A Presentation by OI Analytical

PFPD Training Course – Part 1
Introduction, Theory, and Selectivity

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ISO 9001 SGS

O·I·Analytical
A World of Solutions

PFPD Development

- Originally developed and patented by Dr. Aviv Amirav
  - Professor of Chemistry at the University of Tel Aviv, Israel
- Licensed by OI Analytical
  - Design development
  - Sales & service
  - Training
  - Applications support

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Pulsed Flame Photometric Detector

- PFPD, the newest generation of Flame Photometric Detectors

- Main Advantages:
  - Increased selectivity (10x)
  - Increased sensitivity (10x)
  - Linear, equimolar response
    - Easier calibrations!
  - Minimal maintenance
  - Decreased gas requirements

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PFPD Theory of Operation

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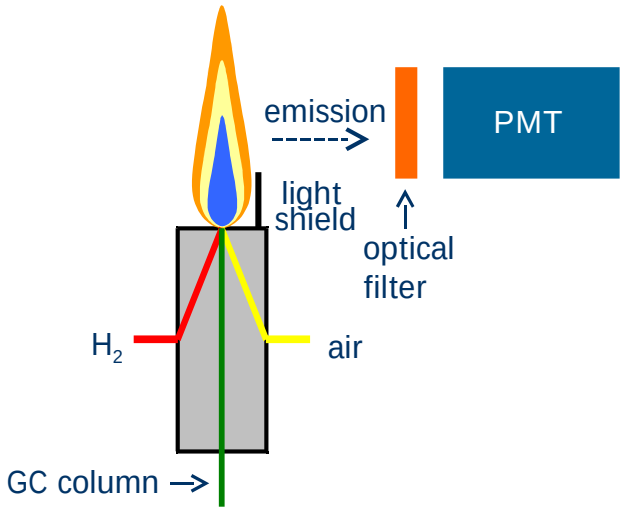
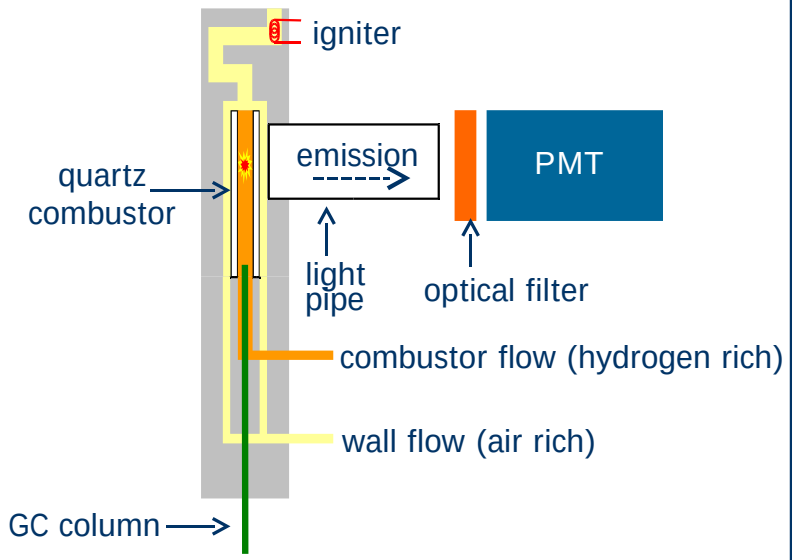
PFPD Compared to FPD

FPD Configuration



PFPD Configuration



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PFPD Compared to FPD

FPD

- Continuous H_2/air flame
- Analyte combustion in flame yields simultaneous emissions CH*, C_2*, OH*, HPO*, S_2*
- Selectivity based on light shield/alignment, narrow-pass interference optical filter, PMT

PFPD

- Pulsed H_2/air flame
- In each “pulse”, combustion yields time-dependent emissions from CH*, C_2*, OH*, HPO*, S_2*
- Selectivity based on time dependent emissions, broad-bank optical filter, PMT, multi-gate technique

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Q. What is a “Pulsed Flame”?

- A flame which propagates (travels) from the source of ignition along a pathway to its gas supply, where it is extinguished
- The timeframe for each “pulse” is measured in milliseconds
- Termination is at a small hole <1 mm in diameter

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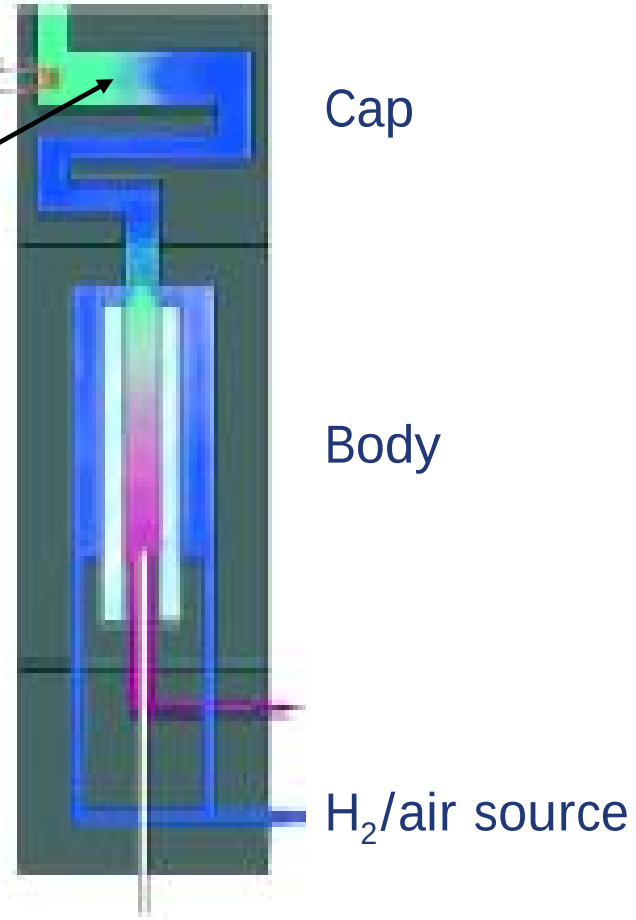
The PFPD Pulse Cycle

<u>Stage 1 – Gas Filling</u>

Combustible mixture of H_2/air (shown in blue and purple) fills detector body, combustor and cap from the bottom up



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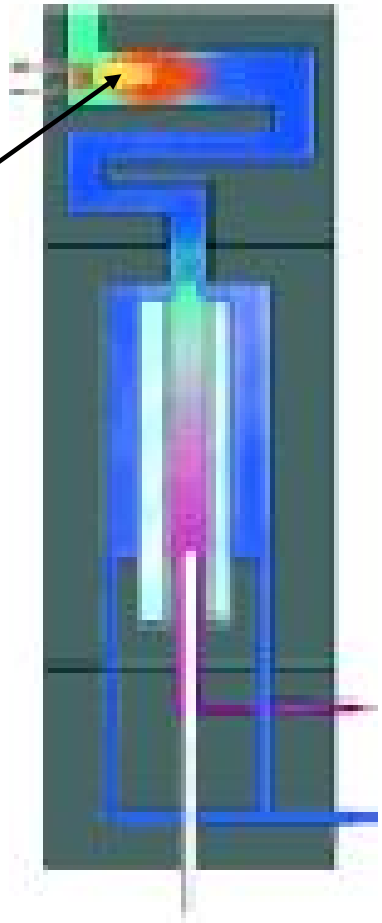
The PFPD Pulse Cycle

Stage 2 – Gas Ignition

Combustible H_2/air mixture is ignited in the cap



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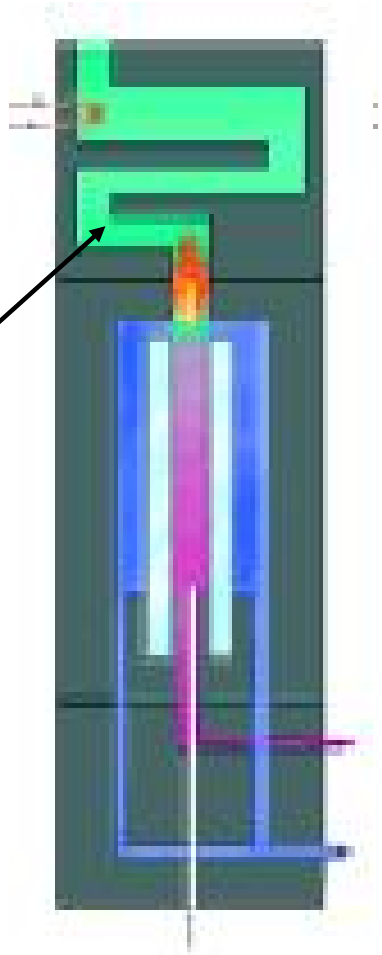
The PFPD Pulse Cycle

Stage 3 – Propagation

Flame begins to travel back along original pathway, consuming (burning) H_2/air fuel along the way



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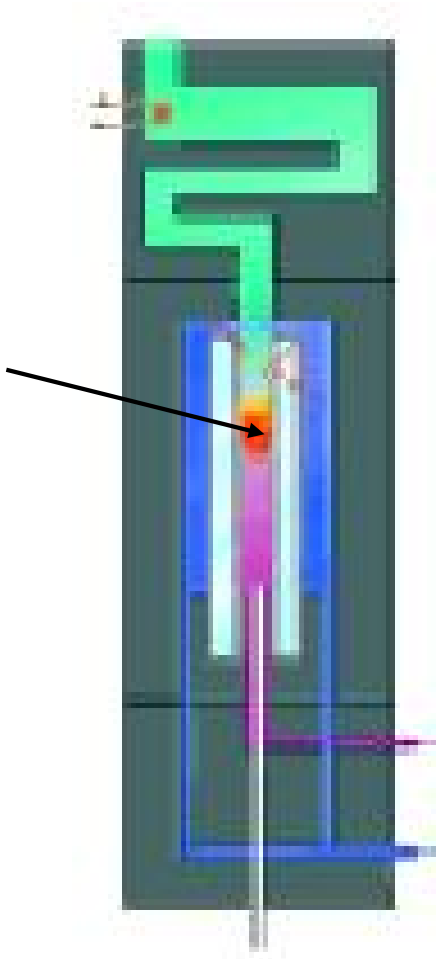
The PFPD Pulse Cycle

<u>Stage 4 – Combustion & Fluorescence Emission</u>

As compounds elute from GC column, they are combusted in the flame; excited species are formed (e.g. HPO*, S_2*) and begin to fluoresce



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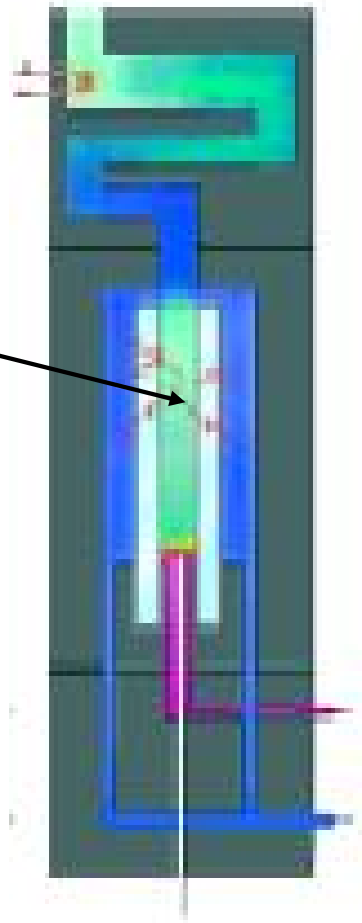
The PFPD Pulse Cycle

<u>Stage 5 – Extinction & Continued Fluorescence Emissions</u>

The flame is extinguished when it reaches the bottom of the detector; the excited species continue to fluoresce for up to 25 milliseconds



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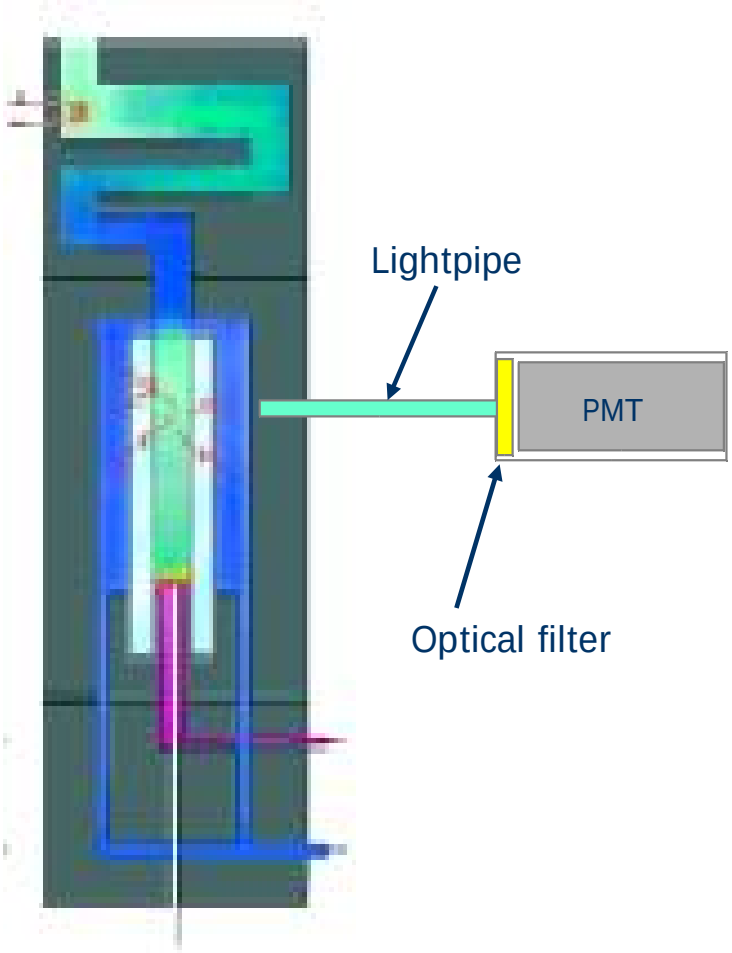
The PFPD Pulse Cycle

Emission Detection

Emissions from the excited species pass along a lightpipe.

