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3D Printed Electrochemical (Bio)devices

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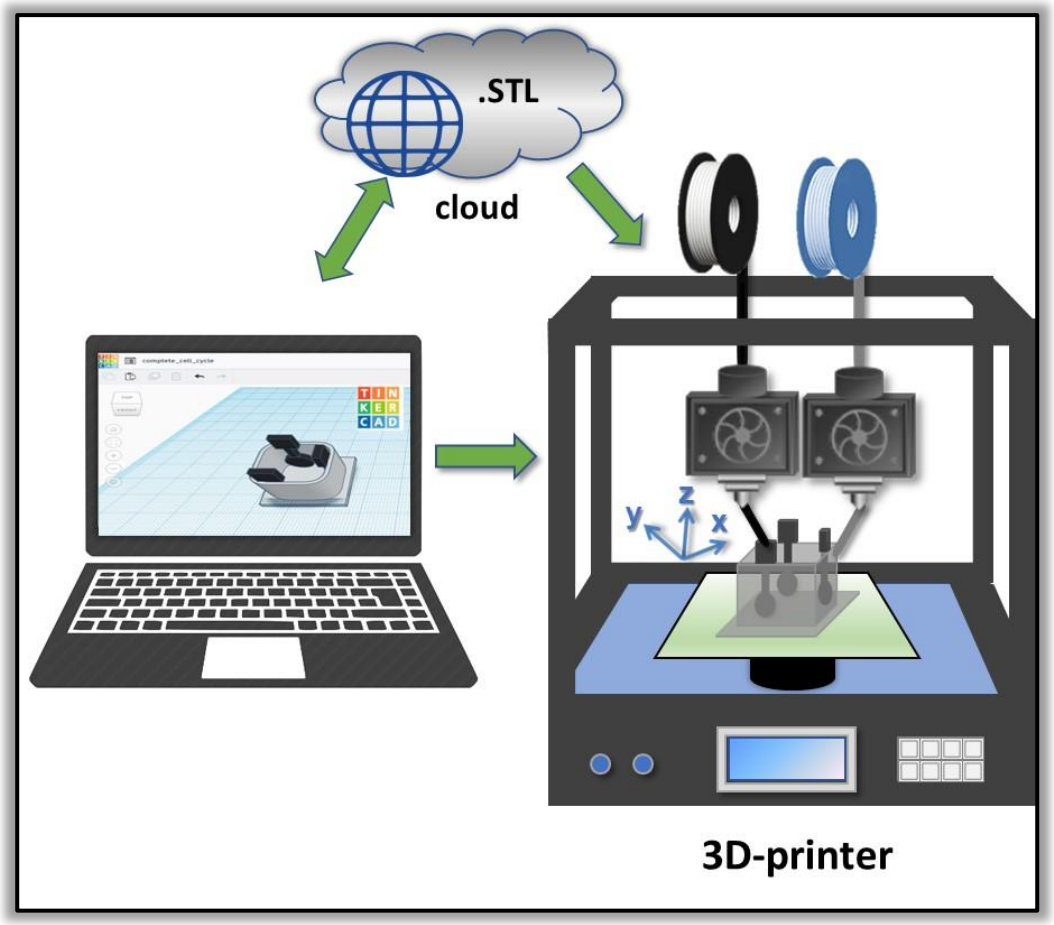
Outline

- 3D printed electrochemical microwells for quantum dots bioassays
- 3D printed enzymatic microchip for multiplexed electrochemical biosensing
- 3D printed e-ring device for glucose monitoring in sweat
- 3D printed wearable e-finger for direct determination of DRDs in spirits

3D printing & electrochemistry

- Fused deposition modeling (FDM) is based on the CAD design of the sensor and its printing from thermoplastic filaments. The filaments are heated to their semi-molten state and extruded on a platform and through their solidification, the programmed sensor is formed.

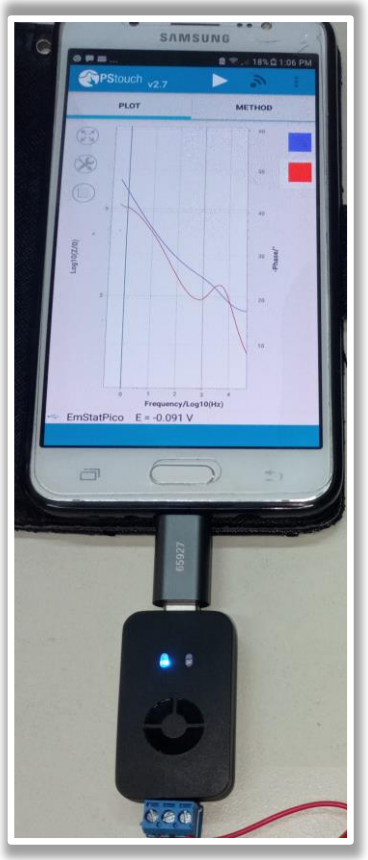


Advantages of 3D printed sensors

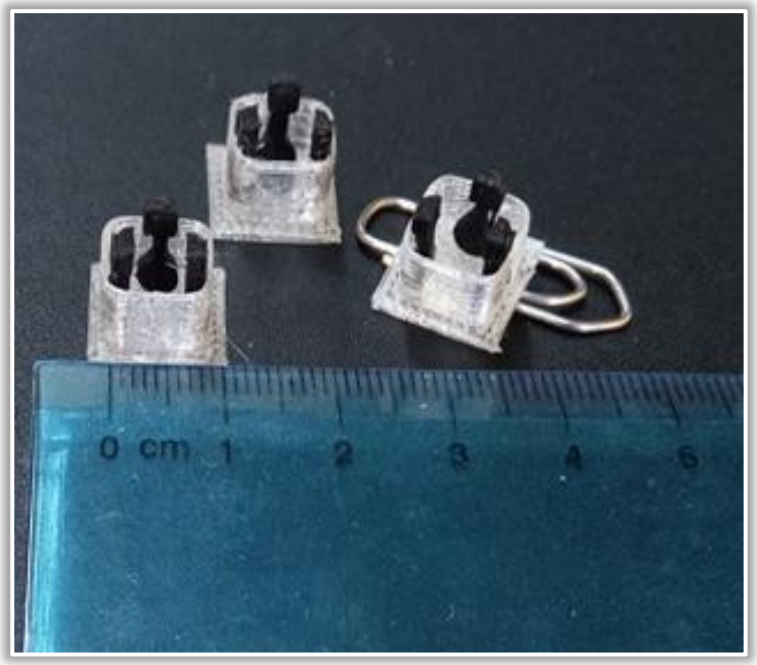
- Desktop-sized equipment (no sophisticated laboratory facilities)
- Flexibility in the design and the construction of sensors (size, geometry)
- Fast prototyping and manufacturing speed
- Extremely low capital, operational and materials costs
- Plethora of filaments with different properties
- Environment-friendly, (no chemicals, no waste)
- Full design transferability between 3D platforms (e-transferable sensors)
- Single-step fabrication of sensors made of different materials (multi-extruders 3D printers)

- ***Meets the core request for specialized (bio)sensors, printed at POC and on time of need***

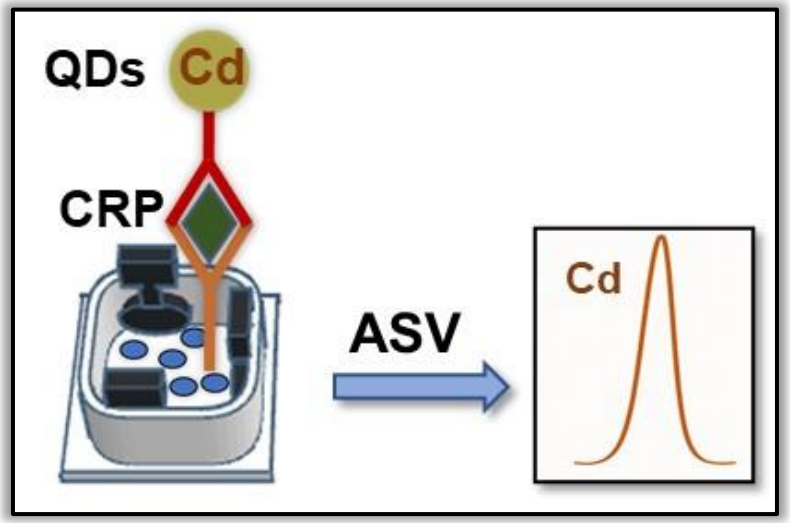
3D printed sensors combined with smartphone potentiostats



