Trapping efficiencies of capillary cold traps for C_2–C_{10} hydrocarbons

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ABSTRACT

The trapping performance of four different capillary cold traps (deactivated, coated, Tenax-TA and Chromosorb 101 packed traps) for C_2–C_5 *n*-alkenes, isoprene, benzene, toluene, *p*-xylene, *o*-xylene, mesitylene, α-pinene, β-pinene, 1,2,4-trimethylbenzene and 1,2,3-trimethylbenzene were determined over the temperature range -20 to $-180°C$. All the hydrocarbons except ethylene were found to be retained by all the traps at different temperatures, but only the Chromosorb 101 capillary trap retained ethylene, and then not completely. The coatings were found to increase the trapping efficiency for the higher hydrocarbons ($\geqslant C_6$), whereas the packings increased the trapping efficiency for all compounds (C_2–C_{10}). A linear relationship was found between the boiling point of the compound and its maximum trapping temperature. The flow-rate of the carrier gas (10–60 ml/min) was found to affect the trapping efficiency of the C_2–C_4 hydrocarbons.

INTRODUCTION

Sampling by adsorption, with subsequent thermal desorption, is widely used for the sampling and analysis of very low concentration volatile organic compounds (VOCs) in ambient air. The whole sample can be analysed in this way, and the best sensitivity of analysis can be obtained. During the process of thermal desorption, the desorbed analytes invariably require reconcentration in a cold trap before being injected on to the GC capillary column for analysis. This is necessary for two main reasons: preconcentration of the sample and solute band concentration. Two types of cold trap are used with different dimensions: packed and capillary cold traps. Capillary cold traps are more compatible with a capillary column in the gas chromatograph than the packed traps. The latter may result in incomplete sample transfer from the trap

to the capillary column because of the differences in the flow-rate required for complete and rapid desorption from a packed trap and the flow-rate through a capillary column in the gas chromatograph [1,2]. Many different capillary traps are available, coated, uncoated, packed and unpacked, etc., and these are all becoming more widely used with the rapidly increasing use of capillary analytical columns [3–14].

Trapping efficiency is one of the most important properties of cold traps. It may vary with the trapping temperature, flow-rate of the carrier gas, coating and packings inside the capillary and the length of the trap etc. Although the commonly used cooling medium, liquid nitrogen, is inexpensive, some capillary traps may not trap some hydrocarbons at all, especially the lighter ones, or cannot trap completely, even at the lowest temperature achievable with liquid nitrogen ($-196°C$). This may lead to errors in the sampling and analysis of VOCs in ambient air, or reduce the sensitivity of analysis. Hence trapping efficiency should be studied as a function of trapping temperature and flow-rate for different

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capillary traps in order to select suitable capillary traps for particular applications. To date little work has been done in this area.

In this work, trapping efficiencies for the C_2–C_{10} hydrocarbons were investigated as a function of both trapping temperature and flow-rate for four different commercially available capillary traps. The relationships between the maximum trapping temperature and the boiling point for each compound are also discussed.

EXPERIMENTAL

Gas chromatographic measurements were made using a Hewlett-Packard 5890 Series II gas chromatograph with flame ionization detection (FID). The carrier gas was helium and the make-up gas was nitrogen. The GC capillary column used was an Ultra 2 (cross-linked 5% phenyl–methylsilicone) of 25 m × 0.2 mm I.D. with a film thickness of 0.33 μm (Hewlett-Packard). The injector temperature was 220°C and the detector temperature 300°C. The sample vapours were injected into the carrier gas stream by means of a 1-ml gas-tight syringe via a Chrompack thermal desorption cold trap (TCT) injector, which was interfaced with the gas chromatograph. The injected vapours were then carried by helium through a heated (230°C) empty Perkin-Elmer stainless-steel tube to the capillary trap, which was cooled by liquid nitrogen. The range of trapping temperatures which can be controlled by the TCT injector unit is from 0 to −180°C. However, a trapping temperature as low as −190°C could sometimes be reached when the temperature on the control unit was a minimum. The trap was then flash-heated to 220°C at 15°C/s for 1 min, and the trapped vapours injected on to the GC capillary column in the splitless mode.

