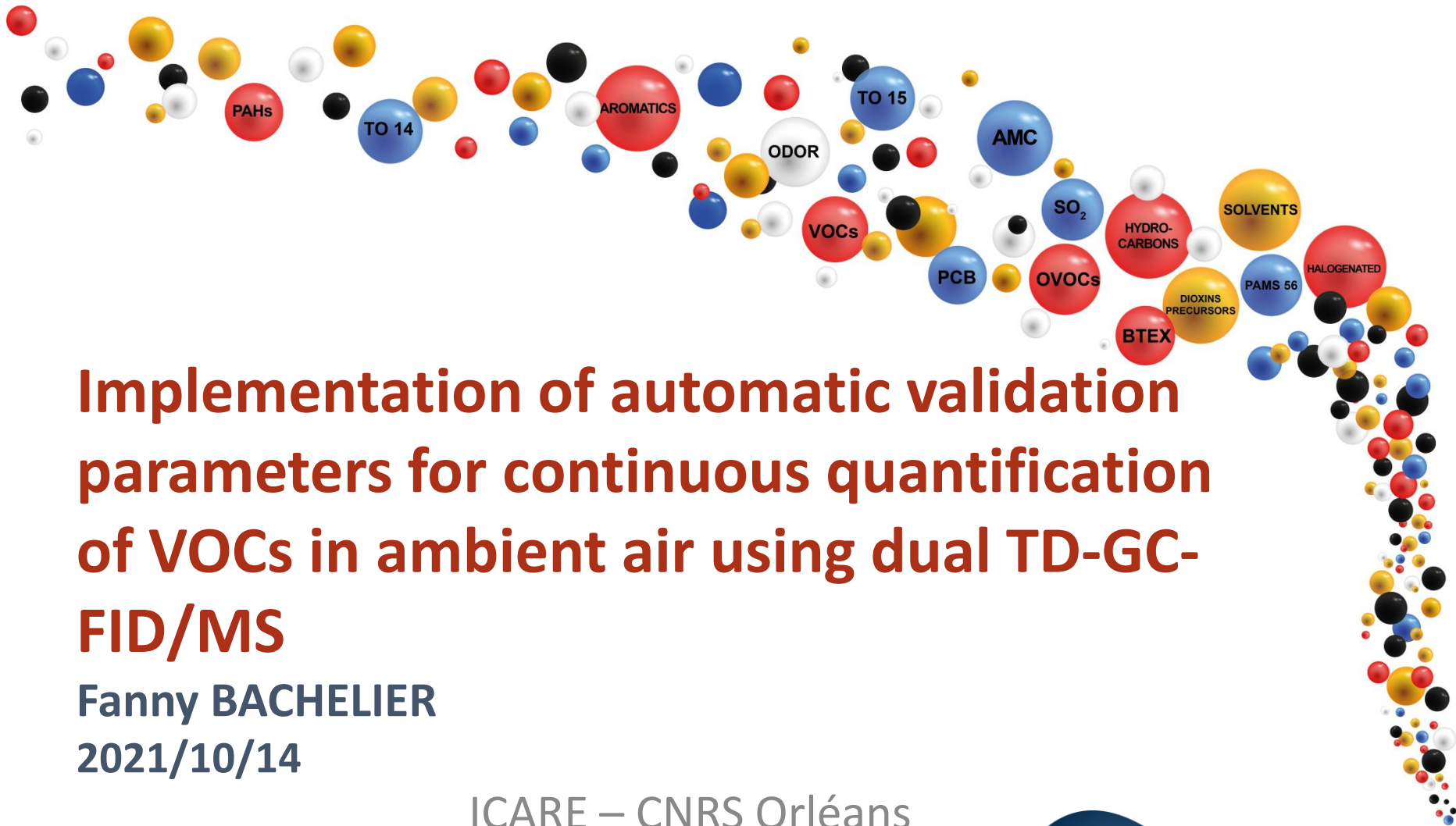




# Implementation of automatic validation parameters for continuous quantification of VOCs in ambient air using dual TD-GC-FID/MS

