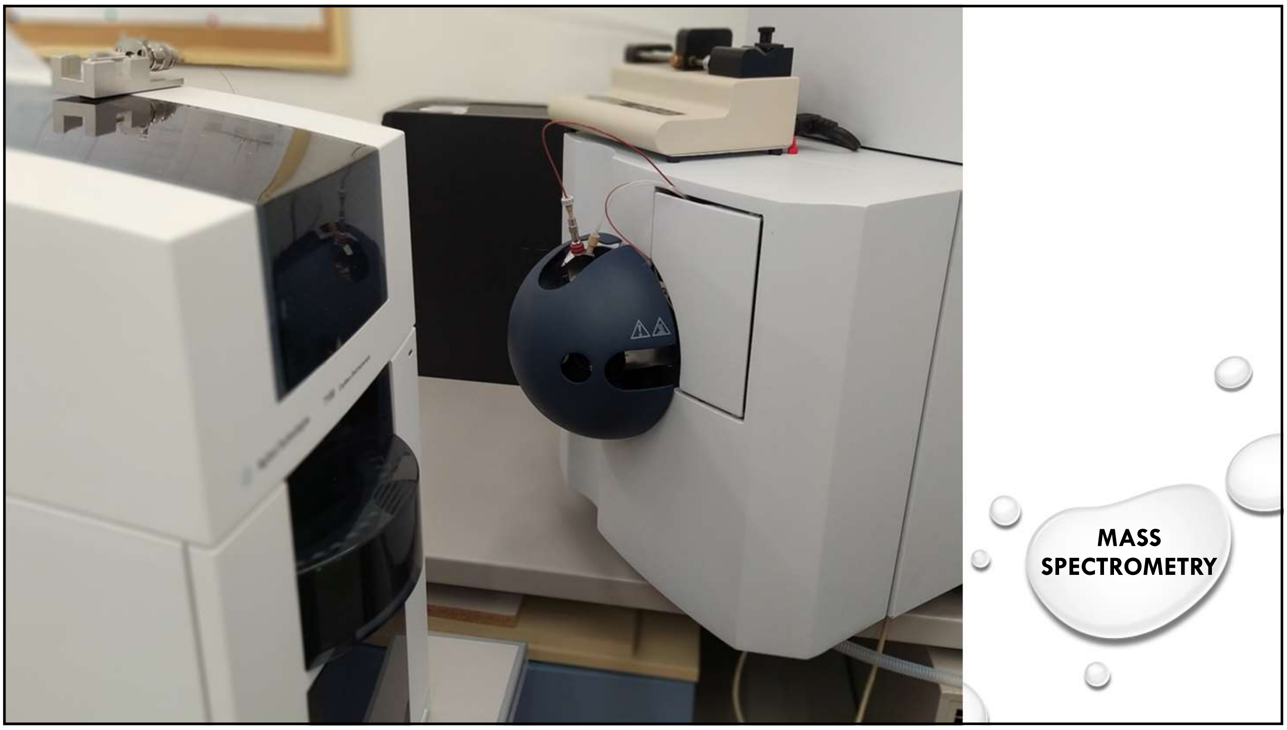


TIME-OF-FLIGHT INSTRUMENTS (TOF)

- **Principle: smaller ions fly faster !**
- typically a **pulse** mass analyzer, because first the ions are accelerated by a very short pulse at the entrance to the analyzer tube, and then the time during which the ions "fly" to the detector is precisely measured, according to which their m/z is determined;
- Mass range m/z is not limited (theoretically);
- **Physical destcription:**
- upon ionization, the all ions gain approximately the same energy and are accelerated by an electric potential V;
- $\mathbf{E_k = 1/2\ m.v^2 = z.V}$
- The time of flight: $\mathbf{t = l/v}$
- where **l** is the length of the tube (= flight path) and **v** is the velocity of the ion
- $\mathbf{m/z = 2.V.t^2/l^2}$

AT WHAT SPEED WILL THE FULLERENE C_{60}^{+} MOLECULAR ION MOVE?
ACCELERATING VOLTAGE IS 19.5 KV.

$$E_k = 1/2\,mv^2 = zV$$

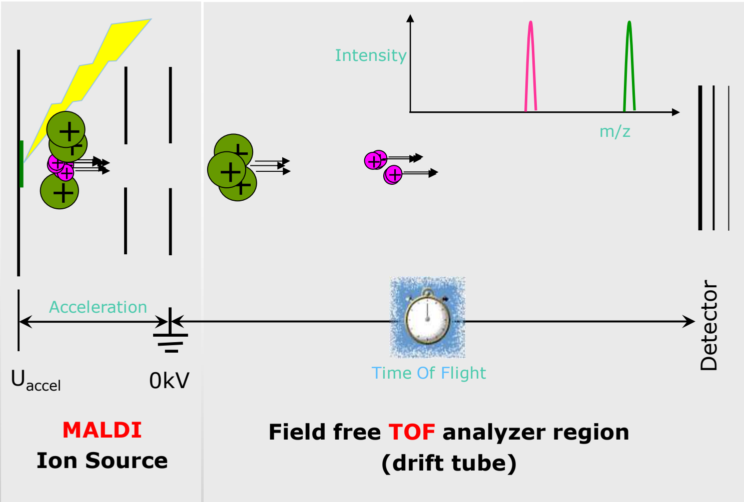
$$v = \sqrt{\frac{2zV}{m}}$$

$$v = \sqrt{\frac{2 \times 1{,}6022 \times 10^{-19}\,C \times 19500V}{60 \times 12 \times 1{,}66 \times 10^{-27}\,kg}} = 72{,}294ms^{-1}$$

