NEPHAR 201
Analytical Chemistry II

Chapter 3
Components of optical instruments

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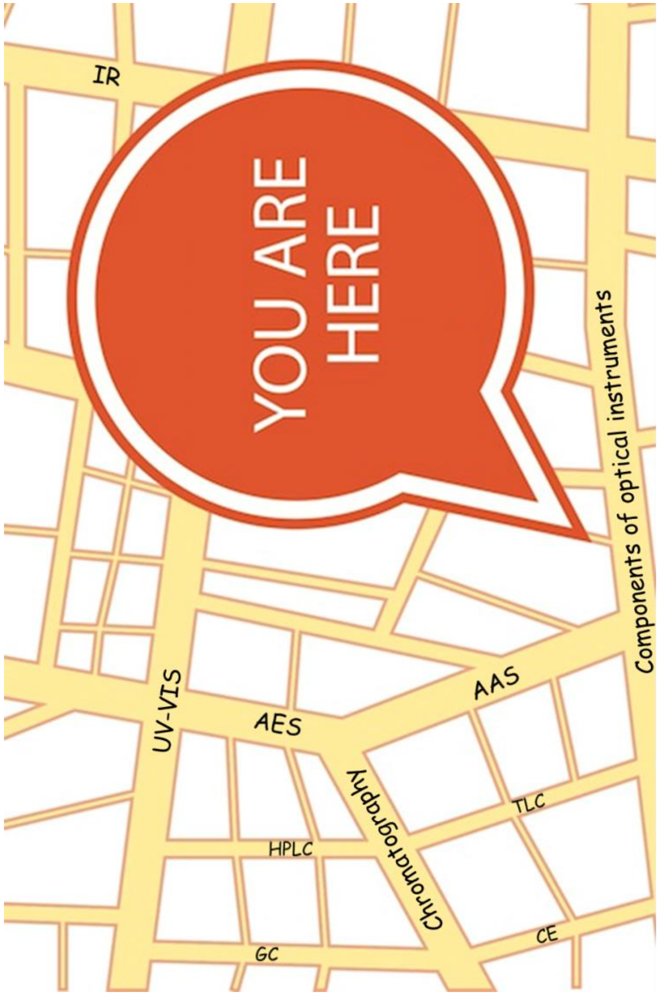
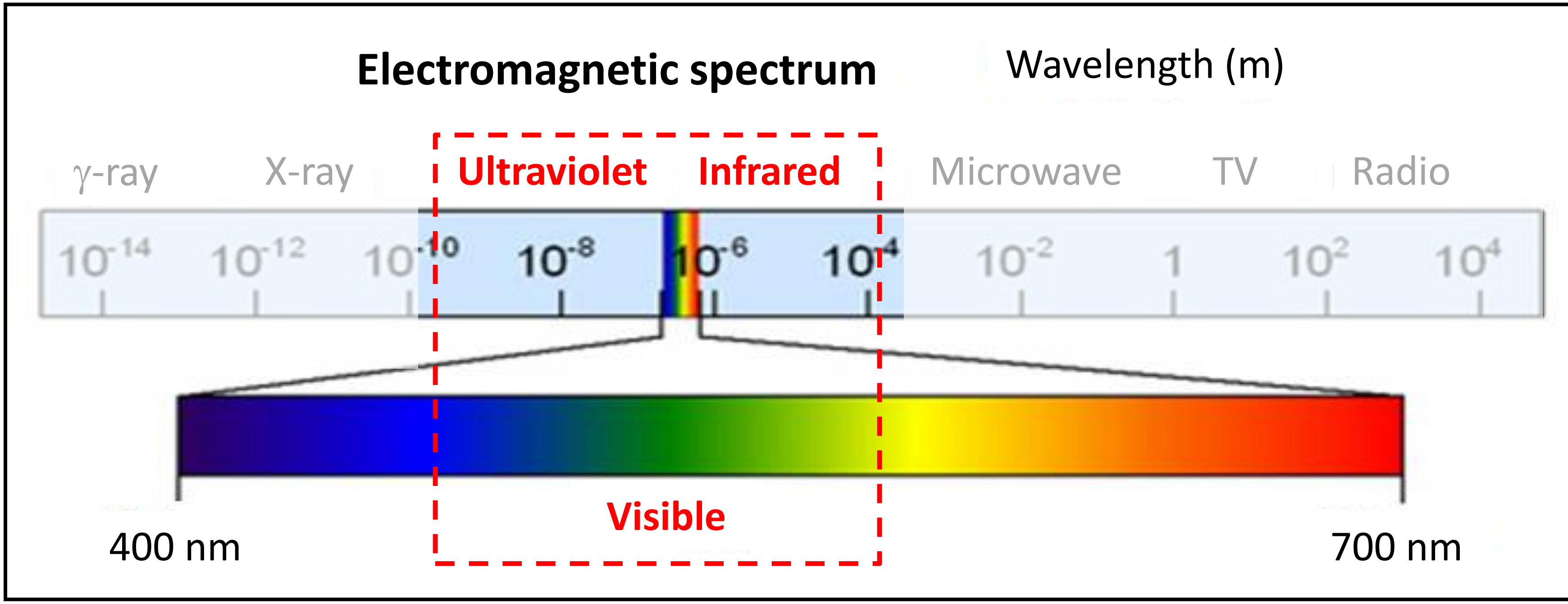


Week	Topic	Reference Material	Instructor
1 [14/09]	Introduction	Instructor's lecture notes	Alshana
2 [21/09]	An introduction to spectrometric methods	• Principles of Instrumental Analysis, Chapter 6, pages 116-142 • Enstrümantal Analiz- Bölüm 6, sayfa 132-163	Alshana
3 [28/09]	Components of optical instruments	• Principles of Instrumental Analysis, Chapter 7, pages 143-191 • Enstrümantal Analiz- Bölüm 7, sayfa 164-214	Alshana
4 [05/10]	Atomic absorption and emission spectrometry	• Principles of Instrumental Analysis, Chapter 9, pages 206-229, Chapter 10, pages 230-252 • Enstrümantal Analiz- Bölüm 9, sayfa 230-253, Bölüm 10 sayfa 254-280	Alshana
5 [12/10]	Ultraviolet/Visible molecular absorption spectrometry	• Principles of Instrumental Analysis, Chapter 13, pages 300-328 • Enstrümantal Analiz- Bölüm 13, sayfa 336-366	Alshana
6 [19/10]	Infrared spectrometry	• Principles of Instrumental Analysis, Chapter 16, pages 380-403 • Enstrümantal Analiz- Bölüm 16, sayfa 430-454	Alshana
7 [26/10]	Quiz 1 (12.5 %)		Alshana
	Chromatographic separations	• Principles of Instrumental Analysis, Chapter 26, pages 674-700 • Enstrümantal Analiz- Bölüm 26, sayfa 762-787	
8 [02-07/11]	MIDTERM EXAM (25 %)		
9 [09/11]	High-performance liquid chromatography (1)	• Principles of Instrumental Analysis, Chapter 28, pages 725-767 • Enstrümantal Analiz- Bölüm 28, sayfa 816-855	Alshana
10 [16/11]	High-performance liquid chromatography (2)		Alshana
11 [23/11]	Gas, supercritical fluid and thin-layer chromatography	• Principles of Instrumental Analysis, Chapter 27, pages 701-724, Chapter 29 pages 768-777 • Enstrümantal Analiz- Bölüm 27, sayfa 788-815, Bölüm 29 sayfa 856-866, Bölüm 28 sayfa 848-851	Alshana
12 [30/11]	Capillary electrophoresis	• Principles of Instrumental Analysis, Chapter 30, pages 778-795 • Enstrümantal Analiz- Bölüm 30, sayfa 867-889	Alshana
13 [07/12]	Quiz 2 (12.5 %)		Alshana
	Extraction techniques	Instructor's lecture notes	
14 [14/12]	Revision	Instructor's lecture notes and from the above given materials	Alshana
15 [21-31/12]	FINAL EXAM (50 %)		

Optical Spectroscopic Methods

- **Optical instruments:** analytical instruments that are designed for measurements in the visible (VIS), ultraviolet (UV) and infrared (IR).

