Large Volume Injection of Semivolatiles by Gas Chromatography Using a Commercially-Available, Unmodified Splitless Injector

Joe Konschnik, Michelle Misselwitz, and Jack Cochran; Restek Corporation, 110 Benner Circle, Bellefonte, PA 16823, USA

Abstract

➢Magni and Porzano described Concurrent Solvent Recondensation Large Volume Splitless Injection (CSR-LVSI) with a special low dead-volume injector, a modified septum head to reduce septum temperature, and the ability to close the septum purge during the injection (and for a period of time after the injection). [1,2]

➢The principles of CSR-LVSI include fast injection with liquid band formation into a liner containing glass wool, a pre-column (e.g. 5m x 0.53mm) press-fitted to the analytical column, and a starting oven temperature below the boiling point of the solvent.

➢In the work presented here, a standard Agilent GC split/splitless injector was employed with a standard single-taper liner with wool and 0.53, 0.32, or 0.25mm pre-columns press-fitted to 0.25mm GC columns to achieve CSR-LVSI.

➢In addition, the use of integrated guard columns (as retention gaps), where no press-fit is necessary were tested.

➢No special cooling was necessary for the GC inlet septum head and the septum purge remained open at 3 mL/min during injection and GC.

➢Repeatable and linear results were achieved for hydrocarbons, PAHs, and other environmental contaminants with injection volumes up to 50µL.

➢CSR-LVSI was also employed for the analysis of EPA Method 8270 semivolatiles, reducing the need for an extended extract evaporation step.

Materials and Methods

➢ To achieve a large volume splitless injection on an unmodified Agilent GC split/splitless injector the following are needed:

- ✓ Fast autosampler injection
- ✓ Single taper/gooseneck inlet liner with wool
- ✓ 5 meter guard column (retention gap, or integrated guard)
- ✓ Initial oven temperature below boiling point of solvent

➢An Agilent 6890/5975 GC-MSD with a standard turbo pump was equipped with a 30m x 0.25mm x 0.25µm Rxi-5Sil MS with a 5m Integra-Guard column.

Results and Discussion

➢ Previous experiments with a 5m x 0.53mm ID guard column with an FID resulted in a linear increase in peak area with an increase in injection volume up to 50µL.

➢ With a mass spectrometer detector the pumping capacity of the turbo molecular pump is a limiting factor.

➢ Using a standard turbo pump on the Agilent 5975 MSD injections of up to 12.5µL were evaluated while monitoring the vacuum ion gauge. **(Figure 1)**

➢ A 10µL injection allows the turbo pump to effectively evacuate the large solvent vapor while still providing a large enough injection that extract concentration can be significantly reduced.

➢ By stopping the concentration at 10mL there is no need to use a micro Snyder column or other further concentration techniques.

➢ Increasing the injection volume from 2.5µL to 12.5µL resulted in a linear increase in peak area for all targeted compounds from phenols to late eluting PAHs. **(Figure 2)**

➢ To prevent the use of a press-tight connection that can be a source of leaks and has a maximum operating temperature of 320°C a seamless integrated guard column was used (Integra-Guard). **(Figure 3)**

➢ The minimum length of the Integra-Guard (0.25mm ID) is 5m with a 10µL injection. Decreasing this length to 4m or 3m resulted in loss of resolution and sample overloading observed by peak fronting. **(Figure 4)**

➢ As the injection volume increased the resolution between closely eluting PAH compounds increased. **(Figure 5)**

➢ Injection to injection repeatability had less than 10% relative standard deviation (RSD) for all target analytes in 7 replicate injections. **(Figure 6)**

➢ A 10µL injection provided good peak shape of early eluting compounds including N-Nitrosodimethylamine and Pyridine. **(Figure 7)**

➢ Setting the solvent delay time is important to protect the MS filament, it is also recommended to set ion-gauge to off during large volume injections.

Conclusion

➢ Using an unmodified Agilent split/splitless injection port for large volume splitless injection is possible. A 5m guard column, single taper liner with wool, and a fast autosampler injection are necessary to achieve CSR-LVSI.

➢ By injecting larger volumes of sample, extract concentration can be reduced by 10x saving time in the lab

References

[1] P. Magni, T. Porzano, J. Sep. Sci. 26 (2003) 1491.
[2] Patent No: US 6,995,709 B2.

Figure 1: Effect of Vacuum Pressure with Increasing Injection Volume

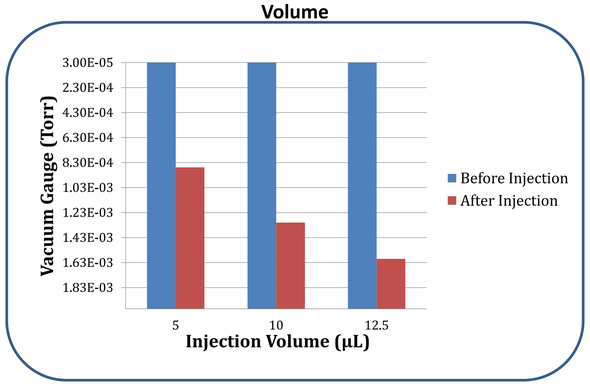

Figure 2: 2,4-Dinitrophenol Linear Increase in Peak Area with Increase in Injection Volume

