



Syringe Injection Techniques

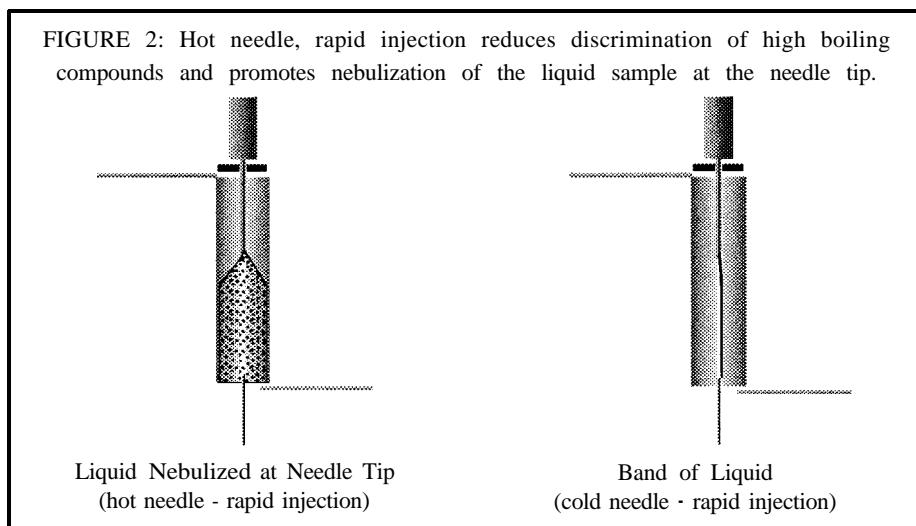
Liquid sample introduction in gas chromatography is usually performed with a hypodermic style syringe. A few guidelines should be followed when performing both vaporizing and cold on column injections.

SAMPLE INTRODUCTION INTO A VAPORIZING INJECTION PORT

Sample introduction into a heated vaporizing chamber via a hypodermic syringe is a convenient method for both split and splitless modes of capillary gas chromatography. Unfortunately, the technique used during this type of sample introduction can drastically affect the amount of analyte entering the analytical column. A comparison of needle handling techniques has been reviewed by Grab' and is summarized in Figure 1.

The most frequent problem created by the syringe needle (usually stainless steel) is the discrimination of higher molecular weight analytes which may be present in the sample. As the needle punctures the injection port septa and enters the heated vaporizing chamber, the temperature of the needle rises to the chamber temperature in a matter of seconds. The volatile solvent and low boiling analytes in this temperature region will rapidly exit the needle but less volatile components will be left behind coating the inner needle surface. When the needle is removed from the injector, these low volatility components are lost.

The most successful technique used to limit the severity of high boiler discrimination is



the hot needle - rapid plunger depression injection technique. For this technique, the sample should be completely withdrawn from the needle into the barrel of the syringe. After the needle punctures the septa, the depression of the syringe plunger is delayed for approximately five seconds allowing the needle to equilibrate in temperature with the injection port. Rapidly depressing the syringe plunger jettisons the liquid sample into the hot needle. Instantaneously, the vapor pressure of the solvent increases, creating high pressure inside the syringe needle which results in a rapid expulsion of the sample through the small needle orifice. This rapid expulsion of the sample not only prevents deposition of high boiling material on the inner needle wall but also promotes nebuliza-

tion of the sample at the needle exit. Dispersing the sample into very small droplets allows their velocity to slow to the speed of the carrier gas providing more time for vaporization to occur before the sample reaches the column and the split point. Solvents with low boiling points and surface tension values such as pentane tend to be nebulized most easily. As a rule of thumb, the injection port temperature should be set at the maximum operating temperature of the analytical column to enhance the effects of the hot needle, rapid injection technique.

The use of autosamplers to increase sample throughput has become common in laboratories responsible for the analysis of large numbers of samples. Unfortunately, some autosamplers cannot be programmed to perform hot needle, rapid injection. With many autosamplers the needle is rapidly thrust through the septa and the plunger is depressed almost instantaneously. This technique is referred to as cold needle, rapid injection, which results in the sample exiting the needle as a liquid stream. This technique also reduces high boiler needle discrimination (due to minimal vaporization in the needle), but does not promote nebulization at the needle tip. Cold needle rapid injection can result in non-linear splitting or sample loss in the splitless mode due to void areas at the bottom of the injection port. The use of fused silica wool or the gooseneck style injection port sleeves can remedy these problems. Figure 2 illustrates potential differences between hot and cold needle, rapid injection.

FIGURE 1: Discrimination of high boiling components due to losses inside the syringe needle of several common injection techniques.

