



**HAL**  
open science

## Development of on-line and field dual TD-GC-FID/MS for automatic and continuous VOCs monitoring in ambient air

Fanny Bachelier, Jean-Philippe Amiet, Véronique Daële, Damien Bazin

► **To cite this version:**

Fanny Bachelier, Jean-Philippe Amiet, Véronique Daële, Damien Bazin. Development of on-line and field dual TD-GC-FID/MS for automatic and continuous VOCs monitoring in ambient air. NOSE 2022 : 8th International Conference on Environmental Odour Monitoring & Control, Sep 2022, Taormina, Italy. hal-03868101

**HAL Id: hal-03868101**

**<https://hal.science/hal-03868101>**

Submitted on 23 Nov 2022

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



# Development of on-line and field dual TD-GC-FID/MS for automatic and continuous odorous VOCs monitoring in ambient air

F. BACHELIER<sup>1,2</sup>, F. AMIET<sup>2</sup>, V. DAELE<sup>1</sup>, D. BAZIN<sup>2</sup>

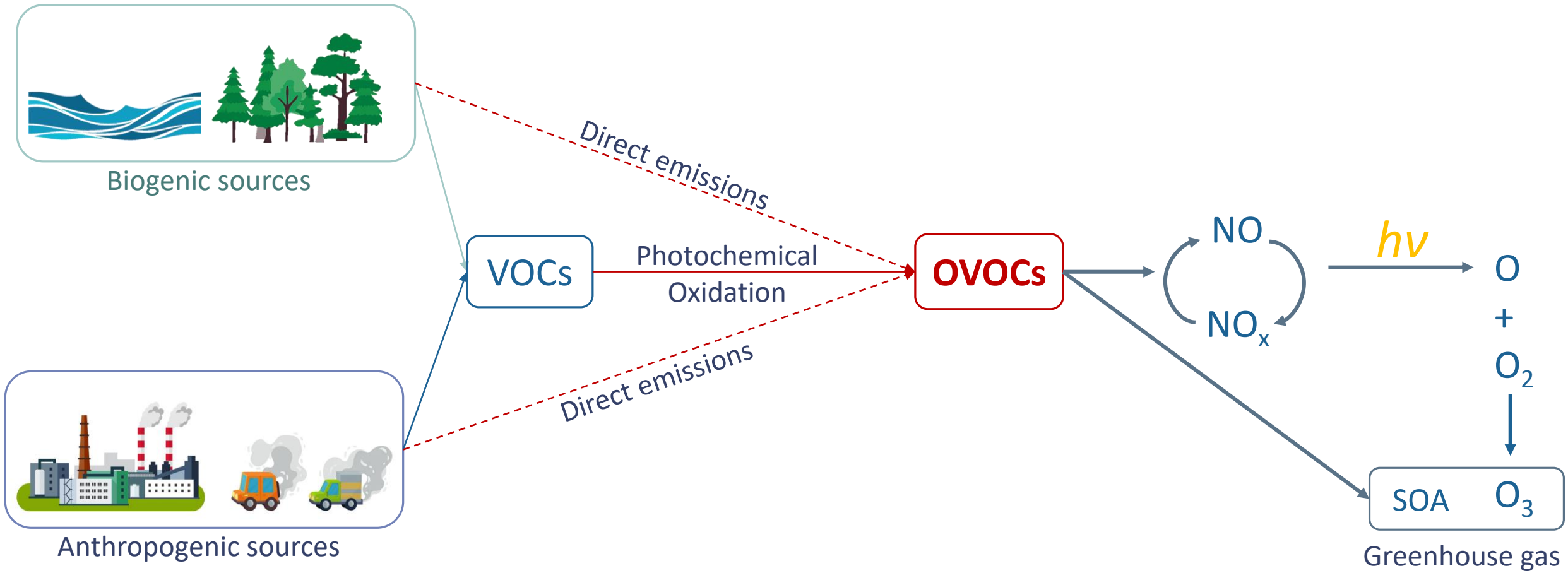
<sup>1</sup>ICARE – UPR 3021 – CNRS, 1C, av. de la Recherche Scientifique CS50060 – 45071 Orléans, France

