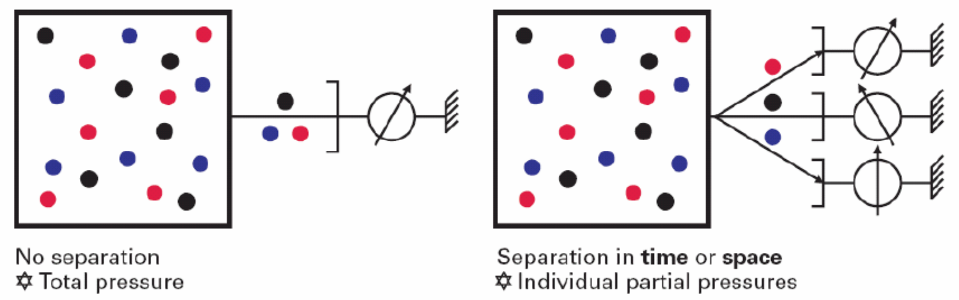
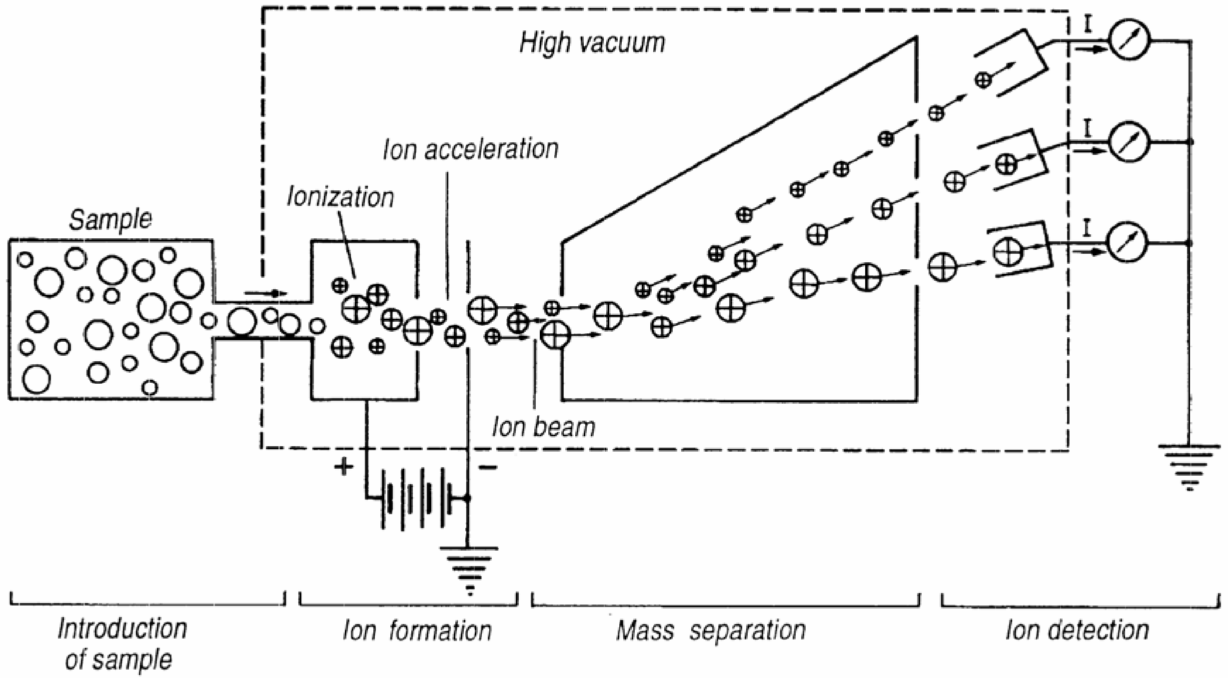
Practical aspects of mass spectrometry

Andrey Tarasov
Lecture on mass-spectrometry
30.10.2015


No separation
✡ Total pressure

Separation in **time** or **space**
✡ Individual partial pressures

Separation of components in the gas phase by mass-to-charge ratio



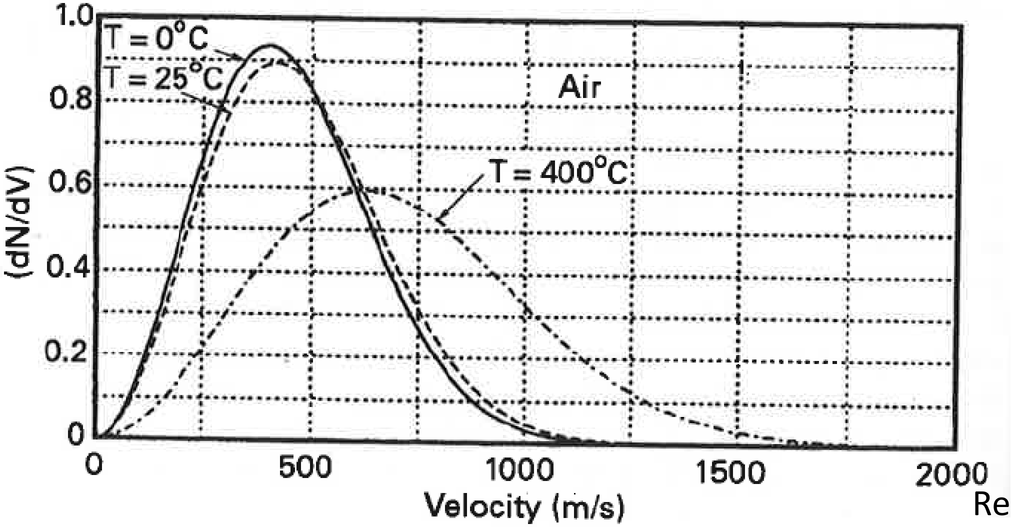
Mass spectrometer

Detection of ion currents

The method is not inherently quantative

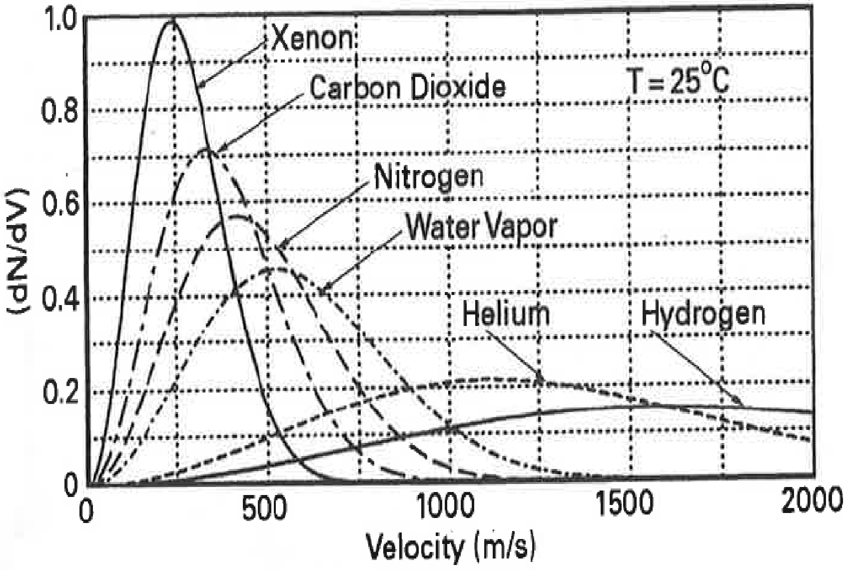
Kinetic picture of gas

Relative velocity distribution of air



@22°C, 10^5 Pa, $2.48\cdot10^{25}$ molecules, $3.4\cdot10^{-9}$m spacing
10^{-7} Pa, $2.48\cdot10^{13}$ molecules, $3.0\cdot10^{-5}$m spacing

Relative velocity distribution of several gases



Maxwell-Boltzmann distribution for ideal gas:

$$\frac{dn}{dv} = \frac{2N}{\pi^{1/2}}\left(\frac{m}{2kT}\right)^{3/2} v^2 e^{-mv^2/(2kT)}$$

$$v = \left(\frac{8kT}{\pi m}\right)^{1/2} \qquad v_p = (2kT/m)^{1/2}$$

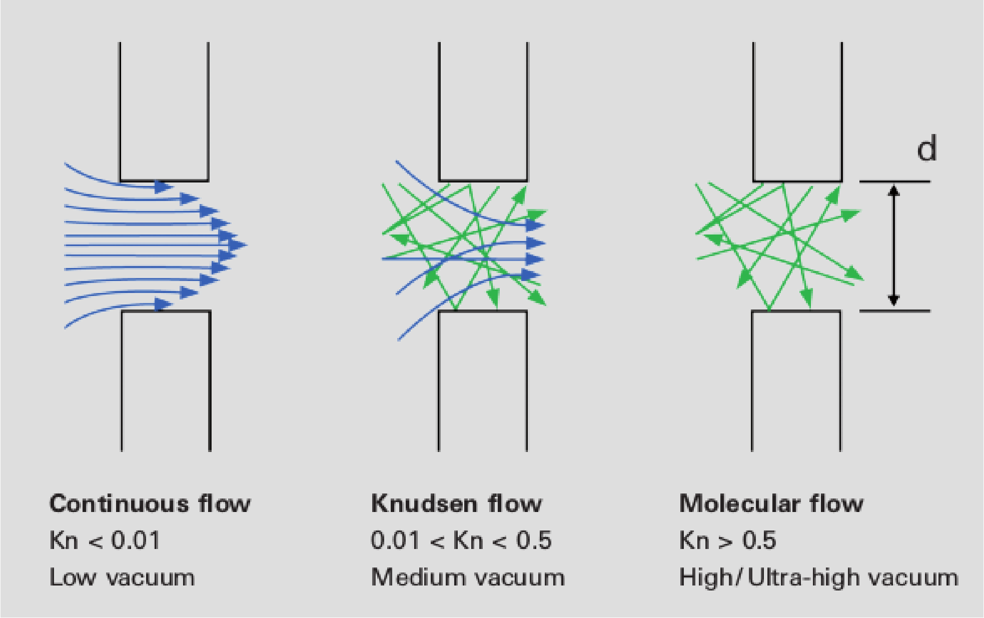
v -mean average velocity, v_p – peak velocity
N – total number of particles
T – absolute temperature
m – particle mass
k – Boltzmann constant

J. F. O`Hanlon, A users guide to vacuum Technology, WILEY, 2003

Flow Regimes

$Kn = l/d$

l – mean free path [m]
d – Diameter of flow chanel [m]
Kn - Knudsen number dimensionless



Flow Regimes

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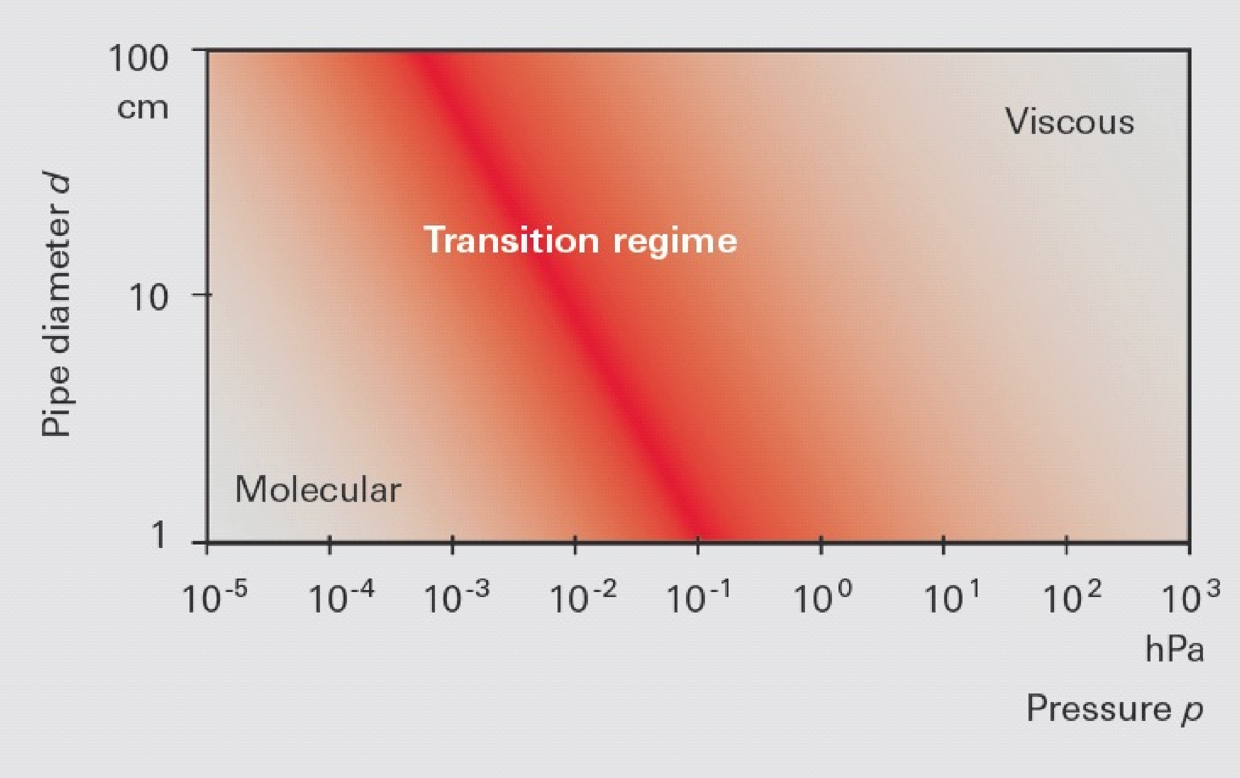
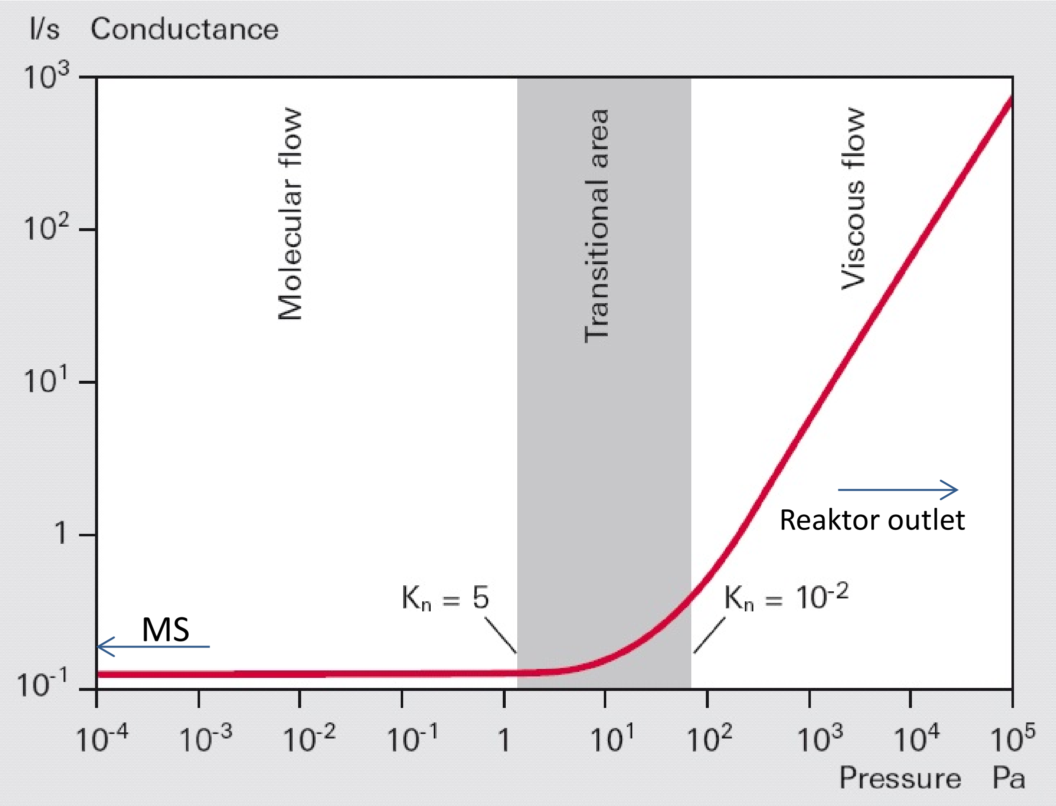


Flow Regimes

$Kn = l/d$ Gass flowing through piping produces a pressure difference at the ends of the piping:



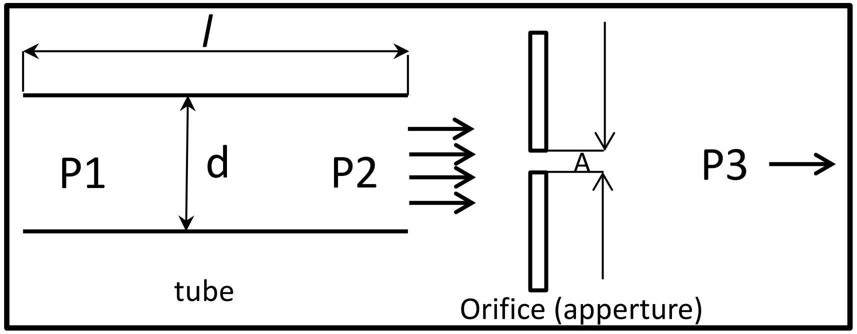
$$C = Q/P_2 - P_1$$

C – conductance [m^3/s]

Q – throughput d(PV)/dt [Pa*m^3/s]

P_2-P_1 – pressure drop at the ends of the pipe

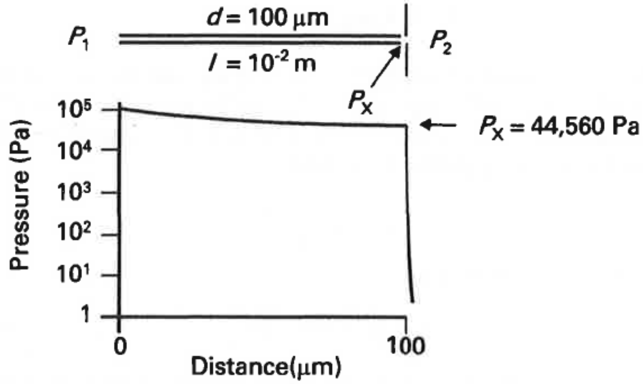
Inlet System



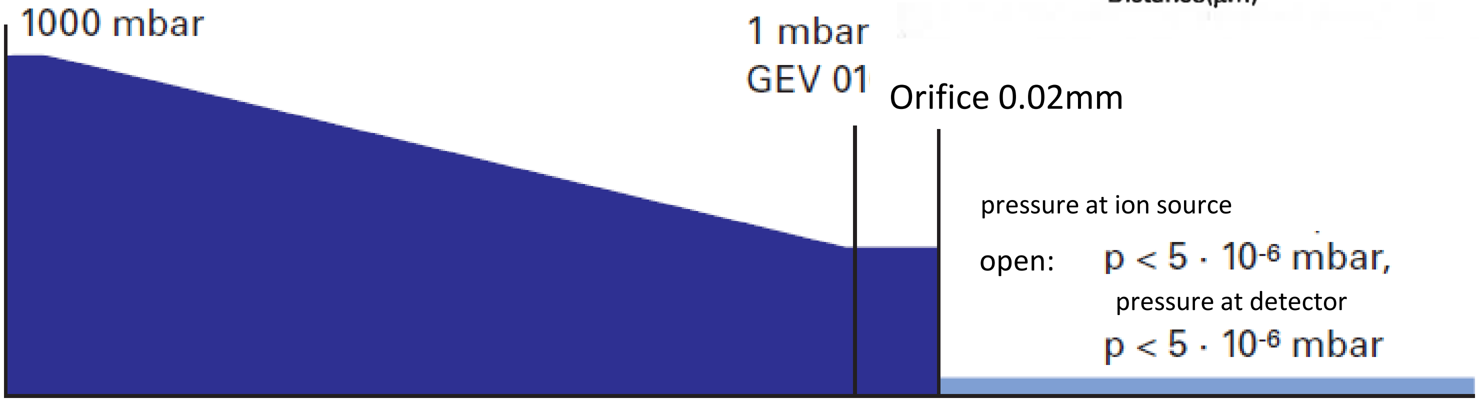
$$Qor, mol = A \cdot \frac{\bar{v}}{4} \cdot (p1 - p2) = A \cdot \sqrt{\frac{kT}{2\pi m_0}} \cdot (p1 - p2)$$

$$Qpipe, mol = \frac{\pi \cdot d^4}{256\vartheta \cdot l} \cdot (p1 + p2) \cdot (p1 - p2)$$

ϑ – viscosity
$\bar{v}$ – mean thermal velocity, (peak velocity v_p)



Continues pressure reduction through the capillary d=0.15mm. L=1.5m



Orifice 0.02mm

pressure at ion source

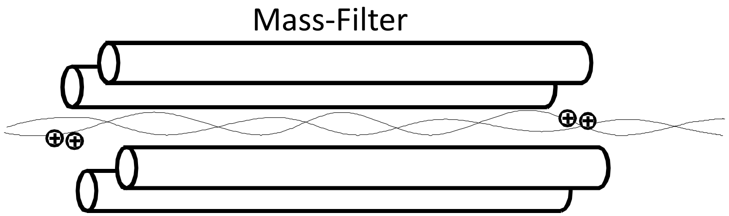
open: $p < 5 \cdot 10^{-6}$ mbar,

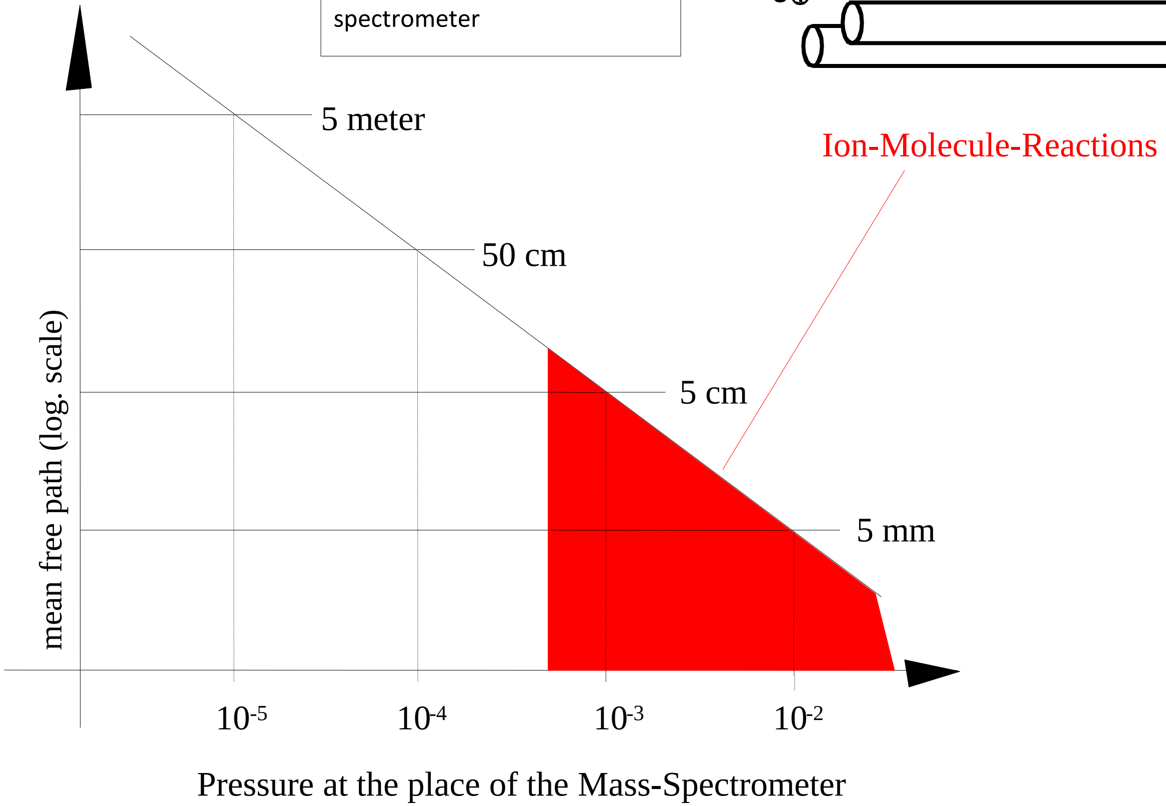
pressure at detector

$p < 5 \cdot 10^{-6}$ mbar

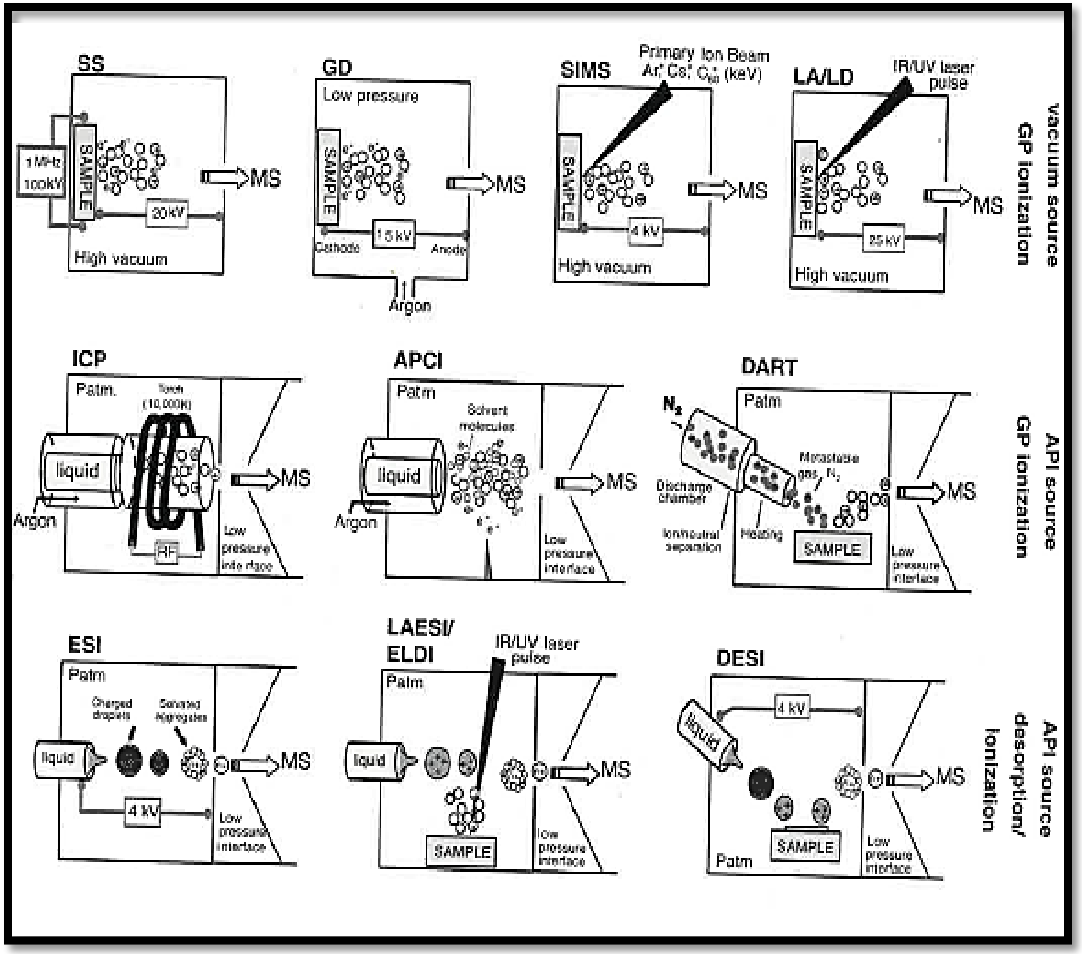
Why is it necessary to work under vacuum?

