Eliminating the Fear Factors

Fundamentals and Troubleshooting of the Split/Splitless Inlet

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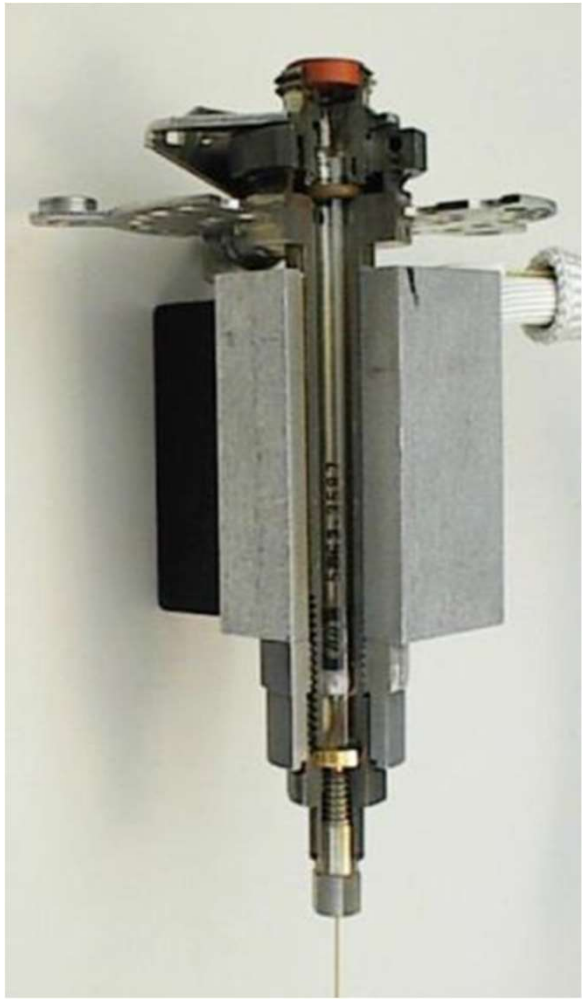
Trusted Answers

Split/Splitless Inlet



GC Sample Introduction

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History of injection

Packed columns – direct injection

Megabore – direct injection

Capillary – Split, Splitless

Other fancy techniques followed

Inlets begin the analysis

Volatile Inlet

Split/Splitless

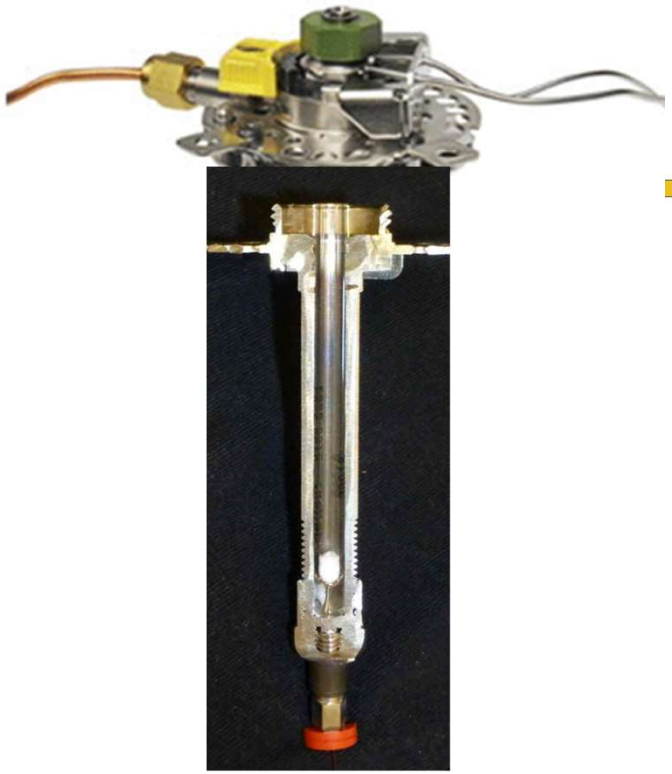
Multi-mode Inlet

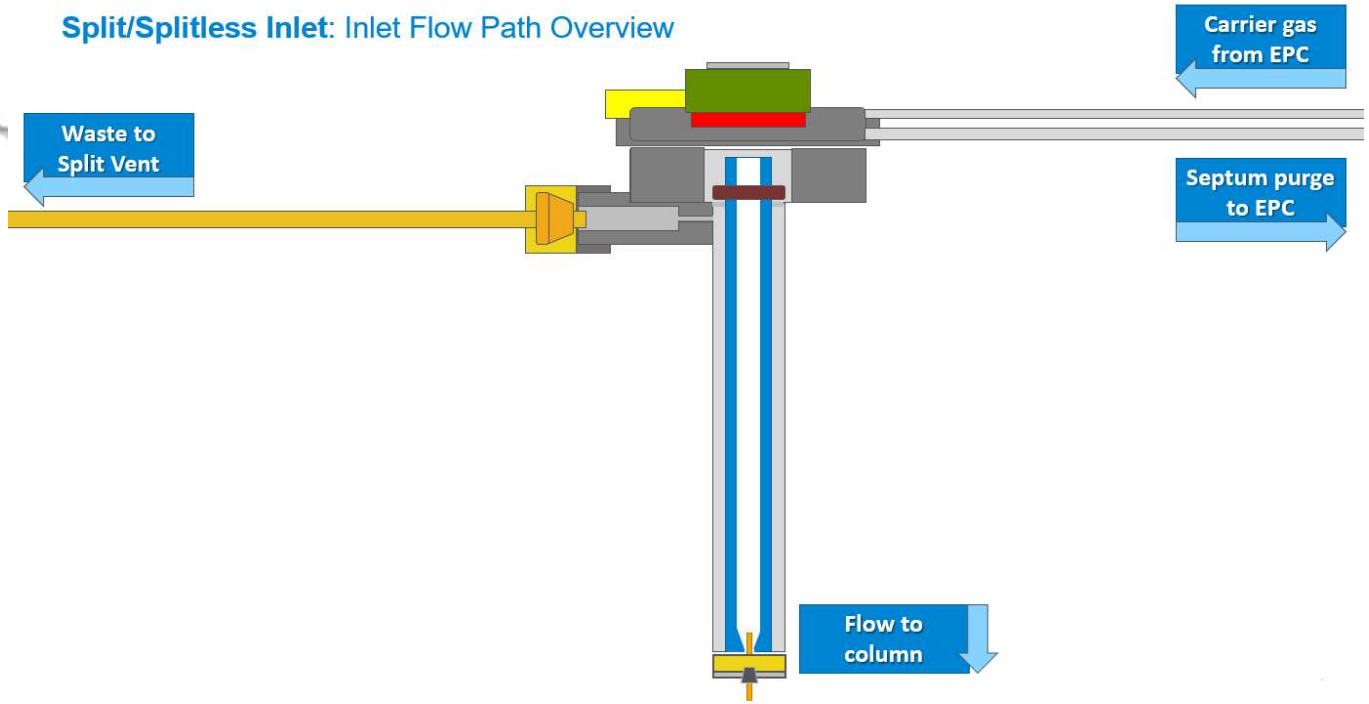
Purge Packed Inlet

Cold On-Column

Programmable Temperature Vaporization Inlet

Split/Splitless Injector





Split/Splitless Inlet

Carrier gas **IN**

- Smaller tube, delivers carrier gas flow from EPC module to inlet, column

Split vent flow **OUT**

- Copper tube carries split flow and waste after splitless purge time from inlet out through trap
- Change trap routinely

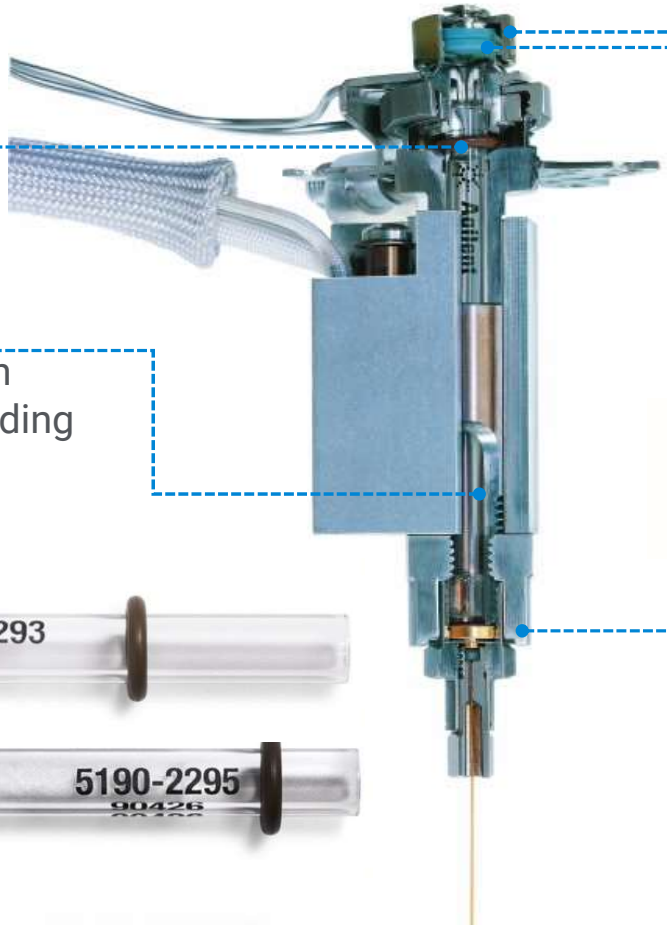
Septum Purge **OUT**

- Larger tube, carries septum purge flow from inlet to EPC
- Used to sweep away semivolatile buildup from heated septum (prevents ghost peaks)

Anatomy of a Split/Splitless inlet

Inlet o-ring
Forms seal between inlet liner and septum nut

Inlet liner
Vessel for sample volatilization
Different configurations depending on analyte, injection type