Selected emissions are transmitted by a broad-band optical filter to the photomultiplier tube (PMT).



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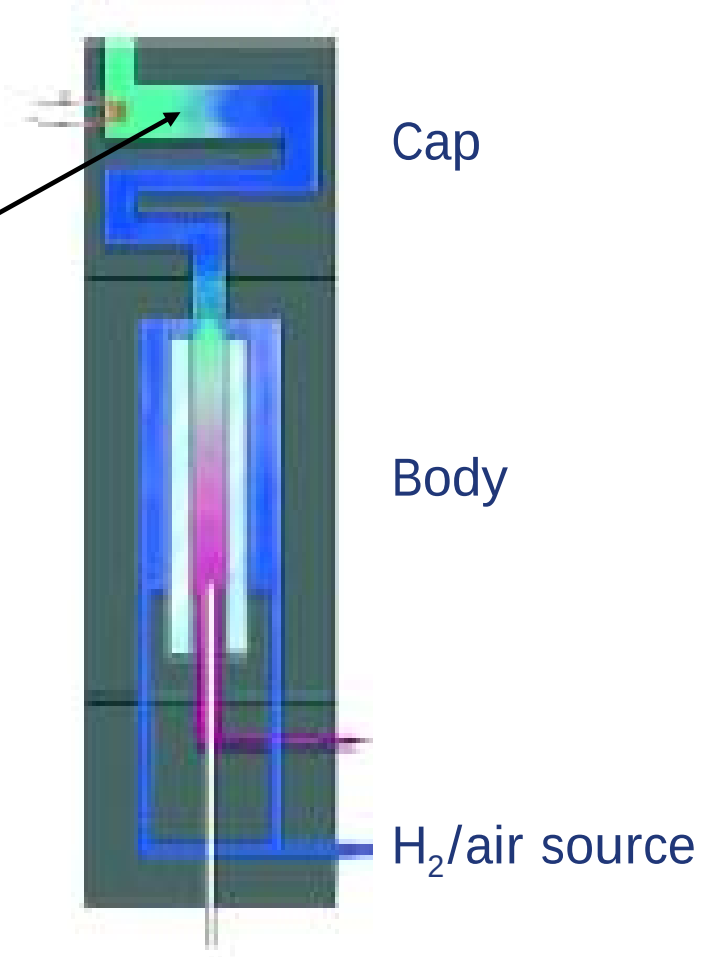
The PFPD Pulse Cycle

<u>Stage 1 – Replenishment</u>

Combustible mixture of H_2/air (shown in blue) re-fills detector body, combustor, and cap from the bottom up

Cycle repeated ~3 to 4 times each second



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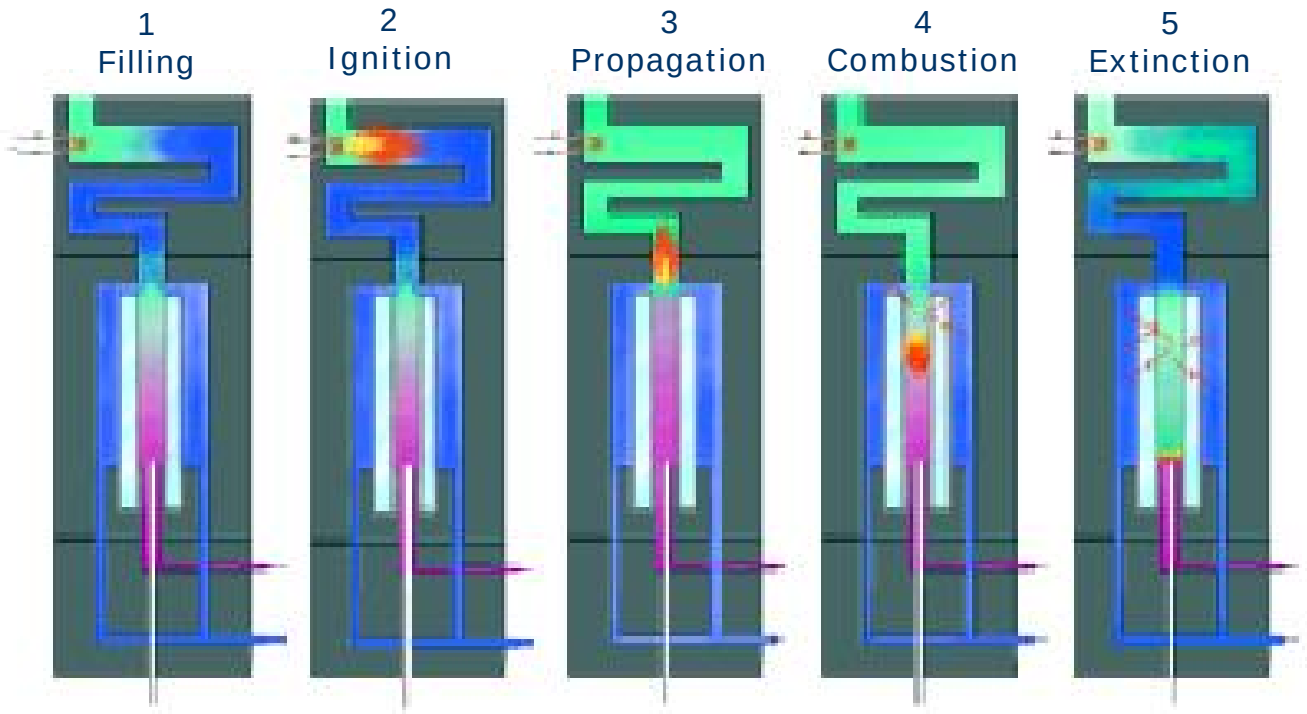
Self-Cleaning Detector



- 2200°C flame
- Pulsing at 3 – 4 times per second
- "Self-cleaning" detector

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Time Domain

- This mode of operation is unique for flame based detection in that it adds time domain information to the detection process
- Each emitting species has a different lifetime (delay) within the flame
  - Sulfur 6-25 msec
  - Phosphorus: 4-15 msec
  - Nitrogen: 2-10 msec
  - Hydrocarbon: 1-3 msec
- The individual S_2*, HPO*, and HNO* heteroatom flame emissions are separated in time

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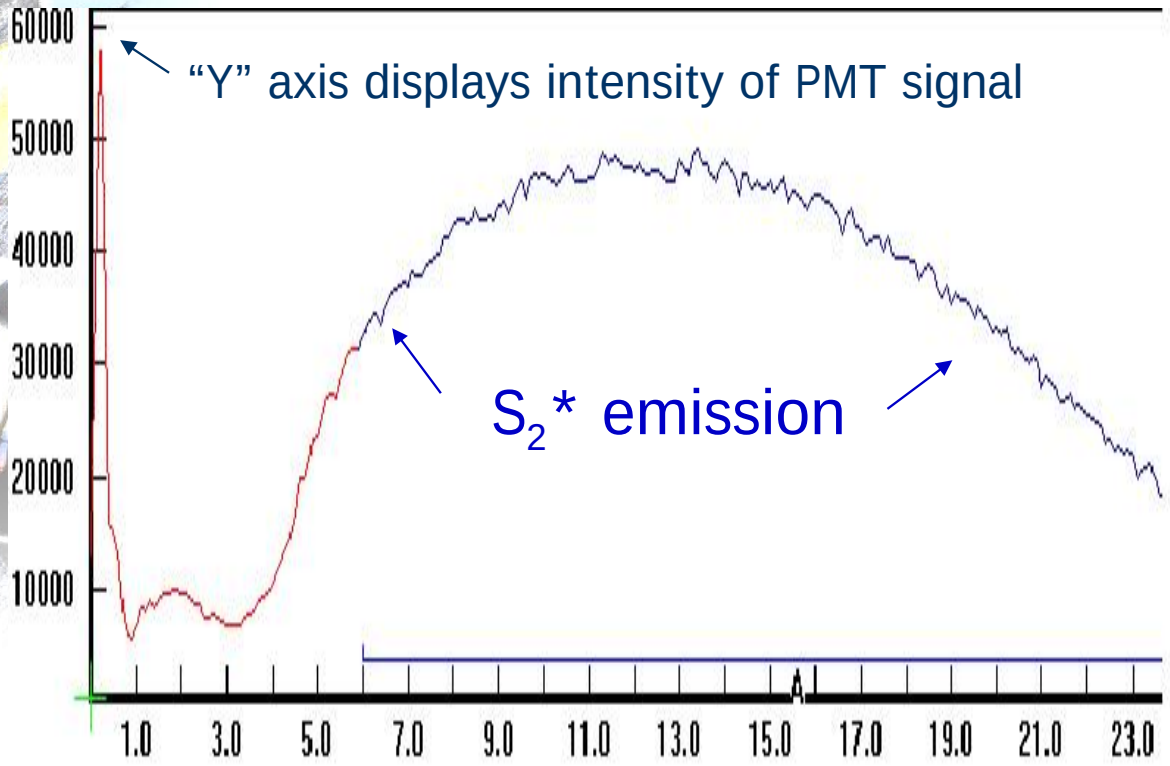
Real-time Emission Display



"X" axis displays time in msec
Time "0" is measured at the initiation of a pulse

- Propagation of the flame produces a time-delayed emission
- Sulfur emits at ~6 to 25 msec
- Real-time display updated 3 to 4 times each second

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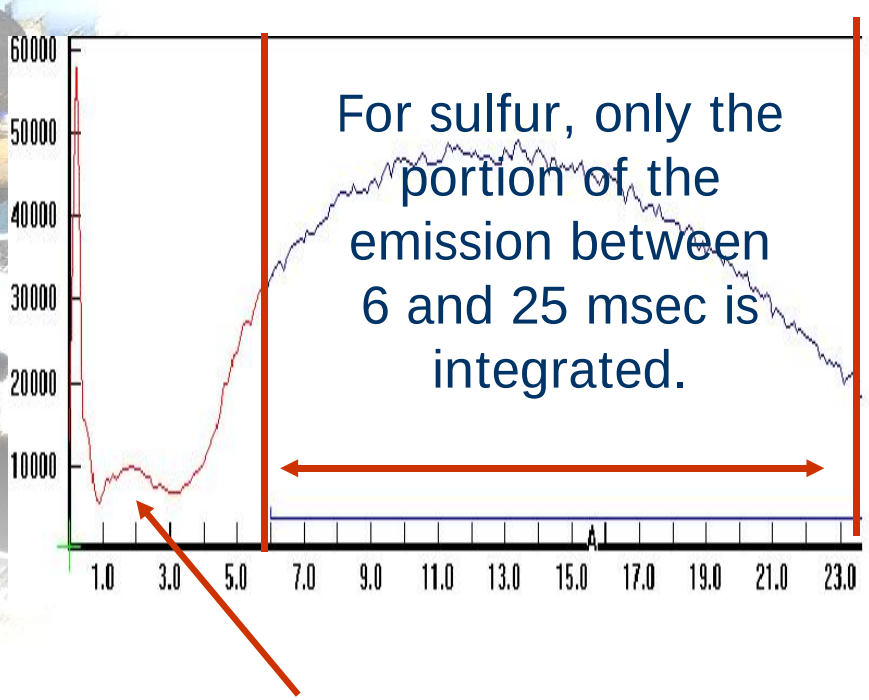
Digital Signal Processing



Emissions from other species can be “filtered” out, not integrated.

