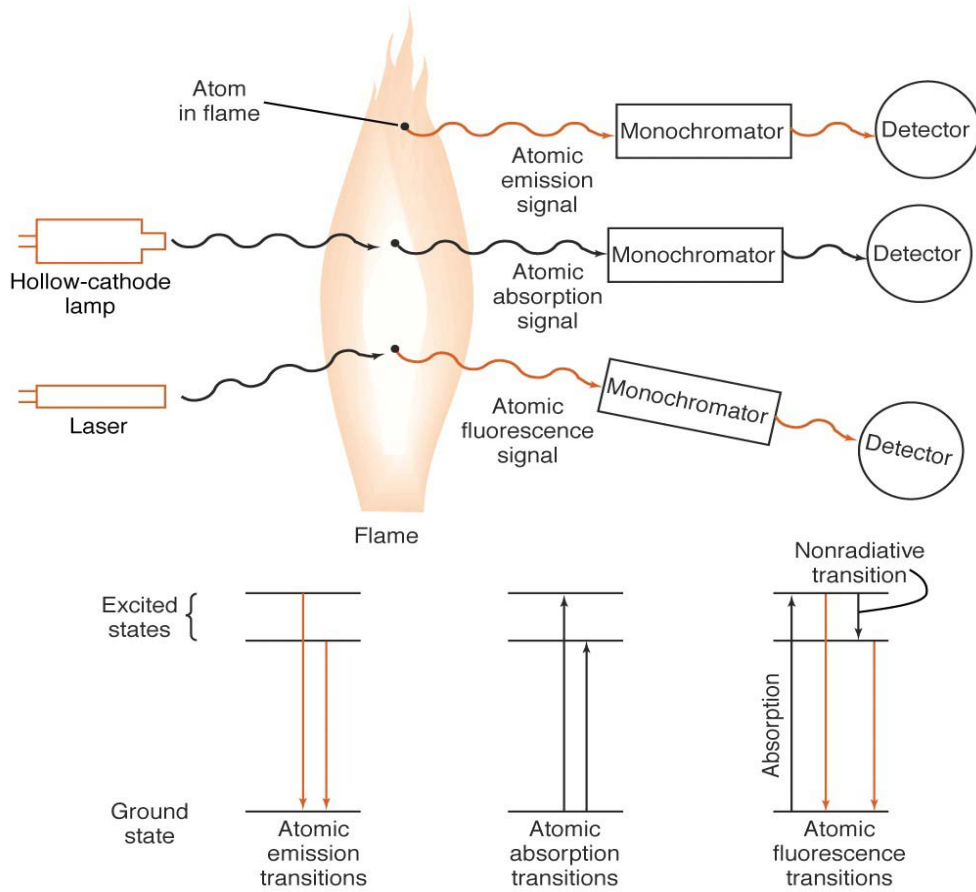


# Atomic Spectroscopy



Atomic spectroscopy – need to convert the analyte to free, unbound atoms or ions (atomization).

## Atomic Spectroscopy

- Unbound atoms, rather than molecules, are the absorbing species.
- Monochromator in atomic absorption or emission is placed after the sample (remove unwanted radiation during atomization process).
- Bandwidths are very narrow (0.002-0.005 nm), often referred to as lines.

### Atomization

a. Flame – premix burner (fuel, oxidant and sample mixed before flame introduction)

- Drawn into pneumatic nebulizer by air (oxidant) and creates small droplets (aerosol).

b. Electrothermal – the graphite furnace

- greater sensitivity and less sample
- maintains constant temperature, reducing memory effects

c. Inductively coupled plasma (ICP), 0.001-50 ng L<sup>-1</sup>

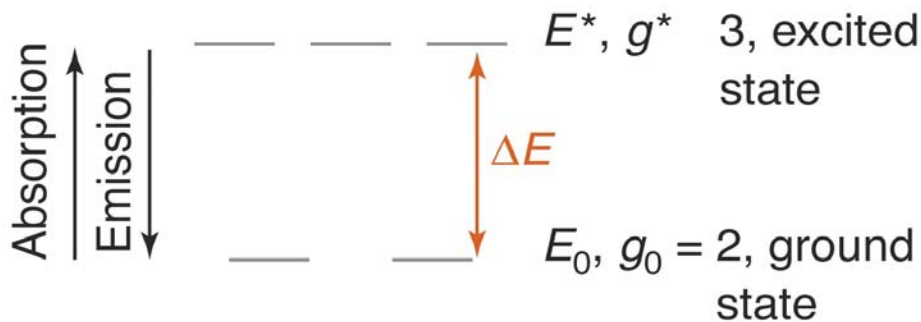
- high temperature, stability and chemically inert Ar environment

<b>Atomization method</b>	<b>Temperature (K)</b>	<b>Measurement Type</b>
Flame	2300-3400	Abs, emission
Electrothermal	2000-3300	Abs, emission
ICP	6000-8500	emission

## Temperature Effects

Boltzmann Distribution – degeneration of energy states (describes the relative populations of diff. states at thermal equilibrium).

