TECHNICAL NOTE

Gas Chromatography/
Mass Spectrometry

Capillary Split/Splitless Injector for the Clarus 590/690 GC

Introduction

The new capillary split/splitless injector for the Clarus® GC platform is an improved version of the venerable capillary splitting injector introduced with the AutoSystem XL. It is designed for use with capillary columns up to 0.53 mm ID, using either the integrated Clarus liquid autosampler or the TurboMatrix Automated Headspace sampling systems, or MultiPrep™ autosampler.

This redesigned injector offers lower reactivity to labile samples and easier access for routine liner and injector maintenance. Also, the new design features liners and consumable items that are common to other GC models and manufacturers, eliminating the need to maintain consumable items of different sizes and types. Programmed Pneumatic Control (PPC) provides for a wide variety of method conditions and sample applications, which may require either a split or splitless mode of operation – all under the control of one instrument method.

System Description

The new capillary splitting injector can be installed in either the A, B or both positions in the Clarus 590 and 690 GC, allowing for two channels of capillary sampling. While similar to the previous inlet model, the new design features changes to the major components that make it easier to use and maintain.

The principle part of the inlet system is the body and split line, as illustrated in Figure 1. Its body has been shortened to accommodate a standard 78.5 mm glass liner of various diameters and internal configurations – keep your favorite liners that you use in other manufacturers' GCs. The septum and liner O-ring are also standard sizes and these consumable items may be used interchangeably with other compatible GCs. For split mode of operation, the liner is packed with glass wool (packed either by the user or using pre-packed liners purchased separately), which serves to wipe the syringe needle and mix the vaporized sample gas thoroughly with the carrier prior to reaching the split point at the bottom of the injector, ensuring reproducible peak areas.

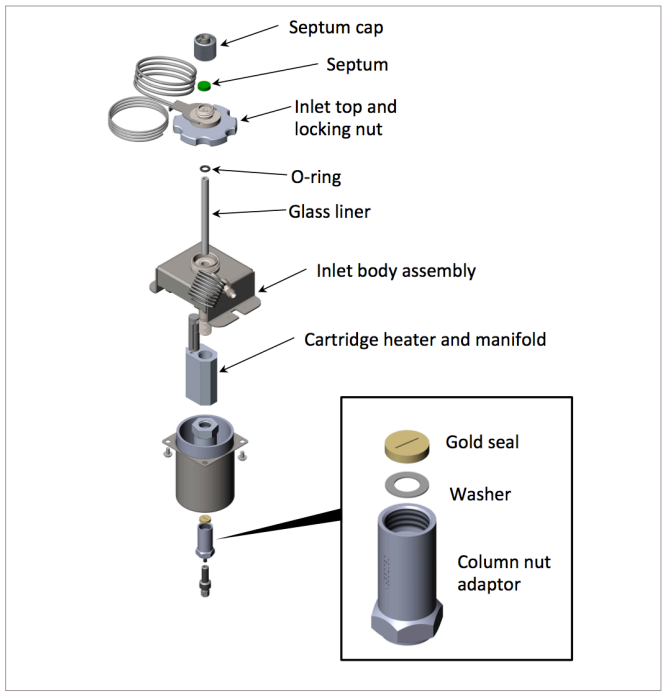

Figure 1. Components of the Split/Splitless Capillary Inlet System.

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The inlet heater is positioned to provide uniform heating across the liner, maintaining an even temperature to avoid cold spots and condensation of the sample vapor once heated, and a cooler septum cap to reduce bleed and prolong septum life. Figure 2 shows the temperature across the injector body (and liner) when heated to setpoints of 50 °C, 100 °C and 300 °C.

The removable top assembly comprises the septum cap, septum, securing nut and septum purge and carrier gas lines, and is easily removed for liner access and maintenance by unscrewing the ergonomically designed nut. No tools are required to change the septum, liner or O-ring. An enlarged access port in the lid surrounding the inlets provides plenty of room to perform maintenance tasks without opening covers.

Septum purge and carrier lines are attached to the top manifold, and are sufficiently flexible to move up and out of the way of the inlet when changing liner and O-ring. The internal design of the manifold provides for a gas flow that isolates sample vapor from the metal walls as it flows down towards and enters the column, reducing the chance of reactivity.

