Etched Ion-track grafting for water pollution detection

M-C. Clochard

Laboratoire des Solides Irradiés
CNRS-CEA-Ecole Polytechnique UMR7642
Institut Polytechnique de Paris
91120 Palaiseau Cedex, France

Location: « Ecole Polytechnique » Engineer School

South of Paris region
Plateau de Saclay (5 km from CEA-Saclay site)

Irradiated Solid Laboratory

emir&a
Réseau national d'accélérateurs pour l'irradiation et l'analyse des molécules et matériaux

EB facility
2,5MeV

SIRIUS

GANIL spiral2
laboratoire commun CEA/DSM CNRS/IN2P3

Mixt laboratory : CEA - Ecole Polytechnique – CNRS, UMR 7642
Management: Michèle Raynaud
90 staff members – 5 teams among them PCnano : 8 permanent staffs

Context and challenges

- Industrial wastes
- Domestic & Agriculture
- Mines & escavations
- Soils erosion
- Leachates & Climate

<u>Toxic metals of interest</u>: Hg, Cd, Pb, As, Cr, Co, Ni, Cu, Zn, Sb, Se, UO2(II)

European legislation on toxic metals

Need for ultra-sensitive devices for analysis, on-site and robust to prevent in real time environmental disasters

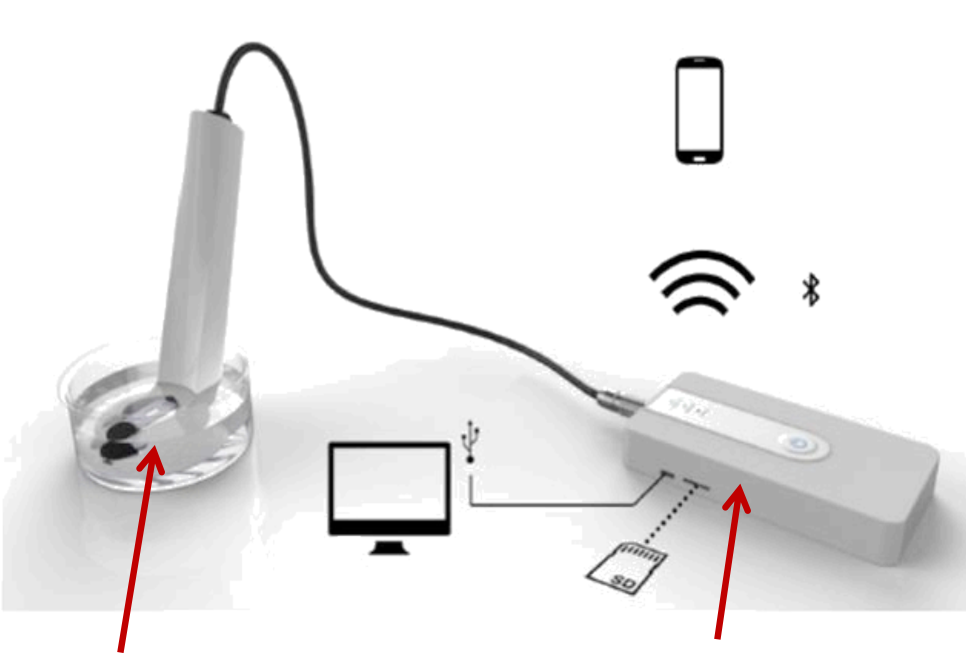
OSPAR regulation for seawater

		µg/L
Metals	Arsenic	60
	Nickel	860
	Cadmium	21
	Chromium	60
	Copper	260
	Mercury	4,7
	Lead	130
	Zinc	300

Tolerables limits are few µg/L (or ppb) to hundred

Scientific Reports (**2020**) 10:5776
Reactive and Functional Polymers 142 (**2019**) 77–86
Journal of Hazardous Materials 376 (**2019**) 37–47

CapTôT Electrochemical analyser



Membrane-based sensor

Potentiometer developed with VALOTEC

- *in situ* sampling
- portable
- quick reading (2mn30s)
- ion speciation data
- compatible with marine environment
- Hg specific detection

Detected ions (few tenths of ppb range):
Pb, Cu, Ni, Co, Hg, UO_2, Mo, Sb, Se, As, Cd, Cr(VI), Zn

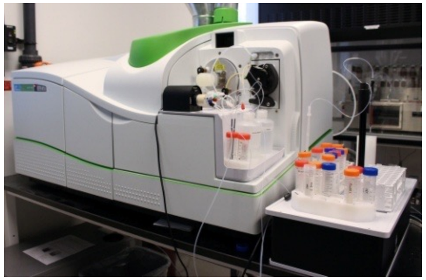
CapTÔT

A key solution for industrials

IDO
Études & Production

Positioning CAPTOT technology

Inductively Coupled Plasma Mass Spectroscopy (ICP-MS)

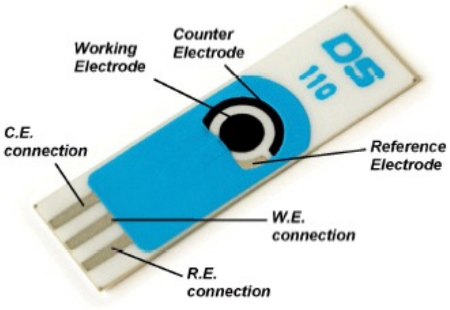


Certified method

Mercury drop Electrode Polarography

www.nordantec.com

Screen Printed Electrode

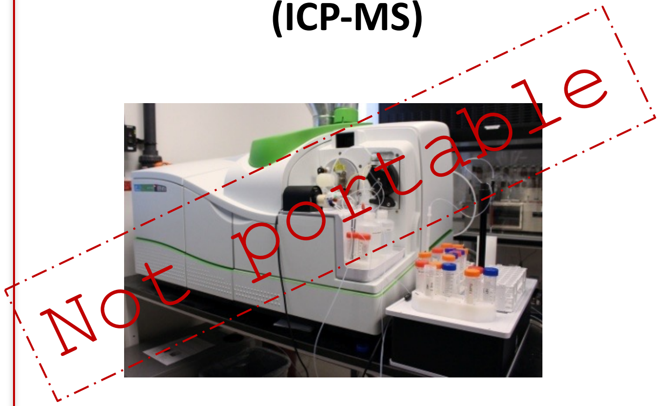


www.dropsens.co.uk

Portable methods

Positioning CAPTOT technology

Inductively Coupled Plasma Mass Spectroscopy (ICP-MS)



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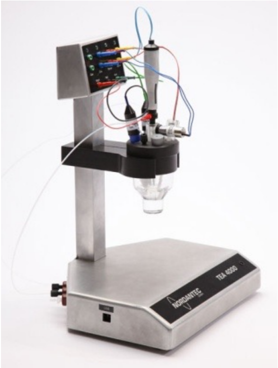

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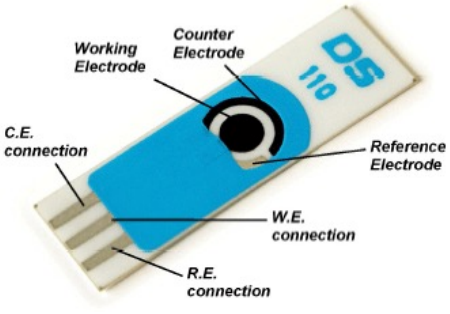
Screen Printed Electrode



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Portable methods

Positioning CAPTOT technology

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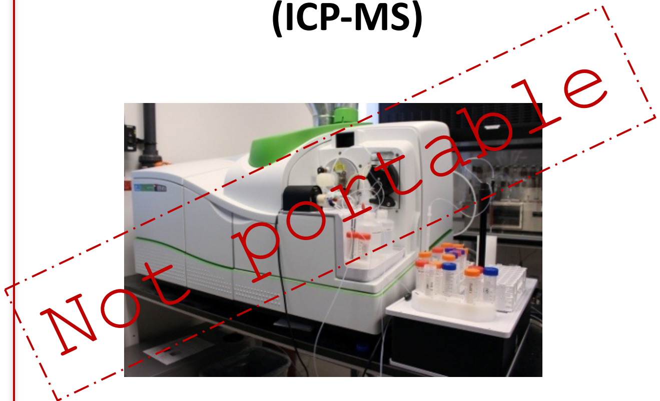

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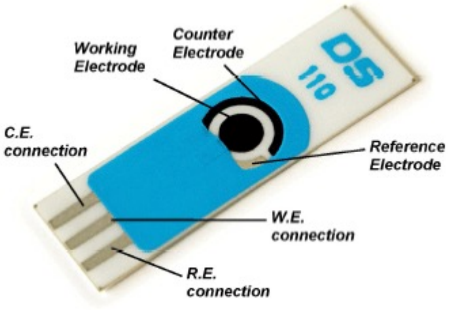

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Portable methods

Positioning CAPTOT technology

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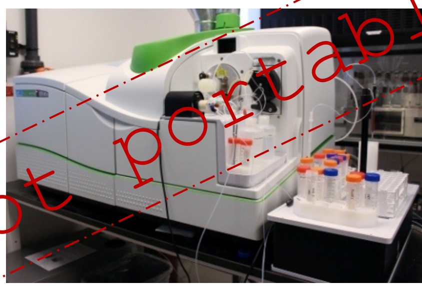

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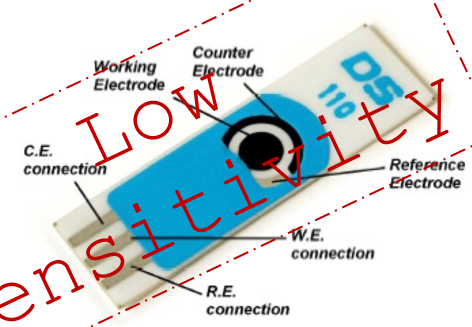

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Portable methods

Positioning CAPTOT technology

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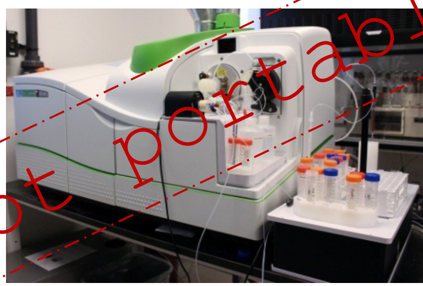

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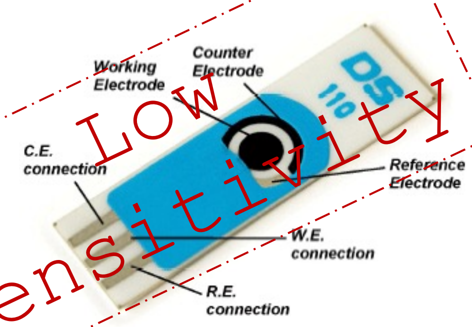


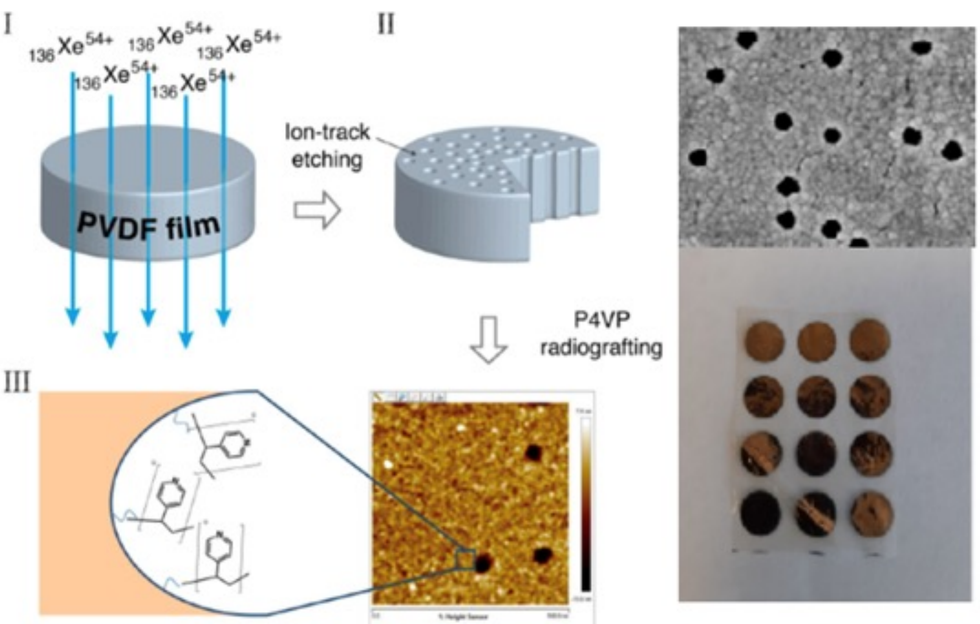
www.dropsens.co.uk

Portable methods

Portable, easy-to-use
Ultrasensitive towards Hg(II)
Speciation of metal ions indication

