Chapter 20

Spectrometers

Spectrometer Components

- source of radiation
- sample
- radiation selection device (monochromator)
- detector
- signal processor
- readout device

Components of Optical Instruments

Emission Flame Photometer

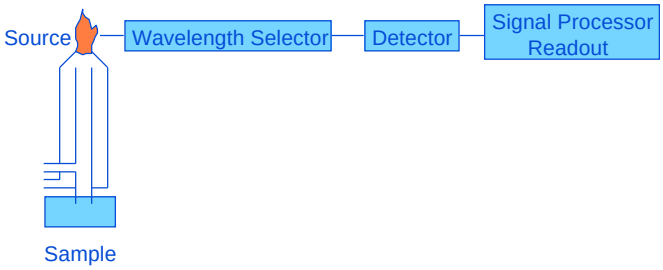
Flame Atomic Absorption Spectrometer

Absorption Spectrometer

Fluorescence and/or Scattering Spectrometer

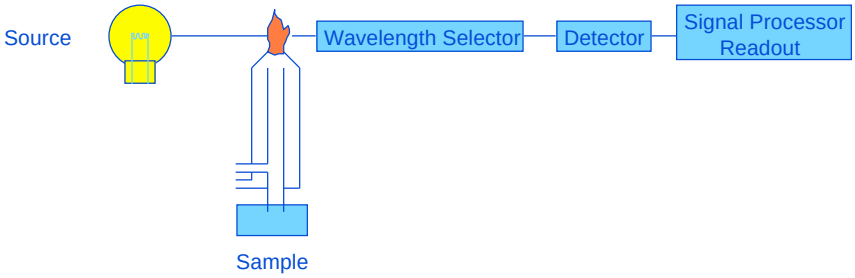
Components of Optical Instruments

Emission Flame Photometer



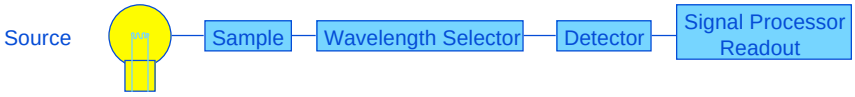
Components of Optical Instruments

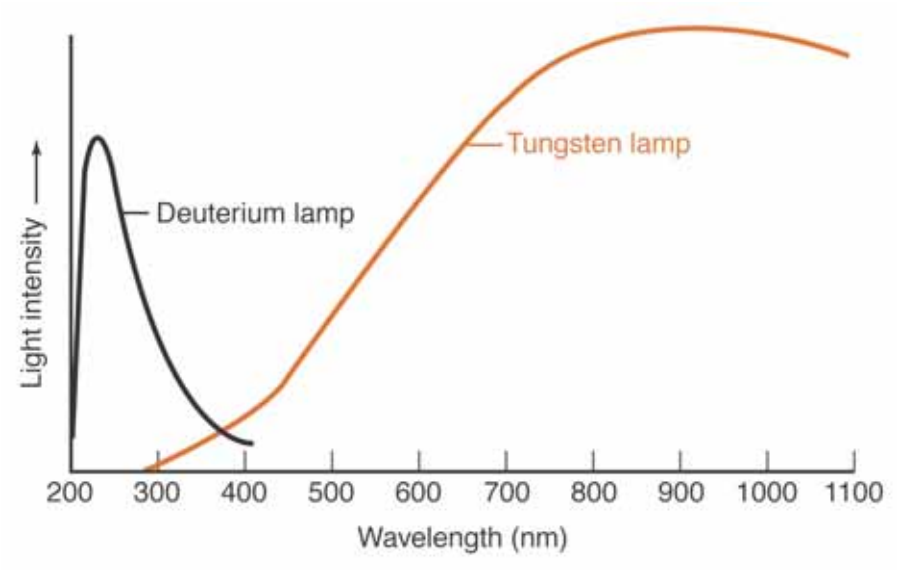
Flame Atomic Absorption Spectrometer



Components of Optical Instruments

Absorption Spectrometer





Sources

UV-Visible-Near IR Region

H2 - D2

160 - 375 nm, must use Quartz windows and cuvettes

Xe arc lamps

250 - 600 nm, max I at 500 nm

W filament

320 - 2500 nm, needs close V control

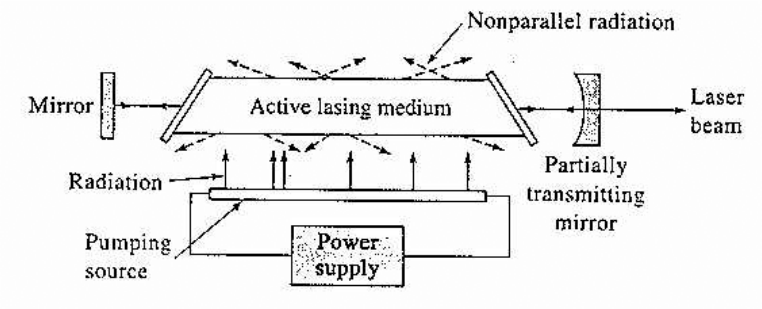
Sources

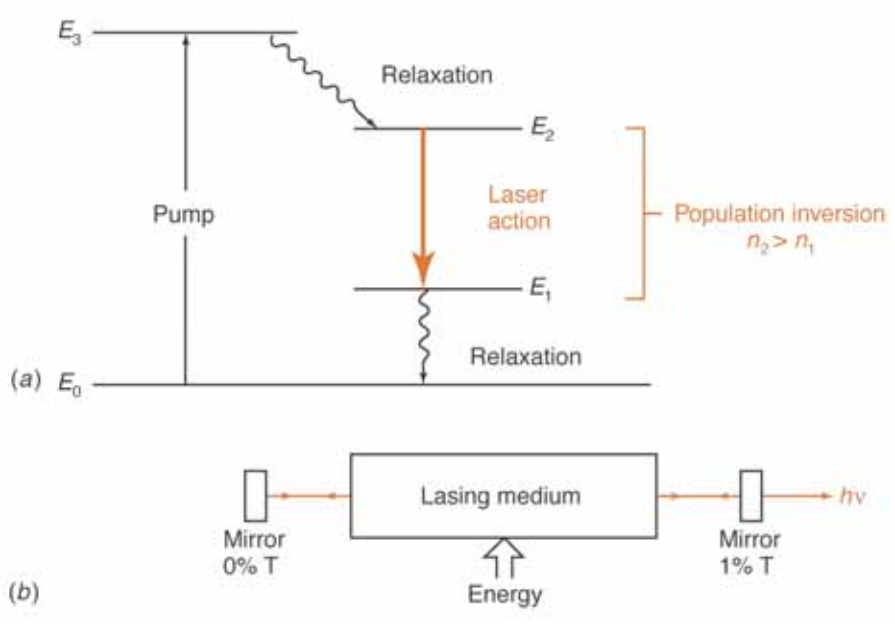
