# Technical contribution to the project

# CNRS – ICPEES ELCOD Team

## Stéphane Le Calvé

***Senior research fellow at the CNRS, Head of the physico-chemistry team of the atmosphere***

Indoor / outdoor air quality: Metrology, instrumental development, sensors' integration, reactivity
Coordination of projects

## Christina Andrikopoulou and Pauline Meyer

***Engineer in Analytical chemistry at CNRS***

Air quality sensors calibration and evaluation, Conception and 3D designs, Rapid prototyping, Communication of the results

## Christophe Sutter

***Personnel of the Technical Pole at CNRS***

Electronics (study, development, troubleshooting), development of software interfaces (Labview), IT, DSC

# Two objectives

## 1- Multi-Sensors Project

Development of a ***monitoring system*** consisting of sensors and the necessary ***fluidic and electronic elements*** for ***integration inside a drone***

**ELCOD Project**

## 2- Development of a Volatile Organic Compounds (VOCs) micro-analyser

presenting the *future perspective* of *integration inside a drone*

# 1- MultiSensors Project


Christina Andrikopoulou[1], Vincent Person[3], Pauline Meyer[1], Christophe Sutter [1], Vedrines Marc [2], Kiefer Renaud [2], Stéphane Le Calvé [1,3]

[1] ICPEES, University of Strasbourg, CNRS
[2] INSA Strasbourg
[3] In'Air Solutions, Strasbourg, France

# 1. Introduction

## Pollutants monitored

- Nitrogen dioxide ($NO_2$)
- Ozone ($O_3$)
- Volatile Organic Compounds (VOCs)

Importance of monitoring

**VOCs + NOx** $\xrightarrow{h\nu}$ **Photo-oxidation products**: $O_3$ , Aldehydes, PAN, $NO_2$

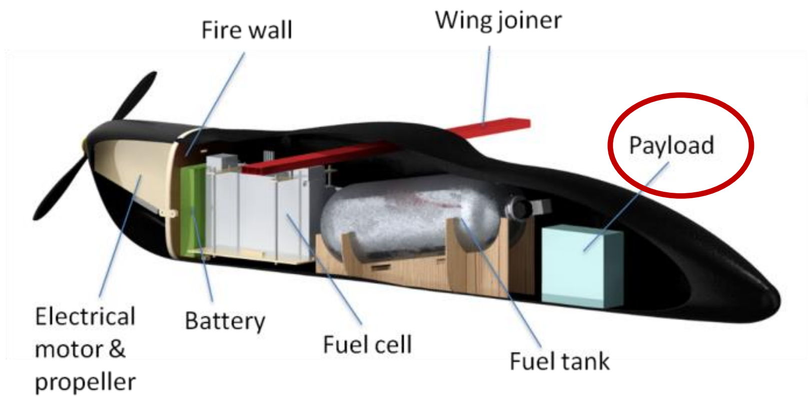
***Smog***

**Paris, France**

**North Rhine, Germany**

# 1. Introduction

## Drone constraints



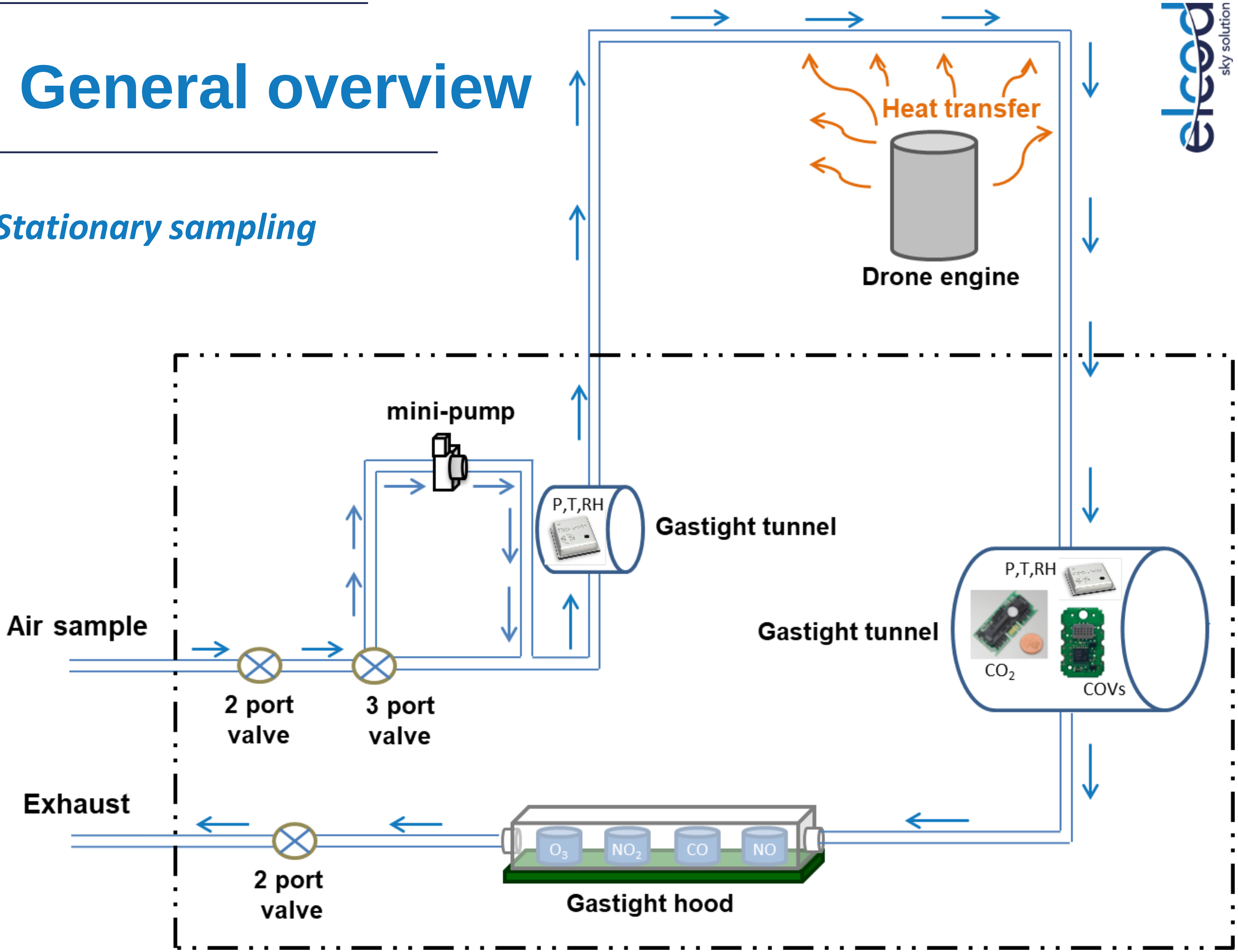

- ✓ Autonomy
- ✓ Low cost
- ✓ Low dimensions / weight
- ✓ Accurate monitoring

***Targeted performance***

| Pollutant / Parameter | Range | Precision |
|---|---|---|
| Volatile Organic Compounds (VOCs) | 31-1000 ppb | 10 % |
| Ozone ($O_3$) | 20 - 1000 ppb | 10 % |
| Nitrogen Dioxide ($NO_2$) | ? - 1000 ppb | 10 % |
| Temperature (T) | -40 to +85 °C | ± 0.5 °C |
| Relative Humidity (RH) | 0 - 100 % | ± 3 % RH |
| Pressure (P) | 0.3 -1.1 bar | ± 1 mbar |

# 2. General overview

## *2.1 Stationary sampling*



# 3. Development: Detection

## Volatile Organic Compounds (VOCs)

0 – 1000 ppb

## Nitrogen Dioxide ($NO_2$)

0 – 20 ppm

## Ozone ($O_3$)

0 – 20 ppm

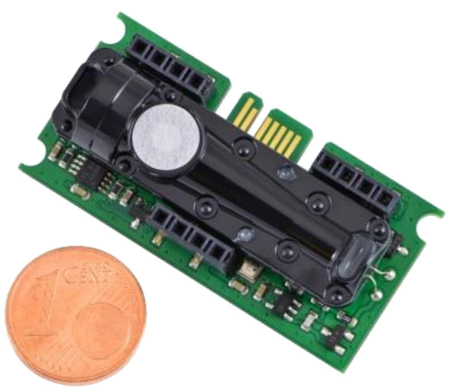
## Nitric Oxide (NO)


0 – 20 ppm

## Carbon monoxide (CO)


0 – 20 ppm

## Carbon Dioxide ($CO_2$)



1 cm

## Temperature (T)

- 40 to + 85 °C

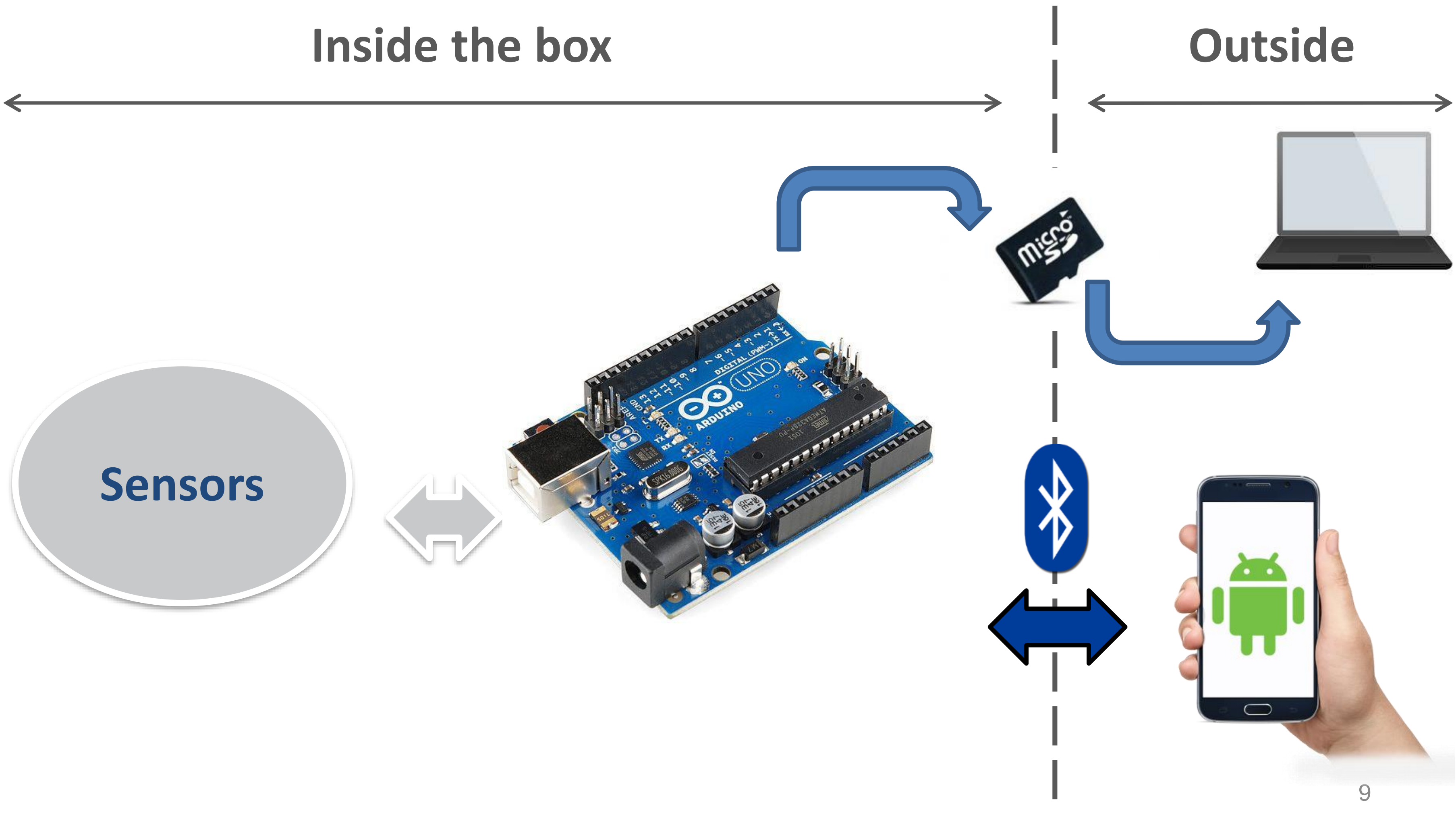
## Relative Humidity (RH)

