Supporting Information

On-chip capacitively coupled contactless conductivity detection using “injected” metal electrodes

Leigh D. Thredgold, a Dmitriy A. Khodakov, a Amanda V. Ellis a and Claire E. Lenehan a b

a Flinders Centre for Nanoscale Science and Technology, Flinders University, GPO Box 2100, Adelaide 5001, Australia.
b School of Chemical and Physical Sciences, Flinders University, GPO Box 2100, Adelaide 5001, Australia E-mail: claire.lenehan@flinders.edu.au
Selection of BGE additive for stable EOF

The interaction of surfactant molecules with PDMS microchannel surfaces can have a significant impact on both the magnitude and stability of the EOF in BGE systems. Native PDMS microchannels are known to produce unstable EOFs due to its hydrophobic nature and ability to adsorb a large range of hydrophobic molecules. For this study, we required the efficient electrophoretic separation of the cations lithium, sodium and potassium. Therefore, it was determined that the surfactant DDM would be most suitable as it has been reported to result in a reduced and stable EOF compared to channels with no surfactant modification. Further, DDM was chosen taking into consideration the short separation channel length (effective length: 37 mm) and consequent need to decrease the cathodic EOF to allow greater time for separation of the cationic analytes.

The effect of adding increasing amounts of DDM on the EOF in the PDMS microchannel was determined using C\textsuperscript{4+}D as previously reported. Increasing the DDM concentration resulted in a sharp decrease in the measured EOF for the 0.1, 0.2 and 0.4 mM solutions, respectively, after which a plateau in the data was observed (Fig. S1 (A)). A stable EOF of \(0.84 \pm 0.03 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}\) was observed at concentrations above 0.4 mM DDM. The decrease in EOF associated with larger concentrations of DDM in the BGE is a result of the dynamic interaction of DDM molecules with the PDMS surface. Zhou et al. have previously reported that the large hydrophobic tails of surfactant molecules are physisorbed onto the PDMS surface effectively exposing the non-ionic maltoside headgroups to the solution (Fig. S1). Further, Huang et al. previously reported that the formation of such a the DDM coating reduces the EOF by effectively covering the charges on the PDMS surface. It follows that the reduced surface charge leads to a decreased zeta potential and a lower EOF observed. Based on these results a DDM concentration of 0.4 mM was used for the remaining experiments.

PDMS microchannel surface modification using surfactant is traditionally achieved by the addition of surfactant to the BGE for preconditioning and/or during analysis experiments, allowing replenishment of the surface coating. To determine the effect on analytical performance of using DDM in the preconditioning and analysis steps (referred to as continuous surfactant experiments) versus only in the preconditioning step (referred to as non-continuous surfactant experiments), both approaches were tested by separating a 0.5 mM mixture of Li\textsuperscript{+}, Na\textsuperscript{+} and K\textsuperscript{+} cations. Continuous surfactant experiments were performed by running BGE (20 mM) with DDM (0.4 mM) for electrophoretic separations. Whereas non-continuous surfactant experiments were performed by flushing the analysis microchannel with BGE (20 mM) and DDM (0.4 mM) for 20 min followed by electrophoretic separations with BGE (20 mM) without surfactant. To compare the analytical performance of both approaches peak height divided by concentration ratios (P\textsubscript{H/Conc ratio}) for each of the three cations were plotted with their associated standard deviation (n=5) (Fig. S1 (B)).

A significant increase in the P\textsubscript{H/Conc ratio} along with a reduction in the standard deviation was observed using the non-continuous DDM surface modification approach (Fig. S1 (B)). These results suggested that the non-continuous surfactant approach resulted in more sensitive and consistent detection of the target analytes. This lead to the conclusion that the presence of DDM during analysis interfered with the conductivity detection resulting in suppression of the analytical signal obtained. It was postulated that this was the result of increased background conductivity and/or the formation of micelles during electrophoresis (CMC\textsubscript{DDM}=0.16 mM) changing the electrophoresis conditions. As a result of these findings it was determined that a non-continuous surface modification approach using DDM be used for all electrophoretic separations.

**Fig. S1 (A)** EOF as a function of concentration for DDM in MES/His background electrolyte (20 mM and 18 mM) at pH 6. The inserted panel illustrates a simplified view of the proposed surfactant molecule interaction with the PDMS surface and **(B)** Comparison of peak height (P\textsubscript{H})/concentration ratios for continuous and non-continuous DDM surface modification approaches as a measure of analytical performance.
Fig. S2 Photograph of PDMS microchip inside housing showing (A) high voltage electrodes for electrophoresis, (B) injected gallium electrodes and (C) custom designed printed circuit board for connection to external electronics. The zoom in depicts the injected gallium Cd electrodes showing (D) the connection of the electrodes to the external electronics through tin plated copper pins protruding from the custom made printed circuit board.

Fig. S3 Effect of BGE concentration on the peak height and S/N ratio of the K⁺, Na⁺ and Li⁺ peaks (5 × 10⁻⁴ M). Operating conditions: microchip 57/37 mm total/effective length; injection voltage, 0.8 kV for 10 s; separation voltage, 1.4 kV. Cd detector: sine waveform of 220 kHz, 5 V p-p. Error bars: ±1 standard deviation.

References