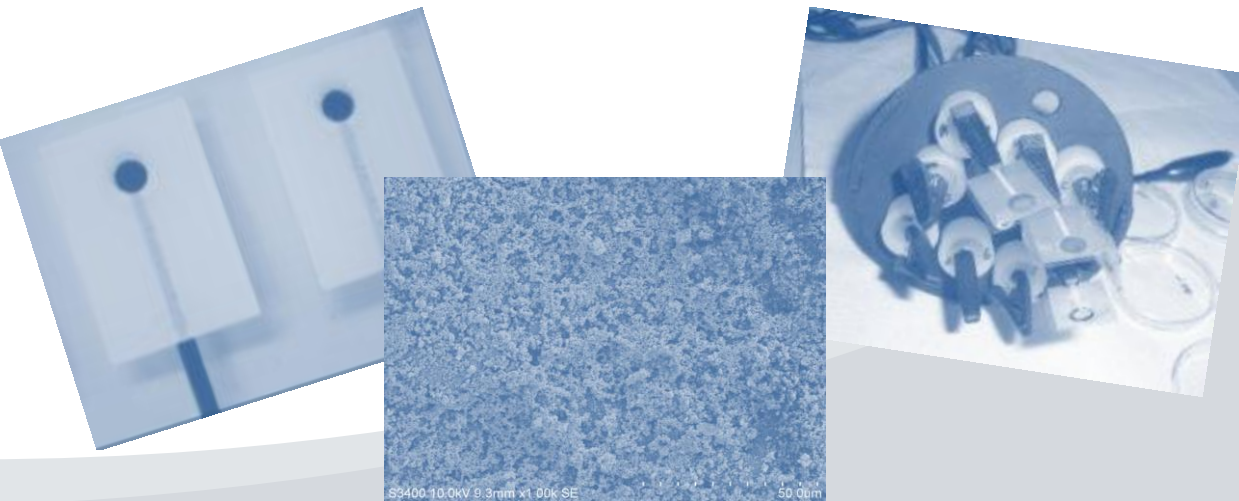




Recent Progress in Disposable Ion-selective Sensors for Environmental Applications

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*CIMTEC 2012,
Montecatini Terme*

Summary

- Introduction

Ion Selective Electrodes (ISEs)

- Pb-ISEs: Conductive polymers (CP) as solid-contact (SC). An optimization study.

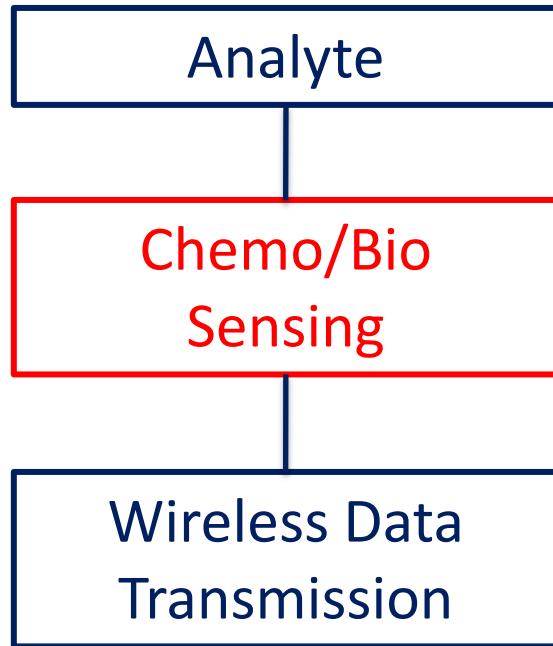
POT

PEDOT

- Pb-ISEs: New materials for the solid contact

Gold Nanoparticles (GNPs)

