

Supplementary material

Voltammetric Determination of Active Pharmaceutical Ingredients Using Screen-Printed Electrodes

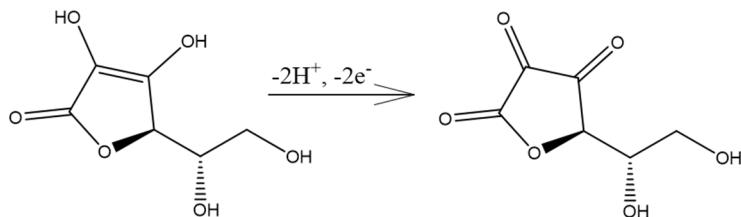
Paula Clares ¹, Clara Pérez-Ràfols ^{1,2,*}, Núria Serrano ^{1,2,*} and José Manuel Díaz-Cruz ^{1,2}

¹ Department of Chemical Engineering and Analytical Chemistry, University of Barcelona, Martí i Franquès 1-11, 08028 Barcelona, Spain; paulaclares99@gmail.com (P.C.); josemanuel.diaz@ub.edu (J.M.D.-C.)

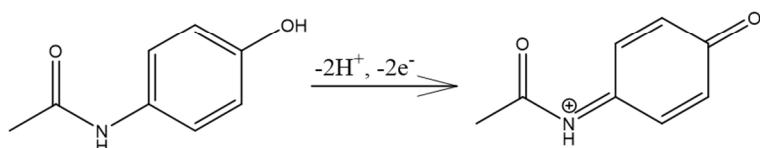
² Institut de Recerca de l'Aigua (IdRA), University of Barcelona, 08028 Barcelona, Spain

* Correspondence: claraperezrafols@ub.edu (C.P.-R.); nuria.serrano@ub.edu (N.S.)

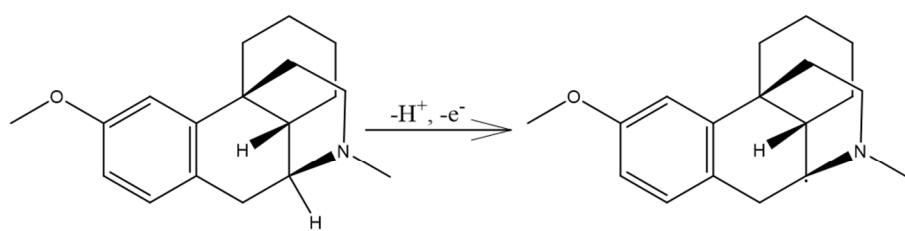
a) Ascorbic acid



b) Paracetamol



c) Dextromethorphan



d) Caffeine

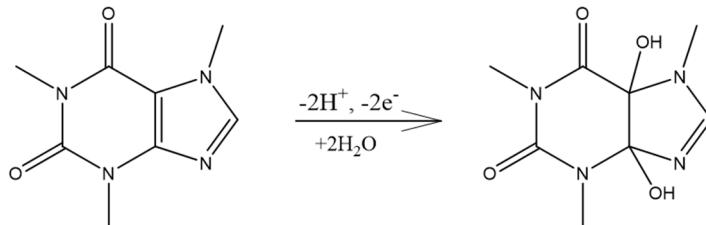


Figure S1. Oxidation reactions for (a) ascorbic acid [27], (b) paracetamol [28], (c) dextromethorphan [28], and (d) caffeine [29].

