PRECONCENTRATION AND ANALYSIS OF ATMOSPHERIC ISOPRENE AND MONOTERPENES

SYSTEM AUTOMATION

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SUMMARY

As part of a study on terpene hydrocarbons in the biosphere–atmosphere exchange processes, an entirely automatic device has been elaborated for sampling, preconcentration and analysis of isoprene and the principal atmospheric mono-terpenes. This device comprises mainly a gas chromatograph for analysis and a programmable controller for the management of the operations. It permits measurement of the concentration and flux rate of terpenes. Automatic and continuous cycles (sampling–analysis) were carried out over several days. They were characterized by a reproducibility lower than 1%; their analytical characteristics were quite acceptable.

INTRODUCTION

In environmental matter, essential problems arise concerning, first, the perturbation, due to human activities, of the biosphere–atmosphere equilibrium, imposed by natural phenomena and then the eventual change in atmospheric air composition. Indeed even if there is no change in proportion of the major atmospheric compounds, there may be one in the composition of the trace compounds. Some of those compounds, CO, hydrocarbons, NO_x, O_3, aerosols, etc., although in low or sometimes very low concentrations, have an important rôle in the planet radiative balance, in atmospheric chemistry, in biomass, in biogeochemical cycles, etc.

The atmospheric vulnerability to external perturbations wherever they come from (solar, natural or human) has consequences, especially for climate, forests, lakes, etc. This inexorable evolution constitutes a problem which is going to increase for the next decades and so retains the attention of the international scientific community.

Aims of research throughout the world are to estimate the actual state on a planetary scale and to comprehend better the emission and evolution of its components, then to predict the future and to propose, if necessary, solutions.

Among the numerous volatile organic compounds present in the atmosphere, emitted by natural sources, isoprene and monoterpenes were the most studied in the

last few years[1-4] because of their predominance in vegetal emissions and their important chemical reactivity. These compounds seem to be implicated in very important tropospheric processes. Under UV solar irradiation, in the presence of nitrogen oxides, they are oxidized by OH radicals, ozone and may participate in many reactions which are sources of "nuclei", aerosols and carbon monoxide[5-9]. Those hydrocarbons can also react by night with the NO_3 radical according to poorly understood chemical mechanisms[10,11].

Although numerous studies[1,12-14] were made to determine the part played by those biogenic compounds in aerosol formation and in the global ozone balance, the results in rural zones are misstated and not sufficient.

Comprehension of the contributions of isoprene and monoterpenes to atmospheric physicochemistry requires knowledge of the variations in their daily, seasonly and geographically concentrations and emissions. This research can be pursued only if an analytical method is available that can characterize and measure terpenes in natural atmospheres in which their concentrations are at the $\mu l/l$ level.

We have devised a totally automatic apparatus for measuring isoprene and monoterpenes in atmospheric air, which operates continuously and sequentially.
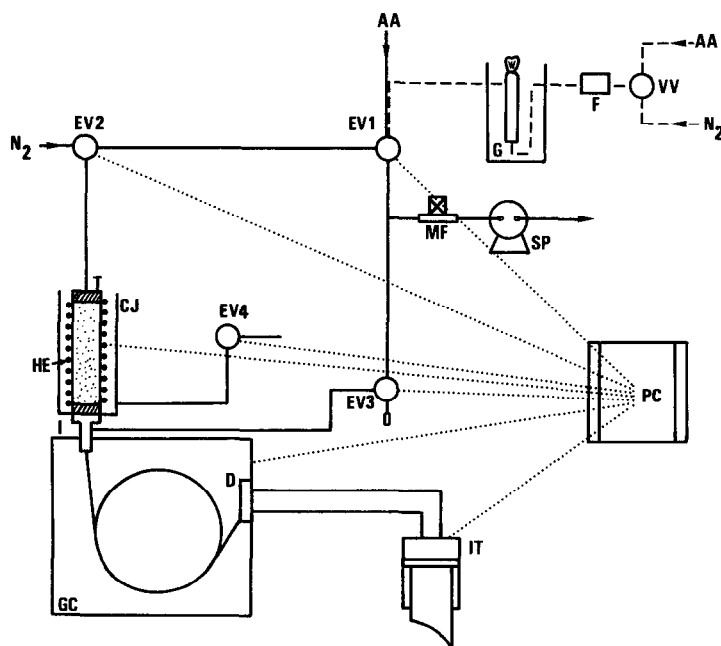

Fig. 1. Automatic device for sampling and analysis $-\rightarrow-$, Standard atmospheres sampling circuit. AA = Atmospheric air inlet for natural atmospheric samples. ......, Programmable controller action. PC = Programmable controller; GC = gas chromatograph; CJ = cooling jacket; D = flame ionization detector; MF = mass flow meter; EV_1, EV_2, EV_3 = three-way electrovalves; EV_4 = two-way electrovalve; F = filter; G = generator; I = injector; IT = integrator; T = trap; HE = heating element; SP = suction pump; VV = three-way valve.