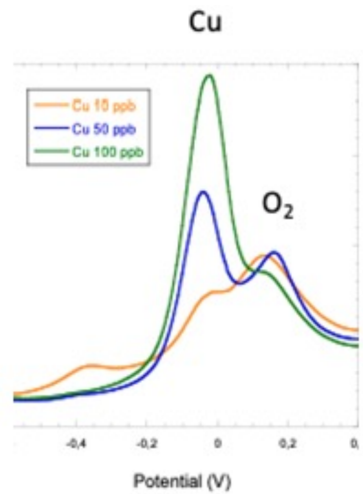
Patented technology

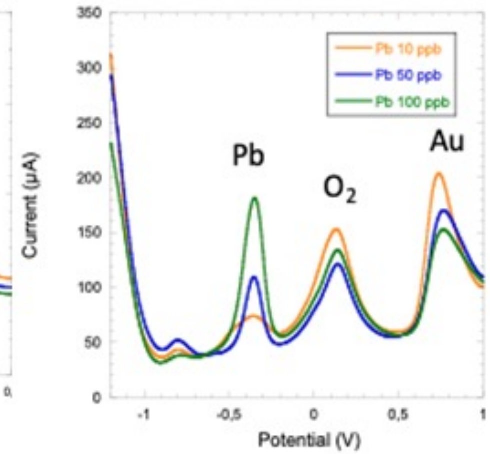
Membrane-based electrochemical sensor

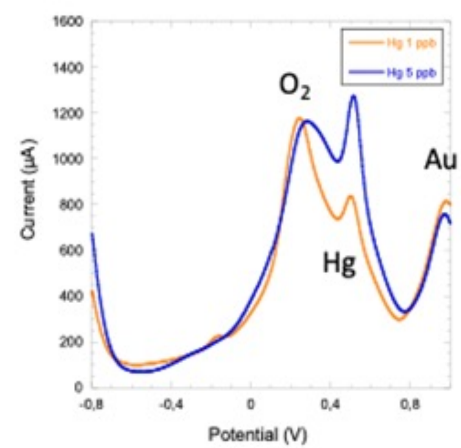


Brevets: EP08305237, EP11305112, EP11306648.4

ASV detection







Membrane-electrode fabrication

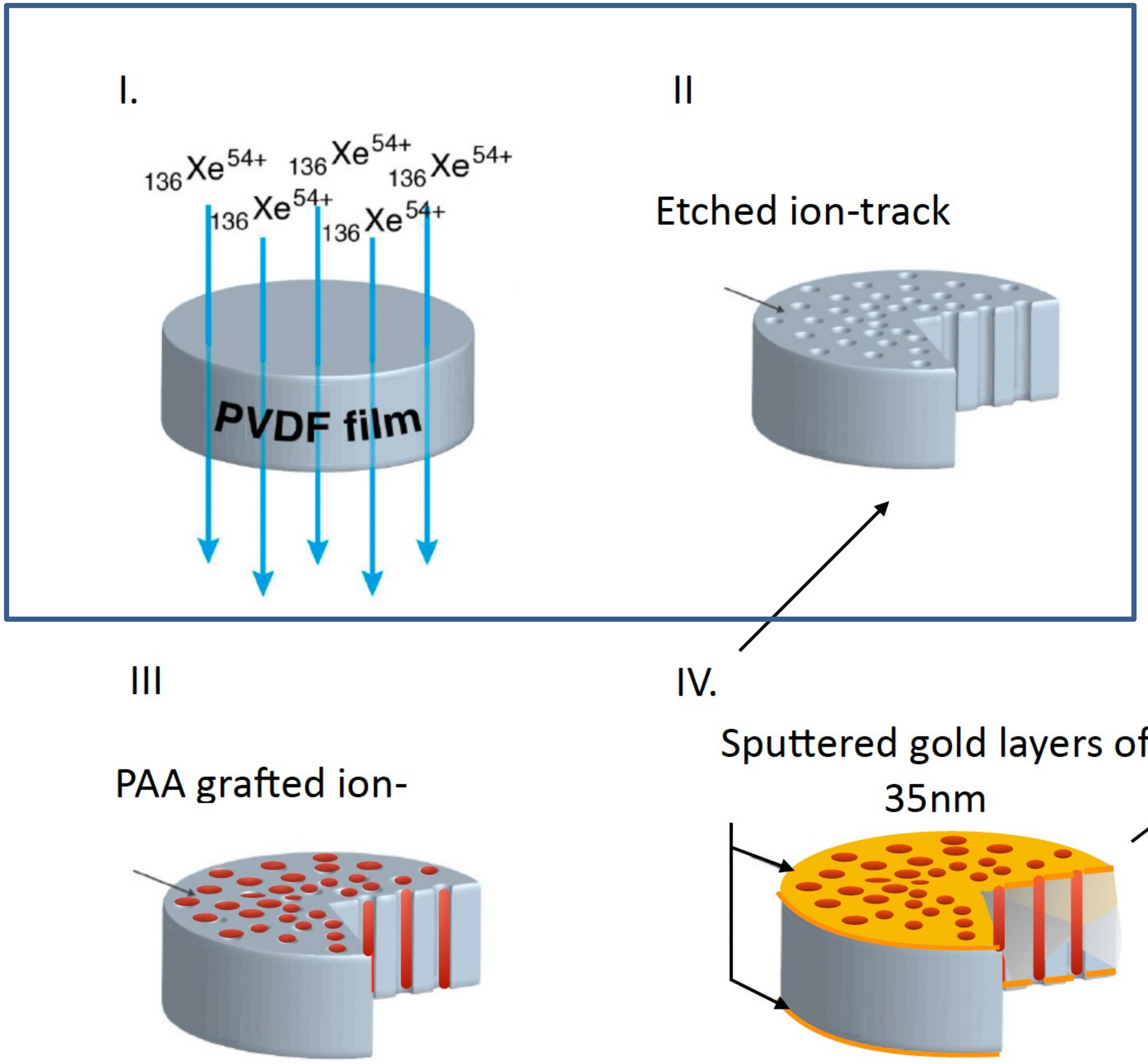
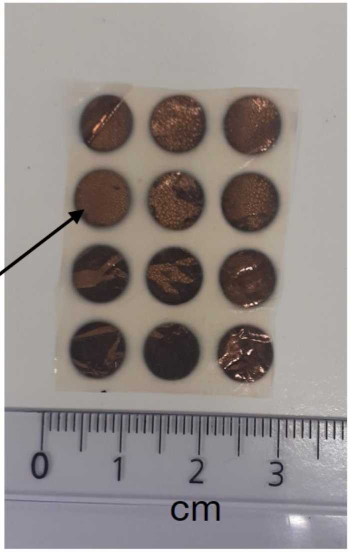
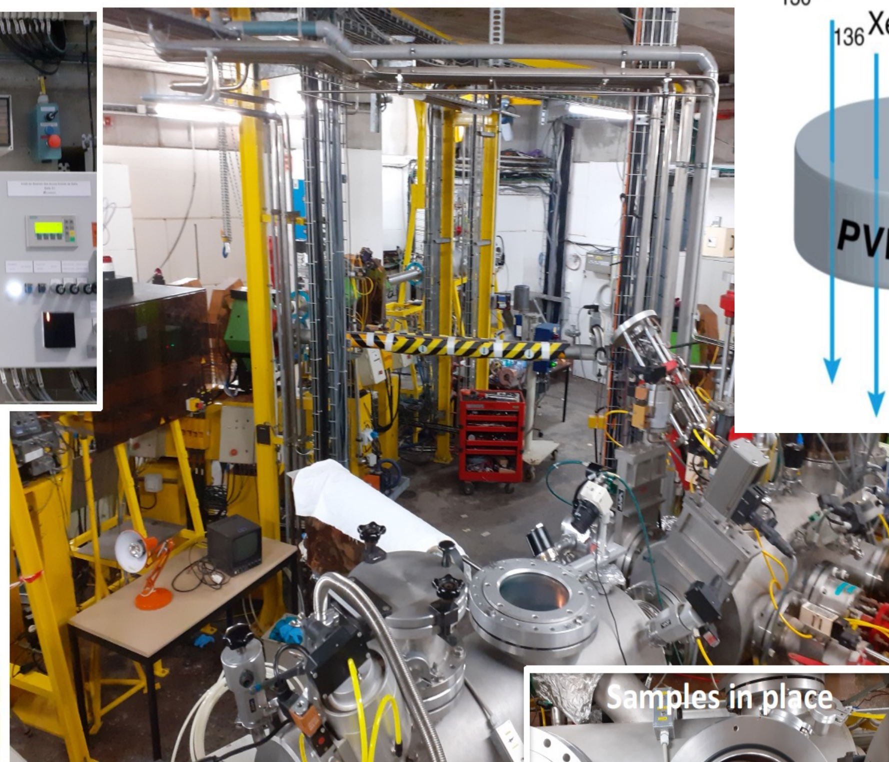
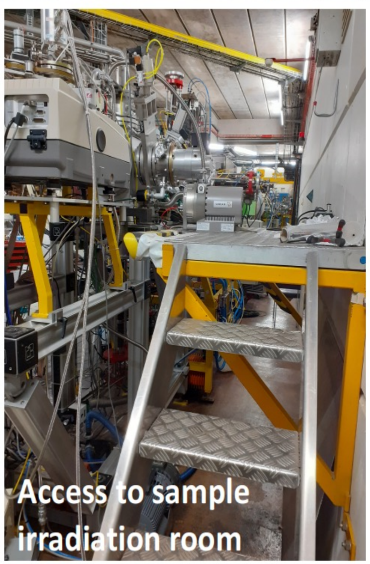


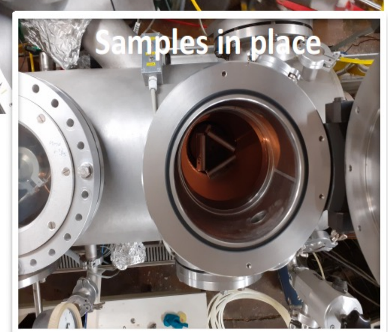
Photo of 12 gold disk electrodes sputtered onto track-etched PAA-g-PVDF membrane



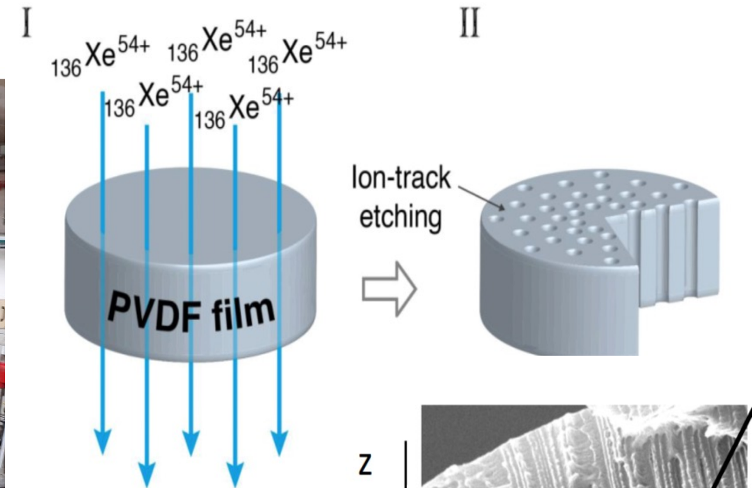
Nanostructuration by Swift Heavy Ions Irradiation and track-etching

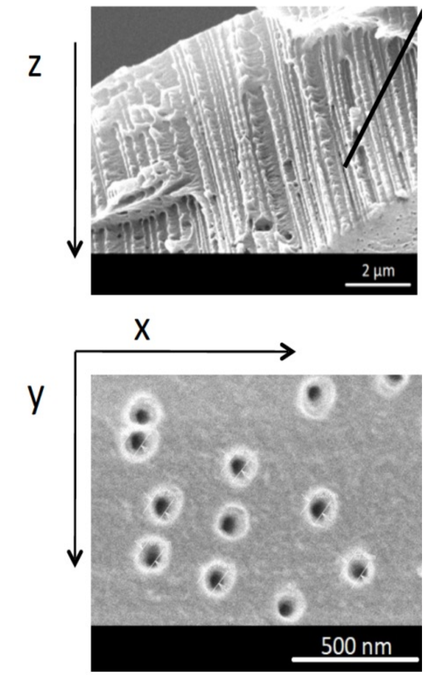






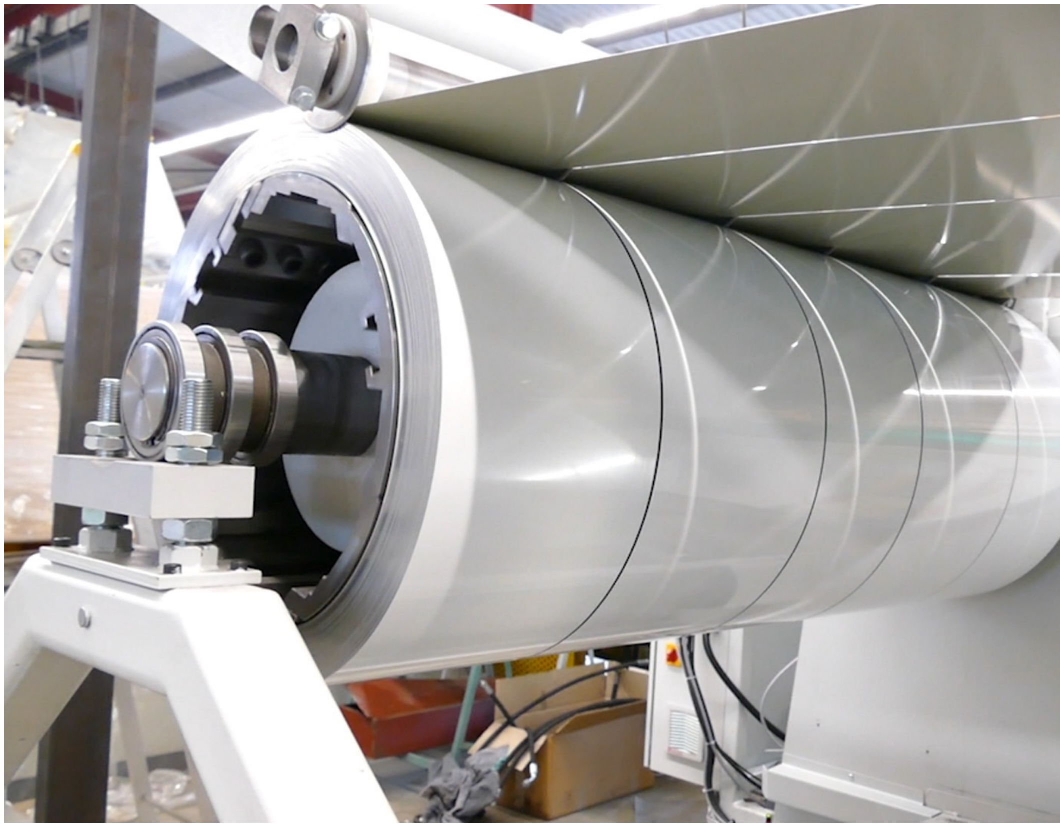
Salle D1 SME



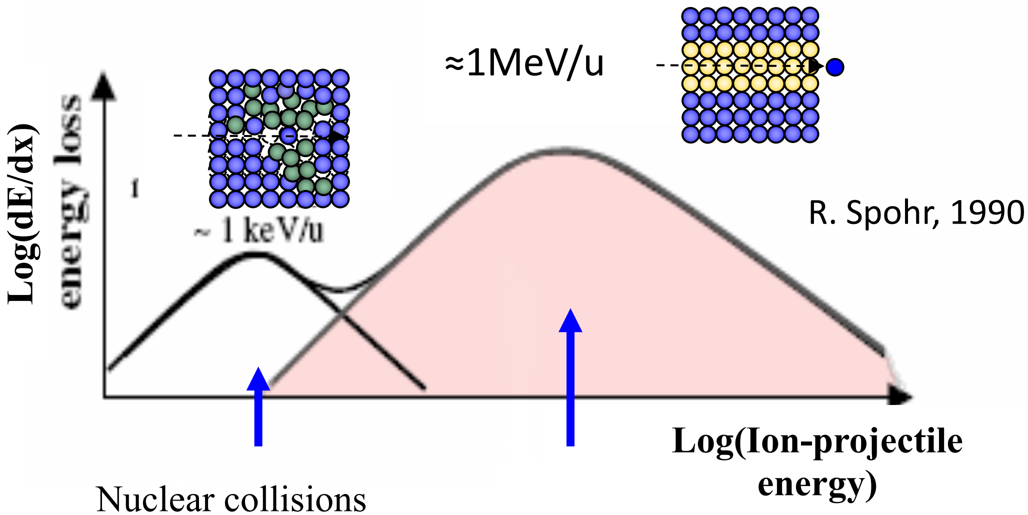


10MeV/mau

Nanostructuration by Swift Heavy Ions Irradiation and track-etching



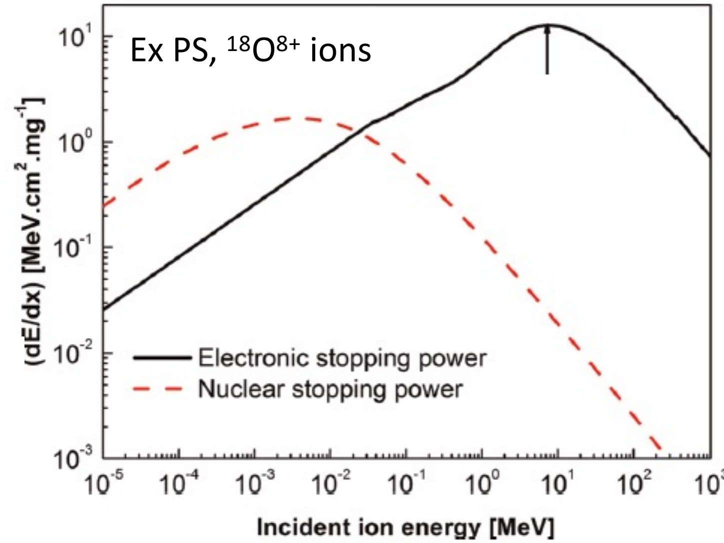
High LET effects and modifications of polymers using swift heavy ions*

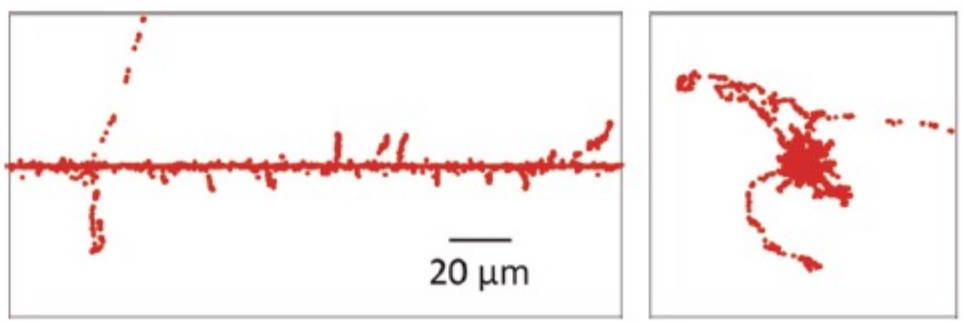


Nuclear collisions
$(dE/dx)_{nuclear}$

Electronic interactions
$(dE/dx)_{electronic}$

Tracks





Calculated track formed by the passage of a 5 MeV He^{2+} ion in polyethylene (Gervais and Bouffard, 1995).

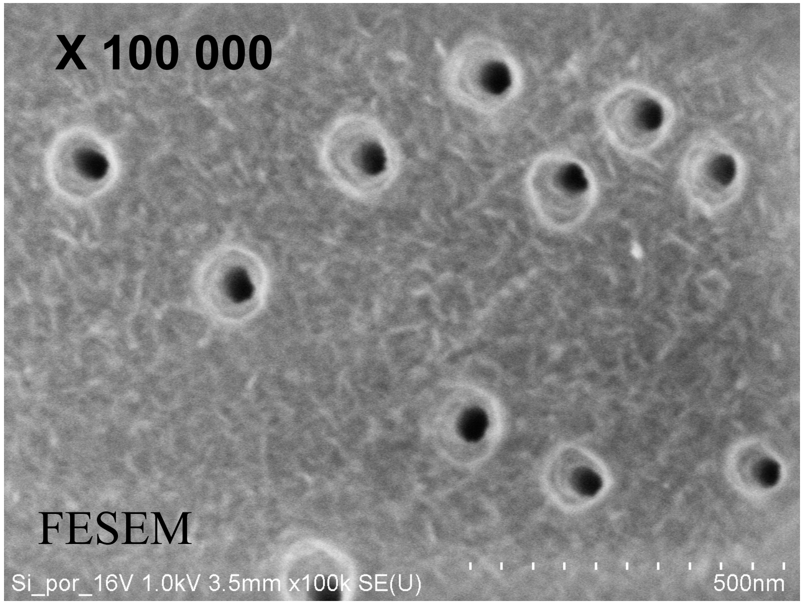
$$D = 1.6 \cdot 10^{-7} \cdot n \frac{dE}{dx}$$

n is the fluence representing ions impacts per cm^{-2}`
stopping power in MeV mg^{-1} cm^2

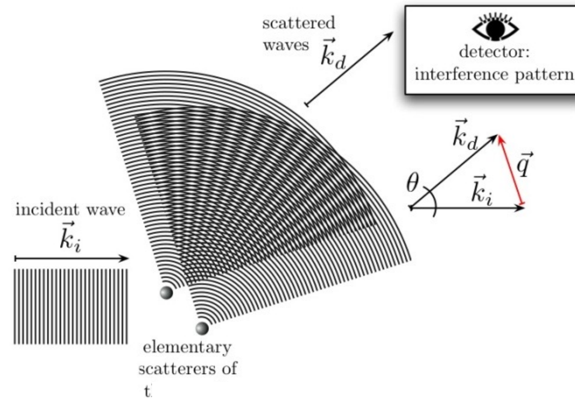
Radiation Physics and Chemistry 142 (2018) 54–59

* Ferry, M.N.; Ngono-Ravache, Y.; Aymes-Chodur, C.; Clochard, M.C.; Coqueret, X.; Cortella, L.; Pellizzi, E.; Rouif, S.; Esnouf, S. "Ionizing radiation effects in polymers". In Reference Module in Materials Science and Materials Engineering; Hashmi, S., Ed.; Elsevier: Oxford, UK, **2016**; pp. 131–149.

