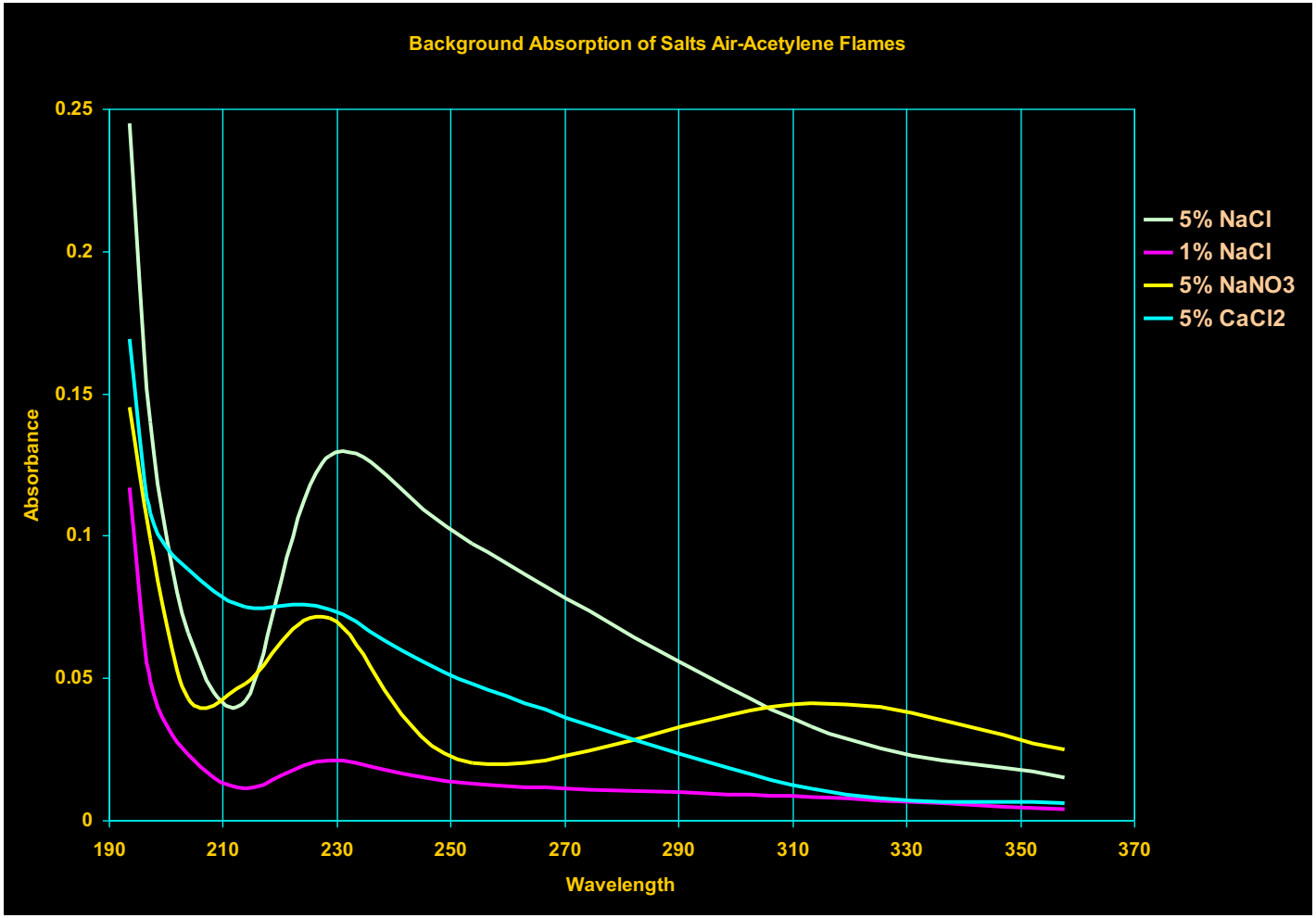
Background Correction

What is Background Absorption

Non specific absorption caused by:

- Molecular absorption in the Gas Phase
- Light scattering by particles in the Light Path

Molecular Absorption in the UV Region



From data supplied by Dr. John Willis

Background

Radiation from hollow cathode lamp is attenuated by NON-ATOMIC source

- Molecular species
- Solid particles
- Absorption
- Scatter

Signal is added to atomic signal

- Results in FALSELY HIGH SIGNAL

Most severe in graphite furnace

- Can exceed 2.0 abs

Background

Background / non-specific absorption is normally very small in flame AA

- Chemically rich flame environment dissociates salt particles and molecules very efficiently

What conditions can lead to background absorption in flame AA?

