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PROPERTIES OF A CAPILLARY COLUMN INJECTOR WITH A CONTROLLED RATE OF INJECTION

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SUMMARY

Gas flow and pressure conditions were investigated in a packed pre-column-type capillary column injector with controlled sample flow during the injection. The injection process was simulated in a bench-top computer and the results are presented. It is shown that injection conditions can be optimized. The roles of the carrier gas, solvent type and injection time are demonstrated.

INTRODUCTION

There are two basic ways of introducing a sample on to a capillary column:

(a) evaporation of the sample or sample solution in the hot injector with successive flushing of vapours into the column with carrier gas;

(b) direct on-column injection of the sample solution, introduced by Grob and Grob¹.

The more precise technique is obviously the latter, if one can inject the sample without spillage. It is limited, however, to clean sample solutions, containing only very small amounts of non-volatile substances. Vapour-phase injection therefore remains the method of choice in most capillary column analyses. The injection of vapour can be performed in several different modes: as a split injection, where only part of the vapour enters the column, as a splitless injection, where the whole volume of the vapour in the injector is (hopefully) flushed into the capillary column, or as a "direct" sample injection, where the solvent is removed prior to the evaporation (*e.g.*, ref. 2).

Three basic requirements have been established for successful split or splitless injection:

(1) the composition of the vapour should correspond with the composition of the sample liquid;

(2) the evaporation of the sample or sample solution and the transfer of vapour into the column should be instantaneous;

(3) the injection process should be reproducible.

Flash evaporation requires rapid injection of the liquid, which causes a sudden pressure increase in the injector, provided that the heat capacity of the internal part of the injector is high enough. The increased pressure causes the expansion of vapour

into peripheral, cold parts of the system and hence partial losses of sample components occur. This is one of the main reasons for the bad reproducibility or sample component discrimination with splitting devices. The volatility difference between the sample and solvent causes different rates of evaporation of the solvent and the sample, which often results in the formation of a sample fog or sample condensation in or on the injection needle. The two main requirements placed on capillary column injectors are thus contradictory.

Numerous papers dealing with injection devices for capillary columns have been published. German and Horning³ described an injector with a packed pre-column, which decreases sample evaporation problems substantially and improves the injection precision, as has been confirmed independently by Schomburg *et al.*⁴.

The problem of volume expansion and/or pressure increase can be overcome by increasing the injector volume or by slow sample injection. A necessary condition for slow liquid injection is the possibility of sample retardation at the column input. This can easily be achieved either by injection on to a cold column or by utilizing the solvent effect⁵.

The liquid evaporation and vapour transfer into the column is a complex process that has been described qualitatively many times. There is, however, a lack of a quantitative description of the process. This paper is the first attempt to provide a quantitative description of evaporative injection on to a capillary column.

EXPERIMENTAL

A digitally controlled injection system has been designed as a part of an automatic gas chromatographic-mass spectrometric (GC-MS) instrument, and a detailed description of the device and its performance has been published elsewhere⁶. The injection system consists in principle of a micro-manifold for sample and solvent dosing and an injector with an exchangeable, tightly packed pre-column (Fig. 1).

