Rennes University

Verres de chalcogénures et microcapteurs environnementaux

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Rennes University

27th International Congress on Glass
January 20-24, 2025
Biswa Bangla Convention Center, Kolkata

Infrared luminescence of chalcogenide glasses doped with rare earth ions and their potential applications

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Pollution of water

Pollution source of groundwater and seawater

nitrate
pesticide
nitrogen compounds

herbicide
Pharmaceutical products
bacteria, virus

hydrocarbons
toxic heavy metal
radioactive substances

Rapid growth of the population, the development of industry and agriculture significant decrease in the quality of air, water and soils.

Environmental Context : Detecting and monitoring pollution in water bodies is a necessity for our current societies

The project has received funding from the European Union’s Horizon Europe Framework Programme under grant agreement No 101092723.

Monitoring water bodies quality and the evaluation of remediation

European issues concerning the development of innovative environmental multisensors

1. Develop of **modular multisensory device** integrating interchangeable sensors that can be manufactured in accordance with green principles.
2. **Achieve real-time monitoring** of multiple potential organic contaminants in various water body forms , including rivers, lakes, and oceans especially in case of accidental pollution
3. **Automated *in situ* multivariate analysis** of contaminants in various water body forms and wastewater treatment plants

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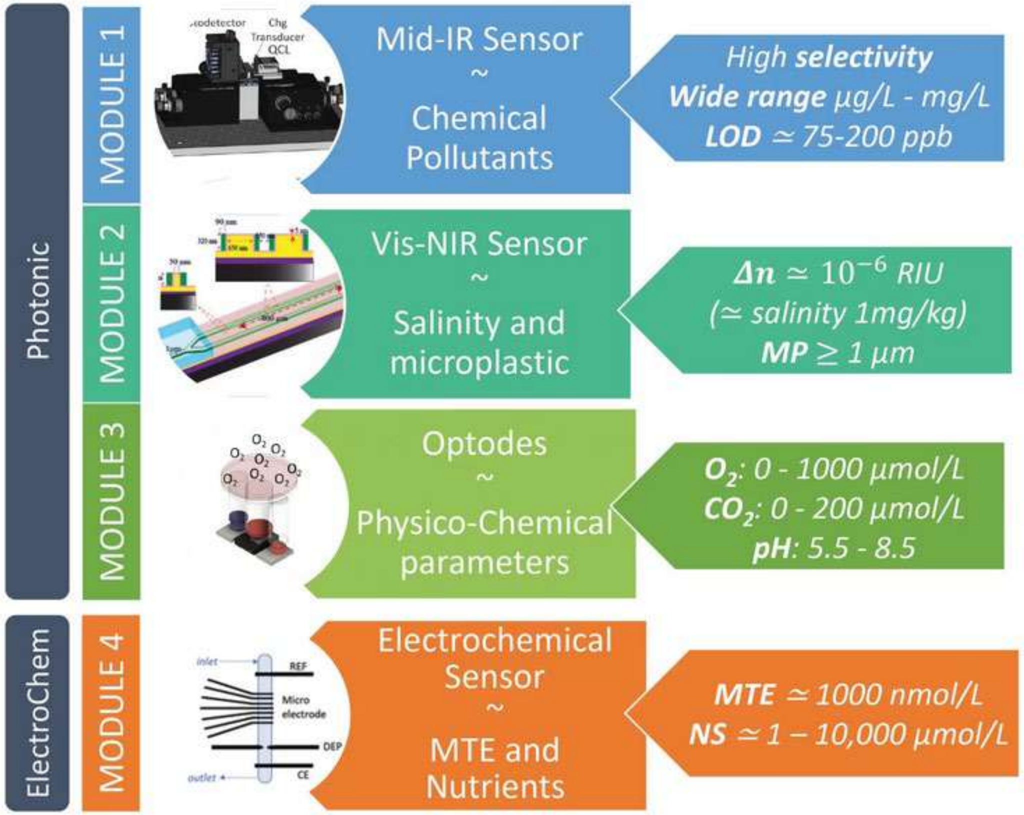
Horizon Europe – IBAIA project

Innovative environmental multi-sensing for water**B**ody qu**A**lity monitoring and remed**I**ation **A**ssessment

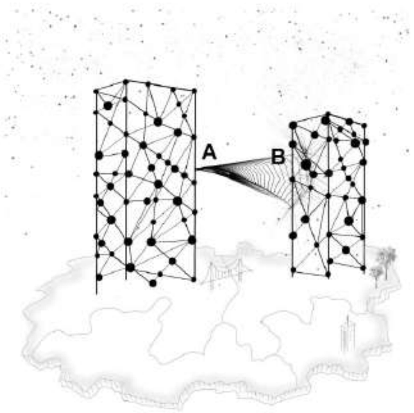


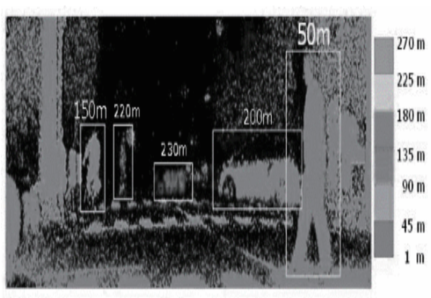
University of Pardubice · Leibniz IPHT · mirSense · Klearia · University of Eastern Finland · brgm · Ifremer · cnrs · Argotech · Tampereen yliopisto Tampere University · Cedre · SCIRPE · VIGO Photonics · MODUS · microLIQUID · Universität Duisburg Essen · UMONS Université de Mons

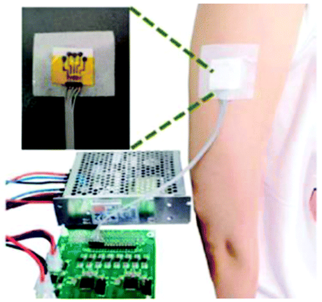
Université de Rennes

Mid-infrared photonics
↓
A key technology for many applications

- Free-space optical communication
- Long-range LIDAR
- Thermal imaging
- Infrared homing
- Biochemical sensing



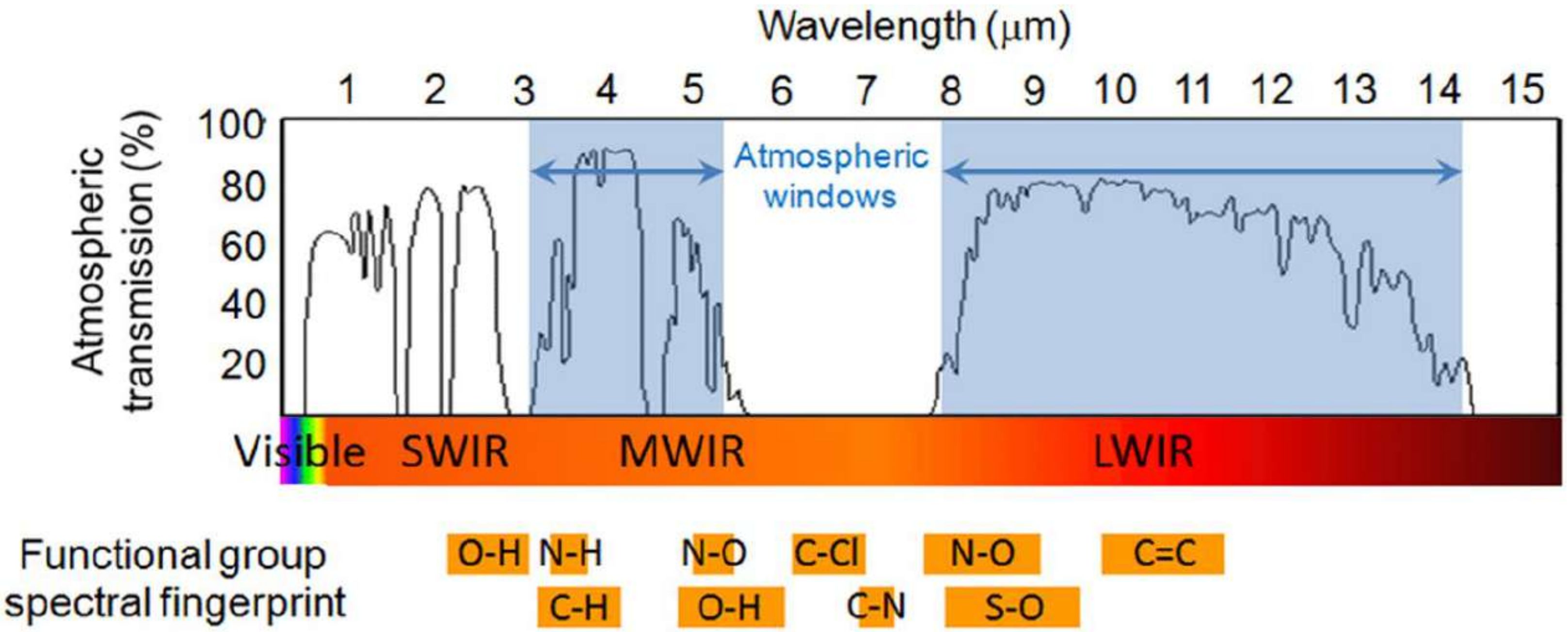




Sensor based on infrared spectroscopy

Mid-infrared range – Detection of bio-chemical molecules

Mid-infrared range contains the **absorption bands related to the vibrations of organic molecules** :
functional group region ($\geq$ 1500 cm^{-1}) and fingerprint region ($\leq$1500 cm^{-1} , $\geq$ 6.7 μm)



Applications in

- Industry
- Defense
- Environment
- Homeland security
- Free space communications
- Healthcare

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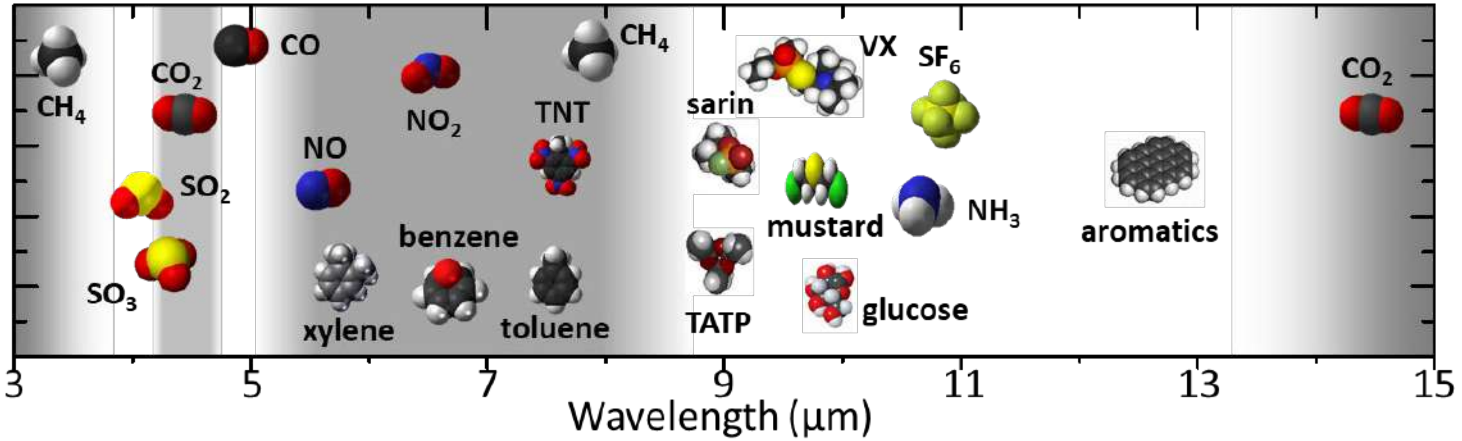
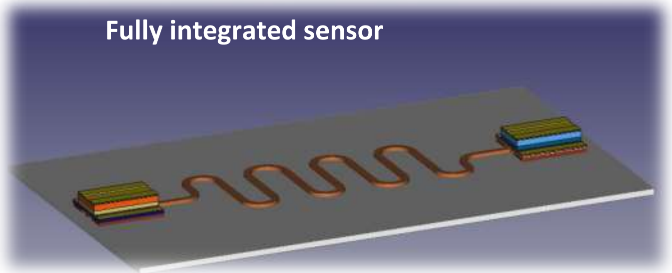
Sensor based on infrared spectroscopy

Identification and quantification of (bio)-chemical molecules have interdisciplinary significance, spanning areas such as security, health, environmental monitoring …



The challenge for mid-infrared sensors lies in the transition from benchtop to microchip.



Increasing scientific interest : mid-infrared photonic circuits for optical sensing applications.
Significant progress : optical sources (QCL, supercontinuum sources) and mid IR detectors

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Optical IR Sensor for water monitoring

- Challenge: Monitoring Accidental pollution and wastewater remediation
- Impact: Affects microbial and aquatic flora, leading to health and environmental problems.

