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## Breakthrough volume of monoterpenes on Tenax TA: influence of temperature and concentration for $\alpha$ -pinene

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### Abstract

The breakthrough volumes (BTV) of several monoterpenes ( $\alpha$ - and  $\beta$ -pinene, myrcene, sabinene,  $\Delta^3$ -carene and limonene) on Tenax TA were determined at very low mixing ratios (0.2–30 ppb, v/v).  $\alpha$ -Pinene, which exhibits the lowest BTV of all the terpenes studied ( $16.3 \text{ l g}^{-1}$  at  $24^\circ\text{C}$  for a mixing ratio of 3 ppb, v/v) was taken as a standard during the atmospheric sampling. A study of the influence of temperature and mixing ratio on its BTV was carried out. The influence of temperature is shown to follow a Van't Hoff-type law of the form  $\log(\text{BTV}) = a + b/T$ , whereas the influence of the concentration follows Freundlich's adsorption isotherm, expressed as  $\log(\text{BTV}) = \log a + b \log C$ .

### 1. Introduction

Perturbations of the equilibrium between the biosphere and atmosphere constitute a major environmental problem. Such perturbations are induced by variations in the concentration of trace components of the troposphere, namely carbon and nitrogen oxides, hydrocarbons, ozone, sulfur compounds and aerosols.

Among the hydrocarbons susceptible to modifying this equilibrium on a local or region scale, isoprenoid compounds are of particular importance owing to their predominance in vegetal emissions and their high chemical reactivity in the gaseous phase [1,2].

A better understanding of the role of these compounds can be assessed by the development

of physico-chemical models able to predict their evolution. However, the validation of such models requires experimental data on the precursors, the intermediates and the products of chemical pollution. Here, a difficulty is the lack of qualitative and quantitative data on the sources of biogenic hydrocarbons.

There is also a technical difficulty in the determination of these compounds close to their source, owing to their very low mixing ratio in the atmosphere (between a few tens of ppt and a few ppb, v/v).

Among different analytical techniques, gas chromatography is the only one that can provide qualitative and quantitative data on most volatile organic compounds that are present in the neighbourhood of sources. In general, the analytical procedure requires the preconcentration of trace components. This is achieved by passing the gaseous samples through a trap in which the

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organic compounds are retained on a solid adsorbent [3].

The solid adsorbent must satisfy a number of requirements, such as (i) total chemical inertness relative to the adsorbed compounds, (ii) a capacity for total desorption and (iii) an adsorption capacity as large as possible for a maximum number of compounds.

The adsorption capacity of an adsorbent towards a given compound is characterized by the breakthrough volume (BTV), which represents the gas volume above which a given compound is no longer totally trapped [4]. This means that the preconcentration of such a compound on an adsorbent can only be quantitative at sampling volumes that do not exceed the BTV of the compound.

Our studies on the quantification of a biogenic monoterpene source are based on analytical techniques requiring preconcentration of terpenes on Tenax TA. For this purpose, we need to determine the BTV of these compounds on this adsorbent.

Although the adsorption capacity of Tenax GC has been evaluated earlier, there are only very few data available on Tenax TA. A study of the BTV of the principal monoterpenes on Tenax TA is presented here.

It has been demonstrated that the BTV depends on numerous factors, such as the temperature [5–7], the concentration of the compound being studied [8,9], the chemical composition of the gaseous mixture [10,11], the relative humidity [12,13], the flow-rate and linear velocity of the carrier gas [14,15], the dimensions of the trap [16], a number of parameters relating to the adsorbent, such as mass [16], granulometry, pore diameter and specific surface area [17,18], repeated re-use and thermal pretreatment [13,19].

However, it appears that the adsorption temperature and the concentration of the adsorbed compound are the main critical parameters affecting the BTV value. We therefore investigated the influence of these two parameters on the adsorption of  $\alpha$ -pinene on Tenax TA. The range of volume mixing ratios considered is representative of that encountered in the atmosphere,

where the mixing ratio in  $\alpha$ -pinene ranges between a fraction of ppb and a few ppb (v/v).

