

## Form & Function II: Understanding the Complex World of GC Inlet Liners An analysis of liner choice on splitless & direct injection techniques

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### Abstract

The performance of a gas chromatograph (GC), a sophisticated piece of expensive analytical instrumentation, can be compromised by a small, low-cost piece of glass housed in the GC's inlet. Though small and relatively inexpensive, the glass inlet liner plays a crucial role in the complex process of sample vaporization that occurs inside the GC. It can therefore define data's accuracy, precision, or representation of the sample. So, it is important to have the right inlet liner. However, there are so many to choose from.

Part 1 of this talk explored the differences that exist in the myriad split liners for split applications. Part 2 will discuss the effect of liner geometry and packing material on the different demands of splitless and direct injection methods. The presentation will focus on a quantitative demonstration of the effect of varying liner geometries on the analysis of samples spanning a relatively wide range of molecular weights. The interaction between splitless and direct injection method parameters and liner configuration will be discussed.

Additionally, the role of wool or other packing materials will be discussed, and we will challenge the belief that relatively slow flow rates during splitless injections eliminate the need for a packing material. Finally, a comparison will be made between the degree of sample transfer during properly configured splitless injections and direct injections.

Liner deactivation will specifically not be discussed in this presentation in an attempt to provide information that spans liner manufacturer, since many of the same or similar geometries are offered by a variety of vendors, but each vendor's deactivation is likely to be different. The best deactivation can still be rendered moot if the wrong liner configuration is chosen for a particular task.



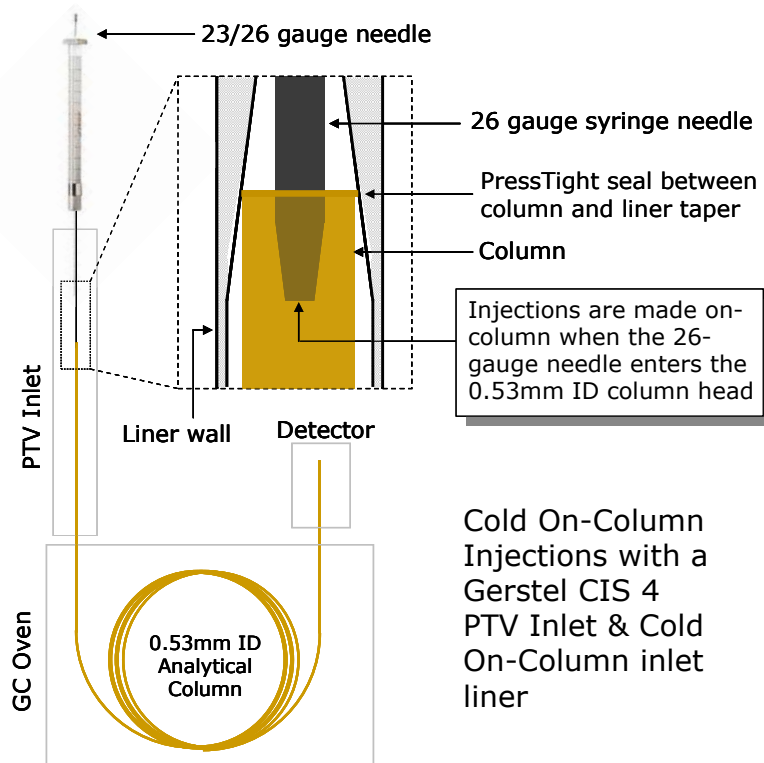
## A Measure of Accuracy

To quantify how much of a sample is transferred onto the column during split or splitless analyses, we must have a measure against which to gauge our observations. For a given mass, the best way to determine its true response is to inject it via cold on-column to completely bypass any loss in the inlet.

