



CAS tutorial on RGA Interpretation of RGA spectra

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CAS on Vacuum for Particle
Accelerators

Why are we interested in RGA spectra?

- Identify **which gas species are present** in vacuum systems; for accelerators, 10^{-9} mbar of H₂ are not equivalent to 10^{-9} mbar of oxygen or pump oil vapour.
- **Monitor processes**; for example thin film deposition.
- **Validate manufacturing and surface treatments**; virtual leaks, remaining contaminations, residual cleaning agents...

Content

1. Mass of molecules
2. Spectra of single and simple molecules:
fragmentation
3. Mixing different gas molecules
4. Case studies
5. Guidelines for diagnosis.



The periodic table of the elements



In UHV system for accelerators

hydrogen 1 H 1.0079	lithium 3 Li 6.941	beryllium 4 Be 9.0122
lithium 3 Li 6.941	magnesium 12 Mg 24.305	magnesium 12 Mg 24.305
potassium 19 K 39.098	calcium 20 Ca 40.078	calcium 20 Ca 40.078
rubidium 37 Rb 85.468	strontium 38 Sr 87.62	strontium 38 Sr 87.62
caesium 55 Cs 132.91	barium 56 Ba 137.33	barium 56 Ba 137.33
francium 87 Fr [223]	radium 88 Ra [226]	radium 88 Ra [226]

Always present
Frequently detected
Only in specific applications
Contaminants

helium 2 He 4.0026	hydrogen 1 H 1.0079	boron 5 B 10.811	carbon 6 C 12.011	nitrogen 7 N 14.007	oxygen 8 O 15.999	fluorine 9 F 18.998	neon 10 Ne 20.180										
lithium 3 Li 6.941	magnesium 12 Mg 24.305	aluminium 13 Al 26.982	silicon 14 Si 28.086	phosphorus 15 P 30.974	sulfur 16 S 32.065	chlorine 17 Cl 35.453	argon 18 Ar 39.948										
potassium 19 K 39.098	calcium 20 Ca 40.078	gallium 31 Ga 69.723	germanium 32 Ge 72.61	arsenic 33 As 74.922	selenium 34 Se 78.96	bromine 35 Br 79.904	krypton 36 Kr 83.80										
rubidium 37 Rb 85.468	strontium 38 Sr 87.62	yttrium 39 Y 88.906	zirconium 40 Zr 91.224	niobium 41 Nb 92.906	molybdenum 42 Mo 95.94	technetium 43 Tc [98]	ruthenium 44 Ru 101.07	rhodium 45 Rh 102.91	palladium 46 Pd 106.42	silver 47 Ag 107.87	cadmium 48 Cd 112.41	indium 49 In 114.82	tin 50 Sn 118.71	antimony 51 Sb 121.76	tellurium 52 Te 127.60	iodine 53 I 126.90	xenon 54 Xe 131.29
caesium 55 Cs 132.91	barium 56 Ba 137.33	lutetium 57-70 Lu 174.97	hafnium 71 Hf 178.49	tantalum 72 Ta 180.95	tungsten 73 W 183.84	rhenium 74 Re 186.21	osmium 75 Os 190.23	iridium 76 Ir 192.22	platinum 78 Pt 195.08	gold 79 Au 196.97	mercury 80 Hg 200.59	thallium 81 Tl 204.38	lead 82 Pb 207.2	bismuth 83 Bi 208.98	polonium 84 Po [209]	astatine 85 At [210]	radon 86 Rn [222]
francium 87 Fr [223]	radium 88 Ra [226]	lawrencium 89-102 Lr [262]	rutherfordium 103 Rf [261]	dubnium 105 Db [262]	seaborgium 106 Sg [266]	bohrium 107 Bh [264]	hassium 108 Hs [269]	meitnerium 109 Mt [268]	ununnilium 110 Uuu [271]	ununnilium 111 Uuu [272]	ununnilium 112 Uub [277]	ununquadium 114 Uuq [289]					

* Lanthanide series

** Actinide series

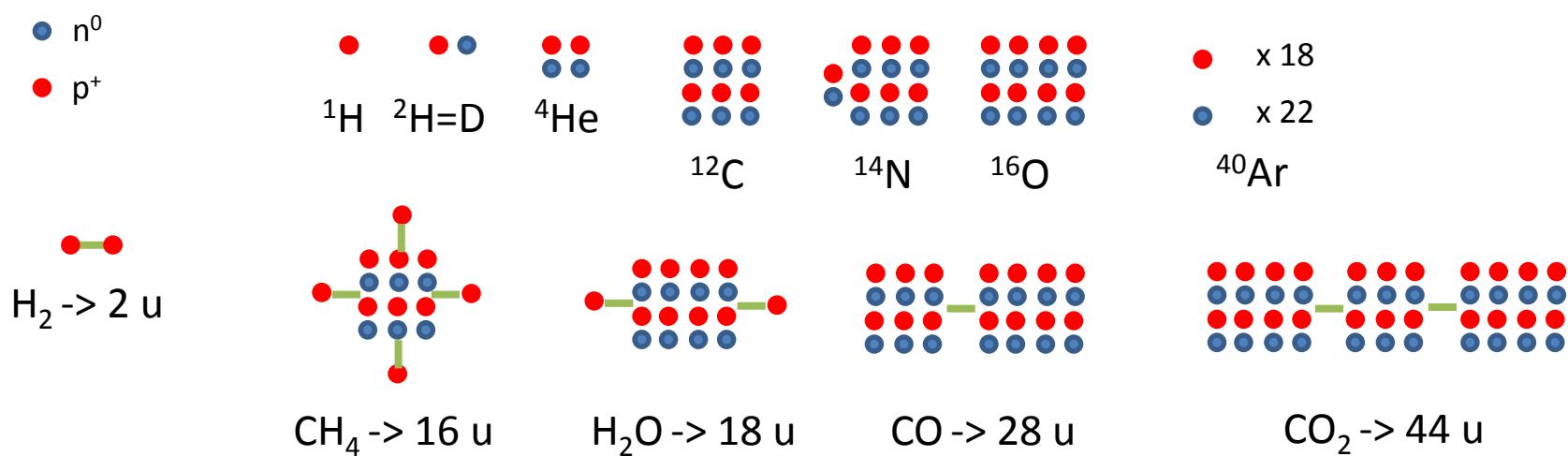
lanthanum 57 La 138.91	cerium 58 Ce 140.12	praseodymium 59 Pr 140.91	neodymium 60 Nd 144.24	promethium 61 Pm [145]	samarium 62 Sm 150.36	europerium 63 Eu 151.96	gadolinium 64 Gd 157.25	terbium 65 Tb 158.93	dysprosium 66 Dy 162.50	holmium 67 Ho 164.93	erbium 68 Er 167.26	thulium 69 Tm 168.93	yterbium 70 Yb 173.04
actinium 89 Ac [227]	thorium 90 Th 232.04	protactinium 91 Pa 231.04	uranium 92 U 238.03	neptunium 93 Np [237]	plutonium 94 Pu [244]	americium 95 Am [243]	curium 96 Cm [247]	berkelium 97 Bk [247]	californium 98 Cf [251]	elsteinium 99 Es [252]	fermium 100 Fm [257]	mendelevium 101 Md [258]	nobelium 102 No [259]

What is the relative mass of a molecule?

- Relative molecular masses are measured in ‘unified atomic mass units’ (‘u’ or Dalton, Da).
- One atomic mass unit is defined as one twelfth of the rest mass of a carbon-12 atom in its ground state.

$$1 \text{ u} = 1/12 (\text{¹²C mass}) = 1.66\ldots \times 10^{-27} \text{ Kg}$$

- One unit is roughly equal to the mass of 1 proton or 1 neutron
- In first approximation the atomic mass unit of a molecule can be evaluated counting its number of protons and neutrons.



Molecule	Symbol	Rel. mass of main isotope	Z = Number of protons	N = Number of neutrons
Hydrogen	H	1	1	
Helium	He	4	2	2
Carbon	C	12	6	6
Nitrogen	N	14	7	7
Oxygen	O	16	8	8
Fluorine	F	19	9	10
Neon	Ne	20	10	10
Chlorine	Cl	35	17	18
Sulfur	S	32	16	16
Argon	Ar	40	18	22
Krypton	Kr	84	36	48

Isotopes

Z	N	M	Rel. abundance
1 H	1	1	≈1
	2	2	10^{-4}
2 He	2	4	≈1
	1	3	10^{-4}
6 C	6	12	0.989
	5	13	0.011
7 N	7	14	≈1
	8	15	3.6×10^{-3}
8 O	8	16	0.998
	9	17	3.8×10^{-4}
	10	18	2.05×10^{-3}
10 Ne	10	20	0.905
	11	21	3×10^{-3}
	12	22	0.092

Z	N	M	Rel. abundance
17 Cl	18	35	0.7576
	20	37	0.2424
18 Ar	18	36	0.003336
	20	38	6.3×10^{-4}
36 Kr	22	40	0.99
	42	78	0.0035
36 Kr	44	80	0.0229
	46	82	0.1159
36 Kr	47	83	0.1150
	48	84	0.5699
	50	86	0.1728

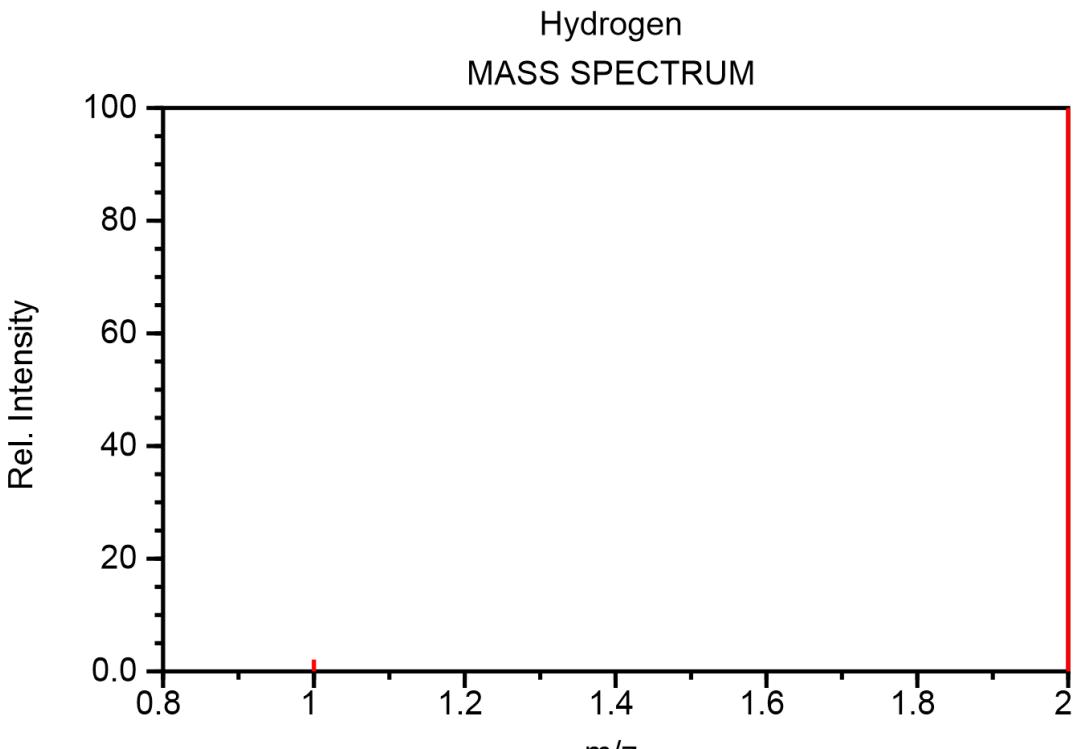
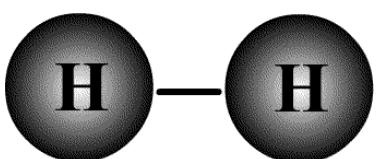
- In general in **UHV**, we have a **limited number of molecules** which are **very light** and easy to identify singularly.

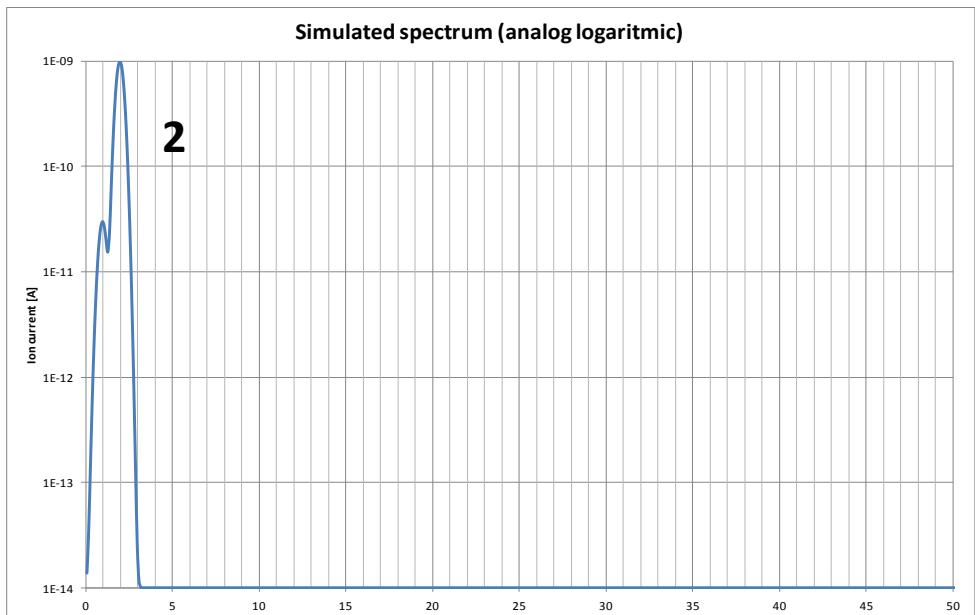
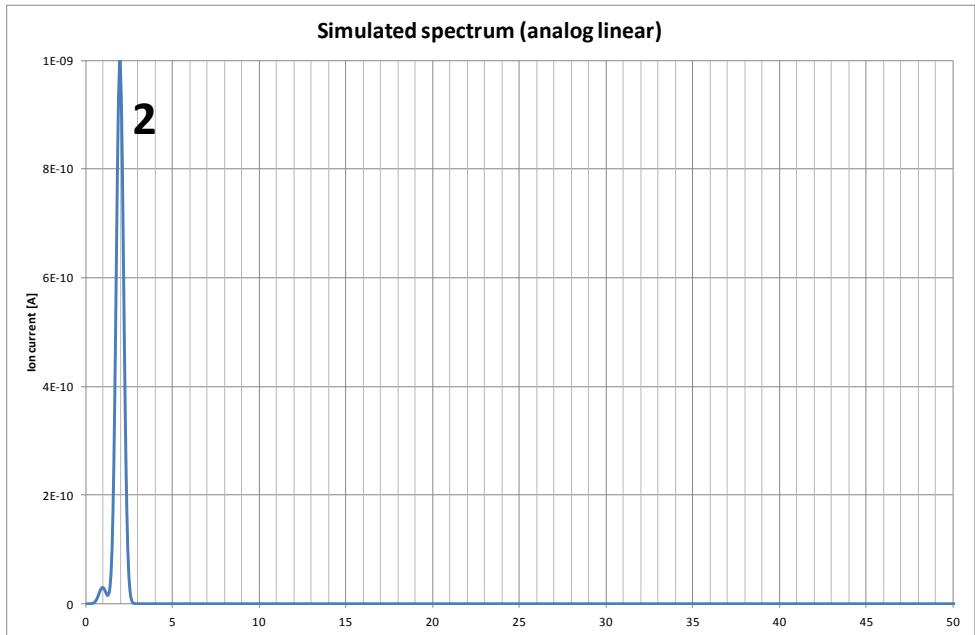
H_2 , He, Ne, CH_4 , H_2O , F, C_2H_6 , CO, $\text{C}_2\text{H}_5\text{-OH}$, O_2 , Ar, C_3H_8 , CO_2 , Kr ...

- However, in the common practise, the gas species of the **residual gas are mixed** and cannot be separated easily and quickly. We do not have a separation equipment in front of the gas analyser as it is the case in analytical chemistry, for example in chromatography.
- The whole set of molecules arrives simultaneously to the quadrupole and the **output signal is the superposition of the single molecule contributions**.
- How can we unbundle the signal and obtain the contribution of each gas in the vacuum system?
- Thanks to the **fragmentation pattern**...

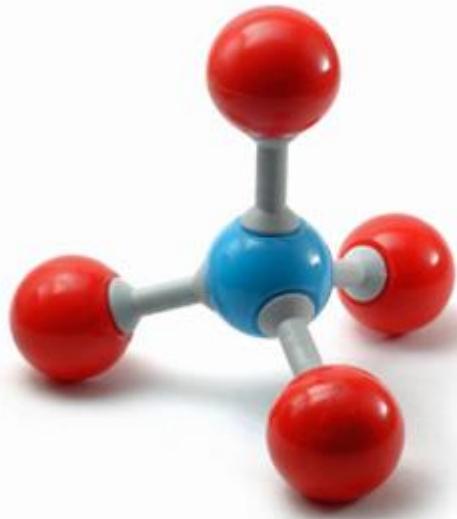
Hydrogen

ions	M	Rel. int.
H ₂	2	100
H	1	2.1

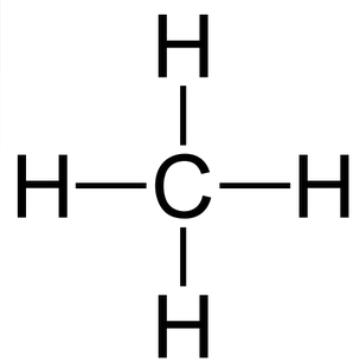




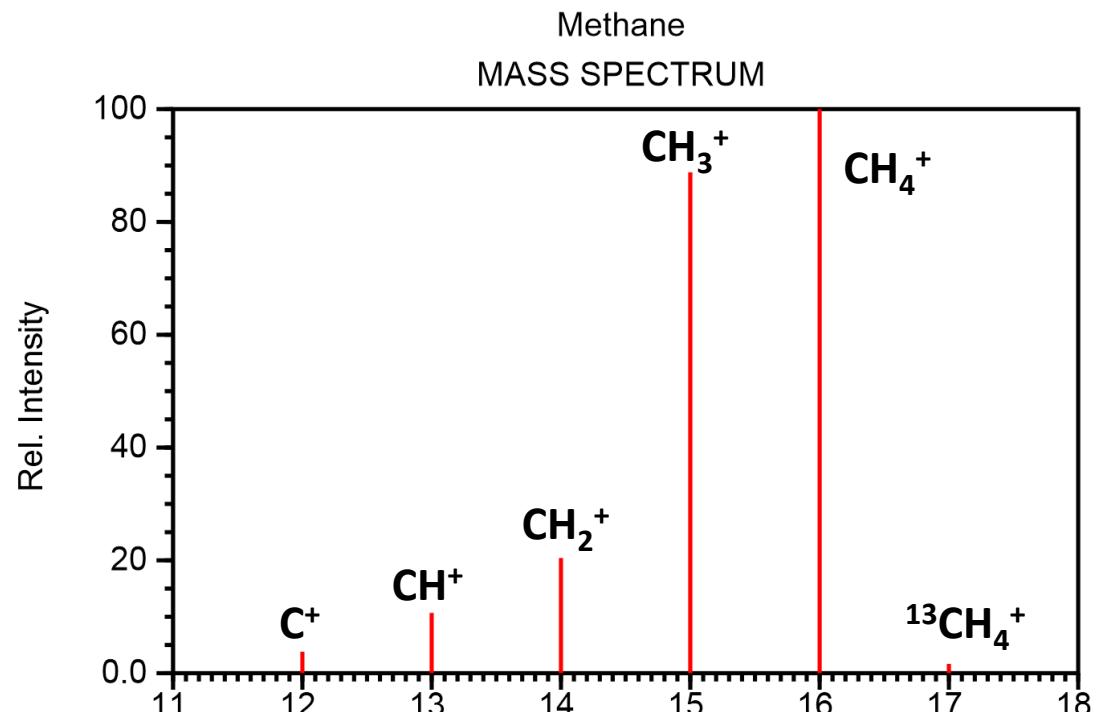
Molecules



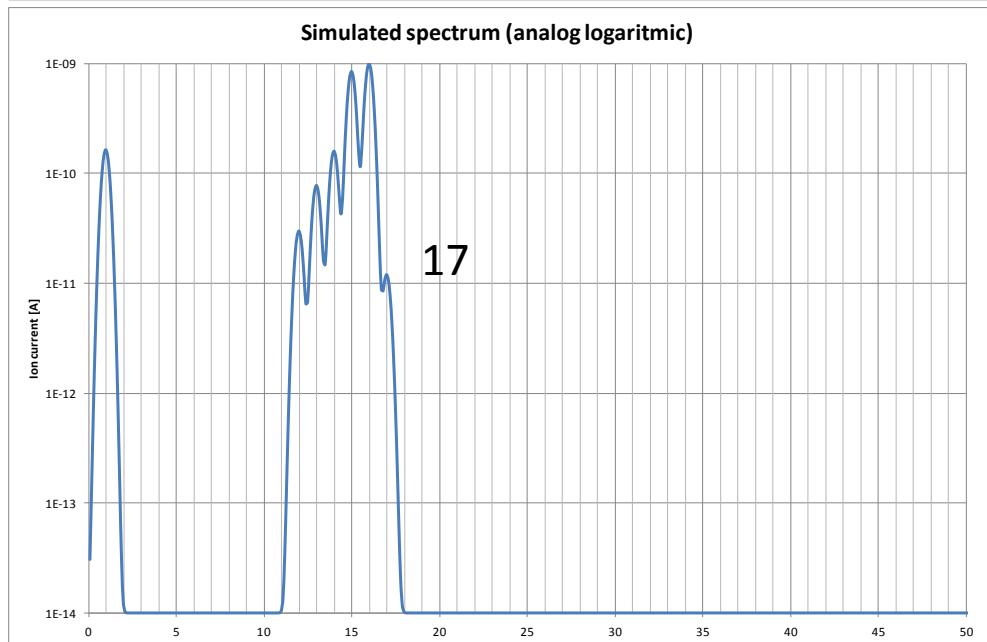
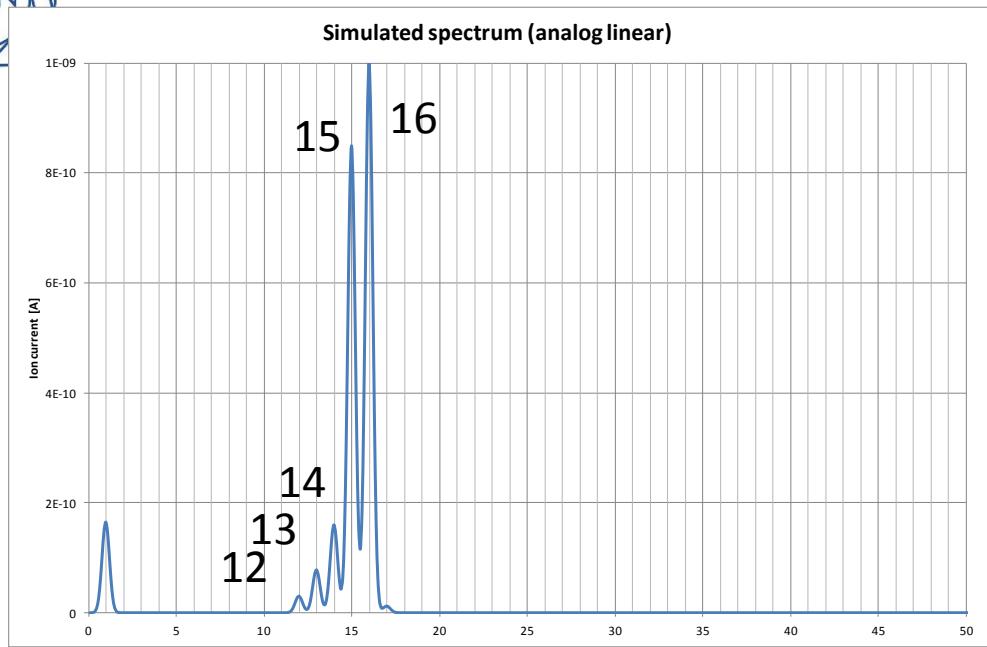
ions	M	Rel. int.
CH_4	16	100
CH_3	15	85
CH_2	14	20.5
CH	13	10.7
C	12	3.8
$^{13}\text{CH}_4$	17	1.1



Methane



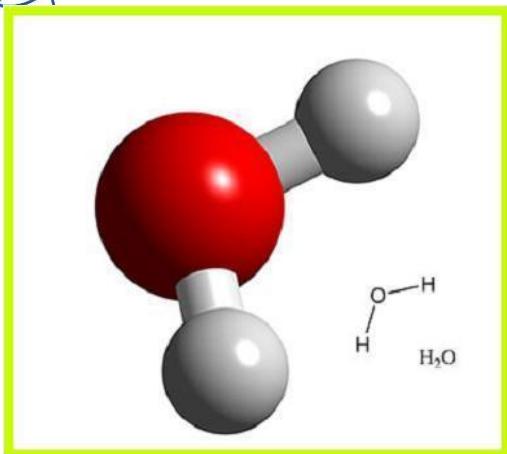
NIST Chemistry WebBook
<http://webbook.nist.gov/chemistry>



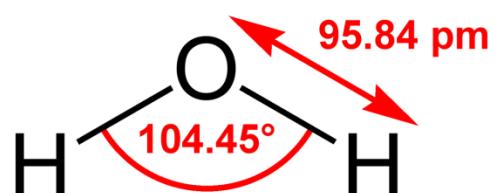
For pure methane:

- $\langle 15 \rangle$ is very close to $\langle 16 \rangle$
- $\langle 14 \rangle$ is lower than $\langle 15 \rangle$
- $\langle 12 \rangle$ is lower than $\langle 13 \rangle$

Molecules

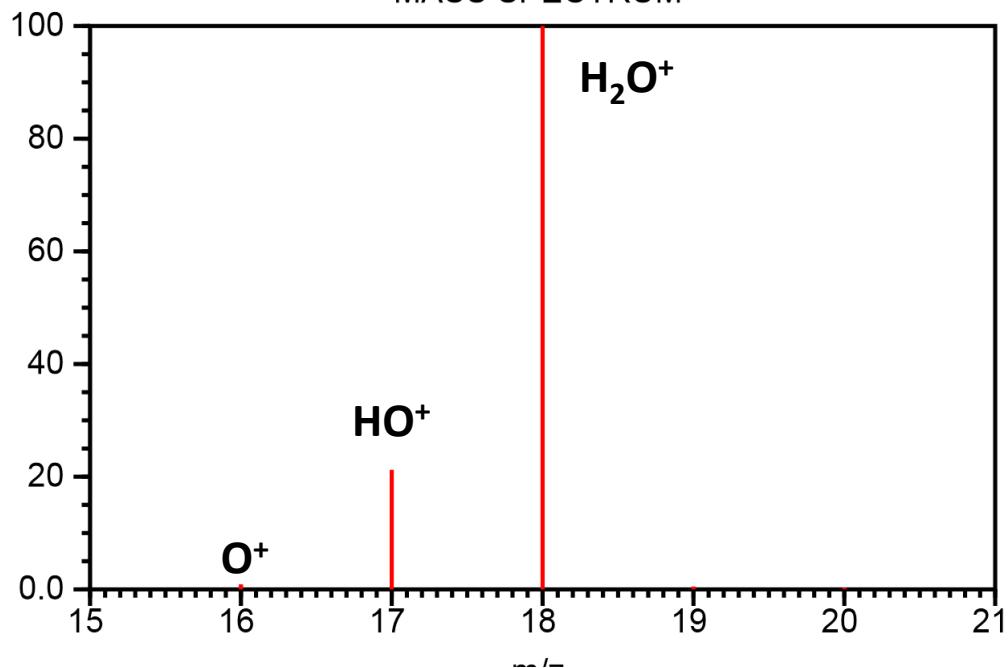


ions	M	Rel. int.
H_2O	18	100
HO^-	17	21
O	16	1
H_2^{17}O	19	0.06
H_2^{18}O	20	0.2

