

Improved Sensitivity and Analysis Time for Semivolatile Organic Compound Analysis by USEPA Method 8270C

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Abstract

The analysis of the semivolatile organic compounds, like those found in USEPA method 8270C, places significant demands on the gas chromatographic column and analytical instrument. Concentrations of target and non-target components may range from low nanograms to milligrams, and the target compound list includes reactive acid and base compounds.

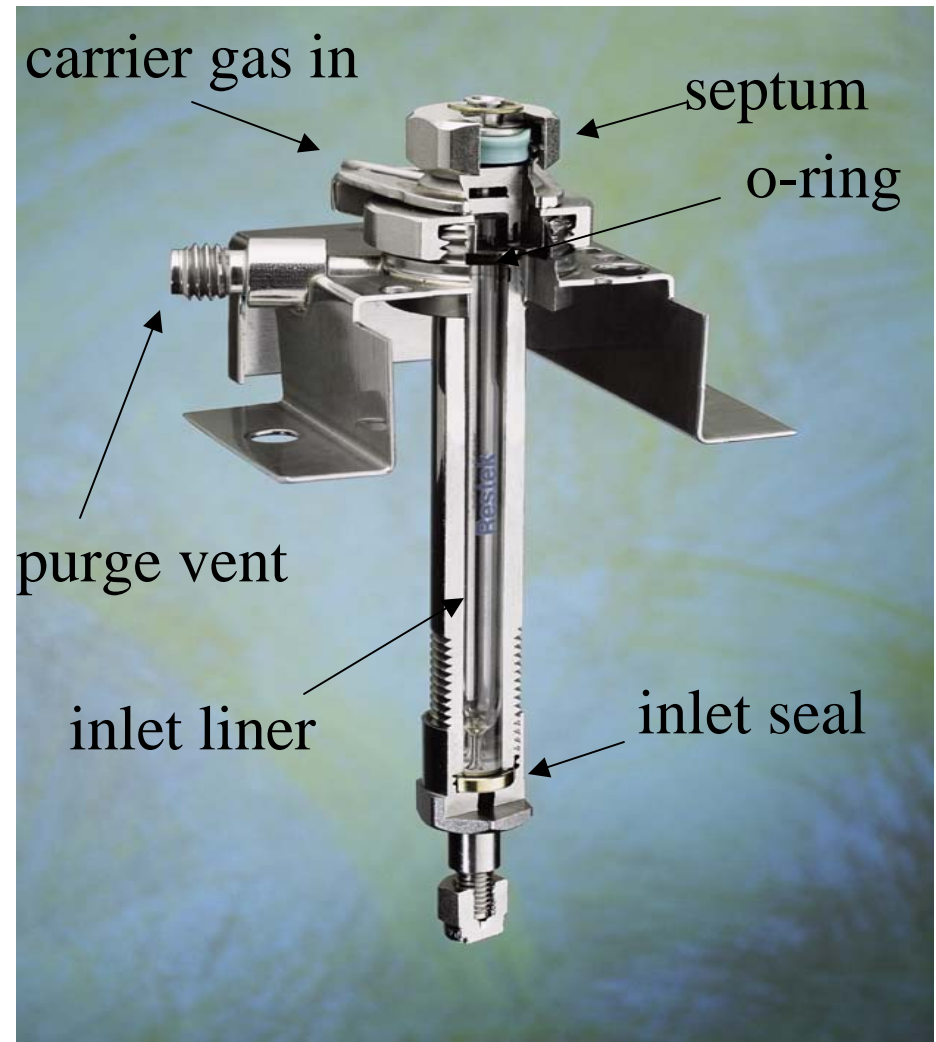
This presentation will demonstrate a method improvement that reduces the concentrations of the target and non-target compounds that are injected onto the column, as well as an instrument modification and new capillary column. These modifications result in less maintenance and instrument down time, while preserving the sensitivity requirements of this method. Finally, an optimized set of chromatographic conditions and column choice yield a superior separation with a minimized total run time.

Introduction

The analysis of semivolatile compounds by USEPA Method 8270C can be very labor intensive. This is due to the continuous need to perform instrument maintenance on the gas chromatographic system. The need for instrument maintenance is caused by sample matrix interferences that are extracted along with the target compounds and cause active sites, or leave nonvolatile residue in the injection port and inlet of the analytical column. The result is low response factors, usually for acidic or basic compounds, and tailing peaks. To meet reporting limits, and continuing calibration criteria, routine maintenance must routinely be performed on the analytical system. In order to increase laboratory efficiency two areas of the GC system can be improved, the injection port, and the cycle time of the analytical run.

Injection Port Configurations

The purpose of the injection port is to quantitatively and reproducibly transfer the analytes from the syringe to the analytical column. The most common injection technique used for Method 8270 is splitless injection. Splitless injection is used because the method requires low-level detection of analytes, and compounds that elute closely to the solvent peak make direct on-column injections unreasonable due to solvent interference.



There are many injection port liner configurations used with split/splitless injection. Figure 1 shows some of the common geometries used for Method 8270C. Each liner has advantages and disadvantages for use with semivolatile sample analysis. The importance of the liners is to shield target compounds from metal surfaces, vaporization of the injected solvent and analytes, and aid in the sample transfer of the extract from inlet to column. Review of these liners (Table 1) show they are all good for these purposes, however the Drilled Uniliner is the more efficient liner for transferring the sample extract from the injection port to the analytical column.

Table 1 - Performance of different inlet liner geometries

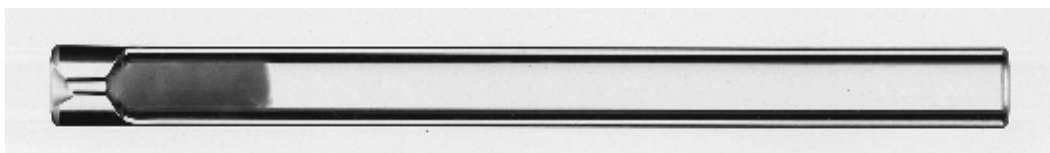
	Vaporization	Inertness	Transfer
single gooseneck w/ wool	very good	variable*	good
double gooseneck	good	good	good
cyclo double gooseneck	very good	good	good
Drilled Uniliner	good	very good	very good

* variability of inertness due to wool

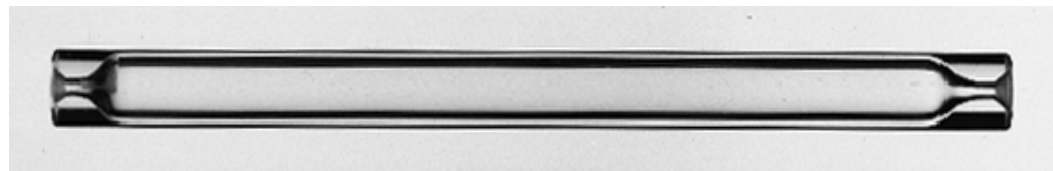
The four common injection port liners are used for this analysis: single gooseneck with fused silica wool, double gooseneck, Cyclo Double Gooseneck, and drilled Uniliner[®] (shown below). Single gooseneck and double gooseneck liners have similar performance characteristics, and can be used with pressure pulse injection, which helps transfer the compounds more quickly from the injection port to the column. Pressure pulse injection decreases the volume of the vaporization cloud, helping reduce contact with active sites outside the injection port liner.

