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A STUDY OF ALTERNATIVE GRANULAR ADSORBENTS FOR BENZENE AND TOLUENE PRECONCENTRATION

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KEY WORDS

Preconcentration, adsorption, VOC analysis, MEMS technology.

ABSTRACT

Introduction

Volatile Organic Compounds (VOCs) are a class of airborne pollutants that include any compound of carbon (excluding carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates, and ammonium carbonate) [1]. These compounds are characterized by their high vapor pressure (≥0.01kPa at 20°C), and their low boiling point. Among these pollutants, benzene and toluene are of interest because they are frequently founded in indoor air. These compounds have adverse effects on human health, for example in the case of toluene, the prolongated exposure may lead to fatigue, loss of coordination or a reduction in reaction time. More serious effects are caused by benzene since it has been classified as carcinogenic to humans (Group 1) by the International Agency for Research on Cancer. Consequently, European Union has established specific guidelines for indoor air quality setting the threshold concentration of benzene to 5 $\mu g/m^3$ (1.6 ppb). In France, this threshold has been decreased to 2 μgm^{-3} (0.6ppb) from 1st January 2018. Nowadays, only bulky laboratory chromatographs can detect such low concentrations since most of portable chromatographic devices have limits of detection in the order of tens or hundreds of ppb, even those having a preconcentration unit. Improvements could be made in this unit to achieve lower limits of detection, but as the device should remain portable, the preconcentration step must be a compromise between energy consumption, size, weight, selectivity and efficiency.
Carbopack B (Supelco, USA) is one of the most commonly used adsorbents for benzene and toluene preconcentration. It has a high surface area (100 m^2/g) which allows to trap a large amount of molecules but it is not selective since it adsorbs a wide range of molecules varying from C5 to C20. In addition, the main drawback of this adsorbent is its high temperature of desorption (between 200-250°C) which increase the energy consumption of the overall system and imposes the use of temperature resistant materials. As a response to these drawbacks, it is necessary to investigate alternative adsorbents with lower desorption temperatures. For these purposes, two adsorbents have been chosen for our study: Basolite® C300 and SBA-16 supplied by Sigma-Aldrich, USA and ACS Materials, USA, respectively. The results will be compared to those obtained on Carbopack B, chosen as a reference.

Materials and Methods

Our reference material, Carbopack™ B (60/80 mesh), is a non-porous graphitized carbon black with a surface area of 100 m^2/g. This carbon is hydrophobic which allows its use in high humidity environments. Carbopack™ B is also proposed by EPA as a standard method for general VOC sampling [1].
The first investigated material is SBA-16. This mesoporous silica has pores of 5 nm and a surface area between 500 and 700 m^2/g, thus higher than Carbopack™ B. This material has been selected because of its lower desorption temperature expected to be about 120°C for toluene, according to previous studies with a similar adsorbent called SBA-15 [2]. The other investigated gas adsorbent, Basolite® C300, also known as HKUST-1 or Cu-BTC MOF, is a metal organic framework (MOF) formed by copper nodes with 1,3,5-benzenetricarboxylic acid struts between them. This structure contains pores with diameters of 0.12, 0.825 and 1.137 nm that can be used for gas storage. The presence of pores results in a very high surface area, between 1500 and 2100 m^2/g according to the supplier. Basolite® C300 was already used for benzene preconcentration in a preconcentrator working by diffusion [3], where the adsorbent was directly exposed to ambient air. In this device, a 5.5µm layer of the material was deposited in a ceramic hotplate and placed close to a metal oxide sensor. This preconcentration step increased up to 10 times the signal of the detector for benzene and toluene. Hence, it could be interesting to evaluate the adsorption performances of this material using a forced air stream that may lead to higher preconcentration factors in less time.
The first step of this work was the characterization of the adsorbents. The most common methods to characterize substances in terms of pore volume and specific surface area are BET (Brunauer–Emmett–Teller) and BJH (Barrett-Joyner-Halenda) analysis. These methods can provide information about specific surface area, size, volume, and pore shape and pore-size distribution. Materials with high surface area and pore size similar to the size of the target molecules will be more suitable to be used as adsorbents for preconcentration. In addition, it is crucial to have interactions between the analytes and the adsorbent strong enough for the adsorption process, but also weak enough to allow the desorption at moderate temperatures.
Apart from surface area, thermostability of the adsorbents was analyzed by simultaneous thermogravimetry and differential scanning calorimetry (TGA-DSC). TGA is employed to analyze the change in the mass of a sample with respect to time or temperature and DSC is applied for measurements of the heat flow rate provided to a sample with respect to time or temperature. Coupling both techniques, it is possible to acquire information about physical absorption and desorption processes, fusion and crystallization events as well as thermal decomposition [4] and, thus, to select a range of desorption temperatures to be employed in the preconcentration tests. Once the range of temperatures has been defined, the setup shown in Figure 1 was used to test the performance of each adsorbent. The system consists of two bottles of gas, nitrogen and BTEX diluted in nitrogen (100 ppb), to generate the targeted benzene and toluene concentrations. The generated gaseous sample passes through a preliminary preconcentrator made of aluminium containing a cavity (7.60 x 4.60 mm) where the adsorbent is placed, a commercial chromatography column to separate benzene and toluene and a photoionization detector. The preconcentration factor is calculated from the ratio of peaks' area obtained with and without preconcentration unit.

