



Using the Periodic Table in our GC-MS Analyses

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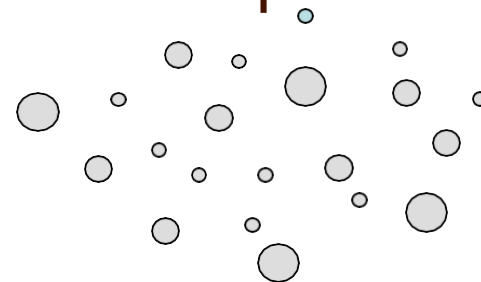
President-Elect, Analytical Division, RSC

Periodic Table & GC

<div>H1</div>		Non-metal										<div>He2</div>																							
<div>Li3</div>		<div>Be4</div>		Non-metallic elements have more varied properties than metals. They are poor conductors of heat and electricity and in reactions they commonly form negative ions. Metalloids have properties that are in between those of metals and non-metals.										<div>B5</div>		<div>C6</div>		<div>N7</div>		<div>O8</div>		<div>F9</div>		<div>Ne10</div>											
<div>Na11</div>		<div>Mg12</div>		<div><div><div></div></div> Metalloid</div> <div><div></div> Unknown</div>										<div>Al13</div>		<div>Si14</div>		<div>P15</div>		<div>S16</div>		<div>Cl17</div>		<div>Ar18</div>											
<div>K19</div>		<div>Ca20</div>		<div>Sc21</div>		<div>Ti22</div>		<div>V23</div>		<div>Cr24</div>		<div>Mn25</div>		<div>Fe26</div>		<div>Co27</div>		<div>Ni28</div>		<div>Cu29</div>		<div>Zn30</div>		<div>Ga31</div>		<div>Ge32</div>		<div>As33</div>		<div>Se34</div>		<div>Br35</div>		<div>Kr36</div>	
<div>Rb37</div>		<div>Sr38</div>		<div>Y39</div>		<div>Zr40</div>		<div>Nb41</div>		<div>Mo42</div>		<div>Tc43</div>		<div>Ru44</div>		<div>Rh45</div>		<div>Pd46</div>		<div>Ag47</div>		<div>Cd48</div>		<div>In49</div>		<div>Sn50</div>		<div>Sb51</div>		<div>Te52</div>		<div>I53</div>		<div>Xe54</div>	
<div>Cs55</div>		<div>Ba56</div>		<div>La57</div>		<div>Hf72</div>		<div>Ta73</div>		<div>W74</div>		<div>Re75</div>		<div>Os76</div>		<div>Ir77</div>		<div>Pt78</div>		<div>Au79</div>		<div>Hg80</div>		<div>Tl81</div>		<div>Pb82</div>		<div>Bi83</div>		<div>Po84</div>		<div>At85</div>		<div>Rn86</div>	
<div>Fr87</div>		<div>Ra88</div>		<div>Ac89</div>		<div>Rf104</div>		<div>Db105</div>		<div>Sg106</div>		<div>Bh107</div>		<div>Hs108</div>		<div>Mt109</div>		<div>Ds110</div>		<div>Rg111</div>		<div>Cn112</div>		<div>Nh113</div>		<div>Fl114</div>		<div>Mc115</div>		<div>Lv116</div>		<div>Ts117</div>		<div>Og118</div>	
				<div>Ce58</div>		<div>Pr59</div>		<div>Nd60</div>		<div>Pm61</div>		<div>Sm62</div>		<div>Eu63</div>		<div>Gd64</div>		<div>Tb65</div>		<div>Dy66</div>		<div>Ho67</div>		<div>Er68</div>		<div>Tm69</div>		<div>Yb70</div>		<div>Lu71</div>					
				<div>Th90</div>		<div>Pa91</div>		<div>U92</div>		<div>Np93</div>		<div>Pu94</div>		<div>Am95</div>		<div>Cm96</div>		<div>Bk97</div>		<div>Cf98</div>		<div>Es99</div>		<div>Fm100</div>		<div>Md101</div>		<div>No102</div>		<div>Lr103</div>					

