Integration of miniature, ultrasensitive chemical sensors in microfluidic devices

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OUTLINE

- Background
- Development of solid-contact ion-selective electrodes
- Development of solid-contact reference electrodes
- Development of platforms for housing of SC-RE and SC-ISEs
- Field experiments

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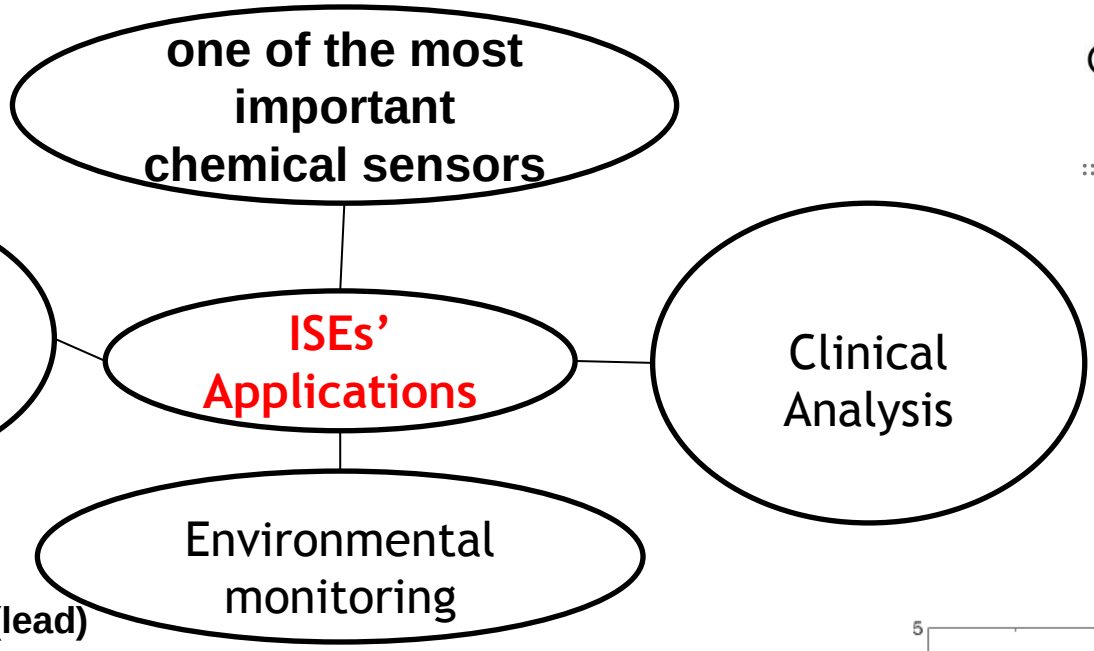
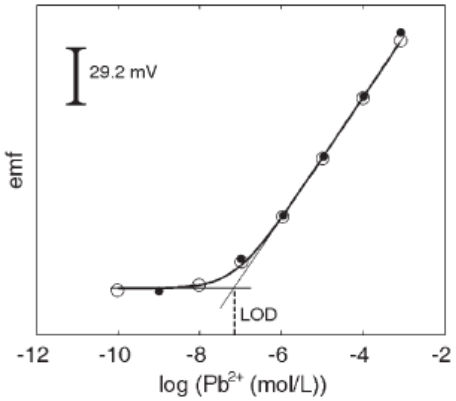
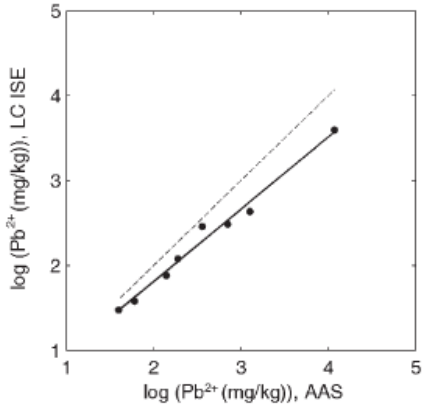


- **quality of drinking water**

pollution by toxic heavy metal (lead)





Evaluation of Liquid- and Solid-Contact, Pb^{2+}-Selective Polymer-Membrane Electrodes for Soil Analysis

Christina M. McGraw,[a] Tanja Radu,[b] Aleksandar Radu,[b] Dermot Diamond[b]

