The Mass Spectrometer as a Laboratory

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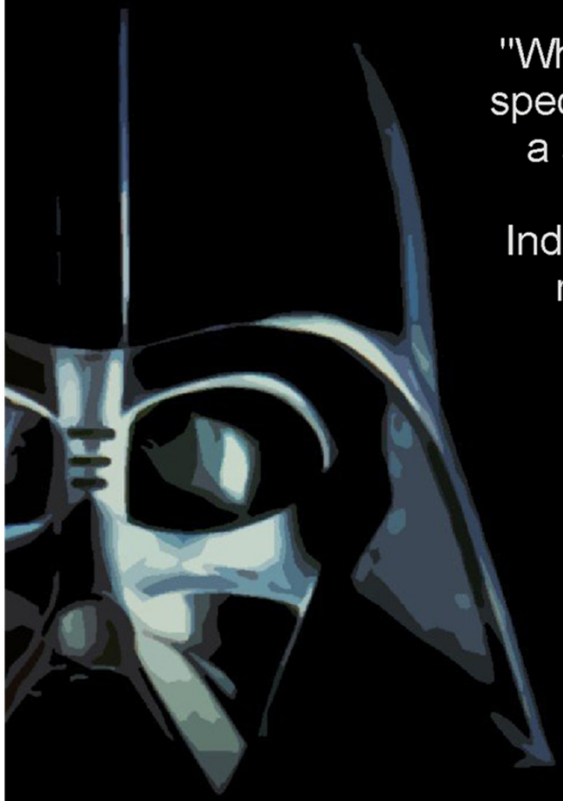
The Dark Side (...of Analytical Chemistry)

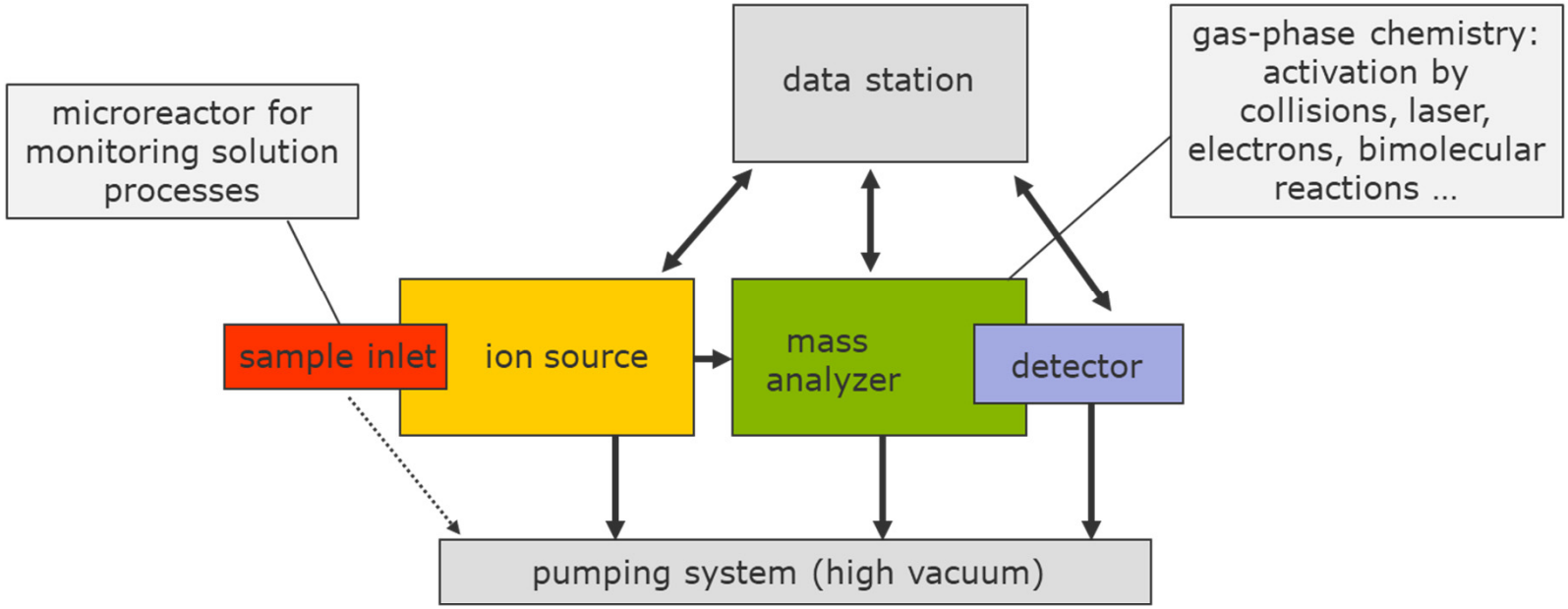


"When non-mass spectrometrists are talking about mass spectrometry, it rather often sounds as if they were telling a story out of Poe's "Tales of Mystery and Imagination".

