J Appl Electrochem (2010) 40:499–505
DOI 10.1007/s10800-009-0021-1

ORIGINAL PAPER

Differential pulse voltammetric determination of chlorphenoxamine hydrochloride and its pharmaceutical preparations using platinum and glassy carbon electrodes

Nour T. Abdel-Ghani · Gouda M. Abu-Elenien · Salwa H. Hussein

Received: 16 May 2009 / Accepted: 25 September 2009 / Published online: 10 October 2009

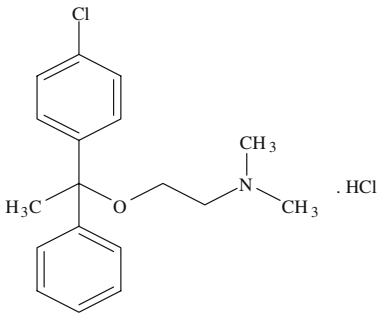
Abstract Voltammetric methods have been used for the determination of chlorphenoxamine hydrochloride (Ch-HCl) in raw material and in its pharmaceutical preparations (Allergex and Allergex caffeine tablet). It was found that Ch-HCl gives a characteristic cyclic voltammetric (CV) and differential pulse voltammetric (DPV) peak in acetonitrile using platinum and glassy carbon working electrodes. The I_p of the DPV peak increases linearly within the concentration range from 4.5×10^{-4} to 1.0×10^{-2} mol L^{-1} of the investigated drug. The concentration of Ch-HCl in raw drug material and in its pharmaceutical preparations was determined using the standard addition method, Randles–Sevcik equation and indirectly via its complexation with sodium tetraphenylborate (NaTPB). The obtained over all average recoveries were 101.44 and 100.49% with SD 0.45 and 0.38 ($n = 4$) for platinum and glassy carbon electrodes, respectively. The effect of scan rate, sample concentration, and supporting electrolyte on the I_p and E_p was also investigated.

Keywords Chlorphenoxamine hydrochloride (Ch-HCl) · Cyclic voltammetry · Differential pulse voltammetry · Acetonitrile · Platinum electrode · Glassy carbon electrode

1 Introduction

Chlorphenoxamine hydrochloride (Ch-HCl) is a well known antihistamine drug, which has been used clinically for many years. Several methods are available for its determination including spectrophotometric with chemometric methods [1–6], potentiometric method using NIO Metrhom electrode [7], thin layer chromatography [8, 9], plastic membrane ion selective electrode based on Tetrakis (4-chlorophenyl)borate [10], indirectly via its complexation with metal ions using Atomic Absorption Spectrometry [11], and polarography [12]. No voltammetric methods have been published for the determination of Ch-HCl.

Ch-HCl does not show inherent voltammetric activity in aqueous media therefore the voltammetric determination was carried out in acetonitrile using platinum and glassy carbon as working electrodes without the need of further extraction or time consuming isolation methods.



Chlorphenoxamine Hydrochloried

2 Experimental

2.1 Apparatuses

The voltammetric experiments were performed using E.G&G Princeton research potentiostat/galvanostat model 263A equipped with computer software (Echem M270). The used cell has a three-electrodes system; a platinum wire auxiliary electrode and silver wire reference electrode

N. T. Abdel-Ghani (✉) · G. M. Abu-Elenien · S. H. Hussein
Chemistry Department, Faculty of Science, Cairo University, Cairo, Egypt
e-mail: noureta2002@yahoo.com

which are 0.5 and 1 mm in diameter, respectively, are used in conjunction with either platinum or glassy carbon as working electrode (2 mm in diameter). An automatic pipet (0–250 μL) (Brand GMBH Germany) was used to deliver the required volumes.

2.2 Reagents and solutions

The active ingredient pharmaceutical drug Ch-HCl (mol. wt: 340.29) and its pharmaceutical preparations Allergex and Allergex caffeine tablets (20 mg/tablet) were provided from EPICO, Egypt. All other chemicals used such as acetonitrile, NaTPB, and supporting electrolytes ($LiClO_4$, Bu_4NPF_6, and Bu_4NCl) were analytical grade reagents (Merk and Fluka). The solutions were deareated with purified Argon. Standard solution 5.0×10^{-2} mol L^{-1} of Ch-HCl was prepared by accurately weighing the appropriate weight and dissolving it in acetonitrile then transferring in a 50 mL measuring flask and completing to the mark with acetonitrile. For tablets solution, 10 tablets of Allergex or Allergex caffeine were weighed, finely grounded and an amount equivalent to the calculated weight of pharmaceutical preparations to produce a 1.0×10^{-2} mol L^{-1} solution was weighed and dissolved in acetonitrile, then filtered in a 50 mL measuring flask and completed to the mark with acetonitrile.