0 – 100 %

## Pressure (P)

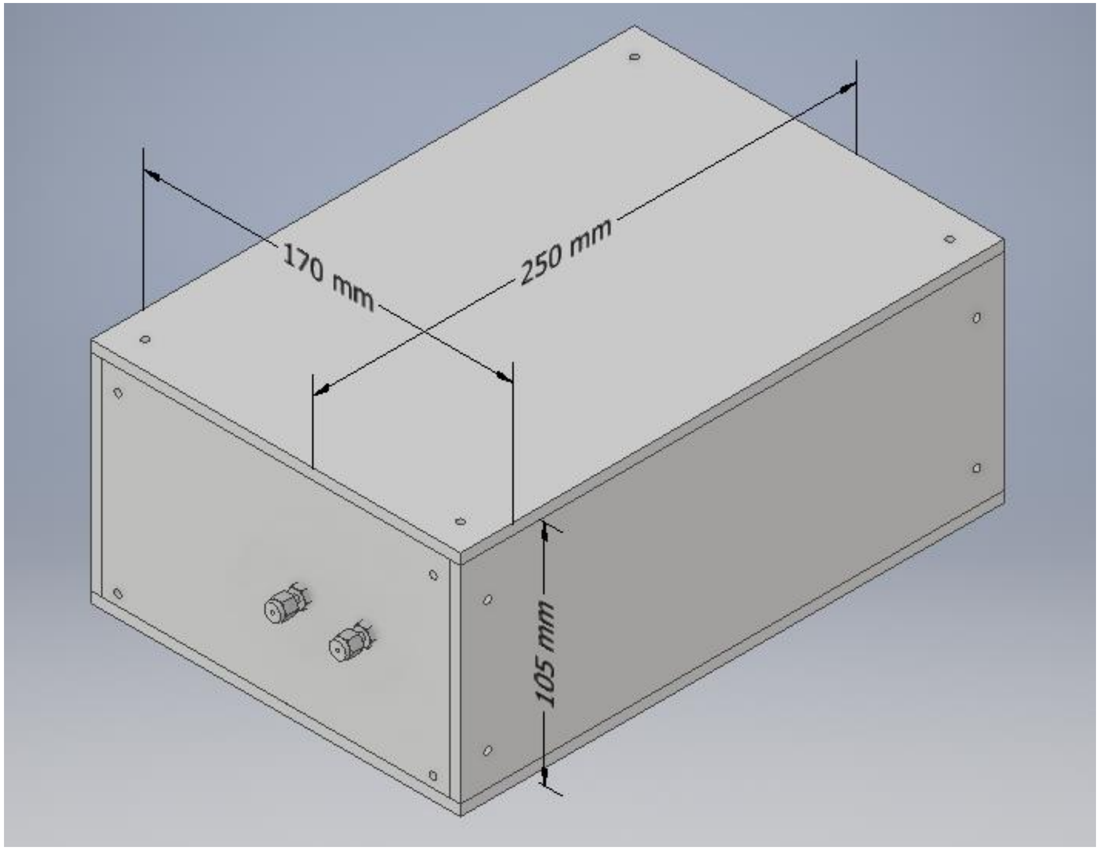
0,3 – 1,1 bar

# 3. Development: Data visualization



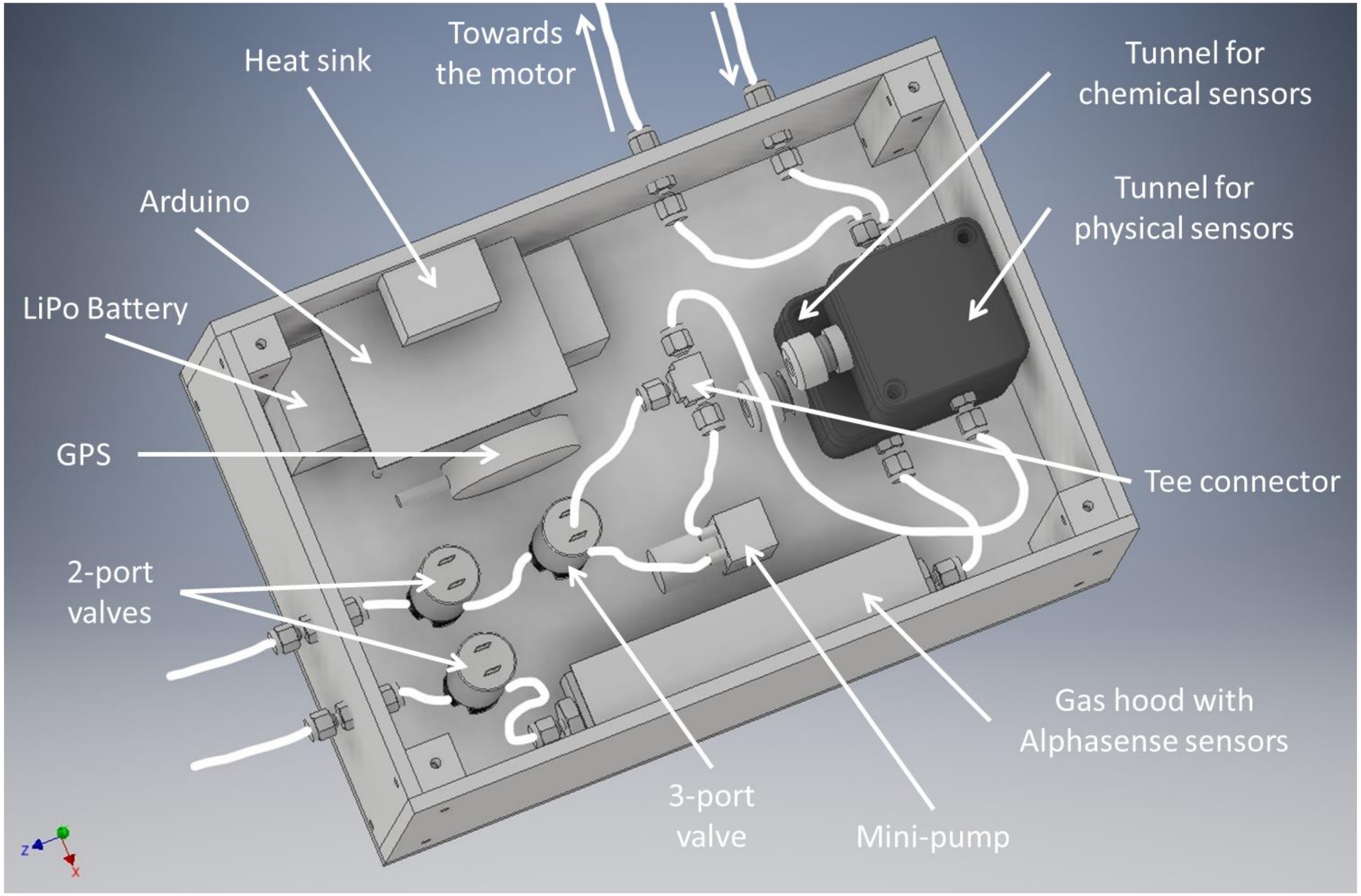
# 3. Development: Mechanics

✓ General 3D design



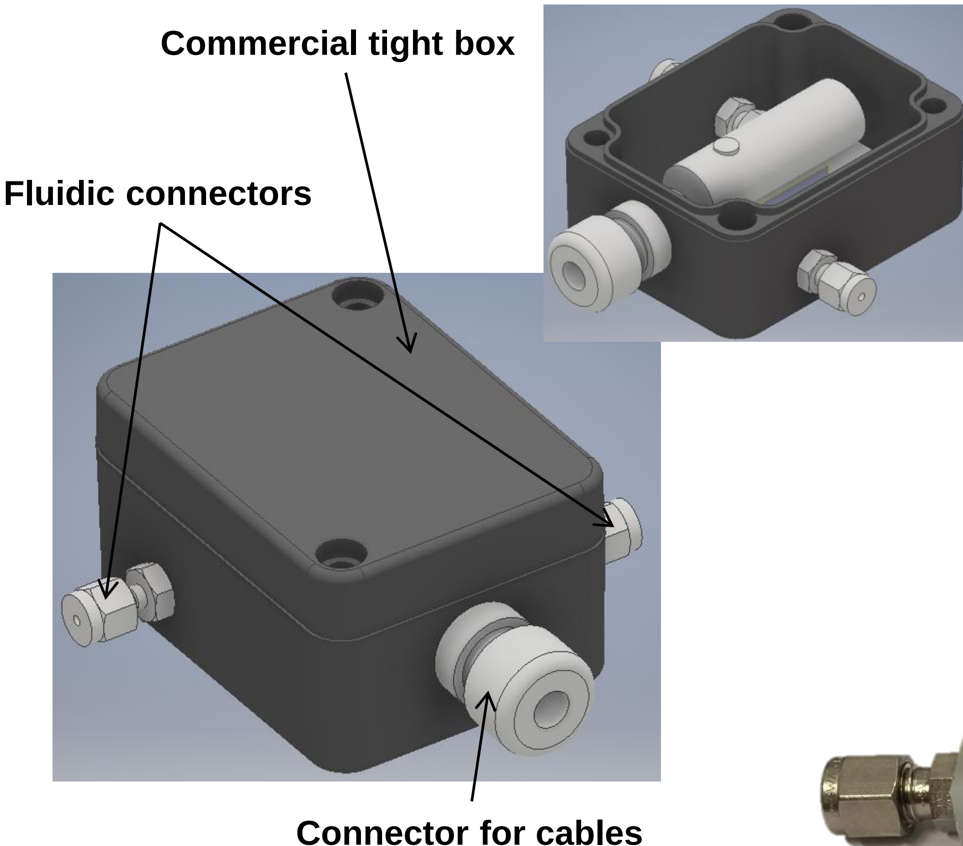
# 3. Development: Mechanics

✓ General 3D design



# 3. Development: Mechanics

✓ 3D design : Tunnel for chemical sensors




✓ Commercial tunnel for Alphasense chemical sensors

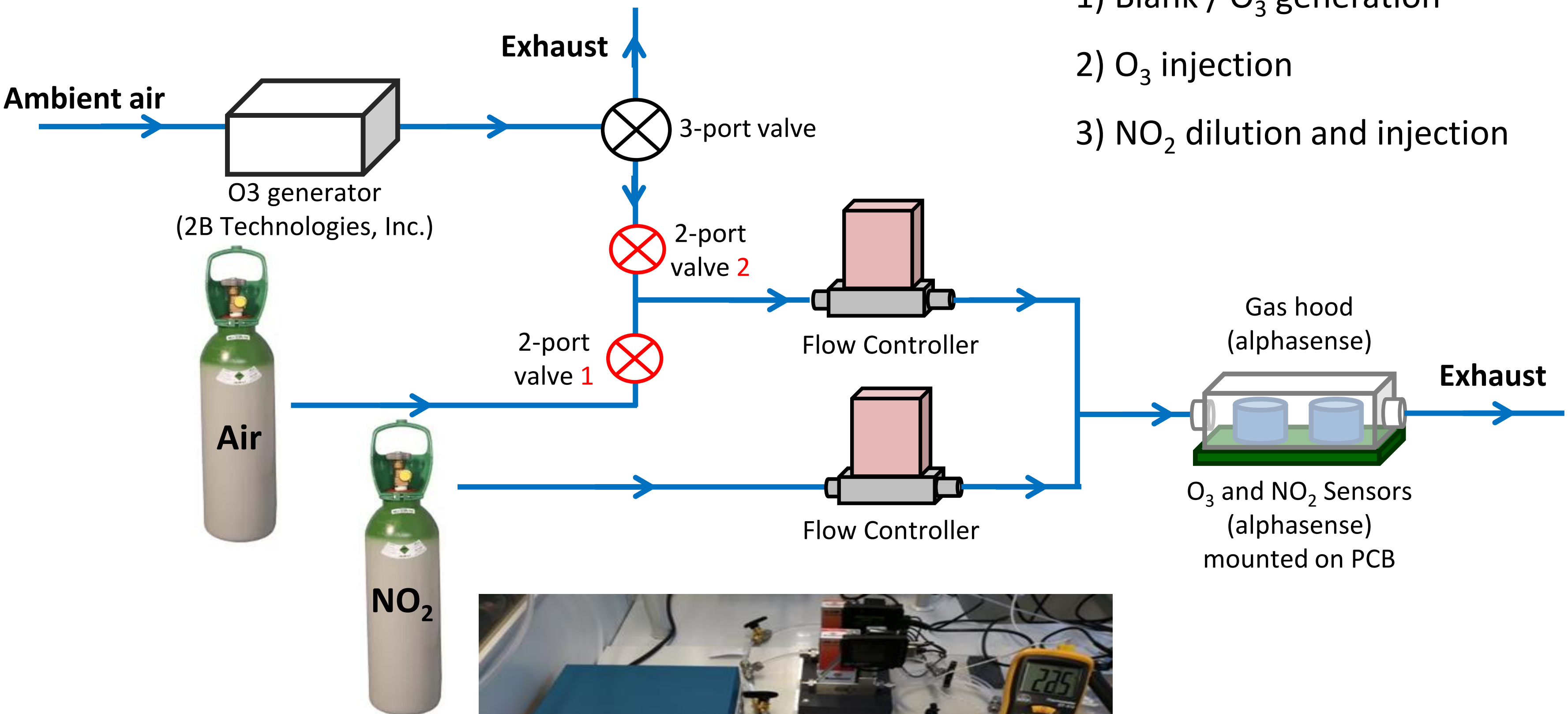
# 4. Results: Detection

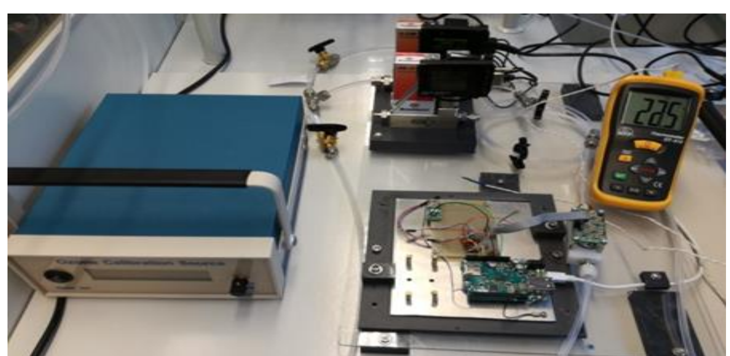
## ✓ Beta laboratory prototype

1) Blank / $O_3$ generation

2) $O_3$ injection

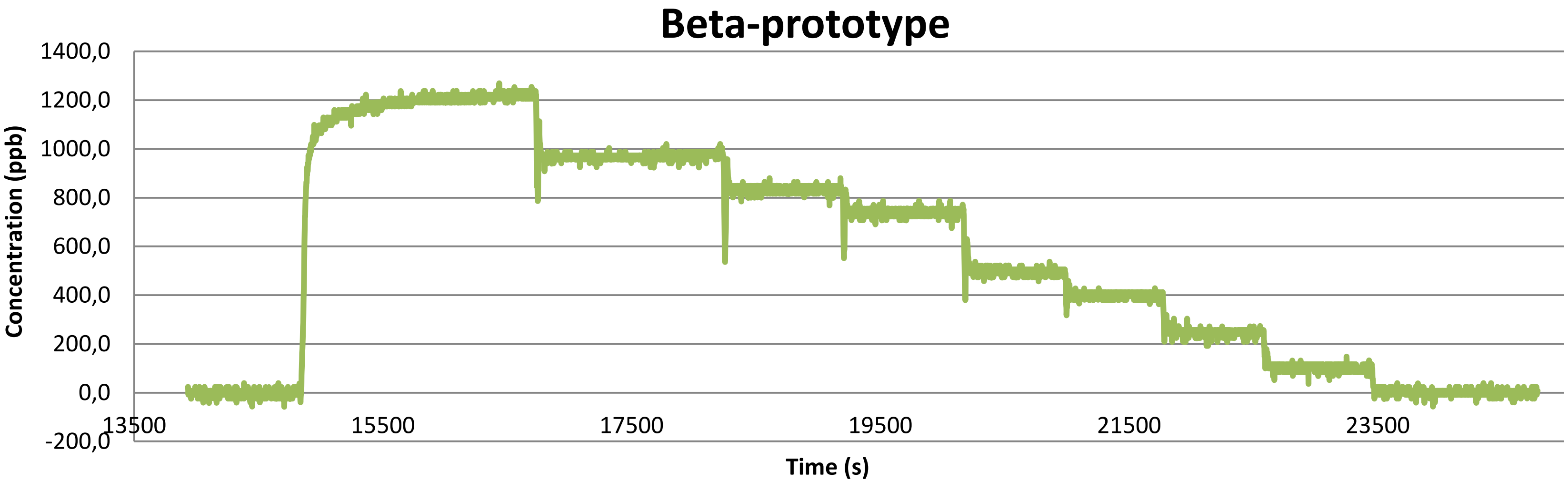
3) $NO_2$ dilution and injection

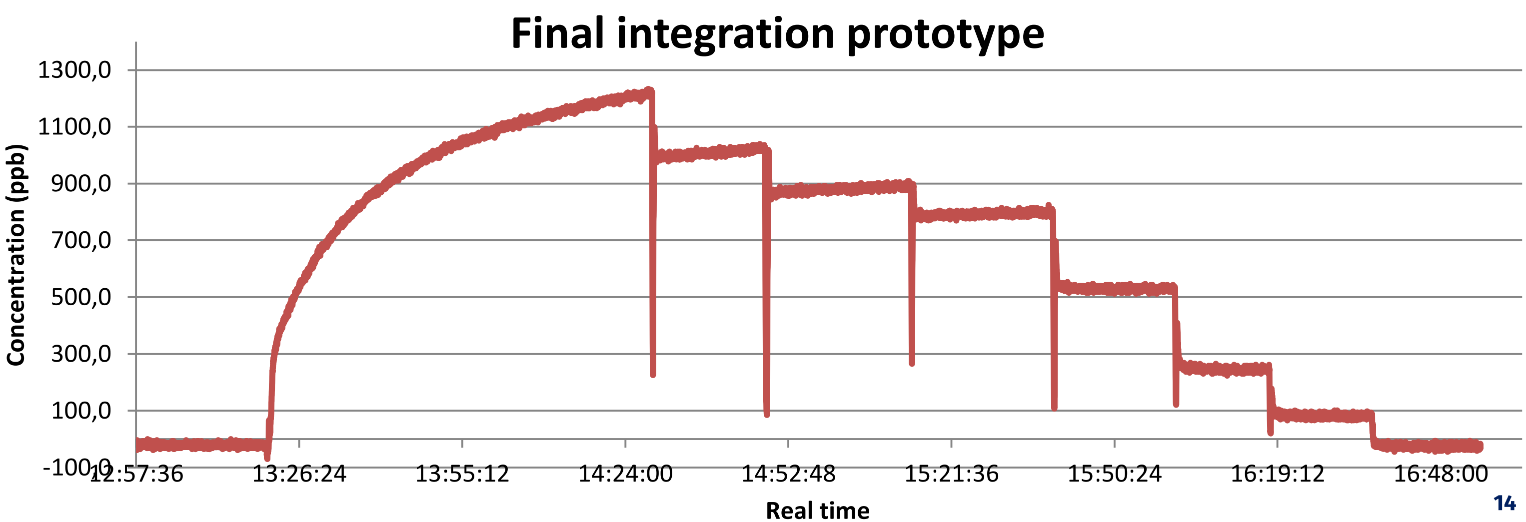


# 4. Results: Detection

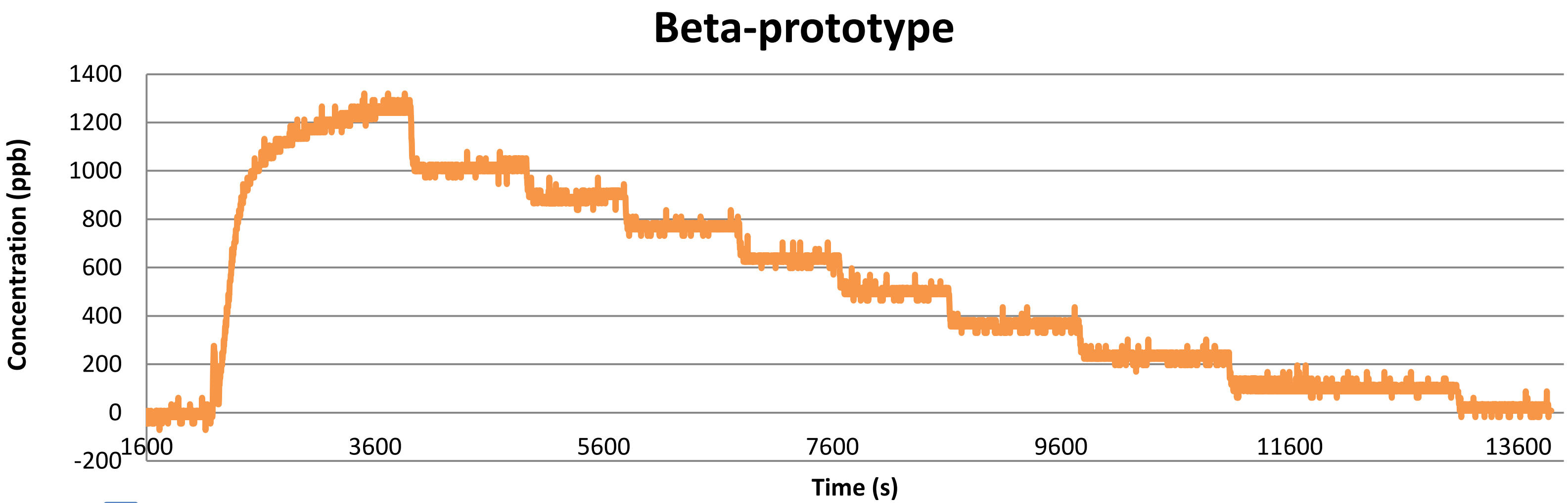
## ✓ Final integration : $O_3$ concentration

