A Presentation by OI Analytical

# PFPD Training Course – Part 3
# Column Installation, Tuning, and Calculating Detectivity

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# GC Column Installation Using The PFPD Column Positioning Tool

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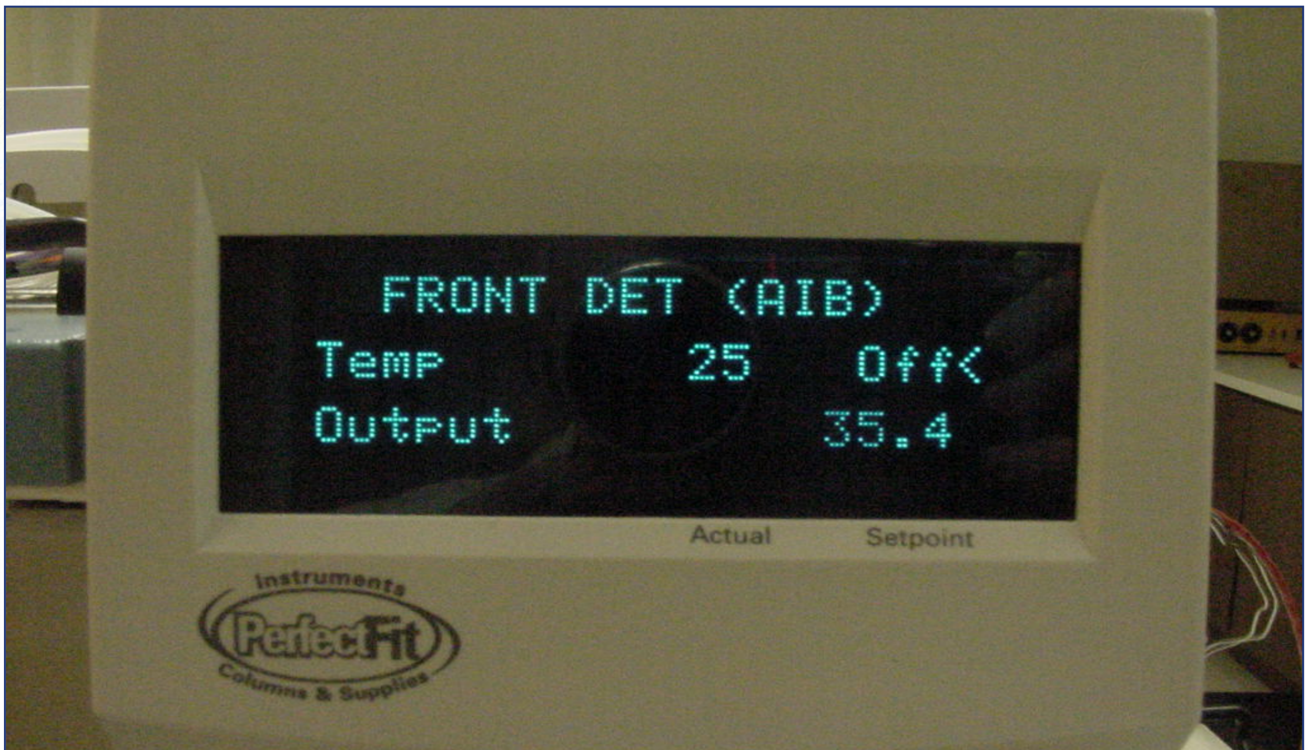
# Step 1

- Turn the detector base heater and igniter (i.e. 5380 controller) off and allow PFPD to cool completely

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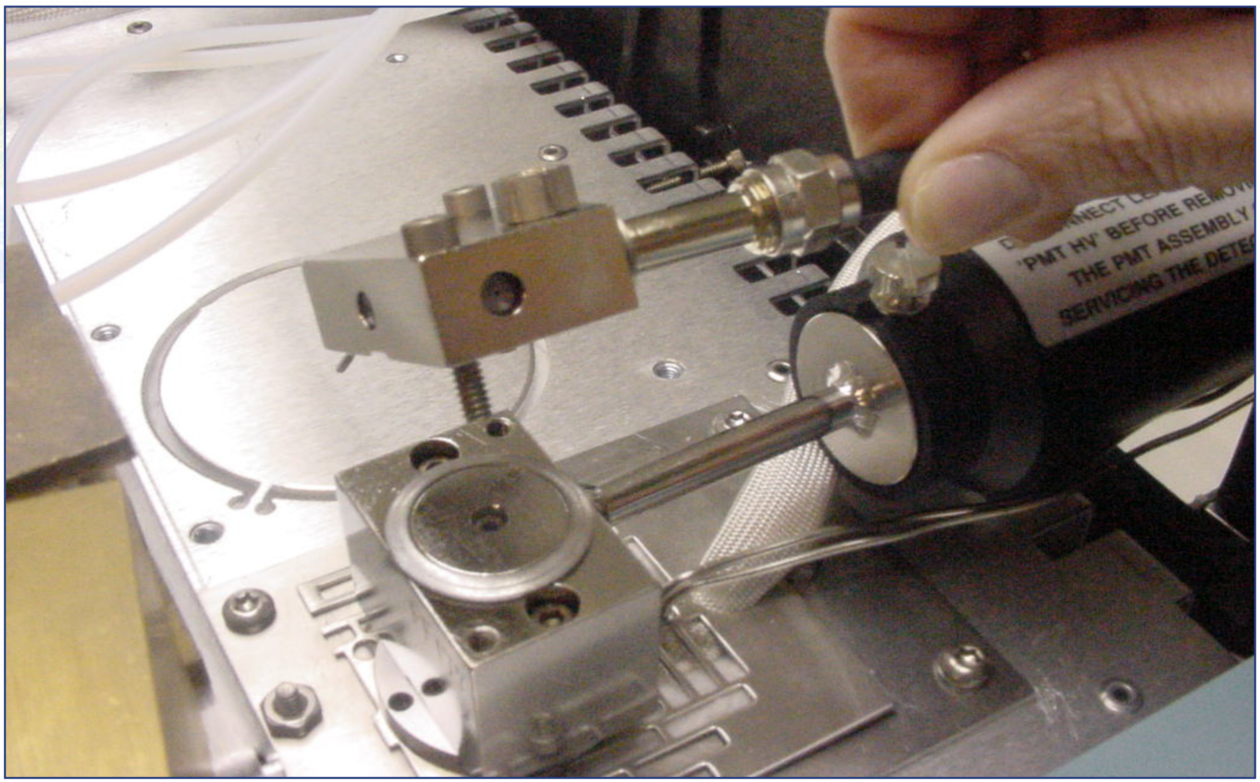
# Note

- Wait patiently for the detector to cool completely before working on it!

# Step 2

- Remove the detector cap and set it to one side on a clean surface



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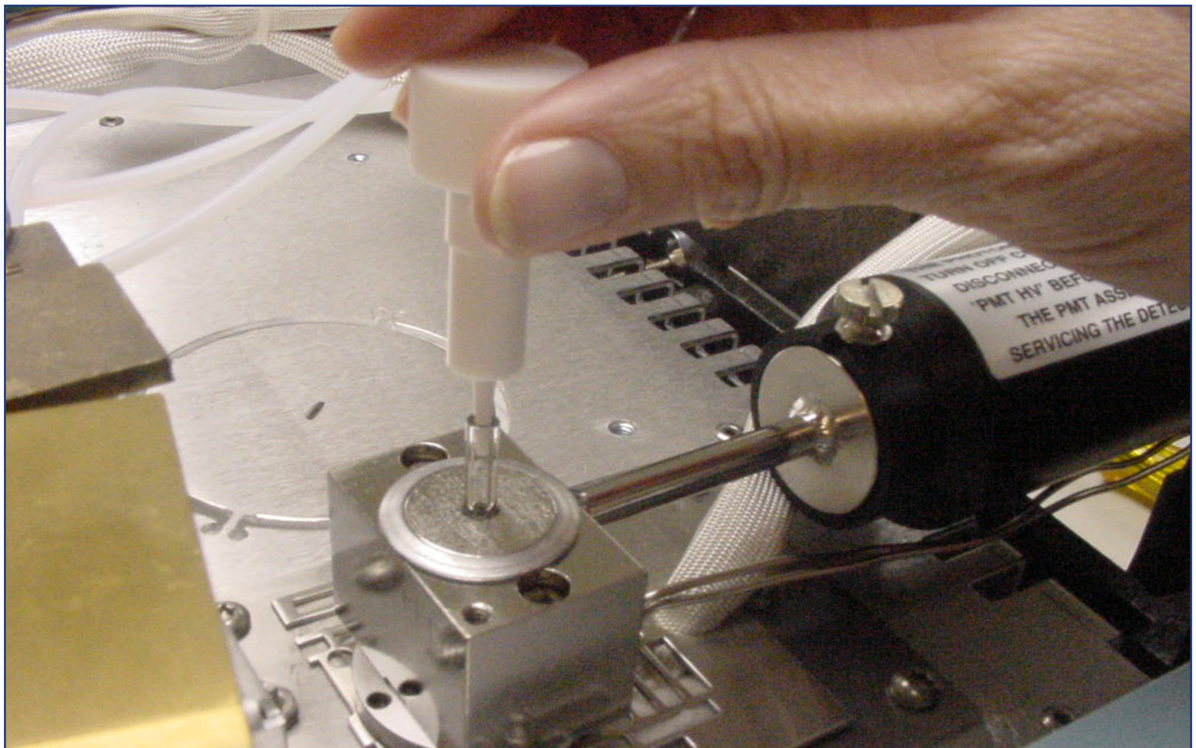
# Step 3

- Remove the combustor using Combustor Extraction Tool, cover and set aside



# Note

- Take necessary precautions to avoid contamination of combustor and inside of cap
- Use Combustor Extraction Tool to maintain proper orientation

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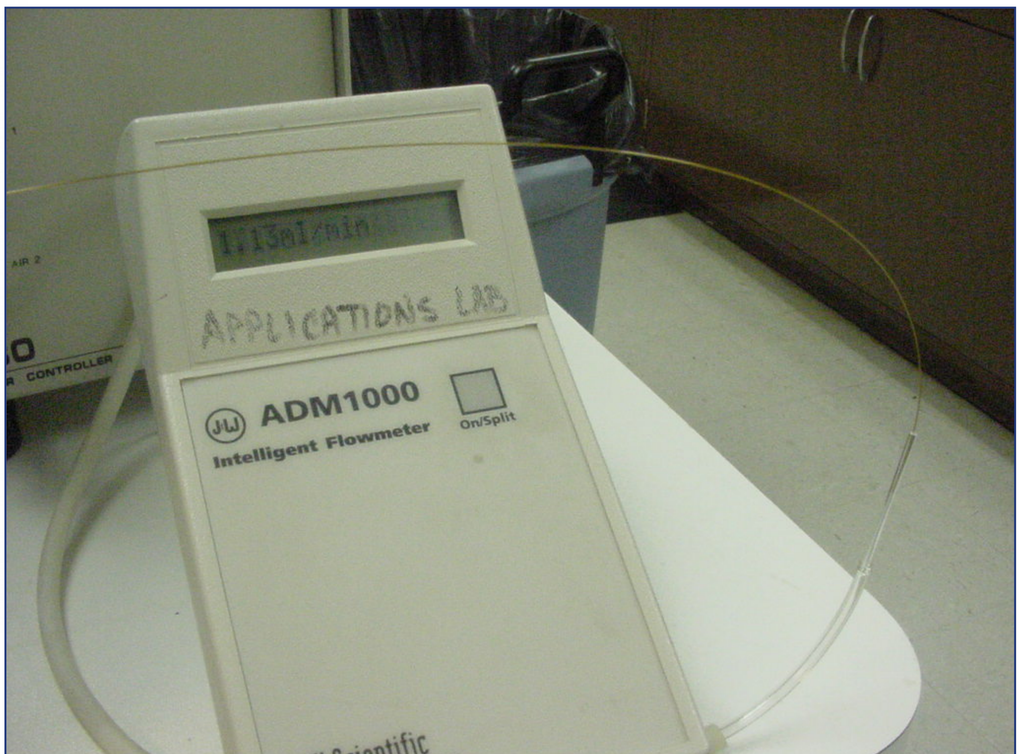
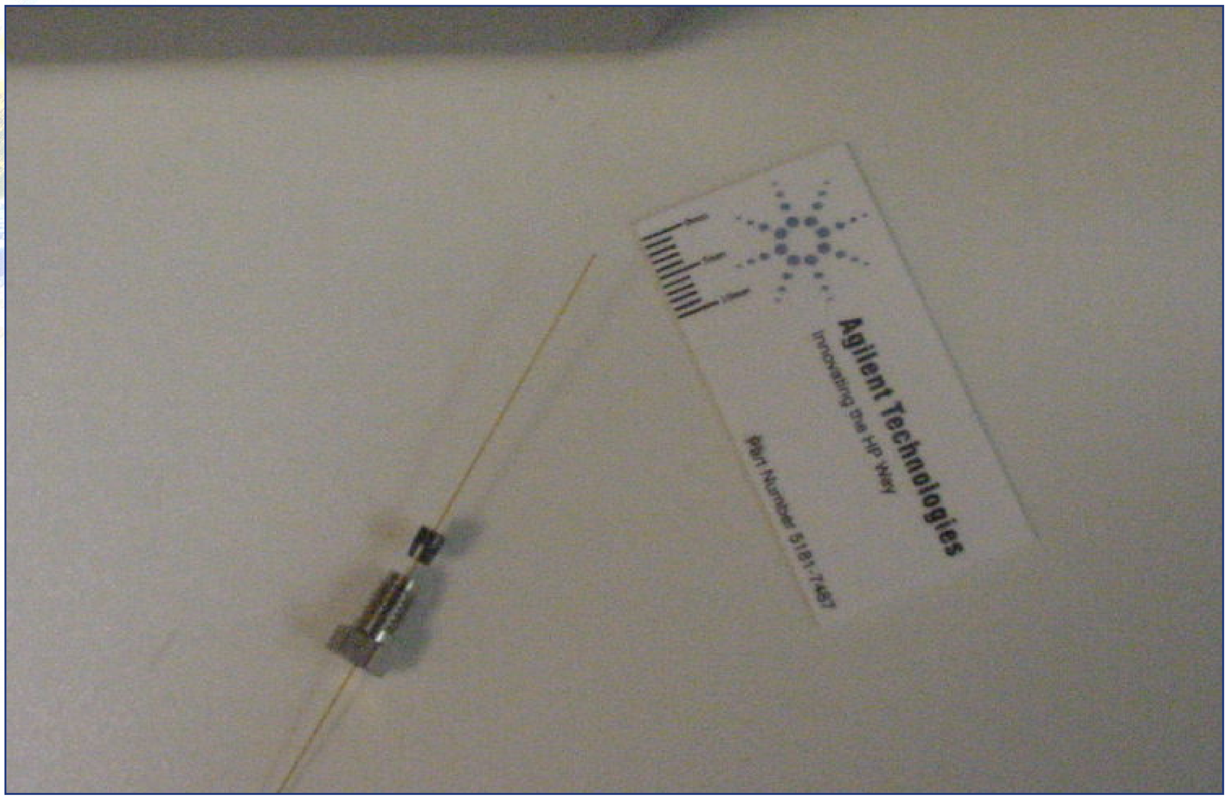
# Step 4

- Measure GC column flow
- Optimally should be < 2 mL/min for He
- Record actual column flow and set point



