AA Optics
AA Optical Components

Spectrometer

- Collimates light from hollow cathode
- Isolates analyte wavelength
  - From other lines
  - From broad band emissions

Detector

- Measures light absorbed by analyte atoms
- References absorbed intensity to initial lamp intensity
Single Beam Optical Layout

- background correction lamp
- hollow cathode lamp
Single Beam Optics

Light from the source traverses ONLY ONE path
Must measure $I_0$ BEFORE inserting sample
Relies on stable light source

- $I_0$ does NOT drift while it is measured
- Modern hollow cathode lamps sufficiently stable
  - Appropriate warm Up period
    - Element dependent
    - Typically 10 minutes
      - Exceptions such as P, Tl, Cu/Zn multi-element
- Change in $I_0 = \text{change in baseline}$
Aging lamps could drift more
  • Use frequent recalibrations and reslopes
  • Particularly necessary for graphite furnace

High volume graphite furnace work - Zeeman or double beam optics recommended
All of the energy from the source passed through sample cell
- Good signal to noise ratio
- SLIGHTLY improved detection limits vs double beam
If fitted with deuterium background corrector - same energy as double beam
Double Beam Optical Layout

- background correction lamp
- hollow cathode lamp
- reference beam
- sample beam

M1, M2, M3
Double Beam Optics

Designed to correct for drift in $I_0$
  - NOT LIKE REFERENCE BEAM IN UV-VIS
Light from source is directed at a beam splitter
  - Optical component designed to reflect a portion of the light energy and allow the remainder to pass though.
  - Normally designed to reflect 50% - pass 50%
Beams recombined before entering monochromator
  - Beams must be time separated
Methods of Time Separation and Beam Recombination

Second beam splitter with rotating perforated disk passing first one beam then the other
  • 50% light loss at first beam splitter
  • 50% light loss at second beam splitter
  • POOR SIGNAL TO NOISE RATIO

Rotating beam combiner (RBC)
  • Alternately passes
    – ALL OF REFERENCE BEAM
    – ALL OF SAMPLE BEAM
  • BEST POSSIBLE SIGNAL TO NOISE RATIO
Advantages of Double Beam Optical Design

Allows intensity ($I_0$ and $I_t$) of BOTH reference and sample beam to be measured at high frequency.

High frequency monitoring provides near instantaneous corrections for variation in source intensity.

Both hollow cathode and deuterium source monitored.
Even with double beam optical design lamp warm up is recommended

- During warm up period emission line profile may change
- Changes in emission profile can cause small changes in the analytical signal
Fast Sequential Lamp Selection
Hollow cathode lamp emits many narrow emission lines
Monochromator isolates single resonance emission line from hollow cathode lamp
IDEALLY monochromator isolates ONLY ONE LINE

• Sometimes easy – Cu
• Sometimes more difficult - Fe
Czerny - Turner Monochromator

Detector PMT

exit slit

grating

entrance slit

spherical mirror

spherical mirror
Czerny - Turner Monochromator

Uses Two Separate Mirrors
  • One to Focus Incoming Light onto Grating
  • One to Focus Outgoing Light onto Photomultiplier

Mirrors Have Different Optical Properties
  • Reduces Aberrations
  • Improves Resolution
  • Improves Light Throughput

Mirrors can be Prepared with Great Accuracy
Heart of monochromator
Light focused on grating is dispersed at different angles according to its wavelength
Rotating the grating focuses a specific wavelength on the exit slit
Spectrum Created by Wave Interference
Monochromator Resolution

Very important

Very high resolution needed for emission
  • Complex spectra generated by high temperature plasma
  • < 0.01 nm

“Medium” resolution needed for atomic absorption
  • “Simple” spectral output from hollow cathode lamp
  • ~ 0.2 nm
Affects spectral isolation of analytical line

- Ability of spectrometer to resolve analytical line from adjacent lines

Normally dictated by nearest adjacent line in spectrum

In practice setting slit width is compromise

- Wide slit
  - High energy - good signal to noise
  - Poor spectral resolution - highly curved calibration

- Narrow slit
  - Lower energy - higher noise
  - Good spectral resolution - more linear calibration
Atomic Spectrum of Fe

Wavelength nm

Intensity

245 246 247 248 249 250

0.00 0.50 1.00 1.20

248nm 248.3nm 249nm
Effect of Spectral Band Width

Resonance Line

Slit Width

Calibration Curvature
Causes of Calibration Curvature

Detector observes non-analyte emission lines

- Hollow cathode lamp fill gas
- Non-resolved spectral lines
Vacuum tube which produces electrical signal proportional to intensity of light reaching it
Light enters a window and falls directly on photoemissive material
Photoemissive material emits electrons
  • More light intensity produces more electrons
Electrons accelerated to dynodes
Dynodes emit secondary electron for each electron striking it
Photomultiplier Tube Operation

*100 Million Amplification of Signal

Photocathode → Light Energy → Window → ***e⁻*** → Anode → Dynode's (9-13)
Photomultiplier Response

![Graph showing the photomultiplier response for different wavelengths.

- **R1516**
- **R4332**
- **R955**
- **R446**

Relative Sensitivity vs. Wavelength (nm)
Factors Influencing Detection Limits

Detection limit reflects the signal to noise ratio

Factors influencing signal to noise ratio

- Optical design
- Standard deviation of blank
- Analytical sensitivity
- Unlikely to be ANY SIGNIFICANT difference between the detection limits for a double beam and D2 corrected single beam instrument