

Mobile water analysis with potentiometric sensors

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16. - 17. 10. 2014

Lichtenwalde (Sachsen)

Potentiometry with ion-selective electrodes

Principle

- measurements of potentials at interface:
ion-selective membrane / solution with analyte ion
- ion exchange at interface: **membrane (ionophor) / solution (ion)**
- membrane composition with **ion-complexing compound (ionophor)**
determines selectivity towards measuring ion

$$E = E_0 + \frac{R T}{n F} \ln a$$

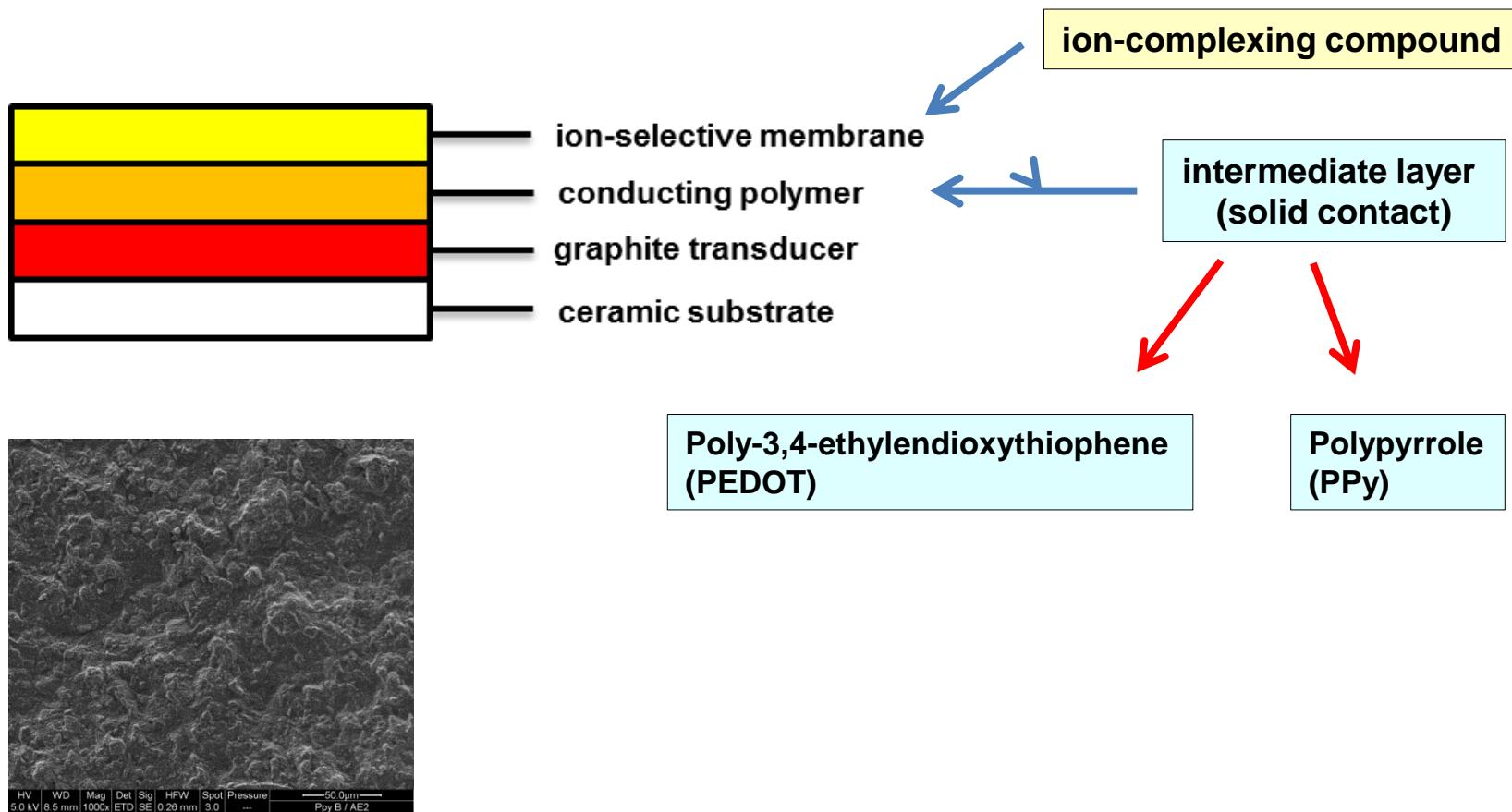
Aim and motivation

- development of new planar screen-printed *All-Solid-State*-ion-selective electrodes and reference electrodes for mobile environmental analysis application fields:
 - heavy metal analysis
 - water hardness (Ca^{2+} , Mg^{2+})
 - NH_4^+ , NO_3^-
- great need for analyzers/sensors for field detection of pollutants