- Analytical wavelengths less than 250 nm
- Low analyte concentrations
- High dissolved solids (salt) solutions
- Fuel rich (cooler) Air/Acetylene flames

General Background Correction

Total absorbance measured

- Atomic + non-specific

Background measured

- Non-specific only

Measurements are time separated

- A few milliseconds

Atomic absorption calculated

- Total absorbance - background absorbance = atomic absorbance

Typical Signals Measured

Graphite furnace signals have rapid rise and rapid decay times

- Up to 20 absorbance units/second

Time separated total and background absorbances need to be rapidly made

- Ideally simultaneously
- 2 - 10 ms intervals in commercial instruments
- Larger time difference - greater error
  - Exception is flame AA where we work with a steady state absorption signal

Background Correction Techniques

Deuterium

Zeeman

Smith-Hieftje

Deuterium Technique

Most common

Continuum source to measure background

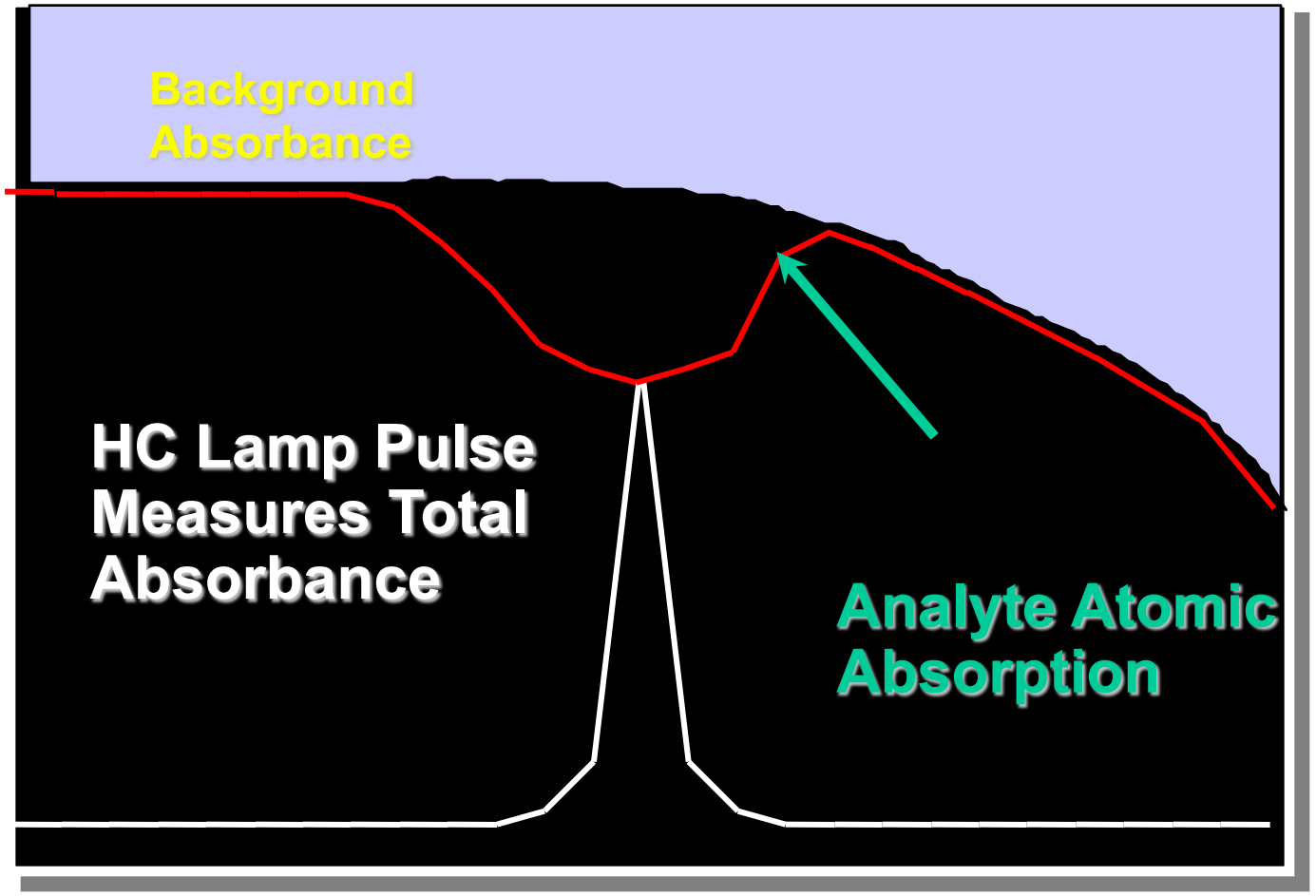
- Deuterium lamp

Operating range from 180 to ~ 425 nm

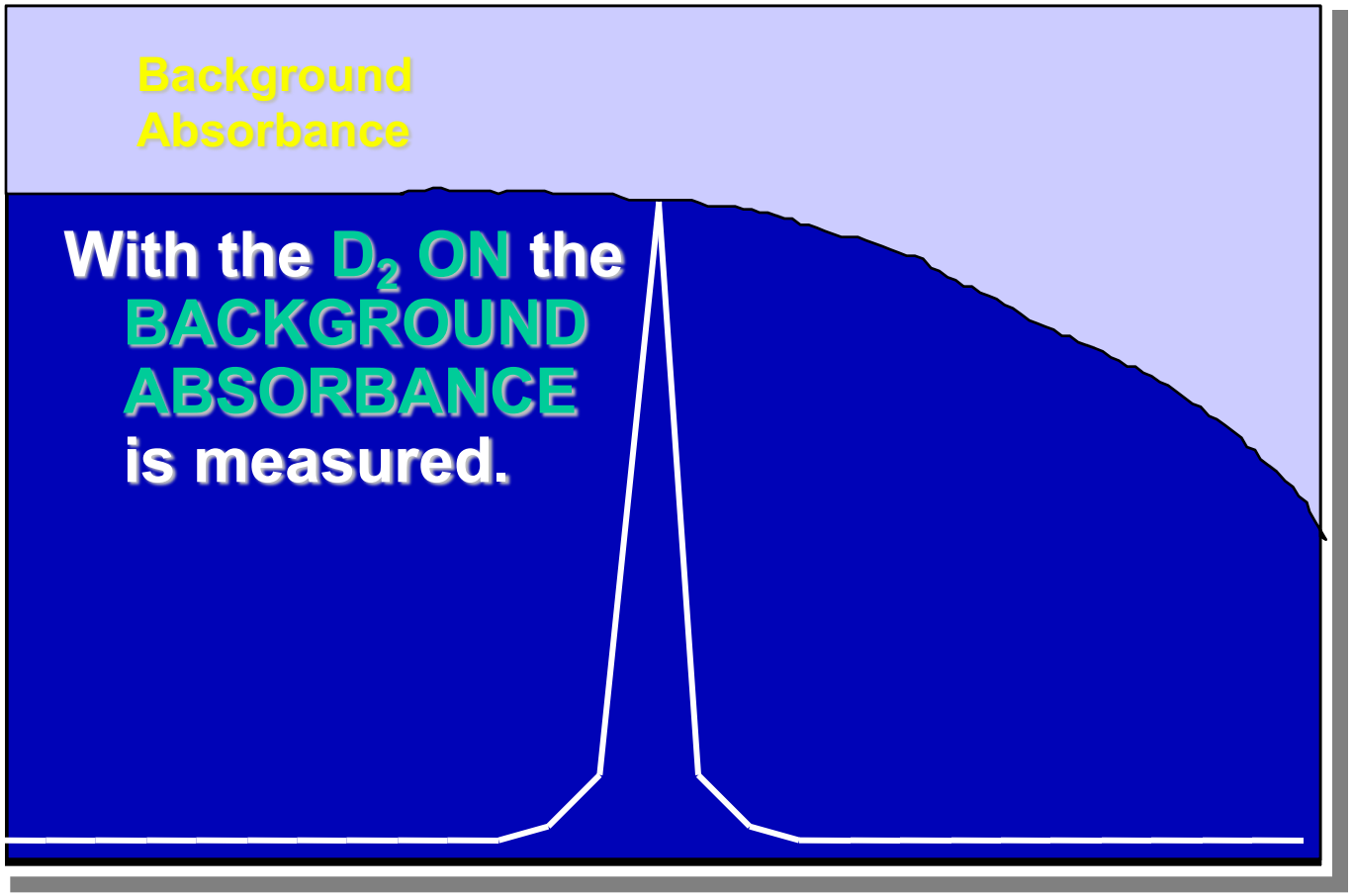
Background is most significant at shorter wavelength