mean free path has to be much larger than the dimensions of the mass-spectrometer

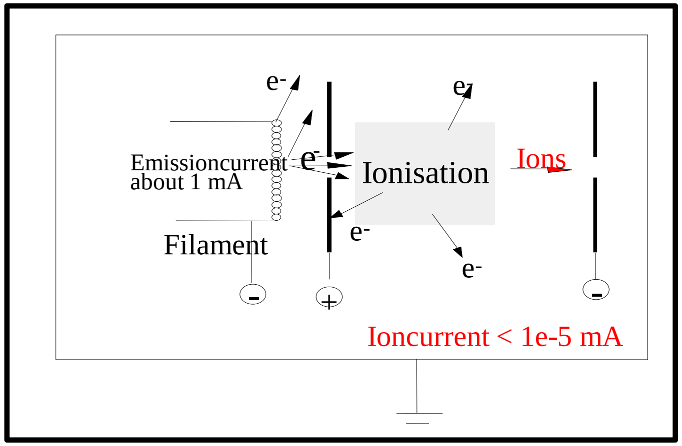




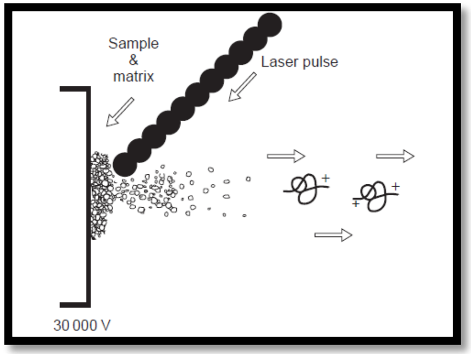
Ionization



EII

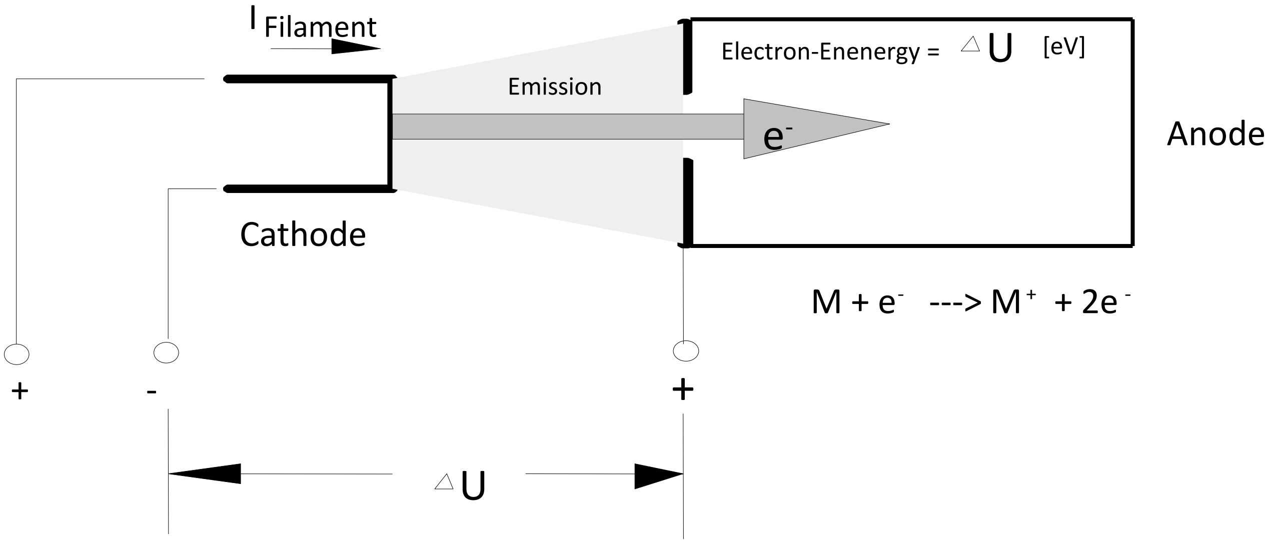


MALDI



Characterization of solid materials and heterogeneous catalysts, Ed. M. Che, J.C. Vedrine; Wiley-VCH, 2012

Ionization (Electron Impact Ionization)



$M + e^- \rightarrow M^+ + 2e^-$

The emission is a function of the filament temperature, the material (work-function), the applied voltage and the geometry (local field strength).

The filament is heating up the ion source by radiation, take the vapour pressure of the material into account!

W_{Re}=4.72 eV, W_W=4.55 eV, W_Y=3.1 eV, W_{Th}=3.4 eV, W_{Ir}=5.00-5.67 eV,

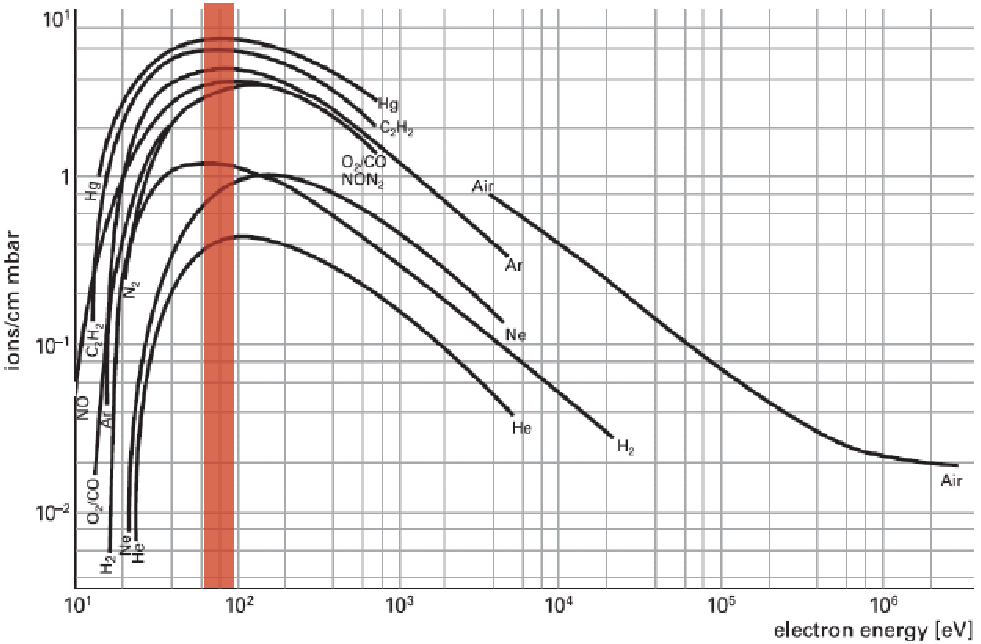
Ionization

Filament materials

Rhenium:	rather high vapour pressure used mainly in High Vacuum
Tungsten	used in the UHV, has a longer lifetime than Rhenium, Tungsten gets brittle WC_x
Yt-Oxide on Iridium replaced thoriated Iridium	rather resistant against air, temperature is much lower compared to pure metall

Ionization

- Small fraction of sample is converted in ionized state (0.1%)
- 20% of all ions are extracted from the ionisation chamber
- Collision enrgy influences the number and type of ions (50-150eV)



60-100 eV

$$I\left[\frac{ion}{sec}\right] = \alpha\left[\frac{ion}{molec}\right]\cdot\rho\left[\frac{molec}{cm^2 sec}\right]\cdot S_{ef}\,[cm^2]$$

α – fraction of the molecules which has been undergone ionization and reached collector i.e.

$\alpha = \omega_1 \cdot \omega_2 \cdot \omega_3$

ω_1- probability that the molecule reaches the ionization zone

ω_2- probability of the ionization of the molecule in the ionization zone

ω_3- probability that the formed ion reaches collector

ρ – molecules flux through the effective area S_{ef}

k – Instrument sensitivity

n – molecules/cm^3

σ – ionization cross section, Å^2

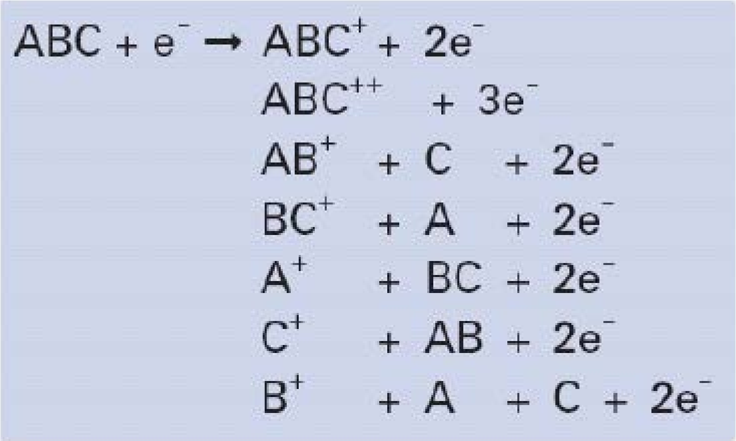
I = k *n *σ

Ionization

Electron-Impact Cross Sections for Ionization at 60eV

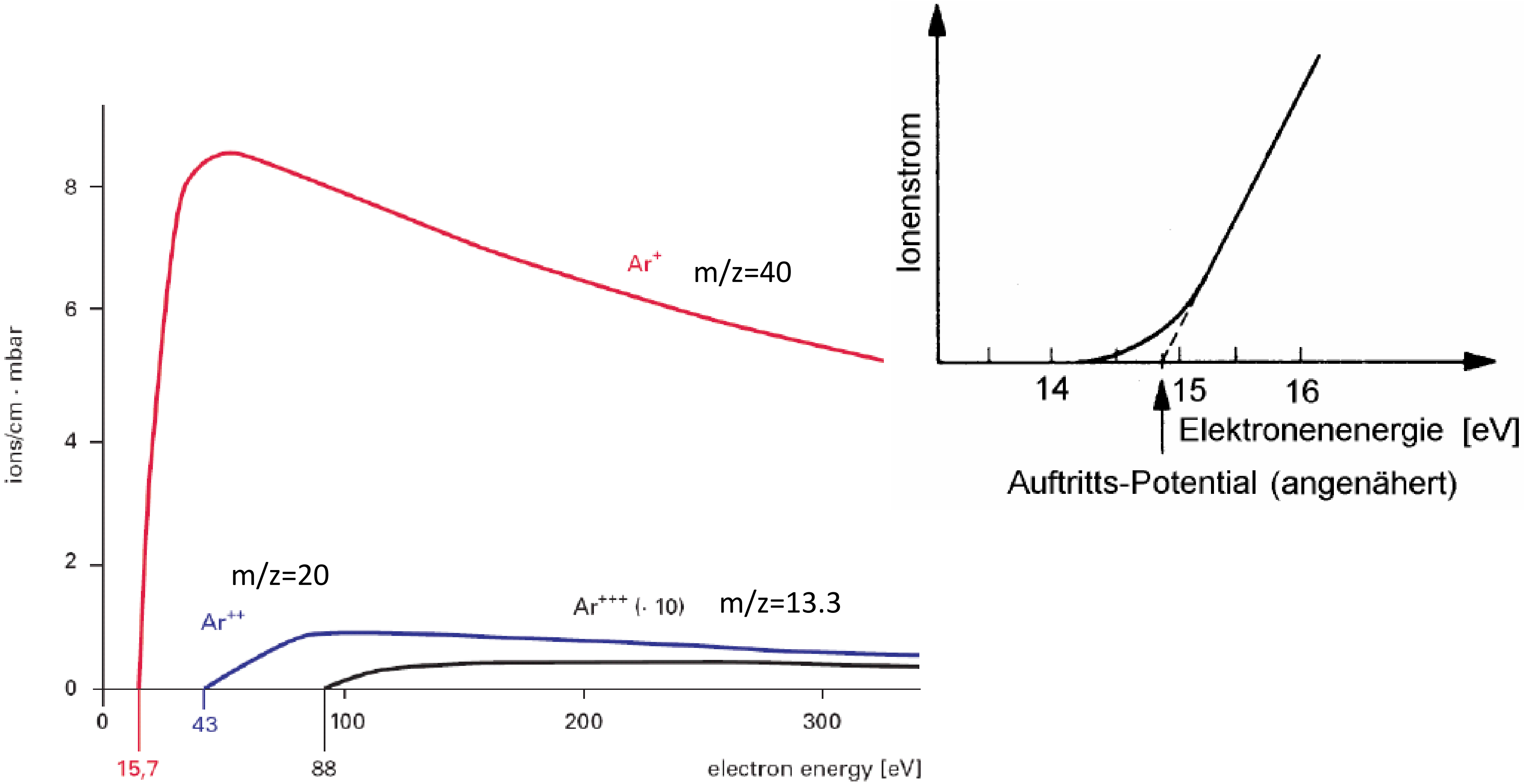
Molecule / ion	σ, Å²
H_2	1.015
N_2	2.381
O_2	2.287
CO	2.395
CO^+	0.813
CO_2	3.317
CH_4	3.471
CH_4^+	0.964
CH_3^+	0.951
N_2O	3.513

$$^{40}Ar + 1e^- \rightarrow {}^{40}Ar^+ + 2e^-$$
$$\rightarrow {}^{40}Ar^{2+} + 3e^-$$
$$\rightarrow {}^{40}Ar^{3+} + 4e^-$$



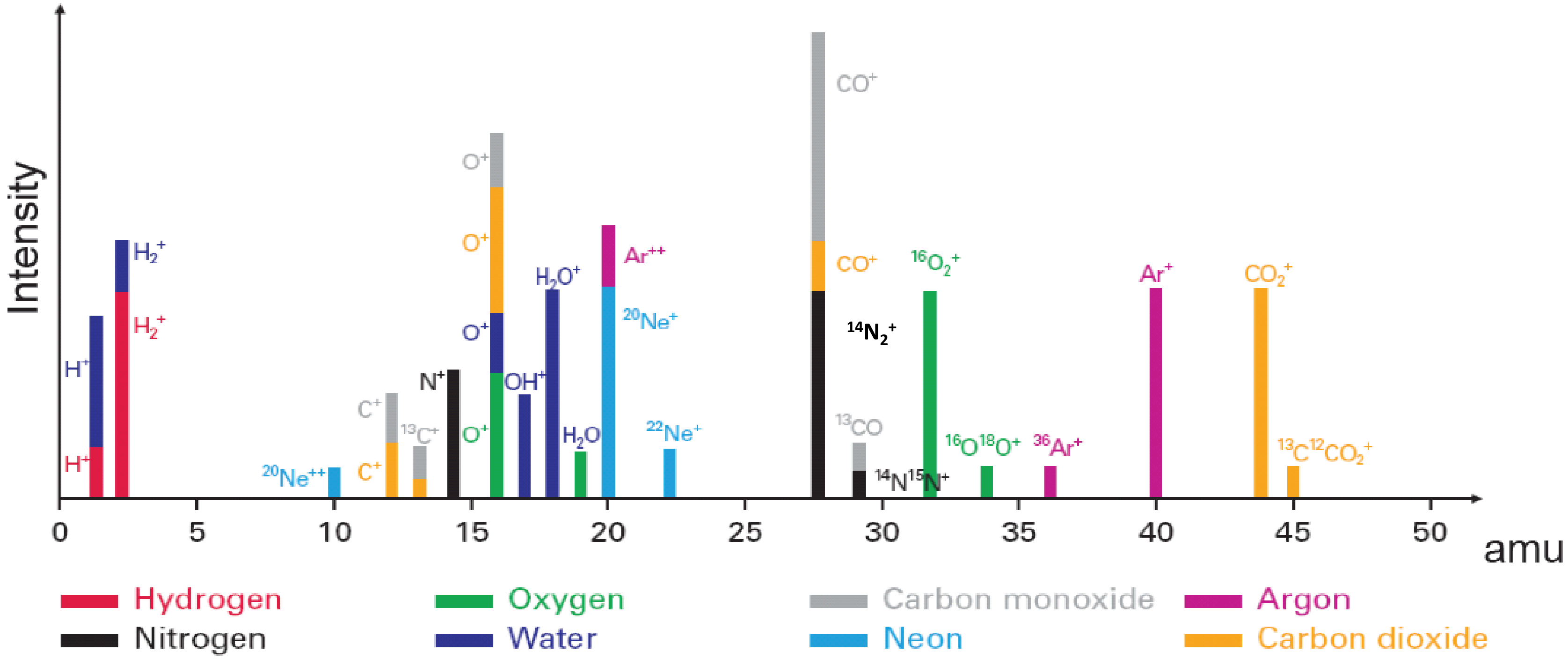
$$\begin{aligned} ABC + e^- \rightarrow\ & ABC^+ + 2e^- \\ & ABC^{++} + 3e^- \\ & AB^+ + C + 2e^- \\ & BC^+ + A + 2e^- \\ & A^+ + BC + 2e^- \\ & C^+ + AB + 2e^- \\ & B^+ + A + C + 2e^- \end{aligned}$$

Ionization

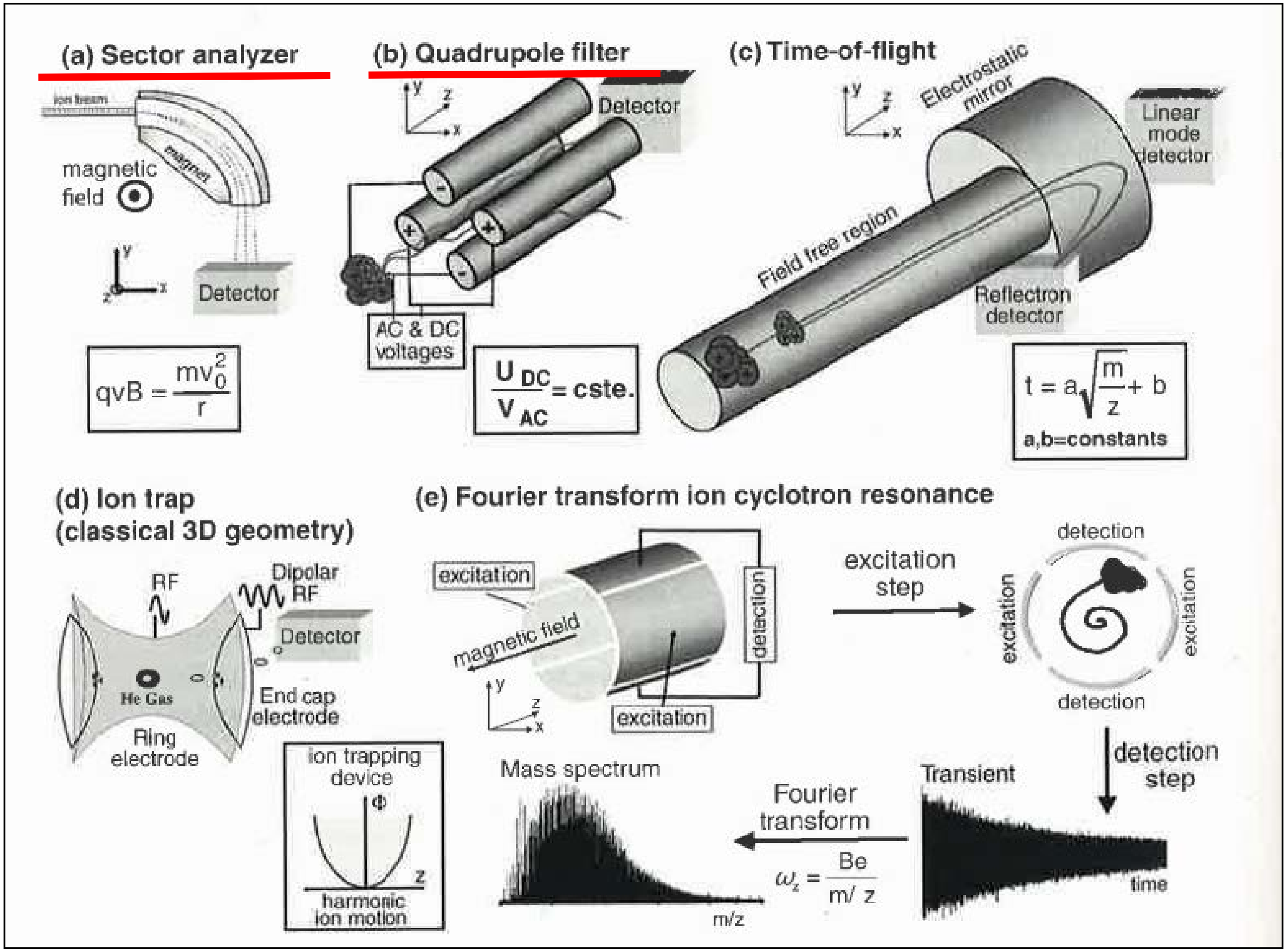


- Decreasing of electron energy in order to reduce overlapping signals from fragments
- HF^+/Ar^{++}, m/z =20, I_{ion} 14eV/43eV
- Multiple charged fragments cause the signals on non-integer mass/charge ration Ar^{3+}

Ionization


Intensity
H+
H+
H2+
H2+
20Ne++
C+
C+
13C+
N+
O+
O+
O+
O+
OH+
H2O+
H2O
Ar++
20Ne+
22Ne+
CO+
CO+
14N2+
13CO
14N15N+
16O2+
16O18O+
36Ar+
Ar+
CO2+
13C12CO2+
0
5
10
15
20
25
30
35
40
45
50
amu
Hydrogen
Nitrogen
Oxygen
Water
Carbon monoxide
Neon
Argon
Carbon dioxide

Mass separation



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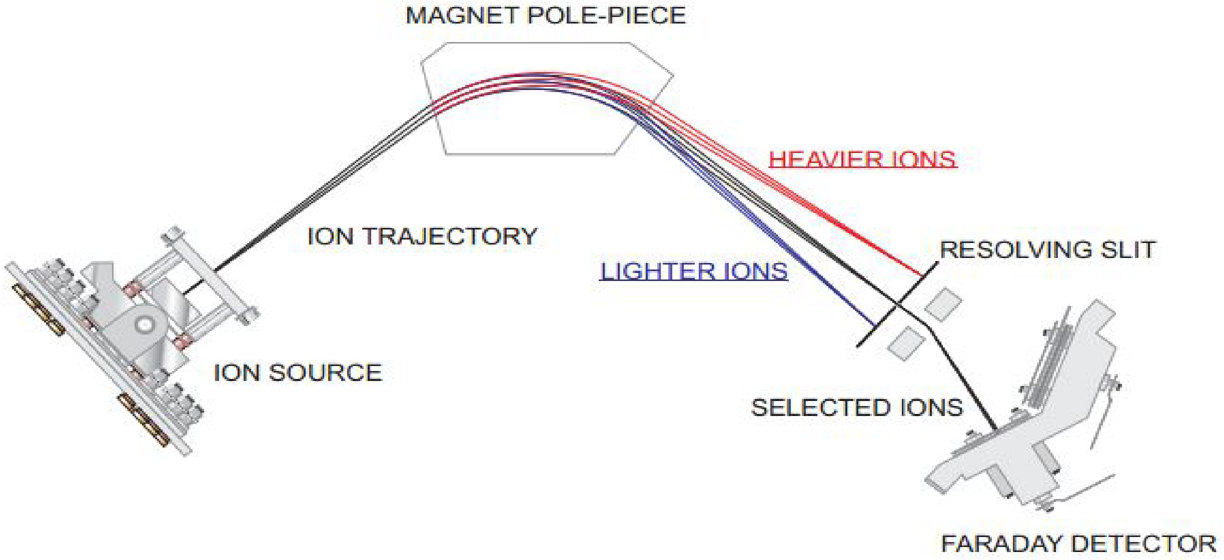
Mass separation

Magnetic sector mass anlyzer



$E_k = E_i$ $\quad$ $\frac{M \cdot v^2}{2} = q \cdot U$ $\quad$ Kinetic energy of ions is determined by the accelerating potential (1.5 – 15kV)

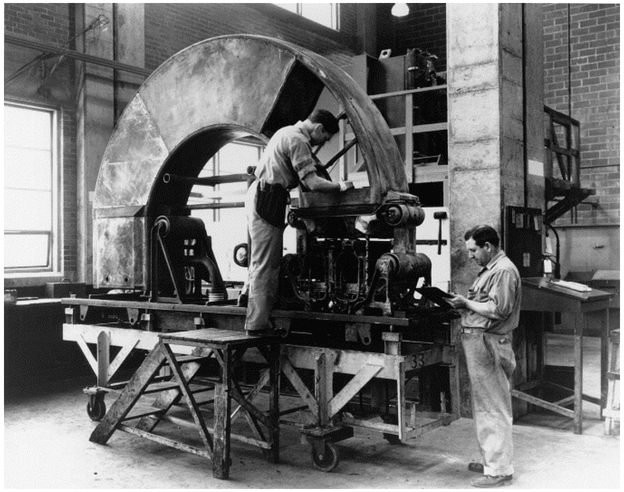
$F_L = F_C$ $\quad$ $\frac{M \cdot v^2}{R} = q \cdot v \cdot H$ $\quad$ Lorenz force is in equilibrium with centrifugal force

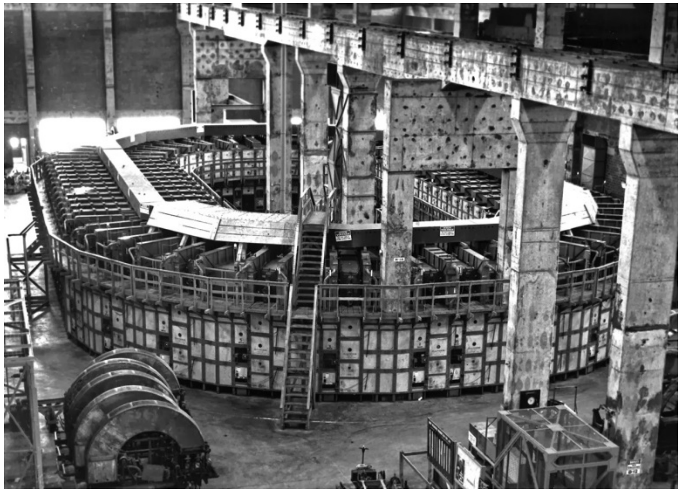
Hence: $\frac{M}{q} = \frac{R^2 \cdot H^2}{2 \cdot U}$ $\quad$ The trajectory radius remains constant e.g. 200mm. To detect the definite M/z one varies the magnetic field induction.

