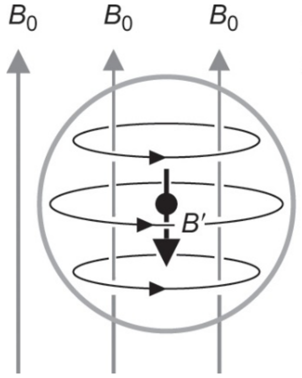
Nuclear Magnetic Resonance – Theory and Techniques

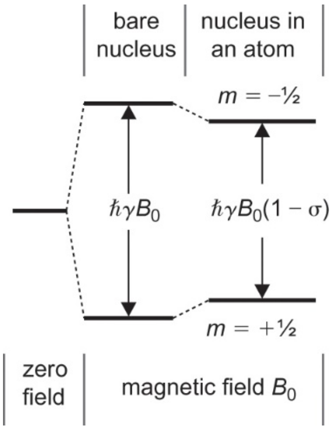
Lecture 2: Chemical Shift – *Ralph W. Adams*

The origin of chemical shift

Chemical shift was discovered by Procter and Yu in 1950 while they were studying the ^{14}N NMR spectrum of NH_4NO_3.



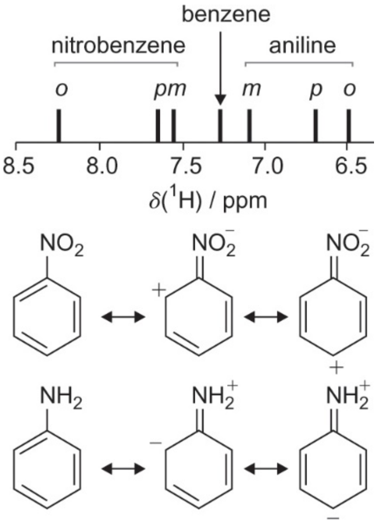
A magnetic field is generated by the motion of electrons, within their orbitals. Applying an external magnetic field B_0 increases electronic motion producing an extra field B’ which reduces the magnetic field, B, experienced by the nucleus.



The effects of chemical shift shown on an energy level diagram with the Larmor frequency changing as a result of interaction of the electrons with the magnetic field produced by electronic motion.

	CH_3F	CH_3Cl	CH_3Br	CH_3I	CH_3H
δ	4.13	2.84	2.45	1.98	0.13
Electronegativity	4.0	3.0	2.8	2.5	2.1

Chemical shift values scale with electronegativity as can be observed for the halogen-substituted analogues of methane. Things can become more complex when both inductive and mesomeric effects some into play. For example, OR groups withdraw electrons due to the electronegativity of O but also the lone pair on the O can be donated back into the electronic structure though double bonds to increase electron density at certain positions.



The chemical shifts of the ^{1}H signals from nitrobenzene are shifted to a higher frequency (also called *down field*) relative to the ^{1}H signals from benzene. This is due to the strongly electron withdrawing mesomeric effects of the nitro group and is known as deshielding. An opposite series of shifts occurs for aniline where the lone pair donates electron density into the π–bonds of the aniline.

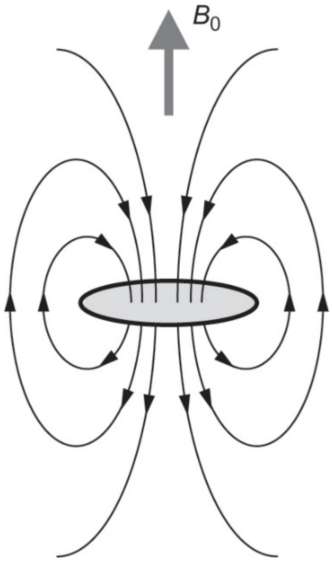
^{1}H nuclei have low electron density and high electronic excitation energies so have a relatively small chemical shift range compared to other nuclei.

Chemical shift is defined relative to a reference compound for a given nuclide using $\delta = 10^6 \frac{\nu_0-\nu_{ref}}{\nu_{ref}}$ which makes chemical shift independent of the magnetic field at which an experiment is performed.

