TECHNICAL ARTICLE

CHOOSING THE RIGHT INLET LINER FOR YOUR APPLICATION

Part One

– Increasing sensitivity of high boiling point compounds.

There is a vast choice of inlet liners available today for the modern chromatographer ranging from straight through liners, to those with glass wool, baffles and laminar cups. Making the right choice can be a difficult task, but is important as it can affect the sensitivity of the analysis.

The liner's ability to transfer heat efficiently depends on its design. The first surface the liquid sample hits will have the largest influence on the amount of boiling point discrimination the sample suffers before it reaches the column. Another factor affecting discrimination is the loss of volatiles from the top of the liner, this affect is not as dramatic as the initial transfer of energy from the liner (or base seal) to the sample. Some liners do not transfer this energy as affectively as others and therefore slow the vaporization process.

When a liquid sample is first injected into a liner by an autosampler it exits the needle at a high speed. In most cases, some of the sample is sprayed slightly, but the majority of it stays together until it collides with a surface. An inlet liner has three surfaces that the liquid sample can hit before it begins to vaporize these are; quartz wool, glass (borosilicate or quartz) and metal (usually plated stainless steel). At the same temperature these materials contain different amounts of energy, therefore, act differently when the sample uses some of that energy to vaporize. Assuming that the affected surfaces of the glass and metal are the same mass, the temperature of the glass surface will not drop as much as the metal when the same amount of energy is used. This is due to the difference in heat capacities of the two materials. An example is shown in **Figure 1a and 1b**:

For our comprehensive range of liners, please request a copy of BR-0072-A.

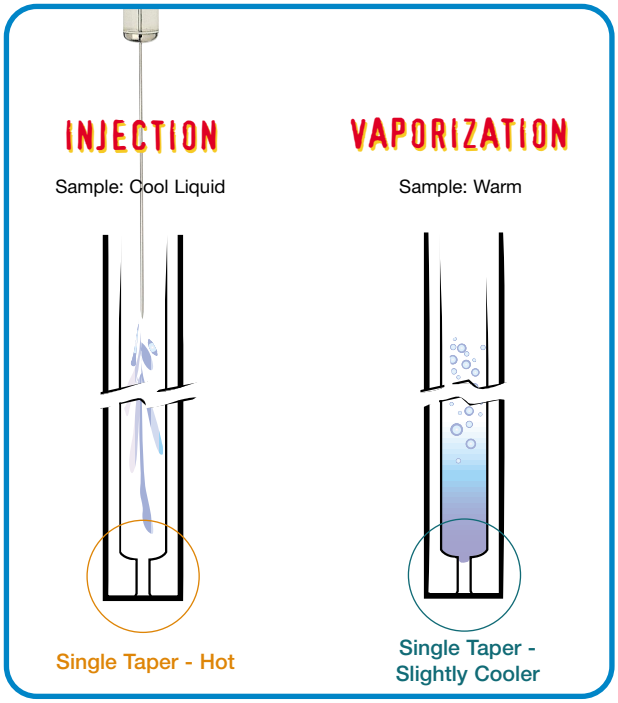

Figure 1a: Vaporization in a Single Tapered Liner.

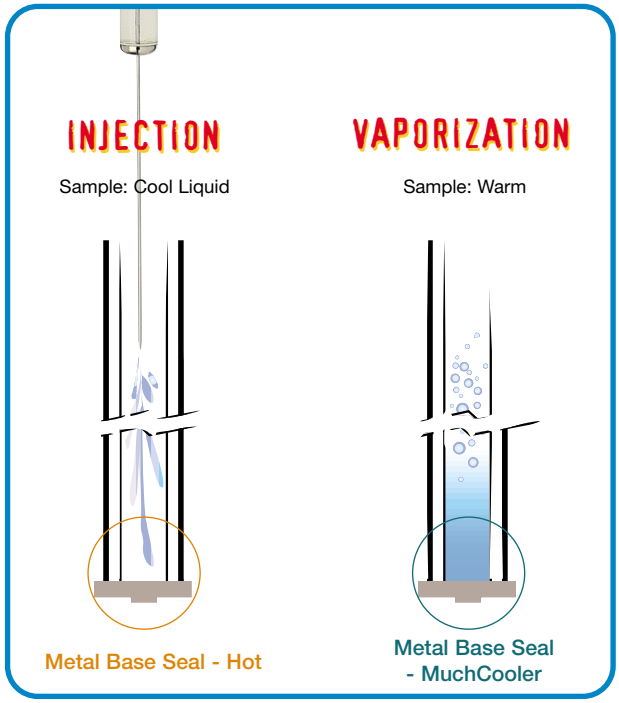

Figure 1b: Vaporization in a Straight-Through Liner.