- Deuterium works well MOST of the time

Deuterium Background Correction



Deuterium Background Correction



Deuterium Background Correction

Radiation from BOTH hollow cathode lamp and deuterium lamp are coincident

- If NOT measurements made on different atom population
  - Significant error

Hollow cathode lamp energy attenuated by BOTH atomic and background species

- Total absorption

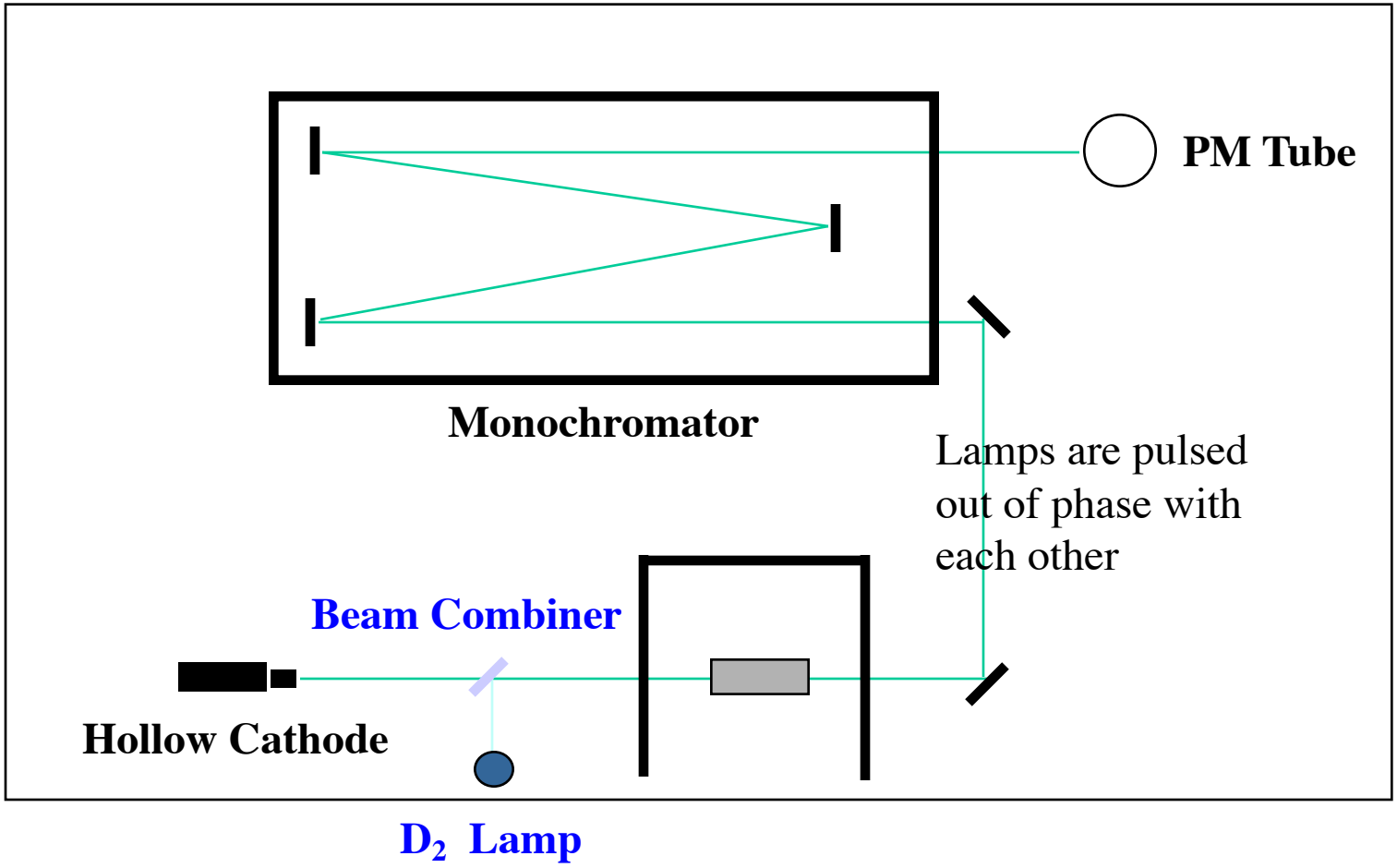
Deuterium energy attenuated by background species

