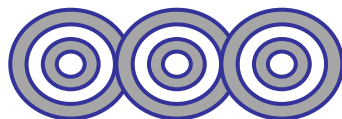




Instrumental Methods of Analysis



Basic Components of Spectroscopic Instrumentation

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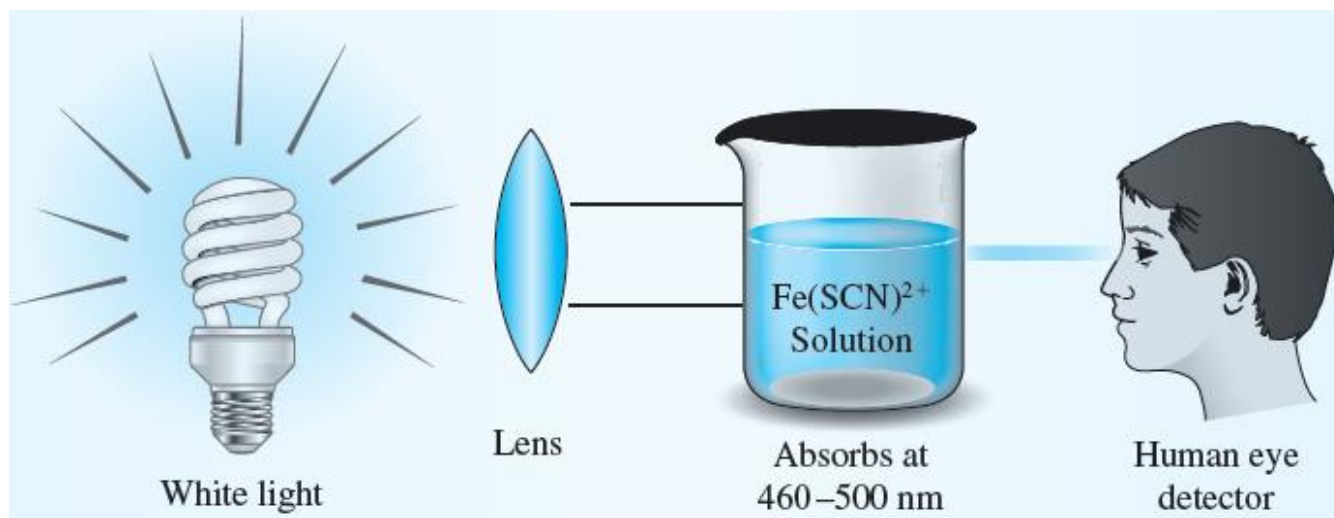
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Basic components of spectroscopic instruments



- A source of energy that can be input to the sample.
- A means for isolating a narrow range of wavelengths.
- Sample container.
- A detector for measuring the signal.
- A signal processor to display the signal in a form convenient for the analyst.

Sources of Energy

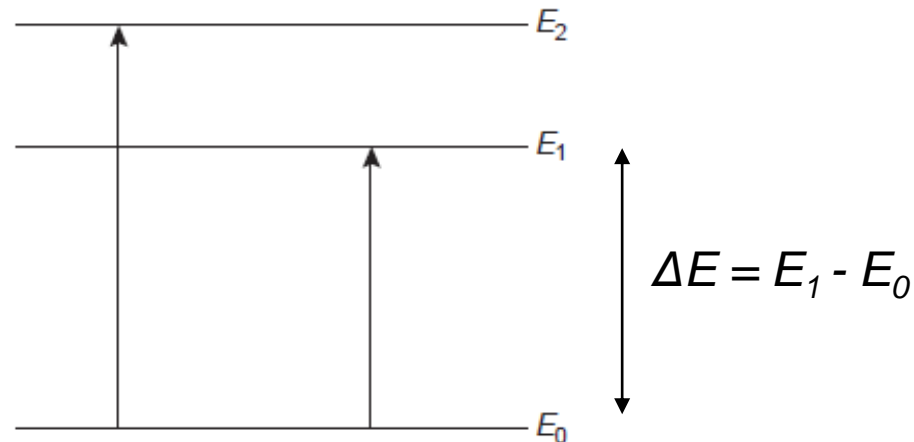
The sources of energy could be in different forms:

(1) Sources of electromagnetic radiation (photons)

A source of electromagnetic radiation must provide an output that is both **intense** and **stable** in the **desired region** of the electromagnetic spectrum.

The energy levels have well-defined values (i.e., they are quantized). Absorption only occurs when the photon's energy matches the difference in energy, ΔE , between two energy levels.

Simplified energy level diagram showing absorption of a photon



Sources of electromagnetic radiation are classified as:

- **Continuum source:** a source that emits radiation over a wide range of wavelengths.
- **Line source:** a source that emits radiation at only select wavelengths (narrow wavelength ranges).

A list of the most common sources of electromagnetic radiation.