- Ground state atoms can absorb light to be promoted to the excited state.
- Excited state atoms can emit light to return to the ground state.



$$\text{Boltzmann distribution: } \frac{N^*}{N_0} = \frac{g^*}{g_0} e^{-\Delta E / kT}$$

Where T is temperature (K), k is Boltzmann's constant ( $1.381 \times 10^{-23}$  J/K)

Ex. Calculate the fraction of sodium atoms in the excited state in an acetylene-air flame at 2600 K.

- lowest excited state =  $3.371 \times 10^{-19}$  J/atom above ground state
- Degeneracy of excited state = 2, ground state = 1

$$\frac{N^*}{N_0} = \left(\frac{2}{1}\right) e^{-(3.371 \times 10^{-19} \text{ J}) / [(1.381 \times 10^{-23} \text{ J/K}) \cdot (2600 \text{ K})]} = 1.67 \times 10^{-4}$$

- fewer than 0.02% of atoms are in the excited state

## The Effect of Temp. on Absorption and Emission

- Excited state population changes by 4% when the temperature rises 10 K...therefore the emission intensity rises by 4%.

**Table 21-3** Effect of energy difference and temperature on population of excited states

Wavelength difference of states (nm)	Energy difference of states (J/atom)	Excited-state fraction ( $N^*/N_0$ ) <sup>a</sup>	
		2 500 K	6 000 K
250	$7.95 \times 10^{-19}$	$1.0 \times 10^{-10}$	$6.8 \times 10^{-5}$
500	$3.97 \times 10^{-19}$	$1.0 \times 10^{-5}$	$8.3 \times 10^{-3}$
750	$2.65 \times 10^{-19}$	$4.6 \times 10^{-4}$	$4.1 \times 10^{-2}$

a. Based on the equation  $N^*/N_0 = (g^*/g_0)e^{-\Delta E/kT}$  in which  $g^* = g_0 = 1$ .

## Read – 21-4 Instrumentation, 21-6 ICP-MS

**Table 21-4** Comparison of atomic analysis methods

	Flame absorption	Furnace absorption	Plasma emission	Plasma–mass spectrometry
Detection limits (ng/g)	10–1 000	0.01–1	0.1–10	0.000 01–0.000 1
Linear range	$10^2$	$10^2$	$10^5$	$10^8$
Precision				
short term (5–10 min)	0.1–1%	0.5–5%	0.1–2%	0.5–2%
long term (hours)	1–10%	1–10%	1–5%	<5%
Interferences				
spectral	very few	very few	many	few
chemical	many	very many	very few	some
mass	—	—	—	many
Sample throughput	10–15 s/element	3–4 min/element	6–60 elements/min	all elements in 2–5 min
Dissolved solid	0.5–5%	>20% slurries & solids	1–20%	0.1–0.4%
Sample volume	large	very small	medium	medium
Purchase cost	1	2	4–9	10–15

SOURCE: Adapted from TJA Solutions, Franklin, MA.

## Analytical Separations

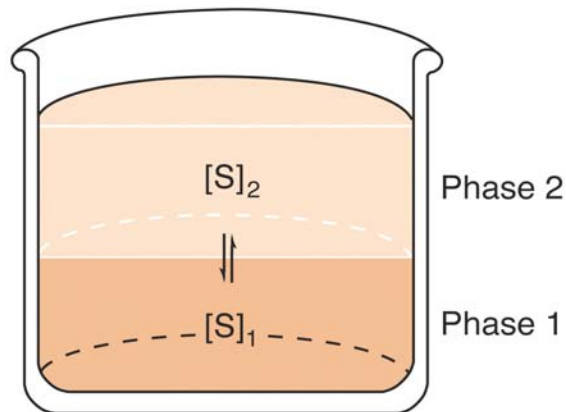
Why do we use analytical separations?

- interferences
- identify
- measure

<b>Gas-Liquid</b>	<b>Gas-Solid</b>	<b>Liquid-Liquid</b>	<b>Liquid-Solid</b>
Distillation	Sublimation	Extraction	Precipitation
Gas Chromatography	Adsorption	Liquid Chromatography	Adsorption
	Molecular sieves		Ion Exchange

### Solvent Extraction

- Transfer of a solute from one phase to another.



