Electronic Supplementary Material (ESI) for Analytical Methods.

First report on the electrooxidation of vinpocetine using a modification free sensing platform: application to pharmaceutical formulations

Adriano Rogerio Silva Lima, Gabriel Chitolina Rodrigues, Alan Carlos Rezende Rodrigues, Caio Raphael Vanoni, Gustavo Amadeu Micke, Giovanni Finoto Caramori, Ricardo Ferreira Affeldt, Glaucio Régis Nagurniak, and Cristiane Luisa Jost

SUPPLEMENTARY INFORMATION

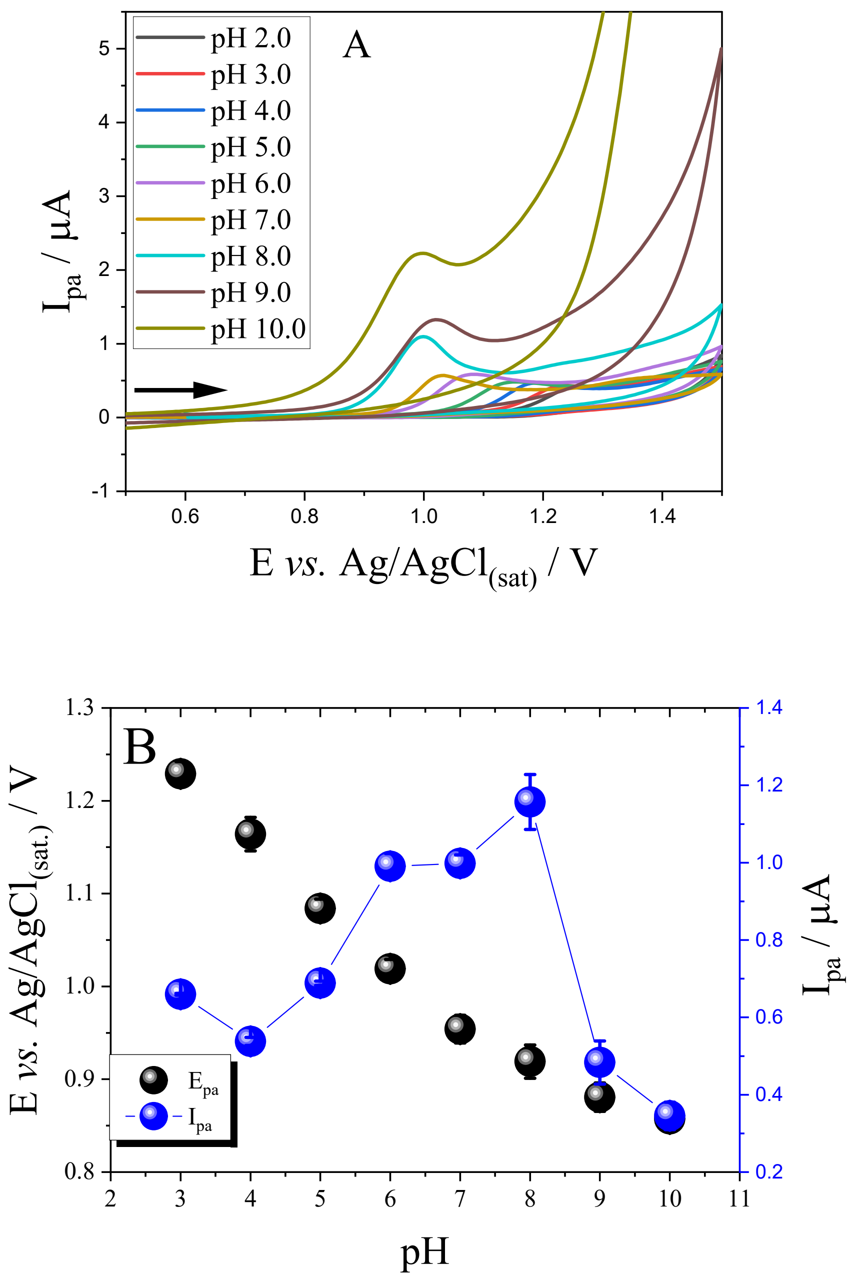
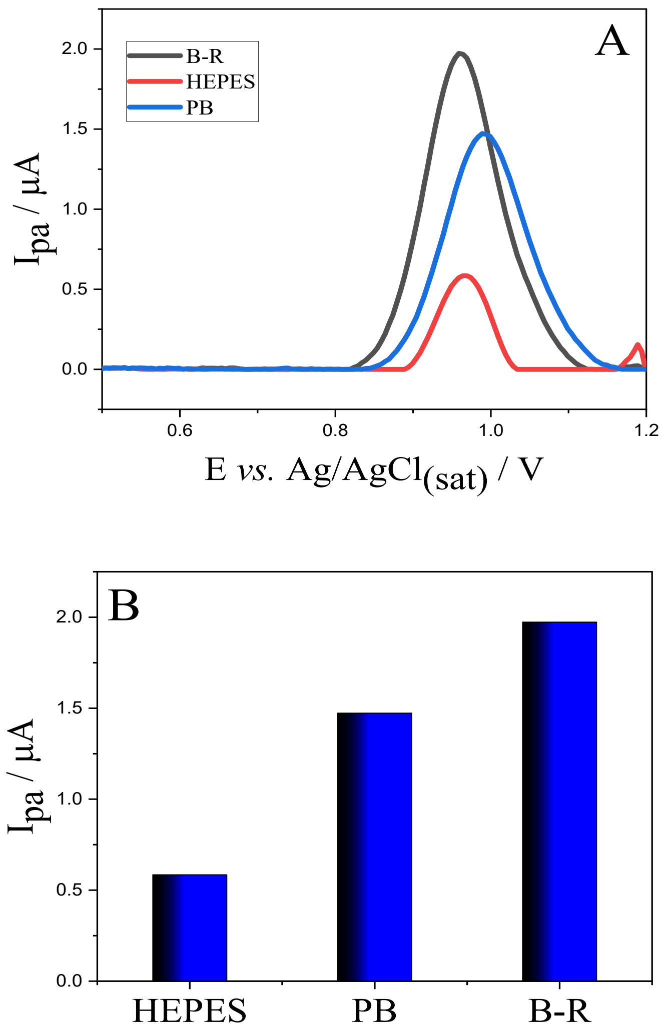
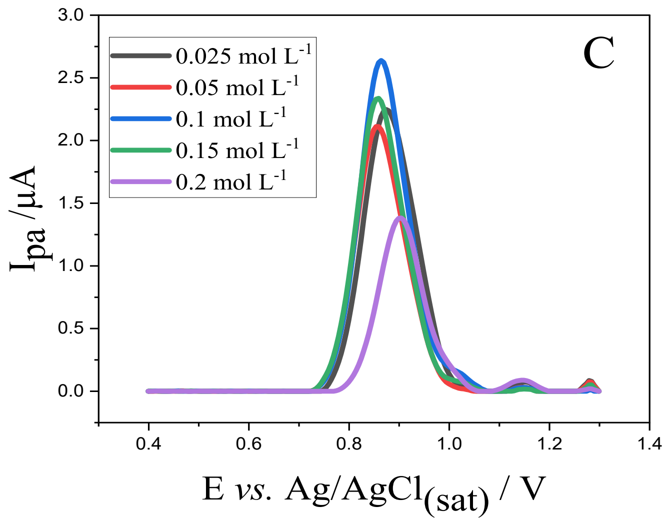


Figure S1. (A) Cyclic voltammograms for VIN 3.5 mg L^{-1} on GCE in B-R buffer at different pH values (2.0 – 10.0); (B) Variation of peak intensity and anodic peak potentials as a function of supporting electrolyte pH.