3D printed bioelectronic microwells



e-wells for micro-volume bioassays



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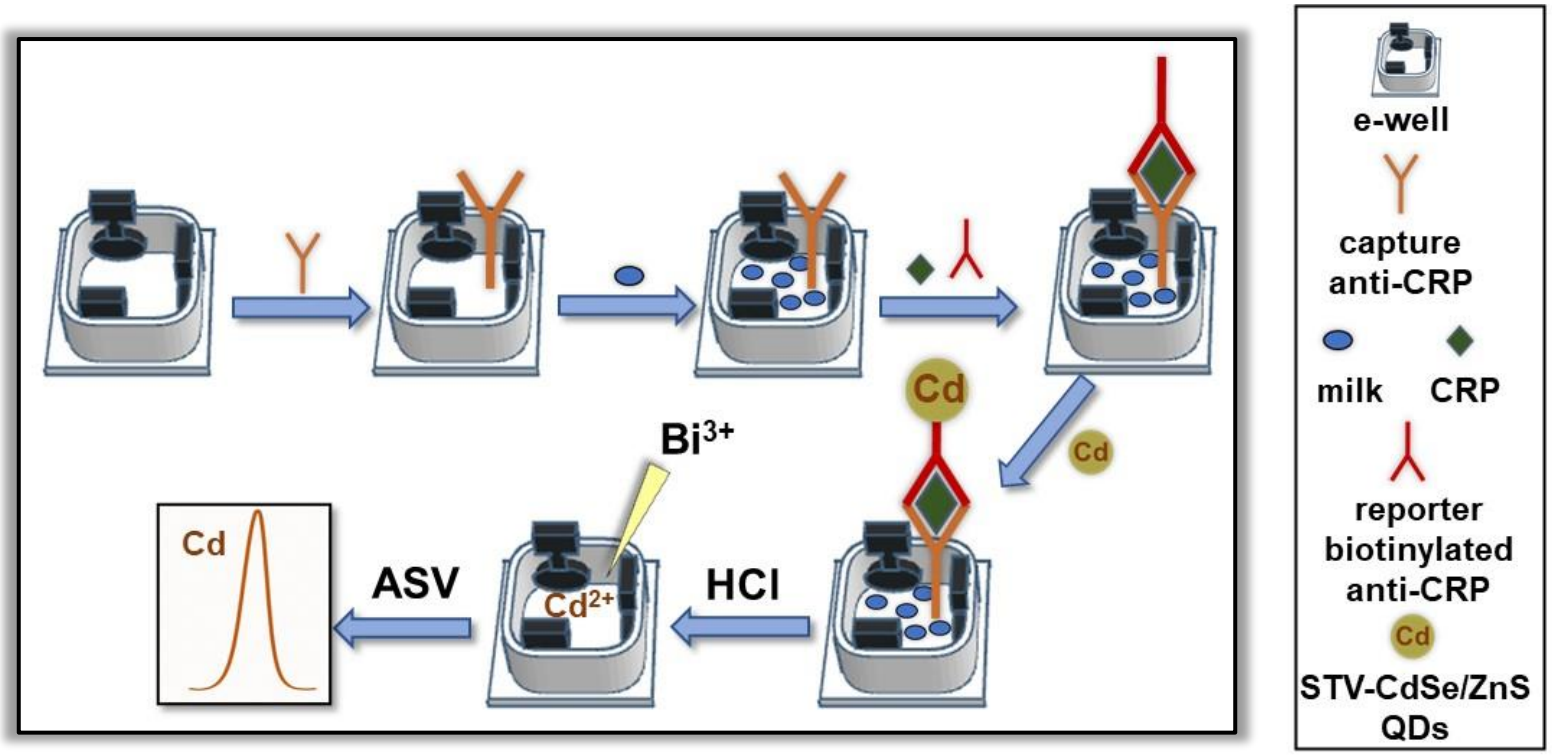
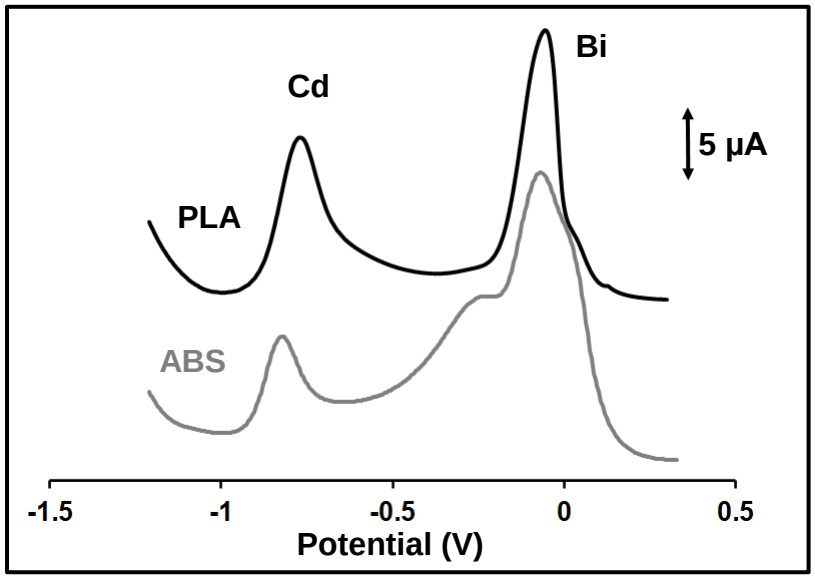
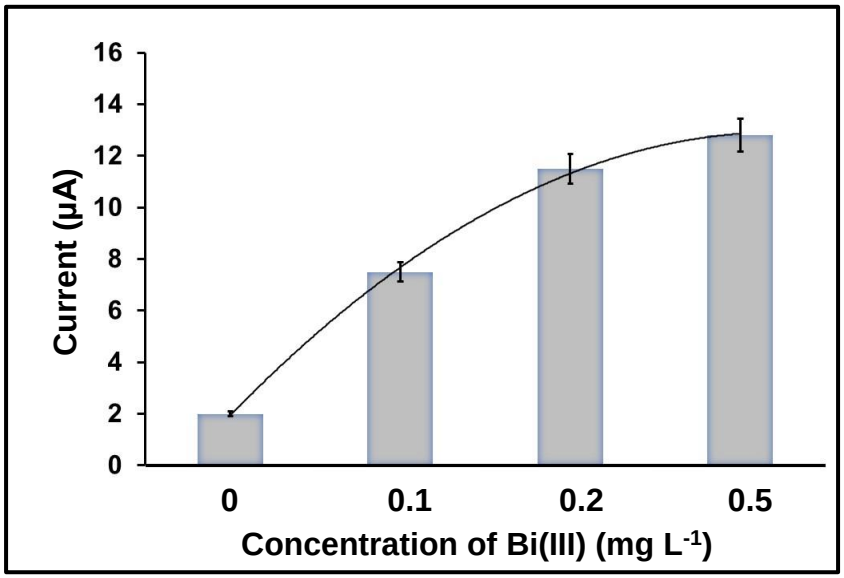
- The e-wells are printed via a single-step procedure by a dual extruder 3D printer and are composed of a miniature well (printed from PLA filament) and of 3 electrodes printed from a carbon black-loaded PLA conductive filament (Proto-Pasta).
- Their bioanalytical capability was demonstrated through the determination of CRP using quantum dots (QDs) as labels and a sandwich-type immunoassay developed directly into the 3D e-well.

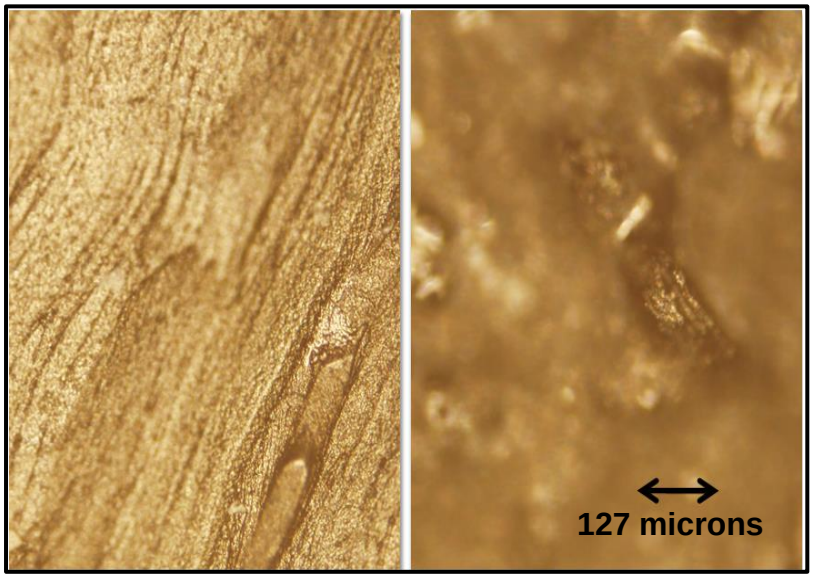




SWASV responses of 30 μg L^{-1} Cd(II) using carbon-loaded WEs PLA and ABS



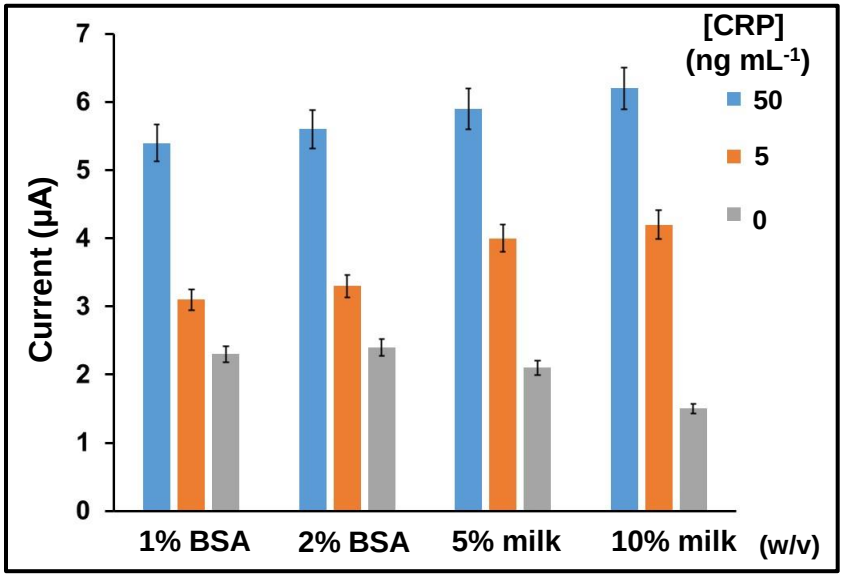
Effect of the Bi(III) plating concentration on the striping peak height of 30 μg L^{-1} Cd(II).