# Step 5

- Place nut and ferrule on column
- Make clean column cut

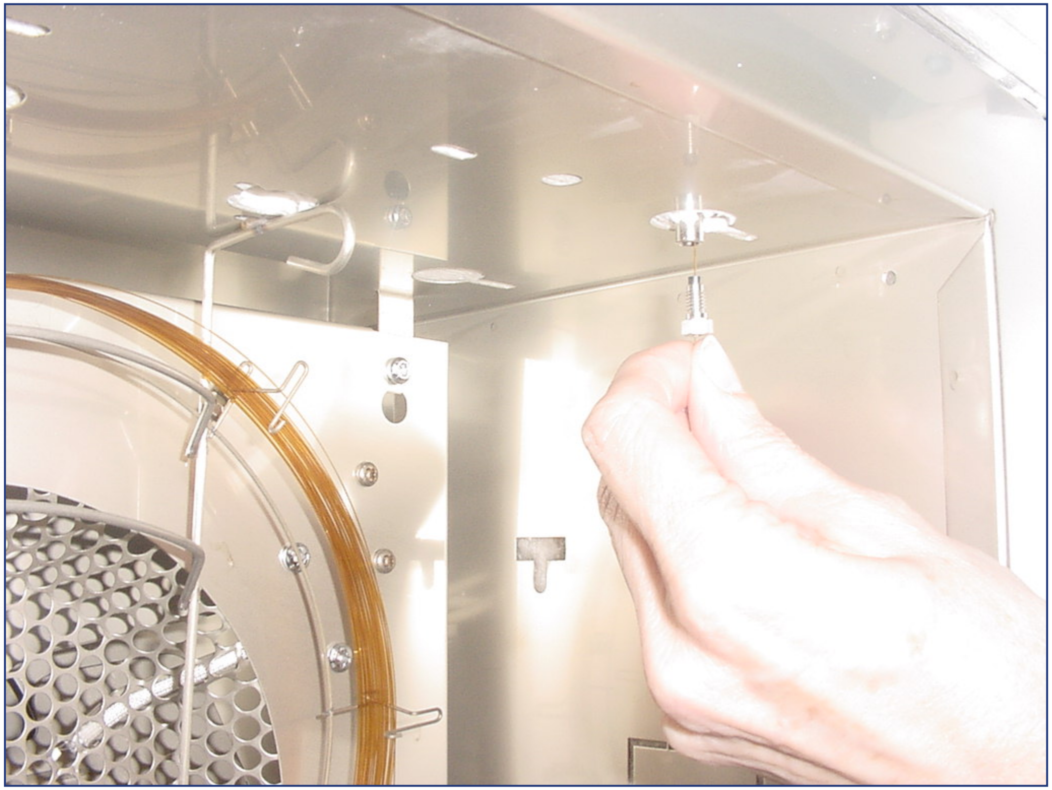


# Step 6

- Wipe column clean using a tissue dampened with MeOH

# Step 7

- Insert the column into the base of the detector, being careful not to damage the end of the column



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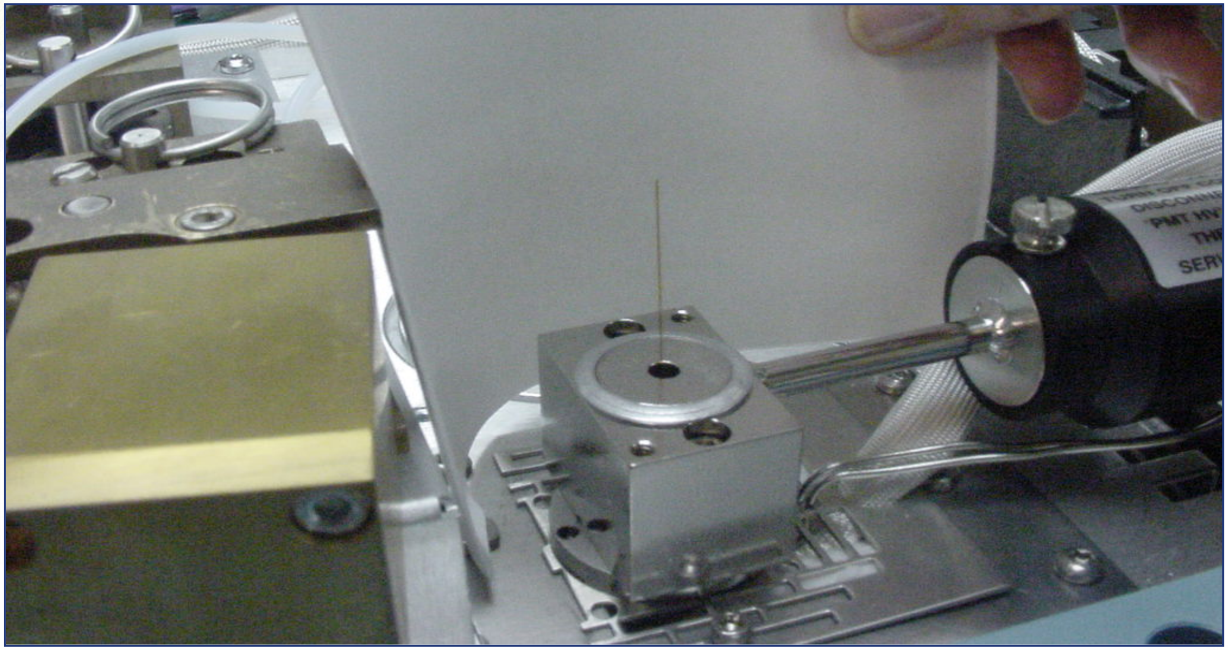
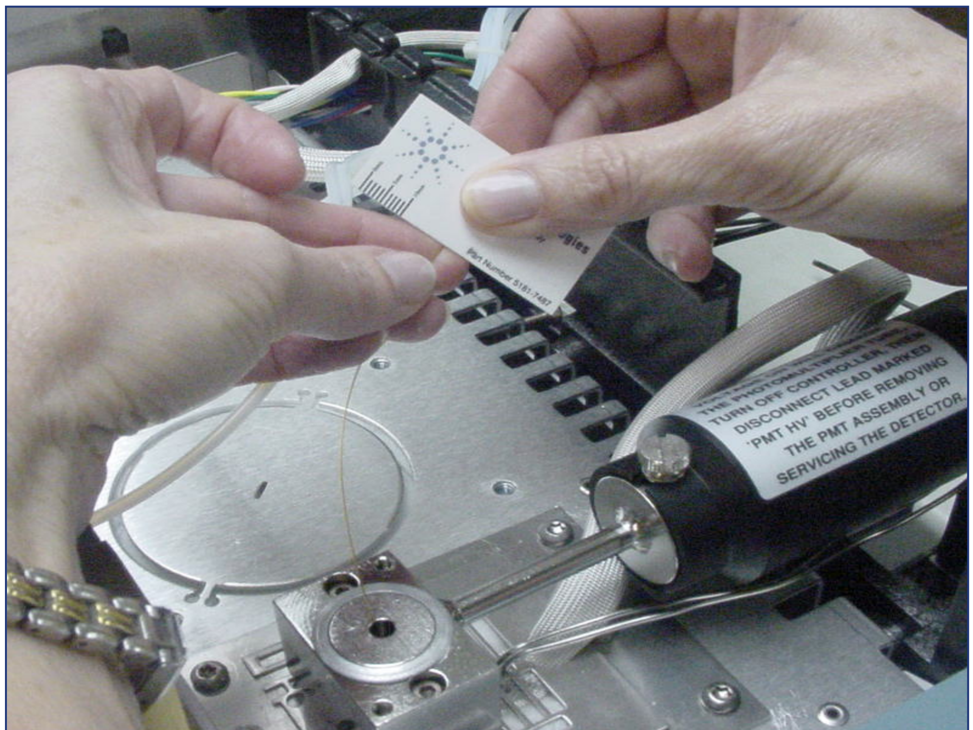
# Step 8

- Push the column up until it extends several inches past the top of the detector body
- Gently snug the column nut so that column doesn’t fall back through



# Step 9

- Bend column to one side and re-score
- Take care not to let small pieces of column drop back into the detector body

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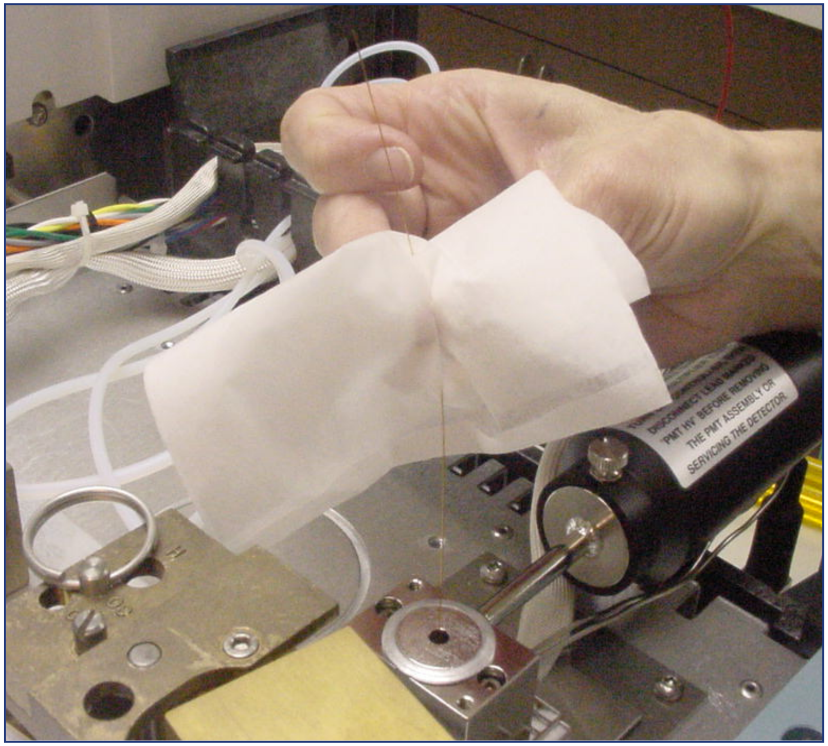
# Step 10

- Wipe the column clean again with a tissue and MeOH to remove dust, bits of column, fingerprints, etc.



# Note

- Don’t stop to answer the phone, just let them leave a message with Audix

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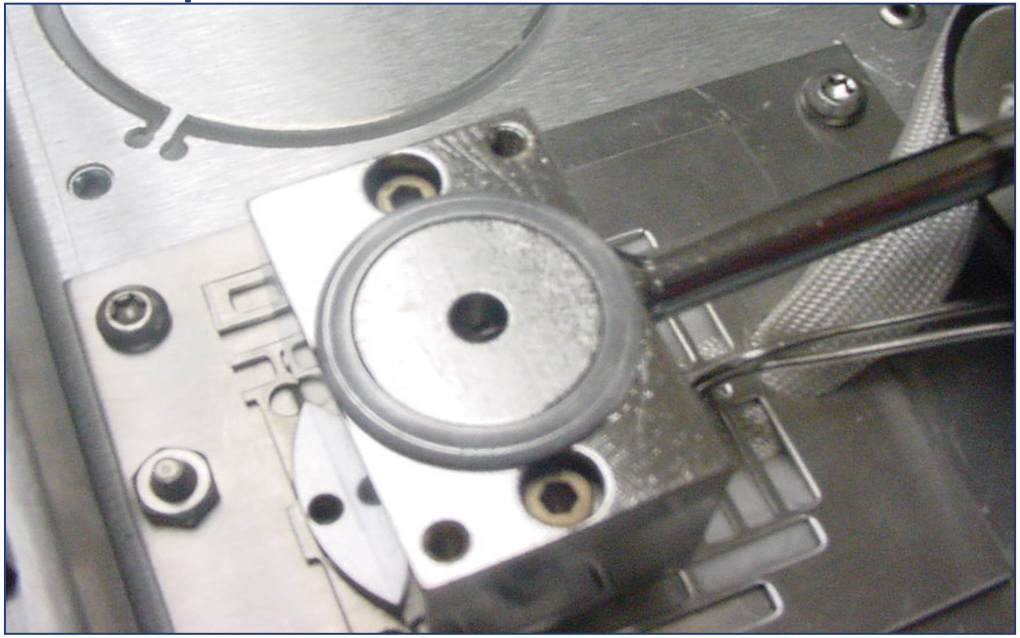
# Step 11

- Retract the column back into the detector body until it is below the level of the combustor support (may take some practice)



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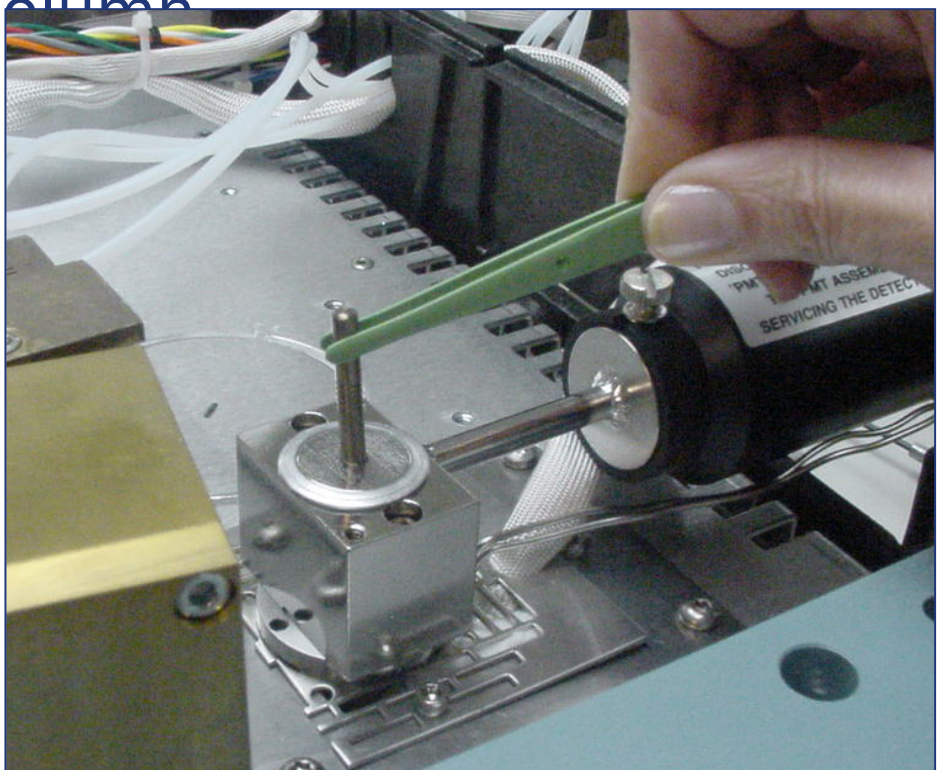
# Step 12

- Using the teflon coated forceps, remove the Column Positioning Tool from its plastic bag
- Important to keep the tool clean, as it will be placed inside the detector body

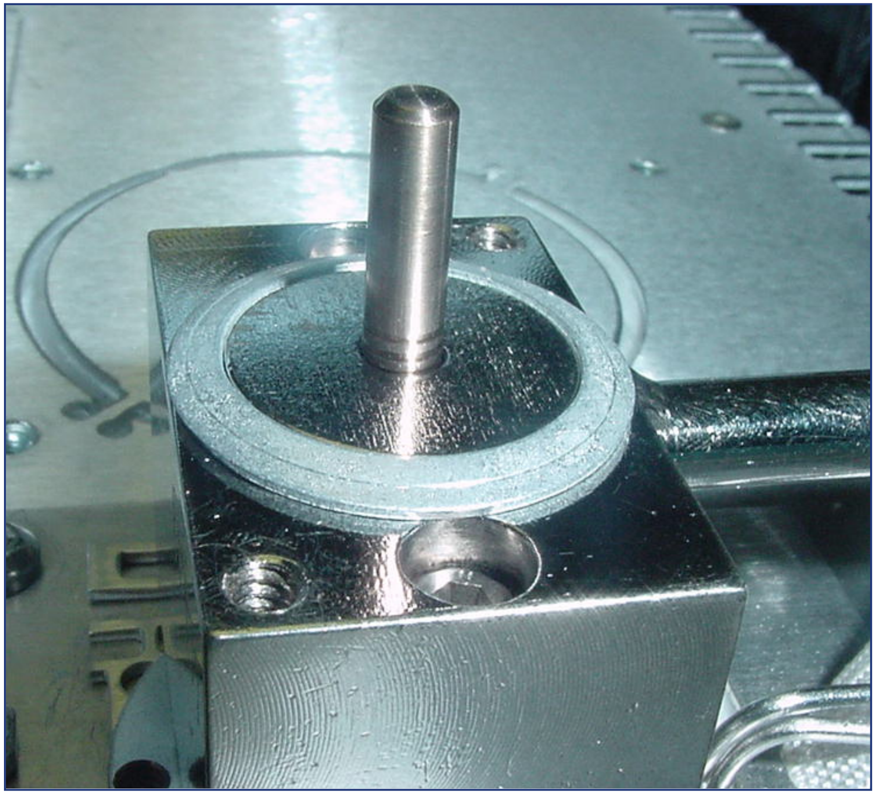
# Step 13

- Carefully place the Column Positioning Tool inside the detector body
- Take care not to drop it on the end of the column



