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Preconcentration of Atmospheric Terpenes on Solid Sorbents

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Hydrocarbons emitted by vegetation, such as isoprene and monoterpenes, seem to play an important role in atmospheric *chemistry*. A better estimation of their *biogeochemical cycle* requires that the levels be testable at any time. The extremely low concentration of these chemicals in the atmosphere necessitates a preconcentration step at the time of sampling. This enrichment was done on 13 solid adsorbents (Tenax G C and T A, Chromosorb 101, 103, 105 and 107, Porapak R and Q, XAD-2, 4 and 7, Amborsorb-XE-340 and Carbosphere). This study allowed us to determine the breakthrough volumes of isoprene and the principal monoterpenes on these adsorbents. Of the adsorbents tested, Tenax G C and T A were those the best adapted to the desorption of compounds as reactive as the terpenes.

KEY WORDS: Breakthrough volume, solid adsorbent, isoprene, monoterpenes.

INTRODUCTION

Because of their high reactivity, it seems that hydrocarbons, such as isoprene and the monoterpenes, play a significant role in the

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physicochemistry of the atmosphere. This is especially true in the formation of particles and in the ozone and carbon monoxide cycles.

Some studies¹⁻⁷ have found that hydrocarbons, after interacting with ozone or monoatomic oxygen generated by NO₂ photolysis, can, through oxidation and polymerization, create condensation nuclei (Aitken nuclei) and aerosols. However, other authors⁸⁻¹⁴ find that these hydrocarbons contribute little to the formation of aerosol particles.

The above-mentioned sources cite that organic products emitted by vegetation consume ozone. They are, however, equally capable of producing it through a series of processes of peroxidation and photolysis of nitrogen oxides.^{3,14,15}

Through ozonolysis and by interaction with °O and °OH radicals,^{3,6,17} terpenic compounds may also be transformed into oxygenated varieties.

Their final degradation appears also to be a strong contributing factor to the global atmospheric carbon monoxide balance.¹⁸⁻²⁰

For any attempt to better interpret the impact of vegetable hydrocarbons on the natural chemical system, it is necessary to be able to test them at small levels of concentration.

Recent studies in rural areas show that the atmospheric concentrations of these products are very low, ranging from a few hundredths ppb to a few ppb.^{16,21-24} To reach the detection threshold, it is always necessary to introduce a preconcentration step into the experimental protocol at the time of sampling. The specimen thus obtained may then be subjected to qualitative and quantitative analysis.

For several years the enrichment technique on solid adsorbents such as active carbons,^{25,26} Carbopacks,^{27,28} Amborsorb series,²⁹ Chromosorb Century series,^{30,31} Porapak series,³² XAD resins^{33,34} and Tenax GC^{25,30,33,35,36} has been well developed. Preconcentration may also be accomplished by cryogenic techniques.^{37,38}

This work describes the study of the preconcentration of atmospheric isoprene and terpenes on solid adsorbents and their thermal desorption, in relation to their quantitative analysis. Until now, the enrichment of isoprene and of the monoterpenes was done with cryogenic traps,^{13,16,21,24,39} or with a few rare adsorbents such as Tenax GC^{16,21,40-43} and Carbopack BHT.⁴⁰

We have undertaken a systematic study of several adsorbents. The

purpose of the study was to identify those adsorbents whose properties best suit the thermal adsorption—desorption cycle and analysis of this type of compounds.

The "best choice" is a function of several factors such as the decomposition of the substances during the preconcentration, stockage and desorption steps, the high temperature stability of the adsorbent, the influence of ambient humidity, the rapid and complete desorption of the mixtures and the action of very reactive mineral compounds (e.g., oxide of nitrogen, carbon and sulphur) on the adsorbent. The most important criterion to determine, however, is the adsorption capacity of the various adsorbents. This is expressed in terms of the breakthrough volume (B.T.V.) which can be defined as the volume of gas passed through a adsorbent bed before the investigated compound begins to be eluted from the container with the adsorbent. The best adsorbent for a given organic substance is that for which the breakthrough volume is the highest.

