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Improvement in breakthrough volume evaluation methods for light adsorbent traps employed for volatile organic compounds determination at atmospheric concentration levels

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Abstract

The use of the thermal desorption (TD) technique with light adsorbents allows for the determination of organic air pollutants at nmol/mol (ppb) level. In this work, two methods to determine the breakthrough volume (BTV) values of sampling devices are proposed as alternatives to the classic methods. The first method proposed obtains extrapolated BTV values (indirect method) and the other, obtains the direct elution profile (direct method). The main advantage of these particular methods is the possibility of working with very diluted samples which are more similar to real conditions, thus avoiding the drawbacks, due to the detection limits, usually encountered with the classic methods. Consequently, the methods proposed here exhibit better sensitivity because the organic content which remains in the device, after passing a given air volume through it, is directly analysed by TD–GC, instead of the method of detecting the organic content of the effluent from the trap. Laboratory tests show that the accuracy of the proposed methods is the same or even better than the accuracy of the classic method.

Keywords: Adsorbents; Thermal desorption; Sampling methods; Air analysis; Environmental analysis; Breakthrough volumes; Volatile organic compounds

1. Introduction

The aim of a sampling process is to obtain, for each sampled species, an amount which is directly proportional to the sampled air volume. Specifically, when using traps containing a solid adsorbent their "sampling capacity", that is the limits within which pollutants from the atmosphere can be concentrated without sample losses, must be evaluated. Consequently, a proper sampling procedure requires a constant adsorbing efficiency during the whole sampling period and that the sampling be stopped before any species of interest are present in the effluent from the tube.

The breakthrough volume (BTV), which is generally considered a parameter related to the sampling capacity [1–14] is defined as the gas volume which passes through the sampler before a given compound begins to be eluted from the sorbent [8], this occurs when the concentration ratio of effluent gas to incoming gas reaches a pre-defined value (from 1% to 50%, according to different definitions [16–22]).

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Moreover, the BTV value is the essential parameter for calculating how the real diffusive uptake rate differs from the calculations based on Fick's first law, in cases of non-ideal systems like the adsorbing devices for passive monitoring [15,17].

In a previous work [5] concerning light adsorbents we demonstrated that the BTV value of a given adsorbent/adsorbate system is an exponential function of the adsorbate concentration, that is, the BTV strongly decreases when the concentration of the species of interest or of the co-adsorbed species, increases. This effect was also described in the case of strong adsorbents beds [10]. These considerations clearly indicate that the precise determination of BTV values, particularly when obtained with the classic indirect method, cannot be proposed as a method of measuring the sampling capacity. However this method is helpful when comparing the performance of different adsorbents. For practical uses, a BTV correction factor is more commonly employed, which allows calculation of a "safe sampling volume" [4].

In most cases, BTV determination is carried out in two ways: the first, an "indirect method", consists of a series of injections of the analyte into a short GC column filled with the adsorbent. The BTV value is then obtained at ambient temperature by extrapolating the straight line of a log V_g (specific volume) against $1/T$ diagram, following the Van't Hoff equation; the second, a "direct method", is usually performed by passing a continuous flow of air containing a given concentration of the analyte through an adsorbing trap kept at ambient temperature; the analyte content in the effluent flow is determined by means of a GC detector [4,5,24,25]. In many cases (e.g., tailed peaks) the effluent peak can be determined only by increasing either the injected amount (indirect method) or the pollutant concentration in the air stream (direct method), however, this can cause a noticeable shift of the retention time.

Some authors [26] suggested a method to improve the sensitivity of the direct method (direct discrete method) consisting of the periodical (repeated) sampling and analysis of discrete volumes of the effluent flow. Only a very recently published work [9] employs a direct method based on the analysis of the amounts remaining in the traps after the elution of multiple discrete volumes, similar to the method described in this work, which allows BTV determination at nmol/mol (ppb) and even sub-ppb levels.

In this work we propose the use of thermal desorption (TD) apparatus for obtaining accurate and repeated results in BTV determination at nmol/mol level; thus an improvement in the sensitivity of both the classic direct and indirect methods, will have been achieved.

