Liquid Injection Techniques

- Flash Vaporization
  - Split injection
  - Splitless injection
  - Direct - Uniliner w/Hole

Flash Vaporization - Split Injection

Advantages:

- Easy to use
- Easy to automate
- Ideal for dirty samples

Disadvantages:

- Sample degradation
- Backflash
- Discrimination
- Not a trace technique

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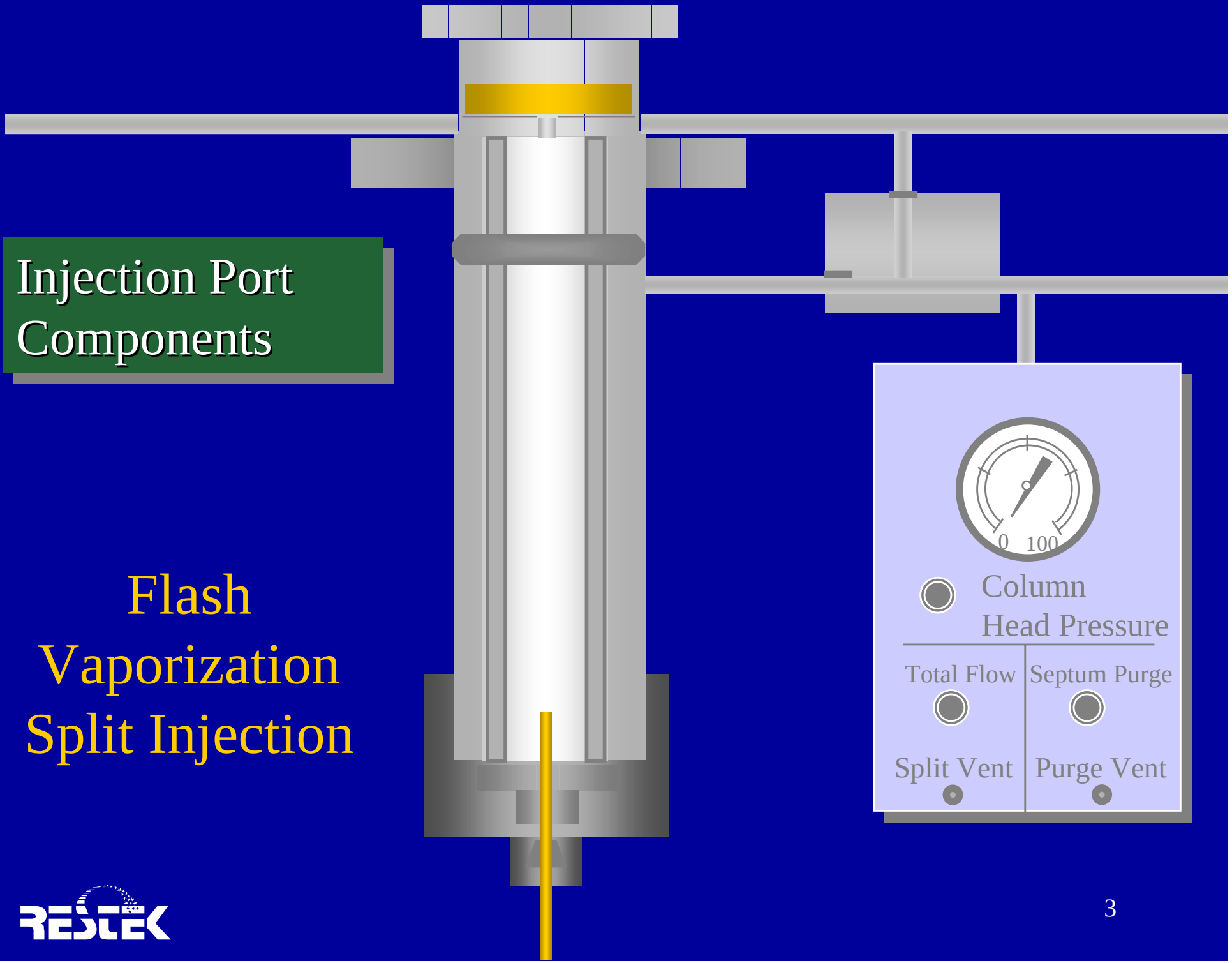
Injection Port Components



Flash Vaporization Split Injection

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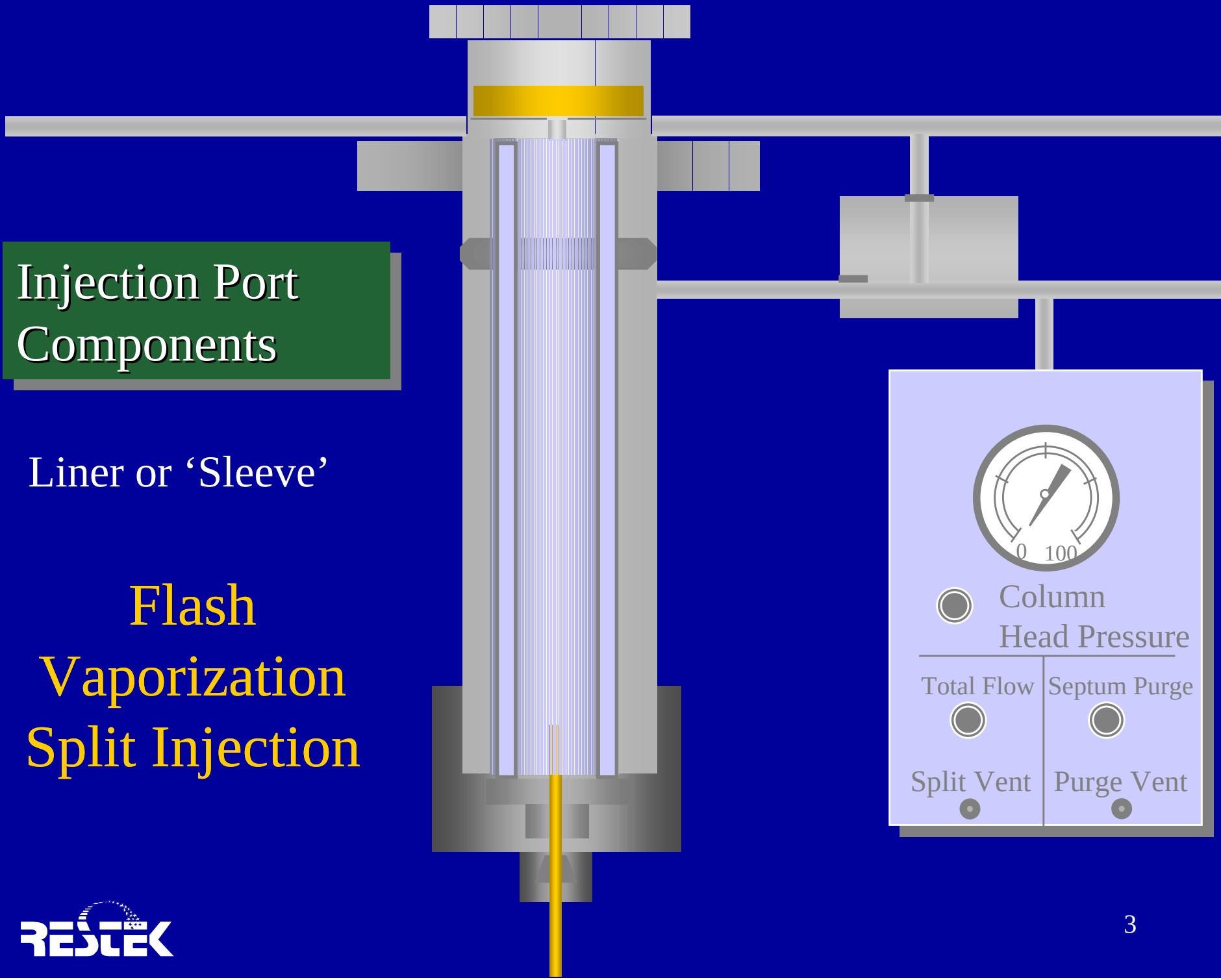
Injection Port Components

Liner or ‘Sleeve’