Introduction



Ion Selective Electrode (ISE) able to detect the analyte of interest

ISE integrated into a wireless device for in situ monitoring

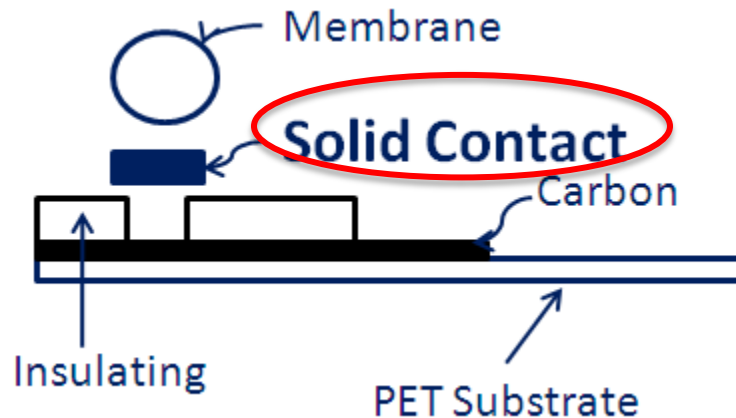


● **Introduction** ● Solid Contact Materials ● Conclusions

How to make an SC-ISE

Screen Printing Technology

- Cost
- Reproducibility



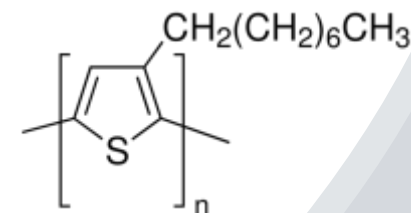
Solid Contact layer in SC-ISEs:
material properties is a key factor
in ensuring sensor reproducibility

• **Introduction** • **Solid Contact Materials** • **Conclusions**

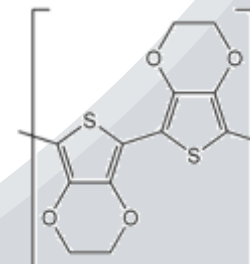
Solid Contact materials

The materials employed in this study:

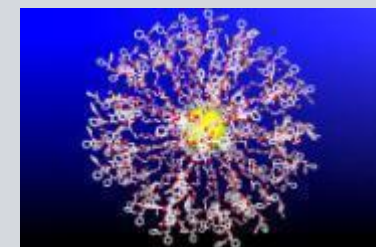
- Poly(3-octylthiophene-2,5-diyl) (**POT**)



- Poly(3,4-ethylenedioxythiophene) (**PEDOT**)

