SHORT COURSE
ICP – MASS SPECTROMETRY
INSTRUMENTATION

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Czech Republic

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WHERE EXACTLY IS BELGIUM?

- **Facts**
  - ***Area: 30,528 km²***
  - ***Population ~ 11,000,000***
  - ***Inhabitation density: 360 /km²***
  - ***Capital: Brussels***
    - *European Parliament*
    - *NATO headquarters*
  - ***Northern part: Flanders (Dutch)***
  - ***Southern part: Wallonia (French)***

WHERE SHOULD I KNOW BELGIUM FROM?

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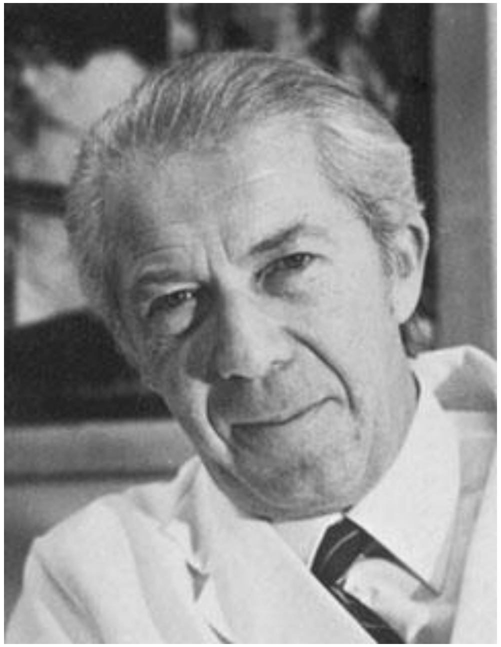
PERHAPS … WHO KNOWS?



***Leo Baekeland*?**
Chemist, inventor
"Father of plastics"
Bakelite
phenol-formaldehyde resin

***Christian de Duve*?**
Biochemist
Nobel Prize for Medicine in 1974
Discovered lysosomes and peroxisomes as cell organelles

PERHAPS … WHO KNOWS?

Eddy Merckx ?
1960-70s,
5 times winner of Tour de France
World Champion
World hour record holder
"The cannibal"

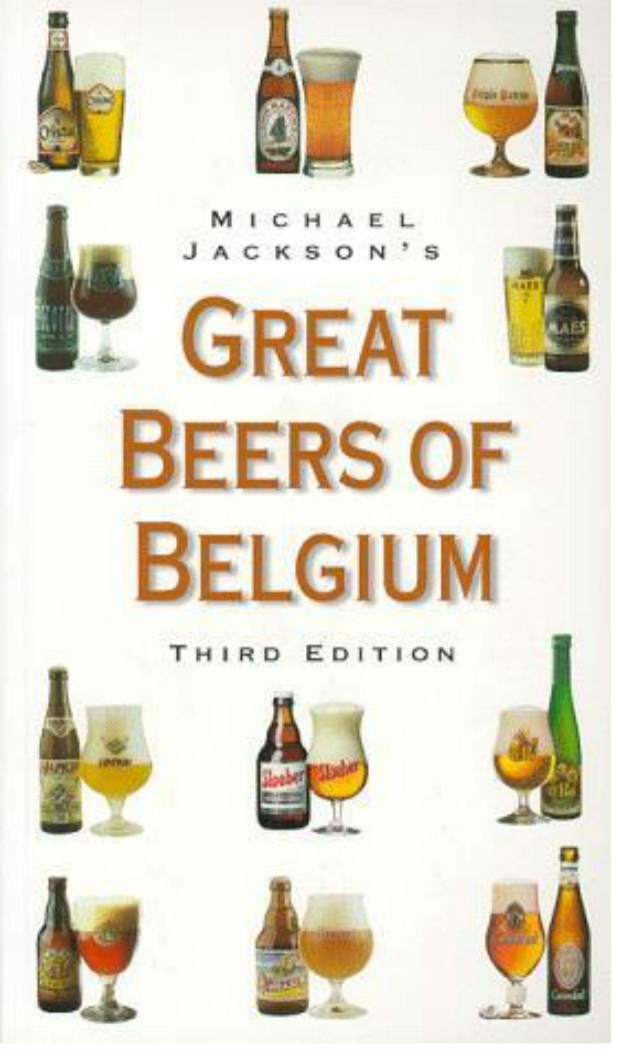
Kim Clijsters ?
Recently "retired"
3 times US open, 1 time Australian open
Achieved nr. 1 world ranking

PERHAPS … WHO KNOWS?

