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Note

Device to transform the liquid chromatographic effluent to a continuous solid plug: a new approach to direct liquid introduction for liquid chromatography–mass spectrometry*

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The effluent from a liquid chromatographic column is generally led into a detector and/or fraction collector. For flame photometric, mass spectrometric and other detection methods used for gas chromatography, the liquid effluent is changed into the vapour state. In the present paper we propose a process in which a liquid effluent is changed into a solid plug continuously.

In the direct liquid introduction interface (DLI) for liquid chromatography–mass spectrometry (LC–MS) it is essential to heat up a nozzle of a capillary tubing from which a liquid jet vapour is sprayed into a vacuum chamber^{1–3}. A thermal supply at least equal to the amount of heat required for evaporation of the liquid is needed. Without such a thermal supply at the nozzle, the liquid becomes solidified at the tip of the DLI interface due to cooling of the liquid below its melting point.

Arpino *et al.*⁴ observed that acetonitrile froze and appeared as a solid mass. We found that the solidification can be controlled by adjusting the thermal supply to the tip of the DLI interface. Thus, the eluent is solidified at the head of the capillary tubing, and the solid is continuously extruded into a vacuum chamber. We call the above process “solidified introduction” and have studied the basic phenomena involved under simulated LC–MS conditions. This process may be useful for sample storage or as an alternative method of DLI LC–MS.

EXPERIMENTAL

An experimental set up for observing the phenomena of solidified introduction under simulated LC–MS conditions is shown in Fig. 1. Instruments used were as follows: injector, Rheodyne Model 7520, 0.5 μ l (Rheodyne, Cotati, CA, U.S.A.); fused-silica capillary tubing, 50 μ m I.D. (S.G.E., Melbourne, Australia); open-tubular capillary tubing (Pyrex glass, 20–200 μ m I.D.); video camera, Victor GX-N4CH (Japan Victor, Tokyo, Japan); microscope, Olympus BH-2 (Olympus Optical, Tokyo,

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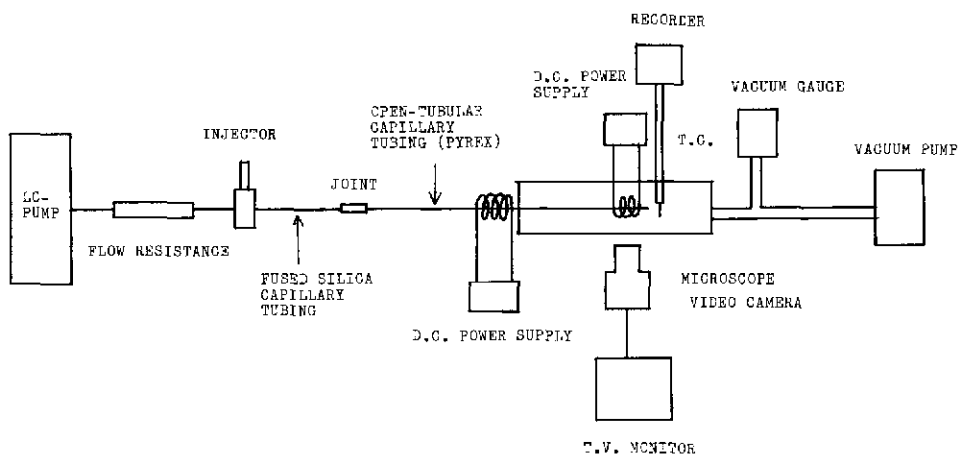


Fig. 1. Diagram of apparatus.

Japan); vacuum gauge, Macleod gauge (Okano, Osaka, Japan); rotary pump (Tokuda, Osaka, Japan) and thermocouple (alumel–chromel wire, 0.1 mm O.D.; The Japan Lamp Ind., Tokyo, Japan).

