Ch. 13 Titrations

Feb 15

A group of analytical methods based on determining the quantity of a reagent of known concentration that is required to react completely with an analyte.

Volumetric – measure the V of a standard

Gravimetric – measure the mass of a standard

Coulometric – measure electrical current needed to complete a reaction

Terms

- Standard solution
  - reagent of known concentration
- Titration
  - slow addition of standard until rxn is judged to be complete.
- Back titration
  - if excess standard is used, the amount of excesses determined by a separate titration.

How will we judge a rxn to be complete?

- Equivalence point
  - the end of a titration
  - → # moles standard = # moles reagent (according to stoichiometry)

ex. AgCl with $AgNO_2$
→ the eq. point is when 1 mole $AgNO_2$ reacts with 1 mole AgCl.

ex. Titrate H_2SO_4 with NaOH
→ 2 moles NaOH to react with each mole of H_2SO_4

How to tell? Indicators.
- present a physical change at or around the eq. point
- this physical change → END POINT

* Standard solutions is key.
→ primary
→ secondary.

EX. 13-1
Prepare 2.000 L of 0.0500 M $AgNO_3$ ($167.87 \frac{g}{mol}$) from the solid

$n_{AgNO_3} = (0.0500 \frac{mol}{L})(2.000\ L)$
$n_{AgNO_3} = 0.1000\ mol$

$m_{AgNO_3} = (0.1000\ mol)(167.87\ g\ mol^{-1})$
$m_{AgNO_3} = 16.98\ g$

HOW do you treat titration data?

Ex. 13-4

50.00 mL HCl required
29.71 mL of 0.01963 M $Ba(OH)_2$ to get to end point.

Need → moles of HCl in 50.00 mL
Have → moles $Ba(OH)_2$

$$Ba(OH)_2 + 2HCl \longrightarrow BaCl_2 + 2H_2O$$

$$n_{Ba(OH)_2} = (29.71 \times 10^{-3}\ L)\left(0.01963 \frac{mol}{L}\right)$$
$$= 5.8 \times 10^{-4}\ mol$$

$$\therefore\ n_{HCl} = (2)(5.8 \times 10^{-4}\ mol)$$
$$n_{HCl} = 1.17 \times 10^{-3}\ mol$$

$$[HCl] = (1.17 \times 10^{-3}\ mol)\left(\frac{1}{50.00 \times 10^{-3}\ L}\right) = 0.02133314\ M$$

Ex. 13-6

→ 0.8040 g of iron ore → dissolve in acid
→ reduce to Fe^{2+} titrate with 47.22 mL of 0.02242 M $KMnO_4$
→ calculate % Fe (55.847 g/mol)

$$MnO_4^- + 5Fe^{2+} + 8H^+ \longrightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$$

$$n_{MnO_4^-} = (47.22 \times 10^{-3}\ L)\left(0.02242 \frac{mol}{L}\right)$$
$$= 1.059 \times 10^{-3}\ mol.$$

$$\therefore\ Fe^{2+} = 5(1.059 \times 10^{-3}\ mol)$$
$$= 5.29 \times 10^{-3}\ mol$$

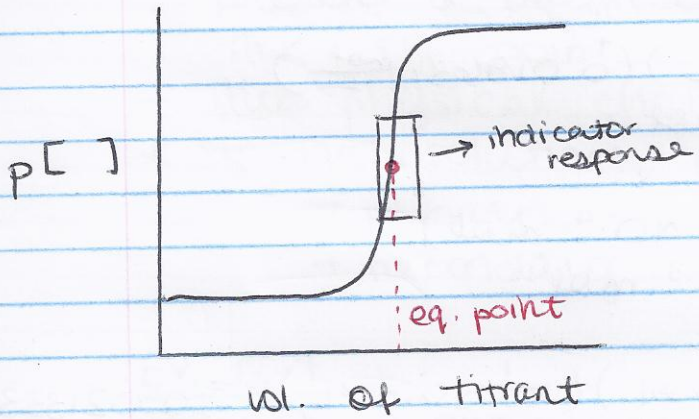
Hilroy

mass Fe^{2+} = 5.29×10^{-3} mol × 55.847 g mol^{-1}
= 0.296 g

% Fe = $\frac{0.296\ g}{0.8040\ g} \times 100$ = 36.77 %

Titration Curves

Sigmoidal curve.



Precipitation Titrations

Eq. point ⟶ precipitate occurs
- precipitate is so small that still need an indicator

Ex. Using Ag^+ to precipitate halides.

Ex. 13-10
50.000 mL of 0.0500 M NaCl reacts with 0.1000 M $AgNO_3$.
$K_{sp} = 1.82 \times 10^{-10}$

① Pre-eq. point : use 10.00 mL $AgNO_3$

$$[NaCl] = \frac{\text{original moles} - \text{moles consumed}}{\text{tot. volume}}$$

→ initial mol NaCl = 2.500×10^{-3} mol

→ Moles $AgNO_3$ in 10.00 mL
= $(10.00 \times 10^{-3}\ L)(0.1000\ M)$
= 1.000×10^{-3} mol

$$NaCl + AgNO_3 \longrightarrow AgCl\downarrow + Na^+ + NO_3^-$$

$$[NaCl] = \frac{2.500 \times 10^{-3} - 1.00 \times 10^{-3}}{60.00 \times 10^{-3}\ L} = \frac{1.500 \times 10^{-3}\ mol}{60.00 \times 10^{-3}\ L} = 0.0250\ M$$

$$[Ag^+] = \frac{K_{sp}}{[Cl^-]} = \frac{1.82 \times 10^{-10}}{0.025\ M} = 7.28 \times 10^{-9}\ M$$

$$p[Ag^+] = -\log[7.28 \times 10^{-9}\ M] = 8.14$$

② At eq. point : $[Ag^+] = [Cl^-]$

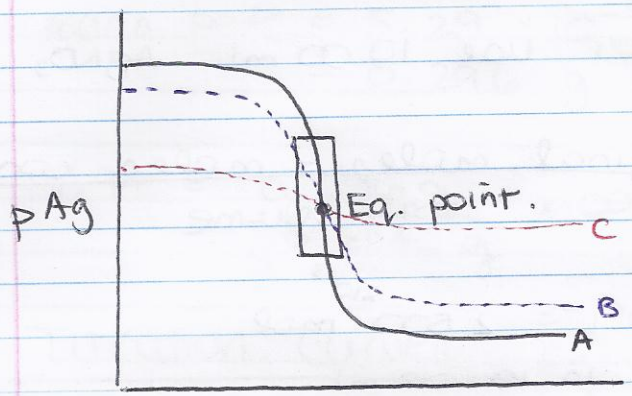
$K_{sp} = [Ag^+][Cl^-]$

$1.82 \times 10^{-10} = [Ag^+]^2$

$[Ag^+] = 1.349 \times 10^{-5}\ M$

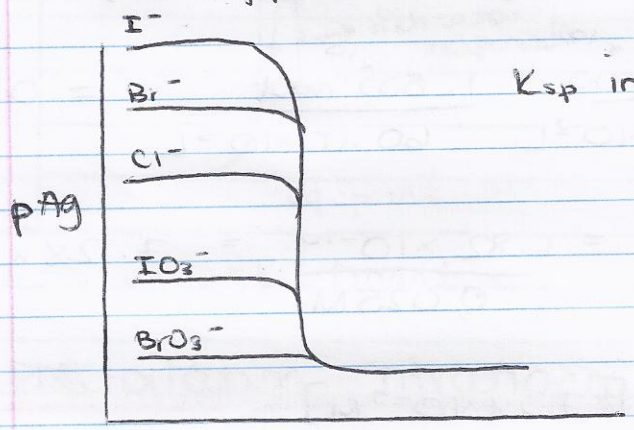
$p[Ag^+] = 4.87 \longrightarrow$ eq. point.

Hilroy



$[B] << [A]$

As concentration drops, titrations become less effective.



K_{sp} increases down the graph

Indicators

- Chemical:
  - chromate ion (Mohr method)

$$2Ag^+ + CrO_4^{2-} \rightarrow Ag_2CrO_4 \quad \text{RED}$$

- Absorption:
  - fluorescan (Fajan's method)
  - binds to solids
  - normally yellow
  - forms a red silver salt

- Volhard Method : uses Fe III
  - titrate Ag^+ with SCN^-
  - back titrate SCN^- with Fe^{3+}

$Fe^{3+} + SCN^- \rightleftharpoons FeSCN^{2+}$ RED

Suggested problems:

13-8
13-13
13-18
13-25
13-26
13-31

Hilroy

Ch. 14 Acid/Base Titrations

Feb 17

Indicators:

$$\underset{\text{acid colour}}{HIn} + H_2O \rightleftharpoons \underset{\text{base colour}}{In^-} + H_3O^+$$

or

$$\underset{\text{base colour}}{In} + H_2O \rightleftharpoons \underset{\text{acid colour}}{InH^+} + OH^-$$

Ex. → for acids:

$$K_a = \frac{[H_3O^+][In^-]}{[HIn]}$$

pH affects the ratio of the 2 forms of the indicator ⇒ colour change.

For the human eye: $\frac{[InH]}{[In^-]} > 10$

" " < 0.1

$\therefore [H_3O^+] = 10 \times K_a$ or $0.1\ K_a$

pH acid colour: $-\log 10 K_a$

$= pK_a - 1$

base colour = $pK_a + 1$

- indicator range: $pK_a \pm 1$

Phenolphthalein:

- acid form = colourless
- in basic solution = red

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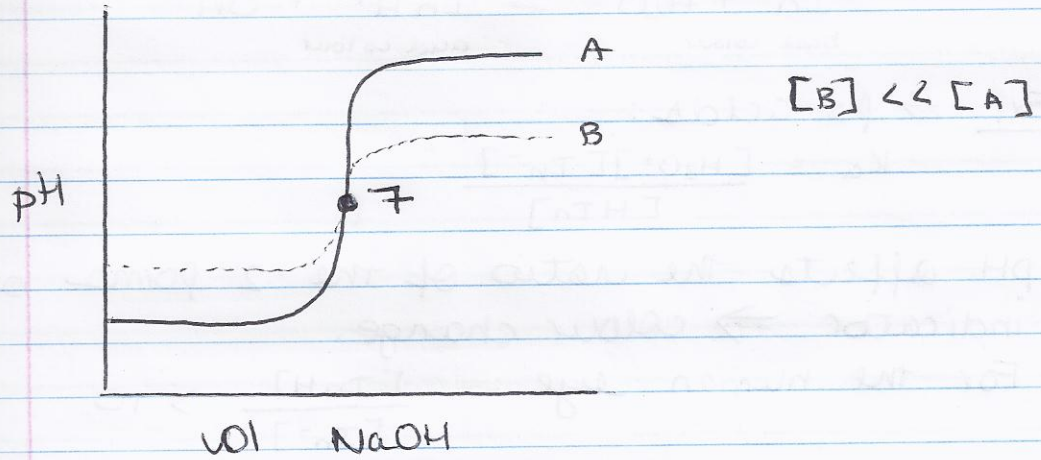
Strong Acid / Strong Base:

Ex. 14-1

Look at example in textbook

Effect of concentration:



[B] << [A]

→ same for strong base / strong acid.

