Split/Splitless Capillary Injector Operations in Gas Chromatography

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A common device used to introduce a small aliquot of a liquid sample into a capillary gas chromatograph is a split/splitless injector. Its purpose is to ensure that the sample loading is within the operating range of both the capillary column and the detector. If too much sample is injected, analyte peaks are likely to be distorted from overloading, the detector may be well above its linear range. It also helps minimize matrix introduction into its detector with mass spectrometers. If the sample loading is too low, the detector may be not able to detect it. Many parameters related to this injector are operator entries and can be optimized for the sample under consideration.

Two split/splitless injector types are commercially available from Scion Instruments. One is labeled PTV for Programmable Temperature Vaporization Injector (previously Varian Model 1079). The injector discussed here is called SSL for Split/Splitless Injector. The Varian Instruments version had been called Model 1177.

This injector operates in two modes – split or splitless, and this choice depends on the characteristics of the measurement. Hardware for split operations and splitless processes are identical, except for some changes in the injector liners and method entries.

Split Mode

This operation is most often used when major components in the sample are targets, and these levels are too high for the capabilities of the column and detector. The process of splitting off a major portion of the sample to vent and allowing a small part to be directed to the head of the column diminishes the stress on overloading the column, lessens the possibility of overloading the detector, reduce the matrix issues for nasty samples, and where clean-up of the sample matrix is difficult. To provide an even split for all components in the sample, this injection must be rapid and turbulent for uniform mixing of the sample with the carrier gas in the injector. This necessity requires the injector liner to have either silanized glass wool, frit or other porous medium stuffed in a 4 mm ID, 6.3 mm OD[1] liner in the injector body, (see Figure1 and Table I), and a rapid injection speed. Split ratios[2] are selected by the operator through an electronic flow controller, so the amount injected into the column is within range of the column capacity and detector range. Carrier gas must be controlled with backpressure regulation, as column flow must remain independent of split ratio. Use of a true flow controller does not work, especially with the high flow often required

Figure 1. Liner for split operations.

Splitless Mode

To overcome a drastic loss of trace components that occurs in the split mode, a sample is injected with the split vent closed. This process is intended to direct much of the components in the sample into the capillary column. A one microliter injection can rapidly expand to typically 100-600 milliliters (see Table II) when volatilized in a hot injector, and most of the backflow from expansion moving away from the split point is solvent. Most trace components reside in the leading edge and directed to the column inlet. Once most of these trace elements are contained in the column, typically 20-60 seconds after injection, the split vent is opened and the residual solvent in the injector is vented off. This action dramatically reduces detection of a tailing solvent peak. To minimize effects of mixing this leading edge with the solvent cloud and to avoid disruption of the proper loading of the column, the injector liner must be chosen to provide near laminar flow to the inlet of the column – either 2 mm ID liner or 4 mm ID liner (see discussion in Thermal Expansion of Solvents). Insertion of glass wool should be avoided, as this produces turbulence and upsets proper sample transfer to the column. Also, the injection speed should be reduced to again minimize turbulence. After several minutes, the split flow can be reduced to save carrier gas. Since actions with the splitter vent require dramatic changes in total flow into the injector, a pressure regulator is mandated to keep flow into the column consistent and allow vent flow to change as required.

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[1] The narrower OD liner (6.3 mm) aids in reducing the restriction around the liner when high split flows are used.

[2] Split ratios are often entered as 1:10, for example. In this case only 9% of the sample injected is loaded on the column. To effectively get a 10% loading, the split ratio should be set to 1:9.

Glass Liner Style	Internal Volume (ml)		Part Number[3]
Split, 4 mm ID, with glass wool, 6.3 mm OD, 78.5 mm length, pkg 5	1.0		Scion 392611936
Split, 4 mm ID, with Frit, 6.3 mm OD, 78.5 mm length, pkg 5	1.0		Restek 23330
Split, 4 mm ID, with CarboFrit, 6.5 mm OD, 78.5 mm length, pkg 5	1.0		Restek 21897-216.5
Splitless, 2 mm ID, 6.5 mm OD, 78.5 mm length, pkg/5	0.25		Scion 392611924
Splitless, 4 mm ID, 6.5 mm OD, 78.5 mm length, pkg/5	1.0		Scion 392611925
Splitless, Topaz, 4 mm ID, 6.5 mm OD, 78.5 mm length, pkg/5	1.0		Restek 23331
Viton O-ring,6.3 mm OD, pkg/10	-		Restek 20296
Viton O-ring, 6.5 mm OD, pkg/10	-		Scion 8850103100
Septa, Marathon Silicone, 9 mm OD, pkg/25[4]	-	-	Scion CR239778
Silanized glass wool, 10 gr	-	-	Scion AL4037
Pencil Filter, Split Vent, 100% Activated Charcoal	-	-	Scion CP742211

Table I. Parts for Scion Split/Splitless Injector (SSL - Model 1177).