Requirements for sensors in field analysis

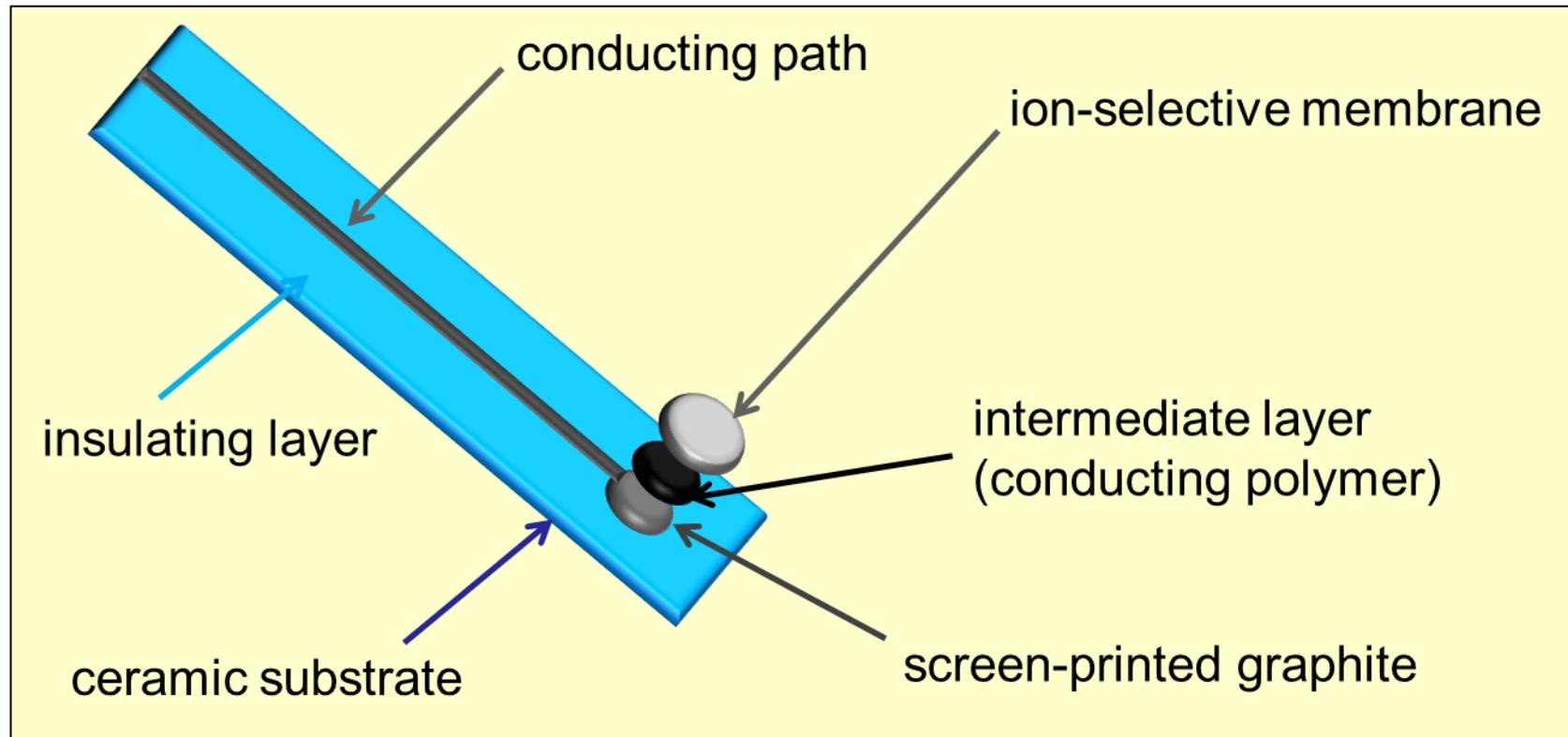
- simple and robust electrode construction
- easy to handle (no liquid components)
- reproducible results

Schematic layer structure of a screen-printed *All-Solid-State* ion-selective electrode

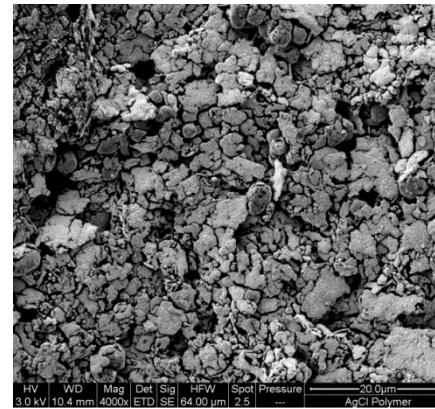
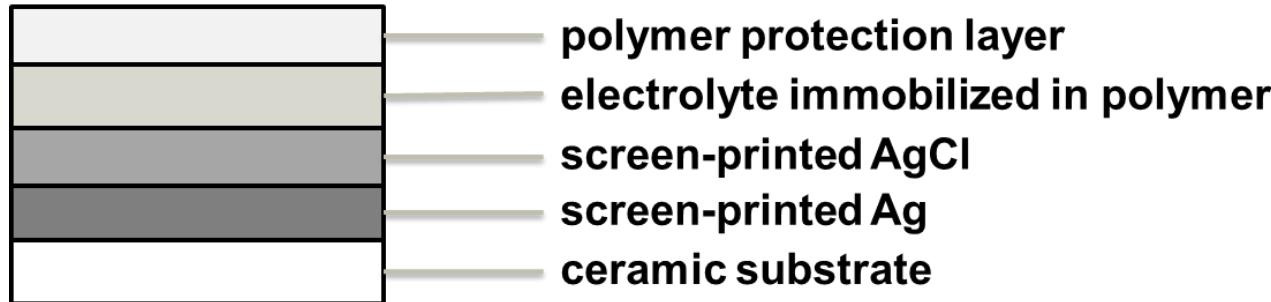