During the course of this work, we have determined the breakthrough volume of different series of adsorbents for isoprene and the principal atmospheric terpenes.

EXPERIMENTAL

Reagents

The isoprene and monoterpenes used were obtained as guaranteed grade products from Fluka (Buchs, Switzerland).

The sorbents used were Chromosorb 101, 103, 105, and 107 (Johns-Manville, Denver, CO, U.S.A.); Porapak Q and R (Waters Assoc., Milford, MA. U.S.A.); XAD 2, 4 and 7 (Fluka, Buchs, Switzerland); Carbosphere and Tenax GC (Alltech Assoc. Deerfield, IL, U.S.A.); Tenax TA (Chrompack, France S. a. r. l.) and Amber-sorb XE-340 (Rhom and Hass Co., Philadelphia, U.S.A.).

Apparatus

Product detection was performed using a Hewlett-Packard model 5880 A gas chromatograph with a flame ionization detector.

The breakthrough volumes of the monoterpenes were determined using a direct method with the apparatus, presented in Figure 1,

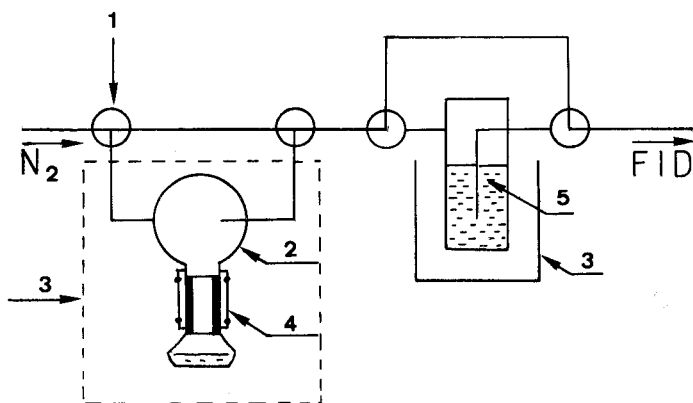


FIGURE 1 Diagram of apparatus used for breakthrough volume determination. (1) Three-way valve; (2) Generator of standard gas mixture; (3) Thermostated bath; (4) Teflon diffusion tube; (5) Adsorbent trap.

which has been described in detail in a previous work.⁴⁴ The apparatus consists of a generator of standard gas mixtures, working by diffusion, comprising a Pyrex reservoir and flask separated by a Teflon tube of known bore and length. It is maintained at $20 \pm 0.2^\circ\text{C}$ in a thermostatted bath. The liquid to be studied is placed in the reservoir and the vapor diffuses into the flask at a constant rate through the Teflon tube and is then carried off by a flow of pure dry carrier gas ($50\text{ cm}^3\text{ min}^{-1}$). The mixture obtained then passes on to the flame ionisation detector either directly or through the trap containing the sorbent to be studied. The circuit does not contain a chromatographic column and should be either of glass or of nickel to avoid any catalytic decomposition of the substances. The entire set-up between the generator and the detector is maintained at a temperature between 90° and 100°C by heating resistors to reduce condensation or adsorption of the compounds onto the equipment walls.

For isoprene, a much more volatile compound than the monoterpenes, we replace the diffusion generator with a permeation generator, presented in Figure 2a. In the upper section is a stainless steel grill on which can be placed one or more permeation tubes. The carrier gas arriving in the lower section of the generator carries the permeated gas. The permeation tube is made entirely of Teflon F.E.P. (Figure 2b). This system allowed us to generate a carrier

