ICP-OES

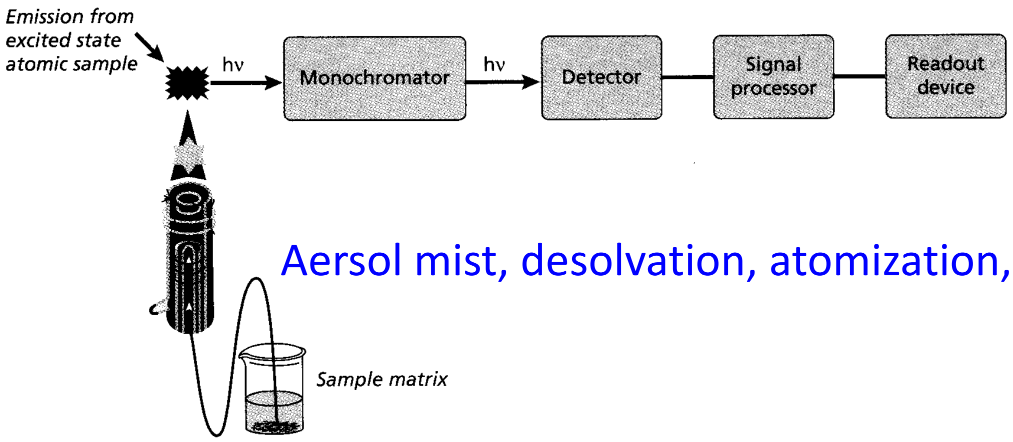


Figure 9.2 Schematic of a generic atomic emission spectrometer.

Aersol mist, desolvation, atomization, excitation

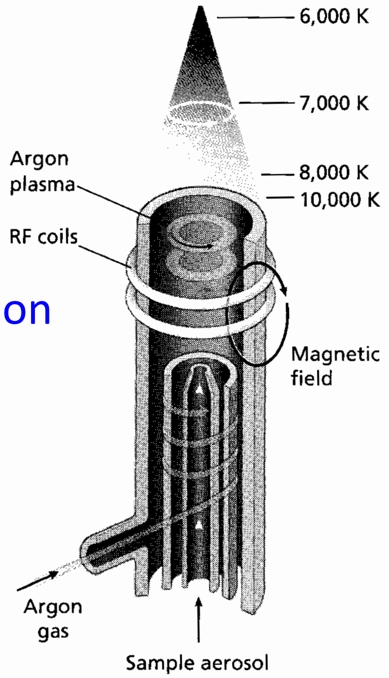


Figure 9.4 ICP torch.

- **High temperatures, more complete atomization – emission.**
- **Multi-element analysis**
- **One set of conditions for all analyses**
- **Inert Ar atmosphere so fewer chemical interferences (metal oxide formation)**

Chapter 13 and 14 – Molecular Absorption Spectroscopy

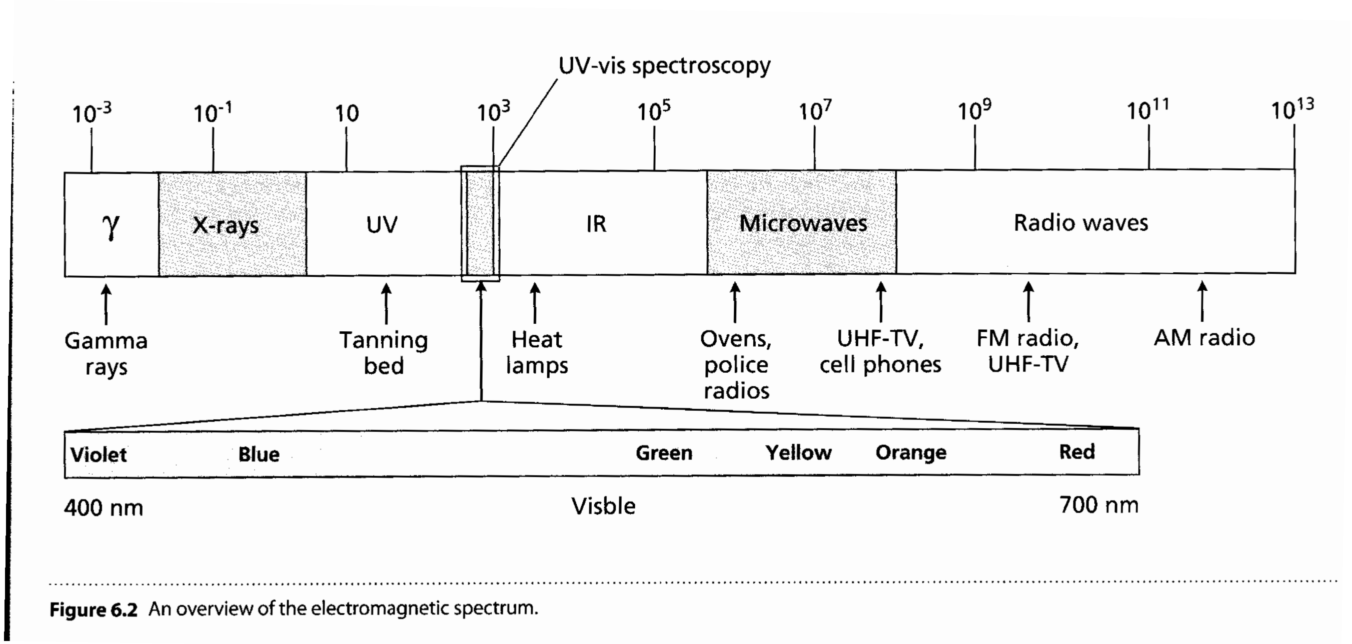
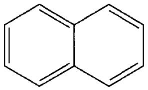


Figure 6.2 An overview of the electromagnetic spectrum.