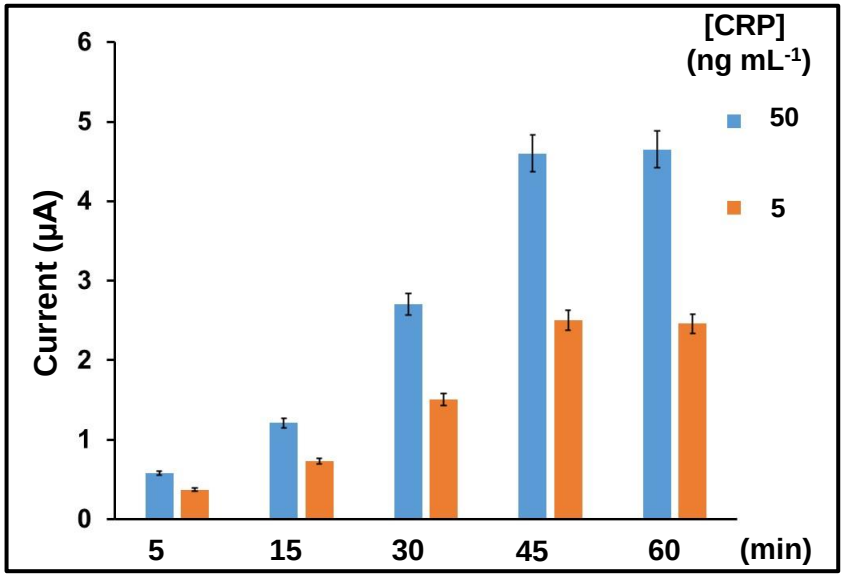
Optical micrograph of the 3D-printed WE surface before (left) and after (right) electrodeposition of Bi(III) film

Potential stability and the within-electrode potential reproducibility of the 3D printed carbon pseudo-RE.

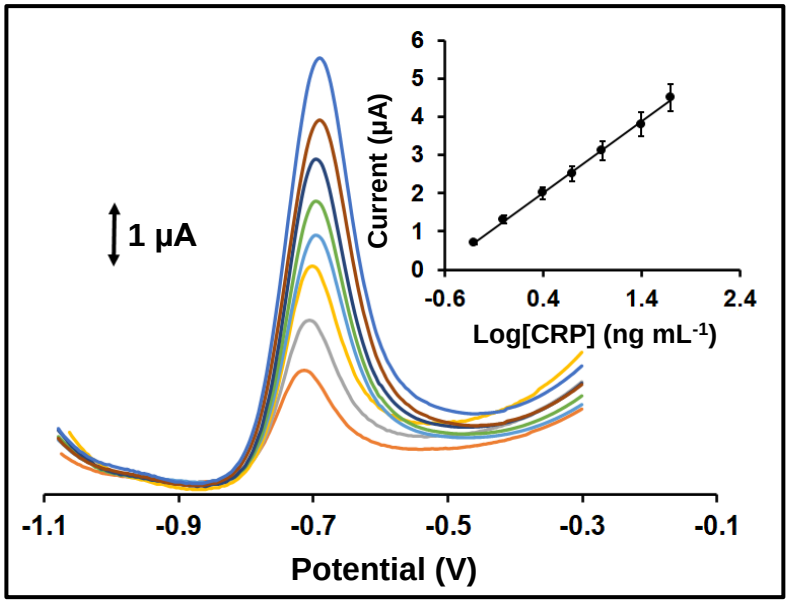
The potential, where the Cd peak appears, remained statistically constant during 20 repetitive measurements, while the % RSD of the peak potential of Cd(II) at the 6 different 3D printed REs was 3.2%,



Effect of blocking solution



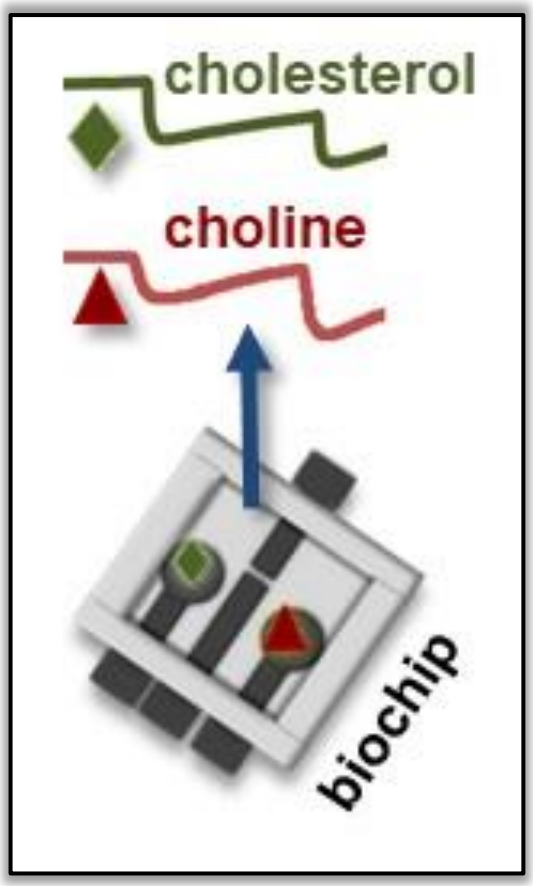
Effect of the immunoreaction time



SW voltammograms for 0 -50 ng mL^{-1} CRP and the calibration curve

- **LOD: 0.06 ng mL^{-1} CRP**
- **Artificial blood samples spiked with 5, 15, 35 ng mL^{-1} CRP were tested. The recovery values ranged from 95 to 103%**

