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Trapping system for trace organic volatiles

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ABSTRACT

A technique is described for the collection and concentration of volatile compounds produced by plants, insects, animals and other materials. The method is a modification of the continuous-flow system based on absorption of volatiles in a low amount of solvent at low temperature. The advantages and disadvantages of the technique used are described in detail.

INTRODUCTION

So far several different techniques have been used for the trapping and concentration of volatile substances: (1) cold trapping and cryogenic trapping (*e.g.* ref. 1–3); (2) trapping on a solid sorbent (*e.g.* refs. 4–7); (3) trapping in a liquid stationary phase coated on a solid support [8–13] and (4) chromatography evaporation of a solvent in a capillary tube [11,14,15]. A short survey of preconcentration methods in capillary gas chromatography has been published by Roeraade [16] and an excellent review concerning headspace–gas chromatographic (GC) analysis of medicinal and aromatic plants and flowers has been published recently by Bicchi and Joulain [17]. So far trapping on a solid sorbent is still the most widespread technique, the properties and use of which have been reviewed by Golub and Weatherston [1], Núñez *et al.* [18] and Günther *et al.* [19].

For an analysis by means of GC, gas chromatography–mass spectrometry (GC–MS), gas chromatography–Fourier transform infrared spectroscopy (GC-FT-IR) or gas chromatography–electroantennography (GC-EAG) it is indispensable to release the volatile compounds from the sorbent. Basically, there are two methods of doing this.

(a) The substances may be washed out with a solvent (if a small amount of solvent is used a quantitative washing out may not be achieved, while when larger amounts of solvent used the eluate must be concentrated, which may lead to quantitative changes in the proportion of the most volatile components.

(b) Volatile substances may be desorbed by heating the sorbent for several minutes, which is usually followed by cryofocusing at the beginning of the chromatographic capillary column, where the substances may not be retained quantitatively [20].

For a thermal desorption of the volatiles, microwave radiation has also been used successfully, but this method has limitations with respect to the choice of sorbent [21,22]. In addition to this, decomposition of substances may take place on the large surface of the sorbent. Thus, desorption of volatiles both from solid sorbents and from the liquid stationary phase requires the use of further equipment [23,24].

The device described in this paper is a modification of the continuous-flow system [25,26], in which absorption of volatiles into a solvent at low temperature is used instead of adsorption [27]. The device works off-line, *i.e.* it is independent of the gas chromatograph. The method was tested by trapping and concentration of volatile substances from natural and artificial sources.

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EXPERIMENTAL

The trapping system

For all experiments described in this paper a tempered desorption vessel of a 30-ml internal volume was used. A U-tube containing 50 μl of solvent had an I.D. of 3 mm at its narrower part and 8 mm at the broader part, which is the section for the trapping of the condensed water. The inner surface of all glass parts of the device was silanized [28] with a solution of dimethyldichlorosilane in toluene (20%, v/v, for 20 min). Air or nitrogen was used as the carrier gas. The carrier gas was purified by means of cartridges packed with silica gel, charcoal (both extracted and activated) and a 5-Å molecular sieve (activated) before entering the desorption vessel. The gas flow-rate was checked with a rotameter and measured using a bubble flow meter. For the cooling of the U-tube with the solvent a mixture of ethanol and dry ice (−78°C) was used. A schematic diagram of the whole arrangement is shown in Fig. 1, and a detailed view of the main part of the desorption device and the location of the sample is shown in Fig. 2.

After each experiment condensed water and a trapping solvent were withdrawn (separately) from the U-tube with a Hamilton syringe and divided into several portions and stored in sealed glass tube (1 mm I.D.) in a freezer.

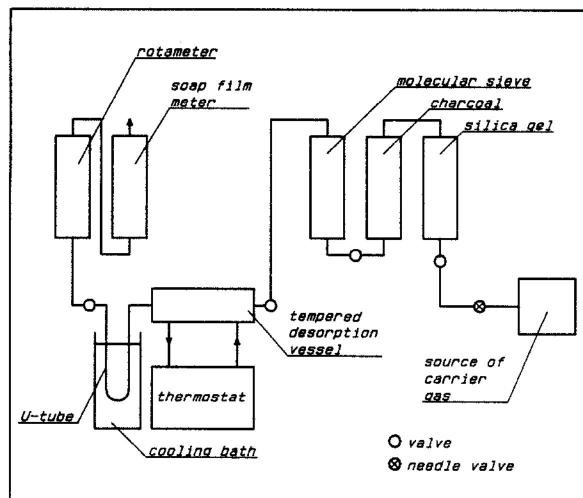

Fig. 1. Schematic diagram of the trapping system.