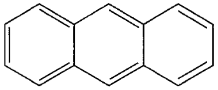
Probing the presence of analytes by the interaction with electromagnetic radiation.

Different regions of the spectrum probe different properties of molecules (electronic, vibrational and rotational states) and atoms (electronic states).

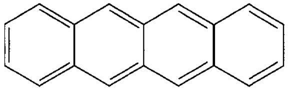
Thought Problem and Experiment Design



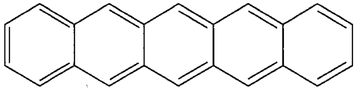
Naphthalene
(colorless)
λ_{max} = 280 nm



Anthracene
(yellow)
λ_{max} = 364 nm



Tetracene
(orange)
λ_{max} = 475



Pentacene
(navy blue)
λ_{max} = 610 nm

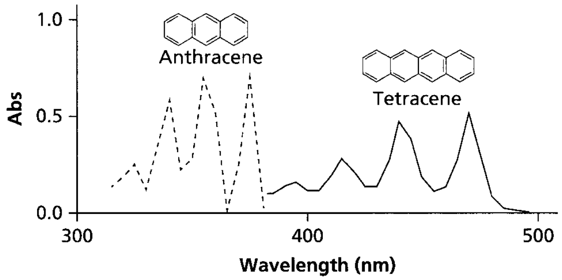


Figure 6.5 UV-vis spectra of anthracene and tetracene.

How would you analyze a solution for these molecules?

How would you quantify them?

Basic Instrument Design

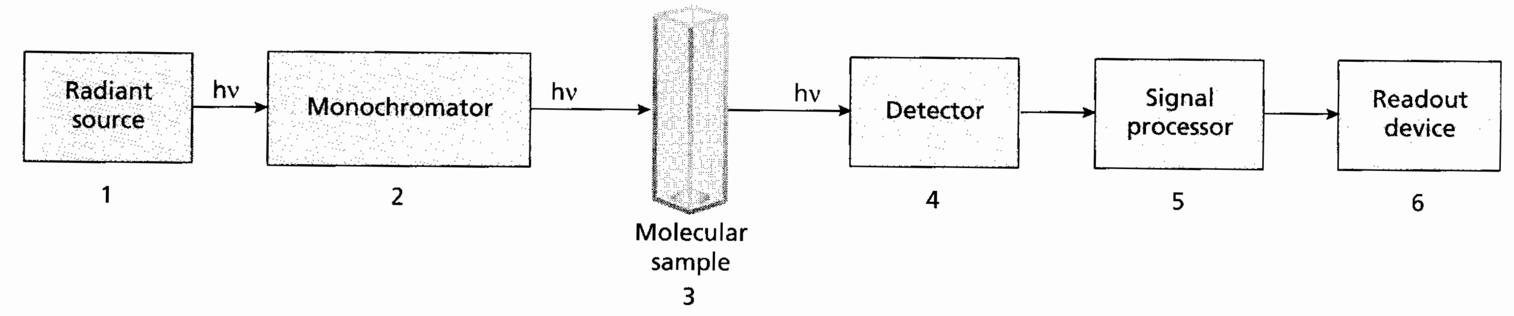


Figure 6.1 Basic schematic of a UV-vis spectrophotometer.

What properties of the different components would be important?

What region of the electromagnetic spectrum is used for these measurements?

What properties of molecules are probed? Qualitative and quantitative analysis?

What Happens in the Molecule When Absorbing Light?

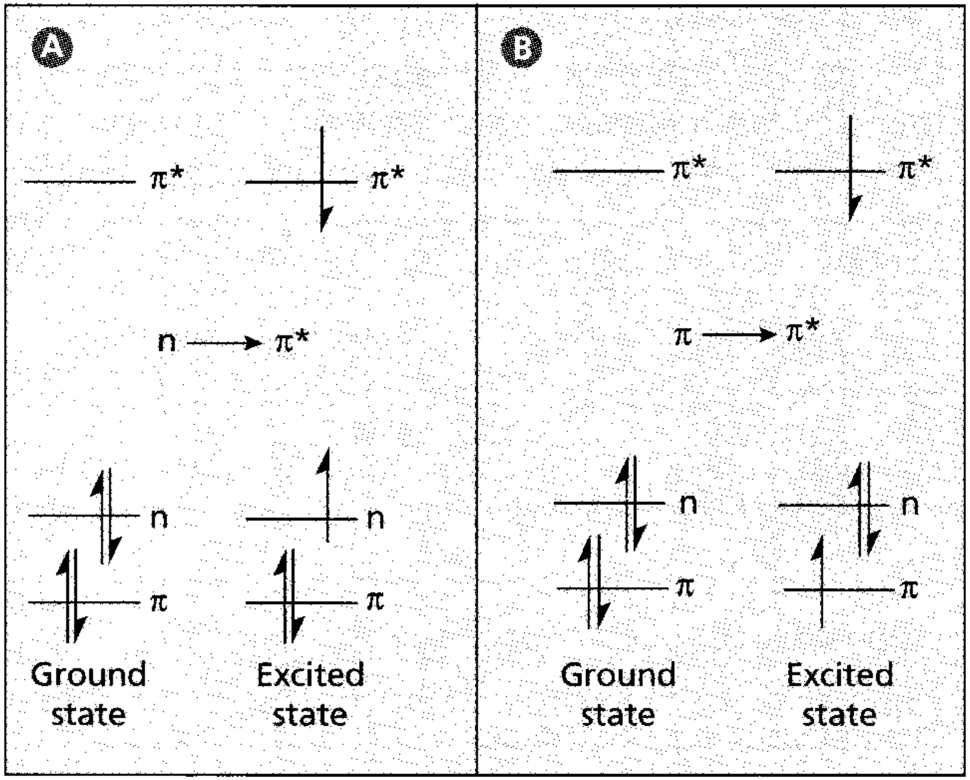


Figure 6.4 A look at two possible transitions in formaldehyde. Here we are looking at only the upper portion of the MO diagram as presented in Figure 6.3. The lower energy (sigma) portion of the MO diagram has been omitted for clarity. Panel (A) shows the n → π* transition. Panel (B) shows the π → π* transition.

