Trace element analysis of geological materials by ICP-MS I

DSP analytical geochemistry

C9067

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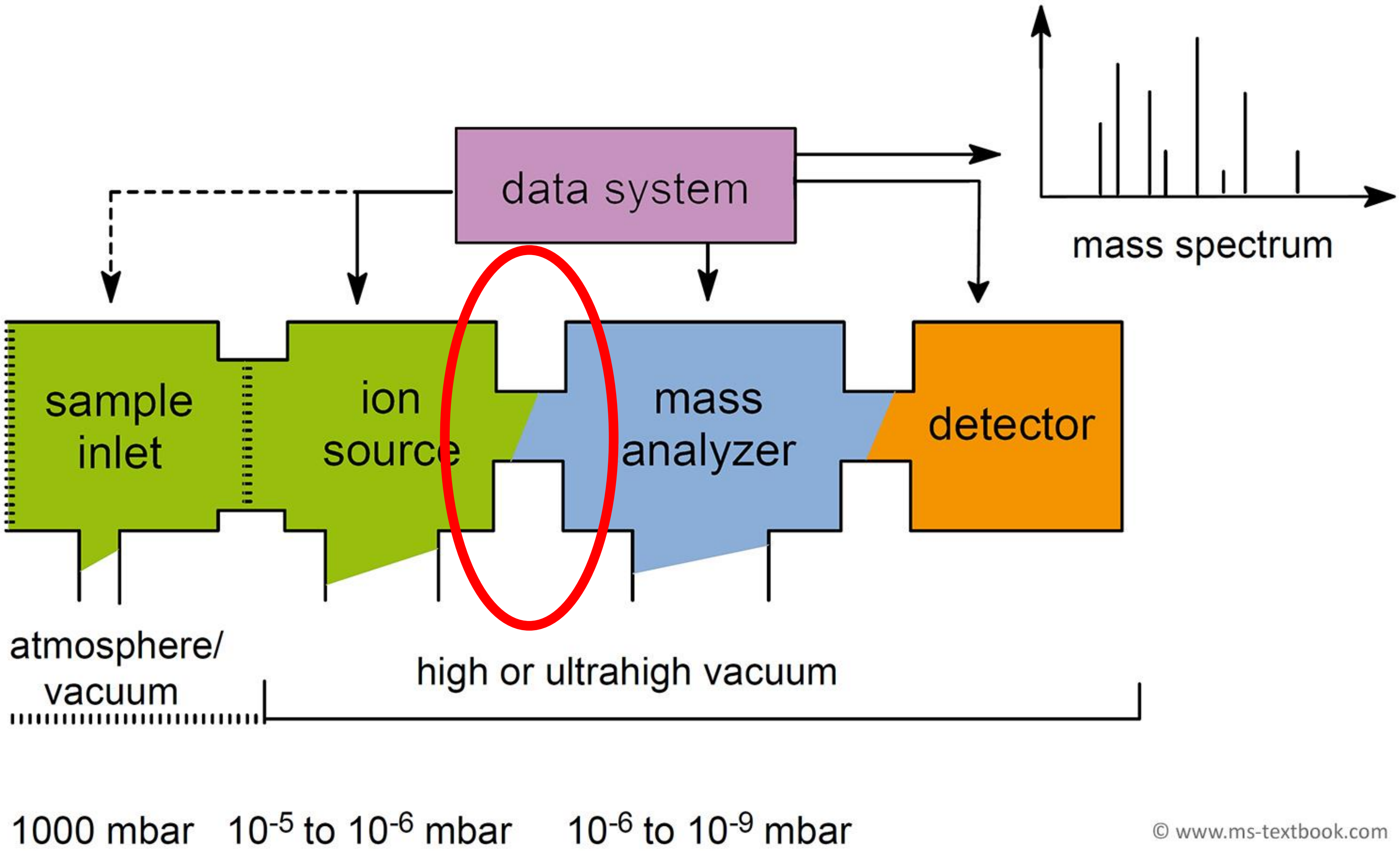
Outline

1. Mass spectrometry. General introduction and history.
2. Ion sources for mass spectrometry. Inductively coupled plasma.
3. Interface. Ion optics. Mass discrimination. Vacuum system.
4. Spectral interferences. Resolution, ion resolution calculations.
5. Mass analyzers. Elimination of spectral interferences.
6. Non-spectral interference.
7. Detectors, expression of results.
8. Introduction of samples into plasma.
9. Laser ablation for ICP-MS.
10. Excursion in the laboratory.


data system
mass spectrum
sample
inlet
ion
source
mass
analyzer
detector
atmosphere/
vacuum
high or ultrahigh vacuum
1000 mbar
10^{-5} to 10^{-6} mbar
10^{-6} to 10^{-9} mbar
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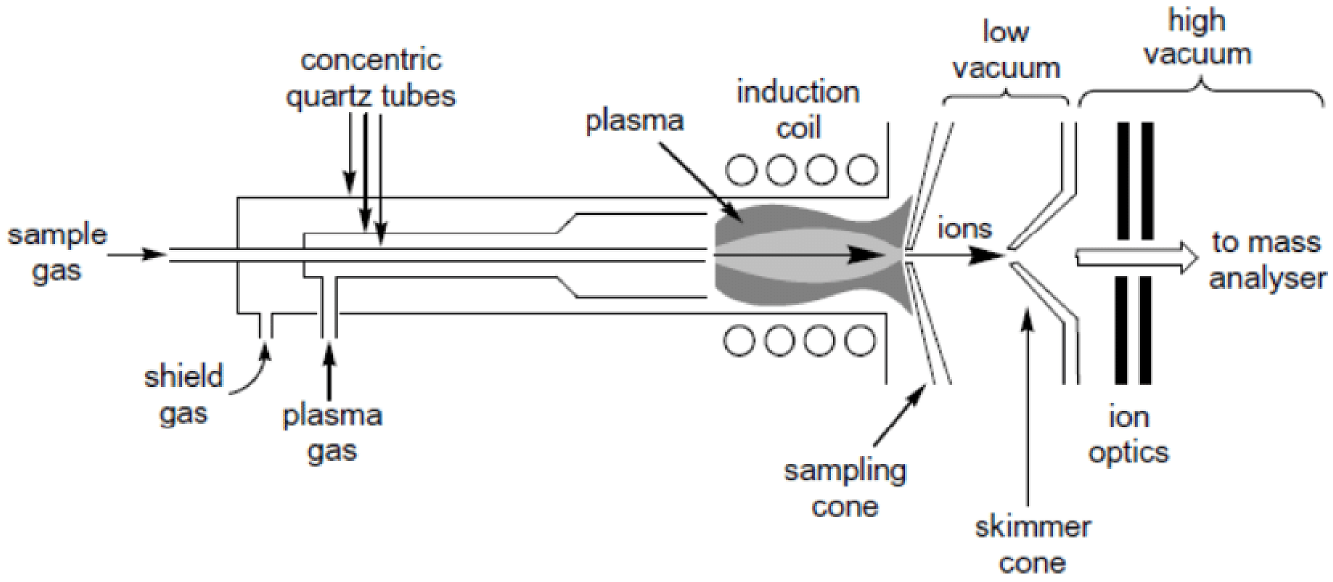
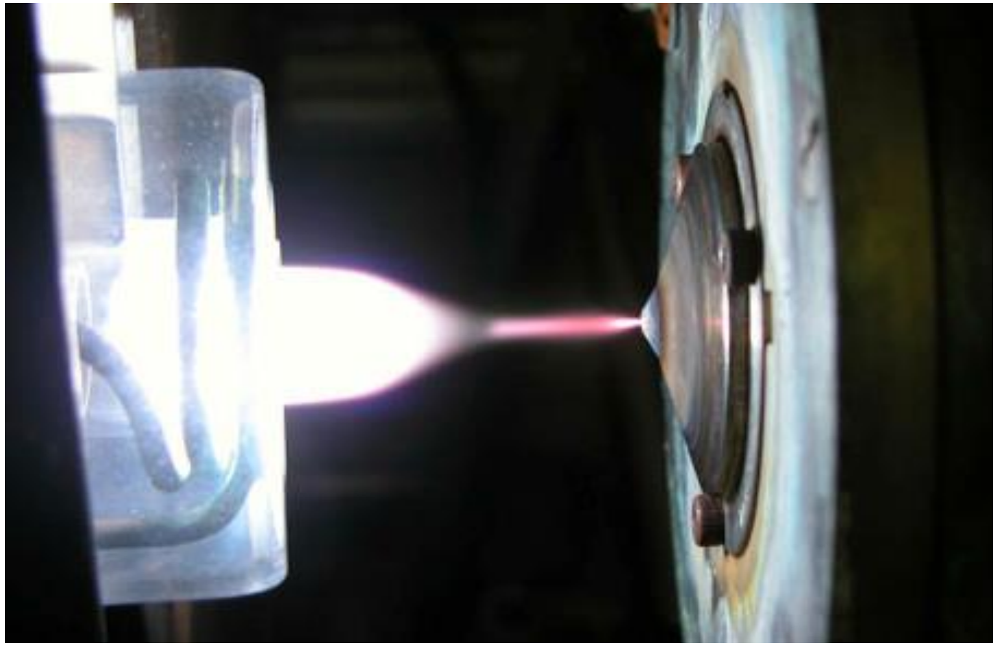
Interface

ICP-MS



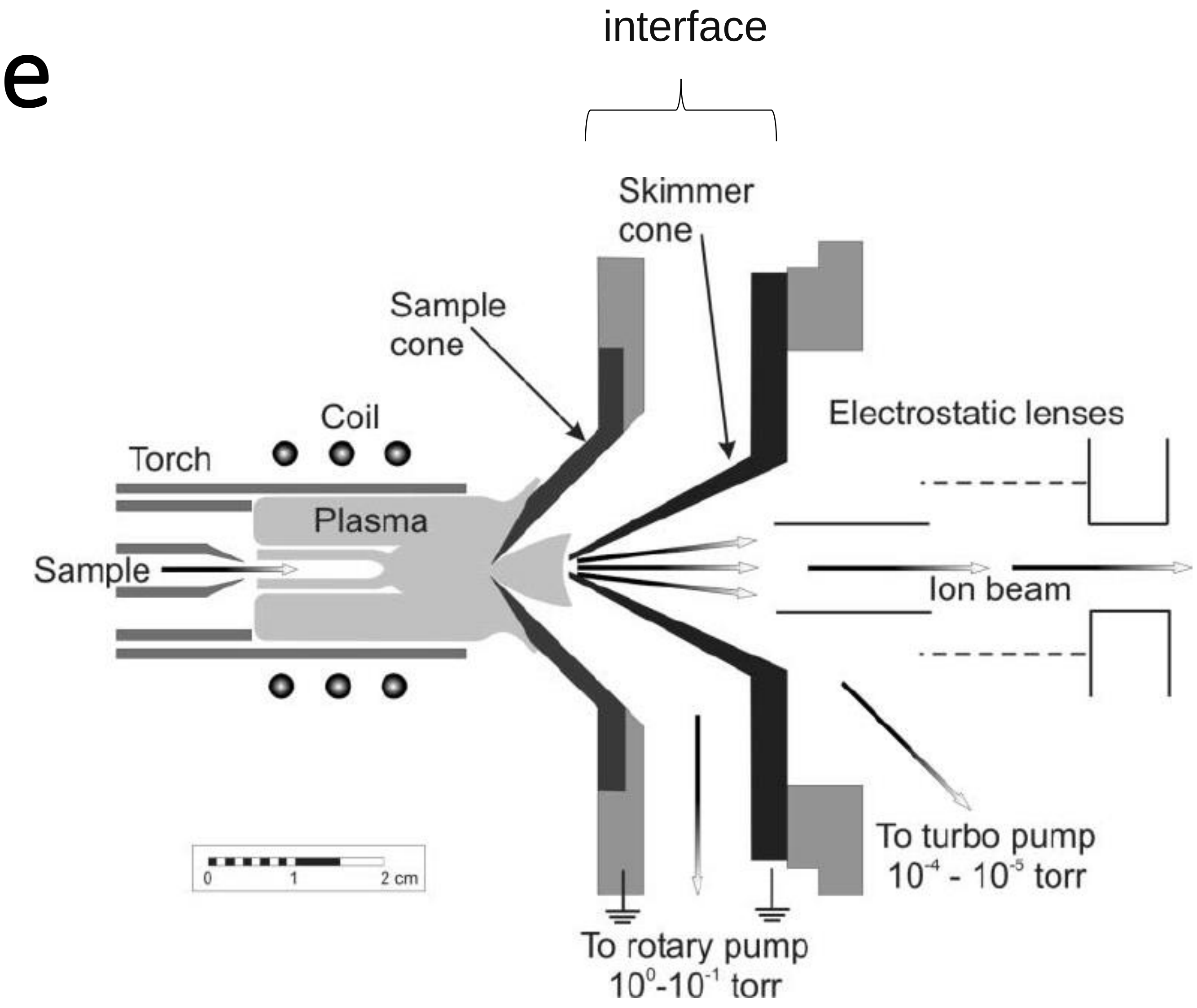


Interface links the atmospheric pressure ICP ion source and the high vacuum mass spectrometer.