Importance of Monitoring Organic Compounds

- Monitoring organic compounds in water is crucial for ensuring public safety.
- A series of techniques (like GC-MS) whose accuracy and analysis speed vary, mainly on laboratory scale.

Challenges in Real-World Applications

- Difficulty identifying specific molecules in mixtures
- Sensitivity and selectivity problems in environmental samples
- Need for reusable and renewable sensors to avoid fouling..

Material Selection

Integrated optical circuits offer several advantages, such as lower manufacturing costs and compact packaging, but require mid-IR transparent materials

Chalcogenide Glasses

16 S sulfur 32.06	34 Se selenium 78.09	52 Te tellurium 127.60

Based on Ge, As, Sb, Ga, In, Si, P

- broad transmission range (Vis-IR)
- high refractive index (2-3)
- high non-linear refractive index
- photosensitivity
- shaping ability (fiber, thin film)
- phase change materials
- ability to be rare earth doped

Reconfigurable lenses/PIC
Modulators
Memories

All-optical signal processing
Supercontinuum generation
Frequency comb generation

Lenses for night vision camera
(Bio)chemical sensors

Fiber lasers
On-chip mid-IR emission

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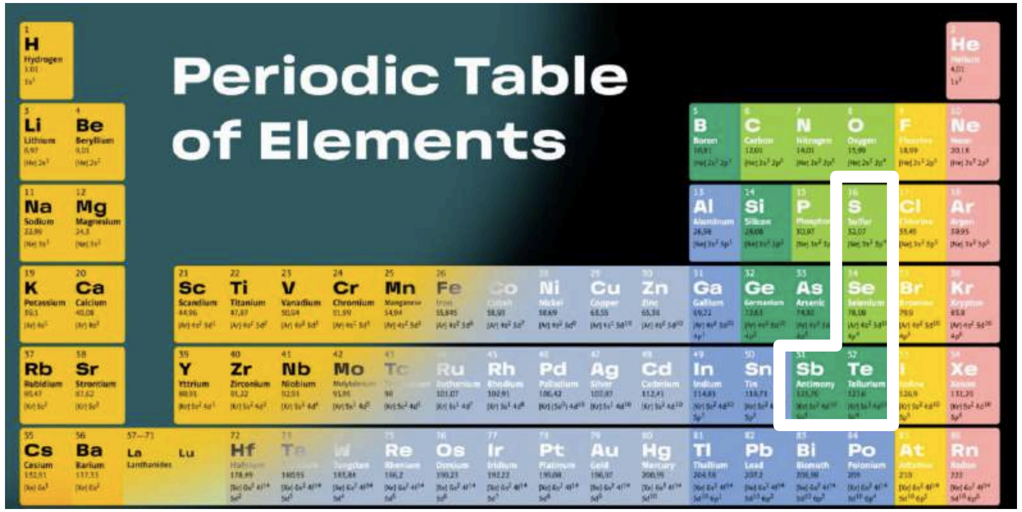
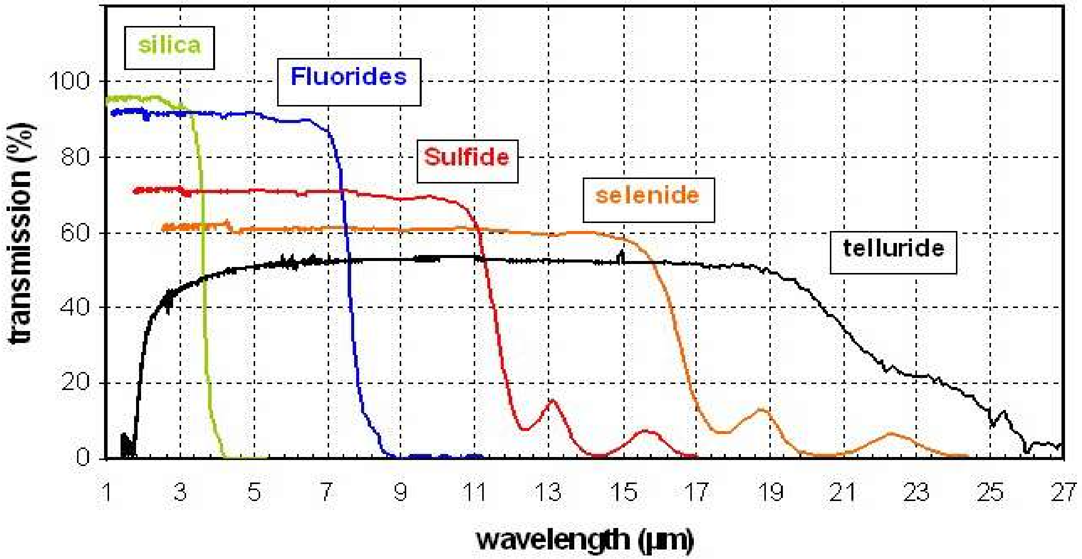
Material Selection

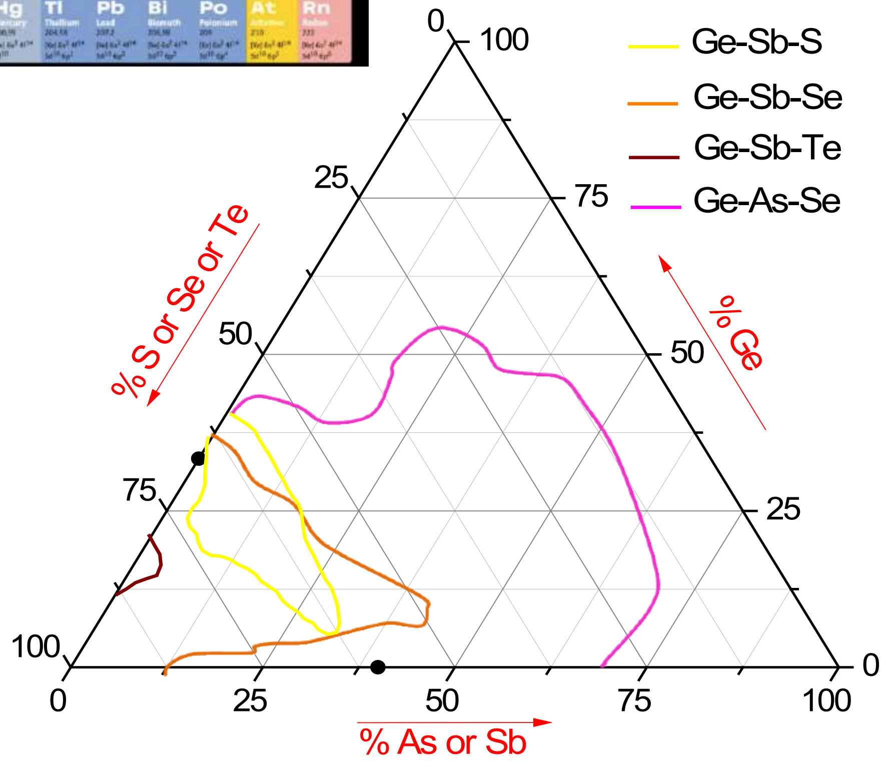
Chalcogenide Glasses

Arsenic-containing chalcogenides would be unacceptable for environmental applications



Ge-Sb-Se offers larger glass-forming region than Ge-Sb-S and Ge-Sb-Te





Selenide glasses present broader transmission window in IR than sulfide

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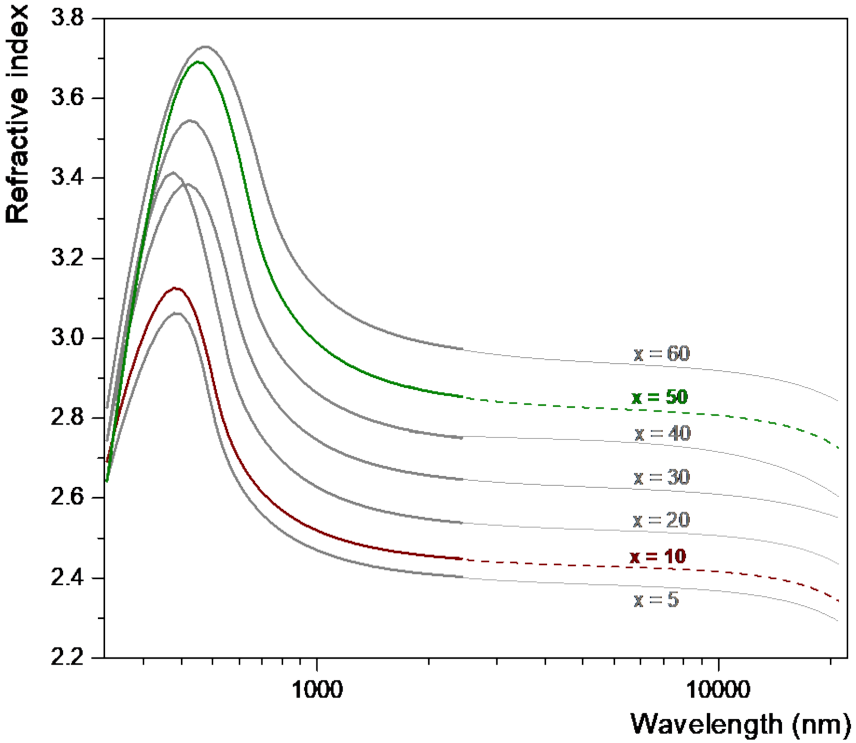
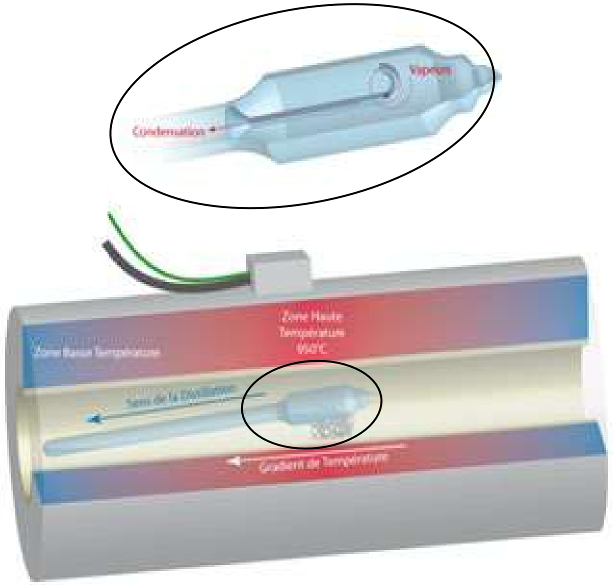
Chalcogenide glasses synthesis

Chalcogenide Glasses Synthesis

$(GeSe_2)_{100-x}\ (Sb_2Se_3)_x$

Glass system

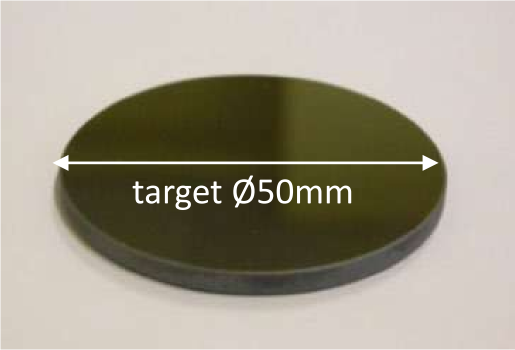




melting

quenching
annealing

cutting
polishing



The project has received funding from the European Union’s Horizon Europe Framework Programme under grant agreement No 101092723.

