Easy-to-manufacture micro gas preconcentrator integrated in a portable GC for enhanced trace detection of BTEX

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ABSTRACT

Air pollution is a current environmental and global public health issue, which requires technological developments to monitor airborne pollutants such as Volatile Organic Compounds (VOCs). These organic species are dangerous for humans even at trace levels.

In this regard, an analytical device can be advantageously coupled with a preconcentration system to improve its sensitivity. In this context, a novel preconcentrator was conceived, manufactured, and tested inside an existing portable gas chromatograph (GC). With a very limited gas sample of 20 mL, the limits of detection achieved are 0.057, 0.150, 0.368, 0.396, 0.418 ppb for benzene, toluene, ethylbenzene, m-/p-xylenes and o-xylene, respectively. These values enable the system to monitor air quality even in the environments with the strictest regulation (0.6 ppb for benzene). Besides, the comparison with the literature demonstrates that the present analytical device is from two to three orders of magnitude more sensitive than the previous ones when detection limit is expressed in pg.

The repeatability and reproducibility experiments show that the measurements are reliable and stable over time, while maintaining a reasonable time resolution of 19 min which can be easily reduced to 15 min by a full automation. Moreover, the average power consumption of the system was limited to 61 W allowing the system to work autonomous and battery powered. Finally, this preconcentrator can be conveniently fabricated without the need for a cleanroom and the simplicity of the design provides an easy way to replace the adsorbent broadening the range of VOC that can be detected.

1. Introduction

Air pollution is a current environmental and global public health issue. Indeed, it is now recognized that indoor and outdoor air pollution is responsible for many effects on human health [1]. This evidence promotes studies on air quality and technological developments to measure atmospheric pollutants. Outdoor air pollution has been studied since the 1950s because it is visible in particular during photochemical smog formation [2]. Indoor air pollution has long been ignored but has been the subject of numerous recent studies, in particular for the two last decades [3–6].

Among the air pollutants, Volatile Organic Compound (VOCs) are of particular interest because they are the most abundant in indoor air [6, 7]. They are precursors of photochemical smog in outdoor air [7] and participate in chemical reactions in indoor environments [8–10]. This group of molecules is defined by the European council as compounds having a vapour pressure of 0.01 kPa or more at 293 K. VOCs includes a broad spectrum of molecules characterized by structures formed by carbon chains and, in some cases, other atoms like oxygen, sulphur, or nitrogen.

Their atmospheric degradation in both outdoor and indoor generates oxidation products in gas phase such as carbonyl compounds (aldehydes, ketones, etc.) [11,12] or Secondary Organic Aerosols (SOA) [13]. VOCs include many sub-families of molecules: alkanes, alkenes, aromatic compounds, aldehydes, ketones, ethers, esters, amines, etc. [11]. Their airborne concentrations usually vary from a few tens of ppt to

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several hundred ppb depending on the considered environment, e.g. indoors and outdoors, and the proximity of pollution sources [6,11,14]. In addition, they can have direct harmful effects on health because some of them are highly toxic or even carcinogenic, even at very low doses in the ppb range. This is for example the case of benzene [14] or formaldehyde [15].

VOCs are usually quantified using optical or chromatographic techniques [16]. Nevertheless, VOCs analysis at these low concentrations remains an analytical challenge. Indeed, such low concentrations imply the development of extremely efficient and sensitive analytical tools to measure them in the atmospheric compartment. This difficulty can be overcome by taking an air sample over a very long period up to a full week, for example on adsorbent tubes. Alternatively, a large amount of air typically varying between several tens to several hundred liters, or even several m^3 can be collected as it is performed in the case of Semi-Volatile Organic Compounds (SVOCs) [17]. After sampling, the organic species are then analyzed off-line in the laboratory using benchtop instruments, chemical (solvent) or thermal desorption, gas or liquid chromatography being the most widely used techniques [17].

Among VOCs, BTEX, i.e., Benzene, Toluene, Ethylbenzene and Xylenes, have been studied extensively because of their relatively high airborne concentrations up to hundreds of ppb, their occurrence in air and their toxicity [12,18]. In 2013, a threshold value of 5 µg m^{-3} (1.6 ppb) for benzene was therefore set by the European Union in public buildings. In France, this limit was decreased to 2 µg m^{-3} (0.6 ppb) in 2018. Thus, many analytical tools incorporating a preconcentration device have been either developed and tested for these specific aromatic compounds [18]– [20].

Nevertheless, detecting such ppt concentrations in near-real time becomes challenging. Some suitable analysers are sensitive enough to quantify some VOCs families and more particularly BTEX but they are still very bulky, heavy, and require high energy consumption [21,22]. Therefore, their use for on-site measurements is limited. These facts evidence the need for a portable and accurate device able to monitor VOCs and BTEX concentrations in near-real time.

However, in the case of a near-real time measurements, a preconcentration system is almost essential to reach thresholds of a few tens or a few hundred ppt. Moreover, many preconcentration systems have been developed in recent years for the detection of different VOCs such as BTEX, alkanes, ketones and alcohols, as illustrated in Table 1. Most of these preconcentrators are based on microfluidic systems manufactured using MEMS-technologies [23]– [27] which are miniaturized and have low energy consumption but still remain fragile and lack of reliable fluidic connections. In addition, the fabrication of these microfabricated devices requires the use of cleanrooms that are not always available in research facilities being often subcontracted which increases the cost and time of the manufacturing process. Recently, 3D printing or micromilling have been employed as alternative fabrication techniques for the fabrication of miniaturized components. At present, these techniques do not allow to fabricate devices as smaller as microfabrication techniques, but these devices are more robust, allow the use of standard fluidic connections and can be fabricated in any laboratory without the need for cleanroom facilities.

This work follows development of a portable and battery powered BTEX analyser operating without any preconcentration step and able to detect concentrations as low as 1−2 ppb within a 10-minutes analysis [28,29], its sensitivity being not sufficient for the standards required by the public authorities for benzene [30,31]. The present work also follows the development of a previous preconcentrator prototype already published by Lara-Ibeas et al. [18]. That system was able to preconcentrate BTEX enough to reduce the limits of detection down to 0.20, 0.26, 0.49, 0.80 and 1.70 ppb for benzene, toluene, ethylbenzene, m/p-xylenes and o-xylene, respectively. However, the system had important energy consumption limitations since it required 210 W of power supply in the heating step. This characteristic is incompatible with a system that needs to be battery-power and stand-alone.

To tackle this issue, the present work aimed to conceive, manufacture, and validate a robust novel preconcentration unit enhancing the sensitivity and combining low energy consumption, fast heating, and rapid cooling while being fabricated by a simple process not requiring specific facilities. The analytical performances of this novel preconcentrator were evaluated under controlled laboratory conditions by testing different concentrations (5−50 ppb) and sample volumes (5−50 mL). Repeatability and reproducibility were also evaluated.

2. Materials and methods

2.1. The existing portable gas chromatograph (GC)

The portable gas chromatograph (GC) employed in this study was codeveloped by the Institute of Chemistry and Processes for Energy, Environment and Health (ICPEES, Strasbourg, France) and In'Air Solutions (µBTEX-1, In'Air Solutions, France). It operates in three steps: sampling, separation and detection [28]. Sampling is performed by means of a SP 570 EC-BL micropump (Schwarzer Precision, Germany) connected to an EL-FLOW flow controller (Bronkhorst, Ruurlo, Netherlands). Air samples are pumped and introduced in a PEEK (Polyether ether ketone) 200 µL sampling loop (Interchim, France) connected to a solenoid 6-port valve (MTV-6LL-N32UF-1, Takasago, Japan). Once the sampling loop is filled, the 6-port valve switched for 20 s, and the sample is injected into the chromatography column. Separation step is carried out using a commercial 20-m long capillary column (internal diameter (ID) 0.18 mm, RXi-624 stationary phase, 1 µm film thickness, Restek, Bellefonte, PA, USA) with nitrogen as a carrier gas. Polydimethylsiloxane (PDMS) is a non-polar stationary phase typically employed for BTEX separation. It provides high resolution but since the interaction of PDMS with aromatic compounds is relatively strong, separation times are long. In environmental monitoring, a balance between short analysis time and reasonable resolution is required, therefore, the column used is slightly more polar (Rxi-624Sil MS). Detection is conducted employing an eVx Blue mini photoionization detector (PID) (Baseline MOCON, Lyons, CO, USA) equipped with a 10.6 eV ultra-violet lamp. This GC prototype is controlled by an integrated computer using a specific GUI (Graphical User Interface) codeveloped by In'Air Solutions and ICPEES.