Let's consider the order of vaporization. If 1.0µL of 100ppm TRPH (Total Recoverable Petroleum Hydrocarbons, C8-C40) in dichloromethane is injected in splitless mode. The solvent and hydrocarbons will all absorb energy at approximately the same rate. However, it will take longer for the high boiling point compounds (>C18) to absorb the extra energy they need to vaporize, thus they will complete their vaporization much later than volatile compounds; i.e. C8 completes vaporization before C30 etc.

The problem is that in this example, 99.99% of the sample is solvent! The solvent will vaporize first, along with the volatile and some semi-volatile compounds. This will take a lot of energy from the liner or base seal (as shown in Figures 1a and 1b), but the high boiling point compounds have not finished vaporizing and the liner or base seal is now cooler than it was before. Depending on the sample size and the specific heat capacity of the solvent and injection port surface, this cooling can be significant enough to affect the rate of vaporization for high boiling point compounds. In other words, C18 and heavier hydrocarbons start to vaporize but the temperature drops quickly on the surface they are on, slowing their vaporization. It will not affect the low boiling point compounds because they have already finished vaporizing. The result is shown in **Figure 2**.

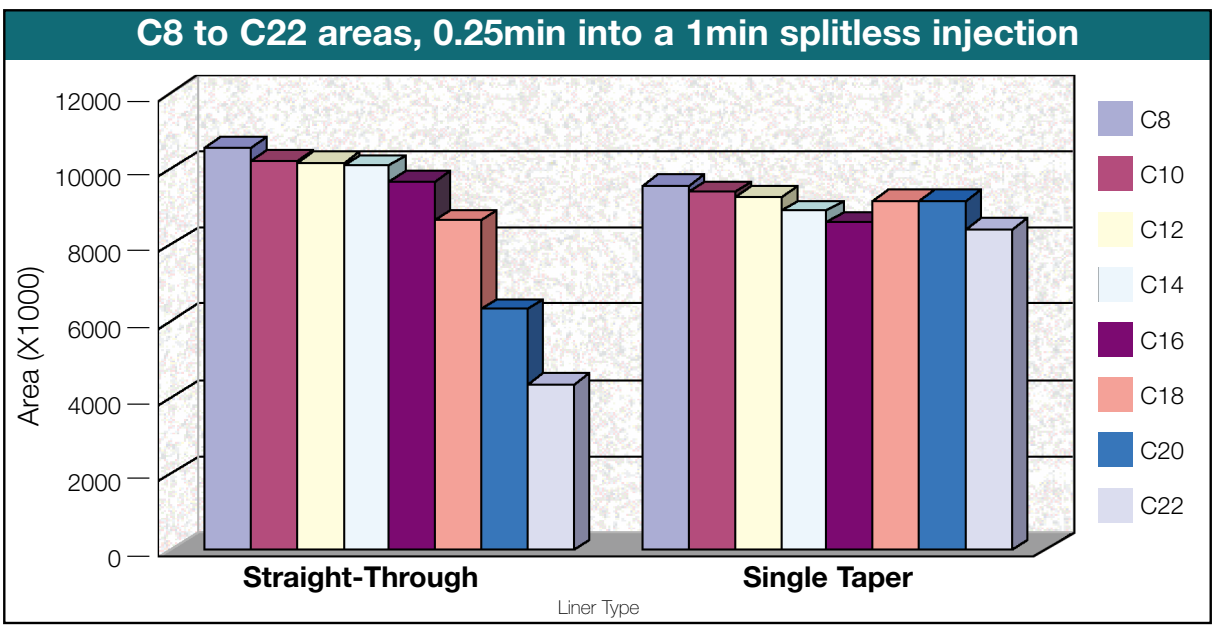

Figure 2: Discrimination caused by the delayed vaporization of heavy hydrocarbons in the straight-through liner.

The bar graphs in **Figure 2** show the area for C22 straight-through liner, is only half the height of the C22 single tapered liner. C22 is still vaporizing in both cases, but the parallel liner is less efficient at transferring energy to the sample because vaporization has cooled the metal base seal more than glass. This could also be attributed to the base seal being in a cooler area of the injection port and therefore it would start at a lower temperature. Eventually heat is transferred back into the base seal and liner but this occurs after the sample has vaporized.