Absorbance Measurements in Gas vs. Liquid Phase

Solvent matters!!!

Polar solvents tend to obliterate the fine structure.

As a rule, same solvent system should be used when comparing absorption spectra for identification purposes.

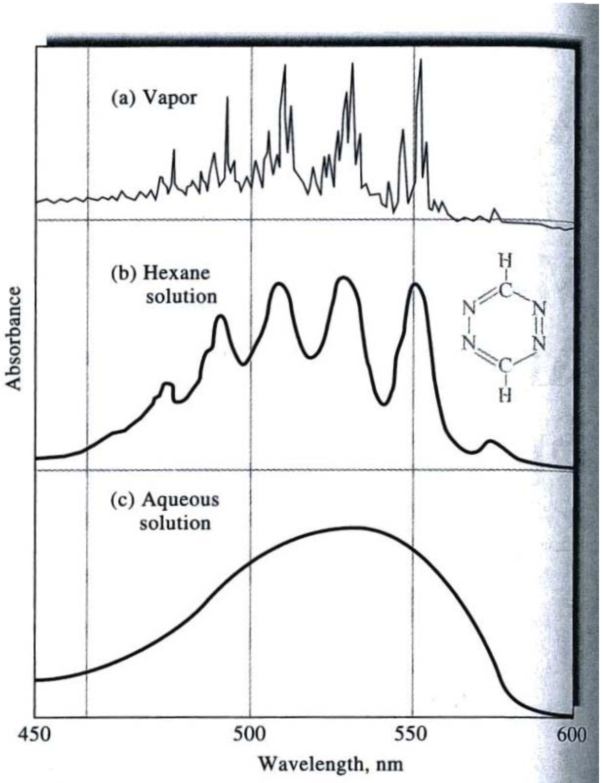


FIGURE 14-1 Ultraviolet absorption spectra for 1,2,4,5-tetrazine. In (a), the spectrum is shown in the gas phase, where many lines due to electronic, vibrational, and rotational transitions can be seen. In a nonpolar solvent (b), the electronic transitions can be observed, but the vibrational and rotational structure has been lost. In a polar solvent (c), the strong intermolecular forces cause the electronic peaks to blend, giving only a single smooth absorption band. (From S. F. Mason, *J. Chem. Soc.*, **1959**, 1265.)

Absorption spectra for vapor shows much fine structure (e.g., numerous rotational and vibrational states associated with excited electronic state are visible.

In condensed state, less rotational freedom so rotational states not observed.

When chromophore is surrounded by solvent molecules, energies of vibrational levels are modified in a nonuniform way . Energy of a given state appears as a broad peak.

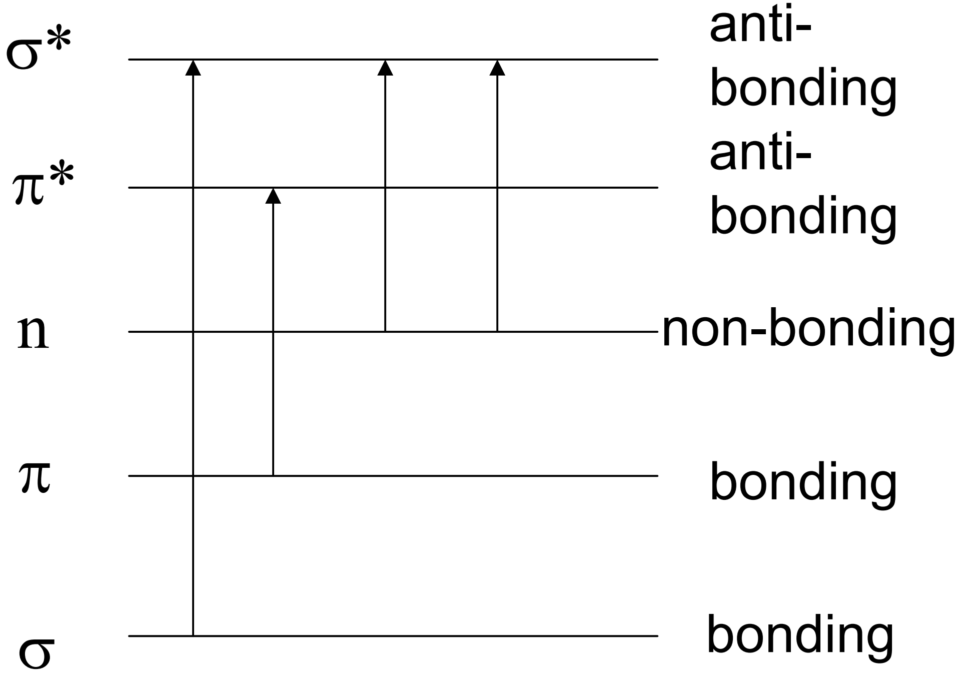
Absorbing Species

$M + h\upsilon \longrightarrow M^*$ Excitation event (10^{-9} s)

$M^* \longrightarrow M$ + heat or light Relaxation event

UV/Vis – excitation of bonding electrons!

Can be used for quantitative purposes and for functional group (type of bonding) information.