A programmable temperature vaporization inlet (PTV) was used to perform this experiment. To effect true on-column injections in a PTV injection port, a novel liner was used that placed the end of a 0.53mm column close enough to the top of the liner that the 23/26-gauge needle of the autosampler syringe could be guided into the column during an automated injection, where it injected the sample. The liner has a dual-tapered restriction where the column is pressed into the lower taper, forming a leak-free seal between the column's polyimide coating and the glass wall of the liner. The top taper guides the needle into the column. Figure 1 illustrates the set-up.

Note: Normally a retention gap is used to help focus the sample, but a connection was undesirable because of possible problems associated with leaks or dead volume.

**Figure 1:** Experimental set-up for cold on-column injections in a PTV injection port using a novel cold on-column inlet liner (PN: 24977)



**Table 1:** Analytical conditions for the cold on-column experiment

**Instrument:**

Agilent 7890A with Gerstel CIS 4 PTV Inlet and an FID detector

**Injector:**

Autosampler; Fast plunger; 1 µL injection from a 5 µL syringe (PN: 21210)

**Inlet:**

PTV; 45 °C (hold 1 min) to 345 °C @ 20 °C/min (hold 2 min); He carrier; splitless with 20 mL/min @ 2 min. Constant Flow @ 5 mL/min

**Column:**

30 m, 0.53 mm, 0.5 µm Rxi®-5ms (PN: 13440)

**Oven:**

40 °C (hold 1 min) to 350 °C @ 20 °C/min (hold 2 min) = 18 min run time

**Detector:**

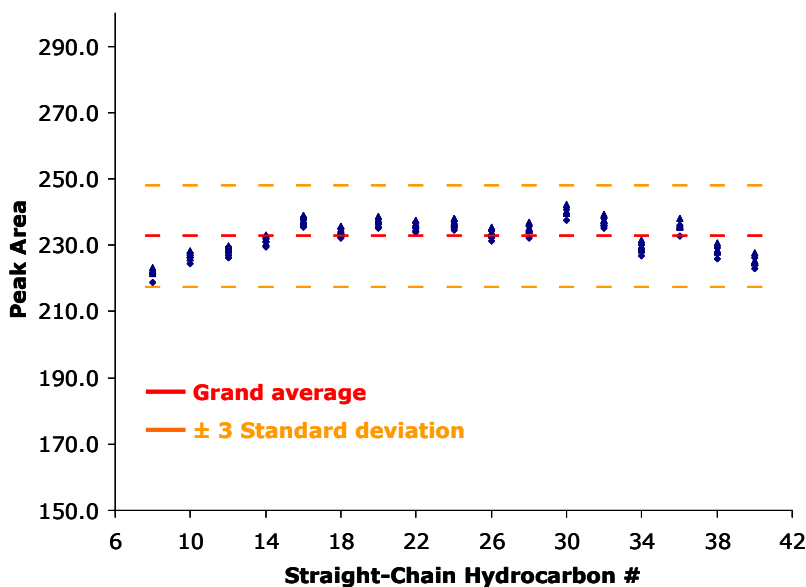
Flame Ionization Detector; 340 °C  
H<sub>2</sub> @ 40 mL/min, Air @ 400 mL/min, N<sub>2</sub> @ 45 mL/min

**Sample:**

10 ng/µL Florida Total Recoverable Hydrocarbons mix (17 straight-chain hydrocabons; C8-C40, the evens)

Using the experimental set up noted in figure 1 and in table 1, seven replicate injections were made of a mix of 17 straight-chain hydrocarbons. All seven data points for each analyte are shown above. Since all hydrocarbons are present at the same mass, it was assumed that they should ideally yield the same response from the FID. As a result, a grand average was taken to represent the ideal “accurate” response, and three standard deviations from that average represent the error in the measurement. These results are presented in figure 2.

