Compact flow system for the analysis of copper in space water treatment units

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Outline

- IMB-CNM & GTQ activities
- ESA project & Motivation
- Microelectrodes: Design and fabrication
- Flow system set-up
- Evaluation results
- Conclusions

Instituto de Microelectrónica de Barcelona (IMB-CNM)

Research and development in fundamental and applied micro- and nanotechnologies

- Located at Campus of the Universitat Autónoma de Barcelona
- Belongs to the Spanish Research Council (www.csic.es)
- 1500 m^2 Class 100-10,000 Clean Room (icts.cnm.es)
- 2.5 µm standard CMOS line

Activities

- Power devices and systems
- Microenergy generation and harvesting
- BioMEMS
- Nanofabrication and functional properties of nanostructures
- Radiation Detectors
- High-K dielectrics
- **Lab on a Chip (LoC) and (bio)chemical Transducers**

IMB-CNM & GTQ activities

- **Lab on a Chip (LoC) and (bio)chemical Transducers**

R&D&I Analytical Microsystems and Lab on a chip (LoC)

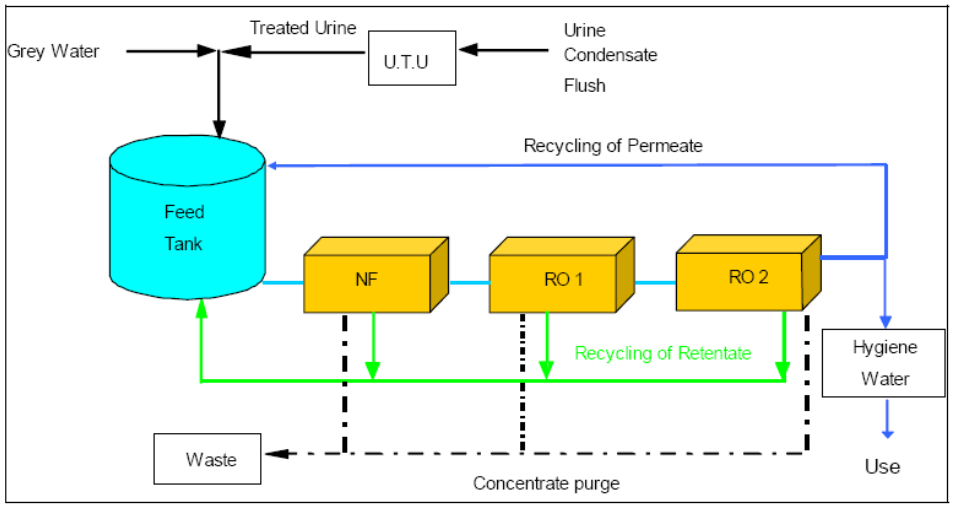
- Chemical Transducers (Electrochemical and optical/photonic)
- Microfluidic components
- Instrumentation

Automation of processes (sampling, analysis and data processing) using very low sample and reagent volumes.

Motivation & ESA project

- Manned space flights of long duration and ISS
- Water recycling systems on board [ESA, NASA and ROSCOSMOS]
- Water treatment units: Conversion of human liquid waste (urine), cabin condensate water and greywater (waste hygiene water) into **hygiene water** or even, if necessary, into **drinking water**

Quality of treated water



Motivation & ESA project

On-line Chemical Water Quality Analysis Equipment

(CN15100-OF-WQA-0001)

Partners:

NTE-SENER Contractor

Cetaqua. Water analysis

UAB. Microsystems & optical sensors technology

CNM. Microsystems & electrochemical sensors technology

Objective

Select, after extensive bibliographic study, preliminary trade-off and capability tests, the best suited analytical technique for on-line water quality monitoring.