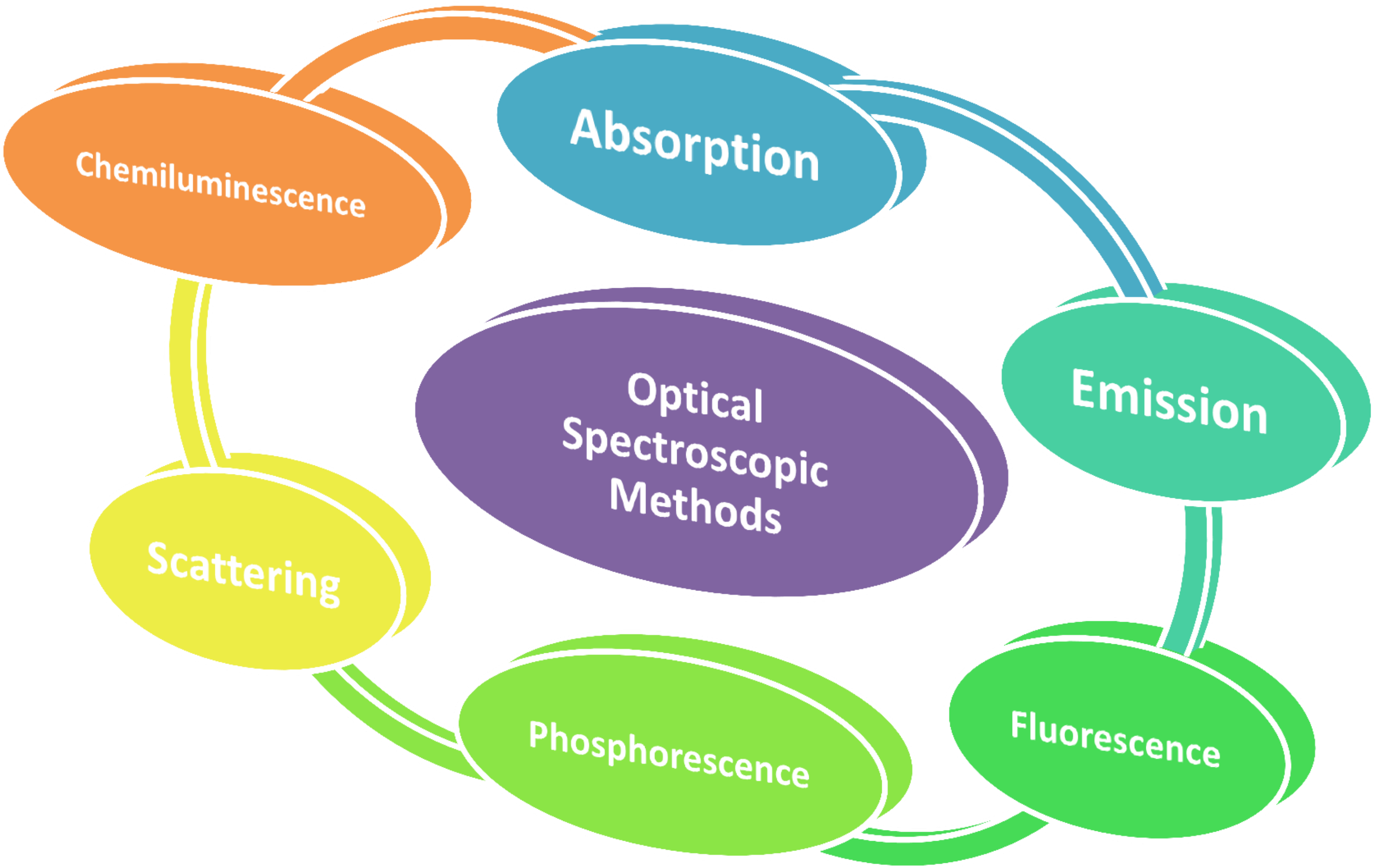


Optical instruments

- Although the human eye is only sensitive to **VIS** but is sensitive neither to **UV** nor to **IR**, they are still called **optical instruments**.

Optical Spectroscopic Methods

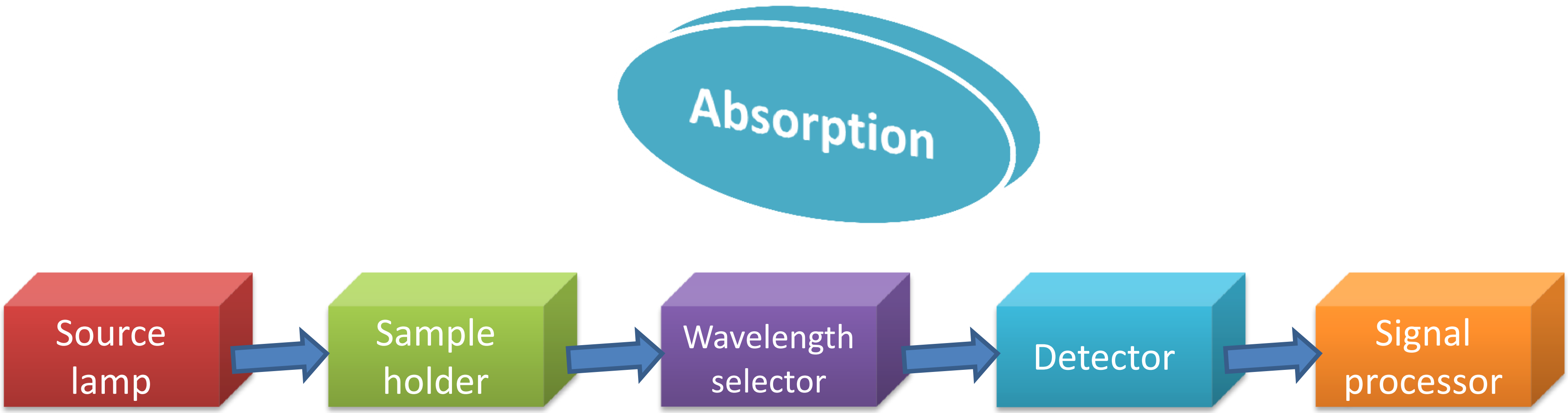
Optical spectroscopic methods are based upon six phenomena:

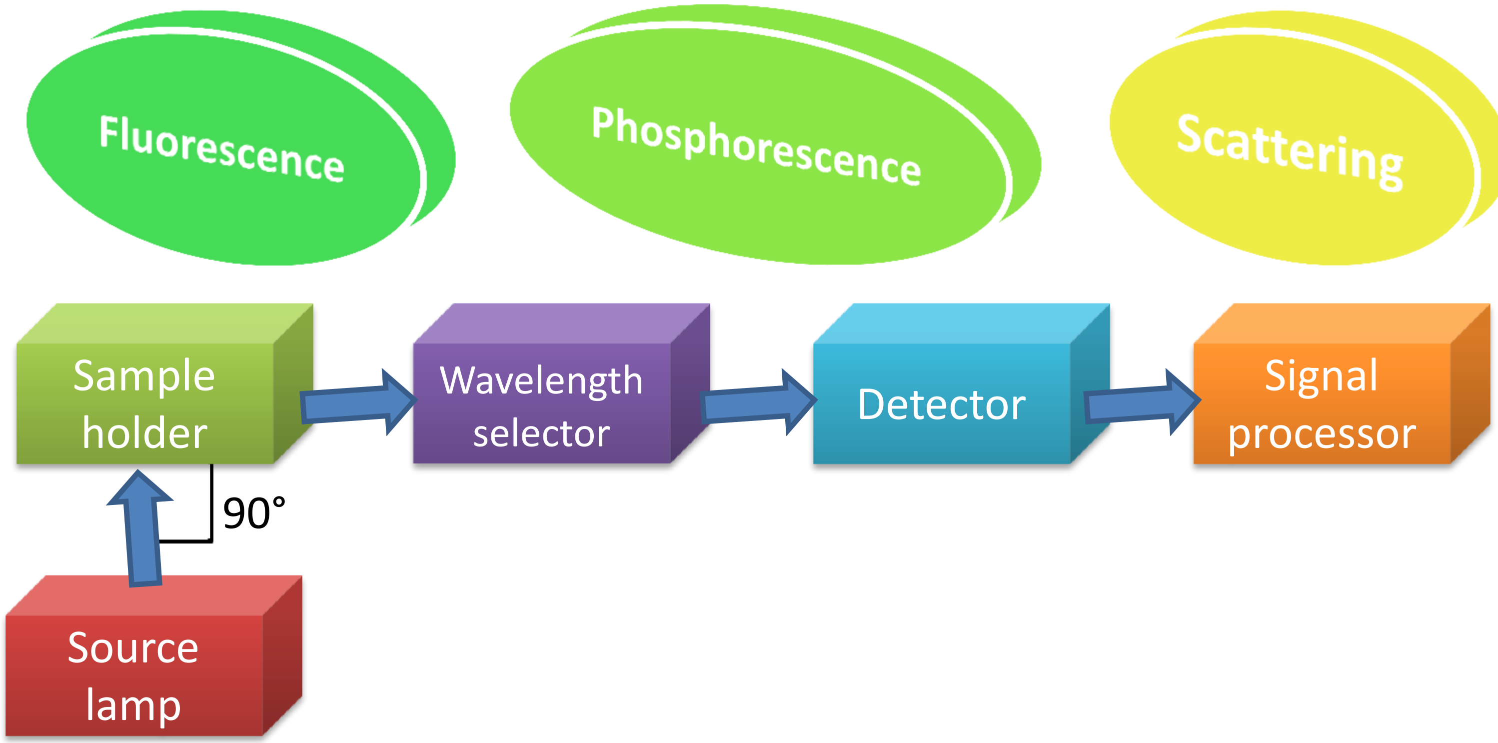


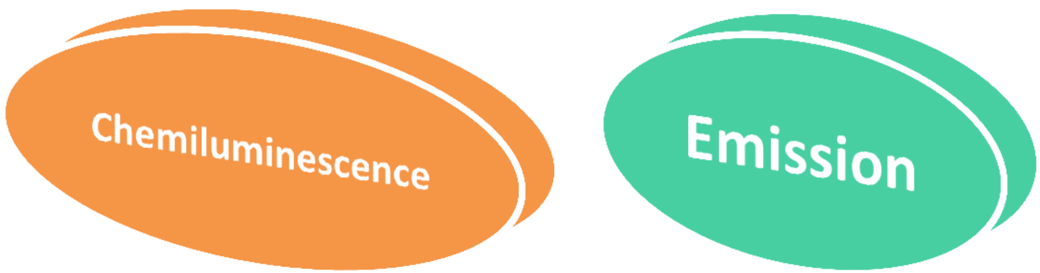
Components of optical spectroscopic methods

- Regardless of whether they are applied to the UV, VIS or IR region, **optical instruments contain five components**:

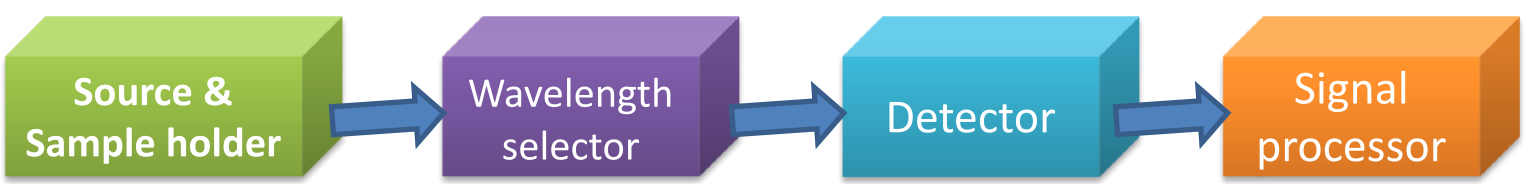
1. A stable **source** of radiant energy,
2. A transparent **container** for holding the sample,
3. A **wavelength selector** to isolate a restricted region of the spectrum for measurement,
4. A **detector** to convert radiant energy to a suitable signal (usually electrical),
5. A **signal processor** to display the result digitally for calculations.







- In emission and chemiluminescence, there is **no need for the source**; the sample itself is the emitter of radiation.



① Sources of radiation

A suitable source for spectroscopic studies:

1. must generate a beam of radiation with **sufficient power** for easy detection and measurement,
2. its output power should be **stable** for reasonable periods of time.

Sources

Continuum

- Deuterium lamp
- Argon lamp
- Xenon lamp

UV region

- Tungsten lamp

VIS region

Line

- Hollow Cathode Lamps (HCL)
- Electrodeless Discharge Lamps (EDL)
- Lasers

Continuum Sources

Deuterium lamp

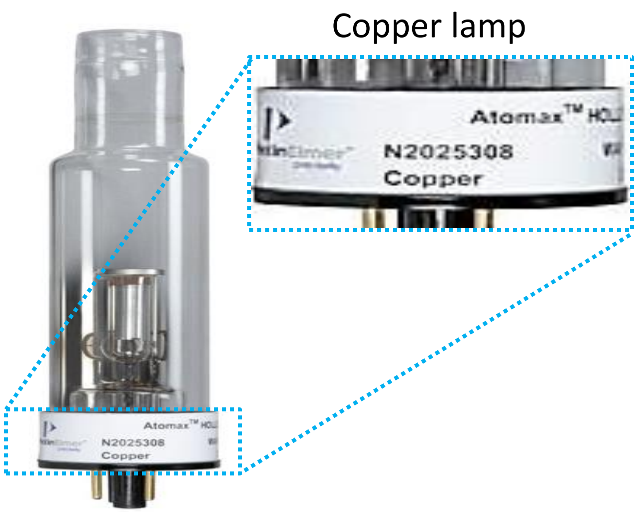
Argon lamp

Tungsten lamp

Xenon lamp

- Continuum sources emit **a wide range of wavelengths**,
- They find widespread use in **absorption** and **fluorescence** spectroscopy,
- For the **UV region**, the most common sources is the **deuterium lamp**.

