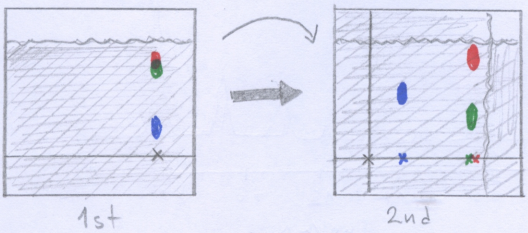
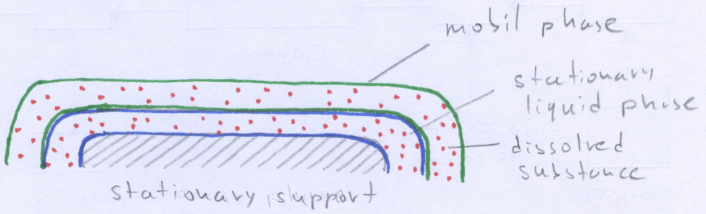
- paper chromatography
  - ↳ solvent - mobile phase stationary phase - water trapped between fibres of paper used
  - ↳ substances have different affinities for solvent and water so move over paper at different rates
  - ↳ some substances seen directly otherwise use locating agent eg: ninhydrin for amino acids
- R_f value - retardation factor
  - ↳ changes with temp, pH, solvent type so must stay constant

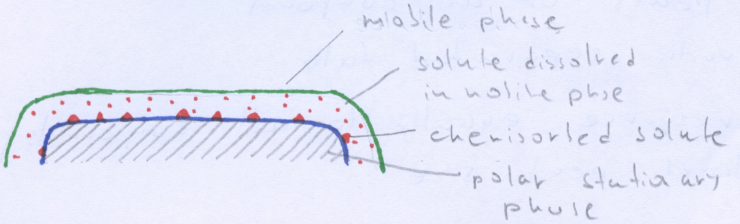
- two way paper chromatography
  - ↳ used if components of a mixture have similar R_f in given solvent
  - ↳ paper chromatography carried out then rotated and repeated with a different solvent

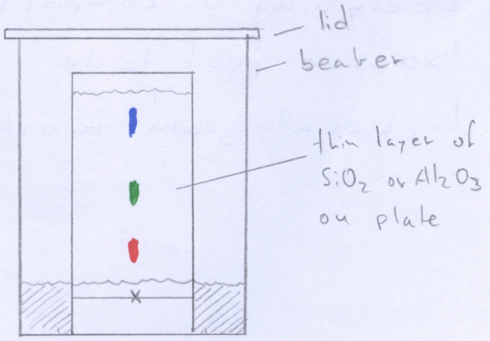




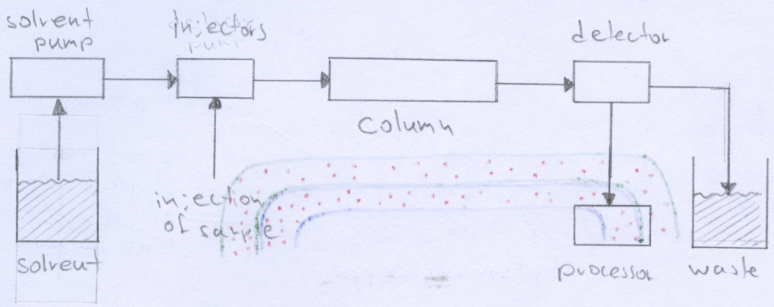
- partition coefficients
  - ↳ different partition coefficients (relative solubilities) of substances in used solvent and trapped water
  - ↳ greater the solubility in mobile phase faster movement R_f ↑

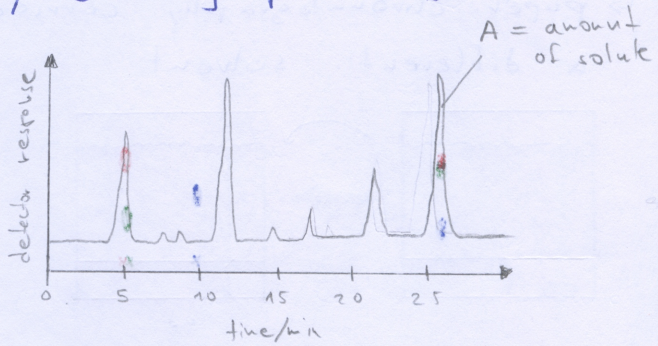
- TLC - thin layer chromatography
  - ↳ solid stationary phase which chemisorbs the molecules of solute
  - ↳ usually Al_2O_3 or SiO_2 made to paste and dried in oven on slide
  - ↳ polar molecules adsorb to polar solid stationary phase more
  - ↳ if slide rehydrated by air partitioning also plays role
  - ↳ Faster than normal paper chromatography and smaller samples can be analyzed
  - ↳ forensic analysis of drugs + explosives