SEM of polypyrrole-modified screen-printed graphite electrode

Screen-printed *All-Solid-State* ion-selective electrode

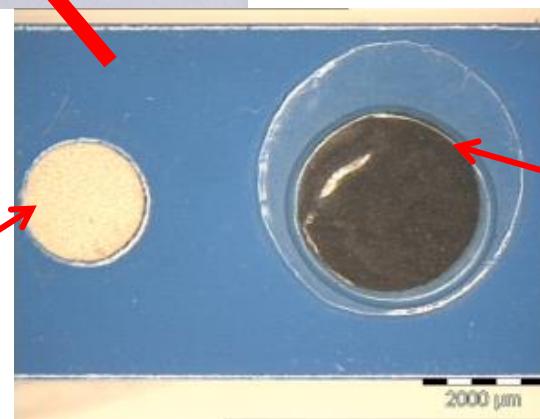
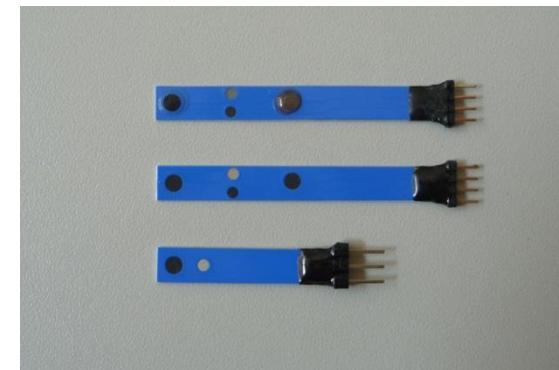
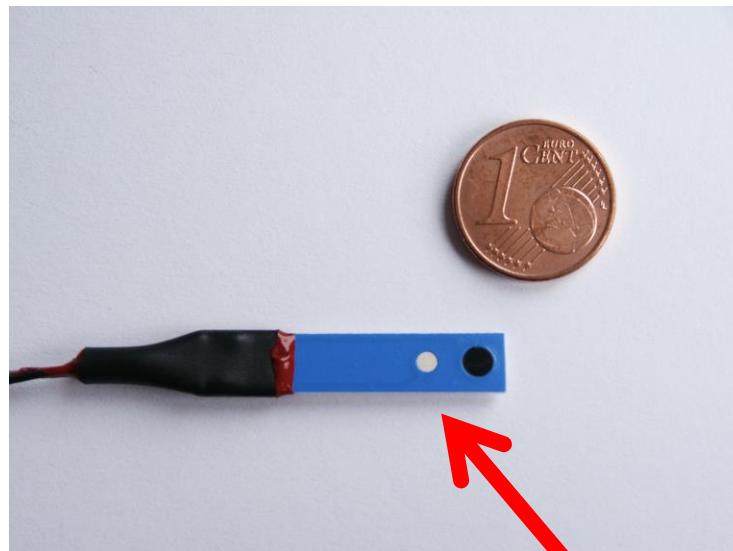


Schematic layer structure of a screen-printed *All-Solid-State* reference electrode



SEM of screen-printed AgCl-layer

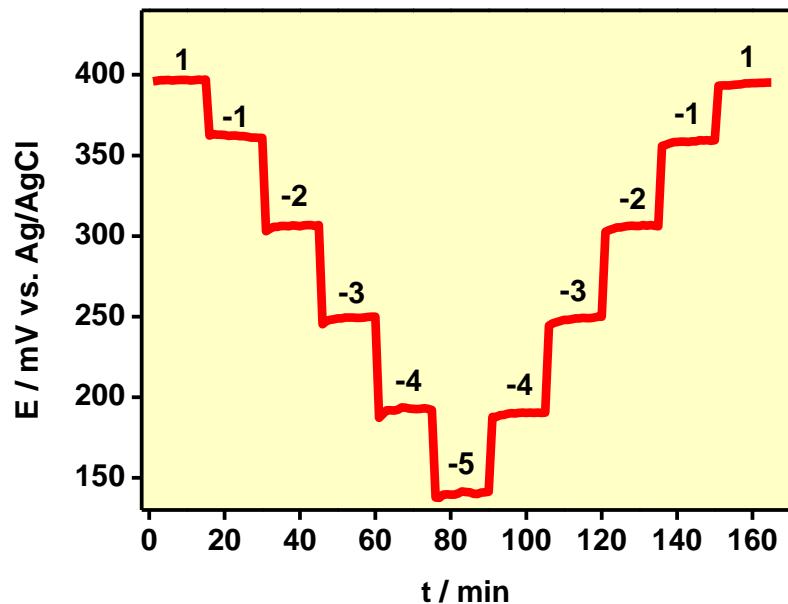
Planar screen-printed *All-Solid-State* potentiometric sensors



reference electrode

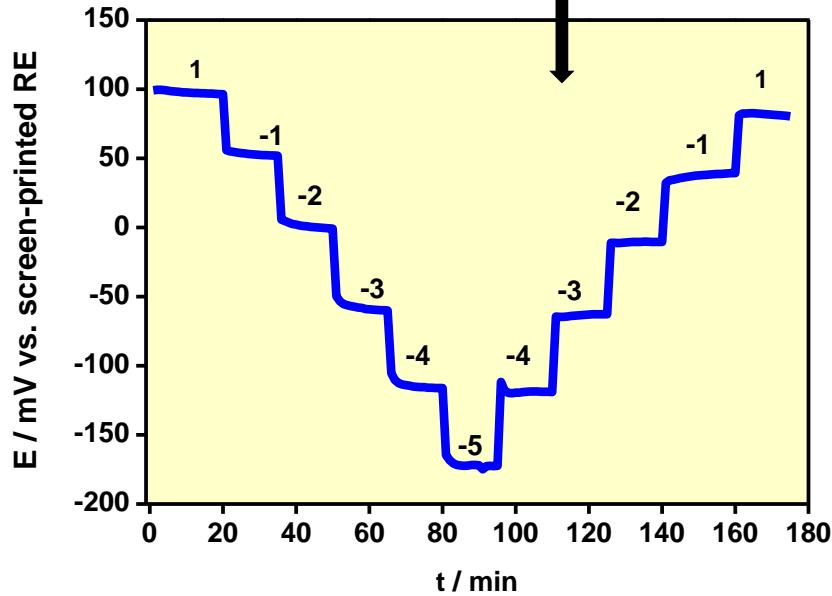
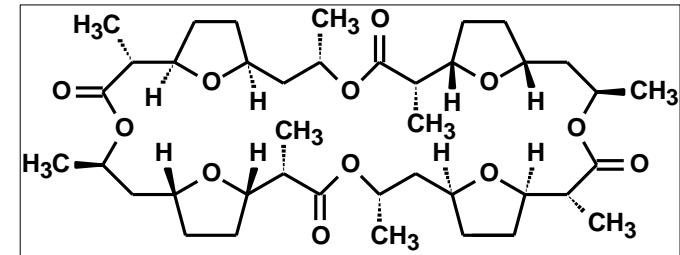
ion-selective electrode

