Ion-selective electrodes: challenges and opportunities for on-site/on-line measurements

Johan Bobacka
Åbo Akademi University
Process Chemistry Centre
Laboratory of Analytical Chemistry
Turku/Åbo, Finland

e-mail: johan.bobacka@abo.fi

Ion-selective electrodes (ISEs)

- ISEs for almost 100 analytes (Na⁺, K⁺, Cl⁻, Ca²⁺, pH, ...)
- ISEs respond to ion activity
- ISEs have a wide linear range (E vs. log a_i)
- Compact, portable, low-cost instruments
- Low power consumption

Reviews:
**Applications of ISEs**

- **environmental analysis**
- **clinical analysis**
- **process analysis**
- **special applications**

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**Every application has its own requirements!**

- **In clinical diagnostics**, ISEs are used all over the world for the determination of pH, Na\(^+\), K\(^+\), Ca\(^{2+}\), Mg\(^{2+}\) and Cl\(^-\) at well-defined concentrations in body fluids.

- **In environmental monitoring**, extremely low concentrations are important (e.g. Pb, Cd, Hg).

- **In process analysis**, each industrial process has its own requirements in terms of species to be monitored and the concentration range of interest.

- **In some special applications**, the ISEs must stand high and low temperatures.
On-line process analysis

ION-SELECTIVE ELECTRODE

Potentiometry

\[ E = E^a + \frac{2.303 \times RT}{nF} \log a_i \]

Ag/AgCl

Ag + Cl^- = AgCl + e^-  

K^+ - selective electrode

Sample solution

Reference electrode

Ag/AgCl

Ag + Cl^- = AgCl + e^-  

Liquid junction

KCl (3 M)

ion-selective membrane

3
Different types of ion-selective membranes

- Glass membranes
  - pH electrode

- Solid-state membranes based on inorganic salt crystals
  - Fluoride electrode based on LaF$_3$
  - Pb$^{2+}$ electrode based on PbS/Ag$_2$S

- Polymer membranes containing ionophores
  - Polymer matrix: PVC, polyacrylates or silicone rubber
  - Plasticizer
  - Ionophore
  - Lipohilic salt

Typical composition of a K$^+$-selective membrane:

- Poly(vinyl chloride) (PVC): 33%
- Valinomycin: 1%
- Potassium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (KTFPB): 0.5%
- Bis(2-ethylhexyl)sebacate (DOS): 65%
Opportunities for ISEs

- Wireless sensor networks
  - Remote analytical monitoring of e.g.
    - Pollutants in the environment
    - Personal health
- Handheld battery operated instruments and wearable sensors, disposable sensors
- Advantages:
  - Fast, low-cost on-site measurements
  - Ion activity is measured


Recent progress in the field of ISEs

1. Low detection limit
2. Solid-contact ISEs
3. Solid-state reference electrodes
4. New membrane materials
5. Advanced theoretical models

Solid-state ion sensors & solid-state reference electrode

1. Low detection limit

Tuned galvanostatic polarization of solid-state lead-selective electrodes for lowering of the detection limit

Grzegorz Liska1,2, Tomasz Sokolski1, Johan Bobacka3, Lena Harju4, Konstantin Mikheelson1, Andrzej Lewenstein1,5,6
1 Laboratory of Analytical Chemistry and Center for Process Analytical Chemistry and Sensor Technology, Poznan, Poland; 2 Chemical Research Institute, Adam Mickiewicz University, Poznan, Poland; 3 Department of Chemical and Environmental Sciences, Aalto University, Espoo, Finland; 4 Department of Chemical and Biological Engineering, Aalto University, Espoo, Finland; 5 Center for Materials and Nanoscience, Aalto University, Espoo, Finland; 6 Institute of Science and Technology, Faculty of Materials Science and Chemistry, Miskolc University, Miskolc, Hungary

Lead (Pb\(^{2+}\)): 
\(10^{-9}\) mol/L = 0.2 µg/L = 0.2 ppb

Challenge no. 1

- Standardized storage, conditioning, calibration and measurement protocols for ISEs are extremely important when measuring low concentrations
## 2. Solid-contact ISEs