In a previous study [32], a nitrogen flow rate of 2.5 mL min^{-1} and a constant temperature of 80 °C were selected as the optimal conditions for BTEX separation. Using these conditions, BTEX analysis was performed in 10 min and detection limits between 1–3 ppb were found for the different species. Analytical performances of this device were validated under controlled laboratory conditions [32] and in real environments [29,33].

2.2. The novel preconcentration unit

As mentioned above, a preconcentration device operates in several stages: 1) adsorption of gaseous molecules at room temperature; 2) desorption of the molecules at a higher temperature and their injection into the GC column for separation and 3) cooling down to room temperature before the next sampling and analysis.

The Fig. 1 displays the preconcentration unit developed in this work including housing and connections. This preconcentrator was manufactured in our research lab using micromachining techniques. An aluminum board of 30 × 15 × 5 mm was machined into the device shown in Fig. 1a. In this piece, the lateral tubes had an outer diameter of 1/8 inch and an inner diameter of 1/16 inch. The dimensions of the central rectangular part were 14 mm long, 12 mm wide and 3.2 mm tall. These cylindrical parts were polished to fit very tight inside the gas connectors as shown in Fig. 1b. This device was fabricated using traditional milling techniques that imply the use of cutting oils to cool and lubricate the material during the machining process. Therefore, once the device fabricated, it was washed several times with acetone in an

Table 1
Summary of miniaturized GC with integrated preconcentrators developed in the last years.

Ref.	Size (cm³)	Weight (kg)	Analysis time (min)	Sample Volume (mL)	Preconcentrator l (mm) × d (μm) × w (mm)	Material	Adsorbent	Heating system	Power cons. (W) / heating rate (°C/s)	Target compounds	Det.	LOD (ppb)	Sensitivity (pg)
This work	32 × 29 × 14	~ 5	19	20	Cavity 4.6 × 350 × 7.4	Al	C-B 5 mg	Ceramic heaters	~44 / 4.8	BTEX	PID	0.06−0.4 (BTEX)	3.6 [b]
PEMM-2 [24]	20 × 15 × 9	~2.1	3	5	2 Cavities (V~4.7 μL)	Si-glass	C-B 2.0 mg C-X2.3 mg	Ti/Pt	1 / -	9 VOC	μCR array	16–600 (150 [b])	2396 [b]
MAP [18]	32 × 29 × 14	~ 5	19	20	Manifold-shaped cavity 4.6 × 350 × 7.4	Al	Basolite C300 5.8 mg	Cartridge	210 / 2.5	BTEX	PID	0.1−1.6 (BTEX)	6.4 [b]
GC-PID [21]	31 × 30 × 20	32	~35	4000	Tube 0.165 cm i.d.	–	ResSil-B 75 mg	–	–	34 VOC	PID	0.002−0.011 (BTEX)	140.6 [b]
Ceramic PC [37]	–	–	~50	200	Manifold shaped cavity 61 × 5.5 mm × 23 mm	Ceramic	C-SII 1.187 g	Tungsten	18 / 0.25	Ethylene	EC	25	5736
GC-MOS [36]	n. d.	n. d.	9	250	Cavity with micro-pillars 10 × 400 × 5	Si-glass	Zeolite DaY ~13 μm	–	–	4 VOC	MOS	24 [t]	22,611 [t]
GC-PID [25]	n. d.	n. d.	6	–	4 Parallel channels n.d × 400 × 0.6 μm	Si-glass	SWNTs 0.15 mg	Cr/Pt	–	5 VOC	PID	< 1 [b]	–
Frog 4000 [40]	25 × 19 × 37	< 2.2	5.5	–	n. d.	Si-glass	Silica gel aerogel	–	–	–	PID	~ ppb	–
GC-PID [19]	n. d.	n. d.	63	600	Parallel channels 25 × 1.3 mm × 12	Si-glass	EtQxBox 10 mg	Pt	- / 50	Benzene	PID	1.25 [b]	2396 [b]
GC-PID [22]	60 × 50 × 10	< 5	16.2	50	Tappered cavity 8.15 × 250 × 2.9	Si-glass	C-B 1.135 mg	Pt	- / 314	50 VOC	μPID	n. d.	–
GC-CMOS [23]	16 × 11 × 11	n. d.	n. d.	–	Cavity with micro-pillars 10 × 250 × 2	Si-glass	Carbon film	Ni-Cr wire	–	7 VOC	CMOS	15 (1,3,5-TMB)	–
iGC3.2 [27]	8 × 10	n. d.	130	24	U shape n.d. × 300 × 1350	Glass	C-B + C-X	Ti/Pt	10.5 / 46	19 VOC	2 CD	10 − 2 (BTEX)	766.7 [b]
Zebra GC [26]	15 × 30 × 10	~1.8	< 12	10	Cavity with micro-pillars 13 × 240 × 13	Si-glass	Tenax TA ~200 nm	Cr/Ni	16 / 25	6 VOC	TCD	~25 (TEX)	942.1 [b]
GC-MOX [20]	n. d.	n. d.	~67	2750	Ten parallel channels 800 *m depth	Si-glass	QxCav	Pt	- / 50	Benzene	MOS	0.1	878.5 [b]

[b]: benzene; [t]: toluene; CR: chemiresistor; S.S.: stainless steel; O.D.: outer diameter; MOS: Metal Oxide Semiconductor; CD: Capacitive Detector. CMOS: Complementary Metal Oxide Sensor. MOX: Metal Oxide sensor. QxCav: Quinoxaline bridged Cavitand; EC: electrochemical sensor; *this PC is not integrated in a miniaturized GC.
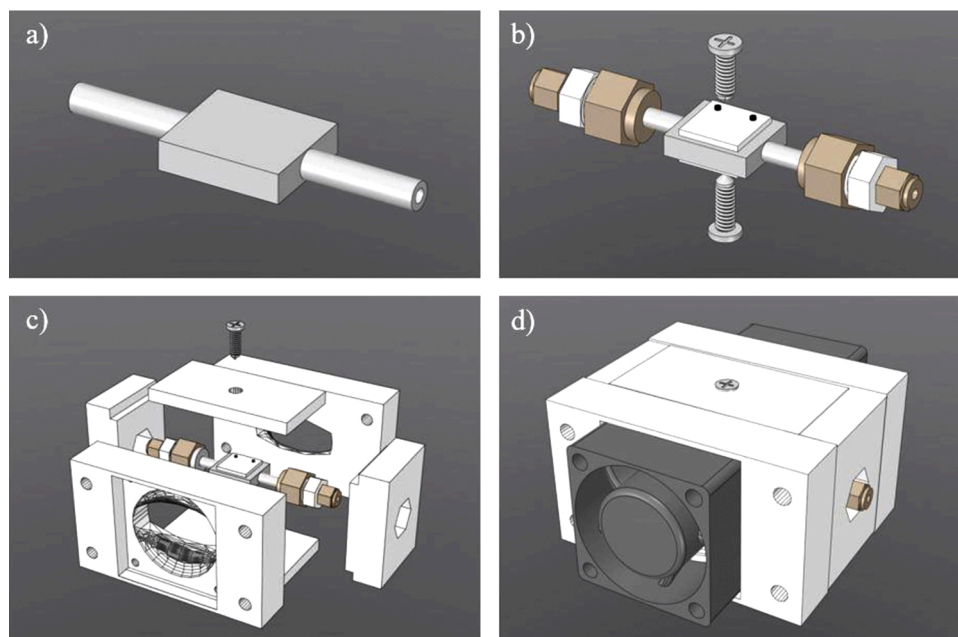
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Fig. 1. Miniaturized preconcentrator 3D design (a) Aluminum block machined and drilled. (b) Aluminum block (light grey), PEEK connectors (brown and white), ceramic resistances (white) and screws (dark grey) (c) System of the Fig. 1b inside its disassembled housing (white). (d) System of the Fig. 1c assembled with fans (dark grey).

ultrasounds bath for 2 h and then rinsed with deionised water. Afterwards, it was heated to 200 °C under a 20 N mL min^{-1} nitrogen flow for 1 h.

