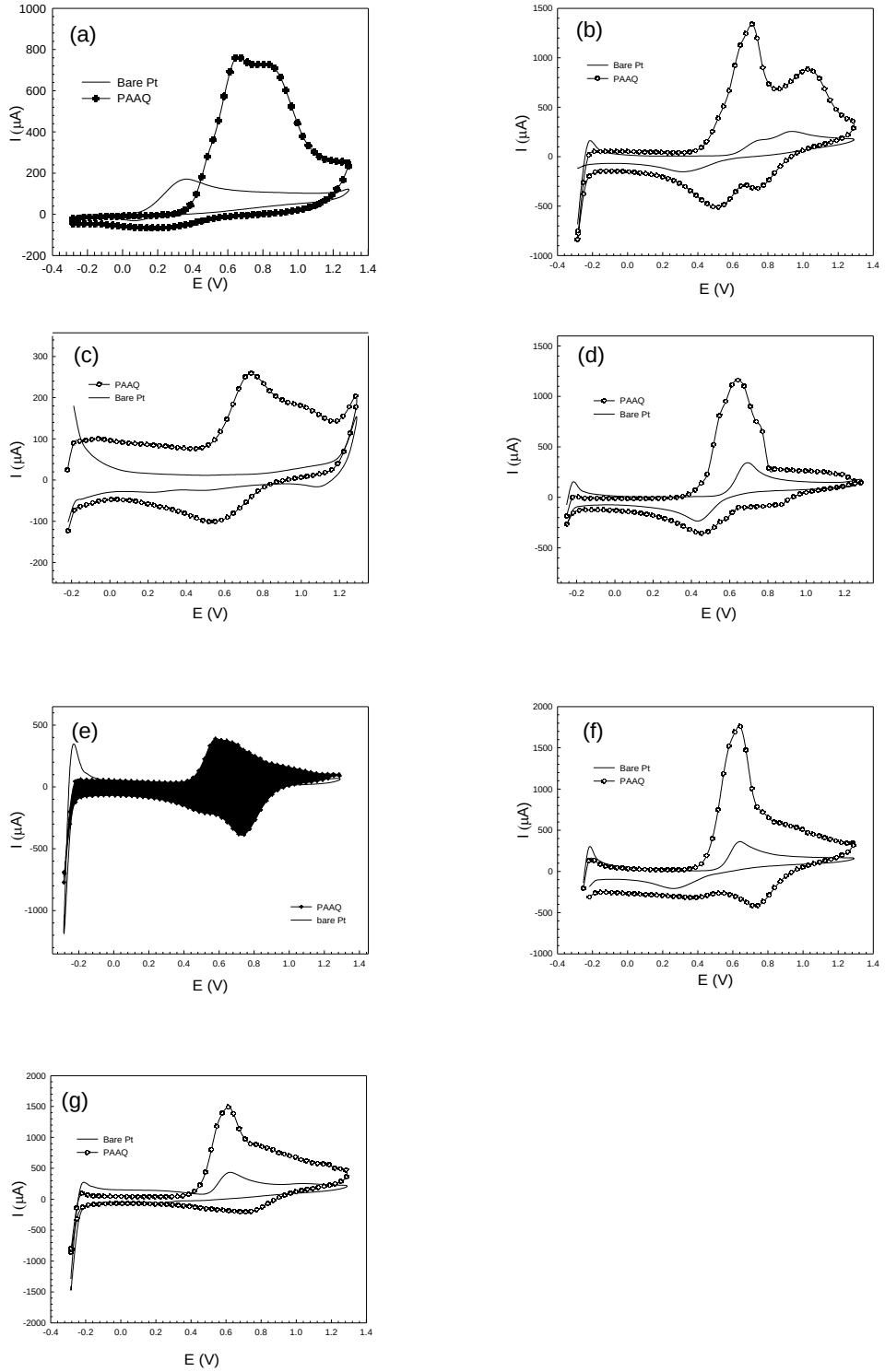

Figure 3. Typical cyclic voltammograms of the electrochemical oxidation of 1.0 x 10^{-2} mol L^{-1} (a) ascorbic acid, (b) catechol, (c) cerium III chloride, (d) dopamine, (e) epinephrine, (f) hydroquinone, and (g) pyrogallol on both the bare Pt electrode and PAAQ modified electrode prepared from non-aqueous medium recorded at 100 mV s^{-1} scan rate in the potential range between -0.3 and +1.3 V at 25±1 ºC.