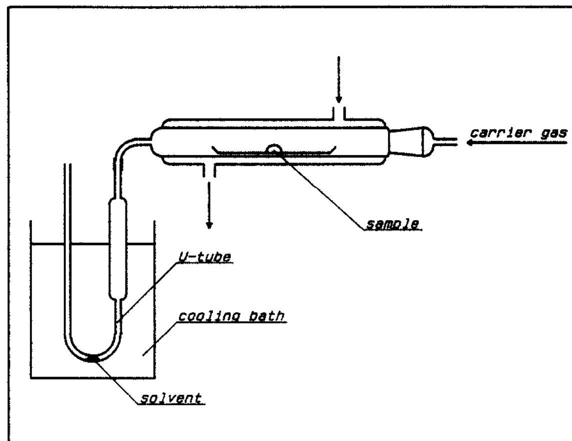

Fig. 2. Detail of the trapping system showing the desorption vessel and U-tube (not to scale).

Testing the device by means of n-alkanes

Fifteen *n*-alkanes (C_8–C_{22}, Applied Science Labs., USA) in equal weight proportions were dissolved in *n*-hexane (10%, w/v) and 5 μl were injected with a Hamilton syringe through a septum directly into the small boat in the desorption vessel. Three equal U-tubes (4 mm I.D.), connected in series, were always used for trapping the volatiles. Each of them contained 150 μl of an absorption solvent. The experiments were carried out: (a) with temperatures in the desorption vessel of 30, 60 and 90°C, (b) at flow-rate of 10, 20 and 30 ml/min and (c) for 1, 2 and 4 h. The retention times (in minutes) of *n*-alkanes (for GC conditions see the Experimental section) were as follows: 14.13 (C_8), 22.30 (C_9), 30.81 (C_{10}), 39.06 (C_{11}), 46.88 (C_{12}), 54.24 (C_{13}), 61.18 (C_{14}), 67.70 (C_{15}), 73.89 (C_{16}) and 79.75 (C_{17}).

Solvents and gases

Prepurified and distilled methanol (99.999%) or *n*-hexane (puriss., p.a., Fluka, Buchs, Switzerland) was used as the absorbing solvent. An air generator (Chrompack) was used as a source of air as carrier gas, while nitrogen was used from a cylinder.

Gas chromatography

An HP 5890A gas chromatograph with flame ionization detector and split–splitless injector was used: injector temperature 200°C; detector temper-

ature, 250°C; oven temperature, 35°C (5 min), then 2°C/min up to 165°C; carrier gas, hydrogen (70 kPa); column flow-rate, 2.0 ml/min; flow velocity, 49.7 cm/s (at 35°C), split ratio, 1:29; injections, always 2 μl; fused-silica capillary column, 30 m × 0.25 mm I.D. with DB-1; film thickness, 1 μm. An HP 3393A integrator was used.

Gas chromatography–mass spectrometry

A combined HP 5890A gas chromatograph and ZAB-EQ mass spectrometer (VG Analytical, UK) using electron-impact ionization at 70 eV was used. The chromatography conditions were the same as for GC experiments.

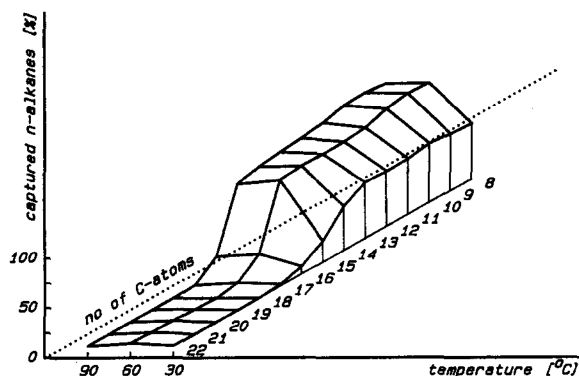

Fig. 3. Distribution of *n*-alkanes trapped at different temperatures in the desorption vessel (time of trapping 2 h, air flow-rate 10 ml/min).

