Comparison of Silonite Coated Injection Port Liners to Glass Liners in the Analysis of Semi-Volatile Organics by Gas Chromatography

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Abstract

The injection port liner is the first surface a sample makes contact with upon injection into a gas chromatograph. This region must be at a temperature between 250 and 300 C to effectively vaporize the sample when analyzing for semi-volatile organic compounds. At elevated temperatures certain compounds can exhibit breakdown if there is any activity in the injection port and primarily in the injection port liner. The material best suited for this purpose is glass, but even glass can be very active and has to have surface deactivation. Our presentation demonstrates breakdown that occurs with glass versus glass that has been specially deactivated by Silonite coating. Silonite coating is a process that bonds fused silica to the surface of glass or stainless steel, creating a very inert surface. Our data shows Silonite coated injection port liners provide the lowest breakdown attainable while maximizing the sensitivity for high molecular weight compounds.

Introduction

Glass liners have been used for decades as a suitable means of delivering sample analyte onto the analytical column of a gas chromatograph, and can provide acceptable results, but there are limitations. The surface of glass is covered with SiOH groups, known as silanols and this active surface will react with certain compounds like Endrin. The only way to prevent the active surface from chemical interactions is to cover the silanols with alkyl groups or other non-reactive end-caps. A very common technique of deactivating glass is to dip the liner in a 2 percent solution of dimethyldichlorosilane in toluene. This will give a usable product but the deactivation will wear off and results in bleed yielding a rising baseline that can reduce sensitivity, lower signal to noise ratios, and even cause damage or contamination of some detectors. Some commercially available liners that work well for Endrin can have problems with high molecular weight compounds. These liners have an absorptive layer like the coating on a GC column

which causes heavier compounds to partition into the phase resulting in lower recovery. Silonite coated liners obtain their high level of inertness without having to apply a thick OV-1 or Silarylene coating. Silonite liners prevent breakdown and maximize the response of high molecular weight compounds.

A very clear demonstration of the benefits of Silonite coating is in the analysis of organochlorine pesticides by EPA method 8081A. In this method a criteria is set for the maximum breakdown of Endrin and 4,4'-DDT. Neither compound is allowed to exhibit more than 15 percent breakdown. An analysis of a solution containing only Endrin and 4,4'-DDT must be performed prior to sample analysis. Endrin can degrade into Endrin Aldehyde and Endrin Ketone, 4,4'-DDT can degrade into 4,4'-DDD and 4,4'-DDE. If the degradation exceeds 15 percent corrective action must be taken before sample analysis can proceed. Chromatograms displayed show the obvious failure of a glass liner, the acceptable results of a common deactivated liner, and the impressive results of a Silonite coated liner.

Experimental

A solution containing only Endrin and 4,4'-DDT at 0.2 mg/ml was obtained from Accustandard (New Haven, Connecticut), and then diluted down to 50 ng/ul in dichloromethane. Several analyses were performed on various injection port liners to compare the percent breakdown of each. Another solution obtained from Accustandard at 2.0 mg/ml each of Polynuclear Aromatic Hydrocarbons (PAH) was diluted to 50 ng/ul in dichloromethane. The PAH standard contained benzo(ghi)perylene which was used to evaluate recovery of high molecular weight compounds. The solutions were injected in split-less mode for 0.3 minutes utilizing a Hewlett Packard 7673 Automatic Liquid Sampler. The gas chromatograph/mass spectrometer was a Hewlett Packard 5890II/5971A operated in full scan mode at 70eV with m/z range of 45- 450. The column utilized was an Agilent DB-5 0.25mm ID x 0.25u film x 30 m. The injection port temperature was set at 300C for breakdown evaluation. Three liners were chosen