2.3 Effect of supporting electrolyte

A 4 mL portion of acetonitrile containing 1.0×10^{-1} mol L^{-1} $LiClO_4$ was added to the three electrode cell and deareated with Argon for 1 min and the background voltammogram was recorded by scanning the potential toward the positive direction using the selected waveform [13]. Then 1 mL 5.0×10^{-2} mol L^{-1} of the investigated solution was introduced to the electrolysis cell and the produced voltammogram was recorded. The previous procedure was repeated with both Bu_4NPF_6 and Bu_4NCl as supporting electrolytes, where the glassy carbon electrode should be polished before each measurement [14].

2.4 Effect of scan rate

Scan rate (v) is one of the most important factors that affect the measurements in cyclic voltammetry since it reflects the type of mass transfer that taking place [15]. The effect of scan rate was studied by recording the voltammograms of 5.0×10^{-3} mol L^{-1} of the investigated drug solution at different scan rates ranging from 30 to 200 mV s^{-1}.

2.5 Construction of the calibration graph

After recording the background voltammogram, different volumes of the drug stock solution, 5×10^{-2} mol L^{-1}, were added using automatic transfer pipette and the voltammograms produced after each addition were recorded. The calibration graph was constructed by plotting I_p versus the concentration. Generally, I_p is measured as the difference between the peak of each voltammogram and that of the supporting electrolyte (background voltammogram).

2.6 Determination of Ch-HCl in pure form and pharmaceutical preparations

The concentration of Ch-HCl was determined using the following methods.

2.6.1 Standard addition method [16]

In this method, the voltammogram of the supporting electrolyte was recorded then a known volume (V_u) of unknown concentration (C_u) of the investigated drug was added and the resulting DPV was recorded and I_{p_1} was measured then a known volume (V_s) of known concentration (C_s) of Ch-HCl was added and the DPV was recorded and I_{p_2} was measured. The C_u can be calculated using the following equation:

$$C_u = \frac{I_{p_2} C_s V_s}{(I_{p_2}(V_u + V_s)) - I_{p_2} V_u}$$

2.6.2 Randles–Sevcik equation [17]

The Randles–Sevcik equation is an equation that correlates peak current (I_p) with concentration (C), $I_p = kC$, where k is a constant that include different cell parameters such as transfer coefficient, number of electrons involved in the reaction, electrode area, diffusion coefficient, and scan rate. The unknown concentration Ch-HCl can be easily determined in two steps; first, determining k by introducing the known concentration of Ch-HCl to the three electrode cell, recording the DPV, and measuring I_p and using Randles–Sevcik equation, the constant k can be calculated. Then under the same conditions the unknown concentration of the investigated drug was subjected to the cell and after measuring I_p the concentration was determined using the previously calculated value of k.

2.6.3 Complexation with NaTPB

NaTPB is a well known complexing agent that is commonly used in potentiometric [18] and conductimetric [19] determinations of pharmaceutical raw materials, and it was found that NaTPB is soluble in acetonitrile and react with Ch-HCl to form a soluble complex which has a characteristic DPV. The I_p of the formed complex increases with decrease of that of Ch-HCl. The concentration of Ch-HCl can be determined by the addition of small volume

increment of known concentration of NaTPB to the unknown concentration of the investigated drug and recording the voltammogram after each addition and the end point takes place by determining the volume where no further decrease on the peak of Ch-HCl occurs.

2.7 Validation of method

The validation of the proposed procedure for the quantitative assay of examined drug was examined via evaluation of the LOD, LOQ, repeatability, recovery, selectivity, and ruggedness.

Linearity and range of the method was done by constructing a calibration curve within the concentration range 1.0×10^{-5}–5.0×10^{-2} mol L^{-1} and finding out the regression equation, limit of detection (LOD), and limit of quantification (LOQ).

Precision and accuracy of the method were demonstrated by repeatability studies where the measurement of standard solutions was repeated four times and the mean recovery and SD were calculated. The selectivity of the proposed procedure was examined in the presence of some common excipients and the mean recovery was calculated.

The ruggedness of the method was carried out by changing the experimental conditions such as, changing the source of reagents and solvent (different manufactures), and changing the supporting electrolytes, working and reference electrodes.

Stability of the analytes, standard, and sample solutions were subjected to long term (3 days) stability studies. The stability of these solutions was studied by performing the experiment and looking for the change in the voltammogram compared with freshly prepared solutions.

