Development and implementation of a portable in-field GC system for plant pests detection

M. Mascles[1*], F. Bachelier[1,2], J.P. Amiet[1], V. Daële[2], D. Bazin[1]

[1]Chromatotec, 15 Rue d'Artiguelongue, 33240 Val-de-Virvée, France

[2] ICARE – UPR 3021 – CNRS INSIS – 1C, av. de la Recherche Scientifique CS 50060 – 45071 Orléans cedex 2

*Corresponding author email address: mathilde.mascles@chromatotec.com

INTRODUCTION

The increasing need for food production coupled with climate change are expected to lead to an increase in the development of plant pests in agricultural and forest plants or plant products. This would greatly enhance the risks of pest-infected plants importation. In this context, the **European PurPest project** aims to develop and implement a brand new and **non-invasive method for field-pest detection**. In-field detection would drastically **decrease the use of pesticides** by only targeting the contaminated area and would reduce the risk of new (or already existing) pest development or importation. The PurPest project aims to identify and quantify **specific Volatile Organic Compounds (VOCs) emitted by plants under stress** induced by various plant pests. Among these VOCs, **terpenes** will most certainly be present and their detection and quantification remain a challenge due to their **low vapor pressure**. This ambitious project requires preliminary work on VOC metrology and more particularly on terpenes monitoring. In this work, a gas chromatograph coupled to a flame ionization detector and a mass spectrometer (**GC/FID-MS**) was used to analyze ambient air and **biogenic volatile organic compounds** (BVOCs) in a field campaign. Some linearity results with a standard cylinder have also been obtained. Preliminary work was also done on the **micro-GC developed for in-field measurements** to compare the analytical performances in outdoor conditions.

BVOCs as biomarkers for pest attacks

It is a well-known fact that plants and pests **communicate their physico-chemical** status to their surroundings by emitting VOCs. These emissions change with **abiotic stresses** (temperature, solar radiation) and/**or with pests attacks**[1]. Biogevic VOCs refer to these hydrocarbons emitted by vegetation.

Most commonly BVOCs emitted by vegetation are **isoprene, terpenes and oxygenated VOCs**. The first two categories account for approximatively 65% of the emissions[2]. The first challenge of the PurPest project is to select **specific BVOCs emitted by plants under stress**. How can a BVOC be specific ?

- The molecule is only emitted by an infected plant
- The molecule is emitted by the healthy plant but not the infected one
- There is a change in the ratio between the healthy plant and the infected one

An analytical method will then be developed for the **specific analysis of these biomarkers**. This can be a challenge as BVOCs can **have limited atmospheric life-times** (**Table 1**). The analytical method must in the end be **implemented on a portable analyzer**. **Figure 1** sums up the goals and strategy of the PurPest project.

Preliminary work on the analysis of BVOCs was done on an **auto-TD-GC/FID-MS.** This was used to monitor VOCs (including some BVOCs) in ambient air. This will be the reference method that will set **the analytical goals for a portable device**. In parallel, a **micro-GC** was used to qualitatively analyze BVOCs emitted by a pine tree in closed space.

