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PORPHYRIN-COATED METALLIC ELECTRODES FOR DETERMINATION OF CHLORINATED PESTICIDES

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ABSTRACT

Determination of organochlorines has become very important due to their chronic toxicity, bioaccumulation, and carcinogenity. The available methods are disfavored as they lack necessary simplicity, inexpensiveness and environmentally friendliness for routine analysis, and consequently, electrochemical methods have shown to be possible alternatives. The use of platinum and gold electrodes for the detection of some selected organochlorine pesticides was demonstrated by modifying them with 5,10,15,20-tetraphenylporphyrinatoiron(III) chloride [Fe(III)TPPCl]. The organochlorines were determined on the modified Pt and Au electrodes using cyclic voltammetry and amperometry. During this process, catalytic properties of the metallic electrodes are preserved while the unwanted characteristics are removed. The reduction potentials of the selected organochlorines on metallic electrodes are lower than those at glassy carbon electrodes under similar conditions. Further, metalloporphyrins are observed to be less firmly bound to metallic surfaces than that of carbon surfaces, resulting in less poisoning effects.

Key words: organochlorine pesticides, metallic electrodes, metalloporphyrins, cyclic voltammetry, amperometry.

1. INTRODUCTION

Certain organochlorine compounds are frequently used as pesticides; which are well known pollutants and toxins, as they have caused extensive pollution problems on the environment, including soil and water resources [1,2], atmosphere [3] and food- stuffs [4,5]. Among different types of pesticides, organochlorines are proven to be highly hazardous, that cause long-term problems as they are persistent in the environment due to low chemical and biodegradability. Their ability of inducing carcinoma [6] and bioaccumulation [7,8] has been investigated extensively. Many such organohalide pesticides in their degradation give rise to more toxic degradation products [9]. Therefore detection of organohalide pesticides has become very important.

Development of alternative methods has become attractive because the methods, such as gas chromatography [10], high performance liquid chromatography [11] established for organohalide determination lack necessary simplicity, low cost and environmentally friendliness.

Electrochemical methods such as differential pulse polarography [12,13], stripping voltammmetry [14], cyclic voltammetry [15] and amperometry [16] have been applied successfully for the detection of organochlorines. However the direct reduction of carbon–halogen bond involves extreme negative over potentials [17, 18], in the range from -1.3 V to –1.6 V, with complete chemical irreversibility. Electrochemical catalysis has thus become important, and metalloporphyrins of transition metals, [18, 19, 20] have been extensively used as catalysts, for the reduction of large number of alkyl and aryl halides.

In the case of metalloporphyrin heterogeneous electrochemical catalysis, the catalyst from a solution is coated on to the electrode surface, usually glassy carbon disk electrodes. Although carbon surfaces act as ideal binding sites for such organic macromolecules that lead to stable coatings, blocking of the electrode surface frequently occurs due to high

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degree of adsorption of analytes. This would lead to early saturation, causing irreproducible results.

On the other hand, electrodes of noble metals, such as Pt and Au show complicated electrochemistry in aqueous solutions. Thus, restrictions arise in the use of these working electrodes. However, attempts have been taken to overcome such complications by covering the metallic surface with substances that inhibit undesired metallic electrochemistry and allow the desired reactions. Platinum electrodes coated with polymers such as poly (4- vinyl-pyridine-co-styrene) together with hexadecylmethane-sulfonate [21] and polyaniline [22] are reported for organic analyses. These applications are important, as certain organic substances such as methanol are prone to adsorb onto metallic surfaces irreversibly, causing the poisoning of electrode surface [23, 24]. Such problems could successfully overcome by careful selection of a modification methodology.

In this study, platinum and gold electrodes, coated with 5,10,15,20-tetraphenyl-porphyrinatoiron (III) chloride [Fe(III)TPPCl] are used for the reduction of organohalogen pesticides without interfering with their own electrochemistry. As transition metals such as platinum and gold are catalysts for certain reactions of organic compounds, this type of use is important, as it preserves the catalytic properties of such metals while avoiding interfering metallic reactions.

