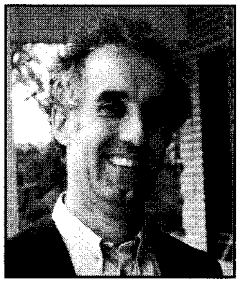
Why 5 cm syringe needles for capillary GC?



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GC is a complex technique. All too often the analyst stands in front of his instrument, surprised about a result, maybe annoyed about a problem, and at a loss for an explanation for what he observes. Often, not even his colleague is able to explain. Another of these CC mysteries? Probably he would have the knack of it if he knew the many details involved in the analytical process. We make numerous choices without being aware of them, overlook variables clinging to the illusion that they had been thoroughly investigated in the past and that an international committee has decided that this or that is the correct choice. The length of the syringe needle is one such frequently neglected detail and is an example of a parameter which has never receivedproper attention.

Many years ago, the manufacturers of GC syringes looked upon their customers and noticed that there was no agreement on how long syringe needles should be for conventional vaporizing (split or splitless) injection. Some said 1.5 inch (the needle protruding 37 mm from the glass barrel), others 3 inch (71 mm), or even longer. So, father syringe producer decided to compromise and have it in between: 2 inch (5 1 mm). Whether or not he died in the mean time, that's how it still is. Some disagreed, but since it seems to be more important that GC is simple than that it is well optimized, the subject was commonly neglected. The subject of needle length seems not to be of sufficient scientific status to justify closer investigation.

As you can check by a few experiments, the length of the syringe needle and the depth by which a long needle is inserted into the injector often have an important impact on quantitative analysis. The reasons are explained below. It is concluded that they need to be adjusted to the situation. The length of the syringe needle determines from which point inside the liner the sample expands during the evaporation process. It may, however, also influence vaporization itself.

HEADSPACE ANALYSIS:

We start by looking at gas or headspace analysis, because the situation is particularly simple since no vaporization interferes. However, the same principals will also apply to liquid samples. We refer to (manual or automated) injection with agastight syringe of 0.5-l ml capacity.

Usually an amount of gas phase is injected that approaches the internal volume of the vaporizing chamber. For instance, a 4 mm ID liner of 80 mm length has an internal volume of 1 ml. A 500 µl sample mixes with carrier gas to form a vapor cloud of close to this volume (inlet pressure compresses the cloud but increased temperature causes it to expand). Care must be taken to release the sample from the syringe needle in such a way that it ends being positioned inside the chamber.

Gas and headspace samples are usually injected in the split mode in order to achieve sharp initial bands. Depression of the plunger at normal speed introduces the sample at around 0.5-l ml/s, i.e. 30-60 ml/min. If the sum of the split and the (comparably small) column flow rate corresponds to the rate of injection, expansion of the sample downwards replaces the gas flow from the rear. Gas supply is stopped; the gas phase running off originates from the syringe (assumption of a pressure-regulation/needle valve system, Fig. 1). At higher split flow rates, the sample is diluted with additional carrier gas from the rear. Under these conditions, basically unlimited volumes of sample can be injected without overloading the injector. A short syringe needle merely entering the vaporizing chamber (2-3 cm) serves the purpose, but longer needles are no drawback.

Since headspace analysis is mostly trace analysis, the split flow rate is usually substantially below the 30-60 ml/min mentioned above. This leaves the choice of injecting at a correspondingly reduced rate or temporarily storing the vapor cloud inside the vaporizing chamber. The latter corresponds to common practice. If more sample is injected than gas runs off at the same time, carrier gas must be displaced within the injection system. Appropriately designed injectors with a pressure regulator at the rear and a needle valve in the split outlet have a relatively large internal volume in the gas supply and a small one in the split outlet, causing the sample to expand backwards (Fig. 2). Long syringe needles are required such that the sample expands from a point near the column entrance towards the rear. If the liner is 80 mm long, the column enters by 5 mm, and the injector head is some 12 mm high, the syringe needle should be around 80 mm

'Figure 1 - Injection at a rate equal to the flow rate of the gas passing through the liner: the flow from the carrier gas supply is substituted by that leaving the syringe needle.