2. Experimental

2.1. Apparatus and materials

The thermal desorption apparatus employed was a TDAS 5000 (Carlo Erba, Milan, Italy) connected to an HRGC 5300 MEGA gas chromatograph equipped with a flame ionisation detector. This equipment allows the pre-setting of the traps: pre-purging, preheating and desorption times, as well as the temperature. The duration of each operative phase can be varied from 0 to 999 s, and the temperature from ambient to 400°C with an accuracy of ±1°C.

A flow controller strictly ensures that the flow through the trap is constant at all times.

Traps were made of glass tubes (10 cm×6 mm O.D.×3.8 mm I.D.) filled with 300 mg of Carbotrap or Carbopack C (Supelco) or with 100 mg of Tenax TA (Chrompack) filling an equivalent of 6 cm of tube.

10 l Tedlar bags were used for containing gaseous standard mixtures.

2.2. Artificial atmospheres

A standard gaseous atmosphere was prepared from a five-component liquid mixture (benzene, hexane, methyl ethyl ketone, methoxyethanol and 1,1,1-trichloroethane, all analytical grade, provided by Fluka). The liquid mixture was prepared by adding 10 g at a time, of each component to a small Pyrex flask and weighing it after each addition. About 0.9 μl of the mixture was injected, through the apposite injection port, into a 10 l Tedlar bag (SKC, USA) filled with pure nitrogen. However, the ethylene oxide was added separately (0.2 μl taken from a frozen ampoule maintained at −15°C and injected

with a cooled syringe through the bags injection port).

The following day the bags content resulted as follows: benzene=53.1 μmol/mol; *n*-hexane=47.2 μmol/mol; methyl ethyl ketone=55.8 μmol/mol; methoxyethanol=40.7 μmol/mol; 1,1,1-trichloroethane=31.0 μmol/mol and ethylene oxide=93.0 μmol/mol.

For the indirect method, the sampling tubes were loaded with 10 ml of this gaseous mixture. This amount corresponds to a three litre sample of an atmosphere with an overall concentration of 107 nmol/mol.

As a comparison with the classic GC method, a short U column packed with 1.2 g of Carbotrap was employed. In this case a standard liquid mixture, obtained by diluting the aforementioned pure components mixture in methylene chloride (1:1000, v/v), was employed; 1 μl was injected at each trial. At times, specifically to detect the peaks of methoxyethanol and other components and when operating at temperatures below 100°C, it was necessary to increase the amounts injected.

A cylinder containing a certified gas mixture of benzene, toluene and ethyl benzene (50, 150 and 100 $\mu g/m^3$, respectively) was used for the direct method trials. The above benzene and toluene values were selected on the basis of the average concentration values which occurred in the urban area of Rome (Italy) in recent years [27]; ethylbenzene acts as "internal standard" or "reference term", as explained below.

2.3. BTV determination procedure

2.3.1. Indirect method

The purpose of the indirect method is to obtain a series of plotted points in a log V_g vs. $1/T$ diagram similar to the classic GC indirect procedure. If a series of different elution times is employed at each temperature, the analyses performed on the traps remaining content after each trial, can be represented on a graph curve which shows the percentage of each species eluted through the trap for each volume. Through these plotted points the outline of the eluted peak is shown, thus establishing the percentage of elution for each elution volume employed, for those compounds which move at a given temperature.

The following procedure was used: sampling tubes were prepared, using equal quantities of adsorbing material, taking care to obtain the same packing density and thus the same number of theoretical plates for each tube.

All the tubes must be carefully purged and their blanks must be tested before use.

A gaseous or liquid mixture of the compounds, for which the BTV must be calculated, is prepared and diluted in an inert gas atmosphere. The concentration of the mixture must be selected by taking into account that the gas volume used to load the tubes is negligible with respect to the BTV value. Moreover, the amount of analyte load has to be of the same order of magnitude as the amount usually collected in real working conditions for both the individual species and total organic content determination (co-adsorption effects).