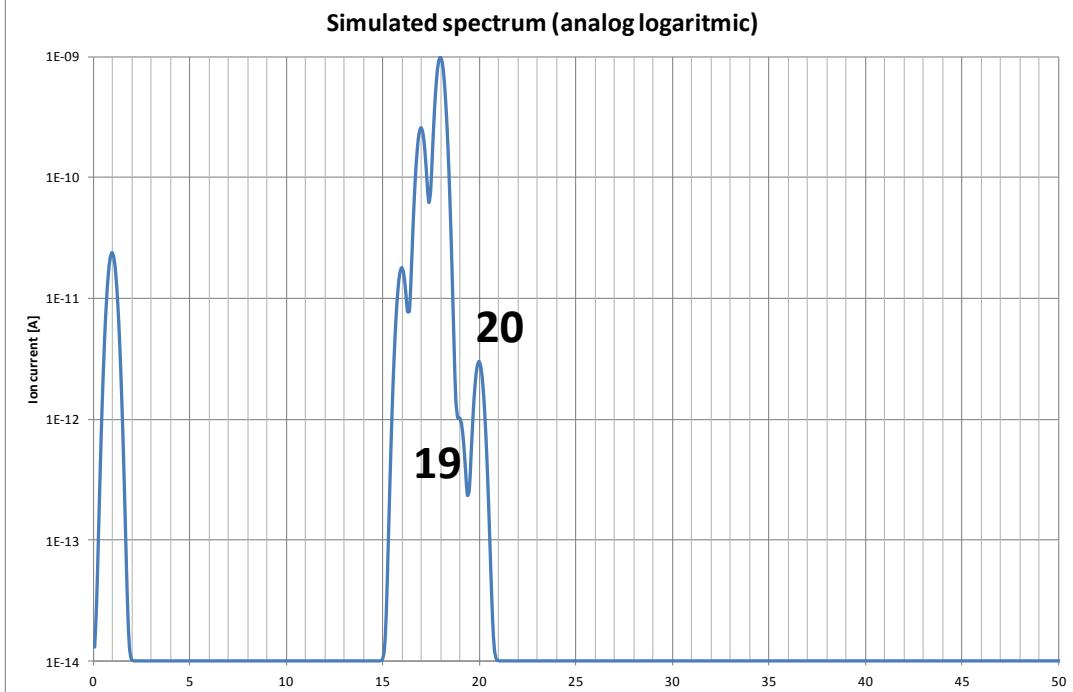
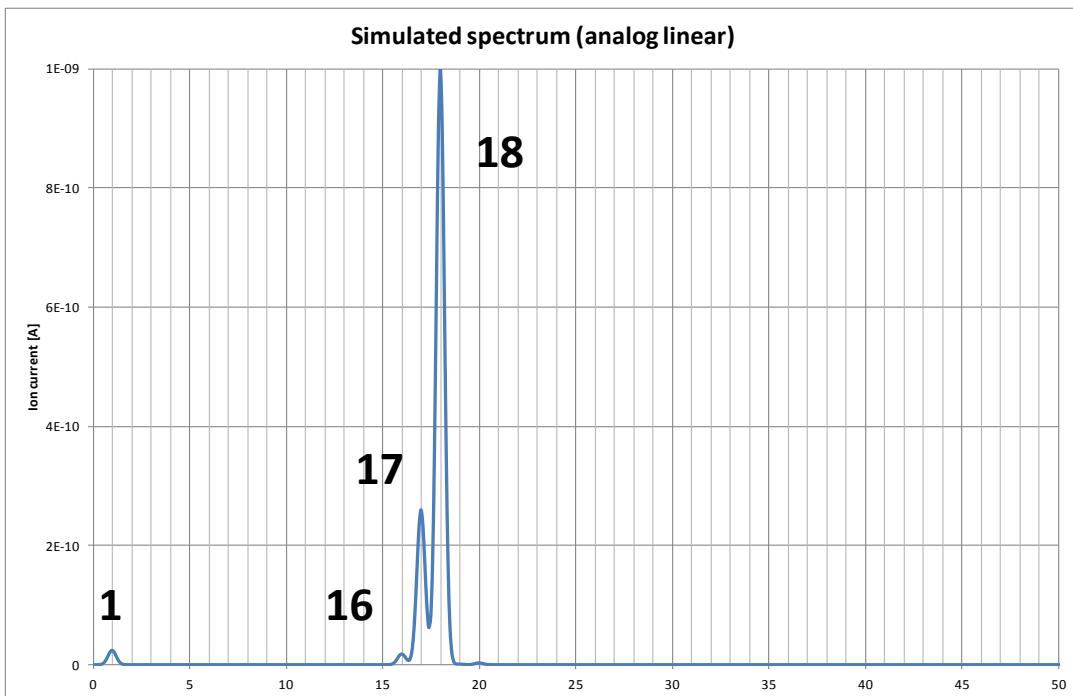


Water

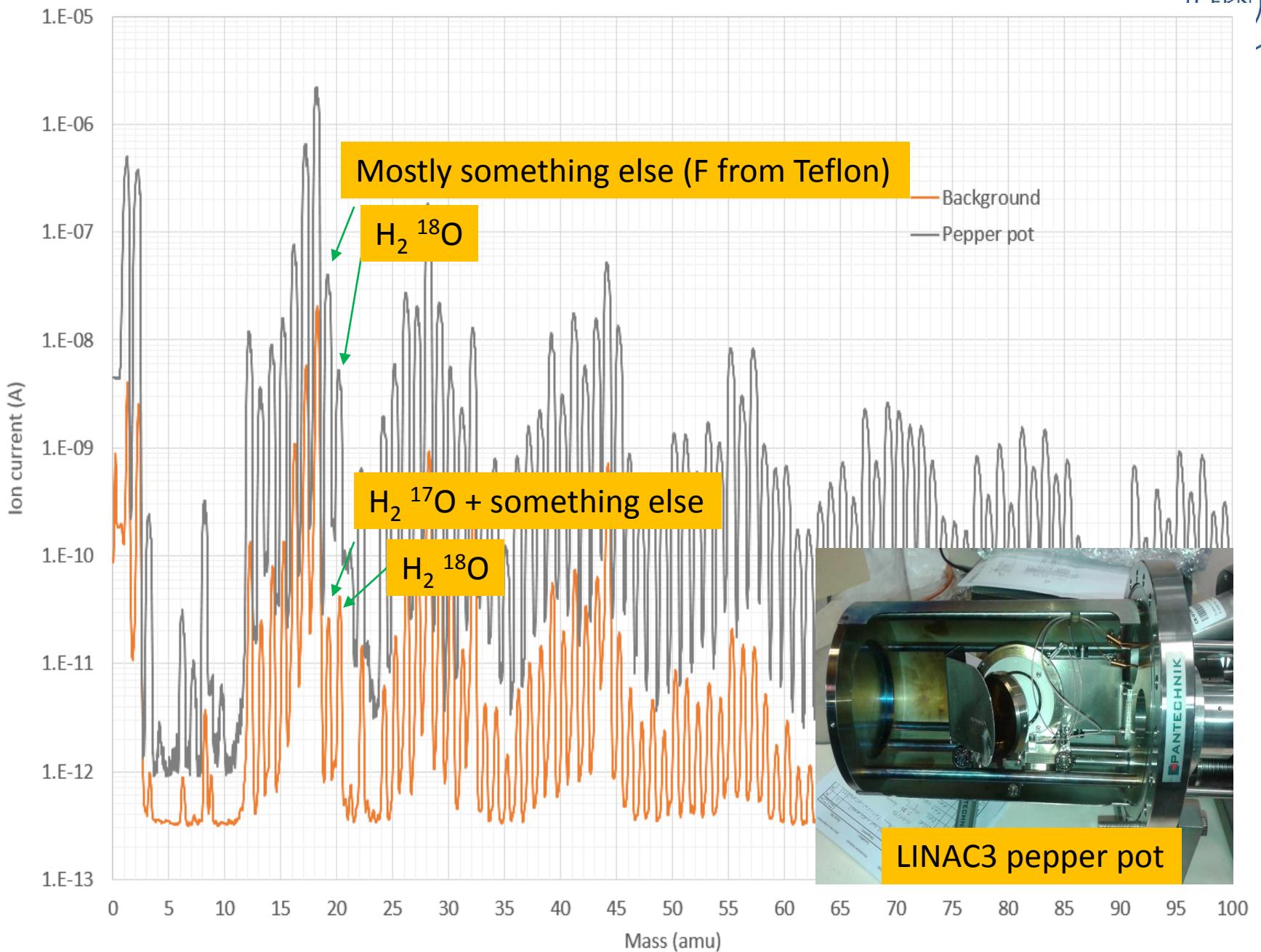
Water
MASS SPECTRUM



NIST Chemistry WebBook
(<http://webbook.nist.gov/chemistry>)

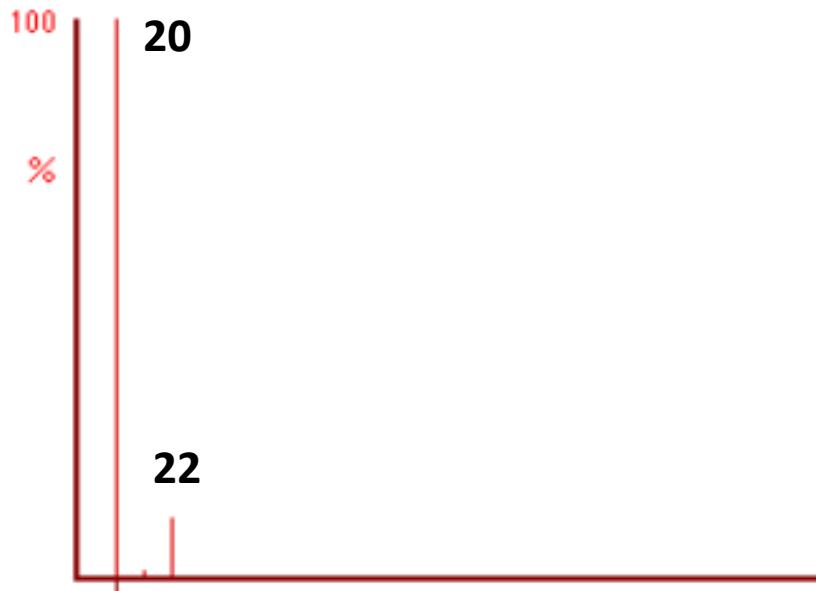


When water peaks are high, <19> and <20> may be detected even w/o F and Ne (or Ar) traces.



Neon

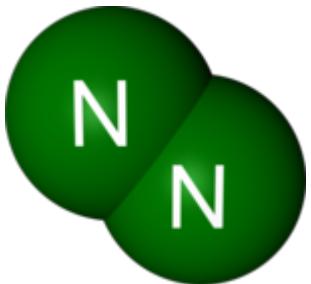
ions	M	Rel. int.
^{20}Ne	20	100
^{22}Ne	22	10.2



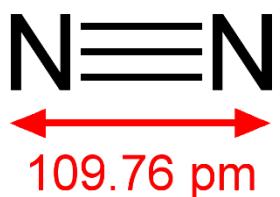
Useful for leak detection in unbaked systems in high helium background

NIST Chemistry WebBook
(<http://webbook.nist.gov/chemistry>)

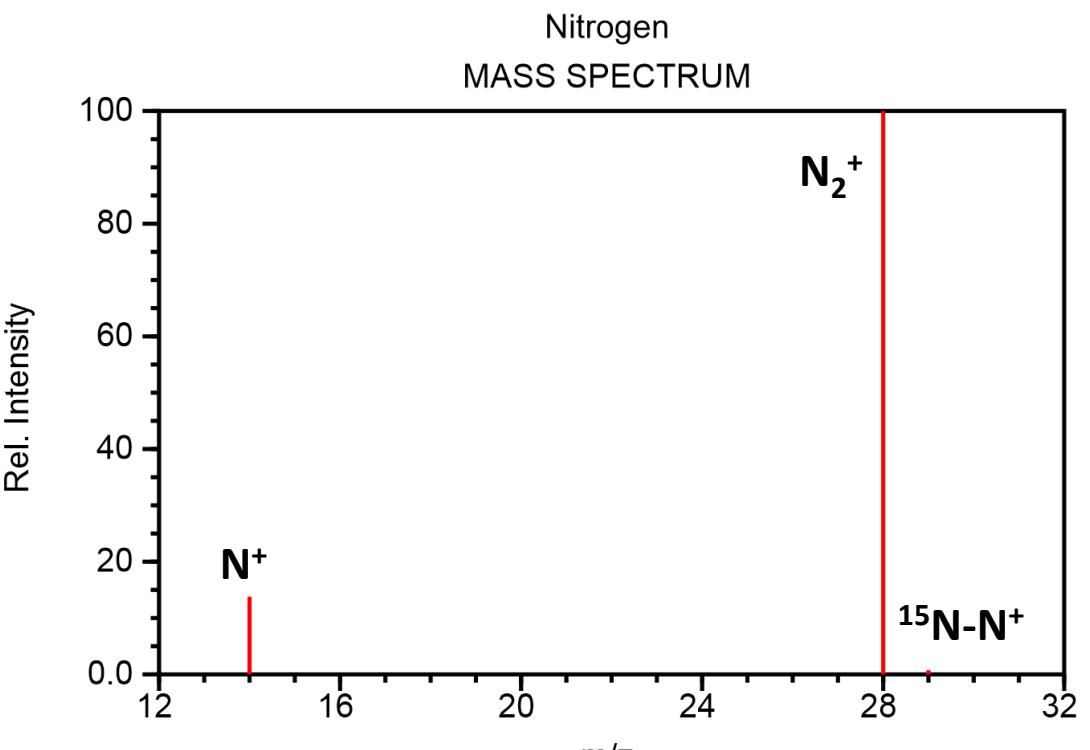
Molecules



ions	M	Rel. int.
N_2	28	100
N	14	14
$^{15}\text{N}-^{14}\text{N}$	29	0.7

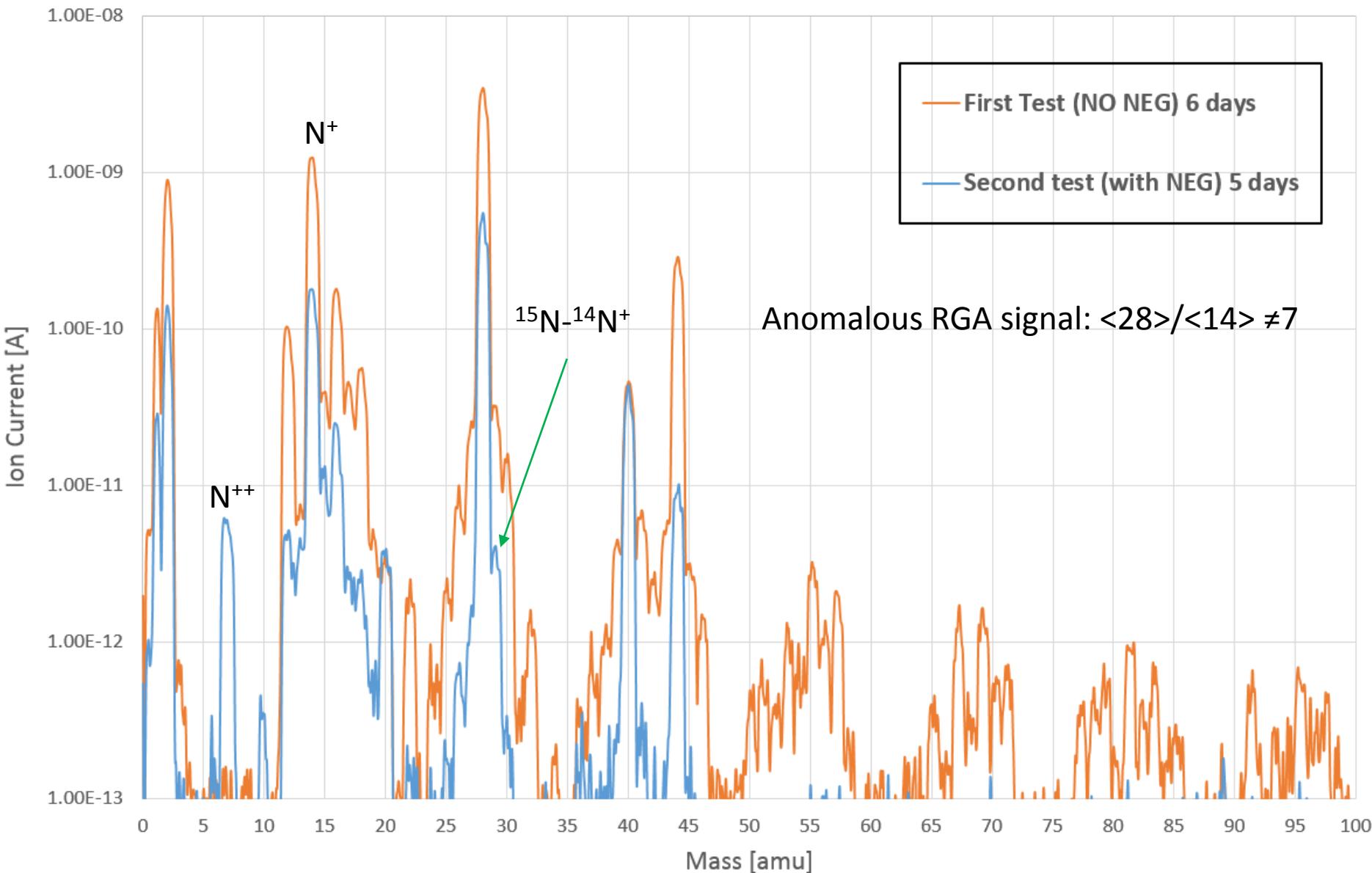


Nitrogen

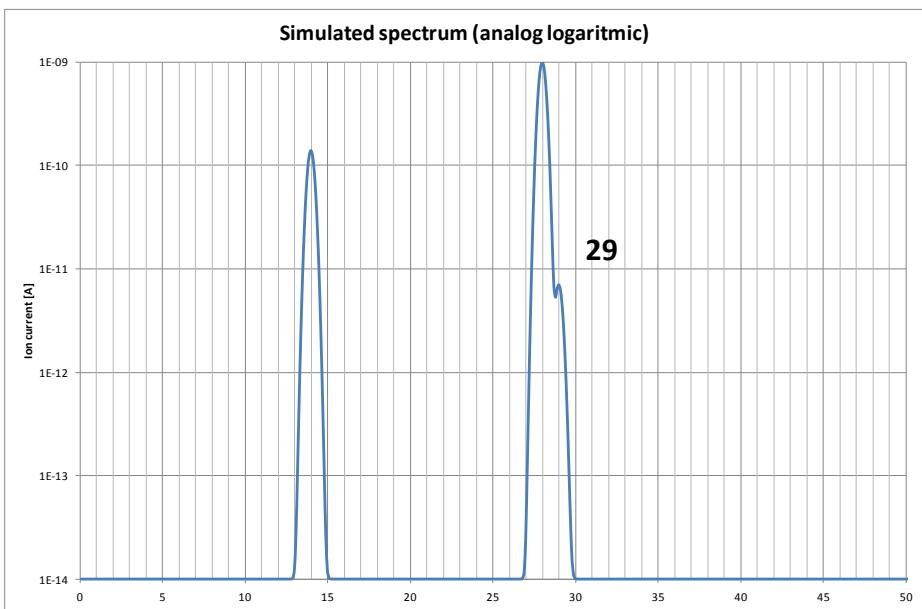
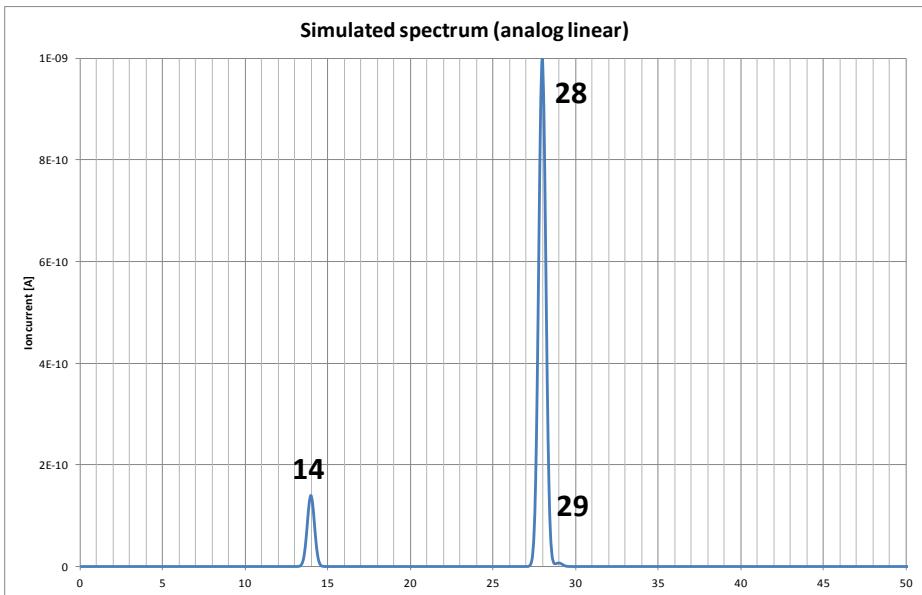


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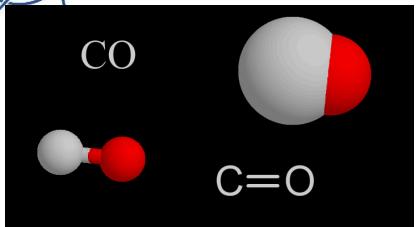
TCSPM prototype collimator



Courtesy of Giuseppe Bregliozi



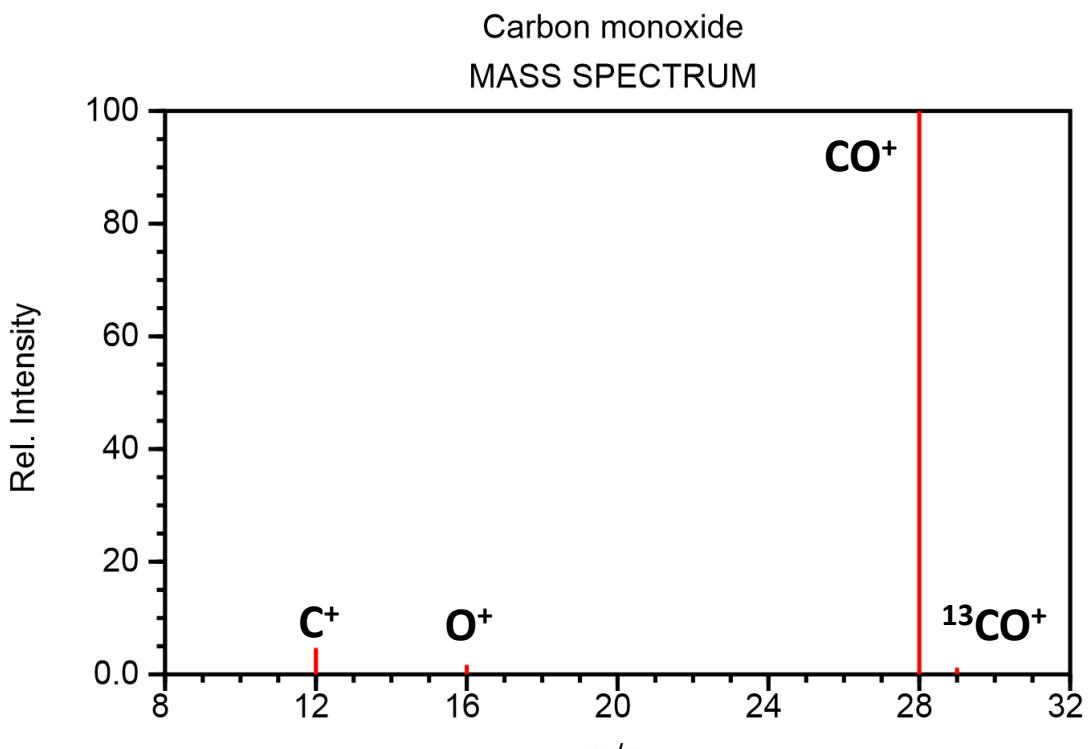
Molecules

**Carbon monoxide**

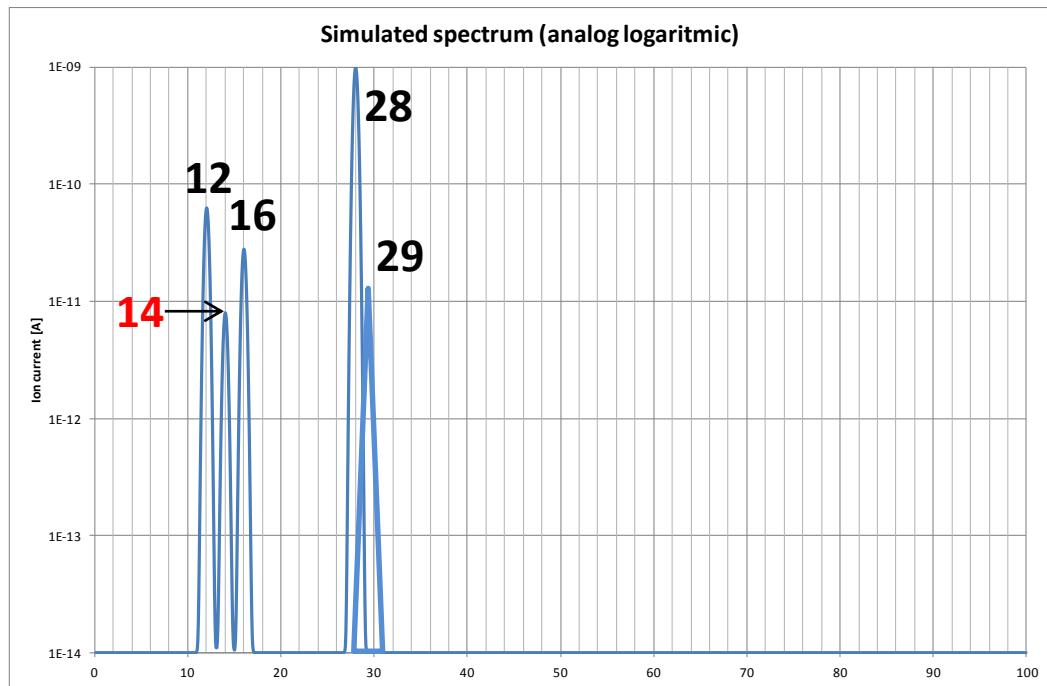
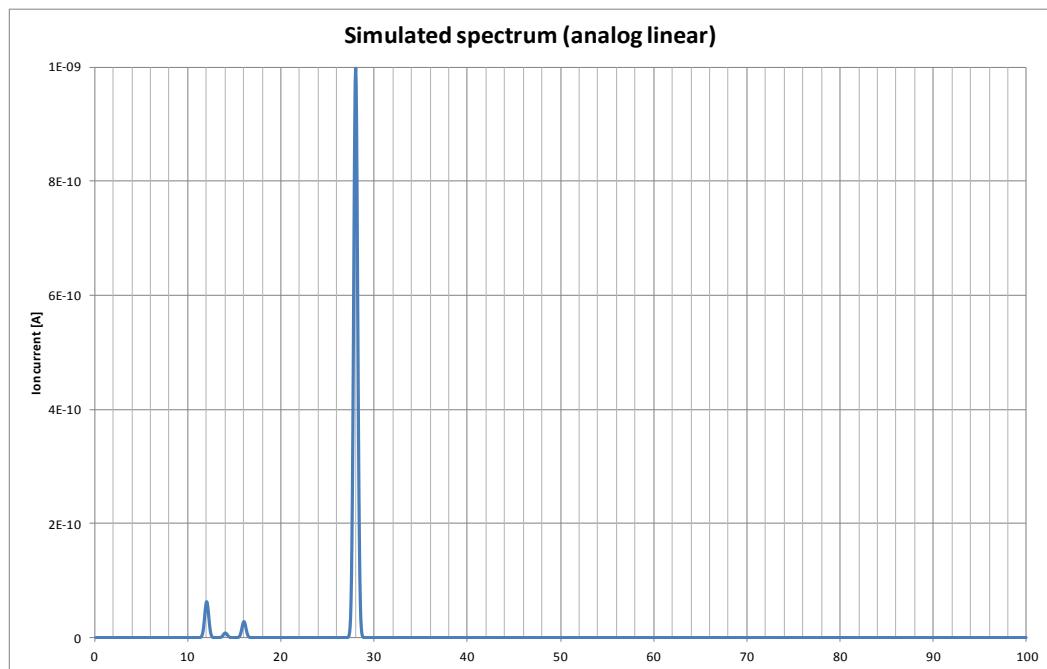
ions	M	Rel. int.
CO	28	100
O	16	1.7
C	12	4.7
¹³ CO	29	1.2



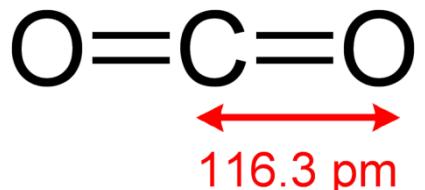
The minimum resolution to separate CO^+ from N_2^+ would be $28/0.011 = 2522 \text{ ☹}$



