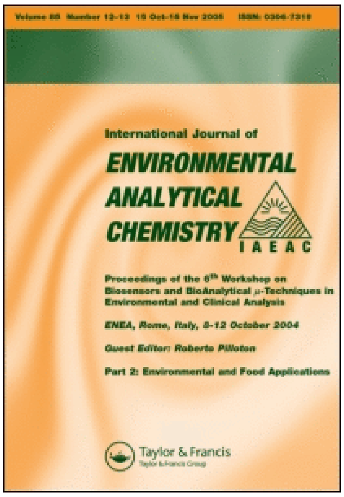

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

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To cite this Article Riba, M. L. , Tathy, J. P. , Mathieu, J. and Torres, L.(1985) 'A Simple, Efficient Device for Determining Terpenes Present as Traces in the Atmosphere', International Journal of Environmental Analytical Chemistry, 20: 3, 255 — 263

To link to this Article: DOI: 10.1080/03067318508077061
URL: http://dx.doi.org/10.1080/03067318508077061

Intern. J. Environ. Anal. Chem., 1985, Vol. 20, pp. 255–263
0306-7319/85/2004-0255 $18.50/0

A Simple, Efficient Device for Determining Terpenes Present as Traces in the Atmosphere†

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(*Received January 12, 1985*)

Up to the present it has been established that natural hydrocarbons, such as isoprene and the monoterpenes, play an important role in the physical chemistry of the atmosphere because of their high reactivity.

However, their true contribution to the natural chemical system has not yet been clearly defined as the seasonal variations in their concentrations are not sufficiently accurately known due to their low content in the atmosphere (a few hundredths of a ppb to a few ppb). We have developed an analysis procedure which enables quantitative trapping to be carried out together with excellent chromatographic separation. It consists of enrichment on adsorbents followed by very rapid thermal desorption and instantaneous chromatographic injection without further cryogenic trapping.

Our adsorption–desorption cycle does not reduce the efficiency of the chromatographic separation at all and does not bring about any decomposition of these highly reactive plant oils.

KEY WORDS: Preconcentration, thermal desorption, solid adsorbent, determination, terpenes, atmosphere.

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†Presented at the 2nd Workshop on Chemistry and Analysis of Hydrocarbons in the Environment, Barcelona, November 19–20, 1984.

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INTRODUCTION

Determining the quantities of the main terpenes present in the atmosphere is most interesting, as these highly reactive natural hydrocarbons play an important role in the physicochemistry of the atmosphere.[1-6] Recent studies in rural areas show that traces of these products are to be found in the atmosphere (a few hundredths of a ppb to a few ppb).[7-12] Such concentrations can only be measured if before any analysis a preconcentration step is performed.

Our analytical system allows a preconcentration on solid adsorbent followed by thermal desorption to be performed. It allows a quantitative trapping of the products and their restitution by means of an almost instantaneous desorption which does not alter their stability or their chromatographic separation which follows the desorption.

This simple method makes an extra cryogenic trapping before chromatographic injection unnecessary. Its great advantage is that it can be used in the field and that it reduces the residence time by the highly reactive terpene compounds in the adsorbent cartridges.

EXPERIMENTAL

Apparatus

Figure 1 shows the apparatus used. With this set, three different configurations are possible.

Configuration 1 (diffusion circuit ➡) Used for calibration of the chromatographic signal according to the quantities of terpenes injected.

The device includes a diffusion generator of standard gas mixtures, the operating of which was described in detail in a previous publication,[13] a VALCO six-way gas valve with a 5 ml calibration loop and heated up to 100°C, which reduces the adsorption phenomenons on the walls of the circuit, and finally a chromatograph in gas phase, a 5700 A Hewlett–Packard model equipped with a flame ionization detector.

