IMPROVEMENTS TO INJECTION TECHNOLOGY IN CAPILLARY CHROMATOGRAPHY

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Introduction

An understanding of the interaction of syringe and inlet liner is important to optimize the chromatographic process and to obtain accurate and reproducible results. Many papers have been written about this phenomenon but the majority of these have not addressed the fundamental issues of dispensing very small samples from the syringe during the injection process. This is particularly important when using high speed autosamplers where the injection process is rapid and little interaction occurs between the syringe needle and the hot injection port.

Work has been undertaken to better understand results of various autosampler syringe and inlet liner combinations. The results of this work has lead to the development of an inlet liner to optimize autosampler injection.

Aim

To study the chromatographic effect of syringe and inlet liner combinations by observing changes to peak shape and chromatographic precision and reproducibility.

Experimental

Syringe used in this experiment

The small injection volume and the low sample exit velocity from the needle of a 0.5µL plunger-in-needle syringe make it ideal for this study. Without needle tip wiping, a sample leaving the tip of this syringe has the tendency to form droplets and wet the needle tip rather than forming a jet of nebulized liquid from the needle tip. Effective tip wiping should improve both peak shape and injection reproducibility.

Packing of Injection Liners

Figure 1 illustrates the six liner packing positions studied in these experiments.
Note: Fine (high-density) quartz wool was used to pack each liner. Subsequent experiments showed that fine quartz wool is superior to course quartz wool in wiping the needle tip.

Chromatographic Conditions

Column:

Column:	SGE, 25m x 0.32mm, BP1, 0.5µm film
Carrier Gas:	Helium
Flow Velocity:	2.3mL/min
Oven Temperature:	120°C

Injector:

Injection:	Split/Splitless Injector
Liner packing positions:	(as specified)
Injector Temperature:	200°C
Split Ratio:	50:1

Detector:

Detector:	FID
Detector Temperature:	300°C

Autosampler:

Injection Volume:	0.1µL
No. of injections per vial:	15
No. of pumps:	6

Sample:
(approx.) 0.02% C_{10} in C_7

Signal Parameters:

Range:	0
Attn:	4

Data Handling:
Delta Chromatography System - calculations based on peak area.

FIGURE 1. Liner Packing Positions

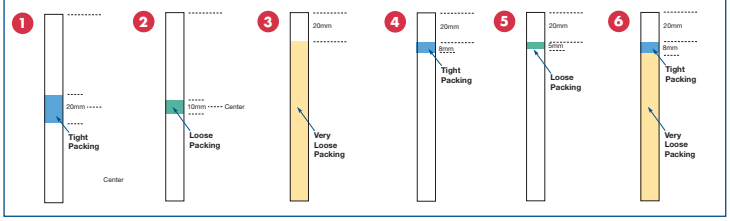

FIGURE 2. Resultant Chromatograms from packed liners shown in Figure 1

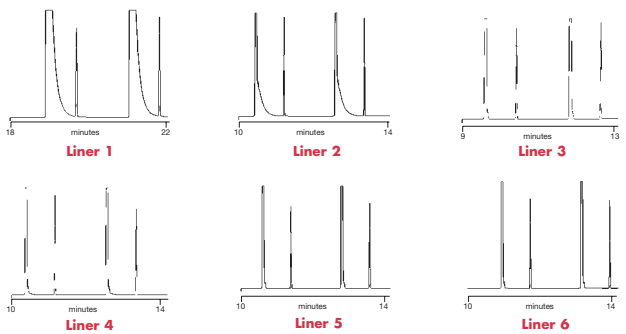

FIGURE 3. FocusLiners™

Results Refer to Figure 2

Liner 1 and 2
The chromatograms obtained from **Liner 1** and **Liner 2** show severe solvent peak tailing. This is consistent with slow volatilization of the sample and/or slow transfer of the sample onto the column. These liners do not wipe the needle tip during injection.

Liner 3

Minor peak tailing was observed from **Liner 3.** On removal of this liner from the injection port, it was found that the needle had pushed the quartz wool beyond the point where it wiped the needle tip during injection.

Liner 4, 5 and 6

Acceptable chromatography was achieved with **Liners 4 to 6.** These were packed to ensure that the needle tip was wiped during injection. However, upon multiple injections, it was found that **Liner 5** suffered the same problem as **Liner 3,** with the packing being pushed beyond the point where it wiped the needle tip. The quartz packing needs to be tight enough to avoid being pushed down the liner by the needle.

Reproducibility:

Chromatographic reproducibility was checked on Liner #1 and Liner #4. The results are tabulated below:

Table #1

Syringe Liner no.	0.3µL(0.5B-0.63) Liner 4	0.3µL(0.5B-0.63) Liner 1
Tailing:	Good	Poor
Mean Area Count	898.55	671.45
Std. Dev. Area Count	5.16	85.49
%RSD (Area Count)	0.57	12.73

Boiling Point Discrimination

Table 2 tabulates recovery results for C_8 to C_{32} hydrocarbon mixture injected onto **Liner 1** and **Liner 4.** The aim of this experiment was to determine if there is any detrimental boiling point discrimination by moving the liner packing from the center **(Liner 1)** of the injection port to a position where the needle tip is wiped **(Liner 4).** The tabulated results below express the ratio of the four highest molecular weight components against C_{11}. *Note: components were not in equal ratios.*

Table #2

Compound Ratio Ratio	Liner 4 Ratio C_x/C_{11} Packed to wipe needle	Liner 1 Ratio C_x/C_{11} Packed-center of liner
C_{22}/C_{11}	0.95	0.95
C_{24}/C_{11}	0.44	0.44
C_{28}/C_{11}	0.47	0.49
C_{32}/C_{11}	0.55	0.54

Conclusion

Severe peak tailing and poor reproducibility is often observed if the needle tip is not wiped during injection when using high speed autosamplers, particularly when injecting small (<2µL) volumes. It occurs when the sample being delivered from the syringe forms droplets that wet the syringe needle tip rather than forming a jet of nebulized liquid from the tip. With the rapid withdrawal of the needle from the injection port; the tip is wiped by the septa causing slow secondary vaporization near the cool septum cap. This is most prevalent on plunger-in-needle syringes.

The peak tailing and poor reproducibility is amplified when using a plunger-in-needle syringe. This is believed to be predominantly due to the larger ID of plunger-in-needle syringes, which results in a larger droplet on the end of the needle.

By placing the liner quartz wool packing in a position where the needle tip is wiped during injection, peak shape and reproducibility is improved without adversely effecting boiling point discrimination.

A commercial product, known as the "FOCUSLINER™", is available with the quartz wool positioned for optimum needle tip wiping. The quartz wool in this liner is held in position by means of two tapered sections in the liner (refer **Figure 3**).

It is also noted that overtightening of the septum cap when using a high-speed autosampler leads to poor peak shape and reproducibility. It is believed that over tightening causes septum deformation and hence leakage during the rapid injection stroke.

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