Figure 1 – Common splitless liner geometries

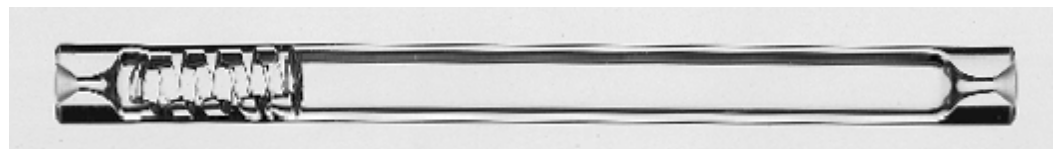
Single Gooseneck



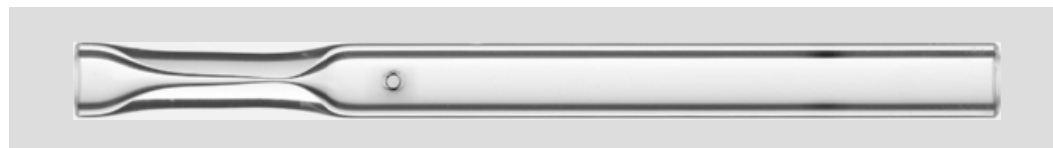
Double Gooseneck



Cyclo Double Gooseneck



Drilled Uniliner[®]



Pressure pulse injection takes place when the initial injection port pressure is increased above the normal operating pressure for the analysis. An example pressure program for a system that starts at 7 psig would be a starting pressure of 30 psig for 0.1 minutes past the splitless hold time, then quickly ramping down the pressure to the normal operating pressure. It is important to decrease the pressure in the injection port after the splitless hold time is complete, to make sure the purge vent is open. This allows the excess carrier gas to quickly escape the inlet. The effect of the increased pressure (30 psig versus 7 psig) is approximately a four-fold increase in flow through the liner.

When using a gooseneck liner, a critical area in Agilent GCs is the inlet seal, which must be replaced during routine maintenance. The seal becomes active due to deposition of non-volatile material on the surface.



Inlet seals with various surface treatments are shown above: stainless steel, Silcosteel[®]-treated, and gold-plated. SilcoSteel[®]-treated and gold-plated inlet seals are more inert than stainless steel seals and should be used for analysis of reactive semivolatile compounds in method 8270.

The drilled Uniliner[®], a new liner geometry used for splitless injection, eliminates contact between analytes and surfaces outside the bottom of the inlet liner. By making a Press-Tight[®] seal between the analytical column and the tapered bottom of the liner, the bottom of the injection port is eliminated from the sample pathway (Figure 2). The benefits are a more inert sample pathway, and minimization of injection port discrimination.

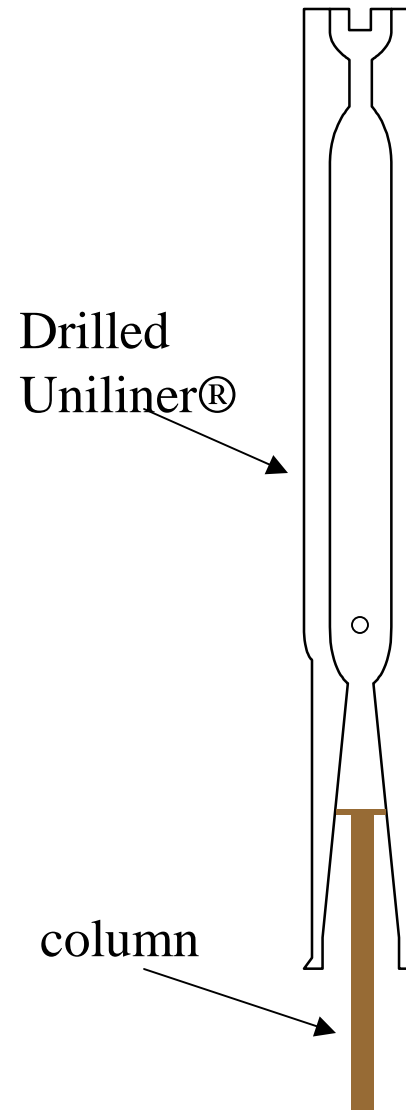


Figure 2 – Drilled Uniliner[®]

There are two styles of Drilled Uniliner[®] liners, one with a hole near the top, and a second with a hole near the bottom of the liner. The choice of liner is dependent on how closely the first compound elutes to the solvent peak. If the first compound elutes near the solvent peak (i.e. 1,4-dioxane), as in Method 8270, the drilled Uniliner[®] with the hole at the bottom of the liner should be used. This allows all the solvent to be flushed out of the entire inlet liner, reducing any solvent tailing, which could interfere with the first eluting compounds. The drilled Uniliner[®] with the hole near the top of the liner works well when the first compounds elute away from the solvent peak as in ethylene glycol in water, or chlorinated pesticide analysis. Figure 3 shows the difference of the solvent peak tail with relationship to the hole placement.

The Drilled Uniliner[®] also helps eliminate injection port discrimination for the late eluting PAHs. This is shown in figures 4 and 5. Figure 4 shows the difference between a pressure pulsed injection versus constant flow for the single gooseneck liner. Figure 5 shows the difference between the Drilled Uniliner[®] and single gooseneck liner under constant flow condition. The Drilled Uniliner[®] exhibits the least amount of injection port discrimination. Also, table 2 shows the results of a calibration sequence utilizing the Drilled Uniliner[®] under constant flow conditions.

