

Evaluation tests and applications of a double-layer tube-type passive sampler^a

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(First received February 14th, 1990; revised manuscript received July 3rd, 1990)

ABSTRACT

Validation tests on a thermally desorbable tube-type passive sampler filled with two different graphitized carbon blacks were conducted in order to determine the influence of air velocity and direction, concentration and sampling time on sampling rate. A specially made apparatus was used to study the behaviour of the passive sampler in dynamic artificial atmospheres. This apparatus permits the simultaneous sampling of 48 tubes at two different air velocities, minimizing errors due to random variations of the operating conditions during a prolonged sampling time, which allows a better stochastic analysis of data to be performed. The results were in agreement with those obtained by actively sampling the same test-tubes. The results of laboratory and field tests showed that the behaviour of tube-type devices having a small cross-section is independent of the environmental parameters checked over a wide range of operating conditions. The constant sampling rate with these samplers in the range from 30 min up to more than 12 h and the high sensitivity of thermal desorption methods allow the determination of organic species down to the ppb level. A field experiment on the evaluation of the indoor pollution in a domestic environment is also described. The use of a double-layer tube-type passive sampler, with the adsorbent of lower specific surface area positioned at the exposed side of the device, allows a better desorption efficiency.

INTRODUCTION

Diffusive samplers are cheaper, smaller, lighter and more comfortable to wear than active devices. However, a series of drawbacks have been suggested by some workers [1]. Evidence indicates that each device needs a proper study of the accuracy and precision of the method and clear instructions for its use. The sampling validity range in relation to the collected species and to the environmental parameters influencing the properties of the devices [2–8] also needs to be properly evaluated.

Thermal desorption offers the best sensitivity, with respect to solvent extraction, when the whole sample is injected into the chromatographic system [9,10]. However, a disadvantage of this technique is that high-boiling compounds are not quantitatively

^a Presented in part at the 8th World Clean Air Congress, The Hague, September 11–15, 1989.

desorbed at low temperatures, while high temperatures may cause pyrolytic effects with some substances [11].

In this work we performed experimental tests in order to evaluate the desorption efficiency of a double-layer packing in a tube-type sampler. We also carried out a series of tests in order to evaluate the behaviour of this sampler in relation to wind velocity [12] and direction [13], exposure time and sampled species concentration.

THEORY

The passive sampling technique is a practical application of Fick's law regarding the transfer of a gaseous species through a fluid. A suitable expression for this law, valid when the mass transfer through a diffusional path having a constant section is considered, is

$$\frac{dQ_i}{dAdt} = -KD_i \cdot \frac{dC_i}{dL} \quad (1)$$

where Q_i (mol) is the amount of species i which passes through a section A (cm²) during time t (s); this term is proportional to the concentration gradient along the mass transfer direction; D_i (cm²/s) is the diffusion coefficient of species i in air; C_i (mol/cm³) is the concentration of species i ; L (cm) is the diffusional path length; and K is the mass transfer resistance term; when the diffusional path is "open", it is assumed that $K = 1$, and when a medium (such as a filter or a septum) is placed in the diffusional path before the adsorbent surface, $K < 1$ and its value must be calculated.

By integrating eqn. 1, the following expression is obtained:

$$C_{i,1} - C_{i,0} = \frac{Q_i L}{KA t D_i} \quad (2)$$

where $C_{i,1}$ is the concentration of the species i at the beginning and $C_{i,0}$ is that at the end of the diffusional path.

In the presence of an adsorbing surface, as in a passive sampler, a concentration gradient occurs. If the adsorbent is strong, the vapour tension of the adsorbed molecules on the surface ($C_{i,0}$) is nearly zero, and we may write

$$C_i = \frac{Q_i L}{KA t D_i} \quad (3)$$

This expression permits the calculation of the environmental concentration C_i if the amount Q_i collected on the adsorbent is analytically determined and L , A , K and t are known. The term $KD_i A/L$ is defined as "diffusive uptake rate" for the species i and is the "virtual" flow through a sampler whose diffusional path has a length equal to L and whose section normal to L is A , which corresponds to the geometrical exposed surface of the adsorbent. The diffusive uptake rate is obviously constant only if we can assume that $C_{i,0}$ remains equal to zero during the whole sampling run. When the sampled amount of the species i begins to saturate the adsorbing surface, $C_{i,0}$ increases

and assumes none-negligible values, leading to a non-linear correlation between exposure time and sampled amount.