3 Results and discussion

Chlorophenoxamine hydrochloride does not show inherent voltammetric activity in aqueous solution, but it shows an anodic response in acetonitrile at platinum and glassy carbon electrodes. This may be attributed to the more basic character of acetonitrile [20] compared with water since acetonitrile can accept the proton of the hydrochloride moiety of the drug to form the conjugate acid $CH_3C \equiv \overset{+}{N}H$ where the hydrochloride moiety of the drug can be added analogous to the addition of water at the first stage of hydration [21]. The peaks were obtained around 1,300 mV for both electrodes and shift to more positive potential with increasing the concentration of Ch-HCl. Changing the supporting electrolyte to $LiClO_4$ resulting in higher I_p and at E_p far from the other peak that appear as the result of

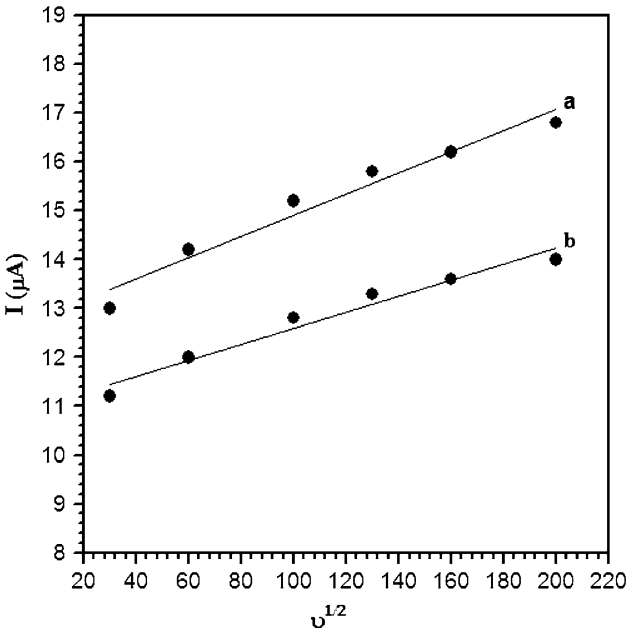


Fig. 1 Variation of I_p of 5.0×10^{-3} mol L^{-1} Ch-HCl with $v^{1/2}$ using (*a*) platinum and (*b*) glassy carbon electrodes

presence of caffeine as excipient with the investigated drug in Allergex caffeine tablets. It was found that the I_p increases linearly with the square root of the scan rate ($v^{1/2}$), Fig. 1, which reveals that the mass transfer takes place via diffusion [22]. All subsequent experiments have been done using $LiClO_4$ as supporting electrolyte and at scan rates of 100 and 130 mV s^{-1} for platinum and glassy carbon electrodes, respectively, because at these values the sensitivity is relatively high and voltammetric curves are well shaped with a relatively narrow peak width.

3.1 Calibration plots and limits of detections

The CV and DPV voltammograms for different concentrations of Ch-HCl were recorded at platinum and glassy carbon electrode as shown in Figs. 2, 3. The CV voltammograms exhibited smaller reverse peaks which resembles EC mechanism, where the product of oxidation of the drug to form a radical cation is chemically removed from the surface [22].

$$O + ne \leftrightarrow R \rightarrow Z$$

The dependence of the DPV peak current on Ch-HCl concentration shows a linear relationship from 4.5×10^{-4} to 1.0×10^{-2} mol L^{-1} for both platinum and glassy carbon electrode. The calibration graphs were constructed three times and the mean slope (*m*) and standard deviation (SD) were calculated. The regression equations were:

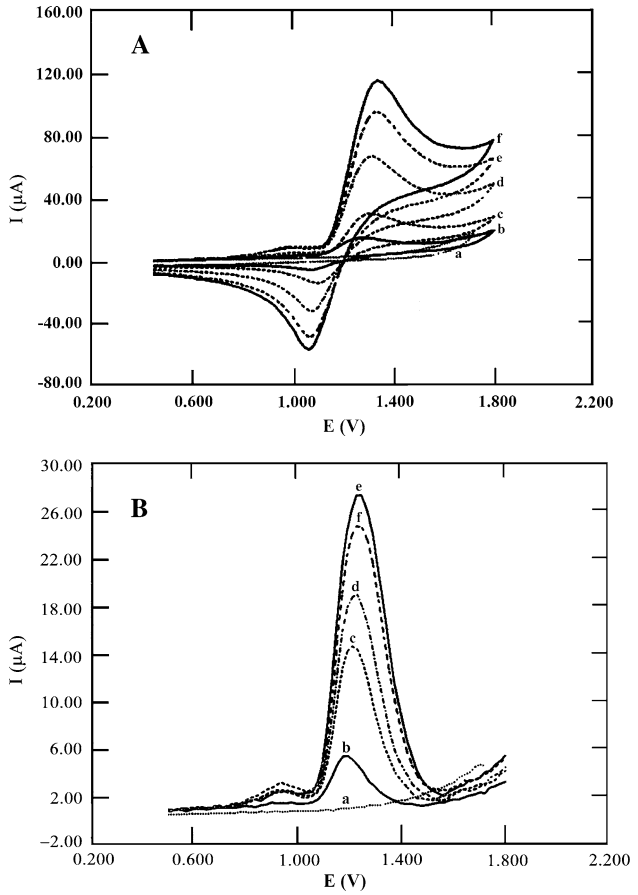


Fig. 2 CV (**A**) and its corresponding DPV (**B**) for different concentrations of Ch-HCl at Pt electrode: (*a*) supporting electrolyte, (*b*) 9.8×10^{-4}, (*c*) 3.7×10^{-3}, (*d*) 5.4×10^{-3}, (*e*) 8.3×10^{-3}, and (*f*) 1.0×10^{-2} mol L^{-1}

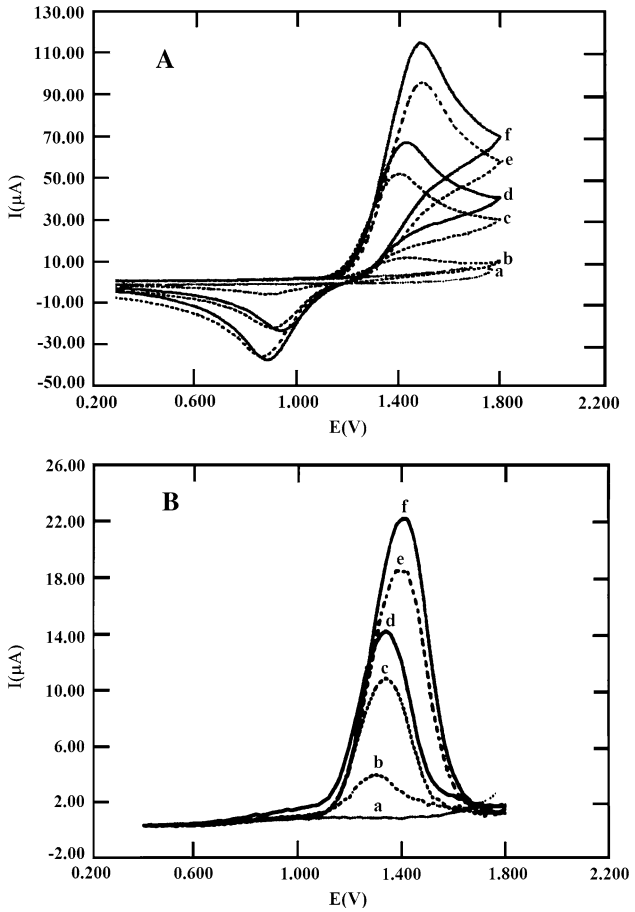


Fig. 3 CV (**A**) and its corresponding DPV (**B**) for different concentrations of Ch-HCl at glassy carbon electrode: (*a*) supporting electrolyte, (*b*) 9.8×10^{-4}, (*c*) 3.7×10^{-3} (*d*) 5.4×10^{-3}, (*e*) 8.3×10^{-3}, and (*f*) 1.0×10^{-2} mol L^{-1}

$I\,(\mu A) = 1{,}732\ C\,(\text{mol L}^{-1}) + 2.4$ for platinum, and

$I\,(\mu A) = 1{,}550\ C\,(\text{mol L}^{-1}) + 2.4$ for glassy carbon electrode

The LOD and LOQ [23] were calculated using the equations LOD = 3SD/*m* and LOQ = 10SD/*m* ($n = 10$). The LOD were 5.1×10^{-4} and 6.7×10^{-4} mol L^{-1} and the LOQ were 1.7×10^{-3} and 2.2×10^{-3} mol L^{-1} using platinum and glassy carbon electrodes, respectively. Figure 4 shows the calibration plots using platinum and glassy carbon electrodes.

