

# Determination of WFD metals in wastewater using micro-machined Boron-Doped Diamond (BDD) sensor

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Water Micro-pollutants: from detection to removal





# Sensor specifications

## Water Framework Directive (2013/39/UE)

### Environmental Quality Standard

Concentration below any expected adverse effect

### Maximum Allowable Concentration

Maximum for any single measurement

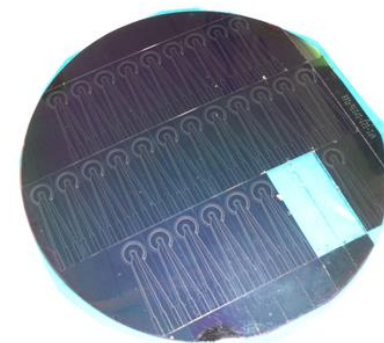
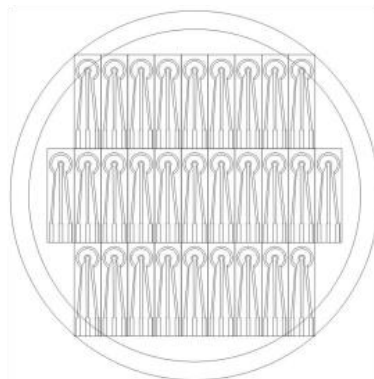
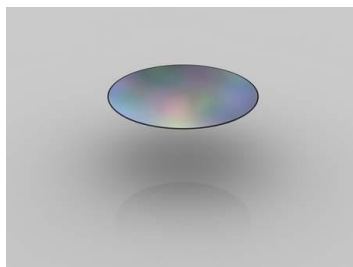
### Two priority hazardous metals

Any emission, discharge or loss must be suppressed

### WFD standards ( $\mu\text{g/L}$ ) MAC-EQS

[Cd]	< 0,45
[Hg]	< 0,07
[Ni]	< 20
[Pb]	< 7,2

# BDD electrochemical micro-cell Design & production



4' wafer of 300 nm  
thick microcrystalline  
BDD (8000 ppm) on a  
silicon layer, isolated  
by 0,5 μm  
Si/SiO<sub>2</sub>/Si<sub>3</sub>N<sub>4</sub> layers

Drawing of  
electrochemical  
microcells on a  
4 'wafer

Cutting at the  
laser  
micromachining  
workstation  
5 kHz, 2.5 W,  
800 nm, 150 fs