$\alpha$ -Pinene was selected as a standard as the value of its BTV on Tenax TA is lower than those of other terpenes.

## 2. Experimental

### 2.1. Apparatus

The apparatus used for this study has been described in detail previously [20,21] and is shown in Fig. 1. It includes principally (i) a generator of standard atmospheric samples which functions by permeation or by diffusion, (ii) a preconcentration–thermodesorption module connected with a Hewlett–Packard Model 5890 gas chromatograph equipped with a 30-m Megabore DB5 column (film thickness 1.5  $\mu$ m), flame ionization detector and an OMRON C28K programmable controller. The whole device is fully automated and operates in a continuous manner.

The preconcentration–thermodesorption module contains a Pyrex glass tube packed with 150 mg of 60–80 mesh Tenax TA (Chrompack) and mounted directly on the chromatograph injector. The adsorbent bed is located in a zone of the trap where the temperature is regulated at  $\pm 1^\circ\text{C}$ .

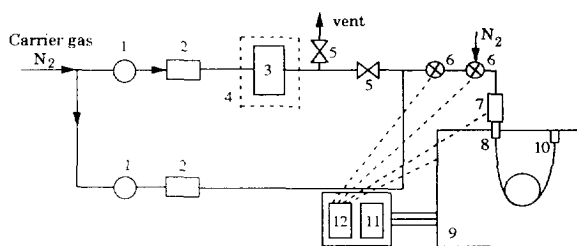


Fig. 1. Experimental device used for the determination of BTV values. 1 = Manometer; 2 = mass flow controller; 3 = terpenes generator (permeation or diffusion); 4 = thermostated bath; 5 = flow controller valve; 6 = three-way electrovalve; 7 = thermoregulated trap module; 8 = injector; 9 = gas chromatograph; 10 = detector; 11 = integrator; 12 = programmable controller.

During trapping experiments, the flow-rate of nitrogen was adjusted to  $150 \text{ ml min}^{-1}$ , corresponding to a linear velocity of  $13.95 \text{ m min}^{-1}$ .

## 2.2. Reagents

The monoterpenes used ( $\alpha$ - and  $\beta$ -pinene, myrcene, sabinene,  $\Delta^3$ -carene and limonene) were obtained as guaranteed products from Extrasynthese (Genay, France).

## 2.3. Procedure

Standard atmospheric samples were obtained either by permeation ( $\alpha$ -pinene) or by a diffusion process ( $\beta$ -pinene, myrcene, sabinene and mixture of  $\alpha$ - and  $\beta$ -pinene). A dilution step was necessary to obtain very low volume mixing ratios in monoterpenes (between a few hundred ppt and a few tens of ppb, v/v).

The BTV was determined by passing a gaseous mixture through the trap. By varying the concentration of the gaseous mixture and the trapping time, it is possible to pass different volumes of gas and different amounts of samples through the trap. It should be noted that the experimental temperatures and the monoterpene volume mixing ratios selected for this study were of the same magnitude as those recorded in the natural atmosphere.

The trapped sample was subsequently desorbed and analysed. The peak area obtained is a function of the mass of compound adsorbed, which was evaluated by comparison with a calibration graph determined for monoterpenes [22].

The masses of adsorbed compounds were plotted against sample volumes. An example is provided in Fig. 2, showing a case in which the mixing ratio in  $\alpha$ -pinene is 1.1 ppb (v/v). Each point represented on the plot is the average of 5–7 experimental measurements. Table 1 gives experimental data with their estimated standard deviations.