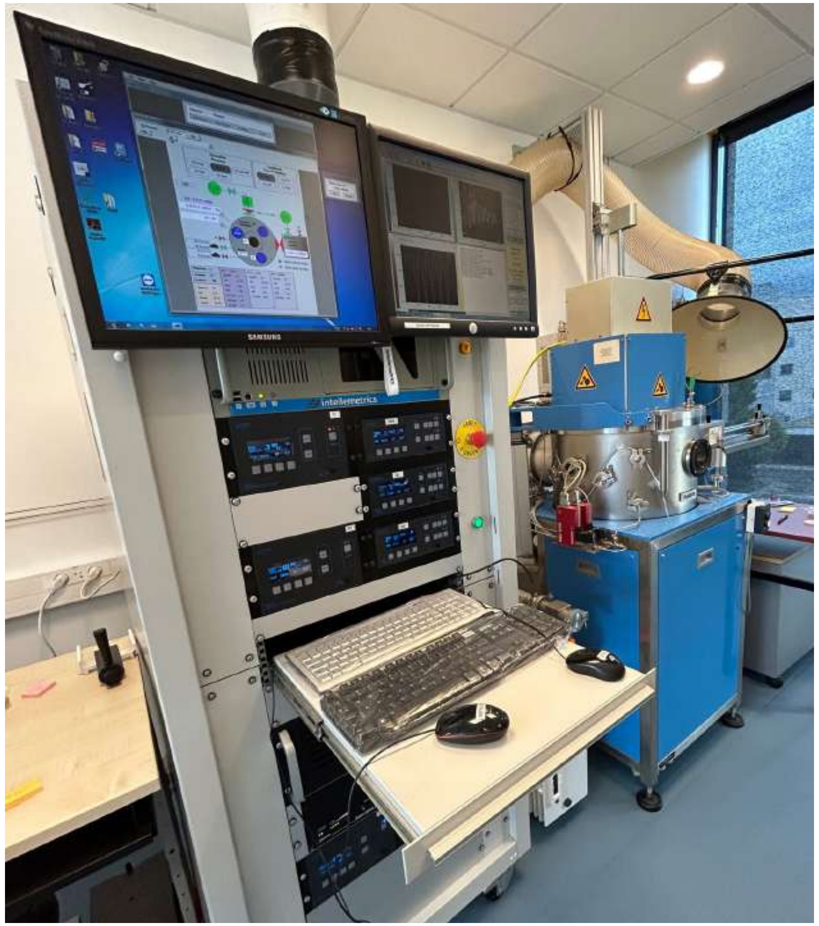
Baudet, E., Selenide sputtered films development for MIR environmental sensor. *Optical Materials Express* **2016,** *6* (8), 2616

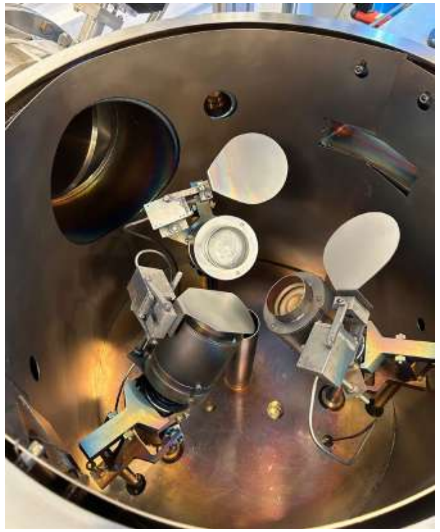
Chalcogenide thin films

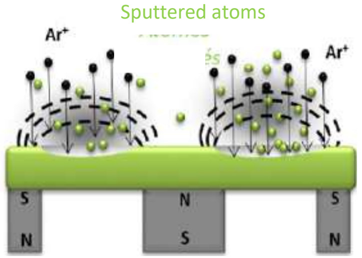
Elaboration of chalcogenide sputtered thin films

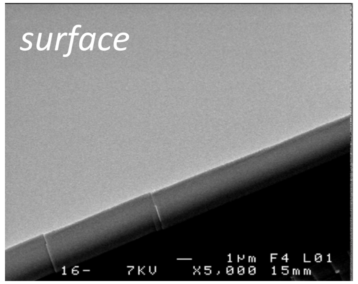
RF magnetron sputtering

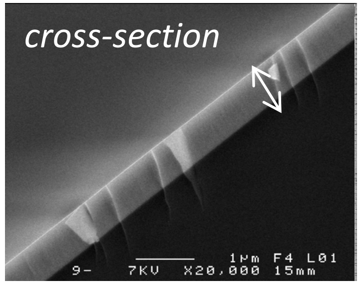
control of composition and thickness good homogeneity





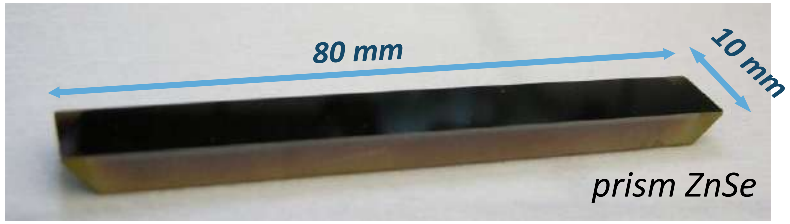






Si substrate

BK7 substrate



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Chalcogenide thin films

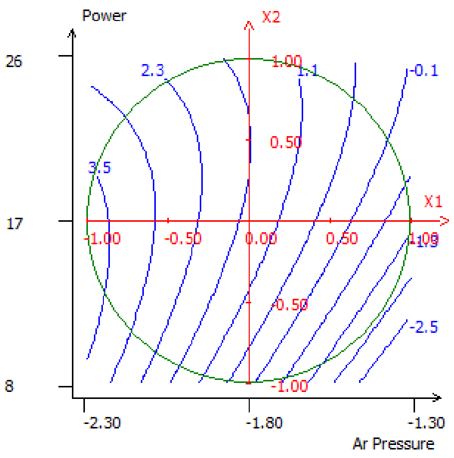
Characterization of sputtered thin films

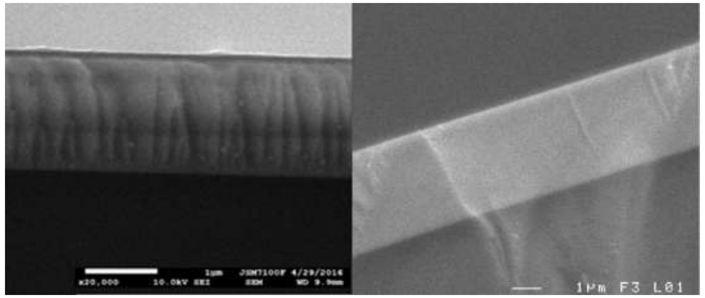
Experimental Design
Doehlert design response surface methodology

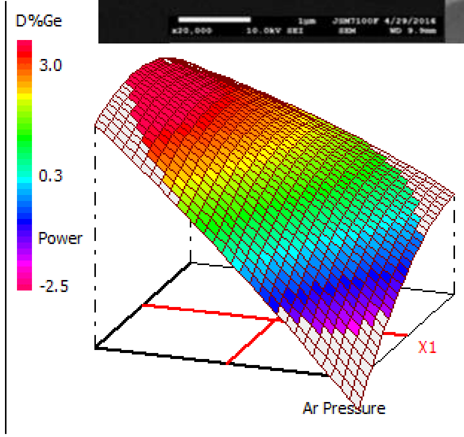
Allowing fast optimization of chalcogenide film deposition
Determine the influence of deposition parameters
To develop an optical integrated system with appropriate characteristics

Parameters
RF power
Ar pressure
Deposition time

Characterization/Response
Chemical composition
Bandgap energy
NIR and MIR refractive index
Deposition rate
Roughness







Baudet, E., Experimental design approach for deposition optimization of RF sputtered chalcogenide thin films devoted to environmental optical sensors. *Scientific Reports* **2017,** *7* (1).

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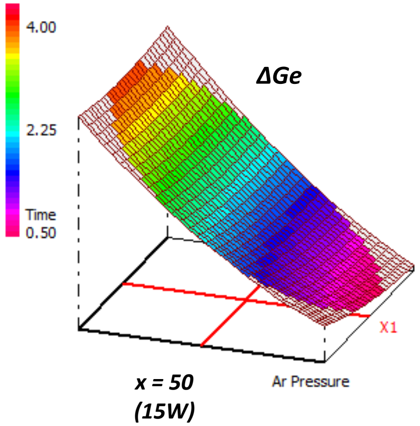
Chalcogenide thin films

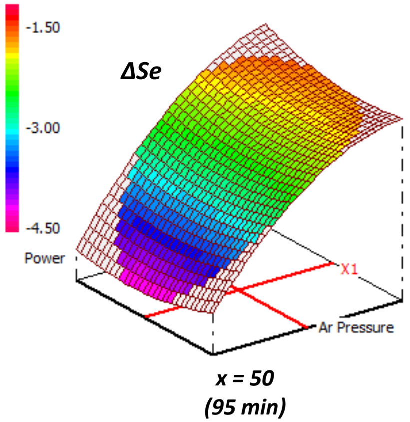
Chemical composition

$(GeSe_2)_{100-x}(Sb_2Se_3)_x$

cladding layer
▫ x = 10
-2.5 < ΔGe < 3.5
-1.1 < ΔSb <1.4
-4.0 < ΔSe < 3.6

guiding layer
▫ x = 50
0.7 < ΔGe < 3.5
0 < ΔSb < 1.4
-4.5 < ΔSe < -1.7





To allow Mid-IR propagation in optical waveguide
Thick layer deposition

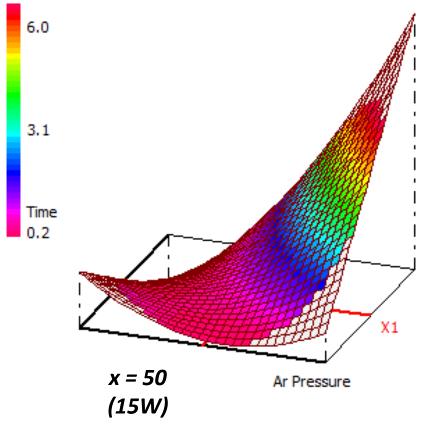
Deposition parameters set
→ no compositional drift
→ even with extended deposition time
high Ar pressure + intermediate RF power
→ composition close to target composition

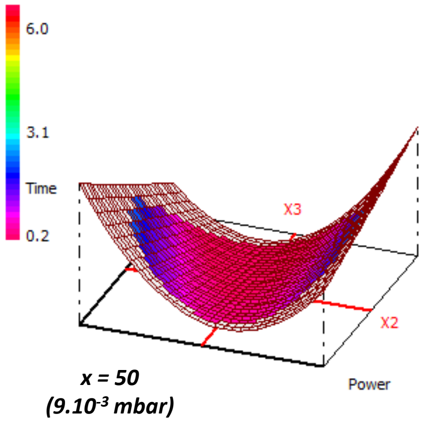
Surface Roughness

$(GeSe_2)_{100-x}(Sb_2Se_3)_x$

cladding layer
▫ x = 10
0.37 < RMS < 6.46

guiding layer
▫ x = 50
0.45 < RMS < 6.26





To reduce optical losses
→ low surface roughness required

Ar pressure is the most influential factor

Surface roughness decreases for
a short time deposition and intermediate RF power

Baudet, E., Experimental design approach for deposition optimization of RF sputtered chalcogenide thin films devoted to environmental optical sensors. *Scientific Reports* **2017,** *7* (1).