Electroanalysis 20, 2008, No. 3, 340 – 346

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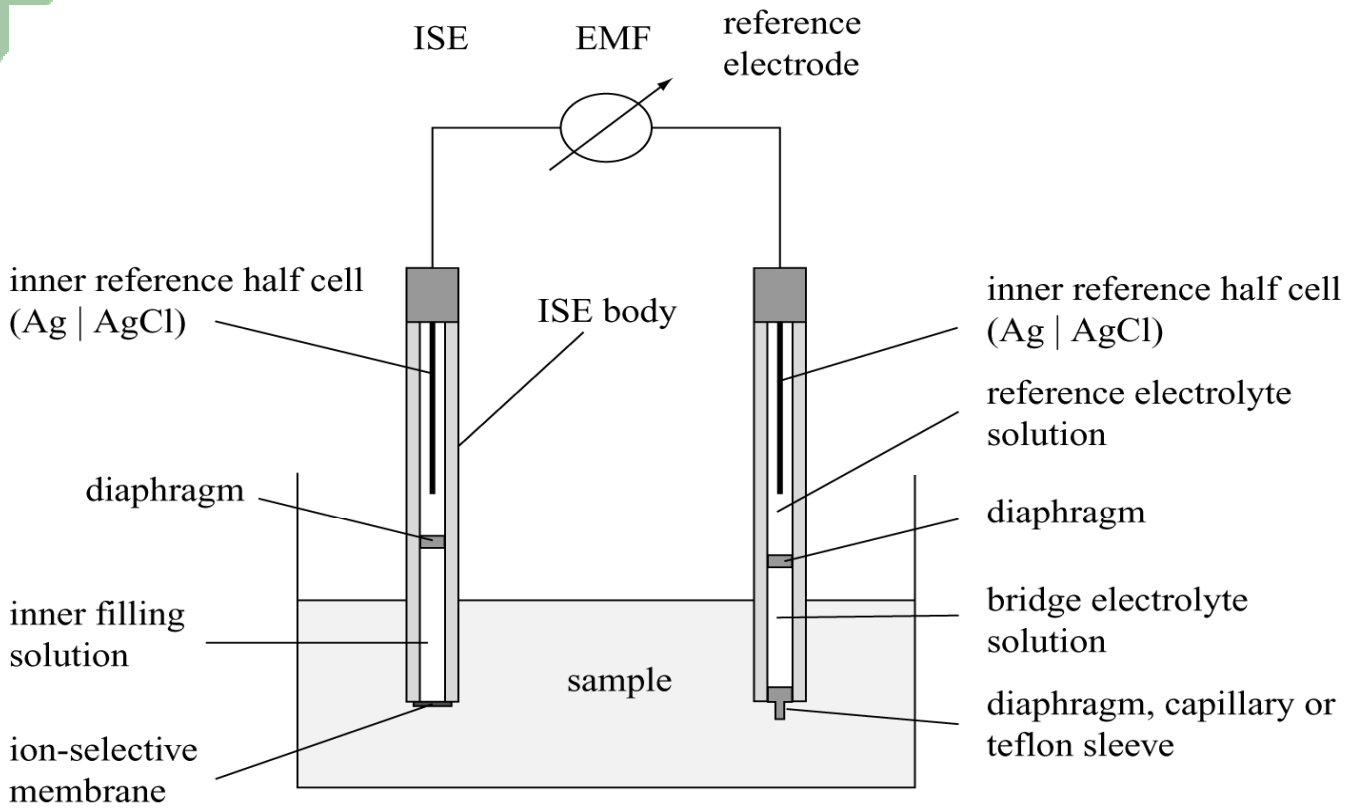
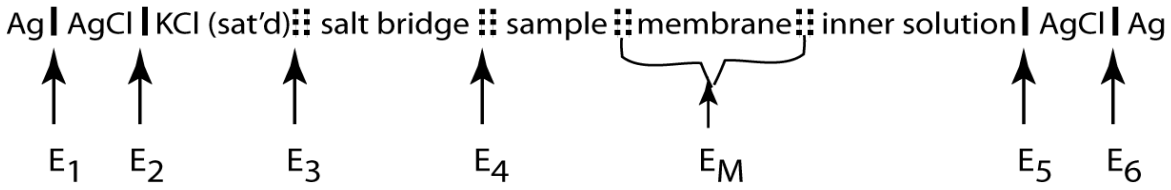
Chemical sensors with potentiometric detection – Ion Selective Electrodes (ISE)





$$E_{cell} = E_1 + E_2 + E_3 + E_4 + E_5 + E_M + E_J = E_{const} + E_J + E_{PB1} + E_{PB2}$$

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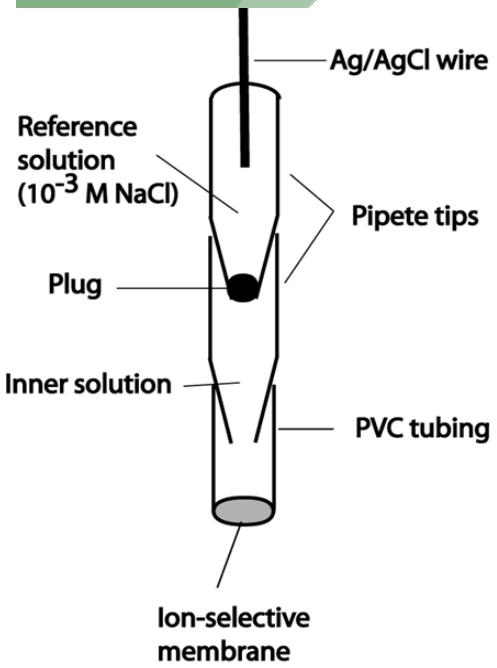
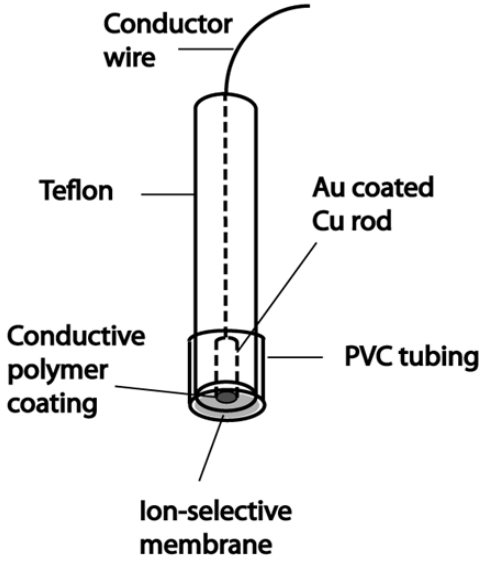
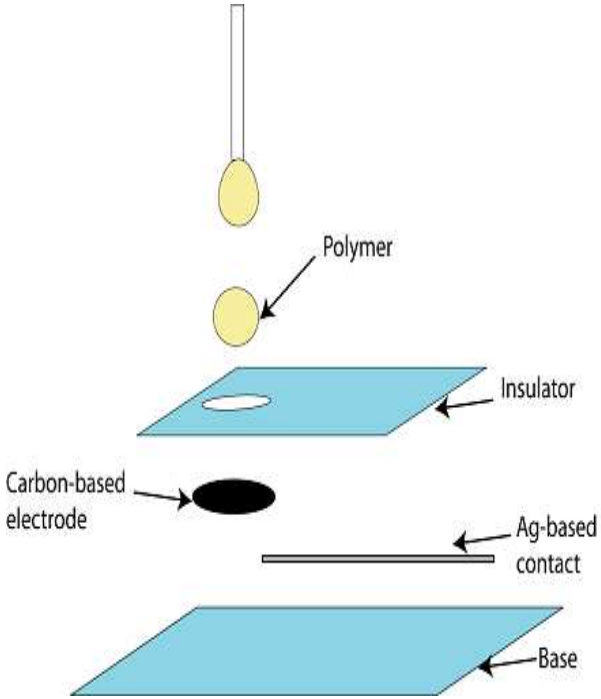
Development of "solid contact" ISEs