Parameters NH_3-NH_4, NO_2, NO_3, **Ni^{2+}, Ag^{+}, Zn^{2+}, Cu^{2+}** and K^{+}

Motivation & ESA project

Water quality analyzers requirements
- Low mass & low volumes
- Microgravity conditions

Standard techniques (Atomic absortion, HPLC, ICP) and probes for in situ analysis does not fit these requirements

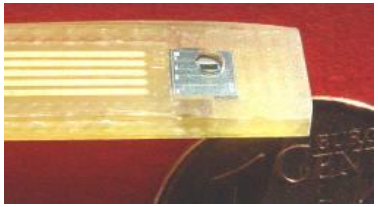
Miniaturization of analytical systems required

Motivation & ESA project

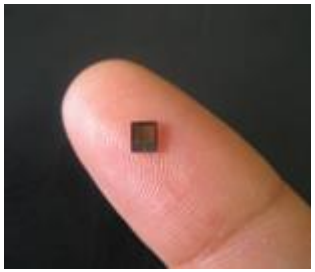
Miniaturization of analytical systems required

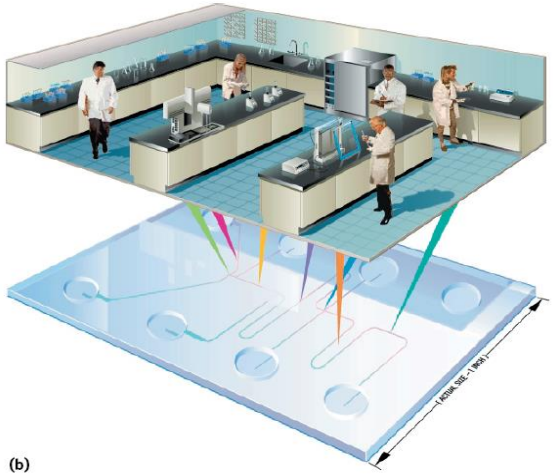
- Low volumes
- Low power consumption
- Microgravity conditions
- Multiparametric systems

Micro Total Analysis Systems (µTAS) or Lab on a chip (LOC)

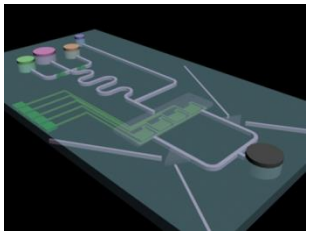


Microsensors





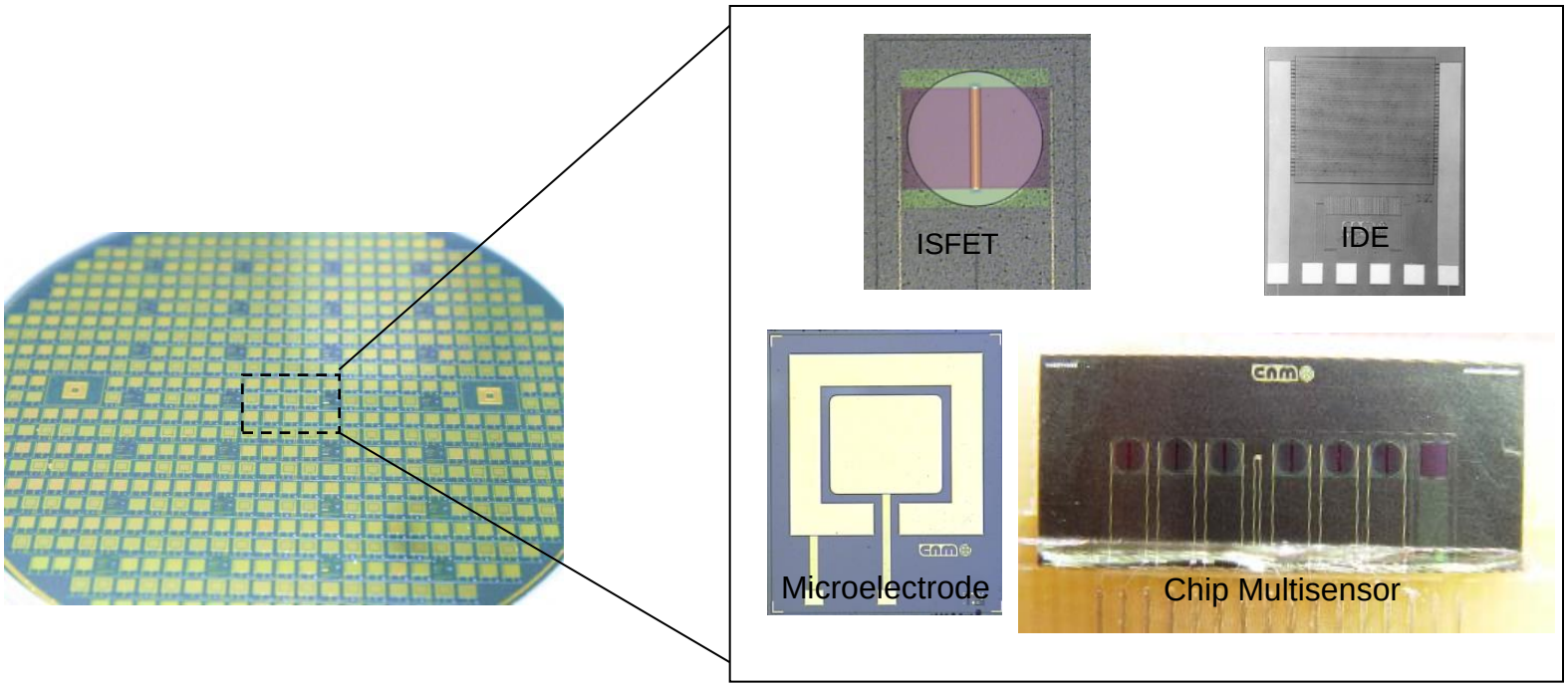
(b)



