TNA User Report

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Project title	Factory boundary pollutants monitoring.
Name of the accessed chamber	EUPHORE
Dates of project	19-27 June 2018
Operators of the chamber	Amalia Muñoz, M. Ródenas, M. Martinez, T. Vera, E. Borrás
Number of users in the project	Blue Industry and Science: Clotilde Vivant and Mélanie Peyrind
Project objectives (max 100 words)	Blue Industry and Science aims at improving air quality for the people by monitoring gas pollutants. To that end, Blue Industry recently released the Blue X-FLR9 gas analyzer. More specifically, the company is completing the validation of an application to monitor the concentration of Benzene, Toluene, Xylenes[1], Hydrogen Chloride, and non-methanic Hydrocarbons (NMHC). When a molecule concentration goes over specific thresholds, an alarm is generated in real-time so that measures can be taken to mitigate the impact of the pollution in a timely manner. Scientific goals are : Validation of the method developed in Blue Industry and Science lab by confronting measurements with the reference method (GCMS analysis after sampling on TENAX cartridges) and also other technologies (FTIR and PTRMS) in real conditions.

[1] Together referred to as BTX in this document

Description of work (max 100 words):	The aim of the project is to test different mixtures of ambient air pollutants at different concentrations. Each day additional conditions were implemented: Addition of HCl, matrix switched from cleaned air (no humidity, no VOC) to ambient air, addition of NOx and sunlight. Sampling for GCMS was performed every hour to provide the reference (reference designated by the regulation), while the 2 high-performance lab instruments installed at EUPHORE (FTIR, PTRMS) provided additional and reliable real-time measurements.

Principal Investigator's and group's information	
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User status[4]	EXP
New user	yes

User 1 Information[5]	
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User status	EXP
New user	yes

[2] Physics; Chemistry, Earth Sciences & Environment; Engineering & Technology; Mathematics; Information & Communication Technologies; Material Sciences; Energy; Social sciences; Humanities.
[3] UNI= University and Other Higher Education Organisation;
RES= Public Research Organisation (including international research organisations and private research organisations controlled by public authority);
SME= Small and Medium Enterprise;
PRV= Other Industrial and/or Profit Private Organisation;
OTH= Other type of organization.
[4] UND= Undergraduate; PGR= Post graduate; PDOC= Post-doctoral researcher; RES= Researcher EXP= Engineer; ACA= Academic; TEC= Technician.
[5] Reproduce the table for each user who accessed the infrastructure

Trans-National Access (TNA) Scientific Report

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Instructions

Please limit the report to max 5 pages, you can include tables and figures. Please make sure to address any comments made by the reviewers at the moment of the project evaluation (if applicable, in this case you were informed beforehand). Please do not alter the layout of the document and keep it in Word version. The report will be made available on the eurochamp.org website. Should any information be confidential or not be made public, please inform us accordingly (in this case it will only be accessible by the European Commission, the EUROCHAMP-2020 project partners, and the reviewers). Please include:

- Introduction and motivation
- Scientific objectives
- Reason for choosing the simulation chamber/ calibration facility
- Method and experimental set-up
- Data description
- Preliminary results and conclusions
- Outcome and future studies
- References

Name of the PI:
Chamber name and location: EUPHORE, Valencia, Spain
Campaign name and period: Factory boundary pollutants monitoring.
Text:

Blue Industry and Science, a start-up created in 2010, developed a brand-new gas analyzer based on the first broadly tunable laser (BTL), in which the optical source has a spectral resolution of a laser (0.01 cm-1) but a much wider tunability (800 cm-1). This enables the analyzers to quantify in real-time multiple molecules, at trace levels, but also to target heavy molecules (such as BTX) that traditional laser-based analyzers cannot measure.

Poor air quality generates a growing urge to monitor pollutants, as reflected in increasing environmental regulatory requirements implemented recently in countries such as China. The Blue X-FLR9 analyzer is tailored for these needs, thanks to its ability to monitor multiple pollutants where multiple technologies would have been required before.

