VARIAN

Pulsed Flame Photometric Detector (PFPD) for CP-3800

Operator's Manual

QUALITY SYSTEM ISO 9001 CERTIFIED

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Section 1
Introduction

1.1 OVERVIEW

1.2 DESCRIPTION OF THE PFPD

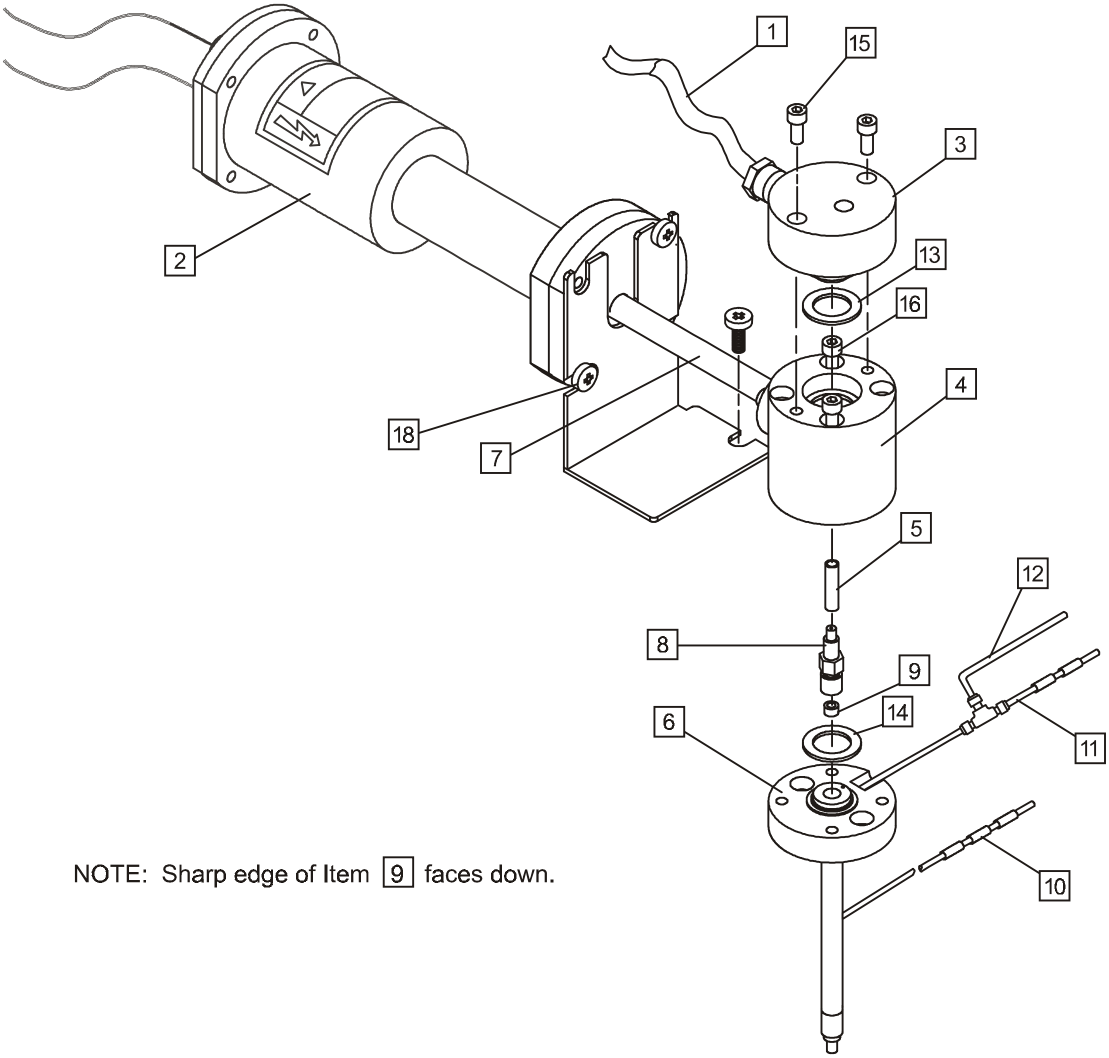
The Pulsed Flame Photometric Detector (PFPD) is the newest member of the family of flame-based gas chromatographic detectors. The PFPD operates in a pulsed-flame rather than continuous-flame mode and offers a number of significant improvements over the conventional flame photometric detector:

- Increased detectivity
- Increased selectivity (relative to hydrocarbons)
- Decreased hydrogen and air consumption

1.2.1 BASIC COMPONENTS OF THE PFPD

- PFPD assembly
- PFPD electrometer board
- PFPD pneumatics

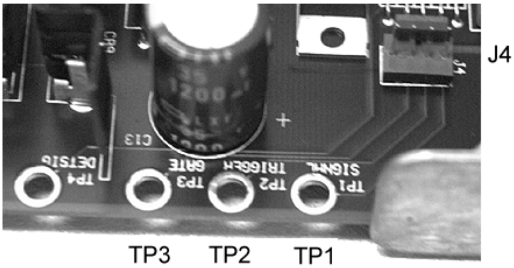
1.2.2 FEATURES OF THE PFPD ASSEMBLY



NOTE: Sharp edge of Item 9 faces down.

Item	Description	Function
1	Ignitor coil assembly	Provides the heat that ignites the flame.
2	Photomultiplier tube (PMT)	Converts the photons emitted in the flame into a current for measurement.
3	Ignitor cap	Holds the ignitor coil and minimizes reflected light from the ignitor coil.
4	Detector tower	Supports the optics, quartz combustor tube, and ignitor cap.
5	Quartz combustor	A transparent inert surface that contains the column effluent for combustion and the transmission of emitted light.
6	Detector base	Holds the detector tower and secures the chromatographic column to the detector.
7	Light pipe	Carries light from the combustion region toward the optical filter and photomultiplier tube.
8	Combustor support	Holds and positions the quartz combustor within the detector tower.
9	Combustor support seal	Seals the space between the combustor support and detector base.
10	Hydrogen-air center flow inlet	Hydrogen-air mixture enters here and flows up through the center of the quartz combustor.
11	Hydrogen-air wall flow inlet	Hydrogen-air mixture enters here and flows along the outside wall of the quartz combustor and into the ignitor chamber.
12	Air_2 inlet	Air_2 enters here and mixes with wall flow.
13	Crunch washer, upper	Seals the space between the ignitor cap and detector tower.
14	Crunch washer, lower	Seals the space between the detector tower and detector base.
15	Allen screws, 9/64"	Secures the ignitor cap to the detector tower.
16	Allen screws, 8/32 x 1 1/2"	Secures the detector tower to the detector base.
18	Phillips-head screws, 8/32 x 3/8"	Secures the photomultiplier tube assembly to the support bracket.

1.2.3 FEATURES OF THE PFPD ELECTROMETER BOARD



Description	Function
J1: Electrometer input signal cable BNC connector	Photomultiplier signal output is directed to the electrometer board through this BNC connector.
J2: Photomultiplier tube high voltage cable TNC connector	High voltage source on the electrometer board is directed to the photomultiplier tube through this TNC connector.
J3: Ignitor cable Molex connector	Current to the ignitor coil is directed through this Molex connector.
SIGNAL (TP1): Test point	With an oscilloscope, used to set the Gate Width and Gate Delay.
TRIGGER (TP2): Test point	Used to monitor the gate trigger (threshold).
GATE (TP3): Test point	Used to monitor when the integration period (Gate Width) begins.
J4: Top ■ Signal ■ Trigger ■ Gate ■ Ground	These are the same signals provided at TP1, 2 and 3, organized to provide easy connection to a cable.

1.3 THEORY OF OPERATION OF THE PFPD

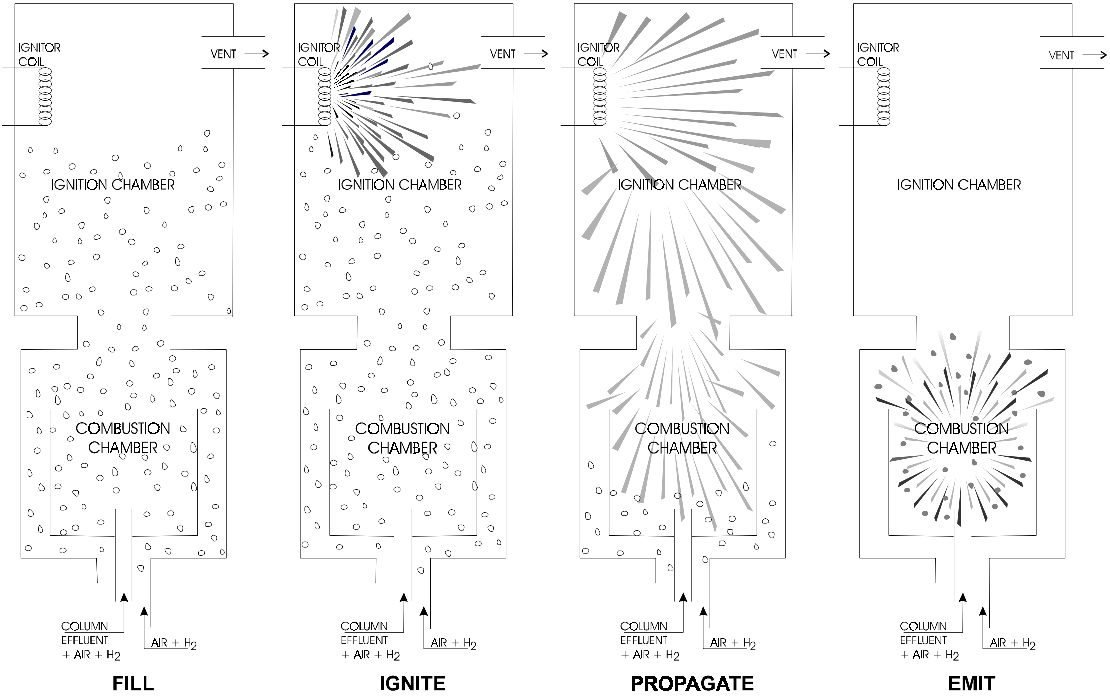
By limiting the flow rates of air and hydrogen to approximately one tenth those typically used in an FPD, the PFPD achieves substantial improvements in both detectivity and selectivity. At these low flow rates, a continuous flame cannot exist. Instead, the combustor and ignitor chambers fill with the combustible mixture of air and hydrogen. When this mixture enters the ignitor, the mixture ignites and a flame front propagates back through the combustor, terminating when the flame reaches the combustor support. The detector then refills with the combustible mixture and the process repeats.

1.3.1 STAGES OF FLAME PULSATION

The flame in the PFPD pulses because the flow rates of hydrogen and air will not sustain continuous combustion. Flame pulsation involves four stages:

- **Fill**: Air and hydrogen mix and enter the combustion chamber at two points. Part of the combustible gas stream mixes with the column effluent and moves upward through the interior of the quartz combustor tube. A second part of the gas stream sweeps along the outside of the quartz combustor tube and into the ignitor chamber.
- **Ignite**: The ignitor chamber contains a continuously heated ignitor coil. When the combustible gas mixture reaches the heated coil, the mixture ignites.
- **Propagate**: The flame front propagates downward into the combustion chamber. At the bottom of the combustion chamber, the flame extinguishes. During this propagation phase, the sample molecules in the flame are broken down into simpler molecules or atoms.
- **Emit:** During and after flame propagation, the sample atoms of interest undergo further reaction to form electronically excited species, from which light is emitted. The flame background emission is complete within less than 0.3 millisecond after propagation, whereas phosphorus and sulfur molecular species emit over a much longer time. This difference in emission times yields the enhanced detectivity and selectivity of the PFPD.

1.3.2 STAGES OF PULSED-FLAME OPERATION



1.3.3 HOW DOES THE PFPD ACHIEVE ITS GREATER DETECTIVITY AND SELECTIVITY?

The enhanced detectivity and selectivity of the PFPD are a consequence of two main factors:

- Separation (in time) of the specific element emission from the background emission
- Concentration (in time) of the emitted light

Background Emission in a Pulsed-flame

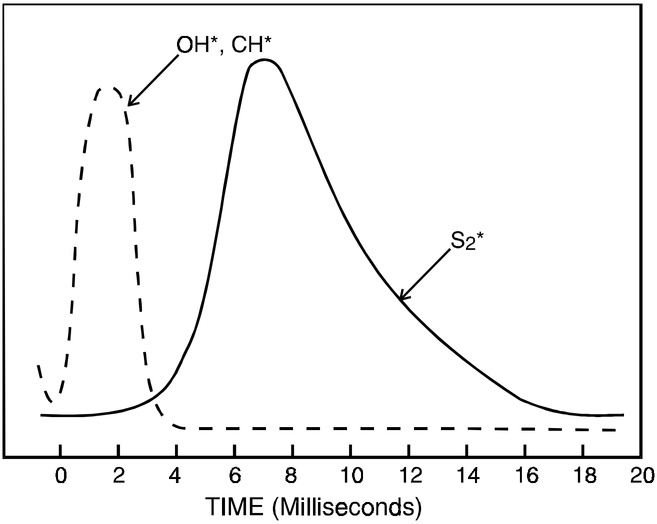
Like the conventional FPD, the PFPD utilizes an air:hydrogen flame. Hydrogen-rich flames favor a variety of gas phase chemical reactions, some of which yield molecular products that emit light (e.g., chemiluminescent reactions). Important excited combustion products include CH*, C_2*, and OH*. The light from such combustion products is referred to as the *background emission*. Hydrogen-rich air:hydrogen flames typically yield chemiluminescence hydrocarbon background emission in the blue region with a maximum near 436 nm.

Time-dependence of Emission Profiles

An important advantage of pulsed-flame operation is the time-dependence of the resulting emission profiles. Flame pulsation enables the molecular emissions of sulfur- and phosphorus-containing compounds to be separated or resolved in time from the flame background emission itself. This resolution is possible because the emission time of the flame background is much shorter than the emission time of the excited molecular products of compounds of analytical interest. As an example, CH* and OH* emission in a hydrogen-rich flame occurs within the time it takes the flame to propagate through the combustor, typically 2 to 4 msec. In contrast, S_2* emission reaches its maximum 5-6 msec after the CH*, and OH* emission has ceased. This separation in time enables the sulfur emission to be monitored when the flame background has dropped to a negligible level. The result is a great improvement in the detectivity and selectivity of sulfur and phosphorus detection.

Emission Profiles

The following figure shows the hydrocarbon and sulfur emission profiles as a function of time (Cheskis, S.; Atar, E.; Amirav, A. *Anal. Chem.* **1993**, 65, 539).



Concentration (in time) of the Emitted Light

In the PFPD, detectivity is greater because all the emission occurs during and immediately following the flame pulse. This increases the brightness of the analytical signal relative to the dark current and other electronic noise. For example, at a typical pulse rate of 2.5 Hz, all the sample eluting from the column during 400 msec is burned in a single pulse, emitting over perhaps 10 msec. This results in a signal which is not only approximately 40 times as bright as that from a continuous flame source, but also is resolved in time from the interference of the flame background.

In addition to the general improvement in detectivity and selectivity as a result of flame pulsation, a further increase in the relative emissions of elements of interest is achieved through the appropriate choice of gas composition. As an example. the formation of S_2^* is favored in cooler hydrogen-rich air:hydrogen flames. Hydrogen content has less effect on phosphorus emission.