Two homemade PEEK reducing unions were inserted in each side of the preconcentrator. These 1/8"-1/16" PEEK connectors were manufactured according to the dimensions of the equivalent connectors in stainless steel provided by Swagelok (Villebon-sur-Yvette, France) and fulfilled two main functions. On the one hand, they had a standard connection of 1/16 inch which allowed the system to be easily integrated into the BTEX analyser. One the other hand, these polymer connectors isolated the metallic part of the preconcentrator avoiding heat losses and allowing the system to achieve 200 °C in 24 s by providing a limited energy, i.e., 24 V and an initial nominal current of 3 A. Note that the current decreased while the temperature increased.

The temperature increase was generated with two ceramic resistances of 7 ohm (Ceramic heating XH-RJ101012, Plexishop, Italy). Its dimensions were 10 × 10 × 1 mm which fitted almost completely the surface of the rectangular aluminum block. These ceramic resistances were pressed towards the preconcentrator using two 3 × 16 mm plain stainless steel screws, one at each side, to assure the contact between the resistance and the rectangular aluminum block. A thermocouple was inserted in a small hole located in the central part of micro-preconcentrator close to the adsorbent bed, in order to accurately monitor the temperature.

A housing consisting of 6 pieces was assembled around the pre-concentrator as shown in Fig. 1c and d. Initially, the assembly had to be done carefully to place the ceramics in the middle of the flat parts of the aluminum block while ensuring good contact to obtain optimal thermal conduction. To facilitate this assembly, the two resistances were glued to the aluminium preconcentrator before the assembly using a tiny amount of liquid glue. Once the resistances were fixed, the preconcentrator was easily installed inside the housing and the two screws were slightly screwed to hold the heating ceramics on place while minimizing the mechanical stress. In this configuration, this housing kept the pre-concentrator in the centre and avoided its contact with other parts except for the screws. Each lateral part of the housing had a square cavity to host a small fan. These fans were used to quickly cool down the system once the desorption step was finished. Thermal paste was tested

but it did not provide any visible improvement in terms of heating rate, tending to prove that the contact between the aluminum block and the two ceramic resistances was optimal in our conditions. Therefore, all the results presented below were obtained without the use of thermal paste.

Before its use, the preconcentration unit was filled with 5 mg of Carbopack B (SUPELCO, Bellefonte, PA, USA). The adsorbent was manually packed inside the cylindrical cavity of the aluminum block and held between two glass wool plugs (Sigma Aldrich, France). Afterwards, it was conditioned at 220 °C under a nitrogen flow of 20 N mL min^{-1} overnight to remove all the volatile impurities. When the resistances are heated up for the first time the glue is evaporated and degraded leaving only a tiny spot of solid, so small that it does not have any significant impact on the heat transfer efficiency. Note that the device does not need to be disassembled once it is manufactured except for maintenance to replace adsorbent or the aluminum block itself filled with a new adsorbent.

The production cost of this preconcentrator was then estimated from the production of a series of 100 units. The combined price glass wool and 5−6 mg of adsorbent was found to be close to one euro per unit. The total subcontracting cost of the production of mechanical parts, i.e., the aluminum board, the two PEEK gas connectors, and the housing, was evaluated at 80–100 euros per preconcentrator unit. The price of two heating resistances, two small fans and two adequate temperature sensors were estimated to be around 40–50 euros per preconcentrator unit, the overall production cost being of the order of 120–150 euros for one preconcentration unit.

2.3. Preconcentrator integration into the GC

The preconcentration unit was placed inside the 3D printed housing and connected to the solenoid 6-ports valve of the existing portable gas chromatograph by means of short 1/16 inch tubing, replacing the 200 μL sampling loop, as displayed in Fig. 2. These tubes had an inner diameter of 250 μm to minimize the dead volumes (see Fig. 2b).

The experimental conditions used for GC analysis are summarized in Table 2. The sampling flow rate was set to 5 N mL min^{-1} for a duration ranging between 1 and 10 min, allowing to obtain a final sampling volume of 5−50 mL. Once the gas pollutants adsorbed into the
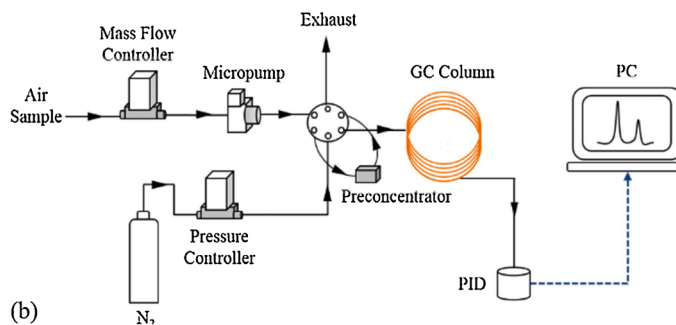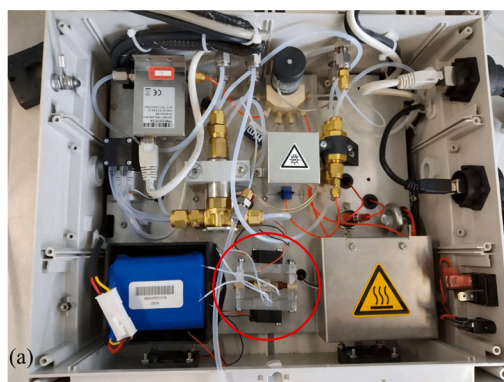
Fig. 2. (a) Picture of the preconcentrator prototype located inside the commercial BTEX analyser (μBTEX-1, In'Air Solutions, France) and **(b)** schematic view of the device.

Table 2
Summary of the experimental conditions employed in a series of tests with the novel preconcentration unit.

Parameter	Setpoint	Parameter	Setpoint
Temperature GC column (°C)	45	Sampling flow rate (NmL/min)	5
Pressure GC column (bar)	4.2	Adsorption temperature (°C)	R.T.
Injection time (s)	75	Desorption temperature (°C)	330 °C

R.T.: room temperature.

preconcentrator at room temperature (22 ± 3 °C), the 6-port valve was switched to injection mode for 75 s and simultaneously the preconcentrator was heated up to the desorption temperature, i.e., 330 °C while the carrier gas flushed the preconcentrator at 2.5 N mL min^{-1} to inject the mixture into the same chromatographic column (20 m, 0.18 mm, 1 μm, Rxi-624Sil MS) used by Nasreddine et al. (2015) [28,29] and Lara-Ibeas et al. (2019) [18] for separation. The pressure at the top of the column was maintained at 4.2 bars.

