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Selection and characterization of adsorbents for the analysis of an explosive-related molecule traces in the air

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ABSTRACT

This study is focused on the development of a 3D micro-preconcentrator for a sensitive analysis of an explosive-related compound: orthonitrotoluene (ONT). A set of potentially efficient adsorbents for the pre-concentration of ONT was investigated here. An in-depth characterization of their textural properties was carried out in order to better understand their adsorption behavior toward the target analyte. More particularly, this study allowed highlighting the interesting adsorption features of a hydrophobic zeolite and a porous activated carbon in relation to their preconcentration performances toward ONT at the ppb level. Moreover, we found a difference in the adsorption mechanism between both selected adsorbing materials.

1. Introduction

The detection of explosives and explosives-related agents is important for preventing terrorism actions in public areas. For example, the analysis of nitro-aromatic compounds (such as trinitrotoluene (TNT) and nitrotoluene isomers) and nitroamines (such as 1,3,5-trinitro-1,3,5-triazacyclohexane (so-called RDX)), widely used in military and industrial applications, is quite complex due to their low vapor pressure [1,2]. When these explosives are left in the environment for a long period, they tend to degrade into a variety of species such as nitrotoluene, nitrobenzene and dinitrotoluene [3,4]. The detection of these explosives-related compounds in the gas phase is then possible due to their vapor pressures higher than explosives species. Nevertheless, highly sensitive devices are required for their detection. The implementation of efficient detection equipments requires at the same time portability, selectivity and low detection limit [5]. In that sense, miniaturization offers functional and economical benefits such as a reduction of sample size, decrease of reagent consumption and inexpensive mass production [6]. Therefore, the use of solid-state gas sensors, especially based on metal oxides, seems to be an interesting option. However, the selective detection of one specific pollutant in a complex mixture (air) is impossible by using a single gas sensor [7]. A chromatographic separation stage is indeed necessary to determine all the chemical compounds in a mixture [8].

Nowadays, there is a growing demand for the use of preconcentrating devices coupled with chromatographic detection systems [9]. The preconcentration process consists in adsorbing the target gas at room temperature on a specific adsorbent. This concentration step is followed by thermal desorption, allowing to generate a higher concentration of the target compound. In this way, the gas micro-preconcentrator lowers the detection limit of the system and improves its performance to detect smaller concentrations (at ppb levels) [10]. The performance of a preconcentrator is commonly evaluated through the determination of the preconcentration factor, which is generally defined as the final concentration of the desorbed sample divided by the initial concentration of the analyte present in the original sample [9]. This factor depends on several variables such as nature and amount of adsorbent, and on preconcentration parameters such as adsorption flow rate and duration, desorption flow and heating rates [11].

On one hand, the nature of the adsorbing material is the most important parameter determining the performance of the gas preconcentrator. For a decade, adsorbents such as carbonaceous

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materials, zeolites and polymers have been widely used in many different applications. Ideally, a suitable adsorbent should have a high adsorption capacity, a strong adsorption affinity, fast adsorption and desorption rates, as well as good stability and durability in use [12]. Activated carbons were found to be promising candidates for the retention of aromatic volatile organic compounds. Moreover, their porous structure can be developed and designed for retaining the target compound through the adjustment of their activation conditions [13,14]. The use of carbonaceous adsorbents such as carbon nanotubes and nanoporous carbons was reported for the adsorption of nitrobenzene [15]. However, the recovery of the adsorbed compound was quite difficult. By contrast, the use of porous resins such as Tenax TA was found to be more interesting, as it allowed to completely desorb the compound at temperatures below 423 K [15]. Surface imprinted periodic porous organosilicas were also employed for trapping TNT before its detection via electrochemical techniques [16,17]. Due to its crystalline well-defined pore structure, zeolite might also be an interesting candidate for preconcentration applications. It is well known that zeolites have a good selectivity due to their homogeneous pore size, and they have indeed been commonly used as molecular sieves [18–20]. Moreover these materials exhibit a strong adsorption affinity allowing the capture of gases at very low concentration. Unlike carbonaceous materials, they can provide a better understanding of the relationships between sorption performances and textural properties. Therefore, the adsorption of organic vapors on zeolites can be an important issue for both theoretical studies and environmental applications [21–23]. Zeolites are also known for their durability in use, high thermal stability, and high resistance to corrosive gases, so that desorption of high-boiling point compounds is possible without a significant degradation in performance [24]. On the other hand, and whatever its nature, the higher is the amount of adsorbent, the higher is the preconcentration factor. Among the different preconcentrating structures proposed in the literature for hosting the adsorbent, three-dimensional structures seem to be more efficient in terms of preconcentration capacity due to the higher amount of adsorbent, which can be hosted inside them [9]. In particular, the 3D cavity design was found to be more efficient than the spiral channel design, due to an easier control of the gas flow distribution and the possibility to avoid the overpressure problems inside the microstructure, leading to higher preconcentration factors.The present study is focused on the development of a 3D cavity-micro-preconcentrator, and especially on the selection of an appropriate adsorbent for the preconcentration of an explosive-related compound (orthonitrotoluene (ONT)). A series of in-depth analyses were performed using a set of adsorbents including porous activated carbon, porous polymer and a hydrophobic zeolite. First, we used some standard analytic techniques to characterize and preselect the best adsorbing materials for the analysis of ONT. Then, we tested the micro-preconcentrator with a chromatographic column in front of a chemical gas sensor in order to evaluate the preconcentration capacities of such detection system.

