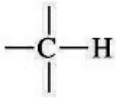
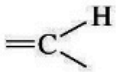
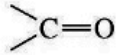
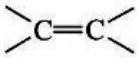
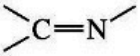
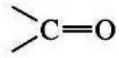
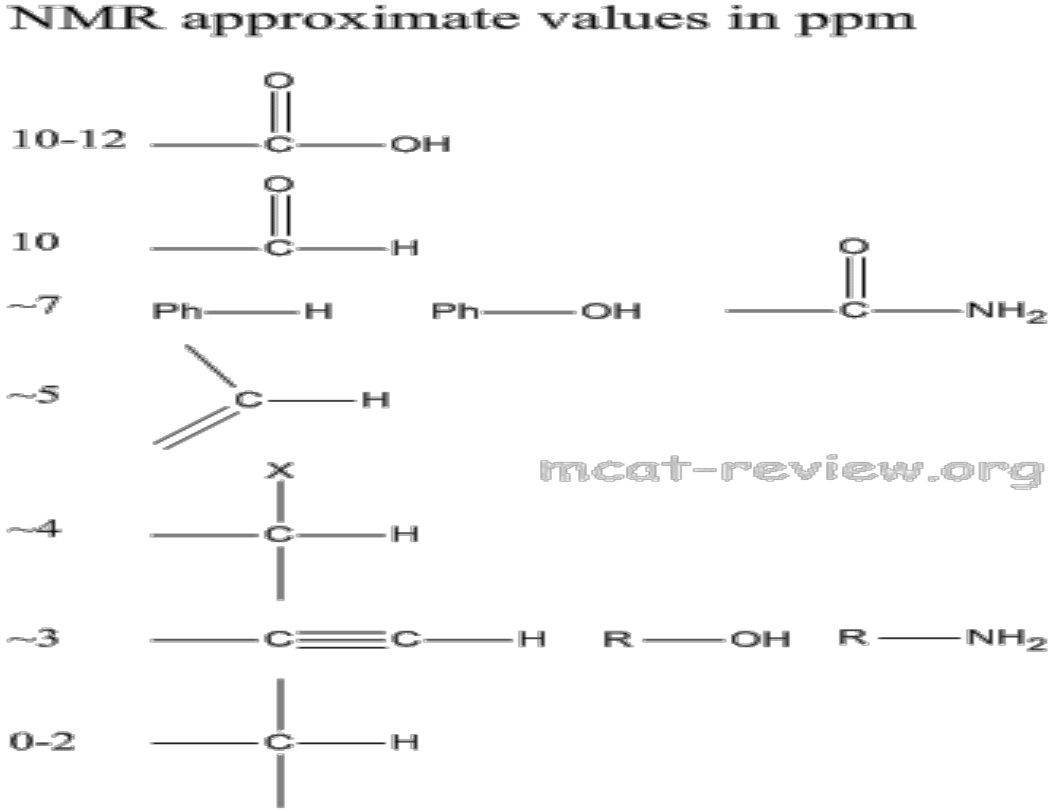
Frequency (cm^{-1})	Functional Group		Comments
3300	alcohol	O—H	always broad
	amine, amide	N—H	may be broad, sharp, or broad with spikes
	alkyne	≡C—H	always sharp, usually strong
3000	alkane		just below 3000 cm^{-1}
	alkene		just above 3000 cm^{-1}
	acid	O—H	very broad
2200	alkyne	—C≡C—	just below 2200 cm^{-1}
	nitrile	—C≡N	just above 2200 cm^{-1}
1710 (very strong)	carbonyl		ketones, aldehydes, acids esters higher, about 1735 cm^{-1} conjugation lowers frequency amides lower, about 1650 cm^{-1}
1660	alkene		conjugation lowers frequency aromatic C=C about 1600 cm^{-1}
	imine		stronger than C=C
	amide		stronger than C=C (see above)

Ethers, esters, and alcohols also show C—O stretching between 1000 and 1200 cm^{-1}.

