Can polymer inclusion membranes be used as an integral tool to facilitate environmental samples analysis? The case of mercury

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Outline

1. Introduction & objective
2. PIMs as extraction phases: water and soils
3. PIM-device as a new sensor for Hg monitoring
4. Conclusions

Environmental samples analysis

Sampling method

Water, solis, air, grab or passive sampling,...

Sample pretreatment

liquid-liquid extraction (LLE), solid phase extraction (SPE), solid phase microextraction (SPME), microwave-assisted extraction (MAE), supercritical fluid extraction (SFE), ...

Instrumental analysis

Organics:
HPLC, GC (UV or MS dectectors,...), ...
Inorganics:
ICP (OES or MS), FAAS, IC, XRF, ...

Environmental samples analysis

Can functionalized membranes help?

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Water, solis, air, grab or passive sampling,...

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Functionalized membranes

Functionalized membranes are specifically engineered to **extract** a particular element.

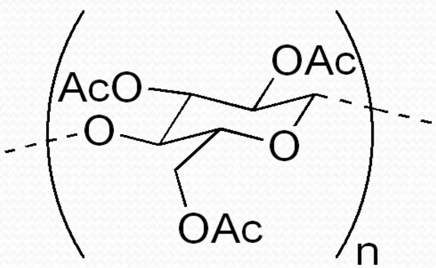
The addition of a suitable **extractant** (carrier) enables the membrane to be specific

- **FUNCTIONALIZED ORGANIC MEMBRANES**
  - **WITH CARRIER**
    - **SUPPORTED LIQUID MEMBRANE**
    - **POLYMER INCLUSION MEMBRANE**
  - **FUNCTIONAL GROUP**
    - **ION-EXCHANGE MEMBRANE**

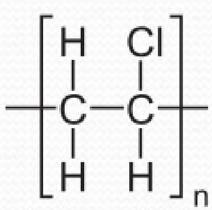
Polymer Inclusion Membranes (PIMs)

PIMs

- **Polymer:** provides mechanical strength
- **Plasticizer:** provides elasticity
- **Carrier:** extracts the analytes

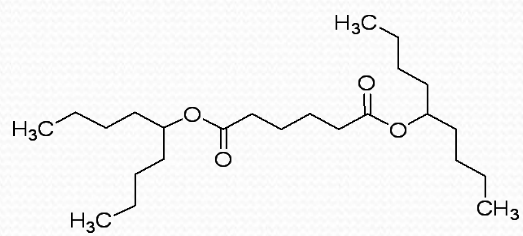


CTA

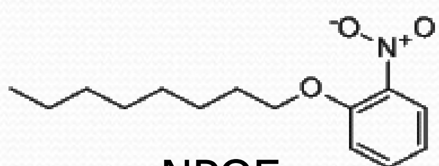


PVC

polymers

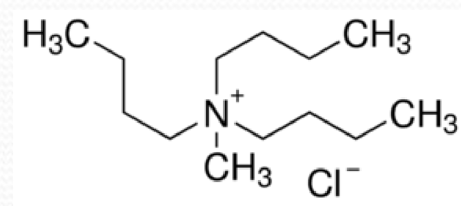


bis(1-butyl pentyl)adipate

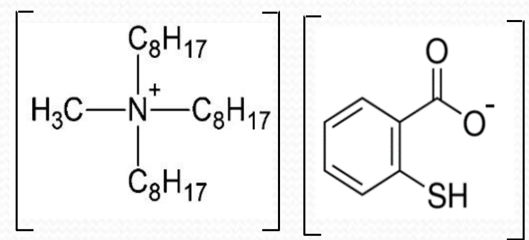


NPOE

plasticizers



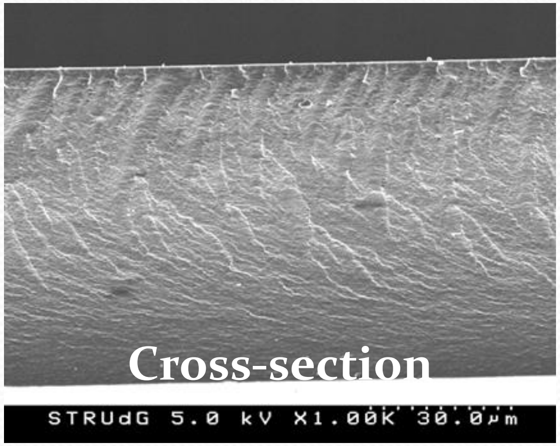
Aliquat 336



TOMATS: [A336][TS]

carriers

Polymer Inclusion Membranes (PIMs)

