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# REAL-TIME MONITORING OF AIRBORNE VOCS USING MICRODEVICES

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## ABSTRACT

Industrial version of a novel micro-device was deployed during an indoor field campaign on air quality in the framework of IMPACT' AIR project in order to validate and demonstrate its ability to highlight rapid changes of atmospheric BTEX concentrations. During this campaign, our instruments have been able to measure continuously the BTEX concentrations for five weeks in two schools and record small changes in concentrations of these compounds over time related to children activities or ventilation. This information added to the data obtained for CO<sub>2</sub>, allowed us to determine the origin of BTEX in different schools, corresponding to an internal source for toluene or an external source for other BTEX. In addition, during this measurement campaign, it was revealed that it was necessary to make a regular weekly calibration to correct the drift of detector response which remains nevertheless moderate in comparison with other techniques. Our micro-device, of about 5 kg and operating with 2.5mL/min carrier gas consumption, appears to be suitable to monitor BTEX concentrations higher than 1 ppb in near real time.

## PRACTICAL IMPLICATIONS

Our study highlights that the temporal variations of indoor BTEX concentrations is highly correlated to the building's ventilation periods and children's activities. The comparison between BTEX and CO<sub>2</sub> concentrations allows us to determine the origin of each BTEX in different schools.

## KEYWORDS

Microfluidic analytical method, indoor field measurements, portable BTEX microanalyser

## 1 INTRODUCTION

BTEX (Benzene, toluene, Ethylbenzene and Xylenes) are among volatile organic compounds (VOC) widely found in indoor air. They present numerous sources such as cleaning products, building materials and outdoor air supply (Guimarães *et al.*, 2010; Missia *et al.*, 2010; Van Veen *et al.*, 1999). BTEX are harmful to human health at high levels but benzene is carcinogenic even at few ppb (Group 1, IARC, 1982). In this context, the French government has established a threshold of 2 µg m<sup>-3</sup> (0.6 ppb) for benzene in indoor air of public buildings starting in 2018. Many methods are available for indoor BTEX



quantification. The gas chromatography (GC) coupled to different type of detectors such as Flame Ionisation detector (FID), Photoionisation detector (PID) and mass spectrometry MS are widely used because of their low detection limit in ppt level (Aranda-Rodriguez *et al.*, 2015; Liaud *et al.*, 2014). However, these techniques do not provide fast answers because of their resolution time higher than 1 hour making them inappropriate for fast temporal variations of VOCs concentrations. Sensors are alternative solution combining both rapidity and portability required for easier *in-situ* measurements. Although the large variety of existing sensors (Ablat *et al.*, 2008; Barber *et al.*, 1995; Chen *et al.*, 2013; Kumar *et al.*, 2015), they still suffer from poor sensitivity (few hundred of ppb to ppm level) and also have various interferences.

GC remains one of the attractive and powerful tools for VOCs detection and BTEX monitoring. Many portable gas chromatographers are commercially available such as Griffin 460® a transportable GC/MS (FLIR systems, Inc. USA), airTOXIC BTX PID® (Chromatotec-France), VOC 72M® (Environment SA-France) and the GC8900 (Baseline mocon-USA) which are transportable GC/PID. But even if high detection limit is achieved with these instruments (ppt level), their gas consumption (21-50 mL min<sup>-1</sup>) and their weight (13 to 45 kg) remain a big limitation for field investigations.

In this context, our research group reported the development of a novel portable device based on gas chromatography coupled to PID for indoor BTEX detection at ppb level. The first industrial version of the device was recently built. The device is very portable; its final weight does not exceed 4 kg with very low consumption of carrier gas lower than 3.0 mL/min and exhibits a time resolution of 10 minutes. This work aims at evaluating this first industrial prototype under real conditions over several weeks. Indeed, in order to verify its analytical performances, our micro GC was used during a field campaign carried out in two primary schools for five weeks. Other objectives of this campaign were to improve indoor air quality in schools and to highlight the possible sources and the temporal variation of indoor pollutants present in the classrooms. In this work, we report the temporal variations of BTEX with a time resolution of 10 min. Among these compounds, toluene was found as the main VOC in both schools.

## 2 MATERIALS/METHODS

### 2.1 Industrial prototype micro-device

The micro device detecting gaseous BTEX at ppb level was detailed elsewhere (Nasreddine *et al.*, 2016) and its industrial version is described briefly below (**figure 1**).