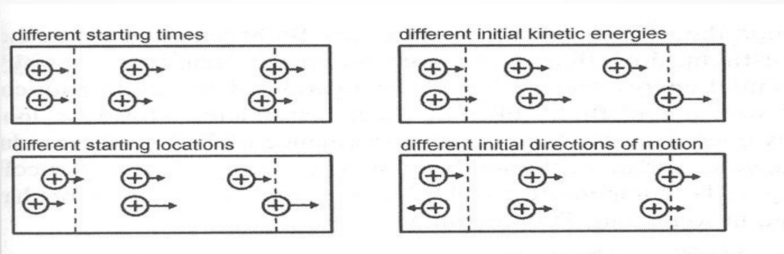
TIME-OF-FLIGHT (TOF)

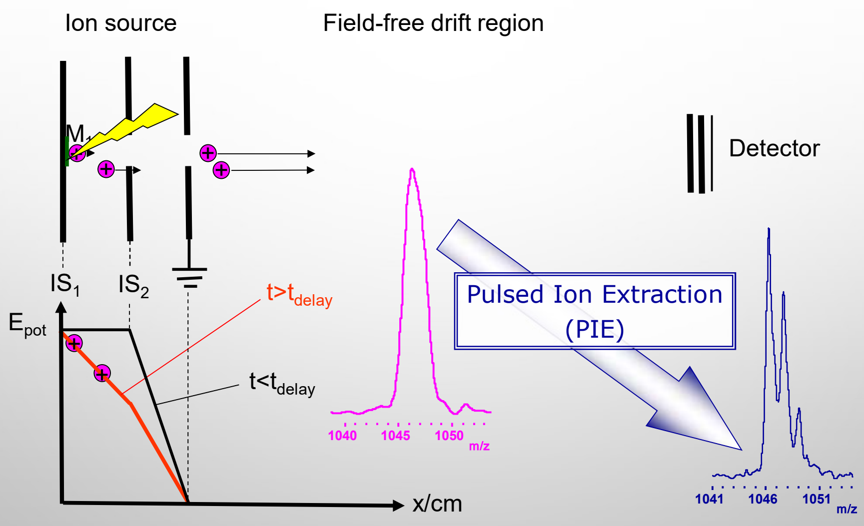
- **The advantages:**

- **i)** the m/z range is unlimited;
- **ii)** a complete mass spectrum is obtained within several μs;
- **iii)** improved transmission, with high sensitivity;
- **iv)** construction is simple and inexpensive;
- **v)** accurate mass measurements and tandem MS experiments;