3D printed enzymatic microchip for multiplexed electrochemical biosensing



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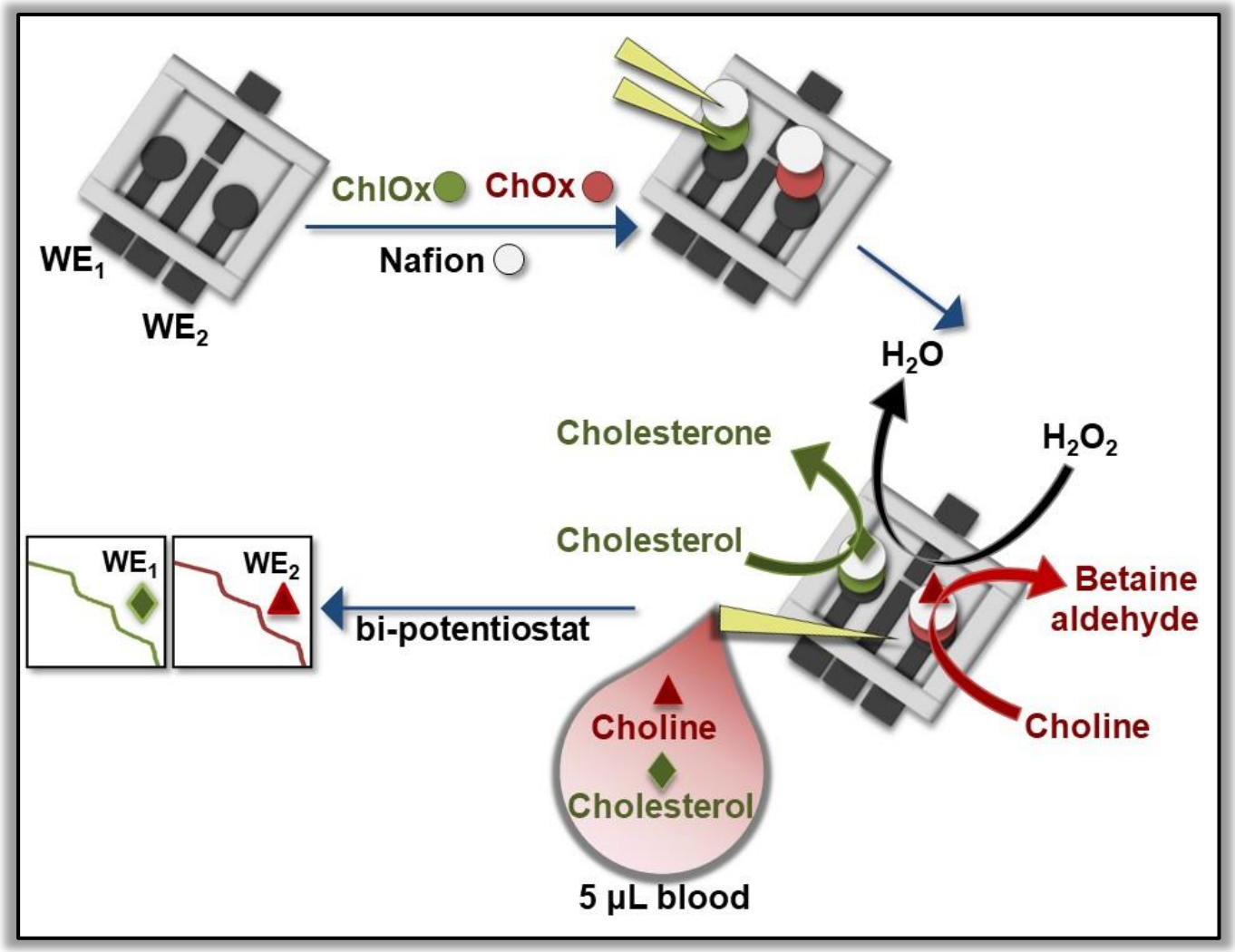
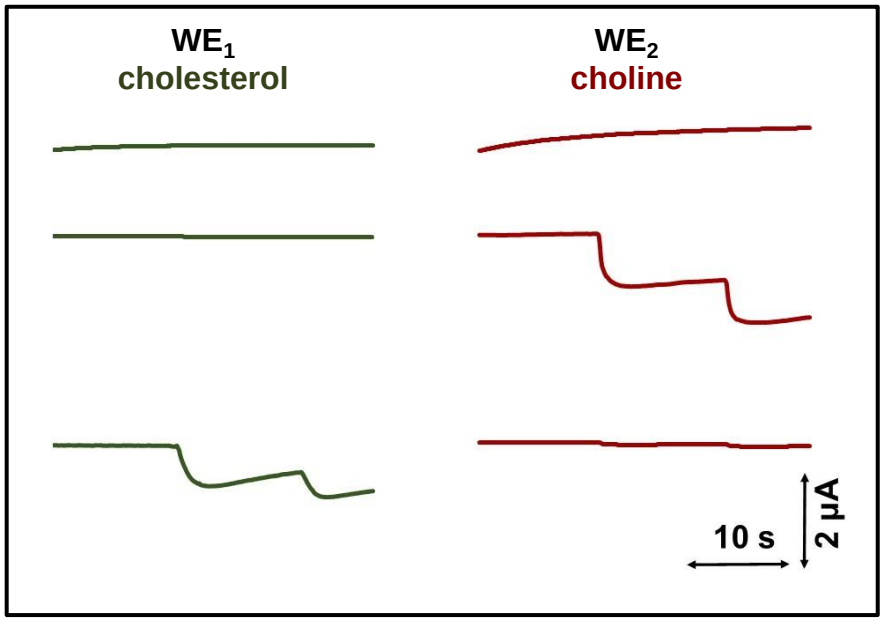
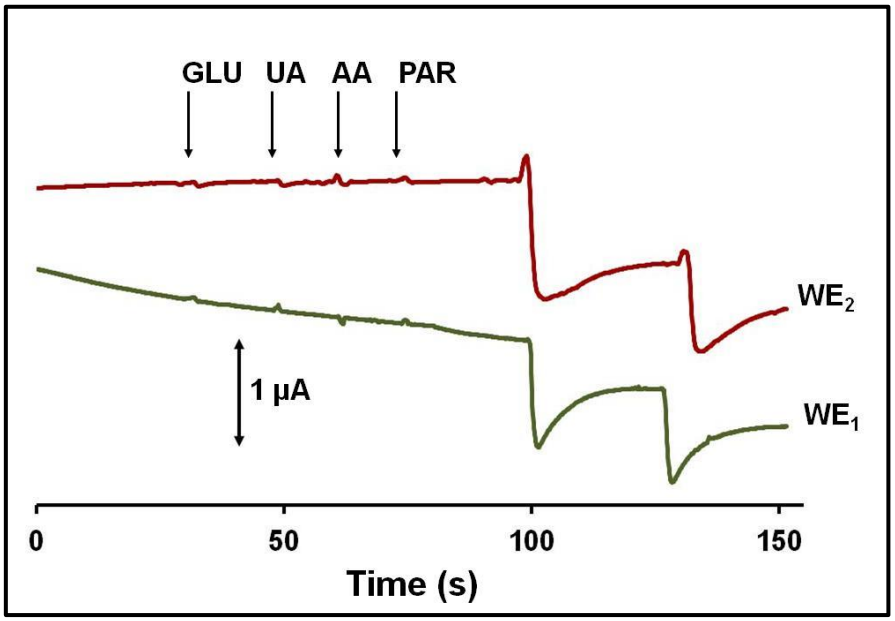
- **The core goal of the biochip is the provision of maximum simplicity and affordability for POC conditions. The whole construction of the multiplexed biosensor lasts 18 min (7 min for the printing and 11 min for the immobilization and drying of the enzymes and nafion)**



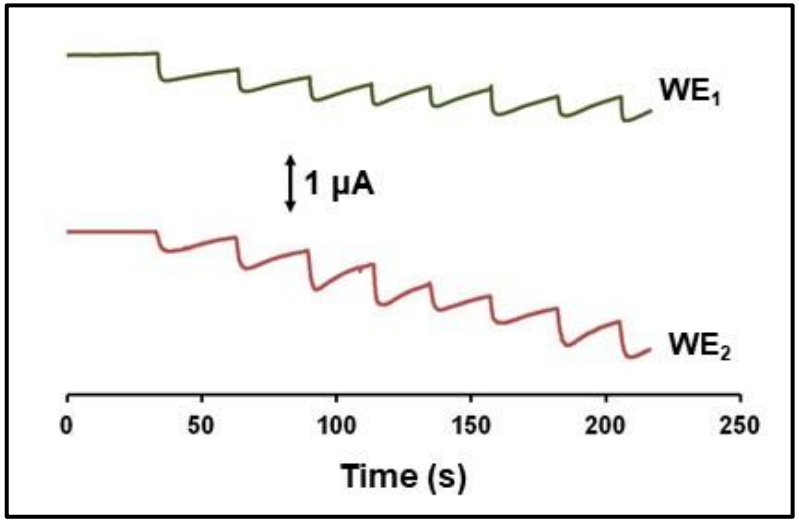
Cross-talk

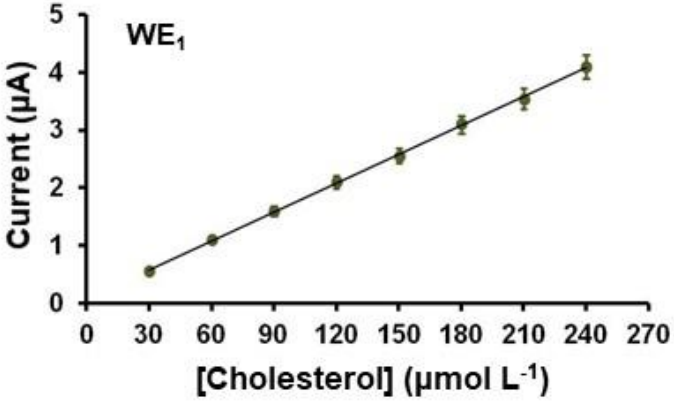


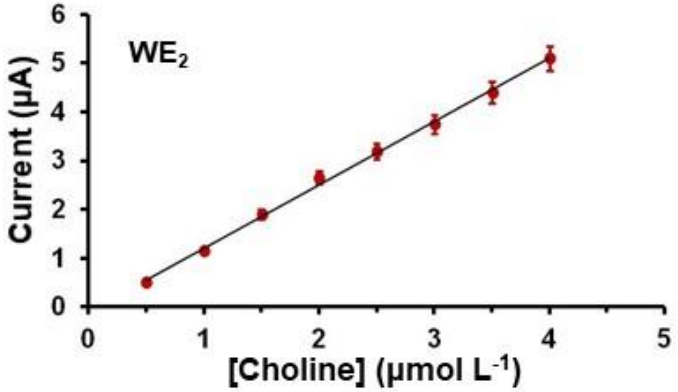


- The center-to-center spacing between the two biosensors is 1 cm and the maximum value for the diffusion coefficient of H_2O_2 is 15 10^{-6} cm^2 s^{-1}. According to the Einstein's diffusion equation ($d = (2 \cdot D \cdot t)^{1/2}$ in which d = average distance traveled (cm), D = diffusion coefficient, and t = time (s)), it is predicted that H_2O_2 will diffuse about 0.08 cm in 225 s.

- The detection of the H_2O_2 at the biochip takes place at a reduction potential of -0.7 V, thus the contributions from electrooxidisable substances are negligible. Besides, the Nafion membrane serves as a barrier towards interferences.



