ROYAL SOCIETY OF CHEMISTRY | APPROVED TRAINING

AnthiasConsulting Ltd
Bridging the Gap

Using the Periodic Table in our GC-MS Analyses

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CAMS
Community for Analytical Measurement Science

Periodic Table & GC

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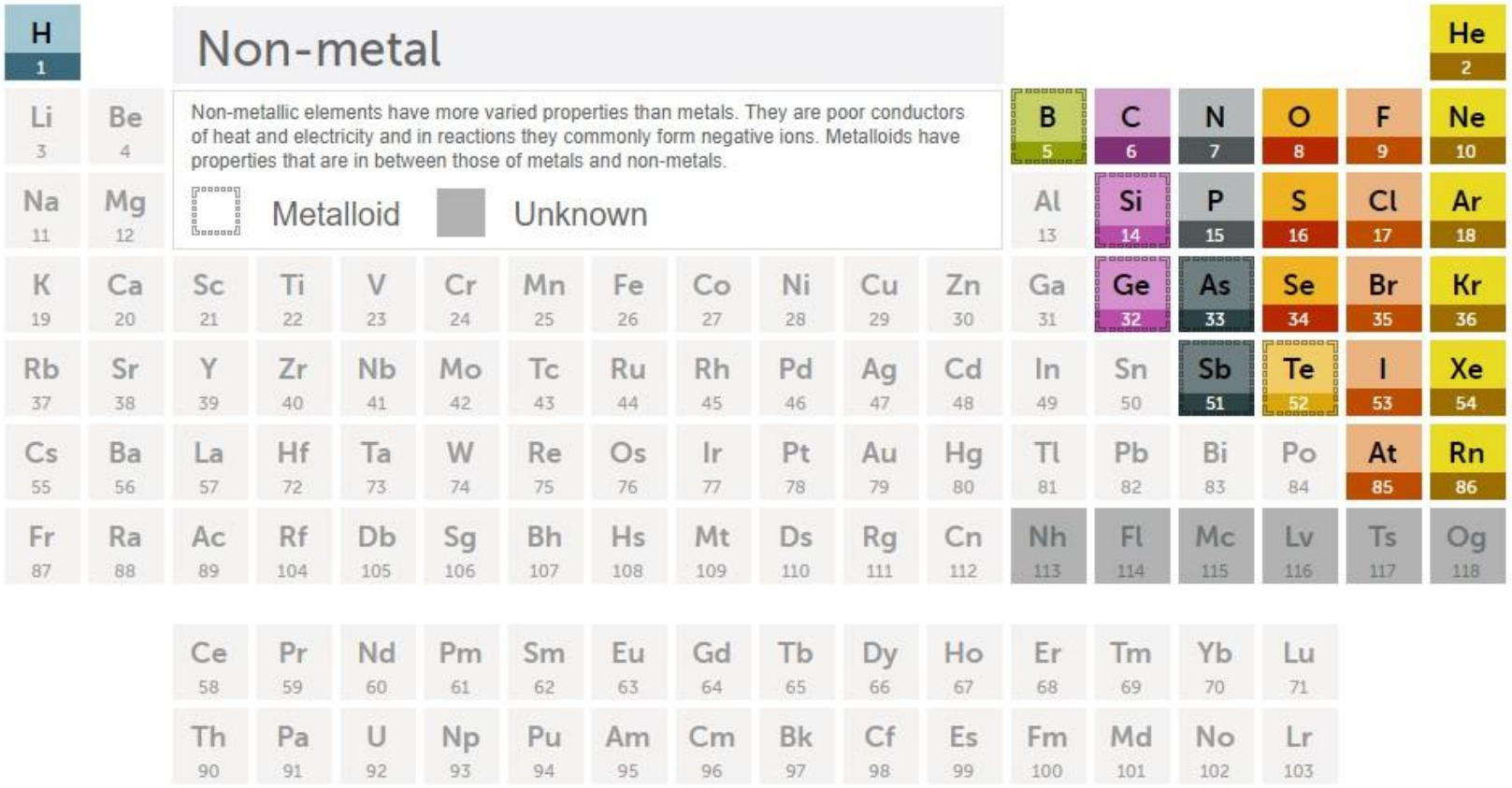

New sample analysis

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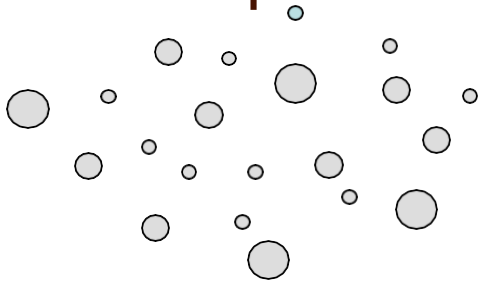
- Start from the basics:
  - Sample phase: gas/liquid/solid/something in-between
  - Chemistry of the targets compounds (analytes): Volatilities? Polarities? Functional groups?
  - Nature of the matrix: Higher MW than analytes? Similar volatility to analytes? Potential interferents? Same or different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



Using the periodic table

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- 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