Indeed, mass spectrometry appears to be regarded as a mysterious method, just good enough to supply some molecular weight information. Unfortunately, this rumor about the dark side of analytical methods reaches students much earlier than their first contact with mass spectrometry."

Jürgen Gross,
Mass Spectrometry - A Textbook, Springer 2004

The General Setup of a Mass Spectrometer



mass spectrometers are operated at pressures < 10^{-8} mbar

exceptions: EI ion source (10^{-5} mbar), CI ion source (10^{-3} mbar), ESI ion source (1 bar)
collision cells (10^{-5} mbar)

Pressure Table

Pressure Conversion Table and Vacuum Terminology

Vacuum Quality	Unit Symbol	Pascal Pa	bar bar	millibar mbar	Torr Torr	mean free path between collisions
Rough Vacuum	P	1,0E+05	1,000	1000,000	751,9	50 nm
	r	1,0E+04	0,100	100,000	75,2	
	e	1,0E+03	0,010	10,000	7,5	
Medium Vacuum	s	1,0E+02	0,001	1,000	0,752	50 µm
	s	1,0E+01	1,0E-04	0,100	0,075	
	u	1,0E+00	1,0E-05	0,010	7,5E-03	
High Vacuum	r	1,0E-01	1,0E-06	1,0E-03	7,5E-04	50 mm
	e	1,0E-02	1,0E-07	1,0E-04	7,5E-05	
		1,0E-03	1,0E-08	1,0E-05	7,5E-06	
		1,0E-04	1,0E-09	1,0E-06	7,5E-07	50 m
Ultrahigh Vacuum		1,0E-05	1,0E-10	1,0E-07	7,5E-08	
		1,0E-06	1,0E-11	1,0E-08	7,5E-09	
		1,0E-07	1,0E-12	1,0E-09	7,5E-10	50 km
		1,0E-08	1,0E-13	1,0E-10	7,5E-11	
		1,0E-09	1,0E-14	1,0E-11	7,5E-12	

1 bar = 1000 mbar = 10^5 Pa; 1 Torr = 133 Pa; 1 psi = 6895 Pa = 68.95 mbar.
Useful ranges are in bold face.