The extent of magnification obtained by means of the TV–microscope system was a factor of 118 on the 14-in. screen. A vacuum chamber, in which the head of the capillary tubing was set, was formed by a quartz tube (50 mm \times 9 mm I.D. \times 12 mm O.D.). Both ends of the quartz tube were sealed with silicone rubber. The pressure in the vacuum chamber was 0.01–0.3 Torr. A kanthal wire (1 mm O.D.; The Japan Lamp Ind.) with windings at the capillary head was used, as shown in Fig. 1. The temperature was adjusted by the application of a voltage from a d.c. power supply to the kanthal wire.

The inner diameters of open-tubular capillary tubings (Pyrex glass) used for the interface were between 20 and 200 μm . The glass capillary tubing was made by using a drawing machine (GDM-1; Shimadzu, Kyoto, Japan). Most experiments were done with 30–40 μm I.D. capillary tubing. For effective heating of the capillary head, it was necessary to keep an appropriate distance between the capillary tubing and the kanthal wire. For the above experimental conditions it was easy to use capillary tubing with larger outside diameters. Therefore, Pyrex glass capillary tubings were selected so as to produce capillary tubings with outside diameters such as 0.6 mm.

The flow-rate of the eluent was 0.3–8.0 $\mu\text{l}/\text{min}$. Coloured solutes, rhodamine 6G and 1-aminoanthraquinone, were used. Each was dissolved in the eluent used.

RESULTS AND DISCUSSION

The process of solidified introduction is shown in Fig. 2. An eluent is passed into a capillary tubing of the DLI interface at L_n , with a linear flow velocity, u , and a temperature at T_n ($^{\circ}\text{C}$). The liquid is gradually cooled, and it starts to solidify and becomes a solid at L_s . Then, the solid is smoothly extruded into a vacuum chamber at L_o . The temperature of the solid at L_o is T^* . At L_s , the heat of solidification, Q_s , is evolved. Electrical heating, YQ_e , is supplied at the head of the capillary tubing, where

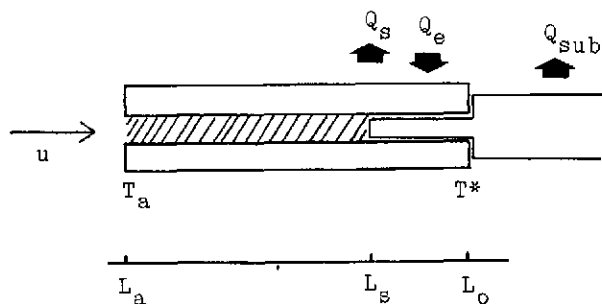


Fig. 2. The process of solidified introduction. See text for definitions.

Y is the efficiency believed to be around a few % or less. After the solid is extruded into the vacuum chamber, the heat of sublimation, Q_{sub} , is lost from the solid. The energy balance in the process of solidified introduction will be discussed elsewhere.

The liquid in the capillary tubing of the DLI interface is solidified, and then the solid is extruded into the vacuum chamber continuously. When the solute reaches L_s it is co-solidified with its solvent, and is carried into the vacuum chamber. These processes were observed by the present TV-microscope system.

The transfer of the solute by solidified introduction is shown in Fig. 3. The processes 1–5 are illustrated by sketches made from the TV screen. The experimental conditions were as follows: pressure of the vacuum chamber, 0.1 Torr; intensive heating at the head of capillary tubing ($30 \mu\text{m}$ I.D.). Water, *ca.* $6 \mu\text{l}/\text{min}$, and rhodamine 6G ($2 \cdot 10^{-3} M$ aqueous solution) were used as the eluent solute, respectively. The amount of rhodamine 6G injected was $0.5 \mu\text{l}$.

