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Short communication

Artifact-free preparation, storage and analysis of solid adsorbent sampling cartridges used in the analysis of volatile organic compounds in air

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Abstract

Technical details on the preparation, conditioning, storage and analysis of solid adsorbent cartridges are given in order to avoid contaminant and artifact formation.

Keywords: Air analysis; Environmental analysis; Sampling cartridges; Adsorbents; Volatile organic compounds

1. Introduction

In a recent study on the passive sampling of airborne volatile organic compounds (VOCs) onto solid adsorbents and subsequent analysis by thermal desorption, gas chromatography (GC) and flame ionization detection, Cao and Hewitt [1] describe experiments with the solid adsorbents Tenax-TA, Tenax-GR, Carbotrap and Chromosorb 106 and the build-up of contaminants on these adsorbents during storage. We have been working over several years with the adsorbents Tenax-TA, Tenax-GR, Carbotrap C, Carbotrap and Carbosieve S-III in a number of different sampling and analysis systems. In our work with these individual adsorbents and with a multistage adsorbent cartridge system (Carbotrap C/Carbotrap/Carbosieve S-III) we have been able to achieve low contaminant levels. This may indicate that the problems encountered by Cao and Hewitt are not from a degradation of the adsorbent but a gradual build-up of these contaminants during storage from passive sampling or introduction of contaminants with the materials used during cartridge assembly or during one of their analytical procedures. Technical details for preparing, conditioning, handling, storing and analyzing solid adsorbent cartridges that circumvent most of the observed difficulties described by Cao and Hewitt [1] are given below.

2. Experimental

2.1. Cartridge preparation

Sampling tubes are prepared from 0.25-in. (1 in. = 2.54 cm) silica-coated stainless-steel tubing (Restek, Bellefonte, PA, USA). Adsorbent is retained in the tubes by inserting stainless-steel retaining springs (Perkin-Elmer, Norwalk, CT, USA) and stainless-steel sieves (Perkin-Elmer).

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These materials are sonicated twice in methanol and baked in an oven at 150°C for 4 h before filling the tubes with adsorbent. A glass-wool plug [silanized glass wool (Alltech, Deerfield, IL, USA)] is used to retain the adsorbent at the inlet side. In the preparation of multibed cartridges individual adsorbent layers are separated by silanized 6 mm diameter glass-fiber filter discs (Tissueglass 2500A0; Pallflex, Putnam, CT, USA). Cartridges are sealed with 0.25-in. stainless-steel Swagelok ferrules and nuts. Lately, we have also been using 85% Polyimide/15% Graphite ferrules (Supeltex M-2A; Supelco, Bellefonte, PA, USA) with similar results. These ferrules have the advantage that they can be removed for cartridge analysis on an automated cartridge thermal desorption instrument (ATD-400, Perkin-Elmer). All materials and tools used in the preparation of the adsorbent tubes are metal or PTFE material and are precleaned in organic solvent before use. During cartridge preparation and also during all following procedures the cartridges are always handled wearing disposable Latex gloves.

2.2. Cartridge conditioning

Ten cartridges at a time are mounted on a manifold, purged with nitrogen at 100 ml min^{-1} and heated in a GC oven. The purge gas used is ultra-high-purity nitrogen which is further filtered through a hydrocarbon scrubber (part 103488; Scientific Glass Engineering, Houston, TX, USA), a high-capacity oxygen trap (part N930-1179, Perkin-Elmer) and an indicating oxygen trap (part N930-1191, Perkin-Elmer). Cartridges are purged in the backflush mode and the outlets are connected to 20 cm × 0.8 mm I.D. stainless-steel tubing, which serve as a diffusion resistance and prevent air from diffusing into the back of the cartridges while they are heated. The temperature during conditioning is 300°C which is 50°C above the maximum desorption temperature during analysis. Cartridges are heated for at least 8 h and taken off the manifold as soon as possible after the heat is turned off (preferably while they are still hot) and capped with Swagelok caps (baked at 300°C with the cartridges).