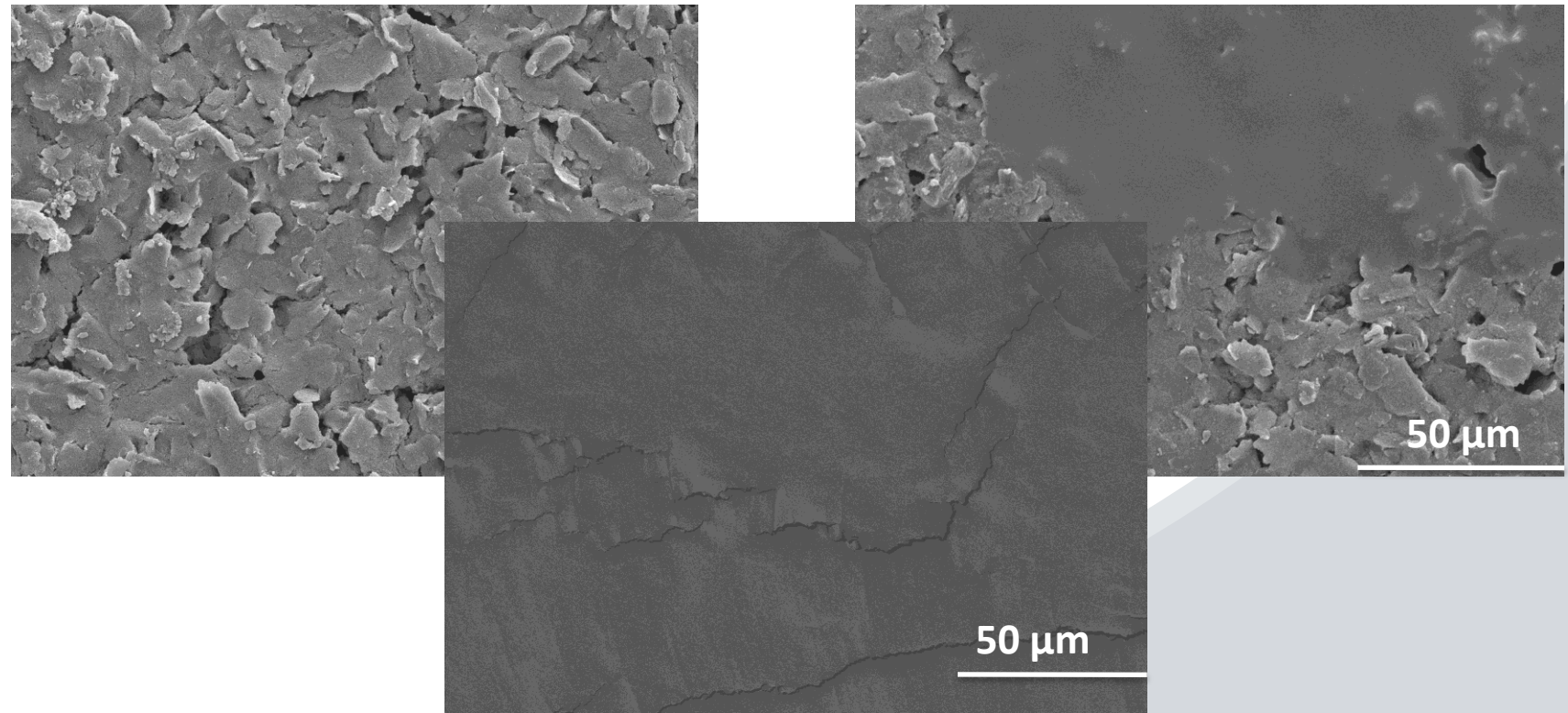


- Thiocctic acid and thiocctic amide gold nanoparticles



POT

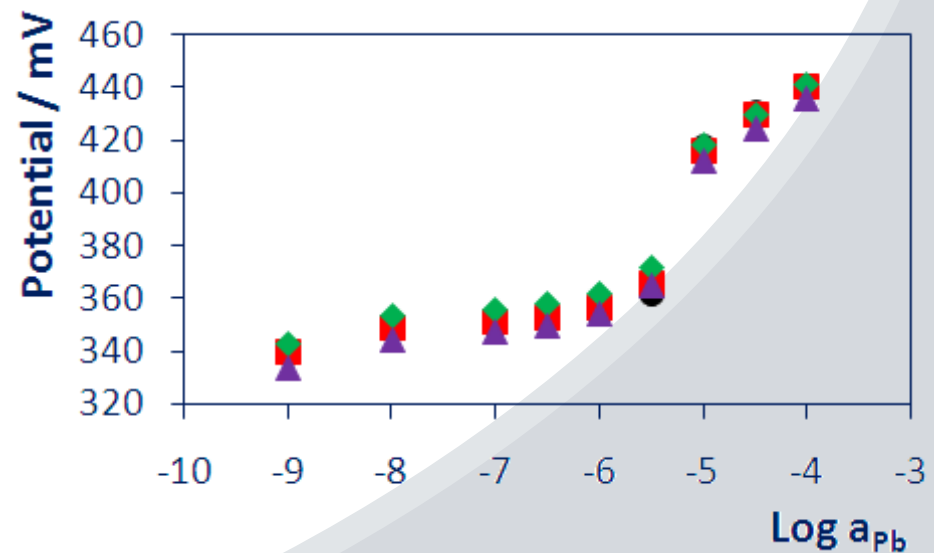
Drop-casting different amounts of POT \longrightarrow **Coverage** changes