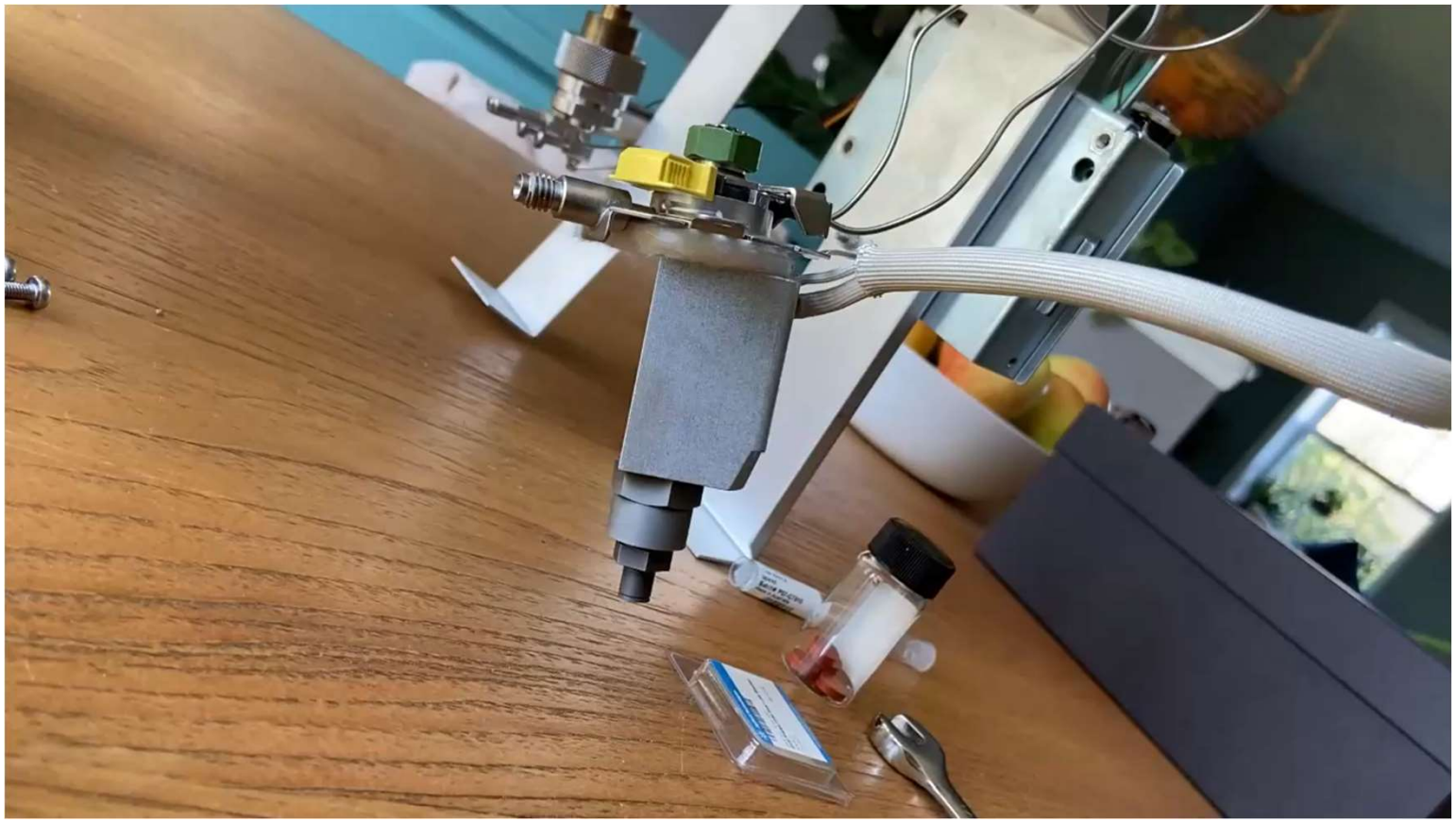


Septum nut
Seals inlet, avoid overtightening

Septum
Forms seal at septum retainer nut, enables syringe injection

Gold seal
Prevents sample contact with hot, active metal surfaces

Inlet Maintenance



Split Injection Overview

- Most common injection technique
- Reduces the amount of sample that reaches the column (majority of sample exits the inlet via the split vent)
- Used primarily for highly concentrated samples (0.1 – 20 µg/mL) and large sample volumes (up to 4 µL)
- Highly efficient injection technique
- Liner must be inserted in inlet so bottom does not contact gold seal (need carrier flow access to split vent)

Split Injection
Major Variables

Split ratio

- determines amount of sample onto column and efficiency of injection (sensitivity vs peak shape)

Liner

- influences efficiency of vaporization/discrimination

Temperature

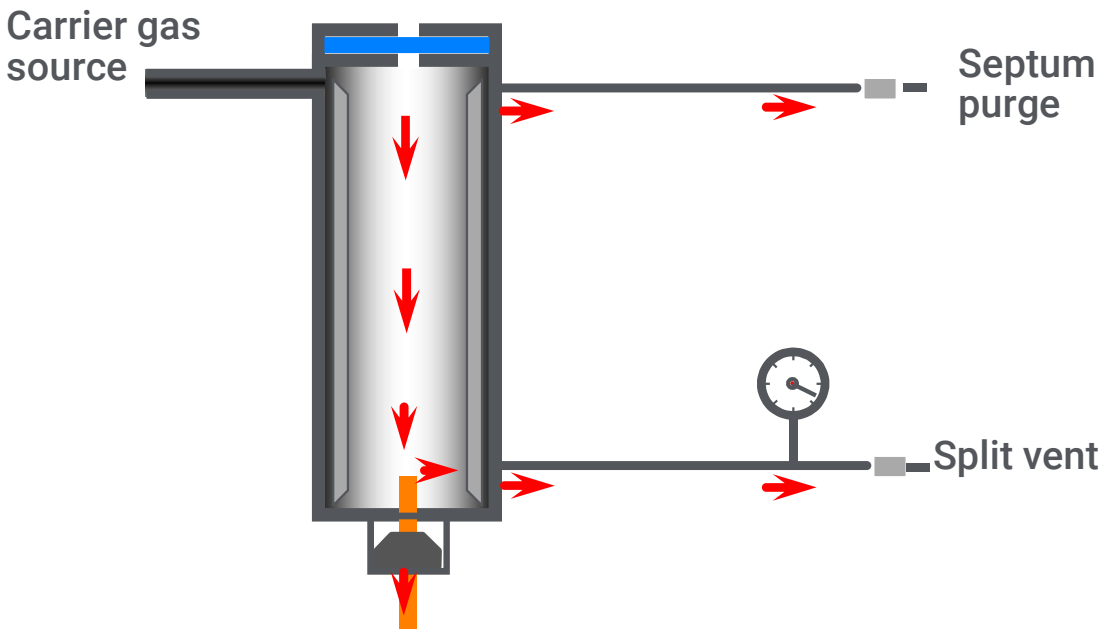
- hot enough to vaporize sample without degradation or causing backflash

Injection volume

- typically 1-3 µL, increasing it does not have as much of an effect as one might think

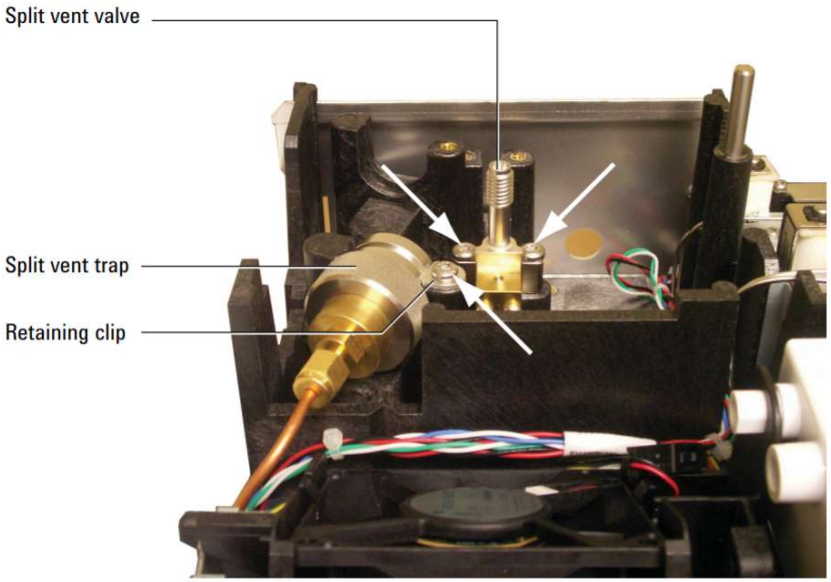
Split Injection

Flow Path



Split Vent Trap

- Filters impurities and waste via split vent during split and AFTER splitless purge time for SSL and MMI inlets
- Should be changed at least every 6 months, or more often for DIRTY samples
- Can cause problems if saturated



Minimum recommended split ratio

Higher flow rates

mm I.D.	Lowest ratio
0.10	1:50 - 1:75
0.18 - 0.25	1:10 - 1:20
0.32	1:8 - 1:15
0.53	1:2 - 1:5

Goal is to have 20 mL/min flow through the inlet

Liner selection

Liner is where sample is volatilized so selection is important

Liner Variables	• Volume • Geometry- taper, glass wool? • Treatment- deactivated?
Application	• Analyte concentration level? • Thermally labile analytes?
Inlet & Injection technique	• Split? • Splitless? • MMI- cold injection, less solvent expansion volume

You may need to experiment with several liner types to find the best one for your method.

Liner treatments or deactivation

- Minimizes possibility of active sample components from adsorbing on active sites on the liner or glass wool surface.
- Unwanted sample adsorption leads to tailing peaks and loss of response for active analytes.
- Although not necessary for all applications, deactivated liners provide added insurance against possible sample adsorption.
- Deactivation of borosilicate glass liners is often done with a silylating reagent like Dimethyldichlorosilane (DMDCS) or by coating with a siloxane (as capillaries are made).

Liner Characteristics

What is glass wool used for?

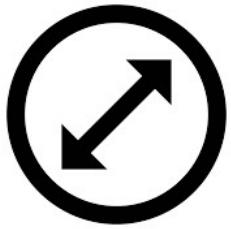
Filtration	• Prevents nonvolatile matrix from entering column
Vaporization	• Provides volatilization surface for liquid injections, promotes mixing with carrier gas
Needle wiping	• Increases reproducibility by wiping needle after injection

Straight or tapered?

Bottom taper	• Focuses sample on the head of the column • Minimizes contact with metal inlet parts
Center taper	• Holds wool in place
Top taper	• Reduces sample backflash

Does liner diameter have an effect?

Inner diameter	• Small or large id for splitless injections • Larger id better for split injections
Outer diameter	• Large od ideal for splitless injection • Slower transfer, snug fit directs flow within liner



Minimizing Sample Discrimination
Some Considerations

Efficient heat transfer to injected sample

Efficient mixing of vaporized sample with carrier gas

Volume of the inlet liner

Liner design

Column position in inlet

Consistent conditions are important

Split Injection

Major Variables

Split ratio - determines amount of sample onto column and efficiency of injection (sensitivity vs peak shape)

Liner - influences efficiency of vaporization/discrimination

Temperature - hot enough to vaporize sample without degradation or causing back flash

Injection volume - typically 1-3 µL

(increasing injection volume does not have as much of an effect as one might think)

Split liners:

Split/splitless liner with glass wool, low pressure drop

Split injections have higher carrier gas flow through liner to help split sample

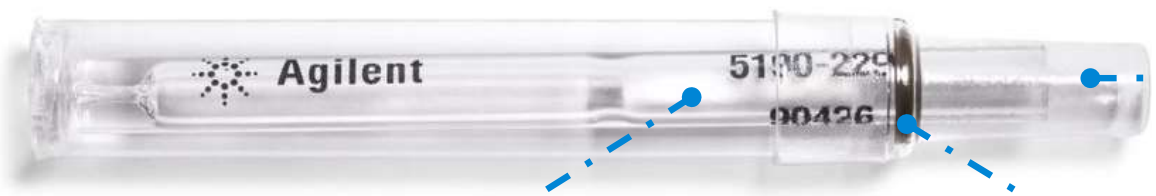
- Faster transfer onto column
- Split liners have a smaller outer diameter than splitless liners to help flow circulate

If potential exists for sample discrimination between low and high boiling components