Solvent Effect with Splitless Mode

A key element in the chromatographic process is partitioning of target analytes into the stationary phase. This phase must be chemically similar to the target analyte for this to occur. Obviously, when a slightly polar analyte is directed into a column with non-polar stationary phase, this compound is not induced to “dissolve” into the phase. However, if the sample solvent is condensed at the head of the column by cooling the column enough below the boiling point of the solvent, the initial portion of the column then becomes very compatible with analytes and allows the target analytes to be focused in the very early portion of the column as a narrow band. As the column temperature rises with programming, the solvent rapidly boils off and quickly passes through the column, leaving the concentrated analytes behind. They eventually elute through the column in much sharper peak shapes, as the column temperature increases. This condensation is very dependent on the dew point of solvent/gas mixture and the column headpressure – a difficult relationship to predict. Settings of the initial column temperature must be optimized experimentally. A suggested starting point is 20 °C below the boiling point of the solvent.

Thermal Expansion of Solvents

Injecting a liquid sample into a hot injector generates rapid expansion inside the injector liner. Table I lists commonly used ones for split/splitless injections. Consideration of the optimum liner type must include the expansion volume of the sample (see Table II). If the expansion volume of the liner is inadequate to accommodate this enlargement, sample can back up inside the innards of the injector and attached gas lines. This episode can yield severe tailing as this overload is flushed out into the liner. In addition, over time residual contaminants that have flashed into the injector tubing may build up and recondense, often resulting in restrictions and pressure fluctuations that can require intense cleaning or injector replacement.

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[3] For Restek parts: www.restek.com/sitesearch/site/liner%20for%201177

[4] Alternate source is www.restek.com/catalog/view/9553, Thermolite Plus, P/N 23862, pkg 50.

[5] www.scioninstruments.com/contact/

Injected Solvent	Liquid Injector Volume (µL)	Injector Temperature (°C)	Column Head Pressure (psiG)	Expansion Volume (µL) at Head Pressure[6]
Benzene	1.0	250	15	240
Butanone	1.0	250	15	236
Carbon Disulfide	1.0	250	15	353
Carbon Tetrachloride	1.0	250	15	220
Chloroform	1.0	250	15	266
Dichloromethane	1.0	250	15	332
Ethanol	1.0	250	15	365
Hexane	1.0	250	15	163
Methanol	1.0	250	15	524
4-Methylpentan-2-one	1.0	250	15	170
Pentane	1.0	250	15	192
Toluene	1.0	250	15	236
Trichloroethene	1.0	250	15	237
2,2,4-Trimethylpentane	1.0	250	15	117
Water	1.0	250	15	1,179

Table II. Expansion Volumes for Common Solvents.

Many liner styles for capillary injectors are available. Some liners have a design incorporating a gooseneck to provide a restriction for this backflow by narrowing the internal diameter at the top. Flow into the injector is accelerated at this point from this restraint, to assist in minimizing sample flow upstream. The Scion SSL injector (Model 1177) is designed for the gooseneck to be located near the top of the injector.

Electronic Flow Controllers (sometimes called Electronic Pressure Controllers)

All injection modes for split/splitless injections mandate use of full pressure control of the column carrier gas to provide consistent operations of the injector independent of changes in parameters, such as split ratios and split vent opening/closing during the run. The Scion 436/456 Gas Chromatographs have available electronic flow controllers (EFC21 and 25)[7] to provide electronic control of inlet pressures. A choice is provided in the method parameters to operate in programmed pressure mode, constant flow set by calculating required pressure settings to maintain constant flow, or constant average linear velocity, again set by computing required pressure settings to achieve constant velocity.

Leak Detection

Operations with pressure control of carrier gas make locating leaks a bit more difficult. If the leak is catastrophic, such as a broken column, the controller senses the dramatic change in total flow required to maintain the pressure setpoint and subsequently shuts down operations with a fatal error. However, small leaks, such seepage through an overused septum, likely will not be picked up. The best method for detection of leaks is use of an electronic leak detector[8] to check around the pneumatic connections and septum.

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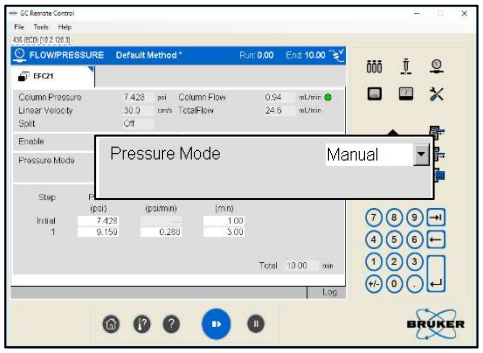
[6] Expansion volume is computed with this formula: $V_{exp} = V_{inj} * \rho * MW * V_m * \frac{T_{inj}+273}{273} * \frac{P_{atm}}{P_{col}} * 10^6$, where V_{exp} is the expansion volume (µl), V_{inj} is the injected volume (µl), ρ is density of solvent (g/mole), MW is molecular weight of solvent (g/mole), V_m is molar gas volume (22.4 L/mole), $\frac{T_{inj}+273}{273}$ is adjustment for temperature of injector (°C), $\frac{P_{atm}}{P_{col}}$ is correction of compression of solvent gas inside the injector at 15 psiG. A different column head pressure, injection volume or injector temperature requires appropriate adjustments.