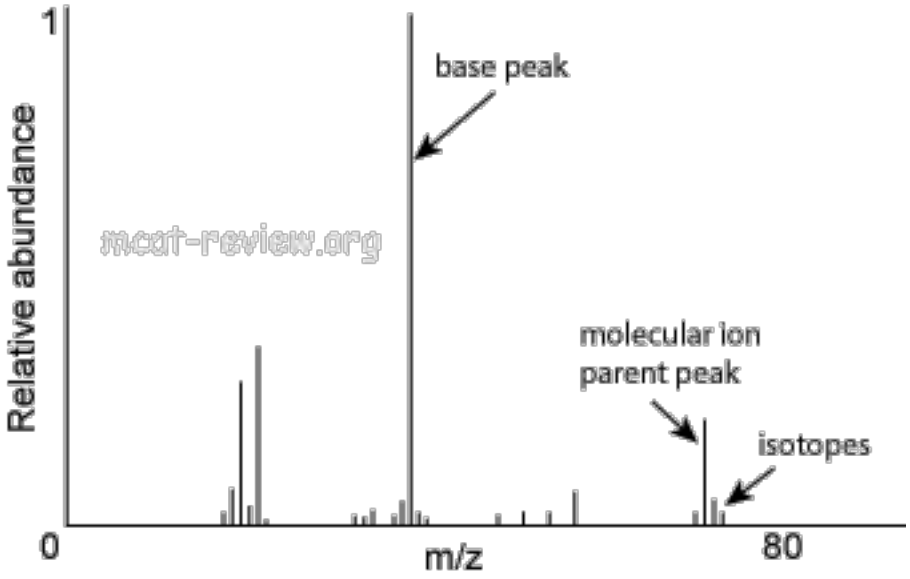
IR is a vibrational spectroscopic techniques that is a valuable tool for qualitative analysis. IR radiation is generally between 10,000-100 cm-1 , but most instruments are limited to the range where most application occur between 4000-400 cm-1 . In this technique, the IR radiation is absorbed and converted by a sample molecule into energy of molecular vibration. The masses of the atoms in the molecule, the force constants of the bonds, and the geometric structure of the molecule determine the frequency of absorption. IR spectra can be used to provide information on the functional groups as well as the structure of a molecule as a whole.

IR spectra are commonly divided into three main regions. The high-frequency region, between 4000-1300 cm-1 (2-7.7 μm), is called functional group region because the characteristics stretching frequencies for important functional groups such as C=O, OH, and NH occur in this region. The middle-frequency region, between 1300-900 cm-1 (7-11 μm) is known as the fingerprint region, in which the absorptions occur are complex and normally due to combinations of interacting vibrational modes, providing a unique fingerprint for every molecule. The spectrum in this region is especially valuable if examined in reference to other regions. The region between 900-650cm-1 (11-15 μm)provides general classification of molecules from the pattern of absorptions, such as substitution patterns on a benzene ring. The absence of absorptions in the low frequency region can provide good evidence for the absence of an aromatic compound. Obtaining a broad, moderately intense absorption in the low-frequency region indicates the presence of carboxylic dimers, amines, or amides. Evaluation of the spectra is normally begun with assigning the bands of high and medium intensities, especially in the functional group region and low-frequency region.



Nuclear Magnetic Resonance is a property of the nucleus of an atom, concerned with what is known as nuclear spin (I). This is equivalent to the nucleus acting like a miniature bar magnet. Although isotopes can have a variety of values for I (including zero), the most useful for spectroscopy are those nuclei which have I = 1/2 . Fortunately this includes hydrogen 1 (^{1}H), carbon 13, fluorine 19 and phosphorus 31, so that some of the commonest elements in organic chemistry can be analyzed using NMR. When a nucleus with I = 1/2 is placed in a magnetic field, it can either align itself ***with*** the field (lower energy) or ***against*** it (higher energy). If radio waves are applied, nuclei in the lower energy state can absorb the energy and jump to the higher energy state. We can observe either the absorption of energy, or the subsequent release of energy as the nucleus "relaxes" back to the lower energy state. Traditionally this was done by scanning slowly through a range of radio wave frequencies (this is called continuous wave, CW). However this has largely been replaced by the faster FT method where one big, broad pulse of radio waves is used to excite all nuclei, then the results are analyzed by computer.

In a real molecule, the effective magnetic field "felt" by a particular nucleus (B_{eff}) includes not only the applied field B_0, but also the magnetic effect of nearby nuclei and electrons. This causes the signal to absorb at a slightly different frequency than for a single atom; it is convenient to reference this resonant frequency to a standard (usually TMS, defined as zero). When we plot the output from this absorption, we obtain a series of peaks known as an **NMR spectrum** (or "spectra" if you have more than one spectrum) such as the typical example shown in Fig. 2. The difference (in parts per million, ppm) from the zero point is referred to as the **chemical shift** (δ). A typical range for δ is around 12 ppm for ^{1}H and around 220 ppm for ^{13}C. It is customary to have the zero point at the right hand end of the spectrum, with numbers increasing to the left ("downfield"). Note: more EN have more electrons…so nucleus is better shielded. But the protons next to more EN atoms experience less electrons, so they are more deshielded (downfield).