RESULTS AND DISCUSSION

The efficiency of the device was tested with a mixture of fifteen *n*-alkanes (C_8–C_{22}). The influence of temperature of the desorption vessel, flow-rate of the carrier gas and time of desorption was determined. The tests showed that approximately 97% of desorbed alkanes were trapped in the first U-tube, while the rest (3%) were trapped in the second one. The third U tube contained only trace amounts of alkanes in some cases. Fig. 3 represents the influence of desorption temperature on the percentage of substances trapped (the injected amount was equal to 100%, time of desorption 2 h and flow-rate 10 ml/min). The effect of temperature is most distinct up to 60°C; a further increase in temperature no longer causes a substantial increase in desorbed material. The effect of temperature is less distinct at desorption of lower hydrocarbons (up to *n*-C_{13}). The influence of the time of desorption or the flow-rate is much weaker than that of temperature. *n*-Heptadecane was the highest hydrocarbon which could still be trapped under any conditions. The resulting quantity was most probably affected by the way in which a 10% solution of fifteen hydrocarbons was injected into the desorption vessel. The hexane solution (5 μl) occupied only a limited area on the glass surface of the small boat. In contrast to

TABLE I

TRAPPING CONDITIONS

Material	Quantity	Temperature of desorption vessel (°C)	Length of trapping (h)	Carrier gas (ml/min)
Coffee beans (Prague mixture type, roast and ground)	0.9 g	90	2	Air, 15
Bark of spruce (*Picea pungens* Engelm. cv. *Argentea*)	1.6 g	50	3	Air, 15
Black pepper (ground)	1.3 g	40	2	Air, 15
Shield bug [*Graphosoma lineatum* (L.1758)]	30 adults	30	2	Air, 15
Polyvinyl chloride (PVC flooring material)	10.5 g (30 cm^2)	50	5	Air, 15
Beer (Sládek 11° lager type)	18 ml	30[a]	2	Nitrogen, 25

[a] A desorption vessel was used for preheating of carrier gas only, the sample of beer was placed in a stripping tube.

this, volatile substances from natural material are evaporated from a much larger surface.

Since the effect of the trapping in the first U-tube was 97%, we always used a single U-tube in further experiments. For a practical testing of our device we concentrated volatile substances from randomly selected samples. The conditions for their analysis are given in Table I. Since a detailed qualitative analysis of the sample was not the main purpose of this study, we identified, by means of GC–MS, only some main components from several samples.

Practically every natural organic material contains a larger or smaller amount of water. As a rule this water causes difficulties during the capturing of the volatiles (*e.g.* ref. 29 and 30). When the device described is used, allmost all of the water condenses and freezes in the wider part of the U-tube, *i.e.* before it can reach the absorption solvent. We found that attention must also be paid to the analysis of water trapped in this manner. Some authors have warned against the presence of water in a sample analysed by capillary gas chromatography (CGC) because this water may change the properties of the chromatographic column [31] or even change retention times [32–34]. In contrast to this, a number of authors currently use aqueous solutions for analyses by CGC [35–37] as well, and they even determine water quantitatively using a thermal conductivity detector (see ref. 38). Under our chromatographic conditions we observed no differences in the retention of substances from aqueous and non-aqueous samples.

During the analysis of our samples we observed several different cases: in the case of coffee beans (roast and ground) the aqueous solution contained approximately six times more volatile substances (by weight) and approximately twice as many compounds as the methanolic solution (Fig. 4). The analysis of volatile substances from the bark of the spruce *Picea pungens* Engelm. cv. *Argentea* represented the other extreme. Volatile substances were captured only in methanol (Fig. 5). In the case of black pepper (ground) only some compounds out of the wide spectrum of volatile substances were present in water (Fig. 6). However, in many cases the water contained approximately the same spectrum of substances as methanol, but in lower concentrations.

