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Short communication

Build-up of artifacts on adsorbents during storage and its effect on passive sampling and gas chromatography–flame ionization detection of low concentrations of volatile organic compounds in air

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Abstract

The levels of blank artifacts on four adsorbents commonly used for air sampling (Tenax-TA, Tenax-GR, Carbotrap and Chromosorb 106) were observed to increase during storage. This may determine the detection limits and hence their suitability for the passive sampling of volatile organic compounds in ambient air. Blank build-up on Chromosorb 106 was very high, and this material cannot be used for passive sampling in ambient air. The blank build-up on Carbotrap was also high, especially in the chromatographic range corresponding to hydrocarbons of $\leq C_5$, but that on Tenax-TA and Tenax-GR was very low. Simultaneous sampling was carried out using different adsorbents, and for compounds that are the main artifacts on adsorbents (e.g., benzene on Tenax, benzene and toluene on Carbotrap) the results from Carbotrap are much higher than those from Tenax-TA and Tenax-GR, and the results from Tenax-TA and Tenax-GR also vary.

1. Introduction

One of the main limitations in the application of passive samplers (e.g., Perkin-Elmer diffusion tubes) to the determination of low concentrations of organic compounds in air [typically sub-ppb (v/v) (ppbv) in rural air] is the blank build-up on adsorbents due to artifact formation during storage and exposure. Although blank levels can be made extremely low by meticulous conditioning of the adsorbing material, artifacts may build up on the unexposed matrix during storage. They may also build up during exposure of the sampler by reaction of ozone with the adsorbent [1,2], and this may raise the detection limits to unacceptable levels. The responses of the reduction gas detector to the blank build-up signals resulting from different adsorbents have been investigated recently [3], and it was found that some adsorbents (e.g., Chromosorb 106) are not suitable for the passive sampling of low concentrations of volatile organic compounds (VOCs) in air. As gas chromatography–flame ionization detection (GC–FID) is widely employed in analyses for hydrocarbons (e.g., Refs. [4] and [5]), it is necessary to study the FID responses to the artifact build-up signals on different adsorbents, and to assess their suitabili-

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ty for the passive sampling and determination of VOCs at low concentrations in ambient air.

In this work, four different adsorbents were used for the passive sampling of VOCs in rural air, and their artifact build-up problem was investigated. The problems with water vapour during passive sampling and analysis are also discussed.

2. Experimental

GC–FID measurements were made using a Hewlett-Packard 5890 Series II instrument. The carrier gas was helium and the make-up gas was nitrogen. The capillary column used was an Ultra 2 (cross-linked 5% phenyl–methyl silicone) (25 m × 0.2 mm I.D., 0.33 μm film thickness) from Hewlett-Packard. The exposed passive sampling tubes were thermally desorbed by a Chrompack thermal desorption cold trap (TCT) injector, interfaced with the gas chromatograph. The flow-rate of the desorption carrier gas (helium) through the tube was 35 ml/min. The desorbed analytes were retrapped by a deactivated fused-silica capillary trap (40 cm × 0.53 mm I.D.) [6] cooled by liquid nitrogen. After sample concentration, the trap was flash-heated to 220°C at 15°C/s for 1 min, and the trapped vapours were injected on to the capillary column in the splitless mode.

Four commonly used adsorbents were studied: Tenax-TA (60–80 mesh, specific surface area 20 m^2/g; Chrompack), Carbotrap (20–40 mesh, specific surface area 100 m^2/g; Supelco), Tenax-GR (60–80 mesh, specific surface area 25 m^2/g; Chrompack) [7–9] and Chromosorb 106 (60–80 mesh, specific surface area 800 m^2/g; Supelco). These adsorbents were conditioned for at least 16 h with a helium flow of 35 ml/min at the maximum temperature possible for each adsorbent. Details of the conditioning and desorption conditions for each adsorbent have been given previously [3]. Perkin-Elmer stainless-steel diffusion tubes packed with adsorbents were used for the sampling of VOCs in a rural area in the vicinity of Lancaster, North-west England, during May–July 1992. The relative humidity varied from 40 to 80% and the temperature from 8 to 25°C. Membrane diffusion caps were used in all instances to reduce the amount of water vapour adsorbed on the adsorbents. The concentrations of organic compounds in air were calculated using the following expression [10]:

$$\text{analyte concentration (ppm)} = \frac{\text{mass uptake (ng)}}{\text{uptake rate (ng/ppm}\cdot\text{min)} \times \text{exposure time (min)}} \quad (1)$$

The uptake rate in Eq. 1 was calculated using the following equation [10];

$$\text{uptake rate (ng/ppm}\cdot\text{min)} = \frac{DA}{L} \quad (2)$$

where D is the diffusion coefficient in air (cm^2/s), A is the cross-sectional area of the diffusion tube and L is the diffusion length of the tube. The uptake rates of the Perkin-Elmer diffusion tube were calculated for some compounds and are given in Table 1.

