Chemistry 4631

Instrumental Analysis

Lecture 14

UV-Vis Instruments

Types of Instrumentation Design

- Single beam
- Double beam in space
- Double beam in time
- Multichannel
- Speciality

UV-Vis Instruments

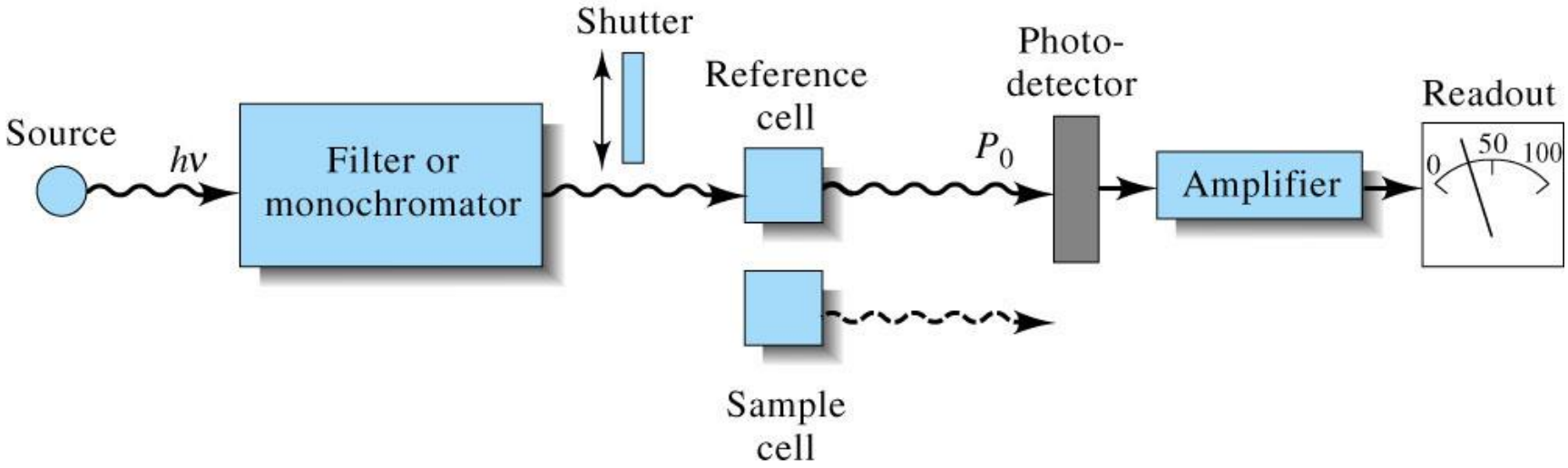
Types of Instrumentation

- **Single beam**
  - **Requires stable voltage supply to keep stable beam intensity.**
  - **Accuracy generally 1-2%**

  Example: Spectronic 20.

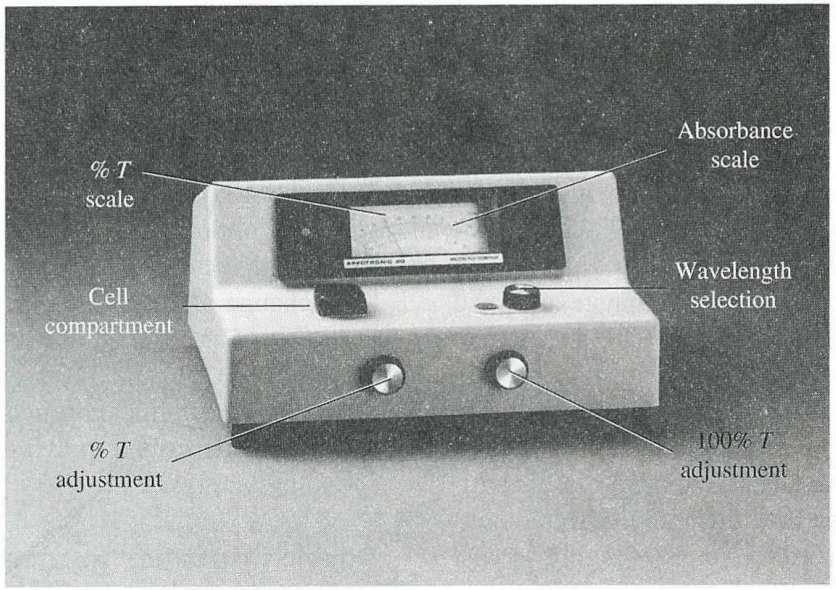
UV-Vis Instruments

Single beam

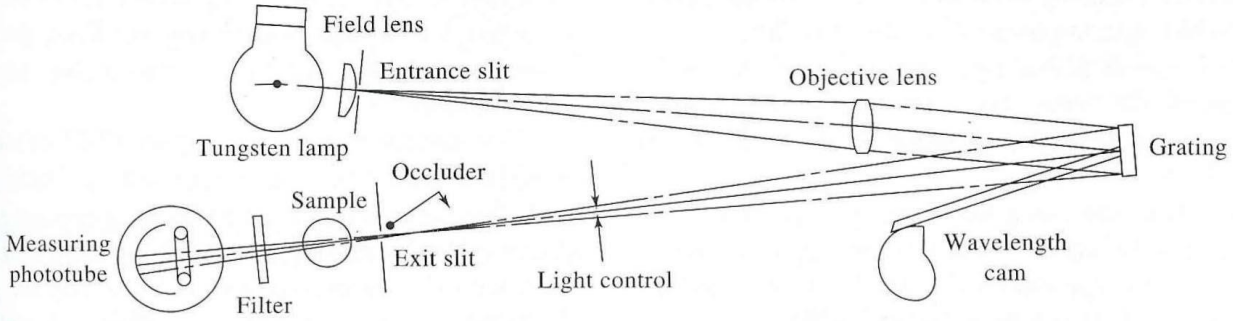


(a)

Spectrophotometers
Single- Beam
for UV/vis



(a)



(b)

Figure 13-17 (a) The Spectronic 20 spectrophotometer and (b) its optical diagram. *(Courtesy of Spectronic Instruments, Inc., Rochester, NY.)*

UV-Vis Instruments

Typical Instruments

Photometers

A Filter Photometer is the least expensive instrument, has lots of light power, only a single wavelength, uses filters, and has good sensitivity.

However cannot take a spectrum with this type of instrument.

UV-Vis Instruments

Visible Photometers

Single or Double Beam

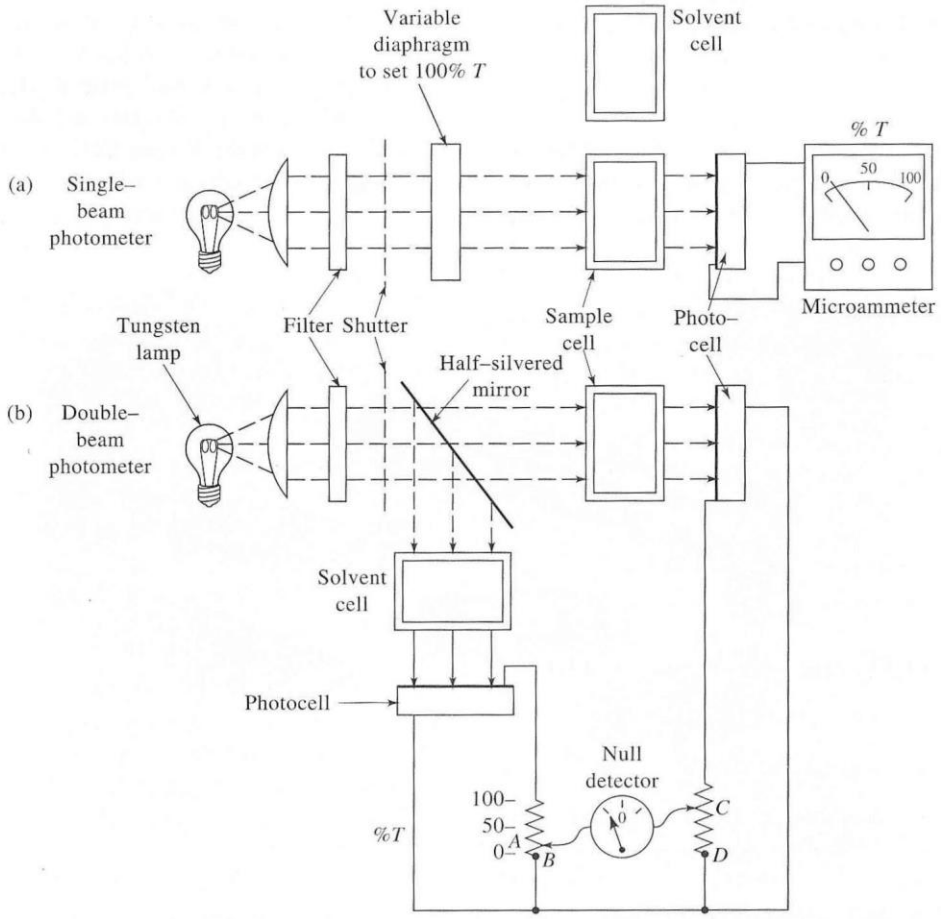


Figure 13-15 A single- and double-beam photometer.