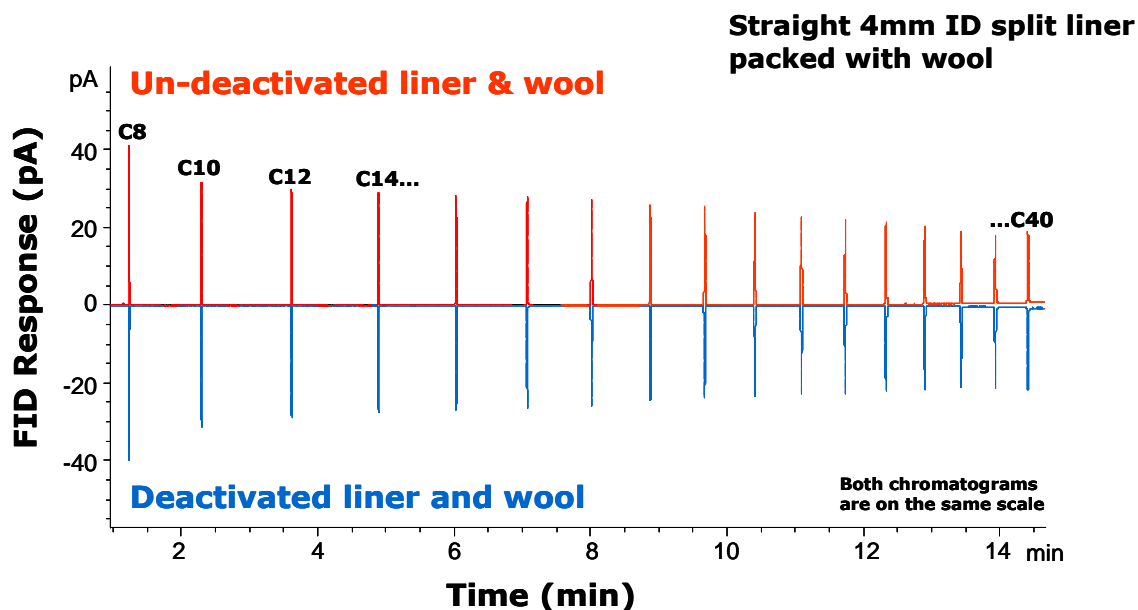
**Figure 2:** Cold on-column results for seven replicate analyses of 17 straight chain hydrocarbons at 10 ng/µL in hexane



### Taking Liner Activity Out of the Equation

To be able to determine the effect of liner configuration and the presence or absence of wool on sample vaporization and transfer it is desirable to remove any effect of liner or wool activity. To be able to do this effectively, it was decided to use a sample that would be insensitive to any activity present. Straight-chain hydrocarbons are able to pass through liners with a considerable amount of activity without effect because their chemistry renders them inert, so a completely inert liner isn't necessary. Figure 3 illustrates how the 17 hydrocarbons used in this study were unaffected by a completely undeactivated liner packed with undeactivated wool. Because of this insensitivity to liner activity, significant differences that are observed can be attributed to the run conditions or liner configuration.

**Figure 3:** Comparison of hydrocarbon response between a liner with wool that was deactivated and a liner with wool that was undeactivated.



## Setting proper splitless and pulsed splitless conditions

Splitless injections are used to increase the amount of sample that is transferred to the column by keeping the split vent valve closed during sample transfer. But eventually the split vent valve opens and the inlet enters split mode. If the sample hasn't been adequately transferred to the column before this event, the analysis won't be as sensitive as it could be. How do you make sure you have the right splitless hold time? There is a convenient tool that Agilent has provided called the HP Flow Calculator that helps with this. With the tool, some knowledge of your liner and run conditions, and a good rule of thumb, you can maximize your sample transfer to ensure the greatest degree of sensitivity. All splitless and pulsed splitless analyses presented in this poster use this technique

**Figure 4:** The HP Flow Calculator software highlighting the inlet flow value and an example of how to use the tool to set the appropriate splitless hold time.

