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Development and validation of on-line auto-GC for the analysis of trace level biogenic VOCs for a field measurement campaign

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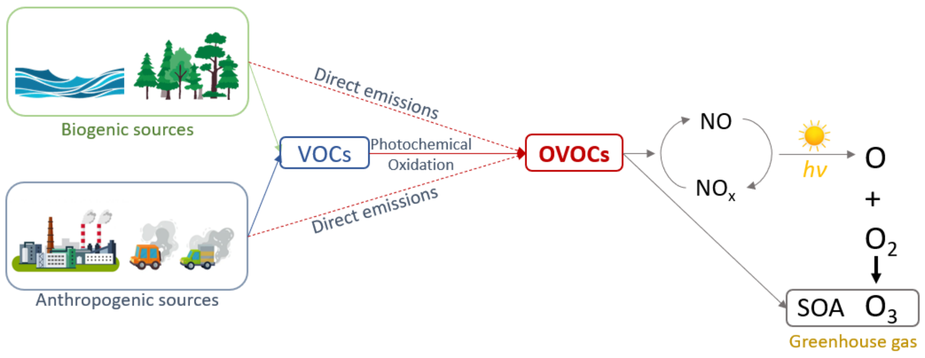
Introduction



Context:

- Volatile Organic compounds (VOCs) play a major role on atmospheric pollution
- VOCs emitted in the atmosphere from natural or anthropological sources(1)
- Biogenic VOCs (BVOCs) = hydrocarbons, isoprene, terpenes & oxygenated compounds (OVOCs)(2)
- These molecules are found in ambient air from ppt to ppb levels that require sensitive analytical systems

Problem:

- Usually laboratory instruments involving one off-sampling and analysis
- Need for continuous on-site monitoring systems and allowing automatic data reprocessing

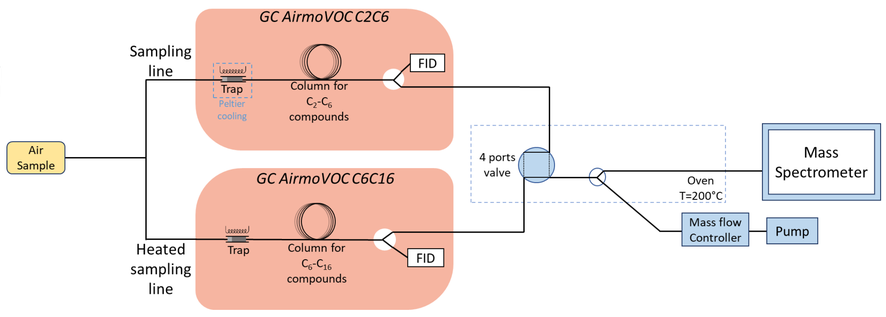
Goal:

- Evaluate suitability of continuous and automatic thermodesorption Gas chromatograph with Flame ionization Detector (FID) and Mass Spectrometer (MS) in parallel for BVOCs measurement in ambient air

Material & Method

TD-GC-FID/MS

AirmoScan C2C16 Chromatotec®



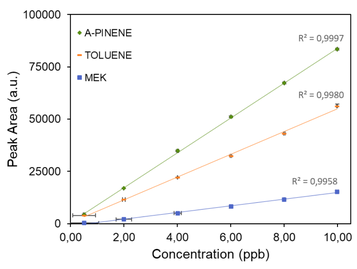
GC AirmoVOC C2C6	GC AirmoVOC C6C16	Mass spectrometer
Carrier gas: H_2 **Flow rate:** 3 mL/min **Sampling flow:** 12 mL/min **Column:** Capillary PLOT column (25m x 0,53mm x 10µm) **Trap:** Carboxen & Carbopack mixture (-10°C) **Thermodesorption:** 220°C **Oven:** 36 – 202°C **Detector:** FID at 170°C	**Carrier gas:** H_2 **Flow rate:** 3 mL/min **Sampling flow:** 20 mL/min **Column:** Capillary MXT30CE column (30m x 0,28mm x 1µm) **Trap:** Carbopack mixture **Thermodesorption:** 380°C **Oven:** 36 – 202°C **Detector:** FID at 190°C	**Single Quadrupole** **EI:** 70eV **Transfer line:** 200°C **Inlet:** 250°C **Detection:** SCAN mode (0 – 300 amu) **SEM voltage** = 1200V
Sampling time: 30 min – Cycle time: 45 min		

Results

Method validation

- To validate the system, certified gas mixtures PAMS 58 and TO15 (Takachiho, Japan) at 100 ppb(V) were used
- Linearity, limit of detection, precision and accuracy calculated according to the Chinese Norm for ambient air measurements(3) for **4 aromatic hydrocarbons**, **11OVOCs** and **1 terpene**
- 4 OVOCs not quantified by FID → coelutions