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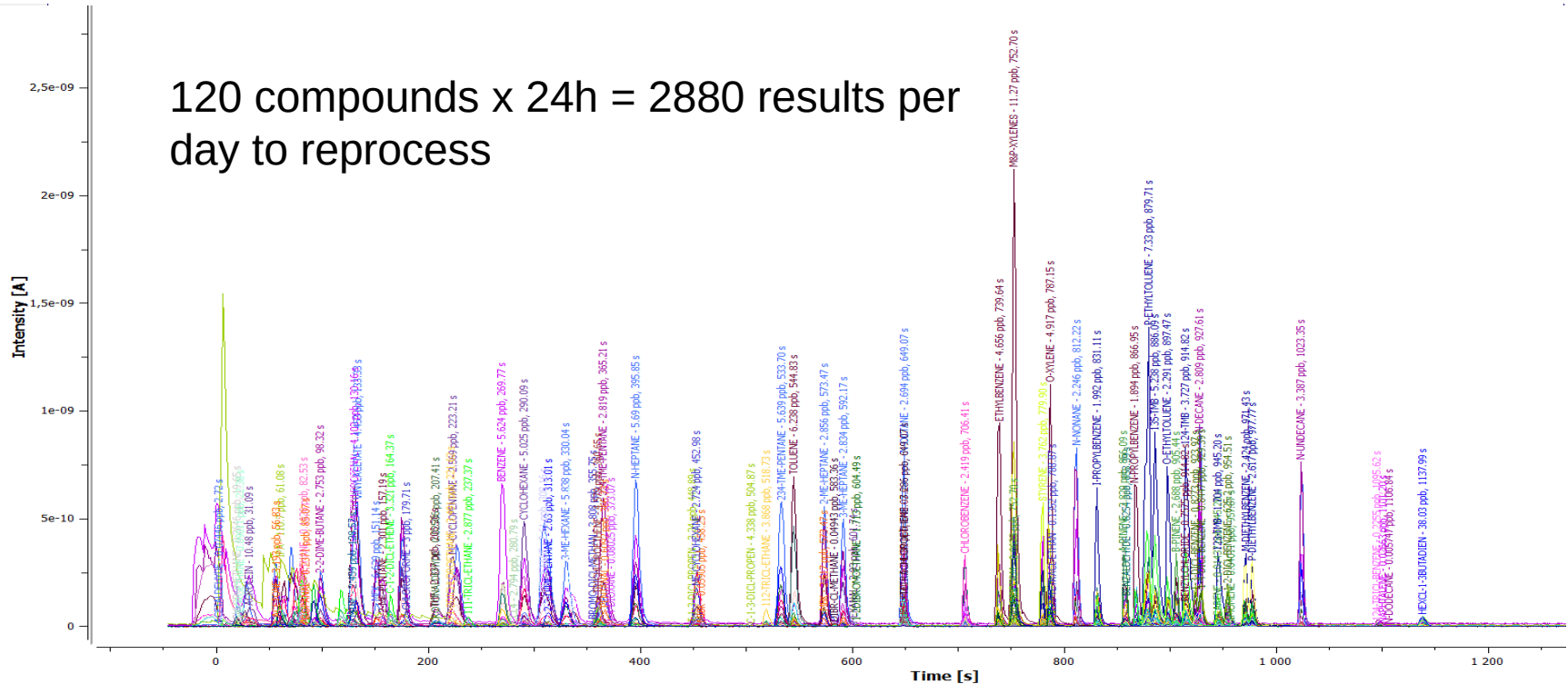
ICARE – CNRS Orléans

Chromatotec®

- VOCs measurements are of great interest for air quality assessment
- Many potential compounds founded in ambient air
  - Anthropogenic or natural
  - Alcanes, Terpens , Oxygenated, Halogenated or sulfur compounds
- Two strategies possible:
  - Collect samples on-site and analyze later in the lab
  - Use continuous on-site gas chromatographs (carry out analyses in real time an without the risk to deteriorate the samples)
    - Laboratory performance studies
    - campaign measurements (Moroccan campaign ATLAS-MOHAMMED V)