IR Region

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

Sources

Laser





Wavelength Selection

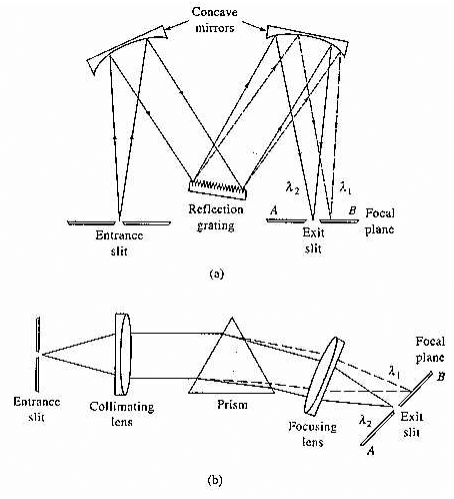
Filters

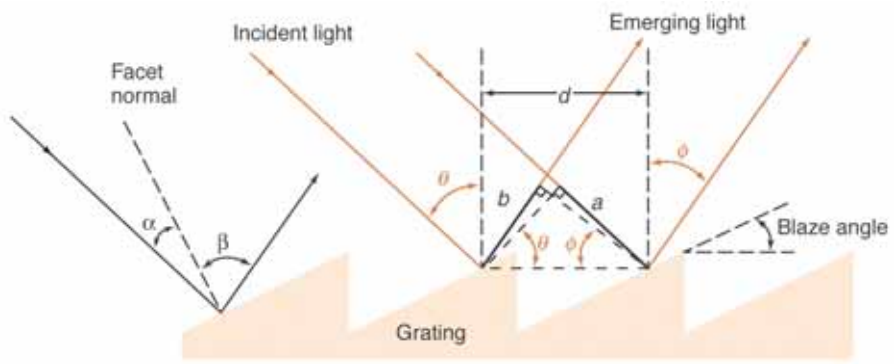
- interference filters
- interference wedges
- absorption filters

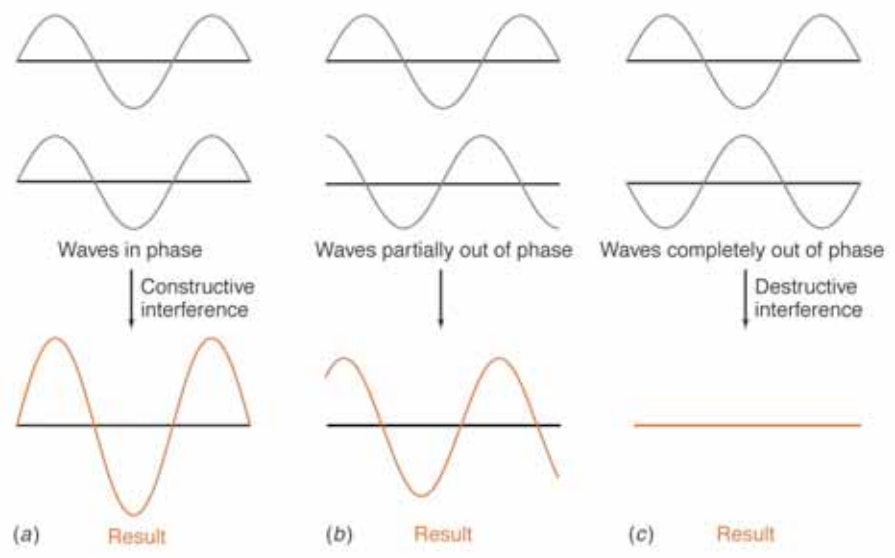
Wavelength Selection

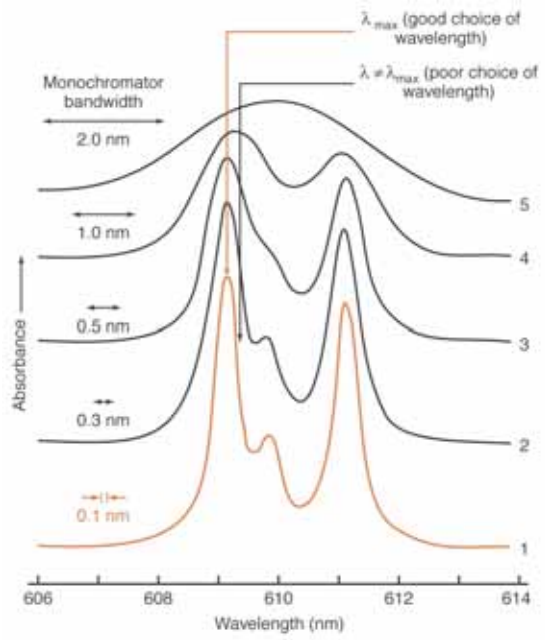
- Monochromators
  - Components
    - entrance slit
    - collimating element (lens or mirror)
    - prism or grating as dispersing element
    - focusing element (lens or mirror)
    - exit slit

Grating vs. Prism




Incident light
Emerging light
Facet
normal
d
θ
b
a
φ
α
β
θ
φ
Blaze angle
Grating


Waves in phase
Waves partially out of phase
Waves completely out of phase
Constructive
interference
Destructive
interference
(a)
Result
(b)
Result
(c)
Result



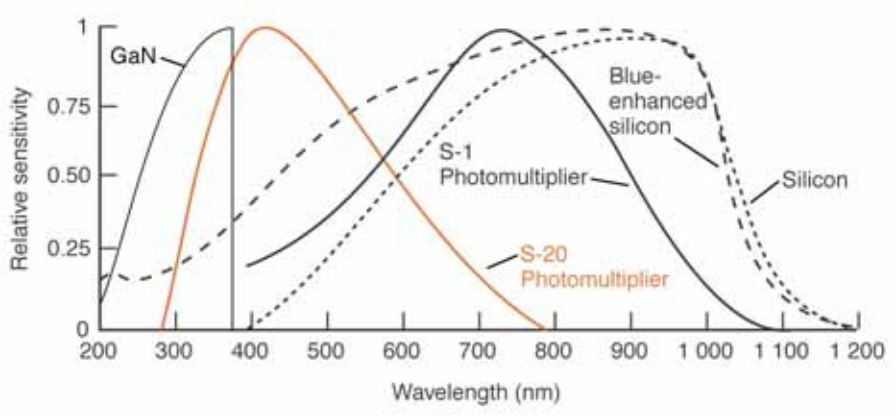
Sample Containers

- Ultra-Violet
  - quartz
- Visible
  - quartz
  - glass
- Infrared
  - NaCl
  - AgCl
  - KBr