New sample analysis

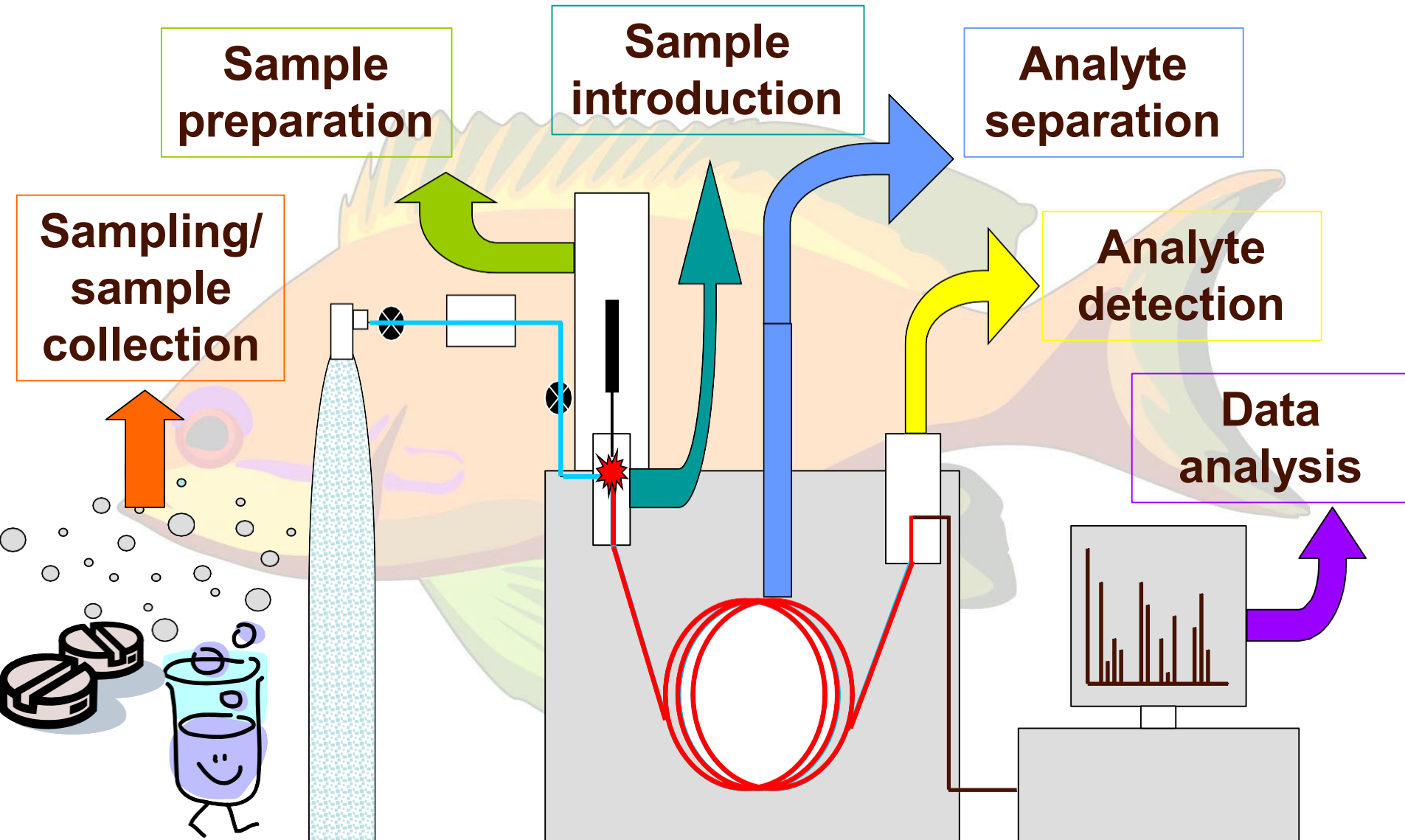
- Start from the basics:
 - Sample phase: gas/liquid/solid/something in-between
 - Chemistry of the targets compounds (analytes): Volatilities? Polarities? Functional groups?
 - Nature of the matrix: Higher MW than analytes? Similar volatility to analytes? Potential interferents? Same or different polarities to analytes?
 - Concentration & relative concⁿ analytes vs. matrix
 - Location of samples
 - Can sub-sample & take to lab or must be sampled *in-situ*?



Using the periodic table

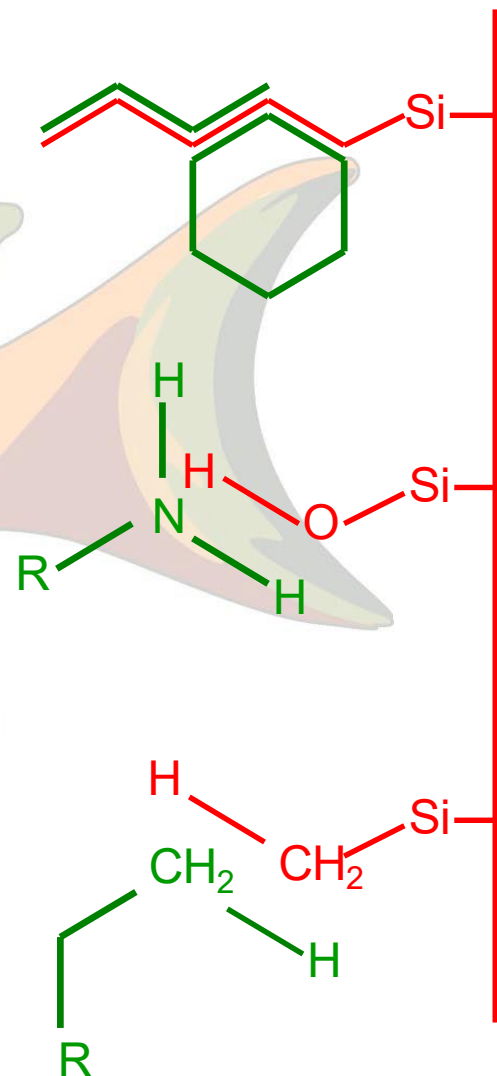
- Samples are complex:
 - Many analytes to separate at possibly low concentration
 - High amount of matrix
 - Presence of matrix interferents
- Many steps in sample collection & analysis
 - Use knowledge about the chemistry of the sample at each step to analyse components of interest & remove/ignore unwanted matrix components
 - Think about interactions that you want/don't want to occur
 - Simplify process: where are the biggest gains?
 - Think about & understand the sample first!

Sample analysis steps



Stationary phase-analyte interactions can be:

- **Dispersion** → caused by temporary charge fluctuations occur spontaneously in all molecules from electron /nuclei vibrations. Also known as London dispersion force or induced dipole-induced dipole. Related to volatility usually of non-polar compounds
- **Dipole-dipole** → permanent, partial charge fluctuations causing distortion of structure:
 - Permanent dipole e.g. alcohols, esters, ethers, nitriles
 - Or dipole induced dipole interactions due to permanent dipoles polar & polarisable molecules