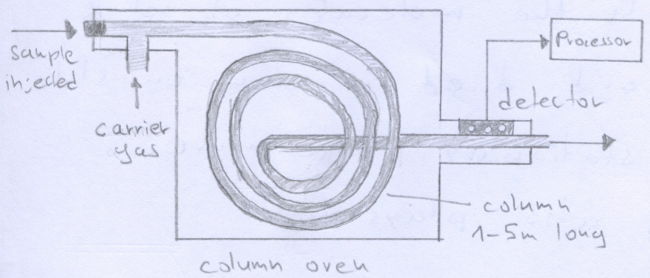


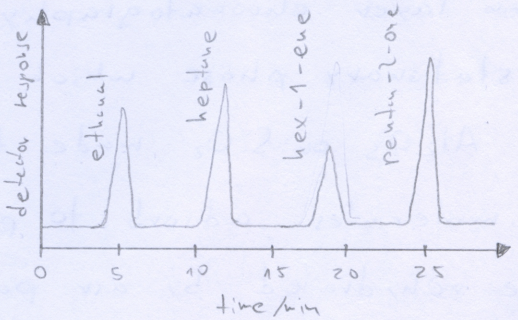
- HPLC - high performance liquid chromatography
  - ↳ stationary phase - non-volatile liquid bonded to solid support tightly packed in a column
    - eg) long chain hydrocarbon bonded to silica beads
  - ↳ solvent in mobile phase - usually polar liquid forced through column under pressure
    - eg) methanol or H_2O
  - ↳ particles in column - ↑ SA so large partitioning effect ∴ ↑ separation
  - ↳ detector measures retention time - time for 'solute' to pass column
  - ↳ A under peaks = amount of solute coming out
  - ↳ retention factor k $R_f = \frac{1}{k+1}$
  - ↳ medicine research, urine test for doping, monitoring pollutants





- GLC - gas liquid chromatography
  - ↳ gaseous sample injected into column
  - ↳ sample propelled by inert gas carrier - mobile phase
  - ↳ used for gases, liquids, volatile solids - vapours
  - ↳ database used to identify known compounds based on retention time
  - ↳ conditions must be controlled





- Determining % composition from GLC
  - ↳ assure peak to be triangle or line
  - ↳ chromatogram must - show all peaks of all compounds
    - all compounds separated fully
    - detector response equally to all compounds so proportional peak size

$$\% \text{ of } X = \frac{\text{peak area } X / \text{peak height } X}{\text{sum of peak areas / sum of heights}} \times 100$$

  - ↳ uses - blood sample, fuel in motorsport

- mass spectrometry
  - ↳ used to measure relative isotopic mass, abundance, identify org compounds
  - ↳ sample vaporised then bombarded by high E e^- which knock out e^- from molecule + brake covalent bonds giving charged fragments
- fragmentation - most commonly C-C C-O C-N bonds broken
- M^+ peak - molecular ion gives highest large peak
  - forms if $1e^-$ knocked out and gives relative molecula mass
- $[M+1]^+$ peak - small peak beyond M^+ due to C-13
  - allways 1.1 % of C is C-13 can be used to find no of C atoms in molecule

$$n = \frac{100}{1.1} \frac{[M+1]^+ \text{peak}}{M^+ \text{peak}}$$

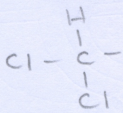
- $[M+2]^+$ and $[M+4]^+$
  - ↳ if sample contains Cl or Br same approach can be used

Cl - 35 - 75 %. Cl - 37 - 25 %. Br - 79 - 50 %. Br - 81 - 50 %.