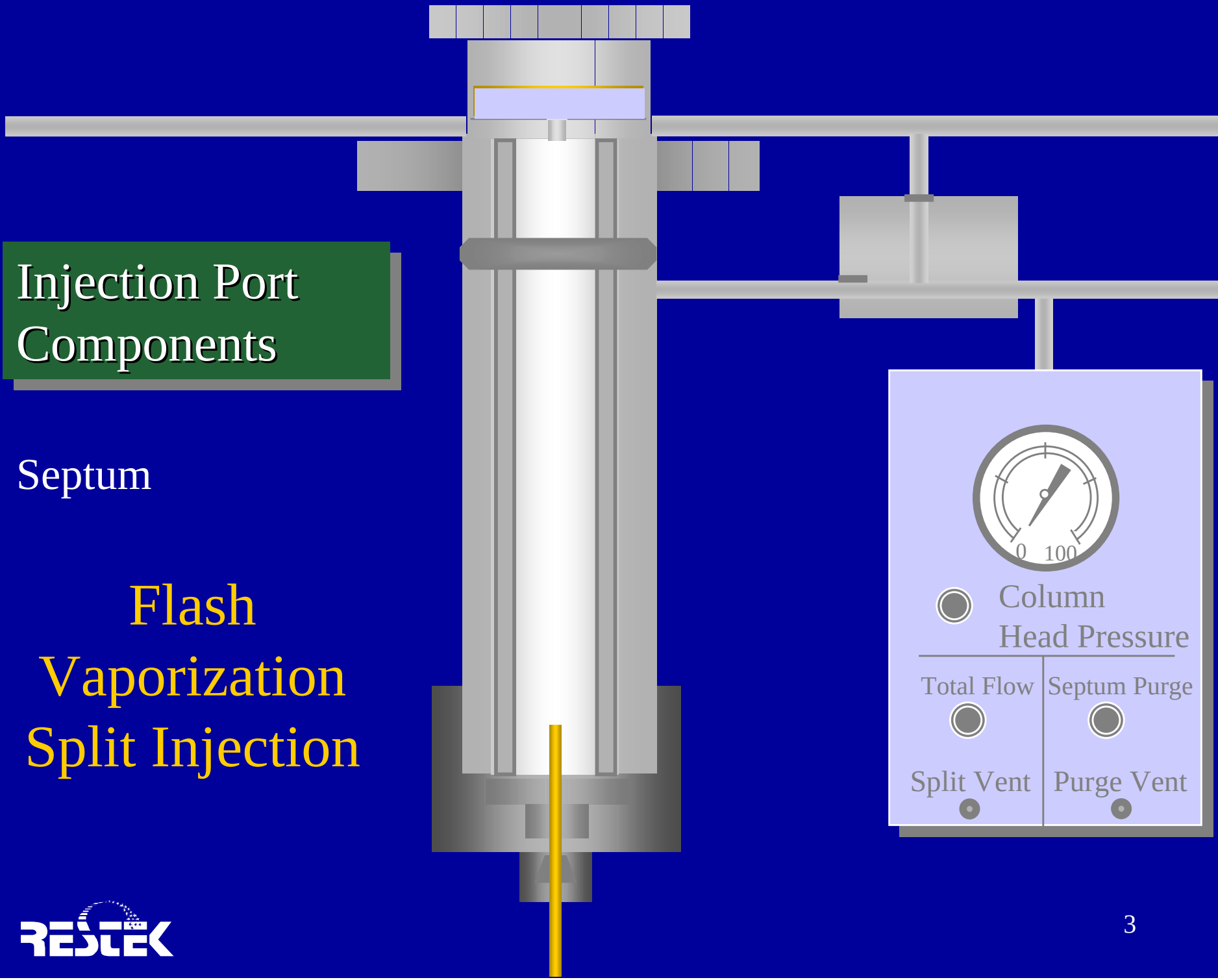
Flash Vaporization Split Injection



Injection Port Components

Septum

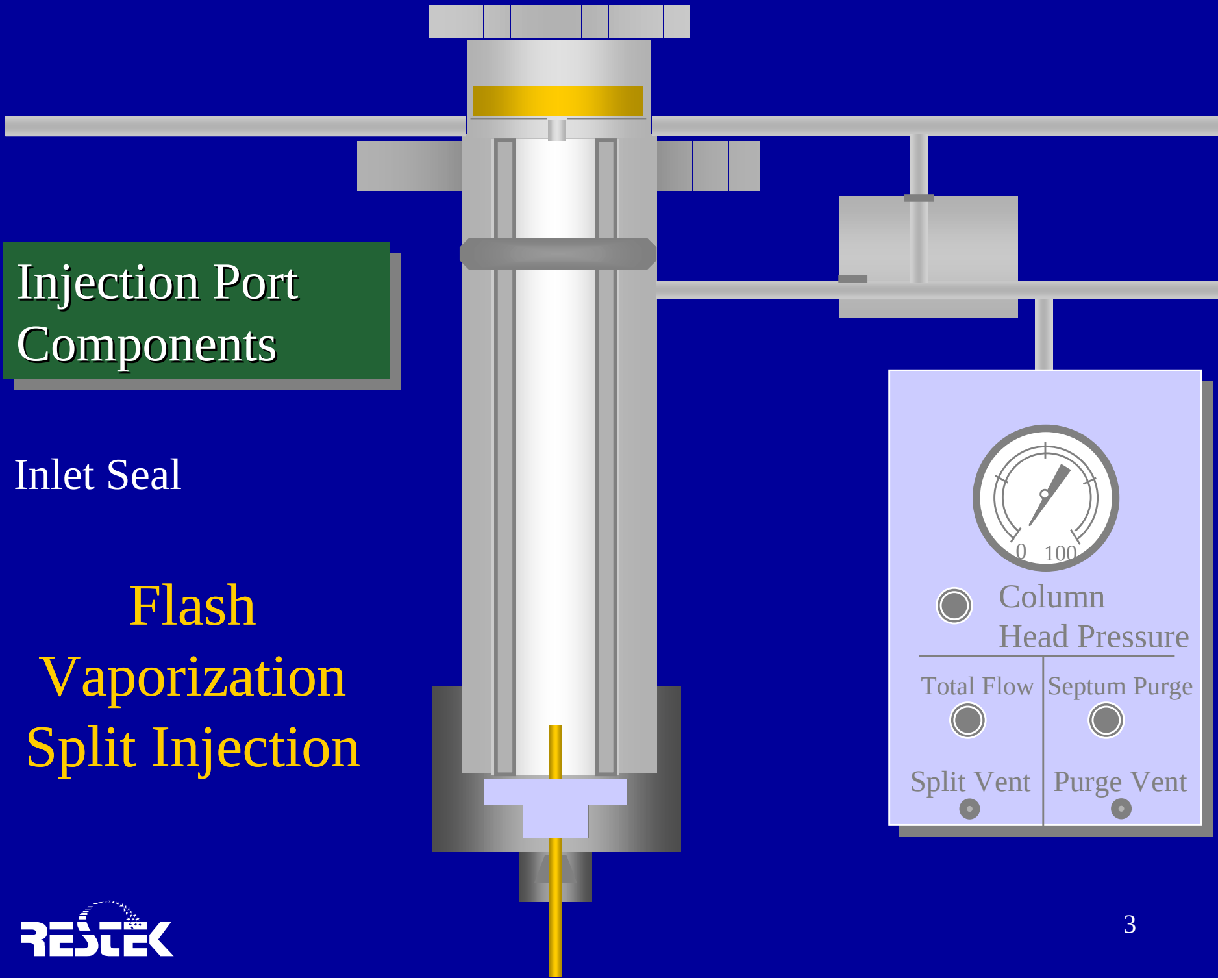
Flash Vaporization Split Injection



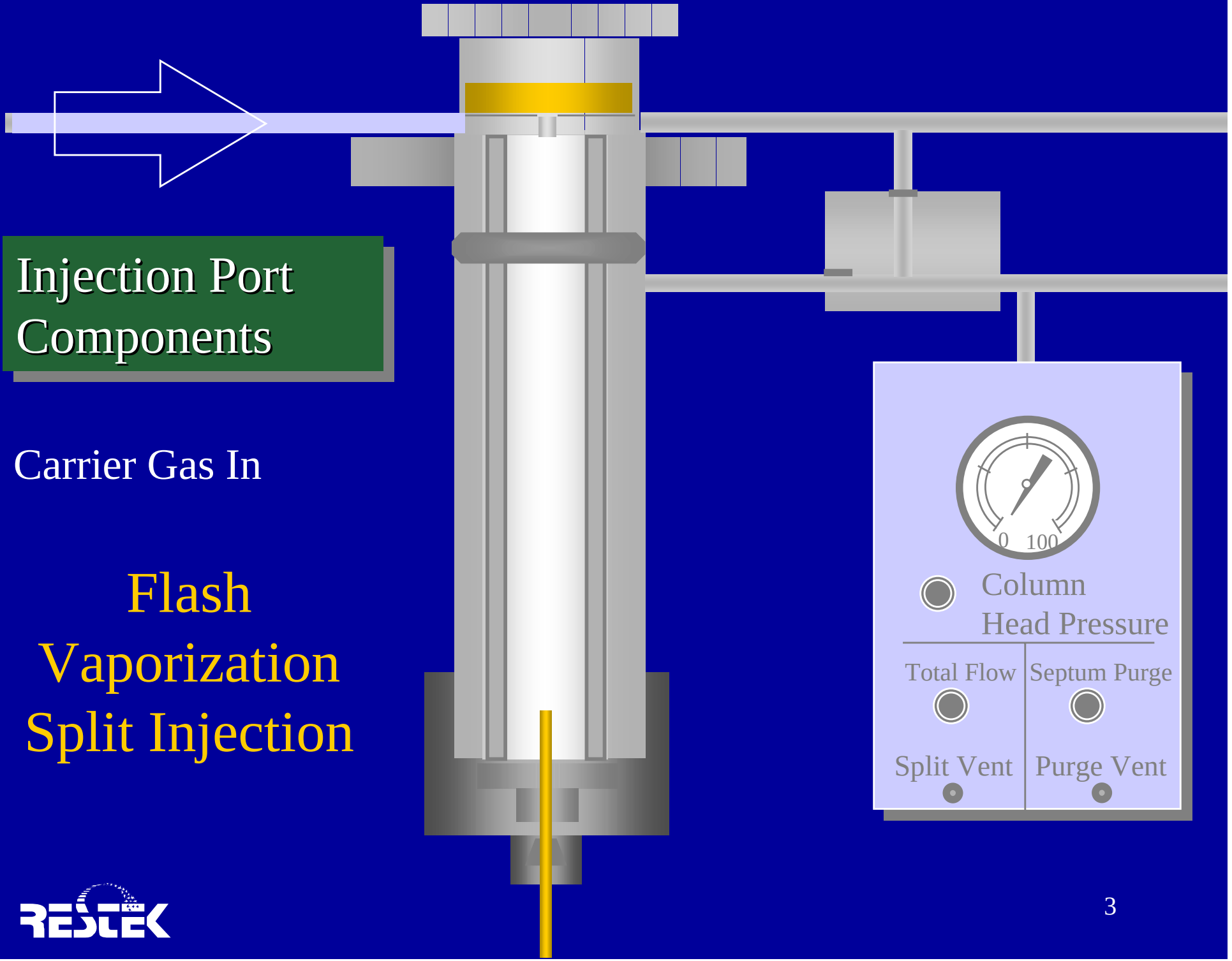
Injection Port Components

Inlet Seal