2.4. Experimental setup for BTEX generation

Different BTEX concentrations were generated using the experimental device shown in Fig. 3. A standard mixture of BTEX purchased from Messer (Folschviller, France) was diluted with nitrogen (99.999 % purity) using mass flow controllers 1 and 2 (Bronkhorst, Ruurlo, Netherlands). The initial concentration of every compound was equal to 100 ppb with a 10 % uncertainty. This setup allows generating different concentrations in the range 2–100 ppb. Mass flow controller 3 was used to select the sampling flow rate which was set to 5 N mL min^{-1} for all the experiments.
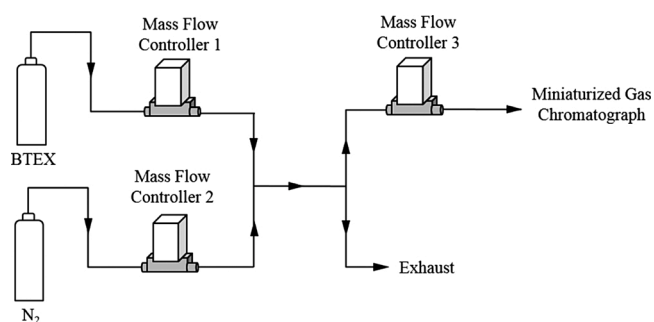

Fig. 3. Experimental setup for BTEX generation.

3. Results

3.1. Heating and cooling

Experiments were conducted by applying a nominal voltage of 28 V and an initial nominal current of 3.00 A for both resistances connected in parallel. The average power consumption over the 70 s of heating was 61 W, decreasing down from 84 W at the beginning of the experiment to 53 W at its end due to the thermal resistance variability. The thermal behaviour of the preconcentrator was experimentally observed by inserting a Type K Thermocouple (RS PRO, Corby, UK) inside the aluminum board close to the adsorbent bed. Several cycles of heating and cooling simulating the adsorption/desorption cycles were performed using two standard screws to maintain the heating resistances, the results being similar in all the cycles. A typical temperature behaviour is presented in Fig. 4a. In this figure the red dashed line represents the end of the heating step while the blue dashed line represents the beginning of the forced-convection cooling with the fans. As it can be observed, 200 °C were reached in 20 s which appeared sufficient for the full BTEX desorption as observed by Liaud et al. (2014) [34] when these authors used an Automatic Thermal Desorber (PerkinElmer, ATD350, France). From 200 °C, temperature linearly goes up and reaches 330 °C in 68 s. These latter conditions were chosen to perform the BTEX analysis experiments detailed below to limit as much as possible the non-desorbed BTEX residues. Note that the absence of automation for the desorption and injection stage did not allow very sophisticated heating ramp as for example to maintain the temperature at 220−250 °C for a given duration. In these conditions, a temperature equal or higher to 200 °C inside the adsorbent bed was maintained for about 55 s during the injection mode corresponding to the time-period from 0 to 75 s. Once the fans switched on, the cooling down to the room temperature, i.e. 20−25 °C, was achieved in approximately 2 min (see Fig. 4a). Note that in absence of forced-convection cooling, the temperature decreases slowly down to the room temperature in 15 min as illustrated in Fig. 4b.

The commercial BTEX analyser runs with a battery having a capacity of 94 W/h, permitting to operate for 4 h in normal conditions, i.e. 16 consecutive analysis of 15 min. The integration of this novel preconcentration unit will lead to an additional theoretical power consumption of 4.74 W/h (61 × 4 × 70 / 3600) for four analysis per hour. The additional power consumption related to the preconcentration unit is thus estimated to 19.0 W for 4 h, which corresponds to about 20 % of the full battery energy. In other words, the integration of the novel preconcentrator would reduce autonomy by 20 %, i.e. 192 min instead of 240 min. This would permit to perform 12 consecutive chromatographic gas analysis.
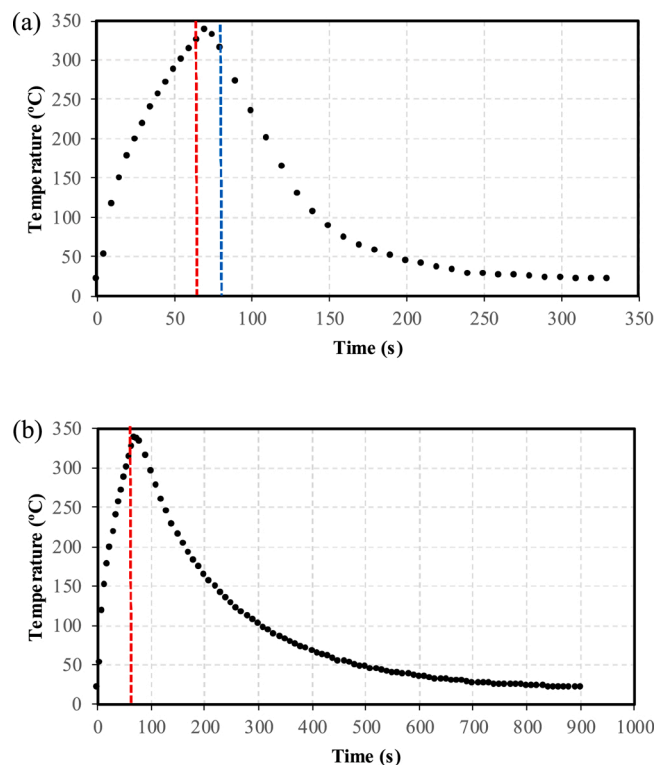
Fig. 4. Heating and cooling performances of the miniaturized preconcentrator using a nominal voltage of 28 V and nominal current of 3 A in combination with a) a forced-convection cooling and b) a natural-convection cooling. Red-dashed line represents the switching-off of the resistances, while the blue-dashed line represents the switching-on of the fans. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

3.2. BTEX analysis

The preconcentrator was tested through a structured sequence of experiments. These experiments aimed to determine the reproducibility, repeatability, and correlation between the amount of BTEX injected and the PID signal detected.

3.2.1. GC calibration as a function of gaseous concentrations
Calibration of the BTEX analyser integrating the novel micro-precontrator was conducted by injecting a series of 20 mL samples of different concentrations ranging from 2 to 50 ppb in triplicate. A
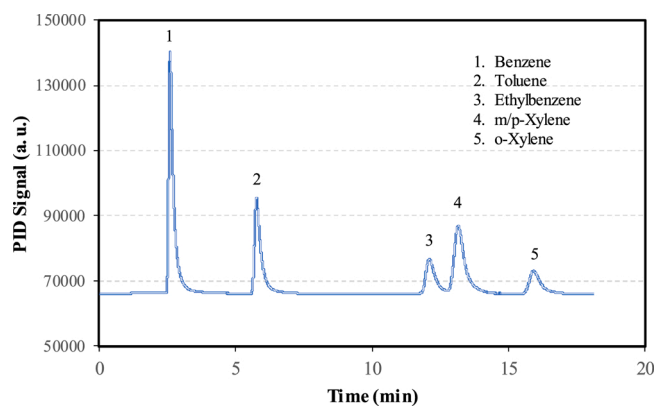

Fig. 5. Chromatogram of BTEX obtained with the BTEX analyzer integrating the micropreconcentrator. Sample volume = 50 mL, C_{BTEX} = 20 ppb, desorption temperature = 330 °C, injection time = 75 s.

chromatogram of a 20 ppb BTEX sample of 50 mL is displayed in Fig. 5. As observed, BTEX peaks are well-defined and much less peak broadening is observed compared with the previous preconcentrator version detailed by Lara-Ibeas et al. (2019). Longer analysis time due to a lower oven temperature (45 °C instead of 70 °C) was necessary to obtain a satisfactory chromatographic separation. The improvement in terms of peak shape is due to the faster temperature ramp inside the micro-precontrator that allows the desorption of analytes in less time, thus producing a narrower peak compared to the previous version developed by Lara-Ibeas et al. (2019). The mean peak areas of the analysed samples were plotted against the injected concentration and the resulting calibration curves are shown in Fig. 6 where the quoted errors correspond to the standard deviation. The peak areas increase linearly with the injected concentration for all the compounds. Determination coefficients R^2 are higher than 0.99 for all compounds as shown in Table 3.