Nanopores characterization



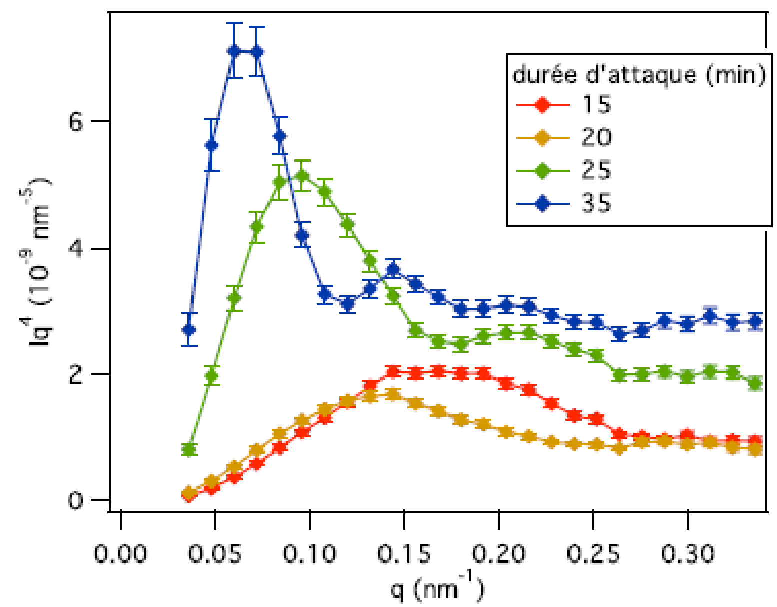
SANS



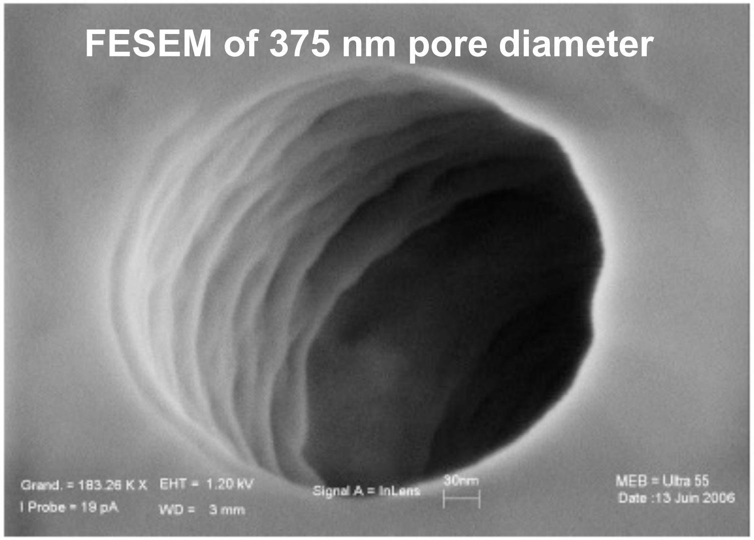
PACE, CEA Saclay
Didier Lairez

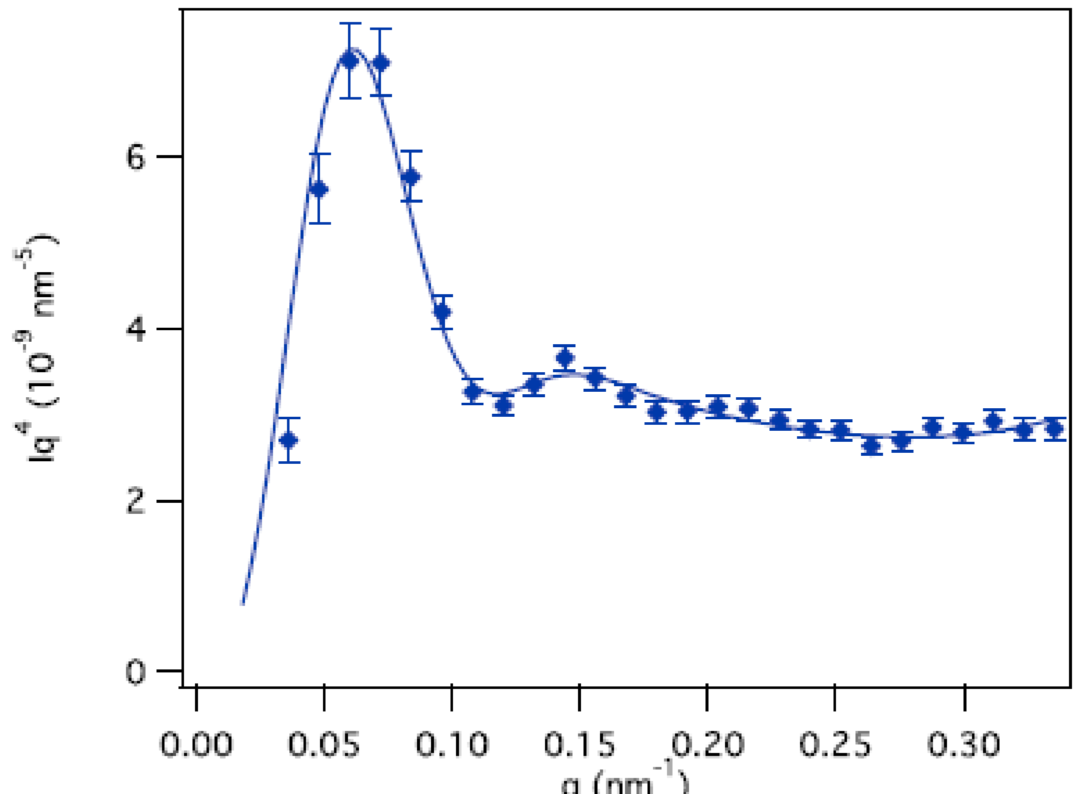
1) Reflections on pore walls (Porod's behaviour): $I \propto 1/q^4$

2) Pore radii r
Periodic Modulations of the signal by Bessel function: $J_1(qr)$



SANS gives also information on pore rugosity

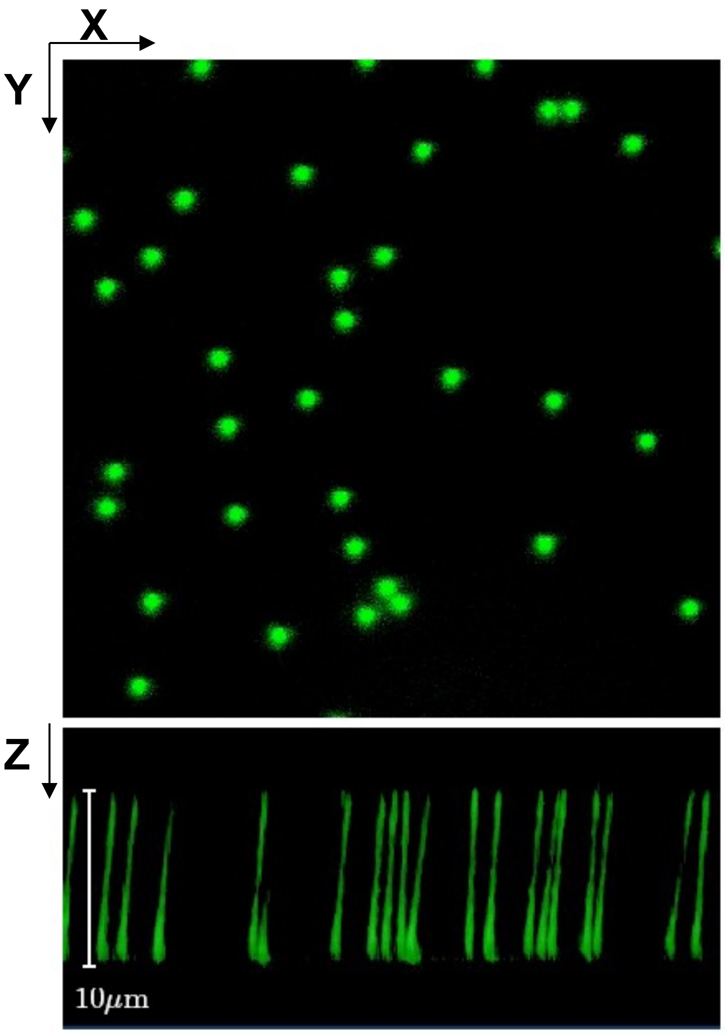




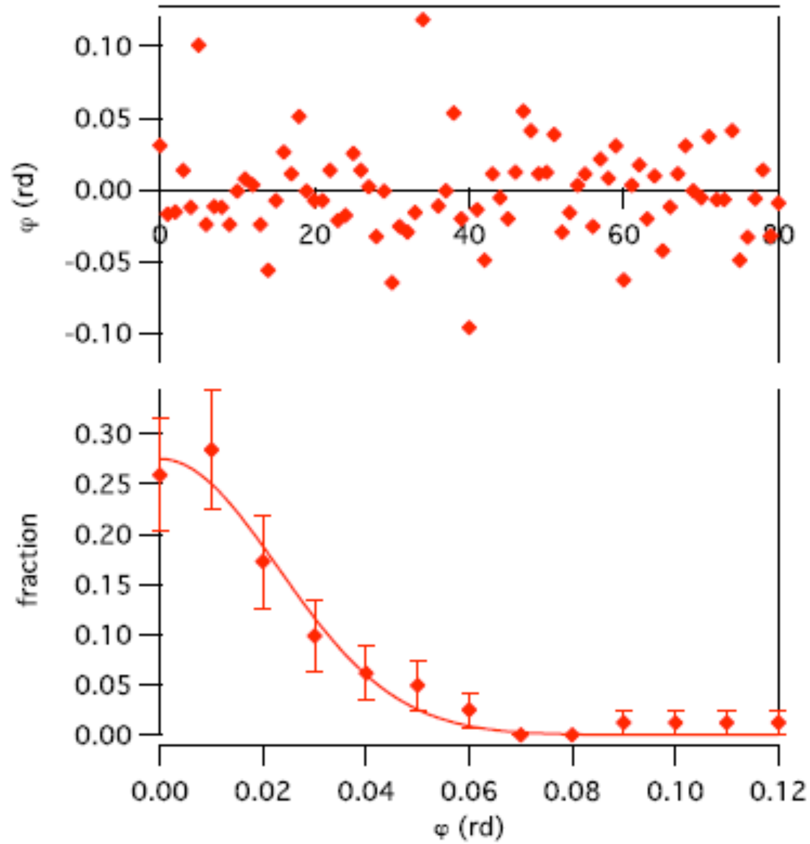
$P_a(r)$ is gaussian of average value r_0 and its standard deviation

$$P(q) = \left(\int p_a(r) r^2 \frac{2J_1(qr)}{qr} dr \right)^2$$

Angle deviation φ of the pores

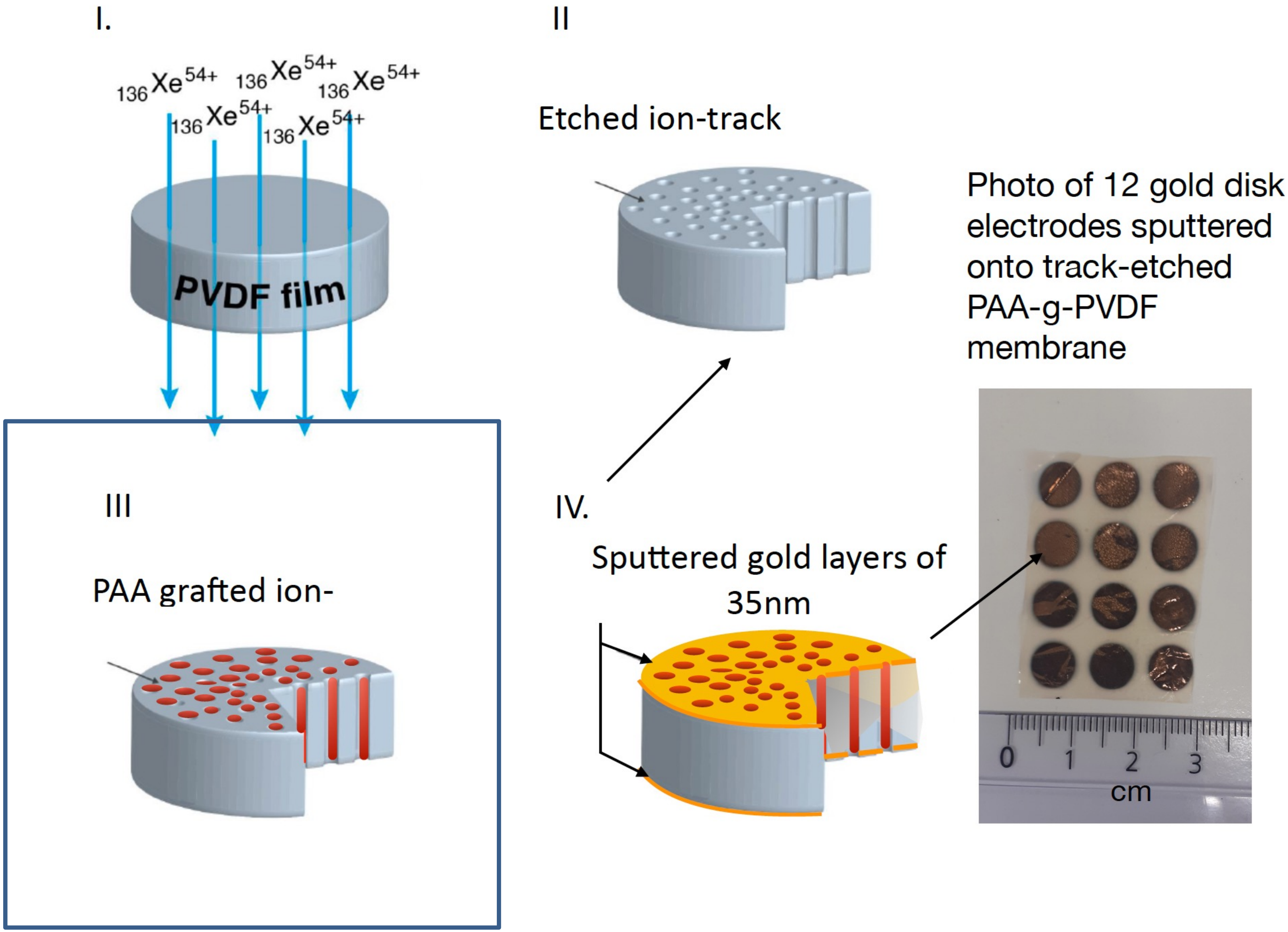


Confocal Laser Scanning Microscopy
of a track-etched PVDF membrane ($5x10^6$ cm^{-2})



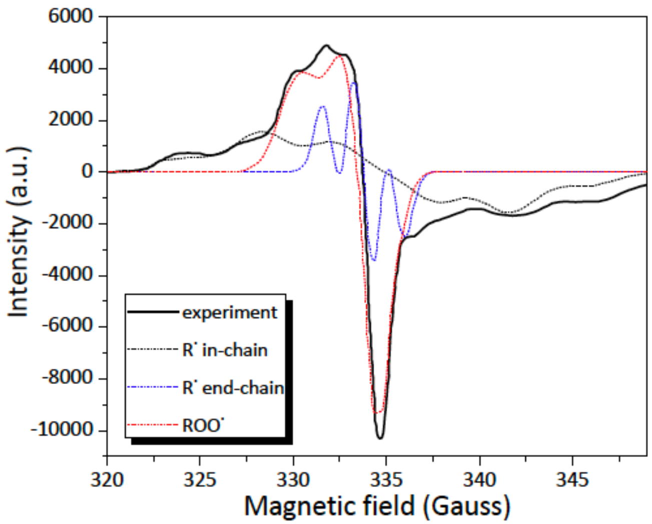
Mean deviation σ_φ = 0.023rd

Membrane-electrode fabrication



Induced radicals + functionalization by radical polymerization

EPR spectra of 9µm β-PVDF films irradiated by (left) e-beam (1.25 MGy) from [41]; (right) Swift Heavy Ions (krypton of 10MeV/mau, fluence of 10^{10} cm^{-2} corresponding to 76 kGy) and e-beam (50 kGy)



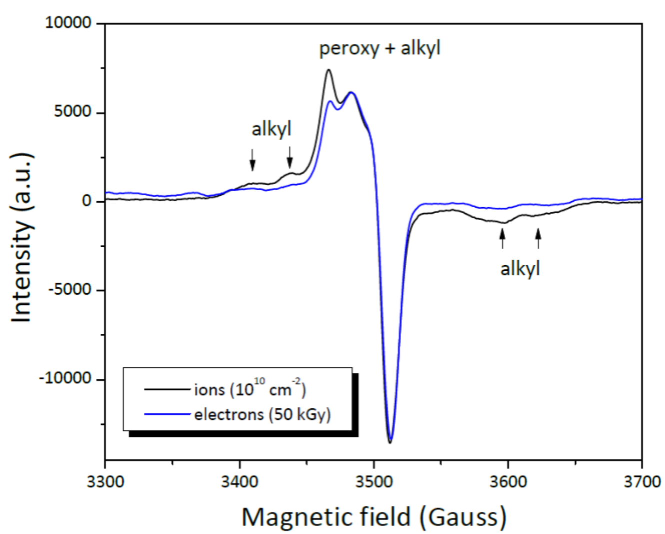
Radical	$-CH_2-CFOO^\bullet-CH_2-$	$-CF_2-C^\bullet H-CF_2$	$-CF_2-C^\bullet H_2$
$g-value$ ΔB_{pp} [Gauss] A [Gauss]	$g_\parallel = 2.0327,\ g_\perp = 2.009$ $\Delta B_{pp}^\parallel = 20,\ \Delta B_{pp}^\perp = 18$ –	$g_{iso} = 2.004$ $\Delta B_{pp} = 33$ $A_F = 43,\ A_H = 23$	$g_{iso} = 2.009$ $\Delta B_{pp} = 12$ $A_H = 16$

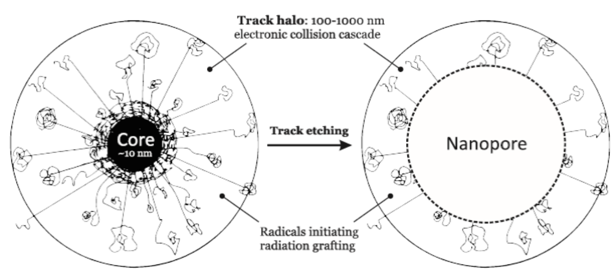
g-values of common radiation-induced radical species in PVDF

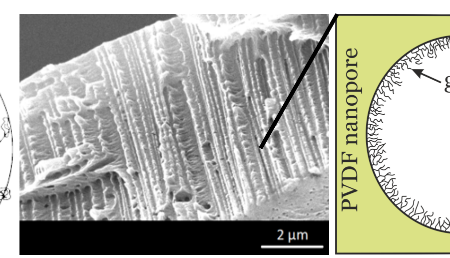
Radio-induced polymerization reactions occurring (so-called radio grating) inside nanopores

$$RH \xrightarrow[vacuum]{irradiation} R^\bullet + H^\bullet$$
$$R^\bullet + M \rightarrow RM^\bullet$$
$$RM^\bullet + nM \rightarrow RM^\bullet_{n+1}$$
$$RM^\bullet_n + RM^\bullet_m \rightarrow RM_{n+m}$$

$$RH \xrightarrow[O_2/air]{irradiation} R^\bullet + H^\bullet$$
$$R^\bullet + O_2 \rightarrow ROO^\bullet$$
$$ROO^\bullet + RH \rightarrow ROOH + R^\bullet$$
$$ROOH \xrightarrow{\Delta} RO^\bullet + {}^\bullet OH$$
$$RO^\bullet + M \rightarrow ROM^\bullet$$
$$ROM^\bullet_n + ROM^\bullet_m \rightarrow ROM_{n+m}$$