EXPERIMENTAL

The proposed samplers are made of 10 cm × 6 mm O.D. × 3.9 mm I.D. Pyrex glass tubes. With the aim of ensuring a precise sizing of the device, two porous glass septa with a porosity of 0 (160–250 μm), 2 mm in thickness, are fixed at both ends of the tube by steel springs. A diffusional path of 8 mm at the side used for passive sampling is obtained. The first 5 mm of the tube are filled with Carboxpack C (Supelco), a low specific surface (area graphitized carbon black (8–10 m²/g) with 20–40-mesh particle size, and the next 7 cm with Carbotrap (Supelco), a carbon with an average specific surface area of 80 m²/g, also 20–40 mesh.

The choice of a 5-mm thickness for the first layer comes from our previous studies [4] in which it was shown that medium- and high-boiling compounds exhibit a low tendency to diffuse in the inner part of the packing, whereas low-boiling species quickly migrate in the back part of the tube. Positioning a reasonable amount of a stronger adsorbent in the second section is also important in order to prevent back-diffusion phenomena.

In order to evaluate the desorption efficiency, two sets of sampling tubes were prepared, the first consisting of fifteen tubes filled with two graphitized carbon blacks as described previously, and the second consisting of fifteen tubes filled with Carbotrap only. All the tubes were sampled by actively collecting a suitable air volume from an artificial atmosphere, generated by bubbling pure air in a very dilute solution of benzene, toluene and ethylbenzene in paraffin oil.

For the analyses we used a two-stage desorption apparatus consisting of a TDAS 5000 sequential desorber connected to an FMA 515 instrument for "focusing" (Carlo Erba, Milan, Italy). The conditions for the primary desorption were 20 ml/min of helium per 30 s after a 30-s pre-heating time, focusing at –150°C; the second stage desorption was carried out at 100°C with a gas flow of 10 ml/min on a Vocol column (60 m × 0.53 mm I.D.) (Supelco, Bellefonte, PA, U.S.A.). An HRGC 5300 MEGA gas chromatograph (Carlo Erba), a flame ionization detector and Hewlett-Packard HP 3396A integrator were also used.

In this trial, five temperatures were employed for the primary desorption, starting from 170 up to 290°C. At each temperature three devices from each kind of packing were used. Results obtained at the higher temperature were selected as a reference standard, by assuming that all the samples were quantitatively desorbed under these conditions.

For the measurements related to the validation of the passive sampling procedure and the evaluation of their behaviour in relation to different environmental conditions, a specially made sampling apparatus was used.

The apparatus used for exposing the samplers to the standard atmospheres (Fig. 1) is made of two coaxially joined tubes, one of diameter 3 cm and the other 9 cm. In each of these tubes there are 24 accesses for the samplers, separated into three groups of eight units, one at a 45° counter flow, one perpendicular to the air flow and one at a 135° angle. The samplers must be fixed at the access point by a series of washers and O-rings to prevent gas leaks. While the tubes are inserted in the apparatus, high-purity