This means that tapered glass liners or focus liners are preferable because they transfer high boiling point compounds more effectively to the column. This will give higher sensitivity for all analysis, not just hydrocarbons.

Next issue:

CHOOSING THE RIGHT INLET LINER FOR YOUR APPLICATION

Part Two – Increasing sensitivity of low boiling point compounds.

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TECHNICAL ARTICLE

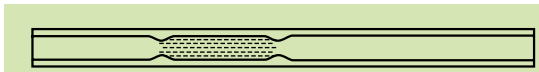
GC Inlet Liners

Which one should I choose?

Q *How do I choose which liner to use for my analysis?*

A There are dozens of different designs for liners. The decision of which one to use is easy.

For Split Injection



Quartz wool in liner:

- Promotes mixing of analytes and results in better quantitation
- Provides a large surface area which aids the vaporization of liquid samples
- Acts as a trap to collect non-volatile residue in the sample
- Protects capillary column from 'dirty' samples
- Prevents sample hitting the bottom of the injector before volatilization

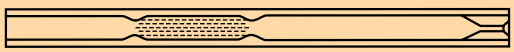
Quartz wool in the liner located at the optimum position (FocusLiner™)

- Excellent reproducibility results from wiping of the sample from the syringe needle and preventing droplet formation.
- Results in lower mass discrimination
- Quartz wool prevents the sample hitting the bottom of the injector

Double glass baffling (FocusLiner™)

- Ensures quartz wool remains in the correct position in the liner
- Top baffle prevents quartz wool shifting towards septum
- Bottom baffle prevents quartz wool being pushed down into the liner

For Splitless Injection



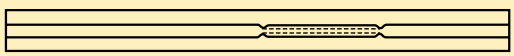
Taper at the bottom of liner

- The taper minimizes contact of analytes with the bottom of the injection port. This is especially important in splitless injection mode because the residence time of the sample in the liner is longer.
- Column installation into the liner becomes more robust because the taper 'channels' the analytes into the column. The distance the column is inserted into the liner is not so critical.

For Splitless Injection – Very Active Compounds

- The taper minimizes contact of analytes with the bottom of the injection port. This is especially important in splitless injection mode because the residence time of the sample in the liner is longer.
- No quartz wool.

For Fast GC Column Analysis



Narrow internal diameter

- Results in smaller peak widths.
- Especially suited for (100μm) Fast columns.

Deactivation

The surface of borosilicate glass is naturally acidic and can contain free silanols, hydrated silanols or

LINER Tip

DO NOT use chromic acid to clean your liner. This reagent will leave metal contamination on the surface of your liner, increasing liner activity.

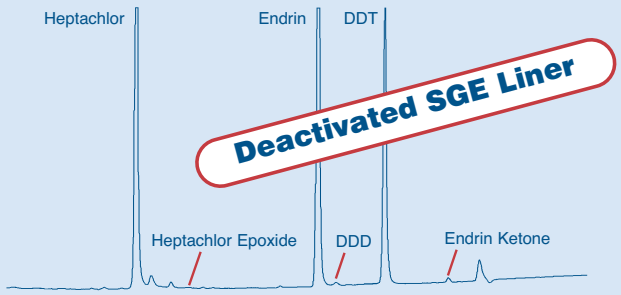
siloxane bridges. Deactivation involves the chemical introduction of a non-polar group to make the surface more inert.

All SGE liners are deactivated using a proprietary HIGH TEMPERATURE gas phase deactivation.

How often should I change my Liner?

The short answer to this is when either quantitation or peak shape deteriorates. Some laboratories injecting very dirty samples will change their liners daily. Other laboratories injecting cleaner samples will only need to change their liner once a month. We recommend a change frequency of at least once a month, preferably once a week.

Figure 1. Chemical Inertness 5pg/Component Level



The above chromatogram illustrates the efficiency of the SGE high temperature deactivation process, effectively NO degradation of the probe compounds (Heptachlor Epoxide, DDD, Endrin Ketone).are observed.

Features and Benefits of SGE's Deactivation Process

FEATURE	BENEFIT
Gas phase deactivation.	More complete coverage of liner and quartz wool surface.
High temperature (400°C) deactivation.	Deactivation won't be stripped when using very hot injectors.
In-situ deactivation.	No manual handling of quartz wool after deactivation, resulting in better stability of deactivation.