UV-Vis Instruments

Types of Instrumentation

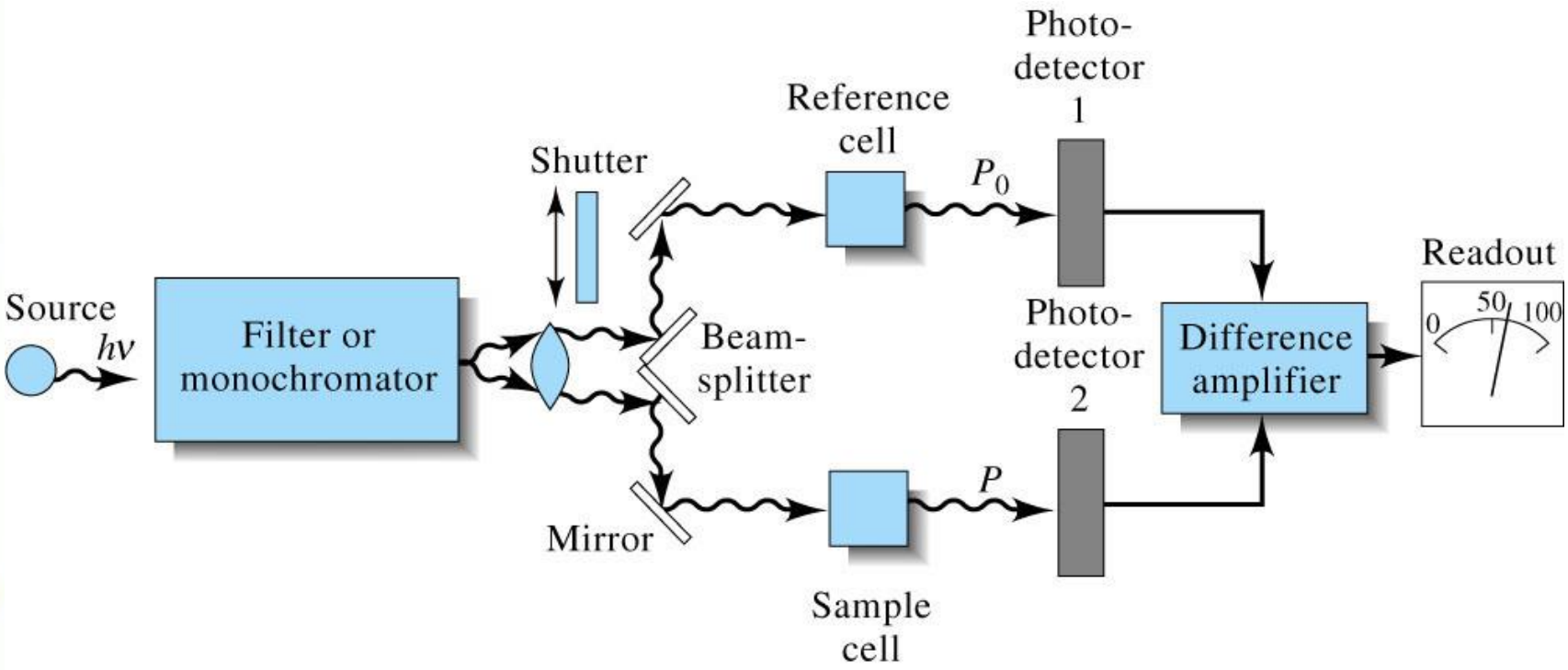
Double Beam

Two beams are formed by V-shaped mirror called a beam splitter.

One beam passes through the reference cell and other through the sample.

UV-Vis Instruments

Double Beam (space)



(b)

UV-Vis Instruments

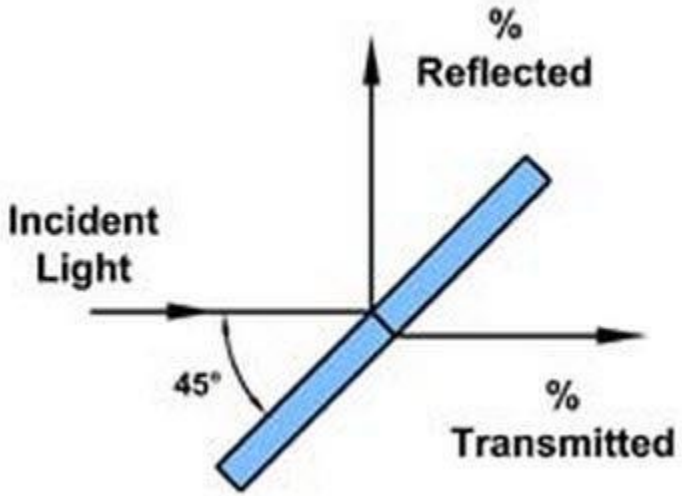
Beam Splitter

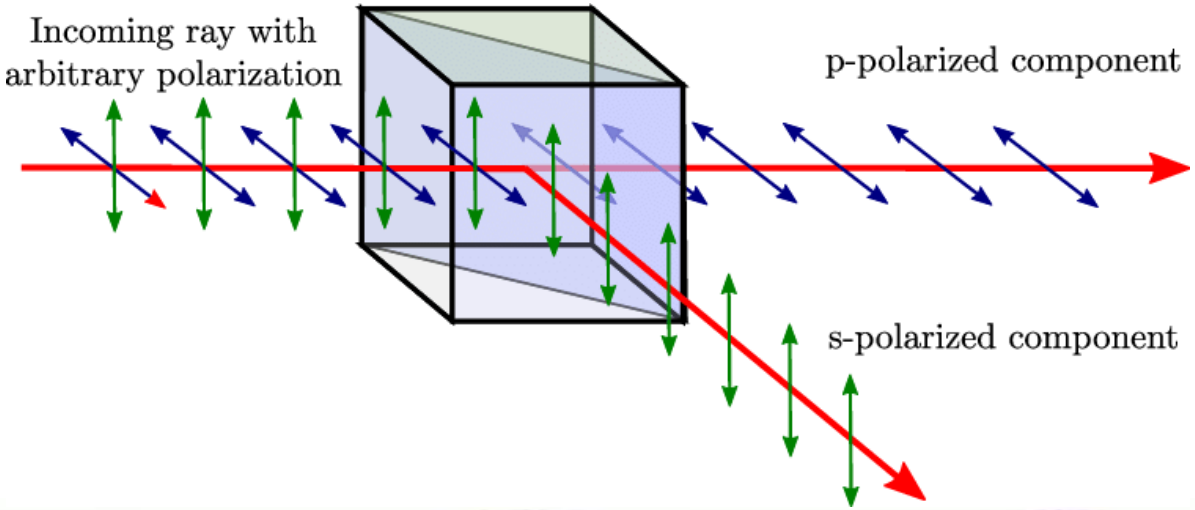
We saw in making holographic gratings and something similar in design of interference filters.

- 2 triangular prisms

- half-silvered mirror (actually Al)

- dielectric coating





UV-Vis Instruments

Double Beam

- **Uses an optical null procedure**
- **An optical wedge is added into the reference beam to make the intensity of the reference beam equal to the intensity of the sample beam.**

UV-Vis Instruments

Double Beam

Or beam can be separated in time by a rotation sector mirror (chopper) that directs beam either through the reference or sample cell.

The beam is recombined on the other side of the cell and sent to detector.

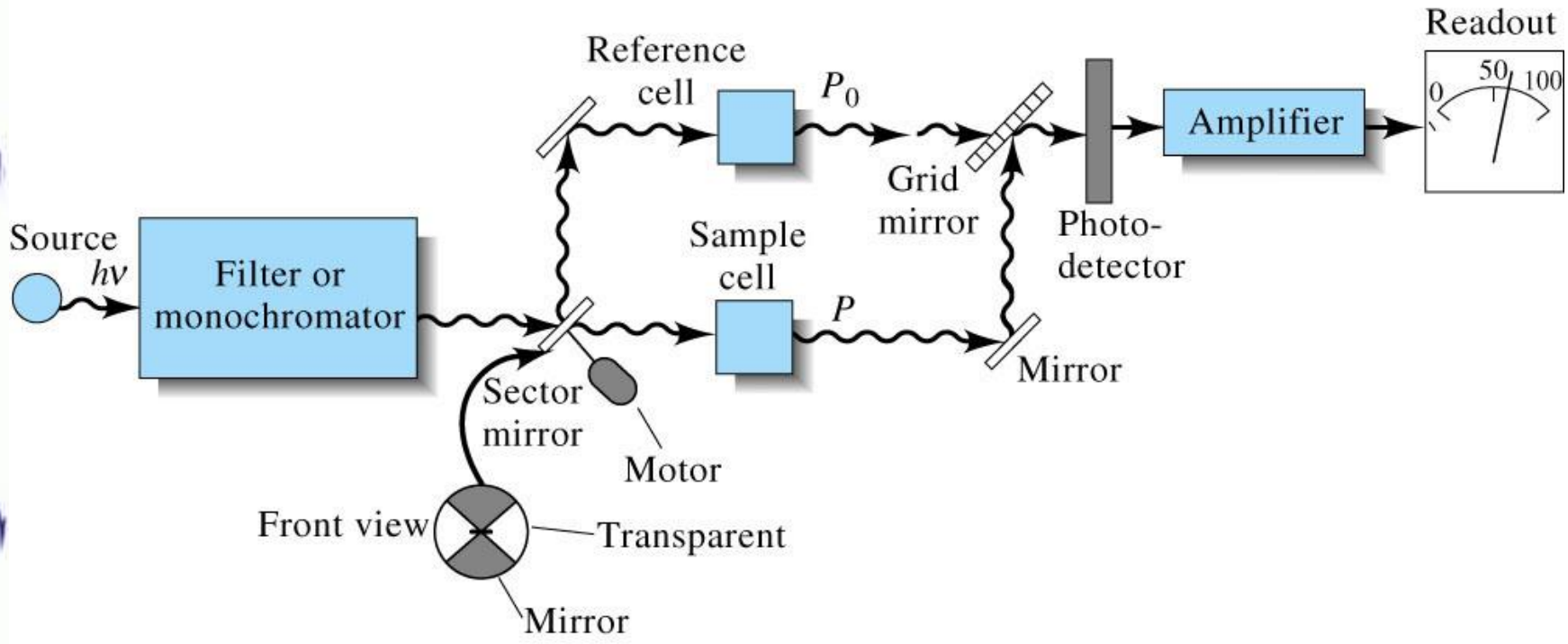
UV-Vis Instruments

Double Beam

- **Rotating mirror face is sectioned with half of segments mirrored and half transparent.**
- **The beam through the reference cell is nulled until intensity matches that of the beam coming from the sample cell.**