Weak Acid / Strong Base:

- 4 calculations to do

1) At the beginning pH is calculated from [W. acid]
2) Prior to eq. point — have a buffer
3) At eq. point — deal with hydrolysis of conj. base of w. acid
4) After eq. point — strong base defines pH.

Q. Titration of 50.00 mL of 0.1000M acetic acid with 0.1000 M NaOH.

→

Initially:

$$AcH + H_2O \rightleftharpoons Ac^- + H_3O^+$$

	AcH	Ac^-	H_3O^+
I	0.1	0	0
C	$-x$	$+x$	$+x$
E	$0.1-x$	x	x

$$K_a = 1.75\times10^{-5} = \frac{x^2}{0.1-x}$$

→ assume $x \ll 0.1$

$$1.75\times10^{-5} = \frac{x^2}{0.1}$$

$$x = 1.32\times10^{-3}$$

$$[H_3O^+] = 1.32\times10^{-3}\ M$$

$$pH = 2.88$$

Add 5mL of NaOH:

Ac^-, AcH, NaAc all in solution.

$$[AcH] = \frac{\overbrace{(50.00\ mL)(0.100\ M)}^{\text{moles initial}} - \overbrace{(5.00\ mL)(0.100\ M)}^{\text{moles used}}}{55\ mL}$$

$$= \frac{4.500}{55.00}\ M$$

$$= 0.0818\ M$$

$$[NaAc] = \frac{5.00mL \times 0.100M}{55.00mL} = \frac{0.500}{55.00}\ M = 0.009\ M$$

$$K_a = \frac{[H_3O^+][Ac^-]}{[AcH]}$$

$$1.75\times10^{-5} = \frac{[H_3O^+](0.009\ M)}{0.0818\ M}$$

$$[H_3O^+] = 1.58\times10^{-4}\ M \longrightarrow pH = 3.80$$

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At eq. point:

- no more ACH left, all is now Ac^- which will hydrolyze. (pH will be slightly basic)

$$Ac^- + H_2O \rightleftharpoons ACH + OH^-$$

- from stoichiometry: $[ACH] = [OH^-]$

	Ac^-	+ H_2O ⇌	ACH	+ OH^-
I	0.1 (volume has changed)			
C				
E				

Initially 50 mL 0.1 M acetic acid

$\therefore$ 50 mL 0.1 M NaOH

→ final volume = 100 mL

$\therefore [Ac^-] = 0.05\ M$

	Ac^-	+ H_2O ⇌	ACH	+ OH^-
I	0.05		~~0~~	~~0~~
C	$-x$		$+x$	$+x$
E	$0.05-x$		x	x

$$K_b = \frac{K_w}{K_a} = \frac{x^2}{0.05} \quad \text{(assuming } x \lll 0.05\text{)}$$

$$x = 5.34 \times 10^{-6}\ M$$

$$pH = 14.00 - (-\log 5.34 \times 10^{-6})$$

$$pH = 8.73$$

After eq. point:

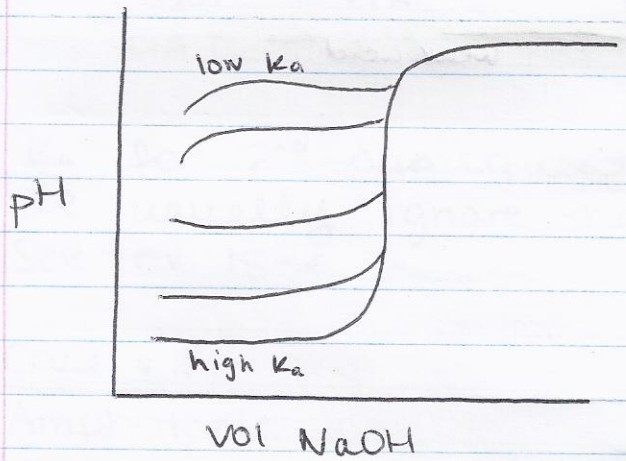
50.01 mL of NaOH

→ only worry about free NaOH

$$[OH^-] = \frac{(50.01\,mL \times 0.1\,M) - (50.00\,mL \times 0.1\,M)}{100.01\,mL}$$

$$= 1.00 \times 10^{-5}\,M$$

$pH = 9.00$



Suggested problems:

14.5	14.41
14.21	14.42
14.23	
14.38	
14.39	

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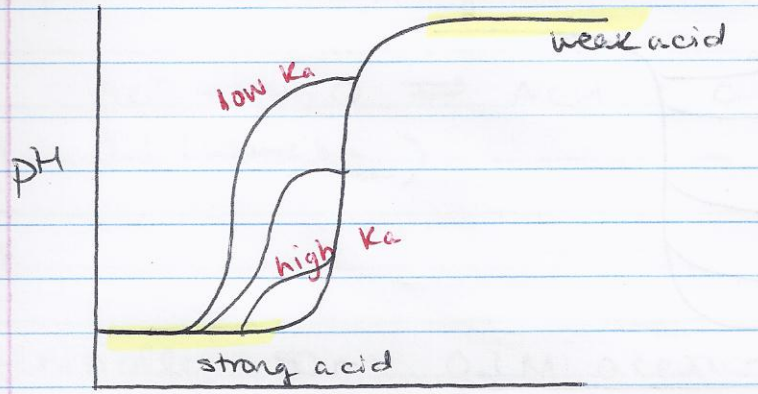
Ch. 15 – Complicated Systems

Case #1

Weak acid & strong acid both present at the same time?



Prior to eq. point:
- pH is dominated by a strong acid

At eq. point:
- need to worry about hydrolysis of weak conj. base

Past eq. point:
- curve looks like weak acid curve

Case #2

Polyfunctional acids / bases

Ex. $H_3PO_4 + H_2O \rightleftharpoons H_2PO_4^- + H_3O^+ \quad : K_{a1}$

$H_2PO_4^- + H_2O \rightleftharpoons HPO_4^{2-} + H_3O^+ \quad : K_{a2}$

$HPO_4^{2-} + H_2O \rightleftharpoons PO_4^{3-} + H_3O^+ \quad : K_{a3}$

$K_{a1} >> K_{a2} >> K_{a3}$

Case #3

Buffers of polyprotic acids

$H_2A \rightarrow HA^-$ ex. $NaAH$

$HA^- \rightarrow A^{2-}$ Na_2A

K_a for 2nd subsequent steps are so small, we usually ignore them.
See ex. 15-4.

Case #4

Amphoteric

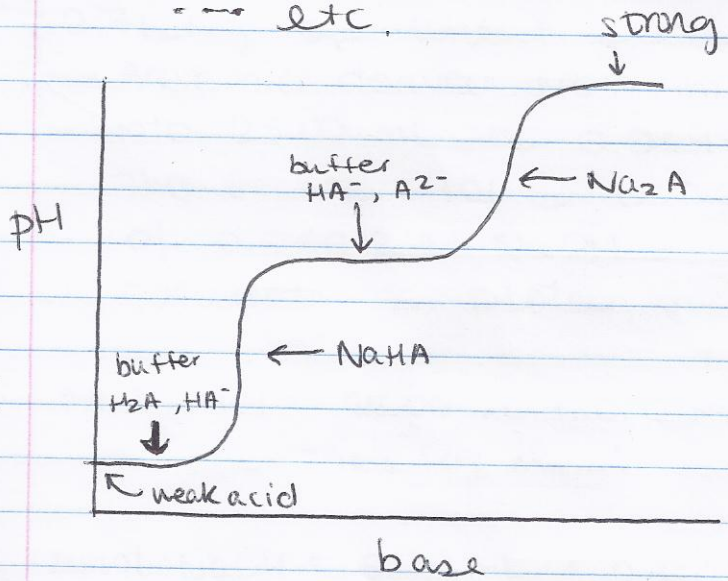
$HA^- + H_2O \rightleftharpoons A^{2-} + H_3O^+$

$HA^- + H_2O \rightleftharpoons H_2A + OH^-$

Solve: $[NaHA] = [HA^-] + [H_2A] + [A^{2-}]$

charge $[Na^+] + [H_3O^+] = [HA^-] + 2[A^{2-}] + [OH^-]$

... etc.



Suggested Problems

15.4
15.6
15.10
15.12
15.25
15.27

Hilroy

Ch. 16 Applications of Neutralization Titrations — March 8

- Review standard preparation

Elemental Analysis

Kjeldahl 1883

- nitrogen analysis
- protein ∝ N
  - ↳ used for determining protein in grains, meat, etc.

1) sample decomposed with heat
2) Concentrated sulfuric acid
   → get the bound N into ammonium ions (NH_4^+)
3) Make the solution basic
   → NH_4^+ becomes NH_3
   → liberated & collected in acid
4) Neutralization titration

Ex.

0.7121 g of wheat flour

→ Ammonia derived from this work up is distilled into 25.00 mL of 0.04977 M HCl. The excess HCl is back titrated with 3.97 mL of 0.04012 M NaOH. Calculate % protein in flour.

$$\text{mmol HCl} = 25.00\ \text{mL} \times 0.04977\ \frac{\text{mmol}}{\text{mL}}$$
$$= 1.2443\ \text{mmol}$$

$$\text{mmol NaOH} = 3.97\ \text{mL} \times 0.04012\ \frac{\text{mmol}}{\text{mL}}$$
$$= 0.1593\ \text{mmol}$$

Hilroy

mmol HCl used up by ammonia
= 1.2443 − 0.1593
= 1.0850 mmol

$$\%\ N = \frac{1.0850\ \text{mmol} \times 0.014007\ \frac{g}{\text{mmol}}}{0.7121\ g} \times 100$$

% N = 2.1341 %

% protein = 2.1341 × 5.70 = 12.16 %

(5.70 = % N in protein)

Check out Table 16-1.

Sulfur:
burn sample → $SO_2 + H_2O_2$ → → H_2SO_4 → titrate

Inorganic Compounds:
- ammonium salts → Kjeldahl
- nitrites / nitrates → reduce to NH_4^+
- carbonates → check out ex. 16-4.