Selection of positive ions - efficient transport & introduction into mass analyser

Interface

ICP-MS



Schematic cross-section of plasma torch and ICPMS interface (after Houk 1986).

Interface

Sampler & Skimmer cones

- Cones are made of ***nickel*** (Ni) most of the time, but they could also be made of Pt, Cu or Al.
- The metal must be characterized by high thermal conductivity, otherwise it will melt! A high melting point is therefore important and it should also be as hard as possible.
- However *thermal conductivity* seems to be the best criteria with regards to performance/price ratio

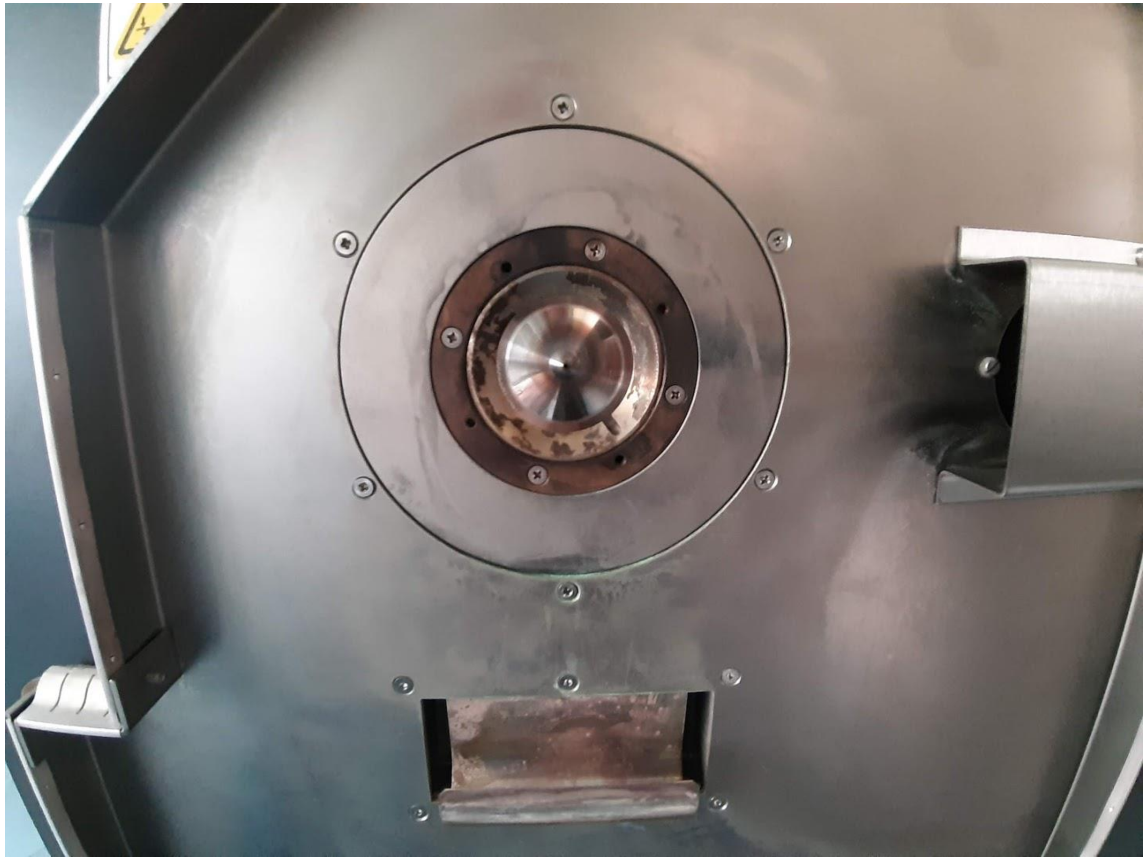
Material	Thermal Conductivity (Wm^{-1}K^{-1})	Melting Point (degrees C)	Hardness
Al	237	660	soft
Cu	401	1083	soft
Ni	90.9	1453	hard
Pt	71.6	1772	hard

Interface

Sampler & Skimmer cones

matrix-induced signal drift (high TDS):

- internal standard
- external standard



Interface

Sampler & Skimmer cones

Wear of cones due to salinisation, settling of samples.

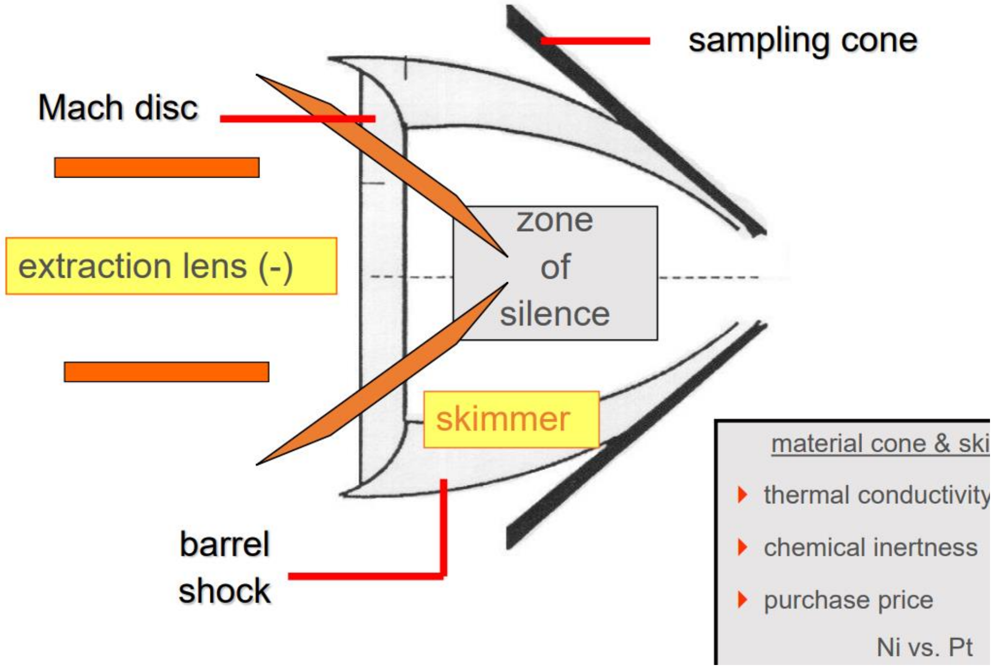
Regular cleaning needed.

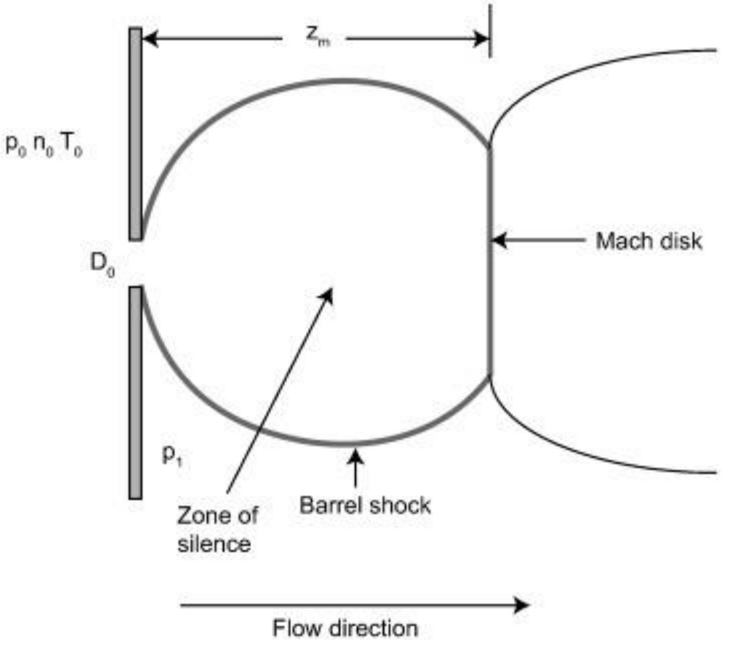
The sampling cone is usually damaged by erosion over time, the skimmer cone is covered with salt deposits, which are formed by the condensation of compounds with a high boiling point during adiabatic expansion in the interface.

Interface

supersonic gas expansion

- transition from 1 ATM to 100 Pa
- supersonic gas expansion
- rapid cooling
- formation of turbulence and Mach disc





The structure of an idealized free jet. Gas expands into a reduced background pressure (p_1) from a source with pressure (p_0), number density (n_0), and temperature (T_0). The expansion through a nozzle with diameter D_0 forms a "zone of silence," bounded radially by a barrel shock and axially by a Mach disk. The distance from the nozzle to the Mach disk is z_m. To achieve ideal skimming, a skimmer cone should be placed with its tip well inside the zone of silence, typically at about 2/3 z_m.

Interface

supersonic gas expansion

Ernst Mach

(18. února 1838 Chrlice – 19. února 1916 Vaterstetten)

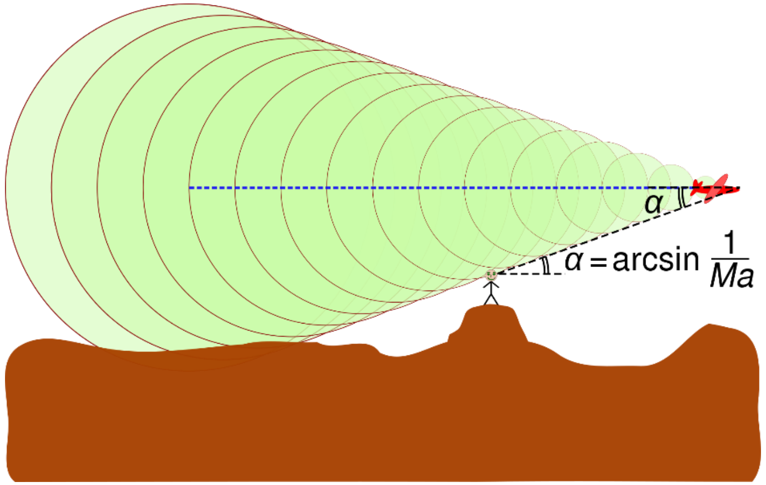
The Mach number (Ma or M), often only Mach is a dimensionless quantity in fluid dynamics representing the ratio of flow velocity past a boundary to the local speed of sound. It is named after physicist and philosopher Ernst Mach.

$$Ma = \frac{v}{c}$$

*where **v** is the local flow velocity, **c** is the speed of sound in the given medium. Speeds Ma less than 1 are subsonic, if Ma is greater than 1 they are supersonic.*

https://www.youtube.com/watch?v=45yQ3nfu3SQ

https://www.milmag.cz/znaceni-rychlosti-letadel/



https://en.wikipedia.org/wiki/Sonic_boom#

Sensitivity of ICP-MS

The increase in the sensitivity of the MS signal with the ion mass is common to all constructions of modern mass spectrometers.