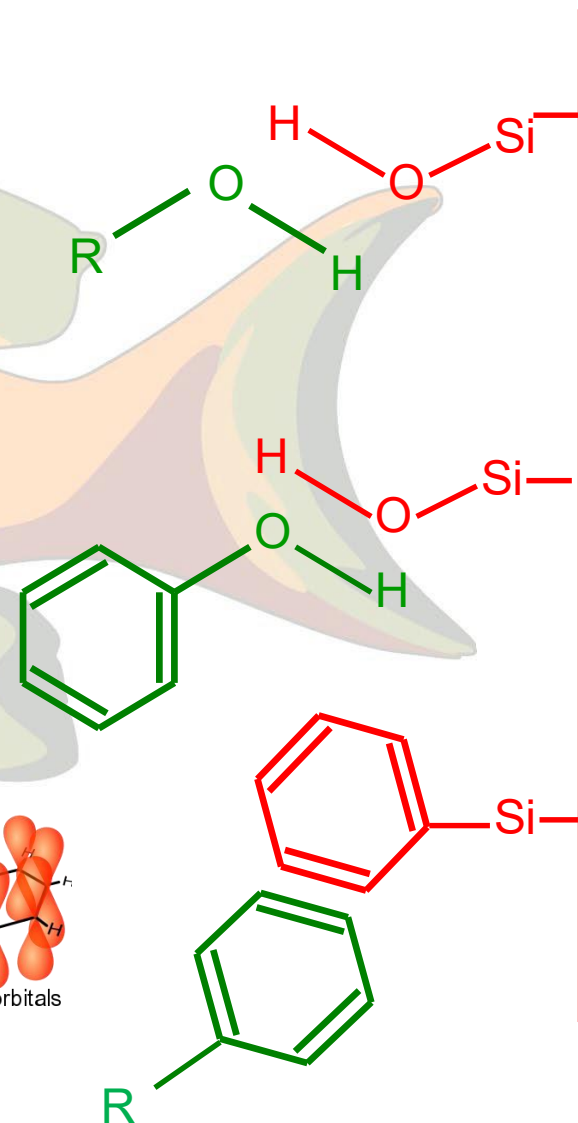
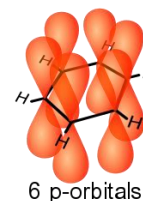


Interactions in GC

- **Hydrogen** → Type of dipole-dipole force. Must have H bonded to very electro-ve atom (F, O, N), enhances partial charge fluctuations. Best known with hydroxyl (-OH) groups. Strongest bond of polar molecules
- **π - π** → Interaction of electron p-orbitals between stationary phase phenyl groups & aromatic molecules

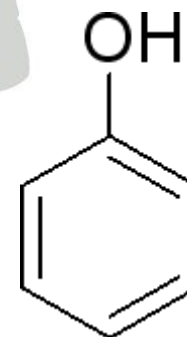
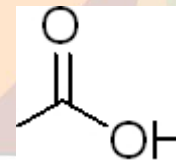
Interaction Energy (kJ/mol)

Dispersive	$\ll 1$
Dipole-Induced Dipole	1
Dipole-Dipole	3.3
Hydrogen bonding	19



Typical active compounds

- Molecules containing only C & H are non-active, therefore anything with additional elements
- In particular, those with active H in their functional group, including:
 - Phenols
 - Organic acids
 - Pesticides
 - Amines
 - Drugs of abuse
 - Reactive polar compounds
 - Thermally labile compounds
 - Sulfur species

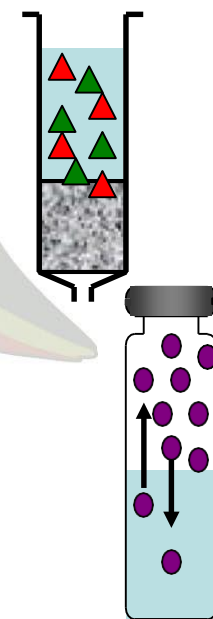


- Aims: To collect a representative sample, enough for analysis, in a suitable manner chosen for sample type & location
- Could be selective for:
 - Volatility (only traps analytes within a certain volatility range)
 - Analyte nature (only traps target analytes with certain characteristics like polarity-functional groups)
 - Avoids matrix interferences (e.g. doesn't trap water)
- Techniques for sampling on-site include:
 - Thermal desorption: selectivity of packing material for analytes not matrix
 - SPME/SBSE/Hisorb: selectivity of phase for analytes not matrix



Sample Preparation

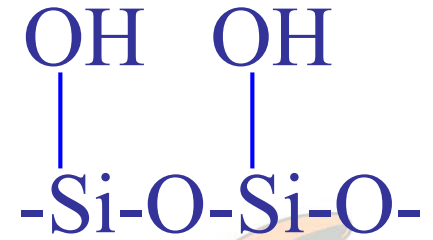
- Aims: to concentrate analytes, make sample GC amenable &/or remove matrix (if possible)
- Negatives: potential loss of analytes & concentration of matrix too
- Techniques:
 - SPE: selectivity of SPE phase(s) for analytes/matrix
 - LLE: selectivity of solvent(s) for analytes/matrix
 - HS: analytes prefer headspace over sample (matrix modification)
 - P&T: selectivity of trap + analytes into gas phase
- Don't lose analytes at expense of removing matrix – could be separate later on



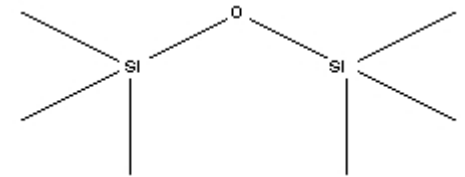
- Aims: to repeatably & reproducibly introduce representative portion of sample onto GC column in narrow sample band with no chemical change
- Problems: mass discrimination, activity, breakdown
- Typical active compounds:
 - Anything that can form hydrogen bonds
- Deactivation of
 - Inlet liner
 - Any seals, e.g. gold seal
 - Inlet body for low-concentration S compounds



Deactivating liners

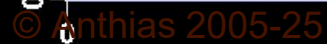


- Liners made of glass or metal
- Activity mainly occurs in liner
→ loss of peaks, tailing peaks, inconsistent results
- Active compounds breakdown/adsorb/react at active sites → interaction of functional groups
- Deactivation applies an inert, integral layer to liner (& packing material)
- Deactivation methods include siltek, or silanisation with e.g. hexamethyldisiloxane
- Max. temp: 400°C (450°C for siltek) but be wary!



