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CONCENTRATION OF HEADSPACE, AIRBORNE AND AQUEOUS VOLATILES ON CHROMOSORB 105 FOR EXAMINATION BY GAS CHROMATOGRAPHY AND GAS CHROMATOGRAPHY–MASS SPECTROMETRY

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SUMMARY

Techniques are described for the collection of volatile material from headspace vapours and the atmosphere and for the direct extraction of volatiles from aqueous solution by traps containing the porous polymer Chromosorb 105. The traps are inserted through a valve into a gas chromatograph which facilitates the desorption and transfer of the volatiles to high-resolution capillary columns. Selected applications of the technique are described.

INTRODUCTION

The use of porous polymers for the water-free concentration of volatiles from headspace vapours or the atmosphere has become a well established practice in many laboratories. An evaluation made recently of the adsorption characteristics of the polymers more commonly used for this purpose[1] cites many pertinent references to their use in headspace and air analysis. In contrast to the considerable effort devoted to the collection of volatiles from the vapour phase, the direct recovery of organic volatiles from aqueous solution by porous polymers has received little attention[2–4].

This paper describes techniques* developed and used in this laboratory over the past five years for (1) the concentration by porous polymers of headspace volatiles, atmospheric pollutants, and volatiles in aqueous solution, and (2) the introduction of the collected volatiles on to capillary columns for examination by gas chromatography (GC) and gas chromatography–mass spectrometry (GC–MS).

EXPERIMENTAL

Trap design

The fundamental component, both for vapour collection and for extraction

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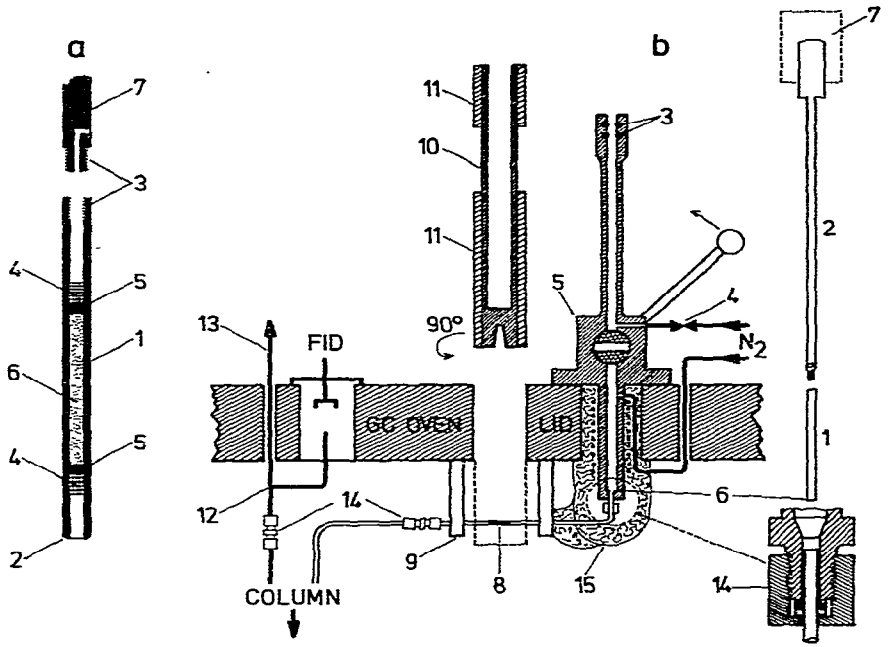

Fig. 1. (a) Chromosorb 105 trap. 1 = Stainless-steel tube 90 × 3.2 mm O.D. × 2.4 mm I.D.; 2 = 60° chamfer; 3 = 6BA threads; 4 = plugs of rolled up 100-mesh stainless-steel gauze; 5 = silanized glass wool; 6 = Chromosorb 105, 50–60 mesh, 100 mg; 7 = tip of insertion rod. (b) Sectional diagram of part of GC lid. 1 = Chromosorb 105 trap; 2 = insertion rod; 3 = silicone rubber "O"-rings; 4 = purge line toggle valve; 5 = ball valve with PTFE seals; 6 = 60° angled faces; 7 = brass weight; 8 = precolumn packed and cooled zone; 9 = precolumn supports; 10 = liquid nitrogen cold probe; 11 = PTFE insulation; 12 = GC effluent splitter; 13 = outlet to sniffing port, collection port, or MS; 14 = low hold-up unions with graphite (Graphlok) ferrules (Scientific Glass Engineering); 15 = asbestos tape lagging.

