Supporting Information

Condensed phase membrane introduction mass spectrometry with *in situ* liquid reagent chemical ionization in a liquid electron ionization source (CP-MIMS-LEI/CI)

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Table S1: Analyte physicochemical properties

<table>
<thead>
<tr>
<th>Phthalate</th>
<th>Molar mass (g/mol)</th>
<th>Water solubility (mg/L)</th>
<th>Vapor pressure (mmHg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bis(2-ethylhexyl)</td>
<td>390.57</td>
<td>0.27</td>
<td>0.000000142</td>
</tr>
<tr>
<td>Diethyl</td>
<td>222.24</td>
<td>1080</td>
<td>0.0021</td>
</tr>
<tr>
<td>Dibutyl</td>
<td>278.35</td>
<td>11.2</td>
<td>0.0000201</td>
</tr>
</tbody>
</table>

Table S2: Proton affinity data for that of the neutral molecule

<table>
<thead>
<tr>
<th>Proton affinity (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetonitrile</td>
</tr>
<tr>
<td>Acetaldehyde</td>
</tr>
<tr>
<td>Ethyl Ether</td>
</tr>
<tr>
<td>Formaldehyde</td>
</tr>
<tr>
<td>Methyl Benzoate</td>
</tr>
</tbody>
</table>

Figure S1: Experimental schematic for condensed phase membrane introduction mass spectrometry coupled to liquid electron ionization with in situ liquid reagent chemical ionization (CP-MIMS-LEI/CI).
Figure S2: Triplicate measurements of 9 mg/L DEHP from 2-propanol by CP-MIMS-LEI/CI using ‘stopped-flow’ mode.

Figure S3: Fragmentation and chemical ionization of ethyl ether
Figure S4: Full scan mass spectra of 70:30 acetonitrile:ethyl ether v/v with LEI/CI – quadrupole mass spectrometry. List of major peaks with proposed molecular formulae: 1) m/z 41 [CH$_3$CN]+; 2) m/z 42 [CH$_3$CN-H]+; 3) m/z 54 [C$_3$H$_7$N]+; 4) m/z 59 [(CH$_2$O)(C$_2$H$_5$)]+; 5) m/z 75 [(C$_2$H$_5$)$_2$O-H]+; 6) m/z 116 [(C$_2$H$_5$)$_2$O(CH$_3$CN)-H]+; 7) m/z 149 [((C$_2$H$_5$)$_2$O)$_2$-H]+.

Figure S5: Bis(2-ethylhexyl) phthalate (DEHP) calibration in 2-propanol (0.5, 9, 25, 35 mg/L) using 5 minute ‘stopped-flow’ analyses. Error bars represent the standard deviations of triplicate measurements.

References