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SOME CRITICAL PARAMETERS IN COLLECTION, RECOVERY AND GAS CHROMATOGRAPHIC ANALYSIS OF ORGANIC POLLUTANTS IN AMBIENT AIR USING LIGHT ADSORBENTS

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SUMMARY

The mutual influence of organic compounds present in the atmosphere on their break through volumes when trapped on light adsorbents is evaluated. The effect of moisture and geometrical characteristics of the traps is also investigated. An explanation of the dependence of the break through volumes on the concentration is given in terms of self deactivation of the adsorbent. This operates as a stationary phase by a mechanism similar to that occurring in gas-liquid-solid chromatography.

INTRODUCTION

In recent years, light adsorbents have been widely used in the evaluation of air pollution from organic compounds¹⁻¹², and the advantages of the heat-stripping technique over collection on strong adsorbents and subsequent solvent extraction prior to gas chromatographic (GC) analysis have been emphasized^{9,11}.

Light adsorbents, such as Tenax GC (Enka, Arnhem, The Netherlands) and Carbopack B (Supelco, Bellefonte, PA, U.S.A.), are particularly useful at room temperature for the evaluation of air pollution in the working place, where, rather than the exposure of workers to dangerous vapours¹³, interest is focussed on the evaluation of pollution sources during certain phases of industrial processes. Furthermore, they are preferred if a high sensitivity is required⁸, or when volatile compounds, with retention volumes similar to that of the solvent and which may evaporate from the solution, are to be monitored.

This paper reports the evaluation of the break through volume (BTV), its variation with the concentration of the organics present in the atmosphere and the mutual interference of the compounds present. The reliability of the measurements has also been studied, as have the effects of grain size and of the presence of water.

EXPERIMENTAL

Generation of artificially polluted atmospheres

The apparatus used for the determination of break through volumes (BTVs) is shown in Fig. 1. A cylinder of extra pure artificial air, obtained by mixing 20% extra pure oxygen with 80% extra pure nitrogen, is connected to the apparatus by means of a system of flow regulators and three-way valves. Known concentrations of various organic compounds are introduced into the mixing chamber by means of permeation tubes. There are eight different inlets to the mixing chamber, although, for the sake of simplicity, only five of them are shown in the figure. A known concentration of water vapour can also be introduced into the mixing chamber through a bubbler that can be kept at different temperatures. The air flow to the total hydrocarbon monitor (THM), either directly or after passing through the trap, is lower than the sum of the flows entering the mixing chamber, so that a venting port is necessary in the latter. About 4 h are necessary to obtain a constant concentration in the mixing chamber, as shown by a constant signal from the THM. The linear gas velocity obtained is the result of the pump and of the overall resistance of the gas lines, and can be regulated.

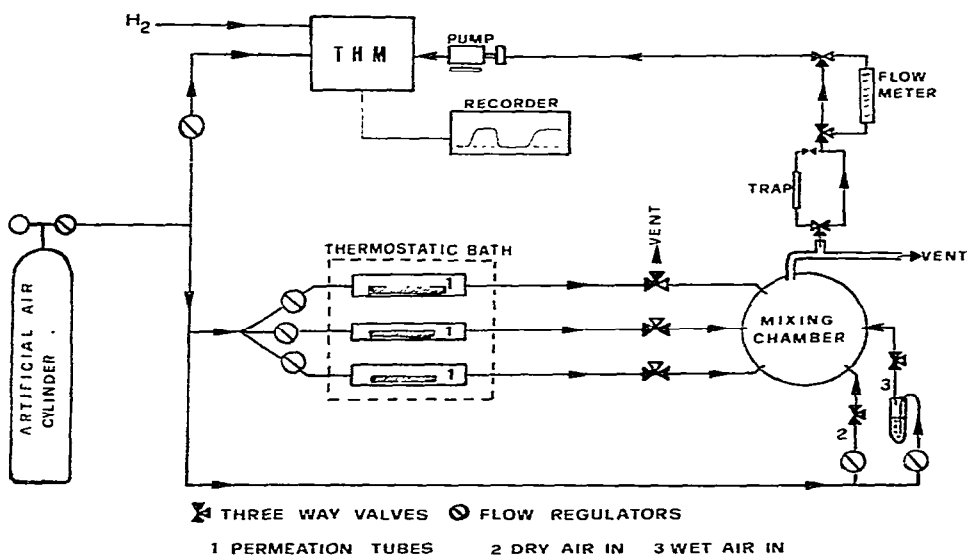


Fig. 1. Schematic view of the apparatus for determination of break through volumes (BTVs).

