

Supplementary material
for

Registration of small (below 1%) changes of calcium ion concentration in aqueous solutions and in serum by the constant potential coulometric method

by
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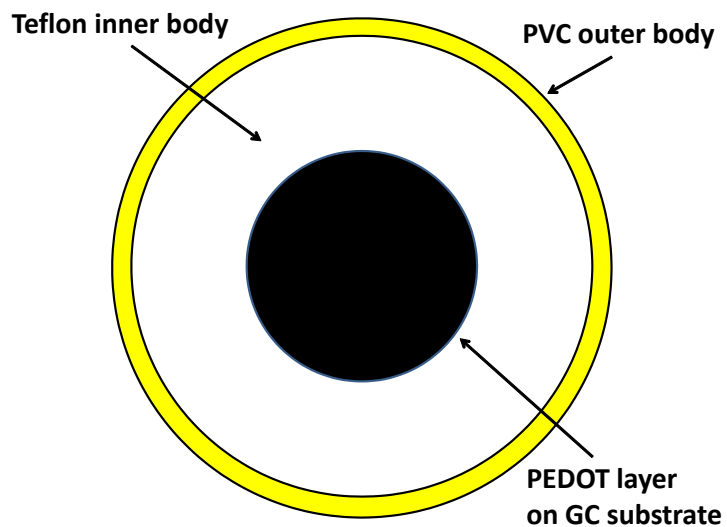


Figure S1. Electrode, top view.

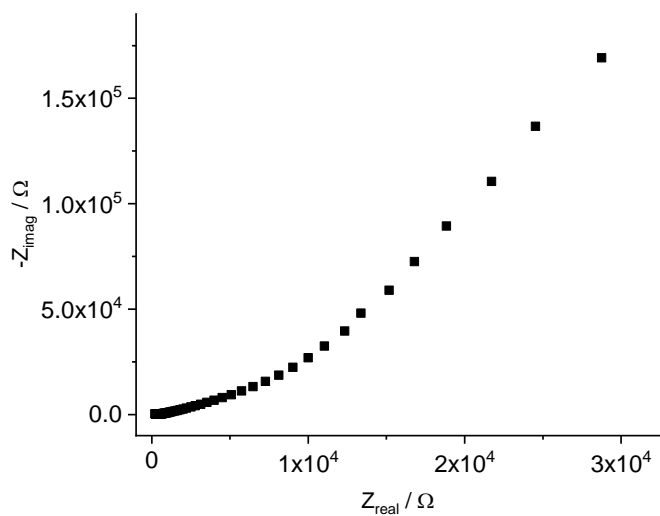


Fig. S2. Nyquist plot of the impedance spectrum of glassy carbon electrode with PEDOT-PSS film recorded in 5 mM $\text{K}_3\text{Fe}(\text{CN})_6$ + 5 mM $\text{K}_4\text{Fe}(\text{CN})_6$.

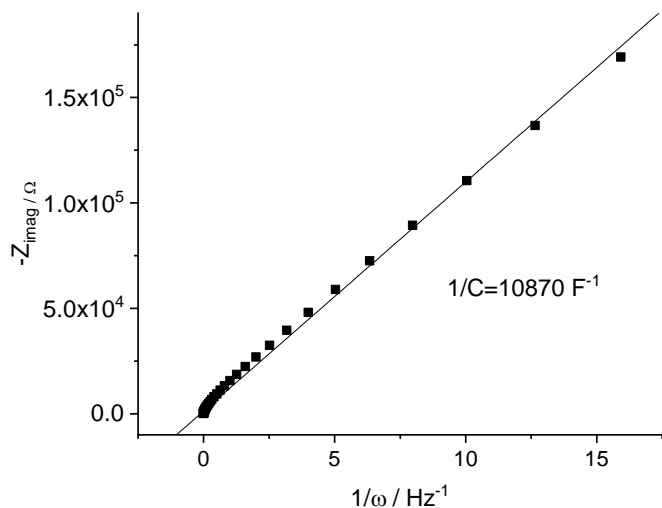


Fig. S3. Estimation of the capacitance of the PEDOT-PSS film from the impedance spectrum shown in Fig. S2.