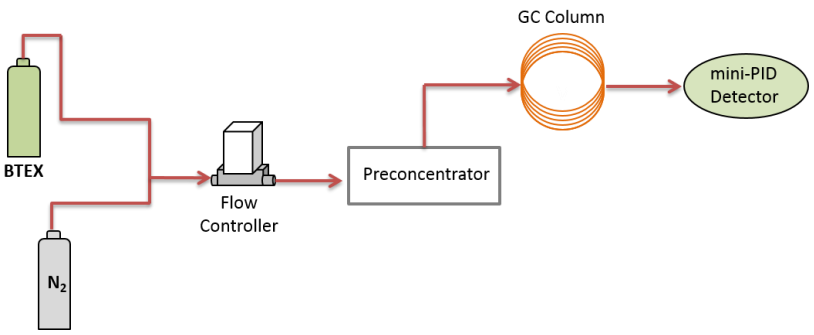

Figure 1. Set up for preconcentration tests

Results and Discussion

The results of BET and BJH analysis for the three adsorbents studied are given in Table 1:

Table 1. Surface area and average pore size obtained for the different adsorbents.

	Type of isotherm	Specific surface area (m^2/g)	Pore size (nm)
Carbopack B	II	100.94	---
SBA-16	IV	563.11	3-4.2
Basolite® C300	I	1733.51	1.8-1.9

These results are consistent with those announced by the manufacturer, the surface area being 100 m^2/g for Carbopack B, and between 500-700 and 1500-2100 for SBA-16 and Basolite® C300, respectively. BET analysis also provide information about the pore size which should be at least as large as the target molecules. As expected, in SBA-16 the pore size is between 3 and 4.2 nm. In the case of Basolite® C300, the size of the pores is lower than 2 nm indicating the presence of micropores. These micropores are big enough to host benzene and toluene molecules since their diameters are 0.492 and 0.535 nm, respectively, thus the material may be suitable for the preconcentration of these compounds. In addition, the hydrophobic character of the benzene linker enhances the hydrophobicity of these small pores [5] promoting stronger interactions between the adsorbent and the analytes.

According to the manufacturer, Carbopack™ B is stable at temperatures up to 400°C. Conversely, no information is available on the thermal stability of the other two adsorbents, thus an TGA-DSC analysis was performed for SBA-16 and Basolite® C300.