Mass separation

Magnetic sector mass anlyzer

Manhattan projekt (1942-1946)





Calutron

Uranium enrichment

^{238}U 99.2%, ^{235}U 0.72%

$^{238}UF_5^+$ m/z 328

$^{235}UF_5^+$ m/z 325

Reactor grade 3-4% U-235

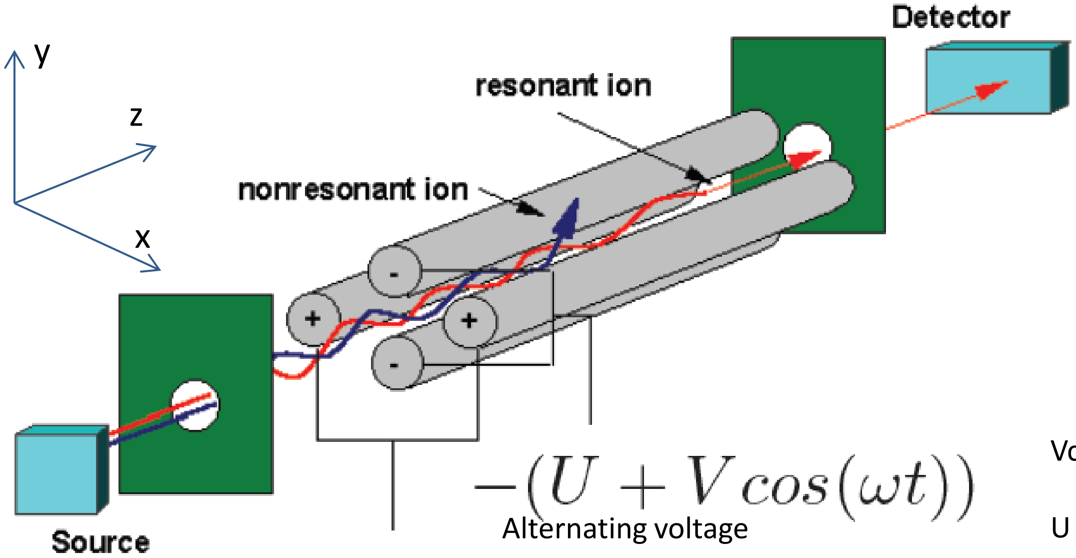
Weapon grade 90% U-235

Later on in Soviet Russia (1969 – 1972)

MS1301

High temperature mass spectrometer for the analysis of the gas phase over hard volatile substances, namely oxides.

Mass separation Quadrupole analzyer



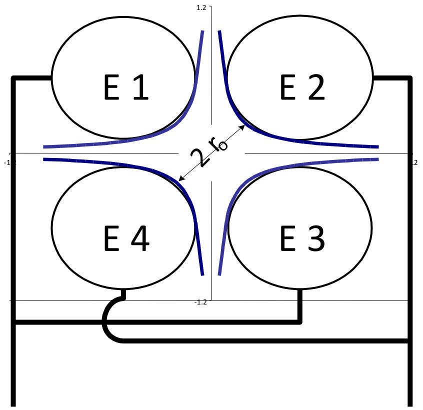
$-(U + V\cos(\omega t))$

Alternating voltage

$(U + V\cos(\omega t))$

Vcos(ωt) - alternating voltage

U - direct voltage



+(U + V cos ω t)

-(U + V cos ω t)

$$\Phi = (U + V\cos\omega t)(x^2 - y^2)/r_0^2$$

Potential between the electrodes

Ex=dΦ/dx Ey=dΦ/dx Ez=dΦ/dz

eE=ma

$$m\ddot{x} + 2e(U + V\cos\omega t)\frac{x}{r_0^2} = 0$$

$$m\ddot{y} - 2e(U + V\cos\omega t)\frac{y}{r_0^2} = 0$$

$$m\ddot{z} = 0$$

Mass separation Quadrupole analzyer

Use of the transformations

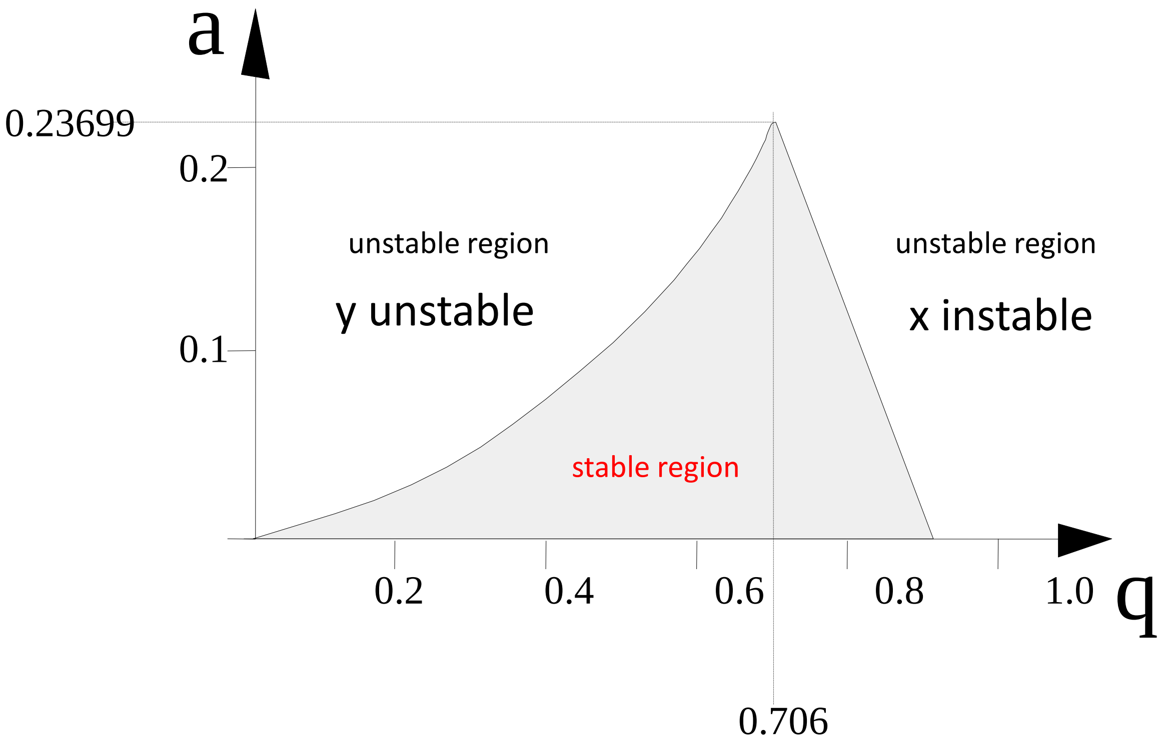
$$a = \frac{8eU}{mr_o{}^2\omega^2} \qquad q = \frac{4eV}{mr_o{}^2\omega^2} \qquad \omega t = 2\xi$$

gives the following differential equations (Mathieu‘s equations)

$$\begin{cases} \dfrac{d^2x}{dt^2} + (a + 2q\cos 2\xi)x = 0 \\ \dfrac{d^2y}{dt^2} - (a + 2q\cos 2\xi)y = 0 \\ \dfrac{d^2z}{dt^2} = 0 \end{cases}$$

Describes the motion of charged particle in the quadrupole field

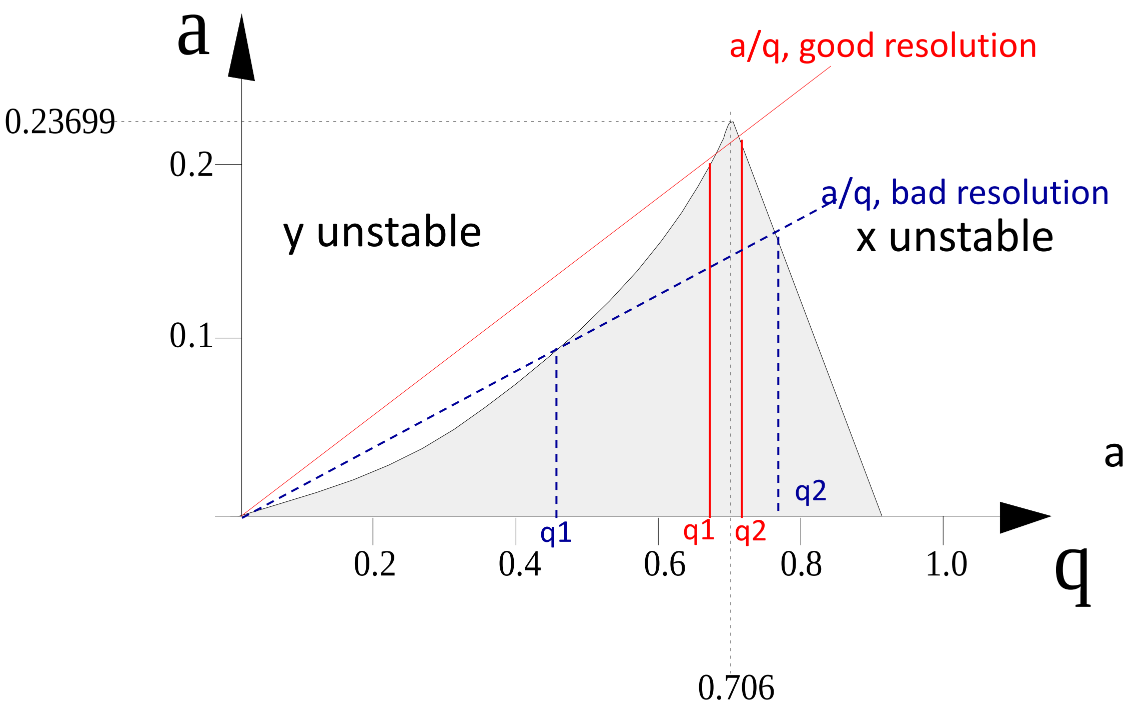
Mass Filter stability diagram



$$a = \frac{8 * e * U}{m * r_0^2 * \omega^2}$$

$$q = \frac{4 * e * V}{m * r_0^2 * \omega^2}$$

Mass separation Quadrupole analzyer



$$a = \frac{8 * e * U}{m * r_0^2 * \omega^2}$$

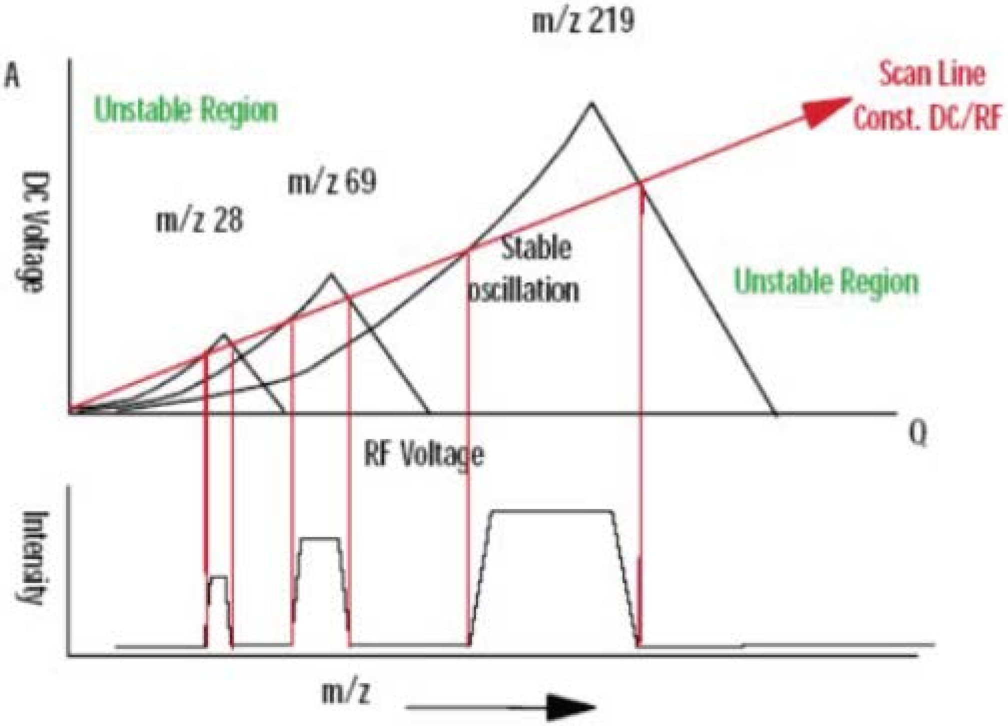
$$q = \frac{4 * e * V}{m * r_0^2 * \omega^2}$$

a/q=2U/V=const=0.1768

- The ratio a/q (which is proportional to U/V) is kept constant and the absolute values of U and V are increased.
- For a/q< 0.1678 (which is the top of the stability-diagram) the stability region is entered periodically for the different masses.
- The slope a/q determines the mass resolution.

$$m_1 = \frac{4eV}{r_0^2\omega^2 q_1} > m > m_2 = \frac{4eV}{r_0^2\omega^2 q_2}$$

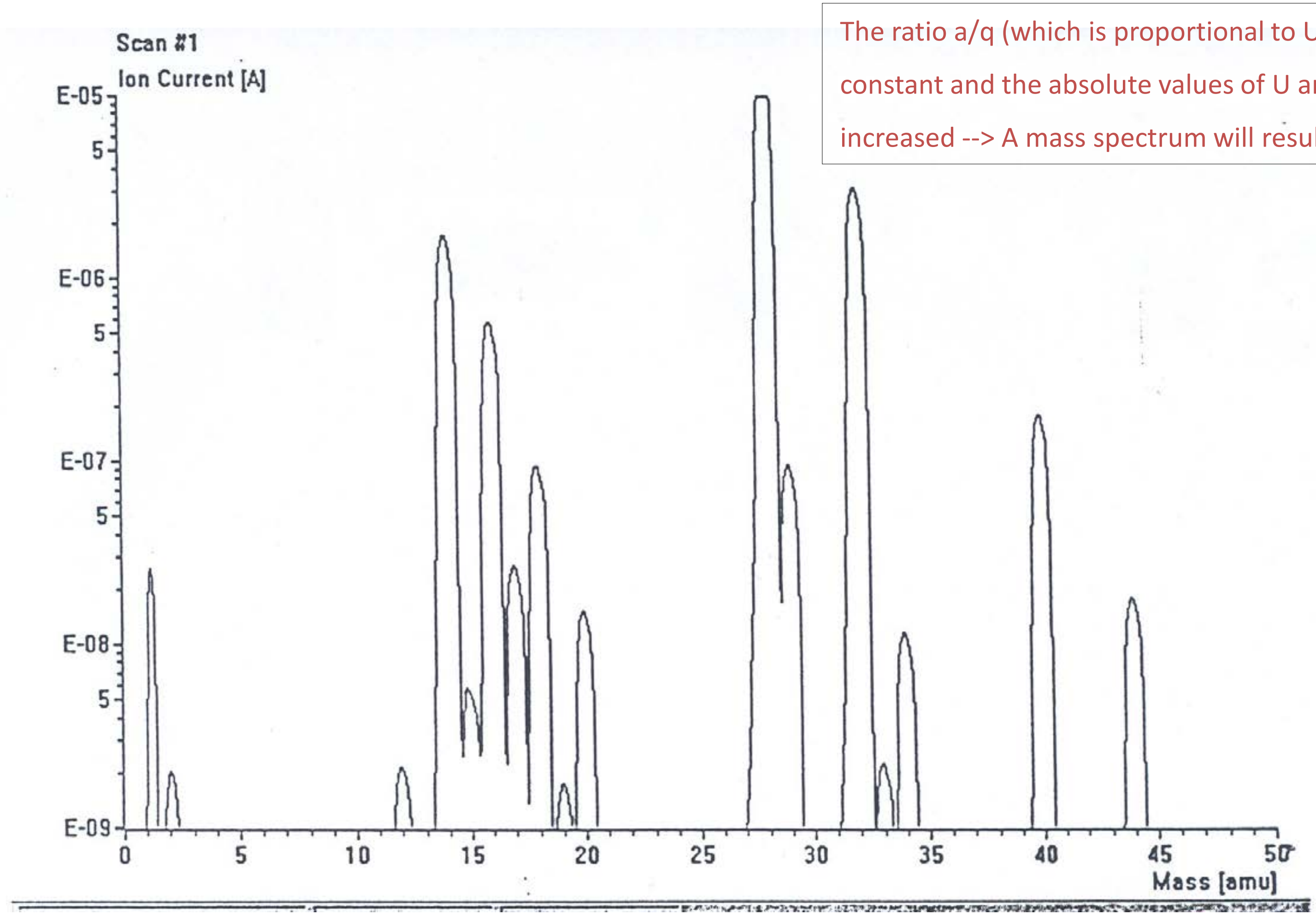
Mass separation Quadrupole analzyer



- Scanning the U/V amplitude ratio gives a mass spectrum
- The scan parameters determine the resolution and transmission
- Lower resolution at higher masses

Mass separation Quadrupole analzyer

The ratio a/q (which is proportional to U/V) is kept constant and the absolute values of U and V are increased --> A mass spectrum will result

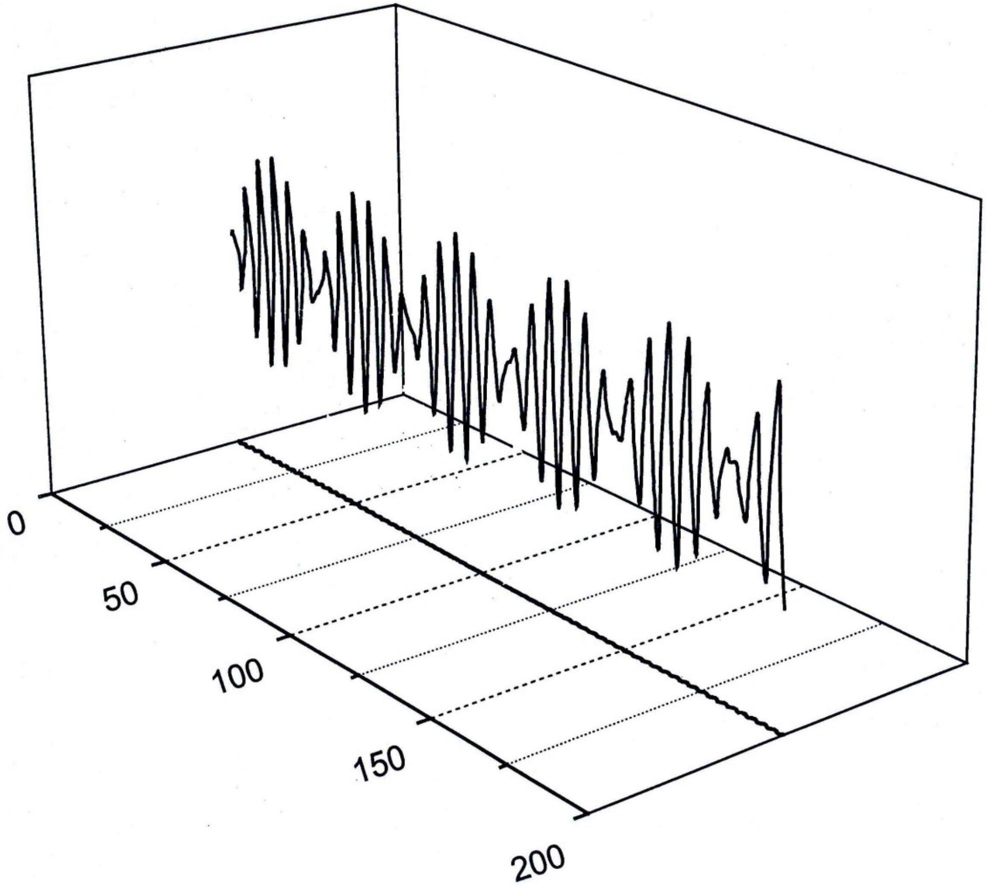


Mass separation

Quadrupole analzyer

Flight path of ions through the mass analyzer

→ Ion mass identical to set mass (transmission full)

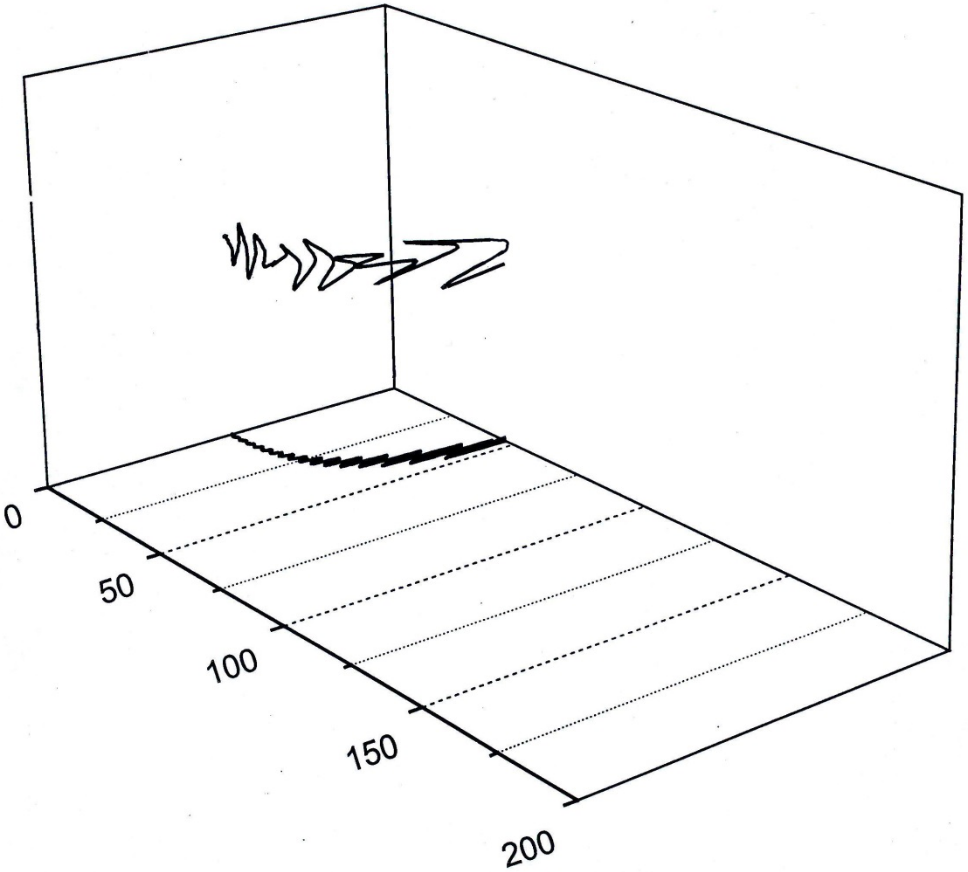


$$\begin{cases} \dfrac{d^2x}{dt^2} + (a + 2q\cos 2\xi)x = 0 \\ \dfrac{d^2y}{dt^2} - (a + 2q\cos 2\xi)y = 0 \\ \dfrac{d^2z}{dt^2} = 0 \end{cases}$$

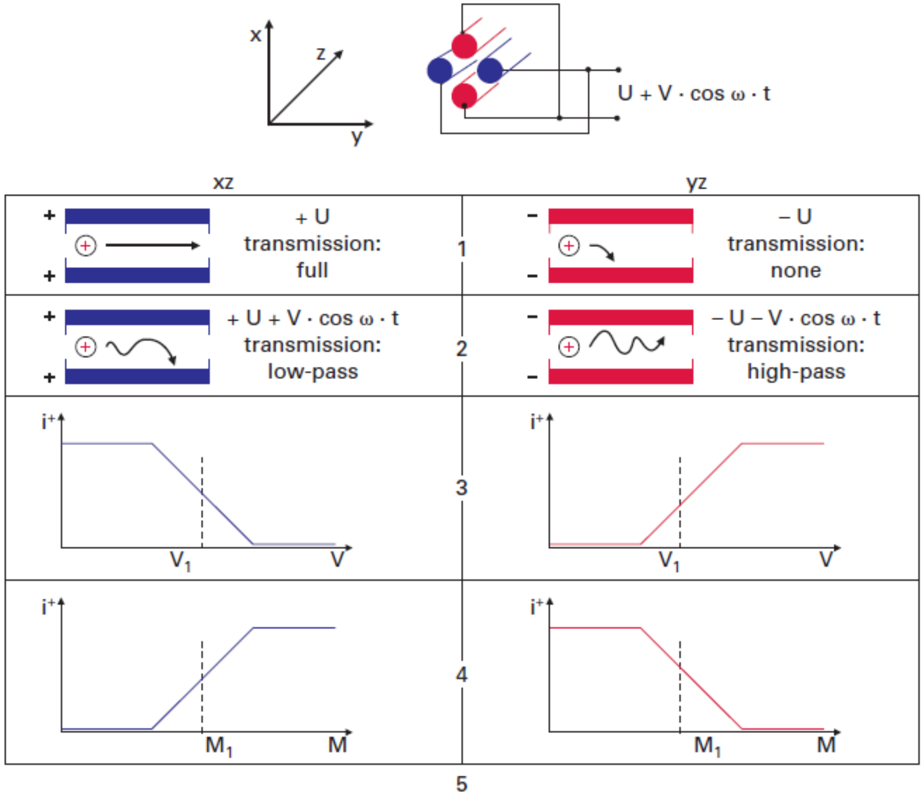
Quadrupole Mass Spectrometer

Flight path of ions through the mass analyzer

→ Ion mass higher than set mass (transmission none)