The BTV is defined as the sampled volume corresponding to the end of the linear domain. The extreme value of the linear domain is evaluated by calculation of the intersection be-

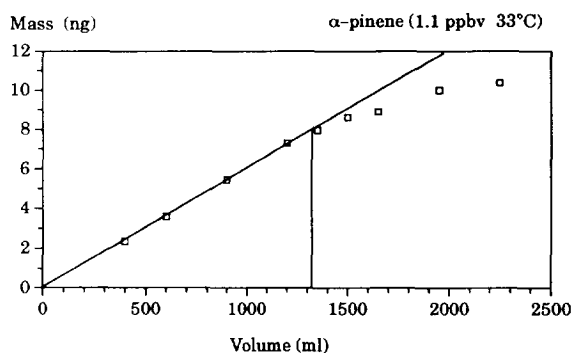


Fig. 2. Plot of mass of  $\alpha$ -pinene (1.1 ppbv, v/v) adsorbed on Tenax TA versus sampling volume.

tween linear and non-linear domains. The linear calibration equation  $y = ax$  is calculated by the least-squares method. Data in the non-linear domain are fitted by a power law,  $y = cx^d$ . The parameters  $c$  and  $d$  are obtained by the least-squares method. Such a mathematical method to determine the BTV was preferred to the statistical method developed by Liteanu et al. [23], which requires a large number of experimental points close to the actual value of the BTV.

Among various direct and indirect methods available for the determination of the BTV [4], the one we employed is well adapted to our automatic device, which can generate very low

Table 1  
Statistical characteristics of the measurements corresponding to Fig. 2

Volume sampled (ml)	Average mass sampled (ng)	No. of measurements	R.S.D. (%)
400	2.35	6	1.5
600	3.59	6	1.2
900	5.45	5	1.9
1200	7.30	5	2.4
1350	7.97	6	6.3
1500	8.61	5	1.8
1650	8.90	7	1.9
1950	10.00	5	1.4
2250	10.40	5	7.6

concentrations and allows automatic programming of the sampling time.

### 3. Results and discussion

#### 3.1. BTV determination for a series of monoterpenes

The BTV values measured on Tenax TA for six monoterpenes characteristic of biogenic emissions are displayed in Table 2. The mixing ratio of these monoterpenes was adjusted to 3 ppb (v/v) and the adsorption temperature on Tenax TA was  $24 \pm 1^\circ\text{C}$ .

It appears that the experimental BTV values are of the same magnitude, and increase in the order  $\alpha$ -pinene < myrcene < sabinene <  $\beta$ -pinene <  $\Delta^3$ -carene  $\approx$  limonene. As  $\alpha$ -pinene exhibits the lowest BTV of the series, it may be selected as a standard and the capacity of Tenax TA for  $\alpha$ -pinene may be reasonably used as a threshold value for all monoterpenes or mixtures of these compounds, provided that their BTV is not modified when they are mixed. Taking  $\alpha$ -pinene as a reference compound, we set out to examine the principal parameters that may influence the value of its BTV on Tenax TA.

#### 3.2. Influence of temperature

Adsorption is an exothermic phenomenon, the BTV being related to the temperature by a Van't Hoff-type relationship:

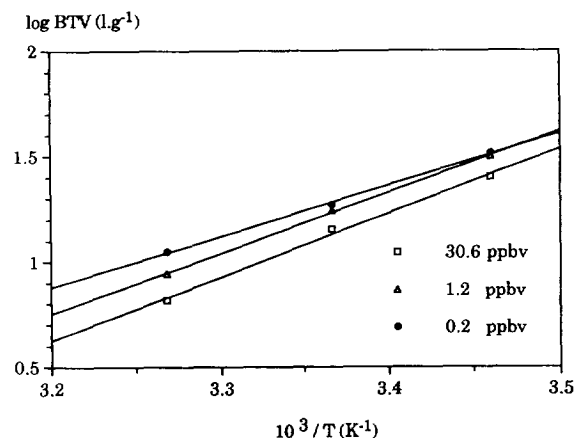


Fig. 3. Variation of  $\alpha$ -pinene BTV versus sampling temperature.