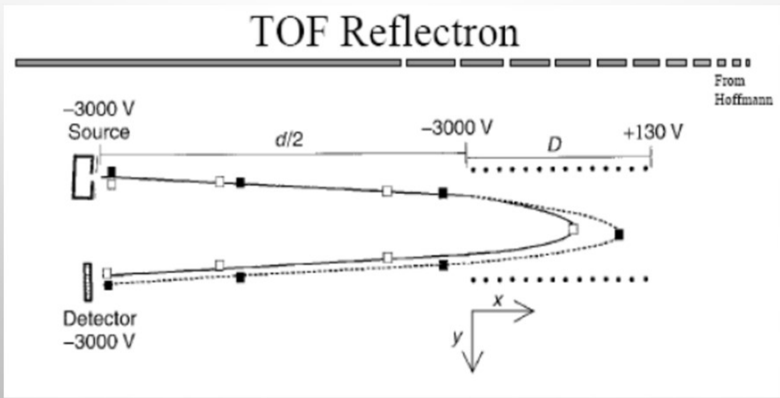
THE POSSIBLE EFFECTS OF DISPERSION - LINEAR TOF

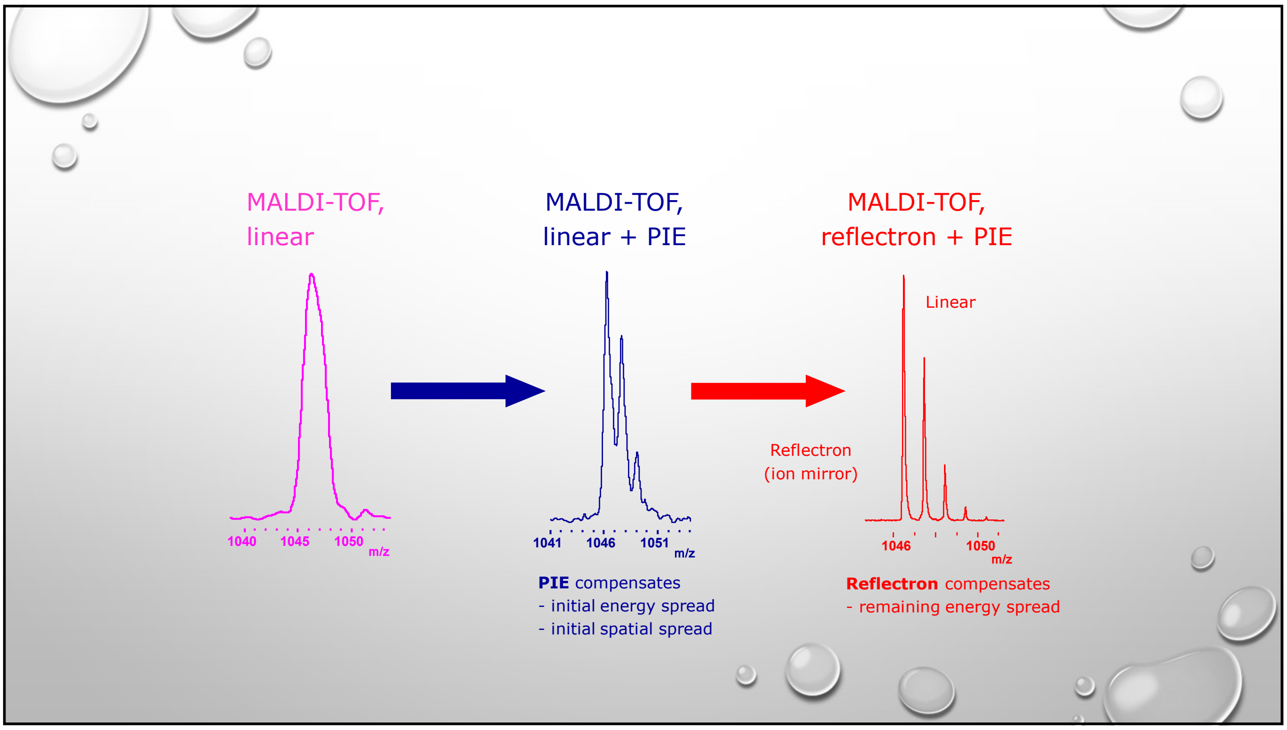




REFLECTOR TIME-OF-FLIGHT ANALYZER

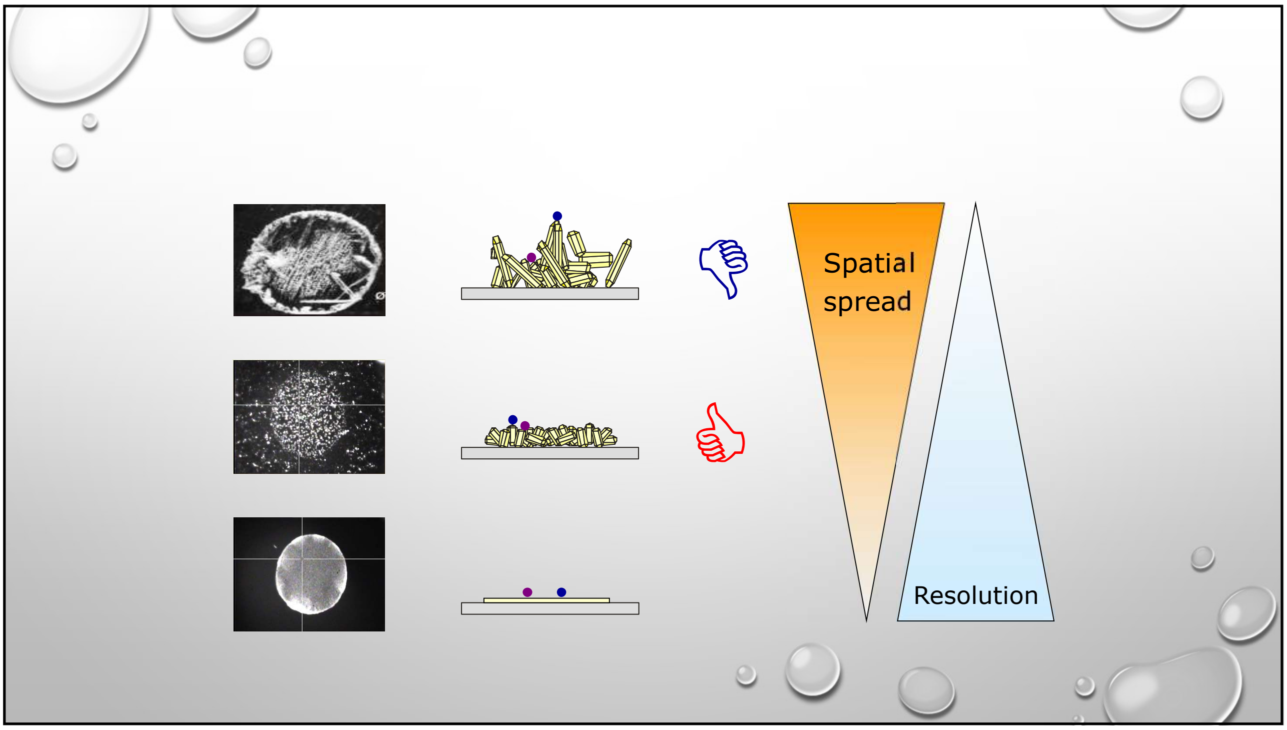
An ion mirror that focuses ions of different kinetic energies in time.
It serves to balance the different kinetic energies for ions with the same m/z value.





