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Production and use of capillary traps for headspace gas chromatography of airborne volatile organic compounds

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ABSTRACT

The production of adsorption traps with activated charcoal particles embedded on the inside surface of glass capillary tubes and of capillary traps containing thick (10–15 μm) and ultra-thick (145 μm) films of an apolar stationary phase is described. The application of these traps to the headspace detection of organic volatiles in various gas samples and in air and the problems involved in the use of these traps are discussed.

INTRODUCTION

Strictly, the determination of airborne volatiles released into the atmosphere by, for example, living organisms or industrial processes is not a headspace analytical problem. With certain adaptations the basic principles can, however, be applied equally effectively to the determination of airborne volatiles in a gas that is not in equilibrium with a liquid or a solid. This field of analytical work has been reviewed by Núñez *et al.* [1] and several books and monographs have appeared on the subject [2,3].

Automated systems for the routine determination of headspace volatiles are commercially available. These systems perform fairly well in normal headspace analyses, but the volumes of headspace gas that can be sampled are often relatively small. The increasing awareness of the deleterious effects of some airborne volatiles on the environment, and the threat to human health from even small concentrations of hazardous chemicals in the atmosphere, have created the need for more sensitive methods of detection in which volatiles can be concentrated from large volumes of air. The trapping of volatiles on various adsorbents in packed traps has therefore become popular. The trapped volatiles are normally desorbed thermally, swept from the trap and transferred to the analytical column by the carrier gas. However, desorption with a solvent, followed by conventional analysis of a sample of the extract, can also be done. Concentrating the volatiles on a trap in an off-line manner has the advantage that samples can be taken at any time at short notice and can be stored for subsequent analysis.

Packed traps, however, have serious disadvantages. One of these is that in many applications such large amounts of adsorbent are used that the formation of artefacts by decomposition during thermal desorption or by concentration from slightly impure solvents cannot be avoided. As pointed out by Grob and Habich [4], packed traps were developed for use in packed-column gas chromatography (GC) and, when applied to

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capillary analysis, have given unsatisfactory results, the most serious problem being incomplete transfer of the sample from the trap to the capillary column. This is due to the difference between 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 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 and complete 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 promising results.

Unfortunately, Professor Kurt Grob died before he could complete his pioneering work on these capillary traps. However, his enthusiasm for this work prompted others to continue with the further development of the technique. Activated charcoal traps were made by Burger *et al.* [5] and used for the GC–mass spectrometric (MS) determination of plant volatiles. Conditions under which thermally labile compounds could be desorbed from activated charcoal traps [6] and a method for the desorption of such compounds with a suitable solvent [7] were developed, and techniques for the introduction of the traps into the injector of the gas chromatograph for the desorption of the volatiles were elaborated [8].

These traps, although suitable for the qualitative detection of organic volatiles in air samples, have relatively low capacities for highly volatile substances. One way to increase the capacity of a capillary trap is to increase its length. A device for the desorption of volatiles from such a long (1 m) capillary trap was developed by Burger and Munro [6], and the capacities of capillary traps coated with a stationary phase and with a combination of stationary phase and several different adsorbents were determined. Such long capillary traps were also used by Bicchi *et al.* [9] for the determination of plant volatiles. Blomberg and Roeraade [10] succeeded in increasing the capacity of these traps considerably by increasing the thickness of the stationary phase film to about 100 μm by immobilizing a thick prepolymer film formed on the column wall during dynamic coating.

Despite a considerable volume of research having been done on both the short and long capillary traps, their application has been limited to use by a few groups with the expertise and instrumentation for their production and use. This is an unfortunate situation, because these traps lend themselves to the trapping of airborne volatiles in emergency situations with which any analytical laboratory might be faced at any time. It is the aim of this paper to give detailed descriptions of the production of various trap types and the techniques for the trapping, desorption and analysis of volatiles from a variety of gas samples.

EXPERIMENTAL

Instrumental

GC analyses were carried out with Carlo Erba Model 4160 and 5300 and Siemens Sichromat 2 gas chromatographs equipped with flame ionization detectors, using helium as carrier gas. All glass and fused-silica capillaries used for analytical separations were coated by the Laboratory for Ecological Chemistry. Column specifications and analytical conditions are given in Figs. 3–8. GC–MS analyses were performed with a Carlo Erba QMD 1000 system.

Production of activated charcoal capillary traps (COTs)

Capillary traps coated with a layer of activated charcoal particles were produced by a method adapted from that used by Grob [11]. Activated charcoal (SCII; Chemviron, Brussels, Belgium) was ground in a TS 250 swingmill (Dickie and Stockler, Johannesburg, South Africa) for 1 min and elutriated through a series of screens. The 25–38-μm fraction was washed with 6 *M* nitric acid to remove heavy metal ions and basic material, whereafter it was washed free from acid on a sintered-glass filter. It was then stirred with distilled water for several days and finally filtered off, dried in an oven at 120°C and stored in an air-tight bottle.

A glass-wool plug with a length of about 3 mm was inserted into a length of glass capillary tubing (20 cm × 1.16 mm O.D. × 0.45 mm I.D.) followed by a thin glass rod (7 cm × 0.35 mm). The rod was used to push the glass-wool plug into the capillary and was inserted into the capillary so that its tail-end was about 3 mm inside the tip of the capillary, which was just sufficiently constricted in a flame to prevent the rod from falling out. The tail-end of the glass rod had an uneven surface to prevent it from forming a gas-tight seal with the constricted tip of the capillary.