Absorbing Organic Molecules Containing σ, π and n Electrons

Absorbing functional groups = *chromophores*

Olefins and aromatics

$\sigma \rightarrow \sigma^*$ < 185 nm

$n \rightarrow \sigma^*$ 150-250 nm

$\pi \rightarrow \pi^*$
$n \rightarrow \pi^*$ 200-700 nm

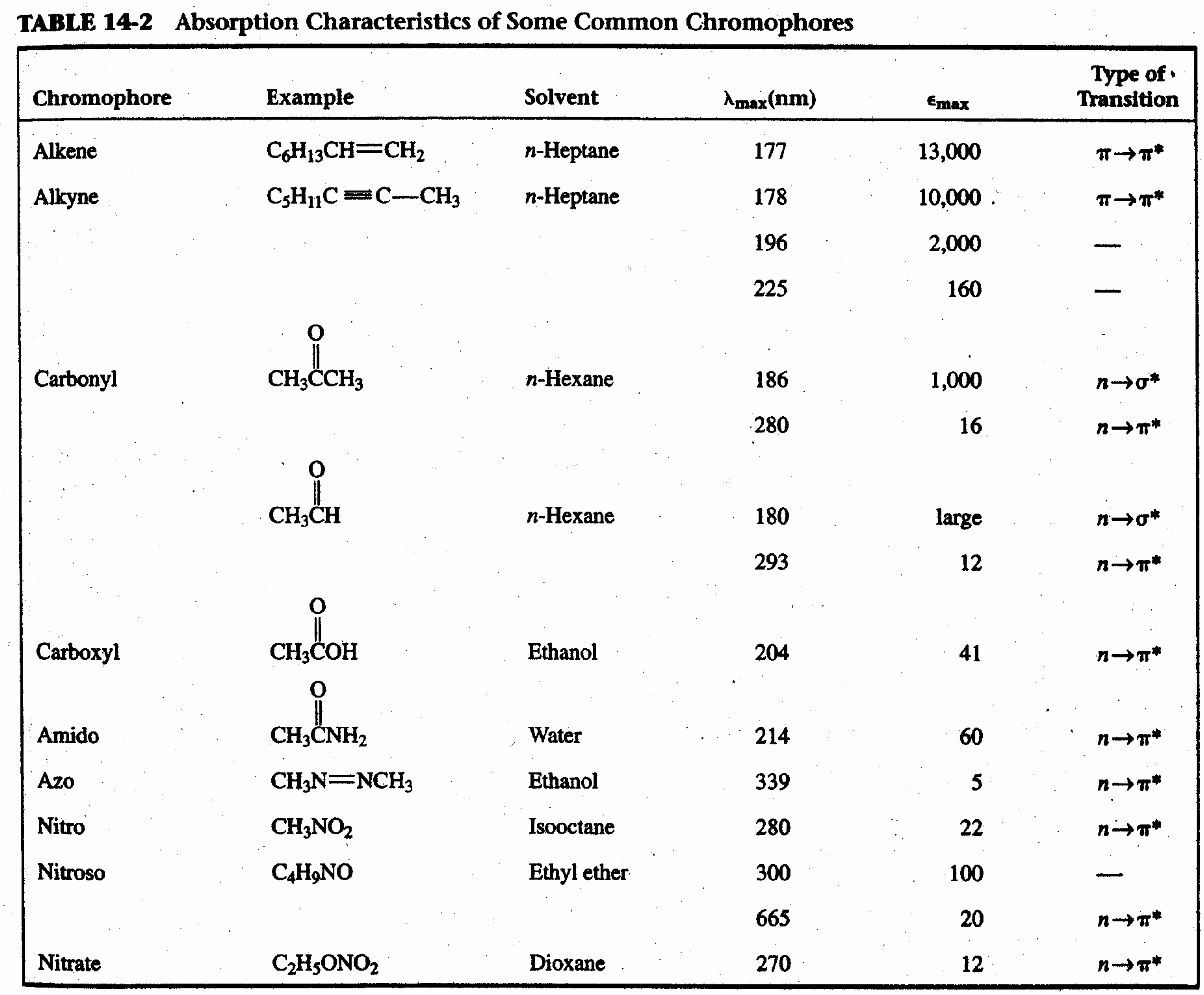


TABLE 14-2 Absorption Characteristics of Some Common Chromophores

Chromophore	Example	Solvent	λ_{max}(nm)	ϵ_{max}	Type of Transition
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	2,000	—
			225	160	—
Carbonyl	$CH_3\overset{\overset{O}{\|}}{C}CH_3$	*n*-Hexane	186	1,000	$n \rightarrow \sigma^*$
			280	16	$n \rightarrow \pi^*$
	$CH_3\overset{\overset{O}{\|}}{C}H$	*n*-Hexane	180	large	$n \rightarrow \sigma^*$
			293	12	$n \rightarrow \pi^*$
Carboxyl	$CH_3\overset{\overset{O}{\|}}{C}OH$	Ethanol	204	41	$n \rightarrow \pi^*$
Amido	$CH_3\overset{\overset{O}{\|}}{C}NH_2$	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	$n \rightarrow \pi^*$

Conjugation = delocalization lowers energy level of π^* orbital

Quantitative Aspects of Absorbance

$$T = \frac{P}{P_o}$$ **Eq. 6.4**

Absorbance is defined as the negative log of the transmittance.

$$A = -\log T = -\log \frac{P}{P_o} = \varepsilon bc$$ **Eq. 6.5**

where

- A = absorbance (unitless)
- T = transmittance (unitless)
- P_o = initial radiant power reaching the detector
- P = radiant power reaching the detector after passing through the sample
- ε = molar absorptivity (L/mole·cm)
- b = path length of the sample (cm)
- c = concentration (M)

Beer's law is a shortened version of Equation 6.5.