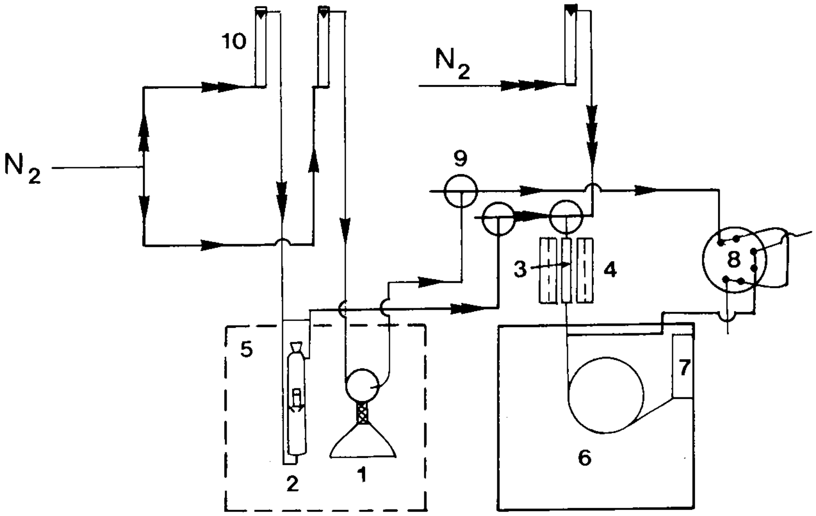

FIGURE 1 Diagram of apparatus. Diffusion circuit ➤ . Permeation circuit ➤➤ . Desorption circuit ➤➤➤ . (1) Diffusion generator; (2) Permeation generator; (3) Sorbent trap + needle; (4) Desorption oven; (5) Thermostated bath; (6) Chromatograph; (7) Detector F.I.D.; (8) Six port valve with sample loop; (9) Three-way tap; (10) Flow rate regulator.

Configuration 2 (permeation, adsorption ➤➤ and desorption ➤➤➤ circuits) The permeation circuit allows the generation of gas mixtures whose terpene concentrations, which are very well known, are close to atmospheric concentrations.

The permeation tubes used, made of F.E.P. teflon, have small dimensions (outside Ø 12 mm, inside Ø 4 mm, useful length of permeation 13 mm); they are filled with terpenes at the start of the experiment, and weighed every fortnight by means of analytical microbalance, a γ 21 N SETARAM model sensitive to 1 μg. The variations between two weighings allows the mass flow of the compound and thus its concentration in the carrier gas to be determined.

The traps used for the preconcentration of terpenic vapours are made of a Nickel tube 14 cm long and $\frac{1}{4}$ inch in diameter. They hold 360 to 380 mg of adsorbent on a 10 cm length. Two 5 mm thick fibre glass stoppers keep the adsorbent down in the tube (Figure 2). The

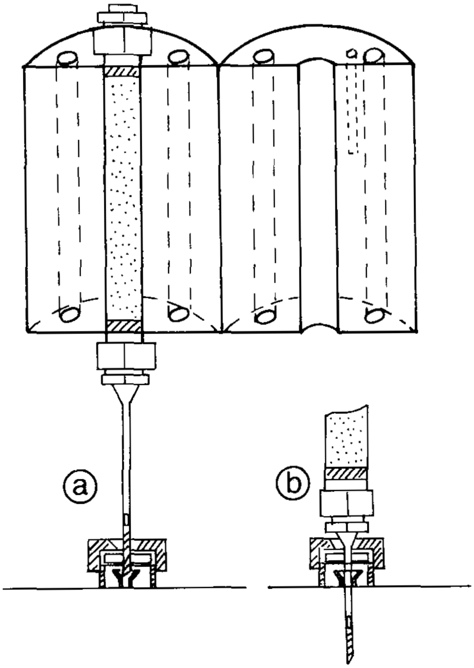

FIGURE 2 Diagram of the trap with desorption oven and injection needle. Position (a): trapping; position (b): desorption and injection.

adsorbent chosen is TENAX GC (Alltech Association, Deerfiel, IL, U.S.A.); a previous study on terpene concentration on various solid adsorbents showed that Tenax GC was best adapted for the determination of the quantities of natural hydrocarbons.[14] The traps are linked to the chromatograph by means of a needle, as shown on Figure 2, drilled with two holes at mid-length, and closed at the end.

Desorption is performed by means of a "sandwich type" oven; Figure 2 shows the diagram of this oven. The heater block is a brass cylinder cut into two halves and drilled with six holes, a central hole for the trap, and five peripheral holes: four of them for 110 W heating resistances and one for the thermocouple linked to the heat regulator.

This set allows adsorption–desorption-analysis cycles to be performed with standard or real atmospheres.

Procedure

Calibration: The exact quantity of terpene injected into the chromatograph is known, by means of a calibrated loop, from the terpene mass flow provided by the diffusion generator and the carrier gas flow. Injection of variable quantities of terpene was made possible by the use of diffusion tubes of different diameters (1 to 2 mm).

