Sistema di Introduzione
DI, MIMS, GC, HPLC, CZE, CEC, ITP

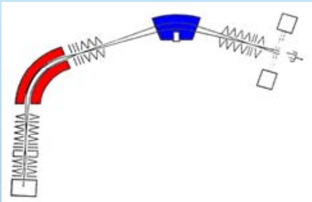
Sorgente
EI, CI, PD, FD, FAB, LSIMS, **ESI**, **APCI, MALDI**

Analizzatore
Settori (EB; BE; EBE …)
Quadrupolo (Q, QqQ)
Trappola ionica, FT-ICR
Orbitrap, Tempo di volo (TOF)
Ibridi (BEqQ; QTOF ….)

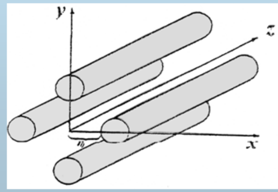
Separazione degli ioni secondo il loro rapporto massa/carica (*m/z*)

Separazione degli ioni
….. nello spazio

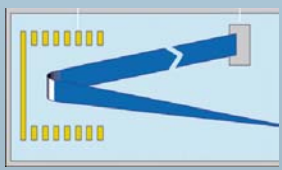
Separazione degli ioni
….. nello spazio



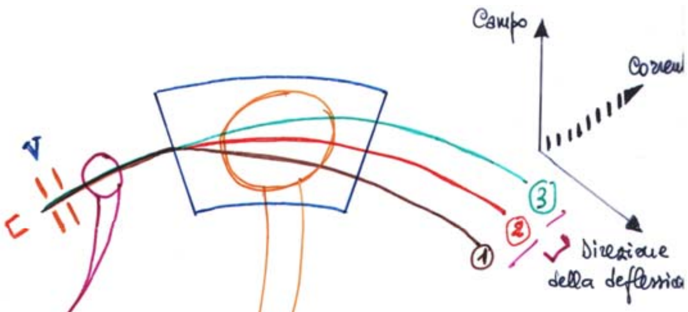
Settori: elettrostatico e magnetico



Quadrupolo



Tempo di volo



$E_{pot} = zeV$

$E_{cin} = \frac{1}{2} m v^2$

$zeV = \frac{1}{2} m v^2$

F. centripeta = $Bzev$

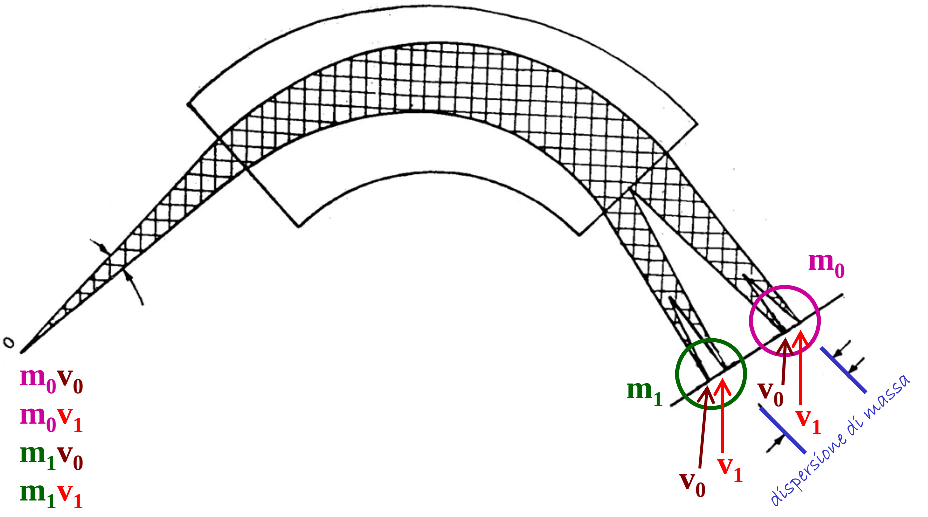
F. centrifuga = $\frac{mv^2}{r}$

$$\frac{m}{ze} = \frac{B^2 \cdot r}{2V}$$

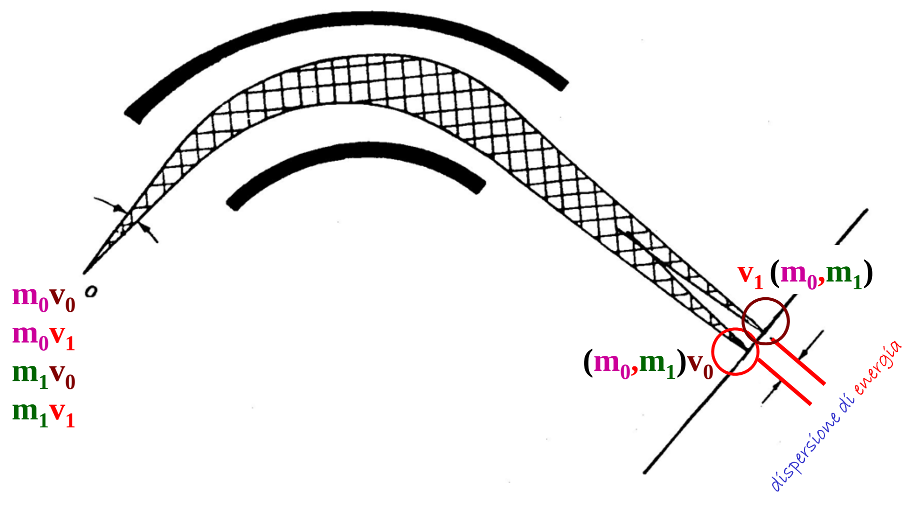
$$\boxed{r^2 \propto \frac{m}{z}}$$

(B, V costante)

PRINCIPIO DI FUNZIONAMENTO DI UN SETTORE MAGNETICO



SETTORE ELETTROSTATICO



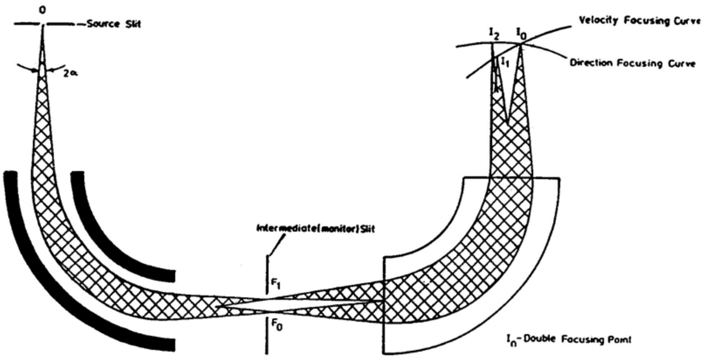
DOPPIO FUOCO

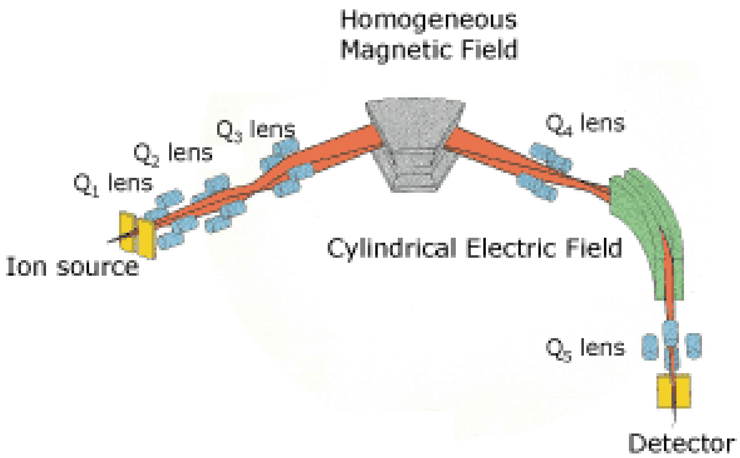
Focalizzazione di un fascio ionico

- **divergente**

e

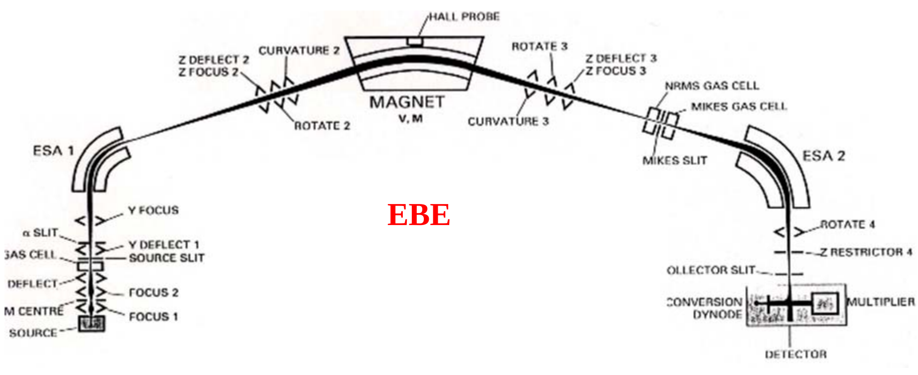
- **non omogeneo in energia**





GCmate II Ion Optics Design

1974

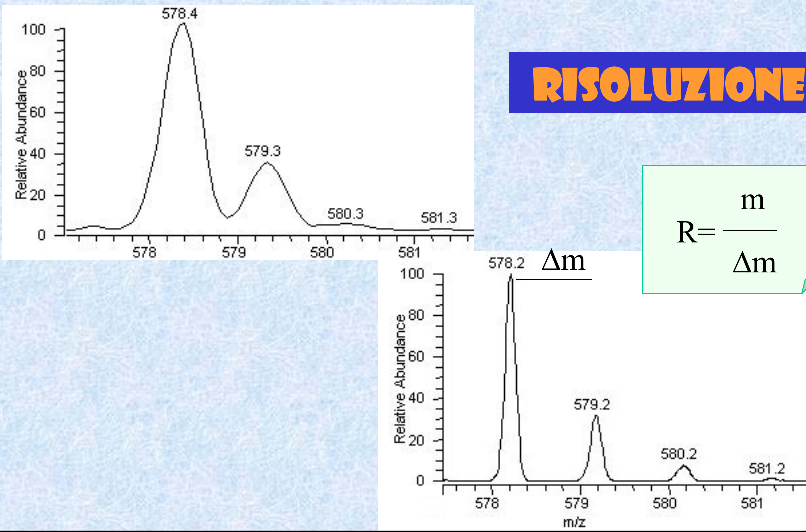

HALL PROBE
CURVATURE 2
Z DEFLECT 2
Z FOCUS 2
ROTATE 2
MAGNET
V, M
ROTATE 3
Z DEFLECT 3
Z FOCUS 3
CURVATURE 3
NRMS GAS CELL
MIKES GAS CELL
MIKES SLIT
ESA 1
ESA 2
Y FOCUS
α SLIT
Y DEFLECT 1
SOURCE SLIT
DEFLECT
FOCUS 2
FOCUS 1
SOURCE
ROTATE 4
Z RESTRICTOR 4
DYNODE
MULTIPLIER
DETECTOR

EBE

EBEBE

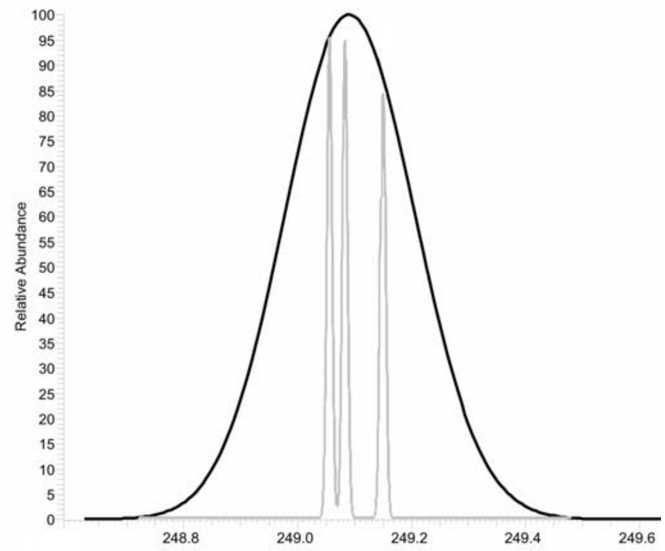
1985-1993

Proprietà degli analizzatori:

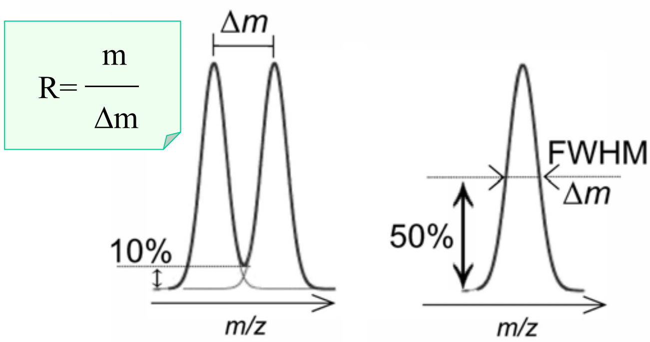


RISOLUZIONE

$$R = \frac{m}{\Delta m}$$

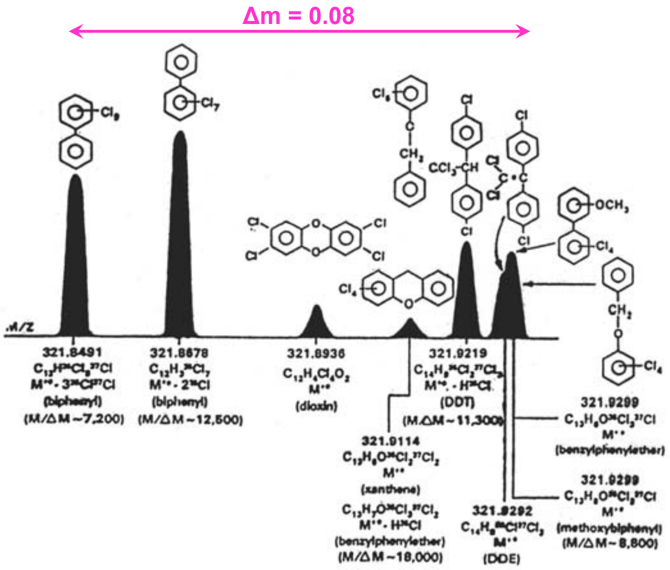


Mass spectra recorded at different resolutions: mass spectrum of a mixture of three isobaric species $[C_{19}H_7N]^+$, $[C_{20}H_9]^+$, $[C_{13}H_{19}N_3O_2]^+$ obtained at low resolution (black line) and at resolving power 50,000 (grey line). It is noteworthy that at low resolution the three peaks are completely unresolved.



Resolution at 10% valley (left) and at full width at half maximum (FWHM, right).

