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HEADSPACE GAS ANALYSIS: THE ROLE AND THE DESIGN OF CONCENTRATION TRAPS SPECIFICALLY SUITABLE FOR CAPILLARY GAS CHROMATOGRAPHY

K. GROB* and A. HABICH
GC Laboratory, ETH Zürich, EAWAG, 8600 Dübendorf (Switzerland)
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SUMMARY

The wealth of recommended headspace techniques causes almost overwhelming evaluation problems. Some techniques work perfectly, and could hardly be improved upon. Many others suffer from their origin; they were developed for use with packed columns and have been improperly adapted to capillary gas chromatography. The critical point is the lack of conformity, particularly in terms of gas flow-rates, of the traditional concentration traps with the requirements of capillary columns. Important advantages (simpler technique, increased quantitative reliability) are gained with narrow-bore and open-tubular traps that permit instantaneous thermal desorption. Two types of such traps, both showing the dimensions of a piece of capillary column are presented and tested. The first type contains charcoal particles melted into the glass surface. Of particular importance, far smaller charcoal particles can be used than for packings. The second type contains extremely thick (12–15 μm) coatings of stationary phase. Some examples of applications show the present state of development. Intensive further development is necessary to provide the basis for a complete evaluation.

INTRODUCTION

There is hardly any special application of gas chromatography (GC) that is so well documented as headspace analysis. The last excellent review, with references to 240 papers, appeared in 1984[1] and several books and monographs[2–5] have been published. We refer to these as sources of both general and specialized information.

The recommended, and successfully used, techniques are so numerous that it is almost impossible not to be confused and to require a comprehensive survey. However, an analyst lacking a survey is in a poor position when he is looking for the ideal technique to handle a particular application. A primary source of confusion is that successful headspace techniques have been developed with *packed* columns. Naturally (but often incorrectly), these techniques have then been adapted to capillary GC without giving sufficient consideration to the important differences between the two column types. The lower success with adapted methods then led to widespread

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remedial work, frequently aimed at the most troubling peripheral details, rather than overcoming the central problems; hence the almost unlimited choice of recommended solutions. The fact that the choice includes both specialized and generally applicable techniques does not make the choice any easier.

We do not attempt here to contribute to a general clarification. Off-line techniques involving sampling and concentration steps clearly separate from the subsequent GC analysis are the most reliable, but not necessarily the most convenient. On-line techniques involving, for instance, direct connection between a concentration trap and a capillary column are most affected by erroneous ideas, and may, therefore, profit most from improvement. This is why we concentrate on the latter exclusively in this paper.

A GAP IN THE RANGE OF HEADSPACE TECHNIQUES

For our purpose, we can hardly avoid a superficial classification of headspace analyses from a purely technical point of view. We doubt, however, whether a reasonably condensed, comprehensive classification is feasible. A classification scheme may be arranged in a variety of ways, and there will always remain unclassifiable methods. Our presentation should be read with this problem in mind.

Full on-line techniques

By "full on-line" we mean that a given volume of headspace gas passes through the entire analytical system up to the GC detector without any interruption or venting/splitting. The simplest case is the direct (ideally on-column) injection of a headspace sample on to a capillary column. The next case involves a concentration trap permanently located before the column. The primary limitation of these techniques is the necessity to allow all sample gases, frequently including large amounts of water vapour, to pass through the system.

Off-line concentration with on-line desorption on to the column

In this group, the headspace sample is concentrated, in the laboratory or elsewhere, on a concentration trap, which is then connected directly to the capillary column. The transfer may be followed directly by the GC separation, or a cold trapping step in an inlet section, or in the whole column, may be inserted. Advantages are the flexibility of sampling and the simplicity of the method, which works without additional equipment, and with a minimized risk of artifacts and quantitative errors.

Techniques involving both off-line concentration and desorption

Whereas sampling may be identical with that in the previous group, the loaded concentration trap is connected to a separate cold trap, from which the sample is transferred on to the column as a last step. Most of the techniques used at present belong to this group, although wide technical variations exist. The single steps can be carried out completely separately, or they can be partly or totally combined by means of three-way valves, splitters, heated lines, etc., located between the functional parts. Advantages of this group are the great freedom in the selection and dimensions of the single parts and in the selection of the operational parameters such as sample type and sample volume.

Techniques involving liquid desorption from a concentration trap

This group contains the most distinct off-line techniques, as sampling and analysis are totally independent. Typical features are maximum qualitative and quantitative reliability, but combined with increased labour. It is evident from the literature that most analysts tends to avoid liquid desorption. The techniques of this group are not used according to their merits.

This paper is limited to the second group and, within this group, to the most direct version, omitting any re-trapping on the column. This extremely simple technique is almost missing from the literature and may, therefore, be termed a gap in the range of techniques used. We wish to show that, based on strict adaptation of the headspace sampling to the requirements of capillary GC, the technique may become rather attractive.