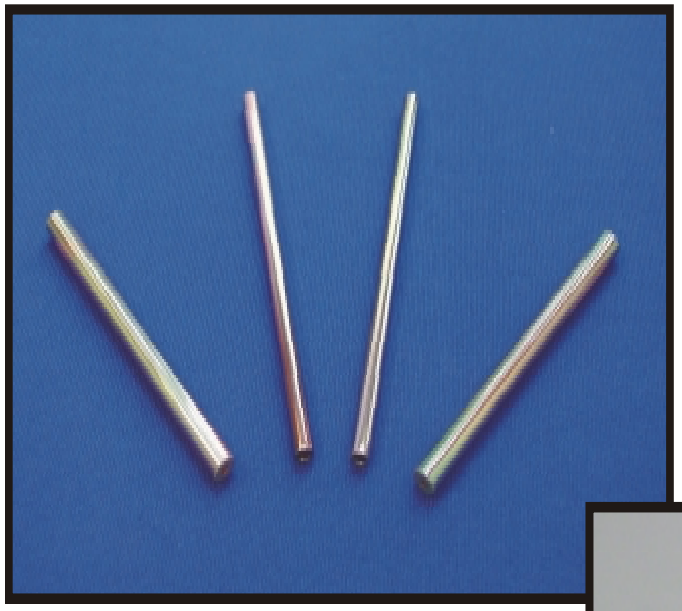
for evaluation, undeactivated glass, a commercially available deactivated liner, and a Silonite coated liner.

Calculation of breakdown:

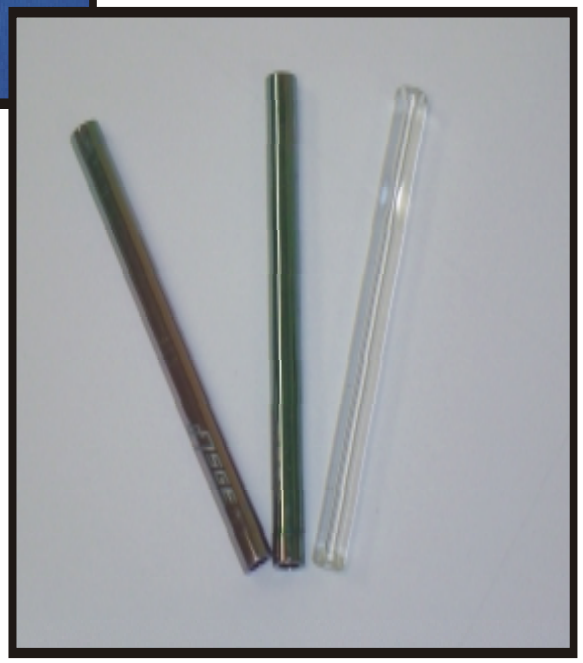
$$\text{Percent Breakdown} = \frac{\text{Sum of all breakdown products} \times 100\%}{(\text{Sum of all breakdown products} + \text{Primary product})}.$$

In addition to breakdown, analyses of the PAH standard were performed to evaluate recovery of the high molecular weight compounds. Benzo(ghi)perylene is a very good indicator for heavy compound recovery. Analysis of the PAH standard was performed with all 3 types of injection port liners using a GC injection port temperature of 250 deg. C to examine the recovery of benzo(ghi)perylene relative to the lighter PAH compounds.