# MS Chromatogram

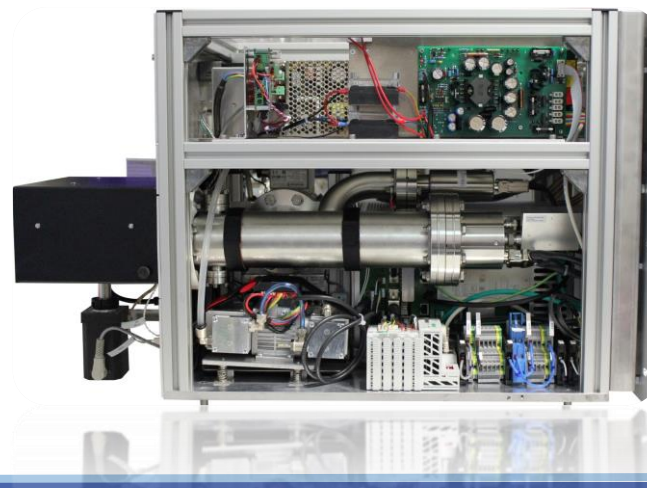
120 compounds x 24h = 2880 results per day to reprocess



- Develop automatic parameters to analyze continuously and automatically chemicals at different concentrations without identification and quantification mistakes

## ➤ Method:

- TD-GC-FID for C6 to C12\*
  - Carrier gas: H<sub>2</sub> - Flow rate: 27.5 mL/min
  - Column: capillary MXT 30 CE (60 m x 1 µm x 0,28 mm)
  - Trap: 2 phases C6
  - Thermodesorption: 380° C
  - Oven : 38 – 200° C
  - Detector: FID at 170 ° C
  - 60 minutes cycle
- DET QMS:
  - Single Quadrupole with Electron Impact ionization (70 eV)
  - Inlet: Deactivated Silica Tube ID 50 µm; T= 170 ° C
  - Transfer line: Deactivated metallic capillary tube; T = 200° C
  - SEM voltage = 1200 V
  - Detection: SCAN or MID (Multiple Ions Detection)

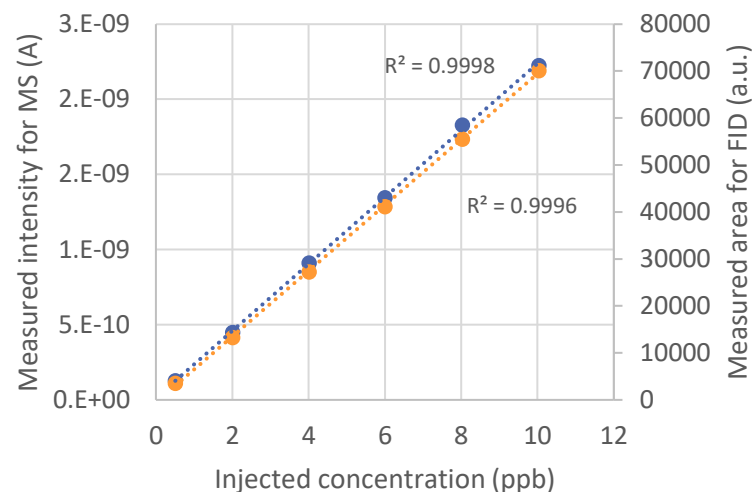


## ➤ Protocol:

- 100 ppb cylinders:
  - PAMS compounds (58 VOCs):  
ambient air representative mix
  - TO15 compounds (64 VOCs):  
industrial air representative mix
- Linearity tests:  
Range 0.5 – 10 ppb(v) generated  
through zero air dilutions  
3 repetitions per concentration
- Precision tests:  
6 repetitions at 4 ppb
- Accuracy tests:  
6 repetitions at 4 ppb

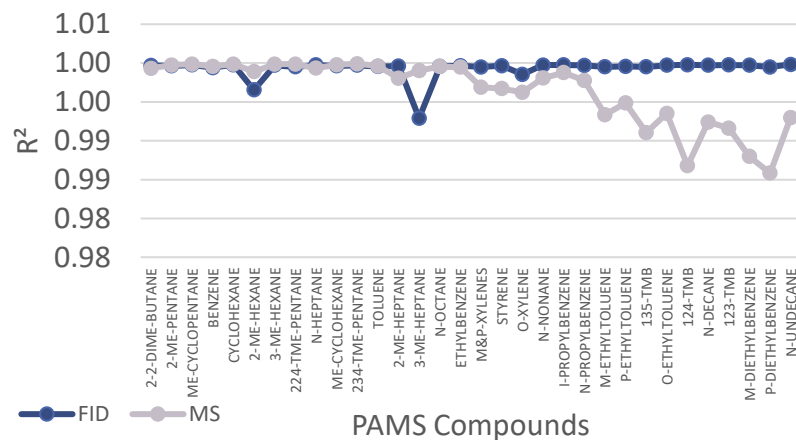
## ➤ Example of cyclohexane performance system:

- Linearity:



|                  | MS     | FID    |
|------------------|--------|--------|
| <b>Precision</b> | 1,60 % | 0,42 % |
| <b>Accuracy</b>  | 98 %   | 100,3% |

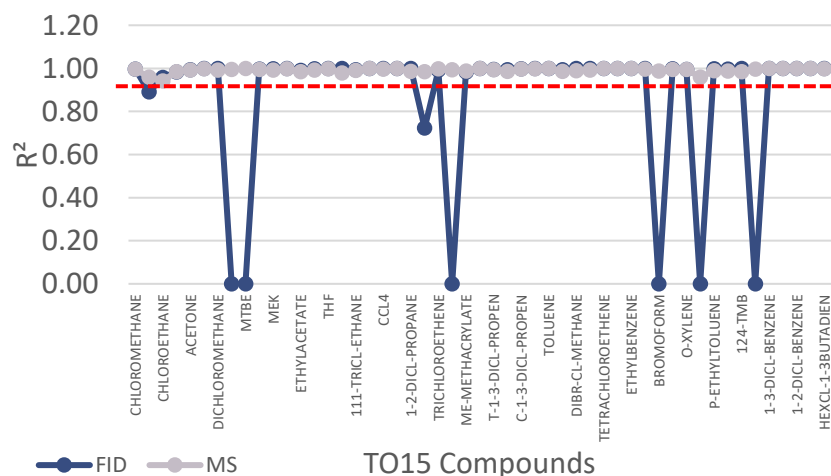
# III – 1) FID vs MS characterization using PAMS cylinder



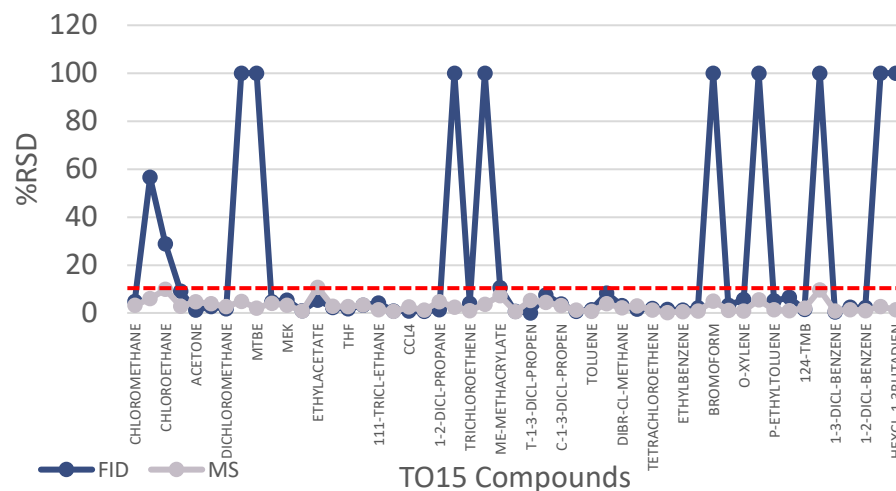
# III – 2) FID vs MS characterization using TO15 cylinder