2.3. Cartridge storage

After conditioning, cartridges are placed into glass jars with sealing metal lids. The jars and lids are cleaned prior to use by heating in an oven overnight at 100°C. One jar can hold about 15 sampling tubes. An activated charcoal adsorption cartridge (Orbo-32, 400/200 mg, Supelco) is utilized to keep the headspace over the cartridges hydrocarbon-free. Both ends of the charcoal tube are open and the tube is placed in the jar together with the adsorbent tubes to serve as passive hydrocarbon sampler. The jars containing the cartridges are stored in a freezer at −30°C.

2.4. Cartridge analysis

Cartridges are purged with helium for 1 min at 25 ml min^{-1} to remove air prior to the thermal desorption. Cartridges are then heated at 25°C min^{-1} to 250°C under a purge flow of 20 ml min^{-1}. Desorbed VOCs are prefocussed on an open tubular 0.53-mm uncoated fused-silica column at −175°C and then flash heated to 75°C and backflushed onto the analytical GC column. About 44 ng of deuterated benzene are added to each sample as an internal standard by filling a sample loop with the gas-phase standard and injecting the contents of the sample loop onto the freezeout trap prior to the thermal desorption of the adsorbent tube. Other analytical details of the instrumentation and procedure will be given shortly [2].

3. Results and discussion

Fig. 1 illustrates a typical example of a blank sample that was obtained in the following manner: the cartridge was prepared and conditioned as described above. The sample cartridge is a multibed system containing 300 mg Carbotrap C, 125 mg Carbotrap, 225 mg Carbosieve S-III (all adsorbents were from Supelco). After conditioning, the cartridge was kept in a freezer for three