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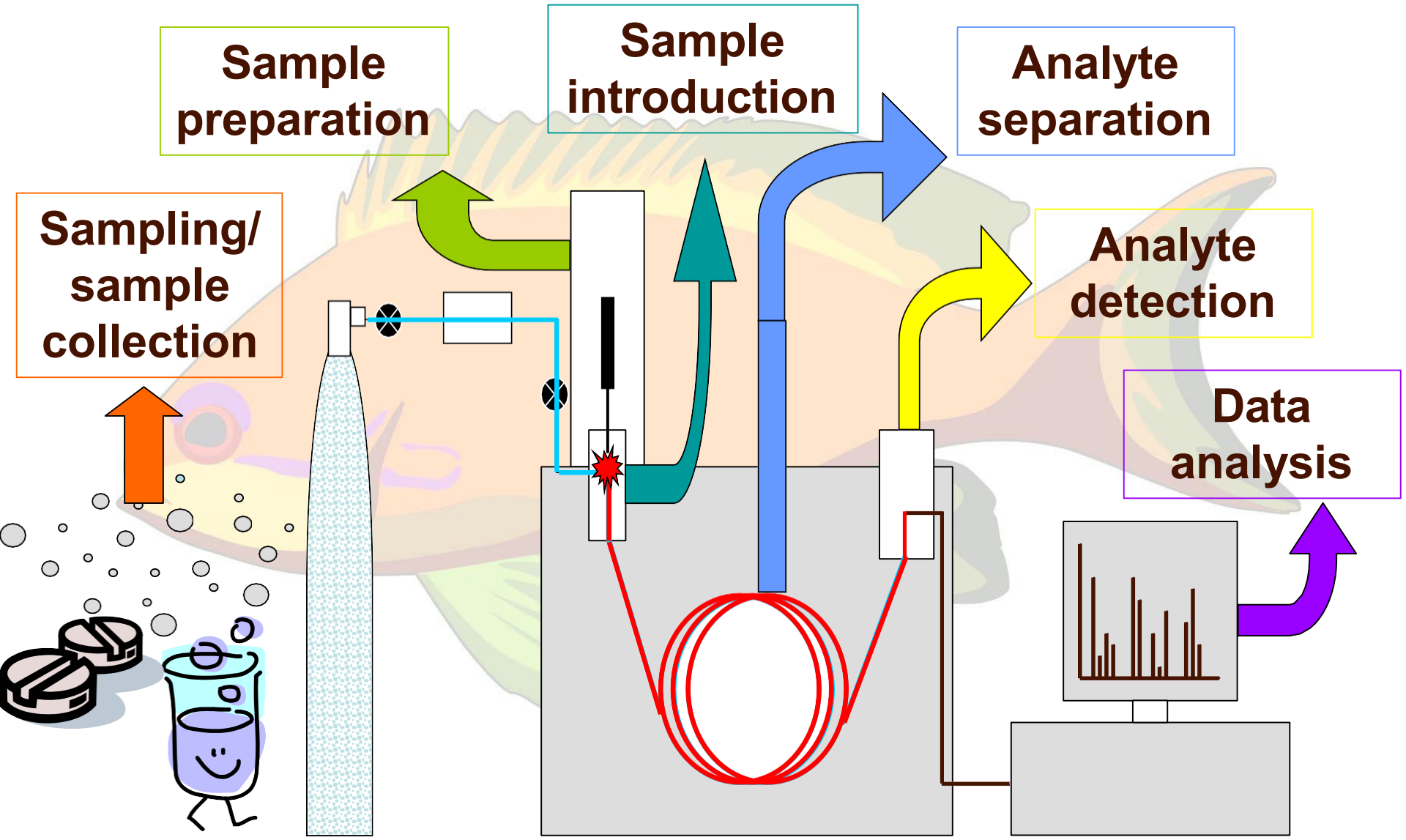

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Interactions in GC

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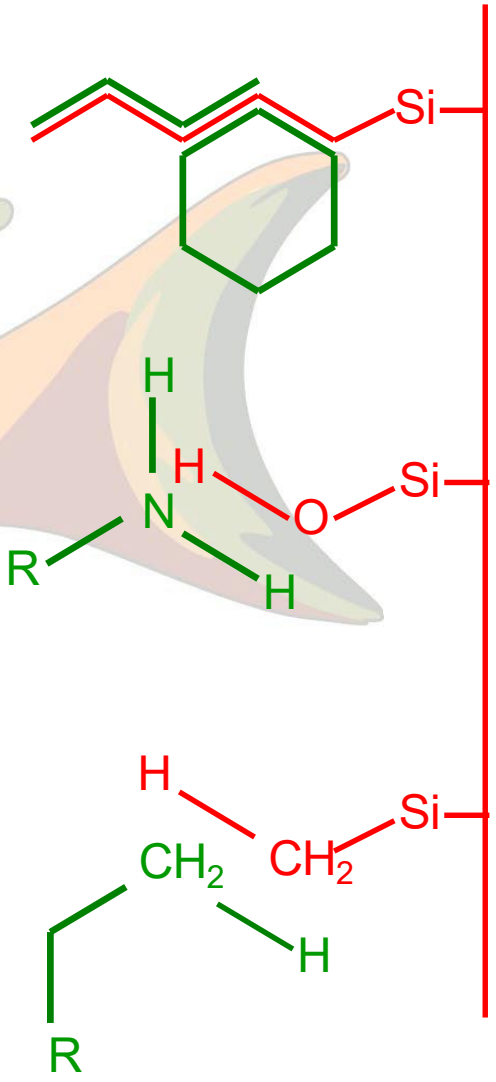
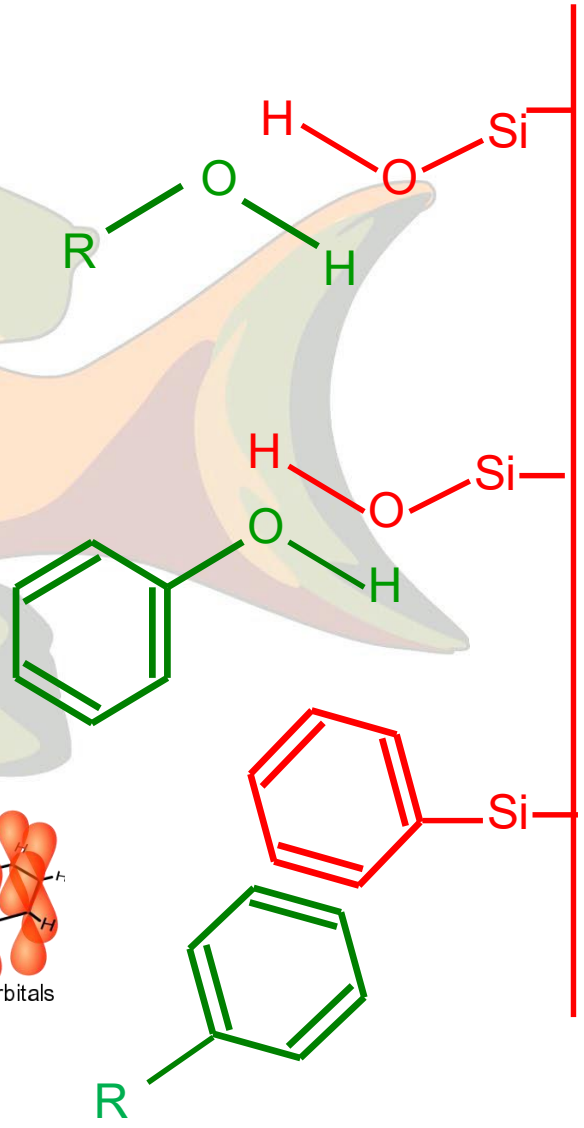
Stationary phase-analyte interactions can be:

- **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

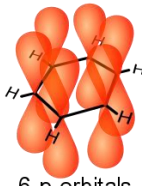


Interactions in GC

- **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

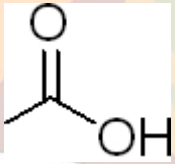


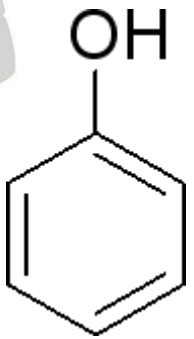
Interaction	Energy (kJ/mol)
Dispersive	<<1
Dipole-Induced Dipole	1
Dipole-Dipole	3.3
Hydrogen bonding	19


6 p-orbitals

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





Sampling/sample collection

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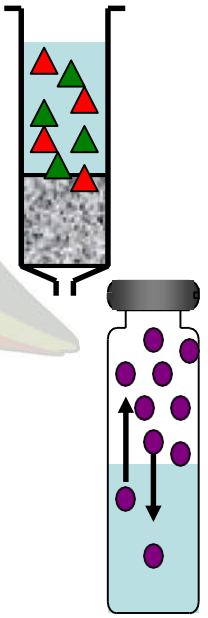
- Aims: To collect a representative sample, enough for analysis, in a suitable manner chosen for sample type & location
- Could be selective for:
  - Volatility (only traps analytes within a certain volatility range)
  - Analyte nature (only traps target analytes with certain characteristics like polarity-functional groups)
  - Avoids matrix interferents (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



Sample Introduction

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- 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

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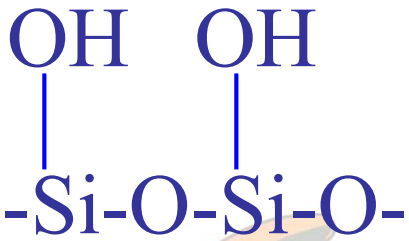
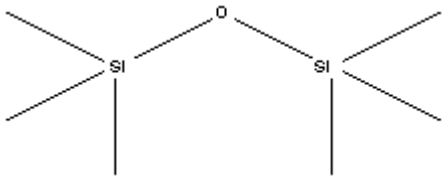


- Liners made of glass or metal
- Activity mainly occurs in liner
  → loss of peaks, tailing peaks, inconsistent results
- Active compounds breakdown/adsorb/react at active sites → interaction of functional groups
- Deactivation applies an inert, integral layer to liner (& packing material)



- Deactivation methods include siltek,
  or silanisation with e.g. hexamethyldisiloxane
- Max. temp: 400°C (450°C for siltek) but be wary!