Table 1
Ideal uptake rate for Perkin-Elmer diffusion tube with diffusion cap

Compound	Uptake rate [ng/ppm (v/v)·min]
Benzene	1.75
Toluene	1.84
Ethylbenzene	1.92
p-Xylene	1.86
o-Xylene	2.02
1,2,4-Trimethylbenzene	1.88

3. Results and discussion

In order to investigate the problem of increasing contamination or artifact formation on adsorbents during storage, sampling tubes were packed with different adsorbents, rigorously conditioned and sealed with Swagelok caps. After storage for one week they were thermally desorbed and analysed by GC–FID as mentioned above. Typical blank chromatograms before and after storage are shown in Figs. 1 and 2, respectively.

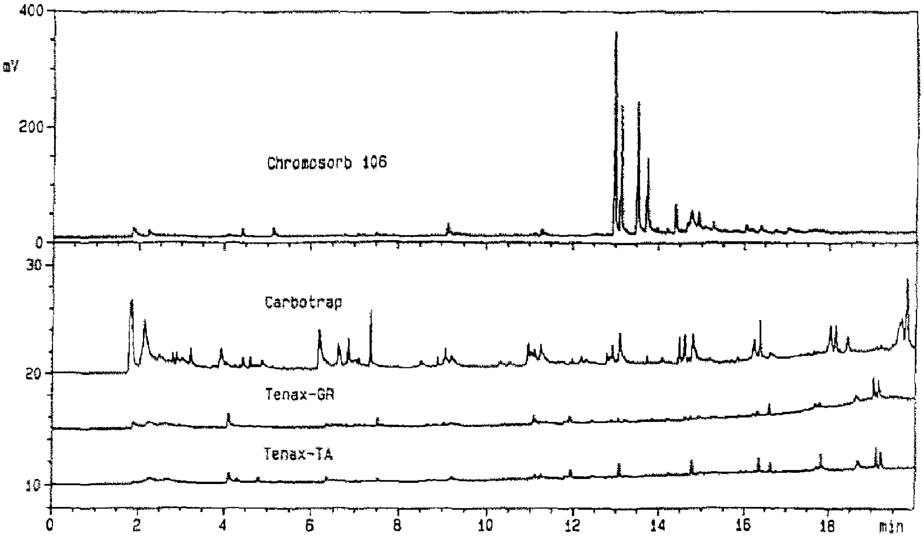

Fig. 1. Chromatograms of blank build-up for different adsorbents before storage. Temperature programme: increased from 35°C (held for 3 min) to 200°C at 10°C/min.

It can be seen from Fig. 1 that after conditioning both Tenax-TA and Tenax-GR are very clean, Carbotrap less so and Chromosorb 106 much less so. Some peaks, e.g., the benzene peaks from Tenax-TA, Tenax-GR and Carbotrap and the unidentified peaks from Chromosorb 106, in Fig. 1 are very small. This is in contrast to the response of the reduction gas detector [3], which has much higher sensitivity and selectivity towards the reactive hydrocarbons than does the flame ionization detector. Fig. 2 shows the chromatograms of the different adsorbents after storage for one week. All four adsorbents showed increased levels of contamination. It is unlikely these peaks represent contaminants from ambient air, adsorbed during storage, as the tubes were sealed with Swagelok caps. Rather it seems likely that they represent residual compounds not completely removed and/or compounds generated within the adsorbents themselves during storage, possibly by degradation of the polymers, or oxidation of the residual compounds by the oxidizing groups on the surface of the Carbotrap. The decomposition and oxidation could take place during conditioning and the compounds then released later during storage. Moreover, the significant increase of the characteristic peaks from Chromosorb 106 (retention times >12.5 min) indicates that the artifact peaks on the adsorbents after storage are produced by the adsorbents themselves and are not contaminants. Such artifact formation processes may be unavoidable, and shortening the sampling and storage period to the minimum practicable or decreasing the amount of adsorbent used may be the only steps that can be taken to obviate the problem.