INSUFFICIENTLY KNOWN PARAMETERS OF HEADSPACE ANALYSIS

In the last few years, important progress has been achieved in the field of capillary GC. Elementary mechanisms of injection processes have, finally, been understood, and new potentials in column technology have been demonstrated. It is not surprising that this progress may create advances in headspace analysis. Some aspects that do not seem to be commonly known are discussed below.

Geometrical considerations

Direct thermal transfer from a concentration trap on to a capillary column has for a long time been a very tempting idea, technical simplicity being the most attractive aspect. However, the literature does not reflect this interest, owing to a lack of practical success. There are even good reasons to suspect that many of the off-line techniques (third group) have been developed, and are used, because the on-line technique worked unsatisfactorily, lacked quantitative reliability and suffered from chromatographic problems.

To describe the basic difficulty, let us consider a practical example. An efficient trap designed for the concentration of dilute headspace volatiles may consist of a 3 mm I.D. tube, packed with a solid adsorbent, which may be directly connected to a 0.3 mm I.D. capillary column. The carrier gas may pass through the column at a flow-rate of 50 cm/sec. As the cross-section of the trap is 100 times greater than that of the column, the linear flow-rate in the trap is only 5 mm/sec. This extremely low flow-rate is, particularly at the elevated temperature of desorption, heavily counteracted by diffusion. Whereas the carrier flow is supposed to push the desorbed sample vapour down to the column, diffusion tends to distribute the vapour upwards, and may even cause it to leave the adsorbent packing at the wrong end. At best, the net effect is severly retarded vapour transfer. Under less favourable conditions, the transfer may remain incomplete, even after an excessively prolonged transfer period. This problem is rarely discussed in the literature, although a clear description was presented in 1978[6]. The situation corresponds to a splitless injection involving the transfer of a large vapour cloud on to a narrow-bore capillary column (where the problem was first studied[7]). Obviously, incomplete sample transfer is an unacceptable basis for quantitative analysis.

The problem may be attacked in several ways. A splitter inserted between the

trap and the column eliminates the necessity to run both the trap and column at the same volumetric flow-rate. At the cost of a severe loss of sample, a suitable flow through the trap could be selected.

Cooling a column section or the whole column or inserting a separate cold trap may overcome peak broadening as a consequence of excessively slow desorption. However, it has no influence on the possibly incomplete sample transfer due to the low flow-rate through the concentration trap.

The safest way to solve the entire problem is to transfer the sample on to a separate cold trap that is not connected to the column. Provided that the cold trap can be run at a sufficiently high flow-rate, rapid and complete desorption can be ensured. However, this approach is technically more demanding.

The solution that has received least attention so far is to reduce the dimensions of the concentration trap to such an extent that it is automatically run with a sufficiently high flow-rate when it is directly connected to the capillary column. In practice, this means reducing the trap dimensions to those of the column. The on-line system designed in this way works so perfectly and rapidly that no additional functions between desorption and separation have to be considered. This provides direct headspace analysis, which, among standard GC techniques, is best compared with on-column injection.

Chromatographic requirements

A basic requirement to be fulfilled by the headspace technique is that the separation efficiency of the subsequent capillary GC analysis should not be reduced. In other words, the ultimate step of the headspace sampling procedure has to concentrate the sample as a sufficiently narrow band in the inlet section of the column. Generally, thermal desorption from a concentration trap occurs with a typical delay and, therefore, produces a prolonged sample band. The same occurs with splitless injection, where solvent trapping is the most common reconcentration principle. As demonstrated 10 years ago[8], solvent trapping by co-injecting a solvent can be combined successfully with headspace sampling. However, its obvious limitations (obscuring effects of solvent, solvent impurities) preclude its introduction as a common technique. Consequently, cold trapping is the only remaining reconcentration method.

Whereas desorption with extremely rapid heating to avoid excessive band broadening has attracted an impressive amount of attention and effort, it is surprising that optimization of the geometric and flow conditions has been widely studied and realized only for adsorption and concentration, and for desorption is virtually missing from the literature, although concentration traps can easily be designed with an optimum geometry providing desorption without any need for a reconcentration step, even without sophisticated rapid heating.

Dissolution versus adsorption as a trapping mechanism

The literature offers a virtually complete theoretical and experimental treatment of the processes that occur on a concentration trap. The commonly used traps contain solid adsorbents. Liquid coatings as an alternative are frequently mentioned, but have been studied less in detail. In a somewhat misleading way, the two trapping materials are presented with too close a relationship, for instance by terming the

corresponding processes physical and chemical adsorption. It may be a consequence of this exaggerated equalization that the essential difference between the two trapping mechanisms seems not to be commonly appreciated.

Quantitative adsorption studies are regularly carried out with pure substances. Breakthrough volumes obtained this way may be irrelevant in the case of mixtures because of displacement processes. We showed in 1971[9] that light components of a mixture may disappear completely from a trap on which they are efficiently trapped as pure substances. In contrast, no displacement occurs on dissolution traps. Light substances may even be trapped more efficiently by a coating that has already dissolved (trapped) a heavy substance.

Obviously, practical interest in coated traps has been modest in the past owing to their low retention as based on the previously available thin coatings. With the presently feasible very thick coatings[10], dissolution traps may receive much greater attention.