- Signal passes from the PMT to an ADC
- Once digitized, a time filter, or “gate”, is applied and only the desired portion of the emission is integrated
- Other emissions are not included in the integration
- Measured value is converted to an analog 0-1v output
- Results in element specificity, selectivity

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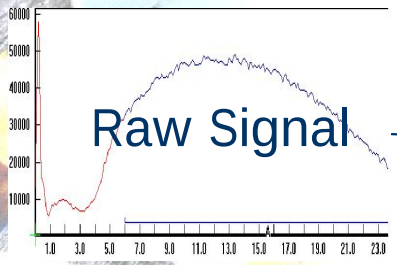
Digital Signal Processing



Electrometer

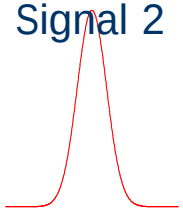
Range Selection
(1, 10, 100)

ACD

Signal 1

DAC A

Signal 2



DAC B

DSP
- Gate
- Attenuation
- Square Root

PC Communication
via RS-232

Memory Storage

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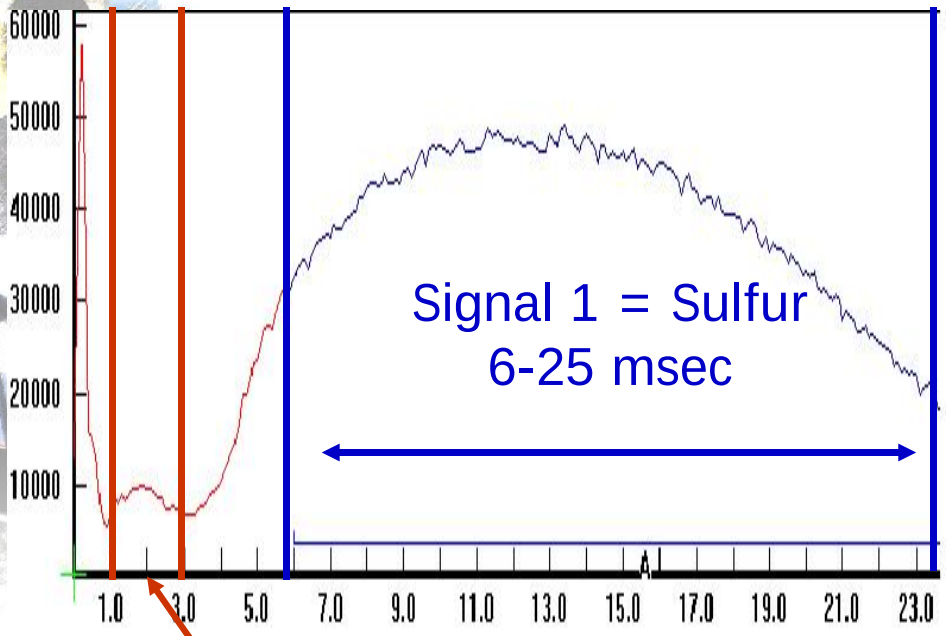
Digital Signal Processing



- PFPD has the capacity to produce two simultaneous signals
- Use two “gates”
- Generate two simultaneous chromatograms

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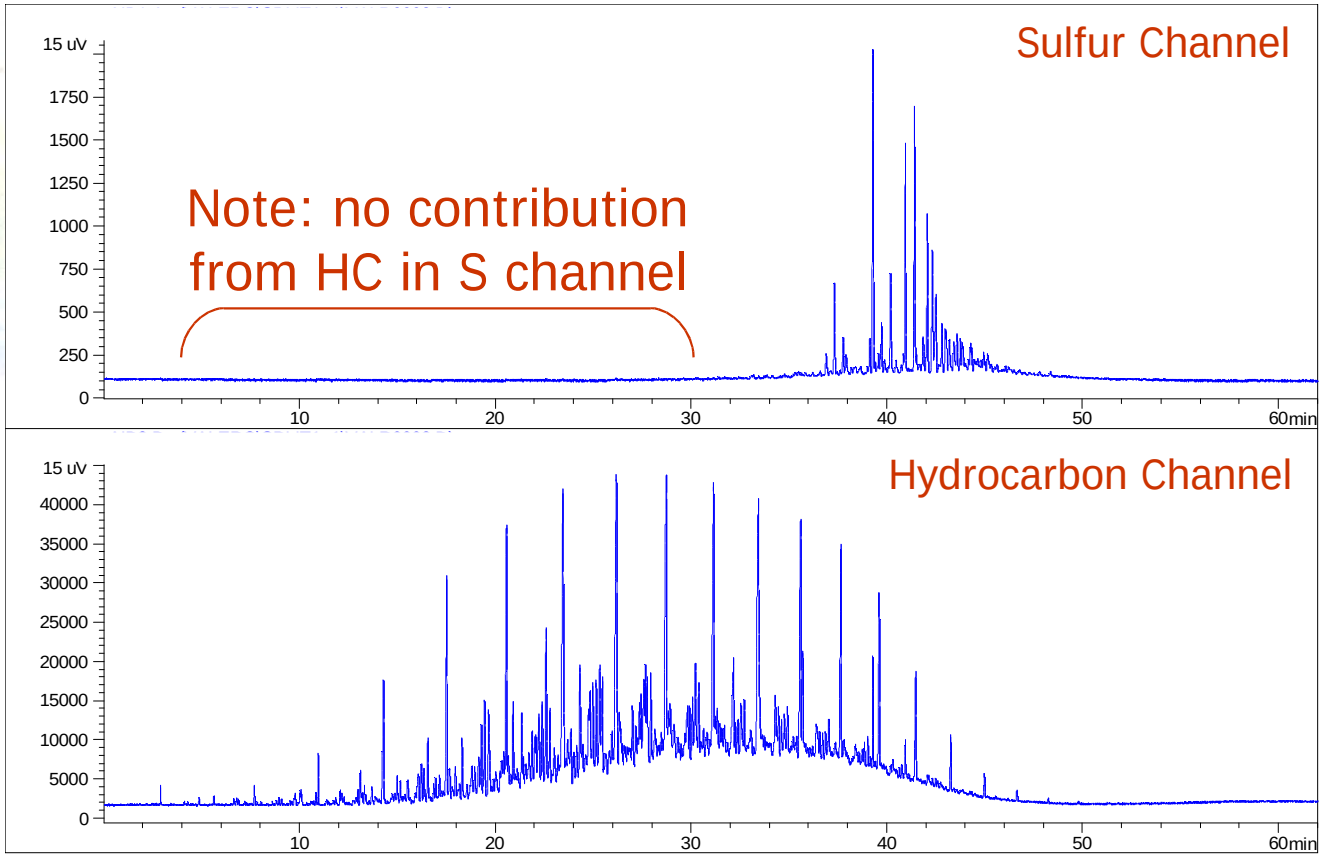
Simultaneous S & HC Chros

302 ppm total sulfur in diesel fuel



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Tools For Selectivity

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28 Elements by PFPD

- S, P (major applications)
- C, N, As, Sn, Se (other key applications)
- Pb, Br, B, Al, Si, V, Cr, Mn, Fe, Ni, Cu, Ga, Ge, Ru, Rh, In, Sb, Te, W, Bi, Eu (21 other compounds)

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Selectivity

- Selectivity is primarily the result of two variables
  - Time separated emissions
  - Selective optical filters
- Other factors can be “tweeked” to optimize performance
  - H_2/air gas flow ratios
  - Combustor size (2 mm or 3 mm)
  - Detector temperature (220îC to 400îC)
  - PMT selection

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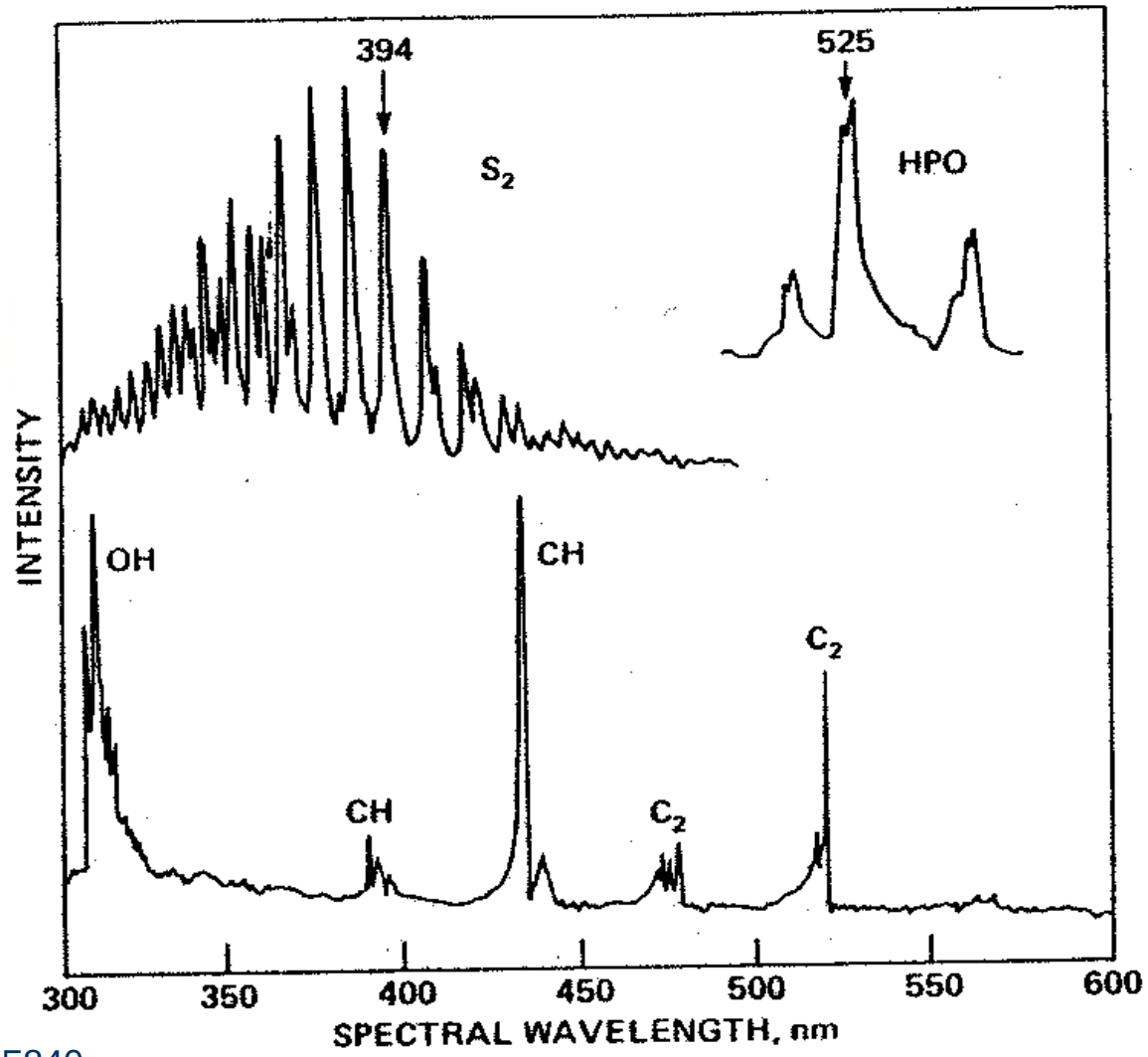
Emissions of Excited Species



From ASTM Method E840

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Tool #1: 3 PMT Choices

Visible EM Spectrum

R1924

300 – 650 nm

R1925

300 – 850 nm (into near infrared)

R5070

300 – 900 nm (for nitrogen)