- Introduction
- **Solid Contact Materials**
- Conclusions

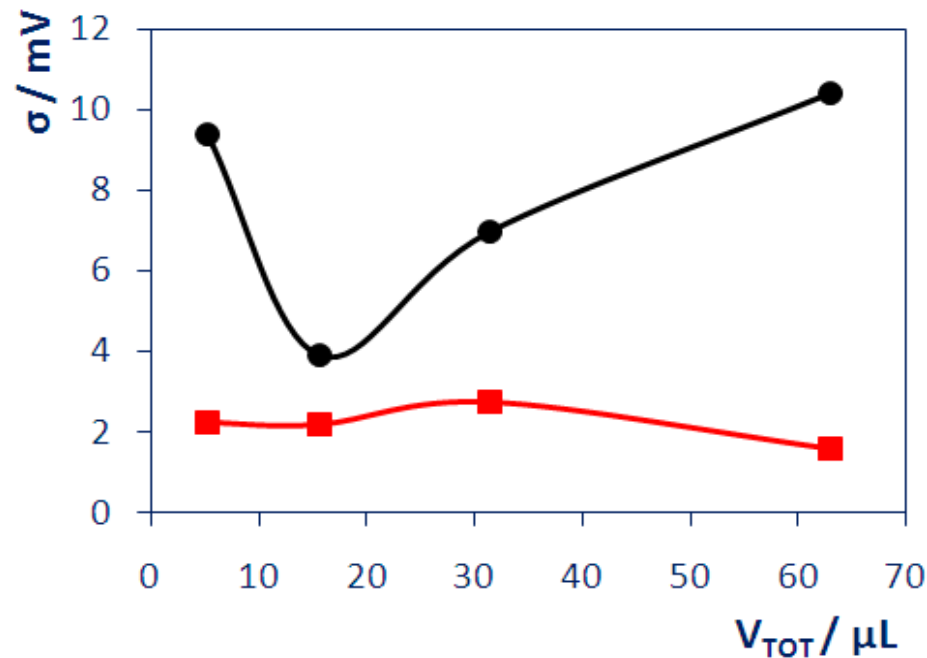
Typical calibration curve realized using POT as solid contact layer

SPE	Sensitivity (mV)	Baseline (mV)
1	48.15	339.3
2	46.36	339.7
3	43.16	343.9
4	44.43	333.7



POT

How the performances of the Lead ISEs were affected in changing the amount of POT drop cast

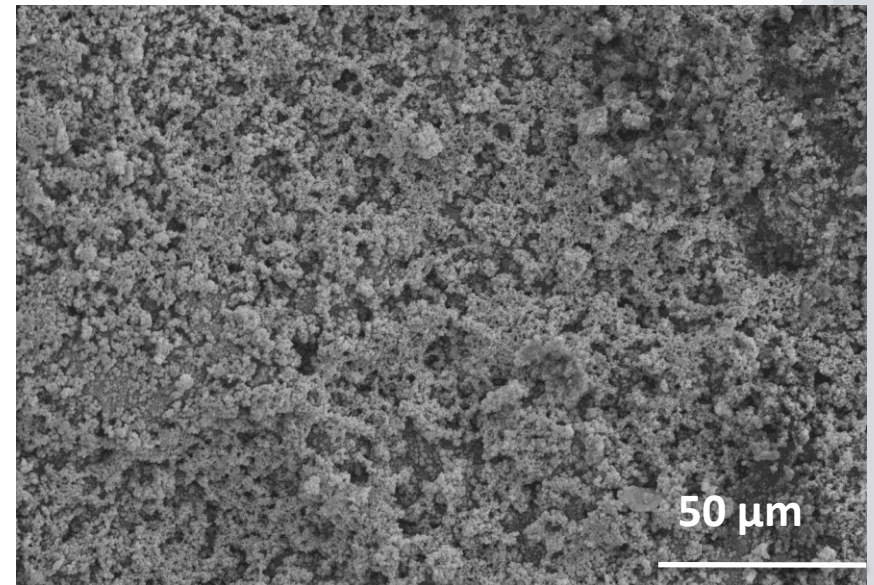
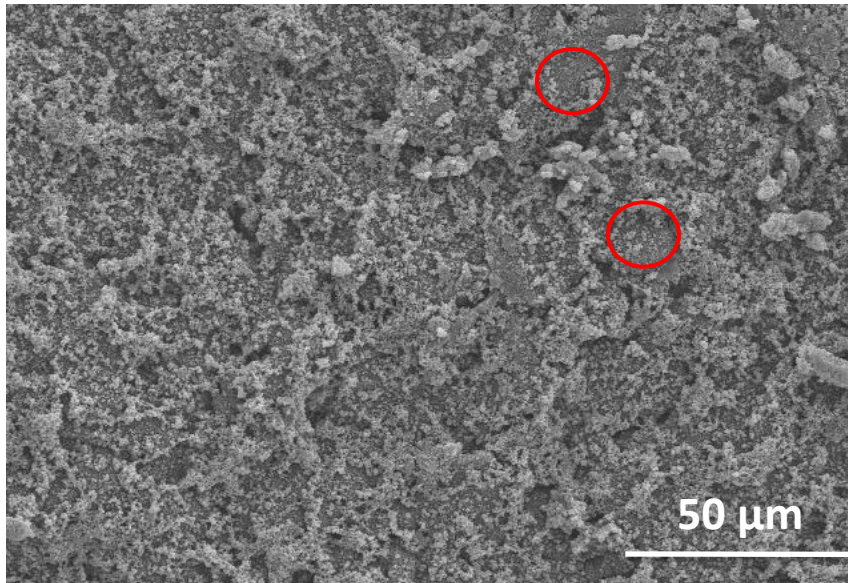