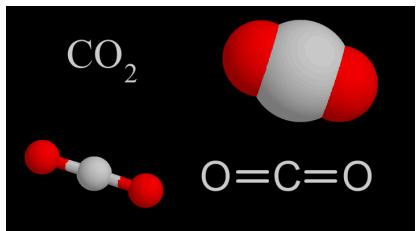
NIST Chemistry WebBook
(<http://webbook.nist.gov/chemistry>)



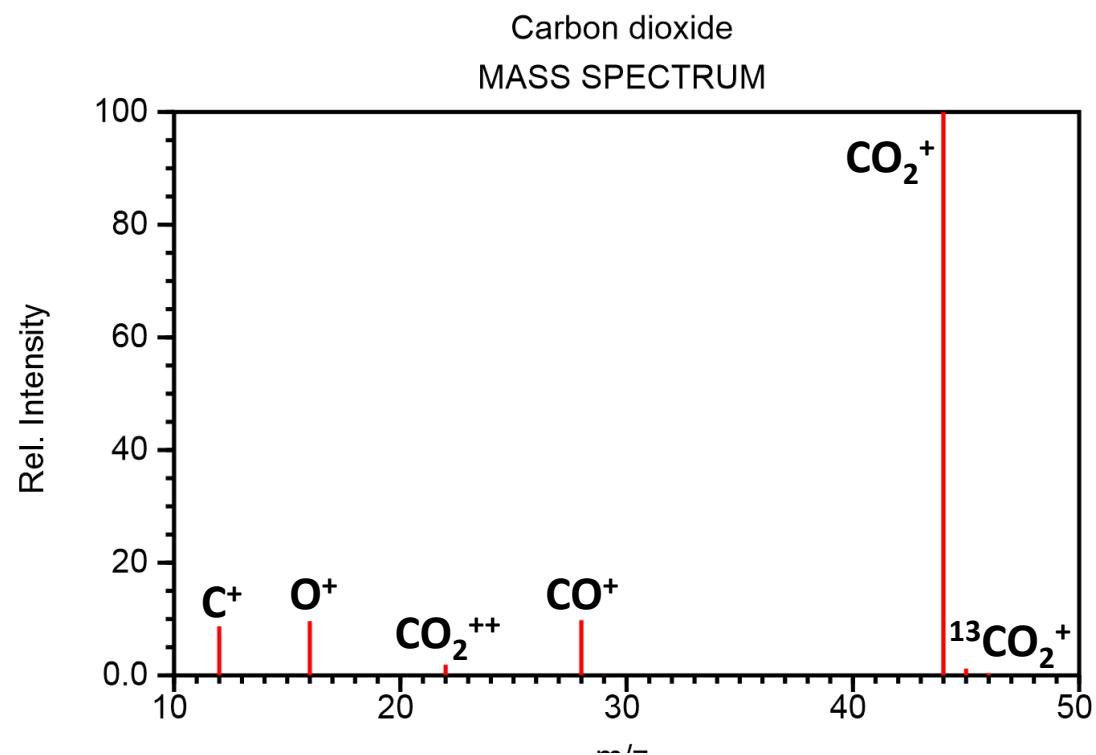
Peak at 14:
CO⁺⁺
 $| \approx \frac{\langle 28 \rangle}{100}$



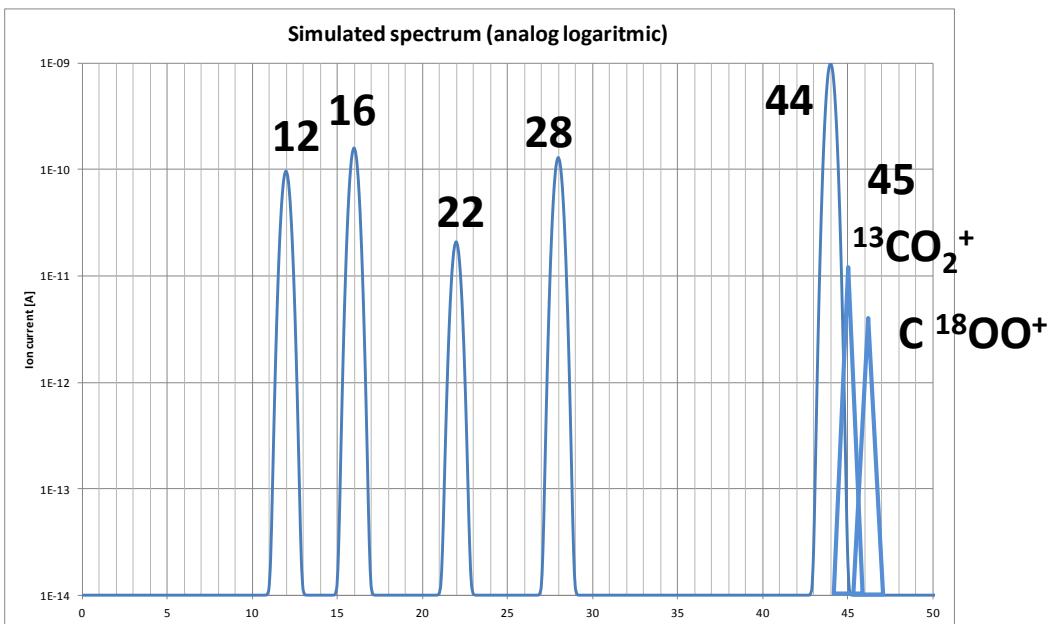
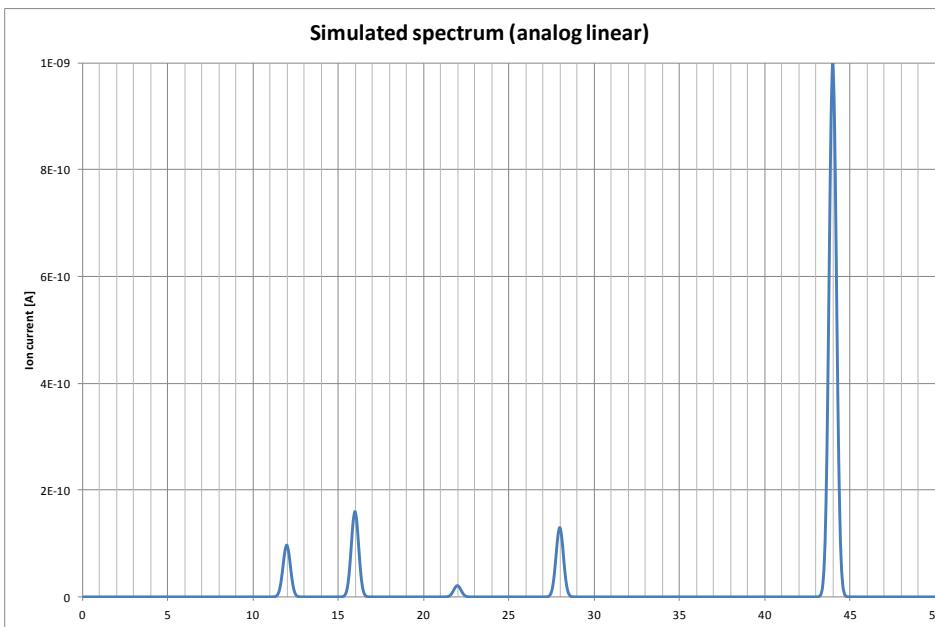
ions	M	Rel. int.
CO_2	44	100
CO	28	10^*
O	16	10
C	12	8.7
$^{13}\text{CO}_2$	45	1.1
$\text{C}^{18}\text{O-O}$	46	0.4
CO_2^{++}	22	1.9



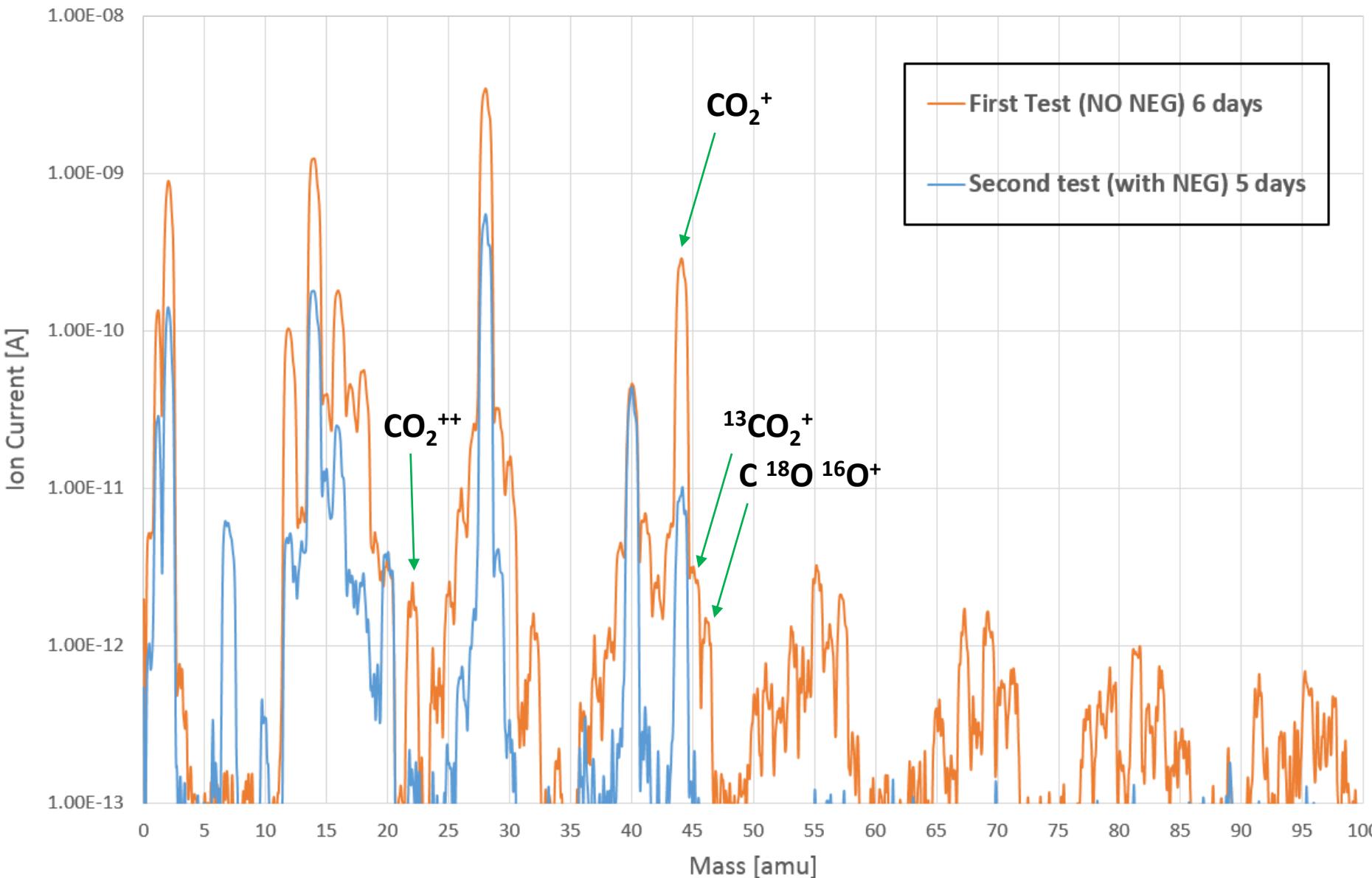
Carbon dioxide



WARNING: (*) strongly system dependent

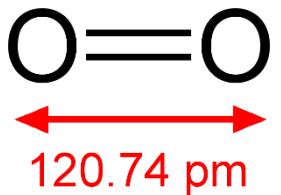


TCSPM prototype collimator

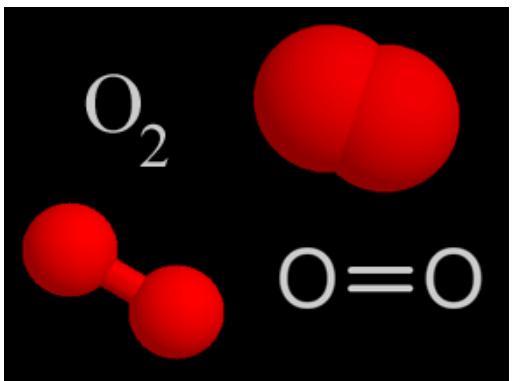


Courtesy of Giuseppe Bregliozi

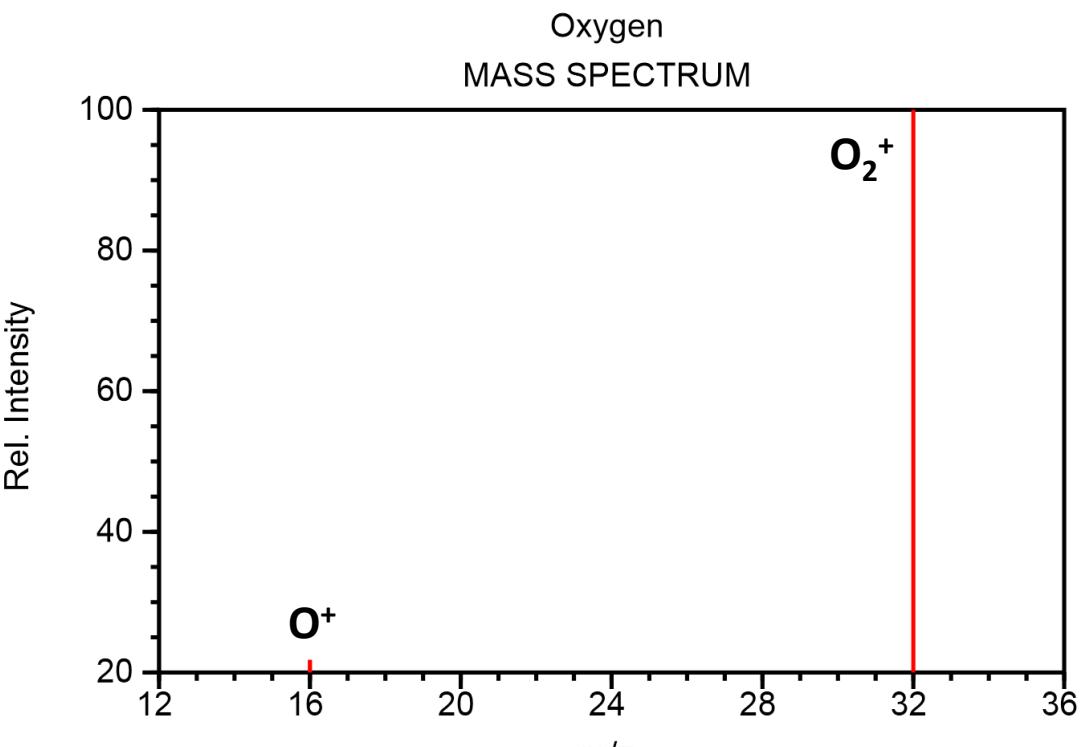
Molecules

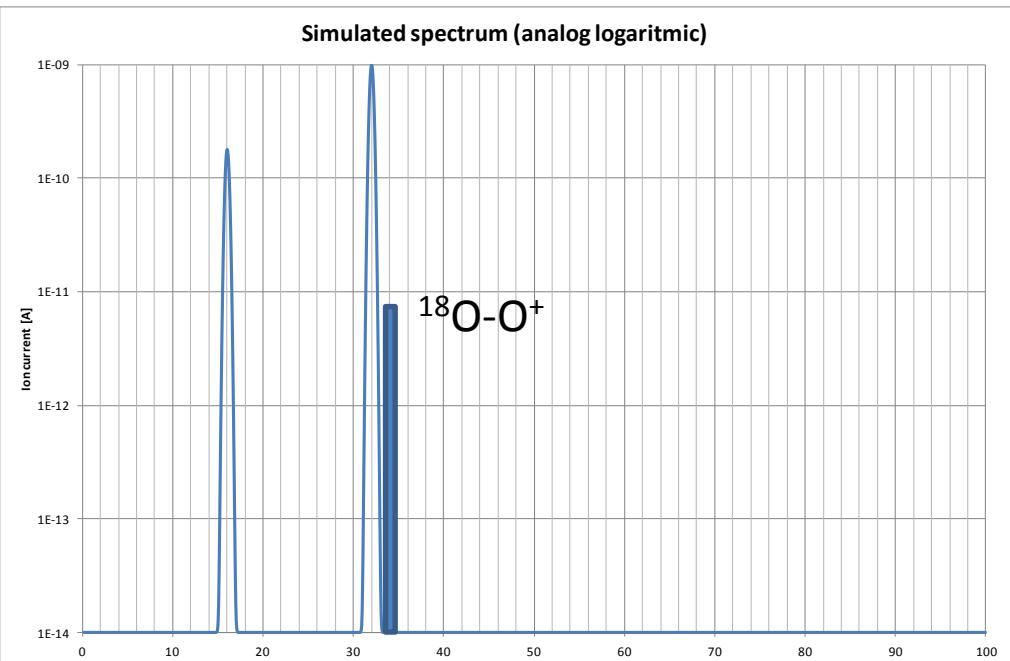
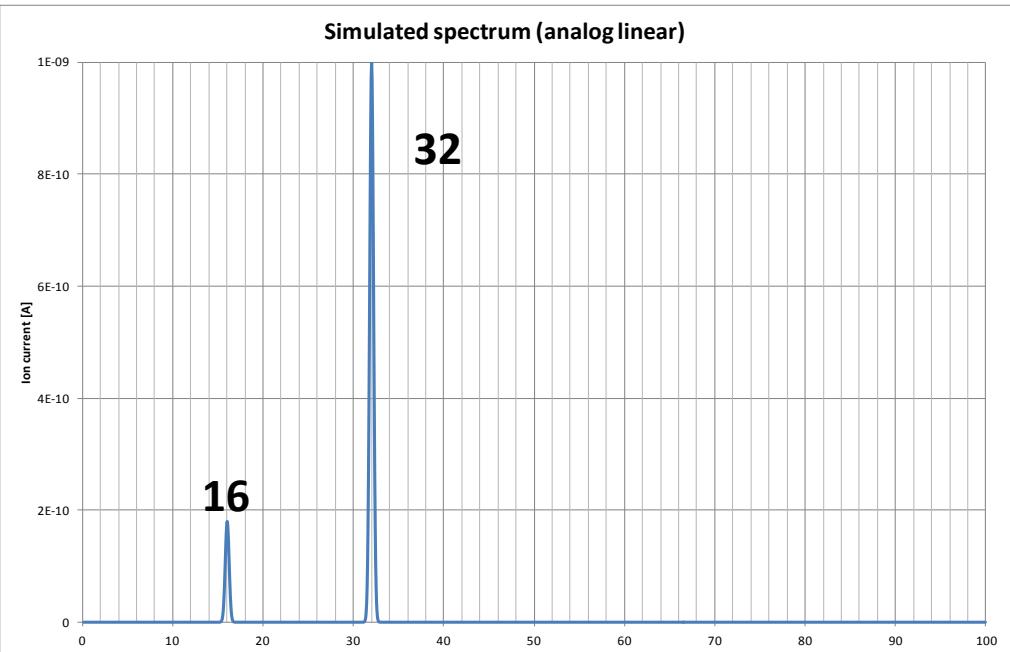


ions	M	Rel. int.
O_2	32	100
O	16	22
$^{18}\text{O}-\text{O}$	34	0.7

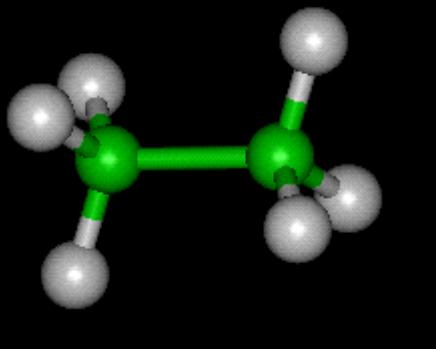


Oxygen



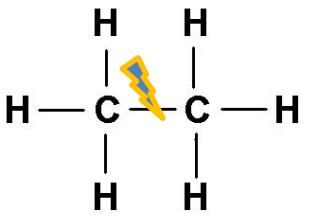
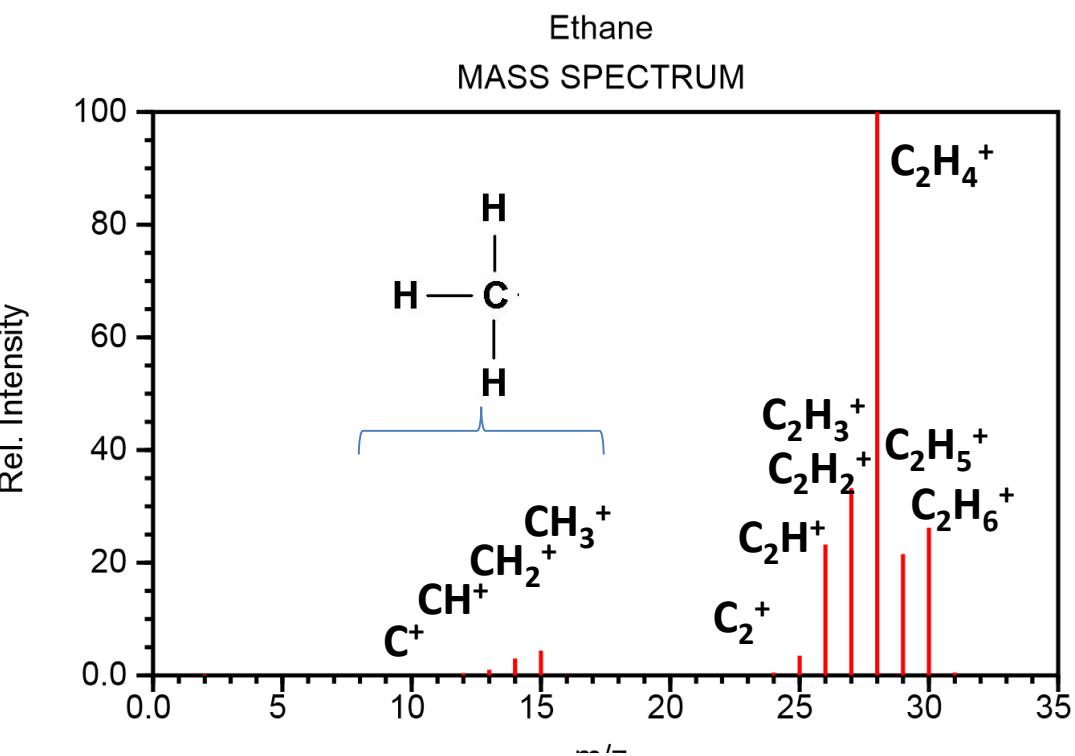


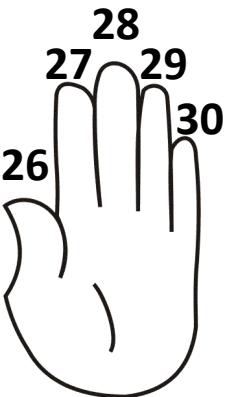
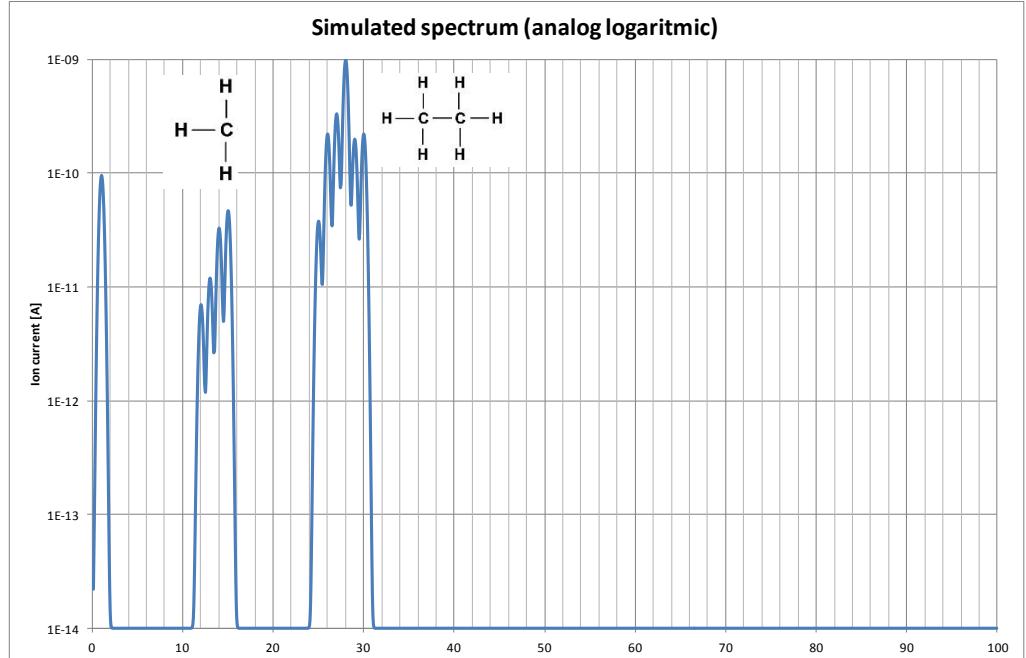
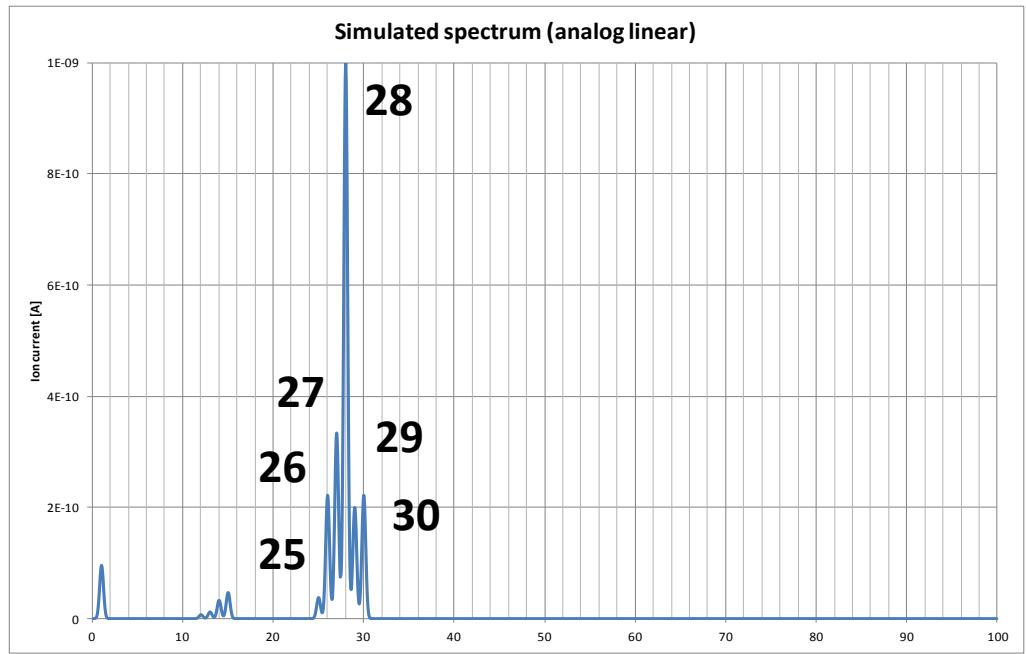
Molecules



ions	M	Rel. int.
C_2H_6	30	26
C_2H_5	29	22
C_2H_4	28	100
C_2H_3	27	33
C_2H_2	26	23
C_2H	25	3.5
C_2	24	0.5
CH_3	15	4.4
CH_2	14	3
CH	13	1
C	12	0.4
$^{13}\text{C}-\text{CH}_6$	31	0.5