- Background only
- Atomic component too small to detect

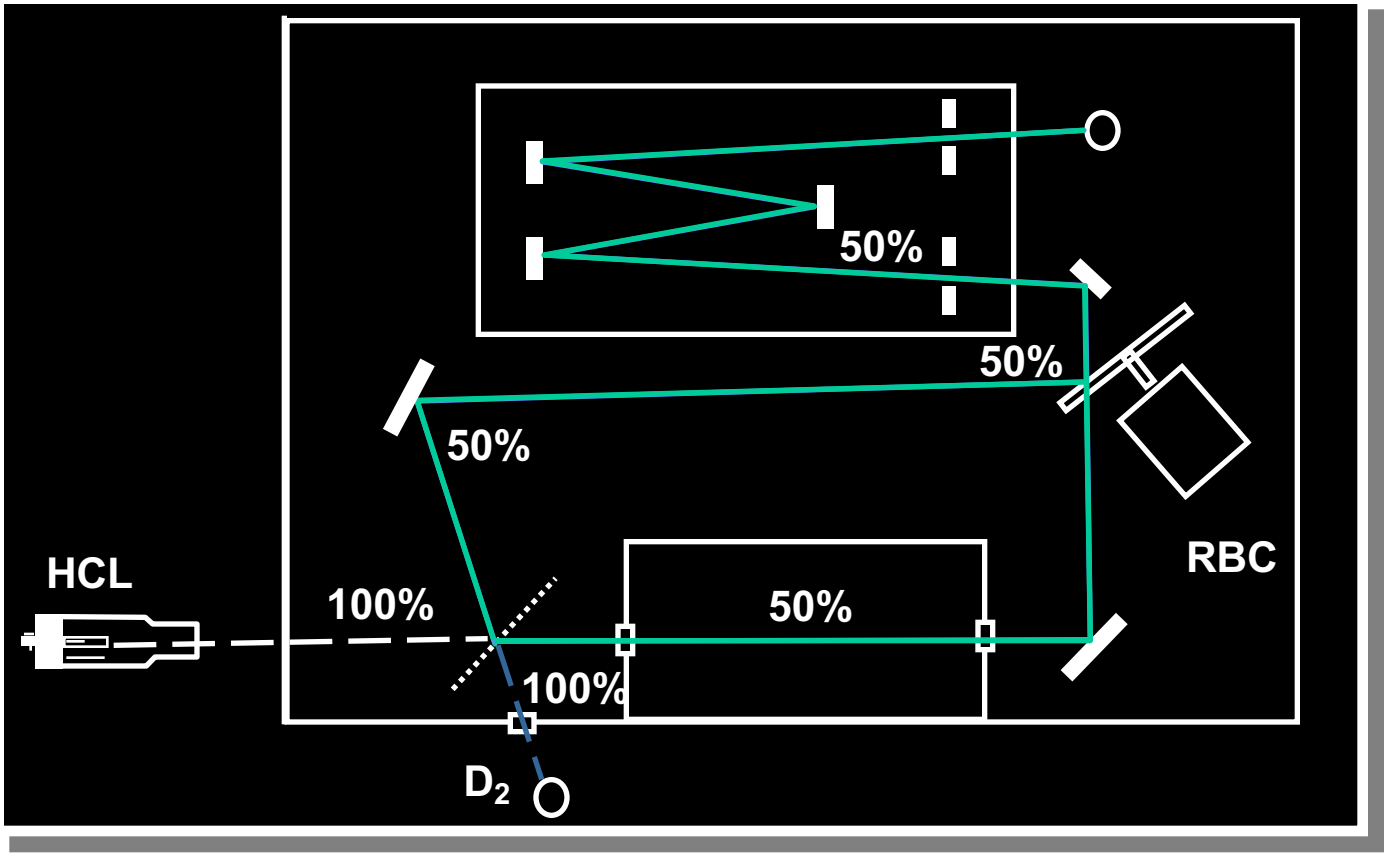
Calculation of Background

Hollow cathode lamp signal	=	AA + BGD
Deuterium lamp signal	=	BGD only
Electronically processed signal	=	AA only

Single Beam Schematic – D_2



Double Beam Schematic – D_2



Zeeman Technique

Limitations of deuterium background correction

- Intensity of continuum inadequate at high wavelength
- Cannot accurately correct for structured background
- Spectral interferences can occur
  - Rare