However, regulatory requirements usually impose the use of normalized measurement technologies. The tests conducted at the EUPHORE chamber are an important step to validate the performance of the Blue X-FLR9 gas analyzer compared to reference measurement methods, in simulated real-life conditions.

With its ability to generate “on-demand atmospheres” and the possibility to provide reference method measurements (sampling and pre-concentration for subsequent GCMS analysis) and to

provide additional real-time measurements with 2 high-performance lab analyzers (FTIR and PTRMS), the EUPHORE chamber was the perfect place to perform this project.

Figure 1: CEAM building with the 2 chambers on the roof

Figure 2: Inside the CEAM's lab

Method and experimental set-up

The Blue X-FLR9 Gas Analyzer, Serial Number Canneberge 004, manufactured on 02/2018, was used for this project.

The calibration of the analyzer was performed at the calibration lab of Blue Industry and Science in Saint Denis, France, before transportation by train to the EUPHORE chamber in Valencia, Spain.
The specific method used to measure BTX and HCl was designed and tested at the applications lab of Blue Industry and Science on gas cylinders.
The spectral characteristics of the method are as follows:
- spectral range: 2840-3100 cm^{-1}
- spectral resolution: 0,09 cm^{-1}, except on spectral range 2900 to 2950 cm^{-1} where is the spectral resolution has been set to 0,03 cm^{-1} to target the sharp peaks of HCl.
- molecules measured: Benzene, Toluene, o-Xylene, p-Xylene, HCl, Water, Methane
Total measurement time: 2 min 58 s

In the EUPHORE chamber, an FTIR analyzer with a custom-made detection cell, and a PTRMS analyzer measure continuously the compounds in the chamber.

- FTIR references are calibrated from well-known databases (e.g. EPA) or by in situ calibrations in the chambers (EUROCHAMP2020 IR database). Measurement time: 5 min.

Figure 3: FTIR in the CEAM lab

- PTRMS is calibrated by introduction of given amounts of compound into the EUPHORE chamber, and by using a gas calibration mixture of BTEX, and an external calibrator system to obtain different concentrations certified by Authorized certifying entity. Measurement time: 3 min.

The 3 analyzers are all directly linked to the chamber.

In addition, every hour VOCs and BTX are collected on pre-concentration cartridges and subsequently analyzed via GCMS
The Blue X-FLR9 analyzer is pumping the air of the chamber thanks to its internal pump and via a 1,5 m PTFE line.

Figure 4: Blue X-FLR9 Gas Analyzer

The volume of the chamber is 200 m3. The compounds are injected in the chamber via an air stream in an impinger. Thanks to this device, a calculated volume of liquid compound can be spread out in the chamber as a gas. It takes 5 minutes to get a homogeneous atmosphere in the chamber.

Figure 5: EUPHORE chamber

Test plan:

- 1st day: the first day was used to prepare the analyzer for the tests.

Calibration of the Blue X-FLR9 analyzer was tested by measuring 1 ppm of benzene and a linearity was performed to check the response of the 3 analyzers.

- 2nd day: linearity on a single compound: toluene, and humidity dependence tests (0-20-50% humidity).
- 3rd day: linearity of BTX mixture in cleaned air (0% humidity, no VOC)
- 4th day: linearity of BTX mixture + addition of HCl (0% humidity, no VOC)
- 5th day: linearity of BTX mixture + HCl in ambient air
- 6th day: linearity of BTX mixture + HCl in ambient air + interferences addition
- 7th day: linearity of BTX mixture + HCl in ambient air with NOx addition and sunlight to generate photooxidation phenomenon.

Results

The tests of the first 2 days were performed to confirm the good functioning of the Blue X-FLR9 analyzer after transportation by train from Paris to Valencia. No drift has been observed. In addition, the first tests also confirmed the non-dependency of the analyzer to humidity changes in the range of 0-50 % of relative humidity.