In order to avoid errors due to imprecision in the injection and dilution and to wall adsorption effects, calibration graphs of the samples should be prepared to determine and evaluate the real concentration values in the standard atmosphere inside the bag.

Tubes are then loaded with a small volume of gas (10–20 ml) extracted from the bag with a gas syringe.

In all phases the flow direction is essential, consequently the different ends of the sampling tubes should be clearly marked.

Sampled tubes are then inserted in the desorbing apparatus and brought to a chosen temperature. A 3 min pre-heating is used [28] to obtain an isothermal elution of the trap content. The tubes are placed in a position that ensures the carrier gas stream to flow into the tube, in the same direction as in the sampling phase; then the elution phase is carried out, during varied lengths of time in order to obtain, by point by point plotting, the elution profile of the compounds (a cold trap can be used during this stage to focus the out coming analyte).

Then each tube is turned, in order to obtain a back-flush, and desorbed; the temperature and duration of the desorption stage must ensure the complete release of the tubes whole organic content. For each temperature a series of chromatograms is thus obtained, showing both the elution phase (from the analysis of the cold trap of the elution concentrate) and the desorption phase (from what remains in the

trap after the elution of a given volume) which will show variations in the peak area.

Fig. 1 represents the results of the application of this procedure to a three-component hypothetical mixture. The first column is the initial loading amount sampled into each trap; the second to fourth columns show the desorption of the remaining amounts recovered after passing three different volumes ($V_1 < V_2 < V_3$) through the trap at the temperature indicated at the head of each line (desorption phase). The fifth to seventh column (elution phase) show the effluent flow content concentrated on the cold traps following the desorption phase.

Fig. 2 shows the diagrams which plot the results from this procedure.

There are three ways to calculate the elution percentage: the first one is to express it as:

$$\%E = 100 \cdot \frac{\alpha - \alpha_1}{\alpha}$$

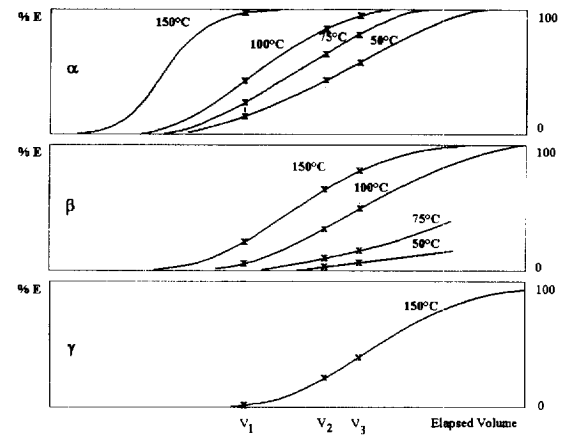

Fig. 2. Determination of the percentage eluted peak (%E) at different temperatures and elution volumes, plotted from calculations indicated in the indirect method (see Section 2.3.1 and Fig. 1).