2. MATERIALS AND METHODS

2.1 Materials

All the electrolytes used throughout the experiments such as NaCl, KCl were of analytical grade (BDH). The catalyst, 5,10,15,20-tetraphenylporphyrinatoiron(III) chloride, was purchased from Aldrich, and used as received. Acetonitrile, used for the preparation of mixed solvent systems was of HPLC grade (Aldrich Chemicals). Commercial formulations of known assay were used for the preparation of propanil and MCPA solutions. Chloroacetic acid (99%),
4- chloro-o- cresol, (99%) and dichloromethane (99%) were purchased from BDH.

2.2 Instrumentation

All the electrochemical experiments were carried out using a BAS cyclic voltammograph and an X-Y recorder. The three-electrode electrochemical system consisted of a saturated calomel (reference), a platinum wire (counter) together with a modified or unmodified glassy carbon, platinum or gold electrode (working). All the experiments were carried out under deaerated conditions with purging of N_2. All the potentials were measured vs. SCE.

2.3 Cyclic Voltammetric Experiments

Pt and Au electrodes were well polished using a polishing pad with alumina slurry. Their electrochemical behavior was observed using pH 7 phosphate buffer system. The study was repeated using 0.1mol dm^{-3} KCl and other buffered systems of pH 1, 3 and 5.

A solution of Fe (III)TPPCl of 5.0×10^{-4} mol dm^{-3} was prepared in CH_2Cl_2 [16]. This solution was used to modify the electrodes using the droplet evaporation method, using two drops at each occasion. The solution electrochemistry of metallic electrodes was re observed in each above solution after modification.

Standard solutions of propanil, MCPA, chloroacetic acid and cresol were prepared in 3: 1 CH_3CN: H_2O system, in 5.0×10^{-3} mol dm^{-3} concentration. Electrochemical behavior of each compound was recorded with modified Pt and Au electrodes. The each experiment was repeated in similar condition with a similarly modified glassy carbon electrode.

2.4 Amperometry

Amperometric experiments were carried out for propanil and MCPA using modified Pt and Au working electrodes at their respective reduction potentials for each compound. Each of those experiments was repeated with modified glassy carbon electrode.

3. RESULTS AND DISCUSSION

Aqueous electrochemistry of platinum electrodes is complicated, which results in many features such as oxide formation, reduction of the oxide, hydrogen adsorption and hydrogen desorption. All these surface reactions can be observed when proper experimental conditions are selected (Fig. 1). Similar characteristics were observed, but to a lesser extent, when other noble metal surfaces, such as gold and palladium, are in contact with aqueous medium.

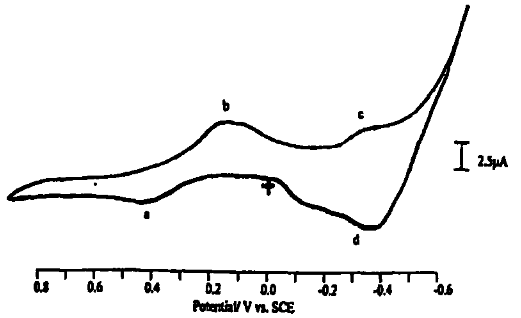

Fig.1 Electrochemical behavior of Pt electrode in pH 7 phosphate buffer and 0.1 mol dm^{-3} KCl media, potential scan rate 25 mV/ S, N_2 saturated. (a) platinum oxide formation (b) platinum oxide reduction (c) Hydrogen adsorption (d) Hydrogen desorption.

When the surface of the platinum electrodes is modified, it is not fully exposed to the solution, resulting in a drastic reduction of the available sites of the metallic surface. Consequently, the extent of the formation of the platinum oxide and the subsequent reduction would be significantly affected as observed in cyclic voltammetric scans, recorded in many buffered systems (Fig. 2).

