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D 3.1
First Sensor System Prototype

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Abstract

This document briefly introduces deliverable D3.1, the portable first sensor system prototype which consists of a compact gas chromatograph and a VOC detector with a preconcentration unit for the efficient collection and detection of target VOCs (biomarkers). This instrument was adapted from a previous version of an AIRMO portable µ-GC and modified to suit the PurPest project's goals.

Public introduction[1]

The current inspection of plants at import sites process faces several challenges, such as the time-consuming nature of visually screening imported plants, the requirement for expert knowledge, low detection accuracy, and the high cost of molecular-based detection kits. Plants emit signaling volatile organic compounds (VOCs) when attacked by pests, and pests themselves release distinctive VOCs. In the scope of the PurPest project, we expect to develop a device to address these challenges by providing a more streamlined and efficient inspection process, capable of detecting pest-infected plants through the analysis of their airborne VOC emissions, resulting in highly reliable outcomes.

[1] According to Deliverables list in Annex I, all restricted (RE) deliverables will contain an introduction that will be made public through the project WEBSITE

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1 INTRODUCTION

Plant inspection requires a compact, self-contained, low-energy, real-time instruments capable of measuring emitted volatile organic compounds (VOCs) that indicate presence of invasive pests.

As gas chromatography is the traditional analytical procedure for VOC detection, there is a strong need to develop miniaturized systems with short sampling times and correct identification of target compounds. Those targeted VOCs constitute the biomarkers needed for detecting and identifying plant pests. The challenge comes to play when sub-ppb (parts per billion) or ppt (parts per trillion) levels are the targeted concentrations. A first sensor system prototype (SSP) containing a sampling, separation and detection constituents in one compact gas chromatograph has been developed for potential detection of these biomarkers.

1.1 Purpose of Developing the Sensor System

The purpose of the development of the SSP is to detect the biomarkers for the targeted pests in the PurPest project. The present deliverable reports the development of a first prototype for a real-time sensor system capable of sub-ppb level detection of the biomarkers. AIRMO, being a partner in the PurPest project, developed along with the efforts of the collaborating partners, SINTEF, Volatile AI, Saftra Photonics and UWAR, the first SSP and was in charge of the deliverable D3.1.

According to the European PurPest Project Grant Agreement, an innovative policy is being followed to go beyond start-of-the-art (SotA) by implementing certain practices for the improvement of the sensors performance for plant pest detection. The portability assessment of the first sensor system prototype, for example, by comparison of current practices versus what is being implemented to attain an improved gas chromatograph performance as a sensor is shown in **Table 1-1**.

Table 1-1: Portability of the first sensor system prototype assessment for the PurPest project[a]

	Parameter	SotA[b] current practice	Implementation	Implemented
Portability of the First ensor System Prototype	Weight	22 kg	5 kg	Yes
	Dimensions (mm) (HxWxD):	222 x 482 x 600	320 x 280 x 150	Yes
	Limit of detection (benzene):	0.01 ppb	0.01 ppb	Yes
	Measurement time:	15 min	10 min	In progress
	Backflush for fast cleaning for short analysis	N.A.	Yes	Yes
	Sample Introduction	Thermodesorption	Thermodesorption	Yes
	N_2 gas consumption	3 mL/min	1.5 mL/min	In progress
	Column Oven	Gradient	Isothermal	Yes
	Detector	PID	PID	Yes
	Second Detector	N.A.	PurPest Developed Sensor	In progress
	Power Source	N.A.	Battery (4 h)	In progress

a: adapted from the European PurPest Project – Grant Agreement 101060634 – PURPEST; b: state-of-the-art.

2 FIRST PROTOTYPE OF THE SENSOR SYSTEM

The first SSP to be used in the field for sensing the biomarkers is shown in **Figure 2-1**. This prototype is adapted from a product of AIRMO's online gas chromatographs (microVOC, Chromatotec, France) for monitoring air quality, mainly for the detection of benzene, toluene, ethylbenzene and xylenes (BTEX) compounds for indoor and outdoor air analysis from 10 ppb to 1 ppm levels with a response time of 10 minutes through loop injection. The prototype consists of a portable gas chromatograph equipped with a mini-detector along with a nitrogen cylinder and manometer for supply of pressurized carrier gas. The adaptation of the prototype is the result of extensive collaborative efforts, including an intercomparison campaign to evaluate the performance of the GC column, newly sensors developed by the project partners

For the PurPest project, this product was modified by replacing the sampling loop with a preconcentration unit to target sub-ppb level of the biomarkers. The system operating principle is comprised of four steps: sampling, preconcentration, separation, and detection. A pneumatic illustration of the system is shown in **Figure 2-2**. After the collection of samples, the samples are actively introduced into a preconcentration unit using a pump. The sampling flow is controlled using a flow regulation (in the meantime a restriction in the integrated sampling tube, or a mass flow controller in the future) in the tube connecting the sample out port of the device to an injection valve. An electrically-actuated injection valve acts as a means of introducing the already-sampled VOCs on the preconcentration unit into the column once sampling is finished.

The pre-concentration unit is a key element in the analysis of very low levels of VOCs. The preconcentration unit is composed of a glass tube that houses an adsorbent bed. A schematic representation of the preconcentration unit along with its dimensions is shown in **Figure 2-3**. The adsorbents adsorb the targeted sample under normal/ambient conditions. When the valve switches to injection mode, the carrier gas, nitrogen, regulated at 4 bars, with a flow of 2.5 mL/min, flushes the thermally-desorbed sample into the column. The desorption parameters of the sample from the adsorbent (temperature and duration) are electrically-controlled using an embedded electrical board (heating temperature up to 380 °C for efficient and rapid desorption). The introduced compounds are then separated using a commercial capillary column of intermediate polarity (Rxi-624, 20 m x 0.18 mm i.d. x 1 µm df, Restek, Bellefonte, PA, USA). The column is housed inside an isothermal oven meaning that its temperature stays constant during the whole analysis. After the compounds are completely separated, they are detected by the means of a miniaturized blue mini photoionization detector (PID) equipped with a 10.6 eV ultra-violet (UV) lamp. The system parameters (date and time, column temperature, humidity, carrier gas pressure, sampling duration, injection duration, analysis time, etc.) can be viewed/controlled using either the LED-touch-screen or an external computer.