Liner Volume and Flashback

Not all solvents will expand to the same volume under a set of conditions. It is important to remember that the gas volume will increase as the molecular weight decreases. Flashback occurs when the volume of the liner is not sufficient to handle the expanded gas volume.

This is one of the reasons why water is a very difficult solvent. Water will expand up to four times the volume compared with methylene chloride. For example, a straight-through liner with an inner diameter of 4 mm and a length of 78.5 mm will have an internal volume of approximately 1.0ml. A 1.0μL injection of methylene chloride at 250°C and an inlet pressure of 10 psi will expand to 0.39mL. Clearly this is OK if the total volume of the liner is 1.0mL. However, for a 1.0mL injection of water, the gas expansion volume will be 1.41mL which is obviously greater than the volume of the liner. If this quantity of water is injected under these conditions, the vapor will expand beyond the liner and end up in the purge lines and the carrier gas inlet lines. Eventually, the vapor will work its way back into the inlet and the column. This effect is known as **Flashback.**

The result of flashback is that solvent and sample can flow back into the inlet and purge gas lines causing contamination of your system. A really bad case can result in the need to replace the plumbing and gas lines.

FLASHBACK can cause severe problems:

- **Erratic quantitation**
- **Ongoing system contamination**
- **Ghost peaks**
- **Peak tailing**

The effect of flashback is much more prevalent in splitless injection systems.

There are a number of ways to prevent flashback. The first point is to be aware that it can happen. By understanding the expansion volume of a liquid to a gas and knowing the volume of the injector, flashback can be avoided.

For further information on our range of GC Inlet Liners please request our "Inlet Supplies" brochure from your nearest SGE office or distributor.

www.sge.com

TECHNICAL ARTICLE

FocusLiner™ (Pat. Pending)

Improve GC accuracy and reproducibility 10 Fold

For most chromatographers poor sample reproducibility is generally observed from one consecutive injection to another. This generally indicates that small variations in the volume of sample injected have occurred and would be overcome if an autosampler was used. Alternatively poor reproducibility can be caused by chromatographic activity of the column or the degradation of the compounds by the glass inlet liner.

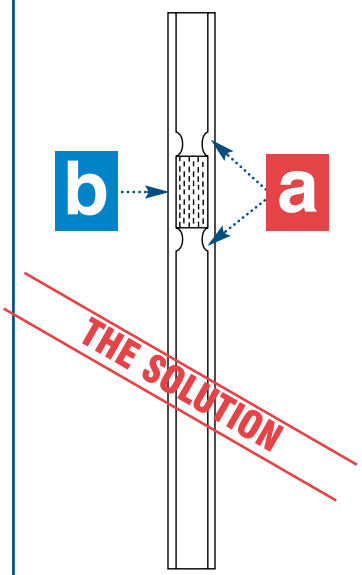
In fact, the major contributor to poor reproducibility in split analyses is the position of the quartz wool in the injection liner. The quartz wool is normally present in the injection port liner to trap sample and to homogenize the vapour prior to splitting and entering to the column. However, what is more important is its location in relation to the needle tip of the syringe during injection. At the point of injection the needle tip must penetrate the quartz wool to maximise vaporisation of the sample and to wipe any droplets that form on the needle tip, before removal from the injector.

Unfortunately, there is no guarantee that once the liner is installed in the injector, that the quartz wool plug will stay in the correct position.

SGE FocusLiner™

SGE now makes available the FocusLiner™, a liner design which overcomes this problem. Using a simple but effective design, the quartz wool is held in the correct position by means of two tapered sections in the liner **(figure 1).** The tapered sections are located to ensure the needle tip penetrates the secured quartz wool plug wiping any residue liquid sample from the needle tip while providing sufficient surface area for volatilisation of the liquid sample.

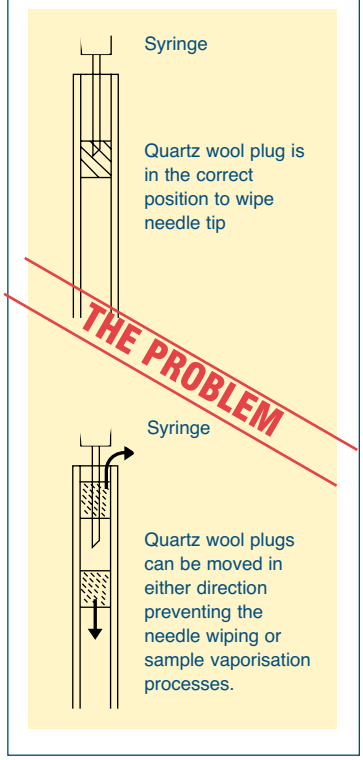
Figure 1.
SGE FocusLiner™



Two tapered section (a) secures the quartz wool plug (b) in the correct position to ensure improved reproducibility