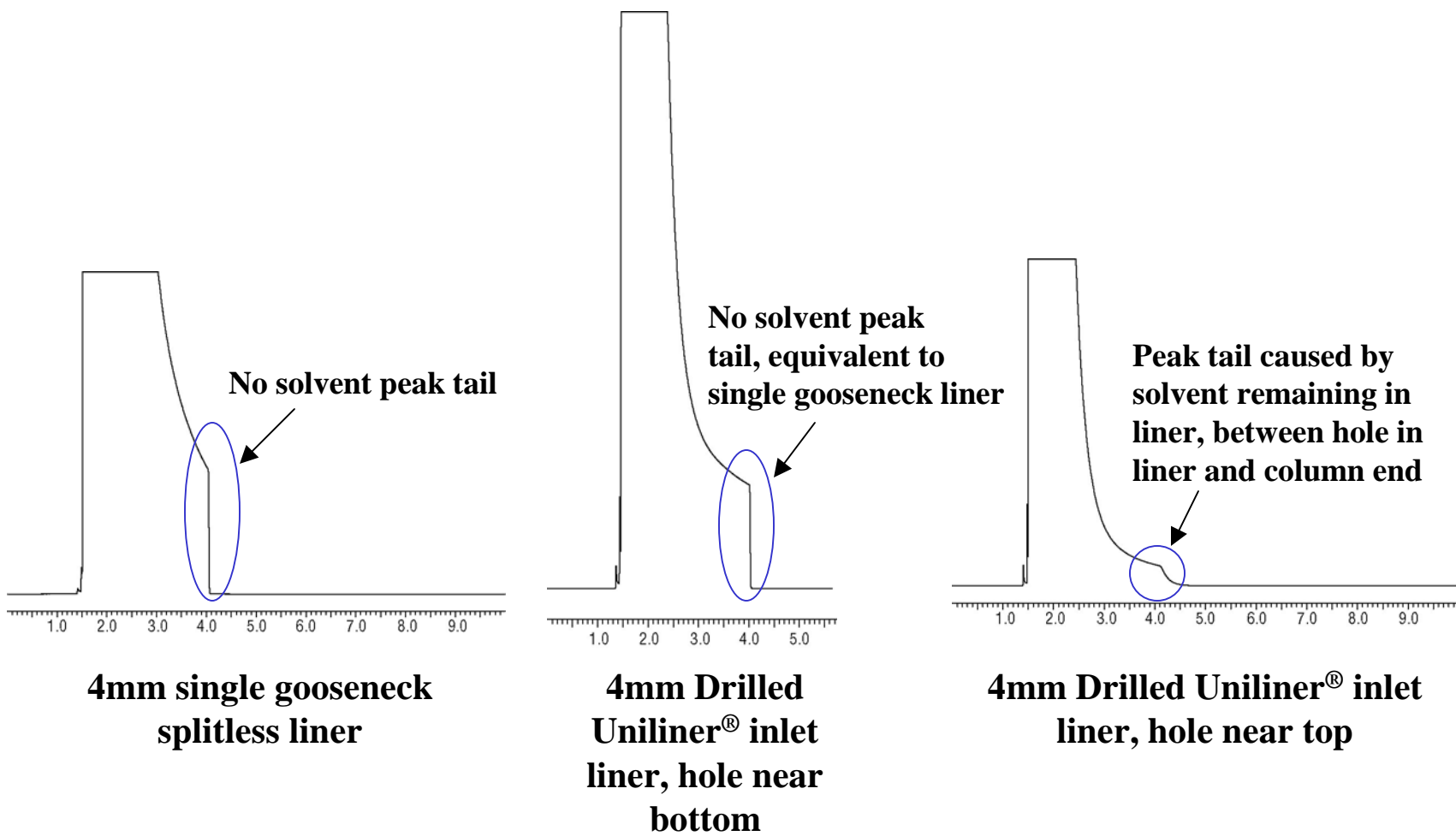


Figure 3 – Solvent peak shape

Figure 4 – Injection port discrimination: Comparing the single gooseneck liner under constant flow and pressure pulsed conditions.

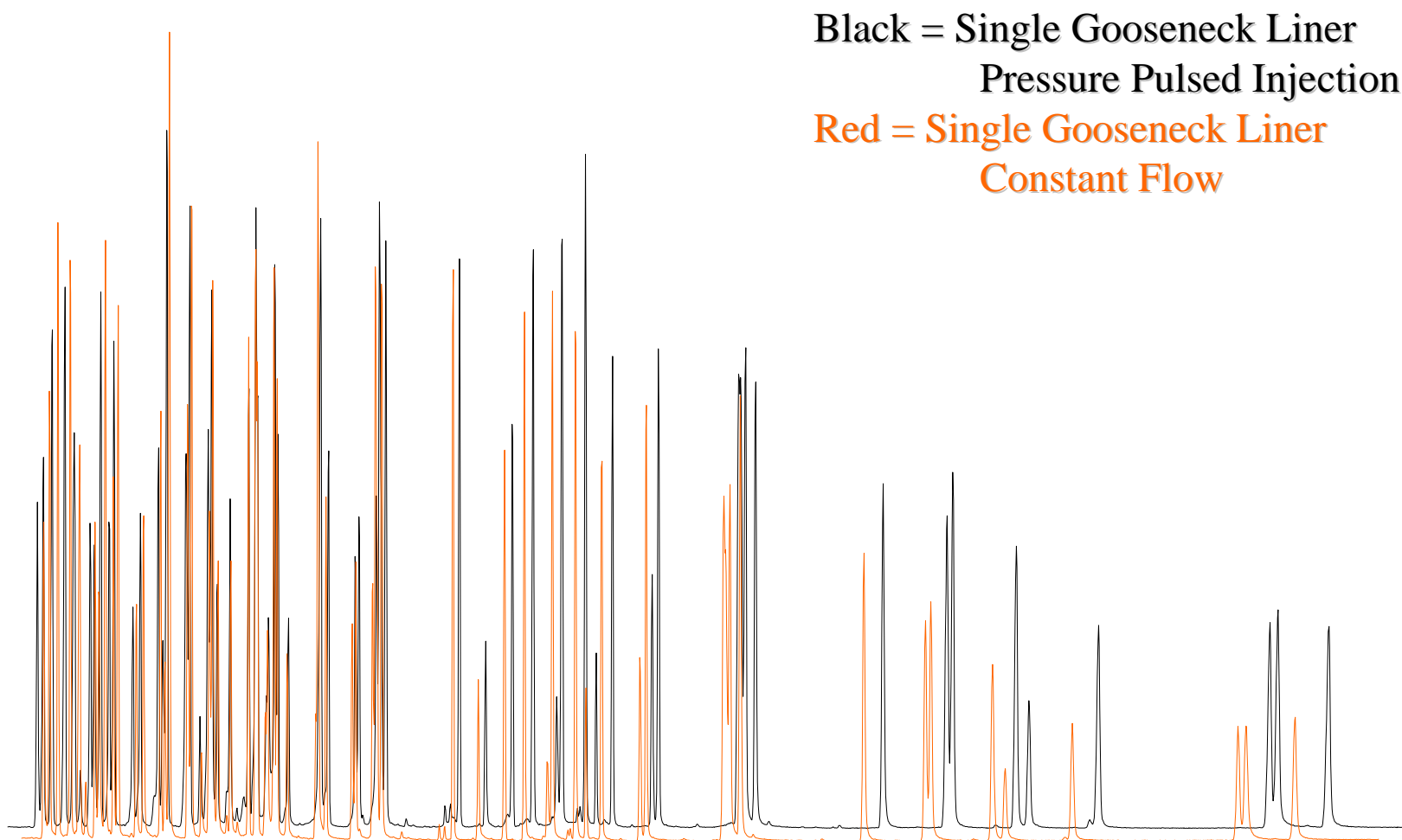
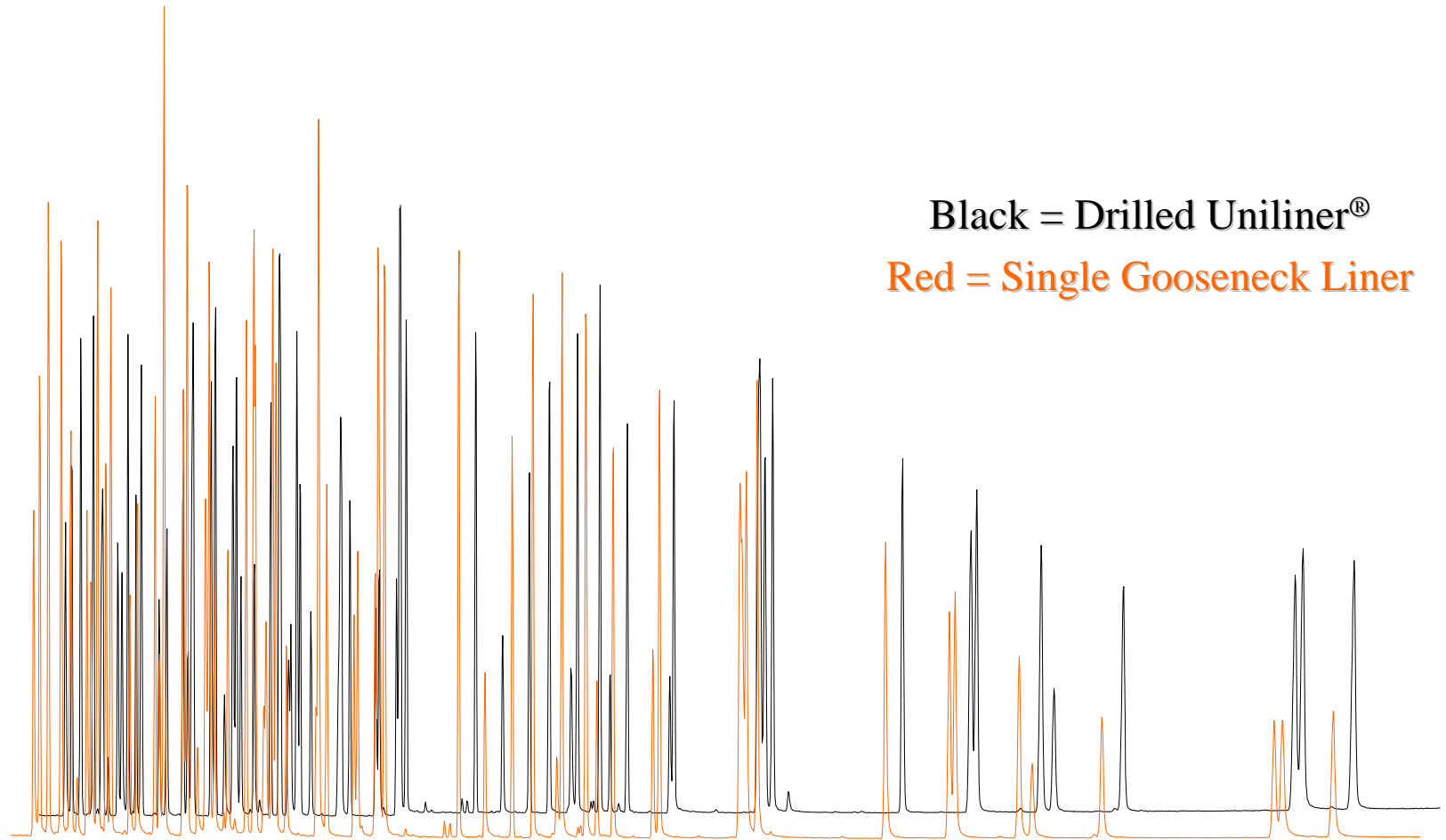