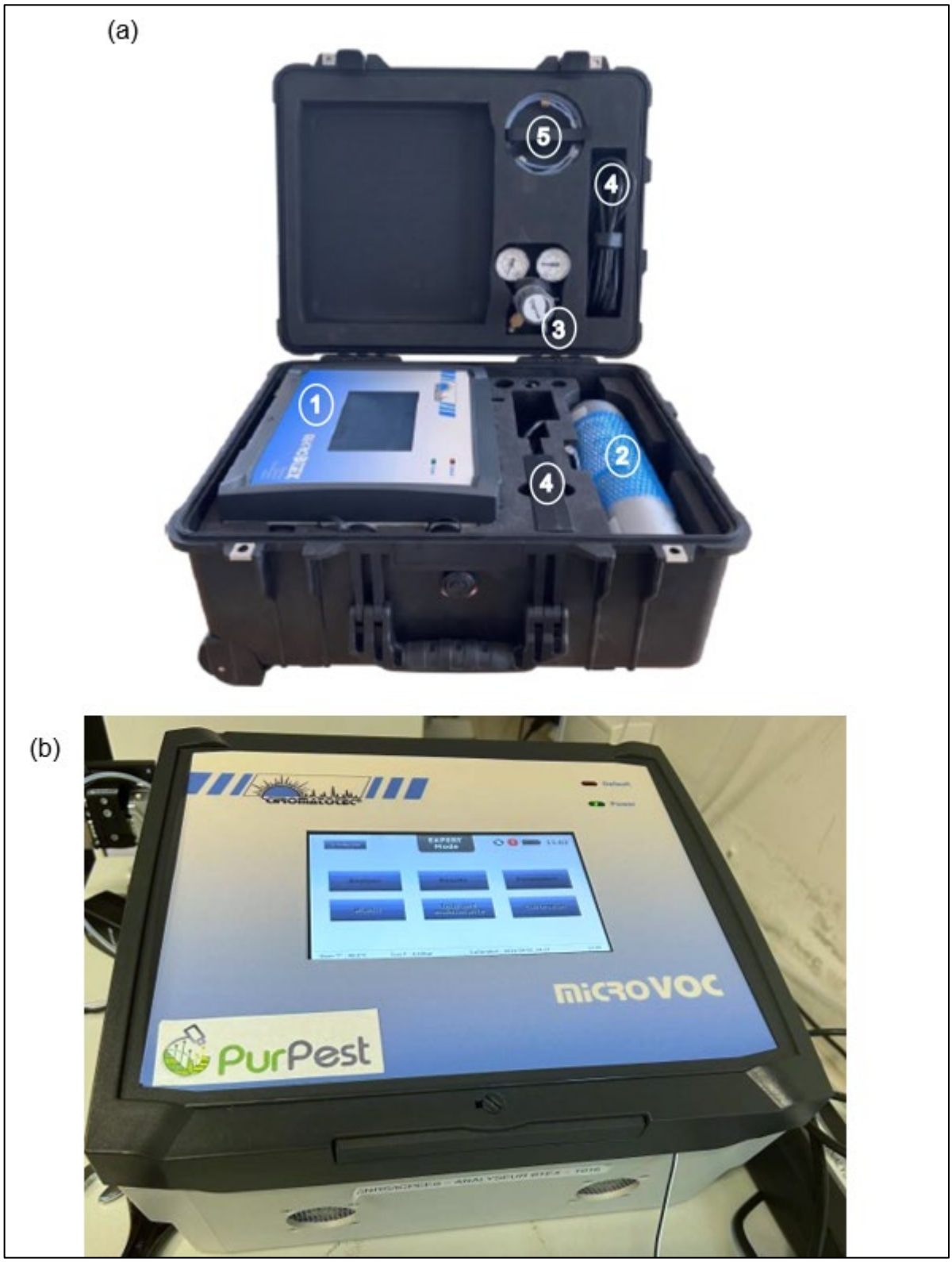


Figure 2-1: (a) Fully assembled first sensor system prototype carrier case that contains (1) the first sensor system prototype, (2) a 58 L nitrogen cylinder, (3) a manometer, (4) battery charger, (6) extra 1/8" Teflon tubing and ferrules; **(b)** a close-up to the first sensor system prototype.

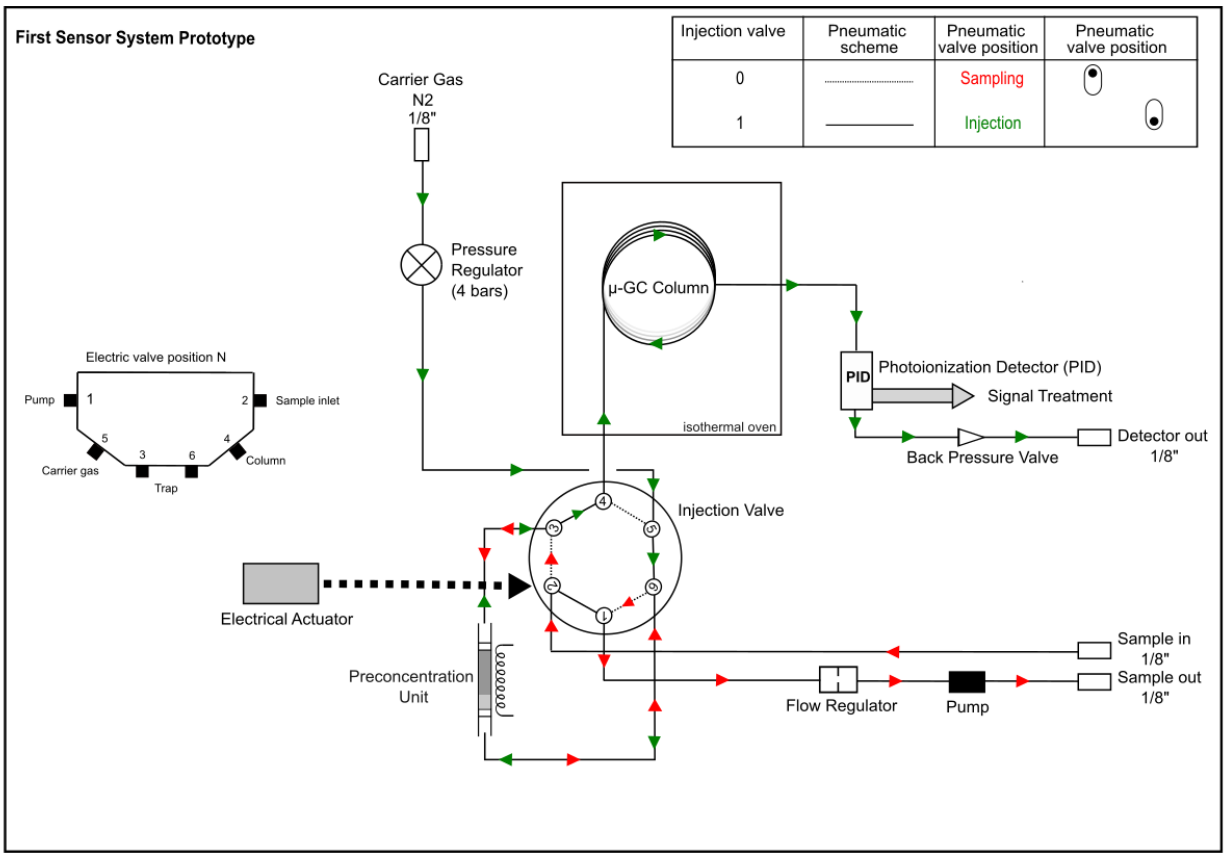


Figure 2-2: Pneumatic scheme of the first sensor system prototype.

