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LOW-COST MICRO-MACHINED PRECONCENTRATOR FOR PPT DETECTION OF BTEX

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KEY WORDS

Preconcentrator, microfluidics, miniaturized gas chromatograph, benzene, VOCs, air quality.

ABSTRACT

Introduction

The concern about air pollution has been rising in the recent years since some relevant studies proved the impact on human health [1]. The majority of the people worldwide spends most of their life inside enclosed spaces. Therefore, controlling the air quality in these environments is crucial, not only because it is the most frequent source of exposure but also because the air-renewing ratio is considerably slower than the one in open-air spaces. Indeed, the impact of chronic exposure to in-air pollution has been already documented [2]. Indoor air pollutants are diverse and can be classified in different families. Among these families, BTEX (Benzene, Toluene, Ethylbenzene and o-, y-, z-Xylene) present in indoor air are particularly harmful [3,4]. In the case of Benzene its carcinogenic and mutagenic effects are well documented [5].

The studies performed by the scientific community and focused on indoor air quality have driven the public authorities to legislate in a way that very low levels of pollutants must be guaranteed in public enclosed environments. In 2013 a threshold value of 5 $\mu g \cdot m^{-3}$ (1.6 ppb) for benzene was set by the European Union in public buildings. In France, this limit was decreased to 2 $\mu g \cdot m^{-3}$ (0.6 ppb) in 2018. Nevertheless, detecting such low concentrations means a big challenge since the current analyzers able to achieve this limit of detection are very large in size, heavy in weight and required high energy consumption, limiting then their use for on-site measurements. These facts evidence the need for a portable and accurate device able to monitor BTEX concentrations in near-real time. In this way, In´Air Solutions in collaboration with the CNRS and the University of Strasbourg has developed a BTEX analyzer which is portable, battery powered and can detect concentrations as low as 1-2 ppb within a 10-minutes analysis [6,7]. However, the sensitivity of this device is not sufficient for the standards required by the public authorities. Thus, the work presented here corresponds to the development of a micro-fluidic preconcentrator and its integration within the BTEX analyzer developed and commercialized by In'Air Solutions.

Preconcentrator

This work is an improvement and therefore follows the development of the macro-preconcentrator already published by Lara-Ibeas et al. [8] 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 has important limitations since it requires 210 watts of power and

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about 65s to be heated up to 200ºC. This is incompatible with a system that needs to be battery-power and stand-alone. Furthermore, we aimed to reduce the limits of detection even further.

The preconcentrator presented in this work is manufactured using micro-machined techniques (its mechanical novelties are not revealed in this work since it is under patent submission). Afterwards the preconcentrator is filled with 5 mg of adsorbent, Carbopack B (Sigma-Aldrich, EG/EC No. 215-609-9).

Two resistances are used for heating up the system while an original cooling system is activated after the desorption step for a quick cool down back to the adsorption temperature. The power consumption decreases with the increase of the temperature, going from 43 watts initially (25 ºC) to 22.15 watts at the end of the heating (250 ºC). These values are considerably lower than the 210 watts of power required in the previous version [8]. Moreover 200ºC are reached in only 22 seconds while in the previous version 65 seconds were required. Finally the cooling part has also been improved, as highlighted in Fig. 1, needing only 150 seconds to cool down back to the room temperature (25ºC) unlike the 2400 seconds of the previous version.
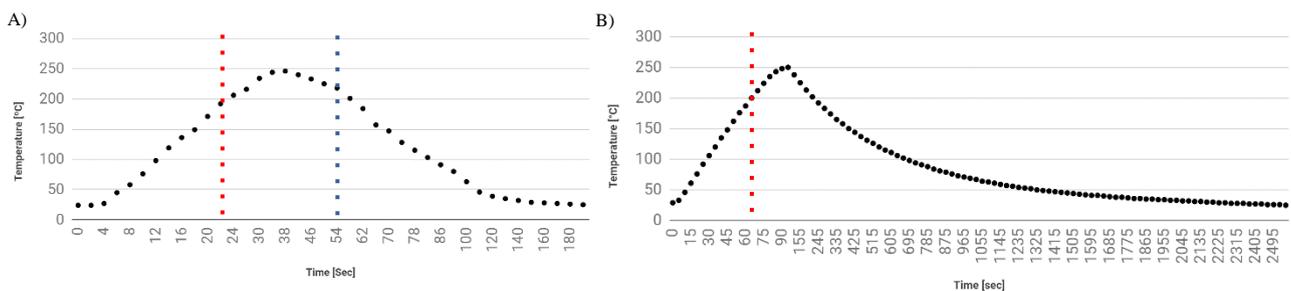
Figure 1. Thermal performance of the two preconcentrator versions.. Red dashed line represents the switching-off of the resistances, while the blue dashed line represents the switching-on of the cooling system. A) Micro-machined preconcentrator [this work]. B) Previous version of preconcentrator [8].