Activated charcoal was filled into the capillary, which was dropped down a 3-m length of glass tubing onto a hard surface to compact the charcoal until a column of 8 cm of activated charcoal had been obtained. A glass-wool plug followed by a thin glass rod was then inserted from the upper end of the capillary and the capillary was carefully bent at an angle of 90° about 5 cm above the glass-wool plug. This prevented the glass rod from being moved upwards by gas expelled from the activated charcoal when heated. The capillary was fastened along the aligned edges of a U-shaped aluminium support (1.5 mm thickness) with bands of aluminium foil, which were in turn firmly stretched over the capillary with the help of elastic insulating tape as shown in Fig. 1. Vacuum (0.01 Torr) was applied to both ends of the glass capillary and the activated charcoal was heated carefully with the flame from a small Bunsen burner, starting from the top of the column of activated charcoal particles and moving downwards. After this step had been repeated two or three times, the packed section of the capillary was finally heated to red heat, again slowly moving downwards along the capillary with the tip of the flame. The capillary was left to cool under vacuum and was then removed from the U-shaped support and trimmed to the required length (*ca.* 7 cm). Activated charcoal particles not in contact with the glass were blown from the capillary with a jet of nitrogen from a length of fused-silica tubing (0.1 mm I.D. × 0.17 mm O.D.). In some instances it was necessary to loosen particles by gently turning the fused-silica tube. The sharp edges of the finished capillary were finally rounded with a small diamond file.

Production of thick-film capillary traps (FTs)

Thick-film capillary traps were produced by coating borosilicate-glass or fused-silica capillary tubing (*ca.* 0.3–0.35 mm I.D.) with a thick film of cross-linked, apolar stationary phase. Traps with a 15-μm film of cross-linked polydimethylsiloxane, for example, were made by using a solution of 2.82 g of PS 255 (vinyl-modified polydimethylsiloxane; Petrarch Systems, Bristol, PA, U.S.A.) and 85 mg of dicumyl peroxide (DCUP) in 15 ml of pentane. Stationary phases such as SE-30 and SE-54 dissolve very slowly and the mixture of stationary phase, DCUP and solvent was therefore left to stand in the dark for at least 1 day.

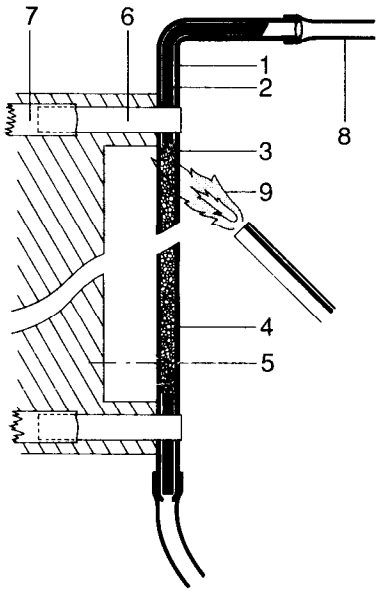

Fig. 1. Production of an activated charcoal open-tubular trap (COT). 1 = Borosilicate capillary tubing; 2 = thin glass rod; 3 = fine glass-wool plug; 4 = activated charcoal particles; 5 = aluminium plate; 6 = aluminium foil strip; 7 = elastic insulating tape; 8 = polyethylene connections to vacuum pump; 9 = flame from small Bunsen burner.

Lengths of fused-silica capillary tubing (*ca.* 2–3 m × 0.32 mm I.D.) were coated with the stationary phase by the static coating technique. To do this, one end of a capillary had to be sealed before the vacuum was applied to the other end to evaporate the solvent from the solution in the capillary. There are several methods to seal off glass and fused-silica capillaries, one of which is to use a plug of hardened waterglass. It must be taken into consideration, however, that waterglass will not adhere to the fused silica in the presence of a highly concentrated solution of the stationary phase. An intermediate plug of a solvent is therefore required. Capillaries were therefore coated as follows: a plug of about 5 cm of pentane was carefully pushed into a capillary using a conventional capillary filling vessel. The pressure was released and the other end of the capillary was closed by inserting in into a piece of silicone-rubber such as a septum in order to prevent the solvent from flowing back out of the capillary. The end of the capillary containing the solvent was then lowered into the stationary phase solution, using another capillary filling vessel. Care was taken not to introduce an air bubble into the capillary between the pentane and coating solution. The stationary phase solution was pushed into the capillary, care being taken not to exceed the maximum allowable pressure in the glass vessel. It is also good practice to use a safety shield during this operation. As soon as the solvent had reached the other end of the capillary the latter was stoppered with the rubber septum. The inlet end of the capillary was removed from the coating solution, wiped clean and also stoppered with a septum. The first septum was removed, the tip of the capillary dipped into a waterglass solution and the longest possible section of the capillary warmed with the

hand or with the help of a piece of cloth soaked in water at 35–40°C. This forced a small volume of pentane out of the capillary. As soon as a few droplets of pentane had left the capillary, the heat source was removed and a short plug of waterglass was sucked into the capillary. The capillary was removed from the waterglass and laid down horizontally in a draught-free location. Extreme care was taken to avoid temperature fluctuations, for example by touching the capillary, to avoid the waterglass being forced out of the capillary by the expanding liquid. The stopper at the other end was removed and the capillary was left for 12–24 h to allow the waterglass to harden. To avoid breakthrough due to the presence of microscopic bubbles in the coating solution or solvent, the liquid in the capillary was pressurized with nitrogen at 1–2 kg/cm^2 for a few hours. This normally does not remove tiny bubbles in the waterglass and it is therefore advisable to use waterglass that has not recently been shaken or poured into a smaller vessel, but rather to fill a convenient vessel with the waterglass a day or more in advance.