Source	Wavelength region	Useful for
H ₂ and D ₂ lamp	continuum source from 160–380 nm	UV molecular absorption
Tungsten (W) lamp	continuum source from 320–2400 nm	Vis molecular absorption
Xe arc lamp	continuum source from 200–1000 nm	molecular fluorescence
Nernst glower	continuum source from 0.4–20 μ m	IR molecular absorption
Globar	continuum source from 1–40 μ m	IR molecular absorption
Nichrome wire	continuum source from 0.75–20 μ m	IR molecular absorption
Hollow cathode lamp	line source in UV/Vis	atomic absorption
Hg vapor lamp	line source in UV/Vis	molecular fluorescence
Laser	line source in UV/Vis	atomic and molecular absorption, fluorescence and scattering

(2) Sources of thermal energy

The most common sources of thermal energy are **flames** and **plasmas**.

-Flame sources use the combustion of a fuel (such as natural gases, hydrogen and acetylene) and an oxidant (such as air, oxygen and nitrous oxide) to achieve temperatures of 1700–3400 °C.

-Plasmas, which are hot, ionized gases, provide temperatures of 6000–10000 °C.

(3) Chemical sources of energy

Exothermic reactions also may serve as a source of energy.

In **chemiluminescence**, the analyte is raised to a higher-energy state by means of a chemical reaction, emitting characteristic radiation when it returns to a lower-energy state. When the chemical reaction results from a biological or enzymatic reaction, the emission of radiation is called **bioluminescence**.

Commercially available “light sticks, glow” and the flash of light from a firefly are examples of chemiluminescence and bioluminescence, respectively.

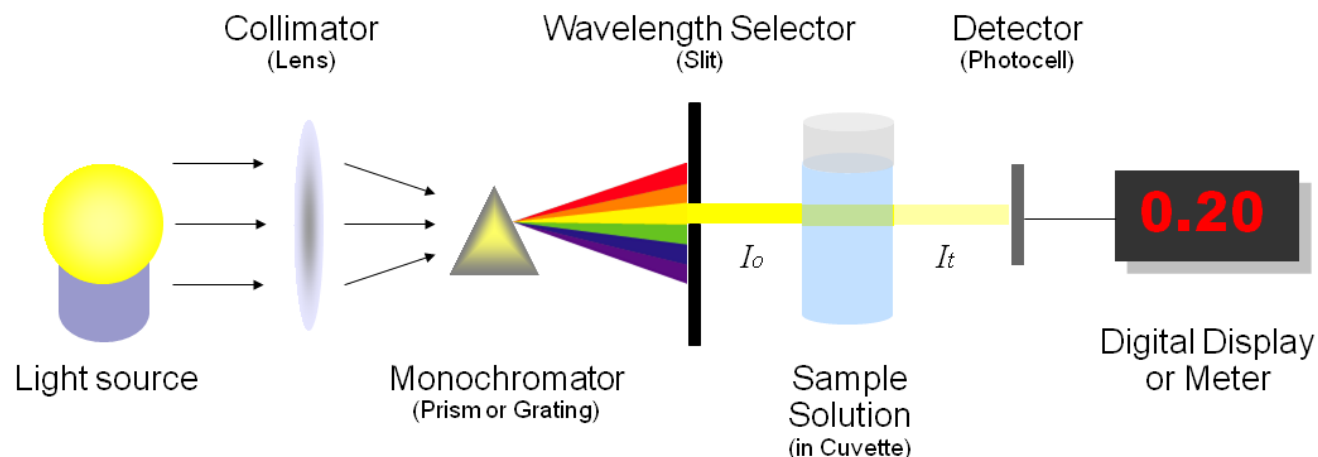


Wavelength Selection

Wavelength selector is a component used to **select** and **isolate** the required wavelengths or range of wavelengths where the analyte is the only absorbing species (to obtain a certain wavelength or a narrow band of wavelengths).

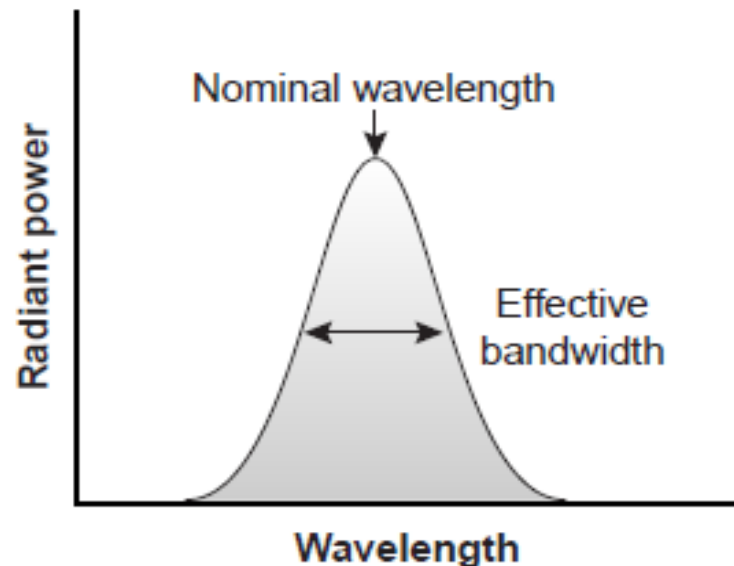
The ideal wavelength selector has;

a **high throughput of radiation** and a **narrow effective bandwidth**.