2. Materials and methods

2.1. Adsorbent description

Various materials can be used as adsorbents for the preconcentration of chemical compounds. The choice of the adsorbing material depends both on the chemical nature and on the dimension of the target molecule. In this research work, we studied three families of adsorbents for the preconcentration of an explosive-related compound, the orthonitrotoluene (ONT) [3,4].

2.1.1. Activated carbons (ACs)

Four activated carbons were prepared from two commercial precursors. One, labeled “N”, was prepared from granular Norit carbon, supplied by SAUF (Norit, Netherlands), and had a grain size of 10–20 μm. The three other ones, labeled “KL_1”, “KL_2” and “KL_3”, were prepared from Kraft lignin supplied by Ligno Ibérica (Spain), and had a grain size below 40 μm. All these activated carbons were chemically activated at 973 K with KOH acccording to the procedure extensively detailed in [25], using an increasingly high KOH to precursor weight ratio from KL_1 to KL_3.

2.1.2. Zeolite

Wessalith® DAY, being a dealuminated Y-type zeolite of faujasite structure, was purchased from Degussa zeolite products and was labeled “DAY”. This material was characterized by a particle size around 3–5 μm and had a high SiO_2/Al_2O_3 molar ratio (>100), making it highly hydrophobic. Due to this, co-adsorption of moisture is minimized, which enables the preferred adsorption of the volatile organic compounds even at very high relative humidity [26,27].

2.1.3. Polymer

One porous polymer was also studied for the adsorption of ONT. 2,6-Diphenylene-oxide polymer resin also called Tenax TA (80/100 mesh) was purchased from Sigma Aldrich and labeled “TA”. The average particle size was around 200 μm with an average pore size of about 200 nm, as specified by the manufacturer [28,29].

2.2. Adsorbent characterization

In order to evaluate the porous textures and adsorption capacities of the different adsorbents selected in this study, we used nitrogen adsorption manometry (ASAP 2020 Micromeritics) and thermogravimetry (TGA 92, Setaram), respectively.

Porous texture parameters such as surface area, pore volume and average pore diameter were determined from the corrresponding nitrogen adsorption–desorption isotherms at 77 K with an automatic instrument. Before each experiment, the adsorbents were first out-gassed at high temperature (573 K for the carbons and zeolite and 473 K for Tenax TA) in order to eliminate any molecule adsorbed at room temperature during the storage period. Adsorption data were recorded over at relative pressures ranging from 10^{-5} to 0.99. The total pore volume was determined at $P/P_0 = 0.99$. The specific surface area of each material was determined using the Brunauer, Emmett and Teller (BET) calculation method. Horvath–Kawazoe and BJH methods were used for the determination of micropore volumes and diameters, and mesopore diameters, respectively. The adsorption/desorption rates and desorption temperature of ONT were determined from TGA experiments. In this case, 4 mg of each adsorbent powder was first out-gassed at 573 K under 100 mL min^{-1} of N_2. Then, each sample was exposed to ONT diluted at a concentration of 22 ppm in N_2, flowing at room temperature at a rate to 100 mL min^{-1}. The desorption of ONT was realized by heating the sample at 503 K with a temperature ramp at a rate of 10 K min^{-1}.

2.3. Micro-preconcentrator fabrication and adsorbent deposition

The gas preconcentrator consisted of a 3D micro-structure etched on a silicon substrate using classical clean room solutions (DRIE). The dimensions of such micro-cavity were 5 mm-wide, 10 mm-long and 400 μm-deep. The micro-structures were equipped with micropillars etched on the silicon substrate in order to fix the adsorbent inside the structure. Each run allowed fabricating 8 micro-structures on a 4 in. silicon substrate. Platinum micro-heaters were deposited by sputtering on the backside of each