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Note

"Inverse" injection system for gas–liquid chromatography with capillary columns

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Injection systems may be classified according to the mode of operation, *i.e.*, split or splitless, the mode of injection, *e.g.*, on-column or, finally, by the physical state of the sample (solid, liquid, gas). As a rule the transfer from one mode of injection to another is time-consuming, requiring a replacement of part or the whole of the evaporator or a rearrangement of the valve positions[1,2].

Here we present an injection system which can operate in any mode without modification either of the arrangement of its parts or of the gas-flow system.

EXPERIMENTAL

The essence of this injection system is the separation in time and space of the evaporation and injection stages. A specimen is placed into a small vial, then this vial is inserted into a cold zone of the injector. Vapour is formed inside the vial by moving the latter into a hot zone and, finally, when the evaporation is complete, further up till the end of the downward directed capillary column reaches the vial bottom. The main features of this inherently versatile and very simple injector are presented in Fig. 1*. The upper part (1) is made of thin-walled stainless-steel tube (5 × 0.5 mm), the lower part (2) of glass (for visual monitoring). Part 3 may be either a simple gas-tight connection (B) or a more sophisticated valve (A). The upper part (evaporation–injection zone) is surrounded by a heater (4), the lower part (20–30 mm) by a water cooling system (5). The vials may be of various sizes and construction (see Fig. 2), in accord with the mode of injection (see below). Transfer of the vial from cold to hot zones is accomplished by use of a glass rod (6 in Fig. 1) with a small magnet on the lower end and an external magnet or magnetic field. Downward movement of the vial is spontaneous under the action of gravity. Normally, the external magnet is employed to move the vial to the uppermost position and then with the magnet upward movement at some point the contact between the internal and external magnets is lost and the vial drops down.

* The essential and critical feature of the present injection system is the counter-current carrier gas flow. This ensures the avoidance of diffusion or contamination from the outside. A recently reported 3 injection system although similar in arrangement is not suitable for the counter-current mode of operation.

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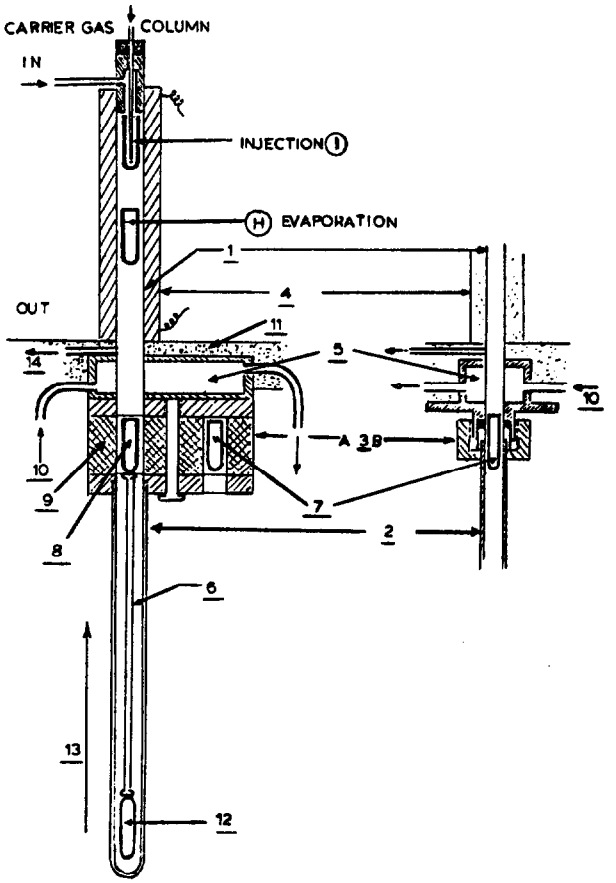

Fig. 1. Diagram of the injection system. 1 = Stainless-steel tube (5 × 0.5 mm); 2 = glass tube; 3(A),9 = PTFE valve; 4 = heating mantle of evaporator; 5 = watercooling system; 6 = glass rod for transportation of vial into evaporation and injection zones; 7 = vial with a specimen at the initial position; 8 = position of vial after rotation into a working channel; 10 = water inlet; 11 = heat insulation; 12 = internal magnet; 13 = external magnet; 14 = regulated injector ventilation.

