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Note

Maximum column temperature during on-column injections of large sample volumes in capillary gas chromatography

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Sample volumes up to several hundred microlitres may be injected by the on-column method on to a column fully coated with an immobilized stationary phase, provided the solvent effects ensure complete reconcentration of the solute bands and the solutes are eluted at or only slightly above the injector temperature (as demonstrated by Fogelqvist and Larsson[1]). If larger temperature increases are involved, a retention gap is required to reconcentrate the bands broadened in space[2].

Maximum column temperature during the sample introduction is desirable, first to minimise the length of the column section that is flooded by the liquid sample and second to accelerate the solvent evaporation (which may last 10–30 min even under optimized conditions). If the sample is injected at excessively high column temperature, the vapour pressure of the sample (solvent) exceeds the pressure of the carrier gas in the column inlet. The solvent vapour created expands in both possible directions, and the route backwards out of the column inlet is far easier owing to the low flow resistance. The returning vapour pushes plugs of sample liquid back out of the column. The solvent peak becomes very broad owing to traces diffusing from dead volumes back into the carrier gas stream. Higher boiling solutes have little chance of being flushed back into the column by condensed solvent. They return with delay (possibly creating memory effects) or not at all.

In contrast to Miller and Barringer[3] we maintain that the sample must remain inside the column and back-flow cannot be tolerated. If no back-flow is accepted, the vapour pressure of the sample in the column inlet must not exceed the inlet pressure of the carrier gas. If they are equal, the solvent vapour replaces the carrier gas and only solvent vapour passes the column. The gas flow at the column entrance is stopped. However in practice the vapour pressure of the sample must be less than the carrier gas inlet pressure because some flow at the column entrance must remain in order to carry the liquid released by the syringe needle further into the column.

If small sample volumes (1–5 μl) are injected, secondary cooling[4] or an equivalent device may prevent sample losses by back-flow even if the vapour pressure of the sample at the evaporation site is higher than the carrier gas inlet pressure. The returning vapour is recondensed in the cooled zone and remains stationary until the normal carrier gas flow is resumed. However, the vapour pressure cannot much exceed the carrier gas pressure even in this instance because of the risk that sample parts will be rejected out of the column by violent evaporation. Such techniques were

developed first by workers at Carlo Erba to avoid band broadening in space[5]. A drastic reduction in the length of the flooded zone was achieved.

Such techniques are not applicable to large sample volumes because very long cooled column sections would be required. Hence the maximum column temperature is more critical for large sample volumes (and cannot be increased by secondary cooling). Further, it is not possible to reduce the length of the flooded zone with similar effectiveness.

EXPERIMENTAL

The maximum column temperatures for the injection of various solvents at different carrier gas inlet pressures were determined by an experiment designed to detect back-flushed material. Two fused-silica capillaries (0.17 and 0.44 mm O.D.) were introduced into a 5-cm piece of glass capillary of 0.62 mm I.D. and sealed with cyanolite glue as shown in Fig. 1. This double column was mounted into an on-column injector (Carlo Erba, Model 4160). The (uncoated) fused-silica capillary of 0.44 mm O.D. and 0.32 mm I.D. had a length of 15 m and its exit section went outside the gas chromatographic (GC) oven to the atmosphere. For the experiments with a 2 atm inlet pressure this fused-silica capillary was elongated by a 50 m × 0.29 mm I.D. glass capillary. The fused-silica capillary of 0.17 mm O.D. was 15 cm long and was glued into a 20 m × 0.3 mm I.D. glass capillary, the exit of which was attached to a flame-ionisation detector.

The samples (mostly analytical-reagent grade solvents) were injected into the wider bore capillary and eluted to the atmosphere. If the sample was back-flushed (during injections into a column at excessively high temperatures) most of the returned material was introduced into the narrow-bore capillary and fed into the flame-ionization detector.

The liquids were introduced into the wider bore capillary through a permanently installed 0.17 mm O.D. capillary reaching about 5 cm into the capillary (similar to normal syringe needles). The rotating valve of the injector was left open and the exit sealed by a soft silicone septum, pressed on to the injector by the device that normally serves as a syringe guide. The fused-silica tube passed through this septum
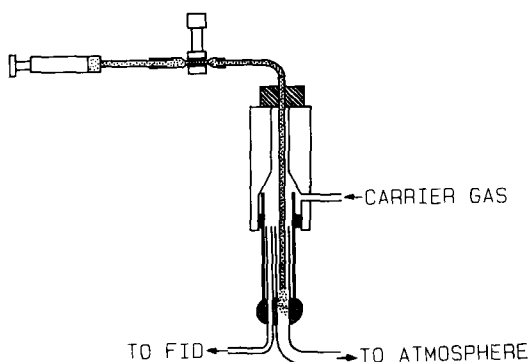

Fig. 1. The two column inlets mounted into an on-column injector with the permanently installed 0.17 mm O.D. fused-silica capillary for sample introduction, as used for the experiment described in the text. FID = flame ionization detector.

and was connected to a piece of shrinkable PTFE tubing, which could be squeezed to close the bore. The other end of the PTFE tube was adjusted to fit on to the needle of a 500-μl syringe. The syringe was filled with 100 μl of solvent, attached to the PTFE tube, the latter was opened and the liquid introduced within about 7 sec. Between two injections the solvent was completely evaporated and purged from the capillary. For each solvent or solvent mixture tested a series of injections was carried out, varying the column temperature by increments of 5°C.

