Topic 3 (Chapters 13-15 & 8-10) Absorption and Emission Spectrometry

1 Jablonski Diagram of Molecules

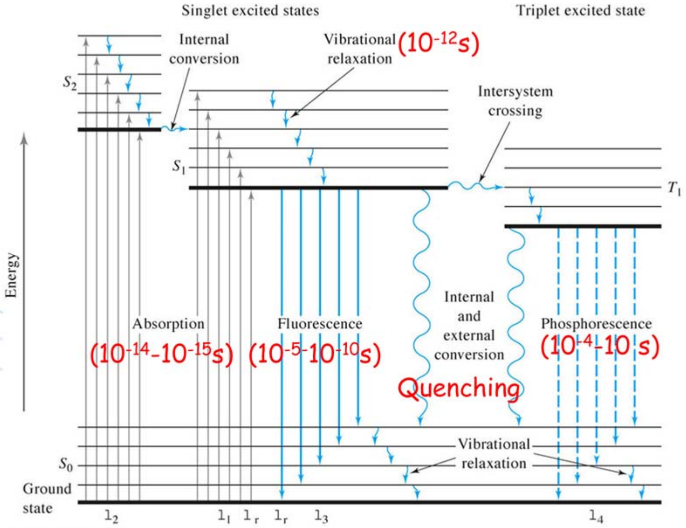

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Fig. 15-2 (p401)

Electronic states

Each electron has a unique set of quantum numbers (**Pauli Exclusion Principle**)

n	principle (1s, 2s, 3s,…)
l	angular momentum (l =0=s, l=1=p)
m	magnetic
s	spin

Any two electrons in same orbital (n,l,m) must have different spins

$s = +½$ or $-½$

$S = |\Sigma s_i|$

Multiplicity

2S+1 (1 = singlet sate, 2 = doublet state, 3 = triplet state, …)

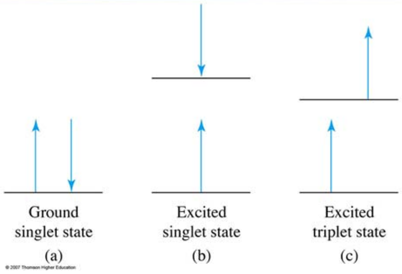


Fig. 15-1 (p401)

Different electronic states:

S_0: common, diamagnetic (not affected by B fields)
S_1: spins remain paired in the excited states
T_1: rare, spins become unpaired, paramagnetic (affected by B fields)

Lifetime (T_1, 10^{-4} ~ several sec) > Lifetime (S_1, 10^{-8} sec)
Energy (S_0) < Energy (T_1) < Energy (S_1)

Absorption:	very fast 10^{-14}-10^{-15} s $S_0 \xrightarrow{Absorption} S_1$
Fluorescence:	emission not involving spin change (S →S), efficient, short-lived < 10^{-5} s $S_1 \xrightarrow{Emission} S_0$
Phosphorescence:	emission involving spin change (T→S), low efficiency, long-lived > 10^{-4} s $T_1 \xrightarrow{Emission} S_0$

.

- **Internal conversion:** intermolecular radiationless transition to a lower electronic state where vibrational energy levels “overlaps” in energy

- **External conversion:** radiationless transition to a lower state by collisions between the excited state and solvent or other solute
  — solvent effects on fluorescence

- **Intersystem crossing:** transition with spin change (e.g. S → T)
  — common in molecules containing heavy atoms

- ***Predissociation:** relaxation to a lower electronic state with enough vibrational energy to break a bond
  — mostly affected by structure

- ***Dissociation:** excitation to a vibrational state with enough energy to break a bond

2 Molecular Absorption and Beer's Law

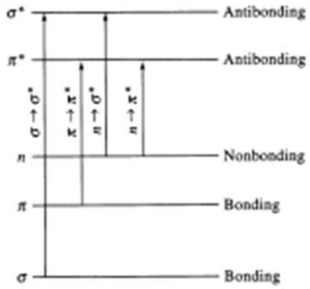
2.1 Excitation of outer valence (bonding) electrons

$$M + h\nu \xrightarrow{excitation} M^*$$

Absorbing species

Organic molecules

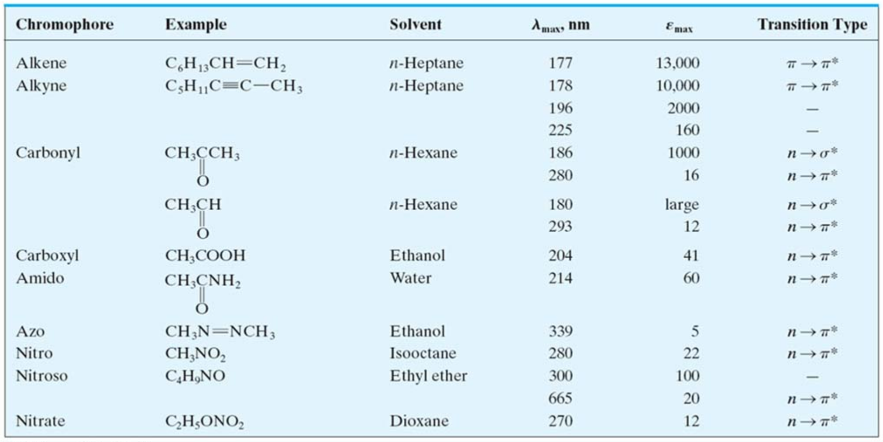
σ, π(bonding), n(non-bonding), σ*, π*(anti-bonding) orbitals



- $\sigma \rightarrow \sigma^*$ large ΔE (λ < 150 nm, out of range)
  ε = 10 -10,000 $Lmol^{-1}cm^{-1}$
- $n \rightarrow \sigma^*$ smaller ΔE (λ = 150 - 250 nm)
  ε = 200-2000 $Lmol^{-1}cm^{-1}$
- $\pi \rightarrow \pi^*$
  $n \rightarrow \pi^*$ smallest ΔE smallest
  (λ = 200 - 700 nm)
  ε = 10-10,000 $Lmol^{-1}cm^{-1}$

Ideal for UV-Vis spectrometry of organic chromophore

TABLE 14-1 Absorption Characteristics of Some Common Chromophores



Chromophore	Example	Solvent	λ_{max}, nm	ε_{max}	Transition Type
Alkene	$C_6H_{13}CH{=}CH_2$	*n*-Heptane	177	13,000	$\pi \rightarrow \pi^*$
Alkyne	$C_5H_{11}C{\equiv}C{-}CH_3$	*n*-Heptane	178	10,000	$\pi \rightarrow \pi^*$
			196	2000	—
			225	160	—
Carbonyl	$CH_3\underset{\underset{O}{\|}}{C}CH_3$	*n*-Hexane	186	1000	$n \rightarrow \sigma^*$
			280	16	$n \rightarrow \pi^*$
	$CH_3\underset{\underset{O}{\|}}{C}H$	*n*-Hexane	180	large	$n \rightarrow \sigma^*$
			293	12	$n \rightarrow \pi^*$
Carboxyl	CH_3COOH	Ethanol	204	41	$n \rightarrow \pi^*$
Amido	$CH_3\underset{\underset{O}{\|}}{C}NH_2$	Water	214	60	$n \rightarrow \pi^*$
Azo	$CH_3N{=}NCH_3$	Ethanol	339	5	$n \rightarrow \pi^*$
Nitro	CH_3NO_2	Isooctane	280	22	$n \rightarrow \pi^*$
Nitroso	C_4H_9NO	Ethyl ether	300	100	—
			665	20	$n \rightarrow \pi^*$
Nitrate	$C_2H_5ONO_2$	Dioxane	270	12	$n \rightarrow \pi^*$

Inorganic molecules

Transition metal ions are colored (absorption in Vis) due to d → d electronic transition

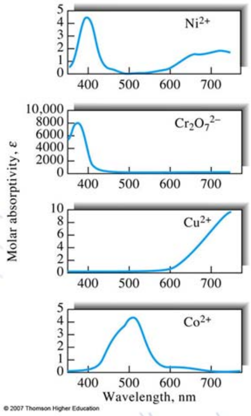


Fig. 14-3 (p370)

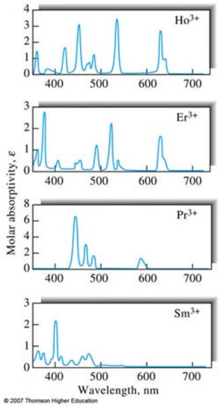


Fig. 14-4 (p371)

Charge-transfer absorption

$$AD + h\nu \xrightarrow{\text{excitation}} A^{+}D^{-}$$

A: electron donor, metal ion

D: electron acceptor, ligand

$\varepsilon > 10{,}000$

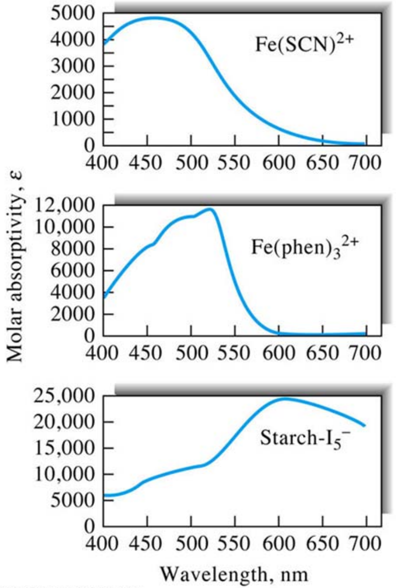


Fig. 14-5 (p371)

2.2 Beer's Law and its limitations

$A = -\log T = \log (P_0/P) = \varepsilon \cdot b \cdot c$

ε: molar absorptivity at a particular wavelength ($L \cdot mol^{-1} cm^{-1}$)

b: path length of absorption (cm)

c: molar concentration ($mol \cdot L^{-1}$)