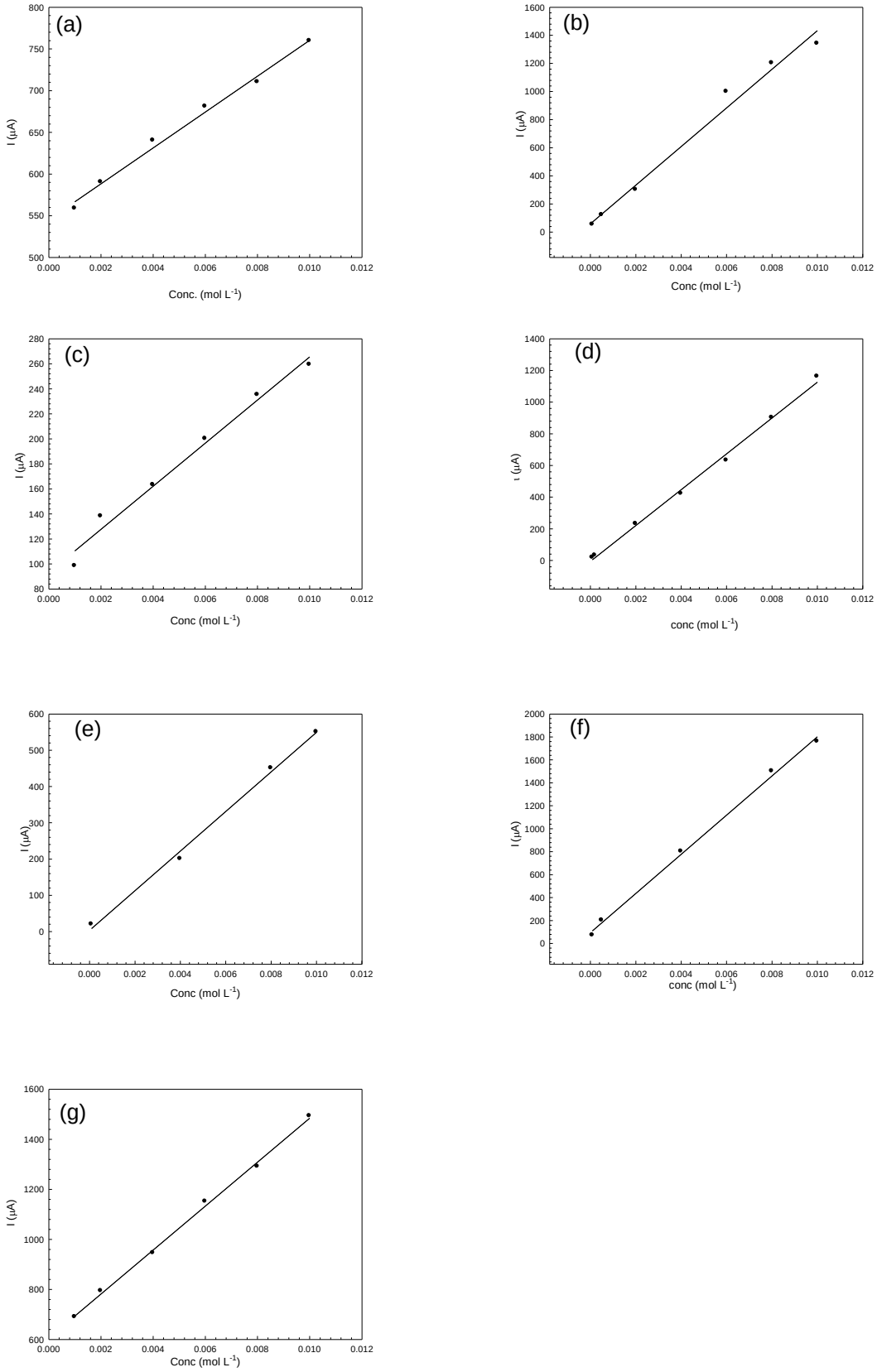

Figure 4. Calibration curves for the electroanalytical determination of a) ascorbic acid, (b) catechol, (c) cerium III chloride, (d) dopamine, (e) epinephrine, (f) hydroquinone, and (g) pyrogallol on the PAAQ modified electrode prepared from non-aqueous medium (the concentration was varied between 1.0 x 10^{-5} and 1.0 x 10^{-2} mol L^{-1}).

Table 1. Oxidation potentials and anodic peak current values for bare Pt and PAAQ modified electrode prepared in non-aqueous media for 1.0 x 10^{-2} mol L^{-1} of each of the tested compounds dissolved in 0.1 mol L^{-1} H_2SO_4 at a scan rate of 100 mV s^{-1}, in the potential range between -0.3 and + 1.3 V vs. Ag/AgCl/Cl^-, at (25 ± 1) ˚C.

Analyte	Bare Pt electrode		PAAQ modified electrode	
	E_{pa} (V)	I_{pa} (µA)	E_{pa} (V)	I_{pa} (µA)
p-aminophenol	+0.867	184.9	+0.610	1206
Ascorbic acid	+0.355	170.3	+0.675	759.3
Dopamine	+0.708	335.3	+0.640	1160
Hydroquinone	+0.643	362.4	+0.620	1759
Catechol	+0.931	254.4	+0.708	1340
Pyrogallol	+0.608	429.8	+0.608	1492
Cerium chloride	-----	-----	+0.739	259.1
epinephrine	+0.771	278.4	+0.516	550.0