Zeeman background correction overcomes these limitations

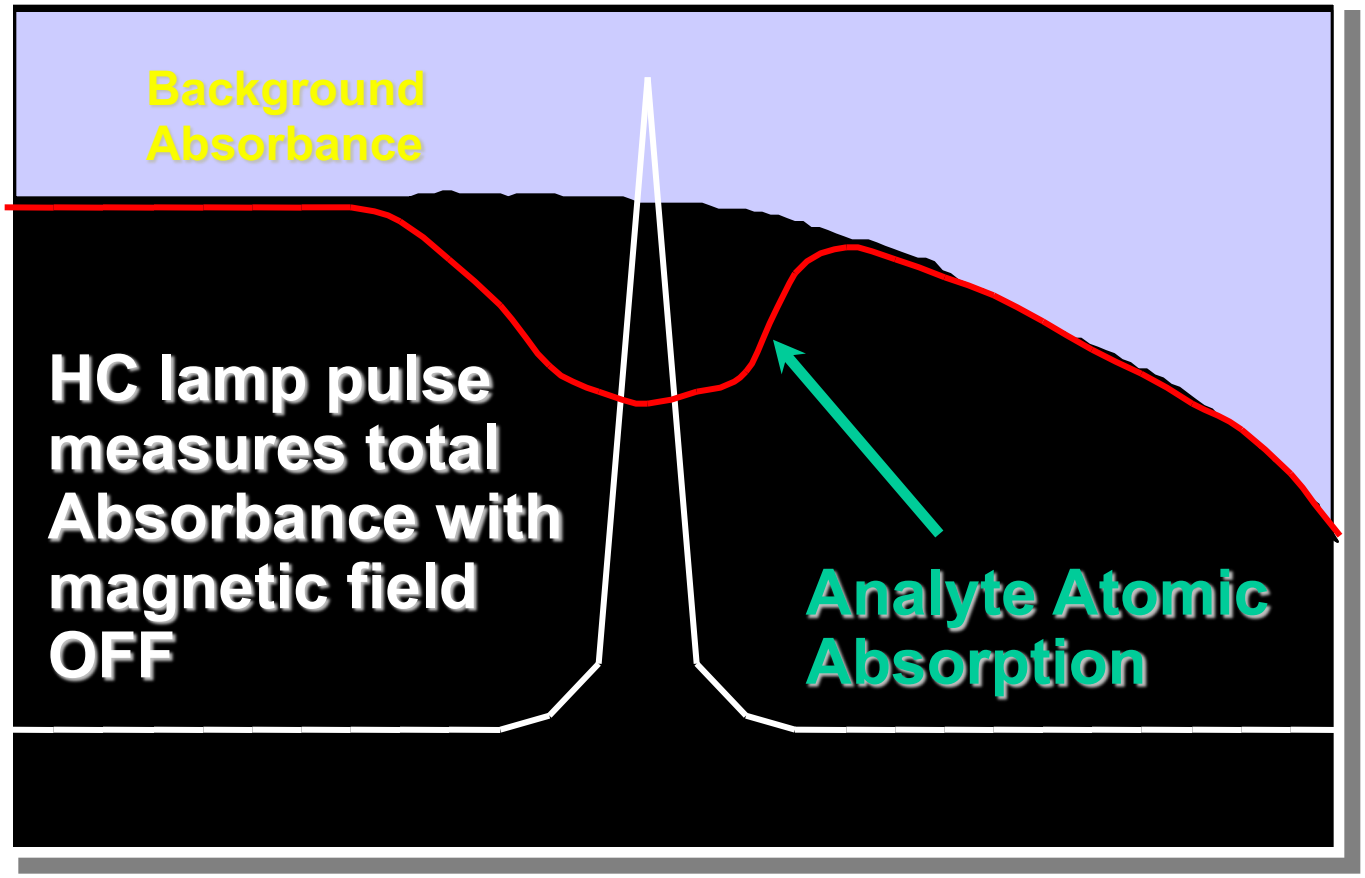
Zeeman Effect

Atomic spectral lines are split in the presence of a magnetic field

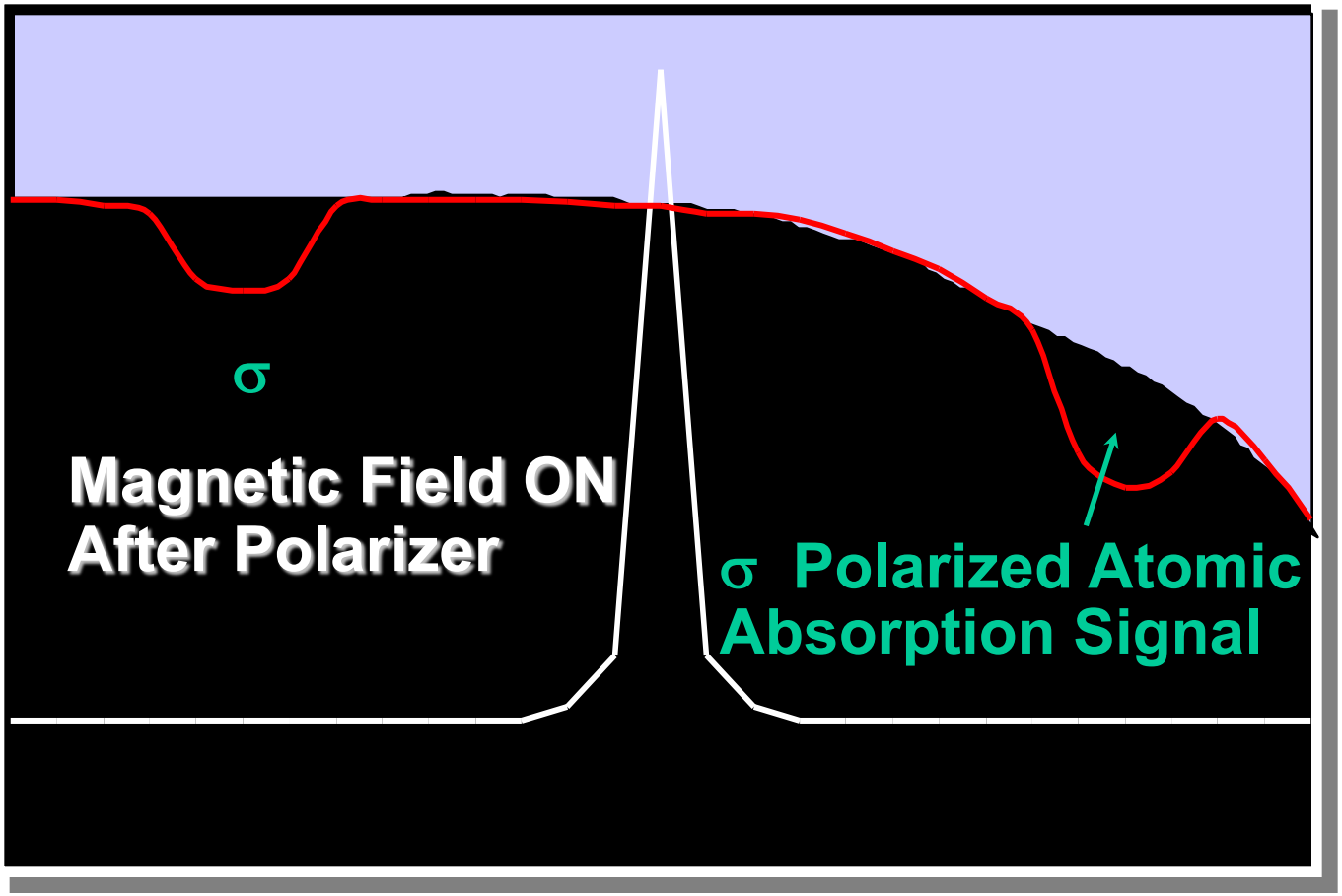
In “simple” or “normal” zeeman effect

- One pi (π) component
  - At original wavelength
  - Polarized parallel to magnetic field
- Two sigma (σ) components
  - Symmetrically displaced around original wavelength
  - Polarized perpendicular to magnetic field