This means, for example, that a 1 ng/ml ^{238}U solution provides a higher signal than a 1 ng/ml ^{7}Li solution.

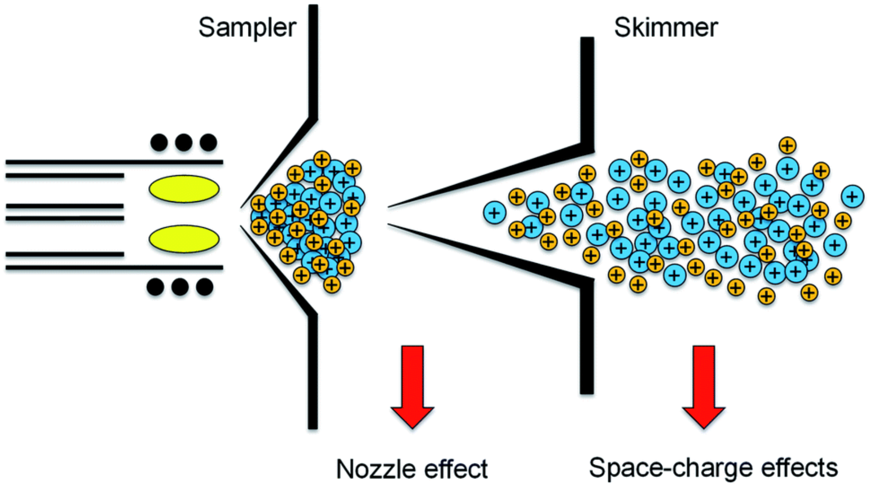
The reason for the higher sensitivity (response) of heavier ions lies in the processes that take place in the ICP/MS interface space and in the following ion optics:

- **Space charge effect**
- **Collisional scattering**

!!! mass discrimination !!!

Mass discrimination

- The phenomenon of non-stoichiometric transition of ions through the mass spectrometer depending on their mass
- **Origins in ICP-MS**:
  - plasma nozzle effect
  - space charge effects in the interface during supersonic expansion of ions through the sampler cone
  - Coulombic repulsion
- **Results in ICP-MS**: measured isotope ratio shows significant bias to the true value
- **Numerical Correction needed**:
  - mass bias drifts with time (**time and matrix dependent**)
  - Instrumental Isotope Fractionation (IIF)



J. Anal. At. Spectrom., 2022, 37, 701–726

Sensitivity of ICP-MS

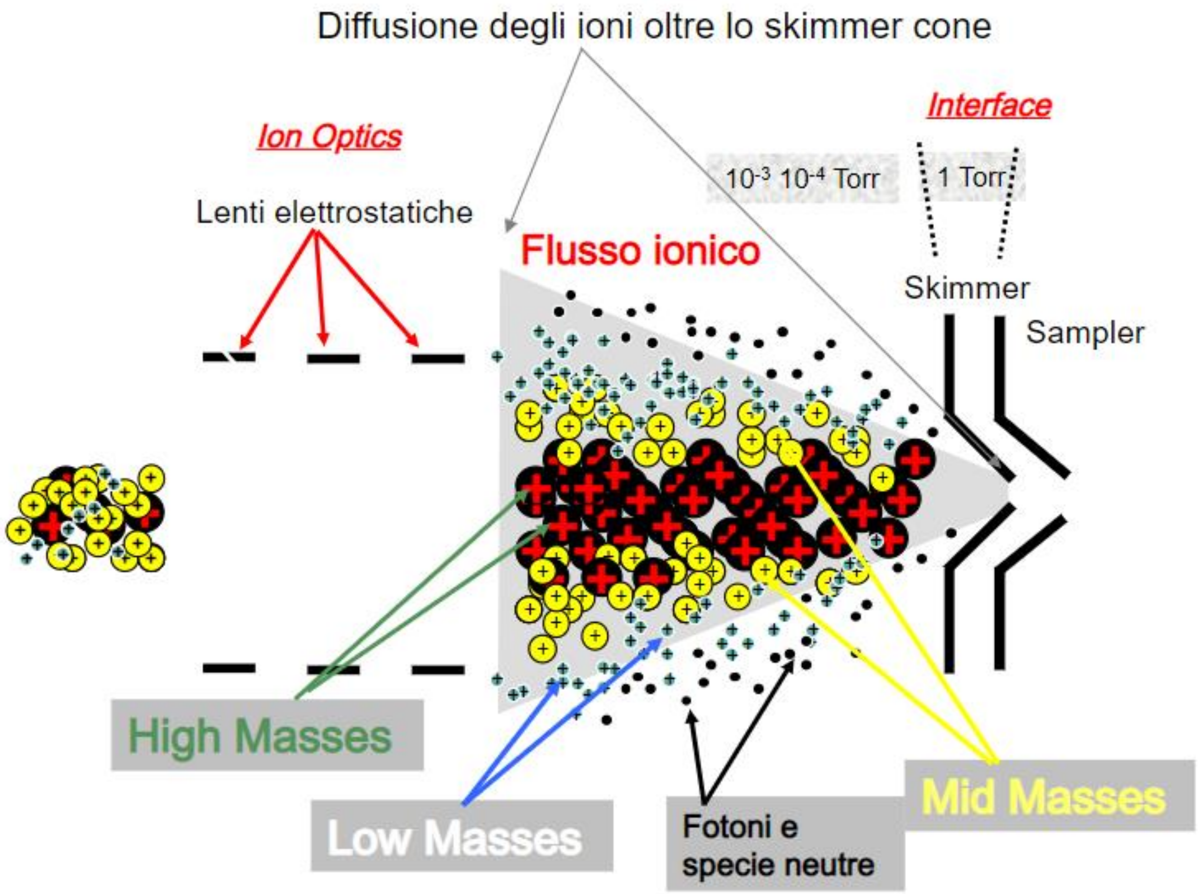
space charge effect

Separation of particles according to their electric charges:

- different mobility of ions and electrons
- differences in particle sizes
- High kinetic energy of electrons

⬇

Light ions with lower kinetic energy are pushed out - **ion optics required**



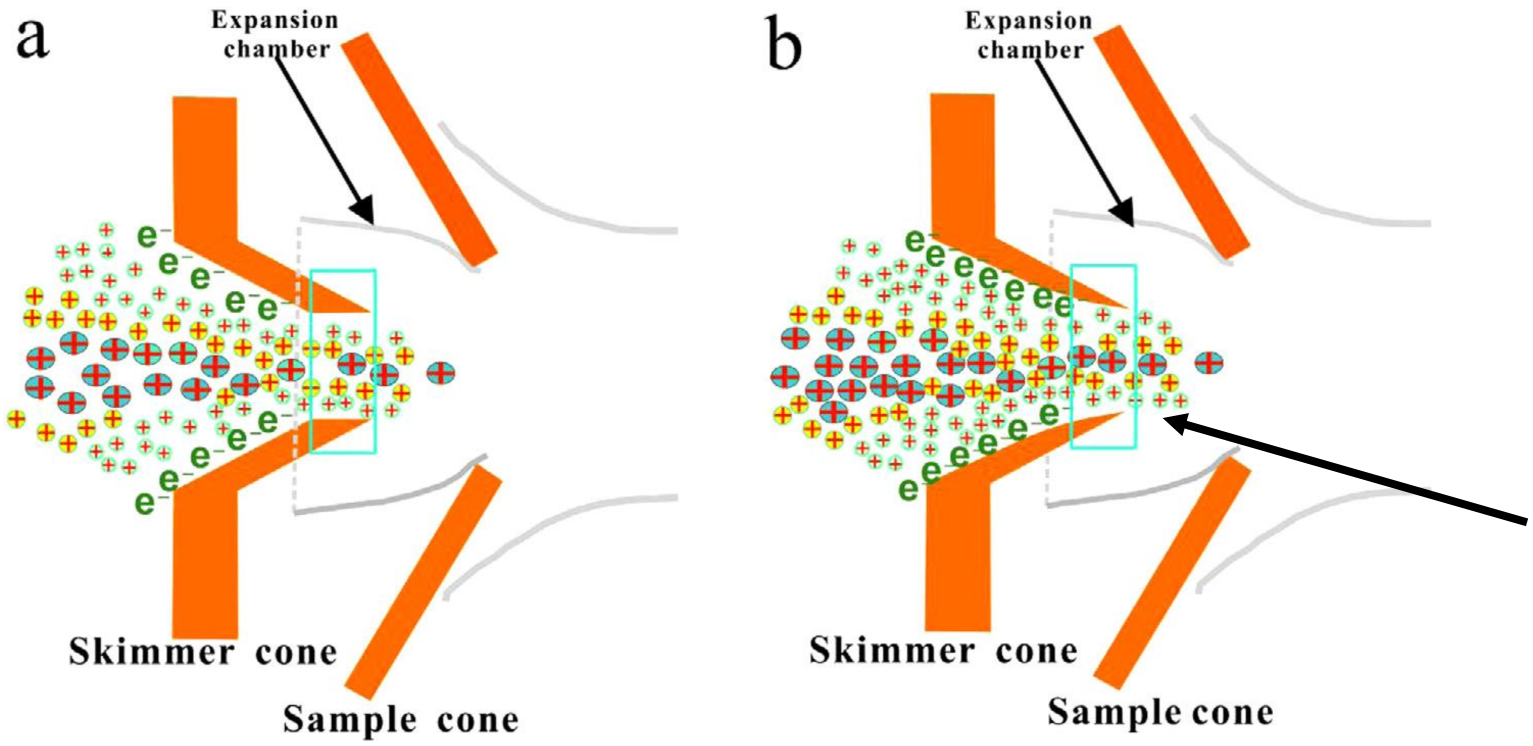
Interface and ion lens to focuse all ions

Sensitivity of ICP-MS

space charge effect

The regular nickel skimmer cone skimmer cone

The nickel X



The sensitivity of inductively coupled plasma mass spectrometers can be significantly improved using different sample and skimmer cones with different orifice diameters and angles.

More of the ion beam can be input to the interface, which introduces more ions into the mass spectrometer and thus improves the instrument's sensitivity.

