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Split injection into a capillary column at very low split ratios

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ABSTRACT

The solute zone in the inlet liner of a split injector at very low split ratios are split because of significant differences between the mean linear velocities in the capillary and in the liner. As the frontal part of the solute zone moves through the liner with a velocity comparable with that in the capillary, radial diffusion is the limiting process. Given the diffusion coefficient of the solute, the radial mixing of the frontal part of the solute zone can be improved both by the inlet liner and the zone extension.

INTRODUCTION

The classical and still frequently used technique of introducing a sample into a capillary column is split injection. Compared with other techniques, such as on-column or splitless injection, the split technique reduces damage to the column caused by large amounts of liquid solvents and by non-volatile contaminants, and enables isothermal separation to be carried out. It is a typical sampling technique: only a part of the vaporized injected sample enters the column and is quantitatively evaluated; the principal open question is how representative is the analysed part with respect to the composition of the original liquid sample. A number of reviews have been published devoted to the split technique [1–4]. Unfortunately, there seems to be a lot of contradictory information, particularly concerning injection of larger sample volumes (*ca.* 2 μl of liquid) at very low split ratios (below 1:10). For example, Schomburg *et al.* [3] emphasize back-diffusion of high-boiling components with subsequent adsorption and condensation in the inlet lines at low split flow-rates, whereas Jennings [4] observed discrimination of more volatile hydrocarbon (C_{13}) compared with the less volatile one (C_{16}) if the split ratio was decreased below *ca.* 1:100. The latter observation seems to agree with that of Grob and Neukom [5]. Similar problems arise with the speed of evaporation of a sample in the liner. Bruderreck *et al.* [6] speak about seconds, but others use terms such as "flash" [1] or "explosion-like" [5] in this context. It was Wang *et al.* [7] who studied the effect of high temperature on solvent

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evaporation. Another question relates to the distribution of solutes in the solvent vapour in the liner. Ettre and Averill [8] contend that the linear function of a splitter is undermined by the absence of any "fractionation in the sample components during splitting because of difference in volatility". Because of this condition, vaporization tubes packed with glass wool plugs should help to "homogenize" the sample [3] or "thoroughly mix" the volatilized sample [1]. In spite of the contention of Ettre and Averill, German and Horning [9] recommend, instead of an inlet liner, a short piece of a packed column, where fractionation follows from the principle.

Practically no information exists about the dynamic behaviour of an inlet system consisting of an inlet valve (whether a part of an inlet pressure controller or a part of a flow controller), a splitter body, a capillary column and an outlet valve (whether an uncontrolled needle valve or a part of a back-pressure controller). Except for the report from Grob and Neukom [5] about the pressure wave that follows sample injection, only the steady-state properties of the basic control systems are discussed.

To study the processes that occur in an inlet liner after sample injection at high flow-rates is hardly possible; at low flow-rates the problem is less severe because we are dealing with a series of consecutive processes, which can be studied separately.

THEORY

Sample evaporation

Evaporation of a polycomponent liquid mixture on the glass wool in the inlet liner involves many factors, of which the following are the most important:

(1) Heat transfer to the boiling liquid, the injector temperature and the rate of evaporation.

(2) Composition of the vapour during evaporation.

(3) The volume changes accompanying evaporation.

(4) The possibility of sample decomposition on a solid hot surface.

The material balance of a binary solution during evaporation is expressed by the Rayleigh equation [10] of simple differential distillation:

$$\frac{\mathrm{d}m}{m} = \frac{\mathrm{d}x}{y - x} \tag{1}$$

where m is the mass of the liquid phase in moles, and x and y are the molar fractions of the volatile solvent in the liquid and the gas phase, respectively. Eqn. 1 is valid provided that the vapour is continuously removed from the boiling liquid.