$$A = \varepsilon bc$$ **Eq. 6.6**

Deviations from Beer’s Law Relationship

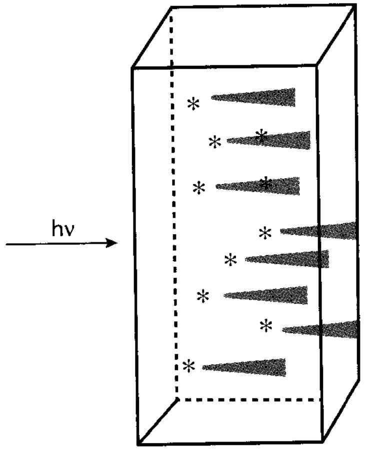
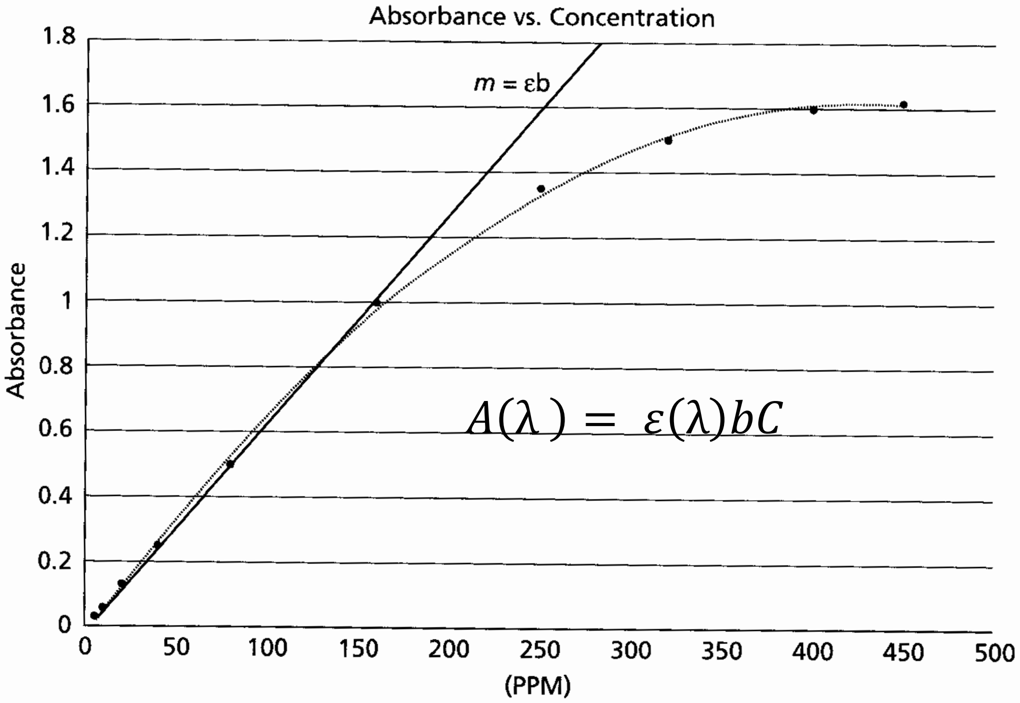


Figure 6.14 A representation of internal screening.



$$A(\lambda) = \varepsilon(\lambda)bC$$

Figure 6.13 A representation of the linearity of Beer’s law as a function of concentration. Beer’s law is generally linear below one absorbance. Above one absorbance, the slope of the Abs. vs. Conc. line usually bends towards zero.

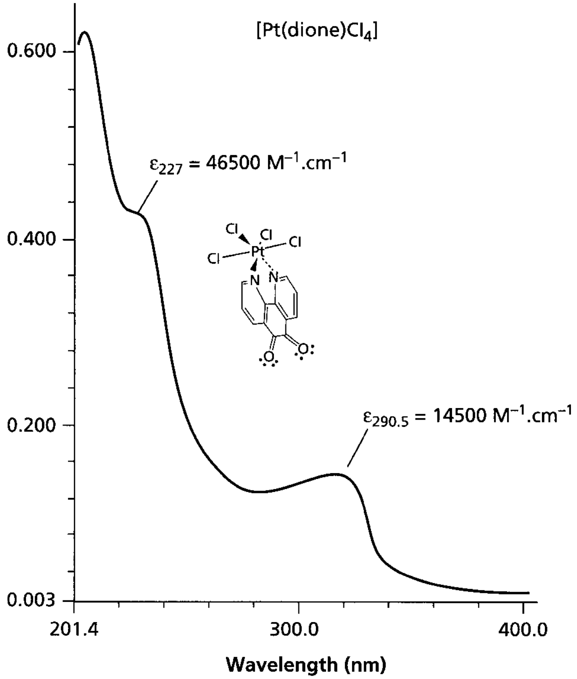
High concentrations!

$\varepsilon = 8.7 \times 10^{19}$ P A

P = probability of electronic transition (0-1)

A = capture cross section area (10^{-15} cm^2)

Spectroscopic Data and Analysis



$\varepsilon_{227} = 46500\ M^{-1}.cm^{-1}$

$\varepsilon_{290.5} = 14500\ M^{-1}.cm^{-1}$

Figure 6.12 UV-vis spectrum of 1-10-phenanthroline-5,6-dione platinum(IV) chloride [Pt(dione)Cl$_4$] in dry acetonitrile.