Table 1: Atmospheric life-times of some well-known BVOCs

BVOC	Lifetime with OH reaction
α-pinene	2.6h
β-pinene	1.8h
Limonene	49min

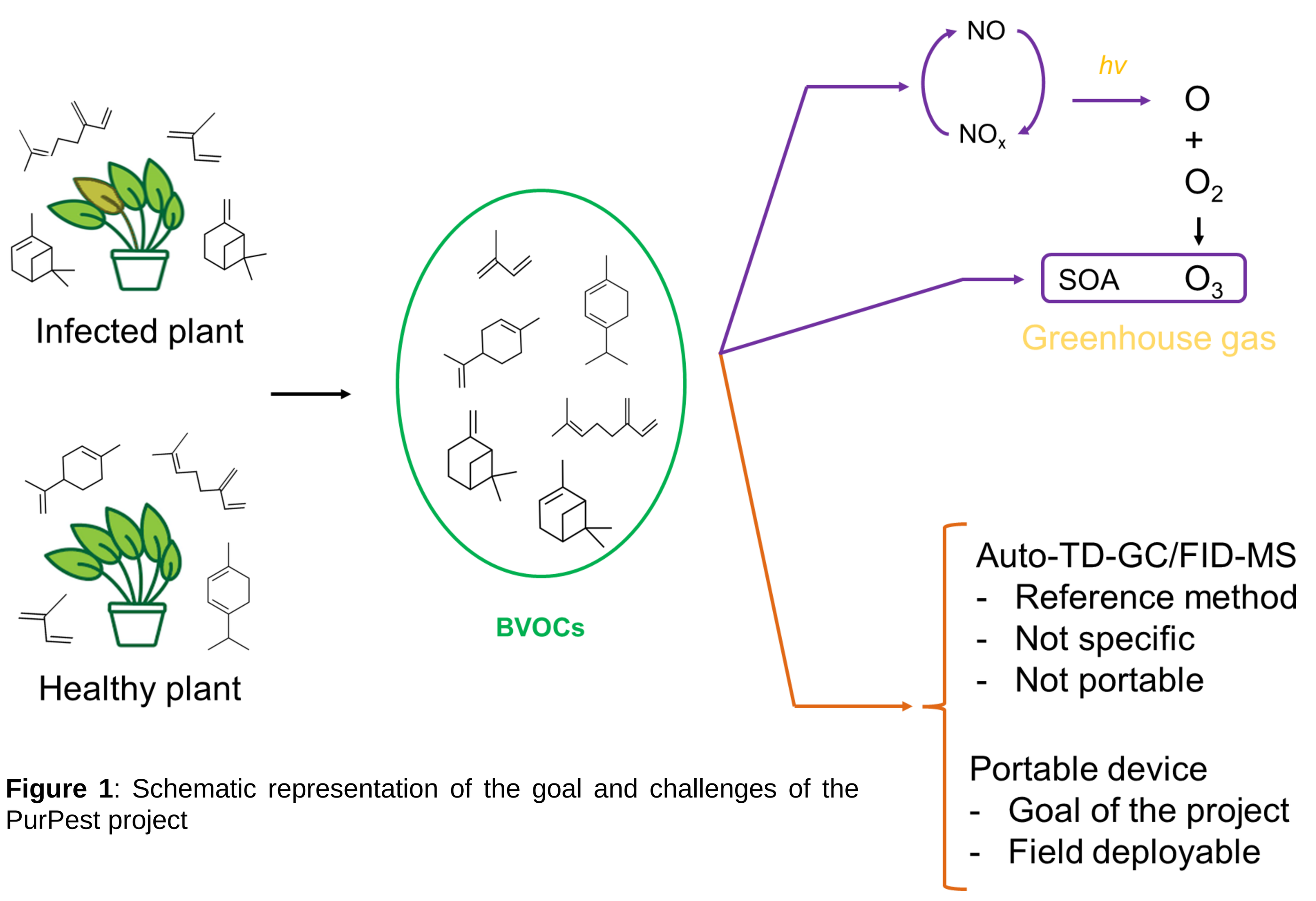

Figure 1: Schematic representation of the goal and challenges of the PurPest project

BVOCs analysis on an auto-TD-GC/FID-MS

Continuous analysis of VOCs in ambient air has been done on **an auto-TD-GC/FID-MS**. This system was specifically designed for the analysis of VOCs containing from 2 to 16 carbon atoms. **Figure 2** represents a schematic view of the system and **Figure 3** is a picture of the system:

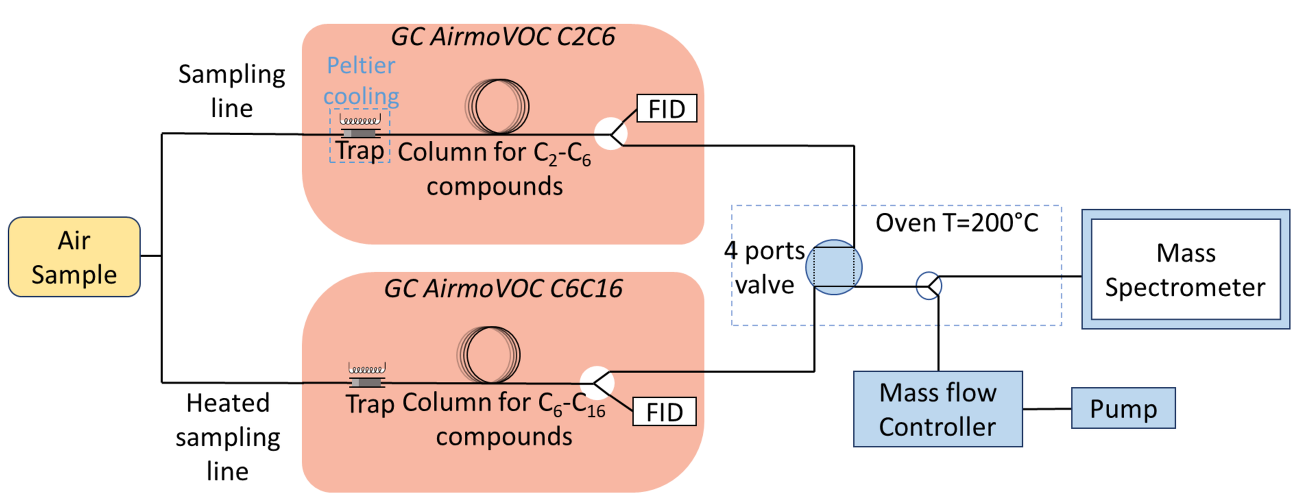

Figure 2: Schematic representation of the auto-TD-GC/FID-MS

Figure 3: Picture of the auto-TD-GC/FID-MS

Air sample is sent on two GC systems. The **airmoVOC C2C6** is designed for the analysis of light, non polar compounds. Analytes are pre-concentrated at low temperature. The **airmoVOC C6C16** is designed for the analysis of semi polar and non polar compounds. They are transferred in a heated sampling line and pre-concentrated at room temperature. Both GC systems use a flame ionization detector. **The MS detector** can be coupled either to the AirmoVOC C2C6 or to the AirmoVOC C6C16.

This system has been used for ambient air monitoring in a **field measurement campaign** in the Rambouillet forest. Several BVOCs have been observed and monitored over time. **Figure 4** represents the evolution of terpenes during the day.

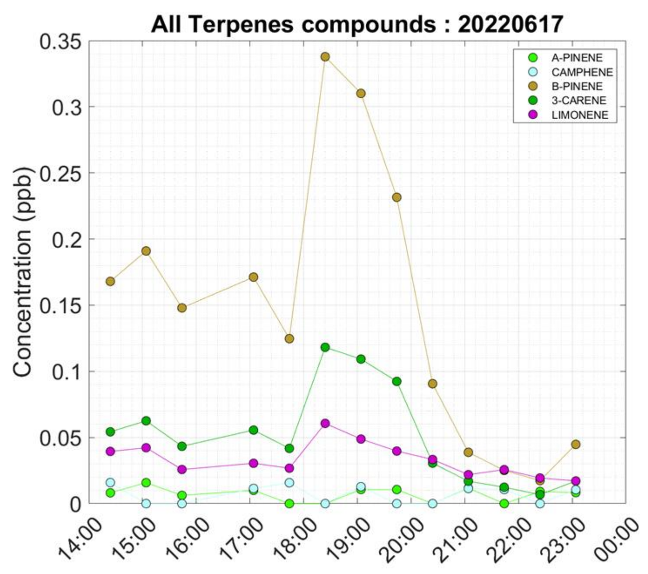

Figure 4: Terpene monitoring during a field campaign in the Rambouillet forest

This clearly shows **the feasibility of terpenes analysis** on this system. To go further, some **linearity tests** have been done on a PAMS and TO15 cylinders containing (among other compounds) acetone, alpha-pinene and isoprene. **Figures 5 and 6** represent the linearity curves obtained for these three compounds on FID and MS detectors with concentrations ranging from **0,5 – 10 ppb**:

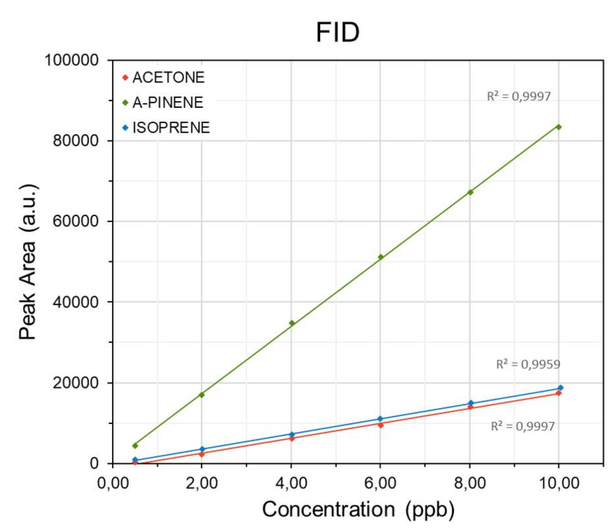

Figure 5: Linearity curves obtained on FID for acetone, alpha-pinene and isoprene