The system operates according to three steps: i) sampling, ii) separation and iii) detection. During the sampling step, the sampling loop of 200 µL connected to the solenoid 6 port valve is filled with the air sample using a mini air pump. At the same time, the carrier gas is continuously injected into the column using a pressure controller placed at the column input and operating in the range 0-8 bar. Once the sampling step achieved, the 6 port valve is switched on and the carrier gas passed through the sampling loop in order to carry the collected sample toward the capillary column (RXi-624, 20 m long, 0.18 mm i.d., 1 µm film thickness, Perkin Elmer) where the VOC are separated. Finally, the detection is ensured by a photoionization detector (PID) (piD-TECH® eVx Blue, Baseline Mocon, CO, USA) equipped with 10 eV UV-lamp and enclosed in a Faraday shield to inhibit the electronic interferences. All fluidic interconnections were 1/8" and 1/16" Teflon (0.5 mm ID x 1/16" OD, Interchim). The analytical system was standalone, fully controlled by an embedded software which ensured real time chromatograms acquisition, automatic integration of BTEX peaks and concentration calculation. The analytical instrument operates in isothermal mode, the temperature is predefined before any analysis step and no temperature ramp is needed. The carrier gas used during the field campaign was nitrogen. According to our previous results, the nitrogen flow rate was fixed at 2.5 mL min<sup>-1</sup> and the oven temperature at 65°C. These experimental conditions provided a full BTEX separation within only 10 minutes.

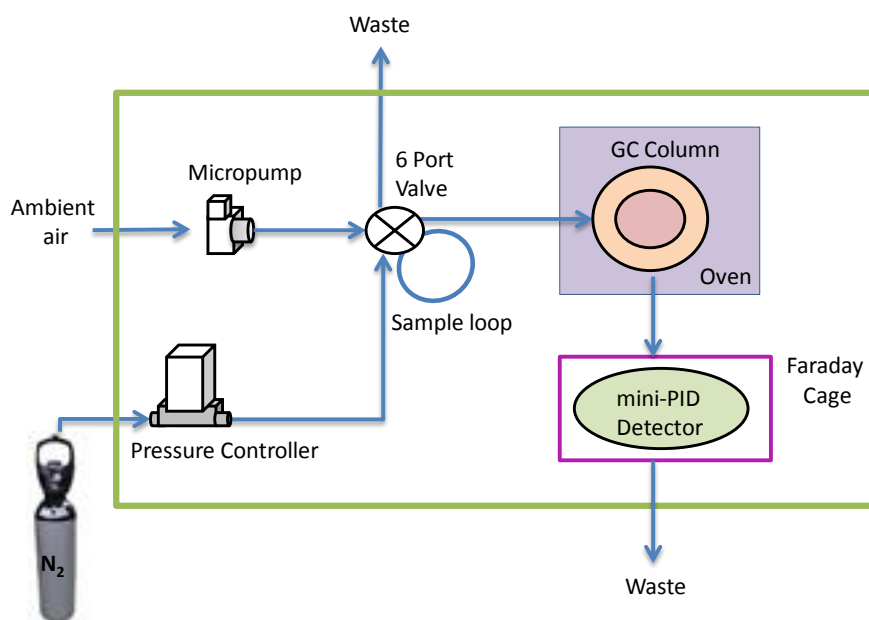


Figure 1 Schematic drawing of the BTEX micro-device operating principle

## 2.2 Description of IMPACT' AIR project

IMPACT' AIR project aims at improving the air indoor quality in schools. This project was carried out in two primary schools of La Rochelle (France) for five weeks. The measurements were performed in a classroom chosen as representative of each school. During this campaign, three regulated pollutants were measured: formaldehyde, benzene and carbon dioxide.

In order to identify the possible sources of pollution and to quantify its contribution, measurements were carried out in different conditions:

- First week: the classroom was empty and no scholar activities were carried out
- Second week: the classroom included the furniture and no scholar activities were carried out
- Three last weeks: the classroom included furniture and normal school activities were carried out

## 3 RESULTS AND DISCUSSION

### 3.1 Instruments calibration

At the beginning of the campaign, a calibration was performed for both instruments, using 3 BTEX concentrations, i.e. 10, 20 and 40 ppb. The detection limit ( $S/N = 3$ ) of our micro-device varied between 1 and 6 ppb depending on the species. The corresponding calibration equations, the correlation coefficient and the detection limits are reported in Table 1.



