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Evaluation of solid adsorbent materials for cryogen-free trapping—gas chromatographic analysis of atmospheric C2–C6 non-methane hydrocarbons

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Abstract

Nine commercial solid adsorbent materials (in order of decreasing surface area: Carboxen 1000, Carbosieve S III, molecular sieve 5A, molecular sieve 4A, silica gel, Carboxen 563, activated alumina, Carbotrap and Carboxen 1016) were investigated for their ability to trap and release C2–C6 non-methane hydrocarbons (NMHCs) in atmospheric samples for subsequent thermal desorption gas chromatography-flame ionization detection analysis (GC-FID). Recovery rates for 23 NMHCs and methyl chloride (CH_3Cl) were determined. A microtrap filled with the three adsorbents Carbosieve S III, Carboxen 563 and Carboxen 1016 was found to allow for the analysis of the widest range of target analytes. A detection limit of approximately 3 pptC [parts per trillion (carbon)] in a 1 l air sample and a linear response over a wide range of volatilities and sample volumes was determined for this configuration. Water vapor in the sample air was found to causes interference in trapping and subsequent chromatographic analysis of light NMHCs. A Peltier-cooled, regenerable water trap inserted into the sample flow path was found to mitigate these problems and to allow quantitative and reproducible results for all analytes at all tested humidity conditions.

Keywords: Atmospheric analysis; Gas chromatography; Volatile organic compounds; Non-methane hydrocarbons; Solid adsorbents; Thermal desorption

1. Introduction

Non-methane hydrocarbons (NMHCs) have received growing interest in atmospheric research, as their concentrations and ratios can yield valuable insight into air mass transport, hydroxyl radical concentrations and photochemical ozone production [1–3]. NMHCs and NMHC ratios have also been identified as tracers for pollution sources such as automobile traffic, fossil fuel exploration and biomass burning [4–12]. These interests have motivated activities towards the establishment of a network of remote automated background stations to monitor NMHCs over a long period of time [13]. Ideally, NMHC monitors to be used for this purpose would have to require low maintenance and be operable without an external supply of cryogen, hydrogen or zero air. Hydrogen and zero air, which are needed for NMHC gas chromatography instruments, can be generated on-site with commercially available gas generators. A preconcentration step is typically required to increase NMHC concentrations to levels that allow analysis by gas chromatography-flame ionization detection (GC-FID). A common technique is the freeze-out of NMHCs in a cold trap that is cooled with a cryogen (such as liquid nitrogen). The supply of liquid nitrogen is cumbersome and can be a substantial expense for long term monitoring purposes especially at remote locations. These constraints make it desirable to use a NMHC focusing and injection system that does not rely on liquid cryogen techniques. Furthermore, one-stage trapping/injection systems are preferable because of their simplicity and reduced design and operational cost. A one-stage system typically requires a low volume microtrap (internal volume <1 cm^3) to ensure rapid sample desorption and narrow chromatographic peak shape. However, the internal diameter of the adsorbent trap needs to be large enough so that the adsorbent-filled trap does not pose a prohibitively large flow resistance in the sampling flow path. Another limiting factor on the microtrap

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volume is that the trap has to be able to hold the required amount of adsorbent. Previous studies have shown that microtraps filled with strong adsorbent materials in combination with moderate cooling (down to −30 °C) by thermoelectric coolers can quantitatively trap selected volatile organic compounds (VOCs) down to the C2–C4 range [14–16].

The ability of an adsorbent to retain NMHCs is typically proportional to its surface area. A review of the physical properties and the production processes of many different adsorbent materials was published by Dettmer and Engewald [17]. The retention of compounds on solid adsorbents is generally inversely correlated with their volatility. Secondly, molecular structure and the abundance of unsaturated carbon–carbon bonds were found to affect adsorption efficiency. This made it especially challenging to quantitatively trap highly volatile compounds, such as C2 hydrocarbons (ethane, ethene and acetylene). Saturated compounds (e.g. ethane, propane) were found to be retained better on carbon molecular sieve adsorbents than unsaturated compounds (ethene, propene) [18]. In agreement with this study, Badol et al. [19] found that acetylene was the most difficult compound to retain quantitatively (despite a higher boiling point than ethane or ethene) on Carbosieve SIII. Approximately 110 mg of this adsorbent were needed to increase the breakthrough volume to >600 ml at −30 °C trapping temperature.