Vacuum (*ca.* 20 Torr) was then applied to the open end of the capillary. This can be done with the capillary in a water-bath, but care has to be taken to avoid any moisture coming into contact with the waterglass, as it will soften and cause breakthrough. We prefer to carry out the removal of the solvent with the capillary in a horizontal position on the laboratory bench where it had been left for the waterglass to dry. After all the solvent had been evaporated from the capillary, it was opened at the other end and purged for several hours with nitrogen. Both ends were sealed with septa, then the capillary was coiled and heated in a GC oven from 160 to 200°C at 0.3°C/min, whereafter it was opened, connected to the injector of a gas chromatograph and conditioned at 270°C for several days. It was used as a long capillary trap or divided into short (5–7-cm) traps.

Production of ultra-thick-film traps (UFTs)

Traps having linings of a cross-linked polysiloxane rubber with a thickness of *ca.* 145 μm were prepared by stretching a polysiloxane–rubber tube (0.65 mm O.D. × 0.30 mm I.D., Silastic, medical grade tubing; Dow Corning, Midlands, MI, U.S.A.) freezing it in liquid nitrogen and inserting it into a fused-silica capillary tube (0.53 mm I.D.). On removal of the capillary from the liquid nitrogen, the rubber tube regained its elasticity and expanded to fit tightly into the capillary, giving a capillary trap with a 145-μm lining and an I.D. of 240 μm. The finished product was conditioned at 270°C for several days with a carrier gas flow of *ca.* 5 ml/min and used as a long (1-m) capillary trap or divided into short traps. A detailed description of the production of UFTs has appeared elsewhere [12].

Loading the traps

The headspace gas was drawn through the trap at a suitable flow-rate (see figure legends), which was regulated by using a length of glass or fused-silica tubing as a restriction. For applications requiring very long sampling times, such as the detection of organic volatiles in the atmosphere or the trapping of semiochemicals in the field, a portable vacuum bottle was made from a 14-l light petroleum gas container fitted with, *inter alia*, a vacuum meter and a needle valve. A T-piece was used for applications requiring sampling in parallel with two traps or trap types. All connections downstream from the traps were made with polyethylene tubing (1.2 mm O.D. × 0.9 mm

I.D.). In applications requiring the headspace gas to be forced through the traps, nitrogen that had been purified by passing it through a column of activated charcoal was used. In these analyses the traps were inserted into the headspace through screw-caps fitted with PTFE-lined silicone-rubber septa. Determinations of the organic volatiles in human breath were done by either drawing a sample of the breath from an inflated PTFE gas sampling bag (BGI, Waltham, MA, U.S.A.) or, preferably, by sampling the breath flowing through a glass breathing tube (2 cm I.D.) at atmospheric pressure. The glass tube was fitted with a simple diaphragm type non-return valve and the breath was withdrawn from the breathing tube through a small hole just downstream from the non-return valve, about 15 cm from the person's mouth.

Owing to the strong adsorption of many compounds on glass and other surfaces, the use of syringes to handle headspace gas samples was avoided except in basic studies in which, for example, gas samples containing highly volatile compounds were used to study the capacity of traps for different compounds.

Desorption of the trapped volatiles

Volatiles were desorbed from short traps in the injector of a gas chromatograph as described by Grob and Habich [4], by inserting the trap into the injector from below (Fig. 2). The column was fitted with a ferrule and the other hardware normally used for its installation. The trap was connected to the column with a short length of shrinkable PTFE tubing. In order to avoid thermal decomposition of the stationary phase in the trap and possibly also in the column, the connection was pre-shrunk on glass capillaries with the same outside diameter as the trap and column.

If a fused-silica capillary column is used, it is possible that the available PTFE tubing will not shrink to the required diameter. It is then advisable to fit the column with one half of a press-fit connector which is connected to the capillary trap with the PTFE tubing as shown in Fig. 2.

In some gas chromatographs the injector has a very small hole which cannot be widened to allow easy passage of the shrinkable PTFE connection between trap and column. In some of these instruments it is possible to remove the septum cap, push the capillary column upwards until it protrudes from the top of the injector, whereafter the trap can be connected to the column. The trap can then be lowered into the injector, the septum cap replaced and the ferrule-retaining nut tightened. If the carrier gas is left turned on during this operation and the split valve is open, the introduction of air into the capillary column is restricted to some extent. However, if the trap has to be introduced into the injector from the top, the method recently described by Grob *et al.* [8] will produce more reliable results.

The desorption of volatiles from a long trap can be done by installing it in a stainless-steel tube which can be ohmically heated [6]. The analyses in this study, however, were carried out using a Siemens Sichromat 2 gas chromatograph. The trap was installed in the first oven with the analytical column in the second. The live switching device of the instrument was not used. The trap was connected to the analytical column with a re-useable butt connector [13] or, in the case of a long ultra-thick-film trap, by using a short length of thinner fused silica, one end of which was permanently connected to the column with a press-fit connector and the other end simply inserted into the trap, the silicone-rubber lining of the trap providing a gas-tight

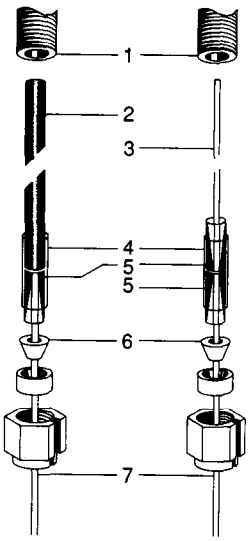

Fig. 2. Connection of capillary traps to a fused-silica capillary column for desorption of trapped volatiles in the injector of a gas chromatograph. 1 = Injector; 2 = borosilicate glass with activated charcoal particles embedded on its inside surface (COT); 3 = fused-silica capillary coated with a thick film of stationary phase (FT); 4 = shrinkable PTFE tubing; 5 = one half of a press-fit connector; 6 = ferrule; 7 = fused-silica column.

connection. All connections were positioned in the first oven to reduce the effect of any possible cold spots and dead volumes in the connections between trap and column. The volatiles desorbed from the trap in the first oven were cryotrapped on the analytical column by selecting an appropriately low temperature in the second oven, or by using solid carbon dioxide.