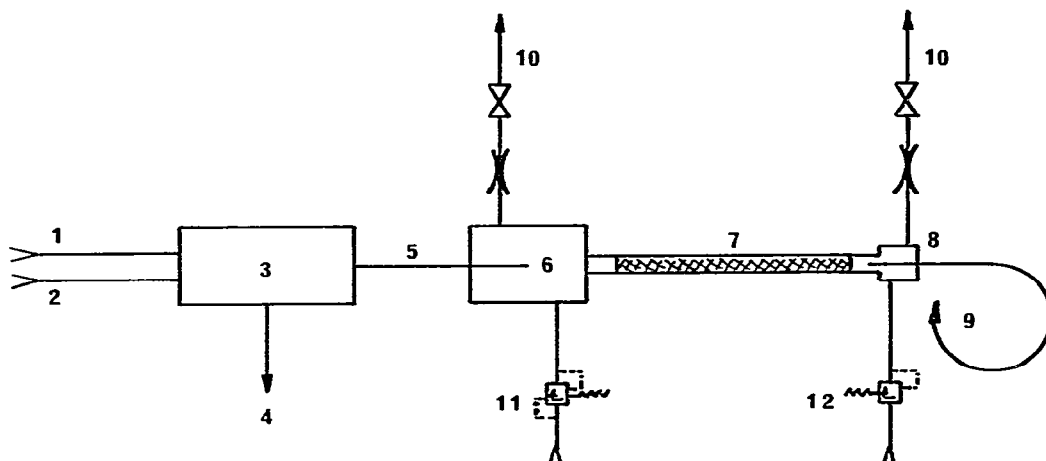


Fig. 1. Schematic diagram of the capillary column injector. 1 = Sample input; 2 = solvent input; 3 = micro-manifold; 4 = waste output; 5 = injection capillary tube; 6 = evaporation chamber A; 7 = packed pre-column; 8 = split chamber B; 9 = capillary column; 10 = auxiliary output; 11 = mass flow controller; 12 = pressure controller.

The injector is composed of two chambers, A and B, connected in series with a pre-column with a defined resistance against flow. Each chamber has its own independent gas supply. The evaporation chamber A is supplied by a constant amount of gas from a mass flow controller, adjustable and controlled by a central computer of the instrument. The sample solution is introduced into this chamber through a narrow capillary. The feed rate of the liquid through the capillary tube 5 is proportional to the pressure difference between the sample vial and the actual pressure in the chamber A. It is a "soft" source of liquid, which stops the flow in case of extreme pressure in the evaporation chamber A. The chamber has an auxiliary output to the atmosphere, which is opened at the end of injection and when backflushing of the pre-column is desired. The gas and vapour mixture flows into the pre-column, where any disperse phase is evaporated and the gas mixture is homogenized.

The pneumatic quality of the pre-column can be expressed as the virtual diameter of the narrow tube. This virtual diameter is easily calculated from the Hagen-Poiseulle equation⁷, the flow of a known gas at a given pressure difference along the tube being measured. The end of the pre-column is connected with an isobaric split chamber B, where the capillary column starts. It is supplied by auxiliary gas from the programmable pressure controller. An auxiliary output vents the excess of gas into the atmosphere when the split injection mode is used.

The quantitative description of an injection process in this injector configuration is based on the following assumptions:

- (a) the material balance of the system must be maintained in a steady state;
- (b) the mass flow of the carrier gas into the evaporation chamber is constant and independent of the chamber pressure;
- (c) the liquid flow through the injector capillary follows the Hagen-Poiseulle law (the assumption is fulfilled after the introduction of the so-called Hagenbach correction⁷);
- (d) the evaporation of the liquid proceeds isothermally (this assumption is not fulfilled exactly; more likely adiabatic evaporation will cause quantitative changes rather than major distortion of the results obtained);
- (e) the gases and vapours follow the equation of state;
- (f) the pressure changes in the system have acoustic velocity;
- (g) the changes in concentration of gases during the injection are equilibrated through mixing during the transport rather than through diffusion;
- (h) the gas mixture is composed of carrier gas and solvent vapours only and the contribution of sample components can be neglected;
- (i) the viscosity of the gas mixture can be calculated from the equation published in ref. 8;
- (j) the gas flow through the pre-column can be described with Hagen-Poiseulle equation with corrections for real tube and gas⁷.

These assumptions, together with the geometrical configuration of the injector, were incorporated in the computer program for the simulation of the injection process.

The main questions investigated were the influence of liquid flow-rate on the pressure development during the injection and the role of different carrier gas and solvent combinations during the injection.