Sample alteration by thermal desorption

The negative role of pyrolysis and other structural alterations owing to thermal desorption can hardly be over-emphasized. As long as such influences are not excluded, one has constantly to be aware of artifacts in perfect chromatograms, which do not provide any warning concerning the possibly wrong information that they convey.

The extent of thermal alteration depends on temperature, duration and surface catalytic effects. It is well known that the surface activity of charcoal, which partly causes the extremely large loading capacity, is also responsible for catalytic effects. It may be less well known how efficiently such effects can be reduced by optimizing the trap geometry with the aim of minimizing the residence time of sensitive substances in the heated trap.

Organic polymers, particularly Tenax, are commonly known for their catalytic inertness. However, in our experience, the greatest inertness is easily obtained with apolar coatings produced the same way as inert high-temperature columns.

NEW TYPES OF CONCENTRATION TRAPS

Basic considerations

The discussion of parameters that characterize the design of concentration traps shows the direction in which the design has to be developed. The prevailing interest is in a trap that permits very rapid desorption. The expected advantages are the following: complete sample transfer with corresponding maximum reliability of quantitative analysis (analogy with on-column injection); extreme simplicity of technique thanks to the removal of a reconcentration step producing a narrow starting band; and a decreased desorption temperature and/or a reduced residence time of the sample in the desorber, both reducing the extent of possible thermal alterations.

The primary parameter influencing the speed of desorption is the carrier gas flow-rate. Provided the trap is directly connected to the column, the improved design has to follow two principles: the internal width of the trap has to approach that of the column to provide a similarly high linear flow-rate (remember that reducing the trap I.D. from 3.0 to 0.3 mm results in a 100-fold change in flow-rate); as an adsor-

bent packing in a small-bore tubing would produce an excessively high flow resistance, the trap has to be open tubular, *i.e.* carrying the trapping material as a layer on the internal walls.

Consequently, a primary consequence of the new design is a strongly reduced trap size including a correspondingly reduced amount of trapping material. Therefore, the critical point of such traps is expected to be retention (resp. loading capacity).

Trapping materials

Fig. 1 shows three tested traps on scale. The packed charcoal trap (CPT) is not included as a recommended version, but rather for comparison with the open types. It was prepared with an I.D. of 0.5 mm because it is difficult to produce it narrower with a still reasonably low flow resistance. For the same reason, it can hardly be made with charcoal particles smaller than *ca.* 30 μm in diameter. For the open trap (COT), there is theoretically no lower limit of particle size. This is an advantage, as desorption from small particles is considerably accelerated. At present, for purely experimental reasons, the lower limit of particle size is 1–2 μm.

We have found that covering the internal walls with charcoal over a length of 10–15 mm is, in terms of retention, sufficient for most applications. Lengthening the carbon layer to increase retention is, of course, feasible.

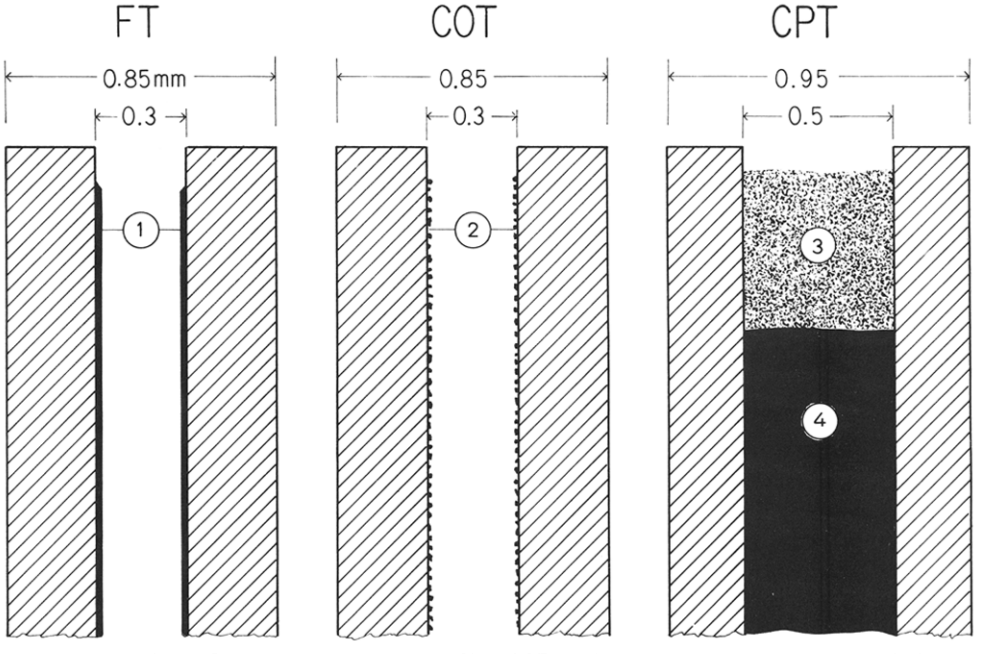

Fig. 1. End sections of the three trap types: FT, film; COT, carbon, open; CPT, carbon, packed. Correct geometric proportions, dimensions in millimetres. 1, Immobilized thick coating (14 μm); 2, charcoal particles, diameter 10 μm, melted into the glass surface; 3, glass-wool plug; 4, carbon particles, diameter 30 μm, kept between two glass-wool plugs. The traps, as designed for Carlo Erba injectors and ovens, are 80 mm long, with the lower 20 mm (non-coated) used for connection to the column. If the heated length of 60 mm is fully used, the FT contains 1.0 mg of stationary phase and the COT 0.15 mg of 10-μm charcoal particles or 0.25 mg of 20-μm charcoal particles.