- Aims: to separate analytes of interest from each other as well as matrix co-extractives
- Problems: enough theoretical plates for large number of analytes/matrix peaks, mixed characteristics: selection of phase good for some classes not others
- Techniques:
 - Select column stationary phase suitable for sample, “like separates like”
 - Heart-cutting: if one stationary phase isn’t enough, transfer remaining co-eluting peaks to different phase
 - GCxGC: separate all peaks on two different column phases
 - LCxGC: use different techniques to selectively separate





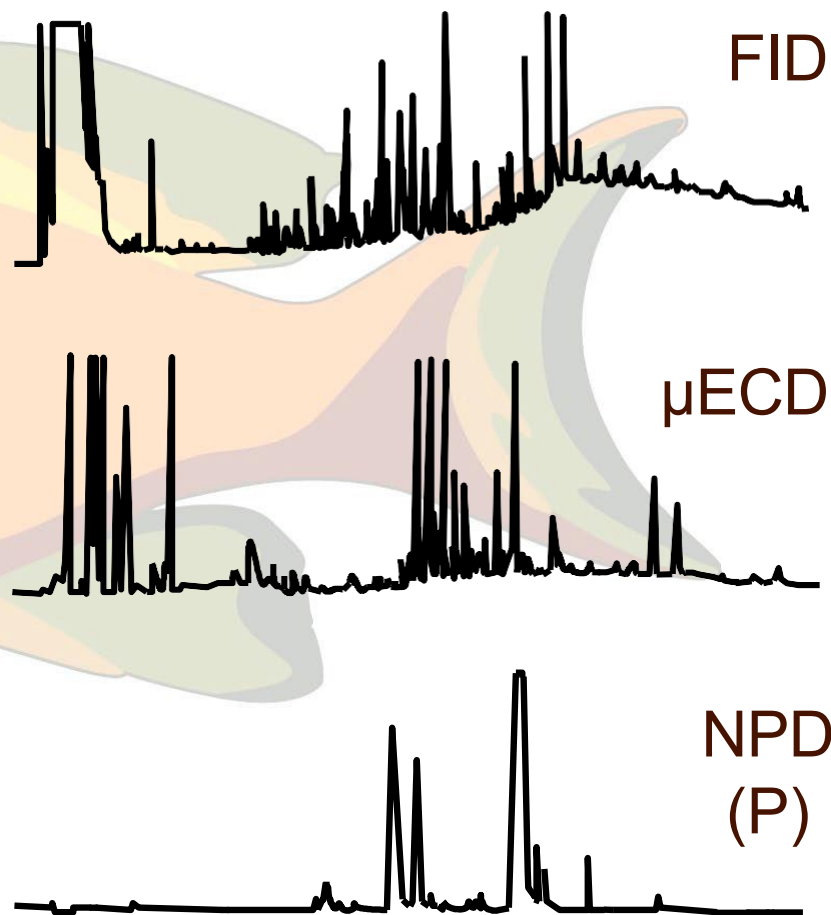
Analyte detection

- Aims: to have adequate sensitivity for analysis with linear response over concentration range, be stable, reproducible & give required information for confirmation of presence/absence
- Detector selectivity can:
 - Improve sensitivity, can get better MDLs
 - Enable observation of only target analyte(s) amongst co-eluting analytes & matrix, thereby reducing matrix interferences
 - Easier quantitation
- Universal:
 - See most organic compounds
 - E.g. FID, TCD, HID
 - E.g. MS in scan mode or TOF



Detector types

- Selective detectors, e.g.:
 - μ ECD: responds only to analytes capable of capturing e^-
 - SCD/NCD/PFPD/NPD: respond to certain atoms
 - MS: another dimension of data
 - NCI
 - SIM
 - MS/MS: secondary ion spectrum e.g. MRM
 - HRMS: 4-5 d.p. mass accuracy