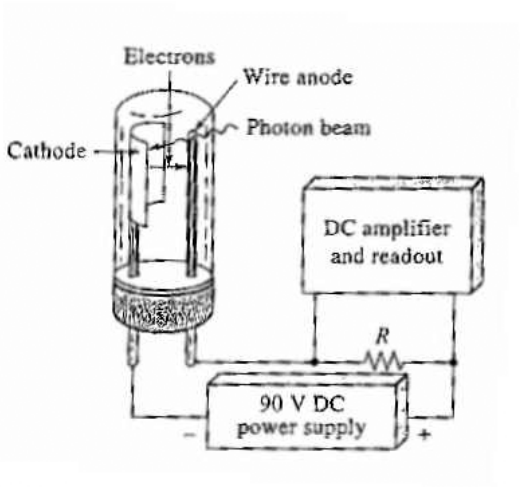
Types of Radiation Detection

UV-Visible
- Photon Detectors
- Vacuum Phototubes
- Photomultiplier Tubes
- Photodiodes
- Linear Photodiode arrays
- Charge-Transfer

Infrared
- Heat Detectors



Phototube



Photomultiplier Tube

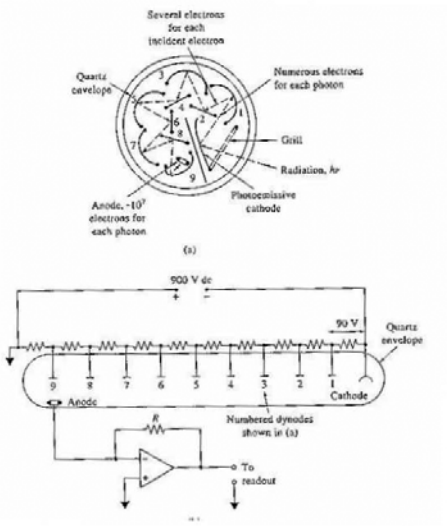
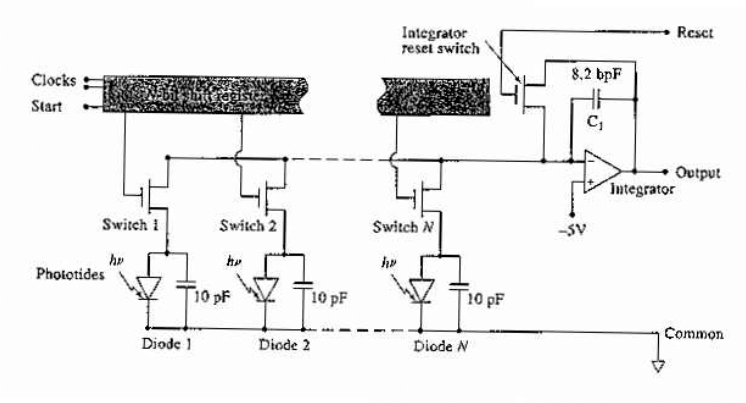