Use the spectroscopic data to determine the concentration of Pt(dione)Cl$_{4.}$

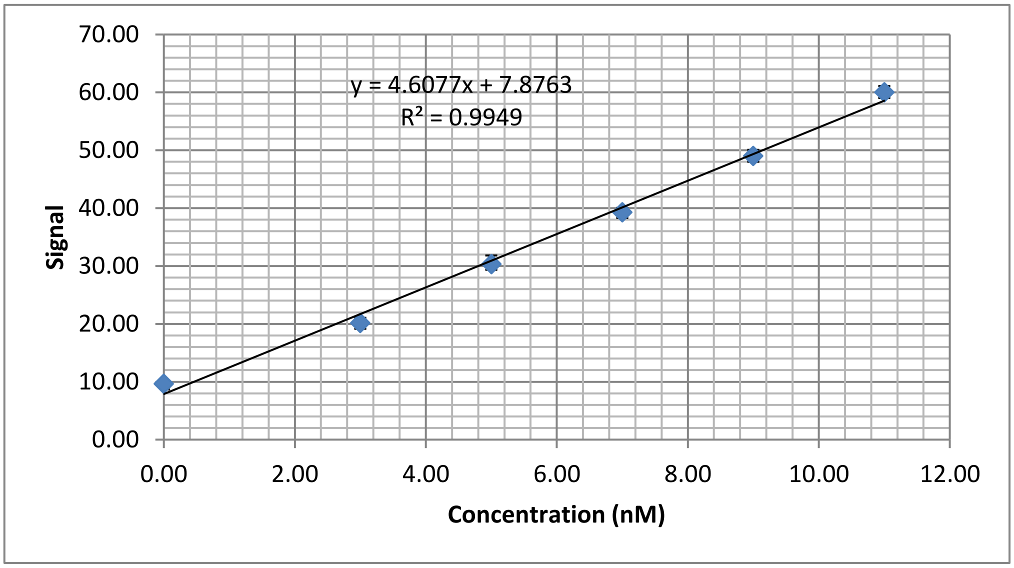
$$C = \frac{A}{b\varepsilon_{290.5}} = \frac{0.145}{(1\ cm)(14500)}$$

$$\varepsilon = \frac{L}{mol - cm}$$

$$C = 10\ \mu M$$

Conc (nM)	**Signal**			**Mean**	**Std Dev.**	**Conc (nM)**	**Mean**	**Std Dev.**
0.00	10.00	9.75	9.25	9.67	0.312	0.00	9.67	0.31
3.00	20.00	21.32	19.15	20.16	0.893	3.00	20.16	0.89
5.00	30.00	32.3	28.75	30.35	1.470	5.00	30.35	1.47
7.00	40.00	39.65	38.26	39.30	0.751	7.00	39.30	0.75
9.00	50.00	47.55	49.5	49.02	1.057	9.00	49.02	1.06
11.00	60.00	61.35	58.75	60.03	1.062	11.00	60.03	1.06

Ymin	10.60		Ymin = Yblank + 3*s	Yblank = mean
Ymin	12.78		Ymin = Yblank + 10*s	
Cmin	0.20	S/N=3	Cmin = (Ymin-Yblank)/m	
Cmin	0.68	S/N=10	Cmin = (Ymin-Yblank)/m	



m =	4.61	7.88	**b =**
sm =	0.17	1.14	**sb =**
R2=	0.99	1.49	**sy =**

Single Beam Spectrometer

Monochromator before sample. Reduces sample heating from full power light.

$$A = -log\frac{P}{P_0} = log\frac{P_o}{P}$$

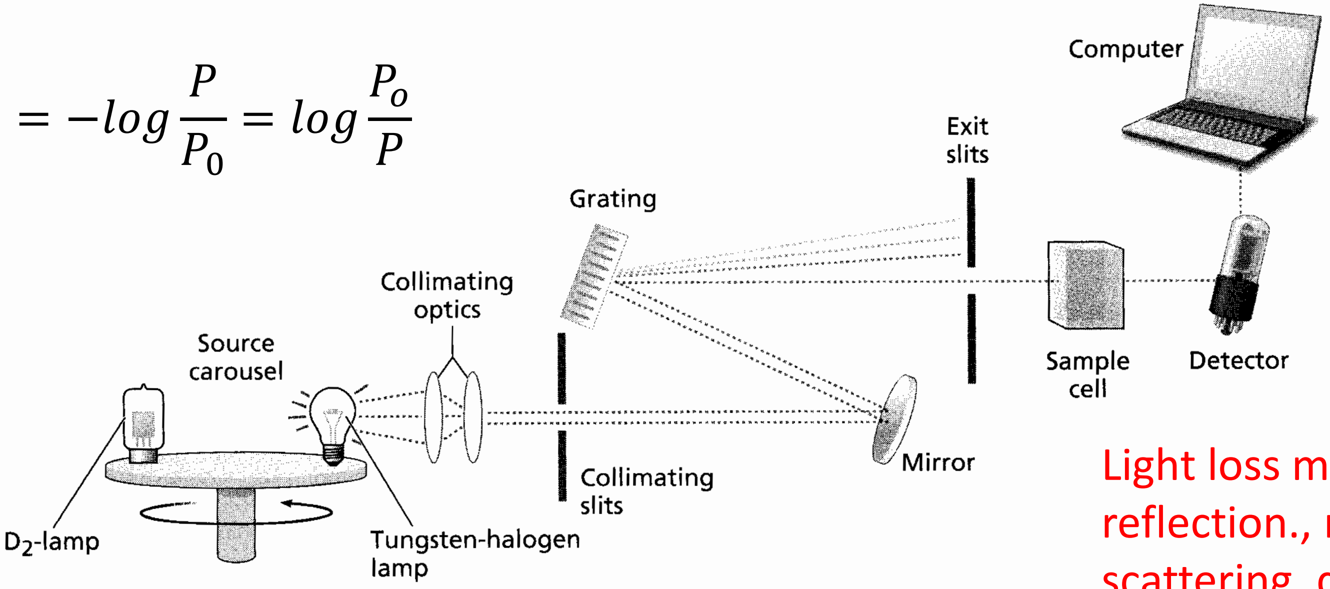


Figure 6.19 Schematic representation of a single-beam scanning UV-vis spectrometer. The source carousel is used to select between a tungsten–halogen lamp (visible) and a D_2 lamp (ultraviolet).