Operation

A liquid (or solid or gaseous) sample is placed into a vial which, is in turn, placed into a cold zone either by disconnection of metal and glass parts (3B in Fig. 1) or with the help of a gas-tight drummer-type PTFE valve (3A in Fig. 1). The vial is then moved upwards into a hot zone (position H in Fig. 1) and left in that position for some time. This time is predetermined by the type of injection procedure, the ease of sample evaporation or other factors, *e.g.*, pyrolytic studies. Normally, the evaporation time is 5–20 sec.

When evaporation is complete the vial is moved to the uppermost position for injection (I in Fig. 1). Here again the injection time, *i.e.*, the residence time at the upper position I), must be adjusted to the specific injection mode ("split", "on-column" or "solvent-effect" mode). For heat-sensitive compounds, *e.g.*, some sugar derivatives, the pre-heating stage (position H in Fig. 1) may be omitted and evap-

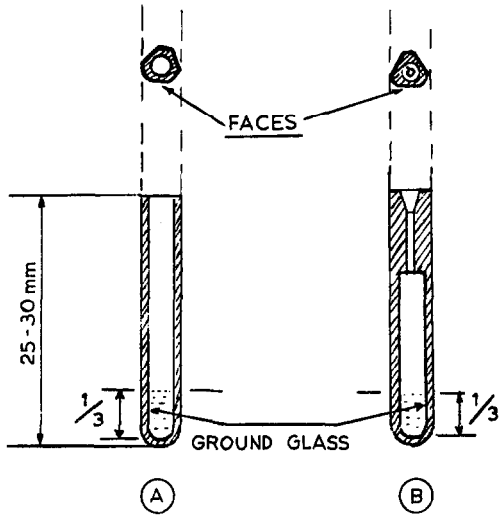

Fig. 2. Construction of the vials for high-boiling samples (A) and for low-boiling samples (B). External diameter: 4 mm; internal diameter = 2.5 mm. The neck of B is 0.7 mm. The faces on the vials are for the free passage of the carrier gas. The lower part of the inside surface (1/3) is of ground glass for better wetting.

oration and injection are synchronous. Normally, the injection time is 0.1–20 sec. The shortest time is for "split injection", *i.e.*, when only a small fraction of the sample is injected, the longest for "solvent-effect" injections. When the system is operating in the split mode the injection from the same vial may be repeated many times. This successive heating and cooling will eventually lead to the enrichment in higher-molecular-weight components. The same technique, *i.e.* heating–cooling but without injections), may be used for direct concentration of dilute solutions of high-boiling components.

Quantitation

The injected mass of a specimen is proportional to the carrier gas flow-rate, v, the vapour concentration, c, and to the duration of injection, t:

$$m = vct$$

Of these parameters, v is normally fixed and t may be varied from very short ("split injections") to intermediate ("on-column injections") to rather long ("solvent injections"); c is controlled by the quantity of the specimen, the vial volume and by the rate of diffusion. If diffusion is not considered, the vapour volume from 0.01 μl of liquid sample will after evaporation be *ca.* 10 μl (at the inlet pressure) and at the flow-rate *ca.* 100 μl/sec the "on-column" injection time will be *ca.* 0.1 sec. In practice, the complete injection takes from four to six times longer. The control of this process (*i.e.*, to check for the sample left-overs) may be performed by its repetition: no vapours should be left in the vial. To avoid fractionation the vial volume should exceed the ultimate vapour volume, or injection and vapour formation should be synchronous (only for "on-column" and "solvent" injections). In practice "on-column" or