Organic Functional Groups:
- carboxylic / sulfuric acids → titrate
- amine → titrate
- esters → saponify

$$R_1\overset{O}{\overset{\|}{C}}OR_2 + OH^- \longrightarrow R\overset{O}{\overset{\|}{C}}O^- + R_2OH \longrightarrow \text{titrate}$$

- hydroxyl groups → esterify with anhydride

$$CH_3\overset{O}{\overset{\|}{C}}-O\overset{O}{\overset{\|}{C}}CH_3 + ROH \longrightarrow CH_3\overset{O}{\overset{\|}{C}}OR + CH_3\overset{O}{\overset{\|}{C}}OH$$

→ unreacted anhydride → acetic acid

$$CH_3-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}CH_3 + H_2O \longrightarrow 2\,CH_3\overset{O}{\overset{\|}{C}}OH \longrightarrow \text{titrate}$$

• carbonyl groups
→ oxime

• titrate

Suggested Problems

16.5	16.25
16.8	16.32
16.12	16.33
16.19	16.35

SPECTROSCOPY

Ch. 24

Photons : waves and/or particles

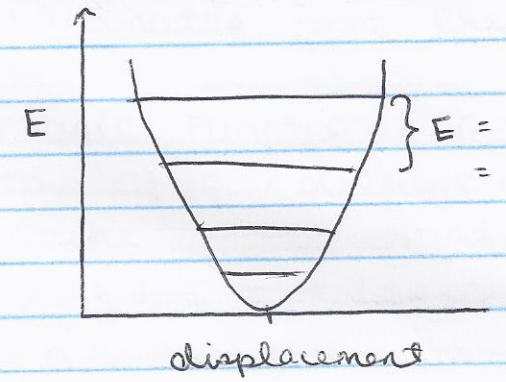
Key element

$$E = h\nu$$

Spectroscopy
- when a species absorbs or emits photons

Key element
- energy of the photon MUST match the transition from one state to another in the molecule
  - → vibrational
  - → rotating
  - → translating : - molecule
    - electrons

Vibrational Motion
- molecule has discrete vibrational energy levels



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

$\lambda \rightarrow$ infrared region of the spectrum

∴ IR Spectroscopy

Rotational Motion

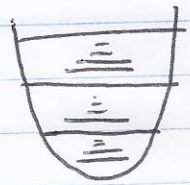
rotational 'states'

E falls into the microwave part of the EMAG spectrum

- Don't use this quantitatively in analytical chemistry

Translational Motion

- only used for electrons



State 2

E is large → UV-VIS region of the spectrum.

State 1

- Most widely used in analytical chemistry

Absorption

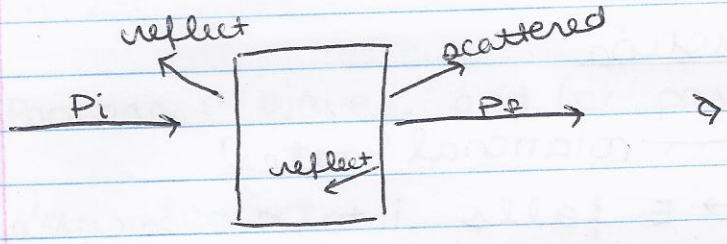
Beer-Lambert Law

- absorbance, $A = -\log T$ ← transmittance

$A = \log \frac{P_0}{P}$ ← radiant power (P_0 is for a blank)

- transmittance:
  - fraction of radiant power decrease going through a sample.

Hilroy



- account for this by running a blank (P_0)

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

a → absorptivity, ε (molar absorptivity)
- take solution of analyte of known concentration, measuring A
- can calculate ε.

b → path length
c → concentration.

See ex. 24-3

- This holds for all spectroscopy
  — selectivity & sensitivity vary

* Beer Law is a limiting law.
- valid below 0.01 M down to detection limit of apparatus

Emission

- transit from an upper state to a lower one.
- useful analytically for atoms:
  → short excited state lifetimes

1) Fluorescence: no spin change between states
   $^1S_2 \rightarrow {}^1S_1$ etc
   - short lifetime, most useful.

2) Phosphorescence : spin change

$^3S_2 \longrightarrow {}^1S_1$, etc

- long lifetime , less useful.

Suggested Problems

24.6 (*)	24.13 (*)	24.21
24.7	24.14	24.24.
24.9	24.19	

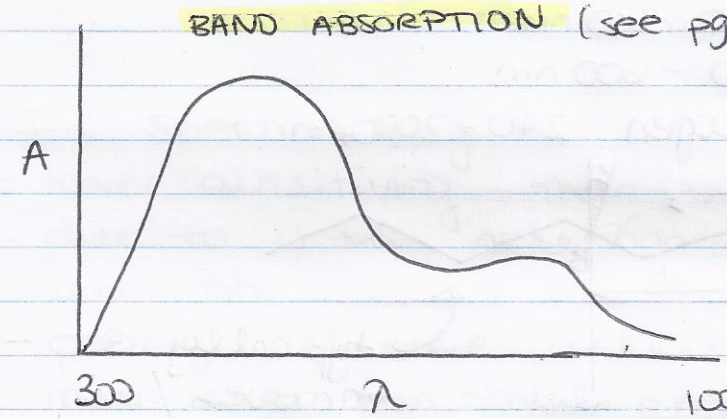
Hilroy

Ch. 26 : Molecular Absorption March 10

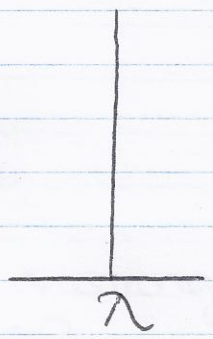
UV - VIS

- most widely applied
- selective
- universal → most organic & inorganic compounds will absorb somewhere in the VIS & near UV
- a wide range of electronic states that often give rise to a band absorption

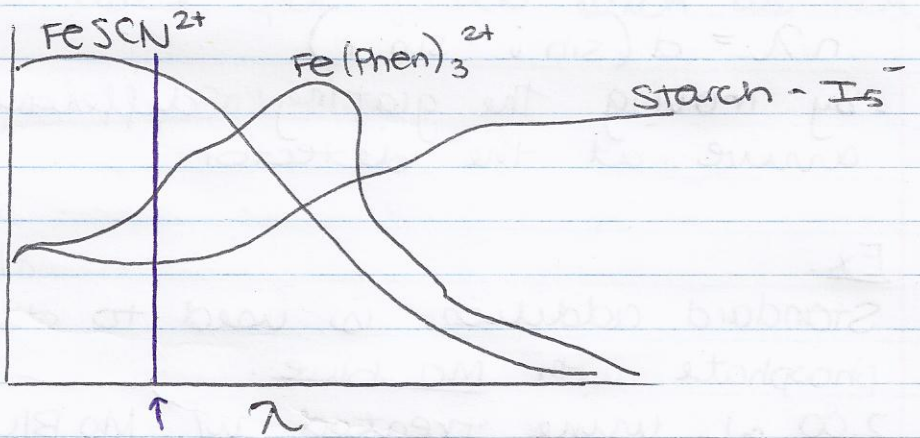
BAND ABSORPTION (see pg. 786/787)



LINE ABSORPTION



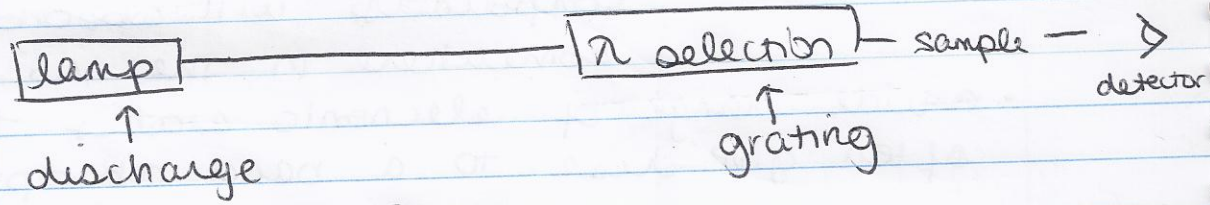
Ex.



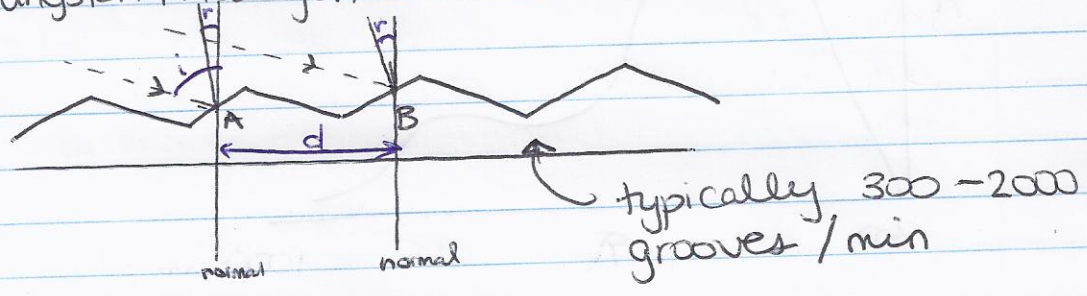
select λ for Beer's Law, can have multiple species absorbing

- tend to use UV-VIS by itself for simple, prepared solutions, not complex matrices
- Often couple UV-VIS to a chromatography technique such as HPLC

Advantages : - sensitivity 10^{-4} to 10^{-5} M
- down to 10^{-7} M sometimes possible
- good accuracy 1-5 %.
- easy to use
→ see ch. 25 to see how it is done



H_2/O_2 160 - 380 nm
Xe 250 - 600 nm
Tungsten / Halogen 240 - 2000 nm



$n\lambda = d(\sin i + \sin r)$

- by moving the grating, different λ's arrive at the detector

Ex.
Standard addition is used to determine phosphate with Mo blue.
2.00 mL urine treated w/ Mo Blue to produce a species absorbing at 820 nm.
Solution is diluted to 100 mL.
25.00 mL is taken & gives an absorbance of 0.428 (solution 1).
Add 1.00 mL of 0.05 mg phosphate to a second 25.00 mL aliquot → gives A = 0.517.
Calculate phosphate in mg/mL specimen.

$$C_x = \frac{A_1 C_s V_s}{A_2 V_1 - A_1 V_x}$$

C_s = [ ] std.

V_s = vol std.

$$= \frac{(0.428)(0.05\ mg\ mL^{-1})(1.00\ mL)}{(0.517)(25.00\ mL) - (0.428)(25.0\ mL)}$$

$= 0.00780\ mg\ PO_4^{3-}/mL$

↳ this is for the diluted solution

$$[PO_4^{3-}] = 0.00780\ mg\ L^{-1} \times \frac{100.00\ mL}{2.00\ mL}$$

$= 0.390\ mg\ mL^{-1}$

↳ in the initial urine sample.

IR Spectroscopy

- lower sensitivity than UV-VIS
- due to Q.M. selection rules for absorption
- poorly selective unless you have a strong absorbing functional group like C=O
- often used for gases such as NO_2, N_2O, etc.