Microelectrodes: Design and fabrication

Electrochemical:

Potentiometric: Ion-selective field effect transistors **(ISFETs)**
Amperometric: Three-electrode electrochemical cells and microelectrode arrays.
Impedimetric: Interdigitated electrodes (IDEs)



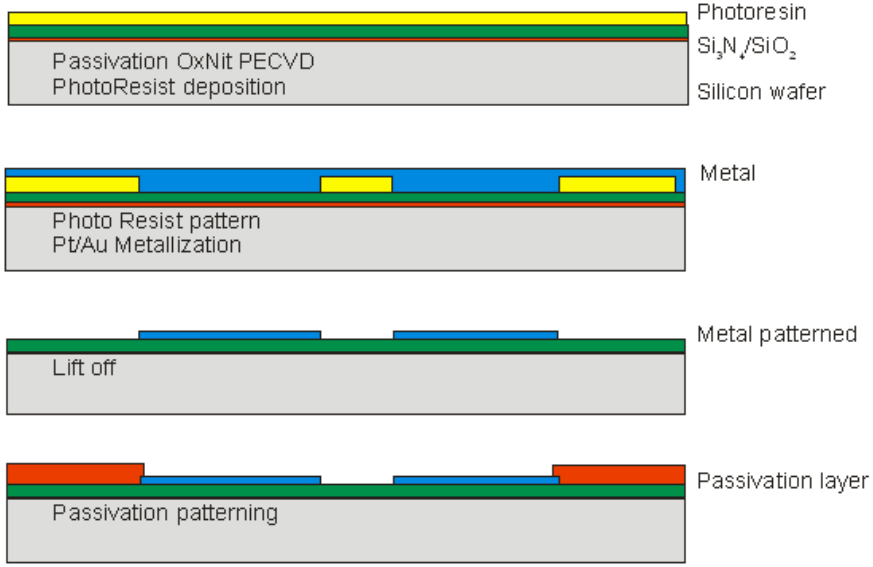
Substrates: silicon and glass.

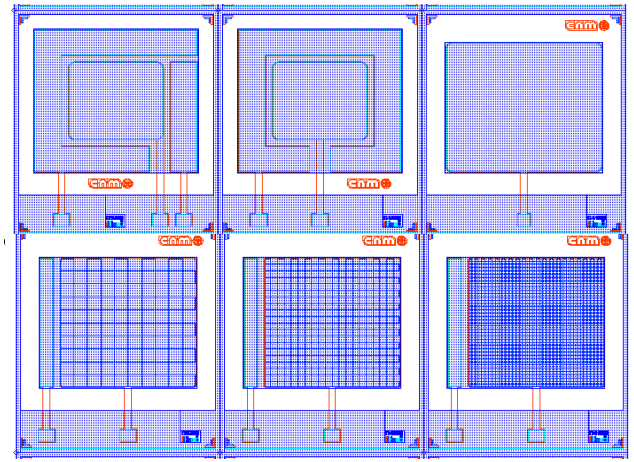
Electrode materials: gold, platinum, silicon, polysilicon, carbon nanomaterials