<sup>2</sup>Chromatotec, 15 rue d'Artiguelongue, 33240 Saint-Antoine, France

2022/09/13

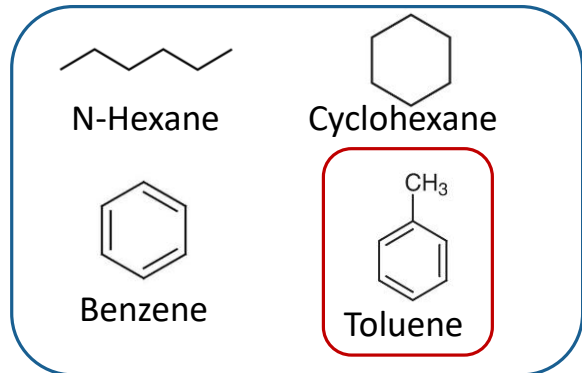


# Introduction

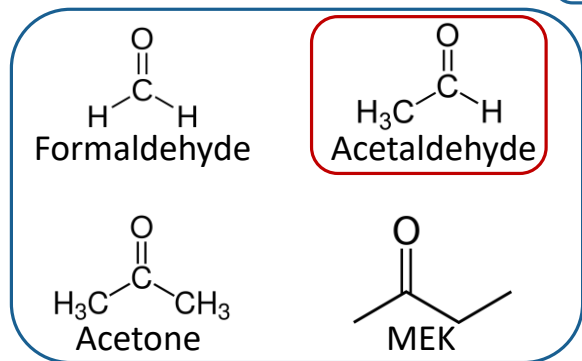


Ehsanul K., et al., 2010, Atmospheric environment, 44, 3492 - 3502

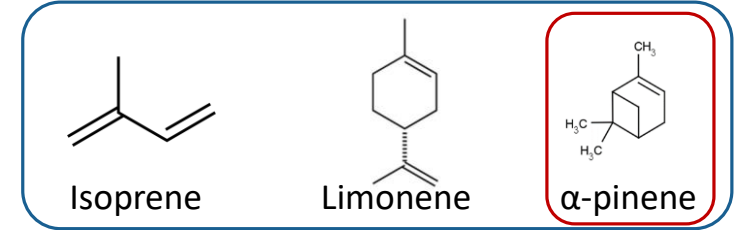
# Introduction VOCs families



NMHCs



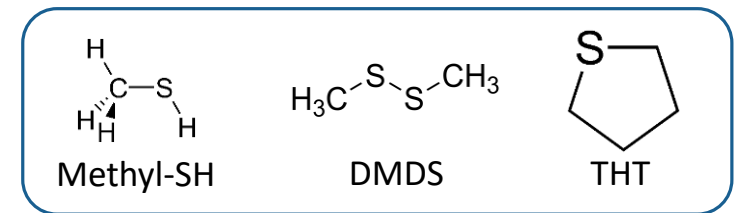
OVOCS



BVOCs

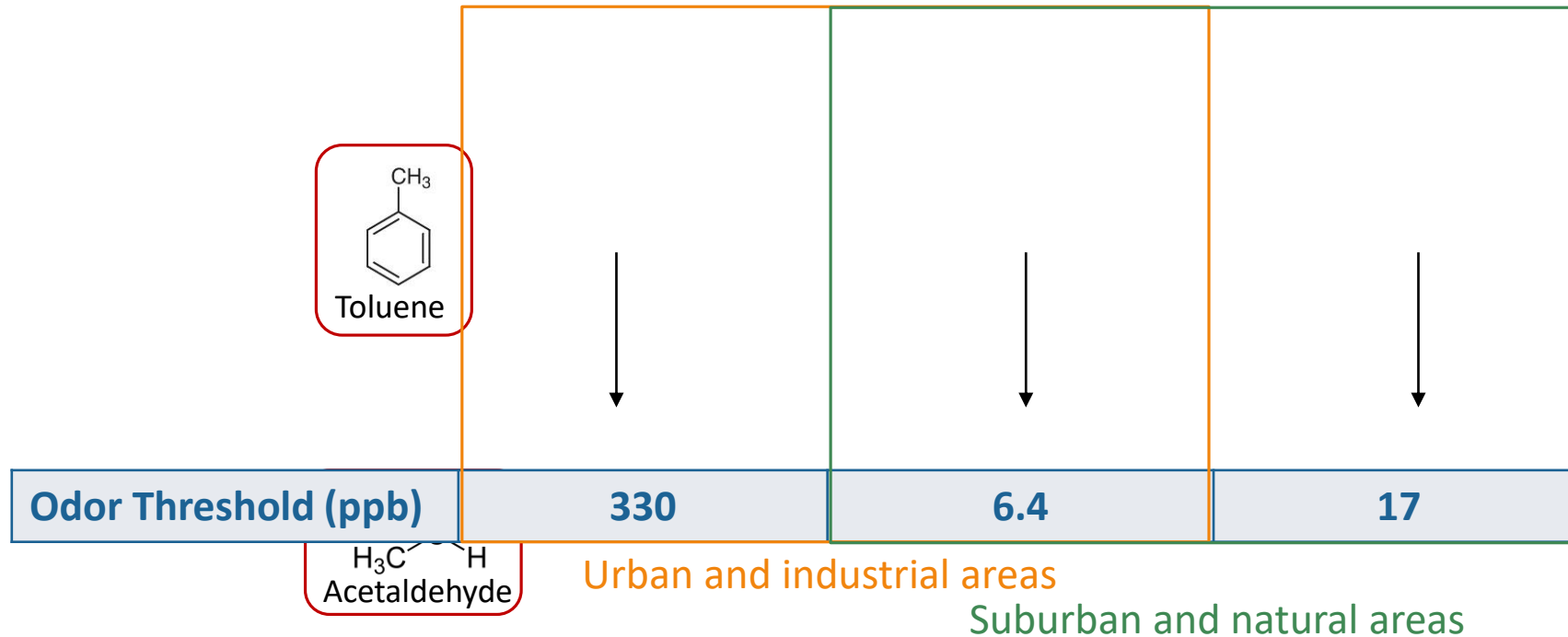
## Some VOCs responsible of odor pollution:

- Environmental nuisances
- Unpleasantness
- Potential health risks



VSCs

# Introduction VOCs families



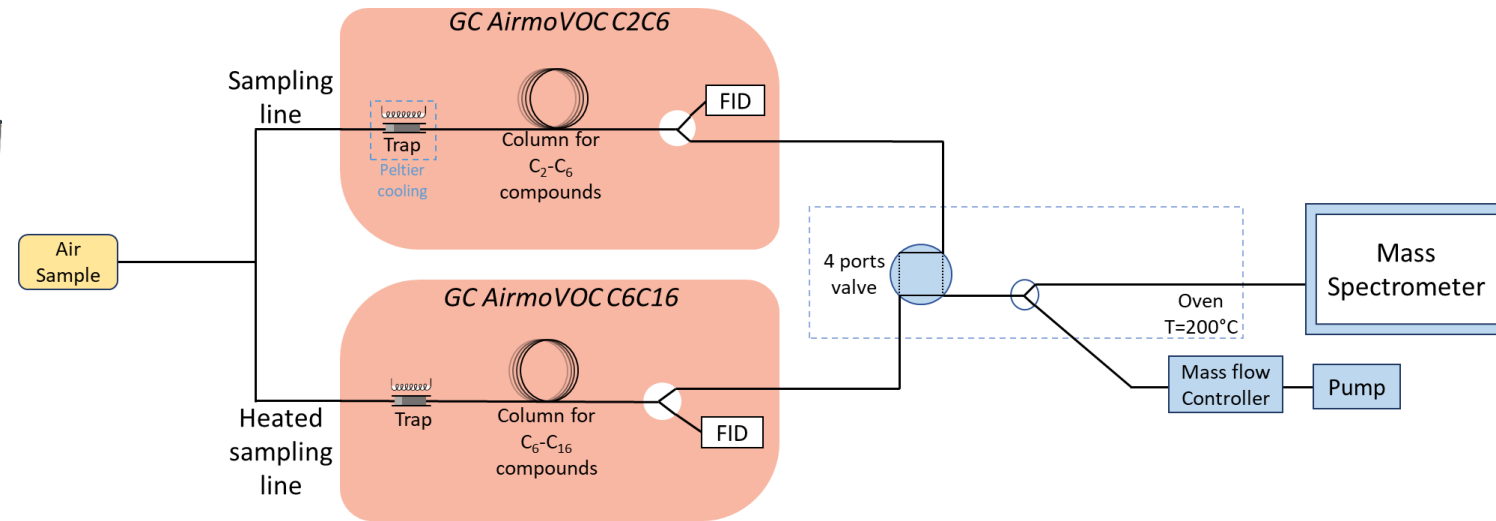
Both areas → **Objective:** Study the performance and limitations of **on-line** **an auto-TD-GC-FID/MS** to identify and quantify these odorant VOCs

Hiroyuki U., 2021, Asian Journal of Atmospheric Environment, 15, 1, 2020085

# Material & Method auto-TDGC-FID/MS: AirmOzone with process MS



- System configuration:



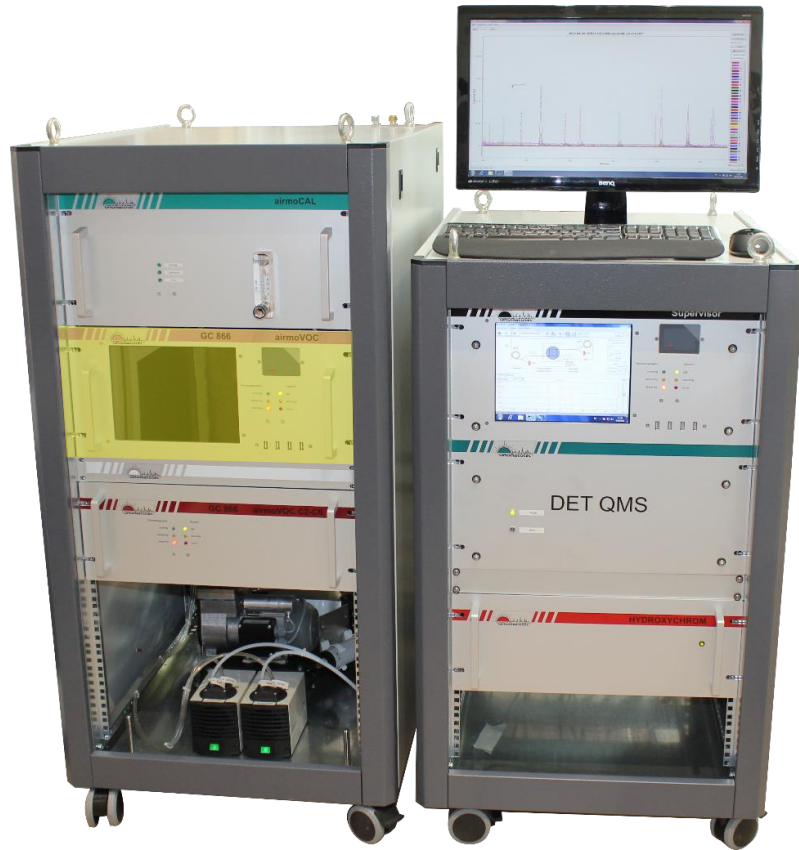
# Material & Method auto-TDGC-FID/MS for C2C6 monitoring



- Carrier gas: H<sub>2</sub>
- Sampling flow: 12 mL/min
- Column: Capillary PLOT column (25 m x 0,53 mm x 10 μm)
- Trap: Carboxen and Carbopack mixture (-10°C)
- Thermodesorption: 220°C
- Oven: 36 – 202 °C
- Detector: FID at 170°C
- Sampling time: 30 min
- Cycle time: 45 min

GC designed for light non polar VOCs containing 2 to 6 carbons

# Material & Method auto-TDGC-FID/MS for C6C16 monitoring



- Carrier gas: H<sub>2</sub>
- Flow rate: 20 mL/min
- Column: Capillary MXT30CE column (60 m x 0,23 mm x 1,0 μm)
- Trap: Carbopack mixture (Room temperature)
- Thermodesorption: 380 °C
- Oven: 36 – 202 °C
- Detector: FID at 190°C
- Sampling time: 30 min
- Cycle time: 45 min