BDD microcells  
made by laser  
micro-machining



# Micro-machined BDD Microcell

*Three electrode micro-cell cut up from the BDD wafer by laser-machining*

Counter-electrode

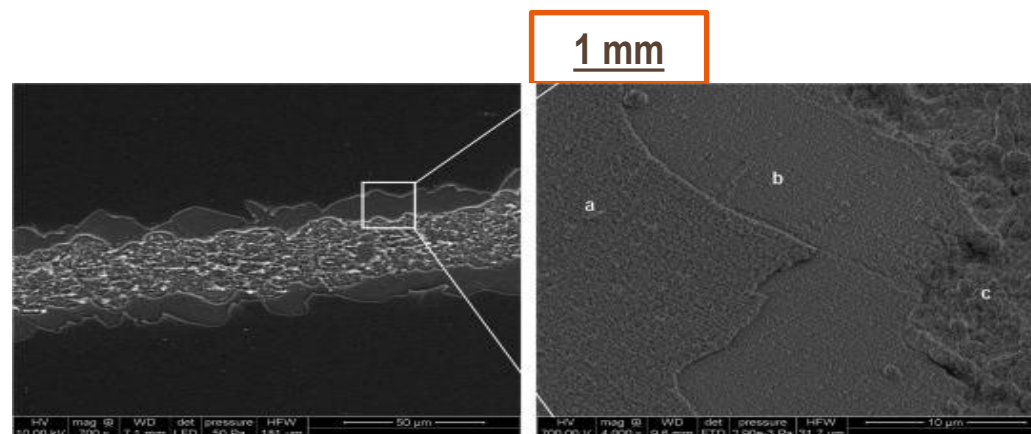
Working electrode

Pseudo-reference

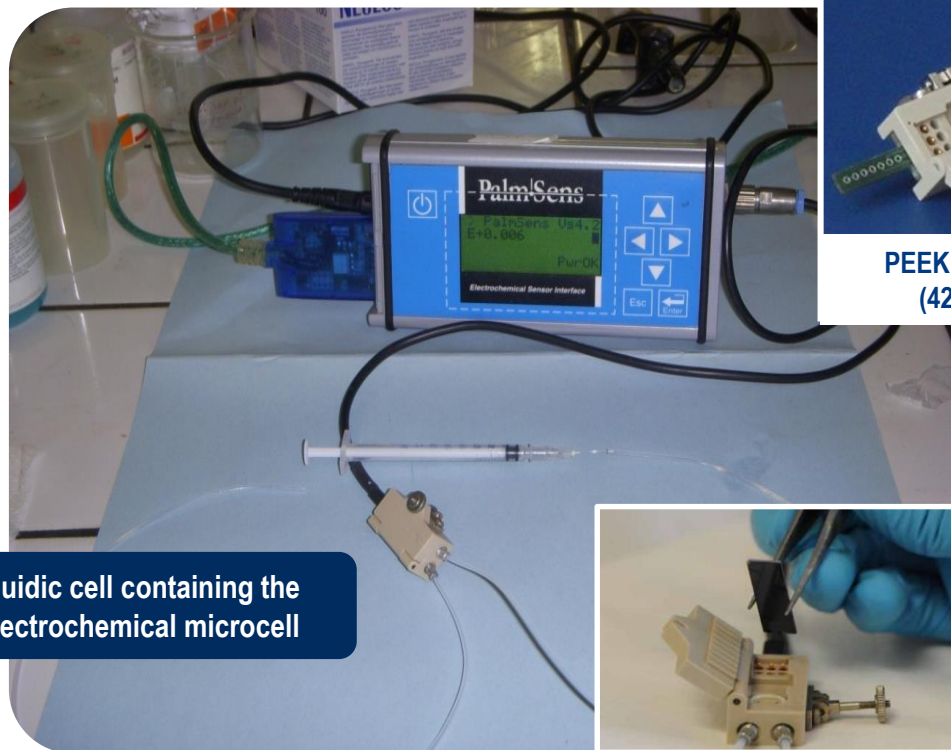


## *Femto Laser Micro-machined Groove Edge:*

- (a) BDD layer*
- (b) Silicon nitride layer*
- (c) Silicon substrate*



# Experimental measurement setup



Fluidic cell containing the electrochemical microcell



PEEK Cell BVT Technologies  
(42 x 24 x 16 mm, 5  $\mu$ L)

Fluidic cell

Handheld potentiostat

Piston pump  
flow rate  $<2$  mL/min ( $<0.1$  L/h)  
Online addition of 0.1 M  
citrate buffer pH 2 (1/5; v/v)