During the week, BTX + HCl mixtures were tested at the following concentrations:

- 1st injection: benzene (200 ppb), toluene (200 ppb), o-xylene (150 ppb), p-xylene (150 ppb), and HCl (100 ppb).
- 2nd injection: addition of benzene (+300 ppb), toluene (+300 ppb), o-xylene (+150 ppb), p-xylene (+150 ppb), and HCl (+100 ppb)
- 3rd injection: addition of benzene (+300 ppb), toluene (+300 ppb), o-xylene (+150 ppb), p-xylene (+150 ppb) and HCl (+ 300 ppb)

It was observed that the change of mixture from “cleaned air” (no VOC, 0% humidity during days 3 and 4) to ambient air (during days 5 to 7) had no impact on the measurement. According to this observation, we are describing below the results of day 5 (June 26th), which provide meaningful measurement points for the application.

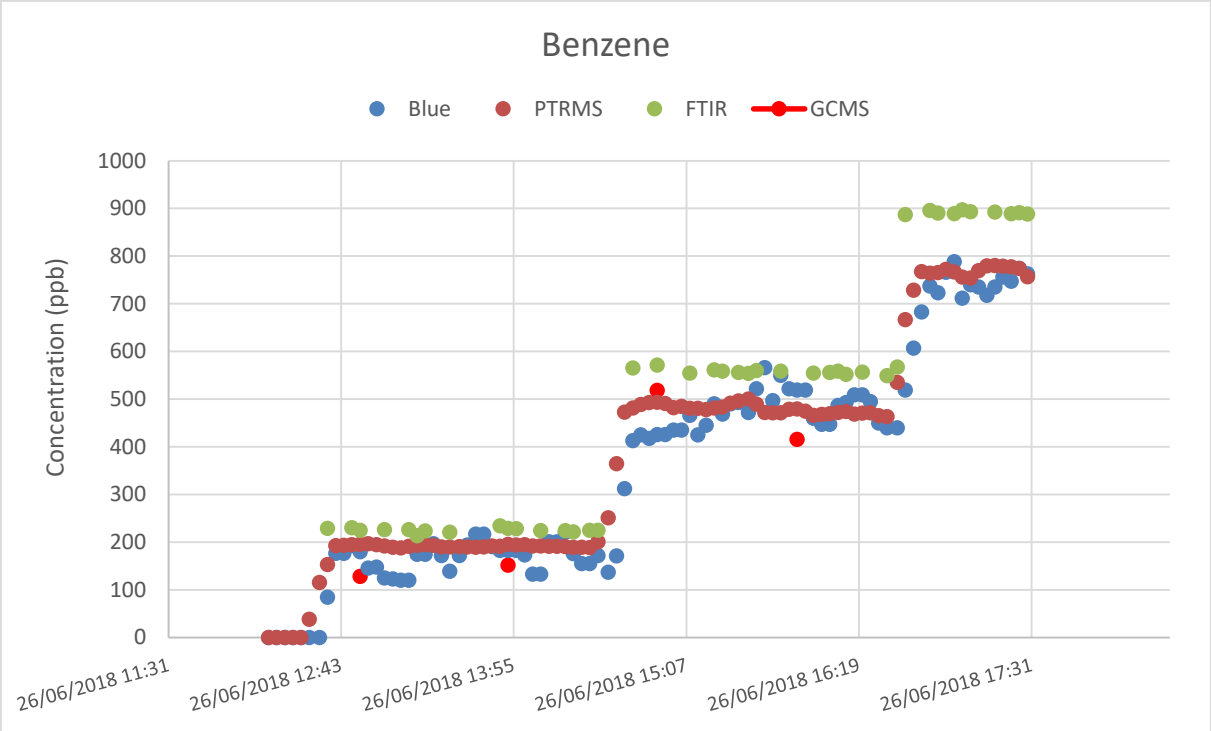
Detailed results of measurements from June 26th : BTX + HCl in ambient air

First, the chamber was filled with ambient air for 4 hours. Then, BTX and HCl were added step by step.