# Step 14

- Manually adjust column position until it is pushing up against the bottom of the tool



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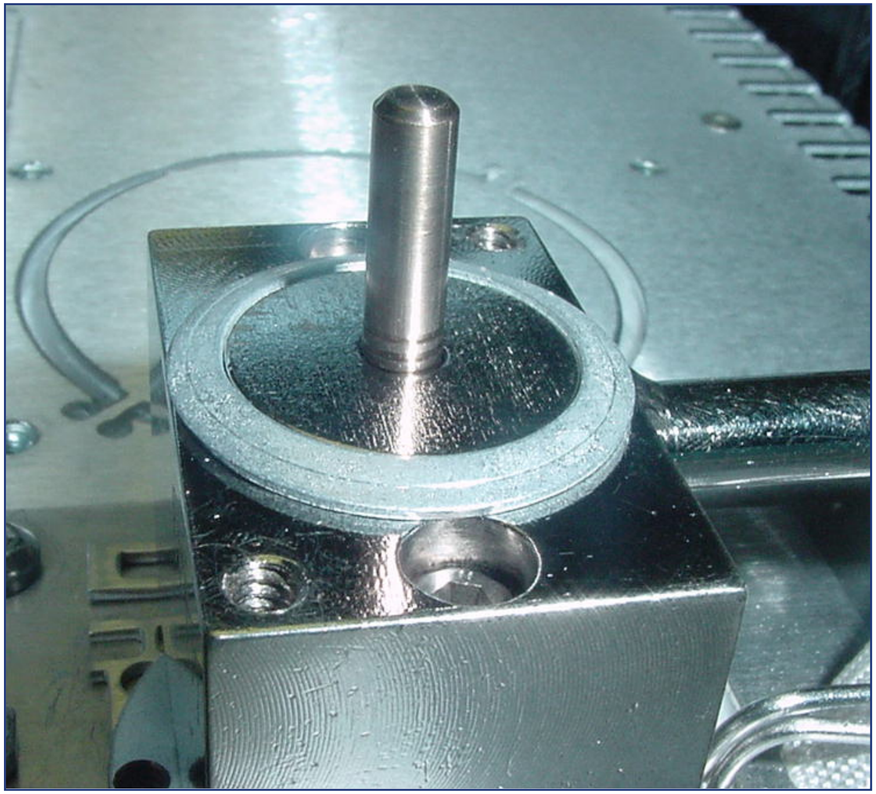
# Step 15

- Use the grooves as a guide to move column up by ~ 1mm (grooves are 1 mm apart)
- Column height should not exceed 1.5 mm



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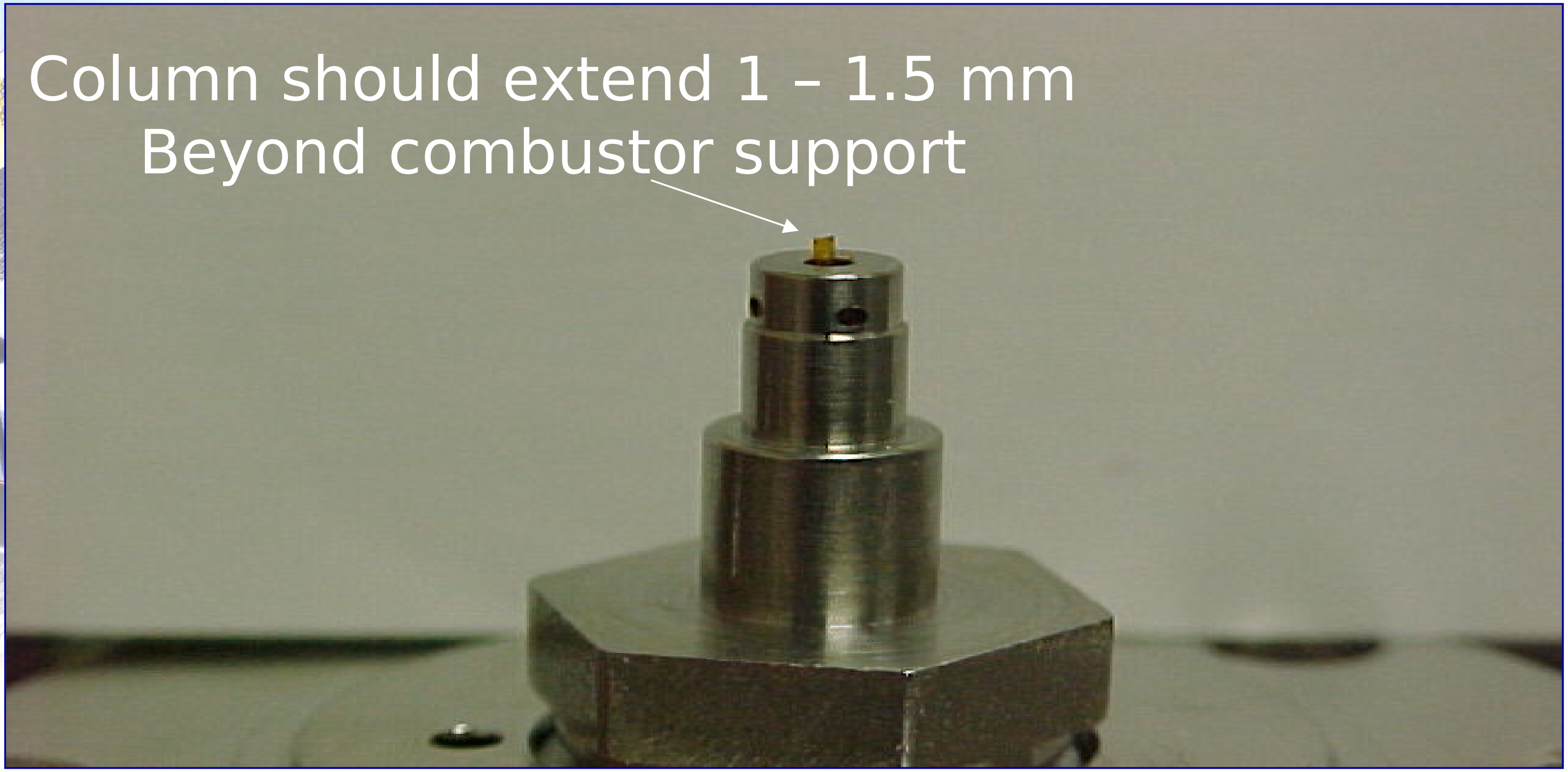
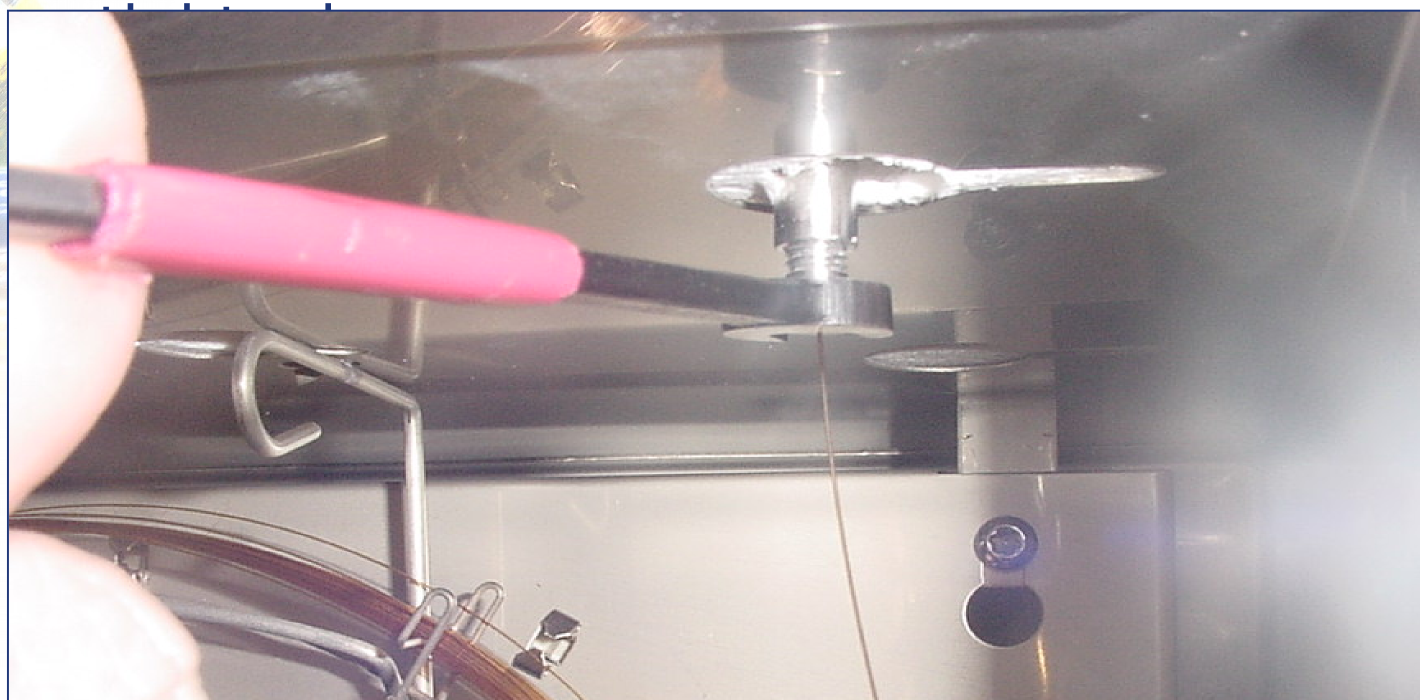
# Proper Column Position




The column can also be installed without the column positioning tool.

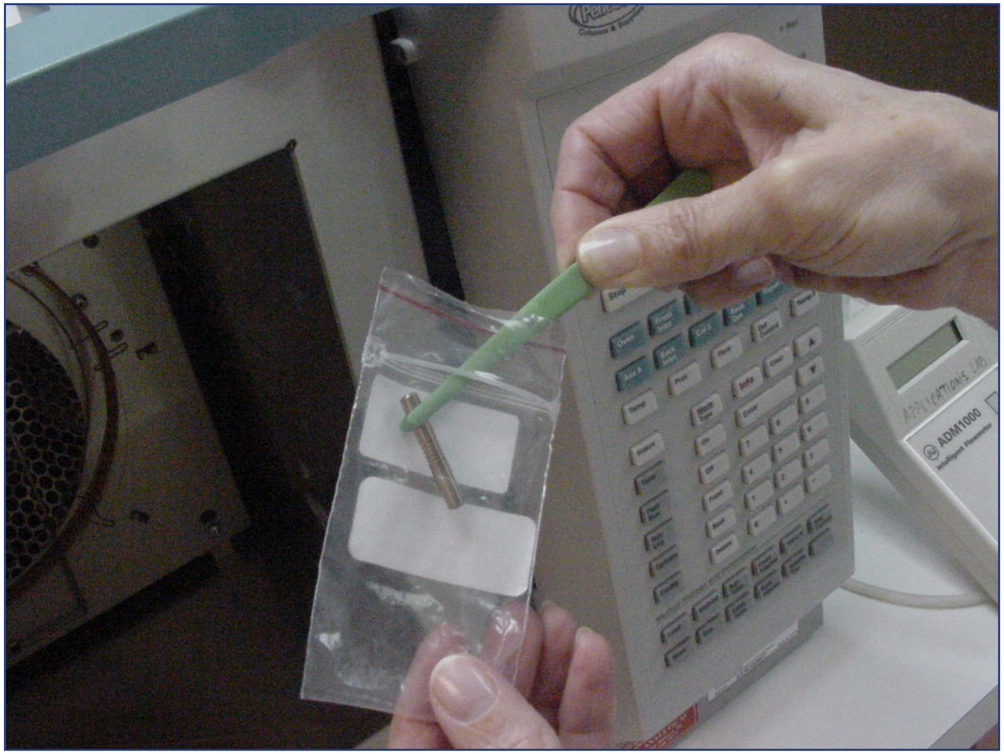
# Step 16

- Tighten the column nut at the base of the detector
- Column may raise up slightly with



# Step 17

- Use the teflon coated forceps to remove the Column Positioning Tool and return it to the plastic bag



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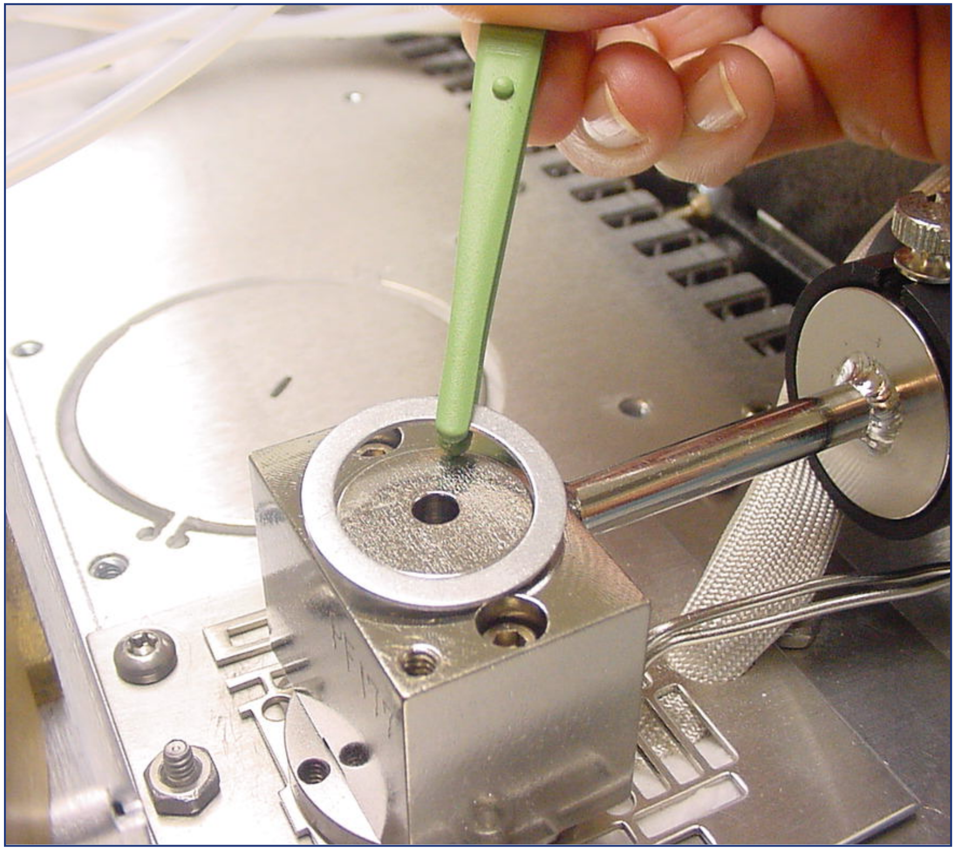
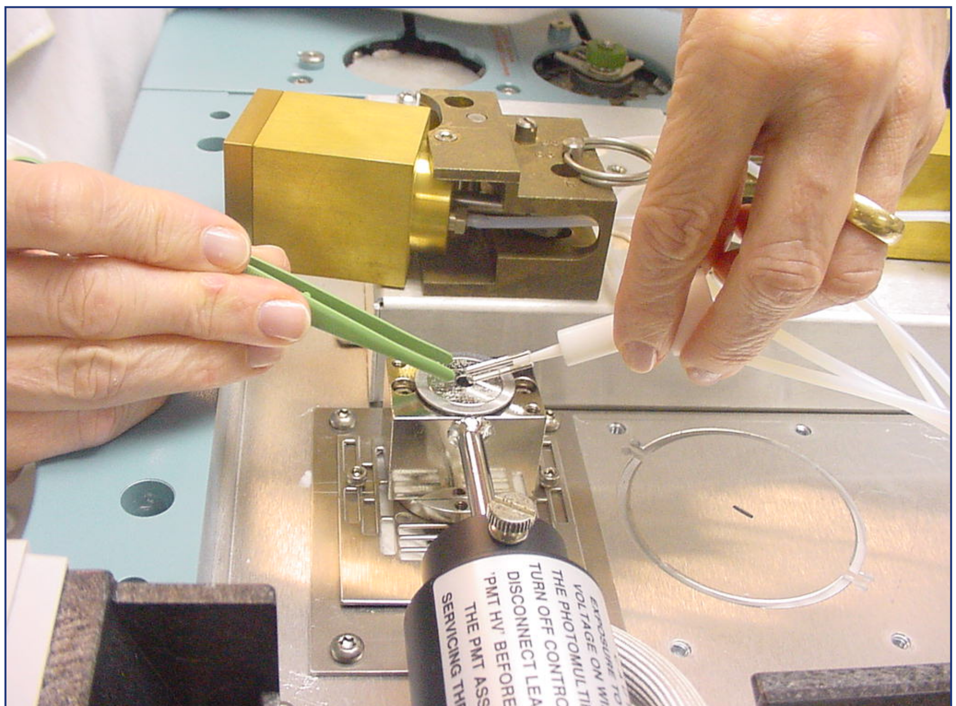
# Step 18