Potentiometric response behavior of PPy-modified screen-printed *All-Solid-State* NH_4^+ -selective electrodes

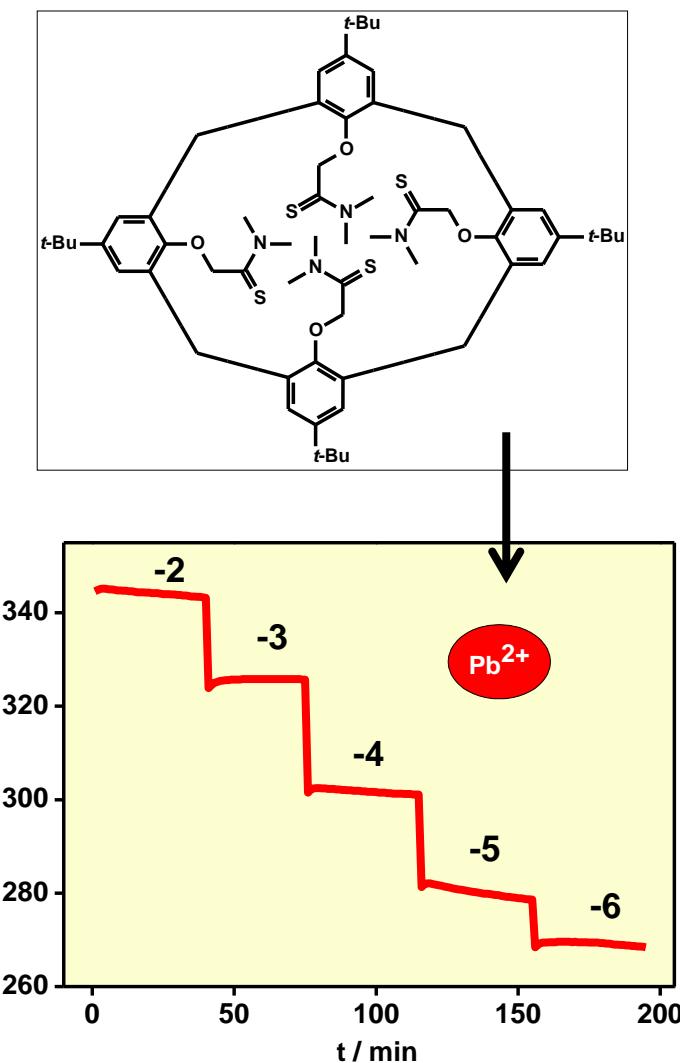
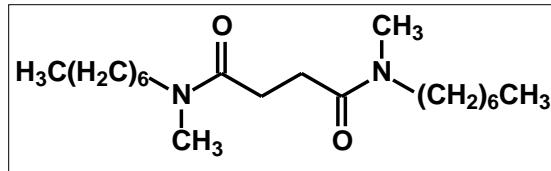
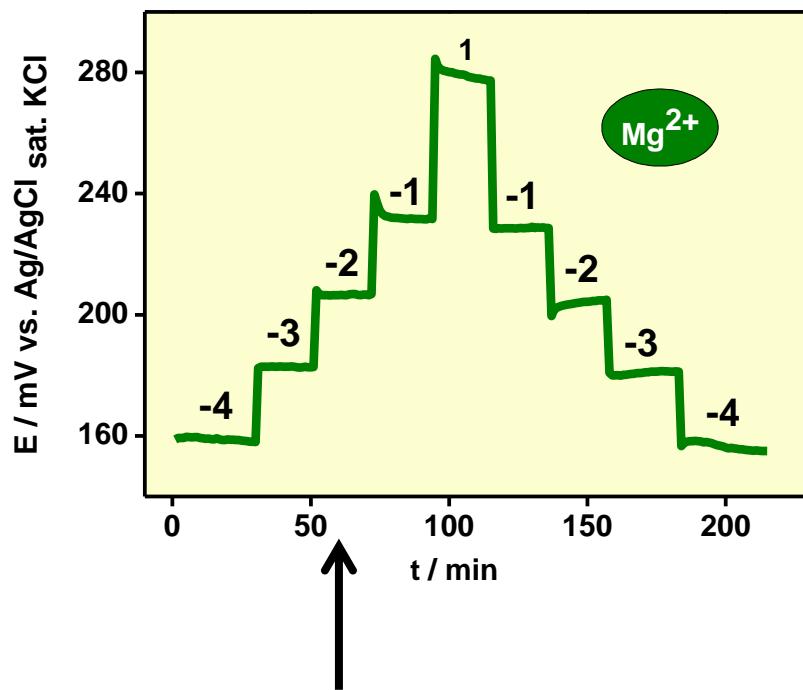


slope: > 56 mV/decade

detection limit: <10⁻⁶ mol/L

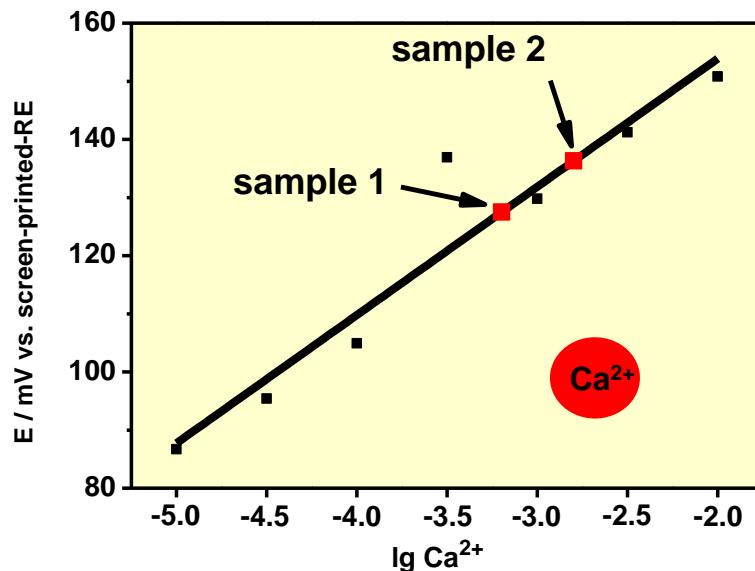


Potentiometric response behavior of screen-printed *All-Solid-State* ion-selective electrodes



