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HEADSPACE GAS ANALYSIS

QUANTITATIVE TRAPPING AND THERMAL DESORPTION OF VOLATILES USING FUSED-SILICA OPEN TUBULAR CAPILLARY TRAPS

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SUMMARY

A system has been devised with which volatiles can be effectively trapped from headspace gas samples at relatively high flow-rates. Material is trapped in fused-silica capillary traps, 1 m in length, and coated with either an immobilized SE-30 layer, or a suitable adsorbent such as activated carbon or a powdered porous organic polymer supported on immobilized SE-30. These fused-silica traps are installed and used in stainless-steel tubes (desorption tubes) through which an electrical current is passed to effect on-line thermal desorption of the trapped volatiles. Thermal conversion of labile compounds such as α-pinene and γ-terpinene can be avoided by temperature-programmed or -controlled desorption in conjunction with cold trapping of the desorbed volatiles on the capillary column. The capacity of different traps was compared for a number of compound types and their versatility demonstrated by carrying out headspace gas determinations on, for instance, wine, urine and an imitation fruit drink.

INTRODUCTION

The compounds employed by insects and mammals in semiochemical communication are normally isolated and identified by extraction of the secretion-producing glands with a suitable solvent and subjecting the extract to the conventional methods of separation, bioassay and identification of the biologically active constituents. If the interest in the active material is merely of a qualitative nature, the rate at which it is released into the surrounding atmosphere, may be considered to be of lesser importance. In recent years, however, it has transpired that semiochemical communication is largely an extremely complex process[1] and that several compounds often have to be present in a specific quantitative ratio to elicit the expected response in the insect or animal[2]. Since semiochemicals are mostly released into the atmosphere in minute quantities, the qualitative and quantitative determination of these air-borne volatiles is essentially a headspace-analytical problem and the techniques developed for the gas chromatographic determination of the headspace volatiles of

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food, beverages, plastics, etc., could therefore, with certain limitations, also be applied to semiochemical research.

The techniques employed in headspace gas analysis have recently been reviewed by Núñez *et al.*[3], and several books and monographs have appeared on this subject[4,5]. However, as Grob and Habich[6] have pointed out, these techniques have been developed for packed column gas chromatography and, when applied to capillary analysis, have given unsatisfactory results, the most serious problem being incomplete transfer of the sample from the trap onto the capillary column. This is due to the difference in the flow-rate required for complete and rapid desorption from, for example, a packed 3-mm I.D. concentration trap and the flow-rate through a capillary column. Grob and Habich[6] approached this problem by using capillary traps with approximately the same diameter as the capillary column, whereby the linear flow-rate through the trap is increased to facilitate rapid sample desorption. Two trap types, a charcoal-coated open tubular trap (COT) and a trap coated with a thick layer of immobilized PS-255 (FT), were used with excellent results.

In our work on the exocrine secretions of the male African sugarcane borer *Eldana saccharina,* extracts of the wing gland and abdominal hair pencil secretions of this moth were found to contain more than 30 compounds ranging from 4-hydroxy-4-methyl-2-pentanone to several unidentified C_{22} compounds[7]. However, *trans*-3,7-dimethyl-6-octen-4-olide (eldanolide), one of the major constituents of the male wing gland secretion, was the only compound eluted from the active charcoal filter when the volatiles were trapped under closed-loop stripping conditions, from air flowing over calling males[8]. The trapped material did not contain any of the other prominent constituents of the exocrine secretions of the male, such as vanillin, which is produced in such quantities that it can be detected by the human nose at a considerable distance from sugarcane plantations infested with this insect. Obviously, the γ-lactone, eldanolide, was adsorbed preferentially on the active charcoal with the exclusion of all the other air-borne volatiles. Although this problem can be eliminated by using several activated carbon filters in series, the coated open tubular traps developed by Grob and Habich[6] presented an alternative approach to the trapping of the semiochemicals emitted by insects.

Any method employed for this purpose must meet requirements imposed by the fact that the volatiles to be determined originate not simply from a large volume of liquid serving as a replenishing reservoir, but from a living organism which, depending on circumstances, will produce varying amounts of material and which will, furthermore, only produce these compounds if natural conditions can be imitated sufficiently accurately to induce calling behaviour in the insect. One possibility is to trap all the volatiles from a brisk stream of air flowing over the calling insect, thus restricting adsorption of the semiochemicals on glass surfaces or on the insect itself. Although some of the compounds secreted by *E. saccharina* were trapped quantitatively on short FTs, almost immediate break-through of vanillin was observed, already at a relatively low flow-rate of 30 ml/min. This flow-rate appears to be too high for this particular compound and the break-through of vanillin is therefore most likely due to its slow dissolution in SE-30 and not to saturation of the trap with this compound.

The composition of this secretion illustrates a situation that is often encountered in semiochemical work where compounds such as acetaldehyde and hexyl hexa-

noate[9] or formic acid and pentacosyl formate[10], *i.e.* compounds with widely different volatilities and polarities may be present in the same secretion and have to be determined in widely different concentrations. Rather than reverting to packed-trap concentration techniques for this type of problem, the feasibility of using longer capillary traps for the trapping of volatiles at reasonably high flow-rates, was investigated. A system which would meet the following requirements, was devised: (1) off-line trapping with on-line desorption of volatiles onto the analytical capillary column, (2) temperature-programmed or at least temperature-controlled thermal desorption of the trapped material, (3) traps in which, depending on prevailing circumstances, the properties and advantages of film- and charcoal-coated open tubular traps can be utilized, and (4) traps which would, as far as possible, give quantitative retention of volatiles at reasonably high flow-rates.

In this paper the preparation of fused-silica traps, 1 m in length and coated with SE-30 or with SE-30 plus an adsorbent, the thermal desorption of volatiles trapped on the capillary traps and experiments carried out to establish the capacity of these traps for a number of reference compounds are described. In addition, several headspace determinations were carried out to demonstrate the applicability of this system to the headspace gas analysis of biological samples, beverages, etc.