Separation of the Element Emission from Background Emission

The flame pulsation in the PFPD yields *time* as an added dimension to flame photometric detection. Both selectivity and detectivity are improved through the ability to:

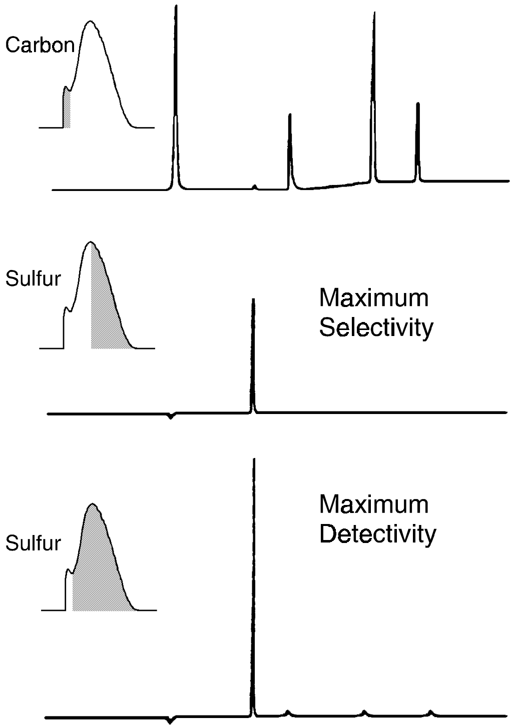
- Resolve emissions of sulfur or phosphorus from the flame emission background
- Resolve emissions of sulfur and phosphorus from each other

As mentioned, the emission times in an air:hydrogen flame of such excited molecular entities as S_2^* or HPO* are generally much longer than the emission times of species responsible for the background emission (e.g., CH*, C_2^*, and OH*). This delay allows the sulfur or phosphorus emission to be integrated after the flame background has dropped to a negligible level. The result is a lower overall noise level and thereby greater detectivity.

The electrometer Gate Delay and Gate Width are used to select the time period of the emission that is to be integrated. In this way, only a small segment of the background noise is integrated during any pulsation. For example, if the time between pulses is 400 msec and the Gate Width is set to 20 msec, 95% of the total background noise is discarded, which further contributes to an improvement in detectivity.

Effect of Gate Control

The following figure illustrates the effect of Gate Delay on selectivity and detectivity.

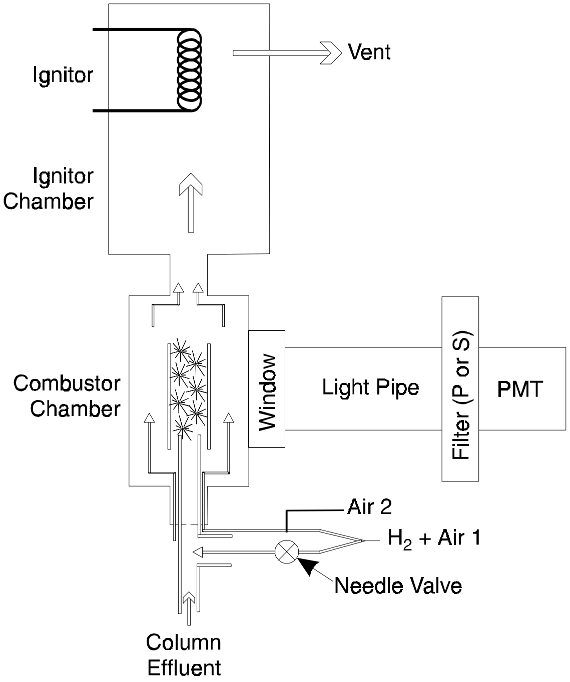


Adjustment of the Gas Composition

The flow rates of air and hydrogen affect the detectivity and selectivity of the PFPD. The total flow rates of air and hydrogen set the operating frequency (rate of pulsation) of the PFPD. Typical operating frequency for the PFPD is near 2-4 pulses/second. The relative proportions of air and hydrogen influence the selectivity by favoring the formation of an emitting species or suppressing the formation of an unwanted interfering species. For example, when detecting phosphorus pesticides in plant tissues, the use of a slightly more air rich flame than usual will suppress formation of the interfering S_2^* molecule, improving P/S selectivity.

1.3.4 FLOW PATH OF THE PFPD

The figure below shows the flow path of gases entering and exiting the PFPD.



The air:hydrogen mixture enters the PFPD at two points: around the outer wall and through the center of the quartz combustor tube. The wall flow is used to refill the upper ignitor chamber of the detector after each pulse, while the combustor flow mixes with the column effluent and refills the combustor. For proper operation, the combustor should refill just slightly faster than the ignitor. The refill rates are balanced by use of a needle valve on the air:hydrogen mixture, and by the flow of air2, which bypasses the combustor and goes directly to the ignitor.

1.3.5 REFERENCES

Refer to the following articles for additional information on the PFPD.

- Cheskis, S.; Atar, E.; Amirav, A. *Anal. Chem.* **1993**, 65, 539.
- Amirav, A.; Jing, H. *Anal. Chem.* **1995**, 67, 3305.

1.4 SPECIFICATIONS OF THE PFPD

Specification	Sulfur Performance	Phosphorus Performance
Detectivity	1 pg S/sec	0.1 pg P/sec
Selectivity	10^6 S/Carbon **NOTE:** The selectivity of Sulfur/Carbon is a function of the sulfur concentration at any time (from 10^5 near its detection limit to ≥10^6 at higher sulfur concentrations).	≥10^5 P/Carbon
Linear Dynamic Range	10^3	10^4
Drift (in 20 minutes)	10 x peak-peak noise	10 x peak-peak noise

1.5 NITROGEN OR OTHER ELEMENT OPERATION

The nitrogen mode enhancement to the Pulsed Flame Photometric Detector extends the range of wavelengths available for detection of element-specific emissions to 900 nm in the near infrared. This not only allows detection of the nitrogen emissions between 700 nm and 800 nm, but also permits the detection of other elements, such as tin and arsenic. Section 4 of this manual gives details of operation in the nitrogen mode, as well as some preliminary information on detection of additional elements.

Nitrogen Mode Specifications

Detectivity:	20 pg N/seconds
Selectivity:	>10^4 N/C
Linear Dynamic Range:	>10^2
Drift:	<10X peak to peak noise in 20 minutes

Section 2
Setting Up the PFPD

2.1 OVERVIEW

2.2 INSPECTING THE PFPD

The PFPD is installed and tested at the factory before the GC is shipped.

Carefully inspect the PFPD. If there is evidence of damage or if parts are missing from the PFPD or its accessory kit, contact:

Customer Service
Varian Analytical Instruments
2700 Mitchell Drive
Walnut Creek, CA 94598-1675
(925) 939-2400

Outside of the USA, notify the nearest International Sales Office listed at the beginning of this manual.

2.3 CONTENTS OF THE PFPD ACCESSORY KIT

The PFPD accessory kit (P/N 03-925190-00) contains tools to disassemble the PFPD and a supply of parts used in its routine maintenance.

Item	Part Number	Qty	Description
1	03-925176-00	1	Quartz combustor (2 mm ID, Sulfur)
2	03-925178-00	1	Combustor support (2 mm ID, Sulfur)
3	03-925180-00	1	Teflon® combustor extraction device (wide bore, 3 mm ID)
4	03-925181-00	1	Teflon combustor extraction device (narrow bore, 2 mm ID)
5	03-925192-00	1	Combustor support wrench
6	29-898500-00	1	Teflon tweezers
7	03-925194-04	1	Allen wrench, 9/64" (cleaned)
8	15-003347-00	15	Crunch washers (Aluminum)
9	03-925138-00	10	Combustor support seal (Aluminum)
10	03-925151-01	1	Filter assembly, Sulfur
11	88-189610-00	1	Teflon pipe thread tape, not shown
12	16-000327-00	1	Reducing union (flow check)

Please note that Item 13, Sulfur Linearization Software, is not used with the 3800 PFPD.

2.4 CONTENTS OF THE PFPD DIFFUSION SOURCE KIT

The PFPD diffusion source kit (P/N 03-925157-00) is supplied as an option to the PFPD.

Item	Part Number	Qty	Description
1	03-925132-00	1	Adapter seal
2	03-925195-00	1	Permeation tube, Sulfur
3	03-925196-00	1	Diffusion source holder
4	03-925200-00	1	Spring
5	03-949786-00	1	Injector adapter
6	88-189610-00	1	Teflon pipe thread tape, 1/2" (not shown)

Section 3
Operation

3.1 OVERVIEW

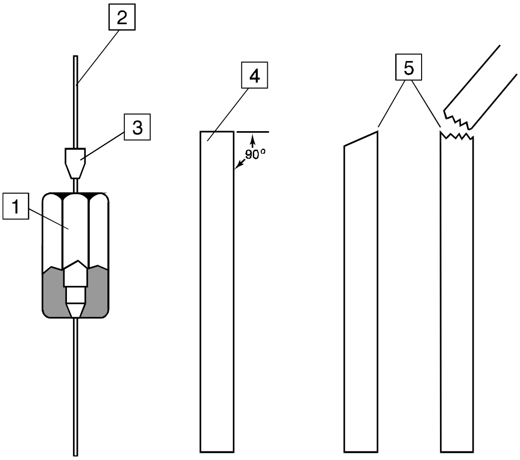
3.2 INSTALLING A CHROMATOGRAPHIC COLUMN

The following procedure describes the installation (or reinstallation) of a gas chromatographic column in a Varian GC equipped with a PFPD.

To ensure good chromatographic performance with the PFPD, the tip of the column must extend 0.5-1 mm above the top of the combustor support.

3.2.1 COLUMN INSTALLATION

Item	Description
1	Capillary Column Nut
2	Capillary Column
3	Ferrule
4	Correct Column Cut
5	Incorrect Column Cut



Tools and Equipment Needed

These tools are needed to complete the following procedure:

- Tungsten carbide pencil (P/N 29-900613-00) or a scoring tool
- Magnifying lens (P/N 00-997369-00)

3.2.2 PREPARE THE COLUMN END

Follow these steps to prepare the end of the chromatographic column for insertion into the PFPD.

1. Before cutting the end of the column, slide the capillary column nut (Item 1) over the fused silica column end (Item 2).
2. Install the appropriate Vespel® or graphite ferrule (Item 3) over the column end.

   Make certain that the tapered edge of the ferrule is toward the inside of the column nut (or away from the column end).

   NOTE: Typically, graphite ferrules contain sulfur as a contaminant. If you use graphite ferrules, expect a higher background during pre-conditioning of the chromatographic column. The background may be particularly high when using a new graphite ferrule that has not be used and conditioned in the past.

3. Hold the column securely between the thumb and forefinger of one hand. Use the scoring tool to score the column once lightly about 1 to 2 cm from the end of the column.
4. With your thumbs and forefingers, grasp the column on each side of the score and bend the column carefully away from the score mark until it breaks at the score mark.
5. Examine the cut with the magnifying lens to decide whether the column was properly cut (Item 4) or improperly cut (Item 5).

   If you observe small splinters of silica or bits of the outer coating on the column end, repeat the above procedure and make a fresh cut.

   If you observe a clean cut, you may use either of two techniques to install the column. If you wish to visually confirm the position of the column end above the combustor support, go to *Disassemble the PFPD*. If you would rather not disassemble the detector, go to *To Install a Column Without Disassembling the Detector.*

3.2.3 PFPD ASSEMBLY

Refer to paragraph 1.2.2 (page 1-2) when disassembling the PFPD, inserting the column, and reassembling the PFPD.

3.2.4 DISASSEMBLE THE PFPD

These tools are needed to complete the following procedure:

- Phillips-head screwdriver
- 9/64" Allen wrench
- Metal forceps
- Teflon combustor extraction device
- Teflon tweezers
- Lab tissues

To Disassemble the PFPD

1. Turn the column oven OFF to stop the oven fan.

2. Open the column oven door and wait for the column to cool to room temperature (or to a temperature at which you can comfortably handle the column).

3. Turn OFF the PFPD electronics.

4. Remove the detector cover from the top of the GC.

5. Before using, thoroughly clean the 9/64" Allen wrench, 1/4" wrench, Teflon combustor extraction device, and Teflon tweezer with methanol or iso-propanol. Set these tools aside on a clean lab tissue.

   NOTE: Dust and dirt inside the combustor can interfere with emission and thereby lower the sensitivity of the PFPD. Therefore, never touch the internal parts of the PFPD with bare hands. Always use a clean lab tissue, Teflon combustor extraction device, or Teflon tweezer to remove or replace detector parts. Place parts on a clean lab tissue as they are removed from the PFPD.

6. Use the 9/64" Allen wrench to remove the 2 Allen screws (Item 1) from the top of the ignitor cap (Item 2). Place the Allen screws on a clean lab tissue.

WARNING:
BURN HAZARD

The ignitor cap and Allen screws may be very hot. Wait until the ignitor cap and Allen screws have cooled or use metal forceps to remove the Allen screws from the ignitor cap.

7. Use the metal forceps to lift the ignitor cap from the detector tower (Item 3). **Place the ignitor cap bottom up** on a clean surface (e.g., a clean lab tissue). The top of the quartz combustor (Item 4) is visible in the center of the detector tower.

WARNING:
BURN HAZARD

The ignitor cap may be very hot. Wait until the ignitor cap has cooled or use metal forceps to remove the ignitor cap from the detector body.

8. Gently insert the appropriate Teflon combustor extraction device into the opening in the top of the combustor. Wait 2-3 seconds for the Teflon combustor extraction device to seat, then lift the quartz combustor from the combustor support (Item 5). Place the quartz combustor on a clean surface (e.g., a clean lab tissue).

9. Use the metal forceps to remove the top aluminum crunch washer (Item 6) from the detector tower. Discard this used crunch washer.

3.2.5 INSERT THE COLUMN

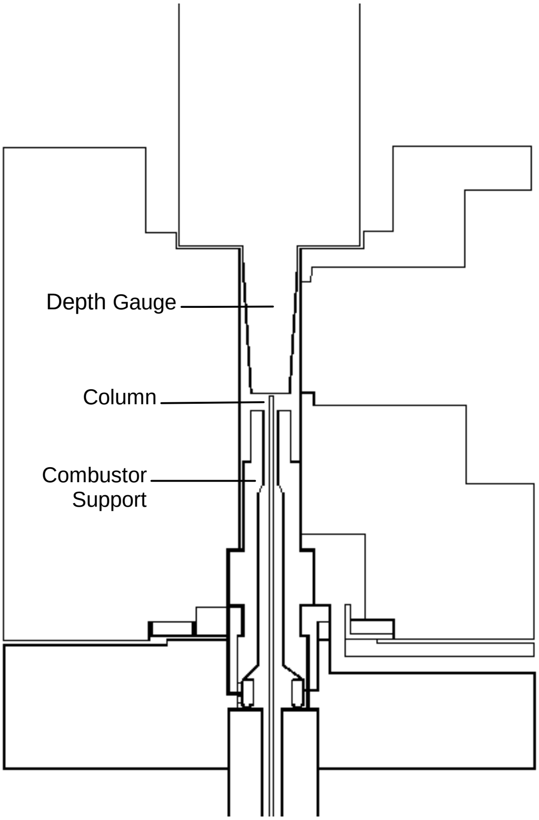
These tools are needed to complete the following procedure:

- Phillips-head screwdriver
- 5/16" wrench
- Capillary pick or combustor support seal extraction tool
- Ceramic scoring tool (P/N 01-900158-00)
- Magnifying lens (P/N 00-997369-00)
- 3 mm combustor extraction tool/Column Depth Gauge (P/N 03-925180-00)

To Insert the Column

1. Check that the capillary column nut and the ferrule (reversed) are installed on the column as described in the manual. Check that approximately 20 cm of the detector end of the column is free so that it can be inserted into the detector.

2. Insert the Column Depth Gauge into the hole from which the combustor was removed. Insert the column into the detector and push the column up until it begins to push up the depth gauge. Tighten the column nut gently until a small amount of force is required to move the column. Gently apply force to the depth gauge to push the column down until the depth gauge contacts the detector tower. See the following figure. Tighten the column nut to secure the column in this position.



3.2.6 REASSEMBLE THE PFPD

Tools and equipment needed to complete the following procedure:

- Phillips-head screwdriver
- 9/64" Allen wrench
- Teflon combustor extraction device
- Metal forceps

To Reassemble the PFPD

1. Use the clean metal forceps to place a new bottom aluminum crunch washer (Item 12) on the detector base.

2. Hold the PMT assembly (Item 11) with one hand and the detector tower with the other. Sight the top of the combustor support (Item 5) through the detector tower. Keep the combustor support centered as you lower the detector tower (Item 3) over the support.

   ⚠ **CAUTION**

   Be very careful not to crush the end of the column.

3. Reinstall the 2 Allen screws (Item 7) that hold the detector tower to the detector base (Item 8). Tighten the screws alternately.