A
B-R
HEPES
PB
2.0
1.5
1.0
0.5
0.0
0.6
0.8
1.0
1.2
Ipa / µA
E vs. Ag/AgCl(sat) / V
B
2.0
1.5
1.0
0.5
0.0
Ipa / µA
HEPES
PB
B-R



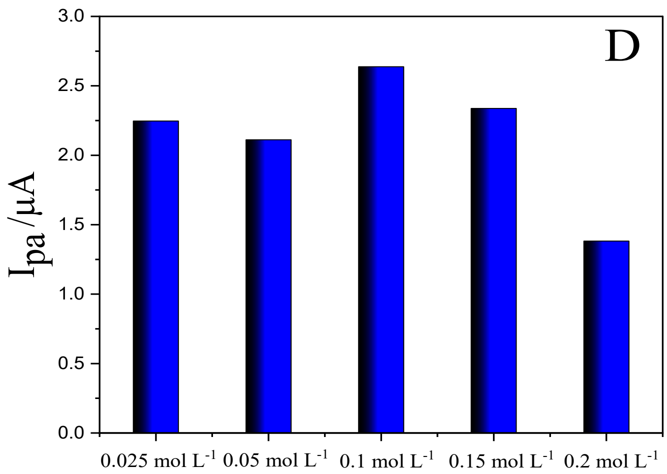
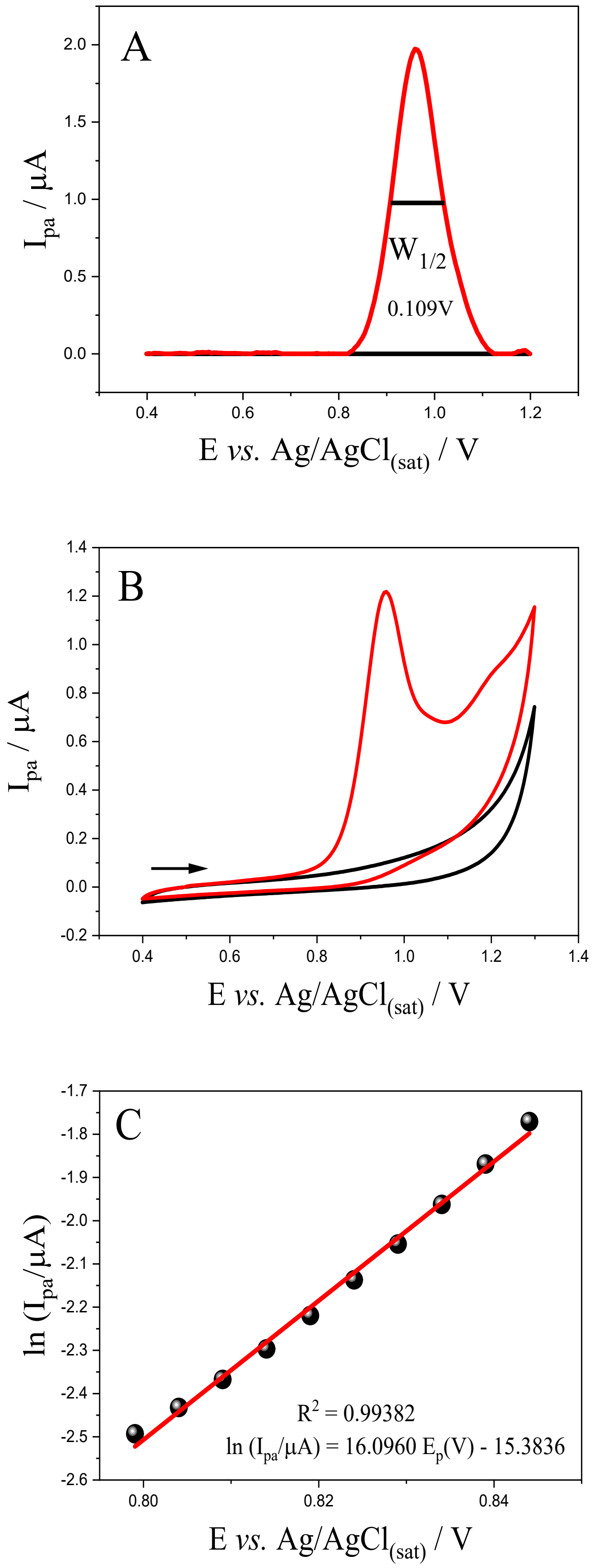


Figure S2. (A) DPV for VIN on GCE in different buffers HEPES, B-R, and PB pH 8.0, 0.1 mol L^{-1}. (B) The anodic current intensities for VIN. (C) DPV for VIN on GCE at different concentrations, and (D) Shows the anodic current intensities for VIN versus B-R buffer concentrations at pH 8.0.


A
I_{pa} / μA
$W_{1/2}$
0.109V
E vs. Ag/AgCl(sat) / V
B
I_{pa} / μA
E vs. Ag/AgCl(sat) / V
C
ln (I_{pa}/μA)
R^2 = 0.99382
ln (I_{pa}/μA) = 16.0960 E_p(V) - 15.3836
E vs. Ag/AgCl(sat) / V

