Cyclic Voltammetric Determination of Methylparaben and Propylparaben in Pharmaceutical Preparations

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الخلاصة

تمت في هذه الدراسة تطوير تقنية جديدة وسريعة باستخدام الفولتامتري الحلقي عند قطب قطرة الزئبق المعلقة لتقدير مركبين شائعا من مركبات البارابين هما المثل باربين والبروبايل بارابين في محلول الماليت المنظم عند الرقم الهيدروجيني(٦) ولقد لوحظ من النتائج المتحصل عليها ان عملية انتقال الشحنة كلها عكسية، وقد تم إستخدام الطريقة لتقدير تراكيزضئيلة للمثيل بارابين وبروبيل بارابين (2.66 ×10^{-8} , 1.0^{7} × 10^{-7}) على التوالي، وطبقت الطريقة بنجاح على المستحضرات الصيدلانية المحتوية على المثيل بارابين والبروبيل بارابين بشكل شراب .

Abstract

In this study, a new technique was developed using rapid Cyclic voltammetry at hanging mercury electrode (HDME) and The anodic oxidation and cathodic reduction for the detrmination of two commonly used parabens (methylparaben (MP) and propylparaben (PP)) in maleate buffer at (pH 6) solution. The results show that the charge transfer processes were reversible. The method is used to determine methyl and propyl paraben in concentration range (2.66 × 10^{-8}, 1.07 × 10^{-7}) M at pH = 6 respectively. This method was applied successfully for the assay of the pharmaceutical preparations of the considered drugs.

Key words: Cyclic voltammetry,methyl and propyl paraben, drugs

Introduction

Cyclic voltammetry (CV) is the application of electrochemical methods for the characterization of colloidal quantum dots (QDs) attracts considerable attention as these methods may allow for monitoring of some crucial parameters, such as energetic levels of conduction and valence bands as well as surface traps and ligands under real conditions of colloidal solution[1] . It is widely used to study a variety of redox processes, for obtaining stability of reaction products, the presence of intermediates in oxidation-reduction reactions and electron transfer kinetics,[2] and the reversibility of a reaction.[3] CV can also be used to determine the electron stoichiometry of a system, the diffusion coefficient of an analyte, and the formal reduction potential, which can be used as an identification tool. In addition, because concentration is proportional to current in a reversible, Nernstian system, concentration of an unknown solution can be determined by generating a calibration curve of current vs. concentration [4-7].

This technique is based on varying the applied potential at a working electrode in both forward and reverse directions (at some scan rate) while monitoring the current. For example, the initial scan could be in the negative direction to the switching potential. At that point the scan would be reversed and run in the positive direction. Depending on the analysis, one full cycle, a partial cycle, or a series of cycles can be performed[8].

Rapid, simple, and safe for the environment voltammetric method for direct determination of total content of esters of p-hydroxybenzoic acid (PHB), named as parabens, in pharmaceutical preparations has been developed[9]. MP and PP, singly or in combination, are the most widely used preservatives. Parabens are recognized as the ideal preservatives because of their inexpensive production, good stability, biodegradability, neutral pH, lack of color, non-volatility, broad antimicrobial activity, as well as their relatively non-irritating and non-sensitizing properties [10,11]. Electrochemical methods such as Cyclic voltammetry are effective techniques for the determination of parabens. In comparison with the other methods, they offer several advantages such as simplicity, ease of sample preparation, short analysis time, and thus the lowering of their cost, comparable sensitivity, selectivity and detection limits. Therefore, electrochemical sensors are often used in conjunction with HPLC as well [12-14]. These methods are based on the electrochemical activity of parabens.

INSTRUMENTAION

Apparatus.

In the electrochemical measurements; we used Cyclic Voltammetry (CV) to indict determination of methyl and propyl paraben that were performed with 797 VA Computrace stand (Metrohm AG, CH-9101 Herisau, Switzerland)

Materials

Methyl Paraben Solution (0.001M).

It was prepared by dissolving 0.0038g in small amount of ethanol and the volume was completed to 25mL with distilled water in a volumetric flask.

Propyl Paraben Solution(0.001M).

It was prepared by dissolving 0.0045g in small amount of ethanol and the volume was completed to 25mL with distilled water in a volumetric flask.

Maleate Buffer Solution (0.05M) [15].

It was prepared by mixing 50mL of (0.05M) maleate acid, with XmL (0.10M) NaOH and diluted in distilled water to the volume up to 100 mL.

Sodium Hydroxide Solution (0.2M)

It was prepared by dissolving 0.8g of Sodium hydroxide in 100mL distilled water in a volumetric flask

Hydrochloric Acid solution, (0.2M)

It was prepared by appropriate dilution of 36% concentrated hydrochloric acid and diluted in distilled water to the volume up to 100 mL.

Acetic Acid Solution (0.2M)

It was prepared by diluting 2.88 mL of concentrated CH3COOH (17.36 N) with deionized water and the volume is completed to 250 mL in a volumetric flask.

Sodium Acetate Solution (0.2M).

It was prepared by dissolving 4.101g of Sodium Acetate in 100mL distilled water in a volumetric flask.

Acetate Buffer (pH 4.5) [16].

It was prepared by mixing volume 25.5mL of (0.2M) acetic acid, with 24.5mL (0.2M) of Sodium Acetate and the volume is completed to 100 mL with deionized water in a volumetric flask.

Removal of Oxygen

Oxygen has been removed from the buffer solution by degassing with nitrogen gas (99.9 %) for 300 seconds [17].

RESULTS AND DISCUSSIONS

Preliminary investigation

The CV Voltammogram of ($4.97x10^{-6}$) M of methyl and propyl paraben in maleate buffer at pH(6) solution (supporting electrolyte), using hanging droping mercury electrode (HDME), was recorded Figure ١ and Figure ٢ show a good CV peak reversible reduction and oxidation, reduction potential of 0.088 V and 0.090 V for reduction and oxidation processes versus Ag / AgCl sat. KCl reference electrode.