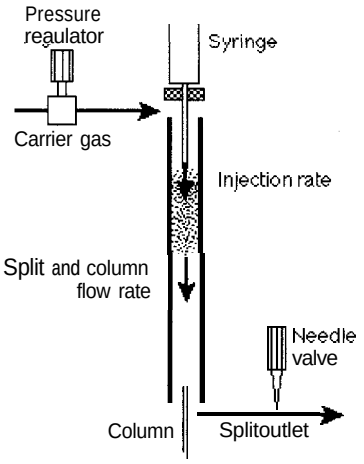
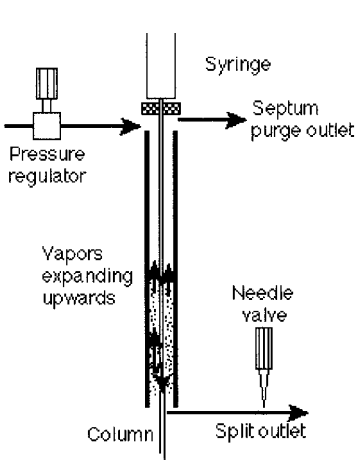


Figure 2 - Headspace injection at a low split flow rate, using gas supply by the pressure regulator/needle valve system: the sample should expand from the column entrance backwards.



long. The commonly used 5 cm needles enter the liner by less than 4 cm and merely exploit the upper half of the chamber. 500 µl 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 2-3 cm (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. 2 µl of a solution in a volatile solvent, such as dichloromethane, creates some 0.9 ml 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. 2 mm), 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, 2 µl of a solution in hexane produce around 500 µl of vapor, in dichloromethane as much as 900 µl, which shows that the internal volume of an 80 mm x 4 mm 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 µl 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.

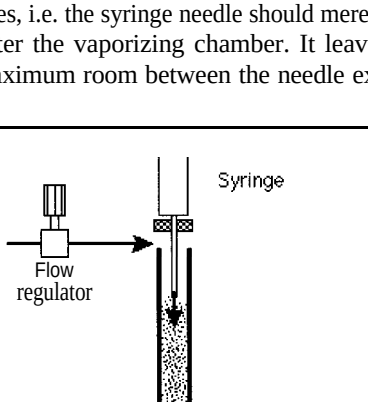
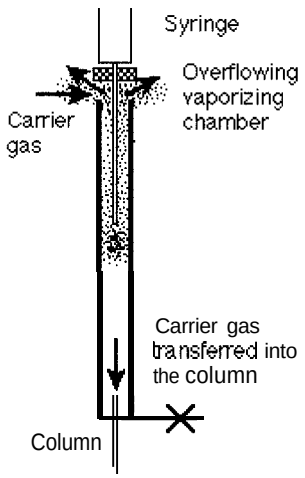


Figure 4 - 5cm syringe needles are too short for splitless injection as the chamber is overfilled even with small sample volumes & some 400µl of carrier gas must be transferred into the column before sample vapors get there.



Knowing how difficult it is to achieve complete sample transfer in splitless injection, this is certainly not the kind of problem we need.

SAMPLE EVAPORATION **INSIDE THE NEEDLE**

As if the subject were not of sufficient complexity yet - the length of the syringe needle also influences sample evaporation. Parts of the sample may be vaporized inside the needle during injection or when the needle content is eluted after the plunger is fully depressed. On the one hand, this often causes problems as more is injected than measured and preferential vaporization of volatile components discriminates against high boilers. On the other hand, it helps nebulizing the sample liquid at the needle exit, which is the prerequisite for sample evaporation in the gas phase of the injector (the most gentle vaporization process, since there are no contacts with packing materials adsorbing or degrading solutes). There is more vaporization inside long needles accentuating these advantages and disadvantages.

CONCLUSIONS

The 5 cm needle for vaporizing GC injectors is a typical compromise: it is between the desirable long and the desirable short needle, but is hardly ever desirable as such. The following table suggests optimum needle lengths.

Optimum Needle Lengths

Injection Technique	Gas Supply System: Pressure reg./ needle valve	Gas Supply System: Flow reg./ back pres. reg.
Splitless	71 mm	71 mm
Split (flow rate >100 ml/min.)	25 mm	25 mm
Split (flow rate <100 ml/min.)	71 mm	25 mm
Split, high boiling matrix	25mm	25 mm

The length of the syringe needle is more critical than usually recognized. Try and see! Although this has been known for more than 15 years, only a few autosamplers give you the choice of varying the injection point. Presumably this is because too many customers ask more about the software for data handling than about the gas chromatograph when they buy a new instrument. Today much emphasis is given to quality assurance. Large amounts of time are invested into general QA procedures, the usefulness of which is not always obvious. Upon such efforts, easily more important optimization of technical aspects is neglected.