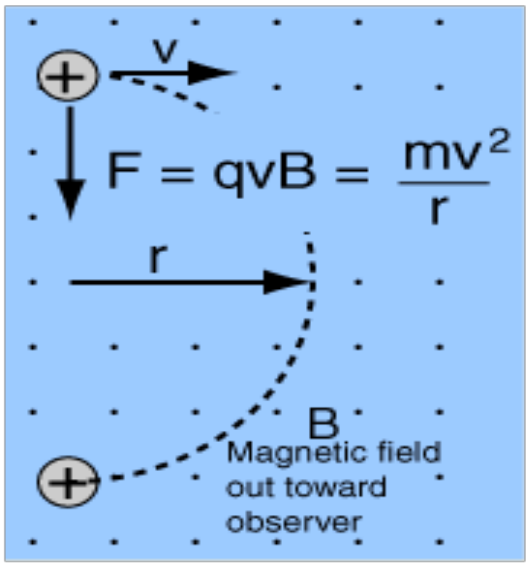
Steps

1. Ionization: via knocking electrons off atom/molecule→positive charge
2. Acceleration: so all ions have same kinetic energy
3. Deflection: magnetic field→deflection; greater deflection with lighter ions and/or more positive charge
4. Detection

Concepts

- For Mass Spec of an element, each line represents a different isotope of the element
- For Mass Spec of a compound, each line represents a different fragment produced from the molecular ion, M+
- M/Z= mass number of ion/charge number; mass to charge ratio
- M+ = molecular ion, has an unpaired electron; unstable, often break up into X+ and Y-
- Base Peak= tallest line on graph, represents commonest fragment ion to be formed
- Line to far right represents the heaviest ion passing through the spectrometer

$$r = \frac{mv^2}{qvB} = \frac{mv}{qB}$$ Radius of path produced by magnetic field



If the velocity v is produced by an accelerating voltage V:

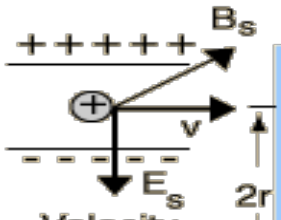
$$\frac{1}{2}mv^2 = qV \; ; \quad v = \sqrt{\frac{2qV}{m}}$$

Substitution gives:

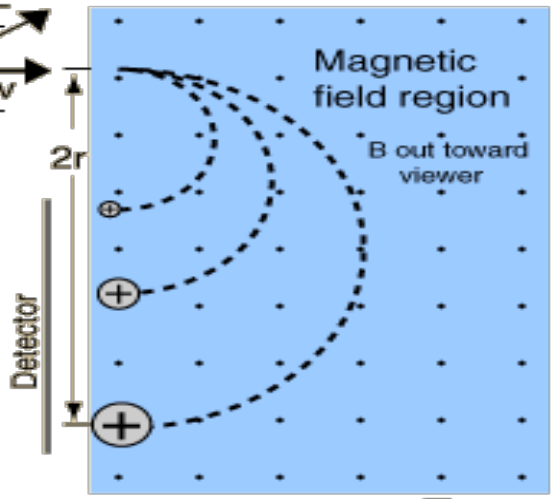
$$r = \frac{1}{B}\sqrt{\frac{2mV}{q}}$$

Ionization

Accelerating voltage applied

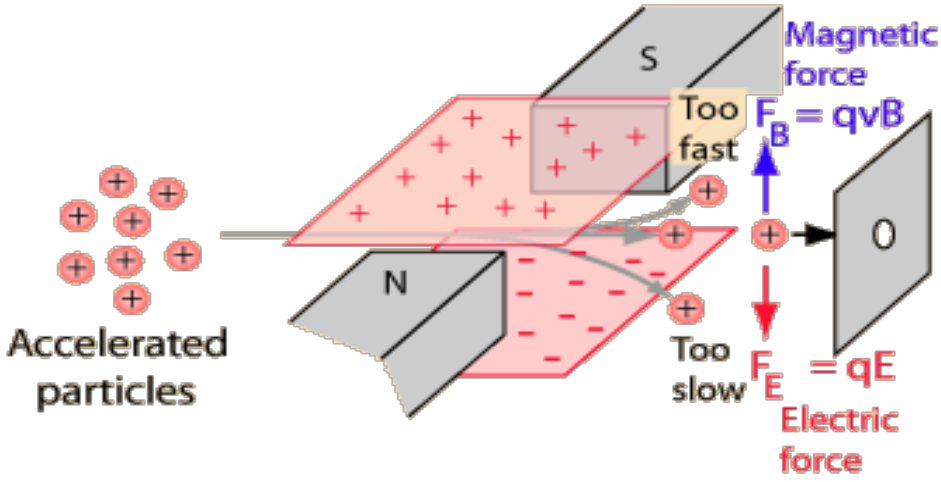


Velocity selector



After ionization, acceleration, and selection of single velocity particles, the ions move into a mass spectrometer region where the radius of the path and thus the postion on the detector is a function of the mass.