- Replace the aluminum crush washer



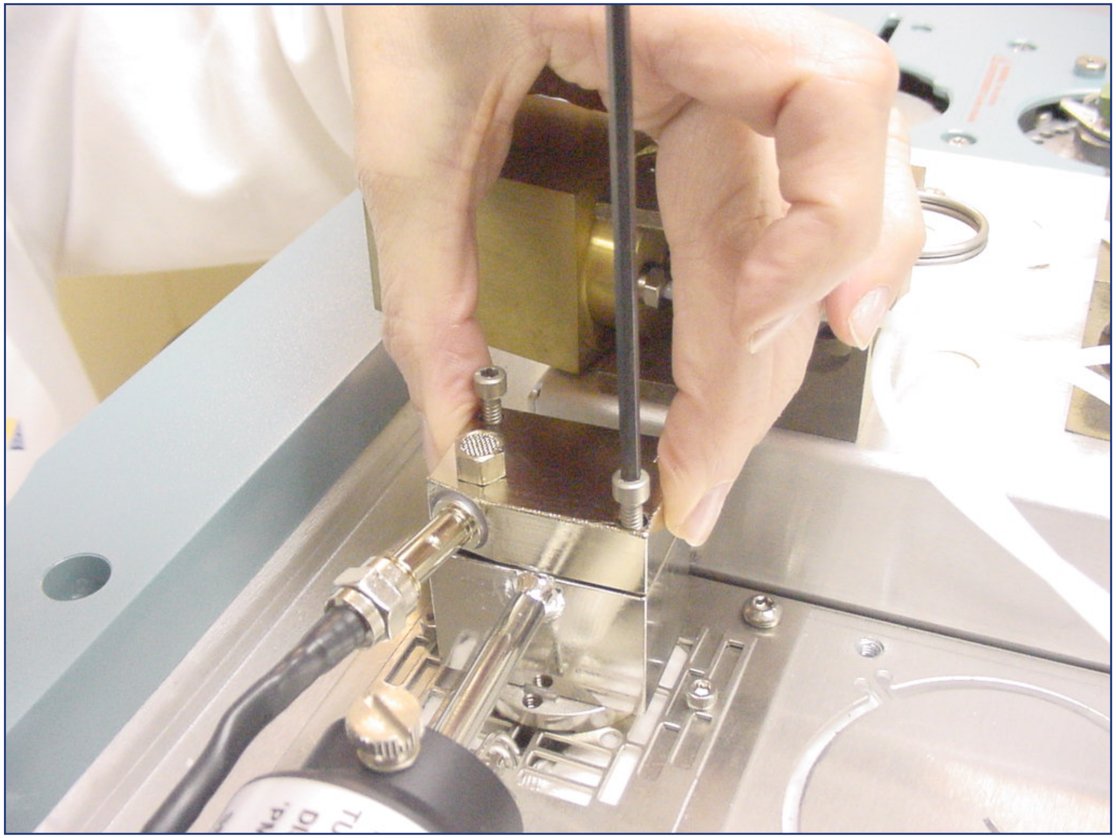
# Step 19

- Carefully re-install the combustor
- Use only the Combustor Extraction Tool and the forceps
- Maintain combustor orientation



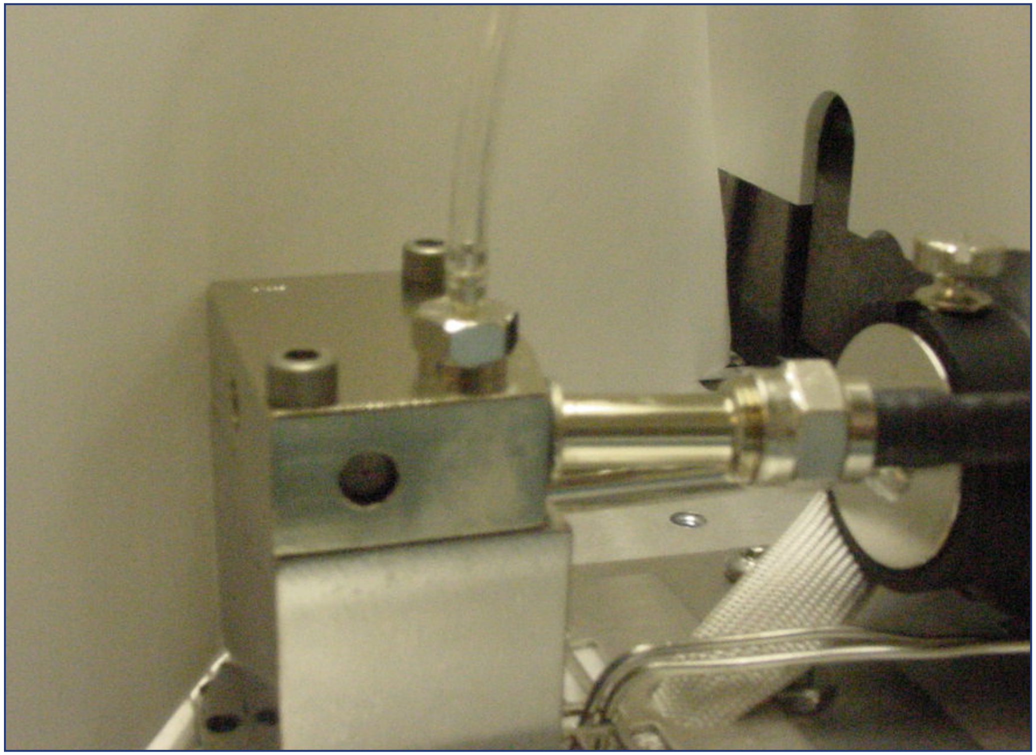
# Step 20

- Re-install the detector cap
- Monitor position of the crush washer



# Step 21

- Use flow-adaptor to re-measure column flow
- Should be within 0.2 mL/min of column flow measured in Step 4, otherwise check for leaks



# Step 22

- Continue to set remaining PFPD $H_2$ and Air flows, or if already set
- Turn on detector body temperature (250°C for sulfur) and wait for it to reach ~100°C
- Turn on 5380 controller
- Detector should begin pulsing within a few moments

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# PFPD Tuning Tips:

# Procedure For Setting The Gas Flows That Will Work Every Time!

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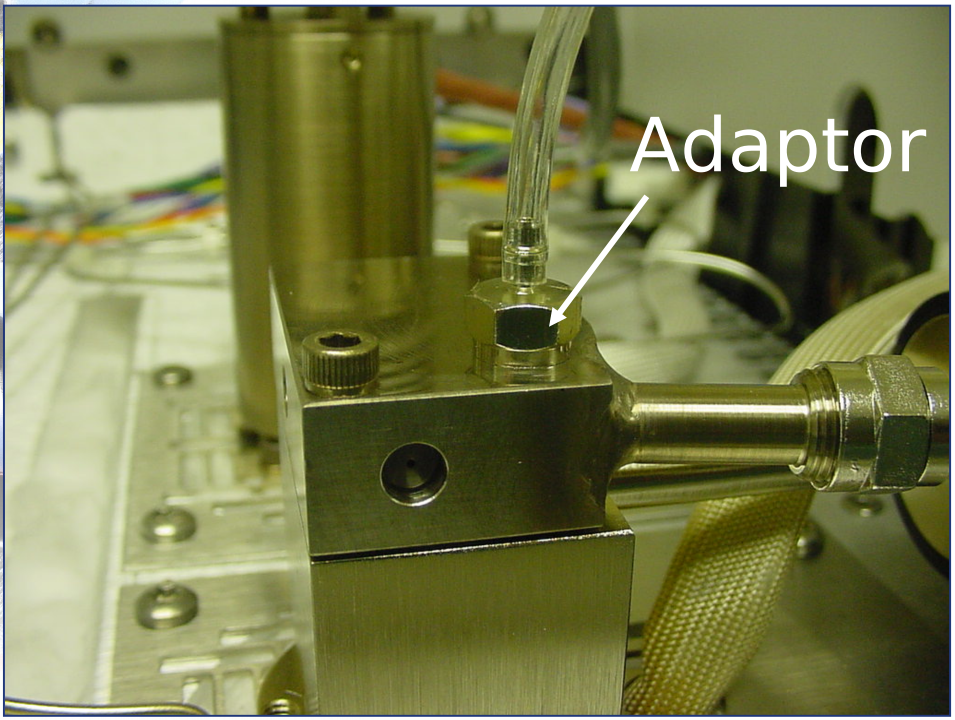
# Step 1

- Turn off the detector body temperature and the 5380 PFPD controller, and allow the PFPD to cool completely
- Turn off all gas flows and close the fine adjust needle valve

# Note

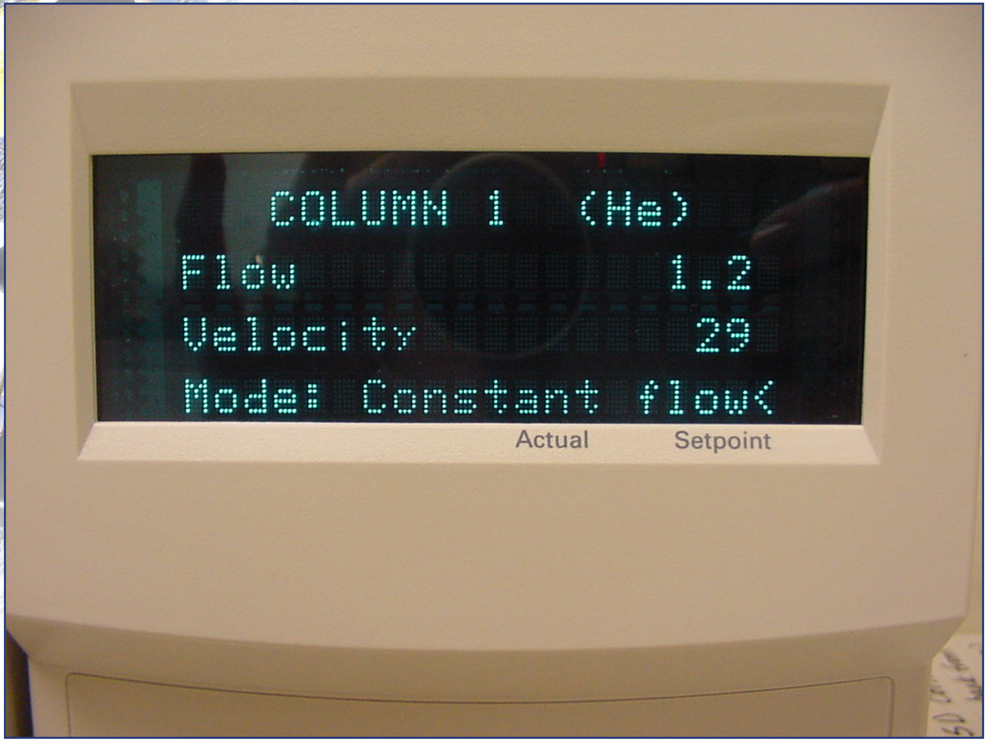
- For models with the manual flow controls, the fine adjust valve is at the top of the controller
- For models with the EPC flow control, the fine adjust valve is on the top of the GC
- Take care not to over tighten

# Step 2




- Use the flow measurement adaptor to attach your flow meter

# Step 3



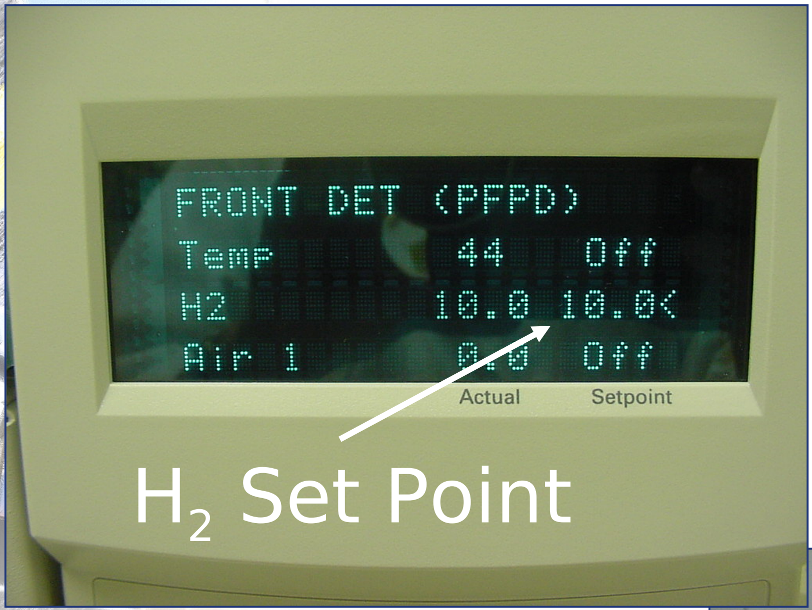

- Set column flow
- Optimum gas setting is < 2 mL/min
  - *He or $H_2$*
  - *Higher flows can be used however may not give optimum performance*
- Where available, always use “Constant Flow” mode
- Record both the measured column flow and the set point

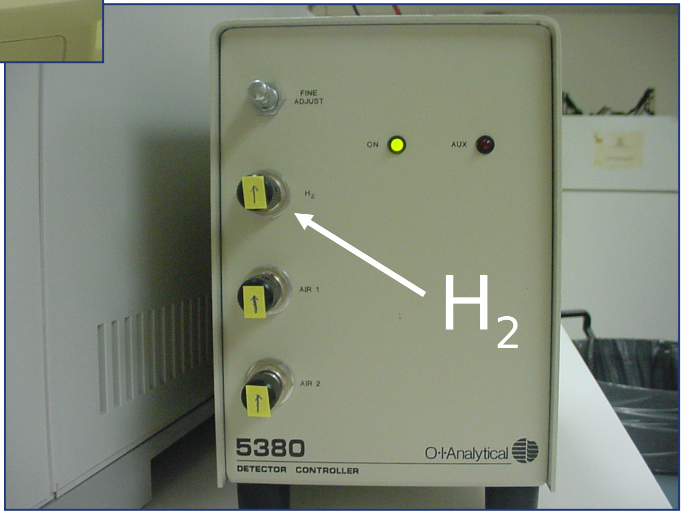
# Step 4


- Open the fine adjust needle valve 3 turns (anti-clockwise)

# Step 5

- Using flow meter, add 11.5 mL/min of $H_2$
  - *If $H_2$ is carrier gas, TOTAL of carrier + detector $H_2$ should be 11.5 mL/min*
- Be sure to include the measured column flow