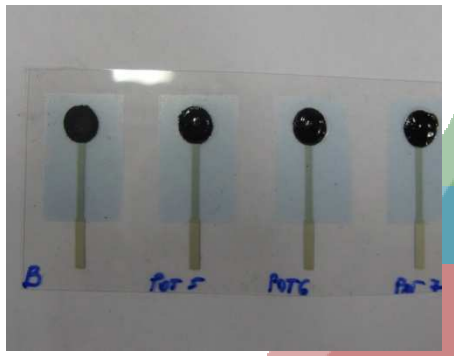
Liquid-contact electrode





Solid-contact electrode

- Lipophilic (does not allow for formation of water layer)
- Known to poses ionic and electronic conductivity



Drop-cast ISE membrane on top of a POT layer (~0.60 mm) thick

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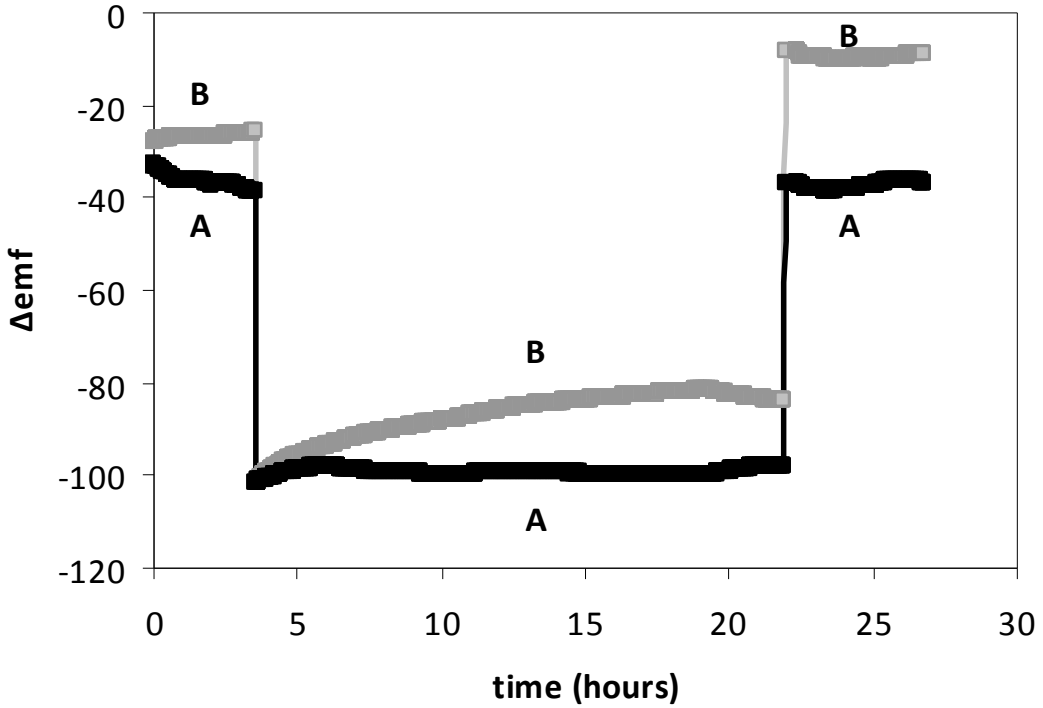
Water layer test



Characterizations of ISEs. Comparison of response of electrode with conductive polymer as inner contact (electrode A) and an electrode having no inner contact (electrode B).

