Ch. 20 & 21

## Emission Spectrum

The spectrum of bright lines, bands, or continuous radiation characteristic of and determined by a specific emitting substance subjected to a specific kind of excitation.

## Absorption Spectrum

- Light shinning on a sample causes electrons to be excited from the ground state to an excited state
- Wavelengths of that energy are removed from transmitted spectra

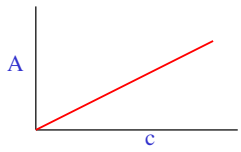
## Absorption Methods - Beer's Law

**A = abc = εbc**

where a => absorptivity
b => path length
c => concentration
ε => molar absorptivity

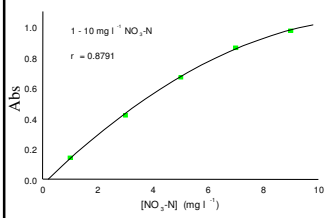
## Absorption Methods - Beer's Law

**A = abc = εbc**




- The light being shined on the sample must be monochromatic (one color or wavelength)
- The analyte must not be participate in a concentration dependent equilibrium

## Limitations to Beer's Law




$$HNO_2 + H_2O \longleftrightarrow H_3O + NO_2^-$$

- Real Limitations – high concentrated solutions, concentrated electrolyte solutions (proximity alters molecular absorption).
- Chemical Limitations – absorbing species participate in association or dissociation reactions, e.g. weak acids in concentrated solutions, complexation.

## Applications

- Health Sciences – 95% of all analyses are performed by spectrophotometry.
- Biological Sciences
- Chemical & Environmental Sciences: Organic, inorganic systems and biochemical systems

## Spectroscopic Procedure

- Have a spectrometer and cuvette(s)
  - Single-beam instrument has one sample holder (swap blank and sample)
  - Double-beam instrument splits light output between two holders (measure blank and sample)
  - A **baseline** spectrum is a spectrum of a reference solution (solvent or reagent blank)

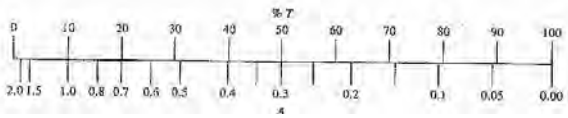
## Spectroscopic Procedure

- Keep the absorbance reading of the sample below 1.
  - % transmittance is related logarithmically with concentration (from 1-99% transmittance you can detect ~ 2 orders of magnitude in analyte concentration)
  - Any orders of magnitude greater than that will be detected in the range of 0-1% T.
- Dilute the solution so that the transmittance reading is not maxed out in that region (for accuracy)

## Relation between Transmittance and Absorbance

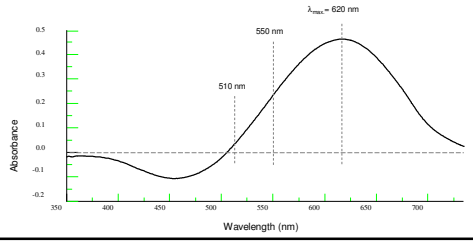
$$A = \log\left(\frac{P_0}{P}\right) = -\log T$$

| T | %T | A |
|---|---|---|
| 1 | 100 | 0 |
| 0.1 | 10 | 1 |
| 0.01 | 1 | 2 |

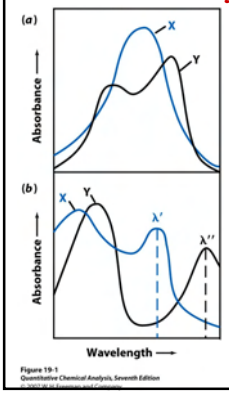



## Spectroscopic Procedure

- Try to do an analysis at the $\lambda_{max}$
  - Sensitivity is greatest at maximum absorbance
  - Curve is relatively flat in case the monochromator drifts and is off by a little in wavelength




## Analysis of Mixtures




$$\text{Mixture}_{Abs} = \varepsilon_X b[x] + \varepsilon_Y b[Y] + .....$$

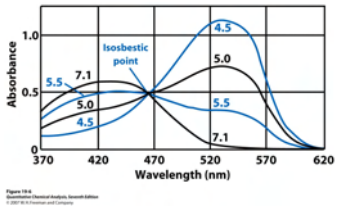
$$A_1 = \varepsilon_1(\lambda_1)c_1 b + \varepsilon_2(\lambda_1)c_2 b$$

$$A_2 = \varepsilon_1(\lambda_2)c_1 b + \varepsilon_2(\lambda_2)c_2 b$$

- What are the knowns and unknowns in the above Eq.?
- Measure Abs at more wavelengths than there are components in the mixture.
- More wavelengths increase the accuracy.