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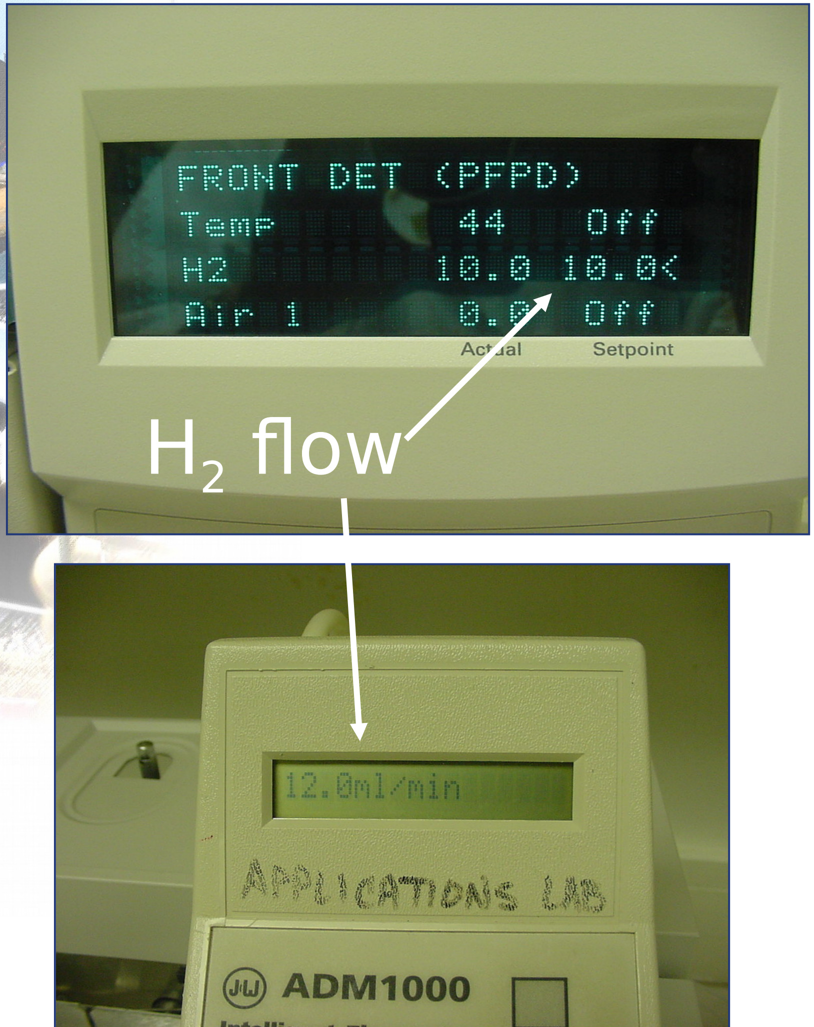
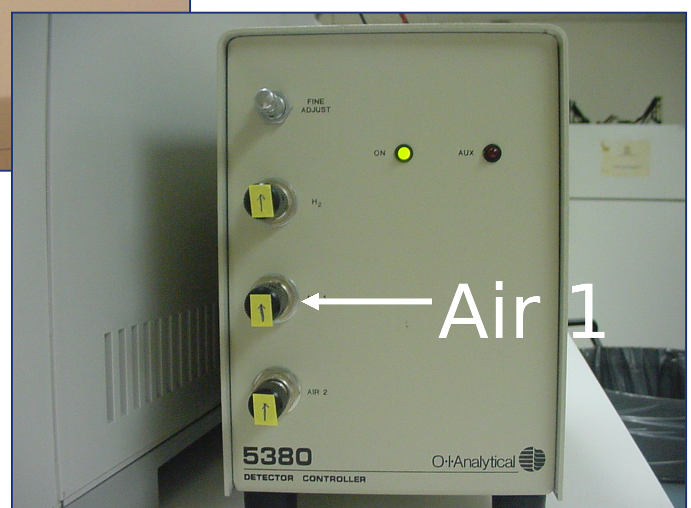
# Note




- For models with EPC, the readout on the flow meter <u>*will not match*</u> the set point on EPC module
- This is normal
- **ALWAYS! Use the <u>measured</u> flow rate to determine when you have the flows set properly**

# Step 6

- Using flow meter, add 10.0 mL/min of Air 1
- Be sure to include the previously measured flows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# Step 7


- Using flow meter, add 10.0 mL/min of Air 2 (Makeup)
- Be sure to include the previously measured flows

- Air 2 is called “Makeup” on the EPC module


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# Step 8



- If using an EPC module, record these “Setpoints”
  - *$H_2$*
  - *Air 1*
  - *Air 2*
  - *Column Flow*
- If using a manual flow control module, mark the position of the knobs (I used tape and arrows in these pictures)

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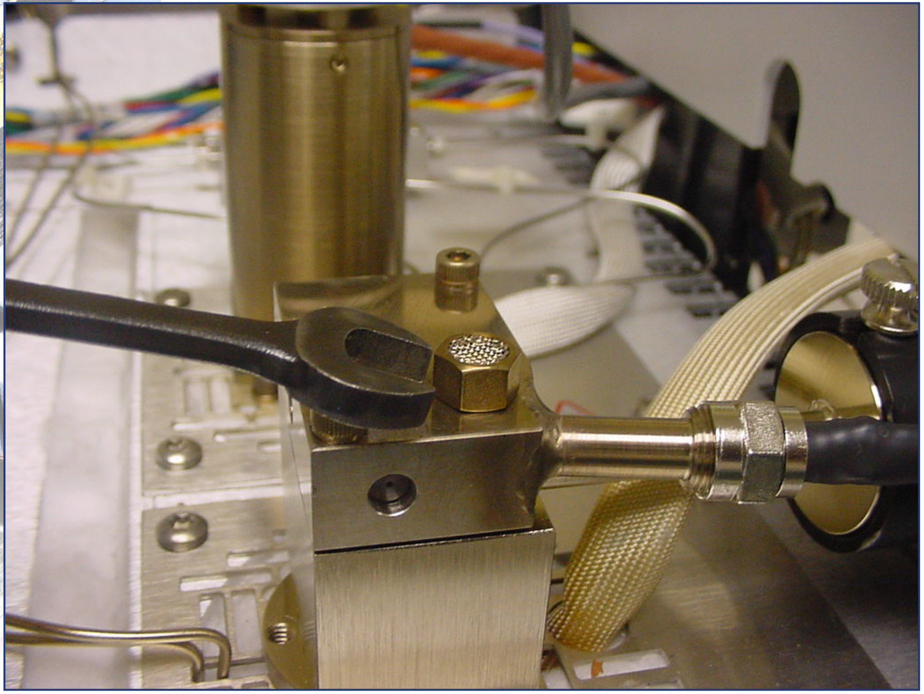
# Step 9



- Remove the flow adaptor and reinstall the flame arrestor

# Step 10


- Turn on the detector base temperature, and wait for it to reach ~100°C
- Turn on the 5380 PFPD controller (turns on the igniter)
- The PFPD should begin pulsing within a few moments
- Wait for all temperatures and the PFPD pulse frequency to stabilize before proceeding to final tuning

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# PFPD Tuning Tips:
# Final Tuning of The Gas Flows

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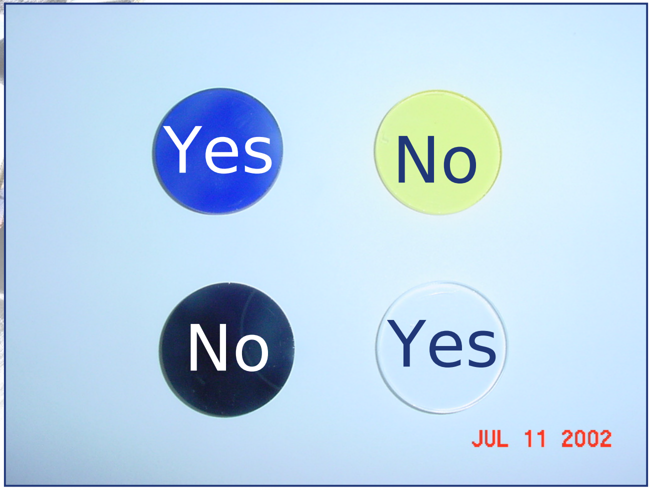
# “The Whole Story”

- The PFPD real time display of the emission profile contains a wealth of information
  - *Gases optimized*
  - *Contamination*
  - *Column position*
- Learn to “read” the emission
  - *Determine PFPD performance*
  - *Diagnose problems*

# Note




- This procedures uses a sulfur source for tuning because of its simplicity, but works very nicely for most phosphorous applications as well.
- Please be sure that you have either the blue or the clear filter installed before proceeding.  Don't use the yellow filter.

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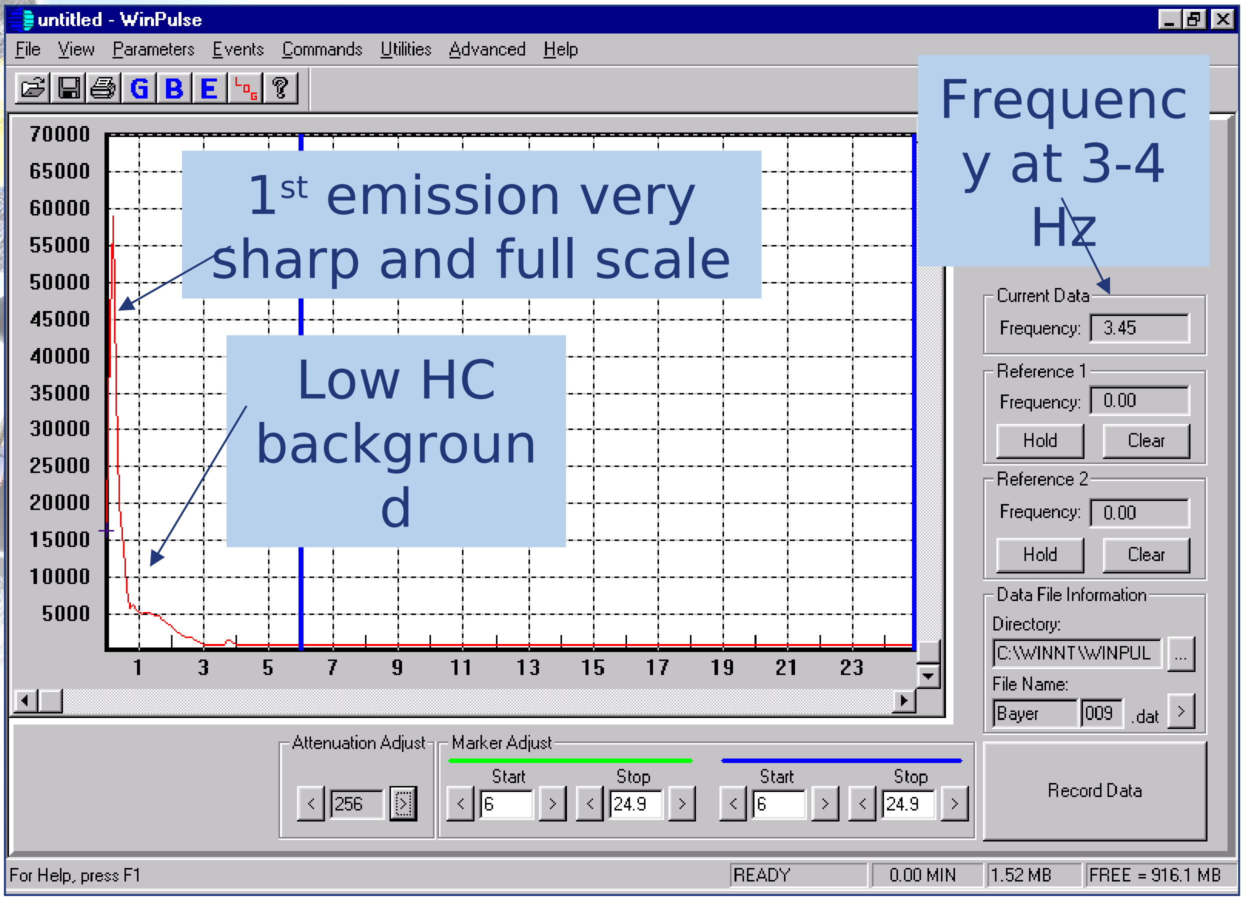
# Step 1




- Wait for all temperatures and pulsing frequency to stabilize
- Check WinPULSE screen for “normal” emission

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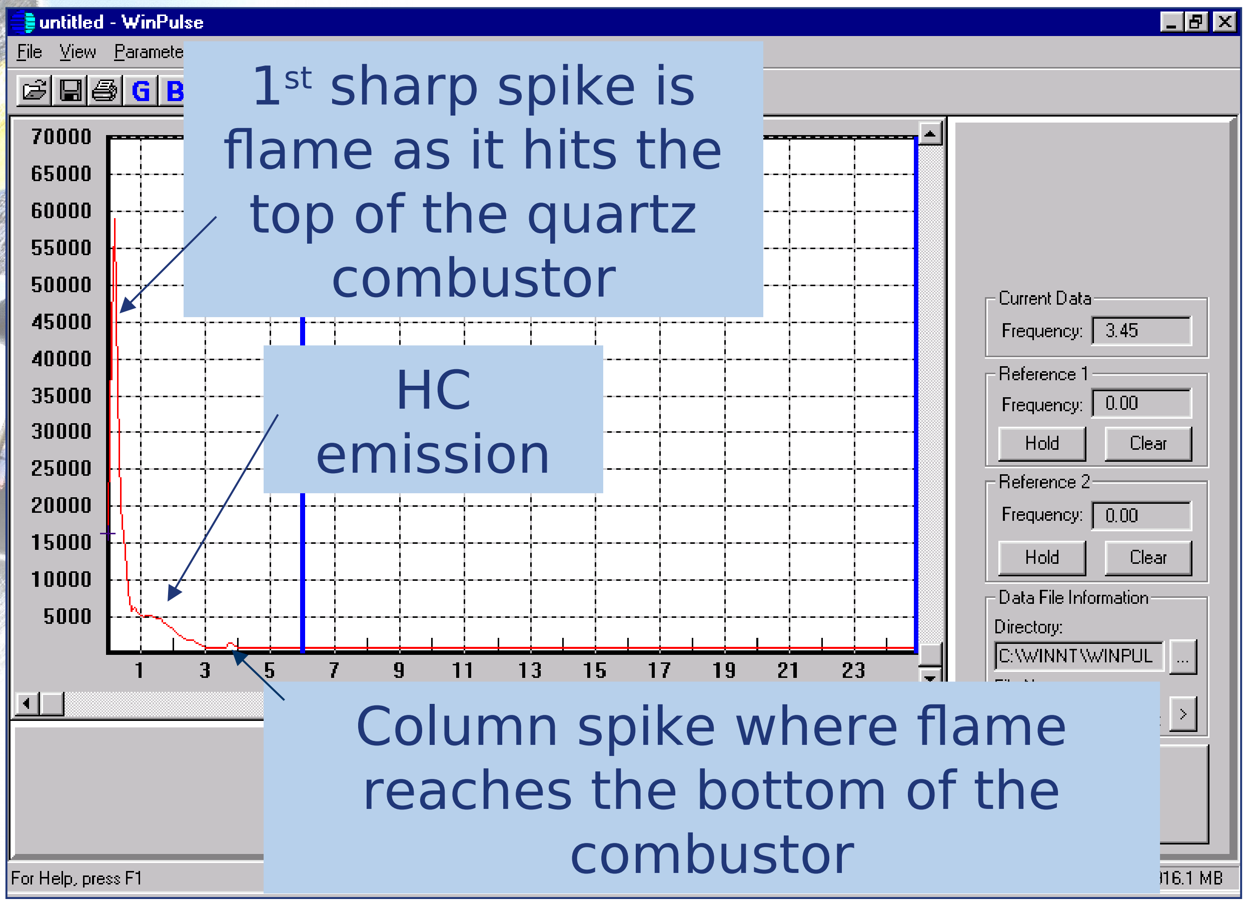
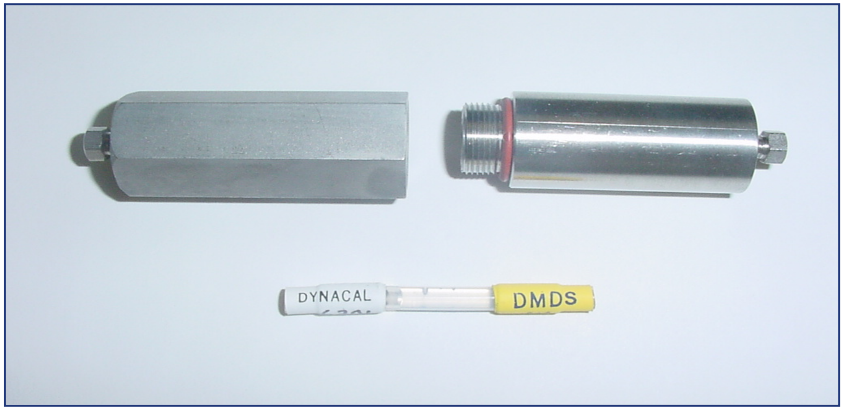
# “Read” the Emission