Benzene results:

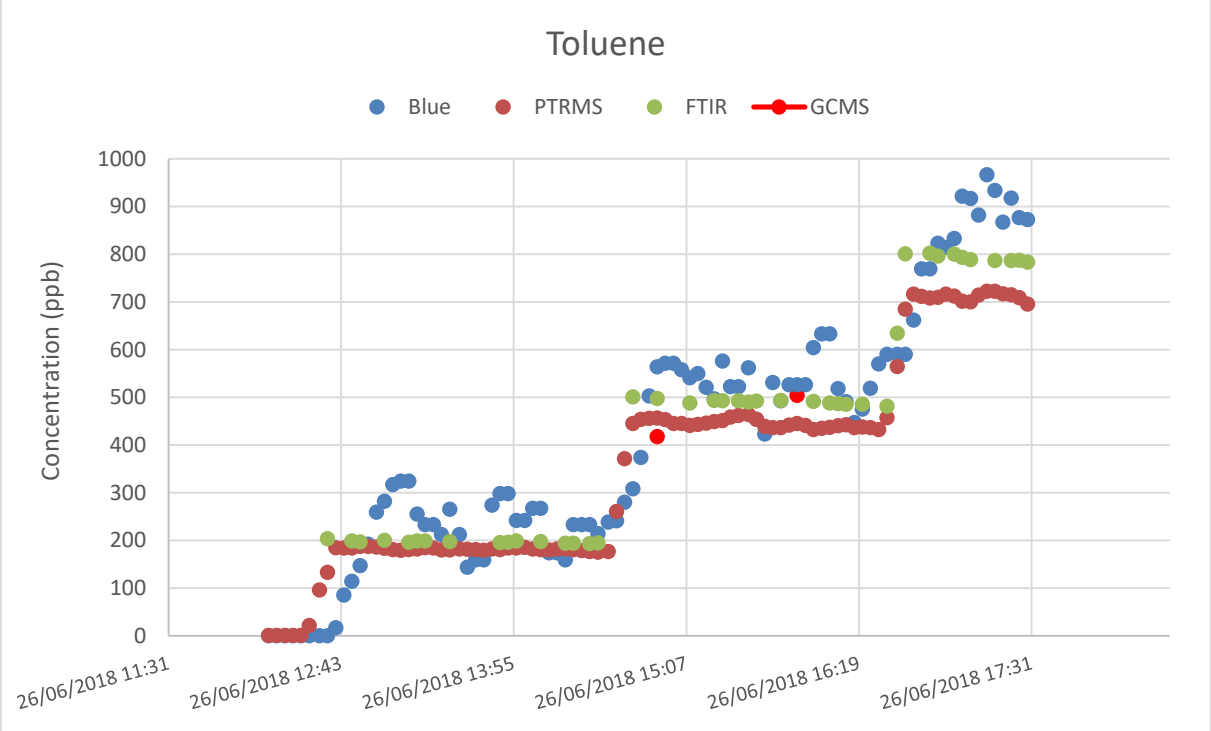
Time (pm)	Injected concentration* (ppb)	Measured concentrations (ppb)	
		GCMS (reference)	BLUE
12:37 – 1:35 pm	203	128	159
1:39 – 2:34 pm	203	152	168
2 :37 – 3:36 pm	514	518	471
3:39 – 4:35 pm	514	416	472
4:38 – 5:29 pm	825	N/A	747

* Theoretical concentrations according to compound weight injected, corrected for temperature and pressure



