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

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Ion-selective electrodes (ISEs)

- *ISEs for almost* ***100 analytes*** *(Na^+, K^+, Cl^-, Ca^{2+}, 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*

ISE + Reference electrode

Reviews:

E. Bakker, P. Bühlmann, E. Pretsch, *Chem. Rev.* **97** (1997) 3083.
P. Bühlmann, E. Pretsch, E. Bakker, *Chem. Rev.* **98** (1998) 1593.
J. Bobacka, A. Ivaska, A. Lewenstam, *Chem. Rev.* **108** (2008) 329.

Applications of ISEs

- environmental analys

- clinical analys

- process analys

- special applications

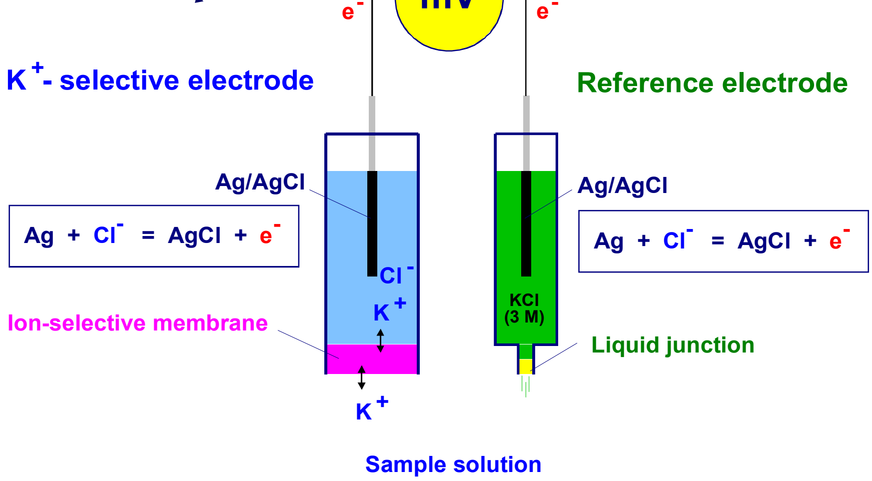
Every application has its own requirements !

- *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

$$E = E^o + \frac{2.303 \times RT}{n_i F} \log a_i$$



Different types of ion-selective membranes

- Glass membranes

- pH electrode

- Solid-state membranes based on inorganic salt crystals

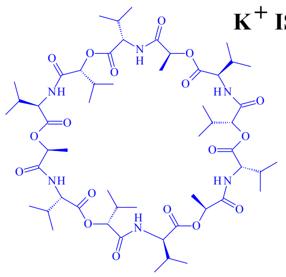
- Fluoride electrode based on LaF_3
- Pb^{2+} electrode based on PbS/Ag_2S

- Polymer membranes containing ionophores

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

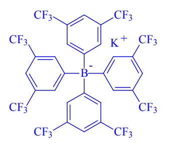
Typical composition of a K^+-selective membrane :

K^+ ISE



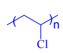
Valinomycin

1 %



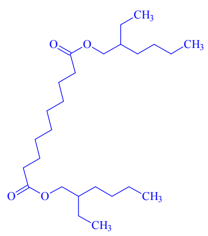
Potassium tetrakis[3,5-bis-(trifluoro-methyl)phenyl]-borate (KTFPB)

0.5 %



Poly(vinyl chloride) (PVC)

33 %



Bis(2-ethylhexyl)sebacate (DOS)