A high throughput is desirable because more photons pass through the wavelength selector, giving a stronger signal with less background noise. A narrow effective bandwidth provides a higher resolution, with spectral features separated by more than twice the effective bandwidth being resolved.

Unfortunately, we cannot isolate a single wavelength of radiation from a continuum source. Instead, a wavelength selector passes a narrow band of radiation characterized by a **nominal wavelength**, an **effective bandwidth**, and a **maximum throughput of radiation**.



Nominal wavelength: the wavelength which a wavelength selector is set to pass.

Effective bandwidth: the width of the band of radiation passing through a wavelength selector measured at half the band's (maximum) height throughput.

Generally these two features of a wavelength selector are in opposition. Conditions favoring a higher throughput of radiation usually provide less resolution. Decreasing the effective bandwidth improves resolution, but at the cost of a noisier signal. For a qualitative analysis, resolution is generally more important. In a quantitative analysis a higher throughput of radiation is usually desirable.

There are two types of wavelength selector:

1. **Filters**
2. **Monochromators**

Filters

Filters are the simplest devices, consisting of only a material that selectively transmits the desired wavelengths and absorbs all other wavelengths. Filters use either an absorption or interference of radiation.

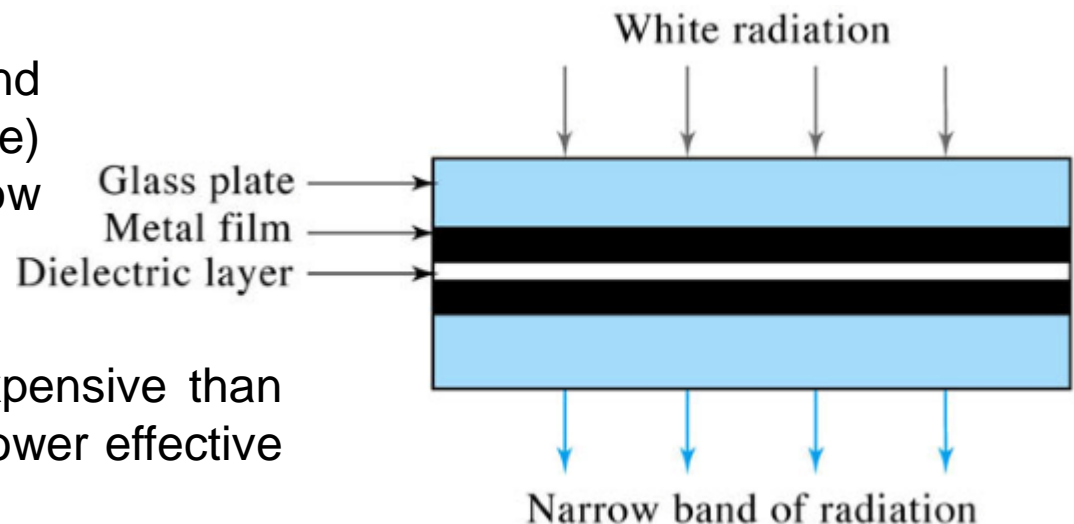
- Absorption filters

work by selectively absorbing radiation from a narrow region of the electromagnetic spectrum. A simple example of an absorption filter is a piece of colored glass.

- Interference filters

use constructive (in phase) and destructive (out of phase) interference to isolate a narrow range of wavelengths.

Interference filters are more expensive than absorption filters, but have narrower effective bandwidths



Monochromators

If measurements need to be made at two different wavelengths, then the filter must be changed in between measurements. Absorption or interference filter do not allow for a continuous selection of wavelength.

Monochromators can give a much narrower range of wavelengths and are easily adjustable over a wide spectral range (scan spectrum, vary λ continuously).