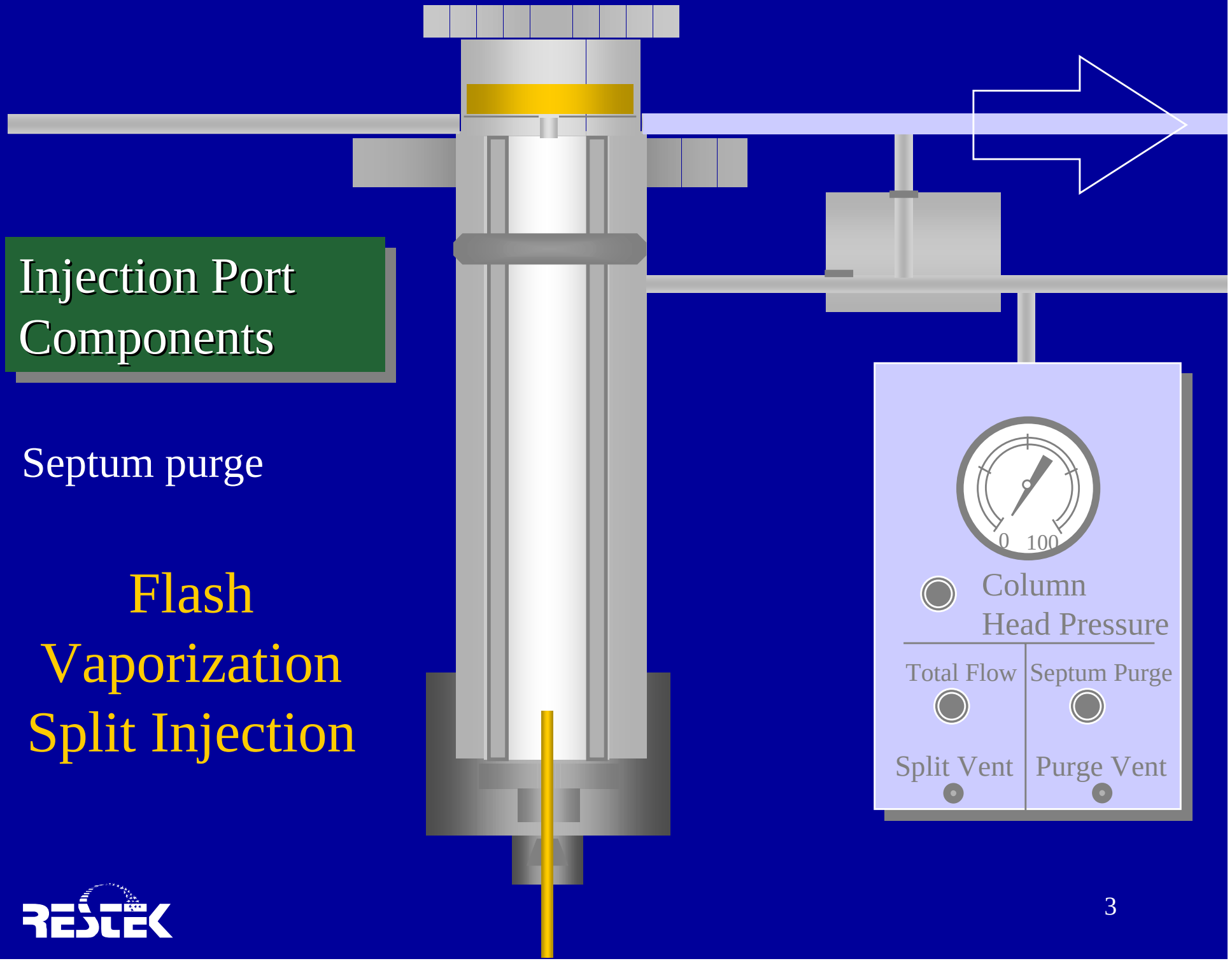
Flash Vaporization Split Injection



Injection Port Components



Injection Port Components



Septum purge

Flash
Vaporization
Split Injection

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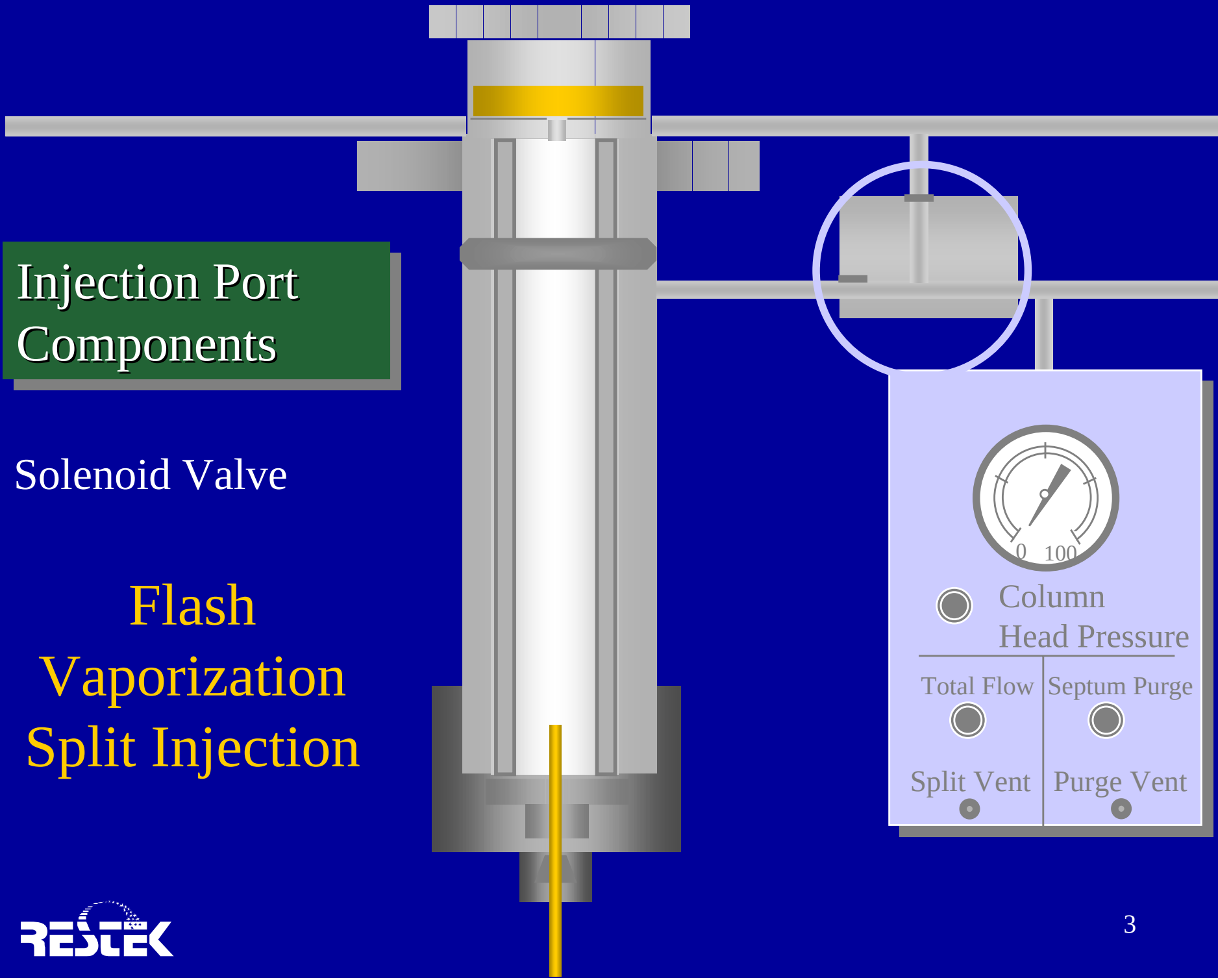
Injection Port Components

