26 Molecular Absorption Spectrometry

26A Ultraviolet and Visible Molecular Absorption Spectroscopy

26A-1 Absorbing species

Molecules Absorbing UV/Visible radiation
- Qualitative
- Quantitative

Absorption by organic Compounds

(1) shared electrons that participate directly in bond formation and are thus associated with more than one atom

(2) unshared outer electrons that are largely localized about such atoms as oxygen, the halogen, sulfur and nitrogen.

Species with unsaturated bonds generally absorb in the UV

Chromophore: unsaturated organic functional groups that absorb in the UV/visible region.

Table 26-1 Absorption Characteristics of Some Common Organic Chromophores

Chromophore	**Example**	**Solvent**	**λ_{max}, nm**	**ε_{max}**
Alkene	$C_6H_{13}CH=CH_2$	n-Heptane	177	13,000
Conjugated alkene	$CH_2=CHCH=CH_2$	n-Heptane	217	21,000
Alkyne	$C_5H_{11}C\equiv C-CH_3$	n-Heptane	178	10,000
			196	2,000
			225	160
Carbonyl	$CH_3(C=O)CH_3$	n-Hexane	186	1,000
			280	16
	$CH_3(C=O)H$	n-Hexane	180	Large
			293	12
	$CH_3(C=O)NH_2$	Water	214	60
Carboxyl	CH_3COOCH	Ethanol	204	41
Azo	$CH_3N=NCH_3$	Ethanol	339	5
Nitro	CH_3NO_2	Isooctane	280	22
Nitrate	$C_2H_5ONO_2$	Dioxane	270	12
Nitroso	C_4H_9NO	Ethyl ether	300	100
			665	20
Aromatic	Benzene	n-Hexane	204	7,900
			256	200

Table 26-2 Absorption by Organic Compounds Containing Unsaturated Heteroatoms

Compound	λ_{max}, nm	ε_{max}	Compound	λ_{max}, nm	ε_{max}
CH_3OH	167	1480	$(CH_3)_2S$	229	140
$(CH_3)_2O$	184	2520	$(CH_3)_2NH_2$	215	600
CH_3Cl	173	200	$(CH_3)_3N$	227	900
CH_3I	258	365			

Absorption by Inorganic Species Fig. 26-2, 3

Charge-Transfer Absorption Fig. 26-4

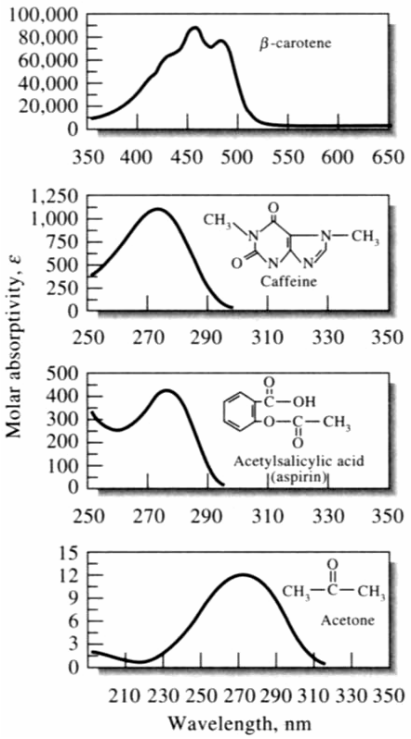

Fig. 26-1 Absorption spectra for typical organic compounds.

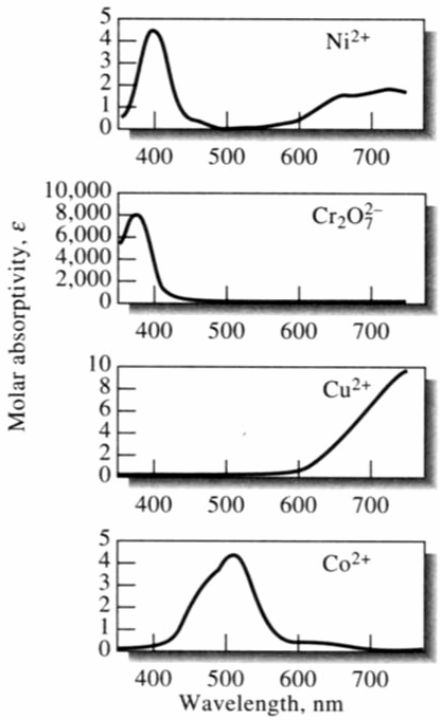

Fig. 26-2 Absorption spectra of aqueous solutions of several transition metal ions.