### Conventional ISE

<table>
<thead>
<tr>
<th>Ag / AgCl</th>
<th>Ag + Cl(^-) = AgCl + e(^-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inner solution</td>
<td>Cl(^-)</td>
</tr>
<tr>
<td>Plasticized PVC</td>
<td>K(^+)</td>
</tr>
<tr>
<td>Solution</td>
<td>K(^+)</td>
</tr>
</tbody>
</table>

### Solid-contact ISE

<table>
<thead>
<tr>
<th>Pt, Au, C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cond. polymer</td>
</tr>
<tr>
<td>Plasticized PVC</td>
</tr>
<tr>
<td>Solution</td>
</tr>
</tbody>
</table>

### Functionalized conducting polymer

<table>
<thead>
<tr>
<th>Pt, Au, C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Funct. cond. polymer</td>
</tr>
<tr>
<td>Solution</td>
</tr>
</tbody>
</table>

### Conducting polymers as ion-to-electron transducers in potentiometric ion sensors

- PANI (1998)
- PPy (1992)
- POT (1994)
- PEDOT (1999)

Stable conducting polymer!

**Ion-to-electron transduction**

- **Ionophore** + $K^+ + A^-$ (Ionophore + $K^+ + A^-$)
- $K^+_{aq}$
- **Carbon**
- Double-layer capacitance

**Redox capacitance**

- PEDOT $+$ e$^- + $K^+$ = PEDOT $+$ $K^+$
- **Carbon**
- **Challenge no. 2**
  - Long-term potential stability

- Influence of light ($h\nu$)
- Influence of O$_2$ and CO$_2$
- Sensor contamination
- Leaching of ionophore etc.

- Electronic conductor
  - Solid-state ion-to-electron transducer
  - Adhesion

- Ion-selective membrane
  - Adhesion
3. Solid-contact reference electrodes

- Conducting polymer coated with a plasticized PVC membrane containing a moderately lipophilic salt


  \[ \text{TBA} \quad \text{TBB} \]
  \(\text{(equitransferent)}\)

- Ionic liquids were also used

Influence of different salts in the sample

Challenge no. 3

- Solid-state reference electrode with reproducible and stable potential
  ± 1 mV change in potential corresponds to ± 4 % change in activity (monovalent ion)
Solid-contact ISEs & Solid-contact RE

Reference electrode

pH-ISEs

Pb$^{2+}$-ISEs
(Detection limit = ca. 2 ppb)


Disposable solid-contact ion-selective electrodes for environmental monitoring of lead with ppb limit-of-detection

Satirina Anastasova†, Aleksandar Radu†, Goony Matzen†, Claudio Zulliani†**, Ulrika Mattinen†, Johan Bobacka†, Dermot Diamond††.

† LAGHT Centro de Ionen Physik, National Centre for Ion Research, School of Chemical Sciences, Dublin City University, Dublin 9, Ireland
** Centro di Chimica dei Materiali e Chimica dei Materiali, University of Rome “La Sapienza”, Italy
†† Centre for Sensors and Sensor Systems, Dublin City University, Dublin 9, Ireland

Upper concentration limit for surface waters = 7.2 µg/L
(European Water Framework Directive)
Challenges & Opportunities

• Contamination/biofouling of the sensor surface from unknown compounds
  – Integration of ISEs with (micro)fluidics for washing, conditioning and calibration of ISEs
  – Disposable ISEs → single use
  – New membrane materials → less fouling

Challenges & Opportunities

• Interference from unknown ions in the sample
  – New membrane materials → better selectivity

• Activity / Concentration
  – Constant ionic strength → concentration
  – Report result as activity
Conclusions

• Solid-contact ISEs for determination of several ions down to ppb-levels of concentration have been demonstrated

• Opportunities exist for fast and low-cost on-site measurements using wireless, wearable and disposable ISEs

• Potential stability of ISEs in long-term continuous use is still a challenge

• “Self-calibrating” sensors with ”self-cleaning” sensor surfaces would be useful

Many thanks to colleagues at the Laboratory of Analytical Chemistry
Thank You!