$$\frac{d[\log(\text{BTV})]}{d\left(\frac{1}{T}\right)} = -\frac{\Delta H_{\text{ad}}}{2.3R} \quad (1)$$

where  $\Delta H_{\text{ad}}$  is the adsorption enthalpy,  $R$  is the gas constant and  $T$  is the absolute temperature. Considering  $\Delta H_{\text{ad}}$  as a constant, Eq. 1 can be expressed as

$$\log(\text{BTV}) = -\frac{\Delta H_{\text{ad}}}{2.3RT} + K \quad (2)$$

or, more generally,

$$\log(\text{BTV}) = a + \frac{b}{T} \quad (3)$$

Fig. 3 shows that the experimental values follow this law for the three mixing ratios volumes considered here, namely 0.2, 1.2 and 30.6

Table 2  
BTV on Tenax TA for different monoterpenes in mixtures where the mixing ratio is 3 ppb (v/v) at  $24^\circ\text{C}$

Monoterpene	BTV at $24 \pm 1^\circ\text{C}$ ( $1\text{g}^{-1}$ )	Boiling temperature ( $^\circ\text{C}$ )	Vapour pressure (mmHg, $24^\circ\text{C}$ )
$\alpha$ -pinene	16.3	156	4.6
$\beta$ -pinene	21.4	164	3.1
Myrcene	17.9	167	1.9
Sabinene	20.9	164	3.1
$\Delta^3$ -carene	>21.4	167	2.5
Limonene	>21.4	178	2.0

Table 3  
Values of the parameters for the experimental law  $\log(\text{BTV}) = a + b/T$

Mixing ratios (ppb, v/v)	<i>a</i>	<i>b</i>	Correlation coefficient	$-\Delta H_{\text{ad}}$ (kJ mol <sup>-1</sup> )
30.6	-9.07	3031	0.99	58.1
1.2	-8.47	2883	1	55.2
0.2	-6.88	2426	0.99	46.4

ppb (v/v). The characteristic parameters *a* and *b* and the correlation coefficients are displayed in Table 3. The influence of temperature seems more pronounced for the two highest mixing ratios considered here (>1 ppb, v/v).

The adsorption enthalpies of  $\alpha$ -pinene on Tenax TA were also determined (Table 3). The average enthalpy,  $\Delta H_{\text{ad}}$ , equal to  $-53.2$  kJ mol<sup>-1</sup>, is of the same magnitude as that reported by Gallant et al. [24] for the adsorption of various hydrocarbons on Tenax GC.

According to Kiselev's classification (see [25]) and considering the value obtained here for the adsorption enthalpy, one may reasonably conclude that  $\alpha$ -pinene–Tenax TA interactions involve both non-specific interactions of the Van der Waals type and London dispersion forces [26] and also specific interactions of the  $\pi$ – $\pi$  type.

The knowledge of *a* and *b* is of great interest as they allow one by extrapolation, to determine theoretical BTV values of  $\alpha$ -pinene on Tenax TA for any sampling temperature.

### 3.3. Influence of concentration

Fig. 4 represents the variation of the BTV of  $\alpha$ -pinene on Tenax TA as a function of the various mixing ratios considered. The resulting relationship, of linear log–log type, is consistent with the expression of an adsorption isotherm satisfying Freundlich's equation:

$$\log(\text{BTV}) = \log a + b \log C \quad (4)$$

where *C* is the mixing ratio volume.