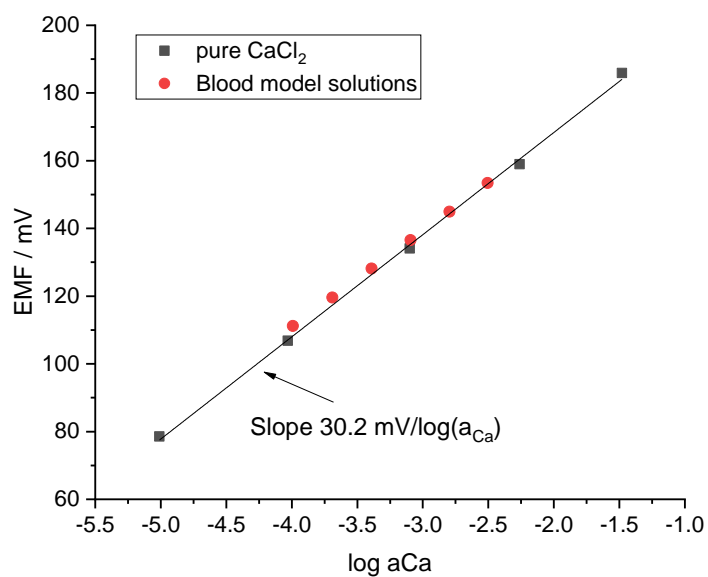


Figure S4. Potentiometric calibration plots of Ca-ISE in pure aqueous CaCl_2 solutions (black) and in blood model solutions without BSA (red).