4. Use the Teflon combustor extraction device (of the correct taper) to insert the quartz combustor (Item 4).

5. Use the clean metal forceps to place a new top aluminum crunch washer (Item 6) on the detector tower.

6. Replace the ignitor cap (Item 2) on the detector tower. Use the 9/64" Allen wrench to reinstall in the top of the ignitor cap the 2 Allen screws (Item 1) that secure the ignitor cap to the detector tower.

7. Reinstall the detector cover on the top of the GC.

8. Turn ON the PFPD electronics and PFPD Oven Power. Be sure that the detector gases are turned on. The detector may not begin pulsing normally until the detector tower has begun to heat up somewhat. Allow the detector to come to temperature and equilibrate for at least 15 minutes. During this equilibration period the polyimide coating on the portion of the column exposed to the flame is burned off, leaving a clean fused silica surface.

9. Did you install a quartz combustor with a different diameter?
    - If **Yes**, go to ***Optimizing the PFPD*** for instructions on optimizing the performance of the PFPD with the quartz combustor just installed.
    - If **No**, the PFPD is ready for operation.

3.3 ADJUSTING THE GAS FLOW RATES

The following procedure describes the adjustment of the flow rates of the gases to the PFPD. If you frequently adjust the column flow rate or change the carrier gas, you may want to calibrate the air and hydrogen flow controllers. Once the flow controllers are calibrated, you can quickly select new flow rates and use the optimization tables that are provided.

If the PFPD detector EFC option is installed on your 3800 GC, detector gas flows are set by pressing the Detector key, selecting the PFPD, then pressing the Adjustments softkey. Air1, hydrogen and Air2 are set on page 2 of the Adjustments. The Split Valve adjustment is described below.

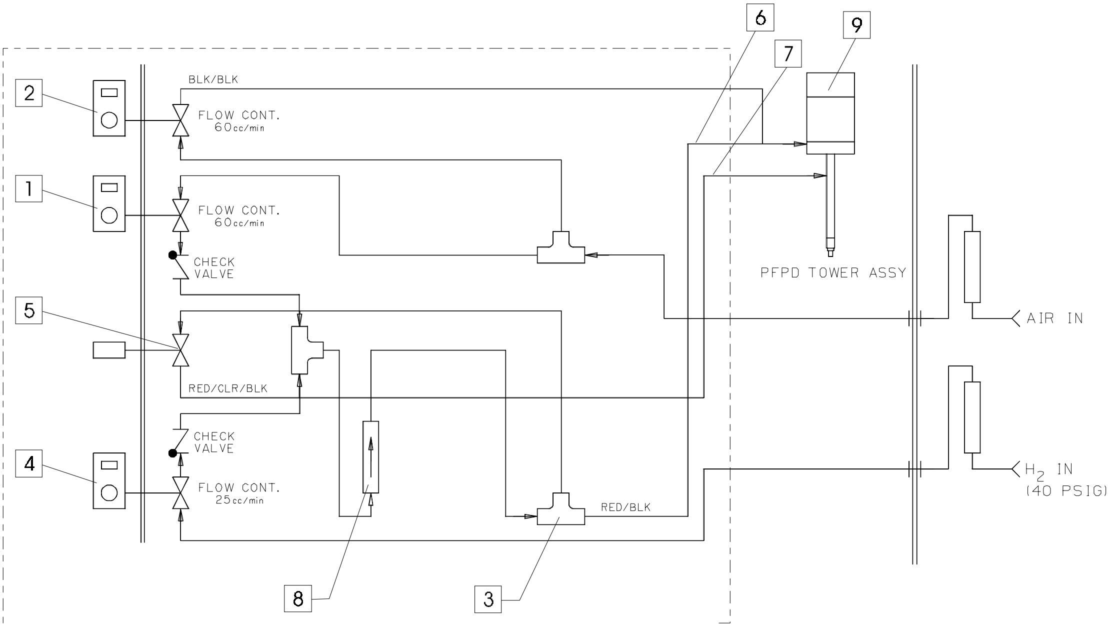
3.3.1 SPLIT VALVE

A split valve is used to finely adjust the flow rate through the combustor section of the PFPD combustor. Follow these directions when adjusting this split valve:

1. Disconnect the outlet line from the needle valve and replace with a flowmeter.
2. With Air 1 and Hydrogen turned on, close the needle valve by turning the knob fully clockwise. The flowmeter should indicate a flow of less than 1 mL/minute. If this is the case, disconnect the flowmeter and reattach the outlet line.
3. If the flow from the needle valve exceeds 1 mL/minute, remove the knob by loosening the set screw. Rotate the valve stem clockwise gently until the flow from the outlet drops below 1 mL/minute. Do not overtighten the valve stem, as the needle valve does not need to shut off completely to function properly, and overtightening can damage the delicate needle in the valve. After making the adjustment, reinstall the knob on the valve stem and secure with the set screw.

3.3.2 PFPD GAS FLOW DIAGRAM

Refer to the following figure when adjusting the flow rates of the gases to the PFPD.



Item	Description
1	Air-1 mass flow controller
2	Air-2 mass flow controller
3	Center flow tee
4	Hydrogen mass flow controller
5	Split valve
6	Wall flow (H_2 + Air-1 + Air-2)
7	Center flow (H_2 + Air-1)
8	Filter
9	Ignitor cap

3.3.3 TO ADJUST THE GAS FLOW RATES

Tools and equipment needed to complete the following procedure:

- Varian Intelligent Digital Flow Meter (P/N 01-900115-00) **or** Soap flow meter (P/N 96-000205-00)
- Stopwatch
- Flow measuring adapter (1/8"-to-1/16" Swagelok® reducing union)
- 1/4" flat blade screwdriver

NOTE: For best stability of flows, flow controllers should have pressure applied to them for at least 24 hours before adjustments are made. A moderate flow of gas through the flow controller during this conditioning period is also helpful in stabilizing the flow controller.

1. Turn the ignitor OFF.

2. Locate the *Air-1* mass flow controller valve (Item 3). Note the current dial setting. Turn *Air-1* OFF.

3. Locate the *Air-2* mass flow controller valve (Item 1). Note the current dial setting. Turn *Air-2* OFF.

4. Locate the *Hydrogen* mass flow controller valve (Item 4). Note the current dial setting. Turn *Hydrogen* OFF.

5. Install the flow measuring adapter (Swagelok 1/8" to 1/16" reducing union). Use Teflon thread tape to make the connection to the ignitor cap gas tight. Measure and record the column flow rate, then turn the column flow OFF. **NOTE:** A Varian Intelligent Digital Flowmeter (P/N 01-900115-00) is highly recommended for this procedure. **IMPORTANT:** Be sure the ignitor seal is completely leak tight before attempting to measure flow rates. This seal can loosen due to temperature cycling during normal operation. This does not affect detector performance, but can lead to serious errors in setting flow rates. Tighten securely before beginning to measure flows.

6. Adjust the *Air-1* mass flow controller valve until flow rate is near 15 mL/min. Write down and save the dial setting for the *Air-1* mass flow controller valve. Turn the *Air-1* flow controller Off.

7. Adjust the *Air-2* mass flow controller valve until flow rate is near 15 mL/min. Write down and save the dial setting for the *Air-2* mass flow controller valve. Turn the *Air-2* flow controller Off.

8. Adjust the *Hydrogen* mass flow controller valve until flow rate is near 12 mL/min. **NOTE:** If you will be using hydrogen as your carrier gas, the total hydrogen flow to the detector should be approximately 12 mL/minute. The flow rate set in this step should thus be 12 mL/min minus the anticipated column flow rate. Write down and save the dial setting for the *Hydrogen* mass flow controller valve.

9. Restore the *Air-1* and *Air-2* flow controllers to the settings recorded above. Restore the carrier gas flow to the column. Remove the flow measurement adapter, remove any Teflon thread tape residue from the ignitor cap. **NOTE:** Leave the flow controllers ON at all times unless you must turn them off to re-plumb or reconfigure the gas chromatograph. If you turn the flow controllers off for an extended period then on again, they must equilibrate overnight before the PFPD can achieve optimum performance.

10. Turn the ignitor ON.

3.4 CALIBRATING THE FLOW CONTROLLERS

NOTE: For best stability of flows, flow controllers should have pressure applied to them for at least 24 hours before adjustments are made. A moderate flow of gas through the flow controller during this conditioning period is also helpful in stabilizing the flow controller.

Tools and equipment needed to complete the following procedure:

- Varian Intelligent Digital Flow Meter (P/N 01-900115-00) **or** Soap flow meter (P/N 96-000205-00)
- Stopwatch
- Flow measuring adapter (1/8"-to-1/16" Swagelok® reducing union)
- 1/4" flat blade screwdriver

To Calibrating the Flow Controllers

1. Turn off the column flow. Or, if you want flow to continue to the column, disconnect the column from the detector and use a column nut and 1/16" no-hole ferrule (P/N 28-694503-01) to seal the detector.

2. Write down the current dial settings for Air-1, Air-2, and Hydrogen, then turn off each flow controller.

3. Install the flow measuring adapter (1/8" to 1/16" reducing union). Use Teflon thread tape to make a gas-tight seal.

NOTE: A Varian Intelligent Digital Flowmeter (P/N 01-900115-00) is highly recommended for this procedure.

IMPORTANT: Be sure the ignitor seal is completely leak tight before attempting to measure flow rates. This seal can loosen due to temperature cycling during normal operation. This does not affect detector performance, but can lead to serious errors in setting flow rates. Tighten securely before beginning to measure flows.

4. Connect the flowmeter to the adaptor. Turn the Air-1 flow controller (clockwise) until the flowmeter indicates flow through the system. Slowly turn the Air-1 flow controller (counter-clockwise) until the flow just stops. Again, write down the dial setting.

   NOTE: It is recommended that the flow controller dial be set so that it reads zero at this setting. Remove the knob then loosen the two set screws holding the dial to the flow controller shaft. While holding the flow controller shaft so that it does not rotate, turn the dial to 000. Retighten the set screws and replace the knob.

5. Set the dial to 100, 200, etc., and allow the flow to equilibrate. Measure the flow and record. When you have completed all measurements, turn off flow.

6. Repeat steps 1-5 for the Air-2 and Hydrogen flow controllers.

   NOTE: **Chart the flow rate versus dial setting so that you have a reference when setting flow rates as suggested in *Optimizing the PFPD* on Page 3-11.**

7. If you removed the column prior to calibrating the flow controllers, reinstall it now.

3.5 OPTIMIZING THE PFPD

The PFPD is optimized to maximize:

- Detectivity of Sulfur or Phosphorus
- Selectivity of Sulfur and Phosphorus to Carbon or each other
- Analytical throughput (shorten total analysis time)

3.5.1 DETECTIVITY

Detectivity is the minimum detectable quantity (MDQ) of Sulfur or Phosphorus (usually expressed as femtograms of Sulfur (or Phosphorus) per second. Detectivity is the preferred method of expressing the sensitivity of a detection method because it includes a consideration of the Signal-to-Noise ratio. Sensitivity alone is insufficient in that the sensitivity of the PFPD can be increased simply by increasing the voltage of the photomultiplier tube, but the noise increases as the signal increases, yielding little enhancement in the minimum amount detectable.

3.5.2 SELECTIVITY

An important question when optimizing the selectivity of the PFPD is, "Selective relative to what?." In some situations, the Sulfur or Phosphorus response is best optimized relative to Carbon (the principal background emission in the air-hydrogen flame). At other times, it may be more important to optimize the Phosphorus response relative to the Sulfur response, as when Phosphorus is analyzed in certain plant tissue extracts that are high in Sulfur content.

3.5.3 THROUGHPUT

The additional selectivity of the PFPD can result in shorter analysis times and thereby greater sample throughput. As an example, by optimizing the sulfur response relative to hydrocarbons, the PFPD may detect fewer peaks thereby simplifying the chromatogram and increasing the chromatographic resolution. With greater resolution, the chromatography can be adjusted such that the peaks of interest elute faster thereby decreasing the analysis time. In addition, when hydrogen is used as the carrier gas, the PFPD can be operated at higher flow rates without greatly affecting the detectivity of the method. Higher carrier gas flow rates translates into shorter analysis times and greater sample throughput.

3.5.4 SUGGESTED FUEL GAS FLOW RATES

The following table lists flow rates for several carrier gases that are often used in common analysis situations when operating the PFPD. Use these flow rates as starting points when optimizing the performance of the PFPD.

Carrier Gas Flow Rate (mL/min)	H_2 (mL/min)	Air-1 (mL/min)	Air-2 (mL/min)
Helium			
2	13	17	10
5	13	20	10
10	20	34	10
Hydrogen			
2	11	17	10
5	9	18	10
10	15	31	10
Nitrogen			
2	14	17	10
5	16	21	10
10	24	34	10

You May Not Need to Adjust Flow Rates

The difference in optimum gas flow rates between sulfur and phosphorus is small. If you don't require the maximum sensitivity for an analysis, leave the flow rates as they are and change only the optical filter, gate delay, and integration time, when shifting between the sulfur and phosphorus detection modes.

3.5.5 SUGGESTED PFPD ADJUSTMENT SETTINGS

The following adjustment settings are recommended for setup and routine operation of the PFPD. These adjustments are accessed by pressing the Adjustments softkey in the PFPD detector section of the 3800 method.

Element	Gate Delay	Gate Width	Trigger
Sulfur	6	20	200
Phosphorus	4	10	200
Nitrogen	3.5	8	200

3.5.6 OPTIMIZATION CRITERIA

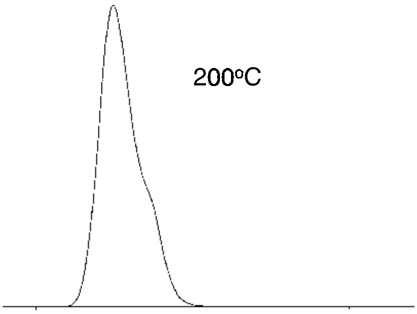
Refer to the table below when optimizing the PFPD.

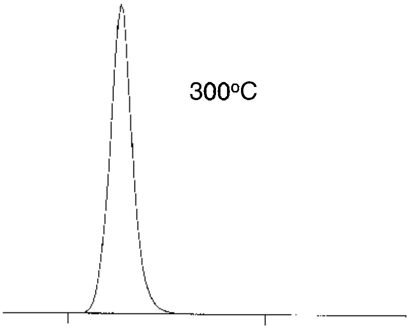
To Maximize ...	Consider ...
Phosphorus response	■ Install wide bore quartz combustor ■ Use moderately hydrogen-rich flame ■ Adjust split valve such that detector is just out of tick-tock ■ Set detector temperature ≥300°C
Sulfur response	■ Install narrow bore quartz combustor. ■ Set hydrogen carrier gas flow rate to a value that is near, but just above, the minimum of the van Deemter curve for the column and maximum column temperature used. ■ Adjust split valve such that detector is just out of tick-tock ■ Use optimum hydrogen-rich flame ■ Increase Air-2 to enhance ignition and flame propagation in the hydrogen-rich flame ■ Set detector temperature ~200°C **NOTE: For some compounds, sulfur response decreases with increasing detector temperature. Set the detector temperature as low as possible while preserving chromatographic peak shape.**
Phosphorus-to-Carbon selectivity	■ Install wide bore quartz combustor ■ Use hydrogen as carrier gas ■ Use *moderately* hydrogen-rich flame ■ Adjust split valve such that detector is just out of tick-tock, then turn counterclockwise an additional 1/2 turn. ■ Detector temperature ≥300°C **NOTE: The Gate Delay can be adjusted to increase or decrease selectivity. However, as the selectivity increases, the detectivity often decreases. Set the Gate Delay to balance these performance criteria at levels that are appropriate to the application. Also, the gate should be set to open (or trigger) as close to the main peak as possible rather than before or after. Setting the gate correctly prevents the hydrocarbon and phosphorus responses from overlapping as the flame propagation slows in hydrocarbon-rich flames.**

To Maximize ...	**Consider ...**
Sulfur-to-Carbon selectivity	■ Install wide bore quartz combustor ■ Use hydrogen as carrier gas ■ Use *moderately* hydrogen-rich flame ■ Adjust split valve such that detector is just out of tick-tock, then adjust counterclockwise an additional 1/2 turn. ■ Set detector temperature ~200°C ■ Increase sample amount injected (inject larger volume or more concentrated form of sample) The trigger level should be set to trigger on the main flame peak. Setting the trigger level correctly prevents the hydrocarbon and sulfur responses from overlapping as the flame propagation slows in hydrocarbon-rich flames. The Sulfur response is proportional to the square of the Sulfur concentration in the flame whereas the Carbon response is directly proportional to the Carbon concentration. Therefore, when the amount of sample that is injected is doubled, the Sulfur-Carbon selectivity doubles (all other parameters being equal).
Phosphorus-to-Sulfur selectivity	■ Install wide bore quartz combustor ■ Use hydrogen as carrier gas ■ Use *slightly* hydrogen-rich flame. Increasing Air1 flow until phosphorus response decreases by a factor of two will improve P/S selectivity greatly. ■ Adjust split valve such that detector is just out of tick-tock ■ Set detector temperature ~300°C ■ Inject the smallest amount of sample consistent with adequate phosphorus signal. Sulfur interference is reduced in direct proportion to the reduction in sample size. For example, a five fold reduction in sample size will result in a 25 fold reduction in sulfur interference response, but only a five fold reduction in phosphorus response, for a net enhancement in selectivity of a factor of 5.