By entering your column, temperature, and column flow rate information the calculator generates an **inlet flow rate** which can then be compared to the volume of the liner used to determine the time necessary to "sweep" one liner volume's worth of gas onto the column. **The rule of thumb is the splitless hold time should be long enough to sweep the liner's volume twice.**

Using the pulse pressure you can determine the appropriate hold time for pulsed splitless injections as well.

### EXAMPLE:

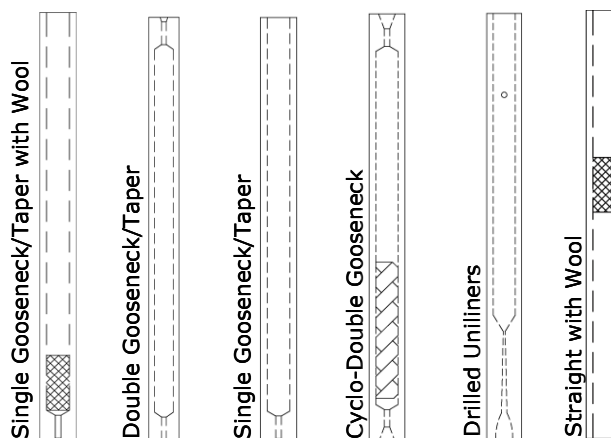
Inlet Flow = 1.80 mL/min

Internal liner volume  $\approx$  0.900 mL for an Agilent-style single gooseneck liner

Time to "sweep" one liner volume =  $0.900 \text{ mL} \times 1 \text{ min} / 1.8 \text{ mL} = 0.5 \text{ min}$

Time to "sweep" two liner volumes =  $0.5 \text{ min} \times 2 = 1 \text{ min} = \text{splitless hold time}$