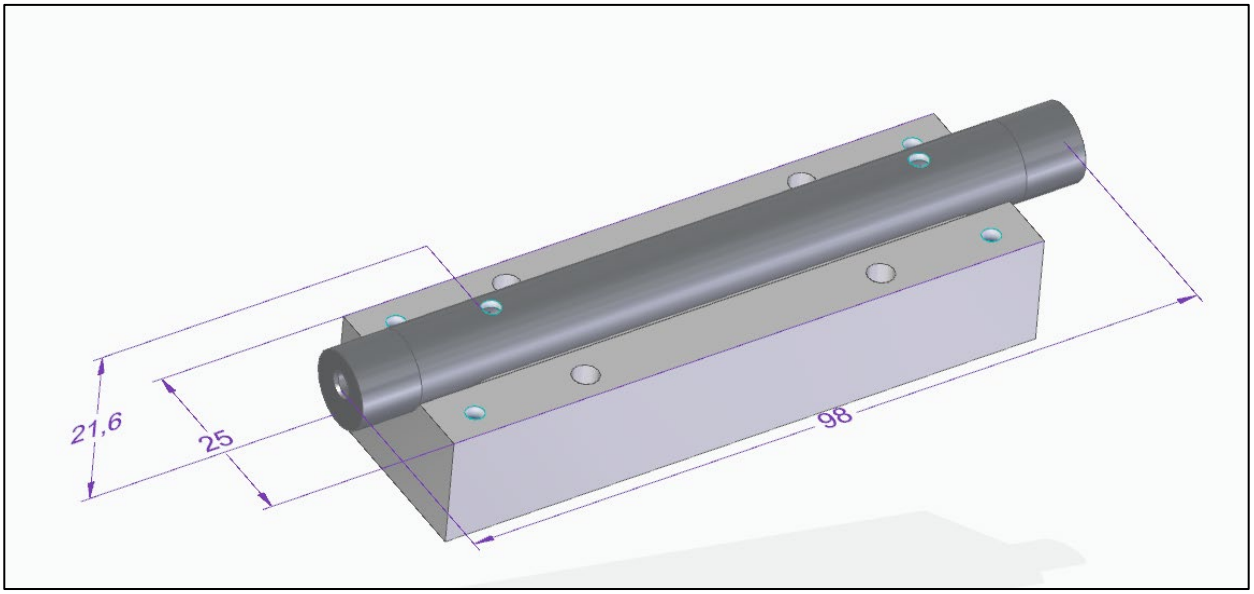


Figure 2-3: Dimensions of the first sensor system prototype preconcentration unit (mm).

3 RESULTS FROM THE FIRST PROTOTYPE TESTS

3.1 First testing using the loop injection

The initial tests for the performance of the first system prototype were made using a 200 µL sampling loop.

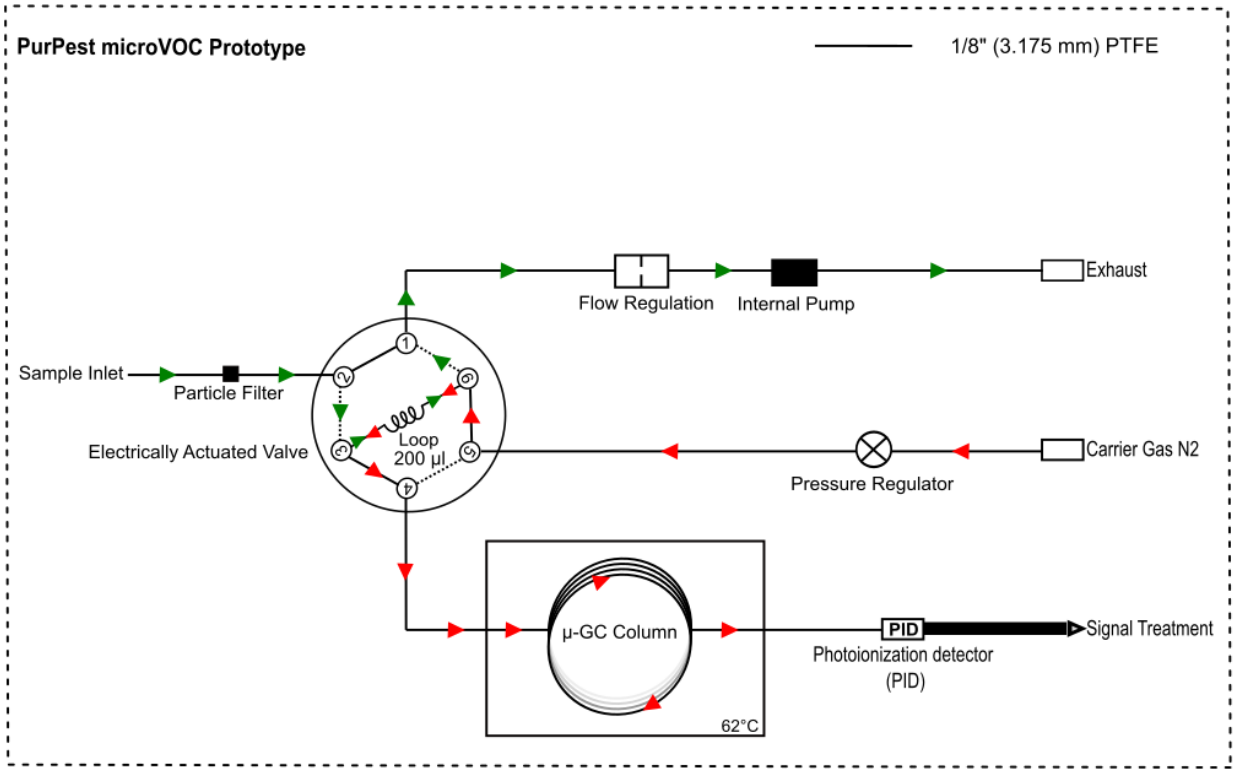
This system was used in the intercomparison held in AIRMO, Bordeaux, France during the second week of April 2024 from 08/04/2024 until 12/04/2024.

During this intercomparison, generation and sensing of several target VOCs, that are produced during several plant-pest interactions, was tested. Several developed sensors from PurPest partners were used to evaluate their performance. All documentation and extensive results are reported in Deliverable D2.2. Report on performance of individual sensor system components (July 05, 2024). In comparison to the results of other PurPest partners sensors that were also tested, the AIRMO sensor was able to detect and quantify all the targeted compounds in the PurPest project with good repeatability.

A schematic representation of the loop configuration that was used in the intercomparison is shown in **Figure 3-1**. Using this previous configuration, sampling a generated single VOC/mixture of VOCs was performed. An AIRMO generation system design for task 3.2 of WP3 (airmoCAL-M) that houses the sources of VOCs through the means of permeation devices was used. The generation system includes temperature regulated ovens that contain permeation devices. Using flow-regulated and pure zero-air, the VOCs are transported from the membranes of the permeation devices into the sensors for detection through a sampling line.

