Supporting Information

Adsorptive stripping voltammetric determination of imipramine, trimipramine and desipramine employing titanium dioxide nanoparticles and amberlite XAD-2 modified glassy carbon paste electrode

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Figure captions

Fig. S1. A plot of peak current (i_p) vs. pH and peak potential (E_p) vs. pH for 5.02×10^{-6} M IMI at GCPE employing DPV; step potential = 5 mV, modulation amplitude = 50 mV.

Fig. S2. A plot of peak current (i_p) vs. pH and peak potential (E_p) vs. pH for 4.83×10^{-6} M TRI at GCPE employing DPV. Other conditions as in Fig. S1.

Fig. S3. A plot of peak current (i_p) vs. pH and peak potential (E_p) vs. pH for 5.35×10^{-7} M DES at GCPE employing DPV. Other conditions as in Fig. S1.

Fig. S4. A bar graph for the effect of various supporting electrolytes employed for 1.0×10^{-6} M IMI , TRI and DES at GCPE employing DPV. Other conditions as in Fig. S1.

Fig. S5. A plot for the effect of amount of XAD2 on the peak current of IMI (5.18×10^{-7} M) at XAD2-GCPE employing DPV. Other conditions as in Fig. S1.

Fig. S6. A plot for the effect of amount of TNP on the peak current of IMI (4.34×10^{-7} M) at TNP-GCPE employing DPV. Other conditions as in Fig. S1.

Fig. S7. Cyclic voltammograms of 5.87×10^{-7} M TRI at GCPE **(- - -)**, XAD2-GCPE (**……**), TNP-GCPE **(.—.)** and XAD-TNP-GCPE **(—)**. Voltammetric conditions: scanning electrode potential between -0.20 and +1.3 V at a scan rate of 10 mV s^{-1} in phosphate buffer (pH 6.0).

Fig. S8. Cyclic voltammograms of 6.91×10^{-7} M DES at GCPE **(- - -)**, XAD2-GCPE (**……**), TNP-GCPE **(.—.)** and XAD-TNP-GCPE **(—)**. Voltammetric conditions: scanning electrode potential between -0.20 and +1.3 V at a scan rate of 10 mV s^{-1} in phosphate buffer (pH 6.0).

Fig. S9. A plot of effect of increment in scan rate in the range of 10 mV s^{-1} to 500 mV s^{-1} on the peak current of (a) IMI (7.75×10^{-7} M), (b) TRI (5.42×10^{-7} M) and (b) DES (6.38×10^{-7} M).

Fig. S10. Influence of accumulation time and accumulation potential on the oxidation peak current of 2.11×10^{-7} M IMI on XAD2-TNP-GCPE. Other conditions as in Fig. S1.

Fig. S11. Influence of accumulation time and accumulation potential on the oxidation peak current of 1.82×10^{-7} M TRI on XAD2-TNP-GCPE. Other conditions as in Fig. S1.

Fig. S12. Influence of accumulation time and accumulation potential on the oxidation peak current of 2.68×10^{-6} M DES on XAD2-TNP-GCPE. Other conditions as in Fig. S1.

Fig. 13. AdSDPV obtained for 4.37×10^{-8} M TRI at four electrodes: GCPE **(- - -)**, XAD2-GCPE **(……)**, TNP-GCPE **(.—.)** and XAD2-TNP-GCPE **(—).** Accumulation potential of -0.40 V was applied to all the four electrodes for an accumulation time of 120 s in phosphate buffer solution (pH 6.0) and the potential was scanned from -0.50 to +1.20 V.

Fig. 14. AdSDPV obtained for 7.44×10^{-8} M DES at four electrodes: GCPE **(- - -)**, XAD2-GCPE **(……)**, TNP-GCPE **(.—.)** and XAD2-TNP-GCPE **(—).** Accumulation potential of -0.20 V was applied to all the four electrodes for an accumulation time of 100 s in phosphate buffer solution (pH 6.0) and the potential was scanned from -0.50 to +1.20 V.

Fig. 15. AdSDPV obtained using XAD2-TNP-GCPE for TRI at different concentrations: (1) 1.16×10^{-9}, (2) 3.88×10^{-8}, (3) 9.74×10^{-8}, (4) 3.12×10^{-7}, (5) 6.46×10^{-7}, (6) 9.05×10^{-7}, (7) 1.81×10^{-6}, (8) 3.37×10^{-6}, (9) 4.75×10^{-6}, (10) 5.48×10^{-6}, (11) 6.87×10^{-6} M. Other conditions as given in Fig. S13.

Fig. 16. AdSDPV obtained using XAD2-TNP-GCPE for DES at different concentrations: (1) 1.43×10^{-9}, (2) 3.28×10^{-8}, (3) 8.01×10^{-8}, (4) 2.03×10^{-7}, (5) 5.48×10^{-7}, (6) 7.89×10^{-7}, (7) 1.43×10^{-6}, (8) 3.02×10^{-6}, (9) 4.12×10^{-6}, (10) 5.07×10^{-6}, (11) 5.68×10^{-6} M. Other conditions as given in Fig. S14.

Fig. S17. Effect of addition of ascorbic acid (0-150 fold excess) on the peak current of 3.8 × 10-8 M IMI.