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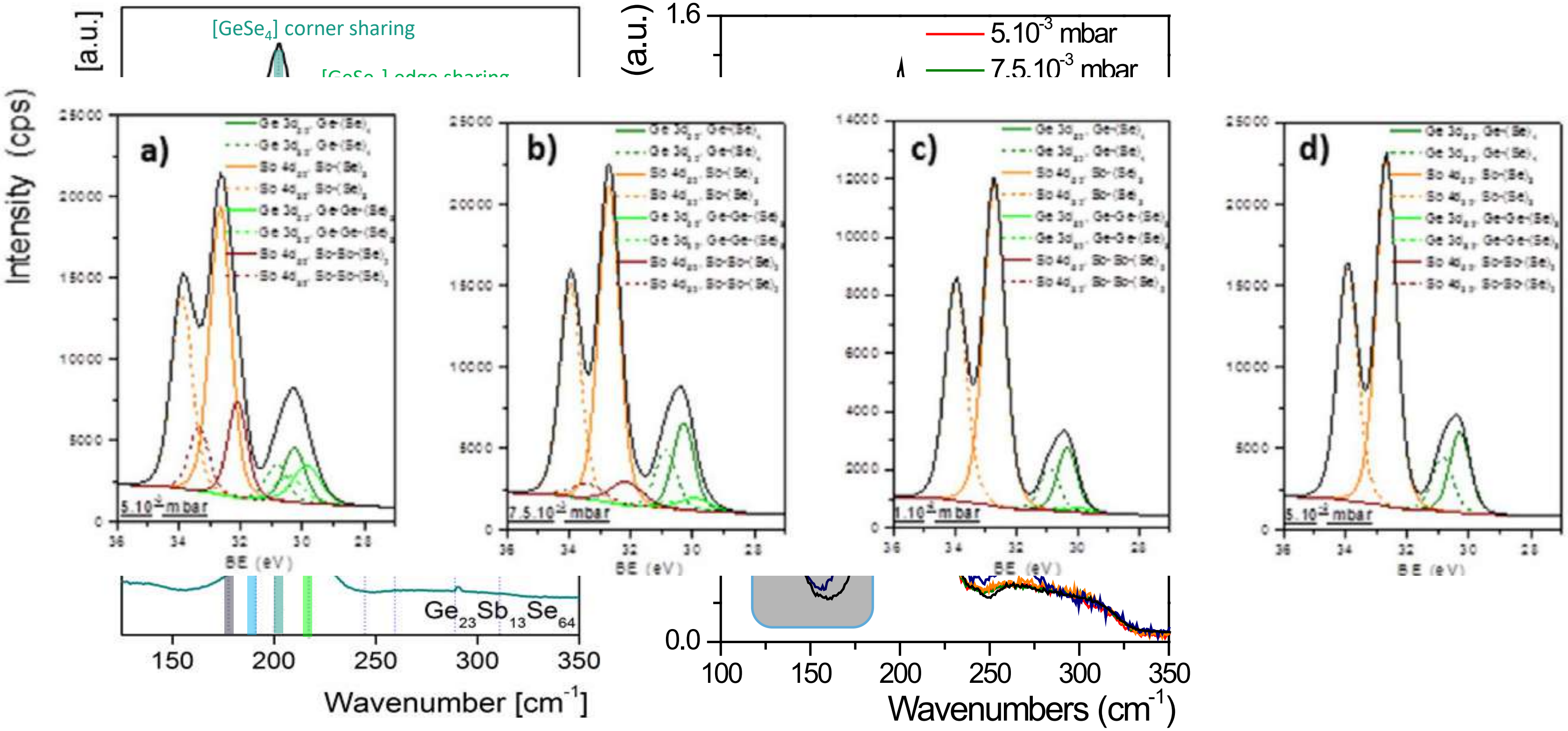
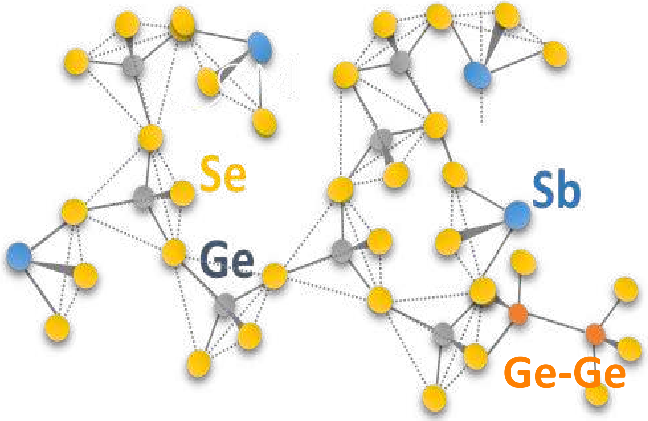
Chalcogenide thin films

Amorphous Structure versus Ar Pressure

Raman and XPS sputtered films analysis



Presence in films of defects (Ge-Ge, Sb-Sb(Ge))



Structure of thin film closer to bulk glass at higher pressure ([$GeSe_{4/2}$] tetrahedra, [$SbSe_{3/2}$] pyramids)

1- Baudet, E. et al, Structural analysis of RF sputtered Ge-Sb-Se thin films by Raman and X-ray photoelectron spectroscopies. *J. Non-Cryst. Solids* **2016,** *444*, 64-72.

2- Baudet, E. et al, X-ray photoelectron spectroscopy analysis of Ge–Sb–Se pulsed laser deposited thin films *J. Am. Ceram. Soc.* **2018,** *101* (8), 3347-3356

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Elaboration of MIR structure

RF magnetron sputtering

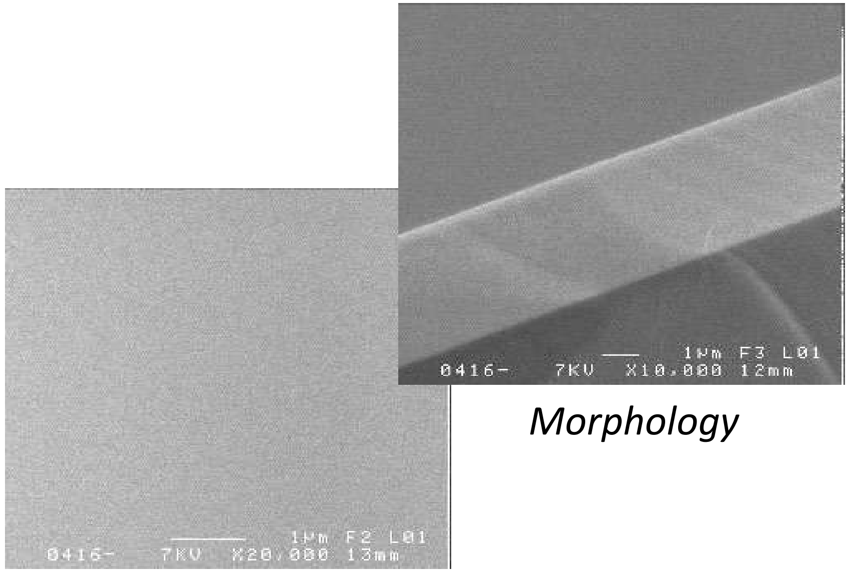
▫ cladding layer (Se2)
▫ guiding layer (Se4)

Experimental parameters defined by the experimental design:
Intermediate Ar pressure, Intermediate RF power, time deposition for thick layer

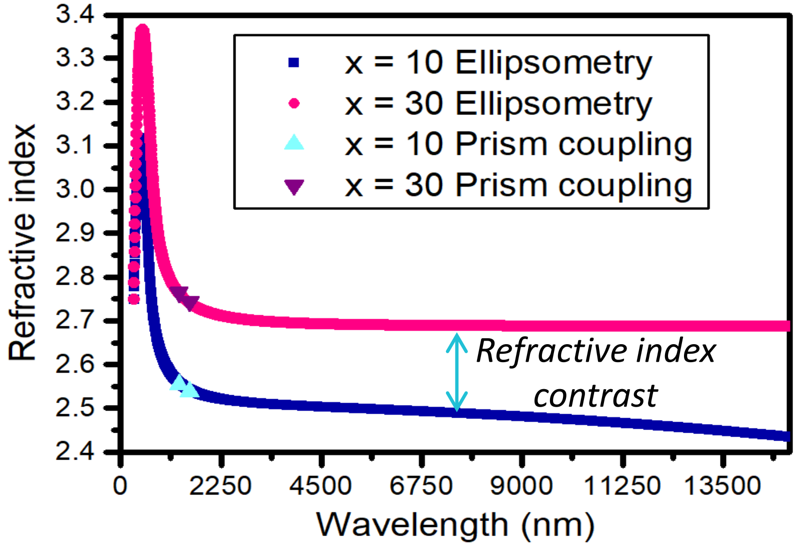
MIR structure

IR-VASE analysis

▫ thickness of each layer
▫ MIR refractive index of each layer



Morphology



University of Pardubice

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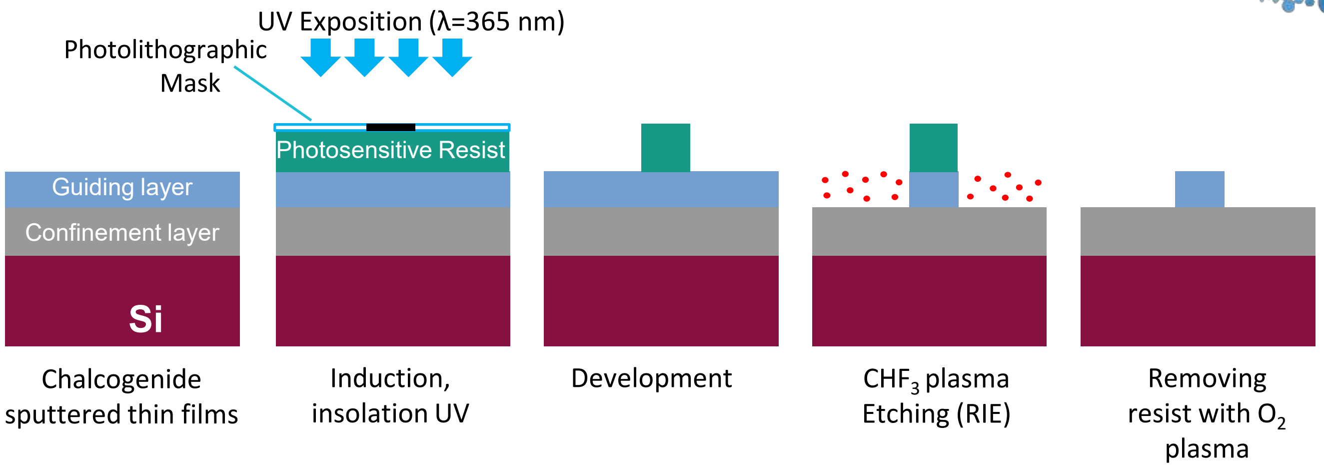
Micro-patterning of chalcogenide

MIR optical waveguide

Objective

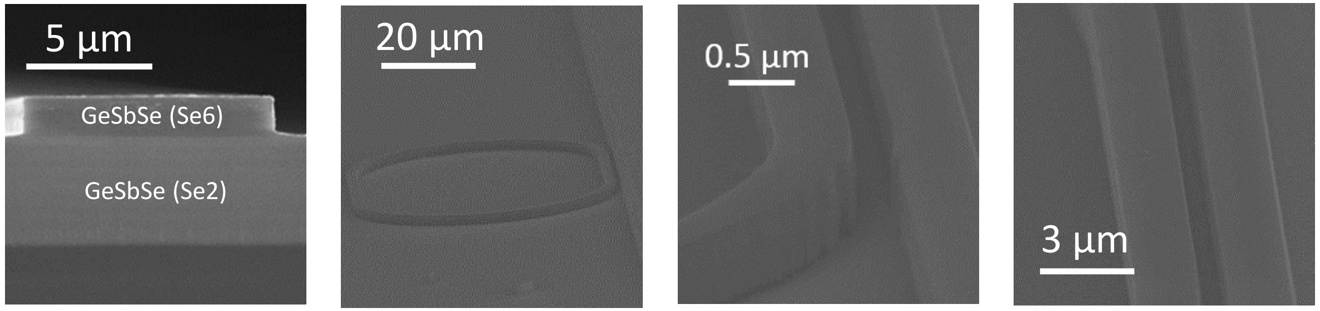
Fabrication of Photonic Integrated Circuit PIC

- straight sidewalls
- low roughness

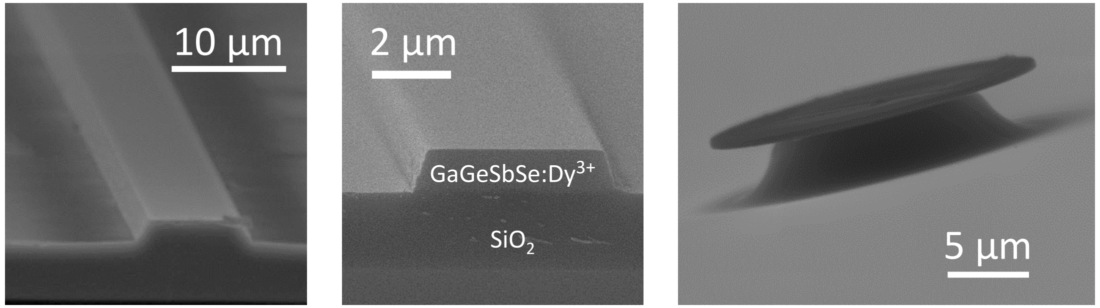


optimization of experimental parameters

(power, gas nature, gas flow…)



Undoped ChG



Doped ChG

L. Bodiou, etal, Carbon dioxide mid-infrared sensing based on Dy3+-doped chalcogenide waveguide photoluminescence, Opt. Lett. 48(5) (2023) 1128-1131

E. Delcourt, et al, Self-phase modulation and four-wave mixing in a chalcogenide ridge waveguide, Optical Materials Express 10(6) (2020) 1440-1450.