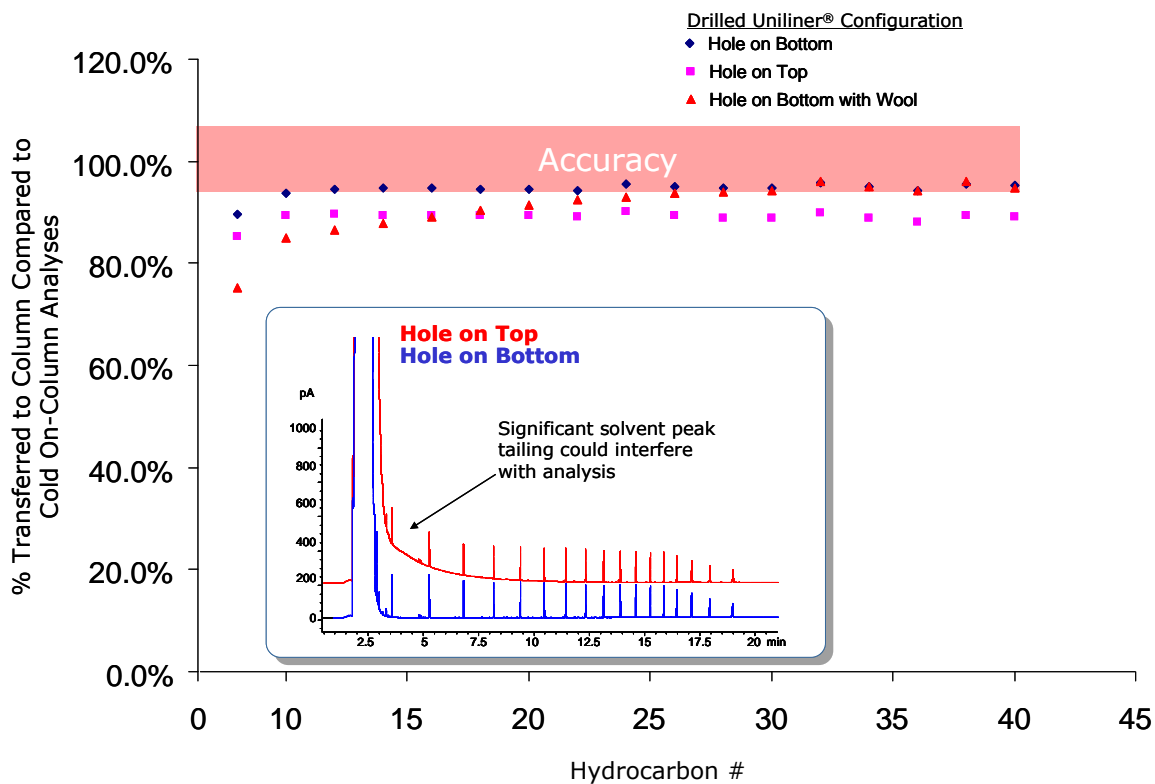
## Liners used in this study



## Direct Injections: Are They Really Better than Traditional Splitless Injections?

The Drilled Uniliner<sup>®</sup> is used to perform “direct injections.” The concept is to direct essentially the entire sample onto the column by forming a connection between the column and the liner. This arrangement increases installation complexity, and comparing figures 5, 5, and 7 would suggest that it does not necessarily produce more mass on column compared to a properly set up splitless injection with a traditional splitless liner.

**Figure 5:** 17 straight-chain hydrocarbons analyzed with three different direct injection liners and compared to cold on-column results. Inset is a diagram of solvent peak shapes for two different liner designs, illustrating the effect of the hole position on solvent shape.



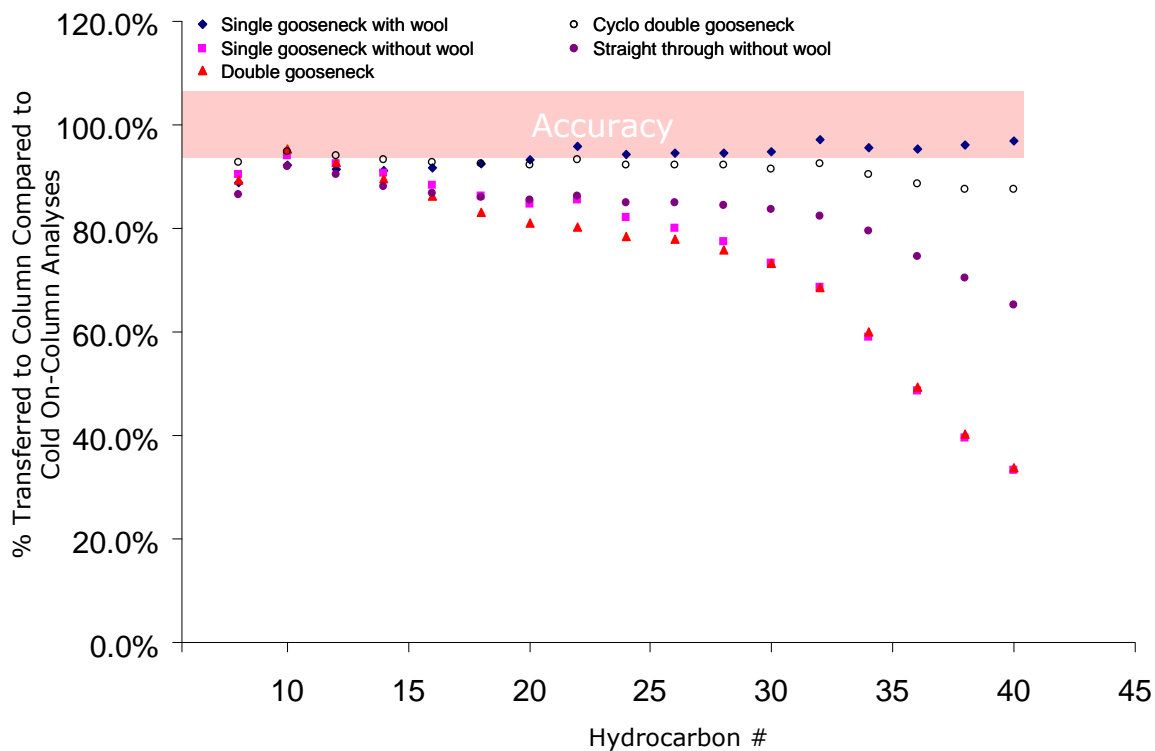
## Does a Slower Liner Flow Rate Really Alleviate the Need for Wool?