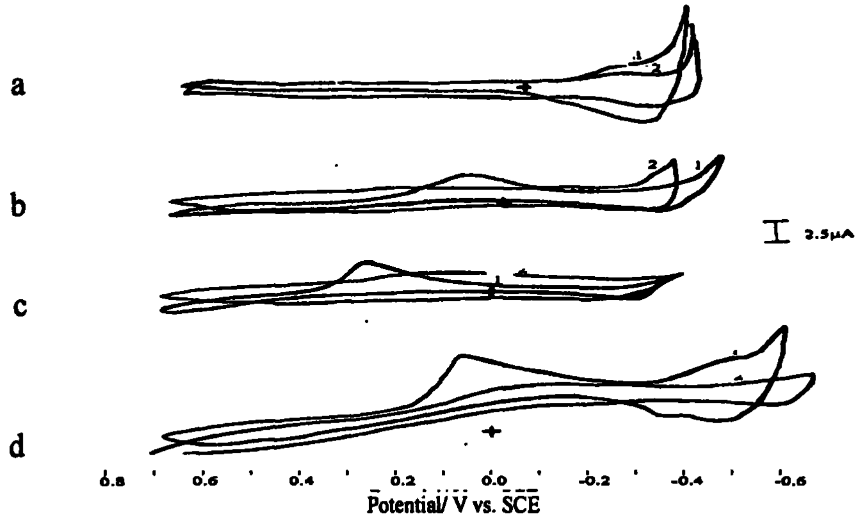

Fig. 2 Comparative electrochemical characteristics of platinum electrode in different buffer systems, potential scan rate 25 mV/ S, N_2 saturated. (a) pH=1 (b) pH=3 (c) pH=5 (d) pH=7 buffers, (1) = response of unmodified electrode and (2)= behavior after modification.

In highly acidic solutions (pH=1 and 3), modification has not very successfully overcome the solution electrochemistry of metallic electrodes. This is probably due to high H^+ concentration, which results in an increased tendency for catalyzing H_2 evolution. Nevertheless, the oxide formation is not found to interfere very much as the acidic conditions disfavor this reaction. At pH 5 and 7, considerable amounts of oxide formation and reduction are observed. The peak associated with the metal oxide reduction would show the highest tendency of interfering with the catalytic reduction peak of organohalides, as both the processes appear at very close potentials. The modification of the surface with the metalloporphyrin successfully overcomes this problem. At such pH values, hydrogen evolution problem is also not serious as in extreme acidic conditions. Similar observations were made with Au electrodes, as expected.

Cyclic voltammetric studies carried out using each organohalogen compound have shown their ability of reduction at both modified metallic and glassy carbon electrodes (Table 1). Electrocatalytic reduction of Propanil at modified glassy carbon electrodes appears at – 0.30 V as expected (16), while Pt and Au electrodes produce the reduction wave at slightly lower potentials (Fig. 3).

Table 1 Reduction potentials of organochlorines at different modified electrodes.

Working Electrode	Propanil	MCPA	4-chloro-o-cresol	Chloroacetic acid
Glassy carbon	- 0.30 V	- 0.20 V	- 0.27 V	- 0.25 V
Platinum (Pt)	- 0.22 V	- 0.12 V	- 0.23 V	- 0.19 V
Gold (Au)	- 0.25 V	- 0.20 V	- 0.25 V	- 0. 22V