Light loss mechanisms: reflection., refraction, scattering, diffraction

- **Smaller footprint and simpler design – low cost**
- **Slow and time consuming – sequential analyte and background scans**
- **Subject to 1/f (flicker noise) – long time, low frequency measurement**

Dual Beam Spectrometer

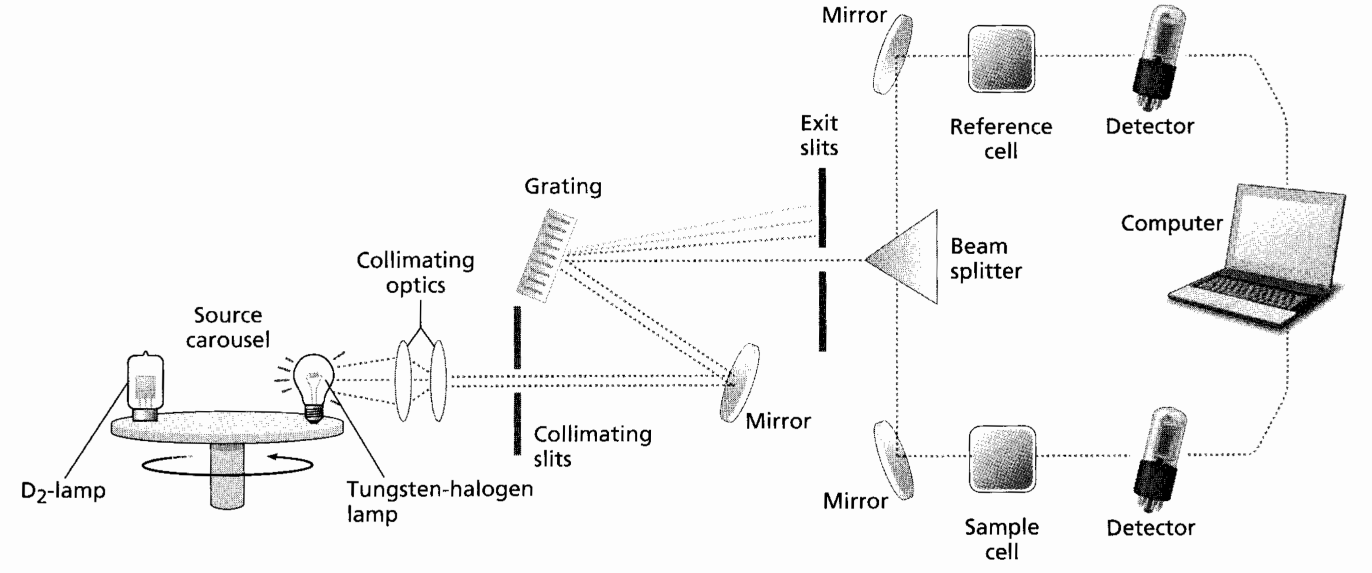


Figure 6.20 A schematic of a dual-beam spectrophotometer. From the source to the beam splitter, the dual-beam spectrometer is conceptually identical to the single-beam spectrometer.

- More complicated footprint and more optical components
- Less time consuming measurements (analyte and background together)
- Less subject to drift

Array Spectrometer

Monochromator after sample. Fast measurement so sample heating not a problem.

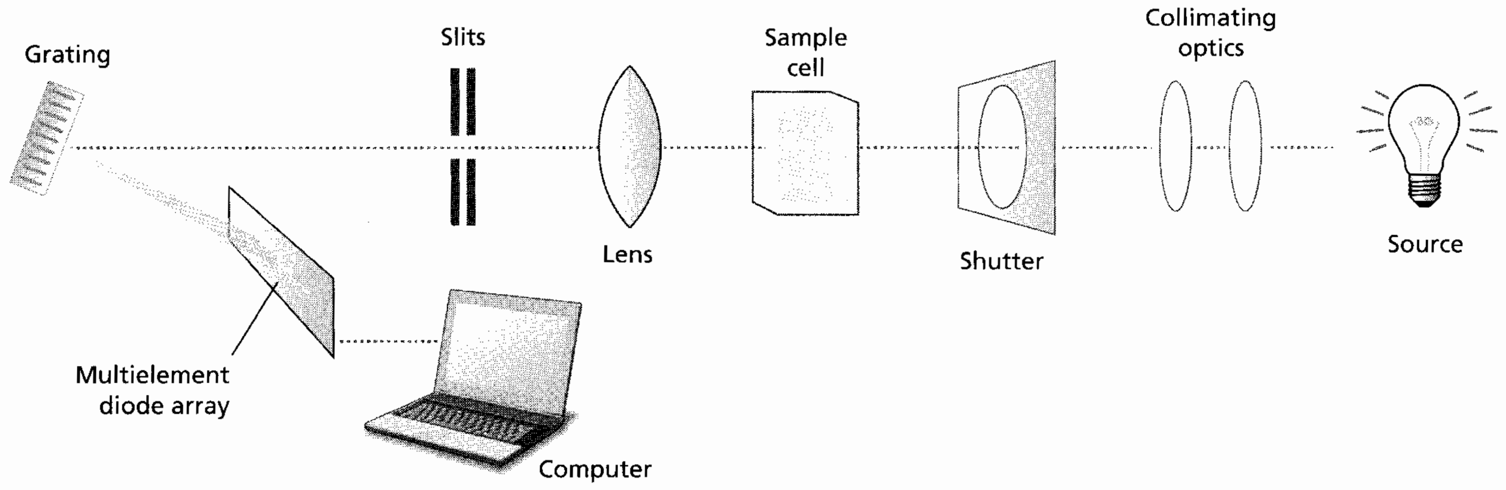


Figure 6.22 A schematic representation of a diode array spectrophotometer.

- **All wavelengths reach the detector simultaneously.**
- **Fast measurements (100’s msec vs. 10’s sec). Kinetic measurements.**
- **Greater sensitivity because one can signal average to improve S/N.**
- **Better design for detecting low levels of light.**

Detectors

Multiple dynodes each about 90 V more positive of the previous one.

