Supplementary material

I. Electrode material

The effect of the electrode's electrochemical pretreatment on HESP DPV oxidation signal (E_{pa2} ~0.710 V) was tested on PGEs electroactivated either by maintaining the working electrode for 60 s at 2.000 V (E = ct) or by cycling ten times the potential in the range -1.000 V to 2.000 V, with a scan rate of 0.500 V/s (CV), in three different supporting electrolytes (Table 1S).

Table S1. The main oxidation peak (a2) currents obtained by DPV for 4.00×10^{-6} M HESP in BRB solution pH 1.81 at H type PGE electroactivated in different conditions

I_{pa2} (A)						
Electroactivation conditions						
CV				**E = ct**		**none**
4 N H_2SO_4	PBS pH 7.40	0.2 N NaOH	4 N H_2SO_4	PBS pH 7.40	0.2 N NaOH	
1.32×10^{-6}	1.28×10^{-6}	2.54×10^{-7}	8.79×10^{-7}	3.77×10^{-7}	1.05×10^{-6}	1.63×10^{-6}

I_{pa2}: current intensity of the oxidation peak from ~ 0.710 V, marked with a2; PBS: phosphate buffer solution

II. Hesperidin Solutions Stabilities

Antioxidants are compounds which can be easily oxidized even by the atmospheric oxygen. Thus, the stability of both HESP stock and working solutions has been tested by monitoring the HESP main DPV oxidation peak (E_{pa2} ~0.710 V) changes in time.

The stability of the 1.00×10^{-3} mol/L HESP in 0.05 mol/L NaOH stock solution was tested using working solutions freshly prepared at different interval times from the same stock solution stored in the refrigerator and at ambient conditions, respectively (Figure 1Sa). After one day, the intensity of peak a2 increased with 4.27% and 8.97% when the stock solutions were stored in the refrigerator and at room conditions, respectively. These results indicated that regardless of the storing conditions, from day to day there were some slow transformations of the analyte and therefore the stock solution was daily freshly prepared.

It is also well-known that voltammetry has the advantage of performing many repetitive recordings using the same solution without changing its composition. However, to carry out multiple measurements needs time during which the solution is exposed to atmospheric conditions (light, oxygen, etc.). Therefore, the stability of the HESP working solution maintained in the voltammetric cell for 100 min at ambient conditions was also tested by recording and measuring the HESP main DPV oxidation peak current at different time intervals (minutes). Figure 1Sb emphasizes a small variation of the monitored anodic signal indicating thus that HESP was stable in diluted working solution (up to 5.00×10^{-5} mol/L HESP) at least 100 minutes, enabling thereby multiple voltammetric recordings without errors due to the analyte transformation. It must be pointed out that the stability of more concentrated solutions, e.g. of 1.00×10^{-4} mol/L HESP was limited to 10 minutes, due to the bioflavonoid's low solubility in acidic medium. However, this time was sufficient to carry out at least five DPV recordings on solutions prepared just prior to the analysis.

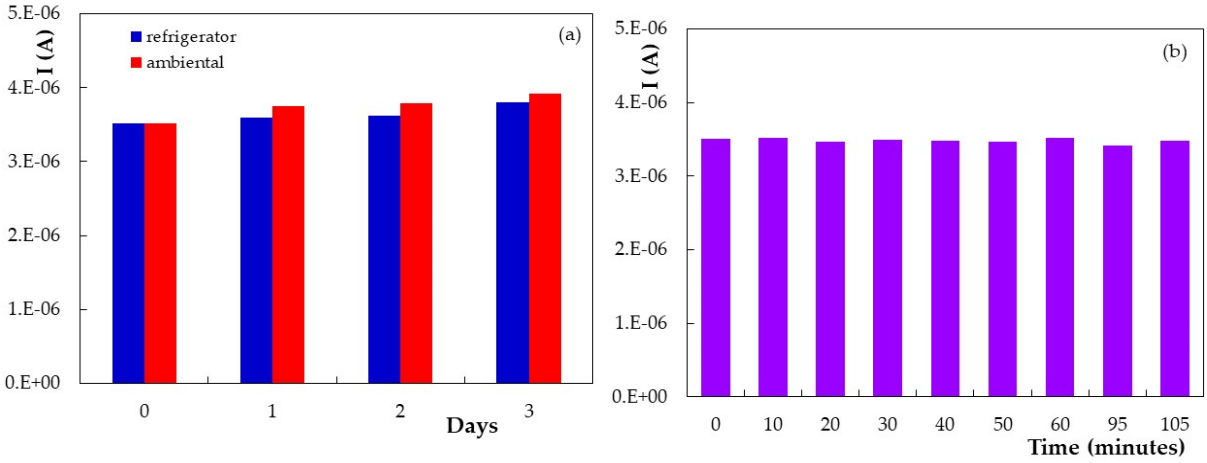

Figure S1. Differential pulse voltammetric peak (E_{pa2} ~0.710 V) currents recorded at H type PGE for 1.00×10^{-5} M HESP in BRB solution pH 1.81 **(a)** prepared on different days from the same stock solution (1.00×10^{-3} mol/L HESP in 0.05 mol/L NaOH) stored in different conditions and **(b)** kept in the voltammetric cell for 100 min.