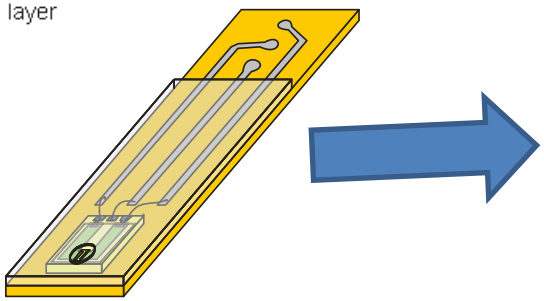
Microelectrodes: Design and fabrication

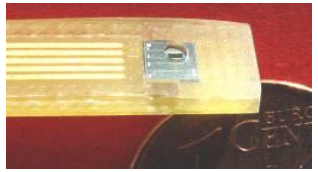
Standard photolithographic technology: Si/SiO_2/Metal

- ✓ Lift-off (patterning)
- ✓ e-beam evaporation (metal deposition)
- ✓ Wet etching (passivation layer)



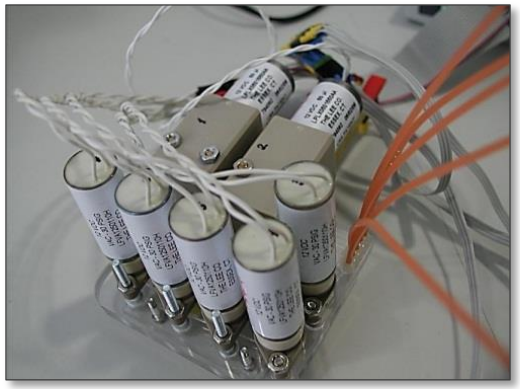


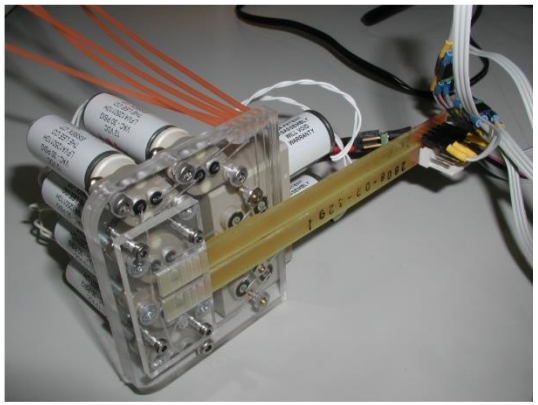




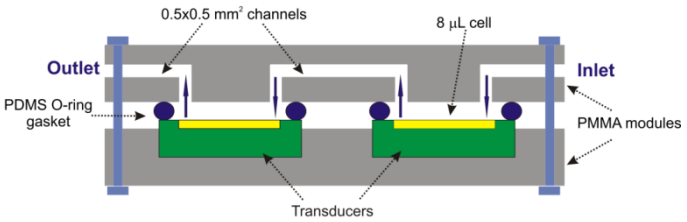