International Journal of Mass Spectrometry 408 (2016) 33–37

Mass bias correction

- specific isotope amount ratio is used to **calibrate** the amount ratio of another pair of isotopes (same or different element) - **SSB (Sample-standard bracketing) correction**
- **mass bias**: time-dependent, mass-dependent

Correction factor:

linear correction law $K_{i/j} = 1 + f(t)(m_i - m_j)$

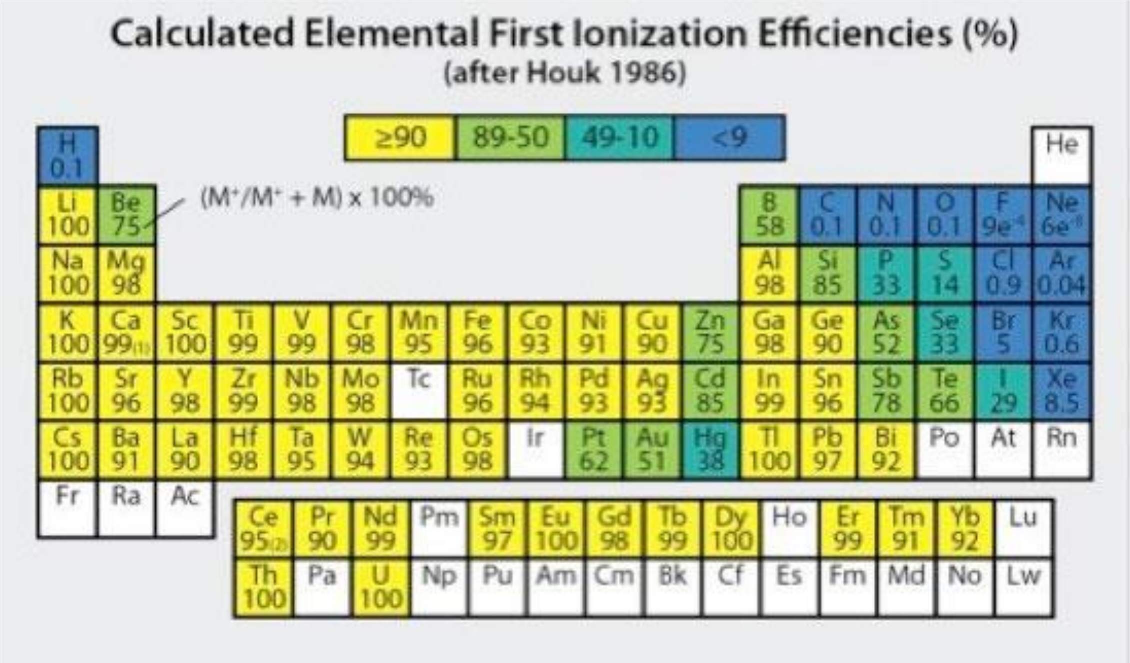
Russell's law $K_{i/j} = (\frac{m_i}{m_j})^{f(t)}$

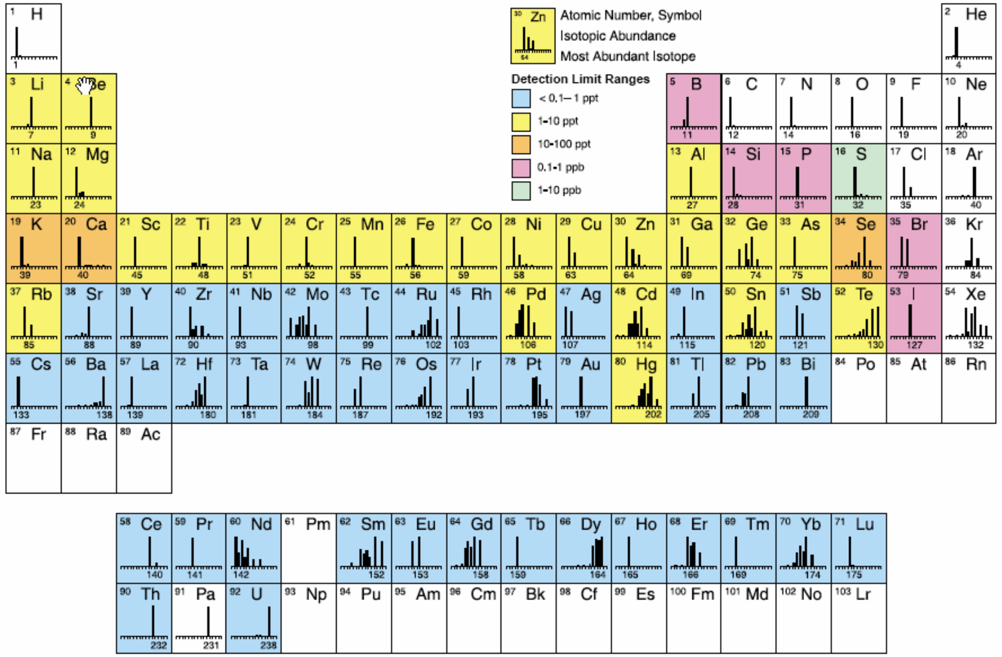
exponential law $\ln K_{i/j} = f(t)(m_i^n - m_j^n)$

- **principle**: calibrator with known isotope amount ratio is measured to obtain the *f(t)* value as a difference between known and measured value; this *f(t)* value is then used to calculate the correction factor $K_{i/j}$
- **Matrix effect:** target element needs to be isolated – separation process

Inductively Coupled Plasma

sensitivity

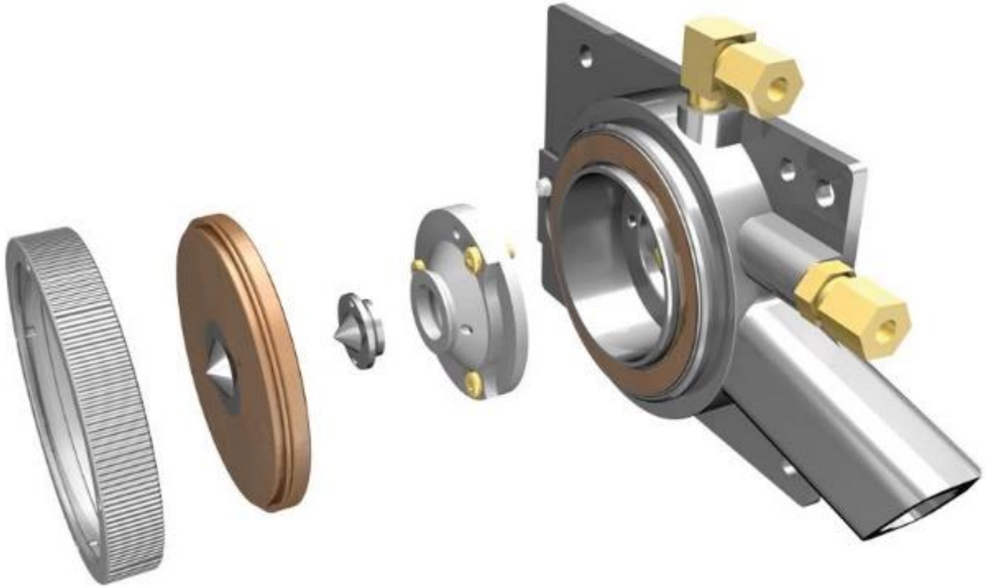


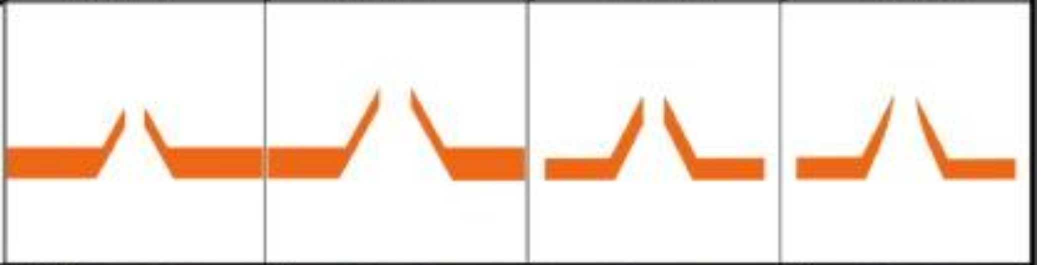


Elemental first ionization efficiencies (as percents) calculated for 7500°K and electron density of 1 x 1015/cm³.

Interface

Sampler & Skimmer cones



Type	Sample cones		Skimmer cones	
Cones	Standard	Jet	H	X
Orifices	0.8 mm [39]	1.2 mm [39]	0.8 mm	0.8 mm
Schematics [a] 				
Photos [a] 				
Geometry	Cylindrical entrance, trumpet-shaped exit			Completely trumpet-shaped

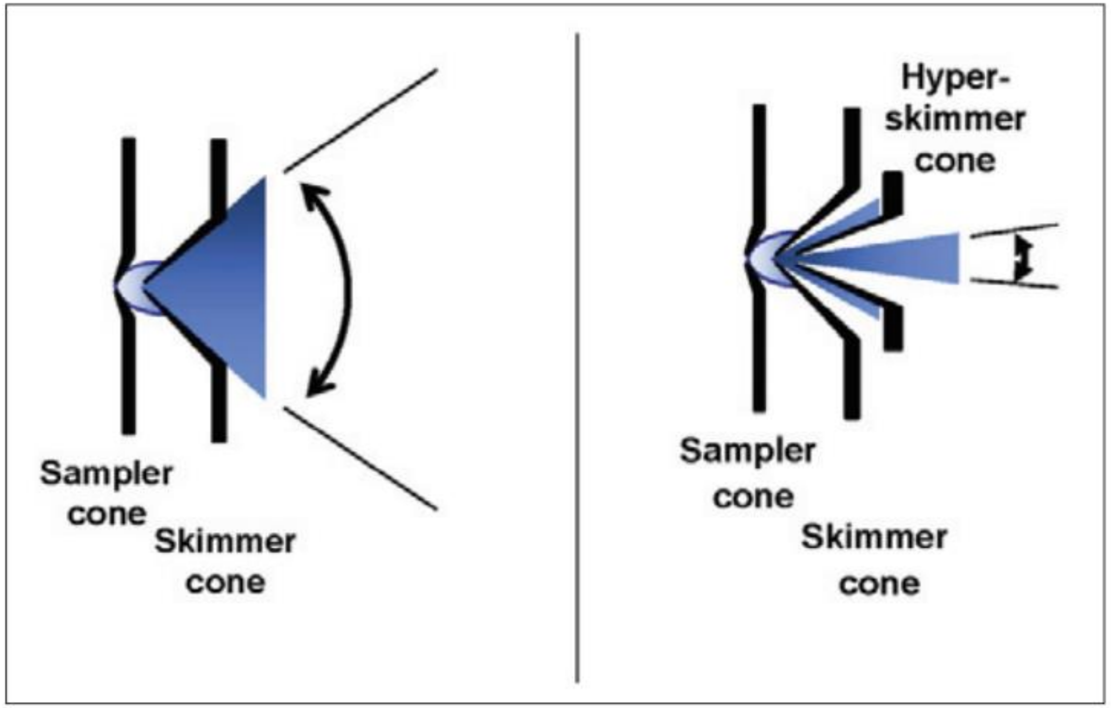
Spectrochimica Acta Part B 146 (2018) 1–8

Sensitivity of ICP-MS

beam divergence

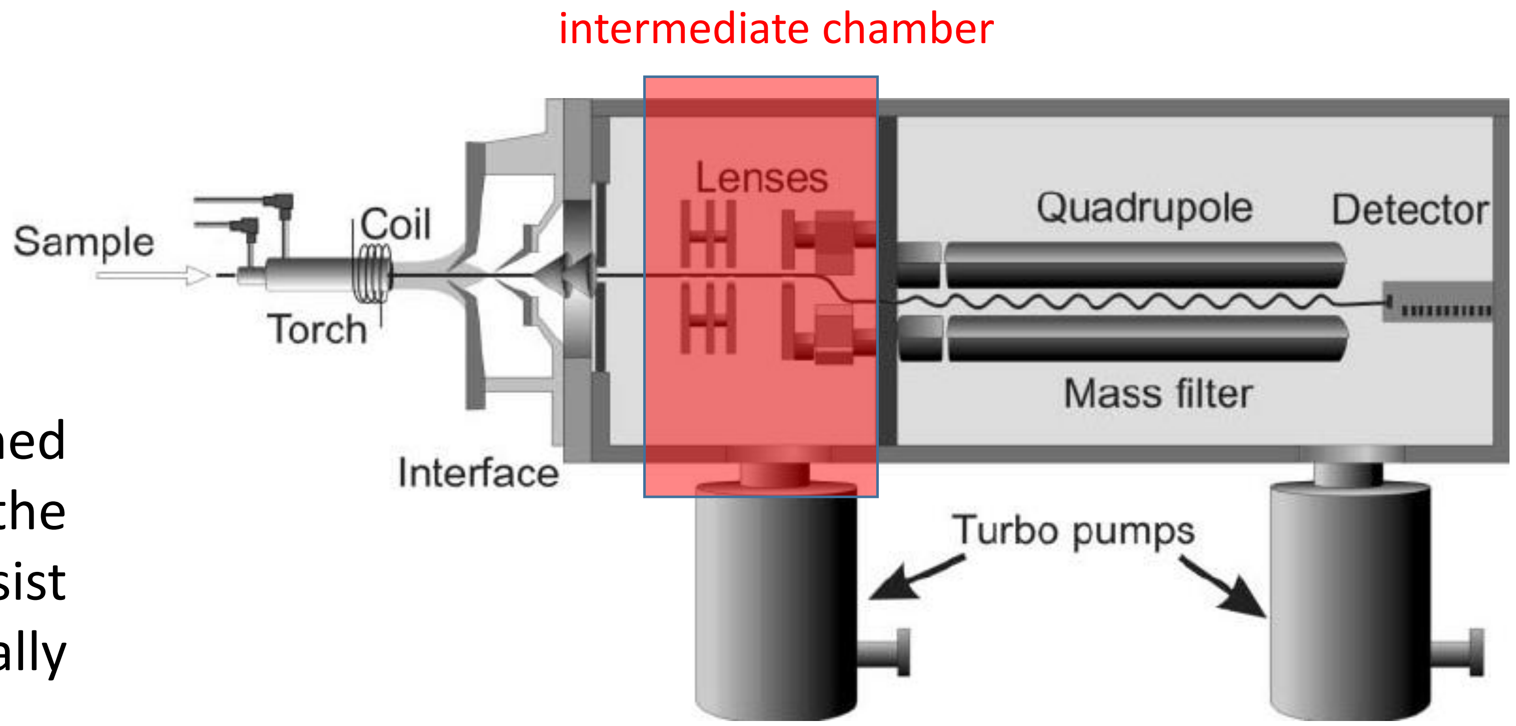
Two-cone design: wide ion beam divergence resulting from a single, large pressure reduction

