

# A New On-Column Injector Liner for a Programmable Temperature Vaporizing Injector: Gas Chromatography of Explosives and Brominated Flame Retardants

Jack Cochran, Scott Grossman, Michael Goss, Jaap De Zeeuw

Restek Corporation, 110 Benner Circle, Bellefonte PA 16823

## Abstract

Nitrate ester (e.g. nitroglycerin and PETN) and other explosives (RDX, Tetryl, HMX) explosives are thermally sensitive, which can lead to problems with sample transfer when using splitless injection – gas chromatography (GC). More brominated flame retardants, especially decabromo diphenyl ether, a member of the group of polybrominated diphenyl ethers (PBDEs), are of low volatility, which can also lead to incomplete sample transfer in splitless injection. Because of these reasons, some analysts turn to cold on-column injection (COC), the most efficient and reproducible introduction method for GC, assuming that samples do not contain large amounts of nonvolatile material.

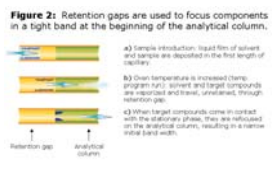
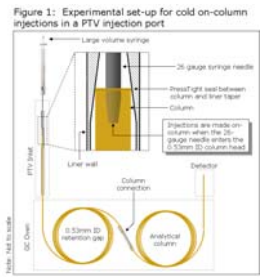
The popular Agilent 6890 and 7890 GCs contain only two slots for injectors. Most analysts use one position for a split/splitless injector (SSI). Those desiring more flexibility often employ a programmable temperature vaporizing (PTV) injector in the remaining position. Unfortunately this eliminates the installation of an on-column injector unless the SSI or PTV is removed from the GC. Recently though, a new liner for the PTV has been developed that allows COC injection via a 23/26s gauge syringe into a 0.53mm retention gap connected to a GC column. The liner expands the capability of the PTV and eliminates the need for a special on-column injector.

This paper will demonstrate on-column injections with the new liner for explosives and PBDEs. The differences in transfer efficiency and reproducibility for SSI and COC will be shown. Large volume (up to 100  $\mu$ L or more) COC injections will be performed. A new robust GC column connector (Alumaseal) will be used to join the retention gap and analytical column.

## Experimental Set-up

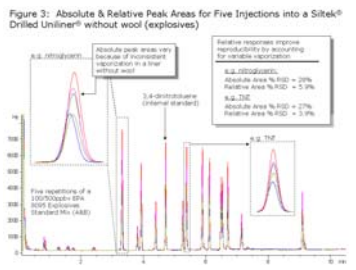
To effect true on-column injections in a PTV injection port, a novel liner was developed that placed the end of a 0.53mm retention gap (5m, 0.53 deactivated guard column) close enough to the top of the liner that the 23/26-gauge needle of the autosampler syringe could be guided into the column during 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.

The retention gap is necessary to focus the liquid sample and maintain good chromatography, especially when large volume injections are used. (Figure 2)



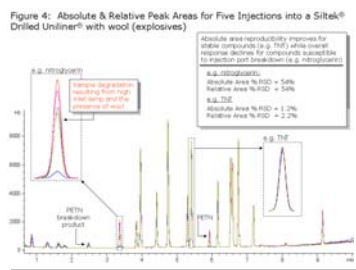
## Reproducibility and Sample Stability

In split/splitless applications, precision and accuracy are linked to the mechanism of sample vaporization and transfer onto the column. If these mechanics are not efficient and consistent, run-to-run reproducibility (as measured by absolute peak area) will suffer, and molecular weight discrimination may cause results to under-represent the actual sample composition. Typically, the use of an internal standard can account for this variation. Figure 3 illustrates the absolute and relative reproducibility for five replicates analyses of EPA Method 8095 explosives using direct injection (the ideal injection technique for split/splitless inlets).



## Reproducibility and Sample Stability

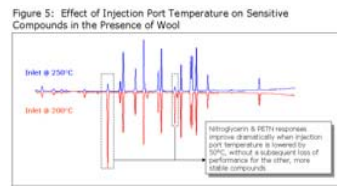
Figure 4 illustrates another sequence of five injections made with a small amount of wool added to the liner (an atypical arrangement for direct injection). The wool clearly helps improve the precision of vaporization and sample transfer for robust compounds (e.g. TNT). However, compounds that are prone to injection port degradation are susceptible to active sites found on the wool. This is clearly demonstrated for two such compounds in the 8095 mix, nitroglycerin (NG) and PETN.