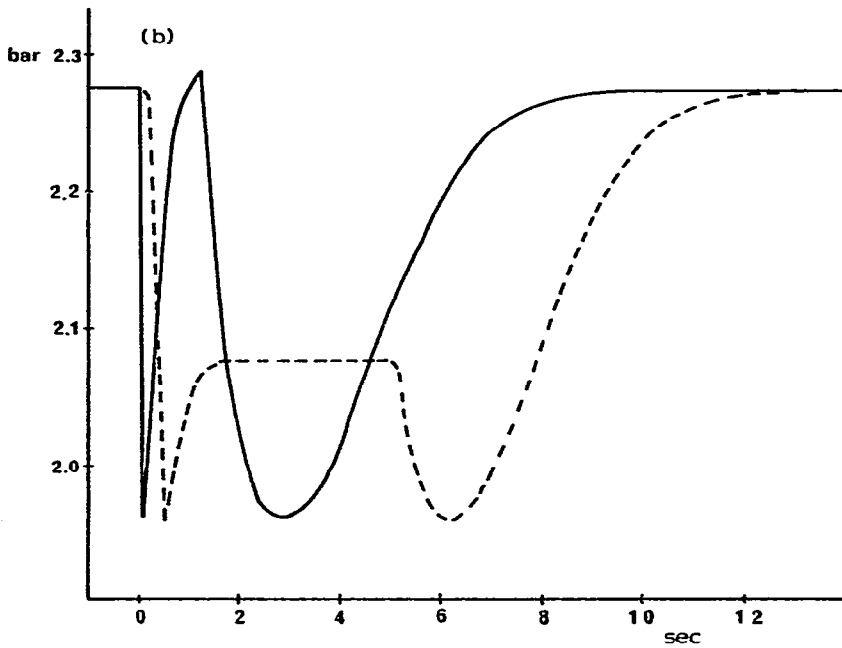
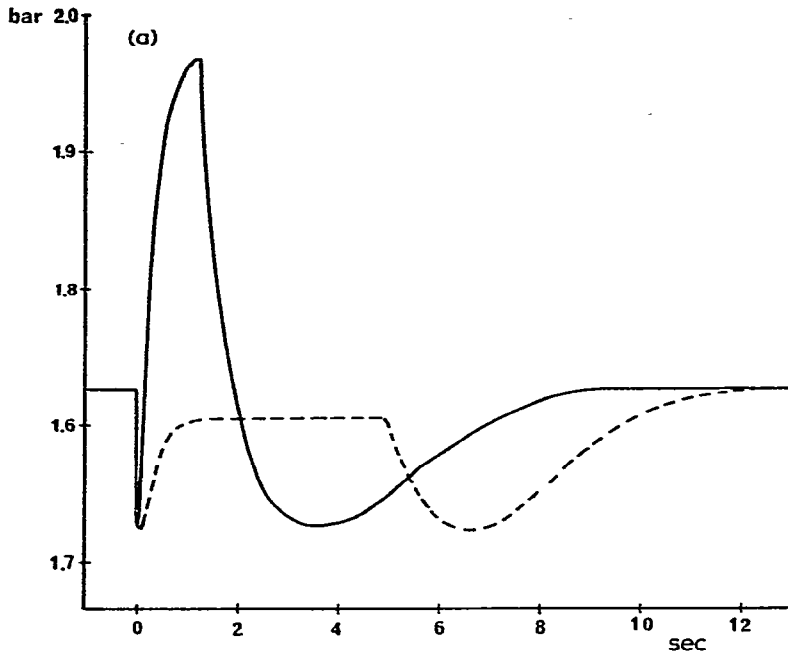


Fig. 2.