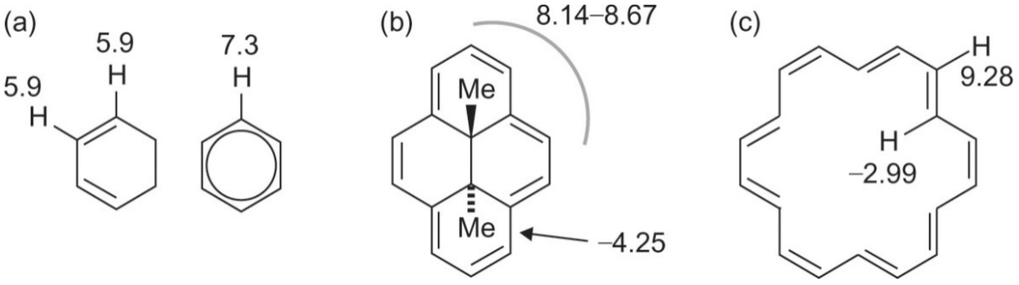
Figures are from *Nuclear Magnetic Resonance (2nd Ed.)* by *P.J. Hore* and *http://chem.ch.huji.ac.il/nmr*

For ^1H and ^{13}C the reference is tetramethylsilane which has a frequency $\nu_{ref} = 0$. Oddly, the IUPAC definition of chemical shift is such that the *unit* ppm (parts per million) is not included when using the format "δ =" to report chemical shift.

Aromatics and ring currents



The electronic structure in aromatic molecules is such that electrons can circulate in a way that will generate a current around the ring(s). Unlike the motion of electrons close to each nucleus, these ring currents deshield nuclei by contributing positively to the magnetic field experienced by nuclei outside the ring.



This effect is shown clearly for (a) cyclohexadiene vs benzene, (b) trans-15,16-dimethyl-15,16-dihydropyrene, and (c) [18]-annulene.

Hydrogen bonding and paramagnetic species

Some of the largest chemical shift values are observed when hydrogen bonding or unpaired electrons are present.

Intramolecular hydrogen bonding is particularly effective at increasing chemical shift values with the OH signals in salicylaldehyde and the enol form of acetylacetone coming at 11.3 and 15.2 ppm respectively.

The magnetogyric ratio of the electron is 660 times that of ^1H which can lead to substantial nuclear (de)shielding effects. Adding paramagnetic lanthanide shift reagents to a sample can simplify ^1H NMR spectra. The commonest lanthanide shift reagents are soluble octahedral complexes of Eu, Dy, Pr or Yb. Different parts of each molecule interact with the shift reagent depending on lone pairs and electronegativity, resulting in a pseudocontact shift of the protons and a change in observed chemical shift.

Temperature

Chemical shift is temperature dependent. Some signals are more temperature dependent than others and this fact can be used to provide an internal thermometer in an NMR sample. The chemical shift difference between the two signals in the ^1H NMR spectrum methanol has almost linear temperature dependence. Ethyleneglycol gives similar results. Some spectrometers have an inbuilt feature where the two ^2H signals in a small amount of methanol-d_4 are constantly monitored to provide the temperature of the sample (in lieu of using an external thermocouple).

Solvent

Interactions of the substrate with the solvent inevitably lead to chemical shift changes. These are normally <1 ppm but complications can be avoided by using solvents such as cyclohexane which will only interact very weakly with most chemicals. Using a solvent that interacts more strongly, such as benzene, can help resolve overlapping signals.

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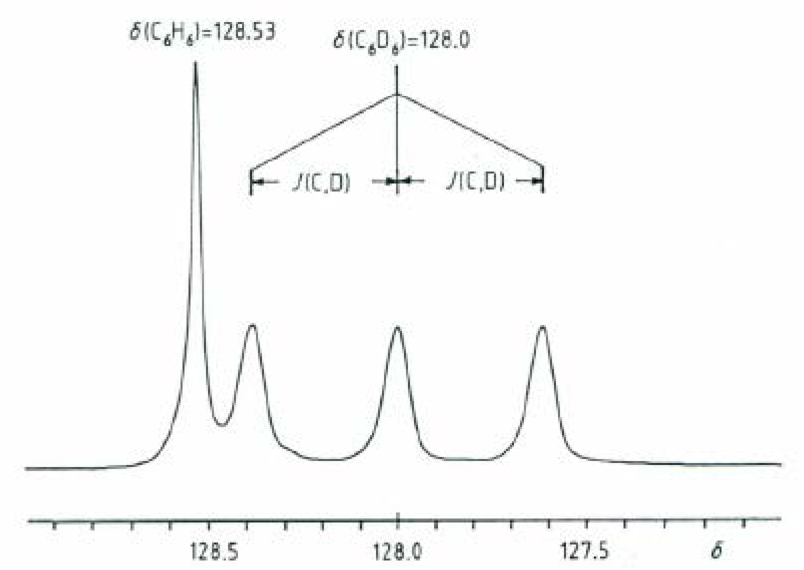
Isotope shifts