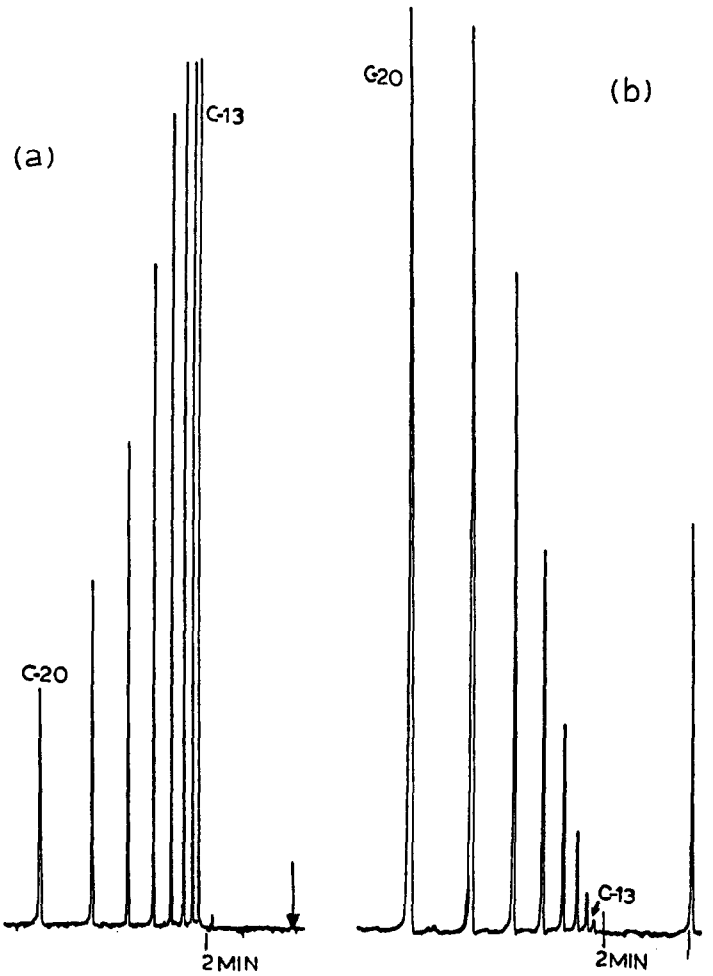

Fig. 3. "Split injection" of a, 0.1 μl of a C_{13}–C_{20} hydrocarbon mixture. Injection (0.2 sec) after 20 sec in the hot zone (220°C). Glass capillary (50 m × 0.25 mm) containing OV-101. Temperature: 185°C. Hydrogen pressure: 1.9 atm. b, Concentration of high-boiling components using the same mixture as above but after ten cycles of evaporation and condensation. Injection (5 sec) after 20 sec in the evaporator. Note the discrimination of low-molecular-weight components (fractionation at evaporation–condensation stages) and relatively broad peaks (long injection time).

"solvent-effect" injections present no difficulties and show excellent reproducibility. The "split" mode gives satisfactory results even with manual operation, especially with very short injection times. For longer injection times a manually operated permanent magnet should be replaced by an electromagnet with a timer for a highly reproducible standard. Practical examples of the operation of "the inverse" injection system will now be described.

"Split" injection

With the conventional split evaporator the major problem is the discrimination of high-molecular-weight components. No such problem exists with the "inverse"

injection system. Actually, the discrimination of low-molecular-weight components may be a problem if the injection is performed with a long delay after the insertion of the vial into the evaporator. The drummer-type insertion port solves this problem as it eliminates waiting for the pressure to build up.

Fig. 3a shows the separation of an hydrocarbon mixture using an injection time of *ca.* 0.1 sec. Fig. 3b shows the result for the same sample after ten cycles of heating, injection and cooling. Note the discrimination of low-molecular-weight components. In comparison with conventional split injection there is no discrimination of light or heavy components after the first cycle. Upon repeated injection the main reason for the discrimination is not the diffusion but rather the fractionation due to the heating–cooling cycle.