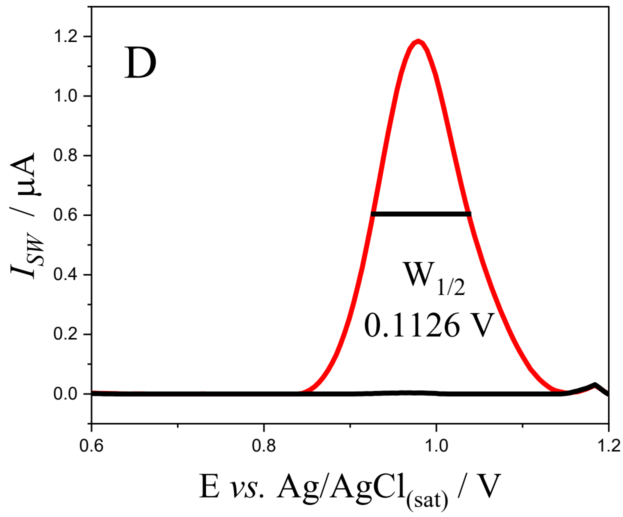
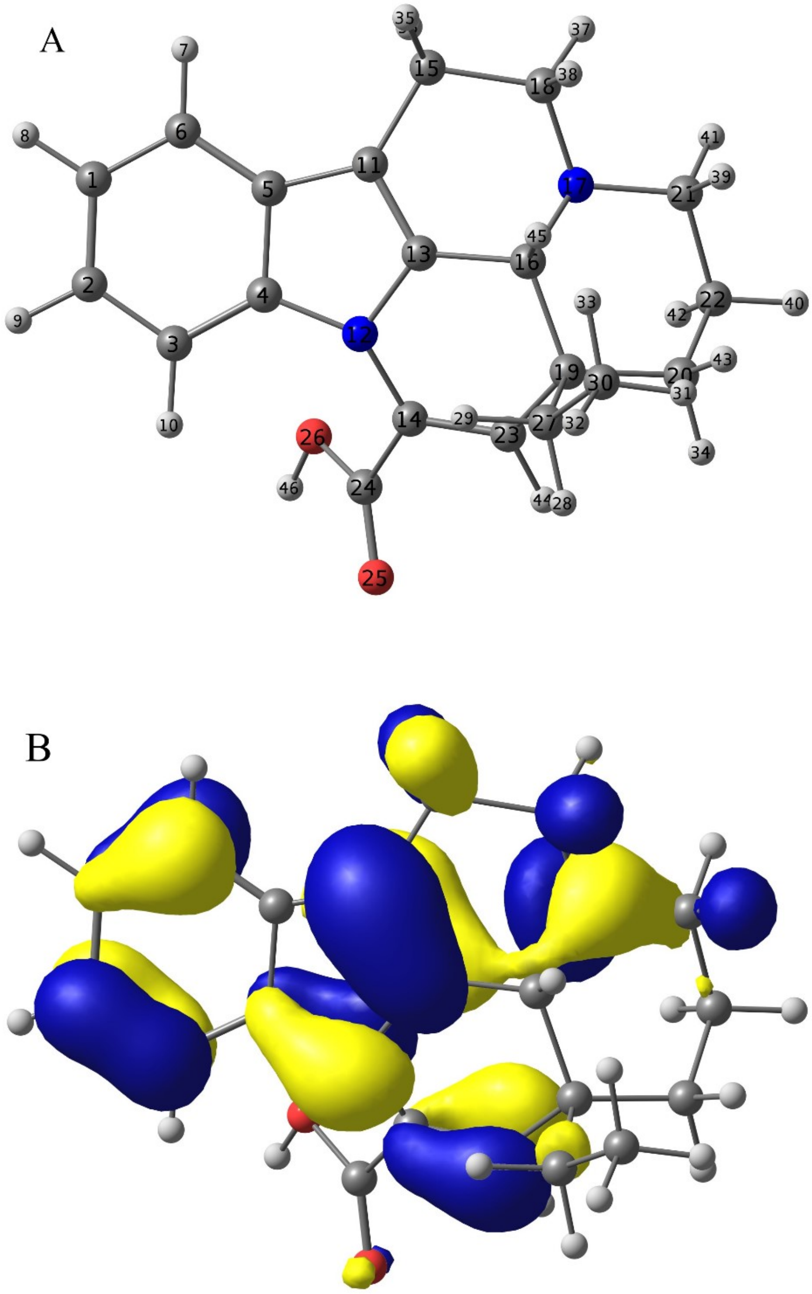


Figure S3. (A) DP voltammogram and the experimental determination of width at the mid-height ($W_{1/2}$) of *ca*. 0.109 V. (B) Cyclic voltammograms for VIN (3.5 mg L^{-1}, red) in B-R 0.1 mol L^{-1} solution (pH 8.0, black), ν = 50 mV s^{-1}, after baseline correction. (C) Tafel plot and the correspondent relation of ln I_{pa} *vs*. E_{pa}. (D) SW voltammogram and the experimental determination of width at the mid-height ($W_{1/2}$) of *ca*. 0.113 V.


A
B

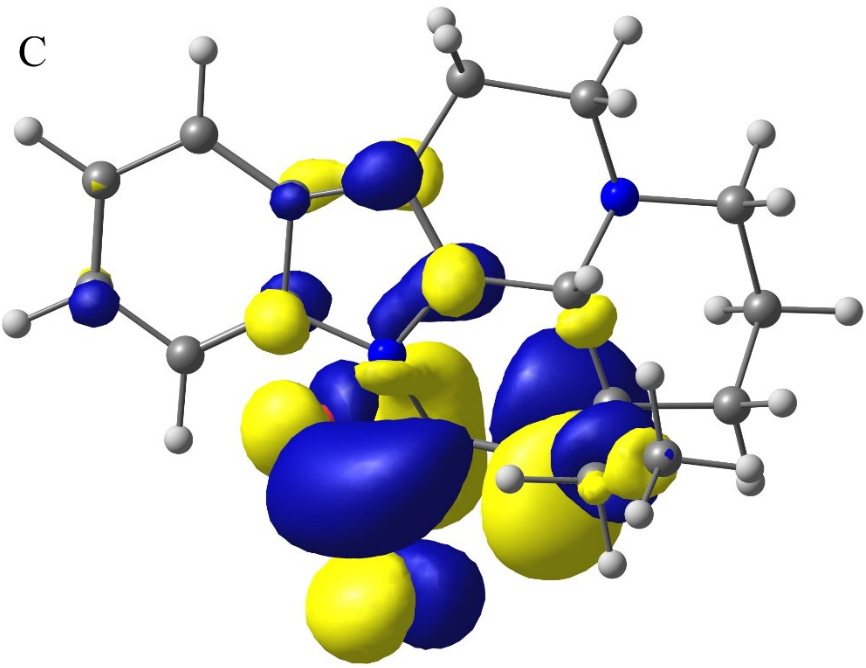
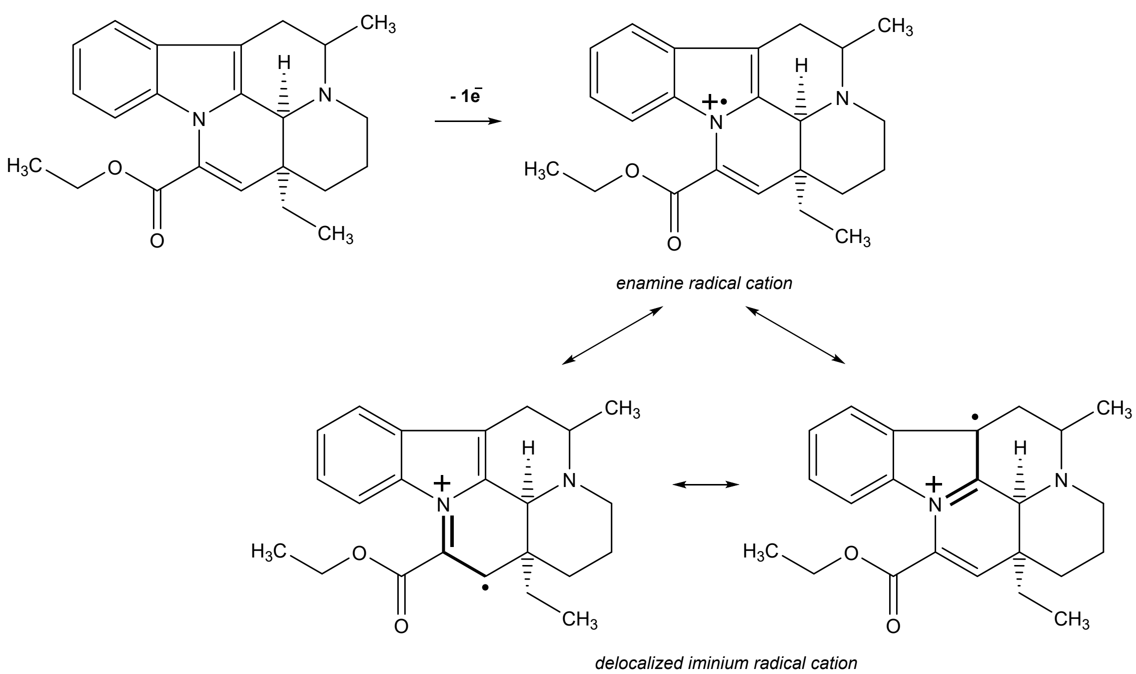


Figure S4. Labeled atoms (A), highest occupied molecular orbital (HOMO) (B), and lowest unoccupied molecular orbital (LUMO) (C) of VIN. The grey, white, blue, and red spheres represent the carbon, hydrogen, nitrogen, and oxygen atoms.