Table 2. Oxidation potentials and anodic peak current values for bare Pt and PAAQ modified electrode prepared in aqueous media for 1.0 x 10^{-2} mol L^{-1} of each of the tested compounds dissolved in 0.1 mol L^{-1} H_2SO_4 at a scan rate of 100 mV s^{-1}, in the potential range between +0.3 and + 0.9 V vs. Ag/AgCl/Cl^-, at (25 ± 1) ˚C.

Analyte	Bare Pt electrode		PAAQ modified electrode	
	E_{pa} (V)	I_{pa} (µA)	E_{pa} (V)	I_{pa} (µA)
p-aminophenol	+0.891	72.06	+0.696	455.4
Ascorbic acid	+0.774	160.1	+0.748	310.1
Dopamine	+0.735	299.7	+0.826	413.4
Hydroquinone	+0.644	368.6	+0.683	406.9
Catechol	+0.748	292.8	+0.774	392.7
Pyrogallol	+0.657	358.6	+0.722	481.3
Cerium chloride	-----	-----	+0.709	77.86
epinephrine	+0.787	261.7	+0.813	320.5

For comparison, the values of the oxidation peak current at a constant concentration of the analyte (1.0 x 10^{-2} mol L^{-1}) measured on bare Pt, PAAQ modified electrode prepared in aqueous solutions and PAAQ prepared in non-aqueous solutions are presented in Tables 1 & 2. It is clear from the data presented in the two Tables that the PAAQ modified electrodes prepared from aqueous solution can be also used for the quantitative determination of the above mentioned different compounds. The cyclic voltammograms of these measurements were recorded and the calibration curves were constructed. These calibration curves are presented in Fig. 5 (a-g) for the different compounds.