Ethane

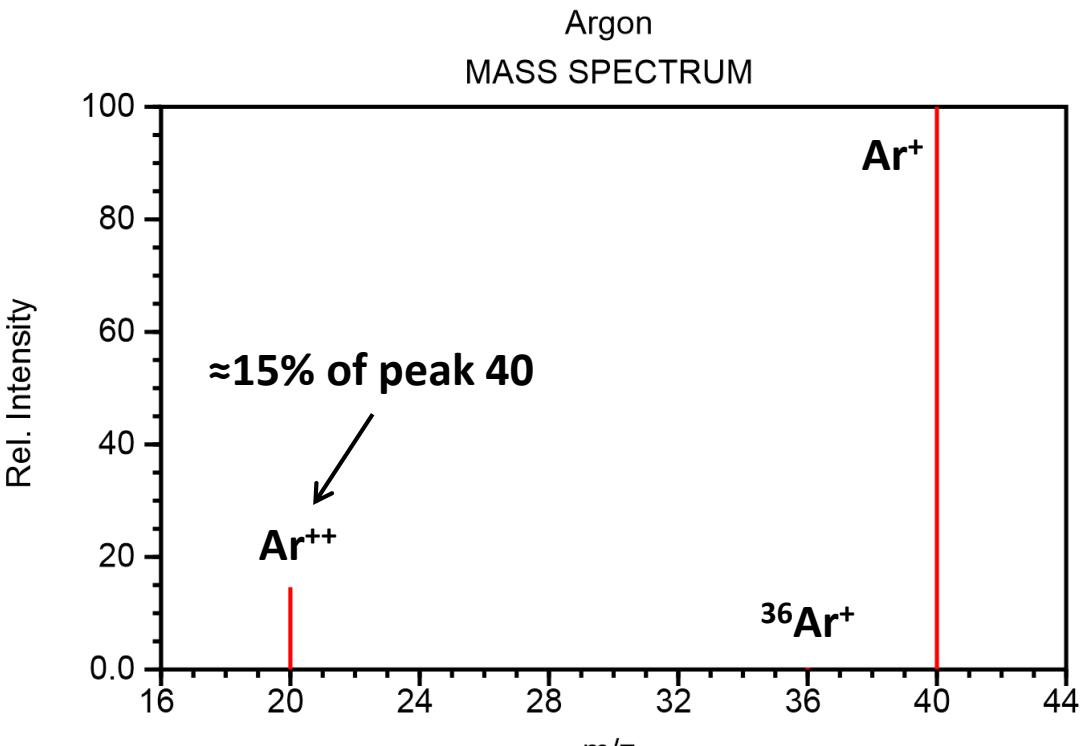


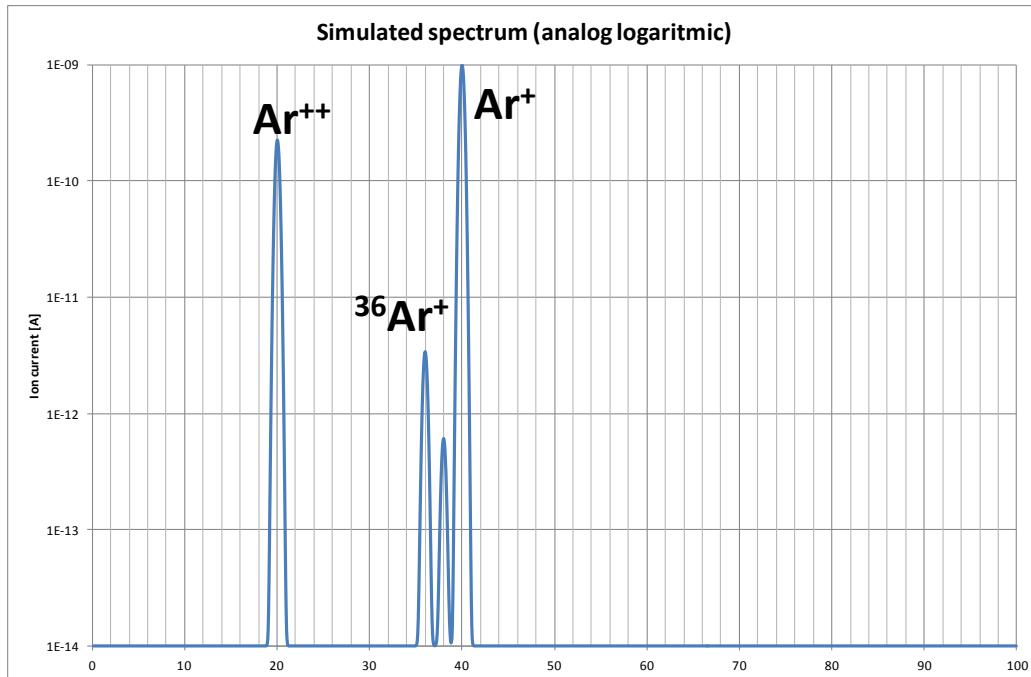
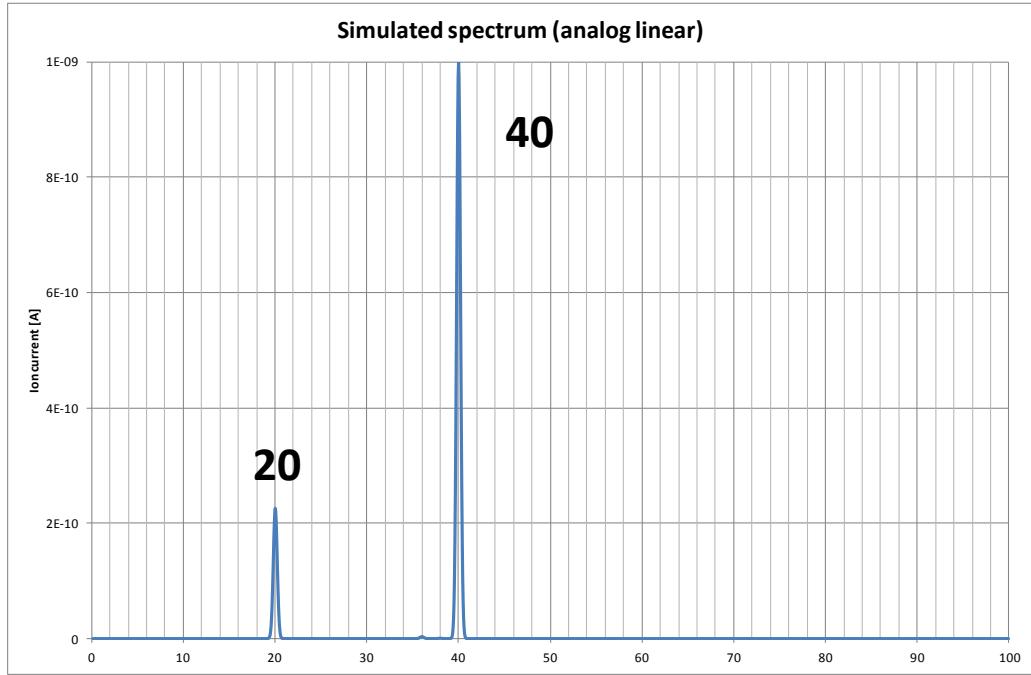


'Molecules'

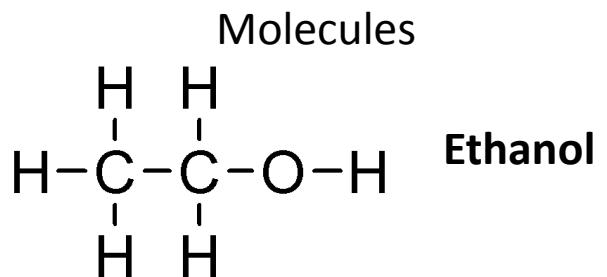
Argon

ions	M	Rel. int.
Ar	40	100
^{36}Ar	36	0.3
^{38}Ar	38	0.05
Ar^{++}	20	14.6

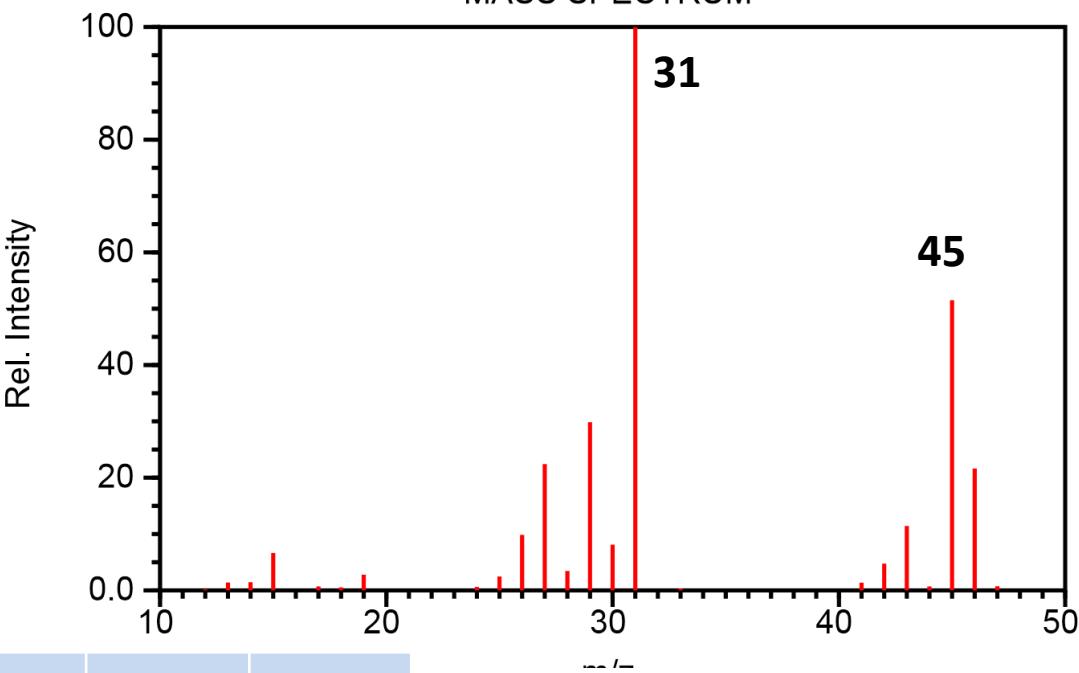
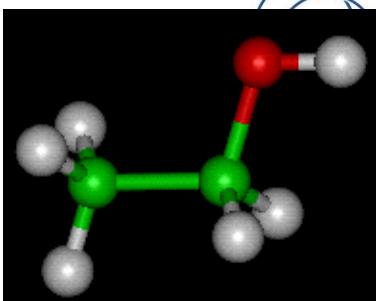




ions	M	Rel. int.
C ₂ H ₅ OH	46	21.5
C ₂ H ₄ OH	45	51.5
C ₂ H ₃ OH	44	0.7
C ₂ H ₂ OH	43	11.4
C ₂ HOH	42	4.7
C ₂ OH	41	1.3
CH ₂ OH	31	100
CHOH	30	8
COH, C ₂ H ₅	29	29.7
CO, C ₂ H ₄	28	3.4
C ₂ H ₃	27	22.4
C ₂ H ₂	26	9.8
C ₂ H	25	2.4
C ₂	24	0.6
H ₃ O	19	2.8
H ₂ O	18	0.55

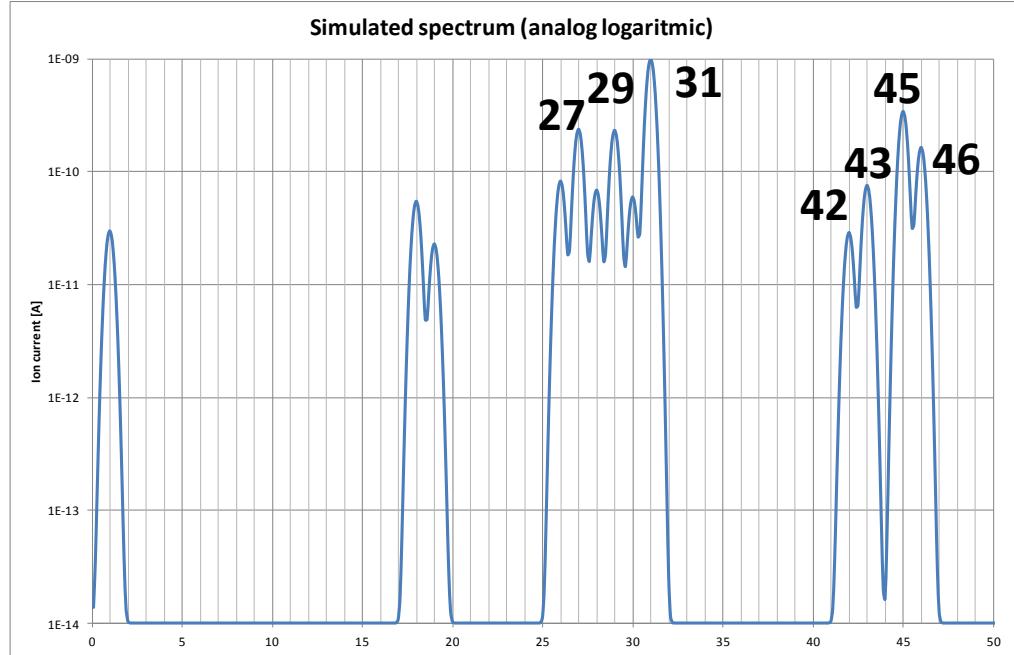
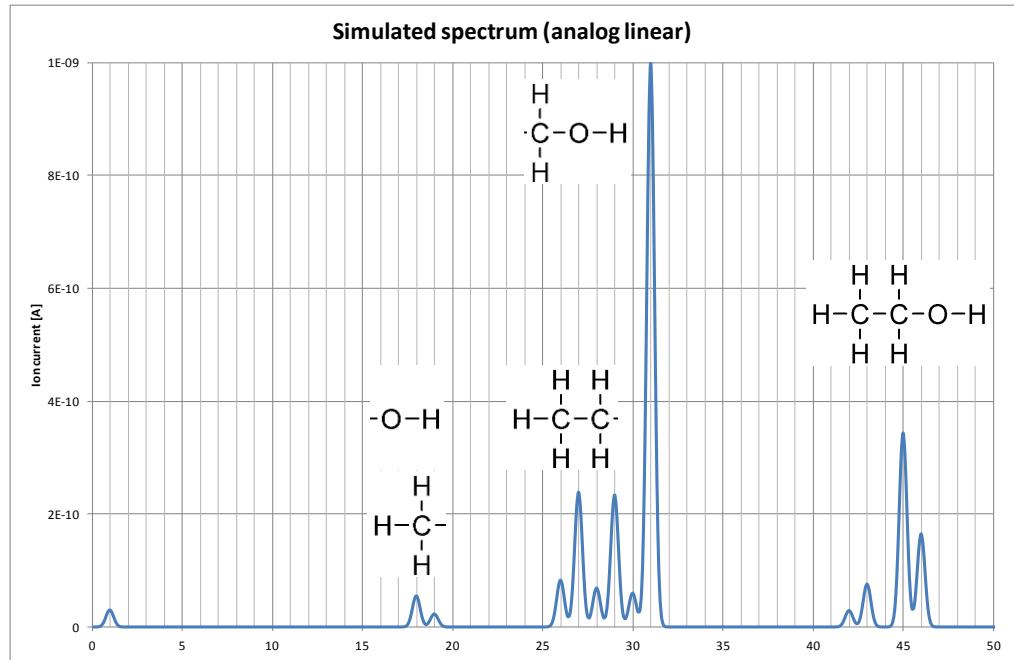


Ethanol
MASS SPECTRUM

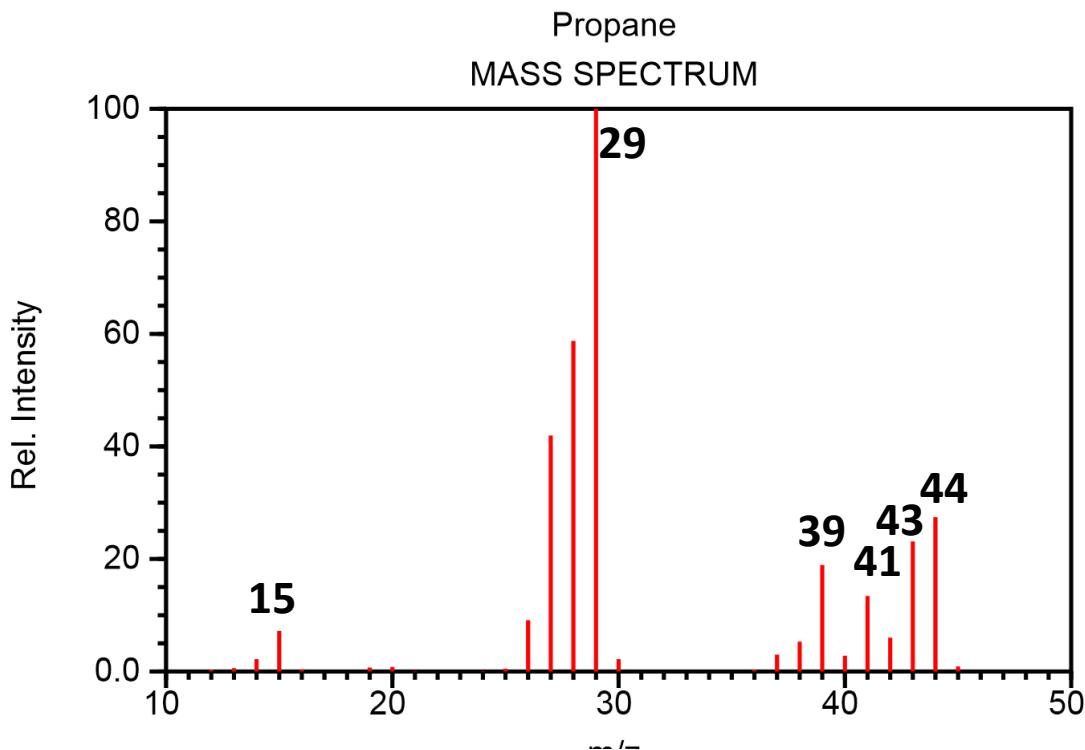
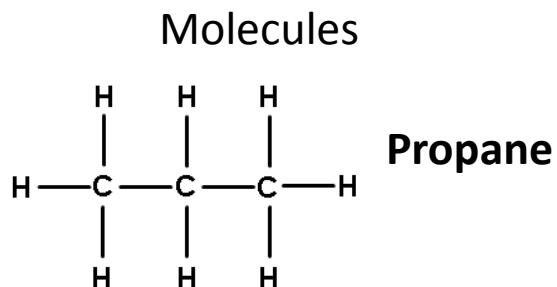


OH	17	0.7
CH ₃	15	6.6
CH ₂	14	1.5
CH	13	1.4
C	12	0.2

46 M⁺ Parent ion
 45 M - H
 31 M - CH₃, CH₂OH⁺
 29 M - OH, CH₃CH₂⁺
 28 M - HHO

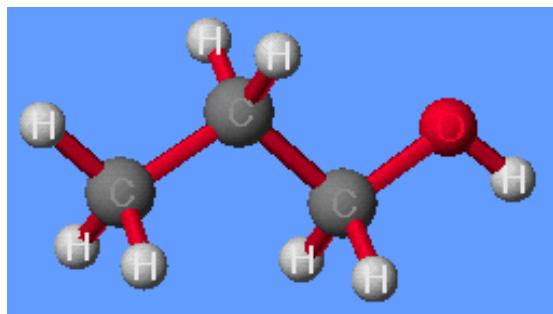


ions	M	Rel. int.
$^{13}\text{C}-\text{C}_2\text{H}_8$	45	0.9
C_3H_8	44	27.5
C_3H_7	43	23
C_3H_6	42	6
C_3H_5	41	13.4
C_3H_4	40	2.8
C_3H_3	39	18.9
C_2H_5	29	100
C_2H_4	28	58.9
C_2H_3	27	42
C_2H_2	26	9
CH_3	15	7.2

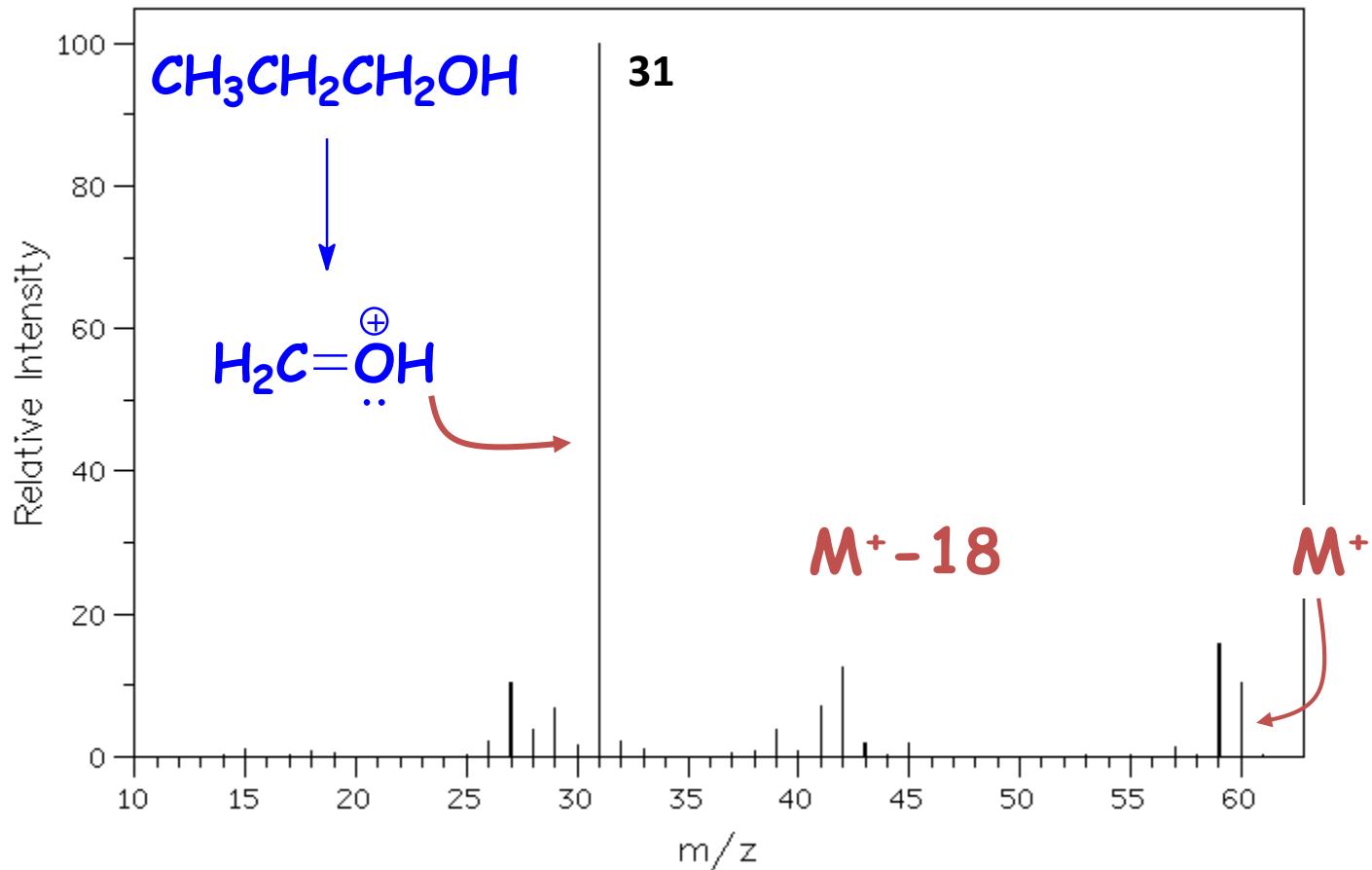


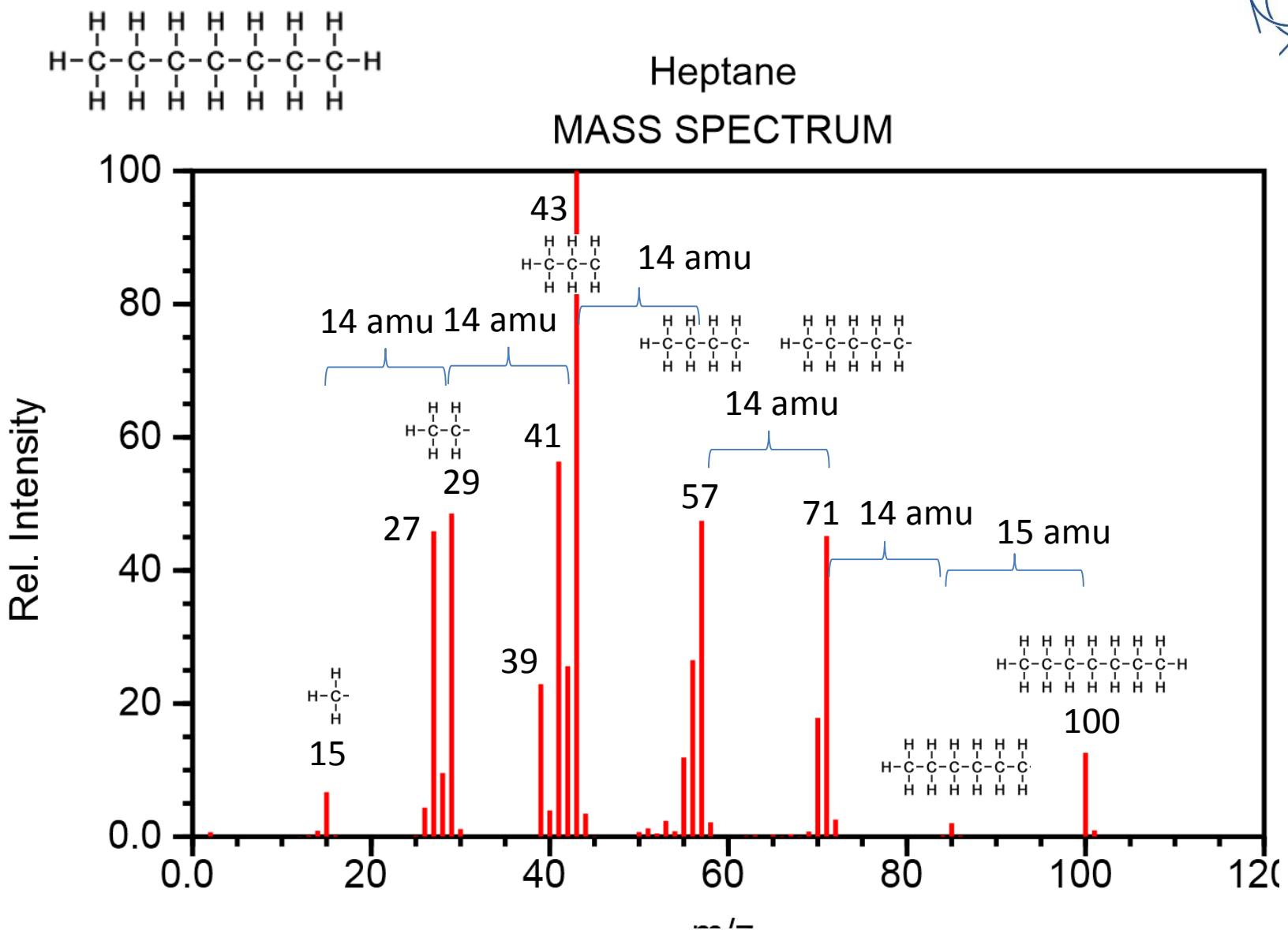
$$\frac{\langle 41 \rangle}{\langle 40 \rangle} = 4.8 \quad \frac{\langle 39 \rangle}{\langle 40 \rangle} = 6.7 \quad \frac{\langle 39 \rangle}{\langle 41 \rangle} = 1.6$$

The ratios $\frac{\langle 41 \rangle}{\langle 40 \rangle}$ and $\frac{\langle 39 \rangle}{\langle 40 \rangle}$ are important to identify Ar and, as a consequence, air.