Match the PMT to expected emission range

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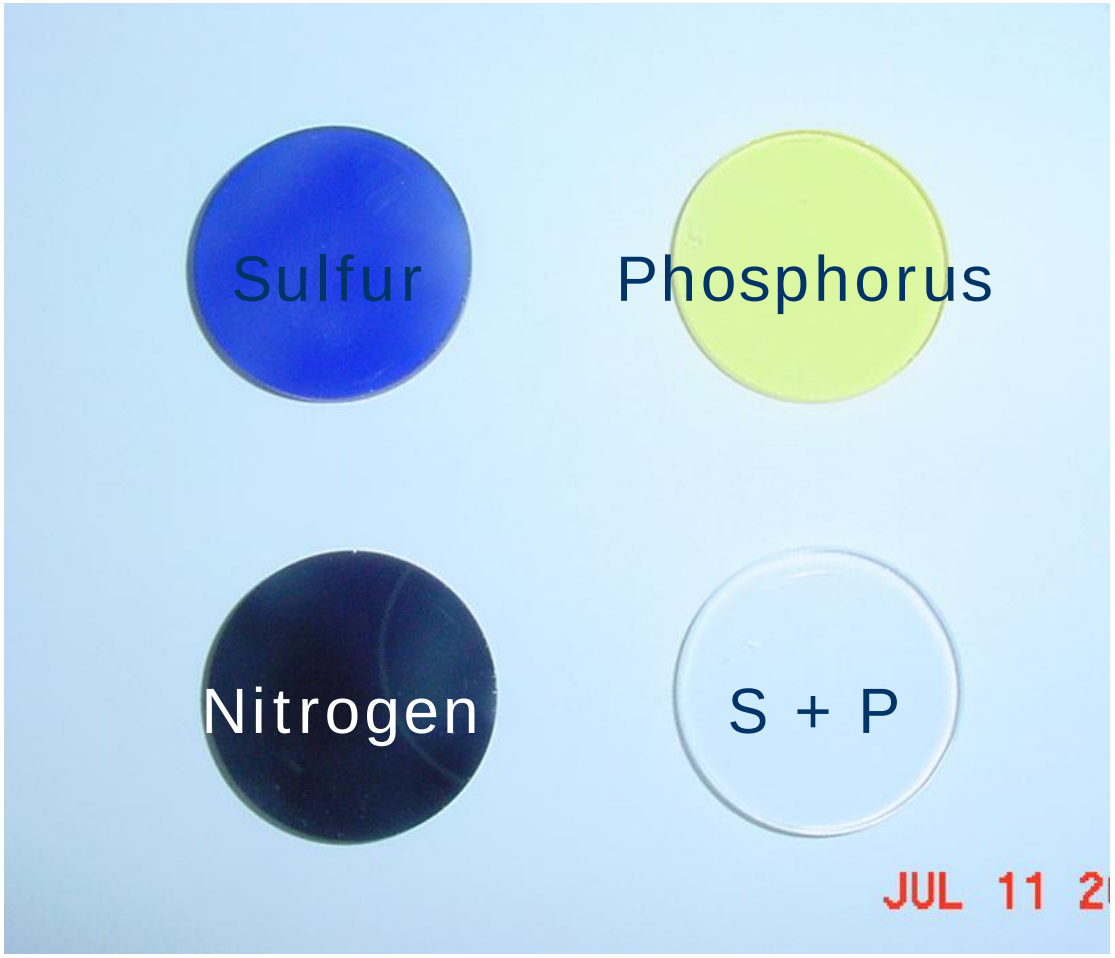
Tool #2: Optical Filter



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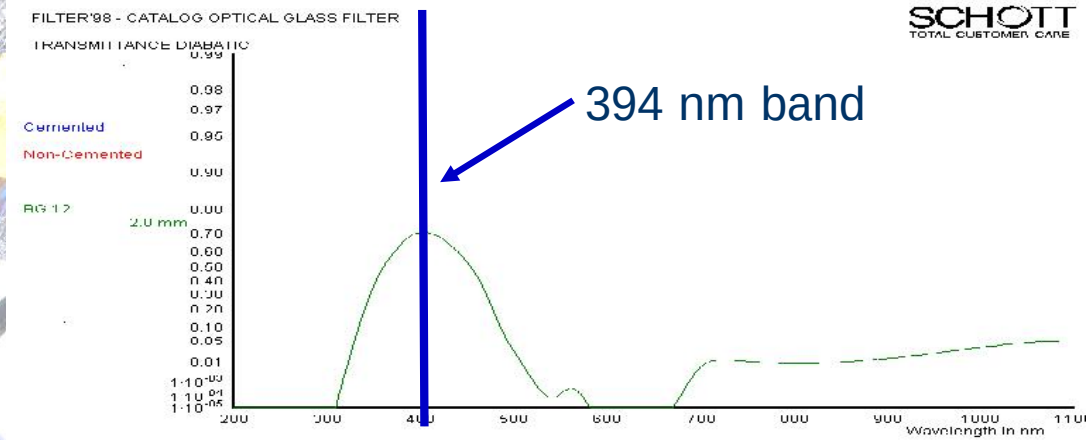
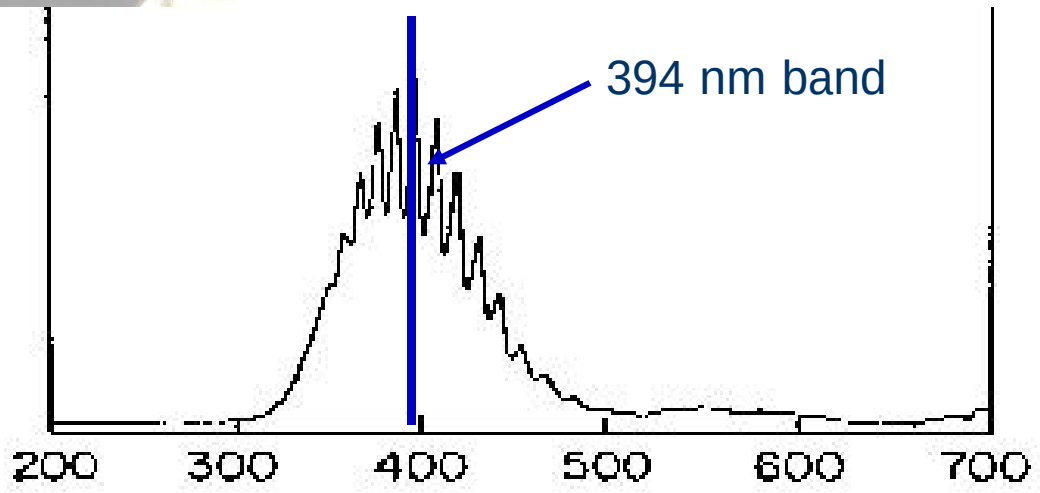
Filter For Sulfur Detection



S_2* emission spans ~300-500 nm



BG-12 broad-band optical filter transmission curve

Improved sensitivity over FPD with narrow-band optical filter (394 nm)

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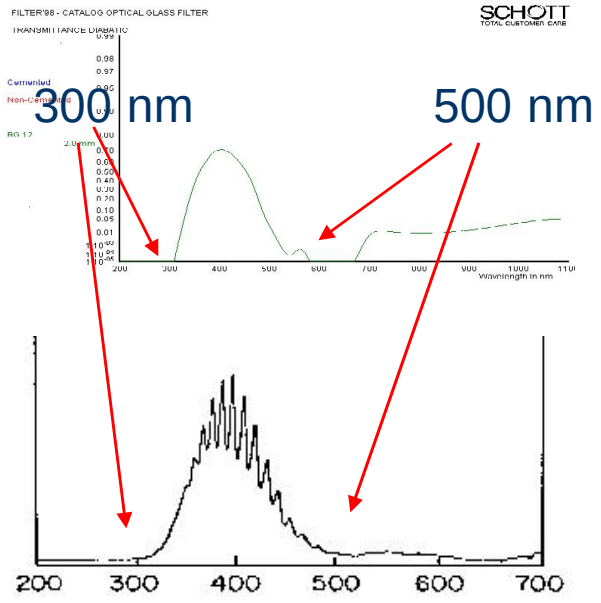
S: Filter and PMT Combination

Visible EM Spectrum

Ultraviolet

Near Infrared

R1924 PMT range 300 – 650 nm



S_2* Emission
~300-500 nm

BG-12 optical filter transmission curve

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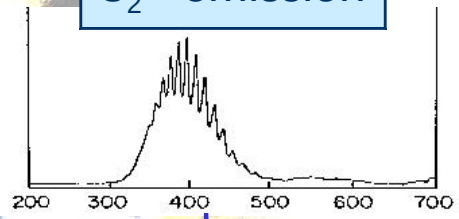
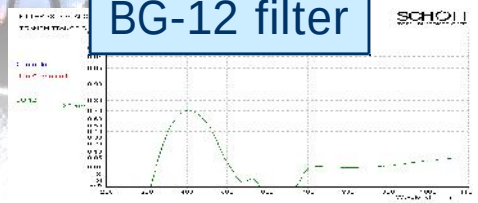
Gate Selection