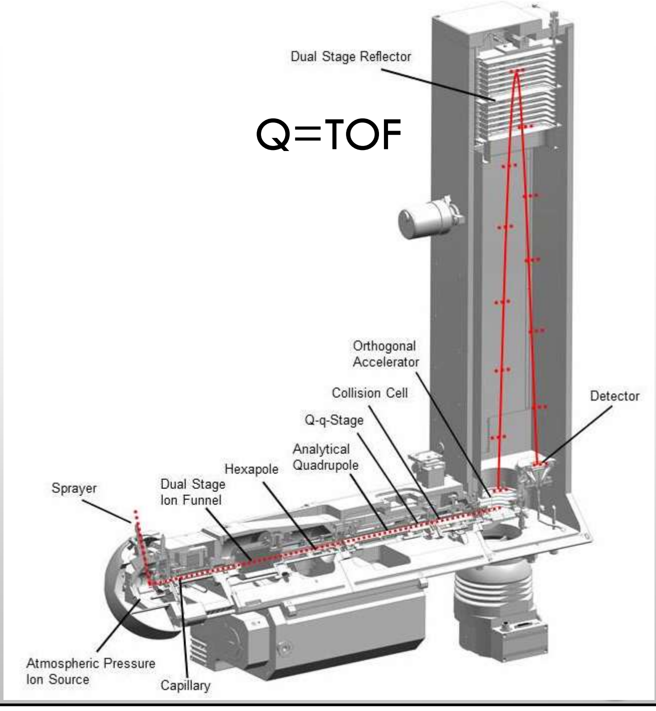
MALDI-TOF,
linear
MALDI-TOF,
linear + PIE
MALDI-TOF,
reflectron + PIE
Linear
Reflectron
(ion mirror)
1040 1045 1050 m/z
1041 1046 1051 m/z
1046 1050 m/z
PIE compensates
- initial energy spread
- initial spatial spread
Reflectron compensates
- remaining energy spread

9



Spatial
spread
Resolution

10



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FOURIER TRANSFORM ION CYCLOTRON RESONANCE (FT-ICR)

- FT-ICR mass spectrometers offer ultrahigh resolving power RP = 10^6 –10^7 ;
- highest mass accuracy Δm = 10^{-4} u ;
- attomol detection limits (with nanoESI or MALDI sources);
- high mass range and MS^n capabilities ;
- all ions are detected at the same time, easy polarity change ;

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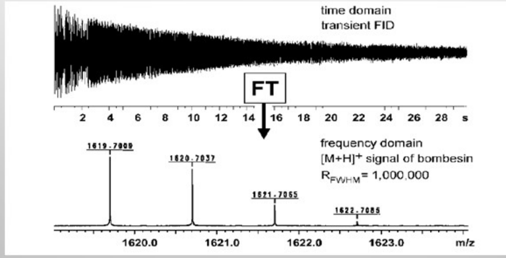
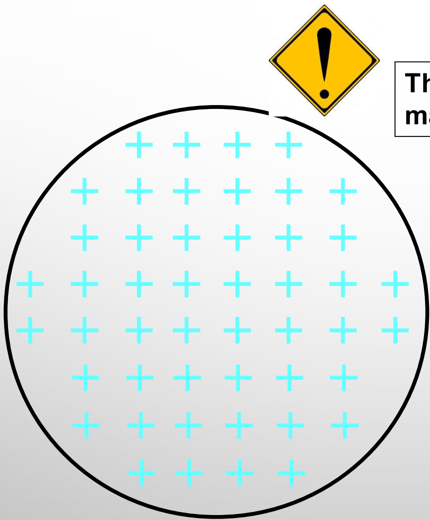
(FT-ICR)

- **principle:**
- the ion begins to move in a strong magnetic field along a cycloidal trajectory with a cyclotron frequency $\omega_c = Bz / m$;
- mass-selective excitation, so-called **resonant excitation**, is achieved by applying a transverse electric field alternating at the cyclotron frequency fc ($\omega_c = 2\pi f_c$) to accelerate the ions;
- magnetic field 7-13 Tesla; low pressure of 10^{-11} mBar;
- each **m/z** has charakteristick ω_c ;
- FT is a mathematical operation that transforms one complex-valued function



Movement of an ion in a magnetic field of very high intensity

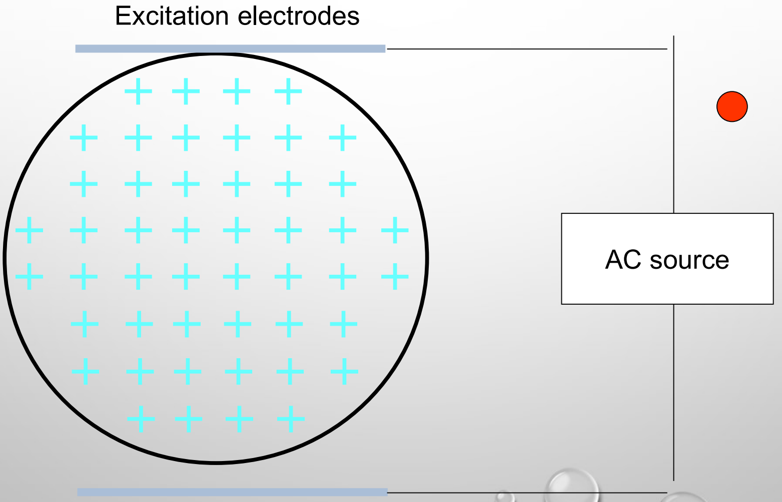


The ion is slowed down by the magnetic field, E_K decreases

$$r^2 = m\frac{2E_K}{e^2B^2}$$

Movement of an ion in a magnetic field of very high intensity (electric field excitation)