Figures for Supporting Information

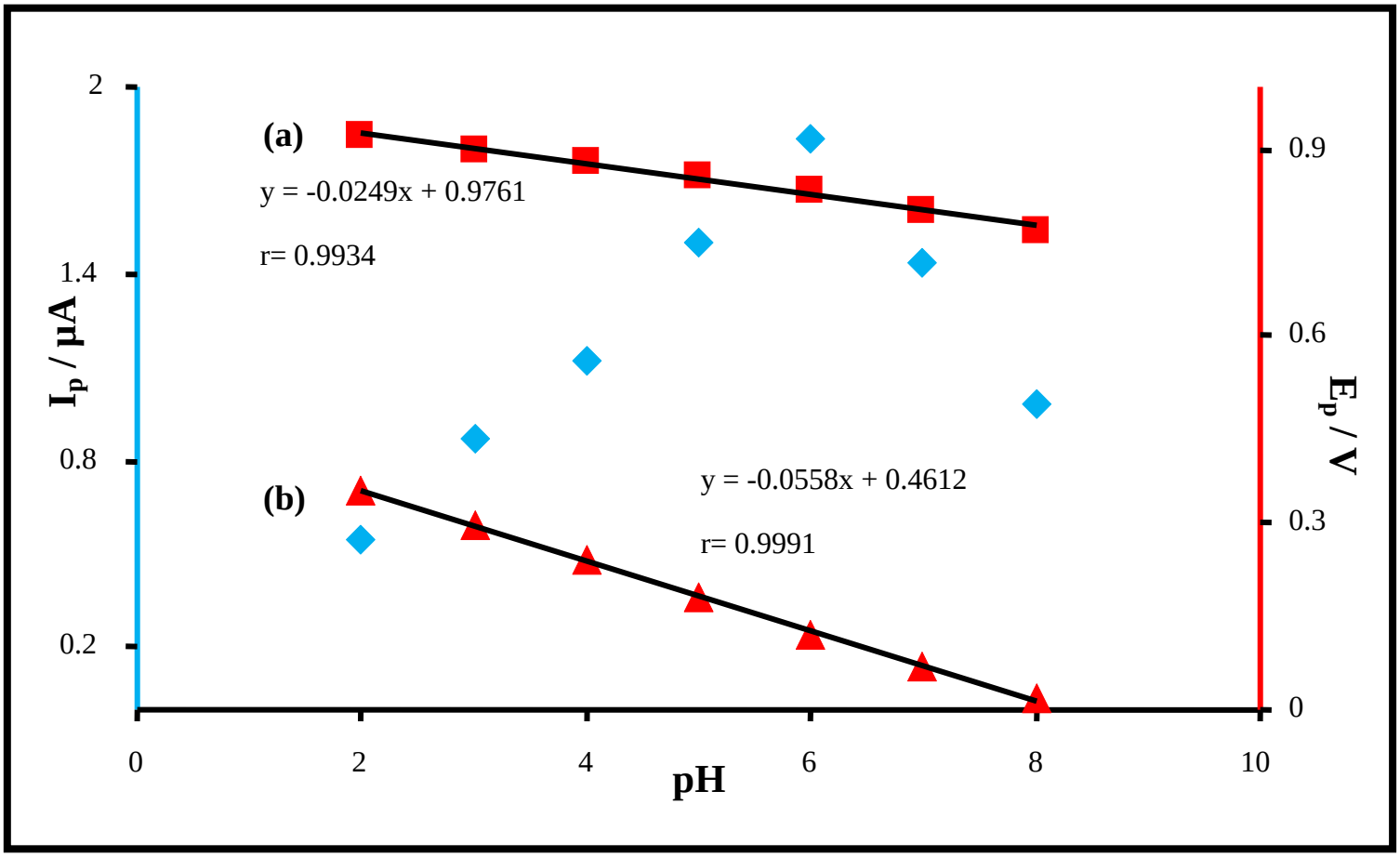


Fig. S1

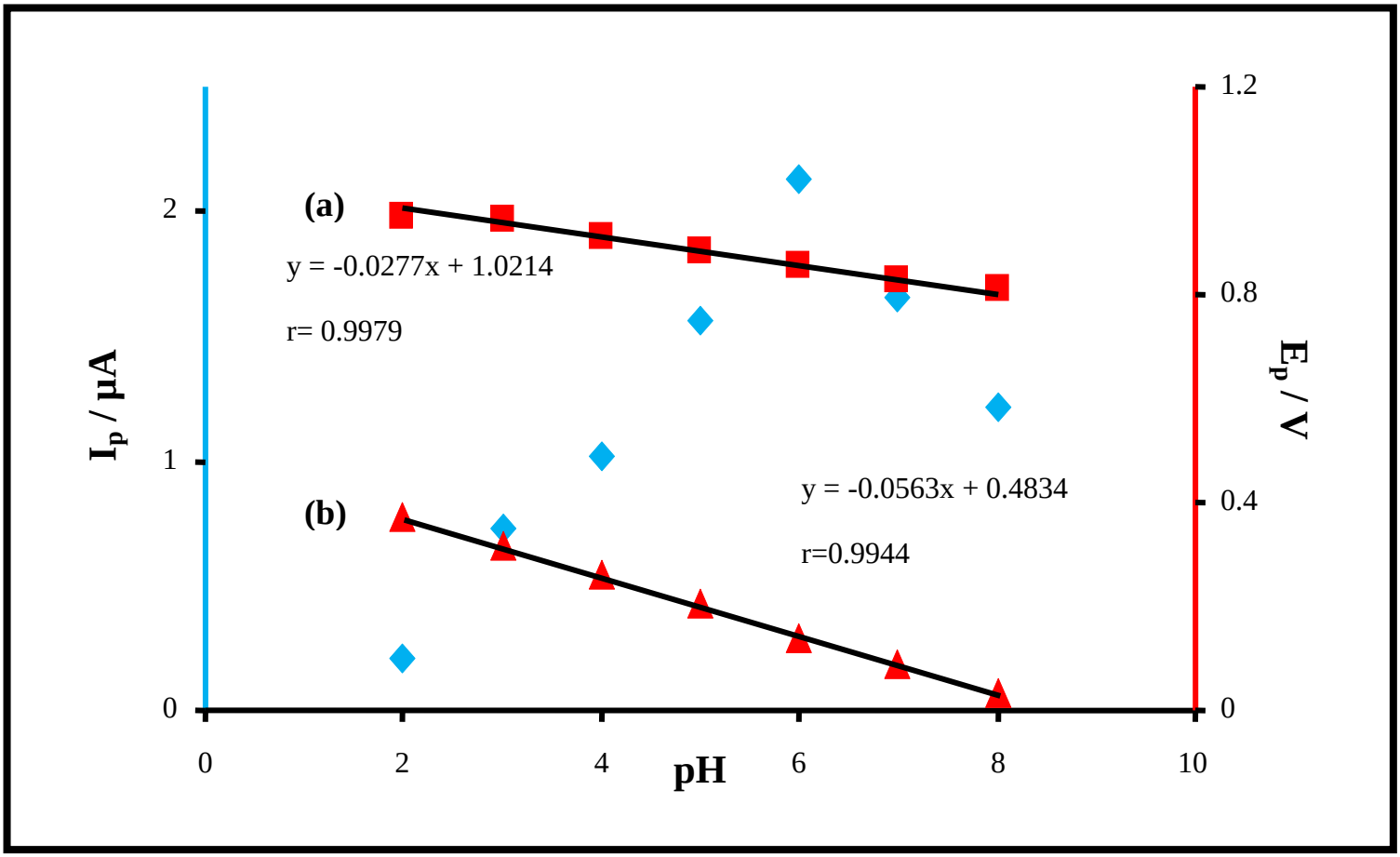
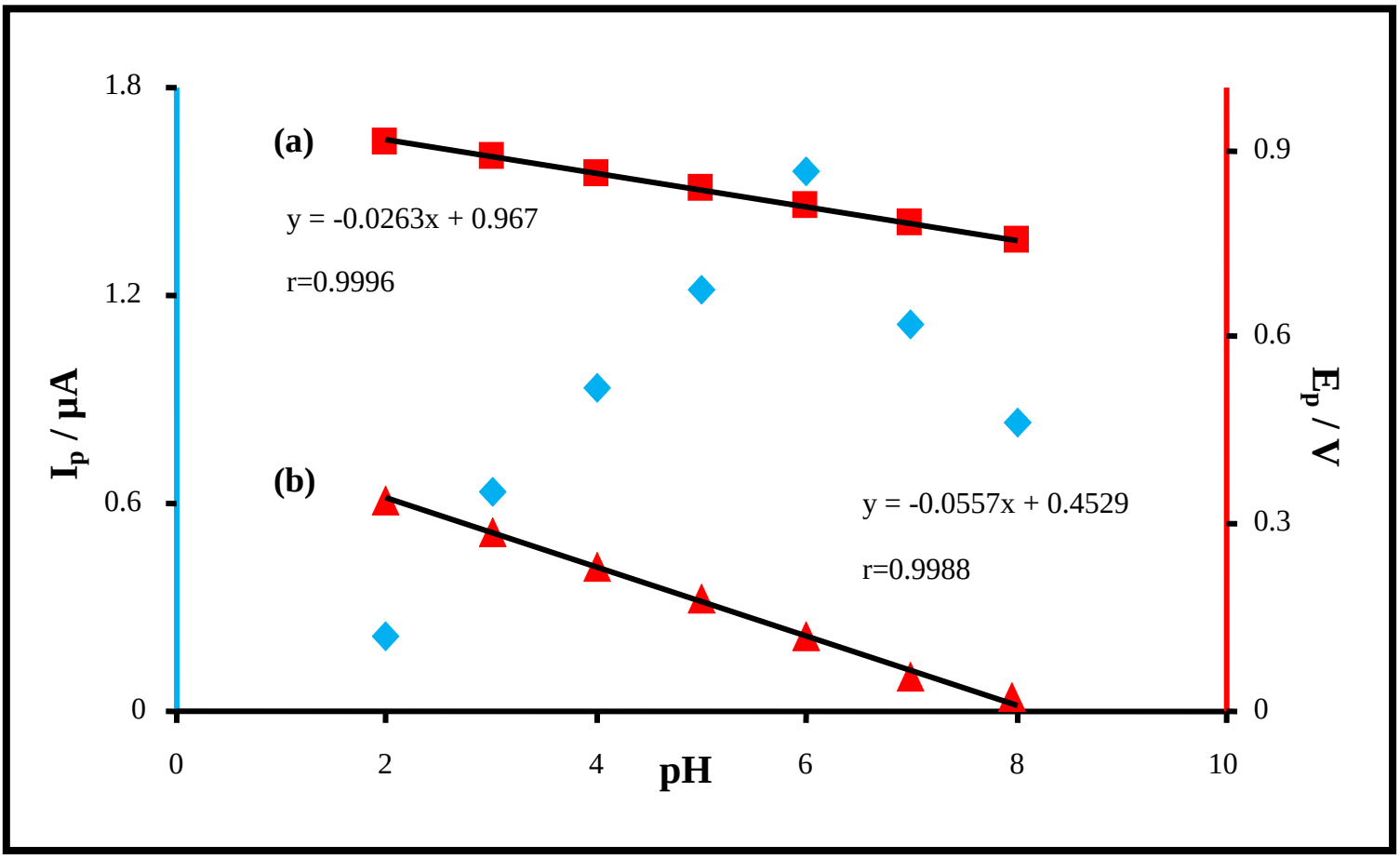


Fig. S2



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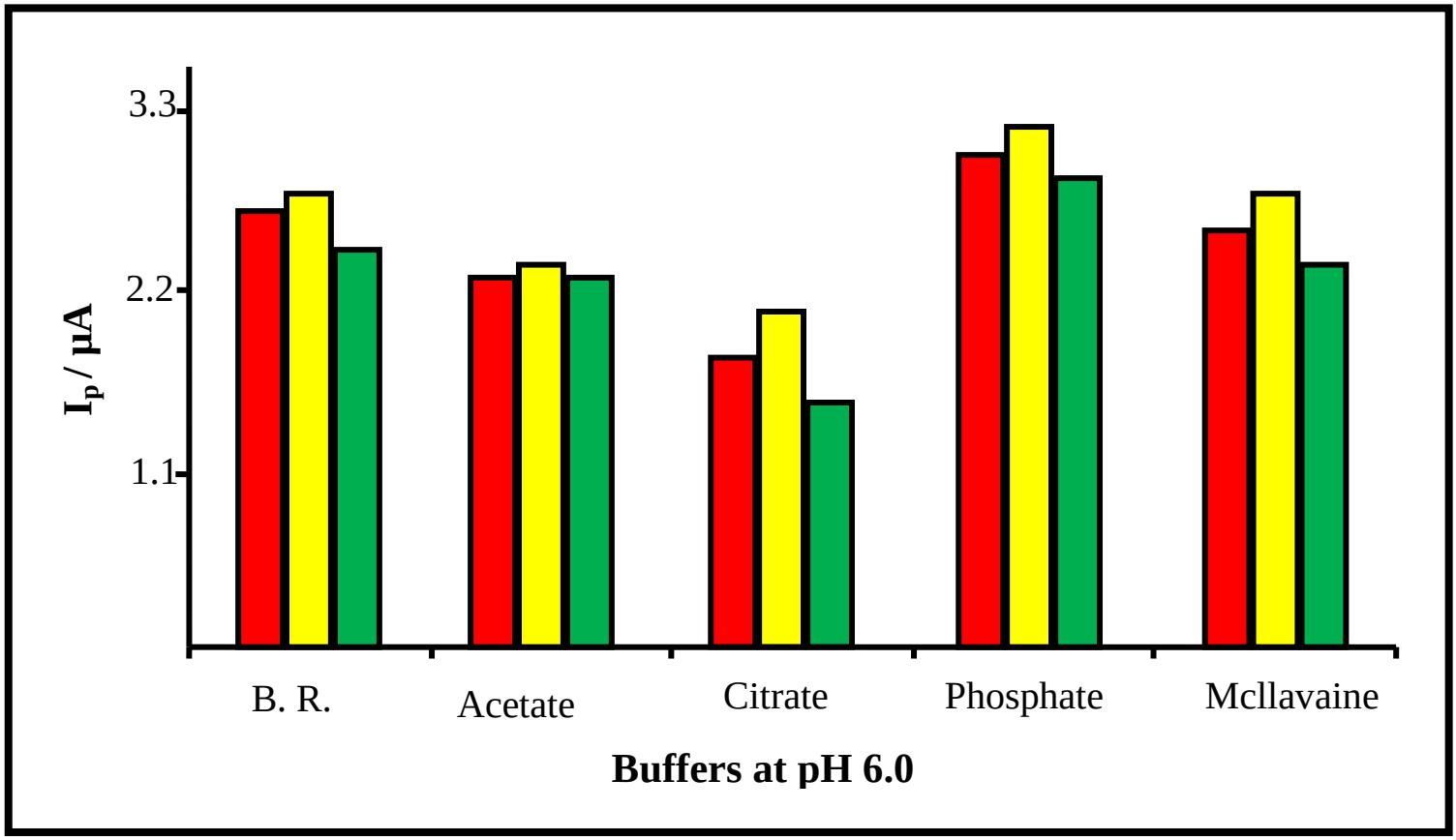

