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Development of a novel portable miniaturized GC for near real-time low level detection of BTEX

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ABSTRACT

This paper reports on the development and optimization of a miniaturized GC/PID system dedicated to BTEX monitoring in near-real time conditions at ppb level. The system consists of a 6-ports valve, a capillary column and a mini-photoionization detector (PID), its final weight is around 4 kg. The system operates at very low flow rate (lower than 4 mL min^{-1}) irrespective of the carrier gas used. The device is controlled through homemade software which provides instrument control and real-time chromatograms collection. The system's performance was studied and optimized with two different carrier gases, namely hydrogen and nitrogen. The optimal experimental conditions of BTEX separation was determined according to the calculated H.E.T.P. and the total analysis time for a single run which was set to a maximum of 10 min. Using the optimal conditions, the detection limit, stability and repeatability of the analytical system were assessed. A detection limit of 1 ppb was found for benzene and toluene with both carrier gases and less than 3 ppb for other compounds of the family. A slight advantage in terms of separation was found with hydrogen especially for ethylbenzene and xylenes using the defined experimental conditions.

1. Introduction

Volatile organic compounds (VOCs) are an important class of pollutants encountered in indoor air [1,2]. Some of these compounds are harmful to human health even at trace levels. Among VOCs, benzene, toluene, ethyl benzene and xylenes isomers known as BTEX are of great concern. Their indoor emission sources are numerous and often caused by human activities. Cleaning products, candles [3], heaters, gas boilers [4], building materials such as paints and varnishes and places where gardening products and automotive fuels are usually stored are the main emission sources [5,6]. Among BTEX, benzene is the most dangerous due to its high carcinogenicity [7]. Consequently, in 2013, the European Union has fixed a threshold value of 5 $\mu g\,m^{-3}$ (1.6 ppb) for benzene [8,9] in public indoor which will be decreased down to 2 $\mu g\,m^{-3}$ (0.64 ppb) in 2018.

Various techniques are available for the determination of airborne BTEX. The most commonly used techniques are based on gas chromatography coupled to various types of detectors such as flame ionization detector (FID), photo ionization detector (PID), mass spectrometry (MS) [10–12] or UV and IR spectroscopy [13–16]. These methods present several advantages such as a part-per-trillion (ppt) detection limit, high selectivity and high accuracy. However, these instruments are very heavy and bulky which represent the two main disadvantages for field monitoring. In addition, most of them do not provide "online" measurements but rather require sampling procedures on the field using for instance Carbopack® or Airtoxics® cartridge before analyzing the sample in the laboratory.

Open-path Fourier transform infra-red (OP-FTIR) spectroscopy and proton transfer reaction coupled to mass spectrometry (PTR-MS) are one of the techniques that could provide both a very low concentration detection and multi-chemical analysis in a near real-time mode [17–19]. However, these instruments are very bulky and very expensive. In addition, the OP-FTIR requires a long optical path (e.g. >100 m) when a very low detection limit is needed. Therefore, these instruments are rarely used for field monitoring.

To overcome these disadvantages, several kinds of portable sensors have been investigated in environmental applications. Quartz crystal microbalance (QCM), [20,21], cata luminescence sensors (CTL) [22], surface acoustic wave arrays (SAW) [23,24] and semi-conductor sensors [25,26] have recently attracted a lot

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Table 1
Weight, size and analytical characteristics of some commercial BTEX analyzers and some laboratory GC with different type of detectors.

		Weight[a] (kg)	Size length × width × height (cm)	LOD for benzene (ppb)	Carrier gas consumption[b] ($mL\,min^{-1}$)	Cycle time (minutes)	Sampling condition and injecting volume	References
Laboratory miaturized gas chromatography	Portable GC/Sensor array	N/A	32 × 32 × 10	28–52 depending on polymer coat	4-(filtered dry air)	4	6 ports valve Multi bed trap (1 L)	[36]
	Miniaturized GC/MOX array	N/A	N/A	0.1	15-(filtered ambient air)	60	2 commercial 3-way valves + Preconcentrator (2.75 L)	[37]
	Miniaturized GC/micro fabricated quartz crystal tuning forks	N/A	N/A	10,000	8-(filtered ambient air)	4	Online sampling	[38]
	μGC/μTCD MEMS technology	N/A	N/A	5000	2-(hydrogen)	3	6 ports valve Sampling loop (500 μL)	[39]
	Compact GC/PID	3	30 × 17 × 8	0.02	21-(purified ambient air)	15	Preconcentrator Multi bed trap (1 L)	[40]
	μGC/μTCD MEMS technology	1.8	30 × 15 × 10	30	3-(helium)	4	Preconcentrator Single trap	[41]
	Miniaturized GC/PID	3	38 × 30 × 15	<1	2.5–3.5 (N_2 or H_2)	10	Without any preconcentration step	This work
Commercial analyzers	GC/PID 8900® Baseline	13.6	44 × 38 × 24	0.05	21 (N_2, 6.0)	12	10 ports valve Sampling loop (300 μL)	[42]
	airTOXICBTXPID® Chromatotec	20	48 × 60 × 22	0.01	54 (N_2, 5.0)	15	Single adsorbent trap (20–240 mL)	[43]
	VOC72M® Environment SA	13	48 × 60 × 13	0.01	15 (N_2, 5.0)	15	Single adsorbent trap (50 mL)	[44]
	Synspec GC955-600® BTX Analyser Enviro Technology Services	19	44 × 39 × 22	0.03	6 (N_2, 5.0)	15	10 ports valve Single adsorbent trap (sampling volume N/A)	[45]
	PetroPro Portable Gas Chromatograph IFICON	6.6	33 × 27 × 13	50	1150 (ultra pure air)	7	N/A	[46]

