Applications of Voltammetric Ion Selective Electrodes to Complex Matrices

Supporting Information

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Figure S1. Structures of ionic liquids.

Table S1: Statistical data from the AEROSET 2 at the John Radcliffe Hospital.

<table>
<thead>
<tr>
<th>Ion</th>
<th>Lower calibrant average activity /mM</th>
<th>Coefficient of Variation</th>
<th>Upper calibrant average activity /mM</th>
<th>Coefficient of Variation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na⁺</td>
<td>122</td>
<td>0.9</td>
<td>156</td>
<td>0.5</td>
</tr>
<tr>
<td>K⁺</td>
<td>2.7</td>
<td>1.7</td>
<td>6.2</td>
<td>0.9</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>1.86 *</td>
<td>1.5</td>
<td>2.77 *</td>
<td>1.1</td>
</tr>
</tbody>
</table>

*total concentration

Figure S2. $E_m$ versus NaCl concentration calibration curve of the TCNQ microcrystal sensor and response using the 10th potential cycle on EPG with an SCE reference electrode (black) and on a planar macrodisc screen printed electrode with an Ag/AgCl reference electrode with no salt bridge (blue).
Figure S3: First three potential cycles in 0.1 M NaCl, 50 mM TRIS and HEPES at a scan rate of 100 mV s\(^{-1}\) of mechanically adhered (a) TCNQ and (b) TTF on screen printed planar electrodes.

Figure S4: Screen printed planar electrodes with 5% w/w TCNQ added to the carbon ink working electrode coated with Nafion in 0.1 M NaCl, 50 mM TRIS and HEPES at a scan rate of 100 mV s\(^{-1}\).

Figure S5. Cyclic voltammetry of a dielectric ink supported thin film VISE with 20 mM Na ionophore VI in 100 mM NaCl at a scan rate of 100 mV s\(^{-1}\) (a) varying amount of dielectric ink (b) varying volume of thin film.
Figure S6. Cyclic voltammetry of a dielectric ink supported thin film in 100 mM NaCl at a scan rate of 100 mV s\(^{-1}\) without ionophore. The numbers 1 and 2 refer to the first and second cycle of the potential respectively.

Figure S7: Voltammetry in 0.1 M NaCl at a scan rate of 100 mV s\(^{-1}\) on an EPG electrode of mechanically adhered (a) TTF (0.5 mM 1,4-benzoquinone, 3\(^{rd}\) potential cycle) and (b) TCNQ (0.1 M TRIS pH9 and 5 mM 1,1\(^{\prime}\)-ferrocenedicarboxylic acid, 3\(^{rd}\) potential cycle). Mechanically adhered TCNQ coated with Nafion with (c) 1 mM 1,1\(^{\prime}\)-ferrocenedicarboxylic acid, 1 M NaCl, 50mM TRIS and HEPES, 12\(^{th}\) potential cycle on an EPG electrode at a scan rate of 200 mV s\(^{-1}\) and (d) mechanically adhered 1,1\(^{\prime}\)-ferrocenedicarboxylic acid in 0.1 M NaCl, 50mM TRIS and HEPES, 1\(^{st}\) potential cycle on a screen printed electrode at a scan rate of 100 mV s\(^{-1}\).
Figure S8. Calibration of a thin film VISE with 10 mM Na ionophore VI in 1 M NaCl at a scan rate of 100 mV s\(^{-1}\) versus Ru(NH\(_3\))\(_6\)Cl\(_3\).

Figure S9: (a) Cyclic voltammetry at an EPG electrode of mechanically adhered TCNQ coated with Nafion at a scan rate of 100 mV s\(^{-1}\), 10\(^{th}\) potential cycle in seawater. (b) 6\(^{th}\) potential cycle of mechanically adhered TTF on an EPG electrode in seawater at a scan rate of 100 mV s\(^{-1}\).

Figure S10. Cyclic voltammetry of a thin film VISE with 20mM Ca ionophore II in plasma varying (a) scan rate of 100 mV s\(^{-1}\) with a 1 µL thin film (b) thin film thickness at a scan rate of 100 mV s\(^{-1}\).
Figure S11. Sensitivity of a 0.2 μL thin film VISE at a scan rate of 100 mV s⁻¹ varying NaCl concentration in pure electrolyte (blue) or high ionic strength calibrant solutions (orange) with (a) 20 mM K ionophore III, (b) 20 mM Ca ionophore II or (c) 20 mM Na ionophore VI.