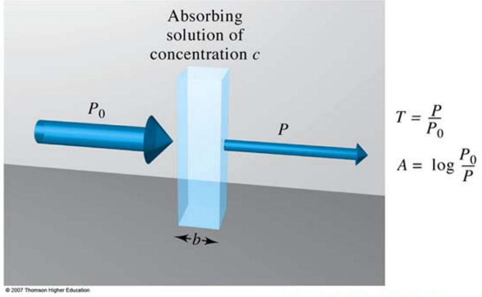


Fig. 6-25 (p158)

Light loss due to reflection (17.3%), scattering, …

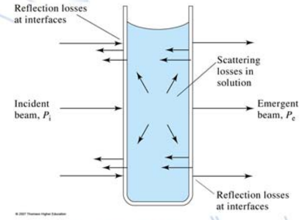
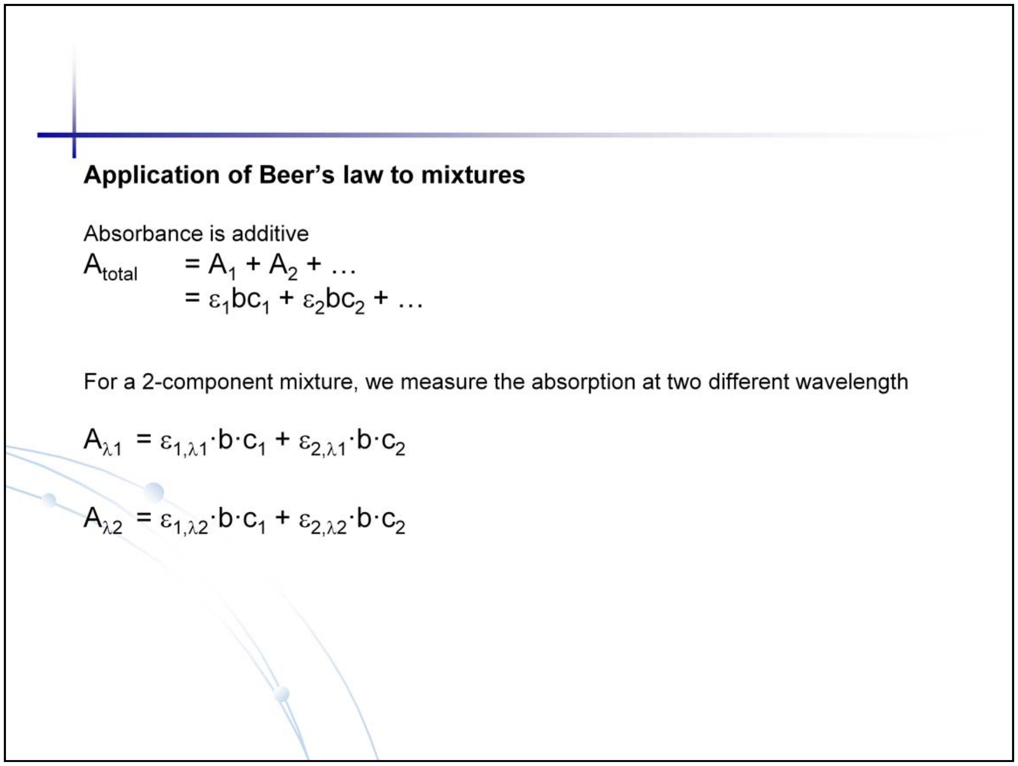


Fig. 13-1 (p 337)

Approximation of T and A

$$T = \frac{P_{solution}}{P_{solvent}} \approx \frac{P}{P_0}$$

$$A = \log \frac{P_{solvent}}{P_{solution}} \approx \log \frac{P_0}{P}$$



Application of Beer's law to mixtures

Absorbance is additive

$$A_{total} = A_1 + A_2 + \ldots$$
$$= \varepsilon_1 b c_1 + \varepsilon_2 b c_2 + \ldots$$

For a 2-component mixture, we measure the absorption at two different wavelength

$$A_{\lambda 1} = \varepsilon_{1,\lambda 1} \cdot b \cdot c_1 + \varepsilon_{2,\lambda 1} \cdot b \cdot c_2$$

$$A_{\lambda 2} = \varepsilon_{1,\lambda 2} \cdot b \cdot c_1 + \varepsilon_{2,\lambda 2} \cdot b \cdot c_2$$

2.2.1 Limitations of Beer's Law

- **Real deviations**

  At low concentration

  A = -log T = log (P_0/P) = $\varepsilon \cdot b \cdot c$

  At c > 0.01 M

  solute-solute interaction, hydrogen bond, …
  can alter the electronic absorption of molecules
  → dilute the solution to remedy problems

- **Chemical effects –** analyte associates, dissociates or reacts with a solvent to produce different species

Example: Acid-base equilibrium of an indicator

$HIn \Leftrightarrow H^+ + In^-$ $\mathrm{K_a} = 1.2\times10^{-5}$

	ε_{430}	ε_{570}	
HIn	6.30 x10^2	7.12x10^3	(measured in HCl solution)
In^-	2.06 x 10^4	9.61 x10^2	(measured in NaOH solution)

What’s the absorbance of unbuffered solution at c = 2 x 10^{-5} M?

$$K_a = \frac{[H^+][In^-]}{[HIn]} = 1.42\times10^{-5}$$

$$[H^+] = [In^-]$$

$$[HIn] = c - [In^-]$$

$$\rightarrow$$

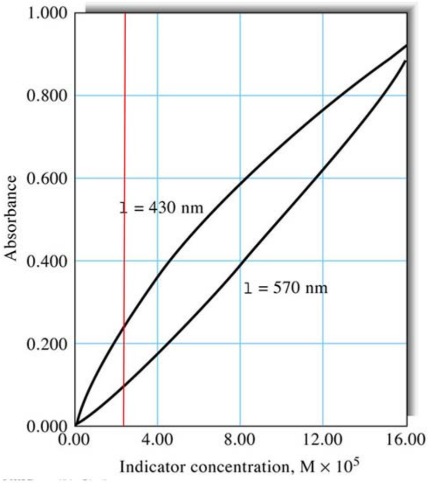
$$[In^-] = 1.12\times10^{-5}M$$

$$[HIn] = 0.88\times10^{-5}M$$

$$A_{430} = \varepsilon_{In^-,430}b[In^-] + \varepsilon_{HIn,430}b[HIn] = 0.236$$

$$A_{570} = \varepsilon_{In^-,570}b[In^-] + \varepsilon_{HIn,570}b[HIn] = 0.073$$

$$HIn \Leftrightarrow H^{+} + In^{-}$$



= [HIn] + [In$^-$]

Fig. 13-3 (p340)

- **Instrumental deviations due to polychromatic radiation**

  Beer's law applies to monochromatic absorption only.

  If a band of radiation consists of two wavelength λ' and λ", Beer's law applies to each wavelength

For first wavelength λ

$$A' = \log\frac{P_0'}{P'} = \varepsilon' bc$$

$$P' = P_0' 10^{-\varepsilon' bc}$$

For the second wavelength λ''

$$P'' = P_0'' 10^{-\varepsilon'' bc}$$

Measured absorbance

$$A_m = \log\frac{P_0' + P_0''}{P' + P''} = \log\frac{P_0' + P_0''}{P_0' 10^{-\varepsilon' bc} + P_0'' 10^{-\varepsilon'' bc}}$$

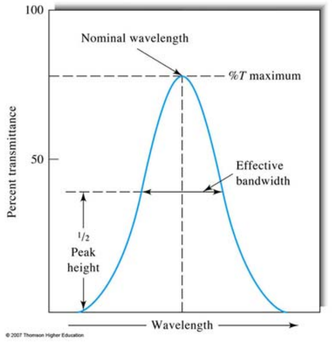


Fig. 7-11 (p176)

Non-linear calibration curve

$$A_m = \log\frac{P_0^{'} + P_0^{"}}{P' + P"} = \log\frac{P_0^{'} + P_0^{"}}{P_0^{'}10^{-\varepsilon' bc} + P_0^{"}10^{-\varepsilon" bc}}$$

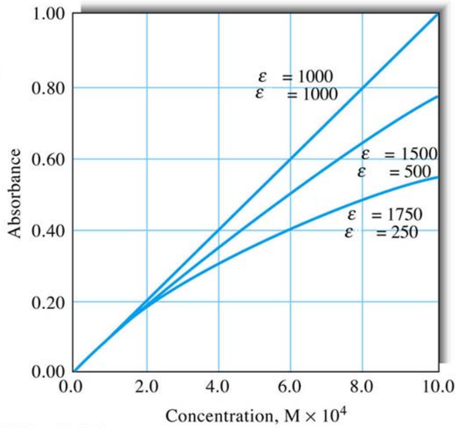


Fig. 13-4 (p341)

How to avoid :

Select a analysis band near the maximum absorption where the absorptivity changes little with wavelength