Results

Initially, as a reference for further comparisons with the preconcentrator results, a group of test were performed using a sampling loop of 200 µL and three different concentrations of BTEX 100ppb, 50ppb and 25ppb. The chromatograms are displayed in the Fig. 2.
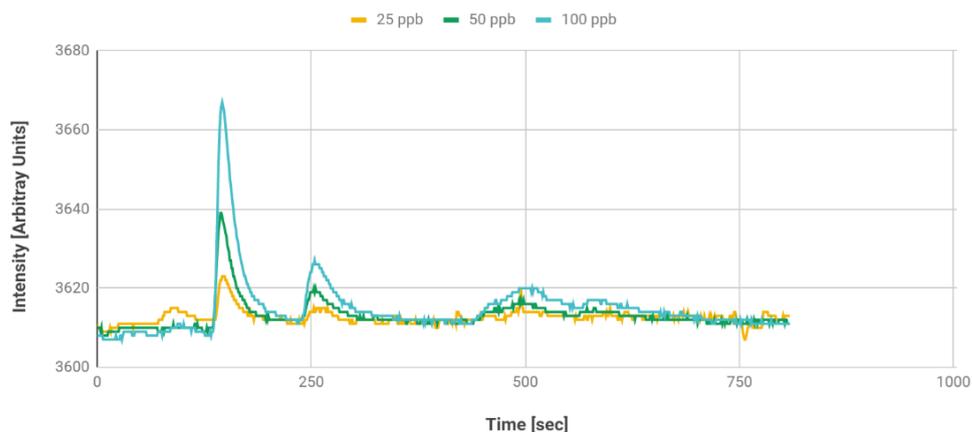
Figure 2: Chromatograms obtained with a sampling loop of 200 microliters used instead of the preconcentrator for concentrations of 100 ppb, 50 ppb and 25 ppb.

In the chromatograms of Fig. 2 and Fig. 3 the first peak corresponds to Benzene, the second is Toluene and the rest, although partially coeluted, come in this order Ethylbenzene, o/p-Xylene and O-Xylene. We have use the area under the peak as a measure of concentration instead of using peak height, since the presence of a preconcentrator can affect the height and with of the peak but does not alter the area for a given concentration.

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The laboratory analyzer used in this work has a limit of detection of 40 ppb for benzene, 60 for toluene and more than 250 ppb for the others. Taking this fact into account three different groups of test were performed: flow rate of adsorption vs signal, total volume of adsorption vs signal, and concentration of BTEX vs signal. The Tab. 1 summarizes the values of the peak area (signal) derived from the chromatograms for every BTEX species and for adsorption flow rates varying between 2 and 40mL/min. The total sample volume and the concentration were fixed to 40mL and 20ppb.

Flow Rate [mL/min]	Benzene [Area under peak]	Toluene [Area under peak]
2	27326	11772
5	27891	11034
10	29820	14896
20	29708	15866
40	29291	14593

Table 1: Peak area depending on the flow rate for an adsorption of 40mL of BTEX at 20ppb with flows of 2 / 5 / 10 / 20 / 40mL/min using the miniaturized preconcentrator.

The peak areas of benzene and toluene are approximately constant in the range of flow rates of 2-40mL/min, the other peak areas were not determined since the separation of ethylbenzene and xylenes were not optimized. In addition, the repeatably has been investigated using a flow rate of 5 mL/min, a sample volume of 40 mL and a concentration of 100 ppb. The results indicate that peak areas of benzene and toluene vary with an uncertainty of 5%.