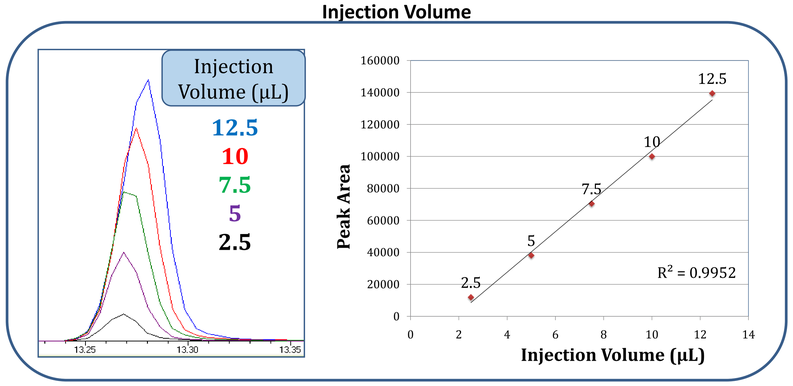

Figure 3: Fast Autosampler Injection, Single Taper Liner w/ Wool and 5m Integra-Guard allows LVSI in Unmodified Injection Port

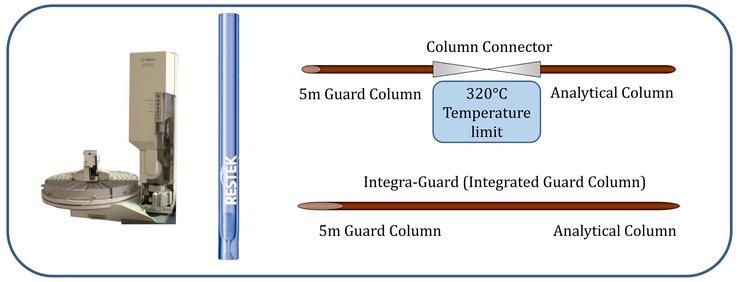

Figure 4: A 5m x 0.25mm ID Integra-Guard is necessary when injecting 10µL

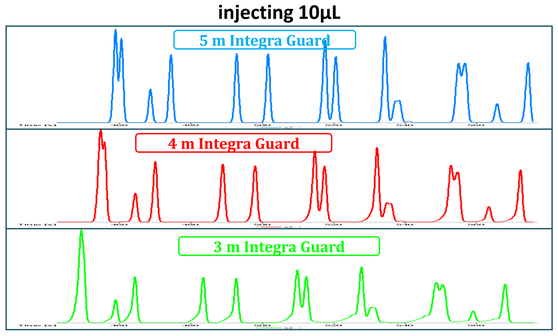

Figure 5: As injection Volume Increases Resolution Increases

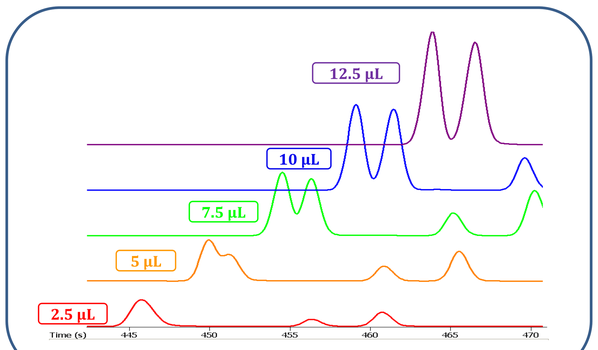

Figure 6: CSR-LVSI Provides Good Injection to Injection Repeatability

Average Response (n=7) Percent Relative Standard Deviation (RSD)	
Compound	**% RSD**
Pyridine	2.32
Phenol	2.26
N-Nitroso-di-n-propylamine	2.16
2,4-Dichlorophenol	1.65
Hexachlorocyclopentadiene	2.65
2-Nitroaniline	2.34
Acenaphthylene	1.39
2,4-Dinitrophenol	8.47
4-Nitrophenol	2.75
4,6-Dinitro-2-methylphenol	3.20
N-Nitrosodiphenylamine	1.37
Pentachlorophenol	1.32
Phenanthrene	1.36
Benzo(ghi)perylene	0.81

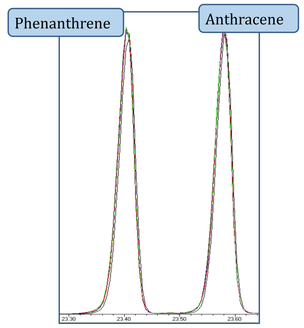

Figure 7: A 10 µL injection of 1ng/µL 8270 Mega Mix on the Rxi-5silMS 30m x 0.25mm x 0.25µm w/ 5m Integra-Guard Using an Unmodified Agilent Split/Splitless Injection Port

GC/MS Conditions

Column	Rxi-5Sil MS w/5m Integra-Guard Column, 30 m, 0.25 mm ID, 0.25 µm (cat.# 13623-124)
Sample	8270 MegaMix (cat.# 31850)
Diluent:	Methylene Chloride
Conc.:	1 ng/µL
Inj. Vol.:	10 µL splitless (hold 1.0 min.)
Liner:	Sky™ 4.0mm ID Single Taper Gooseneck Inlet Liner w/ Wool (cat.# 23303.1)
Inj. Temp.:	250 °C
Purge Flow:	60 mL/min.
Oven Temp:	40 °C (hold 1 min.) to 330 °C at 6.8 °C/min. (hold 5 min.)
Carrier Gas	He, constant flow
Flow Rate:	1.4 mL/min.
Transfer Line Temp.:	280 °C
Source Temp.:	250 °C
Solvent Delay Time:	4.5 min.
Scan Range:	35-550 amu
Instrument	Agilent 7890A GC & 5975C MSD
Notes	Syringe size: 25µL