RESULTS AND DISCUSSION

The production of activated charcoal open-tubular traps (COTs) was demonstrated by Professor Kurt Grob during a course at the University of Stellenbosch in 1986. In principle the method consists in fusing activated charcoal particles into the inside surface of a borosilicate glass capillary tube. This is done by packing the capillary with the charcoal particles, applying vacuum to the open end of the capillary tube and heating the capillary with a small Bunsen burner in order to force the charcoal particles into the soft glass. The charcoal that has not been in contact with the glass is subsequently blown out of the charcoal-coated capillary with a thin fused-silica capillary tube. We have used the same method, but it was found that traps of about 6 cm could be produced only with difficulty as a sudden release of gas from the activated charcoal towards the end of the process often caused the expansion of the traps, which then had to be discarded. Another problem encountered at a later stage was that the charcoal particles did not adhere properly to the glass surface and could easily be blown out to leave an almost empty capillary with a rough inside surface.

These two problems were solved by removing all traces of fine activated charcoal dust from the material to be used in the traps, because restriction of the flow of gas through the capillary was apparently responsible for the sudden expansion of capillaries during the heating process. Fine dust particles sticking to the larger activated charcoal particles apparently also prevented proper contact between these particles and the glass surface. The only way to remove all the fine dust particles was to wash the activated charcoal through a series of sieves with water. It was found that one of the resulting fractions produced by this procedure and having a particle size of 25–38 μm gave perfectly stable COTs. As a further precaution against the expansion of the glass during heating, vacuum was applied to both ends of the capillary tube as shown in Fig. 1.

Activated charcoal traps, although preferred for trapping the more volatile compounds, have certain disadvantages. The first is the high catalytic activity of the material, which often results in decomposition of thermally labile compounds, resulting in the production of artefacts. This is illustrated by a comparison of the results obtained with an FT (d_f 10 μm) and a COT (particle size 25–38 μm) in the headspace analyses of a white wine (Fig. 3). The COT clearly has a very high capacity and even very volatile compounds such as ethanol (eluting at *ca.* 10 min) are retained on the trap. However, with the exception of a few of the constituents normally present in wine, all of the components eluting before ethanol (compare the expanded trace in Fig. 3B) appear to be artefacts. These compounds are not present in the analysis carried out with the FT (Fig. 3C) but, on the other hand, only relatively small amounts of the other highly volatile headspace constituents of the wine were retained on this trap. From a comparison of the gas chromatograms shown in Fig. 3 it appears that, even allowing for a longer sampling time, the later eluting peaks produced by the FT are larger than those produced by the COT. This may be due to irreversible adsorption and/or decomposition on the COT, or otherwise to the preferential adsorption of moisture by the activated charcoal which, consequently, gradually loses its ability to retain the larger molecules. Organic volatiles are retained on the FT by dissolution in the apolar phase layer, which is highly hydrophobic. The water therefore does not have any appreciable influence on the retention of the organic volatiles on the FT. Apparently neither of these traps is ideal for this specific analysis. However, if certain highly volatile and thermally stable compounds have to be trapped, the COT may still be the best trap for the purpose. The FT, again, may be ideal for the determination of thermally labile heavy constituents in a headspace gas. As mentioned earlier, the thermal decomposition of labile compounds can be avoided to a certain extent by temperature-programmed desorption [6], or even more effectively by desorption with solvent, followed by direct transfer of the solvent plus the volatiles to the capillary column for analysis [7].

In some analyses of gas samples with a high moisture content, it was found that the colour of the activated charcoal changed from a dull grey to shiny black, presumably owing to the adsorption or condensation of moisture in the trap. Again only limited amounts of highly volatile compounds were retained when this happened. This is illustrated by an analysis with a COT and an FT in parallel of the air in a chemical factory (Fig. 4).

In view of the often unpredictable behaviour of COTs, we prefer to use FTs in the exploratory stages of an investigation. In principle, pieces of a thick-film fused-silica or