$$r^2 = m\frac{2E_K}{e^2B^2}$$



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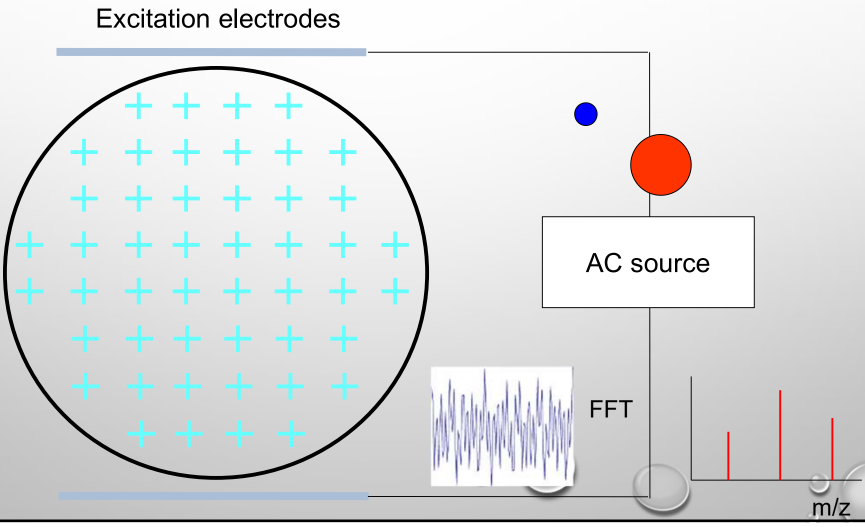
Movement of an ion in a magnetic field of very high intensity (electric field excitation)

$$\omega = \frac{zeB}{m}$$ [rad.s^{-1}]

$$f = \frac{zeB}{2\pi m}$$ frekvence [s^{-1}]



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Orbitrap

Latest on the market with a new type of mass analyzer:
Hybrid instrument combining with a linear trap with the orbitrap;

- Robust Accurate Mass
  - *5 ppm rms external calibration*
  - *2 ppm rms internal calibration*
- High Resolution
  - *60,000 at m/z 400 with a scan repetition rate of 1 Hz*
  - *Maximum Resolution >100,000*
- Mass Range
  - *50-2000; 200-4000*
- Sub-fmol Sensitivity (LC/MS)
- MS/MS and MS^n
- High Dynamic Range
  - *>2,500 within mass spectrum*

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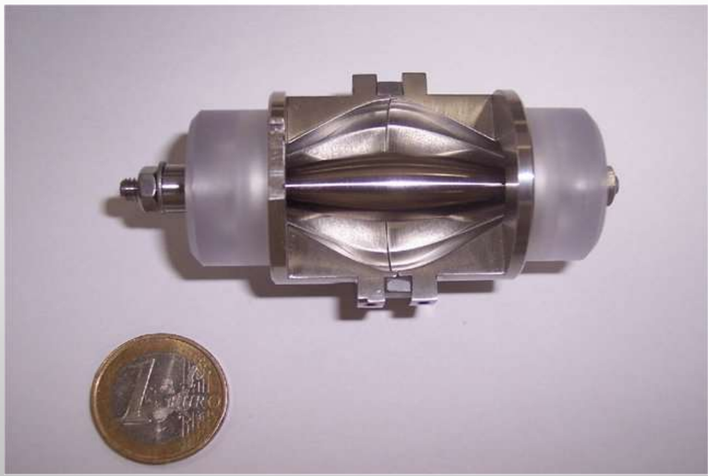
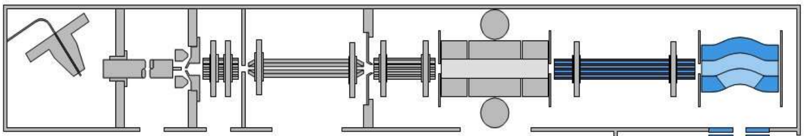
ORBITRAP



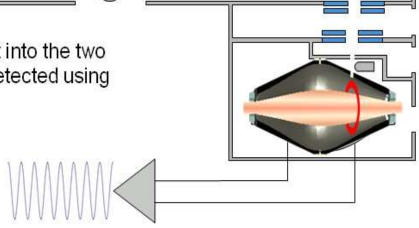
LTQ Orbitrap Operation Principle

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

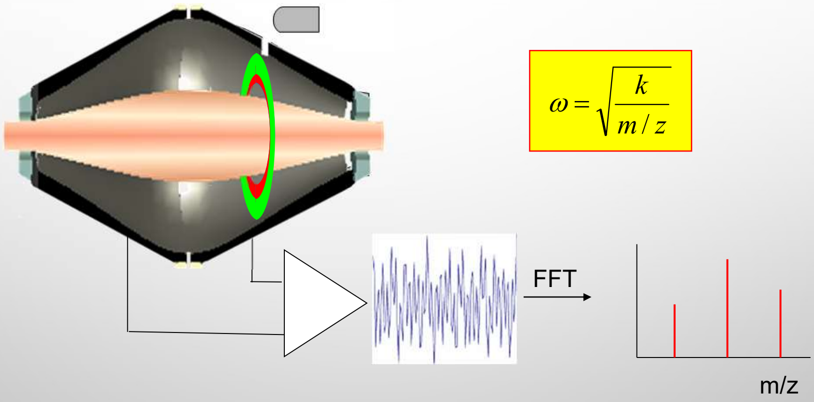


The oscillating ions induce an image current into the two outer halves of the orbitrap, which can be detected using a differential amplifier