The COTs we have prepared so far have been made by melting the carbon particles into the glass surface. This process yields an undesirable, additional activity that is easily removed by rinsing with 20% HCl, followed by regular persilylation in a sealed glass tube.

We are still experimenting with different preparation methods. Therefore, we do not feel able yet to give detailed preparation directions. It seems, however, that the selection of trapping material has been sufficiently resolved. With regard to retention, flow resistance, and feasibility, there is hardly any alternative to charcoal as an adorbent. In contrast, a basic alternative is a coating.

Film traps (FTs)

A given amount of a stationary phase shows far less retention for the same solute than the same amount of charcoal under identical conditions. Therefore, the critical detail of small FTs is sufficient retention.

The traps we have tested are coated with 12–15 μm immobilized PS-255 films over a length of 60 mm. They contain roughly 1 mg of stationary phase. Further optimization of the trap inner diameter and film thickness has to be made with the aim of still increasing retention.

As we have decided to use our regular Carlo Erba split/splitless injector without any modification, the active (coated) trap length can hardly be increased over 60 mm. Of course, lengthening the trap is by far the most practical way to increase retention. We do not doubt that many intermediate solutions can be realized between our short trap and an entire thick-film column. For the latter, there is already practical experience[11].

The preparation of FTs presents no additional problems to the established technique of preparing very thick coatings[10].

Manipulation

For headspace sampling, a trap is connected to a gas-tight syringe and a measured gas volume is sucked through the trap. The gas has to hit the front of the trapping material which will be next to the column during desorption. We have found the flow-rate of sampling to be less critical than expected. As a rule, we suck the sample at a rate of 5 ml/min, although 20 ml/min causes only a slight loss of retention, even for FTs. The loaded traps can be stored; FTs should be stoppered at both ends.

The Carlo Erba injector that we use as a desorber has a 80 mm long cavity, and ends in a 20 mm long, small-bore section reaching into the oven, and carrying at the lower end the column sealing elements. Provided the connection between trap and column is situated above the column seal, it does not have to be absolutely gas-tight, as the pressure is the same outside and inside the tubing. Further, provided the connection remains close to the column sealing ferrule, it has only to withstand the oven temperature. Under these conditions, a simple gliding PTFE connnection is perfectly suitable. One half of a 10–12 mm length of shrinkable PTFE tubing (No. 24) is permanently shrunk on to the non-coated end of the trap and the other half is shrunk on a slightly greased capillary end so as just to glide over the column inlet. The capillary column is mounted in such a way that the inlet protrudes over the sealing ferrule just by the length of the free part of the PTFE connection.

The desorption procedure is as follows. The injector (desorption) temperature

is set, the carrier flow is turned off, the column seal is opened and the column entrance is lowered into the oven. A trap possibly still connected to the column from the foregoing run is now removed. Depending on the column dimensions, a sufficient waiting time is observed, within which the carrier back-flow leaving the column inlet comes to a complete stop. The free PTFE end of the loaded trap is pushed on to the column inlet to yield a butt-to-butt connection between the column and the trap. The carrier gas is turned on again, the trap is shifted into the injector (*i.e.*, against the flowing carrier gas) and the column seal is fastened. Under suitably selected conditions, the analysis can immediately be started without considering the desorption process. The trap may remain inside the injector up to the next run.

Typical features of this procedure are rapidity, simplicity and the need for no modification of the gas chromatograph or additional equipment, provided the injector is of suitable design and the oven dimensions permit convenient manipulation.

EXAMPLES OF APPLICATION

As our laboratory has no application activities, the examples have little relation to specialized practice. The conditions were selected to show typical aspects of the technique, rather than to demonstrate an ideal analysis in a particular field.