Current liner designs which utilise quartz wool to improve vaporisation are frequently positioned incorrectly. Compounding the problem, the unsecured quartz wool plug can be easily dislodged without the chromatographer's knowledge **(figure 2)**. Displacement of the quartz wool can be caused by repeated injections. Each insertion of the needle tip can progressively move the plug until no further contact is made. Dislodging the plug can also occur through a sudden change in inlet pressure. For instance, removing the column from the injector or changing the septum can cause a sudden pressure change in the injector resulting in the movement of the plug.

Figure 2. Dislocation of quartz wool



Relocation of the quartz wool plug from the correct position can also be characterised by excessive tailing of the solvent peak **(figure 4A).** Only when the plug is correctly positioned to wipe the needle tip can sharp solvent peaks as in **figure 4B** be acheived.

Figure 3 illustrates the effects on sample precision (%RSD) from the location of the quartz wool plug in the liner. Another frequently used split liner was also evaluated. This liner design substitutes the quartz wool with a sintered glass frit which can be fixed or removable. In this experiment a 4mm ID fixed frit liner design was used.

When the quartz wool plug is moved to the centre of the liner (as often supplied by other manufacturers), %RSD values are up to 20 TIMES higher than those measured for the FocusLiner.

The fixed sintered glass frit liner is also unable to match the precision provided by the FocusLiner. This result is not surprising as the key element in achieving good sample reproducibility is the needle tip wiping process during injection. Therefore, liners with fixed or removable frits can only ever be used with limited success.

Sample accuracy is also a critical factor in providing confidence in sample quantitation. Peak areas for the probe compounds using the FocusLiner were found to be, on average, 25% higher than a liner where the quartz wool is positioned incorrectly. Solvent peak tailing is also observed **(Figure 4A & B)** if the wool is incorrectly positioned due to slow vapourization near the cool septum cap as the needle is wiped during withdrawal.

Only the FocusLiner provides the levels of reproduciblity and confidence that is needed for split injection analyses.

Figure 4A. Liner centrally packed

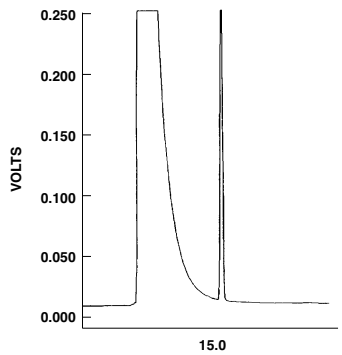


Figure 4B. Liner packed to wipe needle

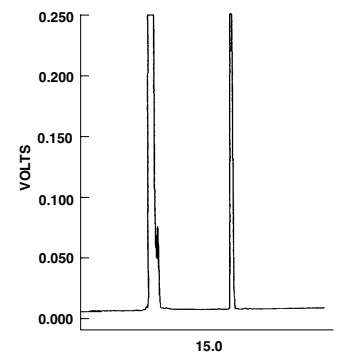
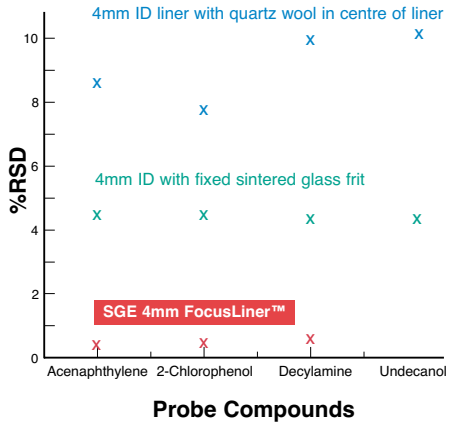


Figure 3. %RSD values for probe compounds using different quartz wool positions



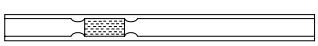
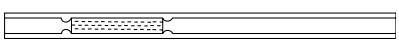
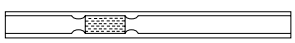
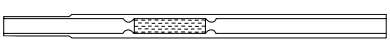
A Complete Liner Deactivation Process

Chemical inertness of the inlet liner is as critical as its design if accurate and reproducible transfer of a sample from the syringe to the column is to occur. The analysis of reactive compounds, like those in the environmental and pharmaceuticals areas, are often limited by the chemical inertness and thermal stability of inlet liners. Complete loss of these types of compounds in the injector are quite common and can occur even after only a few injections.