Flow system set-up

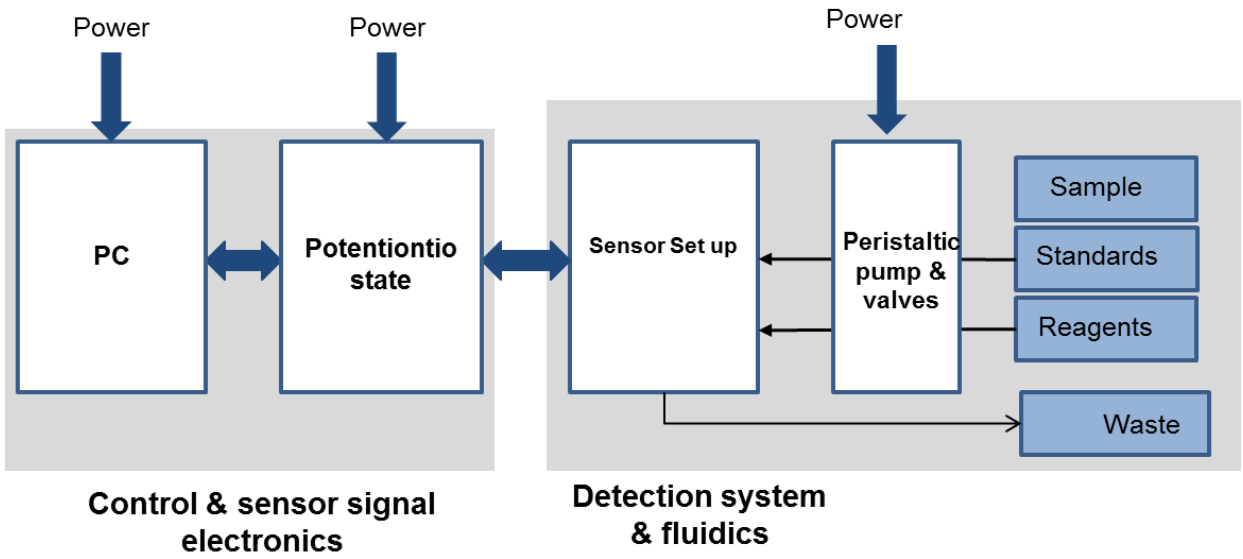
Compact flow system for the analysis of heavy metals





- Flow system Fabricated in PMMA by milling.



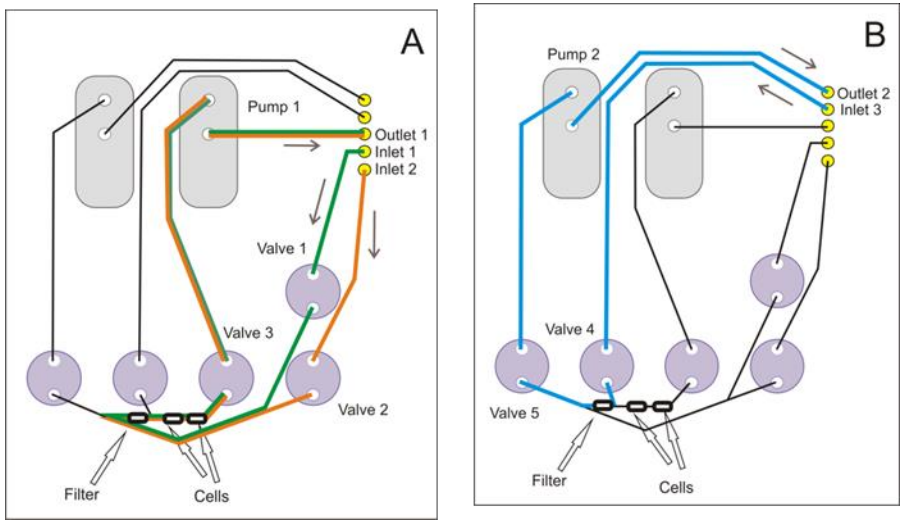


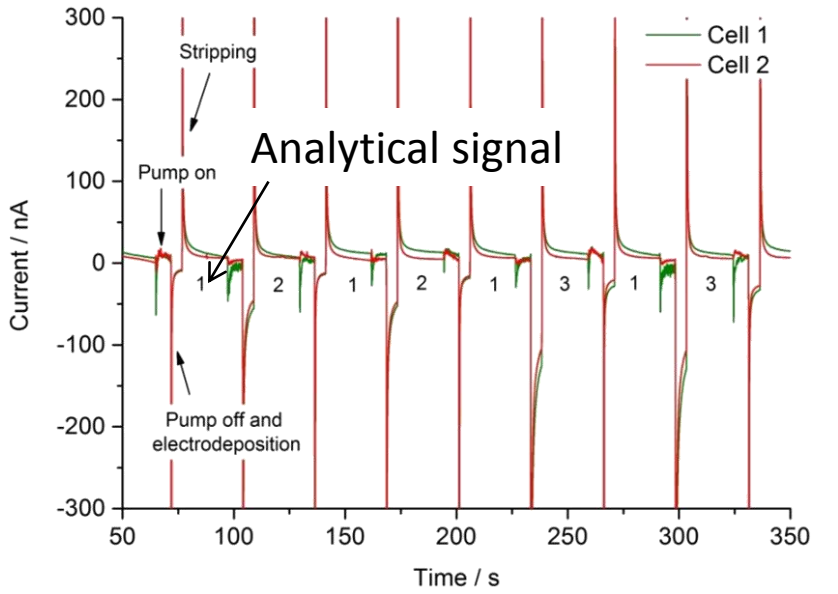
Flow system set-up

Analytical technique:
Anodic stripping chronoamperometry (ASC):
1st step Cu is reduced (signal recorded)
2nd step Cu is stripped