The stream of VOCs was pumped into the microVOC sampling loop. After sampling for 2 minutes, the sample was injected into the analytical column within a short time when flushed with nitrogen. A chromatogram was retrieved within 30 minutes giving the characteristic peak of each compound along with their identification using a reference system. The reference system (GC-FID/MS, airmoVOC C6-C12, Chromatotec, France) acted as an identifier and quantifier of the concentrations of the VOCs.

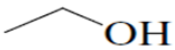
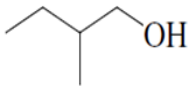
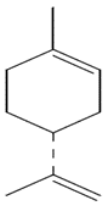
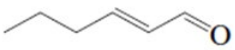
Several interesting compounds in the PurPest project, regarded as biomarkers of the plant-pest infestation, along with other interferents like ethanol, benzene and hexanal were generated using the permeation devices. The biomarkers that were generated are listed in **Table 3-1**.



Pneumatic scheme of the electrically actuated valve	Pneumatic valve position
.....	Injection into the loop
————	Injection into the column

Figure 3-1: microVOC pneumatic scheme (system used in the intercomparison in sampling loop mode).

Table 3-1: Targeted biomarkers generated in the gas phase and tested during the intercomparison.

Targeted Pest	Targeted VOCs	Name	Molecular Weight (g/mol)	CAS number
Phytophthora ramorum		ethanol	46.07	64-17-5
		2-methyl-1-butanol	88.15	137-32-6
Cotton bollworm		d-limonene	136.24	5989-27-5
Brown marmorated stink bug		(E)-2-hexenal	98.14	6728-26-3

The visualization of each peak on the PurPest prototype was done using the LED screen. Each peak had a characteristic retention time that corresponded to each of the biomarkers/interferents. **Figure 3-2** shows the 2-methyl-1-butanol peak along with the detected concentration for a targeted concentration of 0.70 ppm, while **Figure 3-3** shows the d-limonene peak along with the detected concentration for a targeted concentration of 0.62 ppm. **Figure 3-4** shows the (E)-2-hexenal peak along with its detected concentration for a targeted concentration of 0.91 ppm. A mixture of several VOCs was targeted in the last two days of the intercomparison. **Figure 3-5** shows several peaks characteristic of the compounds in the mixture along with their detected concentrations.

Regarding the detection of the VOC biomarkers, some specifications for the PIDs inside the first sensor system prototype have to adapt to the nature of the compounds to be detected. Considering the properties of these compounds, the response on the PID might be improved with adapting those specifications to the properties of the compounds. After studying the effect of choice of 2 PIDs, we can conclude from **Figure 3-6** that one of the two PIDs (PID2) showed much better sensitivity than the other (PID 1) for all the VOCs studied. Indeed, the ratio between the response factors (RF) of the two PIDs (RF_{PID2}/RF_{PID1}) was greater than 1 for all VOCs: benzene (1.5), 2-methyl-1-butanol (6.9), (E)-2-hexenal (5.9), d-limonene (10.7). The gain is therefore greater for polar molecules (3 VOC biomarkers) than for benzene, which is non-polar.

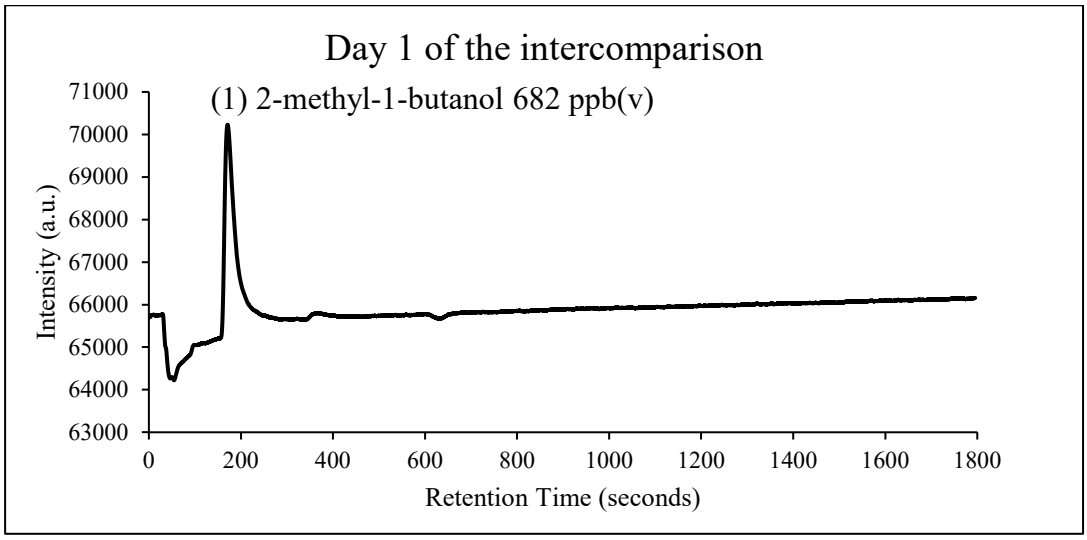


Figure 3-2: (1) 2-methyl-1-butanol peak [retention time = 200 seconds, concentration = 682 ppb(v)] after acquisition of the microVOC chromatograms.

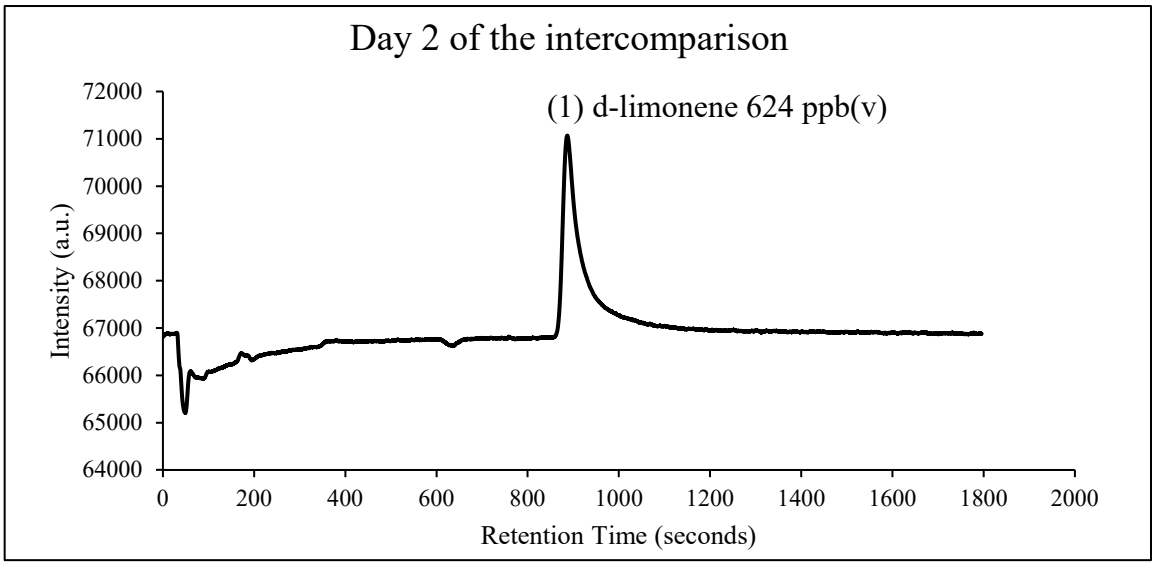


Figure 3-3: (1) d-limonene peak [retention time = 900 seconds, concentration = 624 ppb(v)] after acquisition of the microVOC chromatograms.