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Development of “solid contact” ISEs

- simple construction
- good detection limit
- very low power demand
- simple experimental setup
- miniaturization opportunities arising from solid-contact format
- ISEs an excellent prospect for integration in autonomous sensing devices
- integration in large wireless chemo-sensing networks (new application fields, collaboration with scientist and engineers of different expertise)

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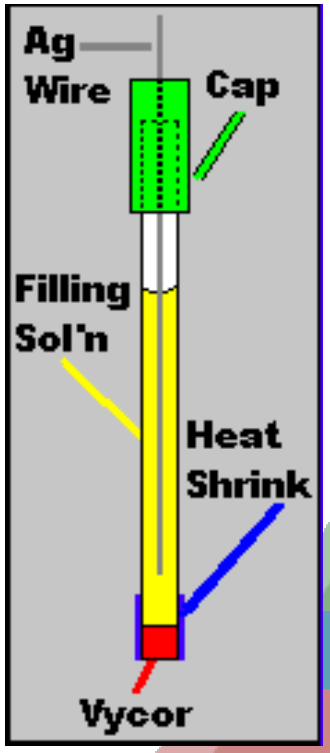
Reference electrode

- Conventional reference electrode
  - Internal solution
  - Require maintenance
  - Vertical working position
  - Cannot be miniaturized
  - Causes a risk of contaminating the sample through leakage of the filling solution



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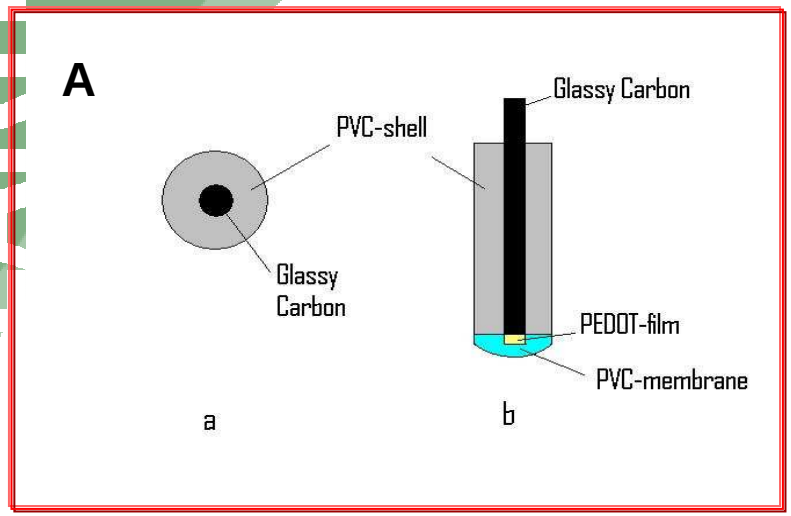
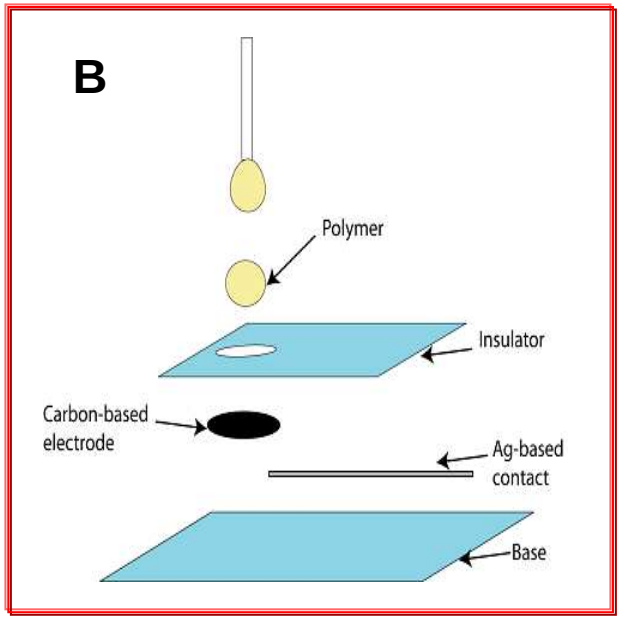
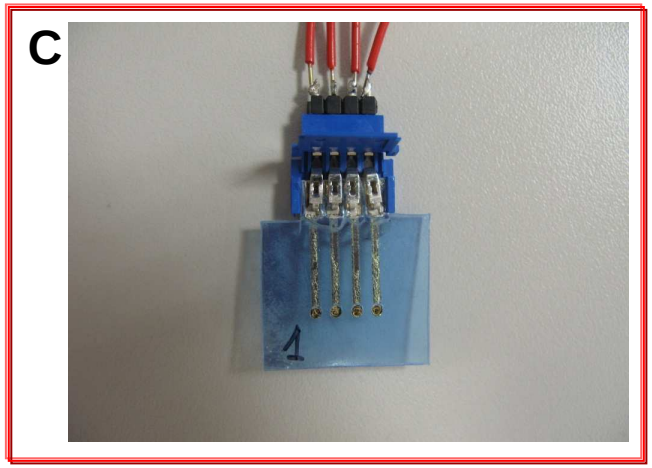
Reference electrodes







Au-PEDOT-PVC-based membrane
pH-ISE: PVC + oNPOE + H II + KTpClPB
Pb^{2+}-ISE: PVC + DOS + PbIV + NaTFPB
Reference electrode: PVC + oNPOE + TBATBB

Ulriika Mattinen, Johan Bobacka and Andrzej Lewenstam, "Solid-Contact Reference Electrodes Based on Lipophilic Salts", Electroanalysis 21 (2009) 1955.

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Micro-chip fabrication

- Development of a microfluidic chip that will incorporate polymer-based ion-selective and reference solid-contact electrodes.

- We will test the series of developed chips for the best design to accommodate these sensors. Initially, we are targeting lead-selective sensors and their application to the monitoring of drinking and natural water quality.

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Micro-chip fabrication

- Microfluidics, also known as “lab-on-a-chip” is an emerging technology that is changing the future of instrument design.
- Microfluidics enables small scale fluid control and analysis, allowing developing:
- - smaller
- - more cost-effective
- - more powerful systems.