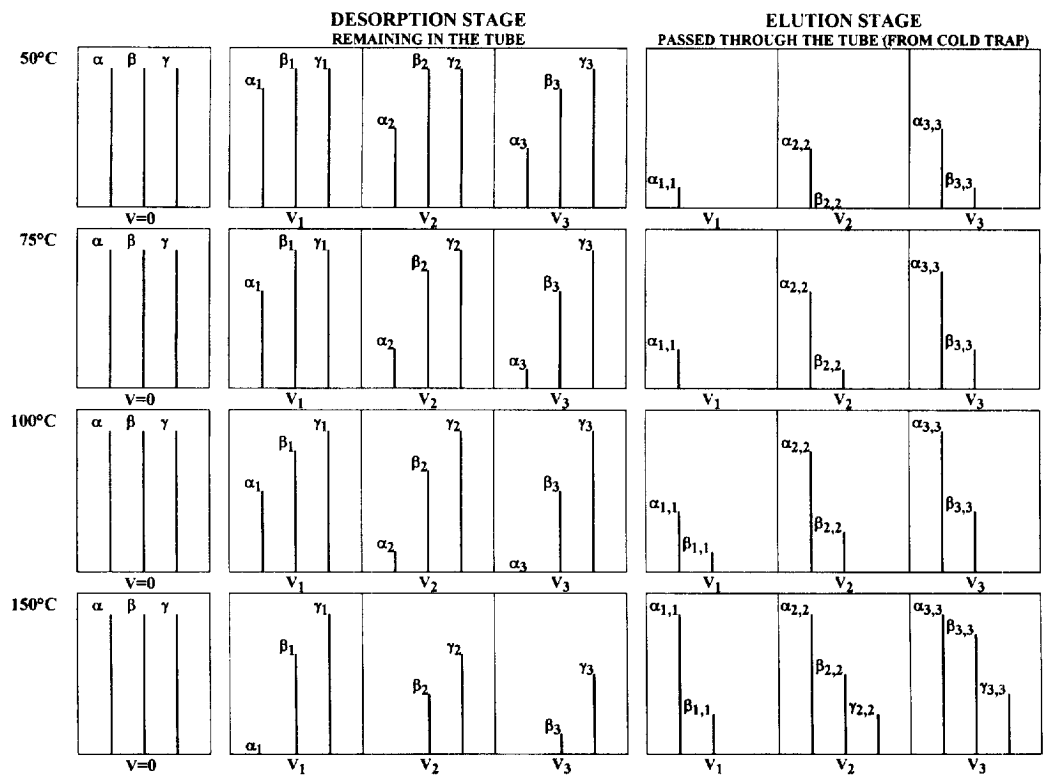

Fig. 1. Bar chart of peak areas determined in some steps of the indirect method application at different temperatures and elution volumes for an hypothetical three component mixture.

where $\%E$ = percentage of the α species eluted through the trap, α is the original peak area ($V=0$) and α_1 is the peak area of the remaining amount after elution of a volume V_1.

This procedure is not more accurate than any external standard calculation and needs particular care when determining temperature, pressure and volume values.

The second way is to consider any compound which has categorically not undergone any elution as an "internal standard" (for example the γ peak at the 50°C trial) as follows:

$$\%E = 100 - \frac{100\alpha_1\gamma}{\alpha\gamma_1}$$

This procedure is more accurate and does not require particular care in trap loading determination, but cannot be applied to the temperature and volume ranges where all the peaks start to be eluted;

The third accurate method of calculation is to apply the formula:

$$\%E = \frac{100\alpha_1}{\alpha_1 + \alpha_{1,1}}$$

where, $\alpha_{1,1}$ is the peak area of the eluted amount of α after elution of a volume V_1 and determined after the adsorption of the eluted amount on the "focusing trap".

As a result, a $\log V_r$ vs. $1/T$ diagram similar to that obtained with the usual gas chromatographic method can be obtained.

The "V_r" term in the $\log V_r$ vs. $1/T$ diagram may refer to any eluted peak percentage value that the operator chooses to represent the BTV. Nevertheless it must be taken into account that the slope of the curves shown in Fig. 2 varies [6] in relationship to the number of theoretical plates N (which is a function of many parameters, like the carrier gas linear velocity, packing length, temperature, amount of analyte etc.). For this reason we found it convenient to use the 50% elution value in comparisons with those values taken from the top of the GC peaks, after comparing our BTV values with those obtained with the classic GC method. This value, following our experience and different theoretical evaluations [6,7] is independent of the N parameter even if Lövkvist and Jonsson [8] maintain the opposite, whereby $N<100$.

2.3.2. Direct method (frontal elution)

Determining BTV by frontal elution usually requires significant volumes of standard mixture, and the most convenient way to provide them is to use a certified cylinder. Of course any other source providing a constant concentration and the required dilution levels may be employed.

A recent work [11] suggests sampling multiple volumes from a gaseous standard mixture and to plot the mass amounts of the adsorbed compounds against the sampled volumes; there the BTV was defined as the sampled volume corresponding to the end of the linear part of the plotted curve. This method exhibits the accuracy of an external standard procedure as far as the experimental points are concerned; moreover, the inflexion point only indicates the BTV starting point, without any quantitative evaluation.