To integrate eqn. 1 we need the equilibrium relation between x and y. For ideal solutions obeying the Raoult law

$$y = \frac{\alpha x}{1 + x(\alpha - 1)} \tag{2}$$

where $\alpha = P_s^0/P_i^0$ is the solvent relative volatility, and P_s^0 and P_i^0 are the saturated vapour pressures of solvent and solute, respectively, at the solvent boiling point. By integration of eqn. 1, using eqn. 2, we have

$$\ln \frac{m_0}{m} = \frac{1}{\alpha - 1}\left[\ln \frac{x_0}{x} + \alpha \ln \frac{1 - x}{1 - x_0}\right] \quad (3)$$

In eqn. 3, m_0 and x_0 are the initial mass of the liquid sample and the initial solvent molar fraction, respectively. For $\alpha \gg 1$ (a solute of low volatility in a volatile solvent) eqn. 3 can be simplified to

$$\frac{m}{m_0} = \frac{1 - x_0}{1 - x}$$

and evaporation of the major part of solvent results merely in concentration of the solute in the liquid phase; the gas phase during a substantial period of evaporation is formed practically by the pure solvent vapour. Consequently, the axial concentration distribution of the vapour plug in the liner is highly inhomogeneous. The front part of the vapour plug consists of pure solvent; somewhere towards the rear part there is a zone of the less volatile solute. The temperature of the boiling liquid remains at the boiling point of the solvent at the column inlet pressure (overheating cannot exceed 1°C), and rises at the end of evaporation to the boiling point of the less volatile solute or to the injector temperature.

If the injector temperature is below the boiling point of the particular solute, the solute saturated vapour pressure is complemented with the carrier to the total inlet liner pressure (distillation in a stream of inert gas), which inevitably leads to excessive dilution of the solute vapour with the carrier gas in the liner and, therefore, to additional broadening of the initial solute zone. Evaporation of larger volumes of a solvent (1–2 μl) on a glass wool plug is accompanied with a rapid local temperature fall. The limiting resistance to heat transfer is between the liner internal wall and the wool, because the wool is a good insulating material. At low split flow-rates the necessary heat excess cannot be transported by the overheated carrier gas and evaporation of less volatile solutes proceeds at a significantly lower temperature than that of the injector body.

The picture is substantially changed if the sample does not obey the Raoult law, and particularly if the solvent and the solute form an azeotropic mixture or if conditions for the extractive distillation prevail. In such cases the front part of the solvent vapour plug in the liner may contain solutes of interest, with consequences, as discussed later, for the pressure control and the liner void volume. This is probably the reason why discrepancies between the results obtained with test mixtures (hydrocarbons) and with solutes in real matrices are frequently reported.

Most chromatographers set the injector temperature somewhere close to the boiling point of the least volatile solute. With relatively volatile solvents, the temperature drop between the boiling liquid and any heated surface in the liner exceeds 100°C, and the solvent evaporation proceeds deep in the Leidenfrost region [11]; this means that every boiling droplet is surrounded by a continuous insulating layer of vapour, which reduces heat transfer to the boiling liquid. As the boiling liquid is in close contact with its vapour, a mutual mass transfer between both phases is possible, and fractionation may proceed behind that specified by eqn. 3. One can hardly speak about a "flash" evaporation in this context (evaporation of 2 μl of chloroform 200°C above its boiling point lasts from 2 to more then 6 s, depending on the I.D. of the liner).

As pointed out many times, the vaporization of an injected liquid sample is accompanied by a large increase in volume in the liner, which manifests itself by a pressure wave propagated with the velocity of sound. The influence of this pressure wave on the liner function depends on the type of pressure control used.

Inlet pressure control

Pressure-control systems used in capillary GC fall into two basic categories. One type controls the supply of carrier gas into the injector by operating the inlet valve to guarantee constant pressure in the liner. The second type operates an outlet valve located in the vent line; an independent constant gas supply source in the inlet line (*e.g.*, a flow controller) is necessary for correct function of the pressure controller.

If the front part of a pressure wave produced by sample vaporization reaches the pressure sensor of a controller of the first type, the controller merely closes the inlet valve and simply waits until the pressure returns to its preset value. Such a controller is generally unable to eliminate the pressure wave. As the vapour propagation proceeds in all directions, some of the sample vapour may easily reach the septum part of the injector. Heavier components may be adsorbed on cooler surfaces and lighter ones may disappear through septum purge if the heated liner volumes on both sides of the evaporation point are not sufficient for the particular vapour volume. At lower split ratios the evaporation should thus proceed somewhere in the middle of the liner. This is probably the reason why Grob [2] emphasizes the importance of the distance between the needle exit and the column entrance.