The following hydrocarbons were selected for study, based on their contributions to the formation of ozone in the troposphere [15–17]: C_2–C_5 n-alkenes, isoprene, benzene, toluene, p-xylene, o-xylene, mesitylene, 1,2,4-trimethylbenzene, 1,2,3-trimethylbenzene, α-pinene and β-pinene. Mixtures of hydrocarbons were prepared by diluting 1000 ppmv Scotty standard calibration mixtures of n-alkenes or injecting known volumes of liquid hydrocarbon into a 1-l flask which had been purged with nitrogen for 3 min. The flask and syringes were kept warm at

55 ± 5°C in order to prevent vapour condensation and adsorption on surfaces. The amount of hydrocarbons injected on to the column for analysis was 10–20 ng.

Four different capillary cold traps (obtained from Chrompack) were investigated: (i) a deactivated uncoated fused-silica capillary (40 cm × 0.53 mm I.D.), catalogue number 4076 [18]; (ii) a fused-silica capillary (40 cm × 0.53 mm I.D.) coated with CP-Sil 8 CB (film thickness 5 μm), catalogue number 16274 [19]; (iii) a fused-silica capillary (40 cm × 0.53 mm I.D.) coated with CP-Sil 8 CB (film thickness 5 μm) and packed with Tenax-TA (length 15 mm), catalogue number 16425 [19]; and (iv) a fused-silica capillary (40 cm × 0.53 mm I.D.) coated with CP-Sil 8 CB (film thickness 5 μm) and packed with Chromosorb 101 (length 15 mm) catalogue number 16426 [19].

RESULTS AND DISCUSSION

Effect of trapping temperature on trapping efficiency
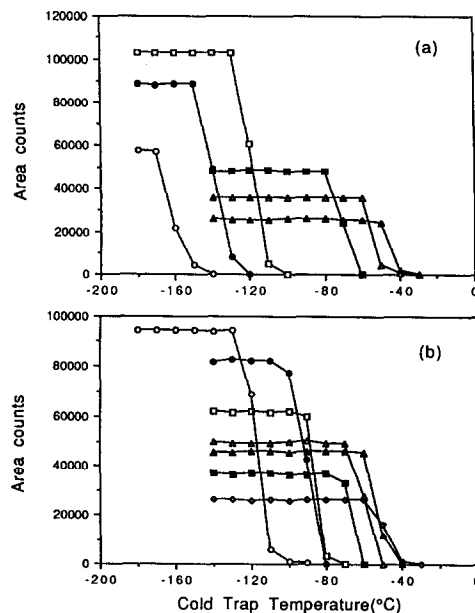
The trapping efficiencies of the four different cap-