Mass separation Quadrupole analzyer



Ions reach the detector

ions are neutralized

Fixed M/q
V>V1 no transmission

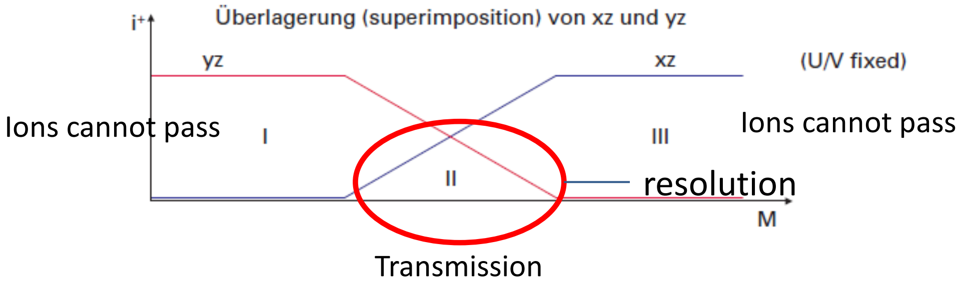
Fixed U/V
M>M1 transmission

ions are neutralized

ions reach the detector

Fixed M/q
V>V1 transmission

Fixed U/V
M>M1 transmission supressed



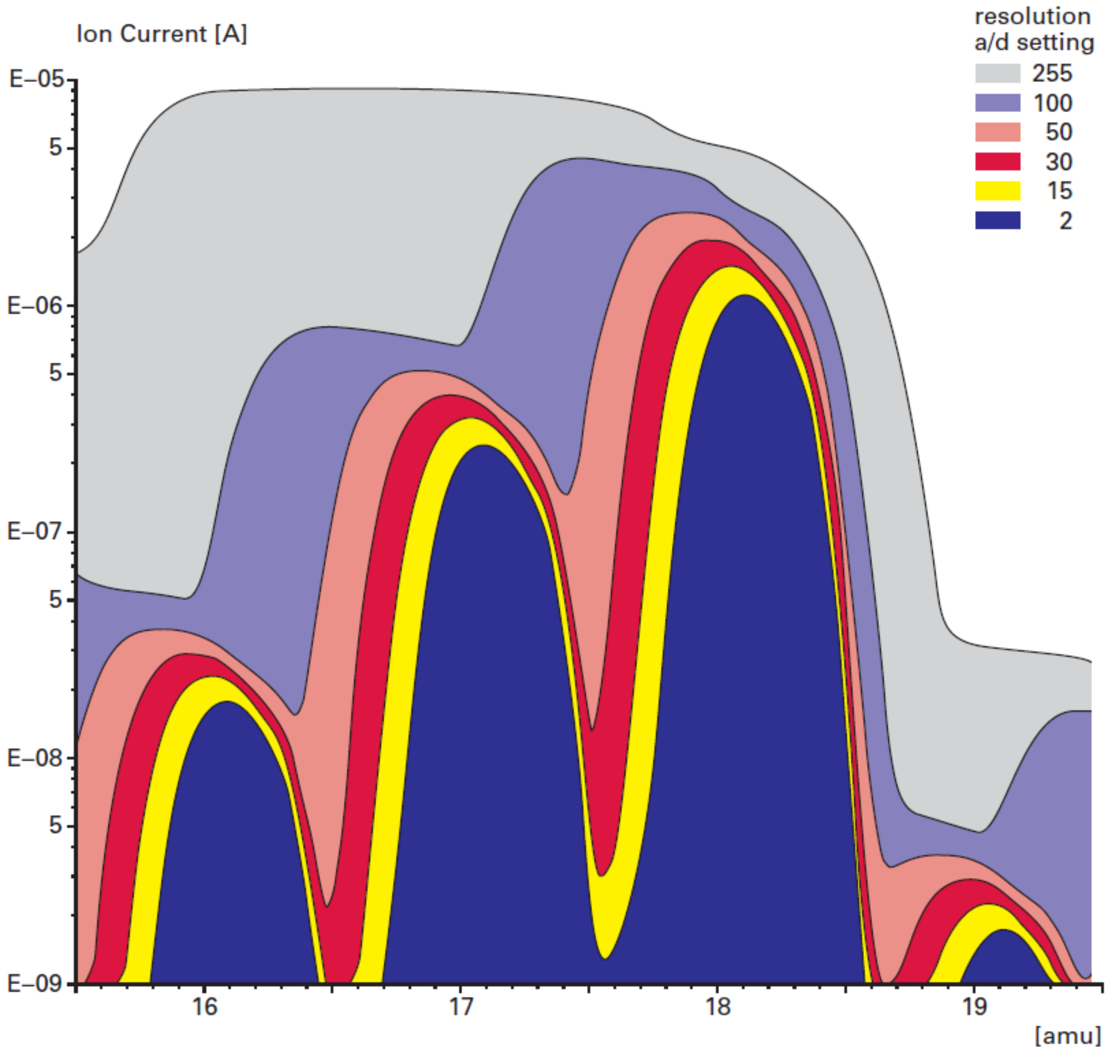
Ions cannot pass

Ions cannot pass

resolution

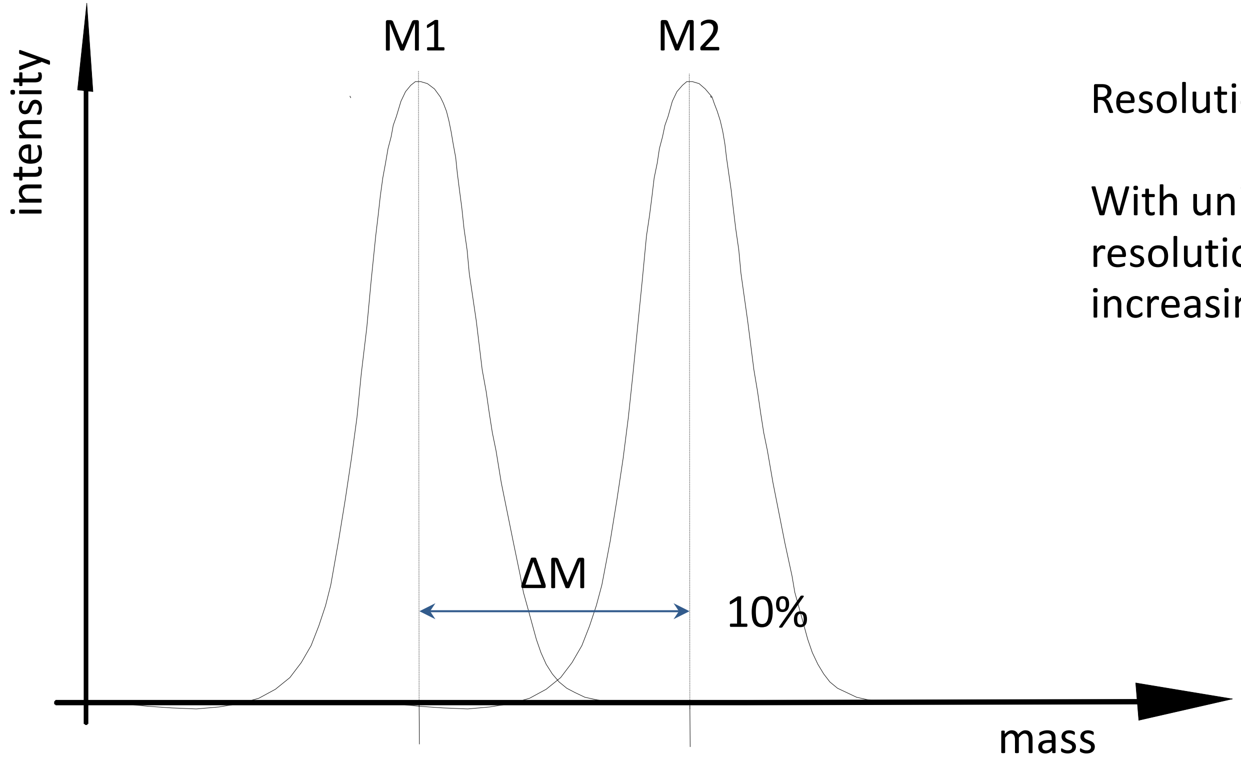
Transmission

Mass separation Quadrupole analzyer



Mass separation Quadrupole analzyer

Unit Resolution (Relative resolution on 10% peak high)



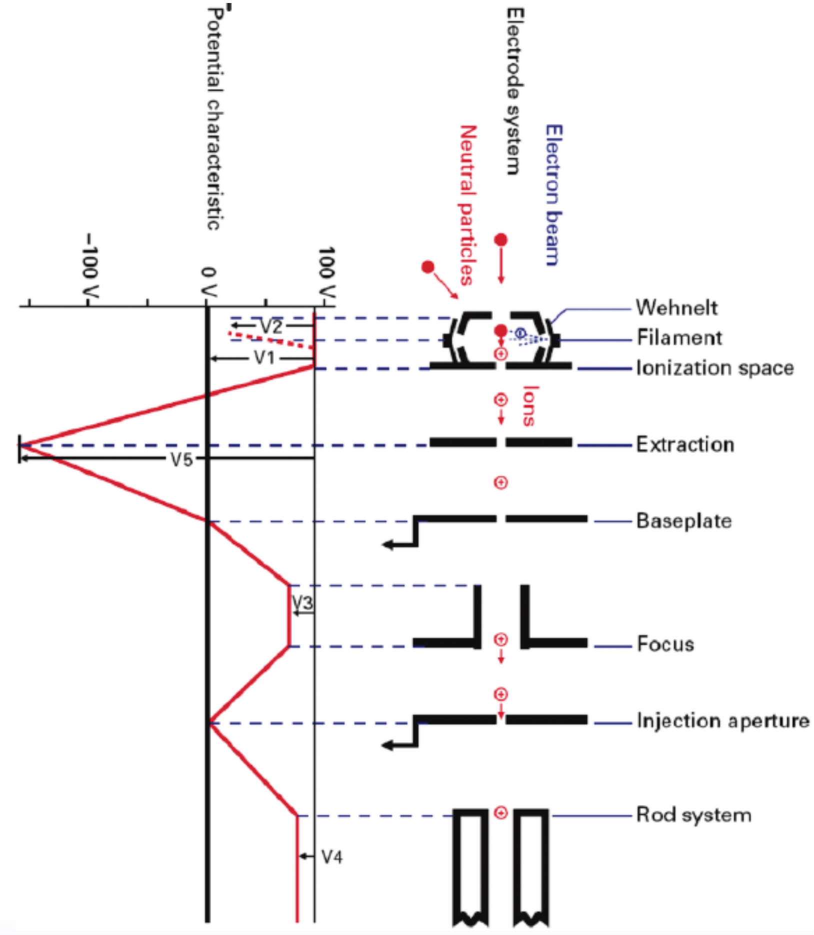
Resolution := M/△M

With unit resolution the resolution increases with increasing mass number

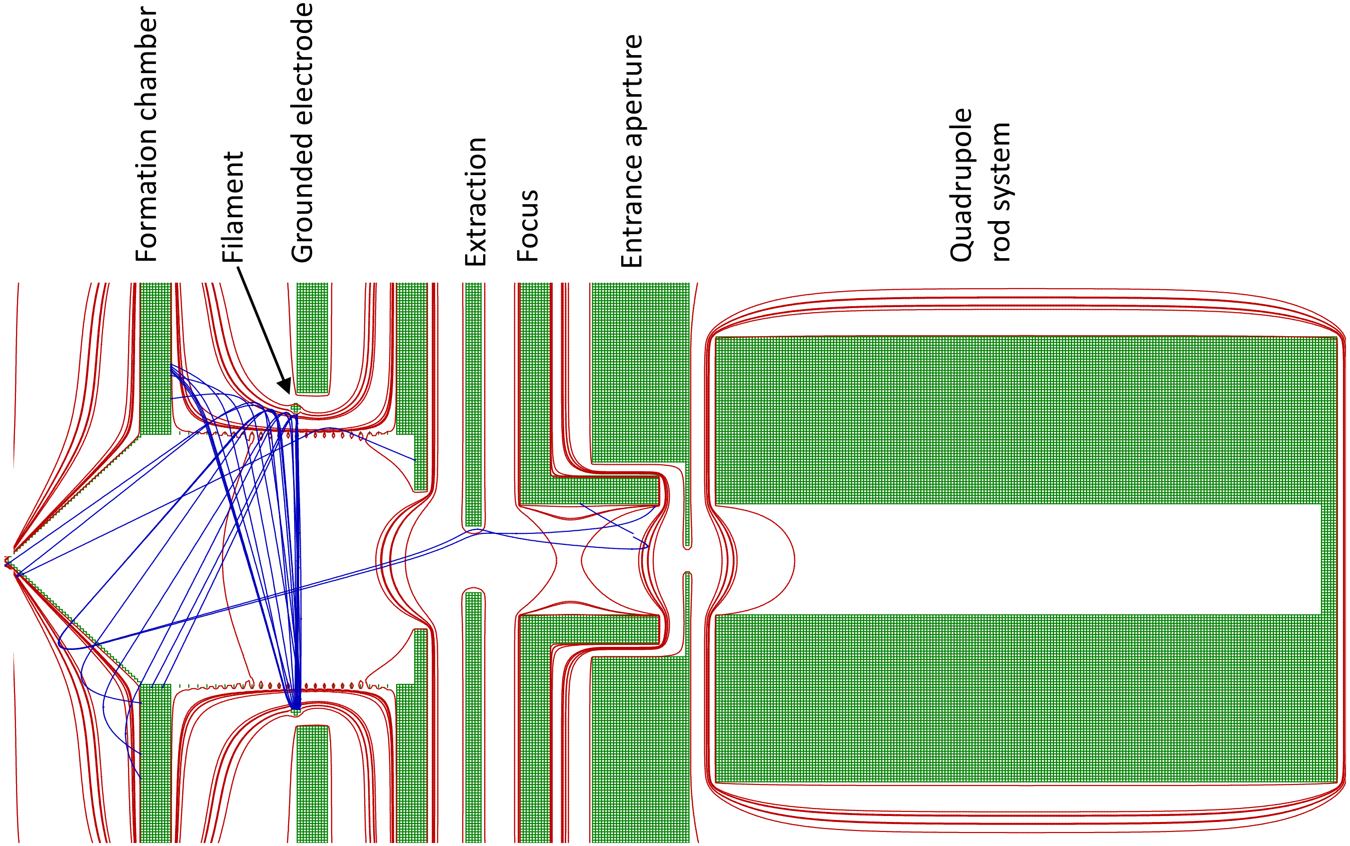
M_1/z 200 $^{200}Hg^+$, M_2/z 201, $^{201}Hg^+$, ΔM=1, Unit Resolution 200

Mass separation Quadrupole analzyer

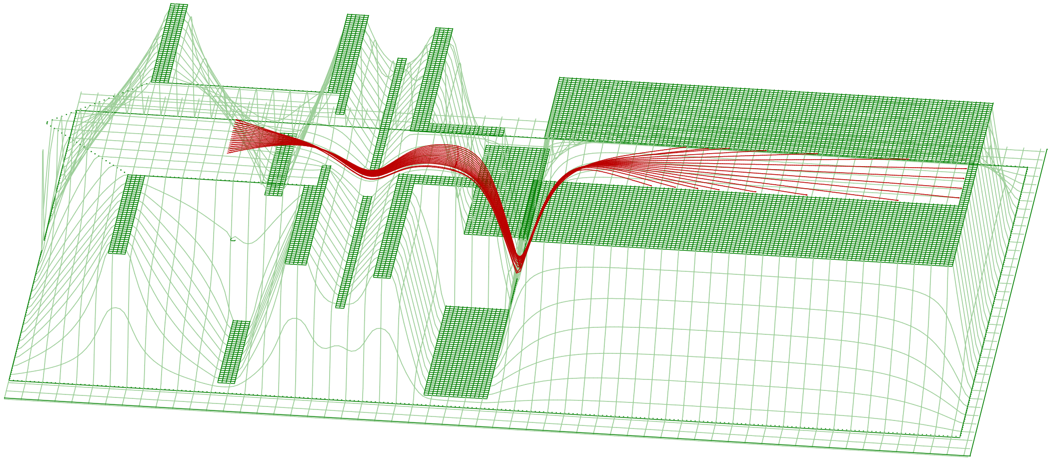
Axial ion source

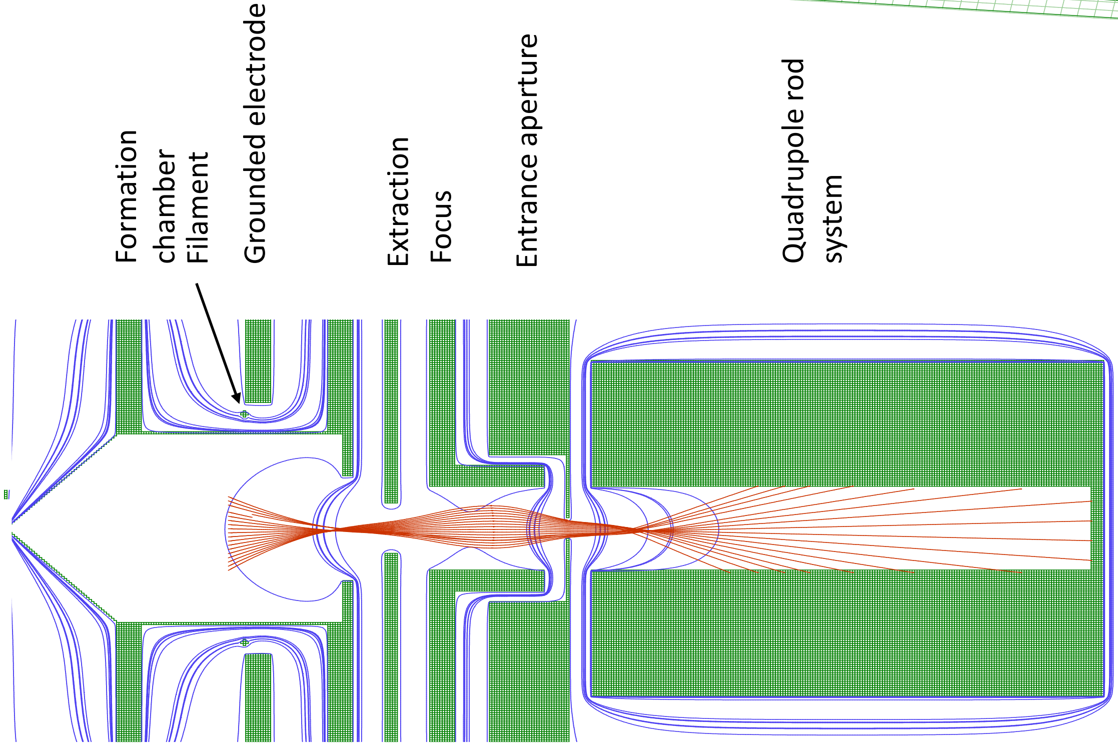


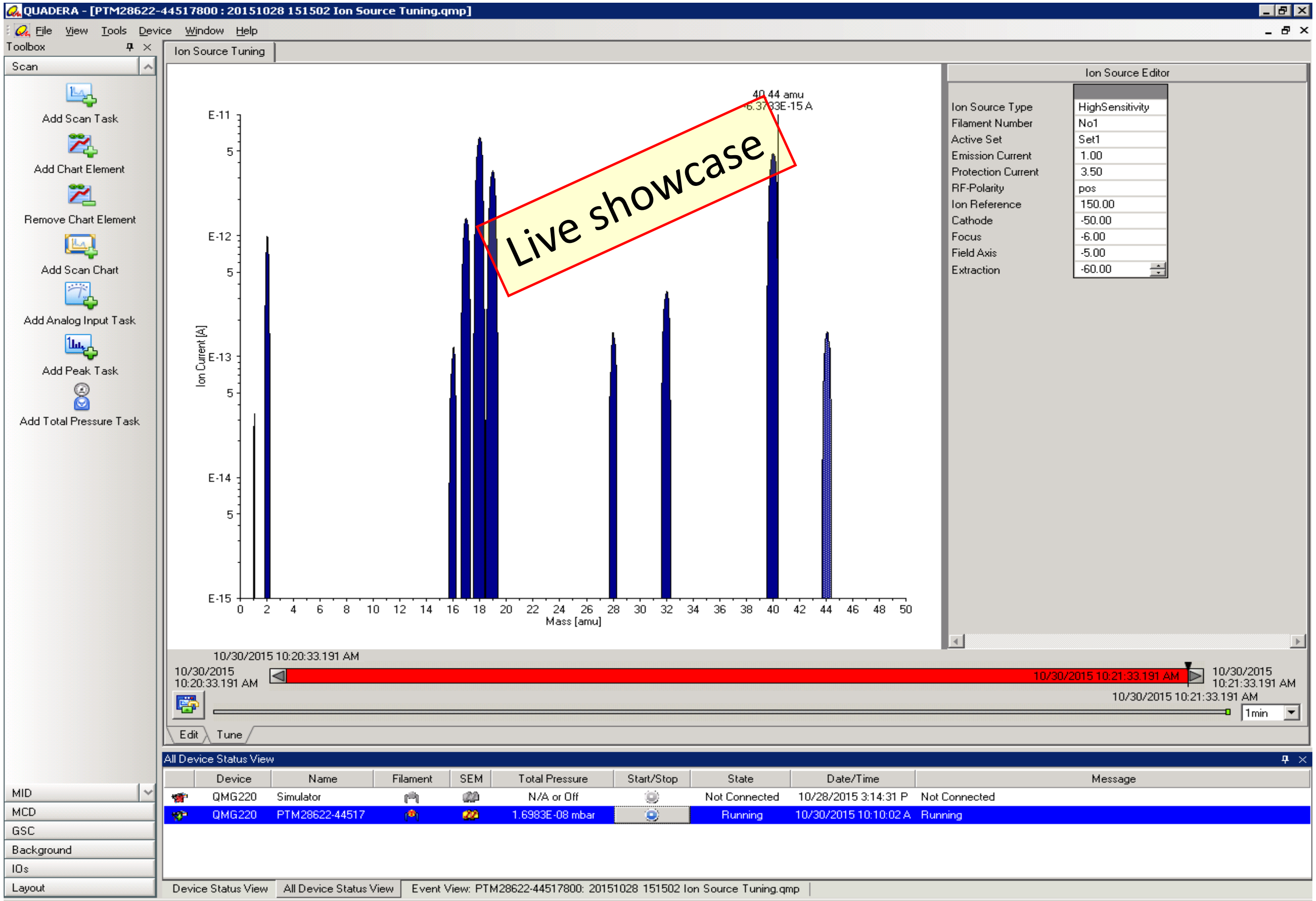
Flight paths of electrons



Flight paths of positive ions







Live showcase

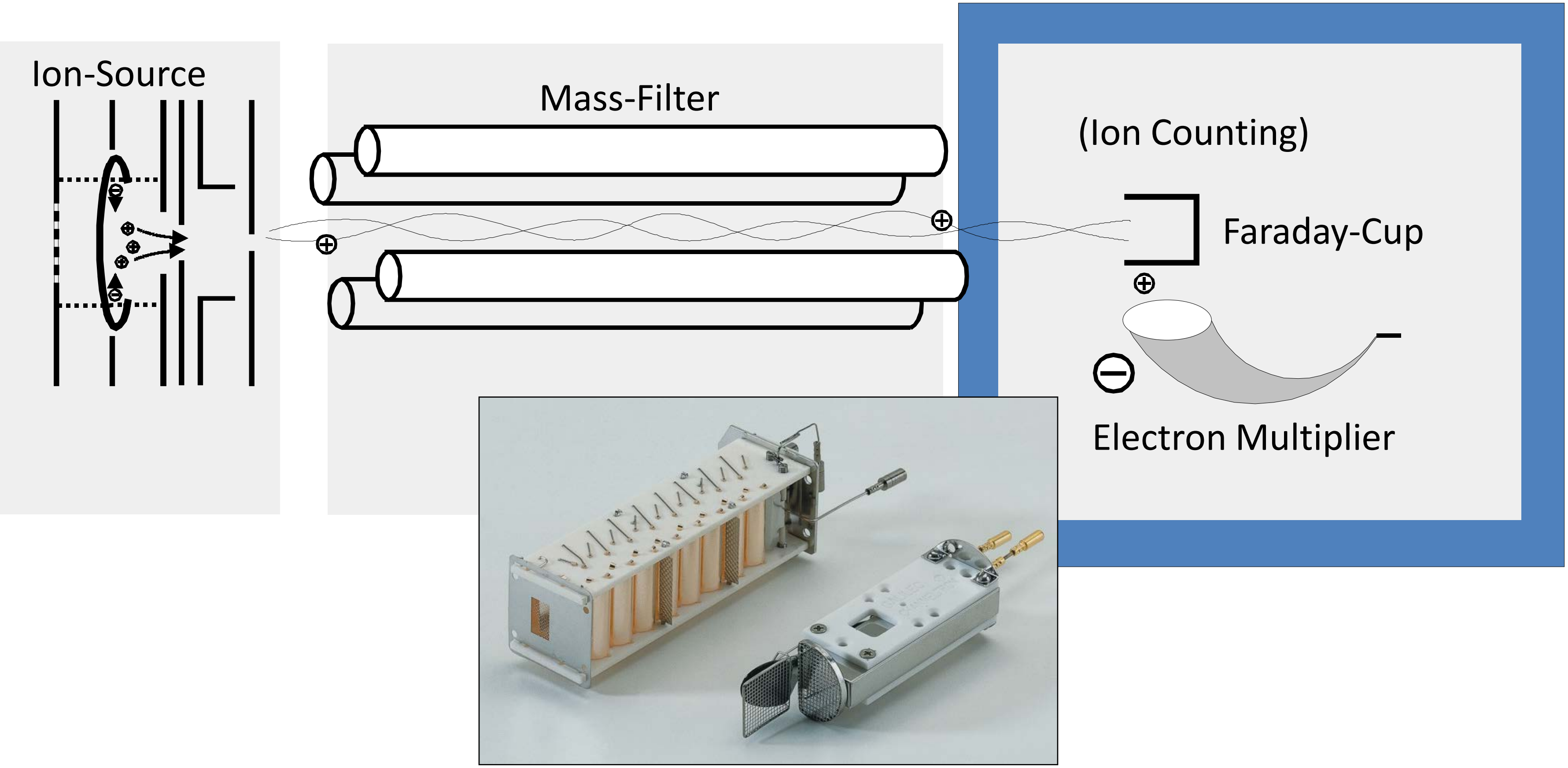
Ion Source Editor

Ion Source Type	HighSensitivity
Filament Number	No1
Active Set	Set1
Emission Current	1.00
Protection Current	3.50
RF-Polarity	pos
Ion Reference	150.00
Cathode	-50.00
Focus	-6.00
Field Axis	-5.00
Extraction	-60.00