The situation with the controllers of the second type is different. As soon as the front of the pressure wave reaches the controller sensor, the controller opens the outlet valve to compensate for the pressure increase by venting out part of the carrier present in the injector. If the pressure sensor is sufficiently sensitive, and if the valve operates rapidly to cope with the pressure changes, the pressure wave can be almost totally eliminated by converting it into a flow-rate wave. In this case the sample vapour is pushed down the heated liner at a speed determined by the sum of the preset injector flow-rate and the rate of evaporation. It is thus reasonable, in this particular case, to evaporate the sample in the upper part of the liner. Such an arrangement is advantageous, as it enables the use of syringes with short needles and reduces the danger of solvent evaporation from the heated syringe needle during injection.

To benefit from these advantages of the back-pressure controller, the dynamic properties of the control system and of the particular controllers (flow and pressure) used must be known. These are obtained by measuring both the transient characteristics of the control system with the open loop (between the sensor and the valve) and the reaction of the control system with the closed loop to pressure disturbances.

Convective diffusion of solute in the liner

As soon as the sample vapour is pushed down the liner, the flow lines that are established are governed by the continuity equation. At low split flow-rates, the mean linear velocity in the capillary is much greater than that in the liner and, consequently, a narrow cylindrical funnel moving significantly faster than the remaining annulus part is formed far above the column entrance. The resulting velocity profiles differ greatly from the parabolic profiles characteristic of open tubes and laminar flow. The convective process associated with the velocity funnel in the centre of the liner

transports the central part of the solute zone down the liner faster than the remaining part of the same solute, and is responsible for the formation of two close but separate zones at different liner depths. Radial solute diffusion transports some of the solute from the axial to the annular part of the liner, and another part of the solute from the annular to the axial part (Fig. 1). We have to deal with a typical axial solute zone splitting in the inlet liner. If there is enough liner length left above the capillary inlet, the split zones will merge by axial diffusion, otherwise we will observe peak splitting for peaks separated isothermally. The peak splitting disappears at temperature-programmed separations because the originally split solute zones are focused in the column. To suppress this unwanted effect of low split flow-rates, sufficient time must elapse for diffusion to occur before the solute zone reaches the column entrance. The stop-flow technique, proposed by Bayer and Liu [12], is unable to help here as convection in the central part of the pressurized liner proceeds even when the vent line is closed. The capacity of the inlet liner from the evaporation glass wool plug to the column entrance must thus be increased to exceed the sample vapour volume by at least a factor of three. The classical liner length (80–90 mm) is too short and should therefore be extended to at least 150 mm.

For ideal solutions following the Raoult law, the insufficient sample capacity of the liner may not be observed as the analyst is not interested in correct solvent splitting; the problems with the liner capacity may become evident for complex real solutions in which some components of analytical interest may be located in the front part of the solvent zone.

The process of sample vapour splitting

Let us consider conditions at the liner cross-section at the column inlet after sample injection and evaporation. For the mass of the i-th component of the mixture entering the column, $m_{c,i}$, in polar co-ordinates (r,Φ) it holds

$$m_{c,i} = \int_0^{\infty} \int_0^{2\pi} \int_0^{R} c_i(r,\Phi,t)\, u_c(r,\Phi,t)\, r\, \mathrm{d}r\, \mathrm{d}\Phi\, \mathrm{d}t \tag{4}$$

where R is the column internal radius, c_i and u_c are the i-th component concentration and linear flow velocity in the column, respectively, and t is time. A similar expression holds for the mass of the i-th component vented out of the liner, $m_{v,i}$:

$$m_{v,i} = \int_0^{\infty} \int_0^{2\pi} \int_{R_0}^{R_1} c_i(r,\Phi,t)\, u_v(r,\Phi,t)\, r\, \mathrm{d}r\, \mathrm{d}\Phi\, \mathrm{d}t \tag{5}$$

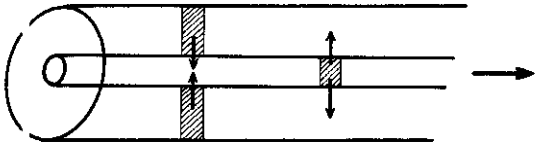

Fig. 1. Mechanism of the solute zone splitting in the inlet liner.

where R_0 and R are the external radius of the column and the internal radius of the liner, respectively, and u_v is the linear flow velocity in the liner. In both expressions the diffusional mass transfer across the plane of interest has been omitted. The experimentally accessible steady-state volume flow-rate in the column, v_c, is

$$v_c = \int_0^{2\pi} \int_0^{R} u_c(r,\Phi)\, r\, dr\, d\Phi \tag{6}$$

and in the liner annulus, v_v:

$$v_v = \int_0^{2\pi} \int_{R_c}^{R} u_v(r,\Phi)\, r\, dr\, d\Phi \tag{7}$$

The ideal function of the liner is characterized by a series of equations

$$\frac{v_c}{v_v} = \frac{m_{c,i}}{m_{v,i}} = \text{const.} \tag{8}$$

for all sample components $i = 1, 2, 3, \ldots, n$, and for any split ratio v_c/v_v.