Chemical Vapor Deposition Coated Silonite Liners



Silonite Coated Glass Injection Liners

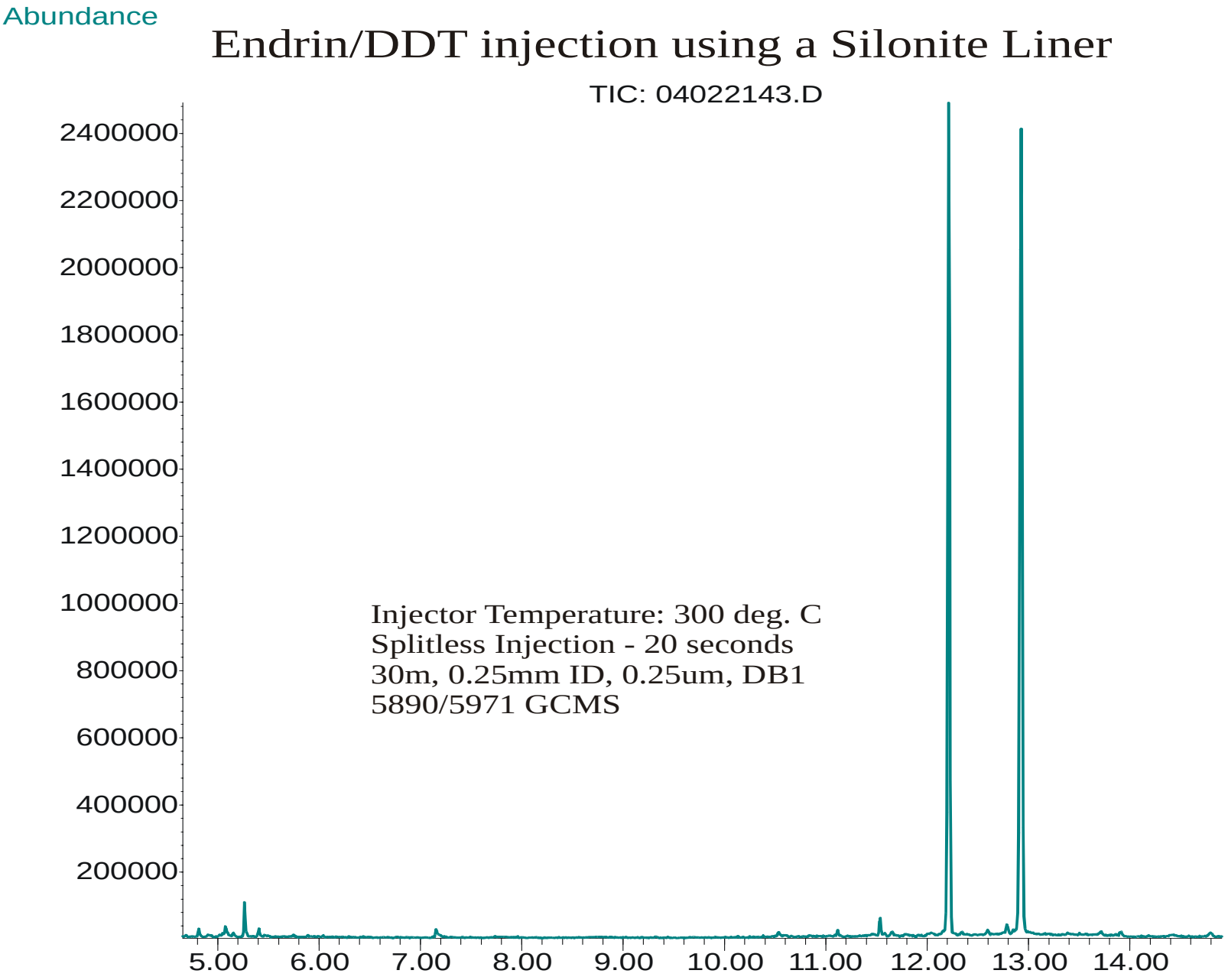


Translucent Silonite Coated Liners next to Uncoated Glass Liner

Discussion

Figures 2-4 show the injection of 4,4’-DDT and Endrin using 3 different types of injection liners at 300 deg. C. The glass liner (Figure 2) exhibits breakdown of 4,4'-DDT of only 0.4 percent but the Endrin breakdown was 16 percent. The glass liner would not be acceptable for EPA Method 8081A, although the high purity borosilicate glass is much better than some lower grade glass which show breakdown products of 30 percent or more. The commercially available siloxane deactivated liner in Figure 3 would be quite sufficient for use with its breakdown of 4,4'-DDT at 0.4 percent and the Endrin breakdown at 3 percent. The most inert liner is the Silonite coated liner (Figure 4) with 4,4'-DDT breakdown at 0.2 percent and Endrin breakdown at 0.7 percent.