Scheme 1. Mechanism suggestion for VIN oxidation process.

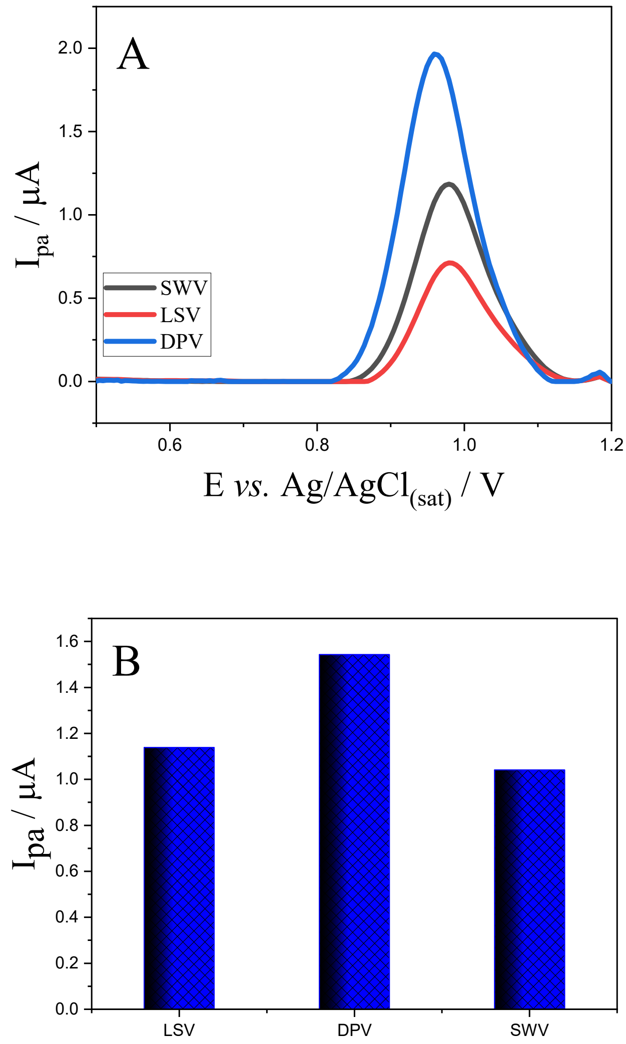


Figure S5. (A) Voltammograms obtained by LSV, DPV, and SWV for VIN 3.5 mg L^{-1} in B-R buffer solution 0.1 mol L^{-1} (pH 8.0) on GCE; ν = 50 mVs^{-1}, after baseline correction and (B) the correspondent data analysis**.**

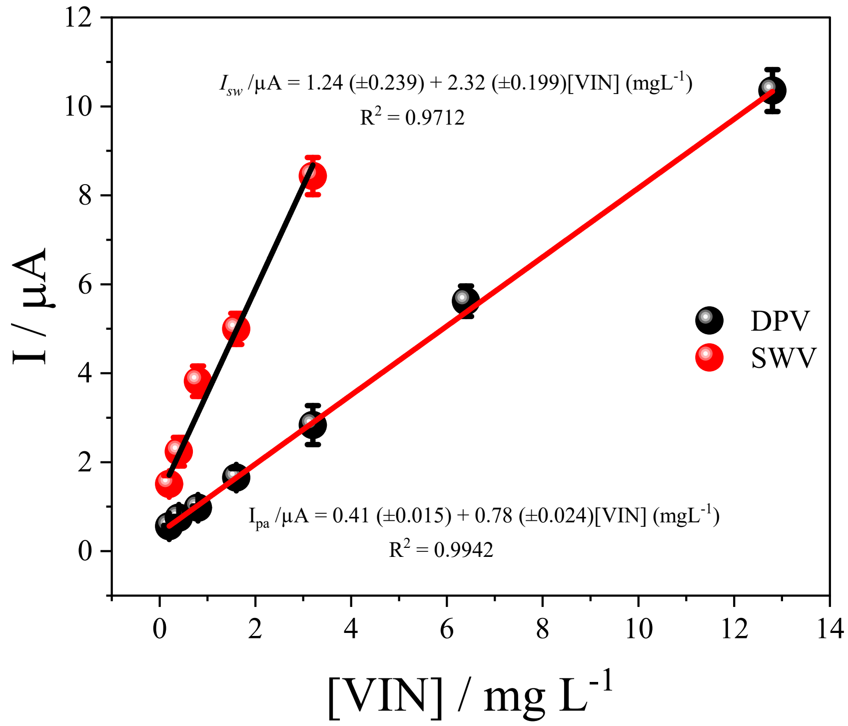


Figure S6. Relationship between the anodic peak current and the concentration of VIN for SWV (red dots) and DPV (black dots).