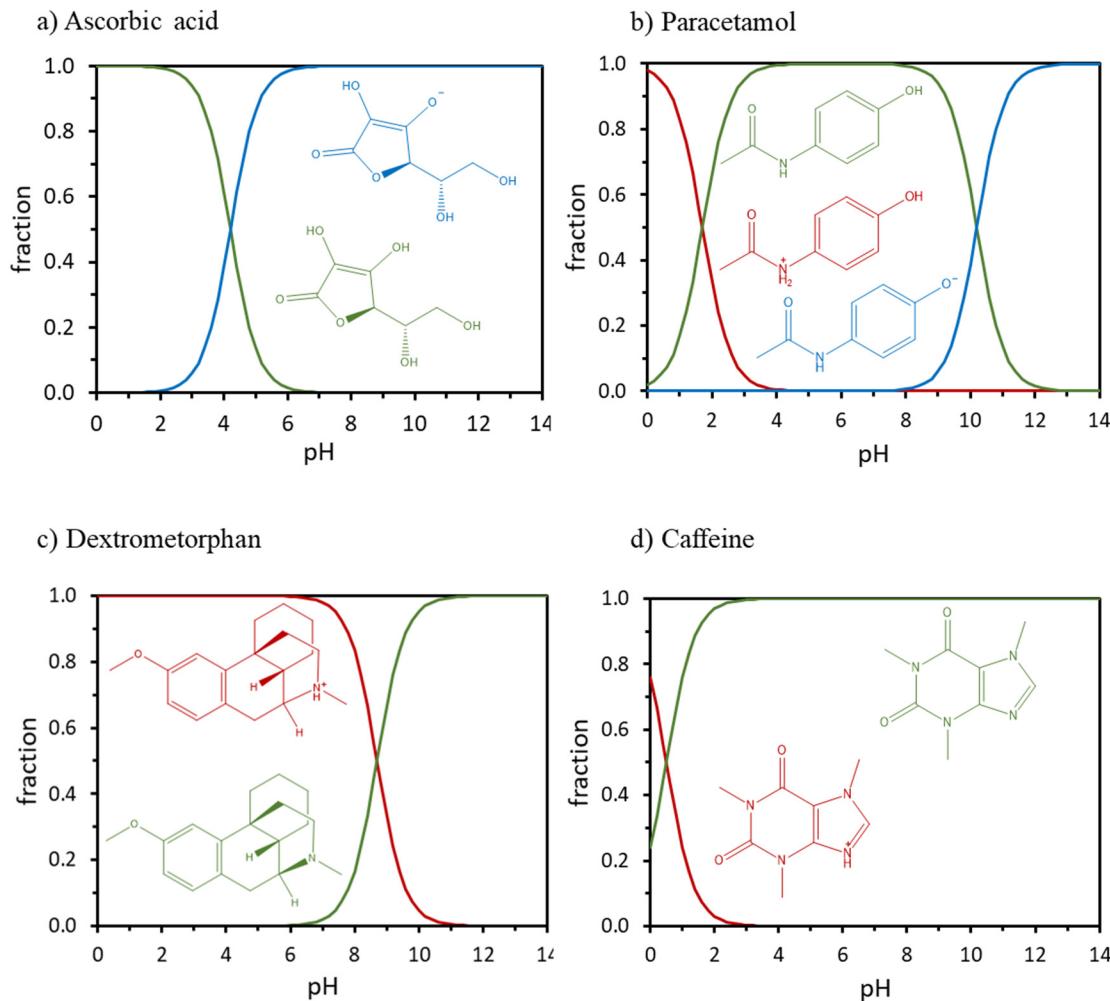


Figure S2. Species distribution diagram as a function of pH for (a) ascorbic acid, (b) paracetamol, (c) dextrometorphan and (d) caffeine. Cationic, neutral and anionic forms are depicted in red, green and blue, respectively.

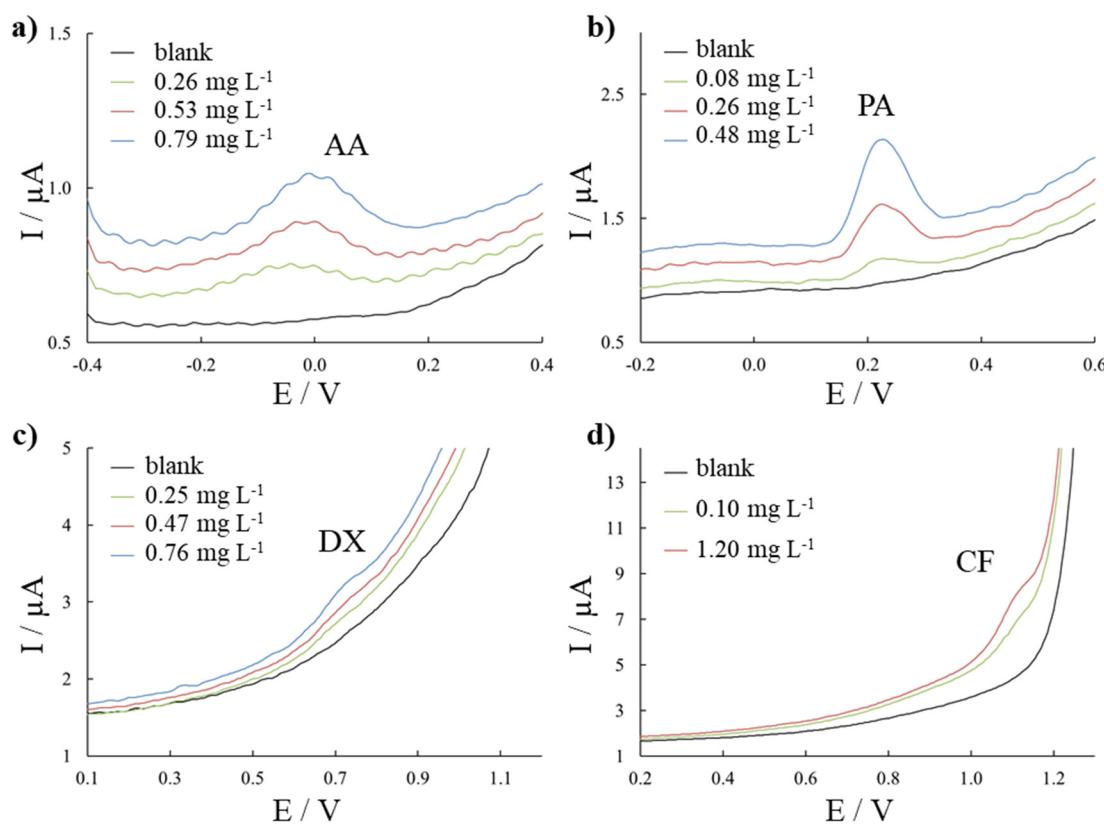


Figure S3. DP voltammograms for low concentrations of (a) ascorbic acid, (b) paracetamol, (c) dextrametorphan and (d) caffeine. Measurements were carried out in 0.1 mol L^{-1} acetic/acetate buffer pH 5.00 using a SPCE.

