Components of Optical Instruments

- **Optical phenomena used for spectroscopic methods:**
  1. absorption
  2. fluorescence
  3. phosphorescence
  4. scattering
  5. emission
  6. chemiluminescence

- **Spectroscopic Instrumentation:**
  1. stable light source
  2. transparent sample compartment
  3. device isolating a restricted frequency/frequency range
  4. radiation detector
  5. emission
  6. chemiluminescence
General instrumentation layout:

Figure 7-1 Components of various types of instruments for optical spectroscopy: (a) absorption; (b) fluorescence, phosphorescence, and scattering; (c) emission and chemiluminescence.
Overview:

![Diagram of Radiation Sources](image_url)

- **Spectral region**
  - VAC
  - UV
  - Visible
  - NEAR IR
  - IR
  - FAR IR

- **Sources**
  - Ar lamp
  - Xe lamp
  - H₂ or D₂ lamp
  - Tungsten lamp
  - Nernst glower (ZrO₂ + Y₂O₃)
  - Nichrome wire (Ni + Cr)
  - Globar (SiC)
  - Hollow cathode lamps
  - Lasers

**Radiation Sources 1**
Laser:

- Laser pumping
- Spontaneous emission
- Stimulated emission
- Absorption
Wavelength Selection 1

- **General:**

  A frequency band/spectral band with a certain **bandwidth** shall be selected. Narrow bandwidth → higher sensitivity (why?) and higher selectivity.

- **Two types of wavelength selectors:**
  - Filters
  - Monochromators

![Diagram of a typical wavelength selector](image)
Filters:

- Interference filters: (UV-IR)
- Absorption filters: (VIS)
**Monochromators:**

Allow to vary the wavelength of radiation continuously over a certain range → *scan* a spectrum.
Performance of Grating Monochromators:

The ability to separate different wavelengths. This depends on the dispersion of the grating.

- **Angular dispersion:**
  for constructive interference:
  \[ n\lambda = (CB + BD) \]
  \[ \rightarrow CB = d\cdot\sin i \quad \text{and} \quad BD = d\cdot\sin r \]
  \[ \rightarrow n\lambda = d\cdot(\sin i + \sin r) \]

  \[ \frac{dr}{d\lambda} = \frac{n}{d\cdot\cos r} \]

- **Linear dispersion:**
  \[ D = \frac{dy}{d\lambda} = F\cdot\frac{dr}{d\lambda} \]
  (reciprocal \( D^{-1} \) in nm/mm)
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\[ D = \frac{dy}{d\lambda} = F \frac{dr}{d\lambda} \]

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- **Optical Resolution:**

The resolving power describes the ability to separate adjacent images with a slightly different wavelength.

\[ R = \frac{\lambda}{\Delta \lambda} = nN \]
Slits:

- Important for the performance of the monochromator.
- If entrance and exit slit are of the same size → image of entrance slit will fill exactly the exit slit when setting corresponds to \( \lambda \).
- The bandwidth is the span of the monochromator settings needed to move the image of the entrance slit across the exit slit.
- Effective bandwidth: \( D^{-1} = \Delta \lambda / \Delta y \)
Influence slit width on spectra:

Figure 7.23 The effect of the slit width on spectra. The entrance slit is illuminated with \( \lambda_1, \lambda_2, \) and \( \lambda_3 \) only. Entrance and exit slits are identical. Plots on the right show changes in emitted power as the setting of monochromator is varied.

Figure 7.24 Effect of bandwidth on spectral detail for benzene vapor: (a) 0.5 nm; (b) 1.0 nm; (c) 2.0 nm. (From H. A. Kabbe, Analyst, 1954, 79, 112. Copyright 1954 International Scientific Communications, Inc.)
Sample Container

➢ **Cuvette:**

Most important → choice of material!

![Graph of spectral regions and materials for optical spectroscopy](image-url)
What do we want?:

- High sensitivity
- High signal-to-noise ratio
- Constant response over a considerable wavelength range
- Fast response time
- Zero output if no radiation is incident
- Electric signal proportional to the radiant power $P$

Detector signal $S = k^*P$ (k ... calibration sensitivity)

What do we get?