Photo Diode Array



Beer's Law
Instrumental response

$G = KP + K'$

Beer's Law
Instrumental response

$G = KP + K'$

dark-current adjust

$G = KP + 0.00$

$K = G/P \;\; ==>> \;\; G/P = 100/P_o$

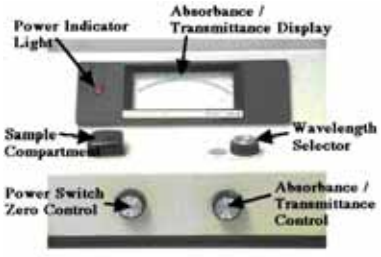
Beer's Law
Instrumental response

$G = KP + K'$

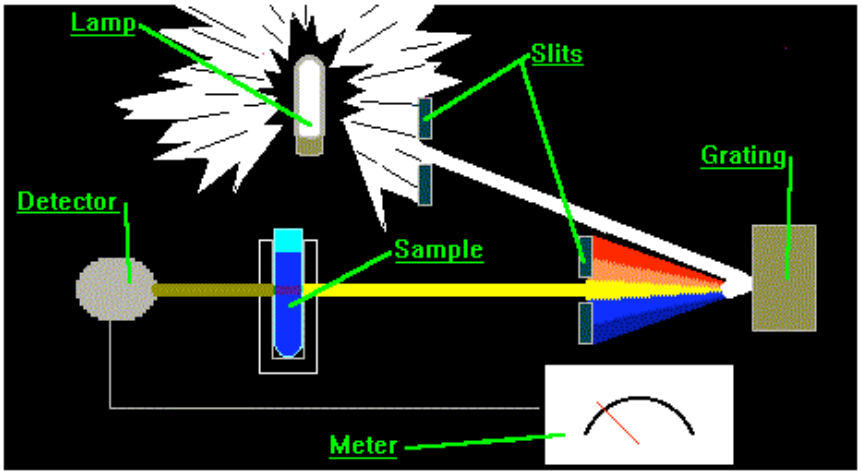
100% adjust, incident radiation

$G_o = 100 = KP_o + 0.00$

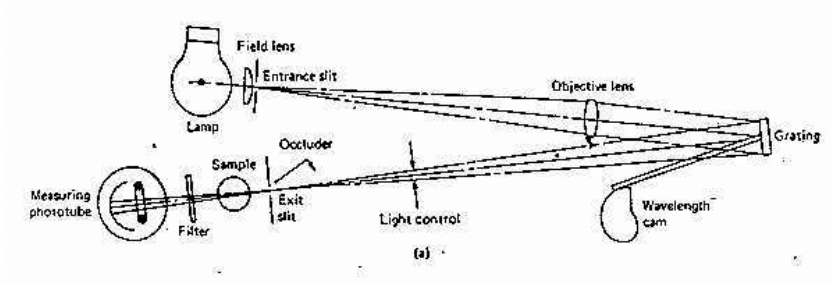
$K = 100/P_o$



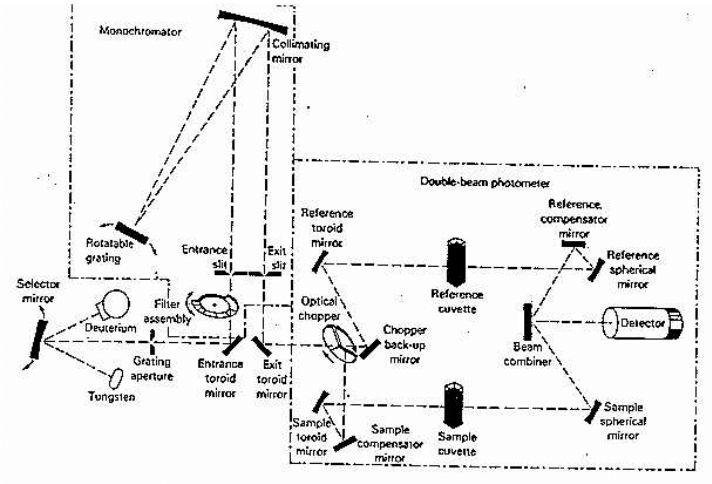
Spectronic 20 optical diagram



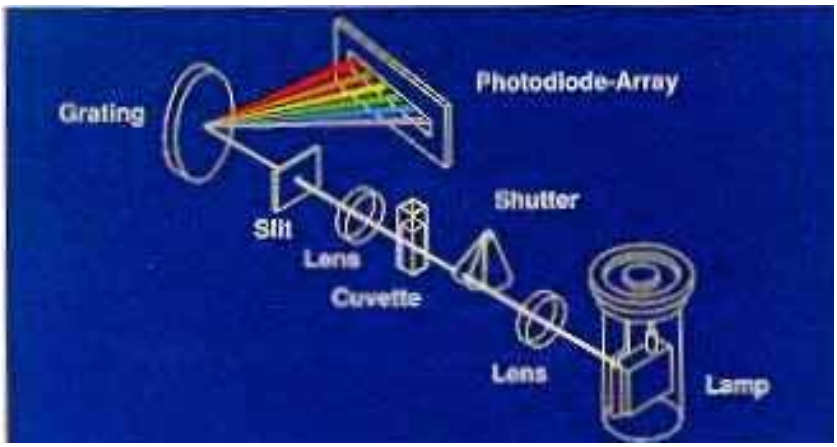
Spectronic 20

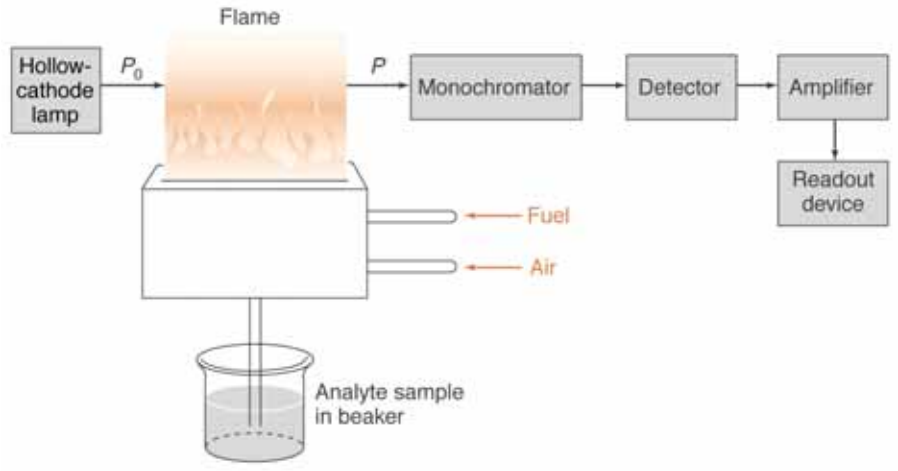


Double Beam Spectrometer



HP 8452a




Flame
Hollow-cathode lamp
P_0
P
Monochromator
Detector
Amplifier
Readout device
Fuel
Air
Analyte sample in beaker

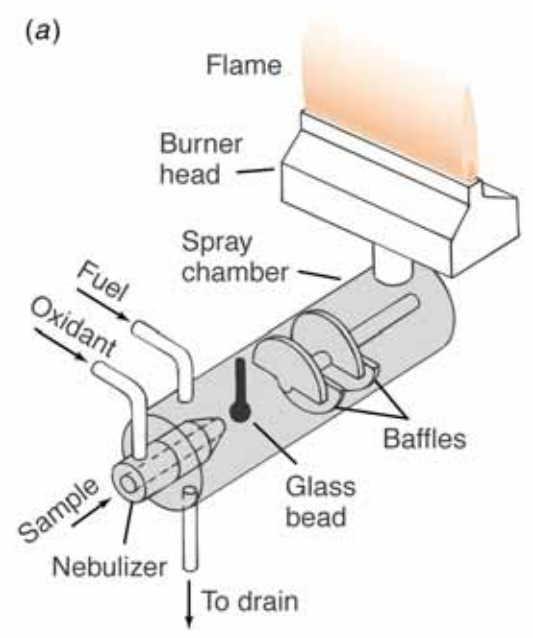
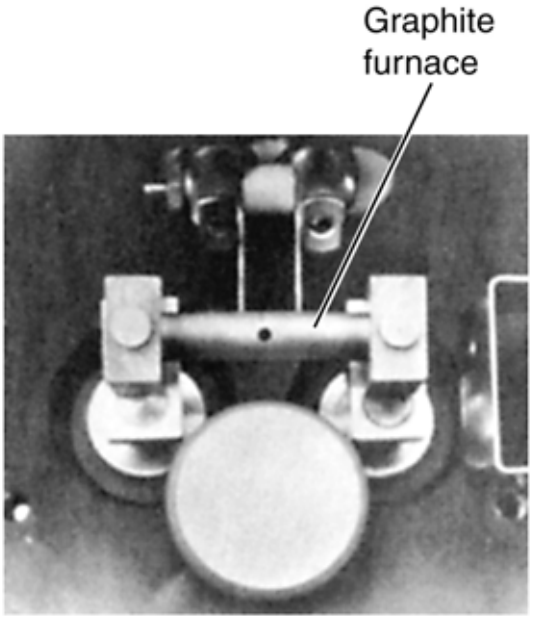
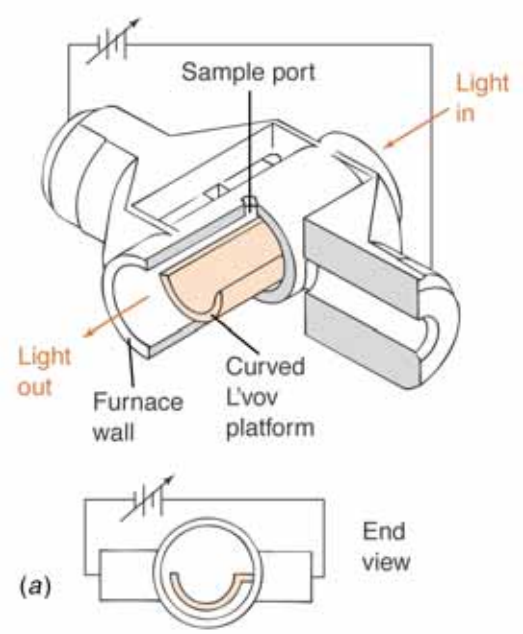
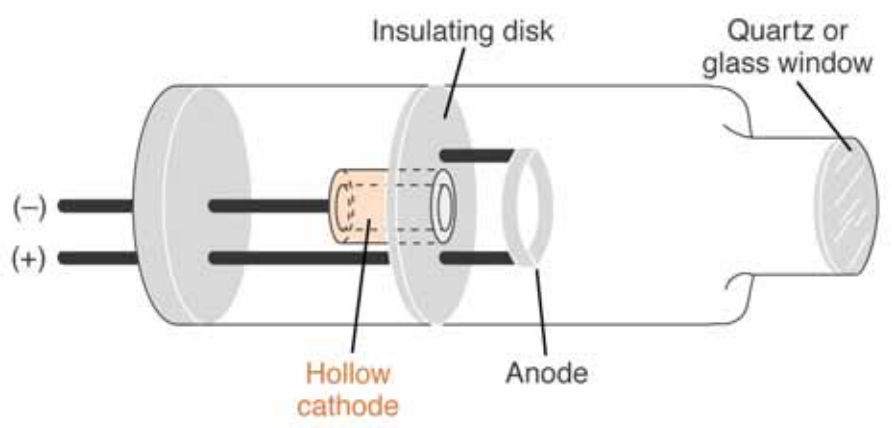