Deactivation by adding a thick polydimethylsiloxane film to cover surface silanols can cause loss of heavier compounds. The best liner is one with minimal silanols requiring a very thin polydimethylsiloxane coating. Figure 6 shows a PAH standard injected into a 250 deg. C GC injector using a Silonite liner. Table 1 compares the 250 deg. C recoveries of Benzo(ghi)Perylene using a commercially available Siloxane deactivated liner and a Silonite liner. Using the lighter Acenaphthene as a normalizing compound, we see that the response of the Benzo(ghi)Perylene is 22% higher with the Silonite liner, probably due to the lack of having to use an absorptive siloxane coating to complete the deactivation.


Abundance
Endrin/DDT injection using a Silonite Liner
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2400000
2200000
2000000
1800000
1600000
1400000
1200000
1000000
800000
600000
400000
200000
Injector Temperature: 300 deg. C
Splitless Injection - 20 seconds
30m, 0.25mm ID, 0.25um, DB1
5890/5971 GCMS
5.00
6.00
7.00
8.00
9.00
10.00
11.00
12.00
13.00
14.00
Time-->

Figure 1

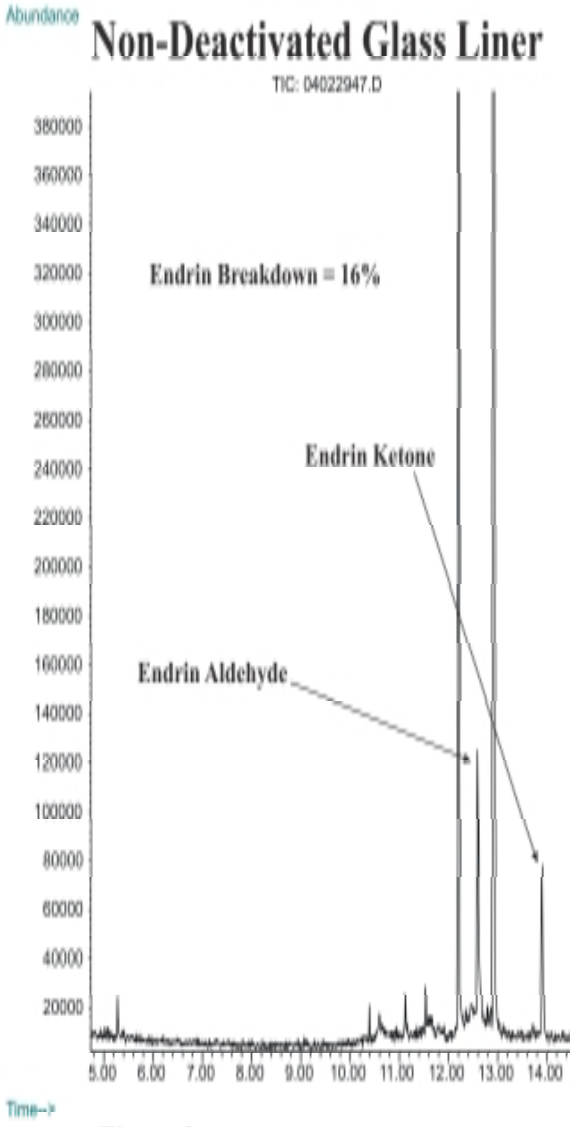

Figure 2

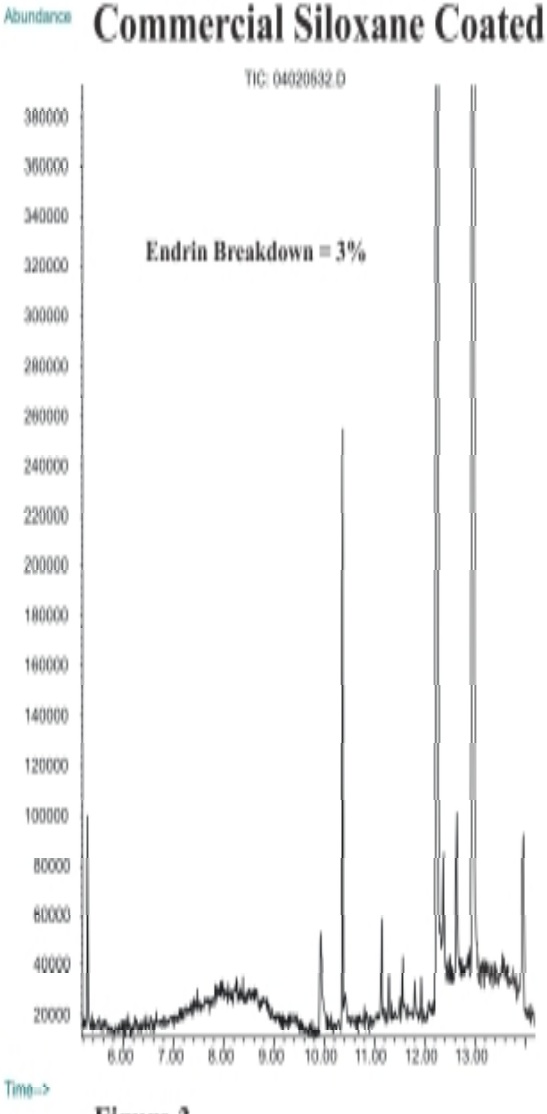

Figure 3

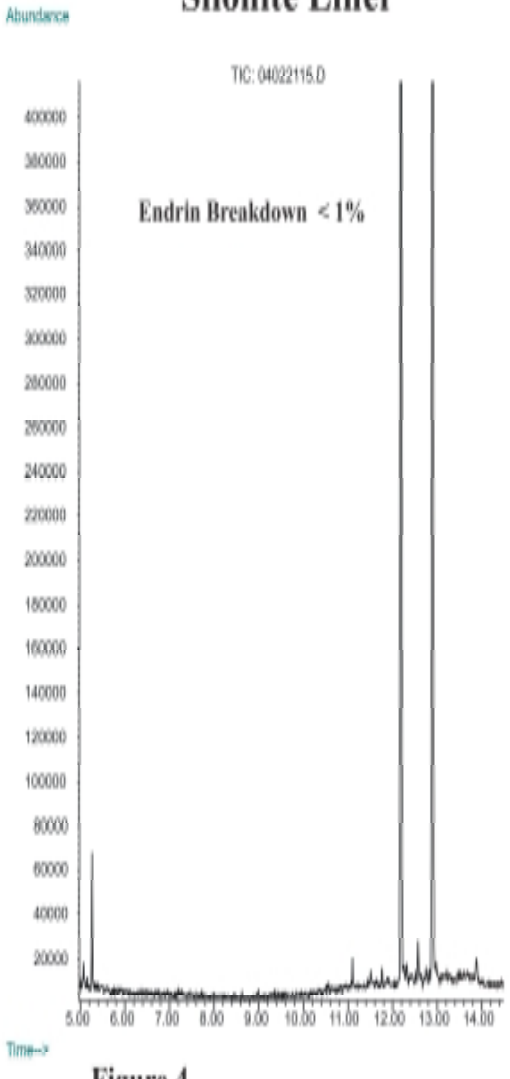

Figure 4

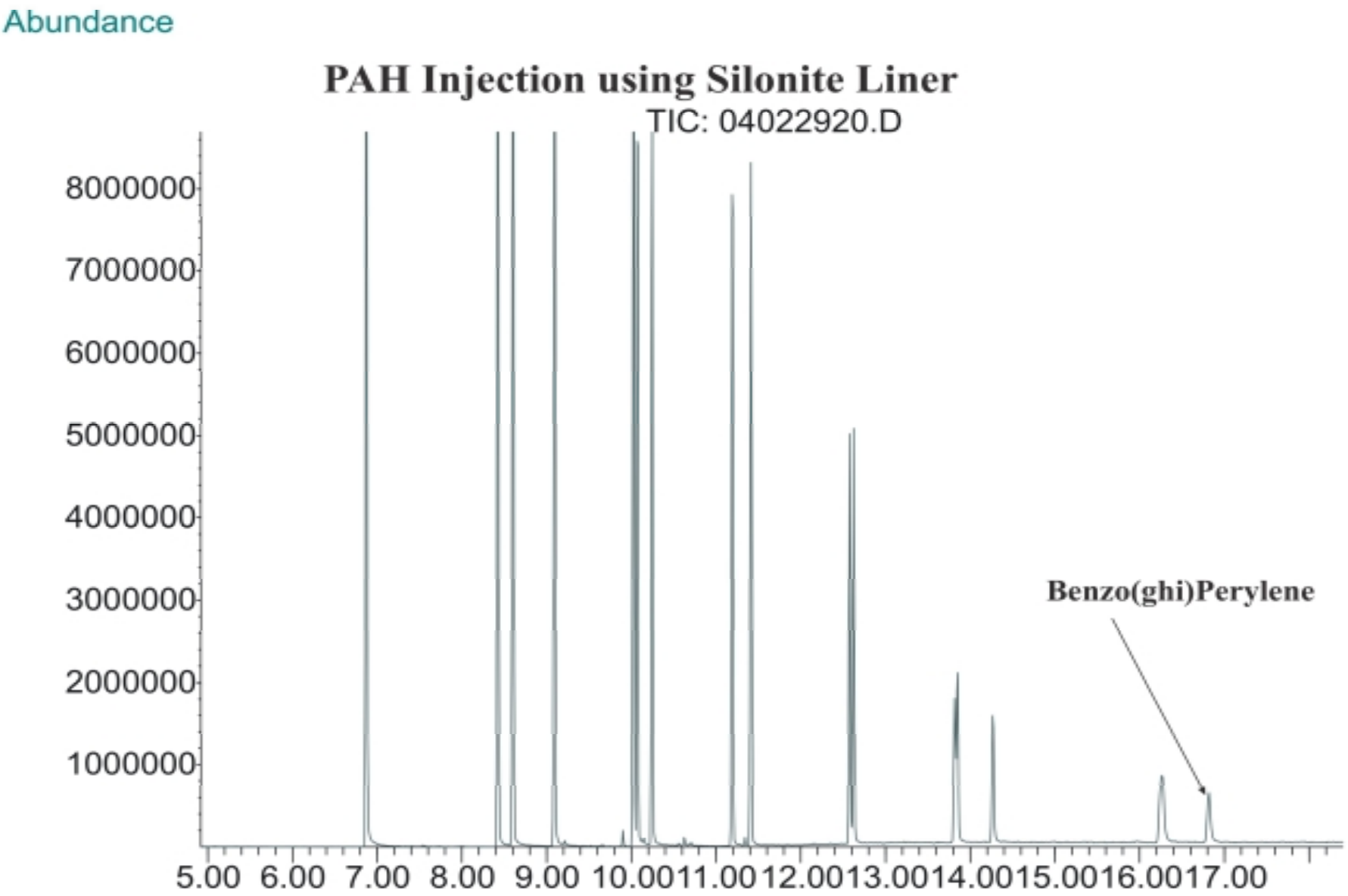
Abundance
PAH Injection using Silonite Liner
TIC: 04022920.D
8000000
7000000
6000000
5000000
4000000
3000000
2000000
1000000
Benzo(ghi)Perylene
5.00 6.00 7.00 8.00 9.00 10.00 11.00 12.00 13.00 14.00 15.00 16.00 17.00
Time-->

Figure 6

Table 1

	Injection Liner		
	Silonite	Siloxane Coated	Relative Response (Normalized)
Acenapthene	50,195,236	53,689,927	1
Benzo(ghi)Perylene	2,319,825	2,038,464	1.22

Conclusion

Glass by itself is far too reactive for the analysis of organochlorine pesticides. Siloxane coated liners improve the inertness of the surface in contact with the sample, but have other drawbacks including the requirement to run the injector at a higher temperature to recover heavier analytes. Silonite coating yields the lowest breakdown of Endrin attainable and at the same time does not need a thick film to cover up active silanols. The combination inertness and a hard surface provides a liner with optimal performance.