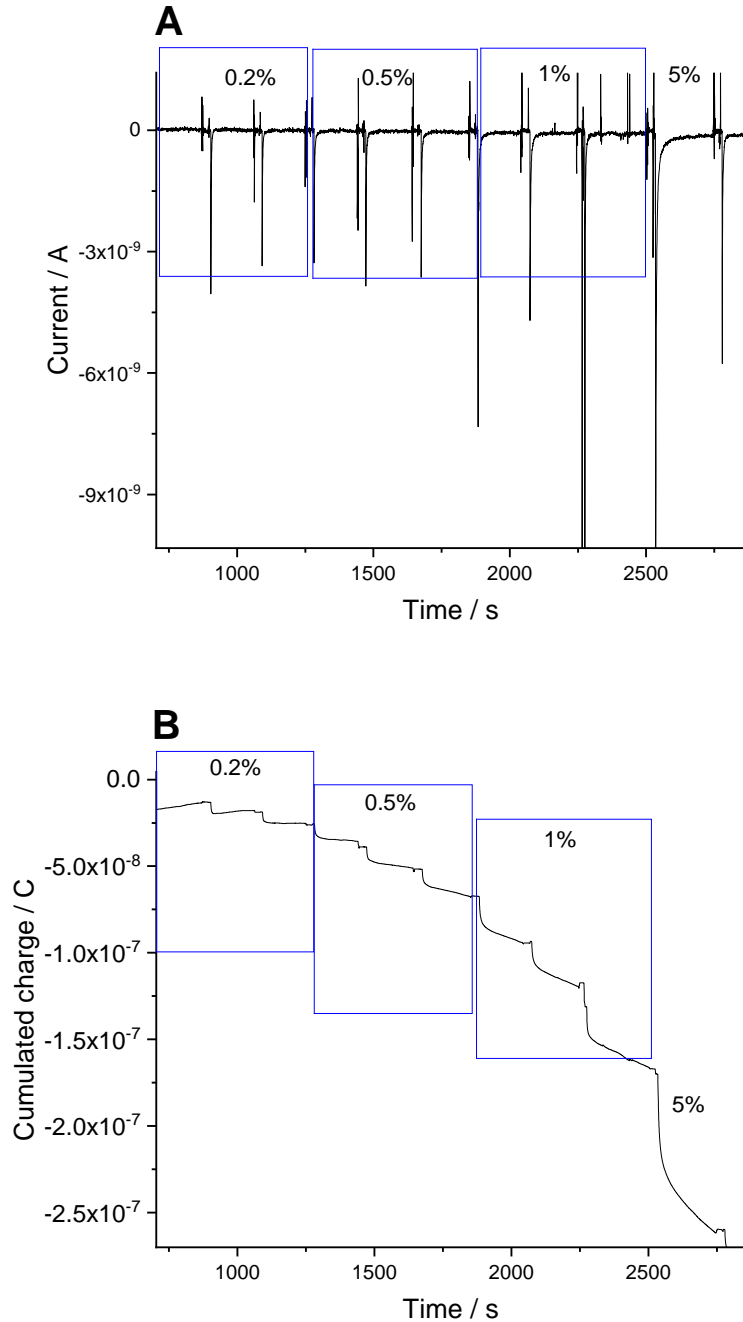


Figure S5. Small additions of 10 mM CaCl₂ to blood model solution initially containing 1 mM Ca²⁺. Three consecutive additions of 2 μ l, then three consecutive additions of 5 μ l, then three consecutive additions of 10 μ l, and finally 50 μ l of 10 mM CaCl₂. Respectively, the initial concentration of Ca²⁺ increased to 1.006 mM (in three steps, 0.2% each), next to 1.021 mM (in three steps, 0.5% each), then to 1.051 mM (in three steps, 1% each), and finally to 1.1 mM (one step).

A – the current curve.

B – the charge curve.

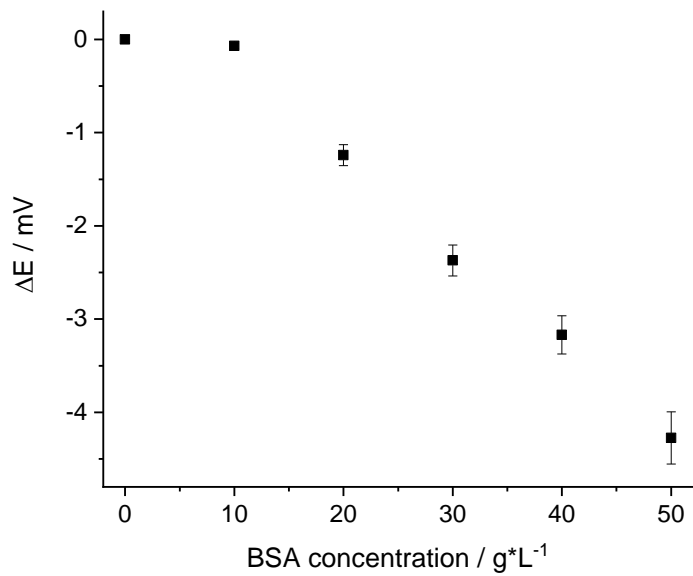


Figure S6. Deviation of the EMF values measured in model solutions containing BSA from the values in model solution without BSA: $\Delta E = E_{BSA} - E$. Total calcium $C_{Ca}^{tot} = 2$ mM.