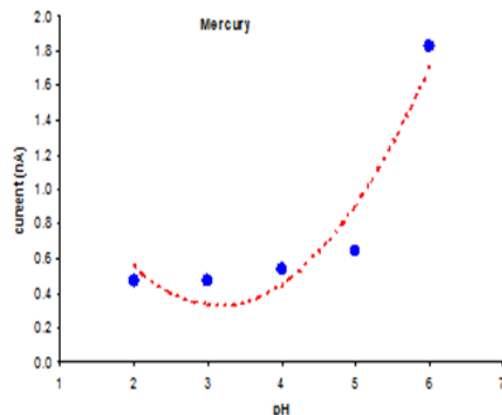
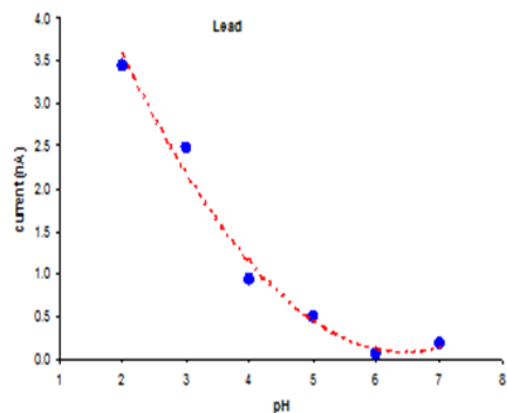
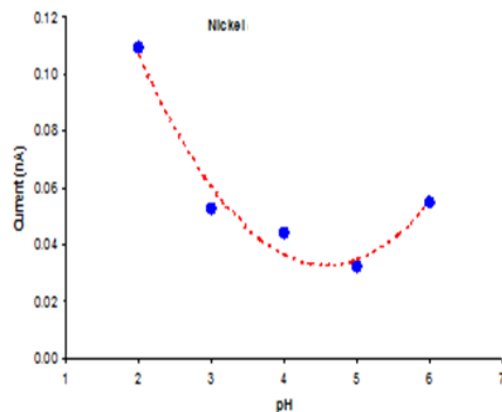
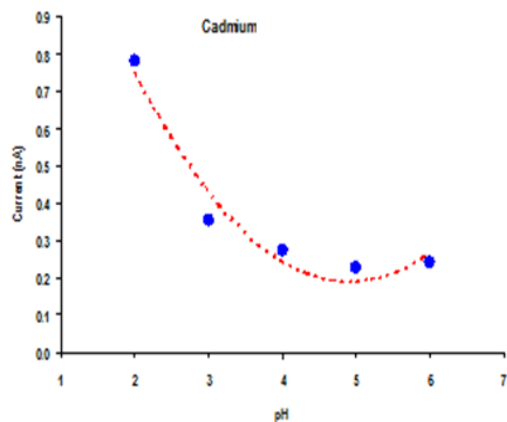
the microcell setting-up  
into the fluidic cell



# Parameter optimisation

A two-level experimental plan was run to optimise voltammetric parameters