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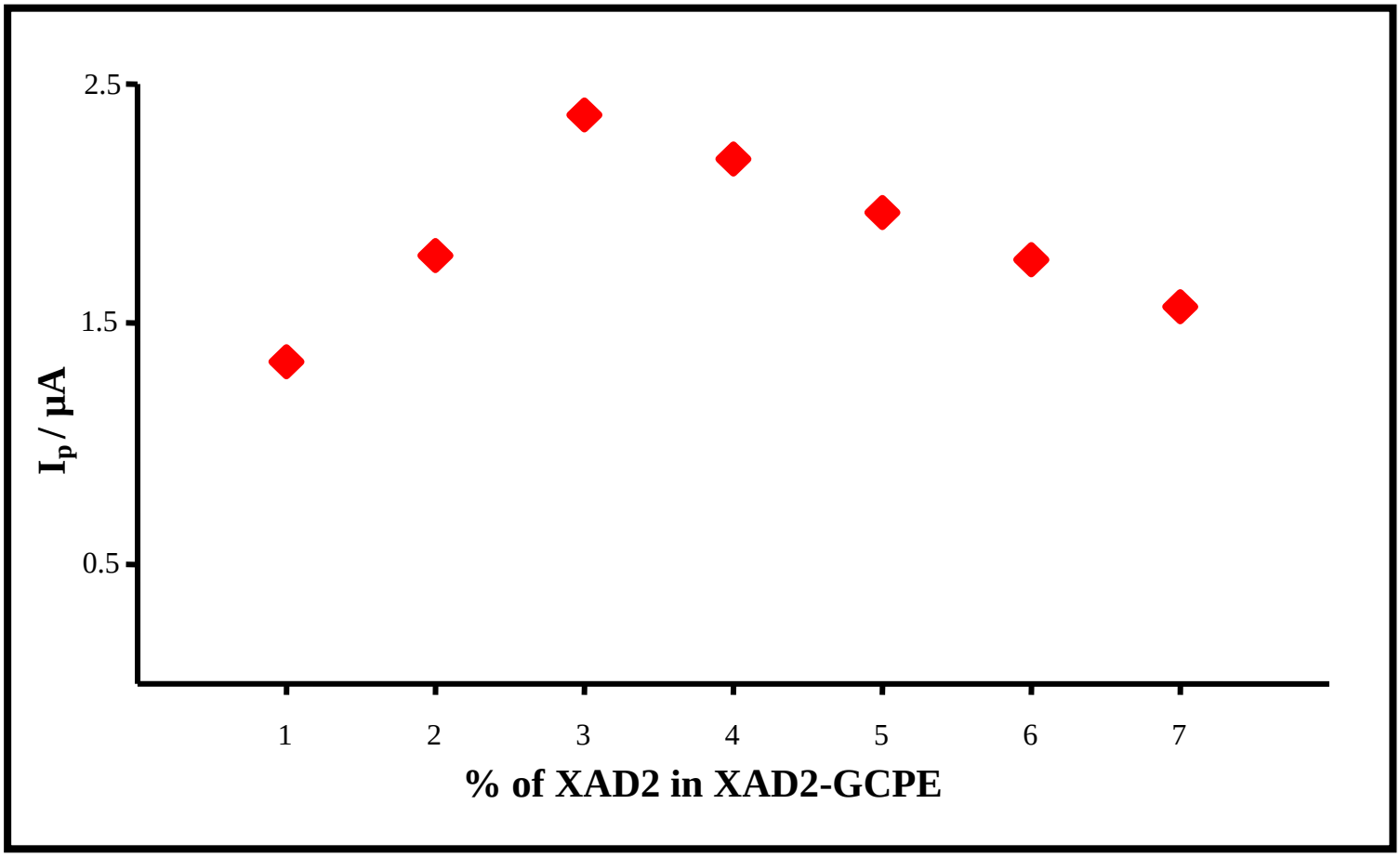

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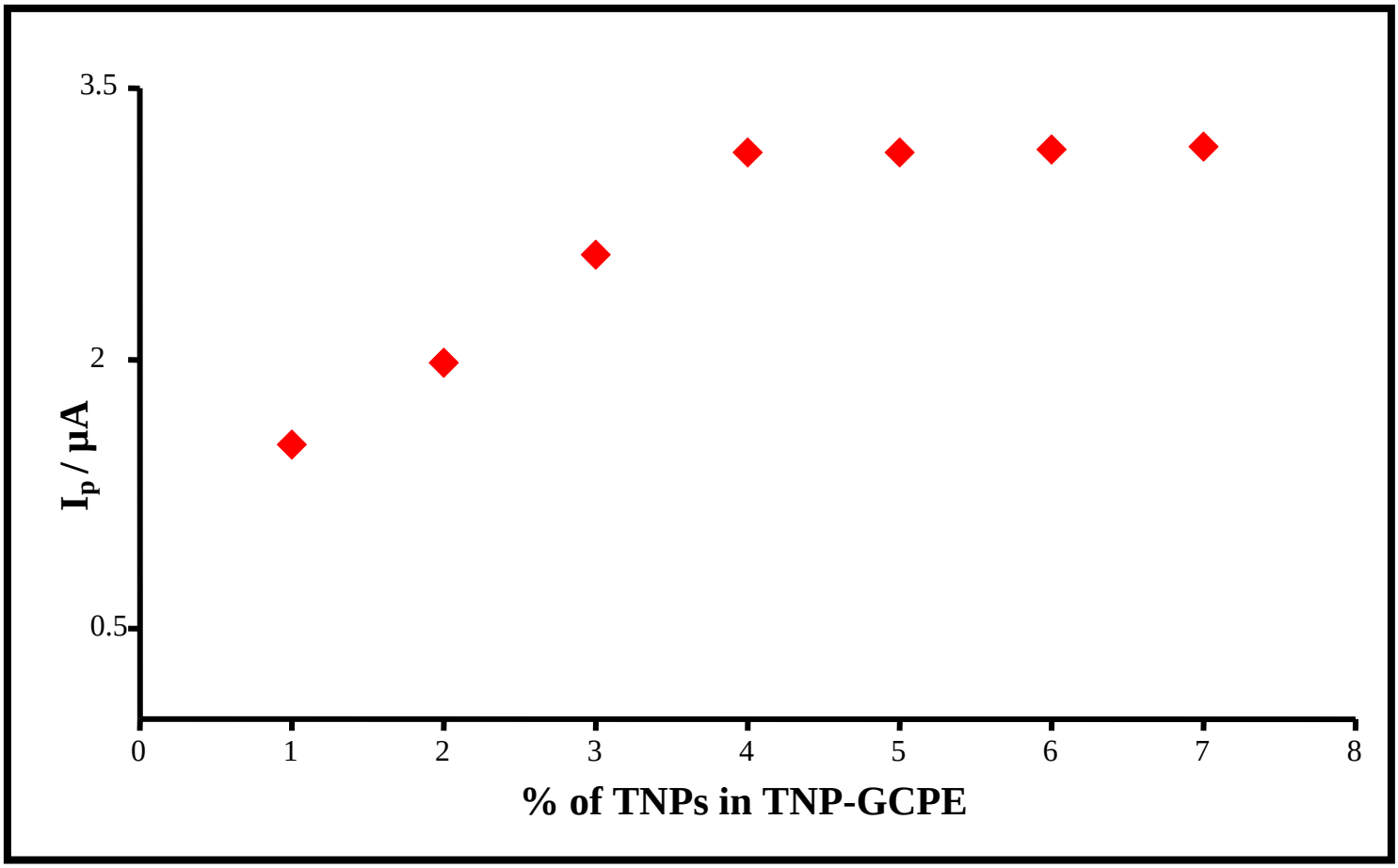