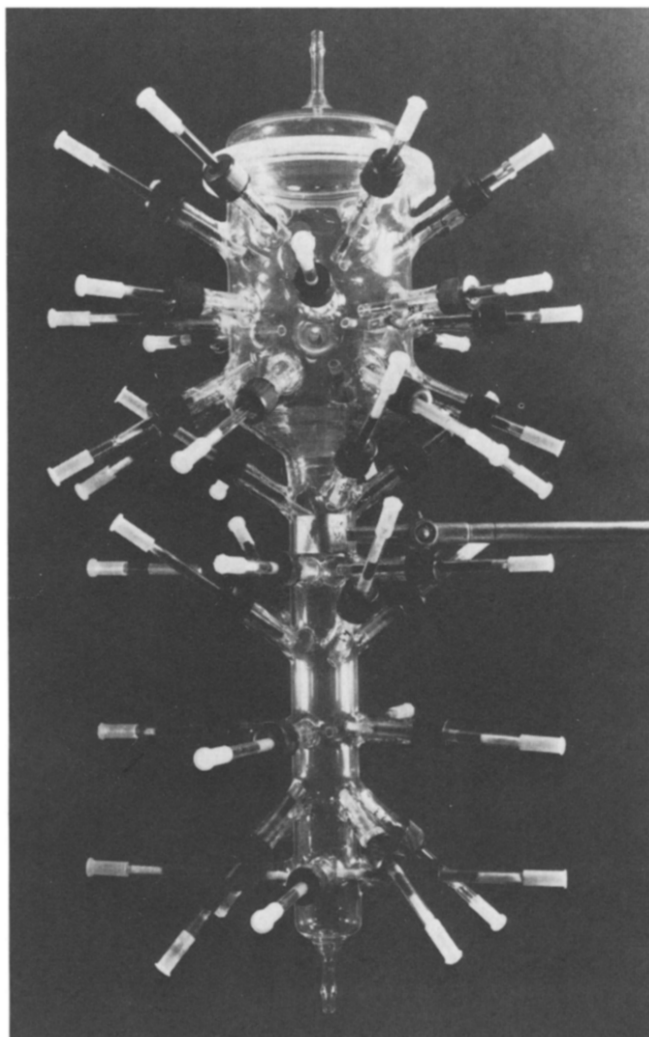


Fig. 1. Apparatus for passive sampling in standard dynamic atmospheres.

artificial air is passed through to ensure that at the beginning of the experiment all the equipment is unpolluted.

To obtain a dynamic atmosphere with the required constant organic contents, a specially prepared pneumatic circuit was constructed. The circuit consisted of three gas lines: the first was used for compressed air, cleaned by means of a active charcoal purifier, the second was connected to an air cylinder certified at a standard content of 100 ± 2 ppm benzene, which also served as a control mixture, and the third was connected to a bubbler filled with a dilute solution of toluene in paraffin with a slow flow of high-purity artificial air passing through. The three lines converged into a tiny mixing chamber. The mixture was then passed into a mechanical volumetric counter, connected to the sampling device by means of a short silicone-rubber tube.

Four devices were actively sampled in each passive sampling trial in order to check the average concentration during passive sampling and to verify if the uptake rate is constant in the experimental conditions selected.

For the analyses we used the previously described apparatus. The conditions employed for primary desorption were 20 ml/min of helium per 30 s with ballistic programming at 300°C, focusing at -150°C; the second-stage desorption was performed at 100°C with a gas flow of 10 ml/min.

A further comparison was carried out by sampling four passive devices and four active devices in the same indoor atmosphere.

RESULTS AND DISCUSSION

Desorption efficiency

In Table I the percentage recoveries of three aromatic compounds obtained with the double-layer samplers are compared with those obtained with samplers filled with Carbotrap only. The values reported for each temperature are the average of three runs for each kind of device. Samplers desorbed at 290°C have been taken as a standard reference, by assuming that at this temperature all the sampled amount is quantitatively desorbed. The results show that the same performance as for the traps filled with Carbotrap only can be achieved by the double-layer traps at a temperature about 50°C lower.

Passive sampling trials

Fig. 2 shows the results obtained for the desorption of passive samplers sampled for different times in a standard atmosphere containing 2 mg/m³ of benzene. The values, obtained from eighteen samples, lie on a straight line with a correlation coefficient of 0.98 and a standard error lower than 7%. The good linearity of the recovered amounts *versus* the exposure time agrees with a constant diffusive uptake rate in the investigated range.