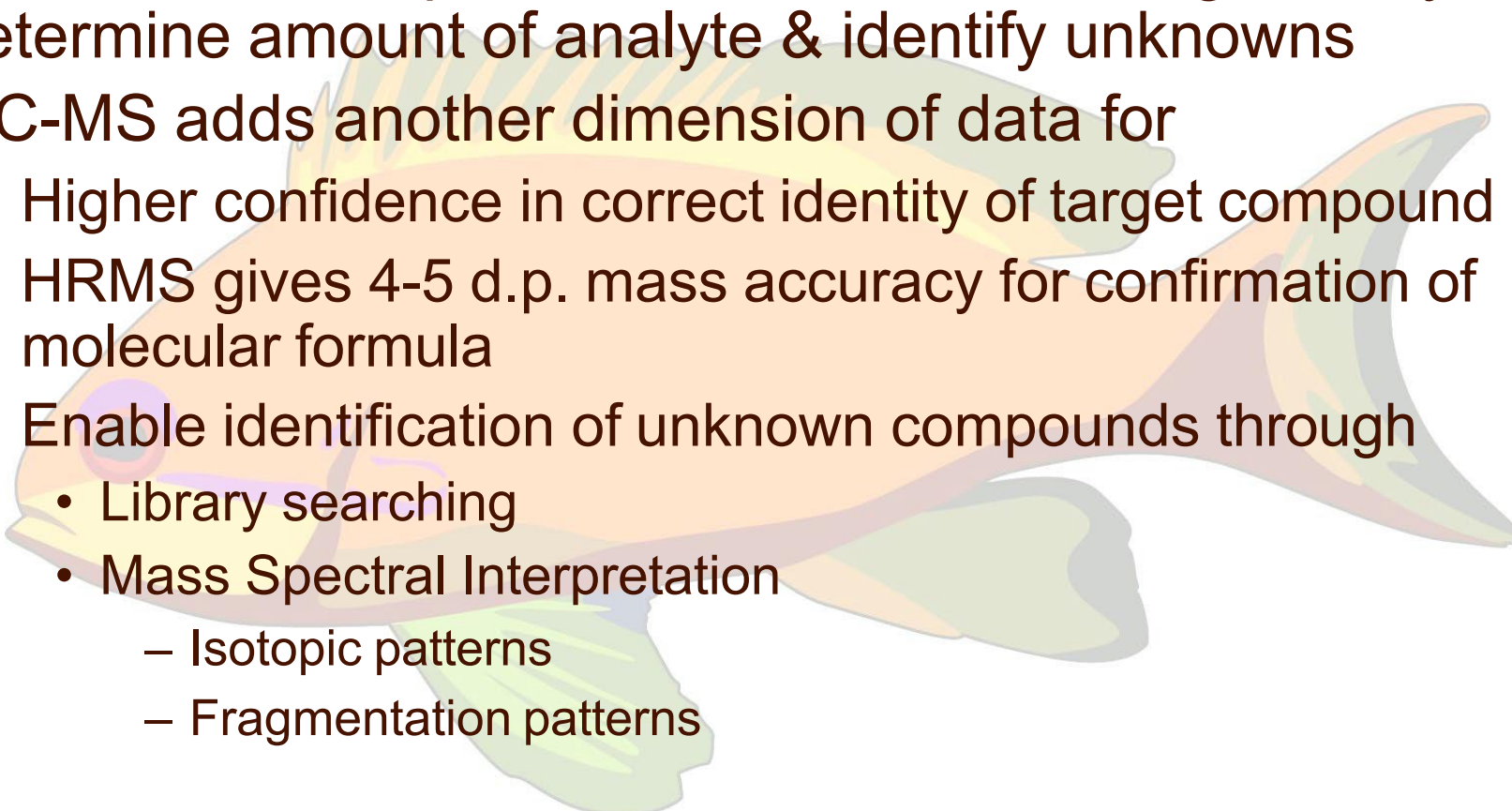


Electron affinity

- Electron affinity is defined as the change in energy (in kJ/mole) of a neutral atom or molecule when an electron is added to the atom to form a negative ion. In other words, the likelihood of gaining an electron

Group →	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
↓ Period																		
1	H 73																	He •
2	Li 60	Be •											B 27	C 122	N •	O 141	F 328	Ne •
3	Na 53	Mg •											Al 42	Si 134	P 72	S 200	Cl 349	Ar •
4	K 48	Ca 2	Sc 18	Ti 8	V 51	Cr 65	Mn •	Fe 15	Co 64	Ni 112	Cu 119	Zn •	Ga 41	Ge 119	As 79	Se 195	Br 324	Kr •
5	Rb 47	Sr 5	Y 30	Zr 41	Nb 86	Mo 72	Tc •	Ru 101	Rh 110	Pd 54	Ag 126	Cd •	In 39	Sn 107	Sb 101	Te 190	I 295	Xe •
6	Cs 46	Ba 14	•	Hf •	Ta 31	W 79	Re •	Os 104	Ir 150	Pt 205	Au 223	Hg •	Tl 36	Pb 35	Bi 91	Po •	At •	Rn •
7	Fr •	Ra •	•	Rf •	Db •	Sg •	Bh •	Hs •	Mt •	Ds •	Rg •	Cn •	Uut •	Fl •	Uup •	Lv •	Uus •	Uuo •
* Lanthanides			La 45	Ce 92	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm 99	Yb	Lu 33	
** Actinides			Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	

Legend
The number mentioned is **Electron affinity** in kJ/mol (rounded)
• Denotes elements that are expected to have electron affinities close to zero on quantum mechanical grounds
For the equivalent value in eV, see: [Electron affinity \(data page\)](#)

- Aims: to confirm presence or absence of target analytes, determine amount of analyte & identify unknowns
 - GC-MS adds another dimension of data for
 - Higher confidence in correct identity of target compound
 - HRMS gives 4-5 d.p. mass accuracy for confirmation of molecular formula
 - Enable identification of unknown compounds through
 - Library searching
 - Mass Spectral Interpretation
 - Isotopic patterns
 - Fragmentation patterns
- 