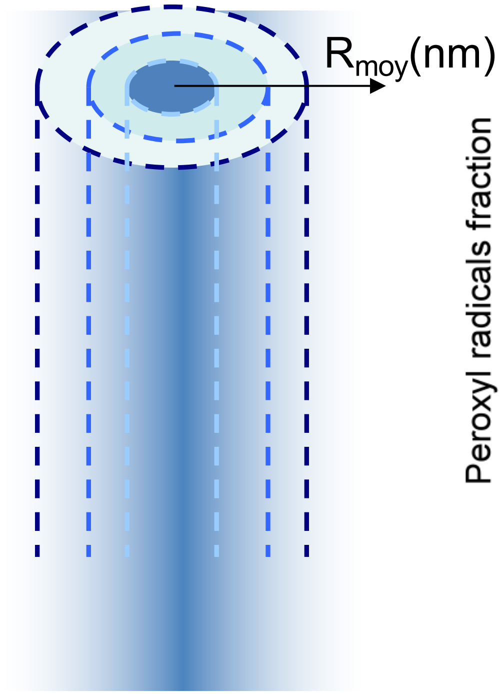


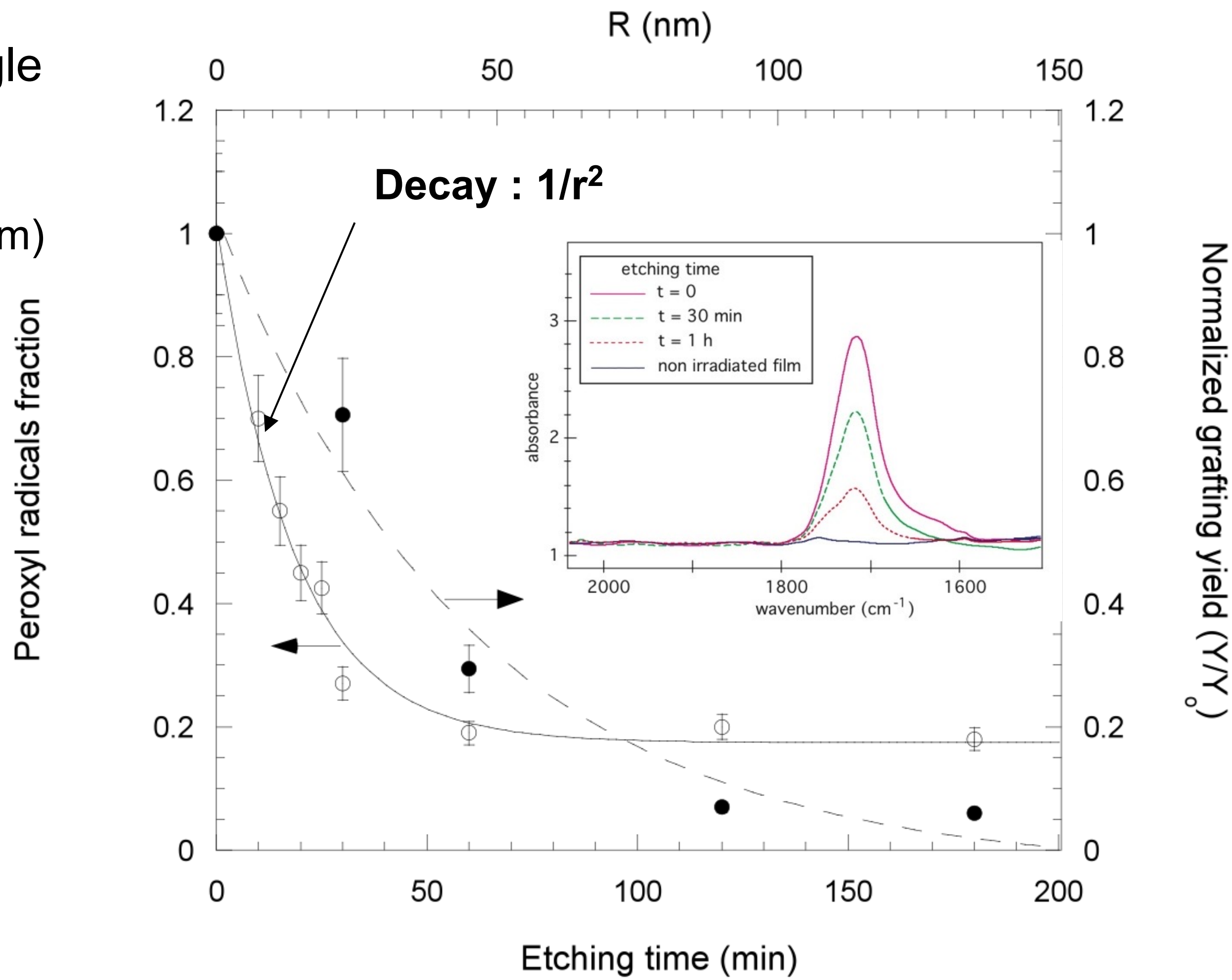
FTIR
NMR
XPS

*Review : Aiysha Ashfaq et al. Polymers **2020**, 12, 2877*

Remaining radical fraction profile per track

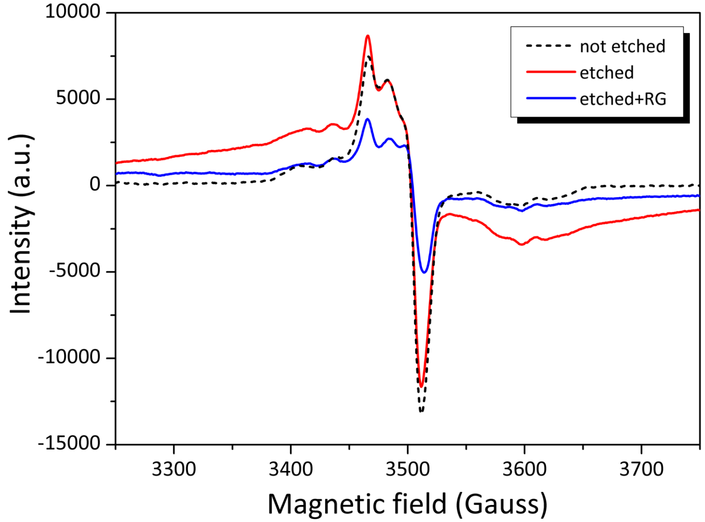
f averaged and normalized to a single track



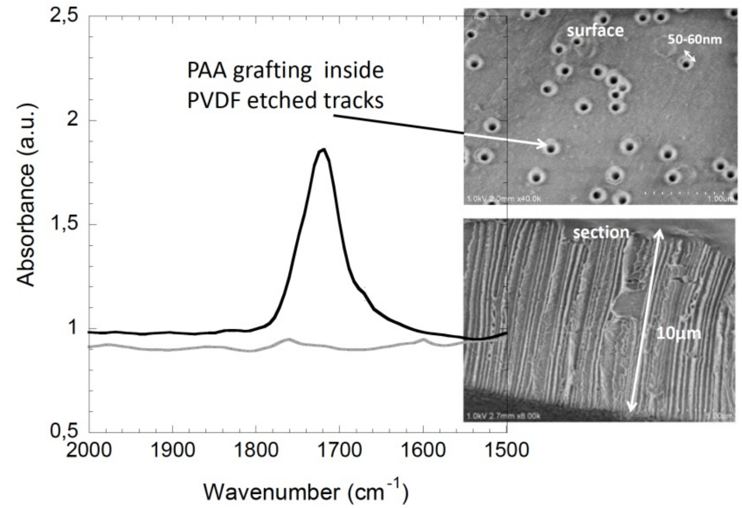


Poly(acrylic acid)-grafted-PVDF membrane

EPR before and after grafting

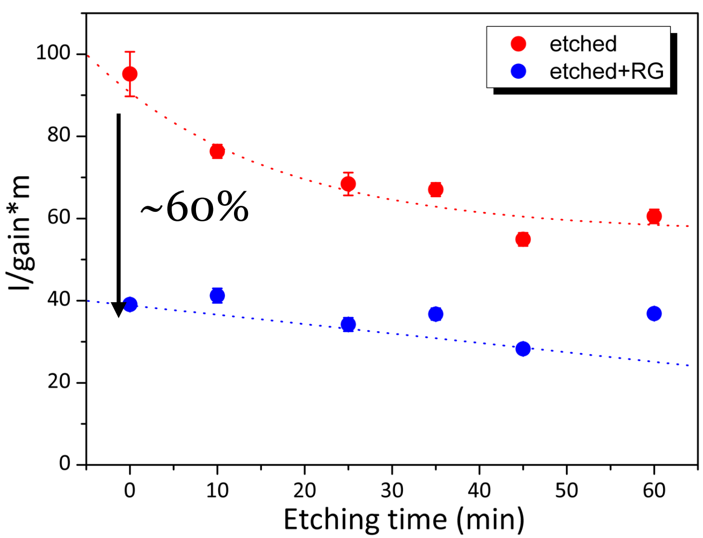


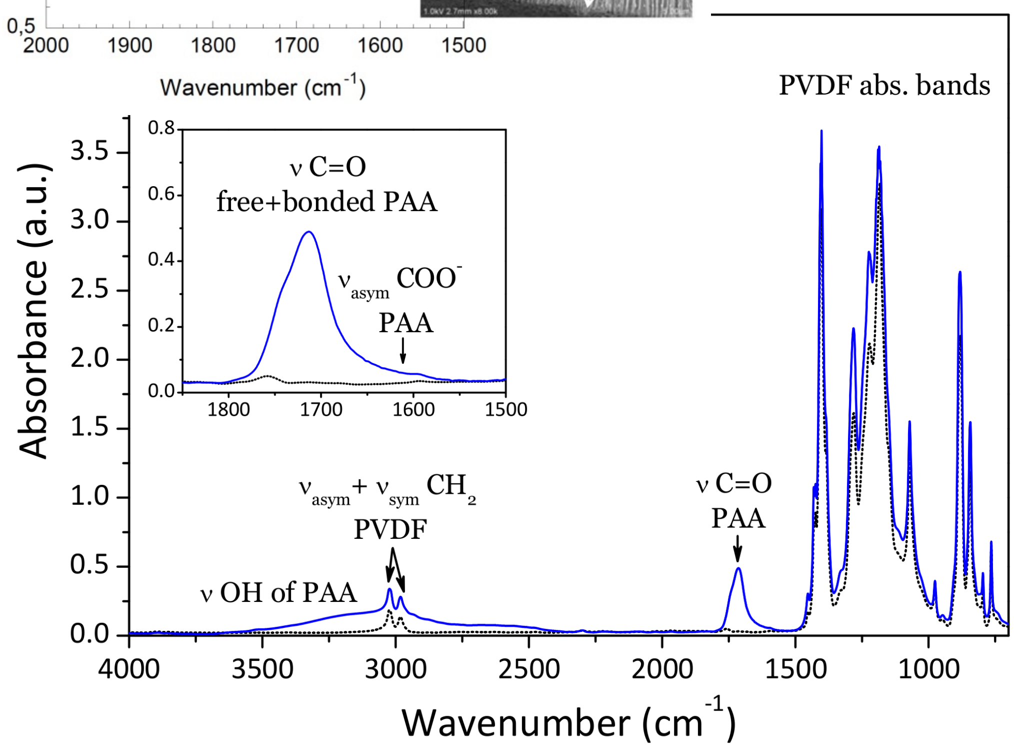
[AA] = 7mM; 1h; 60°C , Mohr salt



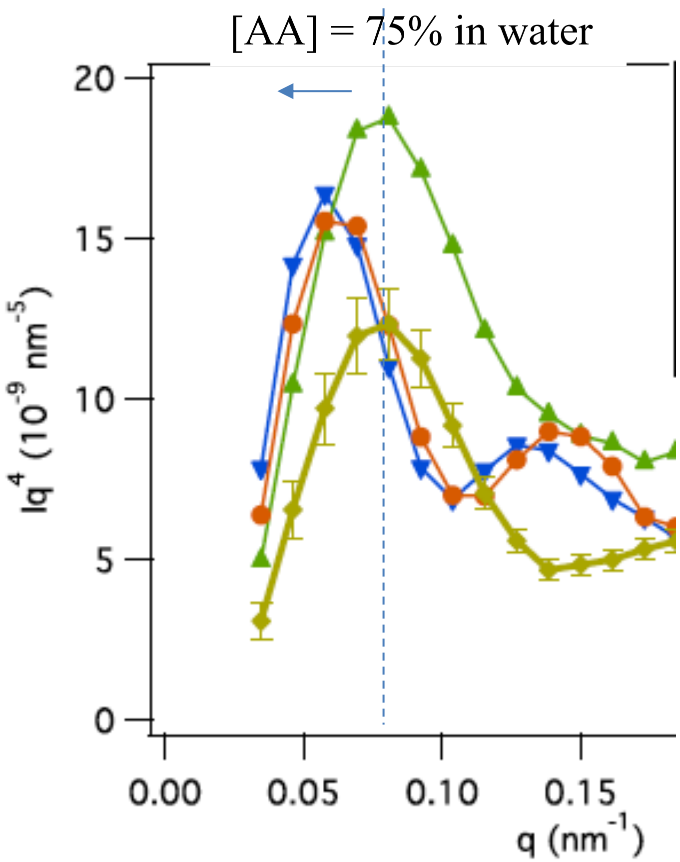
FTIR
& FESEM
characterization

Radical decay due to PAA radiografting



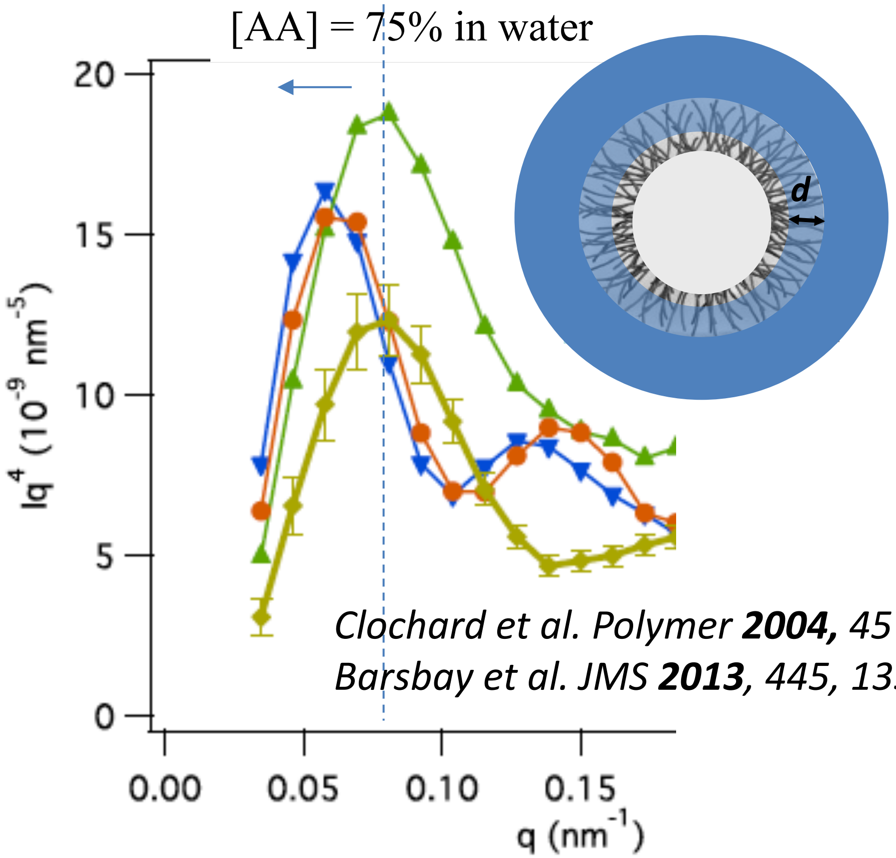


Red: dried state
Blue: acidic solution pH 2
Green triangles: basic solution pH 8



Small Angle Neutron Scattering (SANS) spectra obtained at LLB CEA Saclay, France (PACE spectrometer) for track-etched PVDF membranes exhibiting nanopores of 50 nm of initial radius (light green circles)

Red: dried state
Blue: acidic solution pH 2
Green triangles: basic solution pH 8



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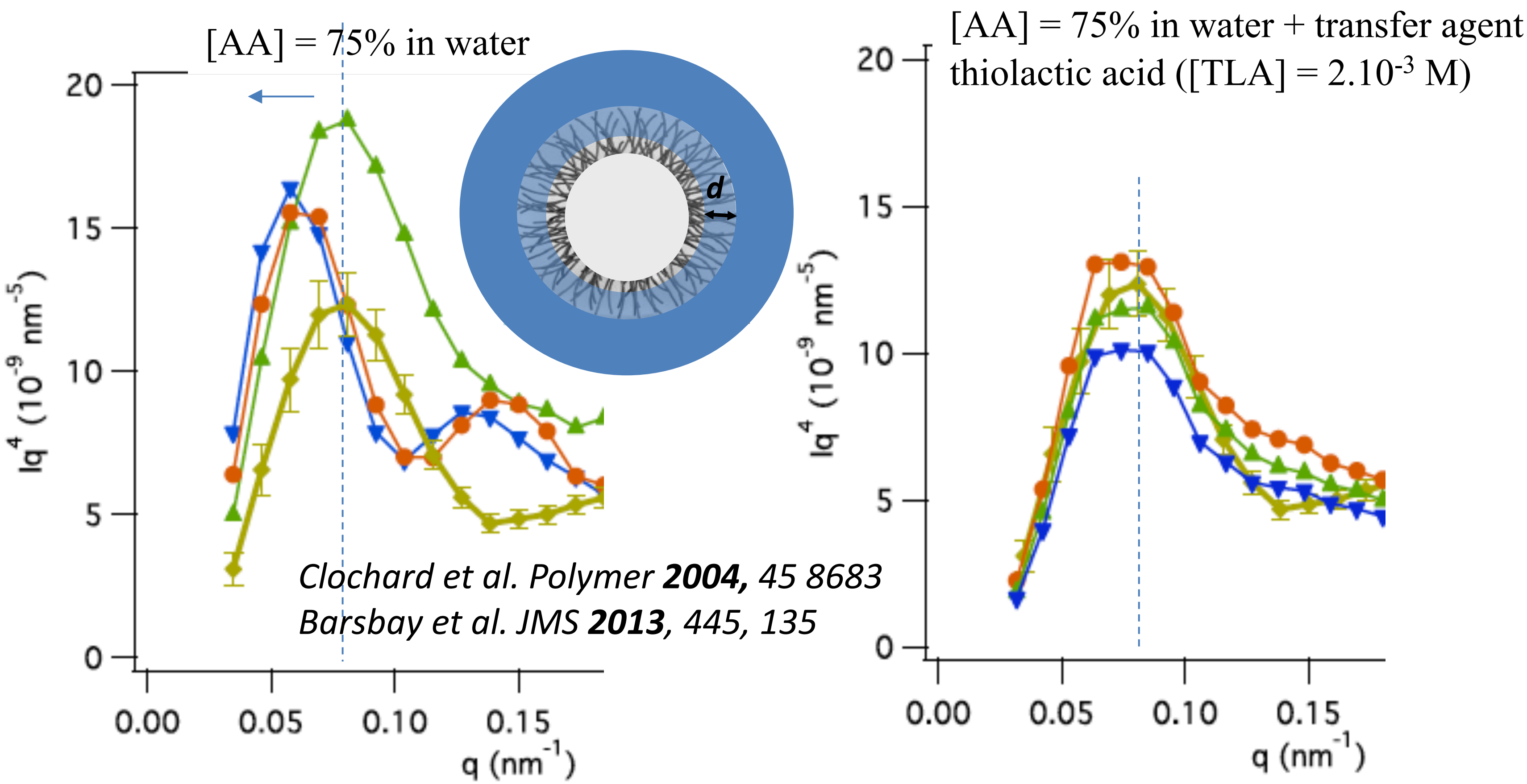