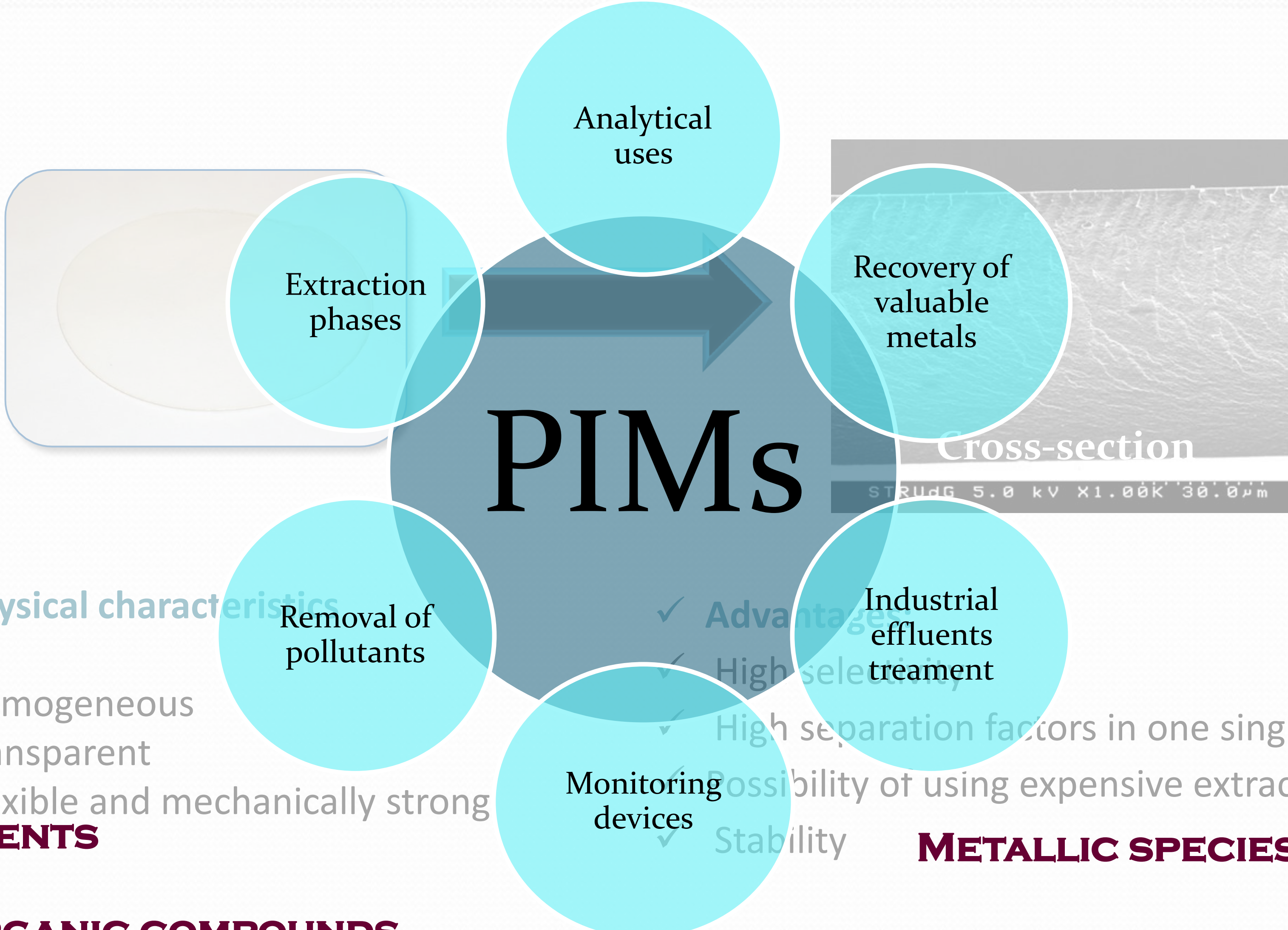


Physical characteristics

Homogeneous
Transparent
Flexible and mechanically strong

- ✓ **Advantages:**
- ✓ High selectivity
- ✓ High separation factors in one single stage
- ✓ Possibility of using expensive extractants
- ✓ Stability

Polymer Inclusion Membranes (PIMs)



Physical characteristics

- Homogeneous
- Transparent
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Advantages

- ✓ High selectivity
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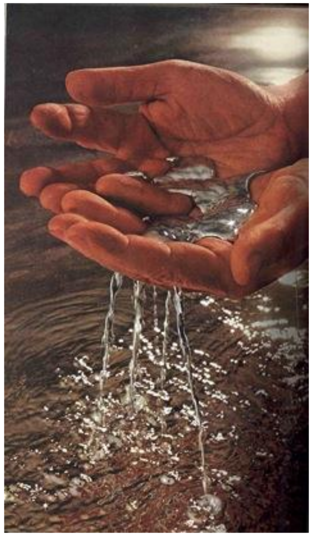
NUTRIENTS

METALLIC SPECIES

ORGANIC COMPOUNDS

OXOANAIONS

Case study: Mercury



- It is a **NATURAL** and **ABUNDANT** element in the Earth's crust
  - present in coal and ore (cinnabar)
  - very used (ancient and modern)

- **UBIQUITOUS** and **TOXIC** element which cycles through the environment (emissions to air, water and land) in various forms

- Ability to **BIOACCUMULATION** in organisms
  - fish, seafood (**BIOMAGNIFICATION**)

- **HIGH TOXICITY** to humans and wildlife
  - can cause <u>severe neurological damage</u>

Hg
High affinity for S-containing compounds

Aim of this work

To explore the use of polymer inclusion membranes to facilitate the analysis of mercury in environmental samples

- Evaluation of PIMs as solid sorbents to collect Hg from water and soils

- Desing and test of a PIM based device for Hg preconcentration and monitoring

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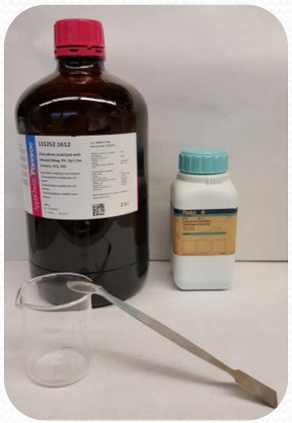
PIMs preparation

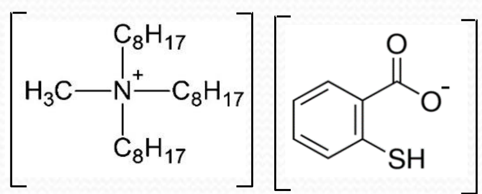


200mg CTA + 20mL $CHCl_3$

5 h

continuous agitation

extractant and plastizicer



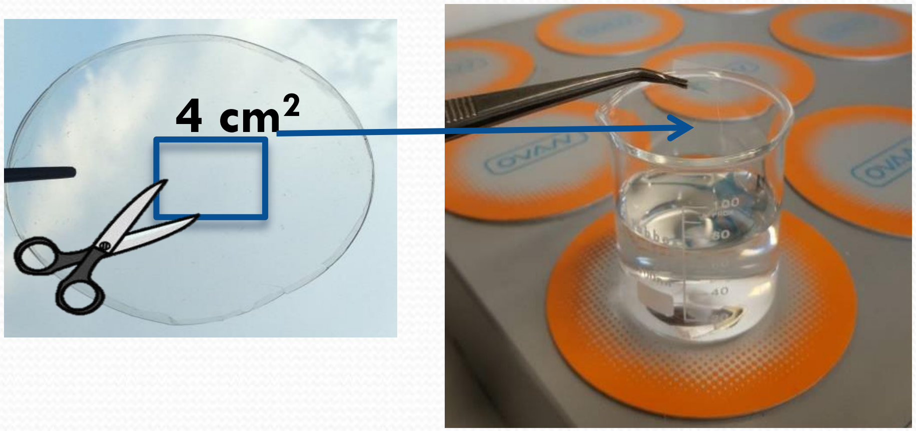
Trioctylmethylammonium thiosalicylate (TOMATS)

