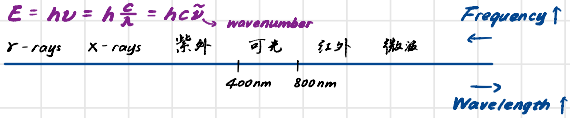
# Spectrometry a

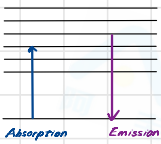
Utilization of light for identification and/or quantification of material.

Intersection of light with matter: Fast, Simple, Low cost

$c = \lambda \nu$

$E = h\nu = h\frac{c}{\lambda} = hc\tilde{\nu}$ → wavenumber




# Spectrometry b




Transmittance: $T = \frac{P}{P_0}$

Absorbance: $A = \log \frac{P_0}{P} = -\log T$

| $\frac{P}{P_0}$ | %T | A |
|---|---|---|
| 1 | 100 | 0 |
| 0.1 | 10 | 1 |
| 0.01 | 1 | 2 |




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

$A_{tot} = \log \frac{P_0}{P'} = A + A'$ (直接相加)

Measurements of optical absorbance:

VIS: Glass

VIS and UV: $SiO_2$

IR: NaCl and KBr

Far IR: Polyethylene

Identifcation: spectral shape: intensity vs. wavelength

Quantification: Beer-Lambert Law, $A = A(c)$

Beer-Lambert Law: $A = \varepsilon bc$ ($\varepsilon$: molar absorbptivity; $b$: optical pass; $c$: conc.)

Beer-Lambert Law condition:

1. monochromatic 单色光
2. a) no scatter light 无反射
   b) medium homogenous
3. absorbers act independently of each other.
4. Analyte do not undergo chemical changes.
5. a) Optical pass is identical for all beam.
   b) Parallel rays. 平行光
   c) Perpendicular to the surface of absorbing material. 垂直于表面
6. Incident radiation must not influence the atoms or molecules. Light shouldn't cause optical saturatio

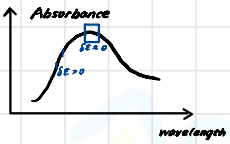
# Spectrometry c

$A^1 = \varepsilon^1 bc = \log \frac{P_0^1}{P} = 1 \quad , \quad P_0^1 = 10P^1$

$A^2 = \varepsilon^2 bc = \log \frac{P_0^2}{P} = 2 \quad , \quad P_0^2 = 100P^2$

$A_m = \log \frac{P_0^1 + P_0^2}{P^1 + P^2} = \log \frac{10P^1 + 100P^2}{P^1 + P^2} = \log \frac{10^{\varepsilon^1 bc} P^1 + 10^{\varepsilon^2 bc} P^2}{P^1 + P^2}$

## 1. Wavelength Selection:




The ε (molar absorptivity) of the analyte only slightly change within the spectral bandwidth of the light.

## 2. Scatter Light effect:

1) Lower measured absorbance.
2) Change in the spectral shape.

## Scattering Material:

1) Absorption by the scatters.
2) Scatter light in the instruments.
3) Spectral change

## 3. Absorbers (atoms, molecules, ions) act independently (Conc. < 0.01M)

At high conc., the average distance is small, influencing charge distribution.

↓

Affect energy levels and absorption spectra.

not valid

At very low analyte concentration, when high electrolyte conc. is present.

~~Vs.~~ 非 electrolyte conc. keep const.

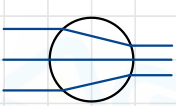
## 4. Do not undergo chemical change as function of conc.

a) Association

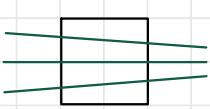
b) Dissociation $HA \rightleftharpoons H^+ + A^-$

c) Reaction with solvent

## 5. The optical pass is identical for all beam



not perpendicular



not parallel

## 6. Identical radiation must not influence the atoms or molecules.

No photochemical reactions.

The light should not cause optical saturation.