10^6 amplification factor

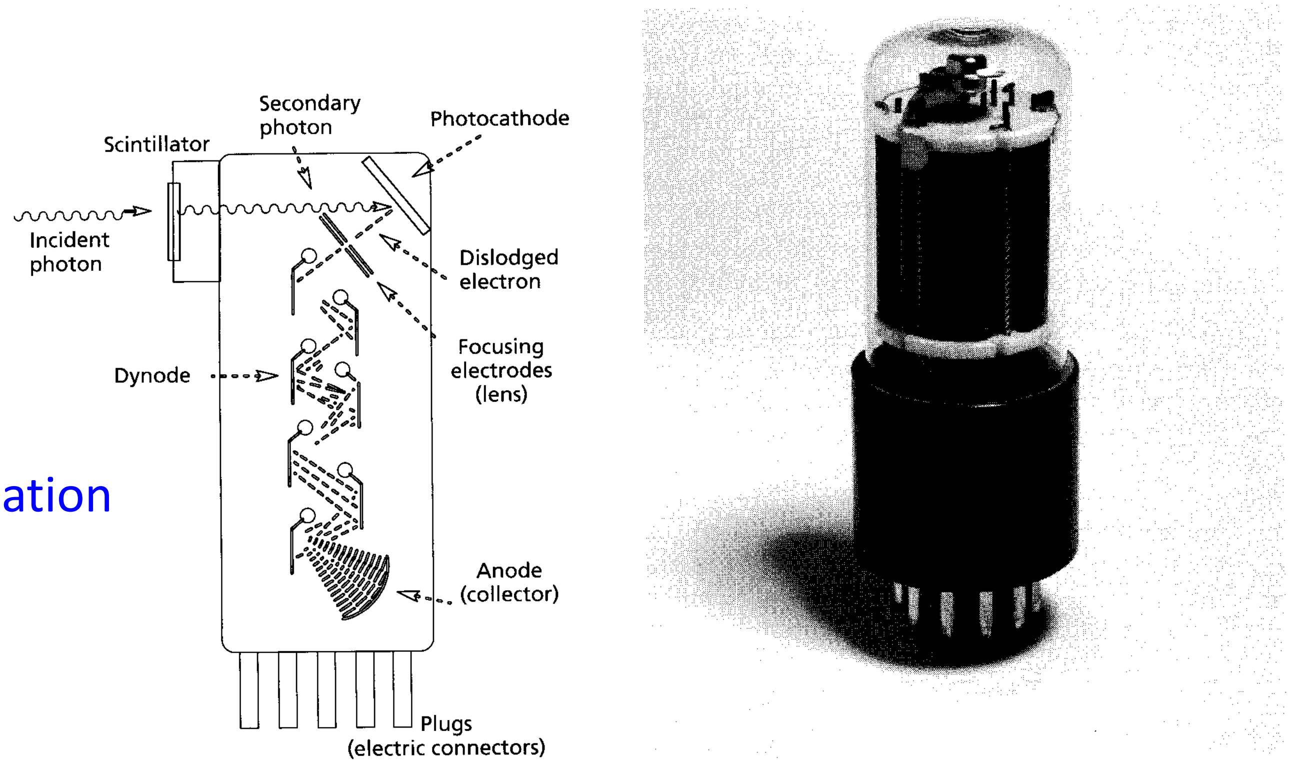


Figure 6.27 (left) A schematic of an eight-stage PMT and (right) a photograph of a PMT. The incident photon dislodges an electron from the scintillator, which initiates a cascade of ejected electrons as they proceed toward the collector.

$$I_{ph} = kP(h\upsilon) + i_{dark}$$

Detectors

Components of array detectors. Individual array elements.

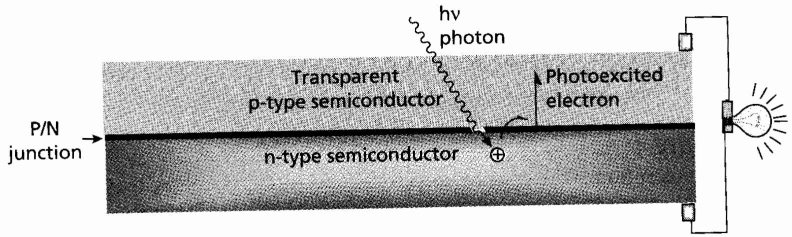


Figure 6.28 A schematic of a photovoltaic p/n junction.

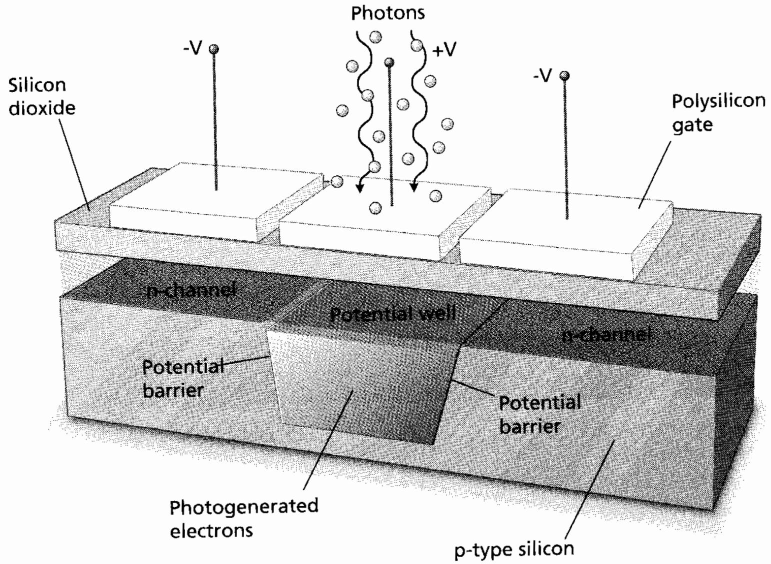


Figure 6.29 An MOS semiconductor used in a CCD detector.