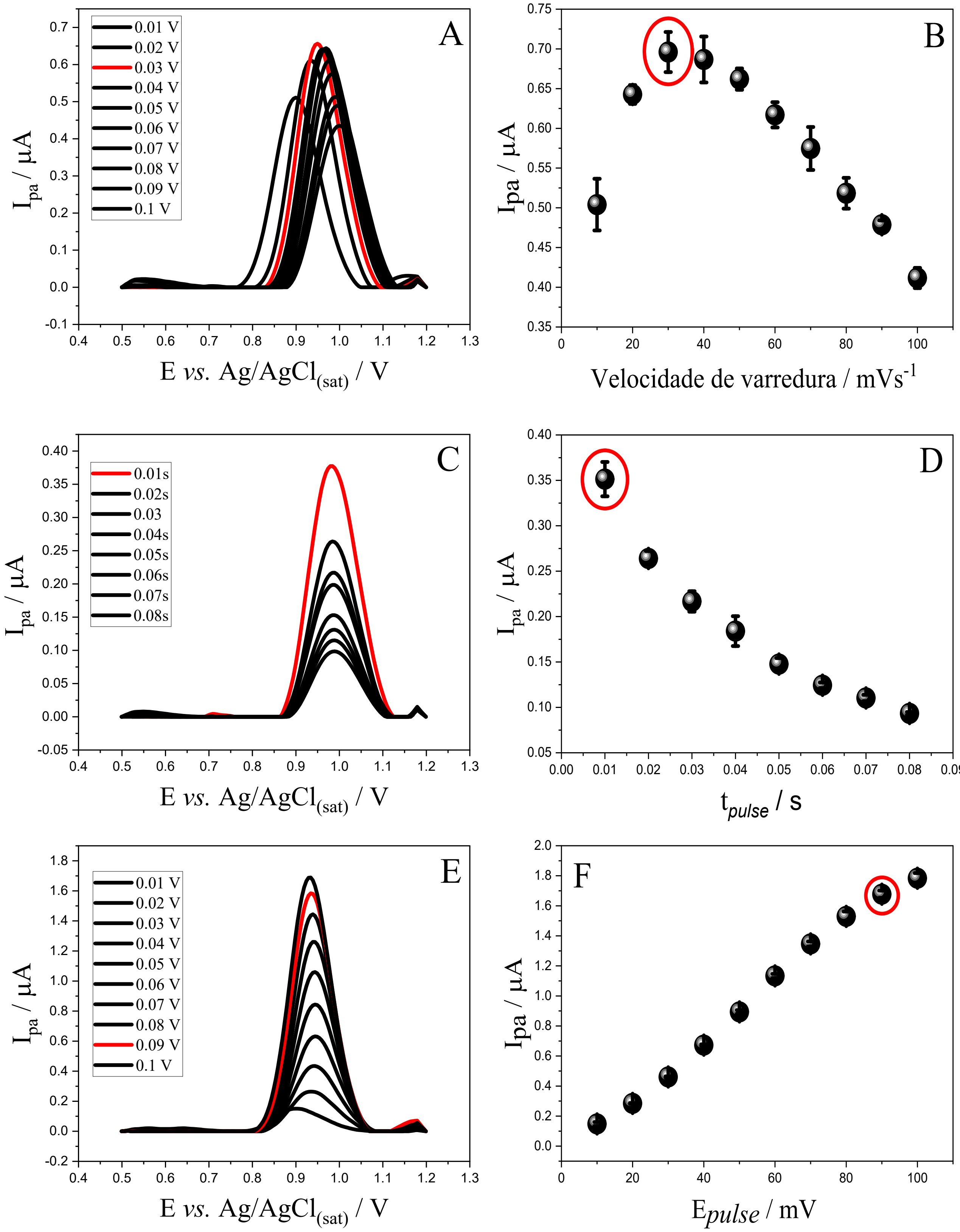
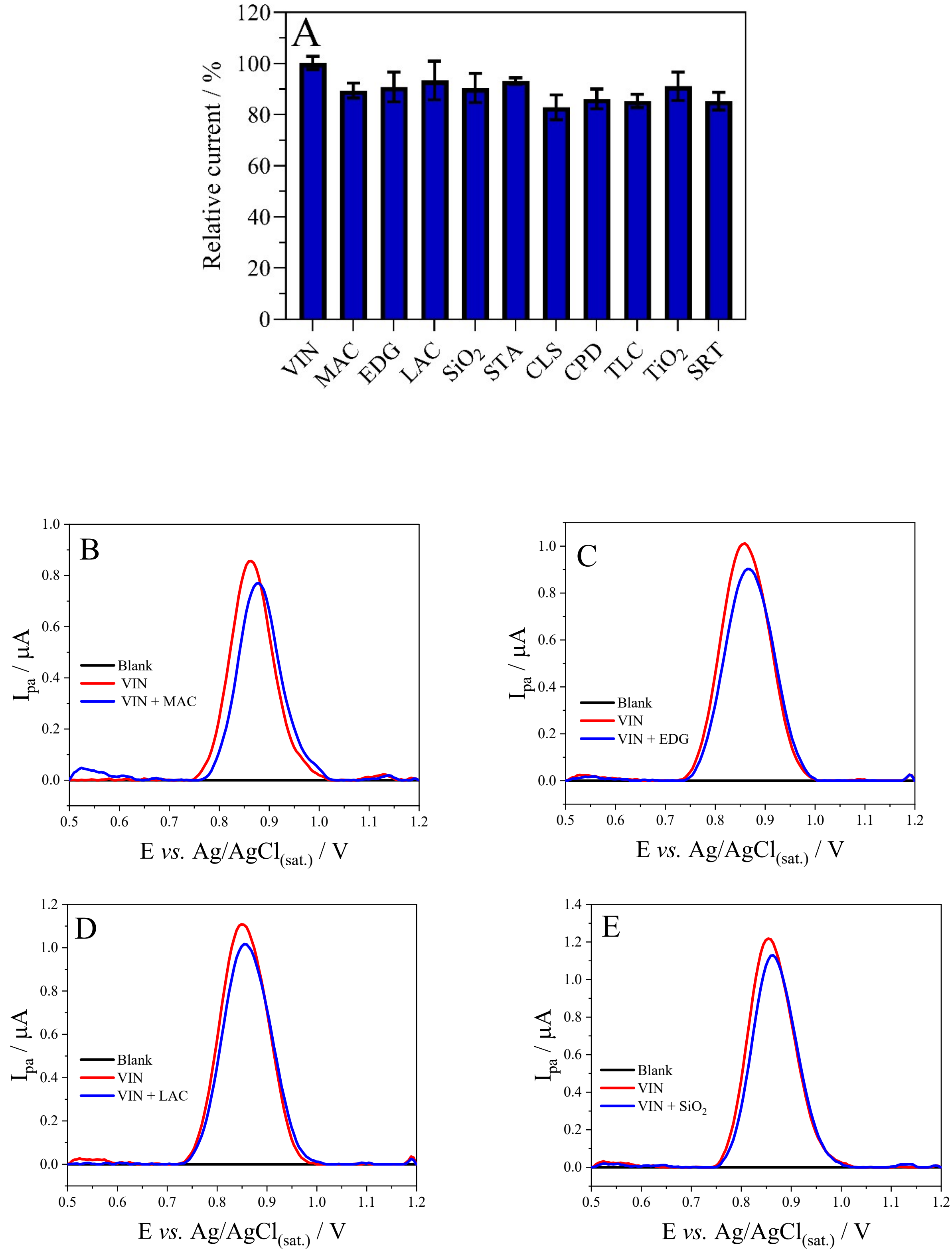
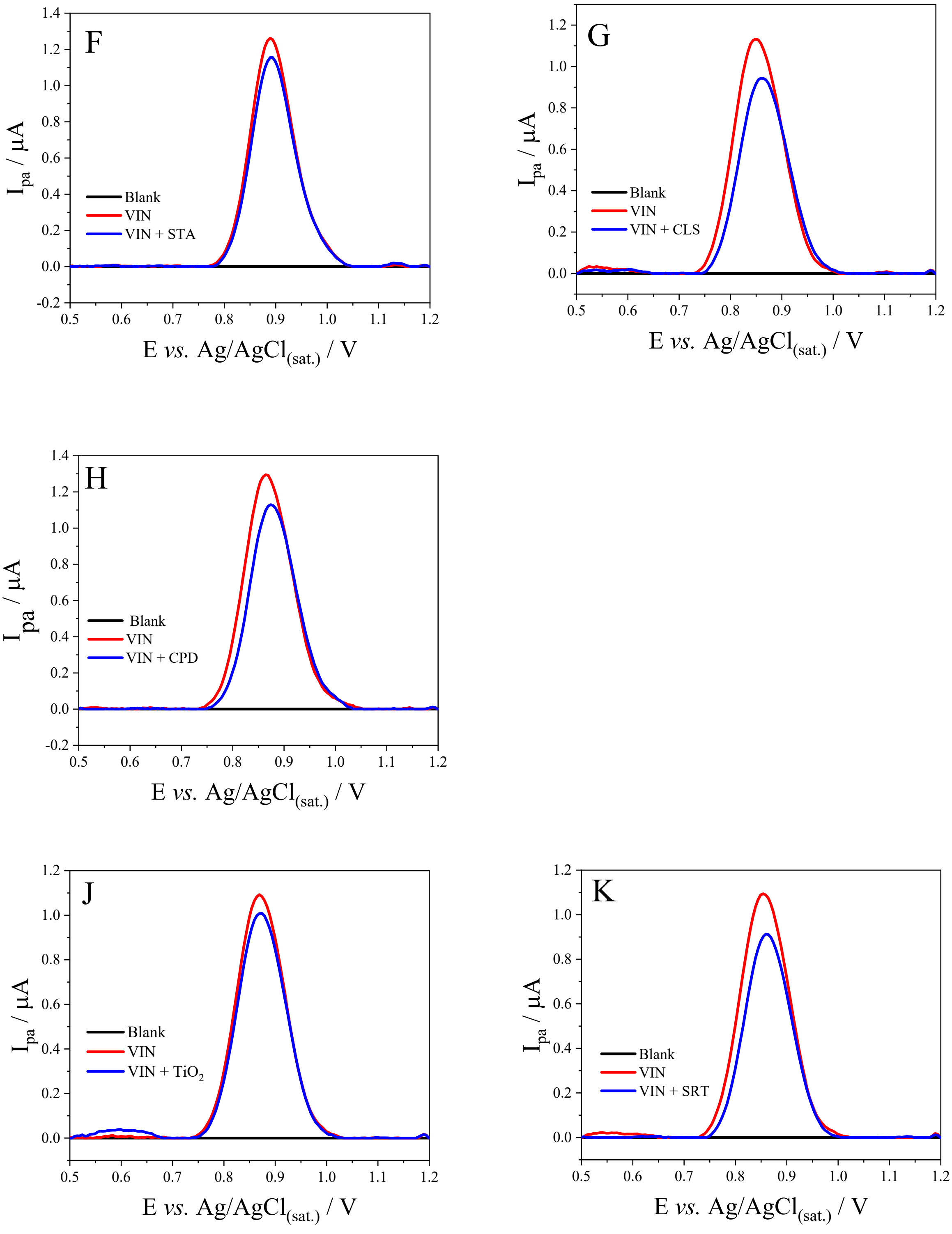
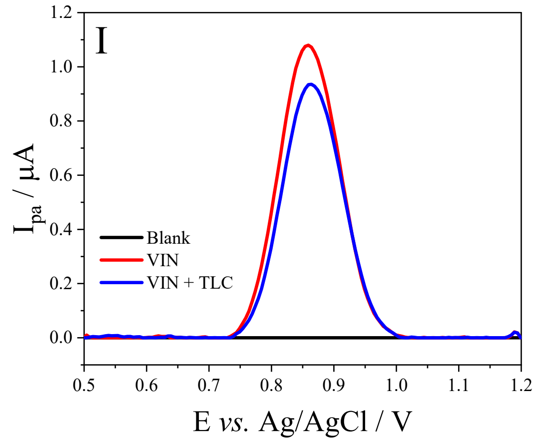