(a)
Flame
Burner head
Spray chamber
Fuel
Oxidant
Baffles
Glass bead
Sample
Nebulizer
To drain

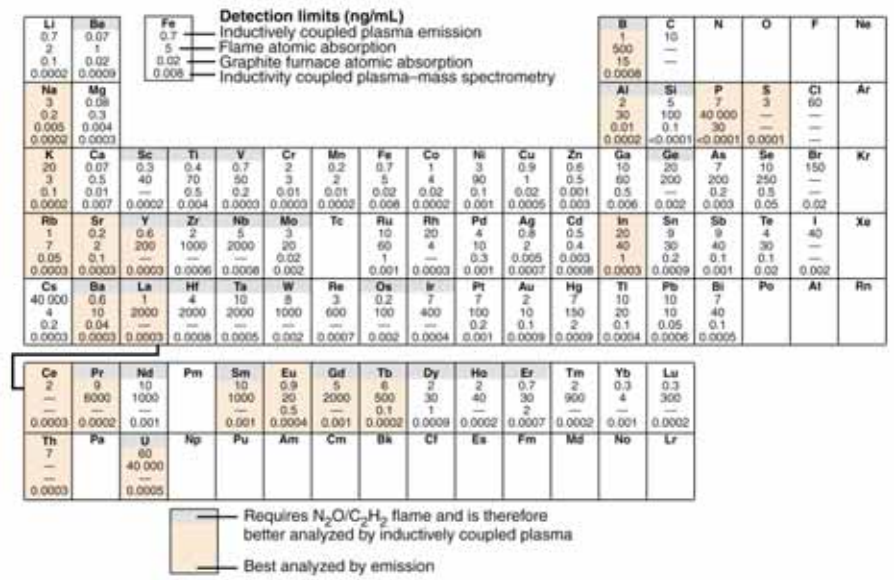
Table 21-1 **Maximum flame temperatures**

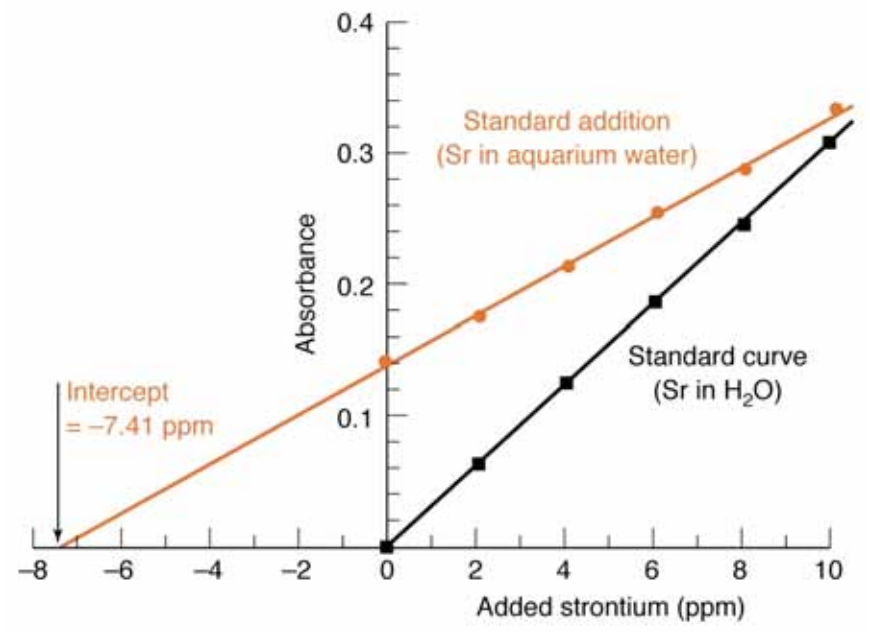
Fuel	Oxidant	Temperature (K)
Acetylene, HC≡CH	Air	2 400–2 700
Acetylene	Nitrous oxide, N_2O	2 900–3 100
Acetylene	Oxygen	3 300–3 400
Hydrogen	Air	2 300–2 400
Hydrogen	Oxygen	2 800–3 000
Cyanogen, N≡C−C≡N	Oxygen	4 800