0,1 M citrate/HCl buffer at various pH



Optimal pH

**pH= 2**

**Cd, Ni and Pb**

**Neutral pH**

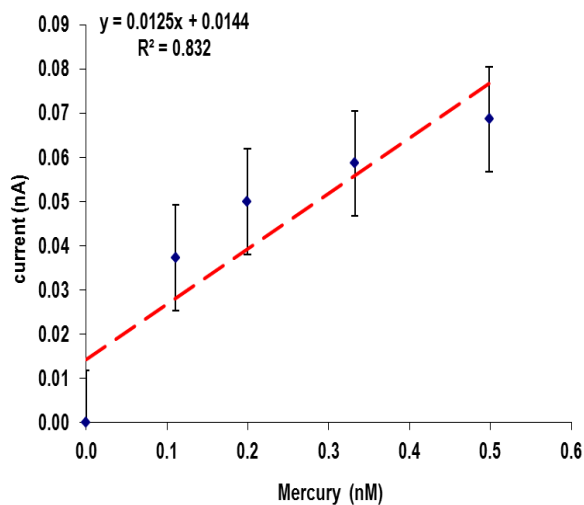
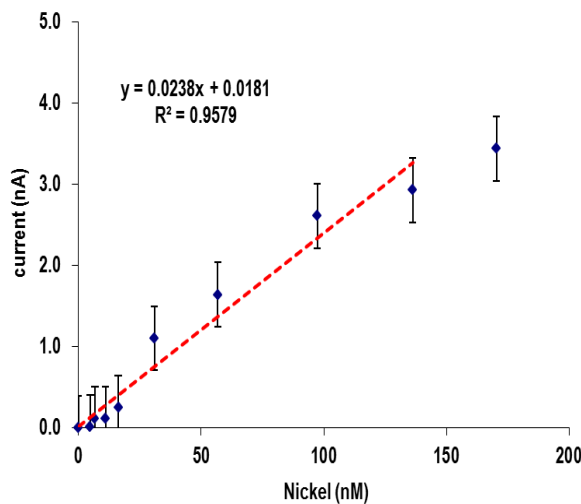
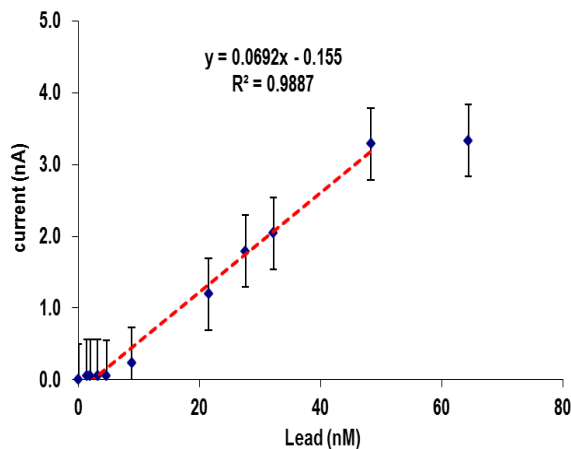
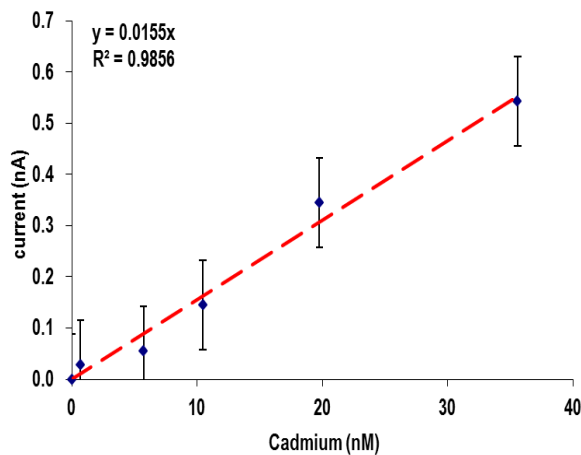
**Hg**