- Use a liner with wool

Ultra Inert liners enable excellent peak shapes for tricky analytes

- 5190-2295 is recommended liner- Single taper, low pressure drop



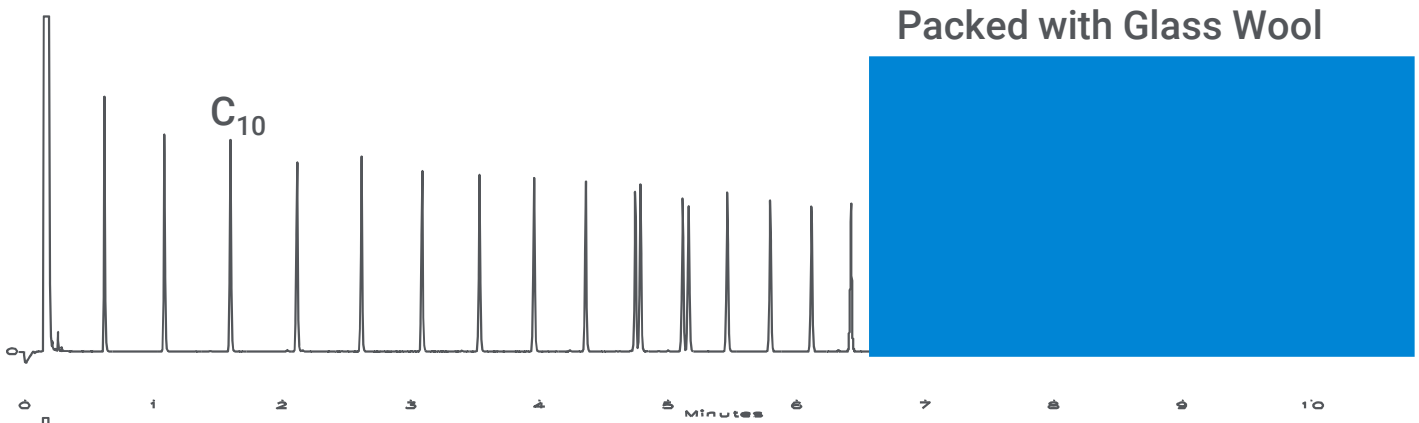
Touchless packaging ensures contamination-free installation

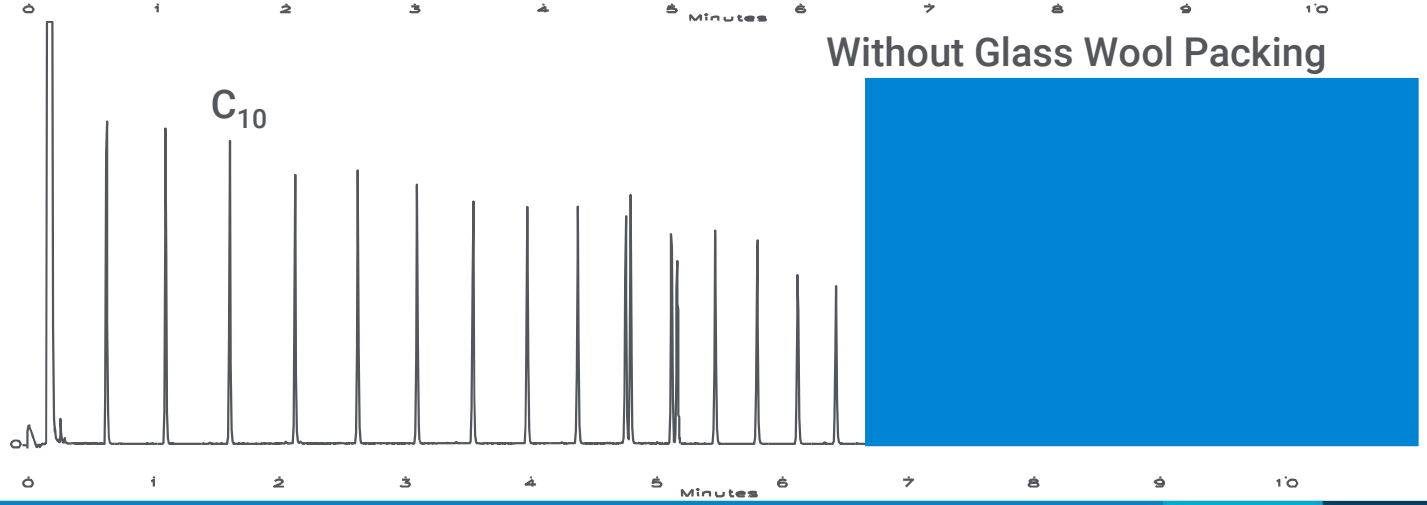
Preinstalled o-ring

Glass wool plug in upper position wipes needle, avoids sample discrimination improves P&A, and collects septum particulate

Low pressure drop bead promotes better carrier gas flow for split injections

Split Liner


Packed with Glass Wool
C_{10}
0
1
2
3
4
5
Minutes
6
7
8
9
10

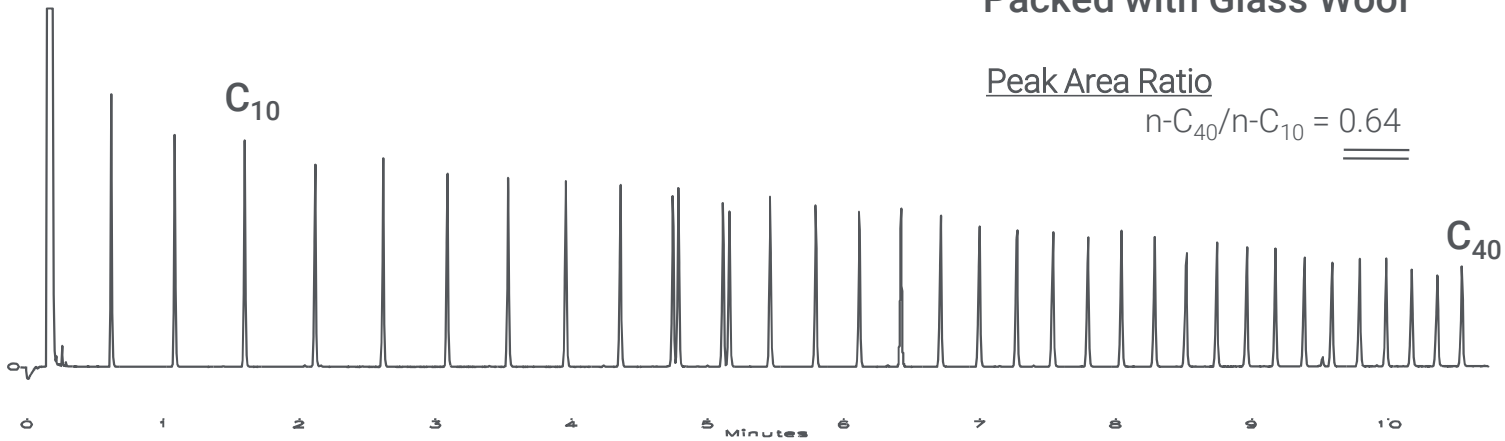

Without Glass Wool Packing
C_{10}
0
1
2
3
4
5
Minutes
6
7
8
9
10

Split Liner

Packed with Glass Wool

Peak Area Ratio

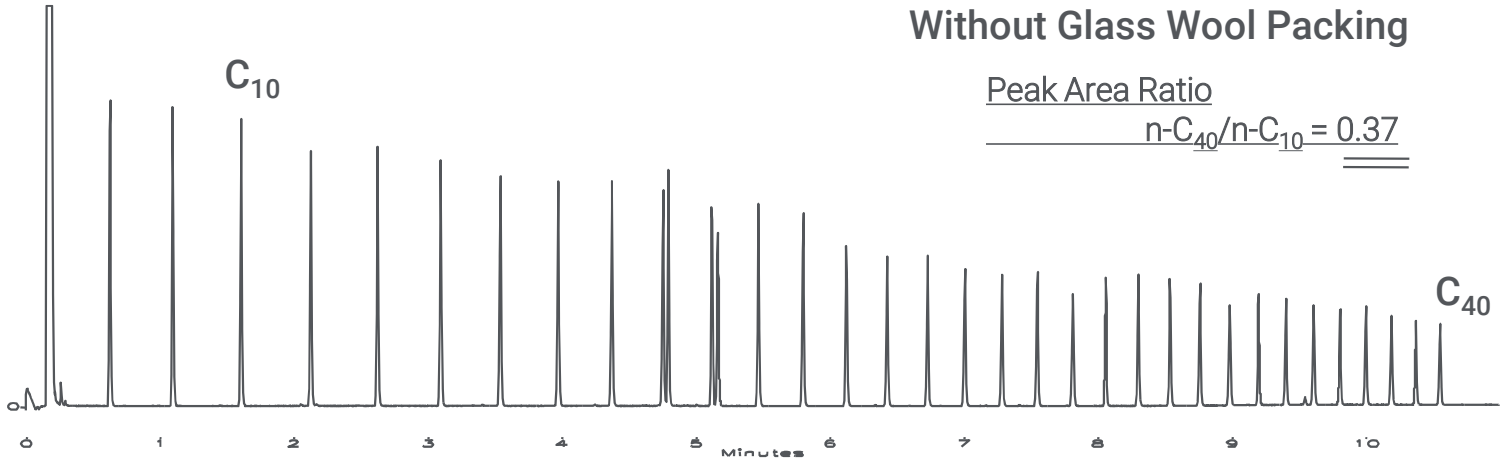
$n\text{-}C_{40}/n\text{-}C_{10} = 0.64$



Without Glass Wool Packing

Peak Area Ratio

$n\text{-}C_{40}/n\text{-}C_{10} = 0.37$



Split Injections - Fast GC Considerations

Faster than splitless because you can start at a higher initial oven temp, thereby decreasing cycle time

Easiest of the injection techniques to speed up

For 100 um i.d. and smaller columns

- narrower i.d. liners may be necessary to maintain input peak width

Using higher flows with normal columns

- Lose some resolution
- Minimize analytes dwell time in potentially active areas
- Minimize contaminating liner due to splitting (remember split vent trap)
- Larger injections possible

Split Injections - Maximizing Response

Increase Injection Volume

- liner dependent (use the Pressure-Volume Calculator)
- 2 µL maximum (previous slides depict larger volumes don't substantially increase response)

Reduce Split Ratio

- go from 50:1 to 10:1
- 5:1 practical lower limit for liquid injections (for 250 - 320 µm i.d. columns)
- 1:1 possible for gas injections with correct liner

Use Pulsed Injection

Utilize Vapor Volume Calculator

Splitless Injection

Overview

Most of the sample is introduced into the column

Used for low concentration samples

Wider peaks are obtained than for split injections

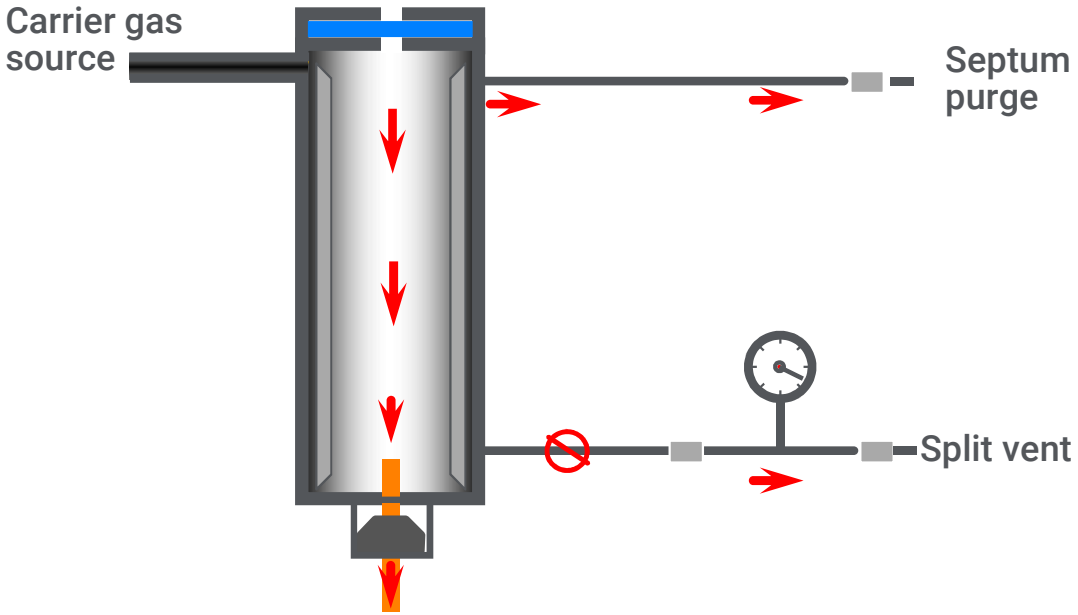
Splitless Injection Overview

For Trace Level Analysis

- Most of the sample is introduced into the column
- Used for low concentration samples
- Wider peaks are obtained than for split injections
- Use split/splitless injection port in the splitless mode (split vent closed until purge time elapses)
- The dilute sample is injected, the sample is volatilized, and majority of analytes condense on column
- Later, the split vent is opened and residual solvent is purged
- Timing, carrier and split vent flows, and oven temperature program are important
- Splitless liners seal against the gold seal at the bottom of the inlet
- Sample has longer residence time in the heated inlet giving more opportunity to vaporize high boiling sample components compared to split injection