from aqueous solution, is a tubular stainless-steel trap (Fig. 1a) containing a bed of porous polymer. Its design allows for its insertion into the introducer (Fig. 1b) of a laboratory-constructed gas chromatograph for unloading and column injection of the trapped volatiles (see below). The dimensions of the resin bed resulted from the author's experience with the larger trap collector used by Dravnieks *et al.*[5] for high-speed collection of atmospheric pollutants. However, the amount of porous polymer in this trap was considered to be excessive for the general collection of headspace vapours and was reduced from 5 g to 100 mg, which allowed it to be contained in a trap of similar size to that already used in this laboratory for the trapping and transfer of GC fractions[6]. Compression of the polymer bed by a spring (to prevent channelling) was difficult to incorporate in the smaller traps. An effective compromise was to hold the bed between plugs of rolled-up stainless-steel gauze and silanized glass pads, the latter providing the necessary cushioning of the polymer bed. When necessary, elimination of contact of the adsorbed organic materials with metal surfaces was allowed for in traps constructed from glass-lined stainless-steel tubing (Scientific Glass Engineering, Melbourne, Australia) and with the wire mesh plug at the inlet to the trap substituted by a sealed-in sintered glass plug.

Choice of porous polymer

Four commercial porous polymers, Chromosorb 102, 105[7] and 106[8] (Johns-Manville, Denver, Colo., U.S.A.) and Tenax GC[9] (obtained from Applied Science Labs., State College, Pa., U.S.A.) have been tried in the above trap. Chromosorb 102, used initially, was found to give unacceptably high and erratic backgrounds presumably due to thermal or oxidative breakdown during the unloading procedure. It has been reported[10] to be sensitive to attack by oxygen at moderately elevated temperatures. For this reason (which was probably also that of Dravnieks and Watson[11]) it was replaced by Chromosorb 105. This polymer, described[7] as "polyaromatic", has a moderately polar surface, a high specific surface area of 600–700 m^2g^{-1} and pores of average diameter 0.5 μm. Its chemical composition has not been divulged by the makers. After initial conditioning in the above trap at 225° for 12–24 h in a stream of oxygen-free nitrogen (10 ml/min) it gave stable and acceptably low backgrounds for the injection conditions used below. The two main products of thermal decomposition have been identified as *m*- and *p*-ethylstyrene. These are detectable only at high GC sensitivity as a partly resolved peak (Linear Index on Carbowax 20M of 1430), the position of which is shown in Fig. 4c by the arrow. After each use the traps are reconditioned overnight in oxygen-free nitrogen at 150–170°. The polymer has a long useful life as no falling-off of adsorptive capacity of the traps has been apparent after routine use for one year. The polymer is renewed after this period.

After an initial conditioning as above, Chromosorb 106, a styrene-divinylbenzene copolymer of high specific surface area (700–800 m^2g^{-1}), also gave a low background which makes it a possible alternative to Chromosorb 105.

In a recent study in this laboratory of vegetable volatiles[12], Tenax GC showed a lower adsorptive capacity than either Chromosorb 105 or 106. This agrees with its much lower specific surface area (18.6 m^2g^{-1})[13] and the results of Butler and Burke[1], in which it ranked poorly against other polymers of high specific surface area. Tenax GC also allowed breakthrough of some components of medium volatility, which was attributed to the selective adsorption of certain classes of compounds commented on by previous workers[14,15]. Tenax GC has not therefore been favoured in this laboratory as an adsorbent for general application, but is certainly the best choice for the collection of stable compounds of higher molecular weight (*e.g.*, environmental polycyclic hydrocarbons) when high recovery temperatures are obligatory.

Collection of headspace volatiles

Fig. 2a shows a simple arrangement for collection from the headspace above liquids. This includes the sampling traps within the flask which allows collection close to the volatile source and so eliminates any risk of contamination by, or adsorption in, connecting lines. It also provides for isothermal conditions between the liquid and collecting trap, thereby avoiding the risk of condensation of water in the trap from the saturated gas stream. Heavy lead collars eliminate the use of clamps and permit the system to be readily assembled.

Quiet magnetic stirring produces a continually renewed surface for the release of volatiles from the liquid. Vigorous stirring, resulting in splashing, must be avoided due to the entrainment of fine droplets and the consequent fouling of the porous polymer. Before collection, stable foam as formed during extraction of some vegetable juices[16] must be removed from the surface by gentle suction through a PTFE tube.

