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TRAPPING EFFICIENCY OF CAPILLARY COLD TRAPS

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SUMMARY

The ability to retain a series of *n*-alkanes (C_3 – C_6 and C_{12}) by cryogenic trapping in different types of simple capillary trap has been studied. The traps were either capillary tube packed with glass beads or open-tubular capillary cold traps. The trapping efficiency was studied as a function of the amount of alkane and the temperature gradient of the trap. The trapping efficiency of open-tubular cold traps is dependent on both these factors, but the packed cold trap retained the alkanes quantitatively.

INTRODUCTION

Cold traps in combination with gas chromatography (GC) are used for two main reasons: enrichment purposes and solute band concentration. Cold traps are included in a great variety of application, such as volatiles in plastics¹, pyrolysis GC², atmosphere analysis³, and in instrumental set-ups, such as multi-dimensional GC^{4,5}.

The utility of cryogenic trapping has clearly been shown in a review by Brettell and Grob⁶. Despite the widespread use of such devices, a search of the chromatographic literature shows a scarcity of papers that discuss the fundamental processes governing cryogenic trapping, *e.g.* with respect to aerosol formation. Takeoka and Jennings⁷ have given a brief discussion of the principles governing cryogenic focusing and Hopkins and Pretorius⁸ have given a more elaborated theory of band broadening during cryogenic trapping.

The wealth of applications of different simple cold traps, however, indicates that from a practical viewpoint cryogenic trapping is of great usefulness. This may well be due to the ease of construction, *i.e.* simply to immerse the trap in a cold medium kept in a Dewar flask, and many of the traps described in the literature are in principle similar to the one shown in Fig. 1. Such cold traps are known to quantitatively retain a variety of organic compounds. However, Graydon and Grob⁹ have reported that they have observed significant breakthrough of volatile organics from a simple open cold trap immersed in liquid nitrogen.

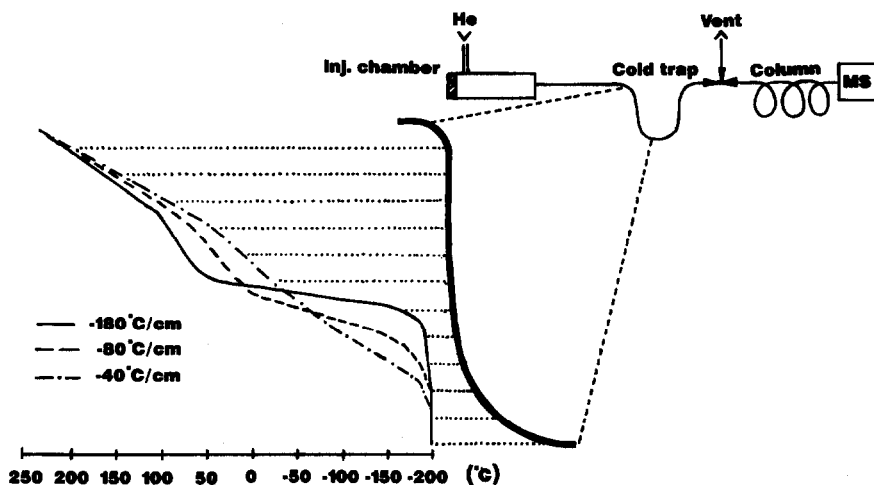


Fig. 1. A schematic diagram of the analytical system, and the profiles of the cold gradients. The distance between two dotted lines indicates 1 cm of the trap.

In our laboratories we have been using simple cold traps for a number of years. For quantitative analysis^{10,11} capillary traps packed with glass beads have been the choice in order to enhance the contact between the vapour and the solid surface. However, in order to minimize dead volumes in capillary multi-dimensional GC⁴, and to avoid flow-splitting arrangements between the cold trap and the capillary analytical column, the use of open capillary (I.D. less than 320 μm) cold traps has become of interest.