[7] Electronic Flow Controllers Types 21 and 25 are intended for use with split and splitless operations in capillary injectors. Type 21 is designed for conventional split/splitless injectors with pressure monitoring feedback directly to the controller from the injector. Type 25 is intended for use when the pathway for connection to the split point is extended beyond the conventional distance to an injector, such as with use of a purge and trap system and with valving.

[8] A recommended leak detector is www.glsciences.com/c-product/gc/gc-accessories/gas-leak-detector-ld-239/.

Constant Pressure Mode



Split/splitless operations require pressure control of carrier gas. When the column temperature is programmed to yield a faster measurement, the carrier gas viscosity rises with temperature. With constant pressure being applied to the head of the column over the temperature program, flow drops due to the higher resistance to flow in the column due to the increase in viscosity of the carrier gas. Figure 2 shows the drop in actual column flow with constant inlet pressure. Figure 6 is a chromatogram of lindane and aldrin with constant pressure. Constant pressure mode can be used with isothermal operations, or to faithfully follow an established protocol listing constant pressure operations.

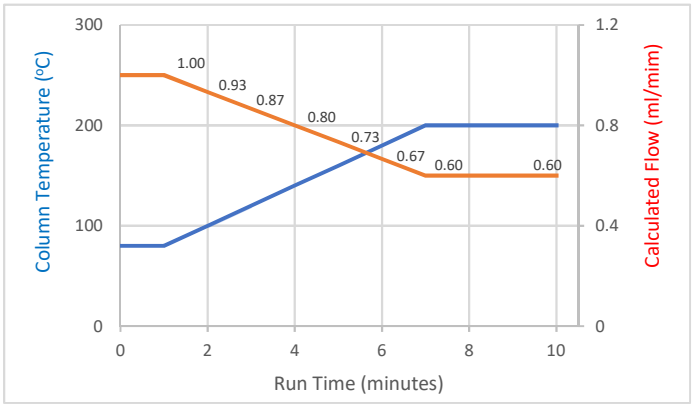
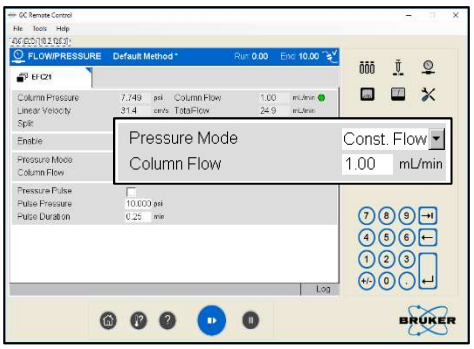


Figure 2. Plot of changes in column flow with constant pressure mode and column temperature programming. Column pressure is constant at 7.8 psiG.

Constant Flow Mode



Constant flow can be critical to maintain performance of some detectors that are flow sensitive, including thermal conductivity (TCD), electron capture (ECD), pulsed photometric (PFPD) and mass spectrometers (MS). The Scion 436/456 Gas Chromatographs can be set up to provide a constant flow mode and vary the pressure as needed during column oven ramping.

Conversion of pressure to flow is computed with Poiseuille's equation for non-compressible fluids[9], which relates flow to column inlet and outlet pressures, dimensions of the capillary column and carrier gas viscosity:

$$F = \frac{\pi \left(\frac{d}{2}\right)^4 \left(P_i{}^2 - P_o{}^2\right)}{8\eta l P_o}$$

[9] en.wikipedia.org/wiki/Hagen–Poiseuille equation; a modification of this relationship involves a condition where the mobile (carrier) phase is compressible.

where F is column flow at the column exit, P_i is column inlet pressure, P_o is column outlet pressure, d is capillary internal diameter[10], η is viscosity of the carrier gas[11] and l is the length of the capillary column. Viscosity is adjusted for its impact from temperature by $\eta = \eta_0 \frac{(T_o+273+\ )}{(T+273\ \ )}\left(\frac{T+273}{T_o+273}\right)$, where η_0 is viscosity at 0 °C (19 μPa∗s),[12] T is the input temperature (°C), T_o is the reference temperature (°C), and C is Sutherland's constant[13] (352.4 °K) for helium.[14] Since viscosity changes over a temperature range, the inlet pressure must rise to maintain constant flow. Figure 3 shows the increase in actual inlet pressure with constant column flow. Figure 7 depicts a chromatogram of lindane and aldrin with constant flow. This calculation of flow based on inlet and outlet pressures is not applicable when the outlet of the column is inserted into a mass spectrometer, as P_o is then nearly zero from the hard vacuum, and with P_o as a divisor, flow becomes very large and unpractical. This new relationship is not presented here.