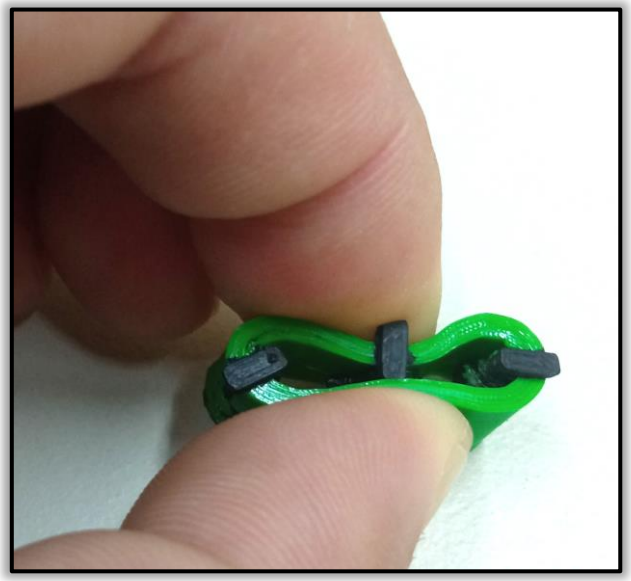


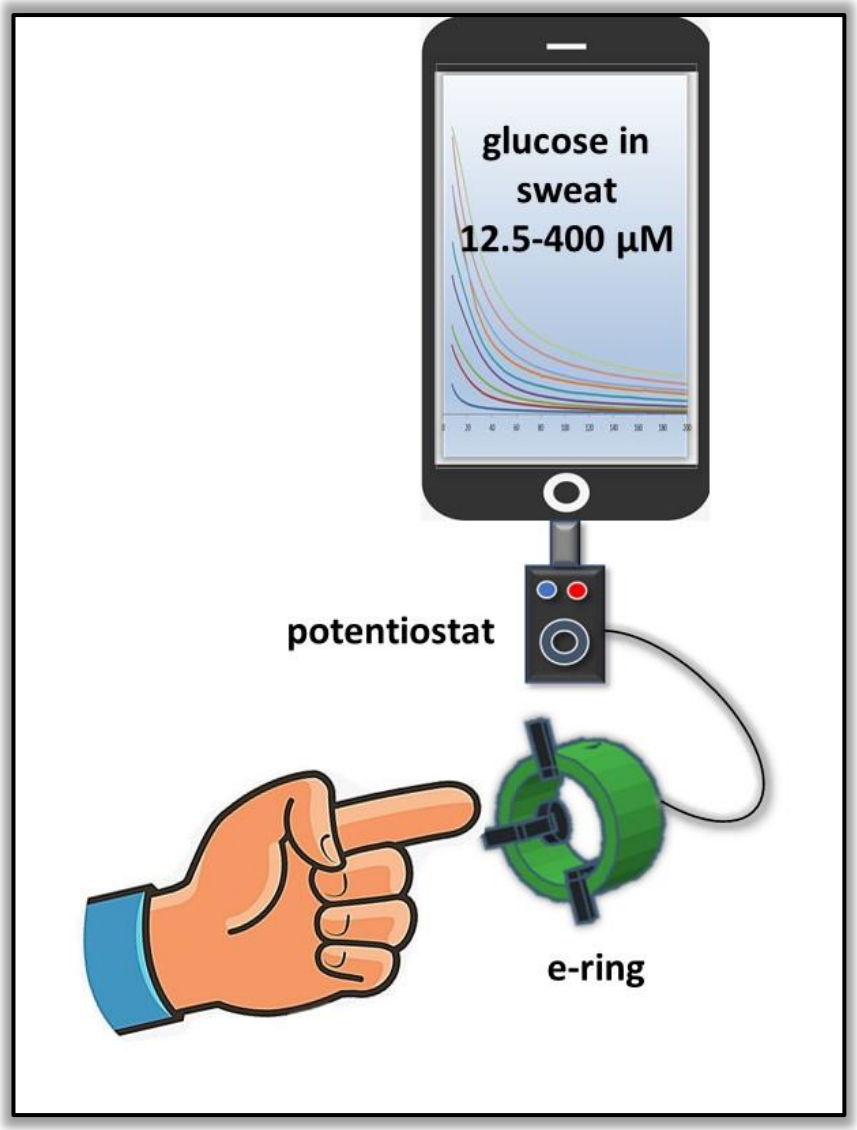


The LODs of cholesterol and choline were 3.36 and 0.08 μmol L^{-1}, respectively (much lower than their cut-off levels in blood for coronary syndromes). These LODs permit the dilution of the clinical samples, resulting to the minimization of their strong matrix effects.

Two artificial blood samples spiked with different concentrations of both biomarkers (4 mmol L^{-1} cholesterol + 30 μmol L^{-1} choline & 7 mmol L^{-1} + 50 μmol L^{-1}, respectively) were analyzed. The recovery values ranged from 96 to 102%

3D printed wearable sensors (e-ring)





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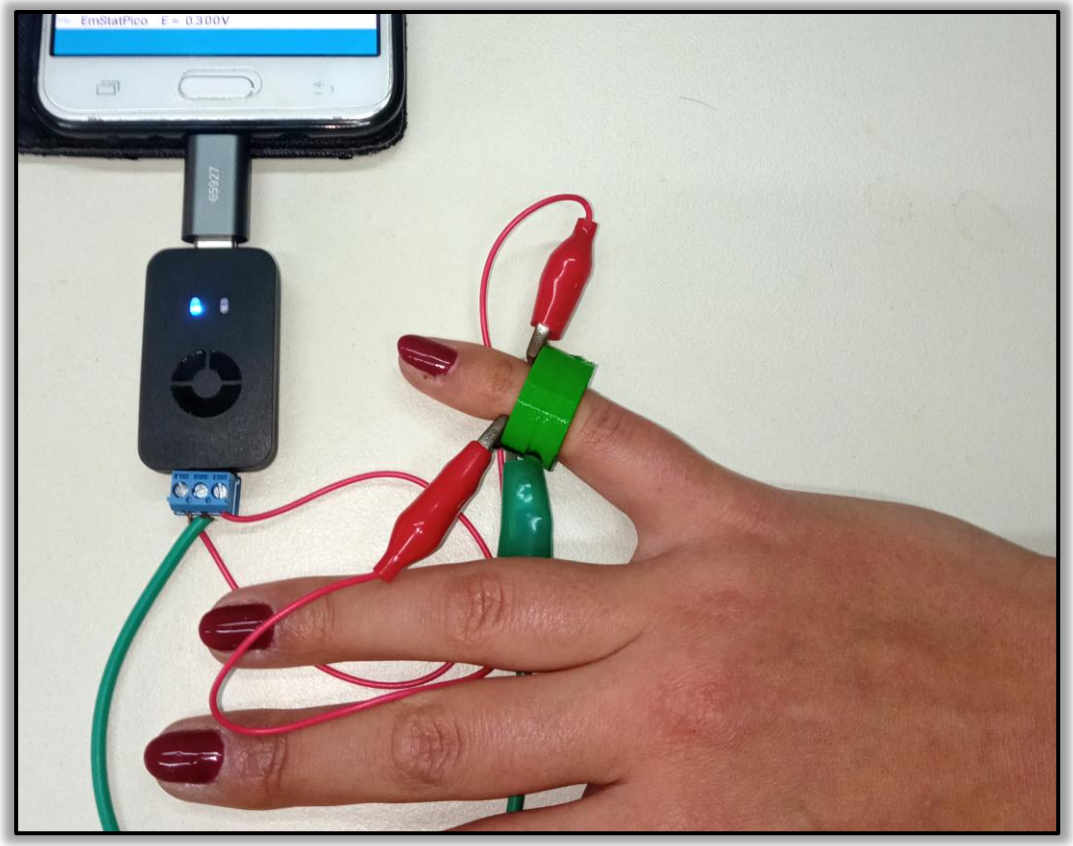
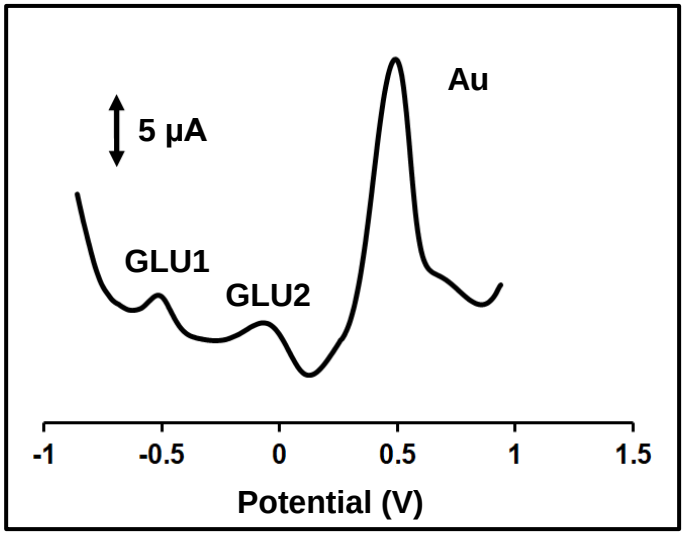
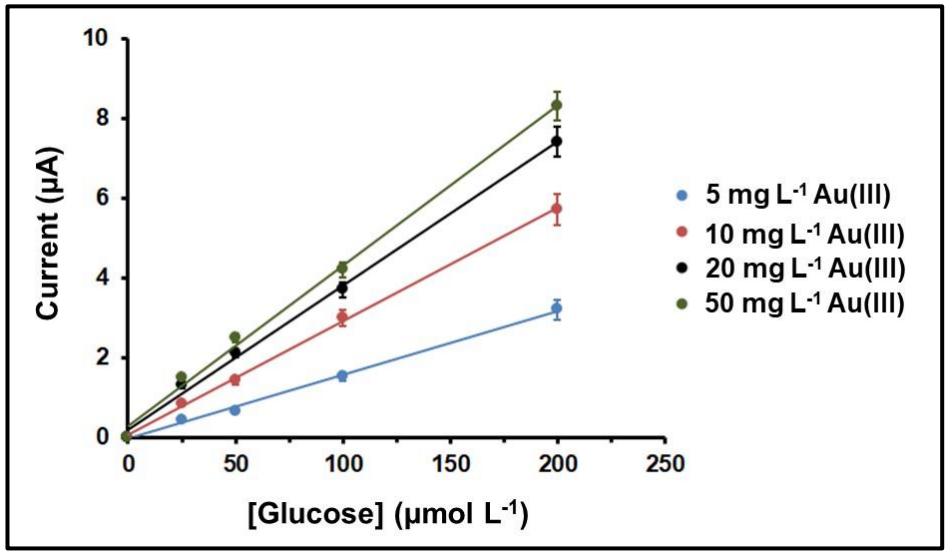
- The e-ring is composed of TPU holder and of 3 carbon black-loaded PLA electrodes. The e-ring is modified with an electrodeposited gold film for the nonenzymatic amperometric glucose monitoring in human sweat.
- The e-ring is coupled to a commercial miniaturized potentiostat operating directly addressable by a smartphone via an Android application.