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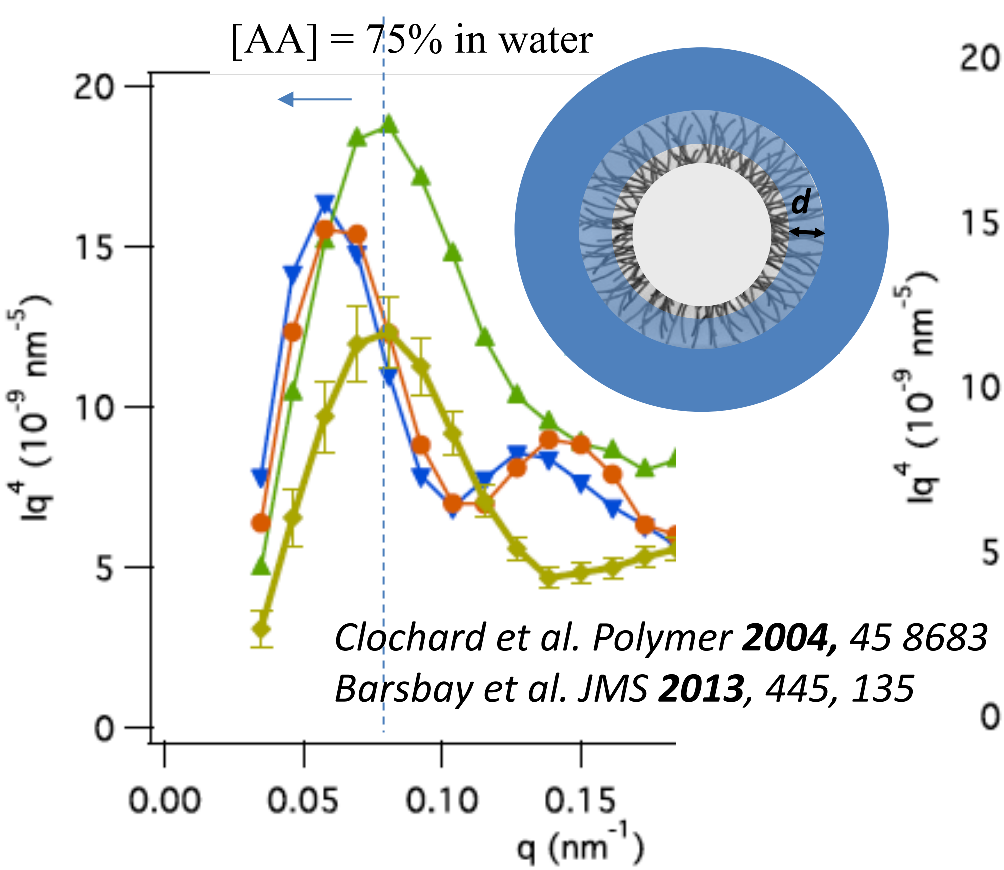

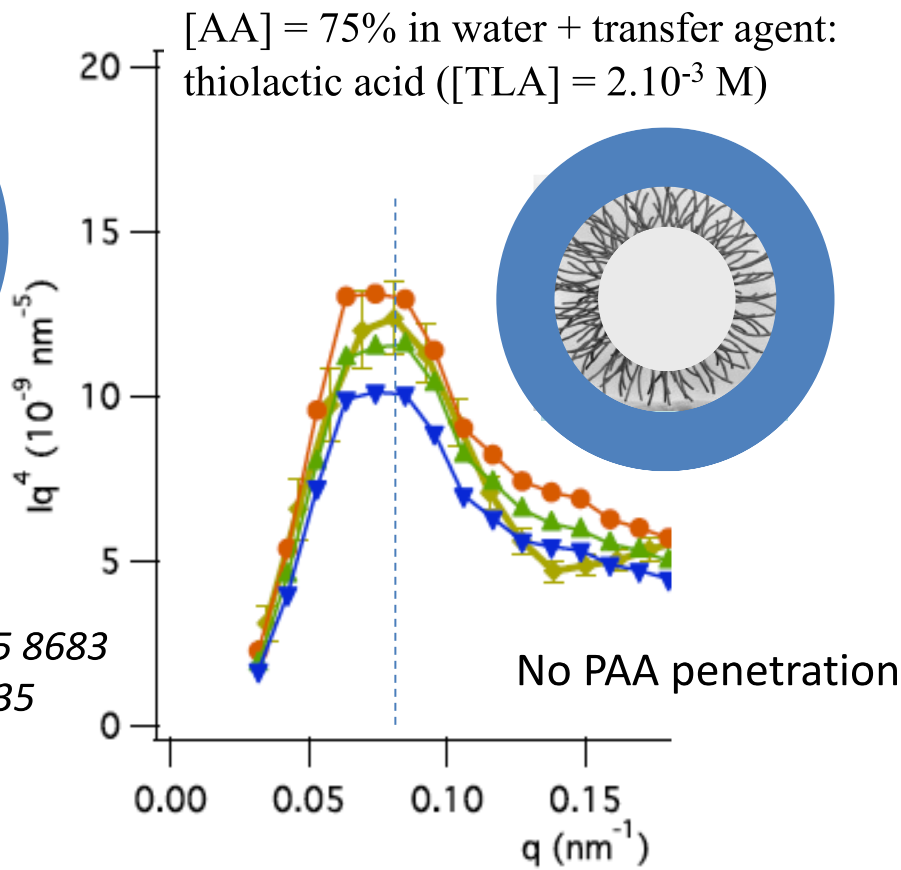

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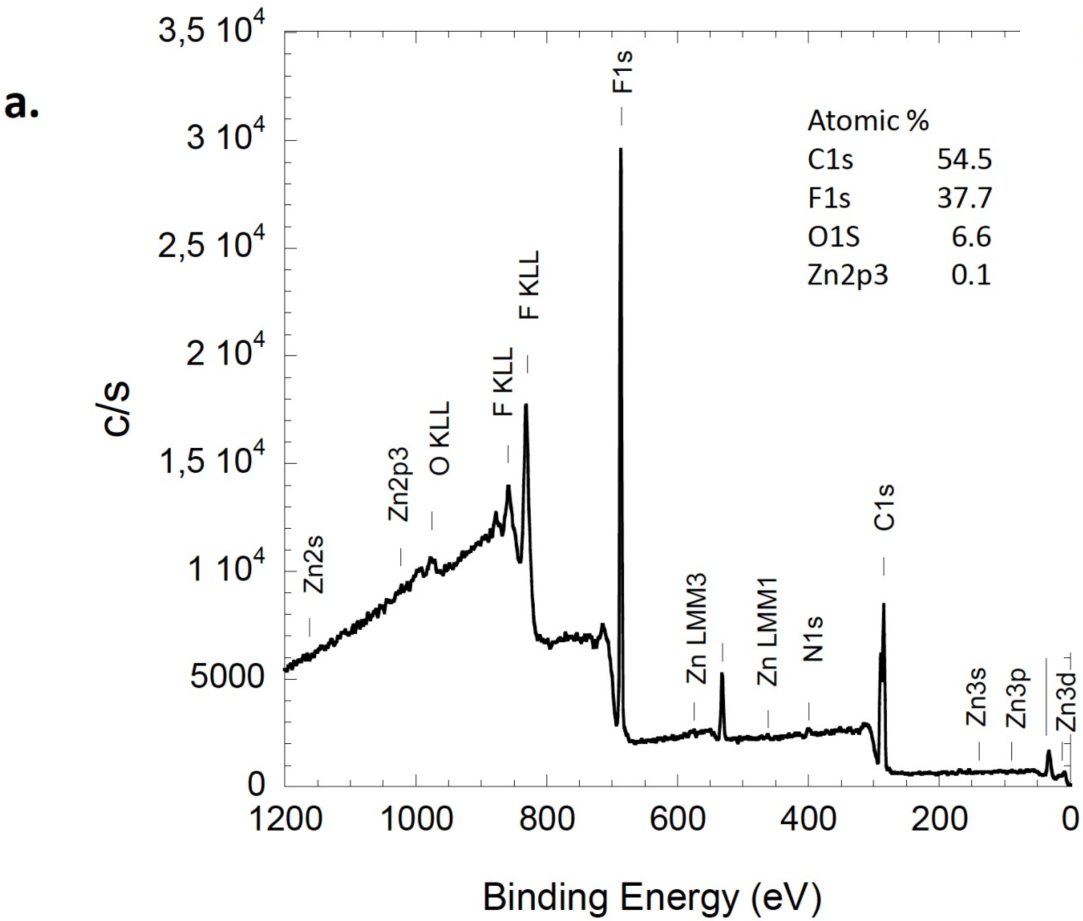
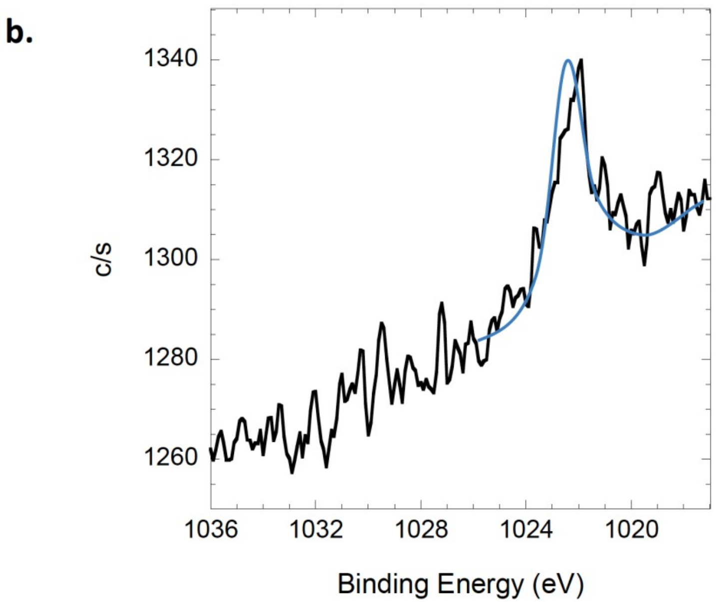
Review : Aiysha Ashfaq et al. Polymers ***2020****, 12, 2877*

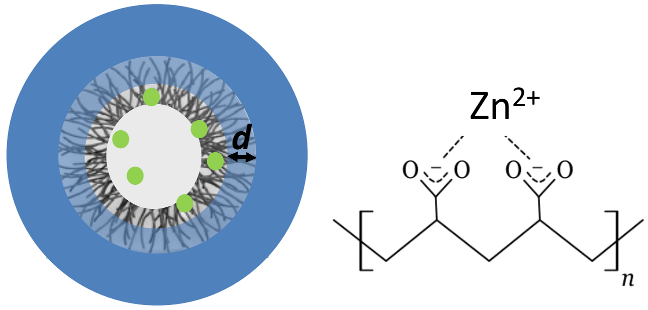
Zn adsorption in PAA-grafted-PVDF membrane nanopores by XPS

XPS survey spectrum



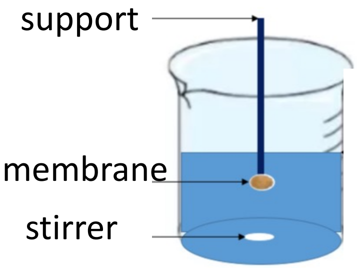
region of $Zn2p_{3/2}$ peak at 1022.14 eV





Electrostatic interaction

Zn adsorption capacity of PAA-grafted-PVDF nanoporous membrane

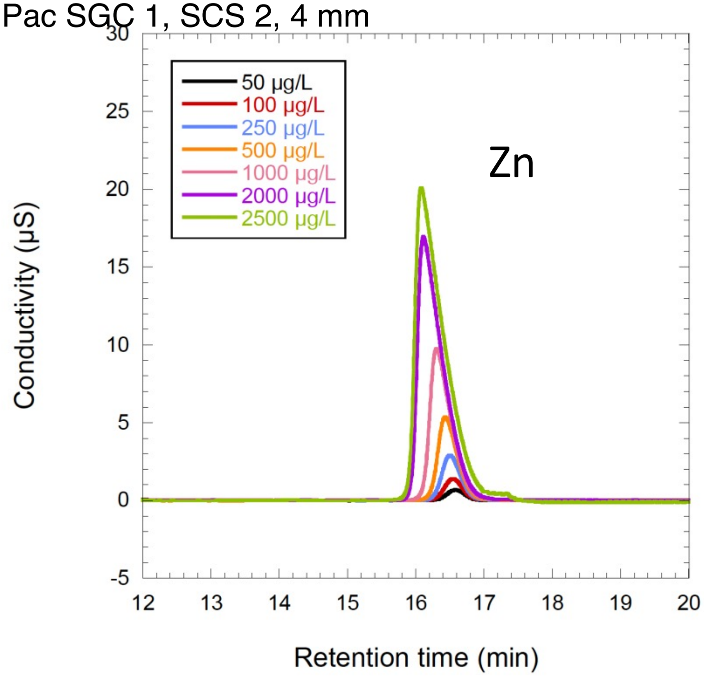


Langmuir model

$$q = \frac{q_{max} b c_{eq}}{1 + b c_{eq}}$$

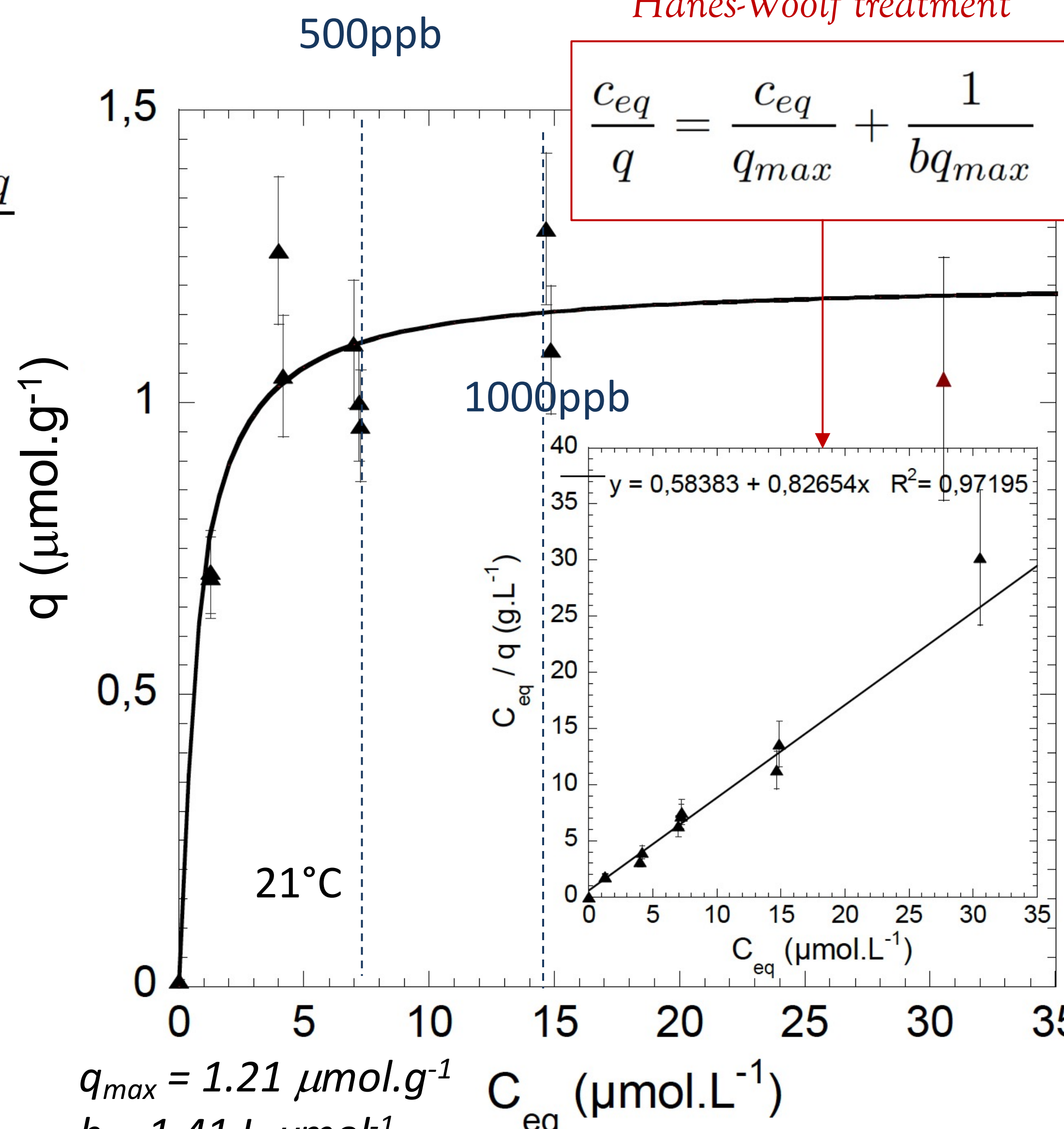
Ion chromatography

Dionex EASION IC, 1mL.min^{-1}
2.5 mM MSA / 0.8 mM oxalic acid
IonPac TCC, LP1, 4x25 mm
IonPac SGC 1, SCS 2, 4 mm