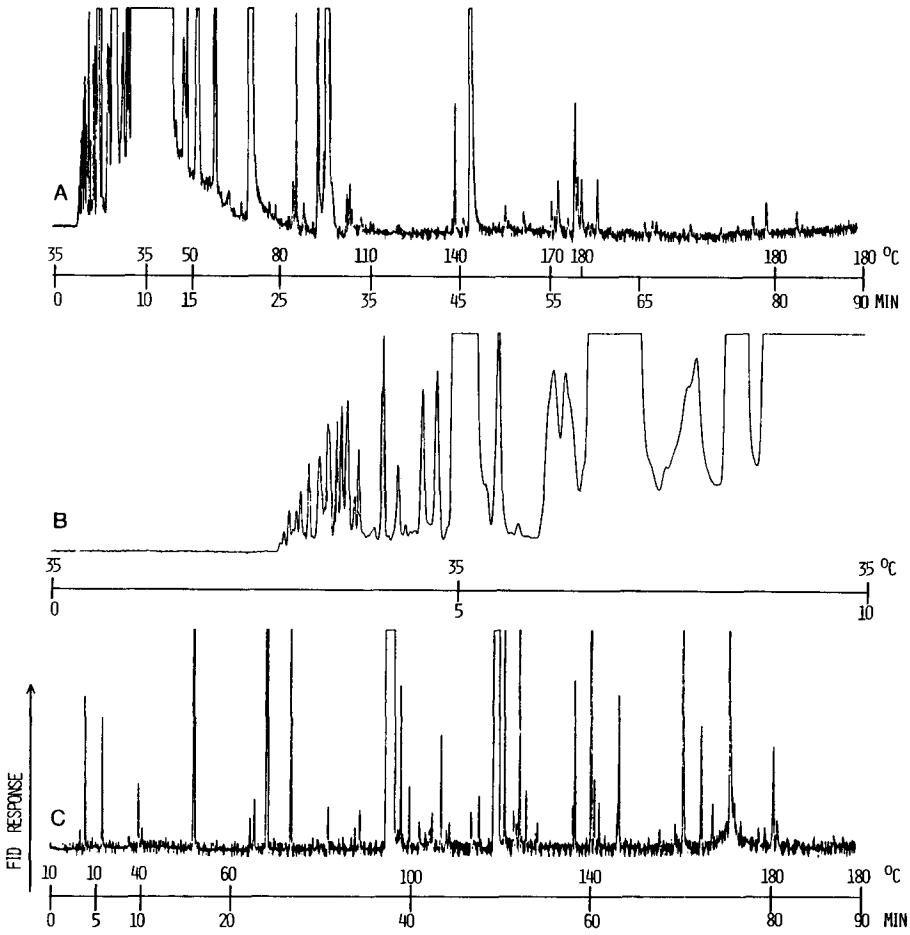

Fig. 3. Chromatograms from the headspace gas of a white wine (Chenin blanc). Column, 30 m × 0.32 mm I.D. fused silica, 0.25-μm cross-linked Carbowax 20M; helium as carrier gas at 25 cm/s. (A) Volatiles trapped from 11 ml of headspace gas drawn through a COT (particle size 25–38 μm) at 3.4 ml/min, desorbed by temperature programming the injector from 100 to 300°C at *ca.* 20°C/min and cryotrapped on the column with solid CO_2; column held at 35°C for 10 min and then programmed from 35 to 180°C at 3°C/min. (B) Expanded section of (A). (C) Volatiles trapped from 34 ml of headspace gas drawn through an FT (film thickness 10 μm) at 3.4 ml/min; desorbed in the injector of the gas chromatograph at 180°C for 5 min and cryotrapped on the column with solid CO_2; column held at 10°C for 5 min and then programmed from 30 to 180°C at 2°C/min. Data acquisition was started after completion of the desorption step. FID = Flame ionization detection.

glass column can be used as short film traps. However, most applications require traps having much thicker stationary phase films than those used in commercially available columns and prospective users of this technique therefore have to be able to produce traps in the laboratory. The problems involved in obtaining straight lengths of glass capillary tubing with the correct dimensions, coating the tubing and coupling the trap to the capillary column, are probably responsible for the apparent lack of interest in