Solenoid Valve

Flash Vaporization Split Injection



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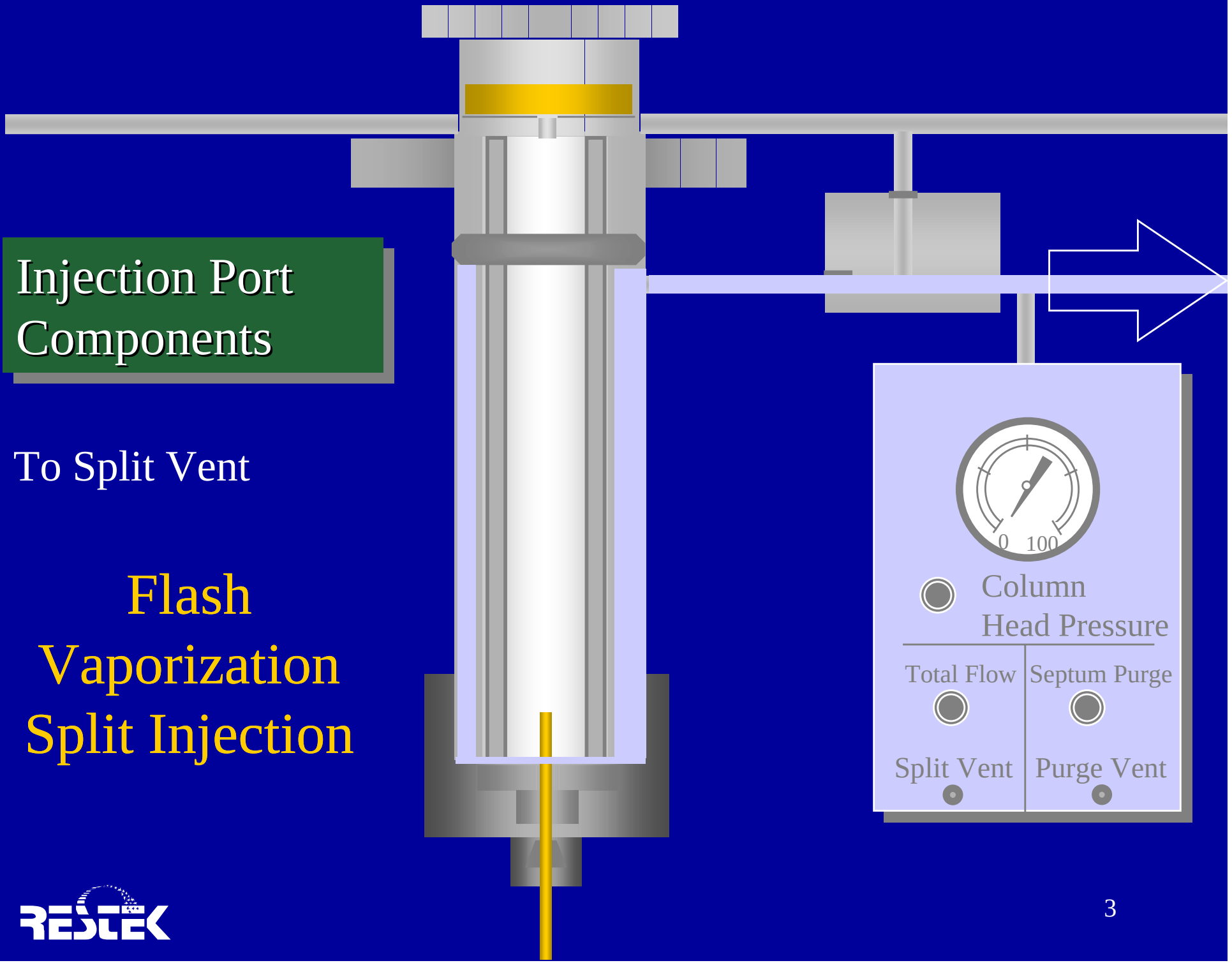
Injection Port Components



Flash Vaporization Split Injection

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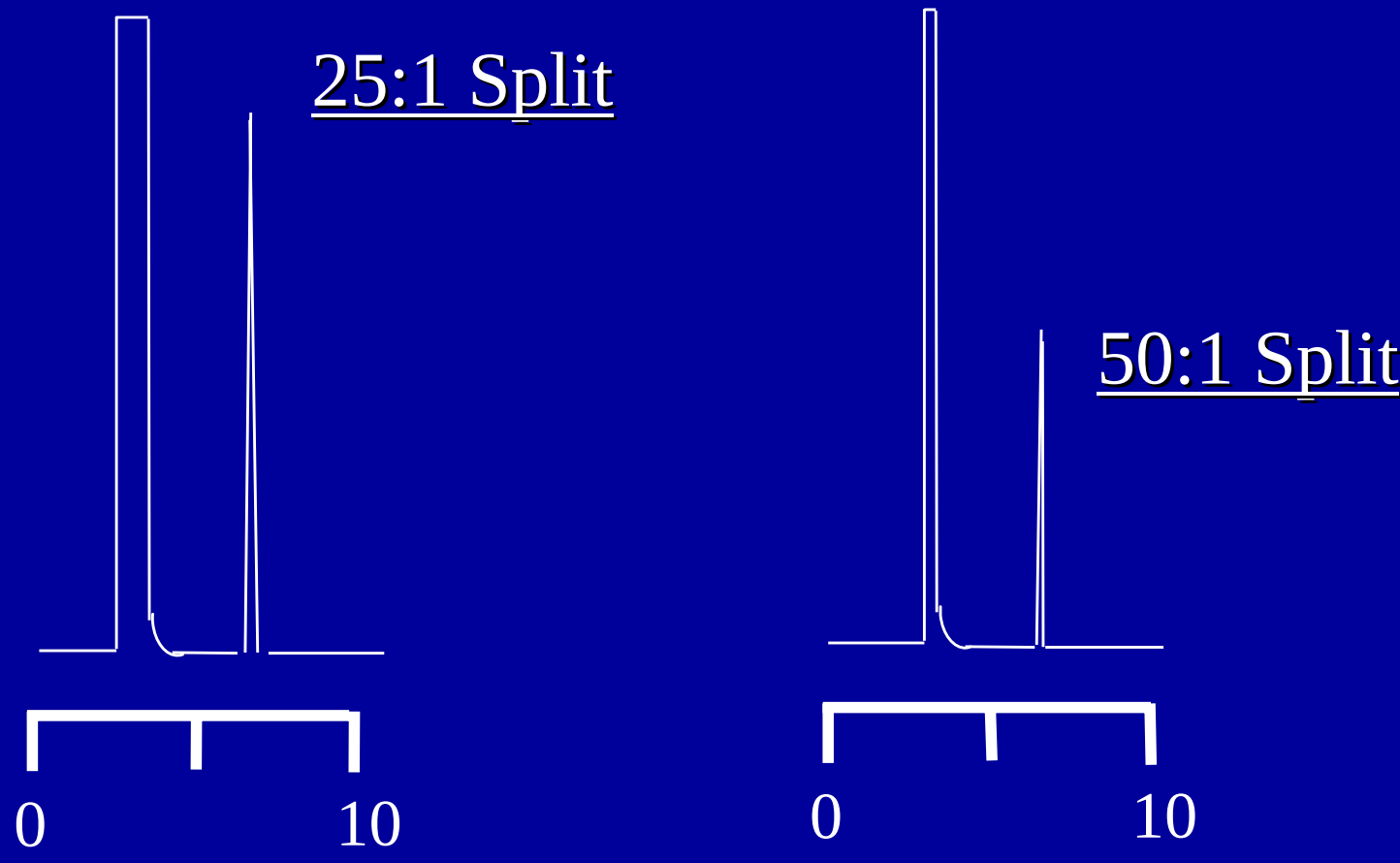
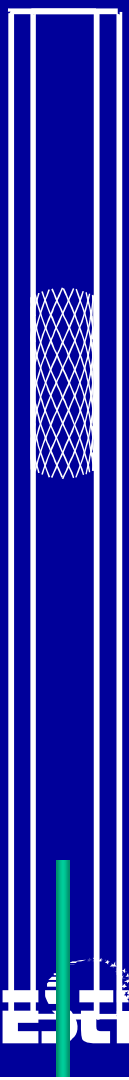
Flash Vaporization - Split Injection

Increasing the split ratio decreases the peak area,
if all other variables are equal.