2 h

24 h

PIMs (%,wt)	*50% CTA + 50% TOMATS* *50% CTA + 30% TOMATS+ 20% NPOE* *70% CTA + 30% TOMATS*

Water samples: Hg extraction



Aqueous phase:
Different natural waters with Hg added

PIM: 50% CTA + 50% TOMATS

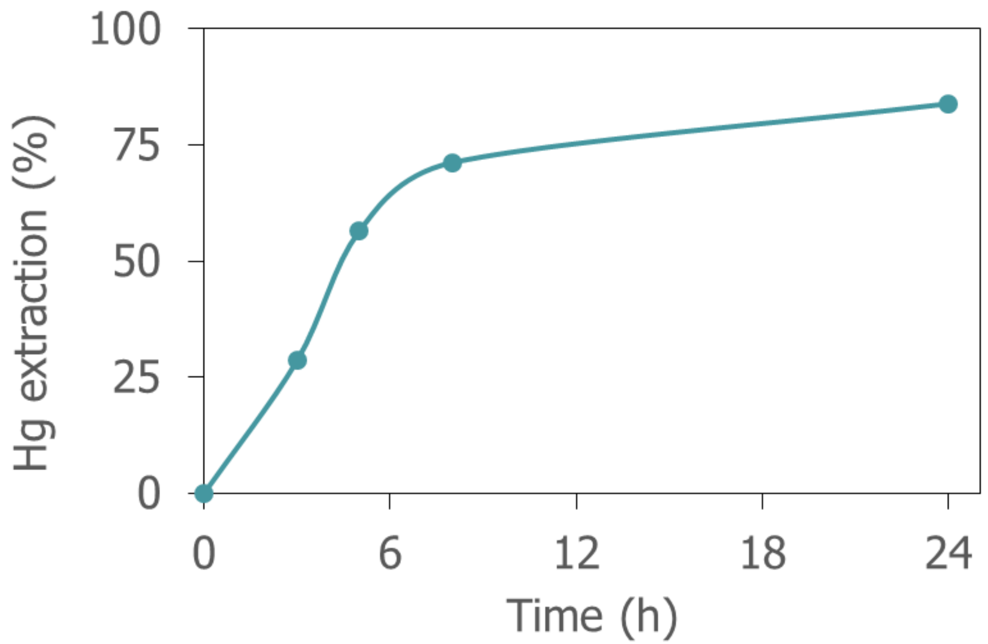
Orbital agitation

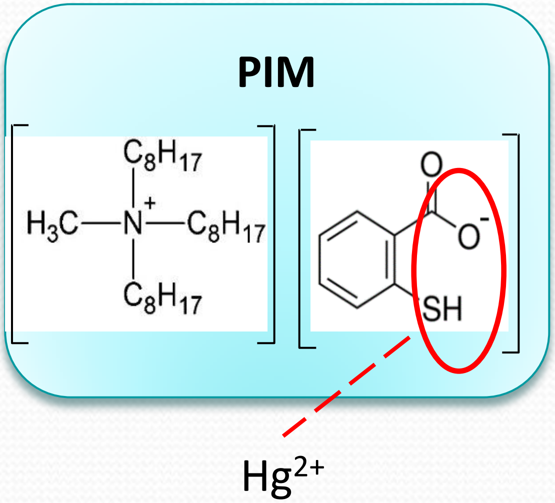
Contact time: 24 h

Hg analysis **(aqueous sample)**: ICP-OES /ICP-MS

$$Extraction\ (\%) = \frac{[Hg^{2+}]_{initial} - [Hg^{2+}]_{final}}{[Hg^{2+}]_{initial}}\ x\ 100$$

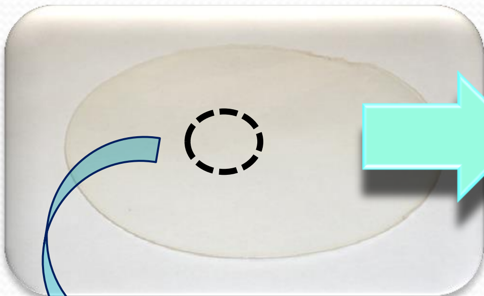
Water samples: Hg extraction

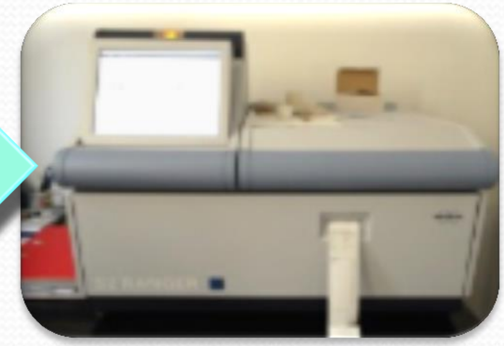




Aqueous phase: 25 mL Hg^{2+} 1 mg L^{-1} in natural water.
PIM: 50% CTA + 50% TOMATS (2x2 cm)
Orbital agitation.

Hg extraction and its determination by XRF

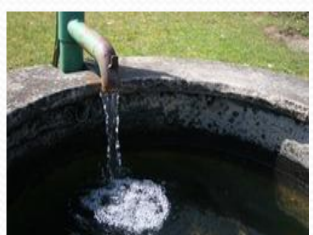




Ø = 3 cm

V (mL) = 100
[Hg] = 10 – 500 µg L^{-1}

Bruker S2 Ranger LE EDXRF spectrometer.



Bruker S2 Ranger LE EDXRF spectrometer	
Voltage (KV)	40
Filter	Al500
Sampler holder	
Film	PROLENE 4.0µm
Disk	Teflon
Measuring time	100 s
Air	Vaccum
Analytical lines	Hg $L_{\alpha1}$

Hg extraction and its determination by XRF

Chemical characteristics of the water samples (mg L^{-1}).