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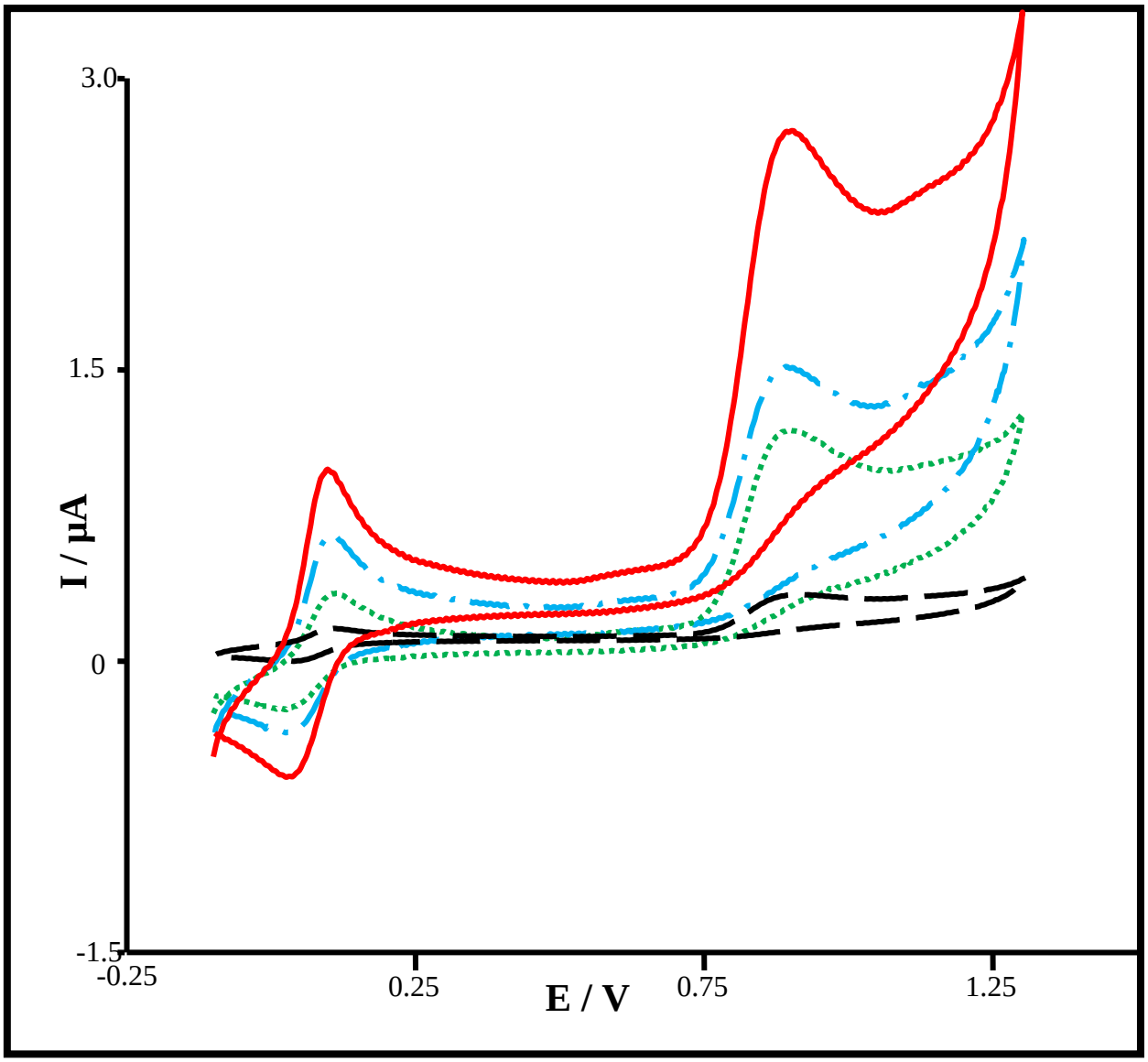

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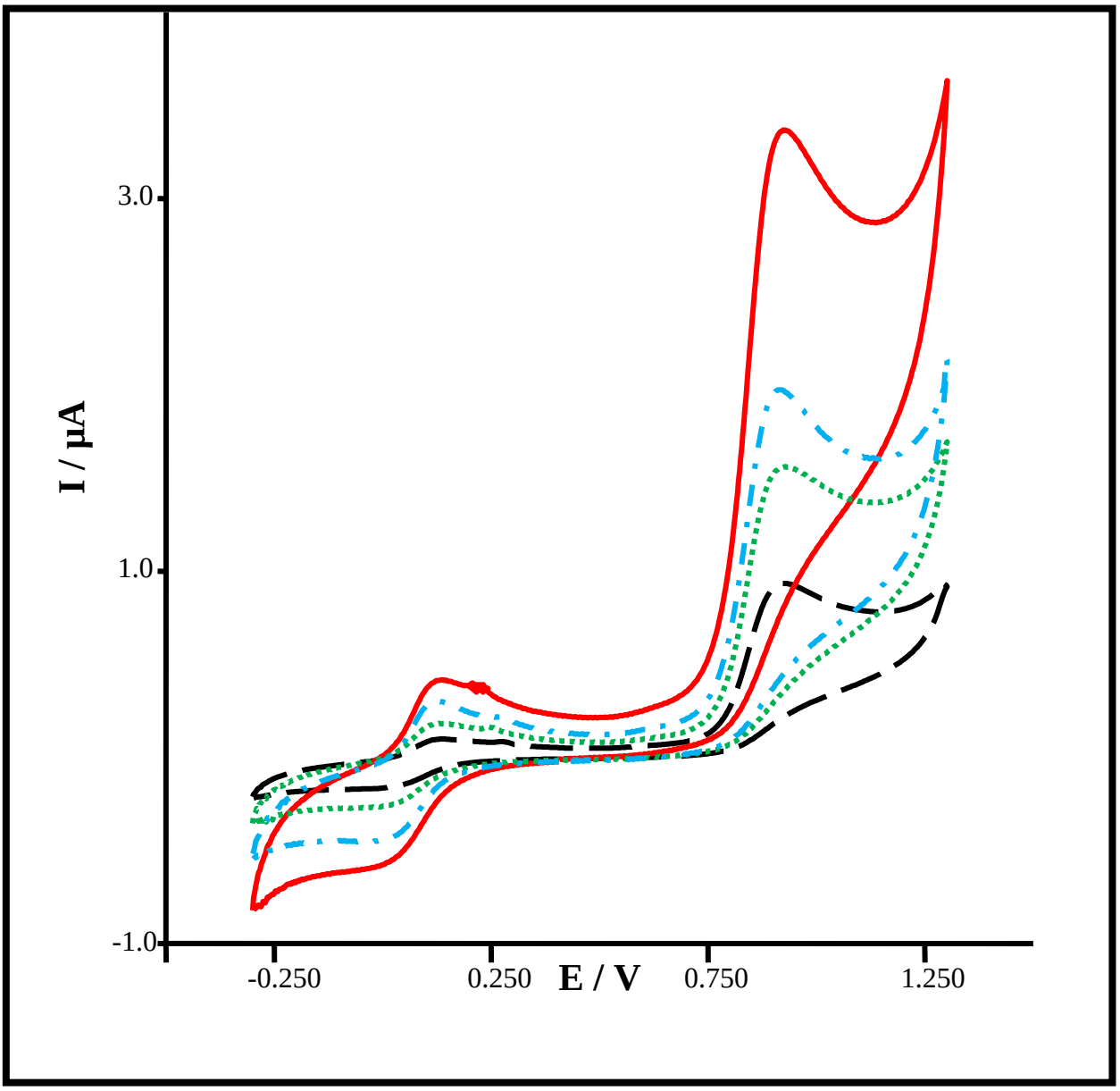

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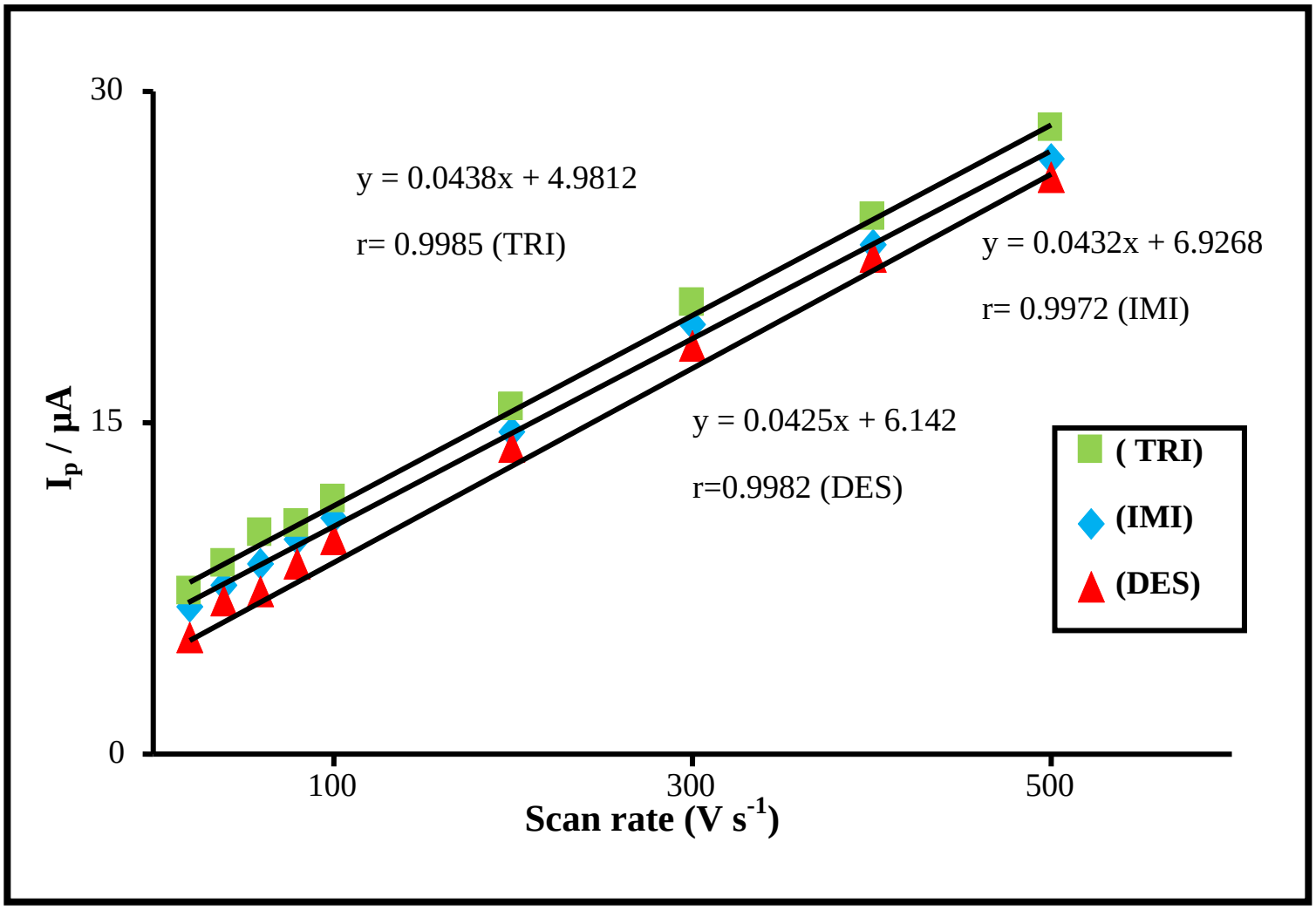