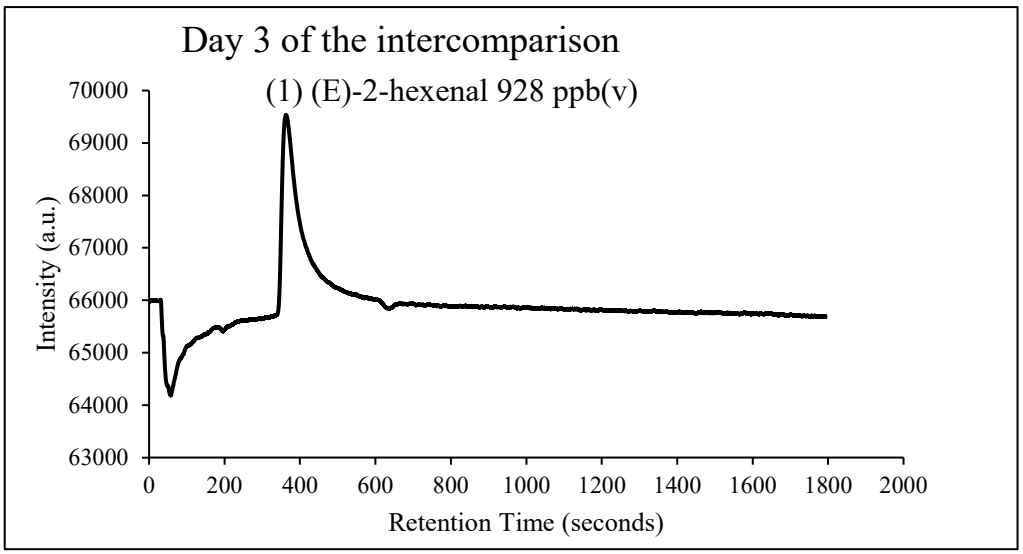


Figure 3-4: (1) (E)-2-hexenal peak [retention time = 400 seconds, concentration = 928 ppb(v)] after acquisition of the microVOC chromatograms.

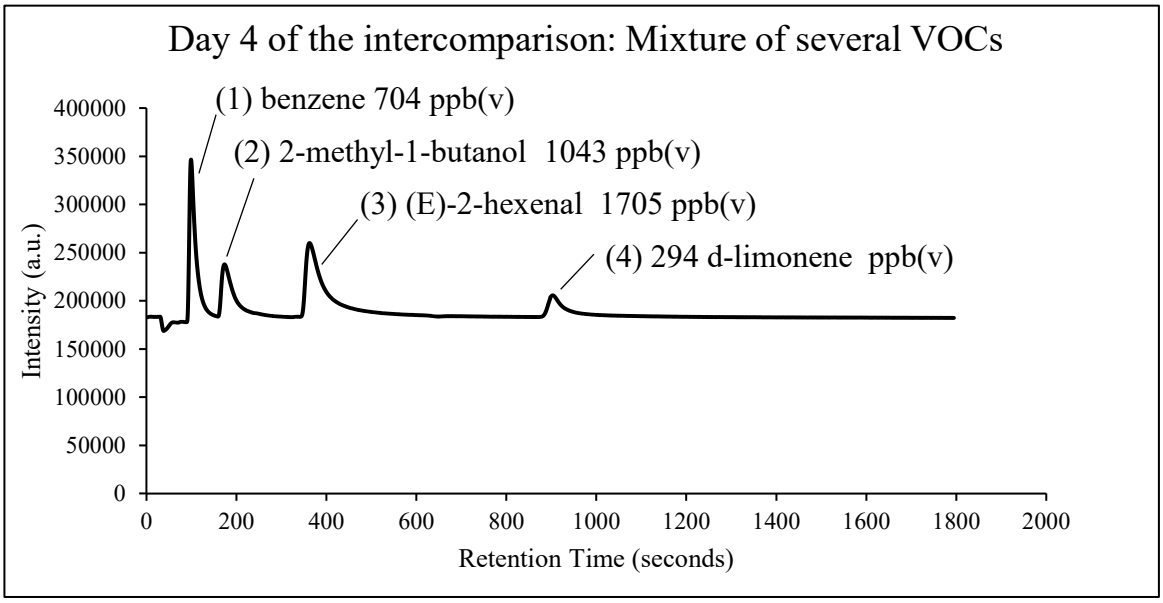


Figure 3-5: microVOC chromatogram of the mixture of the targeted VOCs in the intercomparison, *apparent* compounds listed in order of elution: *(1)* benzene [retention time = 180 seconds, concentration = 704 ppb(v)], *(2)* 2-methyl-1-butanol [retention time = 360 seconds, concentration = 1043 ppb(v)], *(3)* (E)-2-hexenal [retention time = 660 seconds, concentration = 1705 ppb(v)], *(4)* d-limonene [retention time = 965 seconds, concentration = 294 ppb(v)].