This paper examines the utility of simple cold traps to retain highly volatile organic compounds. The effect of three different negative temperature gradients over the cryogenic trapping zone and the influence of different amounts of compound are studied. Moreover, some basic cold trap design considerations are presented.

EXPERIMENTAL

The analytical system used in this study is described elsewhere¹². The cold trap was coupled to a gas chromatograph (Packard 428) interfaced to a Jeol D-300 mass spectrometer and Incos 2400 data system.

Three different traps were investigated: one U-shaped glass tube (30 cm \times 1.6 mm O.D. \times 0.7 mm I.D.) packed with glass beads (40–60 mesh), one uncoated, deactivated fused-silica capillary (30 cm \times 0.22 mm I.D.), and one fused-silica capillary (30 cm \times 0.22 mm I.D.) coated with OV-101 (film thickness 0.55 μm).

The fused-silica capillary was situated in a U-shaped glass tube (0.8 mm I.D.) similar to the packed cold trap, in order to fix and retain the shape of the cold trap and to facilitate temperature measurements along the fused-silica capillary. The temperature measurements, to determine the temperature gradient of the trap, were carried out with a thin type K thermocouple (0.0125 mm O.D., Omega Engineering, Stamford, CT, U.S.A.) placed between the wall of the fused-silica capillary and the

glass wall. Owing to the thin dimensions of the thermocouple, the packed cold trap could be filled with glass beads even though the thermocouple was placed inside the glass tube prior to packing. Different temperature measuring points were obtained by simply sliding the thermocouple along the inside of the trap. The trap was kept in a Dewar flask (200 ml; I.D. 40 mm) filled with liquid nitrogen. To obtain the different negative temperature gradients the Dewar flask was filled with different levels of liquid nitrogen and was flushed with nitrogen gas at different flow-rates. Cryogenic trapping was studied at the following negative temperature gradients: $-40^{\circ}\text{C}/\text{cm}$, $-80^{\circ}\text{C}/\text{cm}$, and $-180^{\circ}\text{C}/\text{m}$. The first of these was obtained by lowering the trap 2.0 cm into the liquid nitrogen (ca. 55 ml) and flushing the liquid nitrogen surface with 300 ml/min of nitrogen gas. The $-80^{\circ}\text{C}/\text{cm}$ gradient was generated by lowering the trap 3.0 cm into the liquid nitrogen and flushing at 150 ml/min, and the $-180^{\circ}\text{C}/\text{cm}$ gradient by lowering the trap 4.5 cm into the liquid and without any flush. The temperature gradients were determined by linear regression analysis of the temperature curves in the interval -150 to 50°C (Fig. 1).

The experimental procedure was as follows. Each compound in turn, with 100- μl headspace, was injected at three different concentration intervals and three different cold gradients. Injection was performed with a gas-tight syringe through a septum into the quartz tube of the headspace chamber ($n=4-6$ at each concentration level and cold gradient). The injected compound was then carried by helium gas to the trap. After a trapping time of 5 min, the Dewar flask was lowered and the trap heating was switched on. The trap was heated to 250°C by applying a high voltage for 2 s to a Kanthal A wire coiled around the glass tube. The voltage was then reduced. The trapped compound was reinjected onto the capillary column (SE-54, 25 m \times 0.22 mm I.D.) with a split ratio of 1:10. The breakthrough was monitored by the mass spectrometer. The same amount of the same compound was then injected directly to the gas chromatograph through the heated trap. The compounds studied were *n*-propane, *n*-butane, *n*-pentane, *n*-hexane and *n*-dodecane.

The carrier gas velocity during the trapping and the reinjection was 87 cm/s in the column, and the flow-rate through the trap was 20 ml/min. The flow-rate was kept constant by a flow regulator (Porter VCD-100, Porter Instrument, Hatfield, U.K.). The headspace chamber was kept at 250°C and the oven temperature and the interface between the gas chromatograph and the mass spectrometer was maintained at 150°C . The mass spectrometer was scanned from m/z 35 to 250 at a cycle time of 1 s. The ionization energy was 70 eV.