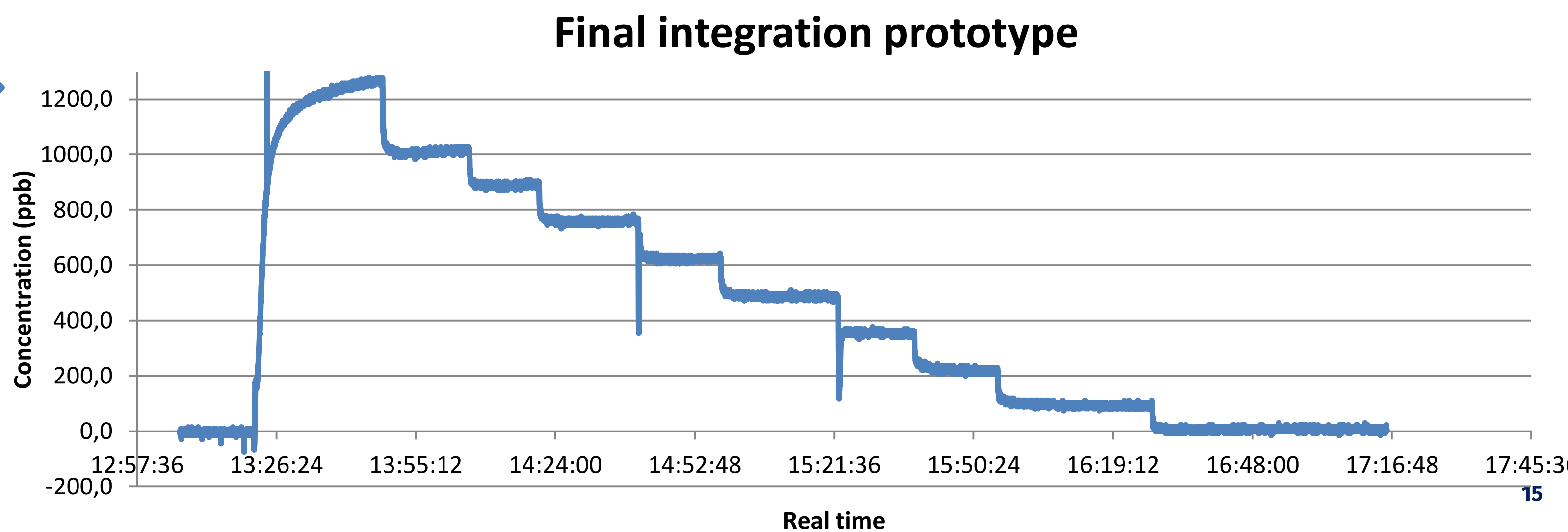


# 4. Results: Detection

✓ Final integration : $NO_2$ concentration



# 4. Results: Detection

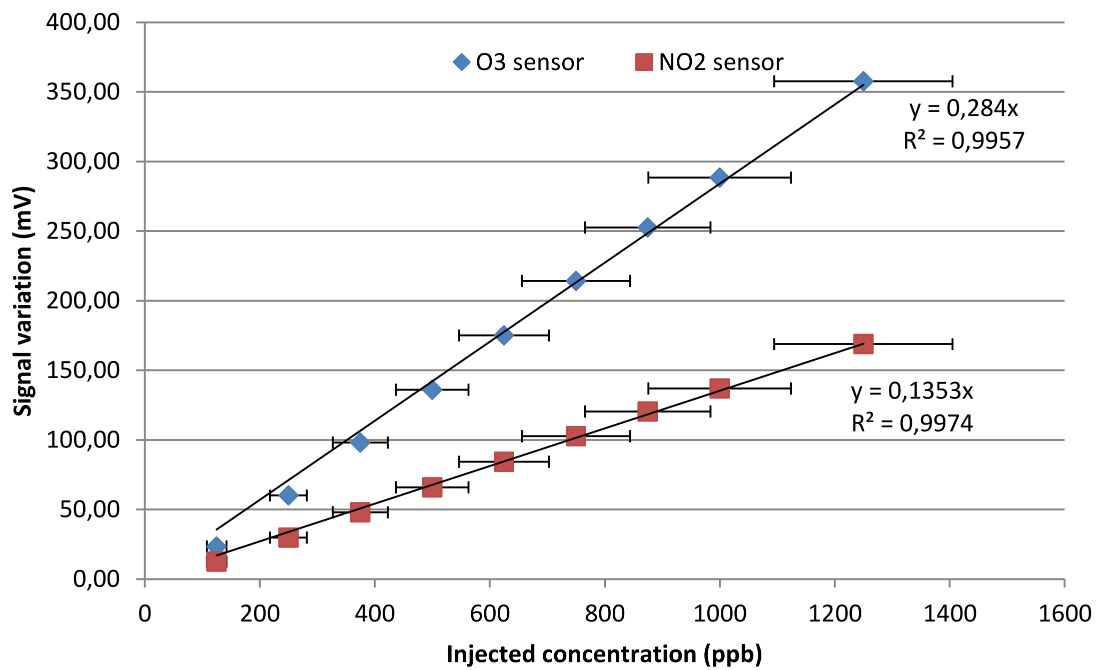
✓ **Final integration : calibrations with $O_3$ and $NO_2$**

- ➢ **flow rate : 400 mL/min**
- ➢ **blank performed with cleaned air from the ozone generator**

✓ Linear response In accordance with the injected concentrations

LOD = 108 ppb

LOD = 193 ppb

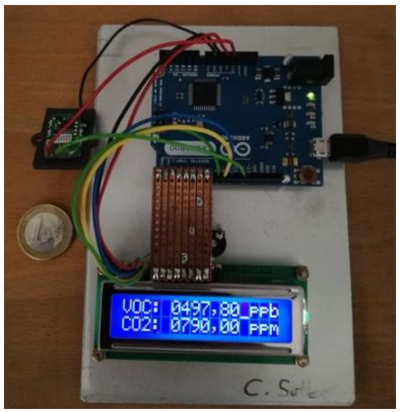



**Electronic/software enhancements :**

- Arduino Leonardo replaced by Arduino Mega
- Analog-to-digital converter 16 bits focused on the ±1V range : theoretical resolution of 0.125 ppb.
- Software filters to reduce the noise : LOD = 10-20 ppb

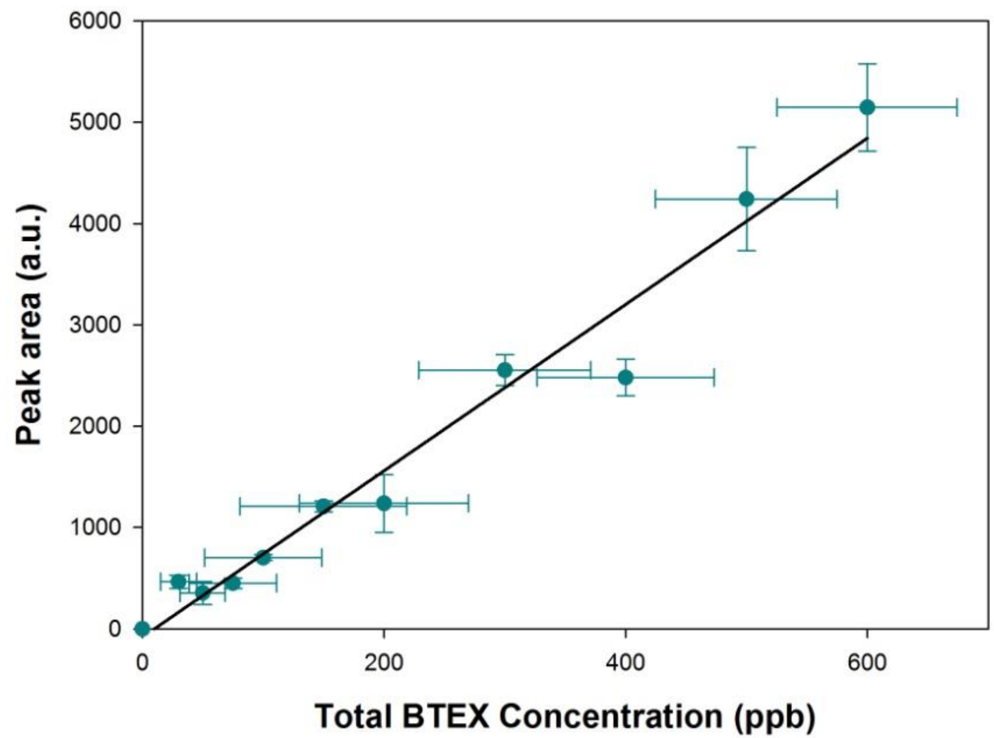
# 4. Results: Detection

✓ **Tests and calibration of VOCs sensors**




***MiCS-VZ89 ($SnO_2$ sensor)***
SGX Sensortech

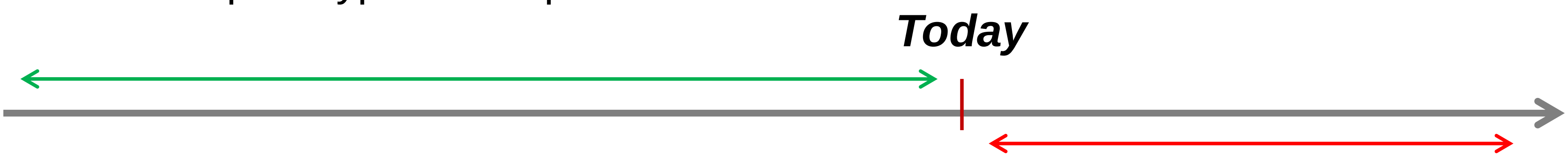
**Calibration with injection of BTEX :**
**Benzene, Toluene , Ethyl Benzene, Xylenes**




***Detection limit : 31 ppb***

# Conclusions & Perspectives

- ✓ Conception and designs
- ✓ Materials chosen
- ✓ Sensors mounting on arduino
- ✓ Sensors testing and calibration
- ✓ Final prototype development




- ✓ Sensors' calibration finalisation
- ✓ Prototype indoor testing
- ✓ Demonstration during flight

# 2- Development of a VOCs microanalyser

Christina Andrikopoulou [1] Irene Lara-Ibeas[1], Vincent Person [1,2], Stéphane Colin[3], Stéphane Le Calvé[1,2]

[1] ICPEES, University of Strasbourg, CNRS

*[2] In'Air Solutions, Strasbourg, France*

*[3] INSA Toulouse, France*

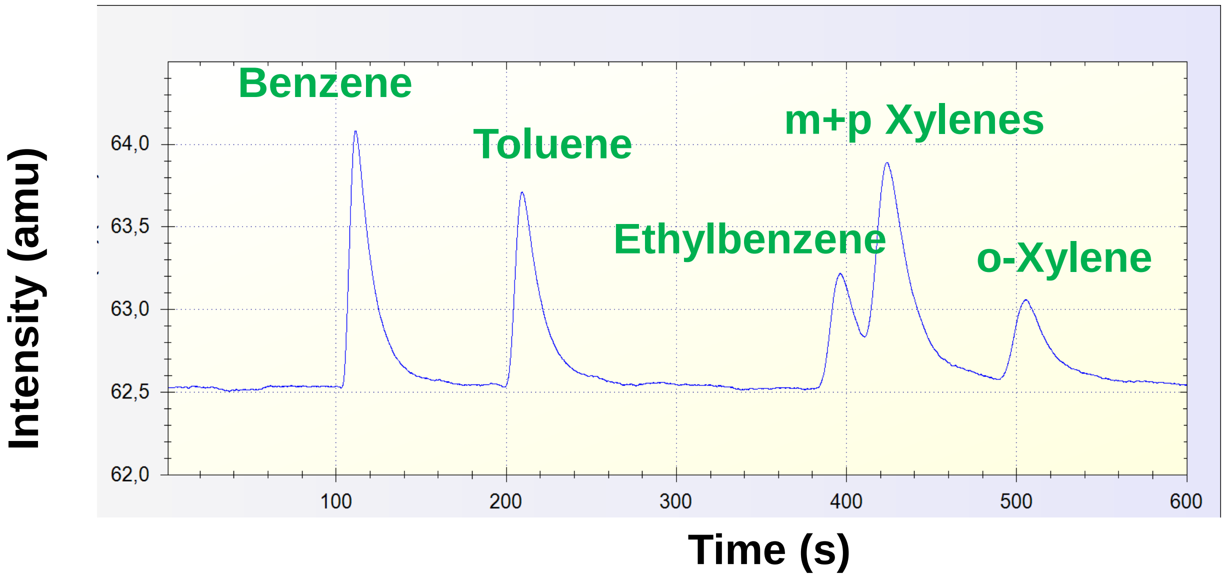
# 1. Introduction

## Detection of Volatile Organic Compounds (VOCs)

**1.1** Total detection of VOCs (VOCs sensor: see before)

**1.2** Detection of each VOC separately

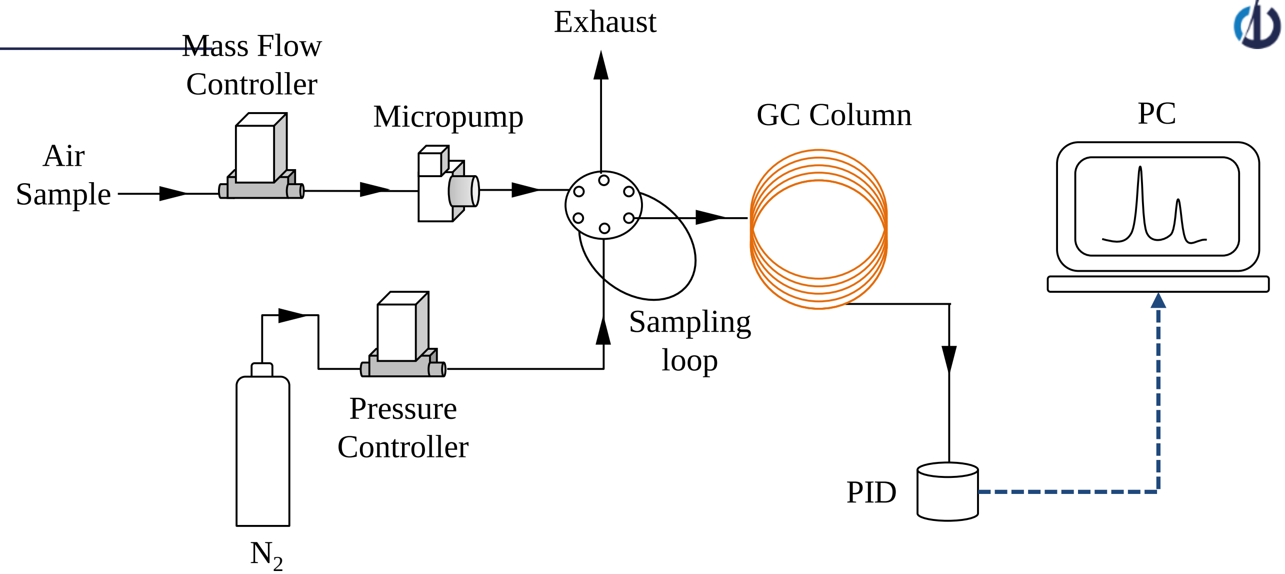
BTEX analyser (In'Air Solutions)