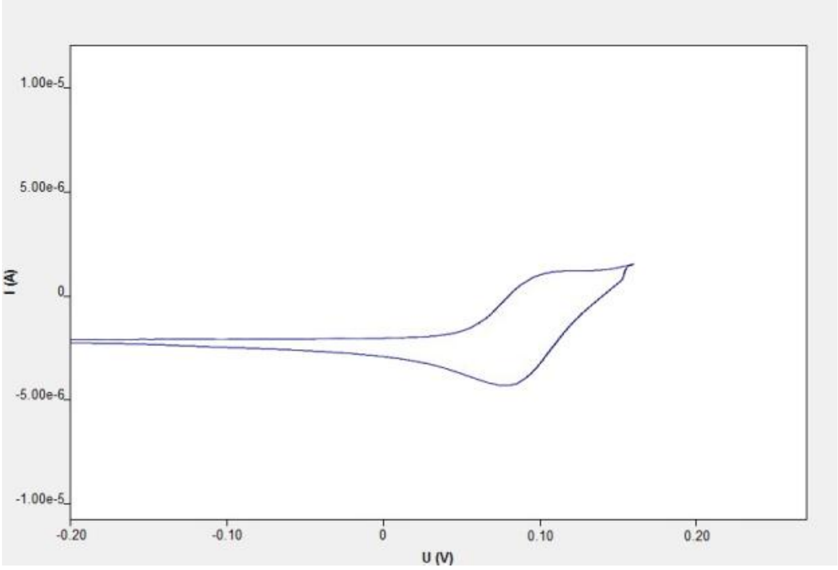

Figure 1: CV Voltammogram of Propyl Paraben

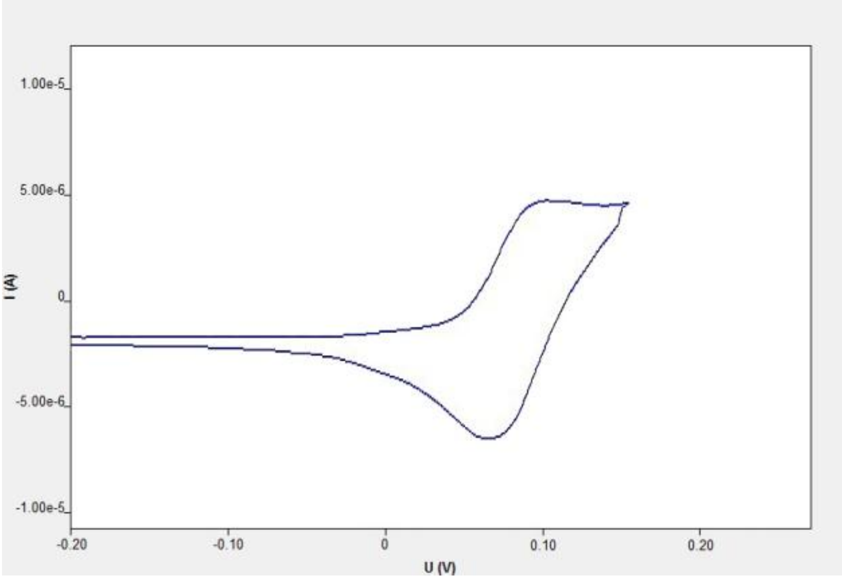

Figure 2: CV Voltammogram of Methyl Paraben

Study of Optimum Conditions at HDME.

A set of CV Voltammogram experiments were carried out in deareated solution containing ($4.97x10^{-6}$) M of methyl and propyl paraben in maleate buffer solution at pH (6). The measurements were performed by changing one of the operating conditions continuously and leaving all other constant. The best results obtained are represented by the heightest peak current or the best shape for reduction and oxidation of CV Voltammogram.

Effect of pH

The effect of pH on the cyclic voltammogram has been recorded in a solution containing ($4.97x10^{-6}$) M of methyl and propyl paraben in 10 mL of maleate buffer solution of various pH (2-10). The peak current anodic oxidation Ipa and cathodic reduction Ipc , peak reduction potential and peak oxidation potential are shown in the Table 1.

Table 1: Effect of pH on the Cyclic Voltammogram

pH	Ep (V) Cathodic	Ep (V) Anodic	Ip_a/Ip_c methyl paraben	Ip_a/Ip_c propyl paraben
3	0.031	0.02	1.60	1.66
4	0.051	0.034	1.50	1.51
5	0.073	0.057	1.50	1.62
6	0.098	0.078	1.40	1.48
7	0.12	0.099	1.65	1.52
8	0.14	0.13	1.59	1.61

the results demonstrate at pH ٦ optaiend highest peak current was used as optimum condition for all studied.

Effect of Drop Size

The effect of drop size on ($4.97x10^{-6}$)M of methyl and propyl paraben was studied for ionic in malate buffer solution at (pH 6), at different drop size between 1-9µl. Table 2 shows that 5µl drop size gives the heightest peak current of methyl and 6µl drop size gives the heightest peak current of propyl paraben.

Table 2: Effect of Drop Size for CV of Methyl and Propyl Paraben.

Drop Size µl	Cathodic methyl paraben		Anodic methyl paraben		Cathodic propyl paraben		Anodic propyl paraben	
	Ep (V)	Ip (Corr.) $\times10^{-٦}$ (A)	Ep (V)	Ip (Corr.) $\times10^{-٦}$ (A)	Ep (V)	Ip (Corr.) $\times10^{-٦}$ (A)	Ep (V)	Ip (Corr.) $\times10^{-٦}$ (A)
1	0.092	2.76	0.079	6.68	0.090	2.14	0.076	3.22
2	0.092	2.81	0.081	6.98	0.092	2.19	0.075	3.88
3	0.091	3.67	0.082	7.04	0.089	2.55	0.074	4.20
4	0.093	3.96	0.080	7.30	0.092	2,67	0.075	4.31
5	0.097	4.66	0.075	7.45	0.093	2.47	0.073	4.38
6	0.098	4.33	0.084	7.40	0.095	2.73	0.073	4.64
7	0.093	4.41	0.089	7.11	0.094	2.41	0.073	4.11
8	0.090	4.22	0.089	6.99	0.093	2.30	0.074	3.53
9	0.088	4.13	0.089	6.54	0.090	2.33	0.072	3.33

Effect of Cleaning Time

CV Voltammograams were recorded on HDME using ($4.97x10^{-6}$) M methyl and propyl paraben in 10mL maleate buffer solution at (pH 6), at a different Cleaning time between (0-50) Sec. The results are shown in table 3

Table3: Effect of Cleaning Time for CV of Methyl Paraben and Propyl Paraben.