Analyte separation

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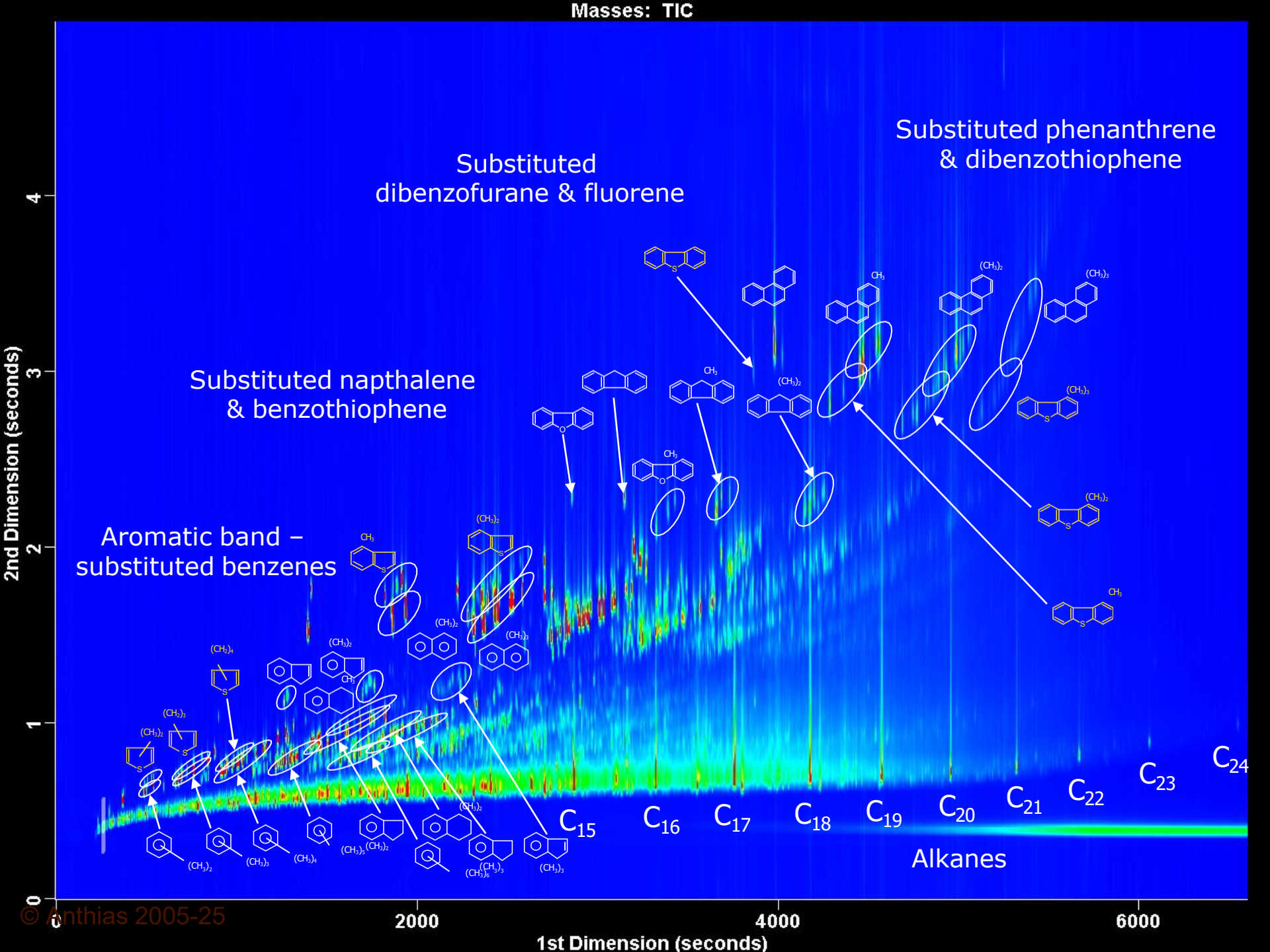
- Aims: to separate analytes of interest from each other as well as matrix co-extractives
- Problems: enough theoretical plates for large number of analytes/matrix peaks, mixed characteristics: selection of phase good for some classes not others
- Techniques:
  - Select column stationary phase suitable 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

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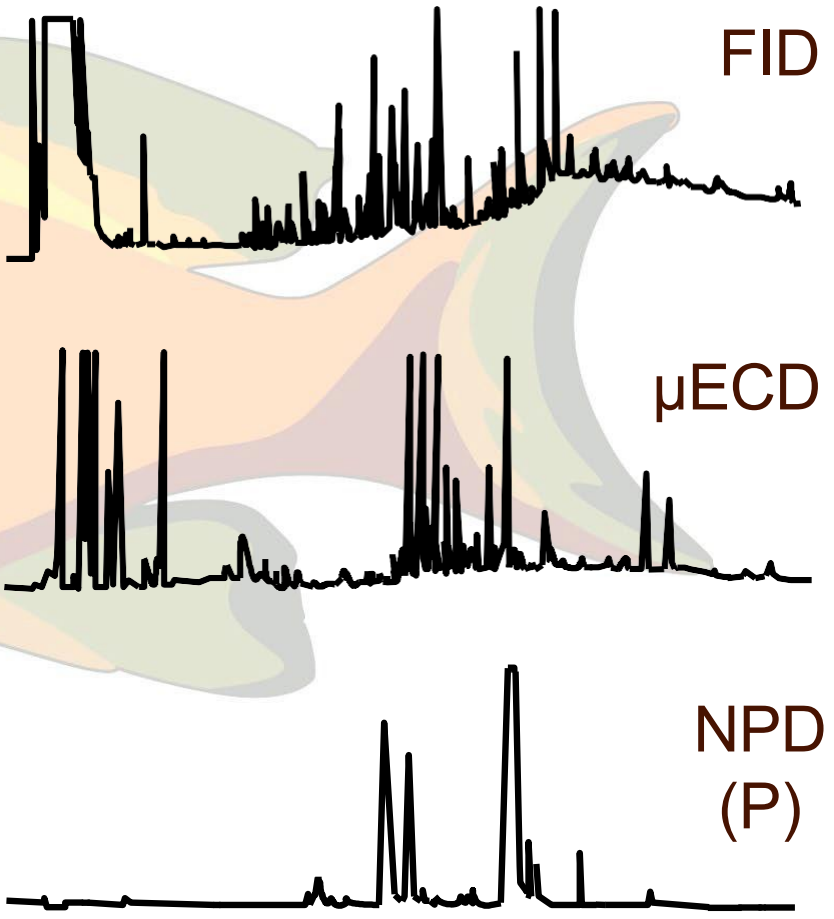
- Selective detectors, e.g.:
  - μECD: responds only to analytes capable of capturing e^-
  - SCD/NCD/PFPD/NPD: respond to certain atoms
  - MS: another dimension of data
    - NCI
    - SIM
    - MS/MS: secondary ion spectrum e.g. MRM
    - HRMS: 4-5 d.p. mass accuracy