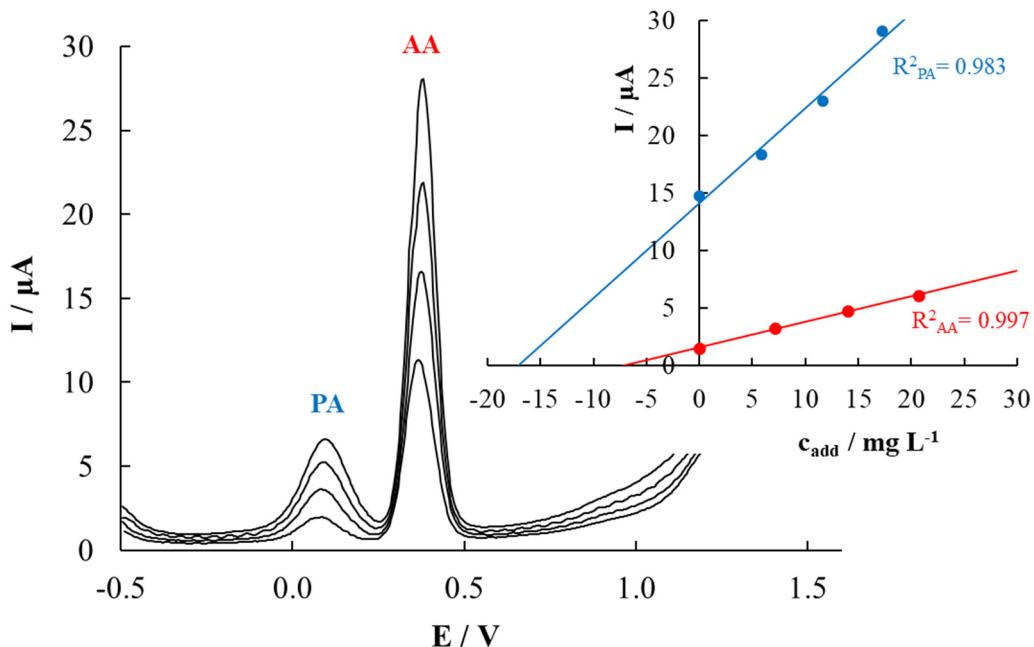


Figure S4. DP voltammograms for the simultaneous determination of ascorbic acid and paracetamol in Frenadol® Complex. Measurements were carried out in 0.1 mol L^{-1} acetic/acetate buffer pH 5.00 using a SPCE. Inset: standard addition calibration plot.

Table S1. Summary of E vs. pH plots obtained from relevant data published in [30].

Substance	Plot of E (V) vs. pH				Comments
	pH range	Slope (V)	Intercept	R ²	
AA	2.0–5.0	−0.062	0.47	0.940	Compatible with a 2H ⁺ , 2e [−] process (slope ideally −0.059 V) starting from the protonated form of AA
	5.0–8.0	−0.026	0.30	0.947	Compatible with a 1H ⁺ , 2e [−] process (slope ideally −0.029 V) starting from the deprotonated form of AA
PA	3.0–10.0	−0.050	0.67	0.997	Compatible with a 2H ⁺ , 2e [−] process (slope ideally −0.059 V)
CF	4.0–10.0	−0.011	1.37	0.957	Too low slope for a 2H ⁺ , 2e [−] process (ideally −0.059 V)

References

27. Osial, M.; Warczak, M.; Kulesza, P.J.; Krysiński, P.; Gniadek, M. Hybrid Polyindole-gold Nanobrush for Electrochemical Oxidation of Ascorbic Acid. *Journal of Electroanalytical Chemistry* **2020**, *877*, 114664, doi:10.1016/j.jelechem.2020.114664.
28. Amiri, M.; Rezapour, F.; Bezaatpour, A. Hydrophilic Carbon Nanoparticulates at the Surface of Carbon Paste Electrode Improve Determination of Paracetamol, Phenylephrine and Dextromethorphan. *Journal of Electroanalytical Chemistry* **2014**, *735*, 10–18, doi:10.1016/j.jelechem.2014.10.006.
29. Petrucci, R.; Zollo, G.; Curulli, A.; Marrosu, G. A New Insight into the Oxidative Mechanism of Caffeine and Related Methylxanthines in Aprotic Medium: May Caffeine Be Really Considered as an Antioxidant? *Biochimica et Biophysica Acta - General Subjects* **2018**, *1862*, 1781–1789, doi:10.1016/j.bbagen.2018.05.011.
30. Marín, J.; Serrano, N.; Ariño, C.; Díaz-Cruz, J.M. A Chemometric Survey about the Ability of Voltammetry to Discriminate Pharmaceutical Products from the Evolution of Signals as a Function of PH. *Chemosensors* **2020**, *8*, 46, doi:10.3390/CHEMOSENSORS8030046.