

CHROM. 15,327

Note

How efficient are capillary cold traps?

J. W. GRAYDON* and K. GROB*

Swiss Federal Institute for Water Resources and Water Pollution Control (EAWAG), CH-8600 Dübendorf (Switzerland)

(Received September 8th, 1982)

Cold traps of various types have been used for many years for the recondensation of solute vapours at the inlet of gas chromatographic columns. With large vapour volumes this recondensation narrows the solute band, thus ensuring maximum resolving power of the column. Cold traps have proved especially useful for the determination of trace organic compounds desorbed thermally from solid adsorbents. This application is becoming popular in environmental analysis, and the need for a simple and efficient cold trap is apparent.

Cold traps described in the literature vary from simple capillary trapping loops immersed in coolant^{1–3} to microprocessor-controlled cryogenic focusers⁴. One assumption common to this previous work is that cold trapping with liquid nitrogen can quantitatively trap even the lightest organic solutes (except methane) from a stream of carrier gas. It is our experience that this is not so. In the course of developing a method for thermal desorption from activated carbon filters used in the closed-loop stripping method⁵, we have observed significant breakthrough of volatile organics from a simple capillary cold trap immersed in liquid nitrogen.

EXPERIMENTAL

Thermal desorption was carried out by direct insertion of activated carbon filters into the heated injector port of a Carlo Erba 4160 gas chromatograph interfaced to a Finnigan 4021C mass spectrometer and an Incos 2000 data system. Care was taken to have the air flushed from the carbon before the filter reached the heating zone. Initially, our trap consisted of a coiled loop of uncoated persilylated glass capillary, of which 25 cm was immersed in liquid nitrogen. One end was inserted in the injector as usual and the other was connected with PTFE shrink tubing to a 40 m × 0.32 mm I.D. SE-54 column. To support the resolution of very volatile organics (Freons, vinyl chloride, etc.), a very thick (2.3 μm) film of SE-54 was selected. With this configuration, an inlet pressure of 1 atm of helium gave a flow-rate of 3 ml/min during the 7-min desorption period. A more detailed description of the equipment, materials and procedures is given elsewhere⁶.

* Present address: Department of Anesthesia, Stanford University, Medical Center, Stanford, CA 94305, U.S.A.

RESULTS

Initial results showed extremely poor recovery of the most volatile components of the standard mixture (Table I) used to evaluate the method. Mass spectral acquisition during the desorption process (with the liquid nitrogen trap in place) revealed large, broadened peaks for these components. Peak-area comparisons showed that for the ten most volatile compounds of the mixture (dichlorodifluoromethane to chloroform), an average of 59% of the material escaped recondensation. On an individual compound basis, we observed breakthrough ranging from 87% for the most volatile component (dichlorodifluoromethane) to 4% for the least volatile (tetrachloroethylene).

TABLE I

REFERENCE MIXTURE USED FOR THE EVALUATION OF VARIOUS COLD TRAP DESIGNS

The efficiency of the cold trap is shown for 400 ng each of components 1-5 and 200 ng each of components 6-17 stripped from 200 ml of blank water and adsorbed on 5 mg of activated carbon⁵. Desorption: 200°C; He, 3 ml/min; 7 min. Chromatography: liquid nitrogen removed after 7 min 45 sec; column, 40 m × 0.32 mm I.D., 2.3 μm SE-54 immobilized; 3 min at 25°C, then programmed at 4°C/min to 160°C.

No.	Compound	Molecular ion (<i>m/z</i>)	Quantitation ion (<i>m/z</i>)	Retention time (min:sec)	Proportion retained by coated cold trap (%)	Proportion retained by packed cold trap (%)
1	CCl ₂ F ₂	120	85	9:25	14	99
2	CH ₃ Cl	50	50	10:05	17	99
3	ClHCCH ₂	62	62	10:30	17	99
4	CH ₃ Br	94	94	11:30	21	99
5	ClH ₂ CCH ₃	64	64	11:35	28	99
6	Cl ₂ CCH ₂	96	96	14:42	77	100
7	Cl ₂ CH ₂	84	86	15:28	73	100
8	ClHCCHCl	96	96	17:10	ND	ND
9	Cl ₂ HCCH ₃	98	63	17:52	ND	ND
10	CHCl ₃	118	85	20:00	93	100
11	Cl ₃ CCH ₃	132	99	21:44	96	100
12	ClC ₄ H ₉	92	63	21:56	97	100
13	CCl ₄	152	117	22:40	ND	ND
14	C ₂ HCl ₃	130	134	25:00	97	100
15	CHBrCl ₂	162	85	25:25	96	100
16	C ₆ H ₅ CH ₃	92	65	29:02	96	100
17	C ₂ Cl ₄	164	170	31:35	96	100