Splitless Injection

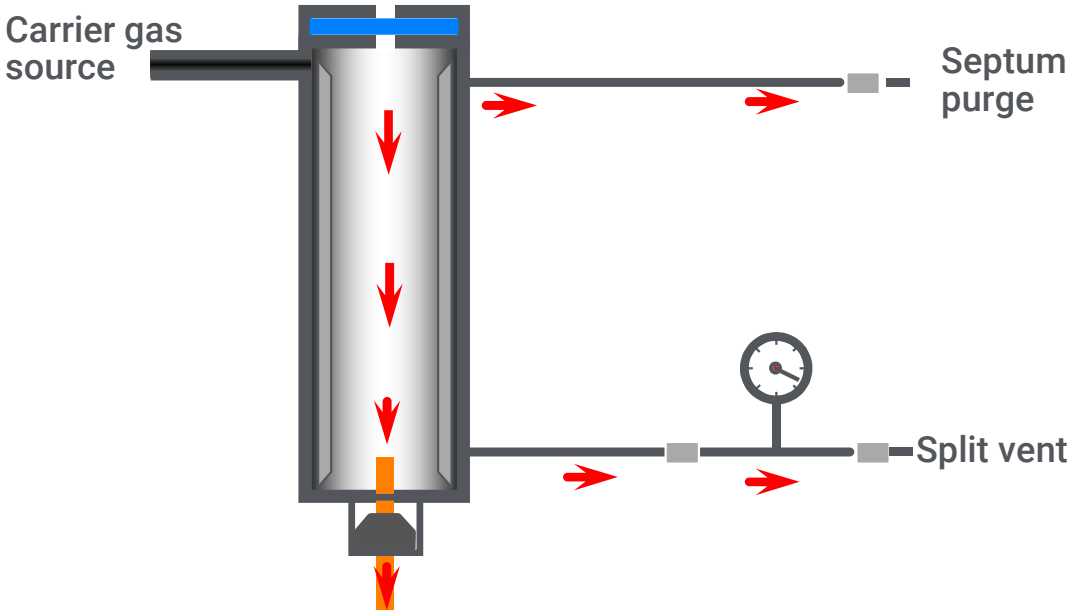
Purge Off At Injection



Flow through injector = Column flow only

Splitless Injection

Purge On After Injection



Flow through injector = Column flow + Split Vent Flow

Splitless Injection
Major Variables

Purge activation time - determines amount of sample onto column and efficiency of injection(sensitivity vs peak shape)

Liner - preventing backflash more critical than vaporization properties (double tapered type recommended)

Injection volume - typically 1µL or less (avoid backflash)

Temperature – long residence times allow for lower temps

Splitless liners

Single Taper with or without wool

Splitless has lower flows through liner

- Splitless liners are typically wider for a more snug fit
  - Ensures all available flow funnels through the liner, not around
- Do NOT do split injections on a splitless liner
  - Poor reproducibility, not enough room for flow

Ultra Inert liners enable excellent peak shapes for tricky analytes

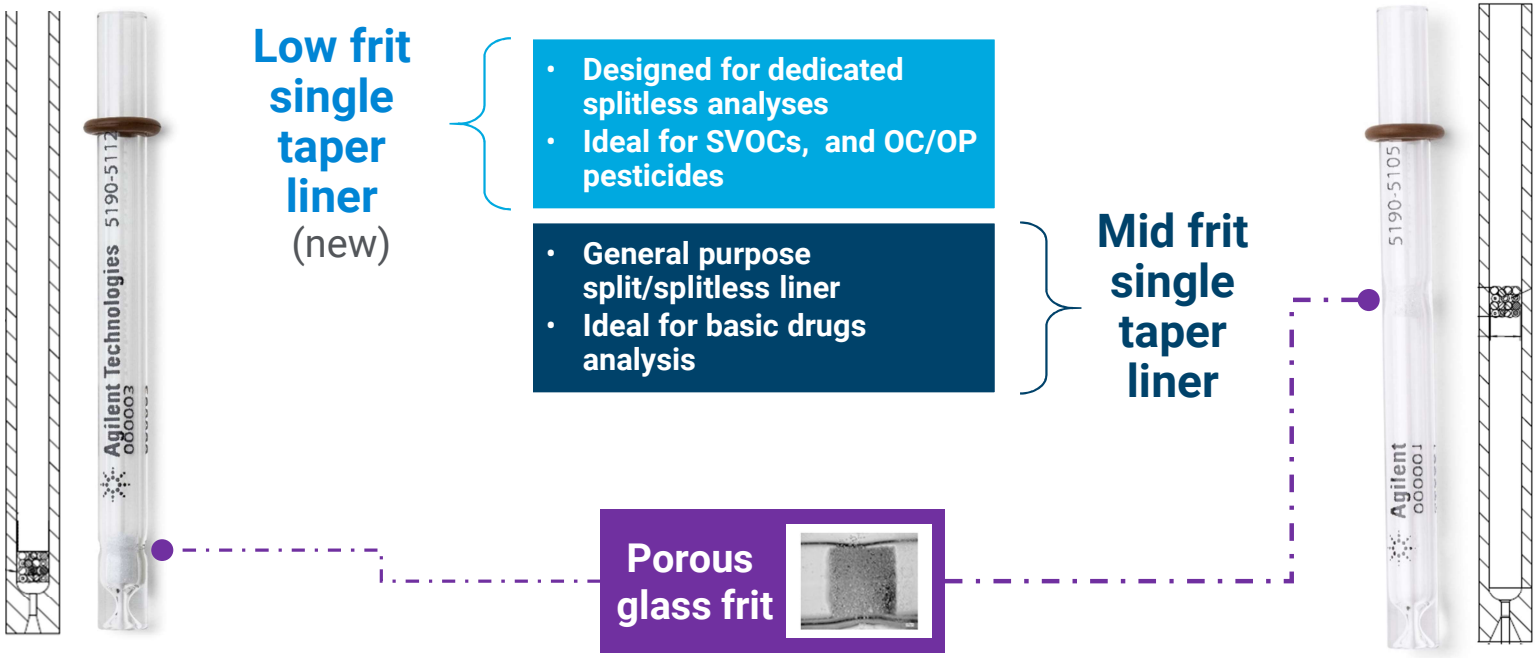
- 5190-2293 is recommended splitless liner- Single taper, with wool

In low carrier gas flow splitless analysis, a **bottom taper** helps focus analytes onto head of column

Small plug of **glass wool** near bottom of liner filters matrix

What's new? Glass wool alternative liners

Ultra Inert liners with sintered glass frits



Glass Fritted Liner

Splitless Fritted Liner

Low Frit Liner

Excellent results in EPA 8270 soil extract work (GC/MS)

- Double lifetime over similar wool liners
- Recovery of responses and criteria with new liner installation

Excellent results for pesticides in food analysis (GC/MS/MS)

- Great calibration curve results
- Great repeatability and reproducibility
- Good peak response maintenance through 70 matrix injections

Split or Splitless Fritted Liner

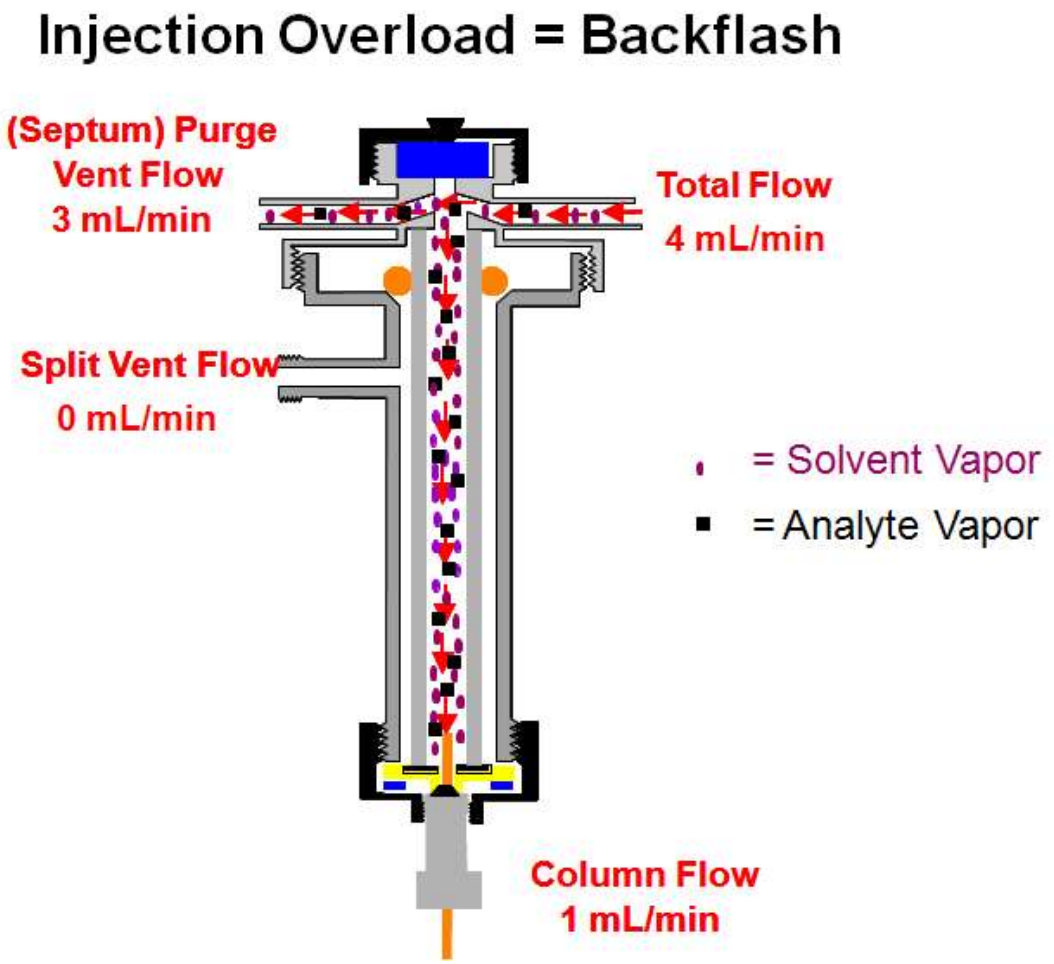
Universal (Middle) Frit Liner

Excellent results for White powders/Drugs of Abuse analysis

- Good amines and opioid peak shapes, including mixtures with both classes together
- Excellent repeatability and reproducibility
- Compounds have good resistance to matrix build-up with Tylenol extract lifetime testing
- Recovery of response with new liner installation