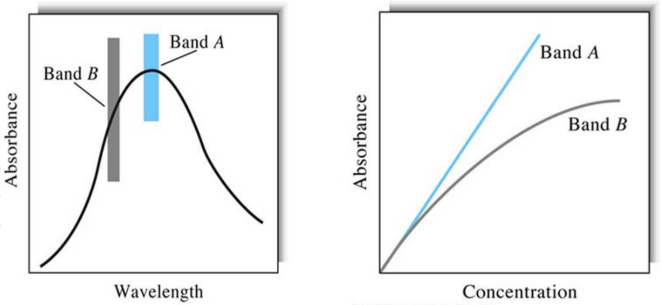


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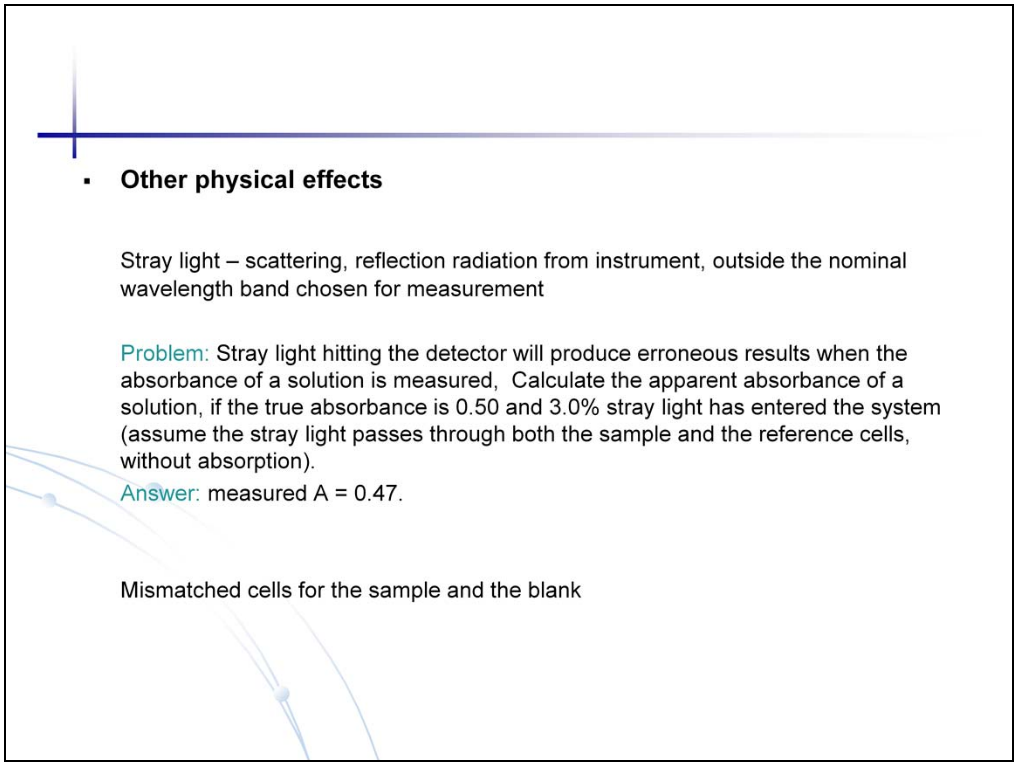
Fig. 13-5 (p341)



- **Other physical effects**

Stray light – scattering, reflection radiation from instrument, outside the nominal wavelength band chosen for measurement

Problem: Stray light hitting the detector will produce erroneous results when the absorbance of a solution is measured, Calculate the apparent absorbance of a solution, if the true absorbance is 0.50 and 3.0% stray light has entered the system (assume the stray light passes through both the sample and the reference cells, without absorption).

Answer: measured A = 0.47.

Mismatched cells for the sample and the blank

3 Instrumentation for Molecular Absorption

3.1 Designs

a. Single beam

b. Double-beam-in-space

c. Double-beam-in-time

Advantage of double beam configuration

- Compensate for fluctuation in the radiant output, drift in transducer, etc.
- Continuous recording of spectra

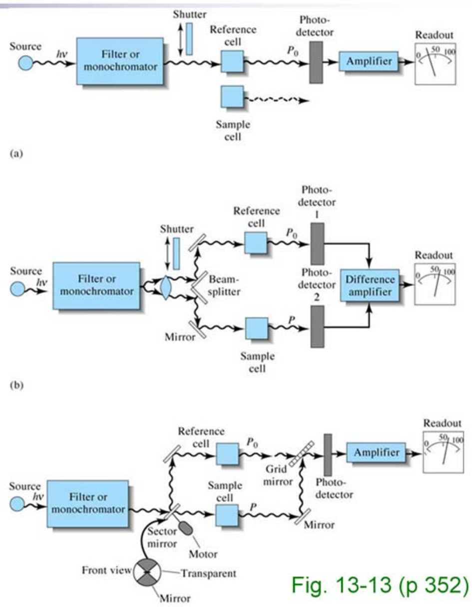
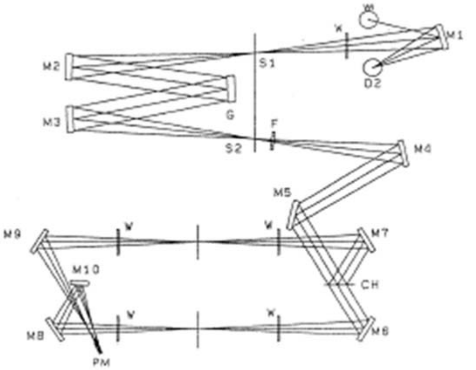


Fig. 13-13 (p 352)

Shimadzu UV-2450 Spectrophotometer

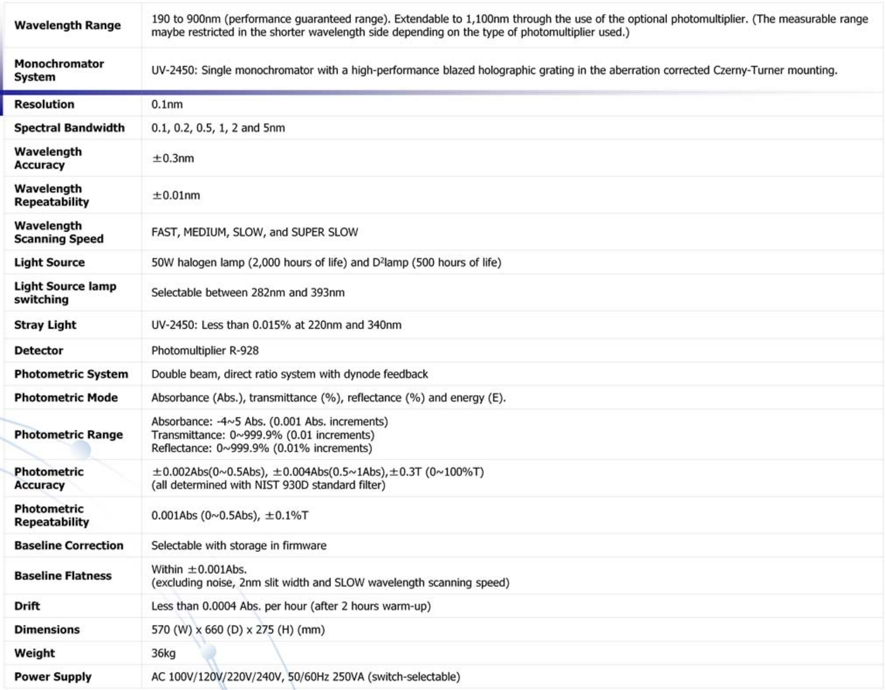


D2:	Deuterium lamp	G:	Diffraction grating
WI:	Halogen lamp	S2:	Exit slit
S1:	Entrance slit	F:	Filters
W:	Quartz windows	CH:	Beam chopper
M1 - M10:	Mirrors	PM:	Photomultiplier

Fig. 3.3 Optical Schematics of UV-2450

The light emitted from the light source (deuterium lamp, D2 or halogen lamp, WI) is reflected by the mirrors M1 and M2 and projected onto the monochromator. The light source is switched automatically depending upon the wavelength as follows:

D2 : 190 nm - light source switching wavelength
WI : light source switching wavelength - 900 nm
(The light source switching wavelength is selectable from 282 - 393 nm.)



Wavelength Range	190 to 900nm (performance guaranteed range). Extendable to 1,100nm through the use of the optional photomultiplier. (The measurable range maybe restricted in the shorter wavelength side depending on the type of photomultiplier used.)
Monochromator System	UV-2450: Single monochromator with a high-performance blazed holographic grating in the aberration corrected Czerny-Turner mounting.
Resolution	0.1nm
Spectral Bandwidth	0.1, 0.2, 0.5, 1, 2 and 5nm
Wavelength Accuracy	±0.3nm
Wavelength Repeatability	±0.01nm
Wavelength Scanning Speed	FAST, MEDIUM, SLOW, and SUPER SLOW
Light Source	50W halogen lamp (2,000 hours of life) and D^{2}lamp (500 hours of life)
Light Source lamp switching	Selectable between 282nm and 393nm
Stray Light	UV-2450: Less than 0.015% at 220nm and 340nm
Detector	Photomultiplier R-928
Photometric System	Double beam, direct ratio system with dynode feedback
Photometric Mode	Absorbance (Abs.), transmittance (%), reflectance (%) and energy (E).
Photometric Range	Absorbance: -4~5 Abs. (0.001 Abs. increments) Transmittance: 0~999.9% (0.01 increments) Reflectance: 0~999.9% (0.01% increments)
Photometric Accuracy	±0.002Abs(0~0.5Abs), ±0.004Abs(0.5~1Abs),±0.3T (0~100%T) (all determined with NIST 930D standard filter)
Photometric Repeatability	0.001Abs (0~0.5Abs), ±0.1%T
Baseline Correction	Selectable with storage in firmware
Baseline Flatness	Within ±0.001Abs. (excluding noise, 2nm slit width and SLOW wavelength scanning speed)
Drift	Less than 0.0004 Abs. per hour (after 2 hours warm-up)
Dimensions	570 (W) x 660 (D) x 275 (H) (mm)
Weight	36kg
Power Supply	AC 100V/120V/220V/240V, 50/60Hz 250VA (switch-selectable)

Effects of the monochromator exit slit width on spectra

Narrow exit slit width improves the spectrum resolution
but it also significantly reduce the radiant power