Adsorption–desorption-analysis cycle: While the adsorption step is performed, the needle is outside the injector (position a, Figure 2). The carrier gas which goes into the generator carries the terpene mixture which is to be adsorbed in the trap; the carrier gas only goes through the trap and is evacuated through the side holes of the needle.

During the desorption step, the needle is pushed into the injector (position b, Figure 2). By switching the valves, the gas coming from the permeation circuit is sent into the atmosphere; the pure carrier gas (desorption circuit) runs through the trap and the chromatograph. When the carrier gas flow and the chromatographic signal have been stabilized, the oven is placed around the trap; the trapped products are then thermically desorbed at a temperature of 300°C, and pushed instantaneously into the chromatographic column.

Analysis of an atmosphere sample: In order to trap the terpene present in the atmosphere, air, at a given flow, must be routed into a trap, by means of a NO 22 A18 type KNF Neuberger membrane pump.

After adsorption, the trap is connected to the desorption circuit and the carrier gas runs through it for 1 to 2 min. The needle is in a high position. The desorption step starts with the introduction of the needle in the injector and is carried out as previously.

RESULTS AND DISCUSSION

Numerous possibilities are offered by the above-mentioned device. In fact, thanks to this set, the chromatographic signal can be calibrated in relation to the mass of samples studied, standard atmospheres can be simulated, adsorption–desorption cycles followed by an adjusting of the chromatographic separation can be performed and the

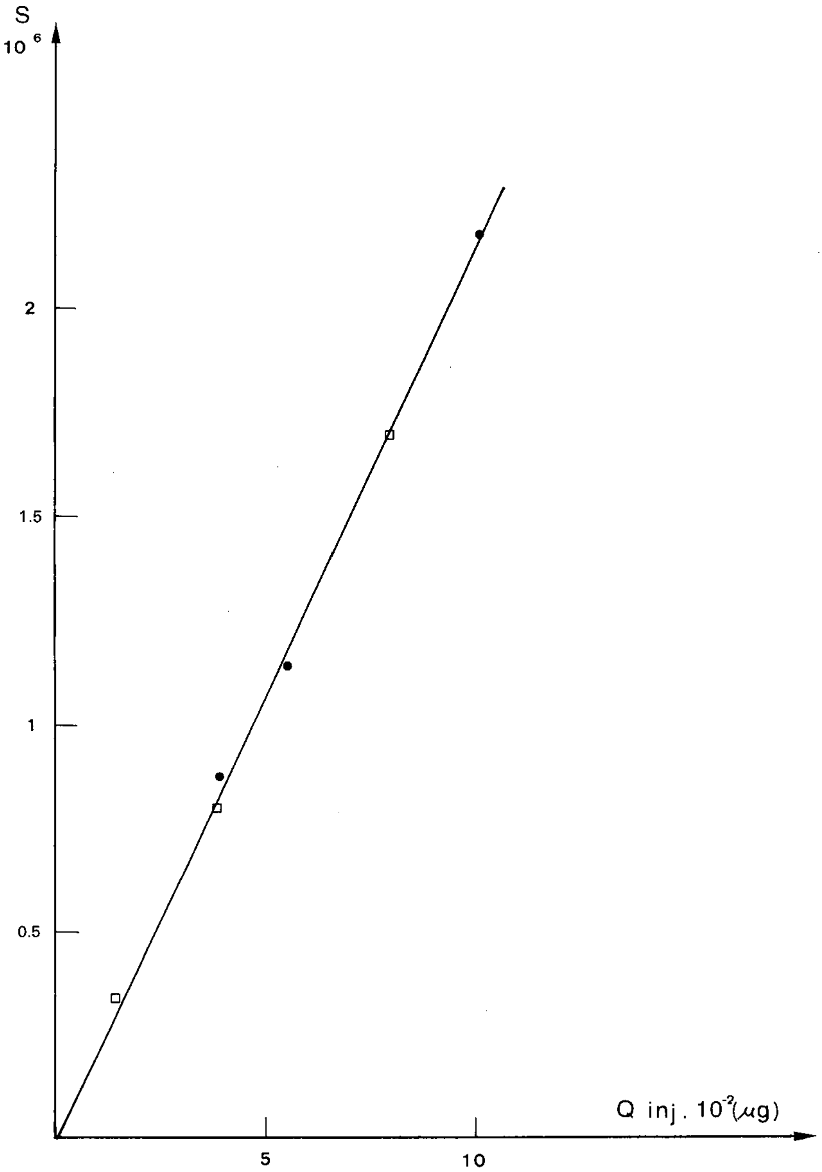

FIGURE 3 Calibration curves concerning α- and β-pinene. ●: α-pinene; □: β-pinene.

efficiency of the operation calculated by means of the calibration curves.