As expected, calibration slopes decrease with the volatility of the compound, being considerably steeper for the most volatile compounds, i.e. benzene and toluene. Between injections, a cleaning step consisting of rising the temperature from 250 to 350 °C five times was performed to ensure the complete desorption of BTEX before the next analysis (more details on the residuals analysis are given below in the "GC calibration as a function of sample volume" section). It should be noted that this was done manually but could be automated and driven by the software in the future, when this preconcentrator will be integrated into the commercial device.

Detection and quantification limits of the GC system were calculated from a signal-to-noise ratio of 3 and 10, respectively, from the lowest injected concentration, i.e. 2 ppb. Detection limits are in the hundreds of ppt order or even less for benzene with only 20 mL of sample for all compounds whereas quantification limits exceeded the ppb in the case of ethylbenzene and xylenes (see Table 3). It is important to note that this extraordinary sensitivity meets the requirements of the indoor air quality French legislation fixing a benzene threshold value of 0.6 ppb in public buildings.

3.2.2. GC calibration as a function of sample volume
As increasing the sampling volume can improve the sensitivity of the instrument, it is important to study this parameter. GC linearity was also evaluated when varying the injected sample volume from 5 to 50 mL for a fixed gaseous BTEX concentration of 20 ppb. All these samples were injected in triplicates. Mean peak areas obtained are plotted versus the sample volume as illustrated in Fig. 7 where the quoted errors correspond to the standard deviation. Peak area increases linearly with the sample volume for all species, as highlighted by the calculated determination coefficients $R^2 \geq 0.99$ (see Table 4).

During the series of experiments where sample volume was varied, the carryover inside the preconcentrator adsorbent was evaluated after each analysis by performing a blank right after desorption. Similar carryover percentage was observed after the injection of different sample volumes, indicating that the residuals were proportional to the injected BTEX amount. These average percentages were found to be 1.6, 2.6, 9.2, 7.1 and 6.8 % for benzene, toluene, ethylbenzene, m/p-xylenes and o-xylene, respectively, being higher for the less volatile compounds since, logically, they need higher temperature to be fully desorbed. Again, this issue could be strongly improved by increasing the desorption time with a precise control of the target desorption temperature related to a fully automatic process.

3.2.3. Repeatability and reproducibility
As any analytical device, repeatability and reproducibility of the GC should be evaluated to ensure reliable results in the long term. To assess repeatability, seven 20 mL samples containing 20 ppb of BTEX were consecutively analysed in the same day using the same experimental conditions (desorption temperature = 330 °C, injection time = 75 s). Between two consecutive samples, a cleaning step was conducted as already mentioned above. Peak areas and retention time obtained are
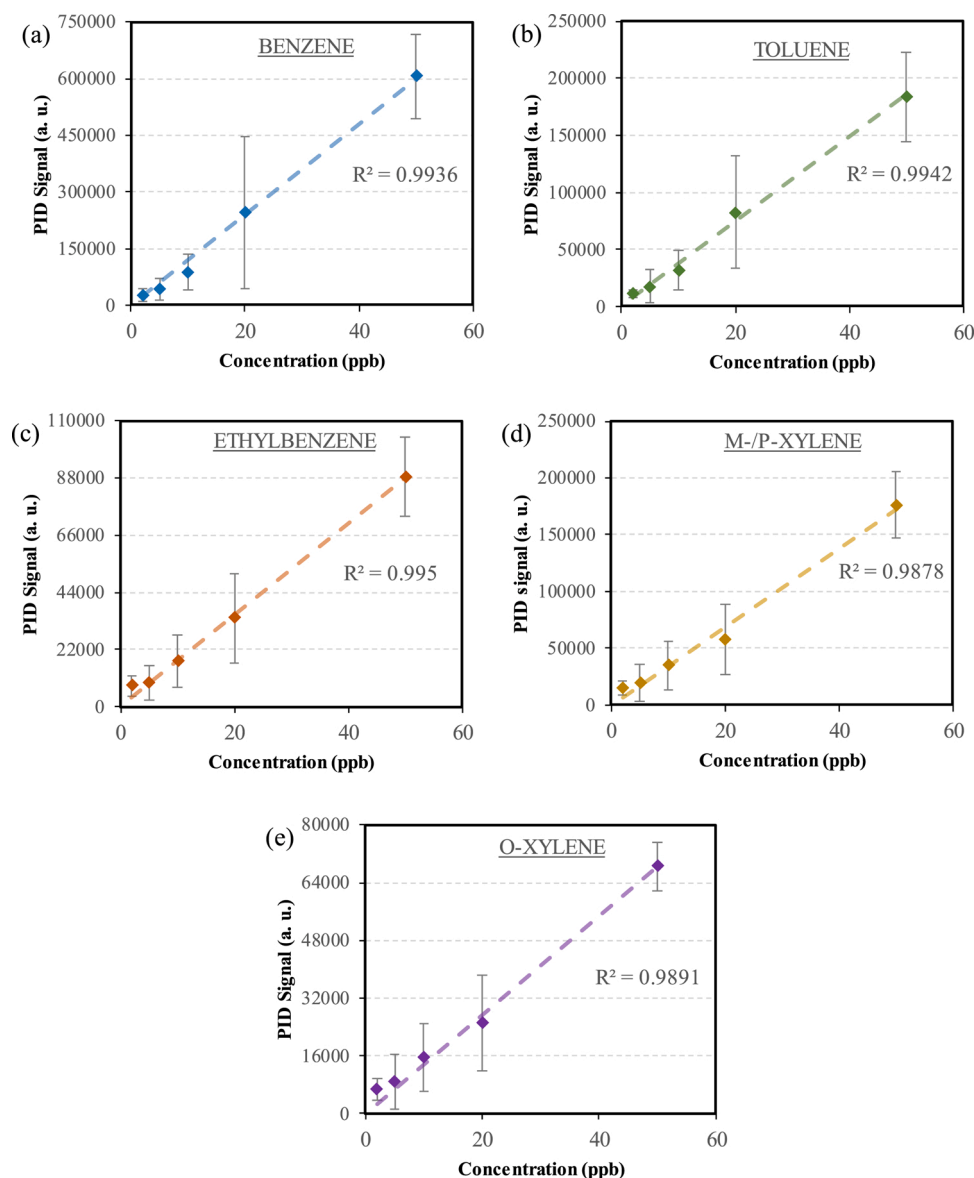
Fig. 6. Calibration curves of benzene (a), toluene (b), ethylbenzene (c), m/p-xylenes (d) and o-xylene (e) using preconcentrator filled with Carbopack® B. Sample volume = 20 mL, sampling flow rate = 5 N mL min^{-1}, desorption temperature = 330 °C, injection time = 75 s. Vertical error bars represent the standard deviation of triplicates.

Table 3
Performances obtained for the GC prototype equipped with the novel preconcentrator filled with Carbopack® B.

Compound	Calibration Equation[a]	R^2	LOD[b] (ppb)	LOQ[c] (ppb)
Benzene	y = 9618.8 x	0.9940	0.057	0.191
Toluene	y = 3761.5 x	0.9930	0.150	0.499
Ethylbenzene	y = 1828.7 x	0.9891	0.368	1.226
m/p Xylenes	y = 1776.2 x	0.9974	0.396	1.319
o-Xylene	y = 1403.7 x	0.9941	0.418	1.393

[a] y and x correspond to the PID signal and the gaseous concentration, respectively.
[b] LOD: Limit Of Detection.
[c] LOQ: Limit Of Quantification.

presented in Fig. 8a and b, respectively. Moderate variability was observed in peak areas of different samples whereas the variation in the retention time of different samples was almost negligible. Relative standard deviation (% RSD) of peak area was calculated to be 4.9, 3.7, 4.3, 8.0 and 5.6 % for benzene, toluene, ethylbenzene, m/p – xylenes

and o-xylene, respectively. These values below 10 % for all the compounds demonstrate that the analyses performed with the BTEX analyser integrating the micropreconcentrator were repeatable even in manual injection mode. The corresponding % RSD was also calculated for the obtained retention times, being equal to 0.1 % for all the analytes. Due to the possible inadequate isolation of the GC oven, retention times can shift in portable GC; however, this parameter appears to be very stable in our instrument. In this BTEX analyser integrating the micropreconcentrator, both sample injection and data acquisition were automatized; therefore, although the sampling time was manually controlled, the obtained results were very satisfactory and the repeatability of the measurements in terms of peak area and retention time was considerably improved compared to the previous preconcentrator version (Lara-Ibeas et al., 2019) [18].