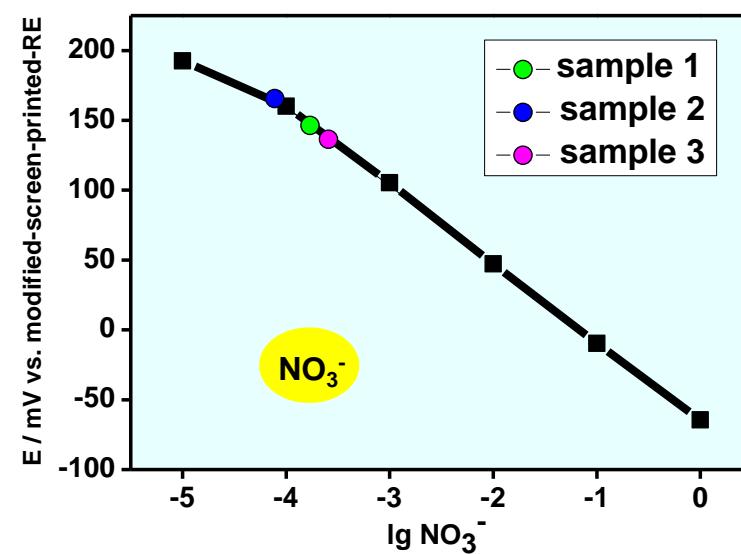
Applications in environmental samples

Calibration curves of PPy-modified screen-printed graphite-based ion-selective electrodes



Ca^{2+} -concentration

sample 1: tap water Freiberg (Sachsen) 28 mg/L
 sample 2: tap water Minkwitz (Sachsen) 66 mg/L

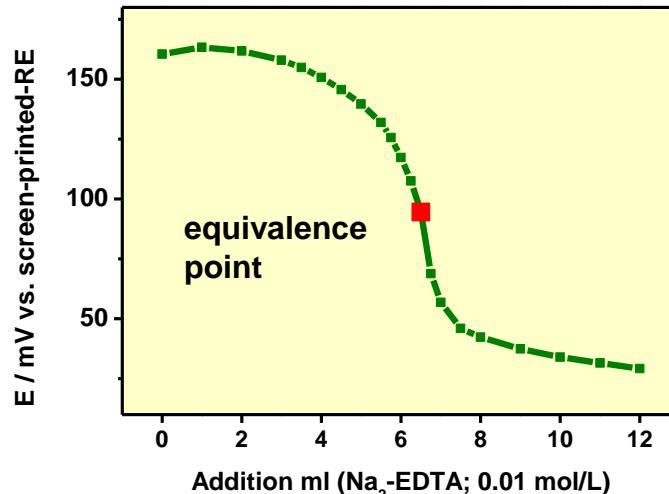


NO_3^- -concentration

sample 1: tap water Freiberg (Sachsen) 11 mg/L
 sample 2: tap water Hammer (Bayern) 4 mg/L
 sample 3: tap water Chemnitz (Sachsen) 16 mg/L

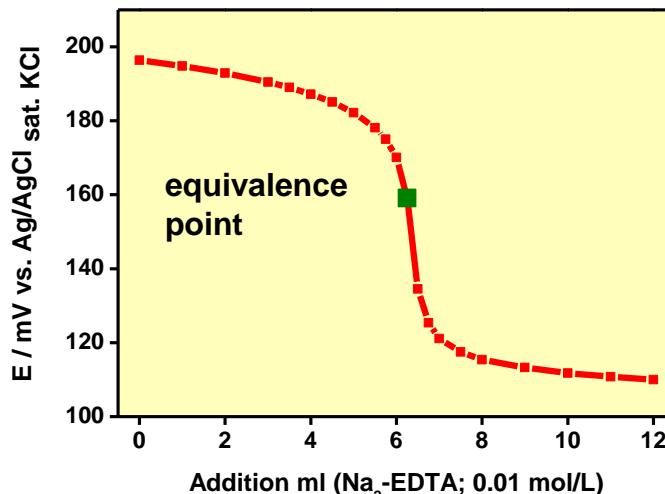
Applications in water analysis - Potentiometric titration

Indicator electrode: new PPy-modified Ca^{2+} -selective *All-Solid-State* electrode



Ca^{2+} : 52 mg/L (1.30 mmol/L)

sample: tap water
Enkenbach (Germany)

