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► **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-03868101v1>

Submitted on 23 Nov 2022

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

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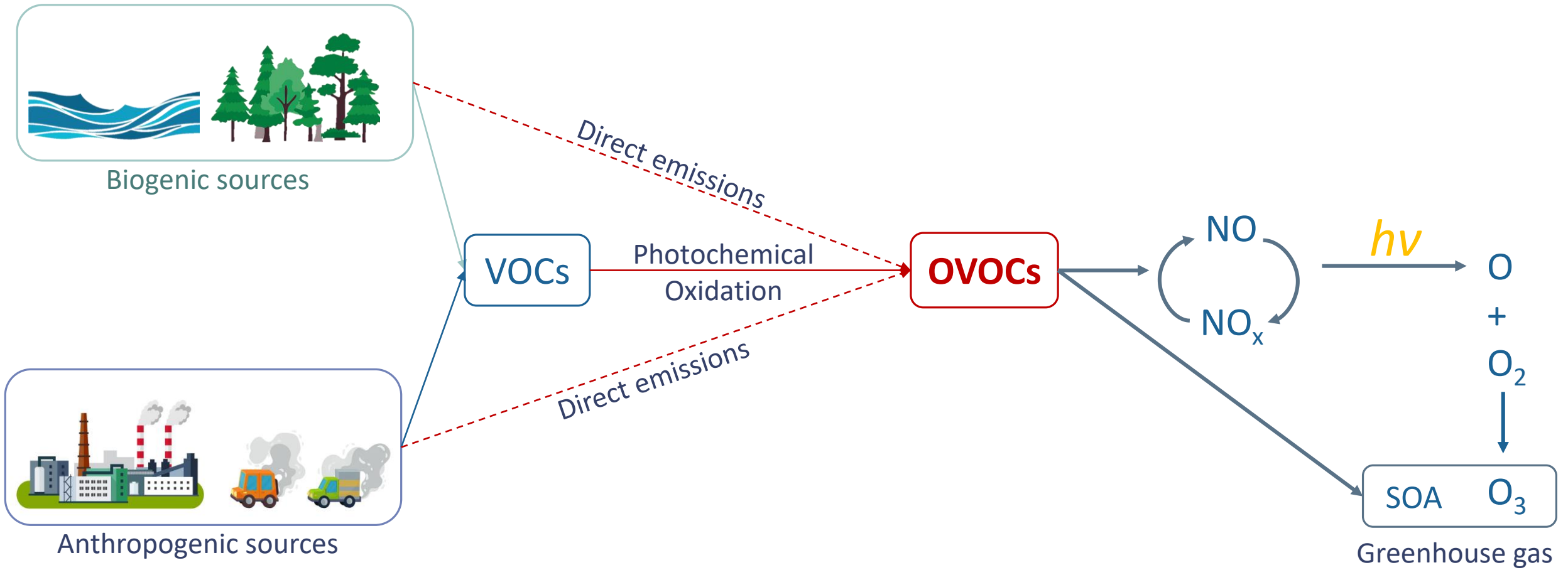
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2022/09/13