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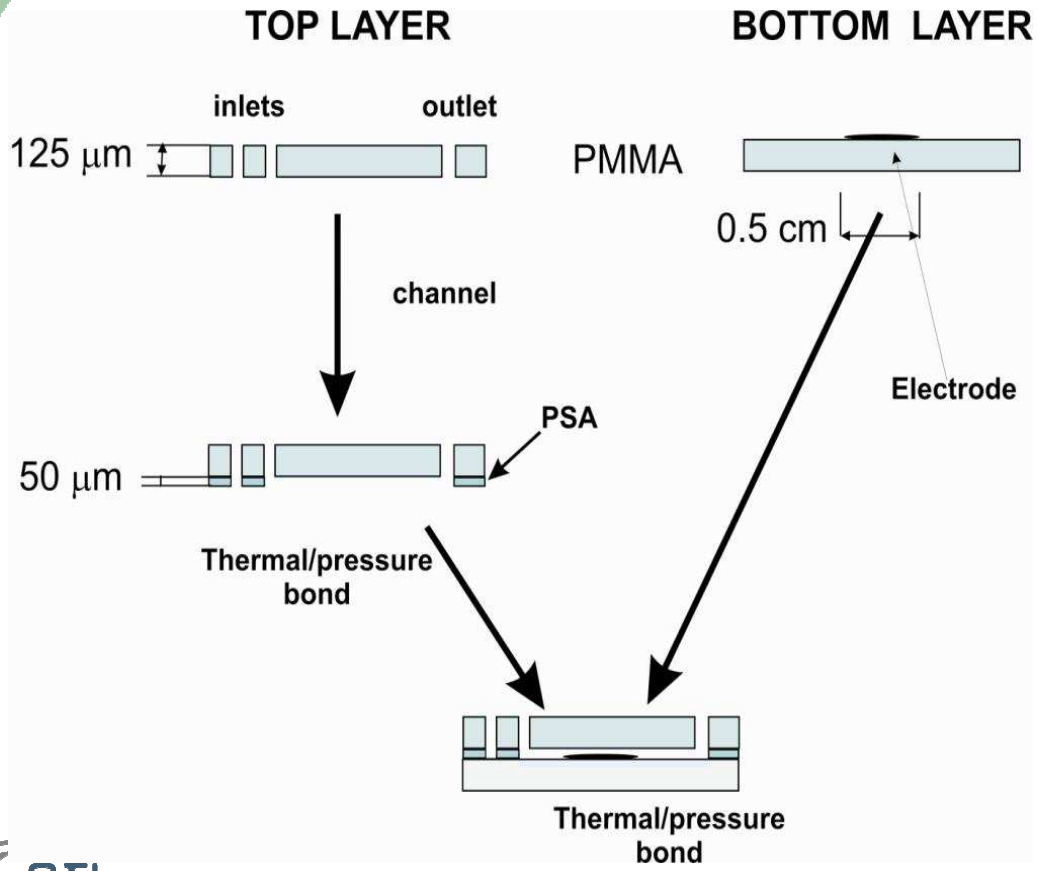
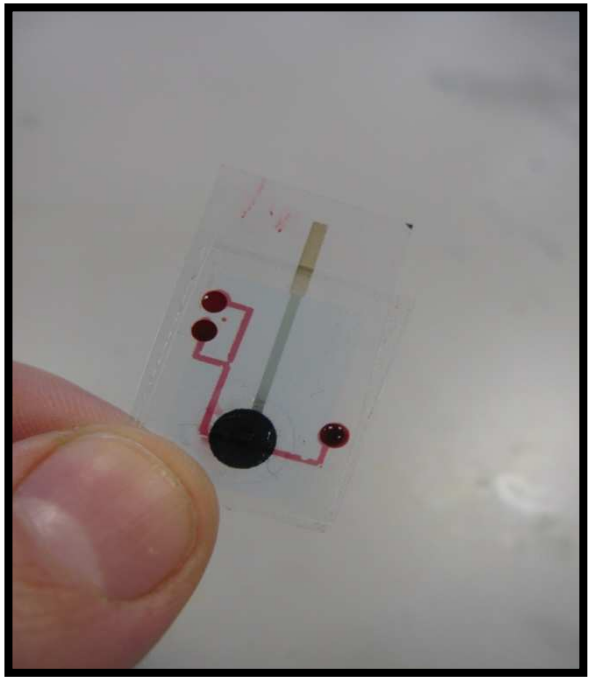
Micro-chip fabrication

1- Channels: Micromaster LASER System (CO_2 laser) – 400 µm width
2- Thermal/pressure laminator system
Materials: PMMA and PSA polymers





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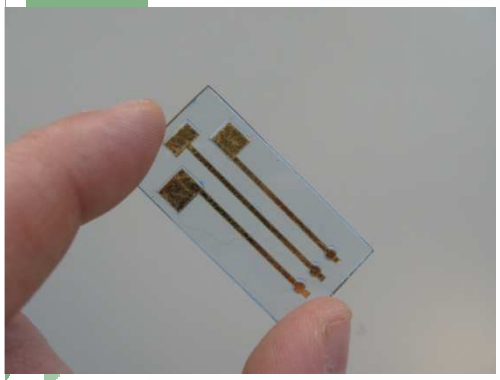
MICROCHIP FABRICATION