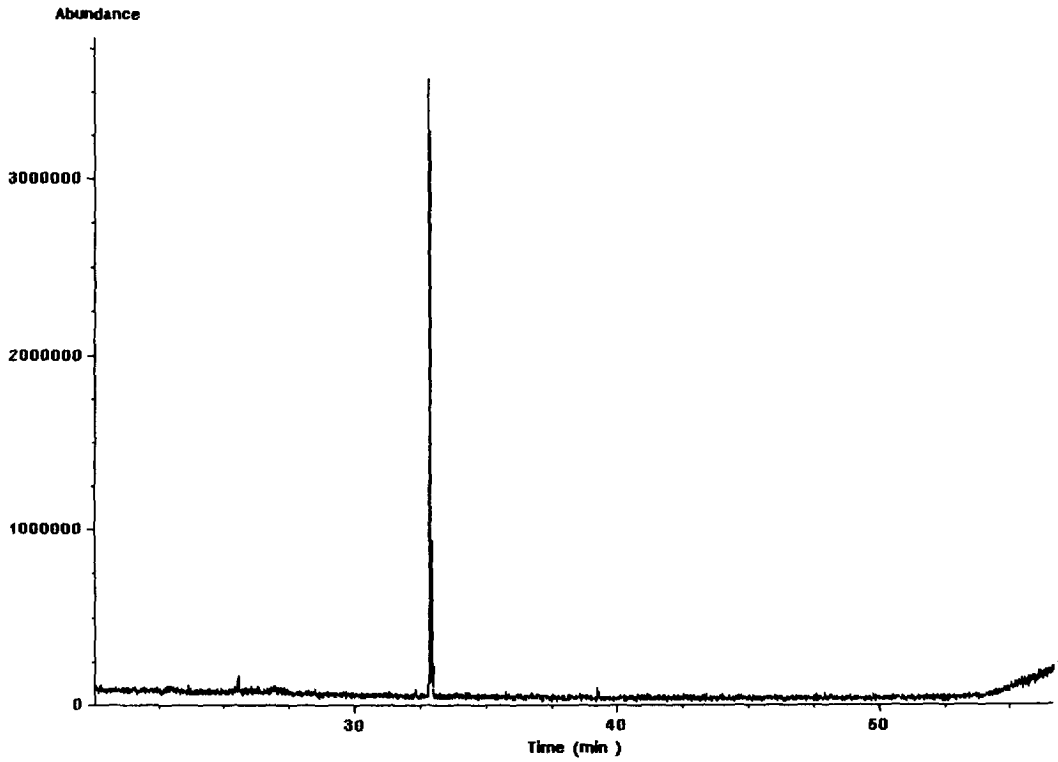

Fig. 1. GC–MS chromatogram of a blank sample (multibed adsorbent cartridge containing Carbotrap C/Carbotrap/Carbosieve S-III) analyzed after three months of storage.

days, then taken to a field site and kept at about 0°C in an ice chest for five days. During this time the jar that contained this particular cartridge was opened and closed about 15–20 times to remove and return other cartridges that were used for sample collection. The jar was brought back to the laboratory and kept in a freezer at −30°C. For the next 1–5 days the jar was again opened and closed about 10–15 times to remove sample cartridges that were analyzed as soon as was possible. The blank cartridge, however, was kept in the freezer for another 78 days before it was analyzed by thermal desorption, cryogenic freezeout and temperature programmed GC with mass spectrometric detection as described above. This method covers the VOC volatility range of about C_3 to C_{15}. The chromatogram in Fig. 1 reveals low blank levels. Except for the deuterated benzene internal standard signal at t_R = 32.86 min, only very minor peaks at 25.56 min [trichlorofluoromethane (F-11)], 32.33 min (1,1,1-trichloroethane), 39.30 min [hexamethyltrisiloxane (column bleed)] are observed. A benzene signal at $t_R = 32.94$ min is almost baseline separated from the deuterated benzene and is an impurity in the internal standard source. From the internal standard amount added to this sample, it can be estimated that all contaminants are below the 500 pg level. This results in a maximum contaminant uptake rate of about ≤5 pg per day. This rate is substantially lower than the uptake rates observed by Cao and Hewitt [1], which were in the range of 100–300 pg per day for the major contaminants observed.

In a different experiment we conditioned a set of ten Carbotrap 300 tubes (Supelco, these tubes contain 300 mg Carbotrap C, 200 mg Carbotrap B and 125 mg Carbosieve S-III) and stored five of them under the detailed conditions in a freezer and the other five capped with standard

Perkin-Elmer O-ring-sealed PTFE caps in laboratory air at room temperature. Analysis of both sample sets was performed after a two weeks storage time using the ATD 400 and temperature-programmed GC–flame ionization detection. The comparison of the two data sets revealed substantially lower blanks under the freezer storage conditions: the total detected peak area count was more than ten times higher in the set of tubes stored in laboratory air with the O-ring-sealed caps than in the sample set stored with Swagelok caps under clean headspace atmosphere in a sealed jar at −30°C.

Because of the consistently low contaminant levels observed from activated charcoal type (Carbotrap and Carbotrap C) and molecular sieve type (Carbosieve S-III) adsorbents these adsorbents are now preferably used. In contrast, our earlier results with Tenax TA and Tenax GR showed that these adsorbents are more prone to contaminant build-up and also to artifact formation during sampling by reactions with other air constituents, in particular with ozone and water. These characteristics have been well established in a number of other studies [3–6].

4. Conclusions

In conclusion, our experiences and the examples given here show that low blanks and good storage stability of solid adsorbent cartridges have been achieved with the described analytical steps of cartridge preparation, conditioning, storage and analysis. Important measures to reduce contaminant levels involve conditioning of adsorbent tubes at higher temperatures than used for thermal desorption during analysis, preventing the diffusion of air into the tubes during conditioning, capping of the adsorbent tubes with Swagelok ferrules and caps during storage and storage under a purified atmosphere and at freezer temperatures.

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