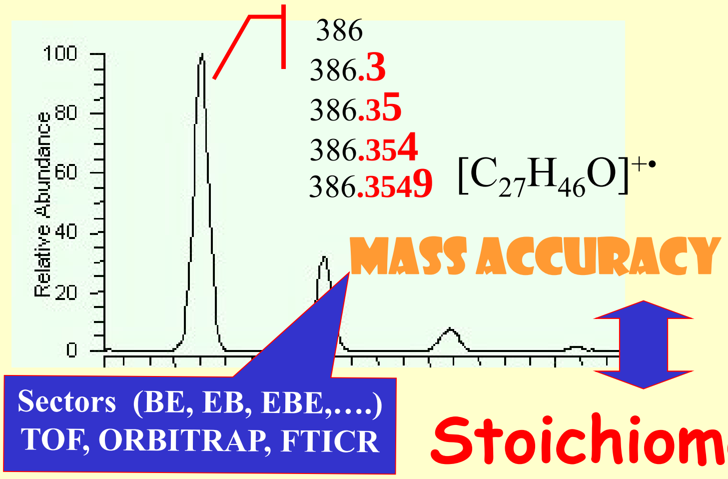
Summary of some PCDDs mass spectral interferences of environmental origin



PCDDs=polychlorinated dibenzo-*p*-dioxins

Performances of analyzers:

Mass accuracy



Stoichiometry

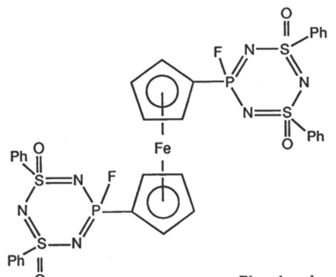
Exact mass

The **calculated mass** of an ion or molecule containing a single isotope of each atom

Accurate mass

An **experimentally determined mass** of an ion that is used to determine an elemental formula

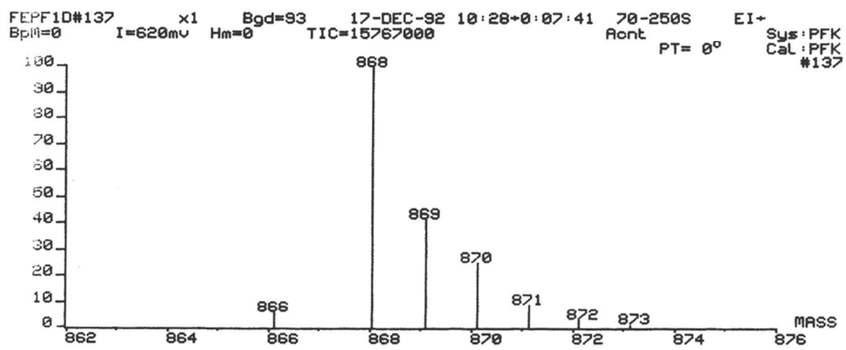
Mass Spec Terms Project: http://mass-spec.lsu.edu/msterms/index.php/Category:Mass_spectrometry_terms

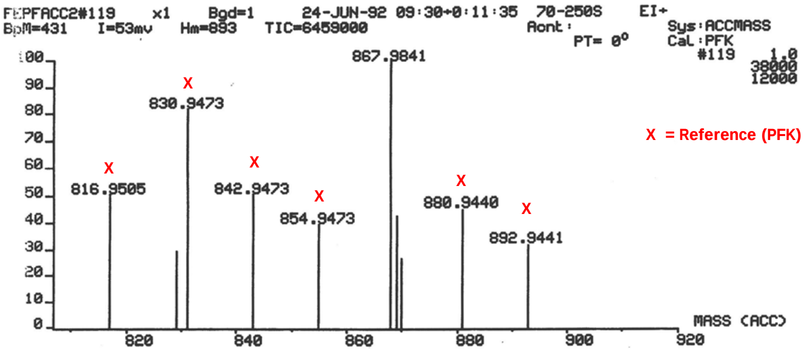


Ph= phenyl

VG 70-250S
m/z 900-200
10 sec/dec
Res=8.000 (10% valley)

$C_{34}H_{28}N_6O_4FeS_4P_2F_2$





FEPFACC2 #119 x1 Bgd=1 24-JUN-92 09:30+0:11:35 70-250S
BpM=431 I=53mv Hm=893 TIC=6459000 Acnt:
PT= 0°

M/E	C 12	C 13	H	N	FE	S	F	P	O	PPM	DBE	ACC.MASS
868	40	0	20	6	1	2	2	2	4	7.0	34.0	867.9780195
	40	0	23	6	1	3	1	2	3	4.4	33.0	867.9802486
	37	0	24	6	1	3	2	2	4	3.1	29.0	867.9813915
	36	1	23	6	1	3	2	2	4	8.2	29.5	867.9769213
	40	0	25	6	1	4	0	1	4	-7.7	32.0	867.9907185
	39	1	24	6	1	4	0	1	4	-2.5	32.5	867.9862483
	40	0	26	6	1	4	0	2	2	1.8	32.0	867.9824777
	39	1	25	6	1	4	0	2	2	7.0	32.5	867.9780075
	37	0	27	6	1	4	1	2	3	0.5	28.0	867.9836206
	36	1	26	6	1	4	1	2	3	5.7	28.5	867.9791504
	40	1	21	6	1	4	2	0	3	-7.9	33.5	867.9909016
	40	1	22	6	1	4	2	1	1	1.6	33.5	867.9826607
	34	0	28	6	1	4	2	2	4	-0.8	24.0	867.9847635
	33	1	27	6	1	4	2	2	4	4.3	24.5	867.9802933

C 0÷100
H 1÷100
N 0÷8
Fe 0÷1
S 0÷6
F 0÷4
P 0÷4
O 0÷6

Single mass

Mass: 474.25725

Max. results 10 Calculate

Idx	Formula	RDB	Delta ppm
1	$C_{21}H_{32}O_4N_9$	10.5	0.154
2	$C_{20}H_{36}O_8N_5$	5.5	2.974
3	$C_{25}H_{36}O_6N_3$	9.5	-5.508
4	$C_{19}H_{40}O_{12}N$	0.5	5.794
5	$C_{26}H_{32}O_2N_7$	14.5	-8.328
6	$C_{15}H_{36}O_{10}N_7$	1.5	11.456
7	$C_{14}H_{36}O_9N_9$	1.5	-12.230
8	$C_{30}H_{36}O_4N$	13.5	-13.990

File... List Simulate

Limits

Charge: 1

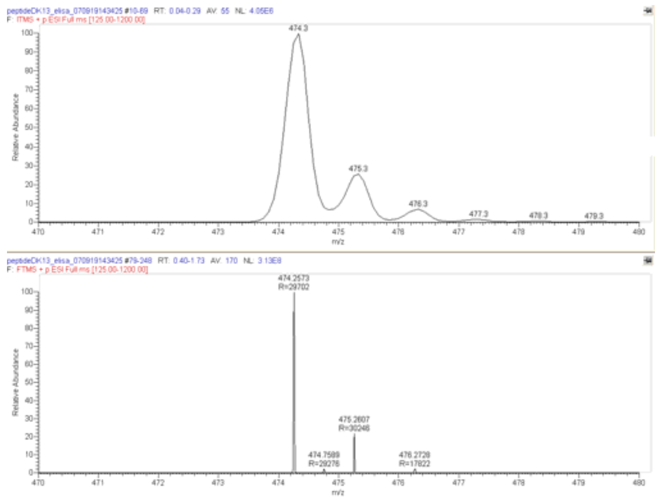
Nitrogen-Rule: Even electron ions

Mass tolerance 140.00 ppm

RDB equiv: -1.0-100.0

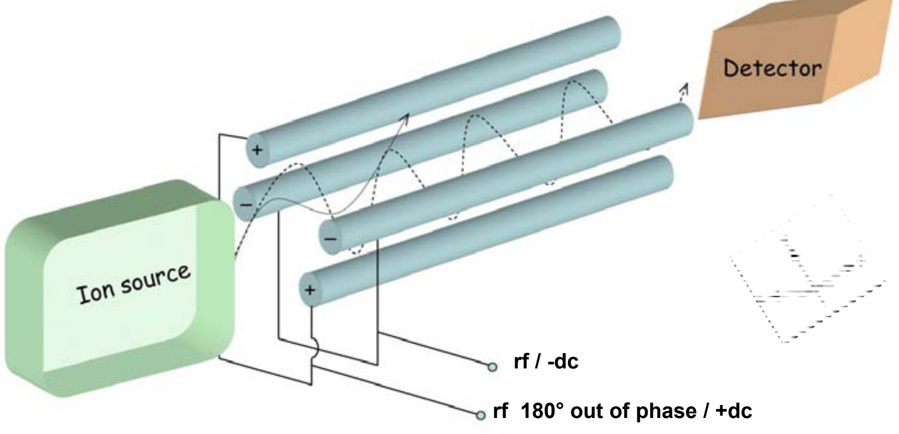
Elements in use

Isotope	Min	Max	DB eq.	Mass
14 N	0	10	0.5	14.003
16 O	0	15	0.0	15.995
12 C	0	30	1.0	12.000
1 H	0	60	-0.5	1.008

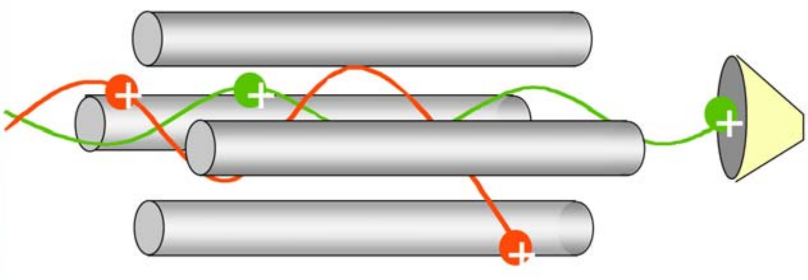


Analizzatori: il quadrupolo

Four rods arranged an equal distance from each other in a parallel manner

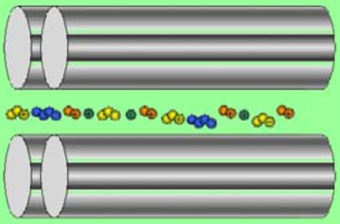


Quadrupole Mass Analyser

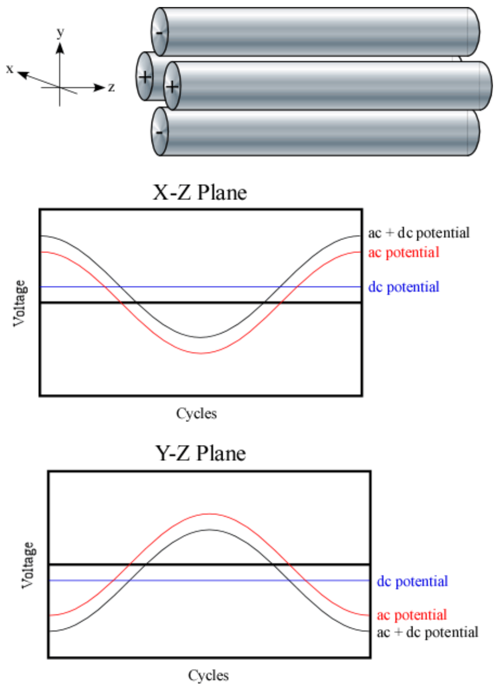


The ion is transmitted along the quadrupole in a stable trajectory Rf field. The ion does not have a stable trajectory and is ejected from the quadrupole.

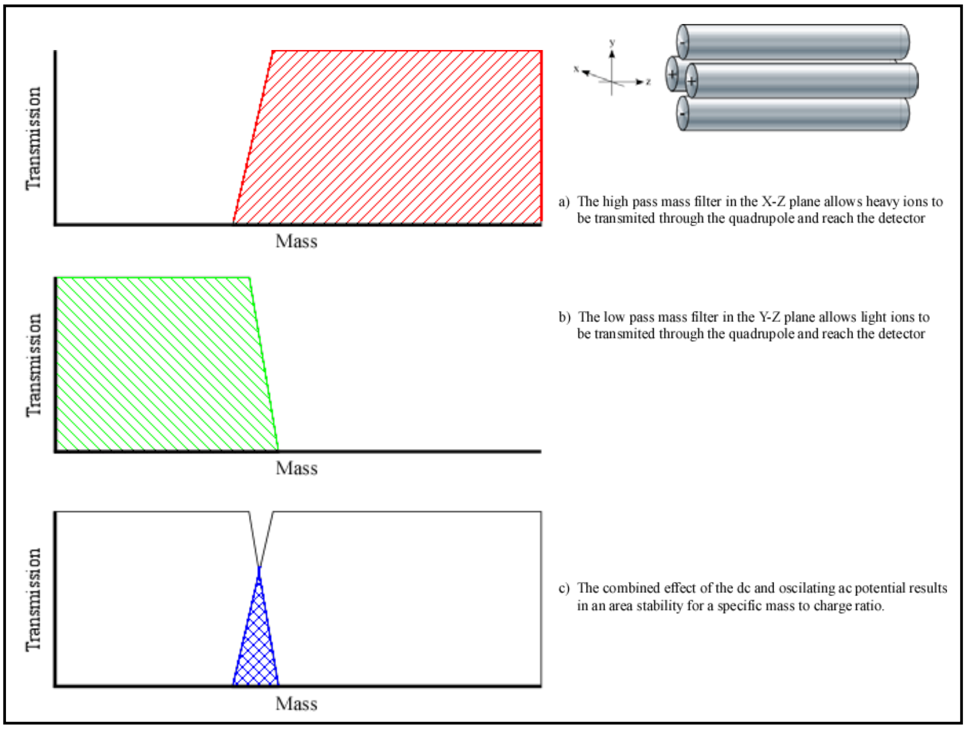
Il movimento degli ioni all'interno del quadrupolo dipende da:

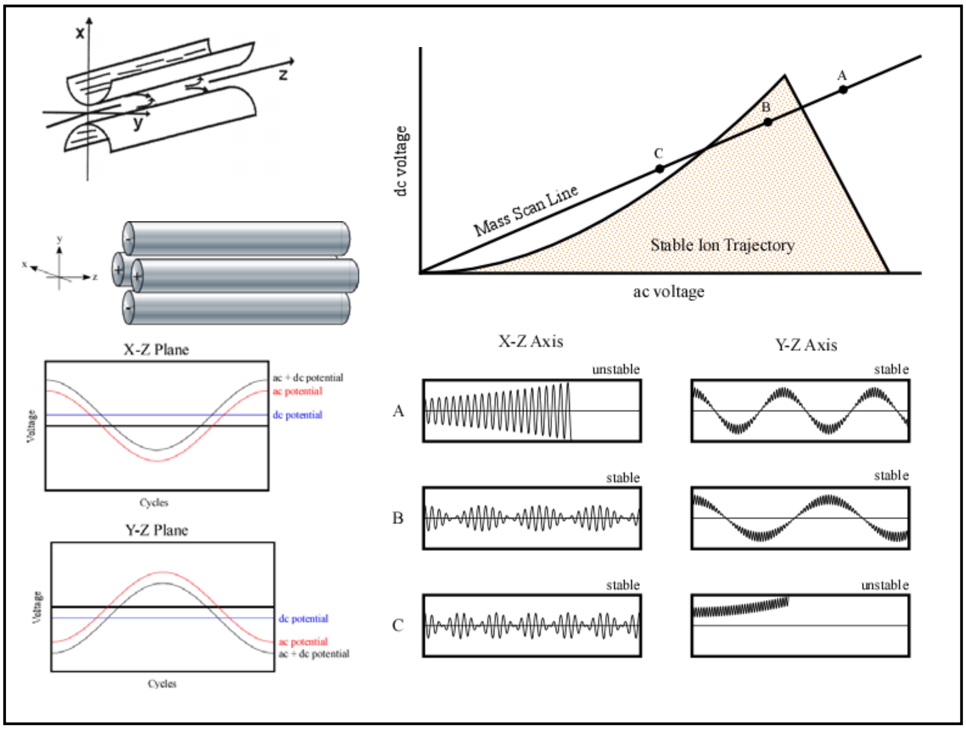


1. Il loro rapporto *m/z*
2. Le dimensioni del quadrupolo
3. Intensità potenziale dc (U)
4. Intensità potenziale rf (V)
5. La frequenza del potenziale rf



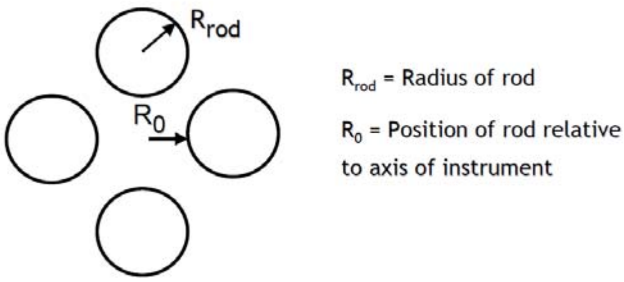
http://people.whitman.edu/~dunnivfm/C_MS_Ebook/CH5/5_2.html


Transmission
Mass
a) The high pass mass filter in the X-Z plane allows heavy ions to be transmited through the quadrupole and reach the detector
b) The low pass mass filter in the Y-Z plane allows light ions to be transmited through the quadrupole and reach the detector
c) The combined effect of the dc and oscilating ac potential results in an area stability for a specific mass to charge ratio.

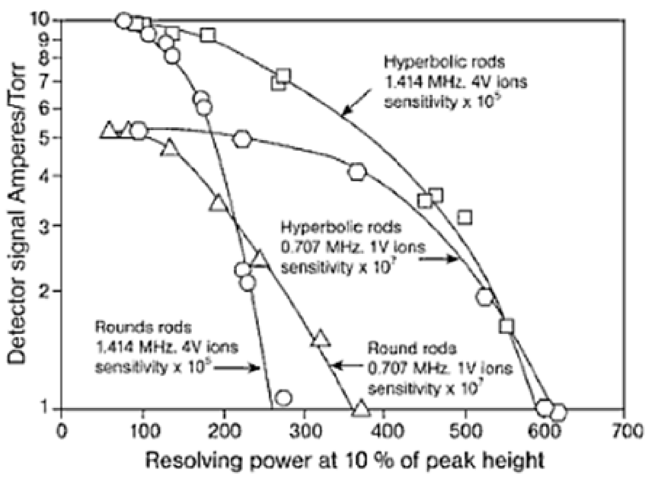

x
y
z
X-Z Plane
ac + dc potential
ac potential
dc potential
Voltage
Cycles
Y-Z Plane
dc voltage
ac voltage
Mass Scan Line
Stable Ion Trajectory
A
B
C
X-Z Axis
Y-Z Axis
unstable
stable

Hyperbolic rods

Round rods can only approximate the field generated by hyperbolic rods - most ideal when R_{rod}/R_0 = 1.16.



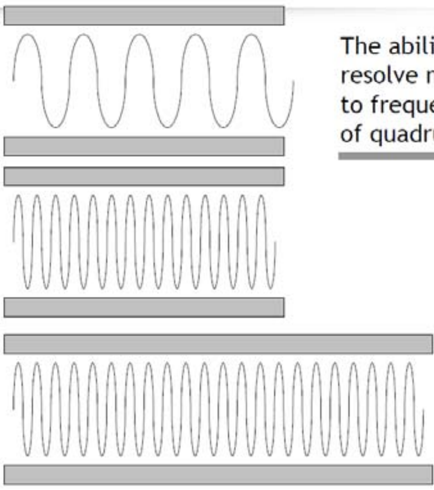
Manufacturing such a kind of rods is non-trivial



Ion transmission of round and hyperbolic quadrupole systems (resolving power ag. ion transmission), first documented investigation by Brubaker 1968 (two curves left: round rods; two curves right: hyperbolic rods).

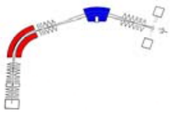
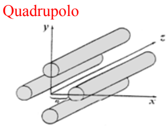
Hyperbolic Rods Quadrupoles

Resolving Power of a quadrupole



The ability of a quadrupole to resolve masses is proportional to frequency of AC and length of quadrupole

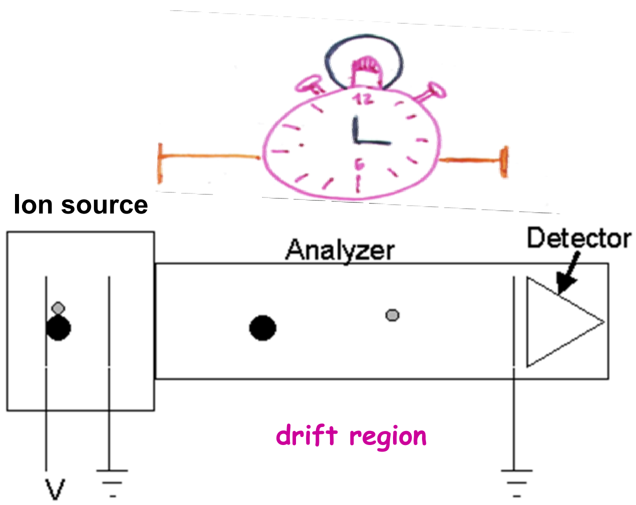
Separazione degli ioni nello spazio

Analizzatore	Forza	Separazione in base a	Range m/z	Risoluzione	Massa accurata
Doppio fuoco (EB, BE) 	Campo magnetico + campo elettrico	Momento degli ioni + energia cinetica	10.000	10.000	< 1ppm
Quadrupolo 	Campo elettrico e radiofrequenza	Stabilità/instabilità	2.000-4.000	Unitaria (0.2 u FWHM)	No (>20ppm)

1946

William Stephens at the Univ. of Pennsylvania proposed the concept of

time of flight



In an ideal case, all ions leave the source with the same kinetic energy:

$$eV = \frac{1}{2}mv^2$$

where V = accelerating voltage, v = ion velocity.

As

$$v = \frac{D}{t}$$

where D = drift length and t = the flight time

$$\boxed{t = \left(\frac{m}{2eV}\right)^{1/2} D}$$

MW = 1000 Dalton; z=+1; D=1.5m; V=15 kV

$$\boxed{t = \left(\frac{m}{2eV}\right)^{1/2} D}$$

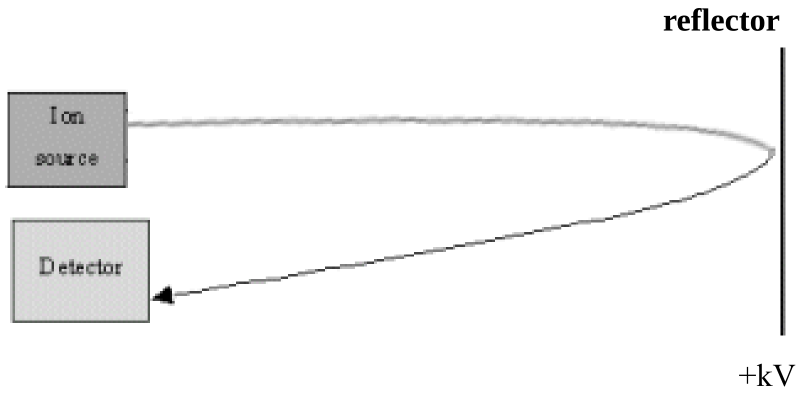
$$t = \sqrt{\frac{1000\text{Da} \times 1.672621 \times 10^{-27}\ \text{kg Da}^{-1}}{2 \times 15000\ \text{V} \times 1.602 \times 10^{-19}\ \text{C}}} \times 1.5\ \text{m} =$$

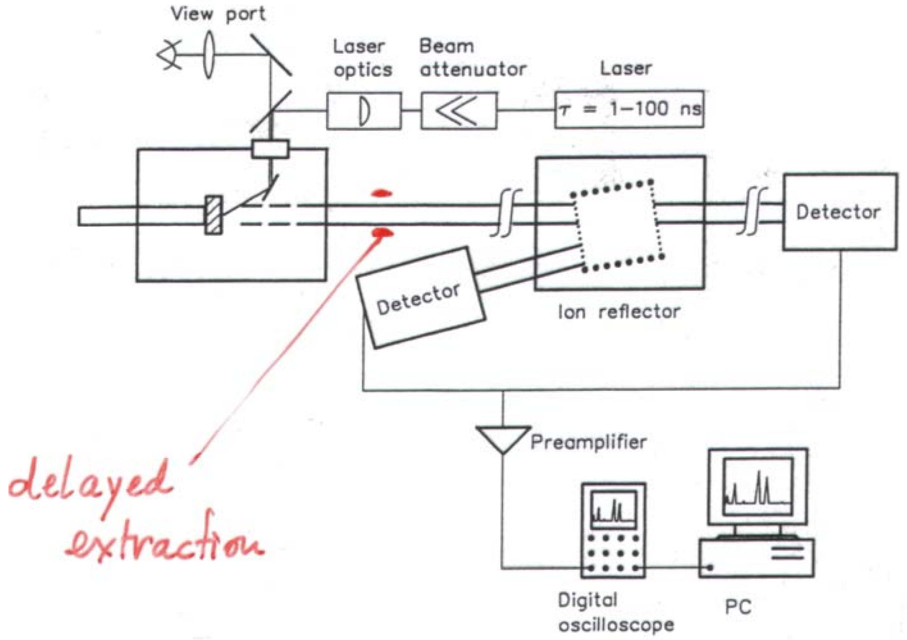
$$= 2.792 \times 10^{-5}\ \text{s} \approx 28\ \mu\text{s}$$

MW = 10000 Dalton V=15 kV $t \approx 88\ \mu s$

MW = 10000 Dalton V=30 kV $t \approx 63\ \mu s$

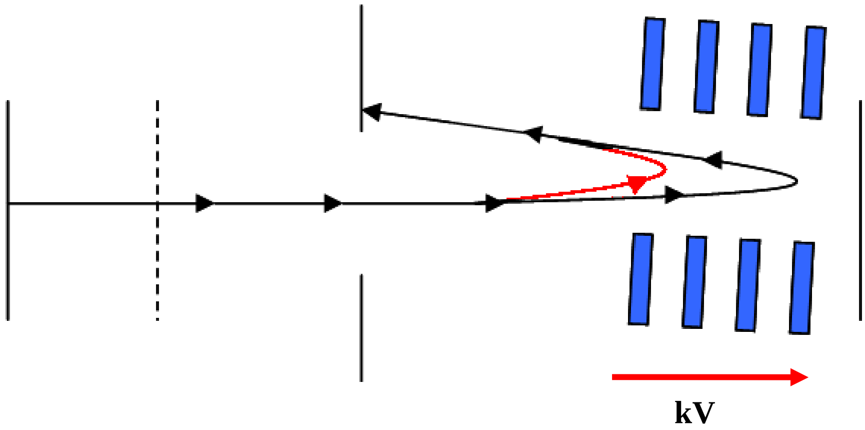
MW = 100000 Dalton V=30 kV $t \approx 20\ \mu s$

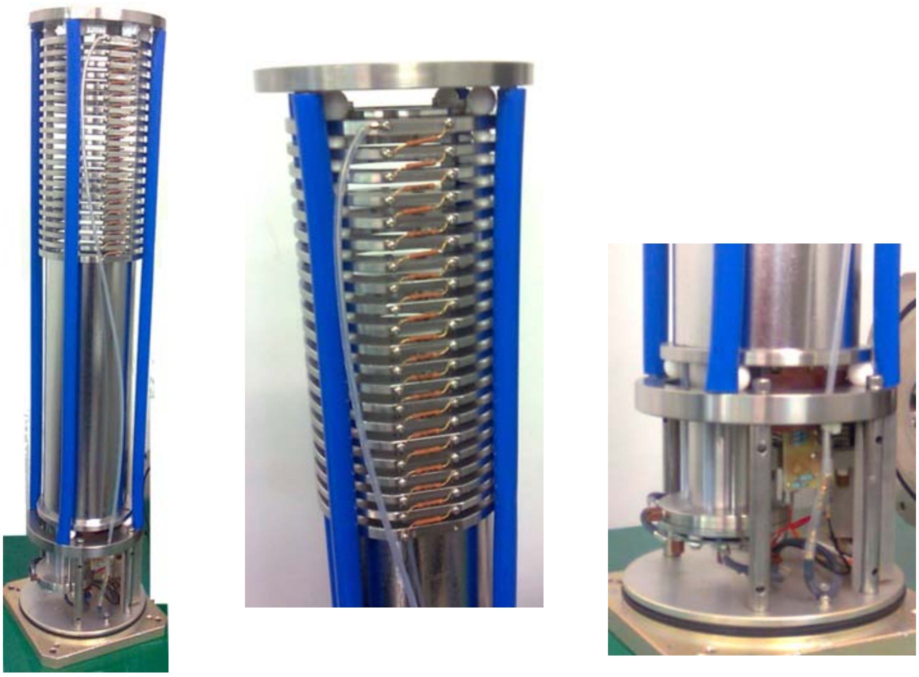


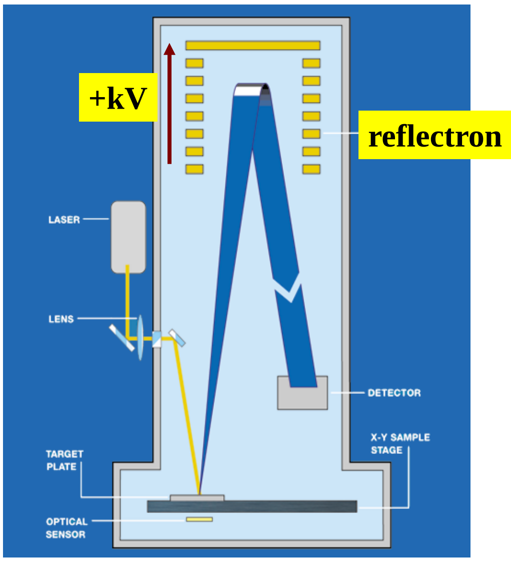


Schematic drawing of a laser desorption/ionization TOF instrument.