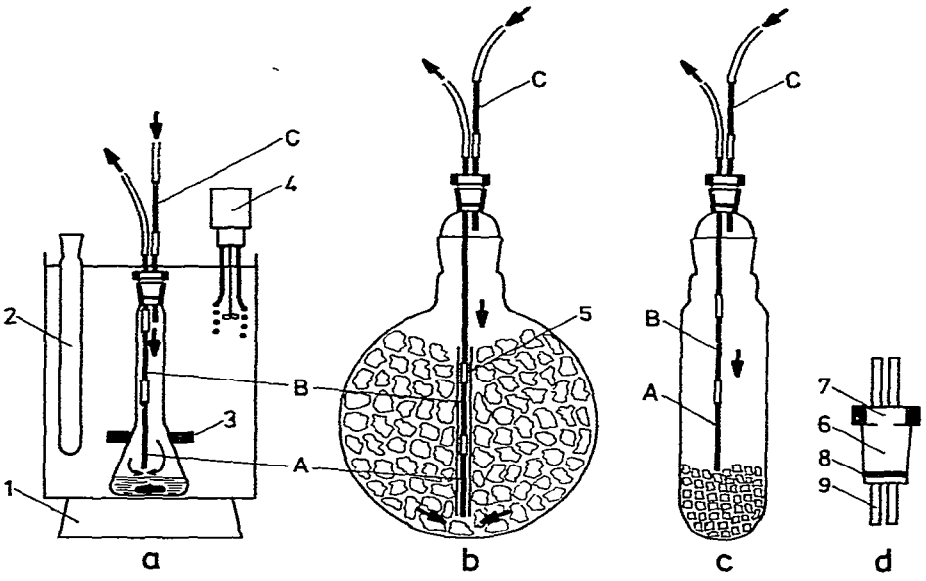

Fig. 2. Arrangements of traps for headspace collection of volatiles from liquids (a), light-weight materials (b), and dense solids (c); (d) PTFE stopper "O"-ring assembly. 1 = Magnetic stirrer; 2 = purge tube; 3 = lead collar; 4 = stirrer-temperature controller; 5 = PTFE tubing; 6 = PTFE stopper 14/23; 7 = flats; 8 = Viton "O"-ring; 9 = stainless-steel tubing 3.2 mm O.D. See also text.

Under these conditions no protecting filter, which itself could have some adsorptive surface, need be attached to the collecting trap. The gap between the inlet of the first trap and the liquid surface was arbitrarily set at about 15 mm, which ensures that the incoming gas must sweep reasonably close to the surface.

Conical flasks used to obtain a good surface-to-liquid volume ratio have, depending on the application, ranged in size from 1 l with 400 ml liquid through intermediate sizes down to 10 ml accommodating 1–3 ml of liquid. The overall height of all flasks is the same to accommodate two traps in series.

A flow-rate of oxygen-free nitrogen, chosen as 40 ml/min as most suitable for the amount and cross-section of the polymer bed, was controlled by the cylinder pressure regulator in series with a finer pressure regulator (Model IW215; Airmate, Sydney, Australia) and a mass flow controller (Model 42300080; Veriflow, Richmond, Calif., U.S.A.). Dependent on the application, the total volume of nitrogen passed has varied from 500 ml for fruit juices to as much as 250 l needed for the concentration of some trace constituents from vegetables for GC–MS examination[16].

On account of the risk of change to thermally labile constituents or of artefact formation from thermally induced reactions, collection above biologically active liquids (*e.g.*, fruit juices and urine) is made at or near ambient temperature using a water-bath controlled by an immersion stirrer controller (Braun Junior). With systems low in volatiles this has involved long collection periods but no great disadvantage has been experienced for routine analysis as the general simplicity of the collection equipment allows it to be readily replicated and to be operated overnight.

Analytical-grade sodium chloride, previously heated in an air oven at 120° to

drive off any adsorbed material, is added before collection to give approximately a 30% (w/v) solution. While this will have some effect of enhancing the concentration of volatiles in the headspace, the main purpose of salt addition is to inhibit the growth and activity, respectively, of micro-organisms and enzymes present which might otherwise give rise to volatile artefacts.

The traps A, B, and C (Fig. 2) have the following functions. A is the main collecting trap which, with low volumes (0.5–2 l) of the sweep gas usually retains all volatiles normally encountered in flavour investigation, but even with large volumes has been found to completely retain volatiles of moderate and low volatility, as examples below show. B is used as a check on the degree of adsorption by trap A. C, situated in the inlet line, removes any organic contaminants from the inlet gas stream and obviates the need for a liquid nitrogen trap. Flexible connections between the flow control system and the collection flasks are made by thin-walled PTFE tubing, and short lengths (2–3 cm) of the same tubing are used to connect trap A to trap B and B to the outlet tube. The PTFE stopper assembly (Fig. 2d), small in diameter to withstand the back pressure of the traps without retaining clamps, is common to all headspace assemblies. When multiple collection is required, a stopper with three outlet tubes is used to take three sets of traps in parallel.

