

Electronic Supplementary Information (ESI)

On-chip electrochemical detection of glucose towards the miniaturised quality control of carbohydrate-based radiotracers

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1. Setup of the screen-printed electrodes (SPEs)

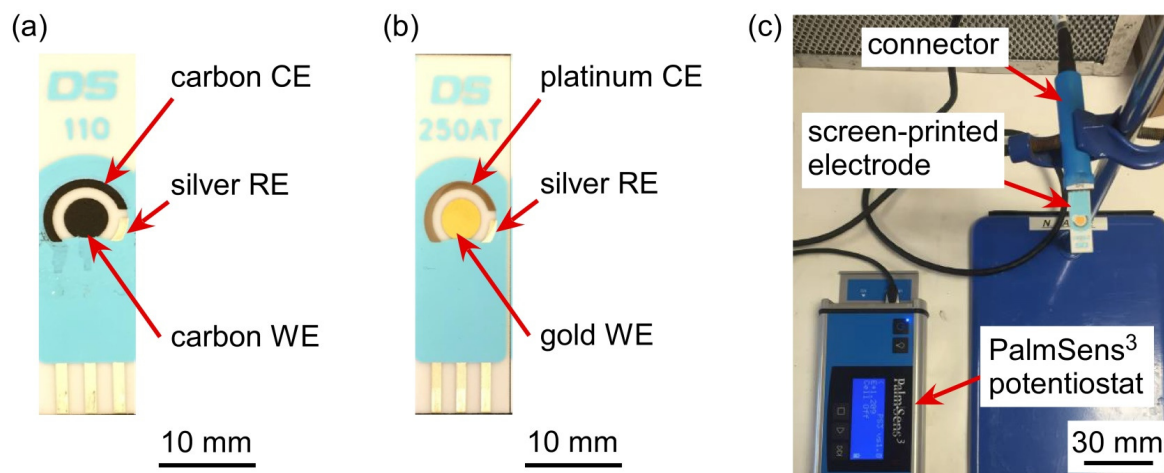


Fig. S1 Setup of the screen-printed electrodes (SPEs). (a) Metrohm DropSens DRP-110 screen-printed electrode with a carbon working electrode (WE; 4 mm \varnothing), a carbon counter electrode (CE), and silver reference electrode (RE). This electrode was used for testing the microfluidic “SPE-chip” by performing cyclic voltammetry (CV) of potassium ferricyanide. (b) Metrohm DropSens DRP-250AT screen-printed electrode with a gold WE (4 mm \varnothing), a platinum CE, and a silver RE. This electrode was used for performing pulsed amperometric detection (PAD) of glucose in an SPE-chip. (c) Connection of an SPE (chip not shown) to a PalmSens³ potentiostat via a Metrohm DropSens DRP-CAST connector cable. The setup was the same when using an SPE-chip, which was assembled onto the electrode.