- Standard deviation for the offset of the ISEs calibration curves

- Standard deviation for the slope of the ISEs calibration curves

● Introduction ● **Solid Contact Materials** ● Conclusions

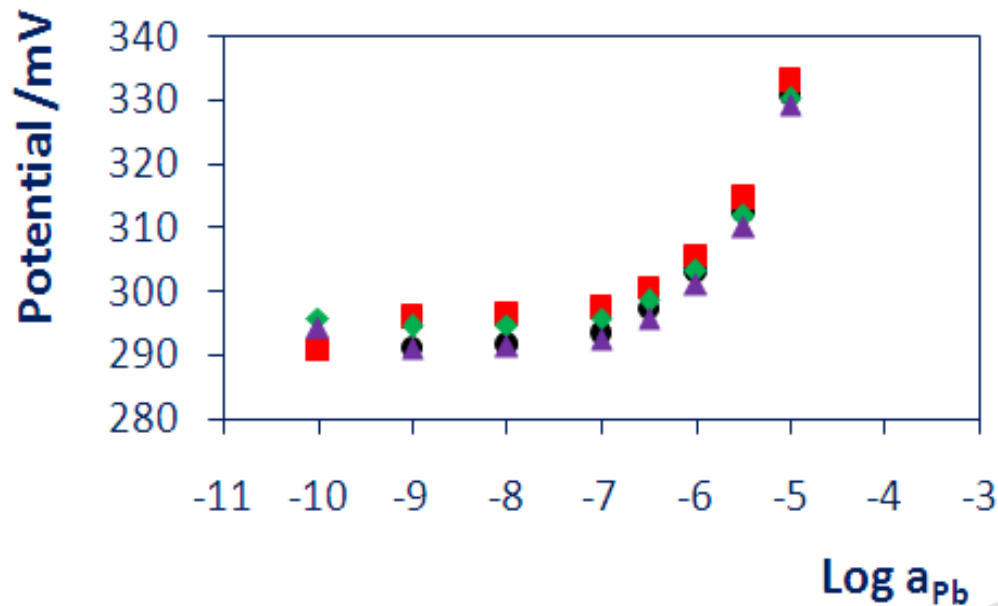
PEDOT



- Introduction
- **Solid Contact Materials**
- Conclusions

PEDOT

Typical calibration curve realized using PEDOT as solid contact layer

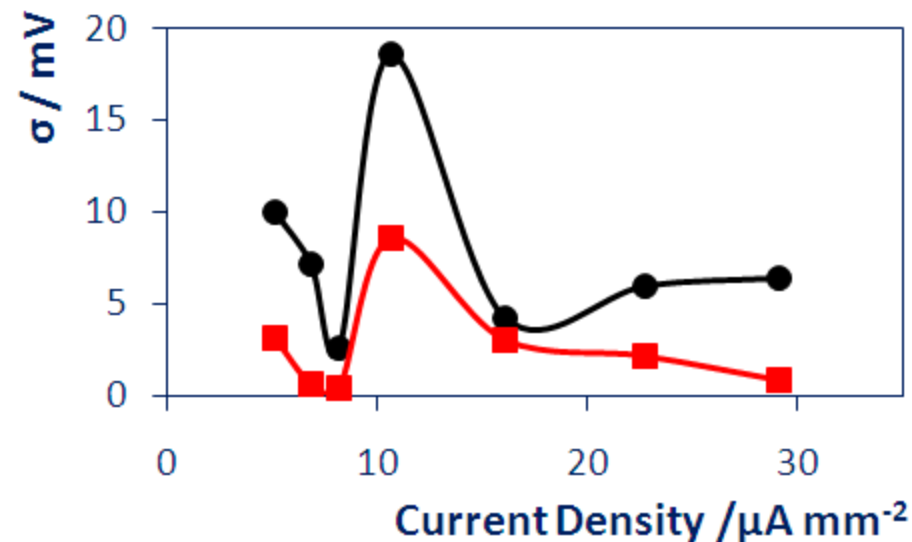


SPE	Sensitivity (mV)	Baseline (mV)
1	27.57	289.1
2	27.45	294
3	27.06	292.7
4	28.02	288.8

- Introduction
- **Solid Contact Materials**
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PEDOT

For PEDOT the performances are affected by the thickness and the redox state of the conducting polymer



- Standard deviation for the offset of the ISEs calibration curves