Zeeman Background Correction



Zeeman Background Correction



Zeeman Background Correction

Total absorbance measured with magnet OFF

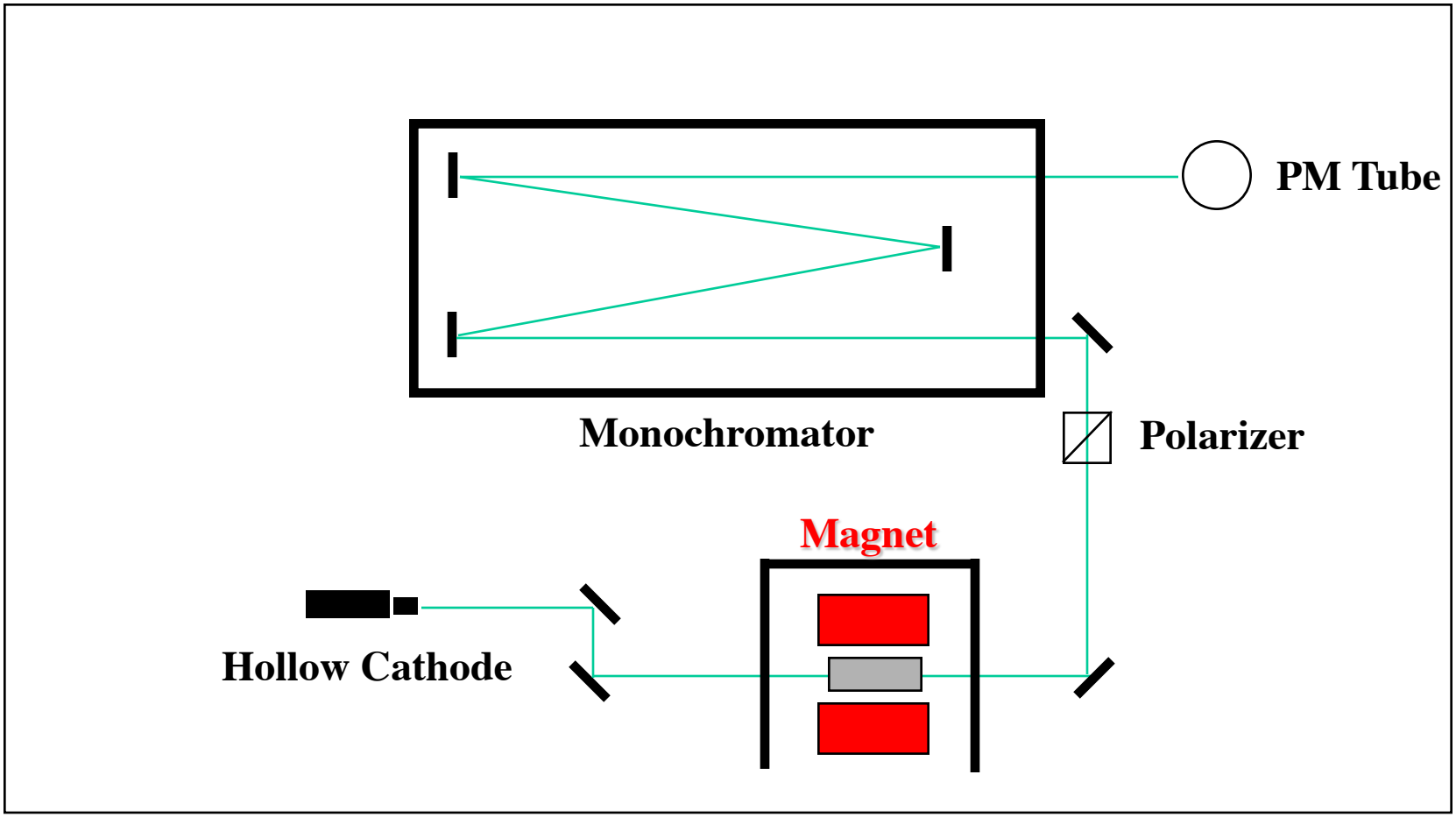
- Same measurement made by Deuterium or Smith-Hieftje systems

Background absorbance measured with magnet ON

- Polarizer excludes pi (π) component
- Measurement made exactly at the analyte wavelength