To Maximize ...	Consider ...
	■ Decrease Gate Delay and Gate Width as much as possible while maintaining an acceptable Carbon selectivity. **NOTE: Because phosphorus emits sooner than Sulfur, a shorter Gate Delay and Gate Width improves the Phosphorus-Sulfur selectivity. Also, because air-rich flames favor Phosphorus emission over Sulfur emission, decrease the hydrogen-to-air ratio to increase the Phosphorus-Sulfur selectivity.**
Analytical throughput (decrease analysis time)	■ Install wide bore quartz combustor. ■ Use hydrogen as the carrier gas at flow rates up to 10 mL/min. ■ Bracket only the region of the chromatogram that the PFPD can detect and for which the detector conditions have been optimized. **NOTE: Because the van Deemter curve for hydrogen is flat at very high flow rates, there is little loss of efficiency as the flow rate is increased to shorten the analysis time. The wide bore quartz combustor permits the use of higher flow rates, but this may not be a good choice if maximum Sulfur response is also the objective of the application.**
Effect of PFPD temperature	An initial detector temperature of 200°C is recommended when optimizing the PFPD, but your sample may require a higher detector temperature to adequately separate and detect higher boiling sample components. The figure below shows the effect of increasing the PFPD temperature by 100°C. The sample eluted from the column at a column temperature of 260°C. At a detector temperature of 200°C, the peak is broad with a slight shoulder. When the detector temperature was increased to 300°C, the peak sharpened and the shoulder disappeared.

To Maximize ... **Consider ...**





3.5.7 ESTABLISHING TICK-TOCK

Tick-tock occurs when the combustible mixture ignites in the ignitor chamber but does not propagate into the combustor chamber because the combustor has not yet filled with a combustible gas mixture. Optimum performance is generally achieved when the detector is operating near, but not in, the tick-tock mode.

Follow these steps to adjust the gas flow rates for optimum performance of the PFPD. This adjustment should be done with the column oven at the highest temperature which will be used in the analysis. This will assure that the detector will remain in the normal operating mode throughout the column temperature program.

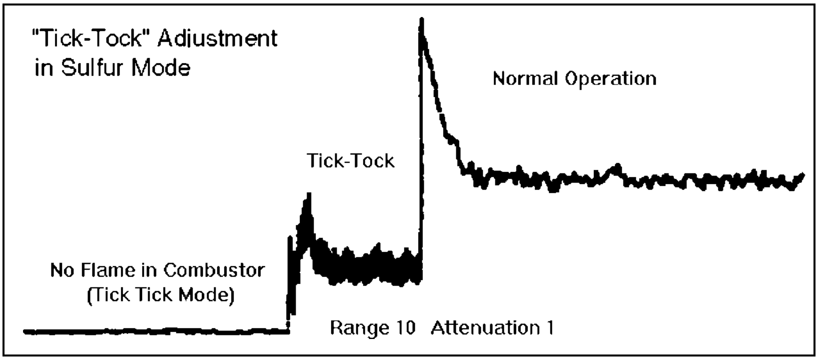
1. To monitor the detector baseline, connect a strip chart recorder to the detector analog output. Turn off the AutoZero function (in the Detector section of the GC method). Set the Gate Delay to 4 msec and the Gate Width to 10 msec. Leave the trigger level at the default value, 200 mV. (This makes Tick-Tock easier to observe. Remember to switch back to the desired gate delay and width settings after setting the needle valve.)

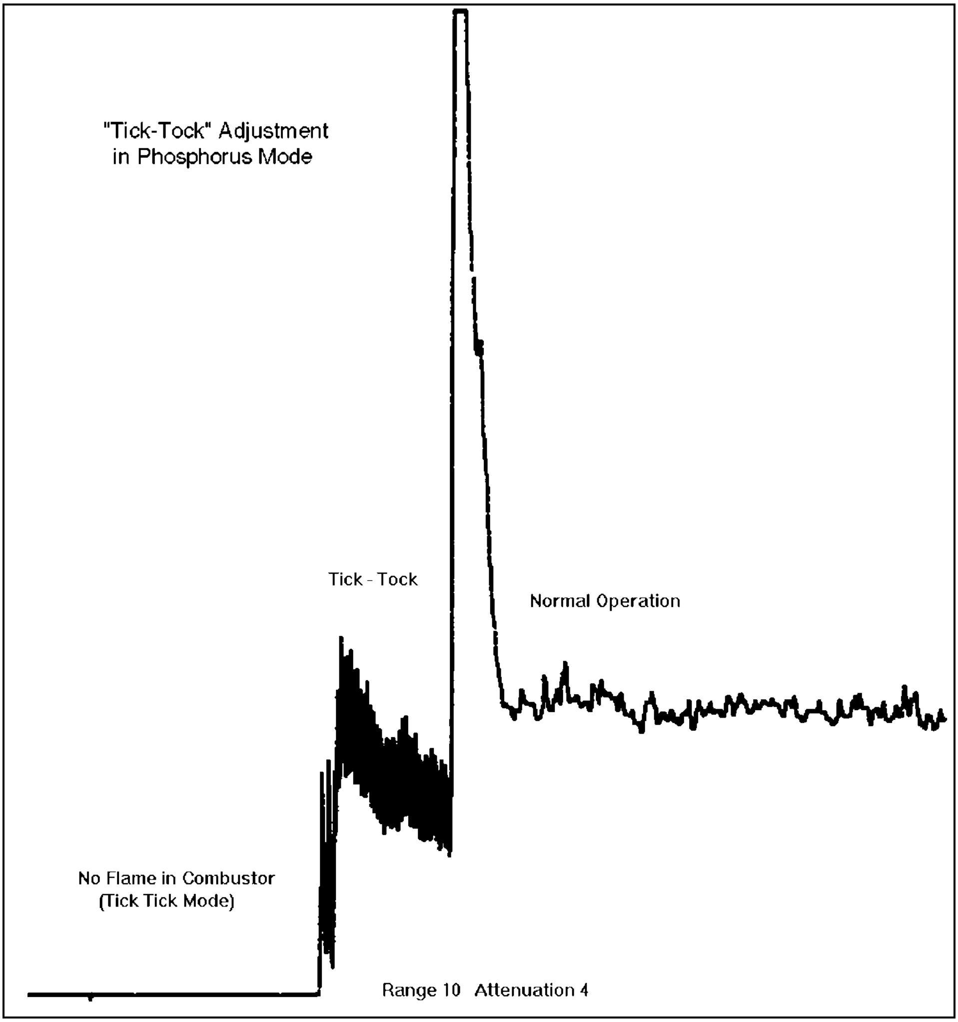
2. Adjust the gas flow rates so that the PFPD is pulsing at about 2-4 Hz (pulses/second).

3. Adjust the Air-Hydrogen needle valve fully clockwise. This shuts off the flow of air-hydrogen to the combustor chamber while permitting the air-hydrogen mixture to pass around the outside of the combustor and enter the ignitor chamber. The pulse rate should increase . As the flame stops propagating into the combustor, the detector baseline drops and becomes smoother (less noisy).

   NOTE: At low column flow rates (particularly with the 3 mm combustor), there may be enough diffusion of fuel mixture into the combustor chamber that the baseline is not completely smooth (noiseless).

4. Slowly turn the Air-Hydrogen needle valve counter-clockwise. With each turn of the needle valve, more of the combustible mixture enters the combustor chamber. As the amount of combustible mixture entering the combustor chamber increases, the flame begins to propagate into the combustor chamber. First, the flame propagates into the combustor chamber on every third or fourth pulse and then, as the flow rate of the combustible mixture increases, on alternate pulses (tick-tock mode), and then finally on every pulse. As you increase the flow rate of combustible mixture that enters the combustor, the baseline should rise sharply and become very noisy as the detector enters tick-tock. As the detector leaves the tick-tock mode, the baseline will rise and then fall and become less noisy. The pulse rate will also decrease as you pass through tick-tock, since more of the combustible mixture is burned on each pulse as you adjust the needle valve for normal operation.


"Tick-Tock" Adjustment
in Sulfur Mode
Normal Operation
Tick-Tock
No Flame in Combustor
(Tick Tick Mode)
Range 10 Attenuation 1


"Tick-Tock" Adjustment
in Phosphorus Mode
Tick - Tock
Normal Operation
No Flame in Combustor
(Tick Tick Mode)
Range 10 Attenuation 4

5. Once the baseline reaches a steady value, you may adjust the needle valve an additional 1/2-turn counter-clockwise to ensure stable operation of the PFPD. If you changed the gate delay and width, reset them to the proper values for your analysis.

3.5.8 PHOTOMULTIPLIER TUBE (PMT) HIGH VOLTAGE

The PFPD detector is shipped with the electrometer and detector set up for the mode specified or the phosphorus mode, if not specified. The PMT high voltage is set at 510 volts typically for phosphorus. For the sulfur mode, the recommended voltage is somewhat higher, usually 550 volts. For the nitrogen mode, 580 - 620 volts is typical.

3.5.9 ADJUSTING THE PHOTOMULTIPLIER TUBE (PMT) VOLTAGE

The following procedure describes how to adjust the PMT voltage when changing from one mode to the other, or to compensate for aging of the PMT over time.

1. If you have not already done so, adjust the detector gas flow rates for the mode of operation desired (Sulfur or Phosphorus). Use flow rate values that you determined previously or the recommended flow rates listed in the *Gas Flow Rates* table on Page 3-13.

2. When the detector is pulsing normally, press the *Detector* key on the GC control panel. Select Front, Middle, or Rear (the position in which the PFPD is installed). Press *Enter,* then Page Down until the PMT voltage entry field is displayed.

3. If the PMT voltage is:

    - within 10-20 volts of the nominal value for the desired mode of operation, you may not need to make any further adjustment.

    - not within this range, enter a new PMT voltage while observing the PFPD output on a strip chart recorder or on the Workstation System Control display.

4. If you want to optimize the detector sensitivity with respect to PMT voltage:

    - Set up the PFPD to operate in the desired mode.

    - Slowly adjust the *HV* setting while watching the baseline noise (displayed on a strip chart recorder or other output device).

- When the noise approaches the values noted below, begin making injections of test sample and calculating signal to noise ratio for the peaks of interest. Increase the PMT voltage in increments of 20 to 50 volts until the signal to noise ratio no longer increases, or until the noise becomes unacceptably large.

NOTE: For the sulfur mode, the noise should be about 1% of full scale (for Attenuation = 1, Range = 10). For the phosphorus mode, the noise should be about 1% of full scale (for Attenuation = 4, Range = 10).

5. Note the *HV* value displayed on the GC Detector Status display as above.

NOTE: **As the PMT ages, the voltage required to generate adequate sensitivity gradually increases. Replace the PMT when you can no longer achieve adequate sensitivity within the range of HV available.**

3.5.10 OPTIMIZING THE PFPD

The PFPD can be optimized in two ways:

- Repeated injections of standard
- Continuous infusion of standard

Tools and Equipment Needed

These tools are needed to complete the procedure for optimizing the PFPD using the method of repeated injections of standard:

- Flat tipped screwdriver
- Printer/plotter or stripchart recorder
- FPD test sample (P/N 82-005048-03)
- 10 µL syringe (P/N 47-000007-00)

3.5.11 REPEATED INJECTIONS OF STANDARD

Follow these steps to optimize the PFPD using the method of repeated injections of a standard.

1. Install the test column.
2. Set the Detector temperature to 200°C. Set injector temperature to 200° for isothermal injectors; 80° initial, 0 hold, program to 200° for 1079. Set column oven to 80° initial, hold 0.5 minutes, then program at 25°/minute to 200°, and hold 2 minutes, or until the last peak of interest elutes..
3. Allow the chromatographic system to equilibrate for ~1 hour.
4. Turn the stripchart recorder or other display device ON.
5. Adjust the gas flow rates to those recommended for your carrier gas and flow rate in the *Suggested Fuel Gas Flow Rates* table *on Page 3-12.*
6. If necessary, adjust the *Air-2* flow rate to give a flame pulse rate of ~2-4 pulses/second.
7. Inject 1.0 µL of the FPD Test Sample split ~20:1 if using a 1079 split injection. Inject 1 µL of a 20:1 dilution of the test sample in iso-octane if using a 1079 splitless or on-column injection or a 1041/1061 injector.
8. Note the peak height of the sample peak eluting last, methyl parathion. When the GC is Ready again, increase the hydrogen flow by 20 digits on the counter, inject the sample again, and note whether the peak height increases. If so, continue to increase the hydrogen flow and reinject the sample until the peak height no longer increases.

   If the peak height does not increase by increasing the hydrogen flow, then decrease the flow by 20 digits on the counter and reinject the sample. Continue this procedure until the methylparathion peak is maximized.

   NOTE: Allow the system to equilibrate for ~2-3 minutes between flow rate adjustments so that the air and hydrogen filters are completely flushed with the new gas composition.

9. When the peak height is maximized, tune the fill time of the ignitor volume to be just slightly greater than the fill time of the combustor volume. See *Establishing Tick-Tock on Page 3-17.*

Tools and Equipment Needed

These tools are needed to complete the procedure for optimizing the PFPD using the method of continuous infusion of standard:

- Printer/plotter or stripchart recorder
- Sulfur diffusion source kit (P/N 03-925157-00)

3.5.12 CONTINUOUS INFUSION OF STANDARD

Follow these steps to optimize the PFPD response using the method of continuous infusion of a standard.

1. Install the Sulfur diffusion source.

   Disconnect the column at the injector end. Insert the sulfur permeation tube (P/N 03-925195-00) into the diffusion source holder (P/N 03-925196-00), wrap the threads of the holder with Teflon thread sealant tape and attach the injector adaptor. Tighten the cap just enough to make a gas-tight seal.

   Insert an aluminum adaptor seal (P/N 03-925132-00) in the end of the injector adaptor. Check that the crunch washer is properly seated at the bottom of the holder and not resting on the threads. Screw the injector adaptor-end of the diffusion source holder onto the injector outlet fitting. Tighten the holder just enough to make a gas-tight seal.

   NOTE: If the permeation tube has not been used recently, set the injector and column temperature to 50°C and pass carrier gas over the permeation tube for ~1/2 hour. This decreases the surface concentration of the permanent.

2. Install the test column.

   If the test column is installed, shorten the length of column extending above the injector nut to ~5 mm.

   Insert the column into the column-end of the diffusion source holder. Tighten the column nut as usual. The outlet of the holder uses the same fitting as the injector outlet except that the holder requires an insertion depth of only 1-2 cm.

3. Set the Injector and Column temperatures to 60°C.

   NOTE: The concentration of standard that enters the detector is adjusted by increasing or decreasing the Injector and Column temperatures. However, 60°C should be near optimum for the optimization procedure.

4. Adjust the column flow rate as required (~2 mL/min for the 320µ test column). Allow the chromatographic system and permeation tube and diffusion source holder to equilibrate for ~1 hour.