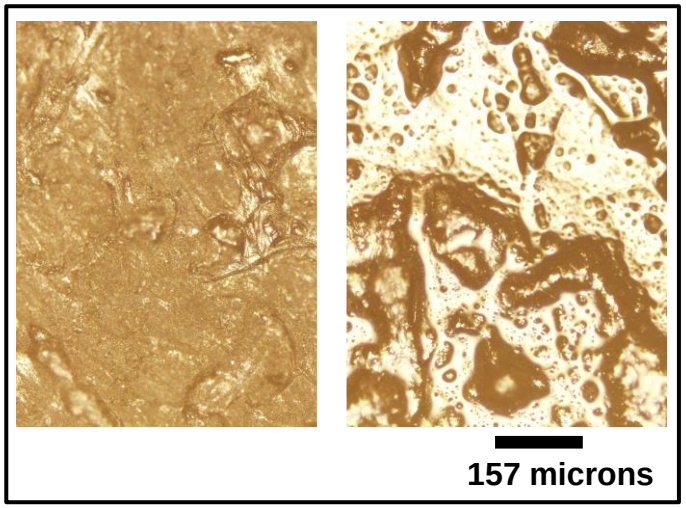




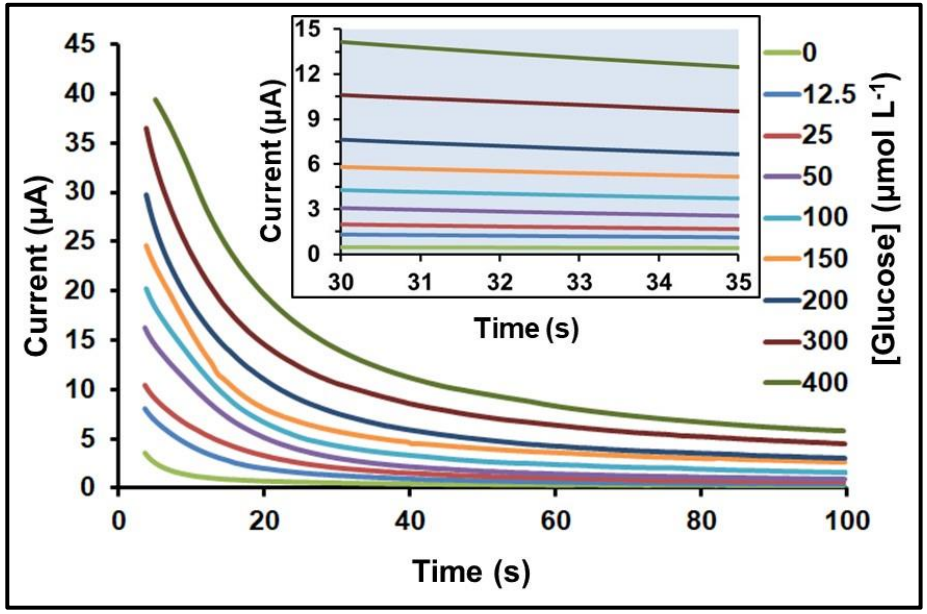
DP voltammogram of 100 µmol L^{-1} glucose 0.1 mol L^{-1} phosphate buffer pH 4.0

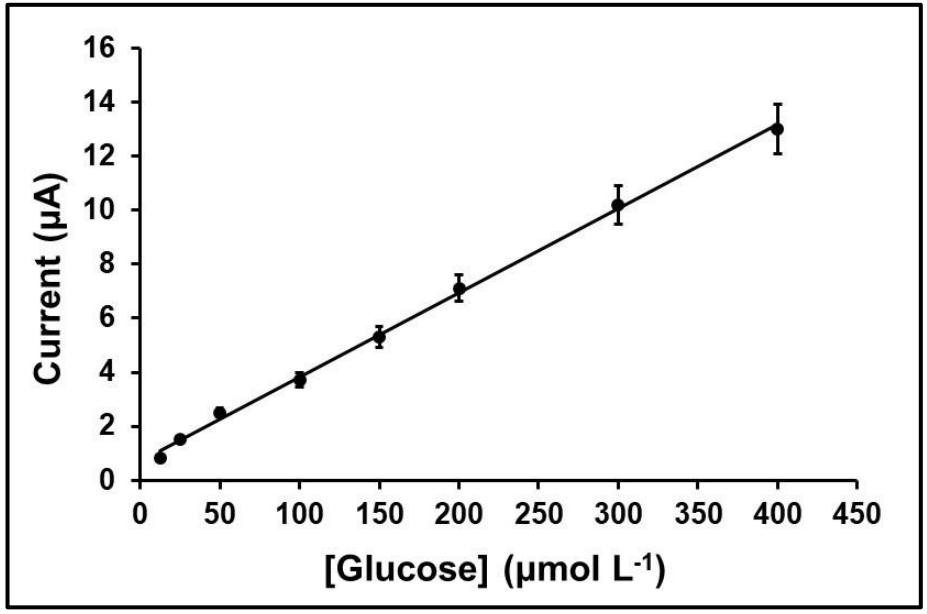


The effect of the thickness of gold films on glucose sensing

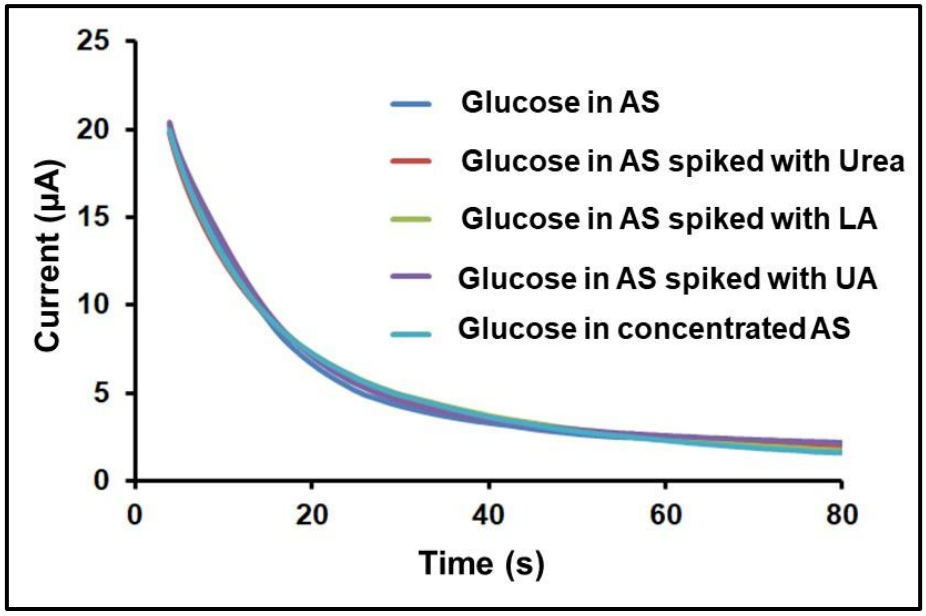


Optical micrograph of the 3D-printed WE surface after (left) and before (right) electrodeposition with Au(III)

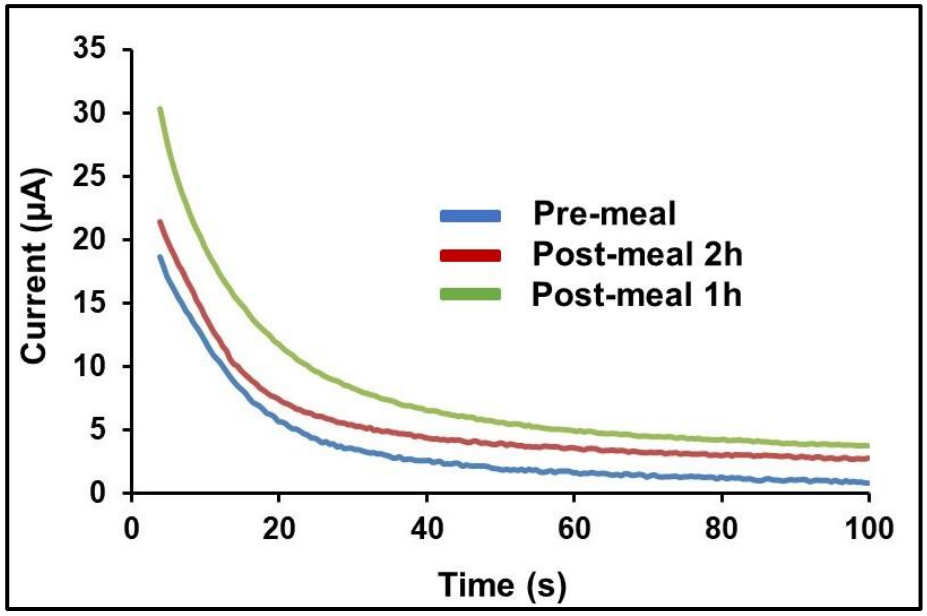




Amperometric responses of the e-ring to glucose (0 to 400 μmol L^{-1}) in artificial sweat and the calibration curve.