S_2* emission

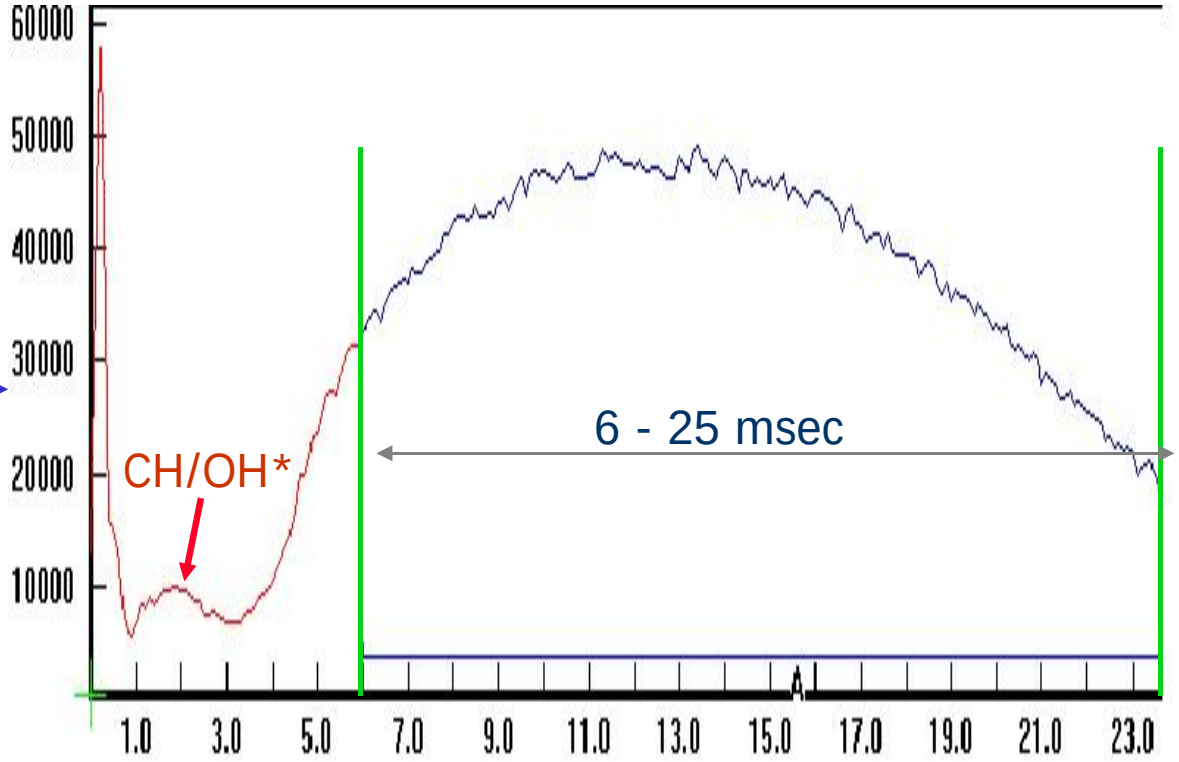


BG-12 filter



R1924 PMT

Gate set to select for sulfur and exclude hydrocarbon



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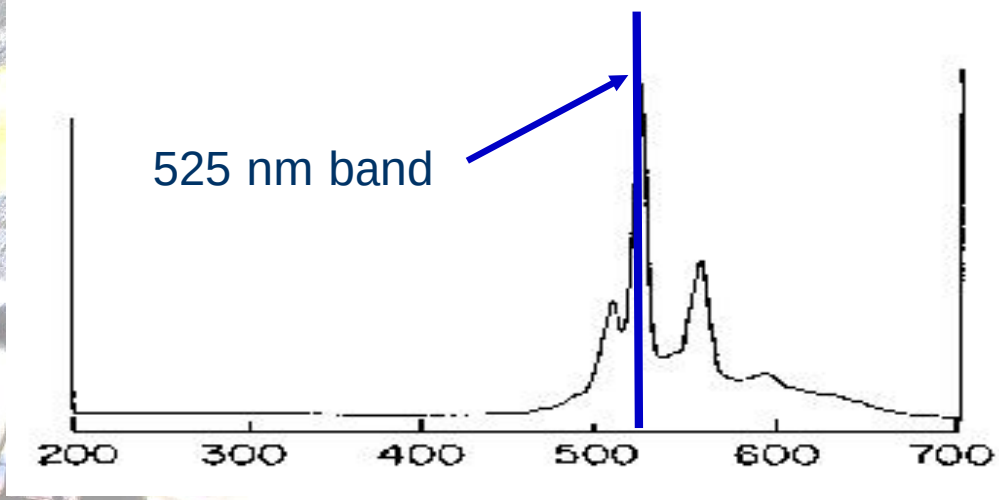
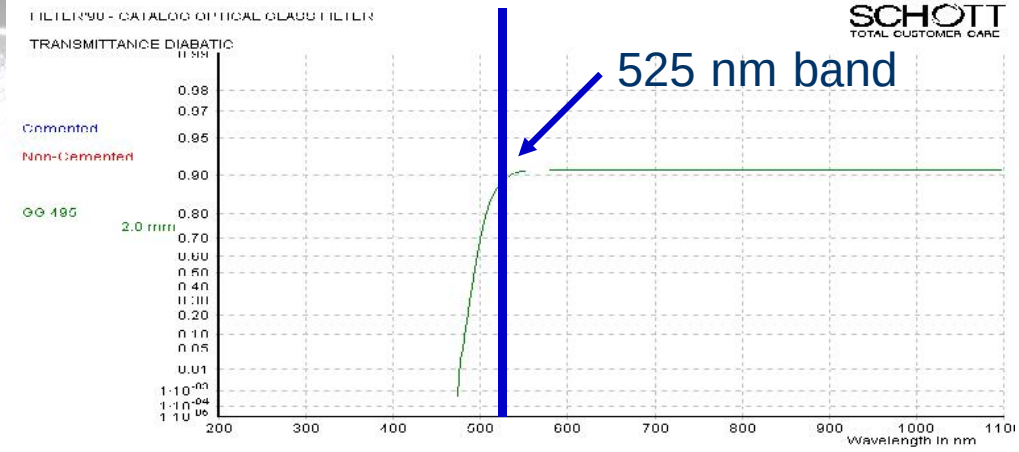
Filter For Phosphorous Detection



HPO* emission spans ~500-650 nm



WG-495 broad-band optical filter transmission curve

Improved sensitivity over FPD with narrow-band optical filter (525 nm)

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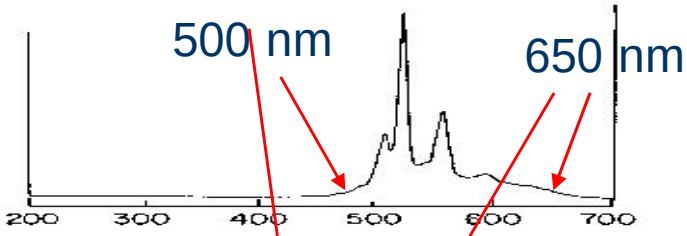
P: Filter and PMT Combination

Visible EM Spectrum

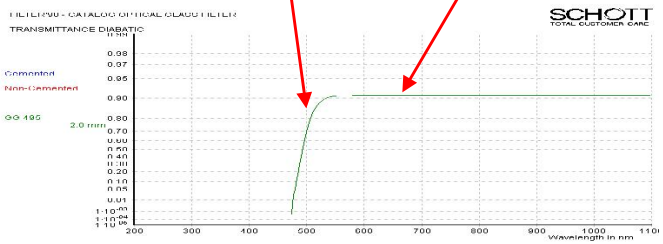
Ultraviolet

Near Infrared

R1924 PMT range 300 – 650 nm



HPO* Emission
~500-650 nm



WG-495 optical filter transmission curve

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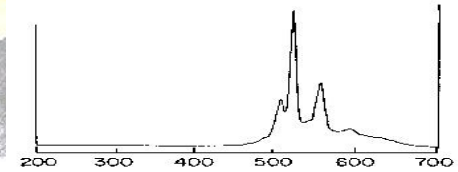
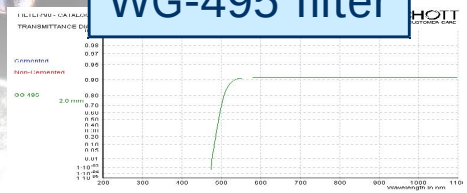
Filter and Gate For Phosphorous

HPO* emission

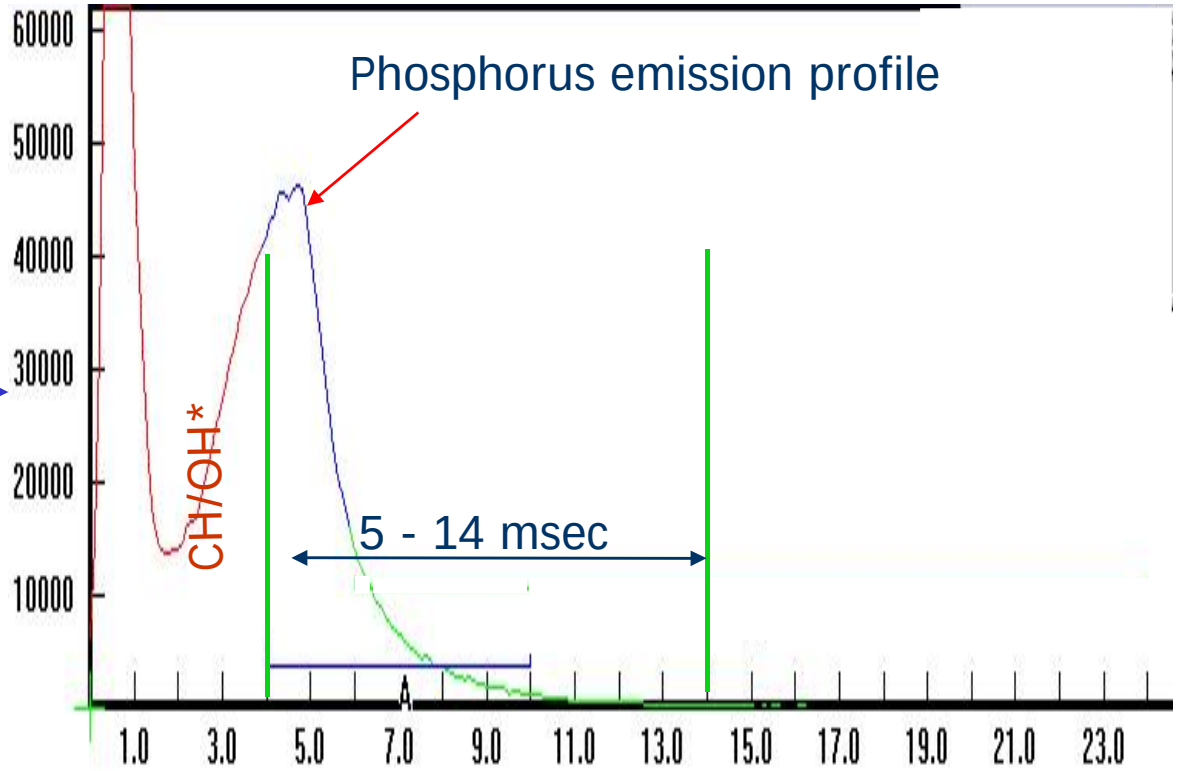


WG-495 filter



R1924 PMT

Gate set to select for phosphorus and exclude hydrocarbon



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Tool #4: Fine Tuning

Sulfur

- 2 mm combustor
- H_2/air ratio of ~1.15
  - Slightly more H_2 than for P
  - Slightly cooler flame than for phosphorus
  - Favors formation of S_2*
- 250°C detector temperature
- Constant column flow
  - ~1 to 2 mL/min (He)
  - Higher flows possible with H_2 as carrier gas

Phosphorus

- 3 mm combustor
- H_2/air ratio of ~1.05
  - Slightly less H_2 than for S
  - Slightly hotter flame than for sulfur
  - Favors formation of HPO*
- 300°C detector temperature
- Constant column flow
  - ~1 to 2 mL/min (He)
  - Higher flows possible with H_2 as carrier gas

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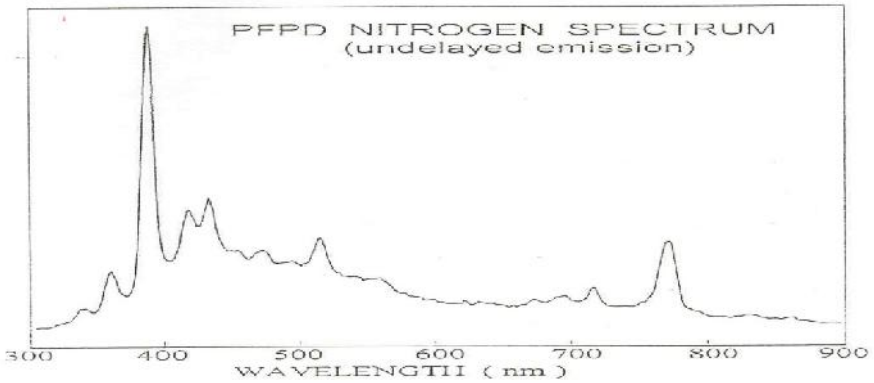
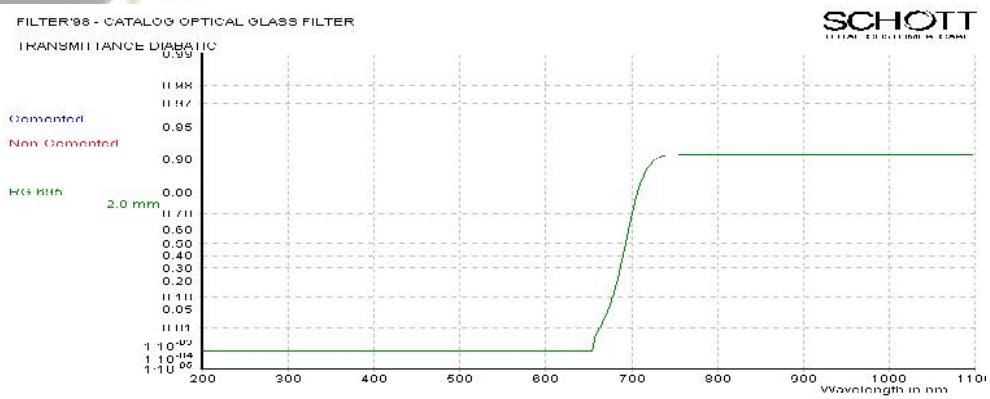
Filter For Nitrogen Detection



HNO* emission spans ~300-800 nm



WG-695 broad-band optical filter transmission curve

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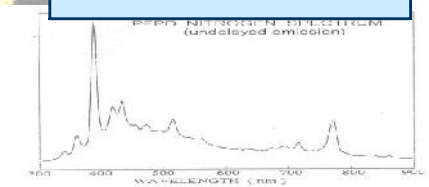
Filter and Gate For Nitrogen