Take note of the relative sensitivity for both PETN and NG between Figures 3 & 4. There is clearly sample loss through degradation.

In split/splitless injections, one way to mitigate the sample loss for thermally sensitive compounds is to optimize the injection port temperature. For example, the suggested injection port temperature for EPA Method 8095 is 250°C. Lowering the temperature to 200°C dramatically improves the response for NG and PETN without degrading the response for the other compounds, even the late eluting HMX. (See Figure 5) System cleanliness may become an issue at lower temperatures.

With cold on-column injections the entire liquid sample is placed inside the column directly. Solvent and sample vaporization occurs at a programmed rate, so there is not the initial "shock" of flash vaporization. As a result, accuracy and precision for sample injections are high, and sample degradation inside the injection port is minimized.



These effects are clearly illustrated in Figures 6 & 7 for explosives and polybromodiphenyl ethers (PBDE's), respectively. Note the reproducible and sensitive response for decabromodiphenyl ether.

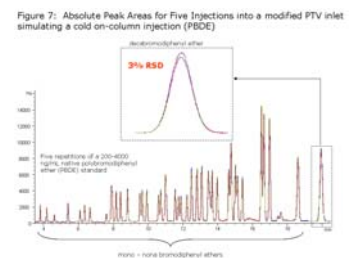
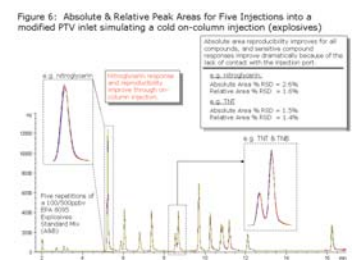


Table 1: Chromatographic conditions for Figures 6 & 8

**Sample:** 100/500 ng/mL EPA Method 8095 Mix A & B with 100 ng/mL 3,4-DNT as IS  
**Injection:** Slow injection speed (300 $\mu$ L/min)  
**Inlet:** PTV Injection Port; 55°C to 285°C @ 10°C/min. (hold 10 min), splitless (15mL/min @ 0.35min). Cryo on @ 125°C with a timeout @ 10min.  
**Column:** Figure 6: 5m, 0.53mm guard column attached to a 6m, 0.53mm, 0.5 $\mu$ m Rxi®-5MS via a Press-Tight® connector.  
 Figure 8: 5m, 0.53mm guard column attached to a 6m, 0.53mm, 0.5 $\mu$ m Rxi®-TNT via a Press-Tight® connector.  
**Oven:** 50°C to 280°C @ 10°C/min (hold 10min)  
**Detector:**  $\mu$ ECD @ 300°C with N<sub>2</sub> make-up gas @ 60mL/min  
 \* Note, IS was not included in Figure 8

Table 2: Chromatographic conditions for Figure 7

**Sample:** 20-400 ng/mL Native BFR mix in toluene  
**Injection:** Slow injection speed (300 $\mu$ L/min)  
**Inlet:** PTV Injection Port; 105°C (hold 0.5min) to 150°C @ 25°C/min. to 305°C @ 10°C/min (hold 5 min) splitless (15mL/min @ 0.5min), Cryo off  
**Column:** 5m, 0.53mm guard column attached to a 6m, 0.53mm, 0.5 $\mu$ m Rxi®-5MS via a Press-Tight® connector.  
**Oven:** 100°C (hold 0.5min) to 150°C @ 25°C/min. to 300°C @ 10°C/min (hold 5 min)  
**Detector:**  $\mu$ ECD @ 310°C with N<sub>2</sub> make-up gas @ 60mL/min

## Large Volume Injections

Split/splitless injection ports rely on rapid flash vaporization to turn a liquid sample into a gas. The sample volume dramatically increases upon flash vaporization, and the volume of the inlet liner where the vaporization occurs can typically only accommodate expansion from about 1 $\mu$ L of liquid (and this is very solvent-dependent).

Samples are injected as liquids in either PTV or cold on-column injection techniques. The temperature of the injection port is ramped to initially vent or elute the solvent and then the analytes of interest. Consequently, sample expansion volume is not much of a consideration, opening the door to larger volume injections

Figure 8 illustrates both the chromatography and the linearity of increasingly larger volume injections. The peak shapes are largely maintained even with a 100 $\mu$ L injection volume. Additionally, as injection volume increases, peak area increases linearly.

One artifact of larger and larger volume injections, however, is a shift in retention time, especially for early eluting compounds. Figure 9 illustrates this effect for EPA 8095 explosives.