Cleaning time (Sec)	Cathodic methyl paraben		Anodic methyl paraben		Cathodic propyl paraben		Anodic propyl paraben	
	Ep (V)	Ip (Corr.) $\times10^{-٦}$ (A)	Ep (V)	Ip (Corr.) $\times10^{-٦}$ (A)	Ep (V)	Ip (Corr.) $\times10^{-٦}$ (A)	Ep (V)	Ip (Corr.) $\times10^{-٦}$ (A)
0	0.097	4.66	0.075	7.45	0.095	2.47	0.073	4.44
10	0.098	4.72	0.073	7.60	0.097	2.54	0.072	4.69
20	0.090	4.55	0.076	7.46	0.097	2.35	0.072	4.41

30	0.088	4.22	0.078	6.55	0.097	2.39	0.069	4.34
40	0.088	4.10	0.078	6.51	0.096	2.43	0.071	3.73
50	0.089	3.66	0.079	6.34	0.096	2.25	0.071	3.67

The results in table above shows that (10) sec gives the heighest peak current of methyl and propyl paraben and the purpose of cleaning time to remove impurities

Effect of Deposition Time.

Voltammograms were recorded for ($4.97x10^{-6}$)M methyl and propyl paraben at different deposition time between (0-60) Sec. The results shown in table (4)

Table 4: Effect of Deposition Time for CV of Methyl Paraben and Propyl Paraben.

Deposition time (Sec.)	Cathodic methyl paraben		Anodic methyl paraben		Cathodic propyl paraben		Anodic propyl paraben	
	Ep (V)	Ip (Corr.) $\times10^{-6}$ (A)	Ep (V)	Ip (Corr.) $\times10^{-6}$ (A)	Ep (V)	Ip (Corr.) $\times10^{-6}$ (A)	Ep (V)	Ip (Corr.) $\times10^{-6}$ (A)
0	0.097	4.09	0.075	7.15	0.095	2.07	0.073	4.19
5	0.098	4.72	0.073	7.60	0.097	2.54	0.073	4.69
10	0.090	4.66	0.076	7.45	0.097	2.47	0.073	4.44
20	0.088	4.22	0.078	6.55	0.097	2.39	0.069	4.34
30	0.088	4.10	0.078	6.51	0.096	2.43	0.071	3.83
40	0.089	3.66	0.077	6.34	0.096	2.25	0.071	3.98
50	0.097	4.76	0.072	7.85	0.097	2.97	0.073	4.84
60	0.097	4.63	0.072	7.32	0.096	2.66	0.073	4.22

Table (4) shows that (50) sec gives the heightest peak current of methyl and propyl paraben .

Effect of Equilibrium Time

For $(4.97x10^{-6})$M paraben compounds CV Voltmmograms were recorded at different equilibrium time on (HDME) between (0-8) second at deposition time (50) sec. Table (5) shows that (5) and (6) sec. for equilibrium time gives the best current peak shape for anodic oxidation Ipa and cathodic reduction Ipc..

Table5: Effect of Equilibrium Time for CV of Methyl Paraben and Propyl Paraben.

Equilibrium time (sec)	Cathodic methyl paraben		Anodic methyl paraben		Cathodic propyl paraben		Anodic propyl paraben	
	Ep (V)	Ip (Corr.) $\times 10^{-6}$ (A)	Ep (V)	Ip (Corr.) $\times 10^{-6}$ (A)	Ep (V)	Ip (Corr.) $\times 10^{-6}$ (A)	Ep (V)	Ip (Corr.) $\times 10^{-6}$ (A)
0	0.097	4.09	0.07	7.15	0.095	2.07	0.07	4.19
1	0.098	4.72	0.07	7.60	0.097	2.14	0.07	4.29
2	0.090	4.66	0.07	7.45	0.097	2.47	0.07	4.44
3	0.088	4.22	0.07	6.55	0.097	2.39	0.06	4.34
4	0.088	4.76	0.07	6.85	0.096	2.43	0.07	3.83
5	0.089	4.88	0.07	7.98	0.096	2.97	0.07	4.84
6	0.097	4.73	0.07	7.81	0.097	3.10	0.06	5.02
7	0.096	4.51	0.07	7.74	0.097	2.79	0.07	4.65

Effect of Voltage Step

The effect of voltage step for $(4.97x10^{-6})$ M methyl and propyl paraben was studied on HDME using maleate buffer solution at (pH 6), at different voltage step between (0.01-0.002) V.

Table 6: Effect of Voltage Step for CV Methyl Paraben and Propyl Paraben.

Voltage step (V)	Cathodic methyl praben		Anodic methyl paraben		Cathodic propyl paraben		Anodic propyl paraben	
	Ep (V)	Ip (Corr.) $\times 10^{-8}$ (A)	Ep (V)	Ip (Corr.) $\times 10^{-8}$ (A)	Ep (V)	Ip (Corr.) $\times 10^{-8}$ (A)	Ep (V)	Ip(Corr.) $\times 10^{-8}$ (A)
0.002	0.09	4.66	0.07	7.45	0.097	2.45	0.07	4.24

0.004	0.09	4.88	0.07	7.98	0.098	2.97	0.06	4.84
0.006	0.1	4.93	0.07	8.02	0.098	3.23	0.06	5.31
0.008	0.09	4.44	0.07	7.78	0.098	2.25	0.07	4.98
0.01	0.1	4.63	0.07	7.61	0.098	2.90	0.06	4.82

Table (6) shows that (0.006) voltage step gives the heightest peak current of methyl and propyl paraben.

Effect of Sweep Rate

Voltammograms were recorded on HDME using (4.97×10^{-6}) M methyl and propyl paraben in 10 mL maleate buffer solution at (pH 6), at a different sweep rate between (0.1-0.9) Sec. The results are shown in table 7 and Figures ٣ and ٤.