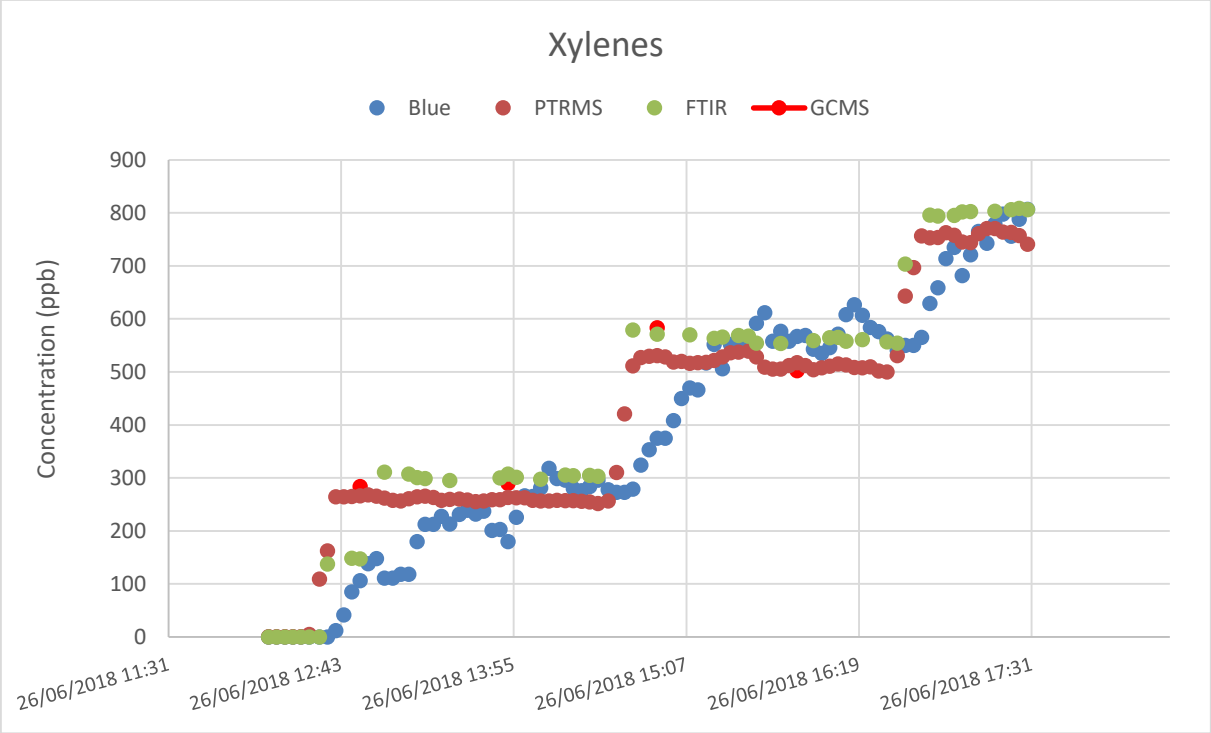
Toluene results:

Time (pm)	Injected concentration (ppb)	Measured concentrations (ppb)	
		GCMS (reference)	BLUE
12:37 – 1:35 pm	201	191	252
1:39 – 2:34 pm	201	193	219
2 :37 – 3:36 pm	502	418	530
3:39 – 4:35 pm	502	504	547
4:38 – 5:29 pm	803	N/A	899



Sum of the xylenes:

Time (pm)	Injected concentration (ppb)	Measured concentrations (ppb)	
		GCMS (reference)	BLUE
12:37 – 1:35 pm	293	284	186
1:39 – 2:34 pm	293	290	287
2 :37 – 3:36 pm	586	584	521
3:39 – 4:35 pm	586	502	576
4:38 – 5:29 pm	878	N/A	760