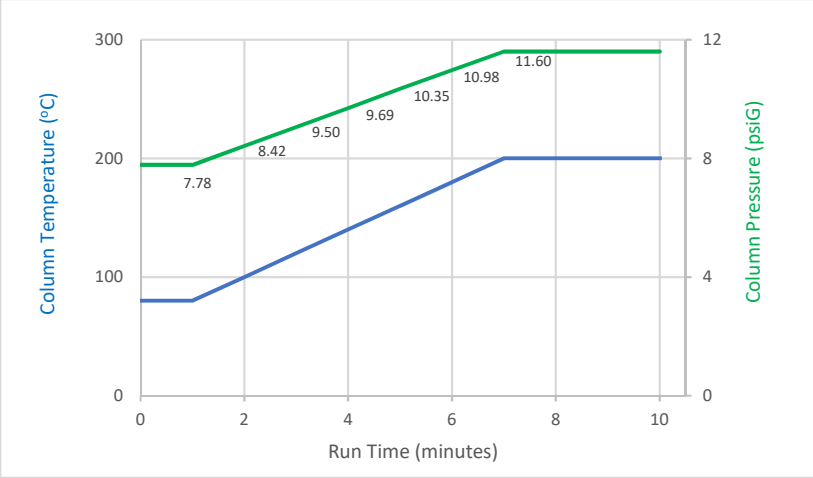
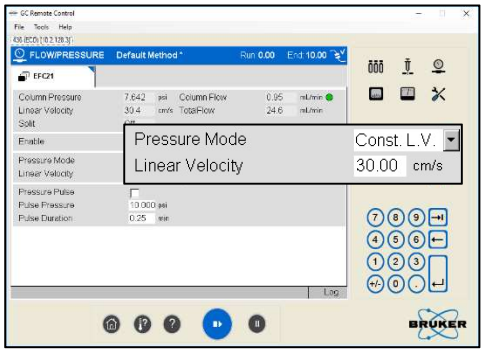


Figure 3. Plot of changes in column pressure with constant flow mode and column temperature programming. Calculated column flow is constant at 1.0 ml/min.

Constant Average Linear Velocity



Flow has a dramatic impact on the separation power of a capillary column. Too slow results in analytes migrating by diffusion along the length of the column and widens the resulting peaks. Flow too fast allows analytes to skip past the stationary phase and also distorts peak shapes. A compromise in flow rate is needed to yield the best performance of the capillary column. Van Deemter plots[15] displays this optimization. To make the curve independent of column diameter, this display uses the average linear velocity for the length of the column. Optimum average linear velocity for helium is 20 cm/s, with an acceptable range of 18 to 40 cm/sec without much effect on separation power. For hydrogen, these values are 40 cm/sec and range of 25 to 60 cm/sec. A setting in the upper ranges dramatically shortens run times without much compromise in separation capabilities.

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[10] Typical tolerance for capillary internal diameters is ± 4.8%. This variation range can result in an error of up to ± 22% in measured flow.

[11] www.engineeringtoolbox.com/gases-absolute-dynamic-viscosity-d_1888.html.

[12] www.engineeringtoolbox.com/gases-absolute-dynamic-viscosity-d_1888.html

[13] Sutherland, W., "The Visocisty of Gases and Molecular Force", Philosophical Magnetic Series 5 (1893), 36: 223, 369-331, http:adxdoi.org/10.1086/14786449308620508

[14] jullio.pe.kr/fluent6.1/help/html/ug/node294.htm.

[15] van Deemter JJ, Zuiderweg FJ and Klinkenberg A (1956). "Longitudinal diffusion and resistance to mass transfer as causes of non ideality in chromatography". *Chem. Eng. Sci.* **5**: 271–289. doi:10.1016/0009-2509(56)80003-1

Average linear velocity can be computed from the length of the column divided by time required for an unretained peak to move through the column. Any compound that has no retention in the chromatographic setup can be used, but a typical analyte used for the measure is methane. Its relationship to pressure is not simple to interconvert:[16]

$$\bar{u} = \frac{d^2 P_o j}{64\eta l}\left[\left(\frac{P_1}{P_o}\right)^2 - 1\right]$$

where $\bar{u}$ is average linear velocity, d is column diameter, P_i is the inlet pressure, P_o is the outlet pressure, j is correction for gas compressibility computed by: $\frac{3}{2} * \left[\left(\frac{P_o}{P_1}\right)^2 - 1\right] \Big/ \left[\left(\frac{P_i}{P_0}\right)^3 - 1\right]$, η is viscosity of the carrier gas at the column temperature and l is column length. Viscosity is adjusted for its impact from temperature by $\eta = \eta_0 \frac{(T_o+273+C)}{(T+273+C)}\left(\frac{T+273}{T_o+273}\right)$ with η_0 is viscosity at 0 °C (19 μPa∗s),[17] T is the input temperature (°C), T_o is the reference temperature (°C), and C is Sutherland's constant (352.4 °K) for helium.[18] Figures 4 and 5 show the increase in actual inlet pressure and a decrease in column flow with constant average linear velocity. Figure 8 represents a chromatogram of lindane and aldrin with constant average linear velocity.