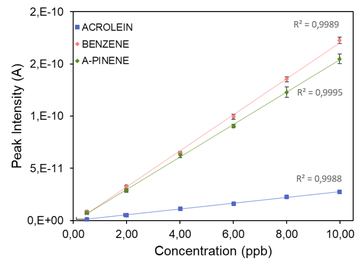
FID detector



Calibration curves of Methyl Ethyl Ketone (MEK), Toluene and α-pinene

- **R^2:** 0,9829 – 0,9992
- **Limits of detection:** 0,035 – 0,325 ppb
- **Precisions at 4 ppb (RSD%):** 0,65% - 5,79%
- **Accuracies at 4 ppb (RSD%):** 0,62% - 18,2%

MS detector



Calibration curves of Methyl Ethyl Ketone (MEK), Toluene and α-pinene

- **R^2:** 0,9871 – 0,9995
- **Limits of detection:** 0,048 – 2,110 ppb
- **Precisions at 4 ppb (RSD%):** 0,66% - 10,6%
- **Accuracies at 4 ppb (RSD%):** 0,33% - 21,4%

Development of automatic reprocessing

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

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

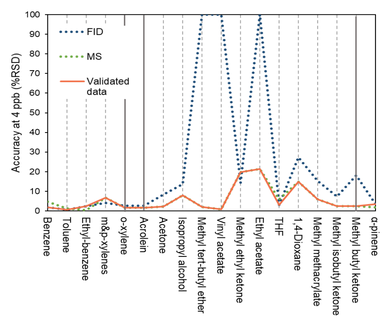
→ Twice as many results
Need to simplify data reprocessing

Algorithm and validation parameters implemented in data reprocessing software :

If [FID] – [MS] < CST_C_GAP
Or
If $\frac{[FID]-[MS]}{[MS]}$ < PCENT_C_GAP
Then FID value selected
Otherwise MS value

With CST_GAP and PCENT_C_GAP = **Validation parameters** optimized for each VOC

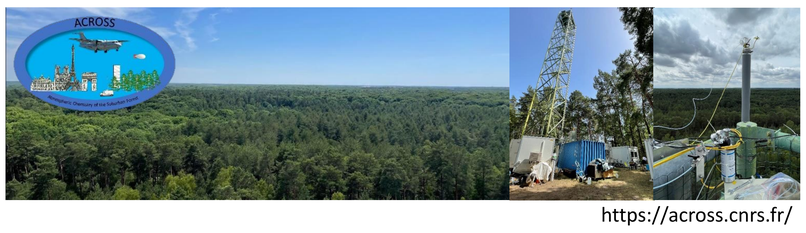
Algorithm efficiency evaluation



FID, MS and validated data accuracies at 4 ppb of aromatic hydrocarbons, OVOCs and terpene

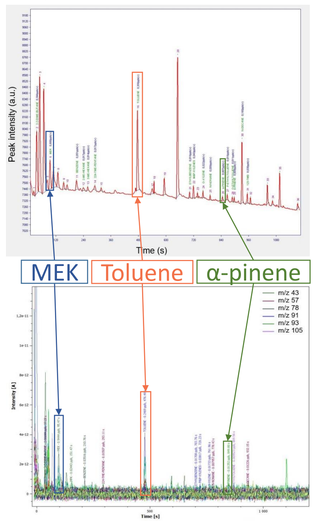
- RSD% of validated data ranged from 0,07% to 21.4%
- Implementation of validation parameters leads to very good overall accuracies

In field measurement campaign



https://across.cnrs.fr/

- **ACROSS campaign:** Atmospheric ChemistRy Of the Suburban ForeSt (15 June – 25 July)
- **Location:** 3 sites in Paris including Rambouillet Forest (80 km from Paris)
- **Aim:** Understand physico-chemical interactions of urban and biogenically air masses
- **TD-GC-FID/MS objective:** Measurement of Biogenic compounds above the trees



FID and MS chromatograms of 3 potential BVOCS identified and quantified in Rambouillet field

VOC	[Validated data] (ppb)
MEK	0,944
Toluene	0,357
A-pinene	0,007

Conclusion

- Performance studies of TD-GC-FID/MS were evaluated to quantify 16 VOCs: 4 aromatic hydrocarbons, 11 OVOCs and 1 terpene in ambient air
- Algorithm optimized to simplify data reprocessing and select accurate result between FID and MS
- 3 potential BVOCs identified and quantified with the system during the ACROSS campaign in Rambouillet site

Perspectives:

- Performance studies with an internal standard
- Data analysis and comparison with other instruments deployed during the Rambouillet campaign

Acknowledgements

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References

(1): Gu et al., (2019) China, Ecotoxicology and Environmental Safety 169, 797 – 806

(2): Dörter et al., (2020), Science of the total Environment 731, 139 – 201

(3): HJ 1010-2018 (2019), Specifications and Test procedures for Ambient Air Quality Continuous Monitoring System with Gas Chromatography for Volatile Organic Compounds