Courtesy of Agilent

Electron affinity

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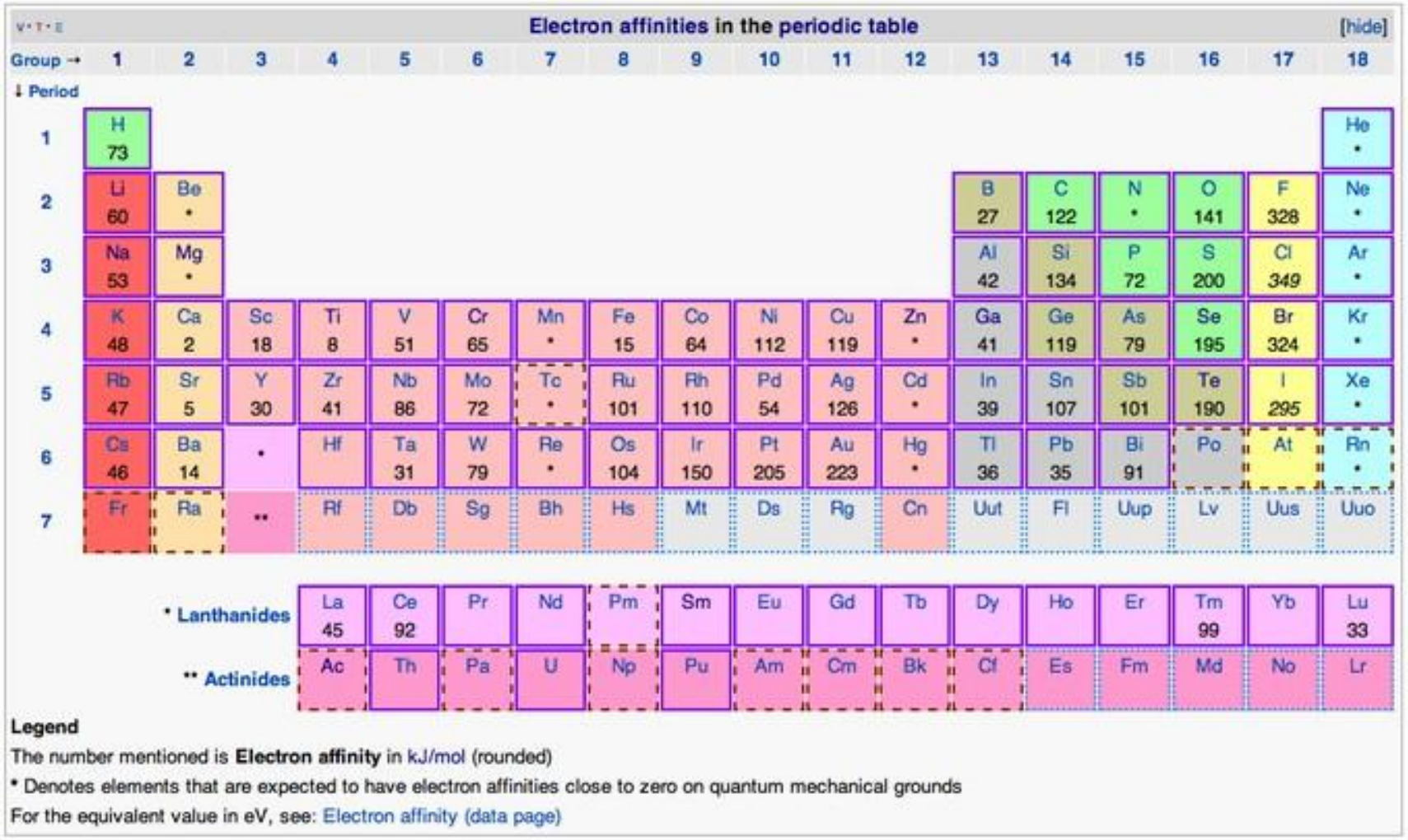
- Electron affinity is defined as the change in energy (in kJ/mole) of a neutral atom or molecule when an electron is added to the atom to form a negative ion. In other words, the likelihood of gaining an electron



Electron affinities in the periodic table [hide]

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)

Courtesy of sciencetrends.com

GC-MS Data Analysis

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- 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

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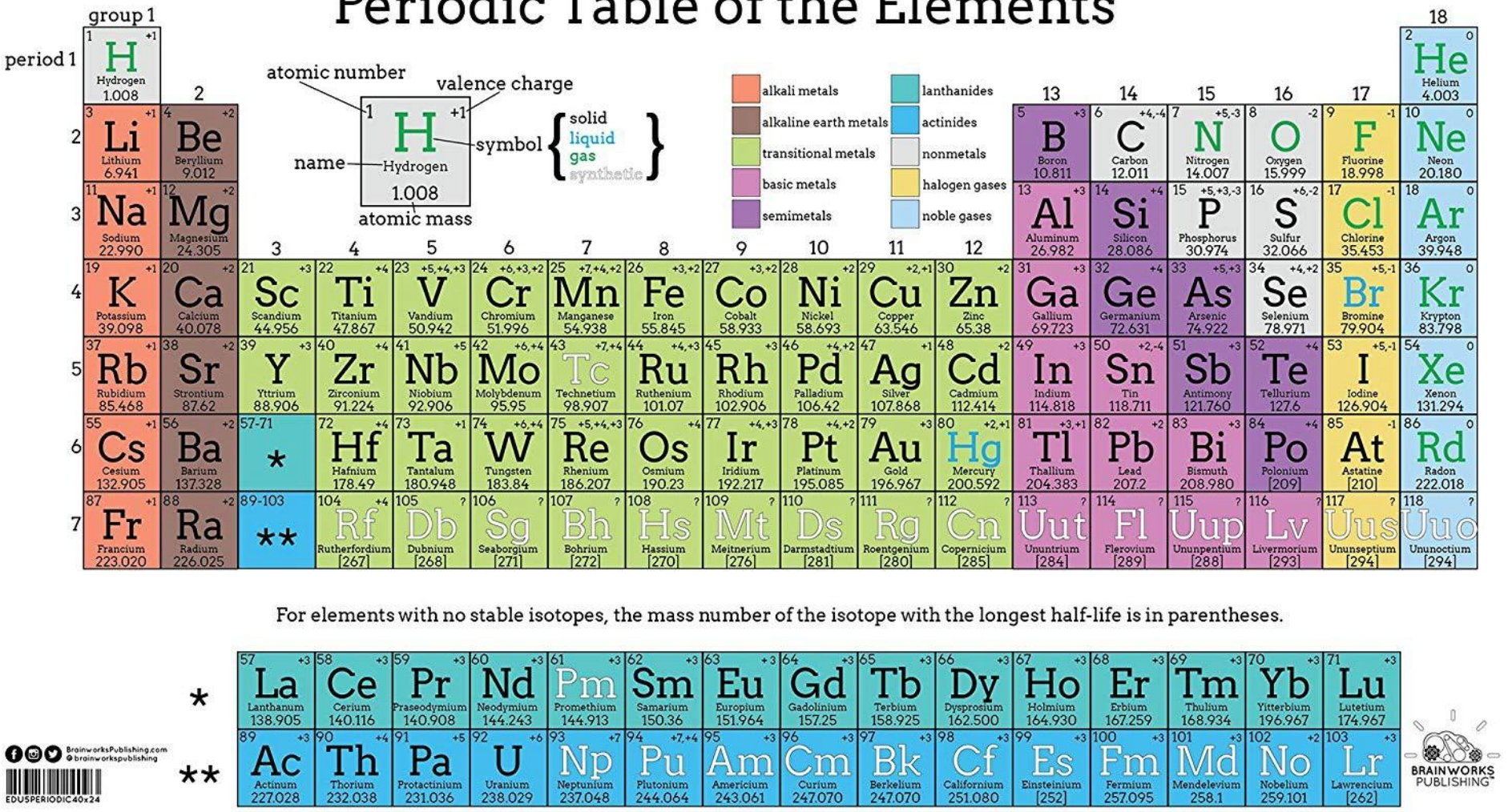