Figure 5 - Injection port discrimination: Comparing the single gooseneck liner to the Drilled Uniliner[®], both under constant flow conditions.



A comparison study to show the affects of the different liner geometries was performed using 8270 standard mixes. Calibration curves ranging from 4-80ng on-column were acquired using each of the four different liners. Included in the study was the affect of constant flow versus pressure pulsed injections. Figure 6 shows the average response factor results from the six point curve, and figure 7 shows the linearity results in percent relative standard deviation (%RSD).

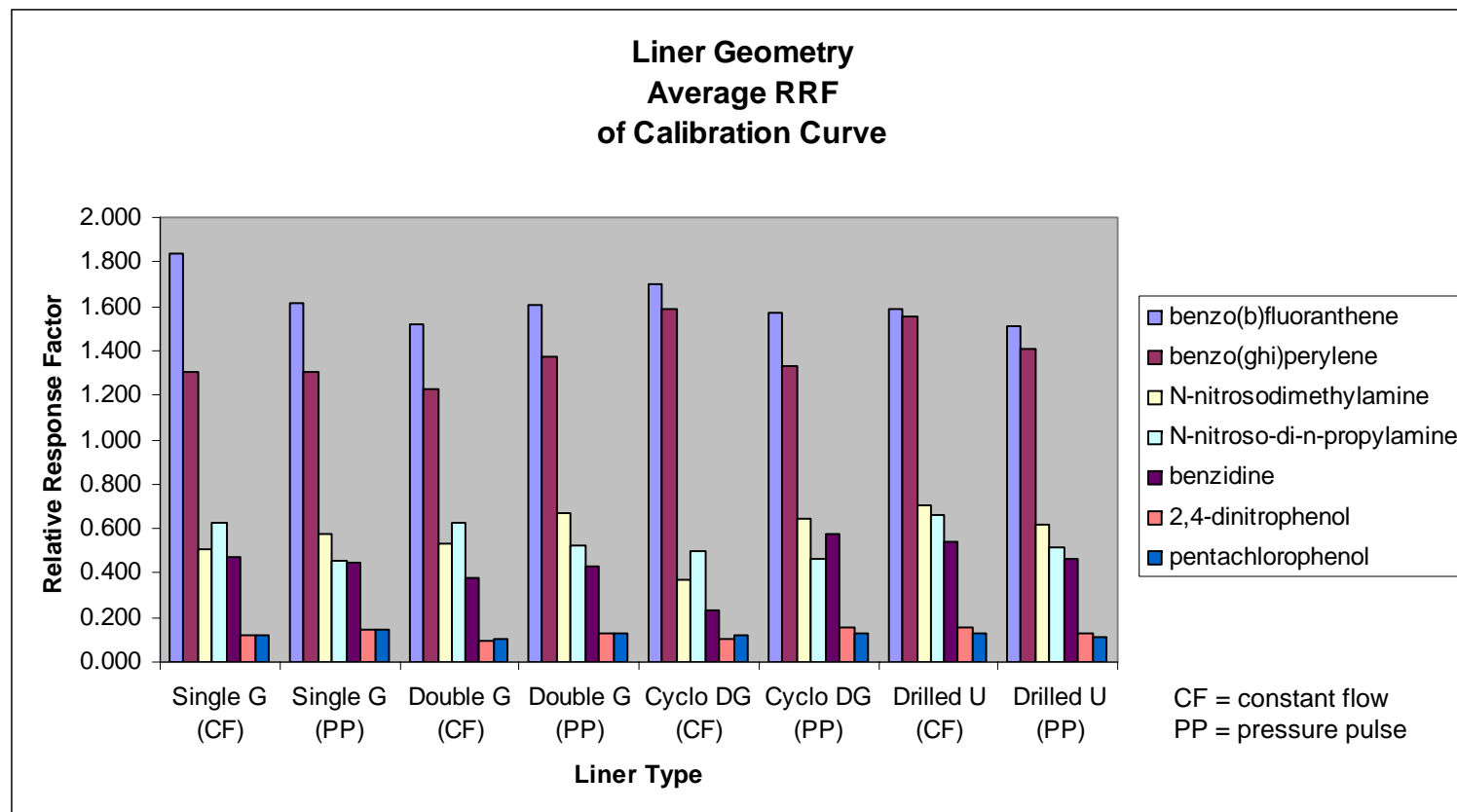


Figure 6 – Average response factor from six point curve (4 – 80ng on-column)