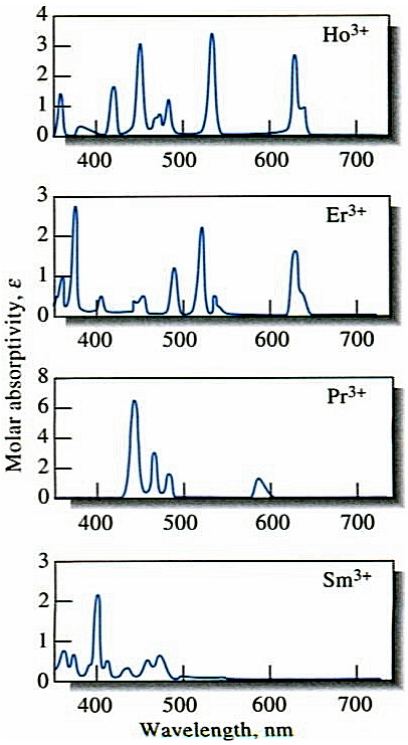

Fig. 26-3 Absorption spectra of aqueous solutions of rare earth ions.

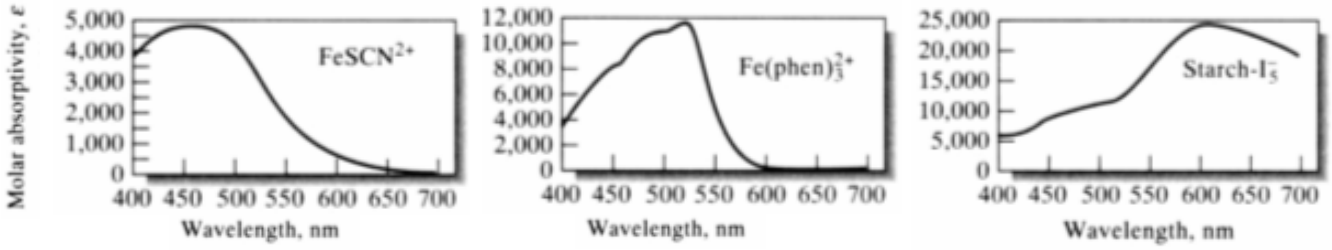

Fig. 26-4 Absorption spectra of aqueous charge-transfer complexes.

Quantitative: UV/visible spectrophotometry

Qualitative: infrared spectrophotometry

26A-2 Qualitative Applications of UV/Visible Spectroscopy

Table 26-1

Solvents (Fig. 24-14, Table 26-3)

The Effect of Slit Width (Fig. 26-5)

The Effect of Scattered Radiation at the Wavelength Extremes of a Spectrophotometer (Fig. 26-6)

Table 26-3 Solvents for the ultraviolet and visible regions

Solvent	Lower wavelength limit, nm	Solvent	Lower wavelength limit, nm	Solvent	Lower wavelength limit, nm
Water	**180**	**Cyclohexane**	**200**	**Acetone**	**330**
Ethanol	**220**	**Cellosolve**	**320**	**Dioxane**	**320**
Hexane	**200**	**Diethyl ether**	**210**	**CCl_4**	**260**

Fig. 26-5 Spectra for reduced cytochrome c obtained with four spectral bandwidths: (1) 20 nm, (2) 10 nm, (3) 5 nm, and (4) 1 nm. At bandwidths < 1 nm, peak noise became pronounced.

Fig. 26-6 Spectra of cerium(IV) obtained with a spectrophotometer having glass optics (A) and quartz optics (B). The false peak in A occurs when stray radiation is transmitted at long wavelengths.