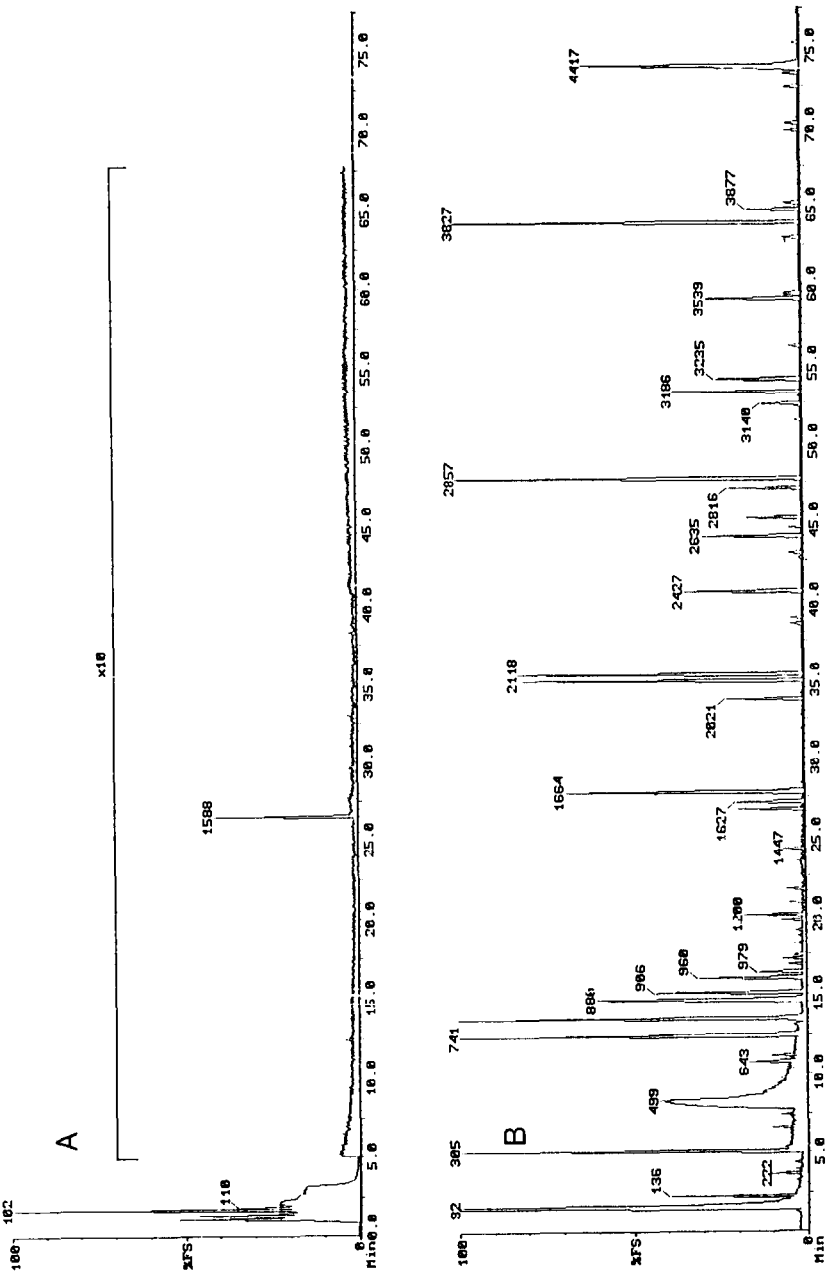

Fig. 4. GC–MS analysis of airborne organic volatiles in a chemical plant. Column, 40 m × 0.3 mm I.D. glass, 0.6-μm PS 089-OH; helium as carrier gas at 28.6 cm/s; temperature programme, 40–250°C at 2°C/min; 450 ml of air sampled at 30 ml/min. Activated charcoal and film traps used in parallel. (A) Volatiles trapped on a COT (particles size 25–38 μm) and desorbed by temperature programming the injector from 120 to 220°C at *ca* 20°C/min; the volatiles were cryotrapped on the column with solid CO_2. (B) Volatiles trapped on an FT (film thickness 10 μm), desorbed at 200°C and cryotrapped on the column with solid CO_2. Data acquisition started after completion of the desorption step.

capillary trapping techniques. We prefer to prepare short capillary traps from straight lengths of glass capillary tubing, as it is possible to seal off a filled glass capillary with a tiny flame and to remove the small gas bubble that is formed during the process within less than 1 min. In this paper the production of short traps from fused-silica tubing is described, as this material is readily available. It is possible, however, that shrinkable PTFE tubing that will shrink tightly onto fused silica with O.D. 0.45 mm may not be available. This problem can be solved by increasing the diameter of the column by making use of a press-fit connector cut in half. One half of the connector is permanently connected to the column and the other half to the fused-silica trap, whereafter the trap and column can be connected to each other with shrinkable PTFE tubing in the usual manner (Fig. 2). It is advisable, however, to pre-shrink the connecting PTFE tubing on the two sections of the press-fit connector before they are fitted to the column and trap, to avoid damaging their stationary phase layers.

The limited capacity of short film traps was a serious problem until Blomberg and Roeraade [10,14,15] developed short and long capillary traps with film thicknesses of up to 100 μm. These traps therefore have stationary phase layers that are about six times as thick as those obtainable with static coating procedures. They used an

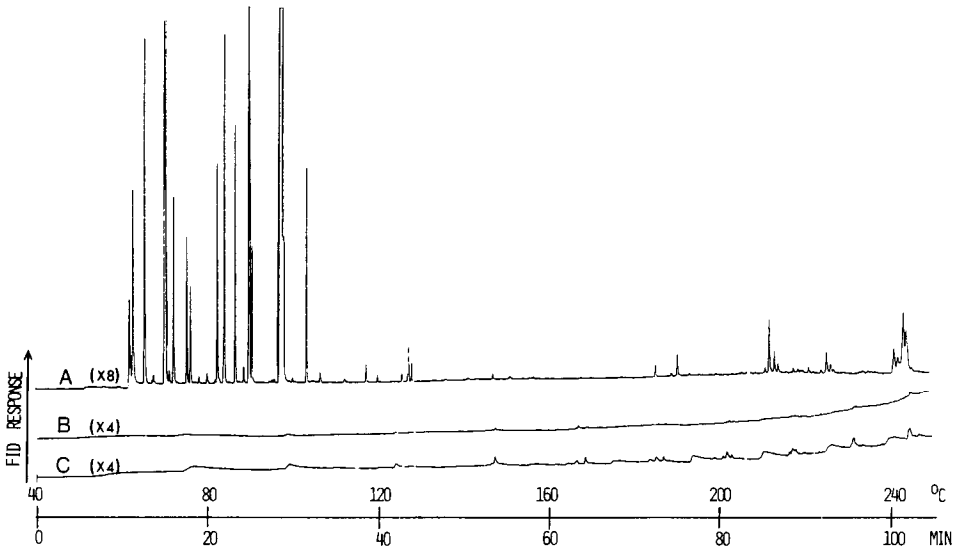

Fig. 5. Quantitative analysis of the headspace gas from 20 g of the pulp of a yellow monkey orange (*Strychnos madagascariensis*). Column, 40 m × 0.3 mm I.D. glass, 0.4-μm OV-1701-OH; helium as carrier gas at 28.6 cm/s; temperature programme, 40–250°C at 2°C/min. (A) Headspace gas (1 ml) was pushed through two short (7-cm) ultra-thick-film traps (film thickness 145 μm) connected in series to the 1-l flask containing the fruit at 0.5 ml/min; trapped volatiles desorbed at 220°C. Constituents determined: 1 = 1-butanol (0.7 μg); 2 = methyl butanoate (1.5 μg); 3 = ethyl 2-methylpropanoate (2.6 μg); 4 = ethyl butanoate (29.8 μg); 5 = butyl acetate (1.4 μg); 6 = ethyl 2-methylbutanoate (1.1 μg); 7 = propyl butanoate (1.6 μg); 8 = butyl propanoate (2.6 μg); 9 = methyl hexanoate (1.9 μg); 10 = butyl 2-methylpropanoate (16.2 μg); 11 = butyl butanoate (45.1 μg). Quantification was done by on-column injection of a mixture of the synthetic compounds as external standards. The desorbed volatiles were not cryotrapped, and the analysis was started directly after the traps had been installed in the injector. (B) Gas chromatogram of volatiles desorbed from the second trap; desorption at 220°C. (C) Blank analysis; desorption at 250°C.