Reproducibility was also evaluated according to the following method: three 20 mL samples containing 20 ppb of BTEX were consecutively analysed over three different days. Fig. 9a and b display the results obtained for the peak areas and the retention time of each sample, respectively. Peak areas obtained in three different days were
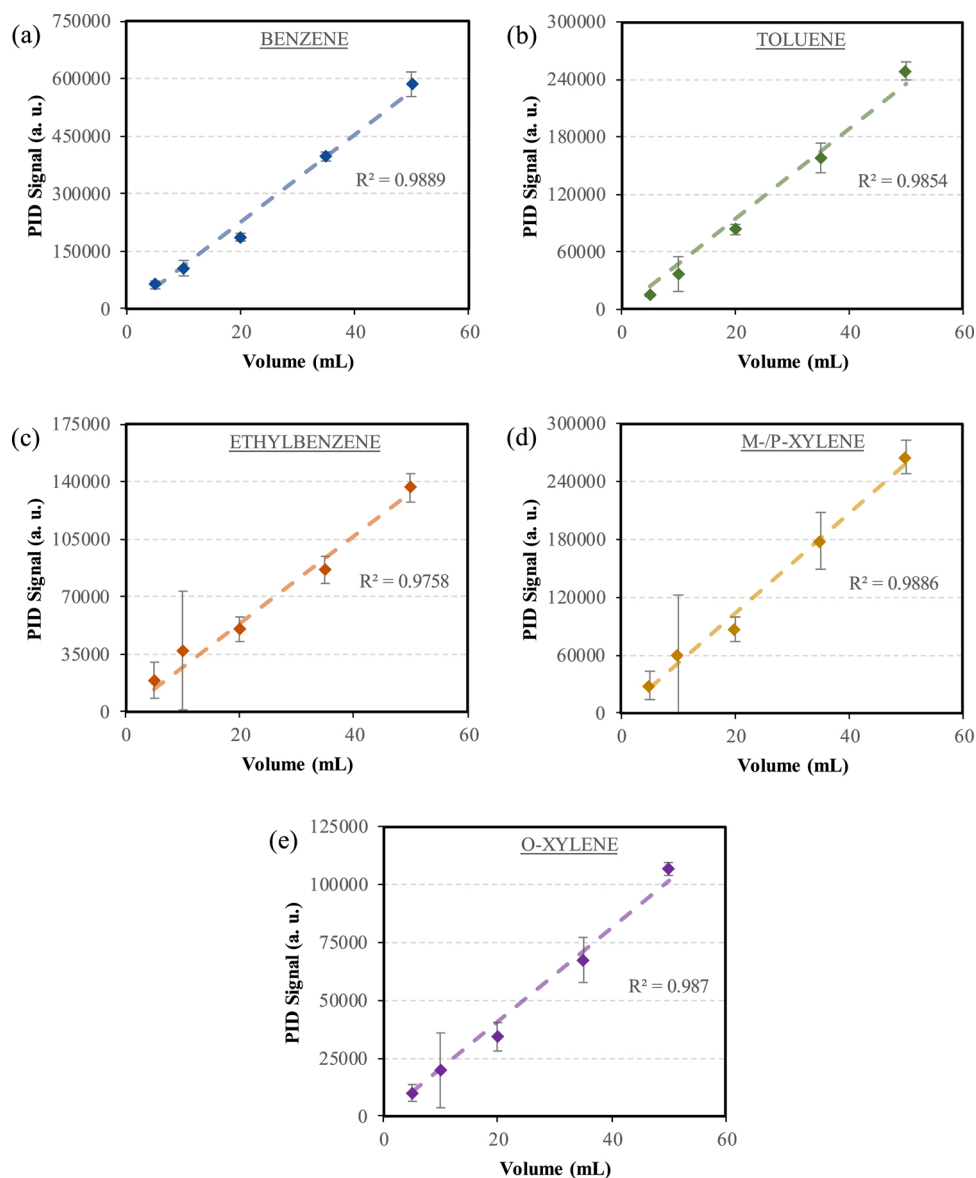
Fig. 7. Mean peak areas vs the sample volume injected in preconcentrator filled with Carbopack® B. BTEX concentration = 20 ppb, sampling flow rate = 5 N mL min^{-1}, desorption temperature = 330 °C, injection time = 75 s. Vertical error bars represent the standard deviation of duplicates. (a) benzene, (b) toluene, (c) ethylbenzene, (d) m/p-xylenes (e) o-xylene.

Table 4
Equation and determination coefficients obtained in sample volume variation tests.

Compound	Equation	R^2
Benzene	y = 11009.7 x	0.9930
Toluene	y = 4743.3 x	0.9942
Ethylbenzene	y = 2616.3 x	0.9940
m/p-Xylenes	y = 5139.6 x	0.9896
o-Xylene	y = 2120.1 x	0.9978

comparable and % RSD was calculated to be 3.2, 10.1, 21.8, 13.8, 13.9 % for benzene, toluene, ethylbenzene, m/p – xylenes and o-xylene, respectively. The variation obtained in this case was obviously higher than the one obtained for the analysis performed in a single day; however, all the RSD, except the ethylbenzene one, were less than 15 %.

Slightly higher RSD were also observed for the retention time

compared to the repeatability experiments, being 1.0, 0.7, 0.5, 0.5 and 0.4 % for benzene, toluene, ethylbenzene, m/p – xylenes and o-xylene, respectively. Despite this small increase, the variation observed in the retention times was relatively minimal and the values can be considered as highly reproducible over time.

The results obtained in the repeatability and reproducibility tests highlight the stability of the measurements conducted with this prototype over time, even with relatively low BTEX concentrations of 20 ppb and despite the use of manual injection mode.