26A-3 Quantitative Applications

1. **Wide applicability.**
2. **High sensitivity**
3. **Moderate to high selectivity**
4. **Good accuracy**
5. **Easy and convenience**

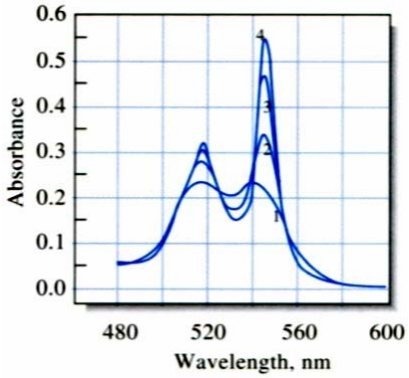

Fig. 26-5

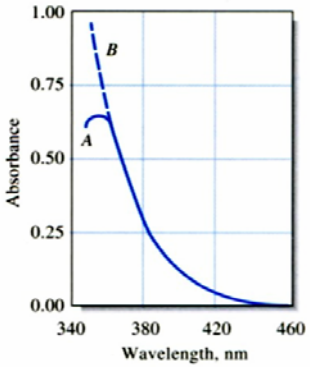

Fig. 26-6

Direct measurement

Nitrate in nature water: NO_3^-: 220 nm

1. Absorbance at 220 nm
2. Absorbance at 270 nm (correct for the interference)

Indirect measurement

$$12\ MoO_4^{2-} + H_2PO_4^- + 24\ H^+ \Leftrightarrow [H_2PMo_{12}O_{40}]^- + 12\ H_2O$$

12-molybdophosphoric acid, 12-MPA (yellow)

↓ ascorbic acid or stannous chloride

molybdenum blue (650~890 nm strong absorbance)

Application to Absorbing Species

common organic chromophore (Tab. 26-1)

inorganic species: ions of transition metals and their complexes (color), nitrite, nitrate, chromate ion, oxides of nitrogen, element halogens and ozone.

Applications to Nonabsorbing Species

react with chromophoric reagents → products that absorb strongly in the UV and visible regions

Inorganic reagent	Analyte	Organic chelating agent	Analyte
thiocyanate	Fe, Co, Mo	diethyldithiocarbamate	Cu
anion of H_2O_2e	Ti, V, Cr	diphenylthiocarbazone	Pb
iodide	Bi, Pd, Te	1,10-phenanthroline	Fe
Ce(IV)	low-molecular-weight aliphatic alcohol	dimethylglyoxime	Ni

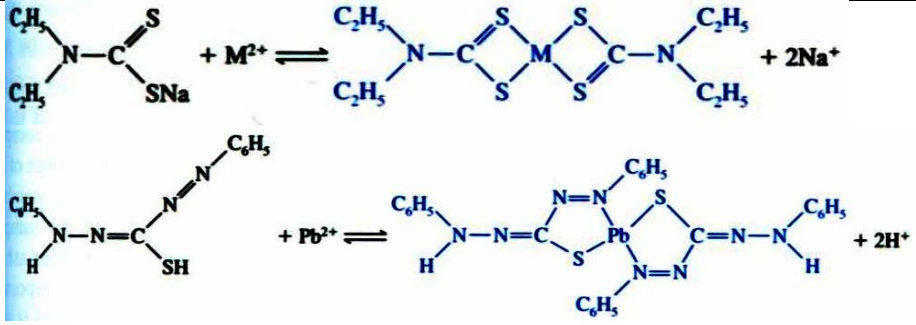

Fig. 26-7 Typical chelating reagents for absorption. (a) Diethyldithiocarbamate. (b) Diphenylthiocarbazone.

Procedural Details

development of conditions that yield a reproducible relationship (preferably linear) between absorbance and analyte concentration.

1. Wavelength Selection

made a wavelength corresponding to an absorption peak → maximum sensitivity

2. Variables That Influence Absorbance

solvent, pH of the solution, temperature, high electrolyte concentrations and presence of interfering substances.

3. Determination of the Relationship Between Absorbance and Concentration

Calibration standards

The measured absorbance of a given solution will usually vary somewhat from instrument to instrument. Thus, determination should *never* be based on molar absorptivities found in the literature.