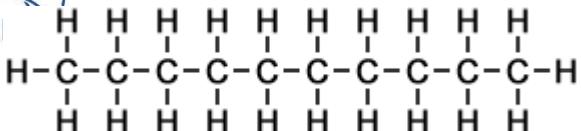


Propanol



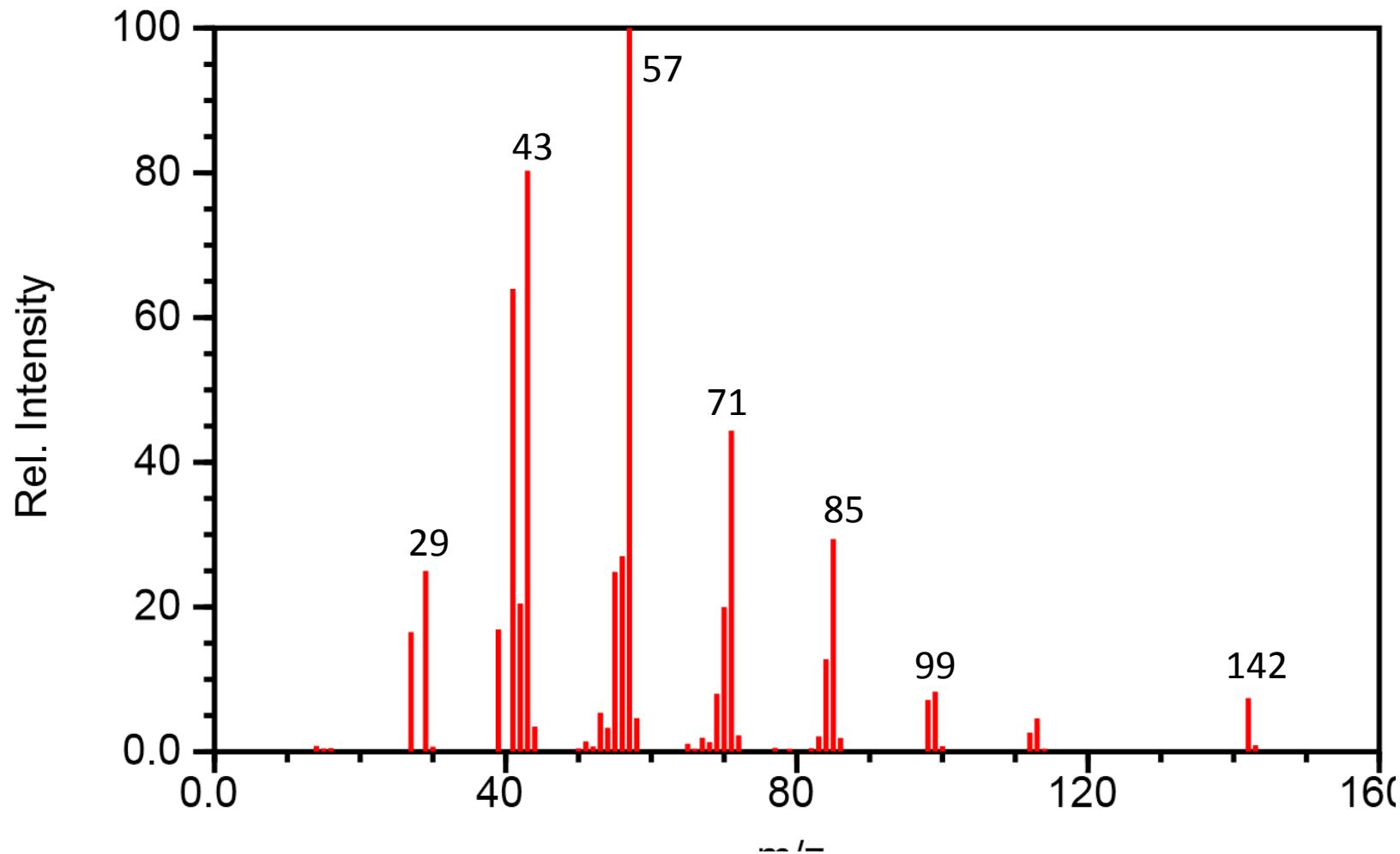


$$\frac{\langle 41 \rangle}{\langle 40 \rangle} = 14.1 \quad \frac{\langle 39 \rangle}{\langle 40 \rangle} = 5.75 \quad \frac{\langle 39 \rangle}{\langle 41 \rangle} = 0.41$$



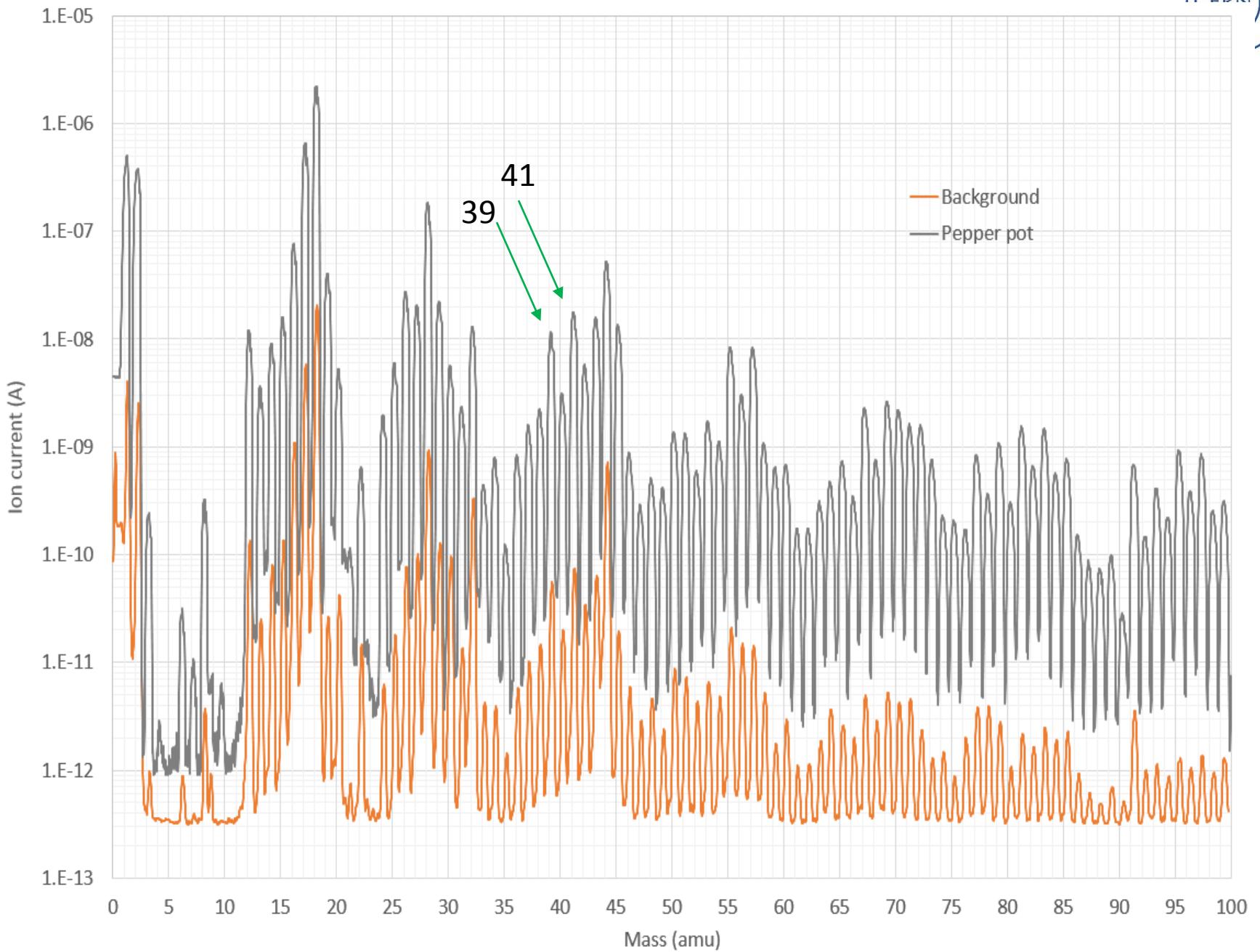
Decane

MASS SPECTRUM

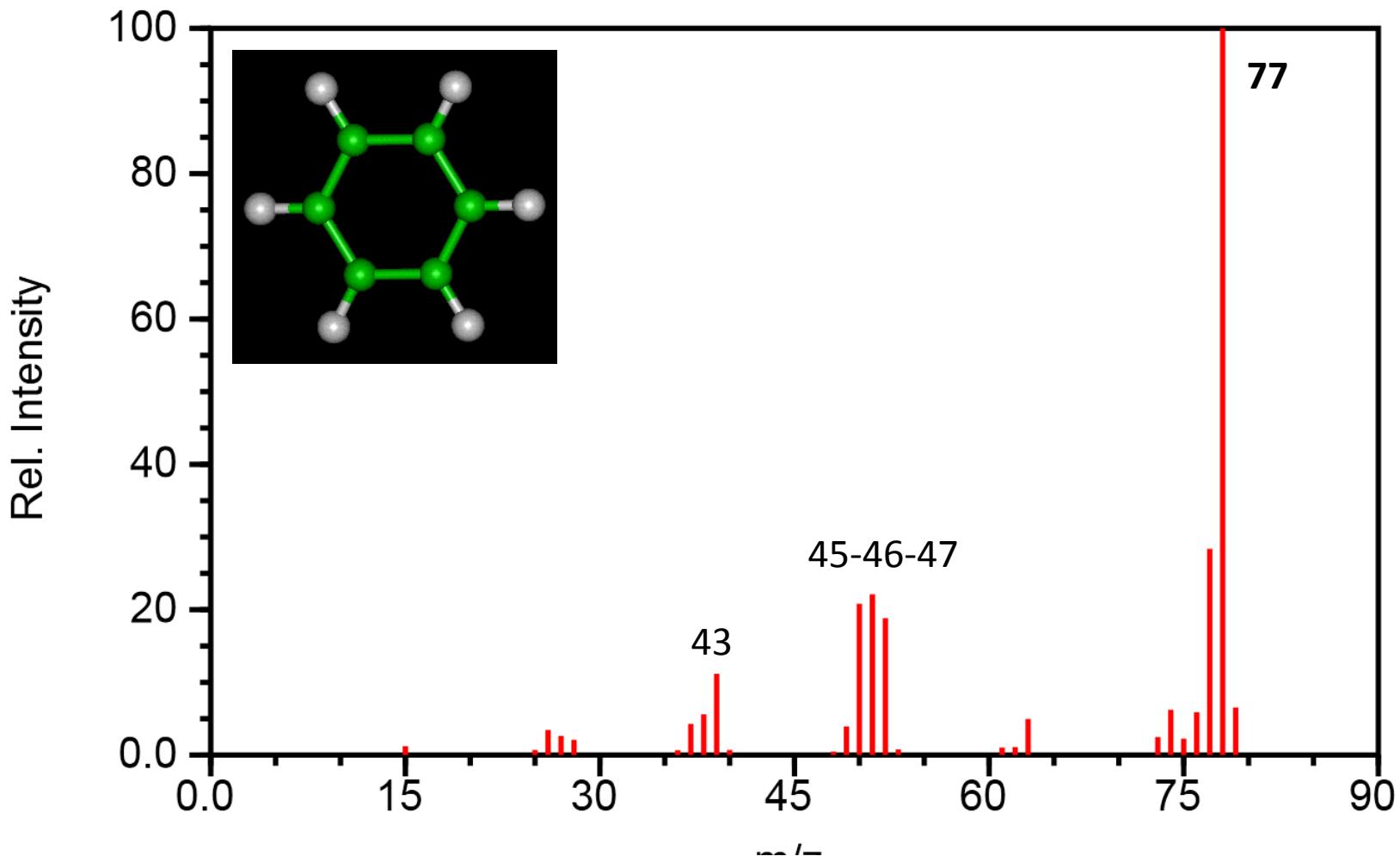


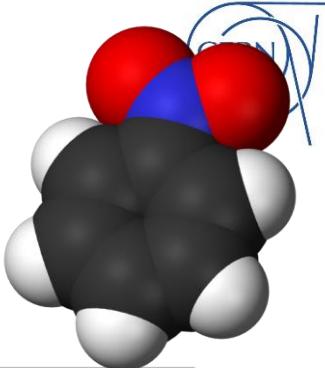
$$\frac{\langle 41 \rangle}{\langle 40 \rangle} = ? \quad \frac{\langle 39 \rangle}{\langle 40 \rangle} = ? \quad \frac{\langle 39 \rangle}{\langle 41 \rangle} = 0.26$$

Heavier the alkane molecule, lower the ratio $\frac{\langle 39 \rangle}{\langle 41 \rangle}$

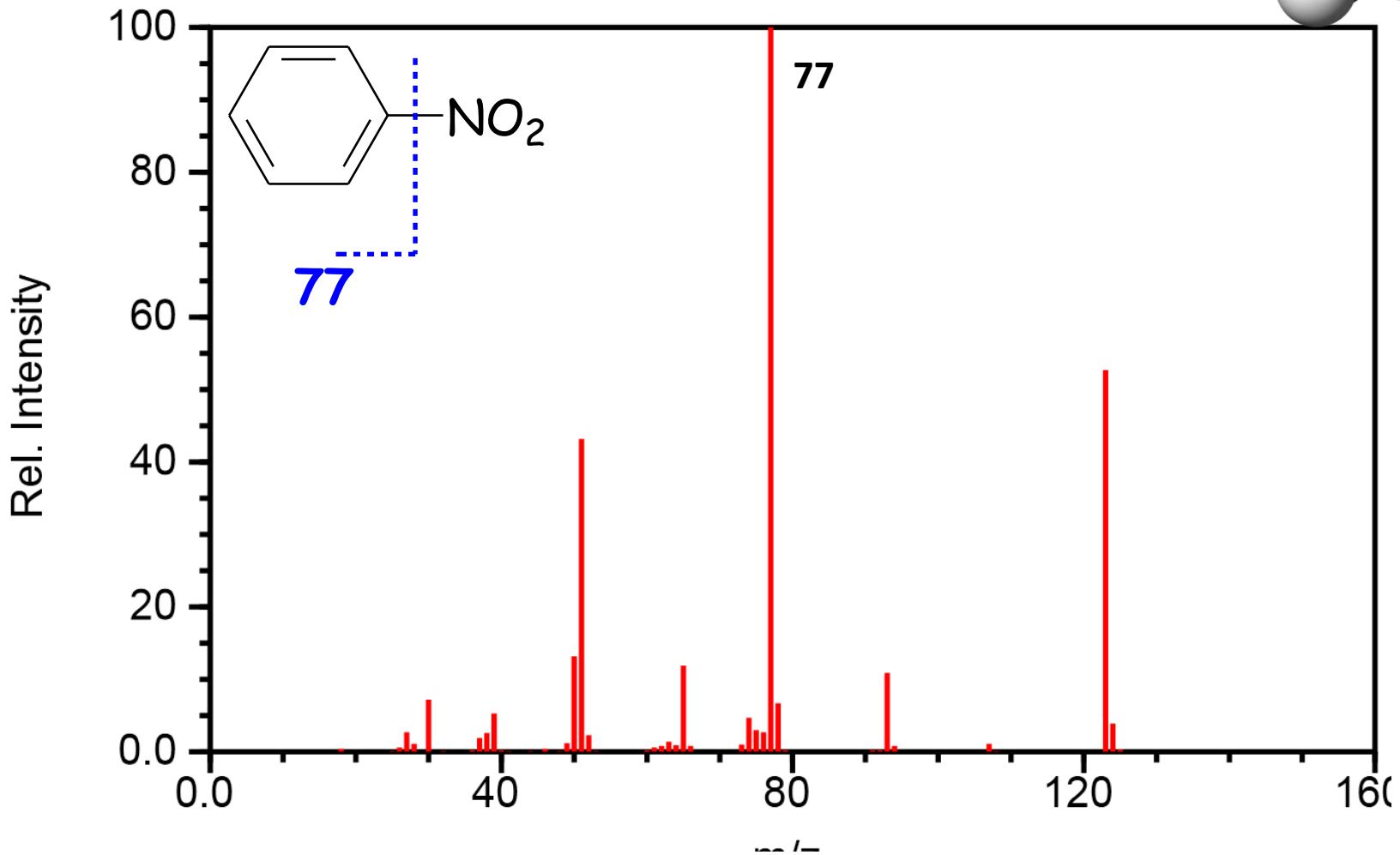


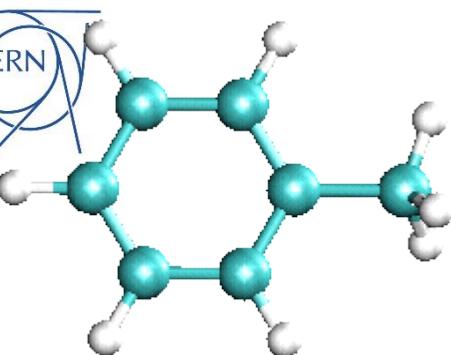
Benzene
MASS SPECTRUM





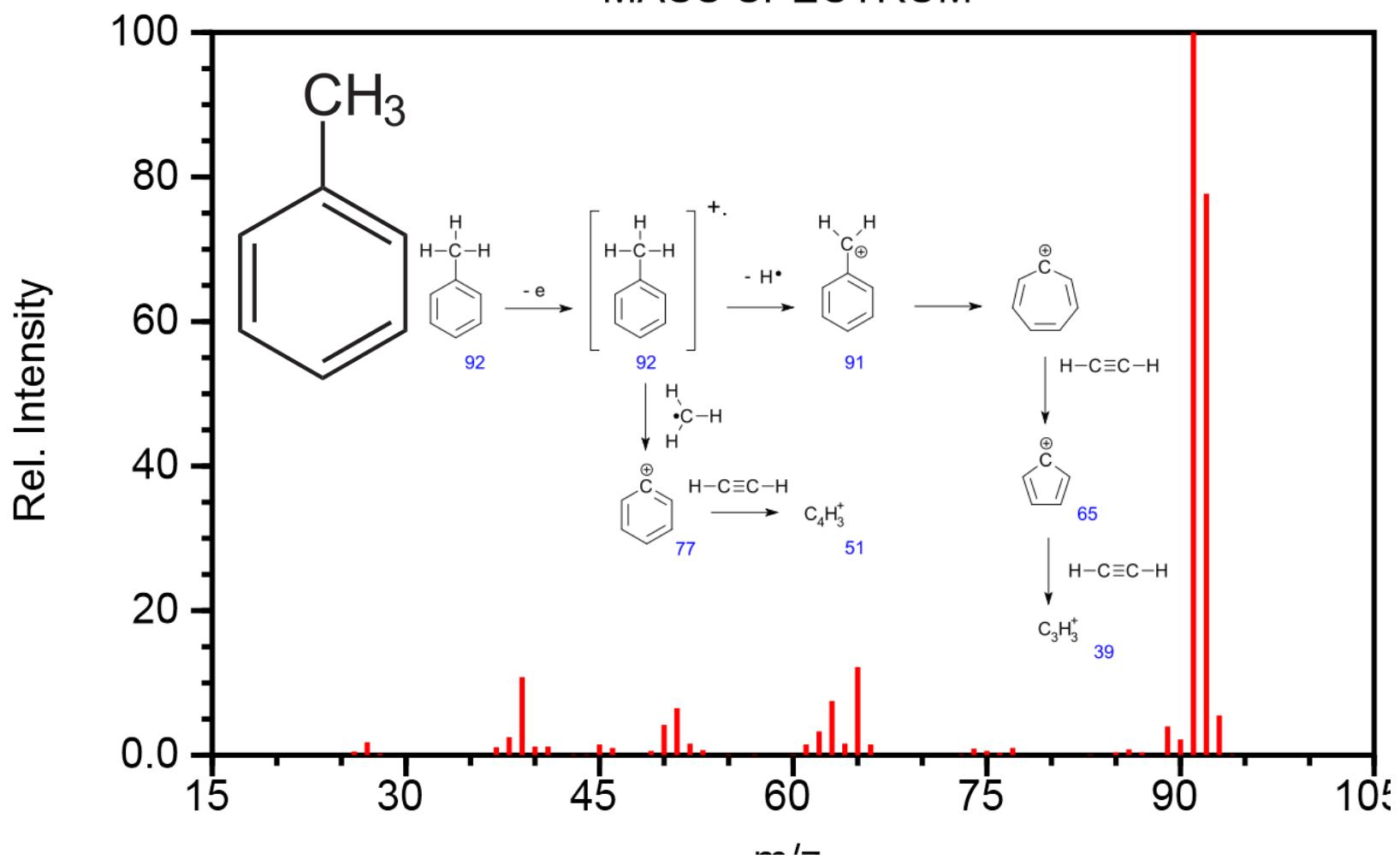
Benzene, nitro-
MASS SPECTRUM





Toluene

MASS SPECTRUM



Pump Oil Contamination

A **mineral oil** is any of various colorless, odorless, light mixtures of alkanes in the C15 to C40 range from a non-vegetable (mineral) source, particularly a distillate of petroleum

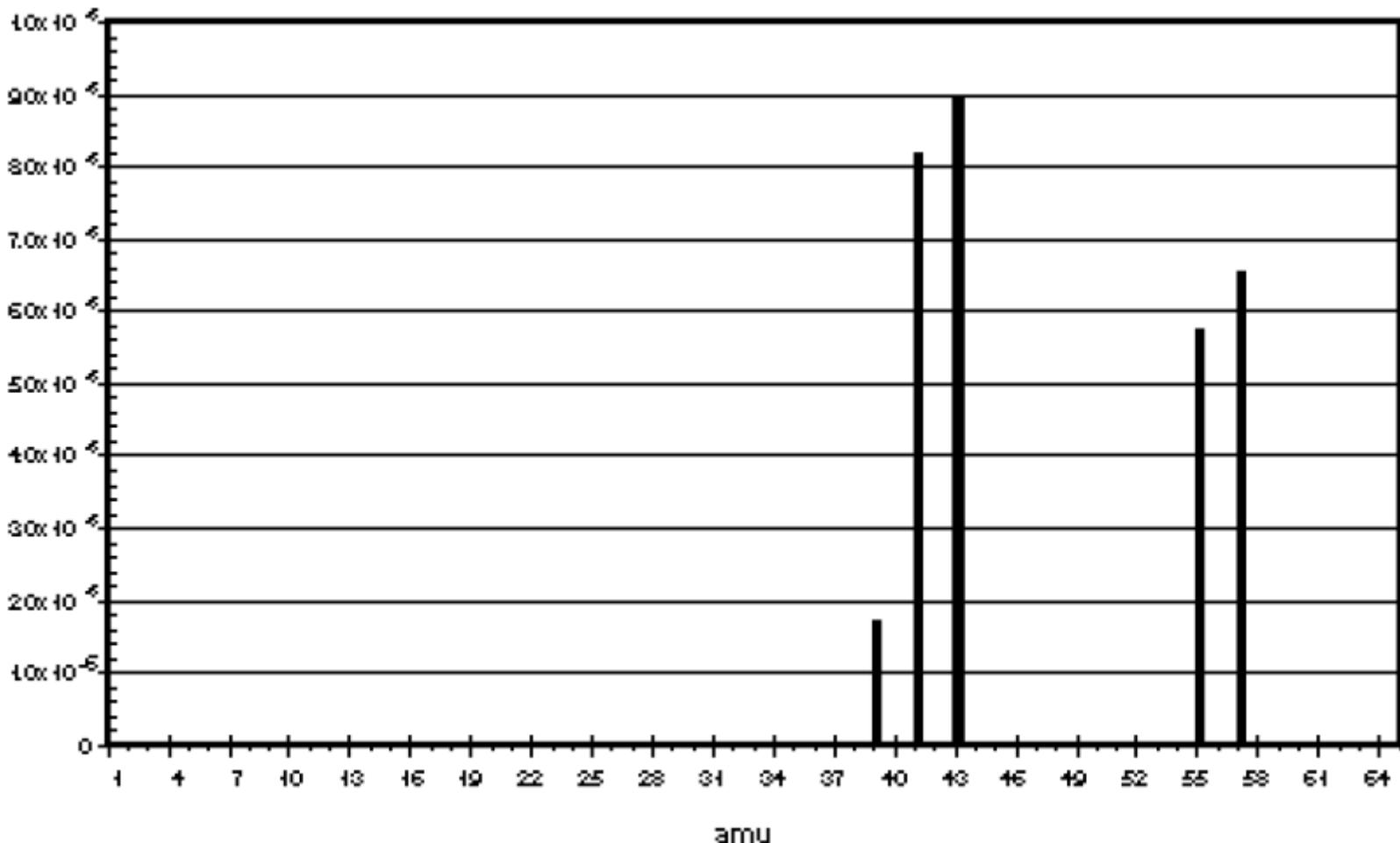
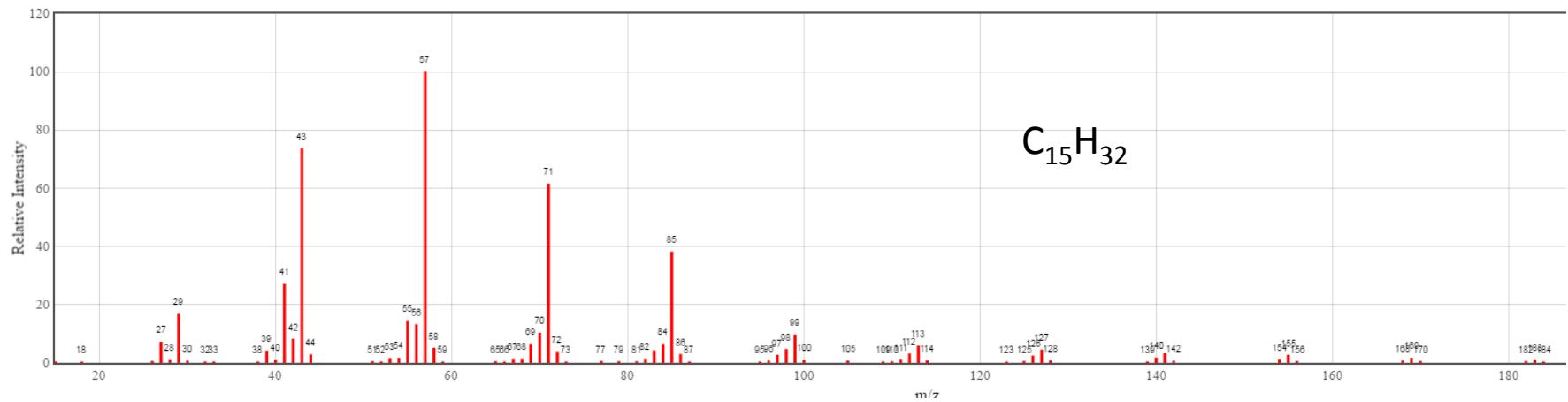
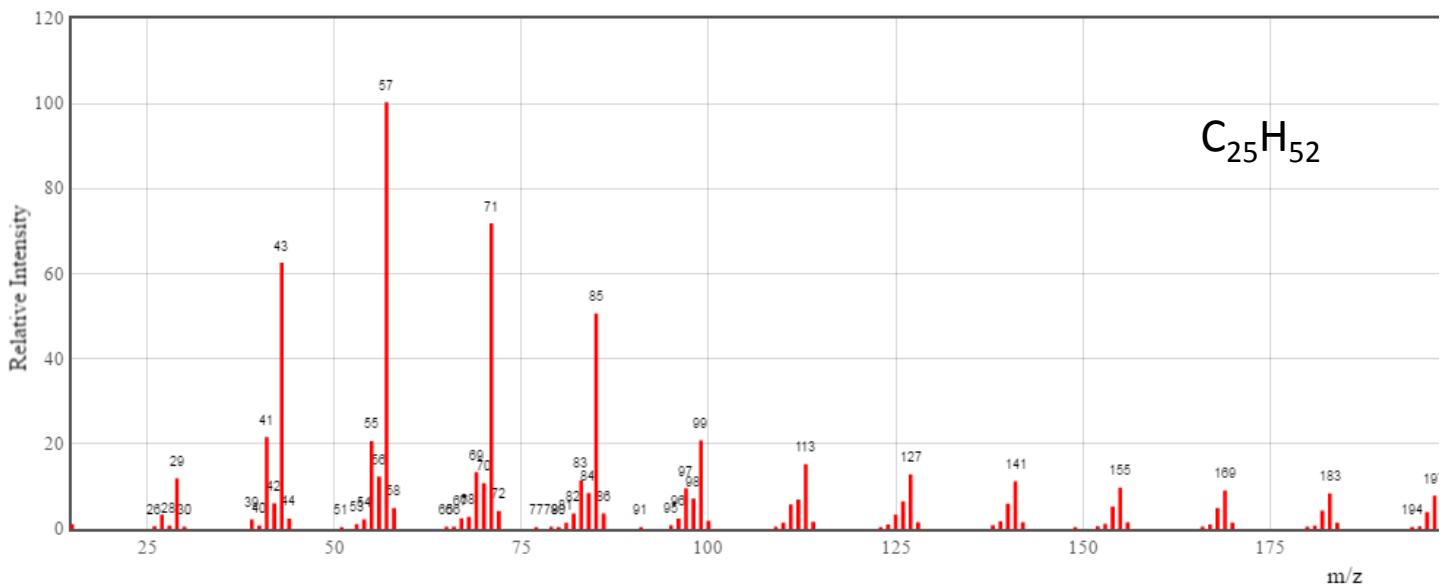