What is required is a deactivation process which can deliver the level of inertness and thermal stability expected for a high performance capillary column. SGE has utilised the same technology used in the preparation of the BPX range of columns and adapted it to the deactivation of inlet liners. This process is performed at very high temperatures under well controlled conditions to produce a silanized surface treatment which exhibits both excellent thermal and chemical stability.

Only when both of these properties are achieved can the maximum operating life of an inlet liner be realised.

FOCUSLINER™ FOR AUTOSAMPLER GENERAL DEACTIVATION TYPE: HIGH TEMPERATURE

	Liner Description	Liner Dimensions	Pkt size	Part No.
	**Agilent Technologies (HP) 5890/6890** Split/Splitless	4mm ID 78.5 x 6.3mm OD	5 25	**092002** **092219**
	**Shimadzu, model 17A** Split/Splitless	3mm ID 95.5 x 5.0mm OD	5	**092062**
	**Varian, models 1075/1077** Split/Splitless	4mm ID 72 x 6.3mm OD	5	**092022**
	**Perkin Elmer, Autosystem** Split/Splitless	4mm ID 92 x 6.2mm OD	5	**092092**

Inlet Liner Geometry and the Impact on GC Sample Analysis

INTRODUCTION

The function of the GC Injection Port or Inlet is to vaporize a liquid sample and introduce a portion of that sample onto the GC Capillary Column so that an effective separation can take place. Today there are a multitude of GC Inlet Liner geometries and packing options available on the market. Coupled with the various injection modes that are available, choosing the optimal Inlet Liner for a given application is increasingly difficult or in most cases, ignored.

Choosing the correct liner design and packing can significantly impact analytical performance. The use of glass quartz wool in Inlet Liners is well documented. Quartz wool on the positive side helps volatilization, as long as it is properly positioned inside the liner. On the negative side, quartz wool even if fully deactivated can cause breakdown of very active analytes. Liner choice also affects molecular weight discrimination. The best Inlet Liner allows all compounds, regardless of boiling point, to load onto the column equally and in a sharp band. In some cases optimization of the inlet system can improve sensitivity. Conversely, choosing the wrong liner geometry can significantly decrease the reproducibility and quality of a given analysis.

Using a series of controlled injection parameters, we report the differences between various GC Inlet Liner designs for a group of analytes across a wide boiling point range.

EXPERIMENTAL

All experiments were performed on a Shimadzu GCMS QP2010, fitted with a single standard split/splitless inlet using an SGE BPX50 (50 % phenyl polysilphenylene siloxane) column (20 m x 0.18 mm x 0.18 µm).

The best way to show the result of mass discrimination is to analyze a series of compounds from low to high molecular weight (i.e. from high volatility to low volatility). For this reason, a 1 µL injection of 20 ng/µL of the components in Table 1 were analyzed.

ID Number	Name
1	naphthalene
2	2-methylnapthalene
3	1-methylnaphthalene
4	acenaphthylene
5	acenaphthene
6	fluorene
7	phenanthrene
8	anthracene
9	fluoranthene
10	pyrene
11	benzo(a)anthracene
12	chrysene
13	benzo(b)fluoranthene
14	benzo(k)fluoranthene
15	benzo(j)fluoranthene
16	benzo(a)pyrene
17	indeno(1,2,3-cd)pyrene
18	dibenzo(a,h)anthracene
19	benzo(g,h,i)perylene

Table 1. Sample components in the test mix. Solvent methylene chloride.

Injection parameters and GC Settings

Inlet temperature 300 °C
Transfer Liner 300 °C
Initial temperature 60 °C
Initial hold 1 minute
Rate 1 35 degrees °C / minute
Rate 1 final temperature 230 °C
Rate 2 6 degrees °C / minute
Rate 2 final temperature 240 °C
Rate 3 50 degrees °C / minute
Rate 3 final temperature 265 °C
Rate 4 4 degrees °C / minute
Rate 4 temperature 320 °C
Hold 4 1 minute

MS – Source temperature 260 °C
Scan – 35-400 amu in 0.5 sec / scan
High Pressure Injection (35 psi) Splitless for 1 minute

The different GC Inlet Liners for evaluation were chosen to demonstrate the impact of quartz wool, wool position, and internal volume on liners and how they contribute to boiling point discrimination of analysis of samples:

Inlet Liner Geometry	Design	Volume of Inlet Liner
Long Taper no quartz wool (P/N 092290)		600 µL
Long Taper quartz wool		575 µL
Short Taper no quartz wool (P/N 092071)		800 µL
Quartz wool at fixed position into quartz wool injection (P/N 092062)		726 µL
Bottom Taper quartz wool at fixed position into quartz wool injection (P/N 092068)		660 µL
Bottom Taper quartz wool at fixed position onto quartz wool injection (P/N 092058)		660 µL
Direct Injection Taper (P/N 092329)		600 µL

Table 2. GC Inlet Liner design parameters.