All Device Status View

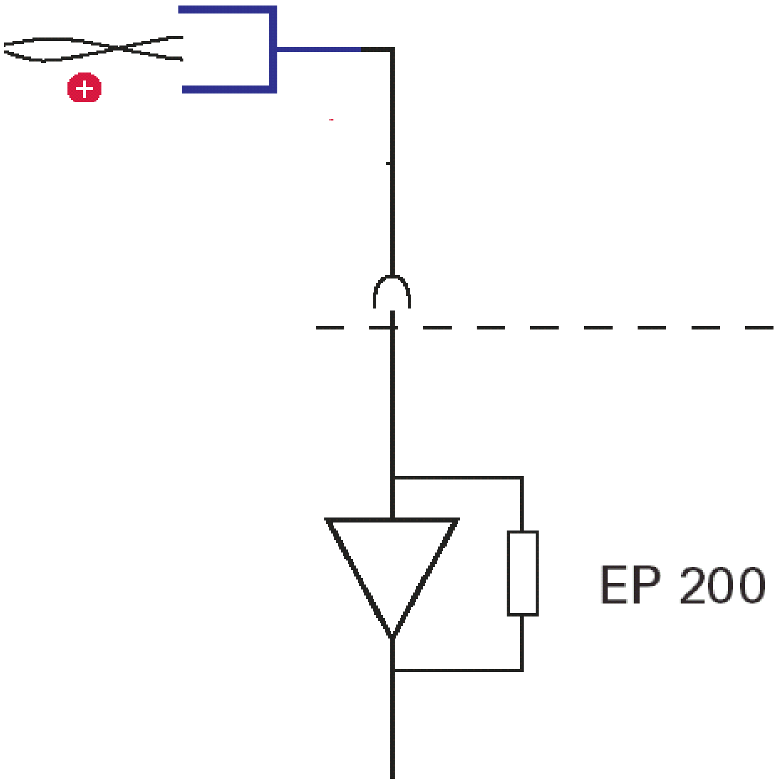
	Device	Name	Filament	SEM	Total Pressure	Start/Stop	State	Date/Time	Message
	QMG220	Simulator			N/A or Off		Not Connected	10/28/2015 3:14:31 P	Not Connected
	QMG220	PTM28622-44517			1.6983E-08 mbar		Running	10/30/2015 10:10:02 A	Running

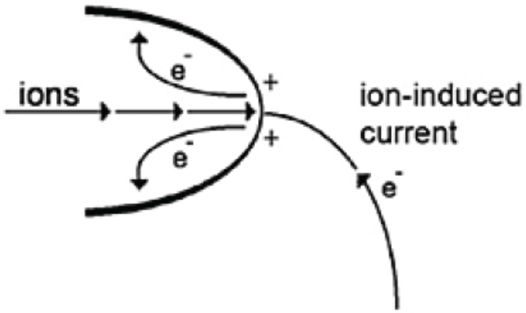
Detectors


Ion-Source
Mass-Filter
(Ion Counting)
Faraday-Cup
Electron Multiplier

Detectors

- Ions leaving the quadrupole mass spectrometer fly into a *Faraday-Cup* and give off their charge
- Charge is measured as a current by an electrometer amplifier
- Measurable currents are from 1E-15 to 1E-8 A


Faraday-Cup

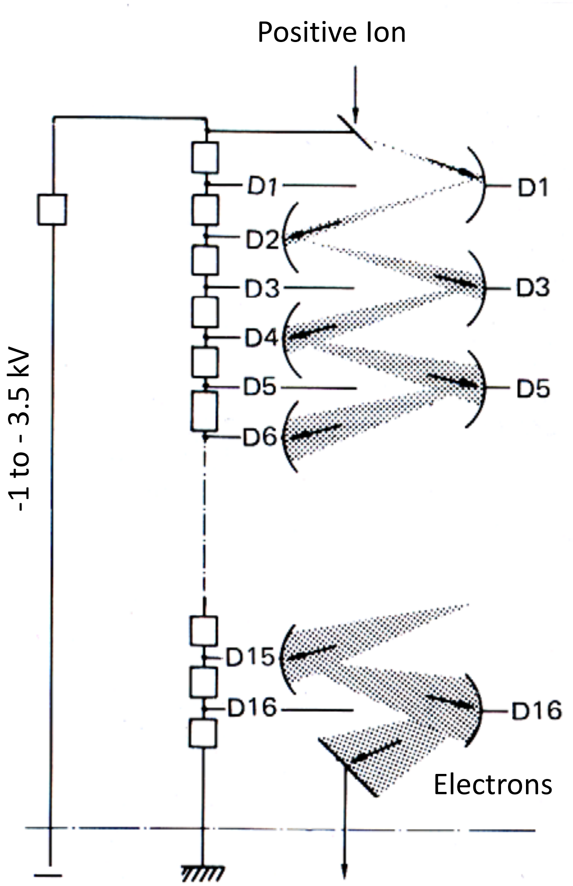


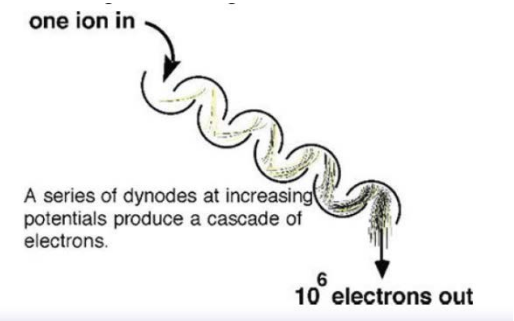
Detectors

Secondary Electron Multiplier, discrete

- Particles (ions, neutrals, electrons, photons) hitting a surface with high energy release several „secondary electrons“
- Use of several dynodes allows for an amplification of up to 10^8
- Low ion currents can be detected easily
- Measuring range 1E-15 to 1E-5A

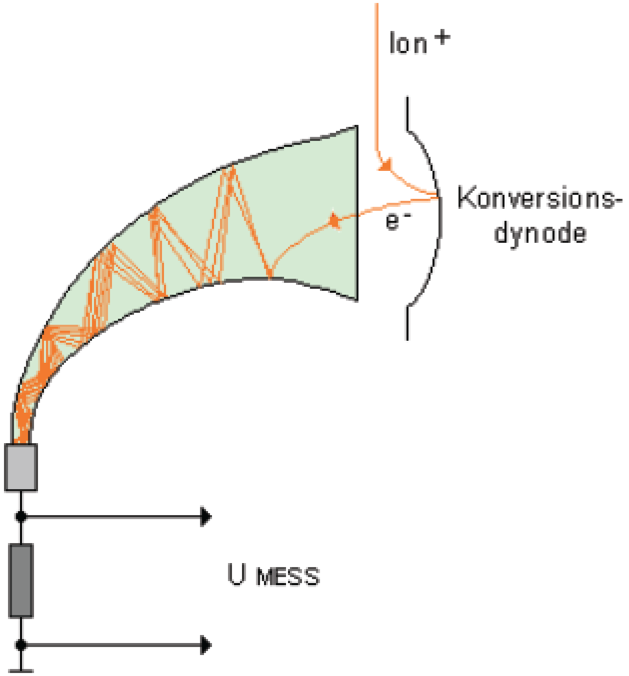
- „Counting“ of individual electron bursts allows for the detection of single ions (1E-19A)

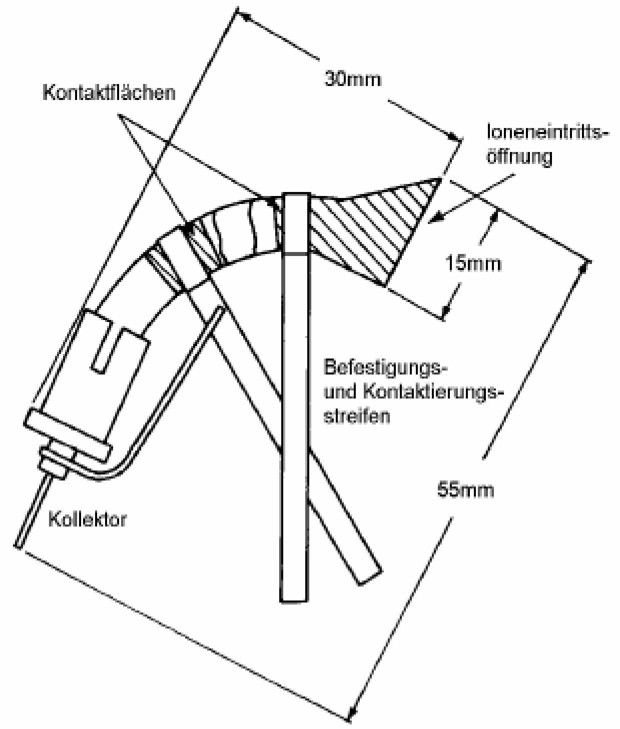




Detectors

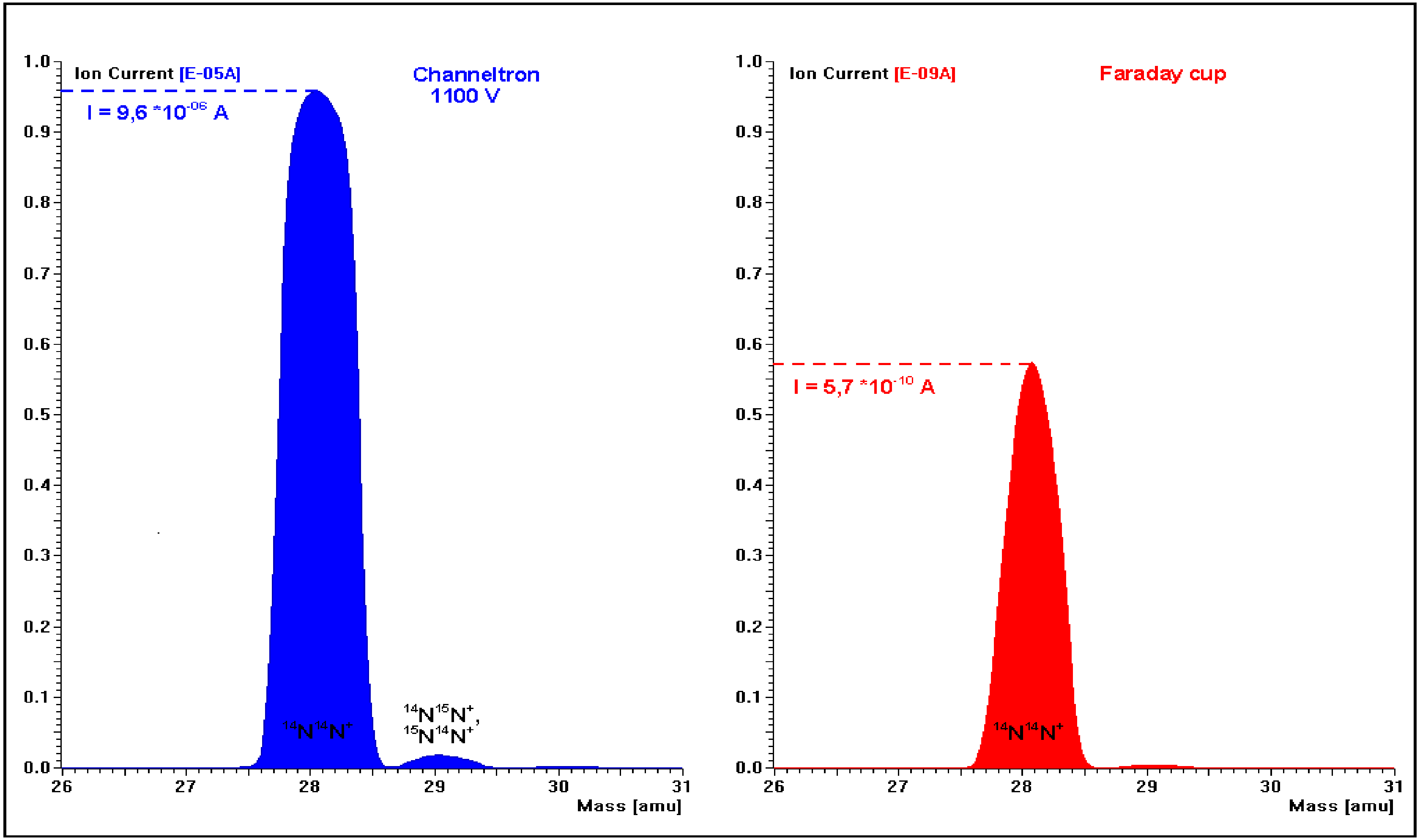
Channeltron

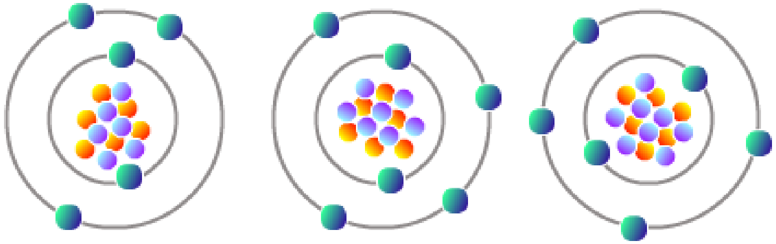




- Glastube covered with antimony based material
- Gain $10^5 - 10^6$
- for voltage amplification high resistance is used

Detectors


Ion Current [E-05A]
Channeltron
1100 V
I = 9,6 *10-06 A
$^{14}N^{14}N^+$
$^{14}N^{15}N^+$,
$^{15}N^{14}N^+$
Ion Current [E-09A]
Faraday cup
I = 5,7 *10-10 A
$^{14}N^{14}N^+$
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
26
27
28
29
30
31
Mass [amu]



Carbon
6 Protons
6 Neutrons

Nuclear number
= 6 + 6
= 12

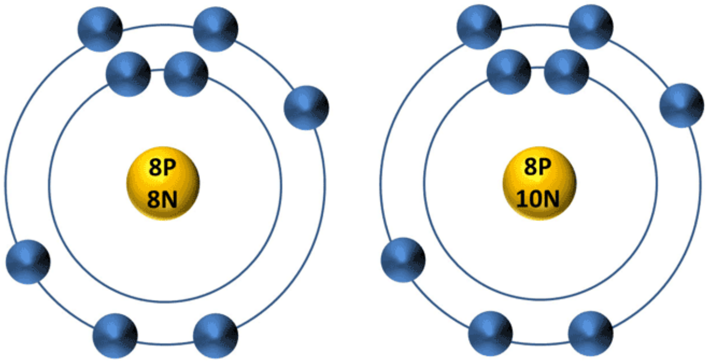
Carbon-13
6 Protons
7 Neutrons

Nuclear number
= 6 + 7
= 13

Carbon-14
6 Protons
8 Neutrons

Nuclear number
= 6 + 8
= 14

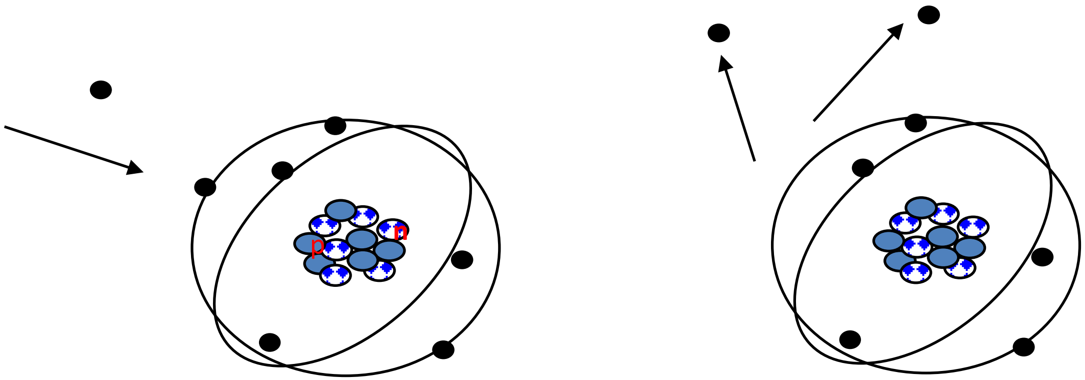
Oxygen Isotopes



^{16}O Isotope

^{18}O Isotope

- Ionization



$$^{12}C + 1e^- \rightarrow {}^{12}C^+ + 2e^-$$

Fragmentation

Molecular ion

ABC + e^- → ABC^+ + $2e^-$

Fragment ion

→ $AB + C^+ + 2e^-$

→ $AB^+ + C + 2e^-$

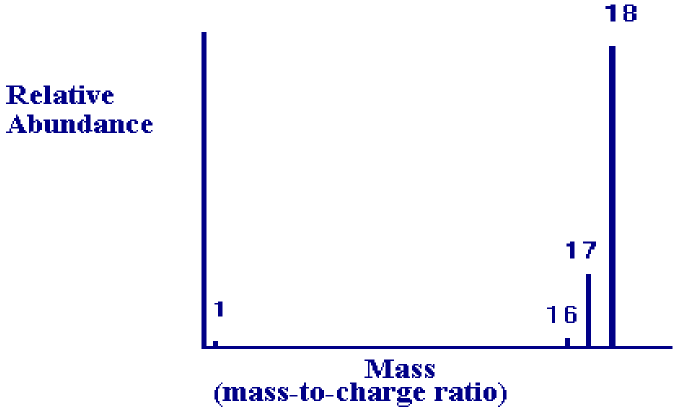
→ $A + BC^+ + 2e^-$

→ $A^+ + BC + 2e^-$

→ $AC^+ + B + 2e^-$

→ $AC + B^+ + 2e^-$

Mass Spectrum of Water



Fragmentation

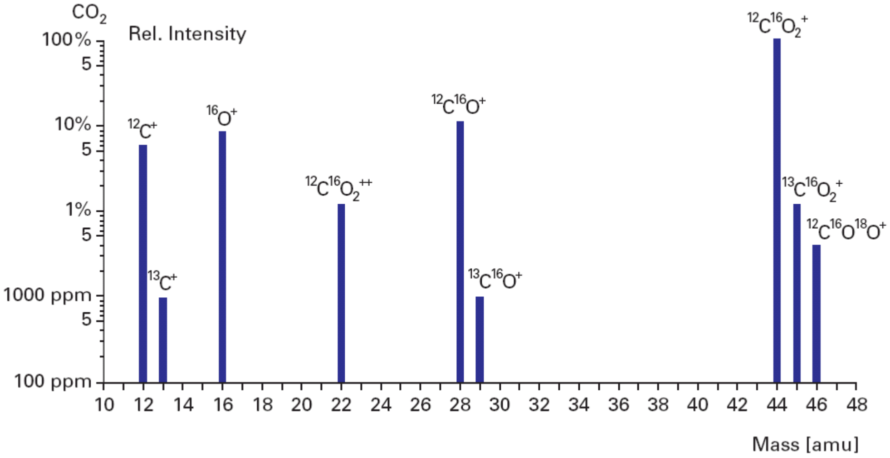
Molecule + electron

- ➔ **Ionization of molecule**
- ➔ **Fragmentation of molecule**
- ➔ **Multiple charged ions**
- ➔ **Isotopic effects are shown**

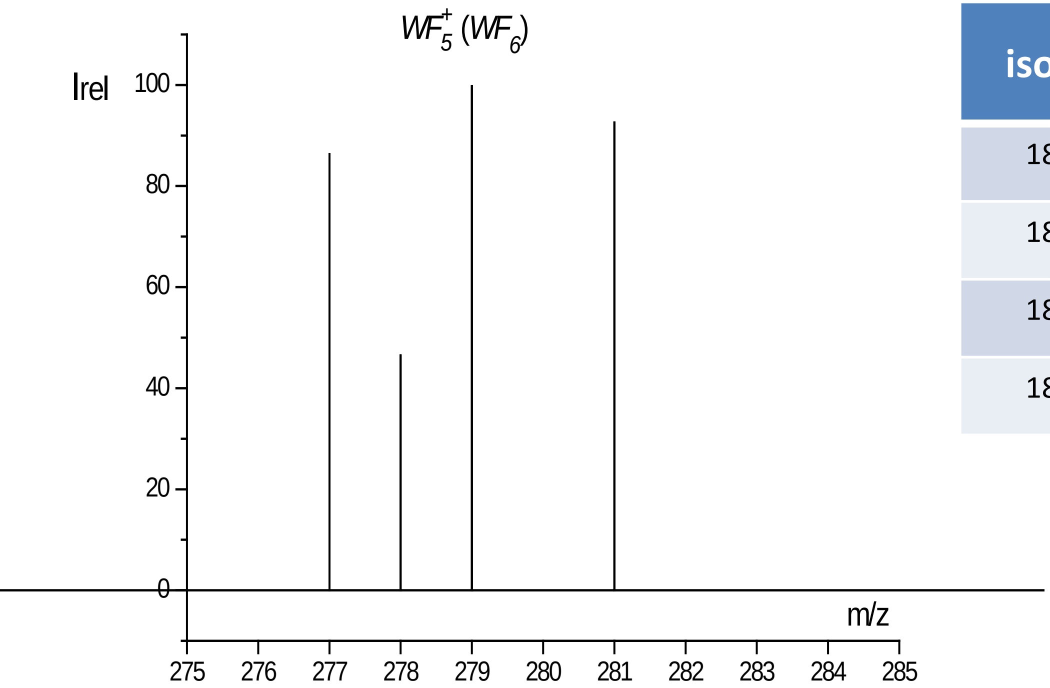
Example:

$CO_2 + e^-$ (70eV)

➔ $CO_2^+ + 2e^-$	**44 m/e**
➔ $C^+ + 2e^-$	**12 m/e**
➔ $O^+ + 2e^-$	**16 m/e**
➔ $CO^+ + 2e^-$	**28 m/e**
➔ $CO_2^{++} + 3e^-$	**22 m/e**
➔ $^{12}C\ ^{16}O\ ^{18}O^+ + 2e^-$	**46 m/e**



Equilibrium distribution of isotopes



isotope	Natural Abundance, %	Irel, %
^{182}W	26.5	83.7
^{183}W	14.3	45.2
^{184}W	31.6	100.0
^{186}W	28.4	89.8

- Isotopic pattern is a fingerprint of all chemical elemets and compounds

Isotope scrambling

Theoretical pattern of CO_2^+

1) $CO_2 \rightarrow {}^{12}CO_2 + {}^{13}CO_2$ $\quad {}^{12}C=0.99 \quad {}^{13}C=0.01$
2) $C^{16}O_2 \quad C^{16}O^{18}O \quad C^{18}O_2$
3) ${}^{16}O - x$, ${}^{18}O$ - (1-x)

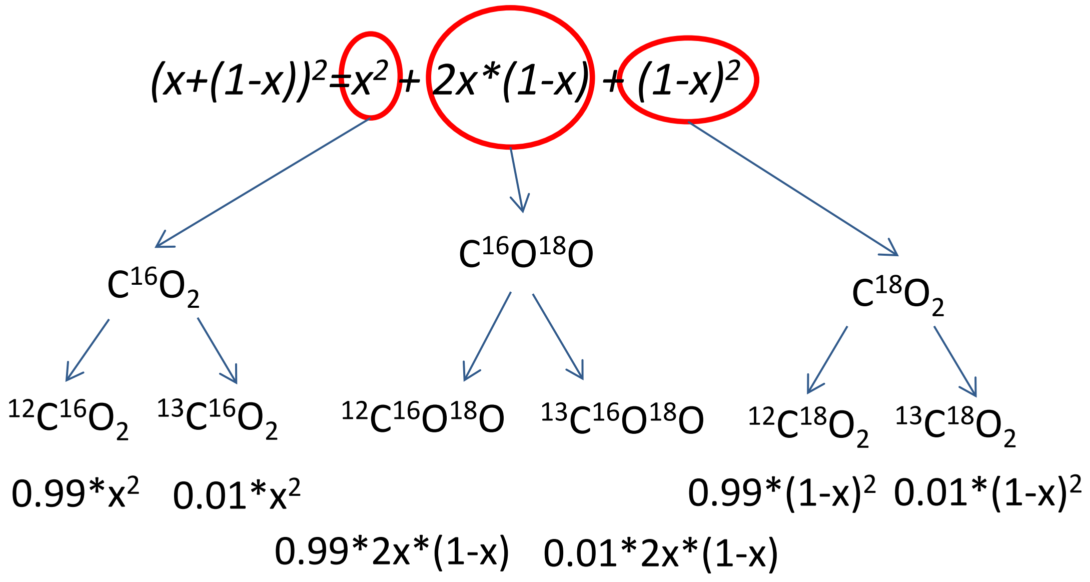
${}^{16}O = 0.998$, ${}^{18}O = 0.002$

$$(a+b)^n = \sum_{k=0}^{n} \binom{n}{k} a^{n-k} b^k$$

n – number of equivalent postions, row number, 2
a, b, abundance of isotopes, x , 1-x.