$$r = \frac{mv}{qB} = \frac{mE_s}{qBB_s}$$

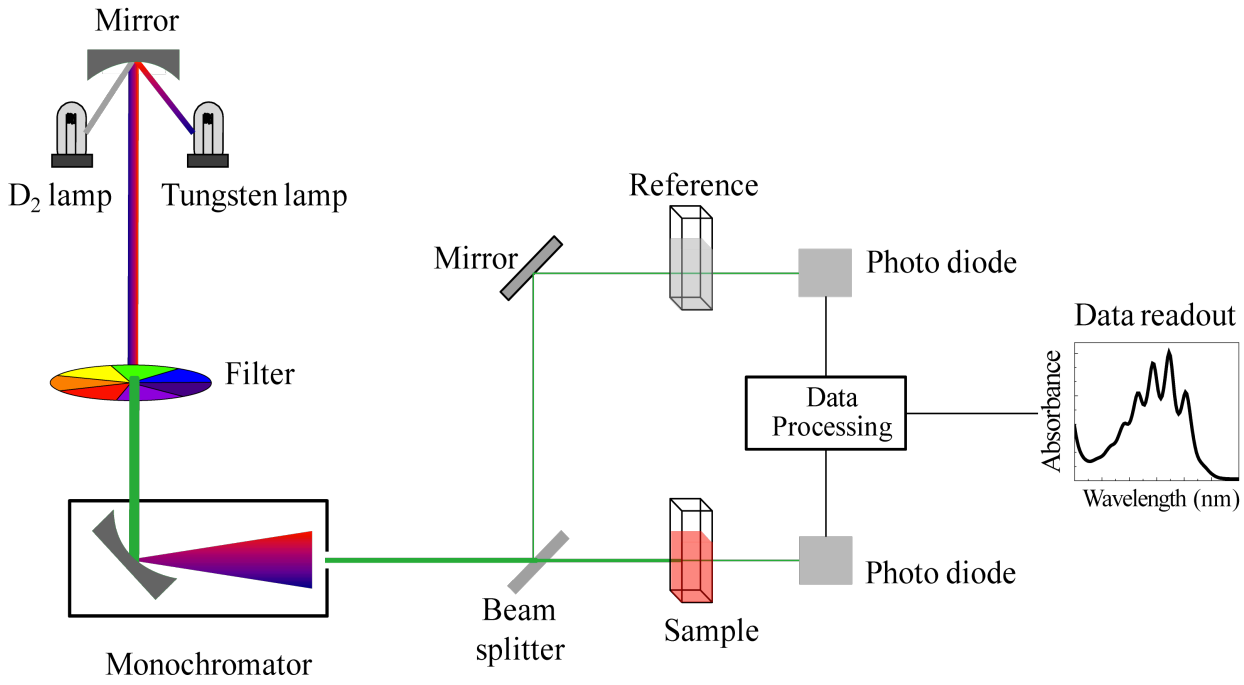


Accelerated particles

Undeflected particles

$v = \frac{E}{B}$ Selected velocity

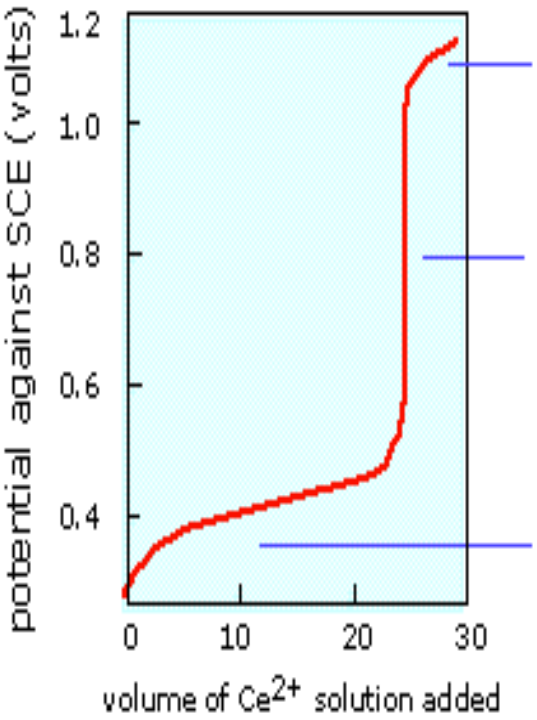
From setting electric force equal to magnetic force



Ultraviolet and visible (UV-Vis) absorption spectroscopy is the measurement of the attenuation of a beam of light after it passes through a sample or after reflection from a sample surface. Absorption measurements can be at a single wavelength or over an extended spectral range. Ultraviolet and visible light are energetic enough to promote outer electrons to higher energy levels, and UV-Vis spectroscopy is usually applied to molecules or inorganic complexes in solution. The spectra have broad features that are of limited use for identification but very useful for quantitative measurements. The concentration of an analyte is determined by measuring the absorbance at some wavelength and applying the Beer-Lambert Law in a calibration curve analysis.

The absorbance of a solution increases as attenuation of the beam increases. Absorbance is directly proportional to the path length, *b*, and the concentration, *c*, of the absorbing species. *Beer's Law* states that ***A = ebc***, **e** is a constant of proportionality, called the *absorbtivity*.

Different molecules absorb radiation of different wavelengths. An absorption spectrum will show a number of absorption bands corresponding to structural groups within the molecule. For example, the absorption that is observed in the UV region for the carbonyl group in acetone is of the same wavelength as the absorption from the carbonyl group in diethyl ketone.



Beyond the end point there is no more Fe^{2+}, so the potential rises rapidly to that of a Ce^{4+}/Ce^{3+} cell with excess Ce^{4+}.

Equivalence point at steepest part of plot

Initially, the solution is mostly Fe^{2+}. As Ce^{4+} is added, the iron is oxidized and the potential slowly rises as the Fe^{2+}/Fe^{3+} ratio decreases.

You want to isolate a mixture of compounds, and you do this by taking advantage of the bascicity and acidity of certain compounds. It is also important to note those structures that are rather neutral. Some key concepts are, bases will react with acid and vice versa. Also, the aqueous layer will contain a charged molecule, or ion, most of the time.

Step 1: Upon dissolving the mixture in a good solvent such as methylene chloride, a strong acid is added to the mixture.

The strong acid is added so that it will react with any basic compounds in the mixture, which wil lead it into the aqueous layer. Thus, one of the compounds has been separated. Adding base will deprotonate the proton from the nitrogen and give you the isolated product in the organic layer.