RESULTS AND DISCUSSION

The cold traps are generally either U-shaped or straight tubes, and, like columns, they can be either open or packed. Some of packing materials that have been used are glass beads^{10,11}, adsorbents such as Tenax¹³⁻¹⁵, Porapak Q¹⁶ and activated carbon^{13,17,18}. In the present study the tubes were U-shaped in order to facilitate immersion in a Dewar flask.

The ability of cold traps to retain compounds is dependent, among other factors, on the lowest temperature of the trap. However, since liquid nitrogen is inexpensive, convenient and a commonly used cooling medium, this study has focused on other factors affecting the cryogenic trapping efficiency.

To the best of our knowledge the importance of a negative temperature gradient during trapping was first discussed by Kaiser¹⁷. He concluded that a too sudden cooling or too low a temperature could cause a micro fog, which could be prevented by a gradient enrichment. In several later publications^{2,3,5,7,19,20} the importance of a negative temperature gradient has been stressed. However, few experimental data have been presented to support such conclusions. The importance of the temperature gradient in aerosol formation and growth is, however, apparent in the more fundamental studies on aerosol formation²¹.

In this work the influence of three different negative temperature gradients on the trapping efficiency of propane, butane, pentane, hexane and dodecane was experimentally examined. Packed cold traps are known to retain highly volatile compounds, such as ethane, at a temperature of -196°C ²². Under the experimental conditions given in the experimental part no breakthrough could be observed for propane, butane, pentane, hexane and dodecane in the packed cold trap. The three amounts of compounds studied were 0.17–0.35 μg , 0.86–1.26 μg and 1.90–3.84 μg . The lower limit of detection was *ca.* 1 ng.

The ability of open cold traps to retain the studied compounds has been examined with uncoated and coated fused-silica traps. The results are summarized in Tables I and II. So that the results can be presented in a manageable form, the injected amounts of the compounds have been grouped in three sets. The variance within each set is large, with a average relative standard deviation (R.S.D.) of 29%, and this is reflected in the large R.S.D. of the breakthrough values. However, the correlation was examined by linear and non-linear regression analysis of the non-

TABLE I

TRAPPING EFFICIENCY OF A DEACTIVATED OPEN FUSED-SILICA TUBE

Percent breakthrough for propane, butane, pentane, hexane and dodecane at three different amounts and at three different cold gradients. The cold trap was a deactivated open fused-silica tube (30 cm \times 0.22 mm I.D.). The R.S.D. was calculated on the basis of six experiments for each amount injected and each cold gradient. The experimental conditions are given in Experimental.

Compound	Quantitation ion (<i>m/z</i>)	Amount injected (ng)	Breakthrough (%)		
			$-40^{\circ}\text{C}/\text{cm}$	$-80^{\circ}\text{C}/\text{cm}$	$-180^{\circ}\text{C}/\text{cm}$
Propane	44	290 (32%)	2.5 (22%)	9.8 (29%)	15 (67%)
		960 (23%)	3.2 (16%)	20 (32%)	24 (34%)
		3300 (36%)	10 (30%)	33 (45%)	50 (79%)
Butane	58	266 (26%)	0	3.8 (42%)	13 (62%)
		1040 (28%)	0	6.2 (23%)	20 (32%)
		3160 (20%)	2.0 (55%)	18 (36%)	39 (14%)
Pentane	72	260 (28%)	0	0.8 (32%)	7.0 (60%)
		1060 (25%)	0	4.2 (50%)	13 (25%)
		3550 (15%)	0.7 (29%)	10 (45%)	24 (43%)
Hexane	86	300 (18%)	0	0	1.8 (40%)
		1060 (35%)	0	0	9.2 (65%)
		2960 (30%)	0	1.2 (55%)	19 (62%)
Dodecane	170	210 (40%)	0	0	0
		860 (38%)	0	0	0
		1900 (35%)	0	0	0

TABLE II

TRAPPING EFFICIENCY OF A COATED OPEN-FUSED SILICA TUBE

Percent breakthrough for propane, butane, pentane, hexane and dodecane at three different amounts and at three different cold gradients. The cold trap was a coated (0.55 μm OV-101) open-fused silica tube (30 cm \times 0.22 mm I.D.). The R.S.D. was calculated on the basis of four experiments at each amount injected and each cold gradient. The experimental conditions are given in Experimental.