- Wait for all temperatures and pulsing frequency to stabilize
- Check WinPULSE screen for “normal” emission

# Step 2

- Introduce a source of sulfur for tuning the gases
  - *Permeation device (shown below)*
  - *Matrix containing lots of sulfur peaks (e.g. gasoline, onion or garlic extract, etc.)*
  - *Known sulfur standard (e.g. calibration mix)*

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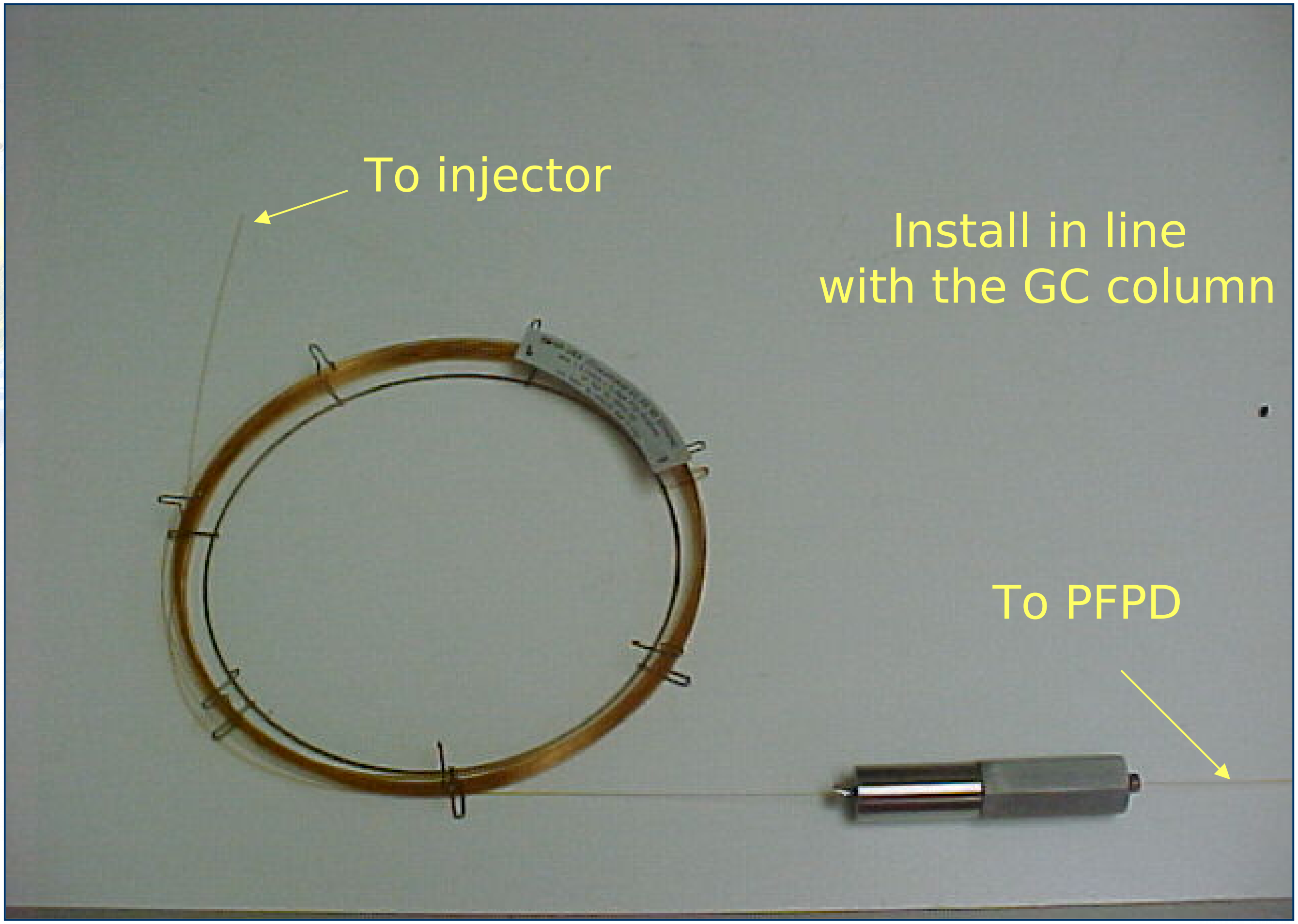
# Perm Device Installation

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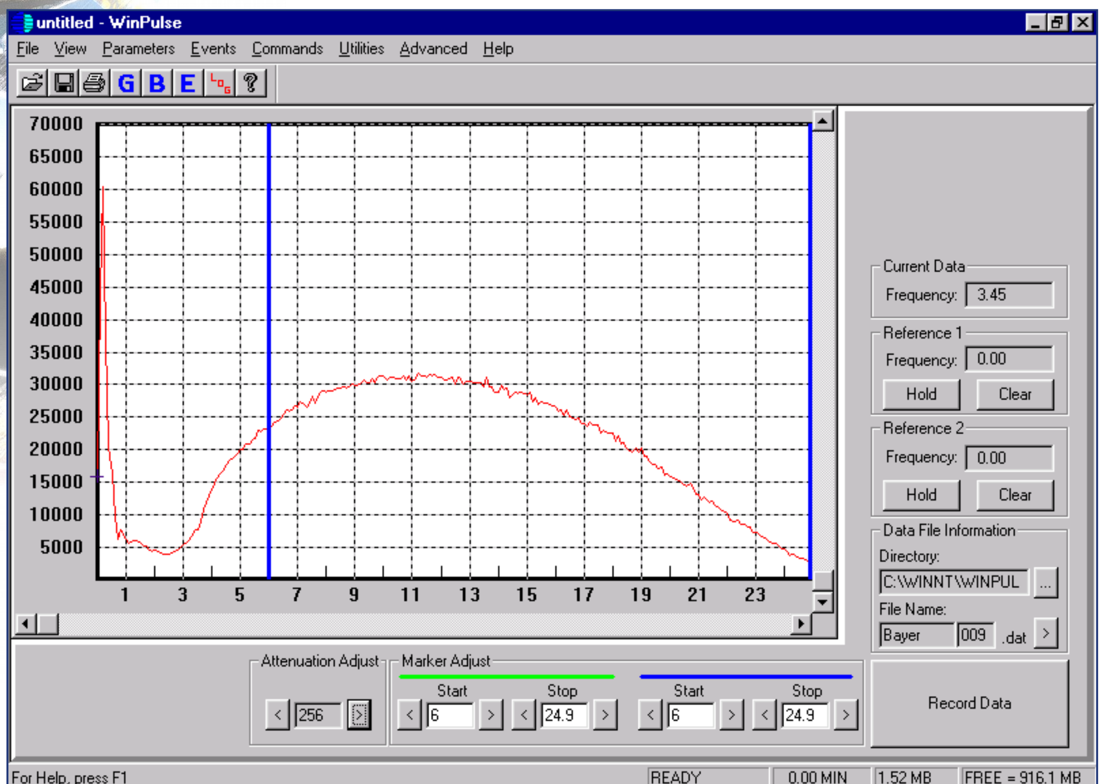
# Step 3

- Check WinPULSE screen for proper appearance of sulfur emission




<u>Important Emission Features</u>:

Characteristic shape

Extends all the way out to 25 msec with 2mm combustor

Slightly shorter lifetime, ~20msec

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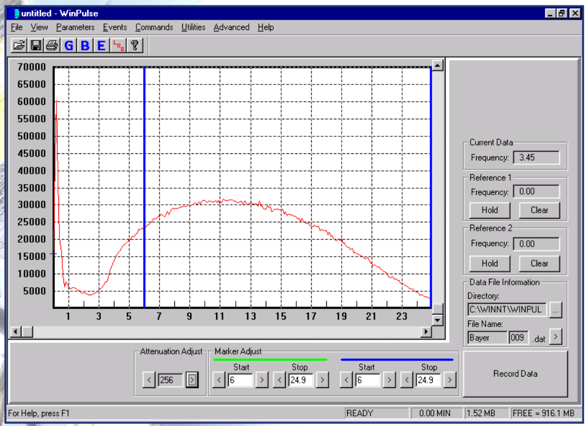
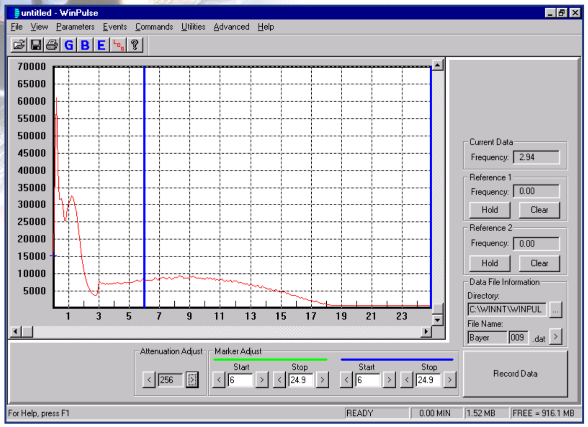
# Notes





- Your emission profile may not have this characteristic appearance initially
- It may look more like the bottom picture. Don't panic!
- The shape is dependent upon the ratio of $H_2$/Air1 gas flows
- The emission shape will change as the ratio of the $H_2$/Air 1 changes
- Air2 is used to adjust the frequency (more on this later)

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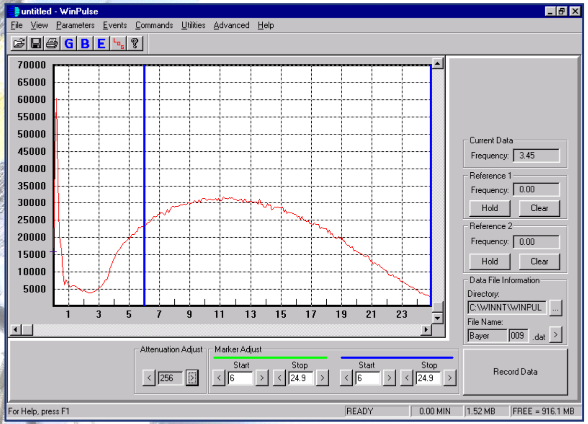
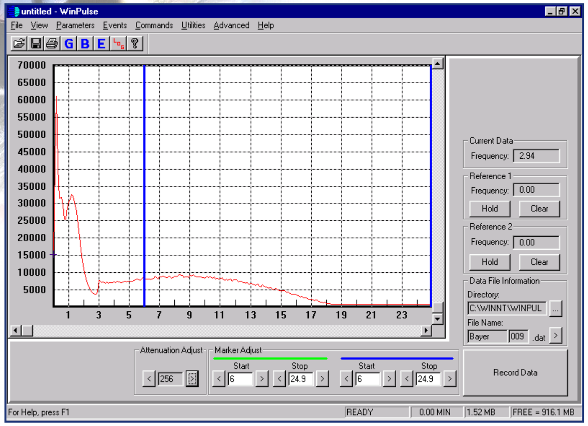
# Step 4: Adjust $H_2$/Air1 Ratio




- Adjust the $H_2$ flow up or down as necessary to achieve the best profile

  Or,

- Adjust the Air 1 flow up or down as necessary to achieve the best profile
- Since it is only the ratio of $H_2$/Air1 that determines the shape, you only need to adjust one or the other, not both (I usually use $H_2$)

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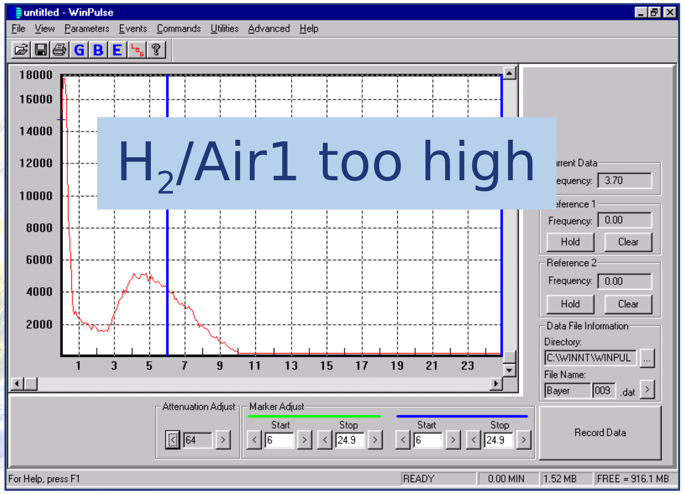
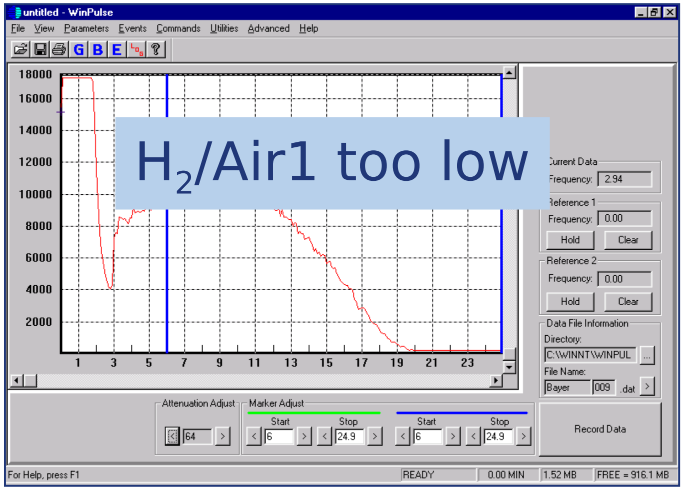
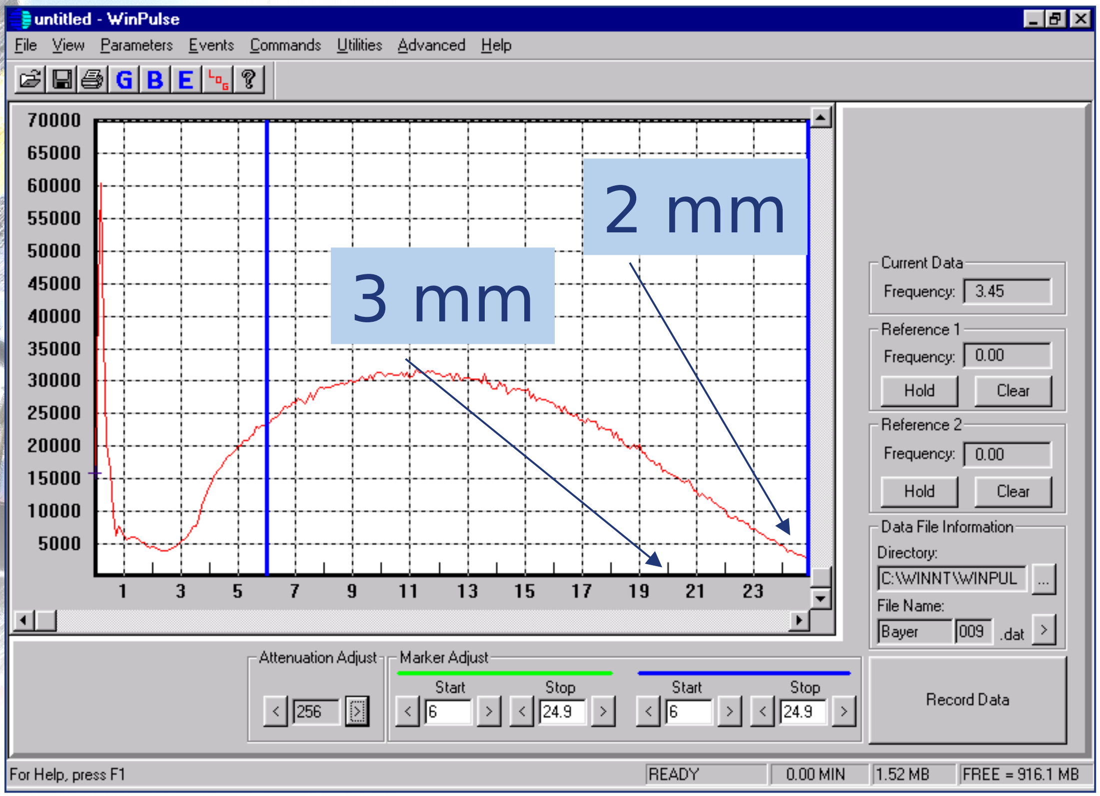
# Notes