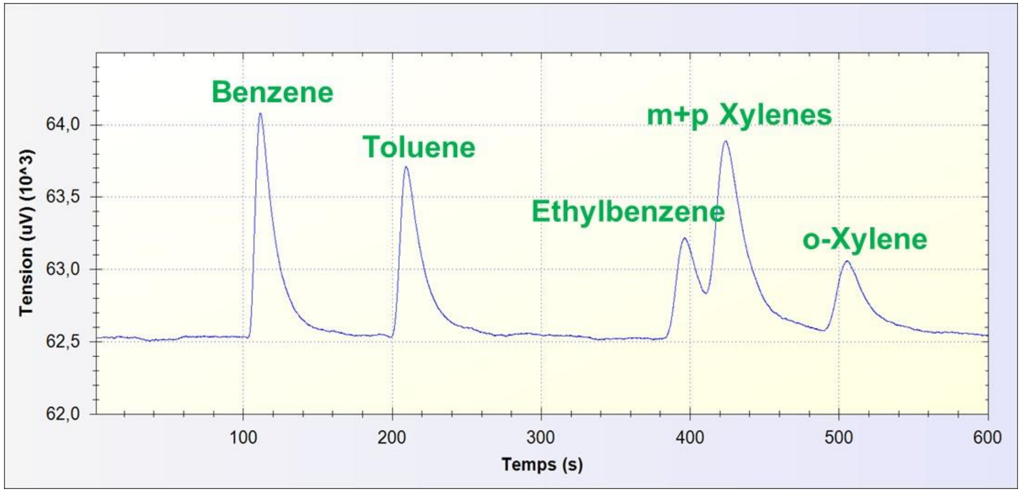



# 1. Introduction: no preconcentration

Three steps analysis:

1. Air Sampling
1. Separation
1. Detection



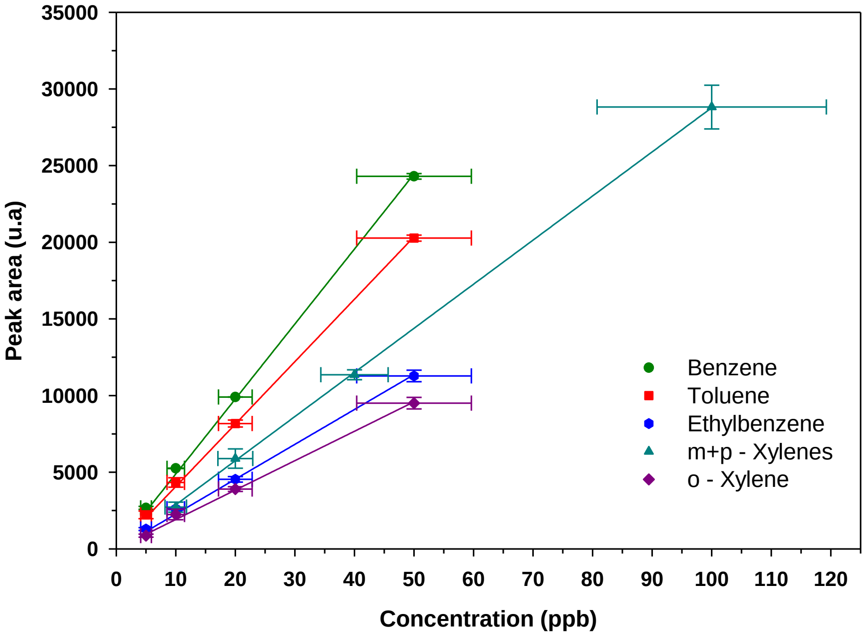

Temperature: 65°C
Carrier gas flow: N2 at 2.5 mL/min
Time of analysis: 10 min

**Nasreddine, R. et al.** (2016), *Sensors and actuators B Chem.*, **224**, 159–169.

# 1. Introduction: no preconcentration

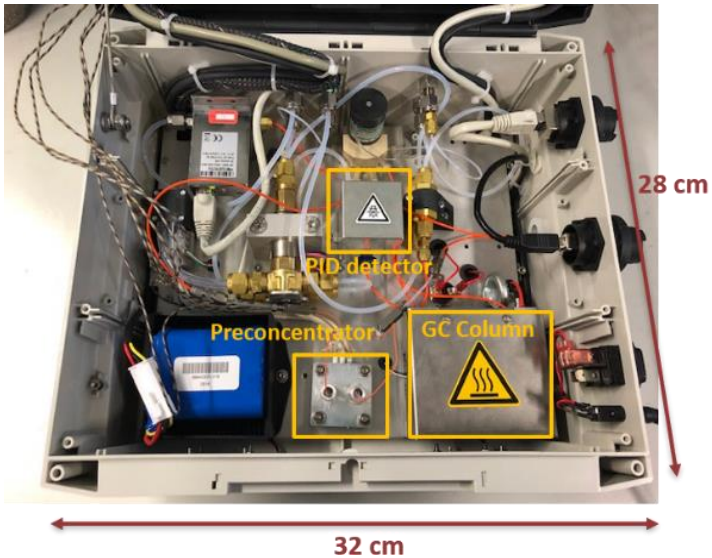
## Current analyser <u>without</u> preconcentrator


**PPB MiniPID 2**
IonScience




***Detection limit : 1- 6.6 ppb***

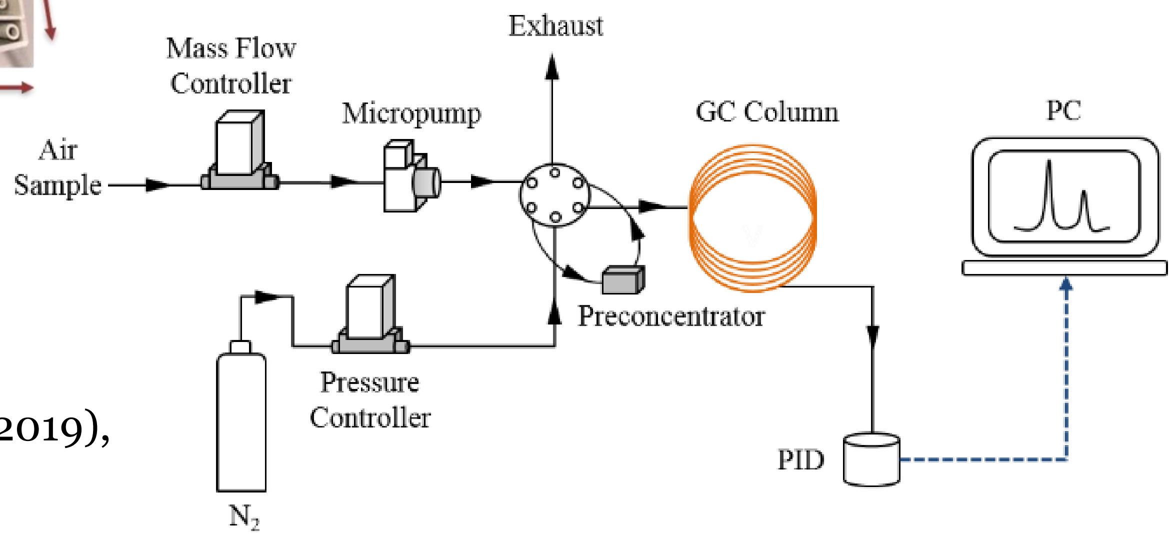
# 1. Introduction: with preconcentration




Four steps analysis:

1. Air Sampling (adsorption in a preconcentrator)
2. Injection / desorption at high temperature
3. Separation
4. Detection

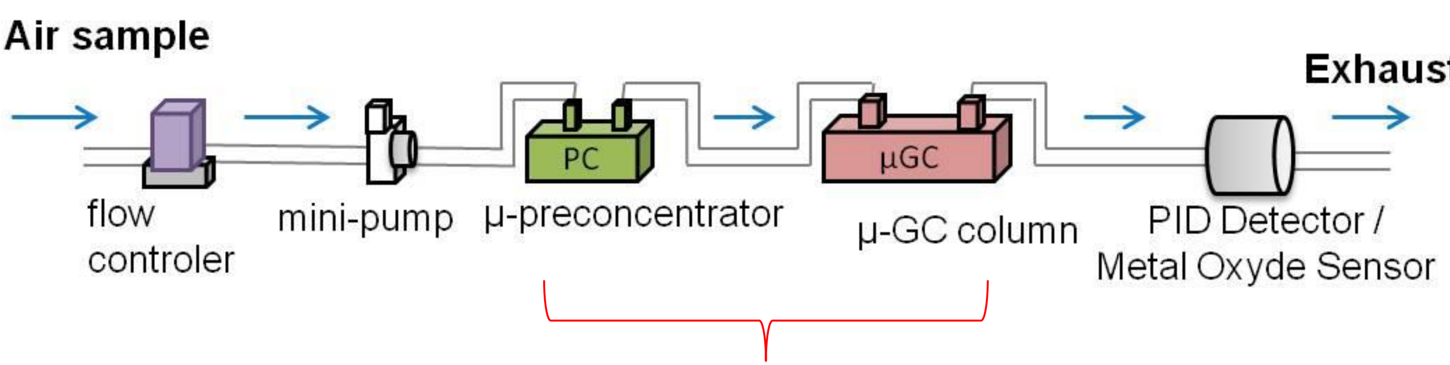
**Lara-Ibeas et al.** (2019), *Micromachines*, **10**, 187.



# 1. Introduction: with preconcentration

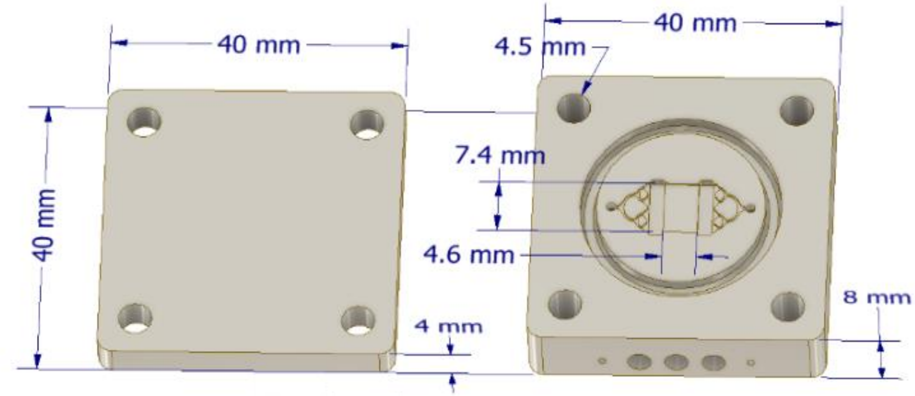
**Operating principle**

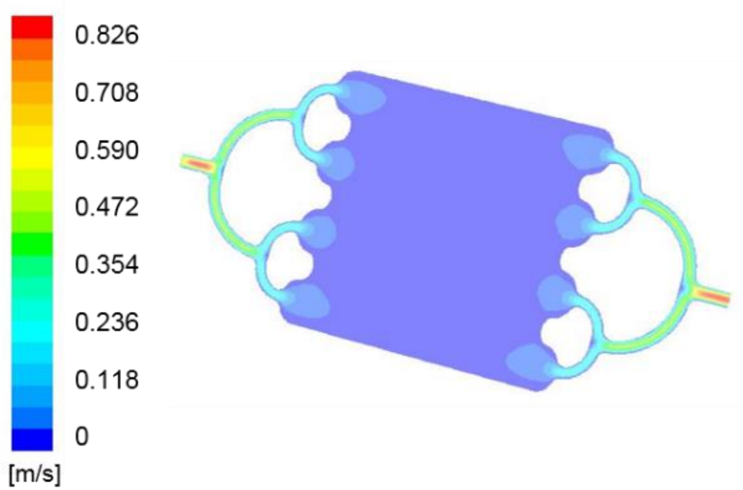
Sampling → Preconcentration → Separation → Detection