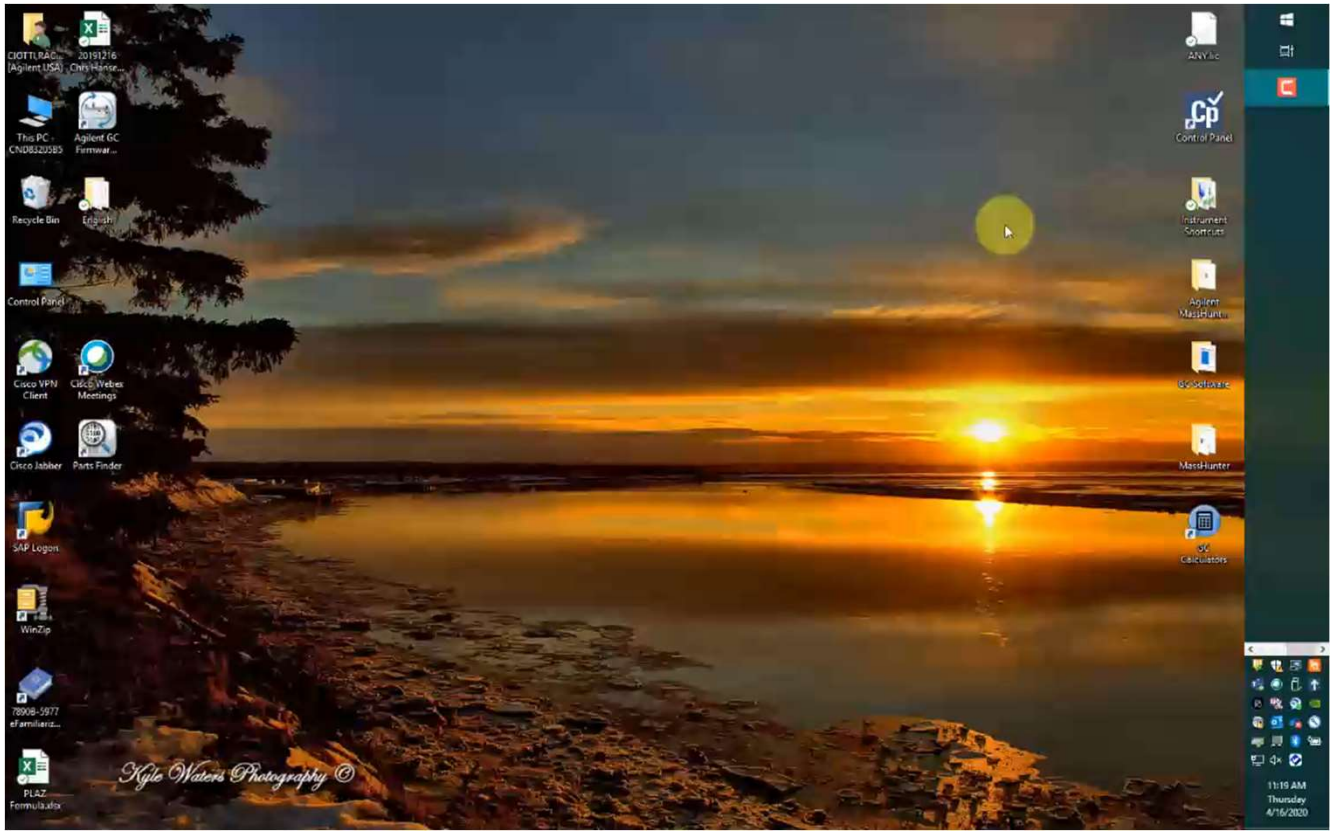
Ghost Peaks
Backflash

Backflash occurs when vapor condenses on a cooler part of the injector. This condensed sample will still have a “headspace” which can be swept forward to the column and cause ghost peaks.



Vapor Volume Calculator

A valuable tool for preventing backflash



Tips to avoid backflash:

Reduce injection volume

Lower inlet temperature

Consider a large volume liner

Pressure pulsed injection

Change solvents

https://www.agilent.com/en/support/gas-chromatography/gccalculators

Splitless Injection

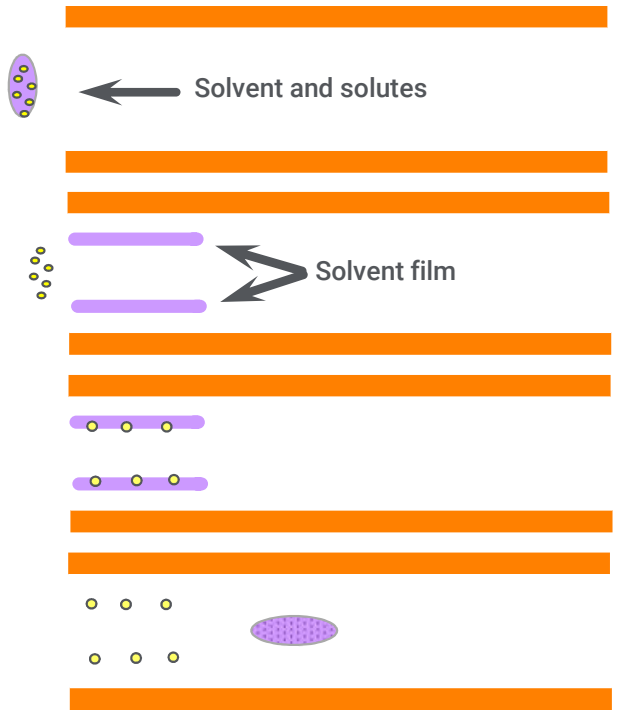
Solvent Effect

Initial column temperature at least ***10°C below*** sample solvent boiling point

Required to obtain good peak shapes unless cold trapping occurs

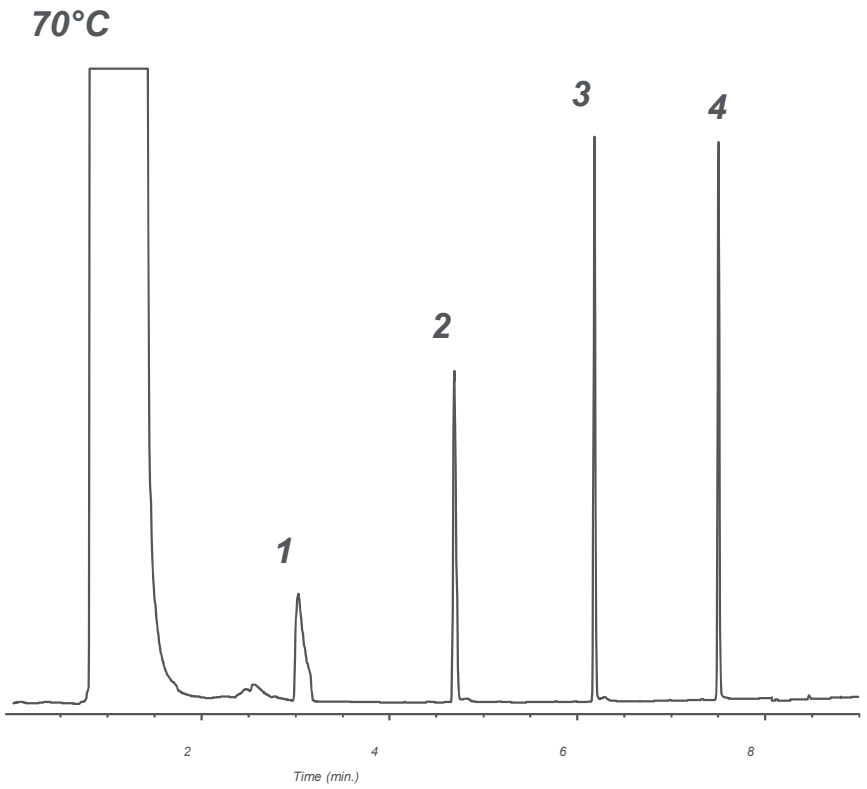
Rule of thumb, if solute BP >150°C above initial column temperature, the solute will cold trap

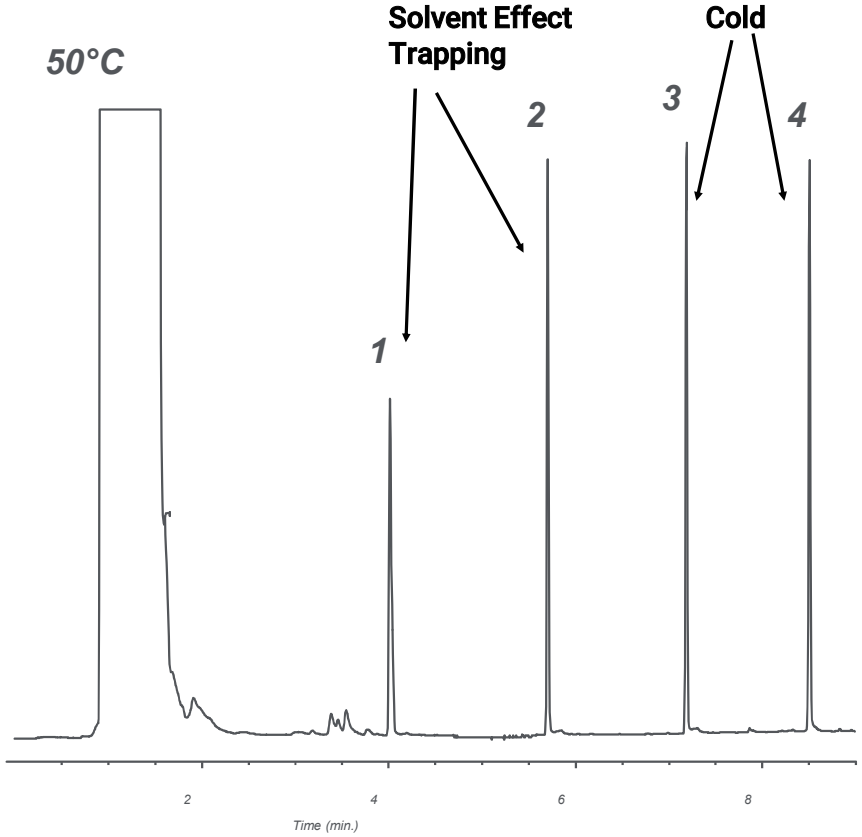
Cold trapping has greater efficiency than solvent effect



Splitless Injection

Initial Column Temperature Hexane Solvent (BP = 68-69°C)

