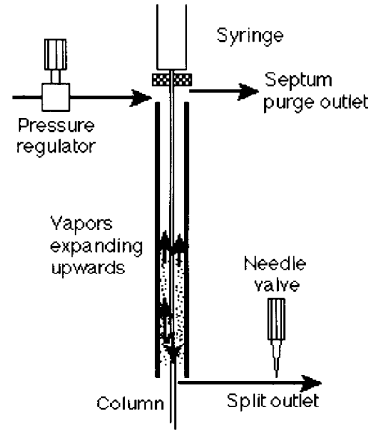
Figure 2 **Headspace injection at a low split flow rate, using gas supply by the pressure regulator/needle valve system: the sample should expand from the column entrance backwards.**



long. The commonly used 5cm needles enter the liner by less than 4cm and merely exploit the upper half of the chamber. 500 ul thus injected already overfill the injector liner, i.e. cause sample material to be expelled through the septum purge outlet or to penetrate the carrier gas supply line.

Systems with flow-regulated carrier gas supply and a back pressure regulator in the split outlet (e.g. Hewlett Packard) behave differently. Pressure increase by injection causes the back pressure regulator to open widely and increase the split flow rate. The sample cloud expands downwards (Fig. 3). As the volume of the injector can only be exploited by releasing the sample at the top of the chamber, the syringe needle should be no longer than 2-3cm (or a longer needle should be introduced only partially).

A drawback of this type of gas supply is the split flow rate during the splitting process is rather ill defined.

SPLIT INJECTION OF LIQUID SAMPLES

Split injection of liquids resembles gas/ headspace injection except that the rate of vapor formation cannot be controlled. Injection must occur rapidly in order to avoid excessive evaporation inside the syringe needle. 2u1 of a solution in a volatile solvent, such as dichloromethane, creates some 0.9ml of vapor in maybe 0.5, i.e. vapors are formed at 1.8 ml/s (108 ml/min). With a split (and column) flow rate of 108 ml/min at least, the situation of Fig. 1 applies, i.e. the syringe needle should merely enter the vaporizing chamber. It leaves maximum room between the needle exit and the column entrance for sample evaporation and mixing across the vaporizing chamber. If the split flow rate is lower, i.e. vapors are formed more rapidly than gas is discharged, a long or a short needle is best suited depending on the carrier gas supply system involved (Fig. 2 or 3).

Samples with high boiling matrices, such as many undiluted liquids, evaporate slowly; discharge of the vapors is a problem only if the split flow rate is extremely low. Such liquids are easily transferred to the wall of the liner (no repulsion by vapors). If an empty liner is used (preferably of narrow bore, e.g. 2mm), short syringe needles render such transfer more reliable as the risk of shooting the sample liquid by the column entrance becomes small.

SPLITLESS INJECTION

In splitless injection, the sample vapors must be stored in the vaporizing chamber until they are transferred into the column, which may take over a minute. Before being diluted with carrier gas, 2ul of a solution in hexane produce around 500ul of vapor, in dichloromethane as much as 900 u1, which shows that the internal volume of an 80mm x 4mm ID liner must be fully exploited.

As the split outlet is closed there is only one way of filling the vaporizing chamber: from the bottom to the top, displacing the carrier gas backwards. The syringe needle must be adjusted to situate the center of sample evaporation slightly above the column entrance. The distance between the needle exit and the column entrance must account for the distance the droplets travel before evaporating, i.e. l-2 cm. For the usual geometry of the injector this means using 3 inch (71 mm) needles (or rather the vaporizing chamber was designed such that standard 3 inch needles would fit). There is a second reason for depositing the sample close to the column entrance. As shown in Fig. 4 (on the following page), a 5 cm syringe needle leaves a distance of some 40 mm to the column entrance, representing a plug of some 400 ul of carrier gas. Before substantial amounts of sample vapor reach the column, this gas must be discharged into the column, i.e. during 10-20s primarily carrier gas is "injected".

Figure 3 - Sample expanding downwards in the instance of a system with flow regulation/ back pressure regulation.