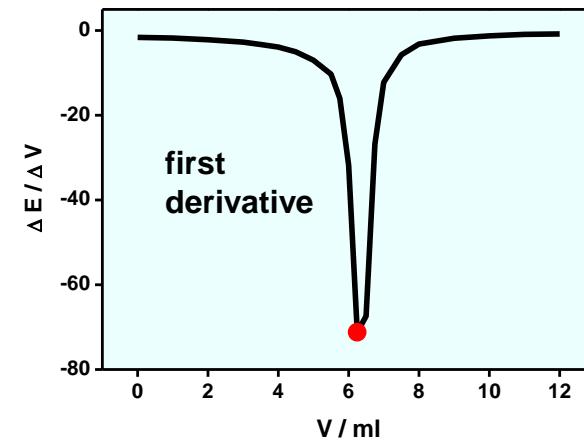
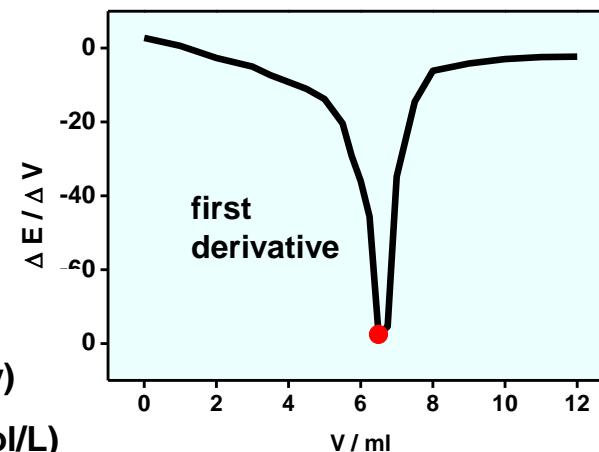


water hardness:

middle

reference methods:

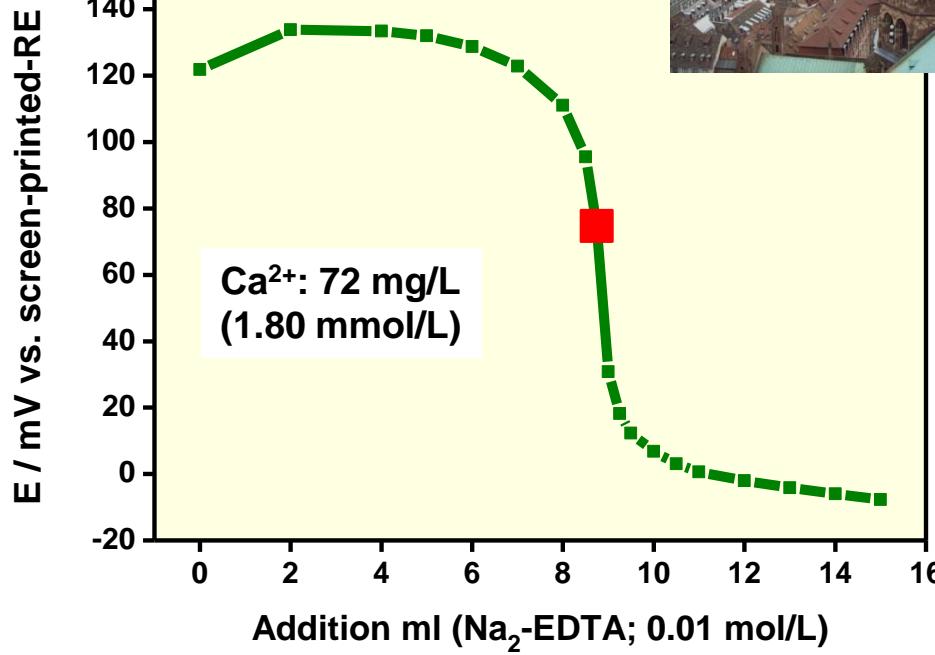
- ion chromatography
- colorimetric titration



Applications in water analysis - Potentiometric titration

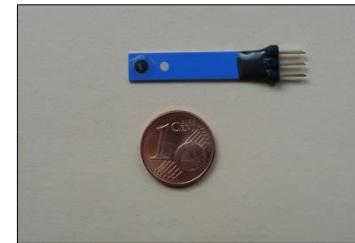
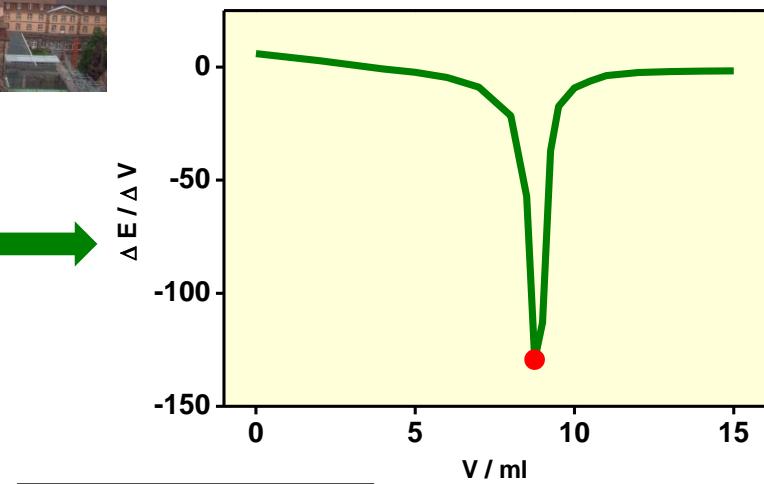
Indicator electrode: new PPy-modified Ca^{2+} -selective *All-Solid-State* electrode

tap water Strasbourg (France)