3.2 Determination of Ch-HCl in raw material and pharmaceutical formulations

Different weights of the investigated drug ranging from 3.50 to 17.00 mg were determined in raw material using the three proposed methods (Standard addition method, Randles–Sevcik equation, and via complexation with NaTPB). The determination was repeated four times to calculate both average recovery (*R*) and standard deviation (SD). The

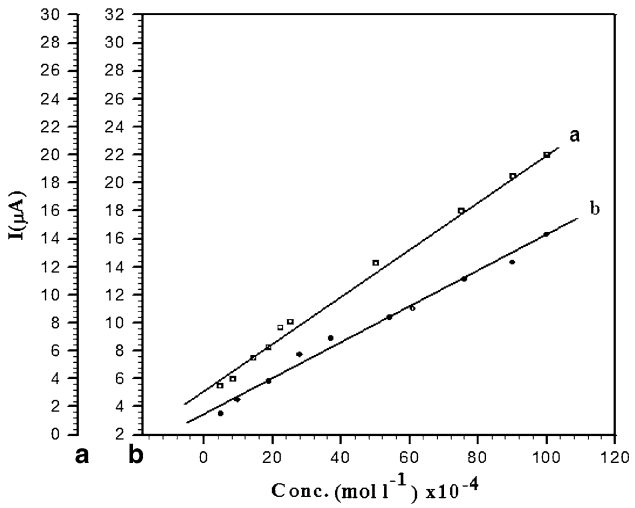


Fig. 4 Calibration curves obtained for Ch-HCl using (*a*) platinum and (*b*) glassy carbon working electrodes

Table 1 DPV determination of Ch-HCl in raw material using the three proposed methods

Taken weight (mg)	Standard addition method						Randles–Sevcik equation						Complexation with NaTPB					
	Pt electrode			Glassy carbon electrode			Pt electrode			Glassy carbon electrode			Pt electrode			Glassy carbon electrode		
	F^a (mg)	R^b (%)	SD	F^a (mg)	R (%)	SD	F^a (mg)	R^b (%)	SD	F^a (mg)	R^b (%)	SD	F^a (mg)	R^b (%)	SD	F^a (mg)	R^b (%)	SD
3.50	3.62	103.30	0.40	3.60	103.02	0.24	3.59	102.77	0.50	3.64	103.30	0.16	3.60	102.86	0.30	3.40	97.14	0.45
7.00	7.25	103.63	0.36	7.12	101.75	0.41	7.26	103.75	0.30	7.025	100.37	0.38	7.43	106.25	0.40	7.20	102.85	0.36
10.00	10.39	103.90	0.30	9.76	97.60	0.27	10.38	103.80	0.27	10.04	100.40	0.19	10.00	100.00	0.47	10.00	100.00	0.52
14.00	14.50	103.60	0.69	14.24	101.75	0.47	14.58	104.20	0.69	14.50	103.50	0.17	13.12	93.75	0.27	14.43	103.07	0.71
17.00	16.95	99.70	0.50	16.50	97.05	0.36	16.81	98.88	0.40	17.2	100.58	0.35	18.27	107.50	0.45	16.15	95.00	0.63

[a] Found

[b] Average recovery ($n = 4$)

results, shown in Table 1, support the validation of these methods for the determination of the investigated drug where the average recoveries ranges from 97.85 to 104.18% with standard deviation ranging from 0.03 to 0.6 by applying the three mentioned methods.

Ch-HCl was also determined in both Allergex and Allergex caffeine tablets (20 mg/tablet) (Fig. 5). The results obtained in Tables 2, 3 prove the success of the proposed methods for the determination of Ch-HCl in Allergex and Allergex caffeine tablets where the recoveries range from 98.11 to 105.18% with SD ranging from 0.03 to 0.6 and from 96.00 to 104.3% with SD values of 0.06 to 0.8 for Allergex caffeine and Allergex tablets, respectively.

Figure 6 shows the DPV developed during the complexation of 5 mL (1×10^{-2} mol L^{-1}) of the investigated drug in Allergex caffeine tablets with 2.5×10^{-2} mol L^{-1} NaTPB using Pt as working electrode.

It is worthy to mention that although Ch-HCl reacts with NaTPB in water with 1:1 molar ratio, this ratio has been changed to 1:2 in acetonitrile which has been confirmed using conductimetric titration [19] (Fig. 7) and this may be attributed to the fact that electroanalytical measurements reflect the activity of species in the liquid phase which in turn is related not only to the concentration of the species present, but also to the total concentration of electrolytes in the solution. A change in the dielectric constant of the solvent causes the response to vary where the solute can dissociate or polymerize on solution and the degree of change varies with the concentration of material present and with the nature of the solvent being used [20].