Gutierrez-Arroyo, A. et al, Optical characterization at 7.7 µm of an integrated platform based on Chg waveguides for sensing applications in the mid-infrared. Opt. Express **2016,** 24 (20), 23109

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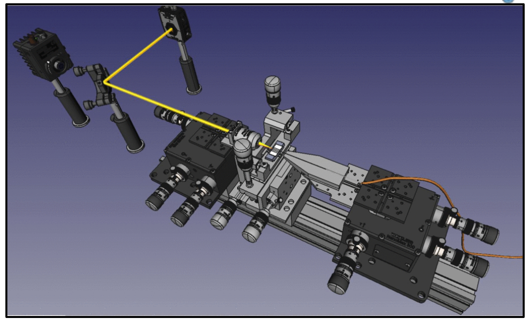
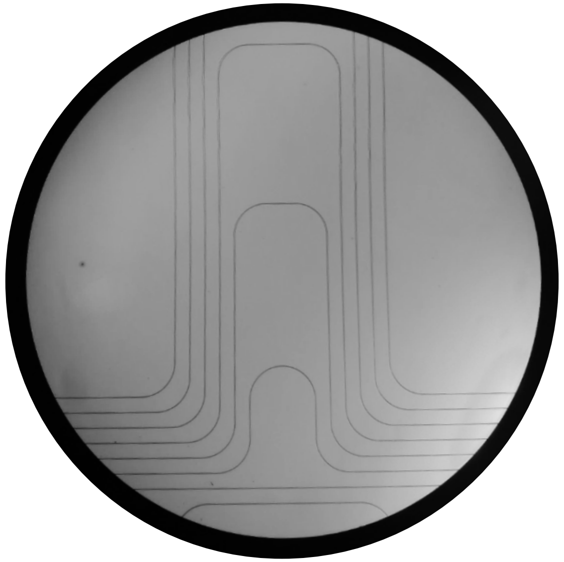
Characterization: mid-IR optical losses

Mid-IR tunable laser → Chalcogenide fiber → **Transducer** → Microscope objective → **Mid-IR Detector**



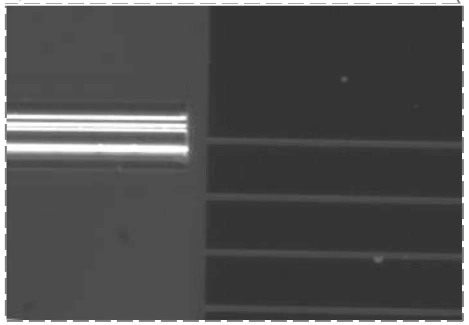
Broadly tunable QCL sources covering
λ = 3.9 – 4.7 µm (QCL1)
λ = 6.9 – 9 µm (QCL2, QCL3, QCL4)

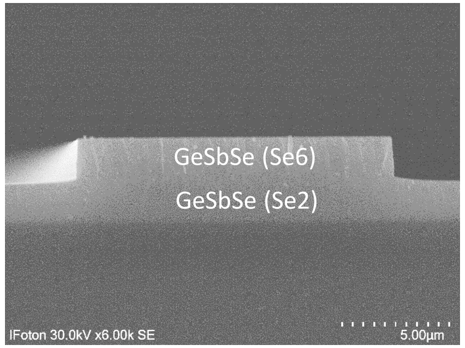
Cutback method



Top view sample

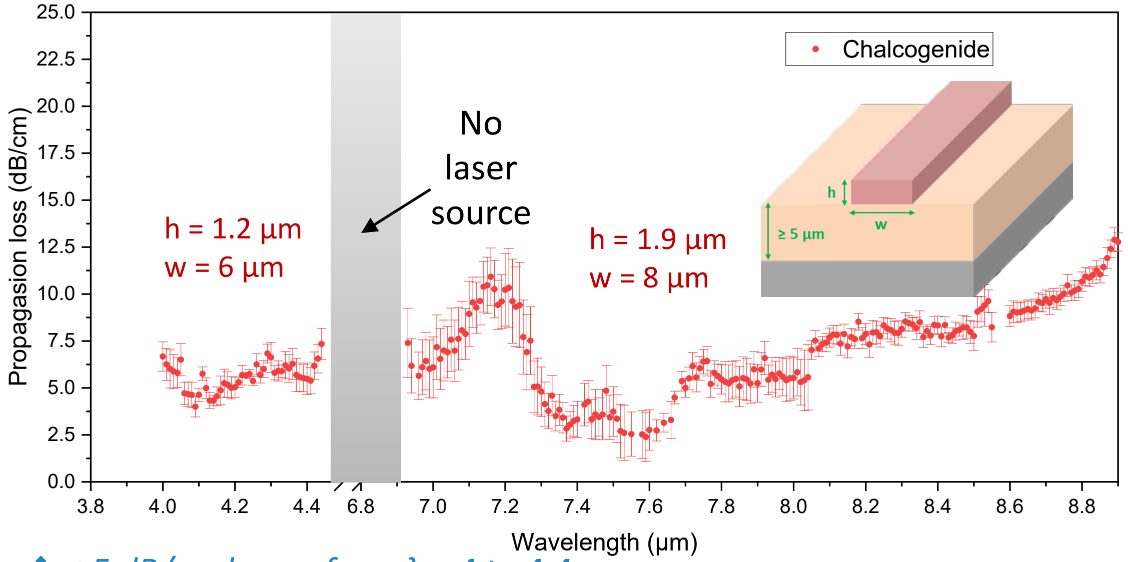
Top view fiber-waveguide light coupling





Chg waveguide

Propagation losses in Mid-IR of Se_6 on Se_2 waveguide



- *~5 dB/cm losses from λ = 4 to 4.4 µm*
- *Transparency up to 9 µm*
- *Losses increase induced by the fluorine-based etching*
- *Min losses = 2.5 dB/cm at λ = 7.5 µm*

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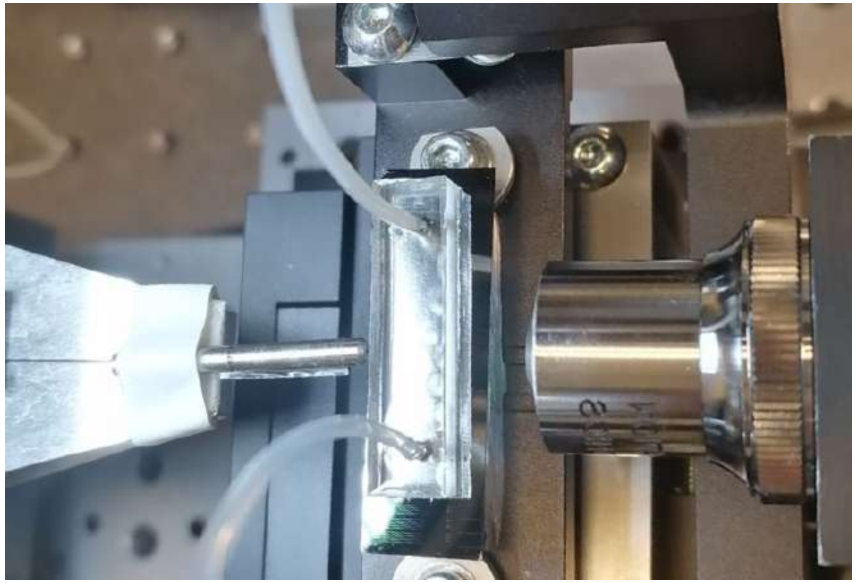
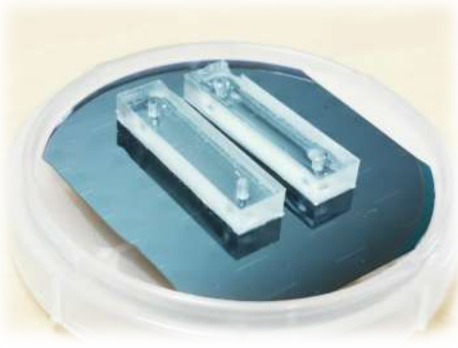
Sensing: Liquid sensing experiments



interaction length: 7.8 mm

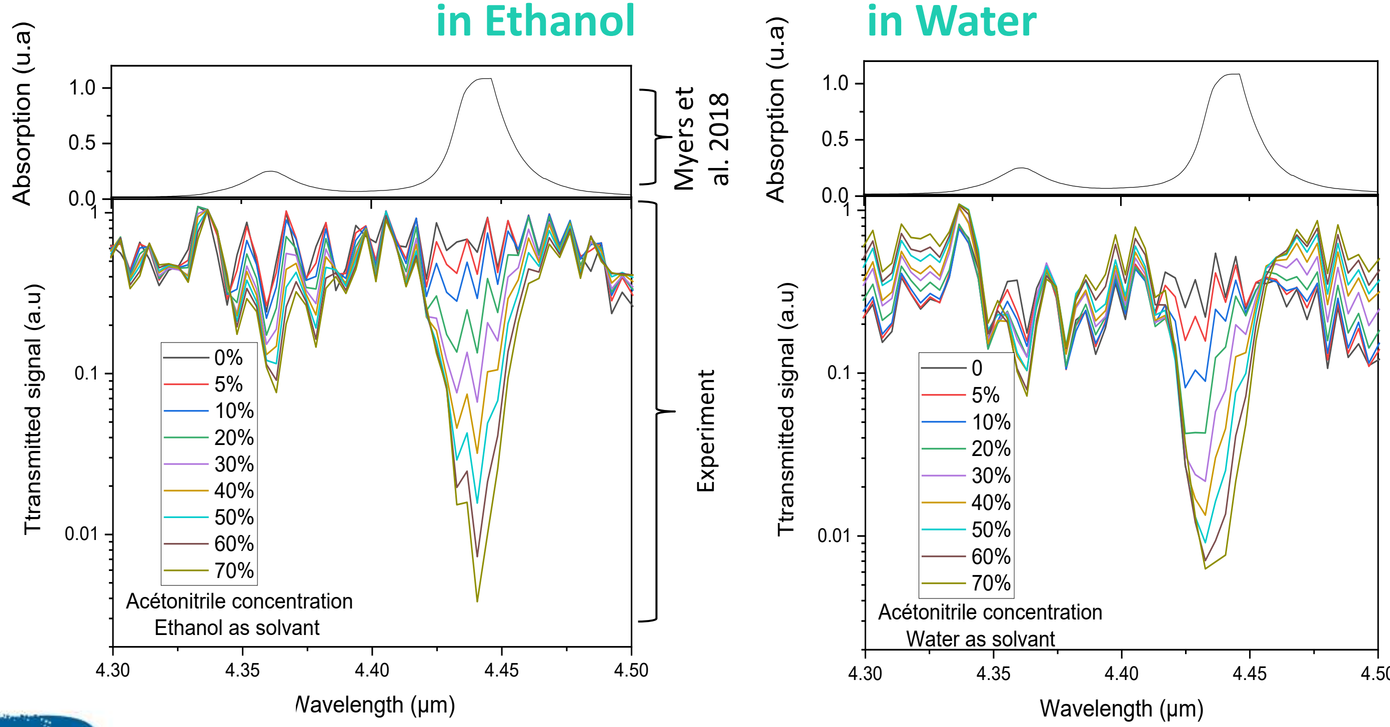


PDMS fluidic cells are bounded to control the interaction length

Sensing platform

Acetonitrile diluted

in Ethanol in Water



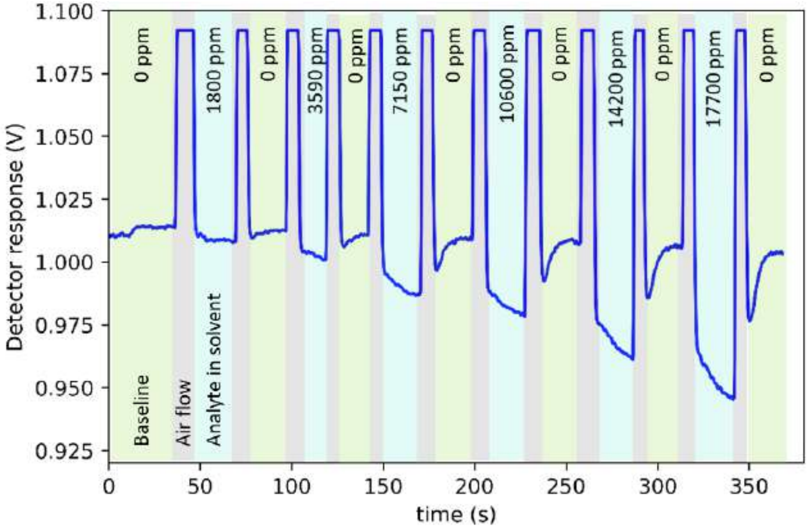
Ifremer

The project has received funding from the European Union’s Horizon Europe Framework Programme under grant agreement No 101092723.