Suggested Problems

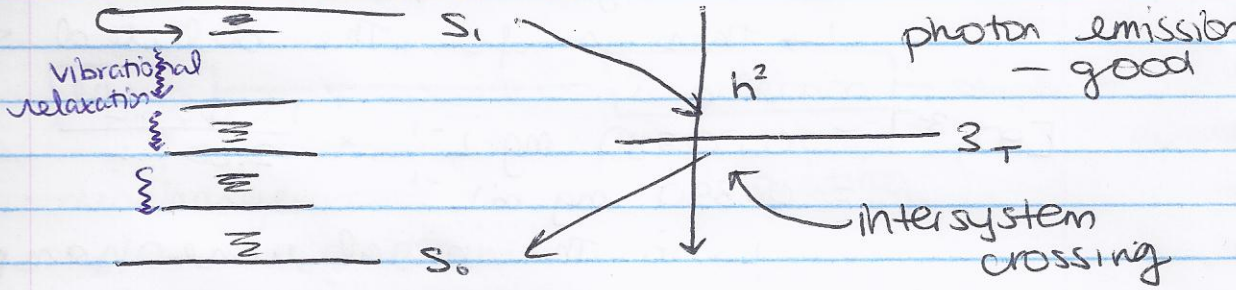
26.1
26.5
26.18
26.32

Hilroy

Ch. 27: Molecular Fluorescence

Fluorescence

- occurs when a species is in an excited state & emits a photon taking it to a lower state



- what you see depends on timescale
- lifetime of S_1 is too great, vibrational relax etc cuts away at the fluorescence yield

Fluorescence Power, F

$$F = K'(P_0 - P)$$

P_0 = power incident beam promoting system to the upper state

K' = efficiency of fluorescence (as opposed to other things)

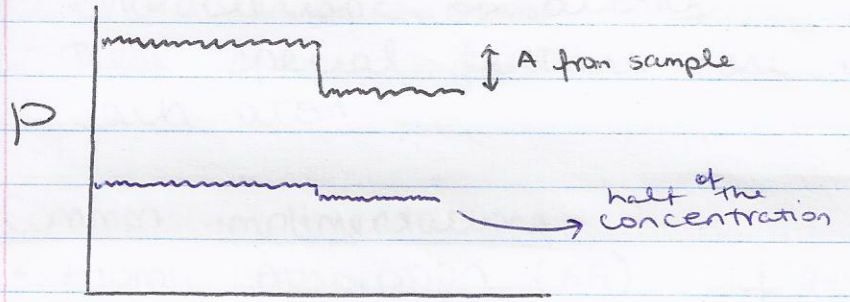
$\frac{P}{P_0} = 10^{-\varepsilon bc}$ (beer's law)

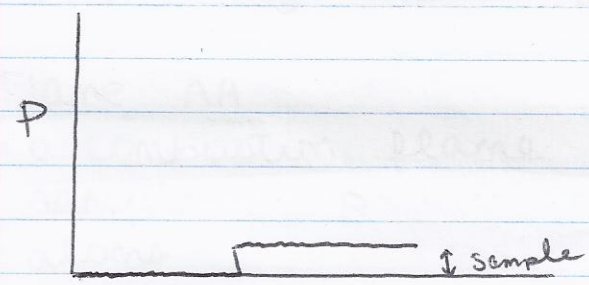
$\therefore \quad F = Kc$

Plot fluorescence vs. [ ], should get a straight line (at low [ ])

- can make this more practical by covalently adding a probe to our target.
- popular in bio
  → matrices are very complicated, limiting the fluorescence of most species
  see pg. 832

- fluorescence has lower detection limits than absorption





→ here the base line is 0 ∴ signal is better
∴ lower [ ]'s possible

So, the ultimate spectroscopy tool in analytical chem?
- fluorescence
- species with ns or less excited state lifetimes

Hilroy

Ch 28. Atomic Speciation

March 15

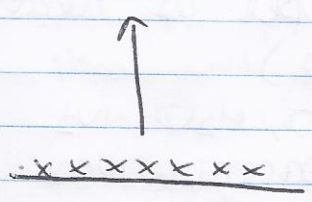
Molecular spectroscopic methods such as UV-VIS or IR (usually FTIR) tend not to be as useful on their own due to the complexity of the absorption spectra of polyatomic molecules.

Atomic spectroscopy is useful due to:
- few, discrete, absorption/emission lines characteristic of atoms
- these special features are indicative for each atom

Common implimentations:
- Atomic Absorption (AA) – flame
  – furnace
- Inductively-coupled plasma (ICP)

Flame AA

- a combustion flame used to atomize a sample & produce electronically excited atoms
- goal in AA is to produce ground state atoms that will absorb incident light of the appropriate wavelength



- because we are reducing molecular compounds down to atoms, we lose all info about the chemical environment of the atom.

Sample Pretreatment

- All samples need to be dissolved into solution
- Most often accomplished with a concentrated acid such as nitric acid
- Any wet chemistry can potentially cause interferences in AA
  → care must be taken to record everything that is done

ex. if you are analyzing for Cr, don't use steel utensils, etc.

Sample Delivery

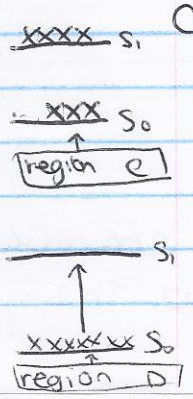
- Typically done by nebulyzing the liquid & passing the droplets into the flame
  → nebulizing: turning the liquid into a fine mist (like perfume)

The Flame

- Desire laminar flow (gas flow in which lines of flow are parallel & change smoothly in time & space)

Flame Regions

A) Premix region — no combustion
B) Preheat region — sample is heated
C) Reaction zone (blue cone)
   - rxn to produce CO_2, CO, H_2O, N_2
   - high radical & ionic concentrations
   - no thermal equilibrium
   - net reducing conditions
   - highly excited species produce emissions that can interfere with detectors



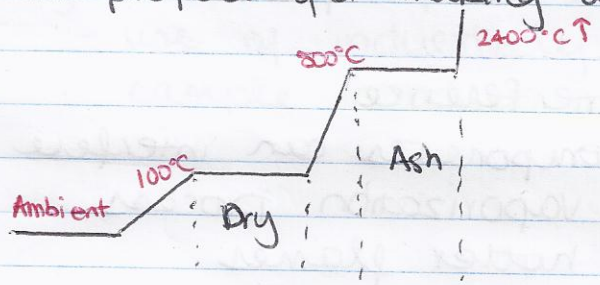
D) Interconal zone (faint colour)
- thermal equilibrium achieved producing mostly ground-state atoms

The absorption of light is monitored.

Graphite Furnace AA

- RATher Than using a flame to atOmize The analyte, we can also simply heat a droplet in a furnace
- **Advantage:**
  - not wasting sample ∴ The ability to use very small amounts of sample
  - some solids can be analyzed directly.

Time profile for making a GFAA measurement:



Interferences

#1) **Background absorption:**
- so many species in a flame, some may absorb the λ passing through
- this will raise the detection limit of the analysis (base line)
- usually corrected for by use of a blank.

#2) Spectral line interference

- occurs when species other than analyte absorb the same λ
- due largely to the bandpass (resolution) of the monochromator

ex.

Mg has a triplet absorption
403.1 403.3 403.5
and Ga 403.3

CaOH absorbs in a band that extends 543 - 622 nm that will interfere with Na (589, 589.6)

Solution — try to find a λ for an atom that is interference

#3) Vaporization interference

- some sample components can interfere in the salt particle vaporization process.
- reduced by hotter flames
- metals such as Al & Ti tend to form very stable oxides which prevent formation of atomic Al, Ti in the flame.
- use of releasing agents
  - can add another metal that out competes the target analyte for interferences

ex

Adding La or Sr to a Ca solution prevents phosphates of Ca to be formed.
Also EDTA.

#4) Ionization interference

- At high flame T, atoms with low IE tend to be ionized which changes their absorption spectra
- TO solve, add excess of very low IE material such as K, Cs or Sr.
  → they will charge transfer with ionized analyte

$$M^+ + K \longrightarrow K^+ + M$$

BOTH FAA & GFAA are absorption techniques.
→ Can also operate in emission (or fluorescence) mode:

AES (Atomic Emission Spectroscopy)

- tends to have wider dynamic range
- can suffer from spectral interference more often
- multi-element analysis
- very common implimentation:
  - use of inductively-coupled plasma sample introduction

March 17

Inductively Coupled Plasma (ICP)

- atmospheric electrical discharge
- "electrical flame"
- Ar^0, Ar^+, e^-, analytes?
- Robust
- High gas temperature
- High e^- # density
- Efficient ion source

ICP Torch & Plasma

- Load coil: copper tube — water or Ar cooled
- Power from the load coil is coupled to the plasma by electrical induction
- RF: 27, 40 MHz. Free running.

Plasma initiation

- free electrons are injected into the plasma gas (ie. Tesla coil)
- electrons are excited by RF magnetic field & collide with Ar atoms
- this generates more electrons & the process rapidly becomes self-sustaining

Aerosol Sample

Diffusion
↑
Ionization $M^+_{(g)}$
↑
Atomization $M_{(g)} + X_{(g)}$
↑
Vaporization $MX_{(g)}$
↑
Particle $MX_{(s)}$
↑
Liq. droplet $M^+_{(g)} + X^-_{(g)}$

Hilroy

Plasma Ionization

Argon gas T_g = 4500 - 8000 K

Electron T_e = 7000 - 10 000 K

Consider that the plasma is in local thermodynamic equilibrium.

$$M \rightleftharpoons M^+ + e^-$$

* know how it works & the key features (such as the temp).

Suggested Problems

28.1, 28.2 (*), 28.9, 28.15, 28.17 (big one)

Ch. 30 : Analytical Separations

The first step in any method is the extraction of the target analyte from the sample matrix.
→ involves separating the analyte preferentially from the matrix.

Precipitation:
- lower the solubility of an analyte until it leaves solution

Liquid - liquid:
- mixing water & chloroform in a separatory funnel to extract non-polar compounds from aqueous solution

There are many types of extractions. Chromatography is related to the extraction.

All analytical separations are based on the distribution law.
When two immiscible solvents (2 liqs, a liq + solid, or gas + solid etc.) come into contact, analyte A will distribute itself between them.

$$A_{solv_1} \rightleftharpoons A_{solv_2}$$

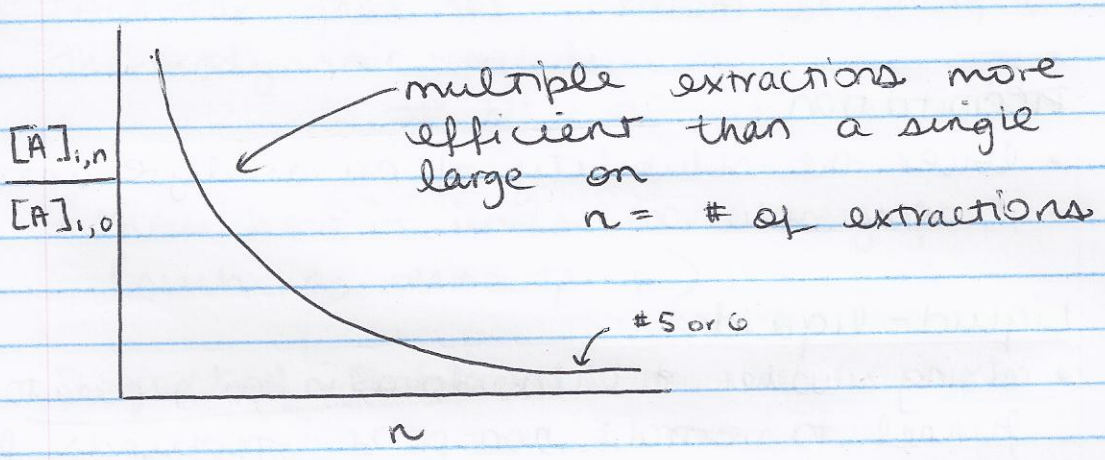
$$K = \frac{[A]_{solv_2}}{[A]_{solv_1}}$$

K, the equilibrium constant is called:
partition coefficient
OR
distribution coefficient

Hilroy

see textbook for explanation of derivation.