Three-cone design: small ion beam divergence resulting from two small pressure reductions



https://resources.perkinelmer.com/corporate/cmsresources/images/44-74849tch_icpmsthirtyminuteguide.pdf

Ion optics



The ion optics are positioned between the skimmer cone and the mass separation device, and consist of one or more electrostatically controlled lens components.

The function of the ion optic system:

- to take ions from the plasma at atmospheric pressure via the interface cones and steer them into the mass analyzer, which is under high vacuum.
- to stop particulates, neutral species, and photons from getting through to the mass analyzer and the detector.

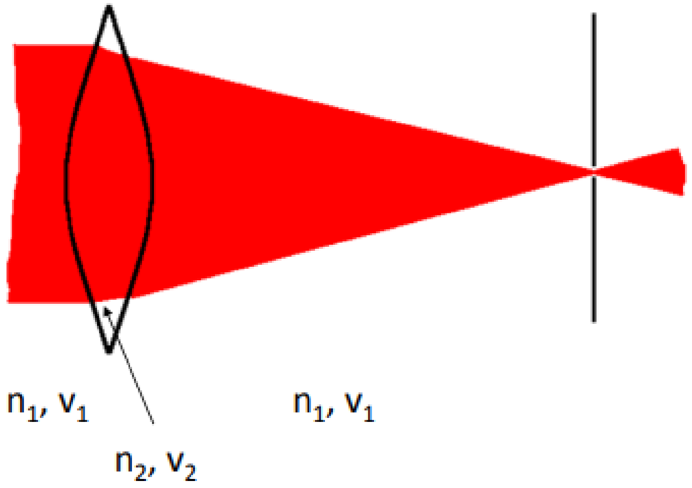
Ion optics

comparison with light optics

no focusing lenses

only small fraction of light makes it thru slit

Use <u>lens</u> to focus beam into slit

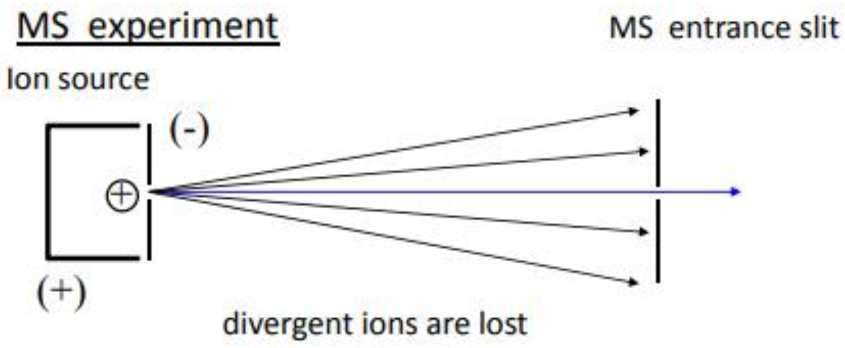


velocity of beam <u>changes inside lens</u>

lens surface curved ⇒
off-axis rays are deflected and focused

Ion optics

comparison with light optics



Insert lens between source and slit

collimate divergent ions thru slit

improve transmission and sensitivity

set of metal lenses: circular apertures or cylinders
apply DC voltages to focus

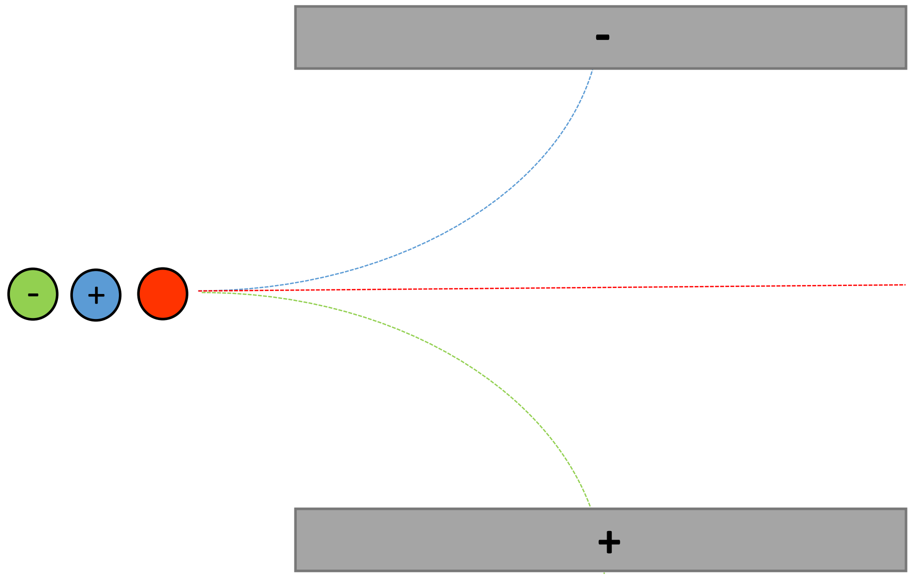
Objective	Optical Lens	Ion Lens
CHANGE VELOCITY	pass beam into medium of different density	pass beam thru region of different E field
DEFLECT BEAM	curve/tilt boundary of different media	curve/tilt potential contours

https://engineering.purdue.edu/BioMS/Pdf/Lecture%20Notes%20for%20MS%20Short%20Course/L9-L10%20Instrumentation_Fina.pdf

Mass Spectrometry

basics

Moving of particles in an electric field



The electric (Coulomb) force F_{el} exerted by the field on the positive charge is:

$$F_{el} = q\,E = \frac{m\,v^2}{r}$$

q *charge magnitude*
E *electric field (N·C^{-1}; V·m^{-1})*
m *mass (kg)*
v *velocity (m·s^{-1})*
r *radius of the ion path*

$$r = \frac{m\,v^2}{q\,E}$$

Ion optics

Einzel lenses

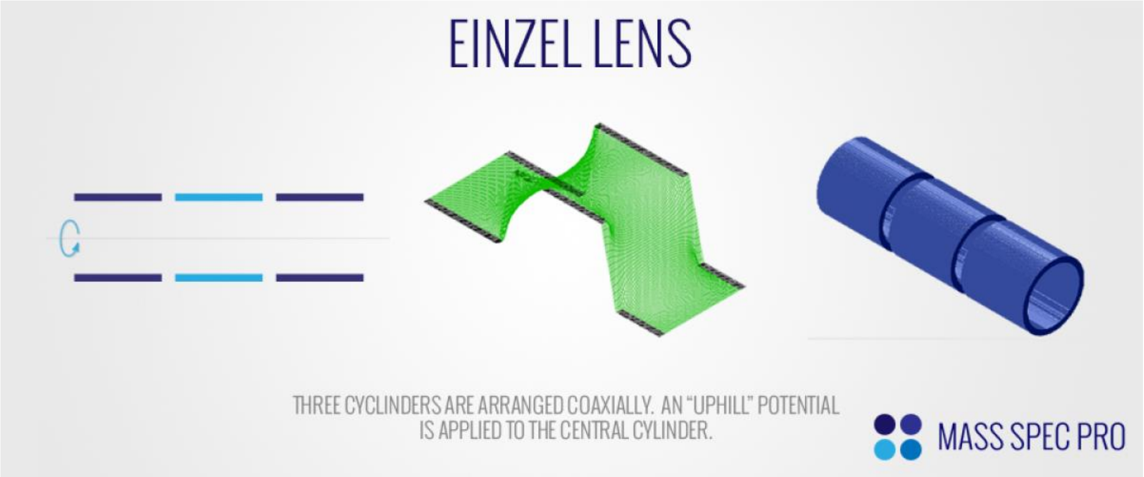
After entering into the evacuated region, a number of lenses are used to manipulate the path of the ions flowing from the plasma. First and foremost are the **accelerator lenses**. An accelerator lens consists of two to three plates with a relatively large hole in them (typically larger than the hole in the cones). **Each plate has an increasingly negative charge placed across them that result in the attraction of the cations towards the plate increasing their kinetic energy. The hole in the center allows most of the cations to pass directly through the plate.** The imposed kinetic energy is needed to pass the cations through the subsequent reaction cell, mass filter, and on to the detector with sufficient energy to dislodge electrons on the surface of the detector (an electron multiplier device).

The next type of lens used in the MS is a focusing lens that centers the cations into a small beam.

Ion optics

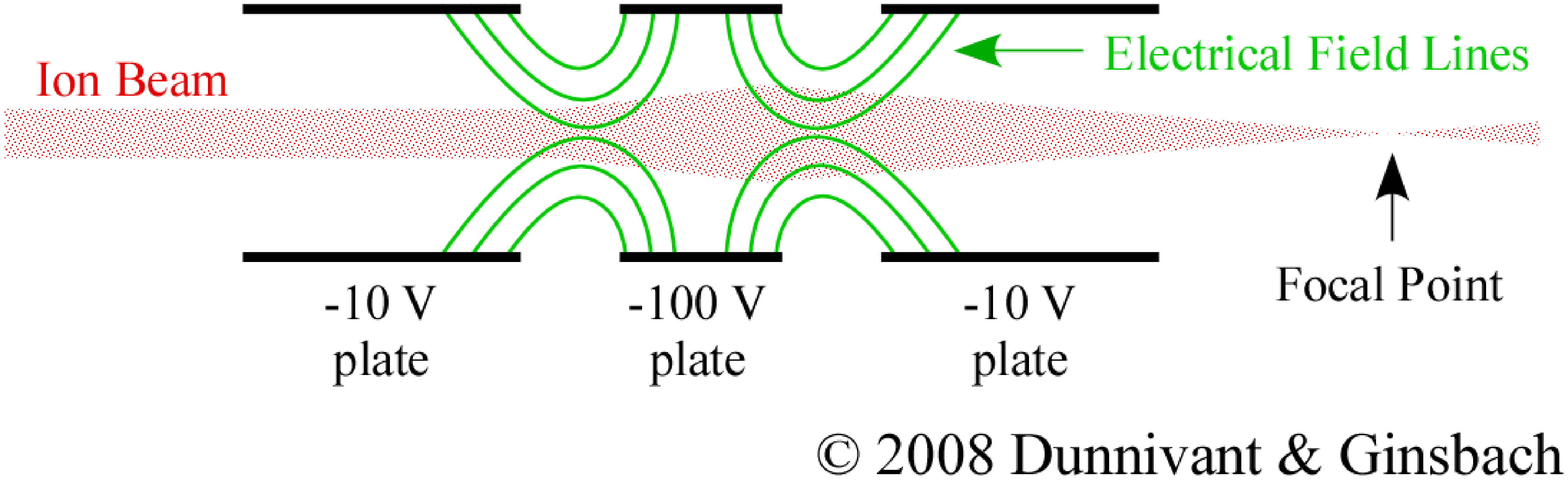
Einzel lenses

An Einzel lens is comprised of three metal cylinders/electrodes arranged coaxially in a row. The first and third electrodes have the same voltage applied to them, while the second electrode has a voltage that is "uphill" to ions of the polarity of interest.