EXPERIMENTAL

Instrument design

The automatic sampling and analysis device is shown in Fig. 1. Its principal elements are a gas mixture generator (G), a trap (T), a NO A18 Type KNF membrane suction pump (SP) (Neuberger, Village-Neuf, France), a gas chromatograph (GC) and a programmable controller (PC). The generators used, working by permeation or by diffusion, have been discussed previously[15,16]. The traps consisted of pretreated nickel tubes (15 cm × 4.5 mm I.D.) packed to a depth of 120 mm with approximatively 350 mg of 60–80 mesh Tenax GC (Alltech-Assoc., Deerfield, IL, U.S.A.) were mounted directly on the injector (I); the trap is surrounded by a brass cooling jacket (CJ) in which compressed air can circulate. A heating element HE (Thermocoax, Paris, France) coiled round the tube supplies heat to the adsorbent heating. The trap and its mode of attachment to the injector is shown in Fig. 2.

The chromatographic system consisted of an Hewlett-Packard Model 5890 A equipped with a split–splitless injector, a flame ionization detector (D), a fused-silica semi-capillary column OV-1 (30 m × 0.53 μm) and a Model 3390 integrator (IT) (Hewlett-Packard). The programmable controller is a Syrelec Model SLP 3001 (Bordeaux, France) with electronic technology containing 24 input interfaces and 8 output interfaces.

The dead volumes of the gas circuits after the trap were systematically reduced. For this purpose the trap was directly connected to the chromatographic injector (Fig. 2).
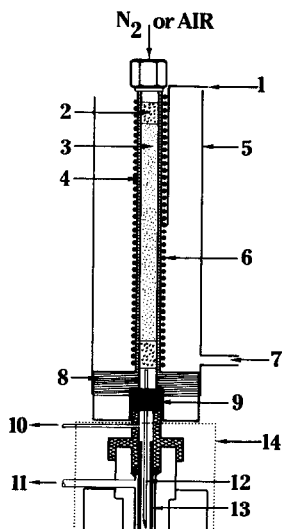

Fig. 2. Trap and its mode of fixing to the injector. 1 = Thermocouple; 2 = glass-wool plug; 3 = adsorbent; 4 = trap; 5 = cooling jacket; 6 = heating element; 7 = compressed air inlet; 8 = cooling jacket fixing nut on injector; 9 = septum; 10 = septum purge; 11 = split vent; 12 = fused-silica needle; 13 = insert; 14 = injector.

System operations

The automation of the whole apparatus was done with an electronic programmable controller which controls, in real time, machines or sequential logic processes. Its role consists in collecting information appropriated by the probes:
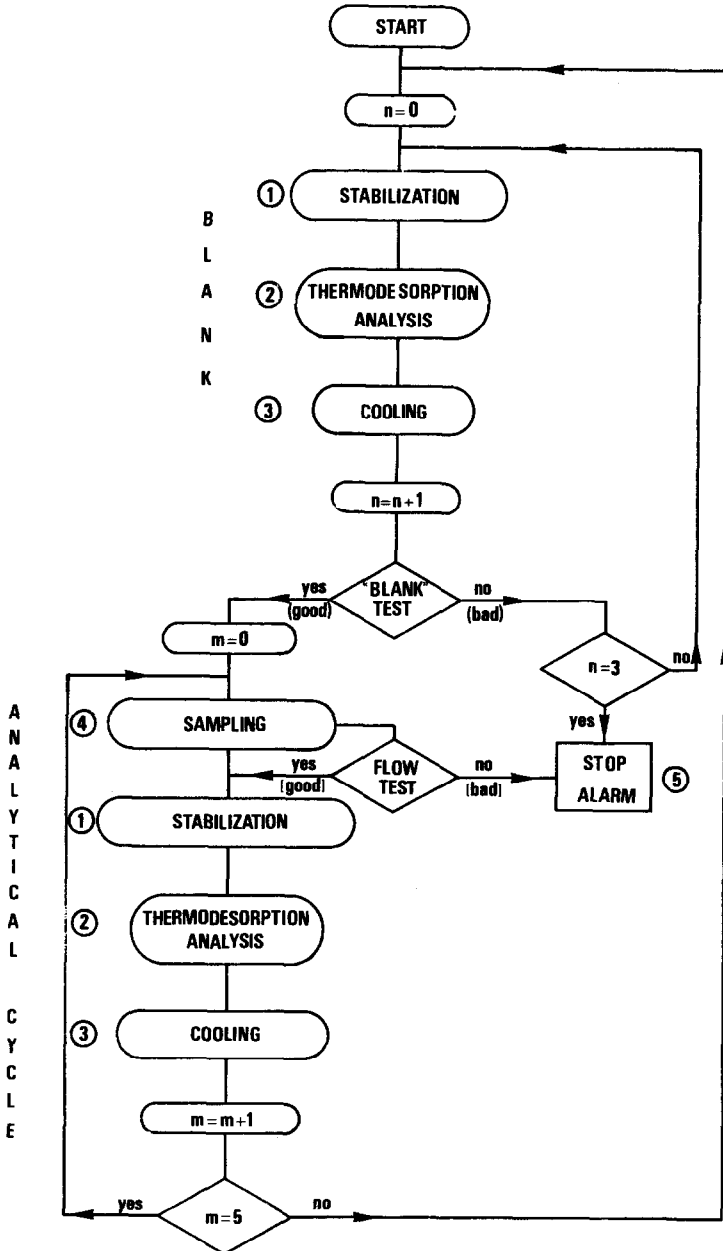