In order to approach to the liner ideal function, we have to satisfy two basic conditions:

(1) Perfect radial mixing of the solute in the liner.

(2) Steady flow conditions before the first sample component reaches the entrance of the column.

According to the first condition, c_i does not depend on r and Φ, and according to the second one, u_c and u_v do not depend on t; therefore

$$m_{c,i} = v_c \int_0^{\infty} c_i(t)\, dt \tag{4a}$$

$$m_{v,i} = v_v \int_0^{\infty} c_i(t)\, dt \tag{5a}$$

and eqn. 8 hold since the integrals in both eqns. 4a and 5a are identical, provided that condition 1 holds. It should be noted that the axial concentration profiles (*e.g.*, axial inhomogenities as split zones) expressed in the convection process as time functions $c_i(t)$, do not play any role here.

Unfortunately, any model based on perfect radial mixing is far from reality. This becomes clear if we include the velocity profiles in the liner above the column inlet in our considerations. The most critical zone with respect to radial diffusion is the frontal zone of each solute as it moves faster.

In practice, we are unable to guarantee steady flow immediately after the sample injection as required by eqns. 4a and 5a; steady flow conditions can be reached only after a certain time interval t_0. The magnitude of this interval is determined by the amount of the sample injected, by the heat transfer rate at the sample evaporation zone, and by the properties of the pressure control used.

It should be emphasized that all conclusions are valid only for totally evaporated samples. Splitting of two-phase systems, such as aerosols, is a matter of statistics and cannot be treated by tools developed for the physics of continuum. The conclusions made above are not valid either for injections into an empty liner, as sample droplets leaving the syringe needle hit the liner hot surface at various depths and the composition of the vapour and the corresponding diffusional paths are unpredictable.

EXPERIMENTAL

All experiments were carried out using the Chrom 61 gas chromatograph (Laboratorní Přístroje, Prague, Czechoslovakia). This apparatus is equipped with computer-controlled two-channel pneumatics for the carrier, hydrogen and air [13]. The original A-channel injector for packed columns was changed for a laboratory-made split injector (Fig. 2). The length of the quartz liner was 145 mm and the I.D. was 3.5 mm. The inlet part of the liner was packed with the glass wool (the plug length was 30 mm). The design of the top part of the liner enabled the 50-mm syringe needle to penetrate 15 mm deep into the liner (10 mm deep into the plug).

A glass capillary column (15 m × 0.25 mm I.D.) covered with immobilized SE-30 phase was used. The column ends were extended by standard fused-silica capillaries of 20 cm length. The column inlet was located 10 mm above the lower end of the liner.

Special attention was given to the design of the back-pressure controller. Grob and Neukom [5] explained discrimination by split-ratio changes during the various phases of a pressure wave accompanying the sample evaporation. To suppress the pressure wave, we need a very fast back-pressure controller that is able to cope with the rate of sample evaporation.

The control valve design is similar to that described earlier [13] in connection with the digital mass flow controller. The valve connected to the vent line of the injector consists of a short inlet tube (1.5 mm I.D.) followed by a seat (0.7 mm I.D.) and a closing element driven by a magnetically controlled lever. The valve mechanics is located inside the valve body of *ca.* 40 ml volume; the valve body is open to atmosphere. The valve operates with a constant period of 40 ms duration. At the beginning of each period the valve is opened for a calculated time interval; for the rest of the period the valve seat is closed. The opening intervals are set in 2 μs multiples.