Split Injection Liner Designs



Split with wool or CarboFrit™

Use only a small amount of wool

Laminar Cup

Excellent vaporization, expensive

Cyclosplitter®

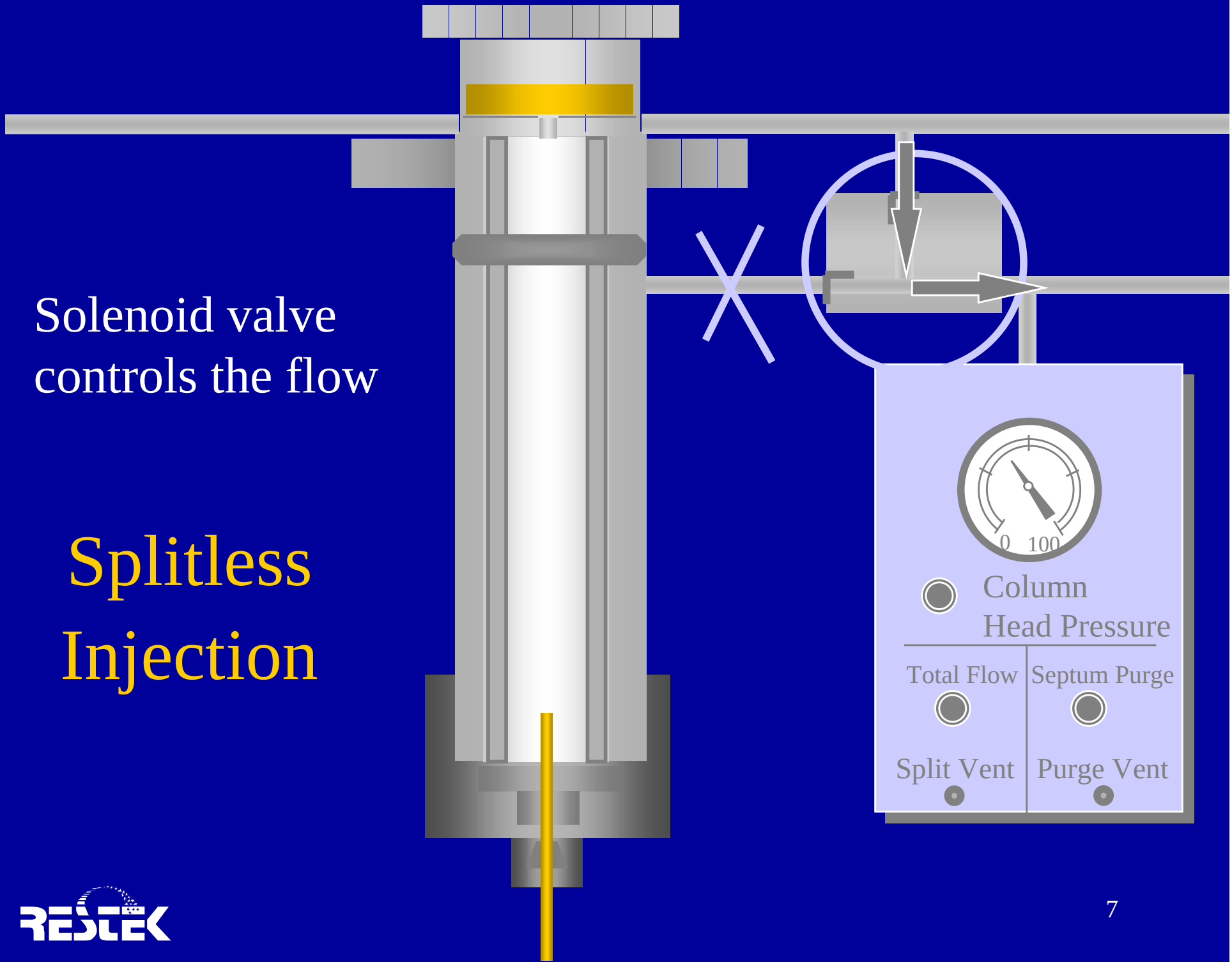
Keeps contamination out of column

Flash Vaporization - Splitless Injection

- Used for trace analysis
- Mode of operation of a split injector
- Slow sample transfer to column
  - Long contact time with the liner promotes vaporization
  - Long initial sample bandwidth, so solvent focusing is important
  - Requires careful optimization

Solenoid valve
controls the flow

Splitless Injection



Splitless Injection Characteristics

- Slow sample velocity through liner
- Long residence time can lead to compound breakdown
  - Injection port inertness is critical
- Requires careful optimization
  - Oven temperature, solvent type, liner volume, solenoid hold time...

Splitless Injection
Factors Affecting Performance

- Hold time
- Solvent focusing:
  - Solvent boiling point
  - Solvent polarity
- Incomplete sample vaporization due to rapid auto injection
- Surface deactivation

Factors Affecting Splitless Injection
Hold Times

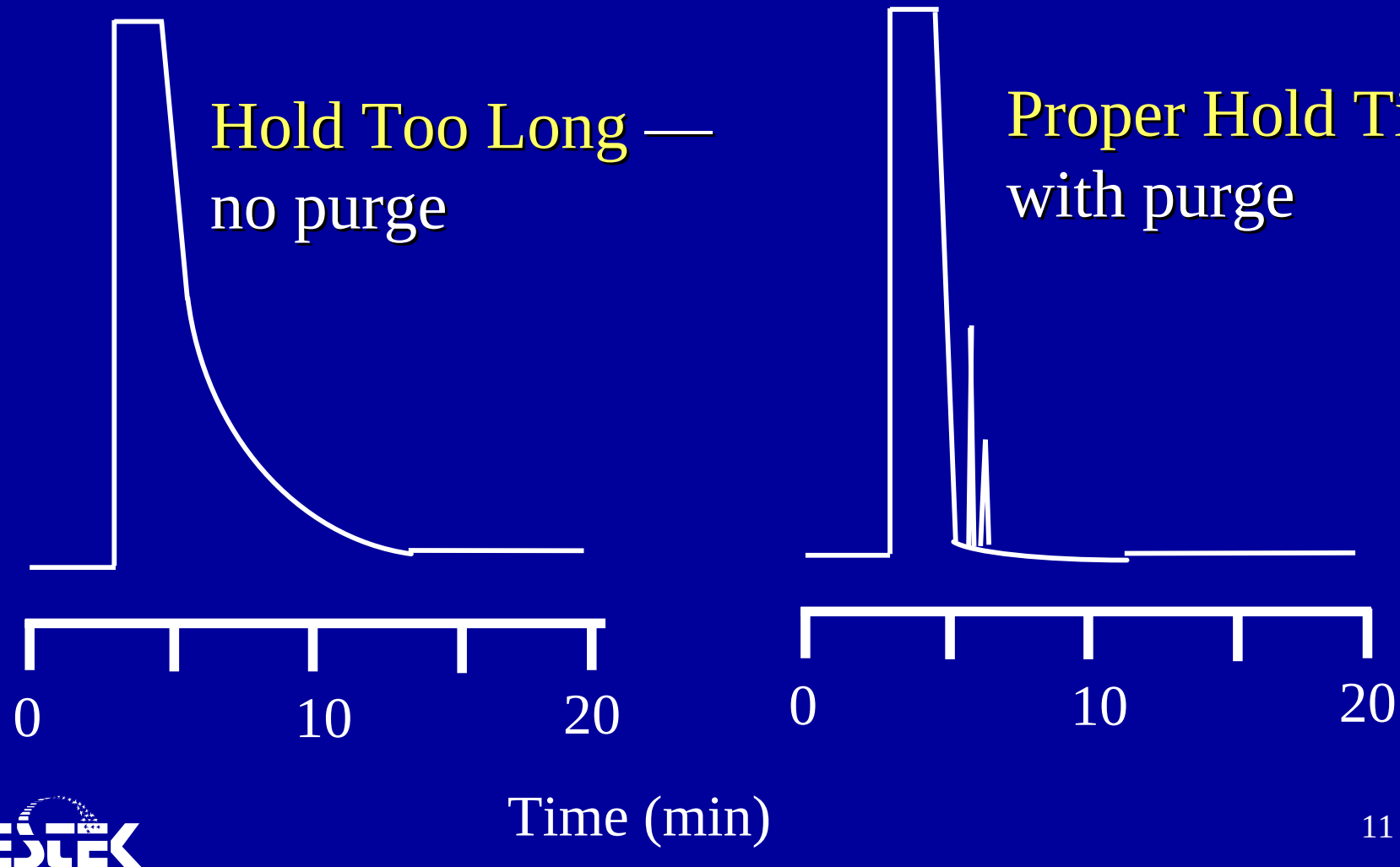
Column ID (mm)	Column Flow Rate (cc/min.) He	Approx. Hold Time
0.18	0.3	3 min
0.25	0.7	1.5 min
0.32	1.2	45 sec
0.53	2.6	30 sec

Determine empirically

Note: based on a 2µL injection volume of CH_2Cl_2 = 0.8 mL sample expansion value @ 250°C & 10 psig.