It has been commonly said that the slower flow rates through the liner during splitless injections obviates the need for wool as a vaporization aide. However, the data in figure 6 demonstrates that for a broader range of molecular weights this assumption is not observed except for the cyclo double gooseneck.

Additionally, when compared to the drilled Uniliner<sup>®</sup> results shown in figure 5, a properly chosen splitless liner used under properly set splitless run conditions (shown in table 2) will allow for almost total analyte transfer onto the column. This would suggest that for this analysis, direct injection doesn't provide a mass transfer benefit.

One interesting thing to note is the relatively small degree of molecular weight discrimination observed with the straight liner without wool compared to the single gooseneck liner without wool. It has been observed by Beiri, et al, that when using an autosampler in fast plunger mode (as was used in this study), some of the sample may "slither" between the column and the taper at the bottom of the liner and become somewhat trapped under the taper. It is hypothesized that this might account for the differences seen between the single gooseneck without wool and the straight liner without wool, which would presumably not suffer from that potential effect.

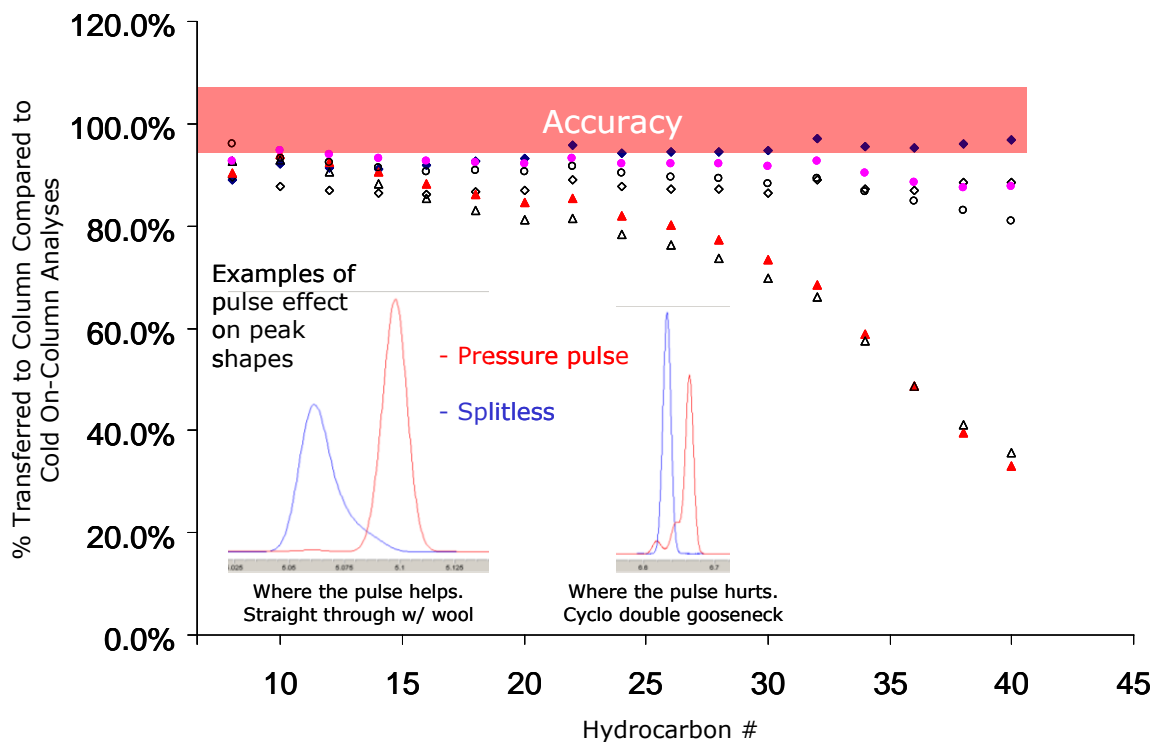
**Figure 6:** 17 straight-chain hydrocarbons analyzed with five different splitless injection liners and compared to cold on-column results.



