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Review

Gas phase micro-preconcentrators for benzene monitoring: A review

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ABSTRACT

Benzene is an illustrative example of cancerigenic compounds at low ppb level, which can be found as contaminant in petrochemical industry applications. The pre-concentration of this compound is an important step prior to gas detection allowing to reduce significantly the detection limit of current detection systems. Nowadays, huge advancements have been made for developing gas miniaturized pre-concentrators to be used as an injection unit in front of gas microdetection systems for benzene monitoring. Herein, a comparative review about gas microconcentrators for benzene is reported, starting from available microstructures design to the main adsorbents and their application in detection systems.

Contents

1. Introduction

Environmental monitoring has become, in the recent years, more stringent since the society has taken conscience about the importance of the presence of trace contaminants that affect human health and environmental safety. Benzene is one of the most studied volatile organic compounds (VOCs) in literature due to its carcinogenic effects at very low concentrations [1]. Occupational exposure to this vapor is likely to occur in air from petrochemical manufactures or stations, from automobile exhaust, etc. [2]. Each country, through an environmental quality agency, sets tolerance limits for benzene. For example, in the United States, the threshold tolerance limit for this compound was fixed at 500 ppb in ambient air by the U.S. Environmental Protection Agency [3].

Benzene could also be found as contaminant in CO_2 used for gaseous beverage production such as sodas and beers. In this context, the International Society of Beverage Technologists (ISBT) has defined the quality standards for the CO_2 to be used in this application, defining a threshold limit for benzene in 20 ppb, while other hydrocarbons like methane can be present in concentrations up to 30 ppm [4].

The safety exposure limits of benzene are being continuously reviewed to lower levels. Therefore, a pre-concentration stage is being introduced in front of gas micro-detection systems in order to decrease their detection limit. In particular, the pre-concentration effect allows ppb level detection for a wide range of chemical compounds [5,6].

As general definition, the pre-concentrator relies on an adsorbing material deposited on the active area adjacent to the heating element [6]. Ideally, the sorptive material must absorb selectively one or more chemical species of interest over a time period necessary to concentrate the chemical compound in the absorptive material. Then, the sorptive layer must be heated with a pulse of temperature for providing narrow desorption peaks with relatively

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high concentration to the connecting detectors (*e.g.* gas sensors, electronic nose or conventional analytical detectors such as gas chromatograph/mass spectrometers). This process must allow the analytes present in a large air volume to be purified and concentrated, so increasing the efficiency of detection.

Nowadays, the microfabrication technology has allowed fabricating low cost and low power consumption microstructures which can be incorporated with the detection analytical systems or MEMS based gas sensors on the same chip [6,7]. The pre-concentrator can perform sample extraction and injection into a single device for on-site analysis without human intervention in the transfer of sample from extraction media to the detector inlet. The first microsystem that includes a micromachined pre-concentrator was designed by the ChemLab at Sandia national laboratories in 1999 [8]. Since then, many works have been carried out. In literature, different pre-concentrating microstructures are now available in different designs and are combined with a wide range of adsorbents [5–7]. However, these systems are still confined in the research laboratories and are not yet commercially available due the difficulty to produce reliable and reproducible systems. Herein, we will review and compare the performance of such structures toward benzene pre-concentration and their practical applications with detection systems.

2. New advancements on benzene preconcentration

A look into the literature allows evaluating the huge number of works devoted to the development of gas preconcentrators for benzene. However, it remains difficult to compare the performance of such structures because the authors use different criteria to define it. One of the most common criteria is the "concentration factor" (CF). This parameter has been commonly used as a metric to estimate the performance of pre-concentrators, and is defined as the ratio of the concentration of the analyte in the sample delivered to the detector to the concentration originally present in the inlet airflow [6]. However, there is no standard definition for the concentration factor. The most common definition is the concentration of the pre-concentrated sample relative to the original concentration [9] or the sampled volume by the desorbed volume [10]. Other definitions include sample container volume to desorption volume [11] and breakthrough time difference [12]. It should be noted that CF on its own is ambiguous. This is because the CF depends on the analyte concentration, how long one collects them, and at what flow rate and desorption heating rate and in what dead volume, thus, is not strictly an intrinsic property of the pre-concentrator itself [9]. Apart from the high concentration factors, desirable pre-concentrator features include operation at high flow rates, low driving electrical power, uniform thermal heating with short time constants for minimum pulse width during the desorption process and selective sampling toward the analyte of interest. The sorbent layer should, in fact, collect only the analyte and must allow passing its intereferents.