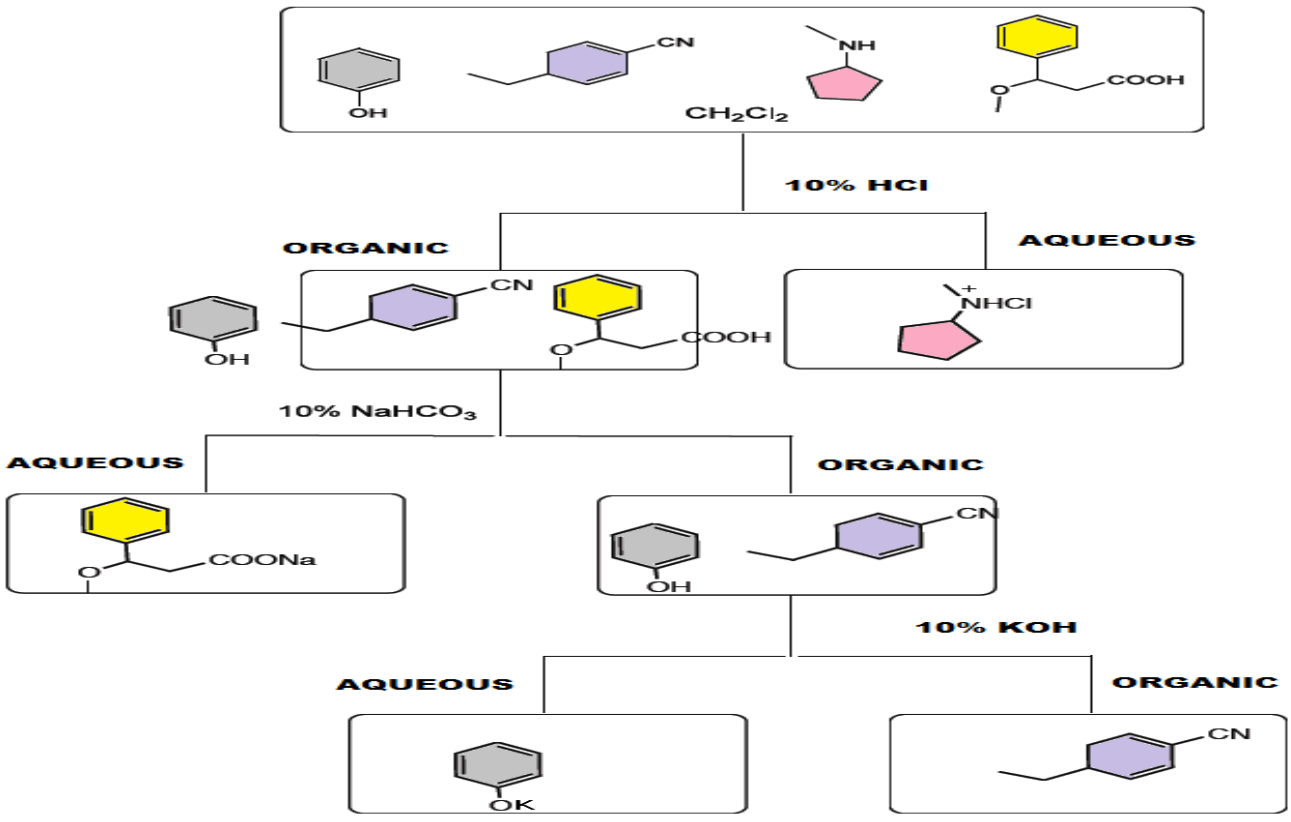
Step 2: To the remaining 3 compounds, a weak base is added, such as sodium carbonate.

The weak base will deprotonate the most acidic of the hydrogens, which is in this case, the carboxylic acid. The carboxylic acid containing structuer will be separated into the aqueous layer. Keep in mind, that the base is not limited to only deprotonating one structure, but this all just depends on the acidity of the compounds.

Step 3: To the final 2 compounds, a stronger base such as potassium hydroxide which will deprotonate the phenol.

Generally phenols are not very acidic, that is why a strong base must be used. The cyano containing compound is left in the organic layer.

Reaction Complete. All 4 compounds have been isolated into either aqueous or organic, and as mentioned eariler, it is very easy to bring an aqueous compound back into the organic, that is by adding the complementary acid or base.