UV-Vis Instruments

Double Beam (time)



(c)

Spectrophotometers
Double Beam
for UV/vis

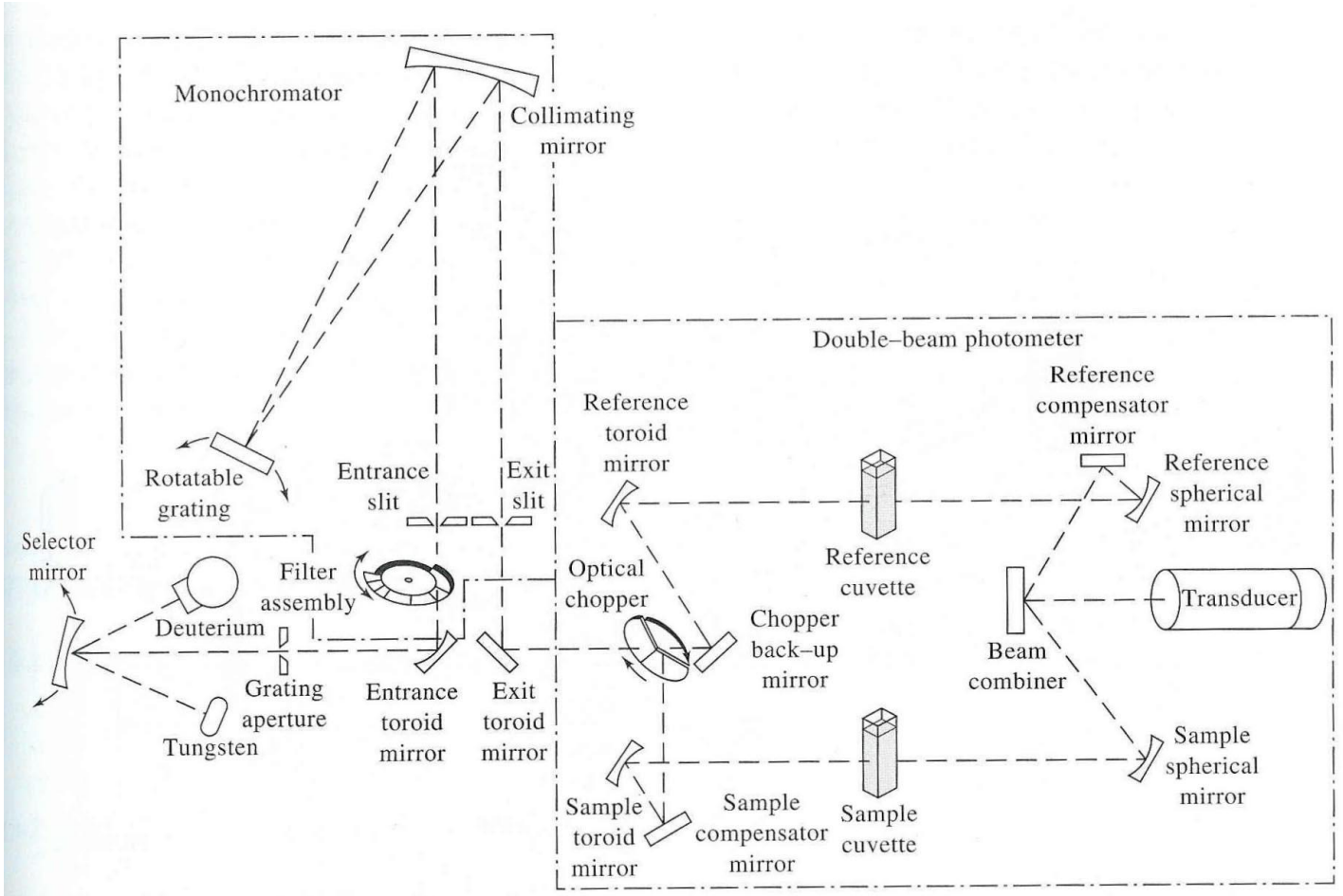
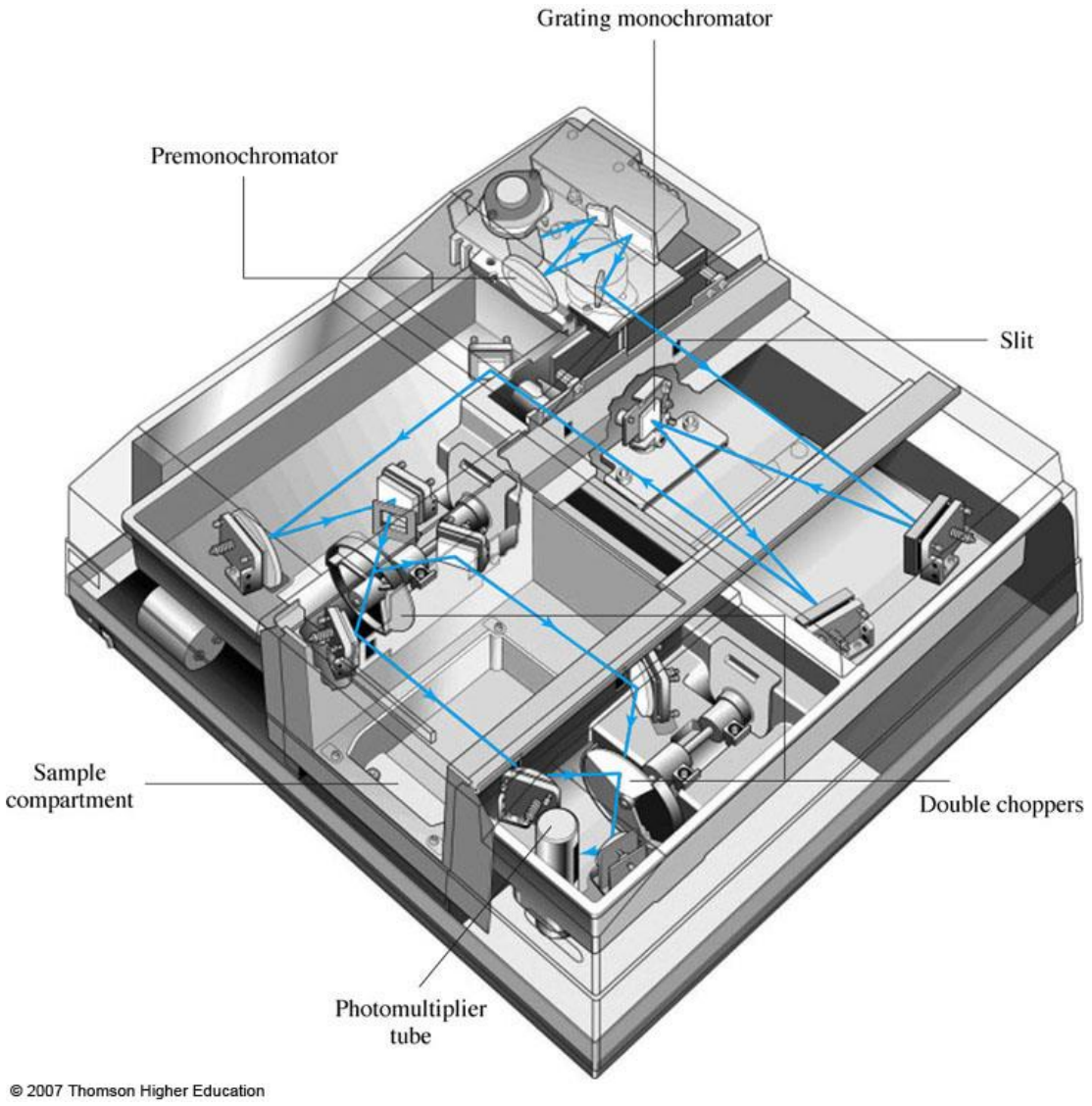


Figure 13-20 A double-beam recording spectrophotometer for the ultraviolet and visible regions; the Perkin-Elmer 57 Series. *(Courtesy of Coleman Instruments Division, Oak Brook, IL.)*

Spectrophotometers
Double Beam
for UV/vis



UV-Vis Instruments

Double Beam

Advantage of double beam:

Compensates for most fluctuations in radiant output of source.

UV-Vis Instruments

Types of Instrumentation

- Single beam
- Double beam in space
- Double beam in time
- **Multichannel**

UV-Vis Instruments

Types of Instrumentation

- **Multichannel**
  - **Based on array detectors**
  - **Usually single-beam designs**

UV-Vis Instruments

Multichannel

Diode Array Spectrometer

Radiation from the source is focused on the sample and passes to a monochromator with a fixed grating. The dispersed radiation hits a photodiode array transducer.

UV-Vis Instruments

Multichannel

Diode Array Spectrometer

The transducer (chip) consist of a linear array of several hundred photodiodes (256, 512, 1024, 2048).

The chip is 1 – 6 cm in length and individual diode widths are 15 – 50 μm. Each diode has a capacitor and an electronic switch.