$S = k^*P + k_D$ ($k_D$ ... dark current)
Types of detectors:

- Photon transducers:
  (photoelectric detectors, quantum detectors)
  All detectors reacting directly to photons incident on an active surface, which absorbs radiation. The absorbed energy causes emission of electrons and a photocurrent or promotes electrons into the conduction bands resulting in enhanced conductivity (photoconductivity). The electric signal results from a series of individual events.

- Thermal transducers:
  Respond to the average power of incident radiation. Hence, thermal noise limiting rather than shot-noise at photon transducers. Relative sensitivity almost independent of wavelength, but much less sensitive than photoelectric devices.
**Photovoltaic cell:**

- Maximum sensitivity: at approx. 550 nm
- Usable range: 350 – 750 nm
- Iron electrode
- Semiconductor (e.g. Selenium)
- Collector electrode (gold or silver)
- Radiation → covalent bonds in semiconductor broken → formation of $e^-$ and holes → $e^-$ migrate towards collector electrode, holes towards bottom electrode → $e^-$ migrate through external circuit to recombine with holes → photocurrent (10-100 µA)
**Vacuum Phototube:**

- Maximum sensitivity: at approx. 400 nm
- Usable range: 200 – 1100 nm
- Semicylindrical cathode
- Wire anode
- Evacuated transparent cylinder
- Cathode has layer from photoemissive material → emits electrons when irradiated → potential applied (approx. 90 V) across electrodes → emitted e⁻ flow to anode and generate photocurrent (0.1 - 1 µA) → due to high electrical resistance → high amplification possible
- Dark current due to thermally induced emission of e⁻
- Photomultiplier Tube:
  - Maximum sensitivity: at approx. 300 nm
  - Usable range: 300 – 800 nm
  - Cathode with photoemissive layer
  - Several dynodes (each at 90+ V)
  - Collector anode
  - Evacuated transparent cylinder
  - Cathode emits electrons when irradiated \( \rightarrow e^- \) accelerated to dynode 1
  - Each \( e^- \) causes emission of several \( e^- \)
  - Cascading effect from dynode 1-9 (\( 10^7 \) to \( 10^9 \) \( e^- \) induced for each incident photon \( \rightarrow \) collected at anode and amplif.)
  - Single photon detection
  - Dark current due to thermally induced emission of \( e^- \)
Silicon Diodes:

- Maximum sensitivity: at approx. 1000 nm
- Usable range: 190 – 1200 nm
- Reverse-biased pn-junction formed on silicon chip
- Reverse bias creates depletion layer → conductance of junction close to 0 → chip irradiated → holes and e⁻ formed in depletion layer → swept through device causing a photocurrent proportional to radiant power
- More sensitive than phototube but less than photomultiplier

Figure 7-30 (a) Schematic of a silicon diode. (b) Formation of depletion layer, which prevents flow of electricity under reverse bias.
Photoelectric Detectors 5

➤ **Multichannel Detectors:**

- Photodiode array:
  64 – 4096 silicon diodes on one chip

- Charge-transfer devices (CTD)

- Charge-injection devices (CID)

- Charge-coupled devices (CCD)

![Diagram of a reverse-biased linear diode-array detector: (a) cross section and (b) top view.](image-url)
Photoelectric Detectors 6

- **Photoconductive Detectors:**
  - Maximum sensitivity: at approx. 1000 nm
  - Usable range: 0.75 – 3 µm
  with cooling: up to FIR
  - Crystalline semiconductors with decreasing resistance upon absorption of radiation (e.g. sulfides, selenides, lead, cadmium, gallium, indium etc.)
  - Cooling to suppress noise from thermally induced transitions
  - Absorption of radiation promotes some of the bound electrons into an energy state where they are free to conduct electricity → this change in conductivity can be measured
General remarks:

- In the infrared photons lack the energy to cause photoemission of e⁻.
- Hence, photoconduction or thermal detectors used for IR.
- Incident radiation is absorbed by a black body → temperature rise → measured.
- Radiant power IR $10^{-7} - 10^{-9}$ W → heat capacity of absorbing detector element as small as possible to maximize detectable change → small, thin elements (max. 2 mm²).
- Thermal noise → vacuum and cooling.
Thermal Detectors 2