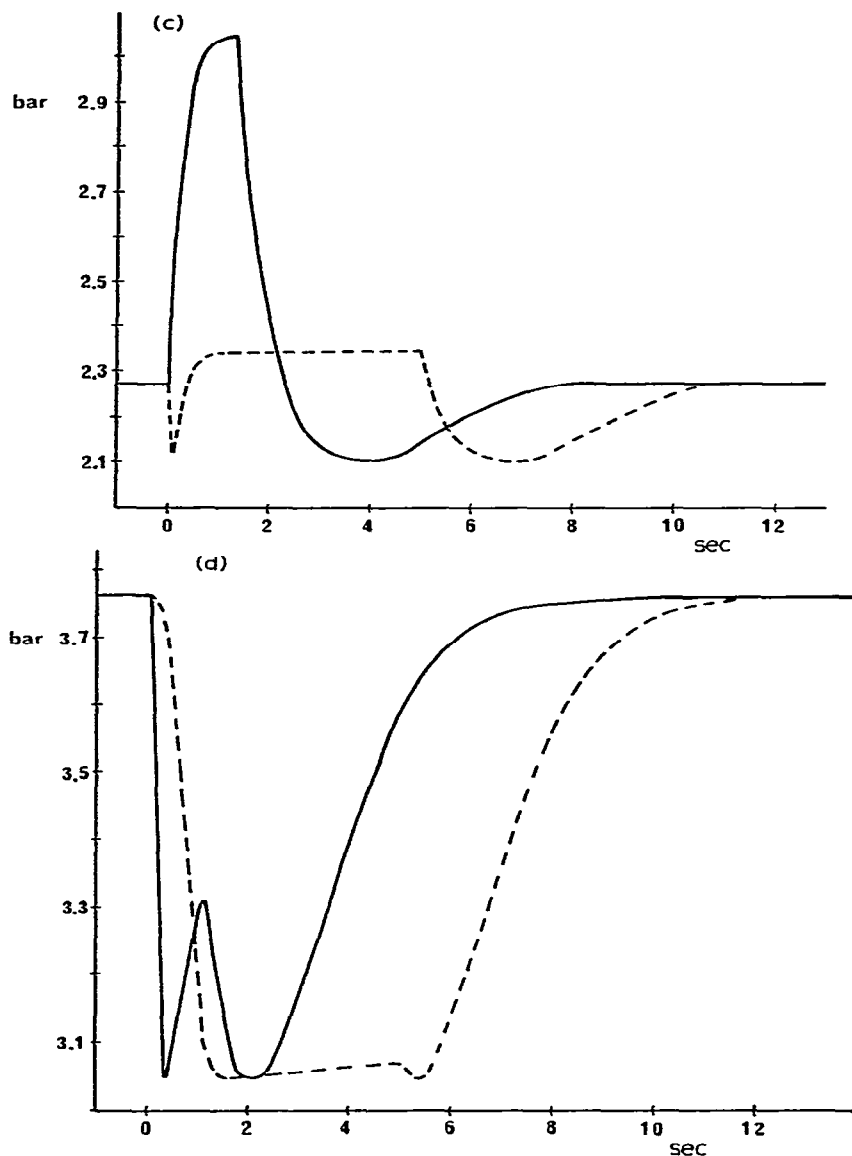


Fig. 2. Dependence of pressure in the injection chamber A on the injection time. Injection time: solid line, 1.25 sec; broken line, 5 sec. Carrier gas: helium, flow-rate (a) 5, (b) 20, (c) 20 and (d) 80 ml/min. Solvent: (a) *n*-hexane; (b) *n*-hexane; (c) dichloromethane; and (d) *n*-hexane.

RESULTS AND DISCUSSION

The injector configuration designed offers several advantages. The positioning of the main flow restrictor of the system (which is the pre-column) in front of the capillary column and stabilizing the pressure in the split chamber give the possibility of continuous, reproducible control of splitting ratios starting from zero (splitless

injection). Common capillary column injectors with one gas controller (usually a pressure controller) have the column mouth in the region of a variable pressure zone, where the variations are dependent on the type and flow-rate of the carrier gas and the