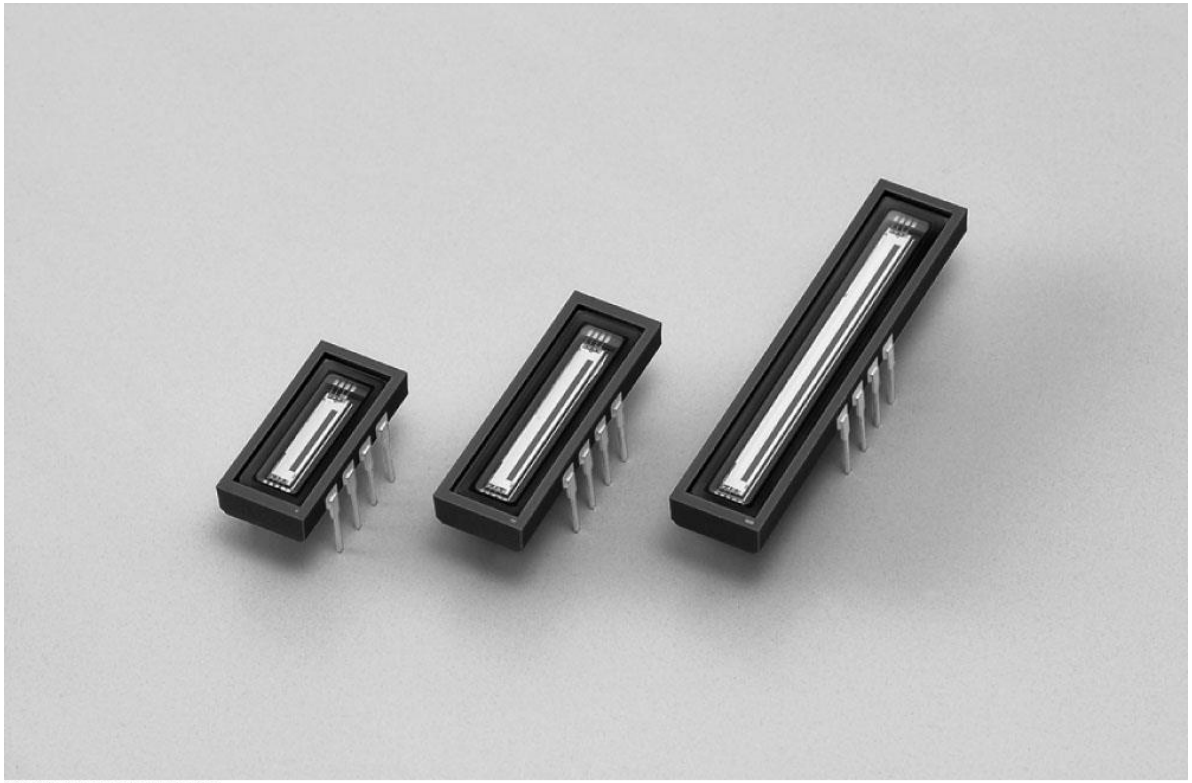
UV-Vis Instruments

Multichannel

- **Diode Array Spectrometer**
- **Each capacitor is charged to –5V. Radiation hitting the diode partially discharges the capacitor.**
- **The lost charge is replaced in the next switching cycle.**
- **The entire spectrum can be obtained in one second.**

UV-Vis Instruments

Multichannel



Spectrophotometers

Diode Array

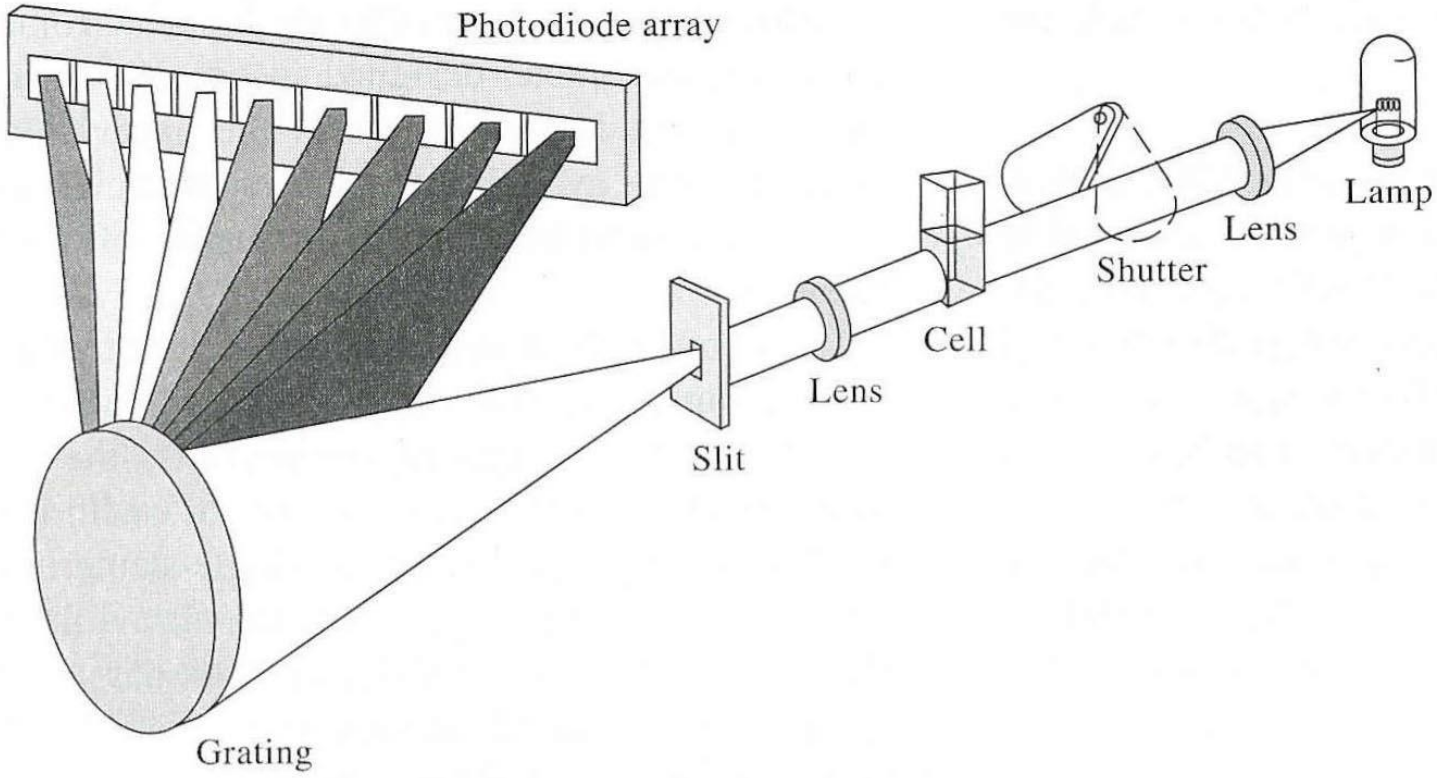


Figure 13-22 A multichannel diode array spectrometer; the HP 8452A. *(Courtesy of Hewlett-Packard Company, Palo Alto, CA.)*

UV-Vis Instruments

Multichannel

Diode Array Spectrometer

Advantages:

- Used for transients intermediate measurements
- Used for kinetic studies
- Can combine with chromatography

Disadvantages:

- Limited resolution (1-2 nm)

UV-Vis Instruments

Typical Instruments

- **Probe-Type Photometers**
- **Uses optical fibers to transmit and collect radiation.**

UV-Vis Instruments

Fiber Optics

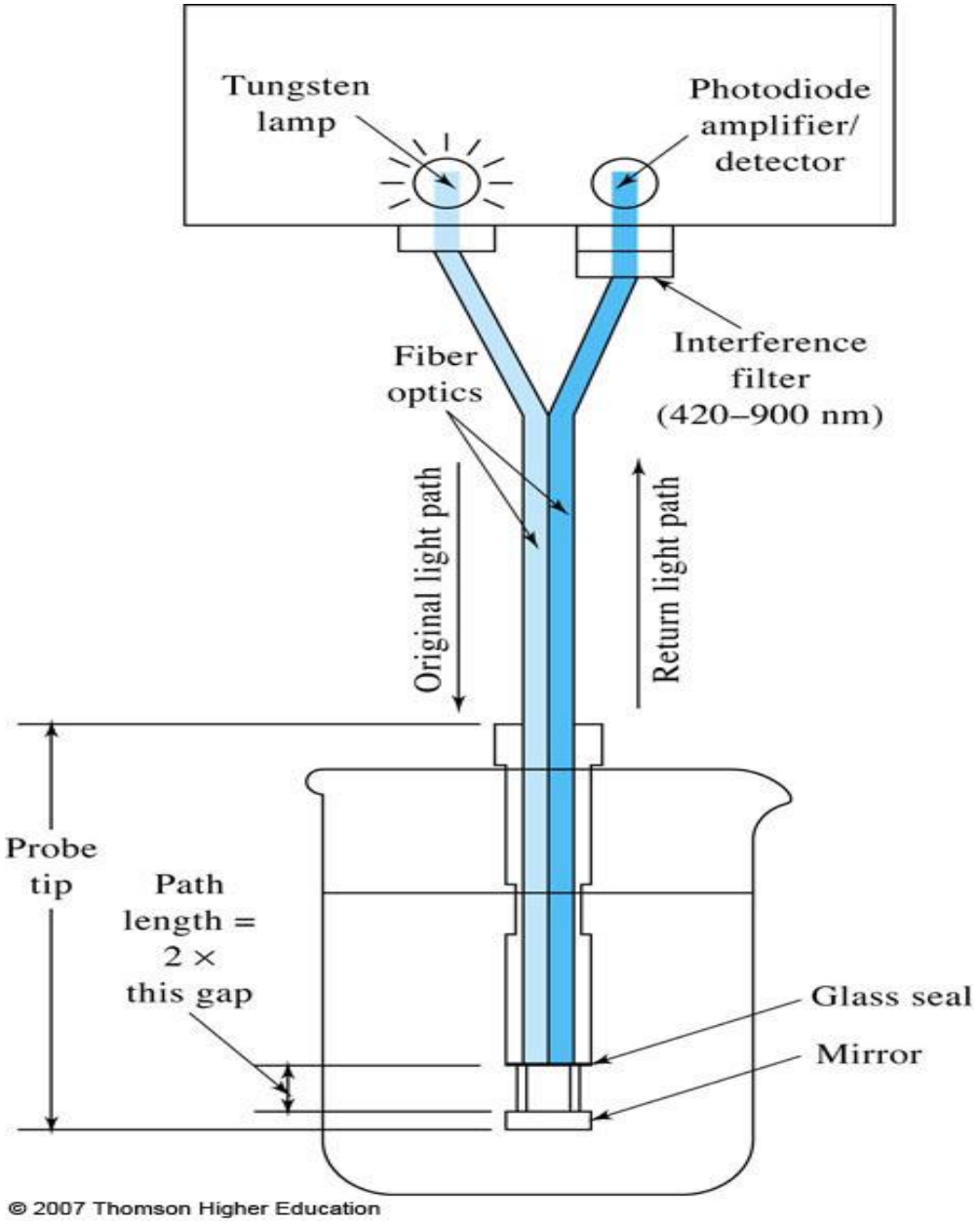
Optical fibers are fine strands of glass or plastic that can transmit radiation several hundred feet or more.