Typically, breakthrough was most pronounced during the first moments of trapping, and was followed by a rapid increase in trapping efficiency. We attributed the increase to the coating of the internal capillary surface with condensed material. Consequently, we tried to avoid the initial breakthrough by using a coated (0.15 μm SE-54) and longer (38 cm) trap. The results from the modified trap were essentially the same as from the original (Table I). Breakthrough of dichlorodifluoromethane averaged 86% and that of tetrachloroethylene averaged 4%. The importance of coating the trap has been emphasized by Rijks *et al.*⁷, who used dry-ice-methanol as a

trapping coolant. The missing effect of the coating in our work is easily explained by the lower trapping temperature at which all practical coatings behave as solids.

Consequently, the only remaining option was to increase the rate of collision between vapour molecules and the solid surface. A 2-cm section of a 15 cm \times 0.32 mm I.D. glass capillary trapping loop was packed with 120–140-mesh persilylated Chromosorb W. On this trap we observed almost complete recondensation even for the most volatile compounds in our standard mixture.

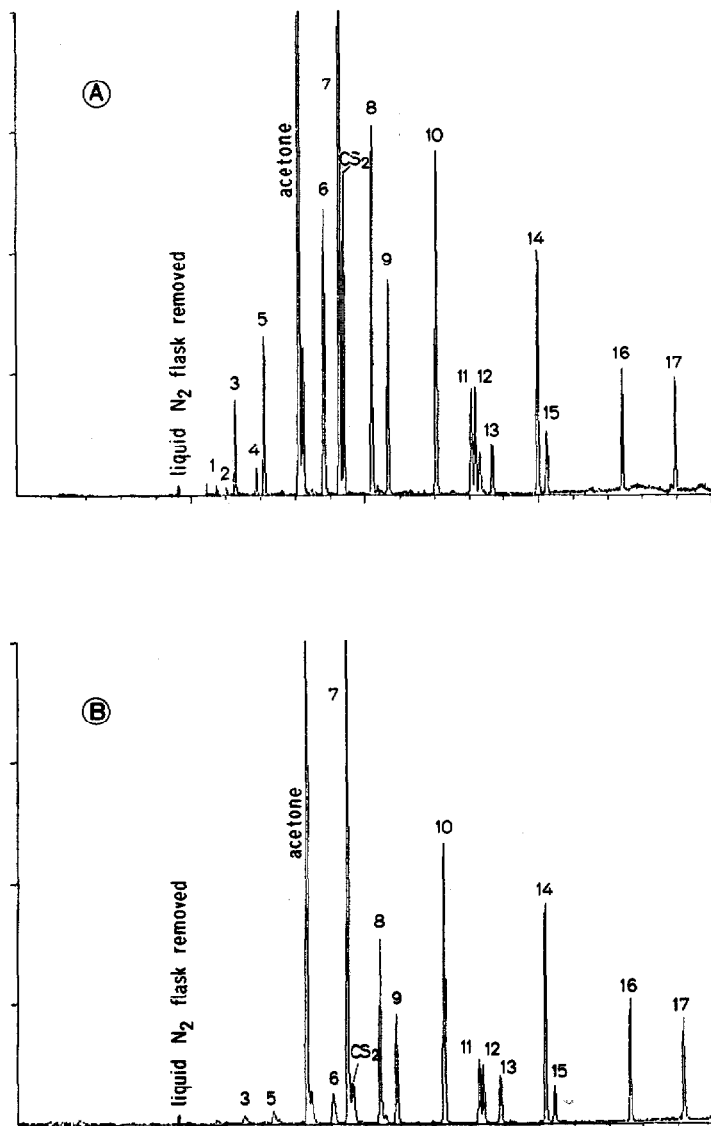


Fig. 1. Comparison of chromatograms of the reference mixture (substances numbered as in Table I) thermally desorbed from activated carbon on to (A) the packed capillary cold trap (A) and (B) the coated capillary cold trap. The acetone and carbon disulphide peaks are artifacts of the carbon filter washing procedure.