Table 7: Effect of Sweep Rate for CV of Methyl Paraben and Propyl Paraben.

Sweep Rate (V/Sec.)	Cathodic methyl paraben		Anodic methyl paraben		Cathodic propyl paraben		Anodic propyl paraben	
	Ep (V)	Ip (Corr.) $\times10^{-٦}$ (A)	Ep (V)	Ip (Corr.) $\times10^{-٦}$ (A)	Ep (V)	Ip (Corr.) $\times10^{-٦}$ (A)	Ep (V)	Ip (Corr.) $\times10^{-٦}$ (A)
0.1	0.1	3.87	0.071	7.11	0.098	2.45	0.068	4.20
0.2	0.1	3.99	0.071	7.43	0.098	2.54	0.068	4.21
0.3	0.1	4.31	0.071	7.47	0.098	2.56	0.068	4.30
0.4	0.1	4.38	0.071	7.51	0.098	2.71	0.068	4.34
0.5	0.1	4.76	0.071	7.54	0.098	2.75	0.068	4.87
0.6	0.1	4.80	0.071	7.66	0.098	2.88	0.068	4.89

0.7	0.1	4.87	0.071	7.90	0.098	2.89	0.068	4.99
0.8	0.1	4.90	0.071	7.94	0.098	3.0	0.068	5.11
0.9	0.1	5.0	0.071	8.03	0.098	3.30	0.068	5.41

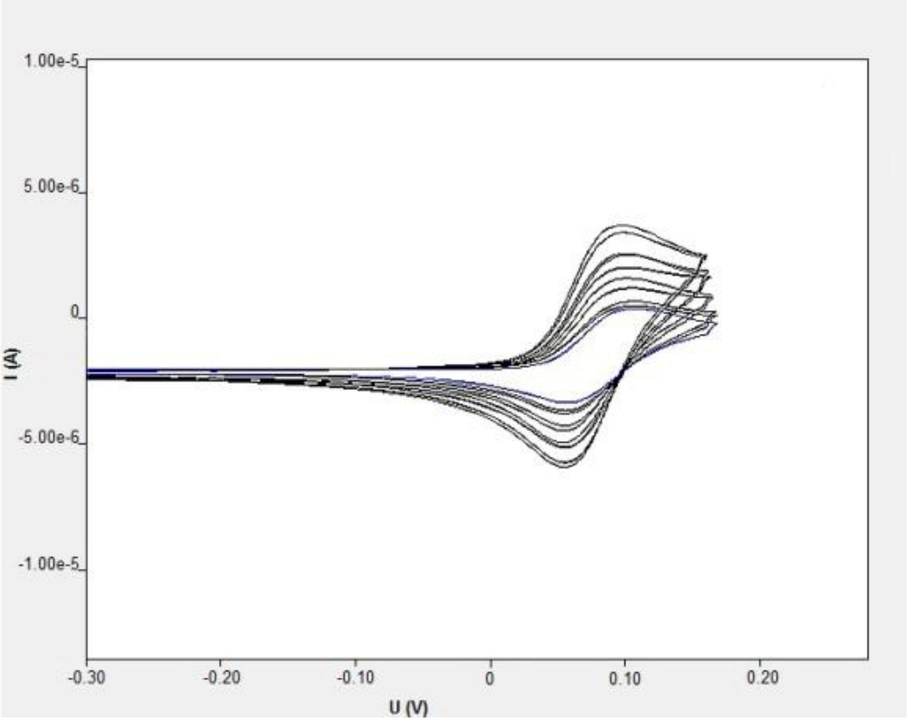

Figure 3: Effect of Sweep Reat for CV Propyl Paraben(4.97 × 10^{-6}M).

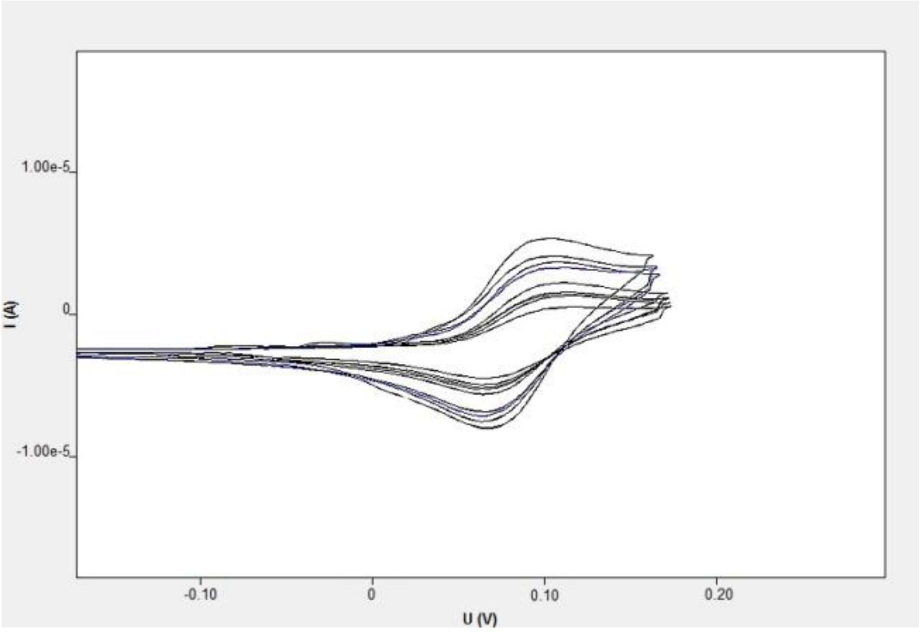

Figure 4: Effect of Sweep Rate for CV Methyl Paraben(4.97 × 10^{-6}M).

Results in Table 8 and Figures 5 and 6 indicate increasing diffusion current of cathodic Ipc and anodic Ipa with a sweep rate, which shows that the process of oxidation and reduction is transmission charge only (E-process only)[18,19

Table 8: Optimum Condition for Methyl Paraben and Propyl Paraben.