Samples containing substances of extreme volatility

In the development of small traps, there are conflicting interests. On the one

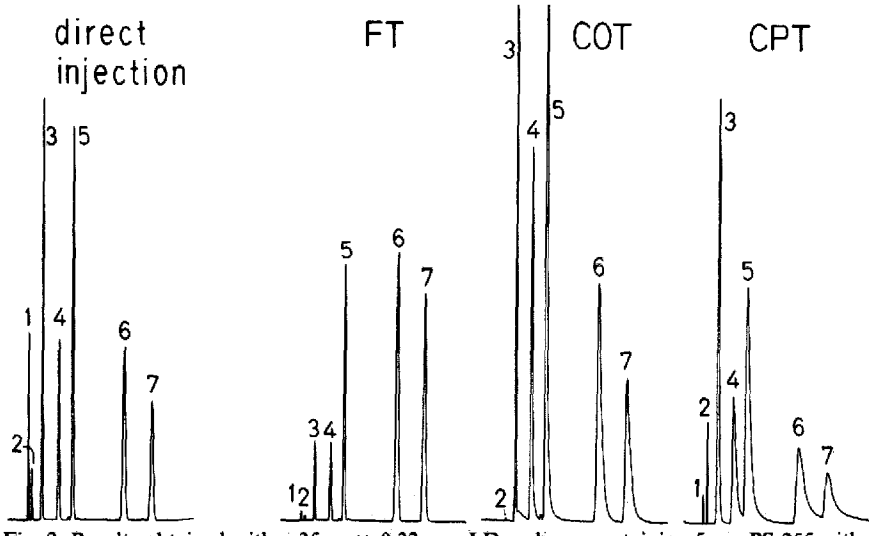

Fig. 2. Results obtained with a 35 m × 0.32 mm I.D. column containing 5 μm PS-255 with nitrogen as the carrier gas (20 cm/sec), isothermal at 28°C. Concentrated gas mixture: to 1 liter of N_2 were added technical gases: 2 ml of fuel gas, 2 ml of propane, 3 ml of butane; liquids: 2.5 μl of isopentane, 2.5 μl of *n*-pentane. 1, Methane; 2, ethane; 3, propane; 4, isobutane; 5, butane; 6, isopentane; 7, *n*-pentane. Direct injection: 0.2 ml of concentrated gas; splitting ratio, 1:5. Traps according to Fig. 1. Diluted gas mixture: 100 ml of concentrated mixture added to 1 l of N_2, 2 ml of diluted gas sucked through the traps within 30 sec. Desorption (injector) temperature, 120°C; attenuation, × 64. Note that the peak broadening with COT and CPT would also be observed with a reversed direction of carrier gas flow, *i.e.*, with the adsorbent front first hit by sample gas directed towards the carrier supply.

hand, there is the convincing conformity of a small trap with a capillary column, particularly with respect to thermal desorption. On the other hand, there is the possible problem of insufficient retention. We were primarily interested, therefore, in observing the behaviour of small traps in contact with the most volatile hydrocarbons (see Fig. 2). The aim was to test them under extreme conditions; we did not expect them to be suitable for the determination of methane and ethane (compare the behaviour of far larger Tenax traps in contact with this sample).

The results may first be checked for breakthrough effects. Studying breakthrough is simple and consistent; two traps connected with one of their PTFE connections are inserted between sample and syringe, and any substances that break through the first trap are found in the second trap. It is useful to select a second trap with particularly high capacity (it does not have to be identical with the first trap).

All three types of traps retained *n*-pentane completely. On the FT the first breakthrough occured with isopentane (*ca.* 15%). The COT showed complete retention down to isobutane and *ca.* 10% loss of propane. On the CPT the first loss (*ca.* 30%) was with ethane. In summary, the retention behaviour shows the expected relationship with the amount of charcoal and with the typically lower retention of a coating, respectively.

It is very interesting, however, to check some details. As stated, the COT retains propane almost completely. In contrast, it traps ethane almost 50 times less efficiently. In other words, ethane suffers a 50-fold discrimination with respect to propane. Below ethane there is complete breakthrough; above propane there is complete trapping. The FT behaves very differently. The strongest discrimination in the entire spectrum is not even 3-fold. However, almost identical discrimination is observed between methane and isopentane. In other words, the FT retains some methane, which the COT, regardless its far higher overall retention, is unable to do.

The explanation follows directly from what is said under *Dissolution versus adsorption as a trapping mechanism*. If the charcoal surface is occupied by propane and heavier substances, all lighter molecules have no chance to be adsorbed; hence the sharp limit where discrimination starts. In the absence of heavier substances, methane and ethane are retained, but are displaced as soon as heavier substances enter the trap. In contrast, an apolar coating containing dissolved pentanes is at least as efficient a solvent for lighter substances as is the pure coating. Therefore, the observed relatively small discriminations are in direct relation with the vapour pressures of the pure substances over their solution in the coating.

A different subject of comparison is the rate of thermal desorption. The comparison is straightforward. Desorption from the FT occurs almost instantaneously and all peaks have the same width as obtained by direct (split) injection. From the COT isobutane is the first substance to show slight peak broadening, which means that isobutane, and also all heavier substances, are desorbed with an observable delay. On the CPT the corresponding limit is shifted to propane. We emphasize that the conditions (injector temperature 120°C!) were selected to favour the demonstration. Of course, perfect chromatograms from COT and CPT can easily be obtained after just raising the desorption temperature.