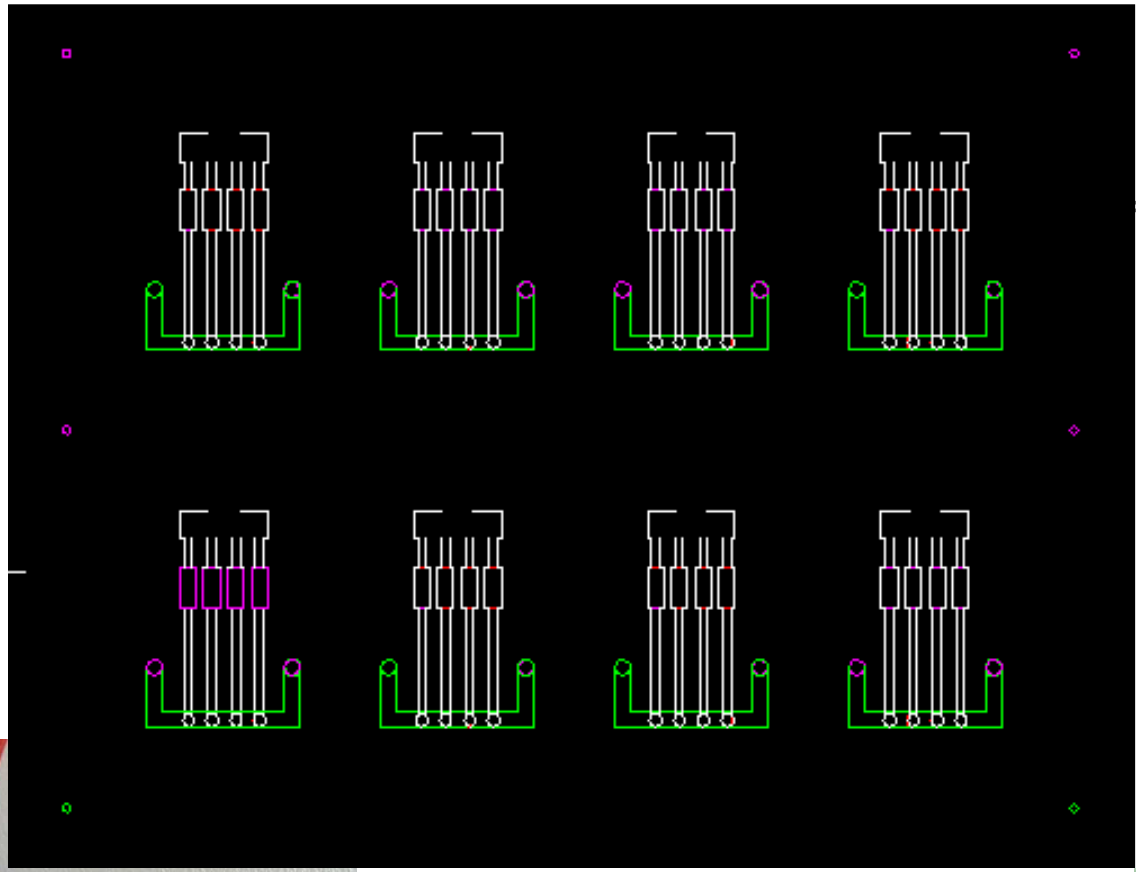
1- Channels: Micromaster LASER System (CO_2 laser)