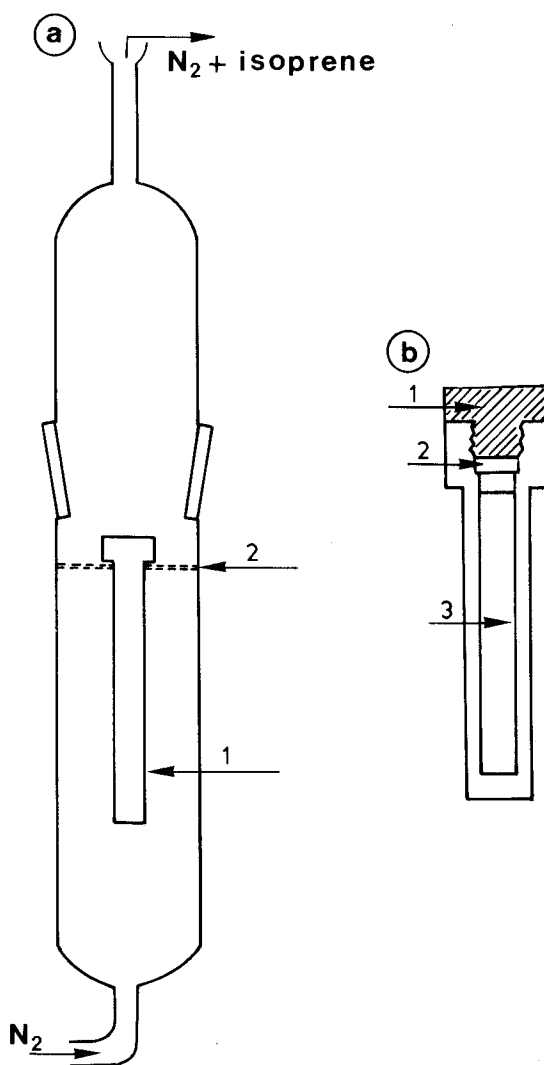


FIGURE 2 a—Generator of permeation. (1) Permeation tube; (2) Stainless steel grill. b—Permeation tube schematic. (1) Stopper; (2) Elastomer membrane; (3) Isoprene. Tube dimensions: outer ϕ external 7 mm, inner ϕ 5 mm, useful length of permeation 80 mm.

gas/isoprene mixture, the concentration of which (20 ppm) was comparable to the range obtained from the terpene diffusion (4–20 ppm).

The diffusion rates were determined, after stabilization, by weighing the diffusion cell or permeation tube every 4 days with the aid of a semi-microbalance sensitive to 0.01 mg to obtain the significant mass losses.

The traps we used were of Pyrex glass (Figure 1) and contained an adsorbent column 1 cm high, the mass of which was between 0.2 and 1 g.

Procedure

The breakthrough volume determination protocol has been described in detail in previous works.^{44, 45} The following, therefore, is only a brief summary (Figure 3). After the generation has stabilized (a few hours for diffusion and a few days for permeation) the gaseous mixture containing the vapor under study is passed through the trap (t_0). After a time lapse t_B the first traces of the substance appear at the trap exit and arrive at the chromatographic detector. The trap is then isolated and we proceed to the thermal desorption. Knowing

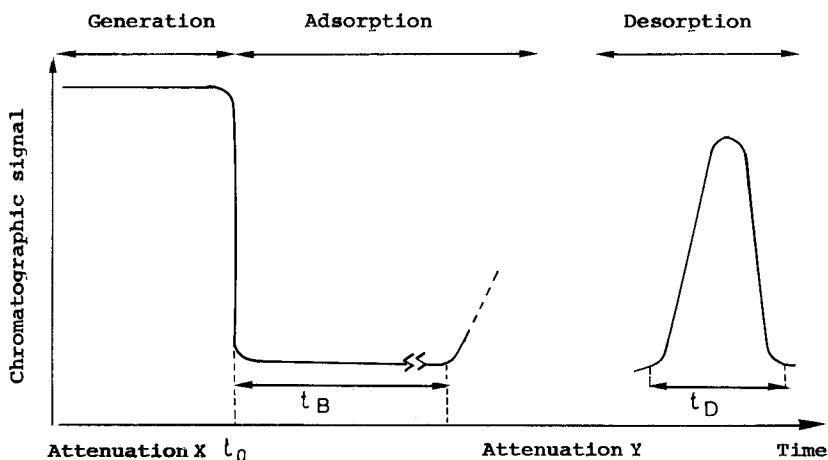


FIGURE 3 Schematic chromatogram allowing the breakthrough time (t_B) and the desorption time (t_D).

the breakthrough time t_B and the carrier gas flow rate, we can calculate the breakthrough volume of the adsorbent per mass units.