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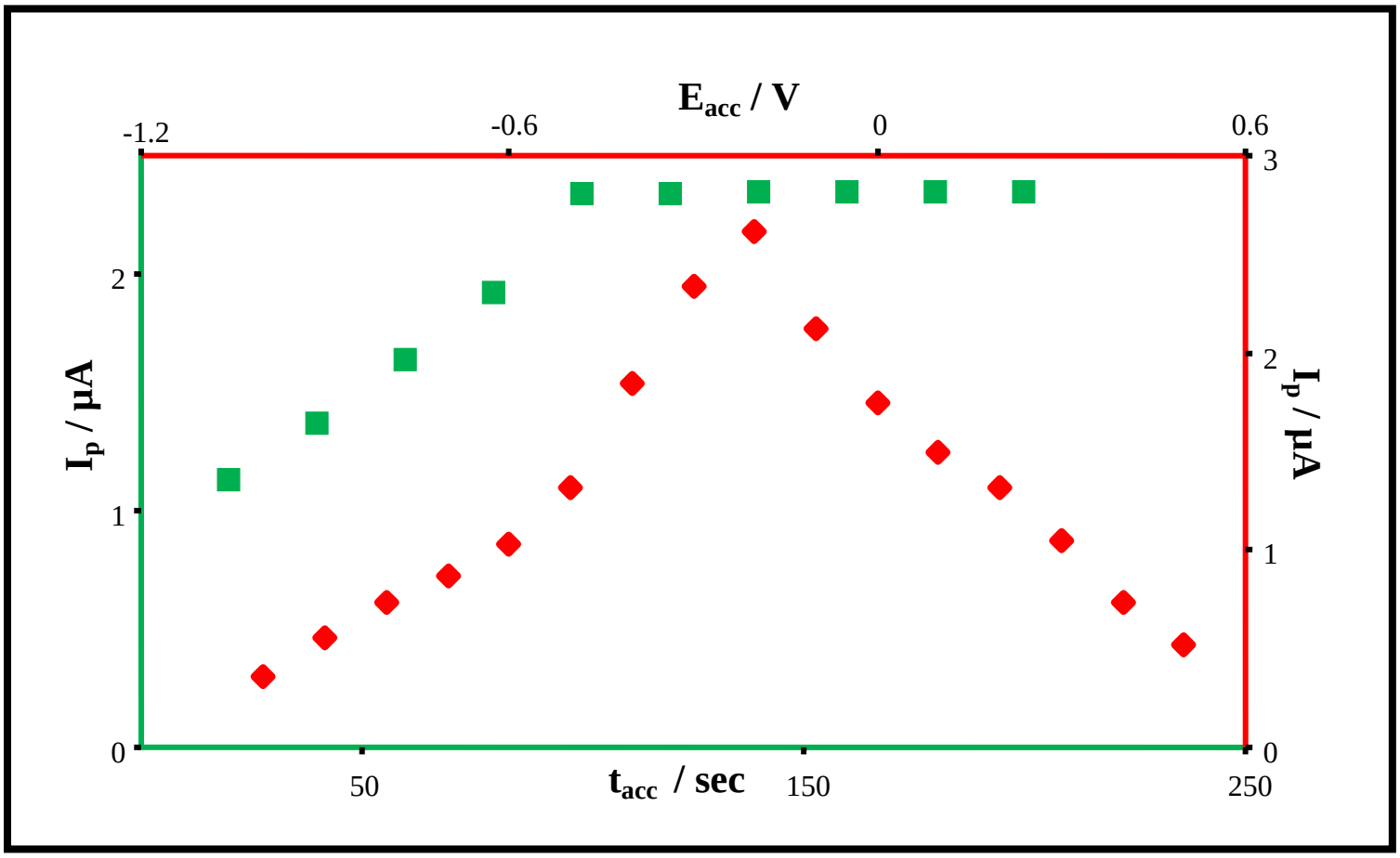

Fig. S10

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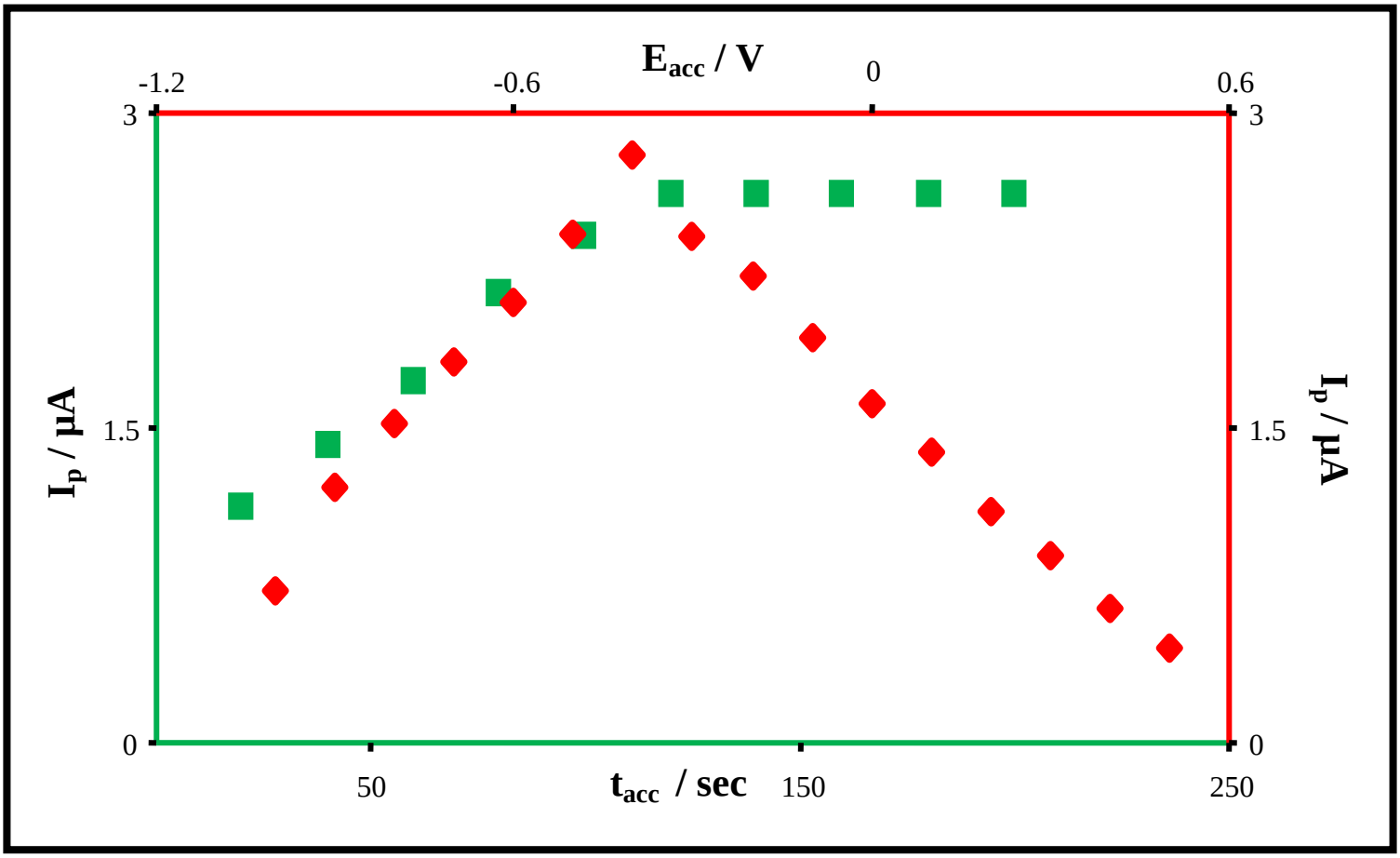