**Table 1** Equations of calibration curves and detection limits (LOD) of BTEX obtained with both instruments at the beginning of the campaign.

Compound	micro-device		
	Equation	R <sup>2</sup>	LOD* (ppb)
benzene	y = 696x	0.998	1.0
toluene	y = 396x	0.999	1.6
ethylbenzene	y = 225x	0.972	3.5
m-xylene	y = 174x	0.994	6.7
p-xylene			
o-xylene	y = 696x	0.940	6.6

\*LOD (ppb) is determined from S/N = 3.

In addition, punctual short calibrations were performed during the campaign using two chosen concentrations. Table 2 presents the variation of slopes for one BTEX microanalyser calculated by comparison with the first calibration made at the beginning of the campaign (day 1). The micro-device exhibited an acceptable reproducibility with variations lower than 15% along the first 9 days, except for ethylbenzene. These variations reached 10-40% after 21 days. Such observations show a significant loss of sensitivity of this analytical instrument may be due to either the decreasing of its PID lamp power or quartz window soiling of PID. These results highlight the necessity of a regular calibration when the instrument works continuously for a long time (typically more than one week).

**Table 2** Variations percentage of calibration curves of industrial prototype of BTEX microanalyser obtained after 9 and 21 days respectively by comparison with the initial full calibration performed at the beginning of the field campaign (day 1)

Compound	Variation of slopes during field campaign	
	day 9 (%)	day 21 (%)
benzene	-3.7	-10.5
toluene	-5.4	-20.4
ethylbenzene	-25.7	-39.3
m-xylene	-15.2	-33.2
p-xylene		
o-xylene	-3.7	-10.5

### 3.2 BTEX monitoring in the studied classrooms

Once the instruments installed and calibrated, indoor air sampling began for 5 consecutive weeks and instruments worked continuously. In order to identify the possible sources of BTEX, BTEX concentration measurements were performed in different conditions. During the first week, the classroom was empty, doors and windows were closed and nobody was allowed to enter inside the investigated classroom. The second week, the furniture was added but still nobody could enter in the classroom and the doors and windows were closed. Over the three last weeks, normal activity in the classroom occurred.

During the first two weeks, BTEX were not detected (except the second week when paint was applied in the corridor of one of the schools). Consequently, construction materials and furniture did not emit any BTEX. Last three weeks, all BTEX were detected. Among BTEX, the major pollutant found in both classrooms was toluene. Its concentration varied between 0 and 30 ppb depending on children's activities and ventilation. For the other compounds of the family, their concentrations ranged from 0 to 11 ppb, except when paint was applied in the corridor of one of the schools. After painting, concentrations of m+p-xylènes and o-xylène reached very high concentrations, i.e. 60 and 41 ppb respectively.



Carbon dioxide was also continuously monitored by ATMO Poitou-Charentes. The comparison of the different BTEX and CO<sub>2</sub> concentrations reveals the origin of the source of these compounds. For example, concentrations of toluene and CO<sub>2</sub> are correlated together as observed in **figure 2**, suggesting that the origin of toluene is inside of the classroom. Besides, other BTEX concentrations are not correlated to CO<sub>2</sub> one as illustrated in **figure 3** showing that benzene is coming from outside.

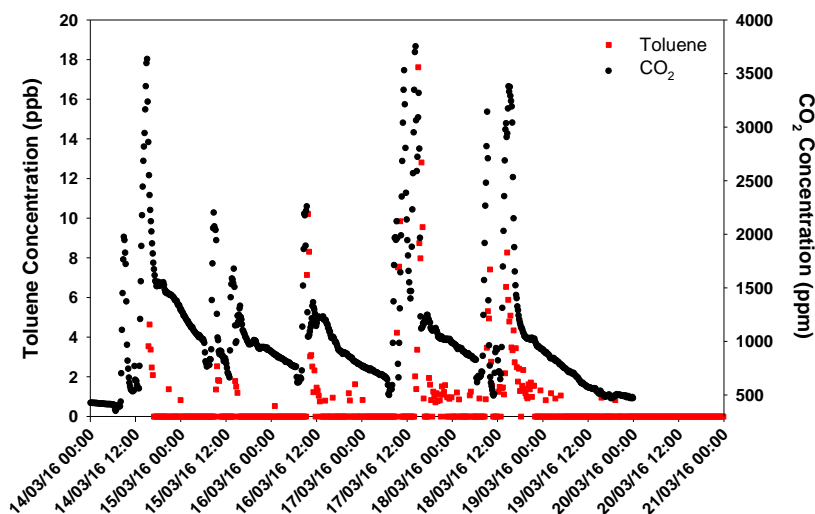


Figure 2 Toluene and CO<sub>2</sub> concentrations measured the fifth week in one of the schools