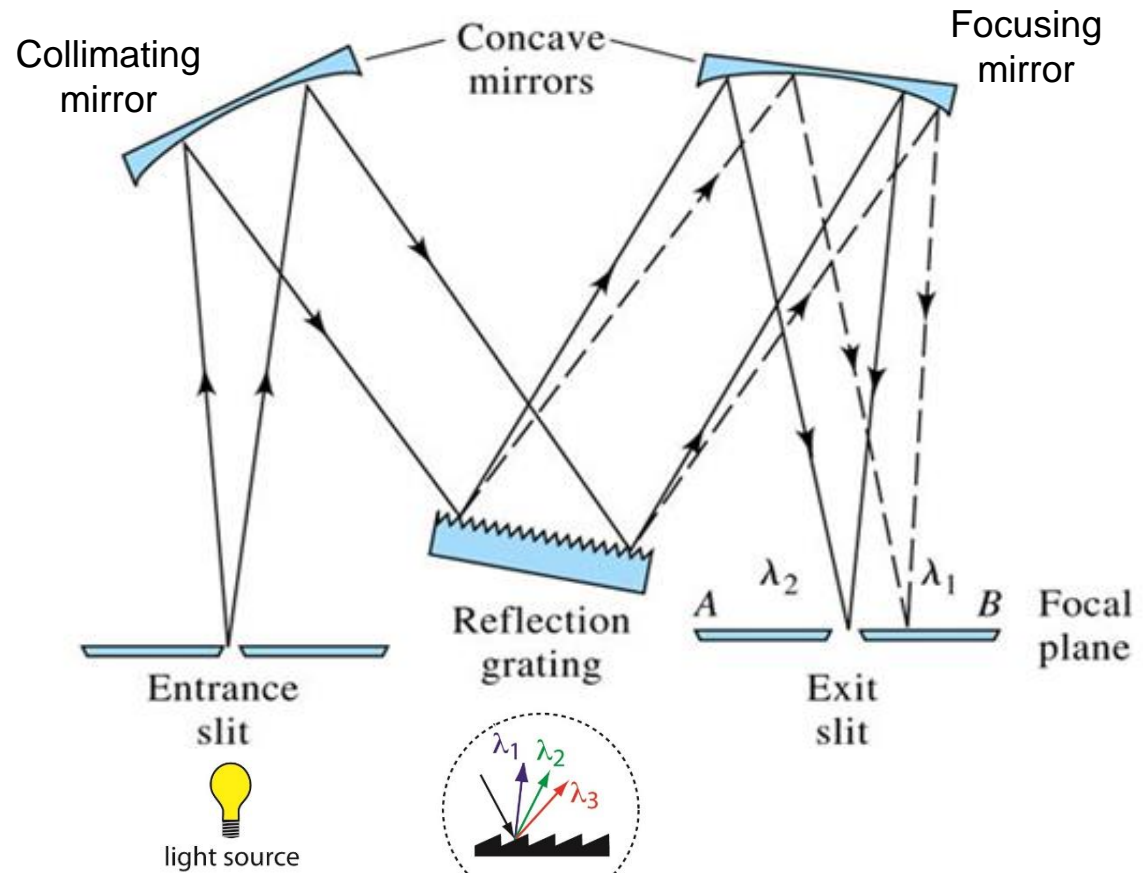
The dispersing element may be a **prism** or a **grating**.

As a result, a **polychromatic** source of radiation at the entrance slit is converted at the exit slit to a **monochromatic** source of finite effective bandwidth.

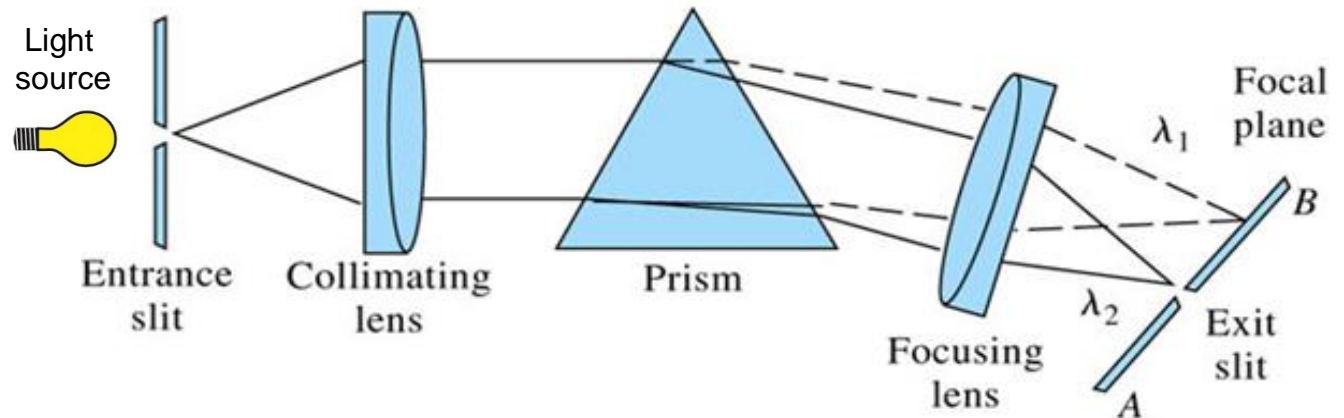
The choice of which wavelength exits the monochromator is determined by rotating the diffraction grating. A narrower exit slit provides a smaller effective bandwidth and better resolution, but allows a smaller throughput of radiation.

Types of
monochromators:

Grating
monochromator



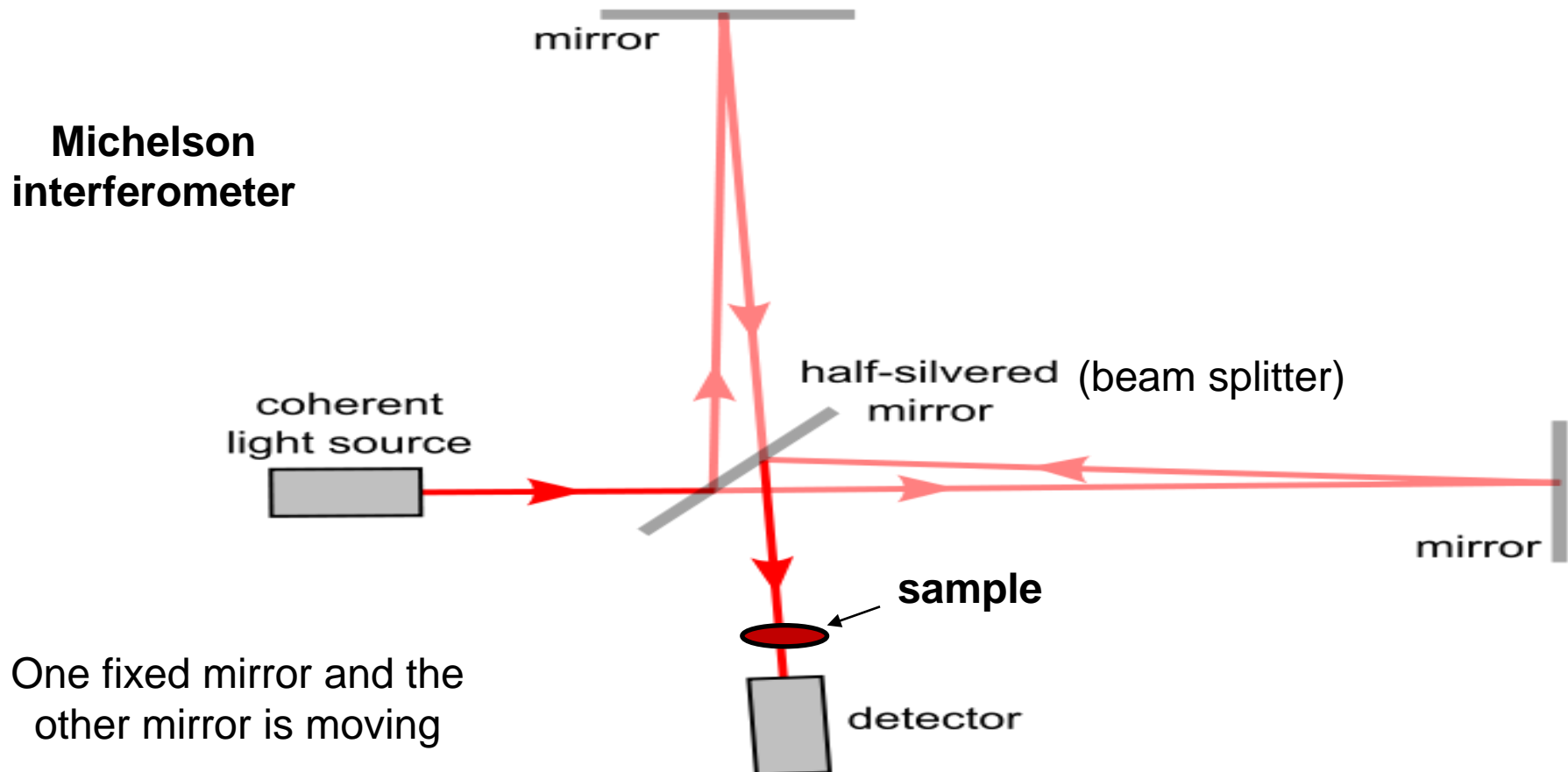
Prism
monochromator



Interferometers

An **interferometer** provides an alternative approach for wavelength selection. Instead of filtering or dispersing the electromagnetic radiation, an interferometer simultaneously allows source radiation of all wavelengths to reach the detector.

Michelson interferometer



Sample Containers (Holders)

The cells or cuvettes that hold the samples must be made of material that is transparent to radiation in the spectral region of interest. Sample containers should also be compatible with the sample type, size and state (solid, solution and gas).

Quartz or fused silica is required for work in the ultraviolet region (below 350 nm), both of these substances are transparent in the visible region.

Silicate glasses can be employed in the region between 350 and 2000 nm.

Plastic containers can be used in the visible region.

Crystalline NaCl is the most common cell windows in the IR region.