Atomic mass

Periodic Table of the Elements

group 1 2 13 14 15 16 17 18

period 1

atomic number

valence charge

name

symbol

atomic mass

alkali metals

alkaline earth metals

transitional metals

basic metals

semimetals

lanthanides

actinides

nonmetals

halogen gases

noble gases

1 H Hydrogen 1.008	2 He Helium 4.003																
3 Li Lithium 6.941	4 Be Beryllium 9.012																
11 Na Sodium 22.990	12 Mg Magnesium 24.305																
19 K Potassium 39.098	20 Ca Calcium 40.078	21 Sc Scandium 44.956	22 Ti Titanium 47.867	23 V Vanadium 50.942	24 Cr Chromium 51.996	25 Mn Manganese 54.938	26 Fe Iron 55.845	27 Co Cobalt 58.933	28 Ni Nickel 58.693	29 Cu Copper 63.546	30 Zn Zinc 65.38	31 Ga Gallium 69.723	32 Ge Germanium 72.631	33 As Arsenic 74.922	34 Se Selenium 78.971	35 Br Bromine 79.904	36 Kr Krypton 83.798
37 Rb Rubidium 85.468	38 Sr Strontium 87.62	39 Y Yttrium 88.906	40 Zr Zirconium 91.224	41 Nb Niobium 92.906	42 Mo Molybdenum 95.95	43 Tc Technetium 98.907	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.906	46 Pd Palladium 106.42	47 Ag Silver 107.868	48 Cd Cadmium 112.414	49 In Indium 114.818	50 Sn Tin 118.711	51 Sb Antimony 121.760	52 Te Tellurium 127.6	53 I Iodine 126.904	54 Xe Xenon 131.294
55 Cs Cesium 132.905	56 Ba Barium 137.328	57-71 * Lanthanides	72 Hf Hafnium 178.49	73 Ta Tantalum 180.948	74 W Tungsten 183.84	75 Re Rhenium 186.207	76 Os Osmium 190.23	77 Ir Iridium 192.22	78 Pt Platinum 195.085	79 Au Gold 196.967	80 Hg Mercury 200.592	81 Tl Thallium 204.383	82 Pb Lead 207.2	83 Bi Bismuth 208.980	84 Po Polonium [209]	85 At Astatine [210]	86 Rn Radon 222.018
87 Fr Francium 223.020	88 Ra Radium 226.025	89-103 ** Actinides	104 Rf Rutherfordium [261]	105 Db Dubnium [268]	106 Sg Seaborgium [271]	107 Bh Bohrium [272]	108 Hs Hassium [270]	109 Mt Meitnerium [276]	110 Ds Darmstadtium [281]	111 Rg Roentgenium [280]	112 Cn Copernicium [285]	113 Uut Ununtrium [284]	114 Fl Flerovium [289]	115 Uup Ununpentium [288]	116 Lv Livermorium [293]	117 Uus Ununseptium [294]	118 Uuo Ununoctium [294]

For elements with no stable isotopes, the mass number of the isotope with the longest half-life is in parentheses.

*
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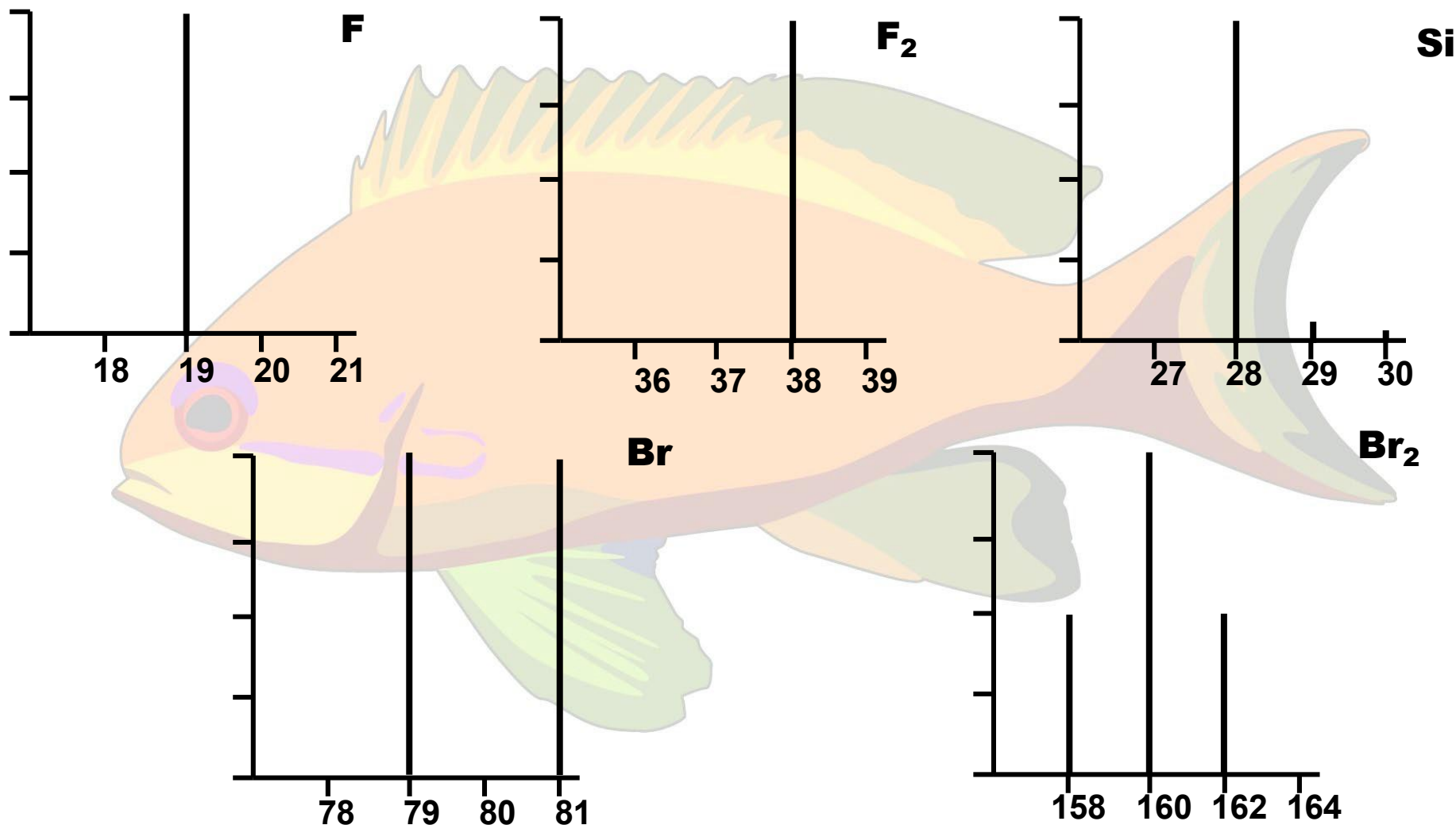
57 La Lanthanum 138.905	58 Ce Cerium 140.116	59 Pr Praseodymium 140.908	60 Nd Neodymium 144.243	61 Pm Promethium 144.913	62 Sm Samarium 150.36	63 Eu Europium 151.964	64 Gd Gadolinium 157.25	65 Tb Terbium 158.925	66 Dy Dysprosium 162.500	67 Ho Holmium 164.930	68 Er Erbium 167.259	69 Tm Thulium 168.934	70 Yb Ytterbium 173.054	71 Lu Lutetium 174.967
89 Ac Actinium 227.028	90 Th Thorium 232.038	91 Pa Protactinium 231.036	92 U Uranium 238.029	93 Np Neptunium 237.048	94 Pu Plutonium 244.064	95 Am Americium 243.061	96 Cm Curium 247.070	97 Bk Berkelium 247.070	98 Cf Californium 251.080	99 Es Einsteinium [252]	100 Fm Fermium 257.095	101 Md Mendelevium 258.1	102 No Nobelium 259.101	103 Lr Lawrencium [262]