The whole set of operations can be performed on all sorts of pollutant or nonpollutant compounds, which can be found as traces in confined or open atmospheres.

The quantitative determination, for example, of α- and β-pinene, the main terpenes present in the atmosphere was performed in our laboratory. Figure 3 shows the lines of the chromatographic calibration ($y = ax$ equation) obtained by means of the method of least squares method. The two lines are practically identical; the respective values of their slopes are: $0.2156\ 10^8$ and $0.2137\ 10^8$. This result was to be expected since the two compounds have the same empirical formula.

The chromatographic separation achieved with such a system is excellent too, considering the experimental conditions. The separation of a standard mixture of isoprene, of α- and β-pinene, of carene and of limonene, after a direct injection or after an adsorption–desorption-analysis cycle are practically identical (Figure 4). This can be due to the considerable reduction of the dead volumes in the whole circuit and particularly in the introduction system.

The set of results obtained shows the good technical qualities of this apparatus which proved easy to use and very reliable as far as the results are concerned.

This simple and portable set was used in the field during the ATILA campaign (action of isoprene and terpenes on the atmosphere) in the Landes Forest (France) in September 1984. We were able to determine the quantities of atmospheric terpenes, and to follow the daily variation of their concentration. The results, now under study, will be the subject of a forthcoming publication.

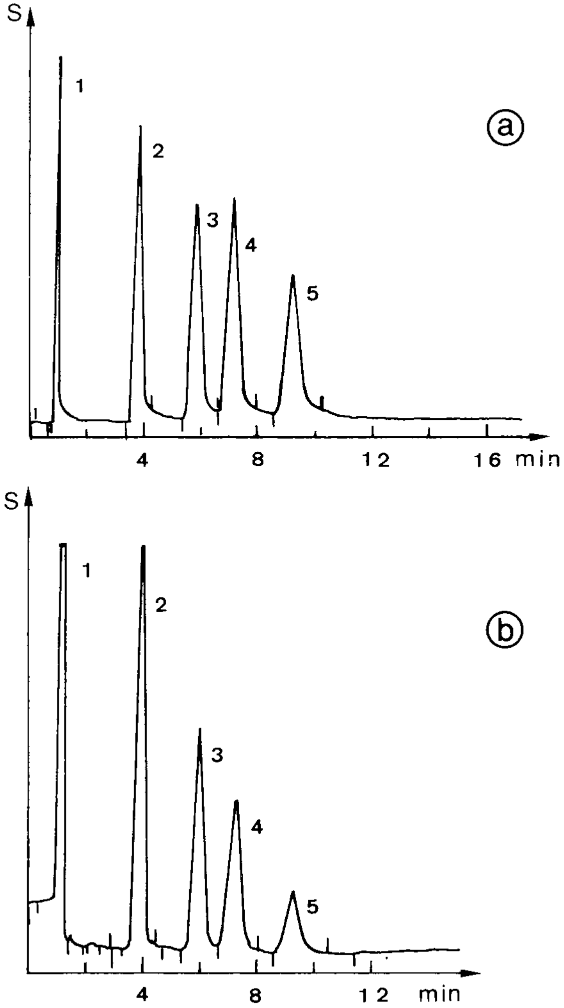

FIGURE 4 Chromatograms of an isoprene and 4 monoterpenes mixture after direct injection (a) or after adsorption on Tenax GC and desorption at 300°C (b). (1) isoprene; (2) α-pinene; (3) β-pinene; (4) carene; (5) limonene.

—4 m long and $\frac{1}{8}$ in. diameter stainless steel column (10% Carbowax 20 M on Chromosorb WAW-DMCS (75–94 mesh)).

—carrier gas flow (N_2): 30 ml/min.

—injector $T = 200$°C.

—column $T = 90$°C.

—detector $T = 250$°C.

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