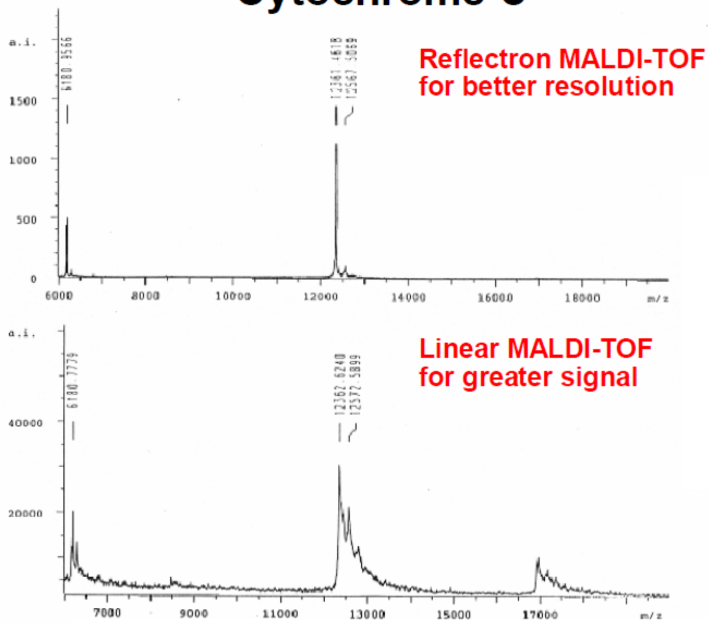
Reflectron



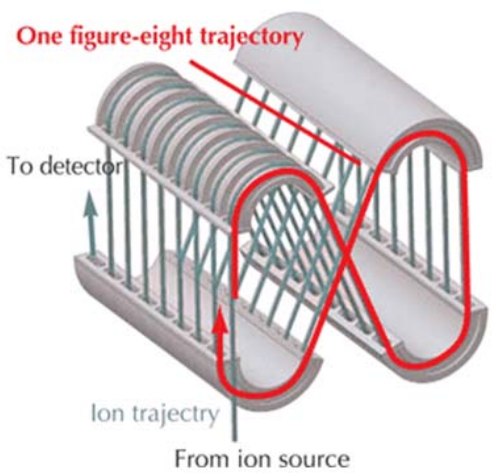




Cytochrome c



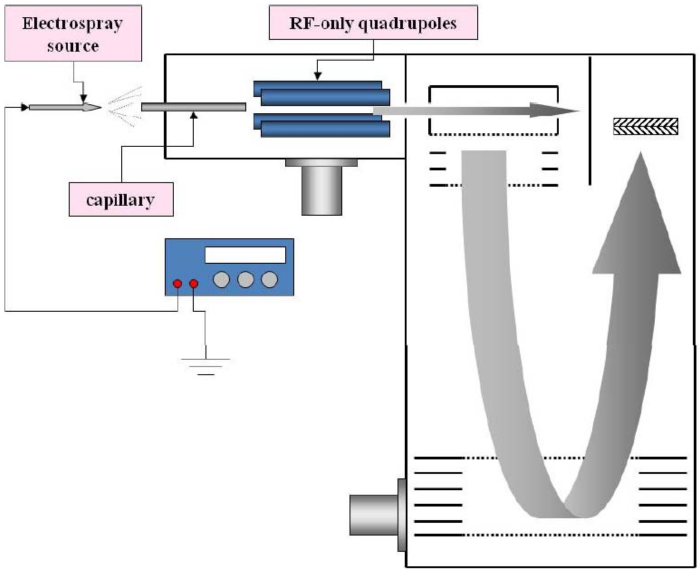
Spiral TOF



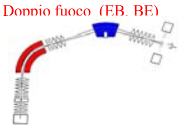
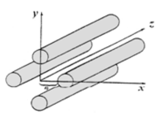
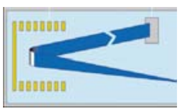
The spiral path is composed of 4 layered toroidal electrodes each incorporating 9 Matsuda plates inside its cylindrical electrode.
Ions are accelerated to 20 kV in the ion source, and then pass through each layer of the 4 layered toroidal electrodes, reaching the detector.

Ion path = 17m

oa-TOF with an ion guide and reflectron

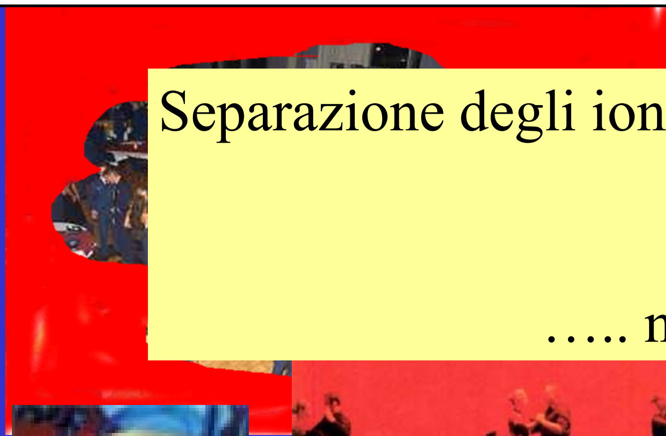


Separazione degli ioni nello spazio

Analizzatore	Forza	Separazione in base a	Range m/z	Risoluzione	Massa accurata
Doppio fuoco (EB, BE) 	Campo magnetico + campo elettrico	Momento degli ioni + energia cinetica	10.000	10.000	< 1ppm
Quadrupolo 	Campo elettrico e radiofrequenza	Stabilità/instabilità	2.000-4.000	Unitaria (0.2 u FWHM)	No (>20ppm)
Time of flight 		Velocità	>100.000	>10.000	2-5 ppm

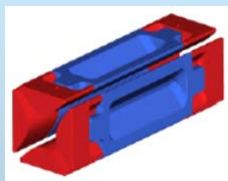
Separazione degli ioni

….. nel tempo

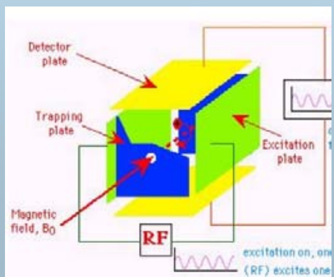


Separazione degli ioni
….. nel **tempo**

Trappola ionica **3D**

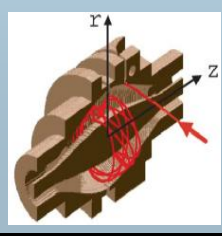


2D



Cella a risonanza ciclotronica

Orbitrap



The Nobel Prize in Physics 1989

The Royal Swedish Academy of Sciences has awarded this year's Nobel Prize in Physics for contributions of importance for the development of atomic precision spectroscopy

Hans Dehmelt
University of Washington
Seattle, USA

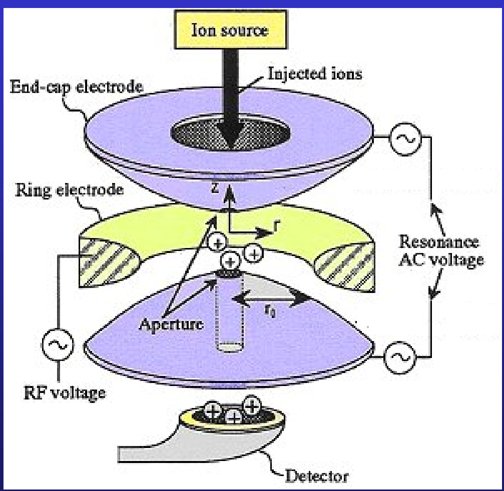
Wolfgang Paul
Universität Bonn
Federal Republic of Germany

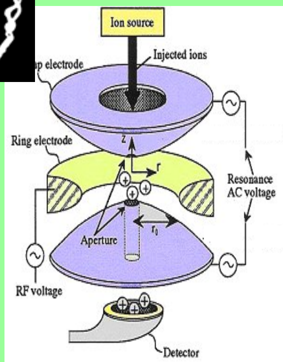
Norman F. Ramsey
Harvard University
Cambridge, USA

for the development of the ion trap technique

for the invention of the separated oscillatory fields method and its use in the hydrogen maser and other atomic clocks

La trappola ionica





Il movimento degli ioni all'interno della trappola dipende da:

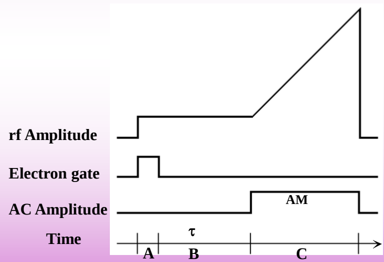
1. Il loro rapporto *m/z*
2. Le dimensioni della trappola (r)
3. Il potenziale dc (U) (elettr. anello)
4. Il potenziale rf (V) (elettr. anello)
5. La frequenza Ω del potenziale (elettr. anello)

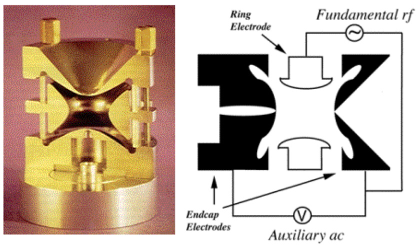
$$a_u = \frac{8eU}{m r_0^2 \Omega^2} \qquad q_u = \frac{4eV}{m r_0^2 \Omega^2}$$

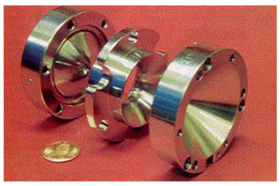
Equazione di Mathieu

Analizzatori:

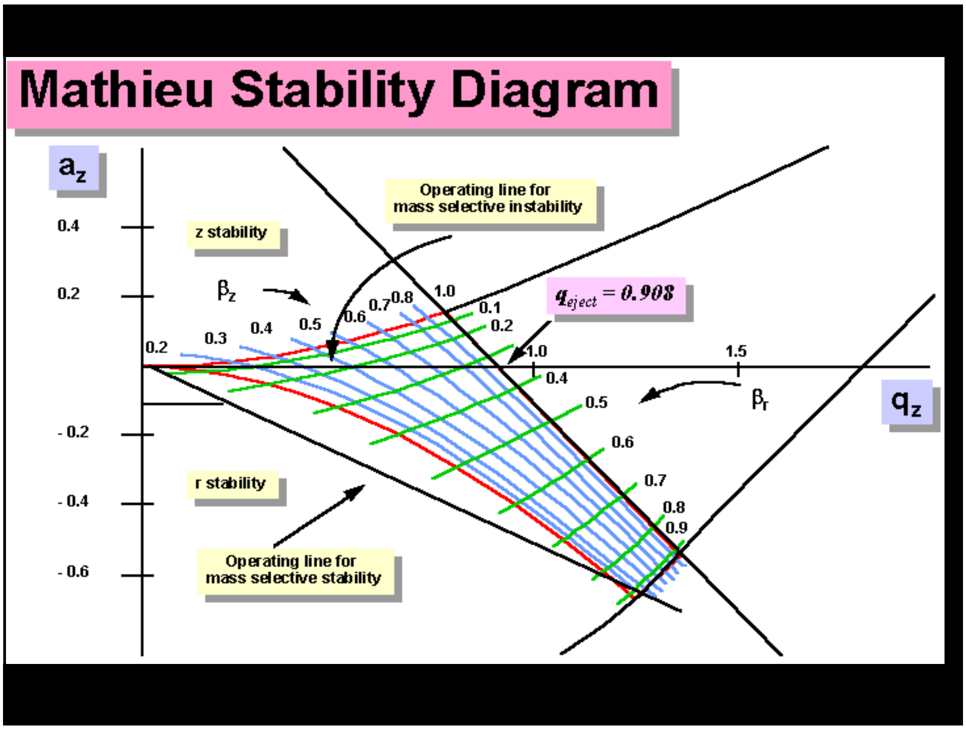
La trappola ionica



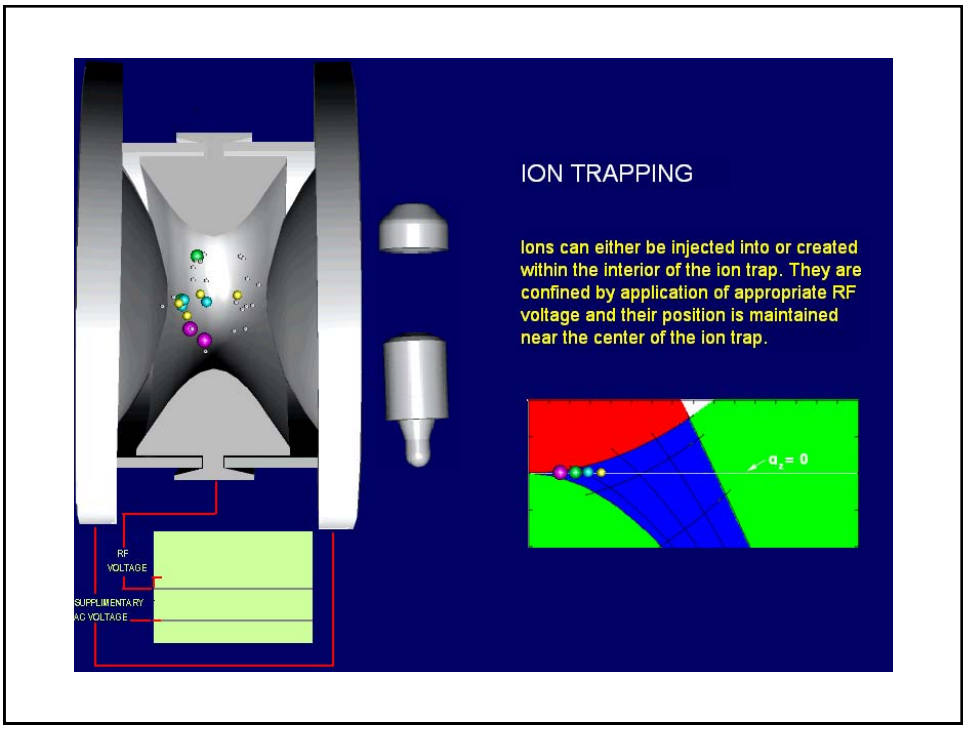




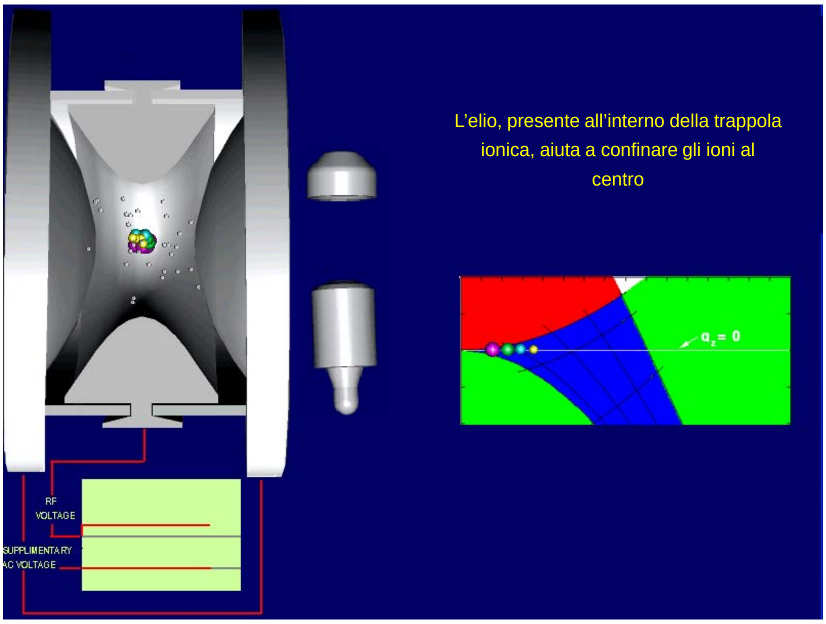
Separazione degli ioni nel tempo



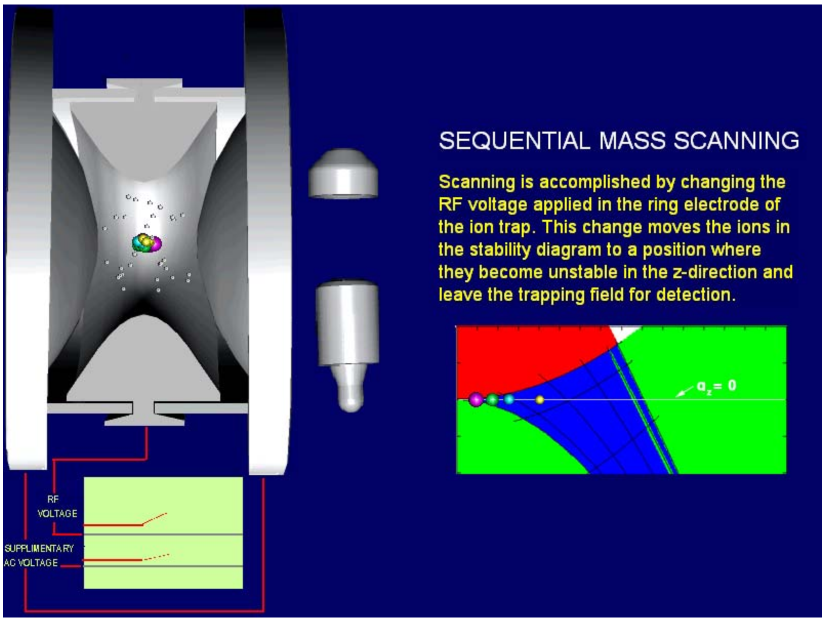
Mathieu Stability Diagram
a_z
0.4
0.2
- 0.2
- 0.4
- 0.6
z stability
r stability
Operating line for mass selective instability
Operating line for mass selective stability
β_z
β_r
$q_{eject} = 0.908$
0.2
0.3
0.4
0.5
0.6
0.7
0.8
1.0
0.1
0.2
1.0
0.4
0.5
0.6
0.7
0.8
0.9
1.5
q_z



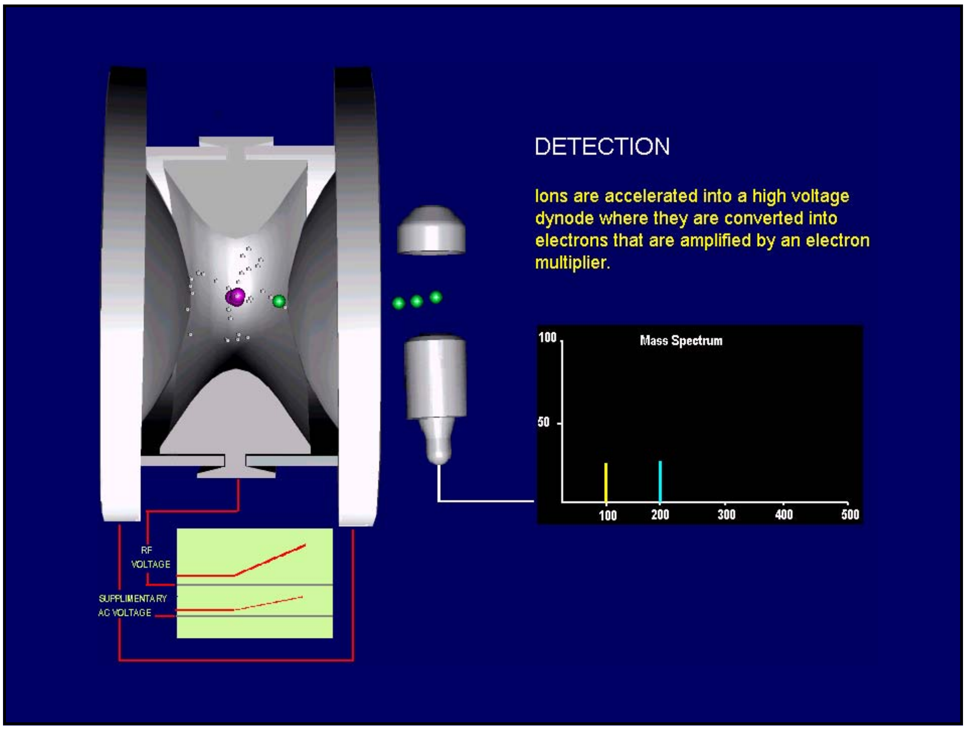
ION TRAPPING
Ions can either be injected into or created within the interior of the ion trap. They are confined by application of appropriate RF voltage and their position is maintained near the center of the ion trap.
RF VOLTAGE
SUPPLIMENTARY AC VOLTAGE
$a_z = 0$



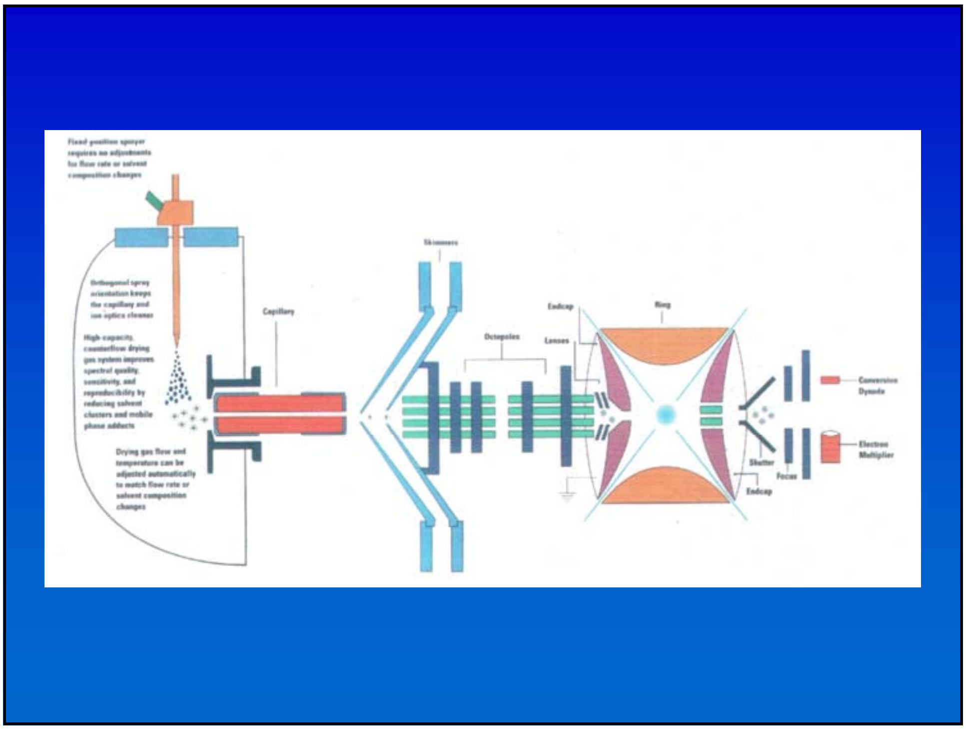
L'elio, presente all'interno della trappola ionica, aiuta a confinare gli ioni al centro
$a_z = 0$
RF VOLTAGE
SUPPLIMENTARY AC VOLTAGE



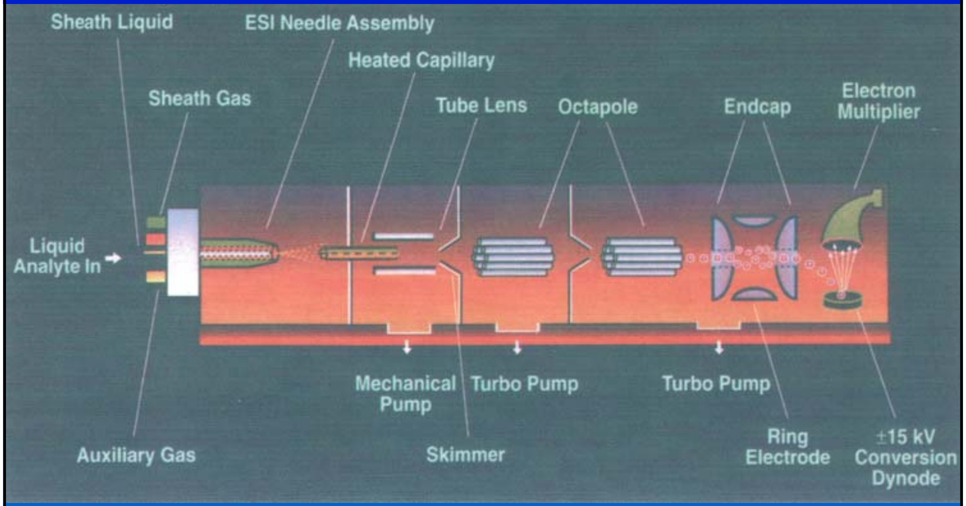
SEQUENTIAL MASS SCANNING
Scanning is accomplished by changing the RF voltage applied in the ring electrode of the ion trap. This change moves the ions in the stability diagram to a position where they become unstable in the z-direction and leave the trapping field for detection.
$a_z = 0$
RF VOLTAGE
SUPPLIMENTARY AC VOLTAGE



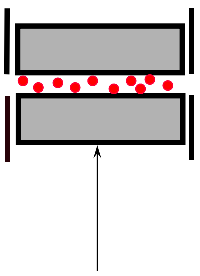
DETECTION
Ions are accelerated into a high voltage dynode where they are converted into electrons that are amplified by an electron multiplier.
Mass Spectrum
100
50
100
200
300
400
500
RF VOLTAGE
SUPPLIMENTARY AC VOLTAGE

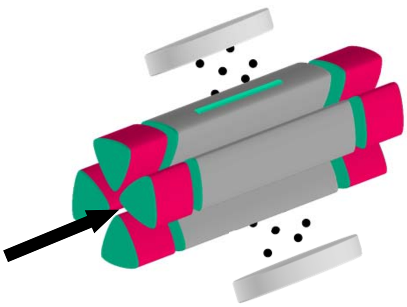


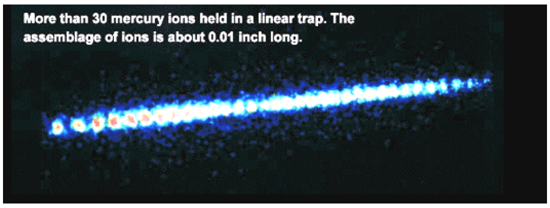
Fixed-position sprayer requires no adjustments for flow rate or solvent composition changes
Orthogonal spray orientation keeps the capillary and ion optics cleaner
High-capacity counterflow drying gas system improves spectral quality, sensitivity, and reproducibility by reducing solvent clusters and mobile phase adducts
Drying gas flow and temperature can be adjusted automatically to match flow rate or solvent composition changes
Capillary
Skimmers
Octopoles
Lenses
Endcap
Ring
Shutter
Focus
Endcap
Conversion Dynode
Electron Multiplier

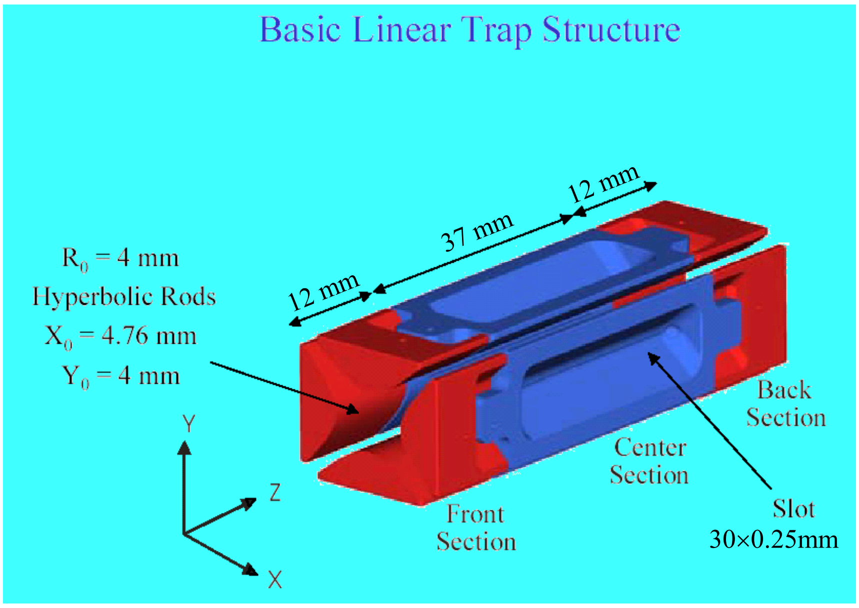


Trappola ionica lineare (2D)