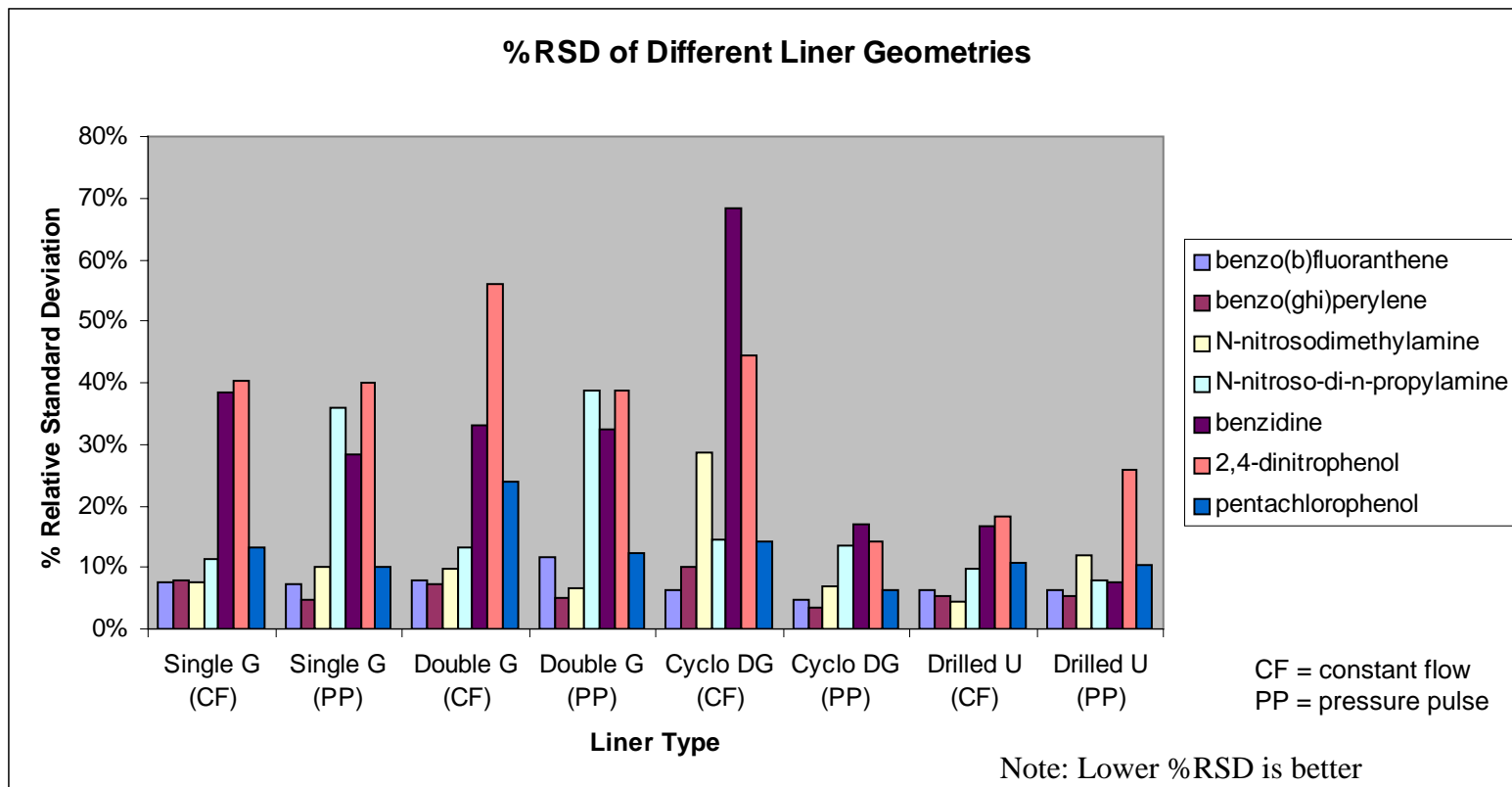


Figure 7 – %RSD from six point curve (4 – 80ng on-column)

GC Column and Temperature Program

In order to reduce the run time of the GC column flow and closely eluting compounds with the same quantitation ions had to be considered. Carrier gas flow rate was set at 1 ml/min constant flow allowing this method to be used with many of the GC/MS currently on the market using diffusion pumps. Closely eluting compounds include the following:

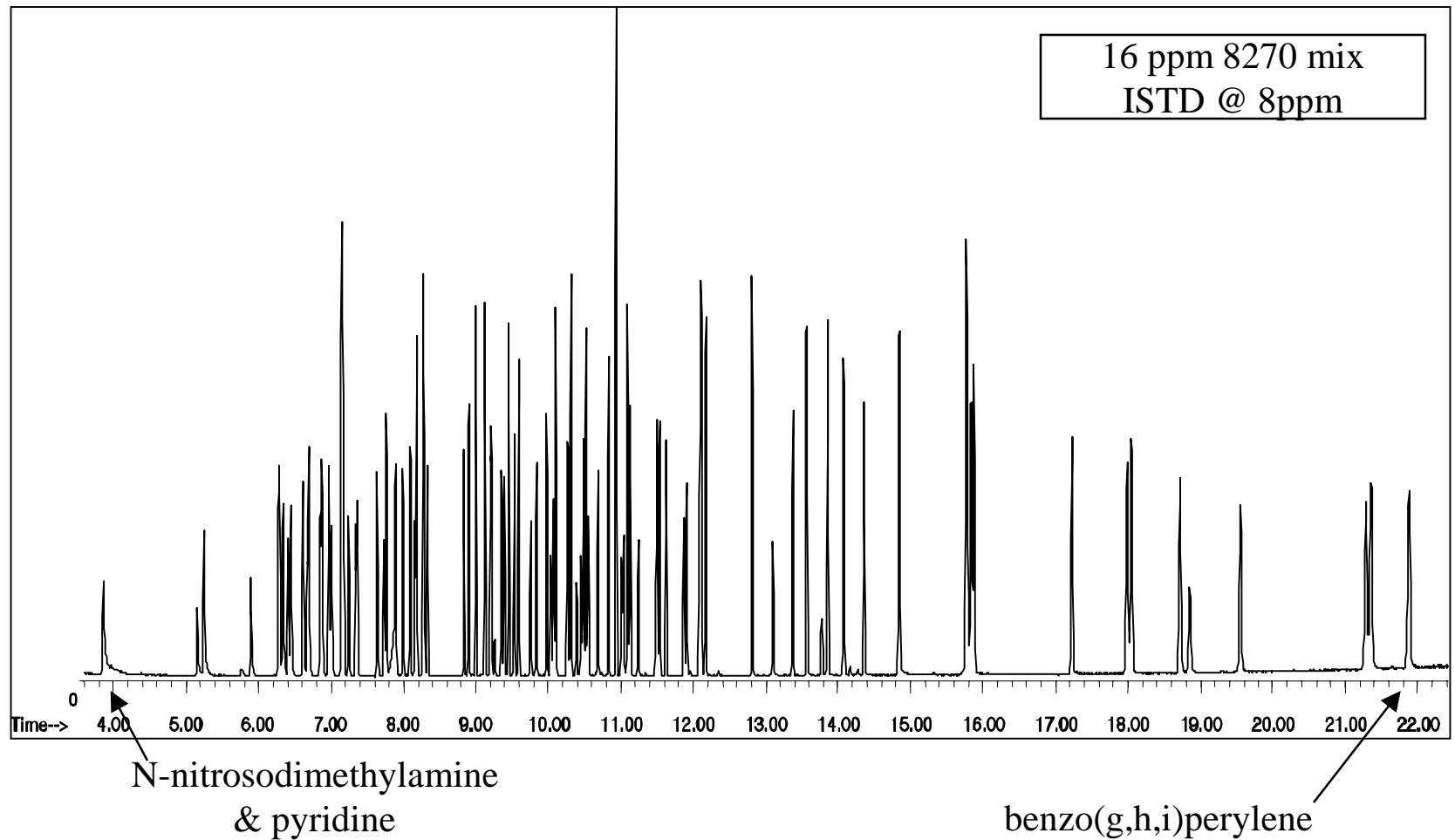
- phenol / aniline / bis(2-chloroethyl)ether
- 1,3- & 1,4-dichlorobenzene
- 2- & 1-methylnaphthalene
- 2,4,6- & 2,4,5-trichlorobenzenes
- phenanthrene / anthracene
- benz(a)anthracene / chrysene
- benzo(b)fluoranthrene / benzo(k)fluoranthrene

Some of the highlights of the study showed that the early eluting compounds (phenol / aniline / bis(2-chloroethyl)ether) could be resolved by changing the hold time at 35C. The second challenge was to separate the late eluting polycyclic aromatic hydrocarbons (PAH) compounds. This was accomplished by keeping the PAH compounds eluting on the temperature ramp. It was observed the PAH compound peak shape would broaden quickly on isothermal holds. The broadening of the peaks masked any increased resolution. Following are the run conditions and resulting chromatogram from the work performed:

- Rtx-5Sil MS (30m x 0.25mm, 0.25um film)
- 1.0 ml/min helium constant flow
- Injection port temperature: 270 C
- Injection volume: 1ul
- MS transfer temperature: 280 C
- Temperature program:
 - 35 C (2 min) 20 C/min to 260C(0 min) 6C/min 330(1 min)
- Analysis performed on HP6890 w/5973 MS

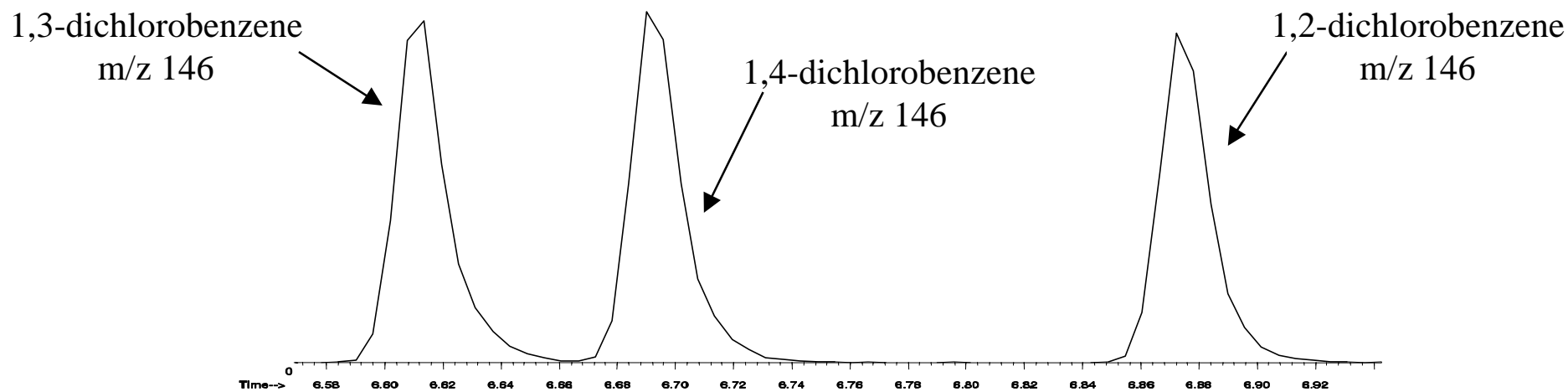
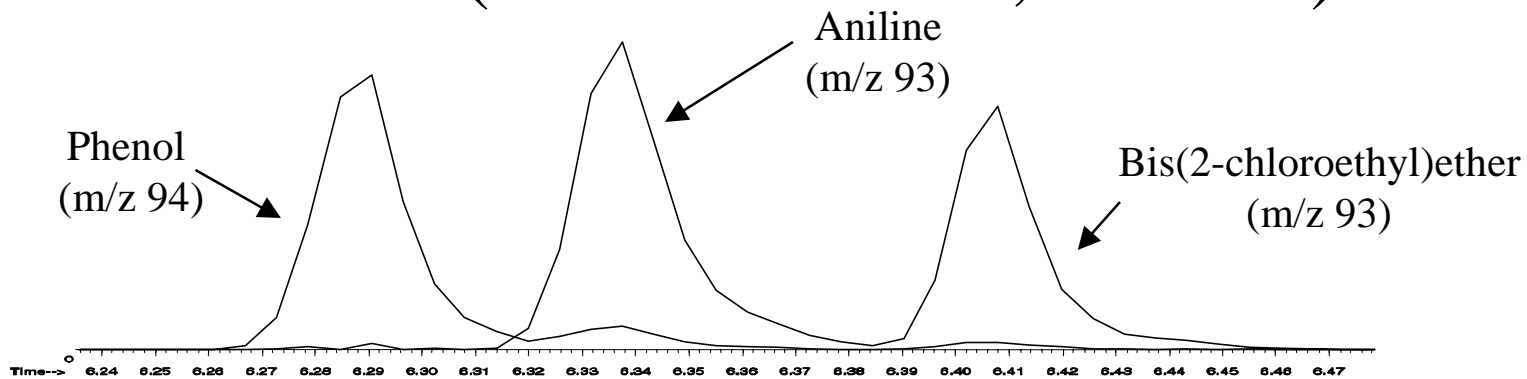
Rtx-5Si1 MS

(30m x 0.25mm ID, 0.25um film)



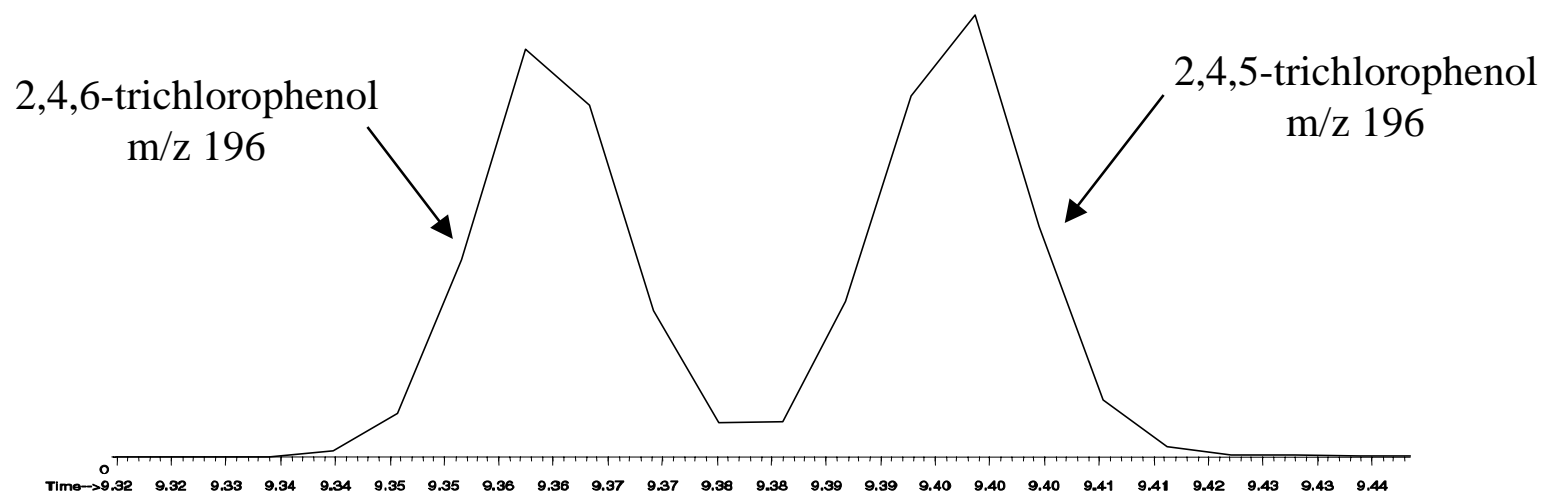
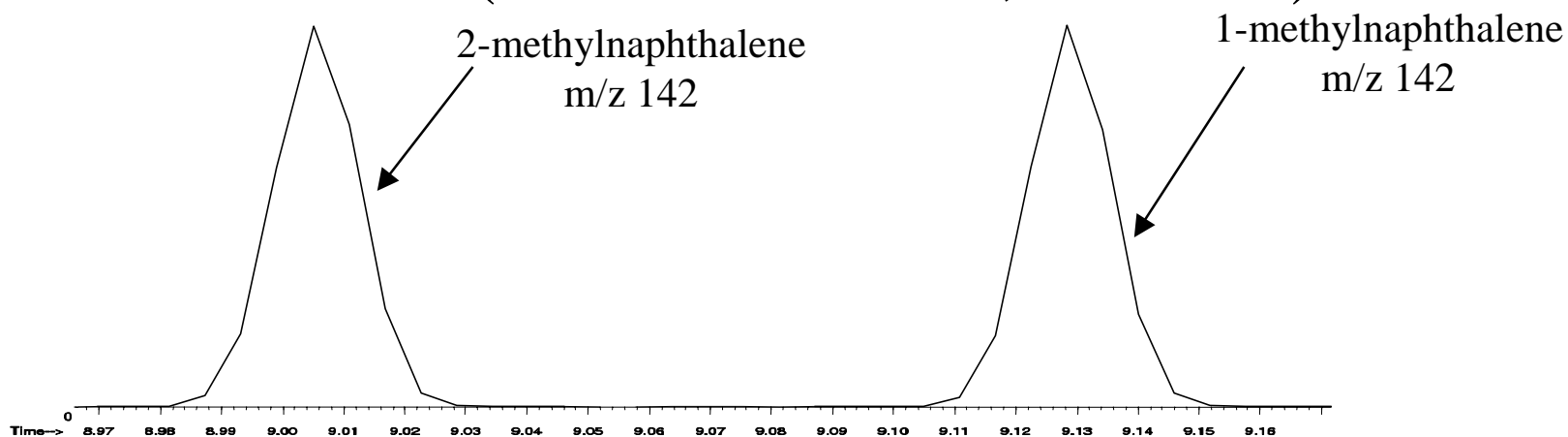
Separation of Critical Pairs