Trade-off between resolution and S/N ratio

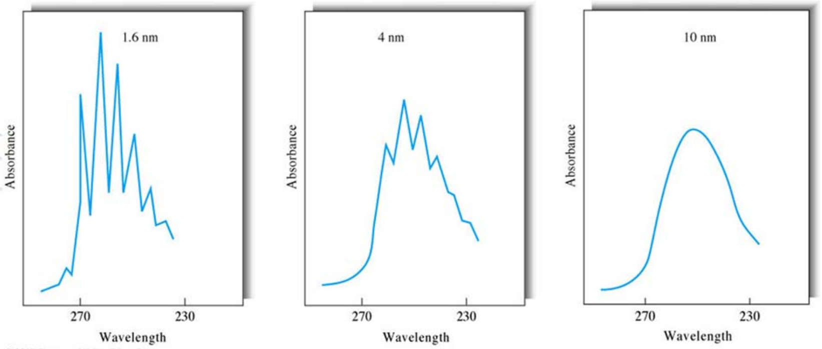


Fig. 13-8 (p347)

Another configuration − Multichannel spectrometer

No monochromator,

Disperse transmitted light and measure “all wavelength at once”

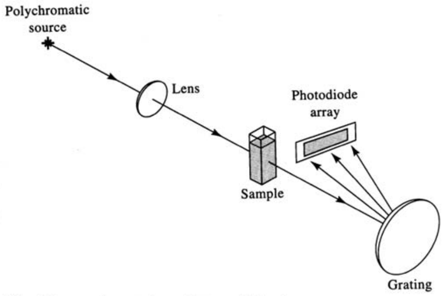


Fig. 13-15 (p353)

No Scanning-simple and fast

More expensive

Limited resolution

3.2 Noise of spectrophotometric analyses

$$c = -\frac{1}{\varepsilon b}\log T$$

$$\frac{\partial c}{\partial T} = -\frac{0.434}{\varepsilon b T}$$

$$\sigma_c^2 = (\frac{\partial c}{\partial T})^2 \sigma_T^2$$

$$s_c = \sqrt{\sigma_c^2}$$

$$s_T = \sqrt{\sigma_T^2}$$

$$\frac{s_c}{c} = \frac{0.434 s_T}{T \log T}$$

Use calculus to show that the minimum uncertainty occurs at 36.8%e, assuming the S_T is independent of concentration

Sources of instrumental noise

Case I $s_T = k_1$

Limited readout resol. (3-1/2 digit displays → 0.1% uncertainty from 0% -100% T)
Thermal noise in thermal detector, etc.

Case II $s_T = k_2\sqrt{T^2 + T}$

Shot noise in photon detector (random emission of photon from light source or e^- from PMT cathode)

Case III $s_T = k_3 T$

Flicker noise
Fail to position sample and blank cells reproducibly in replicate measurements (as a result, different sections of cell window are exposed to radiation, and reflection/scattering losses change)

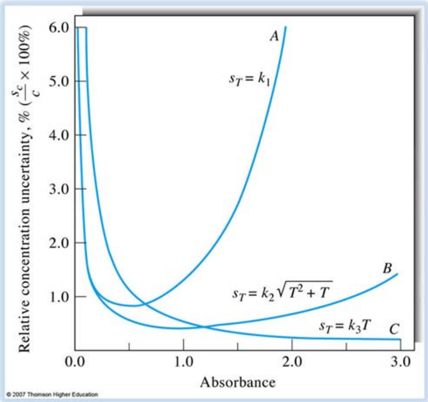


Fig. 13-7 (p345)

4 Fluorescence and Instrumentation

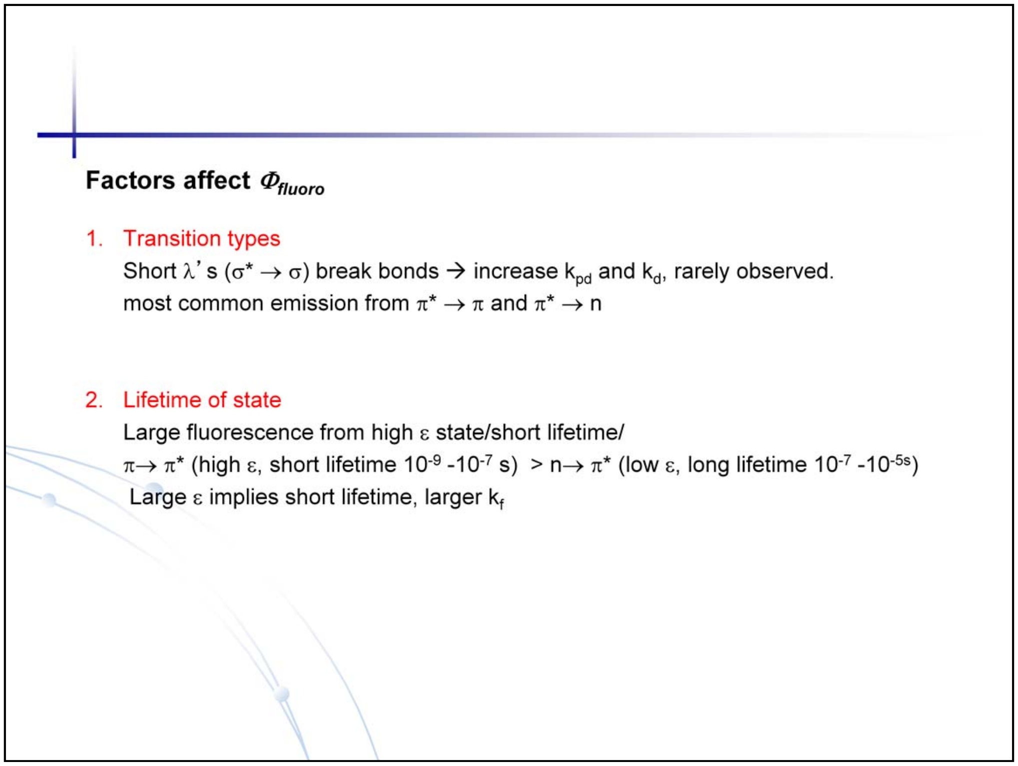
4.1 Fluorescence quantum yield

– ratio of number of molecules fluorescing to number excited

$$\Phi_{fluoro} = \frac{\text{number of photons fluorescing}}{\text{number of molecules excited}}$$

$$= \frac{k_f}{\underbrace{k_f + k_i + k_{ec} + k_{ic} + k_{pd} + k_d}_{\text{rate constants for deactivation processes}}}$$

- k_f, k_{pd} and k_d reflects structural effects,
- the remaining *k's* reflect chemical environments
- Not all molecules are able to fluoresce



Factors affect Φ_{fluoro}

1. Transition types

   Short λ' s ($\sigma^* \rightarrow \sigma$) break bonds → increase k_{pd} and k_d, rarely observed.
   most common emission from $\pi^* \rightarrow \pi$ and $\pi^* \rightarrow n$

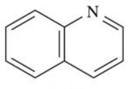
2. Lifetime of state

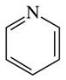
   Large fluorescence from high ε state/short lifetime/
   $\pi \rightarrow \pi^*$ (high ε, short lifetime 10^{-9} -10^{-7} s) > $n \rightarrow \pi^*$ (low ε, long lifetime 10^{-7} -10^{-5}s)
   Large ε implies short lifetime, larger k_f

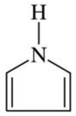
3. Structure

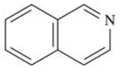
   a) Many aromatics fluoresce, fluorescence increased by # of fused ring

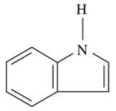
   - short S_1 lifetime, no/slowly accessible T_1


quinoline


pyridine


pyrrole


isoquinoline

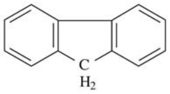

indole

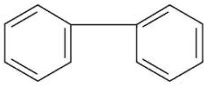
   b) substitution on/in ring

   - heterocyclic, COOH or C=O on aromatic ring decrease energy of n→π*, ↓ Φ
   - heavy atom substitution increase k_i, ↓ Φ

4. Rigidity

   Rigid structures fluorescence (decrease k_{ic})
   increase in fluorescence with chelation


fluorene


biphenyl

5. Temperature, pH, solvent
   ↑ temp, ↑ k_{ec}; ↓ viscosity, ↑ k_{ec};
   pH affects electronic structure of acidic or basic substituents;
   dissolved oxygen (paramagnetic), ↑ k_i
   heavy atom effect(solutes and solvent), ↑ k_i

6. Concentration

$$\overbrace{F}^{Fluorescence} = K'\overbrace{(P_0 - P)}^{Absorbed} = K'P_0(1-10^{-\overbrace{\varepsilon bc}^{A}})$$

$$= K'P_0(2.303\varepsilon bc - \frac{(2.303\varepsilon bc)^2}{2!} + \frac{(2.303\varepsilon bc)^3}{3!} + \cdots](\text{Maclaurin series})$$

$$= K' \cdot 2.303\varepsilon bc \cdot P_0 \text{ (when A} < 0.05)$$

$$= K \cdot c$$

* only works at low A (<0.05), otherwise high-order terms become important
* self quenching (collision between excited states)
* secondary absorption (emission reabsorbed by other molecules in solution)