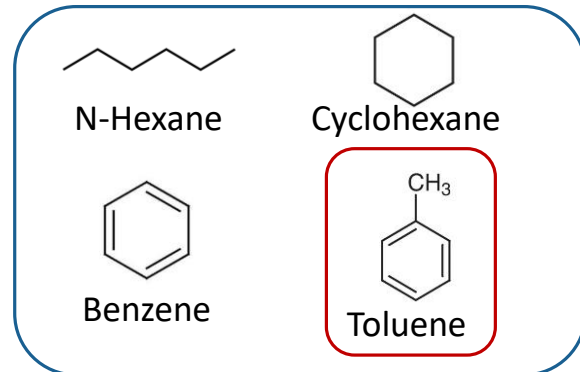


Introduction

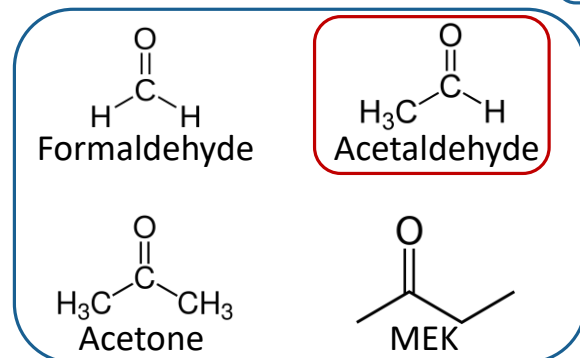


Ehsanul K., et al., **2010**, Atmospheric environment, 44, 3492 - 3502

Introduction VOCs families



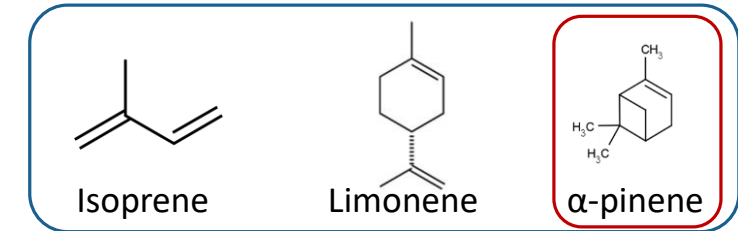
NMHCs



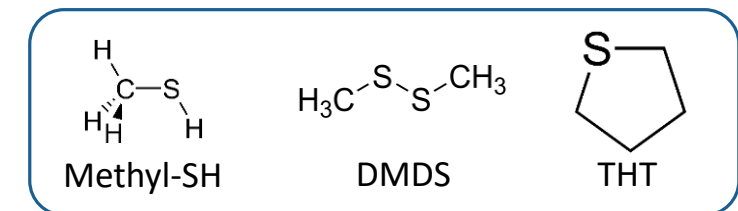
OVOCS

Some VOCs responsible of odor pollution:

- Environmental nuisances
- Unpleasantness
- Potential health risks

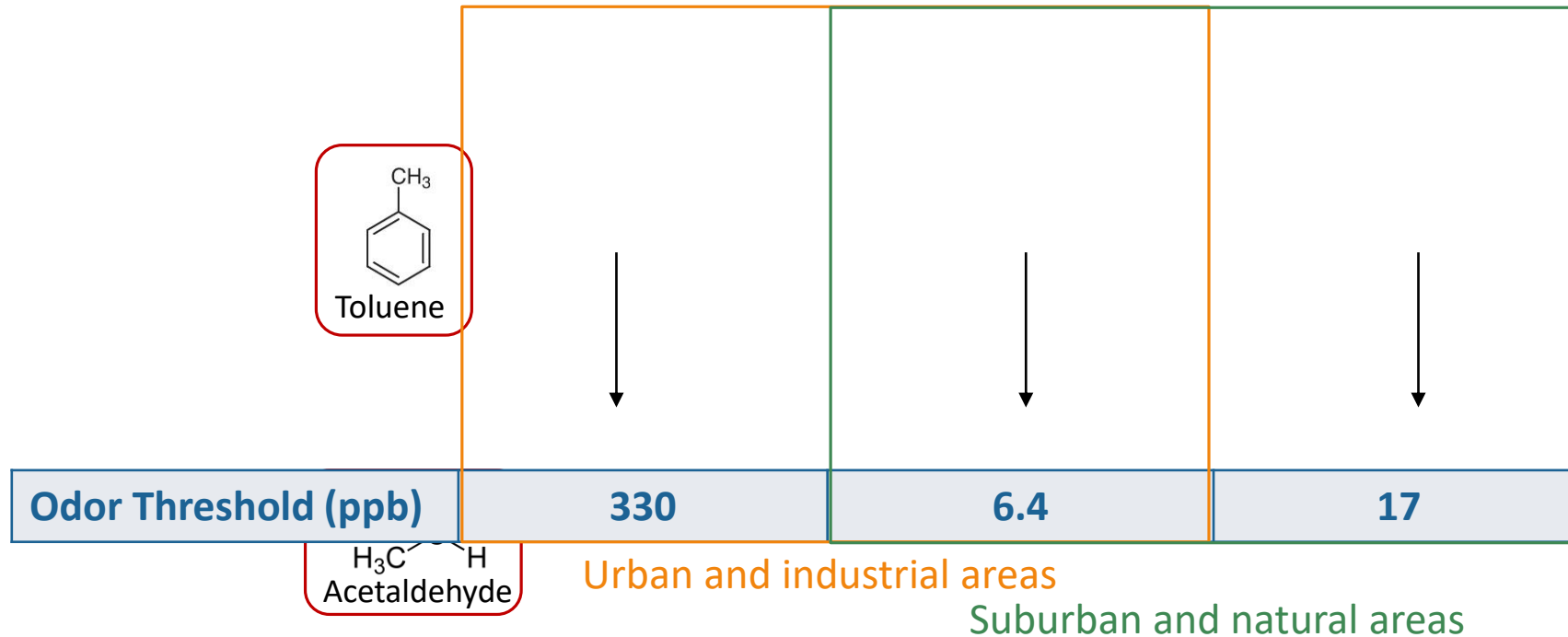


BVOCs



VSCs

Introduction VOCs families



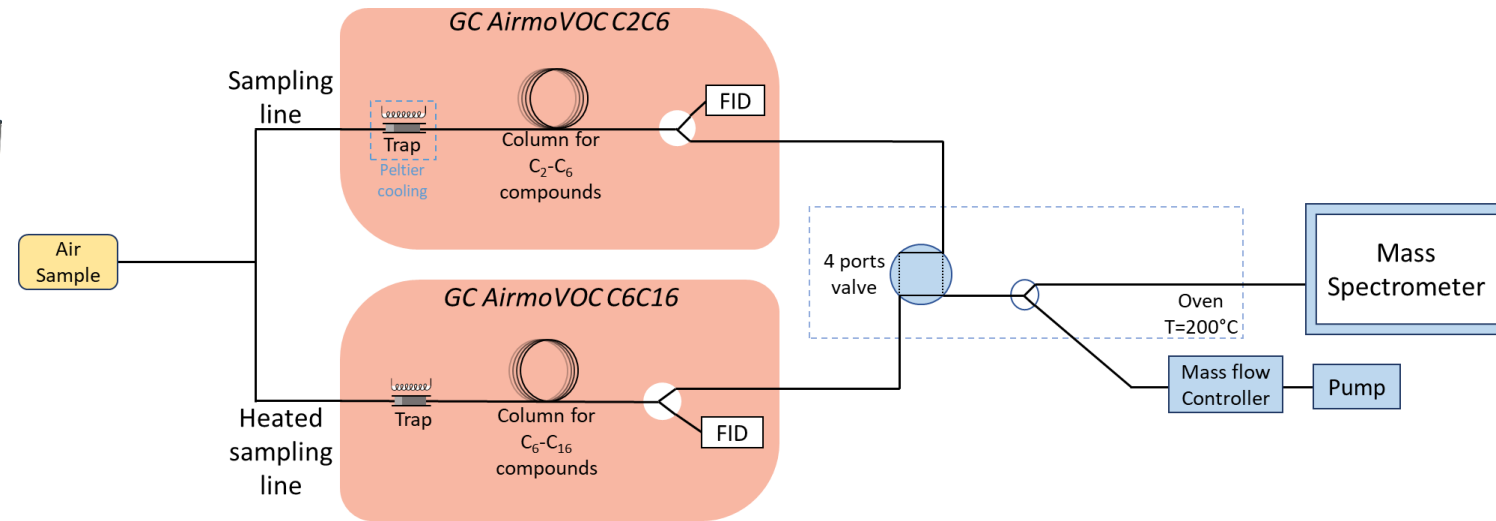
Both areas → **Objective:** Study the performance and limitations of **on-line** **auto-TD-GC-FID/MS** to identify and quantify these odorant VOCs

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

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



- System configuration:



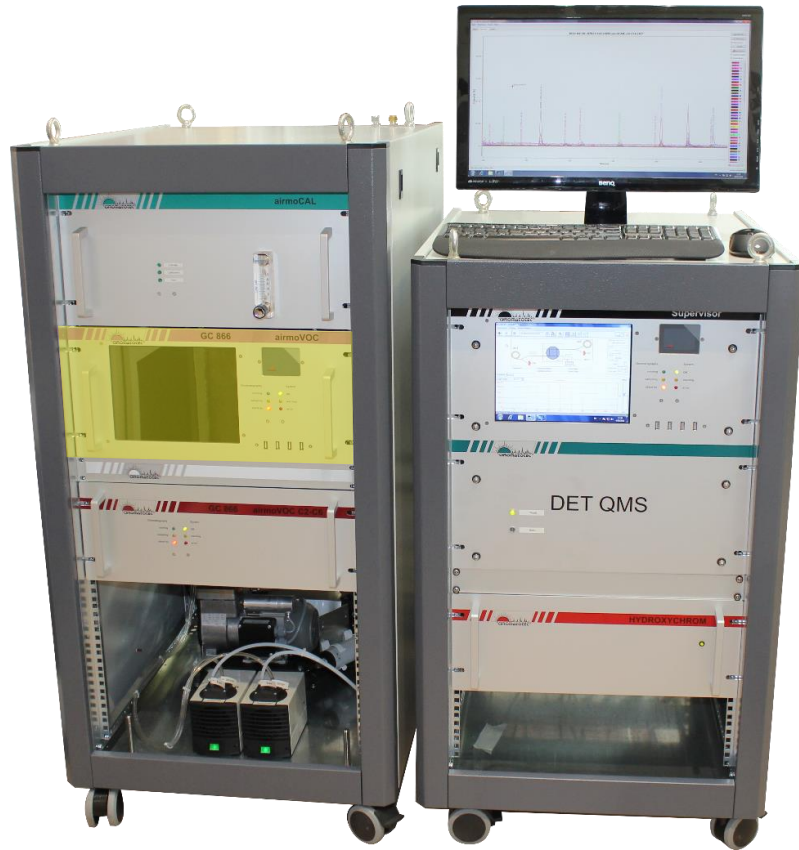
Material & Method auto-TDGC-FID/MS for C2C6 monitoring