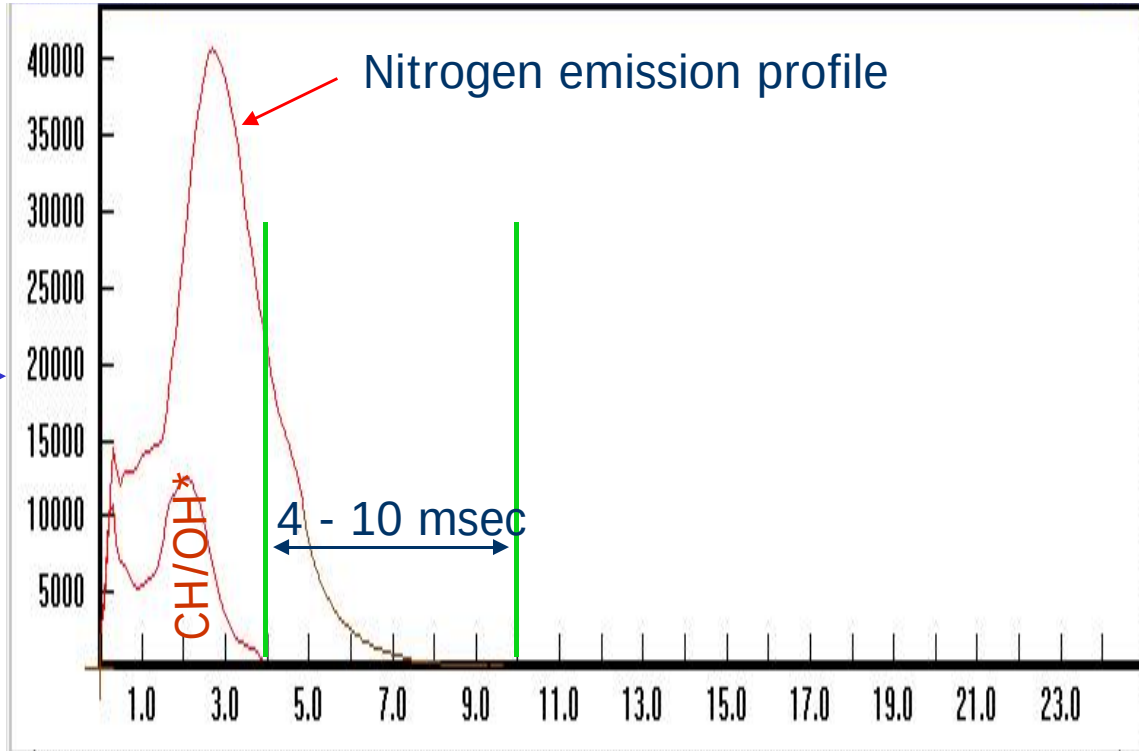
HNO* emission



RG-695 filter

R5070 PMT

Gate set to select for nitrogen and exclude hydrocarbon



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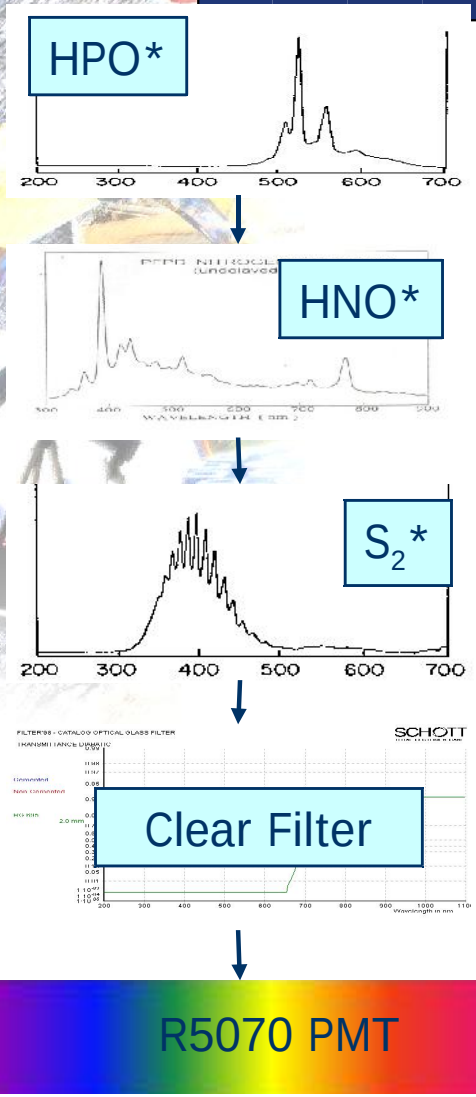
Simultaneous S, P, and N



Nitrogen and phosphorus emission lifetimes are similar (~5-10 msec). Contributions from N and P cannot be distinguished in compounds that contain both elements.

Sulfur contribution can be isolated by using either delayed gate or dual gate subtraction.

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Tool #5: Dual Gate Subtraction

- "Dual gate subtraction"
- For simultaneous detection of two elements with overlapping emissions
- E.g. sulfur emission ~6-25 msec & phosphorous emission ~4-14 msec
- Overlap region between 6-14 msec
- Use non-overlapping gates. For example:
  - P gate 4 – 14 msec
  - S gate 14 – 25 msec
  - 14 msec border is a parameter for optimization
- Use clear optical filter

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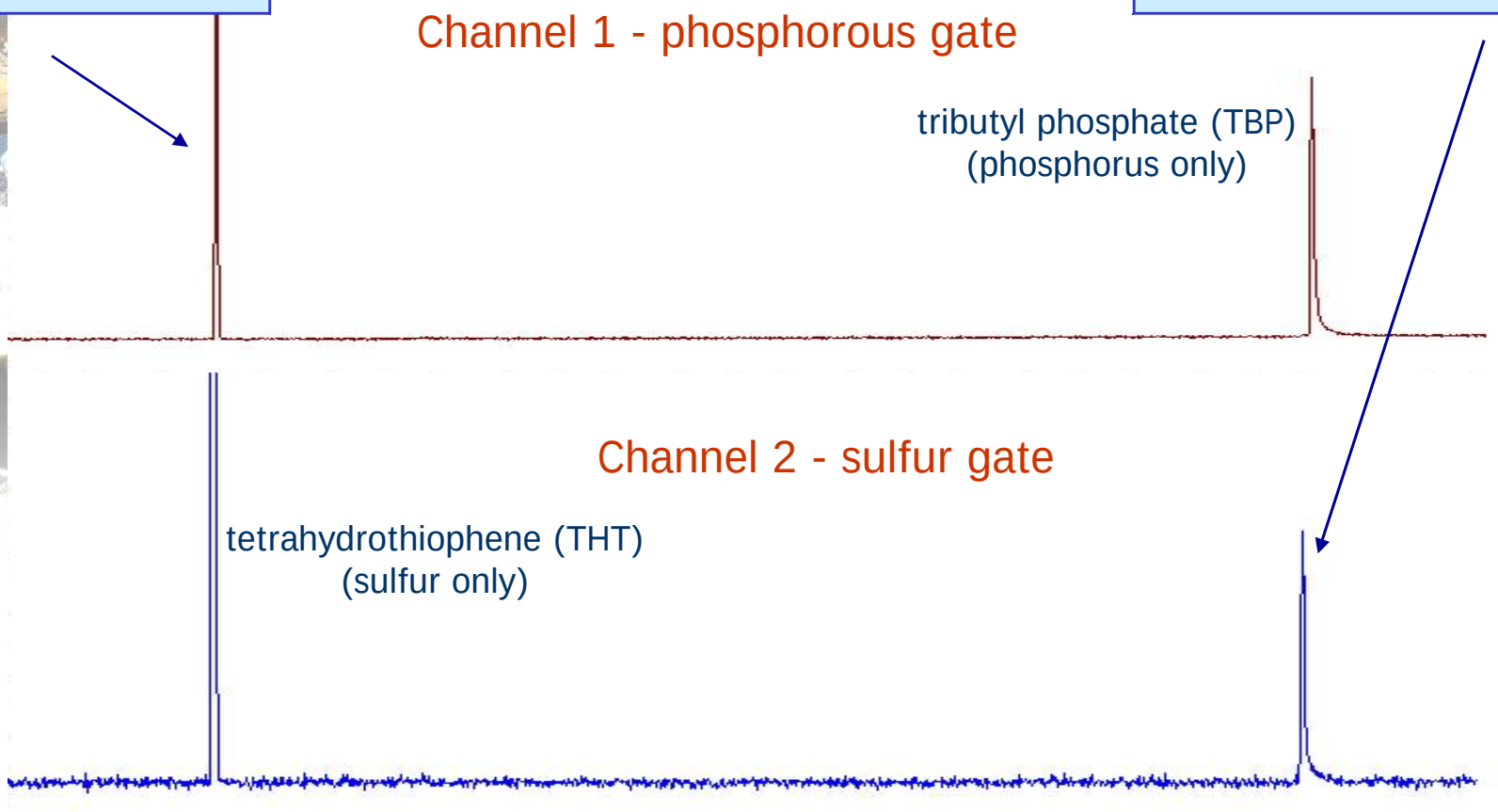
Overlapping Gates

S response in P channel

P response in S channel



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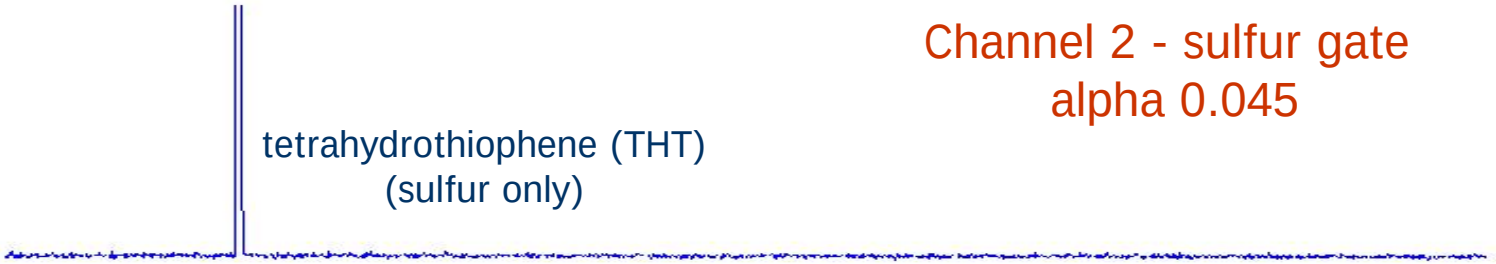
S-only & P-only Chromatograms

Channel 1 - phosphorous gate
alpha 0.370

tributyl phosphate (TBP)
(phosphorus only)

tetrahydrothiophene (THT)
(sulfur only)

Channel 2 - sulfur gate
alpha 0.045



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Summary: Tools for S, P, and N

	S	P	N	S+P	S+N
Combustor	2 mm	3 mm	3 mm	3 mm	3 mm
PMT	R1924	R1924	R5070	R1924	R1925
Optical Filter	Blue	Yellow	Black	Clear	Clear
Time Filter (Gate)	6-25 msec	5-14 msec	4-10 msec	Dual Gates	Dual Gates
Detectivity	<1 pgS/sec	<100 fgP/sec	~30-50 pgN/sec		

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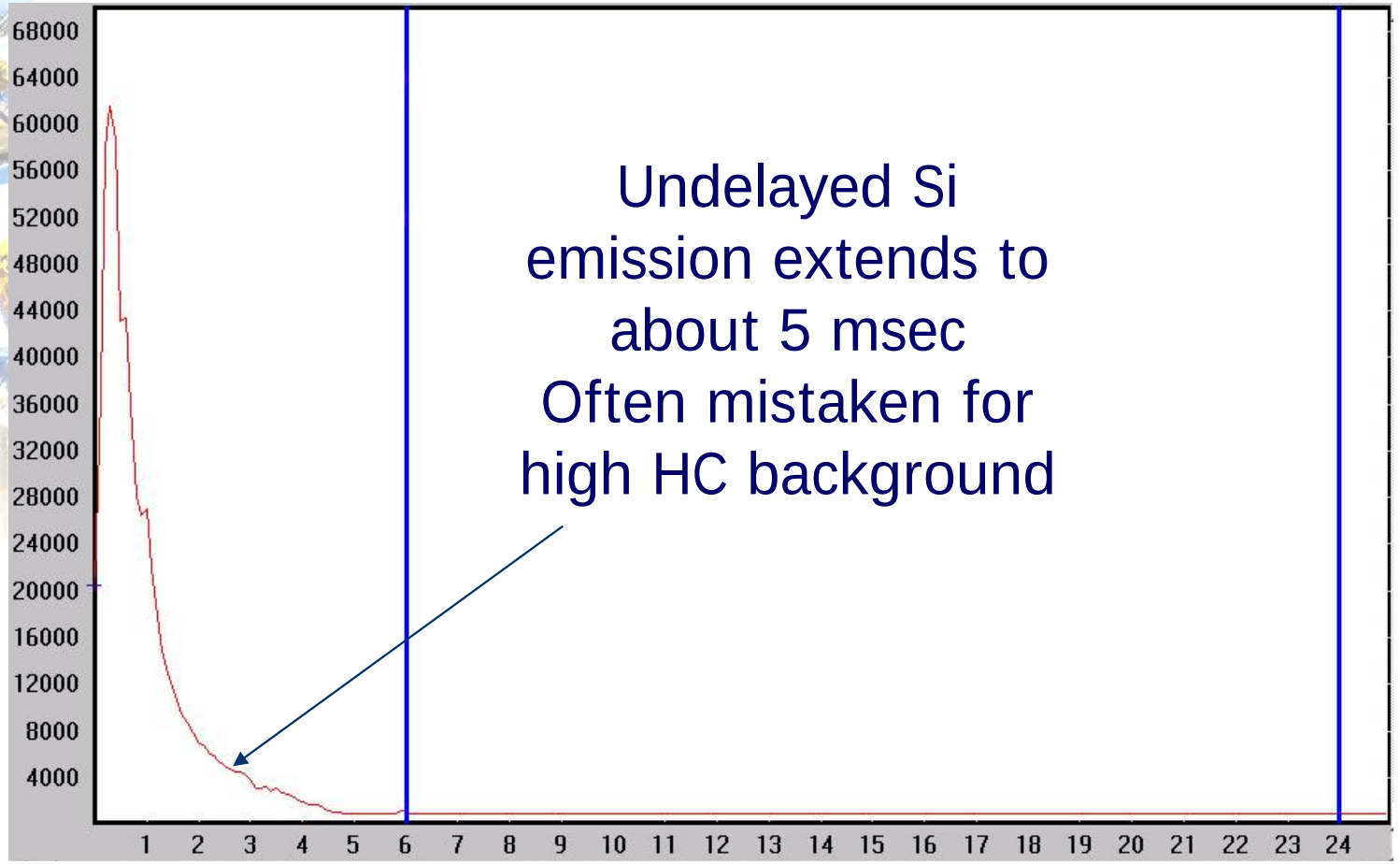
Silicon Emission Profile