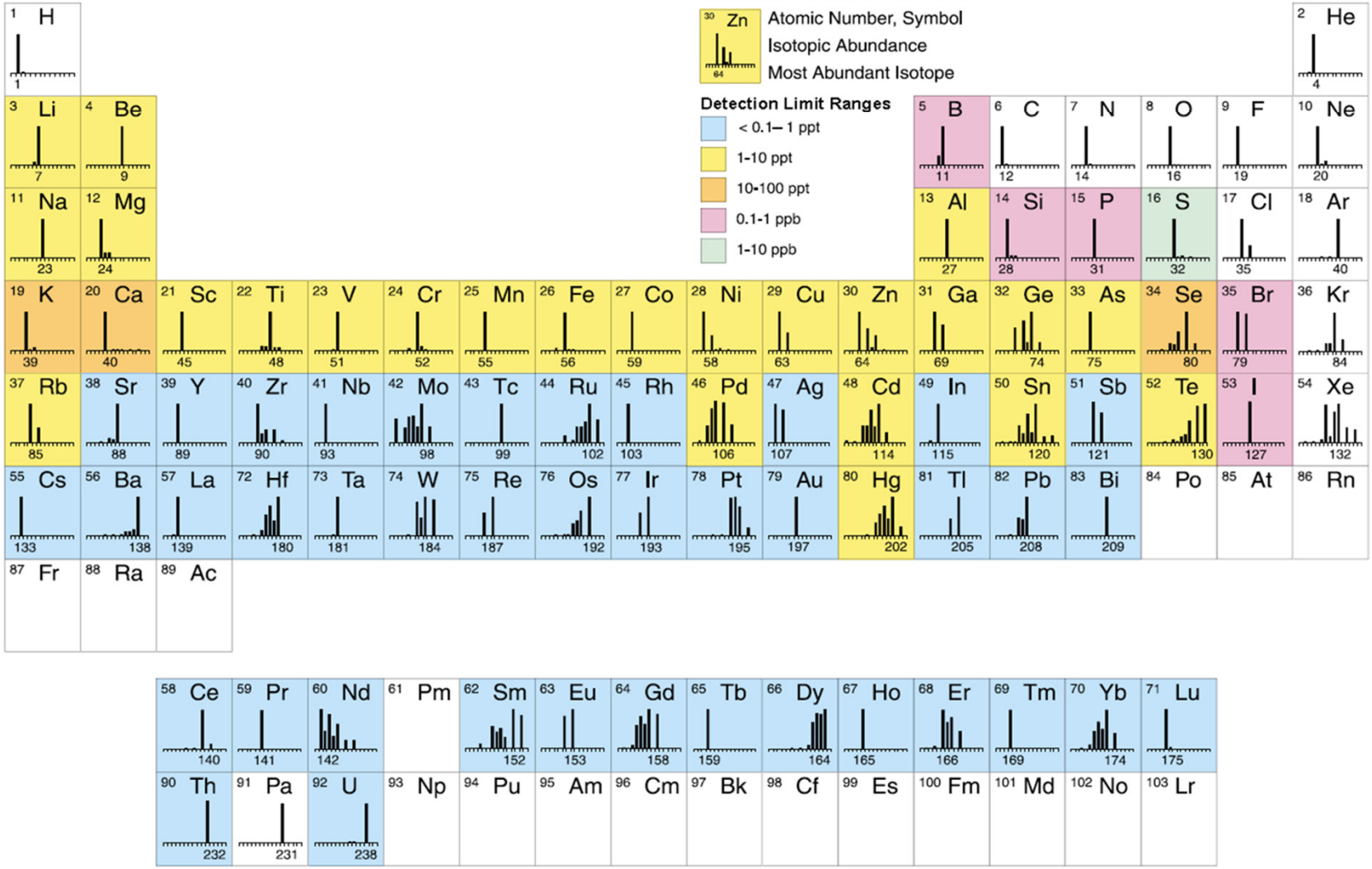
Mass Definitions and Mass Defect

relative mass:	weighted average over all isotopes of each element summed up for the elemental composition
nominal mass:	calculated using the rounded mass of the most abundant isotope of each element
isotopic mass:	exact mass of a certain isotope
monoisotopic mass:	exact mass of most abundant isotope is used for every element
exact mass:	difference to monoisotopic mass is the electron mass (0.000548 amu)
most abundant mass:	mass of the most intense signal in the isotope pattern

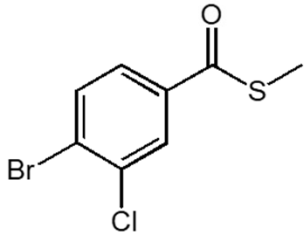
mass defect: binding energy of elementary particles in nucleus causes a relativistic mass defect which is large enough to be measured

^{1}H: 1.007825	^{4}He: 4.002603	^{9}Be: 9.012182	^{12}C: 12.000000
^{14}N: 14.003070	^{16}O: 15.994915	^{28}Si: 27.976927	^{52}Cr: 51.940654