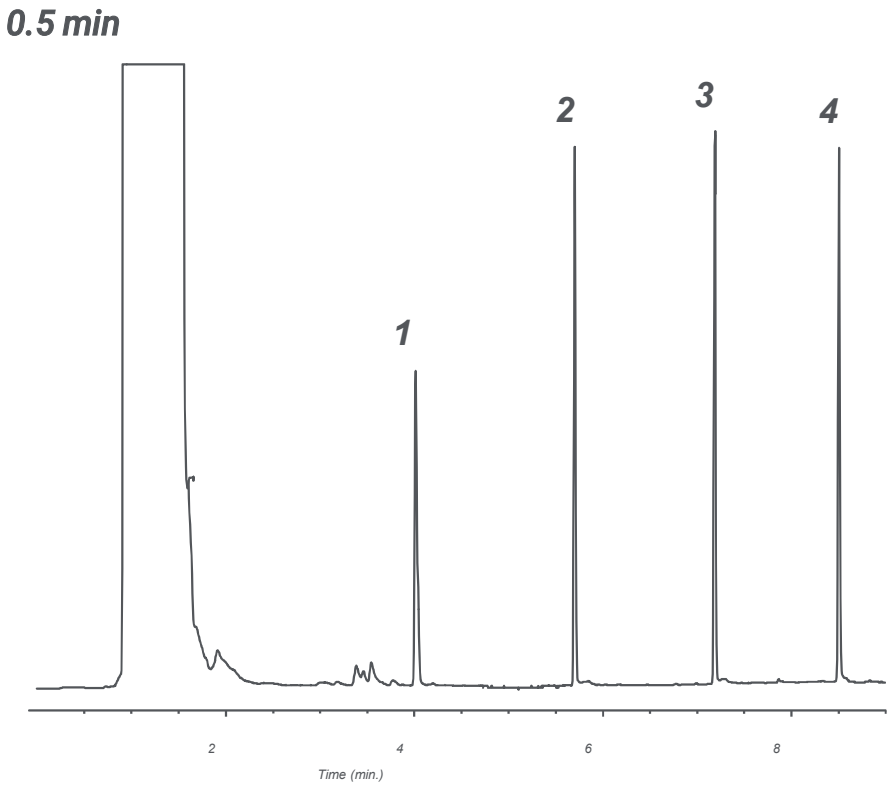


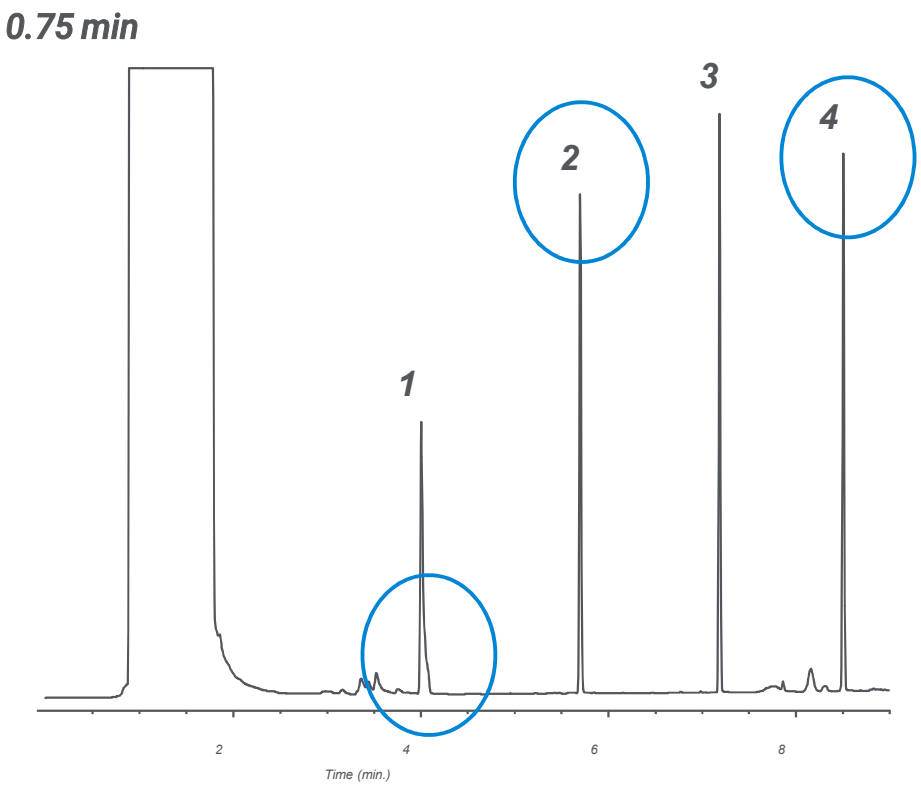


DB-1, 15 m x 0.25 mm I.D., 0.25 µm
50°C or 70°C for 0.5 min, to 210°C at 20°/min; Helium at 30 cm/sec
1. n-decane 2. n-dodecane 3. n-tetradecane 4. n-hexadecane

Splitless Injection

Purge Activation Time

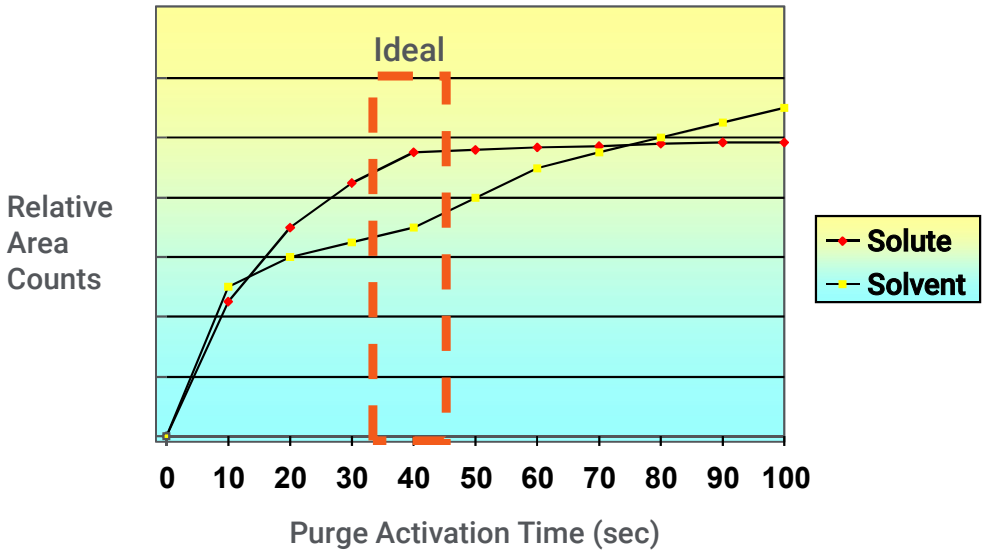




DB-1, 15 m x 0.25 mm I.D., 0.25 µm
60°C for 1 min, 60-180°C at 20°/min; Helium at 30 cm/sec
1. n-decane 2. n-dodecane 3. n-tetradecane 4. n-hexadecane