GC designed for VOCs containing 6 to 16 carbons



# Material & Method

## Mass spectrometer for C2-C16 monitoring

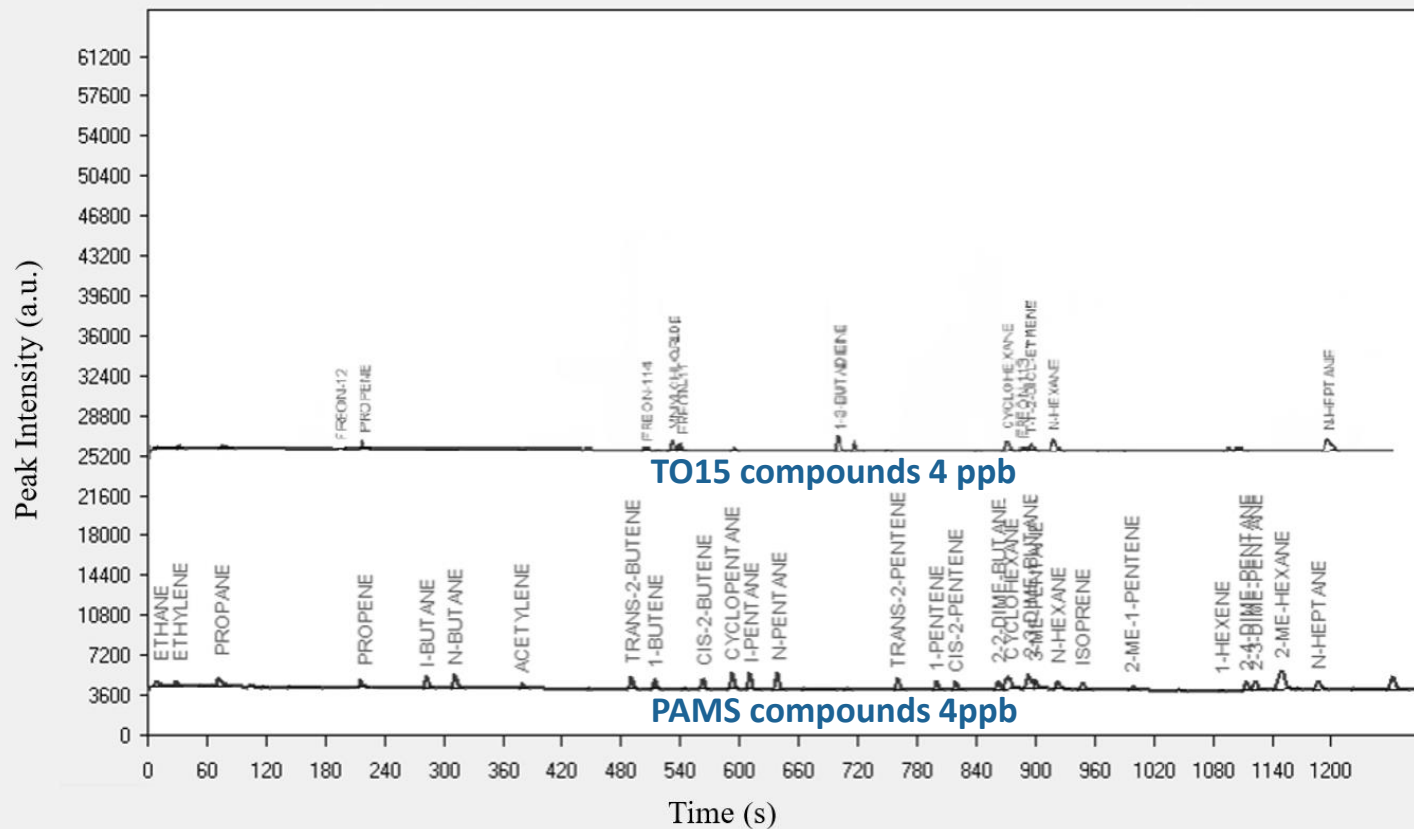


- Single Quadrupole with Electron Impact Ionization (70 eV)
- Inlet:
  - Deactivated Silica Tube ID 50  $\mu\text{m}$
  - Temperature = 170  $^{\circ}\text{C}$
- Transfer line:
  - Deactivated metallic capillary tube
  - Temperature = 200  $^{\circ}\text{C}$
- Detection: SCAN mode (0 – 300 amu)
- SEM voltage = 1200V

MS connected to TD-GC(C6-C16)-FID-MS for identification and quantification of coeluted VOCs

# Results

## C2 to C6 measurement



✓ C2C6 system suitable to analyze:

- All light Hydrocarbons (from PAMS cylinder)
- Freons, light chlorinated compounds (from TO15 cylinder)

✗ C2C6 system cannot analyze:

- Light OVOCs: Methanol, Ethanol, Formaldehyde and Acetaldehyde

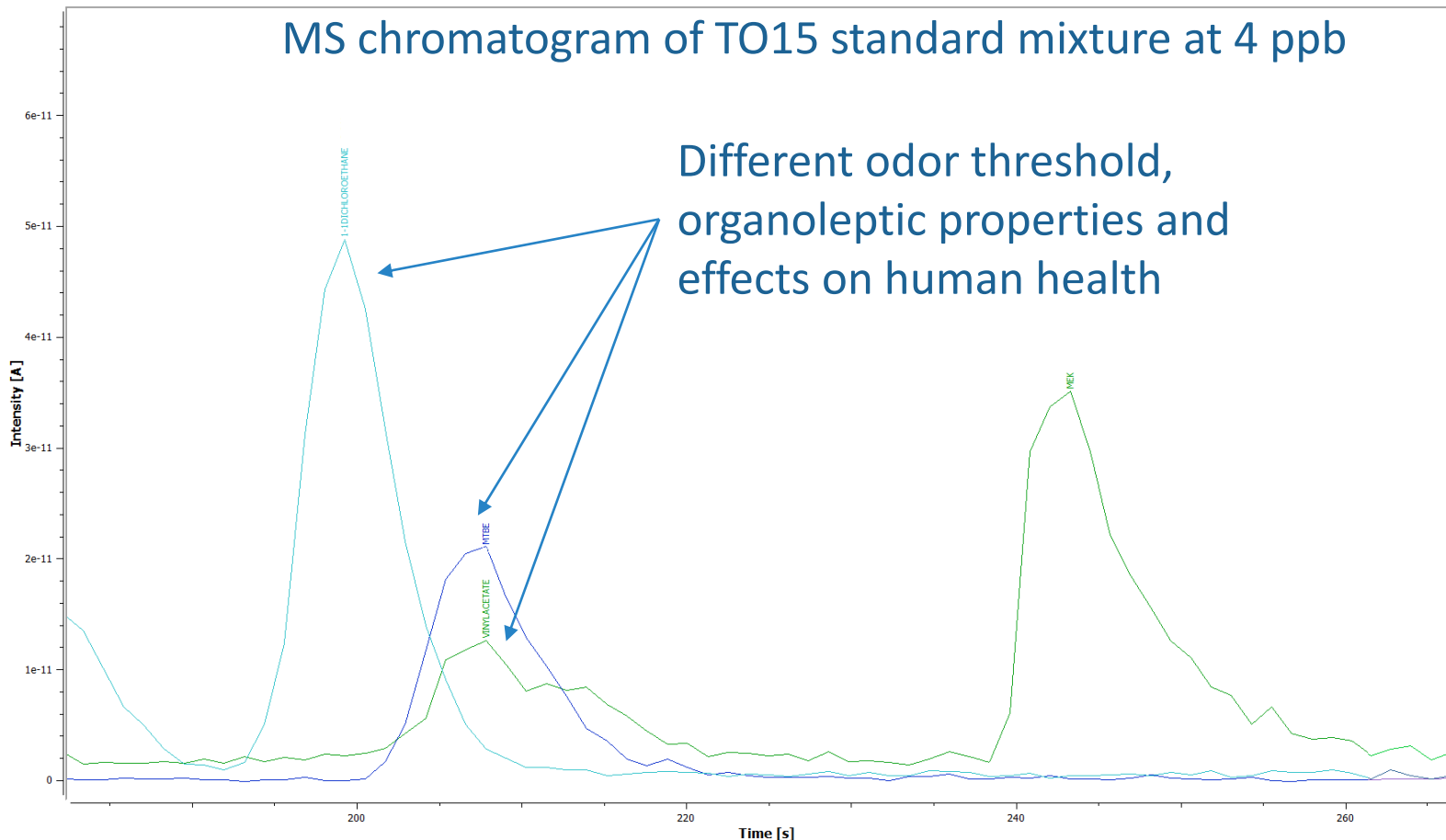
→ Column too polar to elute these compounds



# Results

## C6 to C16 MS measurement

MS chromatogram of TO15 standard mixture at 4 ppb



Compound	Specific m/z	Odor Threshold (ppm)
1,1-Dichloroethane	63	120
Vinyl Acetate	43	0.4
MTBE	73	0.03

→ MS detection allows the quantification of coeluted VOCs thanks to specific m/z of the compounds

Deese D. E. et al., **1969**, AIHA Journal, 30, 449 – 457  
 Smith S. L. et al., **1995**, Chem Health Saf, 2, 3, 32 – 38  
 Verschueren, K. et al., **2001** Handbook of Environmental Data on Organic Chemicals. Volumes 1-2. 4th ed. John Wiley & Sons.

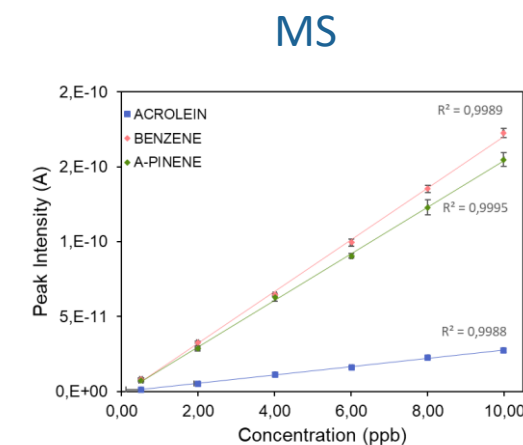
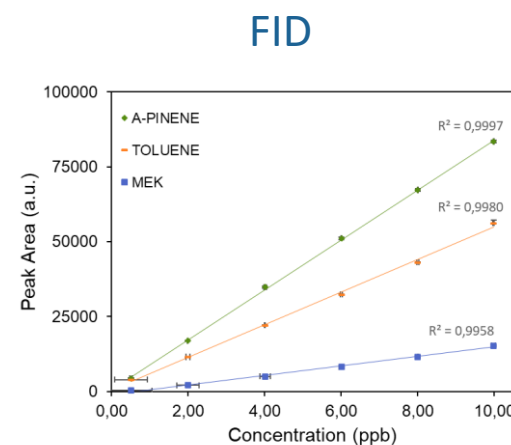
# Results

## Method validation

### ➤ Performance studies:

- 100 ppb certified cylinder:
  - PAMS compounds: containing a mix of 58 hydrocarbons
  - TO15 compounds: containing a mix of 64 oxygenated and halogenated compounds)
- Linearity tests:
  - Range 0.5 – 10 ppb(v): dilution with zero air performed with 2 MFC
  - Calibration curves with 6 different concentrations
  - 10 replicates for the first point and 6 for the others
- Precision and accuracy tests:
  - 6 repetitions at 4 ppb