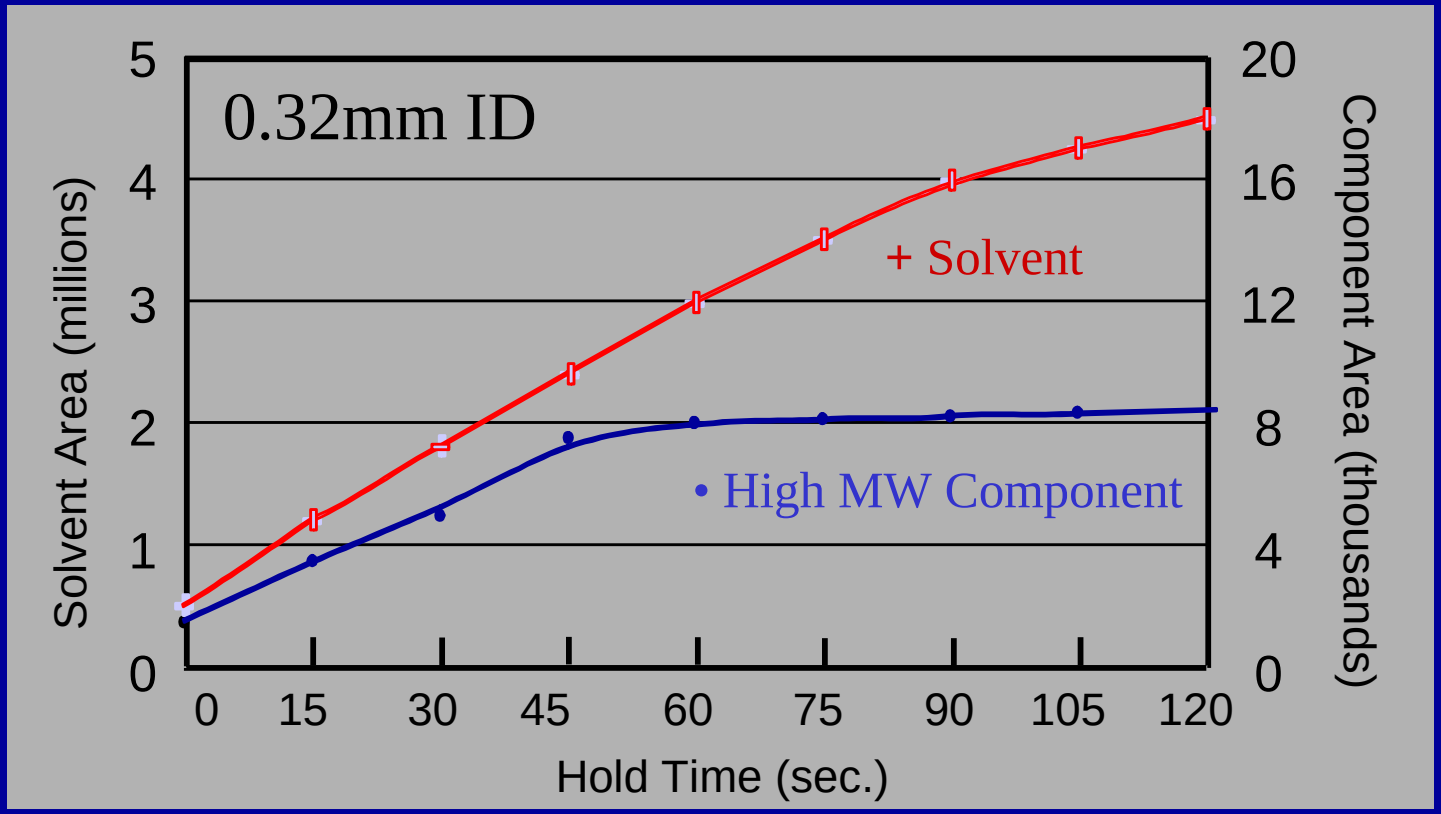
Factors Affecting Splitless Injection

Hold Times



Factors Affecting Splitless Injection

Hold Time Optimization



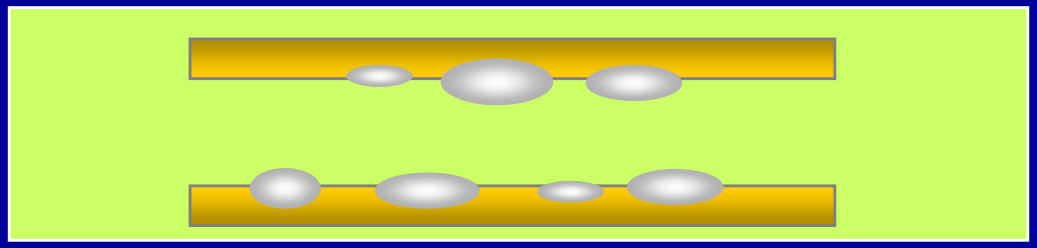
Factors Affecting Splitless Injection
Solvent Focusing, cont'd

	(°C)
pentane	36
methylene chloride	40
acetone	56
chloroform	62
methanol	64.5
hexane	69
1,1,1 trichloroethane	74.1
ethyl acetate	77
ethanol	78.3

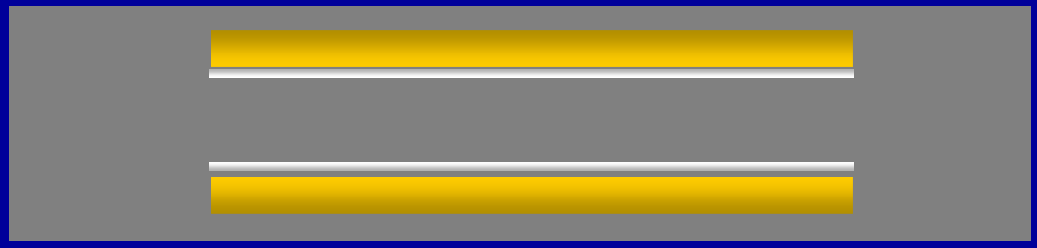
Subambient cooling will improve chromatography

Note: When the first component has a much higher bp than the solvent, you may inject above the bp of the solvent (Analyte Focusing, e.g., analysis of chlorinated pesticides)

Solvent Focusing
Solvent Polarity, cont'd

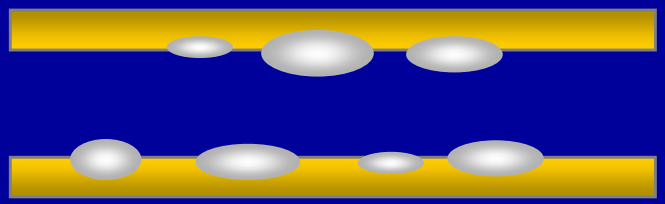


Mismatched Polarity:
The solvent will bead or puddle, causing non-uniform analyte focusing and split peaks