The solid extruded into the vacuum chamber was at first colourless (1 in Fig. 3), and then started to show a faint red colour (2 in Fig. 3). The colour became brighter

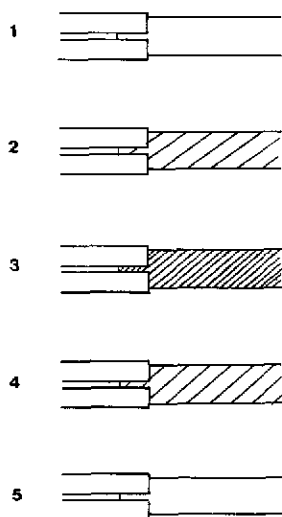


Fig. 3. The process of solute transfer. The solute and eluent were rhodamine 6G and water, respectively. The times for stages 1, 2, 3, 4 and 5 were 0, 6, 9, 15 and 18 s after injection, respectively.

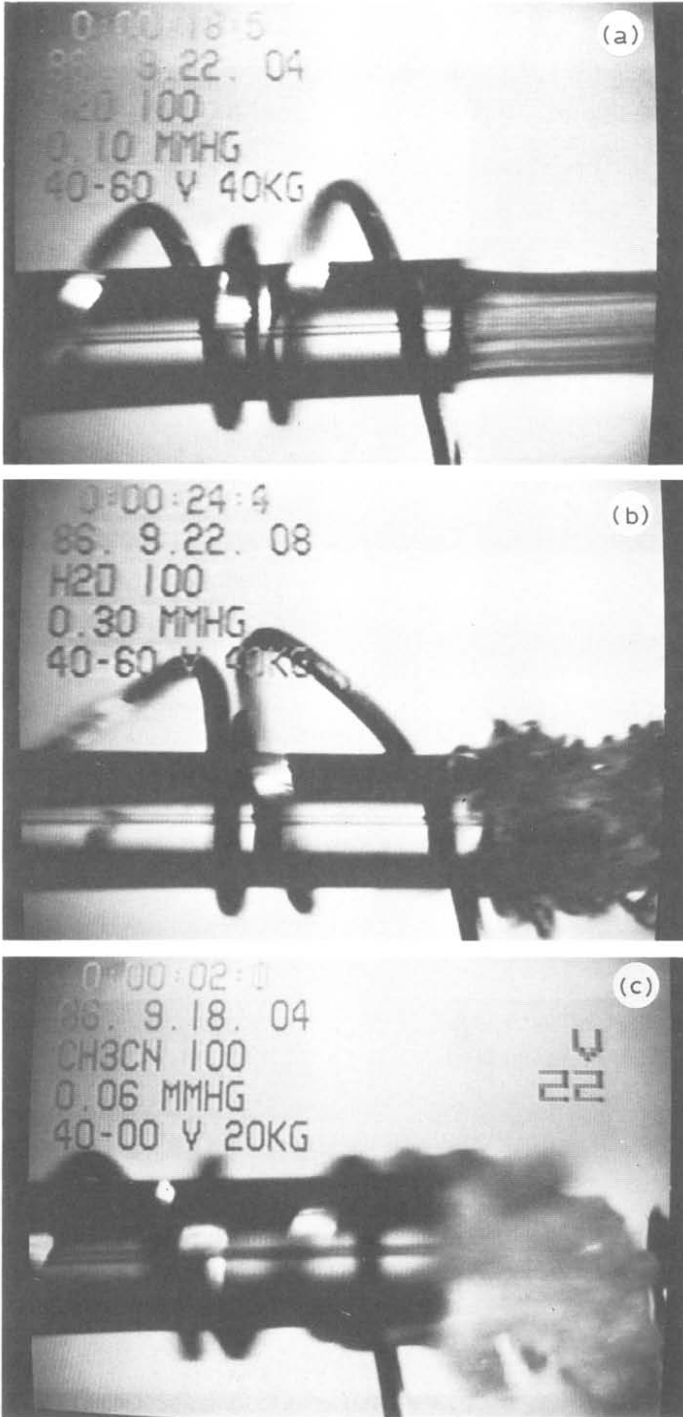


Fig. 4.

