Supplementary Information

Highly efficient and portable laser-scribed graphene-based electrochemical system for forensic-oriented analysis of acepromazine

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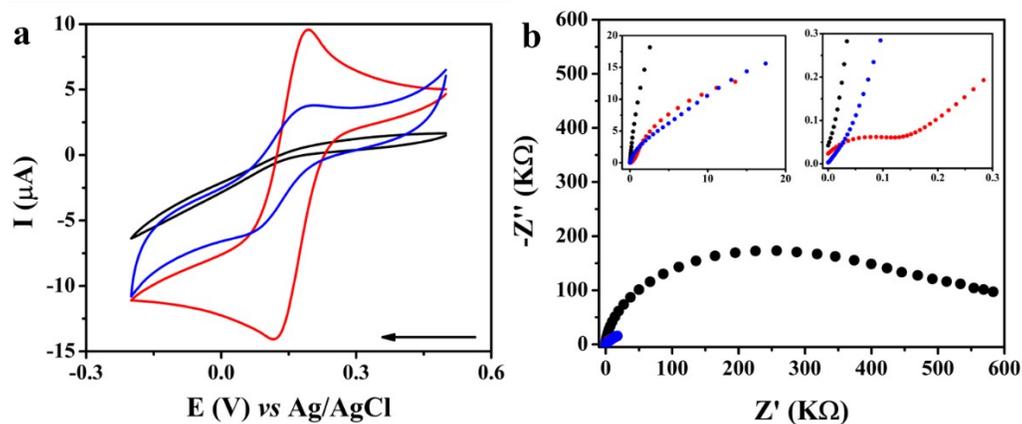
Figure S1: Electrochemical behavior of the LSG sensor under different superficial treatments. (a) CVs were recorded using different electrochemical treatments in a solution of 5.0 mmol L^{-1} $Fe(CN)_6^{-3/-4}$ containing 0.1 mol L^{-1} KCl as the supporting electrolyte at a scan rate of 50 mV s^{-1}. **(b)** Nyquist plots were obtained under the same conditions as in part A (5.0 mmol L^{-1} $[Fe(CN)_6]^{-3/-4}$ containing 0.1 mol L^{-1} KCl). EIS conditions: frequency range from $1x10^5$ Hz to 0.1 Hz and 10 mV amplitude, measurements were performed at room temperature. (●) LSG electrode without electrochemical treatment, (●) LSG electrode with cathodic treatment, and (●) LSG electrode with anodic treatment.