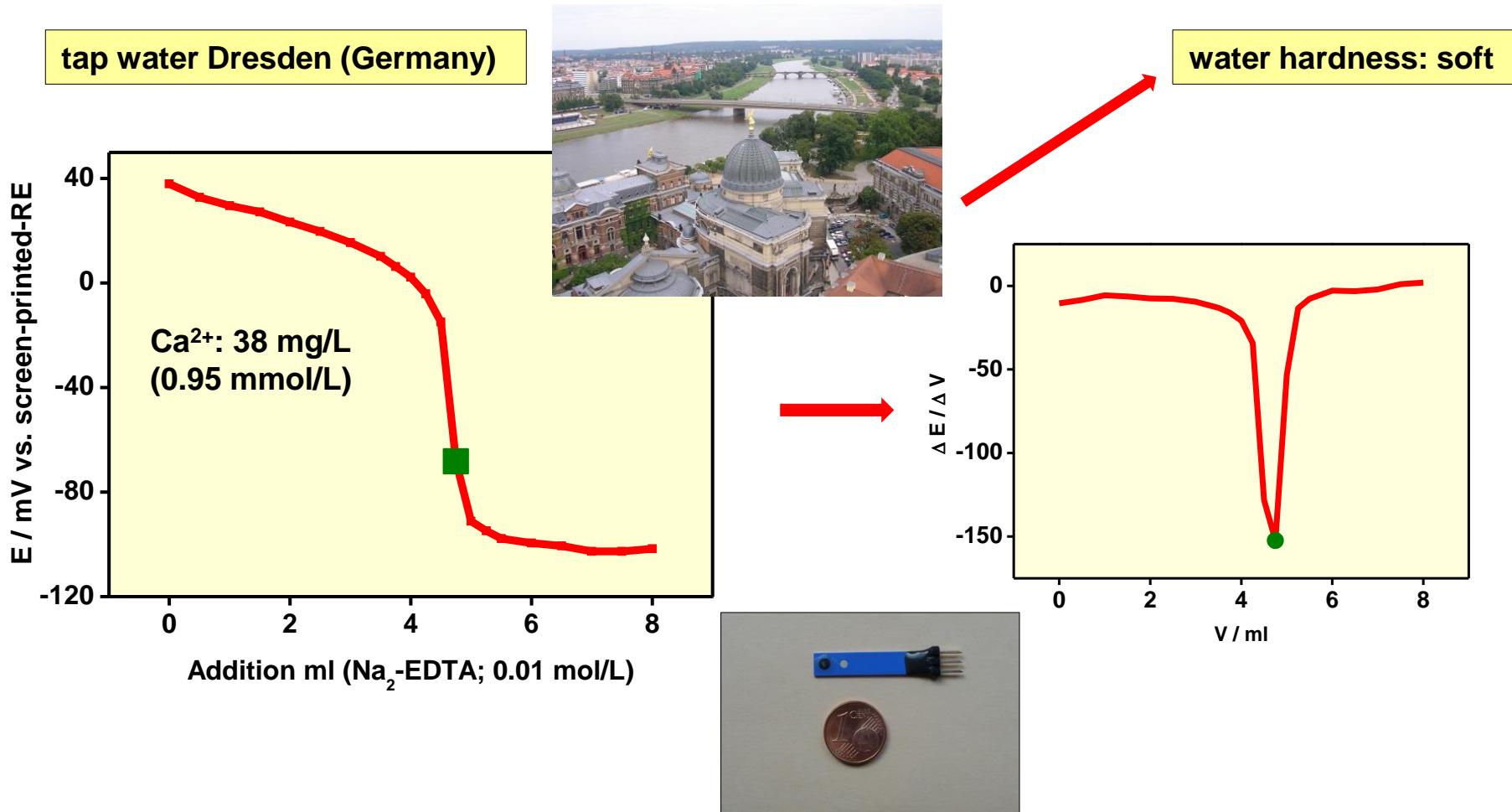
water hardness: middle

$\Delta E / \Delta V$



Applications in water analysis - Potentiometric titration

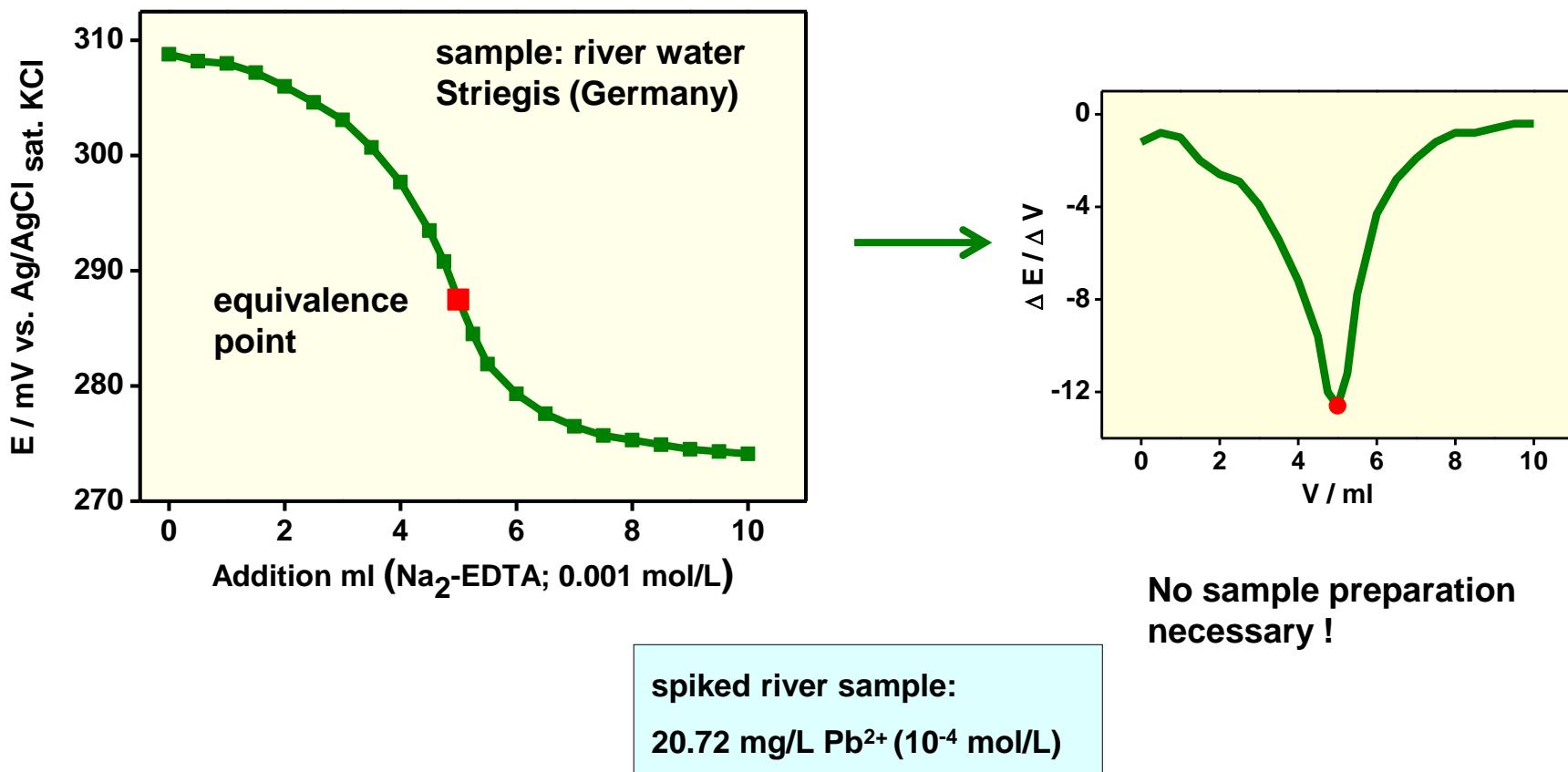
Indicator electrode: new PPy-modified Ca^{2+} -selective *All-Solid-State* electrode