EXPERIMENTAL

Gas chromatographic analyses were carried out with a Carlo Erba Fractovap 4160 gas chromatograph (Carlo Erba, Milan, Italy) equipped with a flame ionization detector, using helium as carrier gas. Fused-silica capillary columns (40 m × 0.32 mm I.D. and 28 m × 0.32 mm I.D.) coated with SE-30 (film thickness 0.84 μm) were used for analytical separations. Gas samples were made up with nitrogen which was purified through a column (200 mm × 30 mm) of activated charcoal. Gas samples were injected onto the traps at specific flow-rates using gas-tight syringes (10 ml or 50 ml) installed in an infusion pump (Sage Instruments, White Plains, NY, U.S.A.).

Preparation of fused-silica capillary traps

Film open tubular traps (FOTTs). Lengths of deactivated[11] fused-silica capillary tubing (*ca.* 1.12 m × 0.32 mm I.D.) were statically coated with SE-30. The stationary phase was thoroughly removed from both end sections of the capillary with *n*-pentane, leaving the coating in the central 1-m section of the capillary intact, whereafter it was immobilized by subjecting the traps to γ-radiation (7.5 MRad) from a ^{60}Co source[12]. The traps were not rinsed with a solvent, but were conditioned at 230°C with a carrier gas flow of 20 ml/min before use. Traps with film thicknesses of 3 μm (FOTT-3) and 12 μm (FOTT-12) were prepared.

Film–activated carbon open tubular traps (FACOTTs). Film traps were coated with SE-30 (3 μm) and the stationary phase removed from the end sections as described above, whereafter the stationary phase in the central section of the traps was coated with a uniform layer of activated carbon by sucking the adsorbent into the traps. The particle size of the charcoal was determined by electron microscopy. Particles of carbon remaining in the end sections of the traps were carefully removed with dichloromethane. The stationary phase layer with imbedded activated carbon was immobilized by γ-radiation as before. Two trap types, FACOTT-10 and

FACOTT-80, were prepared using 1–10 μm and 10–80 μm activated carbon respectively.

Film–organic polymer open tubular traps (FOPOTTs). Traps with particles of Porapak Q imbedded in a layer of SE-30 were prepared using pulverized Porapak Q (1–10 μm) instead of activated carbon. The supporting SE-30 film was also immobilized by γ-radiation (7.5 MRad).

Combination film and film–activated carbon open tubular trap (FOTT/FACOTT). Using the methods described above, a trap was prepared in which one half of the middle 1-m section of a 1.12-m fused silica tube was coated with activated carbon (1–10 μm) supported on SE-30 (3 μm), and the other half with SE-30 (12 μm). This was accomplished by first coating *ca.* 500 mm of the tube with SE-30 and activated carbon, removing all activated carbon particles from the rest of the tube, and then coating the second 500-mm length of the tube with SE-30 from its other end. A short section remained uncoated between the coated sections of this FOTT-12/FACOTT-10 combination trap.

Thermal desorption tube

A stainless-steel tube (1 m × 1.0 mm O.D. × 0.65 mm I.D., 1.2 Ω/m) was silver soldered to a Carlo Erba ferrule-supporting conical washer as shown in Fig. 1. The stainless-steel tube was electrically insulated with PTFE tubing (1.5 mm I.D.). Using crocodile clips and contacts soldered to the desorption tube, the two ends of this tube were connected to the output terminals of a 12-V, 20-A transformer (Osborne Electric Co.) which was in turn plugged into a 2.5-kVA powerstat voltage regulator (Superior Electric Co., Bristol, CT, U.S.A.) as shown in Fig. 1. This arrangement allowed manual control of the temperature of the desorption tube by regulating the current flowing through the tube. For safety it is imperative that a secondary step-down transformer be used in series with the voltage regulator as no more than 10 V should ever be delivered to the desorption tube or its exposed tips. To calibrate this desorption device, a number of slits were made lengthwise in the PTFE insulating sheath, through which crystals of various organic compounds such as, for example, benzoic acid and *p*-nitrobenzoic acid, could be inserted and brought into contact with the desorption tube. By using the melting points of these compounds a calibration curve of the temperature of the desorption tube *vs.* the voltage regulator setting was obtained. Although this calibration procedure was complicated, to some extent, by the sublimation of the crystals near their melting points, sufficiently accurate results for the purpose for which the desorption tube was to be used, were obtained.

Several identical desorption tubes were manufactured. Fused-silica capillary traps were inserted into these desorption tubes as required for various headspace gas determinations.

Manipulation

A series of experiments were carried out to determine the capacity of the different traps for various compounds and compound types.

Break-through curves were recorded for a number of reference compounds by connecting one end of a trap to the needle of one of the gas-tight syringes, using a butt connector, and the other end to the flame ionization detector of the gas chro-