On-column (splitless) injection

Fig. 4 shows the results for the same mixture of hydrocarbons, but using a

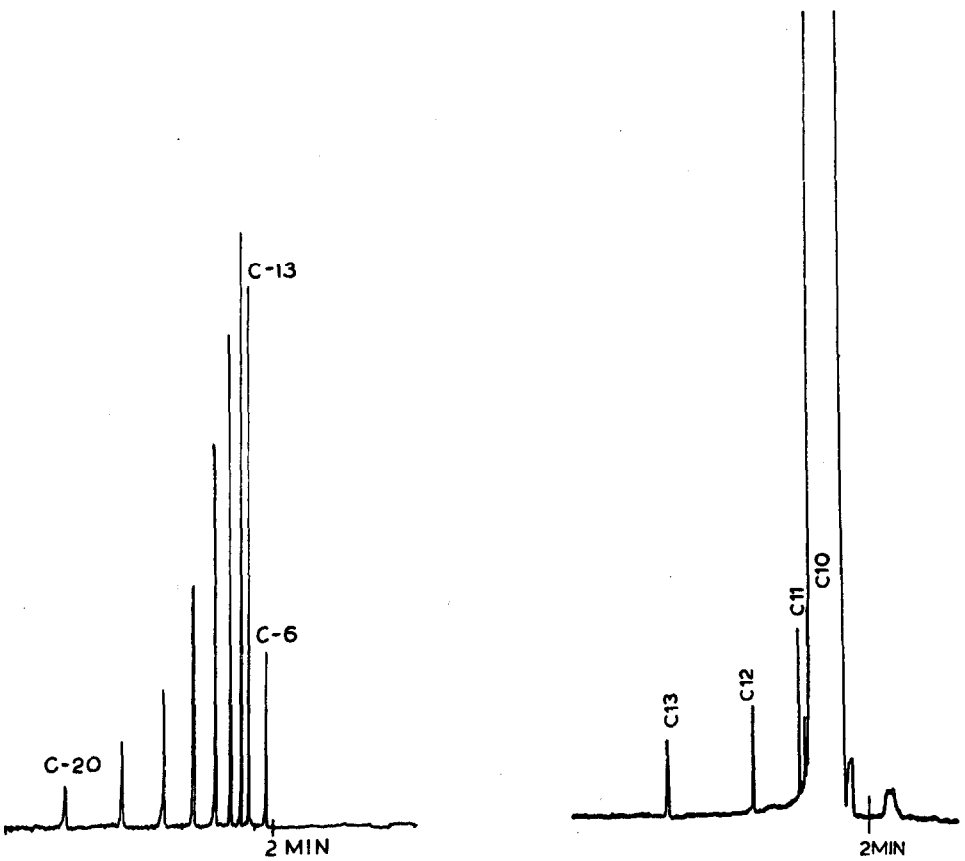

Fig. 4. "On-column injection" of 0.002 μl of the C_{13}–C_{20} mixture. Evaporation time: 30 sec. Injection time: 0.5 sec. Other details as in Fig. 3a.

Fig. 5. "Solvent-effect" injection. Column: OV-101 (50 m × 0.25 mm). Carrier gas: 2 atm H_2. Sample: 0.4 μl of C_{10} with C_{11}, C_{12} and C_{13} (20 ppm). Temperature: 115°C. Injection (10 sec) after 20 sec in the hot zone.

volume of only 0.001–0.005 μl. Such a low volume is placed into the vial with the help of a narrow-bore capillary (*ca.* 0.02 mm). The capillary is dipped into one liquid, the open end sealed with a micro-flame, cutting the excessive length of the filled capillary and the remaining specimen forced into the vial by a micro-flaming of the capillary. Here all the specimen is injected into the column. The experimental injection time is 0.5–1 sec. After this time, repeated injection from the same vial showed that no amount of specimen remained.

"Solvent-effect" injections

Fig. 5 gives an example of injection in a "solvent-effect" mode. Here 0.5–5 μl of a solution are first evaporated (0–20 sec) and then injected (5–20 sec). The temperature giving a maximum effect is specific to each solvent.

Injections of solids or gums, pyrolysis studies, etc.

The technical simplicity of placing a specimen into a vial greatly simplifies this problem. Moreover, a vial with an adsorbent on its internal surface may be effectively used for accumulating specimens from air, etc. This system of injection from a vial makes it especially useful for analysis of reaction mixtures and other "dirty" specimens where the use of a conventional evaporator may ruin the column or create an excessive background current from non-volatile deposits.

CONCLUSIONS

The described "inverse" injection system is very useful for a wide range of problems in gas–liquid chromatography. Advantages of this injection system are a very short injection time, which is important for complex mixtures, great economy in carrier gas consumption (splitless system), cleanness of the evaporation chamber, clean on-column injections and no discrimination in relation to the physical state of the specimen (solid, liquid) or low- and high-molecular-weight compounds.

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