- Carrier gas: H₂
- 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: H₂
- 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

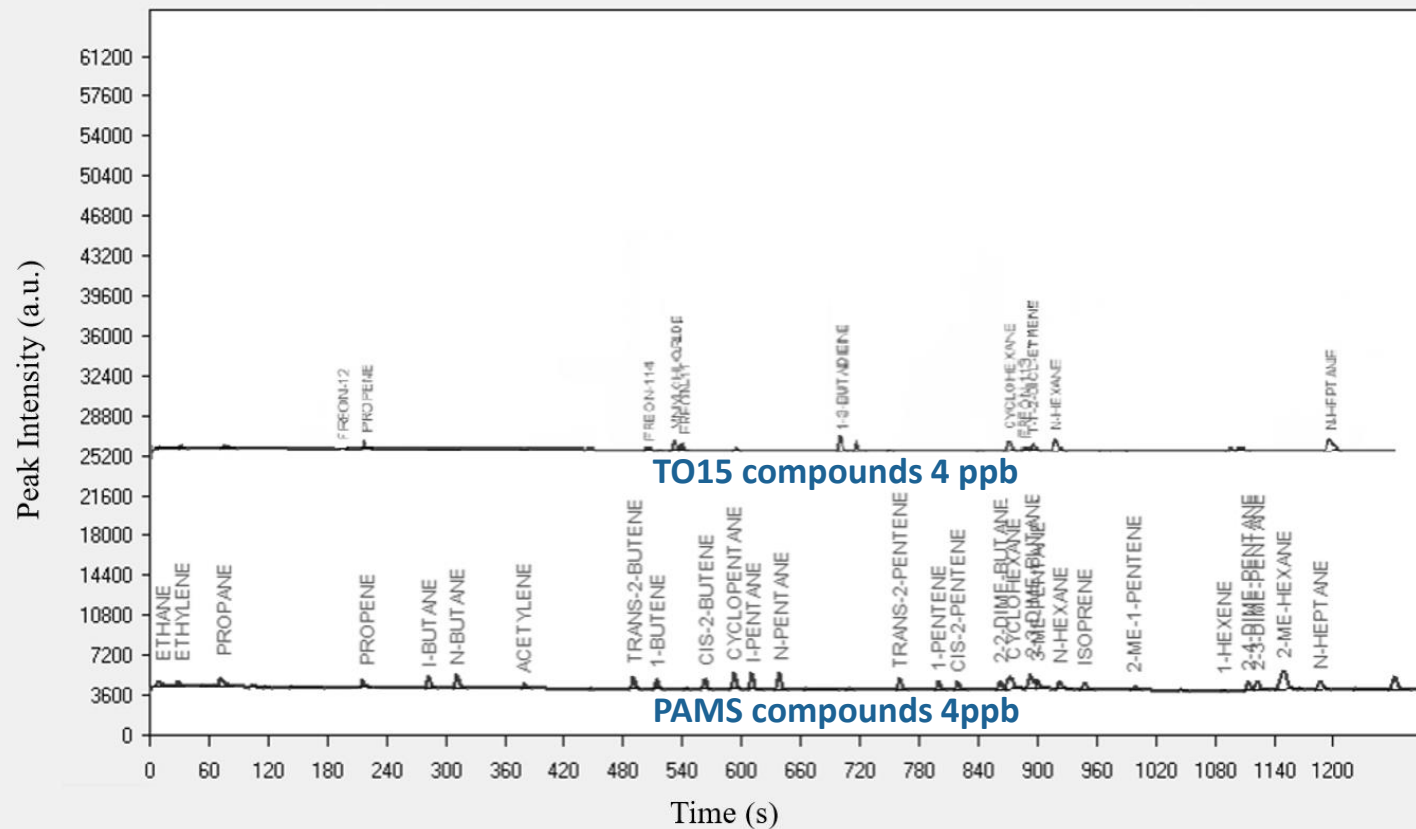


- Single Quadrupole with Electron Impact Ionization (70 eV)
- Inlet:
 - Deactivated Silica Tube ID 50 μm
 - Temperature = 170 $^{\circ}\text{C}$
- Transfer line:
 - Deactivated metallic capillary tube
 - Temperature = 200 $^{\circ}\text{C}$
- Detection: SCAN mode (0 – 300 amu)
- SEM voltage = 1200V