Figure 2b: Library Pump Oil Data

Pentadecane
Mass Spectrum



Pentacosane
Mass Spectrum



To have
 $\langle 57 \rangle / \langle 55 \rangle \approx 1$
We need other molecules than those of alkanes

$$A=2.945 \quad B=-44094 \quad C=1.3677 \quad D=0$$

$$\log(p / \text{atm}) = A + B / T + C * \log(T) + D / T^3$$

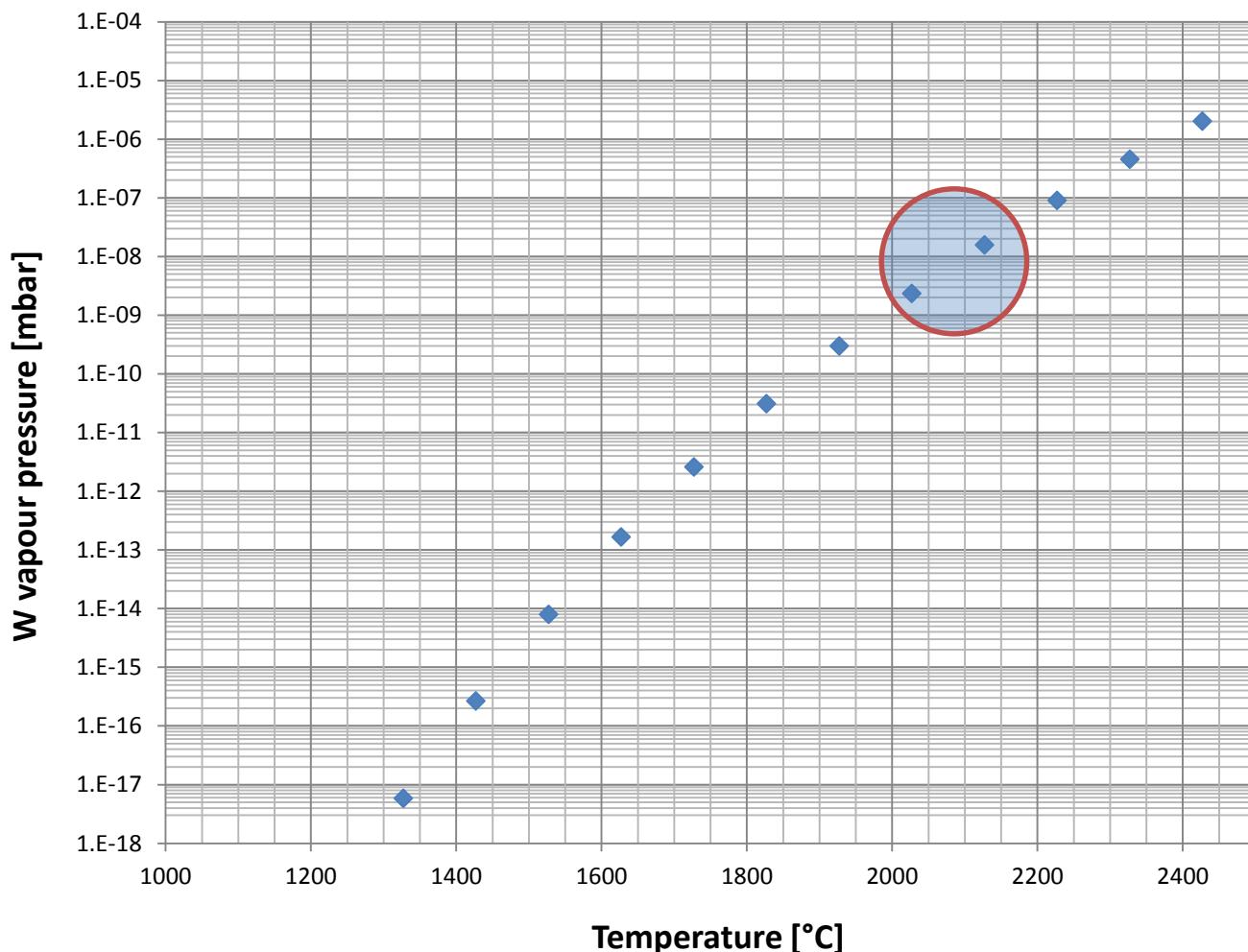
Tungsten isotopes:

^{182}W 26.5% \rightarrow $^{182}\text{W}^{++}$ 91 amu

^{183}W 14.3% \rightarrow $^{183}\text{W}^{++}$ 91.5 amu

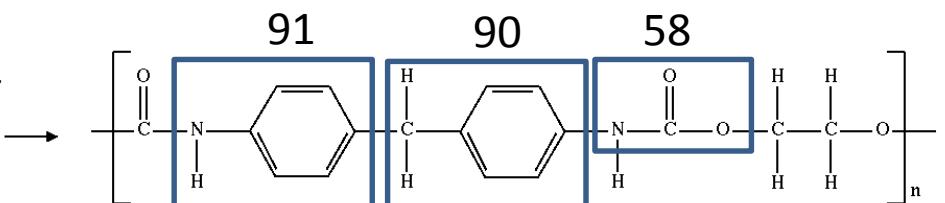
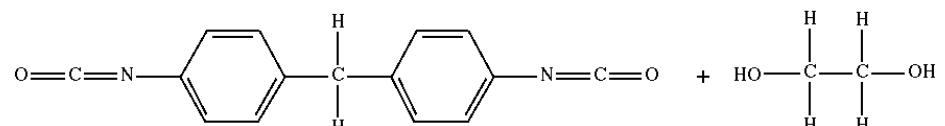
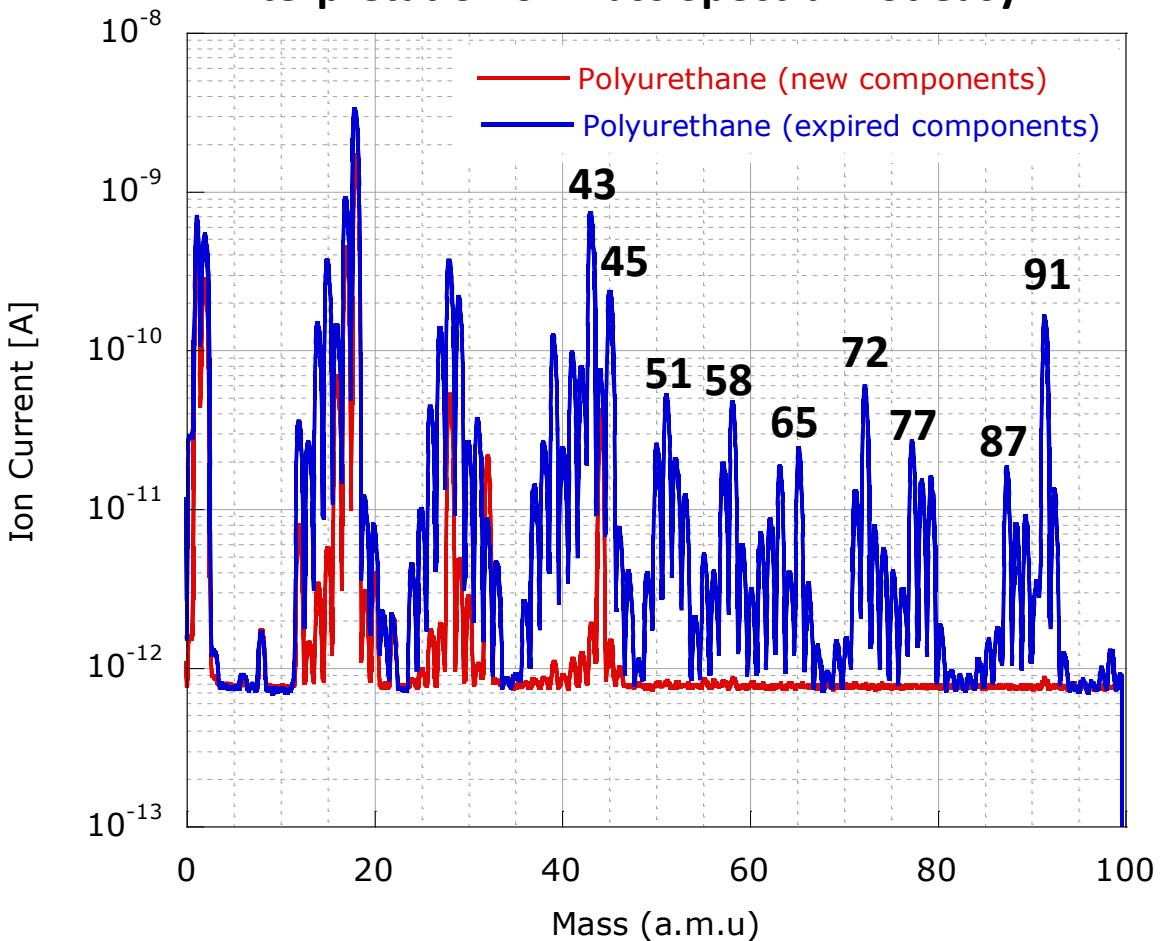
^{184}W 30.6% \rightarrow $^{182}\text{W}^{++}$ 92 amu

^{186}W 28.4% \rightarrow $^{182}\text{W}^{++}$ 93 amu



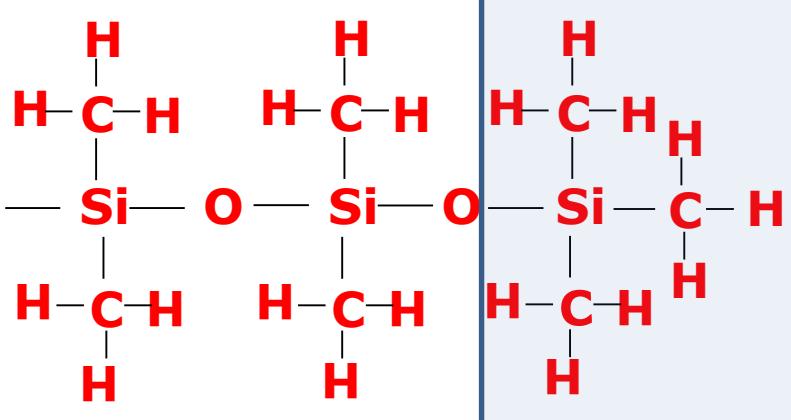
Several peaks superposed in the RGA spectrum

Interpretation of Mass Spectra: not easy

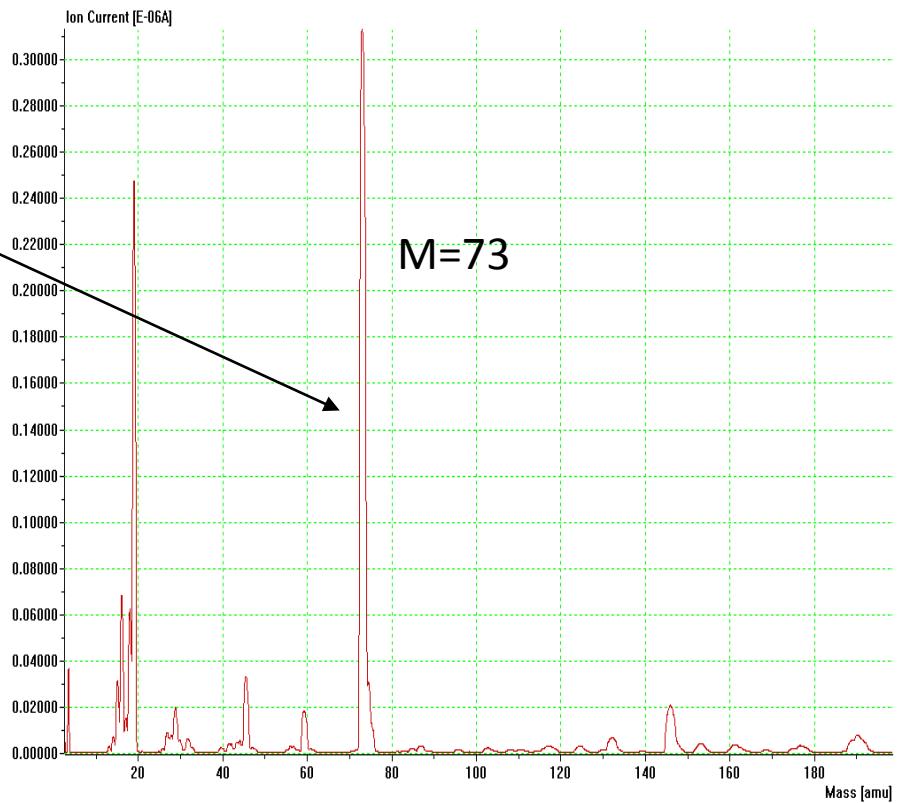
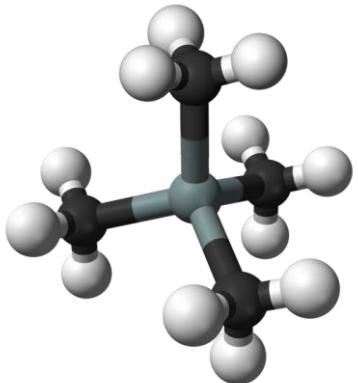


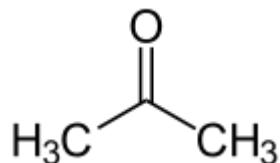
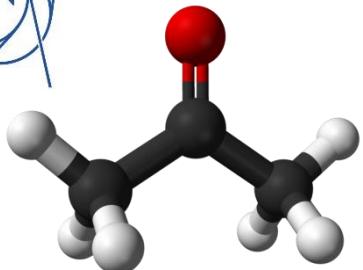
<https://en.wikipedia.org/wiki/Polyurethane>

Interpretation of Mass Spectra: silicone glue



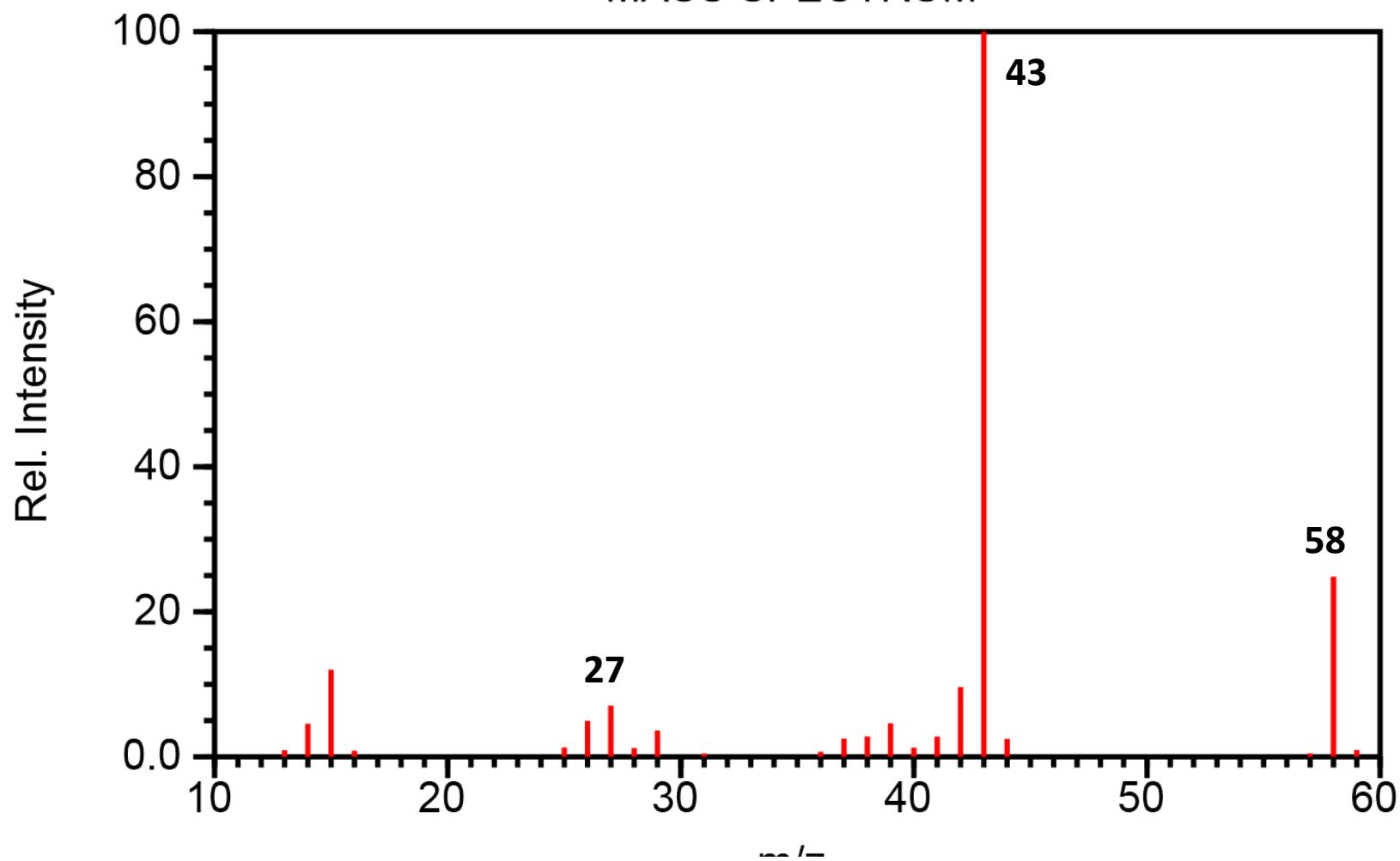
Tetramethylsilane

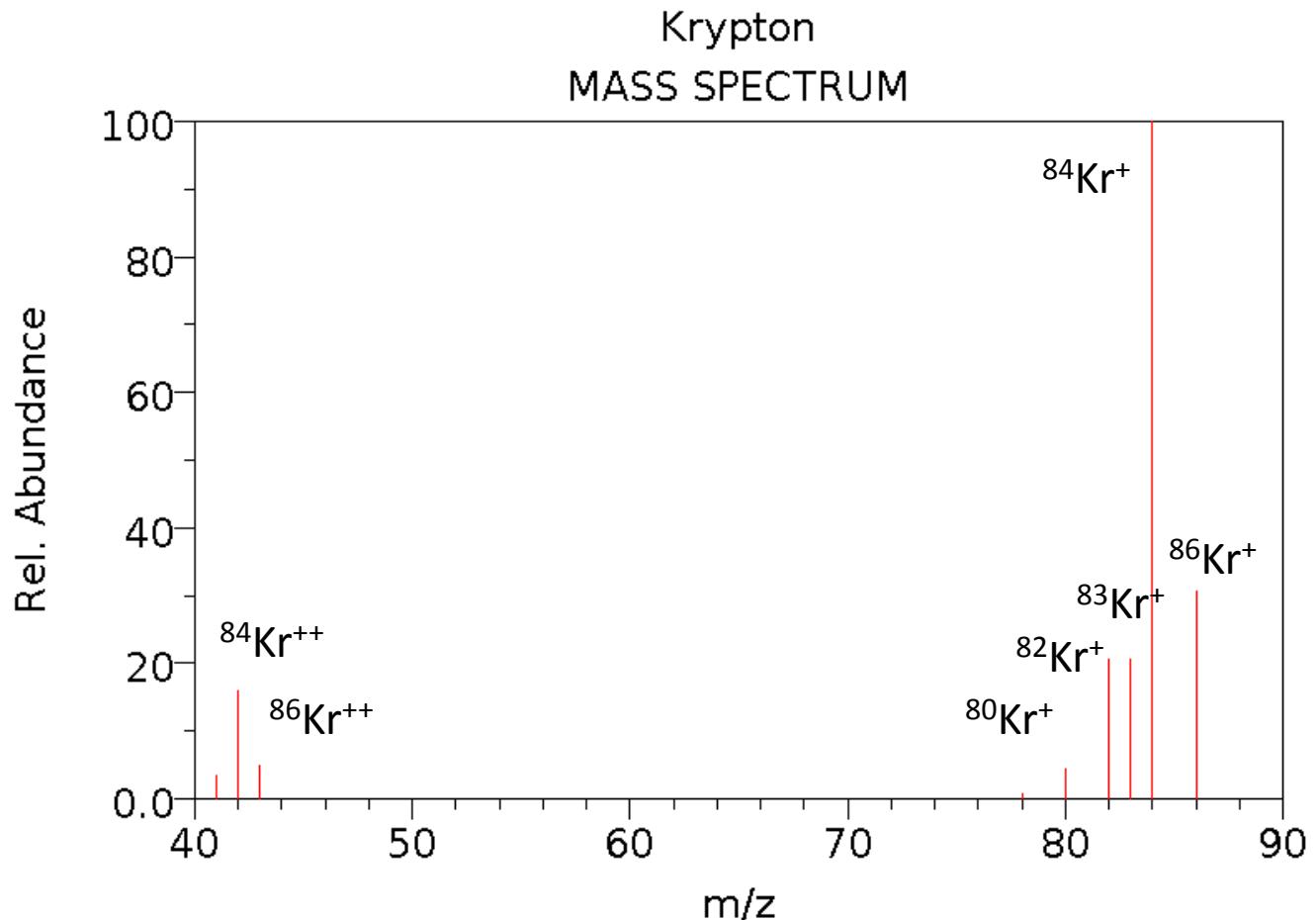




Acetone

MASS SPECTRUM



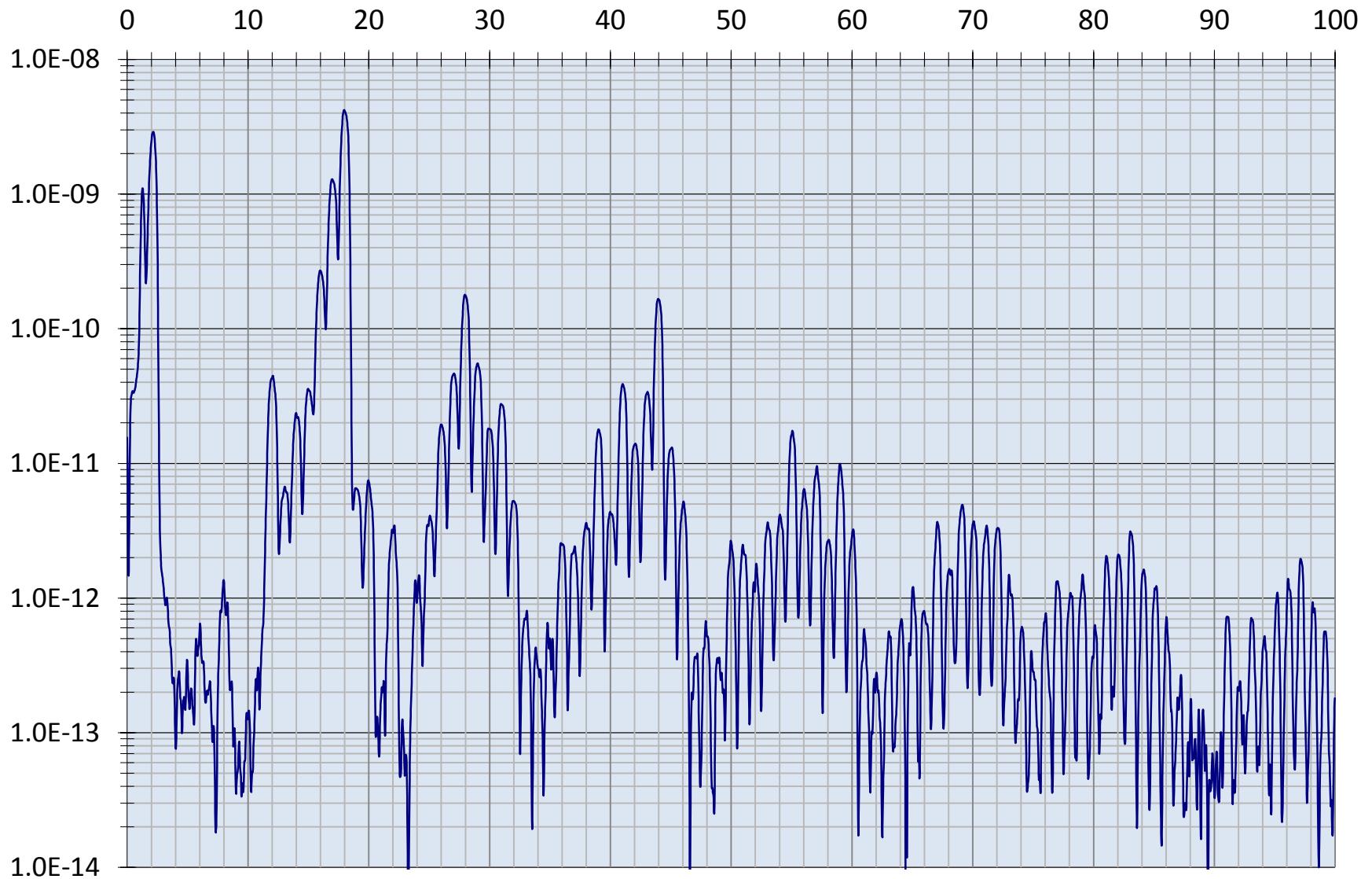


How can we identify an air-leak by RGA

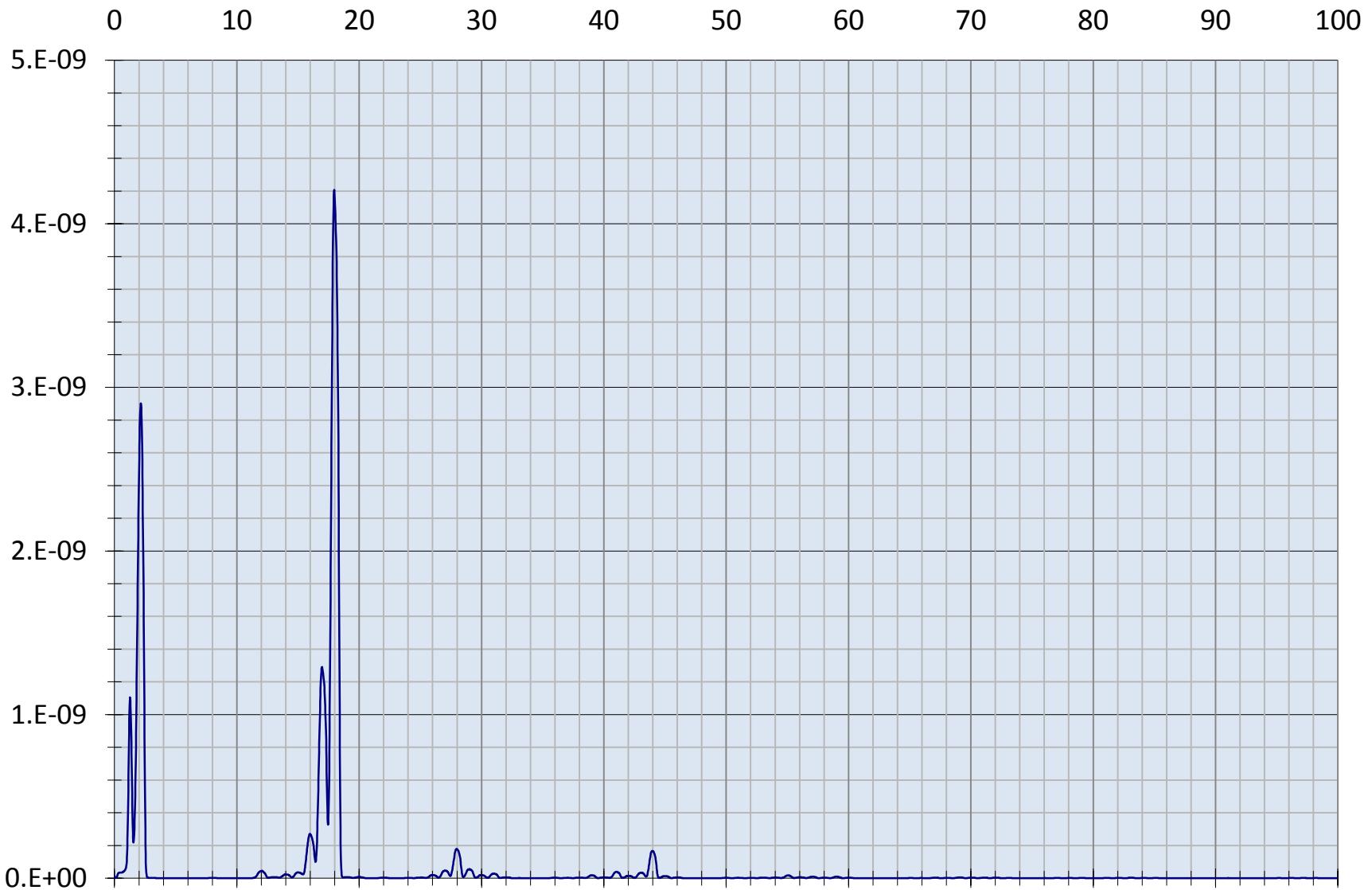
- **Large leaks in unbaked systems:**
 - High 28 - 32 - 40 in the typical ratio for air $N_2/O_2 = 78/21 = 3.7$ and $N_2/Ar = 78/1 = 78$.
- **Small leaks:**
 - Look at mass 14 and 15; **if the ratio $<15>/<14>$ is lower than 4, a leak is not excluded.**
 - If there is a **peak at 20 and not at 22**, Ar could be present.
 - If the ratio **$<39>/<40>$ is lower than 3**, Ar could be present.
 - In baked system, the **absence of peak 32** does not imply the absence of leaks; **baked stainless steel walls adsorb oxygen.**