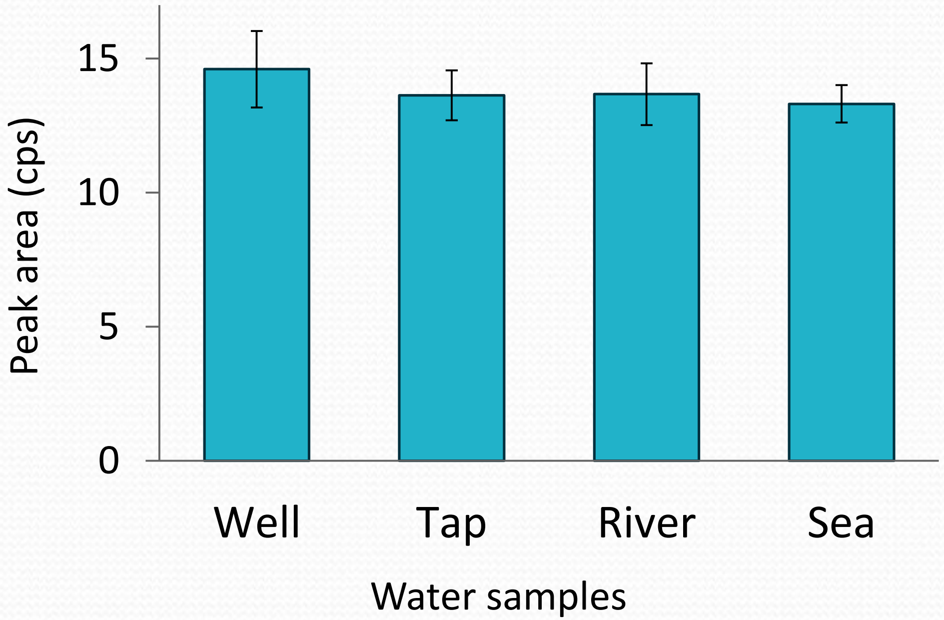
Water	pH	Ca^{2+}	Cl^-	SO_4^{2-}	NO_3^-	HCO_3^-
Well	8.3	96.1	17.2	68.2	1.4	268
Tap	7.8	44.2	29	250	6.3	162
River	7.2	119	48.9	18.99	1.2	203
Sea	8.1	4000	21534.6	2986.7	<LOD	140

Data from MINTEQ software

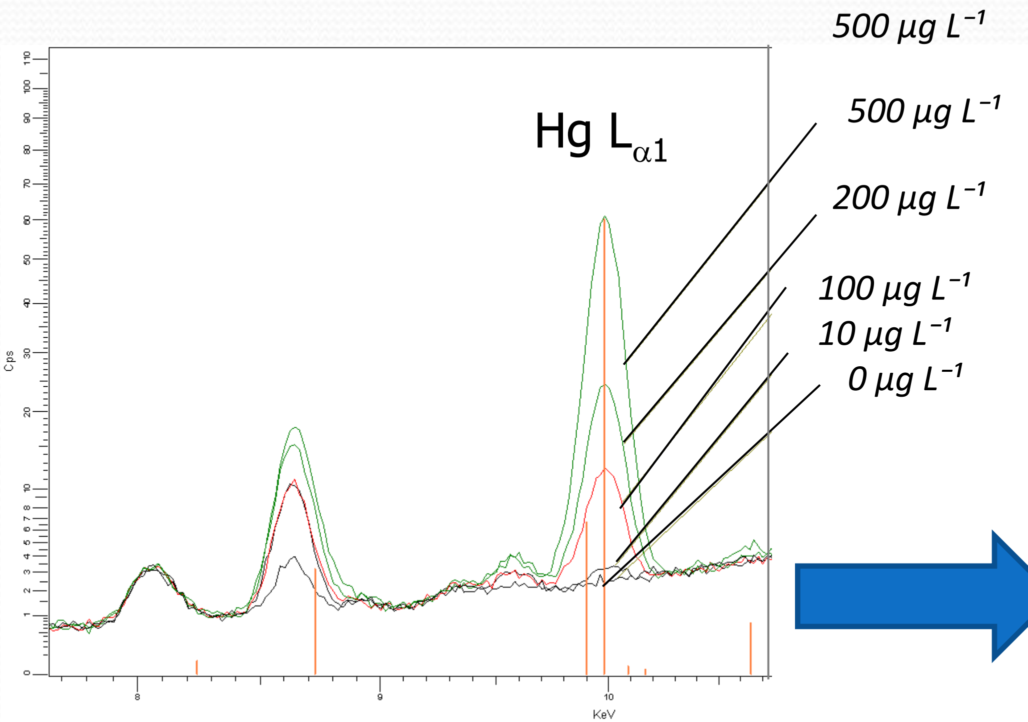
Well/tap water
- 9% $Hg(OH)_2$
- 44.9 % $HgCl_2$
- 44.9% HgClOH

River water
- 11.3% $HgCl_2$
- 40.8% $Hg(OH)_2$
- 47.9% HgClOH

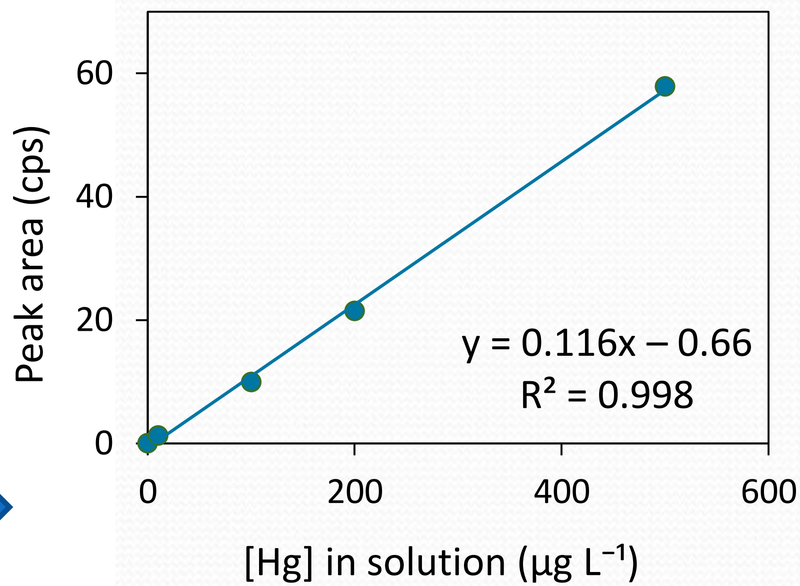
Sea water
- 3.8 % $HgCl_2$
- 20.9% $HgCl_3^-$
- 75.3% $HgCl_4^{-2}$