The lower limits of detection (LOD) and lower limits of quantization (LOQ) were calculated according to the following equations [42]:

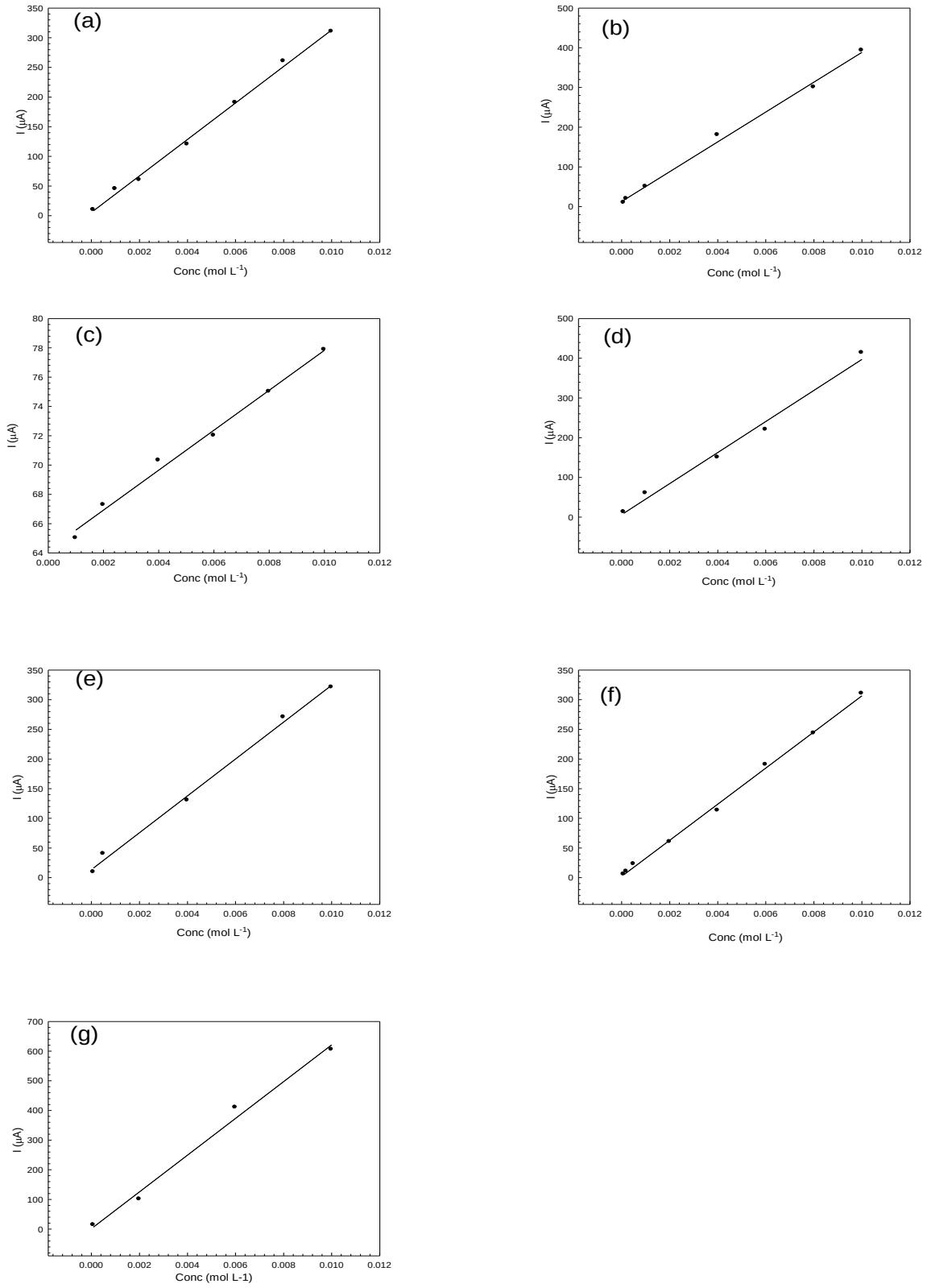

Figure 5. Calibration curves for the electroanalytical determination of a) ascorbic acid, (b) catechol, (c) cerium III chloride, (d) dopamine, (e) epinephrine, (f) hydroquinone, and (g) pyrogallol on the PAAQ modified electrode prepared from aqueous medium (the concentration was varied between 1.0×10^{-5} and 1.0×10^{-2} mol L^{-1}).