In the method described below an additional compound is added to the gaseous mixture sample in order to act as an "internal standard". This compound, which we call "reference term", must have a much higher BTV value than the other compounds. In an homologous hydrocarbon series, for example, a term having one more CH_2 group can be used in addition to the sample compound with a greater molecular mass. In fact, the retention volume increases with the carbon number following an exponential law; thus a linear increase of the "reference term" area against the sampled volume can be expected during the direct BTV determination of the other sample compounds.

Before starting to determine the BTV, the mixture must be carefully analysed to determine, for each species, the ratio K_x of the "reference term" area (A_{r°), to the area (A_{x°) of compound x. For this purpose only a few sampling/analysis cycles (at least three) are needed, by using small sample volumes.

The trap must be connected to the cylinder through a flow regulator. The first step of the BTV determination through frontal elution, consists in passing through the sampling device a carefully measured gas volume about two/three times higher than the supposed BTV of the less volatile component of the mixture. Analysis of the trap content

after the sampling will show significant variations in the relationship between the various peaks. The percentage ratio between values lost in breakthrough and sampled values can be obtained for each x compound with the following formula:

$$\% \text{ passed through} = 100 - \frac{100A_xK_x}{A_r}$$

For example, if the original ratio (K_x) between the reference term compound and the x species is 1, and we then found: $A_x = 2000$ and $A_r = 8000$ after passing through a volume of 4 l, this means that after this volume passed through, 75% of the entered species had come out of the trap. This result does not imply that the BTV begins at 1 l; in fact, the outcoming x front is not a "square" peak but a curve showing the symmetrical sigmoid shape of the Gaussian distribution, which can be determined by means of successive experiments carried out by decreasing and/or increasing the passing-through volumes in the trap. In the above example, if we are looking for the initial BTV point, the next experiment should consist of passing a 1 l volume to determine a lower percentage sample loss; small variations in successive experiments will refine the results.

In order to obtain a curve faithfully showing the outcoming front, expressed as percentage ratio between the passing through concentration and the entering one, a series of multiple volumes must be employed. So the "%BTV vs. passed volume" curve can be plotted by applying the formula:

$$\%\text{BTV} = 100 - \frac{100K_x(A_{x_n} - A_{x_{n-1}})}{A_{r_n} - A_{r_{n-1}}}$$

for each point. The plotted points thus obtained are more accurate as smaller increases in volume, from trial to trial, are passed through.

3. Results and discussion

Fig. 3 shows a log V_r vs. $1/T$ series of diagrams obtained by means of the indirect method (continuous lines and points) with a six component mixture obtained with the procedure described in Section 2.2. Samples were obtained by aspirating 10 ml of the gaseous standard in order to charge the trap with about 1 μg of total organics. The dotted lines and triangles of Fig. 3 refer to the values obtained with the classic GC method by using a short U column filled with 1.20 g of Carbotrap. In order to compare the obtained results we used, as long as possible, the same elution temperatures; in any case both the same temperature intervals and number of plotted points were taken into consideration.

In Table 1 regression analyses obtained with this method are compared with those obtained by the classic GC method. The values used refer to 300 mg of adsorbent phase (Carbotrap in the example), thus the extrapolated BTV values determined with the two