The F- and t-tests [24] were evaluated to compare the average and the SD of the proposed methods with those obtained using spectrophotometric method [3]. The results shown in Table 4 indicate that the calculated F and t values were lower than the tabulated ones indicating that there is no significant difference or constant error between the two methods at the indicated significance level.

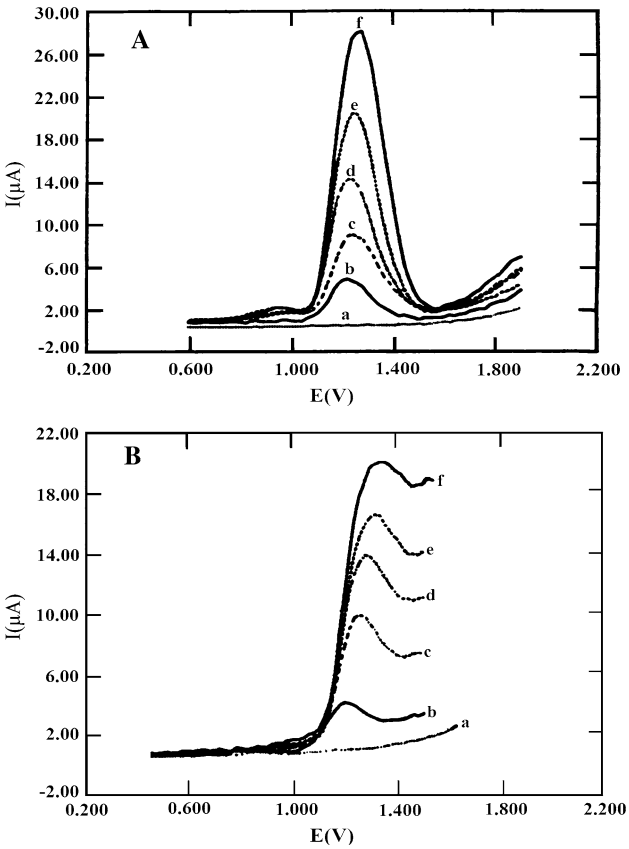


Fig. 5 Variation of I_p with different concentration of Allergex (**A**) and Allergex caffeine tablet (**B**) using platinum working electrode: (*a*) supporting electrolyte, (*b*) 9.8×10^{-4}, (*c*) 2.8×10^{-3}, (*d*) 4.5×10^{-3}, (*e*) 7.6×10^{-3}, and (*f*) 1.0×10^{-2} mol L^{-1}

3.3 Selectivity studies

Ch-HCl was determined in both Allergex and Allergex caffeine tablets (20 mg/tablet) without further extraction or treatment rather than filtering the insoluble ingredient and it was found that after removing the insoluble excipients by

Table 2 DPV determination of Ch-HCl in Allergex tablet (20 mg/tablet) using the three proposed methods

Taken weight (mg)	Standard addition method						Randles–Sevcik equation						Complexation with NaTPB					
	Pt electrode			Glassy carbon electrode			Pt electrode			Glassy carbon electrode			Pt electrode			Glassy carbon electrode		
	F^a (mg)	R^b (%)	SD	F^a (mg)	R^b (%)	SD	F^a (mg)	R^b (%)	SD	F^a (mg)	R^b (%)	SD	F^a (mg)	R^b (%)	SD	F^a (mg)	R^b (%)	SD
3.50	3.62	103.60	0.26	3.60	103.30	0.04	3.63	104.10	0.17	3.70	103.80	0.16	3.45	98.50	0.50	3.50	100.00	0.45
7.00	7.09	101.20	0.16	6.74	96.25	0.28	7.13	101.80	0.12	6.98	99.80	0.11	7.11	101.20	0.62	6.90	98.60	0.29
10.00	10.12	101.20	0.46	9.50	95.00	0.11	10.43	104.30	0.37	9.94	99.40	0.10	10.83	108.30	1.10	10.33	103.30	0.30
14.00	13.87	99.10	1.12	14.18	101.30	0.48	14.14	101.10	0.55	14.40	102.90	0.44	13.56	96.80	0.80	14.87	106.20	0.50
17.00	16.87	99.20	0.52	17.1	100.60	0.70	16.90	99.40	0.80	17.20	101.20	0.75	16.59	97.50	0.60	16.45	96.70	0.60

[a] Found

[b] Average recovery ($n = 4$)

Table 3 DPV determination of Ch-HCl in Allergex caffeine tablet (20 mg/tablet) using the three proposed methods