TO get $a_i \approx 0$ need to do multiple extractions.



There are methods that are equivalent to 5 or 6 experiments but are done all at once.

Solid-Phase Extraction (SPE)

An example of solid-liquid extraction.

Purpose:

- to selectively extract a component ~~form~~ from a liquid by passing it over a solid phase
- the adsorbed is then desorbed from the solid phase by a different, but pure, liquid.

Advantages:

- solid-phase support is in a disposable cartridge.
- after analyte is passed over the cartridge

and then the adsorbed analyte is removed, the cartridge can be reused or disposed of.

Terms to know:

Normal phase

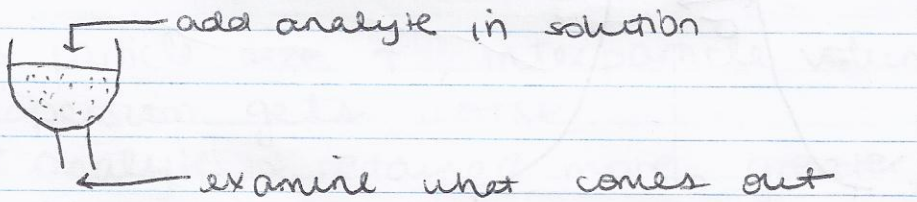
- uses a polar stationary phase (ie. basic silica)
- polar compounds are preferentially adsorbed
  → usually change mobile phase from non-polar to polar

Reverse phase

- uses a modified stationary phase
  → non polar molecule has been added to the surface of the silica packing.
- octadecyl (C18) or octyl (C8) functional groups are very common
- will retain non polars preferentially.

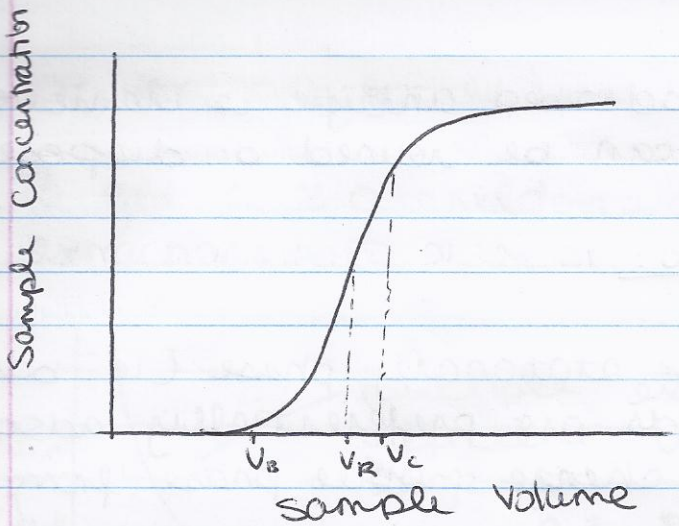
Ion exchange

- column packings that have charge-bearing functional groups attached to a polymer support
- analyte ions displace the charged functional group of the stationary phase.



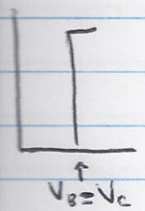
Graph obtained ⟶

Hilroy



Breakthrough volume (V_B)
- volume of sample that passes over the SPE packing at which point the analyte is detected AFTER the column
- ex. column starts bleeding analyte

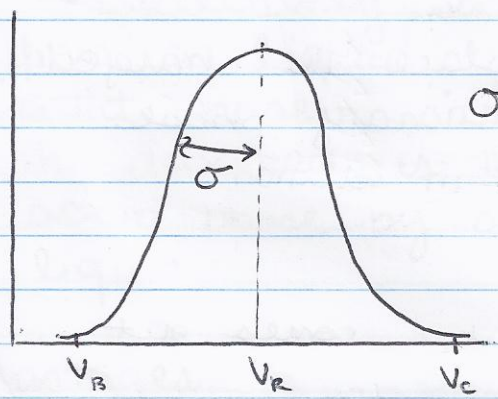
ideally:



Device saturation (V_C)
- volume at which [analyte] entering device = [analyte] exiting
- saturation

By taking the derivative...

ideally



σ = std. dev.

- gaussian distribution

March 22

Plate Height & plate Number

Plate number

- # of times the analyte partitions between the two phases during its passage through the cartridge

$$N = \frac{L}{H} = \left(\frac{t_R}{\sigma}\right)^2$$

L = column length
H = plate height
t_R = time of elution of band centre (corresponding to V_R)

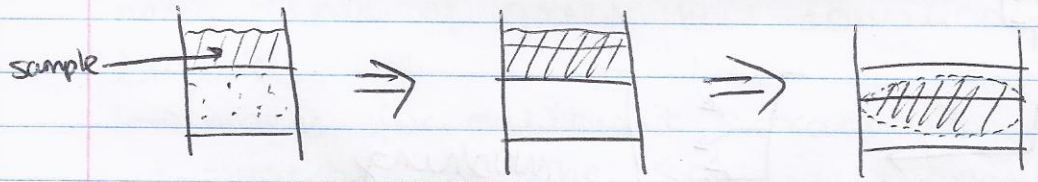
Plate height

- distance analyte moves during one partition

$$H = \frac{L}{N}$$

So, on a column w/ 10 000 theoretical plates that is 1 cm long, $H = 1 \times 10^{-4}$ cm

σ_V comes from axial dispersion.



- As particle size ↑, interparticle volume also ↑ & dispersion gets worse.
- As analyte is retained more, greater dispersion & therefore breakthrough volume goes to lower values

Ideally: $V_B \approx V_c$

→ all sample analyte retained until capacity of SPE stationary phase is exceeded.

There are three sets of parameters we can optimize:

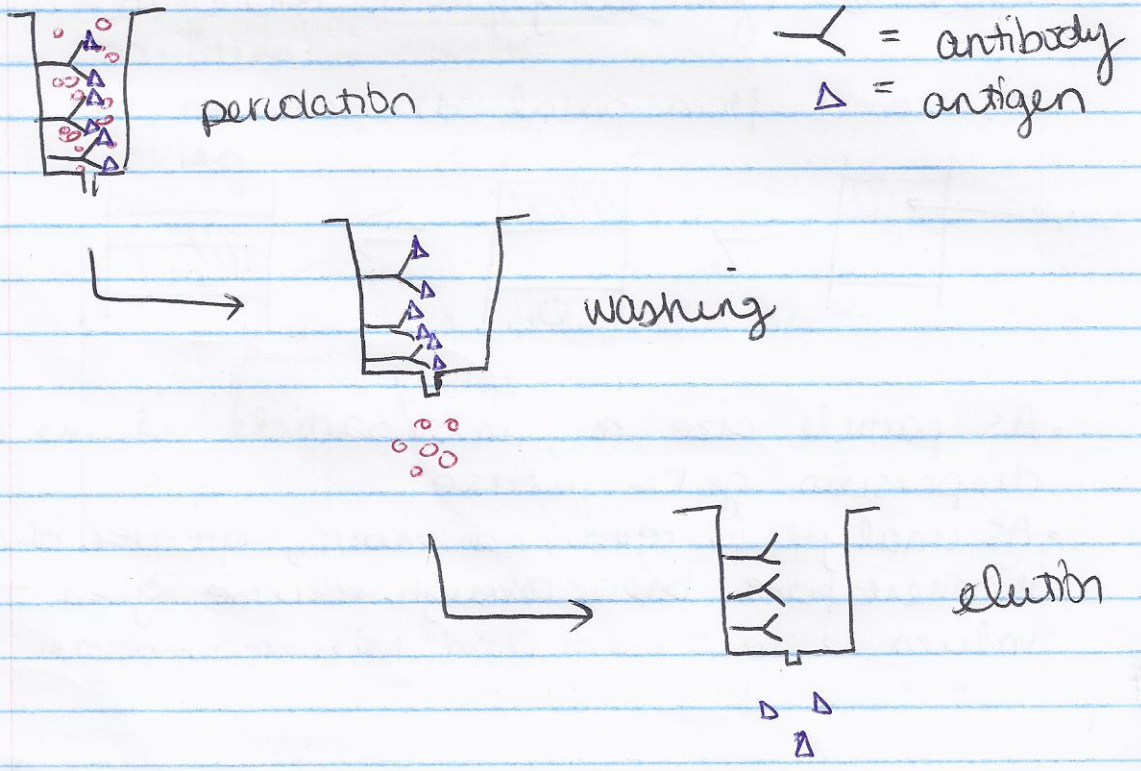
- size (V_m, N)
- kinetics (N, particle size, flow rate)
- retention (N, k, V_M)

$\frac{\Delta P}{L}$ pressure drop across cartridge per unit length. This limits particle size in SPE

As plate #s ↑, $V_B \rightarrow V_c$

More selective way: immunoaffinity

→ very expensive.



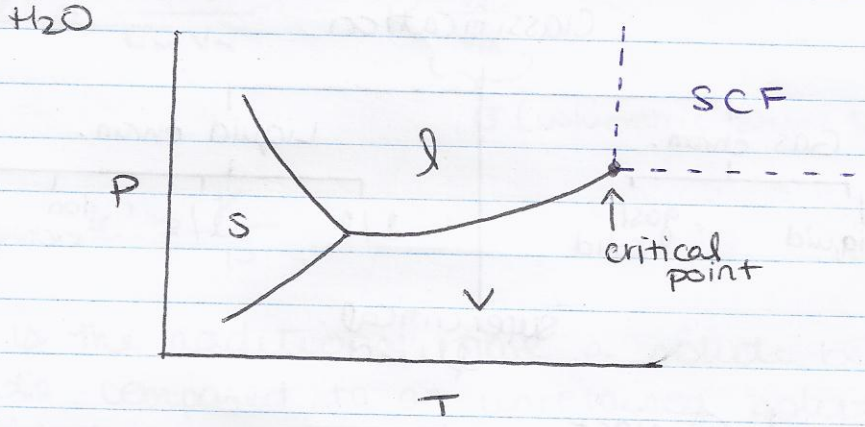
Molecularly Imprinted Polymer

- Mix target analyte (A) with monomer for polymerization (monomer grows around A)
- Add polymer initiator + crosslinker
- Disturb H bonds holding A in polymer with an acidic solution rinse

Super Critical Fluids

→ above the substance's critical point

ex.



Super critical fluids tend to have the viscosities near those of gases but solvation abilities of liquids.