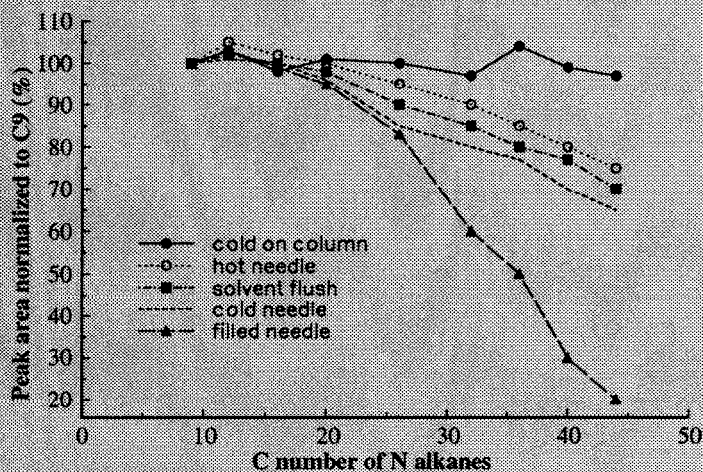
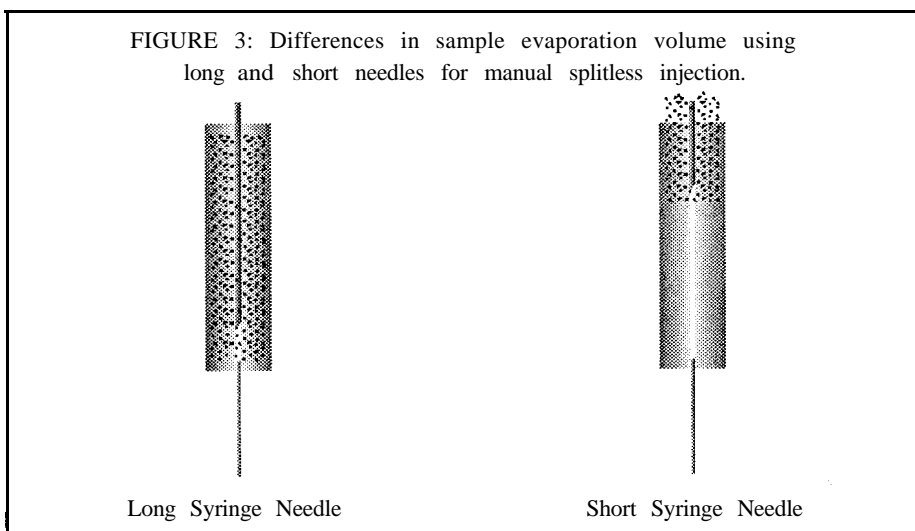




FIGURE 3: Differences in sample evaporation volume using long and short needles for manual splitless injection.



end of the needle. Since the needle and the column wall are in close proximity to one another, sample liquid can be drawn in this space by capillary action allowing part of the sample to be drawn out of the column when the needle is removed. Rapid plunger depression increases the speed at which the sample liquid travels through the needle separating the sample from the needle tip. The sample is deposited some distance below the needle tip on the column wall reducing the chance of sample loss.

The effects of the syringe needle is often overlooked when making injections in gas chromatography. Improper handling of the syringe can result in discrimination or loss of high molecular weight compounds. Needle length can also have an effect on sample loss. Therefore, longer needles that deposit the sample at the bottom of the inlet liner are preferable for manual splitless injection. For cold on-column injection, faster plunger depression will also minimize sample loss.

NEEDLE LENGTH CONSIDERATIONS IN MANUAL SPLITLESS INJECTION

Flow rates through the injection port sleeve in the splitless mode are relatively small in comparison to split injection. Therefore, solvent expansion of the sample in the injection port sleeve can cause sample loss due to the slow transfer of vapor into the column. One way to prevent loss of sample vapor from the top of the sleeve is to deposit the sample near the bottom of the vaporizing chamber. This injection technique provides the greatest amount of sleeve volume to be used for sample containment. For example, injection ports designed to fit 80mm liners would require a syringe with a needle length of 71mm. This length allows for ample space at the bottom of the liner for the addition of a fused silica wool plug to insure the arrest of any unvaporized sample that could potentially reach void (no flow) regions at the very bottom of the injection port.

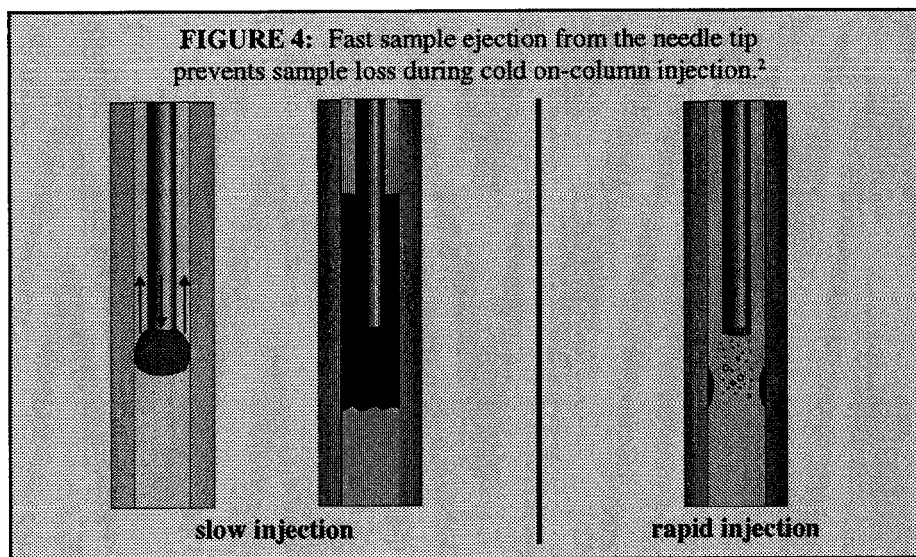
TECHNIQUES FOR COLD ON-COLUMN INJECTION

The data shown in Figure 1 indicates the lack of high boiler discrimination due to needle effects when performing cold on-column injections. This technique eliminates needle discrimination simply because the needle is not heated above the boiling point of the

solvent allowing the sample to exit the needle in liquid form.

The speed at which the plunger is depressed does play a role in sample losses during on-column injection. Depressing the plunger at a slow rate allows a large droplet to form at the

FIGURE 4: Fast sample ejection from the needle tip prevents sample loss during cold on-column injection.²



¹Grab, Konrad, *Split and Splitless injection in Capillary Gas Chromatography*, Huthig, Heidelberg, Germany, 1993.

²Konrad, *On-Column Injection in Capillary Gas Chromatography*, Huthig, Heidelberg, Germany, 1993.

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