A semiconductor tensometric pressure sensor is used to measure pressure in the injector. The normalized sensor signal, taken from the analogue Z-bus of Chrom 61, is converted by a dual-slope A/D converter, one digit of the converter reading corresponds to 100 Pa (0.001 atm). A modified PS controller program is used to control pressure by the 8080A type microcomputer SAPI 1 (Tesla Liberec, Czechoslovakia). The data from the converter are fed to the computer through a parallel input port and every 40 ms the opening time interval is calculated on the basis of the actual sensor reading and sent to the valve through a programmable timer-counter interface.

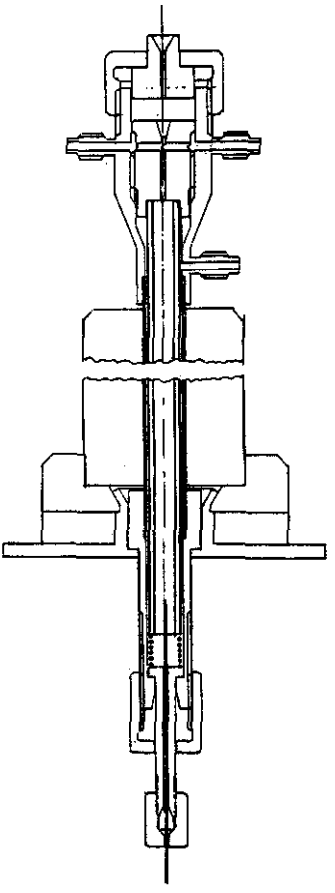

Fig. 2. Injector design.

The same data, along with the normalized pressure readings, are sent to respective D/A converters and plotted as time functions. The schematic diagram of the injector pneumatics is shown in Fig. 3, and the valve and inlet pressure response functions for 0.5, 1, and 2 μl of $CHCl_3$ at various injector temperatures are shown in Fig. 4. The valve responses demonstrate almost complete conversion of the pressure wave into the flow-rate changes in the liner.

As a test mixture, a solution of *n*-decane and *n*-octadecane in chloroform was used. The basic solution contained 0.24 μg of *n*-C_{10} and 0.384 μg of *n*-C_{18} in 1 μl of solution. This solution was further diluted 1:2 and 1:4, so that 0.5 μl of the basic solution contained the same amounts of solutes as 1 μl of the second or 2 μl of the third solution (0.12 and 0.192 μg, respectively). A Hamilton 701 N syringe was used to inject 1- and 2-μl samples, and a Hamilton 7001 N syringe with a needle spacer was used for 0.5-μl samples.

The necessary make-up gas for flame ionization detection (FID) was supplied by the B-channel carrier line. Nitrogen served both as the carrier gas and the make-up gas. The peak-area integration was performed with the CI-105 chromatographic integrator

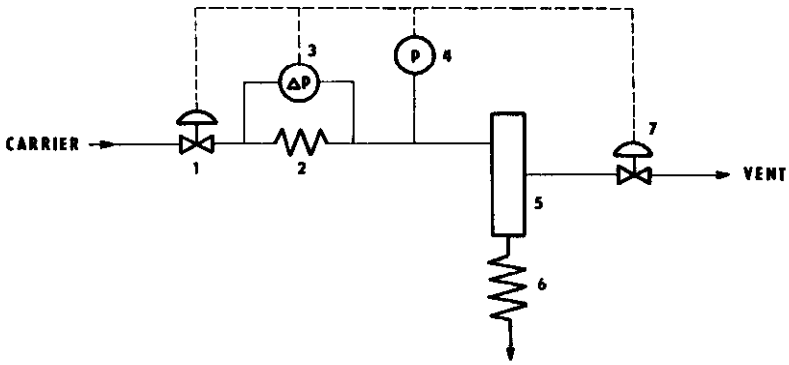

Fig. 3. Injector pneumatics: 1 = inlet valve; 2 = flow measuring capillary; 3 = differential pressure sensor; 4 = inlet pressure sensor; 5 = injector; 6 = column; 7 = outlet valve.

(Laboratorní Přístroje). The standard sampling interval (100 ms) was changed to 50 ms by making the necessary changes in the firmware ROMs.

The separation was carried out at programmed temperature. The programme started isothermally at 90°C, and after 3 min the temperature was raised at 40°C/min to 190°C where it remained for 6 min. The injector temperature was changed during the measurements.

To obtain FID responses to the original sample, 0.5 μl of the basic solution was analysed in a packed column (1.5 m, 3% SE-30 on Chromosorb^{R} W AW) at the same FID and electrometer conditions.