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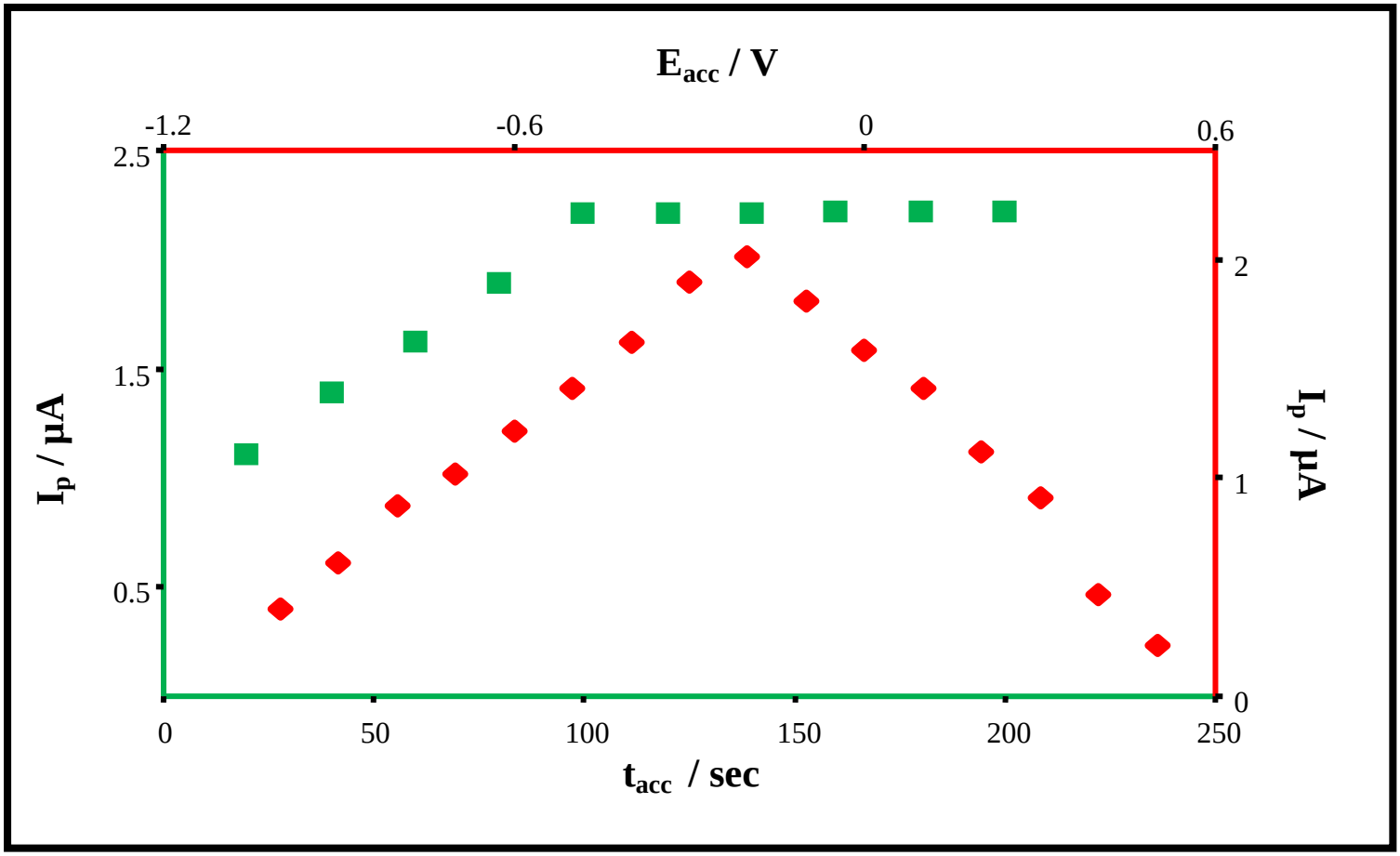


Fig. S12

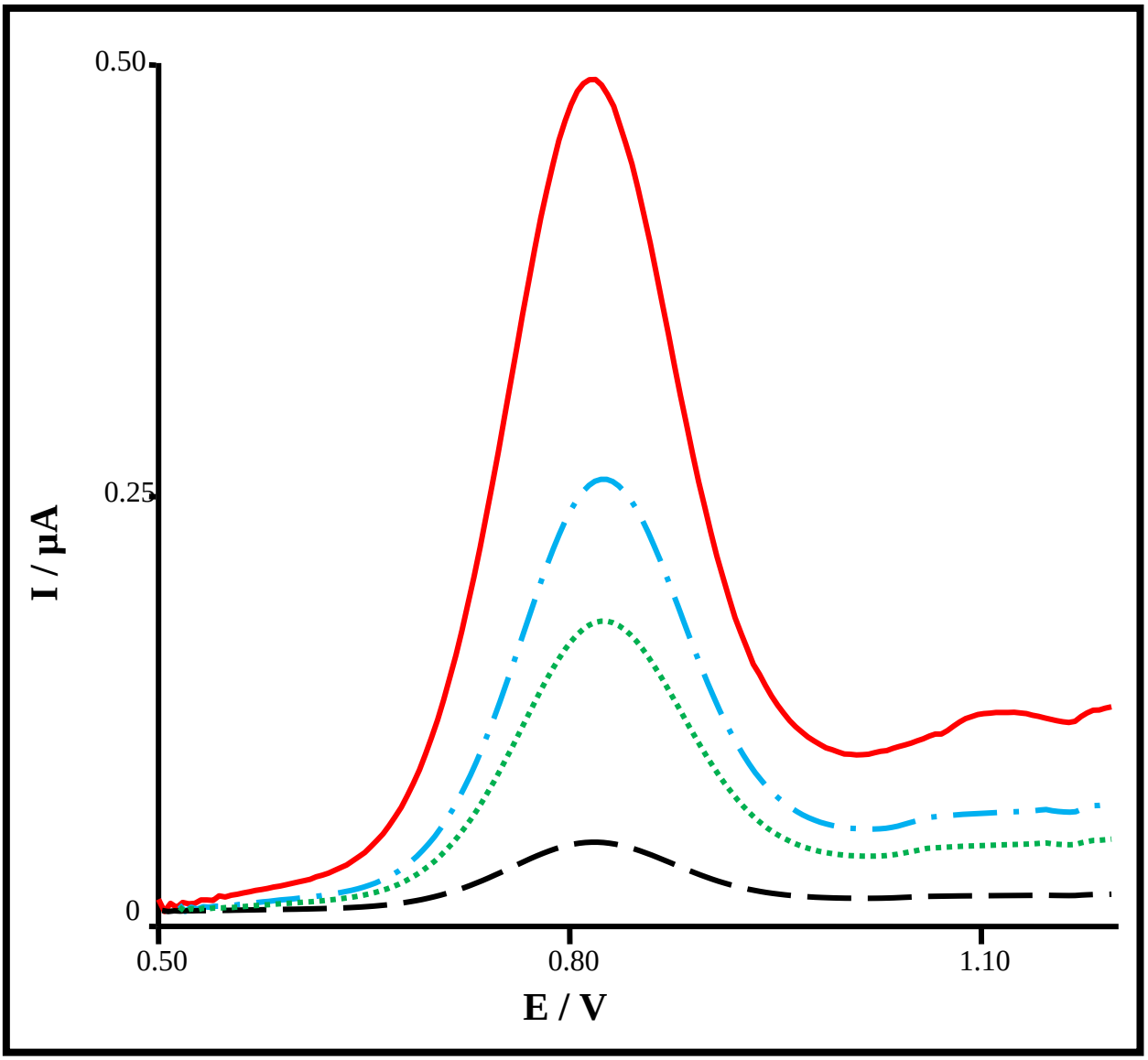


Fig. S13

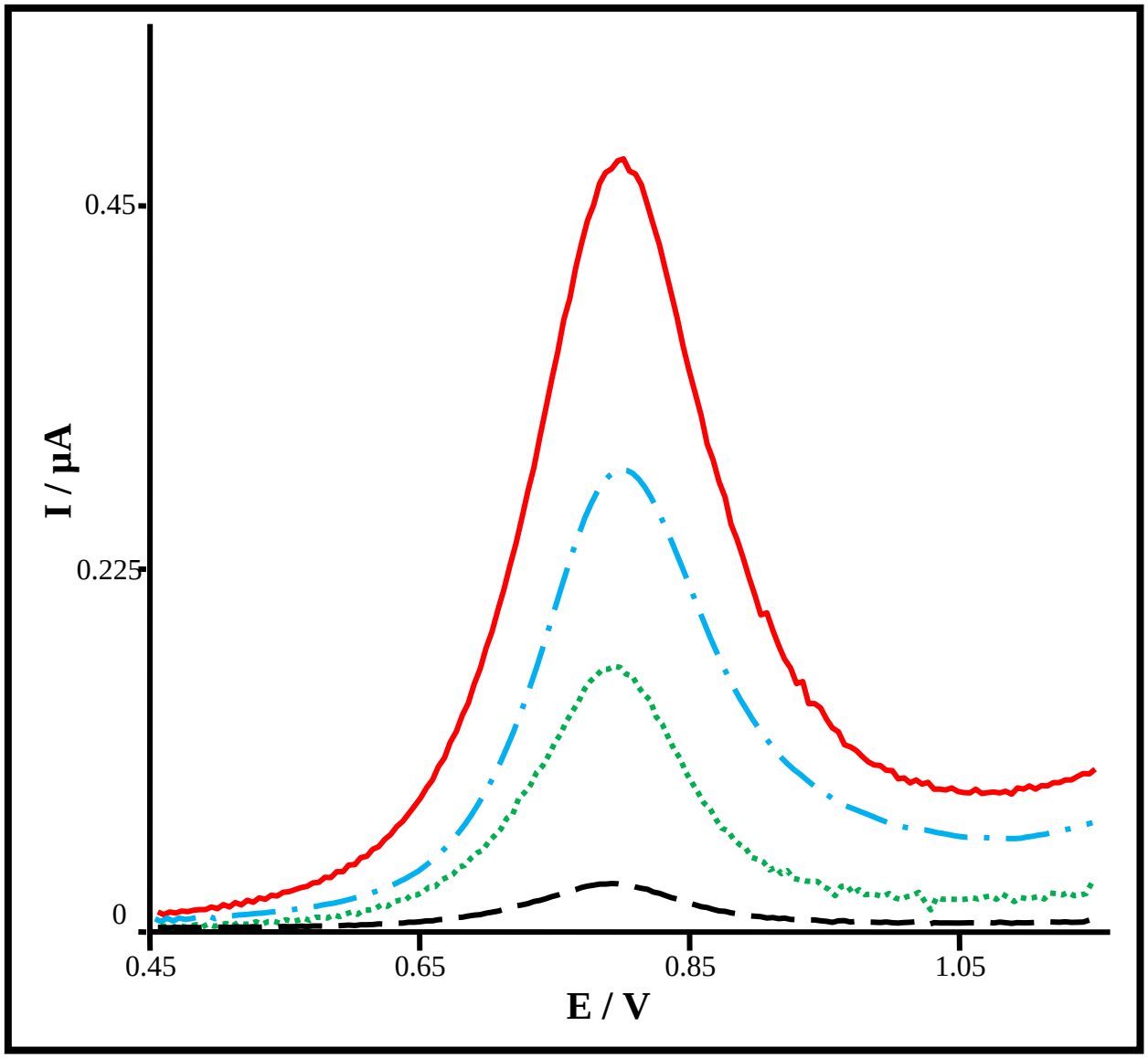
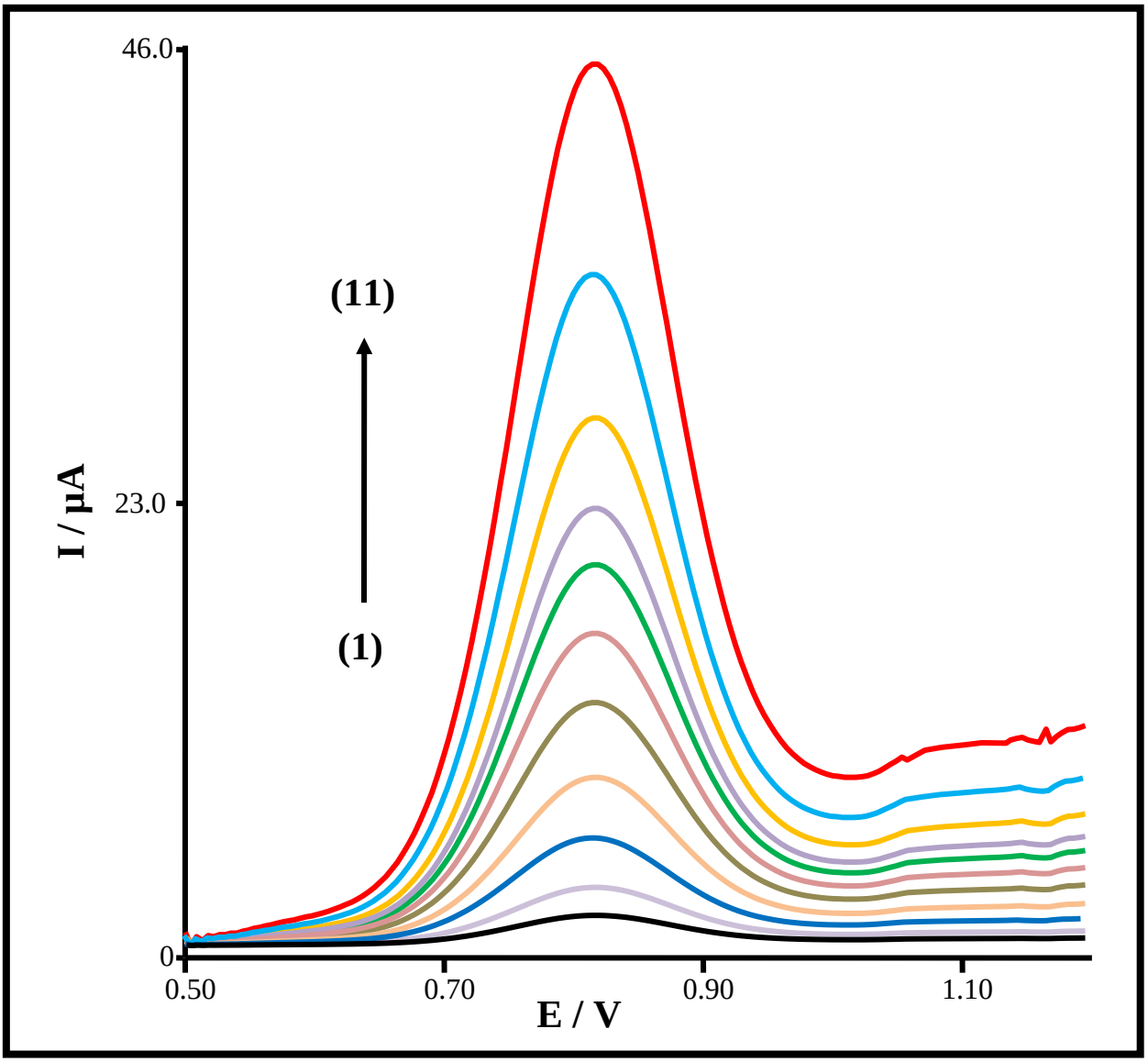