Fig. 1. Trapping curves of the deactivated capillary cold trap for different hydrocarbons. (a) ○ = Propylene; ● = 1-butene; □ = 1-pentene; ■ = p-xylene; △ = β-pinene; ▲ = 1,2,3-trimethylbenzene. (b) ○ = Isoprene; ● = benzene; □ = toluene; ■ = o-xylene; △ = α-pinene; ▲ = mesitylene; ◇ = 1,2,4-trimethylbenzene.
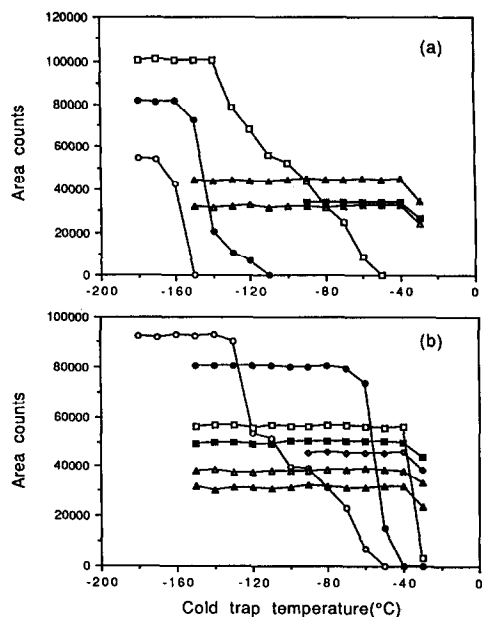
Fig. 2. Trapping curves of the coated capillary cold trap for different hydrocarbons. (a) ○ = Propylene; ● = 1-butene; □ = 1-pentene; ▲ = mesitylene; △ = 1,2,3-trimethylbenzene; ■ = β-pinene. (b) ○ = Isoprene; ● = benzene; □ = toluene; ■ = p-xylene; △ = o-xylene; ▲ = 1,2,4-trimethylbenzene; ◇ = α-pinene.
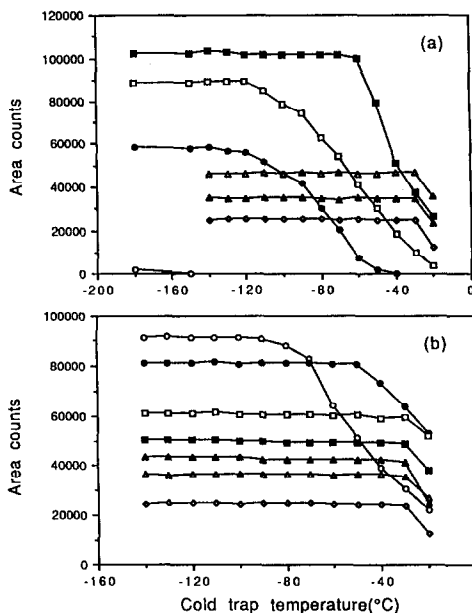
Fig. 3. Trapping curves of the Tenax-TA capillary cold trap for different hydrocarbons. (a) ○ = Ethylene; ● = propylene; □ = 1-butene; ■ = 1-pentene; ◇ = 1,2,3-trimethylbenzene; △ = α-pinene; ▲ = β-pinene. (b) ○ = Isoprene; ● = benzene; □ = toluene; ■ = p-xylene; △ = o-xylene; ▲ = mesitylene; ◇ = 1,2,4-trimethylbenzene.

illary cold traps for the C_2–C_{10} hydrocarbons were determined over the temperature range -20 to $-180°C$ by injecting the same amount of organic mixtures each time. The results obtained are shown in Figs. 1–4. The plateau of each trapping curve indicates the complete trapping of each compound. The maximum trapping temperatures at which compounds can be trapped completely were derived from Figs. 1–4 and are listed in Table I for each trap and each compound.

It can be seen from Table I that the maximum trapping temperatures for the C_6–C_{10} hydrocarbons of the different capillary traps generally have the following order: deactivated capillary trap < coated capillary trap < Tenax-TA capillary trap ≈ Chromosorb 101 capillary trap; and for the C_2–C_5 hydrocarbons, deactivated capillary trap ≈ coated capillary trap < Tenax-TA capillary trap < Chromosorb 101 capillary trap. This indicates that coating a capillary with a liquid film which can increase its trapping capacity may lead to higher trapping

efficiencies for the heavier hydrocarbons ($\geq$ C_6). However, the trapping efficiencies for the lighter hydrocarbons (C_2–C_5) cannot be improved by a liquid film coating. In fact, ethylene cannot be trapped at all in these two traps. This may be because the coatings behave as solids at low temperatures [20,21]. The capillary traps with packings (Tenax-TA or Chromosorb 101) showed higher trapping efficiency than the non-packed traps (both coated and uncoated), especially for the lighter hydrocarbons.