Ions of only one mass generate a sine wave signal



ORBITRAP



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

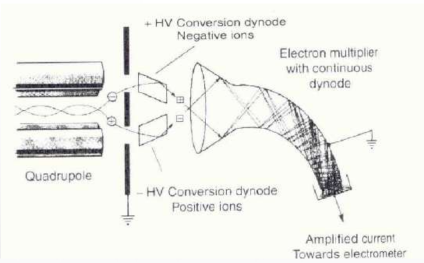
What LTQ Orbitrap Delivers

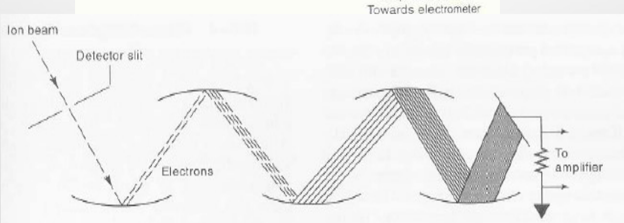
• Mass resolution	> 60,000 at m/z 400 at 1 sec cycle
• Max. resolution	over 100,000
• Mass accuracy	< 5 ppm external calibration
• Mass accuracy	< 2 ppm internal calibration
• Mass range	50 – 2,000; 200 – 4,000
• Sensitivity	sub-femtomole on column
• Throughput	4 scans per second (1 high-resolution scan in the orbitrap + 3 MS/MS scans in the LTQ)

DETECTORS

- **1/ Photographic plate** – intensity is estimated based on exposure shade;
- **2/ Faraday detector** – The simplest ion detector, an ion beam strikes the inner metal surface and is neutralized by electrons. The small electron current is amplified and converted into a voltage. The electron current is proportional to the number of ions striking the surface. (very accurate, used for precise isotopic measurements);
- **3/ Electron Multiplier** – energetic particles hit the surface of a metal, secondary electrons are emitted; the most common, amplification up to 10^7;
- **4/Photo Multiplier**– longer service life-time
- *- 1/ a 2/ the signal is measured directly 3/ a 4/ the signal is multiplied;*

ELECTRON MULTIPLIER

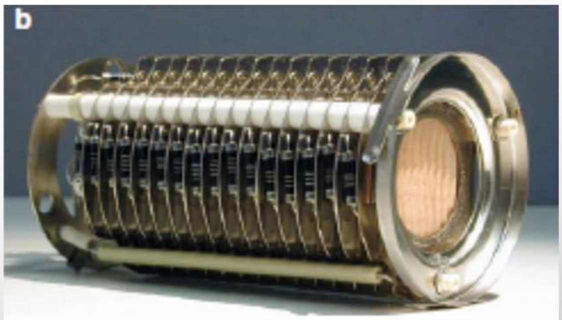




(a)

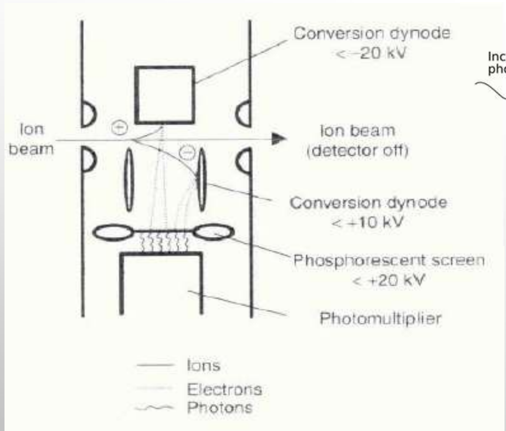
ELECTRON MULTIPLIER

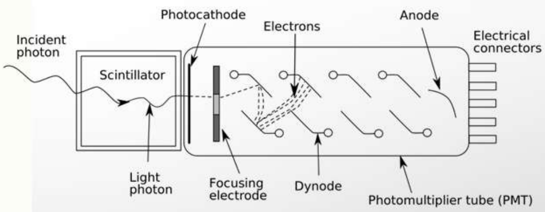
Channeltron multiplier



Discrete dynode electron multiplier

PHOTOMULTIPLIER





VACUUM TECHNOLOGY

- **the mass analyzer** always works under high vacuum, the vacuum value varies according to the type of analyzer;
- **the ion source** also usually works under high vacuum, the exception being ionization techniques working under atmospheric pressure (API);
- to obtain such high vacuum, two or even multi-stage pumping with very powerful vacuum pumps is usually needed;
- 1. pumping stage - rotary pumps (power 80 l/s);
- 2. pumping stage - turbomolecular or diffusion pumps (250 - 2000 l/s);
- **why is a vacuum needed?** ions must have a sufficiently long mean path and collisions with neutral atoms must not occur; during electron ionization, in the presence of atmospheric oxygen, the resistance wire producing electrons would burn out.