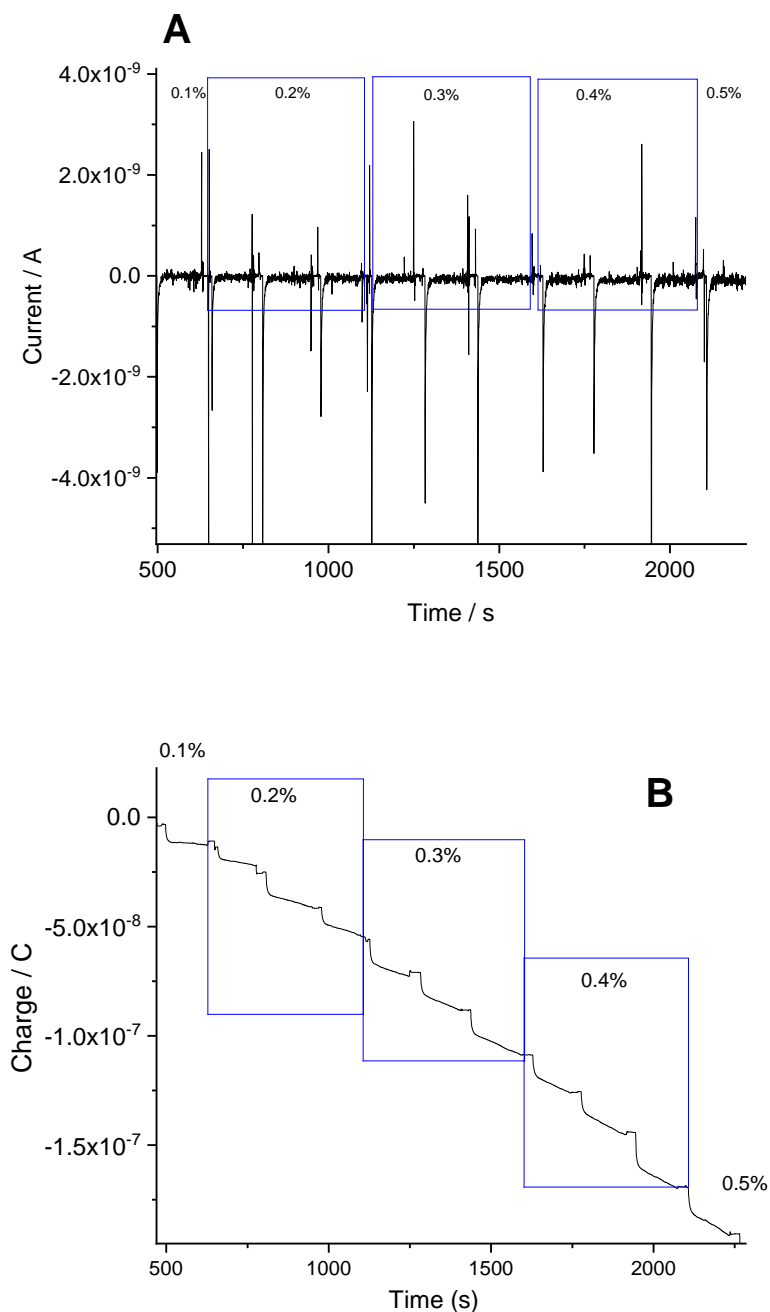


Figure S7. Small additions of 10 mM CaCl_2 to blood model solution initially containing with 40 g/L total BSA and 1 mM CaCl_2 . One addition of 1 μl , then three consecutive additions of 2 μl , then three consecutive additions of 3 μl , then three consecutive additions of 4 μl , and finally 5 μl of 10 mM CaCl_2 . Respectively, the assumed initial concentration of Ca^{2+} of 1 mM increased to 1.001, then to 1.006 mM (in three steps, 0.2% each), next to 1.021 mM (in three steps, 0.5% each), then to 1.051 mM (in three steps, 1% each), and finally to 1.1 mM (one step).

A – the current curve.

B – the charge curve.