Diameter – 0.05 μm – 0.6 cm

Transmit – UV, vis, or IR radiation

Uses: medical, environmental

Probe-Type Photometers



UV-Vis Instruments

Double-Dispersion Instrument

-enhance spectral resolution

-reduce scattered radiation

2-gratings – 2 monochrometers in series.

Spectrophotometers

Double Dispersing (resolution 0.07 nm)

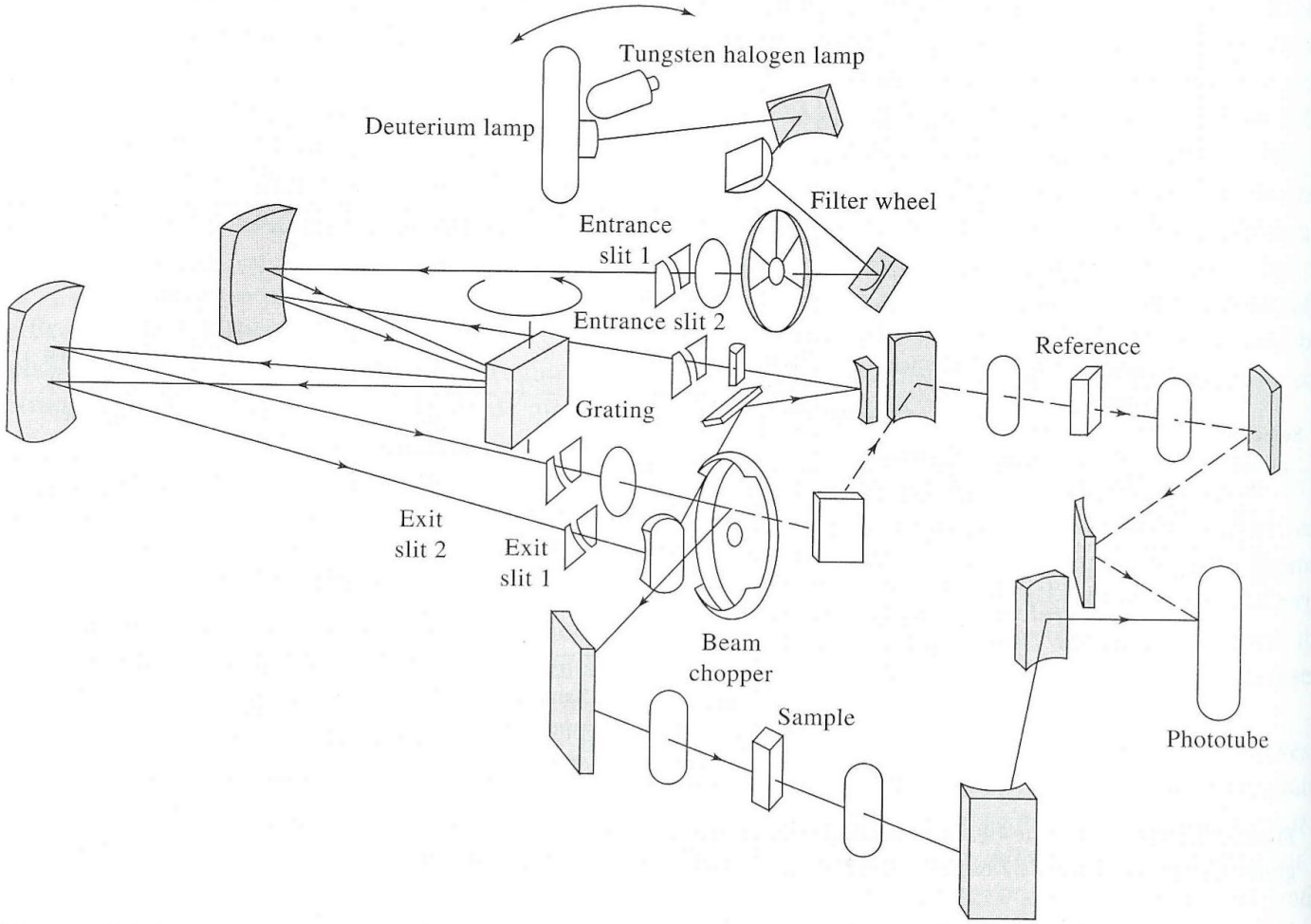


Figure 13-21 A double-dispersing spectrophotometer. *(Courtesy of Varian Instrument Division, Palo Alto, CA.)*

Fluorescence

Instrument designs

Fluorometers

- **If the instrument uses only filters it is called a fluorometer.**
- **Filter photometers very simple, inexpensive, compact, rugged, easy to use can do quantitative fluorescence analysis, cost $1000 - 5000.**

