## Dual Contactless Conductivity and Amperometric Detection on Hybrid PDMS/Glass Electrophoresis Microchips

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**Fig. S-1** Electrophoretic separation of a 50  $\mu$ M equimolar mixture of potassium, sodium and lithium chloride dissolved in water. Separation parameters: run buffer, 20 mM MES/His, pH 6.1; injection voltage, 0.8 kV; separation voltage, 1.2 kV; injection time, 1 s; separation channel effective length, ca. 35 mm. C<sup>4</sup>D parameters: frequency, 500 kHz; excitation voltage, 10 V<sub>peak-to-peak</sub>.



**Fig. S-2** Electrophoretic separation of a 25  $\mu$ M equimolar mixture of potassium, sodium and lithium chloride dissolved in water. Separation parameters: run buffer, 20 mM MES/His, pH 6.1; injection voltage, 0.8 kV; separation voltage, 1.2 kV; injection time, 3 s; separation channel effective length, ca. 35 mm. C<sup>4</sup>D parameters: frequency, 500 kHz; excitation voltage, 10 V<sub>peak-to-peak</sub>.



**Fig. S-3** Electrophoretic separation of a 100  $\mu$ M equimolar mixture of chloride, nitrate and perchlorate dissolved in run buffer. Separation parameters: run buffer, 20 mM MES/His, pH 6.1; injection voltage, -0.8 kV; separation voltage, -1.2 kV; injection time, 1 s; separation channel effective length, ca. 35 mm. C<sup>4</sup>D parameters: frequency, 500 kHz; excitation voltage, 10 V<sub>peak-to-peak</sub>.



**Fig. S-4** Electrophoretic separation of a mixture of 500  $\mu$ M NO2<sup>-</sup> and 100  $\mu$ M NO3<sup>-</sup> in water detected simultaneously by: A) C<sup>4</sup>D (frequency, 450 kHz; excitation voltage, 15 V<sub>peak-to-peak</sub>; effective length, ca. 42 mm); B) amperometric detection (voltage applied to the working electrode, 850 mV; effective length, ca. 47 mm). Separation parameters: run buffer, 30 mM lactic acid-0.75 mM TTAOH, pH 3.5; injection voltage, -1.0 kV; separation voltage, -1.5 kV; injection time, 1 s.



**Fig. S-5** Effective mobility-scaled electropherograms showing the separation of 5 mM NO<sub>2</sub><sup>-</sup> and 1 mM NO<sub>3</sub><sup>-</sup> in a standard mixture detected simultaneously by C<sup>4</sup>D (A) and amperometric detection (B). Other conditions as stated in Fig. 4. The transformation of the time-based x-axis in electropherograms shown in Fig. 4 into effective mobility-scale x-axis was done by considering nitrite as an internal standard (nitrite mobility ~ -69.6 x 10<sup>-9</sup> m<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>).<sup>1</sup>

<sup>&</sup>lt;sup>1</sup> J. Pospíchal, P. Gebauer, P. Boček, *Chem. Rev.*, 1989, **89**, 419.



**Fig. S-6** Effective mobility-scaled electropherograms showing the separation of NO<sub>2</sub><sup>-</sup> and NO<sub>3</sub><sup>-</sup> resulting from the degradation of a peroxynitrite sample detected simultaneously by C<sup>4</sup>D (A) and amperometric detection (B). Other conditions as stated in Fig. 5. The transformation of the time-based x-axis in electropherograms shown in Fig. 5 into effective mobility-scale x-axis was done by considering nitrite as an internal standard (nitrite mobility ~ -69.6 x 10<sup>-9</sup> m<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>).<sup>1</sup>