7. Collision quenching (dynamic quenching) − Stern-Volmer equation

$$\Phi_f^0 = \frac{k_f}{k_f + k_{ec} + k_{ic} + k_{pd} + k_d}$$

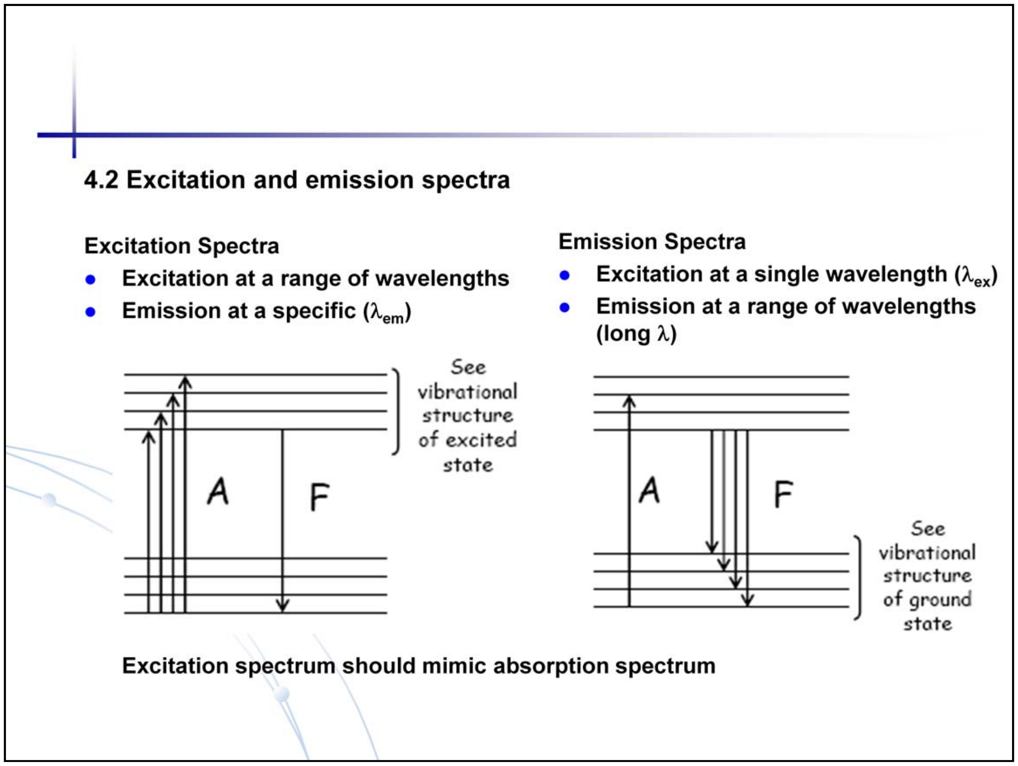
$$\Phi_f = \frac{k_f}{k_f + k_{ec} + k_{ic} + k_{pd} + k_d + k_q[Q]},$$

where k_q is the quenching constant and [Q] is the quencher concentration

$$\frac{\Phi_{\mathrm{f}}^0}{\Phi_{\mathrm{f}}} = 1 + k_d'[Q],$$

where $k_d' = \frac{k_q}{k_f + k_{ec} + k_{ic} + k_{pd} + k_d}$

$$\frac{F_0}{F} = 1 + k_d'[Q]$$



4.2 Excitation and emission spectra

Excitation Spectra

- **Excitation at a range of wavelengths**
- **Emission at a specific (λ_{em})**

Emission Spectra

- **Excitation at a single wavelength (λ_{ex})**
- **Emission at a range of wavelengths (long λ)**

Excitation spectrum should mimic absorption spectrum

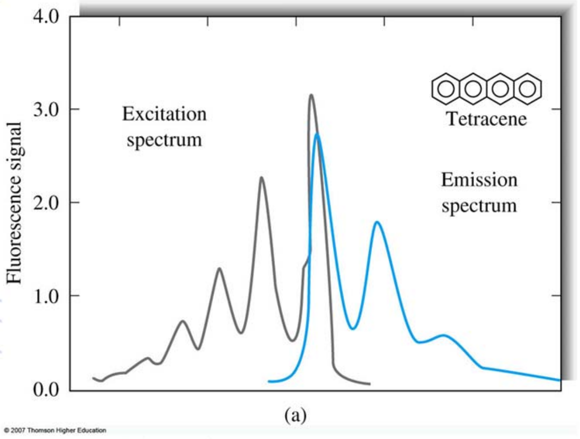


Fig. 15-7 (p411)

Excitation spectrum mimics absorption spectrum

Fluorescence spectrum at lower energy (longer wavelength)

4.3 Fluorometer Designs

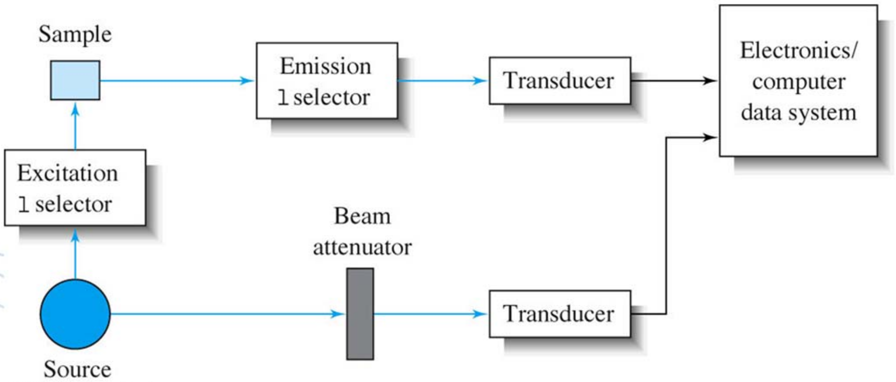


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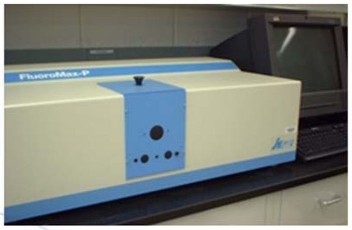
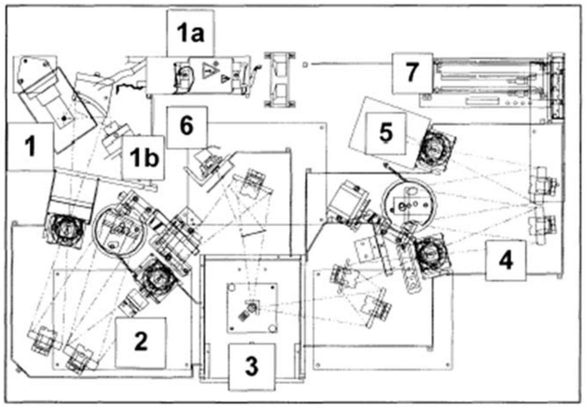
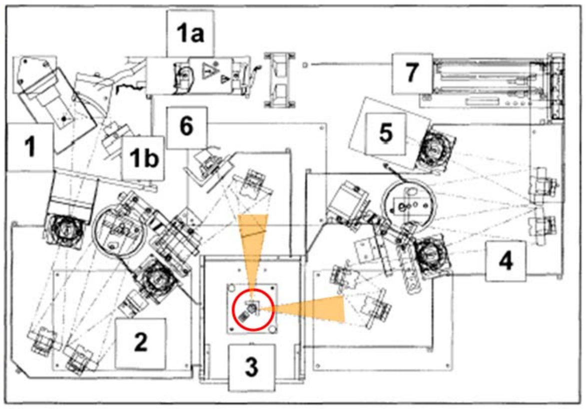
Fig. 15-8 (p412)

FluoroMax-P





1 Xenon arc-lamp and lamp housing
1a Xenon-lamp power supply
1b Xenon flash lamp (FluoroMax®-P only)
2 Excitation monochromator



1	Xenon arc-lamp and lamp housing
1a	Xenon-lamp power supply
1b	Xenon flash lamp (FluoroMax®-P only)
2	Excitation monochromator
3	Sample compartment
4	Emission monochromator
5	Signal detector (photomultiplier tube and housing)
6	Reference detector (photodiode and current-acquisition module)
7	Instrument controller

Phosphorimeter, similar to fluorometer, with two additional components

1. measure the intensity of phosphorescence after a time delay
2. low-temp phosphorescence needs dewar flask

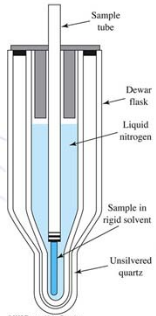


Fig. 15-13 (p417)

4 Applications of Molecular Spectrometry

4.1 Absorption has limited qualitative application

Solvent effects on the UV-Vis spectra
Polar solvents “blur” vibrational features
Polar solvents shift absorption maxima

n → π^*	blue shift
$\pi \rightarrow \pi^*$	red shift

UV-Vis not reliable for qualitative but excellent for quantitative analysis

But it is excellent for quantitative analysis
Determining the relationship between *A* and *c*
External Standards
Standard-Addition

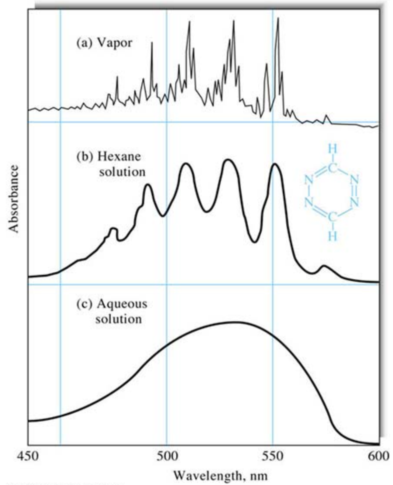


Fig. 14-1 (p368)

Spectrophotometric kinetics

$$A + R \Leftrightarrow P$$

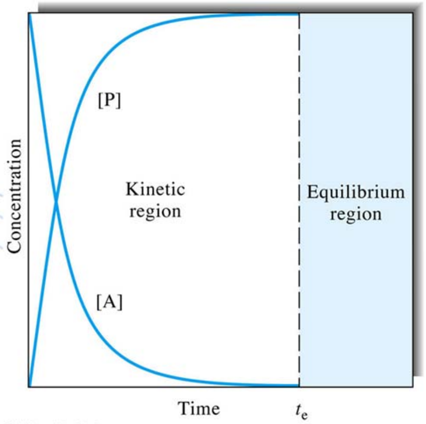


Fig. 14-14 (p382)

Stopped-flow mixing for reactions of 2-4 ms half lives

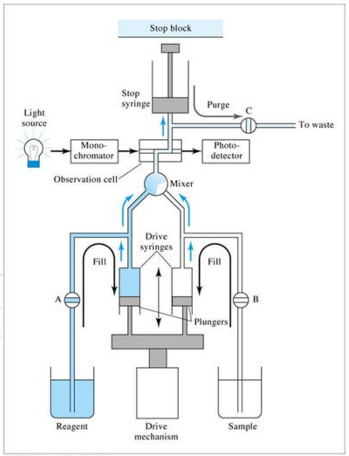


Fig. 14-16 (p384)