RESULTS

Table I shows that the maximum column temperature during the injection using a carrier gas inlet pressure of 0.5 atm was 0–5°C above the boiling point of the solvent. At a 2 atm inlet pressure the difference between the boiling point of the solvent and the maximum column temperature (Δt) was increased to 25–42°C (Table II).

TABLE I

EXPERIMENTALLY DETERMINED MAXIMUM COLUMN TEMPERATURES WITH A 0.5 atm INLET PRESSURE

Solvent	Maximum column temperature (°C)	Solvent	Maximum column temperature (°C)
n-Hexane	70	Dichloromethane–	
Cyclohexane	80	cyclohexane (1:2)	50
n-Heptane	100	Methanol–water:	
Dichloromethane	40	9:1	65
Acetone	55	1:1	80
Methanol	70	1:9	85

The injection speed was found to have only a slight effect on the maximum column temperature. If 100 μl were injected within about 3 sec (using a 2 atm inlet pressure) some liquid was pushed back out of the column inlet at any temperature because the flow-rate of the liquid introduced exceeded the flow-rate through the column (which is lowered owing to the resistance of the plugs of liquid on the column wall). Whether the injection was carried out within 6 or 12 sec resulted in a difference in Δt of only 5°C.

The influence of the carrier gas flow-rate on Δt is negligible as long as the injection speed is adjusted to allow the carrier gas to transport the introduced liquid further into the column. Using a 2 atm inlet pressure and only the fused-silica capillary as a resistance (resulting in a flow-rate of about 12 ml/min) the maximum temperature was identical with that determined with the added 50 m × 0.29 mm I.D. glass capillary (reducing the flow-rate to about 3 ml/min).

The solvent mixtures listed in Tables I and II are of interest as eluents for high-performance liquid chromatography (HPLC) coupled to capillary GC[6].

The maximum column temperatures were lowered by 5–10°C when samples rather than pure solvent were injected.

TABLE II

EXPERIMENTALLY DETERMINED MAXIMUM COLUMN TEMPERATURES AND Δt VALUES FOR VARIOUS PURE SOLVENTS AT 2 atm INLET PRESSURE: COMPARISON WITH CALCULATED Δt VALUES

Solvent	Maximum column temperature (°C)	Boiling point (°C)	$\Delta t_{exp.}$ (°C)	$\Delta t_{calc.}$ (°C)
n-Pentane	70	36	34	32
n-Hexane	110	69	41	35
Cyclohexane	120	81	39	35
n-Heptane	145	98	42	37
Dichloromethane	75	40	35	32
Diethyl ether	70	36	34	32
Acetone	95	56	39	35
Methanol	90	65	25	27
Dichloromethane–cyclohexane (1:2)	95			
Cyclohexane–ethyl acetate (2:1)	110			
Methanol–water:				
9:1	100			
1:1	110			
1:9	125			
Acetonitrile–water (1:2)	115			
Tetrahydrofuran water:				
3%	100			
30%	135			

DISCUSSION

The experimentally determined Δt values were compared with calculated values using the Clausius–Clapeyron equation in the form[1,7]

$$\Delta t = \frac{T(2.8808 - \log p)}{\varphi + 0.15(2.8808 - \log p)} \tag{1}$$

where T is the boiling point of the solvent (sample) at atmospheric pressure, p is the column inlet pressure (mmHg) and φ is the entropy of vaporization at 760 mmHg, estimated according to ref. 7. If the column inlet pressure does not exceed a few atmospheres, eqn. 1 may be simplified to

$$\Delta t = \frac{T(2.8808 - \log p)}{\varphi} \tag{2}$$

Calculated Δt values for an inlet pressure of 2 atm are given in Table II. Reasonable agreement with the experimental values is observed. The experimental Δt values are slightly higher than the calculated values, except for methanol. On the other hand, the experimental Δt values for an inlet pressure of 0.5 atm are slightly below the calculated values. Owing to the changes in the column temperature in 5°C increments the experimentally determined values are up to 4°C too low.

CONCLUSIONS

If large sample volumes are injected, long (20–50 m) retention gaps are needed. Further, it is of advantage to apply high carrier gas flow-rates in order to speed up the analysis (in particular the intermediate step to pass the solutes through the retention gap[8]) and to accelerate the transport of the solvent.vapour through the column. These factors lead to high inlet pressures, which allow injection at relatively high column temperatures.

TABLE III

ΔtVALUES FOR DIFFERENT COLUMN INLET PRESSURES, CALCULATED FOR PURE SOLVENTS AND RECOMMENDED FOR PRACTICAL SAMPLES

Inlet pressure (atm)	Δt (calculated) (°C)	Δt (recommended) (°C)
0.5	11	− 3
1.0	19	8
1.5	25	15
2.0	30	20
3.0	38	30

Some Δt values were calculated according to eqn. 2 for various column inlet pressures, assuming a boiling point of 310°K and φ = 4.8 cal/mol · °K. They are listed in Table III together with recommended Δt values for use in practice, considering the experimentally obtained values and the fact that the boiling point of the solvent may be considerably reduced owing to the sample material in the solvent. It is proposed to add these recommended Δt values to the boiling point of the sample solvent to estimate the maximum allowable column temperature during injection.

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