Compound	Quantitation ion (m/z)	Amount injected (ng)	Breakthrough (%)		
			-40°C/cm	-80°C/cm	-180°C/cm
Propane	44	238 (29%)	2.3 (15%)	8.5 (32%)	21 (36%)
		860 (35%)	8.1 (22%)	25 (43%)	42 (42%)
		3500 (22%)	13 (38%)	45 (56%)	75 (45%)
Butane	58	350 (18%)	0.5 (40%)	6.5 (38%)	8.0 (32%)
		1100 (24%)	1.2 (55%)	12 (25%)	21 (38%)
		3840 (38%)	2.5 (67%)	21 (25%)	38 (40%)
Pentane	72	300 (25%)	0	1.3 (35%)	9 (28%)
		1050 (29%)	0	1.5 (28%)	12 (18%)
		3700 (46%)	1.2 (32%)	4.7 (42%)	19 (25%)
Hexane	86	264 (21%)	0	0	4.5 (29%)
		1260 (32%)	0	0	3.0 (38%)
		2300 (35%)	0	0.7 (36%)	5.0 (42%)
Dodecane	170	170 (18%)	0	0	0
		960 (28%)	0	0	0
		2100 (37%)	0	0	0

clustered data, and the confidence interval of the slope for the curve with the best fit, determined by the correlation coefficient, was tested at the 95% confidence level. For all the compounds examined, except dodecane, the breakthrough is affected by both the temperature gradient and the amount, *i.e.* the concentration (Figs. 2 and 3). Dodecane is probably retained in a region where the effect of the temperature gradient is less pronounced. A comparison of the results obtained reveals that no substantial differences are seen between coated and uncoated traps. This is in accordance with the findings of Graydon and Grob⁹ and indicates that, at the low temperature at which the traps are kept, the coatings behave as solids.

As expected, the greater the difference between the cold trap temperature and the boiling point of the compound (or more probably the dew-point, *i.e.* the temperature at which condensation occurs), the more efficient is the trapping.

Breakthrough is considered to occur predominantly by aerosol formation of the first part of the vapour cloud followed by a rapid increase in trapping efficiency⁹. This hypothesis was found to be consistent with our experimental results, although it was not conclusively proved. As an example, the recorded breakthrough of butane is given in Fig. 4. The breakthrough can be seen as a two-phase procedure. The main breakthrough occurs in the early stage of the passage of the vapour cloud into the trap, and a second phase where the condensed compounds are stripped away due to their own vapour pressure. By use of the more selective detection provided by the mass spectrometer, changes in the baseline could be attributed to flow changes or component breakthrough. This attribution is severely restricted by use of, for example, an flame ionization detector.

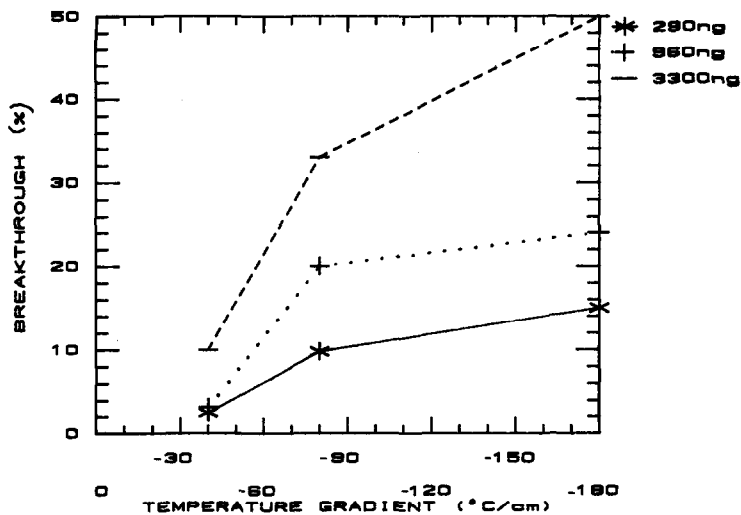


Fig. 2. Trapping efficiency of butane in a deactivated, open fused-silica tube at different temperature gradients and amounts.