Although the trapping efficiencies of the Chromosorb 101 capillary trap for the C_5–C_{10} hydrocarbons are generally similar to those of the Tenax-TA capillary trap, the trapping efficiencies of the former trap for the lighter hydrocarbons (C_2–C_4) are higher than those of the Tenax trap on which ethylene is very inefficiently trapped. This is due to the higher adsorption capacity of Chromosorb 101 (BET specific surface area < 50 m²/g) than that of Tenax-TA (BET specific surface area 20 m²/g). The Chromosorb 101 capillary trap is the only one of the four
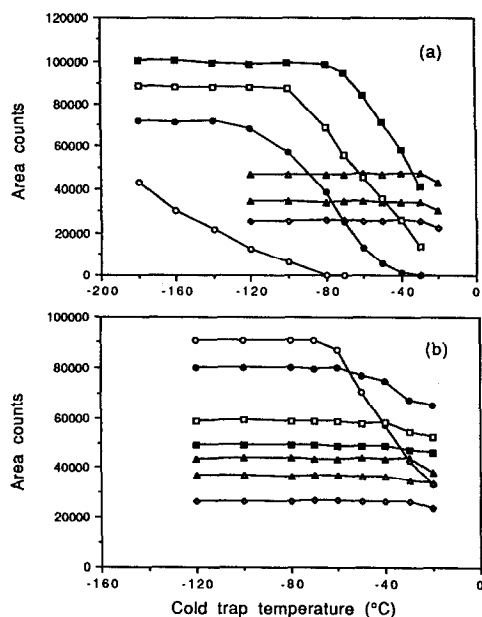
Fig. 4. Trapping curves of the Chromosorb 101 capillary cold trap for different hydrocarbons. (a) ○ = Ethylene; ● = propylene; □ = 1-butene; ■ = 1-pentene; ◇ = 1,2,4-trimethylbenzene; △ = α-pinene; ▲ = β-pinene. (b) ○ = Isoprene; ● = benzene; □ = toluene; ■ = p-xylene; △ = o-xylene; ▲ = mesitylene; ◇ = 1,2,3-trimethylbenzene.

traps investigated which can trap ethylene with a significant efficiency. However, as can be seen from Fig. 4b, the trapping curve for ethylene did not reach a plateau, even at the lowest temperature, which indicates incomplete trapping of ethylene on the Chromosorb 101 trap. Hence stronger adsorbents, such as Carbotrap (100 m^2/g) or Chromosorb 106 (800 m^2/g), are needed for packing capillary traps in order to trap the most volatile hydrocarbons completely.

It is interesting to note from Table I that although the trapping efficiency of the deactivated capillary trap for the C_9–C_{10} hydrocarbons is improved by using a coated capillary trap, there is a very slight improvement by using Tenax-TA packing, and no further improvement at all by using Chromosorb 101 packing. This may indicate that there may be an upper limit for the maximum trapping temperature of −30°C, i.e., the maximum trapping temperature for the C_2–C_{10} hydrocarbons cannot be greater than the upper limit (−30°C) even when the capillary cold trap with the highest trapping efficiency is used.

It can also be seen from the trapping curves in Figs. 1–4 that the trapping efficiency of the uncoated deactivated capillary trap for the C_2–C_{10} hydrocarbons dropped sharply once the maximum trapping temperature for each compound was exceeded.

TABLE I

MAXIMUM TRAPPING TEMPERATURES (°C) OF DIFFERENT CAPILLARY TRAPS FOR C_2–C_{10} HYDROCARBONS

| Hydrocarbon	B.p./m.p. (°C)	Capillary cold trap			
		Deactivated	Coated	Tenax-TA	Chromosorb 101
Ethylene	−104/−169	−	−	−	−180
Propylene	−47.7/−185.2	−180	−180	−140	−120
1-Butene	−6.3/−185.3	−150	−160	−120	−100
1-Pentene	30/−138	−130	−140	−70	−80
Isoprene	34/−146	−130	−140	−90	−70
Benzene	80.1/5.5	−110	−70	−50	−60
Toluene	110.6/−95	−100	−40	−30	−40
p-Xylene	138.3/13.3	−80	−40	−30	−40
o-Xylene	144.4/−25.2	−80	−40	−30	−40
α-Pinene	155.5/−62	−70	−40	−30	−30
Mesitylene	164.7/−44.7	−60	−40	−30	−30
β-Pinene	166/−61	−60	−40	−30	−30
1,2,4-Trimethylbenzene	168/−44	−60	−40	−30	−30
1,2,3-Trimethylbenzene	175.5/−25	−60	−40	−30	−30
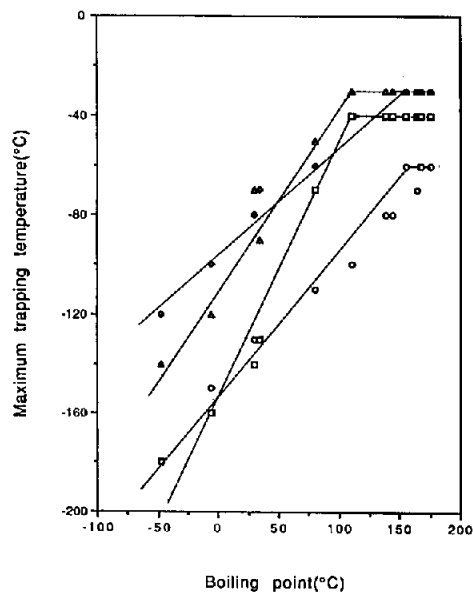
Fig. 5. Variation of the maximum trapping temperature with boiling point for different traps. ◇ = Chromosorb 101; △ = Tenax-TA; □ = coated; ○ = deactivated trap.