Table II summarizes the conditions of concentration, flow-rate and sampling time for five sets of experiments carried out using the above-described apparatus. Concentration values averaged from the active samplings (not reported in Tables II and III) agree in all instances, within the standard deviation, with the values obtained by calculations made on passive samplers. Stochastic analysis was performed on the data

TABLE I
RECOVERY OF SAMPLED AMOUNTS ON SINGLE- AND DOUBLE-LAYER SAMPLING DEVICES

Recovery on Carbotrap (%)			Desorption temperature (°C)	Recovery on Carbopack C + Carbotrap (%)		
Benzene	Toluene	Ethylbenzene		Benzene	Toluene	Ethylbenzene
80 ± 6	36 ± 4	17 ± 3	170	100 ± 7	70 ± 6	49 ± 5
100 ± 7	73 ± 7	42 ± 4	200	100 ± 7	100 ± 7	90 ± 6
100 ± 7	95 ± 7	76 ± 6	230	100 ± 7	100 ± 7	100 ± 7
100 ± 7	100 ± 7	100 ± 7	260	100 ± 7	100 ± 7	100 ± 7

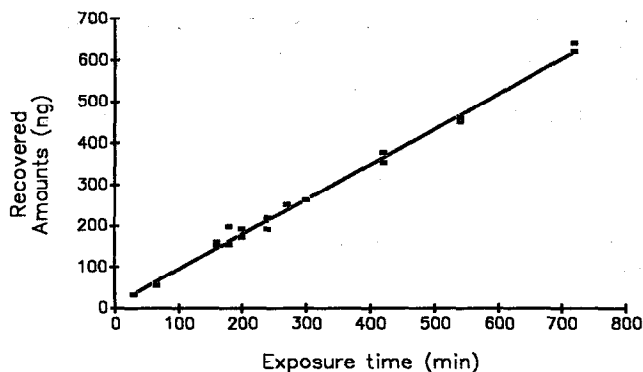


Fig. 2. Recovery of benzene on passive devices at different sampling times.

obtained under various conditions of wind velocity, sampler inclination and analyte concentration.

Table III contains the results obtained in the five tests reported in Table II. The comparison between the samplers kept at 45° and those kept at 135° to the air flow direction demonstrated an average random difference of less than 1%, which is insignificant. All of the values obtained from the angled tubes were therefore grouped and compared with those obtained from the tubes kept perpendicular to the air flow.

According to the literature [9,10], one might have expected a smaller sampling rate from the inclined than from the perpendicular tubes, in proportion to the projection of the orifice diameter on the flow direction and in inverse proportion to the linear velocity. The stochastic analysis of the considered samples, in which two substances were collected together, shows that under the experimental conditions examined there is no variation, as all the values coincide with an insignificant percentage difference. Also, no variation was observed on plotting the uptake rate as a function of the air velocity for values above 0.1 cm/s. Below this value an influence of air speed can be hypothesized, but it is of no interest in practical terms. This observation agrees with experiments already performed [2,3,6] on tube-type samplers characterized by a small sampling surface; this indicates that the influence of air speed decreases with a reduction in diameter.

TABLE II
OPERATING CONDITIONS IN THE SAMPLING RUNS

Test No.	Flow-rate (l/min)	v_1^a (cm/s)	v_2^b (cm/s)	Total average benzene concentration (mg/m ³)	Total average toluene concentration (mg/m ³)	Sampling time (min)
1	0.54	0.14	1.27	10.55	1.00	130
2	0.90	0.24	2.12	1.47	0.31	840
3	3.99	1.05	9.41	0.49	0.42	136
4	6.00	1.57	14.1	3.46	2.70	780
5	10.0	2.62	23.58	10.18	4.55	100

^a Wind velocity through the wide tube of the sampling apparatus.

^b Wind velocity through the narrow tube of the sampling apparatus.