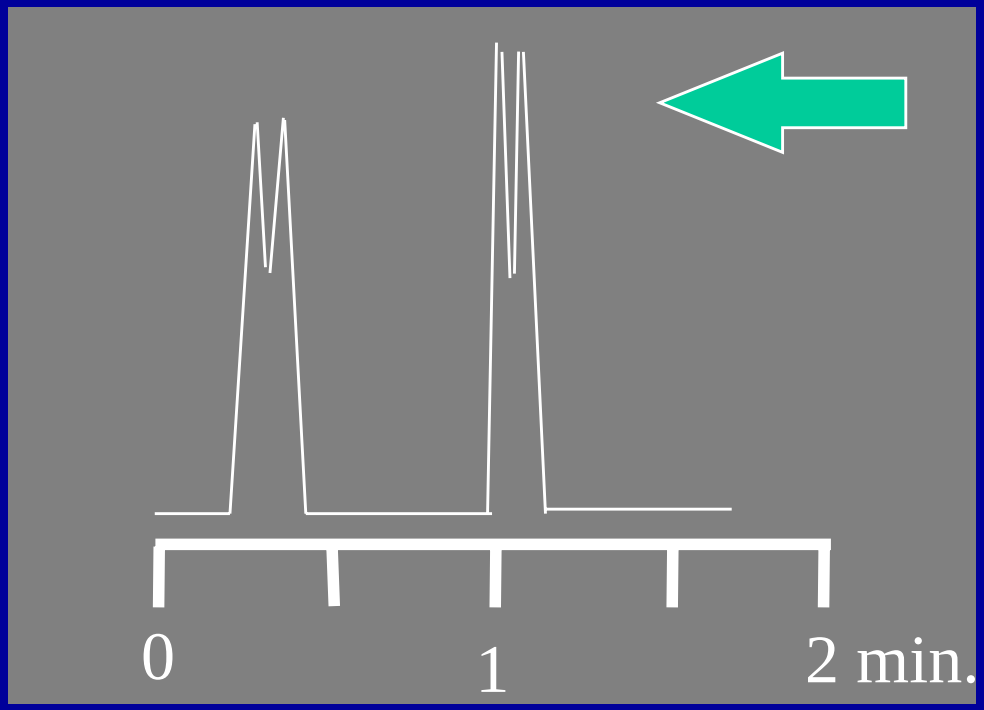


Polarity Match:
The solvent wets the stationary phase

Solvent Focusing
Solvent Polarity



Beading causes non-uniform analyte focusing



Split Peaks

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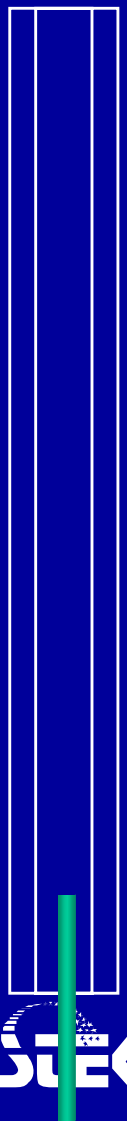
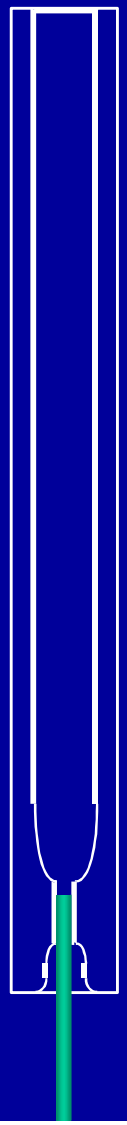
Splitless Liner Designs

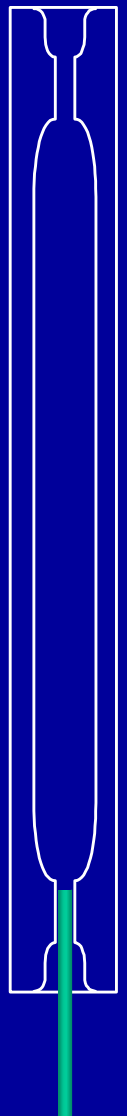
Straight



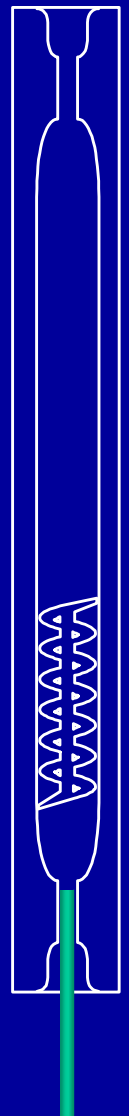
Gooseneck



Double Gooseneck



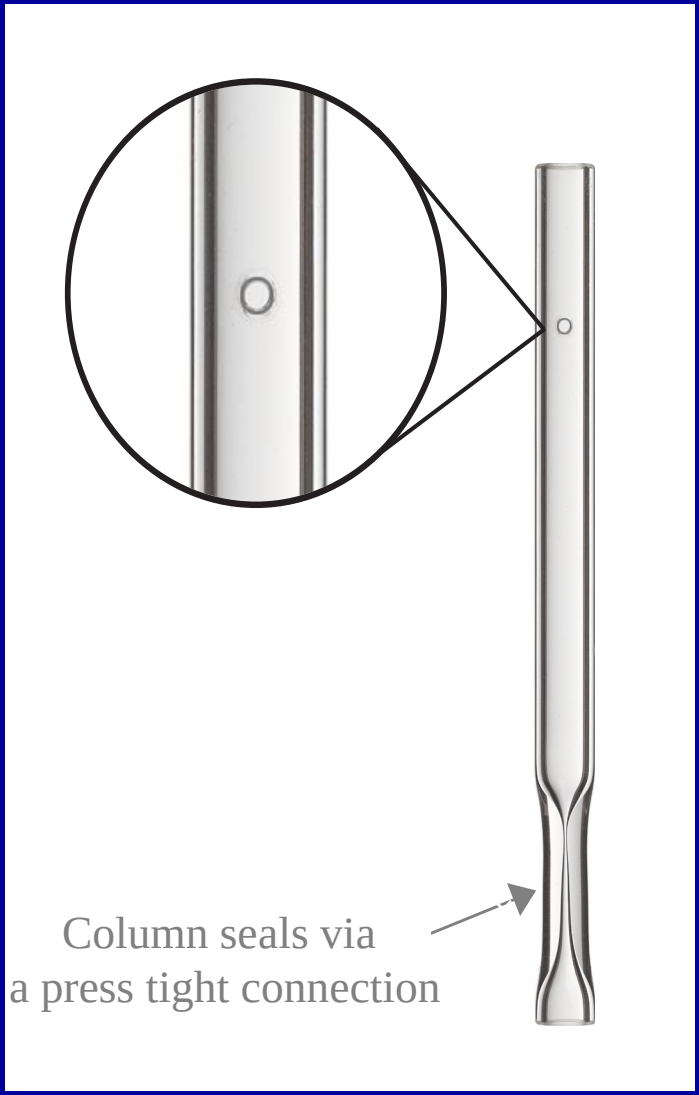
Cyclo Double-Gooseneck



Split/splitless Injection using the Drilled Uniliner

- For trace analysis
- Inlet sleeve has a press-fit connection with column at bottom of sleeve
- More inert sample pathway
- Helps eliminate injection port discrimination

Drilled Uniliner w/ Hole



- Allows DI and Splitless injection methods
- Minimizes injection port discrimination
- Reduces loss of active compounds for more accurate results
- Hole can be placed on bottom or top of liner (each has benefits)

Drilled Uniliners

4mm
IP deactivated

4mm
Siltek deactivated

2mm
Siltek deactivated

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Injection Port Liner
Drilled Uniliner w/ hole

The Uniliner with a hole is a unique liner that can be used for both direct and splitless injection. The column is connected at the bottom of the liner, eliminating any sample contact with metal below the liner. In order for the carrier gas to be routed through the split vent, a hole has been placed on the side of the liner. This hole allows the carrier gas to be vented through the split vent line during the split operation of the injection port.

Injection Port Liner
Drilled Uniliner w/ hole

There are two styles of Drilled Uniliner® liners, one with a hole near the top, and a second with a hole near the bottom of the liner. The choice of liner is dependent on how closely the first compound elutes to the solvent peak. If the first compound elutes near the solvent peak, as in Method 8270, the drilled Uniliner® with the hole at the bottom of the liner should be used. This allows all the solvent to be flushed out of the entire inlet liner, reducing any solvent tailing, which could interfere with the first eluting compounds. The drilled Uniliner® with the hole near the top of the liner works well when the first compounds elute away from the solvent peak as in ethylene glycol in water, or chlorinated pesticide analysis.

The Drilled Uniliner ® also helps eliminate injection port discrimination for the late eluting PAHs. This is shown in figures 5A and 5B. Figure 5A shows the difference between a pressure pulsed injection versus constant flow for the single gooseneck liner. Figure 5B shows the difference between the Drilled Uniliner ® and single gooseneck liner under constant flow condition. The Drilled Uniliner ® exhibits the least amount of injection port discrimination.