This calculation of flow based on inlet and outlet pressures is not applicable when the outlet of the column is inserted into a mass spectrometer, as P_o is nearly zero from the hard vacuum, and with P_o is a divisor, linear velocity becomes very large and unpractical. A new relationship is not presented here.

Alternatively, calculators are available to perform the conversion, based on experimental conditions.[19]

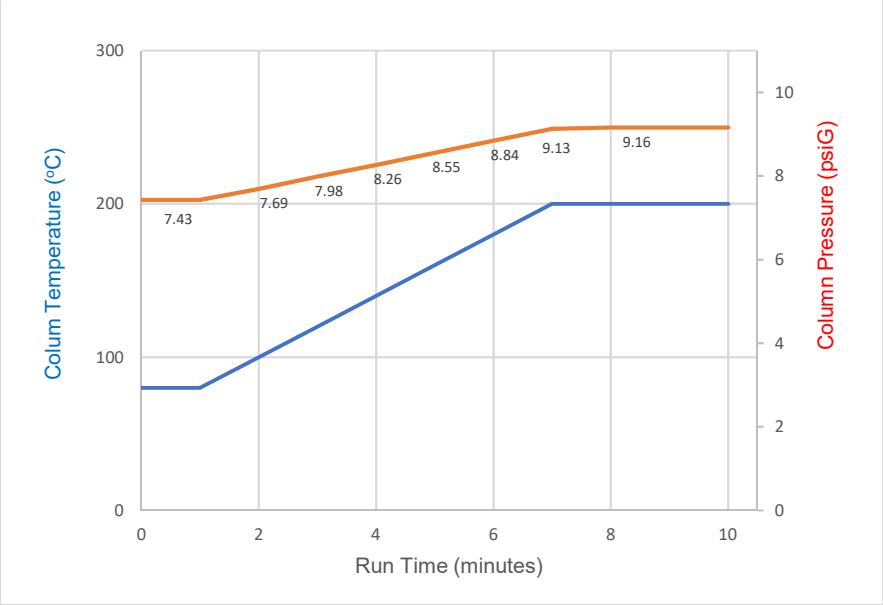

Figure 4. Plot of changes in column pressure with constant average linear velocity mode and column temperature programming. Calculated column average linear velocity is constant at 30 cm/sec.

[16] Engewald, W., Dettmer-Wilde, K., "Chapter 2 Theory of Gas Chromatography", *Practical Gas Chromatography*, 2014, Springer-Verlag Berlin Heidelberg, New York.
[17] www.engineeringtoolbox.com/gases-absolute-dynamic-viscosity-d_1888.html
[18] jullio.pe.kr/fluent6.1/help/html/ug/node294.htm
[19] www.restek.com/ezgc-mtfc

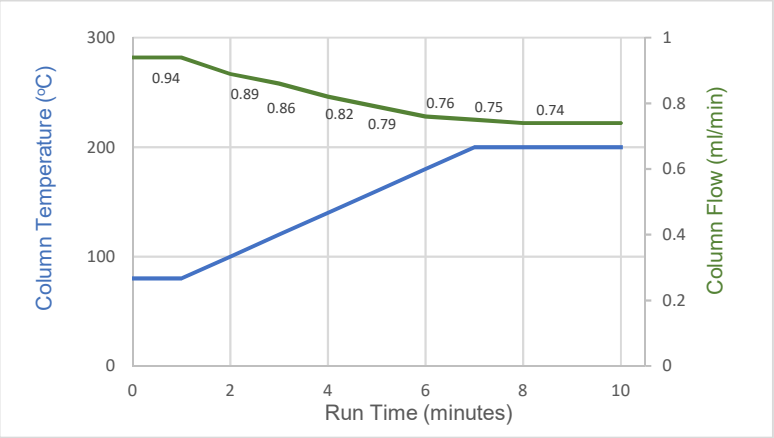

Figure 5. Plot of changes in column flow with constant average linear velocity mode and column temperature programming. Calculated column average linear velocity is 30 cm/sec.