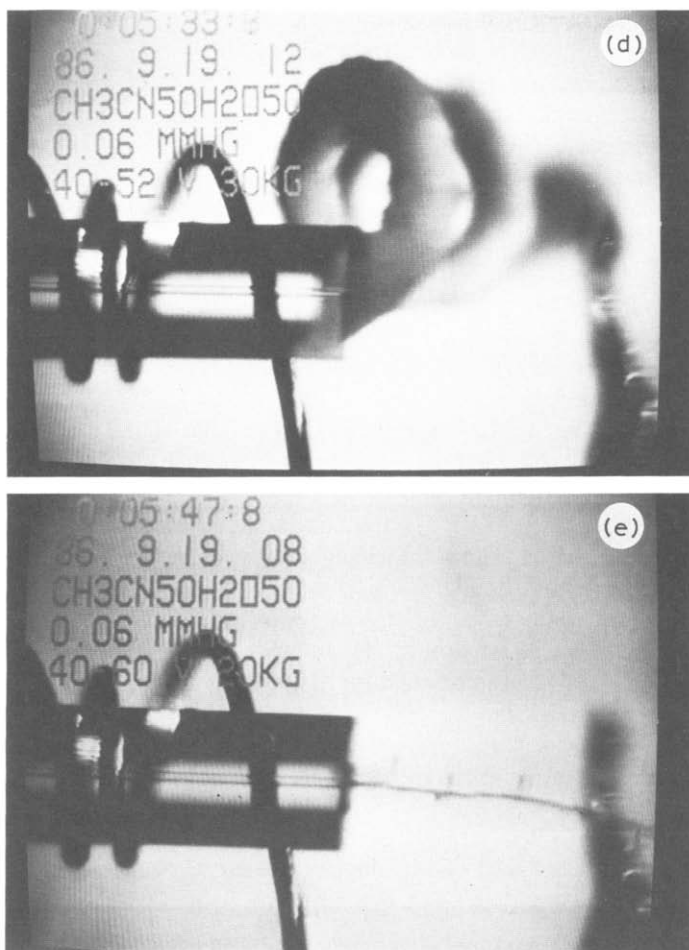


Fig. 4. Different types of patterns in solidified introduction. Each plate shows a glass capillary tubing, 30–40 μm I.D. and 0.5–0.6 mm O.D., a kanthal wire for heating and a solidified bar. In d and e, a thermocouple is seen at the right-hand side. Eluents: water (a and b); acetonitrile (c) and acetonitrile–water (50:50) (d and e). Pressures of the vacuum chamber: 0.10 (a), 0.30 (b) and 0.06 Torr (c, d and e). Other conditions as in the text.

(3 in Fig. 3) and then gradually faded; finally (5 in Fig. 3) the solid became colourless again. The duration of the red colour was about 10 s. Its band width was about 1.5 times that of the original one upon injection, which was simply estimated from the eluent flow-rate and the band width of the solute upon injection. In the present system, the solute in the eluent is smoothly solidified in a very small capillary tubing, and then extruded into the vacuum chamber without much band broadening. After the solidification at L_s , the phase surrounding the solid bar, which is in contact with the inner wall of the capillary tubing, may partly consist of liquid due to the electrical heating.

Five different types of patterns in solidified introduction are shown in Fig. 4. The flow-rates were 4–6 $\mu\text{l}/\text{min}$ for a–d, and 0.5 $\mu\text{l}/\text{min}$ for e. Heating was effected at the head of capillary tubing except in c. In a smooth solidified bar appeared. In b and c, this bar had a rough surface. The surface of the solidified bar in d was smooth, but the bar was bent and formed a circular rod. As the flow-rate in e was only 0.5 $\mu\text{l}/\text{min}$, a very narrow solidified bar appeared. The outside diameters of the solidified bars in a–d were several times larger than the inner diameter of the capillary tubing. In the case of e, these two diameters were nearly equal due to the low eluent flow-rate. Usually a straight bar was obtained, but sometimes a bent one. Although it is not clear why the solidified bar becomes bent, this might be due to the surface condition of the capillary head and/or variations of temperature at the capillary head. The extrusion was continued up to 10 min. Cases a, b and e seem to be favourable for solidified introduction.