The THM monitor (Carlo Erba, Model 370), based on flame ionization, is periodically calibrated with a standard air-methane mixture. The instrument has a sensitivity of 1 ppm full scale. However, measurements at concentrations below 1 ppm are unreliable because of the difficulty in obtaining such low concentrations with an acceptable degree of precision and accuracy.

It is important to note that the flow from each of the permeation tubes is only 10 ml/min, while the total flow to the mixing chamber is greater than 300 ml/min. This means the concentration in the mixing chamber changes only slightly when one or more organic compounds are introduced into the mixing chamber.

Trap shape and particle diameter

The criteria for the choice of trap shape and particle dimensions are based on three considerations:

- (1) the traps should contain a suitable amount of adsorbent
- (2) the permeability of the traps must be such that the flow-rate of a normal packed GC column (2 m × 2 mm I.D., 80–100 mesh) is scarcely affected by the insertion of the traps in the gas line during the injection phase
- (3) the traps should behave as a GC column of reasonable efficiency

The trap dimensions were standardized at the values: 15 cm × 6 mm O.D. × 4 mm I.D.; 9.5 cm adsorbent, two silanized 2.7-cm glass wool plugs. Under these conditions, 0.55 g of Carboxap B or 0.21 g of Tenax GC are contained in each trap. The trap material is Pyrex glass in all cases. The trap desorption and injection system have been described previously⁵.

GC measurements

Retention volumes were determined using a Carlo Erba GI gas chromatograph equipped with a FID and a Carboxap B (20–40 mesh) (Supelco) glass column (50 × 0.4 cm I.D.). The BTV values were obtained by extrapolating to room temperature the retention volumes from the plot $\log V_g$ vs. $1/T^{10,11}$.

Reproducibility of sampling and quantitative analysis was checked by introducing into ten different traps the same artificially polluted air containing seven different pollutants. Trap desorption conditions were kept constant. Also, a fixed volume of air containing a known constant concentration of *n*-hexane was introduced ten times into one trap and desorbed under constant conditions.

Peak area calculations were made using a Hewlett-Packard Model 3380A integrator.

The direct BTV was determined by measuring the time passing between the disappearance of the THM signal due to the adsorption of the organics in the trap and the inflexion point of the curve when the BTV has been attained; values are plotted in Fig. 2.

RESULTS AND DISCUSSION

Changes in BTV with concentration

In Table I the BTV values obtained with the direct (frontal analysis in the trap) and the indirect (GC injection) methods are reported. Very good agreement is observed for the light compounds, but total disagreement for the heavier compounds. This result can be explained by considering the different experimental conditions employed for the two determinations.

In the direct method, the determination is made at room temperature and the break through volume is obtained by extrapolation to 1 ppm of the straight lines in Fig. 2. The equation used is

$$BTV = -K \log C + B$$

which holds in a limited range of concentrations and where *B* is the extrapolated BTV. Within this range, however, correlation coefficients between the points and the straight lines lie in the range 0.91–0.97. Extrapolation to 1 ppm is necessary for