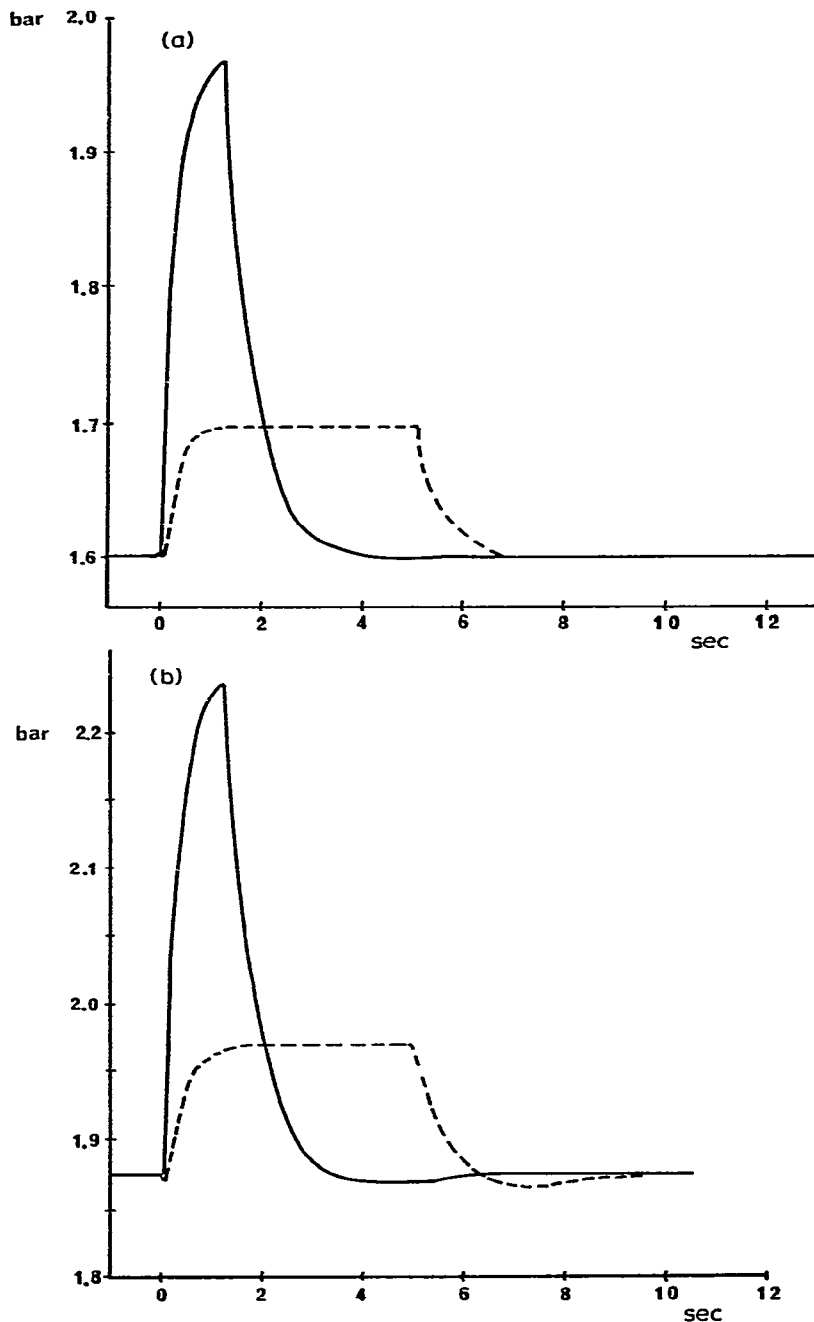


Fig. 3. As Fig. 2, except carrier gas hydrogen, flow-rate (a) 5 and (b) 20 ml/min and solvent *n*-hexane.

actual composition of gas-vapour mixture in the injector. Satisfactory functioning of such splitters can be achieved only when the column flow is negligibly small in comparison with the total carrier gas flow through the injector. Another practical ad-