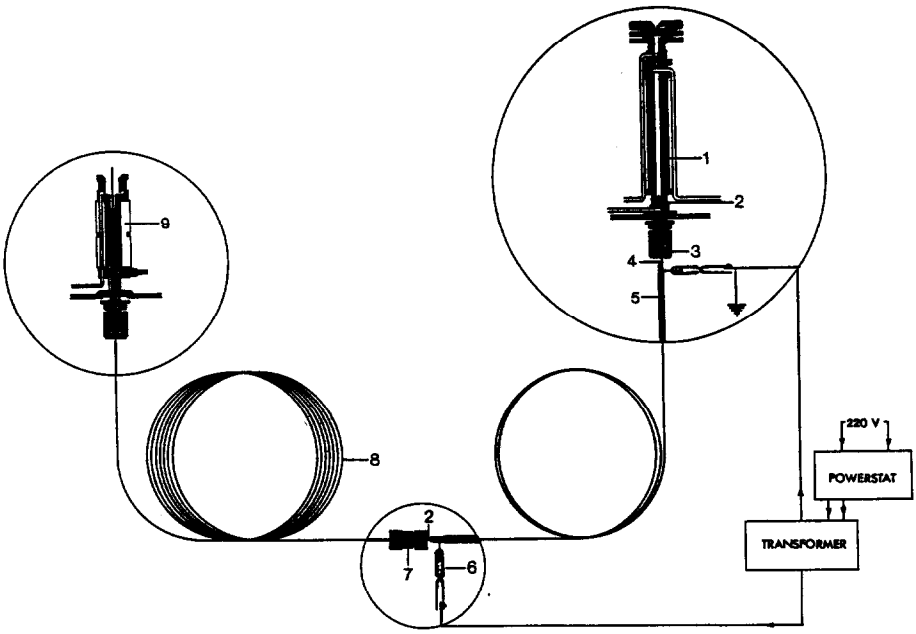

Fig. 1. Installation of a fused-silica open tubular trap in a Carlo Erba gas chromatograph: 1 = injector, 2 = fused-silica trap, 3 = ferrule-supporting conical washer, 4 = stainless-steel desorption tube soldered to conical washer, 5 = PTFE insulating sheath, 6 = crocodile clip attached to contact which is silver-soldered to the desorption tube, 7 = butt connector, 8 = analytical glass or fused-silica column, 9 = detector.

matograph. Gas samples were prepared by adding 1-μl quantities of methanol, chloroform, toluene, *n*-pentane and *n*-octane, respectively, to 5 l of purified nitrogen in 5-l flasks. A gas sample containing propane was similarly prepared by adding 1 ml of propane gas to 5 l of nitrogen. The gas mixtures were pushed through the traps at a steady pre-selected flow-rate using a syringe-type of infusion pump. The detector response was recorded *vs.* the volume of gas passing through the trap. Due to the compressibility of gases, the volume of the gas flowing through a trap lags behind the volume displaced by the plunger of the infusion pump syringe, resulting in a discrepancy which increases with increasing flow-rates. The flow-rate through a trap was, therefore, calibrated at different infusion pump settings by using a bubble flow meter connected to the outlet end of the trap.

The results obtained from these break-through curve determinations were verified for a number of reference compounds on different traps by determination of the percentage break-through at different sample sizes by employing two traps in series.

Applications

Headspace gas analyses using a FOTT-12, FACOTT-10 and FOPOTT-10 were carried out on a gas sample containing limonene, γ-terpinene and α-pinene (1 μl each on some glass wool in 100 ml of nitrogen) to determine the influence of thermal desorption parameters on thermally labile compounds. For comparison, a sample

containing these three terpenes, dissolved in dichloromethane, was injected onto the same capillary column, using split injection. The versatility of the fused-silica open tubular traps was further demonstrated by carrying out headspace gas analyses on citrus peel, a commercial cool drink, wine and a canine urine sample. For these determinations headspace gas samples were transferred from a 100-ml screw-capped bottle onto the traps with either helium from the detector of the gas chromatograph or with purified nitrogen. Sampling was carried out at room temperature (25°C) and sample sizes were measured at the outlet end of the traps using a bubble flow meter. For these determinations all glass-ware and the PTFE-lined gaskets used in the screw-capped bottles, were heated before use in a well ventilated oven at 100°C for 12 h.

RESULTS AND DISCUSSION

Since it is impossible to produce a fused-silica trap coated with activated carbon by the method described by Grob and Habich[6], attempts were made at producing a uniform layer of activated carbon on an inert material such as polyimide resin (Alltech, Deerfield, IL, U.S.A.). Fused-silica capillaries were dynamically coated with the resin, whereafter pulverized activated carbon was sucked into the coated capillaries and the resin cured at elevated temperatures. Although this procedure was found to be feasible for short traps, the carbon particles moving through the capillary, gradually removed the resin from the capillary wall. The front sections of longer traps were thus left uncoated, while the carbon in the rest of the traps was partially covered in resin. The resulting traps were expected to have low capacities and this approach was abandoned. Far superior results were obtained with a gum phase such as SE-30 as supporting layer. Such FACOTTs have the added advantage that they will retain headspace volatiles by dissolution as well as adsorption, thus extending the capacity and efficiency of the traps.

Initially the activated carbon was applied by forcing air-borne particles of the material from a small glass bottle into the capillary with a brisk stream of nitrogen, but as the capillary soon became clogged, the flow had to be regularly reversed to remove the excess of carbon from its front end. Better results were obtained by sucking the activated carbon into the capillary. Since a stationary phase film is expected to support an essentially mono-particulate layer of the adsorbent on the film, the capacity of the trap will depend on the particle size of the adsorbent, larger particles producing layers with a higher capacity. On the other hand, larger particle sizes would result in incomplete and slower desorption, with accompanying unacceptable catalytic effects. This aspect was not investigated in detail, but activated carbon with particle sizes below 1 μm was found to produce traps with such a thin layer of carbon that they remained almost transparent, whereas material with a particle size of 1–10 μm gave a satisfactory uniformly black layer of carbon. When these traps were coupled to the detector of the gas chromatograph for the recording of break-through curves, particles of carbon were transported into the detector resulting in an almost constant production of spikes. The carbon particles, therefore, appeared to adhere rather loosely to the stationary phase. The activated carbon layer could, however, be stabilized and the production of spikes totally eliminated by subjecting the traps to γ-radiation.

The capacity of a trap for a certain compound or headspace sample is usually

determined by using a second trap in series with the first one to trap any material not retained by the first trap. From the relative peak sizes obtained by gas chromatographic analysis of the material desorbed from the two traps, the percentage break-through can then be calculated. The determination of the efficiency with which material is retained on a trap at different sample sizes, usually requires a series of determinations, the results of which can be used to plot a break-through curve of amount of break-through *vs.* sample volume. Similar information can, however, also be obtained by using the flame ionization detector of the gas chromatograph instead of a second trap to detect break-through. Although this method does not give the percentage break-through at a specific sample volume, it can be employed to determine the volume range over which the trap may be safely used with total sample retention. Examples of such break-through curves are given in Fig. 2A–D. In these figures increasing detector response indicates break-through which increases until a situation is reached where the activated carbon is saturated or where the material, transported through the film-coated tube by normal chromatographic processes, reaches the outlet end, whereafter the trap merely acts as a tube conducting the gas sample to the flame ionization detector. The observed fluctuation of the detector response as this stage of the determination is approached, is due to the irregular movement of the syringe plunger.