Line Sources



Hollow Cathode Lamps (HCL)

Electrodeless Discharge Lamps (EDL)

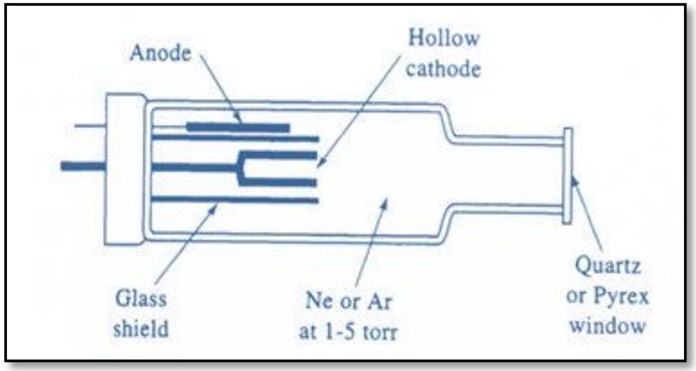
Lasers

- HCL, EDL and laser sources emit a **limited number of lines or narrow bands** of wavelengths,
- They are **specific to the element** to be determined.
- **LASER** stands for **L**ight **A**mplification by **S**imulated **E**mission of **R**adiation,
- They find widespread use in **Raman, molecular absorption and IR spectroscopy.**

HOLLOW CATHODE LAMPS (HCL)

- HCL is a type of lamp used in spectroscopy as a line source.

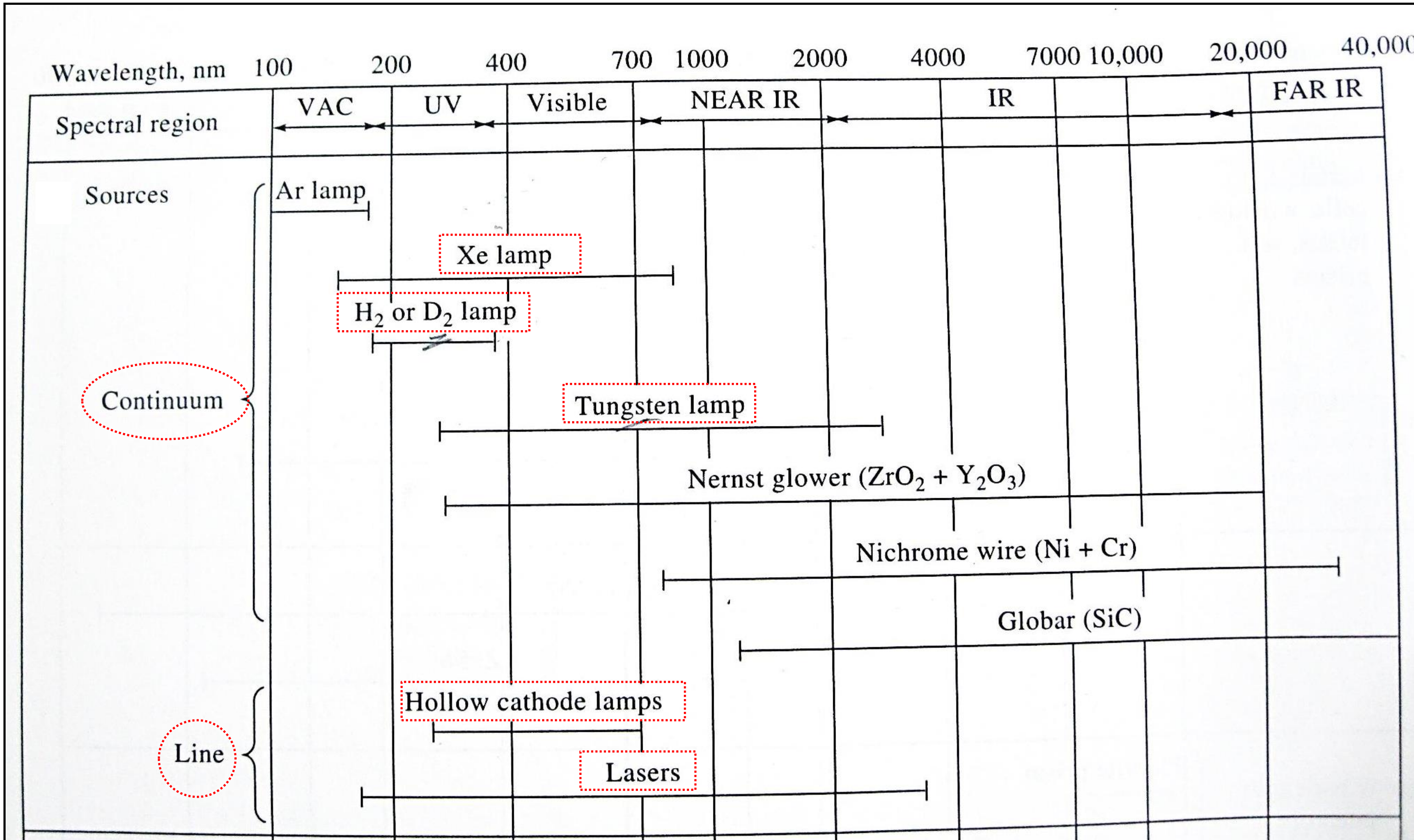
- An HCL usually consists of a glass tube containing a cathode, an anode, and a noble gas (e.g., Ar or Ne). The cathode material is constructed of the metal whose spectrum is desired. For example, if selenium is to be determined, the cathode would be made of selenium.



Schematic cross section of a hollow cathode lamp

- A large voltage causes the gas to ionize, creating a plasma. The gas ions will then be accelerated into the cathode, **sputtering** off atoms from the cathode. Both the gas and the sputtered cathode atoms will be excited by collisions with other atoms/particles in the plasma. As these excited atoms relax to lower states, they emit photons, which can then be absorbed by the analyte in the sample holder.