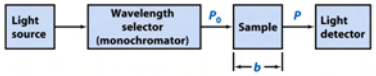
## Isosbestic points

- Good evidence of presence of only 2 species which interchange between themselves (e.g. indicator dye with 2 states)




## Components of Optical Instruments

Single Beam Instruments




Double Beam Instruments

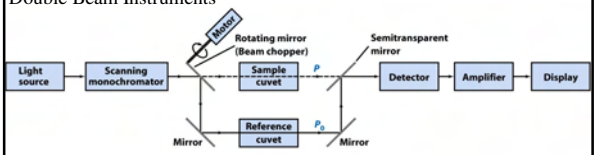



Figure 20-1
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## Instrumentation - Basic Components

(1) Light source

-Tungsten filament lamp (Visible: 320 - 2500 nm); Deuterium arc lamp (UV: 200-400 nm); Nernst glower, globar (IR region).

## Intensity of a Tungsten Filament and a Deuterium Arc Lamp

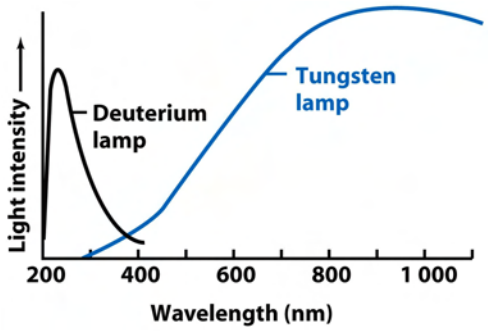


Figure 20-3
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## Instrumentation - Basic Components

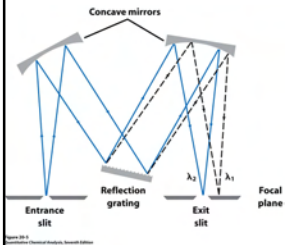
(1) Light source

-Tungsten filament lamp (Visible: 320 - 2500 nm); Deuterium arc lamp (UV: 200-400 nm); Nernst glower, globar (IR region).

(2) Monochromators: disperses light into its component wavelengths and select a narrow band of wavelengths to pass on to the sample or detector.

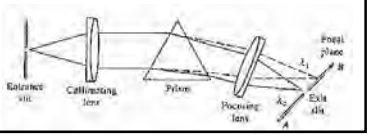
-Gratings & Prisms

## Grating vs. Prism




•Grating: a reflective or transmissive optical component with a series of closely ruled lines; can bend light (diffraction)

•Prism: can bend light (refraction)



## Instrumentation - Basic Components

(1) Light source

-Tungsten filament lamp (Visible: 320 - 2500 nm); Deuterium arc lamp (UV: 200-400 nm); Nernst glower, globar (IR region).

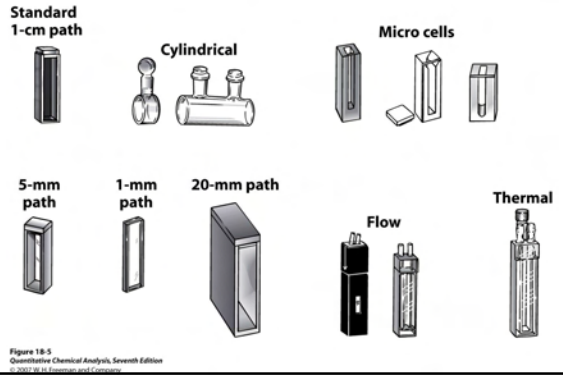
(2) Monochromators: disperses light into its component wavelengths and select a narrow band of wavelengths to pass on to the sample or detector.

-Gratings & Prisms

(3) Sample containers (cuvettes or cells)

-Glass, Plastic & Quartz (usually 1 cm); KBr/NaCl (IR)

## Cells for Spectrophotometry

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-Gratings & Prisms

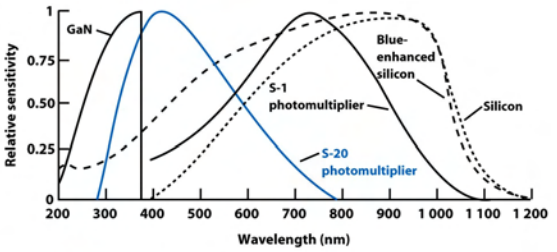
(3) Sample containers (cuvettes or cells)

-Glass, Plastic & Quartz (usually 1 cm); KBr/NaCl (IR)

(4) Detector: produces an electric signal when it is struck by photons

-Phototubes, Photomultiplier tubes, & Photodiode array

## Detector Response




•A function of wavelength of incident light

•The greater the sensitivity, the greater the current of voltage produced by the detector for a given incident irradiance of photons.