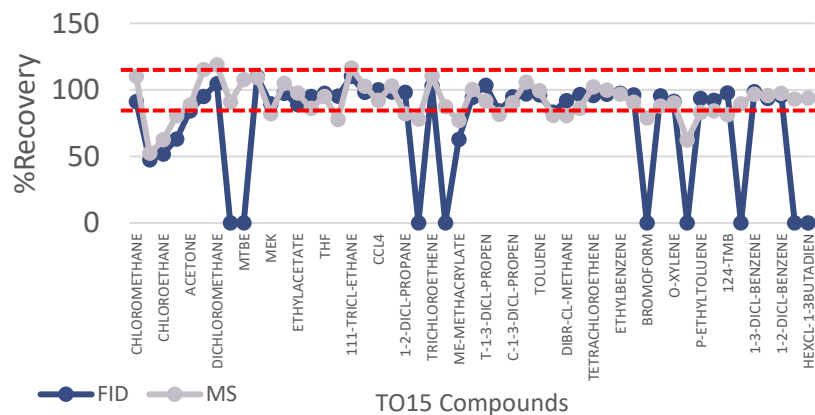
## ➤ Determination coefficients comparison:



## ➤ Precision comparison:



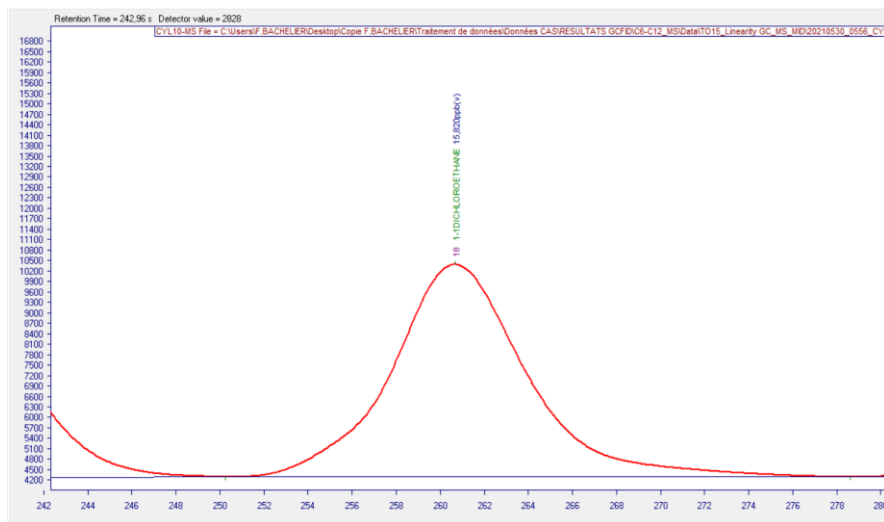
## ➤ Accuracies comparison



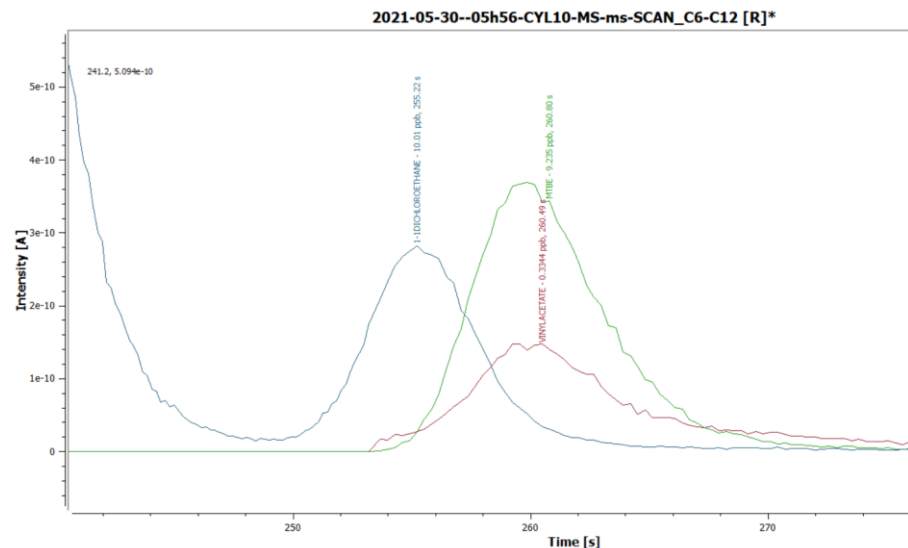
➔ Some TO15 compounds are not detected due to coelutions by FID detection