Fig. 6. Variation of trapping efficiency of the deactivated capillary trap with flow-rate for different hydrocarbons. ○ = propylene; ● = 1-butene; □ = 1-pentene; ■ = isoprene; △ = benzene; ▲ = mesitylene; ◆ = 1,2,4-trimethylbenzene; ◇ = β-pinene.

For the coated and packed capillary traps, the trapping efficiencies decreased gradually as the maximum trapping temperature was exceeded. This shows the important roles in improving the trapping efficiency played by the coatings, especially the packings inside the capillary traps which absorb or adsorb compounds.

As the volatility of the hydrocarbon increases, so the maximum trapping temperature was found to decrease. This is shown in Table I and Fig. 5, where the boiling point of each compound is plotted against the maximum trapping temperature for each capillary cold trap. It can be seen from Fig. 5 that as the boiling point increases, i.e., the hydrocarbon becomes less volatile, the maximum trapping temperature generally increases linearly for all of these four capillary traps until a plateau is reached, which is due to the upper limit of the maximum trapping temperature.

Effect of flow-rate on trapping efficiency

The effect of the flow-rate of the helium carrier gas through the cold trap on the trapping efficiency was investigated for the deactivated, Tenax-TA and
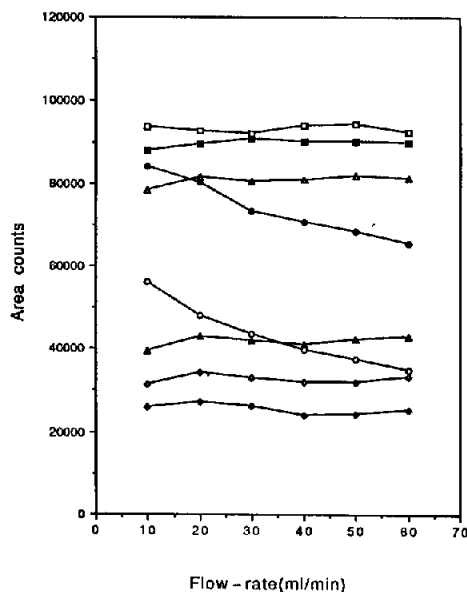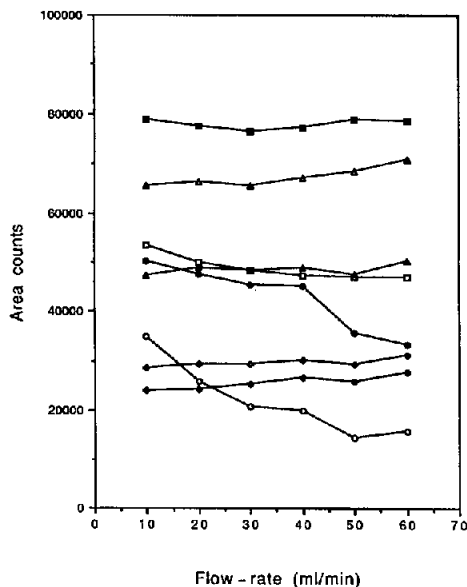