With solid materials a similar arrangement of traps is used. Low-density materials such as foliage or packaging materials are placed in a large flask (Fig. 2b) with the collecting traps, shielded from direct contact with the contents by a loose sleeve of PTFE tubing, positioned with the inlet to trap A close to the bottom of the flask. With higher-density solids the broken-up material is placed in the bottom of an elongated flask (Fig. 2c) in a water-bath and the sample is collected just above the material.

After collection, any residual adsorbed water in the traps is purged before injection into capillary columns. The gas flow is interrupted, the PTFE stopper-trap assembly is fitted into the glass tube (Fig. 2a) and the flow of nitrogen resumed for a period of 2–10 min, depending on collection conditions. The traps are then sealed with PTFE caps and stored above solid carbon dioxide.

Extraction of volatiles from aqueous solution

Volatiles are extracted from aqueous solutions, such as steam distillates and aqueous condensates, by passing the solution through Chromosorb 105 traps connected to a syringe pump (Model 341; Sage Instruments, Cambridge, Mass., U.S.A.), as shown in Fig. 3. The solution is manually drawn into the syringe from a supply through the three-way miniature valve (Hamilton, Calif., U.S.A.). The valve is switched, the drive started, and the solution passed through the traps at about 1 ml/min. By choosing the appropriate size of syringe volumes from 1–50 ml per pass can be conveniently handled. The valve is rotated and some air or nitrogen sucked into the syringe is pushed mechanically through the traps to expel as much bulk water as possible. Nevertheless each trap still retains about 50 μl of water which is removed by attaching the traps to the PTFE stopper (Fig. 2d) and purging them with nitrogen (40 ml/min) for 2 h at 25° in the long purging tube, as for headspace collection. This effectively removes all water from both traps. This purging process usually involves some breakthrough of the lower volatiles into the second trap. This may be an advantage, for instance when recovering volatiles from aqueous distillates which result from

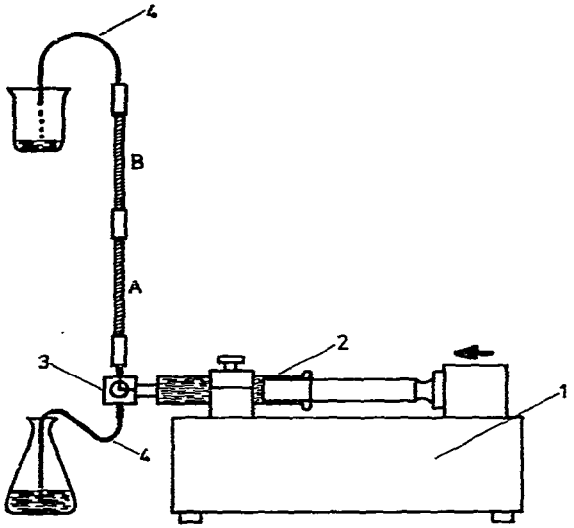

Fig. 3. Arrangement of traps for extraction of volatiles from aqueous solution. 1 = Syringe pump; 2 = syringe; 3 = three-way PTFE valve; 4 = PTFE tubing 1.2 mm O.D.

fermentation or enzyme action and in which excessive amounts of low boilers, such as ethanol, acetaldehyde, or ethyl acetate are usually present. By judicious purging these may be reduced in the first trap to a level which no longer presents an overloading problem on the capillary column.

High-speed sampling from the atmosphere

The large volumes necessary for the collection of atmospheric pollutants in a reasonably short period prohibited the use of the small Chromosorb 105 trap for this application. Consequently, collections are made at flow-rates of up to 4 l/min by a larger trap similar in design and size (100 × 19 mm O.D.) to that used by Dravnieks *et al.*[5] but packed with Chromosorb 105 (50–60 mesh, 5 g) and conditioned as above. After collection, the trap is immediately sealed with Swagelok caps for transport or storage. The adsorbate is recovered by heating the trap to 150° in a small aluminium block oven, drilled to suit the trap, and over a 1-h period the desorbed volatiles are swept by oxygen-free nitrogen (40 ml/min) into two small Chromosorb 105 traps in series and held at 20°. Injection into GC or GC–MS units is then made by the procedure below.