Chromatographic Run Parameters for Test Sample

- Sample: ECD Test Sample, Lindane and Aldrin, 33 µg/µL, diluted 1:9 with isooctane
- Injection Volume: 1 µL
- Injector: Splitless (1177), temperature: 200 °C.
- Liner: Splitless, 4 mm ID, 6.5 mm OD,
- Column: Restek Rtx-I, 15 m, 0.25 ID, 0.25 µ film
- Carrier Gas: Helium
- Pressure Mode: Const Flow, 1 ml/min (calculated)
- Column Temperature Program: 80 °C, hold 1 minute, 20 °C/min to 200 °C, hold 8 minutes
- Detector: ECD, 300 °C, range 10, make-up flow 20 ml/min nitrogen, cell current - CAP
- Detector Frequency: 5 Hz

Chromatograms for Test Sample

Constant Pressure

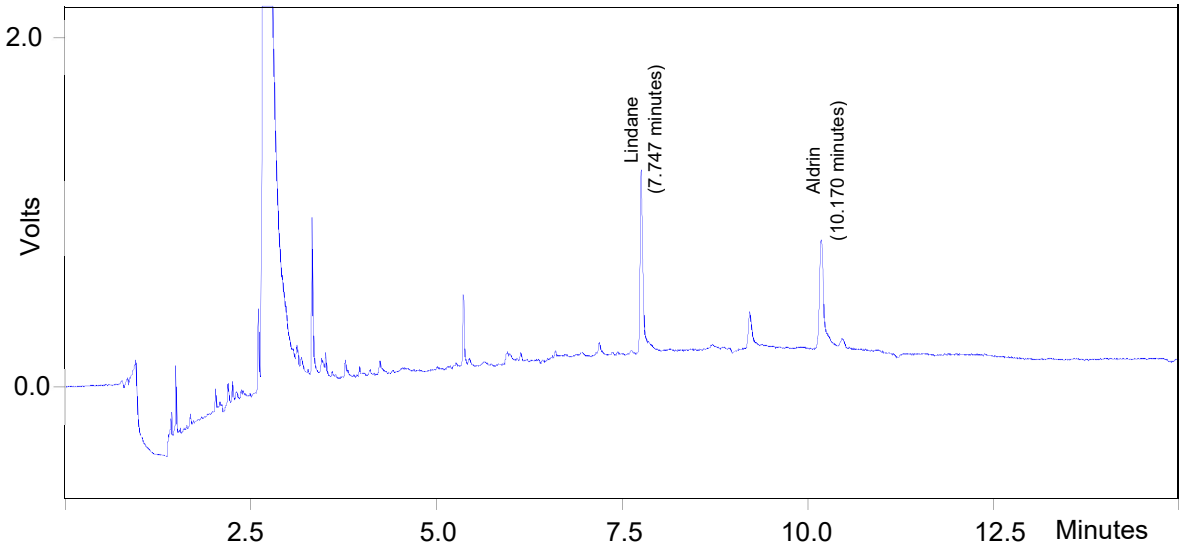

Figure 6. Chromatogram of Lindane and Aldrin (3.3 g/µL), with constant pressure carrier at 7.8 psiG.

With carrier pressure maintained at a constant 7.8 psiG, column flow drops from 1.0 ml/min to 0.6 ml/min. This effect on chromatography has lesser effects on the elution times since column temperature programming induces a stronger impact on retention times.

Constant Flow

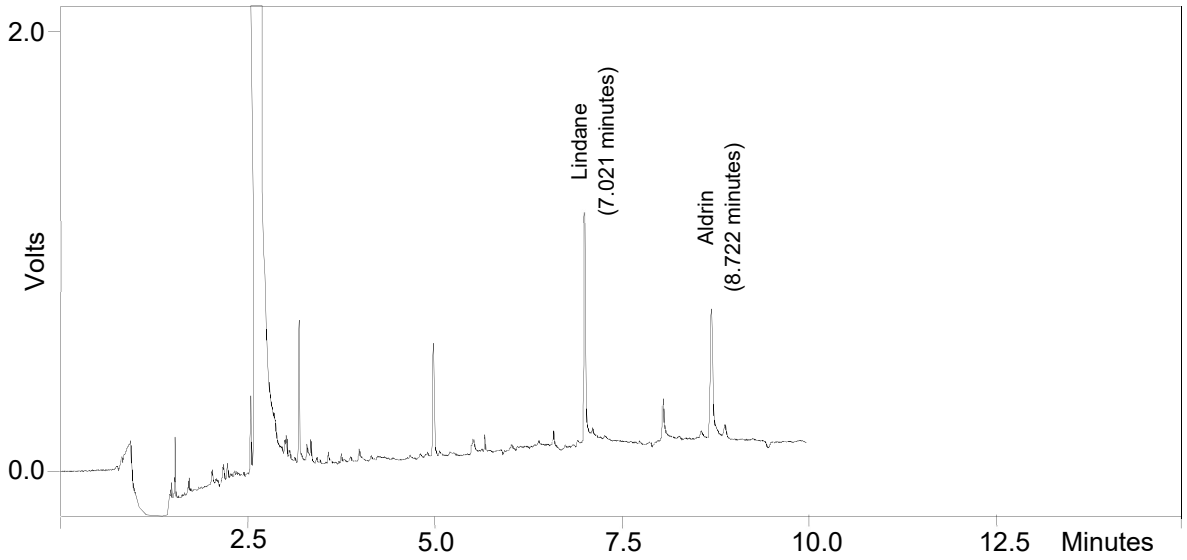

Figure 7. Chromatogram of Lindane and Aldrin (3.3 µg/µL), with constant flow carrier at 1.0 ml/min.