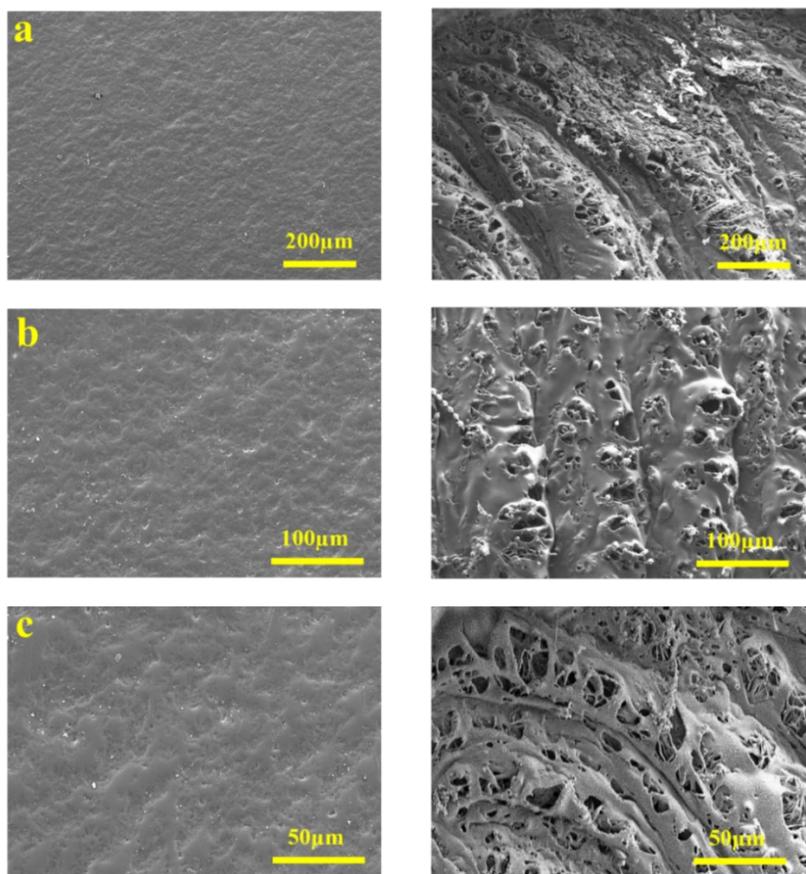
Figure S2: Morphological characterizations. SEM images with different magnifications of the PEI substrate and LSG electrode surface. (a) (200x), (b) (500x), (c) (1,000x).
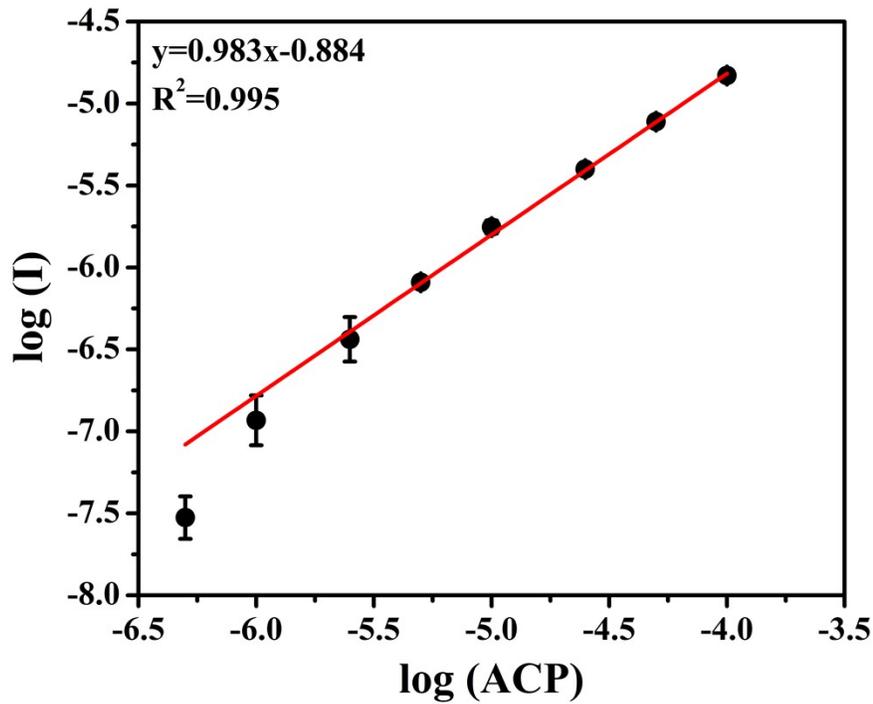
Figure S3: (a) Calibration curve built at different ACP concentrations (0.5, 1.0, 2.5, 5.0 10, 25, 50 and 100 μmol L⁻¹) in 0.1 mol L⁻¹ BR buffer (pH = 8.0), using the logarithm of anodic peak current as a function of logarithm of ACP concentration. The experiments were recorded in triplicate (n=3) at ~30 °C. SWV conditions: step = 7 mV, amplitude = 75 mV, and frequency = 25 Hz
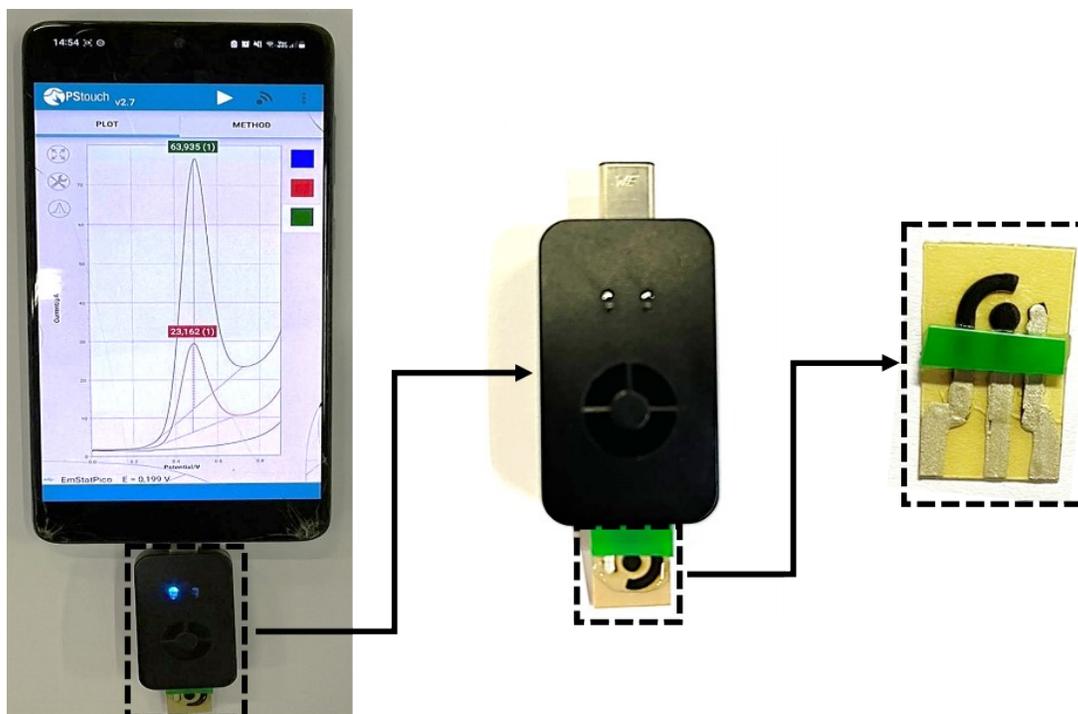
Figure S4: Schematic representation of the portable method employed to detect ACP using the PEI-LSG sensor connected to a miniaturized potentiostat controlled by a smartphone.
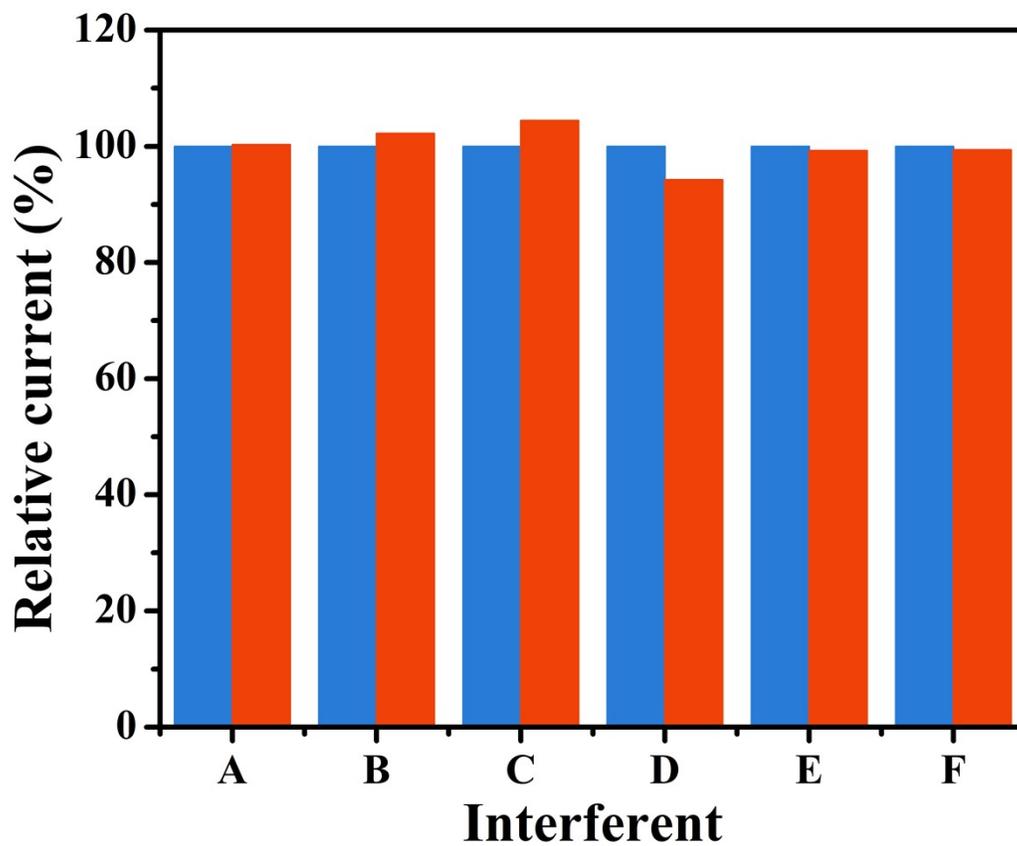