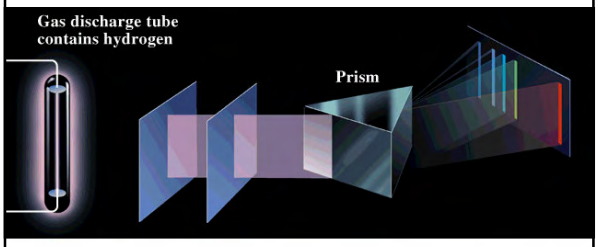
## Atomic Spectroscopy

- Deals with free atoms - the absorption and emission of radiation by atoms.
- Produces line spectra - can be used for elemental analysis (qualitative and quantitative).

## Line Spectrum

A spectrum produced by a luminous gas or vapor and appearing as distinct lines characteristic of the various elements constituting the gas.

## Hydrogen Line Emission Spectrum




The relative simplicity of atomic spectra is due to the small number of possible energy states for the absorbing particles.



## Atomic Spectroscopy - Linewidths

- Atomic spectra have narrow lines: inherent linewidth is ~$10^{-4}$ nm.
- Two main mechanisms can broaden the lines to $10^{-3}$ to $10^{-2}$ nm:

  (1) Doppler broadening: The atoms may move towards slowly or quickly or away from the detector (cause a Doppler shift in the resulting line); greater as the temperature increases

  (2) Pressure broadening: arises from the collision between atoms (cause energy exchanges, shorten the life time of the excited state); greater as the temperature increases.

## Atomic Spectroscopy- Types

- Types of atomic spectroscopy
  - Atomic absorption
  - Atomic emission
  - Atomic fluorescence

## Absorption, Emission, and Fluorescence by Atoms in a Flame

•Atomic Emission:
-emission from a thermally populated radiation.
•Atomic Absorption:
-absorption of sharp lines from hollow0cathode lamp.
•Atomic Fluorescence:
-fluorescence following absorption of laser radiation.

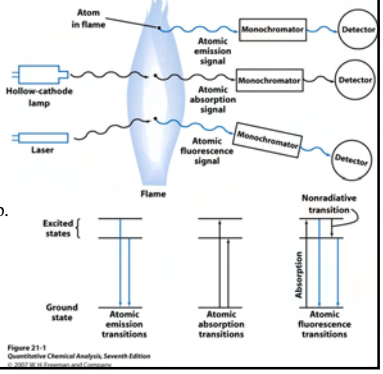



Figure 21-1
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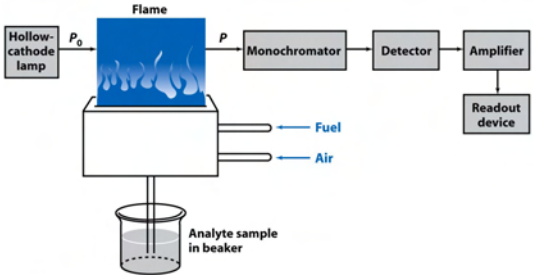
## Atomic Absorption Experiment

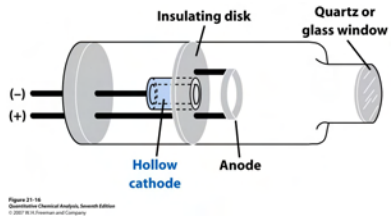



- Atoms absorb part of the light from the source and the remainder of the light reaches the detector.
- The method relies on the Beer's Law (calculations are the same as with molecular absorption methods)

## Sources

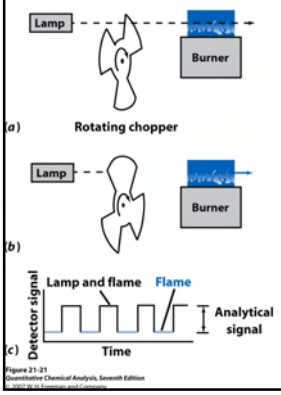
- A molecular spectrophotometer relies on a broad band light source.
- With atomic absorption, a line source is required to reduce interferences from other elements and background.
- Hollow cathode lamp

## A Hollow-Cathode Lamp




Filled with an inert gas like argon or neon. When applies a potential, the gas becomes excited and is driven towards the cathode. Metal atoms are then spitted out the cathode surface, which produces emission lines specific for the element. The cathode must be capable of conducting a current for it to work.