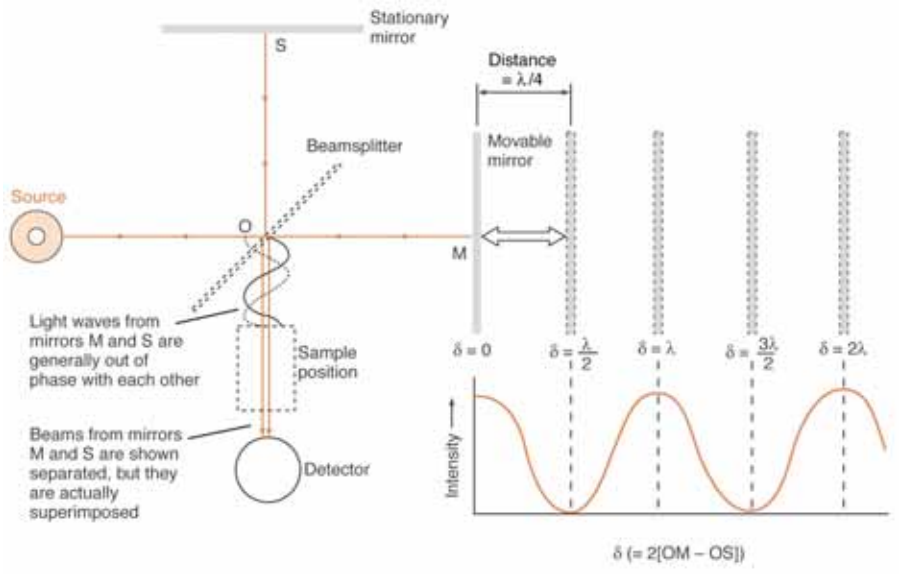


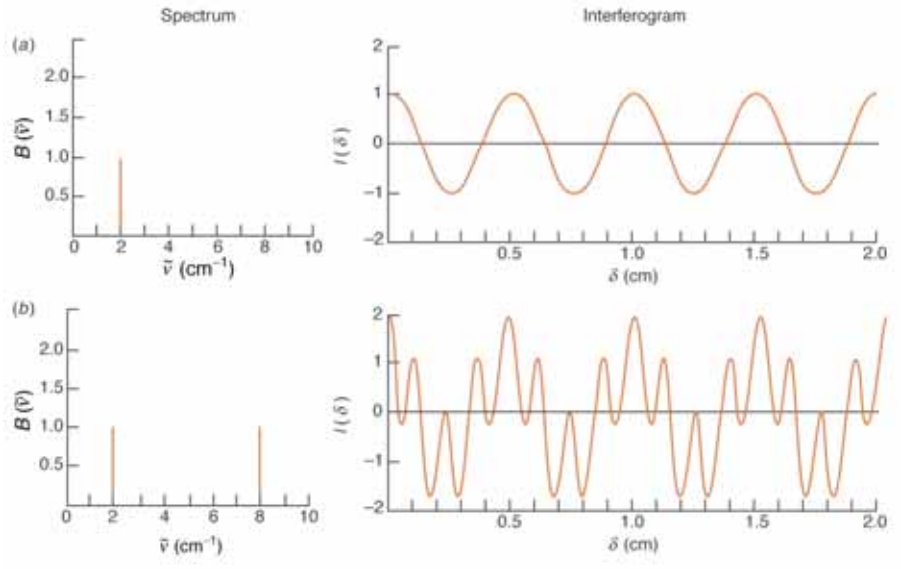

Sample port
Light in
Light out
Furnace wall
Curved L'vov platform
End view
(a)

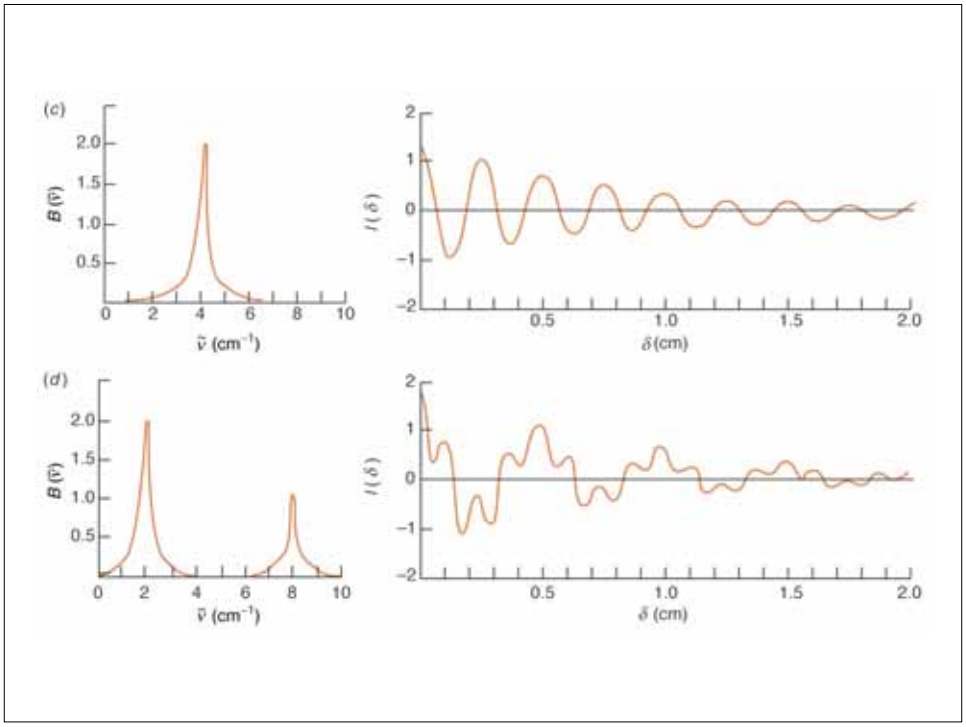

Insulating disk
Quartz or glass window
(–)
(+)
Hollow cathode
Anode

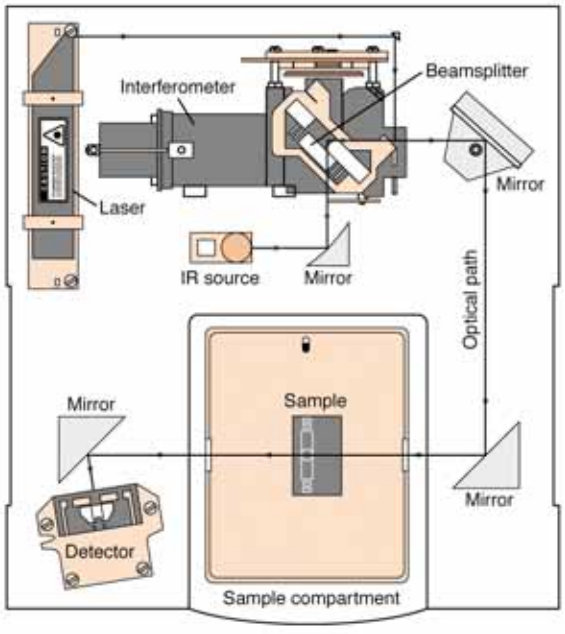

Detection limits (ng/mL)
Inductively coupled plasma emission
Flame atomic absorption
Graphite furnace atomic absorption
Inductivity coupled plasma–mass spectrometry
Requires N_2O/C_2H_2 flame and is therefore better analyzed by inductively coupled plasma
Best analyzed by emission