$$LOD = 3xSD / slope$$

$$LOQ = 10xSD / slope$$

where SD is the standard deviation obtained from at least 4 different runs. The calculated values for each material at both PAAQ modified electrode prepared in non-aqueous and aqueous media are presented in Tables 3 and 4, respectively. The calculated data were then compared with other analytical techniques, like spectrophotometry [43], fluorimetry [44], capillary electrophoresis-UV and capillary electrophoresis-mass spectroscopy [45], flow injection fluorescence [46] and spectrophotometric determination based on polymeric technology [47]. The PAAQ modified electrodes have shown lower detection limit than the other sophisticated techniques as presented in Table 5. Beside the ease of preparation of the sensors and their stability, they can be used several times over more than two weeks.

Table 3. Regression data of the calibration lines for the quantitative determination of ascorbic acid, catechol, cerium chloride, dopamine, epinephrine, hydroquinone, p-aminophenol and pyrogallol at PAAQ prepared from non-aqueous medium using cyclic voltammetry technique.

Analyte	SD	RSD	LOD (mol L^{-1})	LOQ (mol L^{-1})
Ascorbic acid	0.052	$9.3x10^{-3}$	$7.25x10^{-6}$	$2.4x10^{-5}$
Catechol	$5.77x10^{-3}$	0.011	$1.26x10^{-7}$	$4.2x10^{-7}$
CeIII	0.05	0.05	$8.7x10^{-6}$	$2.9x10^{-5}$
Dopamine	0.005	0.03	$1.3x10^{-7}$	$4.4x10^{-7}$
Epinephrine	$5.77x10^{-3}$	0.03	$3.2x10^{-7}$	$1x10^{-6}$
p-aminophenol	$6.35x10^{-3}$	0.01	$1.63x10^{-7}$	$5.4x10^{-7}$
Pyrogallol	0.027	0.04	$4.8x10^{-7}$	$1.6x10^{-6}$
Hydroquinone	$2.887x10^{-3}$	$3.1x10^{-3}$	$1.3x10^{-8}$	$4.3x10^{-8}$

SD = Standard deviation, RSD = Relative SD, LOD = Lower limit of detection,
LOQ = Lower limit of Quantization.
The number of experiments, N = 4 and the regression factor, R = 0.998.

Table 4. Regression data of the calibration lines for the quantitative determination of ascorbic acid, catechol, dopamine, epinephrine, hydroquinone, p-aminophenol and pyrogallol at PAAQ prepared from aqueous medium using cyclic voltammetry technique.

Analyte	N	RSD	LOD (mol L^{-1})	LOQ (mol L^{-1})
Ascorbic acid	4	$5.2\ x10^{-3}$	$4.9x10^{-8}$	$1.6\ x\ 10^{-7}$
Catechol	4	$5.0\ x10^{-2}$	$3.7x10^{-6}$	$1.2x10^{-5}$
Dopamine	4	$4\ x\ 10^{-3}$	$3.8x10^{-8}$	$1.3x10^{-7}$
Epinephrine	4	$5.5\ x\ 10^{-3}$	$4.83x10^{-8}$	$1.6x10^{-7}$
p-aminophenol	4	$6.5x10^{-2}$	$3.4x10^{-7}$	$1.1x10^{-6}$
Pyrogallol	4	$1.4x10^{-2}$	$1.1x10^{-7}$	$1.0x10^{-7}$
Hydroquinone	4	$1.0x10^{-2}$	$4.9x10^{-8}$	$1.6x10^{-7}$

RSD = Relative SD, LOD = Lower limit of detection, LOQ = Lower limit of quantization. The number of experiments (N) = 4 and the regression factor (R) of the data is equal to 0.998. The standard deviation (SD) = 5 x 10^{-4} except for catechol it is equal to 1.0x10^{-3}.

Table 5. The lower limit of detection (LOD) of the different methods used for the determination of dopamine.