Ion optics

Einzel lenses



Ion optics

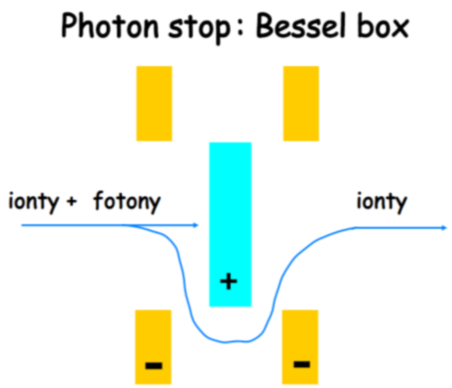
If photons or neutral species reach the detector, they will elevate the background noise and therefore degrade detection capability.

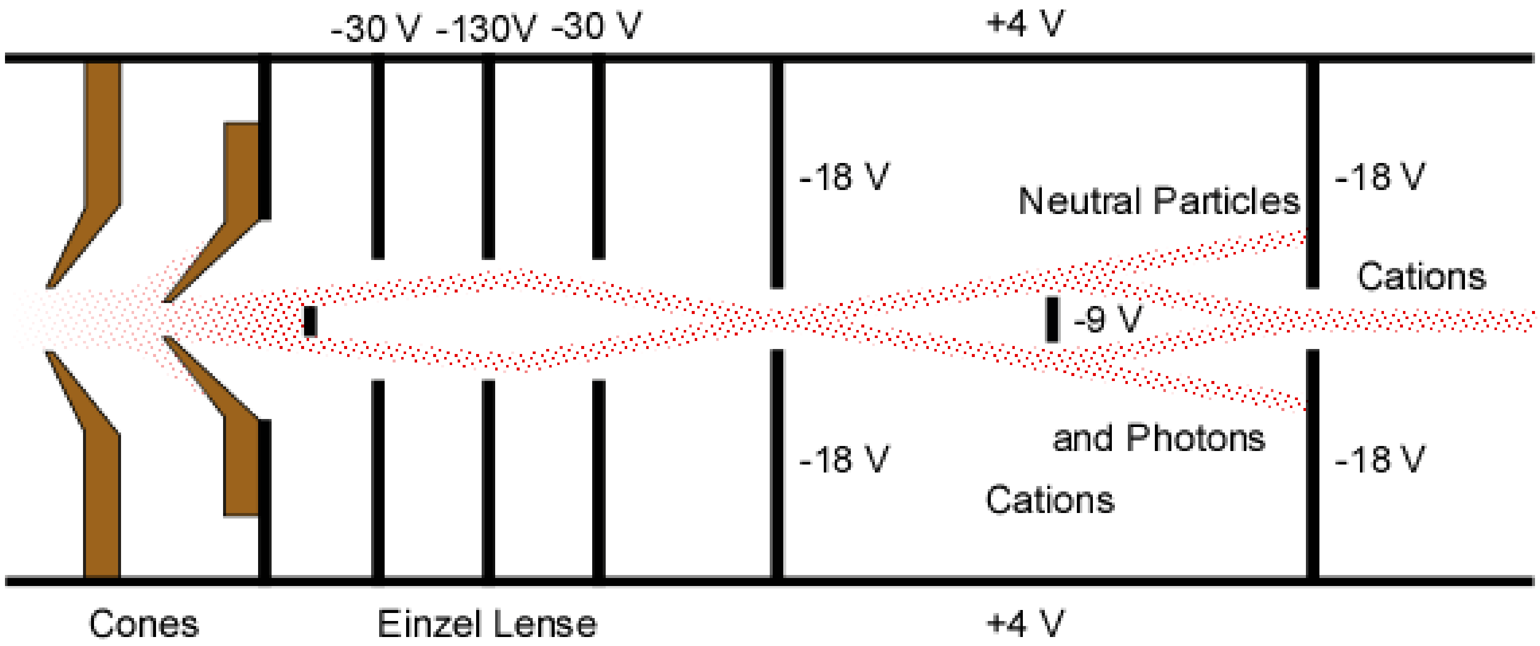
Both photons and neutrals are detected by the universal detector that can give false signals and increase the instrumental noise if they are not filtered. Besides causing increased noise, neutrals passing through the mass filter can become adsorbed onto metal components that can interfere with their proper function. There are two major types of lenses that remove neutral particles and photons; a **Bessel box** and **omega lens.**

Ion optics

Einzel lenses + photon stop

Bessel box, also referred to as a photon stop, is comprised of two photon stops, an Einzel lens, and a set of three lenses. The first photon stop (located before the Einzel lense) prevents particles from flowing directly down the evacuated chamber. The Einzel lens focuses the particles into the Bessel box and around the second photon stop. The positive voltage (+4 V) on the outside of the Bessel box and the negative voltage on the second photon stop (-9 V) direct the cations back to the exit slit. Neutral particles and photons are unaffected by the electrical field and are removed.

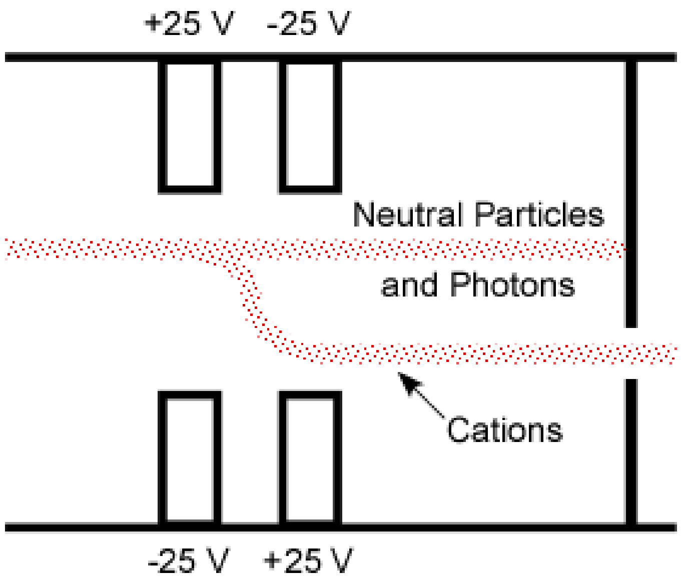


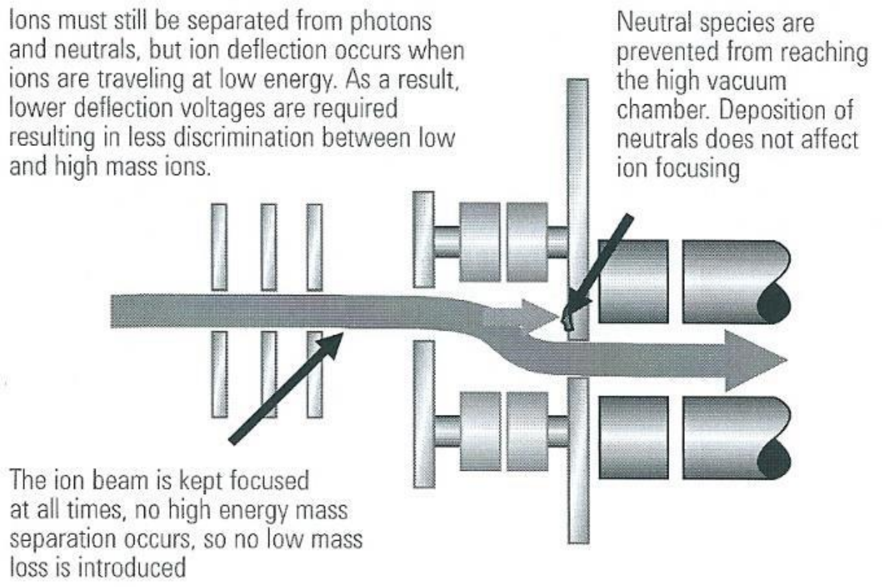


http://people.whitman.edu/~dunnivfm/FAASICPMS_Ebook/CH4/4_2_4.html

Ion optics
Omega lens

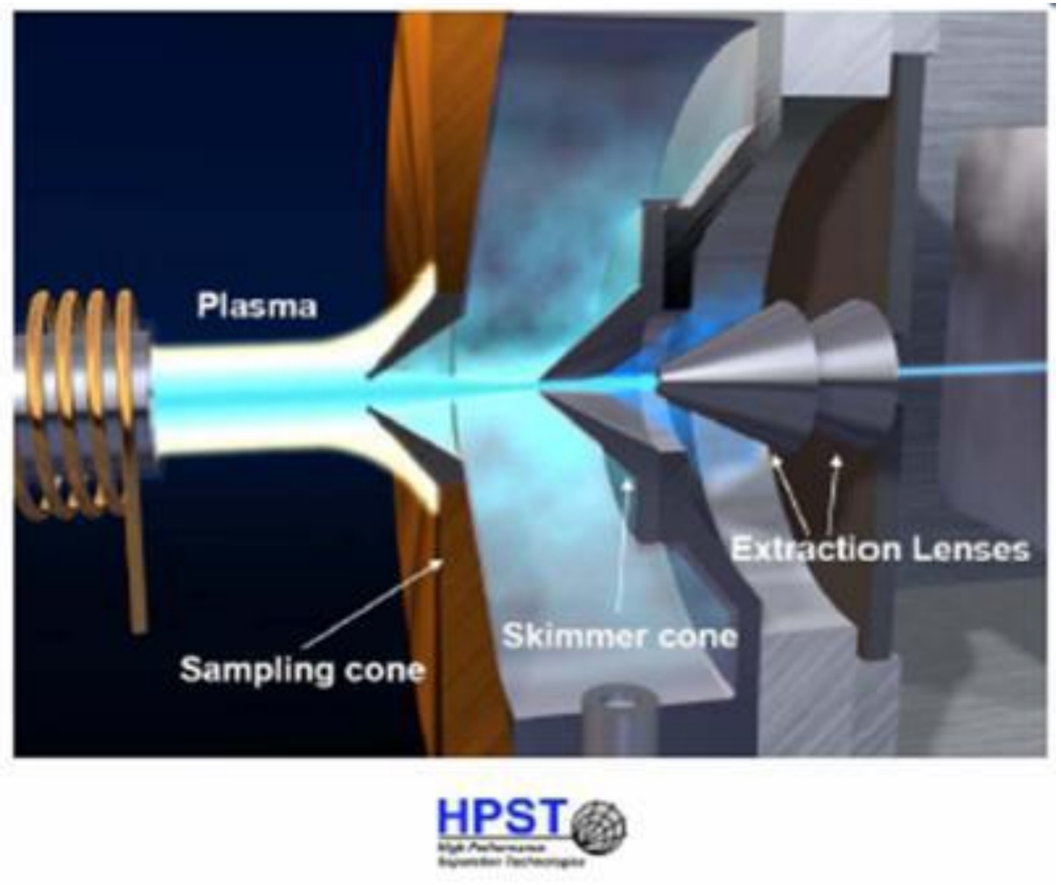
Omega lens, filters out the photons and neutral particles. A cross-section of an Omega lens consists of four electrodes, two near the top and two near the bottom of the ion beam. The lens works by carefully balancing the charges of the electrodes to deflect the beam of cations, but not the neutral species or the photons from the plasma. This deflection is accomplished by placing a positive charge on the first top electrode and a negative charge on the first bottom electrode that acts to deflect the beam of cations downward in the front of the lens