As the vibrational properties of different isotopomers (e.g. ^{1}H vs ^{2}H) differ, each provides a different amount of nuclear shielding, this is known as the *direct isotope* effect. For ^{1}H/^{2}H exchange the isotope effect is relatively large owing to the large ratio of the isotope masses. The effect is much smaller for other nuclei but the effect has been successfully used to identify which ^{13}C in a molecule has Cl attached by observing the different isotope shifts caused by $^{35/37}$Cl.



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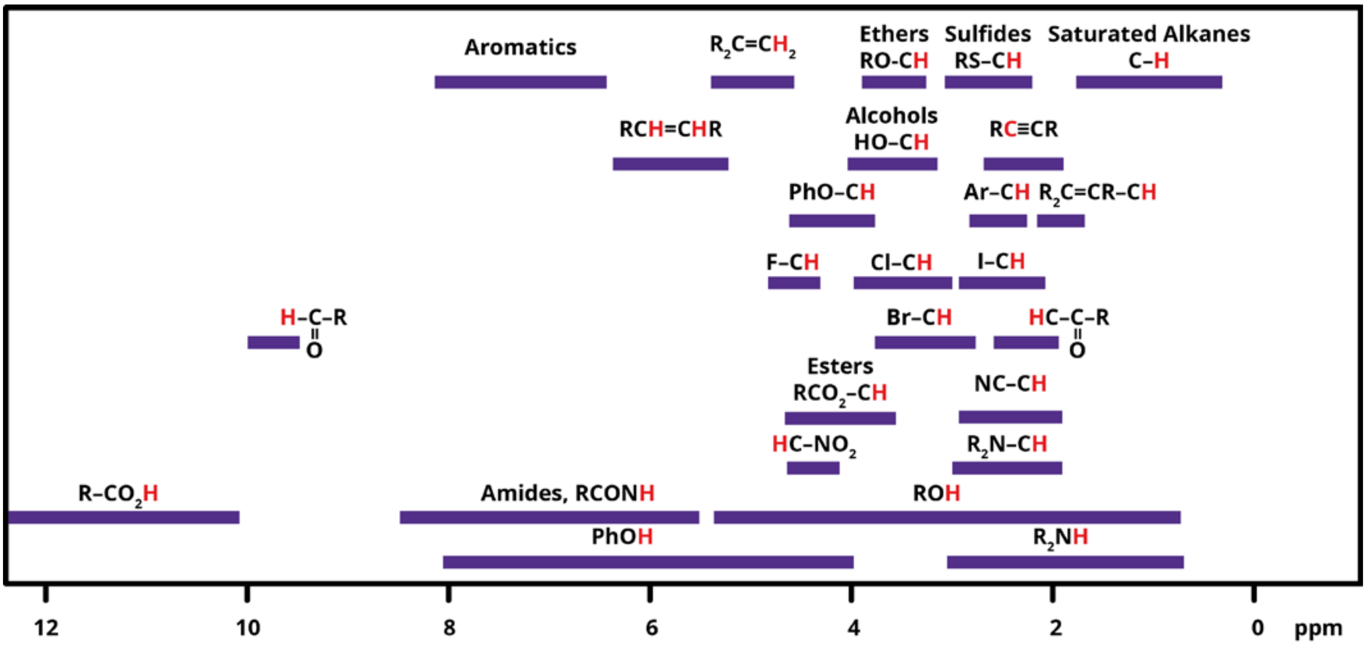
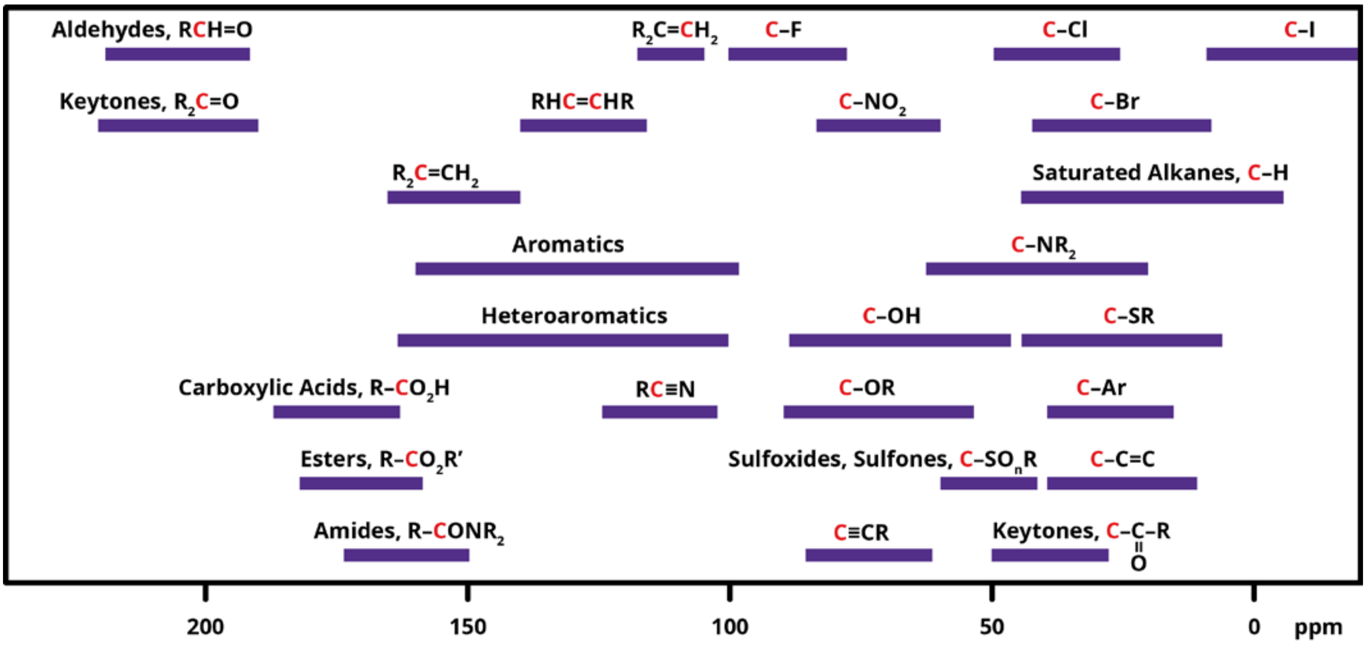
^{1}H and ^{13}C Chemical Shifts