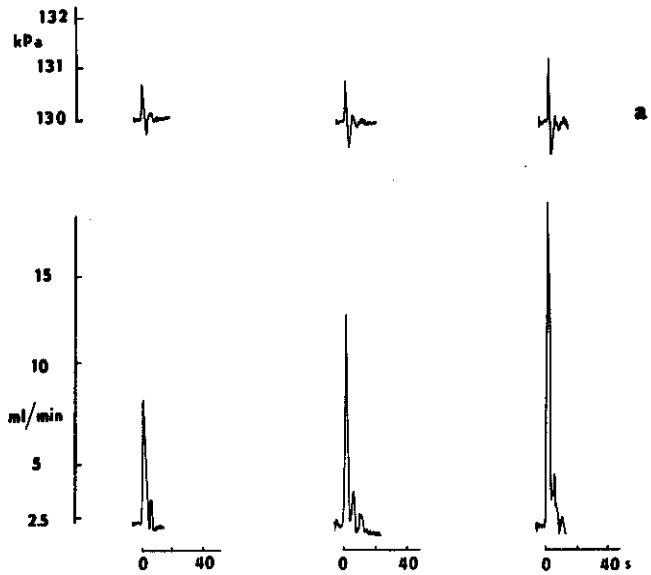

Fig. 4.

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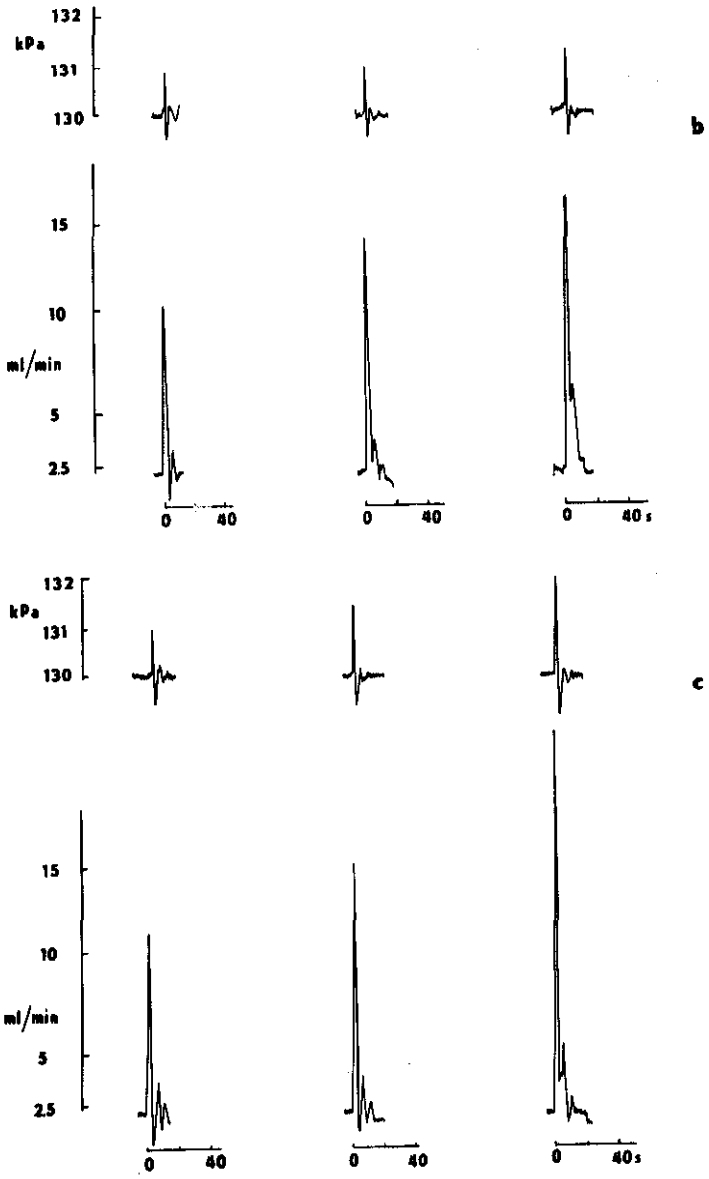

Fig. 4. Absolute pressure and outlet valve response functions to injection of (from the left to the right) 0.5, 1.0 and 2.0 μl of $CHCl_3$. Injector temperature: a = 200°C; b = 250°C; c = 300°C.