In using this method a few precautions have to be taken into consideration. Serious errors may result from the fact that, due to the compressibility of the gas sample, the volume of sample actually flowing through the trap will lag behind the volume displaced by the infusion pump syringe plunger. The resulting discrepancy will increase with increasing flow-rates. Thus, before carrying out a break-through curve determination, a calibration curve has to be set up by plotting the volume flowing through the trap, as measured with a bubble flow meter connected to its outlet end, *vs.* the volume indicated on the infusion pump syringe at the flow-rate to be used in the break-through curve determinations. Corrected volumes are used in the presentation of the results in Fig. 2 A–D and in Table I.

The presence of volatile impurities in the sample under investigation or in the

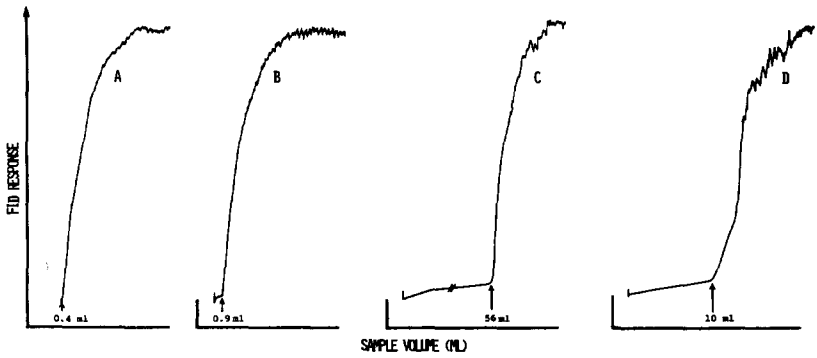

Fig. 2. Break-through curves for 0.2 ppm *n*-pentane in nitrogen determined at 24°C by using the flame ionization detector (attenuation, × 32) to detect break-through. (A) FOTT-3, flow-rate 1 ml/min; (B) FOTT-12, flow-rate 1 ml/min; (C) FACOTT-10, flow-rate 10 ml/min; (D) FOPOTT-10, flow-rate 5 ml/min.

gas which is used in the preparation of gas samples may also result in confusing results as the response of the detector to such volatile impurities may be interpreted as sample break-through. It is therefore essential that the gas used in the determination of break-through curves be purified, for example by passing it through an activated carbon filter. To guard against misinterpretation of results, it is furthermore advisable to desorb and identify the material which had accumulated on the trap when break-through is observed by, for example, retention time comparison. Removal of gas samples from the 5-l flasks in which the gas mixtures were made up, results in the dilution of the material in these flasks. More reliable information would therefore have been obtained by using gas sampling bags. Glass-ware was nevertheless preferred, since contaminants originally present in some bags and the high price of other types precluded their use in this investigation. To keep the dilution of the material in the flasks within limits, a freshly prepared mixture was used when more than 200 ml of the mixture had been removed from such a container.

Examples of break-through curves obtained for *n*-pentane on the FOTT-3, FOTT-12, FACOTT-10 and FOPOTT-10 at a flow-rate of 10 ml/min are given in Fig. 2 A–D. Whereas almost immediate break-through was observed on the FOTT-3, and the FOTT-12 has an only slightly higher capacity for *n*-pentane, the FOPOTT-10 and especially the FACOTT-10 have high capacities for this compound.

Parameters such as film thickness, activity and particle size of the activated carbon, exact length of the coated section of a trap and the temperature at which material is collected on the trap, will influence the capacity of a trap. Break-through curves should therefore only be used to obtain information as to the sample volume range over which the trap may be used without the risk of break-through occuring. This information should be checked regularly. Since information obtained from the break-through curves of gas samples containing single reference compounds are not applicable to the headspace determination of complex samples, it is essential to carry out break-through curve determinations at least for every type of sample under investigation. The break-through curves of simple reference gas mixtures may nevertheless be used to obtain information on the long-term behaviour of a trap or to compare the capacity of different traps and trap types, and is preferred to the time consuming determination of break-through with two traps used in series. In the present investigation the results obtained by break-through curve determinations were nevertheless verified for some traps and gas samples by carrying out percentage-break-through determinations at sample volumes at which, according to the break-through curves, break-through is expected to set in. The results of these determinations are included in Table I.

Whereas reasonably consistent results were obtained when determinations were repeated with FOTTs having the same film thickness, results varied with the FACOTTs, since it is obviously impossible to apply the activated carbon in an absolutely reproducible manner. With *n*-pentane, for example, break-through volumes varying from 40 to 500 ml were obtained with different FACOTT-10s. The increased particle size of the activated carbon used in the FACOTT-80 increased the capacity of this type of trap for *n*-pentane to almost 1.5 l. A break-through volume for propane of 46 ml indicates that this trap should also trap other volatiles quite effectively. On the other hand, however, it may retain thermally labile compounds so effectively that it may not be suitable for general purpose applications. This aspect was not pursued any further in the present investigation.

TABLE I

BREAK-THROUGH VOLUMES OBTAINED WITH DIFFERENT FUSED-SILICA OPEN-TUBULAR TRAPS

Gas samples were prepared by adding 1 μl of the respective compounds to 5 l of purified N_2 in a 5-l flask. The propane sample was prepared similarly by adding 1 ml of propane gas to 5 l of N_2.