Our equipment may also be used for concentration of volatile substances produced by insects and

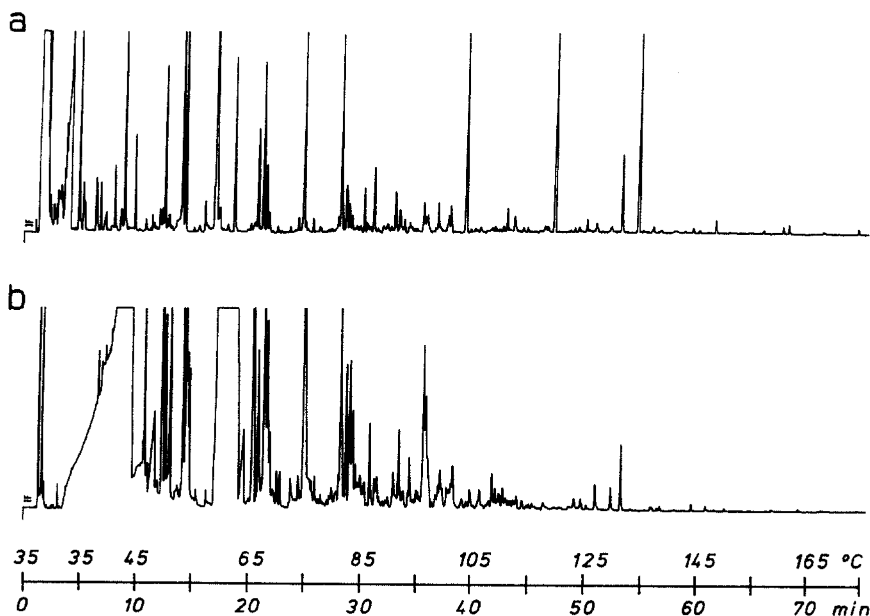

Fig. 4. Gas chromatogram of volatiles from coffee beans (Prague mixture type, roast and ground); (a) methanolic solution, (b) condensed water (for conditions see Experimental section).

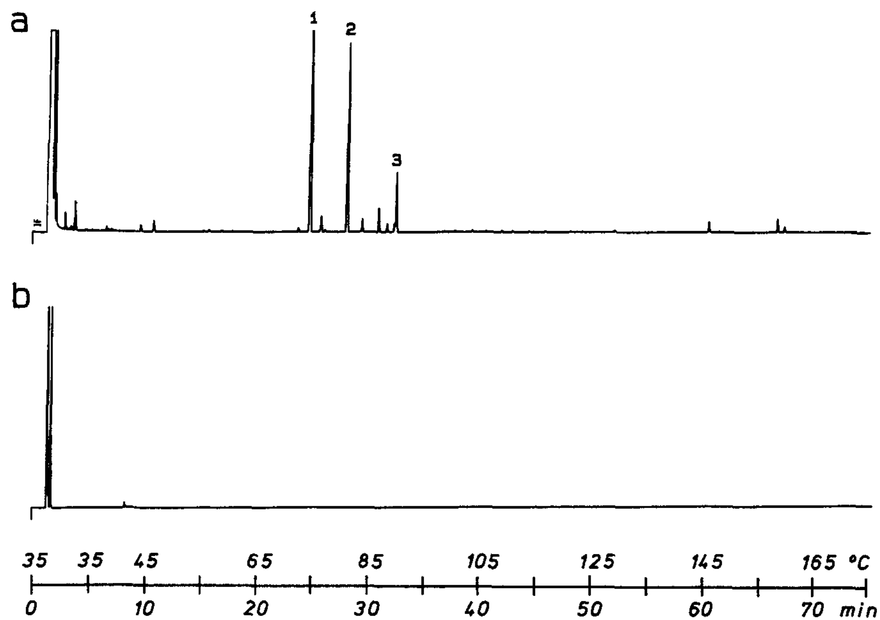

Fig. 5. Gas chromatogram of volatiles from the bark of spruce *Picea pungens* Engelm. cv. *Argentea*: (a) methanolic solution, (b) condensed water. Peaks: 1 = α-pinene; 2 = β-pinene; 3 = limonene.