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:

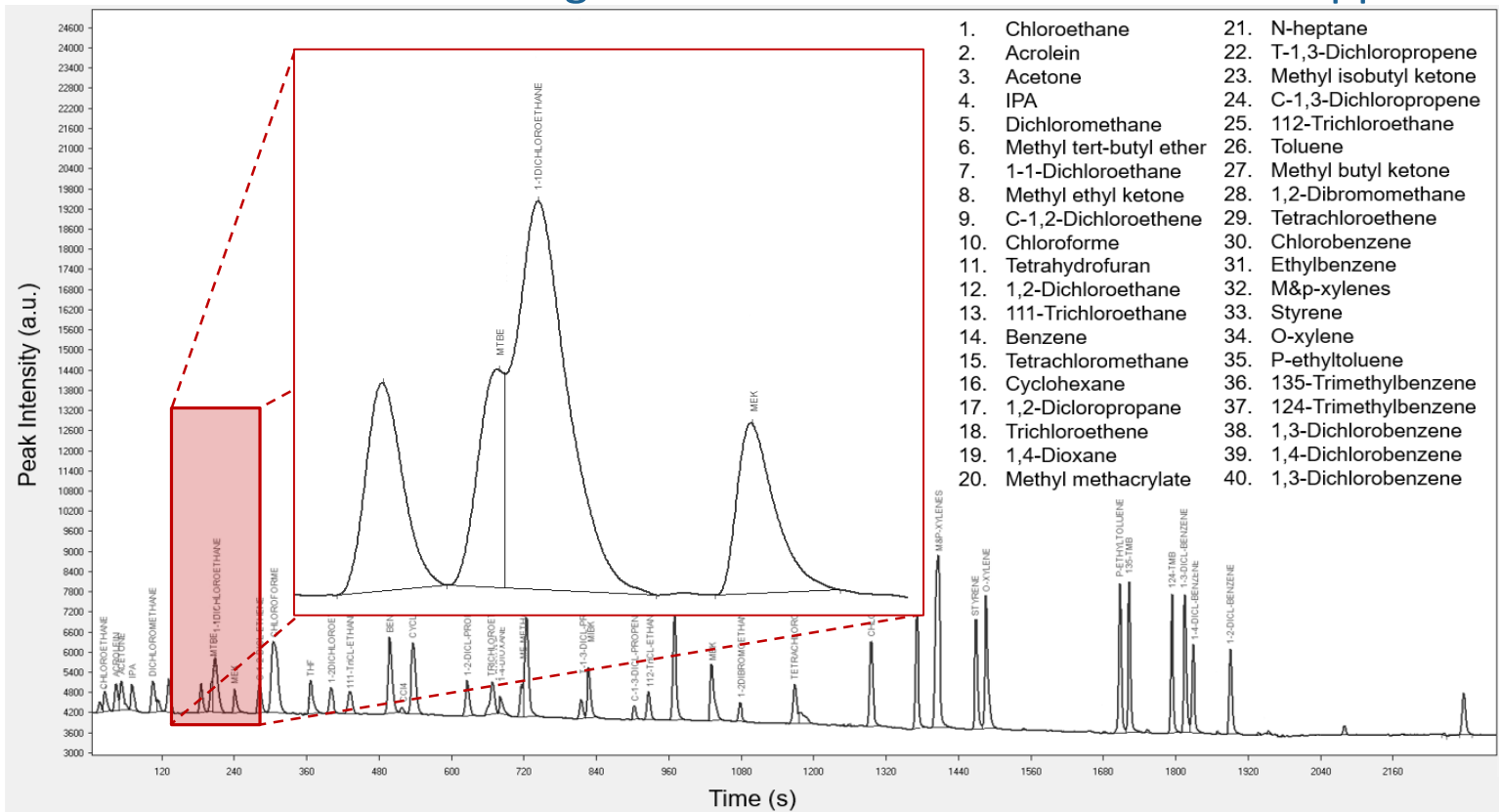
- Light OVOCs: Methanol, Ethanol, Formaldehyde and Acetaldehyde