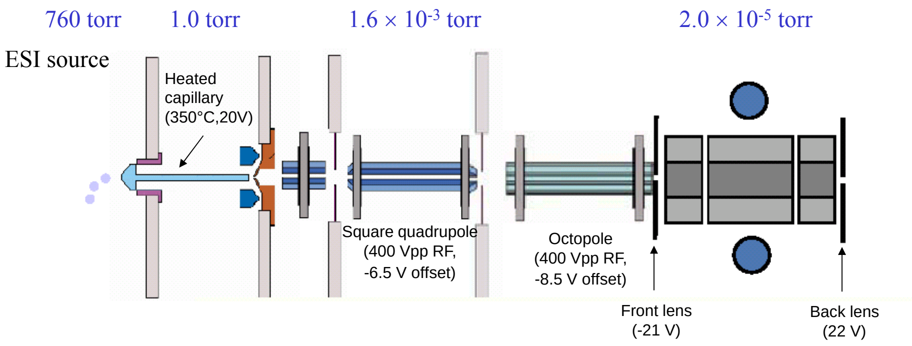






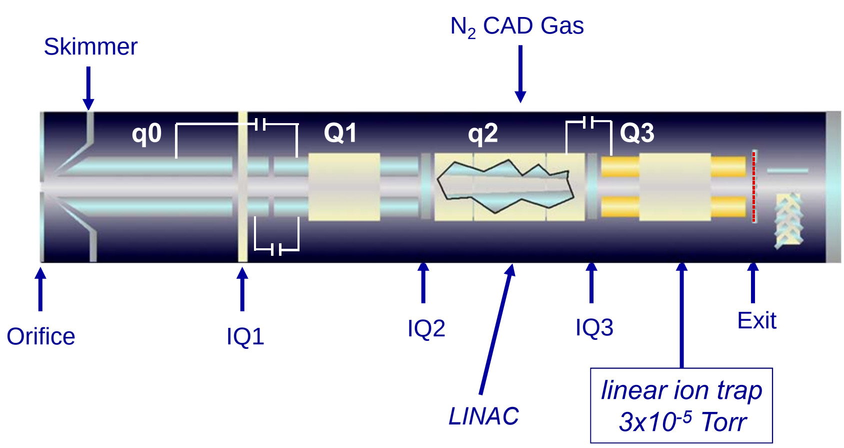

Basic Linear Trap Structure
R_0 = 4 mm
Hyperbolic Rods
X_0 = 4.76 mm
Y_0 = 4 mm
12 mm
37 mm
12 mm
Back Section
Center Section
Front Section
Slot
30×0.25mm
Y
Z
X

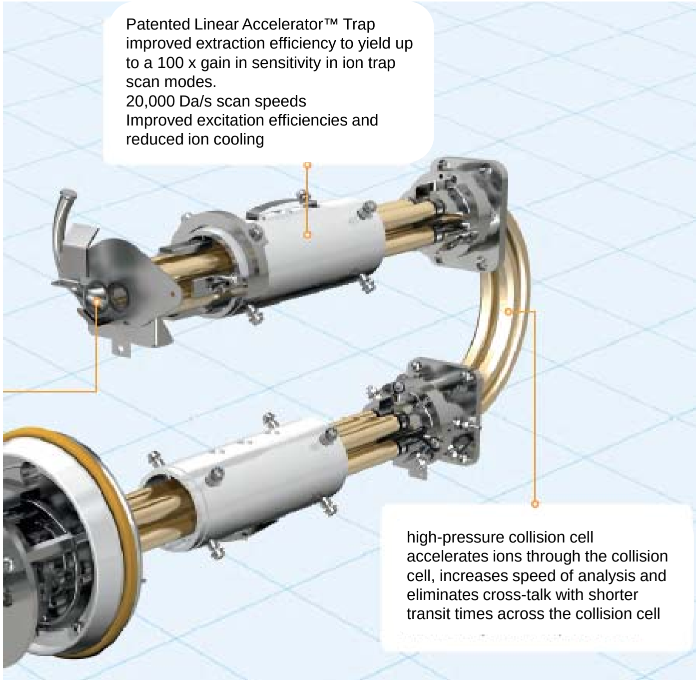
Linear Ion Trap



Analizzatori ibridi ….. QqIT

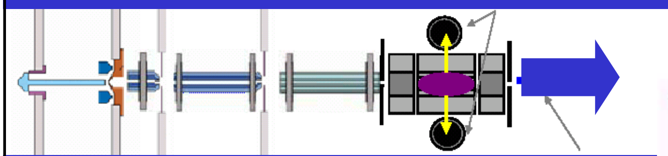
Hybrid Instrument with Q3 Linear Ion Trap

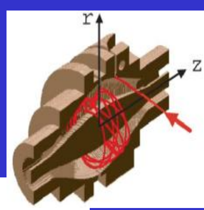


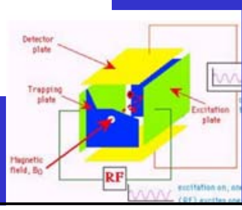


L'espulsione ASSIALE degli ioni permette di accoppiare

la trappola ionica lineare ad altri analizzatori

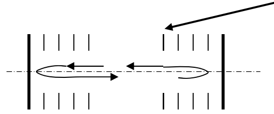


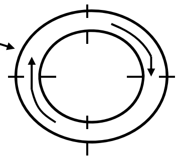




Electrostatic Traps

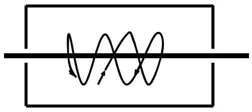
"...Static charges can not be stable in electrostatic fields..."





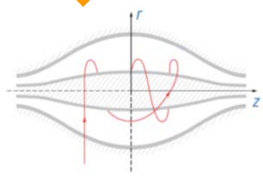
Linear traps

Segmented-ring traps



Orbital traps

Kingdon, 1923



The Orbitrap: a new mass spectrometer

Qizhi Hu,[a] Robert J. Noll,[a] Hongyan Li,[a] Alexander Makarov,[b] Mark Hardman[c] and R. Graham Cooks[a*]

[a] Purdue University, Chemistry Department, West Lafayette, IN 47907, USA

[b] Thermo Electron (Bremen), Hanna-Kunath-Str. 11, Bremen 28199, Germany

[c] Thermo Electron (San Jose) 355 River Oaks Parkway, San Jose, CA 95134 USA

JOURNAL OF MASS SPECTROMETRY
J. Mass Spectrom. 2005; **40**: 430–443

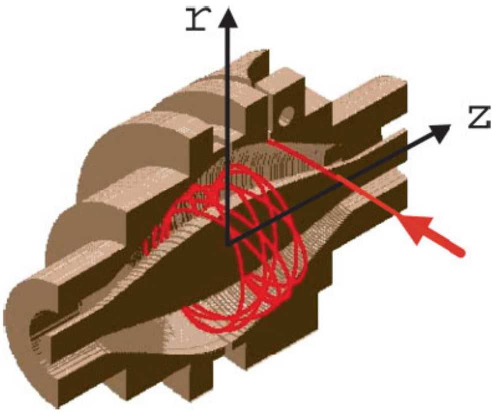
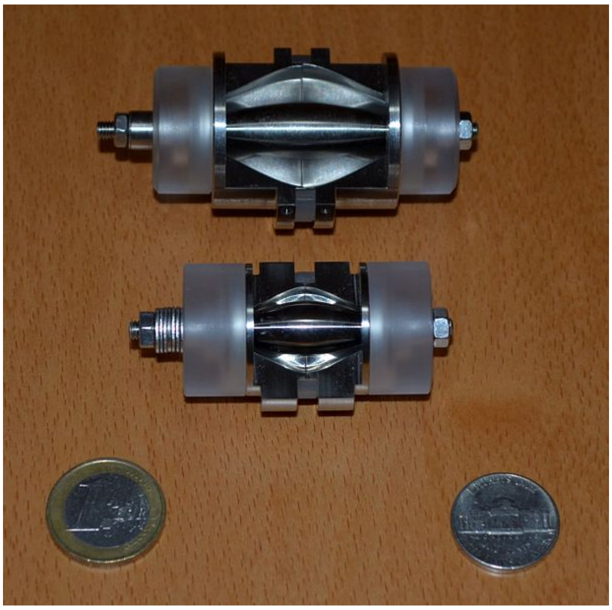


Figure 1. Cutaway view of the Orbitrap mass analyzer. Ions are injected into the Orbitrap at the point indicated by the red arrow. The ions are injected with a velocity perpendicular to the long axis of the Orbitrap (the *z*-axis). Injection at a point displaced from $z = 0$ gives the ions potential energy in the *z*-direction. Ion injection at this point on the *z*-potential is analogous to pulling back a pendulum bob and then releasing it to oscillate.



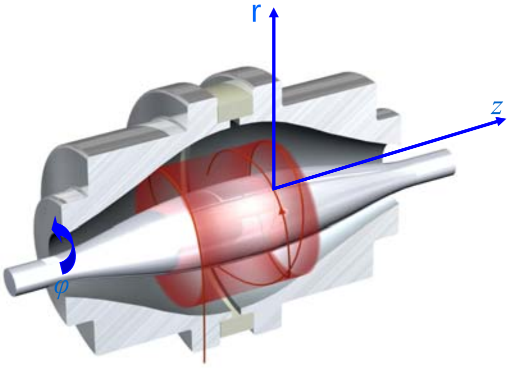
Standard

High-field

Orbitrap mass analyzers

Trajectories in the orbitrap

- Characteristic frequencies:
  - Frequency of rotation ω_φ
  - Frequency of radial oscillations ω_r
  - Frequency of axial oscillations ω_z



$$\omega_\varphi = \frac{\omega_z}{\sqrt{2}}\sqrt{\left(\frac{R_m}{R}\right)^2 - 1}$$

$$\omega_r = \omega_z\sqrt{\left(\frac{R_m}{R}\right)^2 - 2}$$

$$\boxed{\omega_z = \sqrt{\frac{k}{m/z}}}$$

$$U(r,z) = \frac{k}{2}\cdot\left\{z^2 - r^2/2 + R_m^2\cdot\ln(r/R_m)\right\}$$

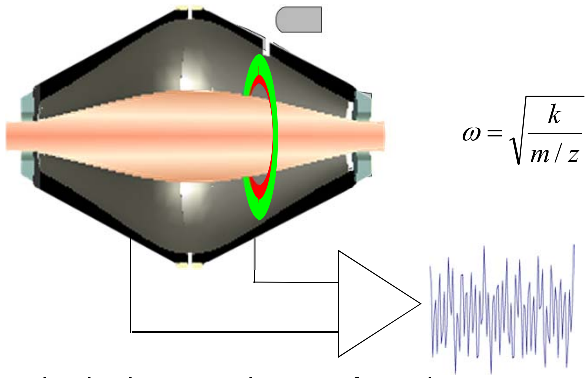
Ion Motion Along z Axis in the Orbitrap

$$\boxed{\omega = \sqrt{z/m \times k}}$$

k = field curvature

ω is to first order independent of ion energy and spatial spread

A Makarov. *Anal. Chem.* **2000**, *72*, 1156.



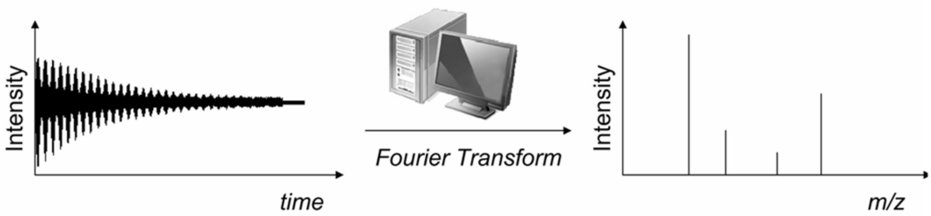
$$\omega = \sqrt{\frac{k}{m/z}}$$

1. Frequencies are determined using a Fourier Transformation
2. For higher sensitivity AND resolution, transients should not decay too fast

Ultra-high vacuum

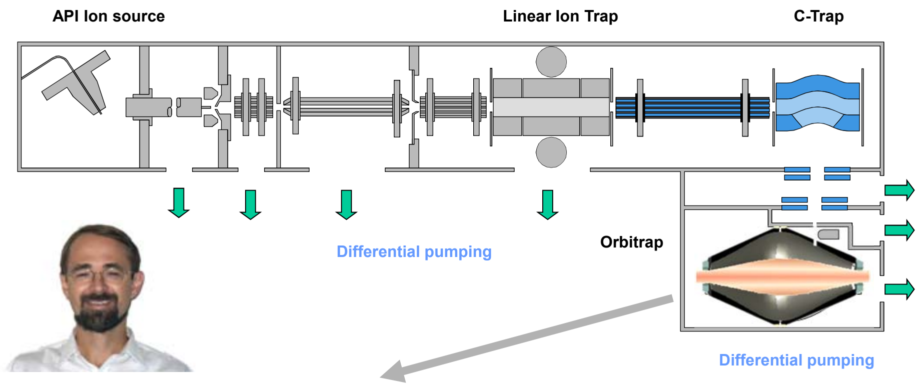
Ultra-high precision

Orbitrap, FT-ICR



LTQ Orbitrap™Hybrid Mass Spectrometer

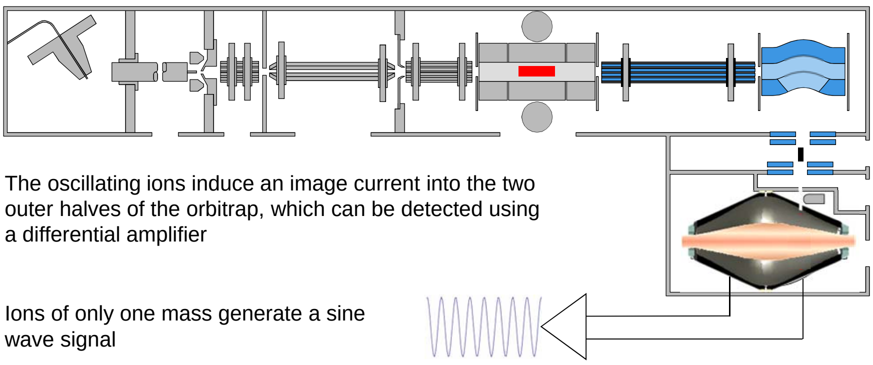
2005 - 2006



Inventor: Dr. Alexander Makarov, Thermo Electron (Bremen)

LTQ Orbitrap Operation Principle

1. Ions are stored in the Linear Trap
2. …. are axially ejected
3. …. and trapped in the C-trap
4. …. they are squeezed into a small cloud and injected into the Orbitrap
5. …. where they are electrostatically trapped, while rotating around the central electrode and performing axial oscillation



The oscillating ions induce an image current into the two outer halves of the orbitrap, which can be detected using a differential amplifier

