

Supplementary Material

Eco-Friendly Differential Pulse Voltammetric Determination of Benzydamine Hydrochloride Using a Gold Nanoparticles-Modified Carbon Paste Electrode

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Experimental

Materials and Reagents

- 0.01 M H₂SO₄ was prepared by transferring 543.0 μL from 18.4 M H₂SO₄ into 1.0 L measuring flask and the volume completed to mark with distilled water and used as the supporting electrolyte.
- Britton-Robinson buffer solution was prepared by mixing a solution of 0.04 M phosphoric acid, 0.04 M acetic acid, and 0.04 M boric acid, and used for the pH study. The desired pH was achieved in buffer solutions by the controlled addition of 0.2 M sodium hydroxide which was prepared by dissolving 0.8 gm NaOH in 100 mL distilled water.
- 0.1 M potassium chloride was prepared by dissolving 0.75 gm KCl in 100 mL distilled water.
- Artificial saliva was prepared by dissolving 0.639 g Na₃PO₄, 0.250 g NaCl, 1.340 g KCl, 0.007 g MgCl₂, 0.122 g CaCl₂, 0.007 g H₂SO₄ and 0.274 g NaHCO₃ in 250 mL of high purity distilled water in a 500-mL beaker using a vortex. Potassium hydroxide used for the pH adjustment to 7.2. The solution was then transferred to a 1.0-L measuring flask and completed to the mark with high-purity distilled water and the flask was sonicated for 15 min.

Procedure

Electrodes Preparation

- **Au-NPs/GCE:** Gold nanoparticles (Au-NPs) were electrodeposited onto a glassy carbon electrode (GCE) using chronoamperometry. Prior to deposition, the GCE was carefully polished with alumina slurry and ultrasonically cleaned in deionized water. The electrodeposition was carried out in 5.00×10^{-4} M HAuCl₄ solution containing 0.1 M KCl. A constant potential of -0.4 V vs. Ag/AgCl was applied for a deposition time of 5 s to obtain a uniform dispersion of Au-NPs on the GCE surface. The resulting electrode is denoted as Au-NPs/GCE.
- **Au-NPs/CNT/CPE:** The carbon paste electrode (CPE) was first modified with carbon nanotubes (CNTs) to obtain a CNT/CPE substrate. Gold nanoparticles (Au-NPs) were then deposited onto the CNT/CPE surface via chronoamperometry, resulting in the final Au-

NPs/CNT/CPE electrode. The electrodeposition of Au-NPs was carried out by applying a constant potential (-0.4 V vs. Ag/AgCl) for a deposition time 5 s from 5.00×10^{-4} M HAuCl₄ solution containing 0.1 M KCl.

Table S1. Elemental composition of EDX spectrum of Au-NPs electrodeposited on SPE.

Element	Weight %	Atomic %	Net Int.	Error %	K ratio	Z	A	F
C K	92.86	97.98	2599.30	6.42	0.4105	1.0124	0.4366	1.0000
Cl K	5.32	1.90	2227.10	1.28	0.0467	0.8394	1.0329	1.0113
Au L	1.82	0.12	78.30	9.55	0.0121	0.5803	1.1066	1.0316

Table S2. Greenness assessment of the developed voltammetric method and the reported potentiometric and HPLC methods for determination of benzydamine hydrochloride by Analytical Eco-Scale.

		Developed voltammetric method	Reported potentiometric method [35]	Reported HPLC method [24]
Analytical Eco-Scale Parameters		Penalty points (PP)		
Reagents	H ₂ SO ₄	2	-	-
	HAuCl ₄ solution	4	-	-
	KCl	0	-	-
	Graphite powder	0	-	-
	Paraffin oil	2	-	-
	Tetrahydrofuran (THF)	-	6	-
	PVC	-	0	-
	Potassium tetrakis (4-chlorophenyl) borate (KTCPB)	-	1	-
	2-hydroxypropyl- β -cyclodextrin (2HP- β -CD)	-	0	-
	Calix[4]arene	-	1	-
	Calix[6]arene	-	1	-
	2-nitrophenyloctyl ether (<i>o</i> -NPOE)	-	0	-
	Acetonitrile	-	-	8
	Methanol	-	-	12
	Ammonium carbonate	-	-	2
	Ethyl acetate	-	-	4
0.1M Sodium Hydroxide	-	-	1	
Instrument	LC-UV \leq 1.5 KWh/sample	-	-	1
	potentiostat/galvanostat <0.1 KWh/sample	0	0	-
	Centrifuge	-	-	1
	Shaker	-	-	1
	Occupational hazards	0	0	0
	Waste	8	6	8
Total penalty points		16	15	38
Analytical Eco-Scale score		84	85	62

Table S3. Green analytical procedure index parameters for the proposed voltammetric method.

Category	Voltammetric method
1- Collection	Off-line
2- Preservation	None
3- Transport	None
4- Storage	None
5- Type of the method: direct/indirect	Simple procedures
6- Scale of extraction	None
7- Solvents/reagents	Benign solvent used
8- Additional treatments	None
<u>Reagents and solvents</u>	
9- Amounts	10 - 100 mL
10- Health hazard	Paraffin oil: NFPA* health hazard rating = 2 H ₂ SO ₄ acid: NFPA* health hazard rating = 3 KCl: NFPA* health hazard rating = 1 Graphite powder: NFPA* health hazard rating = 0 HAuCl ₄ : NFPA* health hazard rating = 3
11- Safety hazard	Paraffin oil: instability score = 0, flammability score = 1 H ₂ SO ₄ acid: instability score = 0, flammability score = 0 KCl: instability score = 0, flammability score = 0 Graphite powder: instability score = 0, flammability score = 0 HAuCl ₄ : instability score = 0, flammability score = 0
<u>Instrumentation</u>	
12- Energy	≤0.1 kWh per sample
13- Occupational hazard	Hermetic sealing of analytical process
14- Waste	> 10 mL/sample
15- Waste treatment	No treatment

* National Fire Protection Association.