ingenious technique to produce these traps, but it is unlikely that the expertise required for the production of the traps will be available in many analytical laboratories. We therefore devised a simple method of inserting a polysiloxane-rubber lining into fused-silica capillaries in order to produce traps with a film thickness of 145 μm and a final I.D. of 240 μm. These traps were expected to have a high background owing to the thermal decomposition of the very thick rubber lining. It was found, however, that background peaks that could be expected to interfere with the detection of minor constituents in a headspace gas, appeared only when the desorption was done at 250°C. In Fig. 5 a quantitative GC analysis is shown of the headspace gas of the fleshy parts of the fruit of the tree *Strychnos madagascariensis* (yellow monkey orange tree). The fruit has a flavour similar to that of the mango and is particularly rich in the esters of butanoic acid. The flavour constituents were trapped under conditions that gave no breakthrough to a second trap, connected in series to the first, and the analysis thus gives an indication of the capacity of an ultra-thick-film trap. Despite the high capacity of the trap, desorption of the esters at an injector temperature of 220°C was rapid enough to give acceptable peak shapes even for the early-eluting constituents, without having to resort to cryotrapping of the desorbed volatiles.

In initial experiments with long ultra-thick-film traps a desorption temperature of 100°C was used in order to avoid the possible generation of background peaks. As expected, the long desorption time of 25 min resulted in peak broadening of the more

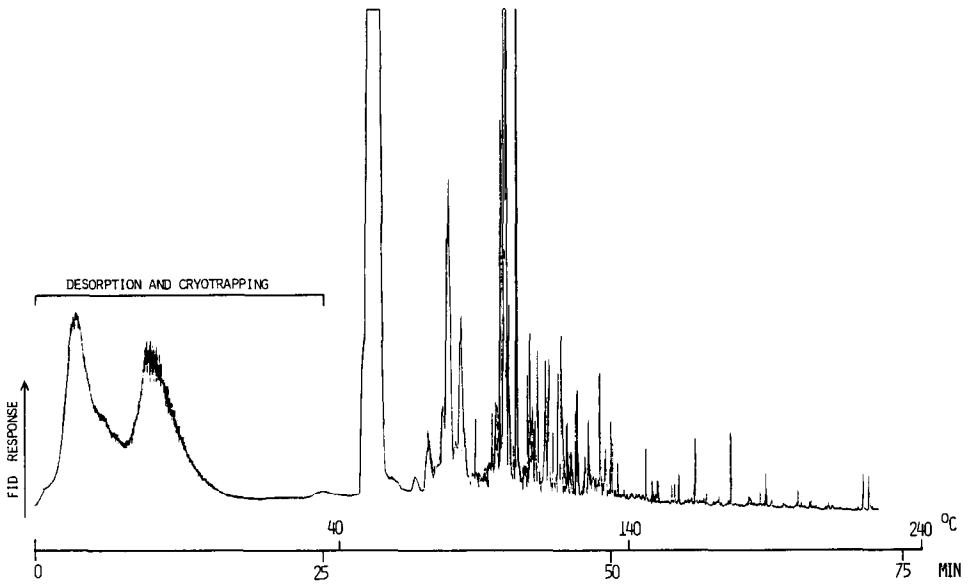

Fig. 6. Chromatogram of the organic volatiles trapped from the air in a synthetic organic chemistry laboratory. Column, 25 m × 0.32 mm I.D. fused silica, 0.75-μm cross-linked PS 255; helium as carrier gas at 28.6 cm/s; temperature programme, 40–250°C at 4°C/min. The volatiles were trapped from 1.2 l of air on a 1-m ultra-thick-film trap (film thickness 145 μm) at a flow-rate of 13 ml/min, desorbed at 100°C for 25 min and cryotrapped at 0°C.

volatile constituents. This is illustrated by a chromatogram of the volatiles from the air in a chemical laboratory shown in Fig. 6. In Fig. 7 two analyses of air sampled from a street in Stellenbosch are shown, illustrating the improved peak shapes of the more volatile compounds obtained by cryotrapping at a lower temperature. Cryotrapping with solid carbon dioxide gave perfect peak shapes in the GC separation of the organic volatiles in human breath shown in Fig. 8.