	Methyl paraben	Propyl paraben
Electrode	HDME	HDME
Drop size µl	5	6
Initial purge time (sec)	300	300
Cleaning time (sec)	10	10
Deposition time (sec)	50	50
Equilibrium time (sec)	5	6
Voltage step (V)	0.006	0.006
Sweep rate (V)	0.9	0.9

The cyclic voltagramme of paraben compounds are two peaks, which presented the oxidation and reduction as in equation below.

Δ E = ECathode – E anode = 0.059/n, then n = 2e-

$\Delta E_{\text{propyl paraben}} = 0.098 - 0.068 = 0.03$ $\Delta E_{\text{methyl paraben}} = 0.1 - 0.071 = 0.029$

The obtained value is near the theoretical value 0.059v indicates is that the oxidation and reduction is a reverse process.

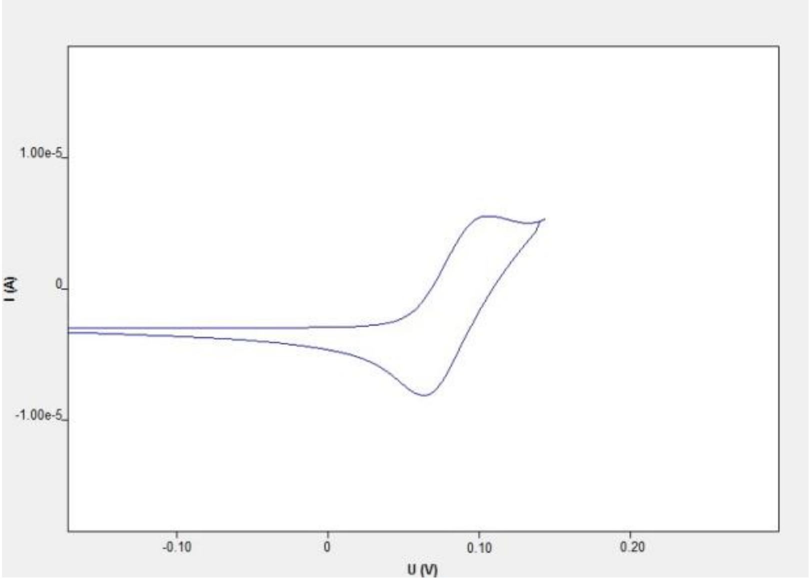

Figure 5: The Final Peak Methyl Paraben After Optimum Condition (4.97×10^{-6}M).

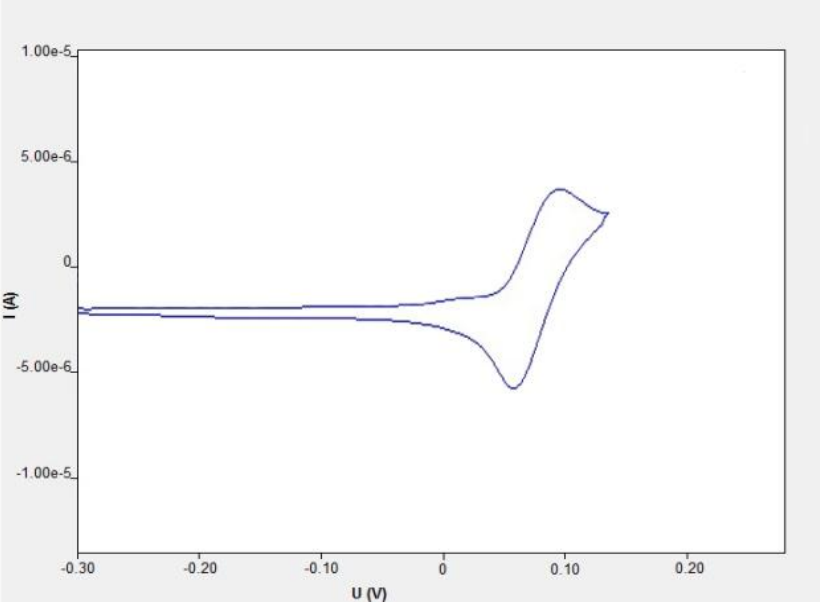

Figure 6: The final Peak Propyl Paraben After Optimum Condition(4.97 × 10^{-6}M).

Calibration curve of Methyl and Propyl Paraben.

Using the optimum conditions (8) CV Voltammogram has been recorded on degassed solution in (4.74x$10^{-6)}$ M methyl and propyl paraben in 10 ml maleate buffer solution at (pH 6) (degassing for 300). Peak current of anodic oxidation $Ip_{\circ a}$ 4.01x10^{-6} and Peak current of cathodic reduction $Ip_{\circ c}$ 2x10^{-6}. Then different amount of (1x10^{-3})M methyl paraben and propyl paraben has been added (degassing 15 sec.) and CV Voltammogram has been recorded again ,(peak current =Ip_a and Ip_c) the increase in peak current (ΔIp) belongs to the concentration of methyl paraben and propyl paraben added ,the equation was applied $\Delta Ip=Ip-Ip_{o.}$ The results obtained are shown in Tables (9) and (10) and figures (7), (8), (9) and (10).

Table 9: The Effect of Concentration on Peak Current(ΔIp) Of Cathodic and Anodic Methyl Paraben at pH(6).

Conc.	Cathodic		Anodic		
×10^{-6} (M)	Ep_c (V)	ΔIp (Corr.) ×10^{-6}(μA)	Ep_a (V)	ΔIp (Corr.) ×10^{-6}(μA)	Ip_a/Ip_c
1.99	0.099	0.97	0.069	1.19	1.22
2.99	0.099	1.67	0.069	2.10	1.25

3.98	0.1	2.30	0.069	3.07	1.33
4.97	0.1	3.00	0.071	4.02	1.34
5.96	0.1	3.60	0.071	4.96	1.37
6.95	0.1	4.33	0.071	5.90	1.36
7.93	0.1	4.90	0.071	6.79	1.38
Intercept		-3×10^{-7}		-7×10^{-7}	
Slope		0.6642		0.9484	
r^2		0.9995		0.9999	