5. Adjust the gas flow rates to the recommended flow rates listed in the *Gas Flow Rates* table of *Optimizing the PFPD* on Page 3-11. Set the detector range to 10. Set Autozero to OFF. Adjust the attenuation to keep the emission on scale.

6. If necessary, adjust the *Air-1* and *Hydrogen* flow rates to give a flame pulse rate ~2-4 pulses/second. Alternately increase or decrease *Air-1* and *Hydrogen* so that the flow rate remains approximately the same as the gas composition is changed. Allow the system to equilibrate for 2-3 minutes between flow rate adjustments so that the air and hydrogen filters are completely flushed with the new gas composition.

   NOTE: When adjusting the flow rate, turn the Air and Hydrogen flow controller dials in increments of 10 or 20.

7. Increase the flow rate of *Hydrogen* by 10 dial units. Examine the emission on the stripchart recorder. Monitor the emission after each flow rate adjustment. If the sulfur emission increases, continue to increase the hydrogen flow rate until the response no longer increases. If the pulse rate increases beyond 4 Hz, reduce the *Air-1* flow by 10 units and continue the procedure. Typically, noise is relatively independent of gas composition so that the relative gas composition can be adjusted with little or no effect on the noise.

   NOTE: Sulfur emission is maximized when the gas mixture is very rich in hydrogen.

8. Once the sulfur emission has been maximized, adjust the fill time of the ignitor volume so that it is just slightly less than the fill time of the combustor volume. *See Establishing Tick-Tock on Page 3-17.*

9. Remove the column from the diffusion device holder, remove the diffusion device holder from the injector outlet, and reinstall the test column or the appropriate analytical column in the injector.

3.6 TESTING THE PFPD PERFORMANCE

The following procedure describes how to test the performance of the PFPD after it has been optimized for the desired detectivity and selectivity.

Tools and Equipment Needed

These tools are needed to complete the following procedure:

- FPD test sample (P/N 82-005048-03)
- 10 µL syringe (P/N 47-000007-00)
- Test column, DB-1 320µ x 4M (P/N 03-912805-99)

3.6.1 TEST THE PERFORMANCE OF THE PFPD

Follow these steps to test the chromatographic performance of the PFPD.

1. Configure the GC as described below:
    - Column: Test column (DB-1 320µ x 4M)
    - Injector: 1079 (preferred)
    - Stripchart recorder
2. Select the mode (sulfur or phosphorus):
    - Turn the PFPD electrometer OFF
    - Remove the GC top covers
    - Install the correct optical filter for the element of interest.
    - Set the Gate Delay and Gate Width for the element of interest.
    - Install a 2mm quartz combustor and support for sulfur mode, or a 3mm combustor and support for phosphorus.

    Replace the GC top covers and turn the PFPD electrometer ON.
3. Set the GC method (or GC Workstation method) for the following bake-out conditions:
    - Oven temperature: 240°C
    - Detector temperature: 350°C
    - Injector temperature: 250°C

Disconnect the test column, cap off the detector, and operate the GC for at least 4 hours to bake out the column. Set the oven temperature to room temperature and wait until the oven and column are cool. Reconnect the test column to the detector.

4. Set the GC method (or GC Workstation method) for the following test conditions:
   - Injector: 200° isothermal or 80° initial, 0 hold, program to 200° for 1079 modes
   - Detector: Temperature 200°, Range 10, Autozero ON
   - Column Oven: 80° initial, 0.5 min. hold, 25°/minute to 200°, hold 2 minutes, or until last peak of interest elutes.

   Set PMT voltage to 530V for phosphorus or 570V for sulfur.

5. Operate the GC for at least 1 hour to ensure that the PFPD and its electronics are thermally stable. Re-optimize the PFPD as recommended in *Optimizing the PFPD*, Page 3-11).

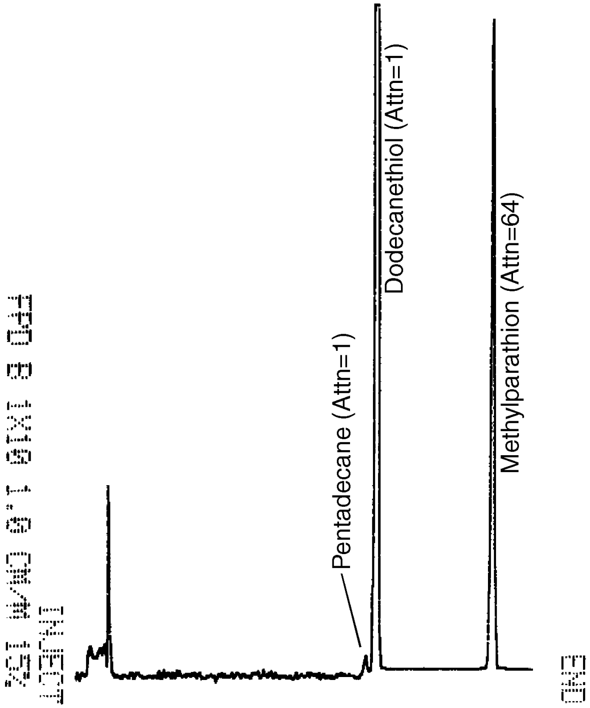
6. If you are using a split injection, inject 1 µL of FPD test mix with a split ratio of 20:1. If you are using a non-splitting injector, dilute the FPD Test Sample 1:20 in iso-octane, and inject 1.0 µL of the diluted FPD Test Sample.

7. The resulting chromatographic peaks should have similar retention times, heights, and resolution to those shown below.

8. Are the peak retention times substantially different?
   - If Yes, adjust the column temperature and/or column flow rate and repeat steps 6-8.
   - If No, replace the test column with the column to be used in your particular application, adjust the GC conditions to appropriate values, and proceed with the analysis.

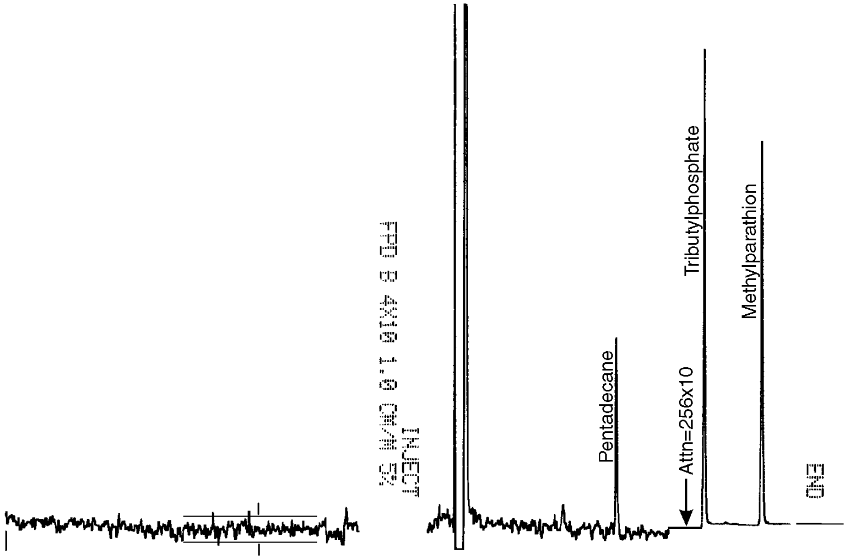
3.6.2 PFPD TEST CHROMATOGRAM: SULFUR PERFORMANCE

Refer to the figure below to check the chromatographic performance of the PFPD for sulfur. Compare the test chromatogram to the chromatogram shown below in terms of peak retention times, peak heights and peak resolution.



3.6.3 PFPD TEST CHROMATOGRAM: PHOSPHORUS PERFORMANCE

Refer to the figure below to check the chromatographic performance of the PFPD for phosphorus. Compare the test chromatogram to the chromatogram shown below in terms of peak retention times, peak heights and peak resolution.



3.6.4 DETECTIVITY

Refer to the instructions below to calculate the detectivity for sulfur and phosphorus with the PFPD:

- Determine the peak-to-peak noise (N_{p-p}) on the baseline. Collect at least 5 minutes of baseline noise at an attenuation which will allow easy measurement of the noise.
- Inject a known amount of standard (~100 x noise) and determine the peak height (H) for Sulfur or peak area (A) for Phosphorus. The instructions above will give a methyl parathion peak which contains 120 pg of both sulfur and phosphorus.
- Determine the width (W) of the peak at half-height ($W_{1/2}$) for phosphorus, or the width at 1/4 height for sulfur. Calculate detectivity (D) according to the formula below:

$$D_{phosphorus} = [Wt \times (2 \times N_{p-p})]/[W_{1/2} \times H]$$

$$D_{sulfur} = [Wt/W_{1/4}] \times SQRT\ [(2 \times N_{p-p})/H]$$

NOTE: **Detectivity is expressed in units of weight/time. Wt is the weight of the specific element injected (e.g., weight of methyl parathion multiplied by 0.12 for either sulfur or phosphorus). $W_{1/4} \cong 1.5 \times W_{1/2}$. The term SQRT means to take the square root of the product in brackets. If you are using peak areas or peak heights that have been calculated by a data system, use the counts-to-mm conversion factor from the data system.**

3.6.5 PFPD TEST CHROMATOGRAM: SULFUR DETECTIVITY

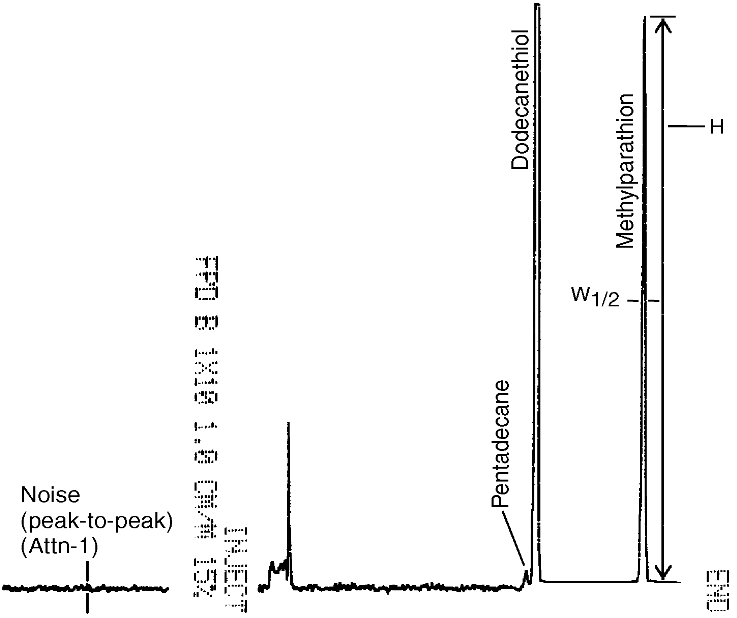
Refer to the figure below to check the detectivity of the PFPD for sulfur.

$$D_S = [W_S / (1.5 \times W_{1/2})] \times \mathrm{SQRT}(2 \times N/H)$$

where D_S = Detectivity (pg/sec) for sulfur, W_S = Weight (pg) of sulfur, $W_{1/2}$ = width (sec) at half height of sulfur peak, N = peak-to-peak baseline noise (mm), H = height (mm) of sulfur peak, SQRT = square root

As an example, for the following test chromatogram: W_S = 120 pg, $W_{1/2}$ = 2.2 sec, N = 1 mm (1 mm x attenuation of 1), H = 4992 mm (78 mm x attenuation of 64) then

$$D_S = [120\ \mathrm{pg} / 1.5 \times 2.2\ \mathrm{sec}] \times \mathrm{SQRT}(2 \times 1\ \mathrm{mm}/4992\ \mathrm{mm}) = 0.73\ \mathrm{pg/sec}$$



3.6.6 PFPD TEST CHROMATOGRAM: PHOSPHORUS DETECTIVITY

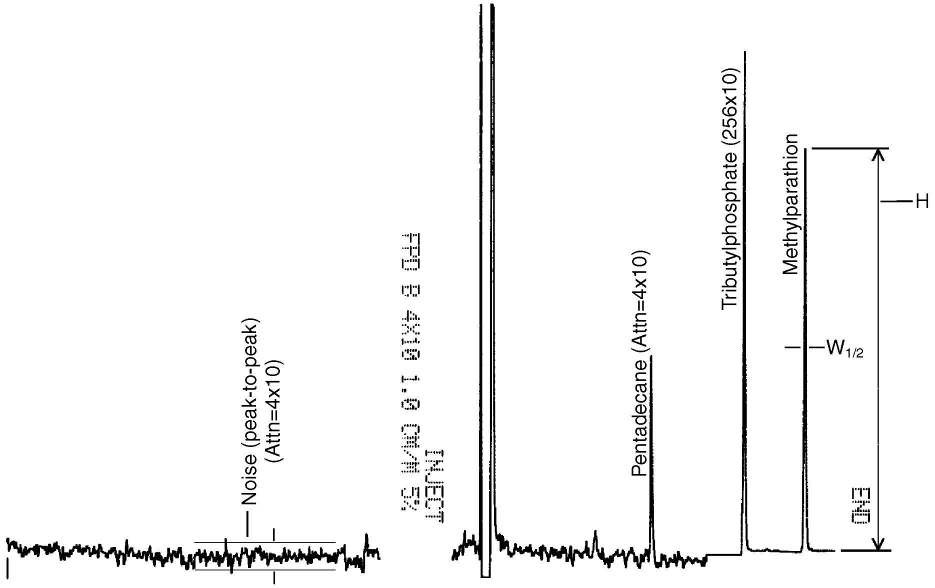
Refer to the following figure to check the detectivity of the PFPD for phosphorus.

$$D_p = [(W_p \times 2 \times N)/(H \times W_{1/2})]$$

where D_p = Detectivity (pg/sec) for phosphorus, W_s = Weight (pg) of phosphorus, $W_{1/2}$ = width (sec) at half height of phosphorus peak, N = peak-to-peak baseline noise (mm), H = height (mm) of phosphorus peak

As an example, for the following test chromatogram: W_p = 120 pg, $W_{1/2}$ = 2.5 sec, N = 16 mm (4 mm x attenuation of 4), H = 17152 mm (67 mm x attenuation of 256) then

$$D_p = [(120 \text{ pg} \times 2 \times 16 \text{ mm})/(17152 \text{ mm} \times 2.5 \text{ sec}) = 0.090 \text{ pg/sec}$$



3.7 USING THE GATE DELAY AND GATE WIDTH PARAMETERS

Through the Gate Delay and Gate Width parameters you have access to the control functions of the gated integrator located on the PFPD electrometer board. These control functions enable you to select the time period (or region) of the emission spectrum that is to be integrated, thereby improving the sensitivity and selectivity of the PFPD.

What Can Be Controlled Through the Adjustments?

Three functions can be controlled through the Adjustments:

- Trigger Level: signal required to start (trigger) the delay and width timer
- Gate Delay: time in milliseconds after triggering before integration of the detector signal begins.
- Gate Width: time in milliseconds after the Gate Delay during which the detector signal is integrated.

The appropriate values for the Gate Width and the Gate Delay are determined from the emission profile (time x emission intensity) of the element of interest. Appropriate values for a number of elements are listed in the following table.

Preset and Range of the Control Functions

Refer to the table below for a description of the preset values and ranges of the functions that can be adjusted.

Function	**Preset**	**Range**
Trigger Level	200 mV	50 - 500mV
Gate Delay	4 msec	0.5 - 20 msec
Gate Width	10 msec	0.5 - 20 msec

For those users interested in gaining a more detailed understanding of the PFPD emission profile, the analog detector signal, the trigger state, and the integrator gate state are available at test points on the edge of the electrometer board, and on the pins of connector J4. When displayed on an oscilloscope, these signals allow detailed investigation of the emission time profiles of the flame background and of elements of interest, so that the detector parameters may be fine tuned for optimum selectivity and detectivity. For more information on the use of these signals, please contact your Varian representative.