Figure S5: Selectivity studies recorded for ACP in the absence (blue bars) and presence (red bars) of interfering species **(A)** ascorbic acid, **(B)** citric acid, **(C)** uric acid, **(D)** creatinine, **(E)** ethanol 20 % (v/v) and **(F)** glucose.
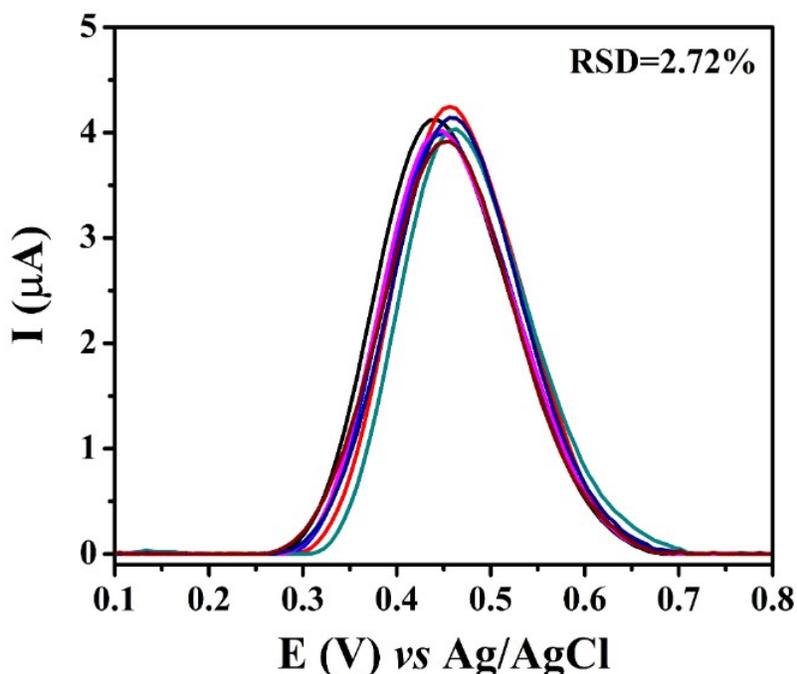
Figure S6: Reproducibility of the LSG sensor carried out by SWV in the presence of 25 µmol L^{-1} ACP. A relative standard deviation (RSD) of 2.72% for the ACP peak current using seven different electrodes was obtained.
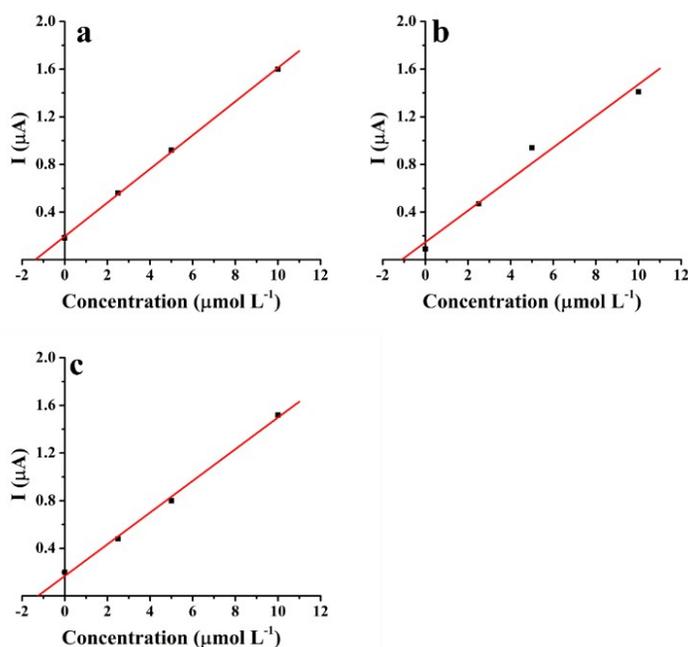
Figure S7: Analysts' comparison study using the PEI-LSG sensor in synthetic urine spiked with ACP solution for 3 different analysts: **(A)** analyst 1; **(B)** analyst 2 and **(C)** analyst 3. The calibration curve was carried out by SWV technique with successive additions of ACP (2.5, 5.0, and 10.0 µmol L^{-1}) in a synthetic urine sample 10x diluted in 0.1 mol L^{-1} BR (pH=8.0). Parameters: step = 7 mV, amplitude = 75 mV, and frequency = 25 Hz.