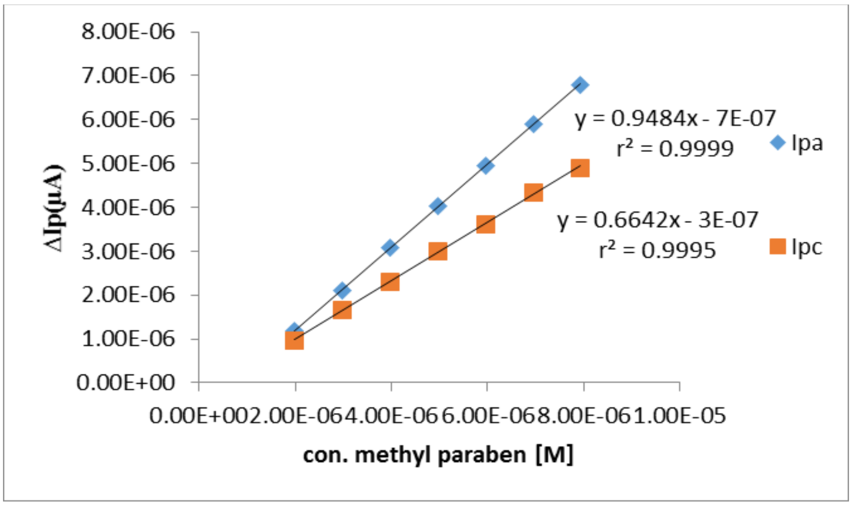

Figure 7: Calibration Curve($1.99\text{x}10^{-6}$- $7.93\text{x}10^{-6}$) M for Methyl Paraben.

From Figure 7 at Epc= 0.1V ,Epa= 0.071 V it has been found that methyl Paraben gives a linear relationship between ΔIp and Concentration over the range($1.99\text{x}10^{-6}$- $7.93\text{x}10^{-6}$) M for Methyl Paraben and correlation coefficient was Ipc(r^2 = 0.9995) and Ipa (r^2 = 0.9999).

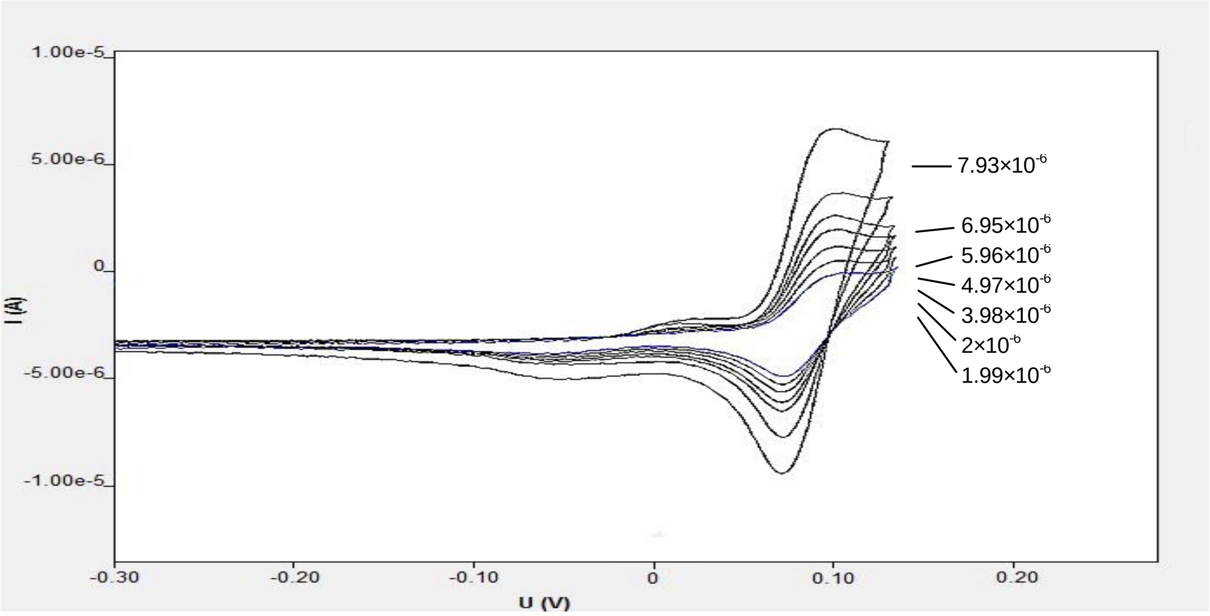

Figure 8: CV Voltammograms for calibration curve of methyl paraben.

Table10: The Effect of Concentration on Peak Current(ΔIp) of Cathodic and Anodic Propyl Paraben at pH(6).

Conc.$\times10^{-6}$ (M)	Cathodic		Anodic		Ip_a/Ip_c
	Ep_c (V)	ΔIp (Corr.)$\times10^{-6}$(μA)	Ep_a (V)	ΔIp (Corr.)$\times10^{-6}$(μA)	
99.9	0.098	0.19	0.068	0.23	1.20
1.99	0.098	0.47	0.068	0.51	1.08
2.99	0.098	0.76	0.068	0.81	1.06
3.98	0.098	1.04	0.068	1.10	1.05
4.97	0.098	1.30	0.068	1.40	1.07
5.96	0.098	1.55	0.068	1.71	1.10
6.95	0.098	1.89	0.068	1.98	1.04
7.93	0.098	2.16	0.068	2.30	1.06
8.9	0.098	2.43	0.068	2.61	1.07
9.8	0.098	2.73	0.068	2.94	1.08
Intercept		-1×10^{-7}		-1×10^{-7}	
Slope		0.2854		0.305	