Hg extraction and its determination by XRF

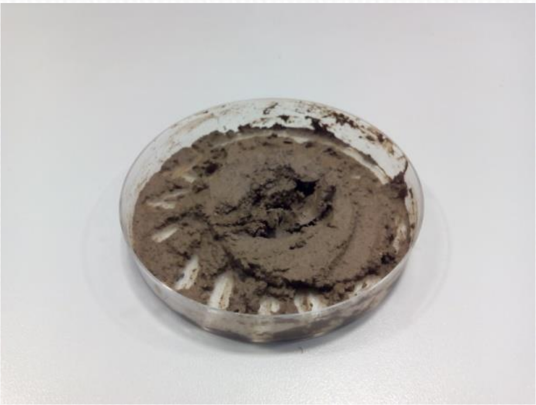


XRF spectra
(10-500 µg L^{-1} in liquid sample)



Calibration curve

Soil samples: Hg extraction



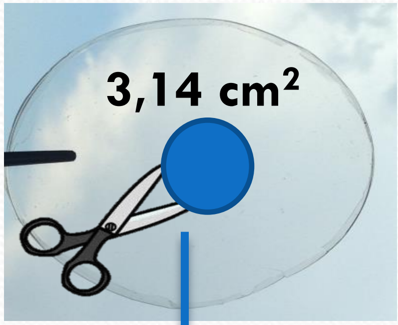
Soil:
Agriculture soils with metals impact (anthropogenic sources)
Barcelona area

PIM:
50% CTA + 50% TOMATS
50% CTA + 30% TOMATS +20% NPOE
70% CTA + 30% TOMATS

Contact time: 24 h

Hg analysis **(PIM)**: Advanced Mercury Analyser

Soil samples: Hg extraction



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Hg analysis **(PIM)**: Advanced Mercury Analyser