Rtx-5Sil MS (30m x 0.25mm, 0.25um)



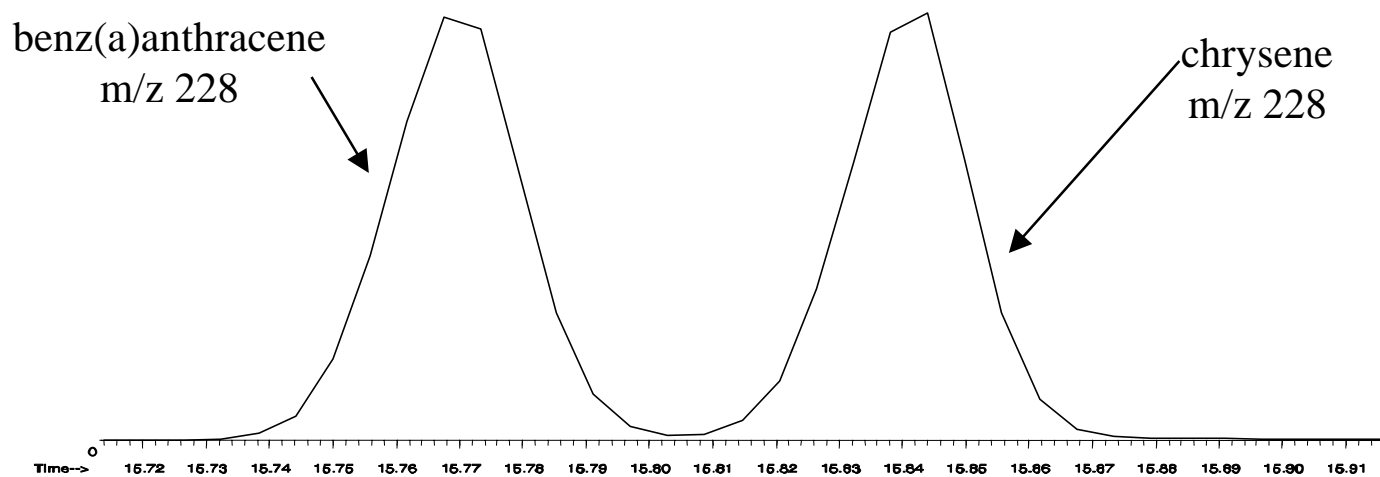
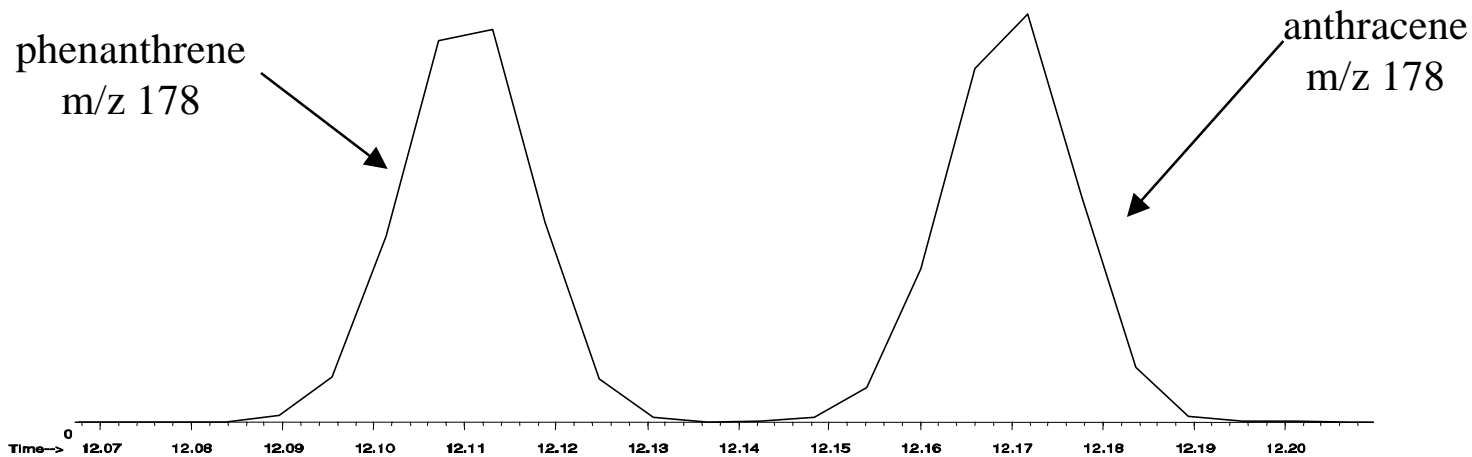
Separation of Critical Pairs

Rtx-5Sil MS (30m x 0.25mm, 0.25um)