r^2		0.9994		0.9992	

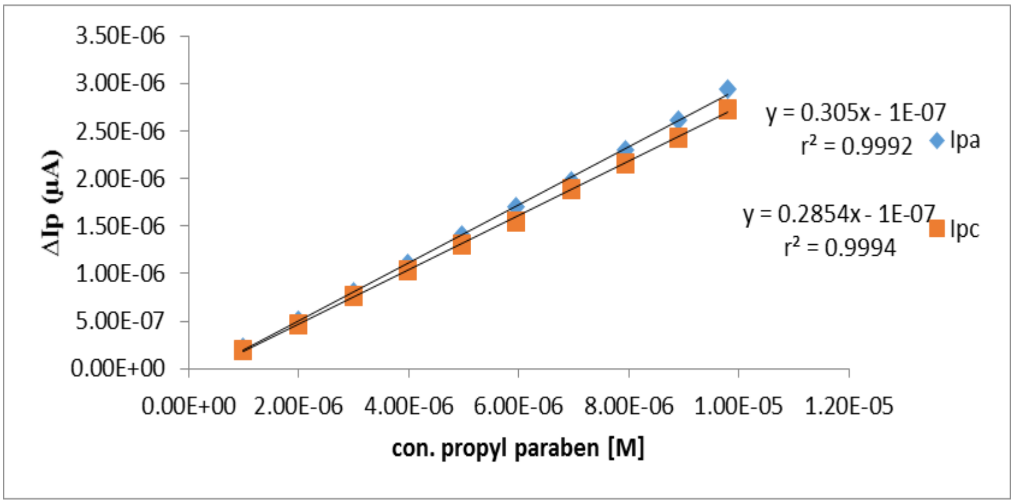

Figure 9: Calibration Curve ($9.99x10^{-7}$- $9.80x10^{-6}$) M for Propyl Paraben.

From Figure 7 at Epc= 0.098V ,Epa= 0.068 V it has been found that methyl Paraben gives a linear relationship between ΔIp and Concentration over the range($9.99x10^{-7}$- $9.80x10^{-6}$) M for Propyl Paraben and correlation coefficient was Ipc(r^2 = 0.9994) and Ipa (r^2 = 0.9992).

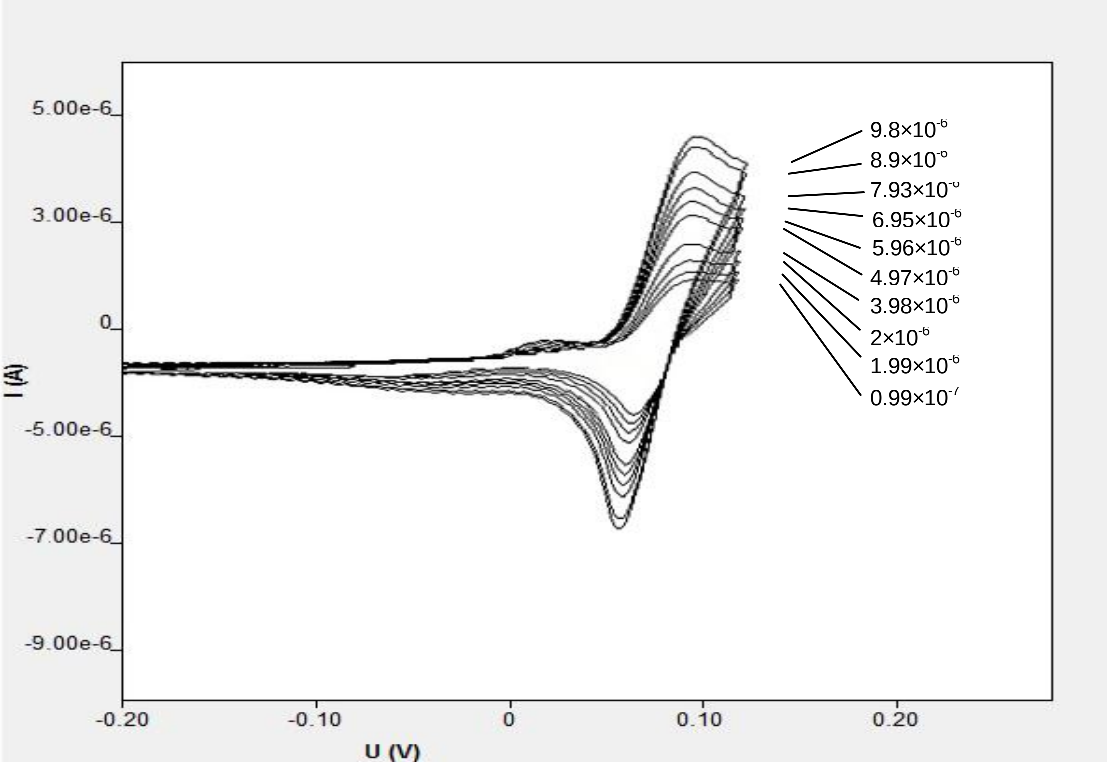

Figure 10: CV Voltammograms for Calibration Curve of Propyl Paraben.

Mechanism of Reaction.

It is possible that the oxidiation and reduction of paraben follow the mechanics:

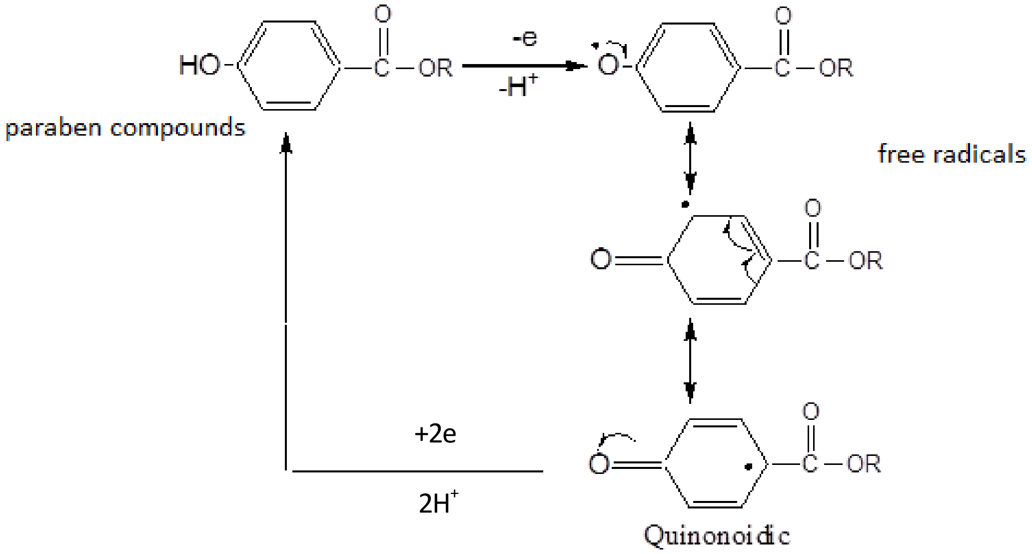

Figure 11: Proposed electrochemical oxidation – redaction mechanism for paraben compounds.