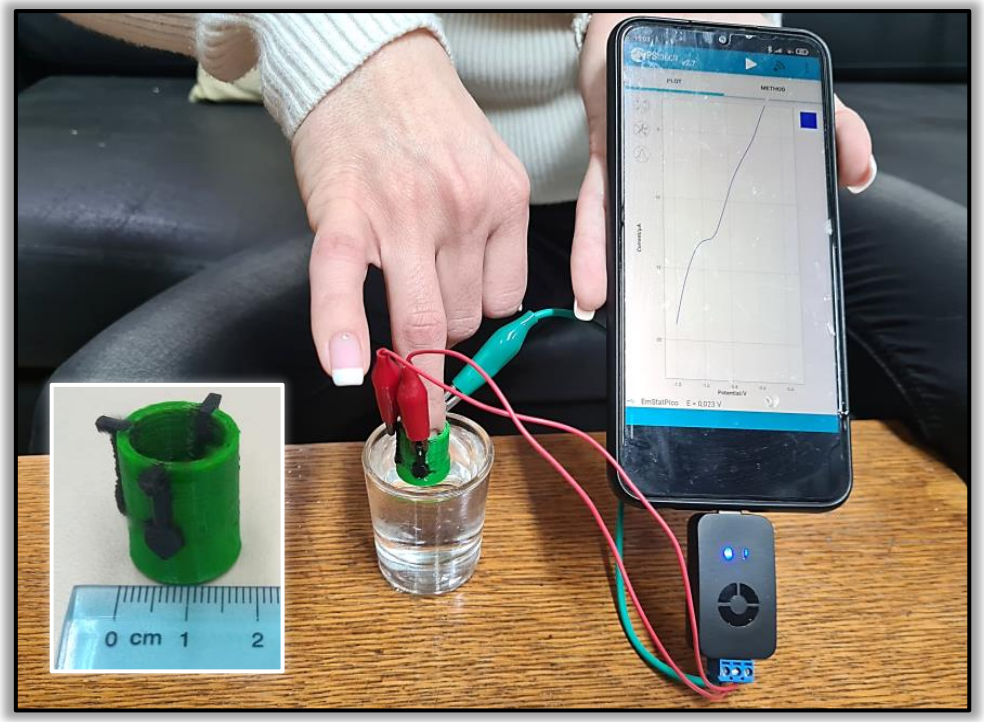


The effect of common electroactive metabolites (10-fold mass concentration excess)



On-body test

e-finger for DRDs screening in spirits



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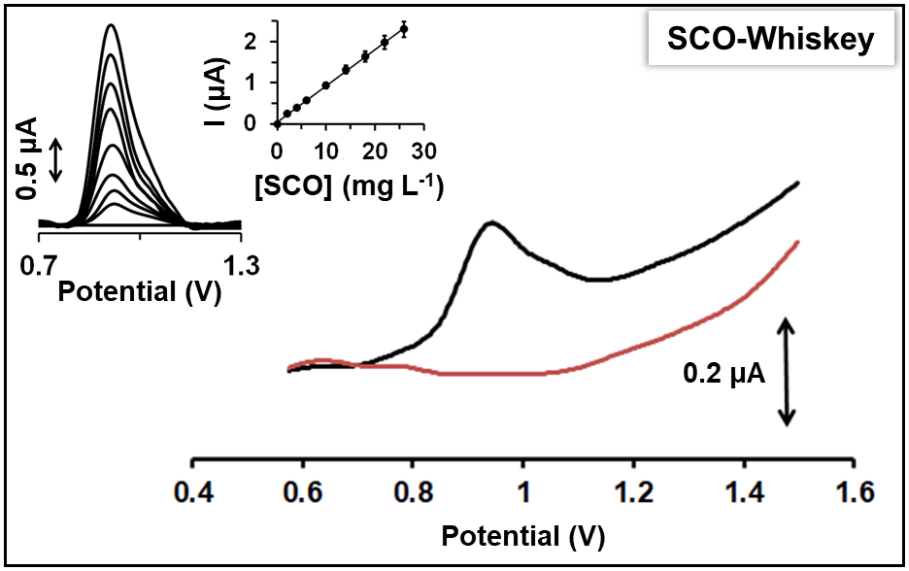
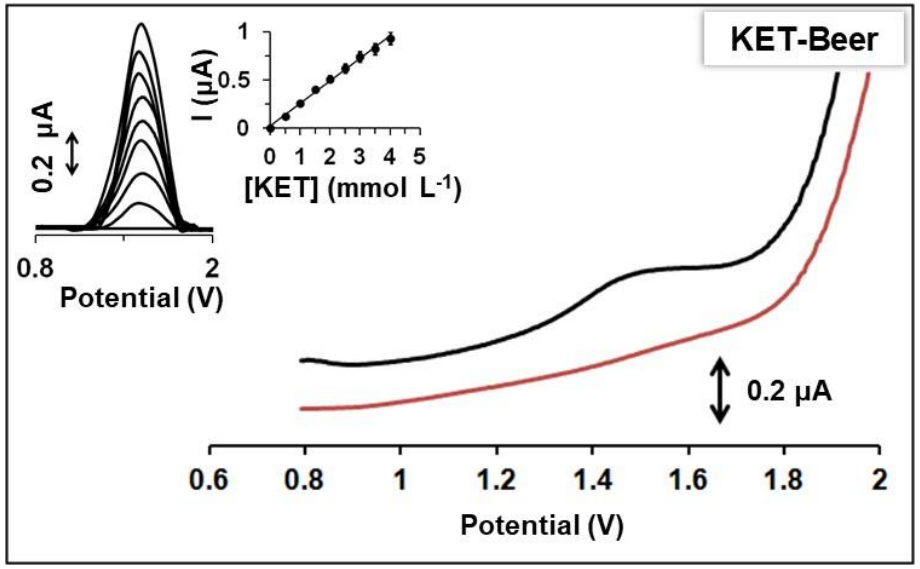
- **DRDs and analgesics are administrated in spirits for "drug-facilitated sexual assault" crimes and for the reduction of the following day hangover caused by low-quality spirits, respectively.**

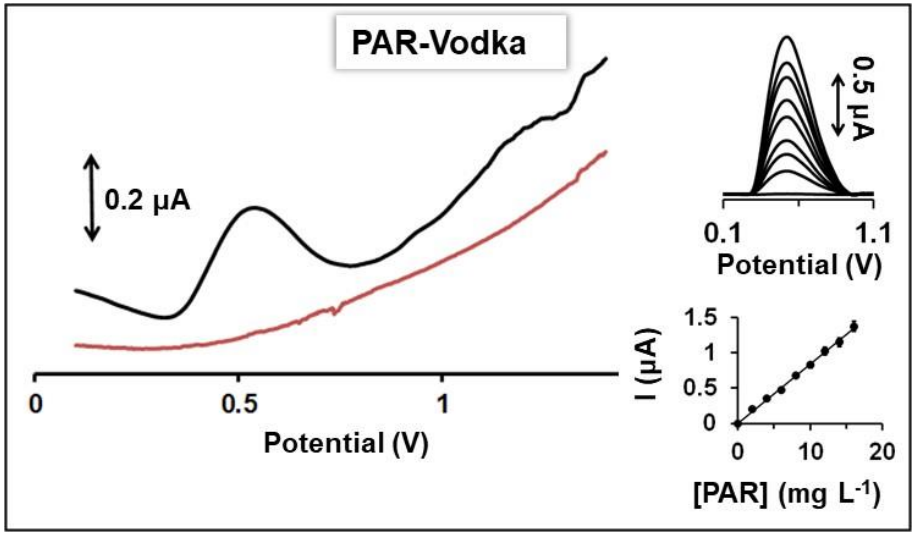
- **The e-finger can be printed in-house at any size by anyone with access to a low-cost domestic 3D printer and it is composed of TPU holder and of 3 carbon black-loaded PLA electrodes.**

- **The 3D e-finger is directly immersed into spirit shot yielding evidence on possible adulteration using a single voltammetric scan.**

- **Each target compound (FLU,SCO,KET,PAR) in the adulterated beverage gives rise to a clearly detectable and well-defined voltammetric peak at a specific potential (due to its electrochemical oxidation or reduction) in contrast to "clear" spirits where no endogenous redox peaks are obtained at the selected potential range.**