3.3. Comparison with the existing instruments

In the last years, great efforts have been made to develop real-time sensitive miniaturized gas chromatographs for a broad spectrum of applications. Most of them include a preconcentration device enabling to achieve very low detection limits. These devices differ in their features (dimensions, manufacturing materials, used adsorbents, power
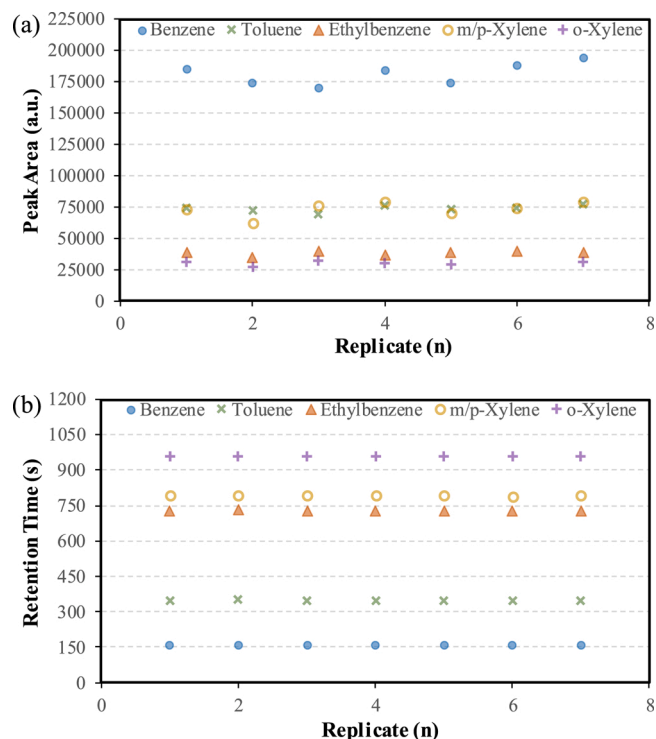
Fig. 8. Repeatability test results obtained for 7 consecutive BTEX samples analyzed in the same day: (a) peak areas and (b) retention time. Sampling volume = 20 mL, BTEX concentration = 20 ppb, sampling flow rate = 5 N mL min^{-1}, desorption temperature = 330 °C, injection time = 75 s.
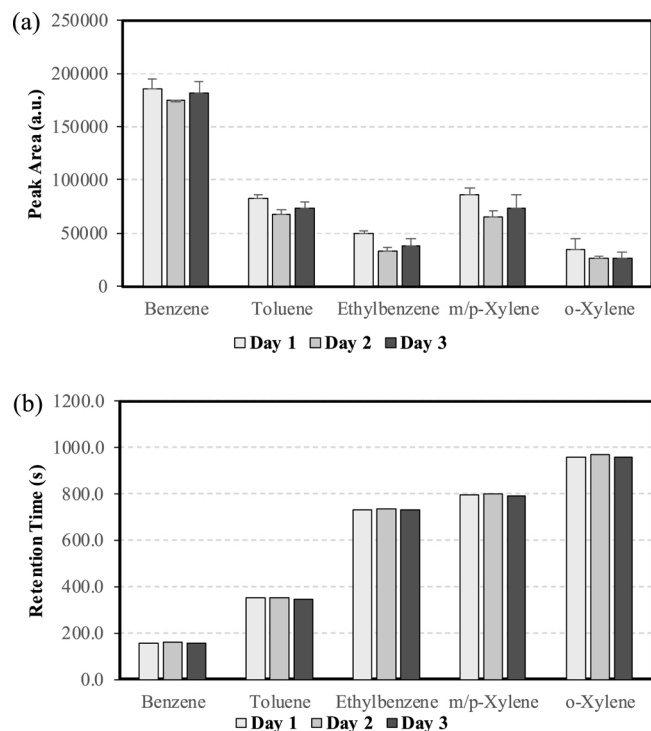

Fig. 9. Reproducibility test results obtained for 3 BTEX samples analyzed over three different days: (a) peak areas and (b) retention time. Sample volume = 20 mL, BTEX concentration = 20 ppb, sampling flow rate = 5 N mL min^{-1}, desorption temperature = 330 °C, injection time = 75 s. Vertical error bars represent the standard deviation of the triplicates.

consumption, etc.) and their analytical performances. However, a simple and direct comparison between them in terms of preconcentration performance is not possible since these results depends on other elements such as the type of detector. Therefore, a comparison between the miniaturized GC existing in the literature with a special focus on preconcentrator features is presented in this section.

Table 1 summarizes the most significant miniaturized GC with integrated preconcentrator (PC) developed for VOC quantification in the last decade. All devices presented are highly portable (weight < 5 kg) and have relatively small dimensions, which makes them suitable for on-site measurements. As can be observed, PID is the most commonly employed detector for VOC quantification in μGC. Indeed, this detector is easy to integrate in the GC system and is more selective and sensitive than metal oxide and chemical sensors. However, these sensors are generally less expensive than PID and enable to detect a larger screening of organic species.

These miniaturized GC were conceived for a wide variety of applications requiring very sensitive instruments such as environmental monitoring [20,35], early cancer diagnosis [23,36] or food quality control [37]. Therefore, all GC systems include a preconcentrator that improves the detector sensitivity to tens or hundreds of ppb in the case of sensors and, to ppb or even hundreds of ppt in the case of PID detectors. These preconcentrators are very different from one another. After the fabrication of the first microsystem including a micromachined preconcentrator in 1999 [38], great efforts were addressed to develop MEMS-based preconcentrators devices. MEMS technology offered indeed the possibility to create miniaturized devices exhibiting great performance with very low power consumption. Therefore, in the last decades, most of these preconcentrators were made from silicon and glass [20,24,26], materials typically used in electronics. However, there are several drawbacks associated with the use of MEMS-based devices. For example, the materials usually employed are fragile and expensive and there are almost not commercially available fluidic and/or electrical connections, leading frequently to leakage problems. In addition, the fabrication process needs suitable facilities (cleanroom) and high level of expertise that results very often in an expensive and time-consuming process. Lately, new fabrication technologies have been developed and those already existing have been improved to reduce the fabrication costs. Laser etching technology, milling or metal 3D printing techniques provide the possibility to use more robust materials such as copper [39], stainless steel [21] or aluminium (this work). Furthermore, standard fluidic connections can be usually integrated since these materials can be micromachined with traditional techniques and their dimensions are generally larger than the MEMS-based counterparts, ensuring better gas tightness. However, these dimensions involve higher thermal mass, leading to high power requirements and slow temperature ramps compared to MEMS-based PC. As illustrated in Table 1, power consumption in MEMS PC varies between 1 and 16 W whereas in metal PC it ranges from 10 to 70 W, except MAP (210 W) that was the first PC developed by our team. Despite the considerable difference of energy consumption required, the consumption of metal PC is still compatible with their integration in battery-powered devices. Nevertheless, the autonomy will be significantly reduced. In this regard, MEMS-based PC are preferred in applications where great autonomy is required. Due to the greater thermal mass, heating rates in metal PC (0.25–5.5 °C/s) are very low compared to MEMS-based PC (25–314 °C/s), while a fast temperature ramp is preferred to generate sharp chromatographic peaks. However, in this study, it was demonstrated that well-defined peaks could be achieved with a heating rate of 5.5 °C/s.

Considering the LOD achieved with these miniaturized GC, it appears that this feature depends more on the type of detector itself than on the preconcentration unit employed, since the instruments having PID detectors are much more sensitive.

Until the present work, only three instruments had LOD in the ppt range. Zampolli et al. [20] proposed a miniaturized GC-PID with a PC filled of an innovative quinoxaline-based adsorbent. LOD down to 0.1

ppb for benzene was reached; however, 55 min of sampling were needed to collect the 2 750 mL required to achieve such a sensitivity. This very long sampling time prevents to establish concentration time profiles that can help to determine occupational exposure or identify pollutant sources [33]. Shorter sampling time of 20 min was employed by Skog et al. [21] to collect a sample of 4 L and achieve LOD from 2 to 11 ppt for BTEX. Sun et al. [25] reported LOD below 1 ppb with a sampling time of only 1 min but the sample volume employed was not mentioned. Since LOD strongly depends on the sample volume, the sensitivity of each system was calculated for the lowest detectable mass of analyte for better comparison. Indeed, it is not necessarily relevant to reason in terms of sensitivity because, as we have shown, the areas of the chromatographic peaks increase linearly when the volume of the sample increases, indicating that this volume can be easily modulated. A relatively small sample volume will provide better temporal resolution while a large volume will provide a lower LOD. To calculate sensitivity, the lowest LOD achieved for each method was multiplied by the sample volume. For example, in our case, benzene LOD (0.18 µg m^{-3} at P =1 atm and T = 25 °C) was multiplied by the sample volume (2×10^{-5} m^3), giving a sensitivity of 3.6 pg.

To our knowledge, the analytical system developed in this work showed the highest sensitivity reported to date for BTEX analysis exhibited by a portable GC as highlighted in Table 1. This instrument achieved LOD from 0.06 to 0.4 ppb (0.18 – 1.82 µg m^{-3} at P =1 atm and T = 25 °C) using a sample volume of only 20 mL (2×10^{-5} m^3). It means that the lowest detectable amount with this compact GC was 3.6, 11.3, 32.0, 34.4 and 36.3 pg for benzene, toluene, ethylbenzene, m/p-xylenes and o-xylene, respectively.