Tintin

The smurfs

WHERE SHOULD YOU KNOW BELGIUM FROM?



Trappist beers – alcohol content: 6 – 12%

WHERE SHOULD YOU KNOW BELGIUM FROM?

What about Ghent?

- *Wikipedia?*
  - ***Ghent started as a settlement at the confluence of the Rivers Scheldt and Lys and became in the Middle Ages one of the largest and richest cities of northern Europe. Today it is a busy city with a port and a university.***

THE MIDDLE AGES IN GHENT
GRAVENSTEEN CASTLE (1180)

THE MIDDLE AGES IN GHENT
FRIDAY'S MARKET SINCE 1199 !

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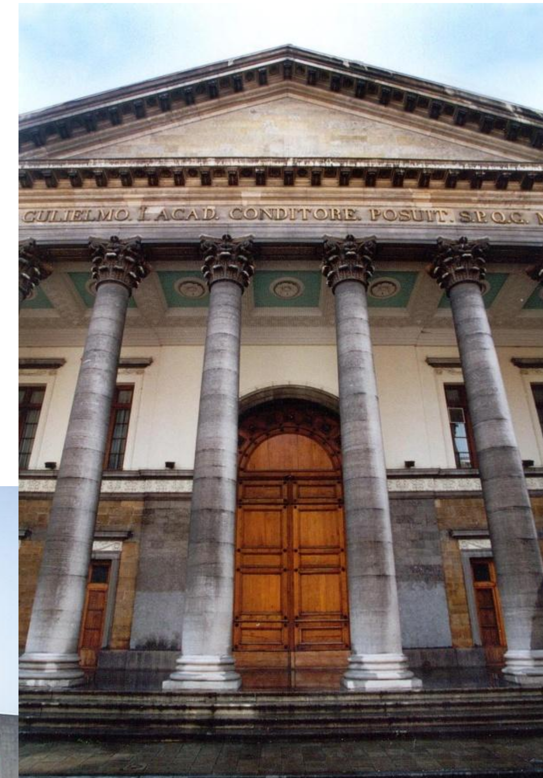
The Middle Ages in Ghent
Graslei – Mediaeval port

THE MIDDLE AGES IN GHENT
THE BELFRY & GOTHIC CHURCHES

GHENT UNIVERSITY

°1817 - ~38,000 STUDENTS & ~7,000 STAFF MEMBERS



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DEPARTMENT OF ANALYTICAL CHEMISTRY