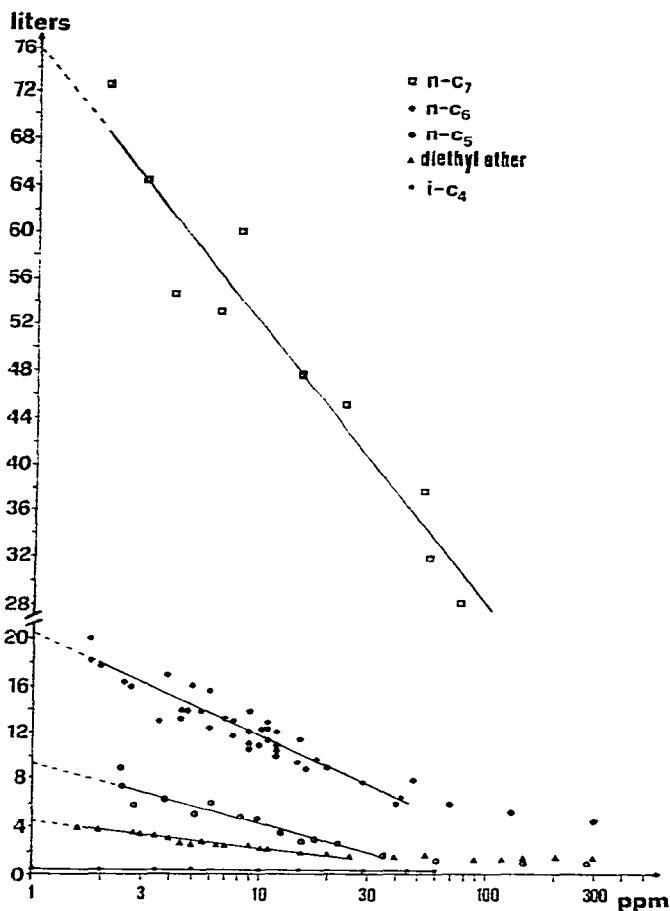


Fig. 2. Plot of the BTV values against the concentration of single compounds in the atmosphere.

TABLE I

BTV MEASURED AT 20°C WITH THE DIRECT AND THE GC METHODS

Compound	BTV (l)	
	GC (extrap. at 20°C)	Direct (extrap. at 1 ppm)
CH_2Cl_2	0.29 ± 0.02	0.18 ± 0.02
iso- C_4	0.40 ± 0.02	0.4 ± 0.02
$CHCl_3$	3.2 ± 0.3	2.9 ± 0.3
Diethyl ether	5 ± 0.5	4.4 ± 0.5
$n-C_5$	8.7 ± 0.5	8 ± 0.5
$n-C_6$	300 ± 30	20.5 ± 2
$n-C_7$	5000 ± 500	76 ± 4

three reasons: the apparatus does not allow precise measurements of BTV, as pointed out before; the retention times in the trap become very high for the high boiling compounds and such low concentrations are of little practical value.

In the GC measurements, the BTV values correspond with those at infinite dilution.

Thus, it may be concluded that the determination of the BTV by the GC method can give false results in practical (polluted atmosphere) conditions. Fortunately, this is true only for strongly retained compounds.

In Fig. 3 the dependence of BTV on concentration of *n*-hexane, is shown. It is seen that water vapour does not affect the BTV on Carbopack B. The same is true of Tenax GC, as was previously observed¹⁴. There is no observable effect on the BTV value caused by a change in the mesh range. The latter result is interesting since it demonstrates that highly permeable traps, such as those of 20–40 mesh, can be used with no problems.

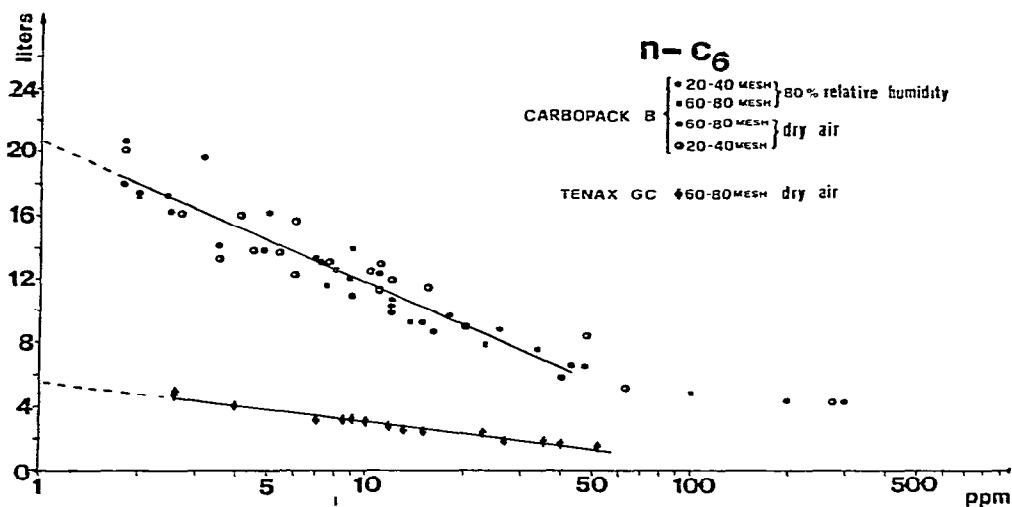


Fig. 3. Plot of the BTV values against the concentration of *n*-C₆ under different conditions.