a. Available microstructures

The main microfabricated structures reported so far can be classified into planar hotplate and three dimensional (3D) structures [6]. On one hand, the planar structure is based on a flat hotplate coated with a specific adsorbing material in order to selectively concentrate a specific analyte. On the other side, in order to increase the active area with low dead volume, 3D structures are being implemented. They are based on microchannels etched in silicon which can be either filled or coated with one or more adsorbing materials, depending on the range of vapors to be concentrated. Exhaustive overviews about those devices are available in [5–7,13].

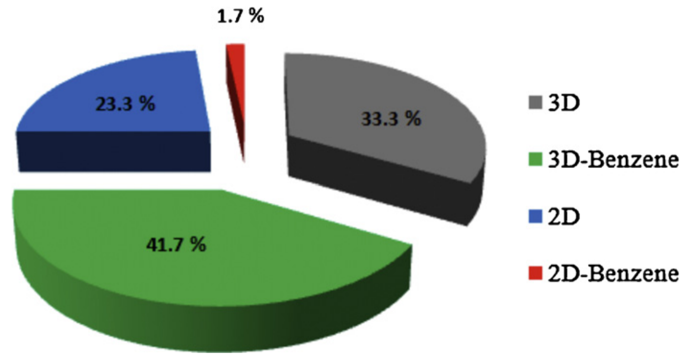

Fig. 1. Statistical classification data about reported pre-concentrating microdevices in general and for benzene 2D and 3D: refer to planar and three dimensional structures used for the preconcentration of gases and vapors in general; 2D- and 3D-benzene: refer to the structures used for the pre-concentration of benzene in particular).

Table 1 summarized the main cycled microfabricated pre-concentrators of benzene reported in literature and their application with detection devices. Fig. 1 presents a statistical data about such devices and sheds some light on the proportion of works dedicated to the special case of benzene. As could be noticed from this figure, almost half of the works reported in literature on gas micro-pre-concentrators focused on the pre-concentration of this compound. Among these latter, 96% of works were based on the 3D structure and only 4% using the planar design.

- Planar pre-concentrators

The first planar micro-concentrator for benzene was implemented by Casalnuovo et al. in 1999 and consisted of a suspended silicon nitride membrane with an area of 2.2 mm × 2.2 mm coated with a microporous polymer which acted as an absorbent material (Fig. 2) [14]. The pre-concentrator was coupled to a spiral micro-column and an array of four chemiresistors based on conducting polymers. This system was aimed at quantifying the mixture of benzene, toluene, xylene, ethylbenzene and chemical warfare agents (CWA). A concentration factor up to 100 was achieved by collecting the vapors during 40 s and desorbing them at 200 °C with a power consumption of 105 mW.

Blanco et al. reported in 2008 a planar pre-concentrator based on activated carbon and commercial Carbopack stuck by Tempflex over a 16 mm^2 alumina-based support equipped with a screen-printed platinum heater (Fig. 3). The pre-concentrator was characterized by a gas chromatograph/mass spectrometer (GC/MS) for the detection of benzene [15]. High concentration factors of about 600 per milligram of adsorbent were achieved by activated carbon, by collecting the analyte during 5 min at a flow rate of 200 mL min^{-1} and desorbing it with a temperature pulse of 200 °C. In another work [16] performed in 2011, activated carbon was deposited by airbrushing, achieving concentration factors up to 1000 per milligram of adsorbent. This planar pre-concentrator

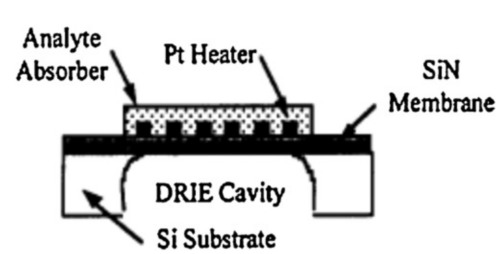

Fig. 2. Schematic cross section of the microhotplate concentrator stage. [1999] IEEE. Reprinted, with permission, from Ref. [14].