Sensing: Liquid sensing experiments

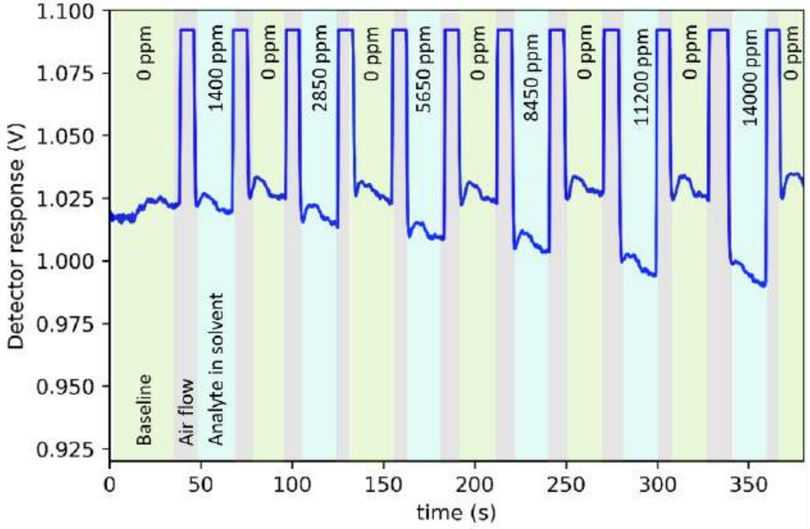
Peak of absorption at λ = 4,28 µm

Acetonitrile diluted in Ethanol

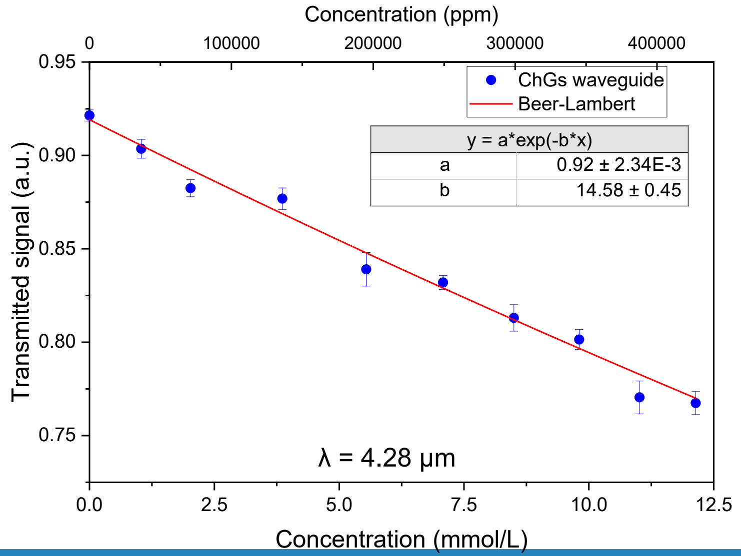


- LoD: 1700 ppm

Acetonitrile diluted in Water



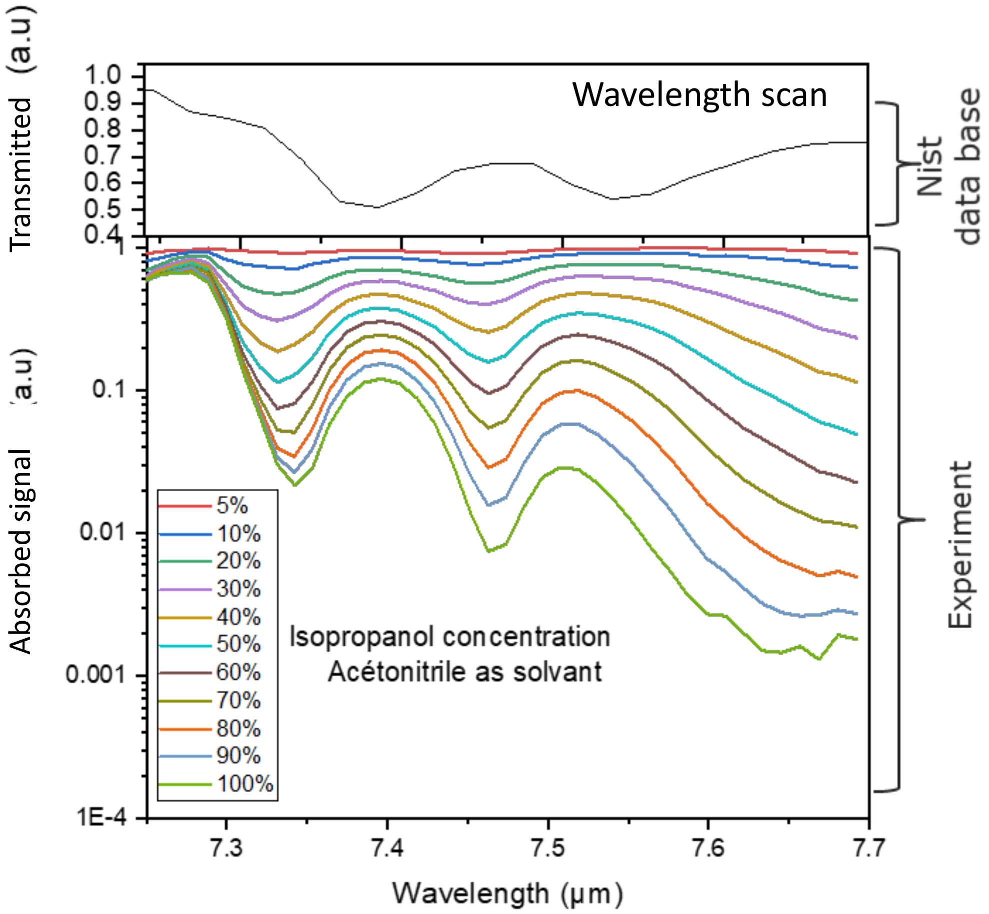
- LoD : 2850 ppm



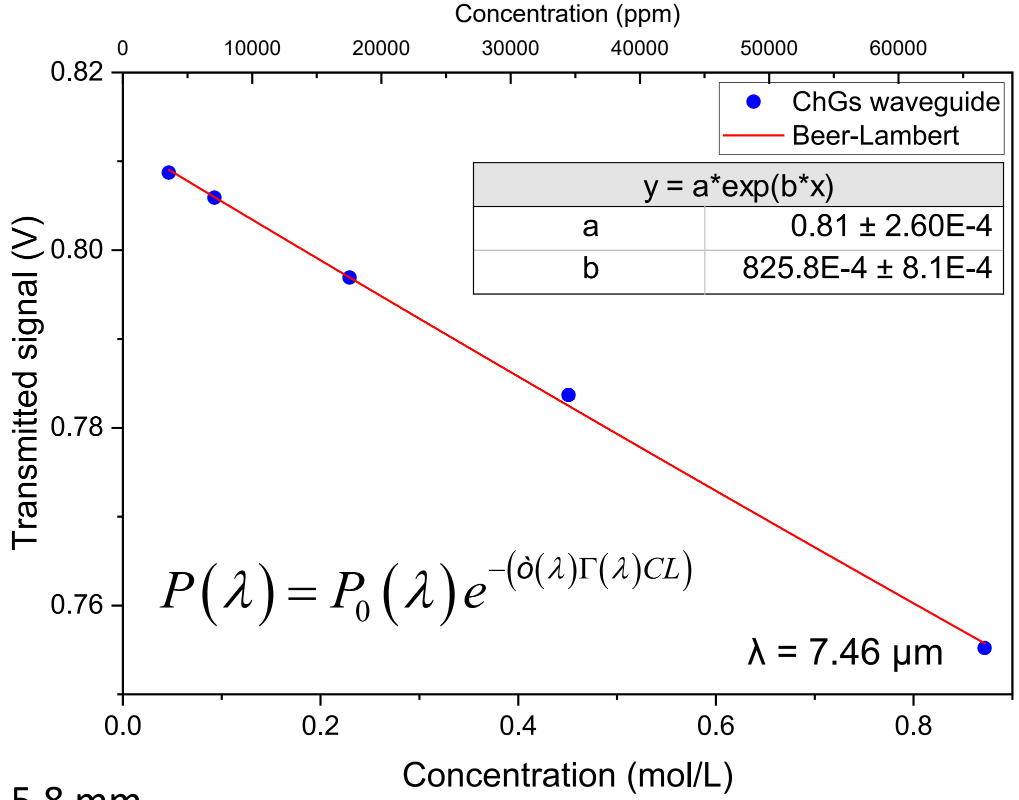
The project has received funding from the European Union’s Horizon Europe Framework Programme under grant agreement No 101092723.

Sensing: Liquid sensing experiments

Isopropanol diluted in Acetonitrile



Fixed wavelength at λ = 7,46 µm



- interaction length: 5.8 mm
- LoD: 610 ppm

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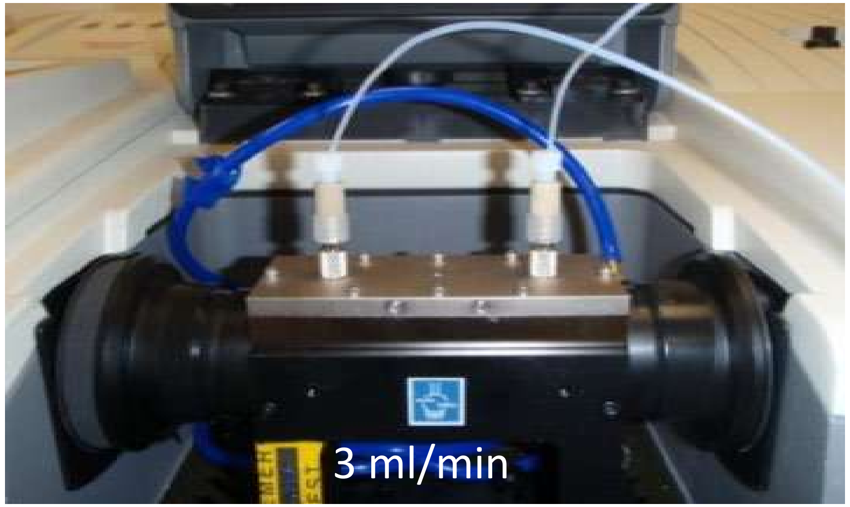
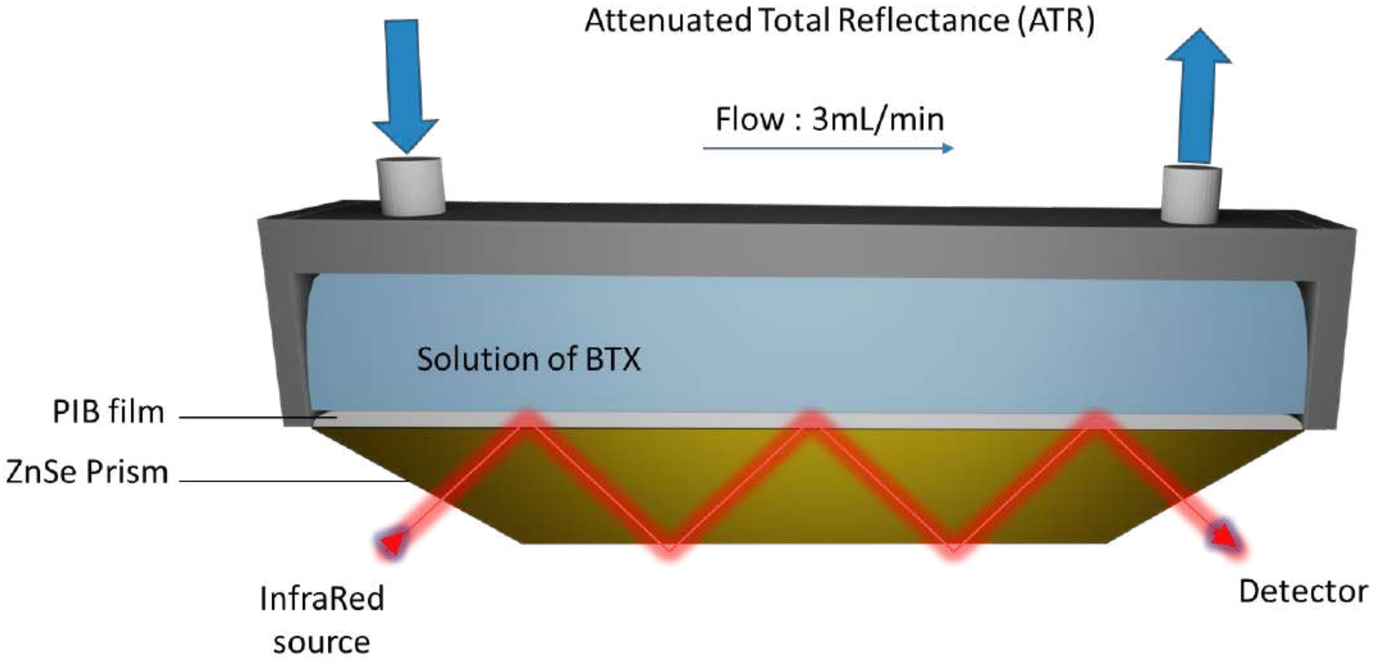
Functionalisation of chalcogenide transducer

Detection of organic molecules requires
hydrophobic material coating onto the waveguide surface