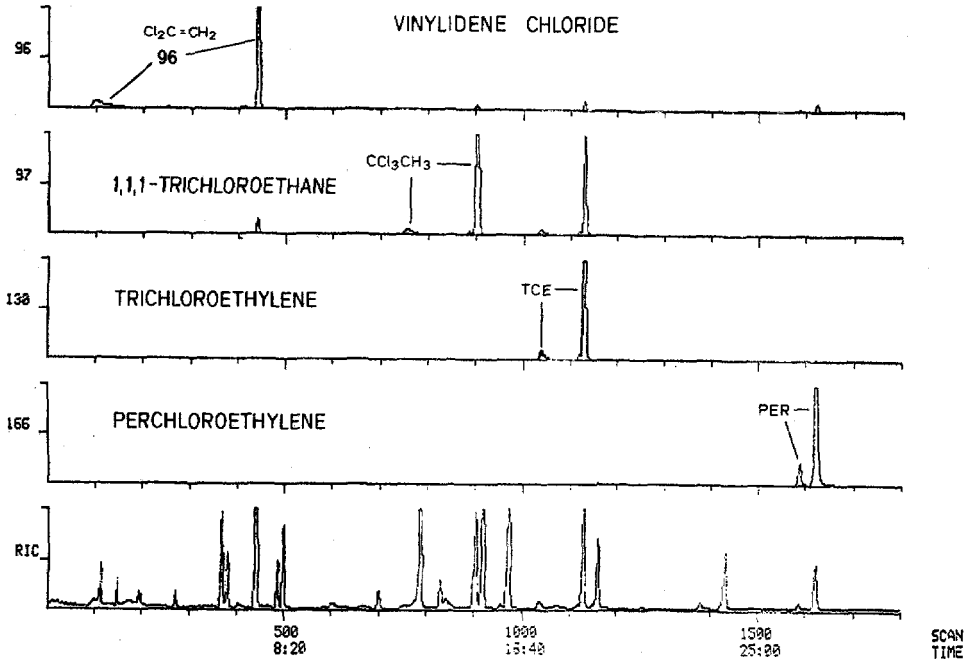


Fig. 2. Mass chromatograms and reconstructed ion chromatogram showing breakthrough peaks and main peaks for vinylidene chloride, 1,1,1-trichloroethane, trichloroethylene and tetrachloroethylene. Typically, the time separating the two peaks decreases with increasing k' .