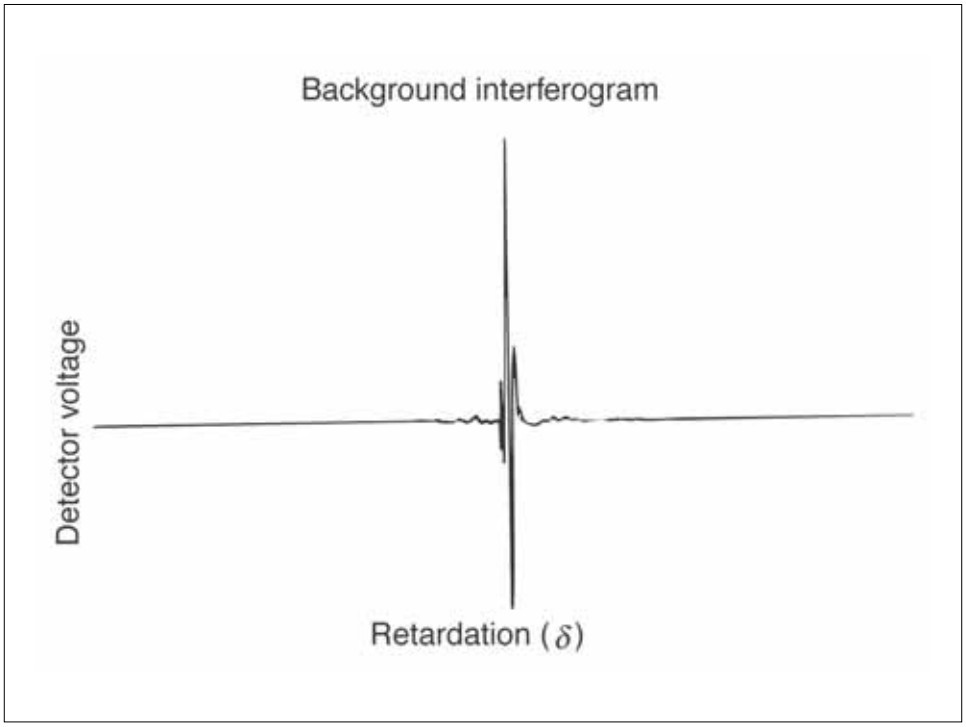

Standard addition
(Sr in aquarium water)
Standard curve
($Sr in H_2O$)
Intercept
= –7.41 ppm
Absorbance
Added strontium (ppm)
0.4
0.3
0.2
0.1
–8
–6
–4
–2
0
2
4
6
8
10

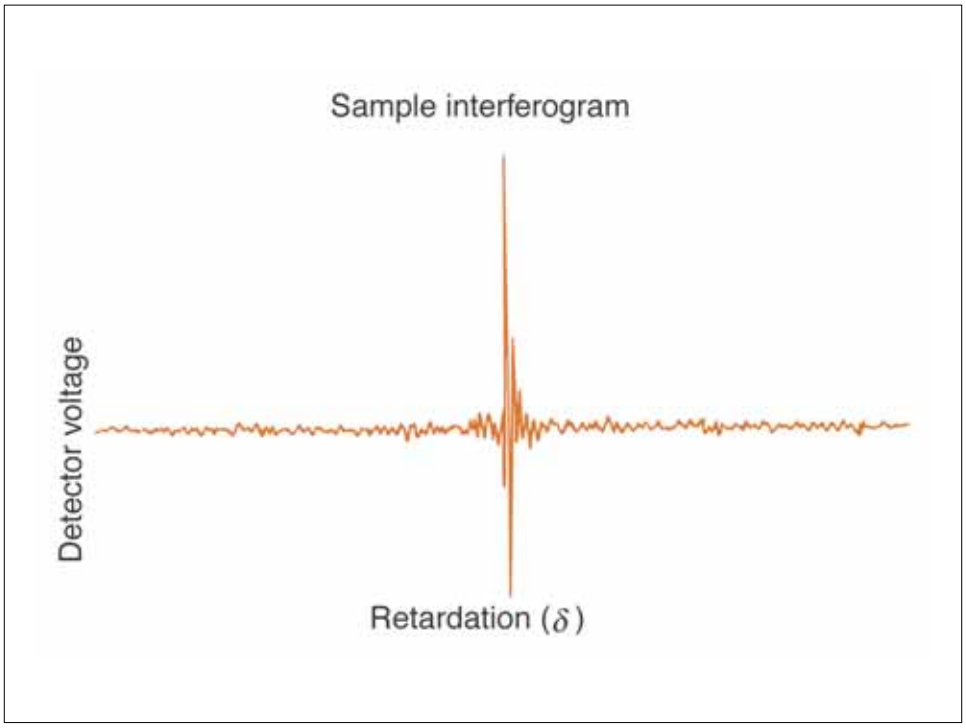

Stationary mirror
S
Distance = λ/4
Beamsplitter
Movable mirror
Source
O
M
Light waves from mirrors M and S are generally out of phase with each other
Sample position
Beams from mirrors M and S are shown separated, but they are actually superimposed
Detector
δ = 0
δ = λ/2
δ = λ
δ = 3λ/2
δ = 2λ
Intensity
δ (= 2[OM − OS])