### What About Pressure Pulses?

From the data shown in figure 7, it appears that pulsing doesn't contribute to a greater mass transferred, but it does transfer the mass to the column in a shorter period of time and can affect the peak shape (positively or negatively, depending on the liner). Comparing figures 6 and 7 suggest that the same mass was transferred in both splitless and pulsed splitless

**Figure 7:** 17 straight-chain hydrocarbons analyzed with three different splitless injection liners and compared to cold on-column results and under splitless and pulsed splitless conditions. The inset chromatograms are examples of the effects of pressure pulses on peak shapes. In some cases, the pulse made unfocused peaks narrower, and in other cases it deformed the peak shape. The examples shown below are for C10, but with different liners. So, the effect is both compound and liner dependent, requiring method specific considerations when deciding whether or not to use pulsed splitless techniques.



- ◆ Single gooseneck with wool - splitless
- ◇ Single gooseneck with wool - pulsed splitless
- ▲ Single gooseneck without wool - splitless
- △ Single gooseneck without wool - pulsed splitless
- Cyclo double gooseneck - splitless
- Cyclo double gooseneck - pulsed splitless

**Table 2:** Analytical conditions for figures 5, 6 & 7.

**Instrument:**

Agilent 7890A with Split/Splitless Inlet and an FID (same used for cold on-column work)

**Injector:**

Autosampler; Fast plunger; 1  $\mu$ L injection from a 5  $\mu$ L syringe

**Inlet:**

Split/Splitless; 300 °C; He carrier; splitless with 50 mL/min @ 1 min. (figures 4,5) or pulsed splitless with a 50 psi pulse for 0.45 min, splitless hold time at 0.43 min, then 50 mL/min (figure 6)

**Column:**

30 m, 0.25 mm, 0.25  $\mu$ m Rxi-5 SIL MS, constant flow at 2 mL/min

**Oven:**

40 °C (hold 1 min) to 340 °C @ 20 °C/min (hold 5 min)

**Detector:**

Flame Ionization Detector; 340 °C

H<sub>2</sub> @ 40 mL/min, Air @ 400 mL/min, N<sub>2</sub> @ 45 mL/min

**Sample:**

10 ng/ $\mu$ L Florida Total Recoverable Hydrocarbons mix (17 straight-chain hydrocarbons; C8-C40, the evens)

## Conclusions

It is evident that the choice of liner can play a role in the successful transfer of analytes onto the column, and therefore the choice should be carefully considered when developing methods.

The analysis of straight-chain hydrocarbons presented in this work also did not show any significant advantages when using direct injection techniques compared to properly chosen splitless run conditions.

Additionally, the introduction of a pulse during the splitless hold time did not seem to directly affect the amount of sample transferred onto the head of the column, but it did affect the rate at which sample was transferred, allowing the same mass to be transferred much faster. This could have implications for the analysis of sensitive compounds where residence time in the inlet could be a factor. Pulsing also had chromatographic effects that were, at times difficult to predict (e.g. the peak splitting observed with cyclo double gooseneck liners), and would suggest that the use of pulsed splitless techniques should be evaluated for a given application, liner, and, while not presented in this work, solvent used.

## Questions?

If you have questions regarding this work, or GC inlet liners in general, please feel free to contact the lead author:

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