3.7.1 SETTING THE TRIGGER LEVEL

Tools and Equipment Needed

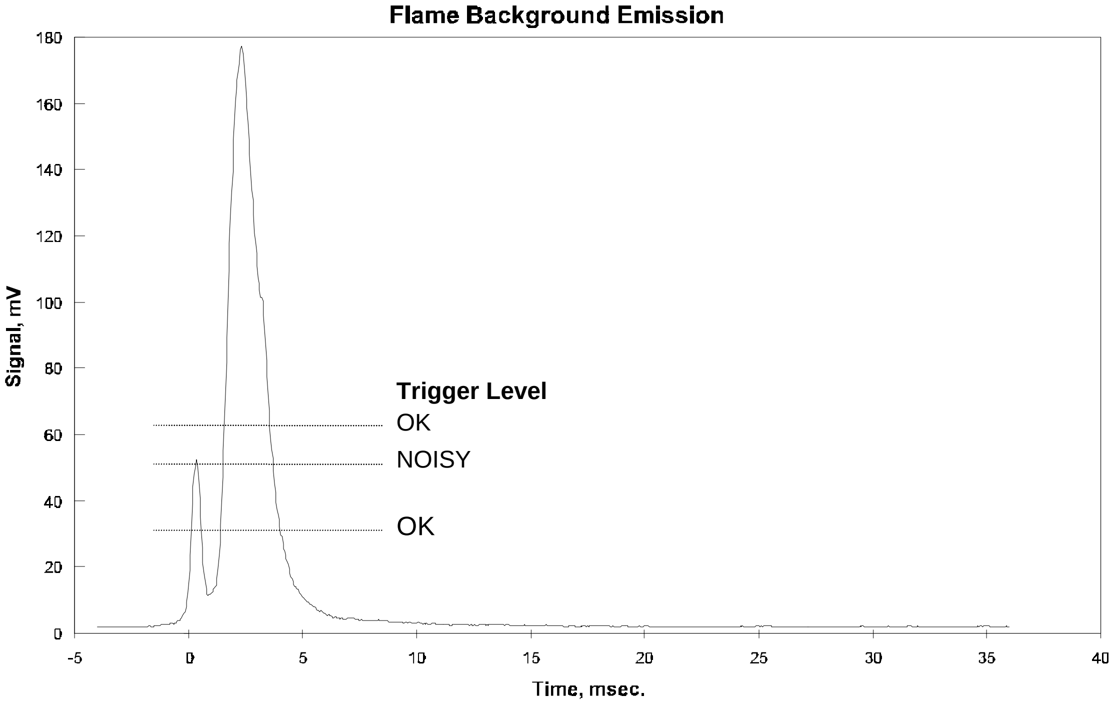
These tools and equipment are needed to complete the following procedures:

- Printer/plotter or stripchart recorder
- FPD test sample (P/N 82-005048-03)
- 10 µL syringe (P/N 47-000007-00)

The trigger level is preset to 200 mV. You may need to set the trigger level lower if you are using a narrow band interference filter which does not transmit much of the flame background. You may need to set the trigger level higher than 200 mV for optimum operation with some elements which have no delayed emission, or very short emission delay times.

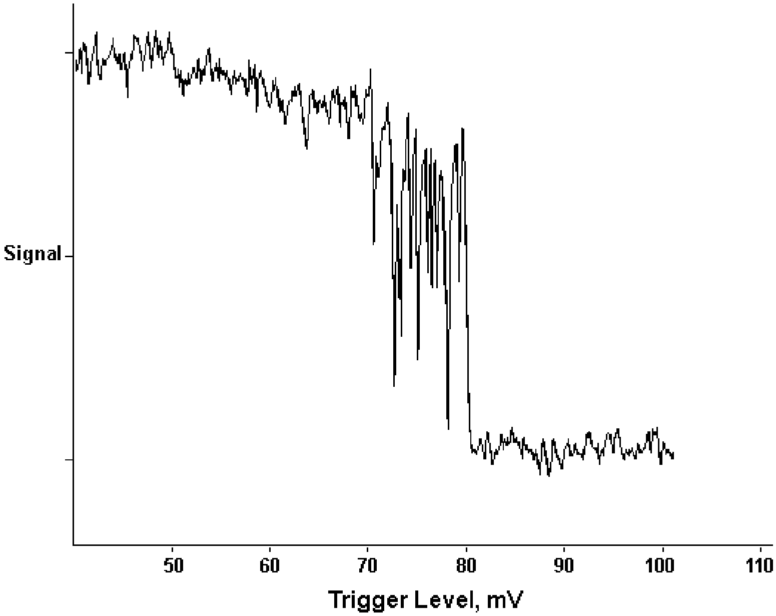
To set the trigger level, follow the steps below:

1. Press the Detector key and select the PFPD you wish to adjust. Turn OFF initial Autozero in the active method.
2. Press the Adjustments softkey to access the integrator parameters. Set Gate delay to 3.5 ms. This allows the tail of the prompt flame background emission to be integrated as a test signal. This figure shows a typical flame background emission profile.



1. Set the trigger level to the minimum and observe the noise on the detector output using a strip chart recorder or the Star Workstation status display. Gradually increase the trigger level. The signal level should decrease and the noise should also decrease. Select a trigger level which gives minimum noise. This will usually be triggering on the preliminary emission pulse.

2. If you will be detecting an element such as nitrogen, which emits very promptly after the main flame propagation, you may get better results by continuing to increase the trigger level until triggering is occurring on the main background emission pulse itself. As you increase the trigger level, the noise will increase substantially at one point. This is due to the trigger occurring sometimes on the apex of the preliminary emission pulse, and sometimes on the main pulse. Increasing the trigger level 10 to 20% above this point should provide very stable triggering for detection of prompt emitting elements. This setting is also preferred when the effects of large amounts of hydrocarbons on emission timing must be minimized. The following figure illustrates the signal observed during such an adjustment.



3.7.2 SETTING GATE DELAY AND GATE WIDTH

The following table contains gate delay and gate width settings which are recommended for routine detection of common elements. Try these settings first when setting up your PFPD to detect these elements.

Element	Gate Delay	Gate Width
Sulfur	6	20
Phosphorus	4	10
Nitrogen	3.5	8

Set the Gate Delay by Repeated Injections of Standard

The appropriate Gate Delay can be determined by injecting a standard and adjusting the Gate Delay until the required selectivity is achieved.

To set the Gate Delay by the method of repeated injections of standard, follow the steps below:

1. Install the test column.

2. Set the Detector temperature to 200°C. Set injector temperature to 200° for isothermal injectors; 80° initial, 0 hold, program to 200° for 1079 mode. Set column oven to 80° initial, hold 0.5 minutes, then program at 25°/minute to 200°, and hold 2 minutes, or until the last peak of interest elutes.

3. Allow the chromatographic system to equilibrate for ~1 hour.

4. Turn the stripchart recorder ON.

5. Adjust the gas flow rates to those recommended for your carrier gas and flow rate in the Suggested Fuel Gas Flow Rates table in Optimizing the PFPD (Page 3-12). The Air-2 flow rate has little effect on the detectivity of the PFPD and can be set to 10 mL/min.

6. If necessary, adjust the Air-1 and Hydrogen flow rates to give a flame pulse rate ~2-4 pulses/second.

7. Inject 1.0 µL of the FPD Test Sample split ~20:1 if using a split injector. Inject 1 µL of a 20:1 dilution of the test sample in iso-octane if using a non-splitting injector. Or, inject another sample of interest.

8. If the desired selectivity has not been achieved, increase the Gate Delay by 0.5 msec and inject the standard to check the effect of this change. Continue to increase the Gate Delay until the desired selectivity is achieved.

   NOTE: In the case of elements which emit very near the flame background peak, selectivity may be improved by opening the combustor flow needle valve somewhat beyond the position determined in the procedure Establishing Tick Tock. An increase of 1/4 to 1/2 turn counterclockwise is usually sufficient.

3.7.3 SET GATE WIDTH

Tools and Equipment Needed

These tools and equipment are needed to complete the following procedures:

- Printer/plotter or stripchart recorder
- FPD test sample (P/N 82-005048-03) or other standard
- 10 µL syringe (P/N 47-000007-00)

1. Set Gate Width to minimum
2. Inject an appropriate standard, calculate the detectivity for this Gate Width.
3. *See: Testing the Performance of the PFPD (Page 3-25) for instructions on calculating the detectivity of sulfur or phosphorus with the PFPD.*
4. Increase Gate Width by 1 msec, inject standard, calculate detectivity.
5. Continue to increase Gate Width as long as detectivity continues to improve.

3.8 BUILDING A GC METHOD

The procedure for building a GC method involves 4 tasks:

- Turn the PFPD electrometer on
- Set the detector temperature
- Set the range of the PFPD electrometer
- Set the gated integrator parameters

To Build a GC Method

1. Press the Detector key and select the PFPD you wish to use.
2. Turn the detector oven ON and set the desired detector temperature.
3. Turn the detector electronics ON.
4. Select the Range you wish to use and turn ON initial Autozero if desired. You may also time program Range and Autozero functions if your analysis requires it.

5. Press the Adjustments softkey to access the Gated Integrator parameters. Enter the Gate Delay, Gate Width, and Trigger Level parameters as determined in the preceding procedures, or from the table provided.

6. If you wish to use the analog output from your detector, select one of the Analog Output ports, enter the position of the PFPD detector you are using (Front, Middle, or Rear) and enter an attenuation value. If the analog output is going to a data system or integrator , an attenuation of 1 is strongly recommended. If the output is going to a strip chart recorder, note that you may time program the attenuation of the analog output port.

3.9 BUILDING A GC WORKSTATION METHOD

The procedure for building a PFPD Detector section as part of a GC method involves 4 tasks:

- Turn on the PFPD electrometer
- Set the detector temperature
- Set the range of the PFPD electrometer
- Set the Gated Integrator parameters

To Build a GC Workstation Method

1. Open the method to which you wish to add the PFPD section. Select the 3800 section, and select the Detector page. Select the position of the PFPD you wish to add (Front, Middle or Rear).

2. Set the Electronics and Detector Oven to ON.

3. Set the Detector Temperature to an appropriate value for your analysis.

4. Set the Range and Autozero as required. Note that these parameters are time programmable.

5. Set the Trigger level, Gate Delay, and Gate Width as required.

6. If you wish to use the Analog Output in addition to the digital signal used by the Star Workstation, select the Analog Output page, select the output channel you wish to use, and select the PFPD position and attenuation.

3.10 QUANTITATION

3.10.1 QUANTITATION WITH THE PFPD

When using the PFPD, it is important to understand how its pulsing flame can affect the accuracy and precision of a quantitative analysis.

As described previously, the combustor and ignitor chambers of the PFPD fill with a combustible mixture of air and hydrogen. The combustor chamber fills with the combustible mixture at about the same time as the ignitor chamber. When the gas mixture enters the ignitor, the mixture ignites and the flame propagates back through the combustor and then extinguishes. The combustor then begins to fill with the gas mixture and the process repeats. The rate of this repetitive process can vary, but for optimum performance of the PFPD, you must adjust the gas flow rates in order to strike a balance between the fill time of the combustor chamber and the fill time of the ignitor chamber. It is important that the combustor chamber fill slightly before the ignitor chamber in order to ensure that the flame propagates completely back to the combustor chamber. However, the combustor chamber should not fill too fast (relative to the ignitor chamber) or some of the sample exits the detector before it is combusted resulting in poorer detectivity.

Because the PFPD pulses, the emission derived from the PFPD appears as discrete signals separated in time. This requires electronics that are quite different from the conventional non-pulsed FPD in which the emission signal increases then decreases without interruption. That is, the PFPD electronics are not sampling discrete points on the eluting peak, as in the case of a conventional FPD. Rather, the PFPD stores the emission output derived during each pulse and generates a peak (or waveform) that may or may not be identical to the actual eluting peak shape, but which contains all the signal information from the chromatographic peak.

Given these unique properties of the PFPD, there are differences between quantitation based on the height or area of the chromatographic peaks.

3.10.2 PEAK AREA QUANTITATION

In general, quantitation based on peak areas is preferred because it is least affected by the pulsing nature of the PFPD and the way the PFPD electronics handles the resulting emission signal. Peak areas are best because once the fill rates of the PFPD are appropriately adjusted, any sample that enters the detector contributes to the resulting signal (i.e., all the sample that enters the detector between pulses is combusted), no matter how narrow the chromatographic peak.

3.10.3 PEAK HEIGHT QUANTITATION

Quantitation based on peak height, on the other hand, is less precise and depends, somewhat, on the widths and resolution of the eluting peaks. Peak height is determined by the pulse which contains the maximum concentration of the eluting peak, and to some extent is dependent on how well centered the concentration maximum of the eluting peak is relative to a pulse. The quantitative precision of the PFPD is not affected much by very narrow or very wide peaks. For very narrow peaks, almost all of the peak is combusted in one pulse and the resulting peak height is thereby equivalent to the total emission. For very broad peaks, the pulsed output follows the chromatographic peak shape. There may be some intermediate width peaks for which peak height precision is worse, but these cases can be addressed by changing the pulse repetition rate appropriately. For these intermediate width peaks, the peak is eluting during 2 or 3 pulses and the position of these pulses relative to the peak position can cause peak height to vary. Peak area is not greatly affected.

3.10.4 PEAK RESOLUTION WITH THE PFPD

Higher repetition rates (up to 10 Hz) are necessary when you must resolve two closely spaced peaks. Higher repetition rates give the best possible peak shape definition (at a small cost in detectivity). However, peak resolution is not usually a problem at lower repetition rates since the number of possible sulfur or phosphorus containing peaks is fairly small at the beginning of a chromatogram where peak resolution is likely to be a problem.

3.10.5 QUANTITATION IN THE SULFUR MODE

Since the electronically excited S_2 molecule is the emitting species in the sulfur mode, the signal generated by the PFPD is proportional to the square of the sulfur concentration in the combustor. Because it takes two sulfur atoms to form each excited S_2 molecule, detectivity is improved by increasing the concentration of sulfur in the combustor by confining the emission to a smaller volume (i.e., 2 mm combustor).

3.10.6 SQUARE ROOT FUNCTION

The PFPD electrometer (through a square root function) converts the quadratic response (sulfur emission varies as the square of sulfur concentration) to a linear response (sulfur signal varies as a direct function of the sulfur concentration) by taking the square root of the response. The square root function can be used for the determination of total sulfur in a hydrocarbon matrix, for example, where individual resolved peaks may not be present, and a total area of sulfur response is needed.

Normal/Square Root setting

The *square root* mode is selected by the NORMAL/Square Root field. When Square Root is selected, the output from the PFPD is the square root of the sulfur emission. When NORMAL is selected, the output of the PFPD is not converted or adjusted. Use this NORMALAL setting when operating the PFPD in the phosphorus mode, and when the sulfur signal is to be processed by a data system using the square root of height.

Detectivity of the NORMAL Versus Square Root Modes

In the Square Root mode, the amplifier signal is applied to the input of a square root circuit which produces an output equal to 10 times the square root of $V_{in}/10$. This output is linear with sulfur concentration but by the nature of the square root function is noisy. Detectivity in the hardware Square Root mode is often 2 to 4 times worse than in the Normal mode under the same detector conditions.

Using the Star Workstation and the Square Root of Height Mode

The square root of height mode of the Star Workstation is most useful for those cases where quantitation of reasonably resolved peaks is required. The peak height reported is the square root of the net peak height, that is, after correction for the position of the baseline. Detectivity is not affected by use of this square root of height. Do not use the square root of height mode when the method is in the SQUARE ROOT mode, since this would result in taking the fourth root of the original signal. The Star Workstation square root of height mode can be used in conjunction with the Multilevel Calibration function of the Star Workstation.

Multilevel Calibration for Sulfur Analysis

Finally, multilevel calibration in the Star Workstation allows you to construct response curves which can be used to obtain quantitative results, even in the presence of interferences which alter the normal quadratic response. The Star Workstation Multilevel Calibration function can be used, with either quadratic or linearized data, for the quantitation of discrete sulfur containing peaks. This function allows for individual calibration of peaks at up to 9 levels of each component and provides accurate quantitation even under conditions where the sulfur response may not be quadratic because of interferences or matrix effects.