The split line is common 1/8 inch copper tubing which exits from the inlet body and is connected using a standard 1/8 inch Swagelok fitting, allowing for easy replacement or cleaning. The split line charcoal filter is mounted at the rear of the GC and contains a standard charcoal filter cartridge, easily removed and replaced as part of routine inlet maintenance – no tools required!

The analytical column connects to the bottom of the inlet body in the column oven by use of an adaptor fitting and an inert capillary inlet gold seal; a modified column nut connects the column and ferrule to the fitting. All parts are easily removed for column replacement or inlet maintenance.

Inlet Assembly

Carrier gas and split vent flows are controlled by the GC using Programmed Pneumatic Control (PPC) modules, as shown in Figure 3. All flows and gas types are set by the user in the control method, allowing for reproducible and resettable pneumatic conditions from run-to-run. The septum purge flow establishes a sweep gas across the inner face of the septum removing residual solvent vapors that may collect there, and the purge flow, fixed at 3 mL/min by a mechanical flow controller, is vented together with the split line flow.

Pneumatics

Carrier gas can be controlled over a wide range of flows and/or pressures, depending on the requirements of the analysis and column. The PPC technology allows for control of the carrier gas by pressure, flow or linear velocity. Whichever parameter is selected as the control, it is maintained at that setpoint and the other two parameters are regulated accordingly by the system to control at the specified setpoint value.

In the split mode of operation, the split vent flow is regulated by a PPC module that will maintain the proper split flow rate,

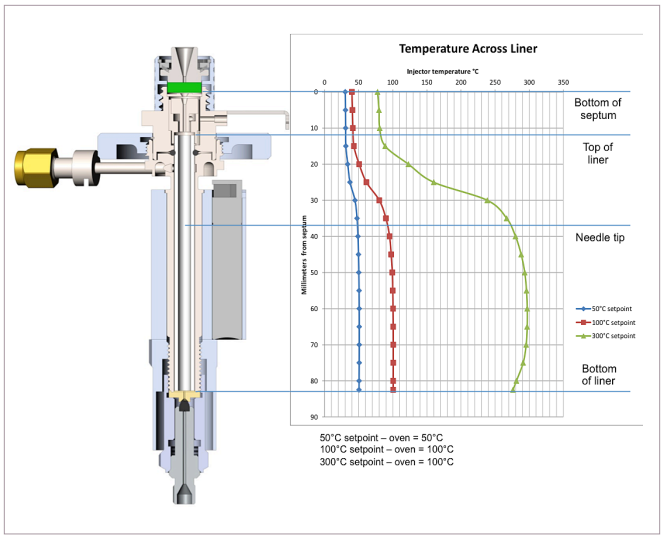

Figure 2. Temperature stability across the inlet body at three setpoints.

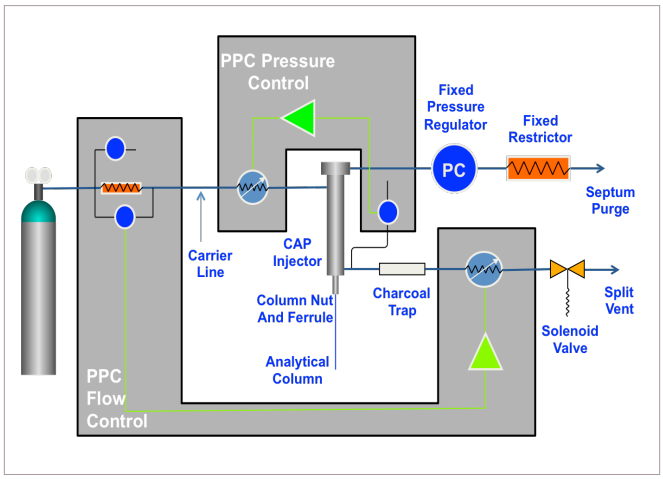

Figure 3. PPC pneumatic diagram of the split/splitless injector (split mode).

based on either ratio or flow as entered by the user. That is, if the user desires the split flow to be maintained at a given flow rate, control by flow is selected. To maintain a constant split ratio throughout the run regardless of changes in the column flow, control by ratio is chosen. The instrument then regulates the split vent flow rate automatically.