Gas chromatography and gas chromatography–mass spectrometry

The volatiles are unloaded from the trap and injected on to a capillary column by a variation of a probe insertion technique[6] used in this laboratory for the past seven years. This allows for the "freezing on" of volatiles on to a pre-column or the column itself and for their plug injection, without disturbance of the carrier gas flow. The unloading and injection procedure is shown in Fig. 1b. The trap (1) brought to ambient temperature if stored, is uncapped, screwed to the insertion rod (2) to form the probe and pushed into the introducer to a point just below the "O"-rings (3). The purge line

is opened at the toggle valve (4) and pure nitrogen (*ca.* 10 ml/min) is passed through the upper introducer and the trap for 1 min and vented to the atmosphere through the hole in the insertion rod. The trap, thus purged of air, is pushed further into the introducer to enclose the vent hole, the purge line is closed, the ball valve (5) is opened, and the probe is pushed right down so that the 60° angled faces on trap and introducer (6) are in contact. A drilled brass weight (7) (150 g) is placed over the probe handle to maintain the seal. The pre-heated carrier gas flow (helium or nitrogen, 10 ml/min, totally oxygen-free by passage through a manganous oxide scrubber[17]) is thus diverted through the probe vent hole and down through the trap in a backflushing direction. The adsorbed material, much of which may be desorbed while the trap is being heated to the introducer temperature, is collected as a narrow frozen zone of 1–2 cm (8) in a pre-column of glass-lined stainless steel (1.6-mm O.D., 0.8-mm I.D.) (Scientific Glass Engineering) clamped into the supports (9). For preference, the pre-column contains a short plug (8–12 mm) of an inert GC column packing (10% Silicone OV-101 on silanized Chromosorb W, 40–60 mesh) situated centrally in the cooled zone and retained by silanized glass wool plugs. The packing provides an extended surface for condensation but may also act as an effective filter for any fog formed. However, satisfactory results have been obtained without this packed plug or when freezing directly onto the beginning of wide-bore (0.75 mm I.D.) open-tubular metal columns, but this may result in some slight breakthrough which, in turn, can be serious when large amounts of low-boiling compounds are present in the volatiles.

The pre-column is cooled by a round hollow copper probe (10) inserted through the lid some minutes earlier, and to which liquid nitrogen is periodically added. The probe straddles the pre-column and good contact is provided by a deep V in the probe (shown at 90°) with the angle of the V curved to closely fit the pre-column. Excessive frosting of the cold probe is prevented by a 5-mm thickness of PTFE insulation (11), while similar insulation permits easy handling. For routine operation, 10 min at an introducer temperature of 150–160° is adequate for complete volatile recovery, after which the 105 trap is withdrawn.

The frozen volatiles are injected into the capillary column by replacing the cold probe by a similarly V-shaped brass probe pre-heated to GC oven temperature or above and withdrawing it after a fixed short period (1–2 min). Although temperature programming has been mostly used with this introduction technique, no difficulties have been experienced with isothermal column operation up to 150°.

All laboratory-constructed GC units, including that coupled to the MS and a commercial instrument (Packard-Becker Model 419) are equipped with the above means of trap injection. By insertion of appropriate lengths of gold wire (0.57 mm diameter) into the glass-lined stainless-steel (0.60 mm I.D.) connections to the FID and outlet (13), the column flow is divided 1:1 between the FID and a sniffing port or alternatively 1:4 between the FID and a collection port. The latter has a heated "O"-ring assembly similar to that on the introducer, which facilitates the collection of fractions and their transfer to columns of opposite polarity[6] or into the GC–MS unit. Although glass SCOT columns (50–85 m × 0.5–0.6 mm I.D.) have been mostly used for the applications reported below, the chromatograms shown in Figs. 4–6 were obtained using a 150 m × 0.75 mm I.D. stainless-steel column coated with Carbowax 20M[6].

APPLICATIONS

The above collection techniques, used in conjunction with high-resolution GC, odour assessment of the column effluent, reaction GC[18] and GC–MS[6] have provided a greatly simplified experimental approach to many investigations carried out over the past five years in this and associated laboratories in Australia.

Vapour collection

The collection of volatiles above liquids as shown in Fig. 2a has been used in the following studies: (1) the GC–MS examination of the volatiles of the juice of the purple passionfruit (*Passiflora edulis*, Sims), the yellow passionfruit (*P. edulis* var. *flavicarpa*), and their commercial hydrids[19], (2) the isolation from purple passionfruit juice of four edulans (Fig. 4a, A–D) a novel class of flavour constituent[20], (3) the isolation and identification of trace vegetable constituents, 3-alkyl-2-methoxypyrazines in many raw vegetables[16], and geosmin from beetroot[21], (4) the identification of behaviourally significant volatile components of the anal gland secretion of the wild rabbit using the excised glands homogenized in saline solution[22], (5) the identification of trimethylamine in the urine of children as being responsible for offensive "fishy" body odours[23], (6) the examination of the volatiles of wines and brandy at the Australian Wine Research Institute (Adelaide, Australia)[24], and (7) investigations of the identification of taints in foodstuffs, refrigerators, and cold storage rooms[25]. Gas chromatograms of a typical collection above a liquid are shown in Fig. 4. These are from a 5.4-l-collection made above 25 ml of the fresh juice of the purple passionfruit at 25°. Except for a partial breakthrough of ethanol and ethyl acetate into the second trap (Fig. 4b), there is total retention of the volatiles by the first trap.