The Fig. 3 displays the chromatograms obtained for different volumes of injection, i.e. the peak intensity plotted in a logarithmic scale as a function of retention time.
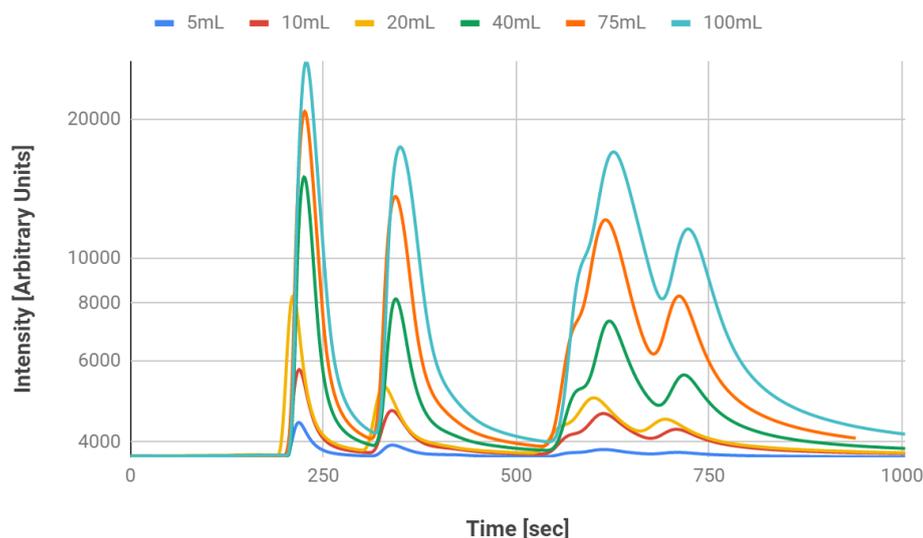
Figure 3. Chromatograms obtained with the miniaturized preconcentrator when injecting different sample volumes ranging between 5 and 100 mL for 100 ppb of BTEX. The y axis is in logarithmic scale.

Finally, a calibration representing the peak area vs concentration was performed using an adsorption flow rate of 20 mL/min for 5 mins of injection, i.e. a total sample volume of 100 mL. Fig. 4 displays the results for every compound, where the concentration ranges between 1 and 10 ppb. It should be underlined that so low concentrations are usually very difficult to generate accurately due to the residual impurities present in pure air used for the dilution of BTEX mixtures.

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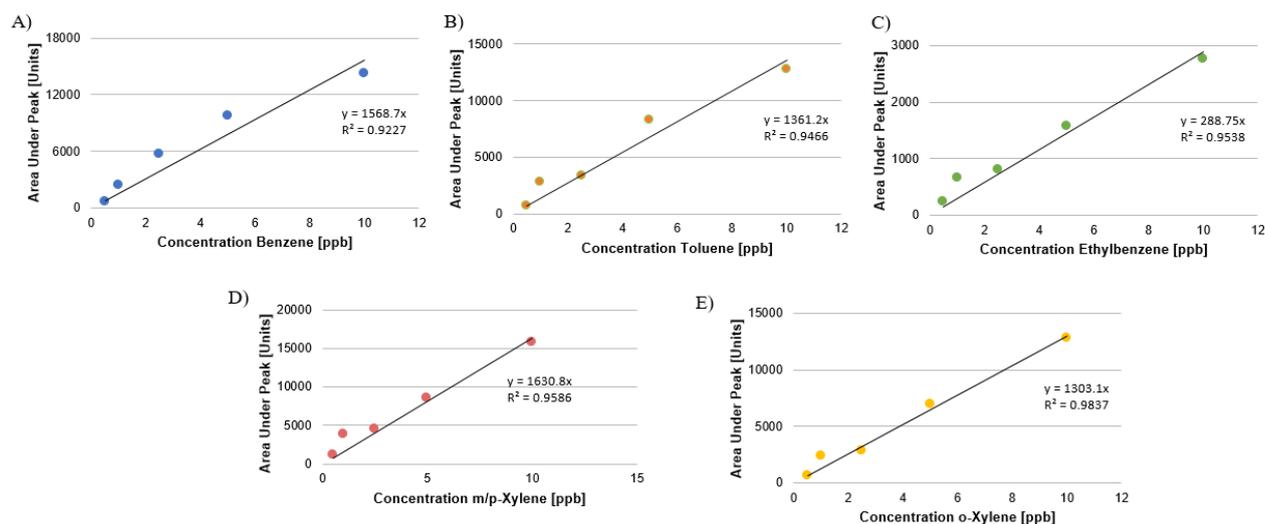
Figure 4. Regression based on the concentration for the BTEX molecules using the area under the curve as a measurement. A) Benzene. B) Toluene. C) Ethylbenzene. D) m/p-Xylene. E) o-Xylene.

The regression coefficients are between 0.93 and 0.98, which can be considered as a reasonably good fit since the theoretical limit of detection has been decreased from 40 ppb, 60 ppb, 250 ppb to 150 ppt, 170ppt and 40 ppt for benzene toluene and the others, respectively.

In conclusion, this upgraded version of a micro-machined preconcentrator is able to detect to 150 ppt for benzene, it needs only 5 mins for sampling, 22 seconds for heating and 150 seconds for cooling down. In addition, this version can be integrated in a portable BTEX analyzer due to its low power-supply requirements.

Acknowledgements

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