Fig. 7. Variation of trapping efficiency of the Tenax-TA capillary trap with flow-rate for different hydrocarbons. ○ = propylene; ● = 1-butene; □ = 1-pentene; ■ = isoprene; △ = benzene; ▲ = toluene; ◇ = o-xylene; ◆ = α-pinene.
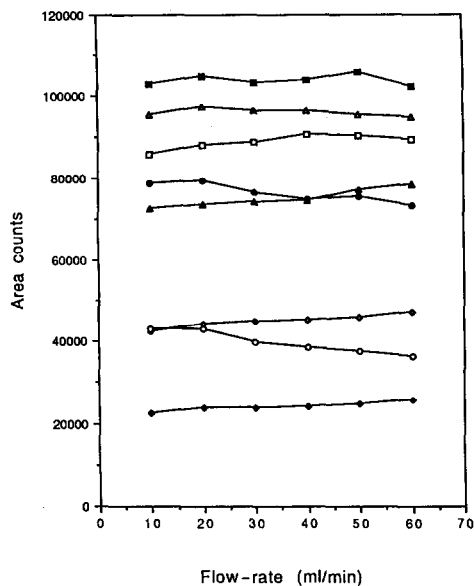
Fig. 8. Variation of trapping efficiency of the Chromosorb 101 capillary trap with flow-rate for different hydrocarbons. ○ = Ethylene; ● = propylene; □ = 1-butene; ■ = 1-pentene; △ = isoprene; ▲ = benzene; ◇ = p-xylene; ◆ = 1,2,3-trimethylbenzene.

Chromosorb 101 capillary cold traps, by injecting the same amount of hydrocarbon mixtures into each trap at −180°C and varying the flow-rate from 10 to 60 ml/min.

Representative plots of area counts against flow-rate for the deactivated trap, the Tenax-TA trap and the Chromosorb 101 trap are shown in Figs. 6, 7 and 8, respectively. It can be seen that the trapping efficiencies of all these traps for the heavier hydrocarbons ($\geqslant C_5$) are generally insensitive to the flow-rate. However, breakthrough did occur for the C_2–C_4 hydrocarbons at higher flow-rates, especially for the deactivated and Tenax-TA traps, which have less affinity for these very volatile hydrocarbons. The trapping efficiencies of the Chromosorb 101 trap dropped only slightly for ethylene and propylene at higher flow-rates, owing to the relatively higher adsorption capacity of Chromosorb 101. Hence care should be taken when using capillary traps to keep the flow-rate of the carrier gas constant, especially for the analysis of these very volatile hydrocarbons.

Blanks of capillary cold traps

One of the primary areas of concern when sampling and analysing very low concentrations of vol-
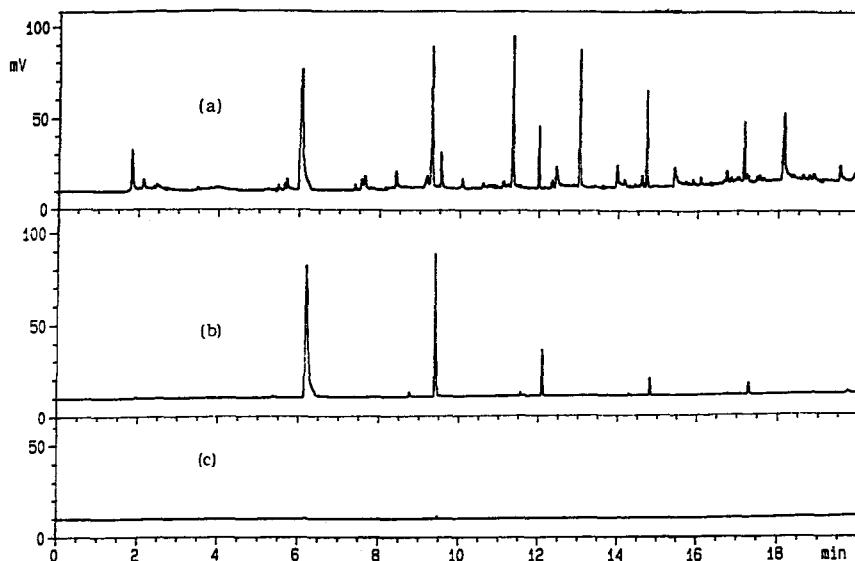