To simulate the conditions of multi-dimensional GC, the test compounds were injected into the cold trap as a narrow band so that they occupied a defined volume. Therefore the trapping efficiency could be interpreted as dependent of the concentration. As the vapour cloud passes through the cold trap the band is sharpened because the distribution constant increases at the front of the band. The compounds are trapped in the space defined by the dew-point and the lowest temperature of the cold trap or, by definition, where the condensation is considered to be complete, *i.e.*

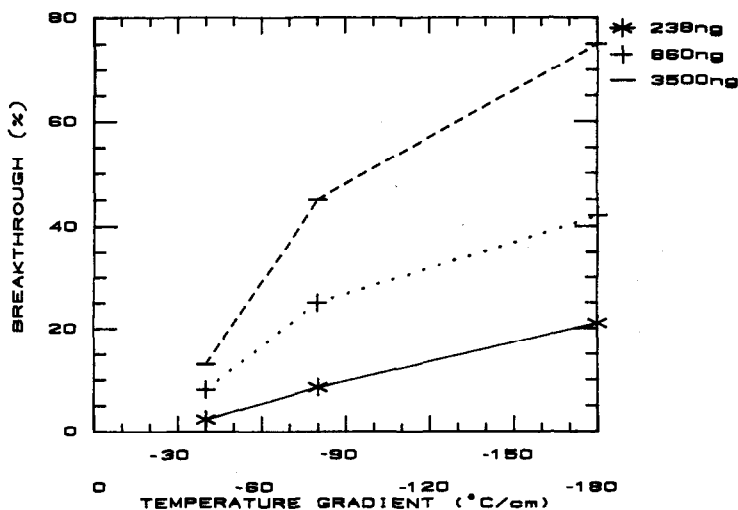


Fig. 3. Trapping efficiency of butane in a coated, open fused-silica tube at different temperature gradients and amounts.