System operation:

1. Pump moves the solution to the flow cells
2. Pump stops
3. Electrodeposition potential applied (-300 mV, 5 s) obtaining a negative current (reduction of Cu^{2+}). Analytical signal
4. Stripping step (+100 mV, 20 s) produces a positive current which tends to zero (re-oxidation of all the Cu).

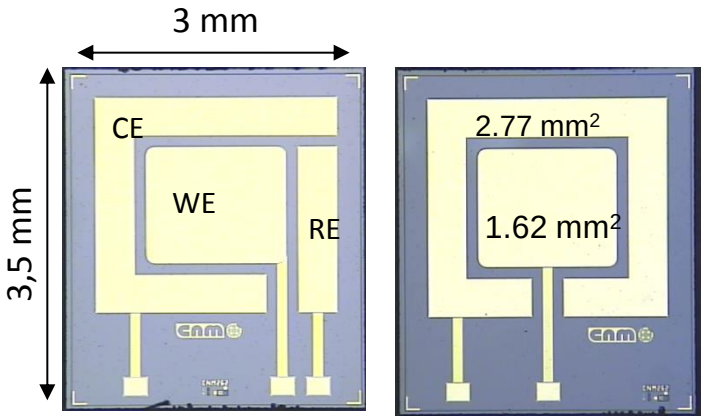




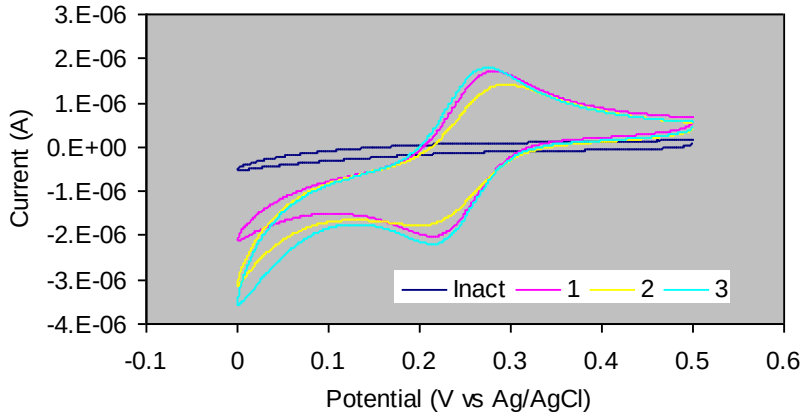
Consumption: 200 µl/sample
Response time: 30 s/sample