4.2 Fluorescence has better sensitivity

Not universally applicable

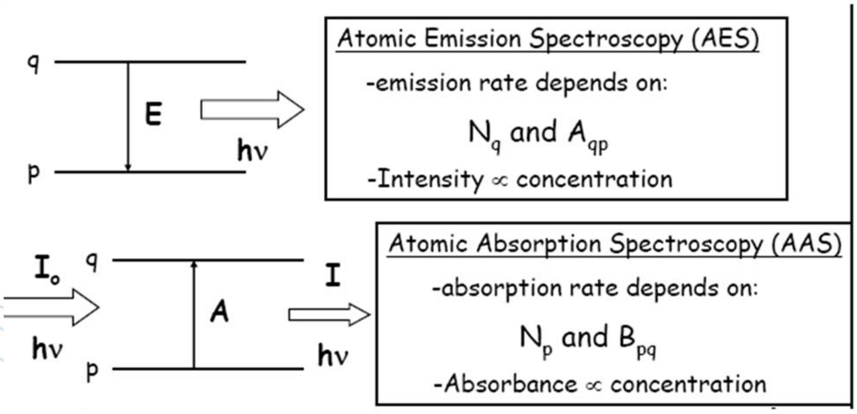
Better detection limit (ppb or below) than UV/VIS absorbance

- Nature of emission versus absorbance measurement
- Signal dependence on source intensity

Limited qualitative analysis

Multi-component analysis requires separation (excellent detection method for HPLC compounds that fluoresce)

5 Atomic Absorption & Emission Spectrometry



Atomic Emission Spectroscopy (AES)

-emission rate depends on:

N_q and A_{qp}

-Intensity ∝ concentration

Atomic Absorption Spectroscopy (AAS)

-absorption rate depends on:

N_p and B_{pq}

-Absorbance ∝ concentration

5.1 Atomic energy level diagrams

Every element has an unique set of atomic orbitals
p, d, f .. split by spin-orbit coupling

Spin (s) and orbital (l) motion create magnetic fields that perturb each other (couple)
if fields parallel – higher energy
if fields antiparallel – lower energy.

Define spin-orbit coupling by J (total angular momentum)
$J = L + S$ ($L=\Sigma l$ $S= \Sigma s$) (positive values only)

Examples:
s electron ($l = 0$, $s = +1/2$ or $-1/2$) $J = 0+ \frac{1}{2} = \frac{1}{2}$
p electron ($l = 1$, $s = +1/2$ or $-1/2$) $J = 1+1/2 = 3/2$ (higher energy) or
$J = 1-1/2 = 1/2$ (lower energy)

Electronic term symbol
${}^{2S+1}L_J$ L written as letter (S, P, D) instead of number
Na = $1s^2 2s^2 2p^6 3s^1$, $L = 0$, $S= 1/2$, ${}^2S_{1/2}$
Na* = $1s^2 2s^1 2p^6 3p^1$, $L = 1$, $S= 1/2$, ${}^2P_{3/2,\,1/2}$

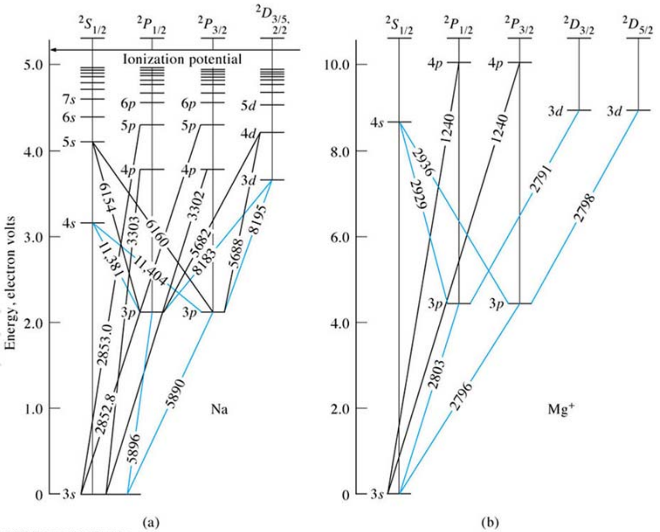


Fig. 8-1 (p216) Energy level diagrams for Na and Mg^+

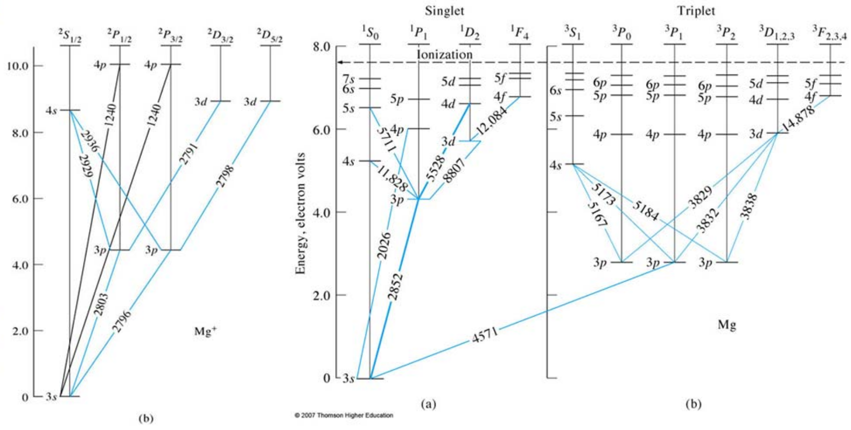


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Fig. 8-1a and 8-2 (p216-217)

Energy level diagram for Mg⁺, and atomic magnesium

- Similar pattern between atoms but different spacing
- Spectrum of an ion different to that of the corresponding atom
- Energy levels measured in electron volts (eV)
  1 eV $= 1.602 \times 10^{-19}$ C × 1 V(J/C) $= 1.602 \times 10^{-19}$ J
  $= 96.484$ kJ .mol^{-1}
- As number of electron increases, the number of levels increases, emission spectra become more complex

5.2 Atomic line widths

5.2.1 Line broadening from the uncertainty principle

Uncertainty principle: must measure for some minimum time to tell two frequencies apart

$\Delta t \cdot \Delta E \geq h$

$\Delta t \cdot \Delta \nu \geq 1$

Δt: minimum time for measurement

$\Delta \nu$: minimum detectable difference in frequencies

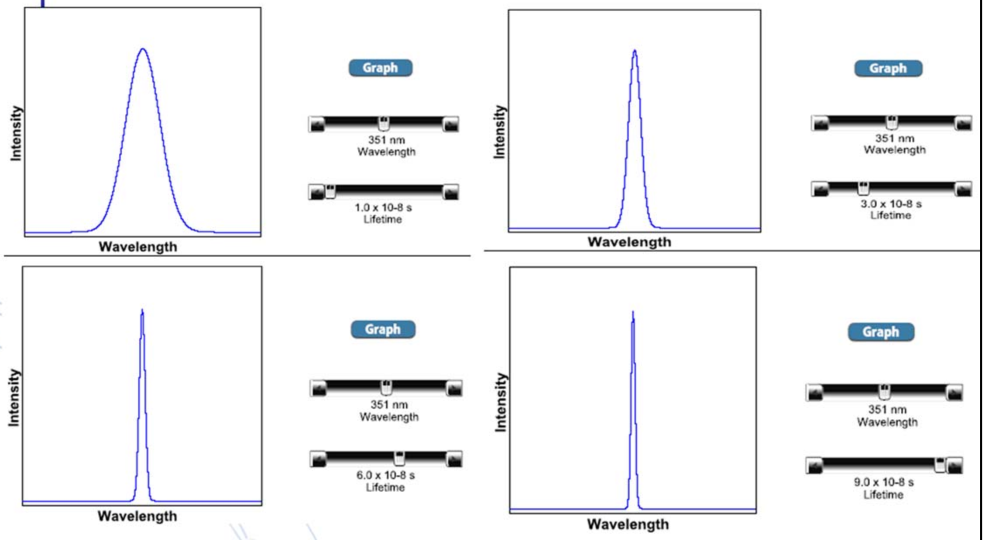
Shows up in lifetime of excited state
- if lifetime infinitely long, ΔE infinitely narrow
- if lifetime short, ΔE is broadened

$\nu = c/\lambda$

Differentiating ν with regard to λ

$d\nu = -c\lambda^2 d\lambda$, $d\nu \approx \Delta\nu$ and $d\lambda \approx \Delta\lambda$

$\Delta\lambda = \Delta\nu\lambda^2/c$ **natural line widths**



351 nm
Wavelength
1.0 x 10-8 s
Lifetime

351 nm
Wavelength
3.0 x 10-8 s
Lifetime

351 nm
Wavelength
6.0 x 10-8 s
Lifetime

351 nm
Wavelength
9.0 x 10-8 s
Lifetime

5.2.2 Doppler broadening

Change in frequency produced by motion relative to detector

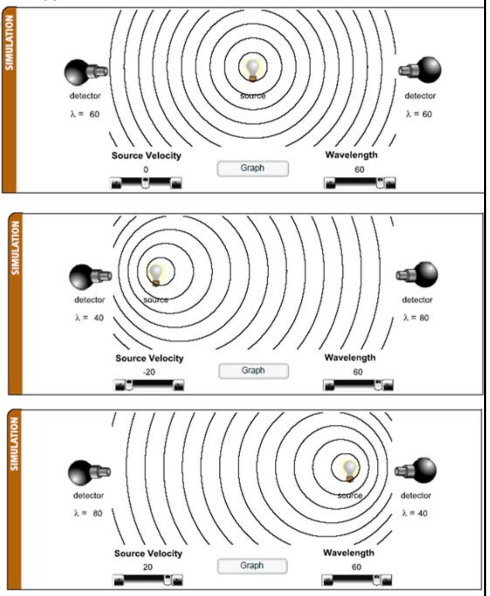
In gas, broadens line symmetrically because of Maxwell-Boltzmann velocity distribution