→ makes for efficient extractions

→ properties of the SCF is tuneable by varying P & T above the critical point

CO_2 is one of the most common SCF used due to the fact that it is cheap & easy to separate from the analyte

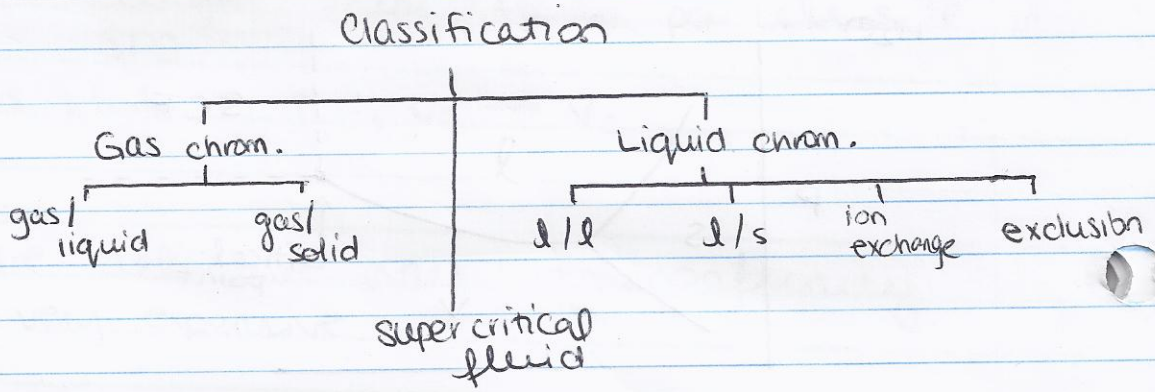
- reduce pressure & the CO_2 evaporates leaving the extracted analyte.

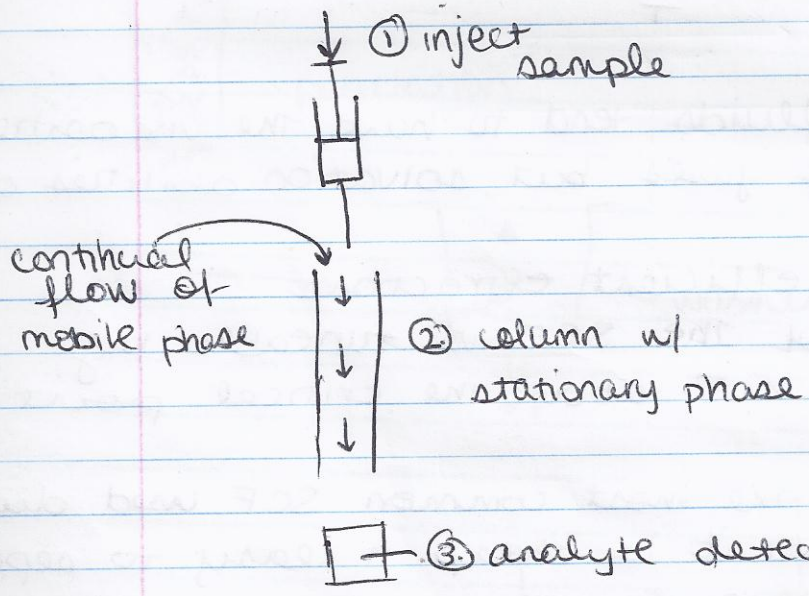
Hilroy

Suggested Problems

30.5	30.25
30.7	30.27
30.11	30.29
30.15	30.31

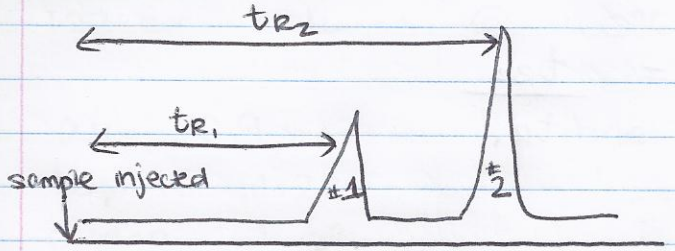
Ch. 30E : Chromatography





Want to separate many possible analytes. Need to add an extra dimension to the separation = retention time.

Retention behaviour



Partition Ratio (k')

$$k' = \frac{C_S V_S}{C_M V_M} = K \underbrace{\frac{V_S}{V_M}}_{\beta \text{ (volumetric phase ratio)}}$$

$$\therefore \quad k' = \frac{K}{\beta}$$

k' is the additional time a solute band takes to elute compared to an unretained solute ($k' = 0$), divided by the elution time of an unretained band

$$k' = \frac{t_R - t_M}{t_M} = \frac{V_R - V_M}{V_M}$$

Ex.

1000 cm tubular column w/ 0.25 mm base

carrier gas velocity is 37 cm sec^{-1}

t_R = 1.27 min

peak width @ half height is 0.88 sec.

$$t_M = \frac{L}{u} = \frac{1000\ cm}{37\ cm/sec} = 27\ sec\ (0.45\ min)$$

$$k' = \frac{t_R - t_M}{t_M} = \frac{1.27 - 0.45}{0.45} = 1.82$$

IN GENERAL: $k' < 1$ → not analytically useful

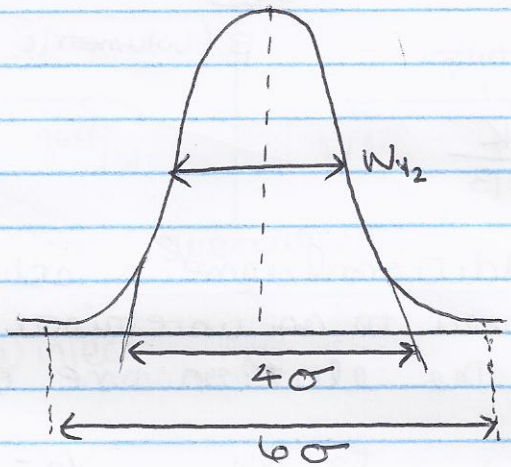
$k' > 10$ → too time consuming (Kilroy)

Relative Retention (α)

$$\alpha = \frac{k_2'}{k_1'} = \frac{t_{R2}}{t_{R1}}$$

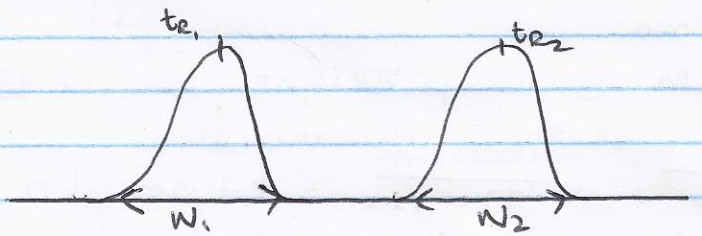
Column Efficiency

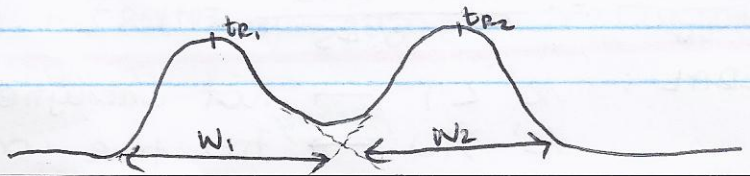
K & k' are independent of total analyte concentration when Henry's Law is obeyed.
→ partitioning is said to be linear



Resolution
- degree of separation of two adjacent bands

$$R = \frac{t_{R2} - t_{R1}}{0.5(W_2 + W_1)}$$





Ex.

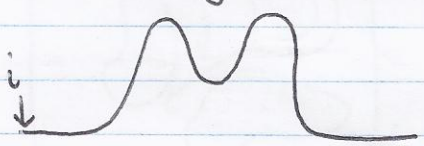
122 cm column @ 160°C

air	0.9 mm	base widths :	0.14	heptane
heptane	1.22		0.20	octane
octane	1.43			

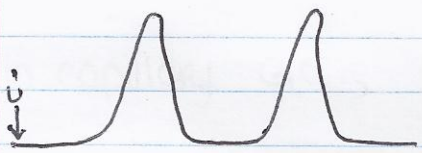
$$\alpha = \frac{t_{R_2} - t_M}{t_{R_1} - t_M} = \frac{1.43 - 0.9}{1.22 - 0.9} = 1.666$$ relative retention time.

$$R = \frac{1.43 - 1.22}{0.5(0.2 + 0.14)} = 1.24$$

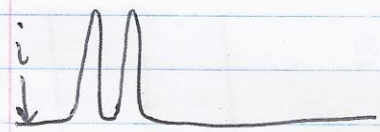
Selectivity, Efficiency, Partition Ratio



reasonable selectivity
poor efficiency



good selectivity & efficiency



good efficiency, poor selectivity & low k'

selectivity ∝ peak separation (rel. ret. time).
efficiency ∝ resolution (plate #)

Hilroy

March 24

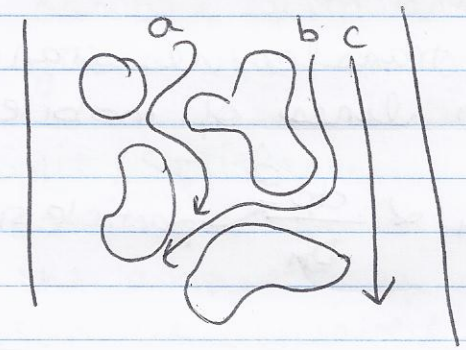
Band Broadening

- several processes occur on a column that lead to broadening of the analyte peaks.

$$\text{Plate Height } (H) = A + \frac{B}{u} + C_s u + C_M u$$

u ↑ avg. linear velocity of mobile phase.

A ⇒ eddy diffusion due to inhomogeneous flow around particles



a, b, c have diff. transit times ∴ peak broadening.

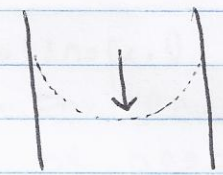
$$A = \lambda d_p$$

λ ↑ uniformity of packing

d_p ↑ particle size.

In capillary GC, $A = 0$

B ⇒ longitudinal diffusion (axial)



$$B = 2\gamma D_M$$

γ ↑ observation factor

D_M ↑ solute diffusion coefficient

B tends to be significant for low mobile phase velocities

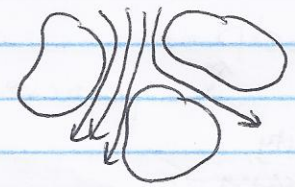
C_s ⇒ results from resistance to mass transfer at solute/stationary phase interface

$C_s \propto \frac{df}{D_s}$ ← thickness of stationary phase

← diffusion coefficient in stationary phase.

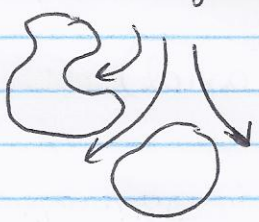
Slow movement in stationary phase means that a fast ~~molecule~~ mobile phase flow = peak broadening

C_M ⇒ radical mass transfer resistance between stream lines of mobile phase



$C_M \propto \frac{dp^2}{D_M}$ ← particle size

- can also get stagment pockets.