Fluorescence

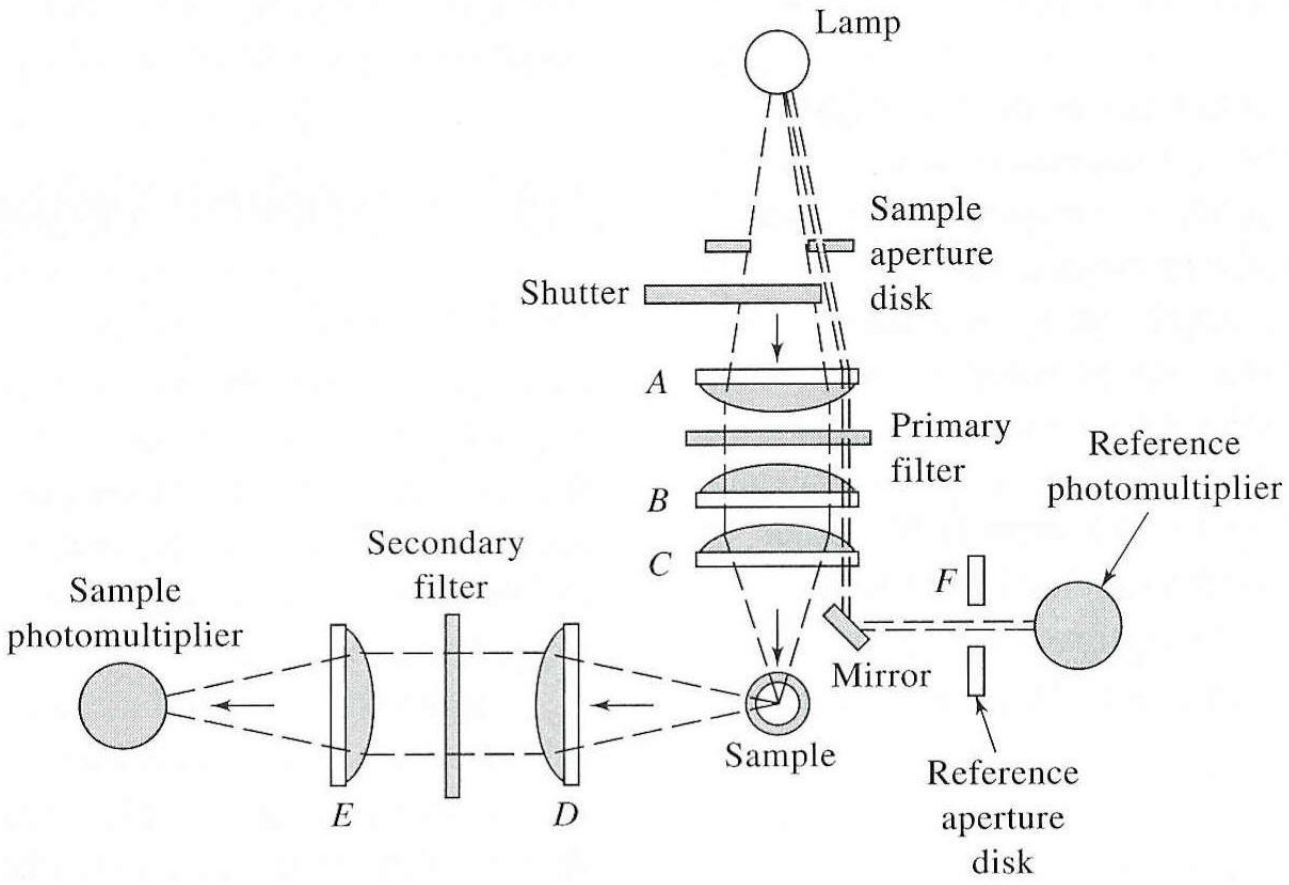


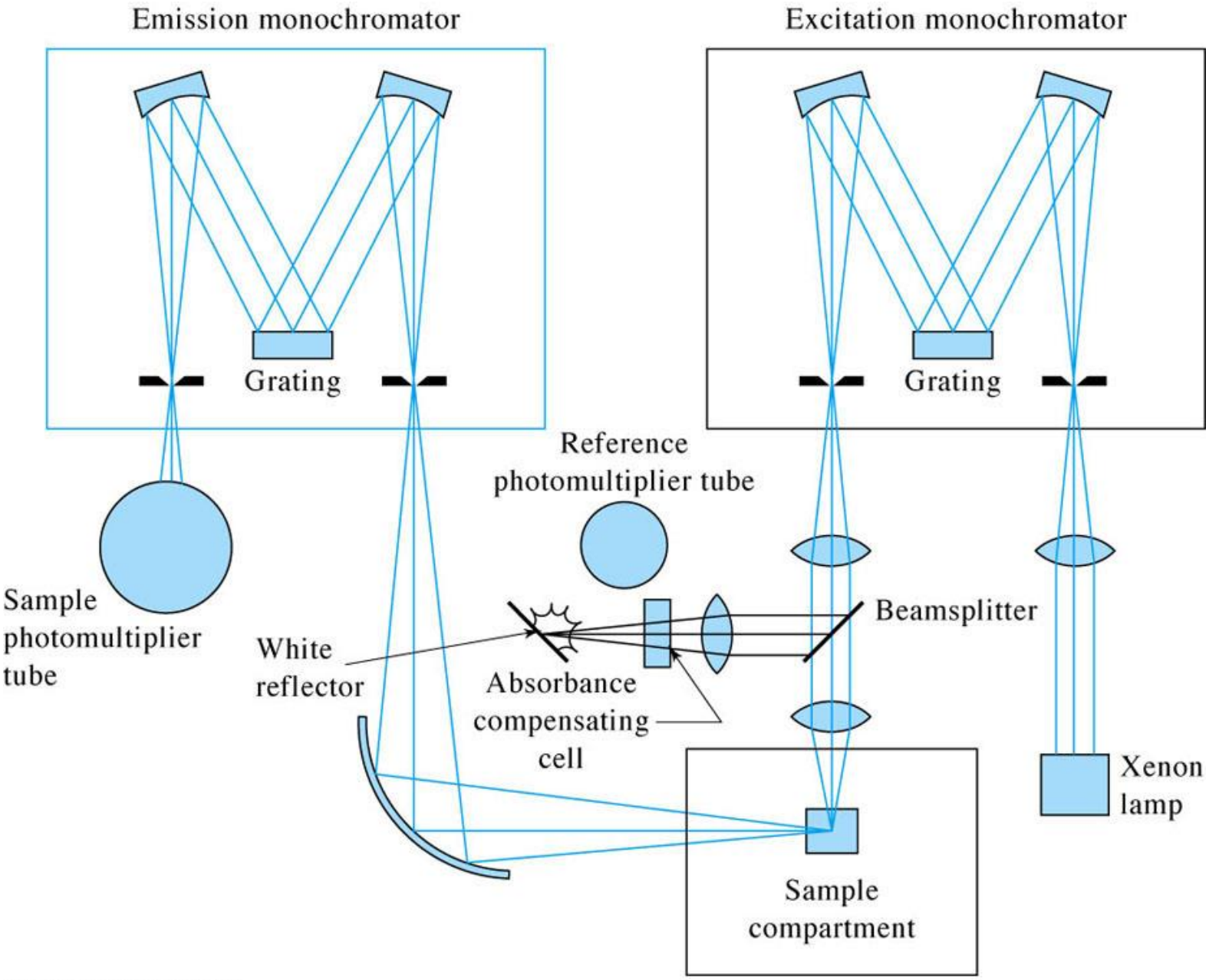
Figure 15-6 A typical fluorometer. *(Courtesy of Farrand Optical Co., Inc.)*

Fluorescence

Instrument designs

Spectrofluorometers

- **Produces both excitation and emission spectra.**
- **Usually has 2 grating monochromaters, radiation from the 1st monochromater is split, part goes to reference PMT and part goes to sample.**
- **The fluorescence coming from the sample goes to the 2nd monochromater and detected by 2nd PMT.**



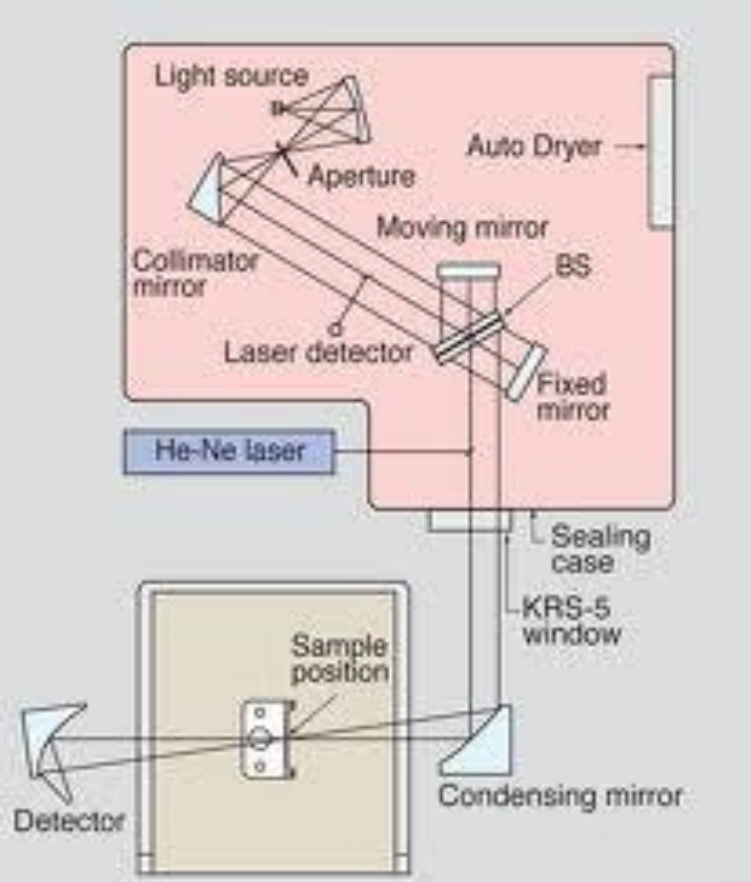
Fluorescence

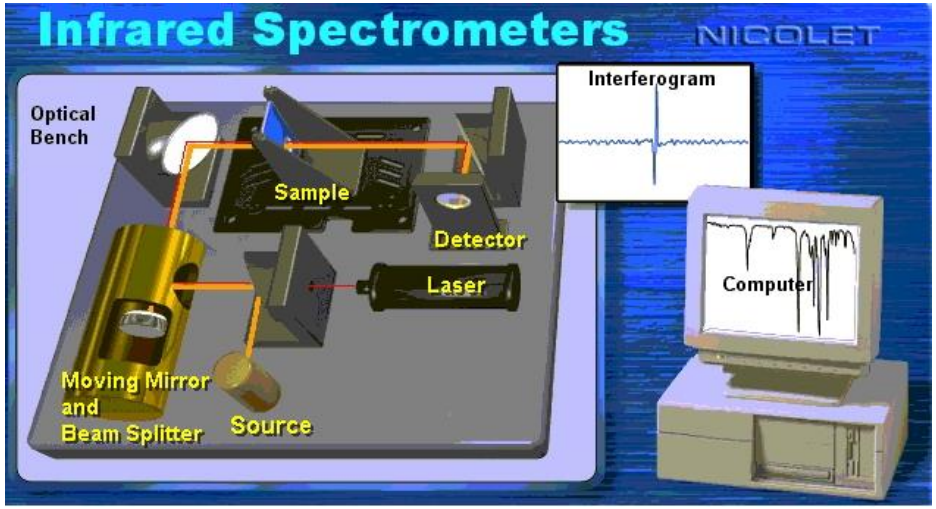
Instrument designs

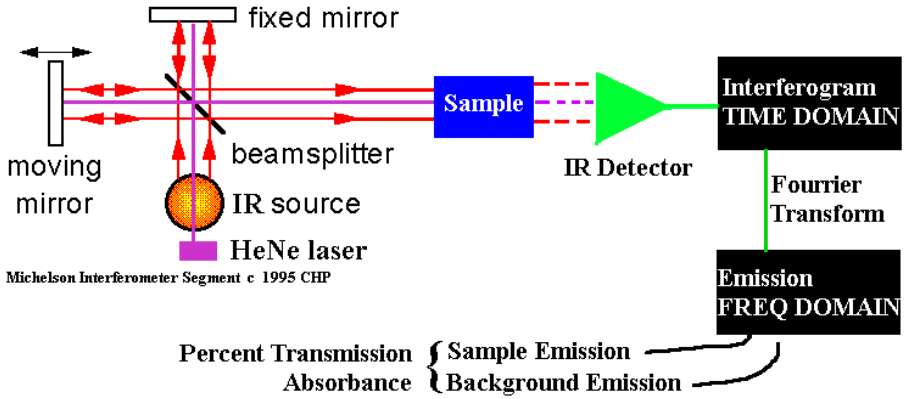
- **Because of day-to-day variations in the instrument, it must be calibrated daily.**
- **A standard solution, such as quinine sulfate (10^{-5} M) is usually used.**
- **Excited at 350 nm and emits at 450 nm.**