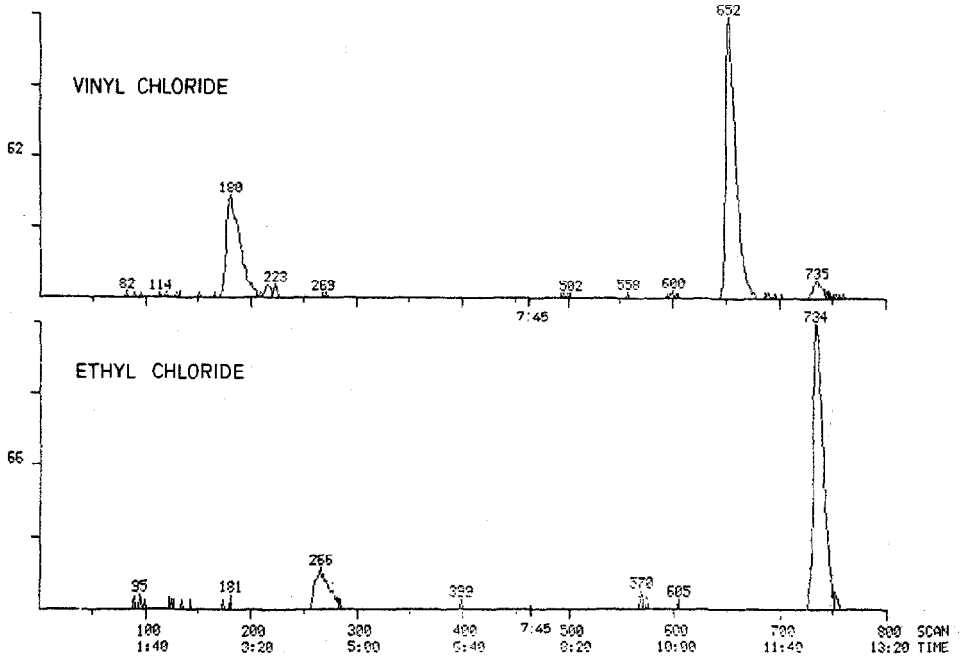


Fig. 3. Mass chromatograms showing the breakthrough of vinyl chloride and ethyl chloride. Note that both breakthrough peaks were eluted before the liquid nitrogen was removed at 7 min 45 sec.

Typical examples showing breakthrough effects, and their dependence on the volatility of the substance and the design of the cold trap, are presented in Figs. 1–3.

DISCUSSION

Given the magnitude of the losses through the cold trap that we have observed, we find the attention given to the problem in the literature to be surprisingly inadequate. Rijks *et al.*⁷ studied the efficiency of a capillary cold trap as a function of trap length, temperature and film thickness for a standard mixture of volatile hydrocarbons. They found insufficient trapping of hydrocarbons lighter than *n*-heptane when using a trap that was not long enough (< 20 cm), not cold enough (> -50°C) or not coated. Extrapolating their results to the most volatile compounds in our standard mixture is difficult, but does at least leave doubts concerning simple capillary trapping.

Other workers have presented evidence for quantitative trapping of compounds as light as ethane¹ and chloromethane^{2,3} using simple capillary traps without the benefit of packing materials. If one considers breakthrough to be a loss of the first part of the vapour cloud passing through the trapping zone and that condensation of subsequent vapour improves the trapping efficiency, then these discrepancies can be explained. In the first instance¹, cold trapping was used in the analysis of gaseous hydrocarbon mixtures at well above trace analysis levels. Here the losses of the first part of the vapour cloud would not amount to a significant percentage of the total material. In the other instances^{2,3}, trace analyses in the ppb and sub-ppb range were performed, but a major difference lies in the film thickness of the analytical column. Our 2.3- μm film allows the reconcentration of materials that escape the cold trapping process into discrete, albeit broad, peaks. The detection would be more difficult when using a column of standard film thickness.

In summary, we have found that highly volatile organic compounds (boiling points < 70°C) cannot be quantitatively recondensed by simple capillary cold trapping even at liquid nitrogen temperature. Enhanced contact between the vapour and the solid surface is required for efficient cold trapping.

ACKNOWLEDGEMENTS

This work was supported in part by the Swiss Department of Commerce (Project COST 64 b) and by F. J. Burrus & Cie, Boncourt, Switzerland.

REFERENCES

- 1 D. E. Willis, *Anal. Chem.*, 40 (1968) 1597.
- 2 D. Kalman, R. Dills, C. Perera and F. DeWalle, *Anal. Chem.*, 52 (1980) 1993.
- 3 A. R. Trussel, F.-Y. Lieu and J. G. Moncur, in L. Keith (Editor), *Water*, Ann Arbor Sci. Publ., Ann Arbor, MI, 1981, pp. 171–186.
- 4 *Master Scheme for the Analysis of Organic Compounds in Water, Interim Protocols*, U.S. Environmental Protection Agency, Cincinnati, OH, 1980.
- 5 K. Grob and F. Züricher, *J. Chromatogr.*, 117 (1976) 285.
- 6 J. W. Graydon, K. Grob, F. Züricher and W. Giger, *J. Chromatogr.*, in preparation.
- 7 J. A. Rijks, J. Drozd and J. Novák, *J. Chromatogr.*, 152 (1979) 195.