2. Setup of the wire electrode chip

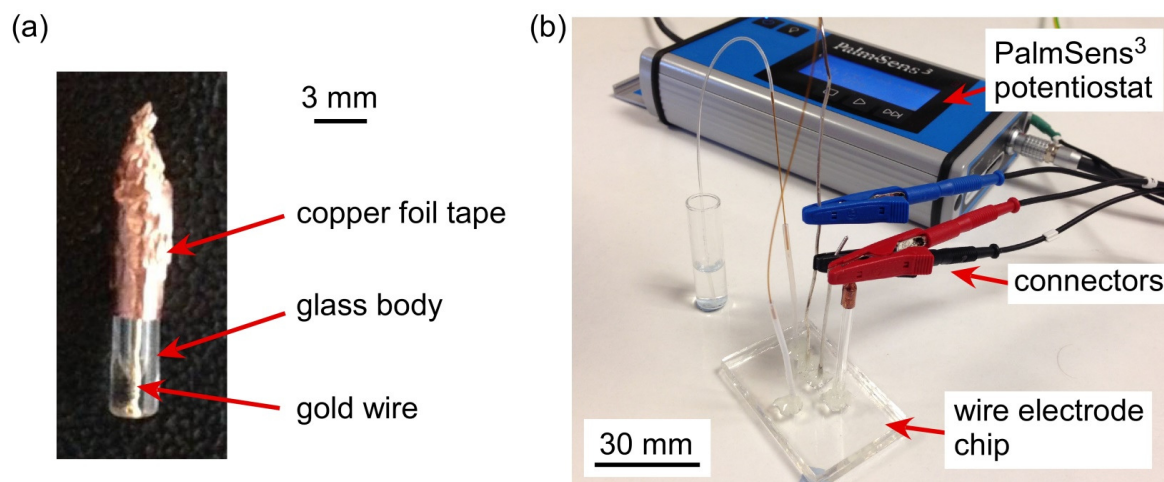


Fig. S2 (a) Working electrode comprising a 1 mm \varnothing gold wire sealed within a 3 mm \varnothing glass body and prepared for connection to a potentiostat via copper tape at the top. The tip of the gold wire was exposed at the bottom of the glass body and was polished with alumina for insertion into the glass microfluidic “wire-chip”. (b) Connection of the wire-chip to a PalmSens³ potentiostat via a Metrohm DropSens DRP-CAC connector cable. Crocodile clips on the connector cable were used to connect to a glass-bodied gold wire WE, a platinum wire CE (1 mm \varnothing), and a silver wire RE (1 mm \varnothing).

3. Flow injection analysis (FIA) setup

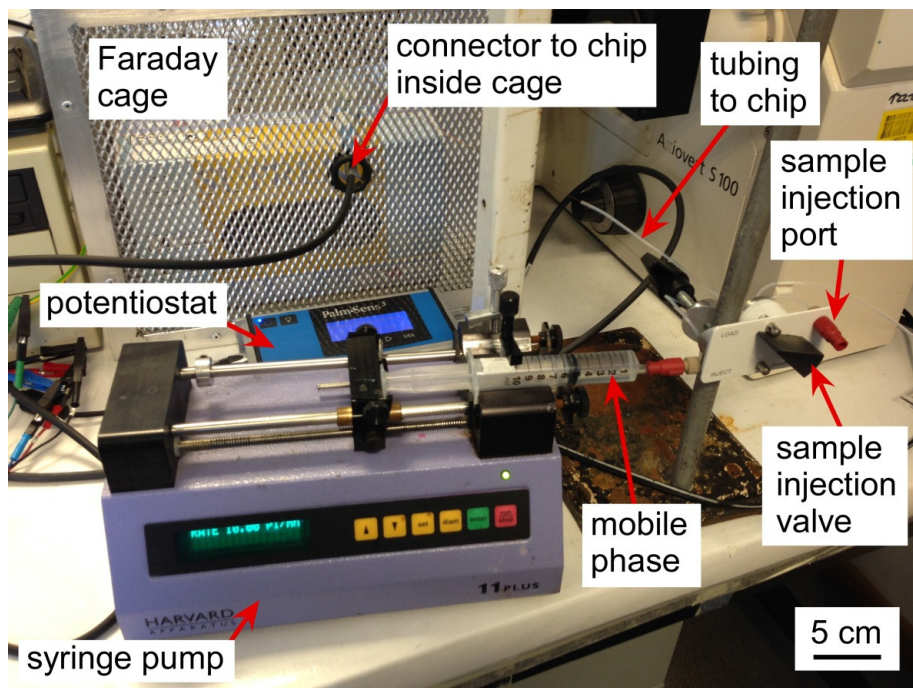


Fig. S3 Photograph of the setup for flow injection analysis (FIA) with pulsed amperometric detection (PAD) of glucose. The SPE-chip was located inside a Faraday cage and the electrodes connected to the PalmSens³ potentiostat (see Fig. S2) positioned outside of the cage, while the fluidic channel was connected to a Diba Omnifit® Labware Low Pressure 6-Port Loop Manual Sample Injection Valve using tubing. A Harvard Apparatus 11 Plus syringe pump was used to continuously pump a mobile phase of 0.1 M NaOH into the SPE-chip. An aliquot (1 μ L) of D-glucose solution was injected into the chip via the injection valve and the resultant PAD signal recorded.