# III – 3) Example of TO15 compounds coelutions

- FID at 262s:** 1,1-dichloroethane



- MS 262s:** at 1-1-dichloroethane + MTBE + Vinylacetate



- FID coelutions are avoided by selected specific ion using MS detection

| Analyzer | FID                                                              | MS                                             |
|----------|------------------------------------------------------------------|------------------------------------------------|
| +        | Better reliability (Linearity, precision, accuracy)              | Possible identification by using NIST database |
| -        | Identification and quantification difficulties when interferents | Results less accurate and precise              |

- Algorithm developed:

CST\_C\_GAP: If  $|[\text{FID}] - [\text{MS}]| < \text{CST\_C\_GAP} \rightarrow \text{FID value}$

PCENT\_C\_GAP: If  $\frac{[\text{FID}] - [\text{MS}]}{[\text{MS}]} \times 100 < \text{PCENT\_C\_GAP} \rightarrow \text{FID value}$

- Validation parameters used:

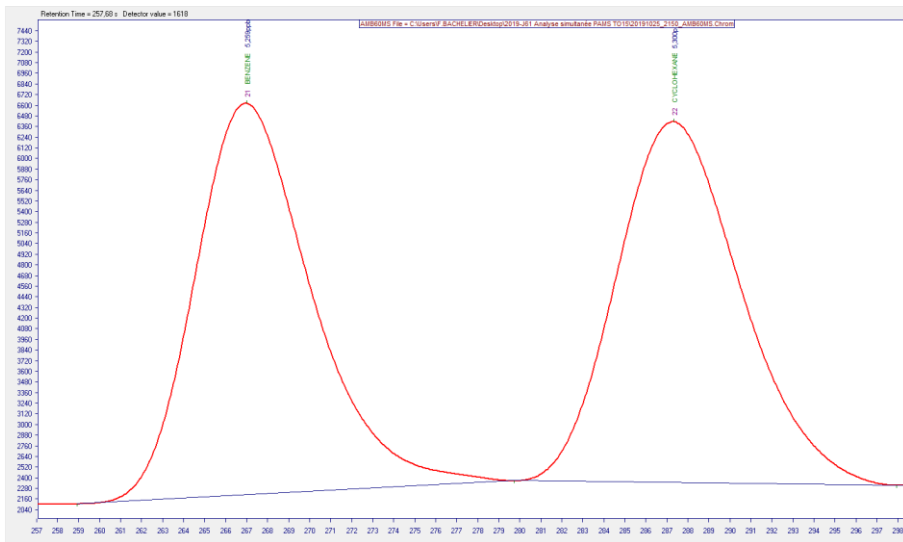
|             | FID MS  | FID MS   |
|-------------|---------|----------|
| CST_C_GAP   | 0,5 ppb | 0,01 ppb |
| PCENT_C_GAP | 20 %    | 1 %      |

These are chosen for each compound by empiric knowledge (for PAMS + TO15 mixture)

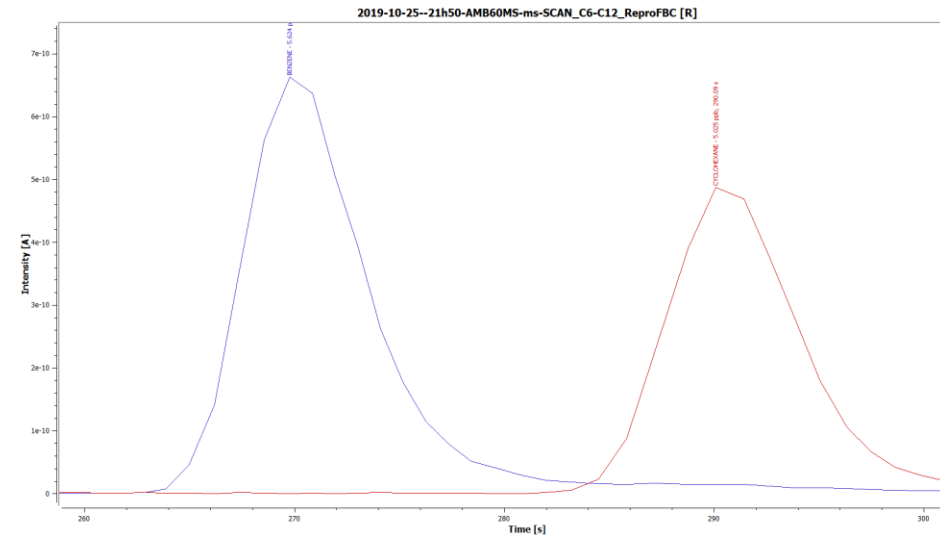
This is uploaded automatically in the quantification software