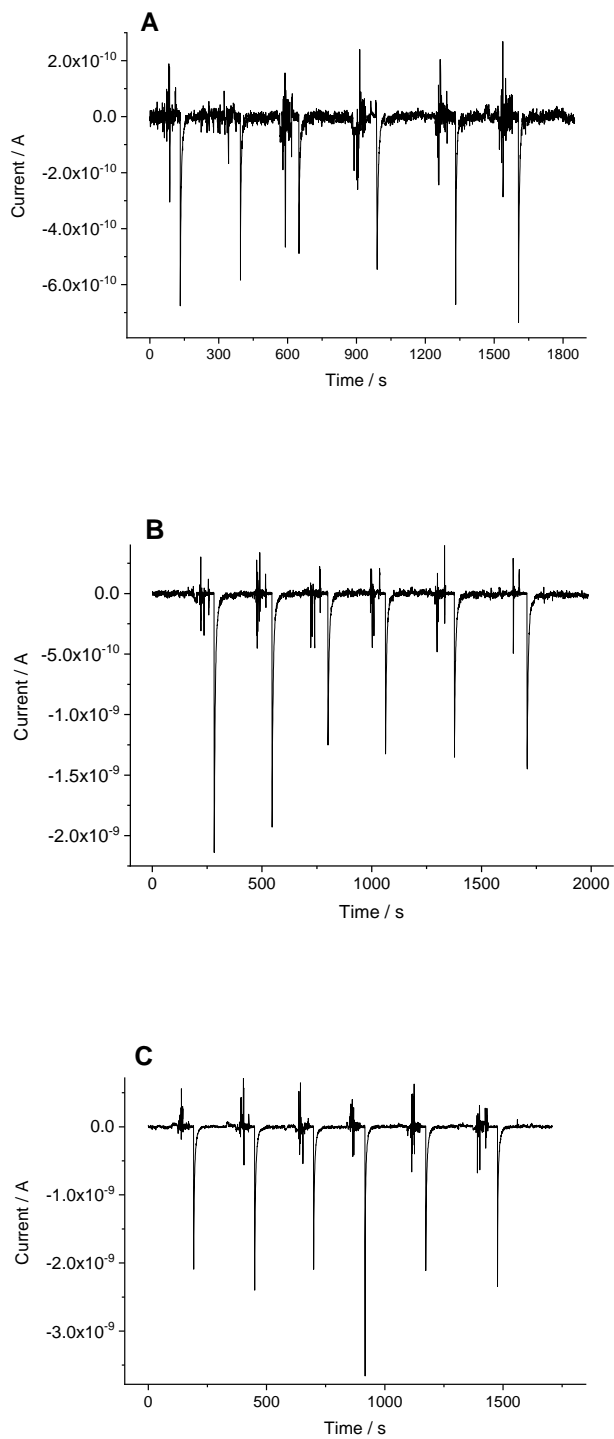


Figure S8. Current curves obtained in Thermo uTroll Control Serum samples with ISEs 1 (A), 2 (B) and 3 (C).

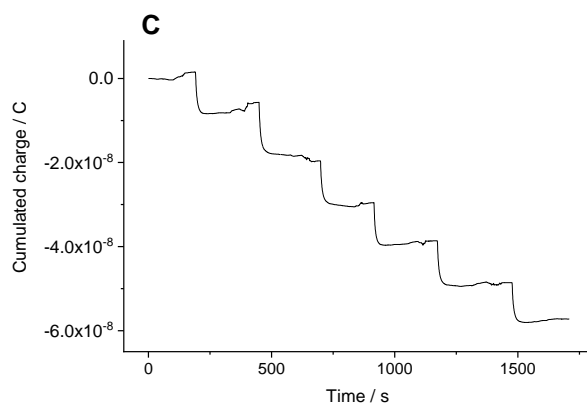
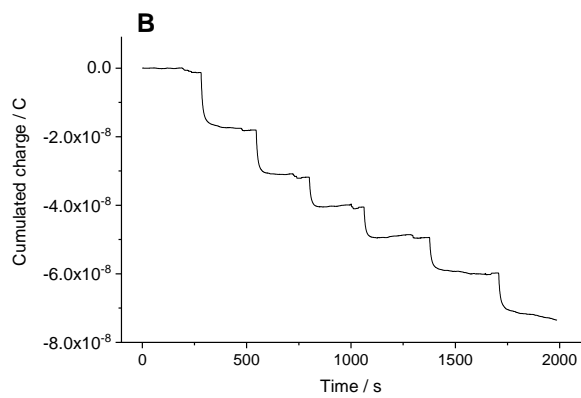
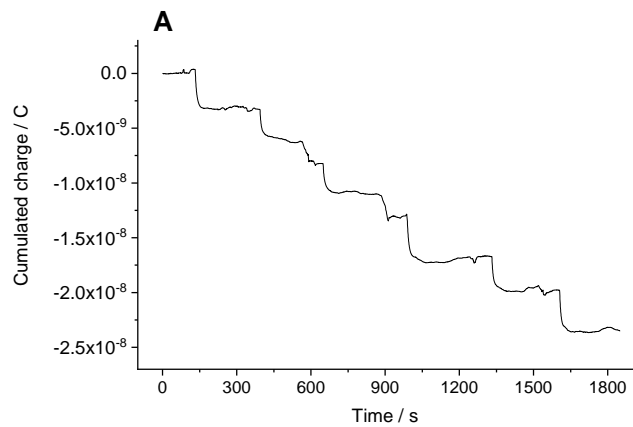


Figure S9. Charge curves obtained in Thermo uTroll Control Serum samples with ISEs 1 (A), 2 (B) and 3 (C).