Evaluation results

Amperometric Microelectrodes



3-cell and 2-cell Au/Pt microelectrodes

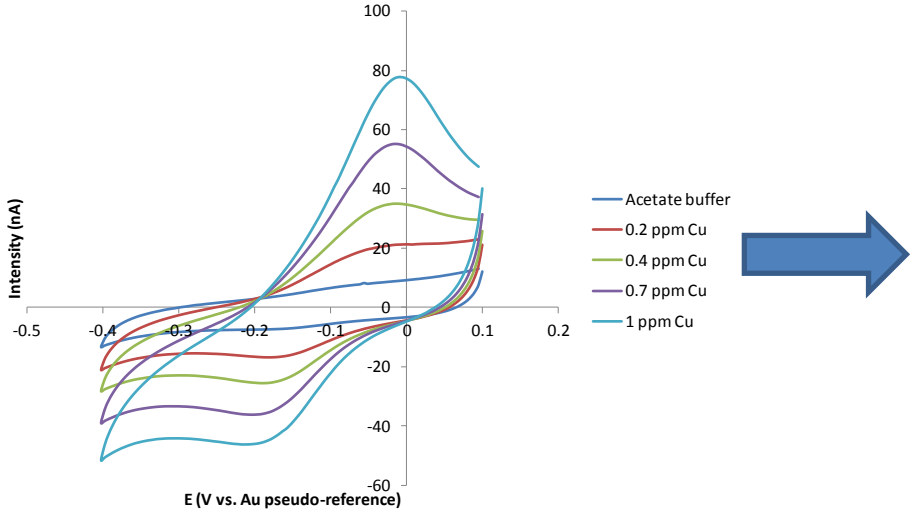


Voltammetric response in PBS/KNO_3/ $K_3Fe(CN)_6$ 1 mM of a Pt microelectrode after metal activation

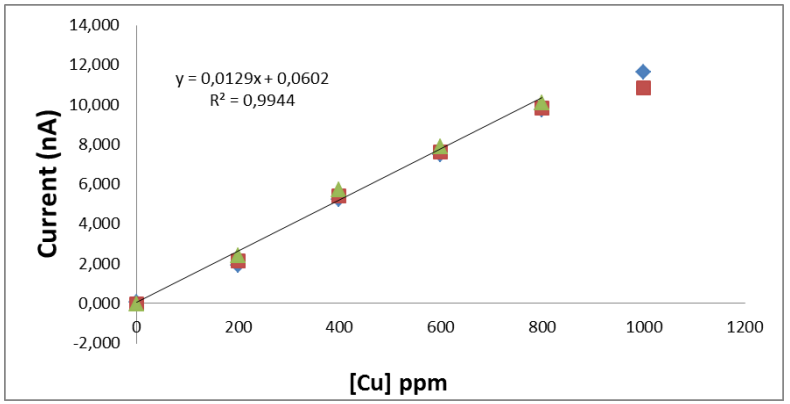
Results of the electrochemical characterization of the microelectrodes fabricated

Type	Metal	n	Surface area / mm²		$i_{red}/i_{ox,}$	ΔEp , V
			Geometric	Electrochemical		
3-electrode	Pt	25	1.62	1.93 (0.06)	1.01 (0.07)	0.071 (0.01)
3-electrode	Au	15	1.62	1.98 (0.04)	1.04 (0.02)	0.070 (0.00)
2-electrode	Au	10	1.62	1.70 (0.26)	0.99 (0.02)	0.074 (0.01)
1 electrode	Au	10	4.51	5.13 (0.01)	1.02 (0.01)	0.071 (0.00)

Evaluation results



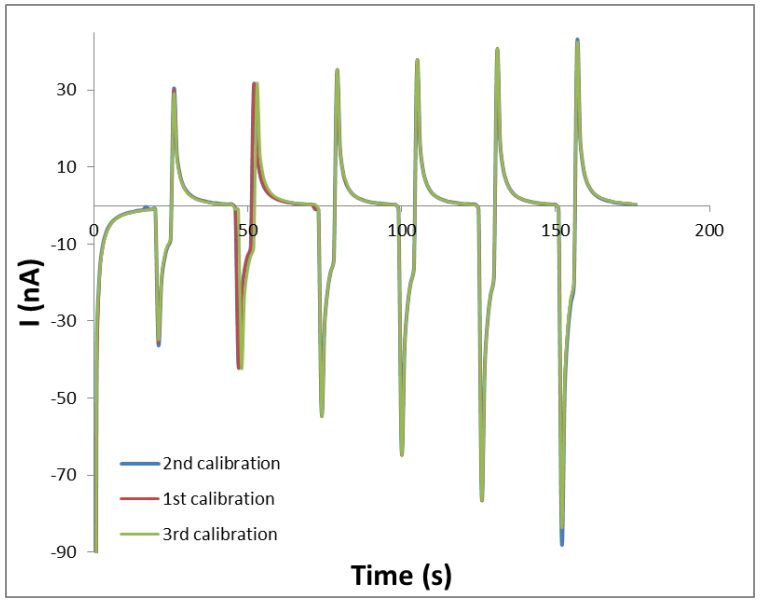
Cyclic voltammograms recorded in 0.1 M acetate buffer with the miniaturized cell using the µAutolab. Scan rate: 100 mV/s.