Accuracy and Precision of the Method.

CV Voltammograms were rcorded at three different concentrations of methyl paraben and propyl paraben in 10 mL of maleate buffer solution at pH(6) under the optimum conditions, table 11.The results obtained are shown in table12.

Table 11: Accuracy and Precision for Determination of Methyl Paraben and Propyl Paraben.

Con.[M] compounds parabn	methyl paraben		propyl paraben	
	RSD%	Recovery%	RSD%	Recovery%
2.99×10^{-6}	0.4360	99.13	0.9345	99.25
4.97×10^{-6}	1.5661	99.02	0.6142	100.29
6.95x10-^{6}	0.6115	100.29	1.5530	98.67

The results indicated that the method has a good accuracy and precision.

Limit of detection LOD.

Table 12: Limit of Detection for Methyl and Propyl Paraben

Compound	Low concentration	SD	LOD=3.C.SD/X
Methyl paraben	1.99×10^{-6}	0.00547	2.66×10^{-8}
Propyl paraben	9.99×10^{-7}	0.04189	1.07×10^{-7}

Interference Effect.

The Interference effect to CV Voltammograms (4.97×10^{-6}) M of methyl and propyl paraben was studied, increasing amounts of interference were added and measured dependent to conditions in the table 8. Table 13 shows the results.

Table 13: Interference Effect

Foreign Compound	**Foreign added µl**	**Recovery%**		**E_{re}%**	
		Methyl Paraben	**proyl paraben**	**Methyl paraben**	**Proyl paraben**
Na^+	20	97.69	100.93	-2.3076	+0.9345
	50	96.92	101.12	-3.0769	+1.1214
	70	102.30	101.86	+2.3076	+1.8691
Ni^{+2}	20	100.76	99.71	+0.7692	-0.2803
	50	101.53	99.62	+1.5380	-0.3738
	70	101.53	101.96	+1.6380	+1.8691
Br^-	20	100.76	100.18	+0.7692	+0.1869
	50	100.84	99.53	+0.8460	-0.4672
	70	102.30	101.68	+2.3087	+1.6822
Sucrose	20	99.84	100.09	-0.1538	+0.0934
	50	99.23	99.34	-0.7692	-0.6542
	70	100.07	98.69	+0.0769	-1.3084
K+	20	99.69	100.09	-0.3076	+0.0934
	50	98.84	99.71	-1.1538	-0.2803
	70	99.84	99.81	-0.1538	-0.1869
Glucose	20	99.61	100.28	-0.3846	+0.2803
	50	98.76	100.93	-1.2307	+0.9345
	70	100.23	99.06	+0.2307	-0.9345
Fe^{+2}	20	99.46	100.09	-0.5384	+0.0935
	50	97.92	99.06	-2.0760	-0.9340
	70	97.53	100.93	-2.4615	+0.945
Cu^{+2}	20	100.76	99.62	+0.7692	-0.3738
	50	101.07	100.37	+1.0769	+0.3740
	70	101.53	100.28	+1.5384	+0.2803
SO_3^{-2}	20	99.15	99.90	-0.8461	-0.0934
	50	99.23	100.65	-0.7692	+0.6542
	70	100.61	101.02	+0.6153	+1.0280

This table shows that there is no highest interference on a high peak current with the presence of some ions and some additives that may be present with the studied materials

Pharmaceutical Applications

The proposed method was applied for the determination of Methyl Paraben and propyl paraben in syrups by the analysis of three different concentrations of samples using the analytical procedure. The results obtained are summarized in Table 14.

Table 14: Application of the Proposed Method for Determination of Methyl Paraben and Propyl Paraben in Pharmaceutical Syrups.

Comp.	**Drug (trade name)**	**Nominal value of compounds (g/100ml syrup)**	**Manufa-cturer**	**Taken (M)**	**Found* (M)**	**RSD%**	**E_r%**	**Rec%**
Methyl paraben	Metronida-zole	0.1	**Samara Drugs of Iraq (SDI)**	$1.99x10^{-6}$	$1.98x10^{-6}$	0.1384	-0.1005	99.89
				$3.99x10^{-6}$	$3.97x10^{-6}$	0.1695	-0.5012	99.49
				$5.96x10^{-6}$	$5.92x10^{-6}$	0.7223	0.6711	99.32
	Samafed	0.15		$1.99x10^{-6}$	$2.03x10^{-6}$	1.9908	2.0101	102.01
				$3.99x10^{-6}$	$3.96x10^{-6}$	0.9225	-0.7518	99.24
				$5.96x10^{-6}$	$5.98x10^{-6}$	0.1608	0.3355	100.34
Propyl parabn	Cameleon	0.09		$1.99x10^{-6}$	$2.02x10^{-6}$	1.2667	1.5075	101.50
				$3.99x10^{-6}$	$4.03x10^{-6}$	3.2950	1.0022	101.00

				$5.96x10^{-6}$	$5.98x10^{-6}$	0.2250	0.3356	100.33
	Antipyrol	0.08		$1.99x10^{-6}$	$2.01x10^{-6}$	1.1489	1.0050	101.01
				$3.99x10^{-6}$	$4.06x10^{-6}$	1.2334	1.7543	101.75
				$5.96x10^{-6}$	$6.13x10^{-6}$	1.3185	2.3372	102.33

* Average of three determinations.

Conclusion

The proposed method proved to be rapid, simple, sensitive and safe for the cyclic voltammetric method for determination of methyl hydroxybenzoate and , propyl 4-Hydroxybenzoic named as parabens, in pharmaceutical preparations has been developed. Performed determinations were based on cyclic voltammetry (CV) at hanging mercury electrode (HDME) in maleate buffer at Ph(6) solution. This developed procedure allows the determination of parabens without the need for their separation from the matrices, and there by aids in achieving desired accuracy, precision, and a low detection limit of the results. The method was applied successfully for the assay of the pharmaceutical preparations of the studied drugs.

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