The portable GC developed by Zampolli et al. [20] had a low benzene LOD of 0.1 ppb (0.32 µg m^{-3} at P =1 atm and T = 25 °C) but it required a large sample volume of 2 750 mL (2.75×10^{-3} m^3) resulting in a sensitivity 878.5 pg for this compound. A lower detection limit was found with the compact GC developed by Skog et al. [21] where a benzene LOD of 0.01 ppb (0.03 µg m^{-3} at P =1 atm and T = 25 °C) was achieved with a 4 L (4×10^{-3} m^3) sample giving a sensitivity of 140.6 pg. Therefore, the sensitivity obtained with the portable GC coupled to the preconcentration unit developed in this work differed by 2–3 orders of magnitude from most of the values reported in the literature, even those reporting very low detection limits [20,21]. For the analysis of BTEX, only the first preconcentrator version (MAP) developed in our previous work yielded similar results with the same sample volume of 20 mL [33]. Despite of the outstanding benzene sensitivity of 6.4 pg achieved with MAP, this new version has improved this feature by a ratio of 1.8. Han et al. [39] reported a sensitivity comparable for the analysis of isoprene. However, this sensitivity does not correspond to a portable GC since the developed preconcentrator in this case was connected to a benchtop GC-FID. These results suggest that the performance achieved by our prototype in terms of sensitivity is close to those typically exhibited by benchtop instruments.

Another crucial aspect of analytical performance is the stability of the measurements. Among the studies presented in Table 1, repeatability was only evaluated for 10 instruments. Despite the importance of repeatability, in some cases this parameter was characterized only graphically by showing the peak shape of triplicates [37,39], which is not useful for comparison purposes. In other studies, repeatability was characterized in terms of % RSD, but the different experimental conditions employed, such as sample concentration and number of replicates, make difficult an objective comparison. Sun et al. [25] evaluate the repeatability by consecutively analysing 8 benzene samples at a high concentration of 1 ppm. They found a very low % RSD of 0.42 % for the peak area. However, this high repeatability may decrease when stability is evaluated in more realistic conditions such as low ppb concentrations. Garg et al. [26] evaluated the repeatability of the Zebra GC using 10 mL samples of a 5 VOC mixture at 100 ppb (1–3.2 ng). The peak areas and retention times showed average % RSD for all analytes less than 1.3 and 4.7 %, respectively, demonstrating the high stability of this compact

GC-TCD. Skog et al. [21] found % RSD between 9 and 30 % for peak areas of BTEX. These high % RSD can be explained by the very low concentrations employed in these experiments, in the order of pg. Wang et al. [20,21] reported also an outstanding stability for the belt-mounted GC for samples up to 9 µg of a 9 VOC mixture. Peak area and retention time stability were assessed in short-term (i.e., 30 min), intraday (i.e., 8 h) for samples collected from the same test atmosphere. % RSD values lower than 2.5 and 5.0 % were found, respectively. Additionally, reproducibility was also evaluated in samples analysed in five different days and % RSD of 7.7 % was reported. It is worthy to mention that no more results of reproducibility tests were found in the literature. In this context, our system seems to have a comparable repeatability in terms of peak area (< 10 %) and very satisfactory in terms of retention time (< 0.1 %) compared to those reported in the literature.

Finally, our compact GC integrating a novel PC exhibited an excellent sensitivity as well as very satisfactory stability of the measurements. In addition, an analysis cycle is performed in a reasonable time of 19 min, enabling to establish accurate concentration time profiles. In the future, this time can be reduced once it will be fully automatized, the next sampling being collected during the analysis step of the current analysis cycle. This automatization will reduce the time between two analysis to only 15 min which will permit to obtain four measurements per hour.

4. Conclusion

A novel preconcentration unit was conceived, manufactured, integrated in an existing portable GC and tested under controlled conditions, demonstrating compliance with the requirements for being a fully functional device.

Considering an air sample of only 20 mL, the quantification limit of the whole device including the preconcentration unit was 0.191 ppb (12 pg) for benzene. This LOQ is lower than the very strict threshold value established for benzene in the recent French legislation concerning indoor air quality (0.6 ppb). Moreover, this sensitivity could be easily improved by increasing the sample volume considered, the benzene LOQ becoming 0.076 ppb with 50 mL of sample, requiring 10 min sampling at 5 N mL min^{-1}.

The addition of a preconcentration step in GC system did not substantially increase the total analysis time, enabling BTEX monitoring in near real-time. While in the case of consecutive analyses, the next air sample can be collected during the separation and analysis of the previous sample. Concerning the energy consumption, the additional power consumption of ~61 W needed for a very short duration estimated to 20 s (time needed to reach the desorption temperature) associated to the preconcentration step is compatible with a portable analytical system.

Following the promising results obtained in this work, further developments are in progress to reduce the heat losses by replacing the screws used in this work by ones with sharp end, wood screws (RS 144-3524, RS, France) or by integrating an insulating and protective material between the ceramic resistances and the metallic screws. The use of two screws with a sharp end limits the heat transfer and, therefore, the heat losses. In this case, a lower nominal voltage of 24 V more compatible with that supplied by standard batteries, instead of 28 V, would permit to decrease the average power consumption of 44 W over the 70 s period of the desorption step (preconcentrator heating) as supported by Figure SI.1. The autonomy of the BTEX analyser will be weakly impacted by this change, i.e., 204 nm instead of 192 min, the temperature increase up to 250 °C during the desorption step is similar for both voltages (see Figure SI.1). In addition, software developments are also underway to automate the device, which will improve repeatability and reproducibility. This software combined with an electronic temperature controller will permit to regulate precisely the desorption temperature, as illustrated in figure SI.1. The red-dashed line represents the predicted thermal behavior of the preconcentrator using 24 V and 3 A once the system will be automated. Unlike other portable GC found in the

literature, the prototype developed in this work was evaluated in terms of both repeatability and reproducibility. The relatively low % RSD < 10 % and < 15 % obtained in these two tests indicate that measurements conducted were stable over time. The stability of the measurements altogether with the extraordinary sensitivity and an acceptable analysis time make this GC prototype equipped with a novel preconcentrator, a good candidate for air quality monitoring applications. However, this instrument should further be tested in real conditions to evaluate the possible influence of interfering compounds and other issues derived from the use in real environments. Other adsorbents could be used and tested in the near future in order to decrease the desorption temperature needed and consequently the energy consumption.

Finally, this preconcentration device can be coupled with other GC systems or optical detection devices and be used for other applications requiring high sensitivity, such as warfare agents and explosives detection or early cancer diagnosis. For chromatography systems, this can be simply done by replacing the PID detector which is fairly specific to aromatic compounds with a more universal detector such as a Thermal Conductivity Detector (TCD), Flame Ionization Detector (FID), a Metal Oxide Semiconductor (MOS), etc.

Declaration of Competing Interest

The authors report no declarations of interest.

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## Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.snb.2020.128690.

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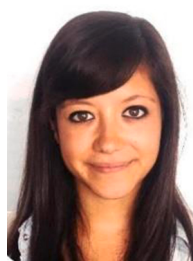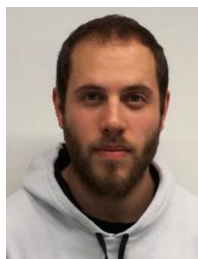
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Michel Wolf has been a mechanic engineer at ICPEES for over 30 years. He has acquired a great expertise in manufacturing unique pieces for researchers in the laboratory. This covers mechanical parts of large volume but also mechanical parts of very high precision to produce miniaturized devices, like the one presented in this work.

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