Table S1: Comparison of some electrochemical parameters reported for different sensors described in the literature.

Sensor	Redox probe	k^0 (cm s^{-1})	ΔEp (mV)	Rct (Ω cm^2)	Reference
SPE/Au/A-EE	[Fe(CN)$_6$]$^{-3/-4}$	5.47 x 10^{-4}	76	-	[1]
SPE/Au/A-DS	[Fe(CN)$_6$]$^{-3/-4}$	5.92 x 10^{-3}	64	-	[1]
SPE/Au/PE-EE	[Fe(CN)$_6$]$^{-3/-4}$	5.94 x 10^{-3}	62	-	[1]
Au	[Fe(CN)$_6$]$^{-3/-4}$	2.61 x 10^{-3}	117.43 ± 12.45	264 ± 69.0	[2]
N-grap	[Fe(CN)$_6$]$^{-3/-4}$	5.82 x 10^{-3}	89.25 ± 3.23	10.0 ± 5.0	[2]
G-PBAT	[Fe(CN)$_6$]$^{-3/-4}$	4.55 x 10^{-3}	-	5.0	[3]
SPE/DropSens	[Fe(CN)$_6$]$^{-3/-4}$	5.76 x 10^{-3}	88	-	[4]
Carbon paste	[Fe(CN)$_6$]$^{-3/-4}$	8.10 x 10^{-4}	386	-	[4]
SPE/Alderon	[Fe(CN)$_6$]$^{-3/-4}$	-	475	-	[4]
GC	[Fe(CN)$_6$]$^{-3/-4}$	2.35 x 10^{-4}	195	38.30	[5]
TC	[Fe(CN)$_6$]$^{-3/-4}$	2.22 x 10^{-3}	125	133.56	[5]
CF	[Fe(CN)$_6$]$^{-3/-4}$	1.60 x 10^{-4}	261	40.07	[5]
CM	[Fe(CN)$_6$]$^{-3/-4}$	2.97 x 10^{-3}	112	14.11	[5]
GR	[Fe(CN)$_6$]$^{-3/-4}$	1.25 x 10^{-2}	74	1.89	[5]
Our sensor	[Fe(CN)$_6$]$^{-3/-4}$	8.66 x 10^{-3}	64.31 ± 5.12	35.0 ± 7.0	This work