Section 4
Advanced Operation

4.1 OVERVIEW

This section describes the operation of the PFPD in the Nitrogen mode, including:

- Theory of operation, describing the basis for nitrogen detection and including suggested gas flow rates.
- Installation of the nitrogen mode parts - for users who are adding the nitrogen mode capability to an existing PFPD. Includes an exploded view of the parts.
- Nitrogen mode operation - provides some suggestions for enhancing or modifying nitrogen mode performance.
- Phosphorus mode/Sulfur mode operation - describes some changes which may be required to detect phosphorus or sulfur using the nitrogen mode PMT.
- Spare Parts and Supplies
- Additional Elements - describes preliminary operating conditions for the detection of the following elements: Arsenic, Selenium, Tin, and Manganese.

4.2 THEORY OF OPERATION

Nitrogen mode is based upon combustion of nitrogen containing compounds to form NO. NO then reacts with hydrogen atoms remaining in the combustor after the flame is extinguished to form HNO*, an electronically excited molecule which emits light in the 700 - 800 nm range of the near infrared. Because these emission wavelengths are beyond the range of the photomultiplier tube used in the standard PFPD, the Nitrogen mode requires a new red-sensitive photomultiplier and PMT holder hardware, along with an appropriate dark red colored glass filter.

Because N mode is based on complete combustion of the sample molecule to form HNO*, the PFPD response is much less dependent on the chemical nature of the sample than is the TSD response, which depends on the presence of a C-N bond in the molecule. Thus even inorganic nitrogen compounds such as ammonia, hydrazine, and nitrogen oxides are detectable by the N mode PFPD, whereas these compounds give no response on the TSD. The only nitrogen compound known to give no useful response on the PFPD is molecular nitrogen,

N_2. Compounds such as nitroglycerin and other nitrate esters, nitroaromatics, and nitroso compounds give a somewhat enhanced response when compared to more reduced nitrogen compounds, but the enhancement amounts to only ~20%, so for most purposes the N mode PFPD can be considered to give a uniform response to all nitrogen compounds, as it does for sulfur and phosphorus compounds. Uniformity of response may be enhanced by increasing the oxygen flow into the combustor, at the cost of some reduction in sensitivity.

Oxidation of nitrogen requires a hotter flame than either phosphorus or sulfur. This is reflected in the following table of recommended flame gas flow rates. In general, the nitrogen mode requires a more air rich flame, and suffers a larger reduction in sensitivity as carrier flow rate increases. Use of the 3 mm combustor provides best detectivity.

4.2.1 TABLE OF OPTIMUM FLOW RATES

		Optimum Flow Rate, mL/minute		
Carrier Gas	**Flow Rate, mL/minute**	**Air 1**	**Hydrogen**	**Air 2**
Hydrogen	2	12.5	7	15
	5	12.5	8	15
	10	28	3	15
Helium	2	14	14	15
	5	17.5	20	15
	10	17	17	15
Nitrogen	2	15.5	18	15
	5	18	19	15

4.3 INSTALLATION OF THE NITROGEN MODE PARTS

If you are upgrading a Phosphorus/Sulfur PFPD to add the Nitrogen mode, you will need to replace the photomultiplier tube housing and filter currently installed on your PFPD with the PMT assembly and filter supplied with your upgrade kit. Refer to the figure below for identification of the components of the N mode assembly. The steps involved are:

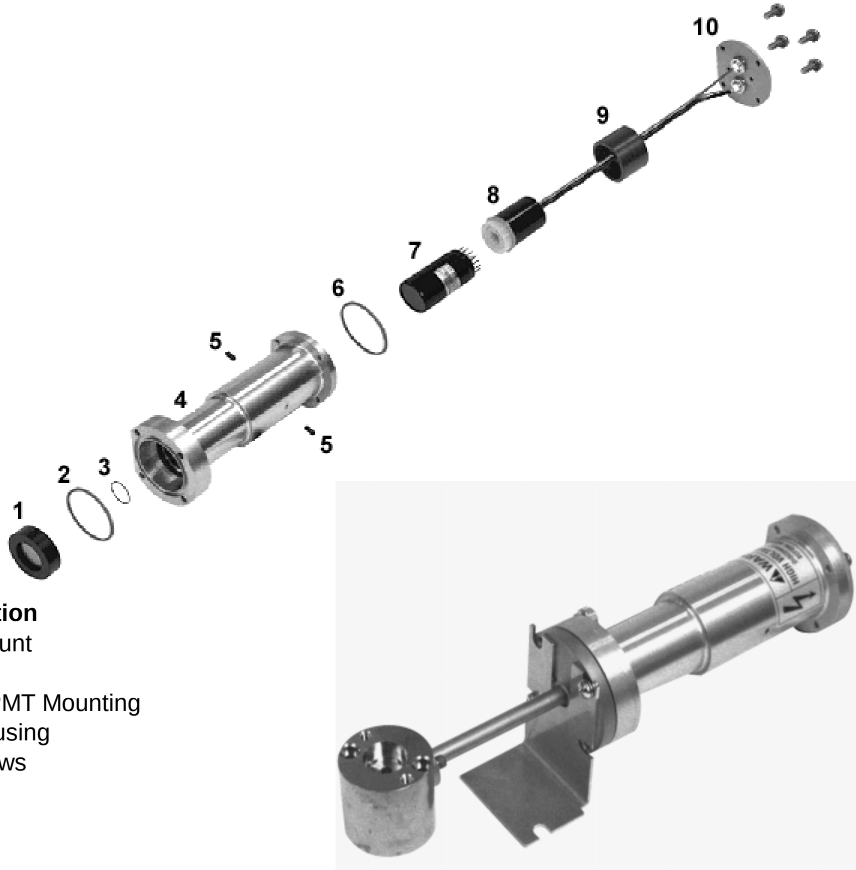
1. Turn off the PFPD. Alternatively, turn off GC power.
2. Disconnect the high voltage and signal cables from the base of the P/S PMT housing.

3. Remove the PMT housing by removing the two thumb screws securing the housing to the light pipe flange. Store the P/S PMT housing so as to protect it from mechanical damage and bright light.

4. Insert the Nitrogen mode filter in the recess in front of the PMT in the N mode housing. Be sure the silicone O-ring is in its place in the groove on the face of the housing flange. Using the two screws supplied with the upgrade kit, attach the N mode PMT housing to the light pipe flange. Be sure that the O-ring makes a light-tight seal.

5. Reconnect the signal and high voltage cables to the connectors on the base of the N mode PMT housing. Restore power to the PFPD.

6. Press the Detector key, select the PFPD, and press the Adjustments soft key. Set a Gate Delay of 3.5 msec, a Gate width of 8 msec, and a PMT Voltage of 600 volts.



Item	Description
1	Filter Mount
2	O-ring
3	O-ring, PMT Mounting
4	PMT Housing
5	Set Screws
6	O-ring
7	PMT
8	Socket
9	Retainer
10	Connectors with Mounting Plate

4.4 NITROGEN MODE OPERATION

Operation in the nitrogen mode is very similar to the sulfur and phosphorus mode operation described in detail elsewhere in the manual. The following differences should be noted:

1. The nitrogen mode uses a Hammamatsu R5070 red sensitive photomultiplier tube. This PMT may be operated at a somewhat higher voltage than the standard phosphorus/sulfur photomultiplier. A typical voltage of 580 volts has been used for the nitrogen mode.

2. Nitrogen emission duration is similar to but somewhat shorter than phosphorus emission, occurring over a period of up to ten milliseconds. A good starting point for Nitrogen mode tuning would be a gate delay of 3.5 milliseconds and a gate width of 8 milliseconds.

3. The Nitrogen mode requires somewhat finer control of the needle valve, since the best sensitivity is achieved just after the tick tock mode of operation is corrected. The needle valve should be opened only enough to bring the detector out of tick tock and reduce the background noise to a usable level. Then evaluate the signal to noise ratio of a nitrogen standard while adjusting the Gate Delay until the optimum signal/noise is achieved.

4. The optimized flame gas flow rates in the table above give the best overall detectivity for all nitrogen compounds, with somewhat enhanced response from oxidized nitrogen species. If you require more uniform response regardless of nitrogen compound type, you may increase the air 1 flow by 10 to 20%. This will enhance the response of reduced nitrogen relative to oxidized nitrogen, at the expense of some loss in overall detectivity. We have found a mixture of 2-nitrotoluene, 2,6-di-t-butylpyridine, and N,N-diethylaniline useful as a probe of response uniformity.

5. When properly tuned, the Nitrogen mode PFPD shows no response to simple alkanes at fluxes up to about 1 microgram/second hydrocarbon. Above this flux the response increases until flame propagation is completely inhibited at about 30 micrograms/second. Selectivity against hydrocarbon interference can be increased by opening the needle valve 1/2 to 1 turn beyond the optimum for detectivity.

6. The near-IR sensitive PMT may respond to emissions from the detector itself at very high detector temperatures. If you need to operate at temperatures above 320°C, you may need to increase the trigger level to be sure that the trigger point is well above the near-IR background. You may also find that addition of a short pass filter which cuts off wavelengths longer than those of your element of interest will improve detectivity and dynamic range.

4.5 PHOSPHORUS MODE OPERATION

Operation in the phosphorus mode is the same with the Nitrogen mode PMT as it is with the standard PMT. To eliminate interference of nitrogen in the detection of phosphorus, a Schott BG39 red blocking filter may be used in conjunction with the Schott GG495 phosphorus filter. The PMT voltage may be run slightly (~20-50 volts) higher than the standard PMT.

4.6 SULFUR MODE OPERATION

No changes in operation are required to use the Nitrogen mode PMT in the Sulfur mode. The PMT voltage may be run slightly (~20 - 50 volts) higher than the standard PMT.

4.7 SPARE PARTS AND SUPPLIES

In general, the parts and supplies needed to operate the N mode PFPD are the same as those used with the P/S mode PFPD. The following are additional parts which may be required.

Part Number	Description
03-925119-01	Filter Mount with Nitrogen Mode (RG9) filter
03-925119-02	Filter Mount with Phosphorus mode (GG495) and Red Absorbing (BG39) filters
03-925128-00	Photomultiplier tube, Nitrogen mode

4.8 ARSENIC SELECTIVE DETECTION

The following recommendations are based upon work reported by Prof. Aviv Amirav and Hongwu Jing, and are accurate to the best of our knowledge. This is an area of ongoing research, so you may find that your application requires modification of some parameters.

4.8.1 EMISSION WAVELENGTHS

Arsenic exhibits a very broad emission spectrum, extending from 360 nm to 800 nm. The choice of the wavelength at which to observe As emission is determined largely by the emission characteristics of interfering elements.

4.8.2 EMISSION TIMING

Arsenic emission is longer delayed than sulfur, with a correspondingly longer emission duration. Use the Gate Delay and Gate Width recommended for sulfur, or increase delay even further for additional selectivity against nitrogen and phosphorus. A 3 mm combustor provides best sensitivity.

4.8.3 FLAME COMPOSITION

Delayed arsenic emission is optimized in hydrogen rich conditions similar to those used for sulfur. Arsenic may also be detected in an air-rich flame, as described below.

4.8.4 FILTERS

Arsenic may be detected at a variety of wavelengths, depending upon the requirements of the analysis. Good detectivity (~6 pg/second As) and selectivity are achieved using an RG9 (nitrogen) or RG695 filter with the Nitrogen mode R5070 photomultilplier tube. Interference by P and N compounds can be reduced by using a long gate delay time. Tailing of the delayed emission can be reduced by operating the detector at the highest practical temperature, or by operating below 200°.

An alternative approach to arsenic detection uses an air-rich flame, a GG495 (phosphorus) filter, and a very short gate delay. This air-rich mode gives very good detectivity, ~3 pg/second As. and very good selectivity against sulfur interference, but at the expense of reduced selectivity against hydrocarbon interference. This air-rich mode also eliminates the tendency to peak tailing observed with the hydrogen-rich flame emission.

Linearity and Dynamic Range

Arsenic response is linear. No information is available on linear dynamic range, although it is expected to exceed 10^3.

Other Considerations

Arsenic detection provides the most opportunities for optimization of any of the common PFPD-detectable elements. Selectivity can be optimized by the choice of air-rich or hydrogen-rich flame conditions, by the choice of gate delay, and by the choice of optical filter. In some applications, it may even be desirable to reduce the selectivity among heteroatoms and instead look to selectivity only against hydrocarbons. For example, the ability to detect simultaneously arsenic, phosphorus, sulfur, and nitrogen, while totally rejecting hydrocarbon response, is extremely important in the detection of chemical warfare agents for treaty verification purposes.

4.9 SELENIUM SELECTIVE DETECTION

The following recommendations are based upon work reported by Prof. Aviv Amirav and Hongwu Jing, and are accurate to the best of our knowledge. This is an area of ongoing research, so you may find that your application requires modification of some parameters.

4.9.1 EMISSION WAVELENGTHS

Selenium exhibits a fairly broad emission spectrum in the PFPD, extending from ~360 nm to ~550 nm, attributed to emission of the Se_2 molecule.

4.9.2 EMISSION TIMING

Selenium emission is somewhat longer delayed than sulfur, with a correspondingly longer emission duration. Use the Gate Delay and Gate Width recommended for sulfur.

4.9.3 FLAME COMPOSITION

Selenium emission is optimized in cool, hydrogen rich conditions similar to those used for sulfur. Since emission is due to Se_2, use the 2 mm combustor and keep all gas flows as low as practical to minimize dilution of the selenium concentration in the flame.

4.9.4 FILTERS

Selenium may be detected using either the BG12 (sulfur) or the GG495 (phosphorus) filter. Best detectivity, ~10 pg/second Se, is achieved using the BG12 filter, but this also gives the most interference from sulfur compounds. Detectivity with the phosphorus filter is ~20 pg/second Se, but sulfur interference is considerably reduced. Either filter gives essentially complete specificity against hydrocarbon interference.

Linearity and Dynamic Range

Selenium response is quadratic, like the sulfur response, and can be treated by the same approaches used for sulfur signal processing. Dynamic range is approximately 10^3 for a given electrometer range.

Other Considerations

Since selenium emission depends upon recombination of Se to form electronically excited Se_2 molecules, use the lowest detector temperature which gives satisfactory chromatographic peak shapes. Selenium also exhibits a prompt emission which may be used to distinguish it from sulfur.

4.10 TIN SELECTIVE DETECTION

The following recommendations are based upon work reported by Prof. Aviv Amirav and Hongwu Jing, and are accurate to the best of our knowledge. This is an area of ongoing research, so you may find that your application requires modification of some parameters.

4.10.1 EMISSION WAVELENGTHS

Tin exhibits a fairly broad emission spectrum in the PFPD. A broad band between ~380 and 540 nm is attributed in the literature to interaction between a tin species and the quartz surface. The sharper bands at 610 and 695 nm have been attributed to SnH emission. The relative and absolute amplitudes of these bands may be a function of the PFPD flame composition.

4.10.2 EMISSION TIMING

Tin emission is somewhat longer delayed than phosphorus, and emission duration is intermediate between phosphorus and sulfur. Use the phosphorus gate delay and width for best sensitivity; use the sulfur gate delay and width for best selectivity against carbon interference.

4.10.3 FLAME COMPOSITION

Tin emission is optimized in hydrogen rich conditions similar to those used for phosphorus or sulfur. Increasing air1, air2, and hydrogen by 50 - 100% each will help to reduce peak tailing. Either the 2 mm or 3 mm combustor may be used, with a slight preference for the 3 mm.

4.10.4 FILTERS

Tin may be detected using either the BG12 (sulfur) or the OG590 filter. Best detectivity, ~100 fg/second Sn, is achieved using the BG12 filter, but this also gives the most interference from high levels of sulfur compounds. Detectivity with the OG590 filter is ~1 pg/second Sn, but sulfur response is considerably reduced. Response with the OG590 filter is best with the red sensitive R5070 photomultiplier tube. A 610 nm interference filter has also been found useful in conjunction with the R5070 PMT.

Linearity and Dynamic Range

Preliminary results indicate that the tin response is linear, and extends over more than three orders of magnitude.

Other Considerations

Tin compounds exhibit tailing in the PFPD, probably due to limited volatility of the tin combustion products. This tailing can be reduced by using higher gas flow rates, and by raising the detector temperature to 350°C to help volatilize the tin compounds. You may also find it helpful to insulate the detector tower, by wrapping the tower with fiberglass cloth, for example, being careful not to cover the outlet.