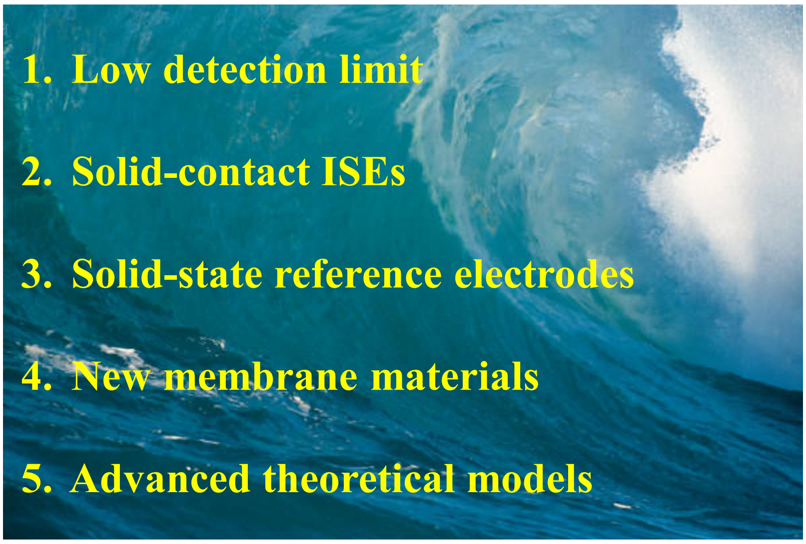
65 %

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

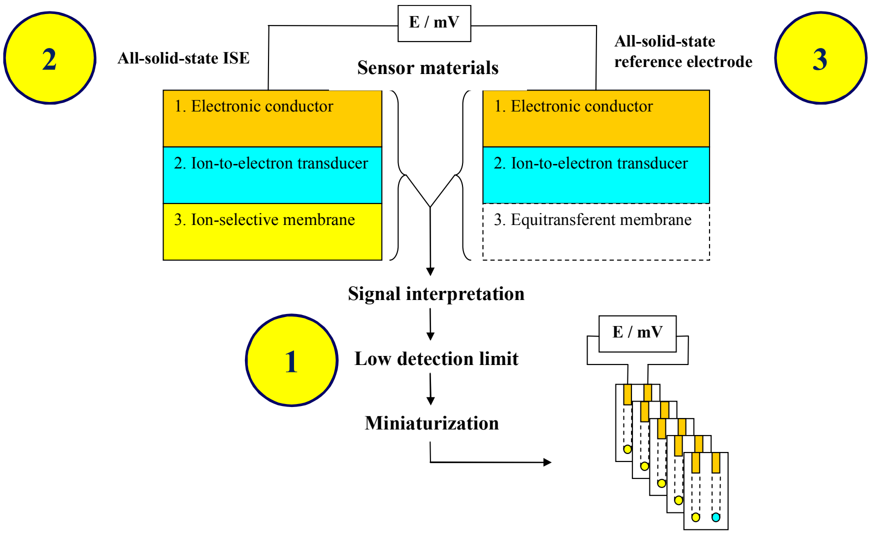
C. Zuliani, D. Diamond, *Electrochim. Acta* 84 (2012) 29.

Recent progress in the field of ISEs



J. Bobacka, A. Ivaska, A. Lewenstam, *Chem. Rev.* 108 (2008) 329.

Solid-state ion sensors & solid-state reference electrode



1. Low detection limit

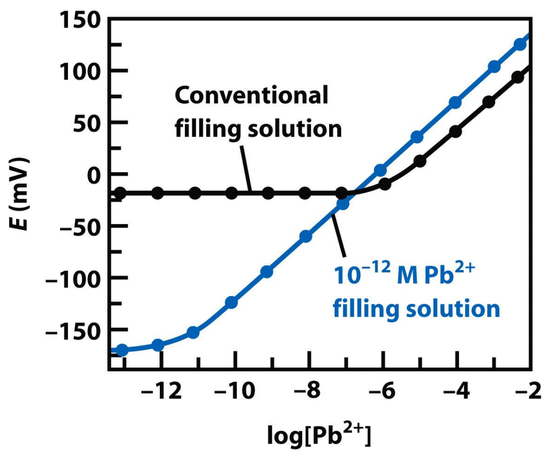


Figure 15-21
Quantitative Chemical Analysis, Seventh Edition

T. Sokalski, A. Ceresa, T. Zwickl, E. Pretsch, *J. Am. Chem. Soc.* 119 (1997) 11347.

Analytica Chimica Acta 707 (2011) 1–6

Contents lists available at SciVerse ScienceDirect

Analytica Chimica Acta

journal homepage: www.elsevier.com/locate/aca

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

Grzegorz Lisak[a,b], Tomasz Sokalski[a], Johan Bobacka[a], Leo Harju[a], Konstantin Mikhelson[c], Andrzej Lewenstam[a,d,*]