Sources for spectroscopic instruments



② Samples and sample holders

Agricultural samples
(e.g., pesticides)

Food samples
(e.g., drug residues)

Clinical samples
(e.g., blood, urine, human milk)

Forensic and crime samples
(e.g., DNA, hair, blood)

Drug samples
(e.g., impurity, humidity)

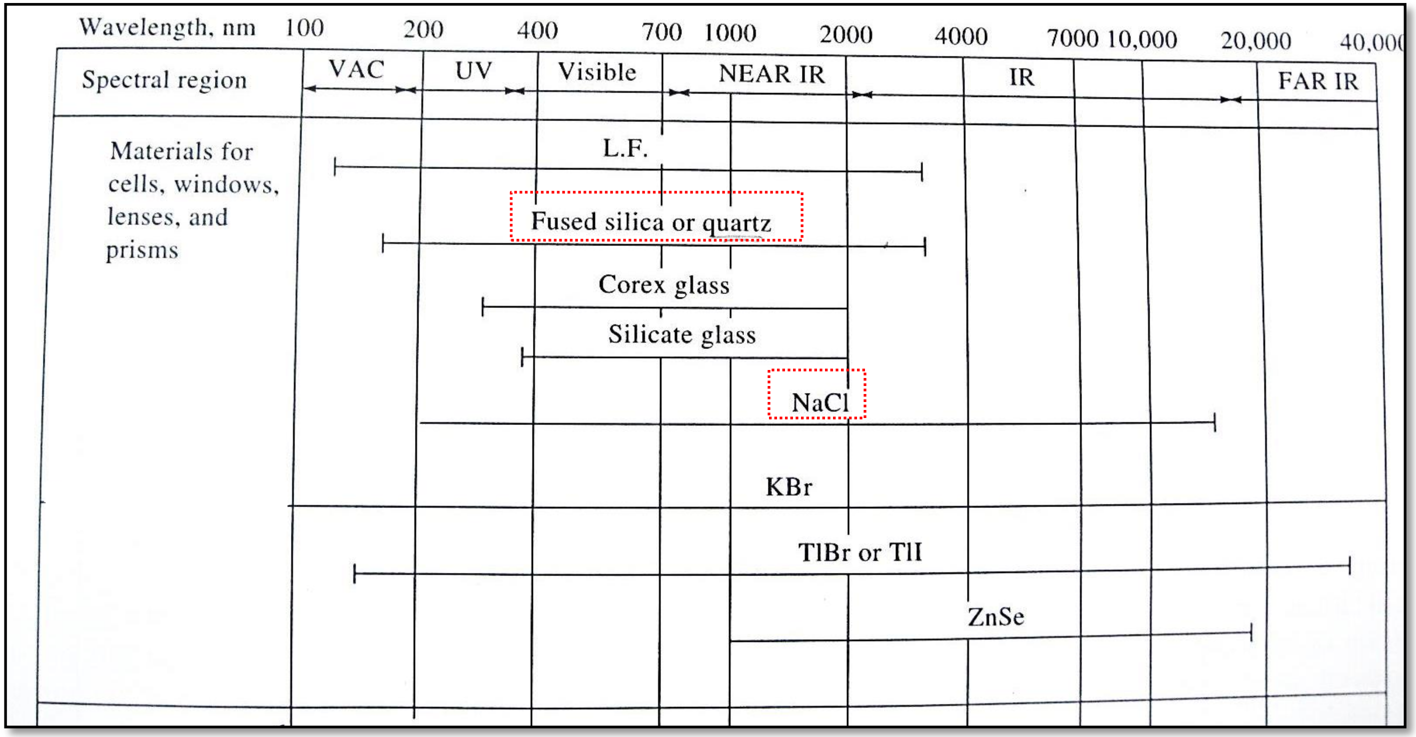
Environmental samples
(e.g., heavy metals)

Narcotic drugs
(e.g., heroin, morphine)

etc....

Sample holders

- Sample holders, also called "**cells**" or "**cuvettes**", are **required for all spectroscopic** methods **except emission spectroscopy**,
- Sample holders must be made of a material that is **transparent** to radiation in the spectral region of interest. For instance, if UV-VIS is to be used, the cuvette must not absorb in the UV-VIS region.



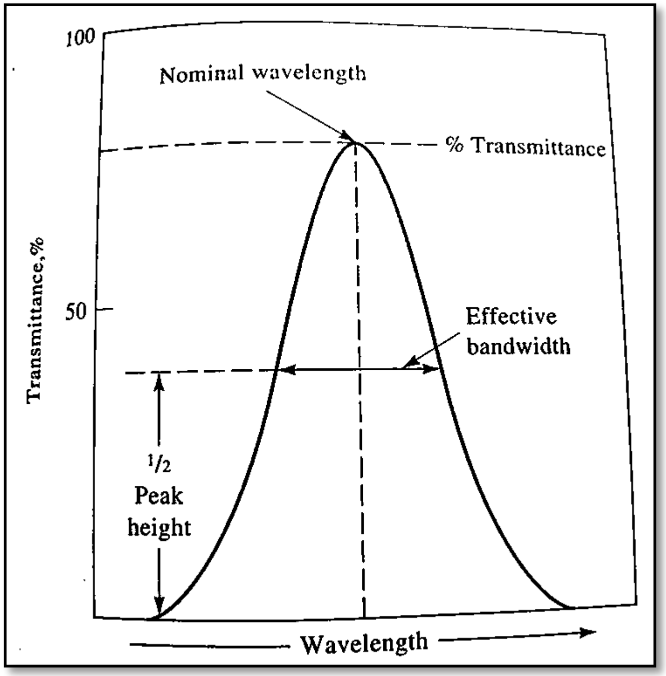
Materials for spectroscopic instruments

③ Wavelength selectors

- For most spectroscopic analysis, radiation that consists of a limited and narrow **band of wavelengths** is required.
- A narrow band enhances both the **sensitivity** and **selectivity** of the instrument
- Ideally, the output from a wavelength selector would be **a single wavelength (monochromatic)**.

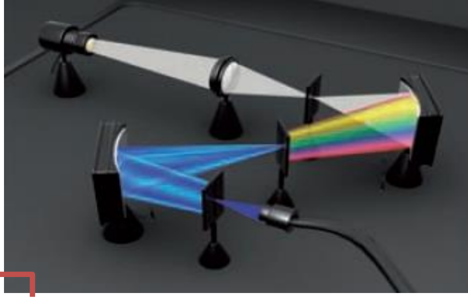
But, in real a band is obtained instead.

- The **effective bandwidth** is a measure of the quality of the wavelength selector.
- Effective bandwidth: the width of the peak at half maximum.
- The narrower the bandwidth, the better the wavelength selector.



Output of a typical wavelength selector

Wavelength Selectors



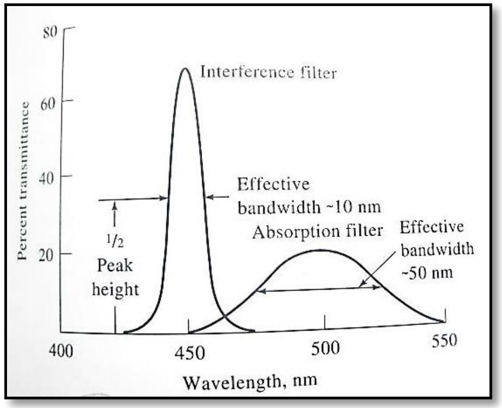
Filters

1. Absorption filters:

- Generally made of colored glass,
- Cheap,
- Have relatively wide effective bandwidth.

2. Interference filters:

- Made of semitransparent metal plates sandwiched between two glass or mirror plates.
- More expensive than absorption filters.
- Provide narrower bandwidth, representing better performance.