Distribution is in equilibrium process:  $S_{aq} \leftrightarrow S_{org}$

For which:  $K_D = \frac{[S]_{org}}{[S]_{aq}}$ , where  $K_D$  is called distribution coefficient

(book: partition coefficient)

Knowing  $K_D$  can help determine the extent to which a solute is transferred.

Let  $m$  = amount of solute (S) in mmoles,  $q$  = fraction of S remaining in the aqueous phase at equilibrium:

$$[S]_{aq} = \frac{(\text{fraction remaining})(\text{total amount})}{\text{volume aq phase}} = \frac{qm}{V_{aq}}$$

$$[S]_{org} = \frac{(\text{fraction transferred})(\text{total amount})}{\text{volume org phase}} = \frac{(1-q)m}{V_{org}}$$

$$K_D = \frac{(1-q)m/V_{org}}{qm/V_{aq}} = \frac{(1-q)V_{aq}}{qV_{org}}$$

$$q = \frac{V_{aq}}{K_D V_{org} + V_{aq}}$$

The fraction of solute transferred to the organic phase is  $1-q$ , or:

$$= 1 - \frac{V_{aq}}{K_D V_{org} + V_{aq}}$$

Fractions remaining after two extractions:

$$q \times q = \left( \frac{V_{aq}}{K_D V_{org} + V_{aq}} \right)^2$$

The fraction remaining in the aqueous phase after  $n$  extractions w/  $V_{org}$  portions of organic solvent:

$$q^n = \left( \frac{V_{aq}}{K_D V_{org} + V_{aq}} \right)^n$$

The percentage of solute transferred to the combined organic phases after  $n$  extractions:

$$\% E = (1 - q^n) \times 100$$

or

$$\% E = \left[ 1 - \left( \frac{V_{aq}}{K_D V_{org} + V_{aq}} \right)^n \right] \times 100$$

Ex: If the  $K_D$  for a metal chelate partitioning between water and chloroform is 6.4, calculate the fraction of chelate extracted when 25.0 mL of  $4.3 \times 10^{-2}$  M ML is shaken with 10.0 mL portion of chloroform.

Fraction remaining after 1 extraction:

$$q = \frac{25.0\text{mL}}{(6.4)(10\text{mL}) + 25.0\text{mL}} = 0.281$$

$$= 1 - q = 1 - 0.281 = 0.719$$

After two successive 10.0 mL portions of chloroform:

$$q^2 = \left[ \frac{25.0\text{mL}}{(6.4)(10\text{mL}) + 25.0\text{mL}} \right]^2 = 0.0790$$

$$\text{the fraction extracted} = 1 - q^2 = 1 - 0.0790 = 0.921$$

## pH Effects

- neutral species more soluble in an organic solvent
- charged species more soluble in an aqueous solution

Consider: basic amine with neutral form (B), has a  $K_D$  between aqueous phase 1 and organic phase 2. Conjugate acid,  $BH^+$ , is only soluble in aqueous phase 1. Also consider its acid dissociation constant as  $K_a$

$$\text{Distribution ratio (coefficient)} = D = \frac{C_{org}}{C_{aq}}$$

$$D = \frac{[B]_{org}}{[B]_{aq} + [BH^+]_{aq}}$$

Substituting  $K = [B]_{org}/[B]_{aq}$  and  $K_a = [H^+][B]_{aq}/[BH^+]_{aq}$

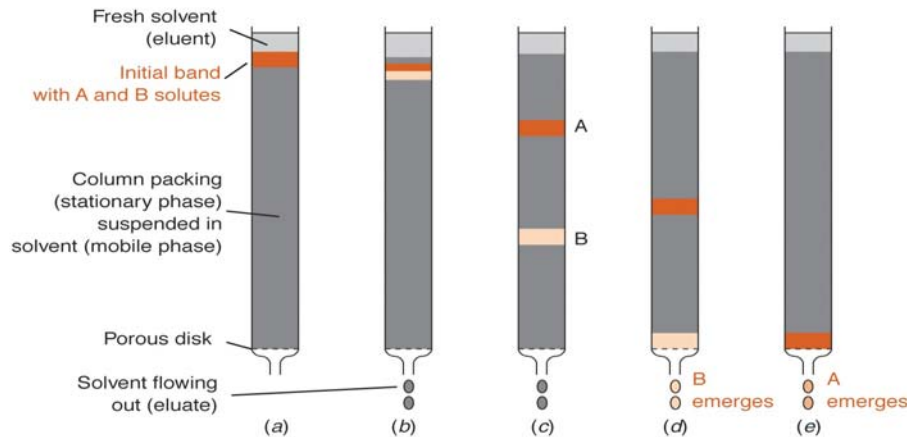
$$\text{Distribution of base between 2 phases: } D = \frac{K \cdot K_a}{K_a + [H^+]} = K \cdot \alpha_B$$