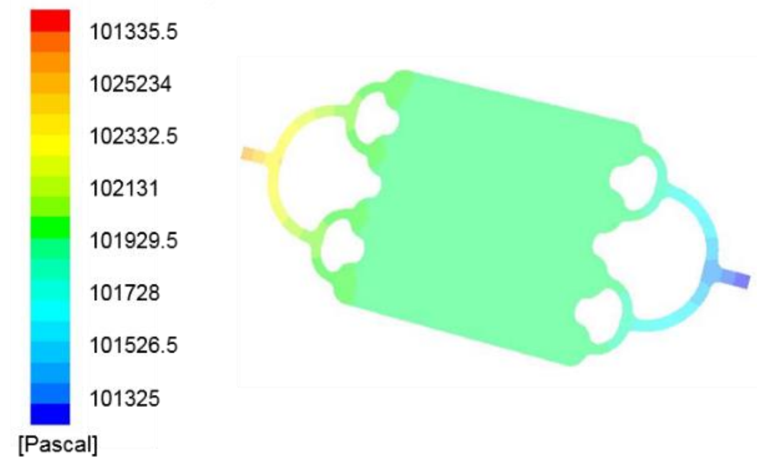



**Most energy consuming**

# 2. 1st Preconcentrator



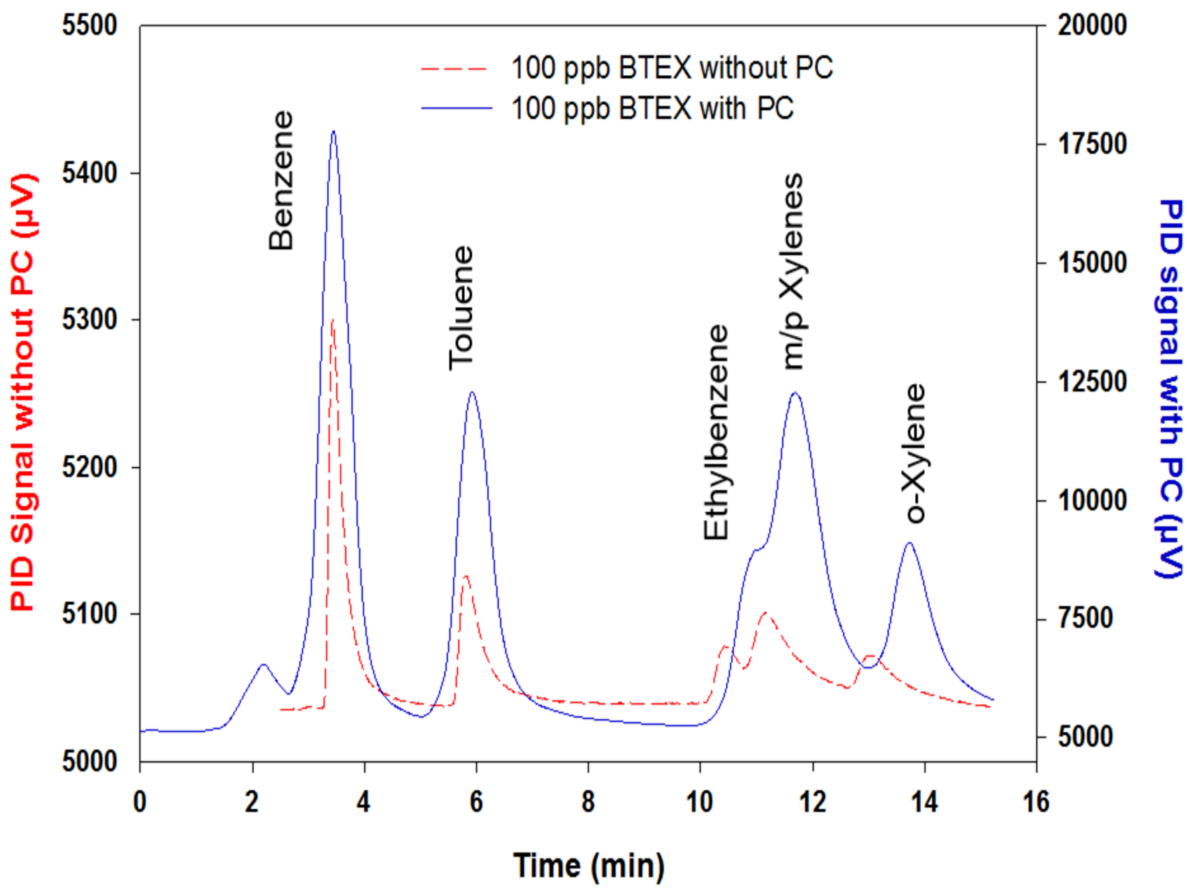




Uniform flow distribution inside the microfluidic cavity

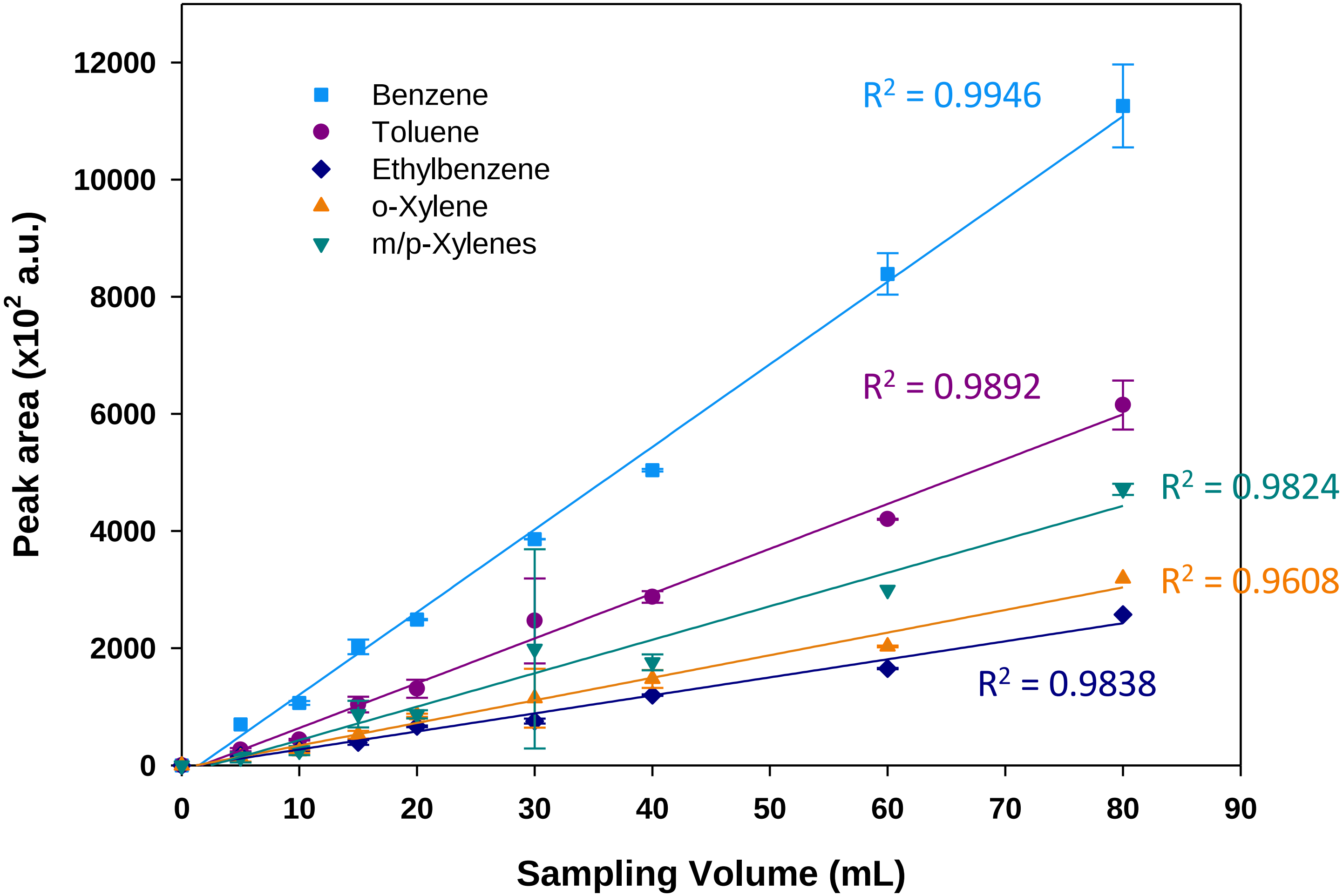
**Lara-Ibeas et al.** (2019), *Micromachines*, **10**, 187.

# 2. 1st Preconcentrator




**Lara-Ibeas et al.** (2019), *Micromachines*, **10**, 187.

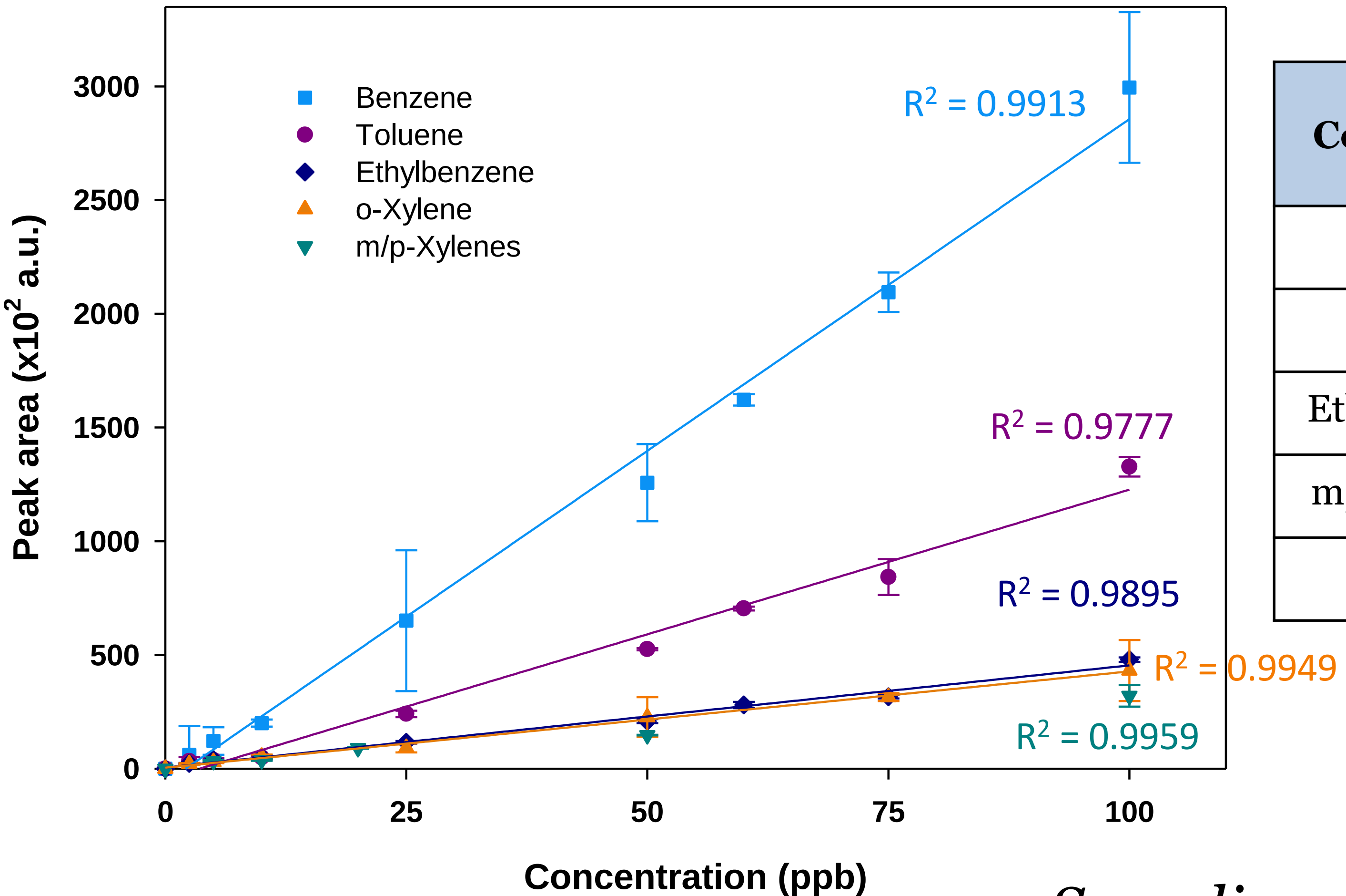
# 2. 1st Preconcentrator




*Concentration = 100 ppb*

**Lara-Ibeas et al.** (2019), *Micromachines*, **10**, 187.

# 2. 1st Preconcentrator



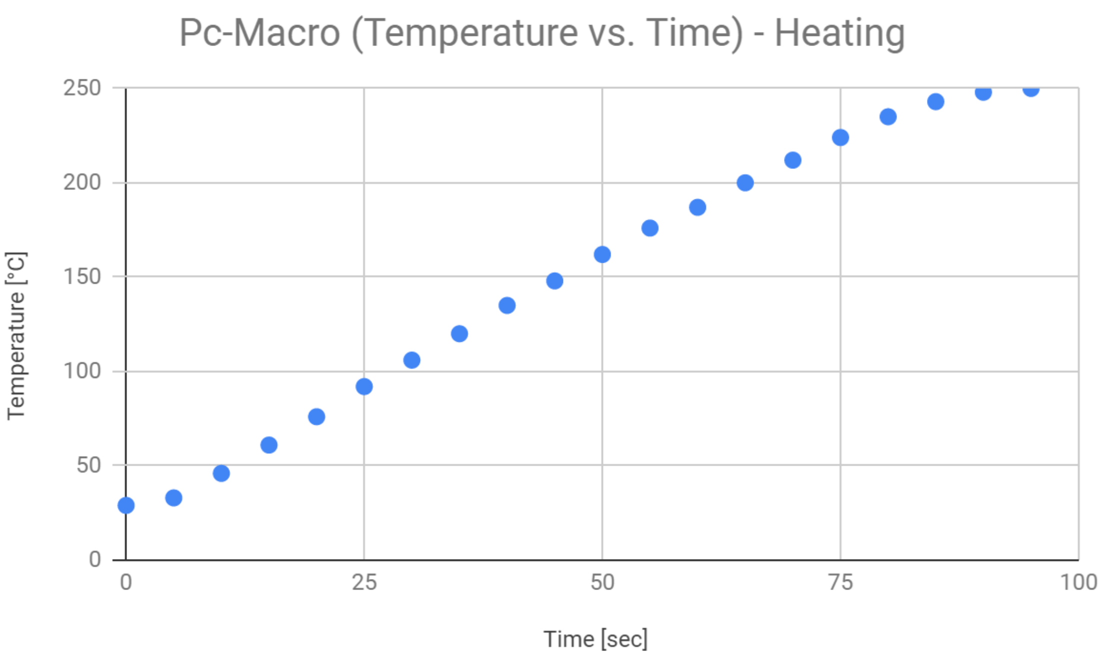

| Compound | LOD (ppb) |
|---|---|
| Benzene | **0.20** |
| Toluene | **0.26** |
| Ethylbenzene | **0.49** |
| m/p-Xylenes | **0.80** |
| o-Xylene | **1.70** |

*Sampling volume = 20 mL*

**Lara-Ibeas et al.** (2019), *Micromachines*, **10**, 187.

# 2. 1st Preconcentrator

The first prototype of preconcentrator takes 65 seconds to rise the temperature up to 200 ªC from room temperature (25ºC). While the energy consumption remains constant at 210 Watts.

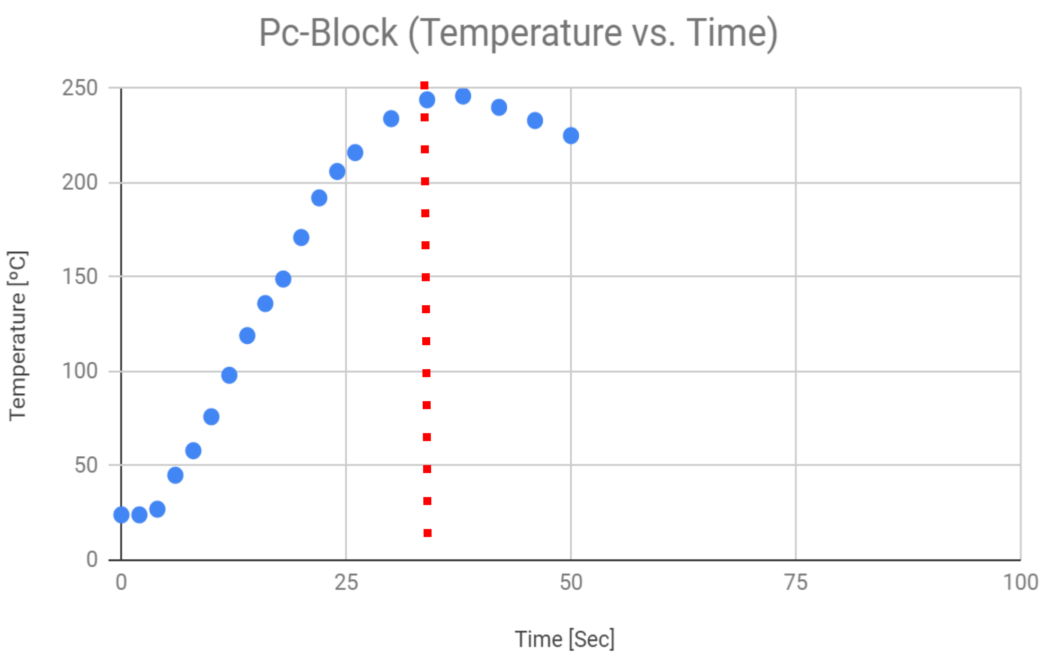



| Heating | Time [Sec] | Temperature [ºC] | Power[w] |
|---|---|---|---|
| | 0 | 29 | 210 |
| | 5 | 33 | 210 |
| | 10 | 46 | 210 |
| | 15 | 61 | 210 |
| | 20 | 76 | 210 |
| | 25 | 92 | 210 |
| | 30 | 108 | 210 |
| | 35 | 120 | 210 |
| | 40 | 135 | 210 |
| | 45 | 148 | 210 |
| | 50 | 162 | 210 |
| | 55 | 176 | 210 |
| | 60 | 187 | 210 |
| | 65 | 200 | 210 |
| | 70 | 212 | 210 |
| | 75 | 224 | 210 |
| | 80 | 235 | 210 |
| | 85 | 243 | 210 |
| | 90 | 248 | 210 |
| | 95 | 250 | 210 |

**Lara-Ibeas et al.** (2019), *Micromachines*, **10**, 187.

# 3. 2nd Preconcentrator

The second prototype of preconcentrator takes 23 seconds to rise the temperature up to 200 ªC from room temperature (25ºC). While, in this case the energy consumption varies from 42..9 Watts to 22.15 Watts .