Precise masses & isotopes

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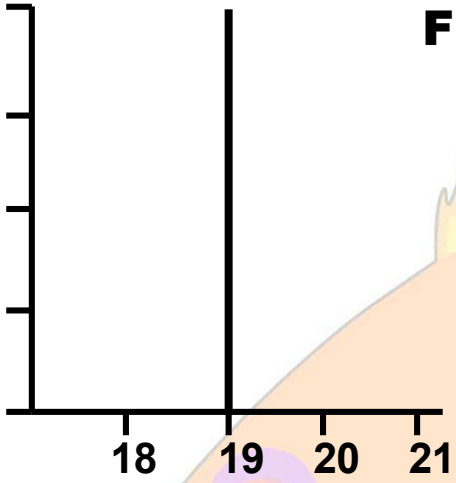
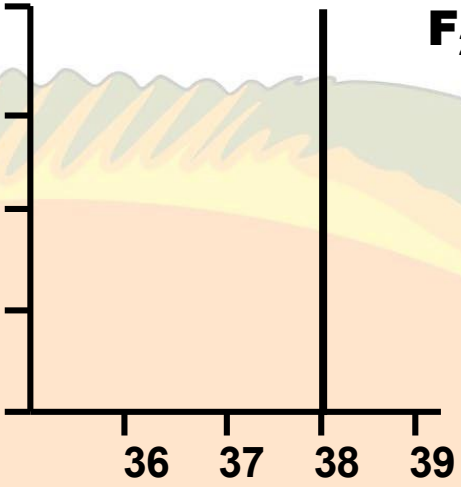
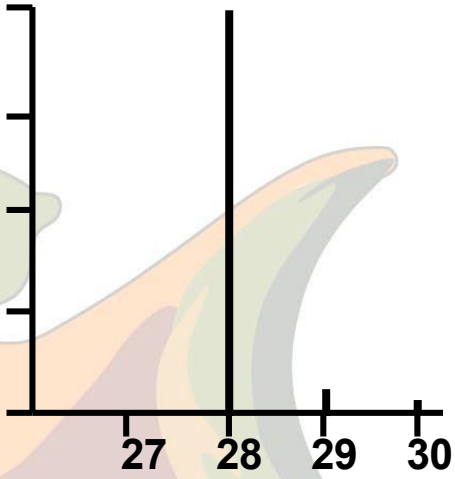
Common Element & their Isotopes found in Organic Compounds

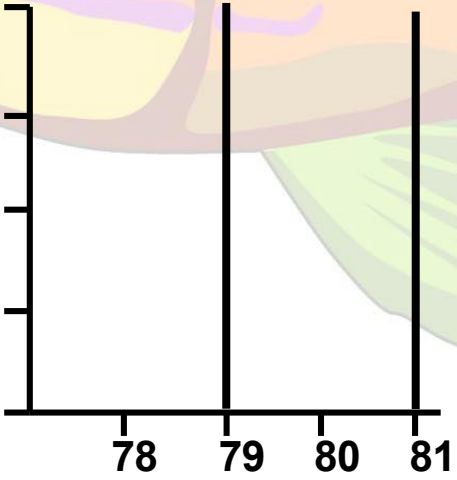
	A Isotope		A+1 Isotope		A+2 Isotope		
	Mass	**%Ab**	**Mass**	**%Ab**	**Mass**	**%Ab**	**Class**
H	1.0078	100	2.0141	0.016			A
C	12.0000	100	13.0034	1.08			A+1
N	14.0031	100	15.0001	0.37			A+1
O	15.9949	100			17.9992	0.20	A+2/A
F	18.9984	100					A
Si	27.9769	100	28.9865	5.10	29.9738	3.40	A+2
P	30.9738	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