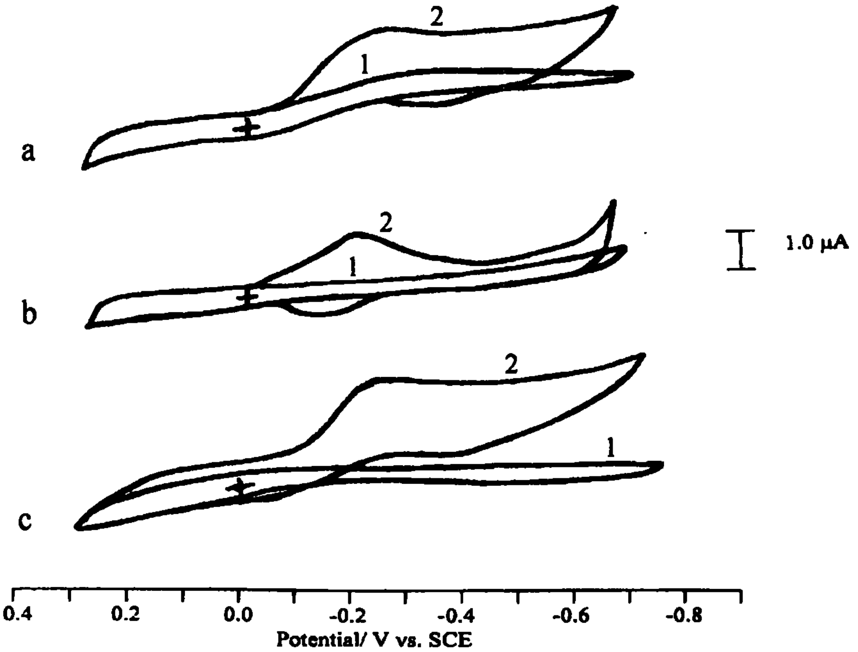

Fig.3 Electrocatalytic reduction of Propanil in CH_3CN/ H_2O (3:1), using Fe(III)TPPCl-modified; (a) glassy carbon (b) Au and (c) Pt electrodes. Potential scan rate, 10 mV/ S, Supporting electrolyte 0.1mol dm^{-3} KCl, N_2 saturated.

In general, for all the organohalides investigated, reduction potentials at the metallic electrodes are lower than those at glassy carbon electrodes, which can be attributed to the surface catalytic role of metallic electrodes. This is a significant achievement in amperometric quantitative analysis.

The reductive electrocatalytic process observed at Pt or Au electrodes would probably follow the same catalytic EC mechanism as reported earlier for glassy carbon electordes, where the electrochemical reduction of the metalloporphyrin produces the active Fe (II) form, which reacts with the organohalide to form an adduct. The adduct is then decomposed with the cleavature of the carbon-halogen bond [16,20]. The reduction potential of such a catalytic process depends on factors, such as type of the carbon–halogen bond, the nature of catalyst and the medium.

According to the steady–state amperometric experiments, carried out for propanil, both glassy carbon and Au working electrodes result in smooth, noise-free responses that are suitable for quantitative analysis.

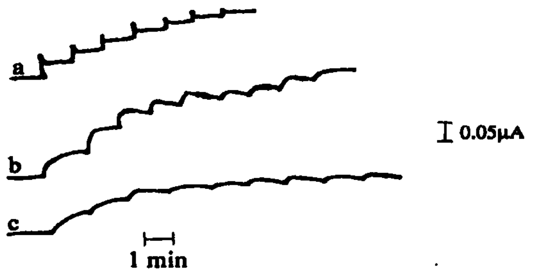

Fig.4 Steady–state amperometric responses for propanil at different working electrodes, modified with Fe(III)TPPCl with 100 µmol dm^{-3} concentration increments, (a) glassy carbon electrode (b) Pt electrode (c) Au electrode.

Although Pt behaves in a different manner (Fig. 4), the background noise may be due to trace amounts of oxide reduction that occurs at the potential of application, as Pt shows a stronger tendency toward the formation of its metallic oxide, as compared to gold. It is suggested that this problem be overcome by modifying the Pt surface with a thicker coating of the catalyst, or alternatively, by mixing the catalyst with an electrochemically inert substance. The ability of glassy carbon and Au electrodes for the detection of MCPA at lower concentrations is evident according to Fig. 5.

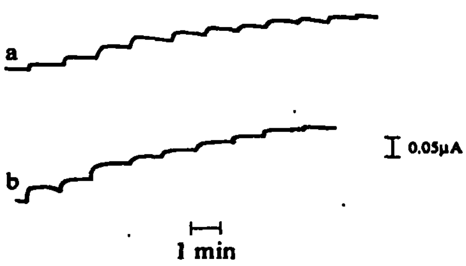

Fig. 5 Comparative amperometric responses for MCPA on modified (a) glassy carbon (b) Au electrodes, with 1.0 µmol dm^{-3} concentration increments.