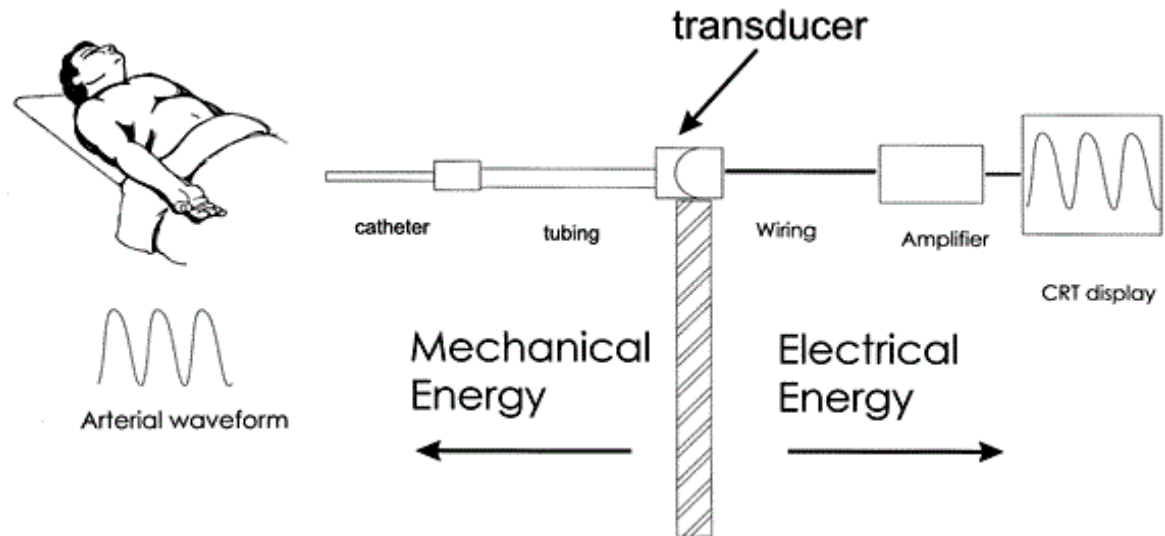
Detectors

The first detector for optical spectroscopy was the human eye (limited to Visible region, limited accuracy and sensitivity to electromagnetic radiation).



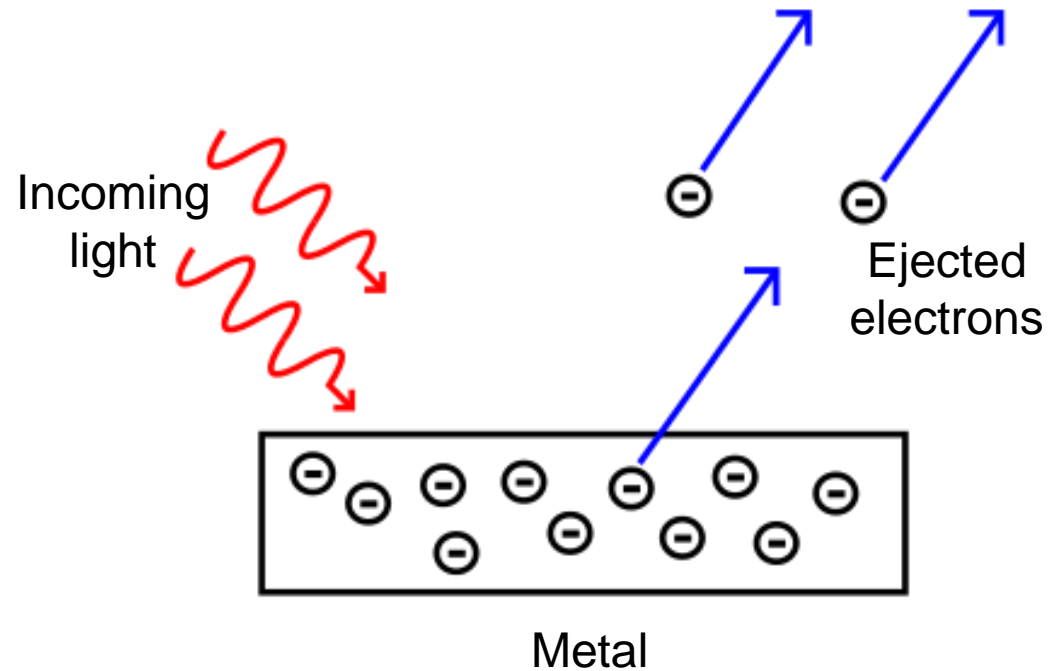
Modern detectors use a sensitive **transducer** to convert a signal consisting of photons into an easily measured electrical signal.

Device converts a signal in one form of energy to another form of energy.



Transducer: a device that converts a chemical or physical property, such as pH or photon intensity, to an easily measured electrical signal, such as a voltage or current.

The **photoelectric effect** is the observation that many metals (such as alkali metals or semiconductor material such as gallium arsenide) emit electrons when light shines upon them. Electrons emitted in this manner can be called **photoelectrons**.



Photon transducer

Phototubes and photomultipliers contain a photosensitive surface that absorbs radiation in the ultraviolet, visible, and near infrared (IR), producing an electric current proportional to the number of photons reaching the transducer.

Other photon detectors use a semiconductor as the photosensitive surface. When the semiconductor absorbs photons, valence electrons move to the semiconductor's conduction band, producing a measurable current.