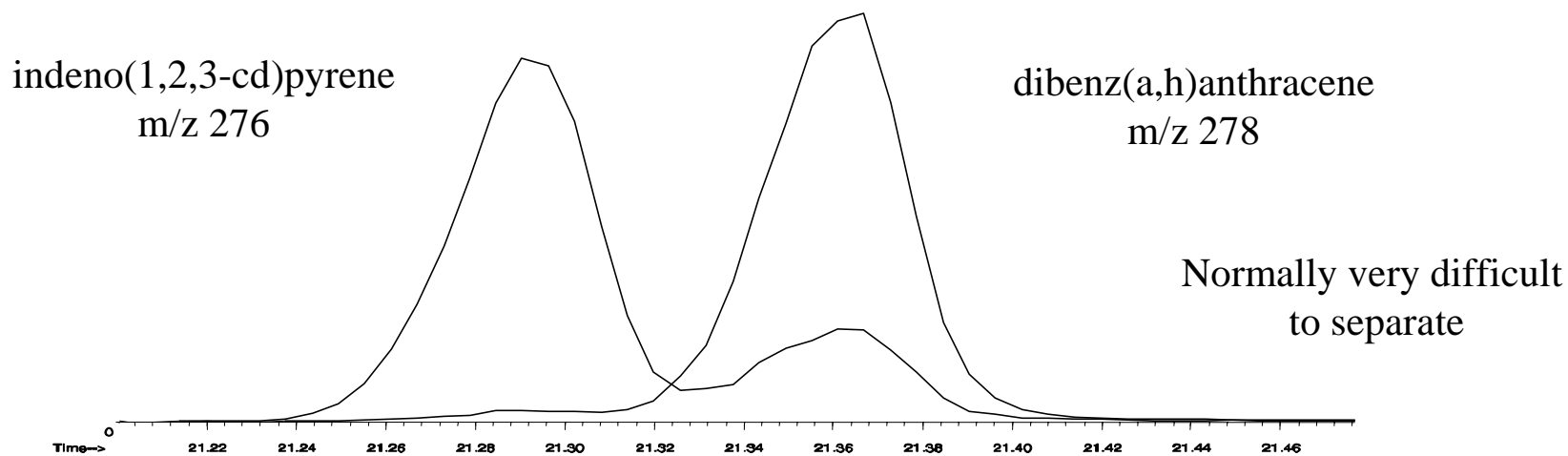
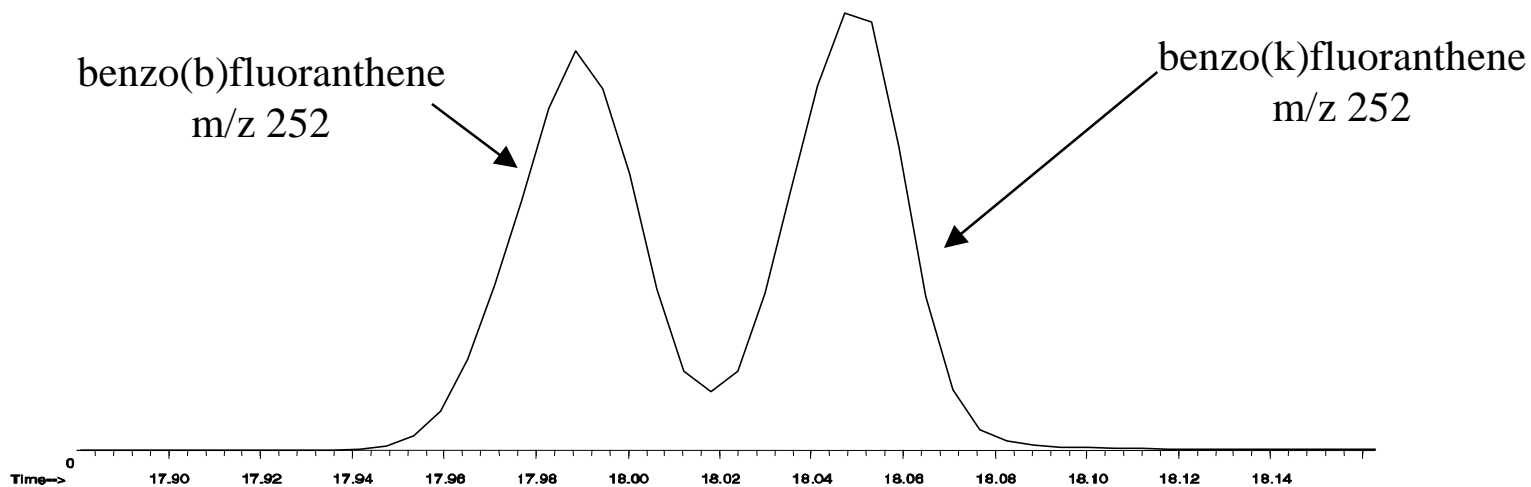
Separation of Critical Pairs

Rtx-5Sil MS (30m x 0.25mm, 0.25um)



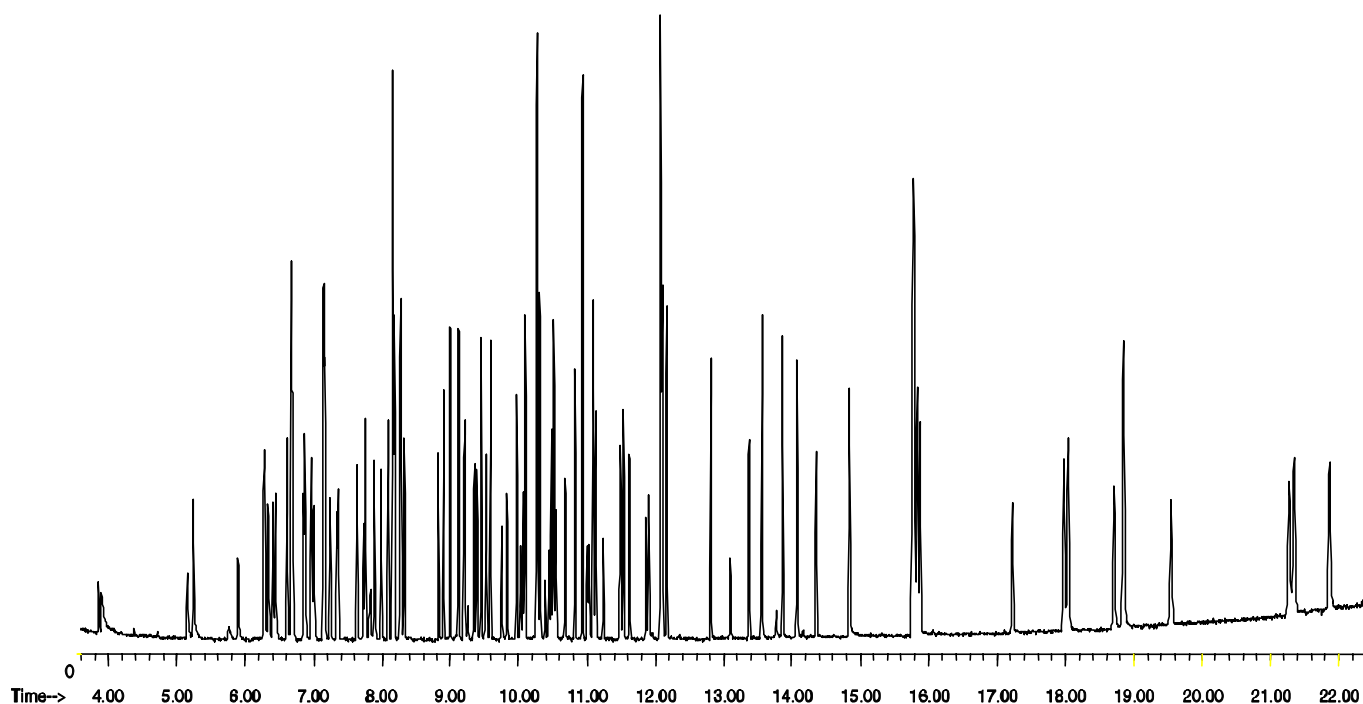
Separation of Critical Pairs

Rtx-5Sil MS (30m x 0.25mm, 0.25um)



4 ppm 8270 Calibration Standard

- Excellent signal to noise for 4 ng on-column injection
- Low column bleed
- Elimination of injection port discrimination



Rtx-5Sil MS (30m x 0.25mm ID, 0.25 um film)

To test the above GC set-up an 8270 calibration sequence was acquired consisting of a six point curve with concentrations at 4, 10, 24, 32, and 80 ppm. The internal standard was at a concentration of 8 ppm. Results of the more troublesome compounds are exhibited in Table 2.

Conclusion

USEPA SW-846 Method 8270 offers many challenges for laboratories, due to the extensive number of target compounds and sample matrix interferences. Improved transfer of the sample extract to the analytical column and faster analysis will lead to longer calibration sequences and increased sample throughput. Utilization of the Drilled Uniliner will enhance the transfer of target compounds as well as reduce active sites in the injection port sample path. Optimizing the GC program will result in faster GC cycle times, allowing more samples to be acquired within allotted time frames.