# Spectrometry d

$A_{sample} = A_{measured} - A_{blank}$

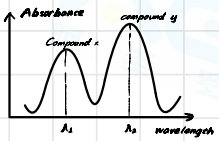
Measuring $P_0$ is not needed, only measuring $P_{blank}$

$A_{sample} = Log \frac{P_{blank}}{P_{measured}}$ 不需要入射光强

## Beer - Lambert Law for mixtures (no interaction between them)

$A_{tot} = A_1 + A_2 + A_3 + \cdots = \varepsilon_1 b c_1 + \varepsilon_2 b c_2 + \varepsilon_3 b c_3 + \cdots + \varepsilon_n b c_n$

## Well separated peaks



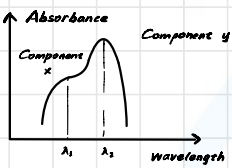

Component x

$A_1 = \varepsilon_1 b c_1$

Component y

$A_2 = \varepsilon_2 b c_2$

## Partially overlapping peaks

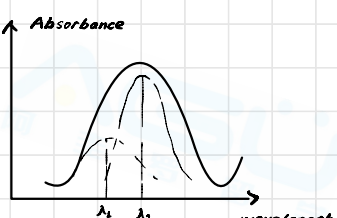



| | Component x | | Component y |
|---|---|---|---|
| $A_1 =$ | $\varepsilon_1 b c_1$ | + | $\varepsilon_2 b c_2$ |
| $A_2 =$ | $\varepsilon_1 b c_1$ | + | $\varepsilon_2 b c_2$ |
| $A_1 =$ | $E_{11} C_1$ | + | $E_{12} C_2$ |
| $A_2 =$ | $E_{21} C_1$ | + | $E_{22} C_2$ |

$$\begin{bmatrix} A_1 \\ A_2 \end{bmatrix} = \begin{bmatrix} E_{11} & E_{12} \\ E_{21} & E_{22} \end{bmatrix} \cdot \begin{bmatrix} C_1 \\ C_2 \end{bmatrix}$$

$A = Ec \rightarrow E^{-1}A = c$

## Much overlapping peaks



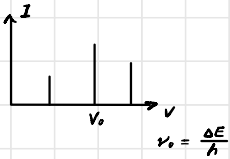

Totally overlapping → No solution.

Partial overlapping, zero measurement error → can be solved

Overlapping higher, effect of the experiment errors are more significant, more information is needed. → Measurement at many wavelength.

$A^{calc} = A^x C_x + A^y C_y$

## The spectral shape




In reality




Measured spectral lines are a convolution of the true spectral shape and instrumental functions.

Spectral shape factors:

Natural broadening, Doppler broadening (无规则热运动), Pressure broadening, Stark and Zeeman broadening (electric field) (magnetic field, 常在同一物理下)

Solvent / matrix effects

一般在气态或非极性溶剂中，能观察到振动跃迁的精细结构，但在极性溶剂中，由于溶剂和溶质分子相互作用增强，使谱带精细结构变得模糊。

## Spectrometry e

| Species | Energy level | Types | Shape |
|---|---|---|---|
| Atoms | Electronic | Absorption<br>Emission | "Lines" |
| Molecules | Electronic<br>Vibrational<br>Rotational | Absorption<br>Emission<br>(Fluorescence) | "Bands" |

$E = h\nu = h\frac{c}{\lambda}$

Molecular Absorption:

Single bond (C-H or C-C) in VUV range, $\lambda < 180\,nm$.

UV-Vis → weakly bounded electrons.

} Absorption Spectra 吸收

Luminescence 冷发光 发光过程中不产生大量的热量，温度没有明显的升高

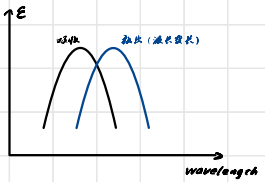
Ground State → Excited State 1 → Excited State 2 → Ground State

vibrational
Rotational

① Fluorescence 荧光 S1 回到 Ground State (单重态)
② Phosphorescence 磷光 T1 回到 Ground State (多重态)

Fluorescence 荧光 吸收能量后自上放光，持续时间短于 $10^{-1}$ 秒.

Phosphorescence 磷光 先吸收能量，过段时间再放光，持续时间在 $10^{-8}$ - $10^{-4}$ 秒.




Emission spectrum of a black body: 只取决于黑体温度