Potentiometric sensing utilizing paper-based microfluidic sampling

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Electronic supplementary information

1. Experimental

1.1. Materials

Poly(vinyl chloride) (PVC) of high molecular weight, potassium tetrakis[3,5-bis(trifluoromethyl)phenyl]-borate (KTFPB), 2-nitrophenyl octyl ether (o-NPOE, ≥ 99 %), tetrahydrofuran (THF, ≥ 99.5%), tetrabutylammonium tetrabutylborate (TBA-TBB, 97 %) and bis(2-ethylhexyl) sebacate (DOS, ≥ 97 %) were obtained from Fluka. Potassium chloride (KCl, purity ≥ 99%), ethanol, KOH and HNO_3 were obtained from J.T Baker, while 3,4-ethylenedioxythiophene (EDOT, > 97 %) was obtained from Bayer AG. Deionized water was obtained with an ELGA Purelab Ultra system (resistivity = 18 MΩ cm). Black ribbon filter paper (pore size = 12–25 μm) and Blue ribbon filter paper (pore size = 2 μm) were purchased from Schleicher&Schuell GmbH., while White ribbon filter paper (pore size = 4–12 μm) was purchased from Whatman GmbH.

1.2. Electrode fabrication

Glassy carbon (GC) disk electrodes with a diameter of 3 mm were polished using 1 μm diamond paste and 0.3 μm Al_2O_3. After polishing, the GC electrodes were immersed in 1 M HNO_3, in 0.1 M KOH, and in ethanol for further cleaning. Finally, the electrodes were placed in an ultrasonic bath with deionized water for 10 minutes. Poly(3,4-ethylenedioxythiophene) (PEDOT) was electrodeposited on the GC disk ,working electrodes from a deaerated aqueous solution containing 0.01 M EDOT and 0.1 M KCl by applying a constant current of 0.014 mA (0.2 mA cm^{-2}) for 714 s. [26] The auxiliary electrode was a GC rod and the reference electrode was a Ag/AgCl/3 M KCl//1 M LiAc (lithium acetate). After electropolymerization, a potassium (K^+) ion-selective membrane (ISM) was drop casted on the GC/PEDOT(Cl^-) electrodes, resulting in solid-contact K^+-selective ISEs (K^+-ISEs). The ISM cocktail contained 1.0 % valinomycin, 0.5 % KTFPB, 65.2 % DOS, and 33.3 % PVC (dissolved in THF at a dry mass of 15 % w/w).[26] Analogously, the solid-contact reference electrode (SC-RE) was prepared by drop casting a reference membrane cocktail containing 12.5 % TBA-TBB, 58.3 % o-NPOE and 29.2 % PVC (dissolved in THF at a dry mass of 15 % w/w) on another GC/PEDOT(Cl^-) electrode.[23]

1.3. Potentiometric measurements

Potentiometric measurements were performed using an EMF16 Interface (Lawson Labs Inc., USA). Before the measurements utilizing paper-based sampling, the Nernstian response of the K^+-ISEs versus the SC-RE was verified in a conventional potentiometric cell by immersing the electrodes directly into the bulk solution (10^{-1}–10^{-3} M KCl). After a Nernstian response was observed, filter paper-based microfluidic sampling was investigated.

Three ashless types of filter papers with different porosity and pore sizes (Black Ribbon = T1, White Ribbon = T2, and Blue Ribbon = T3) were used during the potentiometric

measurement as paper substrates to absorb and hold micro volumes of sample solutions. To optimize the measurement conditions, four shapes/sizes of filter papers were investigated, as illustrated in Fig. S1.

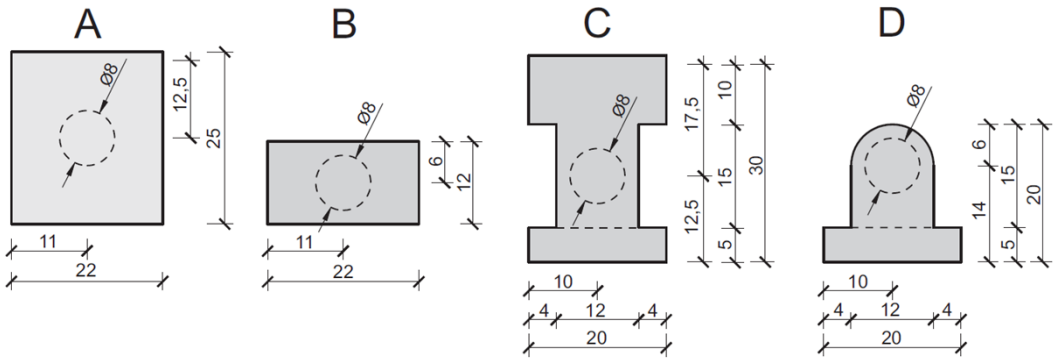

Fig. S1. Illustrations A, B, C and D show the shapes and dimensions (in mm) of filter papers used as microfluidic sampling media for potentiometric sensing. The dashed circles indicate the position where the K^+-ISE and SC-RE were positioned against the paper from opposite sides.