RESULTS AND DISCUSSION

The breakthrough volumes for isoprene, α and β pinene, carene and limonene, determined at $20^\circ\text{C} \pm 0.1^\circ\text{C}$ on 13 adsorbents are listed in Table I. Each result represents the average of 2 or 3 consecutive measurements. As some terpenes have extremely high breakthrough volumes, and great precision is not necessary here, we have shown simply that they are greater than 15 lg^{-1} . It should be noted that, for the porous polymers studied, the isoprene breakthrough volume were inferior to those of the other terpenic derivatives. The capacity of the different adsorbents in relation to isoprene may be represented by the following sequence: Carbosphere \sim Ambersorb XE-340 \geq XAD 4 $>$ Porapak R $>$ Porapak Q \sim Chromosorb 107 $>$ Chromosorb 105 $>$ Chromosorb 101 $>$ Tenax TA $>$ Tenax GC \sim XAD 2 $>$ XAD 7 $>$ Chromosorb 103. On Carbosphere, Ambersorb XE-340 and 7 of the 10 polymers, the four monoterpenes display breakthrough volumes $> 15 \text{ lg}^{-1}$.

Considering only adsorption capacities, the least effective adsorbents were Tenax GC and TA, and Chromosorb 101 and 103. This is probably due to their low specific surface areas (15 to $50 \text{ m}^2 \text{ g}^{-1}$).

Desorption times t_D (Figure 3) for the 5 compounds fall between 4 and 35 minutes. Notice that Carbosphere presents two problems: incomplete desorption and a high retention of trapped substances. Even at high temperature (360°C), there is practically no desorption. Desorption has only been accomplished by "backflushing" which consists of reversing the carrier gas flow in the trap. Even with this technique, however, desorption time is greater than 75 minutes.

It should be noted that certain properties of Tenax GC and TA⁴⁶ make these adsorbents more useful than others when working with terpenes. They are hydrophobic and aid, therefore, in humid environment sampling, and they have good thermal stability which is necessary to desorb such slightly volatile compounds as terpenes. In addition, contrary to the other adsorbents listed in Table I, during the adsorption-desorption cycles, we did not notice the decomposition of products as reactive as isoprene and the terpenes for concentrations in the 100-300 ppb range. The low breakthrough

TABLE I
Breakthrough volumes of isoprene and the principal monoterpenes on various adsorbents. V_b : Breakthrough volume (1 g^{-1}); t_D : Desorption time (min).

Sorbent type	Granulometry mesh	Desorption temperature °C	Compounds (concentrations ppm V/V)											
			Isoprene (20)	t_D	V_b	t_D	V_b	t_D	V_b	t_D	V_b	t_D	V_b	t_D
Tenax GC	60-80	300	1.5	3.6	3.7	6	4.0	6	11.6	13	>15	17		
Tenax TA	60-80	300	1.6	5	4	10	5.6	10	>15	22	>15	22		
Chromosorb 101	80-100	200	1.9	4	2.3	11	2.8	11	—	—	—	—		
Chromosorb 103	80-100	200	0.3	3.4	0.25	11	0.3	9	—	—	—	—		
Chromosorb 105	80-100	200	5.3	5.4	>15	27	>15	20	—	—	—	—		
Chromosorb 107	80-100	200	6.3	5	>15	14	>15	13	>15	17	>15	19		
Porapak R	80-100	200	6.8	4.5	>15	22	>15	14	>15	35	>15	40		
Porapak Q	80-100	200	6.4	5	>15	22	>15	18	—	—	—	—		
XAD-2	20-50	200	1.5	4	>15	14	13.4	14	—	—	—	—		
XAD-4	35-50	200	10	7	>15	28	>15	28	>15	26	>15	28		
XAD-7	20-50	200	1.15	4	>15	15	>15	12	—	—	—	—		
Ambersorb XE-340	—	360	>15	18	>15	24	>15	24	—	—	—	—		
Carbosphere	80-100	360	>15	>35	>15	>75	>15	>35	—	—	—	—		