- Standard deviation for the slope of the ISEs calibration curves

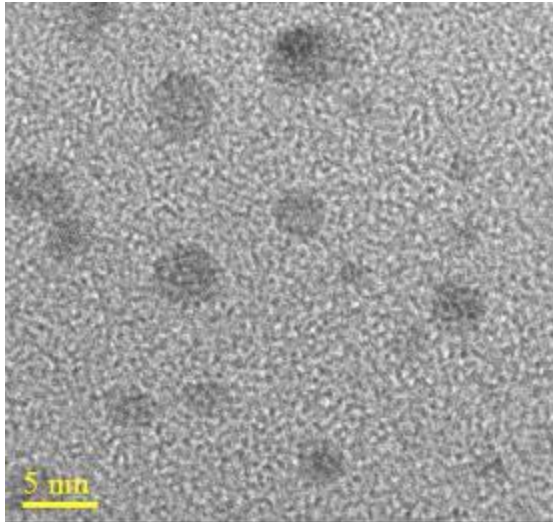
GNPs

Reasons for using GNPs as solid contact :

- Possibility of tuning the ligands and achieve control over hydrophobicity/hydrophilicity of the SC layer
- Ligands may be selected to bind the metal ion of interest, *i.e.*, control ionic fluxes at the membrane/SC layer interface
- Increase in the surface area of the solid contact layer, *i.e.*, increased stability of the ISEs response as demonstrated by the use of CNTs and other carbon nanomaterials

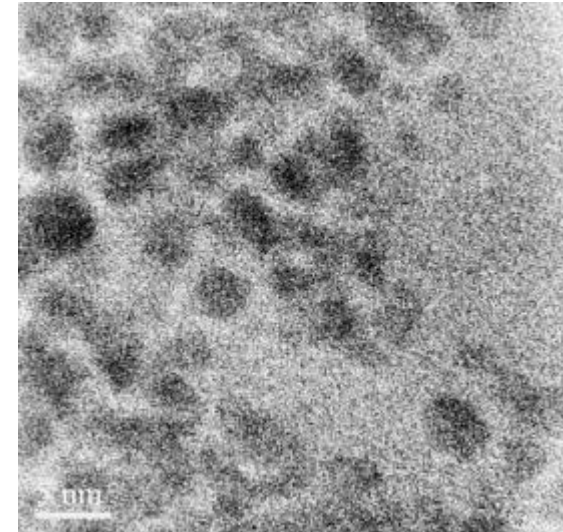
GNPs

TEM of Thiocetic Acid GNPs



- soluble in water
- $d_{\text{mean}} = 3.6 \pm 0.6 \text{ nm}$
- $\text{Au}_{1565}(\text{TA})_{161}$
 $(\text{C}/\text{H})_{\text{exp}} = 1.72; (\text{C}/\text{H})_{\text{the}} = 1.75$