Change in BTV due to the presence of other pollutants

Major changes are observed in BTV when other compounds are present in the atmosphere. This is shown in Fig. 4, where the frontal analysis graphs for three typical compounds are given. The dashed lines refer to the BTV obtained when the atmosphere is polluted by the indicated compound only, present at the concentration defined by the plateau. The effect of the mutual deactivation of the adsorbent is shown by the solid line. The highest effect is observed for the compound with an intermediate BTV (*n*-C₅). This is because of the double deactivating action of diethyl ether and *n*-C₆. The former compound is less affected, because it is the first to be eluted. The influence of smaller molecules on the retention of the latter compound is lower, as would be expected.

The effect of mutual deactivation is well explained by what has been found previously for deactivated adsorbents in gas-liquid-solid chromatography.

From the BTV value for a compound at a given concentration, the percentage of the compound on the adsorbent surface with respect to the adsorbent weight can

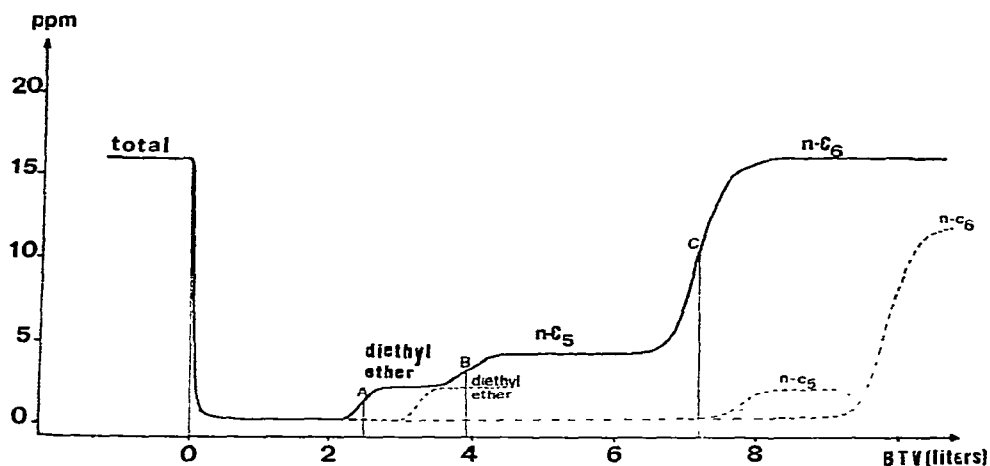


Fig. 4. Frontal analysis for three typical compounds in a Carbpac B trap, showing the mutual influence on the BTV. ---, Single compounds in the atmosphere; —, mixture of compounds.

be estimated. The amount of the adsorbed compound is given by the area between the decrease in signal due to the insertion of the trap and the inflection point of the ascending curve (A, B, C, respectively in Fig. 4). By plotting the BTV values against the amounts adsorbed one obtains the curves of Fig. 5a. These compare well with the graph of Fig. 5b, which shows the well known decrease of the capacity ratio, k' , with the percentage of stationary phase observed in gas-liquid-solid chromatography with Carbpac B¹⁵. It is concluded that the role played by the adsorption of the

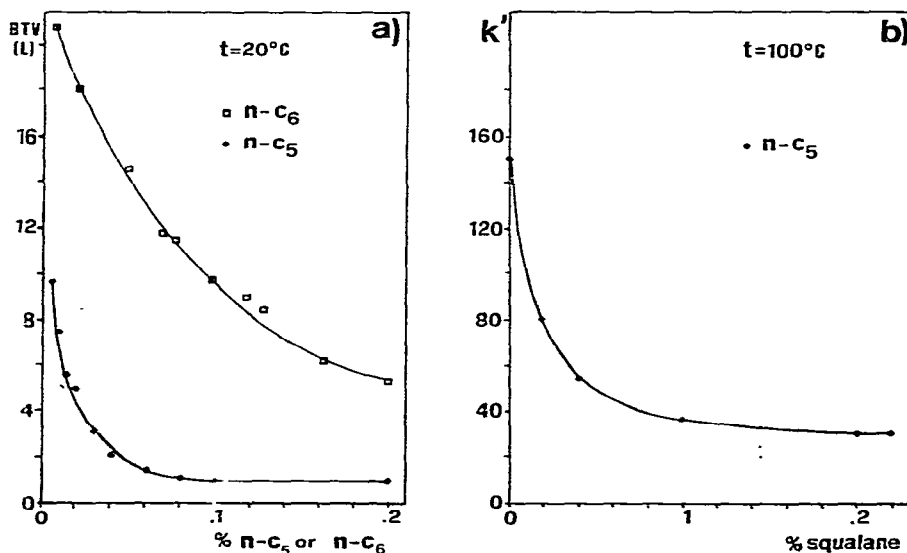


Fig. 5. a, Plots of BTV against percentage (w/w) of $n\text{-C}_5$ and $n\text{-C}_6$ adsorbed in the trap (calculated from the total amount adsorbed before the BTV). b, Dependence of the capacity ratio, k' , for $n\text{-C}_5$ on percentage of squalane on Carbpac B columns.

pollutants in the trap is not different from that which occurs when the adsorbent is covered with a similar amount (in weight) of a stationary phase of analogous structure.