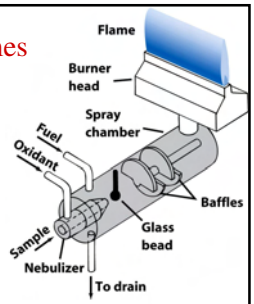
## Chopper



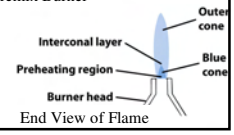

• Provides signal modulation
• Subtracts the signal due to flame background emission to reduce some noise from the atomization source and accounts for instrumental variations.
(a) Lamp and flame reaches detector
(b) Only flame emission reaches detector
(c) Resulting square wave signal

## Atomization Source - Flames

- Atomization source: convert sample to free atoms
- Flame spectrometers:
  - often use a premix burner; have a long, narrow burner head that serves as a sample path (b).
  - Sample is introduced via aspiration.
  - The nebulizer controls sample flow, producing a mist.
  - The mixing chamber assures that the sample mixed with the oxidant and fuel prior to entry into the flame.




Premix Burner




End View of Flame

## Atomization Source - Flames

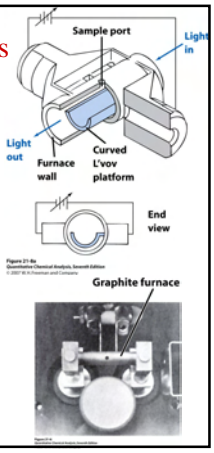
**Table 21-1 Maximum flame temperatures**

| 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 |

•Fuel: the most common one is acetylene.
•Oxidants: air or nitrous oxide ($N_2O$, producing a hotter, noiser flame).
•Sample: must be a fluid; large size (> 1 mL); constantly being consumed.
•Can produce stable signals in the ppm range for most metals

## Atomization Source - Furnaces

- Graphite furnace:
  - Samples are placed in a carbon tube which is heated electrically-graphite furnace (solid samples can be assayed)
  - Improved detection limits and sensitivity.
  - A three stage program: (1) Dry: remove solvent; (2) Char: decompose your matrix (not analyte); (3) Atomization: increase [free atoms].
  - Purge gas- Argon: remove excess material (dry, char, after atomization); reduce oxidation of the tube; as a protective blanket during atomization (cyanogen)

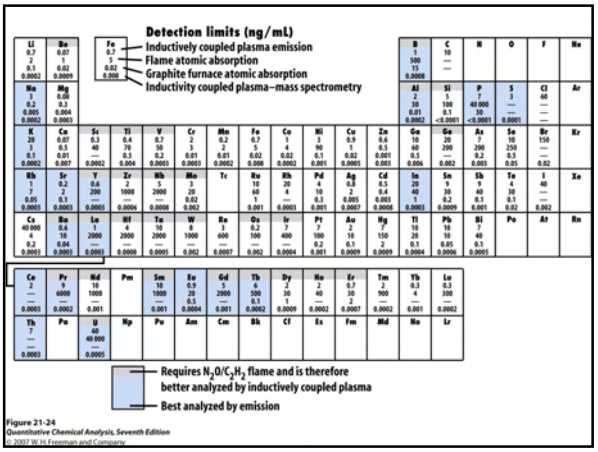



## Monochromator and Detector

- Monochromator: a high resolution, holographic grating
- Detector: photomultiplier tube

## Background Correction Methods

- Background signal arises from absorption, emission, or scatter by everything in the sample besides analyte (the matrix) and by the atomization sources.
- Beam chopping: an easy way to account for instrumental variations and "flam flicker"; not very good at accounting for background absorption or emission.
- Deuterium ($D_2$) Lamp: broad emission from a $D_2$ lamp (mostly background) is passed though the flame in alternation with that from the hollow cathode (sample and background); not very good >350 nm.
- Zeeman correction: when a strong magnetic field is applied, the atom electronic energy level split. Off (sample and background); On (background); directly measure background, but expensive