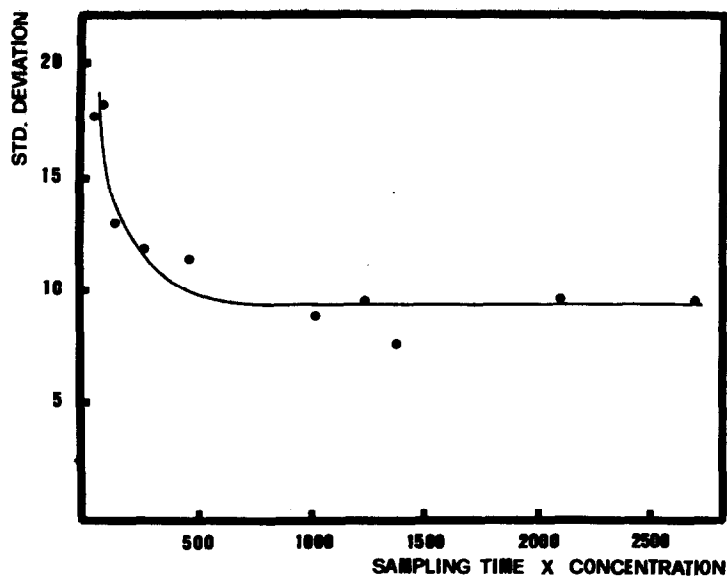


Fig. 3. Plot of percentage standard error vs. sampled amounts.

In Fig. 3 the product of time and concentration is plotted *versus* the percentage standard deviation. The measurement error seems to be strictly correlated with the sampled amount, and is probably a pure analytical error. When more than 200 ng are sampled, the total error is lower than 10%, whereas when sampling less than 10 ng there is a tendency toward an error of more than 20%. Evidently, when the trapped amount is below certain values the percentage influence of any type of interference is enhanced: microlosses in the desorption system, solvent residues in the sampler before use and random distribution of high-energy active sites in the trap, in the lines and in the column, which can obstruct the desorption of favour memory effects.

Fig. 4 shows a comparison between two chromatograms obtained by active and passive sampling in indoor trials in which eight samplers were used. All devices were sampled at the same time, starting at 0.8:00 p.m. and ending at 08:30 a.m. the following day, in the living room of a non-smokers' house.

The average concentration of total hydrocarbons calculated from the active samplers was 0.24 mg/m^3 (expressed as benzene) with a multiplicity of about 60 compounds. For the passive samplers, an accurate quantitative calculation of the ambient concentration requires the identification of each species and a knowledge of its diffusion coefficient. In the presence of many unidentified compounds, the uptake rate was calculated by averaging the diffusion coefficients of the identified main components. The approximate calculated value is 0.39 ml/min ; a total hydrocarbon concentration of 0.21 mg/m^3 can thus be calculated, which agrees with the results obtained from the active samplers. The same multiplicity is also found.

The use of the porous glass septum for maintaining the adsorbent phase *in situ* provides various advantages: absence of dust particles in the desorption lines, mechanical stability during the sampling and desorption and easy positioning within the Pyrex tube. Disadvantages include the fact that this system constitutes a resistance

TABLE III
 INFLUENCE OF WIND VELOCITY AND DEVICE SLOPE ON PASSIVE SAMPLING RATE

Test No.	Benzene concentration (mg/m ³)				Toluene concentration (mg/m ³)					
	v_1^a	v_2^a	Average	45° and 135° slope	90° slope	v_1^a	v_2^a	Average	45° and 135° slope	90° slope
1	10.36±0.63	10.73±0.75	10.55±0.69	10.52±0.56	10.59±0.86	0.94±0.15	1.06±0.10	1.00±0.13	0.996±0.14	1.00±0.15
2	1.49±0.14	1.46±0.14	1.47±0.14	1.47±0.15	1.47±0.13	0.32±0.04	0.30±0.03	0.31±0.03	0.31±0.03	0.31±0.04
3	0.51±0.08	0.46±0.09	0.49±0.09	0.50±0.08	0.47±0.11	0.46±0.09	0.37±0.05	0.4±0.07	0.44±0.09	0.39±0.07
4	3.42±0.34	3.51±0.33	3.46±0.33	3.46±0.37	3.46±0.25	2.63±0.27	2.78±0.25	2.70±0.26	2.71±0.28	2.68±0.25
5	10.32±0.95	10.03±0.84	10.18±0.90	10.36±0.85	10.03±0.93	4.77±0.59	4.33±0.46	4.55±0.53	4.57±0.46	4.53±0.66

^a See Table II.