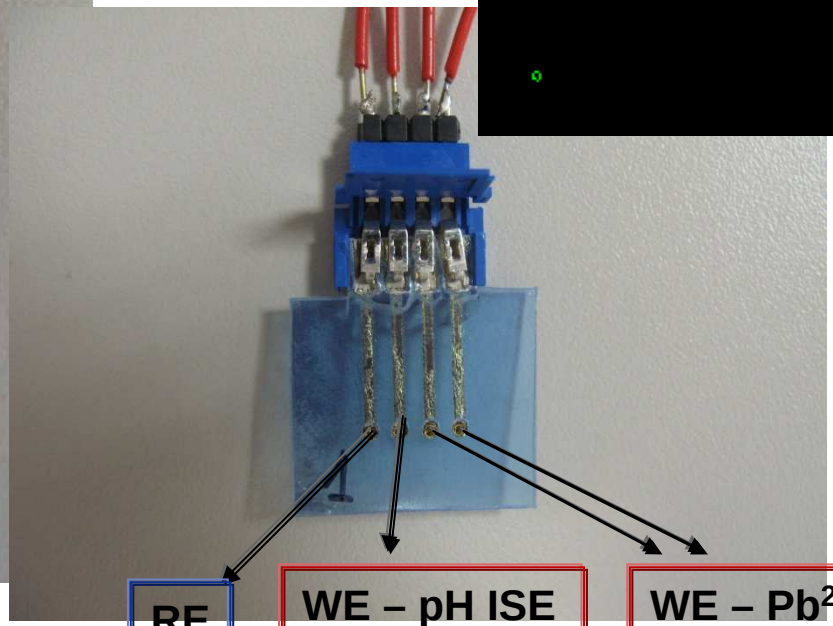
2- Thermal/pressure laminator system

This work is supported by Science Foundation Ireland under grant 07/CE/I1147

MICROCHIP DESIGN and LAYOUTS

MICROCHIP FABRICATION





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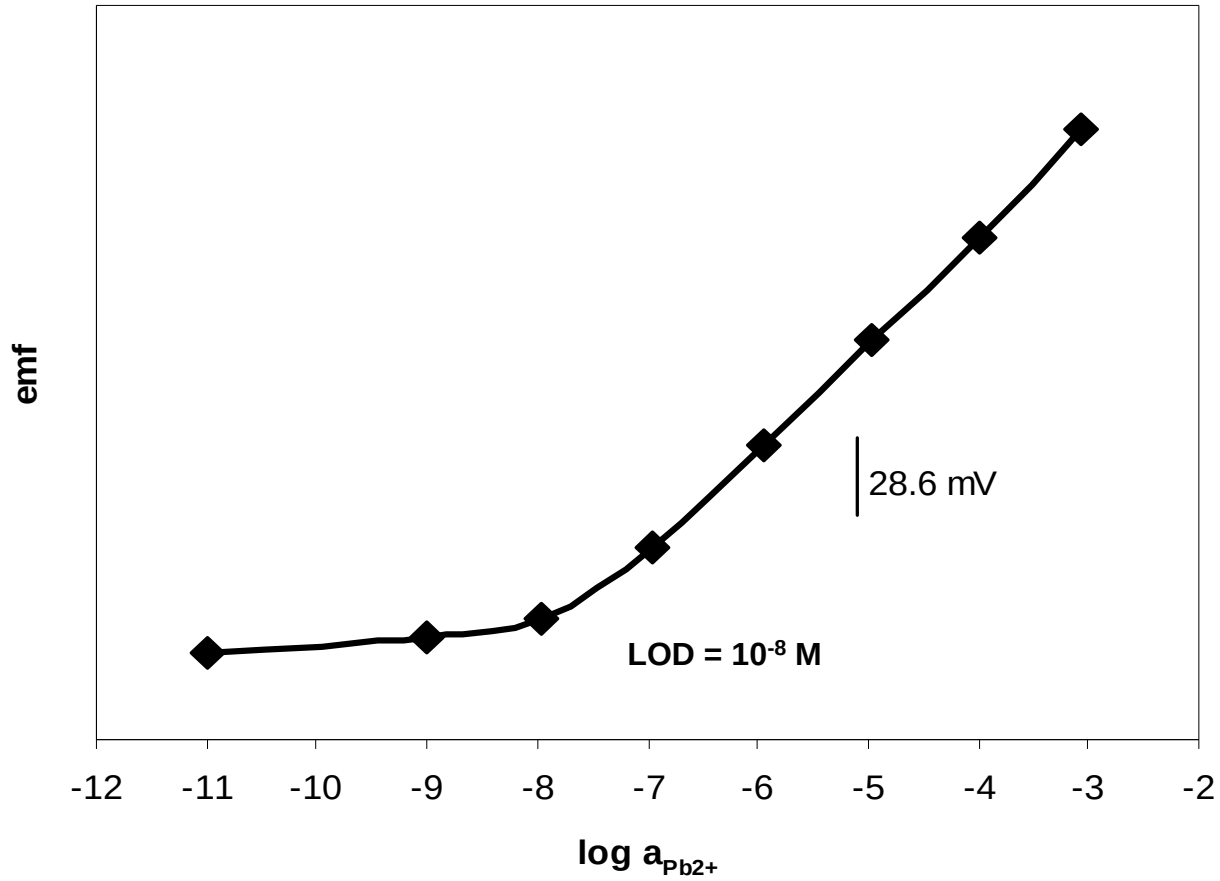
Experiments



Response of solid-contact Pb^{2+} ISEs (■, LOD = 10^{-8} M). The LOD is determined from the intersection of the low –concentration segment of the calibration plot and the extrapolation of the Nerstian segment of the calibration curve.

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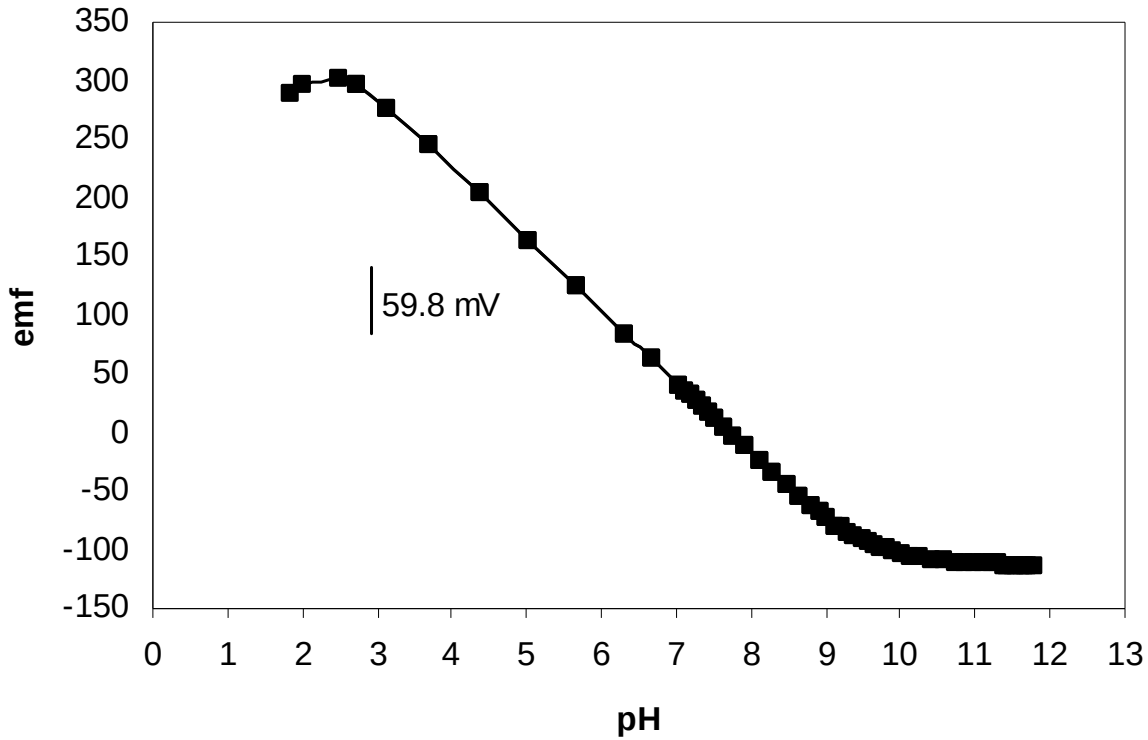
Solid-contact pH ISEs



Response of solid-contact pH ISEs containing NPOE-PVC (2:1), neutral carrier 4-nonadecylpyridine, lipophilic anionic sites KTpClTB. Nerstian response slope (59.8 mV dec $^{-1}$) in the range between pH 2 and pH 9.