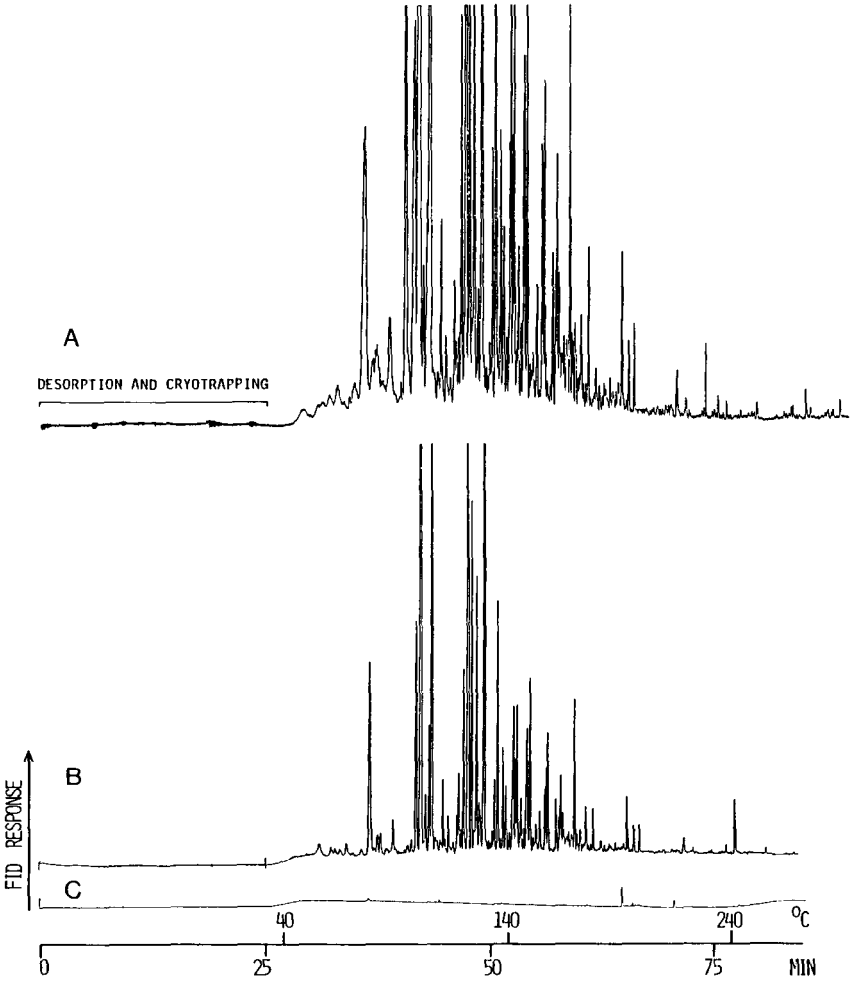

Fig. 7. Chromatograms of the organic volatiles trapped at different times of the day from air on a street in Stellenbosch. The volatiles were trapped from 1.3 l of air on a 1-m ultra-thick-film trap (film thickness 145 μm) at a flow-rate through the trap of 13 ml/min. Gas chromatographic conditions as in Fig. 6. (A) Volatiles desorbed at 100°C for 25 min and cryotrapped at 0°C. (B) Volatiles desorbed at 100°C for 25 min and cryotrapped at −17°C. (C) Blank analysis: desorption at 100°C for 25 min; cryotrapping with solid CO_2.

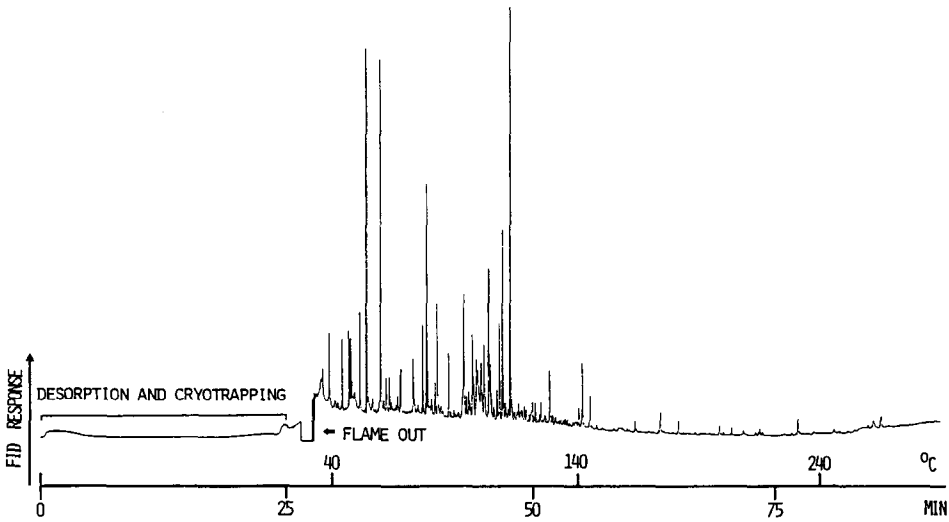

Fig. 8. Chromatogram of organic volatiles trapped from 1.3 l of human breath on a 1-m ultra-thick-film trap (film thickness 145 μm) at a flow-rate through the trap of 13 ml/min. The breath was drawn from a breathing pipe fitted with a non-return valve. The volatiles were desorbed at 100°C for 25 min and were cryotrapped on the column with solid CO_2. Chromatographic conditions as in Fig. 6.

CONCLUSIONS

COTs have a high capacity, and even highly volatile compounds can be effectively trapped on them. However, they behave unpredictably when volatiles are trapped from gas with a high moisture content or when long sampling times have to be employed. Decomposition of thermally labile compounds during the desorption from a COT is a problem. FTs are to be preferred in the exploratory stages of a headspace analytical investigation. Highly volatile compounds are, however, not effectively retained and may be present in the resulting gas chromatogram only in low proportions. Work on the application of UFTs to headspace analytical problems is still in an early stage. The capacity of these traps is expected to be about ten times that of the FTs, but more research has to be done to determine their capacity for specific compounds and compound types, and to establish optimum conditions for their desorption. Fortunately they have a remarkably low bleed in spite of the thickness of the polysiloxane-rubber lining. Except when the headspace contains highly volatile or relatively involatile constituents, it should be possible to analyse almost any headspace gas with these traps.

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