4. Ferricyanide tests on DRP-110 electrode

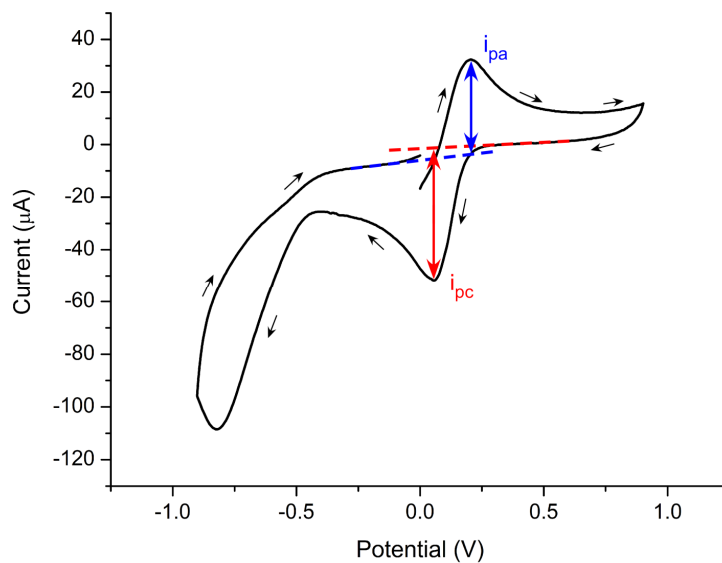


Fig. S4 Example cyclic voltammogram (CV) of the detection of 5 mM potassium ferricyanide in a 0.1 M KCl background electrolyte in stopped-flow conditions on a DRP-110 screen-printed electrode (carbon WE) in the SPE-chip. CVs were scanned in the forward direction from 0 V to +0.9 V, then in the reverse direction to -0.9 V, and finally back to 0 V (the direction is indicated by black arrows on the plot). The scan rate was 0.09 V s^{-1} and the E_{step} value (the incremental step in potential) was set to 0.005 V. The anodic peak current (i_{pa}) for the oxidation of ferrocyanide ($\text{Fe}^{\text{II}}(\text{CN})_6^{4-}$) to ferricyanide ($\text{Fe}^{\text{III}}(\text{CN})_6^{3-}$) was at +0.19 V, while the cathodic peak current (i_{pc}) for the reduction of ferricyanide to ferrocyanide was at +0.05 V.

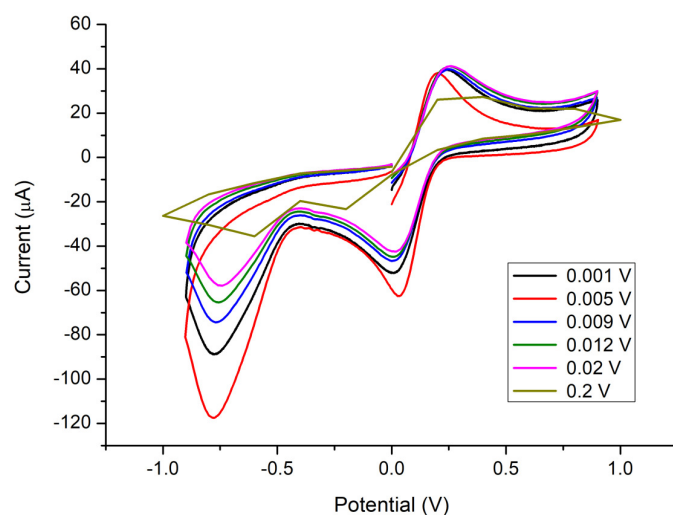


Fig. S5 Cyclic voltammograms showing the effect of changing the E_{step} , with the scan rate set to 0.09 V s^{-1} . The other experimental parameters were as described in Fig. S4. Smaller E_{step} values provided smoother CVs, whilst the peak currents were largely unaffected by E_{step} values between 0.009 V and 0.02 V .