PRESSURE RANGES

Pressure Conversion Table and Vacuum Terminology

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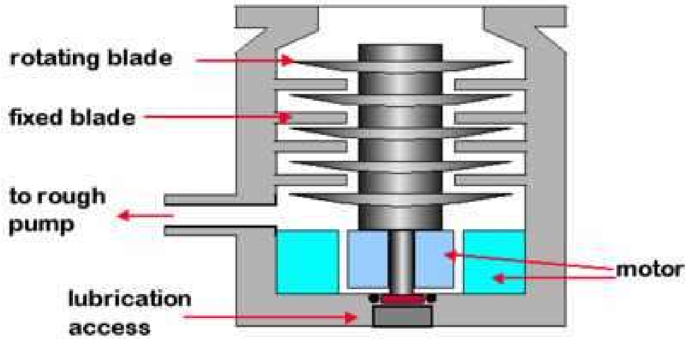
	Unit	Pascal	bar	millibar	Torr	Millitorr	pounds per square inch
Vacuum Quality	Symbol	Pa	bar	mbar	Torr	mTorr	psi
Rough Vacuum	P	1,0E+05	1,000	1000,000	751,9	751880	14,5
	r	1,0E+04	0,100	100,000	75,2	75188	1,450
	e	1,0E+03	0,010	10,000	7,5	7519	0,145
Medium Vacuum	s	1,0E+02	0,001	1,000	0,752	752	0,015
	s	1,0E+01	1,0E-04	0,100	0,075	75,19	1,45E-03
	u	1,0E+00	1,0E-05	0,010	7,5E-03	7,52	1,45E-04
High Vacuum	r	1,0E-01	1,0E-06	1,0E-03	7,5E-04	0,752	1,45E-05
	e	1,0E-02	1,0E-07	1,0E-04	7,5E-05	0,075	1,45E-06
		1,0E-03	1,0E-08	1,0E-05	7,5E-06	7,5E-03	1,45E-07
		1,0E-04	1,0E-09	1,0E-06	7,5E-07	7,5E-04	1,45E-08
Ultrahigh Vacuum		1,0E-05	1,0E-10	1,0E-07	7,5E-08	7,5E-05	1,45E-09
		1,0E-06	1,0E-11	1,0E-08	7,5E-09	7,5E-06	1,45E-10
		1,0E-07	1,0E-12	1,0E-09	7,5E-10	7,5E-07	1,45E-11
		1,0E-08	1,0E-13	1,0E-10	7,5E-11	7,5E-08	1,45E-12
		1,0E-09	1,0E-14	1,0E-11	7,5E-12	7,52E-09	1,45E-13

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

Turbomolecular pump

A turbomolecular pump relies on a series of blades or airfoils that spin at 30,000 - 90,000 RPM. This tends to deflect gas molecules down and out the outlet.



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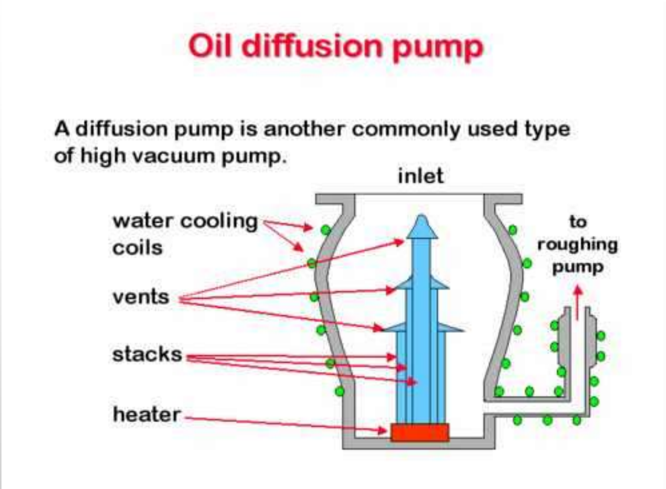
At high speeds and an increase in frictional heat - magnetic bearings.
The pump can be cooled and the rotor is stabilized.
Hall sensors - detection of rotational position.
A turbomolecular pump can only work if the molecules hit by the moving vanes reach the stationary vanes before colliding with other molecules.

Spacing between sets of vanes 1 mm

mean free path - inversely proportional to pressure
At a pressure of about 10 Pa, the mean free path is about 0.7 mm and the pump starts to suck.

Achievable pressure up to 10^{-8} Pa

30



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Diffusion Pump

Provides:

- **high pumping speeds;**
- **low limit pressures;**
- **high performance;**
- **large input pressure tolerance;**
- **low return flow;**
- **noiseless operation;**

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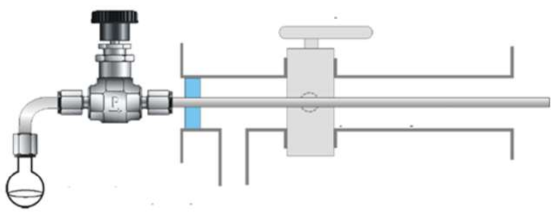
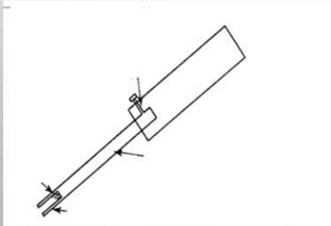
SAMPLE INTRODUCTION METHODS

cold and heated reservoirs – suitable for more volatile samples, e.g. gases;



Inlet system	Principle	Analytes
Reservoir/reference inlet	heated reservoir with sample vapor	low to medium boiling liquids
Direct insertion probe, DIP	sample in heated/cooled glass/metal vial as particles or film of analyte	solids, waxes or high-boiling liquids
Direct exposure probe, DEP	sample particles or film of analyte on resistively heated metal filament	solids of extremely low volatility, especially if thermally labile
Gas chromatograph, GC	elutes directly into ion source	volatile components of mixtures
Liquid chromatograph, LC	connected via particle beam interface	analytes suitable for EI that cannot be separated by GC due to high polarity



DIP probe for direct input - suitable for solid and liquid low-volatile samples;

! take attention to the memory effect !