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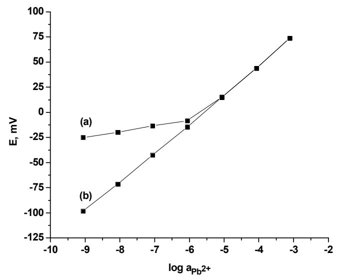
[c] Chemical Faculty, c/o St. Petersburg State University, 26 Universitetskij Pr., 198504 St. Petersburg, Russia
[d] AGH - University of Science and Technology, Faculty of Material Science and Ceramics, Mickiewicza 30, 30-059 Cracow, Poland

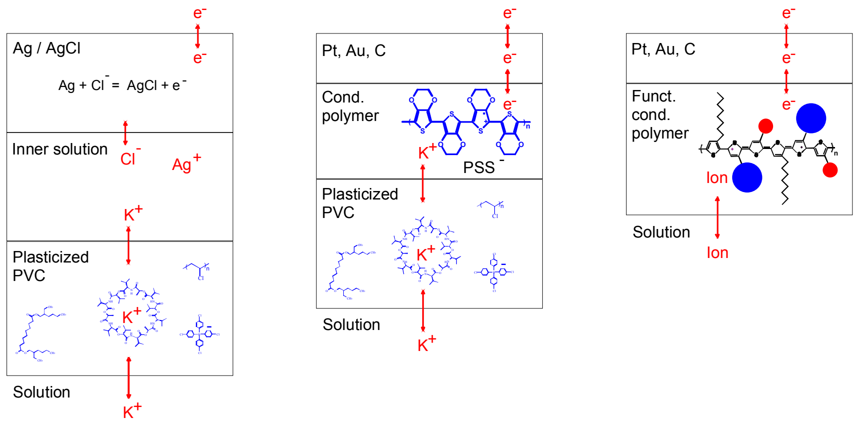


Lead (Pb^{2+}):
10^{-9} mol/L = 0.2 µg/L = 0.2 ppb

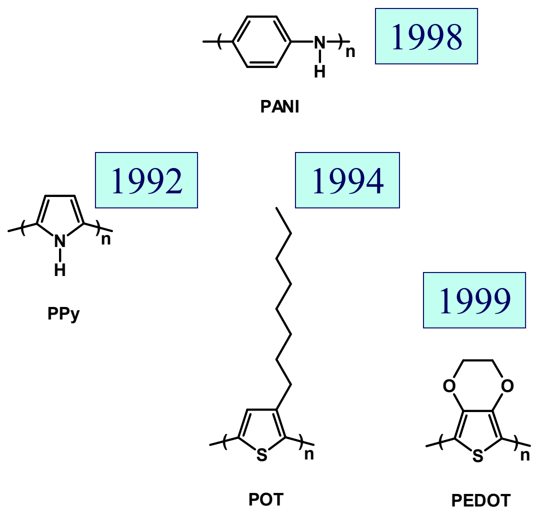
Challenge no. 1

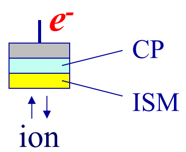
- Standardized storage, conditioning, calibration and measurement protocols for ISEs are extremely important when measuring low concentrations