Taken weight (mg)	Standard addition method						Randles–Sevcik equation						Complexation with NaTPB					
	Pt electrode			Glassy carbon electrode			Pt electrode			Glassy carbon electrode			Pt electrode			Glassy carbon electrode		
	F^a (mg)	R^b (%)	SD	F (mg)	R (%)	SD	F (mg)	R (%)	SD	F (mg)	R (%)	SD	F (mg)	R (%)	SD	F (mg)	R (%)	SD
3.50	3.68	105.18	0.14	3.61	103.2	0.25	3.65	104.6	0.13	3.61	103.40	0.12	3.40	97.14	0.30	3.56	101.7	0.30
7.00	7.25	103.60	0.36	7.21	103.06	0.18	7.23	103.34	0.24	7.14	102.07	0.11	7.00	100.0	0.25	7.43	106.14	0.50
10.00	10.38	103.80	0.49	10.53	105.30	0.50	10.46	104.60	0.27	10.52	105.20	0.34	10.41	104.1	0.45	10.00	100.0	0.35
14.00	14.30	102.00	0.90	13.73	98.11	0.45	14.56	104.00	0.48	14.22	101.60	0.14	13.56	96.87	0.61	14.86	106.14	0.35
17.00	17.10	100.6	0.70	16.90	99.40	0.35	16.80	99.12	0.35	17.30	101.76	0.25	16.59	97.5	0.40	17.42	102.50	0.45

[a] Found

[b] Average recovery ($n = 4$)

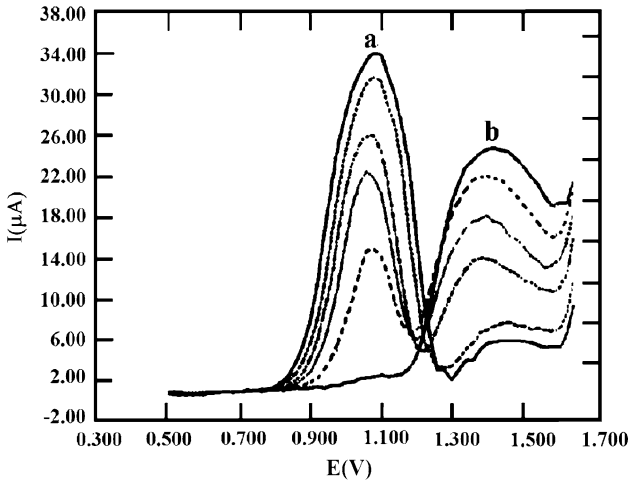


Fig. 6 DPV developed during the complexation of 5 mL (10^{-2} mol L^{-1}) of Allergex caffeine tablet with 2.5×10^{-2} mol l^{-1} NaTPB using Pt working electrode. (*a*) Represent the increase of I_p of the complex formed and (*b*) represent the decrease of I_p of the investigated drug with addition of NaTPB

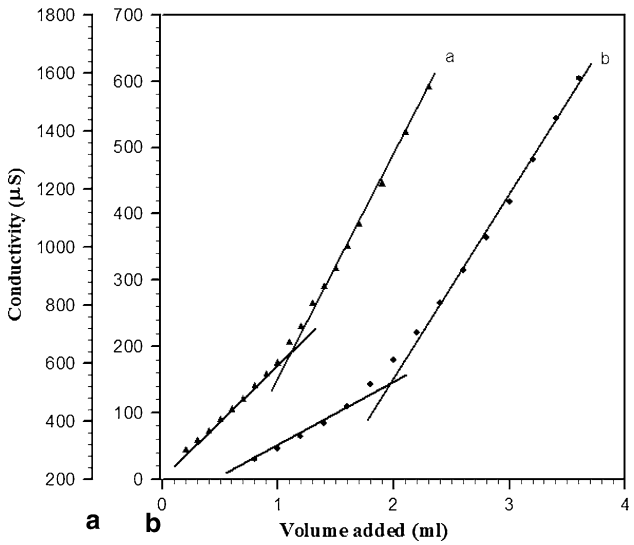


Fig. 7 Conductimetric determination of 1 mL 5.0×10^{-2} mol L^{-1} Ch-HCl using 5.0×10^{-2} mol L^{-1} NaTPB (*a*) in water (*b*) in acetonitrile

Table 4 Statistical treatment of data for Ch-HCl using DPV in comparison with spectrophotometric method [3]