The septum purge gas is fixed at a 3 mL/min flow by a mechanical regulator and fixed frit, which controls the flow at a constant rate regardless of the pressure in the inlet. This flow need not be shut off or changed during normal sample analysis, regardless of the mode being split or splitless. The split flow gas is combined together with the split vent gas flow and both exit the GC through the corresponding split vent fitting.

Inlet Performance

The new inlet design demonstrates excellent chromatographic performance in both the split and splitless modes of operation, as illustrated in the following sections.

Repeatability

A series of injections of an n-hydrocarbon mix from *n*-C10 to *n*-C25 was made to establish peak area repeatability in the split mode of operation. Relative standard deviations (%RSD) were calculated on the raw peak areas, with a typical result of 1.5% or less, going as low as 0.68% as shown in Table 1 below.

The precision of the injections was evaluated by calculating the expected response for each component based on the known amounts in the sample (Area/Component Amt). Two sets of data were collected using two different split flows, representing two split ratios: 50:1 and 150:1. These responses are expressed in Figure 4 for a number of the n-hydrocarbons as a percentage of the expected response, relative to response of *n*-C15 (100%).

For each component at each split ratio the measured responses were within ±10% of the expected values.

Table 1. Split Mode peak area 1 repeatability.

Compound	%RSD Peak Area Split 150:1	%RSD Peak Area 50:1
C10 Decane	0.68	0.89
C11 Undecane	1.05	0.80
C12 Dodecane	1.22	1.01
C13 Tridecane	1.41	1.24
C14 Tetradecane	1.58	1.36
C15 Pentadecane	1.15	1.05
C16 Hexadecane	4.40	3.45
C17 Heptadecane	1.16	1.24
C18 Octadecane	1.15	1.38
C19 Nonadecane	1.13	1.50
C20 Eicosane	1.12	1.66
C21 Heneicosane	1.09	1.78
C22 Docosane	1.07	1.93
C23 Tricosane	1.05	2.07
C24 Tetracosane	1.04	2.14

Split Linearity

It is important for a splitting inlet to maintain accurate peak areas with respect to the amount of sample that enters the column; that is, as the split ratio is changed the proportional amount of sample must reach the column. While good chromatographic practice dictates calibration standards must be run under the same analytical conditions as the sample, the inlet system should still maintain accurate areas as the split flow changes.

Figure 5 shows the linearity on four *n*-C9 sample injections at split ratios from 50:1 to 400:1. As expected, the area counts at each level are halved as the sample fraction that reaches the column decreases in accordance with the following flow equation:

$$\frac{Fc}{(Fc + Fs)}$$ where: Fc = capillary column flow rate (mL/min); Fs = split flow rate (mL/min)

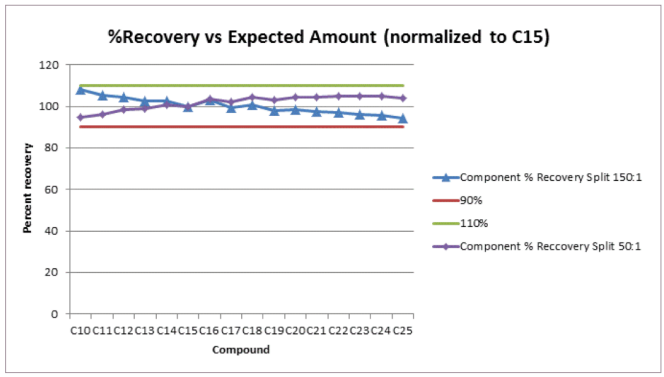

Figure 4. Component percent recovery accuracy – split mode.