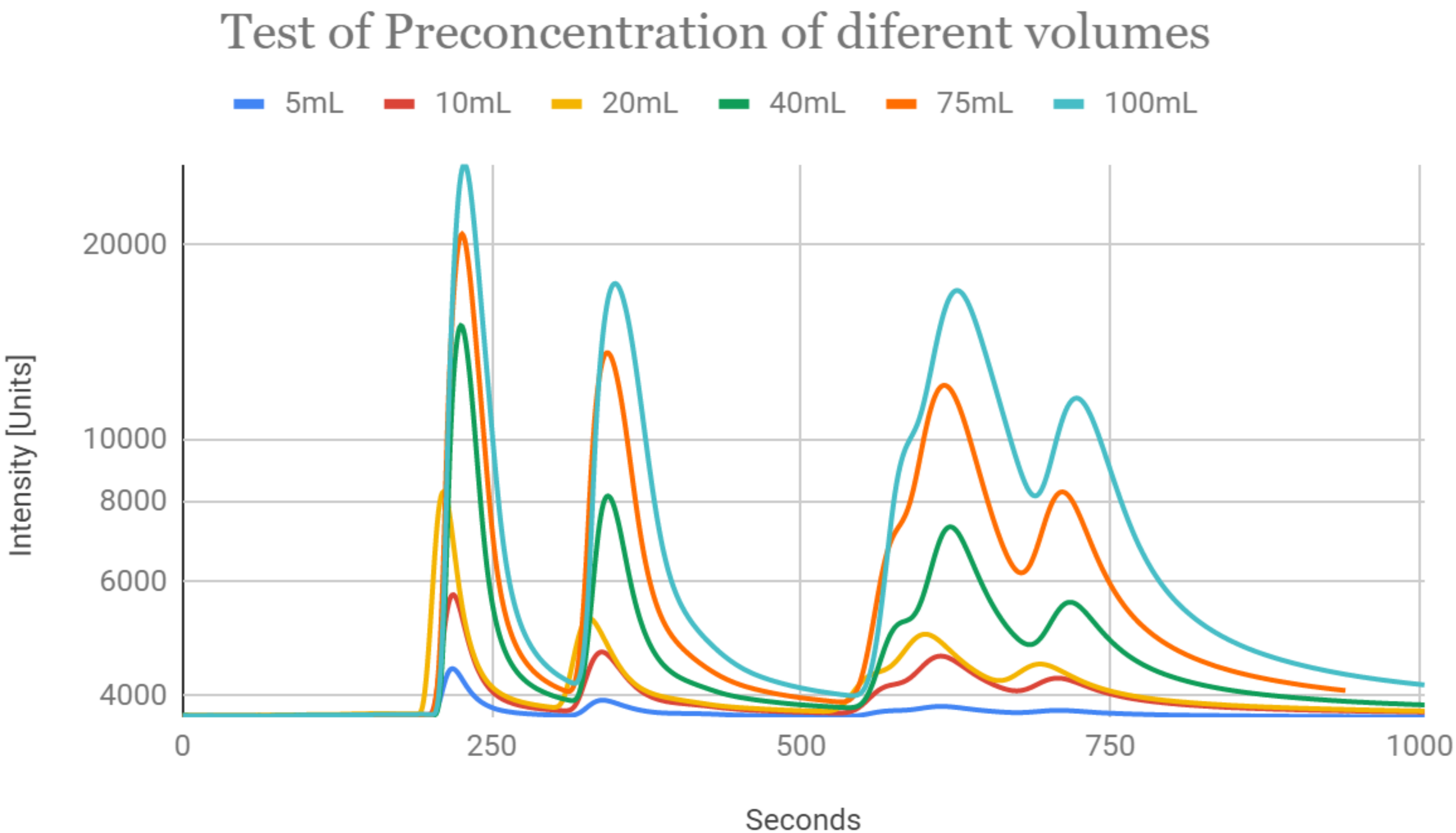



| Heating | Time [Sec] | Temperature [ºC] | Voltage [Volt] | Current [Amp] | Power [Watt] |
|---|---|---|---|---|---|
| | 0 | 24 | 14 | 3.06 | 42.9 |
| | 2 | 24 | 14 | 2.39 | 33.47 |
| | 4 | 27 | 14 | 2.28 | 31.89 |
| | 6 | 45 | 14 | 2.02 | 28.28 |
| | 8 | 58 | 14 | 1.92 | 26.89 |
| | 10 | 76 | 14 | 1.85 | 25.93 |
| | 12 | 98 | 14 | 1.79 | 25.09 |
| | 14 | 119 | 14 | 1.73 | 24.18 |
| | 16 | 136 | 14 | 1.69 | 23.60 |
| | 18 | 149 | 14 | 1.65 | 23.06 |
| | 20 | 171 | 14 | 1.61 | 22.54 |
| | 22 | 192 | 14 | 1.58 | 22.15 |
| | 24 | **206** | | | |
| | 26 | 216 | | | |
| | 30 | 234 | | | |
| | 34 | 244 | | | |
| | 38 | 246 | | | |
| | 42 | 240 | | | |
| | 46 | 233 | | | |
| | 50 | 225 | | | |

**Rodriguez et al.** (2019), publication, *to be submitted.*

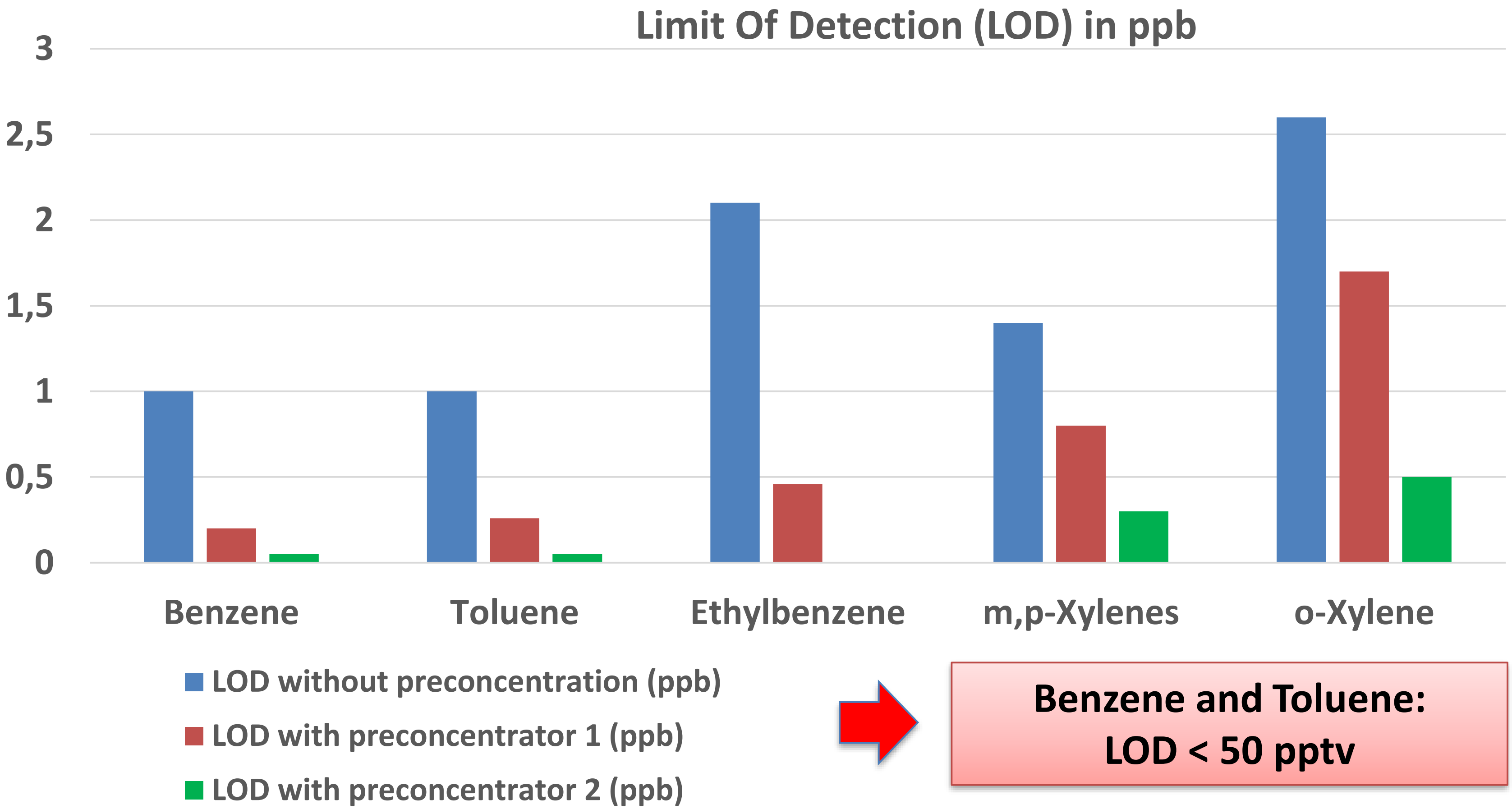
**Le Calvé et al.** (2019), patent, *to be submitted.*

# 3. 2nd Preconcentrator




**Rodriguez et al.** (2019), *to be submitted.*

# 4. Conclusions




**Benzene and Toluene:**
**LOD < 50 pptv**

**Nasreddine et al.** (2016), *Sensors and Actuators B*, **224**, 159-169.
**Lara-Ibeas et al.** (2019), *Micromachines*, **10**, 187.
**Rodriguez et al.** (2019), *to be submitted.*

# Thank you for your attention

# *BACK UP SLIDES*

# Instrumental characteristics by analysis step

# 3. Instrumental characteristics

Sampling

***Note: Approximate values***

| Element | Voltage (V) | Current (A) | Consumption (W) | Dimensions (mm) * | Weight (g) | Price (€ ) |
|---|---|---|---|---|---|---|
| Mini-pump | 12 | 0.16 (max) | 2 | 37 x 16 x 25 | **23** | ***200*** |
| 2 port valves ***(x 2)*** | 12 | - | 2.00 **4.00** | Ø 19.1 x 42.7 | 18.1 **36.2** | 57.51 **115** |
| 3 port valve | 12 | - | 2.00 | Ø 19.1 x 42.7 | **18.1** | ***57,51*** |
| Housing | - | - | - | 50 x 50 x 21 | ***50*** | ***50*** |
| **Total** | 12 | - | 2 | 250 x 170 x 105 | ***127.3*** | ***422.53*** |

Total dimensions



* Length x Width x Height / Diameter x Height

# 3. Instrumental characteristics

Detection

*Note: Approximate values*

| Element | Voltage (V) | Current (A) | Consumption (W) | Dimensions (mm) * | Weight (g) | Price (€ ) |
|---|---|---|---|---|---|---|
| Box with : | - | - | - | 146 x 150 x 60 | 180 | 7 |
| Tunnel 1 | - | - | - | 52 x 50 x 40 | *100* | 5,8 |
| Tunnel 2 | - | - | - | 65 x 50 x 45 | *150* | 12,9 |
| Gas hood with AFE and 4 electrochemical sensors ($NO_2$, $O_3$, CO, NO) | 3.4 – 6.4 | 0.0026 | *0.009 – 0.017* | 115.7 x 28 x 33.3 (Ø 20.2 x 16.5 each sensor) | *168* | ? |
| VOCs (VZ89) | 3.3 | | *0.05* | 22.9 x 14 x 3.2 | *10* | *20* |
| $CO_2$ | 4.75 - 7.5 | *0.0032* | *0.0152 – 0.024* | 45 x 22 x 14.95 | *20* | 113 |
| P, T, HR (x2) | 1.7-3.6 | 0.00071 | 0.0012 – 0.0026<br>**0.0024 – 0.0052** | *22 x 14 x 2* | *5*<br>***10*** | 17<br>**34** |
| **Total** | 3.3-5.5 | - | 0.71 | 250 x 170 x 105 | *638* | |

* Length x Width x Height / Diameter x Height

Total dimensions

# 3. Instrumental characteristics

Electronics

***Note: Approximate values***

| Element | Voltage (V) | Current (A) | Consumption (W) | Dimensions (mm) * | Weight (g) | Price (€ ) |
|---|---|---|---|---|---|---|
| Arduino | 12 | *0.09* | *1.08* | 68.6x23.3x1.7 | *35* | 25 |
| Electronic card | | | | | | |
| Battery | - | - | - | 110 x 34 x 36 | 200 | 30.5 |
| **Total** | 12 | | *1.08* | 250x170x105 | *385* | 446 |

Total dimensions

* Length x Width x Height

# 3. Instrumental characteristics

## Others

***Note: Approximate values***

| Element | Voltage (V) | Current (A) | Consumption (W) | Dimensions (mm) * | Weight (g) | Price (€ ) |
|---|---|---|---|---|---|---|
| GPS | 7.2- 21 (12) | 0.065 | 0.5 – 1.4 (0.8) | 49 x 20 x 12 | 12 | 5.5 |
| ***Connectors*** | | | | | | |
| Bulkhead (x4) | - | - | - | | *35 (140)* | 26 (104) |
| 1/16'' – 1/8'' mm | - | - | - | | 18 | 35 |
| Tee connector | | | | | *20* | *20* |
| **Total** | 12 | 0.065 | 0.8 | 250x170x105 | 202 | 193 |

Total dimensions

* Length x Width x Height

# 5. Preliminary results : Detection

✓ **Final integration**

Electronic enhancements :

- Arduino Leonardo replaced by Arduino Mega

→ **Integration of all the sensors**

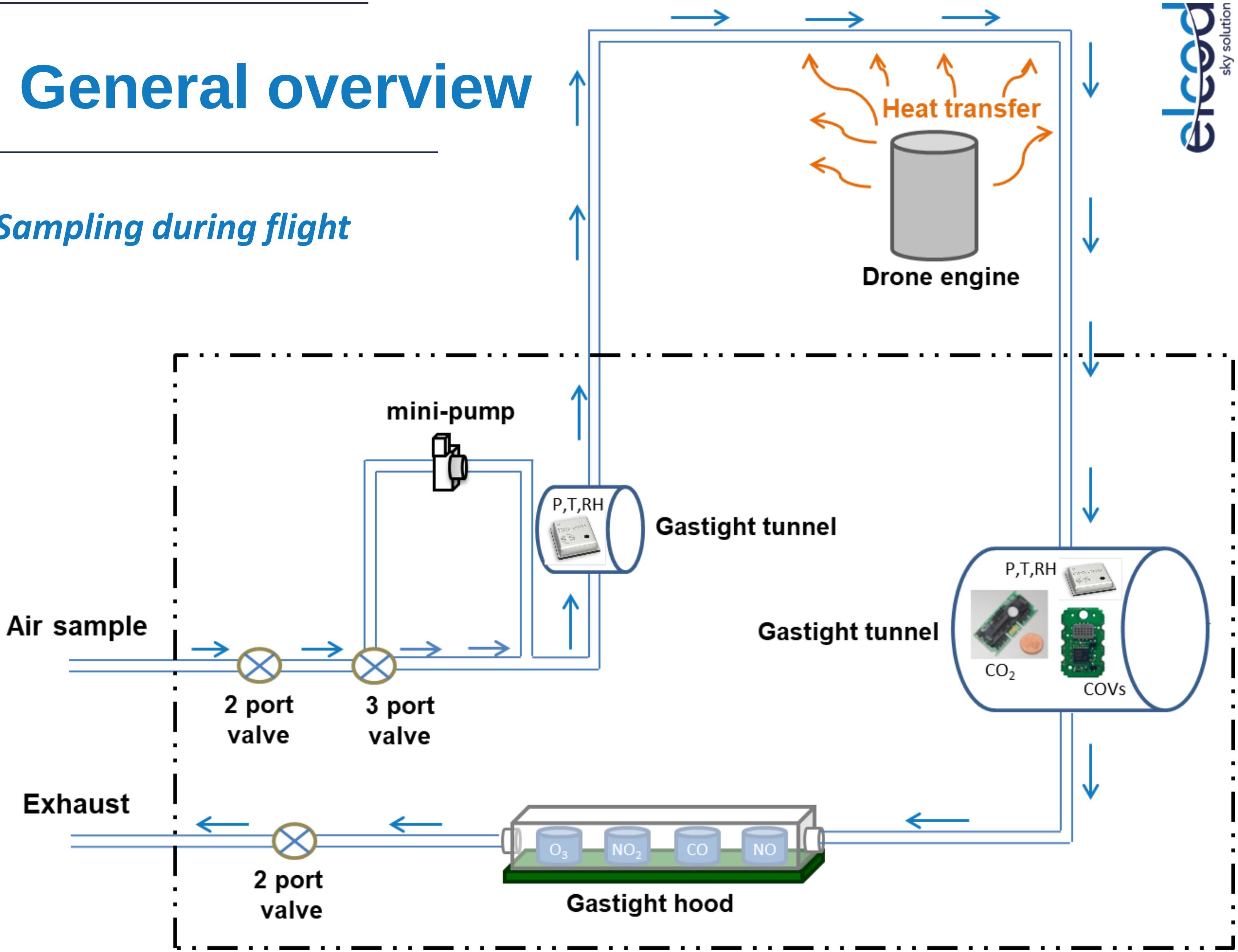
- Analog-to-digital converter 16 bits focused on the ±1V range

→ **Alphasense sensors reach a theoretical resolution of 0.125 ppb**

Signal filtering needed ?