→ Column too polar to elute these compounds

Results

C6 to C16 FID measurement

FID chromatogram of TO15 standard mixture at 4 ppb



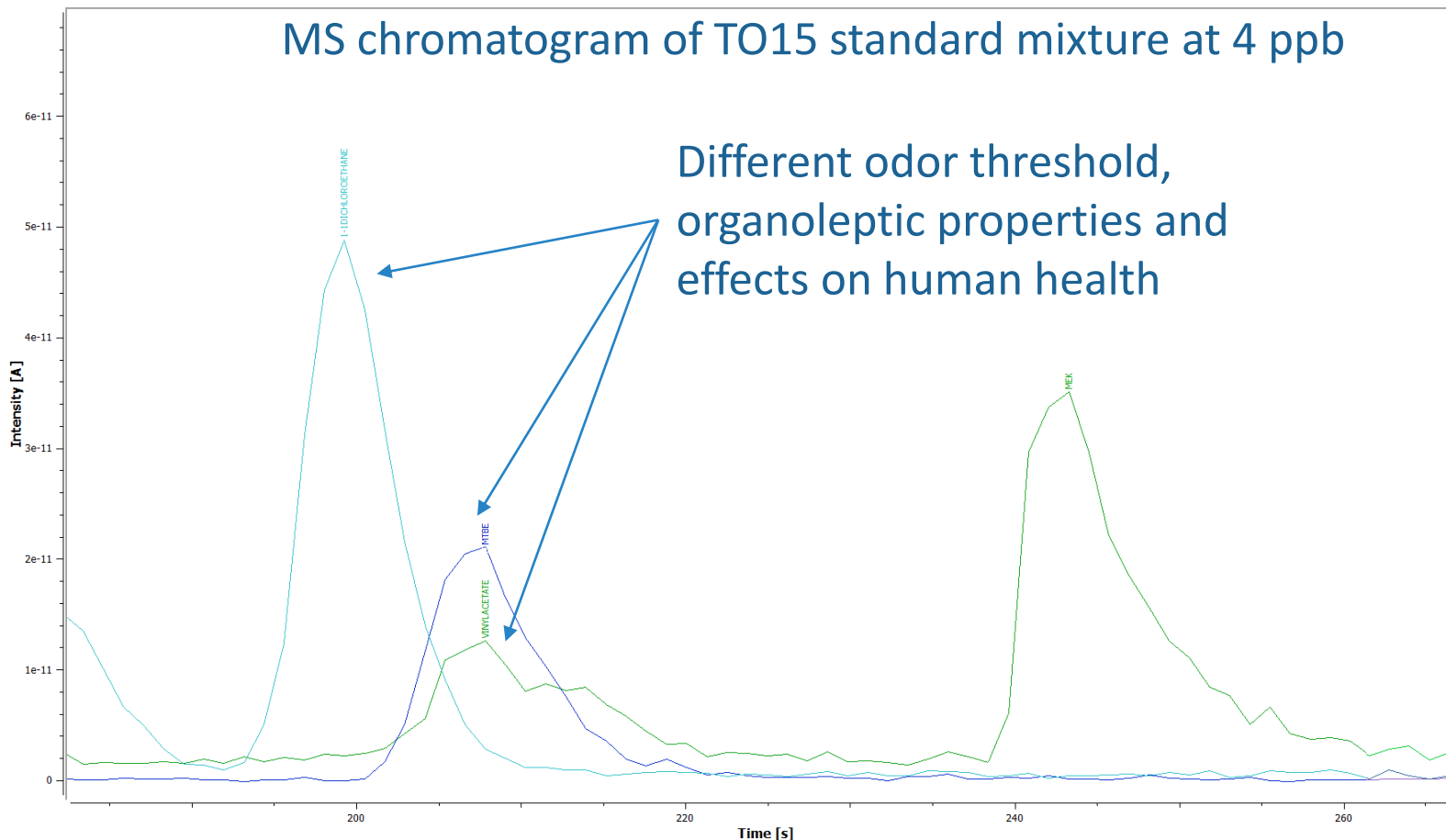
Identification performed with known retention time of the compounds

→ Coelutions occur between some VOCs

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.

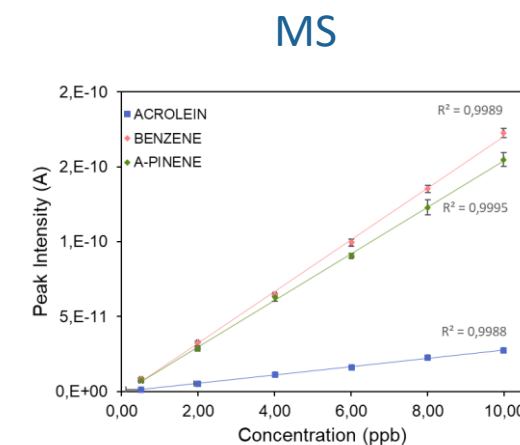
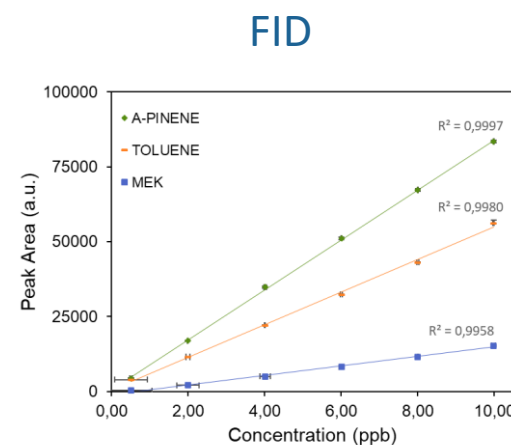
Results