2. Solid-contact ISEs



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

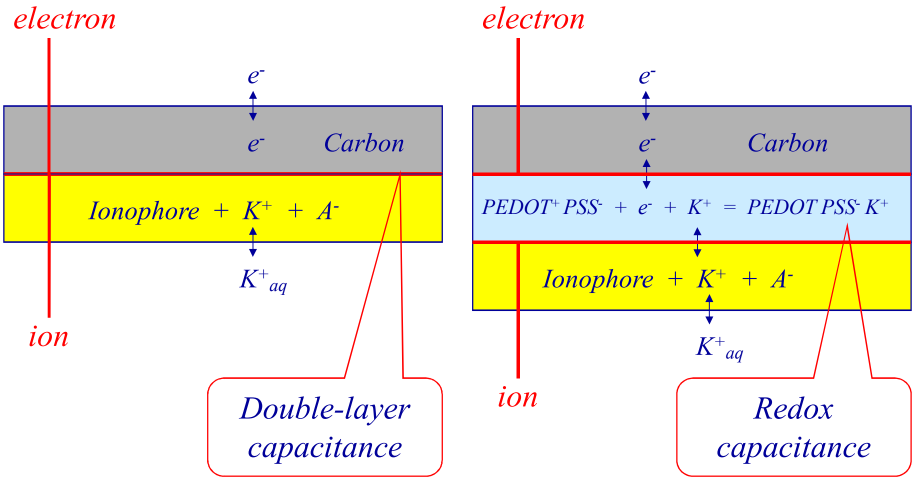




Stable conducting polymer!

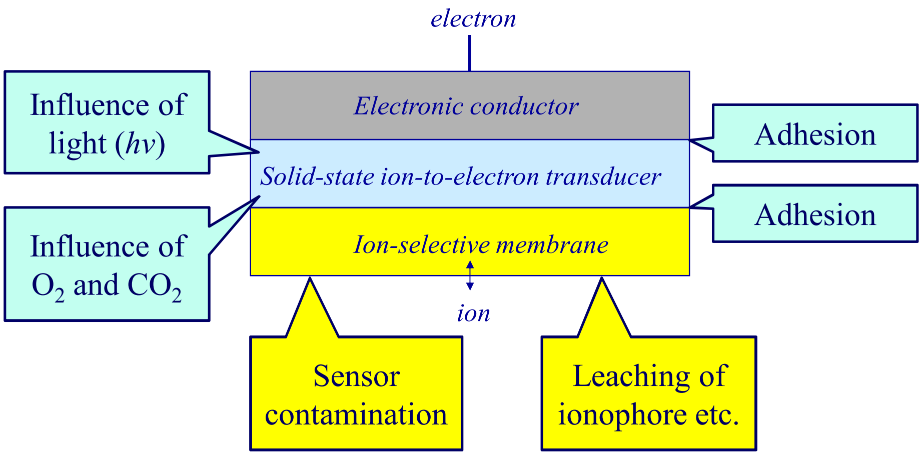
G. Heywang, F. Jonas, *Adv. Mater.* **1992**, *4*, 116 .

Ion-to-electron transduction



Challenge no. 2

- Long-term potential stability



THE JOURNAL OF PHYSICAL CHEMISTRY C

Article

pubs.acs.org/JPCC

Reduced Graphene Oxide Films as Solid Transducers in Potentiometric All-Solid-State Ion-Selective Electrodes

Rafael Hernández,[†] Jordi Riu,[*,†] Johan Bobacka,[‡] Cristina Vallés,[§] Pablo Jiménez,[§] Ana M. Benito,[§] Wolfgang K. Maser,[§] and F. Xavier Rius[†]

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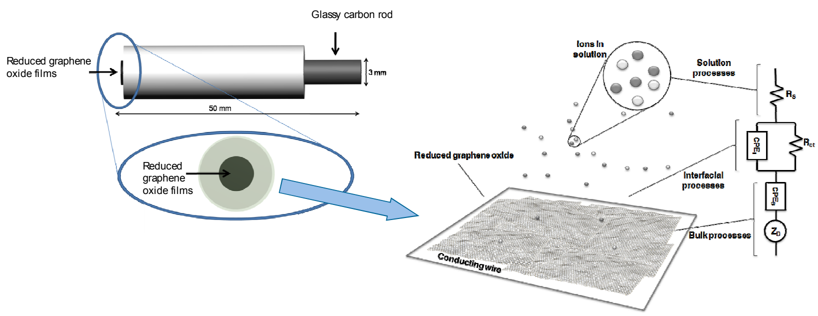
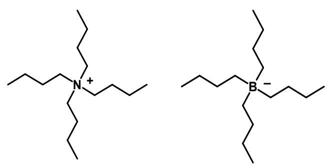