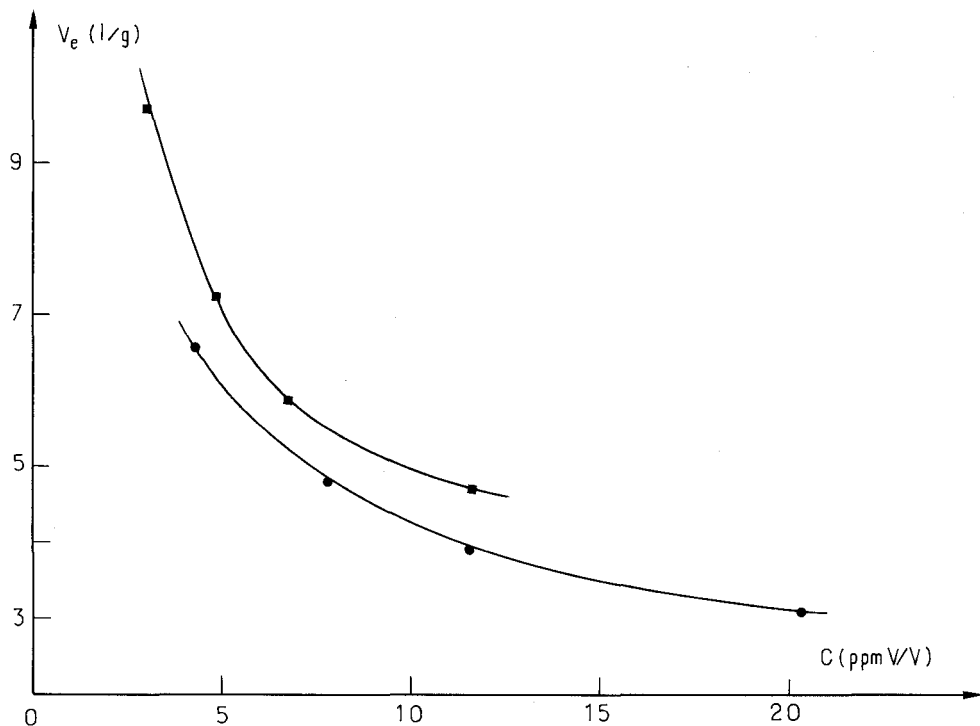


FIGURE 4 Effect of concentration on the breakthrough volume. ●: α -pinene on Tenax GC, ■: β -pinene on Tenax GC.

volumes of Tenax GC and TA for isoprene and α - and β -pinene do not inhibit their use in the analysis of atmospheric terpenes. Actually, one study of breakthrough volume in relation to concentration (Figure 4) shows that this volume increases strongly for concentrations less than 5 ppm (V/V). This result was confirmed by Yokouchi *et al.*⁴⁷ who found a breakthrough volume of 12 l g^{-1} for α and β pinene concentrations of 100 ppb. This agrees with results found by other researchers who studied the adsorption of different compounds (acetone,^{44, 48} sulphur derivatives⁴⁹ and alkanes C_4 to C_7 ⁵⁰) on Tenax GC and various other porous polymers.

We also studied the adsorption capacity of Tenax GC in relation to its age. The breakthrough volumes measured for α -pinene (4.3 ppm V/V) and β -pinene (3 ppm V/V) fall from 7.69 to 6.59 l g^{-1}

and from 9.82 to 9.26 \lg^{-1} respectively after ten assays. These results seem to demonstrate a small decrease (15% and 6% respectively) in the capacity of the adsorbent over the duration of its utilization. Opposite results were found by Sydor and Pietrzyk,⁵¹ who show that Tenax GC improves its performance with each usage. They attribute this phenomenon to a decomposition of the polymer and to an opening of the pores after successive thermal desorptions.

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