Fig. 3 shows representative chromatograms of samples collected with different adsorbents after exposure for about one week to ambient air at the same site. It can be seen that for the very clean adsorbents (e.g., Tenax-TA and Tenax-GR), the amount of analytes adsorbed on the adsorbents is significant compared with their corresponding blank build-up levels (shown in Fig. 2). Even for the Carbotrap, which is less clean than the Tenax materials, the signal-to-noise ratio is also large enough for the successful determination of some hydrocarbons ($\geqslant C_6$) in ambient air. However, this is not so with Chromosorb 106, where artifact formation is too severe a problem for this matrix to be used successfully for this application. The differences in retention times between the separations on

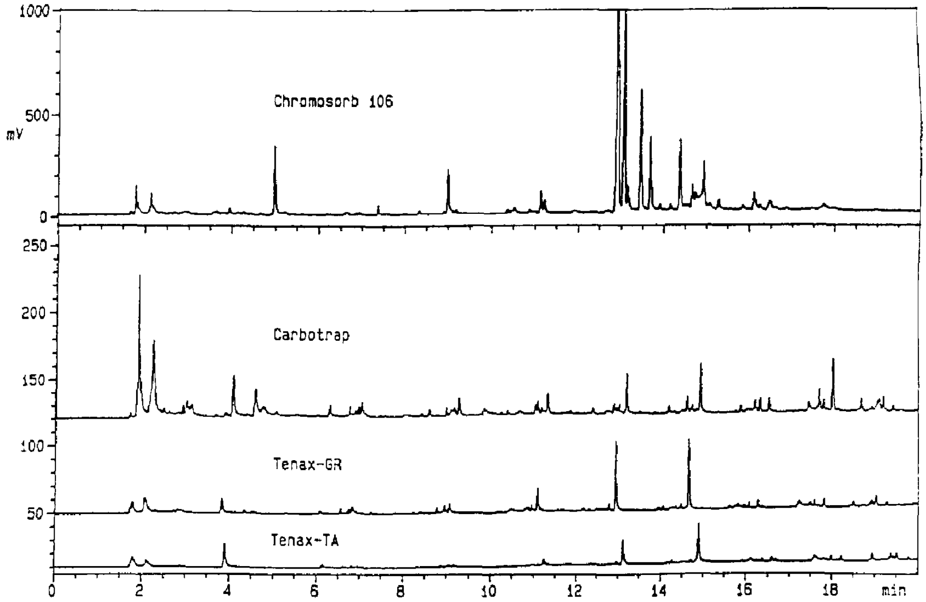

Fig. 2. Chromatograms of blank build-up for different adsorbents after storage for one week. Temperature programme as in Fig. 1.

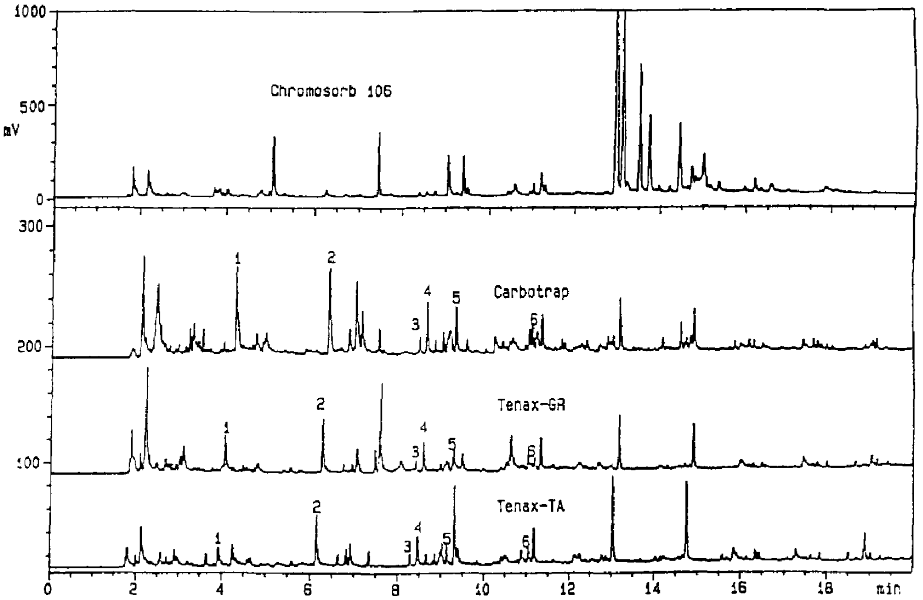

Fig. 3. Chromatograms of passive sampling in ambient air for about one week for different adsorbents. Temperature programme as in Fig. 1. Peaks: 1 = benzene; 2 = toluene; 3 = ethylbenzene; 4 = *p*-xylene; 5 = *o*-xylene; 6 = 1,2,4-trimethylbenzene.