# 2. General overview

## *2.1 Sampling during flight*



# 3. Instrumental characteristics

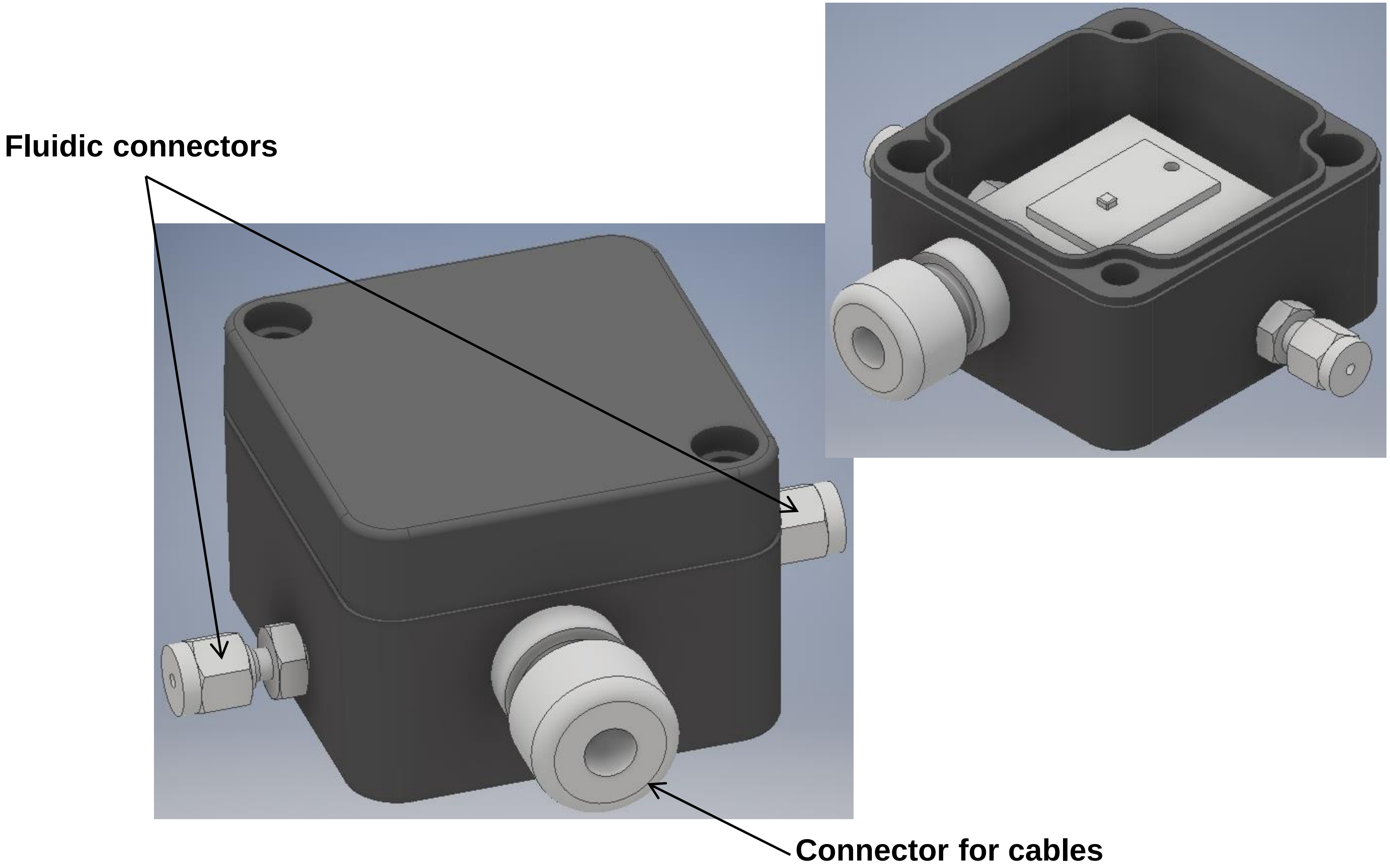
*Estimation based on current progress of the project*

| Analysis step | Voltage (V) | Consumption (W) | Dimensions (mm) * | Weight (g) | Price (€ ) |
|---|---|---|---|---|---|
| Sampling | 12 | 2 | 250 x 170 x 105 | *127.3* | *422.53* |
| Detection | 3.3-5.5 | 0.71 | 250 x 170 x 105 | *638* | |
| Electronics | | | 250 x 170 x 105 | | |
| Others | | | 250 x 170 x 105 | | |
| **Total** | | | 250 x 170 x 105 | | |

* Length x Width x Height

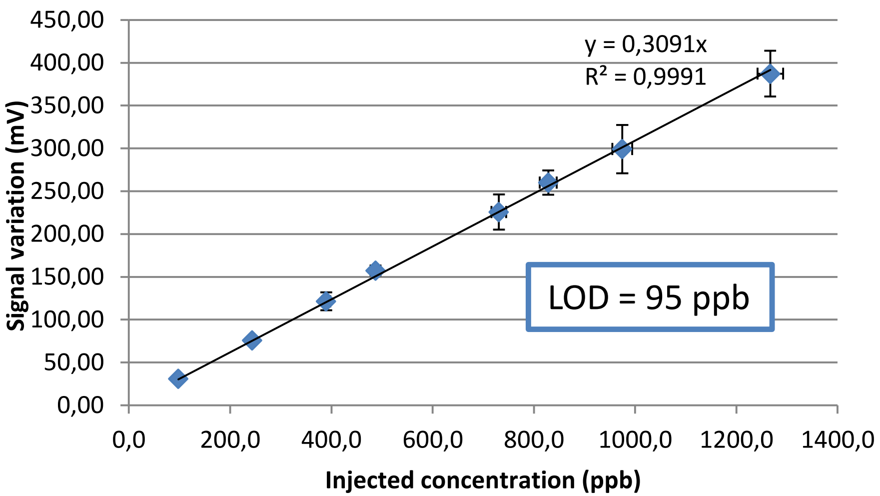
# 4. Preliminary development : Mechanics

✓ 3D design : Tunnel for sensors of meteorological conditions



# 5. Preliminary results : Detection

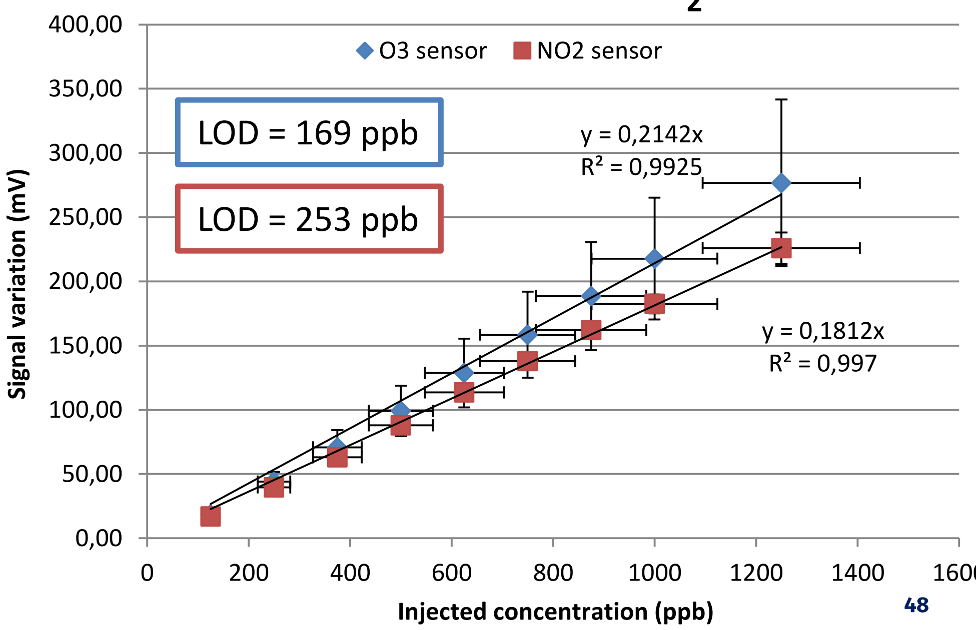
✓ Calibrations with $O_3$ and $NO_2$




- flow rate : 400 mL/min
- blank performed with cleaned air from the ozone generator