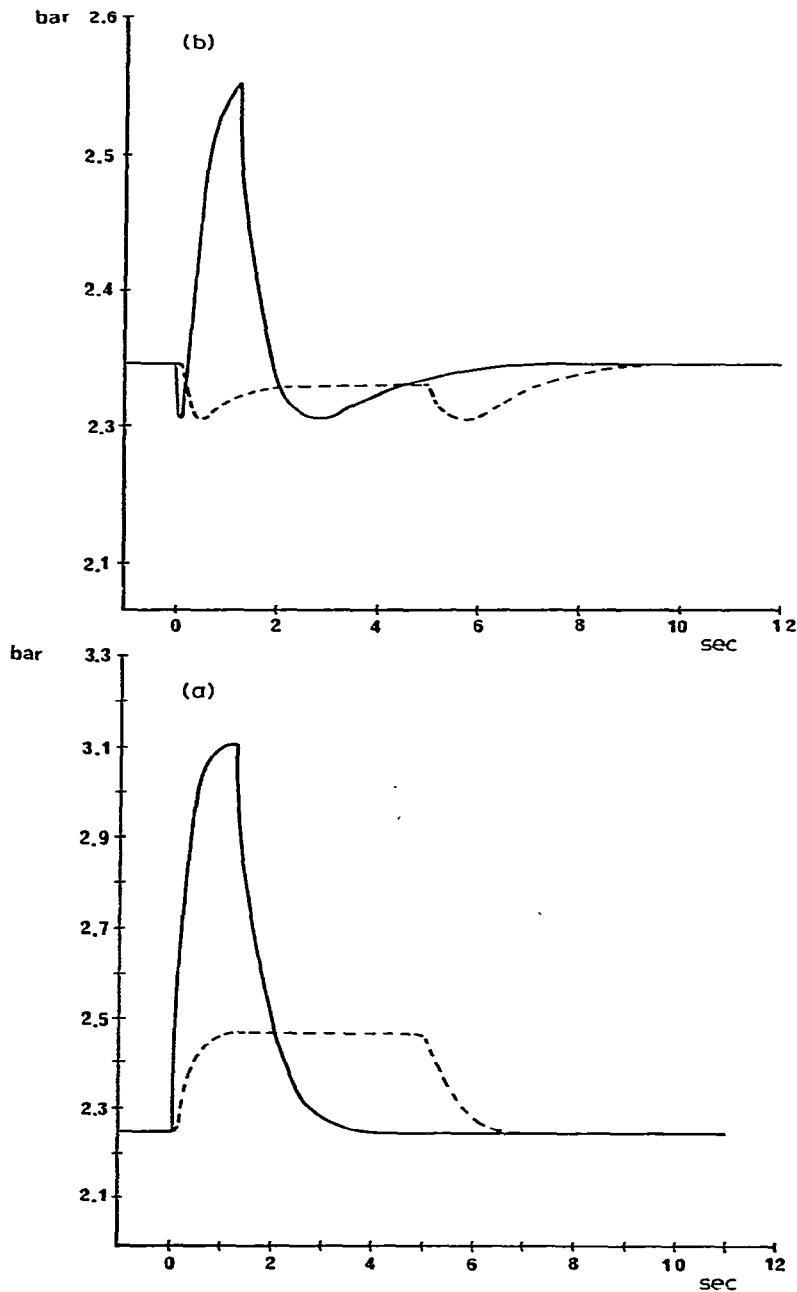


Fig. 4. As Fig. 2, except carrier gas nitrogen, flow-rate 20 ml/min, and solvent (a) dichloromethane and (b) *n*-hexane.

vantage of the injector designed is the ease of pre-column backflushing, which protects the analytical column from all low-volatility sample residues and thus prolongs the column and instrumental active periods.

The computer simulation of the injection assumes a constant carrier gas flow into the injector which is equal to the flow through the pre-column. By maintaining a constant temperature, gas composition and pressure in the split chamber B (typically 1.5 bar), the pressure in the injection chamber A will depend on the pre-column length and diameter. The composition of the gas mixture changes during the injection period, which may have a crucial effect on pressure and flow conditions in the injector. Depending on the viscosity of the mixture (and obviously on the injection rate and the molecular weight of the solvent), the pressure in chamber A during the injection may increase or, surprisingly, decrease. The pressure in the injection chamber decreases during the injection when a high-viscosity carrier gas is used (helium) and the solvent