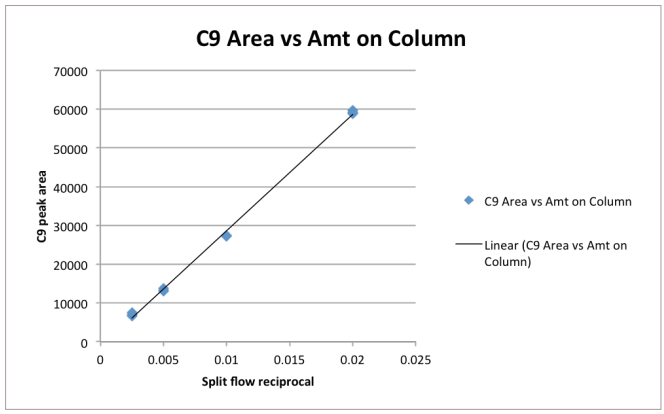

Figure 5. Split Mode linearity at various split ratios, 50:1, 100:1, 200:1 and 400:1.

Conditions: Elite-5 30 m x 0.25 mm ID x 0.5 um film, 40°C hold 1 min 15°C/min to 250°C hold 0.5min; He carrier at 1 mL/min; injector 300°C; FID 300°C; injection 1 uL 1000 ug/mL each component

Figure 6 is a plot of the average relative response factor from each injection calculated by multiplying the peak area by the sample fraction reaching the column. Peak area for *n*-C9 injection is then expressed as a percent of the average. Note that the response of each split ratio falls within a ±10% window. The sample response factor is not adversely affected by changing split flows.

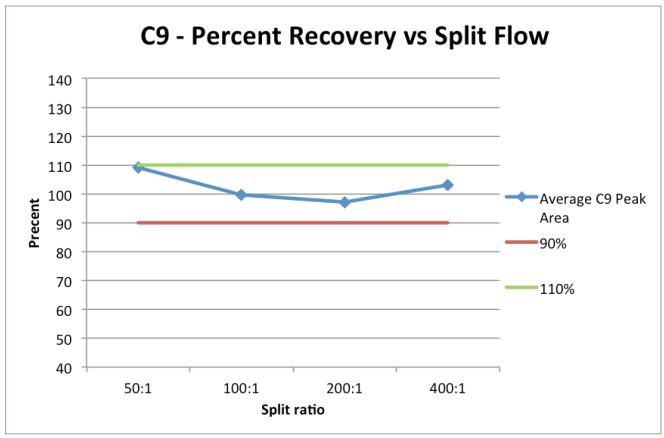

Figure 6. Split Mode percent relative recovery at various split ratios.

Mass Discrimination

The inlet response to a mixture containing *n*-hydrocarbons from C7 to C44 split 100:1 is shown in Figure 7. Relative responses were calculated by dividing the peak area for each component by its corresponding amount injected. Each component is then expressed as a percentage of the RRF for *n*-C20 (100%). All compounds are within a ±5% response, demonstrating a very low discrimination to compounds by mass.

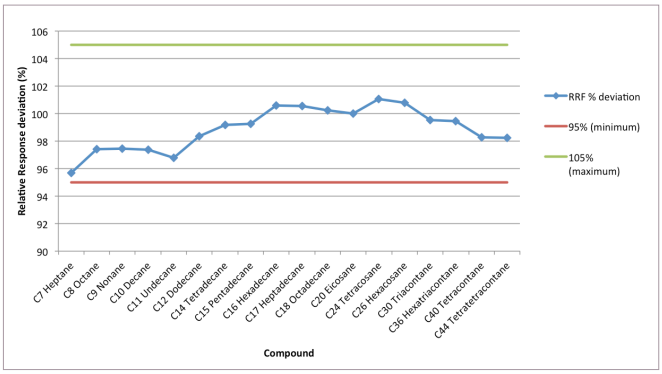

Figure 7. Relative Response Factors in Split Mode C7 to C44; C20 = 100%.

Conditions: MTX-1 Restek #70123 30 m x 0.25 mm ID x 25 um film, 40°C hold one min 15°C/min to 350°C hold 25 min; He carrier at 1 mL/min; split 100:1; injector 375°C; FID 375°C; injection fast mode 1uL 62.54 ng/uL C16 and C18, all others 31.27 ng/uL

Split Carryover

Low carryover from one injection to the next is an important consideration when determining MDQ; sample constituents from previous injections could adversely affect peak areas of interest in subsequent samples if they are retained in the inlet. Table 2 below summarizes 10 injections using a split mode of 400:1; a neat injection of *n*-C16 followed by an injection of Hexane solvent. The presence of *n*-C16 in each subsequent solvent run is shown to be at an acceptable level for all sets of injections.