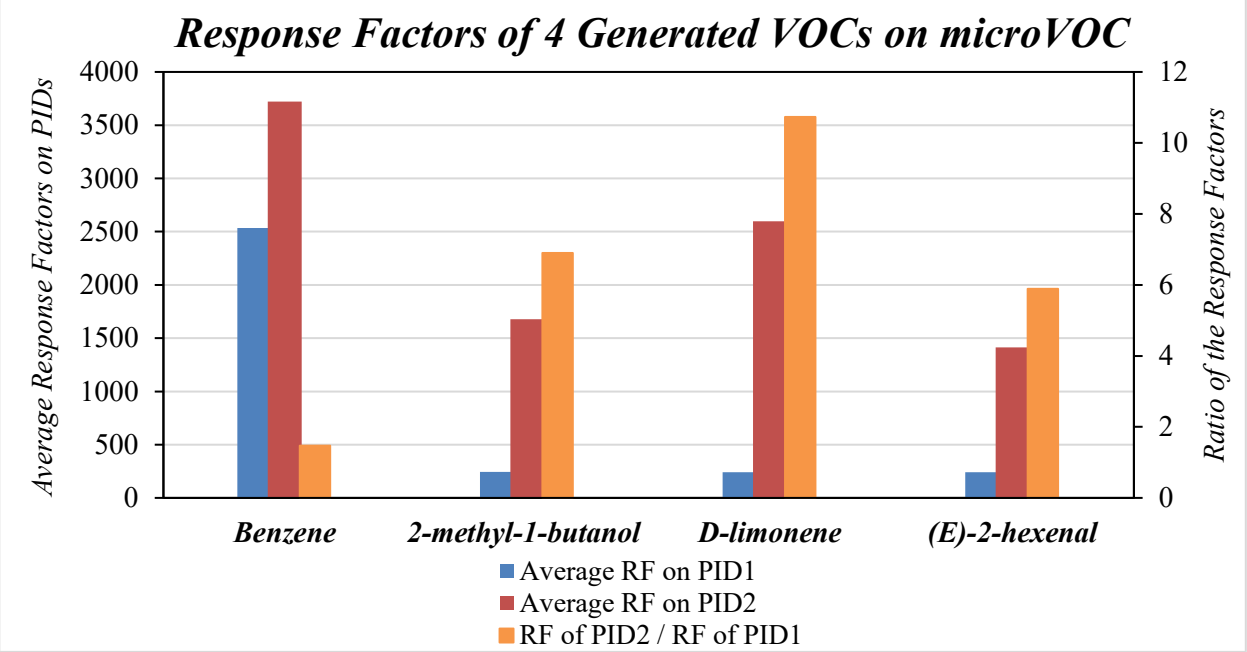


Figure 3-6: Response Factors of 4 Generated VOCs on microVOC using two different PIDs, (RF = Response Factor).

3.2 First testing using the preconcentration unit

Our results obtained with a 200 µL injection loop showed that VOC concentrations between a few ppb and a few ppm can be measured by the first SSP. To achieve concentrations below ppb, it is essential to add a pre-concentration system during the air sampling phase.

The first testing that was made for the first sensor system prototype equipped with a preconcentration unit, was performed using a Tedlar bag sampling that contained the BTEX compounds sampled from a BTEX cylinder (1 ppm) (in alphabetical order: benzene, toluene, ethylbenzene, meta- & para- xylenes, and o-xylene). The sampling duration was 22.5 minutes for a sampling flow of 18 mL/min adjusted using the flow regulation shown in **Figure 2-2**. A sampling volume of 405 mL thus was collected on the preconcentration unit for a target concentration of 7 ppb. The corresponding chromatogram for these results is shown in **Figure 3-7**. Comparison of the result on the first sensor system prototype with the result on the reference system (GC-FID) was also performed to verify the detected concentrations. The chromatogram obtained on the GC-FID is shown in **Figure 3-8**.

Using the same sampling volume, one chromatogram was obtained on both the first sensor system prototype and on the reference system for the two compounds, benzene and d-limonene at 25 ppb and 45 ppb respectively. This is shown in **Figure 3-9** and **Figure 3-10**.

Using the preconcentration unit, concentrations in *sub-ppb to ppt levels* can be targeted. With accurate determination of the emission rate of a permeation device and the required dilution factors to efficiently decrease the concentrations, the preconcentration unit is able

to concentrate the sample. For this, the first tests using the preconcentration unit targeted one reference compound, i.e., benzene. This compound has a well-established response on the reference system. After confirmation of benzene peak identification on the prototype, a first calibration test was performed, with several dilution points ranging from *0.1 ppb (100 ppt) to 5 ppb* after defining optimal sampling parameters. The linearity of the prototype was tested by 5 replicate injections of 60 mL benzene sample generated from the gas-generation system into the preconcentration unit. The benzene sample was desorbed at 380°C to ensure full desorption. A plot of the peak area of benzene versus the measured concentration on the reference system is illustrated in **Figure 3-11**. Although benzene is not considered a biomarker of the plant-pest infestation, some information can be retrieved concerning its detection and quantification limits. A rough preliminary estimation of the detection limit, assuming that the signal of the benzene peak is three times greater than the background noise, gives a value on the order of 10 pptv.

These results obtained with benzene are very promising and they were obtained with a low sampling volume of 60 mL, corresponding to a sampling duration of 4 min with a sampling flow set to 15 mL/min.

In the near future, experiments will be carried out with VOC biomarkers such as 2-methyl-1-butanol, (E)-2-hexenal and d-limonene after further optimization.

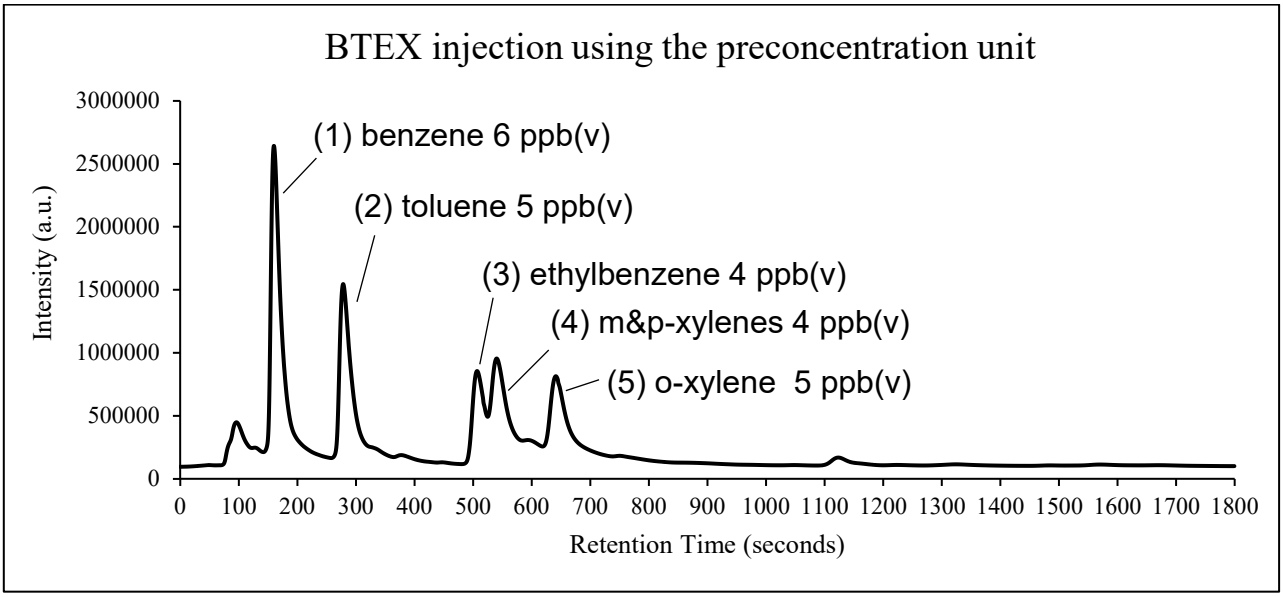


Figure 3-7: A first sensor system prototype chromatogram showing the 5 targeted compounds for a BTEX injection, BTEX compounds listed in order of elution: *(1)* benzene [retention time = 160 s, concentration = 6 ppb(v)], *(2)* toluene [retention time = 278 s, concentration = 5 ppb(v)], *(3)* ethylbenzene [retention time = 507 s, concentration = 4 ppb(v)], *(4)* m&p-xylenes [retention time = 539 s, concentration = 4 ppb(v)], *(5)* o-xylene [retention time = 640 s, concentration = 5 ppb(v)].