4. The Standard Addition Method

standard addition:

a known amount of analyte + a second aliquot sample →

the difference in Abs. → calculate the analyte conc. of the sample

$$A_2 = \frac{\varepsilon\, b\, V_x c_x}{V_t} + \frac{\varepsilon\, b\, V_s c_s}{V_t} = kV_s c_s + kV_x c_x$$

Plot of A_s as a function of V_s →

$\boxed{A_s = mV_s + b}$, $\boxed{m = k}$, $\boxed{b = k\,V_x c_x}$

$$\frac{m}{b} = \frac{kc_s}{kV_x c_x} \rightarrow \boxed{c_x = \frac{bc_s}{mV_x}}, \quad \left(\frac{S_c}{c_x}\right)^2 = \left(\frac{S_m}{m}\right)^2 + \left(\frac{S_b}{b}\right)^2 \rightarrow \boxed{s_c = c_x\sqrt{\left(\frac{S_m}{m}\right)^2 + \left(\frac{S_b}{b}\right)^2}}$$

Ex. 26-1 10-mL aliquots of a natural water sample were pipetted into 50.00-mL volumetric flasks. Exactly 0.00, 5.00, 10.00, 15.00 and 20.00 mL of a standard solution containing 11.1 ppm of Fe^{3+} were added to each, followed by an excess of thiocyanate ion to give the red complex $Fe(SCN)^{2+}$. After dilution to volume, absorbances for the five solutions, measured with a photometer equipped with a green filter, were found to be 0.240, 0.437, 0.621, 0.809 and 1.009, respectively (.0982-cm cells). (a) What was the $[Fe^{3+}]$ in the water sample? (b) Calculate the standard deviation of the slope, the intercept and the [Fe].

(a) c_s =11.1 ppm, V_s = 10.00 mL, V_t = 50.00 mL

m = 0.03820, b = 0.2412

$A_s = 0.03820\ V_s + 0.2412$

$$\boxed{c_x = \frac{bc_s}{mV_x} = \frac{(0.2412)(11.1\,\text{ppmFe}^{3+})}{(0.03820/\text{mL})(100\text{mL})} = 7.01\,\text{ppmFe}^{3+}}$$

(b) $s_m = 3.07\times 10^{-4}$ and $s_b = 3.76 \times 10^{-3}$

$$s_c = c_x\sqrt{\left(\frac{S_m}{m}\right)^2 + \left(\frac{S_b}{b}\right)^2}$$

$$= 7.01\sqrt{\left(\frac{3.07\times10^{-4}}{0.03820}\right)^2 + \left(\frac{3.76\times10^{-3}}{0.2412}\right)^2} = 0.12\ \text{ppmFe}^{3+}$$

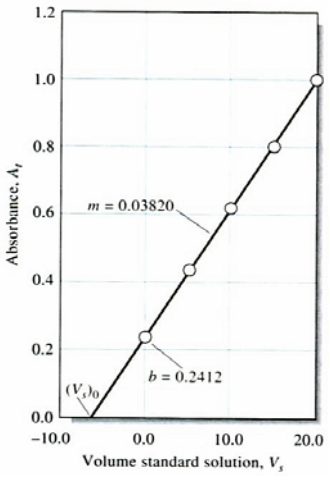

Fig. 26-8 Determination of Fe^{3+} as the $Fe(SCN)^{2+}$ complex.

Ex. 26-2 The single-point standard addition method was used in the determination of phosphate by the molybdenum blue method. A 2.00-mL urine sample was treated with molybdenum blue reagents to produce a species absorbing at 820 nm, after which the sample was diluted to 100.00 mL. A 25.00-mL aliquot gave an absorbance of 0.428 (solution 1). Addition of 1.00 mL of a solution containing 0.0500 mg of phosphate to a second 25.0-mL aliquot gave an absorbance of 0.517. Use these data to calculate the number of milligrams of phosphate per milliliter of the sample.