Table 2. Carry over percent in split mode – injection of C16 neat, followed by hexane solvent.

Sample Type	Split Ratio	Peak Area	C16 Carryover %
C16 neat	400:1	206414	
Hexane	400:1	9	0.00436%
C16 neat	400:1	217246	
Hexane	400:1	6	0.00276%
C16 neat	400:1	212690	
Hexane	400:1	6	0.00282%
C16 neat	150:1	1585626	
Hexane	150:1	62	0.00391%
C16 neat	150:1	1537390	
Hexane	150:1	44	0.00286%

Splitless Injection Mode

Repeatability

A series of ten injections of a mixture of *n*-C9 to *n*-C14 were made in a splitless mode of operation, and the results in Table 3 show good repeatability under 1% for each compound. In Figure 8 each compound is shown within a ±5% tolerance window on percent recovery of expected amount; a larger amount of solvent present in the column shows little effect on response to each component in the sample.

Table 3. Component repeatability – splitless mode of operation.

Compound	Injection Mode	%RSD Peak Area (10 injections)
C9	Splitless	0.80
C10	Splitless	0.82
C11	Splitless	0.85
C12	Splitless	0.9

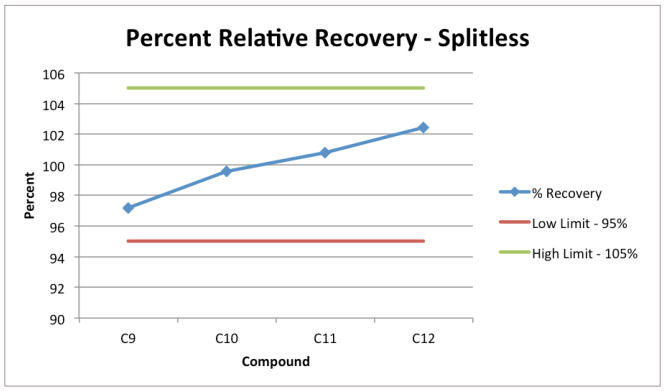

Figure 8. Percent Relative Recovery – splitless mode of operation.

Conditions: Elite-5 30 m x 0.25 mm ID x 0.25 um film, 40°C hold 1min 15°C/min to 200°C hold 0 min; He carrier at 1 mL/min; injector 300°C; FID 300°C; injection 1 uL 0.01% each component.

Splitless Carryover

Carryover tests in the splitless mode were also performed to compare with the results obtained with split injection. Results in Table 4 show similar results with very low carryover of *n*-C16 injected neat when followed by a Hexane solvent injection.

Table 4. Carry over percent in splitless mode – injection of C16 neat, followed by hexane solvent.

Sample Type	Split Mode	Peak Area	C16 Carryover %
C16 neat	Splitless	78253996	
Hexane	Splitless	1839	0.00235%
C16 neat	Splitless	80246473	
Hexane	Splitless	1799	0.00224%
C16 neat	Splitless	80055745	
Hexane	Splitless	1613	0.00201%
C16 neat	Splitless	79657087	
Hexane	Splitless	1784	0.00224%
C16 neat	Splitless	79015641	
Hexane	Splitless	1841	0.00233%

Low Reactivity and Inertness

Pesticides Breakdown

A key change to the design of the capillary injector is the modification to the internal geometry of the inlet which determines gas flows, helping to isolate sample constituents from the hot metal surfaces as they are moved by the carrier gas down through the glass liner and onto the column. That is, the gas conduits within the inlet body have been re-design to be more efficient in moving gaseous sample either into the column or out the split vent with limited contact with reactive surfaces. Additionally, carrier gas flow is directed across the internal surface of the septum, sweeping residual solvent vapor out through the septum purge line, reducing solvent peak tailing effects.

The inside surfaces of the new capillary inlet are electro-polished, reducing the opportunity for sample residuals from 'sticking' to the inside surfaces while headed out the split line. These design features are a critical advantage in reactive compound analyses, and an improvement over the previous PerkinElmer capillary splitting inlet, particularly in sensitive applications such as pesticides.