### ➤ Example of 3 calibration curves of Methyl Ethyl Ketone (MEK), Toluene and : $\alpha$ -pinene



# Results

## Method Validation

OVOCs	FID Detection				MS Detection			
	Determination coefficient (R <sup>2</sup> )	LOD (ppb <sub>v</sub> )	Precision at 4 ppb <sub>v</sub> (%RSD)	Accuracy at 4 ppb <sub>v</sub> (%)	Determination coefficient (R <sup>2</sup> )	LOD (ppb <sub>v</sub> )	Precision at 4 ppb <sub>v</sub> (%RSD)	Accuracy at 4 ppb <sub>v</sub> (%)
Acrolein	<b>0.9992</b>	0.093	2.04	<b>2.62</b>	0.9990	0.277	<b>10.6</b>	1.67
Acetone	0.9960	<b>0.065</b>	<b>5.79</b>	8.27	<b>0.9995</b>	0.253	5.45	2.22
Isopropyl alcohol	<b>0.9829</b>	0.130	<b>1.12</b>	13.6	<b>0.9871</b>	0.404	7.76	7.87
Methyl <i>tert</i> -butyl ether	<i>Coeluted</i>	-	-	-	0.9995	0.216	<b>2.78</b>	2.09
Vinyl acetate	<i>Coeluted</i>	-	-	-	0.9992	0.431	7.49	<b>0.73</b>
Methyl ethyl ketone	0.9960	0.124	2.52	14.2	0.9899	<b>0.068</b>	4.37	<b>19.8</b>
Ethyl acetate	<i>Coeluted</i>	-	-	-	0.9928	<b>2.092</b>	6.79	19.3
1,4-Dioxane	0.9894	0.150	2.44	<b>29.2</b>	0.9978	0.285	7.29	14.9
Methyl methacrylate	<i>Coeluted</i>	-	-	-	0.9984	0.273	3.43	5.92
Methyl isobutyl ketone	0.9986	<b>0.325</b>	1.46	7.36	0.9979	0.760	8.12	2.34
Methyl butyl ketone	0.9970	0.270	2.77	7.68	0.9988	0.159	7.79	2.47

- Linearity: R<sup>2</sup> showed linear calibration curves for FID and MS
- Limit of detection (LOD): Overall higher with MS detection

- Precision (RSD%):
  - < 11 % for FID and MS
  - FID is more repeatable than MS
- Accuracy:
  - < 30 % for FID and < 20 % for MS
  - Overall better accuracy for MS detection

# Results

## Development of automatic reprocessing

- Interest of dual detection FID and MS in continuous and on-site measurements:

- Algorithm and validation parameters implemented in data reprocessing software:

If  $[FID] - [MS] < \text{CST\_C\_GAP}$   
 Or  
 If  $\frac{[FID] - [MS]}{[MS]} < \text{PCENT\_C\_GAP}$   
 Then FID value selected  
 Otherwise MS value

With **CST\_C\_GAP** and **PCENT\_C\_GAP** =  
**Validation parameters**  
 optimized for each  
 VOC