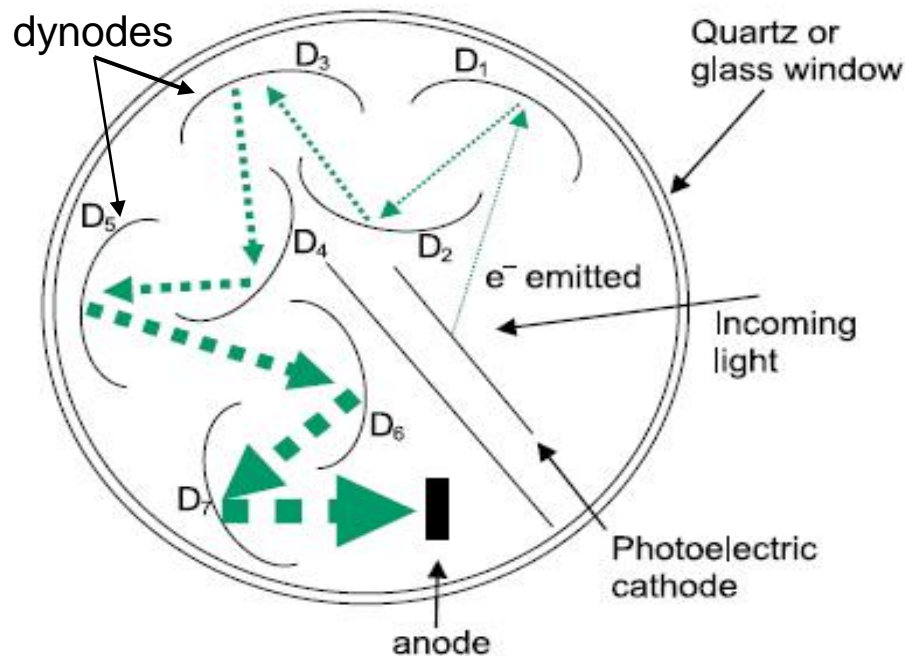
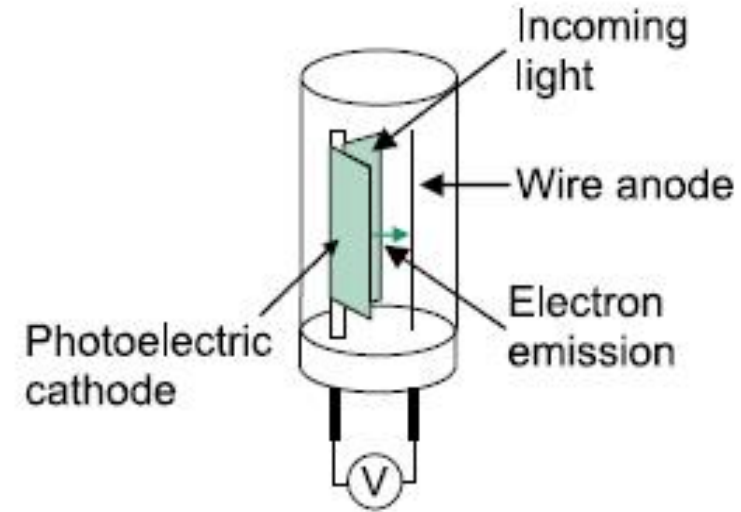
Thermal transducer

Infrared radiation generally does not have sufficient energy to produce a measurable current when using a photon transducer. A thermal transducer, therefore, is used for infrared spectroscopy.

A thermal detector consists of a tiny blackened surface that absorbs infrared radiation and increases in temperature as a result. The temperature rise is converted to an electrical signal that is amplified and measured.

Phototube

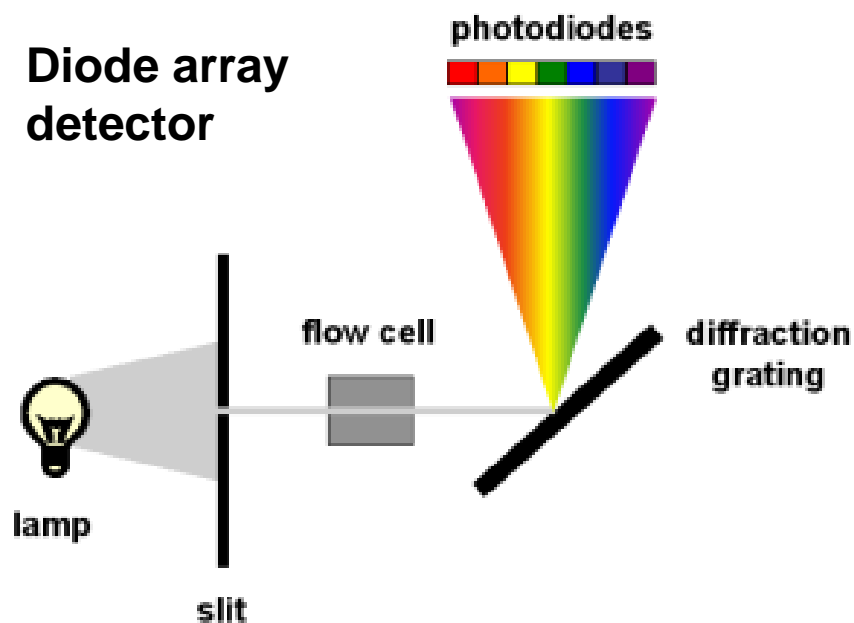
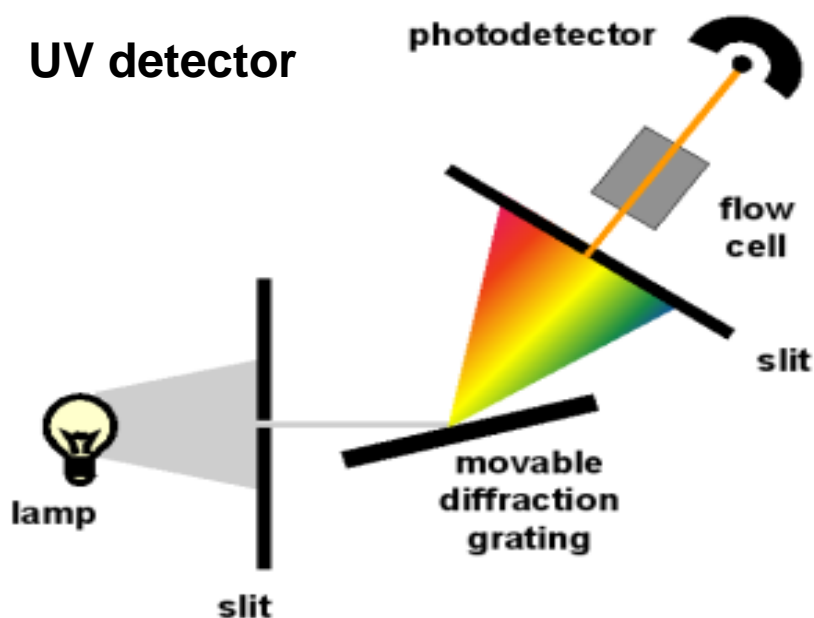
Vacuum phototube, which consists of a semicylindrical cathode and a wire anode sealed inside an evacuated transparent envelope. The concave surface of the electrode supports a layer of photoemissive material that tends to emit electrons when it is irradiated. When a voltage is applied across the electrodes, the emitted electrons flow to the wire anode generating a photocurrent that is generally about one tenth as great as that associated with a photovoltaic cell for a given radiant intensity.