Soil samples: Hg extraction

30 g soil
9 mL MiliQ H_2O

1 x 9

C_i = 0.56 mg Hg/ kg soil

30 g soil
9 mL MiliQ H_2O + Hg added

2 x 9

C_i = 1.60 mg Hg/ kg soil

Stabilization: 24 h

PIM 1. **50%** CTA
50% TOMATS

3.14 cm2

1 x 3

PIM 2. **50%** CTA
30% TOMATS
20% NPOE

3.14 cm2

1 x 3

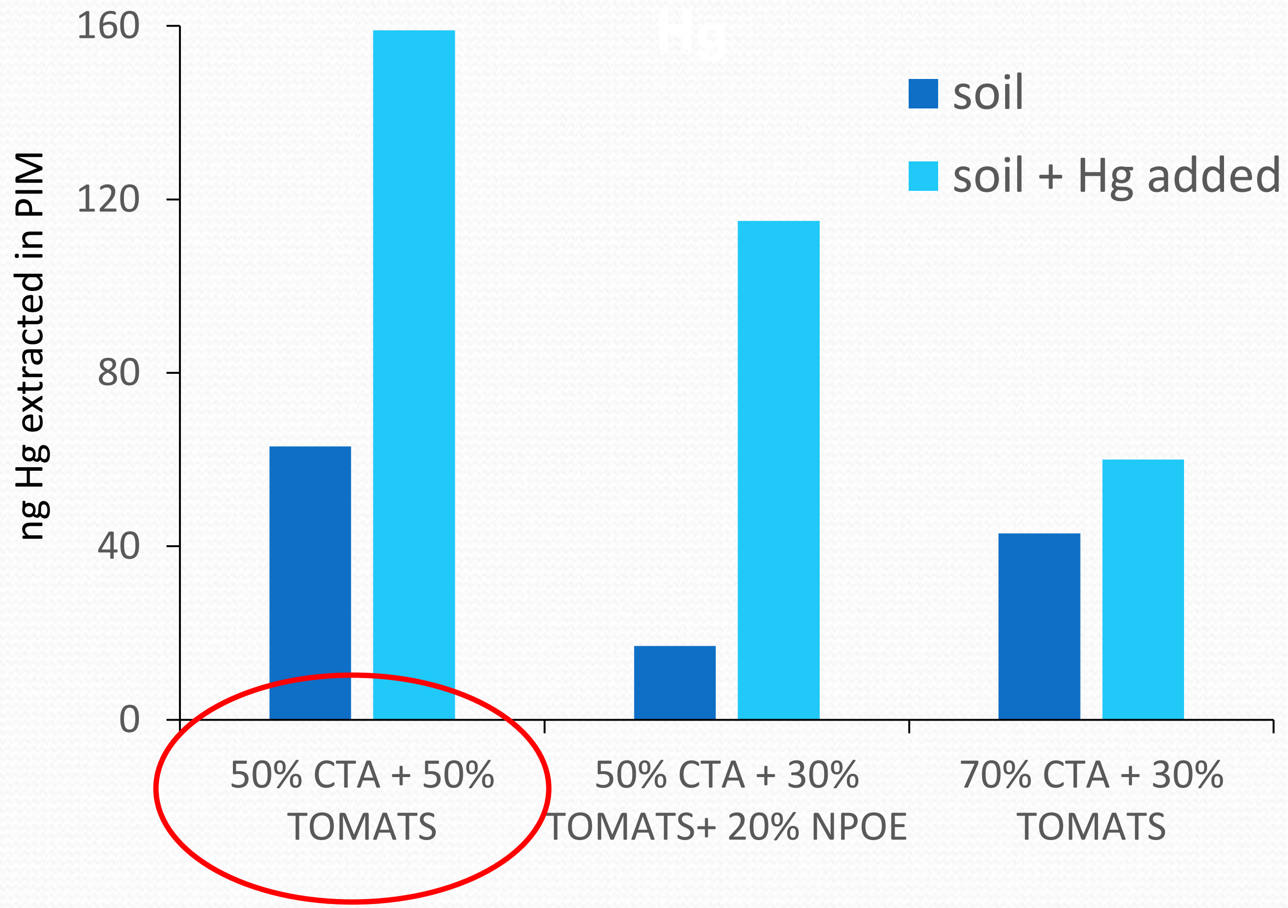
PIM 3. **70%** CTA
30% TOMATS

3.14 cm2

1 x 3

Contact time PIM-soil: 24 h

Soil samples: Hg extraction



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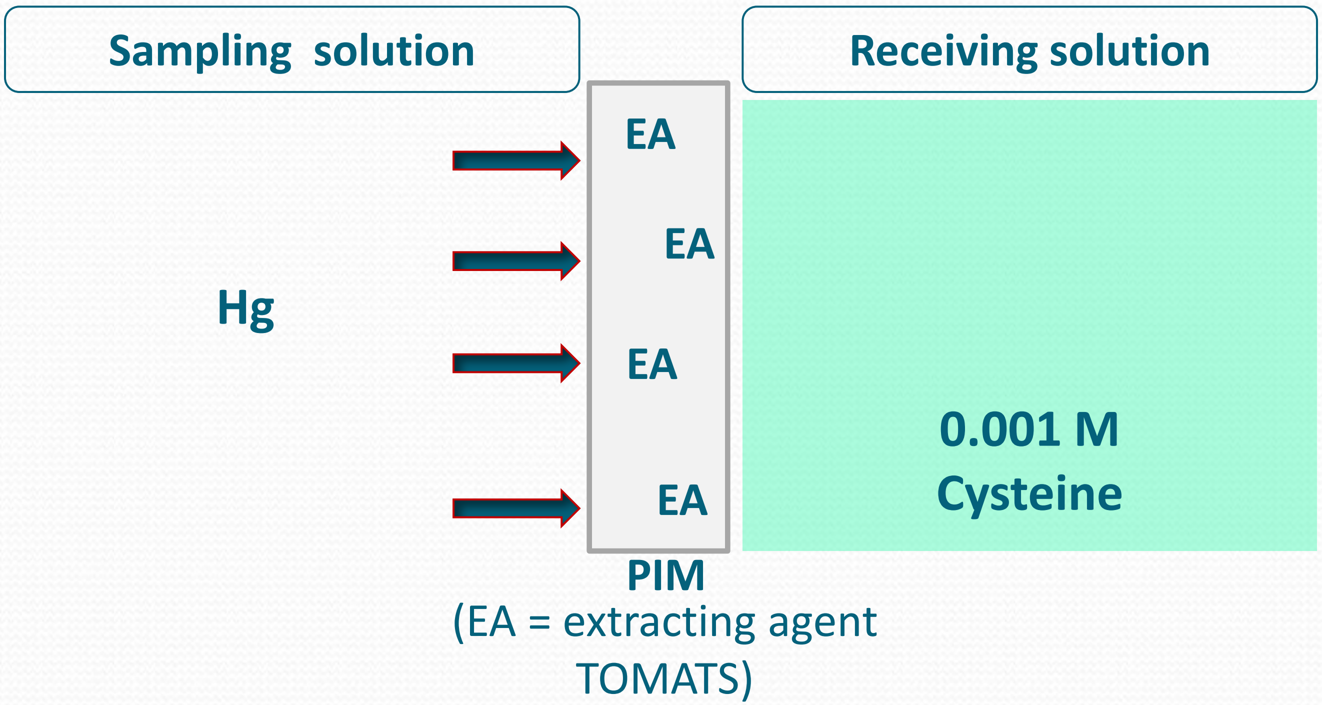
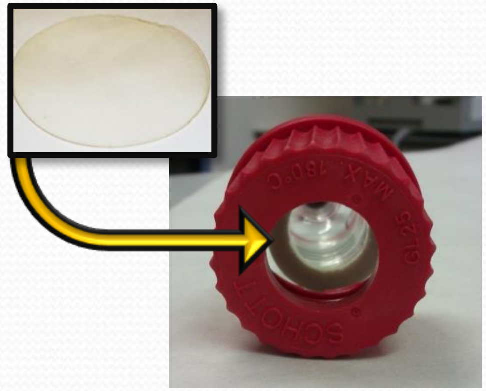
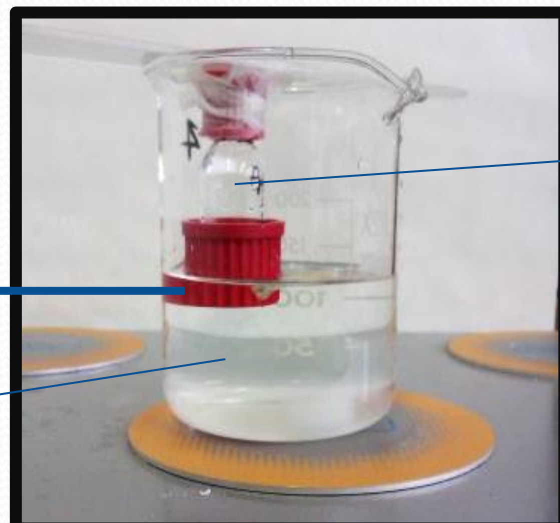
PIM device as a new sensor for Hg monitoring

PIM-device: Hg transport



PIM device as a new sensor for Hg monitoring





PIM:
50%CTA + 30%TOMAS + 20%NPOE

Receiving solution
0.001 M cysteine
(V= 5 mL)