- Distribution is determined by binominal coefficients

n	*k*	
0	1	Row 0
1	1 1	Row 1
2	1 2 1	Row 2
3	1 3 3 1	Row 3
4	1 4 6 4 1	Row 4
5	1 5 10 10 5 1	Row 5
6	1 6 15 20 15 6 1	Row 6
7	1 7 21 35 35 21 7 1	Row 7



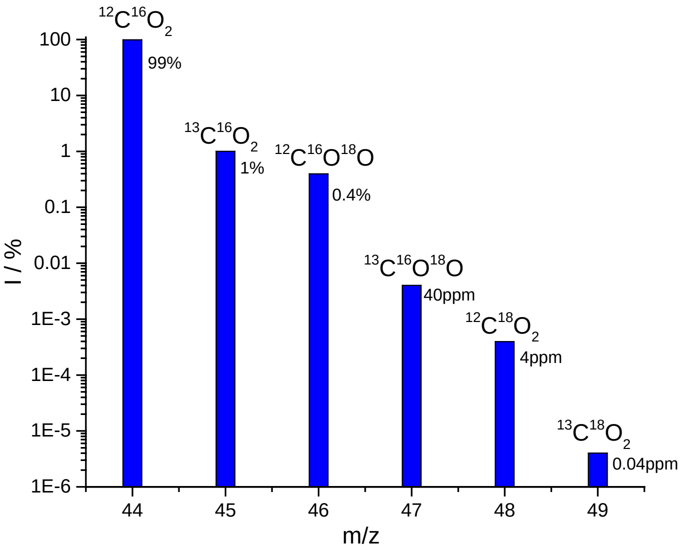
$(x+(1-x))^2 = x^2 + 2x*(1-x) + (1-x)^2$

$C^{16}O_2 \quad C^{16}O^{18}O \quad C^{18}O_2$

${}^{12}C^{16}O_2 \quad {}^{13}C^{16}O_2 \quad {}^{12}C^{16}O^{18}O \quad {}^{13}C^{16}O^{18}O \quad {}^{12}C^{18}O_2 \quad {}^{13}C^{18}O_2$

$0.99*x^2 \quad 0.01*x^2 \quad 0.99*(1-x)^2 \quad 0.01*(1-x)^2$

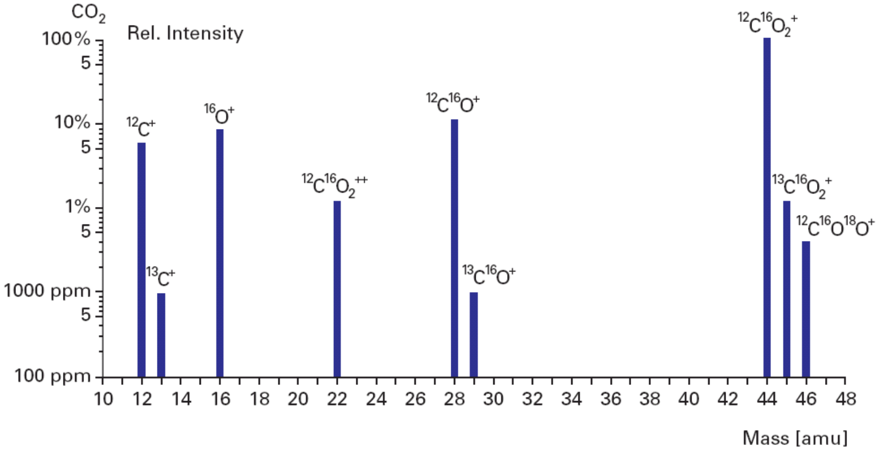
$0.99*2x*(1-x) \quad 0.01*2x*(1-x)$



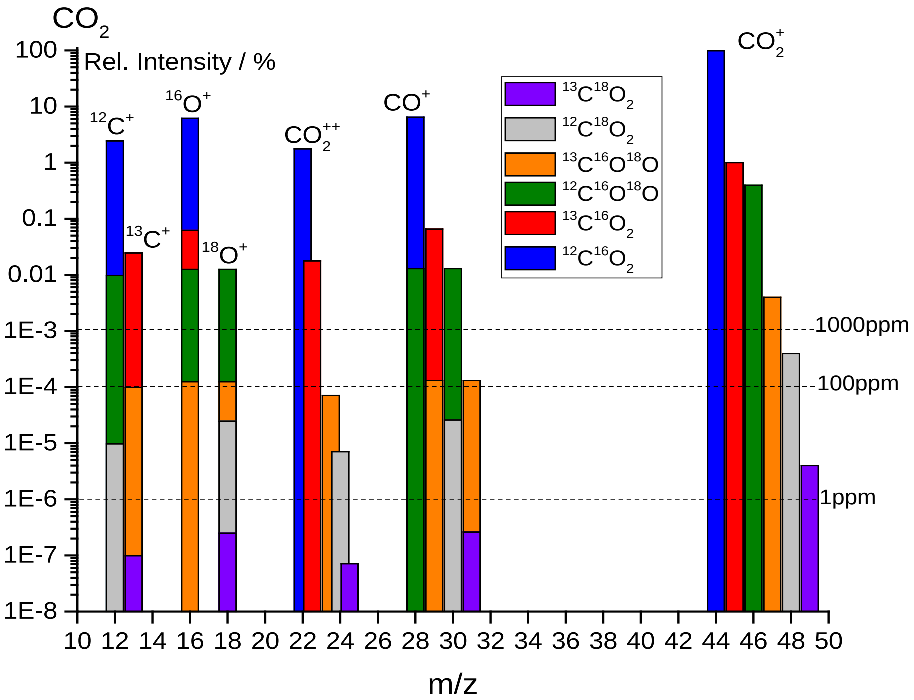
Fragmentation

Cracking pattern of CO_2 (experimental)

Fragmentation distribution at 70 eV



Cracking pattern of CO_2 (calculated)



Deviation of experimental and theoretical spectra caused by:

- Proximity to equilibrium (equilibrium is not reached)
- Kinetic hindrance
- Thermodynamically favorable configuration
- Isotopic composition

Isotope scrambling

Theoretical pattern of NH_3^+

1) $NH_3 \rightarrow {}^{14}NH_3 + {}^{15}NH_3$ ${}^{14}N=0.996$ ${}^{15}N=0.004$
2) NH_3 NH_2D NHD_2 ND_3
3) ${}^{1}H - x$, ${}^{2}D$ - (1-x)

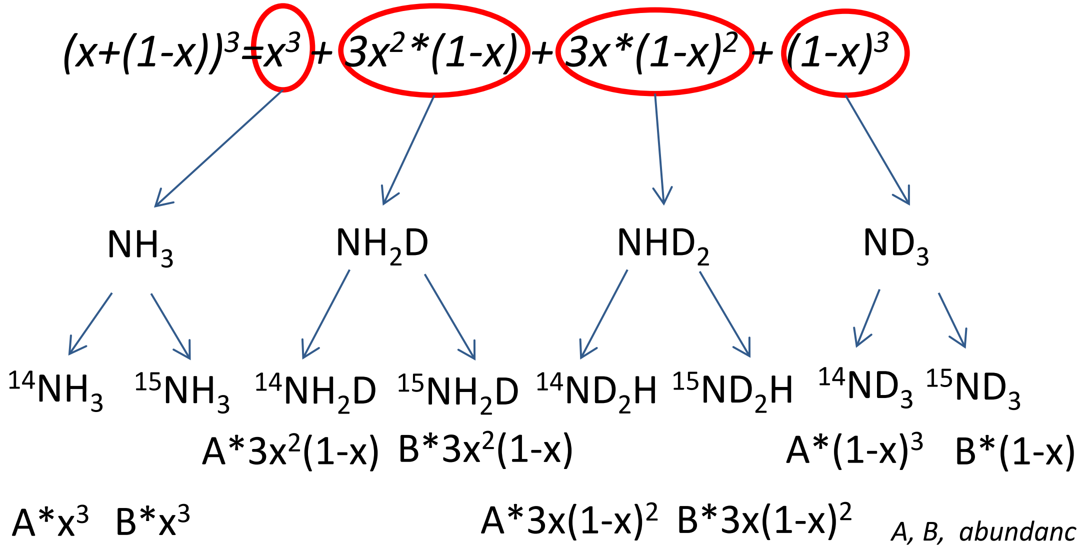
${}^{1}H = 0.9999$, ${}^{2}D = 0.0001$

$$(a+b)^n = \sum_{k=0}^{n} \binom{n}{k} a^{n-k} b^k$$

n – number of equivalent postions, row number, 3
a, b, natural abundance of isotopes, x , 1-x.

- Distribution is determined by binominal coefficients

n	k	
0	1	Row 0
1	1 1	Row 1
2	1 2 1	Row 2
3	1 3 3 1	Row 3
4	1 4 6 4 1	Row 4
5	1 5 10 10 5 1	Row 5
6	1 6 15 20 15 6 1	Row 6
7	1 7 21 35 35 21 7 1	Row 7



$$(x+(1-x))^3 = x^3 + 3x^2*(1-x) + 3x*(1-x)^2 + (1-x)^3$$

NH_3 NH_2D NHD_2 ND_3

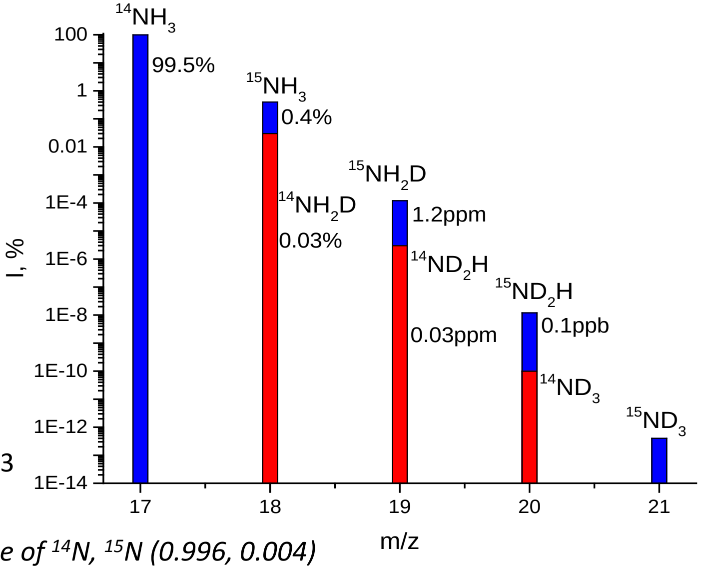
${}^{14}NH_3$ ${}^{15}NH_3$ ${}^{14}NH_2D$ ${}^{15}NH_2D$ ${}^{14}ND_2H$ ${}^{15}ND_2H$ ${}^{14}ND_3$ ${}^{15}ND_3$

$A*x^3$ $B*x^3$

$A*3x^2(1-x)$ $B*3x^2(1-x)$

$A*3x(1-x)^2$ $B*3x(1-x)^2$

$A*(1-x)^3$ $B*(1-x)^3$



A, B, abundance of ${}^{14}N$, ${}^{15}N$ (0.996, 0.004)

Isotope scrambling

Theoretical pattern of CH_4^+

1) $CH_4 \rightarrow {}^{12}CH_4 + {}^{13}CH_4$ $\quad {}^{12}C=0.99 \quad {}^{13}C=0.01$

2) $CH_4 \quad CH_3D \quad CH_2D_2 \quad CH_3D \quad CD_4$

3) ${}^{1}H - x$, ${}^{2}D$ - (1-x)

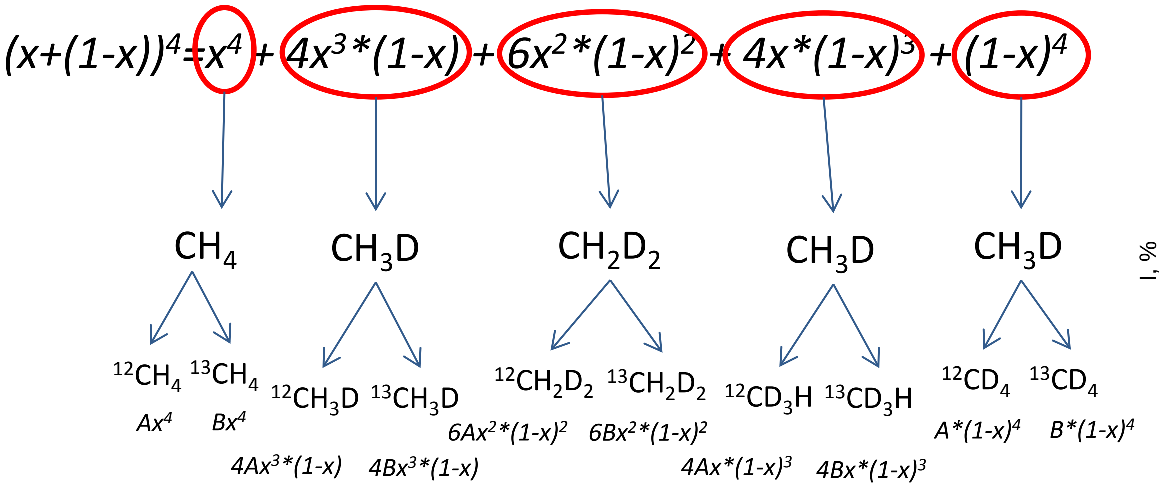
${}^{1}H = 0.9999$, ${}^{2}D = 0.0001$

$$(a+b)^n = \sum_{k=0}^{n} \binom{n}{k} a^{n-k} b^k$$

n – number of equivalent postions, row number, 4
a, b, abundance of isotopes, x , 1-x.

- Distribution is determined by binominal coefficients

n	k	
0	1	Row 0
1	1 1	Row 1
2	1 2 1	Row 2
3	1 3 3 1	Row 3
4	1 4 6 4 1	Row 4
5	1 5 10 10 5 1	Row 5
6	1 6 15 20 15 6 1	Row 6
7	1 7 21 35 35 21 7 1	Row 7



$$(x+(1-x))^4 = x^4 + 4x^3*(1-x) + 6x^2*(1-x)^2 + 4x*(1-x)^3 + (1-x)^4$$

CH_4 → ${}^{12}CH_4$, ${}^{13}CH_4$: Ax^4, Bx^4

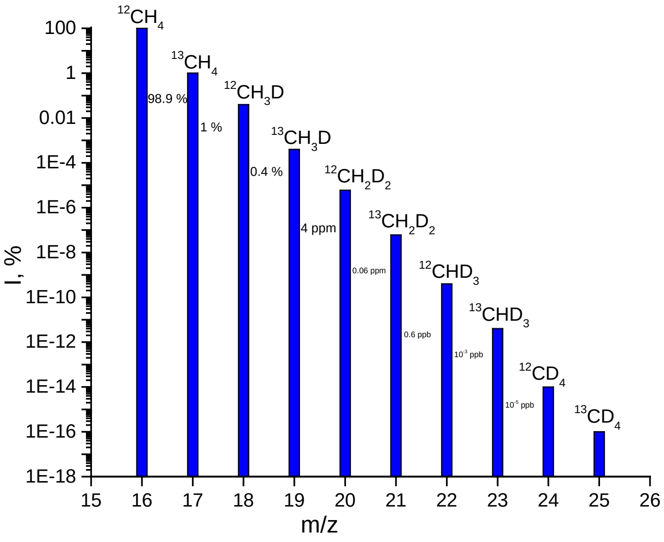
CH_3D → ${}^{12}CH_3D$, ${}^{13}CH_3D$: $4Ax^3*(1-x)$, $4Bx^3*(1-x)$

CH_2D_2 → ${}^{12}CH_2D_2$, ${}^{13}CH_2D_2$: $6Ax^2*(1-x)^2$, $6Bx^2*(1-x)^2$

CH_3D → ${}^{12}CD_3H$, ${}^{13}CD_3H$: $4Ax*(1-x)^3$, $4Bx*(1-x)^3$

CH_3D → ${}^{12}CD_4$, ${}^{13}CD_4$: $A*(1-x)^4$, $B*(1-x)^4$

A, B, abundance of ${}^{12}C$, ${}^{13}C$ (0.99, 0.01)



Isotope scrambling

s - type of particles (number of isotopes of one element)
n – number of particles
C^s_n – number of combinations of n particles with s isotopes (number of lines in spectra)

$$C^s_n = \frac{(n+s-1)!}{n!(s-1)!}$$

TcO_4^-, s=2 (^{16}O, ^{18}O), n=4, (4 + 2 – 1)!/4!(2 – 1)! = 5!/4!1! = 5

$C_2H_4^+$, s=2 (^{1}H, ^{2}D), n=4, (4 + 2 – 1)!/4!(2 – 1)! = 5!/4!1! = 5
s=2 (^{12}C, ^{13}C), n=2, (2+2-1)!/2!(2-1)!=3

$C^2_4 * C^2_2 = 15$ (15 possible lines in spectra for ethylene ($C_2H_4^+$))

$[Mo_2O_7]^{2-}$, s=7 (^{92}Mo, ^{94}Mo, ^{95}Mo, ^{96}Mo, ^{97}Mo, ^{98}Mo, ^{100}Mo), n=2, (2 + 7 – 1)!/2!(7 – 1)! = 28
s=2 (^{16}O, ^{18}O), n=7, (7+2-1)!/7!(2-1)!=8

$C^7_2 * C^2_7 = 224$ (224 possible lines in spectra of $[Mo_2O_7]^{2-}$

Isotope scrambling

Theoretical pattern of $C_2H_4^+$

1) $C_2H_4 \rightarrow {}^{12}C_2H_4 + {}^{13}C_2H_4 + {}^{12}C^{13}CH_4$

${}^{12}C=0.99$; y ${}^{13}C=0.01$; 1-y

2) C_2H_4 C_2H_3D $C_2H_2D_2$ C_2H_3D C_2D_4

${}^{1}H=0.9999$; x ${}^{2}D = 0.0001$; 1-x

$$(a+b)^n = \sum_{k=0}^{n}\binom{n}{k}a^{n-k}b^k$$

- Distribution is determined by binominal coefficients

n	k								
0	1								Row 0
1	1	1							Row 1
2	1	2	1						Row 2
3	1	3	3	1					Row 3
4	1	4	6	4	1				Row 4
5	1	5	10	10	5	1			Row 5
6	1	6	15	20	15	6	1		Row 6
7	1	7	21	35	35	21	7	1	Row 7

n – number of equivalent postions, row number,2 (C) and 4 (H)
a, b, abundance of isotopes, y, 1-y and x , 1-x,

$$(y+(1-y))^2=y^2 + 2y*(1-y) + (1-y)^2 \text{ for carbon}$$

$$(x+(1-x))^4=x^4 + 4x^3*(1-x) + 6x^2*(1-x)^2 + 4x*(1-x)^3 + (1-x)^4 \text{ for hydrogen}$$

$(y+(1-y))^2 \cdot (x+(1-x))^4$ ⟶ *Intensity distribution for 15 possible lines of* $(C_2H_4^+)$

Isotope scrambling

Theoretical pattern of $[Mo_2O_7]^{2-}$

1) Mo

^{92}Mo, ^{94}Mo, ^{95}Mo, ^{96}Mo, ^{97}Mo, ^{98}Mo, ^{100}Mo

a, b, c, d, e, f, g

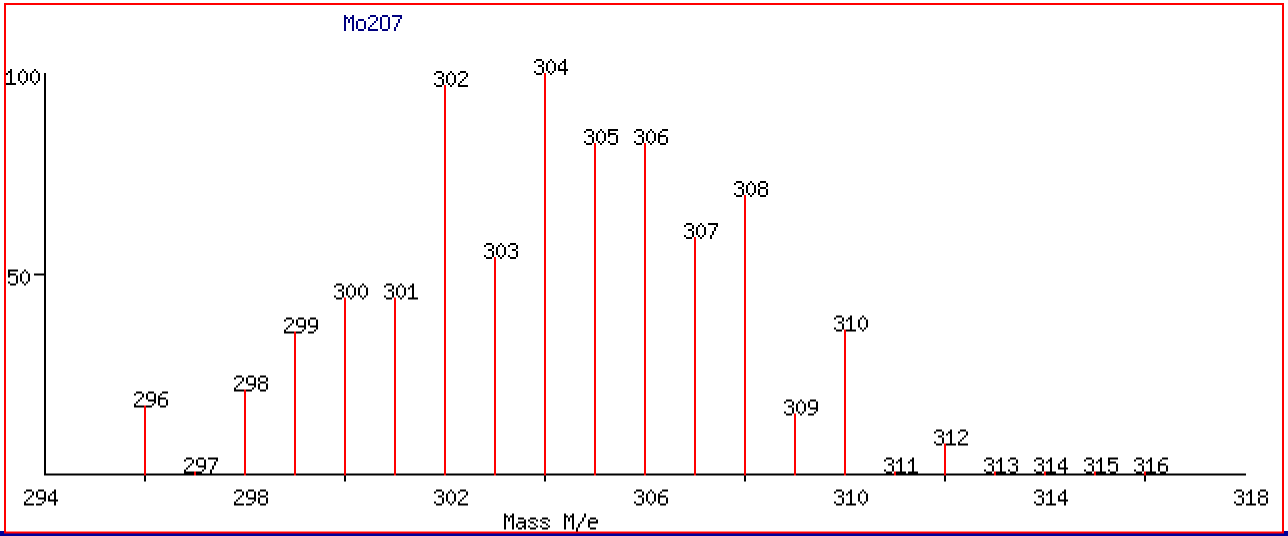
2) ^{16}O – x , ^{18}O - (1-x)

^{16}O =0.998, ^{18}O = 0.002

^{92}Mo 61.5%
^{94}Mo 38.3%
^{95}Mo 66.0%
^{96}Mo 69.1%
^{97}Mo 39.6%
^{98}Mo 100%
^{100}Mo 39.9%

n – number of equivalent postions, row number,2 (Mo) and 7 (O)
a, b, abundance of isotopes, a, b, c, d, e, f, g (Mo); x, 1-x, (O)

$(x+(1-x))^7 \cdot (a+b+c+d+e+f+g)^2$ → *Intensity distribution for 224 possible lines of* (Mo_2O_7)



Quantitative gas analysis

For Isolated spectra

$$P(x) = \frac{total\ ion\ current\ (x)}{GK(x)}$$

$K(x)$ – sensitivity to the specific component*

For overlaping spectra

$$i_{28} = SG[a_{11}P(N_2)+a_{12}P(CO)]$$
$$i_{14} = SG[a_{21}P(N_2)+a_{22}P(CO)]$$

K - instrument sensitivity

G - multiplier gain

$$I_M = KG*\Sigma\ \sigma_{mk}*n_k \sim KG*\Sigma\ a_{mk}*P_k$$

i_m – ion current of the mass M

σ_{mk} – ionization cross section of component (molecule) k with formation of ion with mass M

a_{mk} ~ σ_{mk}/RT– component of cracking pattern, calibration factor

P_k – pressure of the k component.

$$\begin{bmatrix} i_1 \\ i_2 \\ \vdots \\ i_m \end{bmatrix} = \begin{bmatrix} a_{11} & \dots & a_{1k} \\ a_{12} & \dots & a_{2k} \\ \vdots & \vdots & \vdots \\ a_{m1} & \dots & a_{mk} \end{bmatrix} \cdot \begin{bmatrix} p_1 \\ p_2 \\ \vdots \\ p_k \end{bmatrix}$$

$$\begin{bmatrix} p_1 \\ p_2 \\ \vdots \\ p_k \end{bmatrix} = \begin{bmatrix} a_{11} & \dots & a_{1k} \\ a_{12} & \dots & a_{2k} \\ \vdots & \vdots & \vdots \\ a_{m1} & \dots & a_{mk} \end{bmatrix}^{-1} \cdot \begin{bmatrix} i_1 \\ i_2 \\ \vdots \\ i_m \end{bmatrix}$$

---

* For the rough estimation the sensitivity provided by the manufacturer for nitrogen could be used

Quantitative gas analysis

Internal standard calibration

$$\gamma_i{}^k = \frac{I_i}{x_i} \bigg/ \frac{I_{Ar}}{x_{ar}}$$

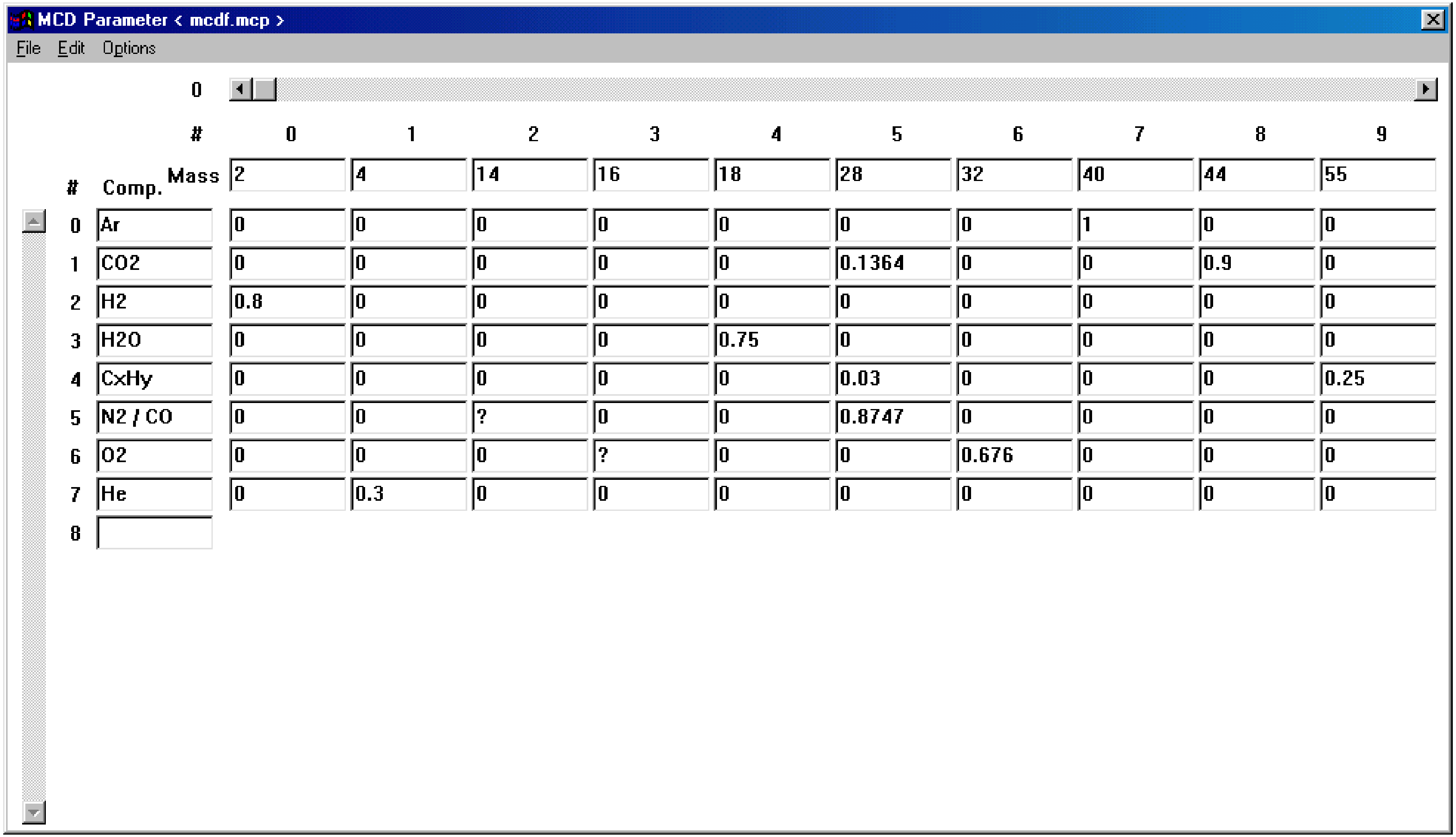
γ_i^k – response coefficient of species i of component k with respect to Ar
I_{Mi} – MS intensities (ion currents of mass M_i)
x_i – the mole fractions.