G-PBAT: graphite-poly (butylene adipate-co-terephthalate); N-grap: nail polish-graphite; Au: gold electrode; PE (polyester), EE (Electrical Engineering Department), A (alumina), DS (DropSens); GC: glassy carbon; TC: template foam; CF: porous carbon foam; CM: porous carbon microspheres; GR: commercial graphite.

Supporting Information 1: Electrochemical treatment of the PEI-LSG device

Electrochemical treatment of the PEI-LSG device was performed by chronoamperometry to ensure optimal performance of the device for ACP detection. The conditions were applied in the positive potential (anodic treatment) and negative potential (cathodic treatment). The anodic treatment was performed by applying +2.0 V for 120 seconds using 0.1 mol L^{-1} NaOH, and the cathodic treatment was performed by applying -2.0 V for 120 seconds using 0.1 mol L^{-1} H$_2$SO$_4$. The performance of the treated electrodes was evaluated by cyclic voltammetry (CV) and electrochemical impedance spectrometry (EIS). CV was recorded in a potential window from 0.5 V to -0.2 V and scan rate of 50 mV s^{-1} using [Fe(CN)$_6$]$^{-3}$ as a redox probe in KCl 0.1 mol L^{-1}. EIS measurements were recorded using a sinusoidal signal with a frequency range of 10^5 to 10^{-1} Hz and an amplitude of 10 mV at 30 °C in the same solution used for CV measures.

Supporting Information 2: Randles-Sevcik equation

$$I_p = (2.69x10^5)\, n^{3/2} A\, D^{1/2} C v^{1/2}$$

where Ip is the peak current, n is the number of electrons transferred (n=1), A is the electroactive area (cm^2), D is the diffusion coefficient of $[Fe(CN)_6]^{-3}$ in 0.10 mol L^{-1} KCl solution $(7.6 \times 10^{-6}$ cm^2 s$^{-1})$ [6], C is the concentration of $[Fe(CN)_6]^{-3}$ $(5x10^{-6}$ mol cm$^{-3})$ and v is the scan rate (V s^{-1}).

Supporting Information 3: Nicholson equation

$$\psi = K^0[\pi D n v F/(RT)]^{-\frac{1}{2}}$$

where ψ is the dimensionless kinetic parameter, $\pi = 3.1415$, F is the Faraday constant (96,485 C mol^{-1}), R is the universal gas constant (8.314 J K^{-1} mol^{-1}), T is the absolute temperature (298.15 K), n is the number of electrons transferred, D is the diffusion coefficient of $[Fe(CN)_6]^{-3}$ in 0.10 mol L^{-1} KCl solution $(7.6 \times 10^{-6}$ cm^2 s^{-1}), and v is the potential scan rate (V s^{-1}).

For this, the values of ψ were obtained using the equation proposed by Lavagnini et al. [7]:

$$\Psi = (-0.6288 + 0.0021 n\Delta E_P)/(1 - 0.017 n\Delta E_P)$$

where ΔE_P is given in mV.

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