Compound	*Trap*	*Flow-rate (ml/min)*	*Break-through volume (ml)*	*Percentage break-through at volume specified (ml)*
Propane	FOTT-12	1	0.2	2.7 (0.2)
	FOPOTT-10	1	0.8	4 (1.0)
	FACOTT-80	10	46	0.1 (47)
n-Pentane	FOTT-3	1	0.4	–
	FOTT-12	1	0.9	12 (1.1)
	FOPOTT-10	5	10	–
		25	10	4 (10)
	FACOTT-10	10	56	–
		100	55	–
	FACOTT-80	10	1480	1 (1510)
n-Octane	FOTT-3	10	7.5	2 (8.5)
	FOTT-12	10	26	–
		25	29	–
		100	28	–
	FOPOTT-10	20	340	–
	FACOTT-10	10	500	0.3 (550)
Toluene	FOTT-12	1	13	6 (13.8)
	FOPOTT-10	10	133	1 (138)
	FACOTT-80	10	> 1000	–
Chloroform	FOTT-12	1	3.5	2 (3.7)
	FOPOTT-10	10	40	4 (41)
	FACOTT-80	10	> 1000	–
Methanol	FOTT-12	1	0.4	5 (0.8)
	FOPOTT-10	1	4.0	1.3 (4.6)
	FACOTT-10	10	32	–
	FACOTT-80	10	233	0.1 (238)

As far as the FACOTTs are concerned, the following observations emerge from a consideration of the data in Table I. The same general trend found in Fig. 2 A–C, *viz.* that the FOTTs have relatively low capacities and that the FACOTT-10 has a much higher capacity, was also observed for other volatile compounds such as propane, methanol, chloroform, and toluene. As expected, chloroform was trapped more efficiently on non-polar FOTTs than methanol, which gave almost immediate break-through on both FOTTs. The high break-through volume of methanol on the FACOTT is therefore almost exclusively due to the contribution of the activated carbon layer. Methanol should be a useful reference compound for the determination

of the adsorptive capacity of a trap or for the comparison of traps containing different types or grades of adsorbent.

At extremely high flow-rates, traps could be expected to exhibit, to a certain extent at least, lower break-through volumes. This was, however, not found to be the case at the flow-rates between 1 and 100 ml/min which had been used in the present investigation. Since the infusion pump motor was not powerful enough to maintain constant plunger motion at high flow-rates, most of the break-through-curve determinations were carried out at a flow-rate of 10 ml/min. Some of the results obtained from successful determinations at higher flow-rates are nevertheless included in Table I.

A strong argument against using activated carbon in headspace traps is the production of artifacts from labile compounds when trapped material is thermally desorbed. However, the high capacity of the FACOTT made this type of trap so attractive for the quantitative headspace gas determination of the complex type of samples often encountered in biological work, that it was decided to investigate possible methods by which material could be desorbed without accompanying thermolysis or rearrangement of thermally labile compounds. Temperature programming of the trap by manually increasing the current flowing through the desorption tube and increasing the flow of the carrier gas through the trap during this step were possible techniques to achieve this goal.

Previous experience in our laboratory has shown that high injector temperatures tended to induce the production of artifacts from γ-terpinene and α-pinene and it was therefore decided to use a gas mixture containing these two terpenes as well as the thermally more stable limonene as test compounds. The results obtained by thermal desorption of these compounds are given in Fig. 3. Desorption of the terpenes from the FOTT-12 and FOPOTT-10 at 150°C for 3 min, the capillary column being kept at 25°C for the same period before starting the temperature programme, did not result in any appreciable production of artifacts. In the resulting gas chromatograms shown in Fig. 3B and C, respectively, the terpenes produced peaks almost as sharp as those obtained by a conventional analysis of a solution of the terpenes in dichloromethane (Fig. 3A). Considerable artifact formation was observed with the FACOTT-10, even when the desorption tube was temperature programmed from 70 to 150°C at 11°C/min (Fig. 3D). Increasing the carrier gas flow during the desorption step from a normal 1.7 ml/min to 3.4 ml/min and programming the trap from 70 to 130°C at 8.5°C/min suppressed, but did not totally eliminate artifact formation (Fig. 3E). However, as is illustrated in Fig. 3F, thermal conversion of the terpene mixture was almost totally eliminated by using a carrier gas flow-rate of 3.4 ml/min and temperature programming the trap from 80 to 120°C at 5°C/min.

The possibility of eliminating the conversion of thermally labile compounds by careful selection of desorption parameters adapted to the compound or sample under investigation, increases the attractiveness of the FACOTT type of trap for work with headspace samples of unknown composition which could possibly contain highly volatile components. The advantages offered by the FACOTT are illustrated by headspace analyses carried out on an imitation fruit drink and fresh citrus peel. In these and all further headspace gas determinations temperature-programmed desorption of the trapped volatiles was employed.