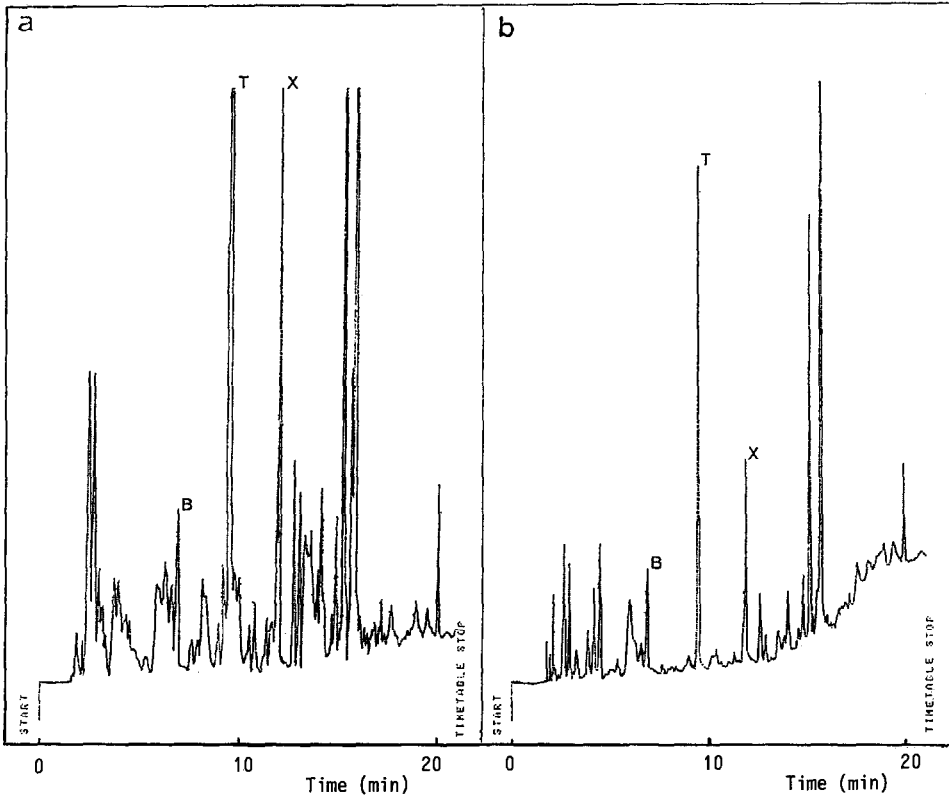


Fig. 4. "Fingerprint" or organics sampled in a domestic living room. (a) Active sampling; (b) passive sampling. B = Benzene; T = toluene; X = xylene.

to the mass transfer. On the basis of the experimental data (see theory) a calculation was made, giving an equivalent sampling rate equal to 0.452 ml/min for benzene, with this value also being confirmed by indoor trial data. Without the septum the theoretical rate should be 0.835 ml/min. The resulting K value is 0.54, which is acceptable because even if the theoretical rate is halved, the order of magnitude of the determinable amounts (about $1 \mu\text{g}/\text{m}^3$ in 10 h of sampling) does not substantially change.

CONCLUSIONS

This series of experiments adds to the knowledge already acquired on this subject. The variations proposed in the construction of the sampler facilitate the standardization of the production process and improve the adsorption and desorption characteristics. The tests demonstrated that the devices are versatile, accurate and precise, beyond the levels normally accepted in this types of determination. The large amount of data obtained at low concentration levels indicates that passive sampling can be used efficiently not only at industrial sites but also for the determination of organic vapours in homes, offices, schools and for indoor pollution in general.

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