$$A_1 = \varepsilon b c_x \qquad A_2 = \frac{\varepsilon\, b\, V_x c_x}{V_t} + \frac{\varepsilon\, b\, V_s c_s}{V_t} = \frac{\varepsilon\, b (V_x c_x + V_s c_s)}{V_t}$$

$$c_x = \frac{A_1 c_S V_S}{A_2 V_t - A_1 V_x} = \frac{0.428 \times 0.0500 \text{mgmL}^{-1} \times 1.00\text{mL}}{0.517 \times 26.00\text{mL} - 0.428 \times 25.00\text{mL}} = 0.00780 \text{mgmL}^{-1}$$

conc. of phosphate = 0.00780 mgmL^{-1} ×100/2.00 = 0.390 mg/mL

6. Analysis of Mixture (Fig. 26-9)

$$\mathbf{A_{total} = A_1 + A_2 + \cdots + A_n = \varepsilon_1 b c_1 + \varepsilon_2 b c_2 + \cdots + \varepsilon_n b c_n}$$

$$\mathbf{A_1 = \varepsilon_{M1} b c_M + \varepsilon_{N1} b c_N}$$

$$\mathbf{A_2 = \varepsilon_{M2} b c_M + \varepsilon_{N2} b c_N}$$

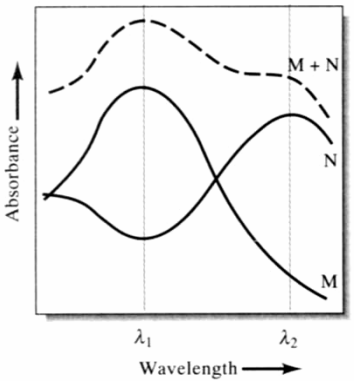

Fig. 26-9 Absorption spectrum of a two-component mixture (M+N), with spectra of the individual components. Wavelengths λ_1 and λ_2 are chosen for the analysis because the individual component spectra are significantly different at these two wavelength.

Ex. 26-3 Palladium (II) and gold (III) can be analyzed simultaneously through reaction with methiomeprazine ($C_{19}H_{24}N_2S_2$). The absorption maximum for the Pd complex occurs at 480 nm, while that for the Au complex is at 635 nm. Molar absorptivity data at these wavelengths are

	Molar Absorptivity, ε	
	480 nm	635 nm
Pd complex	3.55×10^3	5.64×10^2
Au complex	2.96×10^3	1.45×10^4

A 25.0-mL sample was treated with an excess of methiomeprazine and subsequently diluted to 50.0 mL. Calculate the molar concentrations of Pd(II), C_{Pd}, and Au(III), C_{Au}, in the sample if the diluted solution had an absorbance of 0.533 at 480 nm and 0.590 at 635 nm when measured in a 1.00-cm cell.

At 480 nm: $0.533 = (3.55 \times 10^3)(1.00) \times C_{Pd} + (2.96 \times 10^3)(1.00) \times C_{Au}$

$$C_{Pd} = \frac{0.533 - 2.96 \times 10^3 \times C_{Au}}{3.55 \times 10^3}$$

At 635 nm: $0.590 = (5.64 \times 10^2)(1.00) \times C_{Pd} + (1.45 \times 10^4)(1.00) \times C_{Au}$

$$0.590 = 5.64\times10^{2}\times\frac{(0.533-2.96\times10^{3})\times C_{Au}}{3.55\times10^{3}}+1.45\times10^{4}\times C_{Au}$$

$$= 0.0847 - 4.70\times10^{2}\times C_{Au} + 1.45\times10^{4}\times C_{Au}$$

$$C_{Au} = \frac{(0.590-0.0847)}{1.403\times10^{4}} = 3.60\times10^{-5}\,M$$

$$C_{Pd} = 0.53 - \frac{2.96\times10^{3}\times3.60\times10^{-5}}{3.55\times10^{3}} = 1.20\times10^{-4}\,M$$

Au(III) = 7.20×10^{5} and Pd(II) = 2.40×10^{-4} M

26A-4 Photometric and Spectrophotometric Titrations

one or more of the reactants or products absorb radiation or that an absorbing indicator be present.