Where  $\alpha_B$  = fraction of weak base in neutral form, B, in aq phase



## Chromatography

-same principle as extraction, but one phase is held in place while the other moves past it.



eluent → column → eluate

Mobile phase – the solvent moving through the column (liquid or gas)

Stationary phase – stays place inside the column (viscous liquid bound inside column)

## Types of Chromatography

-read pg. 555-556 Harris

## Chromatogram

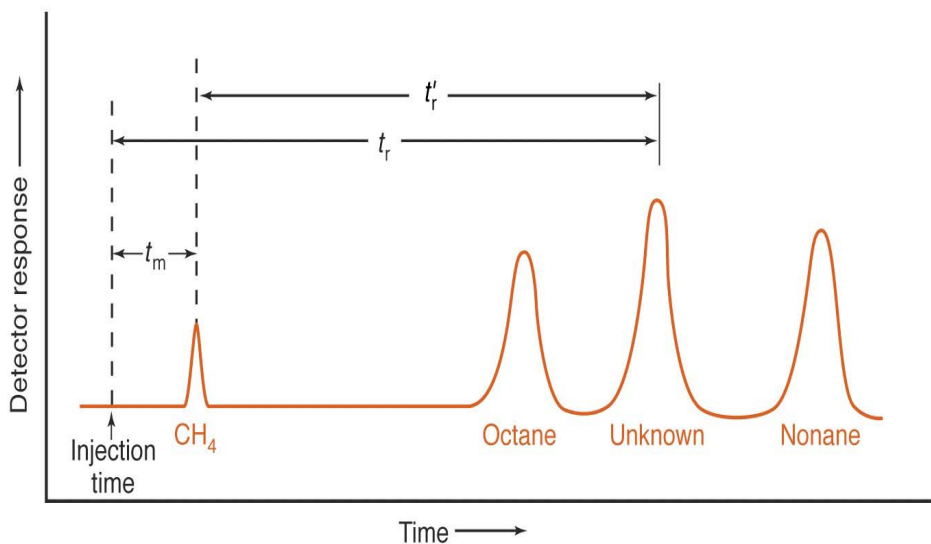
- Retention time ( $t_r$ ) = time needed after injection of the mixture onto the column until it reaches the detector.
- Retention volume ( $V_r$ ) = vol of mobile phase required to elute a solute from the column.
- Adjusted retention time ( $t_r'$ ) = additional time required for solute to travel the length of column, beyond the time required by unretained solvent.

*Adjusted retention time:*  $t'_r = t_r - t_m$

For any two components 1 and 2, the *relative retention*,  $\alpha$ , is the ratio of their adjusted retention times:

$$\text{Relative retention: } \alpha = \frac{t'_{r2}}{t'_{r1}}$$

where  $t'_{r2} > t'_{r1}$ , so  $\alpha > 1$  – the greater the relative retention, the greater the separation between two components.



For each peak in the chromatogram, the *capacity factor*,  $k'$ , is defined:

$$k' = \frac{t_r - t_m}{t_m}$$

Ex. A mixture of benzene toluene and methane was injected into a GC. Methane = 42 s, benzene = 251 s, toluene = 333 s. Find the adjusted retention time and capacity factor for each solute and the relative retention.

Adjusted:

$$\text{Benzene: } t'_r = t_r - t_m = 251 - 42 = 209\text{s}$$

$$\text{Toluene: } t'_r = 333 - 42 = 291\text{s}$$

Capacity factors:

$$\text{Benzene: } k' = \frac{t'_r - t_m}{t_m} = \frac{251 - 42}{42} = 5.0$$

$$\text{Toluene: } k' = \frac{t'_r - t_m}{t_m} = \frac{333 - 42}{42} = 6.9$$

Relative retention:

$$\alpha = \frac{t'_r(\text{toluene})}{t'_r(\text{benzene})} = \frac{333 - 42}{251 - 42} = 1.39$$

Efficiency of separation

-farther the elution time between peaks, the better the separation

-the wider the peaks, the poorer the separation

Resolution:

$$= \frac{\Delta t_r}{w_{av}} = \frac{\Delta V_r}{w_{av}} = \frac{0.589 \Delta t_r}{w_{1/2av}}$$

where  $\Delta t_r$  or  $\Delta V_r$  is the separation between peaks and  $w_{av}$  = average width of the two peaks in corresponding units

Ex. A peak with a retention time of 407 s has a width at the base of 13s. A neighboring peak is eluted at 424 s with a width of 16 s. Find the resolution of these two components.

$$\text{Resolution: } \frac{\Delta t_r}{w_{av}} = \frac{424 - 407}{1/2(13 + 16)} = 1.17$$

Chapter 23, sections 1-4, up to plate theory