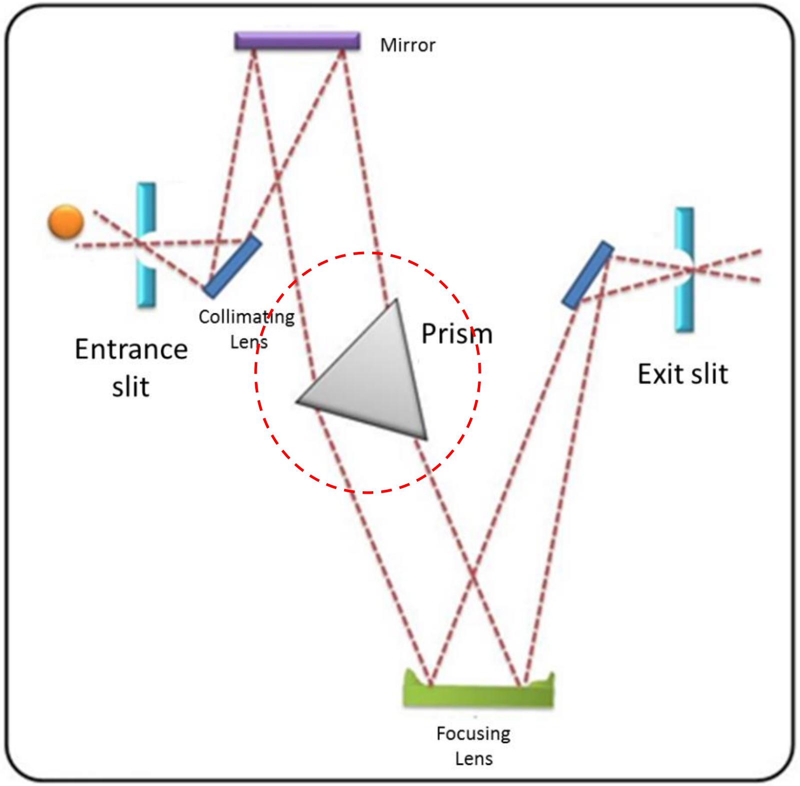


Effective bandwidth for both filters

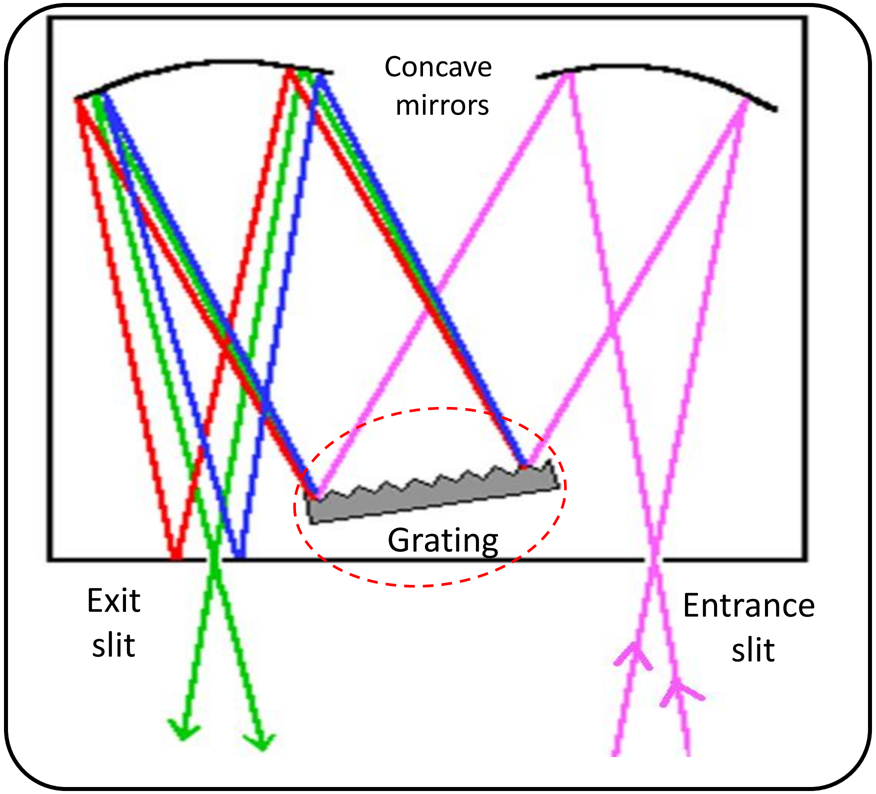
Monochromators

- For many spectroscopic methods, it is necessary to vary the wavelength continuously. This is called **scanning a spectrum**.
- Monochromators are designed for spectral scanning.
- Monochromators for UV, VIS, and IR are similar and employ **slits, lenses, mirrors, windows and gratings or prisms.**
- Two types of **dispersing elements** are found in monochromators: **gratings** and **prisms**.

Types of monochromators



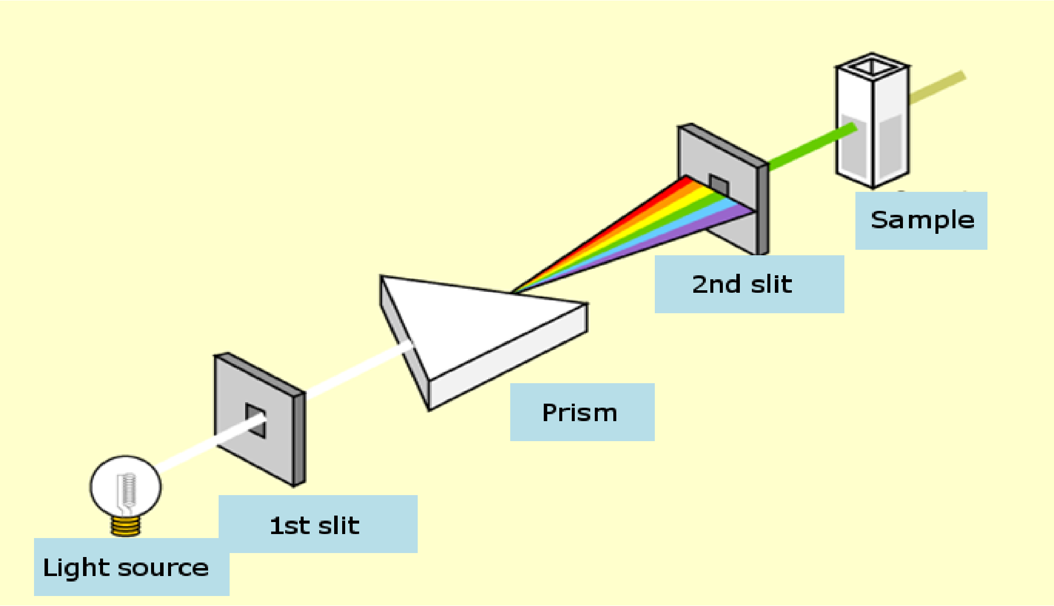
Prism monochromator



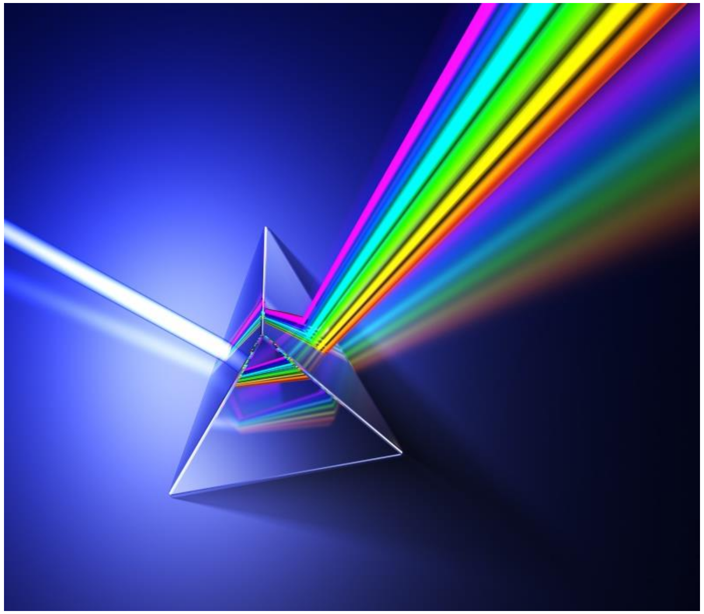
Grating monochromator

Prism Monochromators

- Prisms can be used to **disperse** UV, VIS or IR radiation. However, the material used in these instruments are different depending upon the wavelength region.
- A **polychromatic beam** is passed through the entrance (1^{st}) slit where it is dispersed into **monochromatic light** (or bands of narrower wavelengths). Then, the desired wavelength is directed toward the exit (2^{nd}) slit and allowed to interact with the analyte in the sample.