Fig. 3. Flow chart of an automatic sampling–thermodesorption–analysis cycle.

temperature, flow sampling, chromatographic signal; treating that information according to instructions and data it has received previously: management of sampling time, heating time, automatic stop device if the information does not correspond with the data; producing output signals able to be managed by the processor devices: electrovalve activation, trap heating and chromatograph simultaneous release, integrator start.

The controller can also give information on its own behaviour: visualizing the output states; showing the program or active part evolution; visualizing the inner data evolution: counter values, temporizations; ensuring its own control and uttering alarm signals in the case of failure.

To pass from our experimental definition to its programming we prepared a flow chart which specifies: automation characteristics; the function the controller must ensure; the king of information implicated in the working part automation; safety conditions.

The different steps in the flow chart of the working cycle to be automatized are shown in Fig. 3. The analysis cycle of the atmospheric terpenes starts with a "blank" to test the quality of the analytical apparatus. This "blank" contains three steps.

(1) Stabilization. All the dynamic elements: gas flows, chromatographic signal. During this step the controller simply acts as a timer.

(2) Thermodesorption and analysis. Clean trap heating and the absence of a chromatographic signal control. The trap heating was optimized to subject the adsorbed compounds to a rapid thermic-flash to obtain consequently a rapid injection
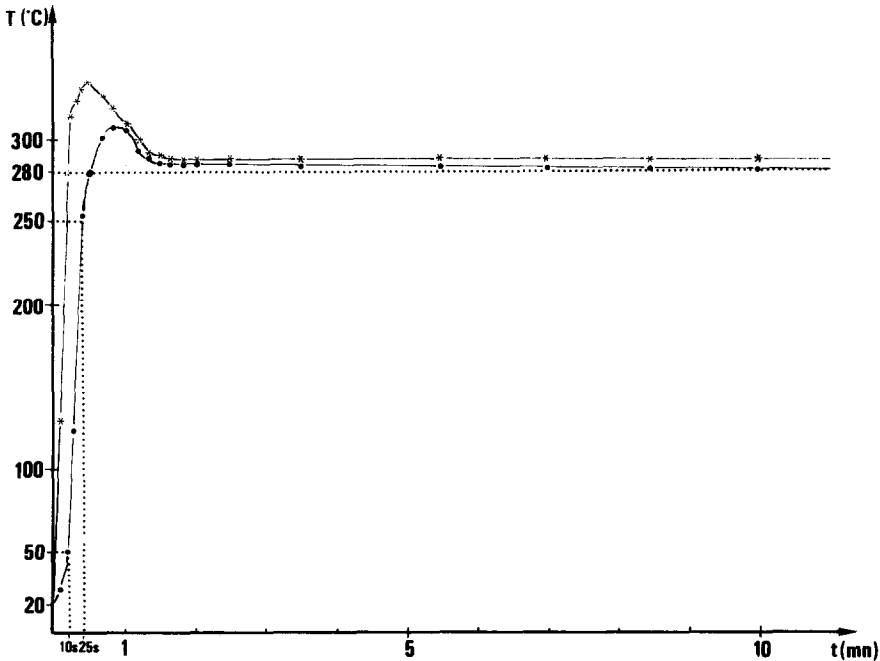

Fig. 4. Trap temperature evolution during thermodesorption. ●—●, Temperature in the adsorbent; *—*, trap external wall temperature.