Molecular species are unaffected by magnetic field

Schematic - Zeeman



Advantages
Zeeman Background Correction

Correction takes place at the EXACT analyte wavelength

Correction over the complete wavelength range

Correction for structure background

Correction for some spectral interferences

Only one light source is required

True double beam performance

- Magnet On - magnet Off
- Automatic compensation for lamp drift

Disadvantages
Zeeman Background Correction

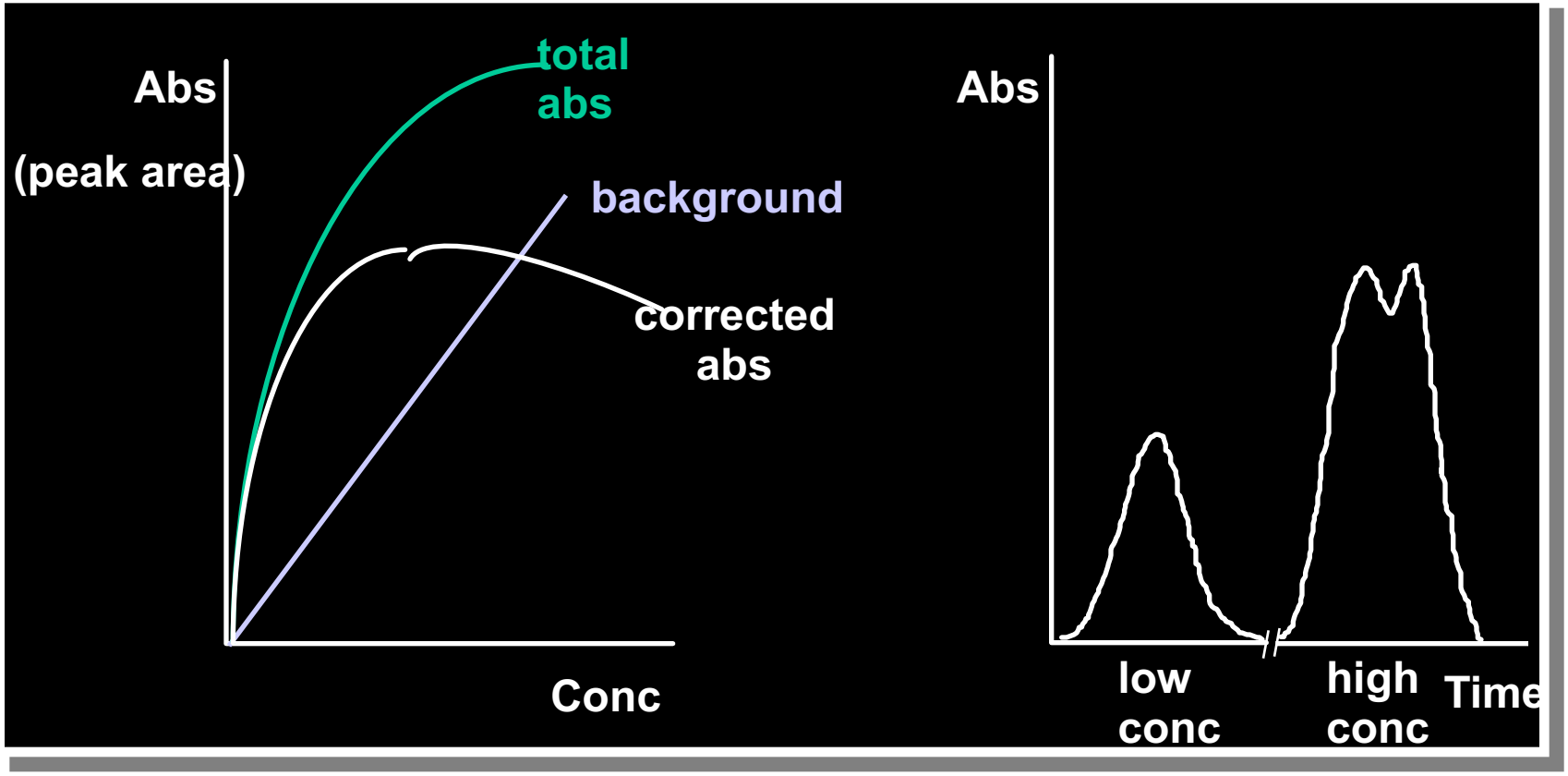
Calibration roll-over

- Degree of roll-over is element dependent

Sensitivity loss for some elements

- Degree of sensitivity loss is element dependent
- Expressed as magnetic sensitivity ratio (MSR)
- Majority of elements MSR loss $\leq$ 10%

Zeeman Calibration Roll-Over



Zeeman Summary

Good for difficult samples

- High background
- Unknown interferences

Good when spectral interferences occur

- Se in the presence of high Fe or phosphate
- As in the presence of high Al or phosphate
- Pb in the presence of high phosphate
  - 217.0 nm only