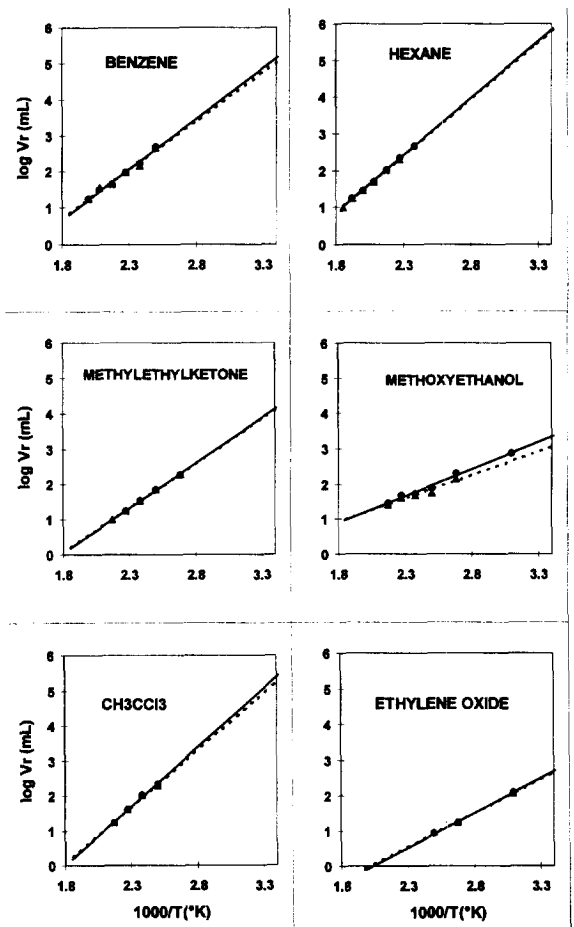

Fig. 3. Comparison of the classic and the proposed indirect methods for the determination of the 50% BTV value on 300 mg Carbotrap filled traps. ——— = proposed method; - - - = classic method.

Table 1
Regression analyses of the log V_r (ml) vs. $1/T$ curves obtained with the classic and proposed indirect methods

Method	Eluate											
	n-Hexane		Benzene		Methoxyethanol		Methyl ethyl ketone		CH_3–CCl_3		Ethylene oxide	
	Classic	Proposed	Classic	Proposed	Classic	Proposed	Classic	Proposed	Classic	Proposed	Classic	Proposed
y Intercept	−4.739	−4.773	−4.105	−4.354	−1.551	−1.867	−4.459	−4.516	−5.761	−6.078	−4.030	−3.837
y S.D.	0.019	0.020	0.079	0.055	0.081	0.068	0.019	0.017	0.068	0.049	0.037	0.032
R^2	0.990	0.999	0.980	0.991	0.937	0.986	0.999	0.999	0.985	0.992	0.998	0.998
x Coeff.	3100.5	3121	2678.1	2792.8	1364.3	1529.8	2515.6	2539.9	3238.2	3379.5	1973.1	1904.5
x Co. S.D.	68.6	50.9	189.8	132.6	203.4	54.8	64.3	54.8	278	202.6	85	74.7
BTV (litres/300 mg)	687	744	107	149	1.27	2.24	13.3	14.1	192	281	0.46	0.50

Referred to the traps containing 300 mg of Carbotrap.

extrapolating methods coincide within standard deviations. The two methods may be considered equivalent both in accuracy and in precision when tailing of the out coming peaks is not severe and the same range of temperatures is used. For tailed peaks the accuracy of the described method is better than that of the GC method, as can be observed on the methoxyethanol graph. Furthermore, a lower standard deviation is also obtained with the proposed method when the working temperatures approach ambient temperature. This condition is more easily met when small quantities of adsorbents are employed, as in the described method.

In Figs. 4–6, profiles of % BTV determined with the direct method are shown. These curves were obtained by desorbing the sample remaining after the elution of discrete volumes of a standard mixture, containing 50 $\mu g/m^3$ of benzene, 150 $\mu g/m^3$ of toluene and 100 $\mu g/m^3$ of ethylbenzene (reference peak), through a 300 mg Carbopack C trap (Fig. 4),

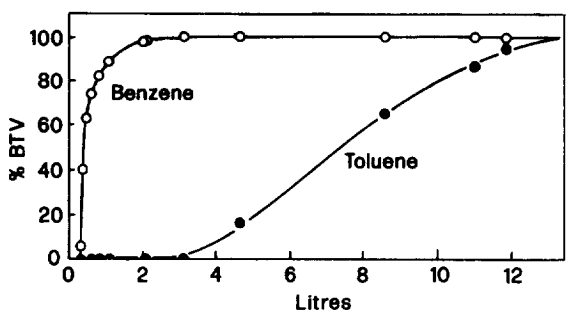

Fig. 4. Determination of the % BTV with the proposed direct method for a 300 mg Carbopack C trap.