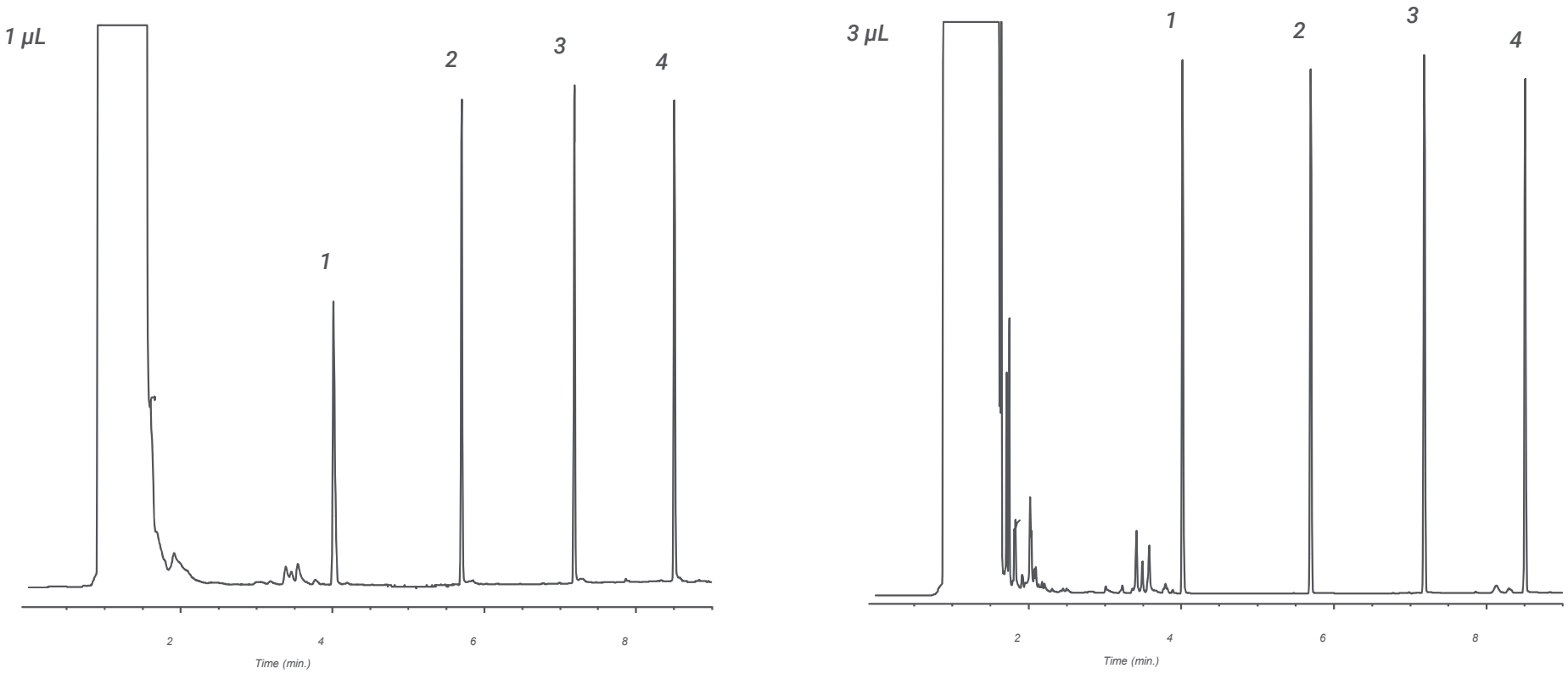
Splitless Injection

Purge Time vs. Peak Size



Splitless Injection

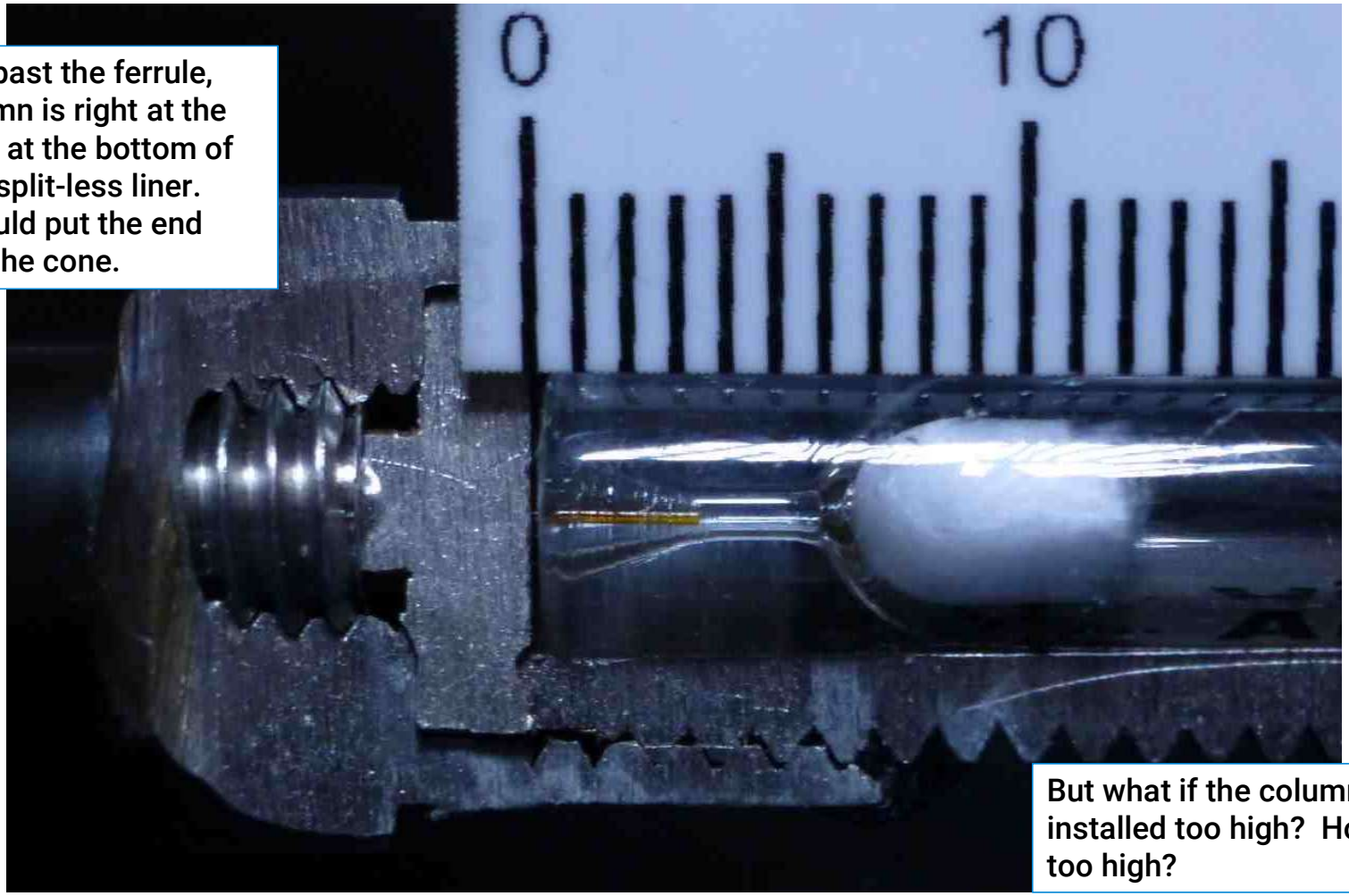
Injection Volume



DB-1, 15 m x 0.25 mm I.D., 0.25 µm
60°C for 1 min, 60-180°C at 20°/min; Helium at 30 cm/sec
1. n-decane 2. n-dodecane 3. n-tetradecane 4. n-hexadecane

SSL inlet column installation

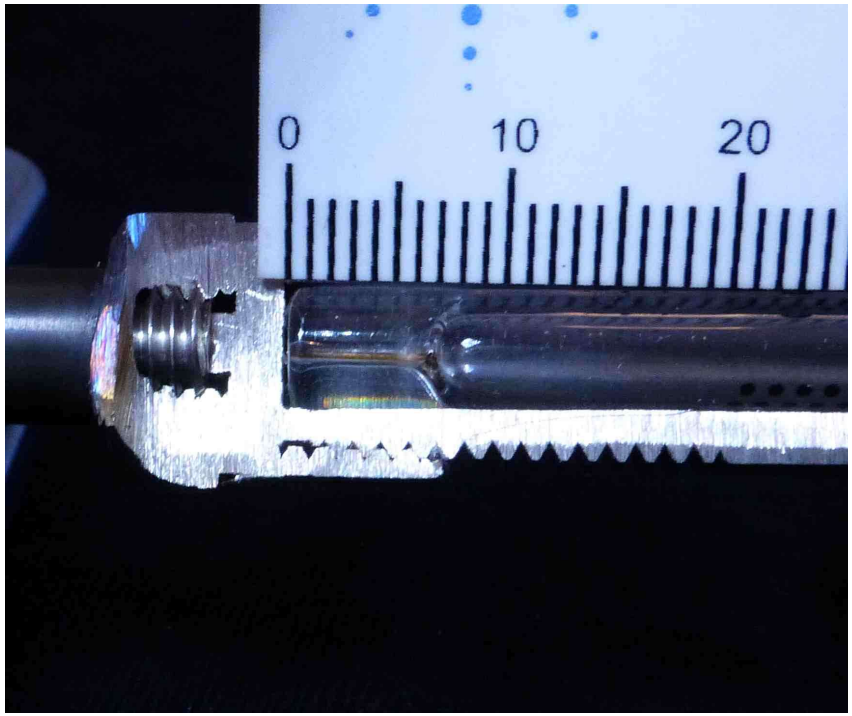
At 6mm extension past the ferrule, the end of the column is right at the top end of the cone at the bottom of this single tapered split-less liner. 4mm extension would put the end near the middle of the cone.

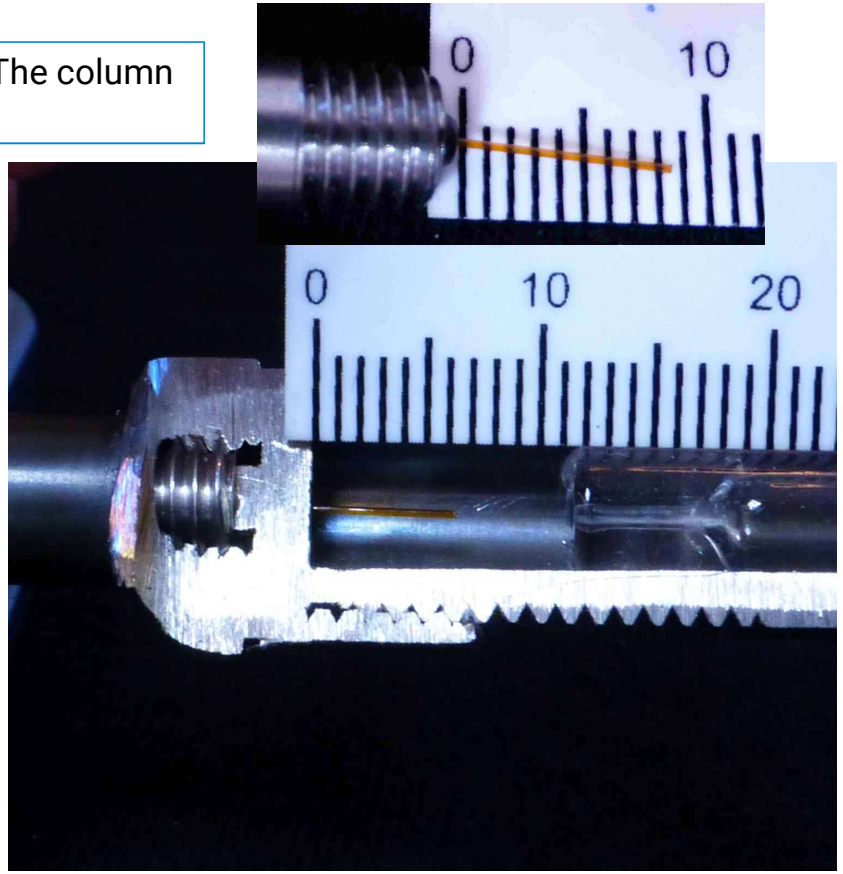


But what if the column gets installed too high? How high is too high?

SSL inlet column installation

This is a Split liner and the column is 8.5mm above the ferrule. The column is right at the bottom of the taper.





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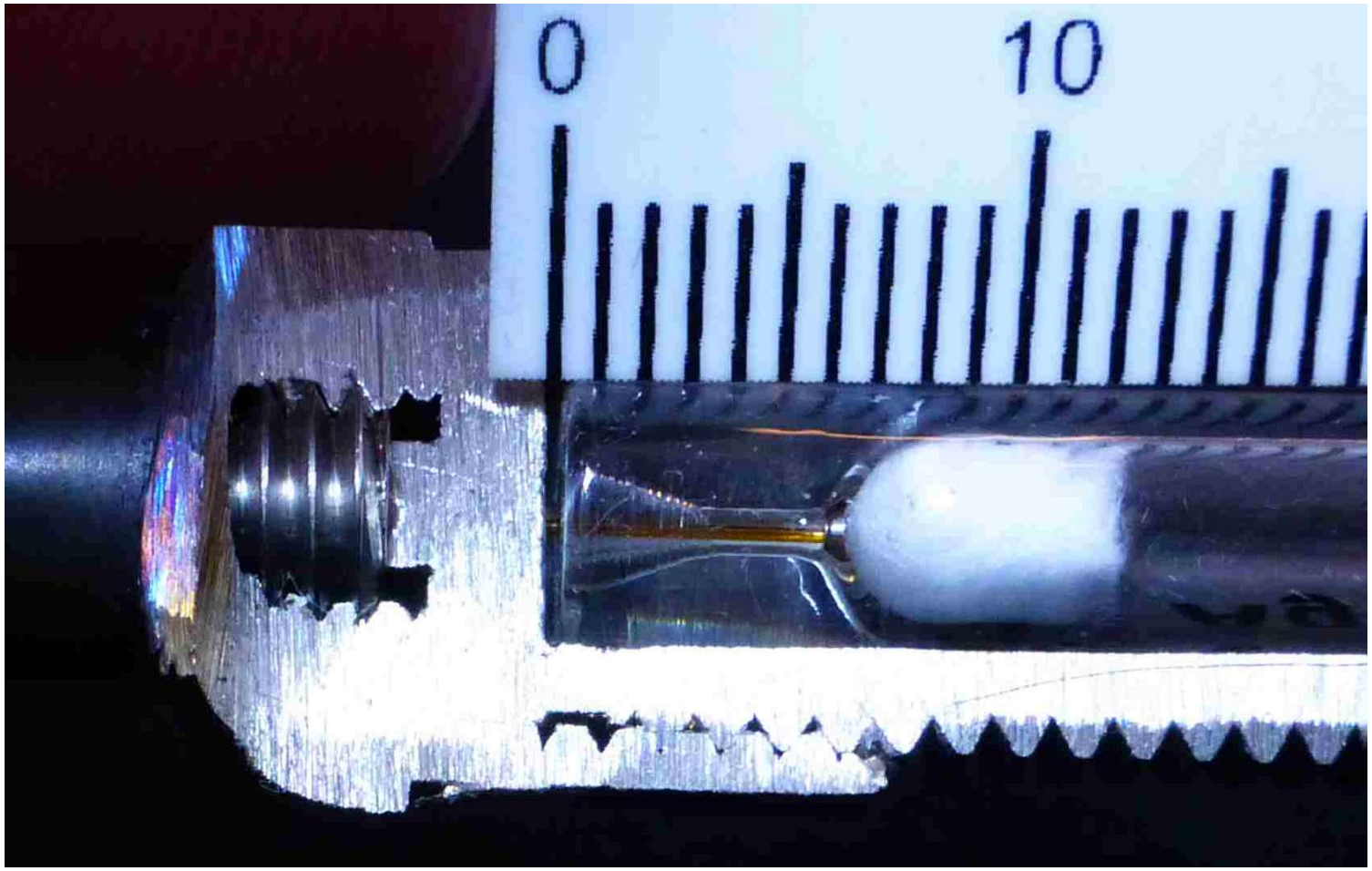
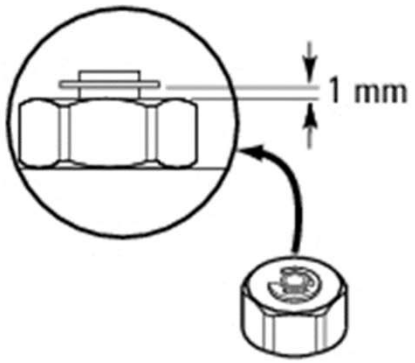
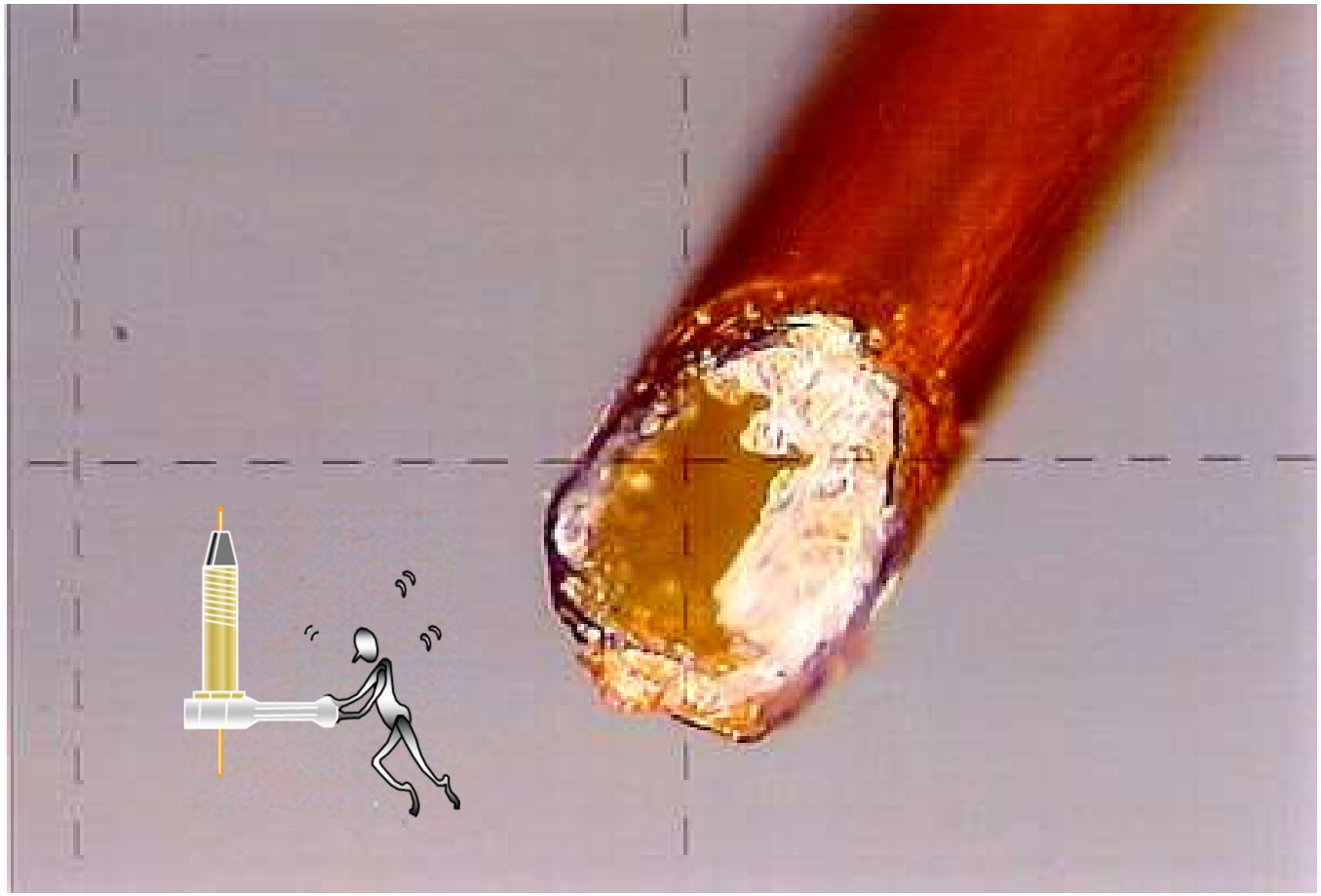