RESULTS

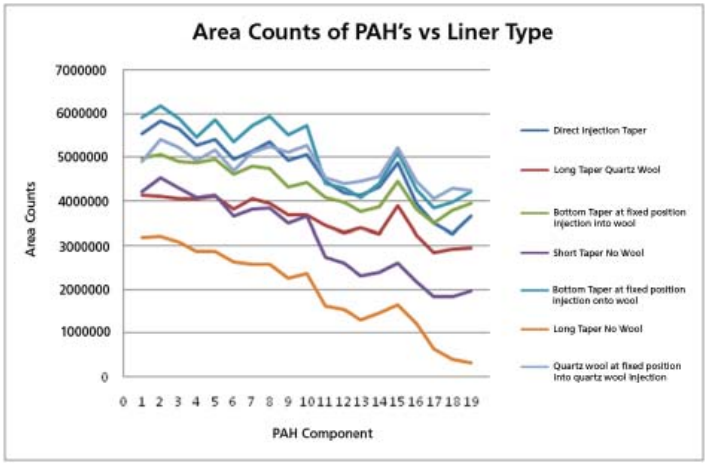


Figure 1. Area counts of the PAH components for each Inlet Liner geometry. Note that the peak area has more than doubled across the range of components between the Inlet Liner with the poorest response, compared with the top performing liners.

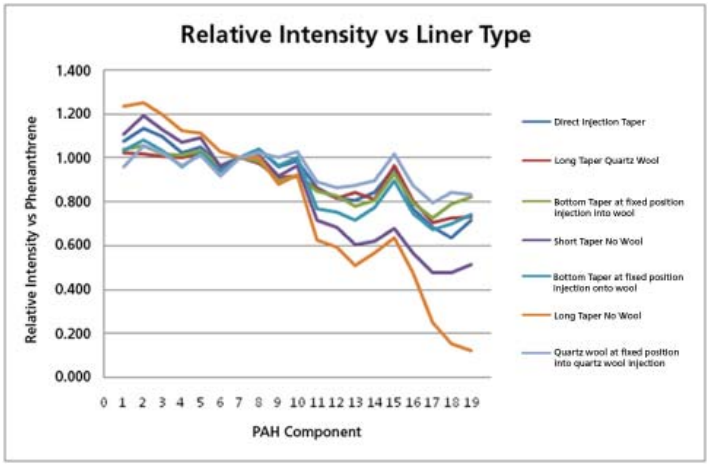


Figure 2. Relative intensity of versus the response for Phenanthrene, for each Inlet Liner geometry. Note how the lack of wool contributes to a loss of response for the later eluting components.

DISCUSSION

Addition of wool

The addition of quartz wool clearly impacts the performance of the Inlet liner regardless of geometry (see Figures 1 and 2) – this is exacerbated for the high boiling point analytes where the inclusion of wool improves recovery as well as the relative response.

Optimal Geometry

Four geometries delivered good recoveries of the PAH's; the optimal geometries based on recovery of the high boiling point PAH's were those liners where the wool was in a fixed position and the sample was injected into the wool regardless of presence of a taper.

Impact of taper length – in this study the length of the bottom taper did significantly impact the recovery of all PAH's. This is most obvious when comparing the relative response of each PAH to phenanthrene – the response for PAH's 17, 18 and 19 is fundamentally doubled when the taper length is reduced (see Figure 2). Hence, there is a complex relationship between liner volume and the temperature gradient across the taper.

Fixing wool position

Introducing a focused zone to secure the quartz wool has previously shown to benefit reproducibility (less than 1 % compared with 5-10 % without the fixed wool position)1. This is due to the sample being injected into the quartz wool, and the needle tip being wiped clean during the injection process, (see Figure 3).