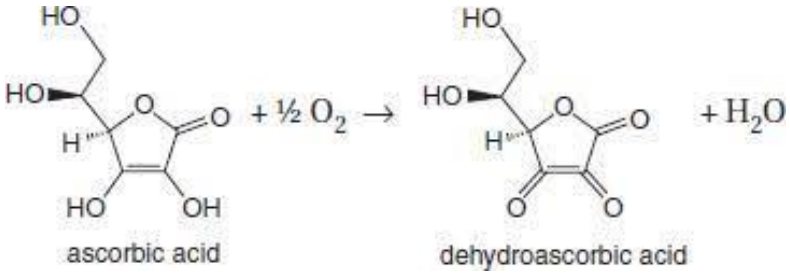
DP voltammograms at the e-finger obtained in undiluted whiskey, beer, vodka, (C) before (red line) and after (black line) spiking with 2 mg L^{-1} SCO, 0.5 mmol L^{-1} KET and 2mg L^{-1}PAR

Metrological features of the DRDs and PAR

		FLU	SCO	KET	PAR
Range		2- 16 mg L^{-1}	2-26 mg L^{-1}	0.5- 4 mmol L^{-1}	2- 16 mg L^{-1}
LOD	Whiskey	0.07 mg L^{-1}	0.83 mg L^{-1}	0.14 mmol L^{-1}	0.54 mg L^{-1}
	Vodka	0.08 mg L^{-1}	0.56 mg L^{-1}	0.11 mmol L^{-1}	0.51 mg L^{-1}
	Gin	0.09 mg L^{-1}	0.98 mg L^{-1}	0.13 mmol L^{-1}	0.68 mg L^{-1}
	Beer	0.11 mg L^{-1}	0.65 mg L^{-1}	0.18 mmol L^{-1}	-
Maximum RSD % within-finger (n=8)		4.4%	5.6%	5.2%	4.9%
Maximum RSD % between-finger (n=5)		7.9%	9.7%	8.8%	8.1%

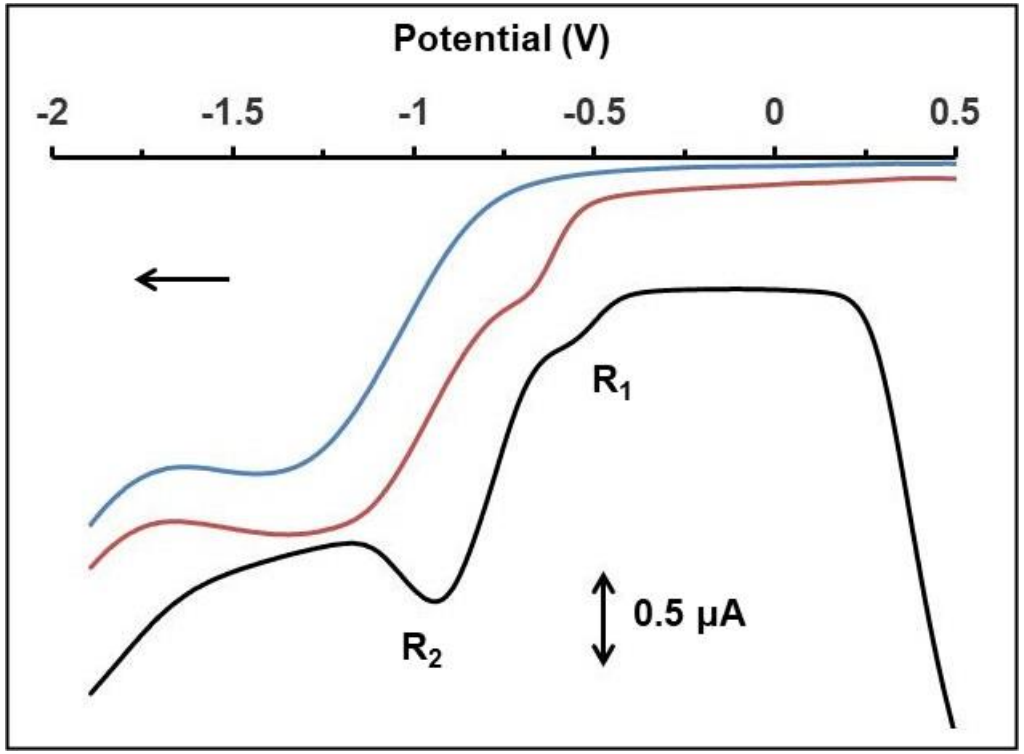
***therapeutic dose* : 25 mg L^{-1} FLU; 7.5 mg L^{-1} SCO, 2.5 mmol L^{-1} KET**

Detection of FLU

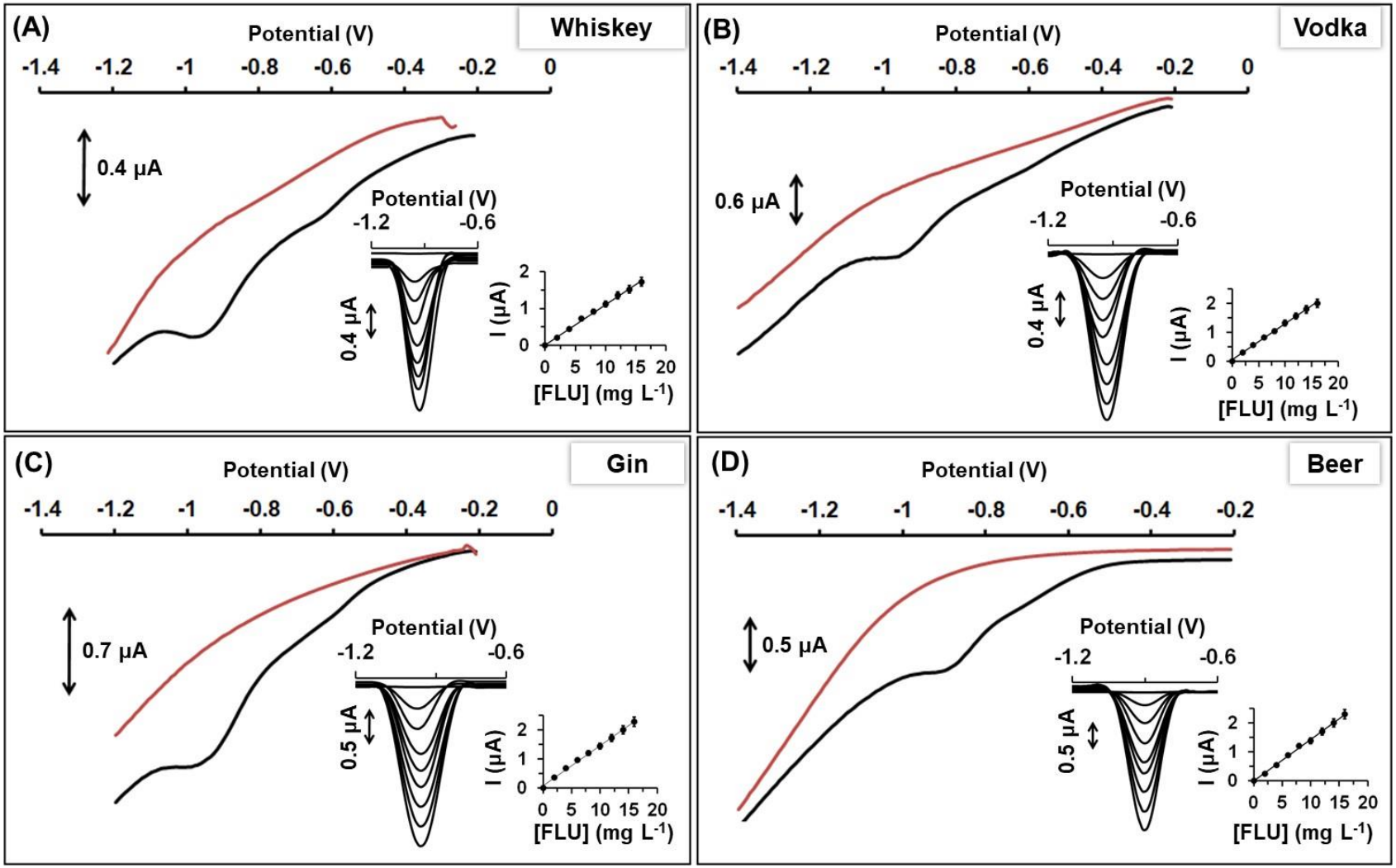


ascorbic acid dehydroascorbic acid

Vitamin C
1000mg



DP voltametric responses of e-finger in the presence of dissolved oxygen in: 0.1 mol L^{-1} PB (pH 7.4) (blue line), after the successive addition of 10 mg L^{-1} FLU (red line) and after the successive addition of 50 mg mL^{-1} ascorbic acid (black line).



DP voltammetric responses of e-finger obtained in untreated (A) whiskey, (B) vodka, (C) gin, (D) beer, before (red line) and after (black line) spiking with 2 mg L^{-1} FLU and 50 mg mL^{-1} ascorbic acid. The insets are the baseline corrected DPV voltametric responses of e-finger for increasing concentrations of FLU (0-16 mg L^{-1}) in each alcoholic drink containing 50 mg mL^{-1} ascorbic acid and the respective calibrations plots.

Acknowledgments

- **My students and researchers**

- **Prof. A Economou from NKUA**

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Thank you for your attention