Ion optics

extraction lenses



Ion optics

transfer lens system – HR-ICP-MS

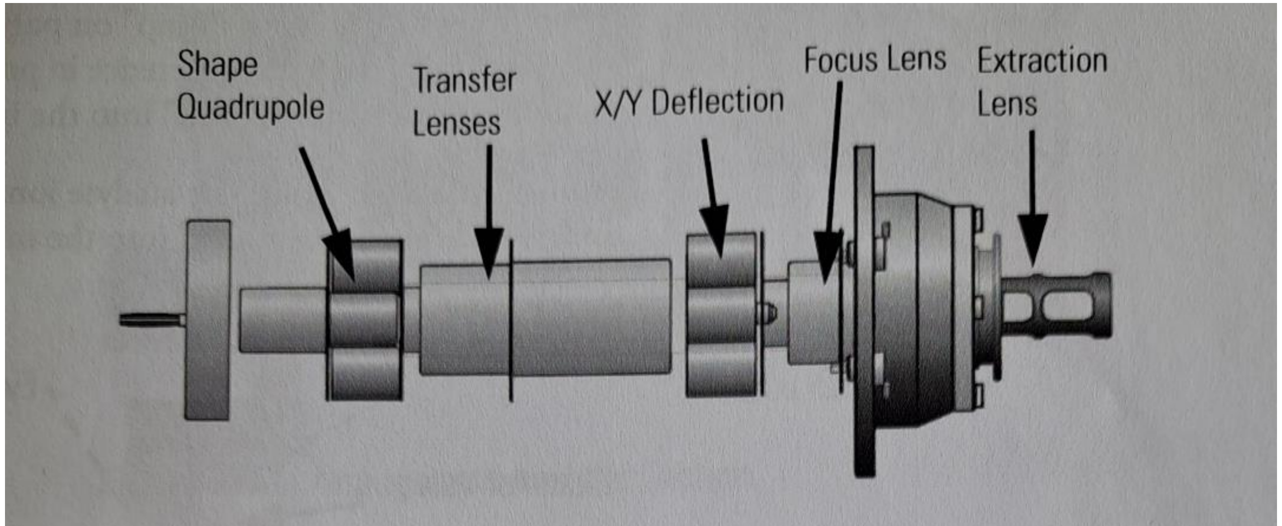


Figure 2-17. Transfer Lens System

The transfer lens system is equipped with the following lenses (right to left):

- **Extraction lens**: attracts ions from the particle stream,
- **Focus lens**: focusses the divergent ion beam onto the entrance slit,
- **X/Y deflection lens**: corrects the direction of the beam with respect to the entrance slit
- **Transfer lenses**: accelerate the ions, and
- **Shape quadrupole**: shapes the beam into a flat shape to fit through the entrance slit.

After passing the above lenses, the analyte ions travel through the focus point (entrance slit) and start to diverge again slightly. With the last two quadrupoles inside the analyzer housing, rotation quadrupole 1 (RQ1) and focus quadrupole 1(FQ1), a slight rotation and a change of the focus of the ion beam can be achieved.

https://www.thermofisher.com/order/catalog/product/IQLAAEGAAMFABWMAFC

Vacuum system

Pressure units:

Pascal: [Pa] = N/m². The basic unit of SI (the International System of Units).

1 Pa = $\frac{1N}{m^2} = \frac{1kg}{m^2 s}$

Standard Atmosphere: [Atm] it is about equal to the atmospheric pressure. Technically, the atm is defined as **101 325 Pa**, but it was originally designated as the air pressure at sea level and 0 ºC.

Atmospheres are most commonly used when the precise air pressure is unimportant. For example, I might say that I heated my sample in dry air at 1 atm. In this case I mean that I didn't measure the air pressure, but I assumed it was basically the pressure of the room, which is more or less 1 atm.

torr: [Torr] = mmHg = 133.32 Pa. 1 Atm = 760 Torr. Outdated, unauthorized pressure unit.

bar: [bar] = 100 000 Pa

With the prefix "hecto-" which means 100, Pa can be easily converted to bar. 1 hectopascal (hPa) is equivalent to 1 mbar.

1 Atm = 101 325 Pa = 760 Torr = 1013.25 mbar

Vacuum system

Why vacuum?

the mean free path (λ) – the distance an atom travels between collisions with other particles

$\lambda(1\text{ atm}) \approx 70\text{ nm}$
$\lambda(10^{-6}\text{ Pa}) \approx 1\text{ km}$

Jennings, S (1988). "The mean free path in air". Journal of Aerosol Science. 19 (2): 159.

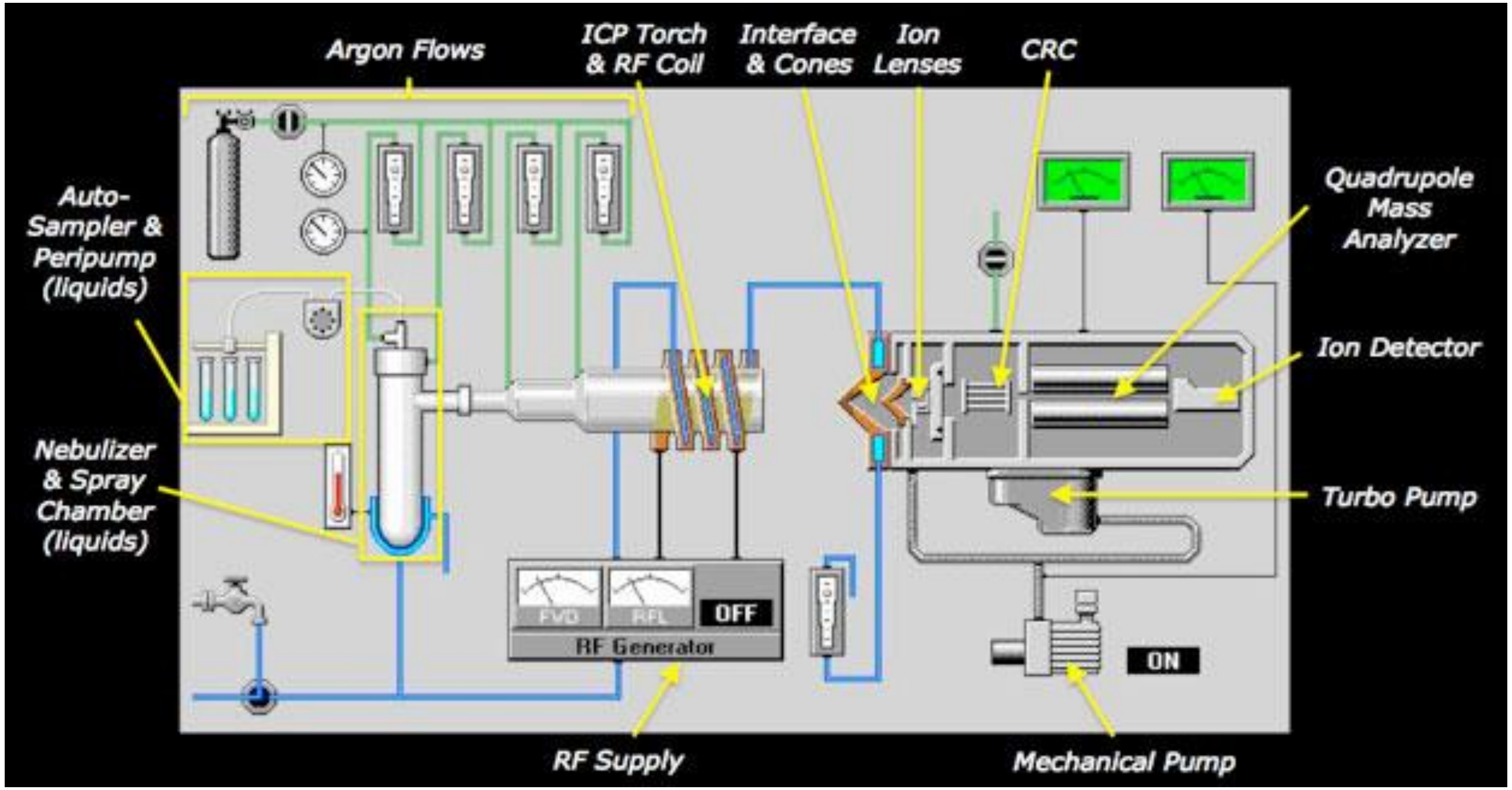
How to reduce pressure?

- lowering the temperature of the system
- increasing the volume of the system
- reduction of the amount of the substance in the system

Vacuum system

Spectrometers always have min. 2 degrees of vacuum.

1. stage – mechanical pump
2. stage – turbo pump



Vacuum system

HR Element2
Five-stage differential pumping system
Atmospheric pressure to a high vacuum < 10^{-7} mbar

- At the *first* stage, a mechanical pump connected to the interface evacuates the region between sample cone and skimmer cone.
- The pumps at the *second* and *third* stage evacuate the housing of the transfer lens and focusing system (analyzer).
- The pump at the *fourth* stage evacuates the flight tube in the magnet and
- the pump at the *fifth* stage evacuates the ESA and the ion detection system.

The following shows the pressure values at the different stages:

Table 3-1. Pumping stages of the ELEMENT2/XR

Stage	Pump	Pressure [mbar]
1st	UNO 30M	~ 2 mbar
2nd	(DUO 05)* TMH 262	~ 3 x 10^{-4} mbar
3rd	TMH 071P	~ 1x 10-5 mbar
4th	TMH 071P	~ 1x 10-7 mbar
5th	TMH 071P	~ 1 x 10^{-7} mbar

*TMH262 is connected to all turbo pumps, serving as a roughing down pump for stages 2 to 5

During standby mode, the skimmer valve separates the vacuum stages 2 to 5 from the atmospheric pressure; the interface pump is switched off.

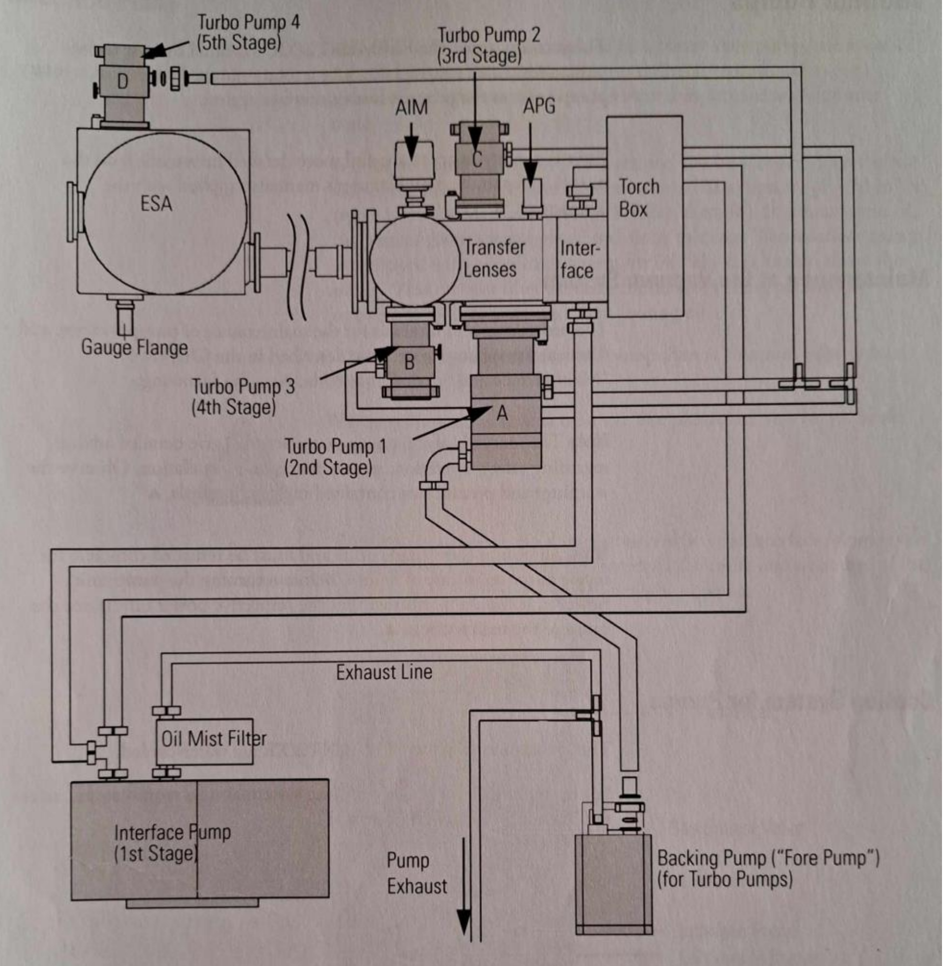


Figure 3-1. Schematic Overview - Pumps in the ELEMENT2/XR

Vacuum system

1. stage

The interface (mechanical) pump is the first pumping stage of the system. It is switched independently and runs only when the system is in operation (i.e. the pump is switched OFF during standby operation).