=

**0,1 M citrate/HCl buffer  
adjusted at pH 2**



# Calibration plots



## BDD Micro-cell Results

### Linear ranges

( $\mu\text{g/L}$ )

[Cd <sup>2+</sup> ]	=	3.9
[Hg <sup>2+</sup> ]	=	1.0
[Ni <sup>2+</sup> ]	=	5.7
[Pb <sup>2+</sup> ]	=	10.0

### Sensitivities

(nA/ $\mu\text{g}$ )

[Cd <sup>2+</sup> ]	=	133
[Hg <sup>2+</sup> ]	=	46
[Ni <sup>2+</sup> ]	=	477
[Pb <sup>2+</sup> ]	=	372

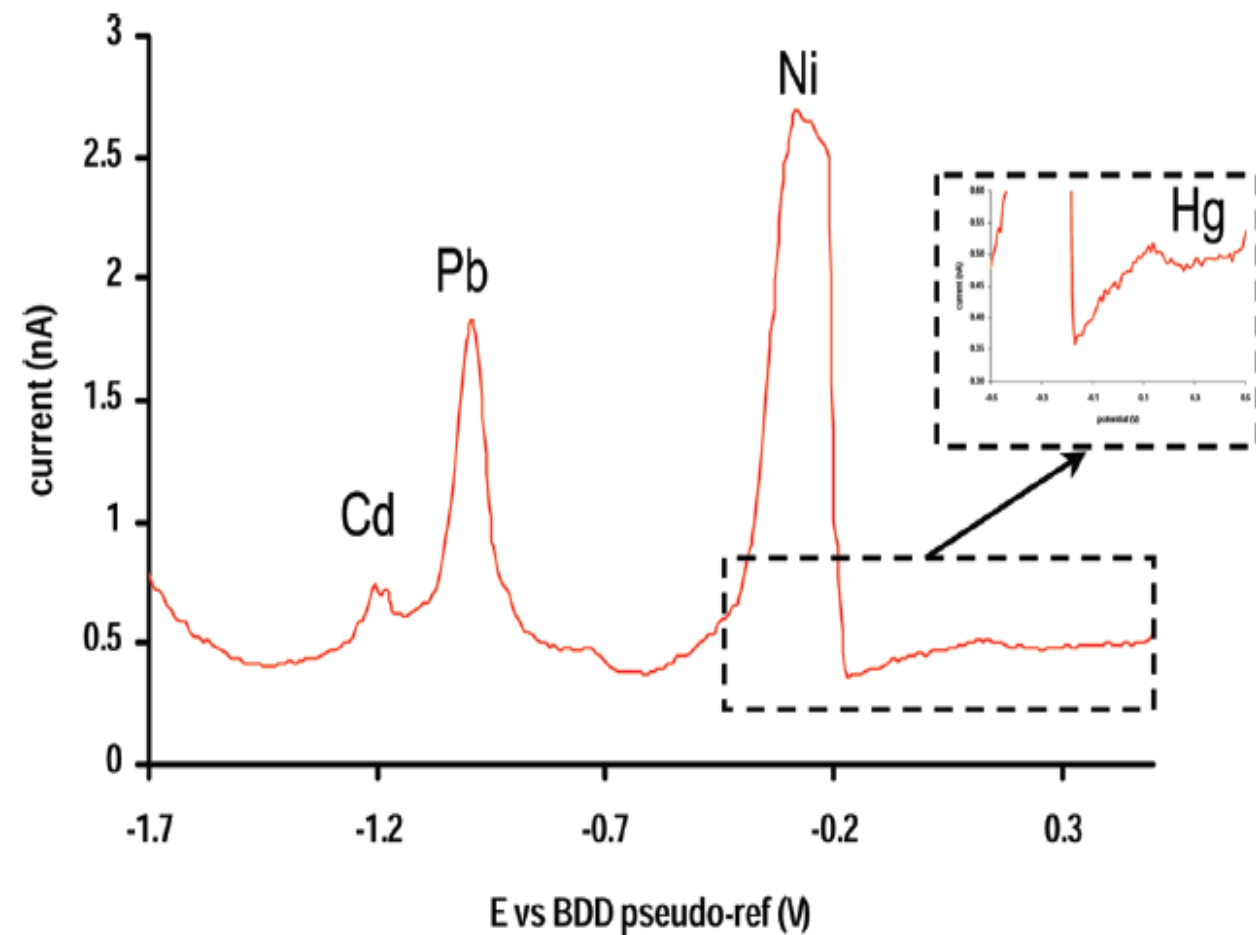
### Limit of Detection

( $\mu\text{g/L}$ )

[Cd <sup>2+</sup> ]	=	0.3
[Hg <sup>2+</sup> ]	=	0.46
[Ni <sup>2+</sup> ]	=	10
[Pb <sup>2+</sup> ]	=	1

Operating conditions:  $E_{dep} = -1.7 \text{ V}$ ;  $t_{dep} = 20 \text{ s}$ ; sweep rate = 50 mV/s

# Urban Runoff Water Analysis



metal determination  
at a average  
concentration ratio  
usually measured in  
runoff waters ( $\mu\text{g/L}$ ):