Average velocity of atoms increases as $(T)^{1/2}$

At room T, line widths 10^{-2} - 10^{-3} A

Total line width typically 1-10 A

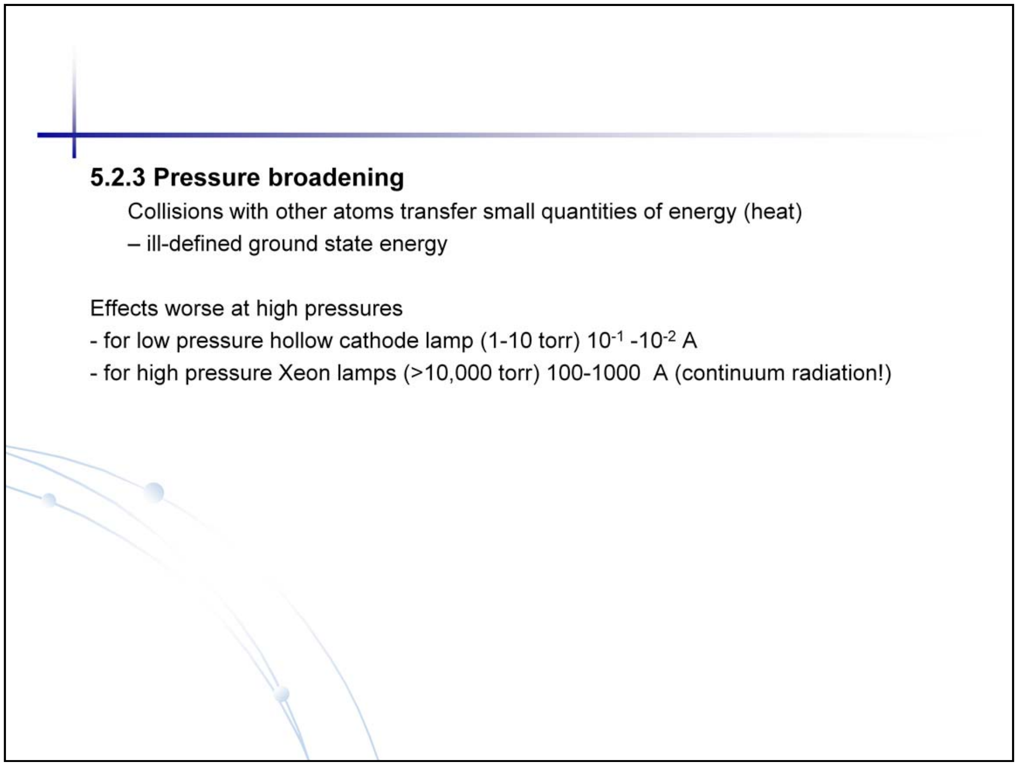
Doppler Effect



λ = 60 λ = 60
Source Velocity 0
Wavelength 60

λ = 40 λ = 80
Source Velocity -20
Wavelength 60

λ = 80 λ = 40
Source Velocity 20
Wavelength 60



5.2.3 Pressure broadening

Collisions with other atoms transfer small quantities of energy (heat)
– ill-defined ground state energy

Effects worse at high pressures
- for low pressure hollow cathode lamp (1-10 torr) 10^{-1} -10^{-2} A
- for high pressure Xeon lamps (>10,000 torr) 100-1000 A (continuum radiation!)

5.3 AAS

- determination of *elements* not compounds
- needs radiation source
- high temperature for atomization

5.3.1 Atomization

- Flame atomizer for solutions

1. Desolvation: solvent evaporates to produce solid aerosol
2. Volatilization: form the gas molecules
3. Dissociation: produce atomic gas
4. {Ionization: ionize to form cations + electrons}
5. {Excitation: excited by heat of flame, emission}

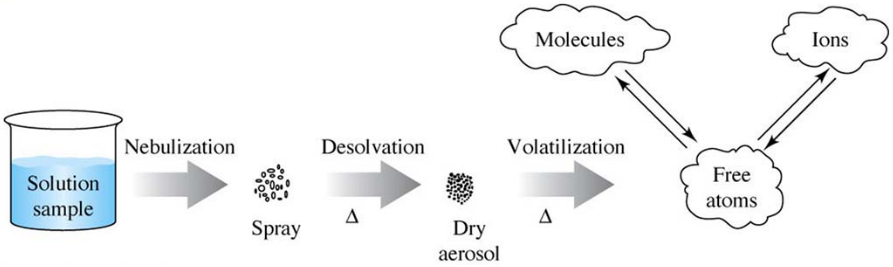


Fig. 8-10 (p225)
Processes leading to atoms, molecules and ions with continuous sample introduction into a flame.

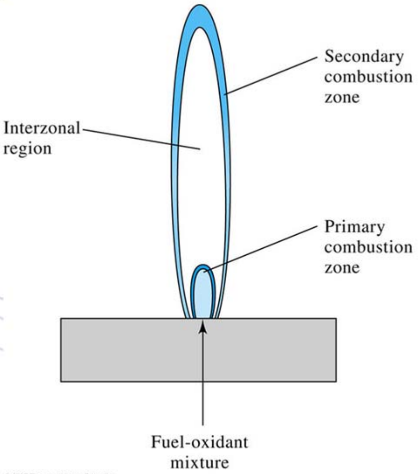


Fig. 9-2 (p231) Regions in a flame

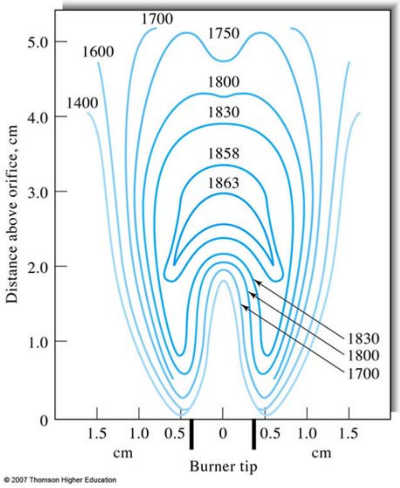


Fig. 9-3 (p232) Temperature (°c) profile for a natural gas-air flame

Flame structure

a. Primary combustion zone:
  - blue luminescence from emission of C_2/CH
  - cool {thermal equilibrium not achieved)
  - initial decomposition, molecular fragments

b. Interzonal region:
  - hottest (several cm)
  - most free atoms, wildly used part

c. Secondary combustion zone:
  - cooler
  - conversion of atoms to molecular oxides {then disperse to surroundings}

Flame temperatures

Fuel	**Oxidant**	**T (°C)**
Natural gas	Air	1700 ~ 1900
H_2	O_2	2550 ~ 2700
Acetylene	O_2	3050 ~ 3000

Sensitive part for AAS

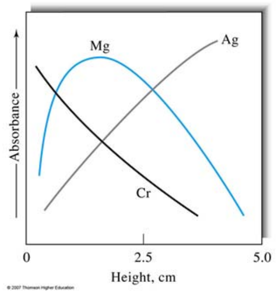


Fig. 9-4 (p232)

- Sensitivity varies with element
  Element rapidly oxides – near burner
  Element poorly oxidizes – away from burner
- Optimize burner position for each element
- Difficult for multi-element detection

Laminar flow burner

- Stable and quite flame
- Long path length for absorption
- Disadvantages: short residence time in the flame (0.1 ms)

  low sensitivity (a large fraction of sample flows down the drain)

  Flashback

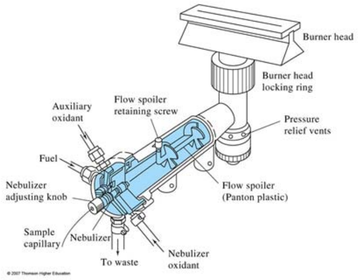


Fig. 9-5 (p233) A laminar-flow burner

Advantages

- Simplest atomization, needs preliminary sample treatment.
- Best for reproducibility (relative error <1%)
- Relatively intensive – incomplete volatilization, short time in beam

- Electrothermal atomization (Method of choice when flame atomization fails)

- Analysis of solutions as well as solids
- Three stages: - dry at low temperature (120°C, 20s)
  - ash at higher temperature(500-1000°C, 60s), removal of volatile hydroxides, sulfates, carbonates
  - atomize of remaining analyte at 2000-3000 °C (ms~s)
- High sensitivity ← less sample and longer residence time in optical path (10^{-10} -10^{-13} g analyte, 0.5-10uL sample, $2x10^{-6}$ -$1x10^{-5}$ ppm)
- Less reproducible (relative precision 5-10%)
- Slow (several minutes for each element)
- Narrow dynamic range

Two inert gas stream are provided

- External Ar gas prevents outside air from entering/incinerating tube
- Internal Ar gas circulate the gaseous analyte

Output signals from graphite furnace

- Drying
- Ashing (both from volatile absorbing species, smoke scattering)
- Atomize (used for analysis)

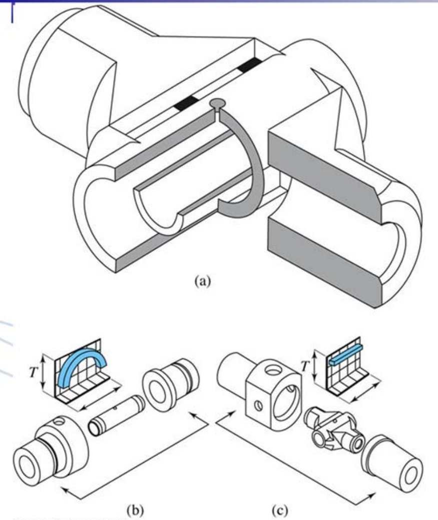


Fig. 9-6 (p234) Graphite furnace electrothermal atomizer

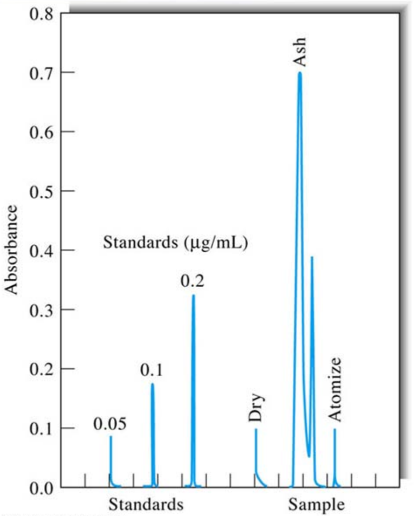


Fig. 9-7 (p235) Typical output from electrothermal atomizer

5.3.2 Radiation source

- Each element has narrow absorption lines (0.002-0.005nm), very selective.
- For a linear calibration curve (Beer's law), source bandwidth should be narrower than the width of an absorption line.