The results of headspace determinations, carried out with the FOTT-12 and

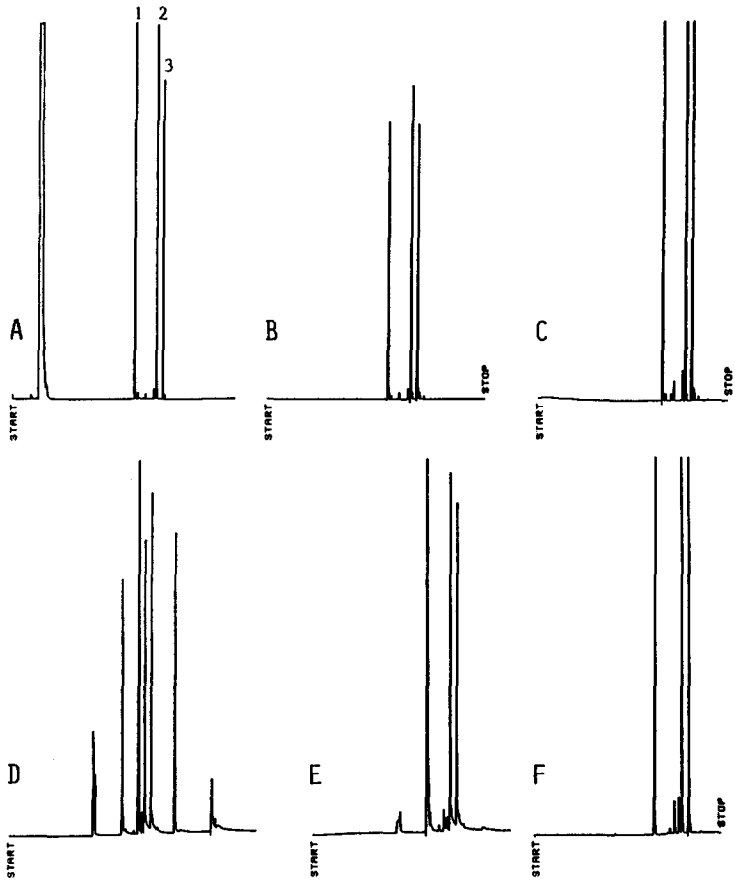

Fig. 3. Analysis of the headspace gas of thermally labile terpenes. Column, 40 m × 0.32 mm I.D. fused silica, 0.84 μm SE-30; temperature programme, from 25 to 180°C at 5°C/min; carrier gas, helium at 28.6 cm/s. (A) Split injection of the mixture of terpenes dissolved in dichloromethane. Injector, 80°C; detector, 220°C. Peaks: 1 = α-pinene, 2 = limonene, 3 = γ-terpinene. Headspace analyses were carried out by trapping 1 ml of a headspace gas sample containing these three terpenes on different traps to determine which desorption parameters would allow desorption without thermal conversion of the compounds. (B) FOTT-12, desorption temperature, 150°C (3 min); flow-rate through trap during desorption step, 1.7 ml/min; on-line desorption and analysis using a butt connector. (C) FOPOTT-10, desorption temperature, 150°C (3 min); flow-rate through trap, 1.7 ml/min; on-line desorption and analysis using a shrink-PTFE connection. (D) FACOTT-10, desorption temperature increased from 70 to 150°C at 11°C/min; flow-rate through trap during desorption, 1.7 ml/min; on-line desorption and analysis using a butt connector. (E) FACOTT-10, desorption temperature increased from 70 to 130°C at 8.5°C/min; flow-rate through trap during desorption, 3.4 ml/min; on-line desorption and analysis using a butt connector. (F) FACOTT-10, desorption temperature increased from 80 to 120°C at 5°C/min; flow-rate through trap during desorption, 3.4 ml/min; on-line desorption and analysis using a shrink-PTFE connection. Material was cold-trapped (25°C) on the capillary column during the slow desorption from the traps.

the FACOTT-10 on equal volumes of the headspace gas of an imitation passion-fruit cool drink, are compared in Fig. 4 and clearly show the much higher capacity of the FACOTT-10, especially for the more volatile constituents of the sample. The quantitative differences between the two analyses as far as the less volatile constituents

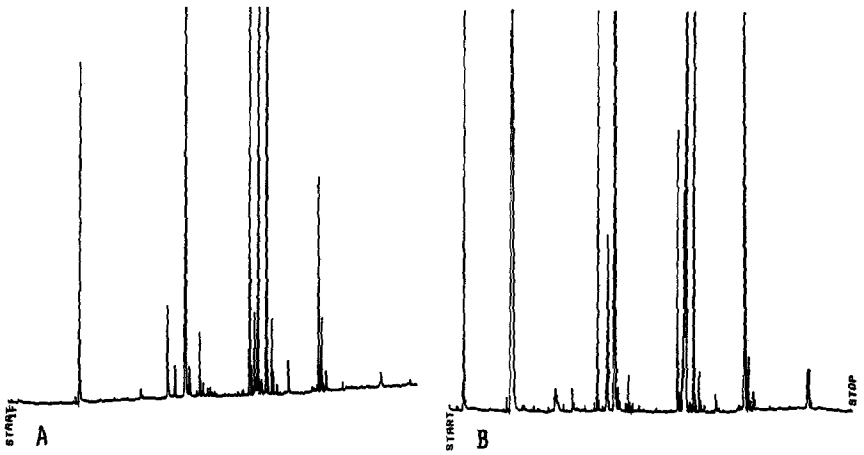

Fig. 4. Analysis of imitation passion-fruit cool drink headspace gas. Column, 40 m × 0.32 mm I.D. fused silica, 0.84 μm SE-30; carrier gas, helium at 28.6 cm/s; temperature programme, 25 to 160°C at 3°C/min; attenuation, × 16; 5 ml of headspace gas; desorption, 70 to 130°C at 12°C/min; on-line desorption and analysis using a butt connector. (A) FOTT-12 (B) FACOTT-10.

are concerned, could be due to the fact that the cool drink sample was not thermostatted and some time elapsed between the two analyses. Similar conclusions can be drawn from the results of the determination of the headspace gas of a 1 × 1 cm piece of citrus (kumquat) peel shown in Fig. 5.

A further number of headspace gas determinations were carried out on more complex samples such as urine and wine. Different trap types were used to collect the volatiles and a second trap was used in series with these traps to determine the

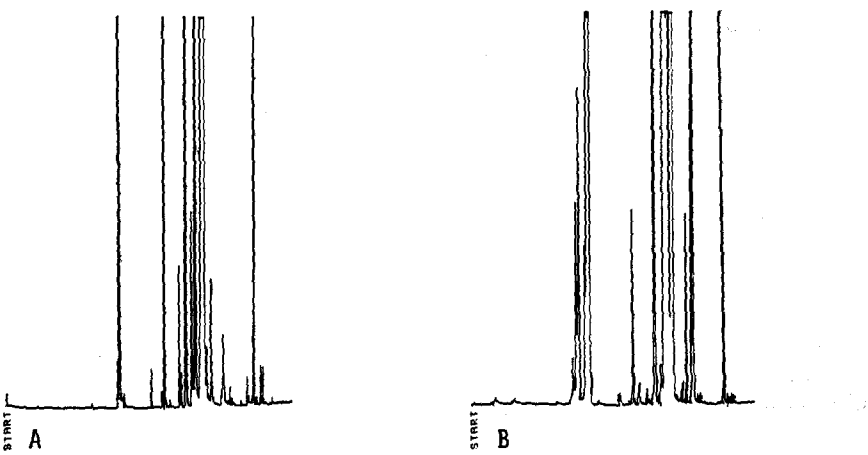

Fig. 5. Analysis of citrus (kumquat) peel headspace gas obtained by leaving a 1 × 1 cm piece of kumquat peel in a 100-ml screw-capped bottle for 2 h. Column, 40 m × 0.32 mm I.D. fused silica, 0.84 μm SE-30; carrier gas, helium at 28.6 cm/s; temperature programme, 25 to 160°C at 3°C/min; attenuation, × 16; 5 ml headspace gas; desorption, 70 to 130°C at 12°C/min; on-line desorption and analysis using a butt connector. (A) FOTT-12 (B) FACOTT-10.

amount of break-through, if any. In order to obtain the best possible gas chromatographic separations of the volatiles on the capillary column, the material desorbed from the traps were focussed on the capillary column by cold trapping using solid carbon dioxide as coolant. In these determinations the traps were removed before the analyses were started and the column connected directly to the injector (on-line desorption, off-line analysis).