Ions of only one mass generate a sine wave signal

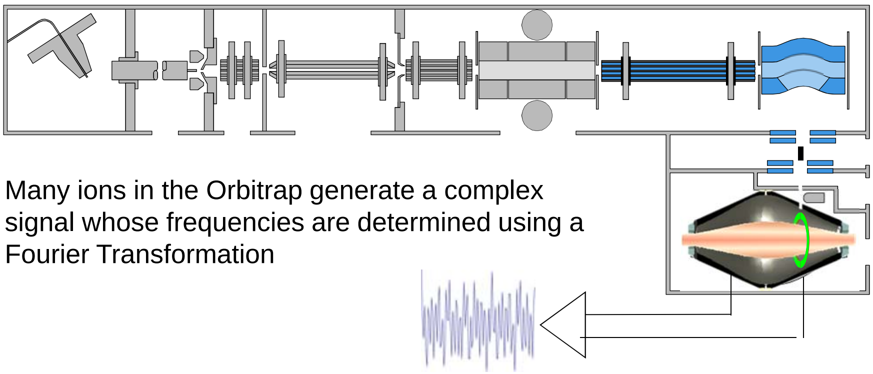
Frequencies and Masses

The axial oscillation frequency follows the formula $\omega = \sqrt{\frac{k}{m/z}}$

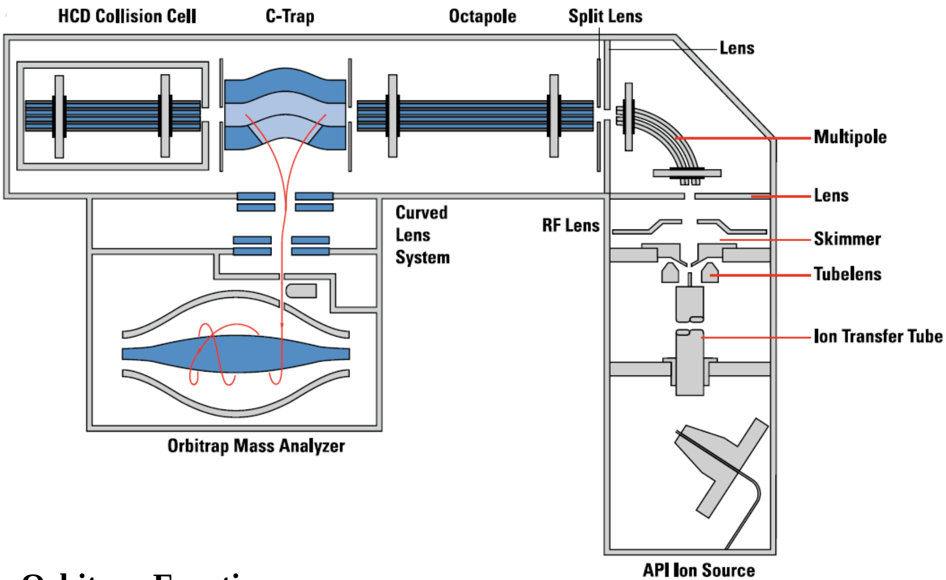
Where ω = oscillation frequency

k = instrumental constant

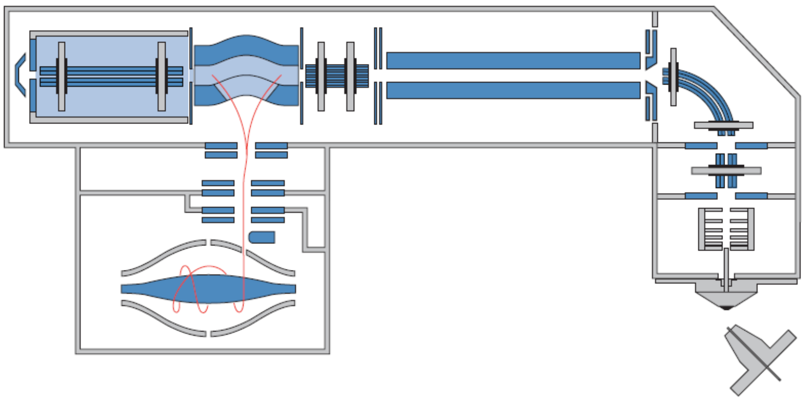
m/z = …. well, we have seen this before



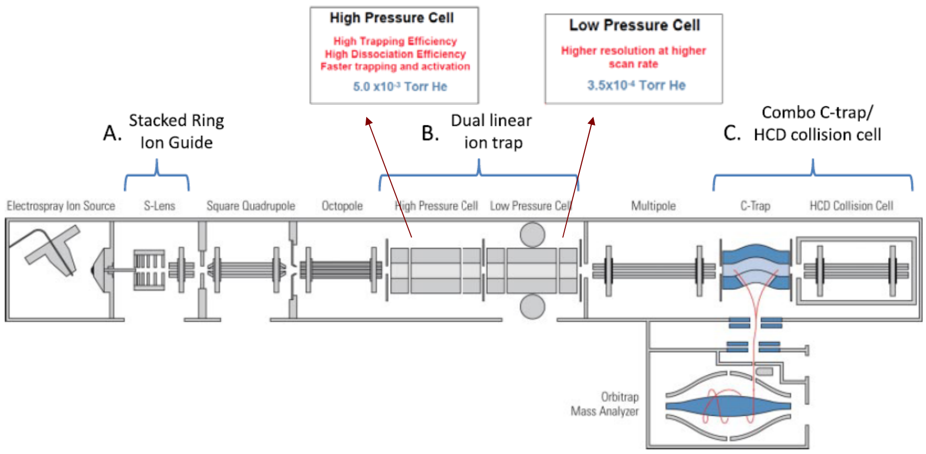
Many ions in the Orbitrap generate a complex signal whose frequencies are determined using a Fourier Transformation



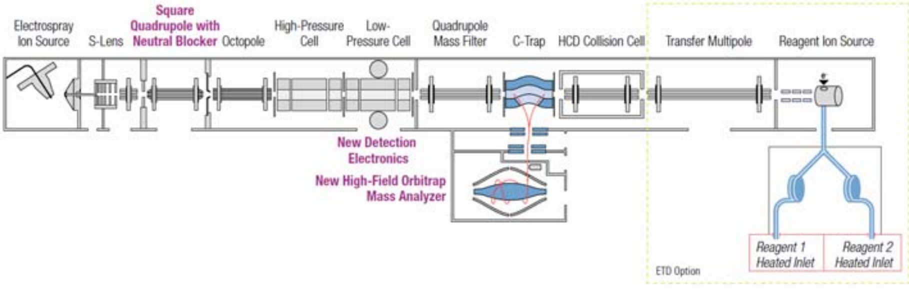
Orbitrap Exactive



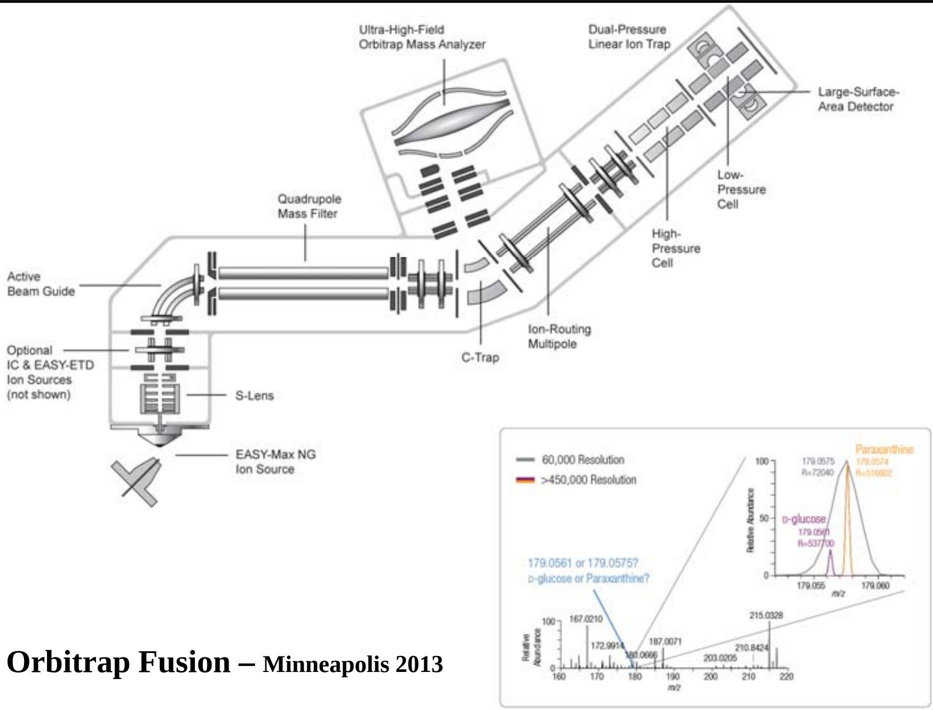
Orbitrap Q Exactive



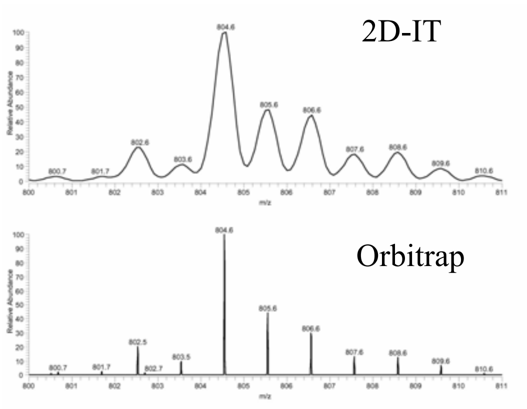
Orbitrap Velos

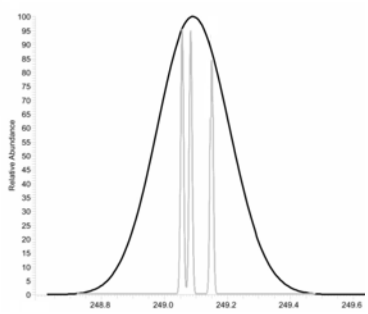


Orbitrap Elite

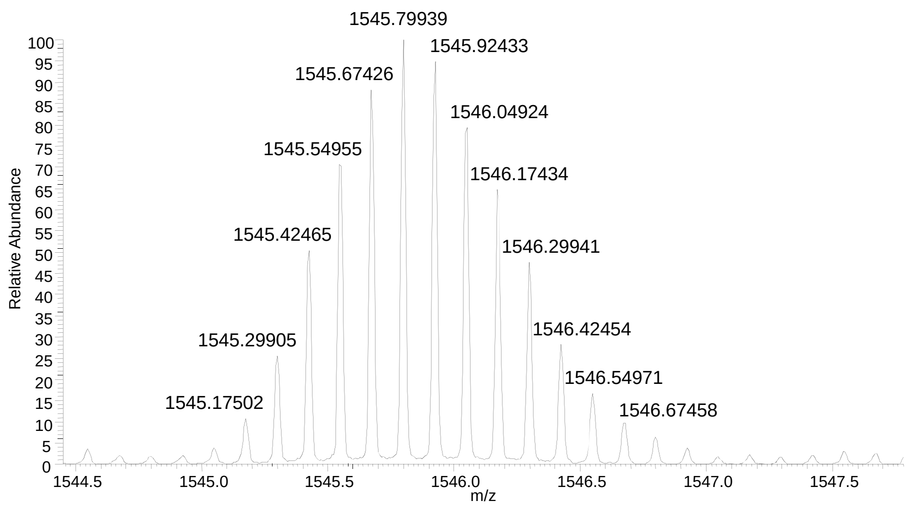


Orbitrap Fusion – Minneapolis 2013





Cytochrome C Zoom on the 8^{+}



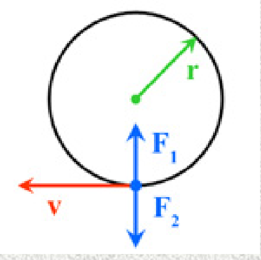
FT-ICR

Fourier Transform Ion Cyclotron Resonance Mass Spectrometry

LA CELLA A RISONANZA CICLOTRONICA

http://www.youtube.com/watch?v=7EHngA4S3Ws

Movimento Ciclotronico



Magnetic field directed upward

F_1 = Magnetic Force

F_2 = Centrifuge Force

r = radius of gyration

v = velocity

Per mantenere lo ione in un'orbita circolare stabile occorre che:

$$F_1 = F_2$$
$$q\,v\,B = m\,v^2/r$$
$$m\,v^2/r = q\,v\,B$$

Ne consegue che la frequenza angolare ω di uno ione con massa m e carica q è data da:

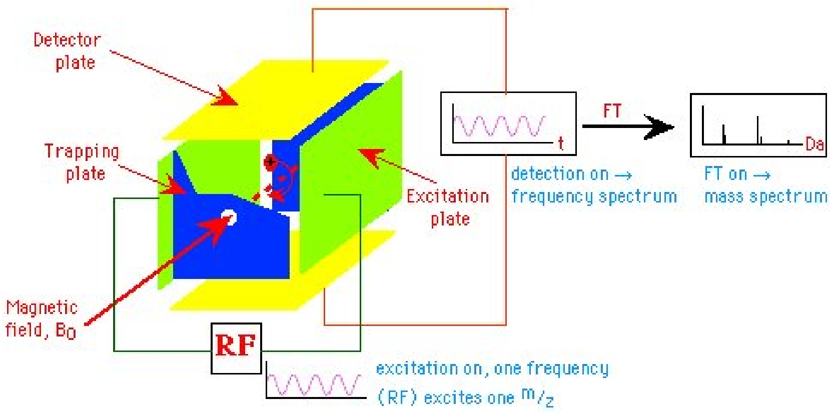
$$v/r = q\,B/m$$

Frequenza ciclotronica ω

$\boxed{\omega = q\,B/m}$ **(radianti/sec)** $\boxed{\omega = (q\,B/m)/2\pi}$ **(Hz)**

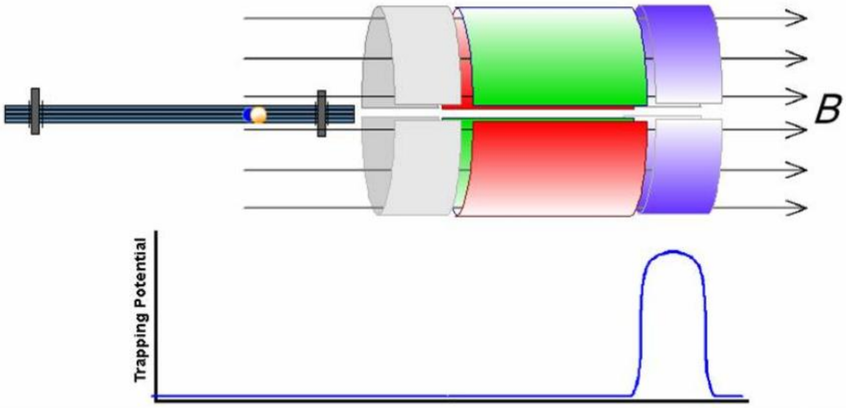
Da notare che **la frequenza ciclotronica NON dipende dalla velocità dello ione.**

Perciò ioni di una stessa massa avranno tutti la stessa frequenza ciclotronica indipendentemente dal tempo in cui entrano nella cella o dalla velocità con cui vi entrano.