For mixture of CO and CO_2 with Ar as internal standart.

$$I_{Mi} = \Sigma\, \gamma_{ik} * C_k$$

$$i_{28} = \gamma_{28}{}^{CO}\,[CO] + \gamma_{28}{}^{CO2}[CO_2]$$
$$i_{44} = \gamma_{44}{}^{co2}[CO_2]$$

Quantitative gas analysis



#	Comp.	0	1	2	3	4	5	6	7	8	9
	Mass	2	4	14	16	18	28	32	40	44	55
0	Ar	0	0	0	0	0	0	0	1	0	0
1	CO2	0	0	0	0	0	0.1364	0	0	0.9	0
2	H2	0.8	0	0	0	0	0	0	0	0	0
3	H2O	0	0	0	0	0.75	0	0	0	0	0
4	CxHy	0	0	0	0	0	0.03	0	0	0	0.25
5	N2 / CO	0	0	?	0	0	0.8747	0	0	0	0
6	O2	0	0	0	?	0	0	0.676	0	0	0
7	He	0	0.3	0	0	0	0	0	0	0	0
8											

Quantitative gas analysis

$$\begin{bmatrix} a_{11} & \cdots & a_{1k} \\ a_{12} & \cdots & a_{2k} \\ \vdots & \vdots & \vdots \\ a_{m1} & \cdots & a_{mk} \end{bmatrix} \cdot \begin{bmatrix} p_1 \\ p_2 \\ \vdots \\ p_k \end{bmatrix} = \begin{bmatrix} i_1 \\ i_2 \\ \vdots \\ i_m \end{bmatrix}$$

$$\begin{bmatrix} p_1 \\ p_2 \\ \vdots \\ p_k \end{bmatrix} = \begin{bmatrix} a_{11} & \cdots & a_{1k} \\ a_{12} & \cdots & a_{2k} \\ \vdots & \vdots & \vdots \\ a_{m1} & \cdots & a_{mk} \end{bmatrix}^{-1} \cdot \begin{bmatrix} i_1 \\ i_2 \\ \vdots \\ i_m \end{bmatrix}$$

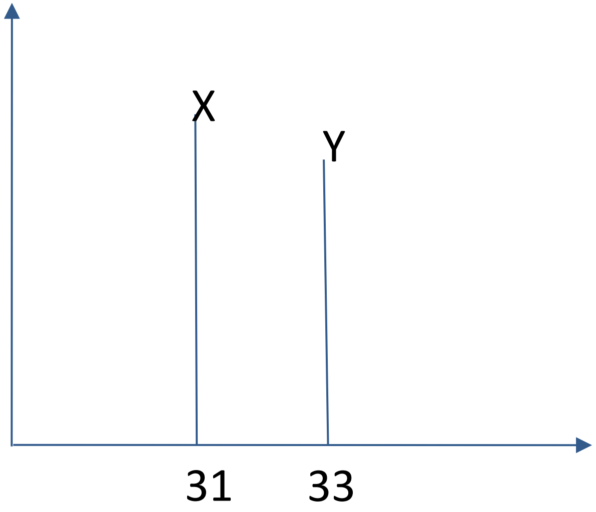
$$\left. \begin{array}{l} ak + bq = X \\ ar + bs = Y \end{array} \right\}$$

$$\begin{bmatrix} k & q \\ r & s \end{bmatrix} \cdot \begin{bmatrix} a \\ b \end{bmatrix} = \begin{bmatrix} X \\ Y \end{bmatrix}$$

Calibration factors

Unknown concentrations

Experimental Ion currents



$$\begin{bmatrix} a \\ b \end{bmatrix} = \begin{bmatrix} k & q \\ r & s \end{bmatrix}^{-1} \cdot \begin{bmatrix} X \\ Y \end{bmatrix} = \frac{1}{ks - qr} \cdot \begin{bmatrix} s & -q \\ -r & k \end{bmatrix} \cdot \begin{bmatrix} X \\ Y \end{bmatrix}$$

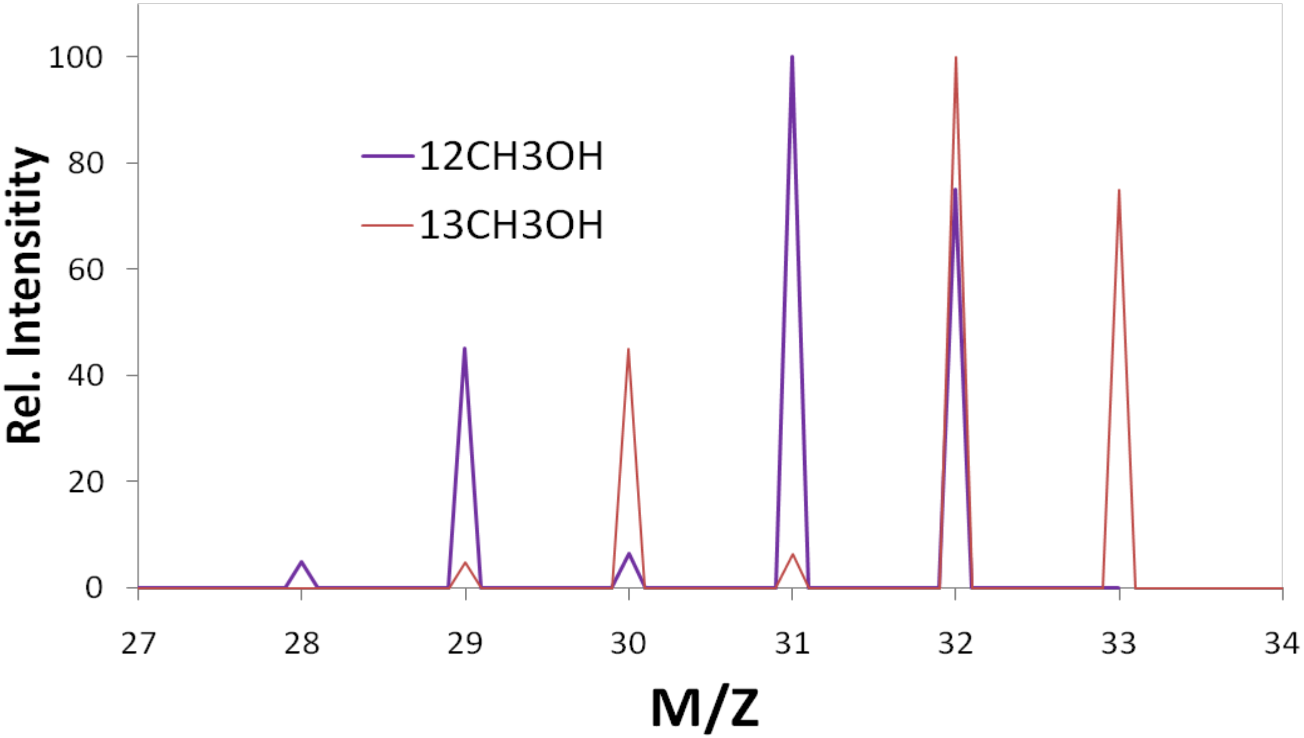
Inverse matrix

Adjugate matrix

ks – qr = D, matrix determinant

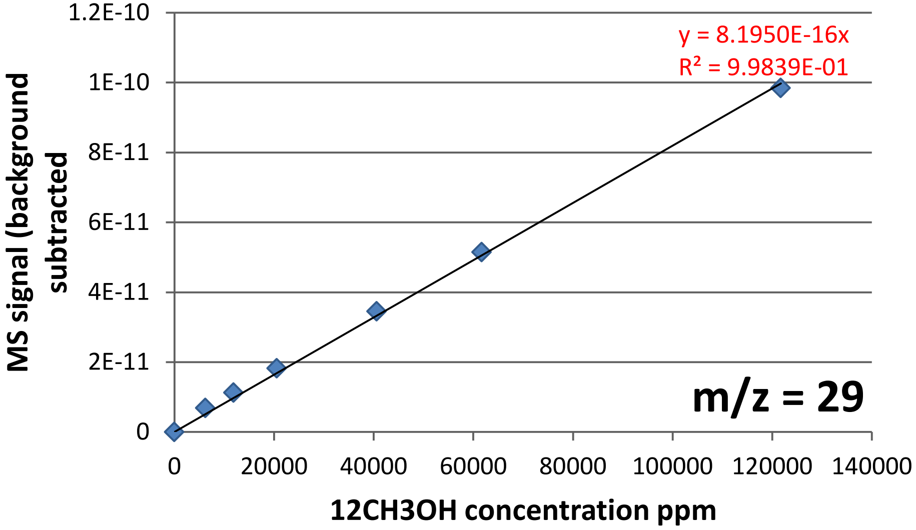
$$a = \frac{sx - qy}{ks - qr} \qquad b = \frac{ky - rx}{ks - qr} \qquad b/a = \frac{ky - rx}{sx - qy}$$

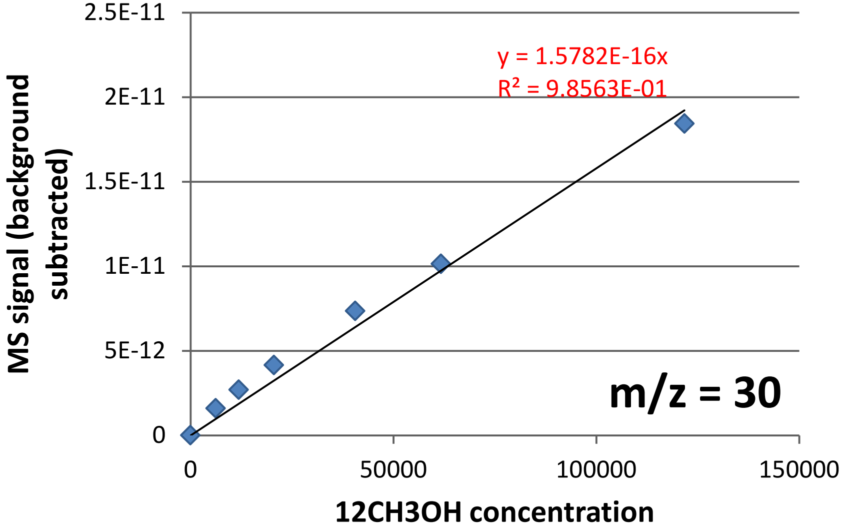
Quantitative gas analysis

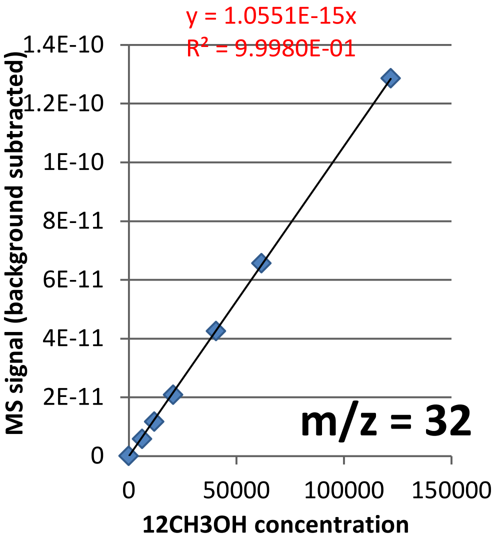


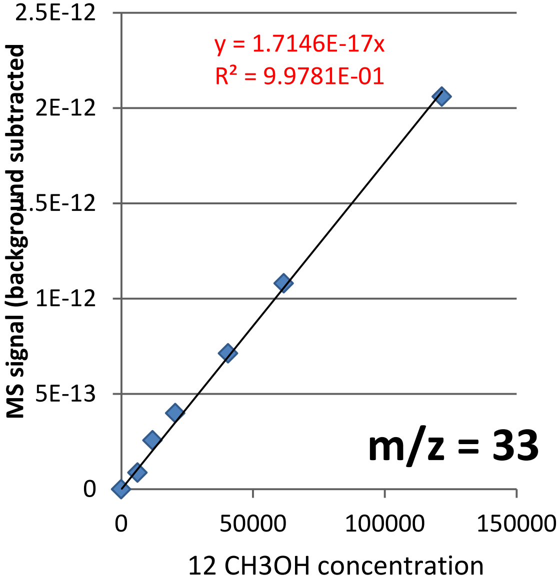
Direct calibration, mass matrix of $^{13}CH_3OH/^{12}CH_3OH$ mixtures

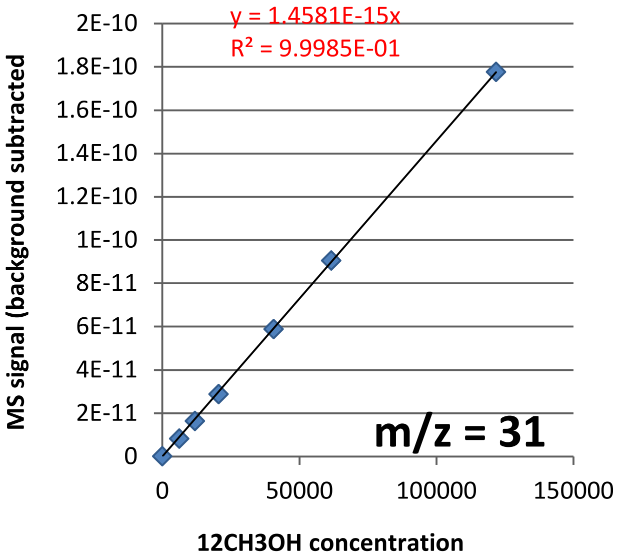
Quantitative gas analysis





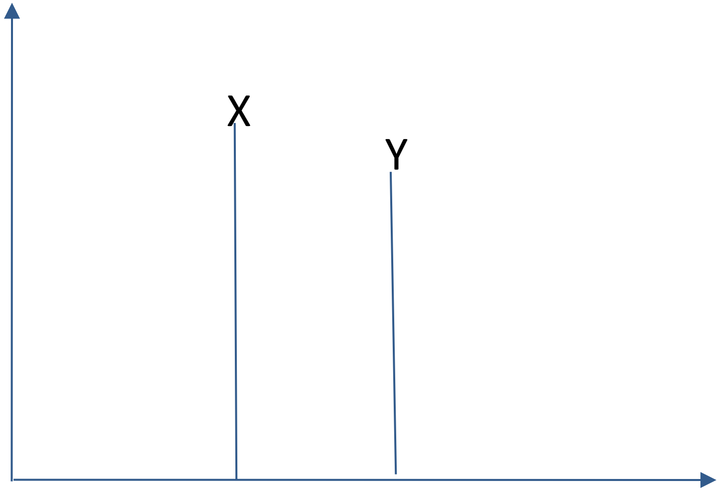






Quantitative gas analysis

Mass Matrix Calculation



We have 2 species a and b. a = C 12 methanol b = C 13 methanol

Fax = Contribution of species a(C12 methanol) to the peak X }
Fby = Contribution of species b(C13 methanol) to the peak Y } ⟹ Sensitivity factors

$$\begin{bmatrix} X \\ Y \end{bmatrix} = \begin{bmatrix} Fax & Fbx \\ Fay & Fby \end{bmatrix} \begin{bmatrix} a \\ b \end{bmatrix}$$

X = a* Fax + b*Fbx
Y = a*Fay + b*Fby

$$fraction\ C13\ methanol = \frac{b}{a+b} = \frac{Fax\cdot y\ - Fay\cdot x}{y\cdot(Fax - Fbx) + x\cdot(Fby - Fax)}$$

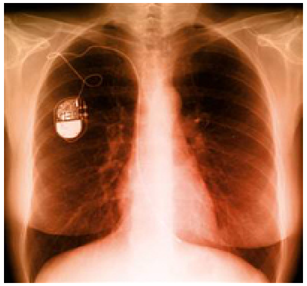
Done By E. Kunkes and N. Thomas in ChemCatChem 2015, 7, 1105-1111

Quantitative gas analysis

Sample	Amount of catalyst Loaded	% of C-13 Methanol		
		GC and MS	MS alone 31 and 33 signals	MS alone 32 and 33 signals
$Cu/ZnO/Al_2O_3$	50mg	93	97	92
Cu/Al_2O_3	1000mg	94	87	87
Cu/MgO	500 mg	91	88	86
Cu/MgO/Zn	50mg	96	94	91

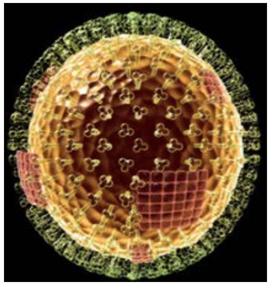
Done By E. Kunkes and N. Thomas in ChemCatChem 2015, 7, 1105-1111