Gas Chromatography (GC)

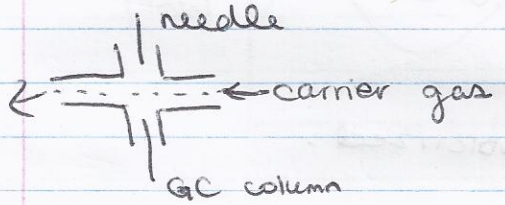
Consists of 6 basic parts:
1) constant flow of carrier gas
2) sample introduction
3) column
4) thermostated chamber (oven)

Sample introduction

- mainly done by volatilying a liquid (or solid) sample with heat.
- gases are OK as is.

Split / Splitless

- sometimes it is necessary to cut back on the amount of sample going on-column. This can be achieved by "splitting" the sample



Some of the sample is carried to the column, the rest is wasted.

- Useful if a large solvent front is undesirable
- For low [ ] samples, splitless mode may be needed to get enough sample on the column.

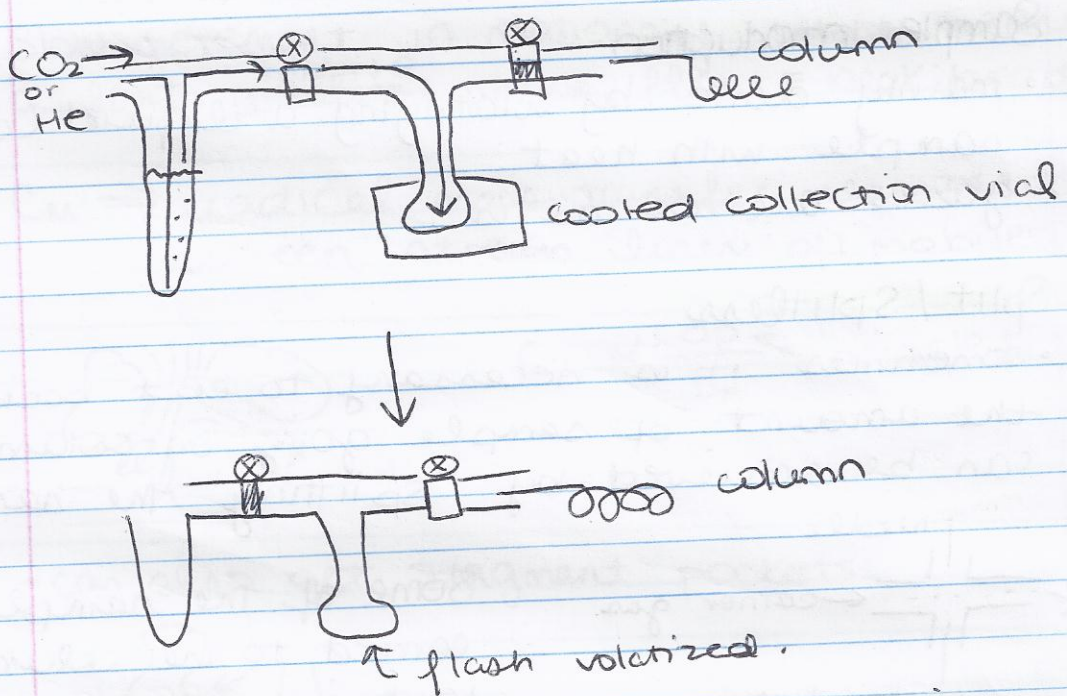
Head space

- gas-tight syringe can be used to sample the gas above a solid or liquid.
- useful for volatile components in complex matrices.

Hilroy

Purge & Trap

- desorb volatile compounds by heating or passing a gas through the sample.
- analytes get concentrated by freezing (typically with CO_2 expansion) then instantaneously heated & injected onto the column.



P & T is very good for direct introduction of volatiles in water.

Pyrolysis

- flash heating of solids to very high temp.
- method of polymer analysis.
- as T↑, more compounds desorb (& decompose)
- need a way to control introduction to GC column (pulsed gas flow for instance).

(CONTINUED IN 3 PAGES)

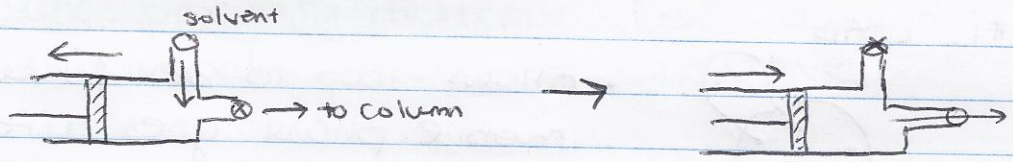
Ch. 32 : HPLC Instrumentation

March 31

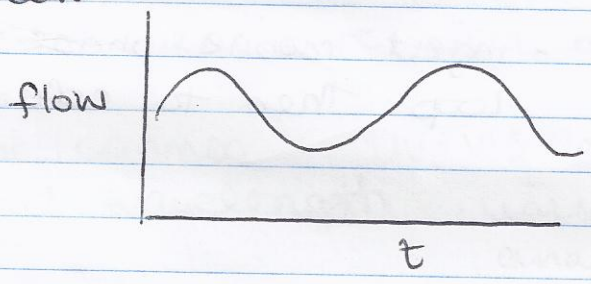
The heart of an HPLC is the pump.

- must deliver mobile phase at high P (~100 atm to 400 atm) at consistent flow rates (0.5 - 3 ml/min)
- as column size ↓, so do flow rates.
- for MS, need ~ 0.02 ml/min
- micro HPLC needs these low flow rates too.

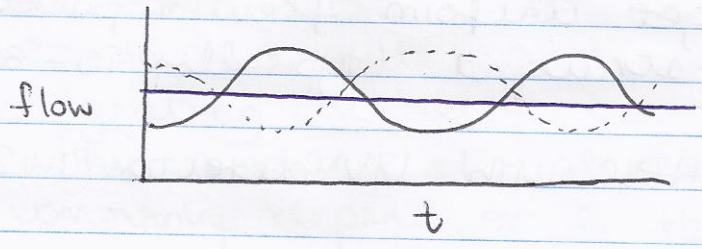
Piston Pump:



- using a single piston can lead to pulsed flows



- by using 2 pistons, 180° out of phase:



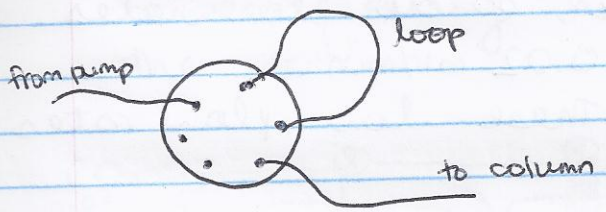
- using 3 pistons gives 120° out of phase.

Hilroy

Sample Introduction

Done via a sample loop — see Rheodyne injector

- filling the loop gives volume injected accurate to less than 0.1 %.



#1. LOAD

- allows loop to be filled, mobile phase goes directly to column

#2. INJECT

- inject mobile phase through loop then to column

Columns

- Standard HPLC column is stainless steel tube containing packing material.
- Easier to get uniform flow & packing if they are straight (typically 10 - 30 cm long)

Analytical HPLC with UV detector : 2 - 4 mm ID

with MS : 1 mm ID (can go down to μm ID)

Flow 2 - 3 mL/min

Narrow bore

ID ↓ by 2 means 4x ↑ in sample signal

Volumetric flow needed to achieve a given eluent velocity is 4x less when ID ↓ x2.
- since volume flow ↓, [ ] analyte is 4x greater ∴ hence detector response ↑ by 4.

Detectors

Bulk property detector (ex. refractive index)
— universal, but not sensitive.

Property detector
- depends on a solute property such as absorbance
- more sensitive but not universal

Most common : UV-VIS spectrophotometer
Fixed wavelength : · usually for dedicated analyses
· uses 1 λ only.

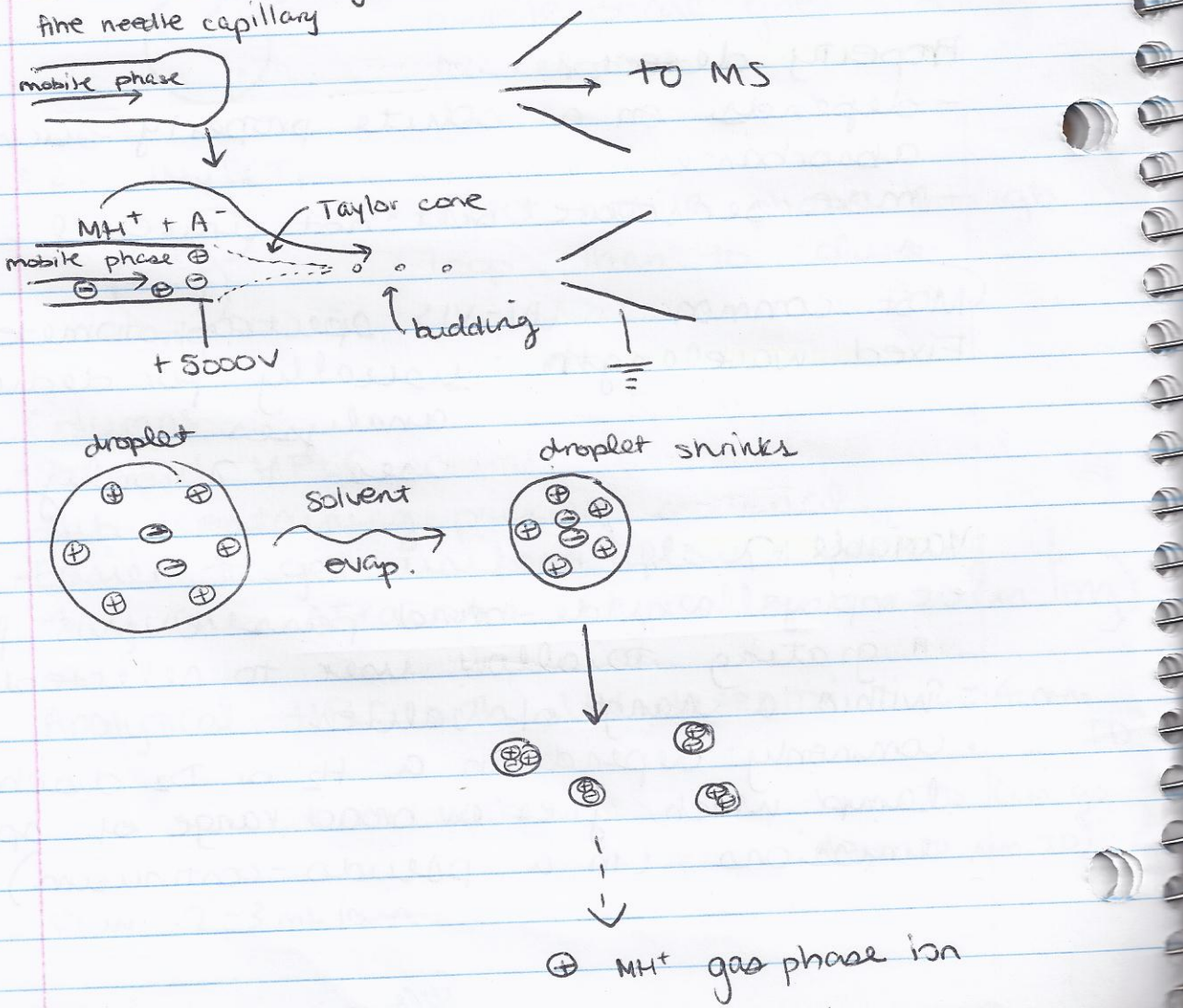
Variable λ :
- employs a wide-band pass UV-VIS filter ∴ grating to allow user to selected λ within a range of values
- commonly depend on a H_2 or D_2 discharge lamp which gives a broad range of spectral emissions (in a pseudo-continuum)

Scanning λ:

- as each solute elutes, the grating scans & a UV-VIS spectrum for that analyte is obtained
- requires array detection to be fast enough.