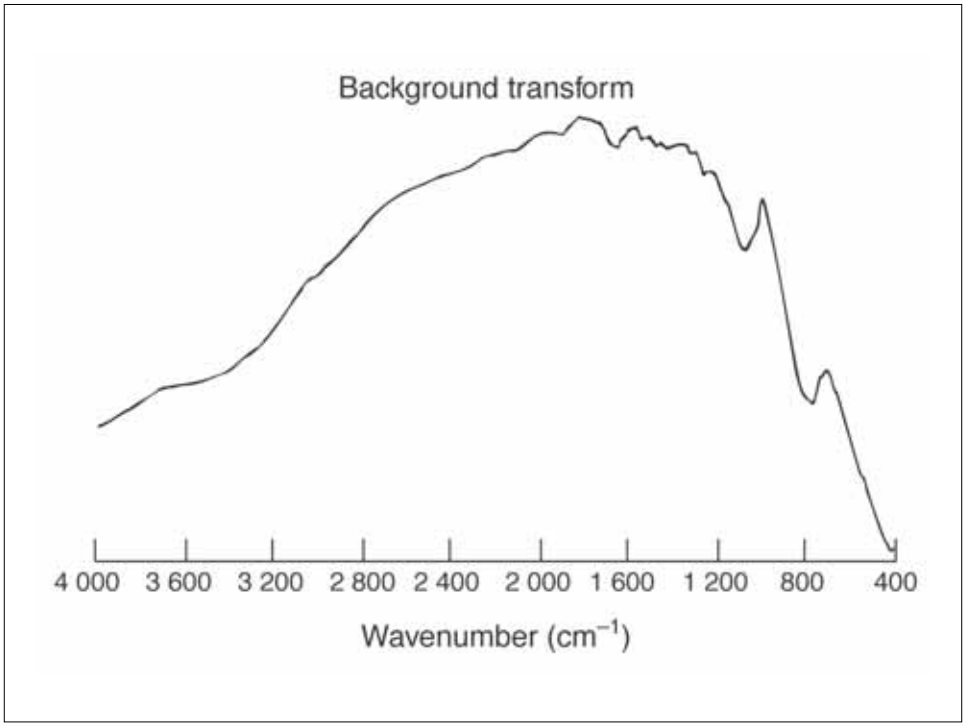

Spectrum
Interferogram
(a)
B (ν̃)
ν̃ (cm⁻¹)
I (δ)
δ (cm)
(b)
B (ν̃)
ν̃ (cm⁻¹)
I (δ)
δ (cm)

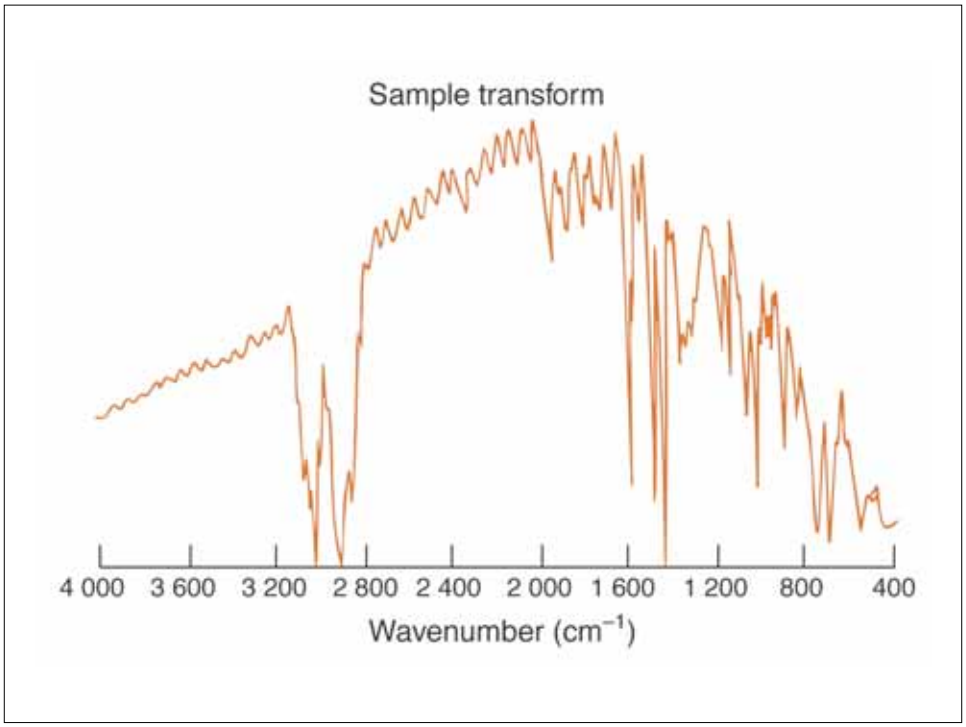

(c)
B(ν̃)
ν̃ (cm⁻¹)
I(δ)
δ (cm)
(d)
B(ν̃)
ν̃ (cm⁻¹)
I(δ)
δ (cm)

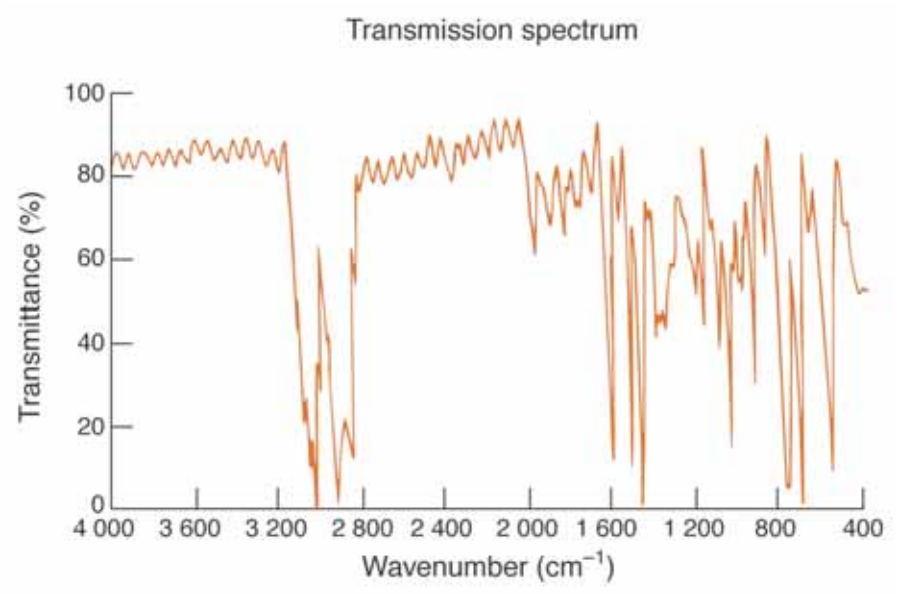

Interferometer
Beamsplitter
Laser
Mirror
IR source
Mirror
Optical path
Mirror
Sample
Mirror
Detector
Sample compartment


Background interferogram
Detector voltage
Retardation (δ)


Sample interferogram
Detector voltage
Retardation (δ)


Background transform
4 000
3 600
3 200
2 800
2 400
2 000
1 600
1 200
800
400
Wavenumber (cm^{-1})


Sample transform
4 000
3 600
3 200
2 800
2 400
2 000
1 600
1 200
800
400
Wavenumber (cm^{-1})


Transmission spectrum
Transmittance (%)
100
80
60
40
20
0
4 000
3 600
3 200
2 800
2 400
2 000
1 600
1 200
800
400
Wavenumber (cm^{-1})