TABLE I
PRESSURE CONDITIONS IN THE INJECTOR WITH AN INJECTION TIME OF 1.25 sec

Parameter	Carrier gas								
	Hydrogen			Helium			Nitrogen		
Gas flow-rate (ml/min)	5	20	80	5	20	80	5	20	80
Gas pressure (bar)*	1.60	1.88	2.72	1.73	2.28	3.76	1.71	2.25	3.84
CH ₂ Cl ₂ maximum pressure (bar)**	2.65	2.95	4.10	2.66	3.05	4.21	2.66	3.12	4.69
<i>p</i> (bar)***	1.05	1.07	1.38	0.93	0.77	0.45	0.95	0.87	0.85
C ₆ H ₁₄ maximum pressure (bar)**	1.97	2.29	3.34	1.97	2.29	3.34	2.01	2.45	4.04
<i>p</i> (bar)***	0.36	0.36	0.41	0.24	0.01	-0.42	0.30	0.20	0.20

* Steady-state pressure in chamber A before the start of injection at pressure 1.5 bar in the split chamber B.

** Maximum pressure reached in the injection chamber A during the solvent injection.

*** Maximum pressure difference along the pre-column during injection.

TABLE II
PRESSURE CONDITIONS IN THE INJECTOR WITH AN INJECTION TIME OF 5 sec

Parameter	Carrier gas								
	Hydrogen			Helium			Nitrogen		
Gas flow-rate (ml/min)	5	20	80	5	20	80	5	20	80
Pressure (bar)*	1.60	1.88	2.72	1.73	2.28	3.76	1.71	2.25	3.84
CH ₂ Cl ₂ injection pressure (bar)**	1.94	2.33	3.34	1.95	2.34	3.67	1.98	2.47	4.06
<i>p</i> (bar)***	0.34	0.45	0.62	0.22	0.06	-0.09	0.27	0.22	0.22
C ₆ H ₁₄ injection pressure (bar)**	1.70	1.97	2.81	1.71	2.08	3.07	1.76	2.23	3.84
<i>p</i> (bar)***	0.10	0.09	0.09	-0.02	-0.02	-0.69	0.05	0.02	0.0

* Steady-state pressure in chamber A before the start of injection at pressure 1.5 bar in the split chamber B.

** Pressure reached in the injection chamber during injection in equilibrated state.

*** Pressure drop along the pre-column during injection in equilibrated state.

vapours has a low viscosity. The viscosity of the mixture will then decrease, which causes an increased flow-rate through the pre-column, with a subsequent pressure drop in the injection chamber. Depending on the solvent flow-rate, this pressure drop may be temporary or permanent during the injection period. The phenomenon is illustrated in Figs. 2-4 and is summarized in Tables I and II.

With optimal carrier gas, solvent and solvent flow-rate, an isobaric injection can be achieved. Hydrogen, with a low viscosity ($176 \mu\text{P}$ at 250°C) and a tendency to exhibit viscosity maxima when mixed with other gases, will always cause a pressure increase during injection. A maximal pressure drop during injection can be achieved with helium (viscosity at $250^\circ\text{C} = 299 \mu\text{P}$) as the carrier gas. The pressure drop will be maximized by using a low-viscosity solvent vapour. Nitrogen will cause a pressure drop during injection only with low-viscosity solvent vapour and with very long injection times (10 sec or longer). Solvents of higher molecular weight, forming low-viscosity vapours, are preferable for GC injections.

Comparison of Fig. 2b with Fig. 2c and of Fig. 4a with Fig. 4b clearly demonstrates the solvent viscosity effect.

CONCLUSION

It has been shown by computer simulation of the injection process that the choice of the carrier gas-solvent combination plays an important role during the injection. The optimal combination can substantially decrease a detrimental pressure effect and thus increase the reproducibility of split or splitless injection on capillary columns. The results, valid for the injector design described, can be generalized, because any capillary column injector contains a narrow tube (usually behind the column mouth) that will function as a viscosity-dependent flow restrictor.

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