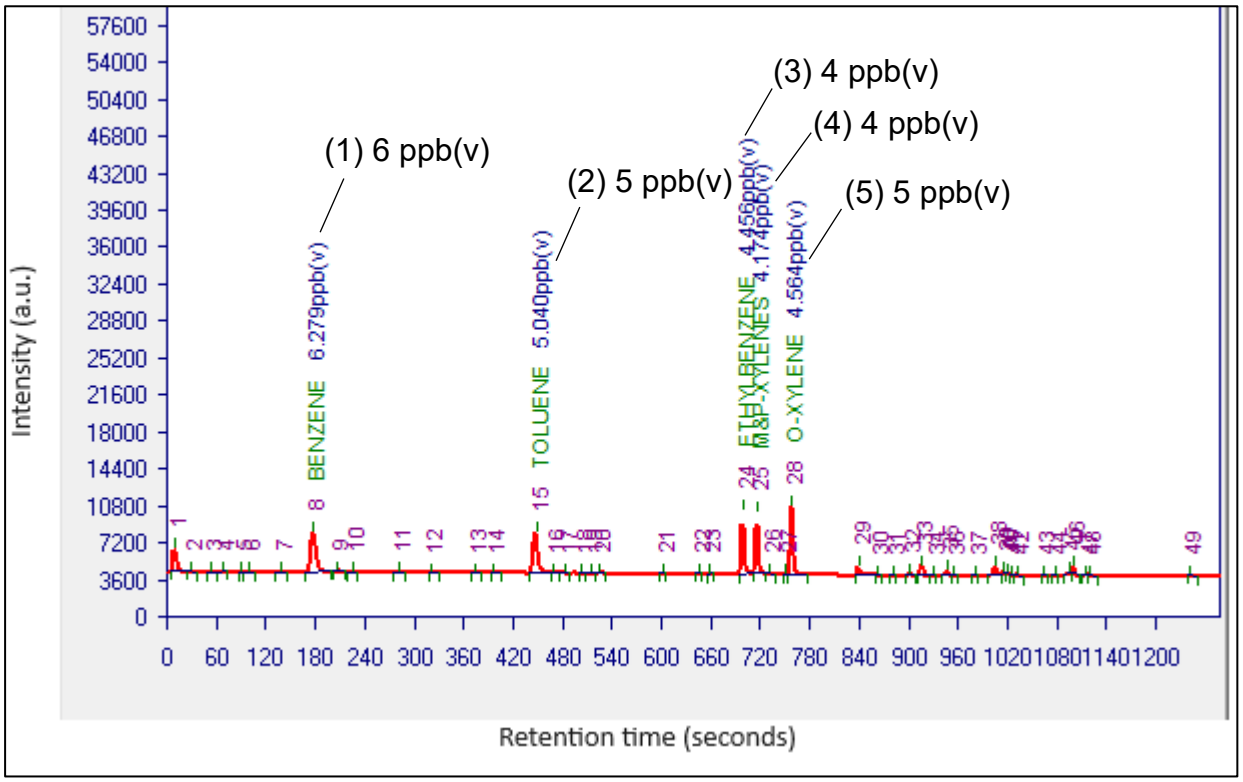


Figure 3-8: Reference system chromatogram showing the 5 targeted compounds for a BTEX injection, BTEX compounds listed in order of elution: *(1)* benzene [retention time = 177 s, concentration = 6 ppb(v)], *(2)* toluene [retention time = 448 s, concentration = 5 ppb(v)], *(3)* ethylbenzene [retention time = 699 s, concentration = 4 ppb(v)], *(4)* m&p-xylenes [retention time = 716 s, concentration = 4 ppb(v)], *(5)* o-xylene [retention time = 758 s, concentration = 5 ppb(v)].

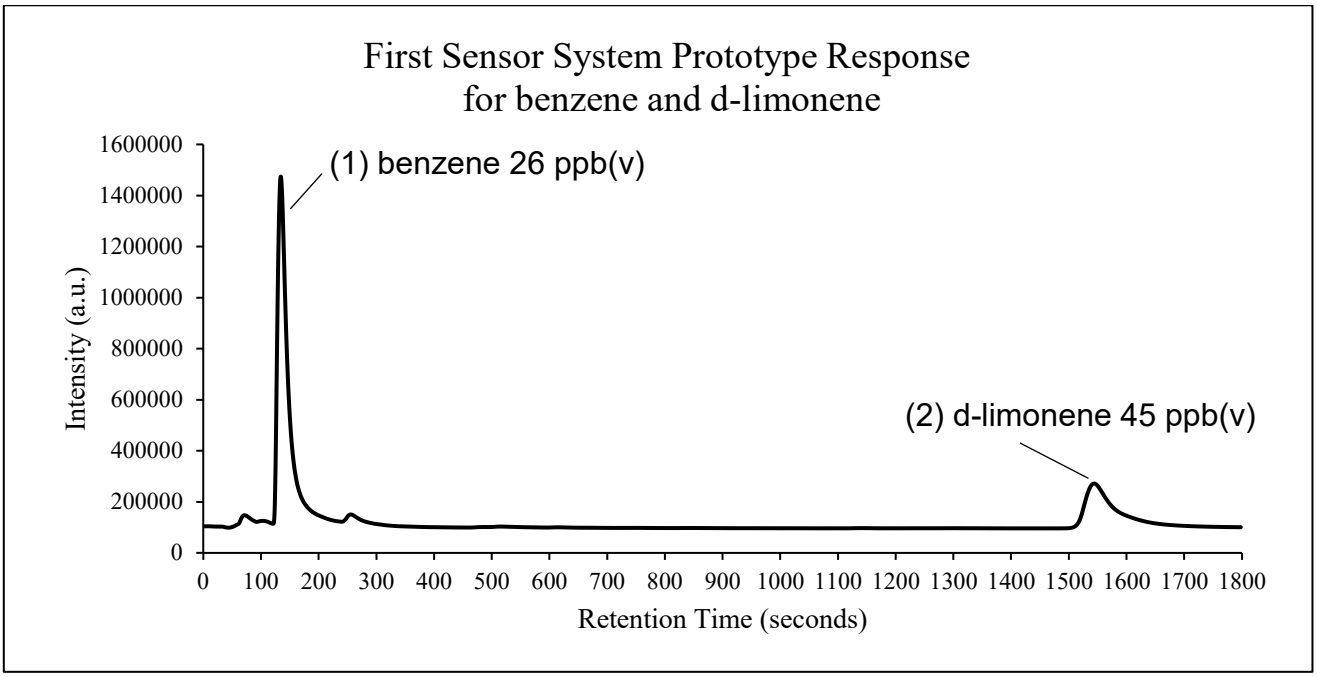


Figure 3-9: First sensor system prototype response for benzene and d-limonene, compounds listed in order of elution: *(1)* benzene [retention time = 135 s, concentration = 26 ppb(v)], *(2)* d-limonene [retention time = 1551 s, concentration = 45 ppb(v)].