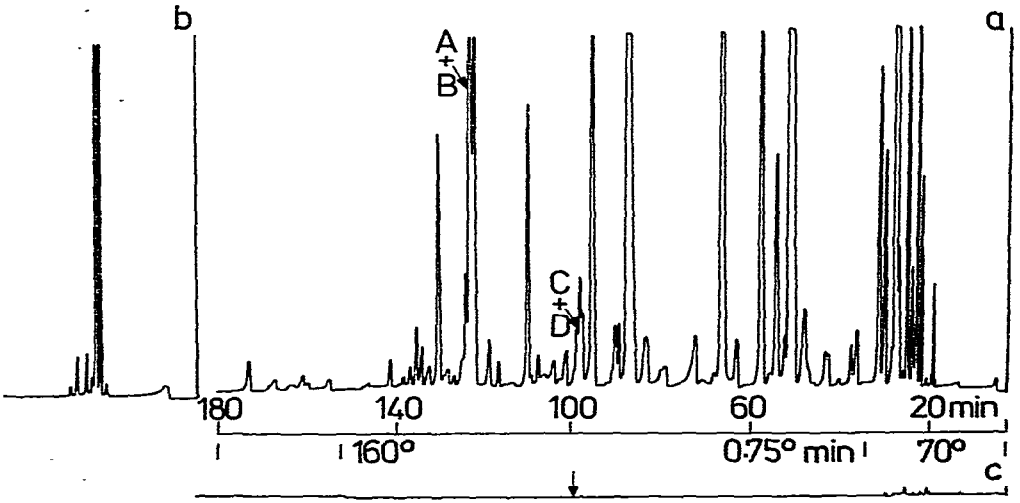

Fig. 4. Chromatograms of headspace volatiles of passionfruit juice. (a) Contents of first trap. (b) Contents of second trap, (c) GC trace of blank collection (50 l) on glass-distilled water (50 ml). GC conditions: sensitivity, 1×10^{-10} A.f.s.; temperature program, 70° for 32 min, 0.75°/min to 160°, then isothermal at 160°.

For the headspace collection of volatiles from solid materials, the arrangement in Fig. 2c has been used for the GC–MS examination of food-tainting volatiles emanating from certain rigid plastics used in the construction of domestic refrigerators[25], and that of Fig. 2b for the collection of volatiles from tainted packaging film[25] and from the foliage of *Lantana camara*. This plant is a serious weed pest on the east coast of Australia[26], and for investigations into its biological (insect) control, a GC method was required to differentiate quickly and to analyse the volatiles of the numerous taxonomic variants of this plant to which insect predators have shown selective preference. Fig. 5 shows the resultant chromatogram from a 51-l (21-h) collection made at ambient temperature (20°) of 150 g of freshly picked terminal branches obtained near the laboratory. Excellent resolution of nerolidol (E) and β-caryophyllene (D), compounds of taxonomic value, are shown as well as the monoterpenes (B) and sesquiterpene hydrocarbons (C). Many low-boiling compounds (A) shown here were not observed in the gas chromatogram of the conventional steam-volatile oil from this plant as these, along with other water-soluble compounds, would tend to be lost during oil recovery. Since only a few early peaks were evident in the second trap, this technique, besides having a low risk of thermal and oxidative changes, must present a composition of leaf volatiles close to that experienced by an insect attracted to the plant and in close proximity to the leaf surface.

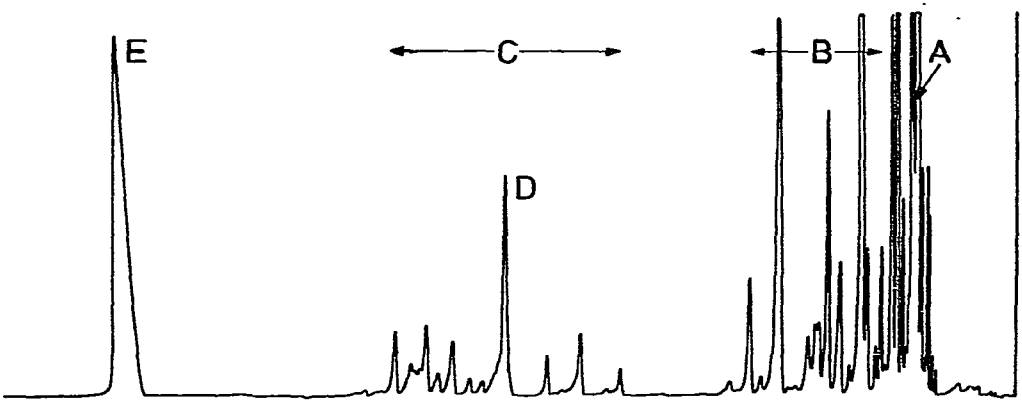

Fig. 5. Chromatogram of headspace volatiles of foliage of *Lantana camara*. GC conditions as in the legend to Fig. 4.