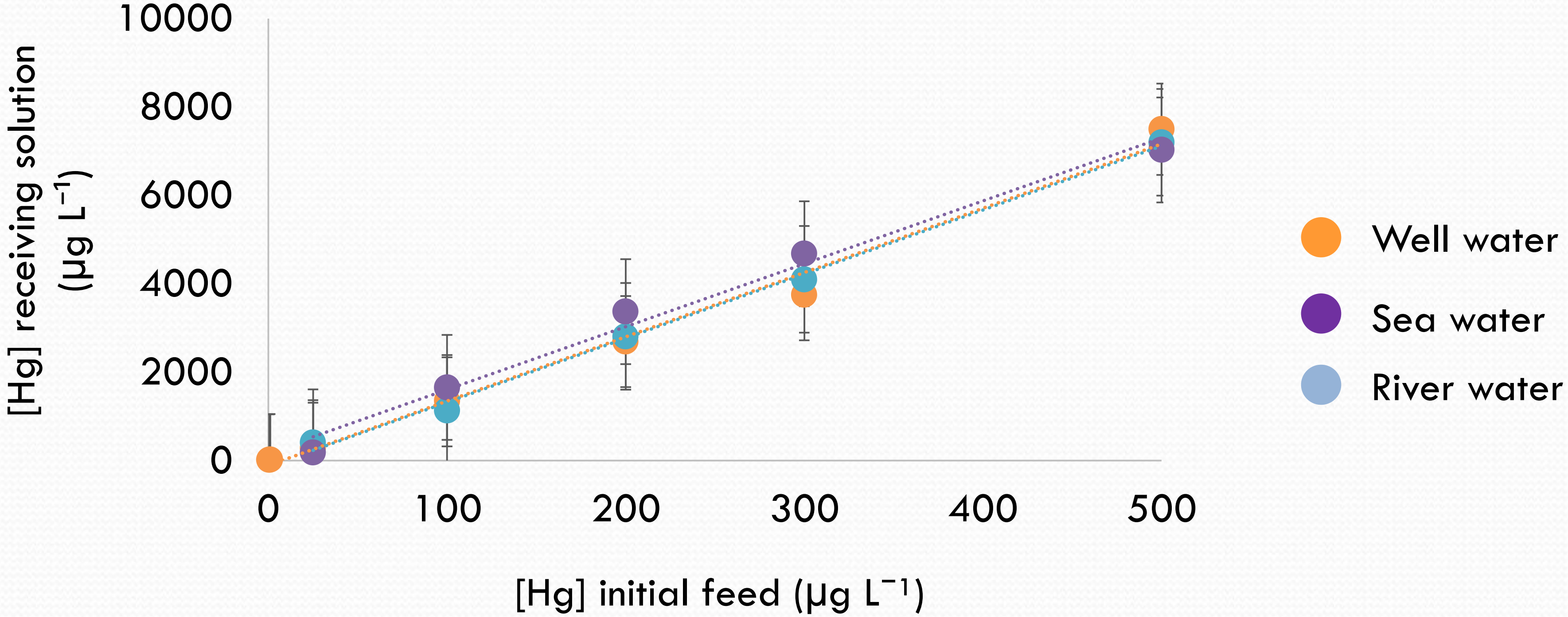
Feed phase
Hg
(V= 100 mL)

Preconcentration factor= 20

$$Transport\ efficiency\ (\%) = \frac{[Hg]_{r.p.}\ x\ V_{r.p.}}{[Hg]_{aq.p.}\ x\ V_{aq.p.}}\ x\ 100$$

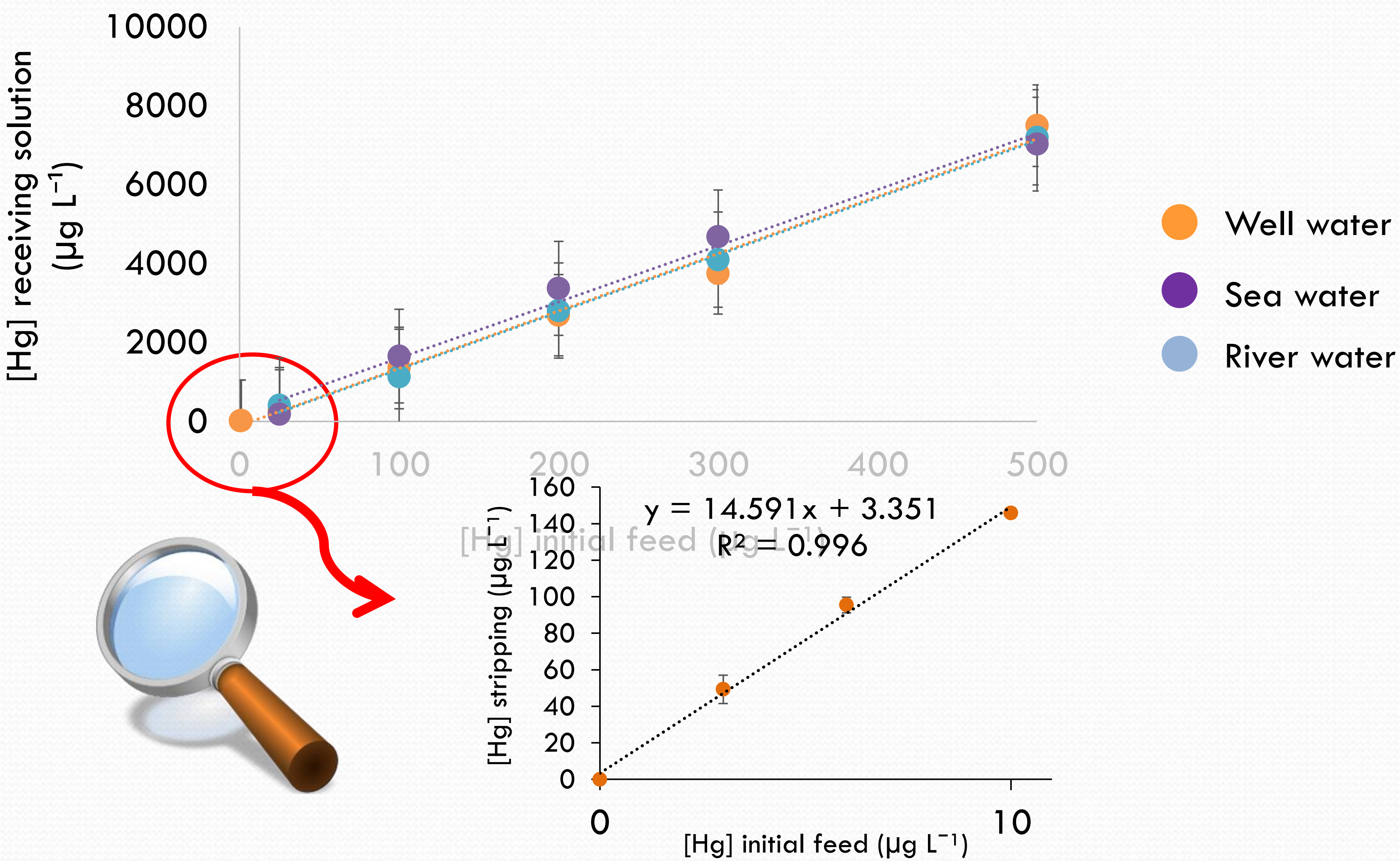
(ICP-OES/ ICP-MS)

PIM device as a new sensor for Hg monitoring



Water sample	Range (ppb)	Slope	r^2
Well	0.5 – 500	14.53	0.991
Sea	25 – 500	14.50	0.997
River	25 - 500	14.23	0.987