IR Instruments

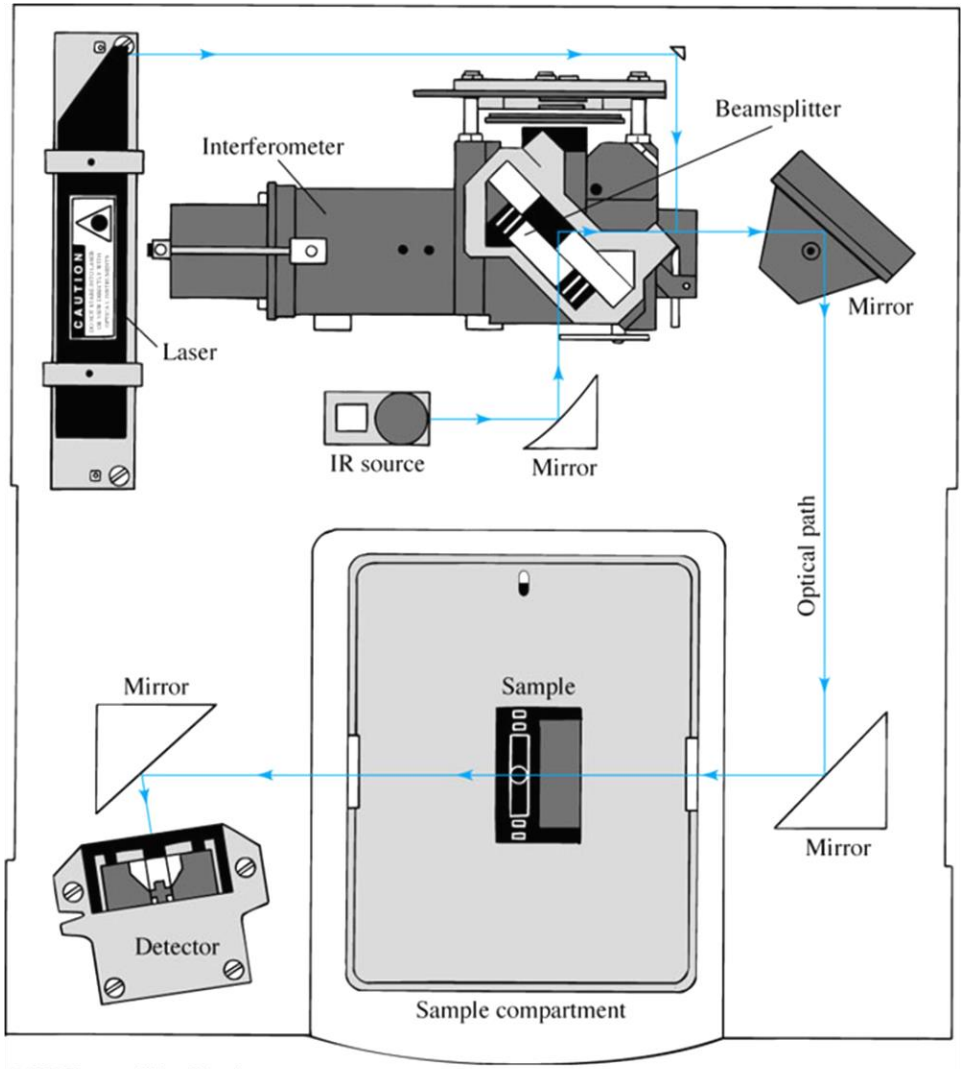
Fourier Transform IR (FTIR)







IR Instruments



IR Instruments

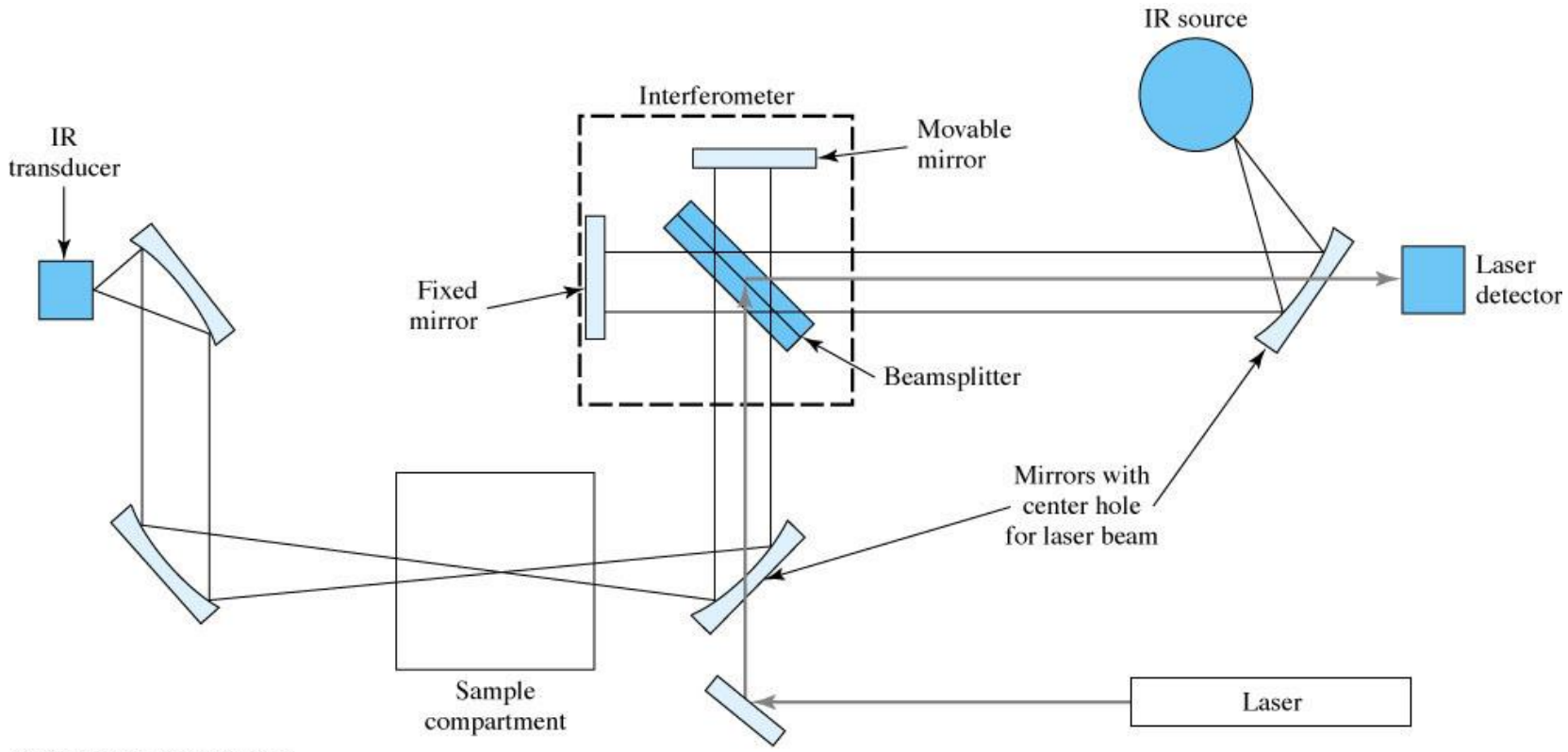
FTIR

Single beam

First obtain the reference interferogram (usually by scanning air) and store, then scan the sample.

IR Instruments

Single beam



IR Instruments

FTIR

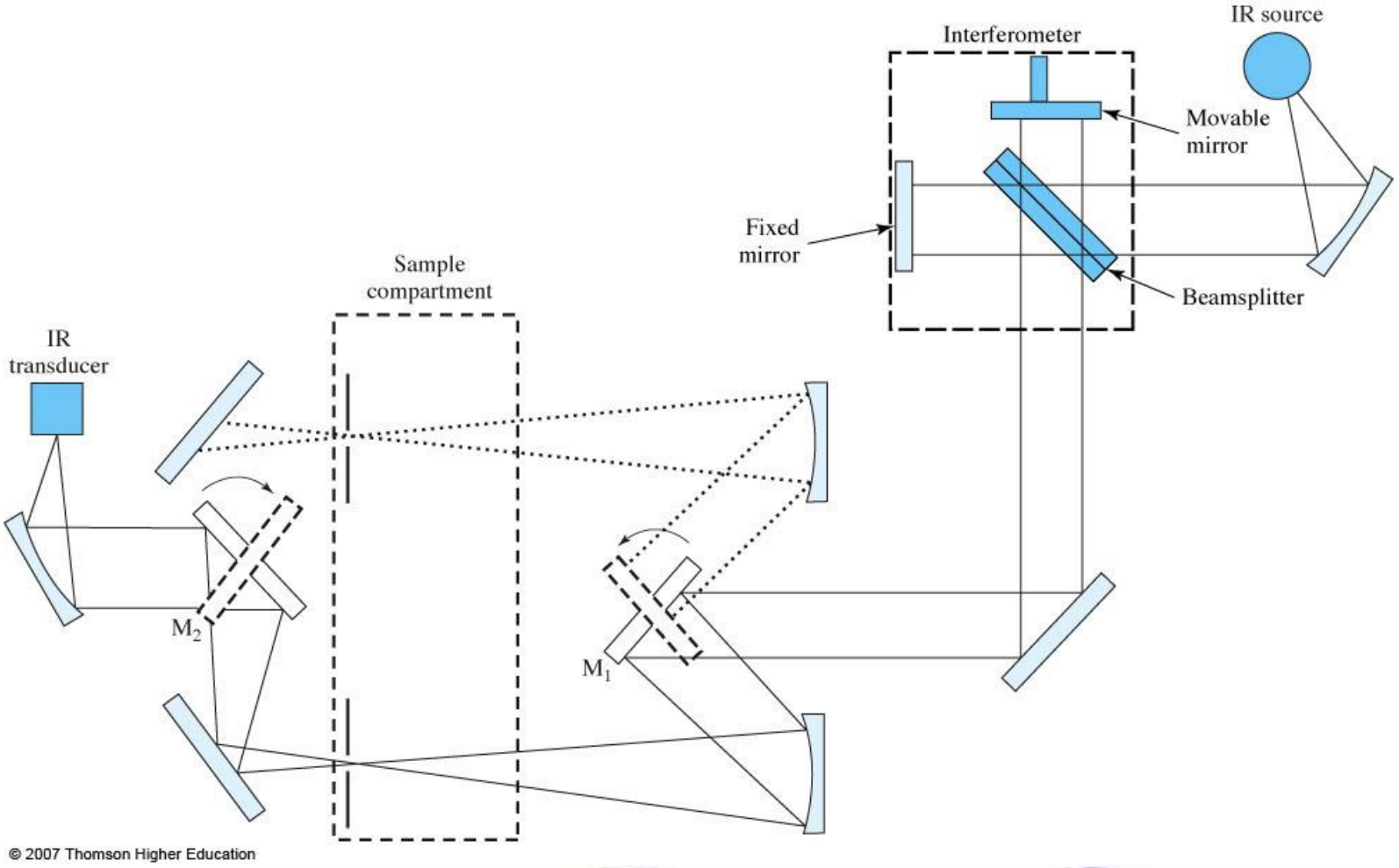
Double Beam

Sample and reference signal is obtained at each mirror position.