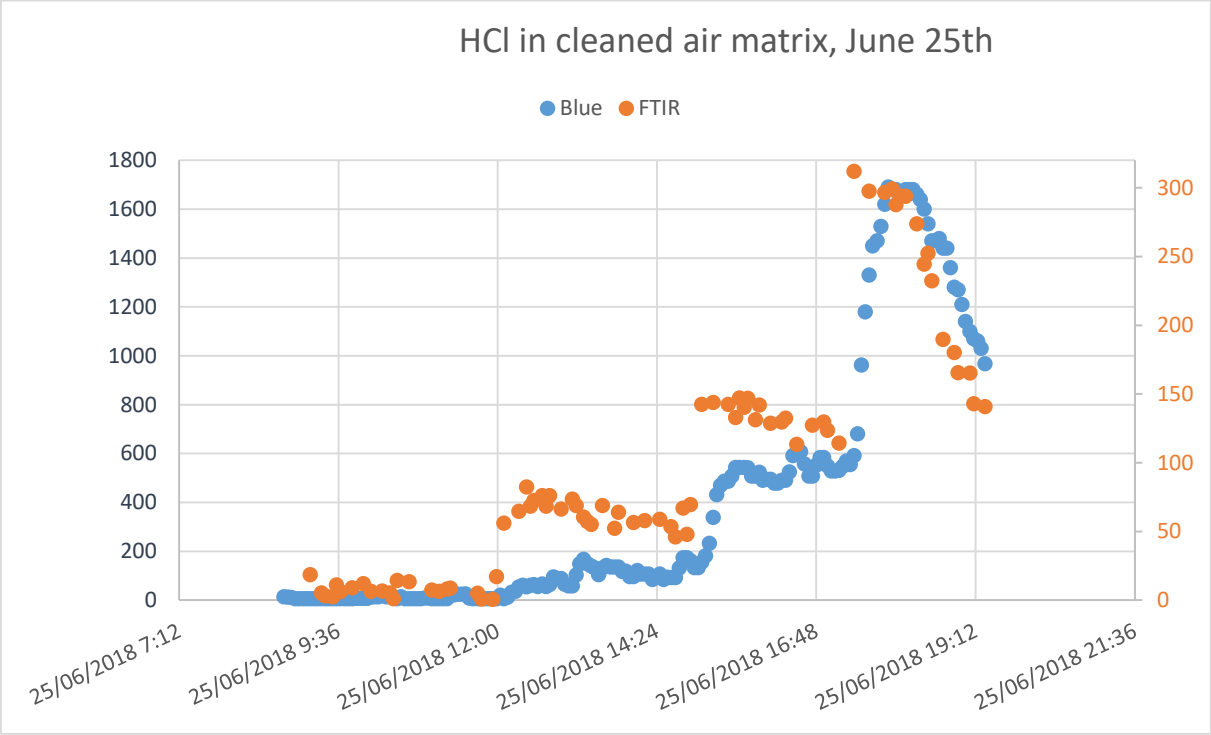
HCl:

HCl was measured by the FTIR and the Blue X-FLR9 analyzers. PTRMS and GCMS do not measure this molecule.

In the absence of a reference measurement, the aim of the experiment was only to study the generic measurement capability of the Blue X-FLR9 analyzer.

First, a phenomenon of wall losses was observed with HCl on the 25th of June when the matrix was "cleaned air" (cleaned of humidity and VOCs, …), the concentration was decreasing faster than for other compounds (see graph below).

Response times might also have to do with the sampling line in Blue's analyzer: when it is saturated, there is no room anymore for the HCl to stick to the lines and therefore next additions can be measured properly and reach the sytem instead of going to the walls.



In addition, on the 26th, when the matrix was ambient air, it was observed that the concentration of HCl disappeared as soon as the HCl was injected. Our hypothesis is a phenomenon of recombination of HCl with the compounds present in ambient air, combined with the specific difficulty of generating stable concentrations of this compound.

The results on HCl were subsequently non-conclusive, however they showed good accordance between the FTIR and the Blue X-FLR9 analyzer.

Conclusion:

During this week of measurements, analysis in controlled environment have been performed. different concentrations of BTX were measured in different situations and in different matrices, and the results were compared between the Blue X-FLR9 analyzer and the reference method. 2 lab analyzers (FTIR, PTRMS) adapted specifically for high performance measurement at the EUPHORE chamber provided additional measurement points. The results show good accordance of the measurements.

It proved difficult to generate stable HCl concentrations in the chamber. Only the FTIR analyzer provided concurrent measurement, which was in good accordance with the Blue X-FLR9 analyzer.

During the tests, it was also noted that the response time of the Blue X-FLR9 analyzer was rather high (up to 30 minutes to get to a stable concentration, an effect particularly visible on xylenes). The analysis of Blue Industry and Science is that this was due to a hardware modification that was performed on the gas line within the analyzer prior to the tests, and that resulted in reducing the flowrate to 50ml.min^{-1}. The analyzers have since been modified to increase the flowrate back to 100 ml.min^{-1} (which is the standard flowrate of the system).

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