Mass spectrometer:

- until recently, joining HPLC to MS was difficult due to the large volume of solvent entering the vacuum system
- electrospray has revolutionized LC-MS



The process is aided by a flow of gas, usually N_2, co-axial to the capillary.
- aids heat transfer ⇒ desolvation

* ions are generated in solution with either acid or base.
E-spray transfers ions into the gas phase

High Performance Liquid Chromatography (HPLC) Optimization

- difficult due to large # of parameters to define (t_M, ΔP, N, etc)
- goal is to find a practical set of experimental parameters

• reduced plate height $h = \frac{H}{dp} = \frac{L}{Ndp}$ ← particle diameter

• reduced velocity of eluent $v = \frac{udp}{D_M}$ ← diff. coef. of in mobile phase

$$v = \frac{Ldp}{t_M D_M}$$

now write h in terms of v

reduced plate height: $h = \frac{B}{v} + Av^{0.33} + Cv$

→ for solid-ion packings $B \sim 1.2$
porous " " $B \sim 2$

Hilroy

For a well packed column : $A \sim 1$
Porous packing $C \sim 0.05$
$C \sim 0.003$ for solid-core packing.

Note:
- h is independent of particle diameter
- contraints are dependent only on how well column is packed
- changing column bore makes no difference

Temperature
T affects viscosity (η), solubility, D_M

Column Performance
ΔP : as $\Delta P \uparrow$, $t_R \downarrow$ but also h can $\uparrow$ due to heat generation
$P > 5000$ psi are not usually practical

dp : typically, performance improves as dp $\downarrow$ but dp $\times \frac{1}{2}$ translates to $\Delta P \times 4$
generally dp < 5 µm

L : smaller particle sizes usually coupled with shorter columns.

η : keep viscosity low
η affects ΔP, D_M

Gas Chromatography (continued) March 29

Columns

- At the beginnings of GC, packed columns were the norm
- Now, capillary glass columns are almost exclusively used.

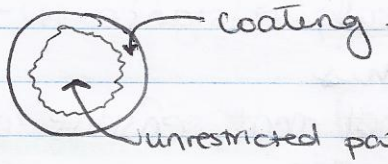
→ made from silica glass

"mega bore" ~0.53 mm id → gc/fid, gc/ecd
- ~2.5 mL/min

→ quadruple instruments : ~0.35 mm id → gc/ms
ex. mass spectrometer

→ high vaccum instruments : ~0.21 mm id → gc/ms
ex. magnetic sector

The most common capillary tubes are open tubular (coated on inside surface).



WCOT : Wall coated open-tubular
→ stationary liquid phase made uniform with a polymer coating.

SCOT : Support coated open-tubular

PLOT : Porous-layer open-tubular

Stationary Phases

- typically looked up in a catalogue

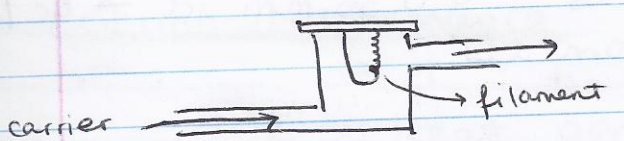
DB-5 : polydiphenyl dimethyl siloxane
85% unsubstituted
- low boiling, large molecular weight range

Column Ovens

- ~~thermo~~stated to ± 1°C for precision separations

Detectors

TCD : Thermal Conductivity Detector



- pass current through wire, heat to constant T
- as organic ~~filament~~ material hits filament, conductivity of carrier decreases.
- therefore, filament retains heat & temp. increases
  → changes the electrical resistance in the wire
  → able to measure this
- fairly universal but not that sensitive or selective

FID : Flame Ionization Detector

- burn a mixture of H_2 & O_2 to form a flame
- ions + free e^- formed in flame hit electrodes which causes a current increase
- responds primarily to C-H bonds
  → not responsive to inert gases such as CO, CO_2, NO_2 ...

TED : Thermionic Emission detector
- employs an H_2 plasma that is low T, suppressing flame ionization for compounds without N or P

ECD : Electron Capture Detector
- one electrode has radioactive β^- emitter
- results in plasma of e^- + ions when N_2 is used as a carrier
- selective for compounds that have positive electron affinities (halo-substituted)

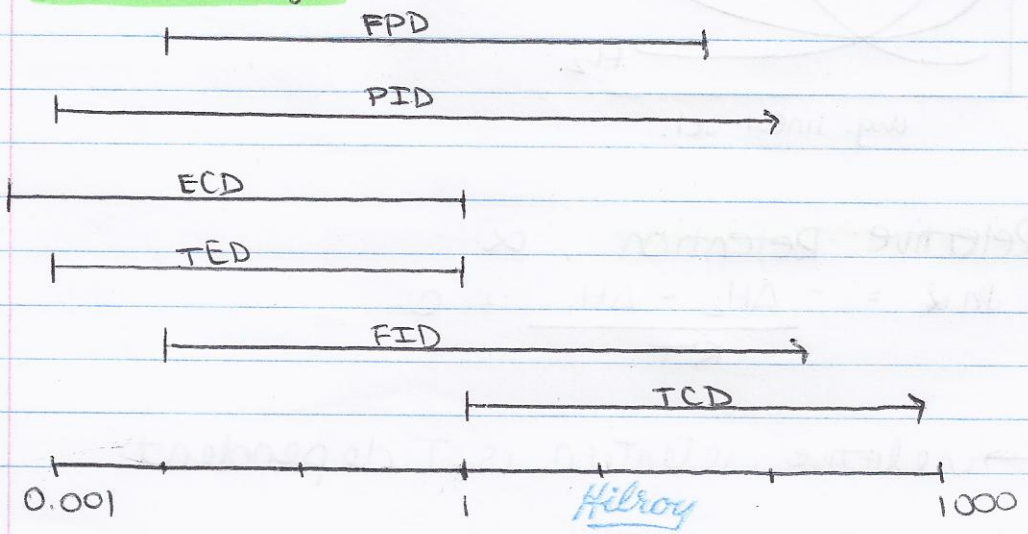
→ method of choice for PCBs

FPD : Flame Photometric Detector
- selectively detects photo emissions from excited HPO (510, 526 nm) + S_2 (394 nm)
- flame detector

PID : Photo Ionization Detector
- uses vaccum UV to ionize molecules

→ usually coupled with mass spectrometer

Dynamic Ranges (see Ch. 31)



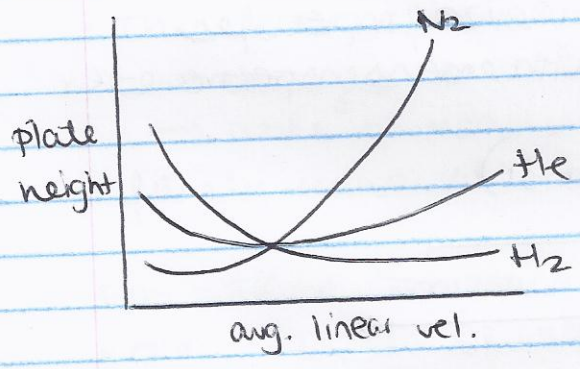
Optimizing GC Conditions

For capillary columns:
- plate height = H
- want H ↓

* Know proportionality

r = column radius — $H \propto r$ ∴ r ↓
k' = partition ratio — $H \propto \frac{k'}{k'}$ → optimize
D_m = solute diffusion coeff. — $H \propto D_m/D_m$ → optimize
u = average linear velocity of mobile phase — $H \propto u/u$ → " "
df = stationary phase thickness — $H \propto df$ ∴ df ↓
D_s = diff. coeff. of solute in stationary phase (dependent on temp.) — $H \propto \frac{1}{D_s}$ ∴ D_s ↑

Carrier gas
- different gases will have different average linear velocities



* H_2 is good.

Relative Retention, α

$$\ln \alpha = \frac{-\Delta H_2 - \Delta H_1}{RT} + C$$

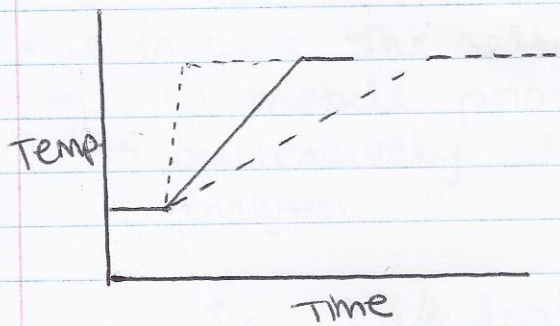
→ relative retention is T dependent

Programming T

- since [ ] of analyte in stationary phase is greater than [ ] in gas phase, able to determine ΔT needed to halve K.

- each compound is unique ∴ need specific T in order to optimize K'.

- change T as it goes, as compounds come in.



- if there aren't many things at low T, we increase T faster to save time to get to analyte's optimum temp.

Suggested Problems

31.1 31.7 31.11
31.6 31.10 31.17.

Gradient Elution

April 5/11

Isocratic elution:
- constant mobile phase make-up
- will not separate a complex mixture in a reasonable amount of time.

Able to change the mobile phase composition (similar to changing T in GC)
→ called a solvent gradient program

- we increase the eluent strength (solvation ability) of the mobile phase during the program
  → successively elute more strongly retained analytes.

$$t_g = t_M \bar{k} \log\left(\frac{2.3\, k_o}{\bar{k}}\right)$$

k_o = k' at time 0
t_g = retention time in a gradient elution
$\bar{k}$ = avg. k' during gradient elution

- at any given time, $1 < \bar{k} < 10$
  → tend to have $\bar{k} \sim 10$ at the beginning of run
  → tend to have $\bar{k} \sim 1$ as analyte comes off column

- since k is dropping during the elution, peaks tend to get narrower ∴ better resolution sensitivity.

Hilroy

Gradients:
- usually select a linear gradient at first
-

Stepwise elution:
- rapid changes in mobile phase composition

Suggested Problems

32.2, 32.3, 32.5

(Ch. 32 A & B)

Exam

65 % Paul — all theory
35 % Wendy — all numerical

16 questions

Q 1 - 11 Paul - short answer (5 marks each)
- describe detector in gas chrom.
- why plate height not plate #

Q 12 - 15 Wendy

Q 16 Paul - long answer (10 marks)

Review DGD — Friday April 15 AM

Hilroy