Precise masses & isotopes

Common Element & their Isotopes found in Organic Compounds

	A Isotope		A+1 Isotope		A+2 Isotope		Class
	Mass	%Ab	Mass	%Ab	Mass	%Ab	
H	1.0078	100	2.0141	0.016			A
C	12.0000	100	13.0034	1.08			A+1
N	14.0031	100	15.0001	0.37			A+1
O	15.9949	100			17.9992	0.20	A+2/A
F	18.9984	100					A
Si	27.9769	100	28.9865	5.10	29.9738	3.40	A+2
P	30.9738	100					A
S	31.9720	100	32.9715	0.80	33.9679	4.40	A+2
Cl	34.9989	100			36.9659	32.5	A+2
Br	78.9183	100			80.9163	98	A+2
I	126.9045	100					A

Fluorine & Bromine



Electronegativity

- Electronegativity, symbol χ , is a chemical property that describes the tendency of an atom to attract a shared pair of electrons (or electron density) towards itself

Periodic Table of the Elements
Electronegativity

<http://chemistry.about.com>
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About Chemistry

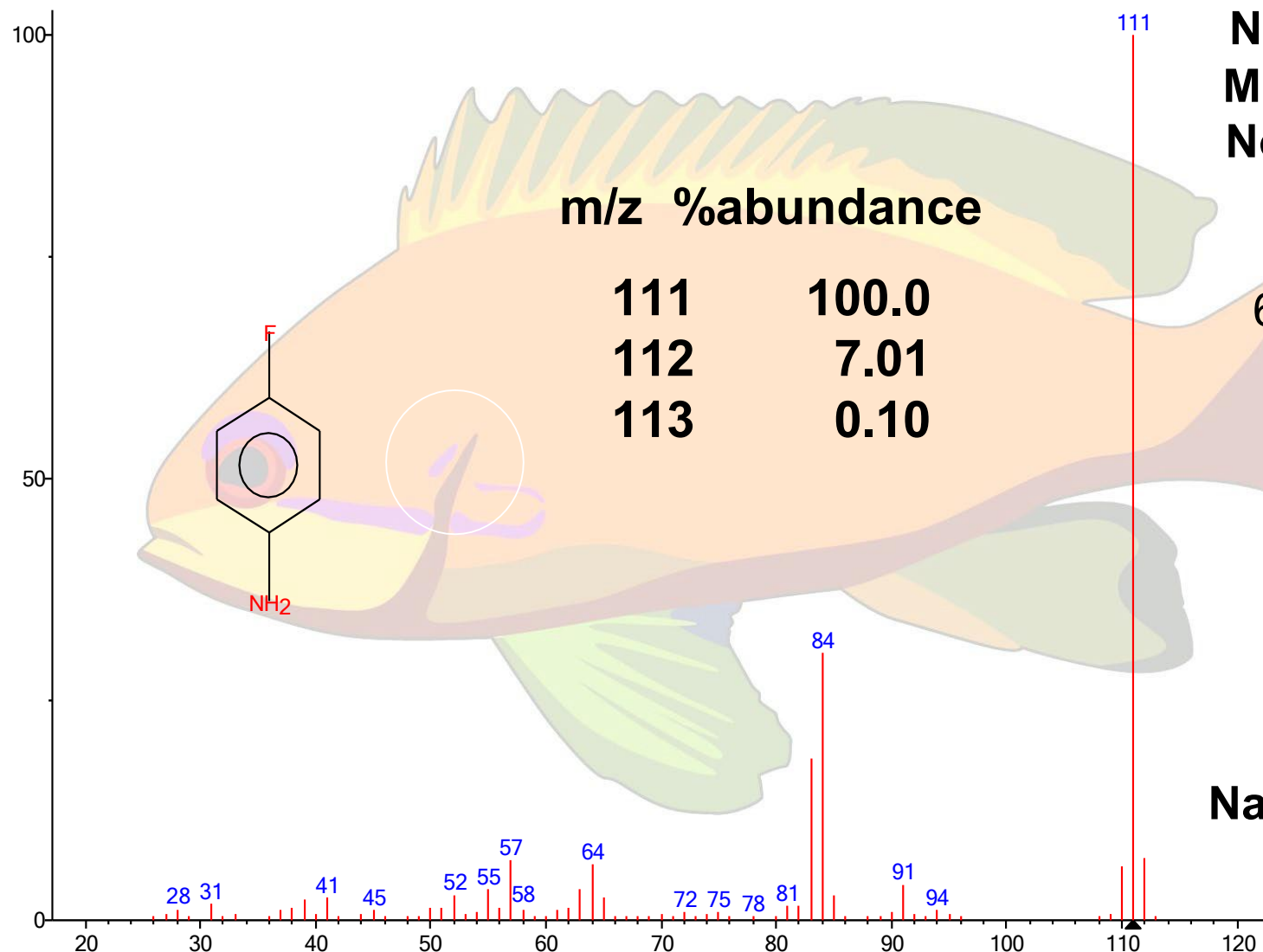
1A 1 H 2.20	2A 4 Be 1.57																	8A 2 He no data
3 Li 0.98	11 Na 0.93																	
19 K 0.82	37 Rb 0.82	55 Cs 0.79	87 Fr 0.7															
20 Ca 1.00	38 Sr 0.95	56 Ba 0.89	88 Ra 0.89															
21 Sc 1.36	39 Y 1.22	57-71 Lanthanides	89-103 Actinides															
22 Ti 1.54	40 Zr 1.33	72 Hf 1.3																
23 V 1.63	41 Nb 1.6	73 Ta 1.5																
24 Cr 1.66	42 Mo 2.16	74 W 2.36																
25 Mn 1.55	43 Tc 1.9	75 Re 1.9																
26 Fe 1.83	44 Ru 2.2	76 Os 2.2																
27 Co 1.88	45 Rh 2.28	77 Ir 2.20																
28 Ni 1.91	46 Pd 2.20	78 Pt 2.28																
29 Cu 1.90	47 Ag 1.93	79 Au 2.54																
30 Zn 1.65	48 Cd 1.69	80 Hg 2.00																
31 Ga 1.81	49 In 1.78	81 Tl 1.62																
32 Ge 2.01	50 Sn 1.96	82 Pb 2.33																
33 As 2.18	51 Sb 2.05	83 Bi 2.02																
34 Se 2.55	52 Te 2.1	84 Po 2.0																
35 Br 2.96	53 I 2.66	85 At 2.2																
36 Kr 3.00	54 Xe 2.6	86 Rn no data																