TABLE I

EXPERIMENTAL CONDITIONS FOR ANALYSIS OF ISOPRENE AND MONOTERPENES

Thermodesorption	Trap temperature	280°C
	Entraining gas	Nitrogen, 10 ml/min
	Desorption time	Time of analysis
Analysis	Column temperature	4 min at 30°C, then programmed at 10°C/min to 90°C during 10 min
	Other temperatures	Injector: 150°C Detector: 300°C
	Carrier gas	Nitrogen, 10 ml/min

in the chromatograph. To avoid damage to the adsorbent (Tenax GC), we were careful to keep its temperature under 310–320°C. Heating was done with an electric element at a maximum initial power (500 W, 80 V) for a few seconds, then under a reduced power (50 W, 25 V). This protocol permits the trap rapidly to attain 280°C and to be maintained at this temperature during the analysis. The passage from one way of heating to another is done automatically by a "home-made" electronic apparatus. Curves of the temperature attained by the trap external wall, and inside the adsorbent, are shown in Fig. 4.

By this step, the controller manages the electrical supply to the heating element, the desorption temperature and their duration. Experimental conditions are given in Table I.

(3) Cooling. By the end of the analysis, the rapid cooling of the trap to ambient temperature is ensured by a compressed air circulation round the trap. At the end of step 3 three ways can be taken: first, if the "blank" test is bad, *i.e.*, the chromatographic baseline has been appreciably perturbed, the test is begun again with three times at most; secondly, if, at the end of the third test the "blank" test is bad again, the whole procedure is stopped and an alarm signal is sounded subject to manual intervention; thirdly, if the "blank" test is good, the analytical cycle is normally done along the steps:

(4) Sampling. Atmospheric air circulation in the trap, in which organic compounds are adsorbed, at ambient temperature. Then, the air is exhausted by the injector "split" circuit.

TABLE II

PROGRAM TO IMPLEMENT AUTOMATED REPETITIVE OPERATION OF A SAMPLING–THERMODESORPTION–ANALYSIS CYCLE

Time (min)	Command	Comments
0	Valves 1, 2, 3 on	Sampling
10	Valves 1, 2, 3 off	Stabilization
15	HE, GC, IT on	Thermodesorption
30	HE, GC, IT off Valve 4 on	Cooling
35	Valve 4 off Valves 1, 2, 3 on	New sampling

(1) Stabilization

(2) Thermodesorption and analysis. The trap is heated, thermodesorbed compounds are carried by carrier gas to the column head and analysed.

(3) Cooling. By the end of this step, the apparatus is ready for another cycle.

Five successive analytical cycles are done, with the same sequence. At the end of the fifth cycle, a new "blank" test is done.

In case of a breakdown of the electric circuit, or a desired end to the procedure, the whole sequence is reset again at step 1.

Table II gives the model program listing the successive cycles of automatic execution. In this example, sampling and analysis last 10 and 15 min respectively.

SYSTEM PERFORMANCE

In a preconcentration process on a solid adsorbent, a general efficiency of the adsorption–desorption of volatile compounds close to 100% is a necessary condition to obtain a quantitative analysis of each compound adsorbed. In this work, we devised an efficiency determination method, called "gaseous deposit" explained in a previous paper[17] and particularly appropriate to very volatile compounds. For isoprene, for example, the general efficiency of adsorption–desorption is 96.5% at 25 $\pm$ 1°C.
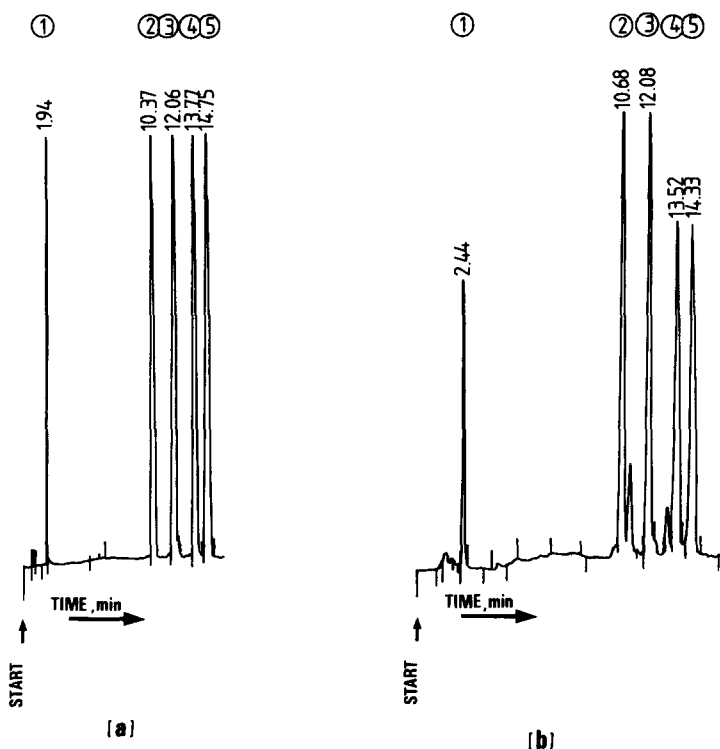