Samples containing heat-sensitive compounds

Many naturally occurring terpenes are known for their thermal lability. We

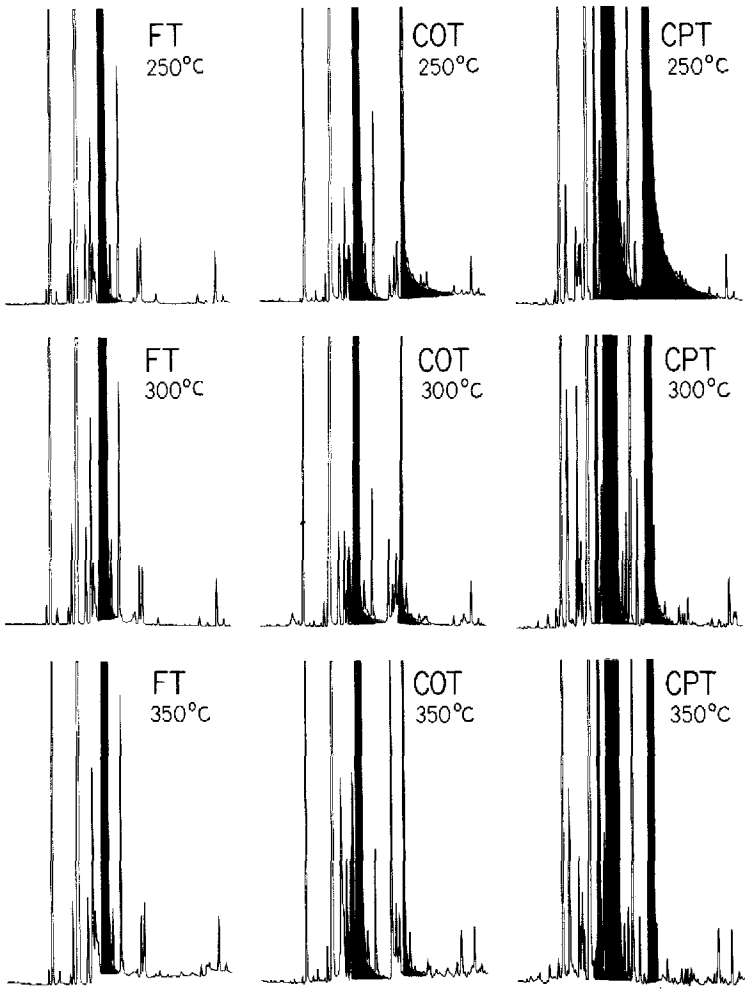

Fig. 3. Headspace of fresh orange juice. Column, 30 m × 0.32 mm I.D., 0.6 μm SE-54; carrier gas, hydrogen (0.5 m/sec); attenuation, ×64; temperature programme, immediately after connecting the trap (with the column at room temperature), from 40 to 160°C at 4°C/min. Traps according to Fig. 1. A 2-ml volume of headspace gas sucked through the traps within 30 sec. Desorption at 250, 300 and 350°C. At all temperatures, no thermal alteration occurs on FT. Alteration increases from COT to CPT and with increasing desorption temperature (see also Fig. 5). Headspace components other than limonene (limonene and its transformation products are indicated in black) are also transformed, producing a more complex chromatogram. At all temperatures, desorption is sufficiently rapid from FT. COT and CPT show delayed desorption at lower temperatures (see also Fig. 4).

selected the headspace gas over freshly pressed orange juice as a typical terpene-containing mixture. A major component is limonene, which may be converted thermally into *p*-menthene and *p*-cymene[12].

By means of two traps in series, we first determined the maximum headspace volume to be sampled on to an FT without any breakthrough. The first losses occurred with 3.5 ml. We used 2 ml as a standard volume. Fig. 3 shows headspace

analyses from the three trap types after desorption at three temperatures. The last large peak in each chromatogram may serve as an indicator of the actual amount of headspace gas sampled for each run. The black peaks represent limonene and its heat-transformation products.

A first, immediately evident result is the strong similarity of runs with FT. Even at 350°C no heat transformation (of limonene) is visible. From a different point of view, one can observe that increasing the desorption temperature causes no harm, but also brings no advantage. We have found that even desorption at 200°C yields an identical, perfect chromatogram.

A second result is the tailing of the major substances desorbed from charcoal, and also the reduced tailing due to the increased desorption temperature. It can be seen also that the tailing is less pronounced with the open-tubular trap (COT). This simply shows that desorption from charcoal is not sufficiently rapid at 250°C. As shown by Fig. 4, however, a relatively mild reconcentration step overcomes the problem. The only difference between the run with COT at 250°C in Fig. 3 and the left-hand run in Fig. 4 is a 2-min waiting period between the start of desorption and the start of temperature programming in Fig. 4. The difference provides a cold trapping effect produced by purely chromatographic means.