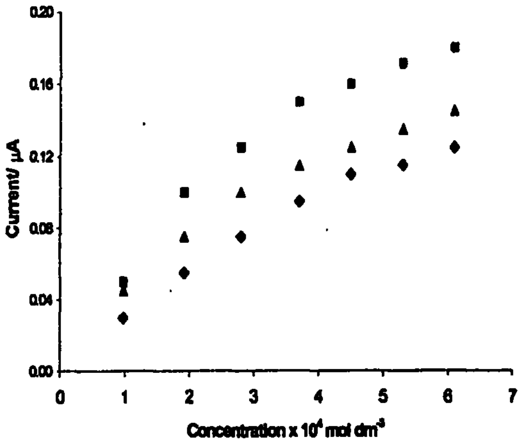

Fig.6 Comparative working curves for determination of Propanil on glassy carbon (◆), platinum (■) and gold (▲) electrodes.

Further the analytical characteristics, determined from the calibration curves (Fig.6) constructed using the steady- state amperograms for the detection of Propanil reveal the usefulness of metallic electrodes over glassy carbon (Table 2).

Table 2 Comparative analytical characteristics for determination of Propanil on glassy carbon, gold and platinum working electrodes.

Electrode	Analytical Characteristics		
	Sensitivity/ μA mol^{-1}dm^{3}	Linear Range/ mol dm^{-3}	^{a}M. D.L./ mol dm^{-3}
Glassy Carbon	0.0186	1.9x 10^{-4}- 4.5x 10^{-4}	8.0x 10^{-5}
Gold	0.0189	1.9x 10^{-4}- 5.5x 10^{-4}	3.0x 10^{-5}
Platinum	0.0240	1.9x 10^{-4}- 5.6x 10^{-4}	3.8x 10^{-5}

(a = Minimum detection Limit, based on S/ N= 3.)

According to a similar comparison between the Au and Pt electrodes for the determination of MCPA, the Au electrode seems to be preferred over the glassy carbon electrode (Fig. 7, Table 3).

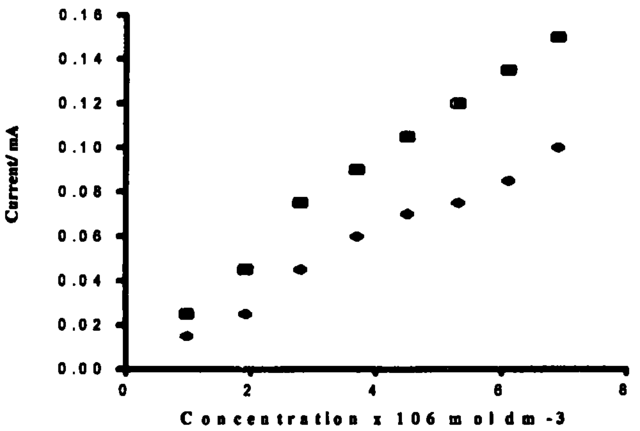

Fig.7 The comparative working curves for determination of MCPA on glassy carbon (◆) and gold (■) working electrodes.

Table 3 Comparative analytical characteristics for determination of MCPA on glassy carbon and gold working electrodes.

Electrode	Analytical Characteristics		
	Sensitivity/ μA mol^{-1}dm^{3}	Linear Range/ mol dm^{-3}	M. D.L./ mol dm^{-3}
Glassy Carbon	0.0209	2.7x 10^{-6}- 5.5x 10^{-6}	9.8x 10^{-7}
Gold	0.0141	2.7x 10^{-6}- 6.8x 10^{-6}	6.0x 10^{-7}

However the coatings made on metallic electrodes were found to be less stable than that were made on carbon surfaces, suggesting that interactions between those metallic surfaces and porphyrins are weaker than that with carbon surfaces. They are found to be unstable after a short period of 2-3 days of use, in contrast to the long-term stability of Fe(III)TPPCl coatings on glassy carbon surfaces [16]. Although this condition restricts the lifetime of sensors prepared with modification of Pt and Au electrodes, it prevents the poisoning of the metal surface. It is particularly important as irreversible adsorption of metalloporphyrins on amalgamated Pt is observed [25].

4. CONCLUSION

Metallic electrodes with porphyrin modification can be used for the determination of organohalides without interfering with their own electrochemistry, further they have proven to be more suitable for quantitative analytical purposes over glassy carbon electrode.

5. ACKNOWLEDGEMENT

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