Undelayed Si emission extends to about 5 msec
Often mistaken for high HC background

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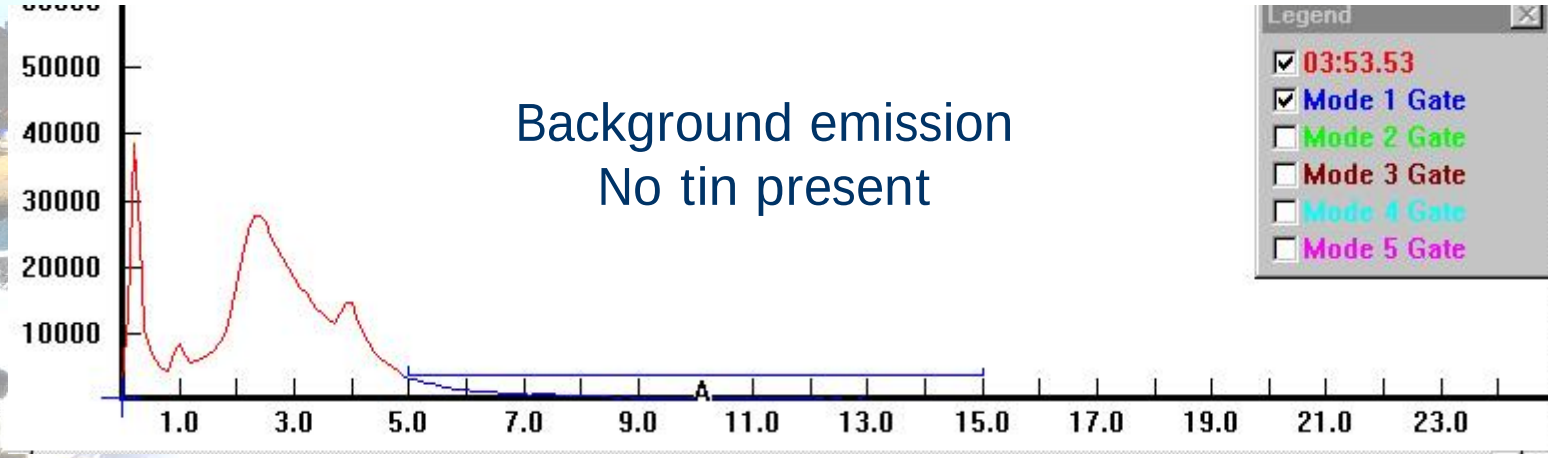
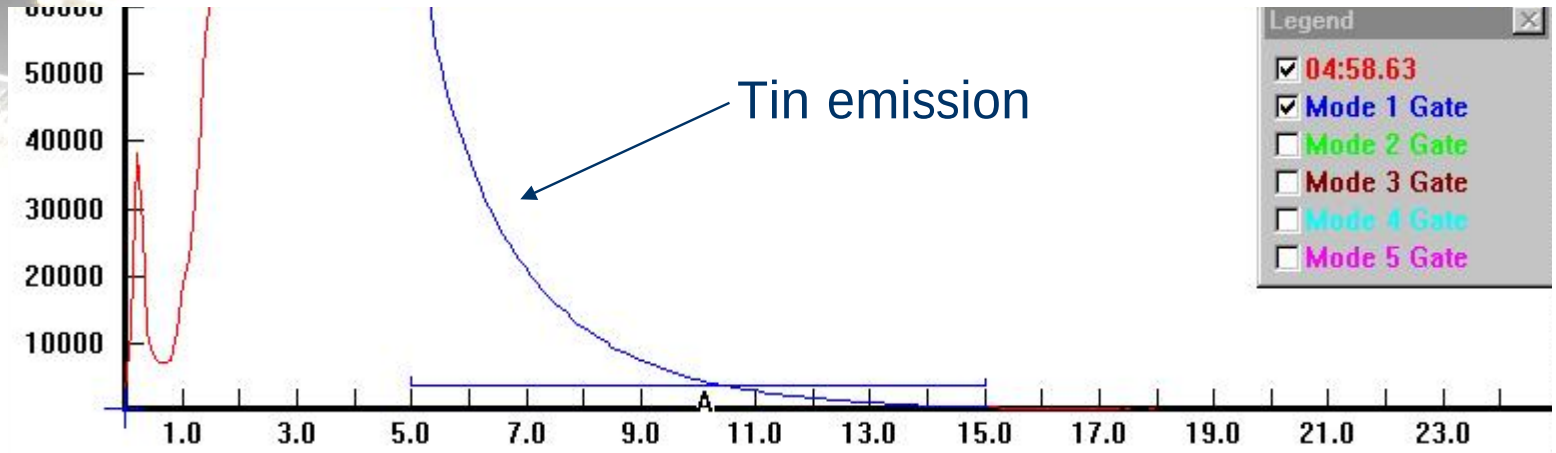
Tin Emission Profile



Background emission
No tin present



Tin emission

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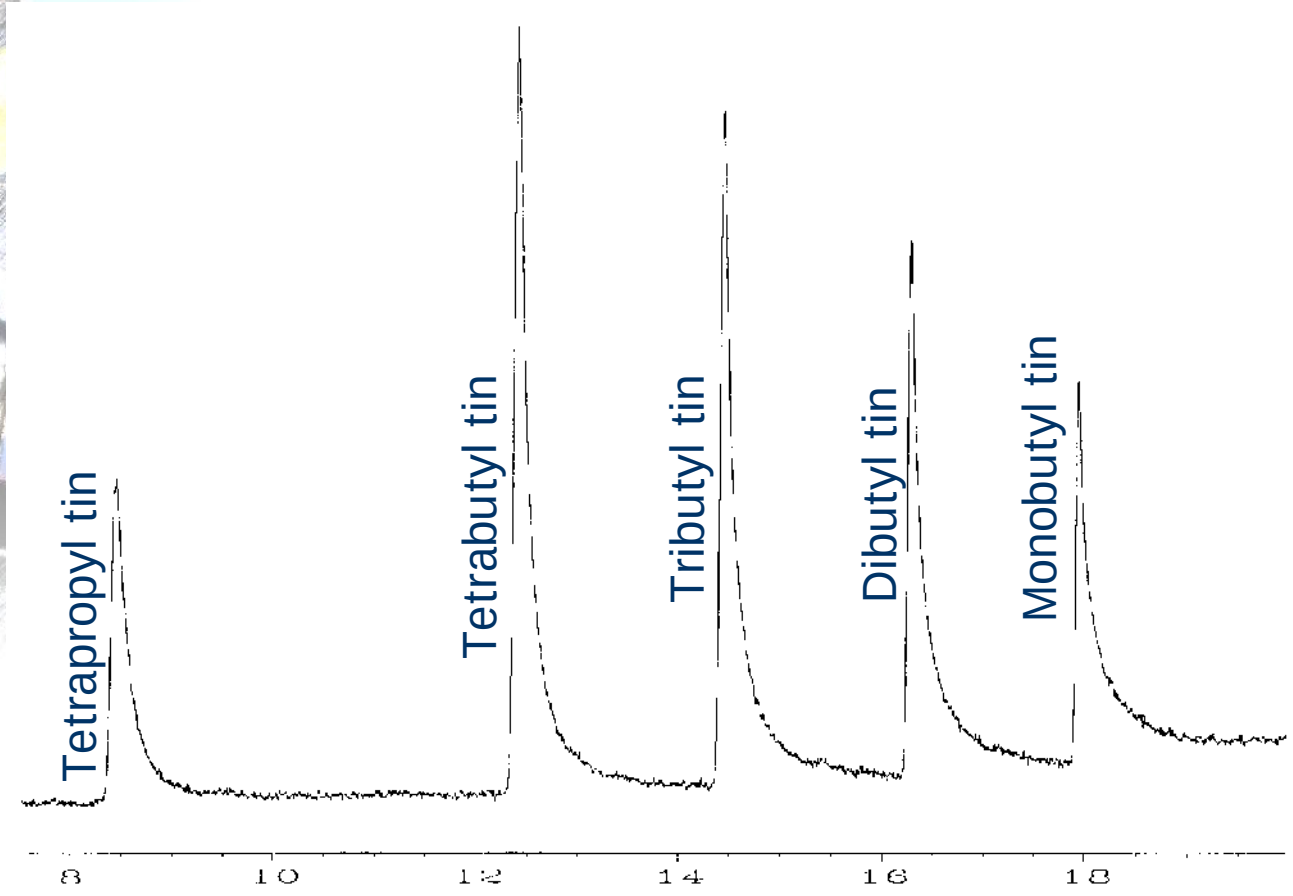
Organo-tin Standard on PFPD



- Rtx-35
- 15 psi constant pressure
- 5.0 pg Sn on column
- 100°C (1 min)
- 10°C/min to 285°C

Chromatogram courtesy of Restek

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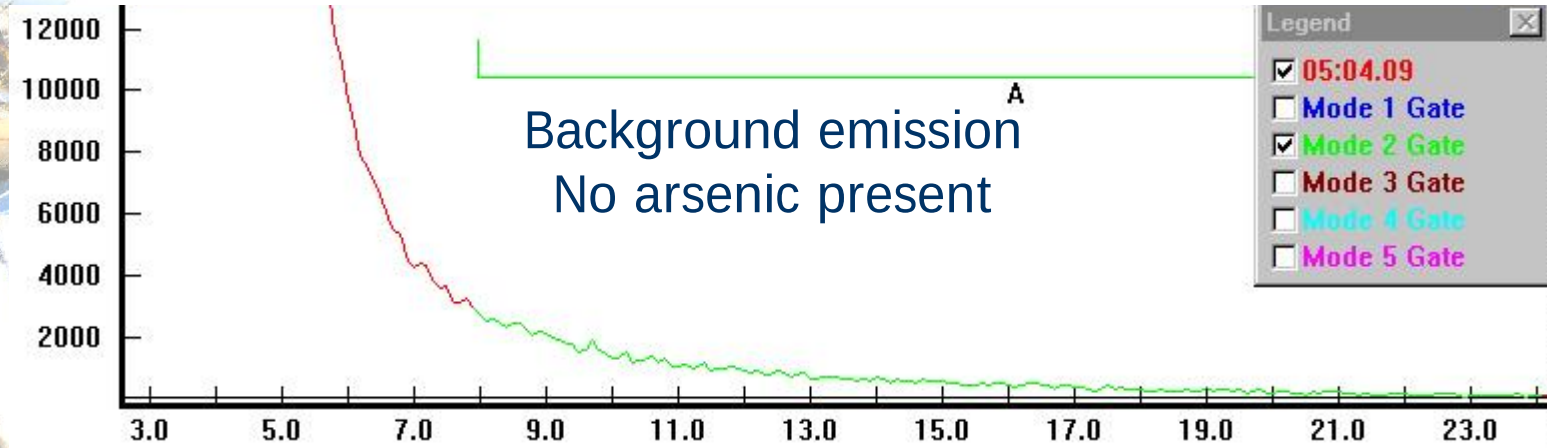
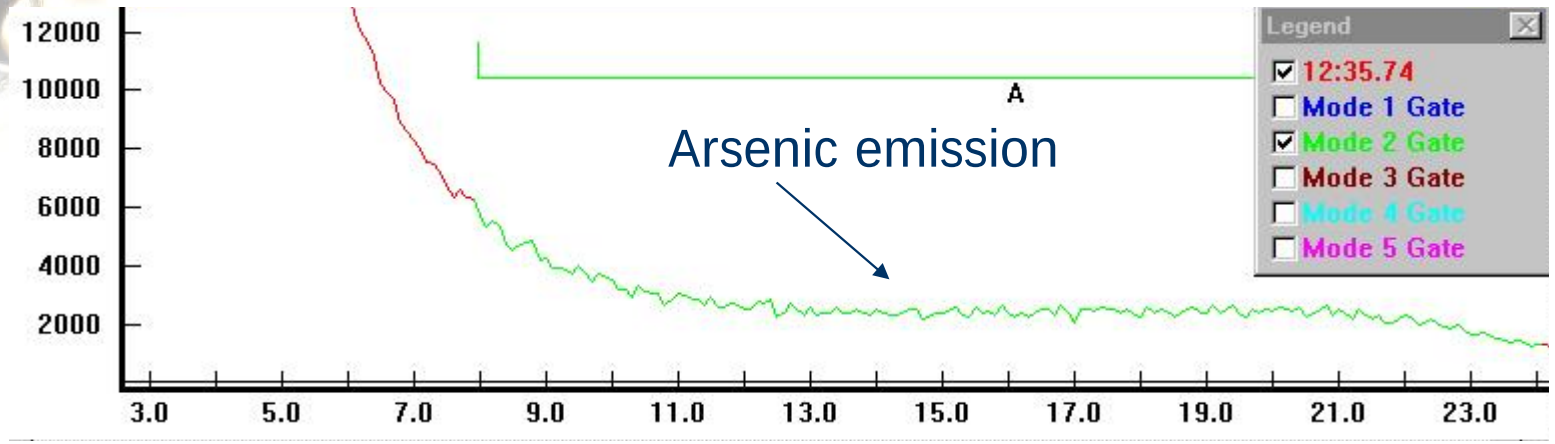
Arsenic Emission Profile