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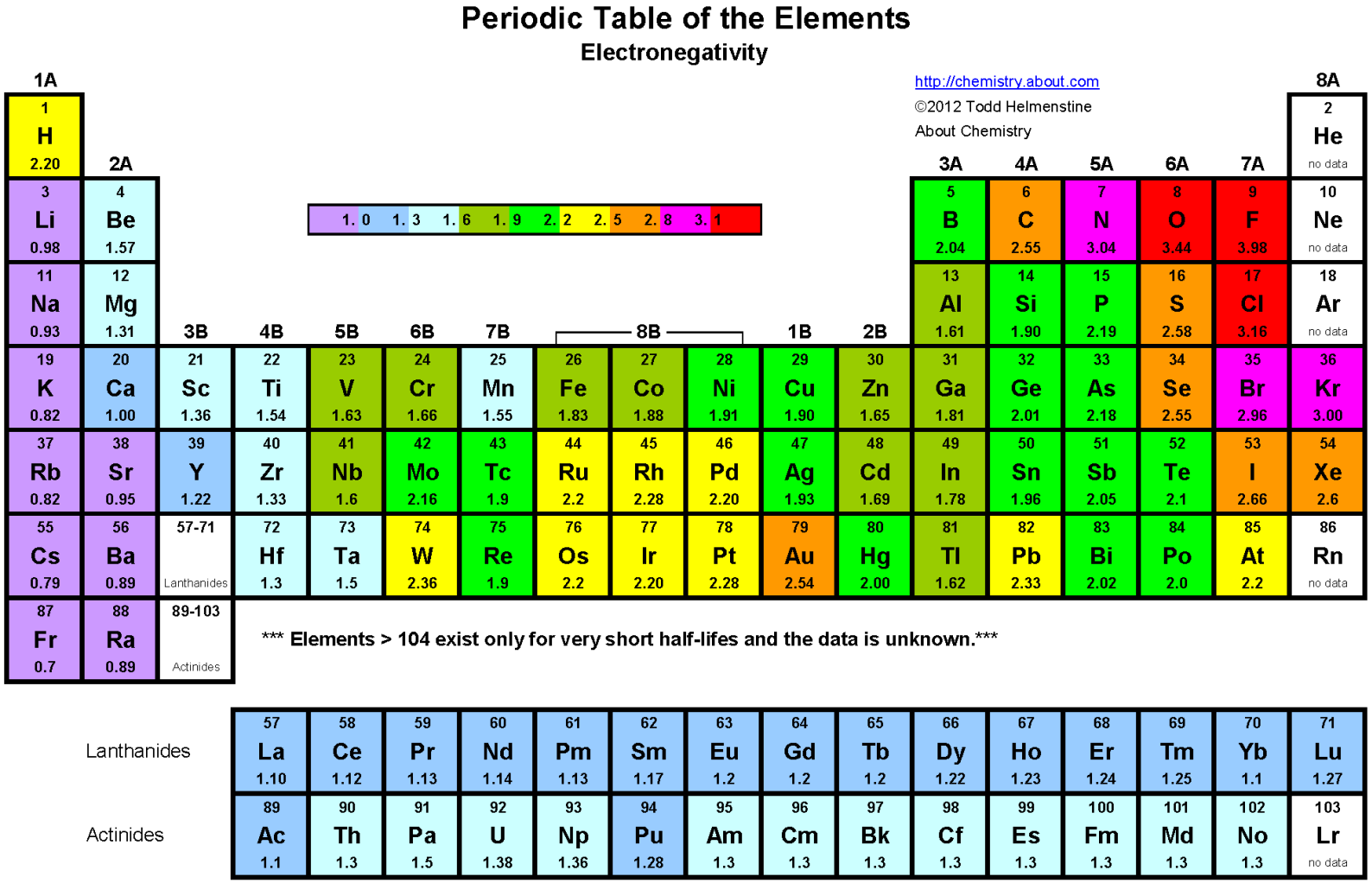
- Electronegativity, symbol χ, is a chemical property that describes the tendency of an atom to attract a shared pair of electrons (or electron density) towards itself



GC-MS Spectral Interpretation

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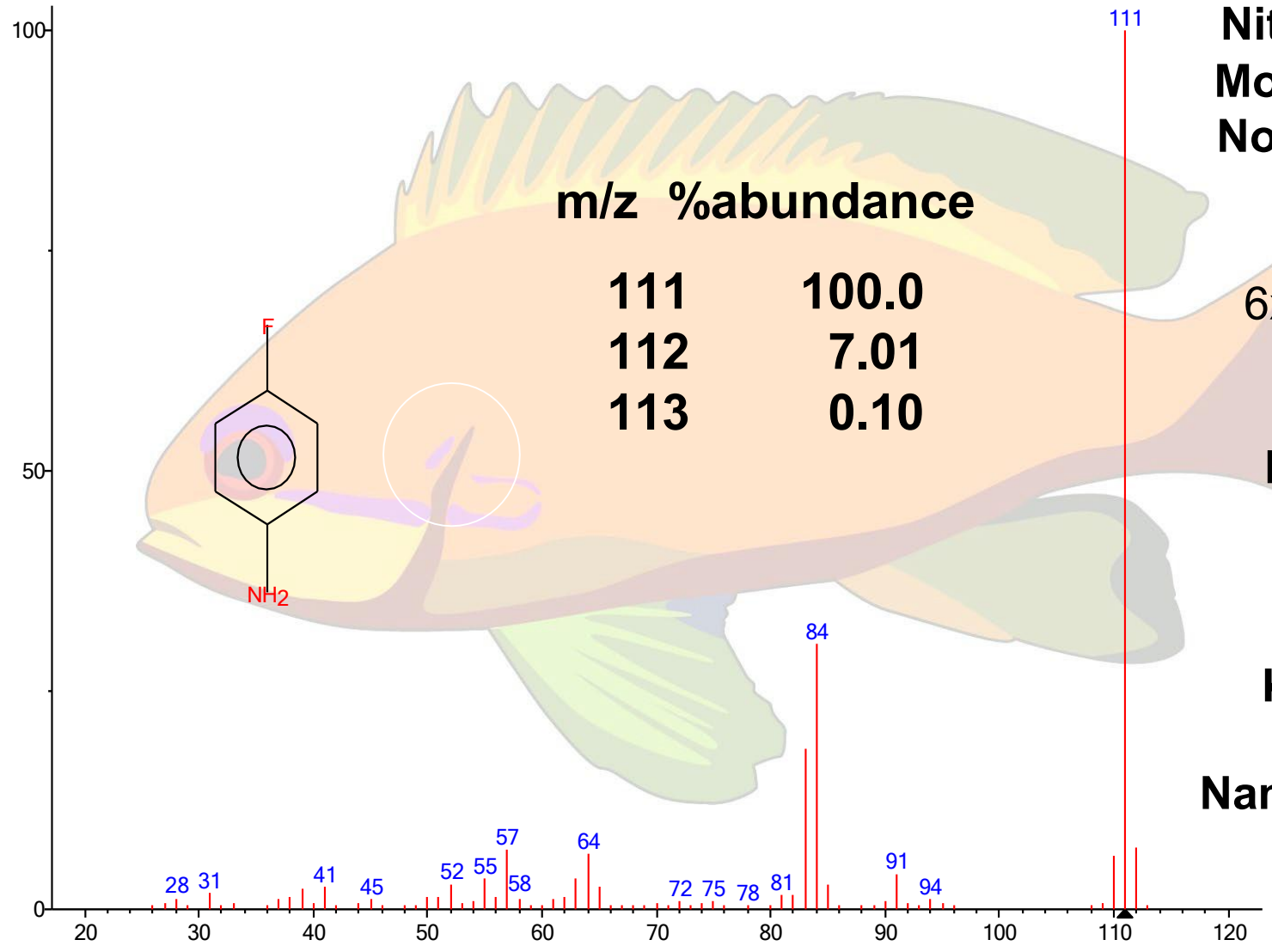