Objectives

- Attenuation of water signal
- Extraction of the analyte from polluted water





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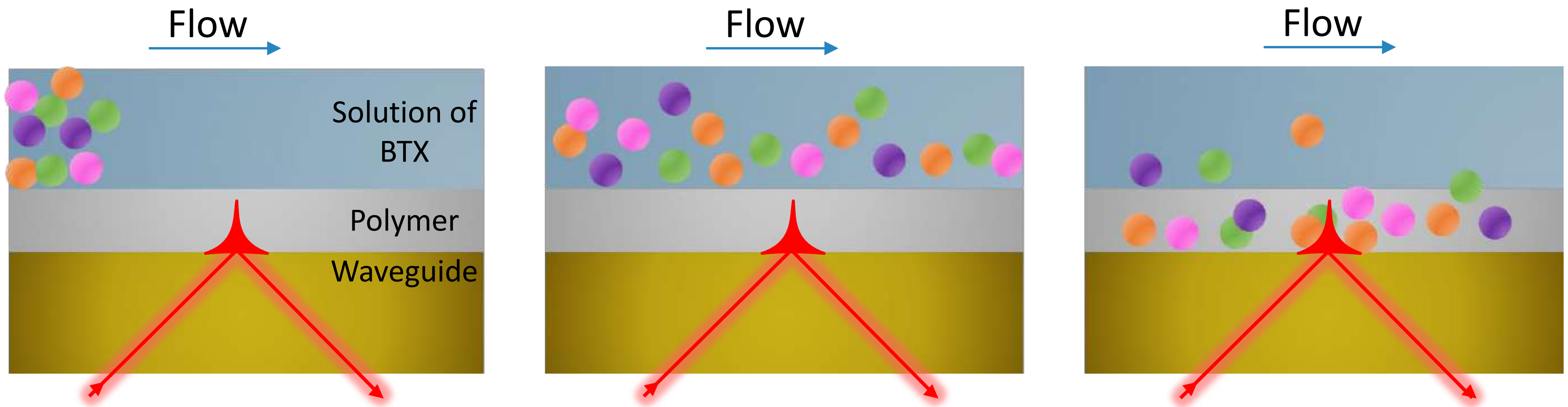
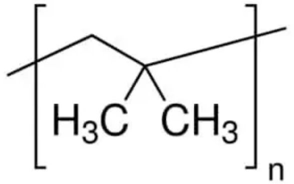
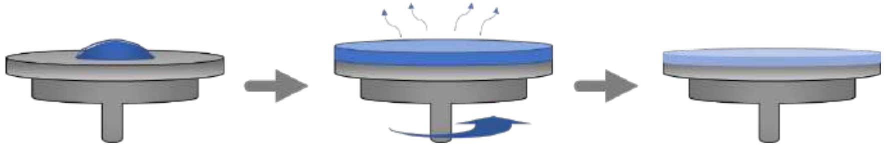
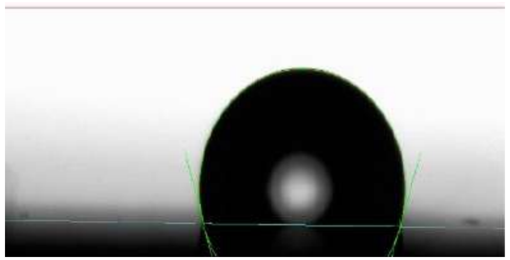


Polyisobutylene (PIB)





Optimization of polymer deposition parameters on ZnSe prism
→ Decrease of water absorption



Contact angle measurement
close to expected value (100-110°)

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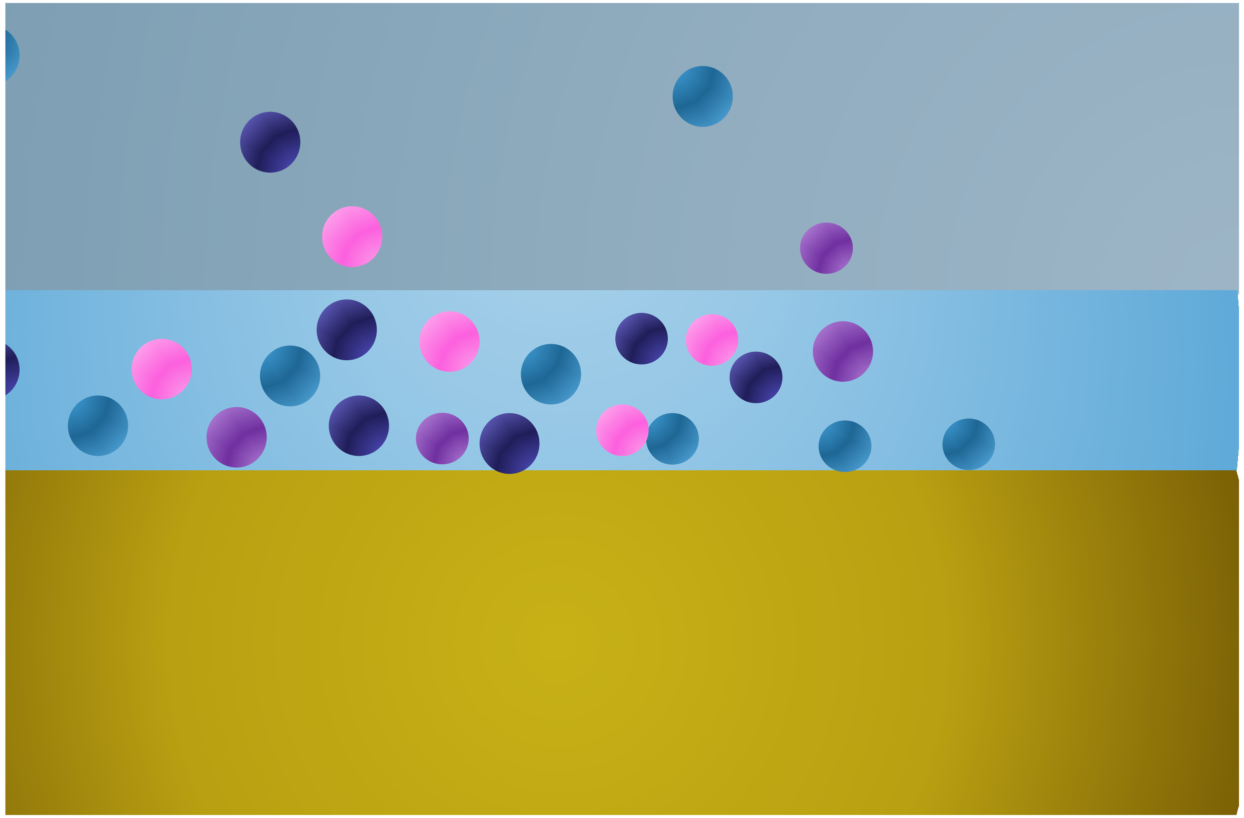
Regeneration of PIB film to extend its life cycle

Water Flow

→



Importance of Reusability

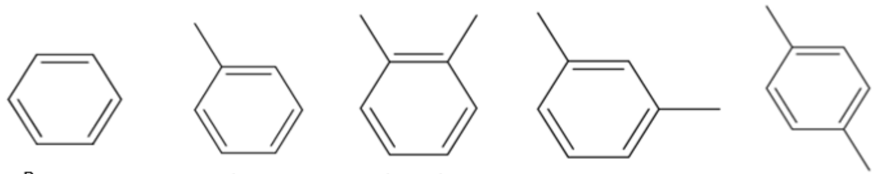
- Minimizes environmental impact and extends sensor life cycle.
- Contrasts with single-use sensors in health and pharmacology.

Functionalisation of chalcogenide transducer

Aromatic Hydrocarbon Detection

- Detection of BTX

benzene - toluene - xylenes
Range 40 ppb – 100 ppm

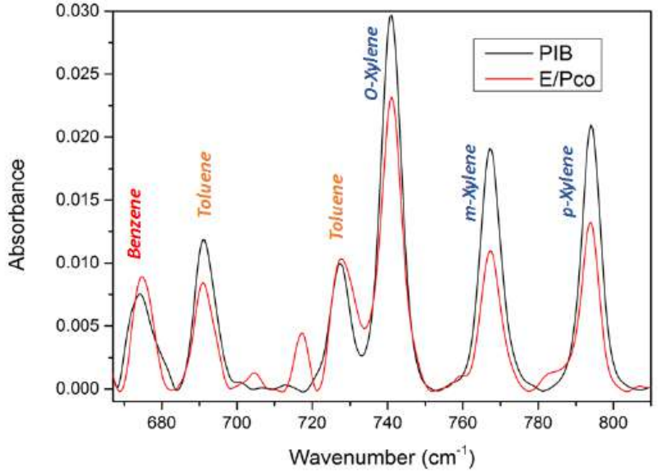


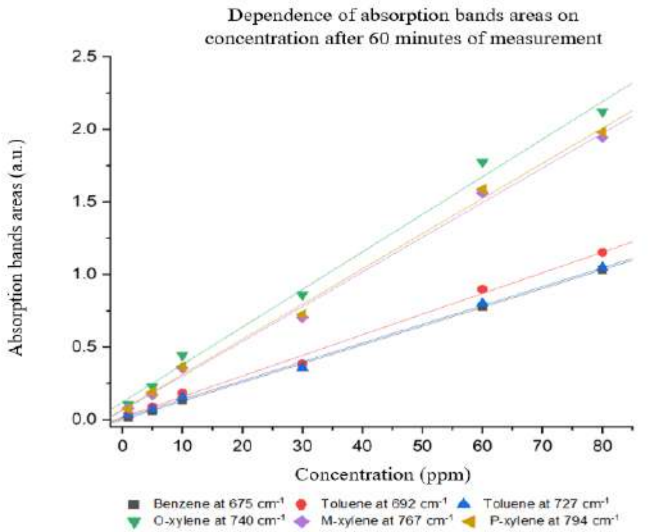
Benzene Toluene Ortho-xylene Meta-xylene Para-xylene

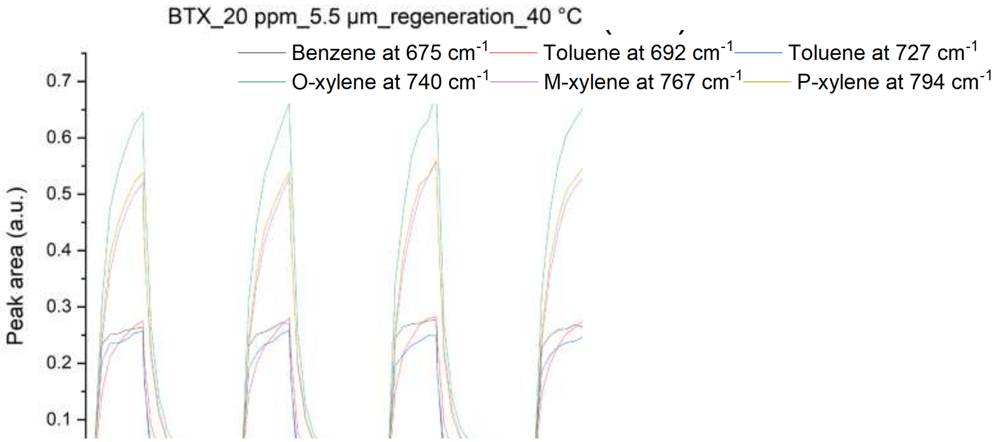
quickly detected
simultaneously

- Regeneration of polymer

polyisobutylene (PIB)
ethylene/propylene copolymer (EPco)







M. Baillieul`et al., Surface Functionalization with Polymer Membrane or SEIRA Interface to Improve the Sensitivity of Chalcogenide-Based Infrared Sensors Dedicated to the Detection of Organic Molecules, Acs Omega 7(51) (2022) 47840-47850.