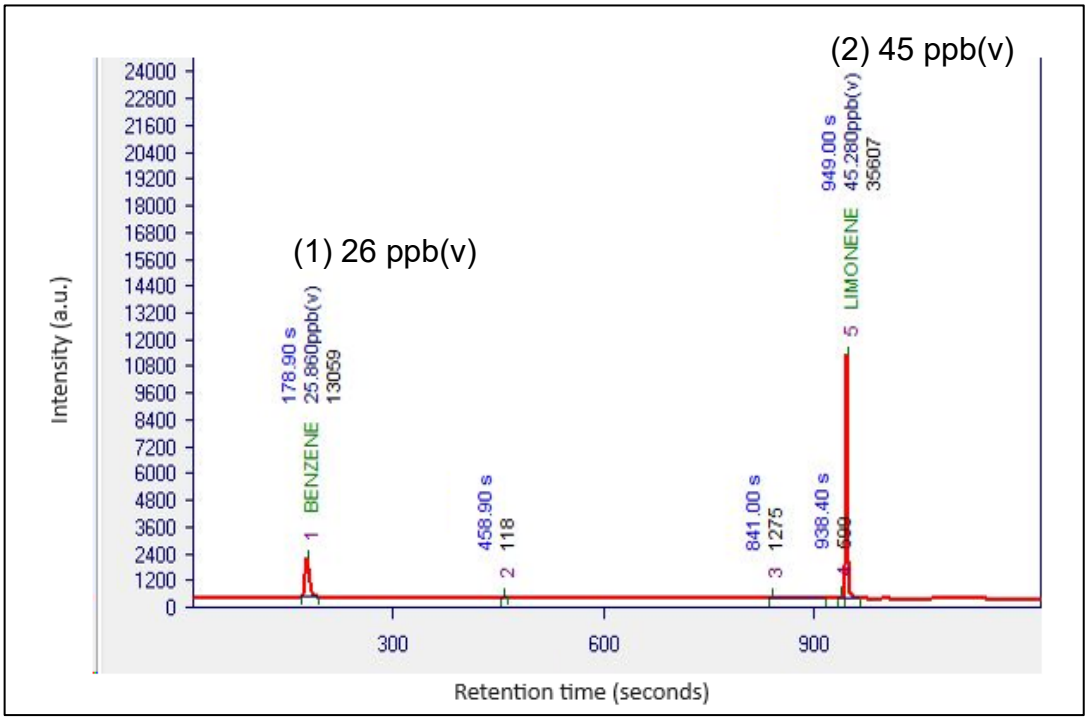


Figure 3-10: Reference system response for benzene and d-limonene, compounds listed in order of elution: *(1)* benzene [retention time = 178 s, concentration = 26 ppb(v)], *(2)* d-limonene [retention time = 949 s, concentration = 45 ppb(v)].

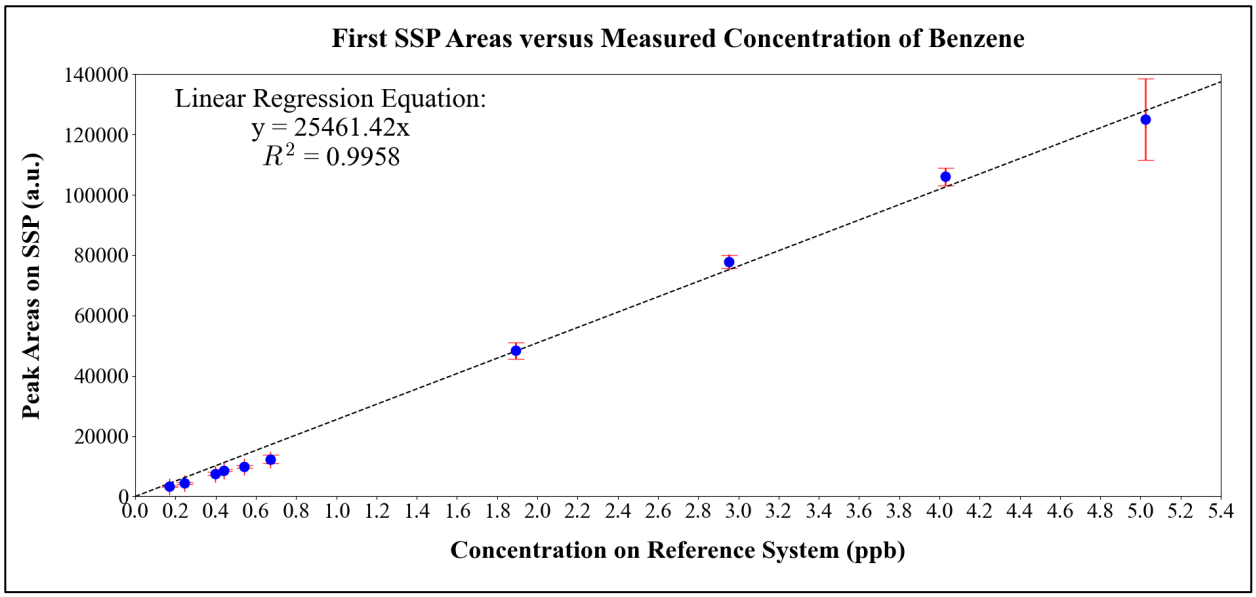


Figure 3-11: Calibration curve of benzene using the preconcentration unit of the first SSP. Sampled volume = 60 mL, sampling flow rate = 15 NmL.min^{-1}, desorption temperature = 380 °C, injection time = 1560 s. Vertical error bars correspond to the standard deviation for 5 replicates of each point. Horizontal error bars correspond to the error on the concentration for 5 replicates of each point.

4 CONCLUSION & PERSPECTIVES

The concentrations of volatile organic compounds emitted by infested pests or plants can typically range in concentration from a few tens of ppt to several tens of ppb.

To achieve the required sensitivities with our SSP, it was therefore necessary to equip it with a pre-concentration unit in the portable µ-GC system. This first stage of development has been successfully completed. The sensitivity of the first SSP was then evaluated for benzene. The detection limit was already equal to 10 ppt with a sampling volume of only 60 mL.

In addition, the second PID modified by AIRMO showed increased sensitivity for all VOCs, and in particular for the targeted VOC biomarkers which are more polar.

Other sensors were tested during a field campaign, but have not yet been integrated into the SSP, as their sensitivities are less promising than those of the two photoionization detectors (PID1 and PID2).

The next experiments will be dedicated to testing the µGC equipped with PID2 and its new preconcentration unit with a series of VOC biomarkers. Meanwhile, a new electronic board is currently being developed with a dedicated new software to obtain the second SSP in the framework of the PurPest project.