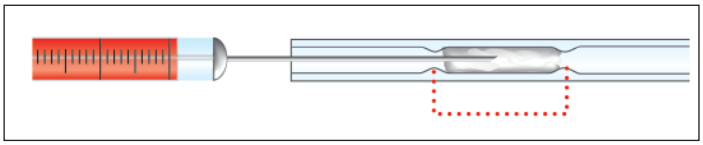


Figure 3. The two tapered sections of a Inlet Liner secure the quartz wool plug effectively wiping the needle tip during injection. This results in improved reproducibility.

The reduction in analyte degradation is due to the cold solvent effect. As the sample is injected into the hot liner the evaporating solvent cools the quartz wool around the analytes. After the solvent has evaporated and as the quartz wool reheats, the analytes dissolve in the gas phase as they reach volatility. They then pass in laminar flow down the column inlet with minimal contact with the liner wall.

Position of wool

While much has been discussed previously about the function of quartz wool at a fixed position to ensure the needle tip has been wiped, some Inlet Liner geometries have the sample being injected on top of the wool rather than into the wool. Comparing two Inlet Liners of this geometry with different quartz wool placement, shows this effect for the range of analytes.

The raw chromatogram suggests an equivalent response (see Figures 4 and 5) for both injecting into the wool and on top of the wool. However, close analysis of the peak areas demonstrates an increased yield for an injection into the wool (see Figure 1). When analyzing active components it is considered better to inject onto the wool, as penetrating the wool can create active sites.

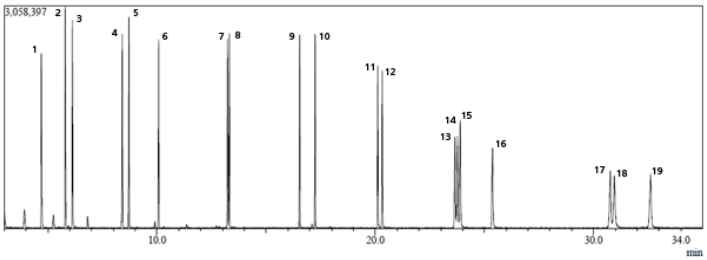


Figure 4. PAH test mix analyzed using a bottom taper and two tapers fixing quartz wool position (Part no 092058) where the sample is injected onto the quartz wool.

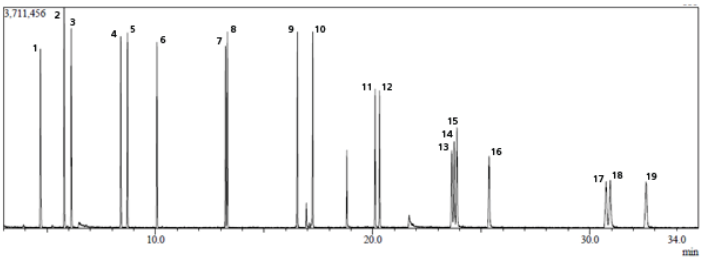


Figure 5. PAH test mix analyzed using a bottom taper and two tapers fixing quartz wool position (Part no 092068) where the sample is injected into the quartz wool.

Direct Inject Liner – direct injection technique

The direct injection tapered liner uses a direct inject technique to ensure full on column injection - effectively bypassing any quartz wool or cooling effect associated with a taper. This Inlet Liner does demonstrate relatively even loading of the analytes onto the column (see Figure 6). The direct injection tapered liner is an excellent choice to improve loading without the use of wool as it has similar loading capabilities to a fixed wool liner.

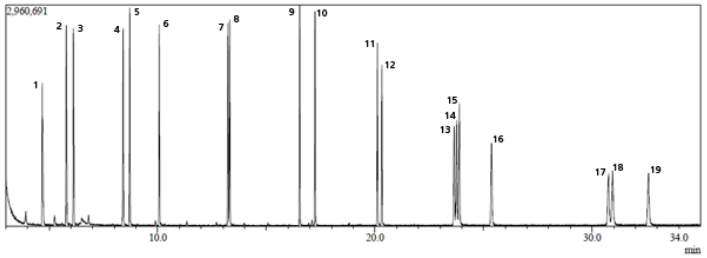


Figure 6. PAH test mix analyzed on a Direct Inject Liner (Part number 092329). Demonstrating excellent recoveries in all components.

CONCLUSION

The geometry of the Inlet Liner impacts the analytical performance and outcome. The bottom taper quartz wool at fixed position is ideally suited to evaluate a large boiling point range of analytes, without compromising the resolution. For those analyses where very sensitive or active samples are being evaluated, and the presence of wool can adversely affect the result, the direct injection tapered liner yields excellent recoveries.

REFERENCES

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