Packets of ions are injected into the ICR cell from the linear ion trap.

They are trapped in the ICR cell by the coaxial magnetic field and voltages applied to the trapping electrodes.



Packets of ions are injected into the ICR cell from the linear ion trap.

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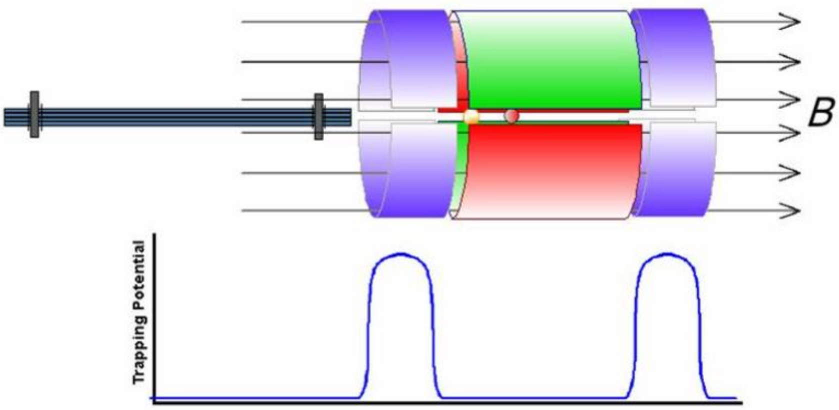
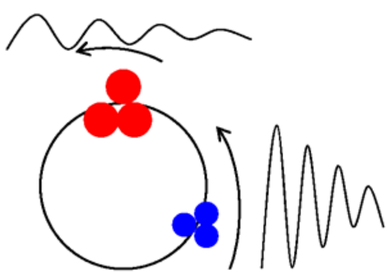
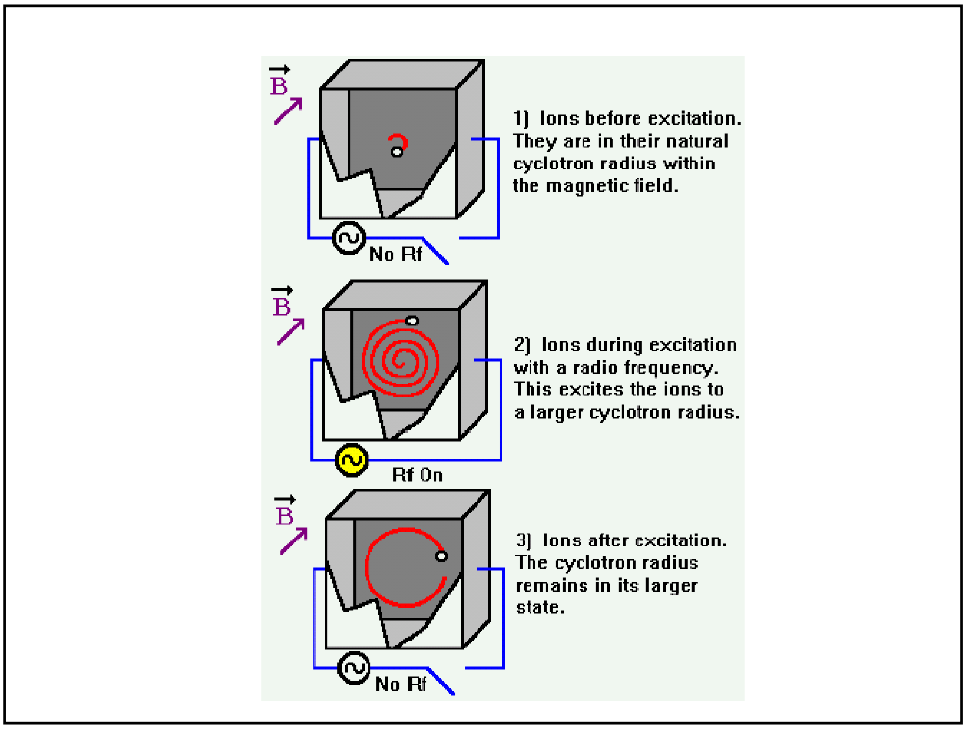


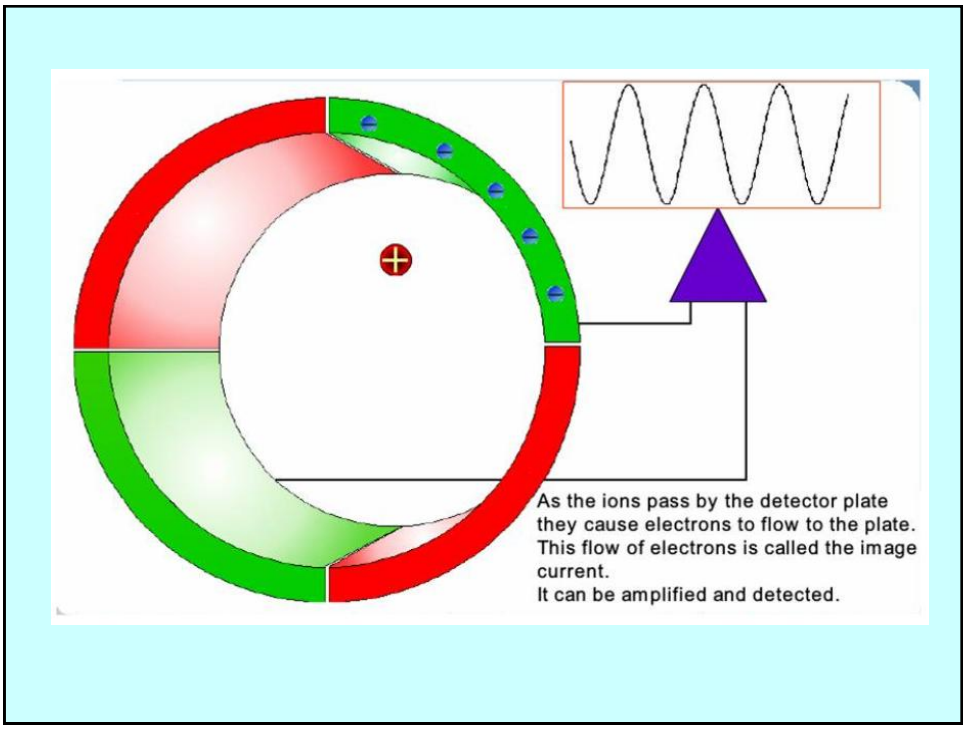
Ad esempio, la frequenza ciclotronica di uno ione monocaricato, con *m/z* 1000 e un campo magnetico di 7.0 Tesla, è di 107.45 kHz, ovvero compie circa 100.000 orbite al secondo.

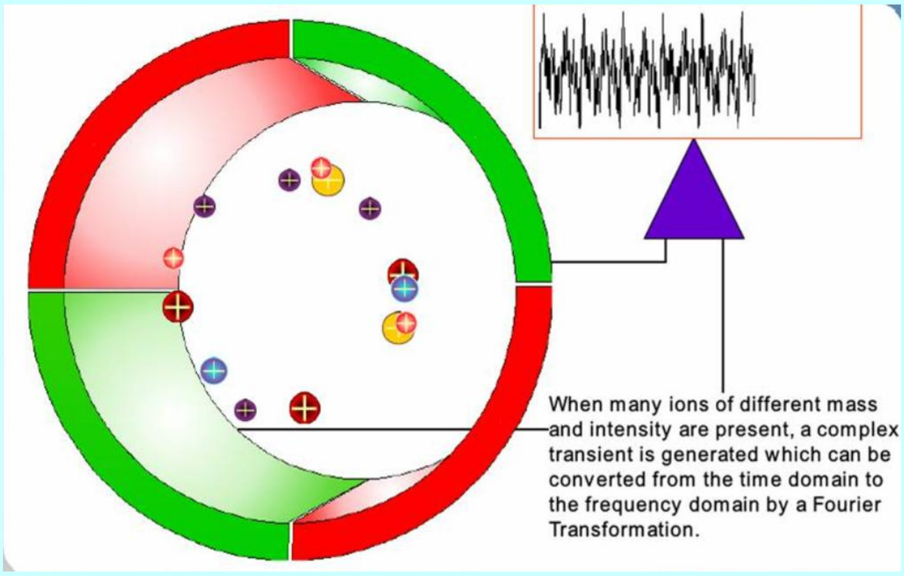
Se il suo stato di carica è +4 il numero di orbite al secondo diventa circa 400.000.

La cella è situata all'interno di una regione di campo omogeneo di un grande magnete superconduttore. Gli ioni si muovono in orbite circolari alle loro frequenze ciclotroniche.
Se all'interno della cella vi sono ioni con diverso valore di *m/z*, essi gireranno su orbite con un raggio molto simile ma avranno frequenze diverse.
Normalmente il raggio di un'orbita di uno ione è di circa 0.1 mm.
Se un impulso RF, sufficientemente largo (8MHz÷100kHz) da coprire l'intervallo delle diverse frequenze ciclotroniche degli ioni che si vogliono osservare, viene inviato all'interno della cella, gli ioni acquisteranno energia dal campo RF e si muoveranno su orbite più larghe.

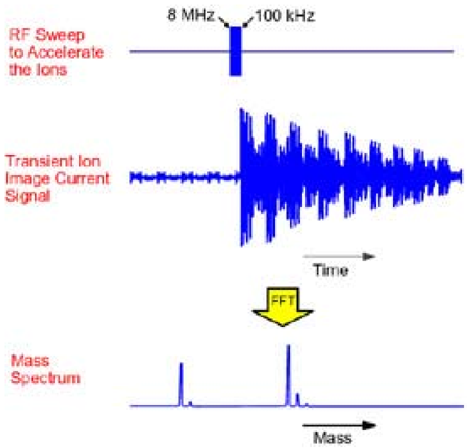



1) Ions before excitation. They are in their natural cyclotron radius within the magnetic field.
No Rf
2) Ions during excitation with a radio frequency. This excites the ions to a larger cyclotron radius.
Rf On
3) Ions after excitation. The cyclotron radius remains in its larger state.
No Rf


As the ions pass by the detector plate they cause electrons to flow to the plate. This flow of electrons is called the image current.
It can be amplified and detected.



Così il segnale complessivo che esce dalla cella è un ***segnale composito*** costituito dalla sovrapposizione delle frequenze ciclotroniche di tutti gli ioni presenti all'interno.
Inoltre questo segnale diminuisce lentamente mentre gli ioni rilassano e ritornano alle loro orbite circolari stabili al centro della cella.
Usando la trasformata di Fourier è possibile deconvolvere il segnale complessivo e identificare le singole frequenze.



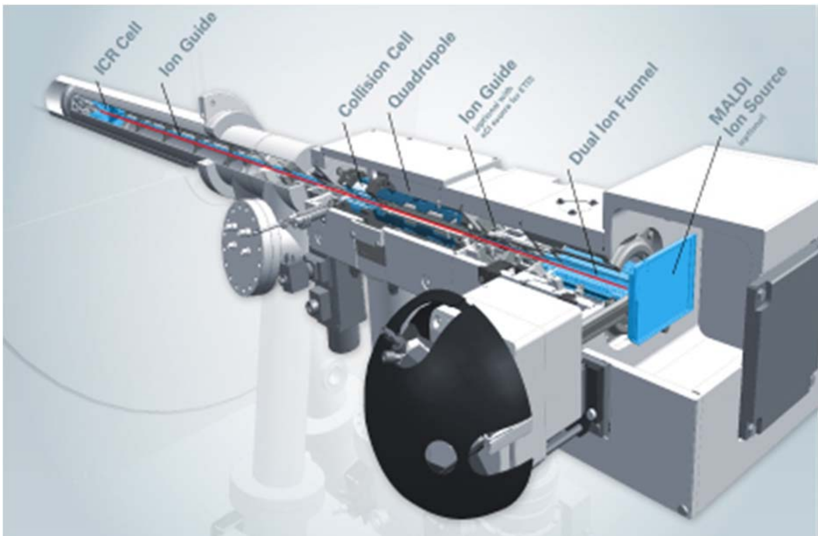
1. **Accelerate all ions with an RF burst.**
2. **Amplify the image current signal: The transient signal is a composite of the cyclotron frequencies of all the ions in the cell.**
3. **Digitize the signal and store it in a computer.**
4. **Use a Fast Fourier (FFT) algorithm to extract the frequency and amplitude for each frequency component.**

A new ultra-high resolution FT-ICR cell with dynamic harmonization

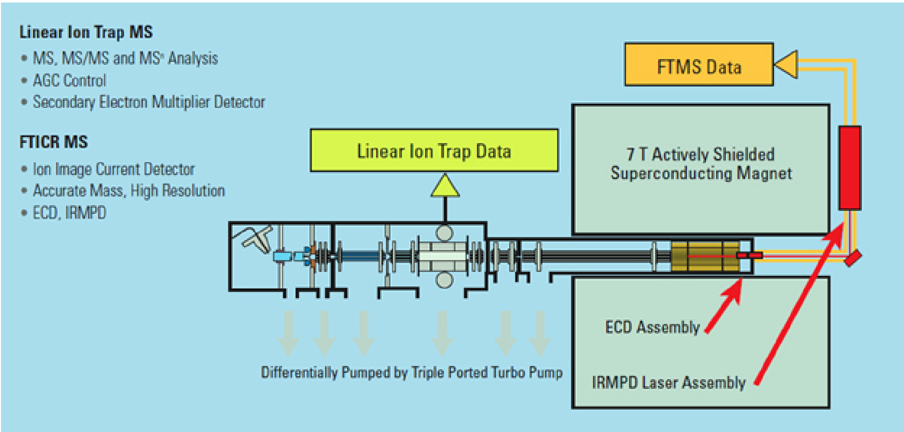
extreme mass resolution greater than 10 million

Nikolaev EN, Boldin IA, Jertz R, Baykut G., *J Am Soc Mass Spectrom.* 2011, **22**:1125-33

Qq-FTICR



IT-FTICR



FT-ICR

ESI (+) of Ubiquitin

1,040,000 Resolution at *m/z* 779