In constant flow mode, column pressure rises from 7.78 to 11.60 psiG with the increased helium viscosity from effects of column temperature programming. As a result, with flow held constant over the program, retention times for the two analytes are shortened by roughly 10%.

Constant Average Linear Velocity

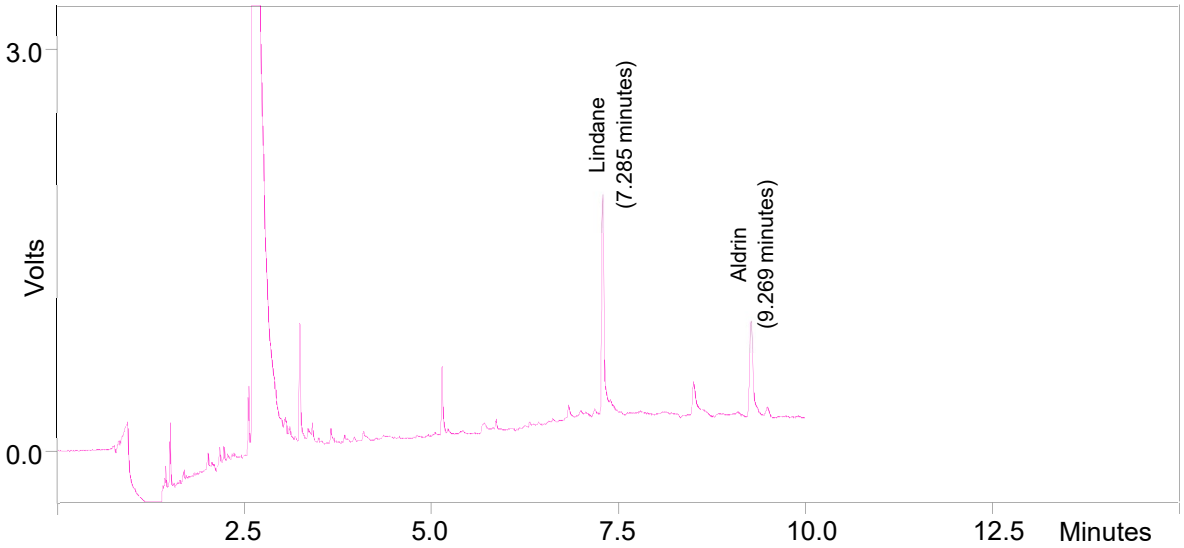

Figure 8. Chromatogram of Lindane and Aldrin (3.3 µg/µL), with constant linear velocity at 30 cm/sec.

The purpose of maintaining constant average linear velocity is to generate optimum separation power over the complete chromatogram with temperature programming. Maintenance of constant velocity requires a change in column pressure. This adjustment then alters column flow from 0.94 to 0.74 ml/min and increases in retention times by approximately 4 percent from those generated from constant flow. No dramatic changes in peak widths are observed between constant average linear velocity and constant flow chromatograms.

Comments on Injector Design

Liquid samples are introduced into a split/splitless capillary injector with a syringe penetrating through a silicone septum on top of the injector body. Silicone septum has the distinct advantages of self-sealing the hole created from the piercing of the syringe needle after removal, and ability to handle the wide temperature range required for proper experimental conditions.

Silicone can slough off volatile materials from thermal degradation that can generate unwanted high backgrounds in a chromatogram, especially with temperature programming of the injector and column. Many chromatographs incorporate a feature that flushes carrier gas across the face of the septum to vent (septum purge), to keep these contaminates from passing on to the column. This flow is controlled by either a needle valve or a flow controller (Scion Instruments Part Number 393302300), which always keeps total flow into the injector constant even when the inlet pressure varies. The actual value of the flow must be entered into the instrument setup parameters to compensate for the impact on split ratio and computed flow/average linear velocity. Figure 9 illustrates possible variations in septum purge flows realized with use of a needle valve. A flow controller maintains constant outlet flow independent of the head pressure.

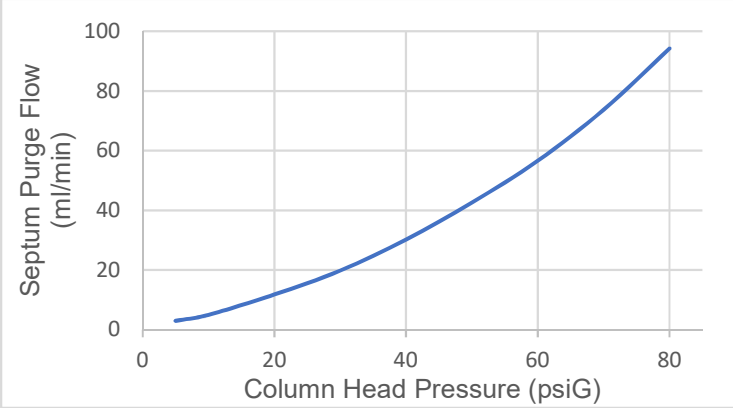

Figure 9. Display of septum purge flow versus column head pressure with needle valve control of purge flow.