# IV- Example of validation parameters implementation for dual MS & FID detection

- FID Benzene & Cyclohexane



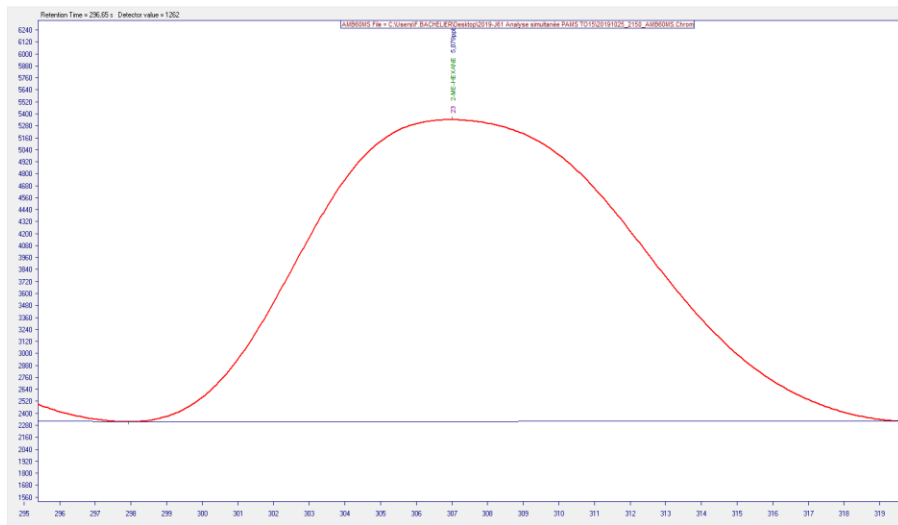
- MS Benzene & Cyclohexane



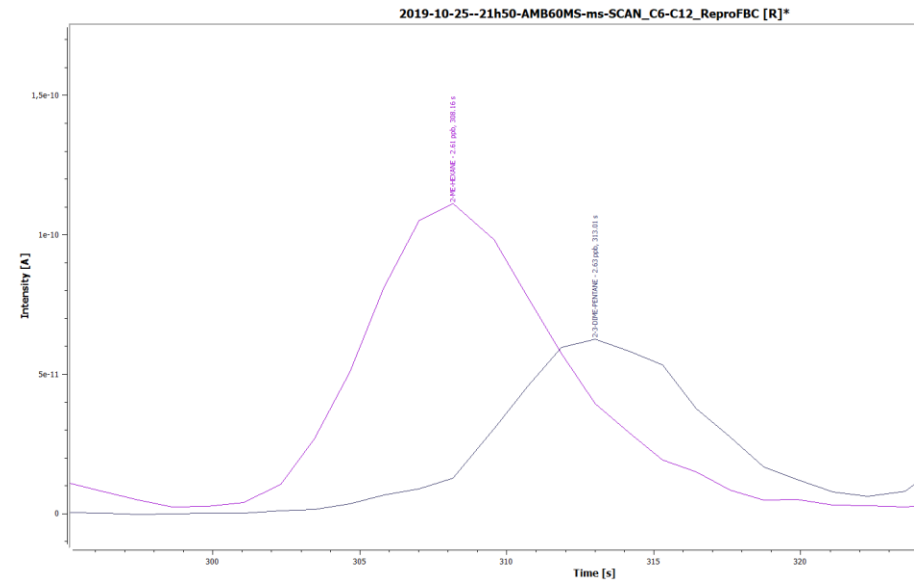
|             | Benzene | Cyclohexane |
|-------------|---------|-------------|
| CST_C_GAP   | 0,5 ppb | 0,5 ppb     |
| PCENT_C_GAP | 20 %    | 20 %        |