An alternative approach to tin tailing is to reduce the detector temperature as much as possible without impairing the chromatography. This reduces the “tail” amplitude, but spreads it out in time. Several minutes may be required for the detector to clean itself of tin deposits.

4.11 MANGANESE SELECTIVE DETECTION

The following recommendations are based upon work reported by Prof. Aviv Amirav and Hongwu Jing, and are accurate to the best of our knowledge. This is an area of ongoing research, so you may find that your application requires modification of some parameters.

4.11.1 EMISSION WAVELENGTHS

Manganese exhibits a strong atomic emission line at 403 nm, along with other weaker lines and bands in the 380 - 600 nm range. The 403 nm line is the only emission of analytical interest with the PFPD.

4.11.2 EMISSION TIMING

Manganese shows no delayed emission, as expected for atomic emission. Use the minimum delay time and a gate width of 2 to 4 msec, depending on your flame propagation rate.

4.11.3 FLAME COMPOSITION

Manganese emission is favored by a hot flame, which is achieved by a stoichiometric or slightly air rich air1/hydrogen mixture and minimum dilution of the flame by carrier gas flow. The manganese emission is not very sensitive to the exact gas composition, so you may vary the composition somewhat to enhance selectivity against other elements. Emission is enhanced by the use of the 3 mm ID combustor.

4.11.4 FILTERS

Because the manganese emission is not separated in time from the flame background emission, a narrow band interference filter is required to provide adequate selectivity against hydrocarbons and other interfering elements. A 404.7 nm interference filter with 10 nm bandwidth was used in Prof. Amirav's work. This filter is commonly available as part of a set of filters for the isolation of mercury emission lines, and may be obtained from many sources of interference filters. Using this filter, detectivity of ~100 fg Mn/second and a selectivity against hydrocarbons of ~10^4 have been observed by Prof. Amirav.

Linearity and Dynamic Range

Manganese response is linear. No information is available on linear dynamic range, although it is expected to exceed 10^3.

Other Considerations

Manganese containing peaks show some tailing due to incomplete clearance of the manganese from the combustor. This tailing is minimized using near-stoichiometric flame conditions. It may be further reduced by using a detector temperature below 225°C, but this may result in long term buildup of manganese deposits in the combustor, although this was not observed by Prof. Amirav.

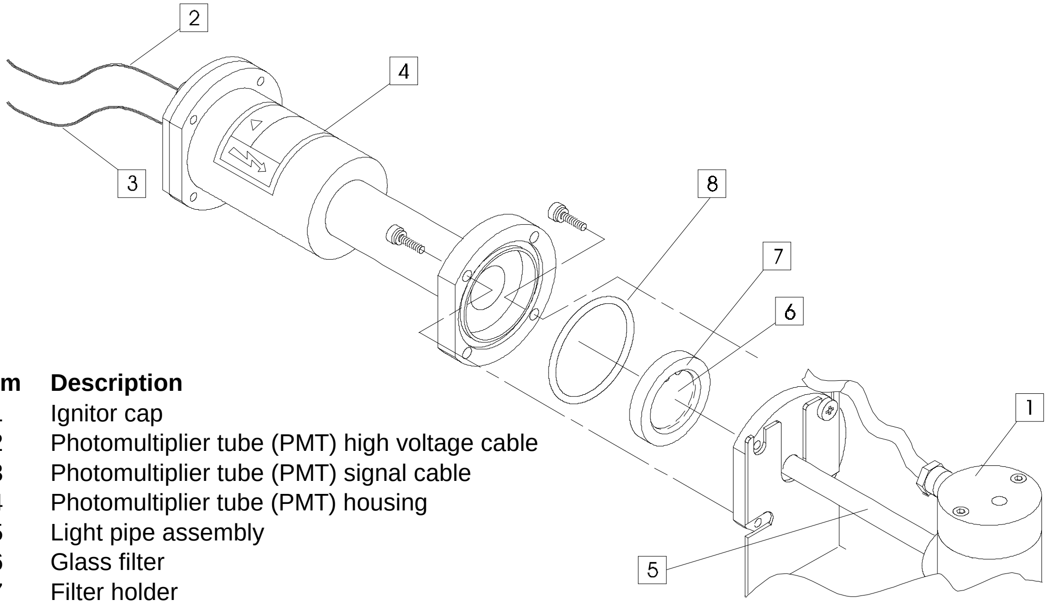
Section 5
Maintaining the PFPD

5.1 OVERVIEW

5.2 REPLACING THE OPTICAL FILTER

The choice of optical filter depends on the detection mode that is to be used.

- Sulfur mode: Use the BG-12 deep-violet glass filter
- Phosphorus mode: Use the GG-495 yellow glass filter
- Sulfur + Phosphorus mode: Use the optional WG-345 glass filter (P/N 03-925158-00)



Item	Description
1	Ignitor cap
2	Photomultiplier tube (PMT) high voltage cable
3	Photomultiplier tube (PMT) signal cable
4	Photomultiplier tube (PMT) housing
5	Light pipe assembly
6	Glass filter
7	Filter holder
8	O-ring

Tools and Equipment Needed

These tools are needed to complete the following procedure:

- Phillips-head screwdriver
- Glass filter in filter holder
- Lab tissues
- Capillary pick

Disassemble the PFPD and Remove the Optical Filter

1. Turn OFF the PFPD electronics.

2. Remove the detector cover from the top of the GC.

3. Remove the 2 thumbscrews holding the PMT housing (Item 4) to the light pipe assembly (Item 5). Carefully remove the PMT housing from the detector tower. The filter (Item 6) is loosely held in the filter holder (Item 7) that is recessed in the end of the PMT housing.

4. Invert the PMT housing over a clean lab tissue and allow the filter holder to drop out of the recess in the end of the PMT housing. If the filter holder should stick in the PMT housing, free it by using gentle pressure with a capillary pick or other clean utensil. Place this filter on a clean surface (e.g., lab tissue) or in its storage container.

   NOTE: Handle the filter holder by its outside edge. Do not touch the optical surface of the filter.

Replace the Optical Filter

1. If you are **cleaning the optical filter**, remove the C-clip holding the filter in the filter holder. Moisten a clean lab tissue with methanol or iso-propanol. Hold the filter by its outer edge and gently wipe both surfaces of the filter with the lab tissue. Wipe away the excess solvent with a clean dry lab tissue. Place the filter in the filter holder and reinstall the C-clip.

2. Hold the filter that is to be installed by its outside edge and slide it into the recess in the end of the PMT housing. Check that the filter is correctly seated so that its surface is flush with the rim of the PMT housing and the O-ring (Item 8) is properly seated in its groove.

3. Carefully join the PMT housing to the light pipe assembly and install and tighten the 2 thumbscrews.

Change the Detection Mode and Reassemble the PFPD

1. Go to the Adjustments page of the PFPD section.
2. Adjust the Gate Delay and Gate Width to correspond with the emission profile of the element(s) you wish to detect.
3. Turn ON the PFPD electronics.
4. Go to Section 3, ***Optimizing the PFPD*** for instructions on optimizing the performance of the PFPD with the optical filter just installed.

5.3 CHANGING THE COMBUSTOR SIZE

Although the PFPD can accommodate both narrow and wide bore quartz combustors, either quartz combustor will work adequately when operating in either the Sulfur or Phosphorus mode. If detectivity is **not** critical, you can switch between the two modes without changing the size of the quartz combustor. However, if you require the maximum detectivity for an analysis, the choice of the appropriate diameter (narrow bore or wide bore) of quartz combustor depends on the detection mode that is to be used.

- Sulfur mode: Use the narrow bore (2 mm ID) quartz combustor for sulfur, selenium, or tellurium detection.
- Phosphorus mode: Use the wide bore (3 mm ID) quartz combustor for all other elements.
- S + P mode: Use the narrow bore (2 mm ID) quartz combustor

NOTE: For column flow rates over 5 mL/min, use the wide bore quartz combustor.

Proceed as described in Section 3.2

5.4 REPLACING A DIRTY COMBUSTOR

The quartz combustor can become fouled after prolonged use, particularly with samples containing high levels of organometallics. However, the PFPD has a remarkable ability to clean itself of many deposits. Therefore, before replacing a combustor, try baking the detector at high temperature with normal pulse rate overnight or longer. If this does not restore expected noise and detectivity levels, proceed as described in Section 3.2.

5.5 ORDERING PARTS AND SUPPLIES FOR THE PFPD

To order parts or supplies for the PFPD, refer to the information below:

- In the USA and Canada, call 800-926-3000.
- In Europe, call your local Country office.
- Or, call your local Varian representative.

Description	**Part Number**
Crunch washers (Aluminum)	15-003347-00
Combustor, quartz (narrow bore, 2 mm ID)	03-925176-00
Combustor, quartz (wide bore, 3 mm ID)	03-925177-00
Combustor support (narrow bore, 2 mm ID)	03-925178-00
Combustor support (wide bore, 3 mm ID)	03-925179-00
Combustor support seal (Aluminum)	03-925138-00
Filter assembly, Sulfur	03-925151-01
Filter assembly, Phosphorus	03-925151-02
Filter, Sulfur + Phosphorus (optional)	03-925158-00
Ignitor assembly with cable	03-925160-00
Diffusion source kit, Sulfur	03-925157-00
Screw, detector tower (8-32 x 1-1/2 SHCS)	03-925194-02
Screw, ignitor adaptor and column guide (8-32 x 3/4 SHCS)	03-925194-01
Adaptor seal, diffusion source holder (Aluminum)	03-925132-00

Section 6
Troubleshooting

6.1 OVERVIEW

The following section describes how to troubleshoot and correct problems with the Pulsed Flame Photometric Detector (PFPD). Refer to the ***Varian GC Operator's Manual*** for instructions on troubleshooting other parts of the chromatographic system.

Using the Troubleshooting Guide

This troubleshooting guide outlines typical problems that you might encounter during the routine operation of the PFPD. To use the guide, first identify the symptom or problem (e.g., the PFPD flame does not ignite). Then, locate the problem in the following guide. Likely causes as well as instructions for correcting the problem are listed.

The troubleshooting guide also refers you to other sections of the ***PFPD Operator's Manual*** or the ***Varian GC Operator's Manual*** that may be helpful. Should you have questions when troubleshooting the PFPD, contact a Varian Customer Service Representative.

Symptom	**See Page ...**
Flame does not ignite	6-2
Baseline noise is too high	6-3
Baseline is erratic (tick-tock)	6-6

6.1.1 FLAME DOES NOT IGNITE

Possible Cause	**Solution**
Gas flow rates are too low or off	Check that the carrier, air, and hydrogen regulators read correct pressures. Check that air and hydrogen are flowing through the PFPD at the expected flow rates.
PFPD electrometer is OFF	Turn the PFPD electrometer ON.
Detector tower too cold	Be sure that detector oven power is On, and allow enough time for the tower to approach the operating temperature. This is particularly important with very hydrogen rich conditions.
Ignitor coil is broken	Use a mirror to check that the ignitor is glowing. If the coil is not glowing, the ignitor coil may be broken. Disconnect the ignitor cable from the electrometer board. Check for continuity. Replace the ignitor coil and assembly if defective.
Detector is leaking gas from around washers and/or seals	Check whether gas is leaking from around the aluminum crunch washers or the light pipe seal.
Air:hydrogen gas composition is incorrect	If the ignitor is glowing dimly, the gas composition may be too rich in hydrogen. To adjust the air:hydrogen composition, proceed as follows: ■ Note the current hydrogen dial setting, then turn the hydrogen flow rate OFF ■ Check that air flow rates are approximately: Air-1 = 10-15 mL/min., Air-2 = 15 mL/min. Reset the hydrogen flow to the correct setting.
Column is installed incorrectly	Check whether the column is leaking or is improperly secured. Install the column correctly.
Carrier gas flow rate is too high	This is a particular problem when using helium as a carrier gas, as helium tends to cool the flame excessively, preventing the flame from propagating into the combustor. Decrease carrier gas flow rate to an appropriate value, or increase Air-1 flow and/or increase the combustor flow to create a hotter flame in the combustor.

Possible Cause	Solution
Problem with hydrogen gas supply	Check the hydrogen gas supply as follows: ■ Is the hydrogen flow rate correct? ■ Is the hydrogen line plumbed correctly? ■ Is a hydrogen gas source connected to the hydrogen line? ■ Are the inlet manifold and tank connections free of leaks or other problems? ■ Is the hydrogen line obstructed (e.g., valve in the hydrogen line is turned off)?

6.1.2 BASELINE NOISE IS TOO HIGH

Possible Cause	Solution
Gas flows are improperly set	Check the gas flow rates and readjust.
Combustor is dirty	Bake the detector at high temperature overnight with flame pulsing. Replace the quartz combustor only if this treatment does not improve the baseline.
Column end is dirty or broken, or extends too far into the combustor.	The end of the column may be dirty, the column may have broken off in the combustor, or the column may be inserted too far into the combustor. If this is the case, splinters of glass may be fluorescing, thereby increasing the background signal. Reinstall the column.
Detector parts are dirty	Detector parts may be contaminated from handling. Mild contamination often responds to a high temperature bakeout. If this proves unsuccessful, clean the parts with reagent grade iso-propanol in an ultrasonic bath. Repeat with several rinses of iso-propanol.
Light pipe window is dirty or broken	Contact Varian Service.
Photomultiplier tube is aging	As the PMT ages the voltage must be increased to achieve the same gain. This results in greater dark current noise. Replace the photomultiplier tube when acceptable detectivity can no longer be achieved.
Photomultiplier tube gain is too high	Decrease the photomultiplier tube voltage to an acceptable level.

Possible Cause	Solution
Gate Width/Gate Delay is incorrect	The Gate Delay has been set too close to the hydrocarbon emission. Reset the Gate Delay.
Normal/Square Root setting is incorrect	Check that the Square Root Mode is not On, unless you wish to operate in that mode, in which case a high noise level is expected.
Gas flow rates are unstable	Check for leaks. Check that the mass flow controllers are operating properly. Replace if necessary. **NOTE: To prevent steps in the baseline when the AutoSampler cycles, DO NOT drive the AutoSampler with the PFPD air line.**
Detector temperature is too high	This is a particular problem when using the near-IR sensitive R5070 PMT at temperatures above 320°C, as the PMT is sensitive to emissions from the walls of the detector itself. If you cannot operate the detector at a lower temperature, you may need to add a short pass filter which will block the near-IR wavelengths.
Detector is in the tick-tock mode	Tick-tock mode indicates that the ignitor volume is filling faster than the combustor volume. The cure is to either slow the ignitor volume fill rate, or speed the combustor volume fill rate. To decrease the ignitor volume fill rate, while viewing the baseline, slowly decrease the Air-2 flow rate until the noise abruptly decreases. Then, turn the Air-2 mass flow controller 1/10 of a turn more. To increase the combustor volume fill rate, turn the split valve counter-clockwise slowly while watching the baseline. When the pulse becomes regular and background becomes constant, increase the split valve an additional 1/2 turn.
Trigger Level Set Incorrectly	Increase or decrease trigger level ~20%. You may need to re-optimize Gate Delay after changing trigger level.

Possible Cause	Solution
Flame propagating past end of the combustor support	A rather characteristic pulse pattern (short pulse-long pulse-pause) suggests that the flame front is propagating past the end of the combustor support. This may happen at high detector temperatures or when using a narrow bore column with hydrogen as the carrier gas. In such situations, the polyimide coating on the column end will be burned off below the combustor support. Increase the *Hydrogen* flow rate by ~10%. This cools the flame and limits the propagation of the flame below the end of the combustor support. Alternatively, you may connect your analytical column to a 15 cm length of 0.53 mm ID deactivated fused silica tubing using a Press-Fit connector, inserting the deactivated tubing into the PFPD in place of your analytical column. This minimizes the clearance between the column and the combustor, preventing unwanted flame propagation.

6.1.3 BASELINE IS ERRATIC (TICK-TOCK)

Possible Cause	Solution
Ratio of combustor flow to ignitor flow is too small.	If possible, increase the center flow rate by turning the split valve 1/4 turn counterclockwise. Decrease the Air-2 flow rate.