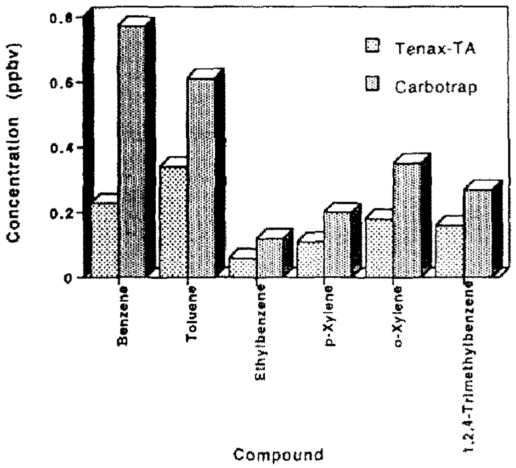

Fig. 4. Concentrations of hydrocarbons in air obtained from simultaneous sampling using Tenax-TA, Tenax-GR and Carbotrap during the period 14–19 June 1992.

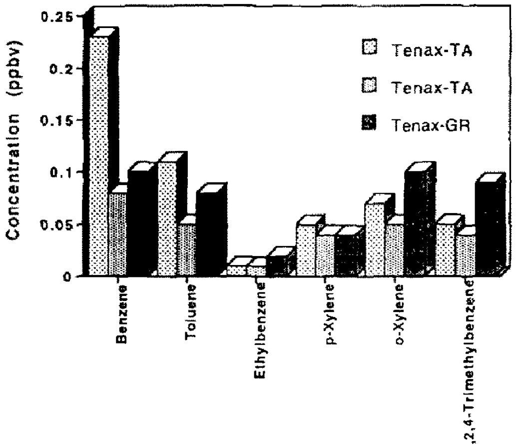

Fig. 6. Concentrations of hydrocarbons in air obtained from simultaneous sampling using Tenax-TA and Tenax-GR during the period 28 July–2 August 1992.

the various adsorbents are due to the variation in the head pressure of the GC capillary column. As Chromosorb 106 cannot be used for passive sampling in rural air, the peaks from it were not identified.

The concentrations of selected organic hydrocarbons in rural air were calculated from the results of Tenax-GR, Tenax-TA and Carbotrap desorption according to Eq. 1. Figs. 4–6 show representative results obtained from simultaneous sampling using different adsorbents. It can be seen that for ethylbenzene, *p*-xylene, *o*-xylene and 1,2,4-trimethylbenzene, which are not present or are present at very low levels as artifacts, the results obtained from Carbotrap generally agree well with those from Tenax-TA and Tenax-GR. The results from Tenax-GR also agree well with those from Tenax-TA for toluene. However, the results for benzene and toluene from Carbotrap are much higher than those from Tenax-TA and Tenax-GR, and the results for benzene from Tenax-TA and Tenax-GR also vary. This is due to the fact that toluene and, especially, benzene, are the main artifacts on the adsorbents, and they exist at higher levels on Carbotrap than on Tenax adsorbents. The uptake rate of benzene on Tenax adsorbent is relatively lower than that on Carbotrap and this may also contribute to this difference. The results from replicate sampling using Tenax-TA (shown in Fig. 6) also show good agreement, except for benzene, which may be due to the difference between the benzene blank levels on these two Tenax-TA sampling tubes before sampling. The average concentrations of the different compounds derived from different adsorbents and the total average values are summarized in Table 2. It can be seen that the results

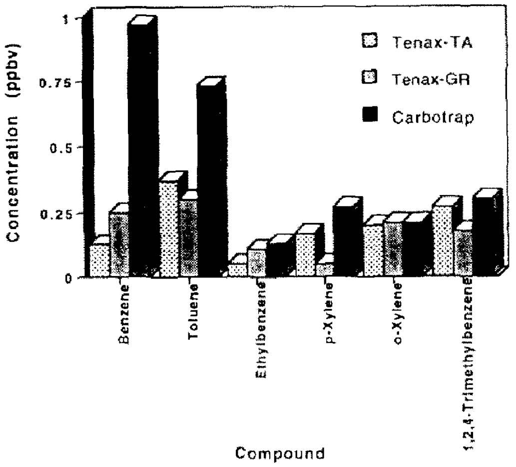

Fig. 5. Concentrations of hydrocarbons in air obtained from simultaneous sampling using Tenax-TA and Carbotrap during the period 18–23 June 1992.

Table 2
Mean concentrations of selected pollutants in ambient rural air in North-west England obtained from different adsorbents during May-July 1992.