Twice as many results  
 Need to simplify data reprocessing

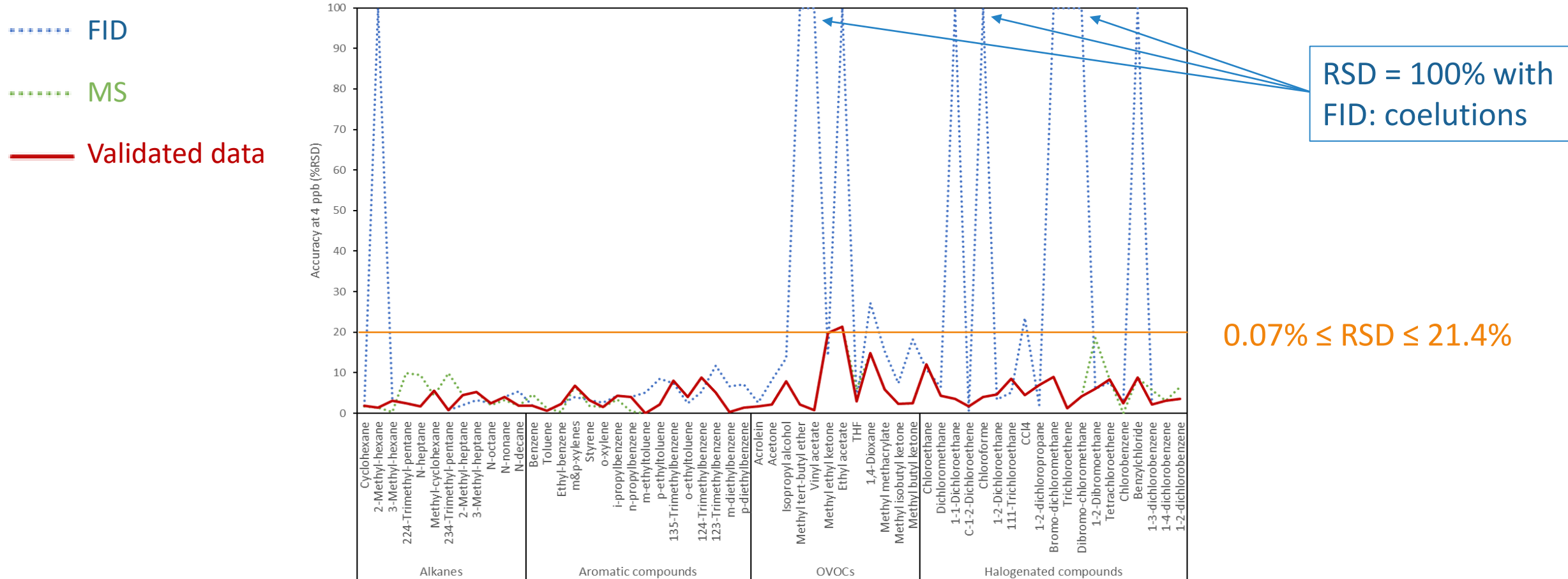
Validation parameter	FID	FID
CST_C_GAP	0.5 ppb	0.01 ppb
PCENT_C_GAP	20 %	1 %

Coelution / bad response

	FID	MS
+	Good reliability (Stable, linear, sensitive)	Sensitive Selective Allows identification (NIST database)
-	Non selective	Time drift

# Results

## Algorithm efficiency evaluation with standard at 4 ppb







# Results

## Algorithm efficiency evaluation in field measurement chromatogram



Algorithm: If  $[FID] - [MS] < \text{CST\_C\_GAP}$   
Or  
If  $\frac{[FID] - [MS]}{[MS]} < \text{PCENT\_C\_GAP}$   
Then FID value selected  
Otherwise MS value

Automatic RP before algorithm: 49 compounds

- FID id: 29
- MS id: 43

Example of results obtained after algorithm implementation:

Compound identified	FID result (ppb)	MS result (ppb)	Valid result (ppb)	Detector selected
BENZENE	0,015	0,022	0,015	FID
1-2DICHLOROETHANE	-	0,037	0,037	MS
C-1-2-DICL-ETHENE	0,051	0,000	Unknown	Unknown
A-PINENE	0,053	0,050	0,053	FID
O-ETHYLTOLUENE	0,385	0,013	0,013	MS
CAMPHENE	-	0,018	0,018	MS

Automatic RP after algorithm: 43 compounds

- Result given with FID detection: 14 (33%)
- Result given with MS detection: 29 (67%)

→ Correction of 6 misidentifications by the algorithm

→ 2 mistakes not detected by the algorithm  
Identification of the noise

# Conclusion and perspectives

---

Performance and limitations of **on-line auto-TD-GC-FID/MS** to identify and quantify odorant VOCs in ambient air studied:

- C2C6:
  - Analysis of light Hydrocarbon, Halogenated compounds and Freons
  - Light OVOCs not detected
- C6C16:
  - Analysis of hydrocarbons, halogenated compounds and OVOCs
  - Method validated to quantify these compounds (Linear, accurate and precise)

→ System suitable to analyze odorant VOCs

Implementation of an algorithm to select the best result between FID and MS detector:

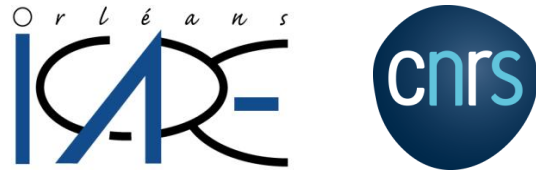
- Algorithm evaluated on standard at 4 ppb
  - Accuracy after algorithm:  $0,07\% \leq RSD \leq 21,4\%$
- Algorithm evaluated in field measurement chromatogram:
  - Efficient at 95%

Perspectives:

- Adjust the algorithm to improve efficiency
- Extend the study for more than 1 chromatogram: 1 day, 1 month or the entire measurement campaign

# Acknowledgements

---



## ICARE CNRS Orléans:

- Véronique DAELE
- Benoit GROSSELIN
- Wahid MELLOUKI
- Max McGILLEN



## Chromatotec group:

- Damien BAZIN
- Analytical team



**Thank you for your attention**



*This work was carried out as part of a thesis with a CIFRE agreement from the National Association for Technical Research (ANRT)*