Fig. S14



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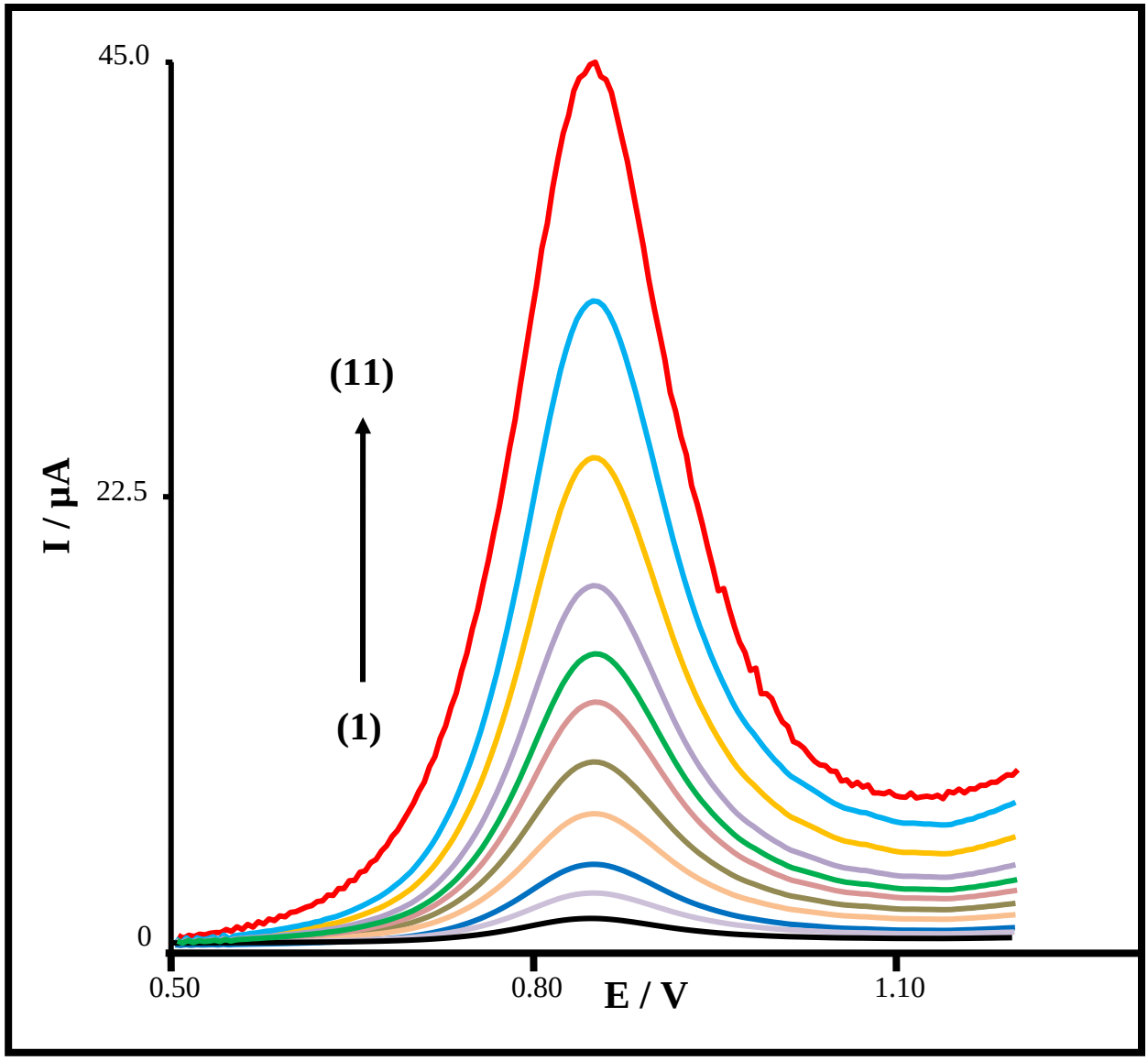

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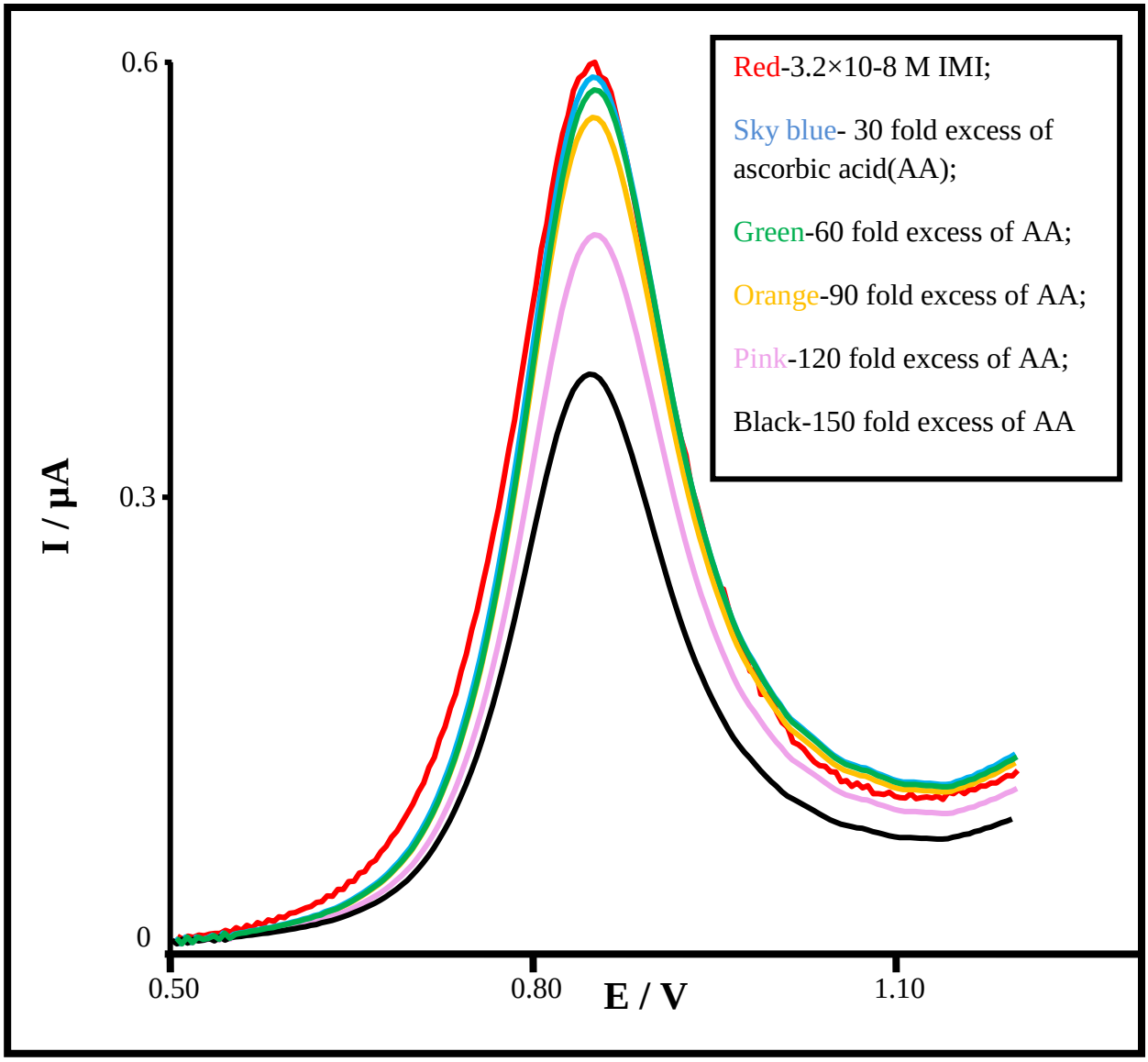