Photomultiplier tubes

A photon of radiation entering the tube strikes the cathode, causing the emission of several electrons. These electrons are accelerated towards the first dynode (which is 90V more positive than the cathode). The electrons strike the first dynode, causing the emission of several electrons for each incident electron. These electrons are then accelerated towards the second dynode, to produce more electrons which are accelerated towards dynode three and so on. Eventually, the electrons are collected at the anode. Each original photon produces about 10^6 - 10^7 electrons.

Photodiode array: a linear array of photodiodes providing the ability to detect simultaneously radiation at several wavelengths. A special feature of diode array detectors is the ability to perform spectroscopic scanning and precise absorbance readings at a variety of wavelengths while the peak is passing through the flow cell.



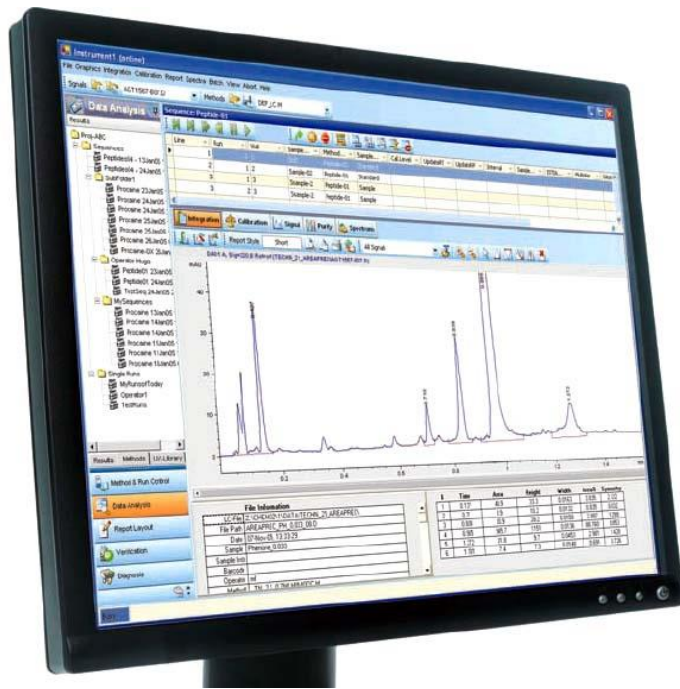
Photodiode array allows for the best wavelength(s) to be selected for actual analysis. This is particularly important when no information is available on molar absorptivities at different wavelengths. The second major advantage is related to the problem of peak purity, absorbance rationing at several wavelengths is particularly helpful in deciding whether the peak represents a single compound or, is in fact, a composite peak.

Detector	Wavelength range	Output signal
Photon detectors		
Phototube	200–1000 nm	current
Photomultiplier	110–1000 nm	current
Si photodiode	250–1100 nm	current
Photoconductor	750–6000 nm	change in resistance
Photovoltaic cell	400–5000 nm	current or voltage
Thermal detectors		
Thermocouple	0.8–40 μm	voltage
Thermistor	0.8–40 μm	change in resistance
Pneumatic	0.8–1000 μm	membrane displacement
Pyroelectric	0.3–1000 μm	current

Signal Processors and Readout

A device that displays the signal from the transducer in a form that is easily interpreted by the analyst.

The signal processor also may be used to control various instrumental parameters, to calibrate the detector's response, to amplify the signal from the detector, to remove noise by filtering, or to mathematically transform the signal.



Examples of signal processors include analog or digital meters, recorders and computers equipped with digital acquisition boards.

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