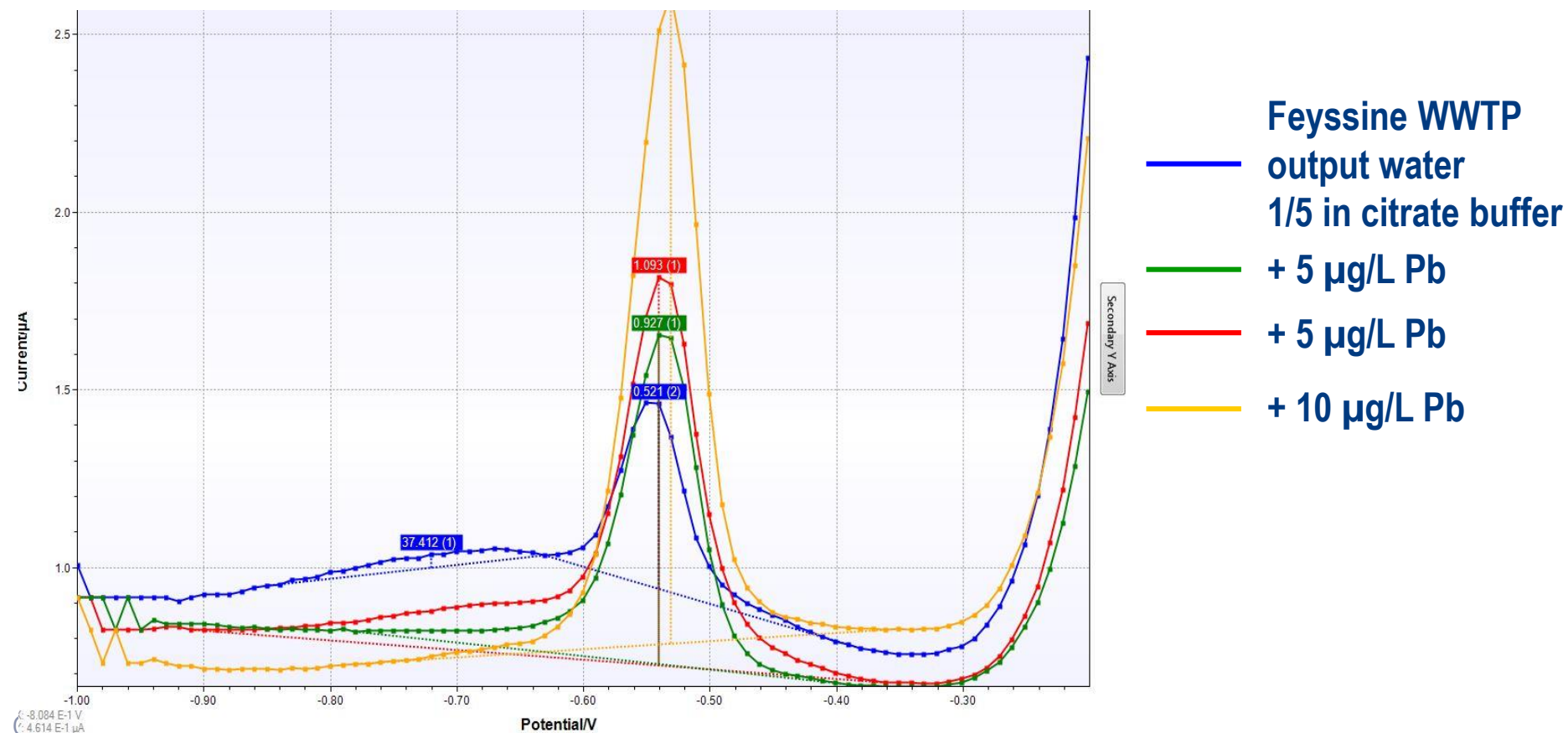
Cd	2.25
Pb	2.28
Ni	2.23
Hg	0.11

in 0.1 M potassium citrate /HCl buffer, pH 2

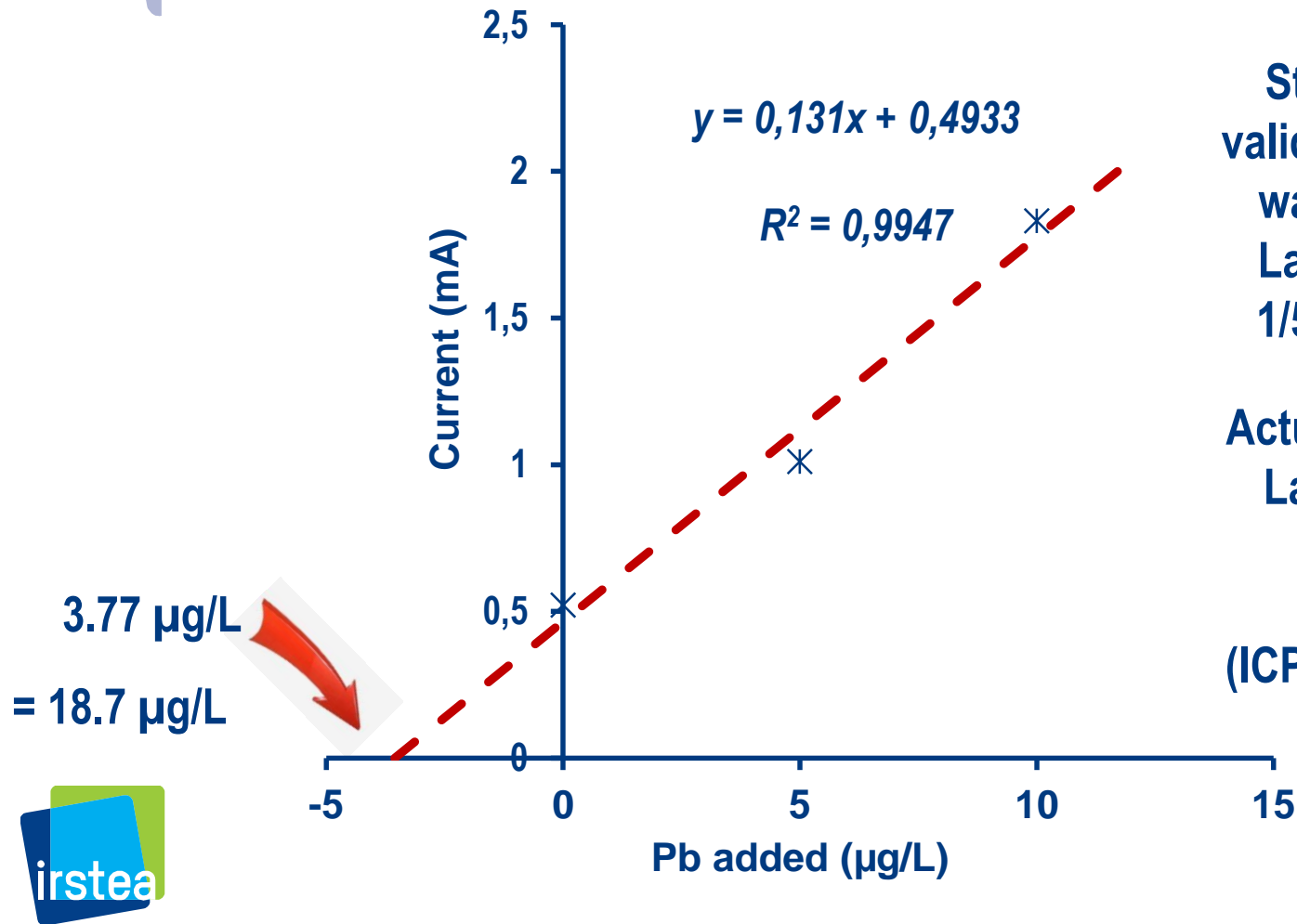


# Wastewater analysis

## Standard additions in a output water sample from La Feyssine WWTP



# Wastewater analysis



# Micro-machined Boron-Doped Diamond (BDD) sensor

## Figures of merit

<b>Micro-cell Results</b>		<b>WFD standards</b>	
	( $\mu\text{g/L}$ )		( $\mu\text{g/L}$ )
	LoD		MAC-EQS
[Cd]	= 0.3	[Cd]	< 0.45
[Hg]	= 0.46	[Hg]	< 0.07
[Ni]	= 10	[Ni]	< 20
[Pb]	= 1	[Pb]	< 7.2



# Conclusions

- **Planar electrochemical micro-cell**, fitting in a fluidic cell, is **micro-machined in BDD**
- **Sensing performances** meet with the **WFD EQS** for **three of the four metals: Cd, Ni & Pb**
- **four heavy metals are detected simultaneously** in **sewage or runoff waters**
- **Onsite monitoring of Cd, Ni and Pb** a near-term reality due to the simplicity of the BDD micro-cell



# Thank you for your attention

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	-1	0	1
1- $t_{\text{pulse}}$ (s)	0,01	0,03	0,05
2- $E_{\text{step}}$ (V)	0,01	0,03	0,05
3- $E_{\text{pulse}}$ (V)	0,01	0,03	0,05
4- $t_{\text{scan}}$ (V/s)	0,01	0,055	0,1