TGA-DSC analysis of SBA-16 shows a loss of weight of about 6% between room temperature and 90°C. This is probably due to the desorption of water, despite the fact that SBA-16 is generally hydrophobic, it can adsorb a small quantity of water as it was reported in other studies [6]. Over the temperature interval between 90°C and 1000°C, there is a variation of total weight of about 5% which means that the compound is thermally stable even at high temperatures. Same analysis was carried out for Basolite® C300. For this material, a change of about from 10% to 30% is observed in the range 70-120°C, again likely due to the desorption of water. Basolite® C300 has a significant affinity towards water since water molecules can coordinate to the free copper sites [5]. The other significant decrease in the total weight of the sample of about 25% is observed at 330°C, apparently corresponding to the degradation of the adsorbent. This temperature is higher to the thermostability of 280°C reported in other studies [7] for Basolite® C300. These results confirm the stability of both adsorbents at temperatures up to 250°C without any degradation.

Once the thermal stability of the adsorbents and the suitability of their pores for benzene and toluene adsorption were confirmed, a series of tests were carried out to quantify the preconcentration performances of each adsorbent. For this purpose, the first step was to inject 200 µL of 100 ppb of benzene and toluene diluted in nitrogen directly to the system without preconcentration stage. This measurement was taken as reference to quantify the improvement in the detector signal due to the preconcentration efficiency of each adsorbent. Then, numerous injections of 40 mL of 100 ppb of benzene and toluene diluted in nitrogen were carried out at different flow rates and desorption temperatures for the selected adsorbents. The results obtained in the optimal conditions are summarized in Table 2.

Table 2. Preconcentration factors obtained for different adsorbents.

	Sampling time (min)	Flow rate (mL/min)	Desorption temperature (°C)	Benzene Preconcentration Factor (PF)*	Toluene Preconcentration Factor (PF)*
Carbopack B	8	5	200	40	43
SBA-16	8	5	225	20	7
Basolite® C300	8	5	150	51	50

**PF defined as the ratio between the peak area obtained with and without preconcentration unit.*

All materials showed high preconcentration factors (P.F.) between 20 and 43, indicating that all of them can be employed as adsorbents for benzene and/or toluene preconcentration. SBA-16 showed an increase of PF

with the desorption temperature, indicating that the interactions of the target molecules with the adsorbent are very strong. As a result, at the same desorption temperature, SBA-16 presents lower PFs than Carbopack B. On the contrary, employing Basolite® C300, the PFs obtained were higher than the ones attained employing Carbopack B. In these experiments with metal organic framework, a PF of 51 and 50 were obtained for benzene and toluene, respectively, at a relatively low desorption temperature (150°C). These results suggest that the use of this adsorbent could potentially increase the efficiency of preconcentration unit and reducing its energy consumption.

Conclusions and Perspectives

A study has been carried out to investigate the performance of two different materials, i.e. SBA-16 and Basolite® C300 as adsorbents for benzene and toluene preconcentration. Surface area and pore size were evaluated and compared with those of Carbopack B, a reference material for benzene and toluene preconcentration. Both materials present high specific surface area due to the presence of pores in their structures. Thermal stability of the proposed adsorbents was confirmed up to 250°C by TGA-DSC analysis demonstrating their potential use for benzene and toluene desorption occurring usually below 250°C. Finally, injections of the same amount of benzene and toluene on the different adsorbents were performed employing different flow rates and desorption temperatures. The results have shown that Basolite® C300 could achieve a higher preconcentration efficiency for the target compounds at lower desorption temperatures. This fact should reduce the energy consumption of the preconcentration stage and, thus, the consumption of the overall analytical device, increasing its autonomy. Desorption at low temperature may also bring the possibility to employ cheaper materials since there is no need for them to be temperature resistant. Future work lays on introducing this adsorbent in a MEMS-based preconcentrator and the integration of the chip in a portable analytical device to evaluate the improvement in the sensitivity of the system.

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