Fig. S17

Supporting Information Tables

Tables

Table S1.

Chronocoulometry data for 4.77×10^{-5} M IMI, 4.23×10^{-5} M TRI and 5.05×10^{-5} M DES.

Molecule	Electrode	Slope ($\mu C/s^{-1/2}$)	Q_{ads} (μC)	Surface coverage (10^{-10} mol / cm^2)	Diffusion coefficient (10^{-6} cm^2 / sec)
IMI	GCPE	0.257	0.171	0.740	4.31
	XAD2-GCPE	1.230	1.269	1.134	4.24
	TNP-GCPE	1.589	3.073	2.181	4.47
	XAD2-TNP-GCPE	2.885	8.181	3.163	4.37
TRI	GCPE	0.213	0.079	0.341	3.72
	XAD2-GCPE	1.019	1.572	1.404	3.64
	TNP-GCPE	1.289	4.724	3.353	3.68
	XAD2-TNP-GCPE	2.396	10.750	4.156	3.77
DES	GCPE	0.285	0.093	0.403	4.66
	XAD2-GCPE	1.386	1.058	0.945	4.72
	TNP-GCPE	1.743	2.437	1.729	4.71
	XAD2-TNP-GCPE	3.226	7.238	2.798	4.79

Table S2.

Table S2(a).
Precision and Bias of assay for standard IMI, TRI AND DES solutions by the proposed procedure (n=5).

No	Molecule	Concentration	Concentration	Recovery	Bias (%)	Precision %
1	IMI	Intra - day				
		5.43	5.41	99.6	0.4	1.84
		Inter - day				
		5.43	5.39	99.3	0.7	2.03
2	TRI	Intra - day				
		4.27	4.23	99.1	0.9	1.12
		Inter - day				
		4.27	4.20	98.4	1.6	1.31
3	DES	Intra - day				
		6.11	6.07	99.3	0.7	1.25
		Inter - day				
		6.11	6.05	99.0	1.0	1.47

Table S2(b). Robustness of the results for 5.43×10^{-8} M IMI, 4.27×10^{-8} M TRI and 6.11×10^{-8}M DES using the proposed procedure

No	Molecule	Variables	Procedural conditions	Recovery	Bias (%)	Precision %
		pH of the medium				
		5.0		100.2	-0.2	1.12
1	IMI	6.0	E_{acc} = -0.2 V, t_{acc} = 100 s	100.1	-0.1	1.05
		7.0		99.8	0.2	1.32
		Accumulation potential, (E_{acc}) V				
2	IMI	0.00		99.5	0.5	2.02
		-0.20	pH = 6.0, t_{acc} = 100 s	99.7	0.3	1.98
		-0.40		99.6	0.4	1.83
		Accumulation time, (t_{acc})				
		70		101.3	-1.3	1.24
3	IMI	100	E_{acc} = -0.2 V, pH = 6.0	100.7	-0.7	0.87
		130		100.8	-0.8	1.03
		pH of the medium				
		5.0		99.6	0.4	1.89
4	TRI	6.0	E_{acc} = -0.2 V, t_{acc} = 100 s	100.4	-0.6	2.01
		7.0		101.2	-1.2	1.61

5	TRI	Accumulation potential, (E_{acc}) V				
		− 0.20		100.5	-0.5	0.55
		− 0.40	pH = 6.0, t_{acc} = 120 s	99.8	0.2	0.63
		− 0.60		99.4	0.6	0.79
6	TRI	Accumulation time, (t_{acc})				
		90		99.4	0.6	1.34
		120	E_{acc} = -0.9 V, pH = 5.0	98.9	1.1	1.41
		150		99.6	0.4	1.56
7	DES	pH of the medium				
		5.0		101.2	-1.2	1.25
		6.0	E_{acc} = -0.2 V, t_{acc} = 120 s	100.3	-0.3	1.21
		7.0		100.5	-0.5	1.20
8	DES	Accumulation potential, (E_{acc}) V				
		0.00		100.3	-0.3	1.37
		− 0.20	pH = 6.0, t_{acc} = 120 s	99.8	0.2	1.45
		− 0.40		100.2	-0.2	1.29
9	DES	Accumulation time, (t_{acc})				
		70		101.2	-1.2	1.09
		100	E_{acc} = -0.2 V, pH = 6.0	100.7	-0.7	0.74
		130		101.1	-1.1	1.12

Table S3. Recovery test for IMI, TRI and DES in pharmaceutical formulations, urine and blood serum samples.

No.	IMI				TRI				DES			
	a	b	c	d	a	b	c	d	a	b	c	d
Tofranil	---	0.79	---	98.8 ± 0.36	---	---	---	---	---	---	---	---
	0.16	0.94	98.9		---	---	---		---	---	---	
	0.32	1.1	99.1		---	---	---		---	---	---	
	0.48	1.25	98.4		---	---	---		---	---	---	
Depsol	---	2.36	---	99.3 ± 0.38	---	---	---	---	---	---	---	---
	0.59	2.94	99.7		---	---	---		---	---	---	
	1.18	3.51	99.1		---	---	---		---	---	---	
	1.77	4.09	99.0		---	---	---		---	---	---	
Surmontil	---	---	---	---	---	0.61	---	97.9 ± 0.75	---	---	---	---
	---	---	---		0.15	0.75	98.7		---	---	---	
	---	---	---		0.3	0.89	97.8		---	---	---	
	---	---	---		0.45	1.03	97.2		---	---	---	
Stangyl	---	---	---	---	---	2.44	---	99.1 ± 0.75	---	---	---	---
	---	---	---		0.81	3.22	99.1		---	---	---	
	---	---	---		1.62	4.01	99.8		---	---	---	
	---	---	---		2.43	4.79	98.3		---	---	---	
Norpramine	---	---	---	---	---	---	---	---	---	0.33	---	98.1 ± 0.41
	---	---	---		---	---	---		0.11	0.43	97.7	
	---	---	---		---	---	---		0.22	0.54	98.2	
	---	---	---		---	---	---		0.33	0.65	98.5	
Pertofrane	---	---	---	---	---	---	---	---	---	0.83	---	98.3 ± 0.89
	---	---	---		---	---	---		0.2	1.01	98.1	
	---	---	---		---	---	---		0.4	1.2	97.6	
	---	---	---		---	---	---		0.6	1.42	99.3	
Urine sample 1	---	ND	---	99.0 ± 0.85	---	ND	---	98.0 ± 0.82	---	ND	---	98.6± 0.69
	1.25	1.23	99.4		0.93	0.92	98.9		1.15	1.14	99.1	
	2.50	2.45	98.0		1.86	1.81	97.3		2.3	2.25	97.8	
	3.75	3.73	99.5		2.79	2.73	97.8		3.45	3.41	98.8	
Urine sample 2	---	ND	---	98.8 ± 0.52	---	ND	---	98.8 ± 0.70	---	ND	---	98.5± 0.60
	2.50	2.48	99.2		1.86	1.84	98.9		2.3	2.27	98.7	
	5.00	4.91	98.2		3.72	3.65	98.1		4.6	4.55	98.9	
	7.50	7.42	98.9		5.58	5.55	99.5		6.9	6.75	97.8	

	---	ND	---		---	ND	---		---	ND	---	
Blood	1.38	1.37	99.3	98.4±	1.05	1.04	99.0	98.4 ±	0.88	0.87	98.9	98.5 ±
Serum	2.76	2.71	98.2	0.79	2.1	2.05	97.6	0.74	1.76	1.72	97.7	0.70
sample 1	4.14	4.05	97.8		3.15	3.11	98.7		2.64	2.61	98.9	
	---	ND	---		---	ND	---		---	ND	---	
Blood	2.76	2.73	98.9	99.1±	2.1	2.06	98.1	98.9±	1.76	1.74	98.9	99.2±
serum	5.52	5.48	99.3	0.21	4.2	4.15	98.8	0.80	3.52	3.5	99.4	0.25
sample 2	8.28	8.2	99.0		6.3	6.28	99.7		5.28	5.24	99.2	

ND : Not detected

a: Standard Drug (IMI/TRI/DES) added (10^{-8} M)

b : Drug (IMI/TRI/DES) found (10^{-8} M)

c : Recovery (%) (n=5)

d : % Average recovery ± %RSD (n = 5)