Fig. 9. Blank chromatograms of different capillary cold traps. GC oven temperature programme: 40°C (2 min) to 200°C (2 min) at 10°C/min. TCT: desorption temperature, 230°C; desorption time, 4 min; injection temperature, 220°C; injection time, 1 min. (a) Chromosorb 101 capillary trap; (b) coated and Tenax-TA capillary traps; (c) deactivated capillary trap.

atile organic compounds in ambient air is the analytical detection limit. This is affected not only by the blank levels of the adsorbents used, but also by the blank levels of the capillary cold traps. It is therefore much better wherever possible to use those adsorbents with the lowest blank levels for sampling VOCs in ambient air. Similarly, the capillary cold trap packings with the lowest blank values will give the lowest analytical detection limits.

The blank levels of all these four capillary cold traps, conditioned overnight at 240°C, were determined under the same conditions. Typical chromatograms are shown in Fig. 9. The blank chromatogram of the coated capillary cold trap is similar to that of the Tenax-TA capillary trap, and is not shown in Fig. 9. It can be seen that the deactivated capillary cold trap is very clean, whereas the coated, Tenax-TA and Chromosorb 101 capillary traps are very "dirty". The blank peaks from the coated and Tenax-TA capillary traps, shown in Fig. 9b, are from the leakage of the coated liquid film of the capillary. The blank peaks from the Chromosorb 101 capillary, shown in Fig. 9a, are from both leakage of the coated film and bleeding from the Chromosorb 101 packing. Hence, although the trapping efficiency of the capillary cold trap may be improved by using coated film or packing, the detection limit may be sacrificed to some extent. For the analysis of $\geqslant C_3$ hydrocarbons in ambient air, therefore, the deactivated capillary cold trap should be used. However, in order to analyse the very volatile hydrocarbons, e.g., ethylene, it is suggested that capillary cold traps be prepared by packing uncoated capillary with "clean" and stronger adsorbents, such as Tenax and Carbotrap, and that rigorous cleaning procedures be used to condition the trap.

It should be mentioned that better blank levels of the capillary traps may be obtained if a lower capillary trap desorption temperature is used, but the oven desorption temperature and desorption time will also affect the blank levels of capillary traps because the upper end of the capillary traps interfaced with the desorption oven is heated by the heat wave from the oven. In environmental analysis, the oven desorption temperature is usually above 240°C for more than 5 min in order to desorb the analytes from the adsorbents with the highest efficiency.

CONCLUSIONS

For the application of capillary cold traps to atmospheric samples, it is very important to select suitable cold traps, because some capillary cold traps may not trap the compounds of interest. The results of this work show that deactivated and coated capillary traps cannot trap ethylene at all, even at the lowest trapping temperature ($-180°C$), and similarly the Tenax-TA capillary trap is also unable to trap ethylene. The Chromosorb 101 capillary trap can retain ethylene at $-180°C$, but not completely. Although coatings inside the capillary can increase its trapping capacity, this has almost no effect on the trapping efficiency compared with the uncoated capillary trap, especially for the $C_2–C_5$ hydrocarbons. Packings inside the capillary can increase not only the trapping capacity but also the trapping efficiency of the capillary trap. It is noted that there is a linear relationship between the boiling point of the compound and its maximum trapping temperature.

Although the flow-rate of the carrier gas (10–60 ml/min) has no effect on the trapping efficiency of the capillary traps for the $\geqslant C_5$ hydrocarbons, breakthrough does occur for the $C_2–C_4$ hydrocarbons at higher flow-rates. Therefore, care should be taken to keep the flow-rate constant in the application of capillary cold traps.

Although the coated and packed capillary cold traps may have improved trapping capacity and trapping efficiency compared with the uncoated, their blank levels are usually very high owing to leakage from the coating or bleeding from the adsorbents. This will adversely affect sensitivity of the method. Therefore, for the analysis of $\geqslant C_3$ hydrocarbons in ambient air, a deactivated capillary cold trap should be used. In order to trap the very volatile hydrocarbons, e.g., ethylene, it is suggested that uncoated capillary cold traps with a packing of preconditioned "clean" and stronger adsorbent, such as Tenax and Carbotrap, be used.

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