Carbon molecular sieves such as Carbosieve and Carboxen materials were found to provide the highest adsorption efficiency for the most volatile (e.g. C2–C4) compounds, while heavier analytes in the C5–C6 range were most often trapped by surface adsorption on carbon blacks. For instance, hydrohalocarbons and halocarbons were best retained on Carbosieve SIII, followed by Carboxen 1000 and 1001, while molecular sieve 5A was a fairly weak adsorbent [20]. Similar results were reported by Betz and Supina [21], who evaluated 10 different solid adsorbents (including: Carbosieve S III, Carbosieve S II, Carboxen 563, 564 and 569 and activated charcoal) and found that Carbosieve S III was the strongest material for trapping ethane. Within the Carboxen product line Carboxen 1000 was the strongest adsorbent [22].

The temperature required to release analytes from the adsorbent bed depends both on the adsorbent strength and analyte volatility. Decomposition reactions became more probable at higher temperatures (e.g. [23]). Weaker adsorbents placed in front of a stronger adsorbent in a multi-layer adsorbent trap can be used to ensure complete thermal desorption at lower temperatures [24].

The trapping efficiency of adsorbent traps increases exponentially with decreasing temperature. However, the increasing co-adsorption of atmospheric water vapor and carbon dioxide at subambient temperatures can cause sampling and chromatographic interferences. Water vapor can affect the trapping procedure in several ways. First, the adsorption efficiency for organic analytes, especially for light NMHCs can be reduced [20,25]. These studies suggested that a monolayer of adsorbed water was formed on the surface of the adsorbent material when air with high water vapor content was sampled. The water monolayer was then occupying a significant fraction of the adsorbent micropores. The adsorption efficiency decreased as these pores were no longer available for the adsorption of volatile organic compounds. The fraction of occupied micropores was found to be proportional to the volume of adsorbed water [26]. Gawrys et al. [27] determined a threshold relative humidity of 35% RH at 30 °C for Carboxen 569, Carboxen 1001 and Carbosieve S III, above which the micropores were slowly filled with water and the recovery of VOCs was reduced. The threshold for Carboxen 1000 was 45% RH at 30 °C sampling temperature.

Secondly, focusing traps were also found to become plugged due to freeze-out of atmospheric water vapor while sampling at sub-zero temperatures, which can restrict the sampling flow to a possibly insurmountable degree. Furthermore, chromatographic and detection interferences could subsequently arise in the chromatography process [20,28]. Carbon molecular sieve type adsorbents were found to exhibit the highest water retention [21,29].

These results underline the necessity to selectively remove water vapor from the sampling air prior to the adsorption step. Different types of water traps and water managing techniques were used to mitigate these problems [30–36]. An increasingly popular technique is to lower the sample dewpoint by freeze-out of water vapor [15,37,38]. Typically, the sample is drawn through a section of thermoelectrically cooled tubing. The water trap is subsequently heated and water is removed by applying a vacuum or by purging the trap with a dry gas. It was proven that this technique required little maintenance and did not interfere with the sampling of C2–C10 NMHCs. These water traps can be operated automatically over a long period of time and are favorable approaches for long-term, remotely operated sampling projects [38,39].

Most of this previous research investigated the use of a particular adsorbent for a narrow range of applications, e.g. for a few targeted compounds. Our goal was to characterize readily available adsorbents for their applicability over a wide range of analyte volatilities. This research was conducted in the context of instrument development for NMHC monitoring at a remote sampling location and for continuous, automated and unattended analysis of a large series of flask samples on a laboratory instrument. Commercially available adsorbent materials, which were previously reported in the literature and appeared to be suited for volatile NMHC preconcentration, were systematically investigated for the cryogen-free trapping of C2–C6 NMHCs. The susceptibility of this analysis towards water vapor in the sampling stream was studied in detail and a freeze-out water trap, suitable for automated, long-term solid adsorption–thermodesorption trapping with GC-FID was thoroughly tested.

2. Experimental

2.1. Instrumental

2.1.1. Inlet system

The experiments were performed using a custom-made inlet system coupled to a commercial GC with FID (HP 5890 Series II, Hewlett-Packard, Palo Alto, CA, USA). A schematic of the instrument is shown in Fig. 1. The GC column was an