J. Phys. Chem. C, **116** (2012) 22570–22578.

3. Solid-contact reference electrodes

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

  U. Mattinen, J. Bobacka, A. Lewenstam, *Electroanalysis* 21 (2009) 1955.



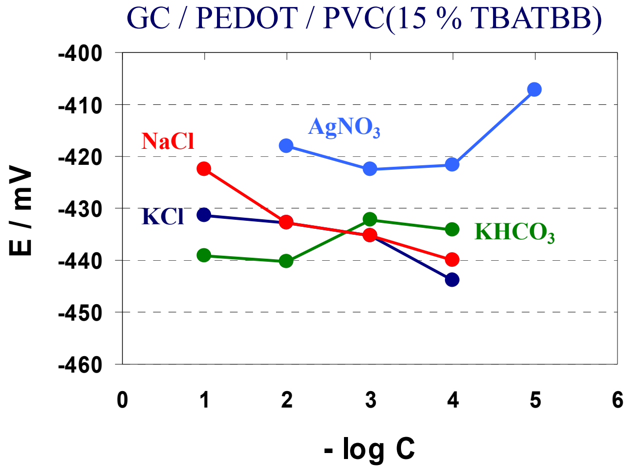
TBA ***TBB***

(equitransferent)

- Ionic liquids were also used

  D. Cicmil, S. Anastasova, A. Kavanagh, D. Diamond, U. Mattinen, J. Bobacka, A. Lewenstam, A. Radu, *Electroanalysis* 23 (2011) 1881.

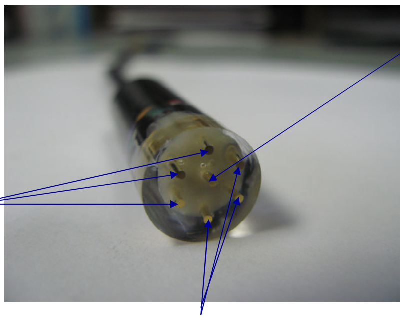
Influence of different salts in the sample



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



pH-ISEs

Reference electrode

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

S. Anastasova-Ivanova, U. Mattinen, A. Radu, J. Bobacka, A. Lewenstam, J. Migdalski, M. Danielewski, D. Diamond, *Sens. Actuators B*, 146 (2010) 199.

Electrochimica Acta 73 (2012) 93–97

Contents lists available at SciVerse ScienceDirect

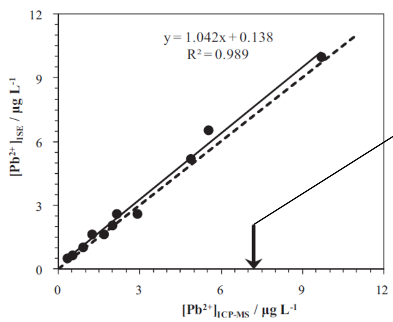
Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

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

Salzitsa Anastasova[a], Aleksandar Radu[a], Giusy Matzeu[a], Claudio Zuliani[a,*], Ulriika Mattinen[b], Johan Bobacka[b], Dermot Diamond[a,*]

[a] *CLARITY Centre for Sensor Web Technologies, National Centre for Sensor Research, School of Chemical Sciences, Dublin City University, Dublin 9, Ireland*
[b] *Åbo Akademi University, Process Chemistry Centre, Laboratory of Analytical Chemistry, and Centre for Process Analytical Chemistry and Sensor Technology 'ProSens', Biskopsgatan 8, FI-20500 Åbo/Turku, Finland*



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

Åbo Akademi University

Many thanks to colleagues at the Laboratory of Analytical Chemistry

ANALYTISK KEMI

Thank You!