Figure 5a - Single Gooseneck Liner
(Constant Flow vs Pressure Pulsed Injection)

White = Single Gooseneck Liner

Pressure Pulsed Injection

Red = Single Gooseneck Liner

Constant Flow

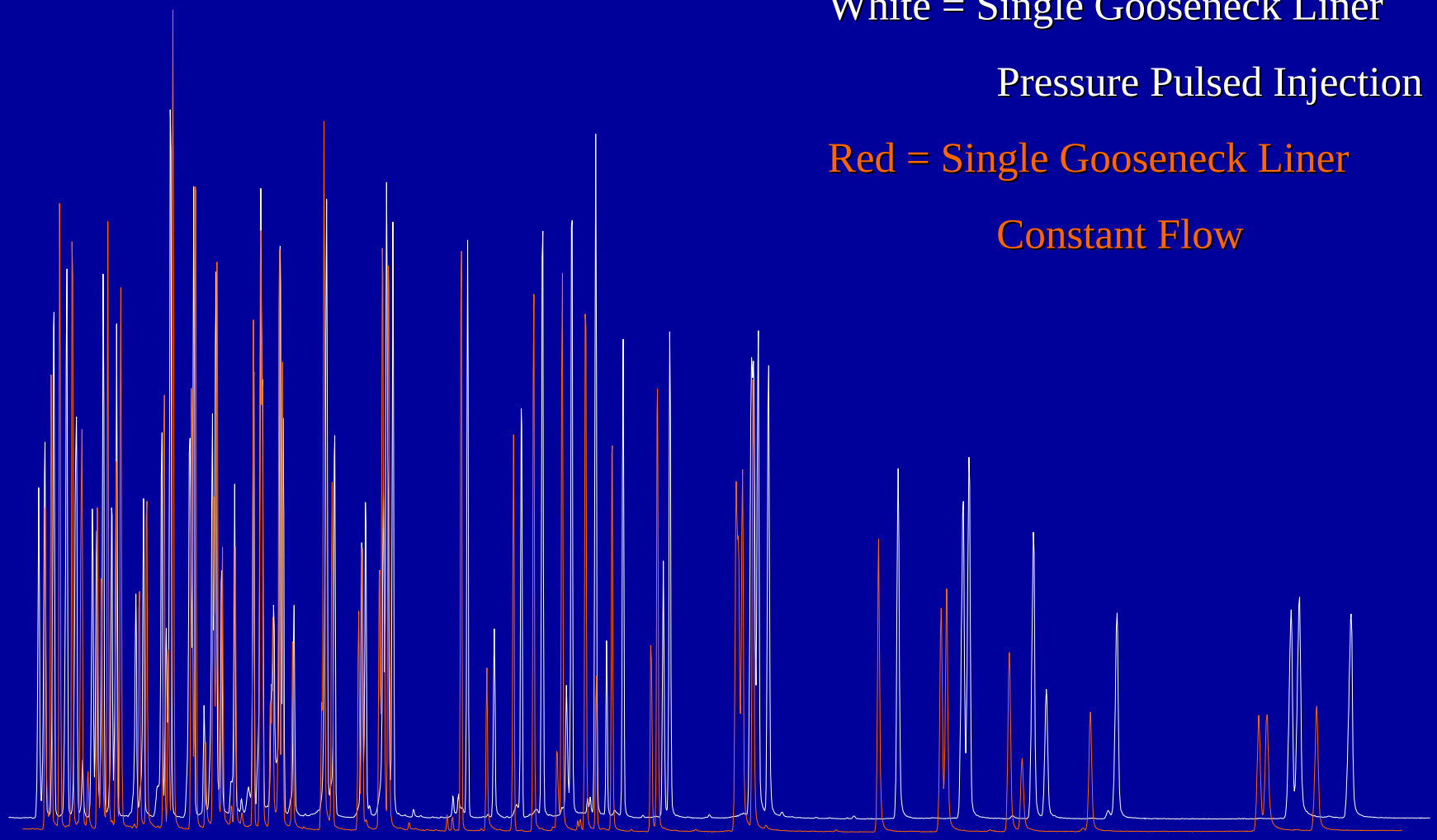

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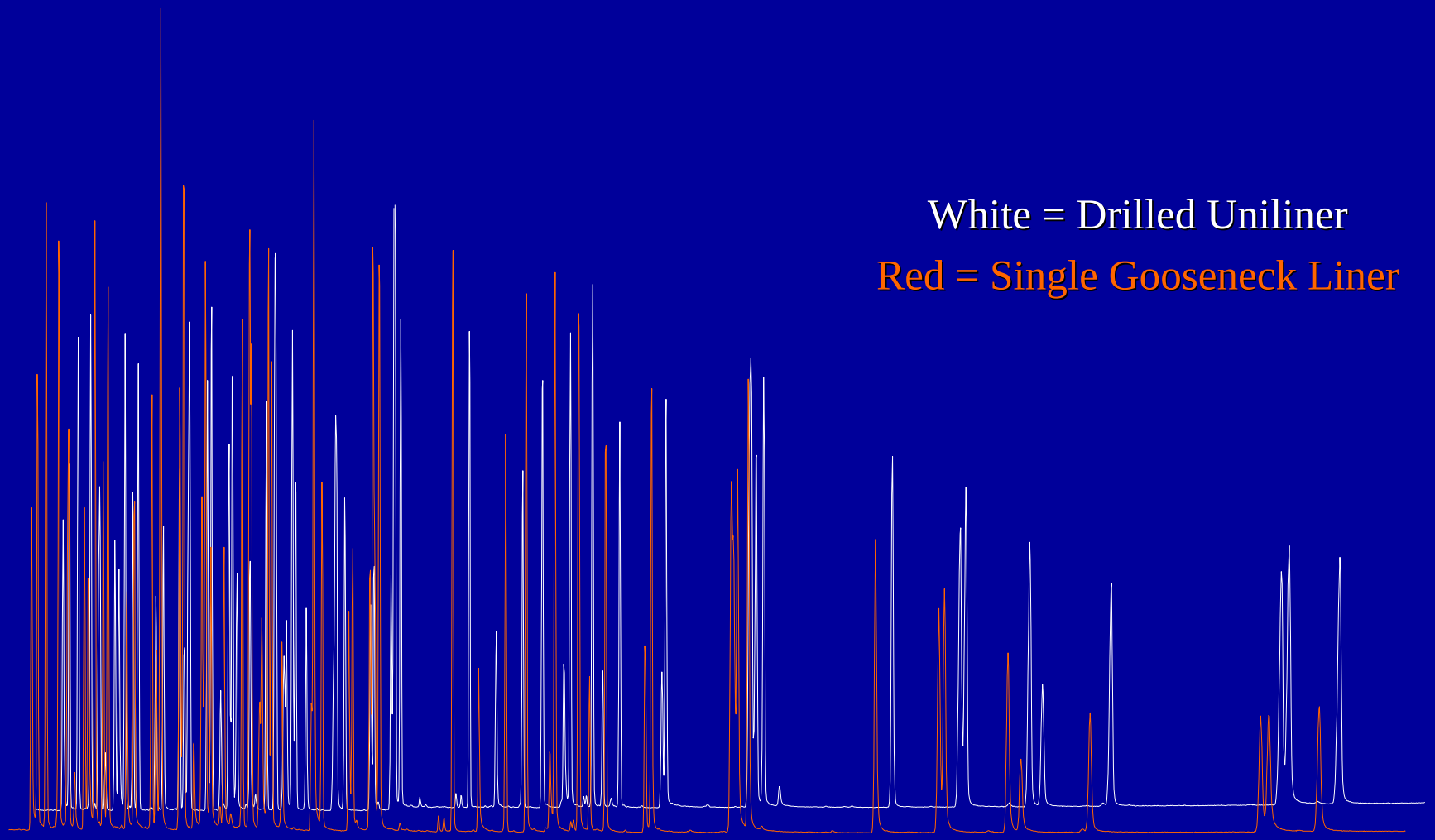
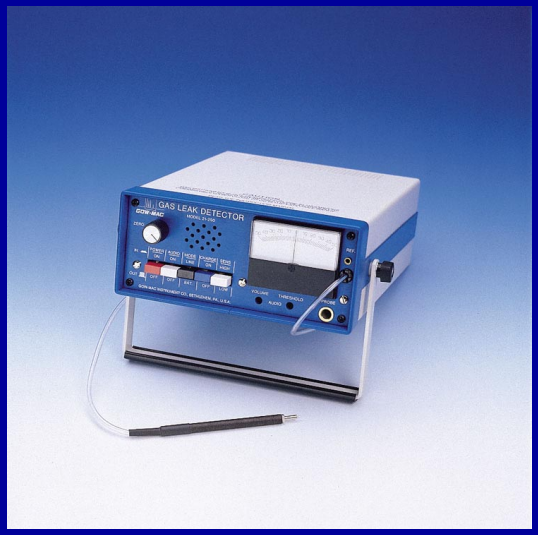
Figure 5b - Single Gooseneck vs Drilled Uniliner® Sleeve (Constant Flow)



White = Drilled Uniliner

Red = Single Gooseneck Liner

Leak Detectors



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