m/z	%abundance
111	100.0
112	7.01
113	0.10

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

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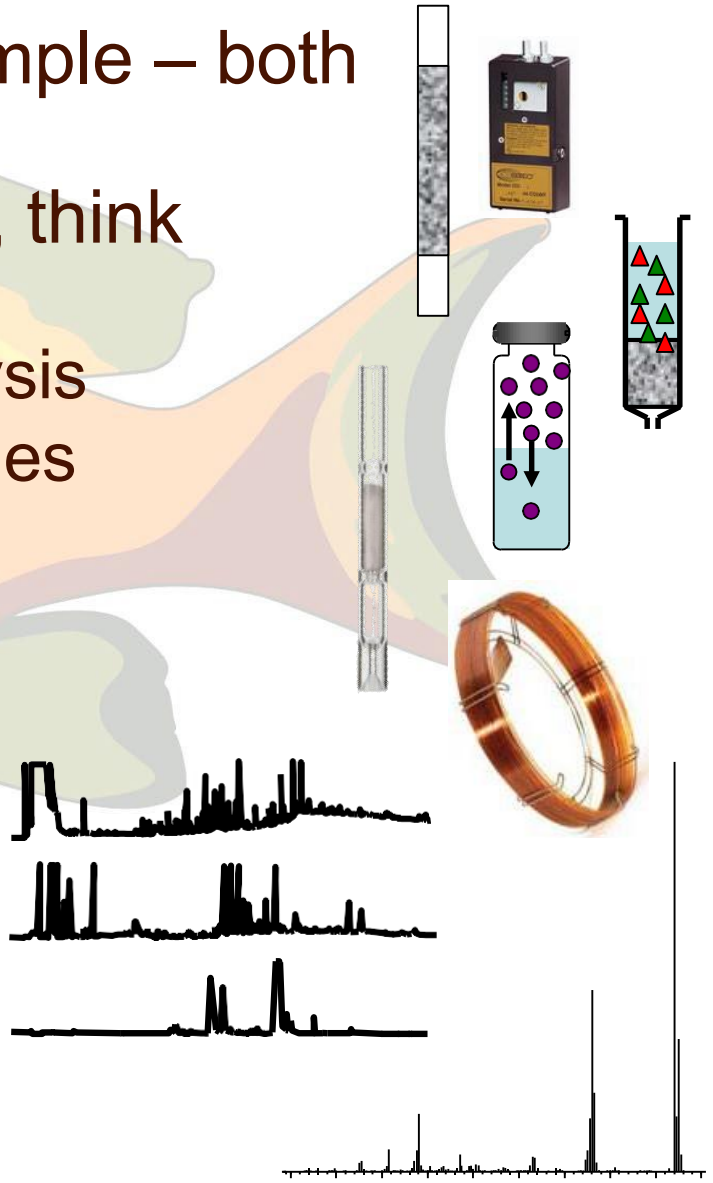
- Always start with chemistry of sample – both target compounds & matrix
- At each stage of sample analysis, think about how chemistries can
  - Be used to improve sample analysis
  - Cause problems in sample samples
- Stages include:
  - Sampling
  - Sample preparation
  - Sample introduction
  - Analyte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



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Thank you for listening!

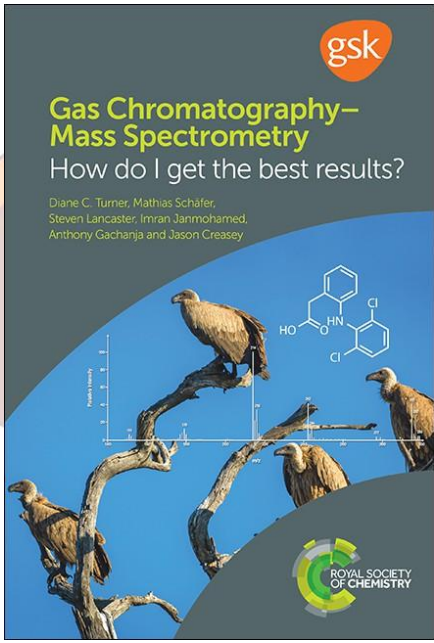
RSC

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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