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 : α -pinene



Results

Method Validation

OVOCs	FID Detection				MS Detection			
	Determination coefficient (R ²)	LOD (ppb _v)	Precision at 4 ppb _v (%RSD)	Accuracy at 4 ppb _v (%)	Determination coefficient (R ²)	LOD (ppb _v)	Precision at 4 ppb _v (%RSD)	Accuracy at 4 ppb _v (%)
Acrolein	0.9992	0.093	2.04	2.62	0.9990	0.277	10.6	1.67
Acetone	0.9960	0.065	5.79	8.27	0.9995	0.253	5.45	2.22
Isopropyl alcohol	0.9829	0.130	1.12	13.6	0.9871	0.404	7.76	7.87
Methyl <i>tert</i> -butyl ether	<i>Coeluted</i>	-	-	-	0.9995	0.216	2.78	2.09
Vinyl acetate	<i>Coeluted</i>	-	-	-	0.9992	0.431	7.49	0.73
Methyl ethyl ketone	0.9960	0.124	2.52	14.2	0.9899	0.068	4.37	19.8
Ethyl acetate	<i>Coeluted</i>	-	-	-	0.9928	2.092	6.79	19.3
1,4-Dioxane	0.9894	0.150	2.44	29.2	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	0.325	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: R² 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

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



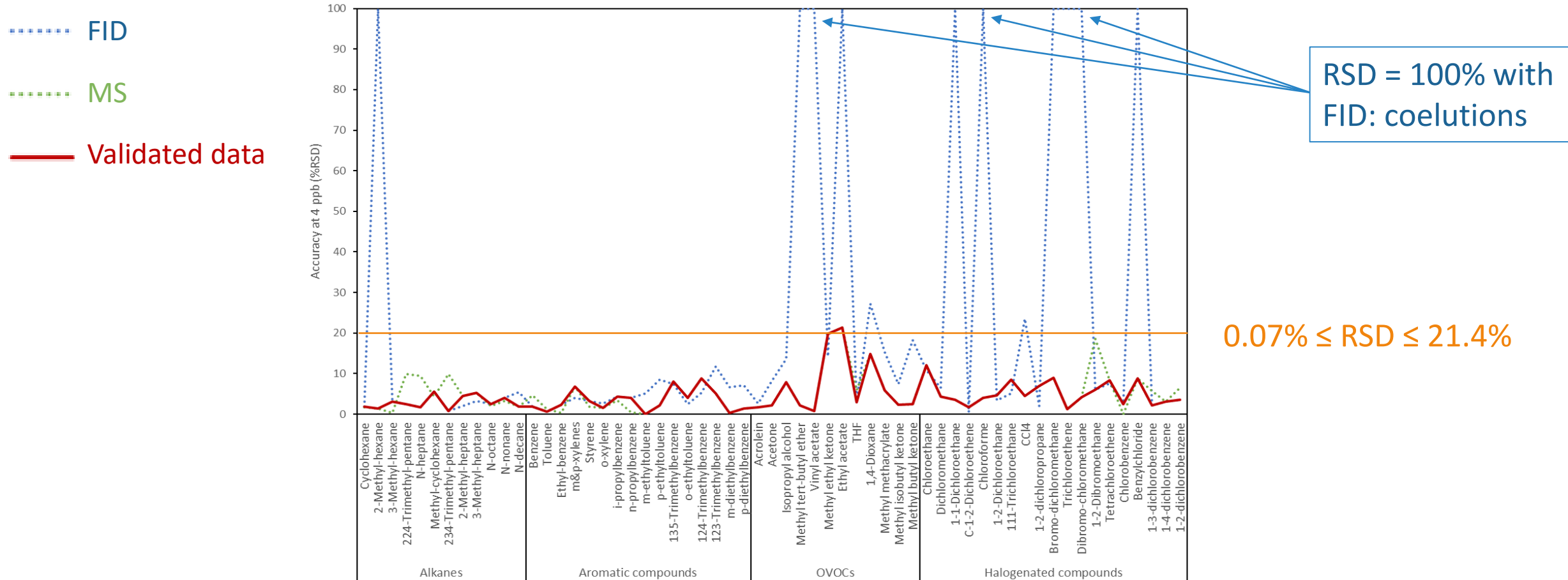
Twice as many results
 Need to simplify data reprocessing