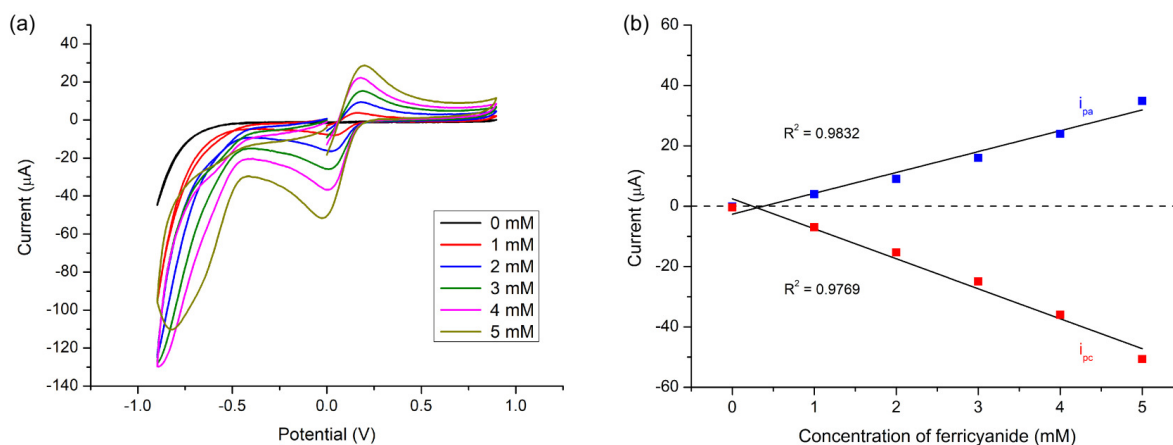


Fig. S6 Calibration of potassium ferricyanide (in 0.1 M KCl) on the DRP-110 screen-printed electrode (carbon WE) in the SPE-chip. (a) CVs of the ferricyanide standards tested. (b) The change in the anodic peak current (i_{pa}) and cathodic peak current (i_{pc}) obtained from the CVs in (a) for the forward and reverse scans, respectively. The scan rate was 0.09 V s^{-1} , the E_{step} was 0.009 V , and the CV was performed in stopped flow conditions. The results demonstrated good linearity that suggested quantitative analysis would be feasible using the SPE-chip.