In the first of these analyses, 35 ml of headspace gas of a sample of urine of the female red jackal, *Canis mesomelas,* was passed through a FACOTT-10 as first trap and a FOTT-12 as second trap. The results presented in Fig. 6 show almost total retention on the FACOTT, only traces of one of the major, apparently very polar compounds, breaking through to the FOTT. In the next set of analyses, the results of which are given in Fig. 7A, the headspace gas of a white wine (Gewürztraminer) was trapped with the FACOTT-10 as first and the FOTT-12 as second trap. The analysis was then repeated with the FOTT-12 as first and the FACOTT-10 as second trap (Fig. 7B). In the first of these analyses only ethanol and small quantities of one or two other volatile components broke through the FACOTT to be collected on the FOTT, whereas, with the FOTT-12 as first trap, major break-through of a large number of volatile compounds was found. The efficiency of the separations on the analytical column and the sharpness of the peaks in the gas chromatograms were found to be quite satisfactory.

A similar analysis was carried out using the FOPOTT-10 as first and the FACOTT-10 as second trap. In this analysis considerable break-through of a number of compounds, subsequently identified as alcohols, was observed. This type of trap could possibly be used to advantage in wine headspace analysis since, as was pointed out earlier, it does not have the strong catalytic activity of activated carbon towards thermally labile compounds and furthermore, it could be used to concentrate com-

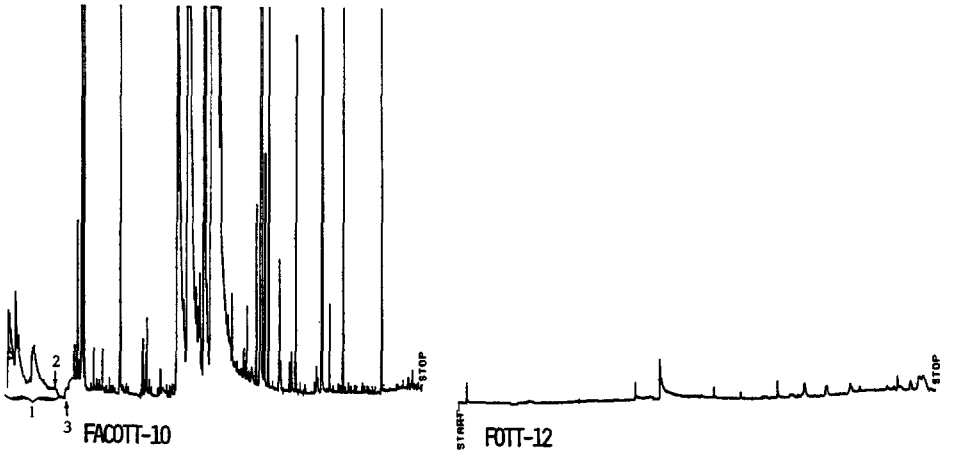

Fig. 6. Analysis of the headspace gas of the urine of a female red jackal (*Canis mesomelas*). Column, 40 m × 0.32 mm I.D. fused silica, 0.84 μm SE-30; carrier gas, helium at 28.6 cm/s; temperature programme, 25 to 180°C at 3°C/min; attenuation, ×8; 35 ml headspace gas; desorption, 70 to 160°C at 13°C/min; peaks: 1 = desorption and cold trapping of the desorbed material on the capillary column with solid carbon dioxide, 2 = shrink-PTFE connection and trap removed, 3 = programme started. FACOTT-10 as first trap and FOTT-12 as second trap.