*** Elements > 104 exist only for very short half-lives and the data is unknown.***

Lanthanides

Actinides

57 La 1.10	58 Ce 1.12	59 Pr 1.13	60 Nd 1.14	61 Pm 1.13	62 Sm 1.17	63 Eu 1.2	64 Gd 1.2	65 Tb 1.2	66 Dy 1.22	67 Ho 1.23	68 Er 1.24	69 Tm 1.25	70 Yb 1.1	71 Lu 1.27
89 Ac 1.1	90 Th 1.3	91 Pa 1.5	92 U 1.38	93 Np 1.36	94 Pu 1.28	95 Am 1.3	96 Cm 1.3	97 Bk 1.3	98 Cf 1.3	99 Es 1.3	100 Fm 1.3	101 Md 1.3	102 No 1.3	103 Lr no data



Nitrogen rule: odd

Molecular ion: 111

No. carbons: 7.01-

0.37=6.6%

6.6/1.1=6C

6x12=72 111-14-

72=25H? F?

25-19=6H

Mol. Formula:

C_6H_6FN

R+DB: 6-

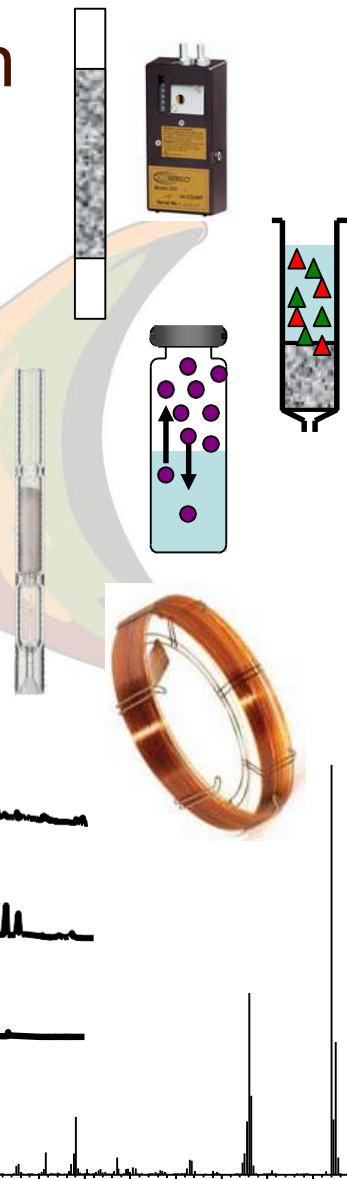
$7/2 + 1/2 + 1 = 4$

Key ions: 91 =
aromatic

Name: Fluoro-aniline

Break the system down

- Always start with chemistry of sample – both target compounds & matrix
- At each stage of sample analysis, think about how chemistries can
 - Be used to improve sample analysis
 - Cause problems in sample samples
- Stages include:
 - Sampling
 - Sample preparation
 - Sample introduction
 - Analyte separation
 - Analyte detection
 - Data analysis



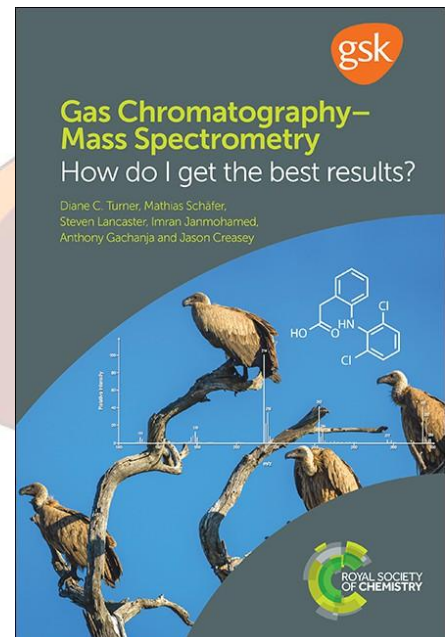
Thank you for listening!

RSC

Colleagues at Anthias Consulting Ltd.

Dr Geraint Morgan & colleagues – SPS, The
Open University, UK

RSC Analytical Division, PACN and Books
Community for Analytical Measurement Science



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