Figure S7. DP voltammograms for VIN using the GCE. (A) Variation of scan rate with (B) the correspondent data. (C) Variation of pulse time with (D) the correspondent data. (E) Variation of pulse amplitude with (F) the correspondent data. Experimental conditions: BR-buffer 0.1 mol L^{-1} pH 8.0 in the presence of 3.5 mg L^{-1} of VIN.

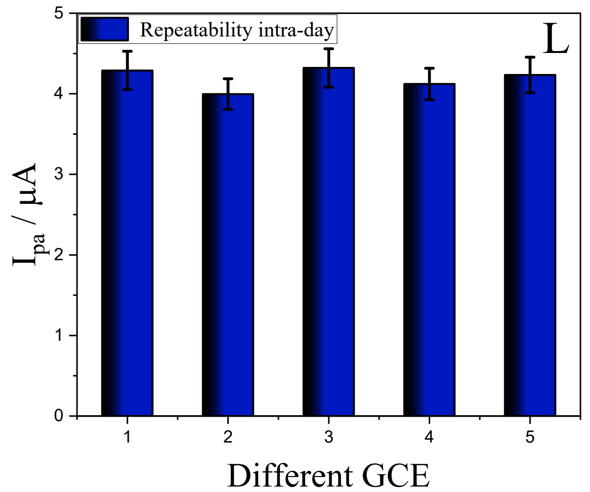

A
Relative current / %
0
20
40
60
80
100
120
VIN
MAC
EDG
LAC
SiO_2
STA
CLS
CPD
TLC
TiO_2
SRT
B
Blank
VIN
VIN + MAC
C
Blank
VIN
VIN + EDG
D
Blank
VIN
VIN + LAC
E
Blank
VIN
VIN + SiO_2
I_{pa} / μA
E *vs.* Ag/AgCl$_{(sat.)}$ / V
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2



F
Blank
VIN
VIN + STA
I_{pa} / µA
E *vs.* Ag/AgCl$_{(sat.)}$ / V
G
Blank
VIN
VIN + CLS
I_{pa} / µA
E *vs.* Ag/AgCl$_{(sat.)}$ / V
H
Blank
VIN
VIN + CPD
I_{pa} / µA
E *vs.* Ag/AgCl$_{(sat.)}$ / V
J
Blank
VIN
VIN + TiO_2
I_{pa} / µA
E *vs.* Ag/AgCl$_{(sat.)}$ / V
K
Blank
VIN
VIN + SRT
I_{pa} / µA
E *vs.* Ag/AgCl$_{(sat.)}$ / V



I
Blank
VIN
VIN + TLC
I_{pa} / µA
E *vs.* Ag/AgCl / V



L
Repeatability intra-day
I_{pa} / µA
Different GCE

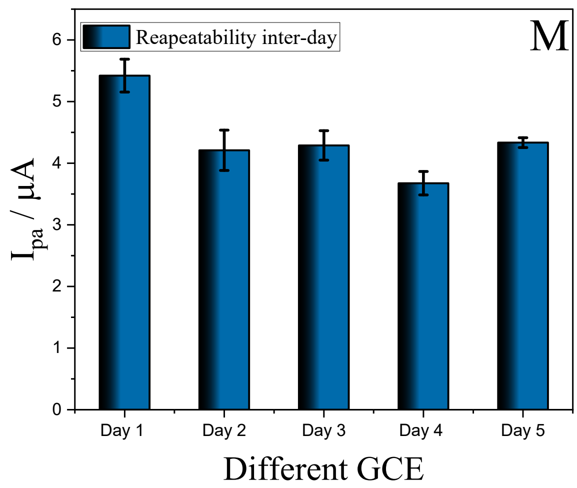


Figure S8. Selectivity and repeatability tests. (A) Peak current intensity using DPV for VIN, and in the presence of possible interferers macrogol (MAC), eudragit (EDG), lactose (LAC), silicon dioxide (SiO_2), starch (STA), cellulose (CLS), crospovidone (CPD), talc (TLC), titanium dioxide (TiO_2) and magnesium stearate (STR), (B-K) Comparative graph of VIN current intensity versus interfering potentials (VIN/Mac, VIN/EDG, VIN/LAC, VIN/SiO_2, VIN/STA, VIN/CLS, VIN/CPD, VIN/TLC, VIN/TiO_2 and VIN/SRT), after baseline correction, (L) Peak current response for intra-day repeatability using GCE and (M) Peak current response for inter-day repeatability using GCE.