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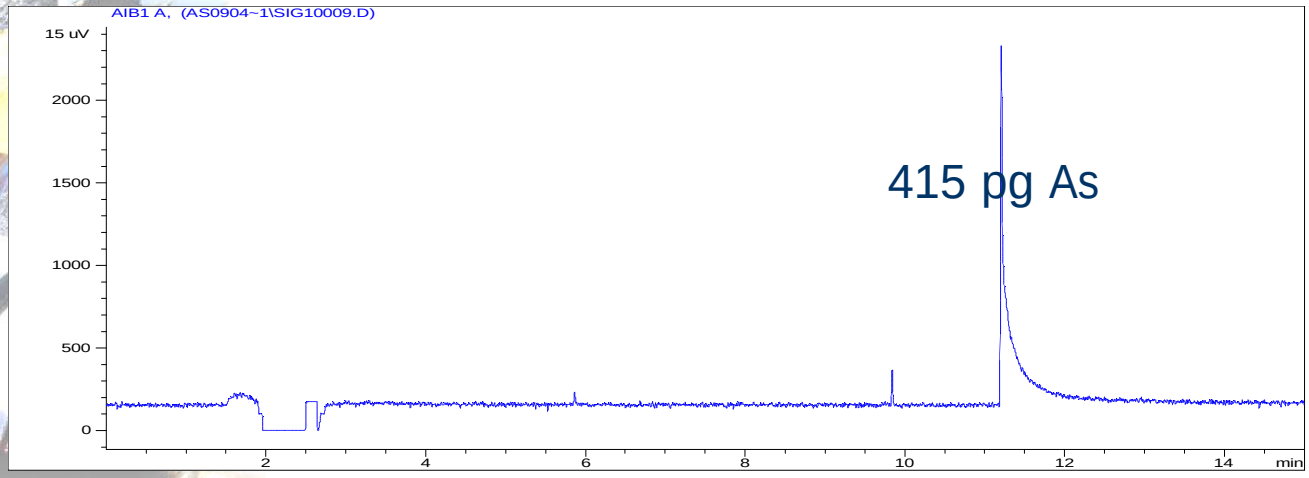
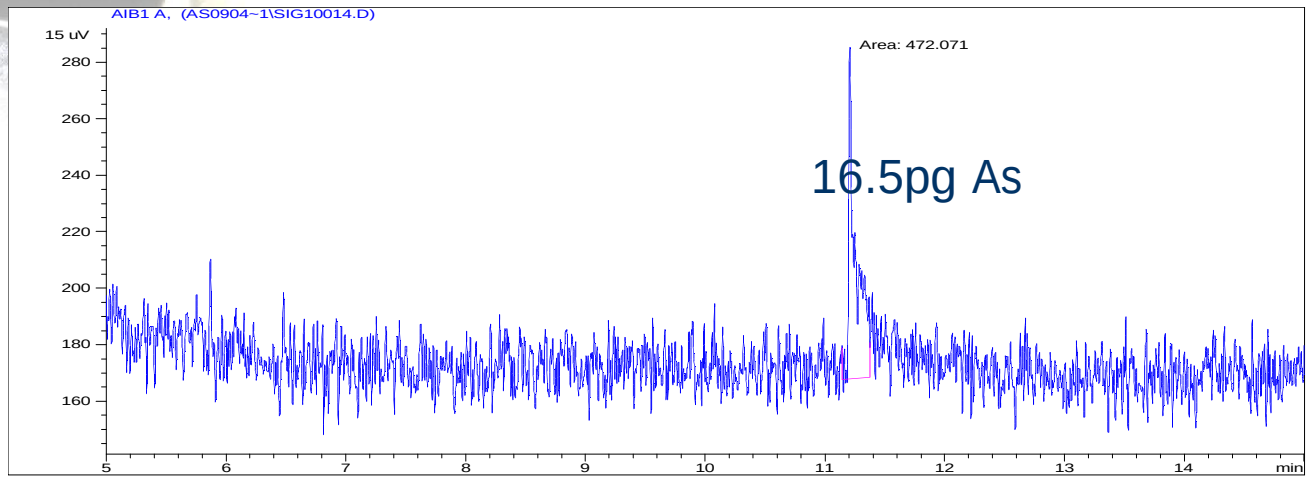
Arsenic Standard by PFPD





- WG-345 optical filter in PFPD
- 300°C detector temperature
- 1 μL injection of triphenylarsine

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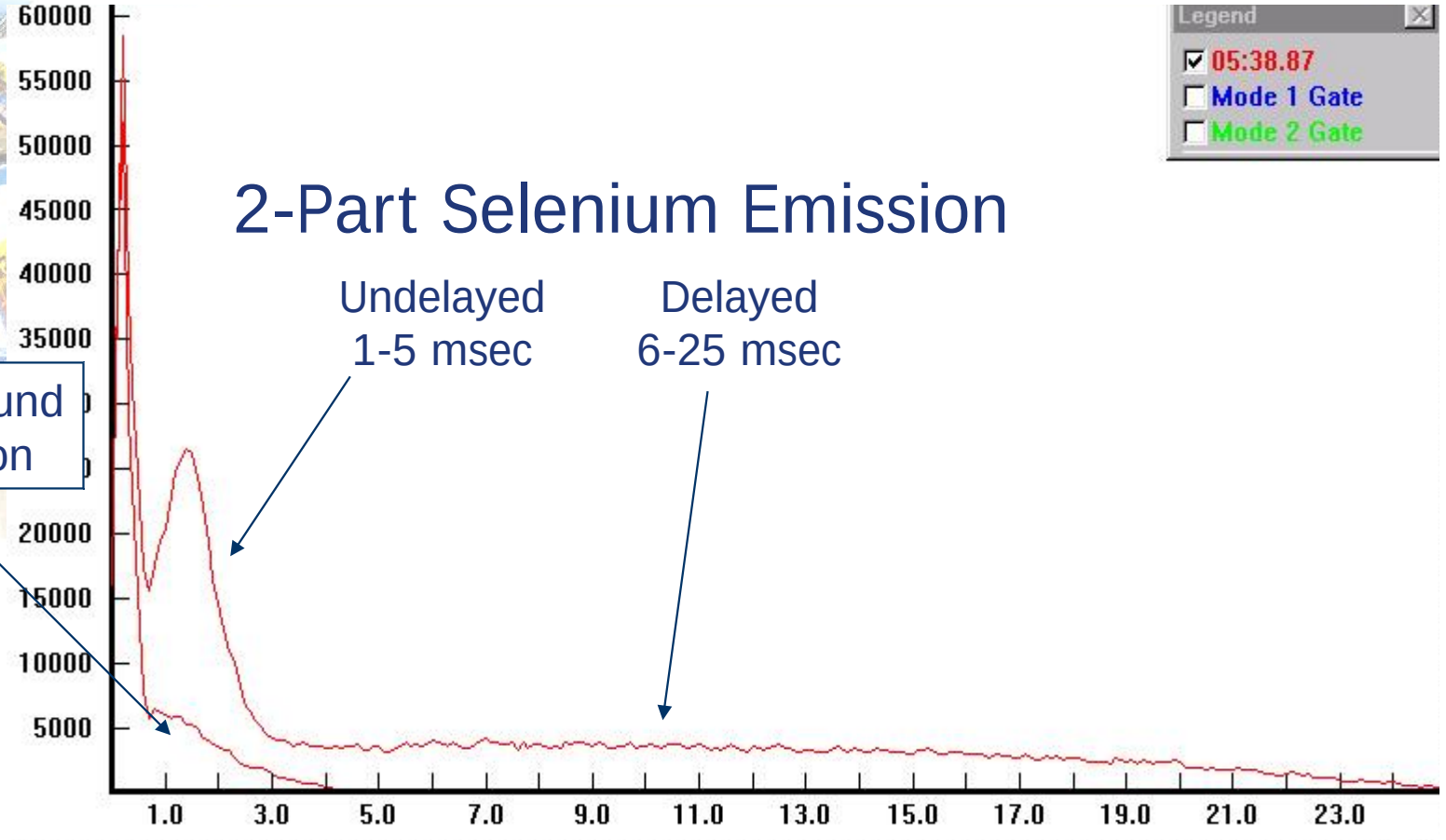
Selenium Emission Profile



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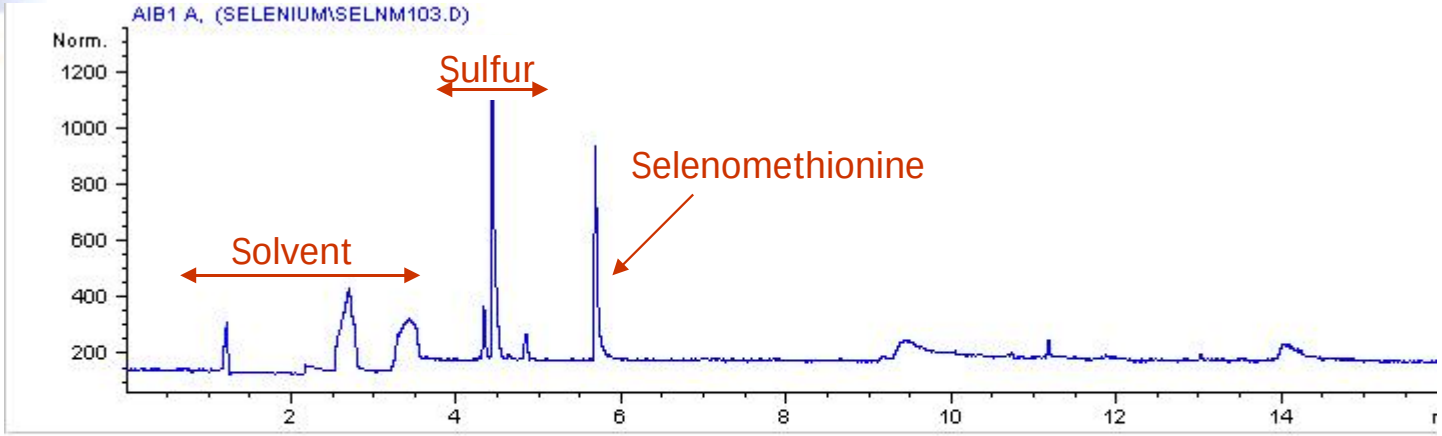
Selenium Standard

- 4 ppm Se as selenomethionine in chloroform
- 1 μL splitless injection
- DB-5MS column; ramped oven program



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Selectivity Tools

- Available Photomultiplier Tubes
  - R1924 300-650nm
  - R1925 300-850nm (For the near IR)
  - R5070 300-900 (N enhanced)
- Available Optical Filters
  - BG-12 blue Band pass -Center 390nm
  - BG-39 clear Short Pass -Cuts IR (600nm)
  - GG-495 yellow Long Pass - 490nm
  - RG-695 black Long Pass - 690nm
  - UV-34 clear Long Pass - 340nm

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