Interpretation of Mass Spectra: Unbaked System 4×10^{-9} mbar



Interpretation of Mass Spectra: Unbaked System 4×10^{-9} mbar



Interpretation of Mass Spectra: Artefacts

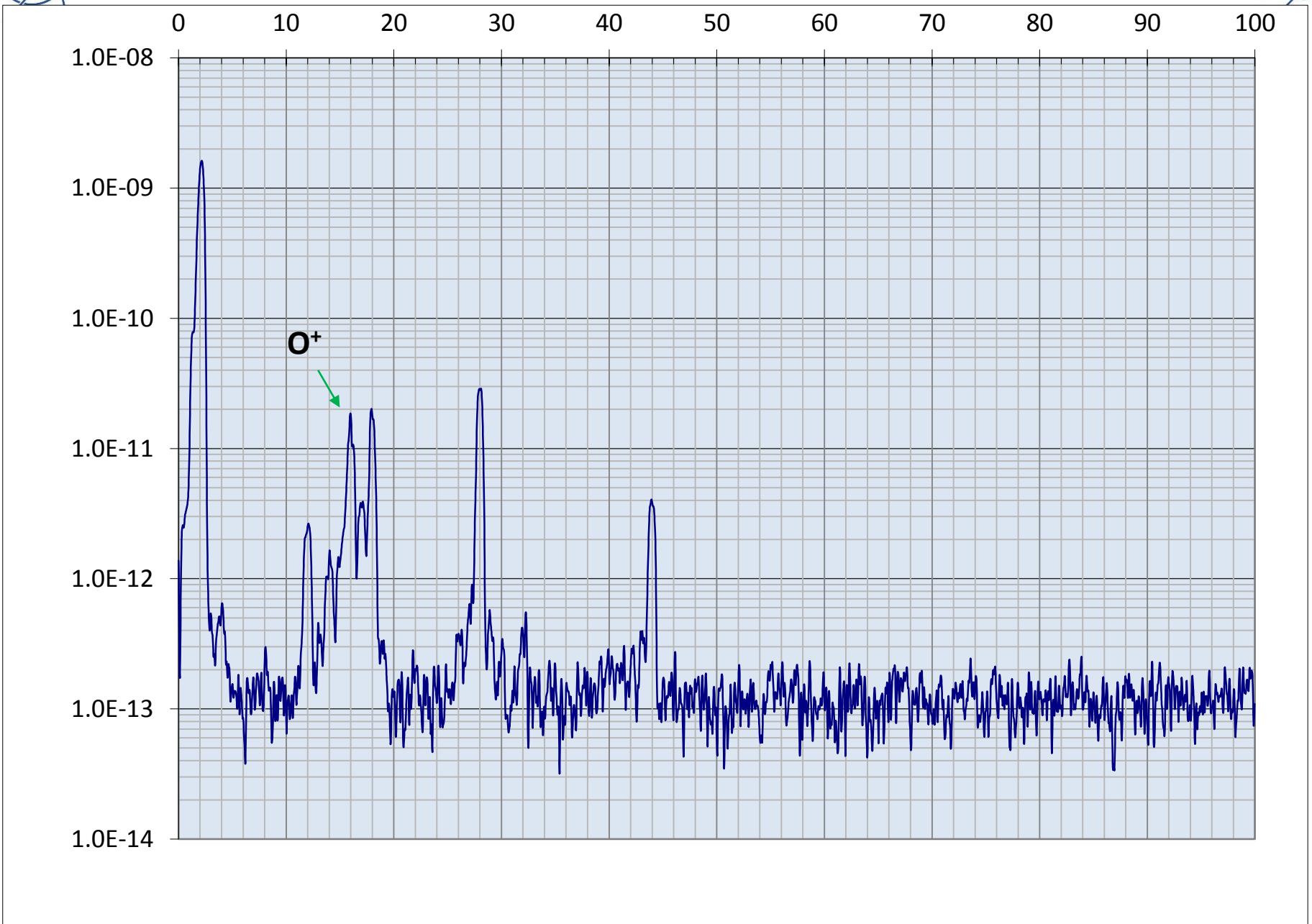
➤ Artefacts:

- The cracking pattern depends on the RGA electrical setting (in particular the energy of the electrons);
- Misalignment could have a role.
- The RGA fragmentation pattern is **indirectly modified by the vacuum system**. For example assume that:
 - CO₂ is the only gas injected in the system
 - the system is equipped with ion pumps and ionization gauges

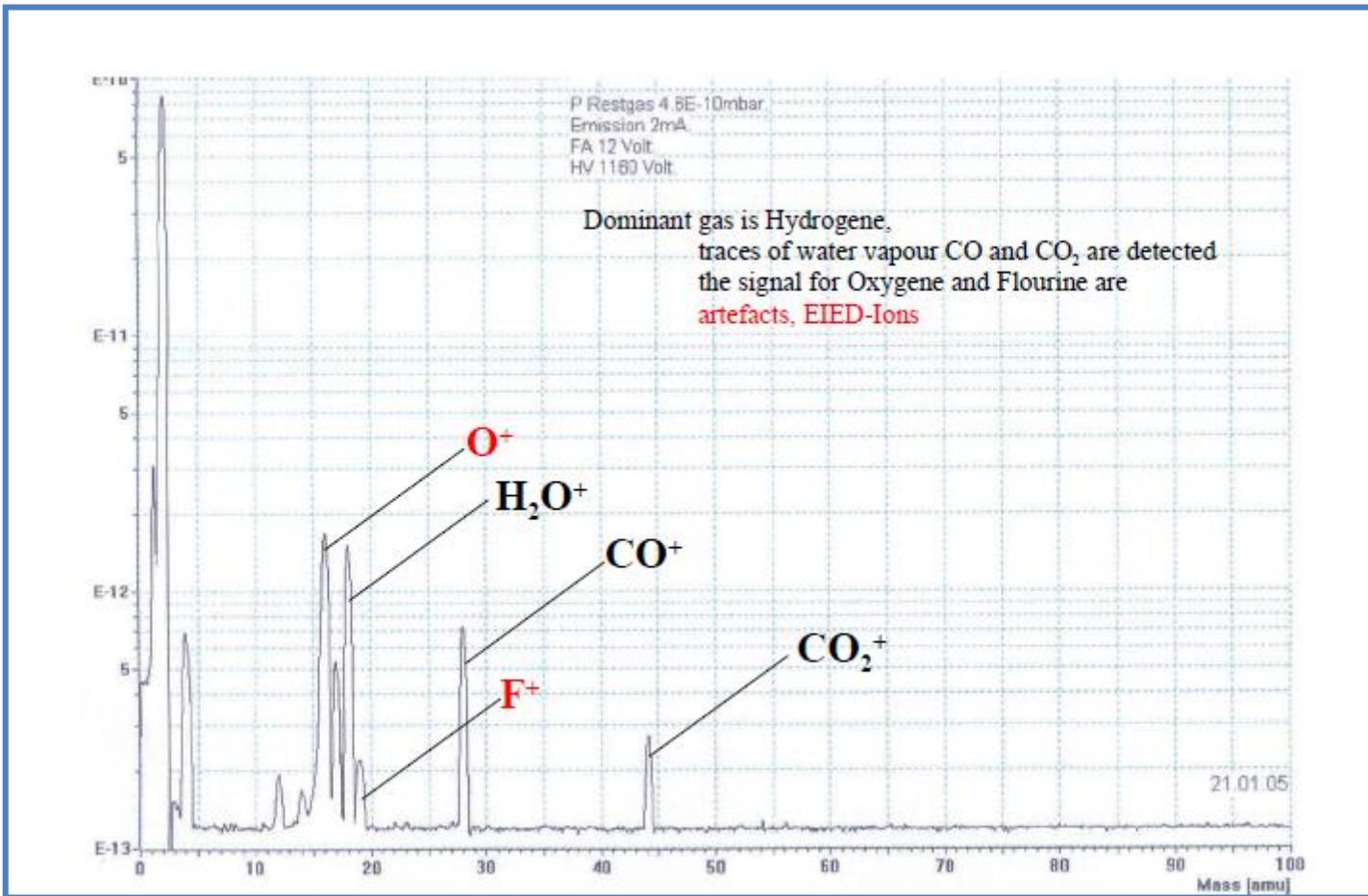
→ CO is generated and the measured 28/44 ratio increases.

- Some peaks not related to gas molecules may appear in the UHV range: **ESD** of gas adsorbed on the grid **may lead to spurious peak** in the mass spectrum. The most common ESD peaks are:

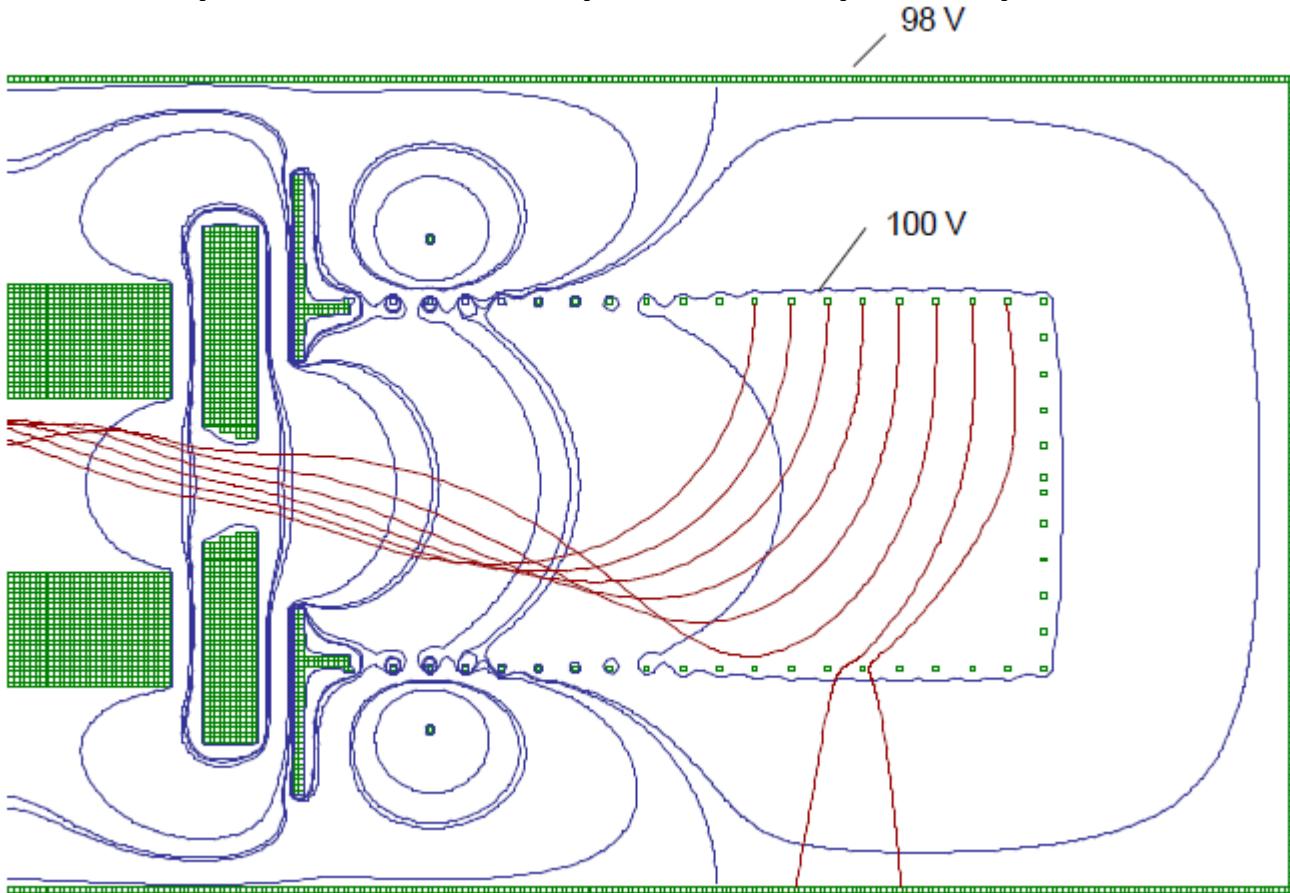
Mass (m/e)	Component
– 1	H+
– 16	O+
– 19	F+
– 23	Na+
– 28	CO+
– 35,37	Cl+
– 39	K+

Interpretation of Mass Spectra: Baked System 4×10^{-11} mbar

Interpretation of Mass Spectra: ESD spurious peak

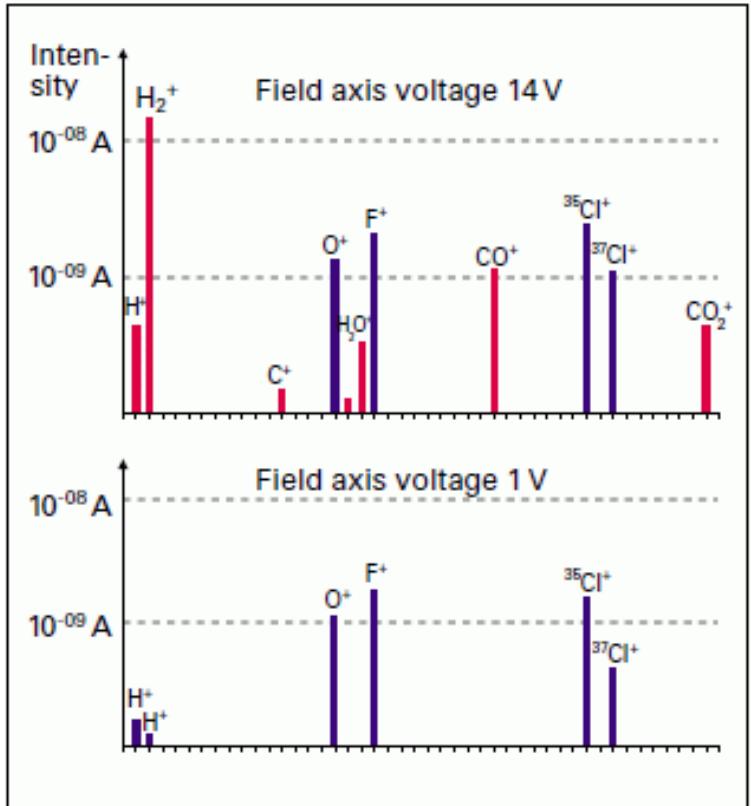


Interpretation of Mass Spectra: ESD spurious peak

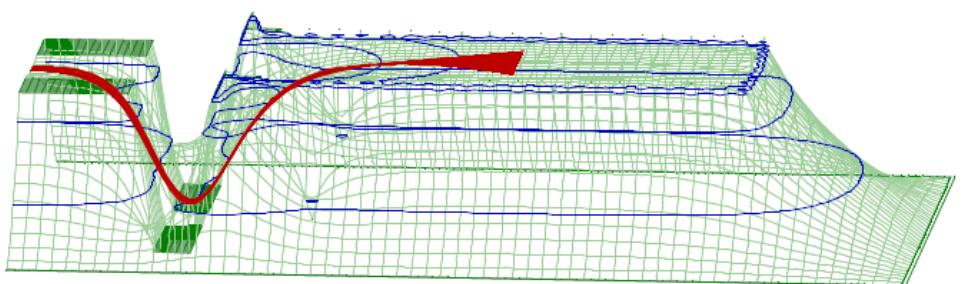


ESD ions acquire a kinetic energy of the order of 1 eV as a result of the electron collision. So, **they move much faster than the gas ion of the same mass** (in average 0.025 eV).

Interpretation of Mass Spectra: ESD spurious peak



- Because they have higher energy than gas ions, they can fly directly into the quadrupole even with a small field axis voltage.

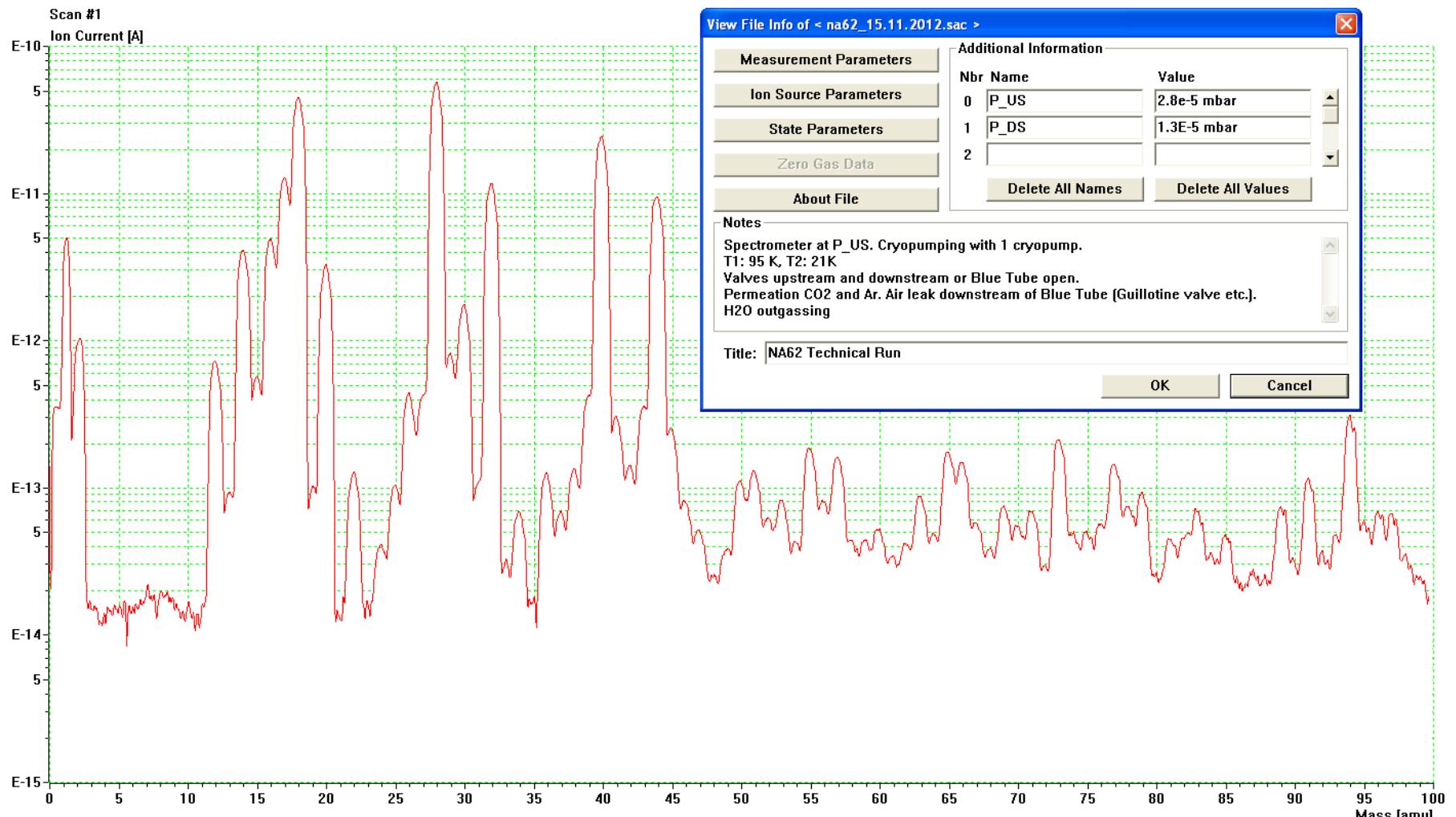


- Reducing the field axis voltage leads to the suppression of the gas ions; in this way, only the ESD spurious peaks are detected.

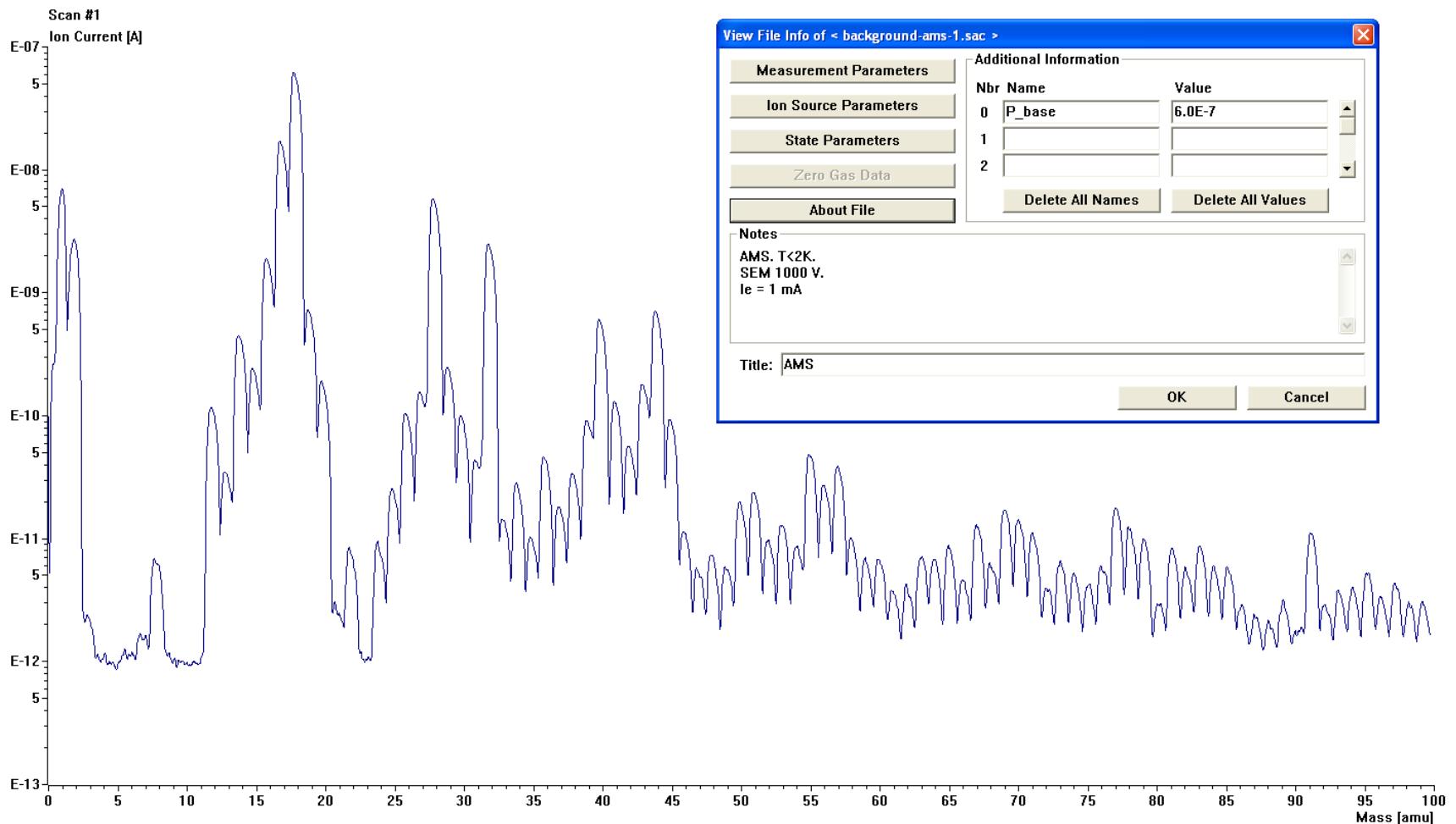


SOME EXAMPLES

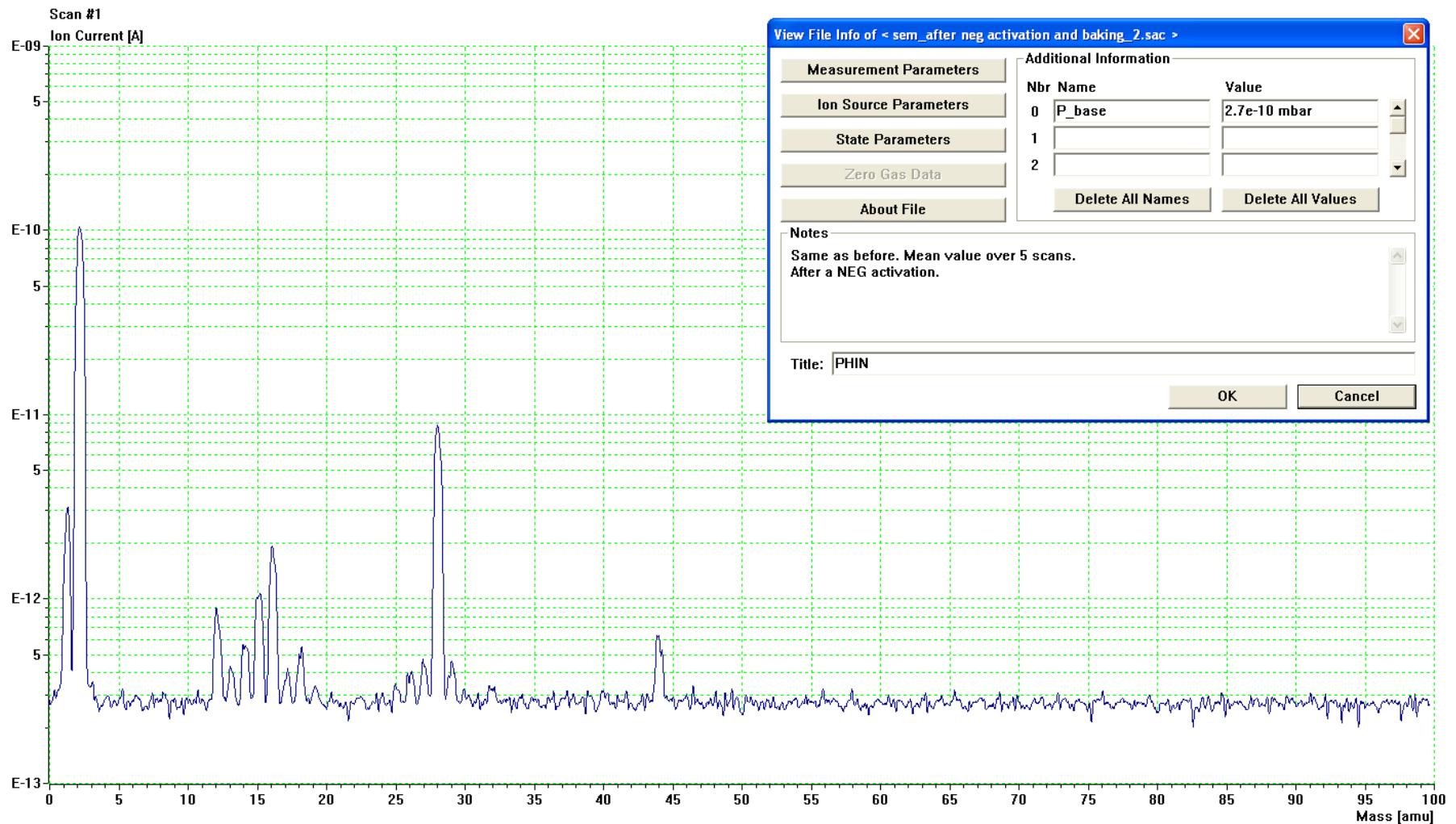
Measured Spectrum NA62 (16.11.2012)