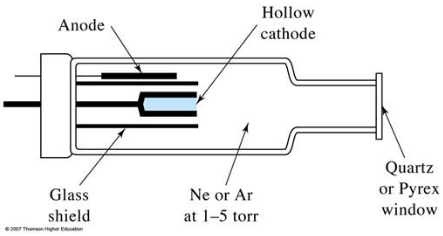
  \- continuum radiation source requests a monochromator with $\Delta\lambda_{eff} < 10^{-4}$ nm, difficult!
- Solutions:
  - LINE source at discrete wavelength,

    resonance line, using 589.6 nm emission line of sodium as a source to probe Na in analyte
  - operate line source with bandwidth narrower than the absorption line width

    minimize the Doppler broadening

    lower temperature and pressure than atomizer

Hollow cathode lamp



Hollow cathode design:

Concentrate radiation in limited region;

Enhance the probability of redeposition on cathode

Fig. 9-11 (p.238)

- Electric discharge (300V) of Ar between tungsten anode and a cylindrical metal cathode in a sealed glass tube filled with Ar (1-5 τ)
- Ar^+ bombard cathode and sputter cathode atoms
- Fraction of sputtered atoms excited, then emit characteristic radiation
- Cathode made of metal of interest (Na, Ca, K, Fe,.. or mixture of several metals) → give intense narrow line source of cathode material

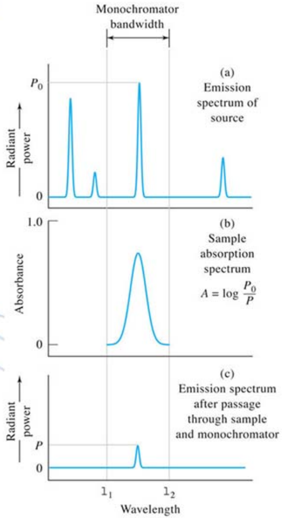
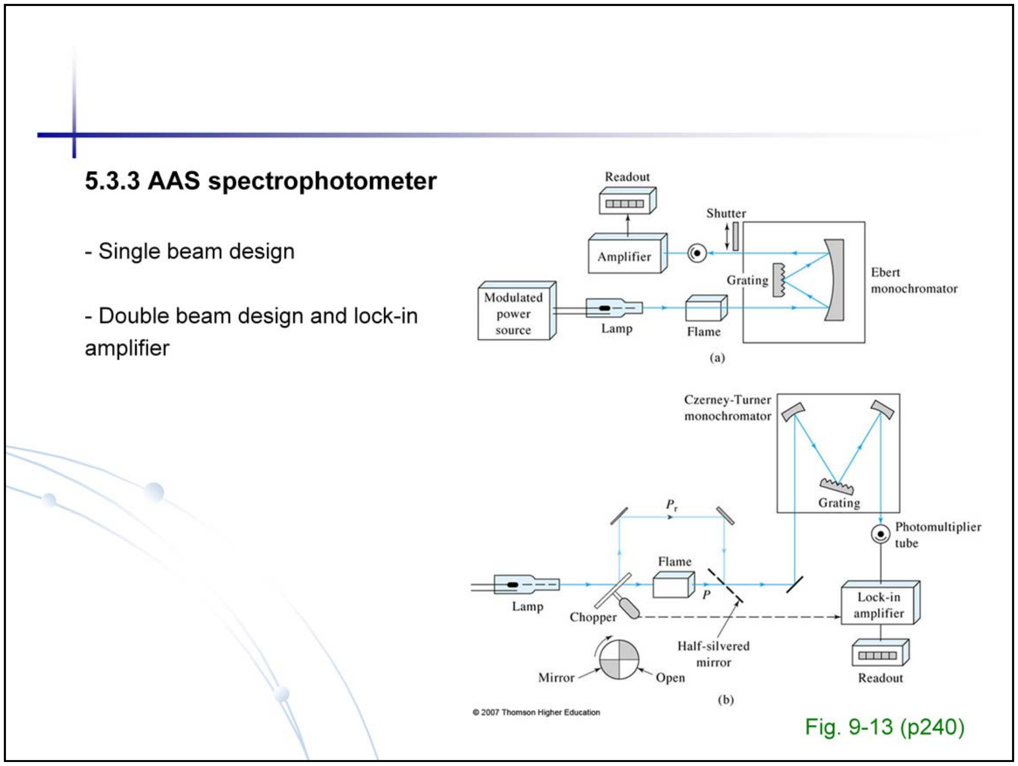


Fig. 9-10 (p238) Absorption of a resonance line by atoms



5.3.3 AAS spectrophotometer

- Single beam design
- Double beam design and lock-in amplifier

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Fig. 9-13 (p240)

5.4 AES

Sample introduction

1. Nebulizer – convert solutions to fine spray or aerosol
2. Electrothermal vaporizer (ETV)
   Only for introduction, not atomization
3. Other methods
   Direct insertion {powder placed inside flame, plasma, arc or spark atomizer}
   Laser ablation {uses laser to vaporize sample}

5.4.1 Atomization for AES

$$\frac{N_j}{N_0} = \frac{g_j}{g_0}\exp\left(-\frac{E_j}{kT}\right)$$

Emission relies on the number of excited atoms, requiring close control of temperature (e.g., at 2500K Na only has 0.02% atoms in the 1st excited state, a rise of 10 K in temperature results in 4% increase of excited atoms)

Less important in absorption, 99.8% atoms in ground state!

Inductively coupled plasma (ICP)

Three Argon flow

1. Plasma gas (10-20 L/min)
2. Nebulizer gas (~1L/min)
3. Optional auxiliary gas (~0.5L/min)

Radio-frequency (RF) power up to 2kW ~ 8000 K

Heated from outside-in

Torch up to 1” diameter

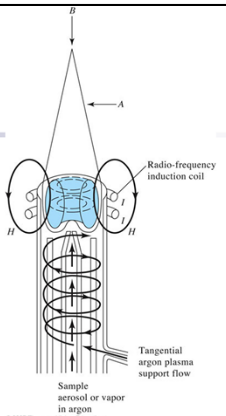

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Fig. 10-1 (p255)

Plasma structure

- Brilliant white core – Ar continuum radiation
- Flame-like tail up to 2cm
- Transparent region (15-20 mm above the core) – measurement made

- Analyte atoms have 2 ms residence time and experience temperature from 5000 - 800K. Atomized in “inert” atmosphere. Little ionization.

- Torch may be viewed radially or axially

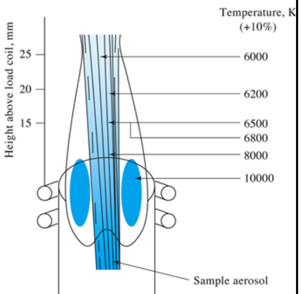

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Fig. 10-4 (p258)

5.4.2 Plasma source AES spectrophotometer

- Sequential (scanning and slew-scanning)

  Slew-scan spectrometers – Rapid scan (slewed) across blank regions

  Slow scan across lines

  Computer control/preselected lines to scan

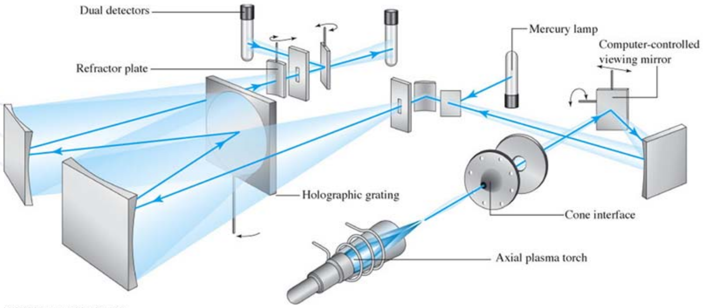

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Fig. 10-6 (p260)

- Multichannel spectrometer

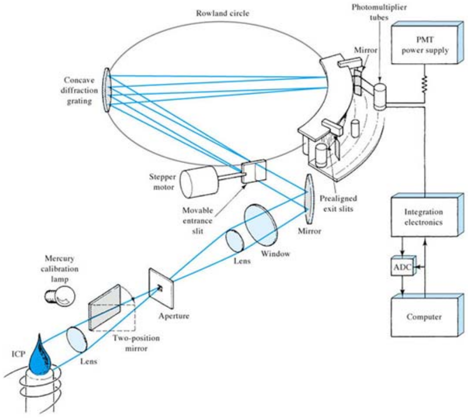

Fig. 10-8 (p262)

5.5 Plasma AES vs. Flame AAS

AAS	**AES**
Similar atomization technique to AES	
Addition of radiation source	No radiation source
High temperature for atomization	Very high temperature for excitation
(flame and electrothermal atomization)	(plasma/arc/spark)
Low cost instrumentation	moderate-high cost
Single element	simultaneous multielement analysis
Quantitative	qualitative and quantitative
Low sample throughput	high sample throughput
Atomization interference	spectral interference (large # of lines)
Detection limit 0.001-0.020 ppm	10ppb
Greater precision	

complementary techniques