- one Cl or Br per molecule
  - ↳ if $[M+2]^+$ peak is $\frac{1}{3}$ of M^+ peak suggests one Cl atom per molecule since abundance 75 : 25 ⇒ 3 : 1
  - ↳ if $[M+2]^+$ peak is same height as M^+ suggests one Br atom per molecule since abundance 50 : 50 ⇒ 1 : 1
- two Cl or Br per molecule
  - ↳ 4 permutations possible 3 of which have different mass

for Cl ratio is 9 : 6 : 1 Br ratio is 1 : 2 : 1

eg.) dichloromethane



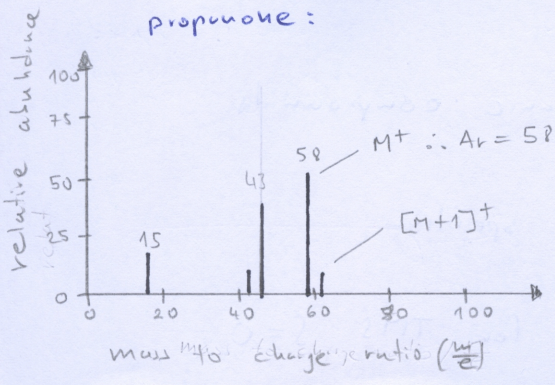
$^{35}Cl\,CH_2\,^{35}C^+$ – M^+ peak 9

$^{35}Cl\,CH_2\,^{37}C^+$ } $[M+2]^+$ peak 6

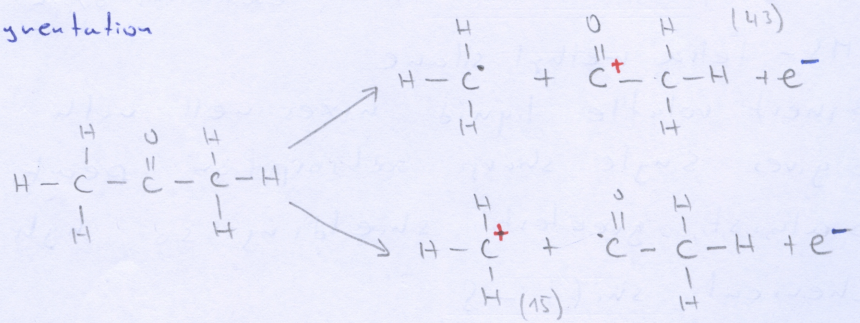
$^{37}Cl\,CH_2\,^{35}C^+$ }

$^{37}Cl\,CH_2\,^{37}C^+$ – $[M+4]^+$ peak 1

propanone:



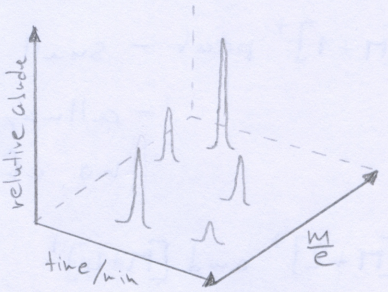
fragmentation



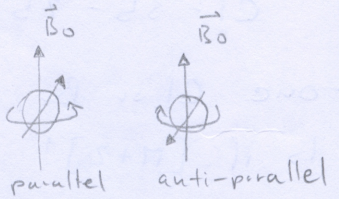
- High resolution mass spectra
  - ↳ can distinguish between ions which otherwise appear to have = mass
  - ↳ enables differentiation of molecules of different atoms due to slight difference in mass as a result of binding energy in molecule

eg) $C_2H_7N^+$ -45.057846 CH_3NO^+ -45.021462

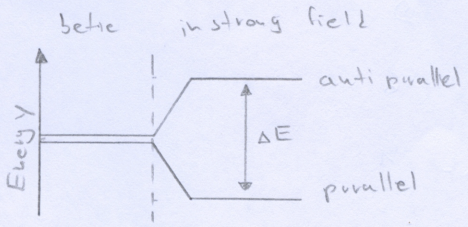
- Applications
  - ↳ used after GLC or HPLC to instantly identify separated solutes
  - ↳ each solute has characteristic retention factor + peaks on mass spectrum
  - ↳ 3D graph of abundance against time and $\frac{m}{e}$
  - ↳ analysis of: pollutants + crude oil
    drugs + toxins

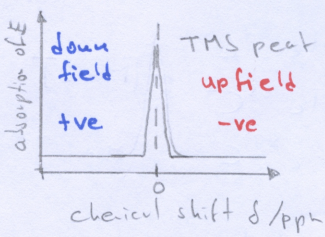


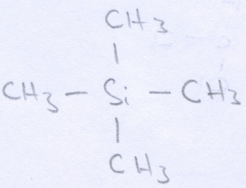
- soft ionisation
  - ↳ no fragmentation but H^+ added by firing H^+ instead of high E e^-
  - ↳ MH^+ peak formed used in biochemical research