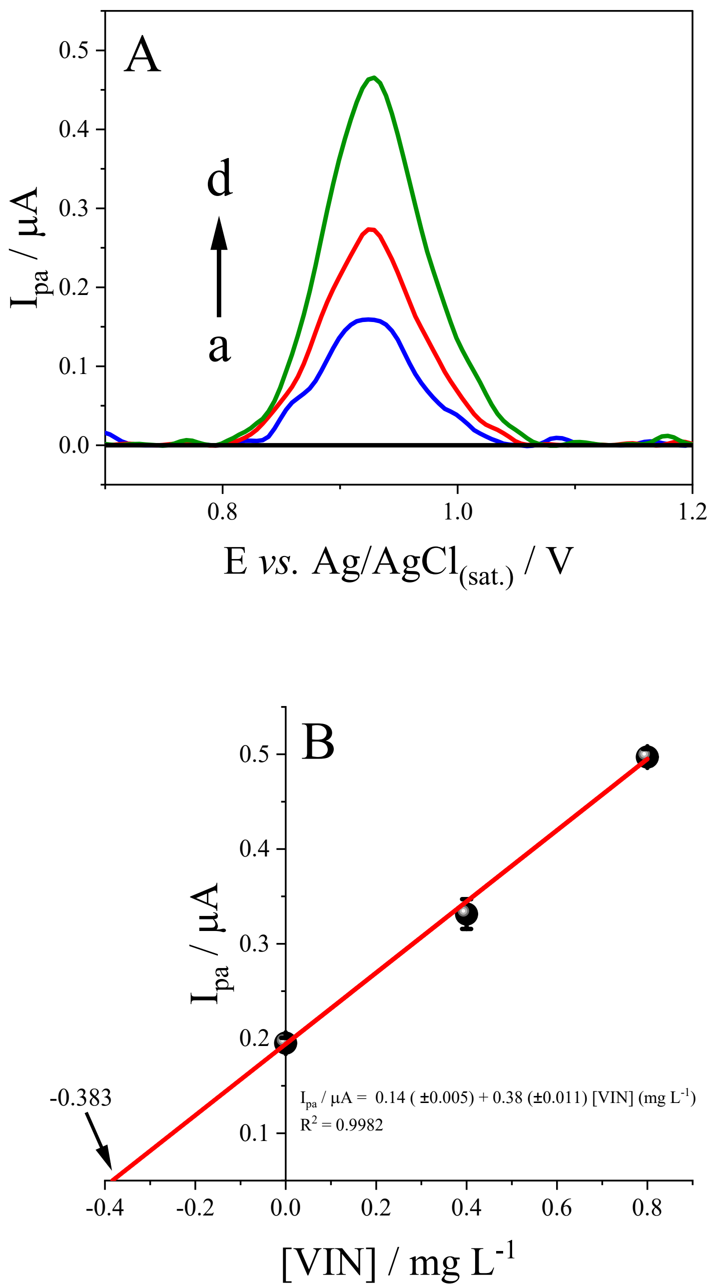


Figure S9. (A) DP voltammograms recorded using the GCE in the presence of VIN: (a) blank; (b) sample; (c-d) successive additions of 20 μL of 10^{-3} mol L^{-1} VIN standard solution in 0.1 mol L^{-1} B-R buffer solution (pH 8.0), baseline corrected. (B) Calibration curve for the relationship between anodic peak current and VIN concentration based on the standard addition method.

Table S1. Hirshfeld charges (*q*), condensed Fukui functions (f^{-}, f^{+}, and f^{0}), and condensed dual descriptor (Δf) for all VIN atoms. The N, (N + 1), and (N – 1) represent the ground, oxidized, and reduced states of VIN, respectively. All the charge values are expressed in atomic units.

Atom	$q(N)$	$q(N+1)$	$q(N-1)$	f^{-}	f^{+}	f^{0}	Δf
1 (C)	-0.0552	-0.0895	-0.0218	0.0335	0.0343	0.0339	0.0008
2 (C)	-0.0535	-0.0974	-0.0028	0.0507	0.0439	0.0473	-0.0068
3 (C)	-0.0574	-0.072	-0.0261	0.0313	0.0146	0.0229	-0.0167
4 (C)	0.0257	0.0149	0.0425	0.0168	0.0108	0.0138	-0.006
5 (C)	-0.0236	-0.046	-0.0142	0.0095	0.0224	0.0159	0.0129
6 (C)	-0.0503	-0.083	-0.0095	0.0408	0.0327	0.0367	-0.0081
7 (H)	0.0385	0.016	0.0603	0.0218	0.0225	0.0221	0.0007
8 (H)	0.0369	0.0122	0.0627	0.0258	0.0247	0.0252	-0.0011
9 (H)	0.0373	0.009	0.0645	0.0272	0.0284	0.0278	0.0012
10 (H)	0.0363	0.0239	0.0517	0.0155	0.0124	0.0139	-0.0031
11 (C)	-0.0369	-0.0775	0.0134	0.0504	0.0406	0.0455	-0.0098
12 (N)	-0.0011	0.0005	0.0287	0.0298	-0.0016	0.0141	-0.0314
13 (C)	0.0187	-0.0027	0.0488	0.0301	0.0214	0.0257	-0.0087
14 (C)	0.0242	-0.0403	0.0328	0.0086	0.0645	0.0366	0.0559
15 (C)	-0.0474	-0.0583	-0.0333	0.0141	0.0109	0.0125	-0.0032
16 (C)	0.0147	0.0159	0.0295	0.0148	-0.0012	0.0068	-0.016
17 (N)	-0.0839	-0.0768	0.0088	0.0927	-0.0071	0.0428	-0.0998
18 (C)	-0.01	-0.0158	0.0097	0.0196	0.0058	0.0127	-0.0138
19 (C)	0.0175	0.0113	0.0199	0.0024	0.0062	0.0043	0.0038
20 (C)	-0.0521	-0.0584	-0.0457	0.0064	0.0063	0.0063	-0.0001
21 (C)	-0.0166	-0.0206	0.0053	0.0219	0.004	0.0129	-0.0179
22 (C)	-0.0555	-0.0602	-0.0458	0.0097	0.0047	0.0072	-0.005
23 (C)	-0.0421	-0.1294	-0.0141	0.028	0.0873	0.0576	0.0593

24 (C)	0.1796	0.1094	0.1857	0.0061	0.0701	0.0381	0.064
25 (O)	-0.2604	-0.344	-0.2252	0.0352	0.0836	0.0594	0.0484
26 (O)	-0.1406	-0.1791	-0.1324	0.0082	0.0385	0.0233	0.0303
27 (C)	-0.045	-0.0556	-0.0382	0.0068	0.0106	0.0087	0.0038
28 (H)	0.0331	0.0215	0.047	0.0139	0.0115	0.0127	-0.0024
29 (H)	0.0303	0.0261	0.0372	0.0069	0.0042	0.0055	-0.0027
30 (C)	-0.0877	-0.1025	-0.0795	0.0082	0.0148	0.0115	0.0066
31 (H)	0.0297	0.0167	0.0409	0.0112	0.013	0.0121	0.0018
32 (H)	0.0372	0.0144	0.0528	0.0155	0.0229	0.0192	0.0074
33 (H)	0.0277	0.0185	0.0316	0.0039	0.0093	0.0066	0.0054
34 (H)	0.0335	0.0228	0.05	0.0165	0.0107	0.0136	-0.0058
35 (H)	0.0345	0.0127	0.0594	0.025	0.0218	0.0234	-0.0032
36 (H)	0.0374	0.0261	0.0635	0.0261	0.0114	0.0187	-0.0147
37 (H)	0.0355	0.0176	0.0569	0.0213	0.0179	0.0196	-0.0034
38 (H)	0.012	-0.0044	0.0503	0.0383	0.0164	0.0273	-0.0219
39 (H)	0.0134	-0.0097	0.0493	0.0359	0.0232	0.0295	-0.0127
40 (H)	0.0349	0.0178	0.0566	0.0217	0.017	0.0194	-0.0047
41 (H)	0.0343	0.0187	0.055	0.0206	0.0157	0.0181	-0.0049
42 (H)	0.0304	0.0255	0.0377	0.0073	0.0049	0.0061	-0.0024
43 (H)	0.0281	0.0132	0.0402	0.0121	0.0149	0.0135	0.0028
44 (H)	0.0427	0.0062	0.0607	0.0181	0.0365	0.0273	0.0184
45 (H)	0.0214	0.0117	0.043	0.0215	0.0097	0.0156	-0.0118
46 (H)	0.1743	0.1404	0.192	0.0177	0.0339	0.0258	0.0162