- $H_2$/Air1 ratio too high or too low may give similar emission profiles
- Be sure to adjust $H_2$ in both directions until the optimum emission profile is attained

# Notes




- A perfect sulfur emission should look like this when done with the 2 mm combustor
- With a 3 mm combustor, the emission will only extend out to about 20 msec

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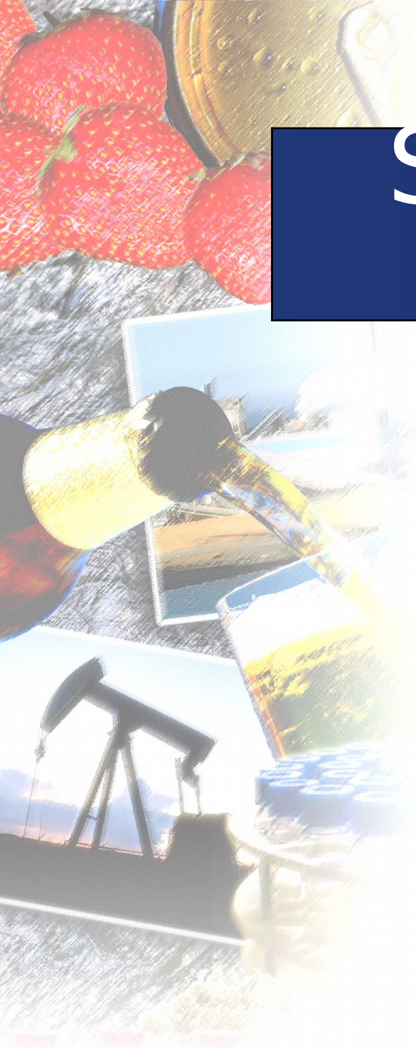
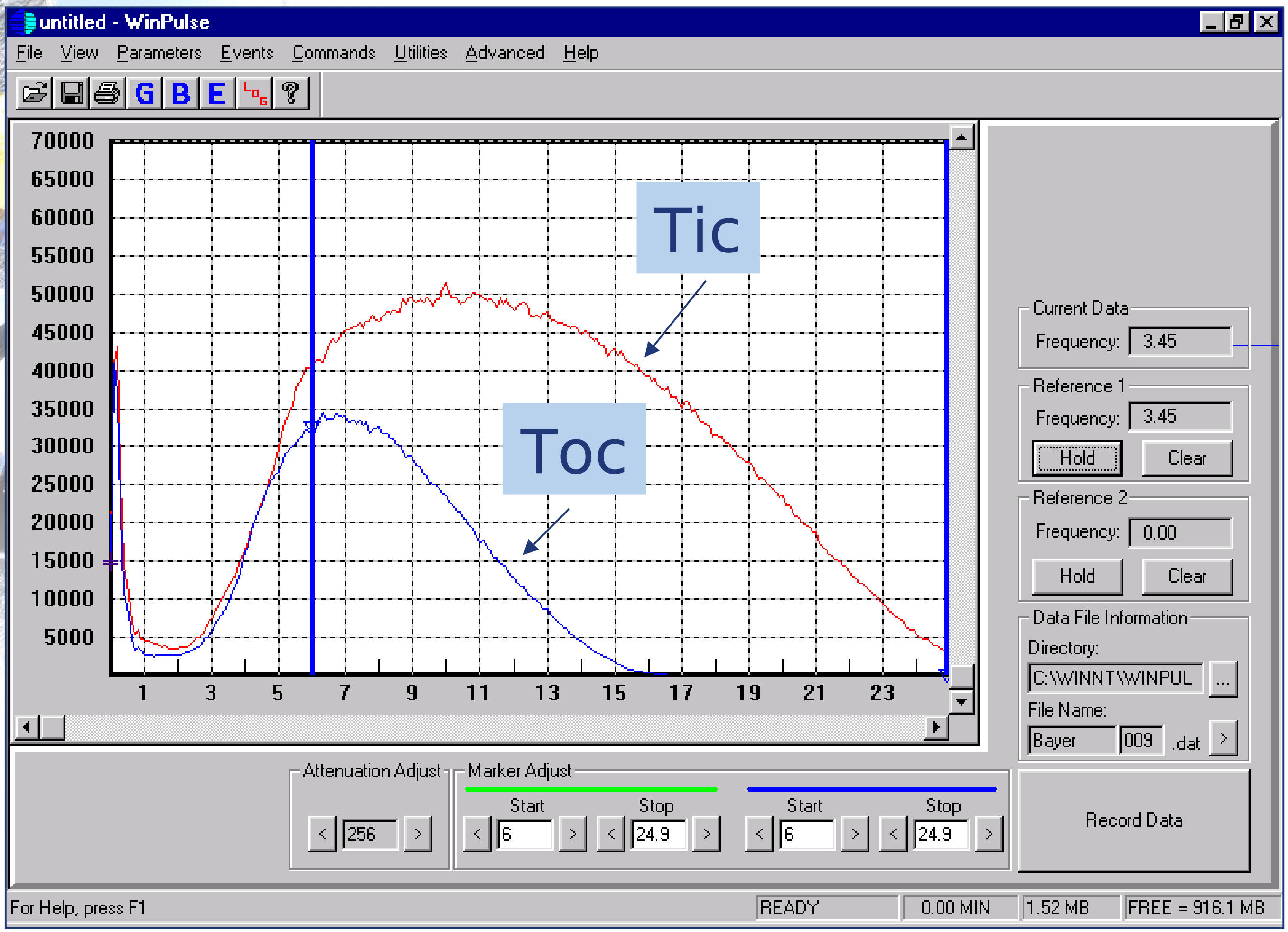


# Step 5: Set The Frequency

- Once you have a “perfect” sulfur emission, use Air2 to adjust the pulsing frequency to between 3 and 4 Hz
  - *Increase Air2 to increase the frequency*
  - *Decrease Air2 to decrease the frequency*
- For very narrow peaks, use a faster frequency
- Do not exceed 4 Hz
- After setting the frequency, recheck the sulfur emission profile and adjust with Air1 if necessary

# Step 6:  Find TicToc




Slowly close the fine adjust needle valve (clockwise) until the PFPD drifts into "TicToc" mode

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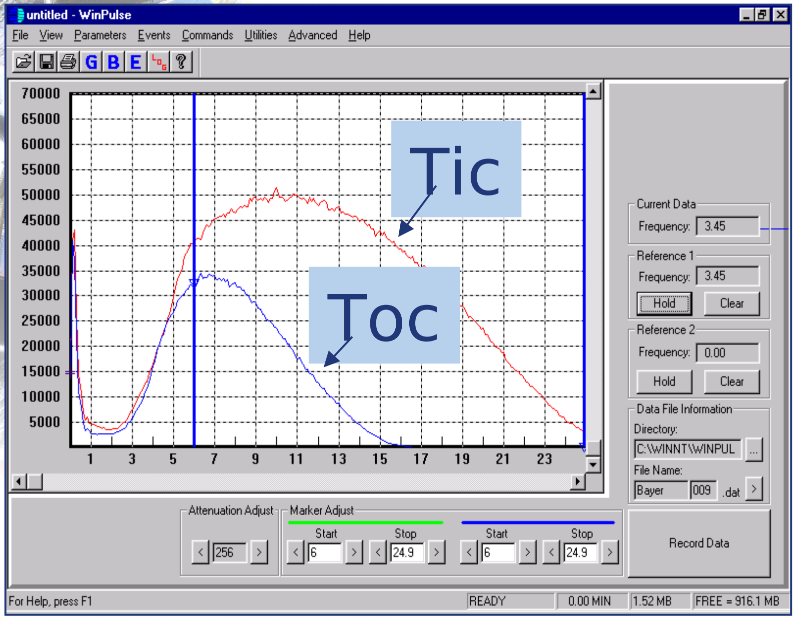
# Notes




- In TicToc only every other pulse makes it to the bottom of the combustor
- There is a distinct change in the audible sound of the PFPD when it is in TicToc
- You may not be able to find TicToc. Just open the fine adjust valve 3 turns and leave it alone

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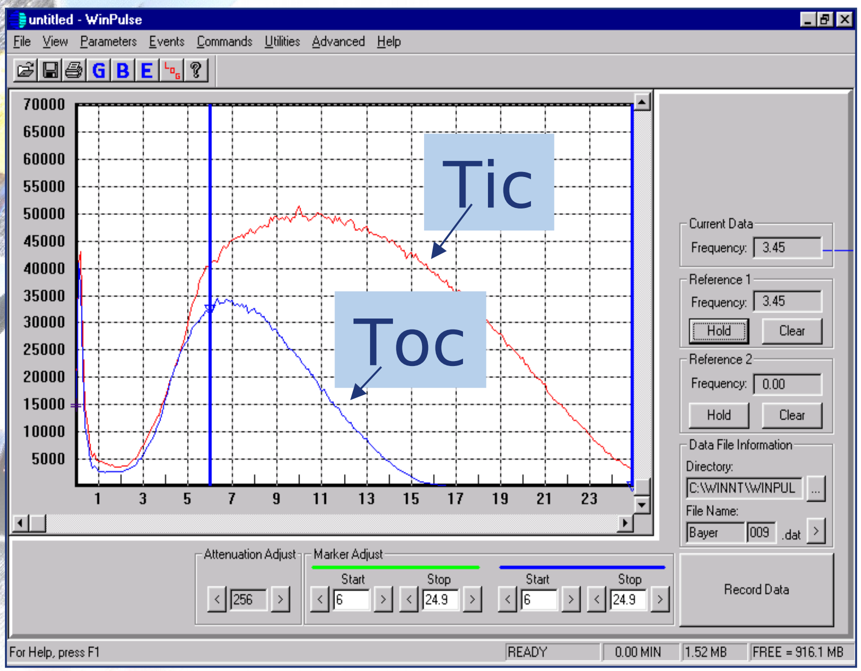
# Step 7




- Once in TicToc, slowly open the fine adjust needle valve just to the point where it stops TicToc-ing
- Open the valve another ½ to ¾ turn

If you don’t have “Constant Flow” mode on your GC, you may drift into TicToc during a ramped GC run. Simply open the valve another ½ turn.

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# Step 8

- The gas flows are now set properly
- Be sure to record the set points (EPC models) or mark the manual flow control knobs
- If you application is analysis of phosphorous compounds switch back to the yellow filter
  - *For P-only applications you may also want to increase the Air1 by 1 to 1 ½ mL/min at this point*
  - *This is not necessary, but OPTIONAL*
- Verify that the board parameters are set correctly and save the PFPD configuration
- Proceed to "Calculating the Detectivity"

# Step 9

## Typical Board Parameters for Sulfur Tuning

| | |
|---|---|
| PMT Voltage | Set so that first spike is at full scale |
| Igniter Current | 2.8 |
| Trigger Level | Set so that first spike intercepts axis at about 1/3 height (~300-400) |
| Range | 10 |

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# Step 9 (cont.)

Typical Board Parameters for Sulfur Tuning

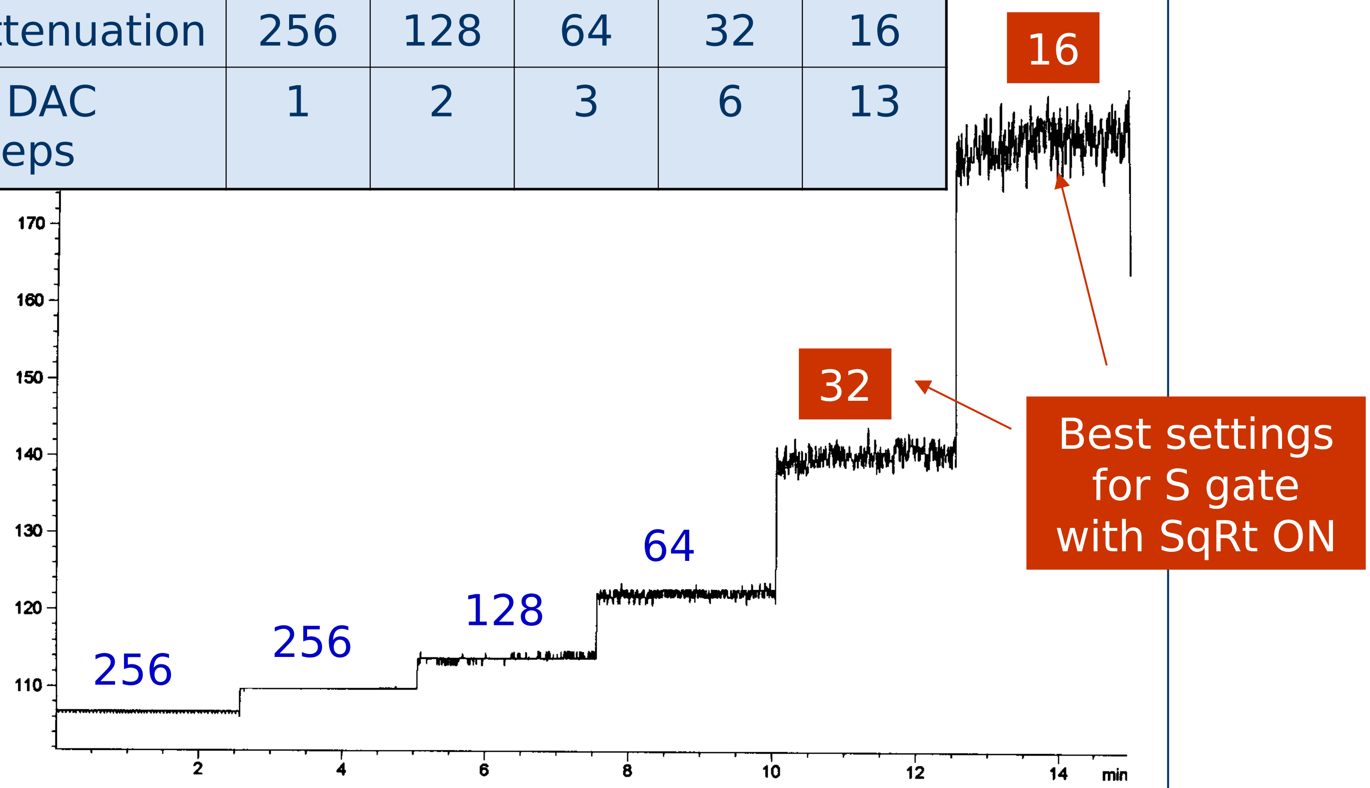
| | |
|---|---|
| Mode | S gate (6 to 24 msec with square root ON) |
| Interpolation | Spline |
| Attenuation | 16 or 32 |
| Zero | Approximately 10-15% below lowest value |

# Why Use an Attenuation Factor?

- Lots of different factors contribute to GC baseline noise
  - *Electrical*
  - *Chemical*
  - *Environmental*
- Attenuation used to minimize absolute peak-to-peak height of the baseline noise
- Still give accurate representation of the true baseline noise
  - *No “flat line”*

# Effect of Attenuation Settings

| Attenuation | 256 | 128 | 64 | 32 | 16 |
|---|---|---|---|---|---|
| # DAC Steps | 1 | 2 | 3 | 6 | 13 |