RESULTS AND DISCUSSION

The results for the capillary column are summarized in Table I. The data obtained with the 7001 (1 μl) syringe are *ca.* 10% lower than those obtained with the 701 (10 μl) syringe. By dividing the area counts for *n*-decane determined in the packed column (Table II) by 3.46 and 7.0, respectively, we obtain the theoretical responses for

TABLE I

CAPILLARY COLUMN DATA

Volume injected (μl)	Split ratio	Injection temperature (°C)	C_{10} area (μVs)	C_{18} area (μVs)	C_{18}/C_{10}
0.5	1:2.46	200	326 814 (2.5)[a]	497 428 (2.7)	1.52 (2.6)
		250	332 754 (2.0)	553 411 (2.5)	1.66 (3.0)
		300	337 959 (3.2)	725 110 (4.7)	2.15 (5.6)
1.0		200	369 771 (4.0)	556 800 (5.2)	1.51 (3.0)
		250	389 466 (1.7)	649 510 (4.0)	1.67 (2.8)
		300	396 583 (3.0)	808 056 (3.0)	2.04 (4.9)
2.0		200	370 048 (1.7)	561 398 (2.0)	1.52 (2.4)
		250	381 985 (1.9)	636 178 (1.7)	1.67 (1.6)
		300	363 677 (2.4)	820 859 (3.5)	2.26 (2.2)
0.5	1:6.0	200	151 282 (2.7)	236 375 (3.1)	1.56 (2.1)
		250	160 223 (2.0)	275 782 (3.7)	1.72 (4.1)
		300	163 868 (1.8)	340 884 (3.7)	2.08 (3.9)
1.0		200	177 050 (4.0)	265 011 (4.7)	1.50 (3.7)
		250	182 099 (5.0)	294 722 (3.6)	1.62 (4.5)
		300	172 236 (3.5)	374 897 (4.6)	2.18 (5.2)
2.0		200	171 587 (2.6)	261 363 (3.4)	1.52 (3.9)
		250	178 240 (1.2)	296 765 (5.3)	1.67 (5.3)
		300	183 359 (2.6)	368 109 (3.9)	2.01 (4.5)

[a] The data in brackets refer to the standard deviations expressed in % and valid for 10 measurements.

the preset split ratio 1:2.46 as 332 726 and for the preset split ratio 1:6.0 as 164 462. Both responses are in good agreement with the data obtained in the capillary. With 2-μl samples at injector temperatures 250°C and 300°C, *n*-decane peak splitting was frequently observed. In those cases both areas corresponding to *n*-decane were summed.

While the area counts for *n*-decane are independent of the injector temperature, a strong dependence of responses for *n*-octadecane on injector temperature is evident. Except for the injector temperature 200°C, the experimental responses exceed the theoretical ones (532 866 and 263 388, respectively). The corresponding C_{18}/C_{10} ratios increase with increasing injector temperature, and are practically independent of the preset split ratio. This fact can simply be explained if we realize that each solute

TABLE II

PACKED COLUMN DATA

Volume injected (μl)	C_{10} area (μVs)	C_{18} area (μVs)	C_{18}/C_{10}
0.5	1151 232 (1.7)	1843 716 (2.6)	1.60

enters into the capillary in the form of two discrete portions. As the velocity of the first portion is determined by the flow in the capillary (by the column inlet pressure), the radial mass transfer is insufficient for components with smaller diffusion coefficients, and more solute enters the column with the first portion as theoretically predicted. Given the velocity and diffusion path (inlet liner length reduced by the solvent vapour volume), the exposure of the first zone to diffusion can be extended by increasing the width of the particular zone. The principle is similar to that utilized by the slot shutter of a camera. The initial zone-broadening is here accomplished by decreasing the injector temperature far below the boiling point of the particular solute. This operation is of course dangerous, as condensation of less volatile components in relatively cold parts of the injector leading to discrimination cannot be excluded. This is probably the reason why the data for 200°C and *n*-octadecane are slightly below the theoretical values.

The correct solution to the problem lies in extending the inlet liner (the length of 250 mm is quite reasonable), in decreasing the liner internal diameter, and in changing nitrogen for hydrogen as the carrier gas. If the diffusional path is sufficient for the particular solute, the results should not depend on the injector temperature (as observed with *n*-decane).

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