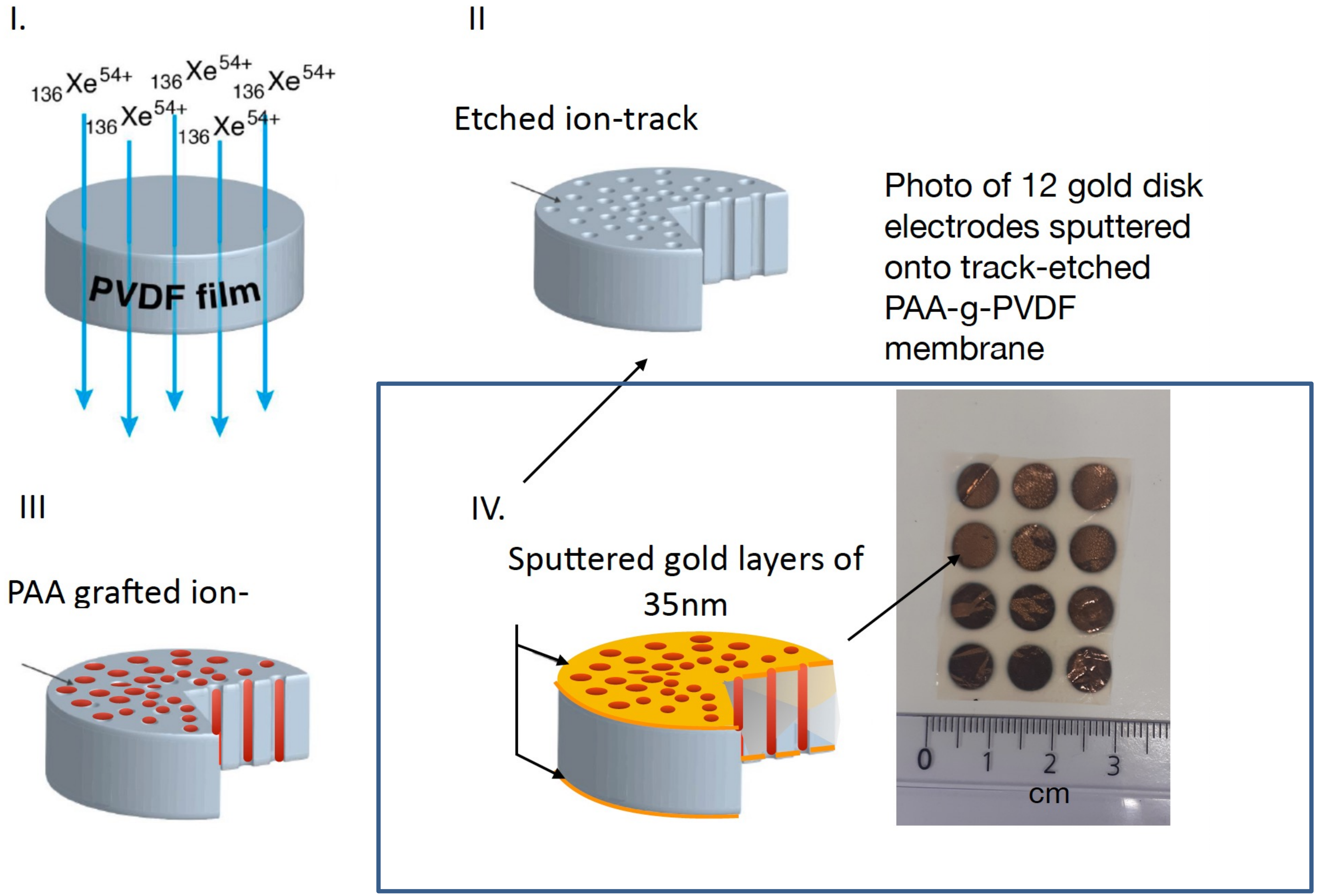
Hanes-Woolf treatment

$$\frac{c_{eq}}{q} = \frac{c_{eq}}{q_{max}} + \frac{1}{b q_{max}}$$

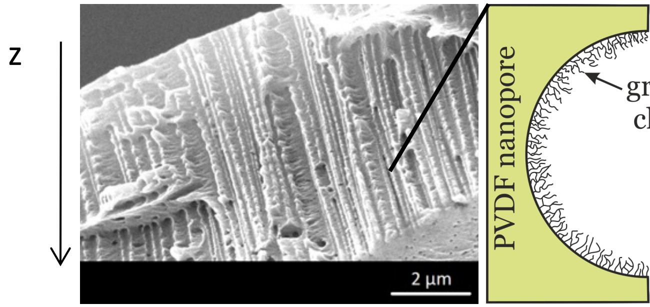


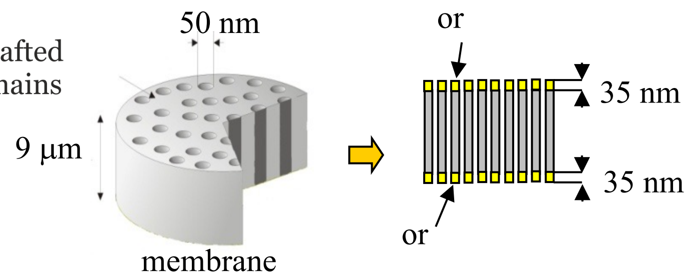
q_{max} = 1.21 µmol.g^{-1}
b = 1.41 L.µmol^{-1}

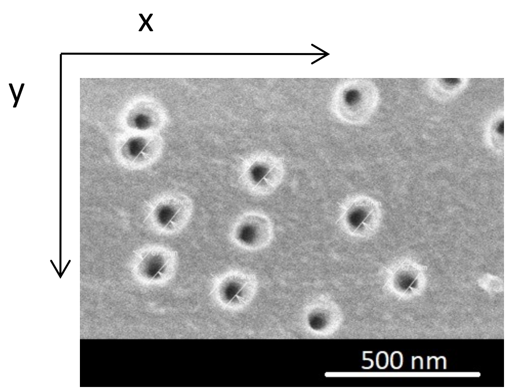
Membrane-electrode fabrication



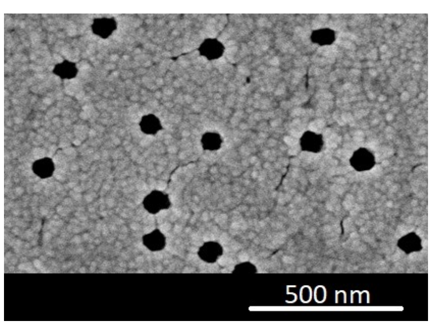
Gold sputtering: changeover into electrodes



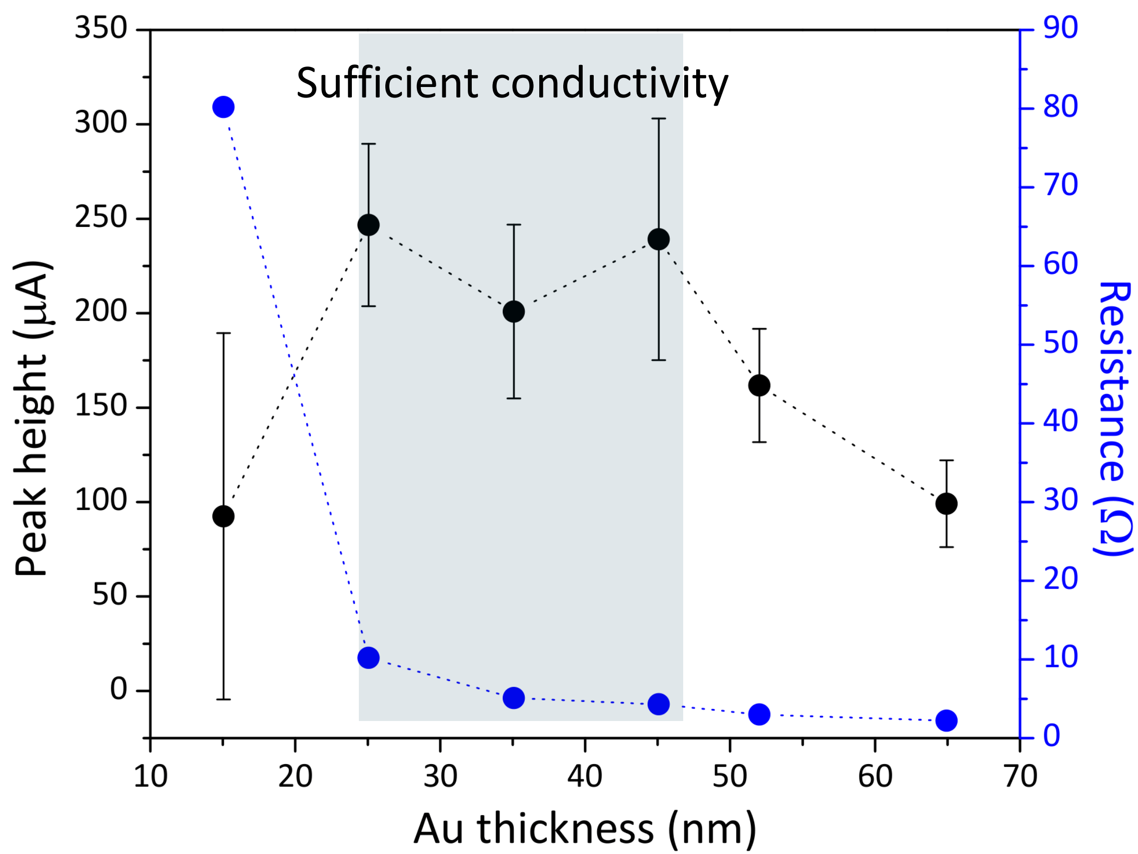




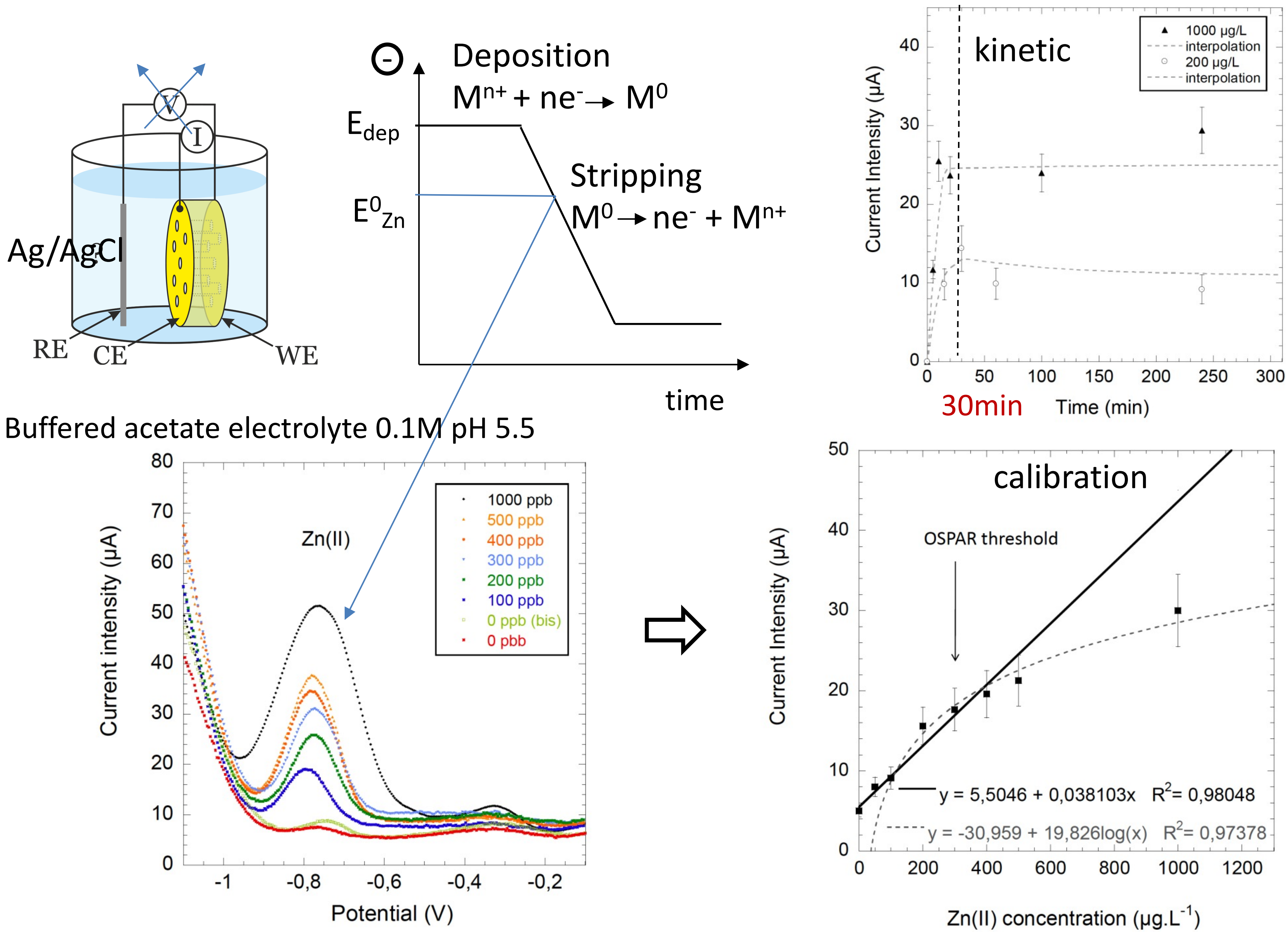
Before Au sputtering



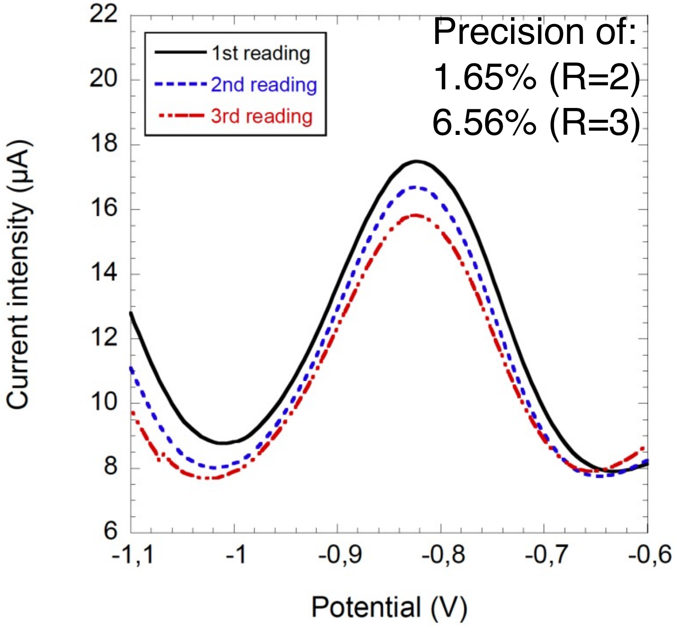
After Au sputtering

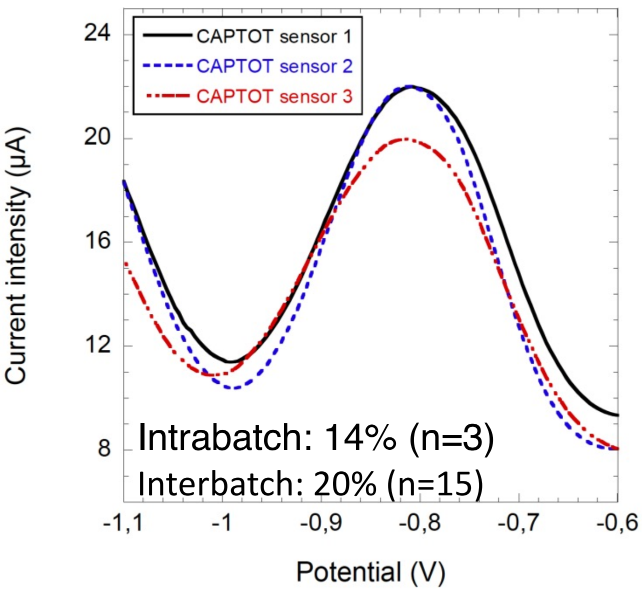


Anodic Stripping Voltammetry detection of adsorbed Zn(II)