Titration Curves

plot of absorbance (correct for volume change) as a function of titrant volume: consists of two straight-line regions with different slopes

→終點: intersection of extrapolated linear portions of the two lines

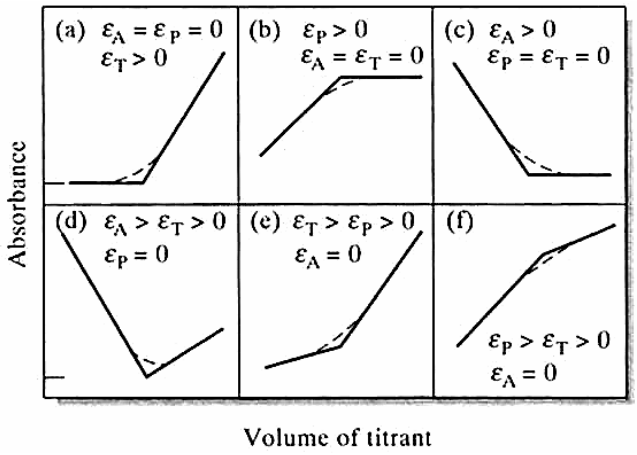

Fig. 26-12 Typical photometric titration curves. Molar absorptivities of the analyte titrated, the product and the titrant are ε_A, ε_P and ε_T, respectively.

(Fig. 26-12)	Analyte	Titrant	Product
(a)	nonabsorbing (ε = 0) thiosulfate	absorbing (ε > 0) triiodide	(ε = 0)
(b)	colorless (ε = 0) iodide	(ε = 0) iodate ion	Absorbing (ε > 0) triiodide

Application of Photometric Titrations

more accurate than a direct photometric determination
presence of other absorbing species may not interfere
more dilute solution may be titrated
photometric end point →applied to all types of reaction

ex: successive titration of Bi(III) and Cu(II). At 745 nm, cations, reagent and the Bi complex no absorb, but the Cu complex → absorbance ↑ additional reagent cause no further abs. change
→ two well-defined end points.

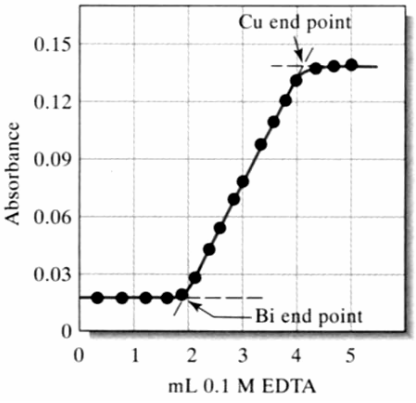

Fig. 26-13 Photometric titration curve at 745 nm for 100 mL of a solution that was 2.0×10^{-3} M in Bi^{3+} and Cu^{2+}

26B Automated Photometric and Spectrophotometric Methods

26C Infrared Absorption Spectroscopy

Qualitative > Quantitative

26C-1 Infrared Absorption Spectra

exception of a homonuclear species, such as molecular H_2, O_2 and N_2, all moleculars, organic and inorganic, absorb IR radiation.

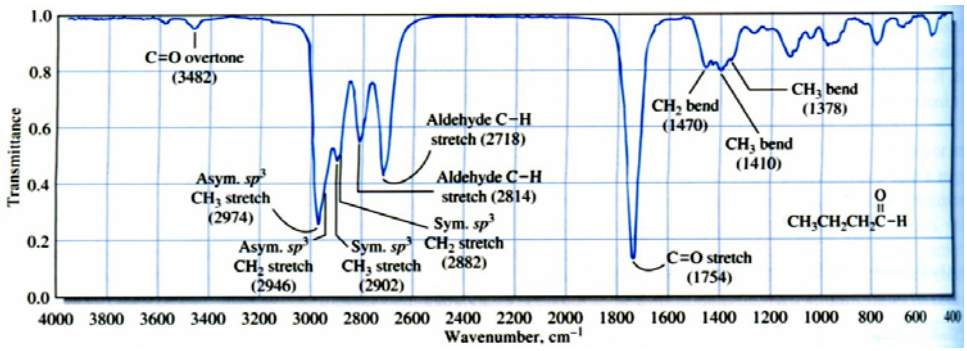

Fig. 26-20

Infrared spectrum for n-butanal (n-butyraldehyde).