Prism monochromator

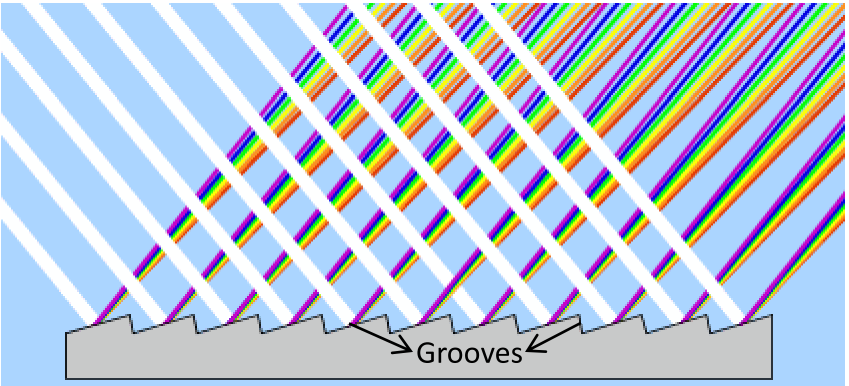


Dispersion by a prism

Grating Monochromators

- Dispersion of UV, VIS and IR radiation can also be brought about by directing a polychromatic beam onto the surface of a **grating**.

- A grating for the UV-VIS typically contains 300 to 2000 grooves/mm. For IR, gratings with 10 to 200 grooves are commonly used.
- Grating is expensive because the process of producing identical grooves is tedious.



Dispersion by a grating

- Performance characteristics of grating monochromators:
  1. Purity of its output,
  2. Ability to resolve adjacent wavelength (i.e., to produce narrow bandwidths),
  3. High light gathering power.

④ Detectors

- Early detectors were human eye or a photographic plate or film. The **human eye is a good detector** but only in the **VIS region**.
- Radiation detectors are found as two types: **photon** and **heat** detectors.

➢ **Properties of an ideal detector:**

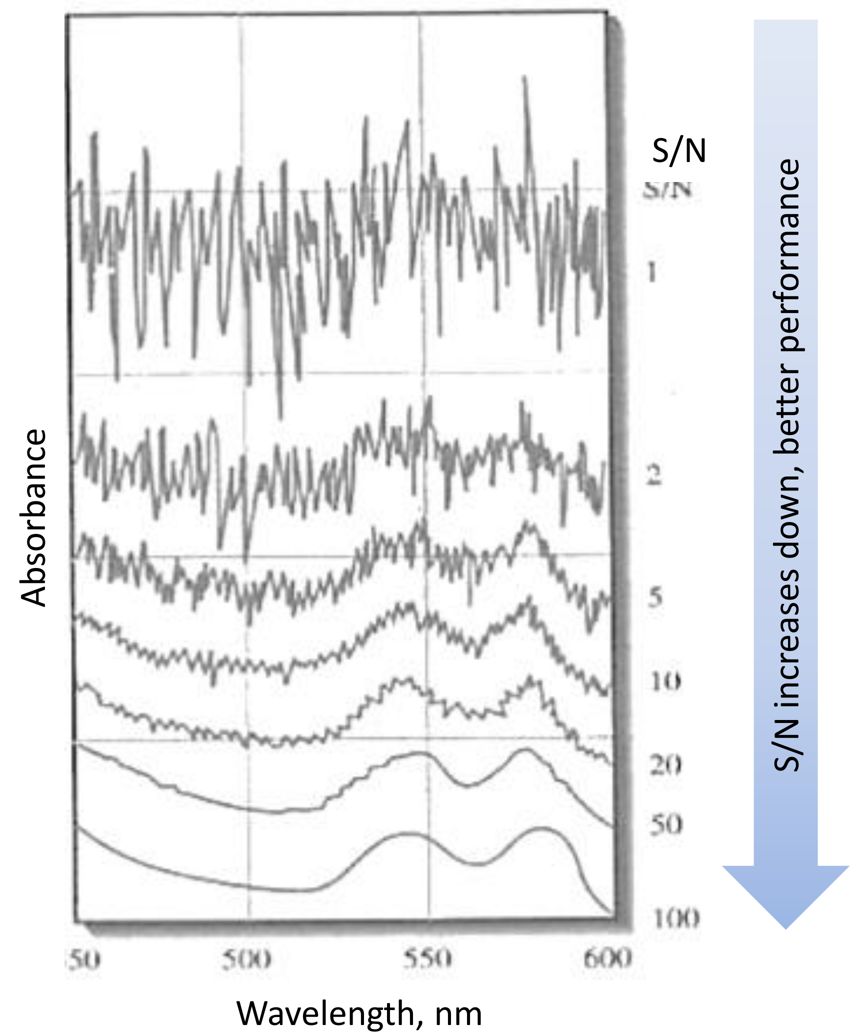
1. would have a **high sensitivity**,
2. would have a **high signal-to-noise (S/N) ratio**,
3. would show a **constant response** over a wide range of wavelengths and time,
4. would exhibit a **fast response**,
5. would have a **zero output** signal **in the absence of illumination** (i.e., light).

Signals and noise

The signal-to-noise ratio (S/N):

- In most measurements, the average strength of the noise (N) is constant and independent of the magnitude of the signal (S). Thus, the effect of noise becomes more important as the signal becomes smaller.

- S/N is a much more useful **figure of merit** than noise alone for describing the quality of an analytical method or the performance of an analytical instrument.