Fig. 5. Chromatograms of mixture of isoprene and monoterpenes: (a) direct injection with a microsyringe; (b) injection after a sampling–thermodesorption–analysis cycle managed by the automatic device. Peaks: 1 = isoprene; 2 = α-pinene; 3 = β-pinene; 4 = Δ_3-carene; 5 = limonene.
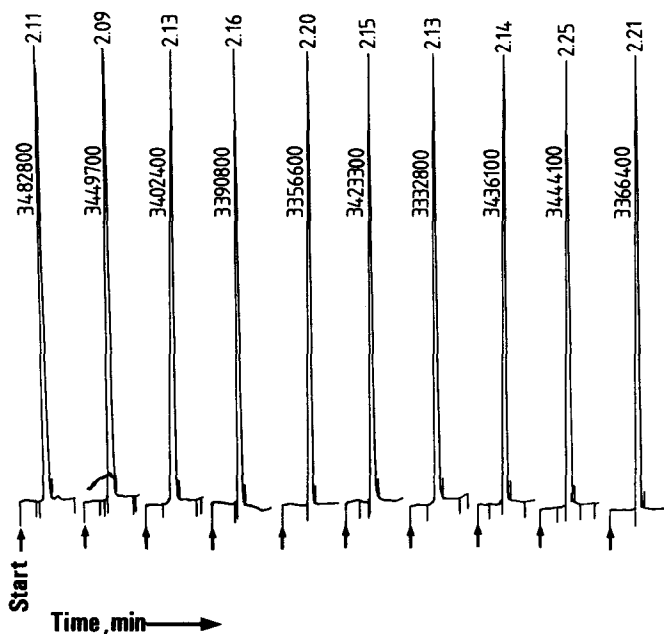
Fig. 6. Repeatability of signals obtained after automatic sampling–thermodesorption–analysis cycles for a mixture of nitrogen gas and traces of isoprene.

The chromatograms shown in Fig. 5 result from the injection of a mixture of isoprene and monoterpenes with a microsyringe (a) and after an automatic preconcentration–thermodesorption–analysis cycle of the same compounds (b). The quantities injected by the two techniques differ. The chromatographic resolution is practically unaffected by the preconcentration–thermodesorption mode. We think this is due to a good injection of the products from the trap. This is a practically instantaneous injection thanks to the rapid thermodesorption resulting from a rapid thermic-flash. The systematic reduction of the dead volumes of the whole trapping and injection circuit leads to a low diffusion of te compounds.

Beside the recovery of the compounds, after adsorption–desorption and the good analytical performance of the apparatus used a most important factor of the automatic apparatus liability is its repeatability over long time periods. This factor is illustrated in Fig. 6 which shows signals obtained from a mixture of nitrogen gas and traces of isoprene, subjected to a complete adsorption–thermodesorption–analysis cycle. We show 10 signals at regular intervals in a series of 60 recording automatically over a 48-h period. The very low coefficient of variation found (0.9%), indicates an excellent repeatability.

In our experimental cycles, the sampling of the compounds on a solid adsorbent and their direct chromatographic analysis after thermodesorption avoids the need for an intermediate cryogenic trapping, while retaining analytical performance. Then, the avoidance of liquid nitrogen makes this device easier to carry out and increases its autonomy.

The apparatus developed permits the measurement of isoprene and monoterpenes present in traces (a few $\mu l/l$) in laboratory prepared atmospheres. Its automatic working over long time periods is confirmed by our results. However, it remains to demonstrate its applicability to natural atmospheres in rural or forest zones, non-polluted or polluted at low levels. Those experiments or studies should be achieved during future international campaigns (DECAFE, BIATEX) in which we will participate. There have been only a few previous realizations[18-22] of devices that can ensure simultaneous sampling–thermodesorption–analysis.

ACKNOWLEDGEMENTS

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