A third result is the appearance of heat transformation products after desorption from charcoal. Note that only limonene and its products are represented in black. Other terpenes also yield new substances; hence the more complex chromatograms obtained from charcoal. It is also evident that more transformation occurs on

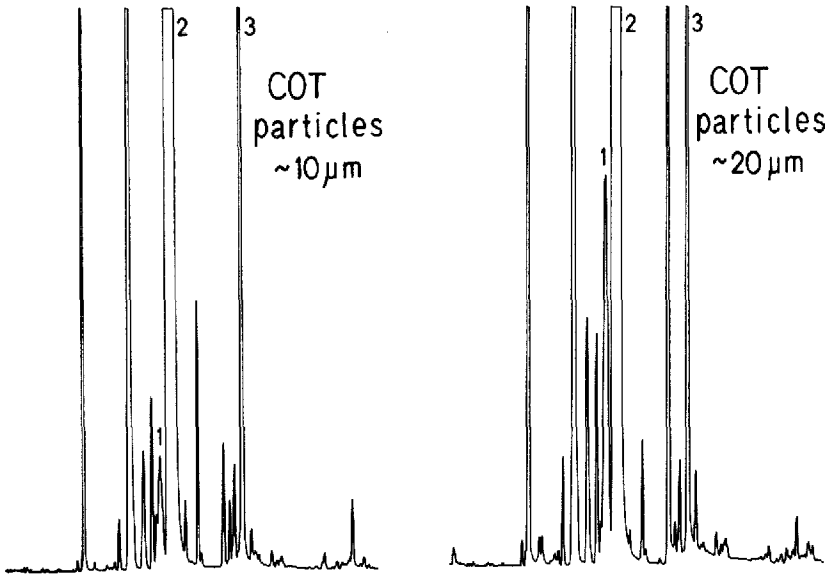

Fig. 4. Repeat of orange headspace analysis with a 2-min waiting period at room temperature (cold trapping effect) before starting temperature programming. Left: same COT as used in Fig. 3, *i.e*, chromatogram directly comparable to middle chromatogram, upper line. Note the strongly improved peak shape. Right: COT with particle diameter doubled. Primary effect: more heat alteration. Secondary effect: slightly more tailing. 1, *p*-Menthene; 2, limonene; 3, *p*-cymene. Other transformation products not identified.

the CPT, owing to the longer residence time of the sensitive substances in the desorber. In a special way this is confirmed by Fig. 4, in which only the first chromatogram was obtained from the same COT as used for Fig. 3. The second chromatogram in Fig. 4 was run under identical conditions, but with desorption from a COT with larger charcoal particles. Although the injector temperature was only 250°C, the chromatogram is very similar to that in Fig. 3 obtained at 350°C. Hence doubling the particle diameter produces increased heat transformation at 250°C, which with the smaller particles occurs only at 350°C. The reason is hindered diffusion of trapped molecules from a larger adsorbent particle, which means a prolonged residence time in the desorber.

Owing to high attenuation, Fig. 3 may produce incorrect quantitative information concerning the relationship between different substances in the same chromatogram, as well as concerning the extent of transformation effects in relation to the desorption temperature. The tailing after slow desorption gives the impression of large peak areas. As shown by Fig. 5, the relative amounts of transformation products increase considerably with increase in the desorption temperature. Both effects of increased desorption temperature, reduced tailing and more pronounced thermal alteration, are visible.

In summary, the typical drawbacks of charcoal, slow desorption and the risk of thermal alteration, are confirmed. However, we have also shown that both effects can be counteracted efficiently by using open-tubular carbon traps with small charcoal particles.

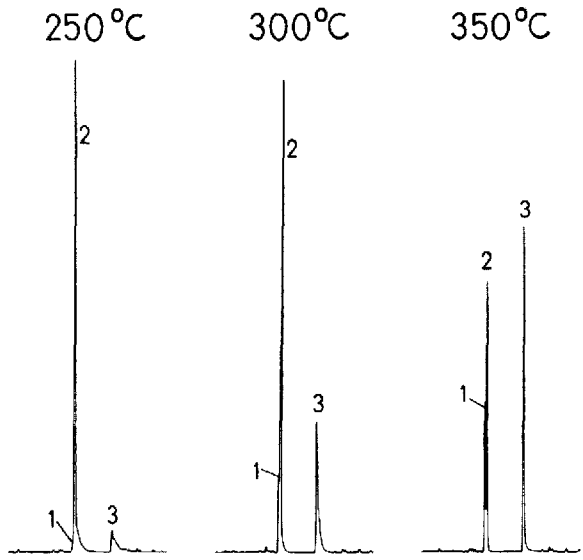

Fig. 5. Analysis of pure limonene headspace. Column, 15 m × 0.32 mm I.D., 0.8 μm PS-255; temperature programme, from 40 to 120°C at 6°C/min; carrier gas, hydrogen (60 cm/sec); attenuation × 128; limonene diluted 1:1000 in XF-1105; CPT; 2 ml of headspace gas; desorption at 250, 300 and 350°C. 1, *p*-Menthene; 2, limonene; 3, *p*-cymene. The figure demonstrates increased thermal transformation with increasing desorption temperature. In Fig. 3, this increase is obscured by changing peak shapes. Accelerated desorption (decreasing tailing) is also visible.

Samples containing adsorption-sensitive components

Rapid desorption from a concentration trap may be hindered when the sample tends to undergo strong adsorption. Wine headspace, with its various alcoholic and other polar components, seemed to be a realistic sample for testing our traps.

