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Portable novel micro-device for BTEX real-time monitoring: Assessment during a field campaign in a low consumption energy junior high school classroom

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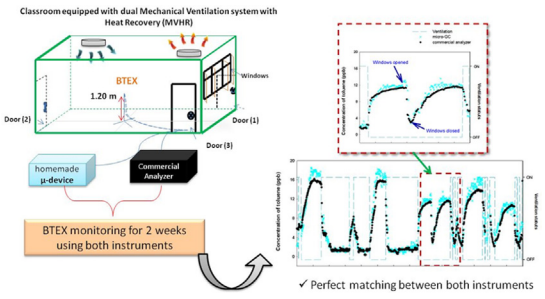
HIGHLIGHTS

- Assessment of a novel portable analytical micro-device during a field campaign.
- Indoor toluene concentration variations according to the ventilation.
- BTEX measurements performed in a low energy consumption junior high school classroom.

GRAPHICAL ABSTRACT



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ABSTRACT

A novel micro-device was deployed during an indoor field campaign to validate and demonstrate its ability to highlight rapid changes of atmospheric BTEX concentrations. The field campaign was carried out in a junior high school recently built respecting the thermal regulation of 2005 and equipped with a modern ventilation. BTEX concentrations were continuously measured using the novel micro-device and a commercial analyzer for two weeks during the winter holidays, both operating with a time resolution of 10 min. Toluene appeared to be the major VOC inside the investigated classroom. Its concentration varied between 1 and 18 ppb and was strongly correlated with the room ventilation status. This latter was partially programmed to mimic the school period. In order to compare the efficiency of the ventilation with natural ventilation, the windows were opened for 1 h when the ventilation was OFF. In all tested conditions, the toluene concentrations measured with our new micro-device were in very good agreement with those provided by the commercial BTEX analyzer. In addition, punctual short calibrations were performed during the campaign for both instruments (after 4 days and 9 days). Results showed that our micro-GC was more stable (gap less than 15% after 9 days) while the commercial analyzer required regular calibrations because of the loose of 60% of its sensitivity after 9 days of

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continuous operation. Therefore, our micro-device, of about 3 kg and fully controlled by homemade software, appears to be suitable to monitor BTEX concentrations higher than 1 ppb in near real time.

1. Introduction

BTEX (Benzene, toluene, Ethylbenzene and Xylenes) are among volatile organic compounds (VOC) widely found in indoor air where their main sources are cleaning products, building materials and outdoor air supply (Guimarães et al., 2010; Missia et al., 2010; Van Veen et al., 1999). Due to their harmful effects on human health and particularly their carcinogenicity, the European Union has established a threshold value of 5 μg m^{-3} (1.6 ppb) for benzene in indoor air of public buildings (Group 1,IARC, 1982), while other compounds of the family such as ethylbenzene and xylenes are considered to be known or probable carcinogens for humans (Group 2A or 2B,U.S. Environmental Protection Agency, 1999).

Many methods are often used for indoor BTEX quantification. These methods could be divided in several following categories.

The first category corresponds to laboratory gas chromatography (GC) coupled to different types of detectors such as Flame Ionization Detector (FID), PhotoIonisation Detector (PID) and Mass Spectrometry (MS) which are the most used (Aranda-Rodriguez et al., 2015; Liaud et al., 2014; Woolfenden, 1997). These techniques are very sensitive, presenting a detection limit at the sub-ppb level. They are often used for off-line analysis, i.e. those performed in the laboratory after passive or active *in-situ* sampling. They can also be used in an on-line mode; they have a typical time resolution higher than 1 h and therefore are not suitable for the monitoring of fast temporal variations of VOCs concentrations.