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Field trials

Comparison of the pH values measured (with pH meter) and pH values from SC ISEs (according to the Nerstian equation using the data from the electrodes) and the difference (Δ) in percentage (%)

Samples	pH meter	pH ISE	Δ, %
Distil water	4.30	4.28	0.52
Rain water	5.85	5.82	0.52
Tap water	7.94	7.92	0.25
Tolka river	7.50	7.49	0.19
Royal Canal (Public library)	7.52	7.50	0.21
Botanic garden	7.95	7.93	0.22
Royal Canal (Shandon gardens)	7.53	7.50	0.35
Tolka park	7.95	7.94	0.17

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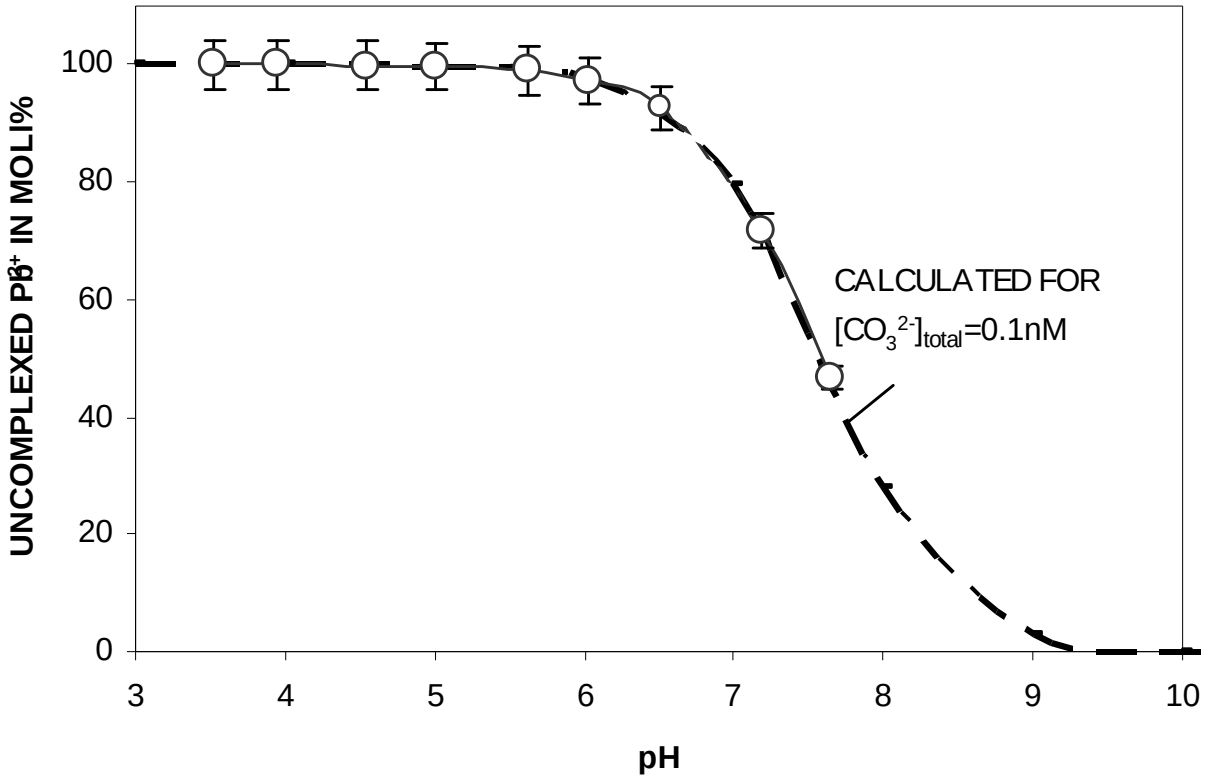
Speciation analysis



- **Direct potentiometric speciation of Pb^{2+} in deionised water spiked with 9.1 ppb Pb^{2+} as a function of pH.**
- **Solid line: expected from anions in the water samples and their complex equilibria with Pb^{2+} for 0.1 nM carbonate concentration. The formation of lead carbonate is dominant.**

This work is supported by Science Foundation Ireland under grant 07/CE/I1147

Conclusions

- Using micro-fluidic chips provide a convenient small platform for rapid analysis and detection.The results demonstrated in this work show that development of solid contact ion-selective membrane and solid contact liquid junction-free polymer based reference electrode can be successfully deposited on one platform and this platform can be successfully used in environmental analysis.

- Using the system pH ISE and all-solid RE we have successfully determined unknown pH of natural samples.

- Furthermore, we demonstrated lead-selective ISEs capable of measurement very low levels of lead.

- Using the array of all-solid contact RE and lead- and pH-selective ISEs we have successfully determined speciation of lead using direct potentiometry.

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Future steps

1. Tests of the platforms in case when we have **PUMPING SYSTEM FOR CONTINUOIUS FLOW.**

2. Microfluidic device that has the capability of wireless data transmission

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