Compensates for source and detector drifts.

IR Instruments

Double Beam



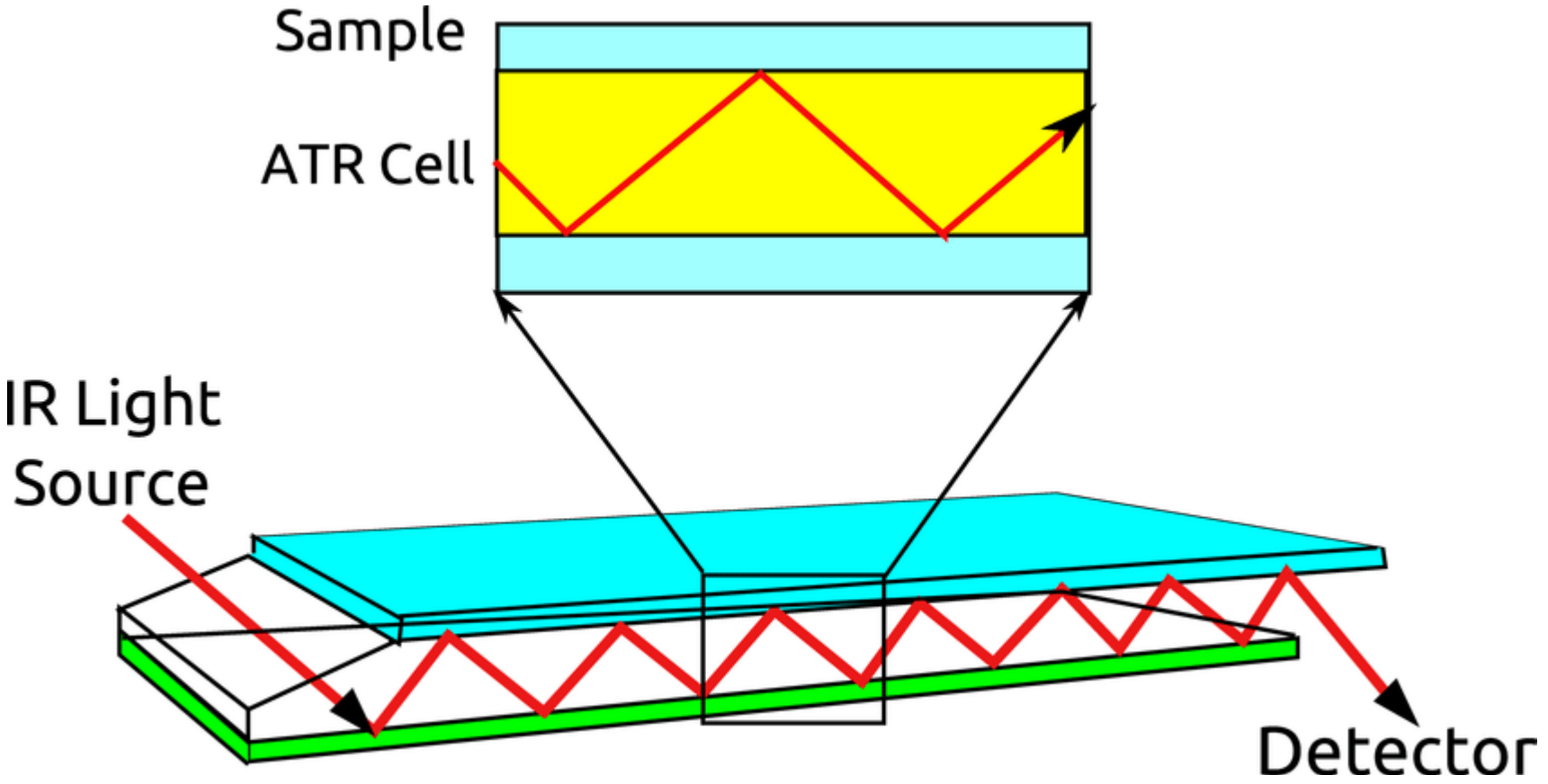
IR Techniques

Attenuated Total reflectance (ATR)

- Sample placed on high refractive index material
- i.e. TlBr/TlI or Ge or ZnSe
- Multiple internal reflections occur in the crystal.

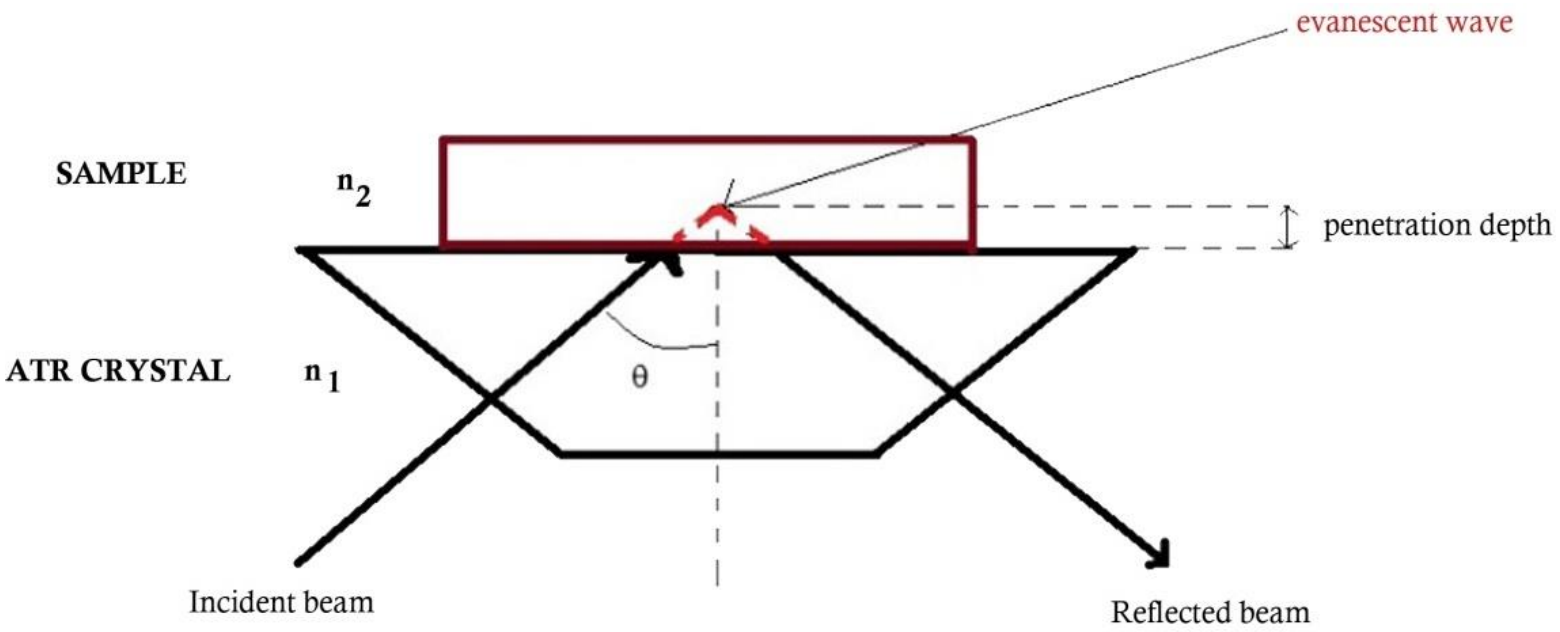
IR Techniques

Attenuated Total reflectance (ATR)



IR Techniques

Attenuated Total reflectance (ATR)



IR Techniques

Transmission vs. ATR

Transmission:

Advantages

- High quality spectra
- Satisfactory for qualitative analysis
- Wide variety of spectra libraries available

IR Techniques

Transmission vs. ATR

Transmission:

Disadvantages

- Solid (KBr pellet)
  - Time consuming
  - Particle size < radiation wavelength to avoid scattering
  - Spectra dependent on sample thickness
- Liquid (NaCl Plates)
  - Water in samples causes plates to fog
- Spectra not particularly reproducible
- Sample can't be recovered after analysis

IR Techniques

ATR

-Liquids and solids loaded directly onto crystal

-Arm Applies pressure to solids for uniform contact with crystal

-PSI can be controlled

IR Techniques

ATR

Advantages

- High Quality Spectrum for qualitative analysis
- Minimal sample preparation
  - Non destructive
  - Time efficient
- Spectra not affected by sample thickness
  - Radiation penetrates only a few micrometers
- Highly reproducible results
- Wide variety of sample types
  - Threads, yarns, fabrics, fibers, pastes, powders, suspensions, polymers, rubbers

IR Techniques

ATR

Disadvantages

- New technique
  - Less spectra catalogs available
- Spectral artifacts
  - Peak shift and intensity differences

Assignment

- See book and manufacturer websites for more instrument diagrams
- Test 2- Lectures 8 to 11 and 14 (not 12 & 13) – Wednesday Feb 28th or Friday March 1st