Some chromatographs are designed to reduce the temperature at the septum location, even with extremely high injector temperatures. Use of a finned injector nut radiates heat away from the septum area to reduce thermal effects on the septum and lengthen its useful life. Figure 10 is a photo of the finned nut mounted on an injector. The lower temperatures realized for the septum area and injector nut are summarized in Figure 11. These lower temperatures extend the life of septa without restricting temperature operations of the injector.

Figure 10. Photo of finned injector nut, with an injector switch to start chromatographic run on injection.

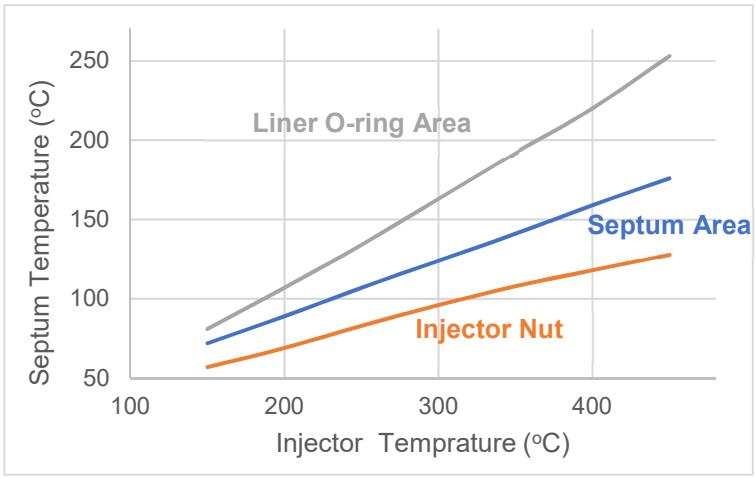

Figure 11. Plots for temperatures of liner O-ring area, septum area and injector nut for various injector temperatures.

Some instruments incorporate a switch attached to the septum nut to initiate chromatographic operations and start data collection (see Figure 10) on injection. In addition, this trigger switch at injection provides confirmation that an injection has occurred with an automated sampler. A failure to detect this signal at injection yields a system fault that halts all operations.

Liners are frequently sealed in place with Viton o-rings installed close to the top of the injector. Viton has a maximum temperature of 260 ºC. Since this o-ring is located near the finned injector nut, its temperature is noticeably lower than the setpoint for the injector body. Figure 11 displays the temperature of the o-ring area. With a set temperature for the injector of 450 ºC, o-ring temperature is only 253 ºC and never exceeds the rated maximum temperature.

Repetitive penetrations of a septum by a syringe needle can cause creation of an enlarged hole or coring in the septum. This can produce a critical source of leaks. Some injector nuts have a tapered entrance for the syringe needle to aid in directing the needle to the same spot in the septum. Typically, this exit hole at the bottom of the nut is 0.035” diameter and provides a tight fit for many syringes with a needle outside diameter of 0.018” (26 gauge). This feature aids in directing the needle to the same locale each time, lengthening lifetime of the septum

Some injector designs incorporate two small “pencil” filters to protect injector components. They are usually mounted as the last hardware components just before the injector (Figure 12). The “silver” one is a combination of molecular sieve and activated charcoal. It is installed in-line with the carrier feed to the injector. Its purpose is to collect any organic outgassing from polymeric surfaces inside pneumatics and possible backflashing of solvent during injection.

Figure 12. Pencil filters are mounted under the left top cover of the Scion 456 Gas Chromatograph.

The “gold” one is activated charcoal and is mounted after the splitter vent to collect excess sample from the split action. This protection keeps excess solvent from passing on from the split injection process to post-injector pneumatic components, including splitter valve and backpressure controller. This filter can fill up with sample vapors and should be replaced after ~1,000 injections.

Some target analytes are sensitive to exposure to raw metal or glass surfaces, resulting in their adhering to the surface or chemical degradation into different species. Possible examples include hydrogen sulfide, organosulfides, alcohols, phenols, free fatty acids, methyl esters of fatty acids, organophophates and other organic acids. Interior surfaces of capillary injectors consist of stainless steel for the primary body and glass liners to hold the vapor cloud at injection. If sensitive compounds are intended to be properly analyzed, these surfaces need to be rendered inert. One manufacturing process involves treating the injector body with chemical vapor deposition to lay down a thin inert layer bonded to the stainless steel. This process turns metal to a blue or blue-gray color. Treated injectors from Scion Instruments are either factory-installed upgrade (P/N 4561999998) or injector body replacement (P/N 392599411). Injector liners are available where their surfaces are deactivated (http://m.restek.com/Landing-Pages/Topaz-GC-Inlet-Liners-Page).