The high-speed sampling technique is being applied to the sampling of hydrocarbons in the C_5–C_{16} range and other compounds from Sydney's urban atmosphere as a part of an extended study of its smog problem. Collections of 50 l over $12^1/_2$ min, followed by GC examination on high-resolution glass SCOT columns, have been found suitable to follow the variation of individual compounds between selected sites and during the course of the day. Samples of 600 l have been used for identification by GC–MS. Some preliminary results have been reported[27]. At the Royal Children's Hospital, Melbourne, the same technique shows promise for fast large-volume collections of body volatiles from patients with metabolic disorders[28].

Extraction from aqueous solution

This technique has been applied in this laboratory as follows: (a) The recovery for GC–MS analysis of volatiles from steam distillates of canned vegetables with a "disinfectant" (chlorophenol) taint[25]. (b) The removal of water remaining in meat flavour concentrates[29] obtained by the technique of distillation of dilute aqueous distillates through a cold condenser. (c) A convenient means in quantitative GC for injecting microgram amounts of highly odorous substances (*e.g.*, the 3-alkyl-2-methoxypyrazines) which are best kept in dilute aqueous solution and extracted as required[16]. (d) In conjunction with vapour sampling it has provided an informative experimental approach to a study of the volatiles associated with the cooking of vegetables[12]. This has involved the extraction of volatiles from the aqueous condensate and headspace collections of the raw and cooked vegetable and of the residual cooking liquor. (e) Promising results have been obtained in the recovery of volatiles from brandy as illustrated by the following example: Ten ml of a 1 : 2 brandy–water mixture was passed through two Chromosorb 105 traps in series at 0.5 ml/min (Fig. 3), followed by purge drying of the traps for 2 h at 40 ml/min of nitrogen at 25°. The liquid eluate had a strong alcoholic aroma but the characteristic brandy aroma had been removed. Figs. 6a and b clearly show that the volatiles beyond the unresolved methylbutanols (A) have been retained almost completely by the first trap with the methylbutanols predominant in the second trap. The vast excess of ethanol and much of the other lower alcohols passed through the first trap and so avoided overloading of the capillary column.

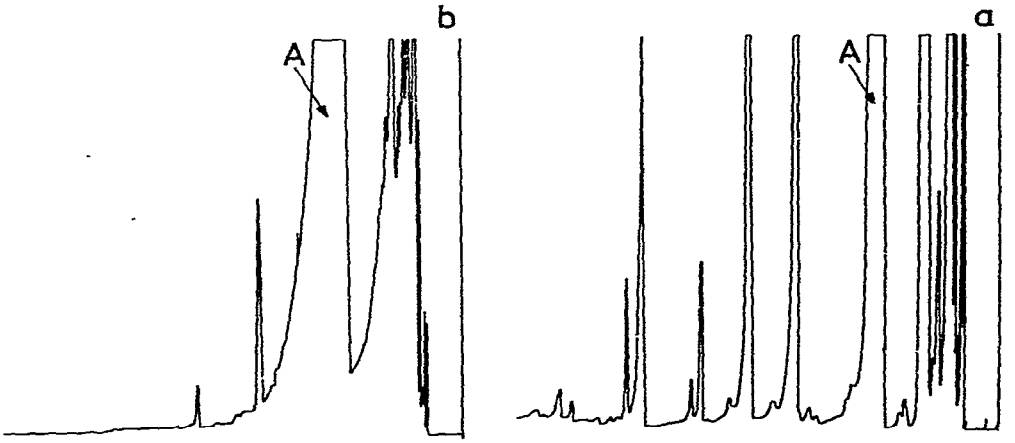

Fig. 6. Chromatograms of volatiles extracted from a brandy. (a) Contents of first trap. (b) Contents of second trap. GC conditions as in the legend to Fig. 4.