Calibration curve for 0-1000 ppb Cu

Test Sample	Obtained [Cu^{2+}]	Recovery
100 ppb Cu	97	97
300 ppb Cu	329	110
500 ppb Cu	475	95
700 ppb Cu	706	101

Results obtained in the determination of Cu^{2+} in tap water samples spiked

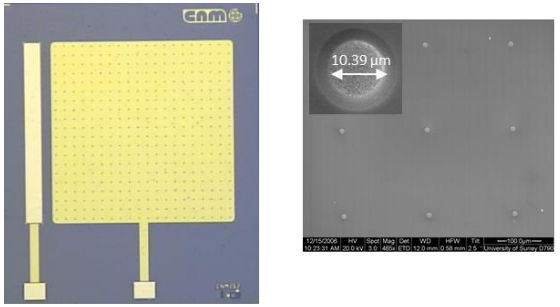


Analysis of other metals

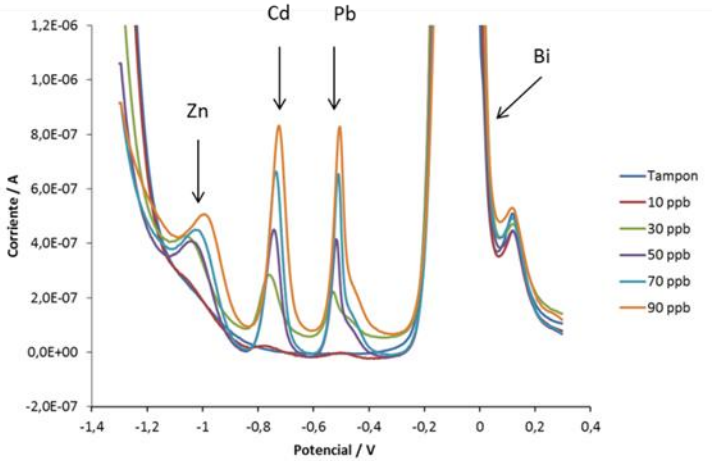
Detection with Ultramicroelectrode arrays (UMEAs)

Zn, Cd and Pb
Co-deposition of metal and Bismute
Background: acetate buffer 0.1 M, pH 4.5 with 2 ppm Bi
Electrodeposition at a potential of -1.3 V during 360 s

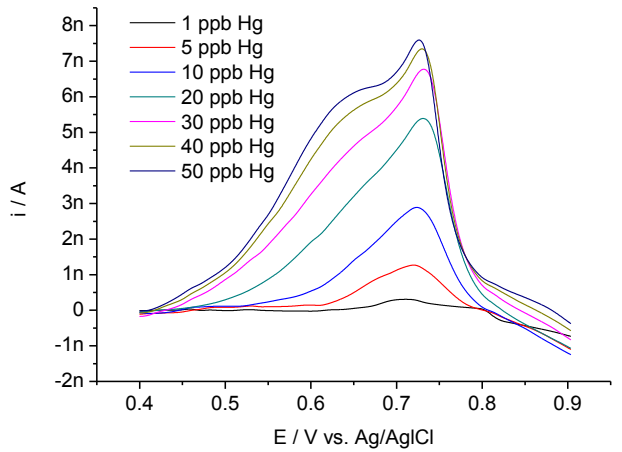
Hg
Direct detection with H_2SO_4
Electrodeposition at a potential of +0.4 V during 180 s



UMEA chip (3x3,5 mm) with detail of 10 µm microelectrode (100 disks with 200 µm separation)



Square wave voltammetry recorded in acetate buffer



Linear voltammograms recorded in 0.1 M H_2SO_4 and additions of Hg. *Scan rate: 100 mV/s.*

Conclusions

- A compact amperometric flow system for Cu detection with low consumption (< 1 ml per sample) and rapid response (< 1 min) has been developed
- Copper is detected with a high sensitivity
- Concentration range and LOQ acceptable for potable water measurements (100 -1000 ppb)
- Real sample analysis in agreement with nominal values
- Extension to other heavy metals: Hg, Zn, Cd, Pb

Acknowledgements

- Christophe Lasseur, Pierre Rebeyre, ESTEC, The Netherlands
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Thanks for your attention!

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