Leaks



„technically“
tight
0.1 µm

„gas“-
tight
0.8 µm

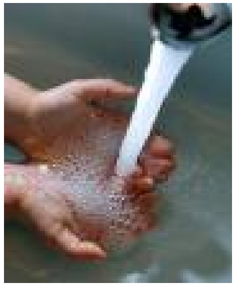


Virus-
tight
3 µm

Bacteria-
tight
10 µm

water-
tight
30 µm

water
drops
100 µm



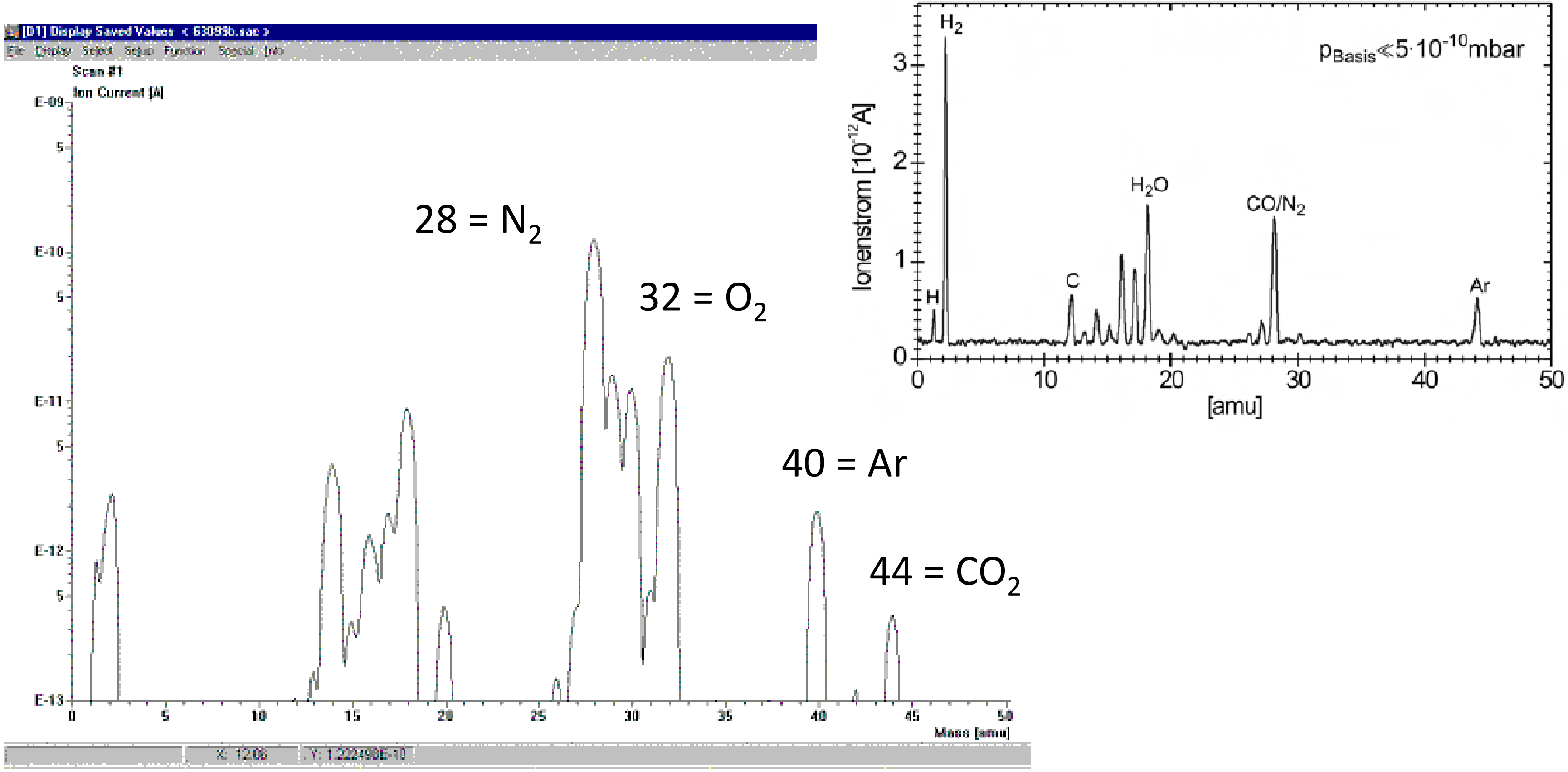
water
flows
1 mm

10^{-11} 10^{-9} 10^{-7} 10^{-5} 10^{-3} 10^{-1} 10^{1} 10^{3} mbar l/s

Lower detection limit
of vacuum methods

Lower detection limit
of snooping methods

Air, residual gas in the system

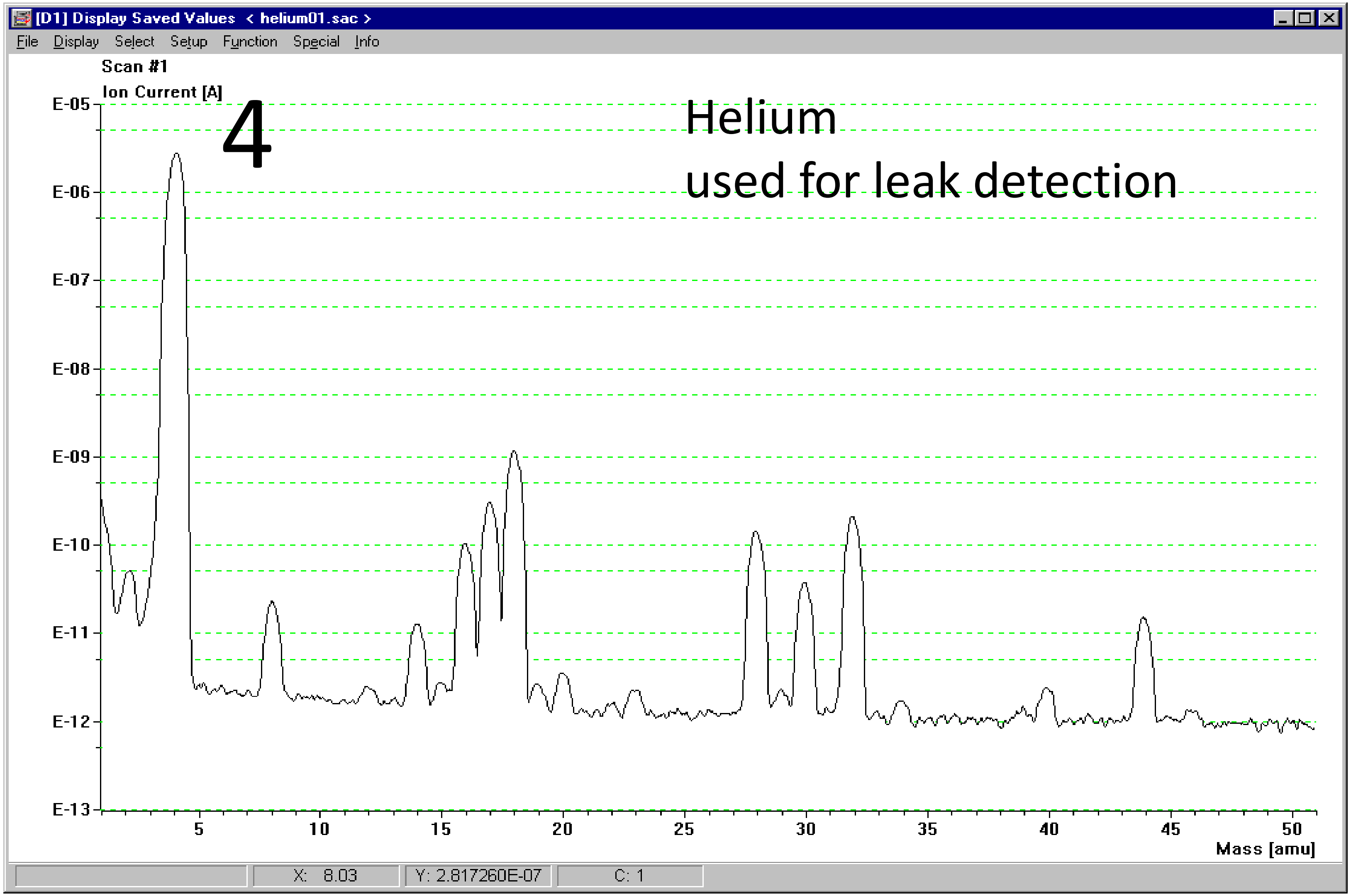


28 = N_2

32 = O_2

40 = Ar

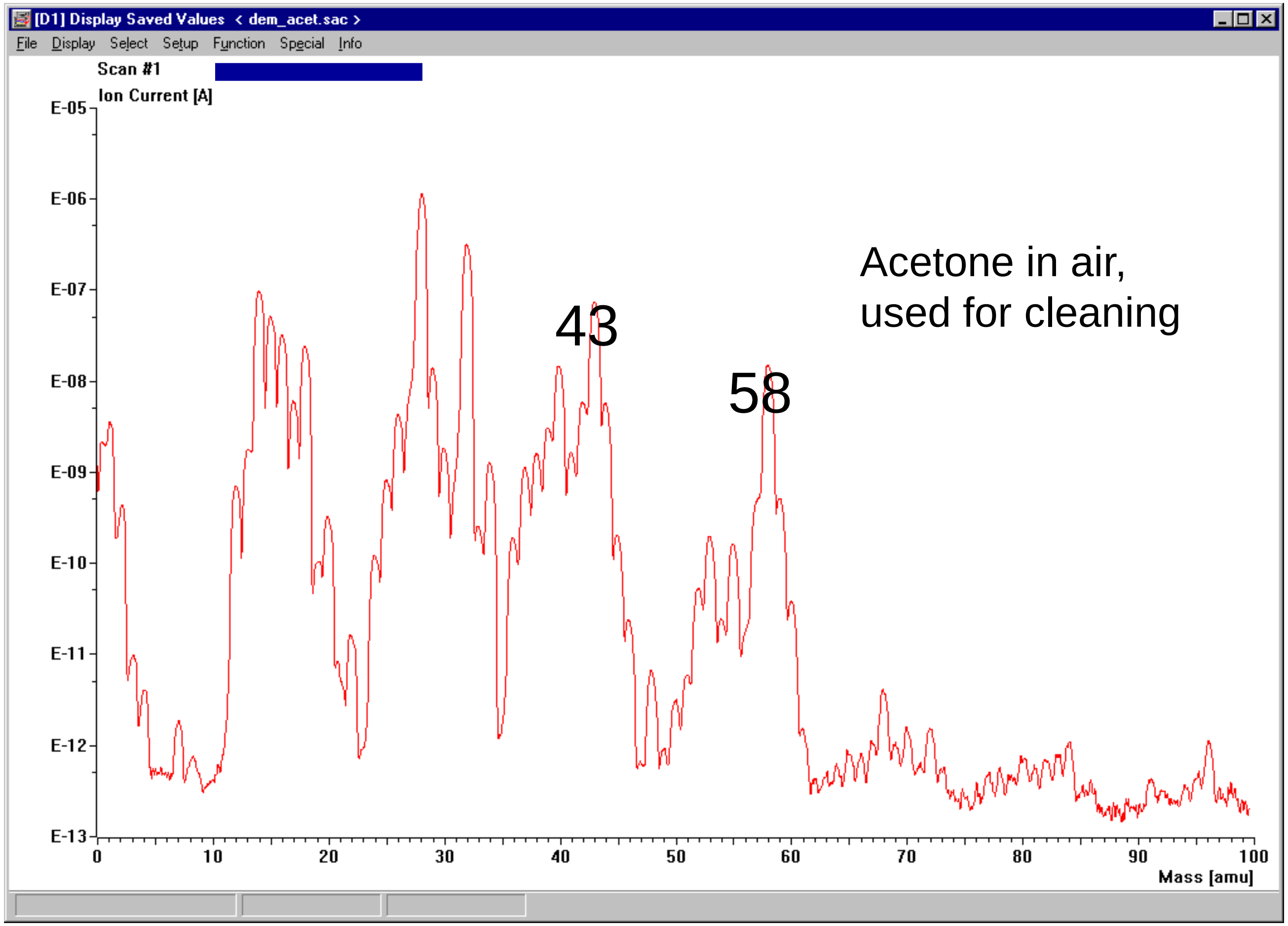
44 = CO_2



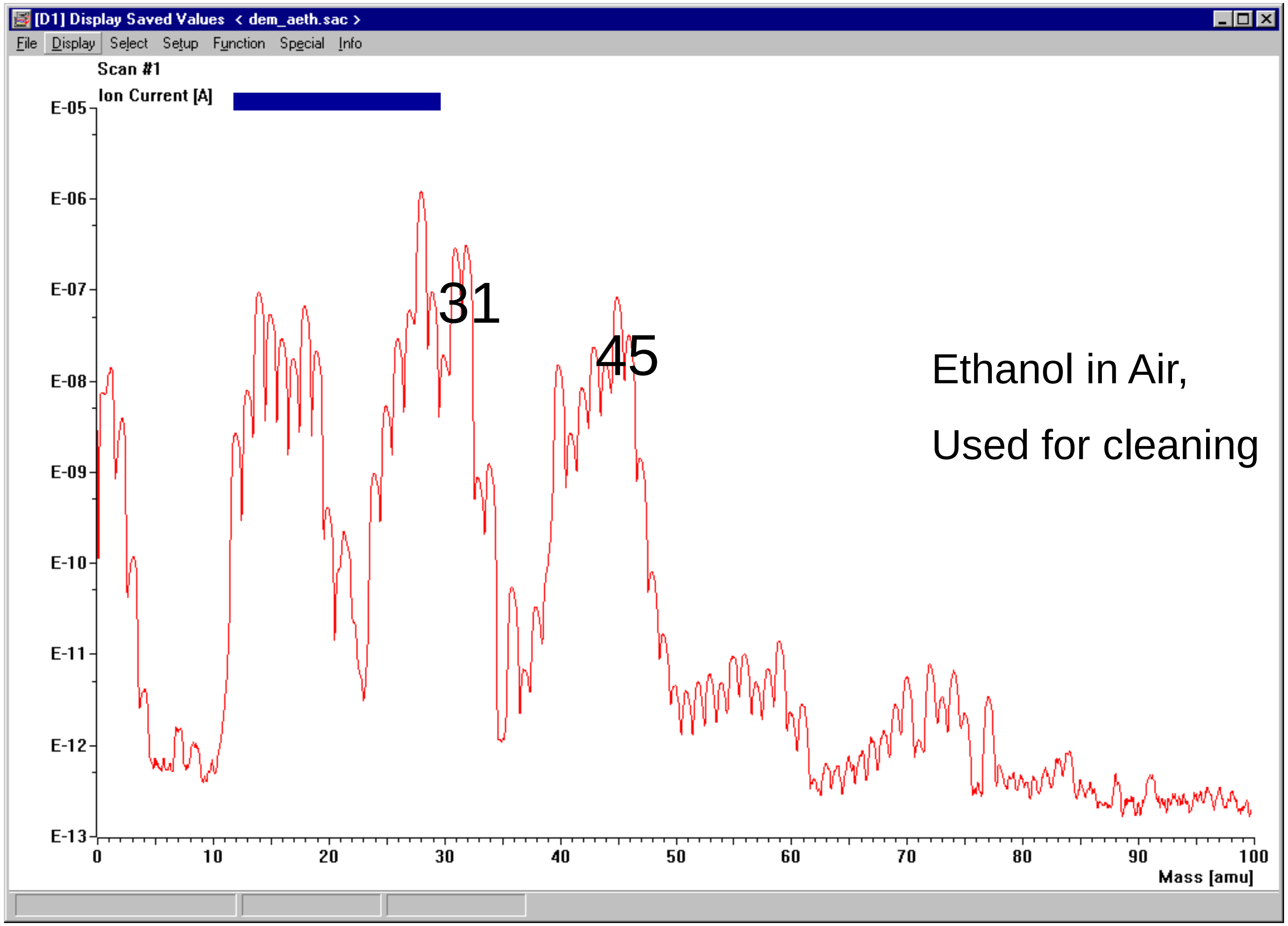
4

Helium

used for leak detection

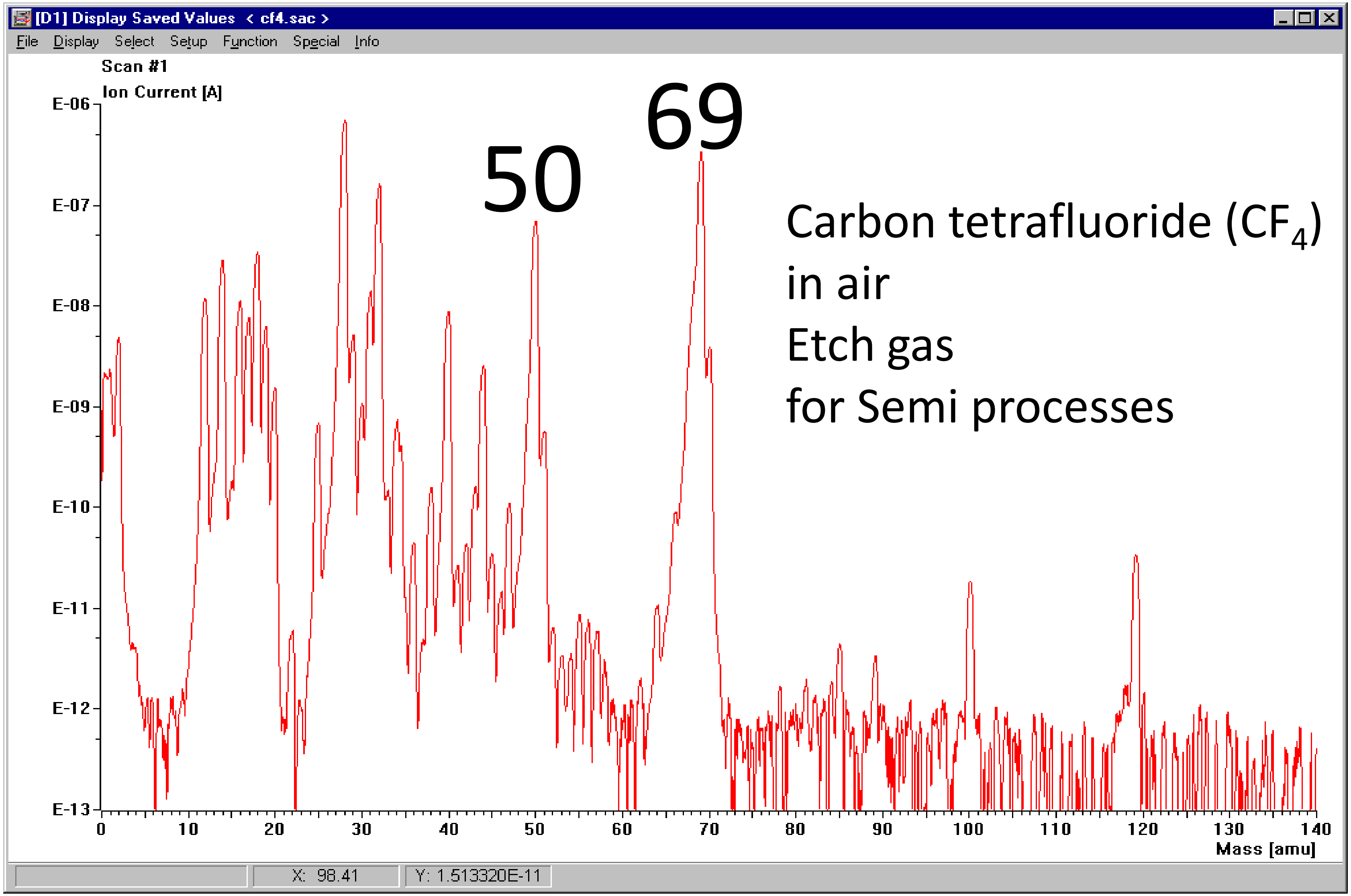


Acetone in air,
used for cleaning

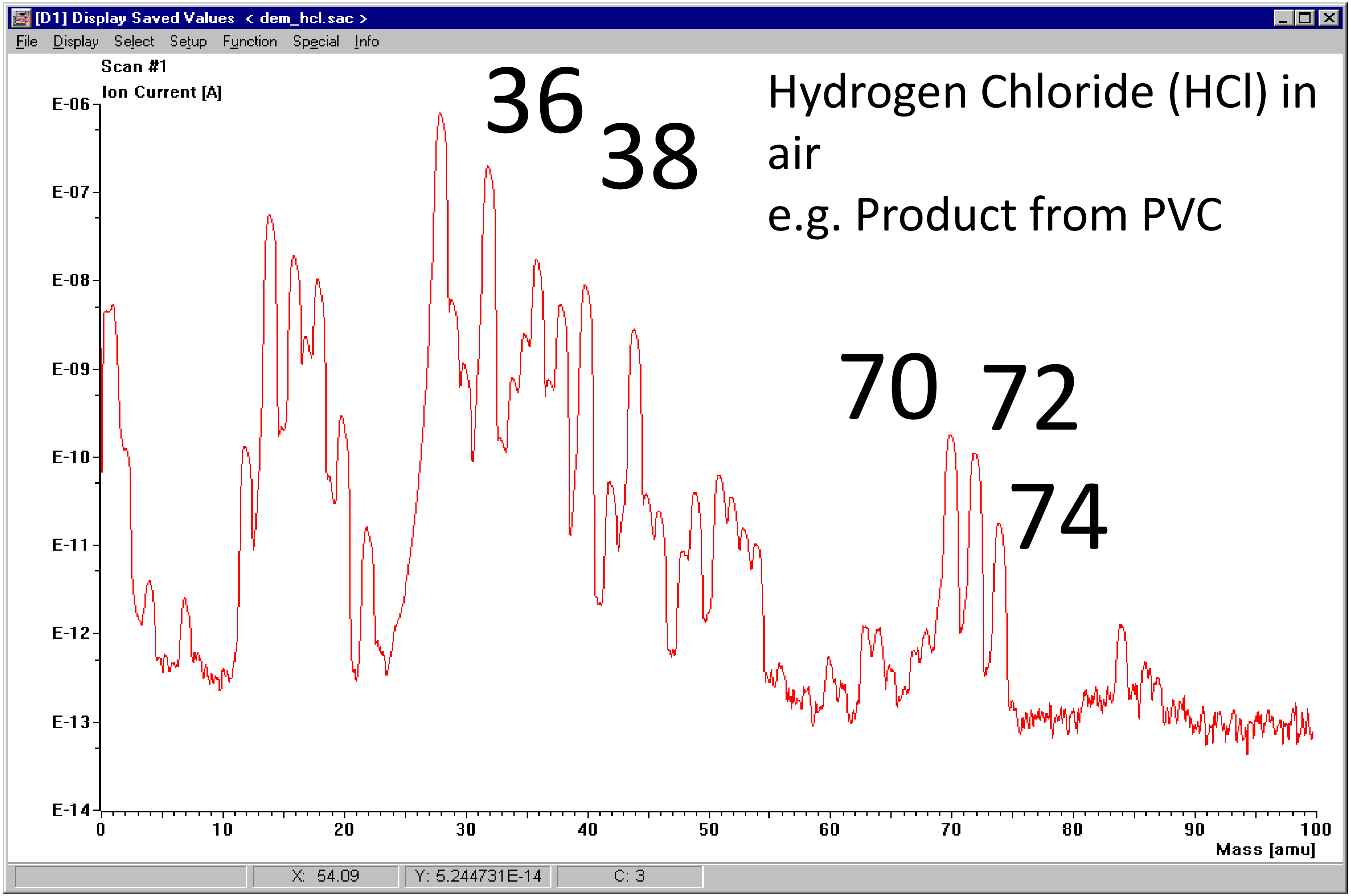


Ethanol in Air,

Used for cleaning



Carbon tetrafluoride (CF_4)
in air
Etch gas
for Semi processes



X: 54.09 | Y: 5.244731E-14 | C: 3

36

38

Hydrogen Chloride (HCl) in air

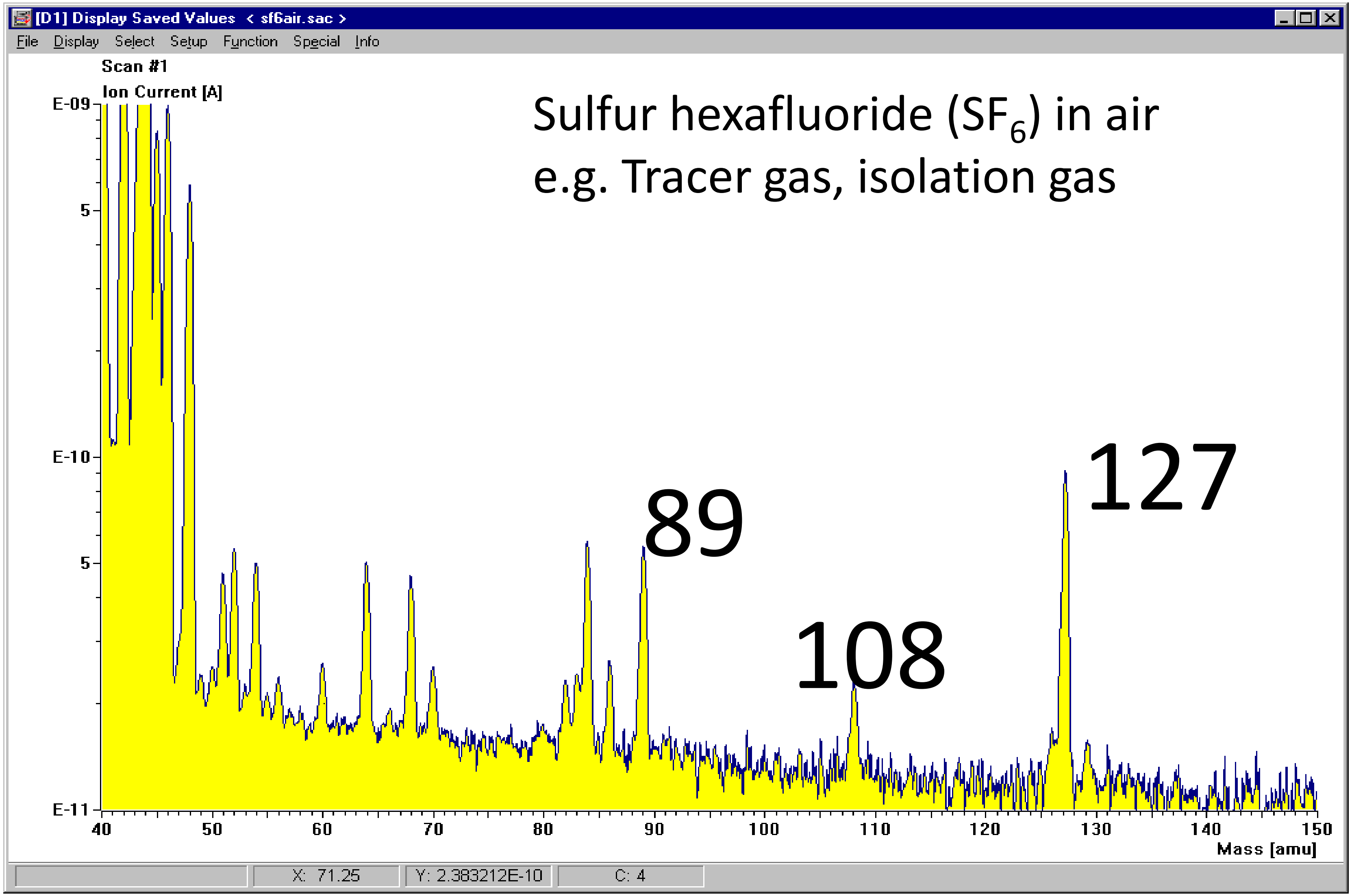
e.g. Product from PVC

70

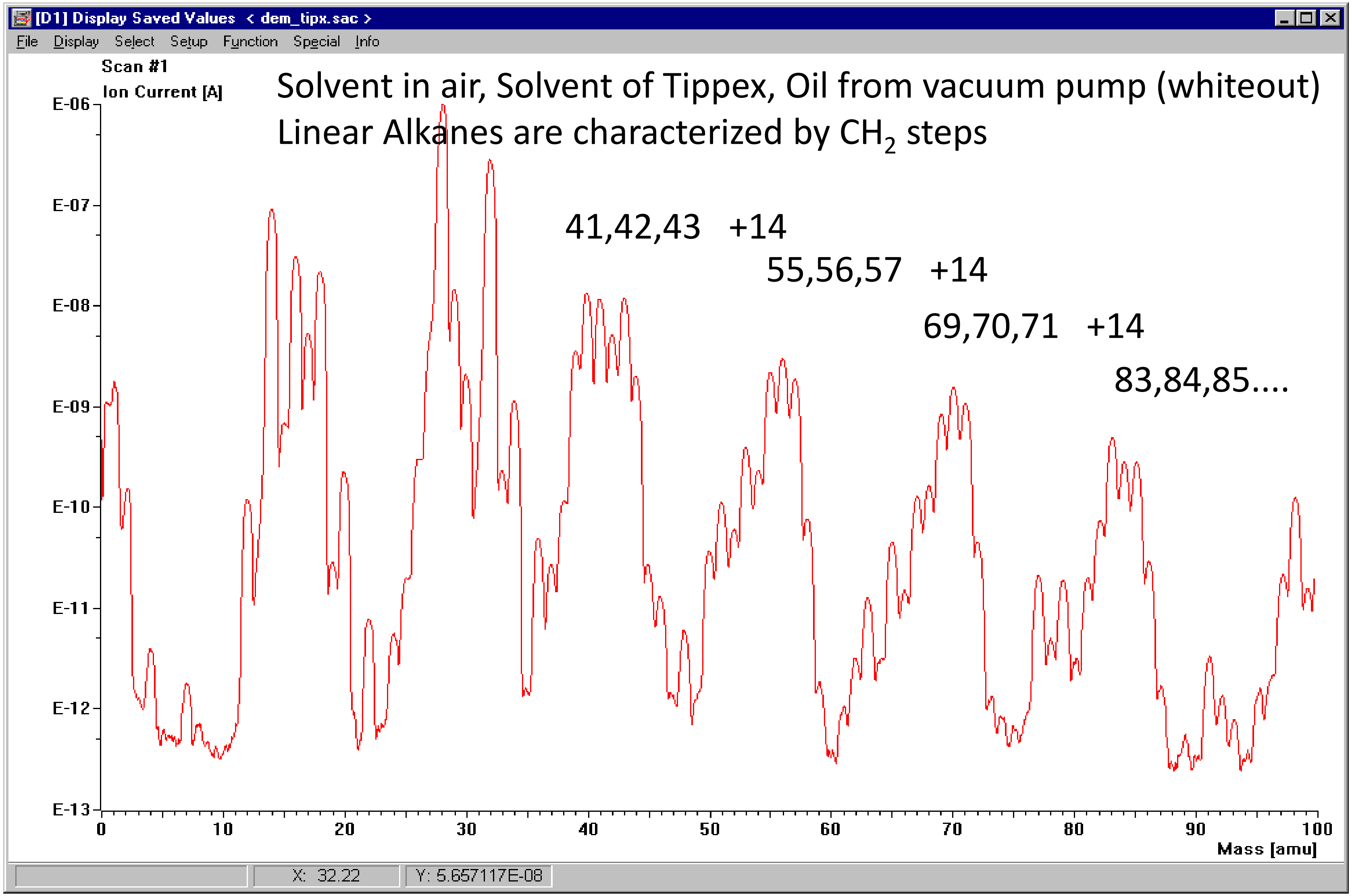
72

74

Sulfur hexafluoride (SF_6) in air
e.g. Tracer gas, isolation gas



X: 71.25
Y: 2.383212E-10
C: 4



Solvent in air, Solvent of Tippex, Oil from vacuum pump (whiteout)

Linear Alkanes are characterized by CH_2 steps

41,42,43 +14

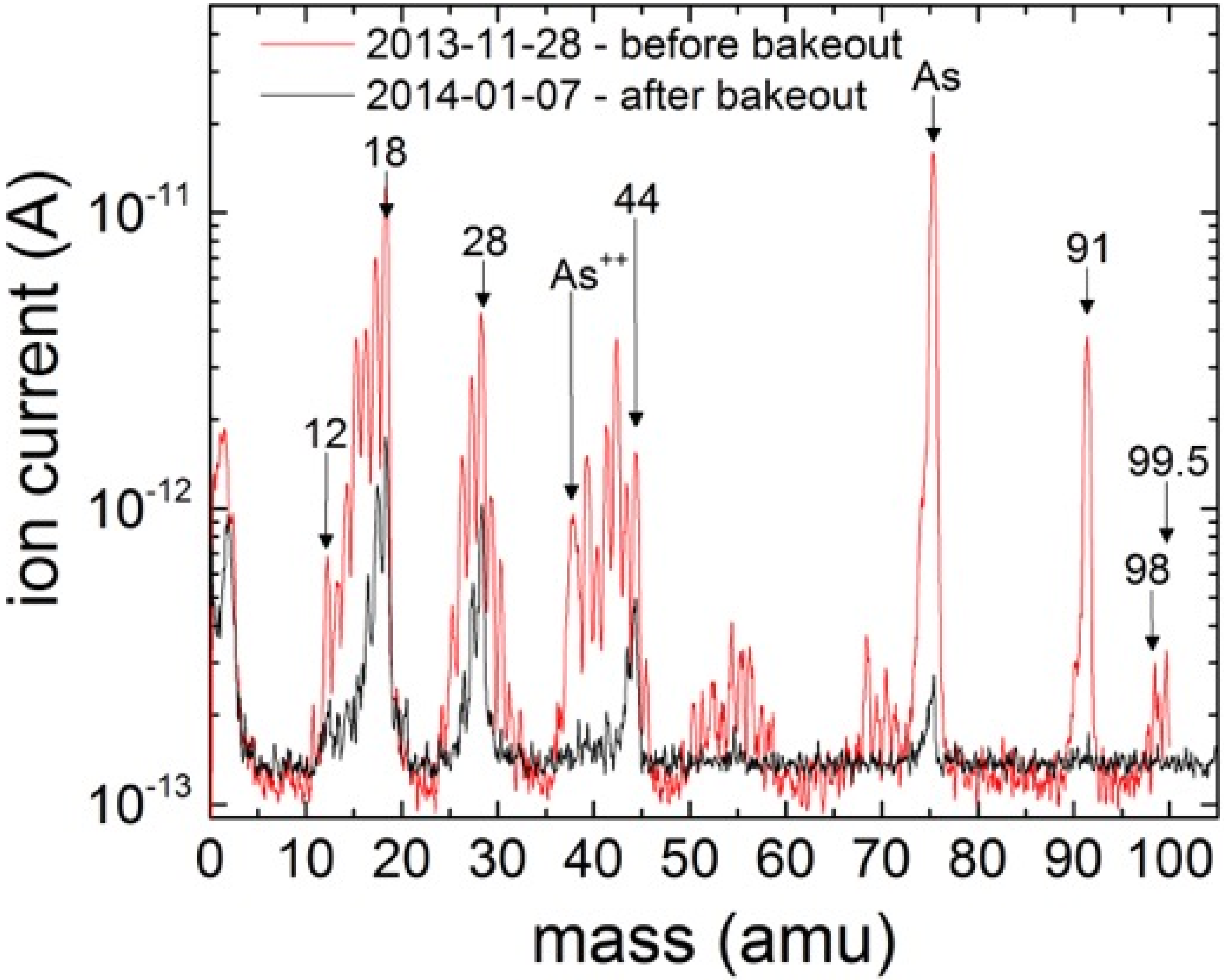
55,56,57 +14

69,70,71 +14

83,84,85....

X: 32.22

Y: 5.657117E-08


2013-11-28 - before bakeout
2014-01-07 - after bakeout
As
18
44
28
As++
91
12
99.5
98
ion current (A)
10-11
10-12
10-13
0
10
20
30
40
50
60
70
80
90
100
mass (amu)

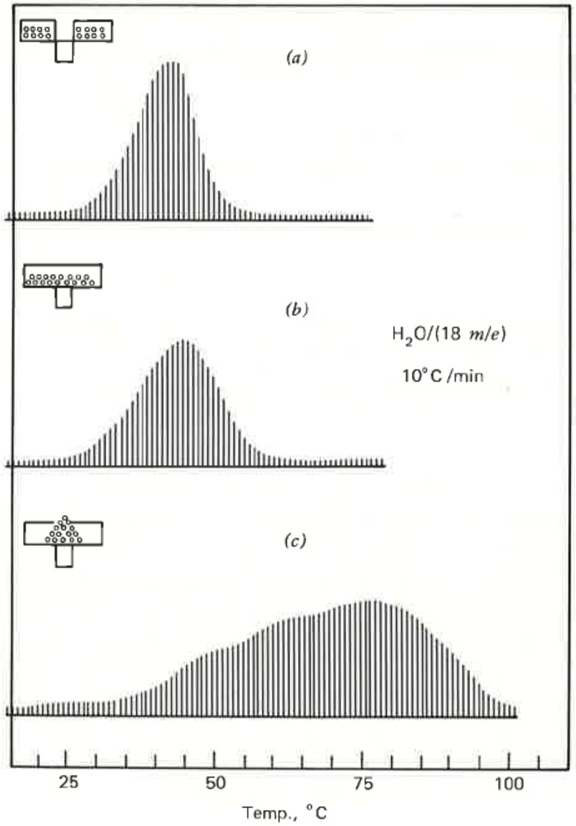


Figure II.13. Effect of sample packing and sample-holder geometry on the evolution of water from $CaC_2O_4 \cdot H_2O$ (43).

W Wendland Thermal methods of analysis. John Wiley & Sons, *1974*.