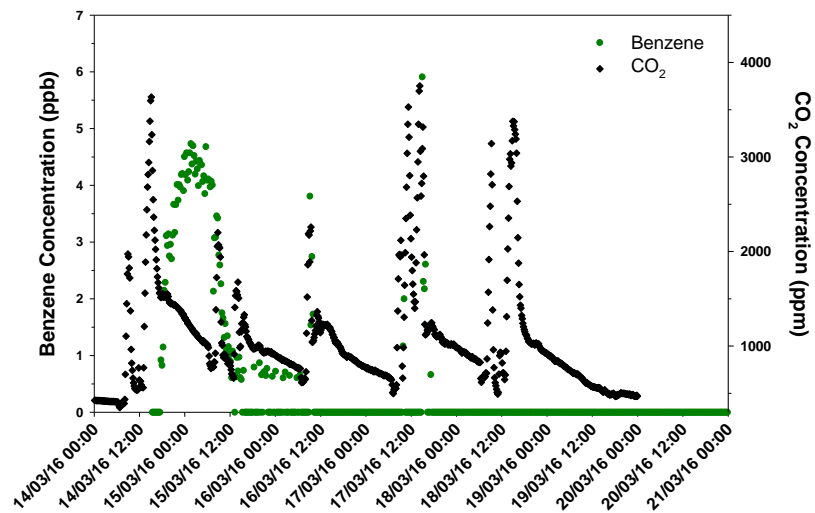


Figure 3 Benzene and CO<sub>2</sub> concentrations measured the fifth week in one of the schools

Furthermore, toluene concentration profiles measured each week of the last three weeks were overlapped in **figure 4**. Some peaks of toluene are observed at very similar given time periods, i.e. Monday, Tuesday and Friday at noon. In addition, toluene was not present during the weekend. These results confirm toluene is emitting by an indoor source and more probably by specific activities of schoolchildren.

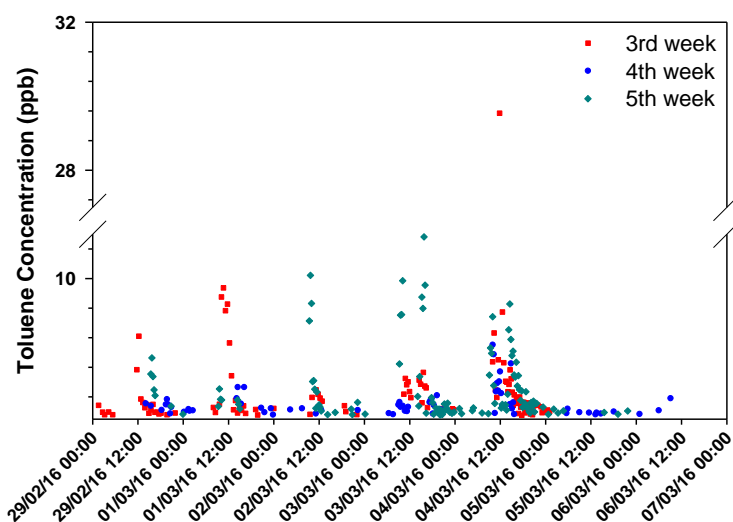


Figure 4 Overlapping of toluene concentrations measured during the last three weeks in one of the schools

## 5 CONCLUSIONS

In conclusion, our compact highly portable and low consumable micro-device has shown its ability to monitor BTEX continuously and to record small changes in its concentration related to children activities or ventilation. In addition, our analyzer presents several significant advantages for field investigations compared to commercial instruments especially in terms of size, carrier gas consumption and electric autonomy thanks to its battery. In, Finally, its low detection limit, consistent with the current guideline value for the indoor air quality, makes our device a perfect tool for indoor air quality monitoring.

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