As with the orange juice, we started by checking the breakthrough behaviour

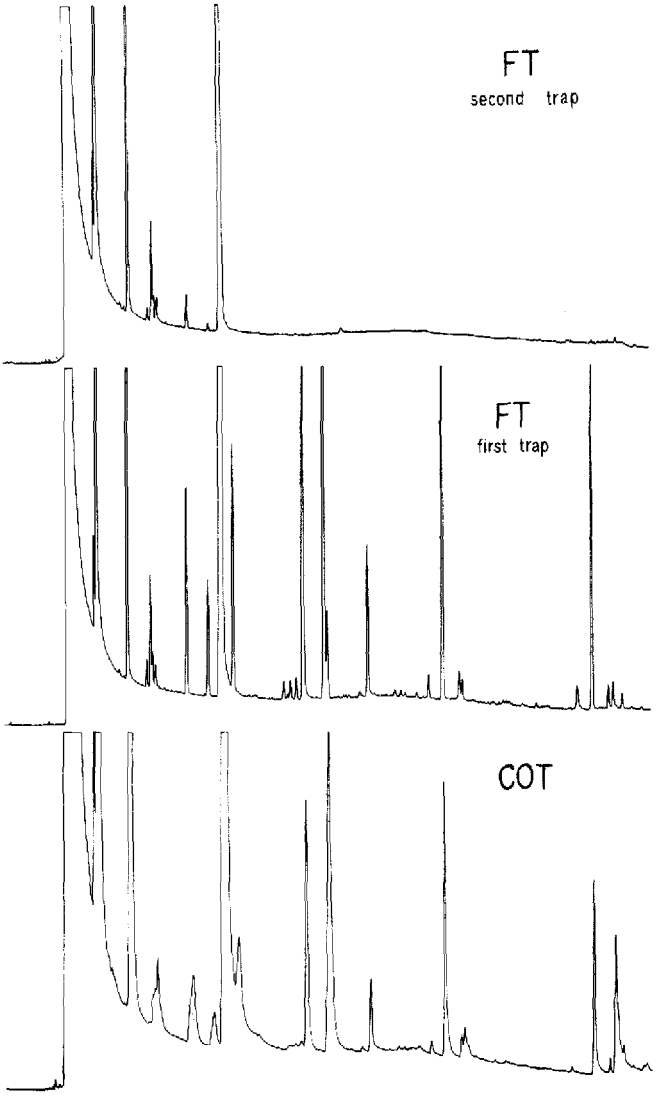

Fig. 6. Analysis of wine headspace. Column, 25 m × 0.30 mm I.D., 0.4 μm OV-1701; carrier gas, hydrogen (0.5 m/sec); temperature programme, 2 min at 40°C, increased from 40 to 70°C at 3°C/min and from 70 to 150°C at 6°C/min; attenuation, × 8; injector temperature, 250°C. Traps according to Fig. 1. A 4-ml volume of wine headspace was sucked through two FTs in series, and, separately, through one COT. The substances eluted from the second FT (top) had passed the first trap. The FT (middle) shows perfect desorption characteristics. The relatively polar components of wine headspace show delayed desorption (broadened peaks) at 250°C from a COT (bottom).

of an FT. Whereas for the orange headspace we selected the conditions to exclude any breakthrough, we did not attempt to achieve full trapping of ethanol. With a sample volume of 1.5 ml, the FT lost methanol, ethanol and some acetaldehyde; no other losses were detected. The analyses shown in Fig. 6 were obtained with 4.0 ml of headspace. As shown by the first chromatogram (from the second filter in series), there was considerable breakthrough of volatiles. As a rule, such double-trap tests should be run whenever the analytical conditions are not completely known. It is then up to the specialist in the field to judge the importance of the observed breakthrough effects.

Desorption on to the column was carried out in the same most direct way as for the foregoing examples. The middle chromatogram, from the first filter, shows that the FT handles the more polar components of wine headspace in the same perfect way as less polar substances.

This did not apply to the charcoal traps. As shown by the lower chromatogram, desorption at 250°C from a COT was too slow. Of course, it can be efficiently accelerated by increasing the desorption temperature. However, this would have little practical meaning, as thermal alterations would then inevitably become troublesome.

SUMMARIZED EVALUATION OF SMALL TRAPS

Headspace analysis with high resolution GC is still in a conflicting situation. The analysis is run on capillary columns, whereas the sampling techniques originate from GC with packed columns (the traps are short packed columns). The problems arising from this basic nonconformity have led to various sophisticated and demanding techniques, a good deal of which might be obviated by sampling techniques that are specifically developed for use with capillary columns.

Regardless of some very strong points, charcoal may not be the ideal adsorbent for small traps, owing to the slow response to heat and to its catalytic activity. It is still unclear, however, how far these drawbacks may be overcome by using even smaller charcoal particles.

The favoured trap is the wall-coated type, which is unequalled in terms of immediate response and inertness. It is also attractive because of the lack of displacement effects. Its weak point is a critically low retention. Future developments should clarify the importance of this aspect.

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