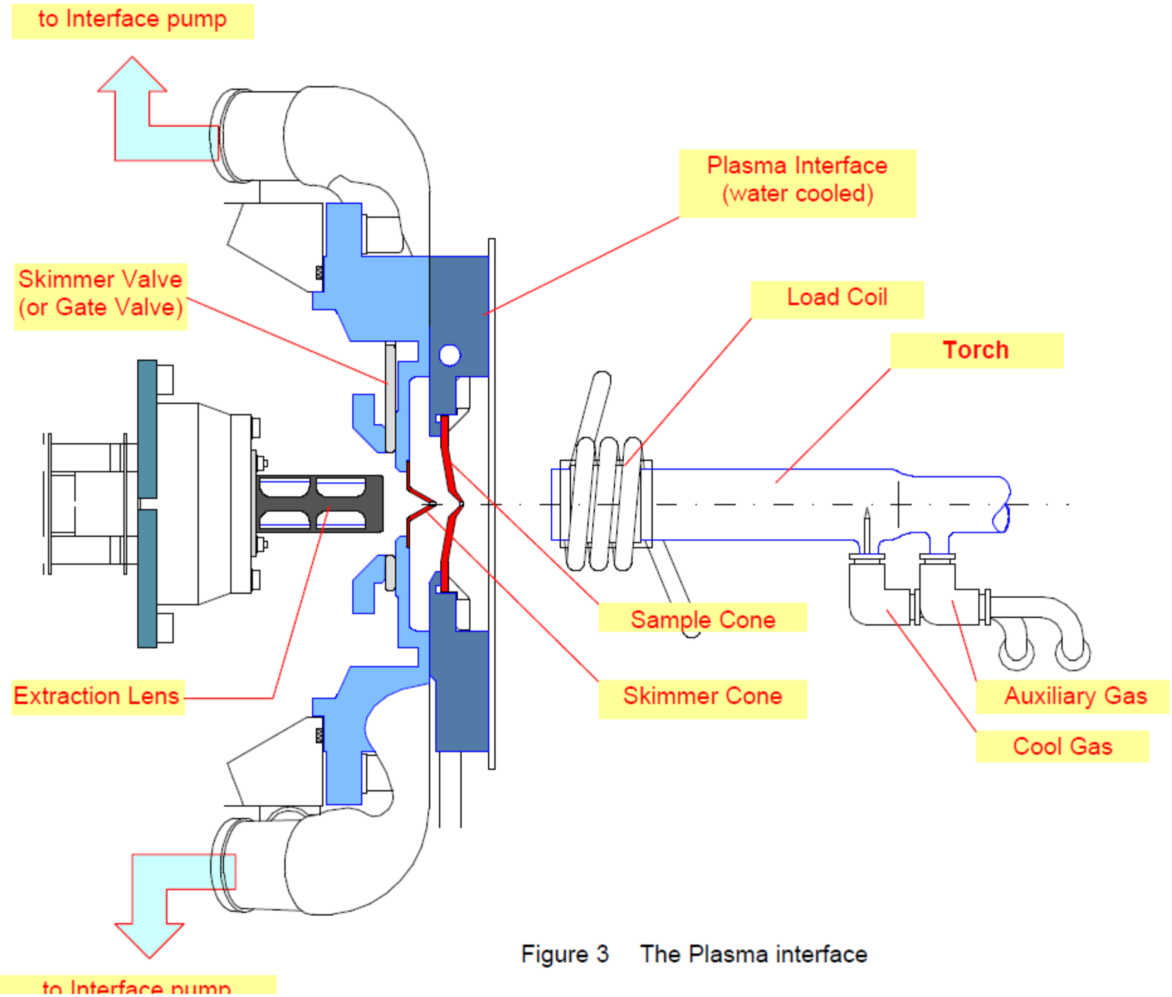
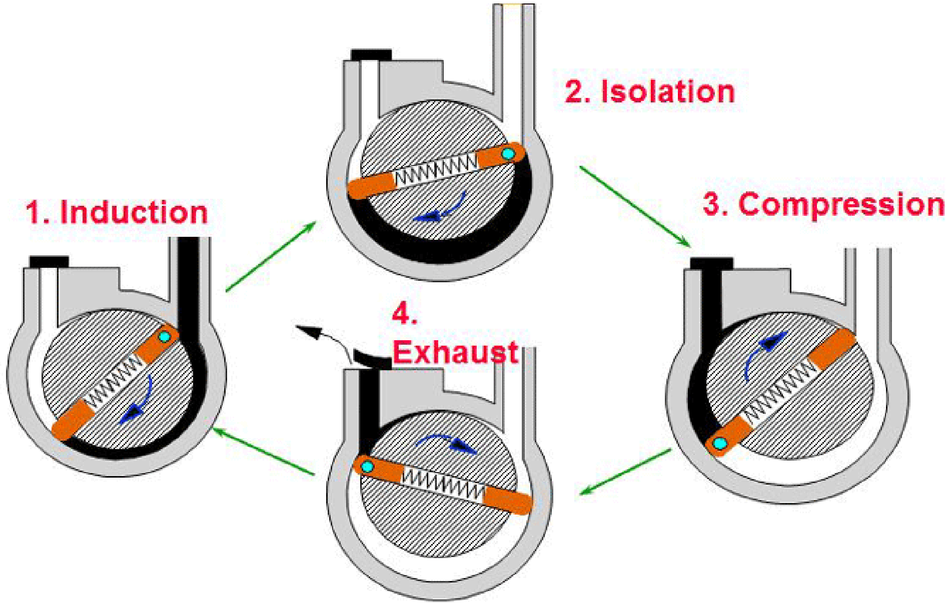


Figure 3 The Plasma interface

Vacuum system

1. stage is provided by **rotary oil pumps** – vacuum approx. 10^{-2} mBar – serves for operation of the 2nd stage of vacuum

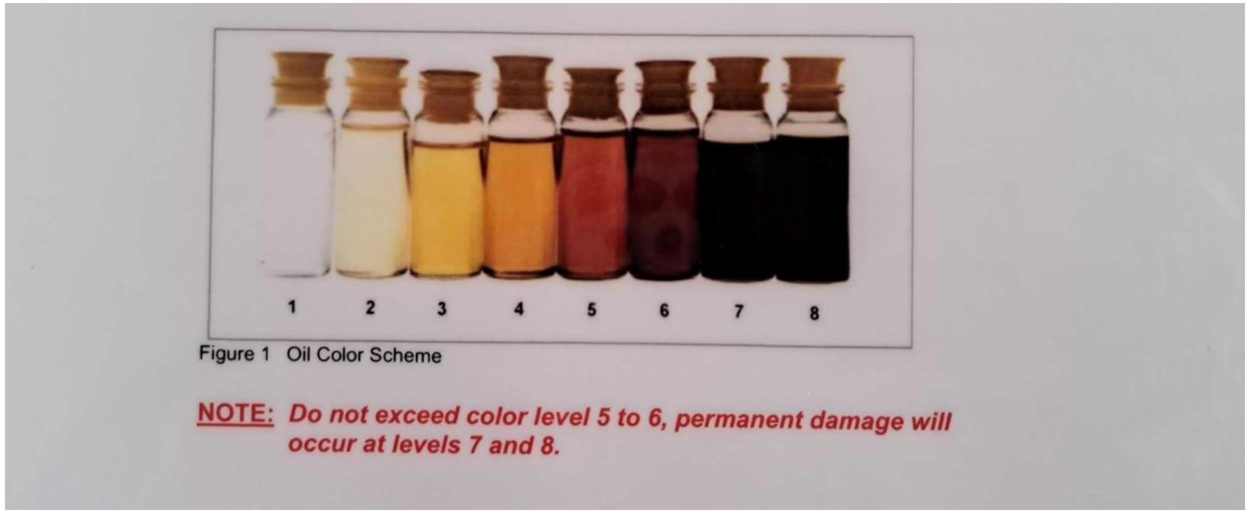


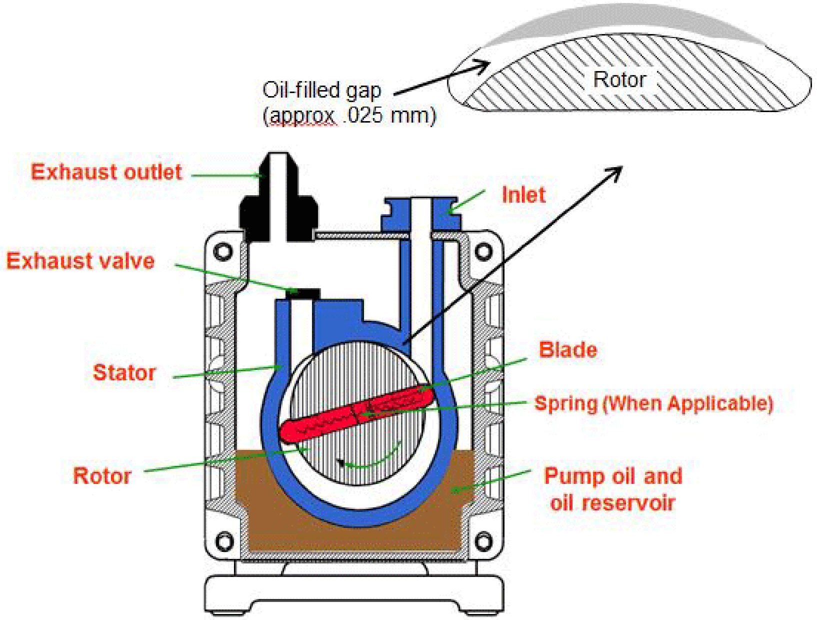
https://www.youtube.com/watch?v=oXgdnnkIKZ4

https://vacaero.com/

Vacuum system

rotary oil pumps maintenance – oil change





The entire assembly is machined and assembled with tight tolerances so that the gap between the top of the rotor and the stator wall (often referred to as the "Dou seal") is approximately 0.025 mm. This seal is filled with oil, providing a seal between the inlet and outlet sides. The oil is circulated from the oil reservoir into the pump interior and is exhausted through the exhaust valve with the pumped gas.

https://vacaero.com/

Vacuum system

2. Stage - turbomolecular pump 10^{-5} – 10^{-8} mBar

does not work at atmospheric pressure => necessity to use a rotary pump

Rotation speed upto 90000 min^{-1}

Oil-free

https://youtu.be/f1SErZyhMe4

Vacuum system

Do not move the device when the turbo pump is on, there is a risk of damage!!!