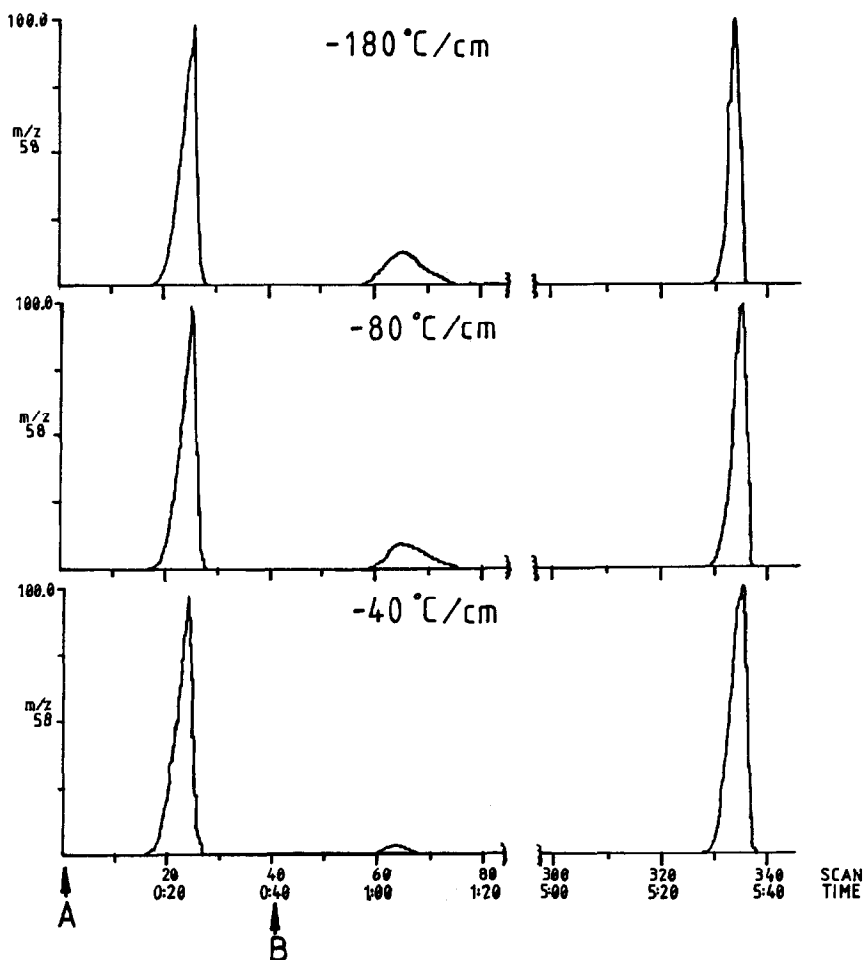


Fig. 4. Mass chromatograms showing the trapping efficiency of butane in a deactivated fused-silica tube at three different temperature gradients; the amount injected was *ca.* 3 μg . (A) Direct injection with heated trap; (B) injection with the cold trap on for 5 min and the liquid nitrogen removed there after.

T_{complete} . The time taken by the solute molecules in the vapour phase of the cold trap to diffuse to the cold wall, t_D , could be calculated by the following equation, which is deduced from Einstein's diffusion law²³:

$$t_D = r_t^2/4D \quad (1)$$

where r_t is the radius of the trap and D is the coefficient of diffusion.

The diffusion equation is valid for a cylinder. The coefficient of diffusion can be calculated for a binary system by the Fuller-Schetter-Giddings equation²⁴:

$$D = \frac{1.00 \cdot 10^{-3} T^{1.75} (1/M_A + 1/M_B)^{1/2}}{P[(\Sigma_A v_i)^{1/3} + (\Sigma_B v_i)^{1/3}]^2} \quad (2)$$

where D is the binary diffusion coefficient (cm^2/s), T is the absolute temperature, P is the total system pressure (atm.), M_A and M_B are the molecular masses (g/mol) and v is an atomic diffusion volume, a special diffusion parameter to be summed over atoms, groups, and structural features of the diffusing species (helium = 2.88, carbon = 16.5 and hydrogen = 1.98); A = carrier gas (helium) and B = the analyte (e.g. propane).

As examples, the coefficient of diffusion for propane is $0.096 \text{ cm}^2/\text{s}$ at -136°C , and that for butane is $0.11 \text{ cm}^2/\text{s}$ at -111°C . Hence, with a cold trap radius of 0.11 mm, we can expect diffusion times of $3.2 \cdot 10^{-4} \text{ s}$ or larger for propane; the corresponding t_D for butane is $> 2.8 \cdot 10^{-4} \text{ s}$. If we further assume that, for the bulk of the compound, condensation occurs between the dew-point and T_{complete} , then the residence time of the corresponding compound could be calculated. In this context T_{complete} is defined as the temperature where the compound under study exerts a vapour pressure of $1 \cdot 10^{-5} \text{ mmHg}$ or less. The dew-point defines the temperature at which a given concentration of a compound begins to condense. By use of the Antoine equation:

$$\ln p = A + B/(C + t) \quad (3)$$

and the iteration procedure of the Newton–Raphson method^{2,5}, the dew-point of the studied compounds could be established:

$$t_{n+1} = t_n - S_n/S'_n \quad (4)$$

$$S_n = 1 - P \sum y_i e^{-[A_i + B_i/(C_i + t_n)]} \quad (5)$$

$$S'_n = -P \sum y_i [B_i/(C_i + t_n)^2] e^{-[A_i + B_i/(C_i + t_n)]} \quad (6)$$