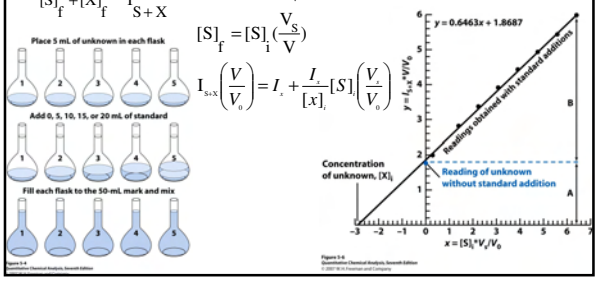

## Standard Methods

- **Standard calibration curve**. (standard curve)
- **Standard addition method** – requires linear response

$$\frac{[X]_i}{[S]_f+[X]_f}=\frac{I_X}{I_{S+X}} \qquad [X]_f=[X]_i\left(\frac{V_0}{V}\right)$$

$$[S]_f=[S]_i\left(\frac{V_S}{V}\right)$$

$$I_{S+X}\left(\frac{V}{V_0}\right)=I_x+\frac{I_x}{[x]_i}[S]_i\left(\frac{V_s}{V_0}\right)$$




## Standard Methods

- **Internal standard method**: a known amount of standard (different species from the analyte) is added to the unknown. Equate ratio of unknown signal to standard signal in the unknown mixture to the ratio of the standard mixture.

$$\frac{\text{Area of analyte signal}}{\text{Concentration of analyte}}=F\left(\frac{\text{Area of Std signal}}{\text{Concentration of Std}}\right)$$

$$\frac{A_X}{[X]}=F\left(\frac{A_S}{[S]}\right)$$

Example: A solution containing 0.0837M X and 0.0666M S gave peak area of Ax=423 and As=347. To analyze the unknown, 10.0 mL of 0.146 M S were added to 10.0 mL unknown, and the mixture was diluted to 25.0 mL in a volumetric flask. This mixture gave Ax=553 and As=582. Calculate [X] in the unknown.

$$\frac{A_X}{[X]}=F\left(\frac{A_S}{[S]}\right)$$

$$\frac{423}{0.0837}=F\left(\frac{347}{0.0666}\right)\Rightarrow F=0.9700$$

$$[S]=0.146M\times\left(\frac{10.0}{25.0}\right)=0.0584M$$

$$\frac{A_X}{[X]}=F\left(\frac{A_S}{[S]}\right)$$

$$\frac{553}{[X]}=0.9700\left(\frac{582}{0.0584}\right)\Rightarrow[X]=0.05721M$$

$$(25.0/10.0)\times 0.05721=0.143M$$

Example: Water from a salt lake is analyzed for Ca (see the AAS data table below). A 100.0 ppm $Sr^{2+}$ standard solution and a 250.0 ppm $Ca^{2+}$ standard solution are used in addition to the unknown in the test tubes indicated in the table. Assume the detector responds of Ca and Sr are the same.

| test tube # | ml $Sr^{2+}$ standrd | $Ca^{2+}$ standrd | $Ca^{2+}$ unkwn | A423 (Ca) | A404 ($Sr^{2+}$) |
|---|---|---|---|---|---|
| 1 (stds) | 2.00mL | 1.00mL | - | 0.885 | 0.342 |
| 2 (unk) | 3.00 | - | 1.00ml | 0.465 | 0.385 |

$$\frac{\{[X]/[S]\}unk}{\{[X]/[S]\}std}=\frac{\{Ix/Is\}unk}{\{Ix/Is\}std}$$

$$\frac{(1/4)[X]}{(3/4)(100ppm)}=\frac{0.465}{0.385}$$

$$\frac{}{(1/3)(250ppm)}=\frac{}{0.885}$$

$$(2/3)(100\text{ ppm})=0.342$$

2x/750 ppm = 0.467 => [X] = 175 ppm

$$\frac{A_X}{[X]}=F\left(\frac{A_S}{[S]}\right)$$

$$\frac{I_X}{I_S}=F\left(\frac{[X]}{[S]}\right)$$

**Example:** A sample containing $Ca^{2+}$ is tested as described in the table below. A 5.00 mM $Ca^{2+}$ standard is added in tube #2 . The instrumental signal is directly proportional (i.e. linear) to the concentration of the analyte.

| Tube # | mL of $Ca^{2+}$ unknown | mLs of $Ca^{2+}$ standard | Signal |
|---|---|---|---|
| 1 | 5.0 | 0.0 | 1.50 |
| 2 | 3.0 | 2.0 | 1.30 |

What is mM of Ca unknown?

$$\frac{[X]_i}{[S]_f + [X]_f} = \frac{I_X}{I_{S+X}}$$

$$\frac{[X]_i}{\frac{2}{5}\times 5 + \frac{3}{5}[X]_i} = \frac{1.50}{1.30} \Rightarrow [X]_i = 7.5mM$$