The small deactivating effect of water is explained by its very low BTV. The effect is only present at extremely low concentrations of the eluted compounds, such as those employed when the BTV is extrapolated from the plot of retention volumes, and only for compounds of low molecular weight.

To confirm the findings from the graphs of Fig. 5, one trap was filled with Carpack B coated with 0.2% squalane and the BTVs for *n*-C₅ and *n*-C₆ measured for concentrations 7.5 and 2.0 ppm respectively. The values found fit very well with those measured for an uncoated trap with a concentration of *n*-C₅ higher than 40 ppm and of *n*-C₆ higher than 200 ppm. This shows that the total BTV is affected by the sum of the surface coverages of the pollutants and by the coverage of the stationary phase at the same extent, in full agreement with a previous comparison¹⁶ of the heats of adsorption of *n*-hexane found by Kiselev and Yashin¹⁷ and by gas-liquid-solid chromatography using squalane as stationary phase.

Reproducibility of sampling and of operating conditions

The most important source of errors in the evaluation of air pollution is the volume measurement. This is complicated by the fact that it is not possible to use an internal standard to adjust the data given by the flow counter of the pump. The volume errors are essentially due to the different permeabilities of the traps, because the traps are made by hand and it is difficult to reproduce the glass wool plugs. Adsorbent packings in the same mesh range have little effect on the permeability. If the traps are chosen at random, the volume errors result in scattering of the measurements by up to 15%. By choosing traps of analogous permeability the scattering can be reduced to 6%, and use of the same trap for a set of ten measurements reduced the error to that of normal GC quantitative analysis, *i.e.*, 1.5–2%.

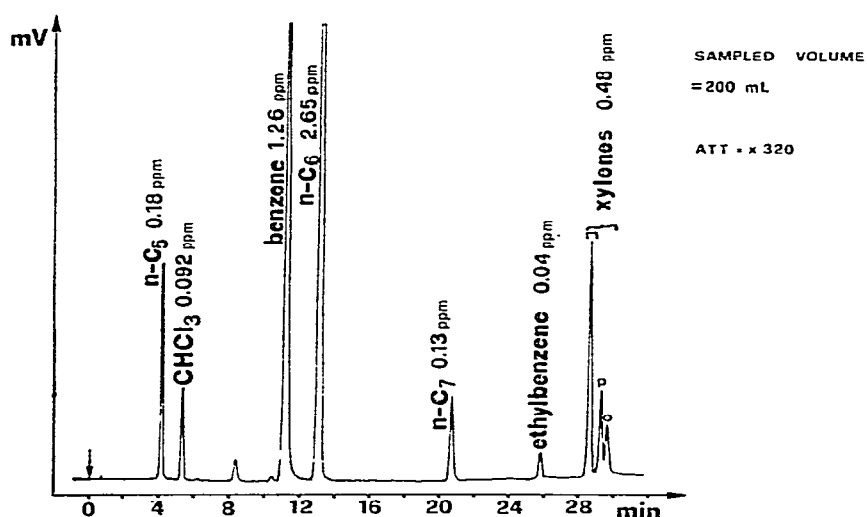


Fig. 6. Chromatogram of seven solvents used for determination of reproducibility.

The desorption oven temperature should be kept constant within 10°C. The desorbing temperature is determined by the molecule size and vapour pressure of the compounds to be monitored. Preliminary experiments were made in order to establish the desorption temperature. It is desirable to keep the oven temperature as low as possible, so traps should be stripped with the carrier gas flowing in the opposite direction to that used in sampling, *i.e.*, they should be back-flushed. Finally, flash heating at a higher temperature is preferred to slow heating at lower temperatures.

A typical chromatogram obtained by using the system described is shown in Fig. 6. Ethylbenzene is present in the test mixture at a very low level. However, it can be determined by sampling only 200 ml of air. This confirms the great advantage of this method with respect to adsorption on charcoal followed by solvent extraction.

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