TEM of Thiocetic Amide GNPs

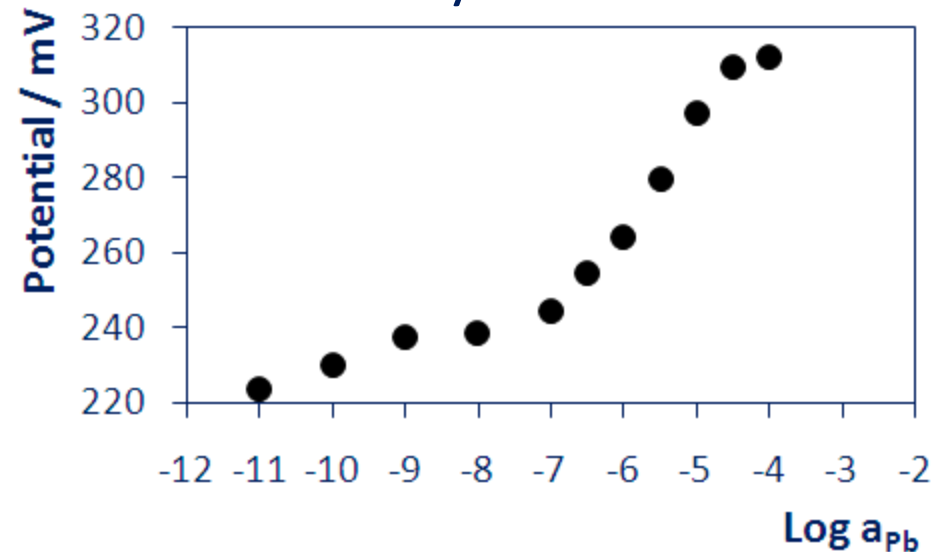


- soluble in DMSO
- $d_{\text{mean}} = 3.5 \pm 0.7 \text{ nm}$
- $\text{Au}_{1314}(\text{TA})_{311}$
 $(\text{H}/\text{C})_{\text{exp}} = 1.88; (\text{H}/\text{C})_{\text{the}} = 1.88$