Compound	Concentration (mean ± S.D.) (ppbv)			
	Tenax-TA	Tenax-GR	Carbotrap	Total
Benzene	0.21 ± 0.08 (11)[a]	0.19 ± 0.11 (8)	0.51 ± 0.30 (10)	0.33 ± 0.25 (29)
Toluene	0.36 ± 0.19 (11)	0.25 ± 0.18 (8)	0.66 ± 0.54 (10)	0.43 ± 0.38 (29)
Ethylbenzene	0.08 ± 0.08 (10)	0.06 ± 0.04 (6)	0.12 ± 0.05 (8)	0.09 ± 0.07 (24)
p-Xylene	0.20 ± 0.16 (10)	0.09 ± 0.07 (6)	0.24 ± 0.10 (8)	0.21 ± 0.19 (24)
o-Xylene	0.23 ± 0.18 (10)	0.15 ± 0.08 (6)	0.31 ± 0.13 (8)	0.26 ± 0.16 (24)
1,2,4-Trimethylbenzene	0.18 ± 0.09 (10)	0.12 ± 0.07 (6)	0.25 ± 0.04 (7)	0.20 ± 0.10 (23)

[a] Number of samples.

obtained from Tenax-TA and Tenax-GR generally agree well, whereas the results for benzene and toluene from Carbotrap are higher than those from the Tenax adsorbents. Therefore, although it is possible to measure the compounds in air after subtraction of their blank signal following artifact formation, the precision and accuracy of the results may be poor, depending on the level of the artifacts on the adsorbents.

The other problem encountered in the passive sampling of VOCs in ambient air is the humidity. The relative humidity of ambient air is highly variable, and may range from 30 to 40% on a fine day, from 60 to 70% during the night and be more than 85% during fog or rain. Water vapour adsorbed on sampling adsorbents may cause two problems: on desorption it may extinguish the flame of the flame ionization detector, and it may block the cold trap, especially the capillary cold trap, which has only a single path, used for sample preconcentration, by the formation of ice. Although the latter problem can be eased by using a multi-path packed cold trap, the large difference between the carrier gas flow-rate through a packed cold trap and that through a capillary GC column necessitate the use of split injection, causing most of the sample to be lost by venting. This causes a severe loss of sensitivity. However, by using a flow-rate restrictor in the packed cold trap, the splitting ratio may be decreased significantly. Although the membrane diffusion cap available for Perkin-Elmer diffusion tubes may be used during sampling to lower the amount of water vapour adsorbed, it does not eliminate it completely under conditions of high relative humidity. Therefore, further development of membrane diffusion caps to exclude water, while allowing the analytes to pass, is required.

4. Conclusions

The main problem in the passive sampling of low concentrations of volatile hydrocarbons in rural air concerns the sensitivity of the method, which is highly dependent on the signal-to-noise ratio in the resultant chromatogram. It is possible to clean the adsorbents used to acceptable levels by the use of rigorous conditioning procedures. However, with time, artifacts form in or on the adsorbent, resulting in an increasingly noisy blank signal. This occurs during storage prior to sampling, during exposure to ambient air and during storage after sampling prior to analysis. Artifact formation on four adsorbents during storage was studied. The problem is at a minimum with Tenax-TA and Tenax GR, is more acute with Carbotrap, especially in the $\leq C_5$ range, and is so severe with Chromosorb 106 that it prevents the use of this material for this application.

The results of simultaneous sampling using different adsorbents show that for compounds that are not present or are present at very low levels in the blank build-up on each adsorbent, the results obtained from Carbotrap generally agree well with those from Tenax-TA and Tenax-GR. The results from Tenax-GR also agree well with those from Tenax-TA for toluene. However, for compounds which are the main artifacts on adsorbents (e.g., benzene and toluene), the results obtained from Carbotrap are much higher than those from Tenax-TA and Tenax-GR, and the results from Tenax-TA and Tenax-GR also vary. Hence, although it is possible to measure the compounds in air by subtraction of their corresponding blank signals on adsorbents, the precision and accuracy of the results may be poor, depending on the amount of the artifact on the adsorbent.

Storage and exposure times should be as short as possible in order to keep the blank build-up level on adsorbents as low as possible. This would be facilitated by the design of a new thermally desorbable passive sampler with much higher uptake rates (by increasing the ratio of A/L of the sampler) and by development of more sensitive detection methods.

The adsorption of water vapour by even the most hydrophobic adsorbents remains a problem and further development of membrane diffusion caps to exclude water, while allowing the analytes to pass, is required.

Acknowledgements

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