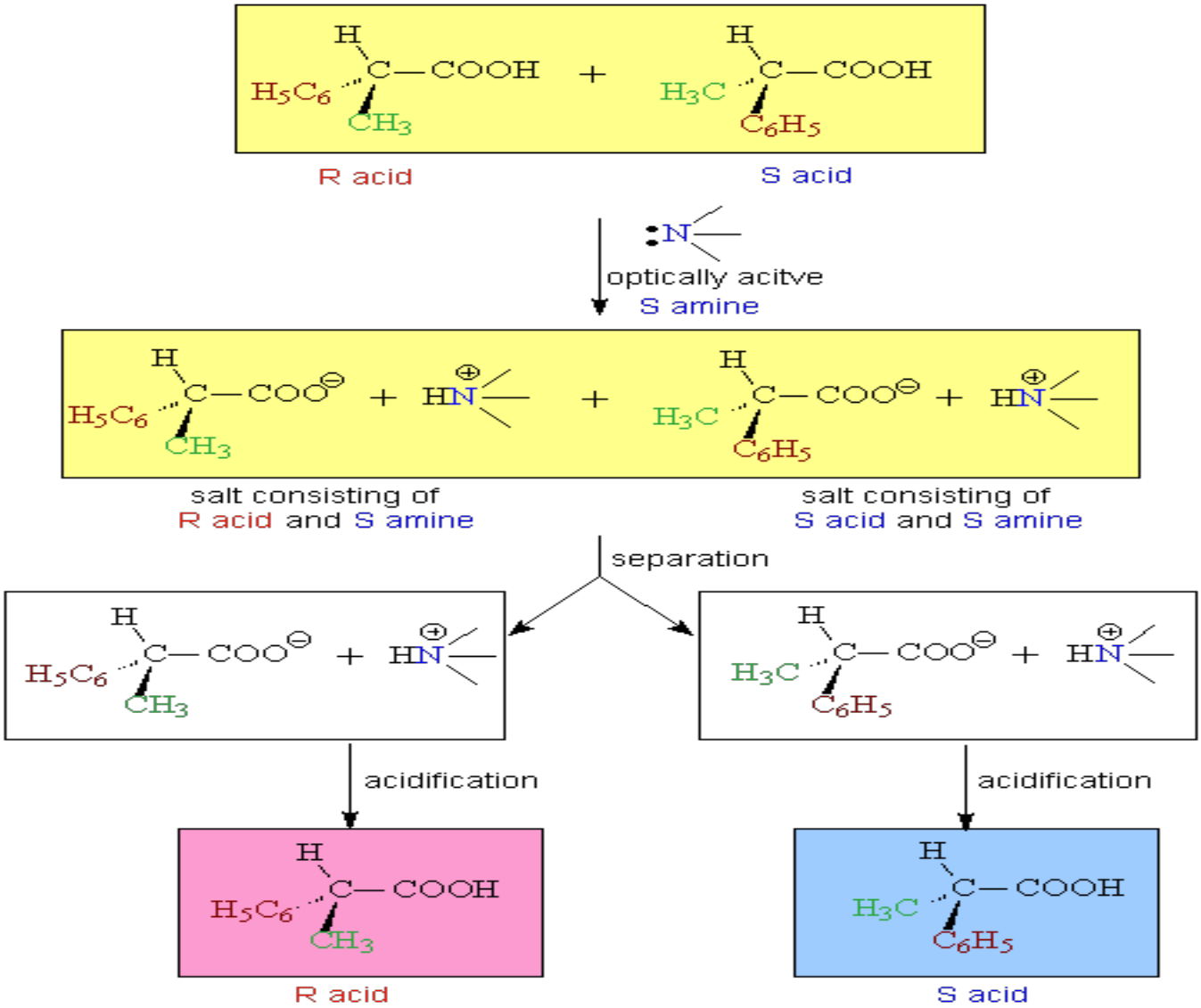


Conversion to diastereomers

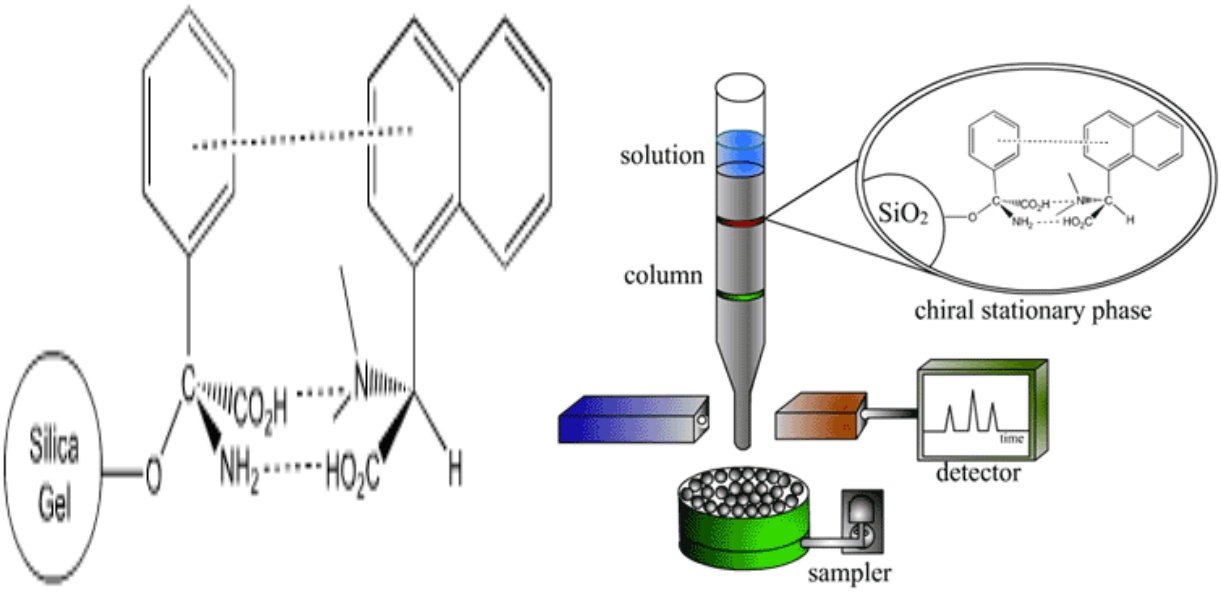
One way to separate enantiomers is to chemically convert them into species that *can* be separated: diastereomers. Diastereomers, unlike enantiomers, have entirely different physical properties--boiling points, melting points, NMR shifts, solubilities--and they can be separated by conventional means such as chromatography or recrystallization.