In eqns. 3–6, p is the vapour pressure (mmHg), S_n is the summation for dew-point, S'_n is the derivative of S_n , P is the total system pressure (mmHg), t is the temperature in $^\circ\text{C}$, A, B, and C are constants with the respective values 15.74, -1875 , and 248 for propane and 15.72, -2176 , and 240 for butane (the constants are calculated for the vapour pressure range 10–100 mmHg), and y_i is the mole fraction of compound i in the vapour phase. In this case, the mole fraction is calculated from an injection time of 1 s into the carrier gas.

For butane (266 ng) these boundary conditions imply that condensation starts at a temperature of -111°C . The calculations of the dew-point are summarized in Table III. The temperature at which butane has a vapour pressure of $1 \cdot 10^{-5} \text{ mmHg}$, T_{complete} , was estimated to be -170°C . This gives a temperature interval of 59°C , which corresponds to a length of the condensation zone of 0.33 cm at the steepest temperature gradient. With a flow-rate of ca. 20 ml/min this corresponds to a residence time (t_{re}) of $3.8 \cdot 10^{-4} \text{ s}$.

Thus, the diffusion time to the wall (t_D) is in the critical vicinity of the time available for condensation. The close time-scales of the two events (t_D and t_{re}) suggests that part of the vapour cloud enters a temperature zone in which the vapour becomes supersaturated before condensation on the wall occurs. The supersaturated vapour would be prone to form droplets, giving rise to aerosols.

TABLE III
DEW-POINT DETERMINATION

Calculation of dew-point for butane by the iteration procedure of the Newton-Raphson method. The gas mole ratio (y) was $3.4 \cdot 10^{-3}$ at 760 mmHg pressure and the starting temperatures for the trials were -100°C and -130°C , respectively.

Trial	n	t_n ($^\circ\text{C}$)	S_n/S_n' ($^\circ\text{C}$)
First	t_0	-100	-28
	t_1	-128	+6
	t_2	-122	+5
	t_3	-117	+4
	t_4	-113	+2
	t_5	-111	0
Dew-point		-111 $^\circ\text{C}$	
Second	t_0	-130	+6
	t_1	-124	+6
	t_2	-118	+4
	t_3	-114	+2
	t_4	-112	+1
	t_5	-111	0
Dew-point		-111 $^\circ\text{C}$	

The numerical interpretation of the concentration dependence is not readily available. Qualitatively, the concentration dependence may be interpreted as a shift of both the dew-point and T_{complete} , or the temperature at which aerosol formation actually takes place, to higher temperatures than for the corresponding lower concentration. However, the temperature at which the aerosols are actually formed is influenced to a greater extent than the dew-point with increasing concentration. Thus, as the concentration increases, a decreasing effective condensate zone is available, *i.e.* the effective residence time decreases.

In order to prevent aerosol formation, sufficiently long residence times with respect to the diffusion time (t_D) of the compound to be enriched have to be generated in open-tubular capillary cold traps. Ways to achieve this are smooth temperature gradients and low flow-rates, or the use of temperatures that sharpen the solute band without causing a supersaturated vapour to form, and hence an aerosol. In open-tubular capillary cold traps, aerosol formation may also be minimized by using loop-type traps²⁶, where the flow through the trap passes zones of different temperature gradients. However, this implies an increase of trap volume, and a consequent increase in the band-width. It should be noted that the cooled trap length at the lowest trapping temperature increased with steeper gradients. Hence, the results can not be explained by any decrease of the trap length.

CONCLUSION

This study has demonstrated the dependence of the open cold trap on the temperature gradient and the concentration. For the packed cold trap no such de-

pendence could be shown. Thus, if the trapping performances of different open cold traps are to be compared, one must take into account not only the lowest trapping temperature, the flow-rate, and the trap geometry, but also the temperature gradient and the concentration.

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