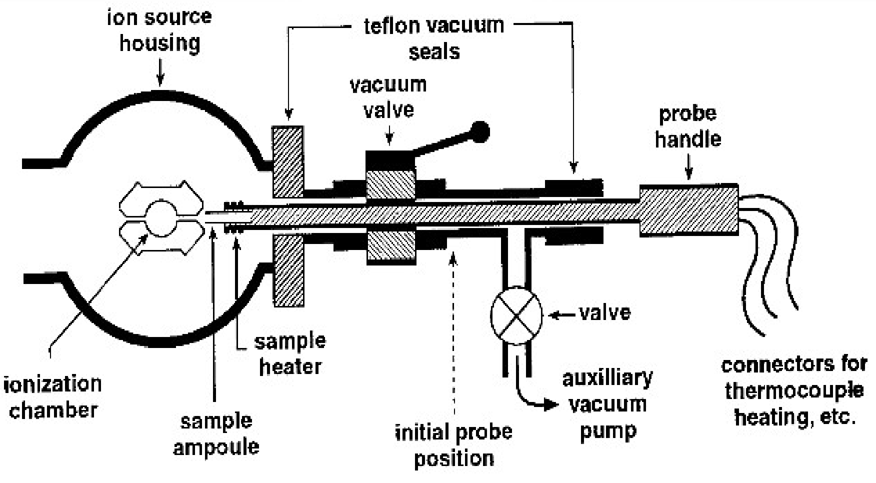
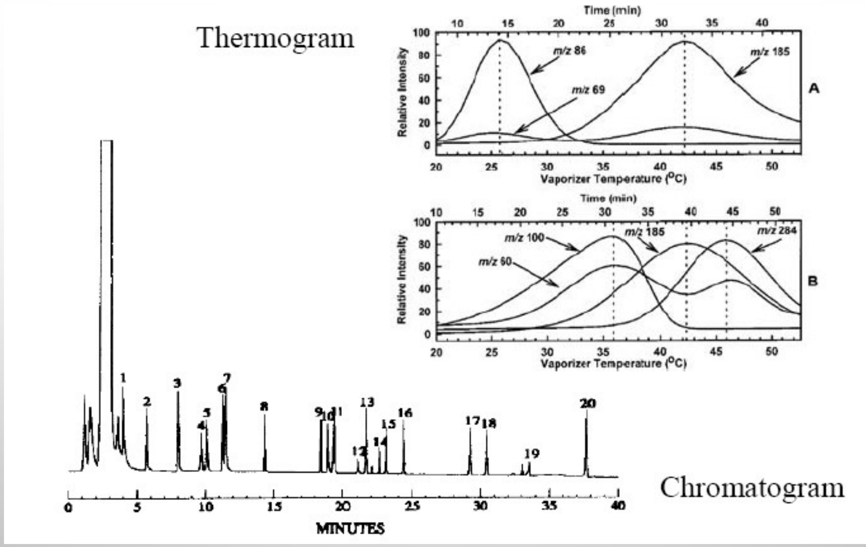


FIG. 6.2. Schematic diagram (showing involvement of vacuum lock) of the direct-inlet probe for solids and liquids having low vapor pressure.


Thermogram
Chromatogram
MINUTES
Time (min)
Relative Intensity
Vaporizer Temperature (°C)
m/z 86
m/z 69
m/z 185
A
m/z 100
m/z 60
m/z 185
m/z 284
B

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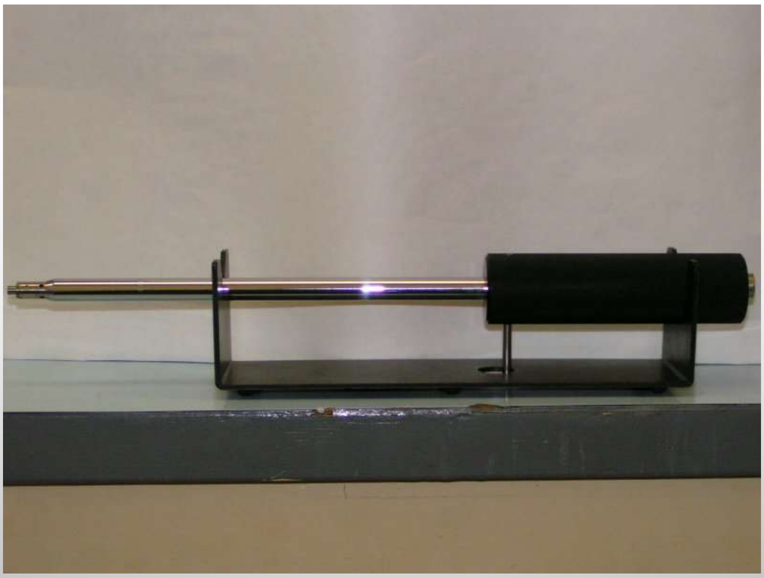

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Finnigan
MAT
DIRECT EXPOSURE PROBE
POWER
CLEAN
RATE
AMPERES
START
CURRENT
FILAMENT
CURRENT
STOP
CURRENT
INITIALIZE
START
RESET

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