If it was desired to separate a mixture of an R and S carboxylic acid, for example, this mixture could be reacted with a single enantiomer of a chiral amine to make the diastereomic ammonium salts that could then be separated. Once the diastereomic salts have been separated, mineral acid can reprotonate the carboxylic acid to reform the original enantiomers. This is a general, three step, technique for separating enantiomers:

1. React the enantiomers with a single enantiomer of another compound to form diastereomers
2. Separate the diastereomers by conventional means (chromatography, recrystallization)
3. Regenerate the original enantiomers, now separated



Another technique for separating enantiomers is chiral chromatography. While enantiomers cannot be distinguished in achiral environments, such as a solvent system or by normal silica gel chromatography, they *can* be distinguished in chiral environments, such as in the active site of an enzyme, or in a chiral stationary phase of a column. In a chiral column, achiral silica gel (SiO_2)is converted into a chiral stationary phase by a reaction with a chiral molecule. Once the enantiomers that need to be separated are run down the column, one enantiomer will "stick" to the stationary phase better than the other, and there will be separation (of course, a disadvantage is that chiral silica gel is much more expensive than standard silica gel).



In this hypothetical example of an interaction between a chiral stationary phase (left) with an enantiomer of a biphenyl derivative (right), there is a three-point interaction, with the carboxy groups aligning with the amino groups and the aromatics lining up with each other to form pi stacking interactions. The enantiomer of this biphenyl would not be able to have all three of these interactions because its groups would not be aligned correctly, and, consequently, it would stick less to the chiral stationary phase and filter off the column first.

Technique	Stationary phase	Mobile phase	Basis of separation	Notes
*Paper chromatography	solid (cellulose)	liquid	polarity of molecules	compound spotted directly on a cellulose paper
*Thin layer chromatography (TLC)	solid (silica or alumina)	liquid	polarity of molecules	glass is coated with thin layer of silica on which is spotted the compound
*Liquid column chromatography	solid (silica or alumina)	liquid	polarity of molecules	glass column is packed with slurry of silica
Size exclusion chromatography	solid (microporous beads of silica)	liquid	size of molecules	small molecules get trapped in the pores of the stationary phase, while large molecules flow through the gaps between the beads and have very small retention times. So larger molecules come out first. In this type of chromatography there isn't any interaction, physical or chemical, between the analyte and the stationary phase.
Ion-exchange chromatography	solid (cationic or anionic resin)	liquid	ionic charge of the molecules	molecules possessing the opposite charge as the resin will bind tightly to the resin, and molecules having the same charge as the resin will flow through the column and elute out first.
Affinity chromatography	solid (agarose or porous glass beads on to which are immobilized molecules like enzymes and antibodies)	liquid	binding affinity of the analyte molecule to the molecule immobilized on the stationary phase	if the molecule is a substrate for the enzyme, it will bind tightly to the enzyme and the unbound analytes will pass through in the mobile phase, and elute out of the column, leaving the substrate bound to the enzyme, which can then be detached from the stationary phase and eluted out of the column with an appropriate solvent.
Gas chromatography	liquid or solid support	gas (inert gas like argon or helium)	boiling point of the molecules	samples are volatilized and the molecule with lowest boiling point comes out of the column first. The molecule with the highest boiling point comes out of the column last.