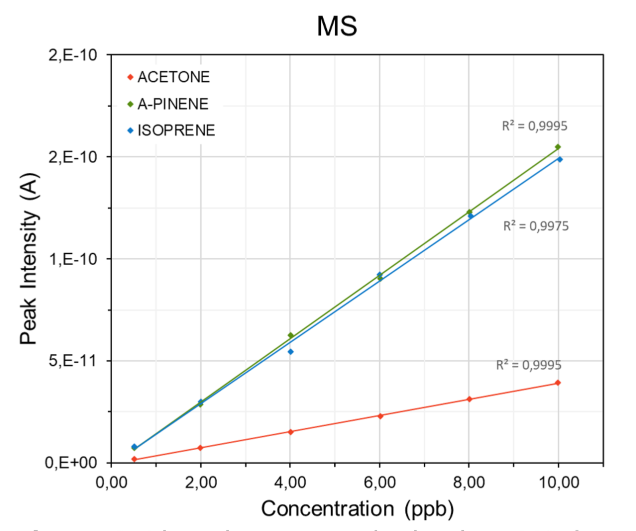

Figure 6: Linearity curves obtained on MS for acetone, alpha-pinene and isoprene

BVOCs analysis on an micro-GC

A portable GC/PID system was used to analyze terpene compounds. The goal of this study was a proof of concept of the **feasibility of analysis of BVOCs emitted by plants** on this portable analyzer.

Some **pine tree** was put in a **closed space** with 60 ml/min of air continuously flowing through it. 18 ml/min of that sample is used to fill up the 200 µL sampling loop of the GC/PID. Then, the analytes are separated on the analytical column heated at 77 °C. The analytes are detected by a **photo-ionization detector**. The cycle time of this experiment was **15 minutes**. **Figure 7** shows a picture of the experiment.

Figure 7: Analysis of pine tree with the micro-GC

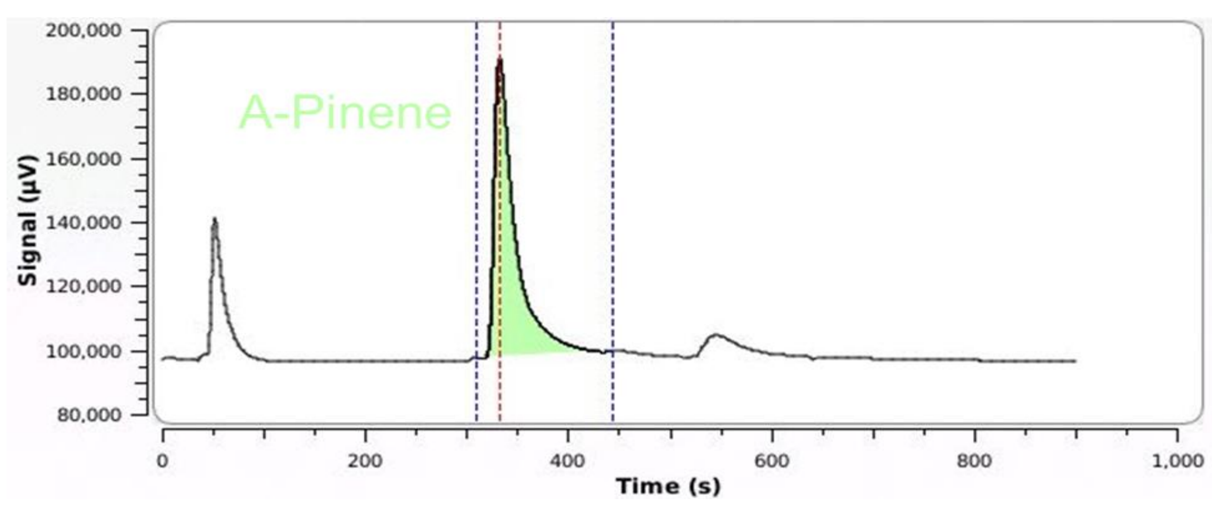

Figure 8: Chromatogram obtained for the analysis of pine tree on the portable analyzer

Figure 8 shows the chromatogram obtained for the analysis of **pine tree in a closed space**. Only **alpha-pinene** was successfully identified as it was verified with a pure standard (**Figure 9**).