The following tests were conducted using the new splitting inlet installed in a PerkinElmer Clarus 590 GC platform. Breakdown criteria for Endrin and DDT are specified in EPA Method 8081B when qualifying the analytical instrument performance. An Endrin/DDT standard of 0.1ug/mL in iso-octane was injected 300 times consecutively into the new inlet system.

The limits for Endrin/DDT breakdown specified in EPA8081B for GC analyses are <15% for each compound over the entire sample set analyzed, and <30% for both analytes combined. This standard measurement is the basis for proving a system has acceptable reactivity while sampling.

Figure 9 summarizes the breakdown percentages over the 300 runs of Endrin/DDT. Starting at injection 1, the breakdown was shown to be 3.5% for Endrin and 2.1% for DDT. Throughout the test, DDT breakdown levels remained rather steady, while Endrin rose somewhat gradually, leveling off after injection 250. The final injection yielded 7.3% Endrin and 2.2% DDT. The proportion of Endrin loss was still well below the EPA standard limit of <15%. Combined, Endrin/DDT breakdown was never found to be greater than 13%, well below the 30% threshold.

A comparison of the breakdown performance in the new capillary inlet with the previous AutoSystem GC model is shown in Figure 10. Over a period of 100 samples, it is clear that Endrin breakdown products drift well past the 15% limit within 40 sample injections, while the new inlet performance remains at a level of <5% for more than 100 injections.

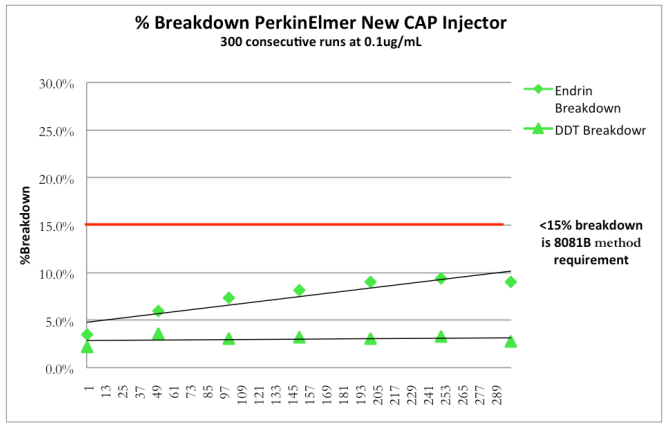

Figure 9. Endrin/DDT breakdown over 300 injections (EPA Method 8081B specifies <15% per compound).

Conditions: Elite-5 30 m x 0.32 mm ID x 0.25 um film, 100°C hold 15 min 25°C/min to 150°C 10°C/min to 250°C 20°C/min to 290°C hold one min; He carrier at 1 mL/min; injector 250°C; FID 300°C; injection splitless 1 uL 0.1 ug/mL each component.

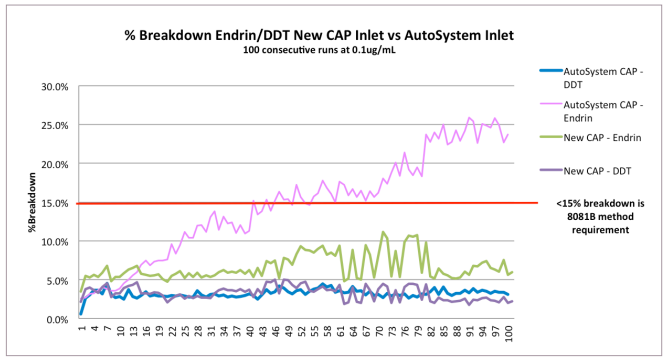

Figure 10. Endrin/DDT breakdown over time CAP injector compared with original AutoSystem XL CAP splitting injector.

Conclusion

The split/splitless capillary inlet demonstrates marked improvements over the original AutoSystem GC model. New features allow easier access to the septum, liner and O-ring- all without tools. Simple column insertion/removal and use of commonly available consumable items, combined with lower reactivity for sensitive samples, all provide for a better performing inlet on the Clarus GC platform. The system provides a highly accurate, sensitive, and repeatable instrument for analytical sampling in both the split and splitless modes of operation.

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