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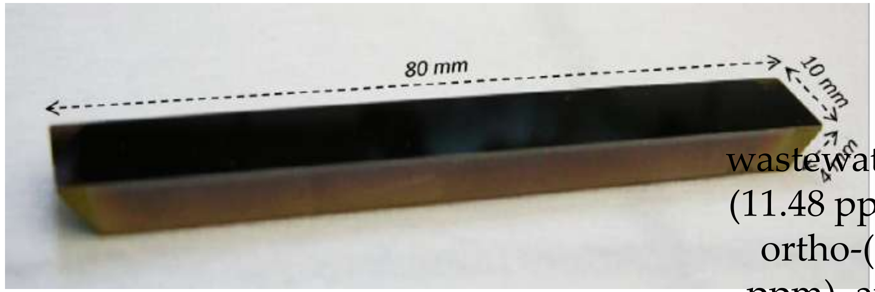
Functionalisation of chalcogenide transducer

Aromatic Hydrocarbon Detection

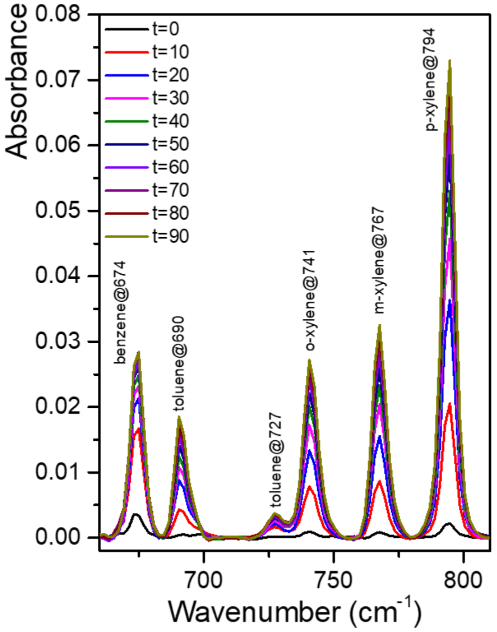
- Polymer compatibility with Chg waveguide

ATR-FTIR flow cell using PIB film deposited on GeSbSe: ZnSe prism



- Natural Water Analysis

wastewater spiked with benzene (11.48 ppm), toluene (0.76 ppm), ortho-(3.08 ppm), meta-(6.04 ppm), and para-xylenes (11.88 ppm) for different time enrichment (from 0 to 90 min).



Rapid and simultaneous detection of BTX in a complex and natural water

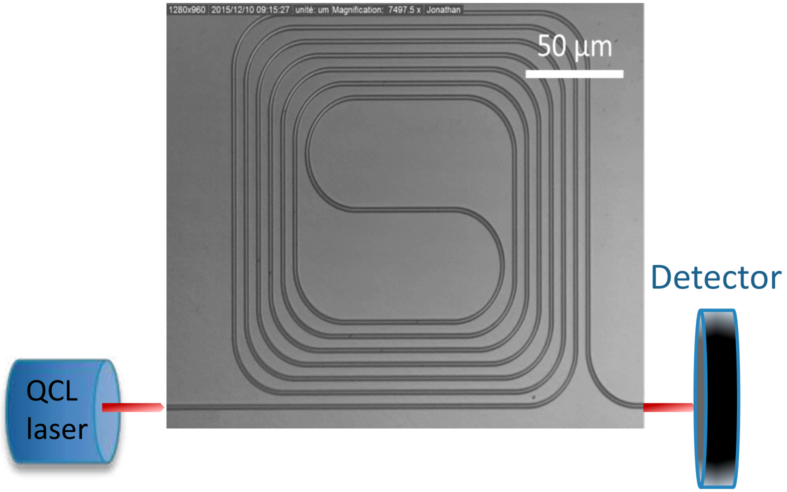
- All hydrocarbons detected after 10 min enrichment
- Wavenumbers of peak are in agreement with previous results

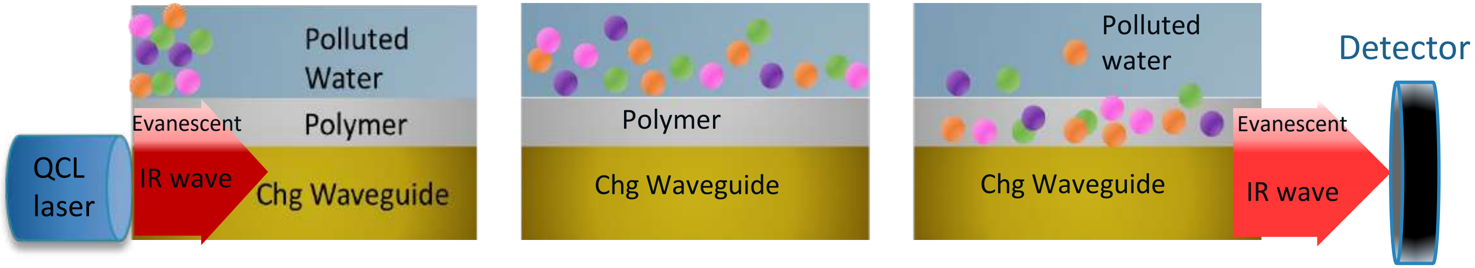
Baillieul, M. et al, Toward Chalcogenide Platform Infrared Sensor Dedicated to the In Situ Detection of Aromatic Hydrocarbons in Natural Waters via an Attenuated Total Reflection Spectroscopy Study. *Sensors* **2021,** *21* (7), 2449.

The project has received funding from the European Union's Horizon Europe Framework Programme under grant agreement No 101092723.

Sensor based on infrared spectroscopy

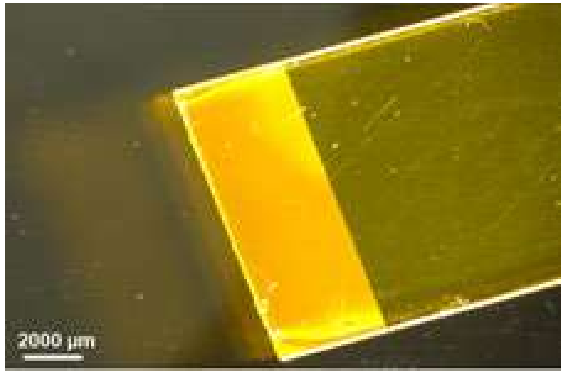
PIC Evanescent wave Spectroscopy





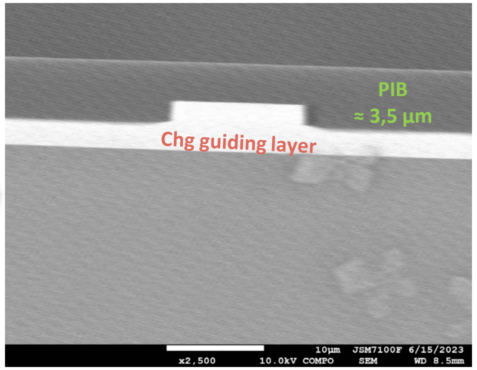
Propagation of the MIR light in the waveguide

The evanescent wave detects pollutant molecules that diffuse on the surface of the waveguide

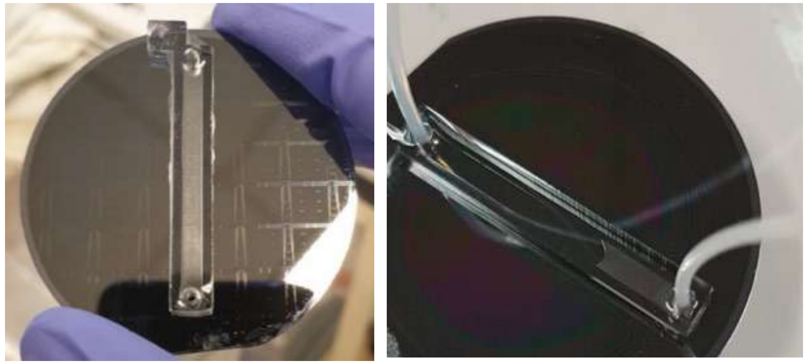


PIB or EPco on ZnSe prism for ATR FTIR spectroscopy

Transfer to Selenide waveguide



PIB on chalcogenide MIR sensor for Evanescent wave spectroscopy



PDMS microfluidic device grafted onto the microstructured chalcogenide substrate and PIB polymer coating filled with water

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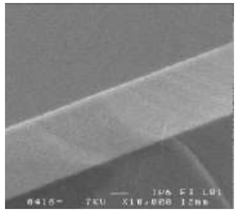
Conclusion and Perspectives

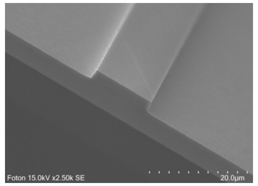
MIR microsensor based on chalcogenides platform

Chalcogenide Glasses
GeSbSe
→ large transmission range
→ high refractive index

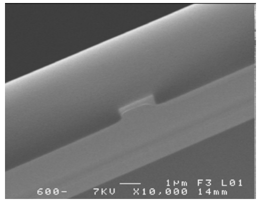
Thin Films
RF magnetron sputtering
→ appropriate experimental parameters



MIR structure
Refractive index contrast
→ IR light propagation

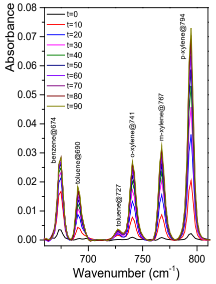


Micro-patterning and Light injection
Ridge waveguide
→ IR light confinement



Surface Functionalization
Hydrophobic polymer
→ increase sensitivity

Detection
BTX detection
→ LOD 250 ppb // 26 ppb
→ natural and complex waters



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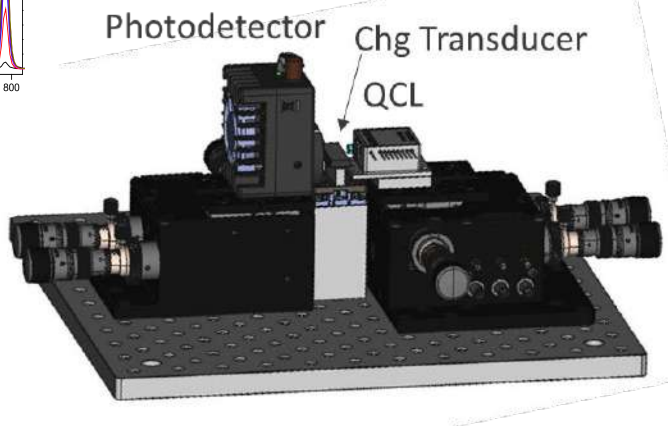
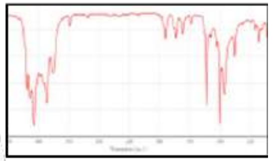
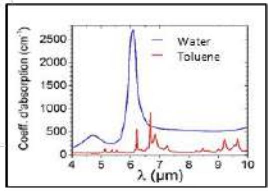


Lab scale



Pilot scale



mir sense

Argotech

VIGO PHOTONICS

microLIQUID

Cedre

SCIRPE www.scirpe.fr Group SCIRPE Wastewater treatment for rural communities

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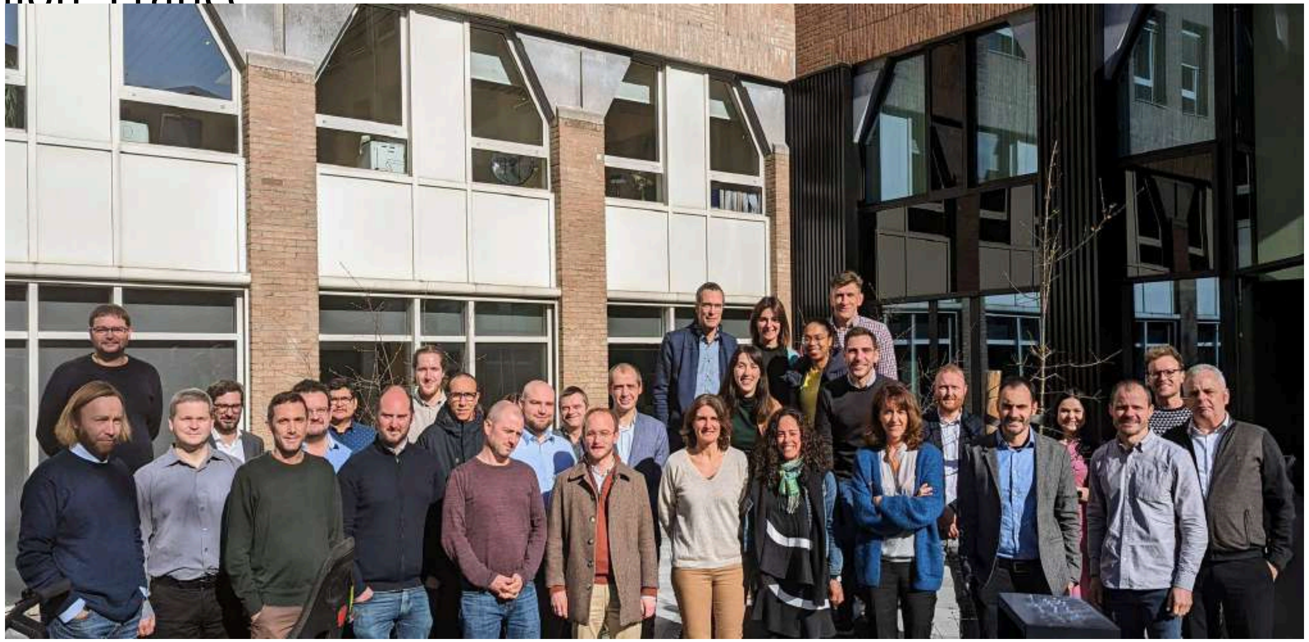

In green PhD Students

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