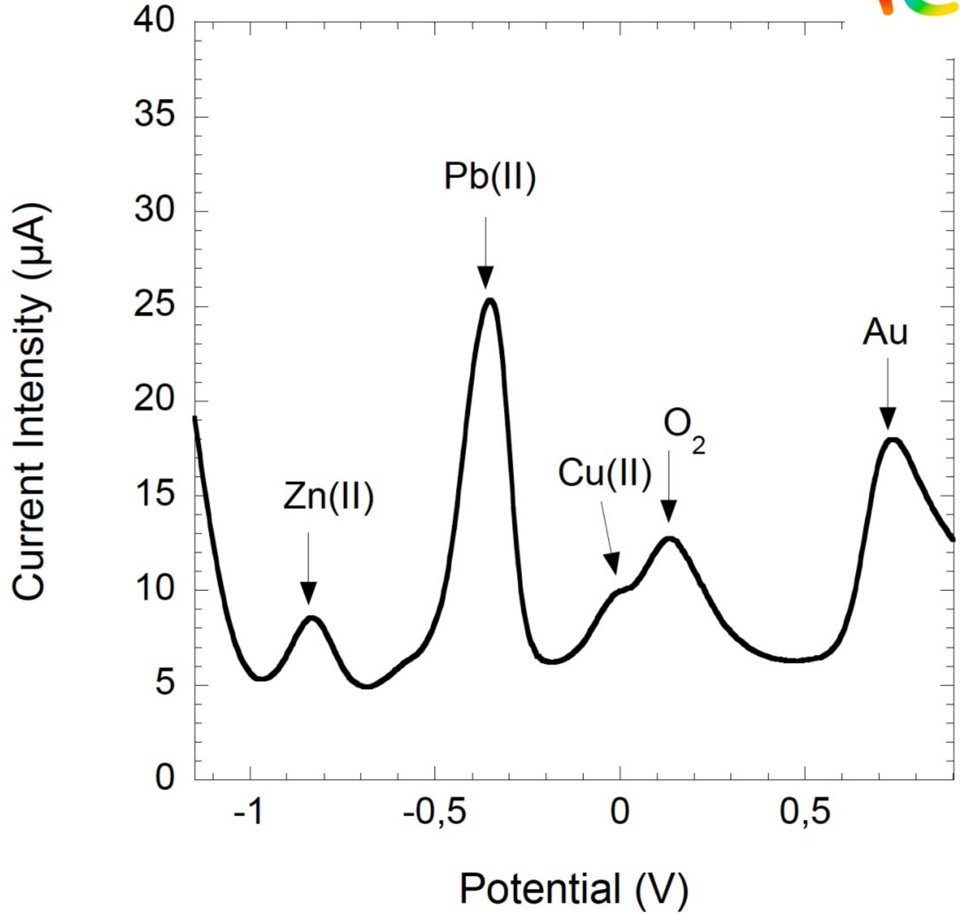


Repeatability, reusability and selectivity in synthetic waters





Synthetic water: 0.80M NaCl, (50g.L^{-1}) 0.80mM KCl, 0.70mM Ca^{2+}, 0.98mM Mg^{2+}, 0.07mM Na_2SO_4, 1.04mM $NaHCO_3$ + oil (59mg.L^{-1} of TOC)



200 µg.L^{-1} (0.96µM) Pb, 200 µg.L^{-1} (3.14µM) Cu and 200 µg.L^{-1} (3.06µM) Zn in 50g. L^{-1} spiked NaCl solution

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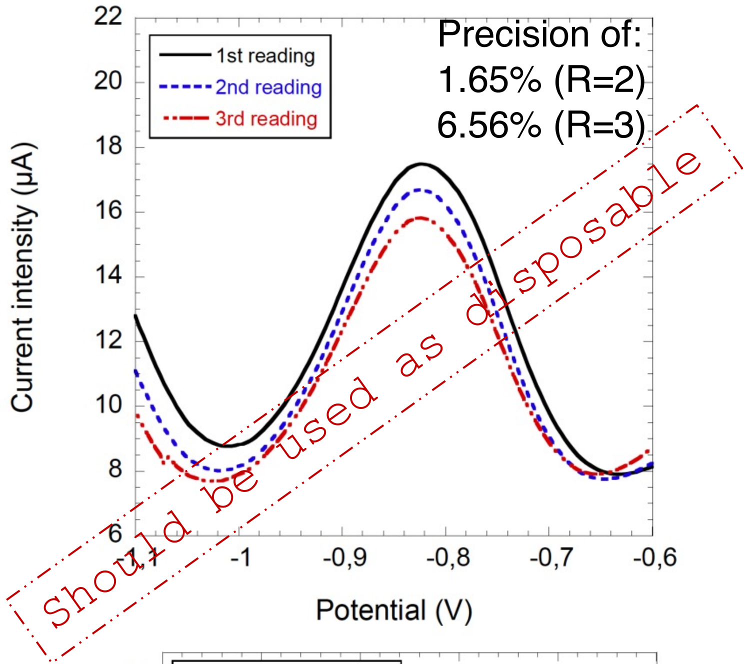

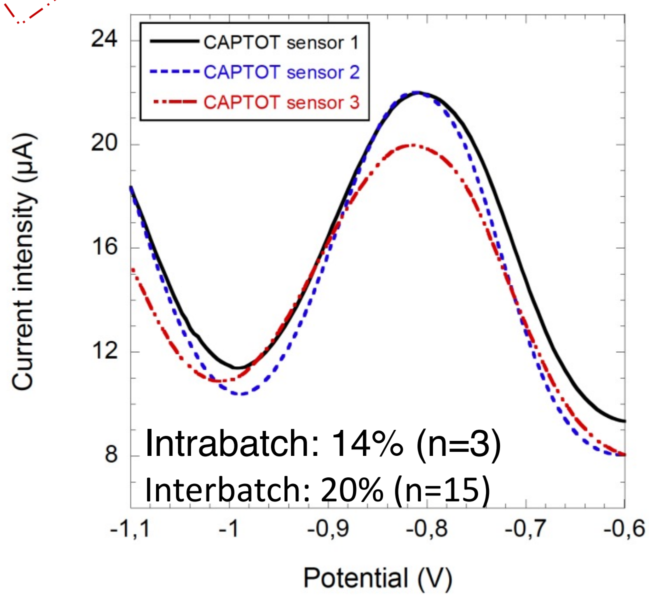

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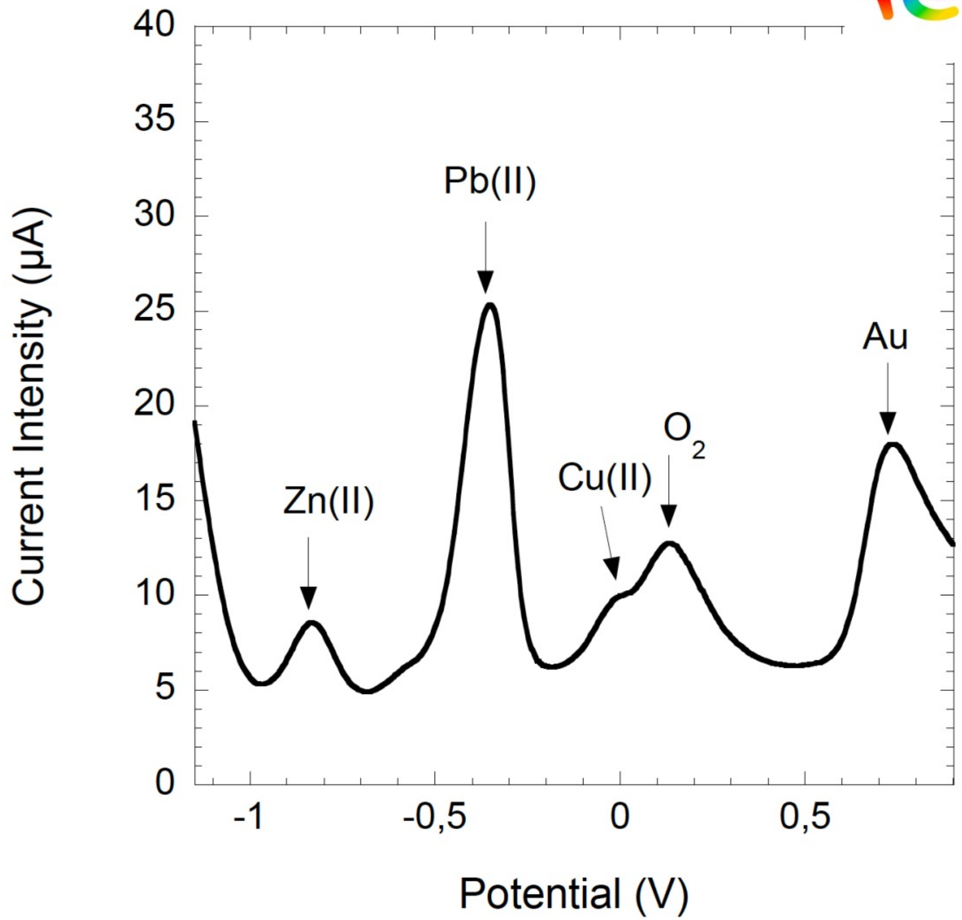

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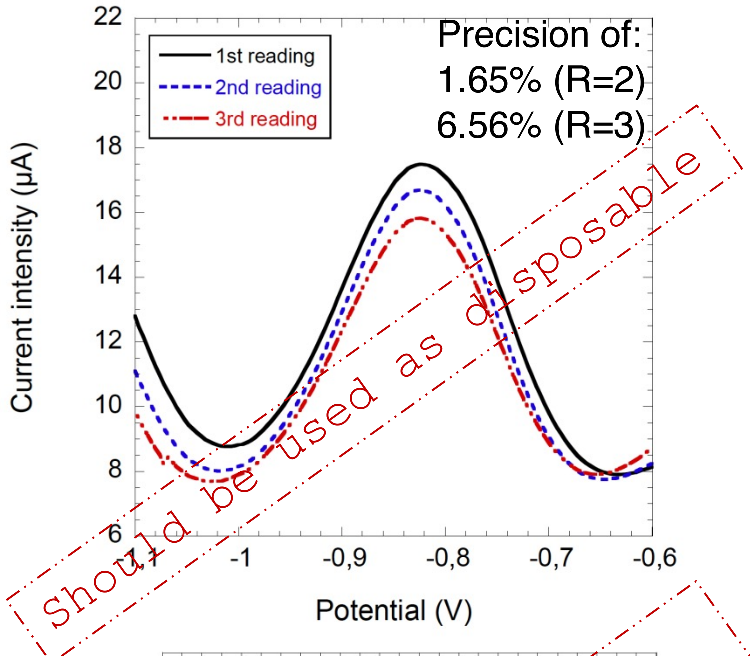

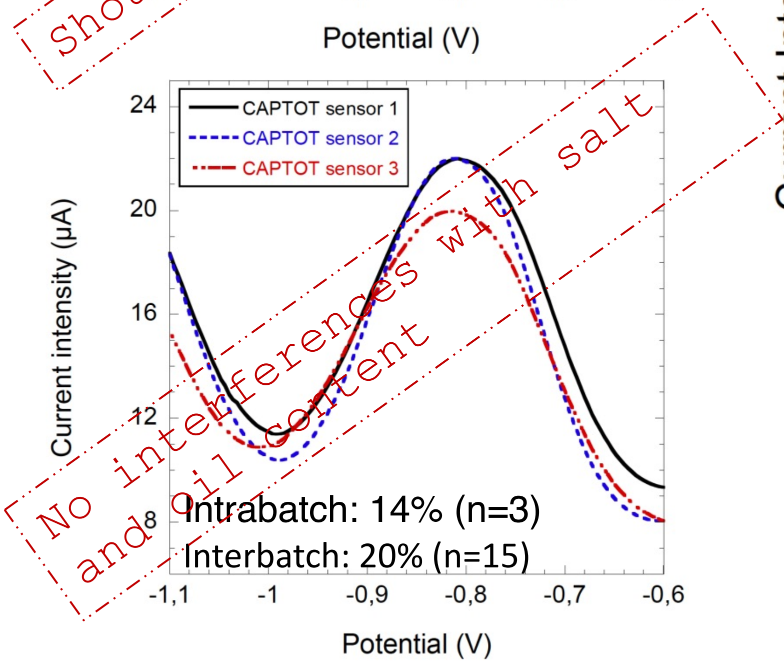

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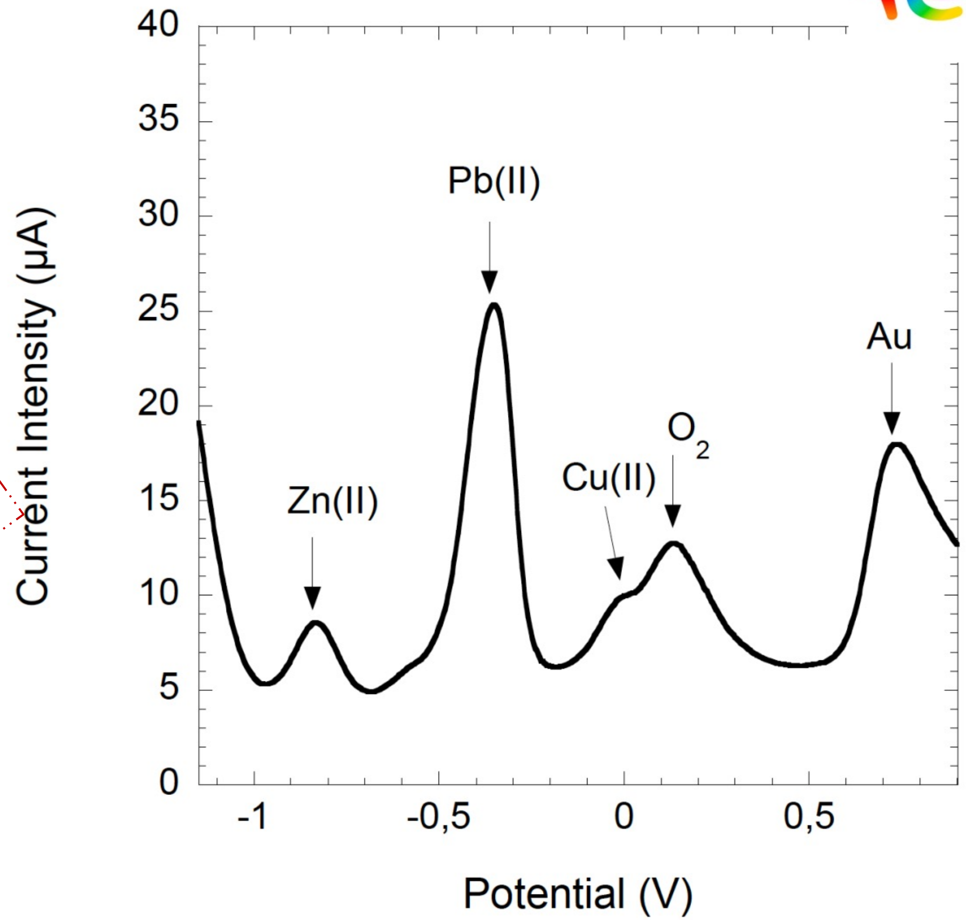
TotalEnergies



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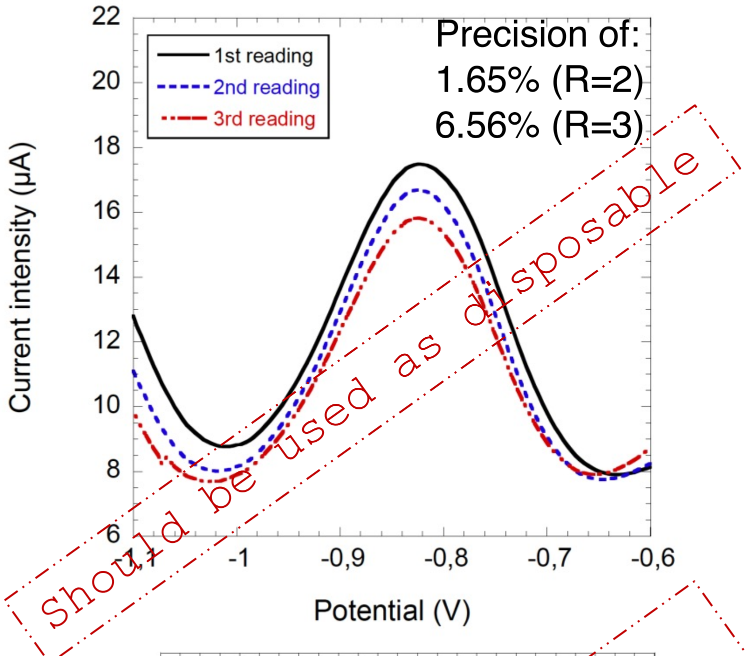