For each isotherm we determined the param-

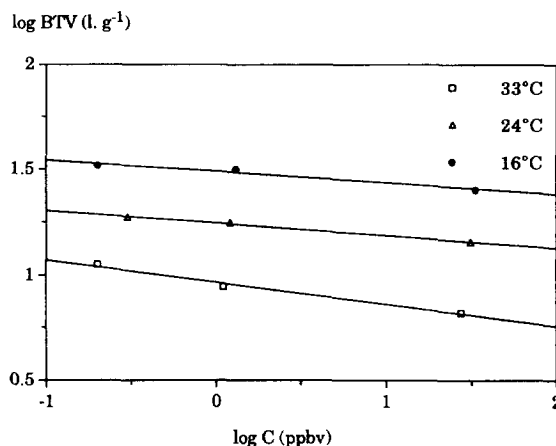


Fig. 4. Variation of  $\alpha$ -pinene BTV versus  $\alpha$ -pinene mixing ratio.

eters *a* and *b* as well as the correlation coefficients (Table 4). The slope of the linear isotherm at 33°C is greater than those obtained at 24 and 16°C.

Thus, prior to any sampling experiment, the BTV value can be evaluated from Eqs. 3 and 4, depending on the sampling temperature selected by the operator and the concentration range to be measured, which should be estimated by excess.

For example, let us calculate the BTV of  $\alpha$ -pinene for sampling temperatures of 16 and 33°C, considering an atmosphere containing  $\alpha$ -pinene at a volume mixing ratio of 100 ppb (v/v). Eq. 4 leads to the corresponding BTV values (Table 5). Considering that the trap contains 400 mg of Tenax TA, volumes lower than 9.6 and 2.2 l would be the maximum sampling values not to exceed the BTV value at 16 and 33°C, respective-

Table 4  
Values of the parameters for the experimental law  $\log(\text{BTV}) = \log a + b \log C$

Temperature (°C)	Log <i>a</i>	<i>b</i> × 10 <sup>2</sup>	Correlation coefficient
16	1.49	-5.35	0.97
24	1.24	-5.89	1
33	0.96	-10.51	0.99

Table 5  
BTV of  $\alpha$ -pinene on Tenax TA at different temperatures and mixing ratios

Parameter	Mixing ratio of $\alpha$ -pinene			
	100 ppbv		10 pptv	
	16°C	33°C	16°C	33°C
BTV ( $l\ g^{-1}$ )	24.1	5.6	39.4	14.7
BTV (l) <sup>a</sup>	9.6	2.2	15.8	5.9

<sup>a</sup> Calculated for 400 mg of Tenax TA.

ly. Atmospheric  $\alpha$ -pinene mixing ratios are generally lower than 100 ppb (v/v).

Let us also consider the example of an atmosphere characterized by an  $\alpha$ -pinene mixing ratio as low as 10 ppt (v/v). In that case, the calculated BTV values (Table 5) indicate that it would be possible to adsorb on 400 mg of Tenax TA a maximum of 15.8 l of  $\alpha$ -pinene at 16°C and 5.9 l at 33°C. In the latter example, the masses of  $\alpha$ -pinene sampled (0.9 and 0.3 ng, respectively) would only be detectable for a sampling temperature of 16°C on our apparatus, and the mass sampled at 16°C would be three times greater than at 33°C, yet not exceeding the BTV value. This clearly means that low values of the sampling temperature favour the detection of the lowest quantifiable concentration.

It is clear that the BTV is a volume threshold value above which the sampling operation is no longer quantitative. Even in the case where this critical volume is collected, the sampling may be subject to uncontrolled variations during the manipulations. As shown above, if one does not control the sampling temperature or the concentration of the compound being studied, the BTVs corresponding to different samplings will be subject to large deviations. One should keep in mind that the temperatures and the concentrations may be subject to large variations at the experimental site, especially between night and day.

Hence it is generally recommended to remain far below this value during sampling experiments. A safe sampling volume (SSV) has been

defined for this purpose, corresponding to a certain percentage of the actual BTV value. Different percentages have been used by different workers. The SSV suggested by Harper [27] corresponds to two thirds of the BTV, whereas the value indicated by the HSE [28] is 70%. In our determinations, we took an SSV value equal to two thirds of the BTV.

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