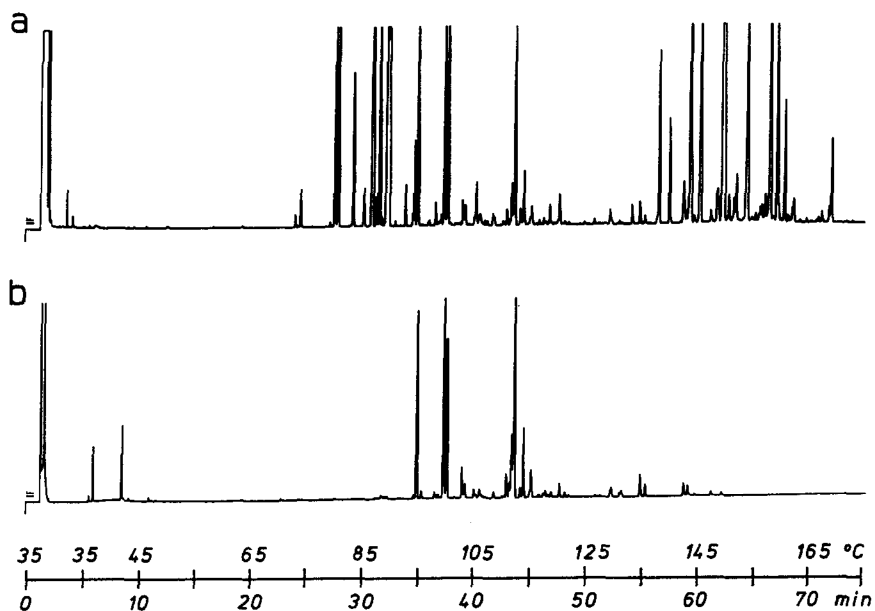

Fig. 6. Gas chromatogram of volatiles from black pepper (ground): (a) methanolic solution, (b) condensed water.

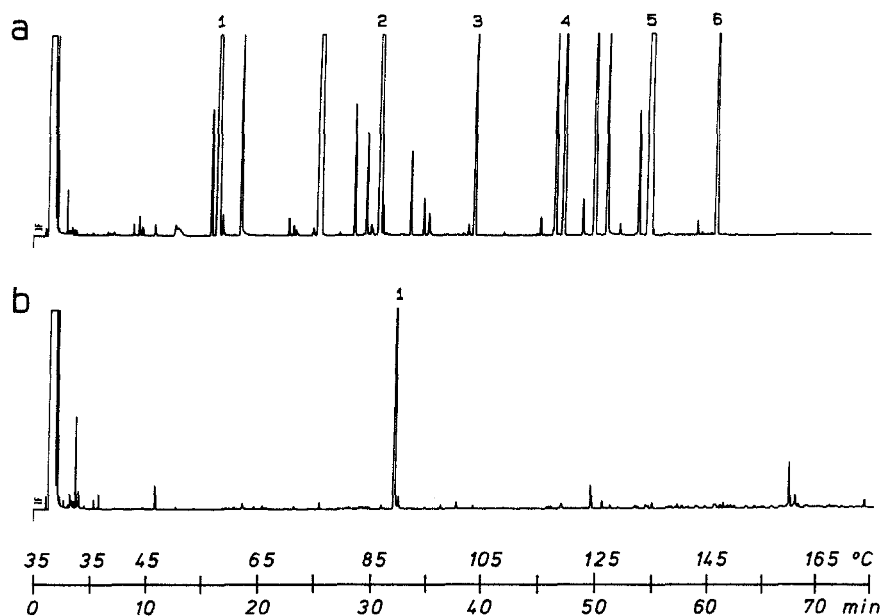

Fig. 7. Gas chromatogram of volatiles. (a) Chromatogram produced by the shield bug *Graphosoma lineatum* (L. 1758); methanolic solution. Peaks: 1 = 2-hexenal; 2 = 2-hexen-1-ol acetate; 3 = n-$C_{11}H_{24}$; 4 = n-$C_{12}H_{26}$; 5 = n-$C_{13}H_{28}$; 6 = 2-decen-1-ol acetate. (b) Chromatogram from PVC flooring; methanolic solution. Peak: 1 = 2-ethyl-1-hexanol.