	Spectrophotometric method	DPV method	
		Pt electrode	Glassy carbon electrode
Linear range	5.8×10^{-3}–1.9×10^{-2} mol L^{-1}	4.5×10^{-4}–1×10^{-2} mol L^{-1}	4.5×10^{-4}–1×10^{-2} mol L^{-1}
Regression equation	Conc. = Abs. × 0.0385 − 0.1551	I (μA) = 1,732 C (mol L^{-1}) + 2.4	I (μA) = 1,550 C (mol L^{-1}) + 2.4
Average recovery ± SE	99.98 ± 0.27	101.44 ± 0.35	100.49 ± 0.45
r	0.995	0.994	0.988
SD	0.851	0.45	0.38
Variance	0.725	0.20	0.15
N	3	4	4
Probability	0.05	0.05	0.05
F-value$^{(3.4)}$ (6.59)		3.6	4.8
t-Value$^{(df = 5)}$ (2.6)		2.07	0.78

filtration no other peaks than that of Ch-HCl appear except in Allergex caffeine formulation where another peak appears at more positive value than that of Ch-HCl which may be attributed to the presence of caffeine as excipient and that has no effect on the determination or the recoveries obtained. Therefore, the proposed method can be considered to be selective.

4 Conclusion

DPV is a simple, rapid, and sensitive electrochemical method for the determination of Ch-HCl. The method has been successfully proven to be suitable for the determination of the studied drug in raw material and pharmaceutical preparations using either platinum or glassy carbon electrode. The method achieves high degree of precision, selectivity and accuracy in comparison with spectrophotometric method, within wide concentration range, that have been confirmed by recoveries, standard deviations, F- and t-values. Also, the proposed method shows clear advantages such as short period of real time of drug analysis and no pretreatment, derivatizing agents or time consuming extraction steps are required. Moreover, because of its low limits of detection and quantification the proposed methods are valid for the determination of the investigated drug and can be used as a shelf stability test in drug companies.

References

1. Kelani KM (2005) J AOAC Int 88(4):1126
2. Dinc E, Palabiyik IM, Ustundag O, Yurtsever F, Onur F (2002) J Pharm Biomed Anal 28(3–4):591
3. Ayad M, Saleh H, El-Bolkiny M, El-Henawee M (1993) Anal Lett 26(5):913
4. Barary MH, Wahbi AM (1991) Drug Dev Ind Pharm 17(3):457
5. El-Henawee MM, Mohamed HS, El-Bolkiny N, Ayad MM (1990) Spectrosc Lett 23(3):273
6. Amine AS, El-Henawee MM (1995) Mikrochim Acta 118(3–4): 177
7. Metrohm Application Bulletin (2001) Technical report 263/1e: 11
8. Bebawy LI, El-Kousy MN (1999) J Pharm Biomed Anal 20(4): 663
9. Goeneches S, Ruecker G, Brzezinka H, Hoffmann G, Neugebauer M, Pyzik T (1987) Arzneim Forsch 37(7):854
10. Zareh MM, Teleb SM, Ahmed ES (2002) Anal Lett 35:17
11. Isaa YM, Amin AS (1996) Analusis 24:139
12. Temizer A, Ozaltin N (1986) J AOAC Int 69(2):192
13. Abdel-Ghani NT, El-Ries MA, El-Shall MA (2007) Anal Sci 23: 1053
14. Svancara I, Ogorevc B, Hocevar SB, Vytras K (2002) Anal Sci 18:301
15. De Btono SF, Garcia AA, Arranz Valentin JF (1999) J Pharm Biomed Anal 20:621
16. Ewing GW (1995) Instrumental methods of chemical analysis, 5th edn. Lippincott/Raven, Philadelphia
17. West DM, Holler FJ, Grouch SR (2004) Fundamental of analytical chemistry, 8th edn. Thomson-Brooks/Cole, USA
18. Abdel-Ghani NT, Shoukry AF, Hussein SH (2002) J Pharm Biomed Anal 30:601
19. Issa YM, Shoukry AF, El-Nashar RM (2001) J Pharm Biomed Anal 26:379
20. Pickering WF (1971) Modern analytical chemistry. Marcel Dekker, New York
21. Nesmaeyanov AN, Nesmaeyanov NA (1986) Fundamental of organic chemistry, 3rd edn. MIR Publisher, Moscow
22. David K, Gosser JR (1993) Cyclic voltammetry simulation and analysis of reaction mechanisms. VCH Publishers, UK
23. Miller JC, Miller JN (1993) Statistics for analytical chemistry, 4th edn. Ellis Horwood Ltd, New York
24. Christian GD (1994) Analytical chemistry, 5th edn. Wiley, USA