Analytical Method	LOD (mol L^{-1})
Spectrophotometry [42]	1.6 x 10^{-7}
Fluorimetry [43]	4.3 x 10^{-7}
Capillary electrophoresis- Ultraviolet [44]	0.7 x 10^{-6}
Capillary electrophoresis- Mass Spectroscopy [44]	1.2 x 10^{-6}
Flow injection fluorescence using photoinduced electron transfer boronic acid derivatives [45]	3.7 x 10^{-6}
Spectrophotometric determination using microfluidic system based on polymeric technology [46]	6.3 x 10^{-6}
PAAQ modified electrode prepared from non-aqueous medium	1.3 x 10^{-7}
PAAQ modified electrode prepared from aqueous medium	3.8 x 10^{-8}

4. VALIDATION OF THE METHOD

4.1. Specificity

PAAQ prepared from non-aqueous medium was found to be specific for the qualitative and quantitative determination of epinephrine, pyrogallol, catechol and cerium chloride where the difference in peak potential amounts to 100 mV. Also, mixtures of ascorbic acid and epinephrine or dopamine and epinephrine can be determined simultaneously using the PAAQ modified electrodes. With the exception of catechol and hydroquinone, which can be determined specifically with high sensitivity, the other phenolic compounds interfere together during their determination using PAAQ prepared from aqueous medium. In such cases we can use the difference in oxidation peak potential height to differentiate between them if they found in the same sample.

4.2. Accuracy

The accuracy of the method for the determination of the different compounds under investigation was performed by the addition of standard concentration of each compound to 10 mL tap water and recording the oxidation peak current.

For example, 5.0 x 10^{-3} mol L^{-1} catechol was added to 10 mL tap water then the current response was recorded using the PAAQ modified electrode. The current recorded by PAAQ modified

electrode prepared from non-aqueous medium was found to be 740 μA which corresponds to 5.05 x 10^{-3} mol L^{-1} as extrapolated from the calibration curve of catechol. The current response obtained by PAAQ modified electrode prepared from aqueous medium was found to be 200 μA which corresponds to 4.98 x 10^{-3} mol L^{-1} catechol.

Although the concentration of the standard sample is relatively high, the percent error did not exceed 1%, also when we went down to $1x10^{-4}$ mol L^{-1} catechol concentration. The measurements have indicated the accuracy of the method.

4.3. Precision and repeatability

Each determination for the eight different compounds has been carried out at least four times. The relative standard deviation was found to be less than 1% indicating the high precision of the method and the confidence in its repeatability.

The detection limits obtained by the use of PAAQ modified electrodes were compared with those obtained by other methods, especially for the determination of dopamine. The data are presented in Table 5, which shows clearly that the PAAQ modified electrodes can detect concentrations down to 10^{-8} mol L^{-1} a ranges lower with an order of magnitude than the other standard methods.

4.4. Robustness

The method was found to be fast where the preparation of the modified electrode does not exceed 30 minutes for PAAQ prepared from non-aqueous solutions and 15 minutes for that prepared from aqueous media.

The method of preparation is easy and does not require special pretreatments or sophisticated designs. The process of determination of the analyte is very fast and is taking place in less than one minute. The PAAQ modified electrode is stable and can be used several times over two weeks. The current response recorded using the previously prepared PAAQ modified electrode was always the same within a range of ±0.01μA. It is recommended to use a freshly prepared PAAQ modified electrode before every measurement, since it is easy and fast to prepare and not expensive.

5. CONCLUSIONS

PAAQ thin films are prepared conveniently and reproducibly by the electropolymerization of AAQ on Pt substrates from either aqueous or non-aqueous media. The polymer films are stable and show good performance as electroanalytical sensors.

The prepared PAAQ modified electrodes were used for the qualitative and quantitative determination of standard solutions of ascorbic acid, catechol, cerium chloride, dopamine, epinephrine, hydroquinone, p-aminophenol and pyrogallol in concentration range between 1.0 x 10^{-5} and 1.0 x 10^{-2} mol L^{-1}. The method is fast, precise, reproducible and economic and can be applied to real biological

samples. It has a better detection limit down to ~ $5x10^{-8}$ mol L^{-1} compared to other standard analytical techniques.

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