VIN	VIN-OXI	VIN-RED
Energy = -1035.707276876883 Hartree	Energy = -1035.466782841832 Hartree	Energy = -1035.700179194273 Hartree
Negative Frequency = none	Negative Frequency = none	Negative Frequency = none
C -3.189412 -2.146459 3.573591	C -3.178377 -1.867663 3.509709	C -3,150355 -2,096008 3,709667
C -3.297412 -3.142816 2.586327	C -3.328331 -2.727415 2.412771	C -3,314790 -3,020093 2,656181
C -2.175077 -3.602029 1.894635	C -2.222929 -3.212589 1.689774	C -2,236258 -3,426637 1,866789
C -0.938859 -3.034536 2.206059	C -0.962261 -2.802340 2.093835	C -0,967399 -2,893140 2,123406
C -0.802971 -2.053675 3.236256	C -0.784997 -1.968405 3.243459	C -0,776320 -1,998558 3,247105
C -1.950288 -1.604342 3.909433	C -1.908893 -1.486029 3.939238	C -1,888526 -1,593793 4,011500
H -1.870103 -0.854621 4.697740	H -1.786752 -0.843442 4.811089	H -1,751356 -0,913040 4,855363
H -4.086200 -1.809787 4.094576	H -4.060876 -1.511676 4.039218	H -4,014522 -1,792331 4,304803
H -4.273432 -3.572719 2.360188	H -4.327446 -3.033904 2.104597	H -4,304114 -3,433769 2,451009
H -2.273053 -4.386210 1.146118	H -2.377328 -3.883120 0.850215	H -2,384368 -4,131780 1,056004
C 0.606394 -1.773708 3.373833	C 0.621220 -1.852987 3.463883	C 0,625587 -1,785624 3,366357
N 0.350336 -3.316017 1.711943	N 0.339216 -3.152112 1.615058	N 0,294859 -3,143932 1,543958
C 1.256565 -2.600021 2.507466	C 1.242959 -2.650332 2.507368	C 1,222377 -2,545216 2,387425
C 0.779095 -3.689782 0.421592	C 0.811721 -3.717809 0.410467	C 0,757267 -3,610274 0,262366

C 1.345893 -0.646812 4.033226	C 1.506520 -1.060557 4.364245	C 1,510918 -0,898016 4,184620
C 2.731502 -2.572469 2.287755	C 2.730884 -2.739108 2.415716	C 2,703321 -2,536719 2,249445
N 3.033282 -1.120897 2.177692	N 3.035567 -1.292588 2.361239	N 3,030639 -1,088896 2,110817
C 2.808894 -0.521653 3.502568	C 2.732564 -0.523954 3.571242	C 2,729428 -0,354935 3,351629
C 3.193395 -3.527898 1.141826	C 3.228520 -3.649151 1.253022	C 3,188454 -3,505394 1,138838
C 4.498568 -3.028053 0.482412	C 4.454161 -3.024550 0.550919	C 4,553817 -3,055045 0,572761
C 4.364791 -0.828535 1.657933	C 4.034284 -0.735643 1.463113	C 4,360672 -0,792534 1,614630
C 4.548392 -1.508866 0.304316	C 4.202630 -1.559964 0.192087	C 4,621344 -1,548585 0,313499
C 2.098176 -3.723289 0.124438	C 2.142181 -3.899994 0.240580	C 2,155489 -3,583578 0,050764
C -0.164734 -3.871688 -0.726488	C -0.061824 -3.983093 -0.783598	C -0,061739 -3,911697 -0,873812
O -0.043017 -4.727954 -1.582419	O 0.116652 -4.910385 -1.541174	O 0,359107 -4,358210 -1,965707
O -1.132690 -2.915531 -0.772956	O -0.996125 -3.014389 -0.970549	O -1,432603 -3,596915 -0,805515
C 3.407554 -4.968913 1.746013	C 3.568463 -5.070435 1.838470	C 3,328352 -4,947926 1,764513
H 3.567489 -5.650274 0.895812	H 3.724055 -5.744716 0.983234	H 3,513903 -5,626843 0,916655
H 2.454727 -5.279563 2.201312	H 2.669134 -5.444746 2.352717	H 2,334666 -5,224184 2,150246
C 4.539954 -5.168854 2.759834	C 4.777090 -5.160516 2.774746	C 4,381837 -5,205003 2,854747
H 5.532701 -4.993222 2.325051	H 5.722661 -4.949987 2.260092	H 5,407588 -5,036641 2,495528

H 4.524173 -6.207146 3.119939	H 4.847319 -6.179897 3.176083	H 4,326368 -6,250941 3,197156
H 4.438933 -4.521194 3.641502	H 4.702215 -4.483086 3.637731	H 4,232497 -4,568029 3,738987
H 4.634113 -3.547134 -0.479192	H 4.690006 -3.616174 -0.345218	H 4,752982 -3,623257 -0,350238
H 1.377207 -0.735525 5.131137	H 1.852547 -1.704407 5.192408	H 1,911113 -1,435234 5,064039
H 0.793949 0.283419 3.821363	H 0.979796 -0.222017 4.835371	H 0,946617 -0,044236 4,589283
H 3.083224 0.540853 3.439361	H 2.530506 0.509012 3.251795	H 2,552018 0,697745 3,074243
H 3.499719 -0.987765 4.242910	H 3.626412 -0.484019 4.224576	H 3,622547 -0,357455 4,022054
H 5.172926 -1.162827 2.353193	H 5.009546 -0.692398 1.995138	H 5,159390 -1,051396 2,360191
H 5.514466 -1.215428 -0.131952	H 5.045736 -1.147723 -0.377274	H 5,611251 -1,270465 -0,083683
H 4.455279 0.264515 1.565861	H 3.753713 0.305008 1.240222	H 4,428670 0,297940 1,457296
H 3.757452 -1.164668 -0.380027	H 3.307431 -1.463694 -0.442665	H 3,861056 -1,262646 -0,428987
H 5.353780 -3.315962 1.112489	H 5.332738 -3.089421 1.210249	H 5,358657 -3,309338 1,284148
H 2.373049 -3.992039 -0.895305	H 2.448043 -4.334316 -0.712000	H 2,478494 -3,900321 -0,939871
H 3.231174 -2.944842 3.210395	H 3.142199 -3.148099 3.357044	H 3,145682 -2,886329 3,214126
H -1.661276 -3.112726 -1.572406	H -1.463923 -3.234828 -1.802890	H -1,715988 -3,840386 -1,706983