# IV- Example of validation parameters implementation for dual MS & FID detection

- FID 2-methylhexane



- MS 2-methylhexane & 2,3-dimethylpentane

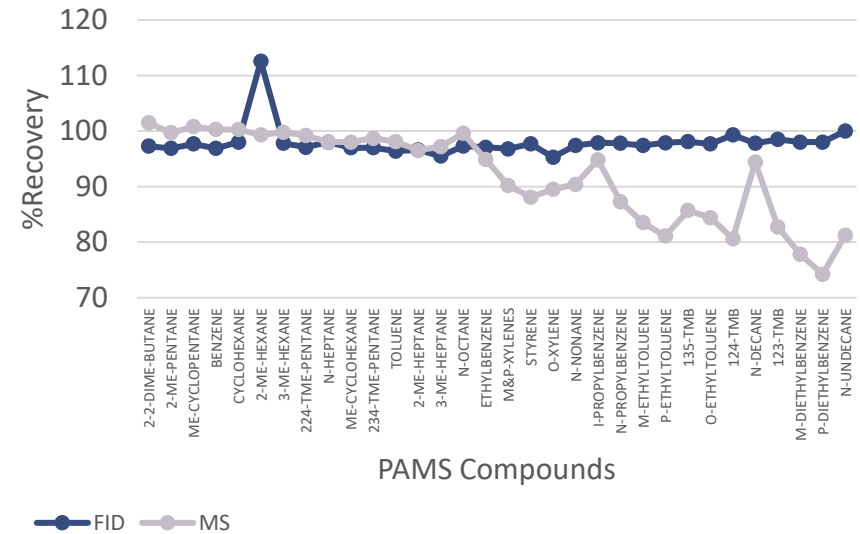
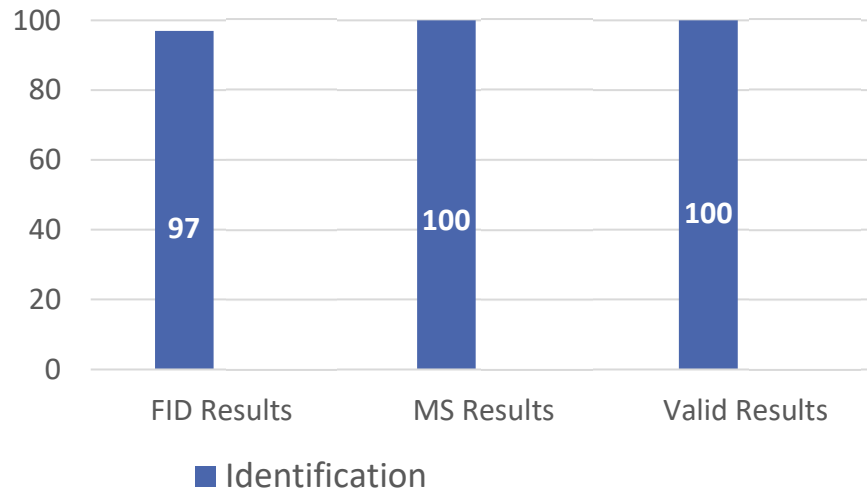


|             | 2-Methylhexane | 2,3-dimethylpentane |
|-------------|----------------|---------------------|
| CST_C_GAP   | 0,01 ppb       | 0,01 ppb            |
| PCENT_C_GAP | 1 %            | 1 %                 |

# IV – 1) Implementation of Data validation parameters



PAMS: identification and quantification for FID and MS



- All identification mistakes are avoided by implementing validation parameters
- Quantification at 4 ppb with less than 20% of uncertainty
- For heavier compounds MS detector less accurate
  - work on MS accuracy of heavier compounds
  - Refine validation criteria



- When dealing with complex air samples, necessity of dual detection
  - Overall good linearity, precision and accuracy for both detectors with results close to CCEP norm criteria<sup>(1)</sup>:
    - Linearity:  $R^2 > 0,98$
    - Precision:  $RSD \leq 10\%$
    - Accuracy:  $100\% \pm 10\%$
- } FID more reliable but coelutions can be avoided by using MS
- Implementation of automatic validation parameters between FID and MS detection are efficient for correcting misidentifications but not suitable enough for reducing quantifications mistakes

## Perspectives:

→ Refine validation parameters to found good compromise between avoiding coelutions risks and results accuracy



Thank you for your attention