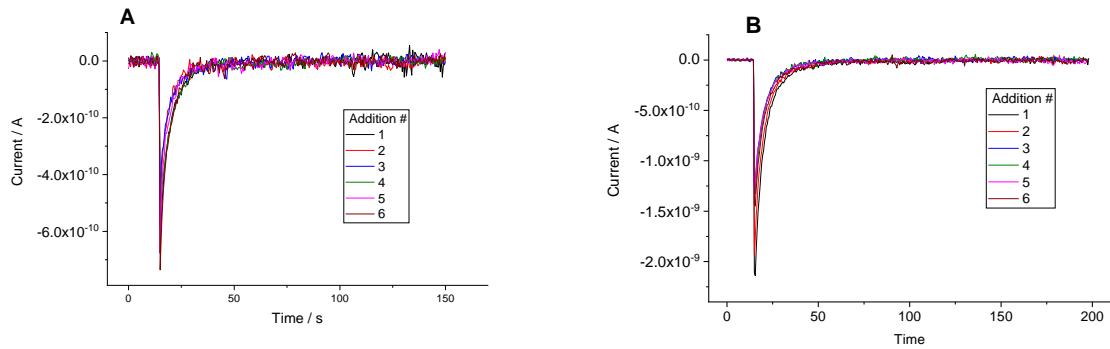


Fig. S10. Currents recorded with ISE 2 (A) and 3 (B) after sequential 0.1% additions of CaCl_2 to serum sample.

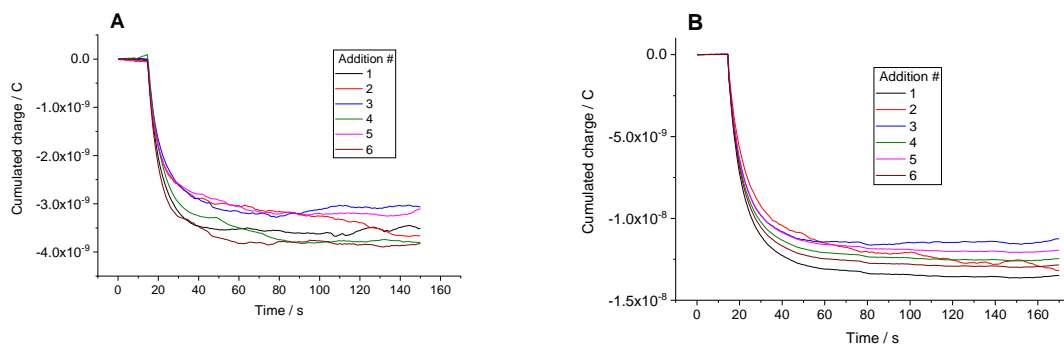


Figure S11. Charge values obtained using ISEs 2 (A) and 3 (B) after sequential 0.1% additions of CaCl_2 to serum sample.

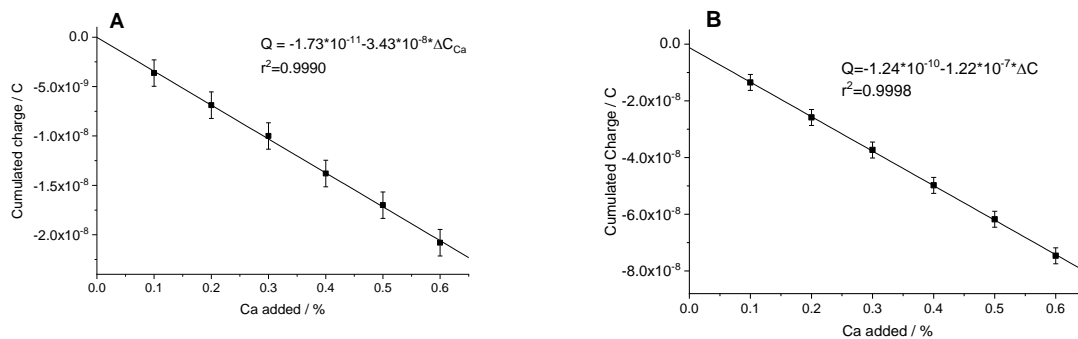


Figure S12. Calibration graph obtained with charge values cumulated by 100 s after additions of CaCl_2 to serum sample. A: ISE 2, B: ISE 3.