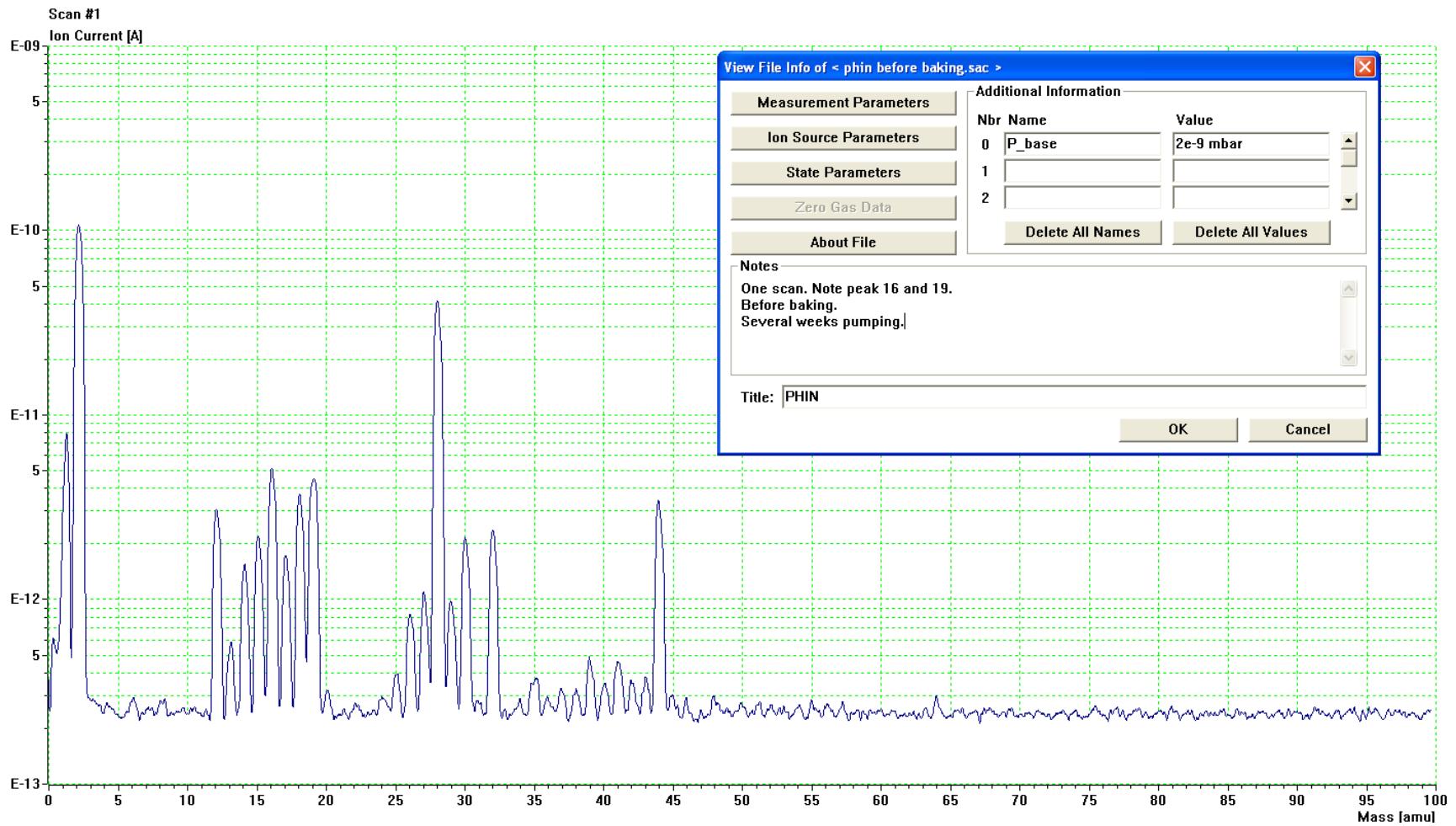
AMS background

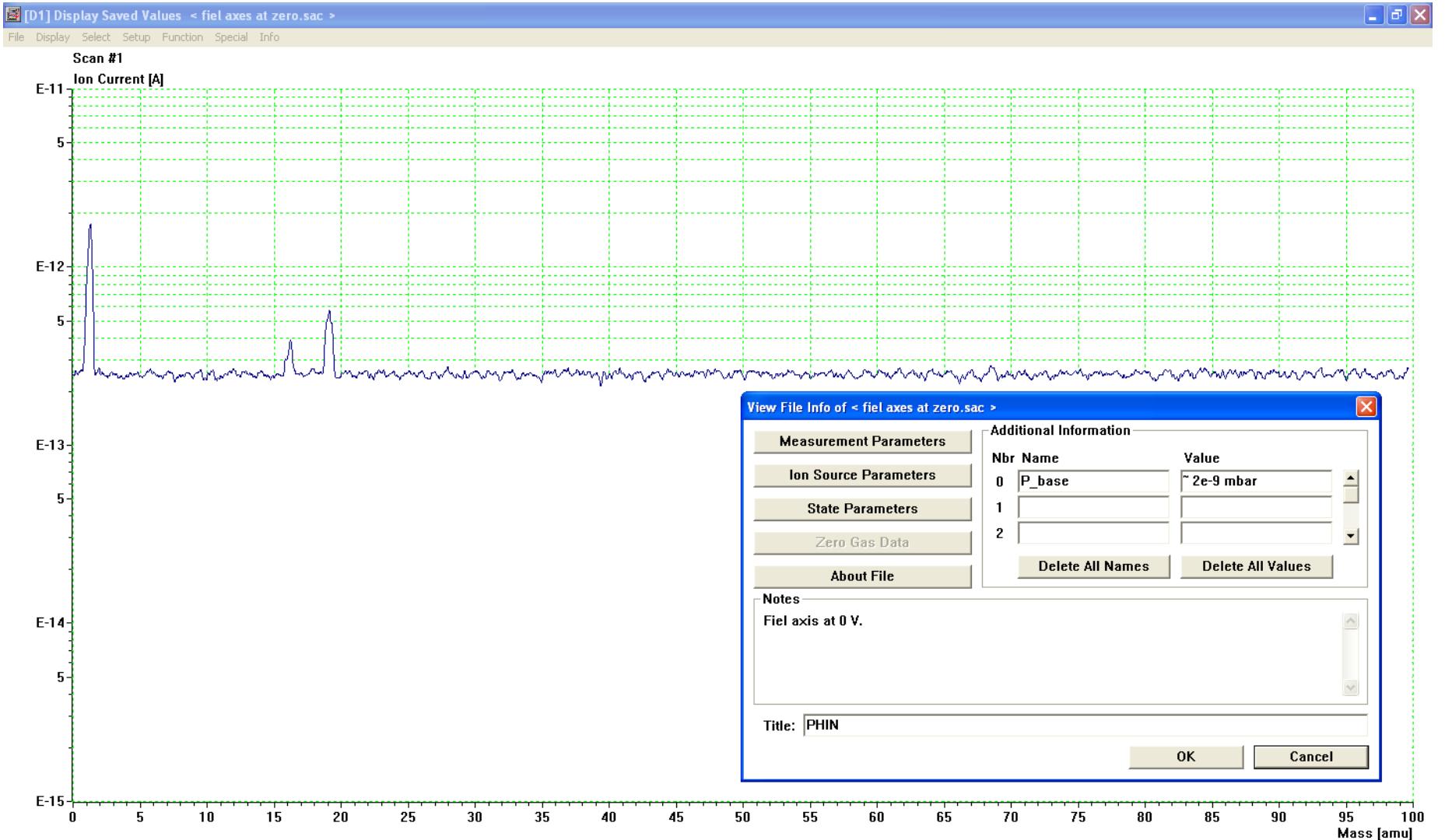


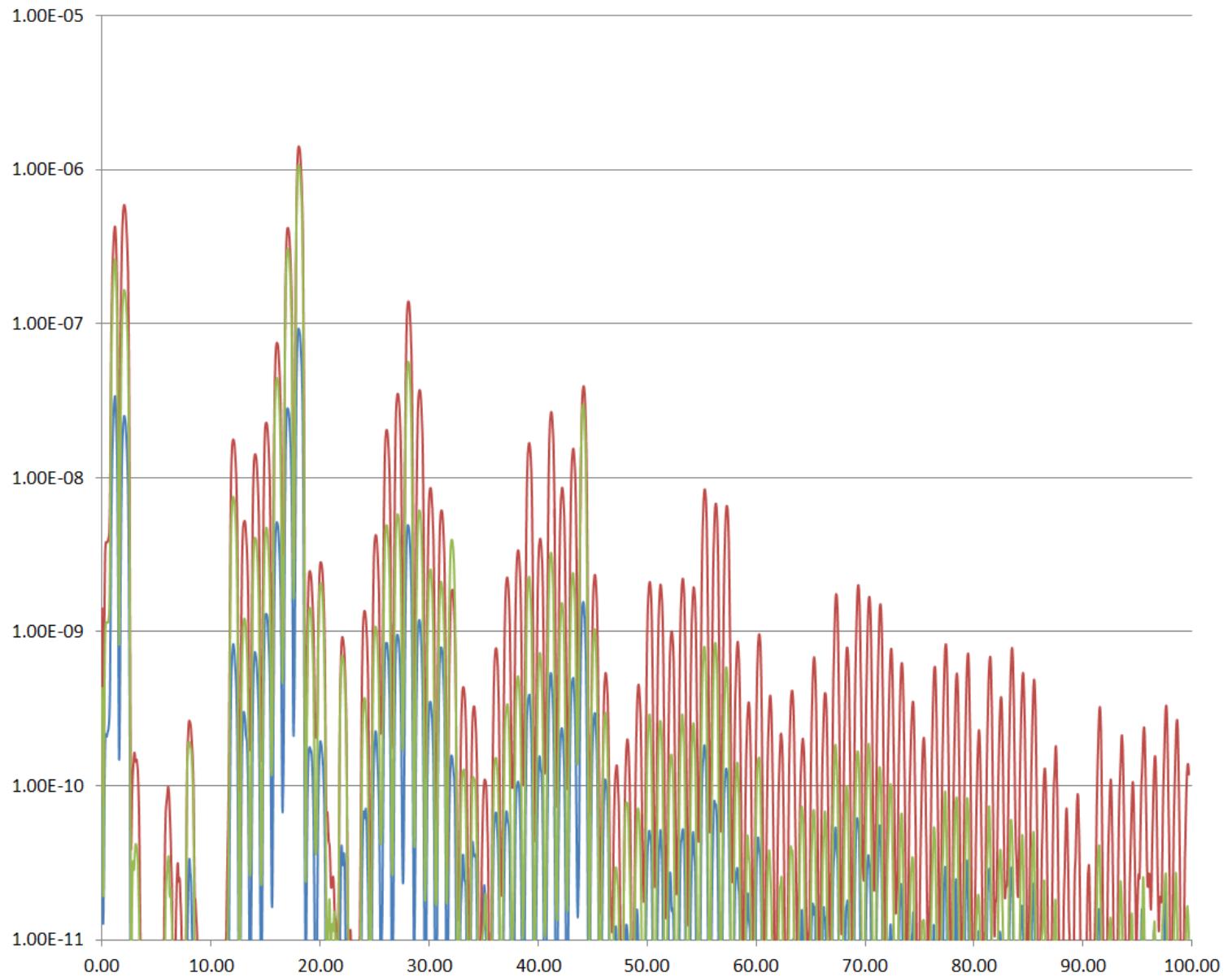
CTF-PHIN



CTF-PHIN







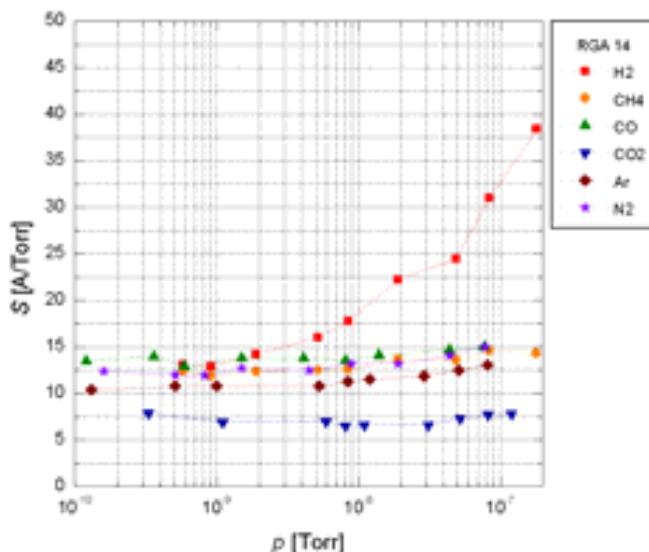
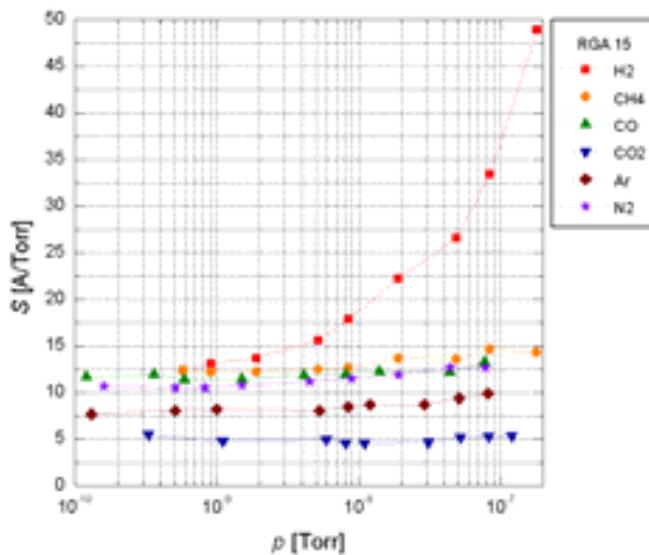
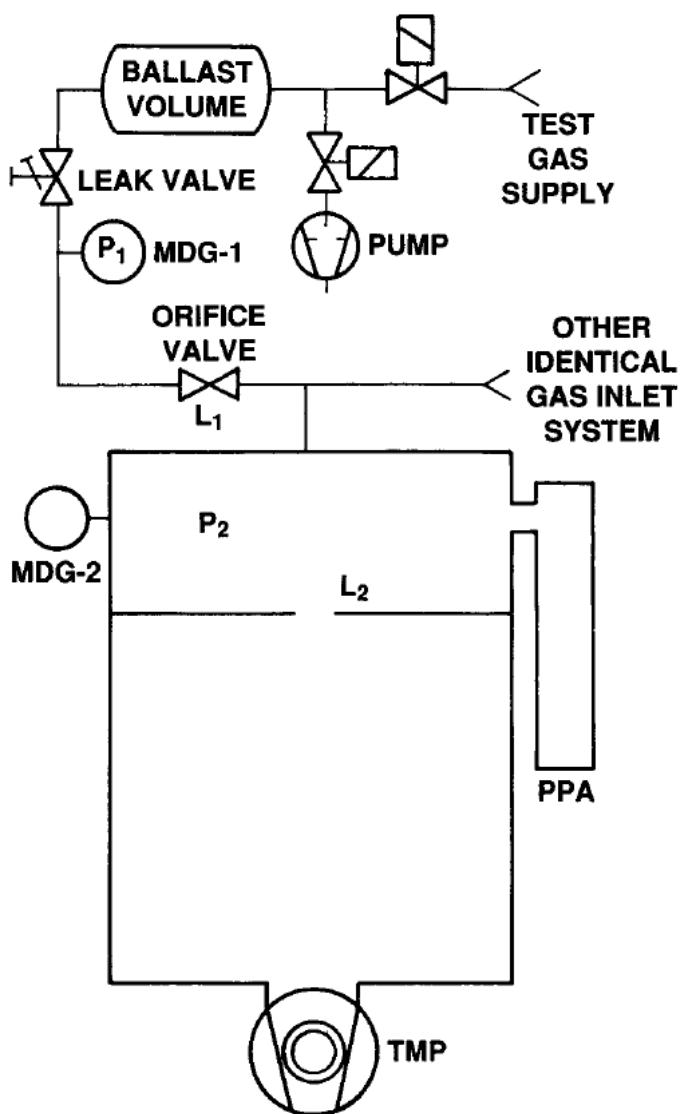
- The calibration of a RGA consists in measuring the **sensitivity [A/Torr]** and the **cracking pattern** for a set of gases.
- The calibration of RGA is a frustrating activity because the **sensitivities** can change quickly and depends on so many parameters that are in most of the cases impossible to keep under control. In particular, gas mixtures affects the sensitivity of a single gas component (**matrix effect**). Pre-exposure to a reactive gas modifies sensitivities of single gases. The time stability is also an issue, in particular when SEM are used.
- For these reasons, **RGA are not calibrated against primary standard**.
- The simplest calibration method is to **compare its signal to that of an ionization gauge**. The sensitivity for the gas 'i' is:

$$S_i = \frac{I_{RGA} - I_0}{P_i - P_0}$$

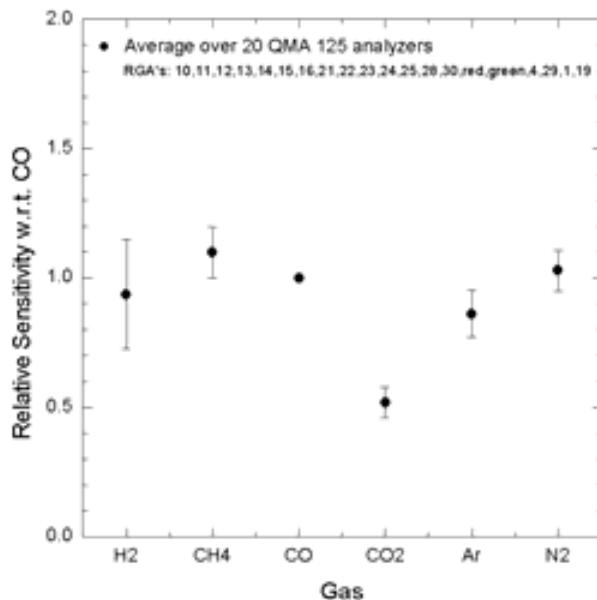
- **The relative sensitivity** is the ratio of the absolute sensitivity for a given gas to the absolute sensitivity for a **reference gas**.

Calibration of Quadrupole Mass Analyzers

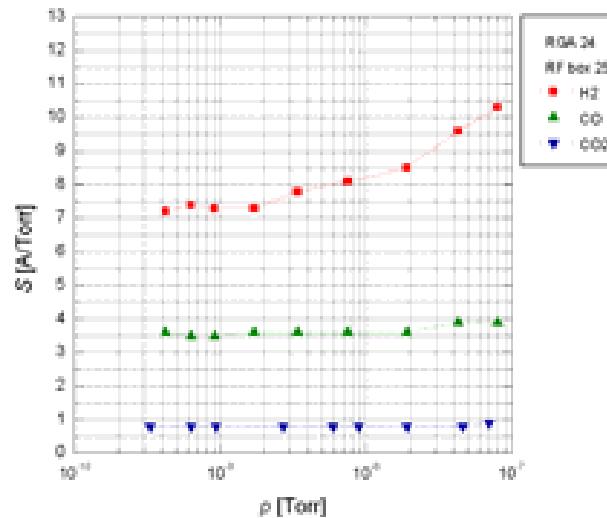
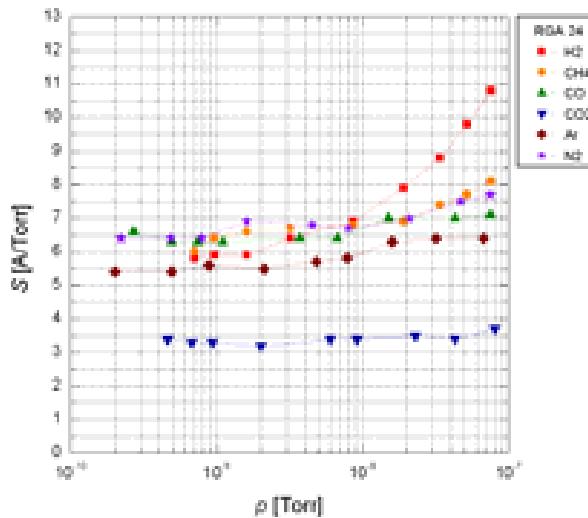
QMA 125, SEM 1600, $I_e = 2 \text{ mA}$, Courtesy of E. Mahner



- If quantitative measurement are necessary, **the RGA has to be recalibrated as frequently as reasonable in situ**. Fortunately the calibration for the full set of gas is not necessary because **the relative sensitivities do not change too much** (E. Mahner data: ±10%, except for H₂ 23%) despite the usual drift of the absolute sensitivity. It is then enough to measure in situ the sensitivity for an ‘heavy’ gas (Ar or N₂) and hydrogen (the gas with the largest spreading in sensitivity).
- As a general rule, when a RGA is used for quantitative measurements, there should be the possibility of gas injection and total pressure reading.
- Another possibility consists in using calibrate leaks, for example for H₂ and N₂.



Calibration of Quadrupole Mass Analyzers

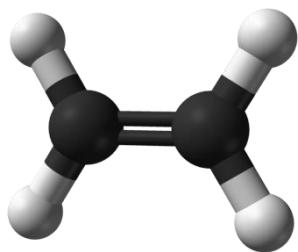


Experience at CERN (E. Mahner) indicates that 'a change of the RF supply can strongly influence the sensitivity of the head. The Pfeiffer's **QMA 125 head and the QME 125 RF box are tuned assemblies**'.

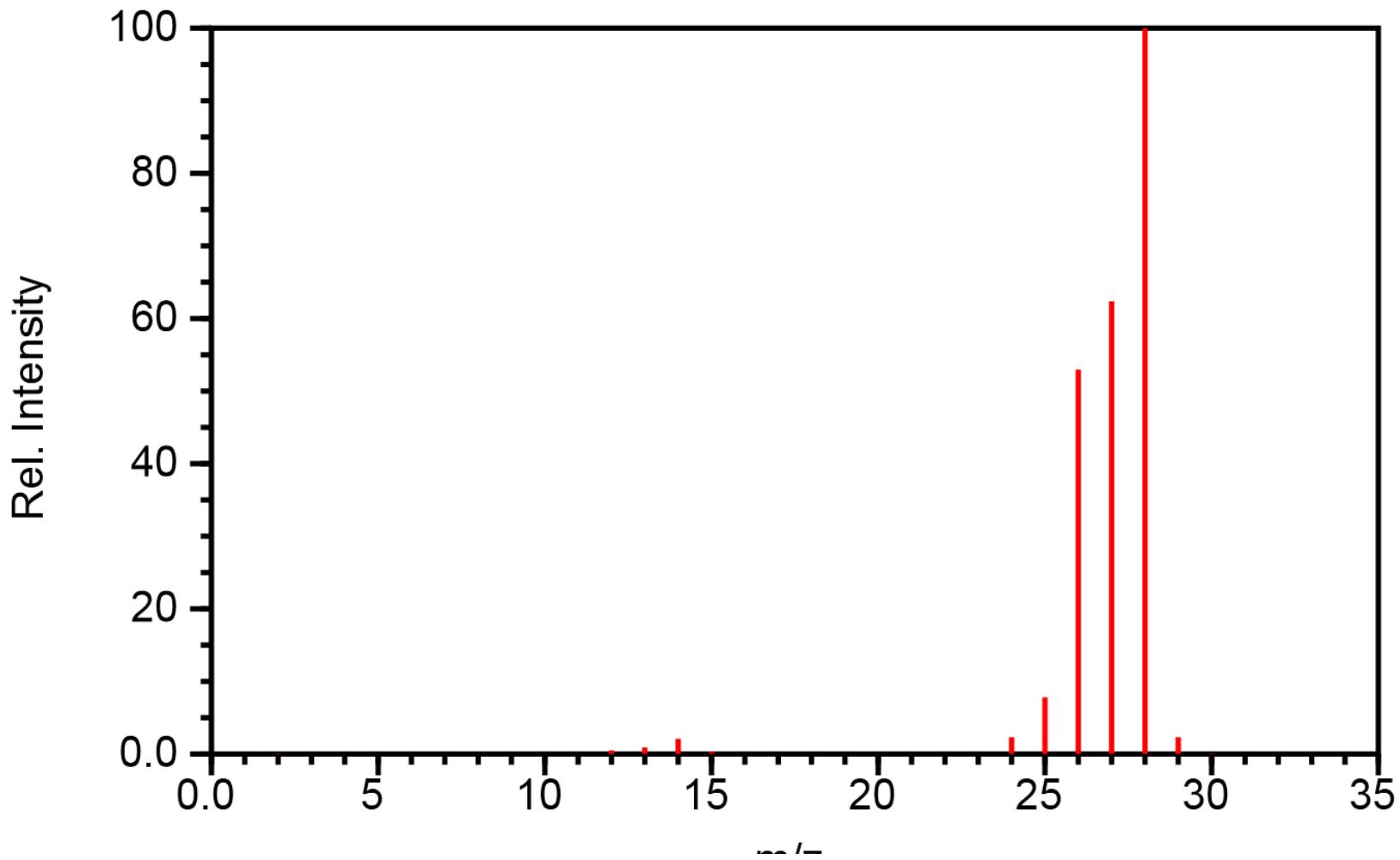
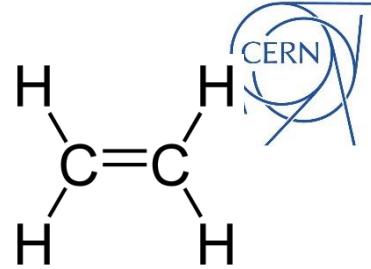


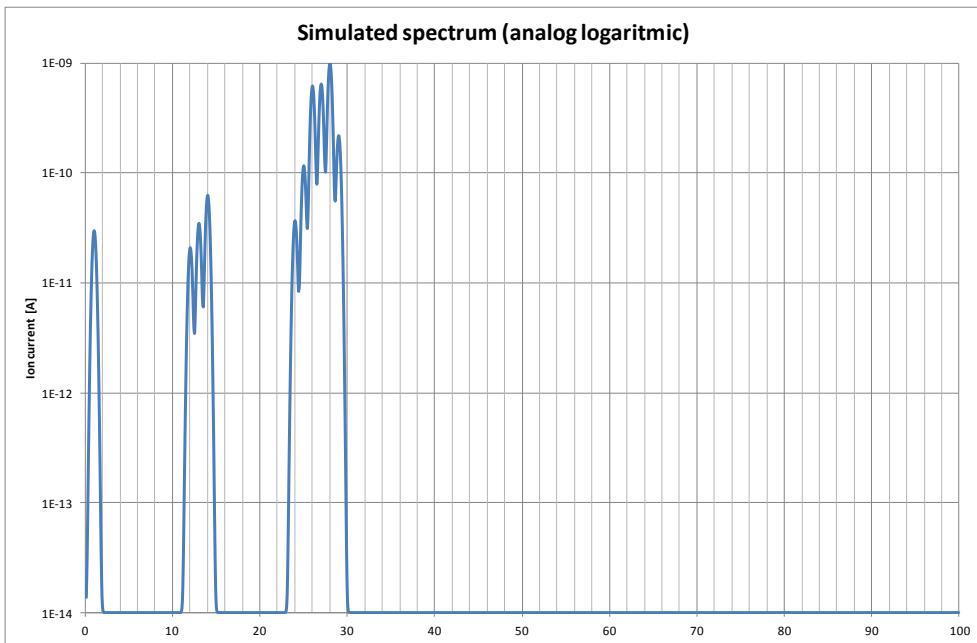
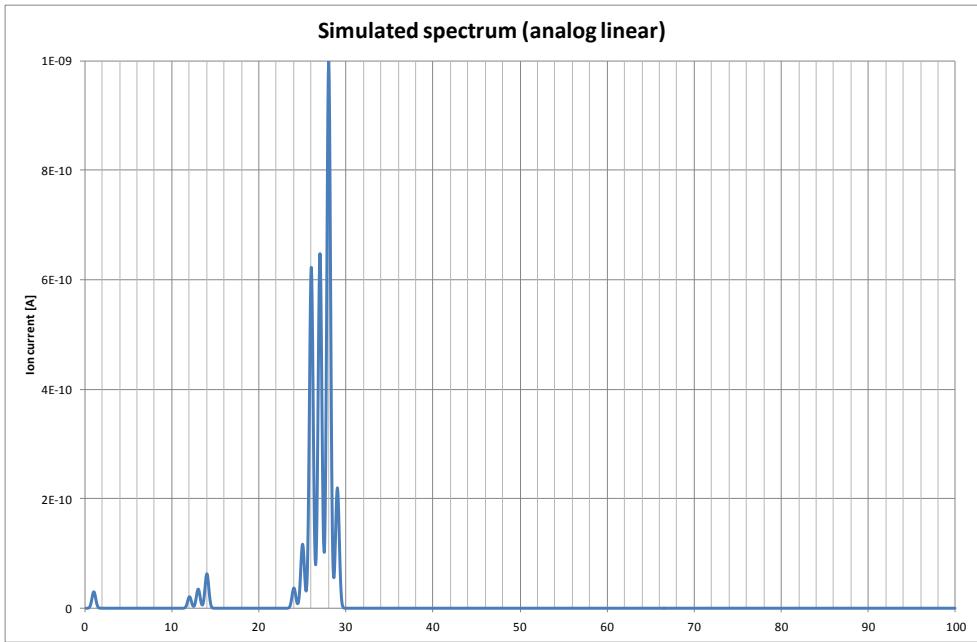
And now let's put into practise...

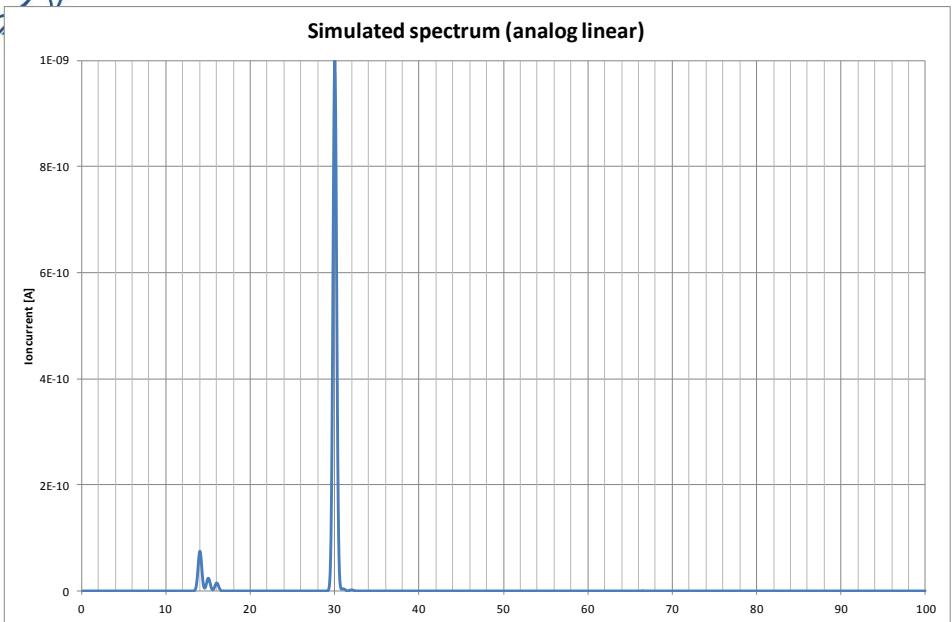




Ethylene
MASS SPECTRUM







NO