As for the other two peaks, the first one probably is **isoprene** because it elutes very early (RT = 60s). The last peak could be **beta-pinene or limonene**. An injection of pure standard would be necessary to confirm the identification.

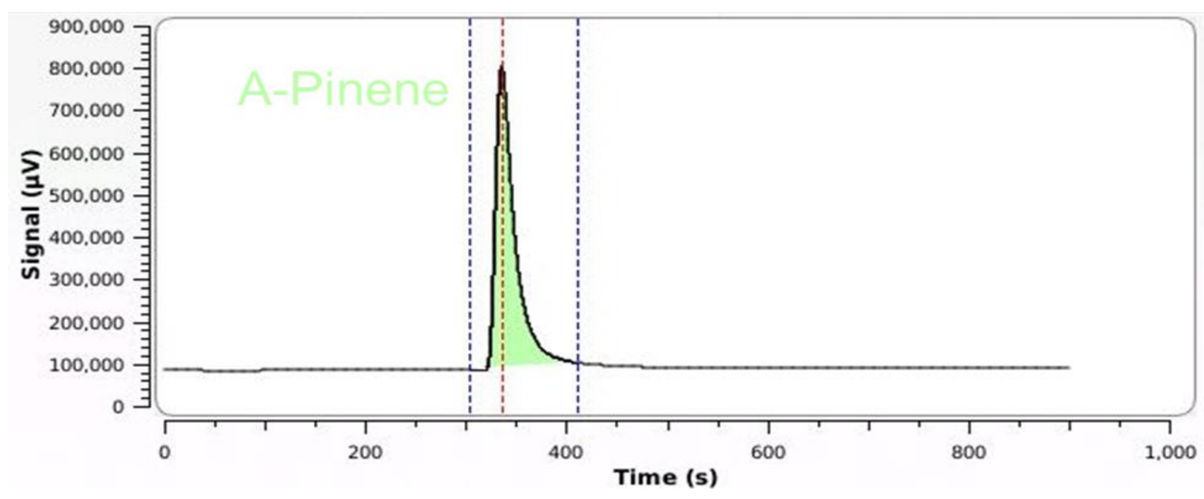

Figure 9: Chromatogram obtained for the analysis of pure alpha pinene

These first **qualitative results** are very promising. The **micro-GC is capable of analyzing BVOCs** in an enclosed space. This analyzer could be useful for analyzing and monitoring BVOCs emitted by plants in an enclosed area. In the scope of the PurPest project, it could be used to control **plants that have traveled in trucks** (enclosed space) to check for pest attacks.

Indeed, this analyzer is easily transportable and portable and only needs small cylinder of N_2 as carrier gas and has an autonomy of at least 4 hours. The **cycle time can be very short** which is ideal given the very short life time of a lot of BVOCs.

CONCLUSION AND PERSPECTIVES

Several BVOCs were monitored and analyzed on two kinds of systems: an **auto-TD-GC/FID-MS** designed for ambient air analysis and **a portable micro-GC** designed for VOCs analysis. The auto-TD-GC/FID-MS showed its capacity to **monitor terpene compounds during a field campaign**. Very good linearity results were obtained on alpha-pinene and isoprene with **R^2 > 0,995 both on FID and MS detectors**. Satisfying preliminary results were obtained on the micro-GC analyzer (GC/PID) with **the analysis of pine tree in a closed space**. Three BVOCs (including alpha-pinene) were observed in less than 10 minutes. The first part of the PurPest project is the identification **of specific BVOCs** emitted by plants under pest attacks. When these BVOCs will be identified, the **auto-TD-GC/FID-MS and the micro-GC will be adapted to see specifically** these molecules. The micro-GC analyzer could be a very **convenient and robust tool** to check plants for pest attacks **directly on the field**.

REFERENCES: [1]Ghimire R. et al., *Effect of bark beetle* (Ips typographus *L.) attack on bark VOC emissions of Norway spruce (*Picea abies Kars.*) trees*, Atmospheric Environment, Vol. 126, 145-152, 2016;

[2] Gomez M. C. et al., *Long-term measurement of biogenic volatile organic compounds in a rural background area: Contribution to ozone formation*, Atmospheric Environment, Vol. 224, 2020.