• Introduction • **Solid Contact Material** • Conclusions

Thioctic Acid GNPs

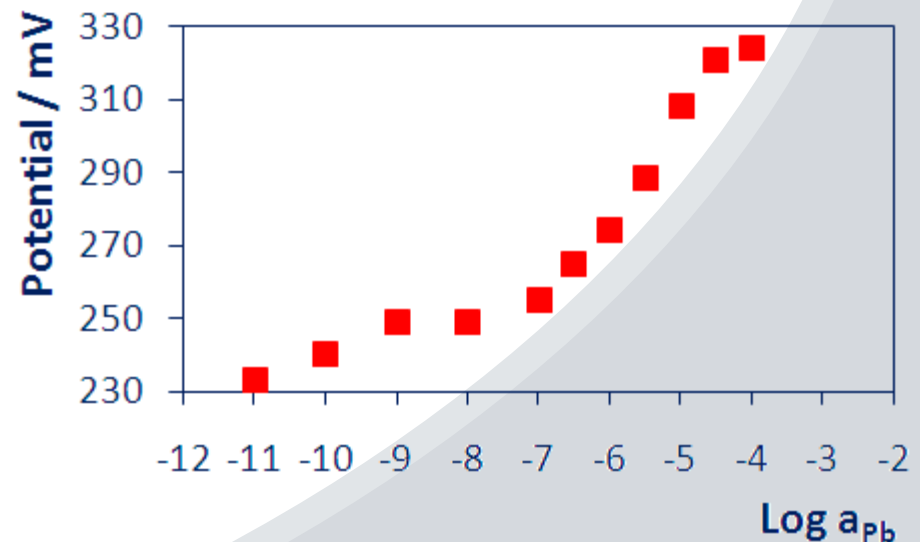
10 monolayers of GNPs as SC



SENSITIVITY: 26.68 mV

LOD: 6.87

50 monolayers of GNPs as SC



SENSITIVITY: 31.91 mV

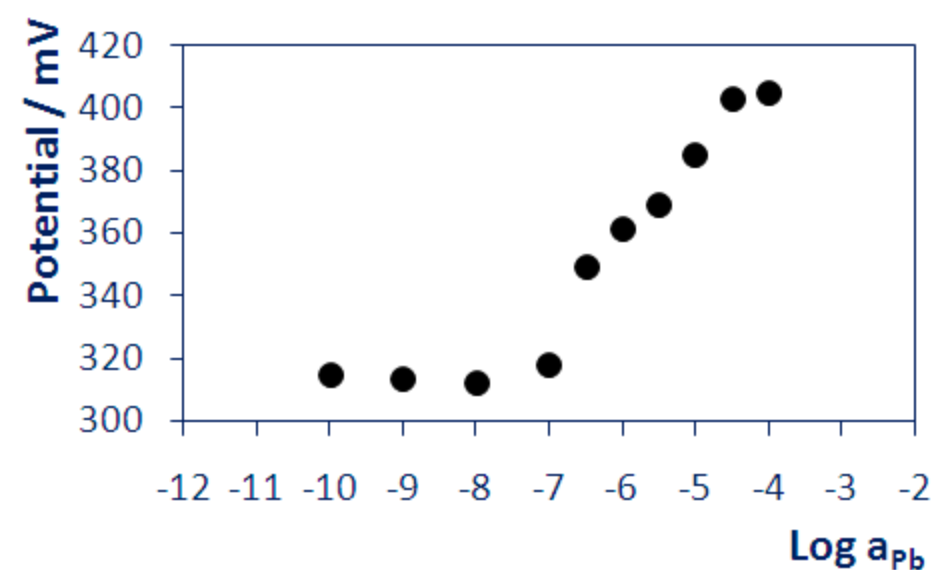
LOD: 6.53

- Introduction
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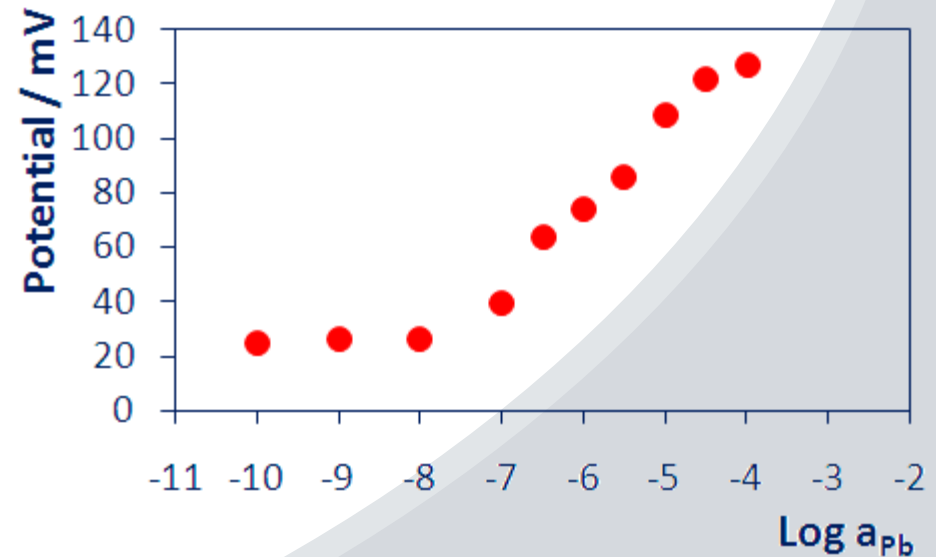
Thioctic Amide GNPs

10 monolayers of GNPs as SC

50 monolayers of GNPs as SC



SENSITIVITY: 33.93 mV
LOD: 7.2



SENSITIVITY: 26.36 mV
LOD: 7.9

- Introduction
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- Conclusions

Conclusions

- POT: depend on the thickness of the conducting polymer
- PEDOT: depend on the thickness and the redox state of the conducting polymer
- GNPs: indicate the possibility of decreasing significantly the LOD replacing the CP with the GNPs in the solid contact layer



Future Work

- Other optimizations needed for improving ISEs performances: **Ion-selective MEMBRANE**
- Exploration of the GNPs as solid contact, *e.g.*, ligand, to fully exploit their potentials
- Preparation of calibrationless sensors directly integrated into wireless platforms for environmental applications



• Introduction • Solid Contact Materials • **Conclusions**

Acknowledgements

- Dr. Claudio Zuliani
- Prof. Dermot Diamond
- All the people in room N205 and SG03
- We would like to acknowledge Science Foundation Ireland - 07/CE/I1147 – supporting "CLARITY: Centre for Sensor Web Technologies"