J. Schwarz, K. Trommer, M. Mertig, Proceedings
11. Dresdner Sensorsymposium 373-375, DOI 105162 (2013)

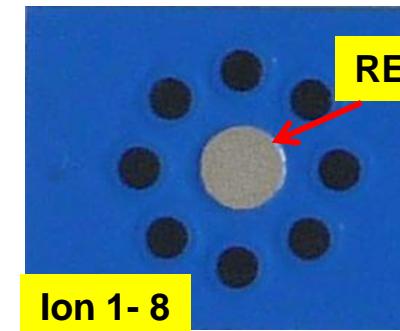
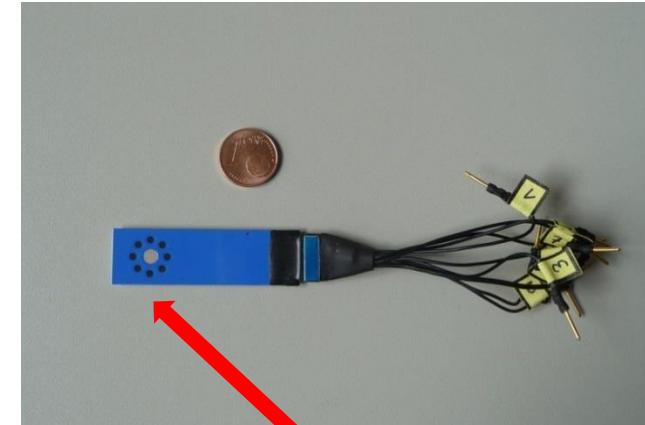
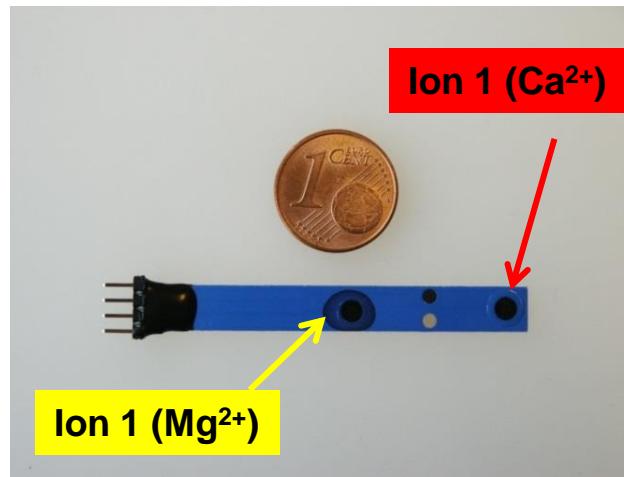
Applications - Potentiometric titration

Indicator electrode: new PPy-modified screen-printed Pb^{2+} -selective electrode



New development - Potentiometric multiparameter sensors

water hardness sensor



Aims

- simultaneous potentiometric detection of different ions
- use of highly ion-selective compounds
- integration of ion-selective electrodes and reference electrodes on common substrate surfaces

Summary

New solid-contacted planar *All-Solid-State* ion-selective electrodes based on functional layers for determination of different ions

- suitable for *on-line* determination and *in-situ* applications
- low cost production, fast response, simplicity in operation
- reproducible layer conformation
- conducting polymer as internal solid-contact (replacing liquid electrolyte)
- determination of electrode parameter (slope, selectivity coefficents, detection limit, electrode life time, drift, response behavior)

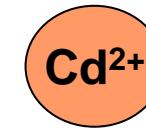
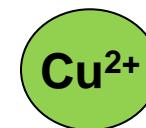
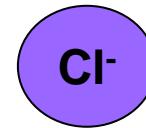
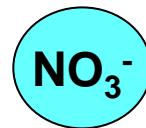
New planar *All-Solid-State* screen-printed reference electrodes

- reproducible layer conformation
- no liquid components
- stable potentials

Summary

Applications in environmental samples

- indicator electrodes in potentiometric titrations (complexometry)
- direct potentiometric ion analysis
- no or few sample preparation steps necessary



Future prospects

- **use of new electrode materials**

- **use of new ion-complexing compounds with high ion-selectivities
(calixarenes, cyclodextrines)**

- **development of an electrochemical multiparameter (ion) analyzer**
 - **integration of ion-selective electrodes and reference electrodes**
 - **use of different electrochemical detection methods**

Thank you !

