Chapter 25

Instruments for Optical Spectrometry

Optical Instruments
• Emission Flame Photometer (ICP—Inductively Coupled Plasma Emission Spectrometer)
• Flame Atomic Absorption Spectrometer (AA)
• Absorption Spectrometer (UV/Vis, FTIR)
• Fluorescence Spectrometer (Fluorimeter)
• Scattering Spectrometer (Raman Spectrometer)

4 Basic Components of Instruments for Chemical Analysis
• signal generators
• detectors (input transducers)
• signal processors (circuits & electrical devices)
• readout devices
Absorption

Fluorescence, Phosphorescence, Scattering

Chemiluminescence

Optical Instrument Configurations

Atomic Absorption Spectrometer

Optical Materials
Optical Sources and Detectors

EMR Sources

- Ideal Properties:
  - High Intensity
easily measured
  - Stable
low noise
  - Tunable
provides desired $\lambda$’s

Two Types of Sources

- Continuum -Band Spectrum (wide $\lambda$-range)
- Line Spectrum (discrete $\lambda$’s)
**Line Sources**

- Most line sources rely on spontaneous emission from thermally-excited **gas-phase** atoms/ions:

\[
E_{\text{Em}} = \frac{q}{A_p} = \frac{N_q}{A_p} \frac{dN_q}{dt}
\]

**Continuum & Line Spectra**

- **Continuum Spectrum**
- **Emission Line Spectrum**
- **Absorption Line Spectrum**

**Most Commonly Used Sources**

- **UV-Visible-Near IR Region**
  - (a) H₂ or D₂ (deuterium) lamps (160-375 nm)
  - \( D_2 + E_{\text{electrical}} \rightarrow D_2^* \rightarrow D(KE_1) + D(KE_2) + h\nu \)

[Link to Hamamatsu Light Sources]

(b) Xenon Arc Lamps (250-600 nm)
$\lambda_{\text{max}} \sim 500$ nm

(c) Tungsten Lamps (320-2500 nm)

(d) Quartz Tungsten Halogen Lamps (200-3000 nm)

- IR Region
  - Nernst glower - rare earth oxides
  - globar - silicon carbide rod
  - incandescent wire - nichrome wire

- Line Sources
  (a) Hg Lamps
  (b) Hollow Cathode Lamps
  (Atomic Absorption Analysis)
Hollow Cathode Lamps

Hamamatsu Produces ~186 HCL Lamps
Can be used to detect ~70 metals

More Details will be discussed in Chapter 9

Sources

Lasers
Light Amplification by Stimulated Emission of Radiation

Silvered Mirror
Nonparallel radiation
Active laser medium
Partialy transmitting mirror
Power supply

Flash Tube
Ruby Rod

Sample Cells

- Must be transparent over desired λ-range
  -- Visible: Glass or Plastic
  -- UV/Vis: Quartz (fused silica)
  -- IR: KBr/NaCl
- Needs to have a stable, fixed pathlength
  -- can be 1 mm to ~ few cm (varies)
- Should have minimal physical defects
  -- to keep losses due to scattering/reflection at a minimum
Wavelength Selectors

• Optical Filters
  – Interference
  – Absorbance
• Prism Monochromators
• Grating Monochromators
• Interferometers

Radiation Transducers: (Detectors)

Ideally:
• high sensitivity
• low noise
• wide wavelength response
• linear output ($S=k\cdot I$)
• low dark current (small current when $I=0$) ($S=k\cdot I+k_d$)

Detectors

■ *Earliest: The Human Eye*
• can detect single photons
• limited to visible spectral region
• quantitation is problematic

■ Two classes to consider:
  1. *Single-Channel*
     • monitor intensity of a single resolution element at a time
  2. *Multi-Channel*
     • monitor intensities of many resolution elements at a time
Single-Channel Detectors

In general:

\[ V_{\text{out}} = i_p R_c \]

Two common types:

1. **Photoemissive**
   - Based on photoelectric effect:
   
   \[ \text{hv} \rightarrow e^- \]
   
   - \( e^- \) released only if \( hv > E_{\text{min}} \)
   
   - \#e^- \propto \#\text{photons}

2. **Photoconductive**
   - Photons striking device cause an increase in electrical conductivity
   - e.g., photodiodes, semiconductors

Multi-Channel Detectors

- Monitors intensities of many resolution elements simultaneously
  - Similar to FT-interferometry (multiplexed measurement), but in the frequency domain
- **Examples:**
  - Photographic plates
  - Photodiode arrays (PDA)
  - CID and CCD detectors
- Most commonly limited to UV/Vis
(A) Photovoltaic cells - metal-semiconductor-metal sandwiches that produce voltage when irradiated (350-750 nm)

(B) Phototube - electrons produced by irradiation of cathode travel to anode. Response depends on cathode material (200-1000 nm) (Photoelectric Effect)

(C) Photomultiplier tube (PMT) - irradiation of cathode produces electrons, series of anodes (dynodes) increases gain to $10^4$-$10^7$ electrons per photon. Low incident fluxes only!
Non-Dispersive Methods

**Fourier-Transform Interferometry**

What if we could measure the oscillating wavefunction of EMR directly?

![Waveform Diagram](image)

**Time Domain**

**Frequency Domain**

**Michelson Interferometer**

- EMR enters and hits beamsplitter
- Port goes to fixed mirror
- Port goes to movable mirror
- Reflected beams recombine at beamsplitter

![Michelson Diagram](image)
Advantages of Fourier Transform Spectroscopy

- Signal to noise enhancement—Multiplex Advantage;
- High throughput advantage—few optical elements and no slits to attenuate radiation;
- High resolution.