Effect of S/N ratio on the spectrum

Sources of noise

Chemical

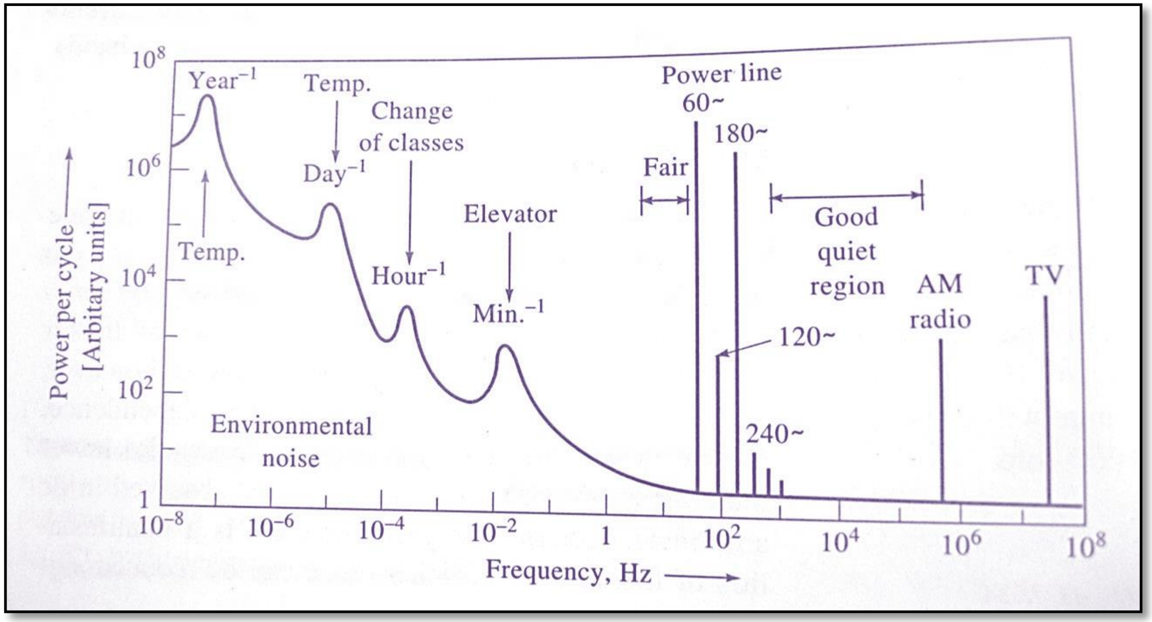
- Examples include: variations in temperature, pressure, humidity etc.
- Laboratory fumes that may interact with samples.

Instrumental

- May be caused by thermal agitation of electrons in resistors, capacitors, wires etc. in the instrument.

Environmental

- Changes that may occur per year, day, hour or minute.
- Climate change, elevators, radio, TV, computers or mobile phones.



Some sources of environmental noise in a university laboratory

Detectors

Photon

- Used mainly in **UV, VIS and near-IR** optical instruments.

1. **Photovoltaic cells:**
   - Radiant energy produces current in a semiconductor.

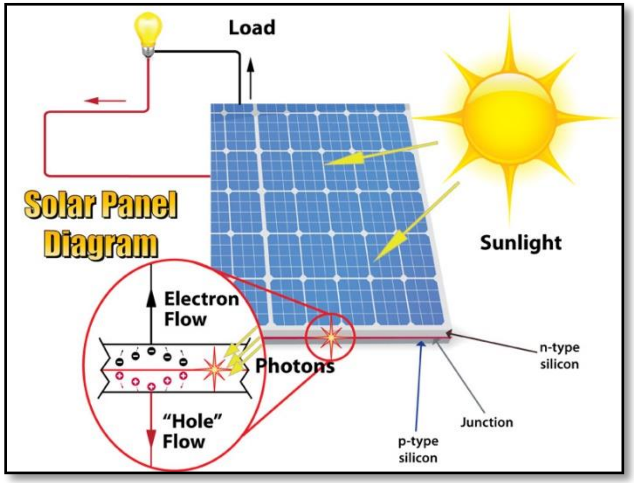
2. Phototubes:
- Radiation causes emission of electrons by the "photoelectric effect".

3. Photomultiplier tubes (PMT):
- Contains many photo-sensitive surfaces to multiply the electrons produced by the "photoelectric effect".

Thermal

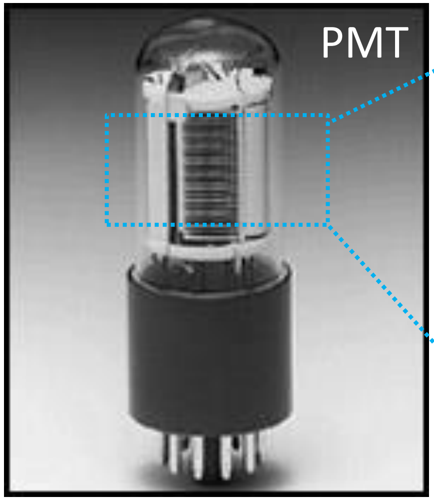
- Used mainly in **IR** optical instruments.

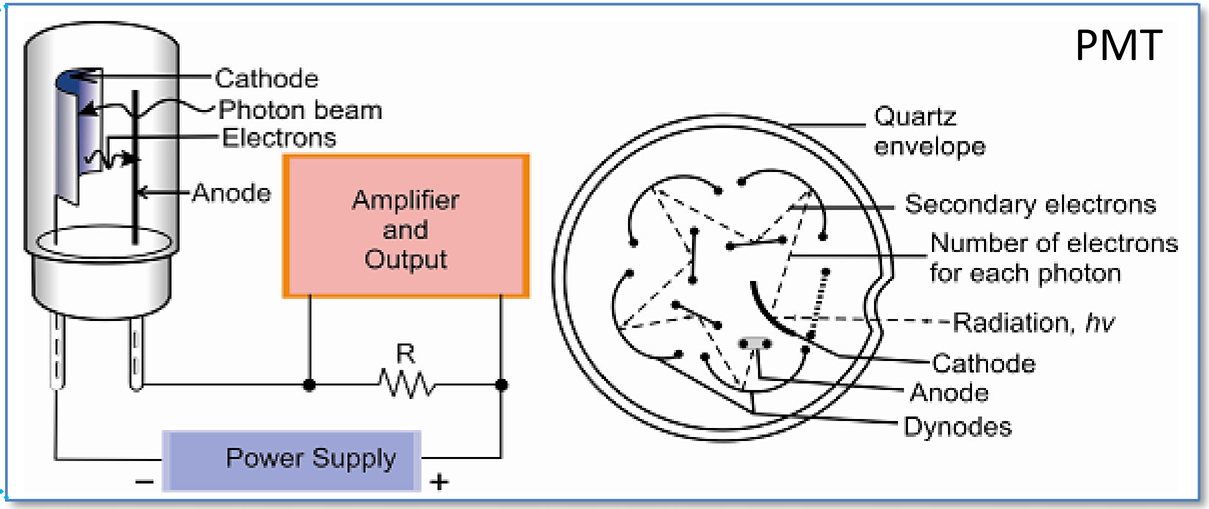
1. **Thermocouples.**
2. **Pyroelectric detectors.**



A photoelectric cell transforms radiant sun energy into electricity.

Photomultiplier tubes (PMT)





- PMTs are extremely sensitive detectors of light in the UV, VIS and near-IR ranges of the electromagnetic spectrum. These detectors multiply the current produced by incident light by as much as **100 million times** enabling even individual photons to be detected when the incident light is very low.
- The combination of **high gain**, **low noise**, **ultra-fast response**, and **large area of collection** has maintained PMTs an essential place in optical instruments.

⑤ Signal processors

- The signal processor is ordinarily an electronic device that **amplifies the electrical signal** from the detector.
- It may change the signal from direct **(DC) to** alternating current **(AC)** (or the reverse).
- It may change the shape of the signal and filter it to **remove** any unwanted components (e.g., **noise**).
- It may be used to perform such mathematical operations on the signal as **differentiation, integration or conversion to a logarithm**.
- The most commonly used signal processors are:

  1) Photon counters,

  2) Fiber optics.