PIM device as a new sensor for Hg monitoring

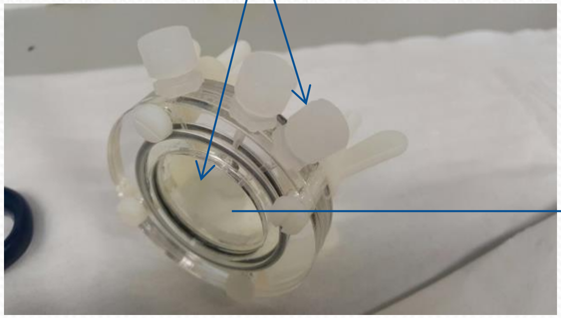


PIM device as a new sensor for Hg monitoring

Improvement: new 2-PIMs device

PIM area: 1.5 cm^2
Receiving phase: 5 mL

2 PIMs



In-between:
Receiving phase: 5 mL

PIM area: 2x 8.55cm^2 = 17 cm^2

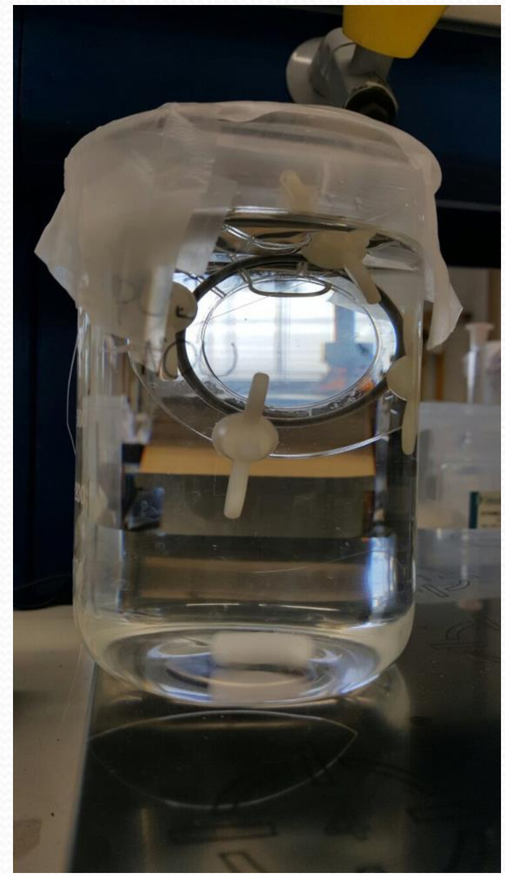
PIM device as a new sensor for Hg monitoring

Improvement: new 2-PIMs device

Feed phase: **500 mL well water with 100 µg L^{-1} de Hg^{2+}**

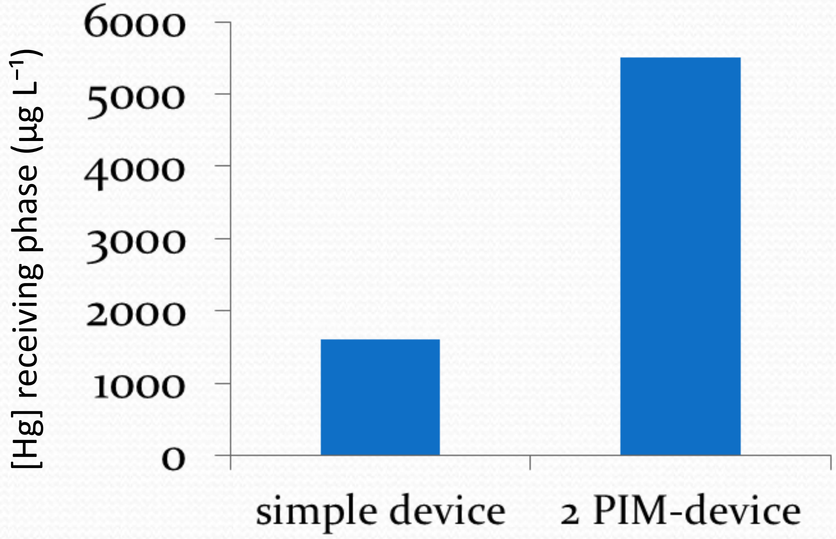
Receiving solution: 5 ml 10^{-3} M cysteine

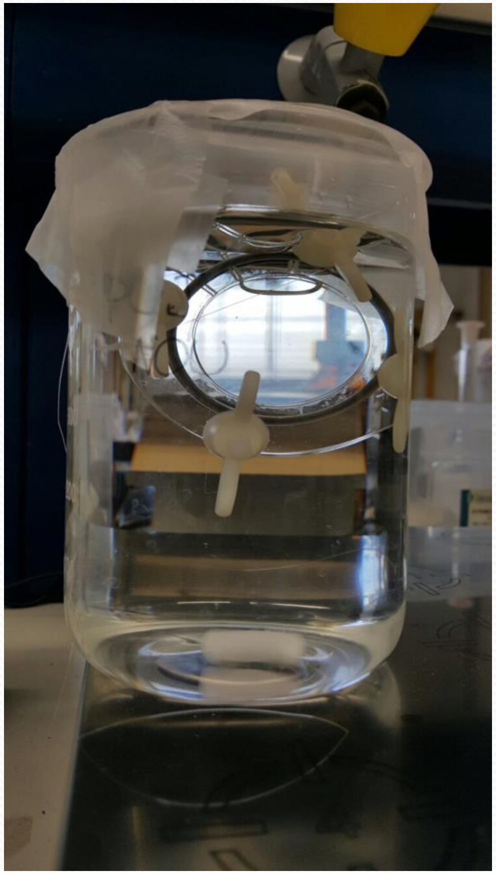
Time: 24 h



PIM device as a new sensor for Hg monitoring

Improvement: new 2-PIMs device





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Conclusions

- PIMs made of CTA as polymer and TOMATS as extractant effectively adsorb Hg from different natural waters at low ppb level.

- A new methodology based on Hg sorption on PIMs followed by EDXRF anaylisis has been developed, and it has been shown that Hg extraction is not affected by water matrix.

- PIMs have also been useful to collect Hg present in soil and better results have been obtained with a PIM made of 50% CTA + 50% TOMATS. Further experiments will be conducted to increase Hg sorption.

- A simple PIM-device including a cysteine solution as a receiving phase has been designed and tested to preconcentrate Hg. This PIM system shows promising results to use this device as Hg passive sampler in natural waters.

Girona and Costa Brava

Thank you very much for your attention!