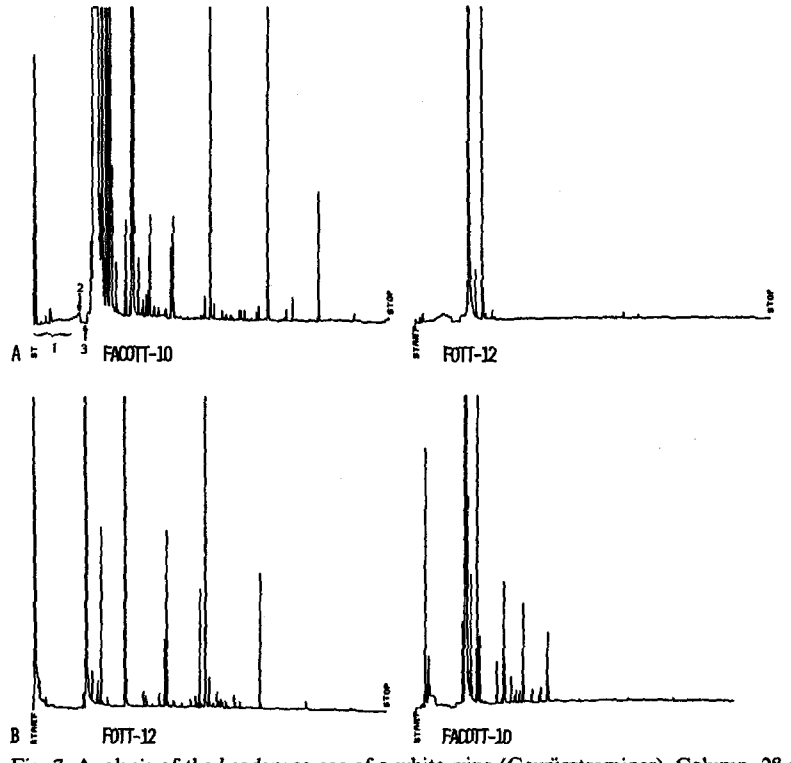

Fig. 7. Analysis of the headspace gas of a white wine (Gewürztraminer). Column, 28 m × 0.32 mm I.D. fused silica, 0.84 μm SE-30; carrier gas, helium at 28.6 cm/s; temperature programme, 25 to 180°C at 3°C/min; attenuation, × 16; 5 ml headspace gas; desorption, 70 to 140°C at 15°C/min; peaks: 1 = desorption and cold trapping of the desorbed material on the capillary column with solid carbon dioxide, 2 = butt connector and trap removed, 3 = programme started. (A) FACOTT-10 as first trap and FOTT-12 as second trap. (B) FOTT-12 as first trap and FACOTT-10 as second trap.

ponents other than the short-chain alcohols, thereby eliminating one of the annoying problems in wine flavour analysis.

Instead of using different traps in series, different phases and adsorbents can be used in different sections of the same fused-silica trap. To illustrate this, a combination FOTT-12/FACOTT-10 trap, having one half of its length coated with SE-30 and the other half with activated carbon supported on SE-30, was prepared. This trap was used with headspace gas flowing through it from the FOTT towards the FACOTT section. Only the most volatile components are thus expected to reach the FACOTT section and to be retained there. Since desorption was carried out with reversed flow, thermally labile compounds will come into contact with the activated carbon layer only if they are also highly volatile, and then only to the extent to which they are not retained by the FOTT section of the trap.

If, in addition, the desorption tube temperature is also carefully increased (manually programmed) it should be possible to restrict the thermal production of artifacts to an absolute minimum by using a combination type of trap. An analysis of the headspace gas of a white wine (Crouchen blanc), using a FOTT-12/FACOTT-10 combination trap, is shown in Fig. 8.

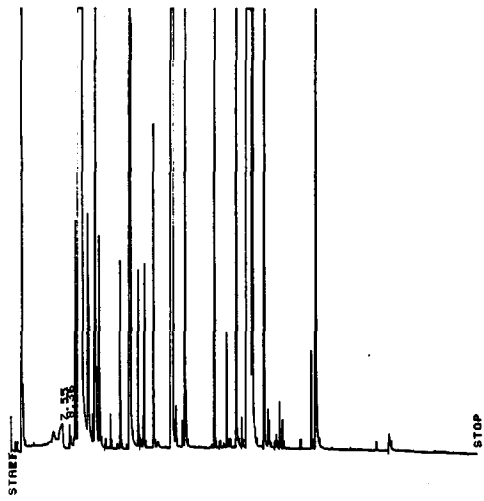

Fig. 8. Analysis of the headspace gas of a white wine (Crouchen blanc) using a FOTT-12/FACOTT-10 combination trap in such a manner that the FOTT section acts as first trap and the FACOTT section as guard trap. Desorption was carried out with carrier gas flowing in the opposite direction and with the trap temperature programmed at 11°C/min from 70 to 140°C. Gas chromatographic conditions as in Fig. 7; attenuation, ×4.

CONCLUSIONS

The present investigation can be seen as an extension of the work of Grob and Habich[6] on the development of open tubular traps for headspace gas analysis. The finger-printing of the volatile secretions produced by insects and other animals requires quantitative trapping of all the compounds in such exudates, which in turn requires traps with a high capacity for a wide range of compound types. In order to remove volatiles quantitatively from the atmosphere surrounding such a secreting organism, traps must preferably also allow quantitative trapping at relatively high flow-rates. A system was devised in which material is trapped on fused-silica open tubular traps coated with a suitable stationary phase or with an adsorbent supported on a film of immobilized SE-30. Trapped material is desorbed by installing the trap in a coiled stainless-steel tube which is heated electrically by passing an electric current through it. Connecting the traps directly to the flame ionization detector of a gas chromatograph when trapping volatile compounds from gas samples containing individual reference compounds, and recording the detector response *vs.* the volume of the gas sample introduced into the trap, proved to be a simple but rigorous test for break-through. From the results obtained with various volatile compounds, a trap coated with activated carbon on an immobilized film of SE-30 is clearly to be preferred to traps coated with the stationary phase only, as some volatiles are lost almost completely from the latter type of trap. Increasing the flow-rate at which a headspace sample is pushed through the traps up to 100 ml/min did not have an appreciable effect on the effectivity with which headspace volatiles are trapped. This is in agreement with the results obtained by Grob and Habich[6].

When using a trap containing activated carbon, thermal conversion of material

during the desorption step can be avoided by gradually increasing the temperature of the trap during this step and using cold trapping to focus the material on the analytical column, instead of employing isothermal desorption at high temperatures to obtain sharp bands of the desorbed material on the capillary column. As expected, increased carrier gas flow-rates facilitated desorption at lower temperatures. In those cases where thermal conversion on activated carbon is expected to take place in spite of programmed desorption at a high flow-rate, artifact formation could possibly be avoided by using a FOPOTT instead of a FACOTT, or otherwise by using a combination FOTT/FACOTT in such a way that the headspace gas volatiles will hit the FOTT section of the trap first. Only the most volatile components will then reach the FACOTT section and if desorption is carried out in the reverse direction, thermally unstable compounds with a lower volatility may not come into contact with the activated carbon at all. The relative lengths of the sections could also be adapted to the type of sample that has to be trapped.

Trapping the headspace volatiles from a number of samples of the type that are often encountered in headspace-analytical work, such as wine, urine, etc., produced such promising results that we believe that using this type of trap could prove to be a valuable addition to the already excellent traps introduced by Grob and Habich, especially in those cases where quantitative trapping of highly volatile constituents is essential in order to obtain an exact aromagram of the headspace sample.

Since the application of these traps to the determination of the material secreted by living organisms introduces further problems peculiar to research on insects and animals, the results of these determinations wil be published elsewhere.

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