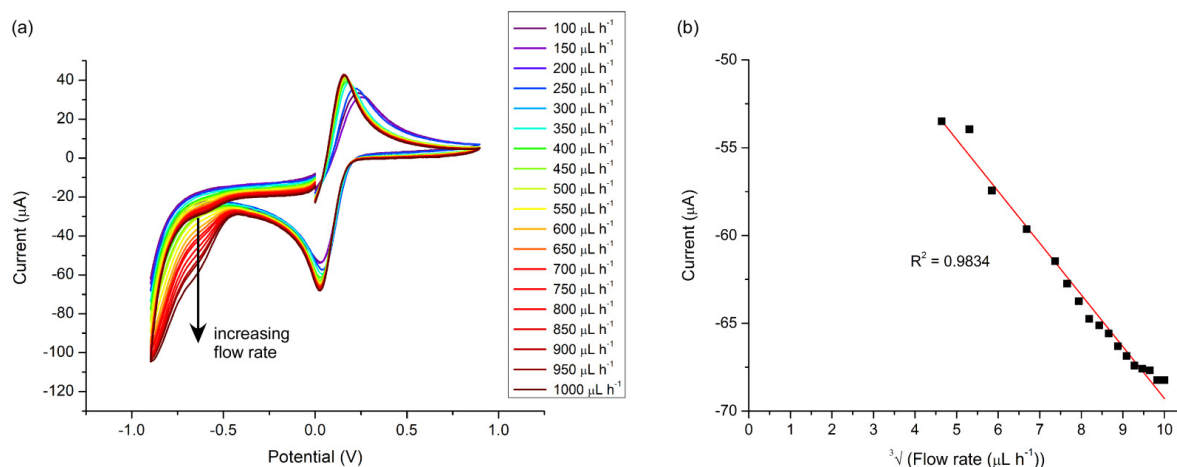


Fig. S7 The effect of flow rate on the detection of 5 mM potassium ferricyanide on the DRP-110 electrode (carbon WE) as it was pumped through the SPE-chip. (a) CVs of potassium ferricyanide at flow rates ranging from 100 to 1000 $\mu\text{L h}^{-1}$ ($1.7\text{-}16.7 \mu\text{L min}^{-1}$). The scan rate was 0.09 V s^{-1} and the E_{step} was 0.009 V. (b) Plot of the peak cathodic current of the reverse scans against the cube root of the hydrodynamic flow rate. The linearity of the data indicates that the SPE-chip operated as expected under hydrodynamic flow conditions, with mass transport being predominantly due to convection rather than diffusion [1,2].

5. Varying the PAD waveform potentials on the SPE signal

The effect of changing the potentials of the PAD waveform was studied for the SPE-chip by varying the applied E1 (measurement step), E2 (electrode cleaning step), and E3 (electrode regeneration step) potentials between 0.25 to 0.45 V, 0.70 to 0.90 V, and -0.20 to -0.40 V, respectively (Fig. S8). Samples of 1000 ppm D-glucose were injected into the FIA system, with a mobile phase of 0.1 M NaOH at $10 \mu\text{L min}^{-1}$. A DRP-250AT SPE with a gold WE was used in the SPE-chip.