Too low is <u>definitely</u> bad. Below 4mm can cause many issues like boiling point discrimination, reproducibility problems, and poor response. A bit too high is definitely better than too low.

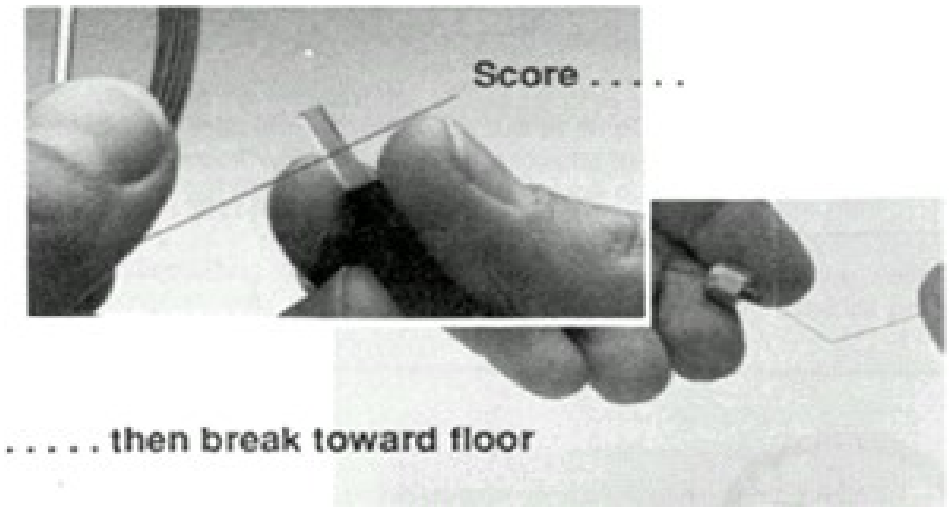
Pay attention to details

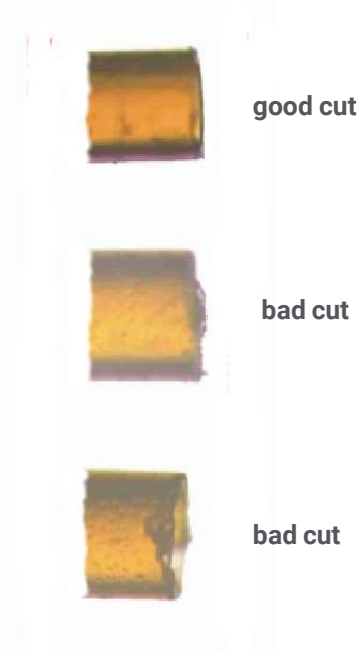


Overtightened Ferrule



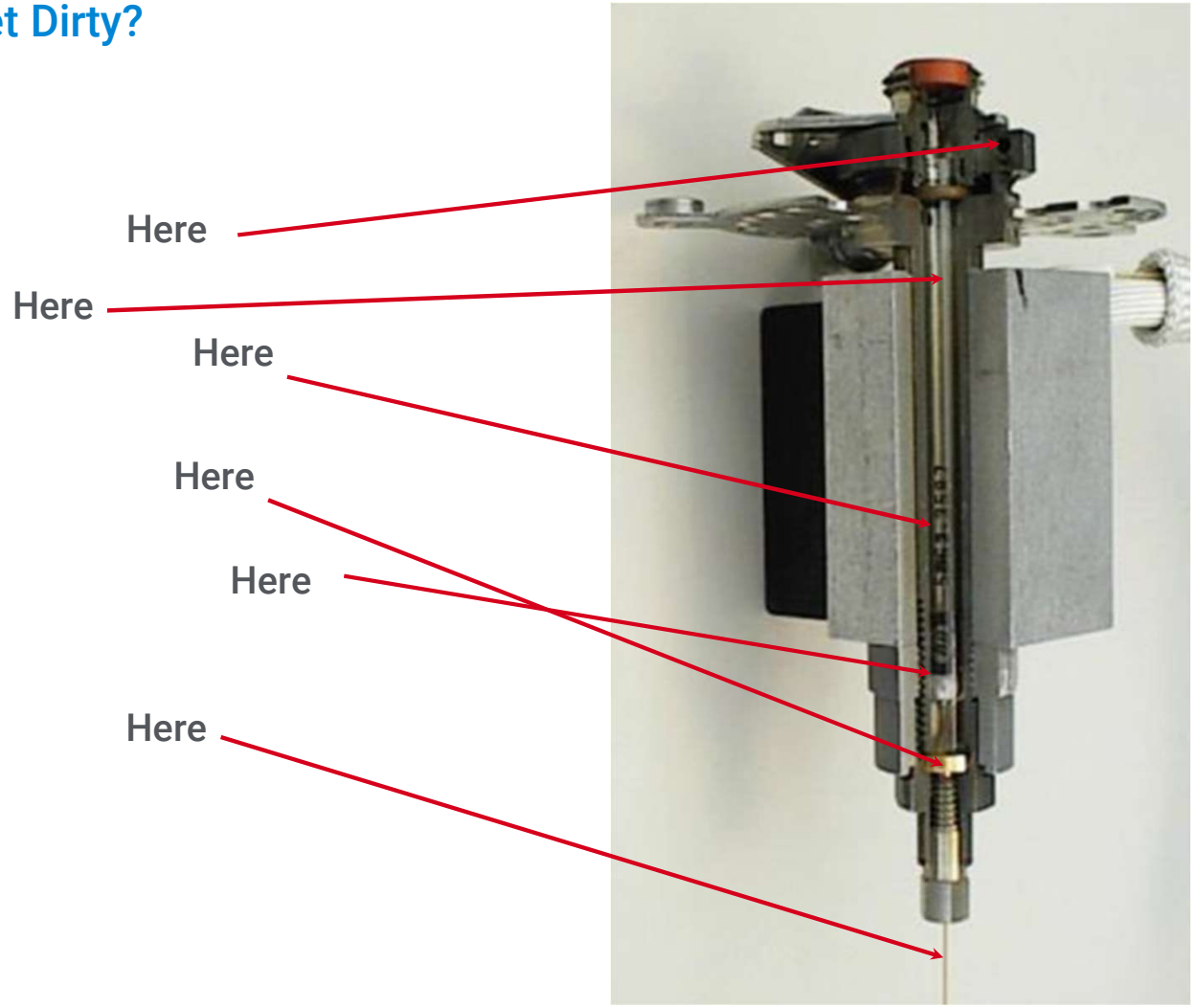
Column Cut Matters





A flat, 90° square cut will be optimal for all connections

Where Does the Inlet Get Dirty?



Common customer question: how often should I complete maintenance?

- Answer: It depends.
  - What types of samples are they analyzing?
  - Do they do any sample prep?
  - How much are they injecting?
  - What is the nature of the analytes?

Less Often — Maintenance Frequency — **More Often**

- Clean samples (gas/headspace injections, drinking water)
- Smaller sample sizes
- More sample prep (SPE, evaporation, filter)
- Smaller injection sizes
- Hydrocarbons, alcohol, solvents

Example applications:
- Blood alcohol analysis
- Residual solvents
- Volatiles in drinking water

- Dirty or high matrix samples (wastewater, soil, food)
- Larger sample sizes
- Less sample prep (Dilute-and-shoot)
- Larger injection sizes
- Active, thermally labile, acidic, or basic analytes

- **Example applications:**
  - Semivolatiles in soils
  - Pesticides in spinach extract
  - Basic drugs in urine

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Program comes with every instrument!

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Most recent version is shipped with Instrument Utilities discs, also available on SubscribeNet

Contact Agilent Chemistries and Supplies Technical Support

1-800-227-9770 Option 3, Option 2:

Option 0 for R&D testing on covid-19 virus

Option 1 for 4 digit callback number

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Questions…

Thank you for your attention