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STUDY OF ALTERNATIVE ADSORBENTS FOR PRECONCENTRATION OF BENZENE AND TOLUENE: IMPROVING THE SENSITIVITY OF A MINIATURIZED GC TO PPT LEVELS

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ABSTRACT

In this work, SBA-16 and HKUST-1 have been investigated as alternative adsorbents for benzene and toluene preconcentration and compared with Carbopack B, the reference material for VOC sampling. They have been fully characterized and assessed in terms of preconcentration performances. For both materials, preconcentration tests shown higher preconcentration factors than the ones obtained with Carbopack B. Using these sorbents in a preconcentrator device, the detection limit of our miniaturized GC prototype was calculated to be 0.2 ppb for both compounds. Both adsorbents are promising for environmental applications in BTEX monitoring.

KEYWORDS: miniaturized GC, BTEX, environmental air monitoring, HKUST-1, SBA-16.

INTRODUCTION

Indoor air quality (IAQ) is a growing concern to the society due to the harmful effects of airborne pollutants on human health. Among the most frequently found pollutants, toluene can be harmful to human health only at high levels but benzene is carcinogenic even at few ppb (Group 1, IARC 1982). Therefore, European Union has established a threshold concentration of benzene to 5 $\mu\text{g}/\text{m}^3$ (1.6 ppb). In France, this threshold has been decreased to 2 $\mu\text{g}/\text{m}^3$ (0.6 ppb) from 1st January 2016. Recently, our research group reported the development of a portable GC-PID for indoor BTEX detection at ppb levels [1]. The aim of this study is to improve the limit of detection of this device to ppt levels by integrating a preconcentrator and thus, to meet with the new regulations. SBA-16 and HKUST-1, were investigated as adsorbent for benzene and toluene preconcentration and compared to CarbopackTM B (C-B), the reference material proposed by EPA as a standard method for VOC sampling.

EXPERIMENTAL

Scanning electron microscopy (SEM), nitrogen adsorption/desorption isotherms (B.E.T.), thermal gravimetric analysis (TGA) and thermal programmed desorption (TPD) analysis techniques were employed to characterize the investigated adsorbents in terms of morphology, specific surface area, porosity, thermal stability and optimal desorption temperature. Once adsorbents characterized, preconcentration tests were carried out by using a microfluidic preconcentrator designed by our team. This preconcentrator has been integrated in the μGC developed by Nasreddine et al. [1] which allowed BTEX analysis in 10 min and had a detection limit of 1 ppb for benzene and toluene without preconcentration unit.

RESULTS AND DISCUSSION

The investigated adsorbents were characterized using the techniques aforementioned. The results are summarized in Table 1. As it was expected, specific surface areas were higher for the porous materials, namely SBA-16 and HKUST-1, our values being in good agreement with the ones given by the manufacturers. Thermal stability of SBA-16 and HKUST-1 in the common range of desorption temperatures ($<250^\circ\text{C}$) was confirmed by ATG-DSC analysis. The optimal desorption temperature of BTEX from the alternative materials was lower than 200°C which may lead to a decrease in the energy consumption of the preconcentration unit in comparison with other employing C-B. A preliminary microfluidic preconcentrator was constructed and integrated in a miniaturized GC system to evaluate the preconcentration performances of the adsorbents. Injections of mixtures of benzene and toluene diluted in nitrogen were conducted at different concentrations and various sampling volumes (see Figure 1). Peak area

increases perfectly linearly with gaseous concentration and sampling volume for both adsorbents. Preconcentration factors (PF) were calculated from the ratio between the peak area obtained with and without preconcentrator.

Table 1: Summary of the adsorbents characterization.

	Specific surface area (m ² /g)	Porosity	Average Pore size (nm)	Micropore Volume (%)	Max. Operating Temp. (°C)	Desorption Temp. (°C)	Water affinity
C-B	112	Non-porous	No	--	< 400	200	No
SBA-16	572	Mesoporous	5	<1%	< 1000	129	Weak (5%)
HKUST-1	1734	Microporous	< 2	77 %	< 330	180	Strong (10-30%)

Employing HKUST-1, PF of 47.5 and 30 were obtained for benzene and toluene, respectively, at a relatively low desorption temperature (150°C) whereas using Carbpac B, the PF were 13.9 and 11.5 for the above-mentioned compounds at 200°C. These results suggest that the use of HKUST-1 could potentially increase the efficiency of the preconcentration unit while reducing its energy consumption. Limit of detection for the system with a HKUST-1-filled preconcentrator was calculated to be 0.2 ppb (S/N = 3) for the target compounds.

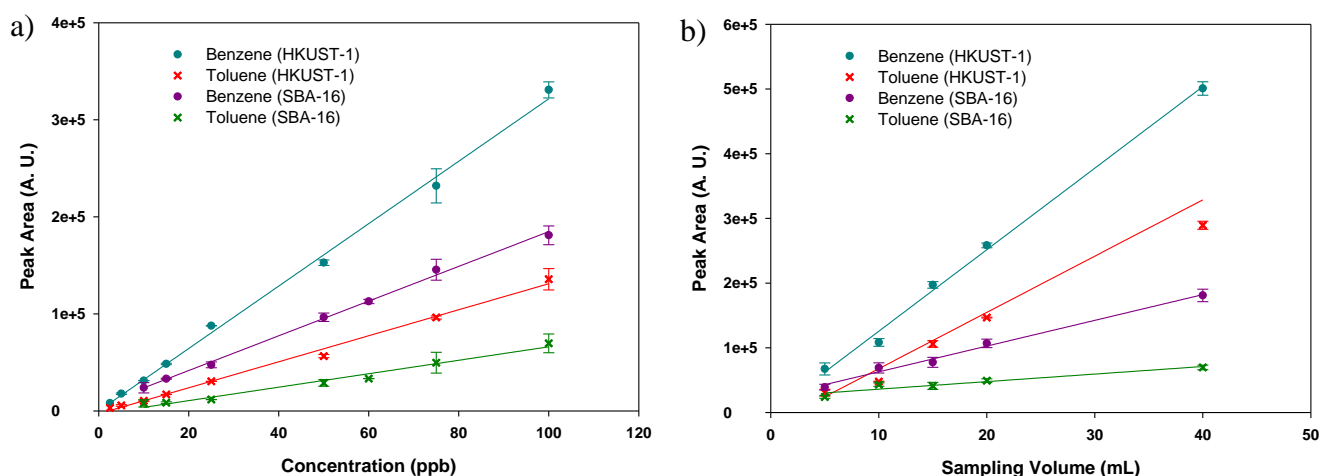


Figure 1: a) Variation of peak area with the gaseous concentration and b) with the sampling volume

CONCLUSION

SBA-16 and HKUST-1 have been characterized and evaluated as alternative adsorbents for benzene and toluene preconcentration. For both materials, the PF obtained are higher than those obtained using the reference material C-B. Using HKUST-1 as adsorbent in our GC prototype, the limit of detection of the system was calculated to be 0.2 ppb for the target compounds. To our knowledge, this is one of the few miniaturized GC prototypes that achieves a limit of detection in order of hundred ppt for benzene and toluene. Once the preconcentration performances demonstrated, a MEMS-based preconcentrator is currently being manufactured to decrease the dimensions and the energy consumption of the device while keeping its sensitivity to ppt levels.

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