Periodic Table of Isotope Patterns



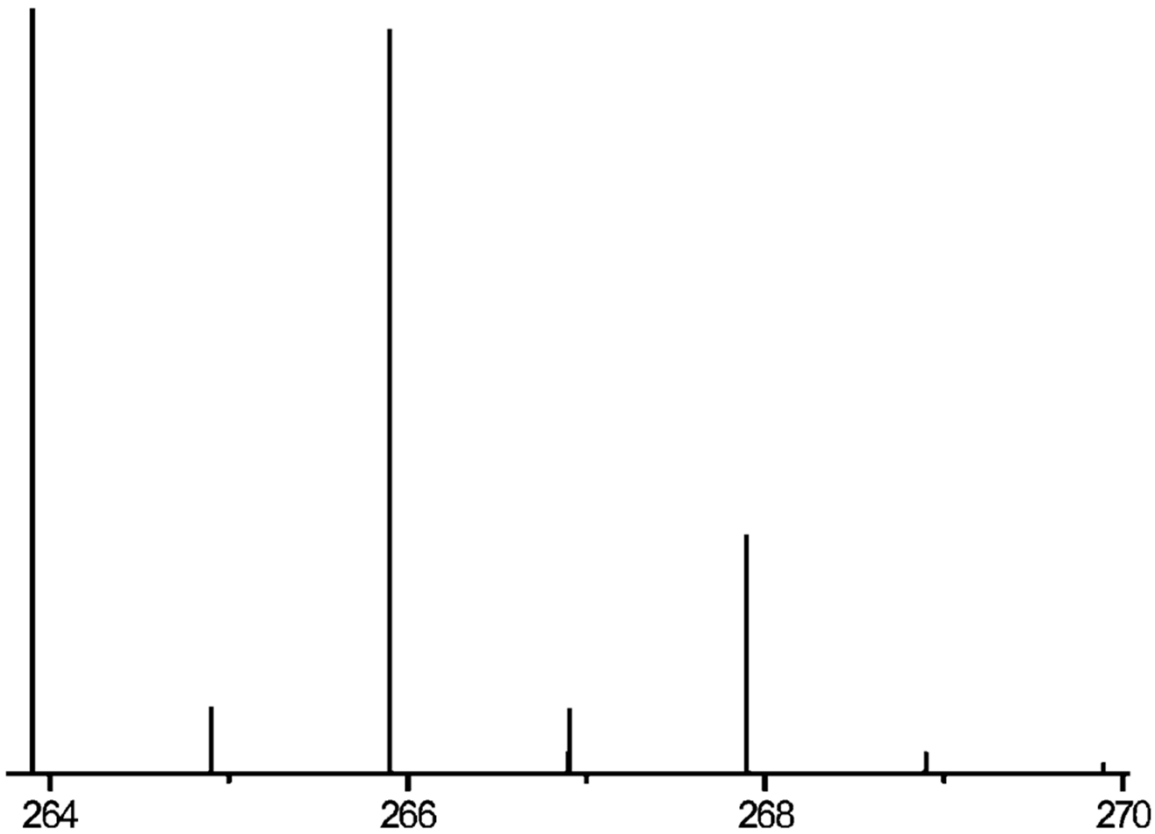
Isotope Pattern Analysis



$C_8H_6BrClOS$

number of visible isotope peaks depends on resolution of instrument

here: 7 visible isotope peaks in low res, 22 in high res mode



Information Content of Mass Spectra

primary information: **mass-to-charge ratio** and **intensity** of any ions formed

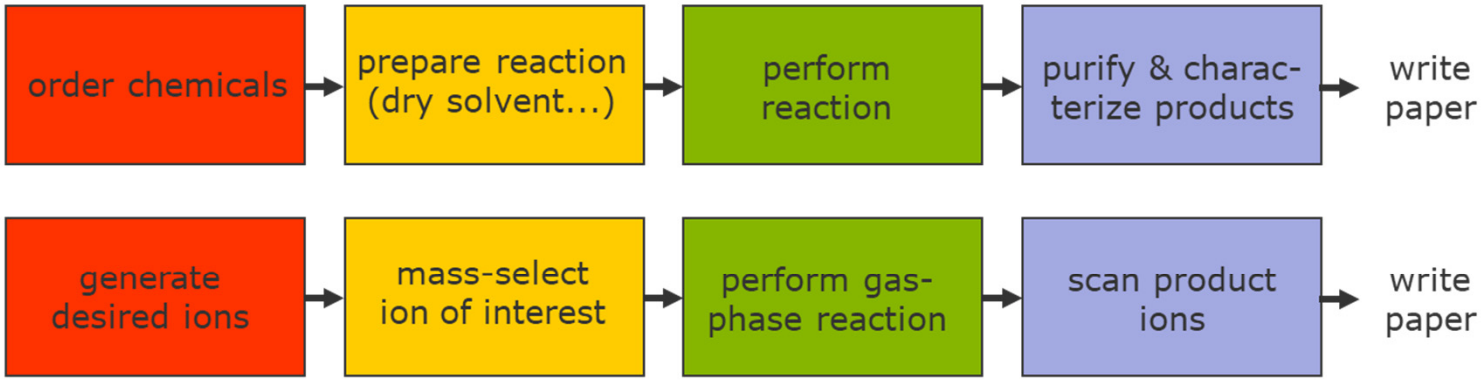
secondary information:

- elemental composition (from exact mass through mass defect and from isotope patterns)
- stoichiometries of non-covalent complexes (**warning:** unspecific aggregation is possible)
- structural information from fragments appearing in the mass spectra (**warning:** determining which signals are fragments and which are impurities sometime difficult)
- reactivity information (in solution as well as in the gas phase)

mass spectrometers are multichannel detectors able to identify components in complex mixtures (each m/z is one channel)

Tandem MS and Gas-Phase Chemistry

compare a reaction in the lab with a tandem mass spectrometric experiment:



what is so interesting about gas-phase chemistry?

extremely precisely controlled experimental conditions: minimal systems can be studied to unravel underlying principles (e.g. the mechanisms of catalytic reactions)

in high vacuum inside a mass spectrometer, ions are isolated (environment-free conditions)
tandem MS monitors intrinsic properties
comparison with solution properties allows to determine the effects of the environment

Understanding Mass Spectrometry

Basics

Ionization Processes
Gaseous Ion Energetics
Time Scales
Isotope Distributions
etc.

Technical Realization

Sample Inlets
Ion Sources
Vacuum Technology
Mass Analyzers
Detectors
GC/LC-MS Coupled Techniques

Mass Spectrometry
Gas-Phase Chemistry

Applications

Sample Identification
Quantification
Gas-Phase Chemistry
Mechanistic Studies
Proteomics
etc.

Interpretation of Mass Spectra

Fragmentation Channels
Characteristic Ions
Characteristic Fragmentation Reactions
etc.