The second one is dedicated to the very sensitive and rapid techniques for BTEX quantification and detection. Open-Path Fourier Transform Infra-Red (OP-FTIR) spectroscopy and Proton Transfer Reaction coupled to Mass Spectrometry (PTR-MS) are the main ones (Brilli et al., 2014; Grutter et al., 2003; Lindinger and Jordan, 1998). Nevertheless, they present a major limitation in terms of weight and prices which limit their use for field monitoring. Sensors are alternative solutions combining both rapidity and portability required for easier *in-situ* measurements. Despite 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 are also prone to various interferences. Other attempts were conducted to develop compact BTEX analyzers based on UV detection and operating in near real time with detection limits of few tens of ppb (Allouch et al., 2013; Ueno et al., 2003) which is again one order of magnitude higher than the threshold value fixed by the European Union.

Finally the third category consists in the portable gas chromatography which remains one of the attractive and powerful techniques for indoor air monitoring and particularly for BTEX detection (Garg et al., 2015; Narayanan et al., 2013; Sklorz et al., 2012; Xu et al., 2010). For instance, some transportable GC/MS such as Griffin 460® (FLIR systems, Inc. USA) are commercially available. Despite its high sensitivity, the instrument's weight of 44 kg remains a big limitation for field monitoring. Other commercial GC coupled to PID are also available, such as GC/PID 8900® (Baseline mocon-USA), airTOXIC BTX PID® (Chromatotec-France) and VOC 72M® (Environment SA-France). All these GC-PID are very sensitive (sub-ppb level) and provide answers in near real time (10–30 min). For example, Liaud et al. (2014) reported detection limits of 0.058 and 0.142 ppb (S/N = 3) for benzene and toluene, respectively. But these transportable instruments are still not totally suitable for field monitoring. Indeed, their weight range between 15 and 20 kg and their carrier gas consumption can reach up to 50 mL min^{-1} because of the use of a makeup gas before the detector.

In this context, we recently reported the development and the optimization of a novel portable micro-GC based on photoionisation detection able to detect BTEX at ppb level (Nasreddine et al., 2015). The device is very portable; its final weight does not exceed 4 kg with a very low consumption of carrier gas, ca. less than 3.0 mL min^{-1}. This new device operates according to two consecutive steps, sampling and analysis. The system is standalone, fully controlled by homemade software and exhibits a time resolution of 10 min.

In order to assess its analytical performance, our micro-GC was used during a field campaign aiming at highlighting the temporal variations of various pollutants concentrations inside a newly built junior high school that follows the French thermal regulation of 2005 under the MERMAID project (Schoemaecker et al., 2014). The campaign was carried out during the winter holidays from February 23rd 2015 till March 6th 2015. The school was equipped with a dual flow controlled mechanical ventilation system with heat recovery (MVHR). The ventilation system aimed to ensure a good Air Exchange Rate (more than 2 h^{-1}) to provide a healthy atmosphere inside classrooms since many studies have shown the relation between the indoor air quality and the student achievements (Bakó-Biró et al., 2012; Mendell and Heath, 2005). In this work, we report with a time resolution of 10 min the temporal variations of toluene which was found as the main VOC in the classroom. The measurements performed with our micro-GC were compared to those obtained with the commercial GC/PID 8900®-Baseline during the two weeks of measurements.

2. Materials and methods

2.1. Prototype of the micro-GC instrument

The micro-GC-PID (Fig. 1) detecting gaseous BTEX at ppb level was detailed elsewhere (Nasreddine et al., 2015) so that only a brief description is given here.

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 ports valve (between ports 2 and 5) (1/16″ valve, MTV-6LL-N32UF-1, Takasago, Japan) is filled with the air sample. The sampling is insured by a mass flow controller with a dynamic range of 0–100 mL min^{-1} (El-Flow, Bronkhorst, France) placed before a mini air pump (270 EC, Schwarzer, Germany) to obtain a constant flow inside the loop. At the same time, the carrier gas is continuously injected into the column using a pressure controller (IQ+ Flow, Bronkhorst, France) placed at the column input and operating in the range 0–8 bar. Once the sampling step is achieved, the 6 ports 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 VOCs are separated. Finally, the detection is ensured by a PID (piD-TECH@plus white, Baseline MOCON, CO, USA) equipped with 10.6 eV UV-lamp and enclosed in