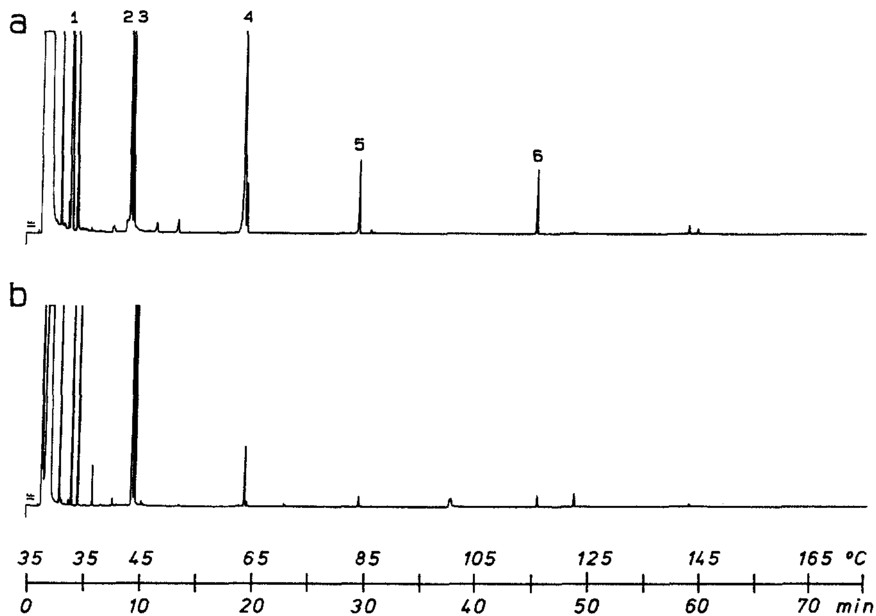

Fig. 8. Gas chromatogram of volatiles from beer (Sládek 11°, lager type): (a) methanolic solution, (b) condensed water. Peaks: 1 = 2-methyl-1-propanol; 2 = 3-methyl-1-butanol; 3 = 2-methyl-1-butanol; 4 = 3-methyl-1-butanol acetate; 5 = ethyl hexanoate; 6 = ethyl octanoate.

animals. As an example we present the analysis of compounds produced by the shield bug *Graphosoma lineatum* (L. 1758) (Fig. 7a).

An example of the concentration of compounds evaporated from floor covering on the basis of polyvinyl chloride (PVC) is shown in Fig. 7b.

The device described was also used for trapping of substances absorbed in liquids (stripping). A test tube containing the liquid was attached to the tempered vessel used to temper the carrier gas, and this was blown through a tube provided with a frit. As expected, a considerable amount of water was also trapped in the U-tube. The water contained practically the same compounds as methanol (Fig. 8).

In view of the fact that the trapping and the concentration of volatile substances was carried out using amounts in the microgram range, we considered it necessary to silanize the inner surface of the glass parts of the device and so minimize the losses caused by adsorption on the surface.

The disadvantages and advantages of the device described above are given in Table II.

TABLE II

DISADVANTAGES AND ADVANTAGES OF THE DEVICE

Disadvantages
1. The device is not suitable for ultramicroanalysis.
2. The selection of solvents is limited (methanol, ethanol, carbon disulfide, *n*-pentane, *n*-hexane, 2,2,4-trimethylpentane); m.p. must be lower than −80°C. Methanol proved to be best because (a) it is obtainable in a very pure state (up to 99.999%); (b) it gives a narrow signal at the beginning of the chromatogram; (c) it miscible with water; and (d) it is stable.

Advantages
1. A concentrated solution of volatiles is obtainable in one operation without any losses.
2. There is no need for desorption equipment and/or to carry out cryofocusing.
3. The amount of sample from one experiment is sufficient for several GC analyses, GC–MS, GC–FT-IR, GC–EAG and biological testing.
4. It is possible to obtain accurate retention times for identification by means of retention indices [39–41] due to split injection technique.
5. Easy quantification of experiments.
6. The device is very versatile in terms of (a) the size of the U-tube; (b) the size and shape of the desorption vessel (from 5 ml to 20 l, special shape for living objects); (c) different desorption temperatures (20–90°C), carrier gas flow-rate (for a U-tube of 3 mm I.D. about 15 ml/min) and length of time of collection; (d) different carrier gases (nitrogen, helium, argon, air) can be used; (e) it is useful for concentration of volatiles from liquid samples (stripping).

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