Typical ^{1}H chemical shifts



Typical ^{13}C chemical shifts

In addition to the chemical shift ranges given above, tables of empirical chemical shift data can be extremely useful for predicting substituent effects and assigning structure. However, scalar coupling and nOe data usually allow more confident structural characterisation.

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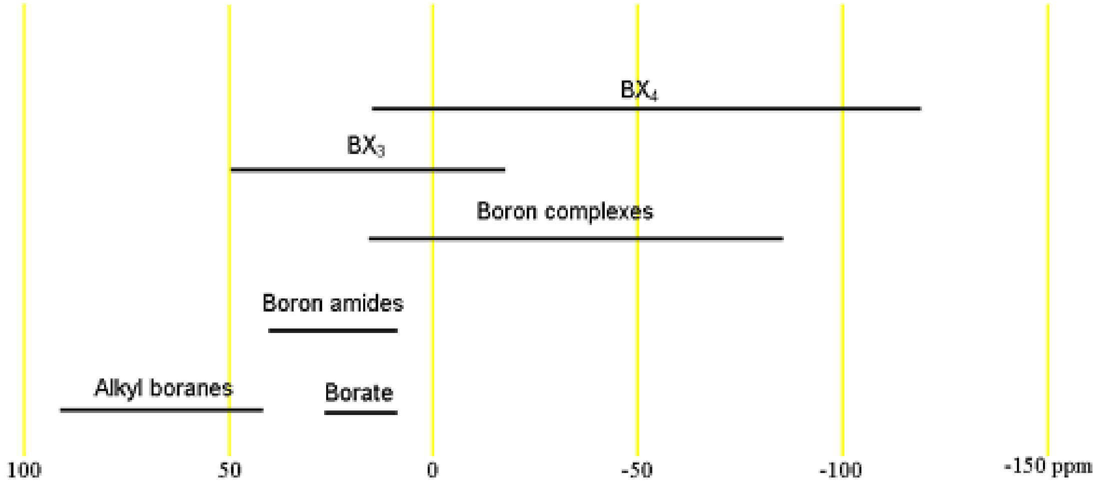
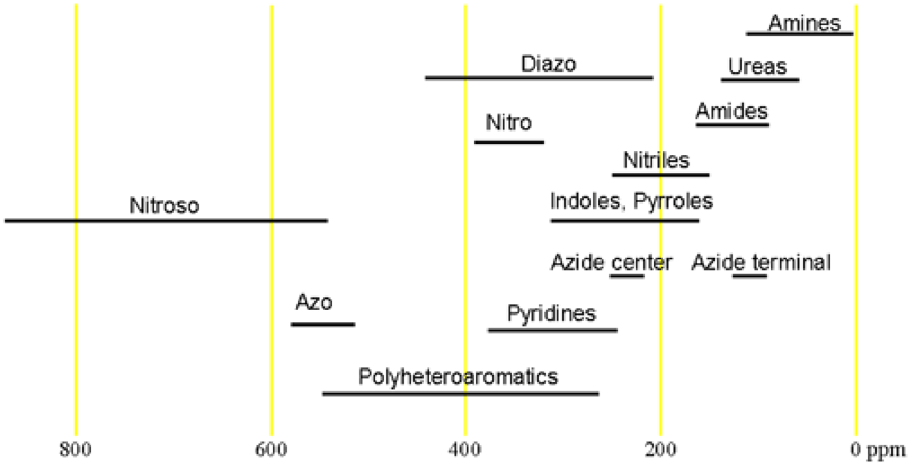
Chemical shift ranges (taken from Roy Hoffman's http://chem.ch.huji.ac.il/nmr/)

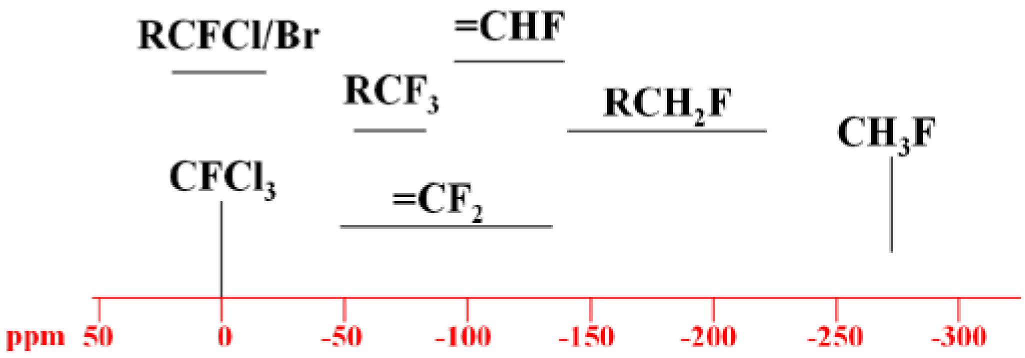
Boron:



Nitrogen:



Fluorine:



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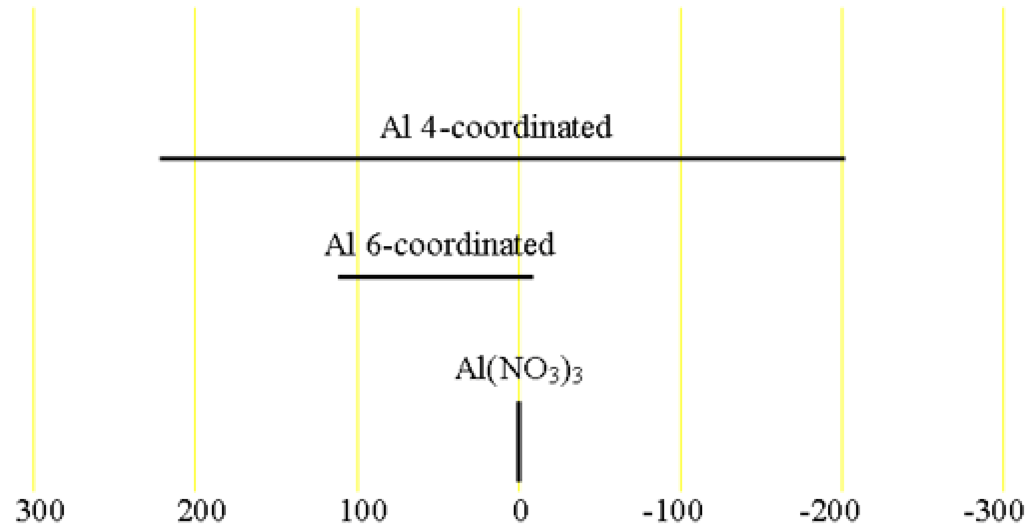
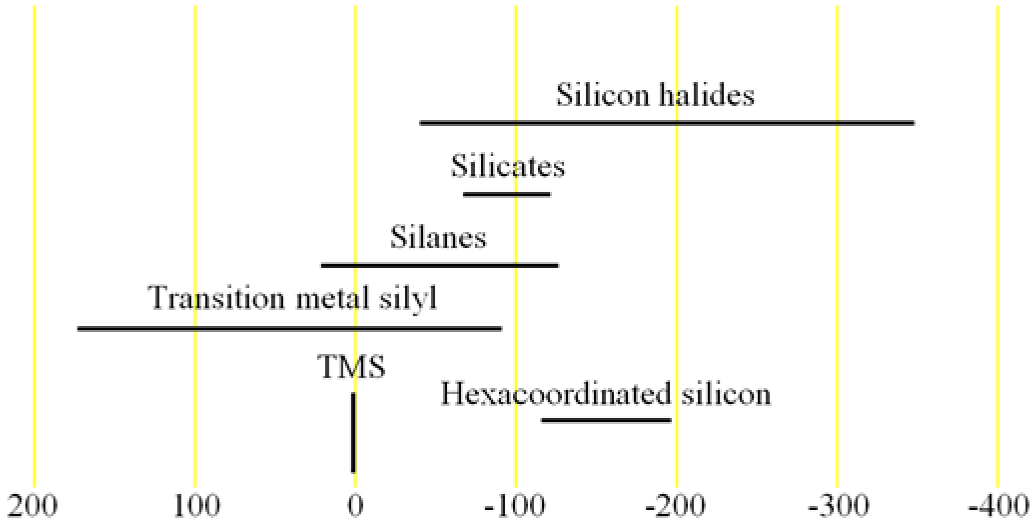
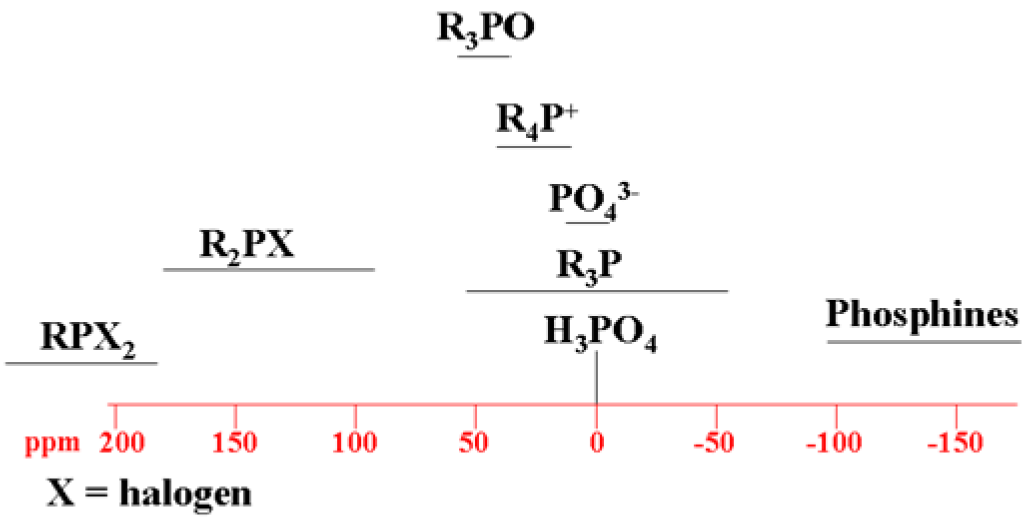
Aluminium:



Silicon:



Phosphorus:



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