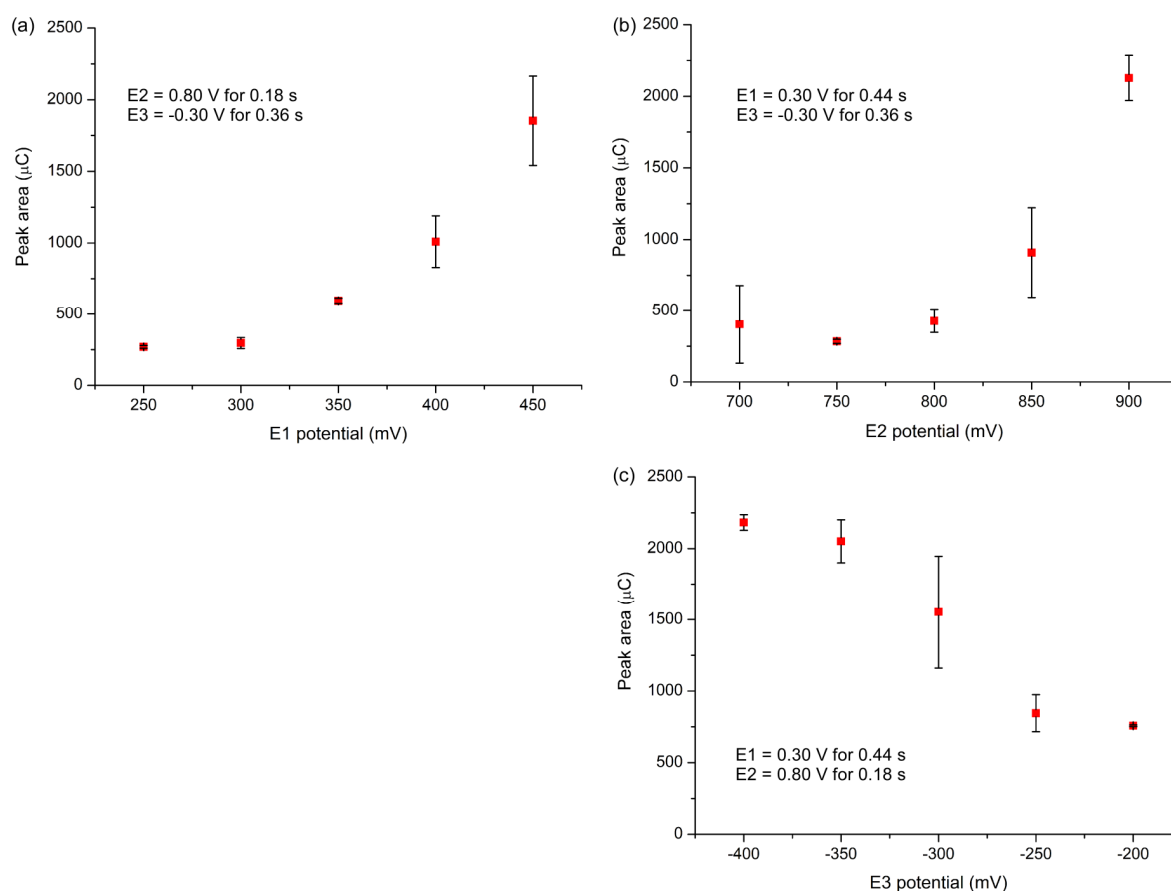


Fig. S8 The effect of varying each potential of the PAD waveform for the detection of D-glucose using a screen-printed electrode with a gold working electrode. (a) Effect of changing the E1 potential (time, $t = 0.44$ s) during injections of glucose into the SPE-chip. (b) Effect of changing the E2 potential ($t = 0.18$ s). (c) Effect of changing the E3 potential ($t = 0.36$ s).

6. Fouling of the gold WE screen-printed electrode

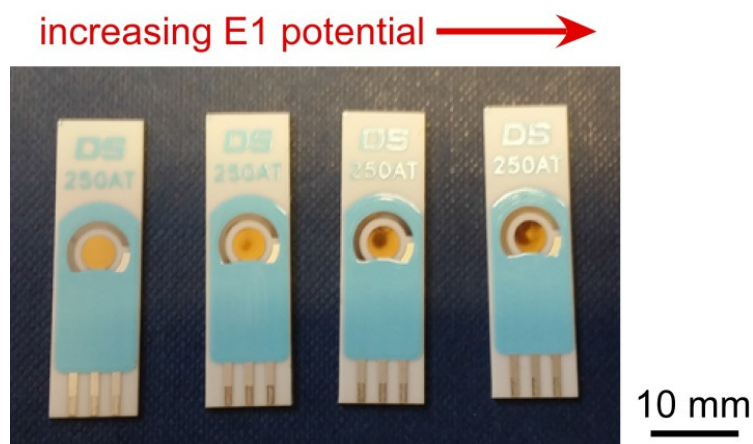


Fig. S9 Fouling of the gold WE of the DRP-250AT screen-printed electrode with increasing E_1 (measurement) potential (time, $t = 0.44$ s) during E_1 potential optimisation. The E_2 (regeneration) potential was set to 0.80 V ($t = 0.18$ s), and the E_3 (cleaning) potential was set to -0.30 V ($t = 0.36$ s). A 1000 ppm solution of D-glucose was injected ($1 \mu\text{L}$) into the SPE-chip with a mobile phase of 0.1 M NaOH at $10 \mu\text{L min}^{-1}$. Each SPE was used for only one analysis, and fouling was found to become much worse at higher E_1 potentials. The spiral design of the microfluidic channel in the SPE-chip could be seen in the fouling pattern of the SPEs used with the greater E_1 potentials

7. References

- [1] R. G. Compton, A. C. Fisher, R. G. Wellington, P. J. Dobson and P. A. Leigh, *J. Phys. Chem.*, 1993, **97**, 10410-10415.
- [2] C. Amatore, N. Da Mota, C. Sella and L. Thouin, *Anal. Chem.*, 2007, **79**, 8502-8510.