DISCUSSION

An attractive feature of the techniques described is that, with the same traps and injection procedure, an investigator has the flexibility when studying volatiles in aqueous systems, of sampling both from the headspace and from derived distillates or vacuum condensates. This could be a great advantage, for instance, in following the

formation and fate of aroma volatiles involved in the processing of many foodstuffs. It could also give greater scope for the GC method of estimating air/water partition coefficients[30], especially in extremely dilute solutions, such as is necessary with powerful odorants (*e.g.*, the 3-alkyl-2-methoxypyrazines).

Success with the direct extraction of volatiles from aqueous solution by Chromosorb 105 prompted the author to attempt similar extractions of the volatiles from passionfruit juice, the juice of raw bell peppers, and from a saline homogenate of rabbit anal glands, after clarifying these liquids by filtration or centrifugation. Results were not promising as little or no adsorption was apparent, particularly of the higher volatiles. A likely explanation is that high-molecular-weight materials (carbohydrates, proteins, pectins) still present in these liquids and known to be strongly retentive of volatiles during freeze drying[31] successfully compete with the porous polymer for the adsorption of the volatiles.

There is no evidence to date that Chromosorb 105 has any chemical reactivity, catalytic activity or specific adsorptive properties. This apparent inertness, its high retentive capacity, the relative ease of recovery of volatiles at moderate temperatures combined with the ability to collect both from headspace and aqueous solution make it a most versatile adsorbent for the concentration of volatiles from many sources.

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REFERENCES

1 L. D. Butler and M. F. Burke, *J. Chromatogr. Sci.*, 14 (1976) 117.
2 R. E. Naipawer, R. Potter, P. Vallon and R. E. Erickson, *Flavour Ind.*, (1971) 465.
3 O. G. Vitzthum and P. Werkoff, *J. Food Sci.*, 39 (1974) 1210.
4 V. Leoni, G. Puccetti and A. Grella, *J. Chromatogr.*, 106 (1975) 119.
5 A. Dravnieks, B. K. Krotoszynski and J. Whitfield, *Environ. Sci. Technol.*, 5 (1971) 1220.
6 K. E. Murray, J. Shipton and F. B. Whitfield, *Aust. J. Chem.*, 25 (1972) 1921.
7 *Chromosorb Century Series Polymer Supports*, Johns-Manville, New York, Pub. FF-202A, 1970.
8 *Chromosorb 106 and Chromosorb 107*, Johns-Manville, Denver, Pub. FF-215A, 1971.
9 R. van Wijk, *J. Chromatogr. Sci.*, 8 (1970) 418.
10 M. G. Neumann and S. Morales, *J. Chromatogr.*, 74 (1972) 332.
11 A. Dravnieks and C. A. Watson, *J. Food Sci.*, 38 (1973) 1024.
12 E. H. Ramshaw, to be published.
13 K. Sakodynskii, L. Panina and N. Klinskaya, *Chromatographia*, 7 (1974) 339.
14 M. Novotny, M. L. Lee and K. D. Bartle, *Chromatographia*, 7 (1974) 333.
15 W. Bertsch, R. C. Chang and A. Zlatkis, *J. Chromatogr. Sci.*, 12 (1974) 175.
16 K. E. Murray and F. B. Whitfield, *J. Agr. Food Chem.*, 26 (1975) 973.
17 E. Schulek and E. Pungor, *Mikrochim. Acta*, (1956) 1116.
18 G. Stanley and B. H. Kennett, *J. Chromatogr.*, 75 (1973) 304.
19 F. B. Whitfield and K. E. Murray, to be published.
20 F. B. Whitfield, G. Stanley and K. E. Murray, *Tetrahedron Lett.*, (1973) 93.
21 K. E. Murray, P. A. Bannister and R. G. Buttery, *Chem. Ind. (London)*, (1975) 973.
22 B. S. Goodrich, E. R. Hesterman, K. E. Murray and R. Mykytowycz, to be published.
23 C. W. G. Lee, J. S. Yu, B. B. Turner and K. E. Murray, *N. Engl. J. Med.* 295 (1976) 937.
24 P. J. Williams, personal communication.
25 F. B. Whitfield, unpublished results, 1975.

26 K. L. S. Harley, *PANS (Pest Artic. News Summ.)*, 17 (1971) 433.
27 M. F. R. Mulcahy, P. F. Nelson, M. Y. Smith, K. E. Murray and F. B. Whitfield, *Proceedings of Symposium, Occurrence and Control of Photochemical Pollution*, Clean Air Society of Australia and New Zealand, Sydney, 1976, paper IV.
28 D. M. Danks, personal communication.
29 K. E. Murray and R. J. Park, to be published.
30 R. G. Buttery, J. L. Bomben, D. G. Guadagni and L. C. Ling, *J. Agr. Food Chem.*, 19 (1971) 1045.
31 M. Karel, *Crit. Rev. Food Technol.*, 3 (1972) 359.