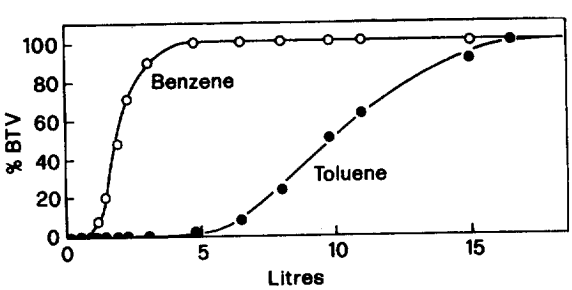

Fig. 5. Determination of the % BTV with the proposed direct method for a 100 mg Tenax TA trap.

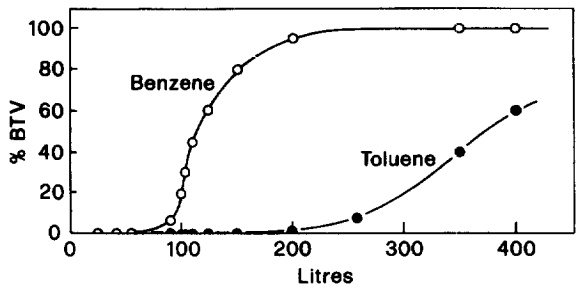

Fig. 6. Determination of the % BTV with the proposed direct method for a 300 mg Carbotrap trap.

a 100 mg Tenax TA trap (Fig. 5) and a 300 mg Carbotrap trap (Fig. 6). A flow stream of 200 ml/min was passed at ambient temperature (20°C) for a series of multiple times. The %BTV curve of toluene on Carbotrap was not completed because of the very high volumes required and of the little interest in determining any values above the 50% BTV.

It is worth noting that the 50% BTV value of benzene on Carbotrap (120 l) agrees with the values obtained from the indirect methods while the 50% BTV value of toluene (350 l) is much lower than the value determined with the indirect method (1500 l). This fact indicates that self-deactivation and co-adsorption effects play a role at any concentration value. Nevertheless, this self-deactivation effect may be considered negligible, with respect to the co-adsorption, for species sampled at low concentration levels. In fact the deactivation of the adsorbing bed finally depends on the w/w adsorbate/adsorbent ratio [5], where the term "adsorbate" must refer to the whole amount of the species carried through, which play a role similar to that of a liquid phase in gas–liquid–solid chromatography [5,29]. For this reason any extrapolated BTV value cannot be used as a precise sampling limit [23] and for practical uses a safety factor must be applied. BTV values determined by the direct method must be considered as more suitable for field applications, particularly if determined by using a mixture corresponding to real concentrations and ratios; moreover, in this case, it is advisable to apply a safety factor that takes into account the variations in field conditions (concentration, temperature, relative humidity, etc.).

In the case of Carbotrap, data show that surface deactivation is significant even when the adsorbed

amount is less than 0.1% (w/w) of the adsorbing material. For this adsorbent the values obtained, with an indirect method, approach the real sampling capacity of a trap only for very diluted atmospheres and when the determined specific volume (V_g) is lower than 300 or 400 l; otherwise this parameter can only be useful for comparing different adsorbents. Moreover, it is natural to consider that values of billions of litres, like those found for high-boiling compounds such as n-C_{11} ($V_g > 10^{10}$ l on Carbotrap), cannot be considered realistic in terms of sampling capacity, unless we want to believe that 300 mg of adsorbent are able to retain many grams of analyte.

4. Conclusions

The proposed methods constitute an inexpensive and sometimes more accurate alternative to the classic methods of BTV determination. They allow easy determination of the BTV values of gaseous mixtures by means of direct and indirect procedures.

These methods apply to any atmospheric concentration and mixing ratio and are particularly suitable for working in the nmol/mol (ppb) range.

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