- **Thermocouple/Thermopile:**
  - Temperature-dependent contact potential formed at each of the two junctions
  - Potential difference measured
  - Several thermocouples connected in series → **Thermopile**
  - Detectable temperature difference: $10^{-6}$ K
Thermal Detectors 3

- **Bolometer:**
  - Resistance thermometer
  - Metal strips (Pt, Ni, semiconductor ...)
  - Large change in resistance as function of temperature
  - e.g. germanium element operated at 1.5 K for 2000 – 25 µm

- **Pyroelectric detector:**
  - pyroelectric material: insulator (dielectric) with temperature-dependent polarization when exposed to an electric field
  - single crystalline wafers, e.g. Triglycine sulfate sandwiched between two electrodes → T-dependent capacitor → T-change due to irradiation changes the charge distribution across the crystal → measurable current occurs
Optical Fibers

- **Time resolved fluorescence:**

![Diagram of time resolved fluorescence setup](image)
Throughput (Jaquinot) advantage:

- Few optical components and no slits → much greater power reaches detector compared to dispersive instruments.
- The aperture right after the source is only required to simulate as close as possible a punctual radiation source.
- The optical throughput for a FT-setup is mainly restricted by the areas of the mirrors and is dependent on the resolution and the maximum wavenumber.
- In contrast to this slit-less setup, the dispersive spectrometer requires a slit to filter out the required wavelength range. The smaller the slit, the better is the achievable spectral resolution. But accordingly, by using a slit the intensity of the radiation incident at the detector is strongly reduced.
Calibration (Connes) advantage:

- The frequencies in the FT-spectrometer need not to be calibrated with a reference material as the retardation of the mirror is exactly determined by a reference laser → all frequencies are obtained in absolute values without prior scaling.
- The dislocation of the moving mirror (or “mirrors”, in other interferometer configurations than the set-up described by Michelson, e.g. Happ-Genzel) in the interferometer from the zero position is determined with the interferogram of a helium-neon (He-Ne) laser with a wavelength of 0.633 µm.
- As the wavelength of the laser is known exactly and remains constant, it may be used as internal standard. With this method a spectral resolution below 0.1 cm\(^{-1}\) may be achieved.
Multiplex (Felgett) advantage:

- Simultaneous detection of all spectral frequencies results in a higher sensitivity and a shorter measurement time.
- With FT-instrumentation the signal/noise-ratio is directly proportional to the root of the measurement time.
- With a dispersive spectrometer the spectral range has to be scanned sequentially. Therefore, the S/N ratio of a dispersive spectrometer is proportional to the root of the number of spectral elements M and the root of the measurement time, with the number of spectral elements M calculated as quotient of measurement range versus spectral resolution.
Time domain/frequency domain spectroscopy:

- Frequency domain spectroscopy:
  Conventional spectroscopy where the radiant power is recorded as function of the frequency.

- Time domain spectroscopy:
  Used in FT-techniques, where the changes in radiant power are recorded as function of the time.
  If only few wavelengths are involved, periodicity (beat) is obvious when waves go in and out of phase.
  If broadband light source, pattern of beats hard to determine, signal power decreases with time as closely spaced wavelengths get more and more out of phase.
  Frequency domain spectra and time domain spectra contain the same information and can be converted into each other by numerical computation.
Figure 7-40 Illustrations of (1) time-domain plots (a) and (b) and (2) frequency-domain plots (c), (d), and (e).

Figure 7-41 Time-domain signal of a source made up of several wavelengths.
Michelson Interferometer:

- Frequency of the radiation in optical spectroscopy usually too fast for direct detection ($10^{12}$-$10^{15}$ Hz) → modulation of the high-frequency signal to a measurable frequency maintaining the proportionality.

Figure 7-42  Schematic of a Michelson interferometer illuminated by a monochromatic source.
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- **Interferograms, 1, 2 and multiple wavelengths:**

![Interferograms and Spectra Diagram](image)

*Figure 7-43 Comparison of interferograms and optical spectra.*