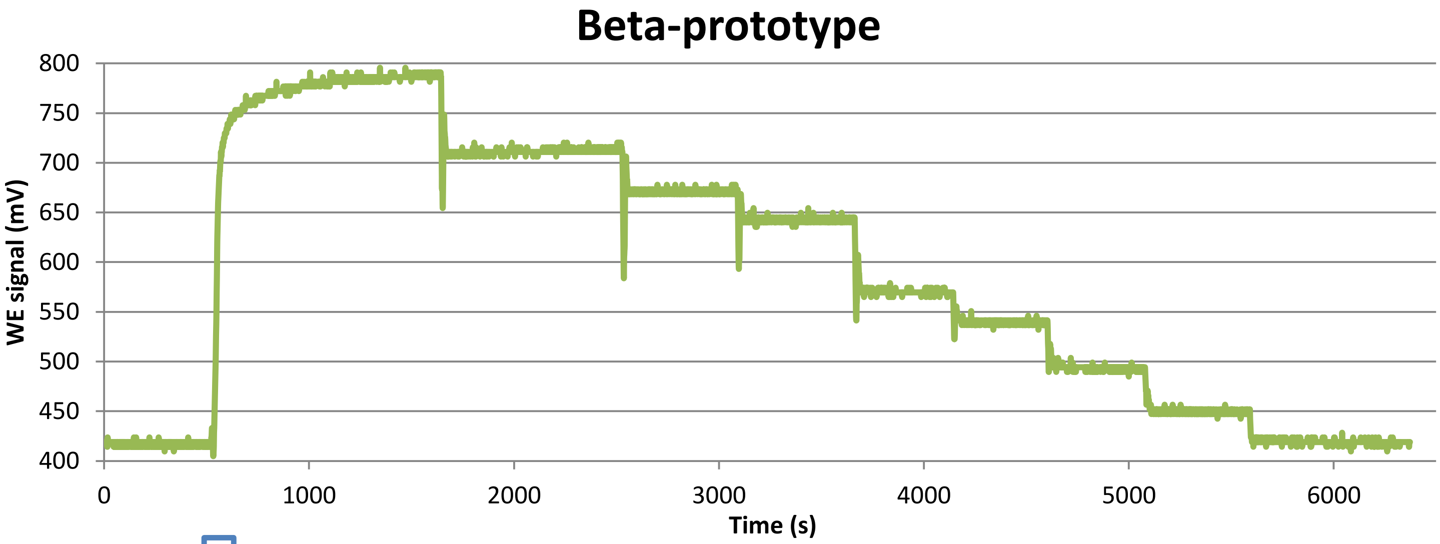
✓ Linear response

✓ In accordance with the injected concentrations

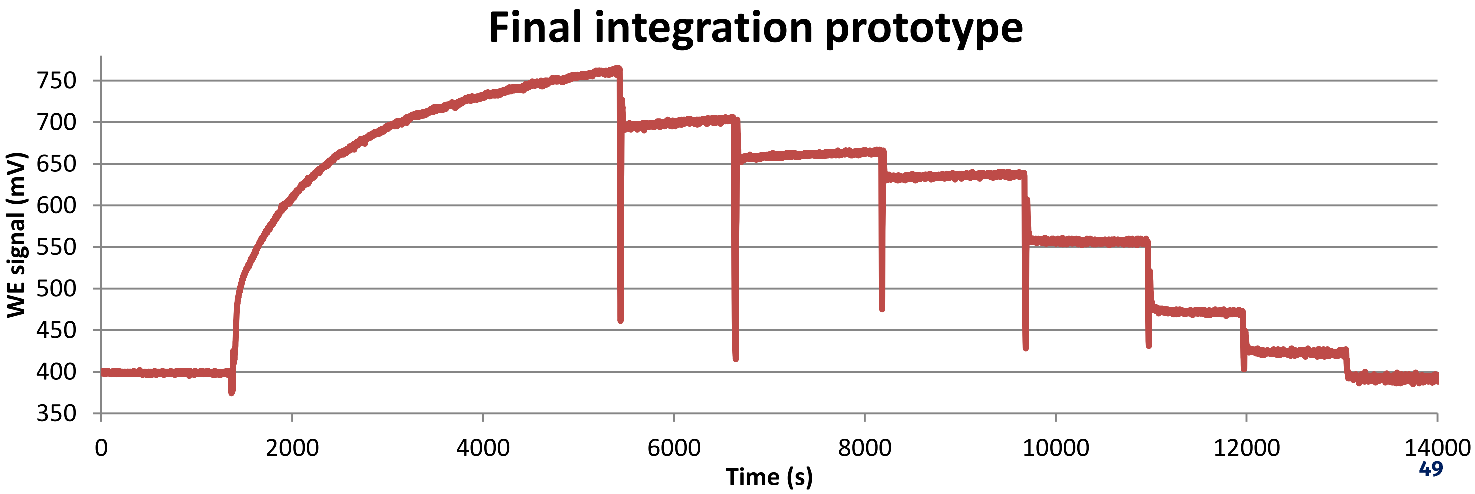


# 5. Preliminary results : Detection

## ✓ Final integration : raw signal with $O_3$ injection



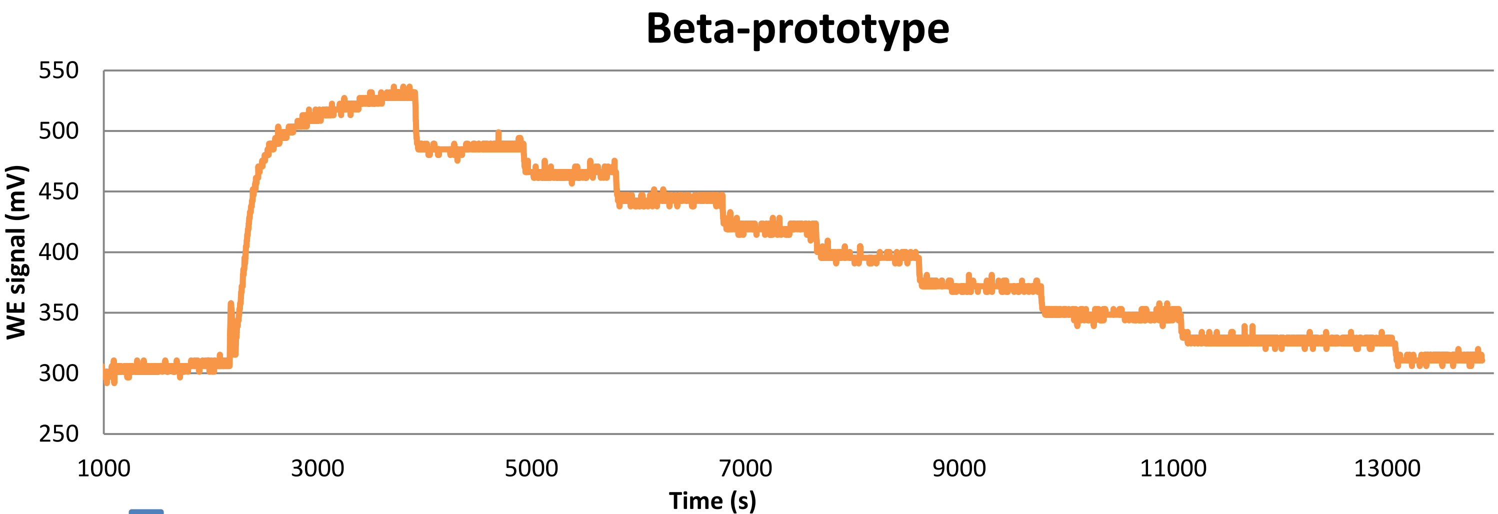

Noise : 18,8 mV




Noise : 6 mV

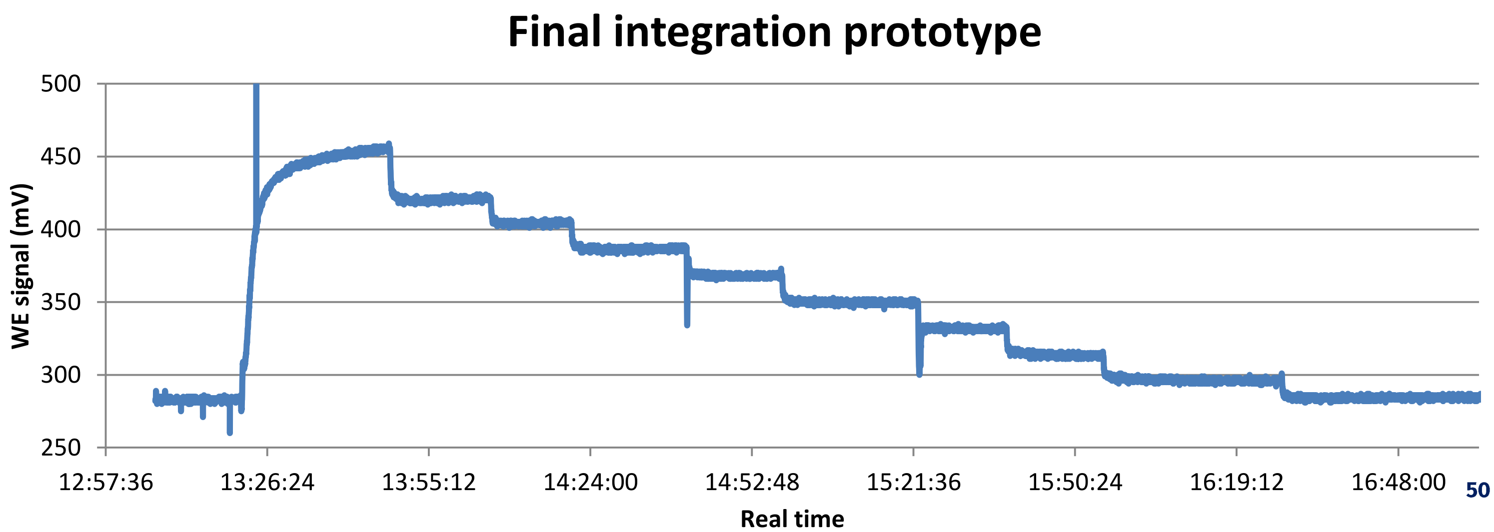
# 5. Preliminary results : Detection

✓ **Final integration : raw signal with $NO_2$ injection**



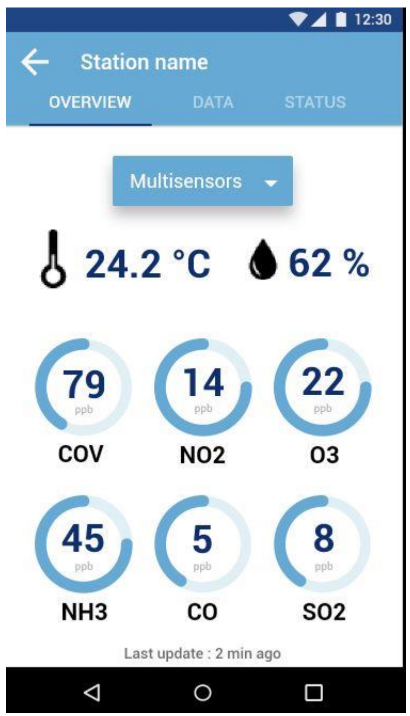

Noise : 14,1 mV

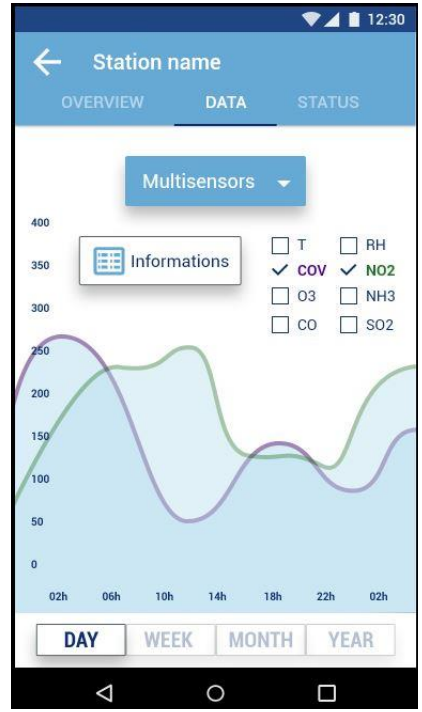
Noise : 6 mV



# 4. Preliminary results : Data visualization

## Android app interface


# 2. Preliminary results: Preconcentration

## *6) Conclusions and future work*

- Linearity and repeatability has been validated
- Calibration has been performed in the range 2.5 - 100 ppb
- LOD less than 2 ppb have been achieved for all BTEX
- More adsorbents are currently being tested for VOCs trapping (zeolites)

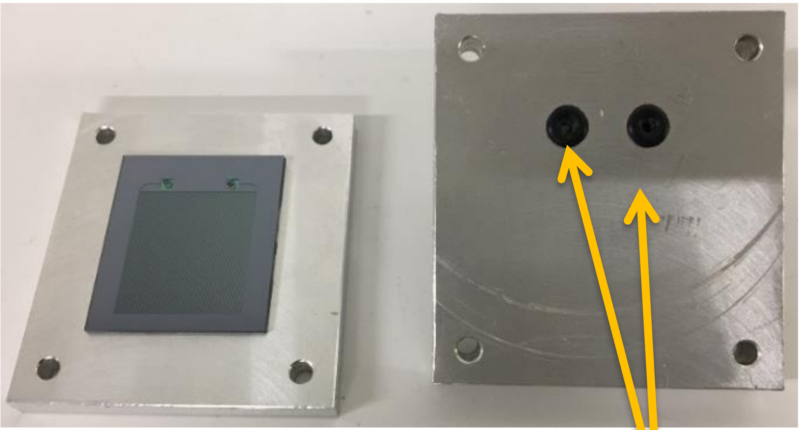
| Main problems: | Solutions: |
| --- | --- |
| • Low heating rate | • Heating cartridges will be replaced by ceramic resistances |
| • High energy consumption | • Energy consumption reduction from 210 W to less than 36 W |
| • Lack of automatization | • Functions will be integrated in the current software (Tronico) |

# 2. Preliminary development : Separation

*3 m GC Column*

***Nanotechnology Plateforme of CNRS-Toulouse (LAAS)***


*Housing*



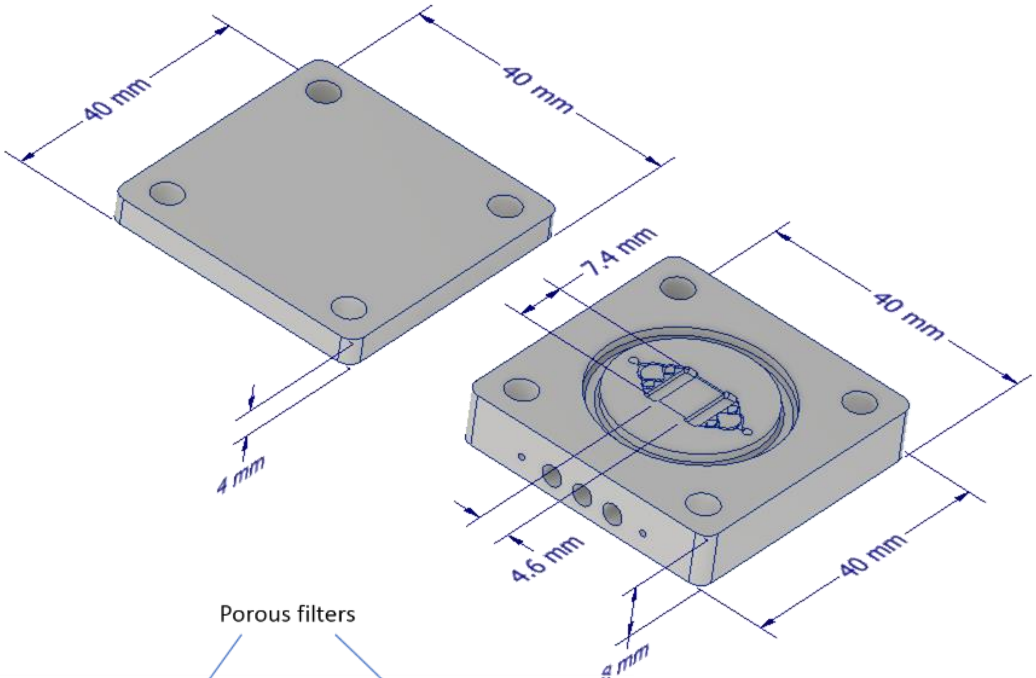
O-ring seals

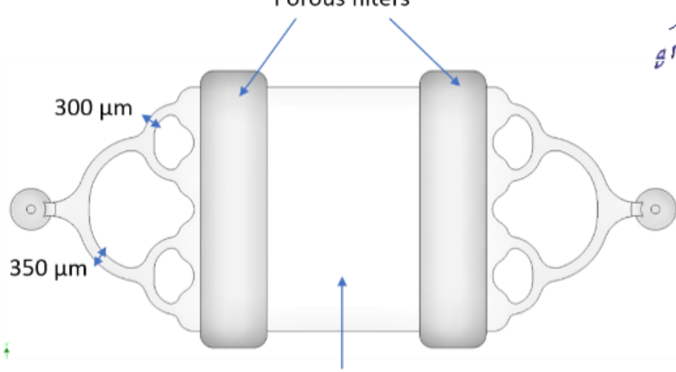
Inlet/outlet
Ø = 1 mm

Inlet/outlet 1/16”

# 2. 1st Preconcentrator

## 1st Preconcentrator




**Study of adsorbents**

**✓Carbopack B**

**✓Basolite C-300**

**✓SBA-16**

*Characteristics:*

- Weight: 54.9 g
- Adsorbent: 5.8 mg of Basolite C300
- Heating system consumption: 210 W
- Heating rate: 150°C in 60 s
- Sampling time: 4 min
- Analysis time: 15 min

# 2. 1st Preconcentrator

## *1) Repeatability*

Ten 20-mL samples containing 100 ppb of BTEX were consecutively injected.

**Retention time RSD (%) < 2 %**

**Peak area RSD (%) < 15 %**

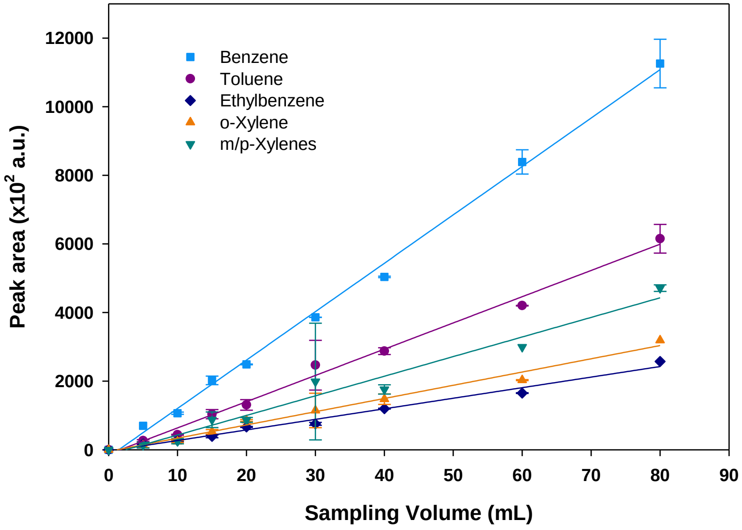
Caused by:

- Co-elution of peaks
- Lack of automatization

Solution:

- Faster heating rate
- Functions integrated in the software

## *2) Linearity*



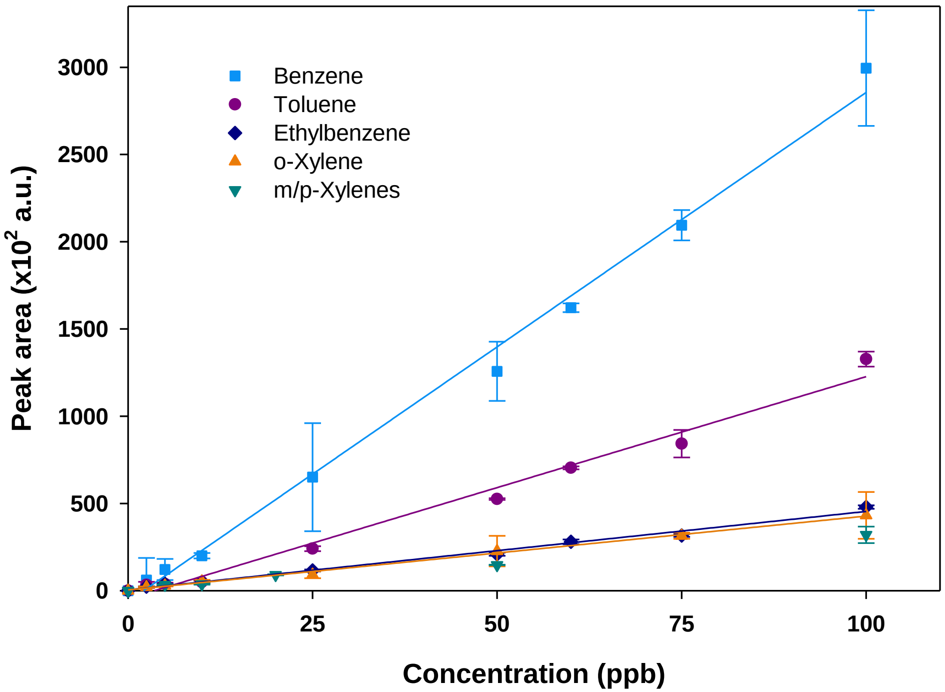

| Compound | $R^2$ |
|---|---|
| Benzene | 0.9946 |
| Toluene | 0.9892 |
| Ethylbenzene | 0.9824 |
| m/p Xylenes | 0.9608 |
| o-Xylene | 0.9838 |

*Linearity is confirmed in the range 5 - 80 mL*

# 2. Preliminary results: Preconcentration

## *3) Calibration*

Calibration was performed using different gaseous concentrations of the targeted compounds in the range 2.5 – 100 ppb. Each concentration was injected in duplicate.

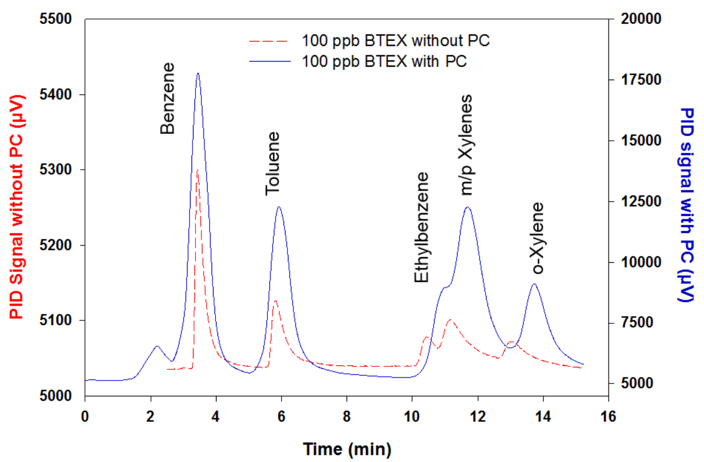



| Compound | Calibration Equation | $R^2$ |
|---|---|---|
| Benzene | y = 2828.2 x | 0.9913 |
| Toluene | y = 1206.3 x | 0.9777 |
| Ethylbenzene | y = 454.2 x | 0.9895 |
| m/p Xylenes | y = 311.9 x | 0.9959 |
| o-Xylene | y = 427.0 x | 0.9949 |

*Analyser response is linear in the range 2.5 – 100 ppb*

# 2. Preliminary results: Preconcentration

## *4) Limit of detection*




| Compound | LOD (ppb) |
|---|---|
| Benzene | 0.20 |
| Toluene | 0.26 |
| Ethylbenzene | 0.49 |
| m/p Xylenes | 0.80 |
| o-Xylene | 1.70 |

*LOD lower than 2 ppb is achieved for all compounds*

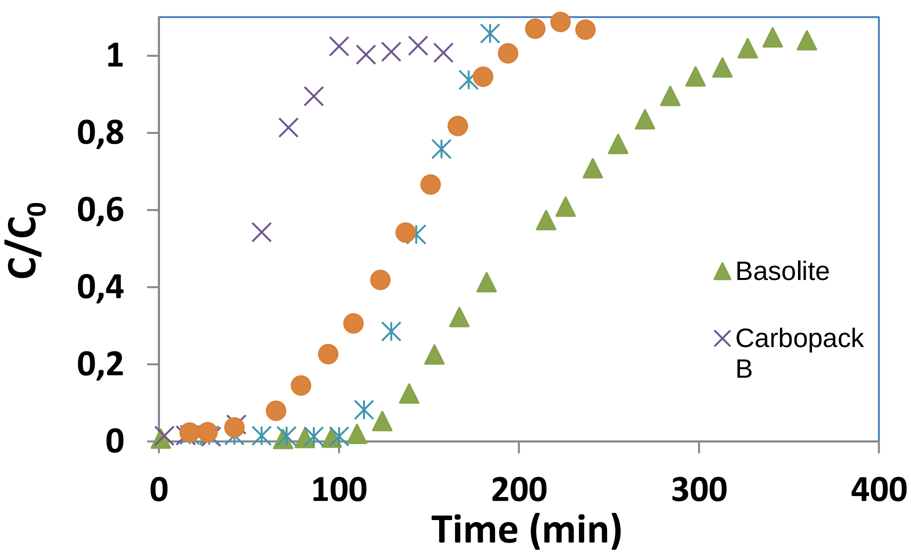
## *5) Adsorbents for VOCs trapping*

Different materials tested as adsorbents for aldehydes trapping

**<u>Conditions:</u> $C_0$ = 3300 ppm    Flow rate = 20 mL/min**

**Adsorbent mass = 50 mg**

**Hexanal adsorption**




*Selected adsorbents exhibited high adsorption capacity for BTEX and hexanal*

# Conclusions & Perspectives

✓ Conception

✓ MEMS GC Column manufacturing

✓ Study of absorbants

✓Preconcentration tests (major drawback : 210 W for heating)

✓ Heating performance tests

***Today***

✓Miniaturization of preconcentrator with lower Energy consumption (patent under submission)