- principles of proton NMR
  - ↳ pt in nucleus has charge + spin so acts as magnet
  - ↳ in magnetic field pt either allined (parallel) or anti parallel to field and these two states have different energies and their difference ΔE falls into RF range
  - ↳ field strength B_0 or frequency varied until resonance occours and states flip giving a peak
  - ↳ size of ΔE depends on molecular environment since a bond pulls e^- away and e^- shield nucleus from magnetic field further away e^- = ↓ ΔE so ↓ δ or stronger field



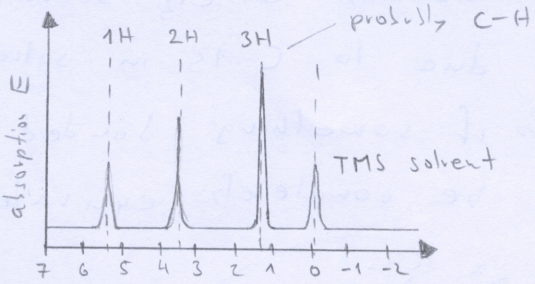




- TMS - tetra methyl silane
  - ↳ inert volatile liquid mixes well with organic compounds
  - ↳ gives single sharp absorption peak
  - ↳ almost greatest shielding so high on spectrum

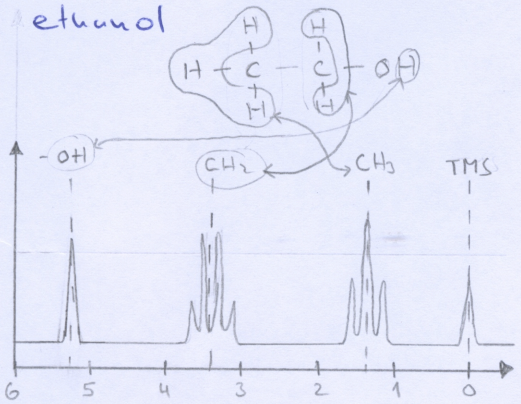
- Chemical shift - δ
  - ↳ measured in parts per million (ppm) for TMS $\delta = 0$

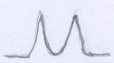
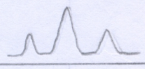
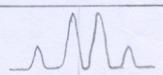
- Low resolution HNMR
  - ↳ shows single peak for each non-equivalent H atom
  - ↳ area of each peak gives relative amount of H atoms responsible
  - ↳ checked against known database



- High resolution HNMR
  - ↳ provides more information to interpret
  - ↳ single peaks on LRNMR give clusters on HRNMR due to interference of magnetic fields of spins on neighbouring nuclei – **spin-spin coupling**
  - ↳ splitting pattern depends on no of H on adjacent C atoms
  - ↳ peak splits into n+1 peaks n is no of H on adjacent C
  - ↳ relative intensity of peaks follows pascals triangle !

eg) ethanol



number of adjacent H atoms	(by n+1 rule) peak splits to	relative intensities	observed pattern
0	1 – singlet	1	
1	2 – doublet	1 : 1	
2	3 – triplet	1 : 2 : 1	
3	4 – quartet	1 : 3 : 3 : 1	

- Identifying –OH and –NH– signal
  - ↳ –OH and –NH– give single peak because they exchange rapidly with H^+ from acid or solvent so average out to single peak
  - ↳ often difficult to identify – wide range of values
  - ↳ add small amount of D_2O (heavy water) and peaks disappear
  - ↳ ^2H and ^1H in dynamic equilibrium
  - ↳ ^1H in –OH and –NH– called **liable proton**

- Carbon 13 NMR
  - ↳ majority of C is C-12 so gives no peak but 1.1% is C-13 which gives peaks of non-equivalent C-13
  - ↳ no splitting since peaks appear as lines
  - ↳ height $\xrightarrow[\text{not !}]{}$ proportional to relative amount of non-equivalent C-13

- Carbon - 13 NMR

↳ usually $CDCl_3$ solvent which gives peak at $\delta \approx 80$ ppm due to C-13 in solvent

↳ if something bonded to benzene ring the C-13 will not be completely equivalent so gives slight splitting of peaks