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

Coelution / bad response

Results

Algorithm efficiency evaluation with standard at 4 ppb

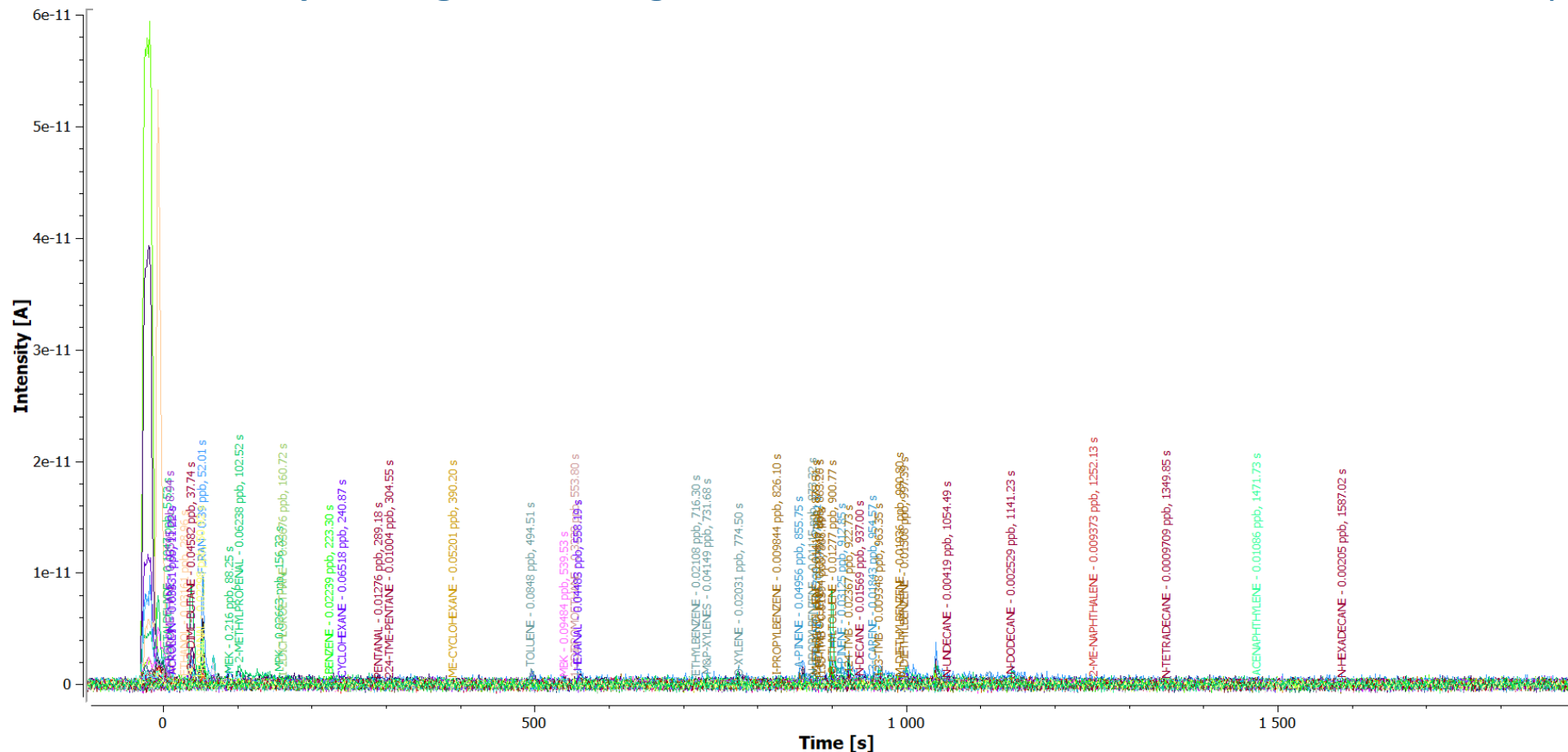


Results

Algorithm efficiency evaluation in field measurement chromatogram



MS corresponding chromatogram of ambient air in a field measurement campaign (forest)



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

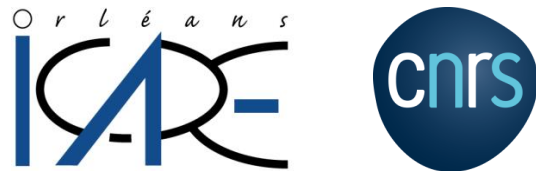
Implementation of an algorithm to select the best result between FID and MS detector:

- 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)