A thin thermocouple (T.C. in Fig. 1) was mounted just in front of the capillary head so as to be in contact with the solidified bar. It is also seen at the right in d and e in Fig. 4. The distance between the thermocouple and the head of the capillary (L_0 in Fig. 2) was about 1 mm. The temperature of ice–water in a vacuum bottle was used as a reference in the thermocouple system. The solid which had just been extruded from the capillary head was contacted with the thermocouple. The output of the thermocouple was recorded with a potentiometer and the temperature of the solid bar thus calculated. A typical temperature measurement is shown in Fig. 5. The experimental conditions were as follows: eluent 6, $\mu\text{l}/\text{min}$; vacuum at capillary head, 0.06 Torr; inner diameter of capillary tubing, 30 μm .

In Fig. 5 a large negative peak with a flat shape and several sharp peaks are observed. These differences in thermocouple responses were due to the different durations of contact of the thermocouple with the solidified bar. The contact duration should be sufficient to enable the real temperature of the solidified bar to be recorded. This temperature, estimated from the response of the large negative peaks in Fig. 5,

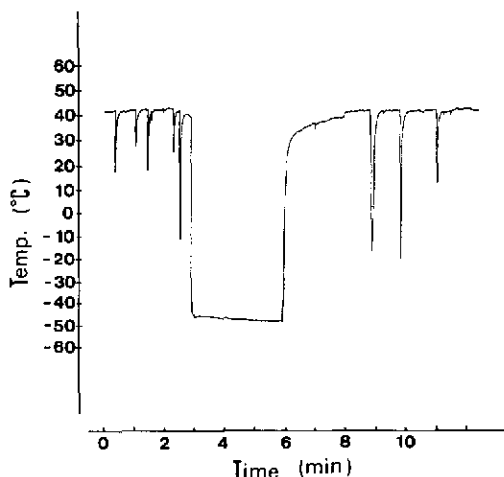


Fig. 5. Temperature of solidified bar, estimated from the output of the thermocouple. Time means the time of recording of the output. The peak widths correspond to the durations for which the solid bar was in contact with the thermocouple.

was about -47°C . Solid acetonitrile was cooled slightly below its melting point, -45.7°C at atmospheric pressure. The sharp peaks in Fig. 4 were recorded when the solid was contacted with the thermocouple for just a few seconds.

If strong heating was applied at the capillary head, the solidified bar melted and liquid was observed in the capillary tubing, which was sprayed into a vacuum room. This case is very similar to the behaviour of the DLI interface in LC-MS (DLI mode). It is possible to select solidified introduction or the DLI mode by adjusting the heating of the capillary head. Eluents such as water, acetonitrile, acetonitrile-water (95:5 or 50:50) and acetonitrile-0.1 M phosphate buffer (50:50, pH 7) were examined and found to be applicable for both modes. With pure water as the eluent, intensive heating was needed to change the solidified introduction to the DLI mode. The use of intensive heating means that the temperature of the kanthal wire itself was around 600°C . With acetonitrile or a mixture containing it, heating at the capillary head was moderate or, in some cases, not necessary for solidified introduction. Eluents containing methanol or ethanol were always in the liquid state (DLI mode) under the present experimental conditions. If the capillary interface is cooled with a coolant, these eluents may be solidified at the capillary head.

If the present process of solidified introduction is utilized for LC-MS, it may be more gentle to a solute than the ordinary process of DLI, because the latter needs at least a thermal supply equal to the heat of vaporization of the liquid used. In the process of solidification, the temperature of the eluent and solid bar is always decreasing toward that of the vacuum room. Therefore, the solidification process is milder to the solute. Thus the present system is suitable for thermally labile and high-molecular-mass substrates.

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