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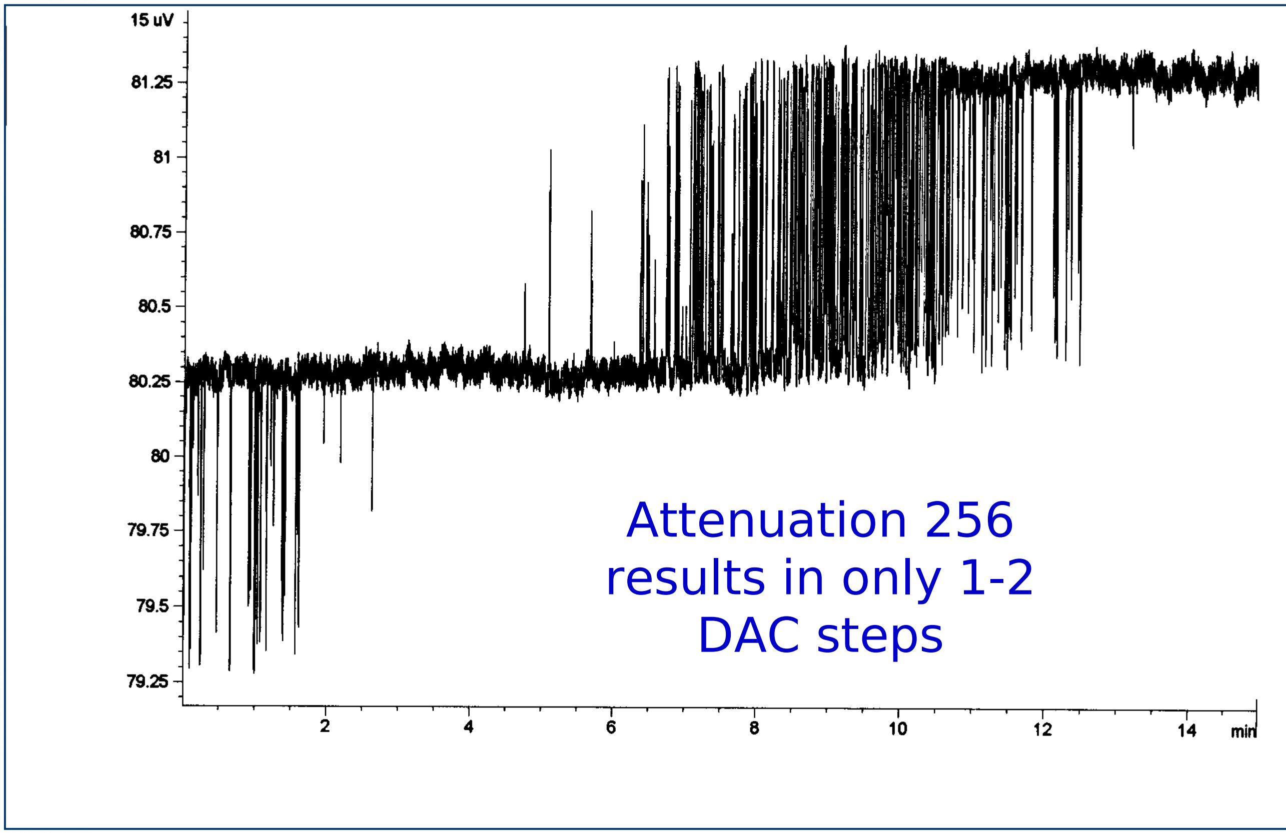
# Attenuation 256 Magnified

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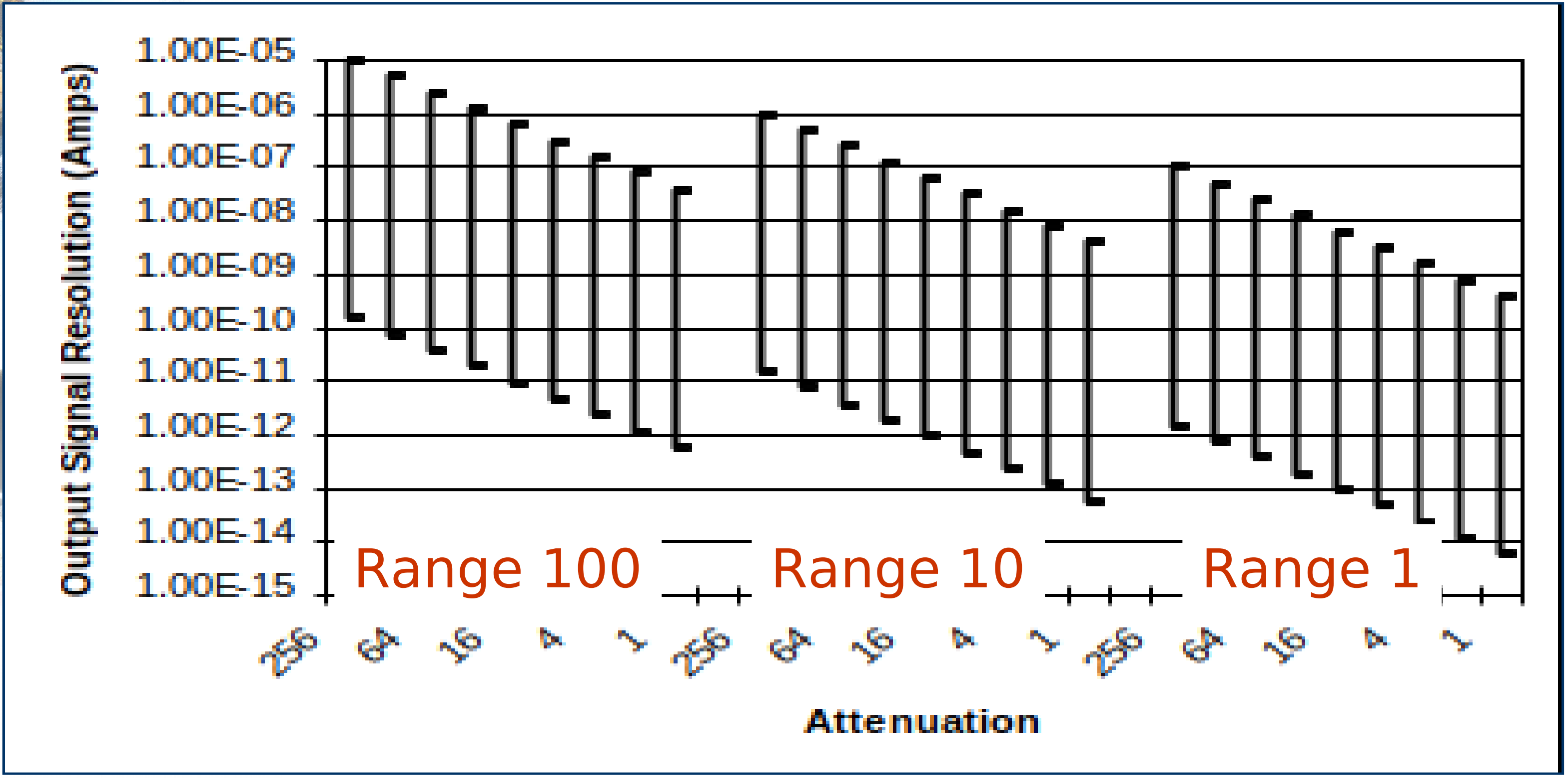
# Why Use an Attenuation Factor?

- Number of bits of information available due to peak integration is greater than the DAC output range
- Use of an attenuation factor permits utilization of this information otherwise not available

$$\text{Output} = \frac{(\text{Response} - \text{zero}) \times 256}{\text{Attenuation}}$$

# Output (log) vs. Attenuation




O·I·Analytical

A Presentation of OI Analytical

# PFPD Tuning Tips:
# Calculate the PFPD Detectivity

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- When you want to calculate detectivity:
  - *The first time the detector is installed*
  - *Anytime you change the configuration*
  - *Anytime you do maintenance or make repairs*
  - *At a set frequency (e.g. once per month) as part of a lab quality assurance protocol*

Detectivity (detectability) is determined by both the peak-to-peak noise level and the sensitivity (response) of the PFPD to a particular species.

The following definitions of detectivity are based on ASTM Standard E 840-81

The minimum detectability for a compound is defined as the mass flow rate of atoms that gives a detectable signal equal to twice the peak-to-peak noise level and is calculated from the measured sensitivity and noise level. The following equation describes "Detectivity":

$$D = 2N / S$$

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Where: D = minimum detectability [pg/sec]

N = peak-to-peak noise [Amp]

S = sensitivity (response) [Amp x sec/pg]

Note that the sensitivity is simply the peak area (A) divided by the mass (m), therefore

**$D = (2N \times m)/A$**

# Step 1

- Select a well behaved compound and prepare a standard that will give a sulfur response with S/N of at lease 10:1 or better
- Don’t use difficult or reactive compounds to calculate detector detectivity (e.g. carbamates or $H_2S$)

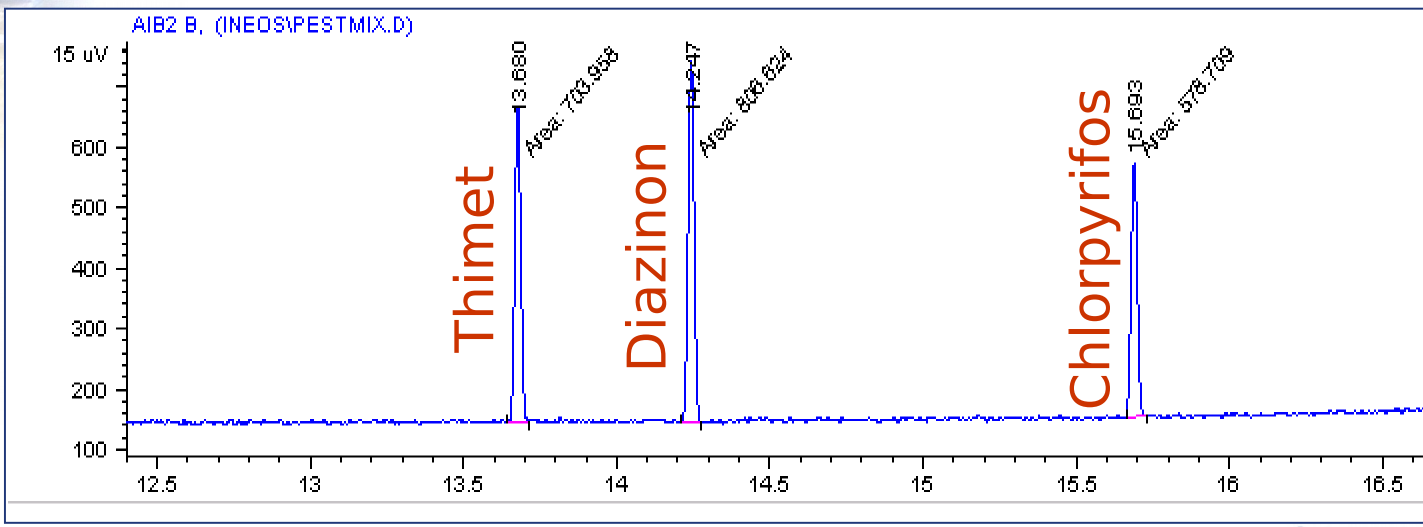
# Note

- Try using the OI Pesticide Mix which comes with the PFPD startup kit (table below)
- Inject 1 μL with a 9:1 split ratio

| Compound | Formula | Concentration | Sulfur Conc. |
|---|---|---|---|
| Thimet | $C_7H_{17}O_2PS_3$ | 500 ppb | 184.7 ppb |
| Diazinon | $C_{12}H_{21}N_2O_3PS$ | 1500 ppb | 158.1 ppb |
| Chlorpyrifos | $C_9H_{11}Cl_3NO_3PS$ | 1500 ppb | 137.3 ppb |

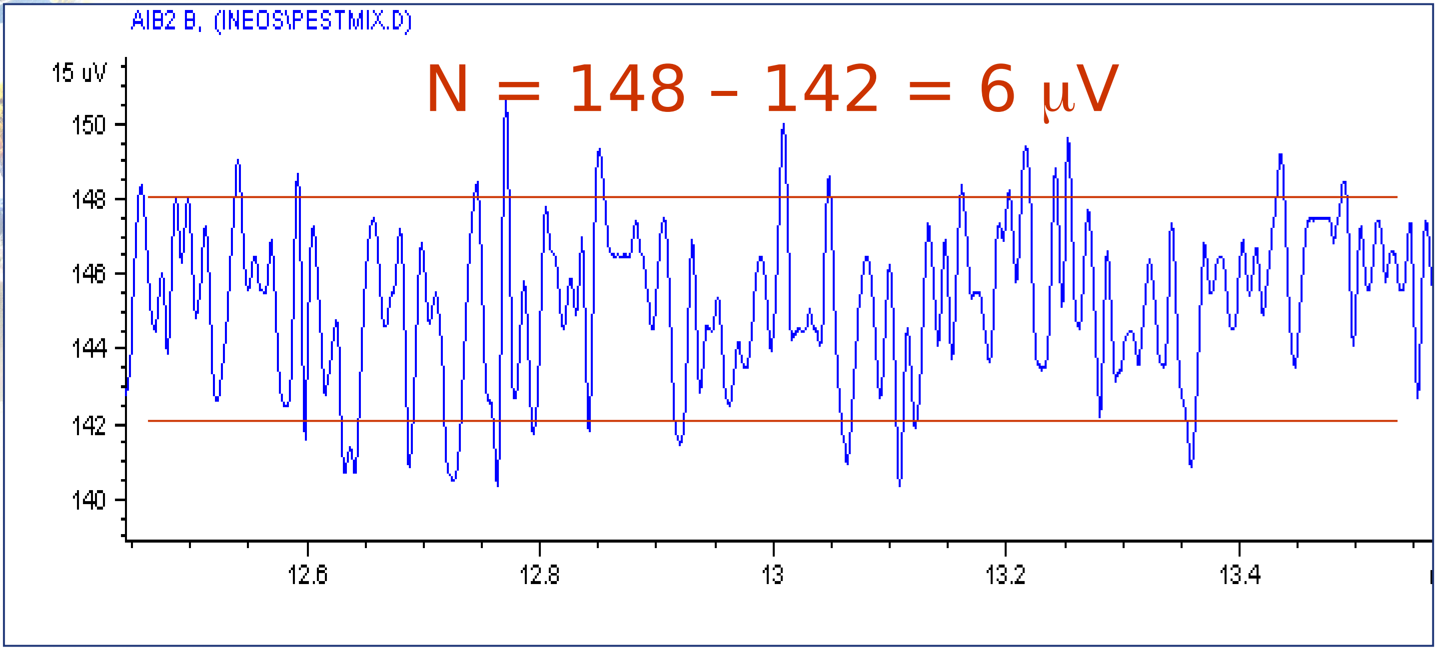
# Step 2

- Inject a known volume (e.g. 1 $\mu$L) with a reproducible split ratio and collect the chromatogram
- Integrate peak areas
- For sulfur, use the PFPD in “Linear” mode



# Step 3

- Measure the peak-to-peak height of the noise

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# Step 4

- Substitute into the equation and calculate detectivity:

$$D = (2N \times m) / A$$

- For Thimet in the previous example:

$$D_{thimet} = (2 \times 6\mu V \times 18.5 \text{ pg S}) / 704\ \mu V * \text{sec}$$

$$D = 0.35 \text{ pg S / second}$$

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# Notes

- Make sure that the mass used in the equation is the mass of sulfur (or phosphorus) that is presented to the detector
- Take into account the injection volume and split ratio
- Do not use the mass of compound
- Make sure that the units for the area measurement are reported in seconds, not minutes (e.g. μV * sec or mA * sec)
- Convert to seconds if necessary

# Step 5

- Calculate detectivity for all three compounds in the mix
- For this case:
  - $D_{thimet} = 0.32$ *pg S/sec*
  - $D_{diazinon} = 0.24$ *pg S/sec*
  - $D_{chlorpyrifos} = 0.29$ *pg S/sec*
- Compare to detectivity specification for the detector
  - *Detectivity for sulfur < 1 pg S / second*
  - *Detectivity for phosphorus < 100 fg P / second*

# Notes

- After you have demonstrated that the detectivity specification has been met, the detector is in good working order and you are ready to analyze samples

# Detectivity for Other Elements

S = 1 pg S/sec

P = 100 fg P/sec

N = 60 pg N/sec

C = 0.5 ng C/sec

Sn = 30 fg Sn/sec

As = 5 pg As/sec