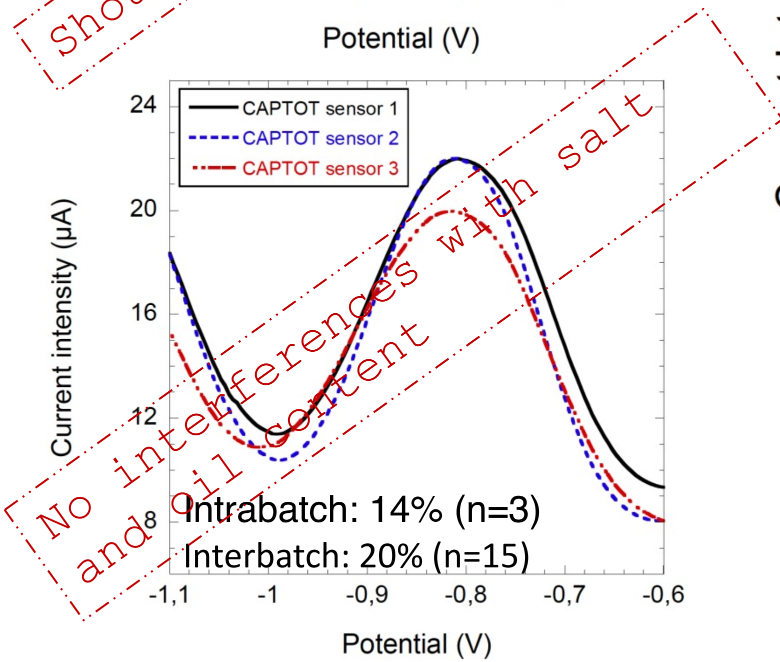

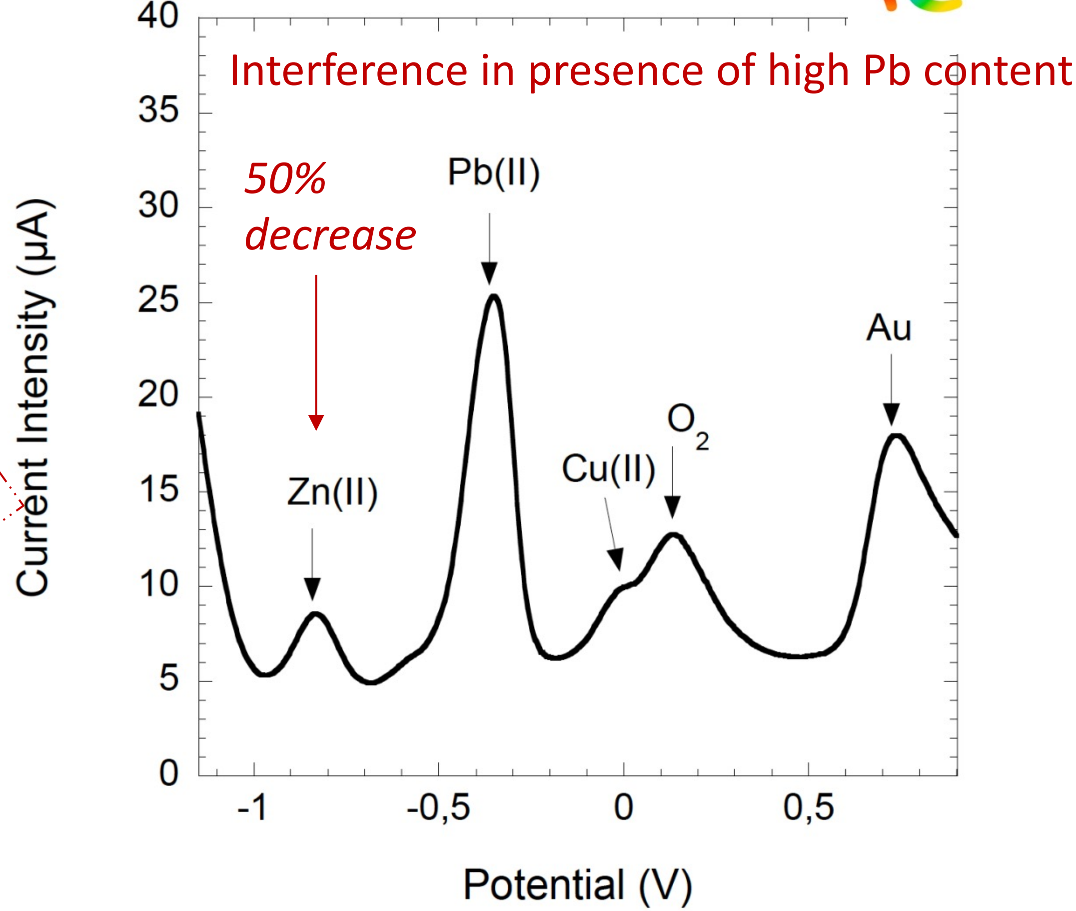

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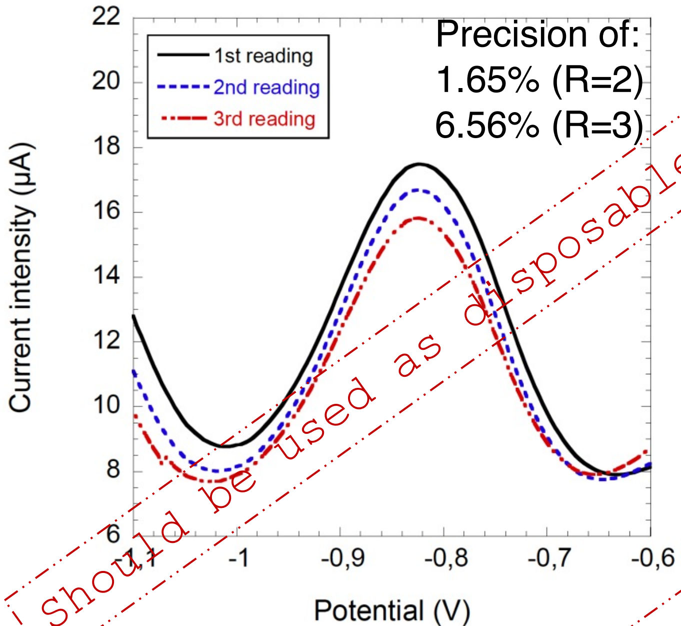

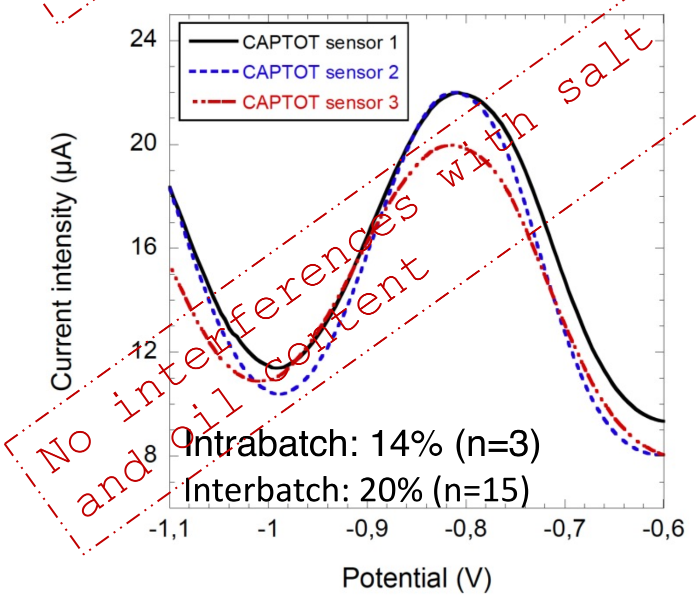

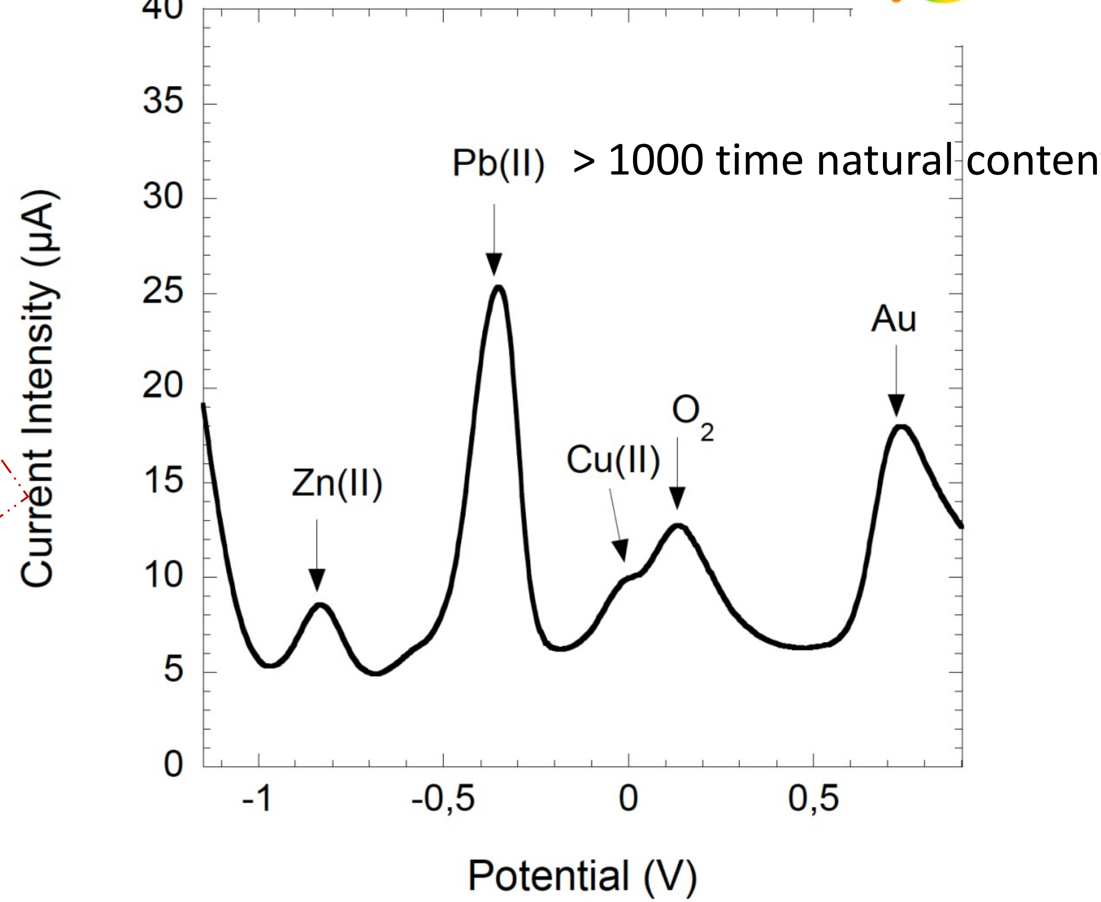

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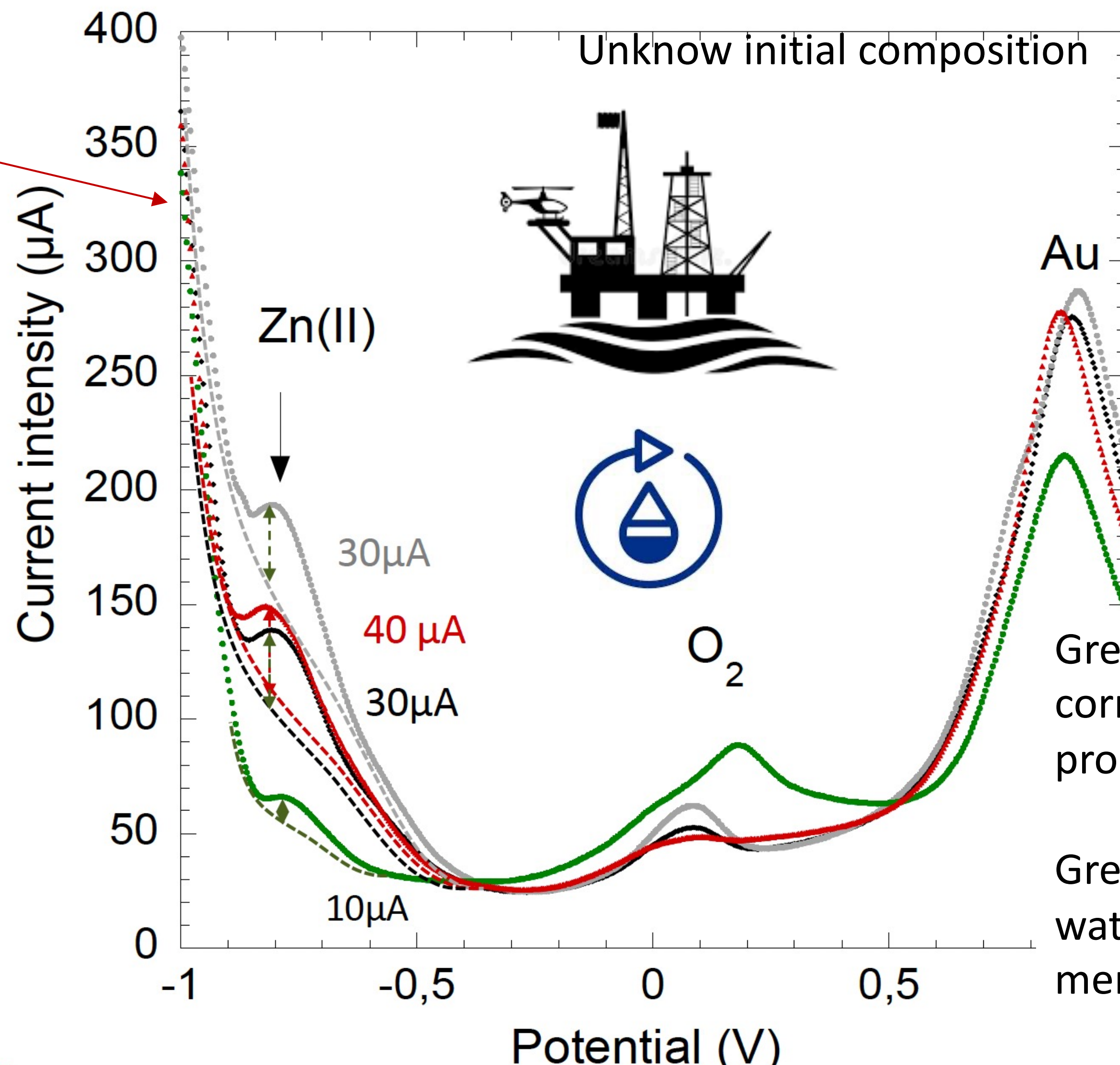
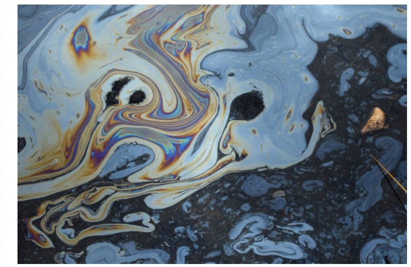
Raw production Water Electrochemical Analysis

Hydrogen wave is shifted to positive potentials due to acidic medium



Buffered acetate electrolyte 0.1M pH 5.5



ICP-MS

Grey and black curves corresponds to raw production water

Green for production water after PVDF-g-PAA membrane sampling

Red 1ppm Zn(II) addition

TotalEnergies

Comparison of Zn(II) electrochemical sensors demonstrating true or high potential application for real seawater analyses with reported sensors

Electrode	Technique - *In-situ* or on-site solution	Deposition time	Linear range (μg.L^{-1})	LOD (μg.L^{-1})	Refs
Hg based electrode	SWASV - Voltammetric *in-situ* submersible profiler	300s at -0.75V and 180s at -0.35V	0.1-10	0.002	[18], [23]
Vibrating gold microwire	SWASV - *ex-situ* measurements with *in-situ* potentiality	300s at -0.9V	0.065-6.5	0.02	[19]
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Poly(sodium 4-styrenesulfonate) wrinkled rGO composite	DPASV - *ex-situ* measurements	300s at -1.4V	0.3-50	0.1	[20]
Thin nanoporous gold disk sputtered onto PAA-g-PVDF membranes	SWASV - on-site solution with submersible probe for *in-situ sampling*	150s at -1.2V	10-500 (100-1000 linear-log fitting)	4.2	this work

[18] Tercier M.L., Buffle J., Zirino A., Vitre R.Rd., In-situ voltammetric measurement of trace elements in lakes and oceans. *Anal. Chem. Acta* **237** 429-437 (1990).

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. None of others techniques :
- can alert on pollution event
- were confronted to oil polluted seawater samples

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Zinc detection in oil-polluted marine environment by stripping voltammetry with mercury-free nanoporous gold electrode

M.-C. Clochard[1]✉, O. Oral[1], T. L. Wade[1], O. Cavani[1], M. Castellino[2], L. Medina Ligiero[3] & T. Elan[3]

1. *Laboratoire des Solides Irradiés, CNRS-CEA-Ecole Polytechnique, UMR7642, Institut Polytechnique de Paris, 91120 Palaiseau Cedex, France*
2. *Department of Applied Science and Technology (DISAT), Politecnico di Torino, C. so Duca degli Abruzzi 24, 10129, Torino, Italy*
3. *TotalEnergies, PERL, Lacq, 64000 Pau, France*

Limits of detection in deionized water

Hg par SW-ASV

10 mM HNO_3 + 10 mM NaCl, -0.8 V, 50 sec, 75 Hz

Hg(II) → LOD ~ 0,01 $\mu g.L^{-1}$ (ou ppb)*

Pb(II) → LOD ~ 2 $\mu g.L^{-1}$**

Zn(II) → LOD ~ 2 $\mu g.L^{-1}$

Cu(II) → LOD ~ 5 $\mu g.L^{-1}$

Sb(III/V) → LOD ~ 10 $\mu g.L^{-1}$

Cd(II) → LOD ~ 10 $\mu g.L^{-1}$

Ni(II) → LOD ~ 10 $\mu g.L^{-1}$

U(VI) → LOD ~ 10 $\mu g.L^{-1}$ (SW-CSV)µ***

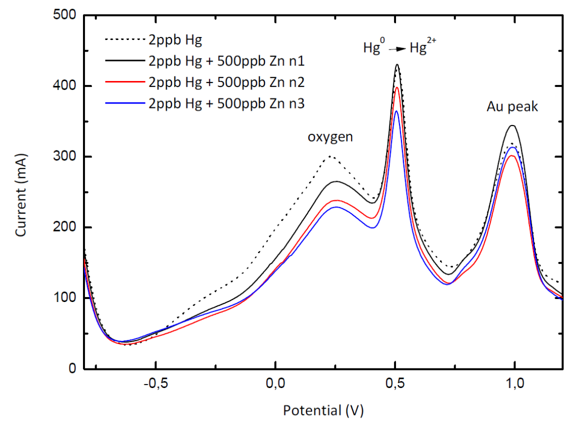
Se(IV) → LOD ~ 50 $\mu g.L^{-1}$

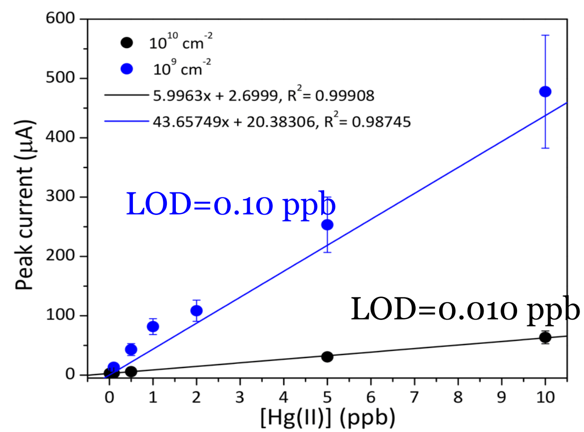
As(III) → LOD ~ 50 $\mu g.L^{-1}$

Mo(IV) → LOD ~ 133 $\mu g.L^{-1}$

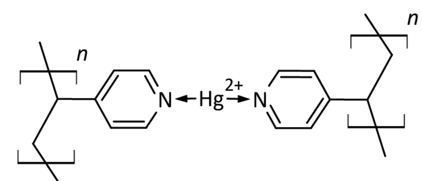
Zn(II) → LOD ~ 2 $\mu g.L^{-1}$

Cr(VI) → LOD ~ 20 $\mu g.L^{-1}$ (SW-CSV)





High affinity for mercury due to Metal : Ligand complex



$[Pyr\text{-}Hg\text{-}Pyr]^{2+}$ complex

*Pinaeva et al. Journal of Hazardous Materials 376 (2019) 37–47

**Bessbousse et al Anal. Methods, 2011, 3, 1351

***Pinaeva et al Reactive and Functional Polymers 142 (2019) 77–86

Thank you all for your attention

Acknowledgements

Fundings

RÉPUBLIQUE FRANÇAISE
Liberté
Égalité
Fraternité

anr agence nationale de la recherche
AU SERVICE DE LA SCIENCE

TotalEnergies

cea

VINCI CONSTRUCTION

International irradiation and neutrons falicities

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Réseau national d'accélérateurs pour l'irradiation et l'analyse des molécules et matériaux

LLB Orphée
Laboratoire Léon Brillouin

Industrial partners for prototyping

VALOTEC

IDO
Études & Production

Academic partner

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1859 1906

CAPTÔT

Protecting water starts with knowing it