[a] It corresponds only to the instrument weight and does not refer to the total weight of the operating system, i.e. it does not include any gas cylinder or generator.
[b] All mentioned commercial analyzers use pure gases as carrier gas (Nitrogen 5.0 or 6.0 for baseline).
N/A, information not available.

of interest. Indeed, they provide a very fast response (less than 1 min) because of the high interaction between pollutants and the sensitive layer of the sensor [26]. Additionally, they are highly portable and perform a continuous monitoring of BTEX. In spite of their advantages, these chemical sensors are complicated to handle, and they have lack in sensitivity with detection limit ranging between few hundred of ppb to ppm and low specificity. Furthermore, they are not sufficiently stable to be used over a long period. For example, polymer-based sensors can suffer from moisture interference. In case of metal oxides sensors, the operating temperature needed for detection is high (300–400 °C) which leads to analytes oxidation thus causing a shifting of signal in time.

Many attempts were made to develop cheap, portable, rapid and highly sensitive BTEX analyzers [27–32]. Analyzers based on UV–visible spectroscopy are actively studied at the moment [27,33–35]. The most developed UV-analyzer was reported by Ueno et al. [34]. According to the authors, the system operates as follows: pre-concentration of ambient air sampled on mesoporous materials, flashed desorption and detection using UV-visible spectroscopy. However, the obtained detection limit of 10 ppb for benzene is still too high regarding the guideline values for indoor air concentrations [9].

Currently, considerable research efforts have been made in the development of micro gas chromatography for online BTEX detection. Griffin 460® (FLIR systems, Inc. USA) is an example of such GC/MS which could be used for online monitoring according to the manufacturer's specifications. But even if a high sensitivity (ppt to ppb level) is claimed, the weight of the instrument which is around 44 kg remains a severe limitation.

Many portable laboratory miniaturized GCs equipped with different kind of detectors have been recently reported [36–41] (see Table 1). Their gas consumption ranged between 2 $mL\,min^{-1}$ for those based on MEMS technology and 21 $mL\,min^{-1}$ for the GC equipped with PID. Their detection limit varied between 0.02 ppb and 10 ppm depending on the detector. On the other hand, commercial analyzers for online BTEX detection are also available (see Table 1).

GC/PID 8900® [42] (Baseline mocon-USA), airTOXIC BTX PID® [43] (Chromatotec-France), VOC 72M® [44] (Environment SA – France), Synspec GC955-600®[45] (Envri Technology, UK) and PetroPRO™ [46] (INFICON, Switzerland) are some examples of commercial transportable GC/PID. All the aforementioned analyzers are very sensitive (limit detection in sub ppb levels) and provide an answer in near real time (6–15 min). Despite their remarkable performances, these instruments are still moderately portable because of their weight (ca. 13 to 20 kg) and the need of a large and heavy gas cylinder for their operation. Thus a B10 cylinder would be used only during 28 days because of the gas carrier or make-up gas flow rates that could reach 50 $mL\,min^{-1}$.

If miniaturized GC/PID remains one of the most promising options for indoor air BTEX detection, the large gas consumption is still a severe drawback. To that extent, the aim of our study was to develop a novel portable miniaturized GC system able to detect BTEX concentrations lower than few ppb. The system should operate with a very low carrier gas flow rate (less than 5 $mL\,min^{-1}$) which means that a B10 cylinder would allow 277 days of operation. And finally, the time resolution should be less than 15 min and the miniaturized GC's weight should not exceed 5 kg including gas cylinder.