ATOMIC & MASS SPECTROMETRY RESEARCH GROUP A&MS

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INDUCTIVELY COUPLED PLASMA – MASS SPECTROMETRY
ICP-MS

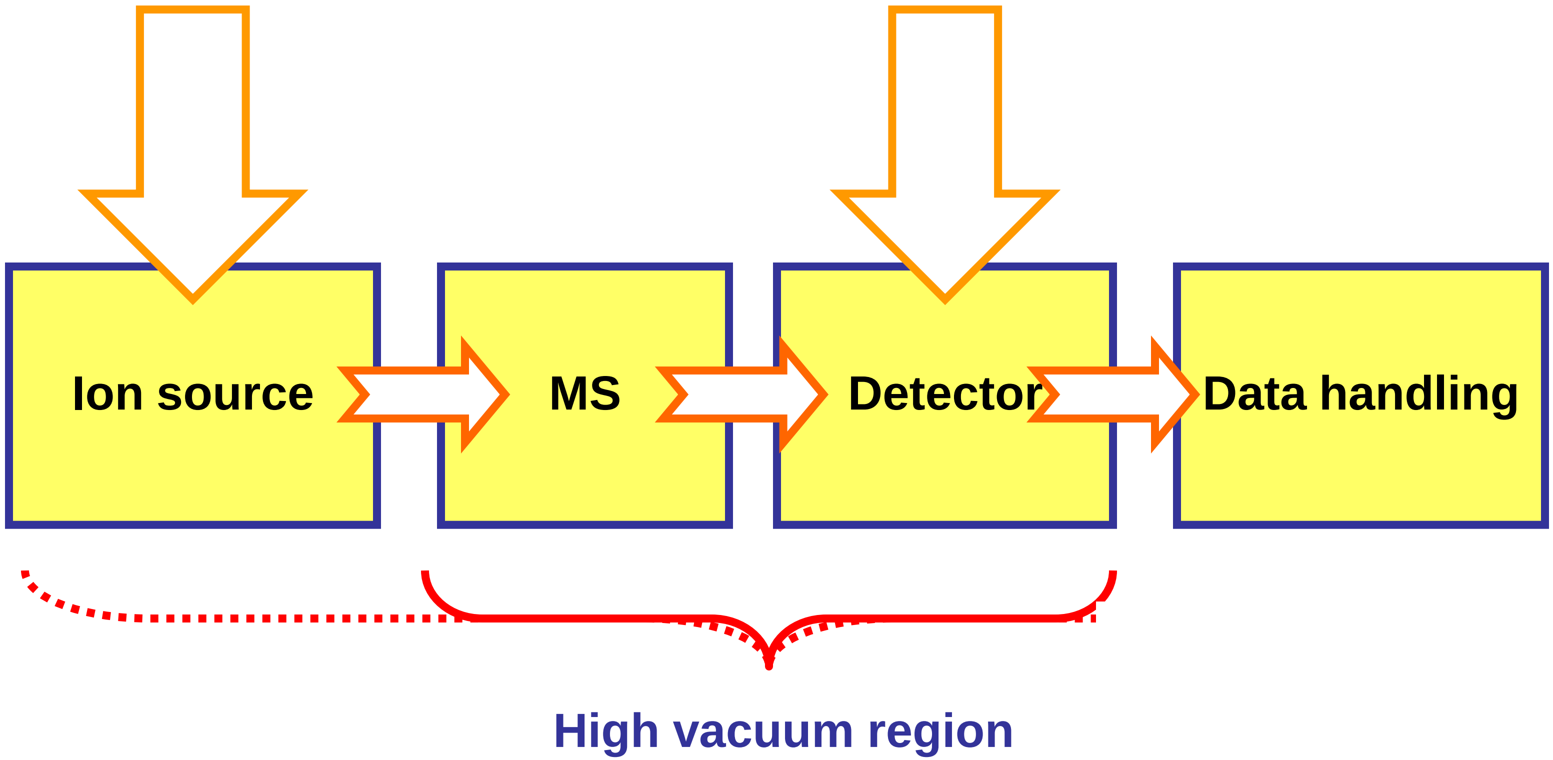
- ***What is ICP-MS?***

  - ***Wikipedia?***
    - ***Inductively coupled plasma mass spectrometry (ICP-MS) is a type of mass spectrometry which is capable of detecting metals and several non-metals at concentrations as low as one part in 10^{12} (part per trillion). This is achieved by ionizing the sample with inductively coupled plasma and then using a mass spectrometer to separate and quantify those ions.***
    - ***Compared to atomic absorption techniques, ICP-MS has greater speed, precision, and sensitivity. However, analysis by ICP-MS is also more susceptible to trace contaminants from glassware and reagents. In addition, the presence of some ions can interfere with the detection of other ions.***
  - ***A powerful technique for the determination of (ultra)trace elements***

ICP – MASS SPECTROMETRY

- ***° 1983, at present: thousands of instruments in use***
- ***Research tool → more robust & well-established technique***
- ***Advantages***
  - ***Low limits of detection***
  - ***Multi-element capabilities***
  - ***Wide linear dynamic range***
  - ***High sample throughput***
  - ***Relatively simple spectra***
  - ***Ability to obtain isotopic information***
  - ***Ease of combination with***
    - ***Alternative sample introduction systems***
    - ***Chromatographic separation techniques***

MASS SPECTROMETRY



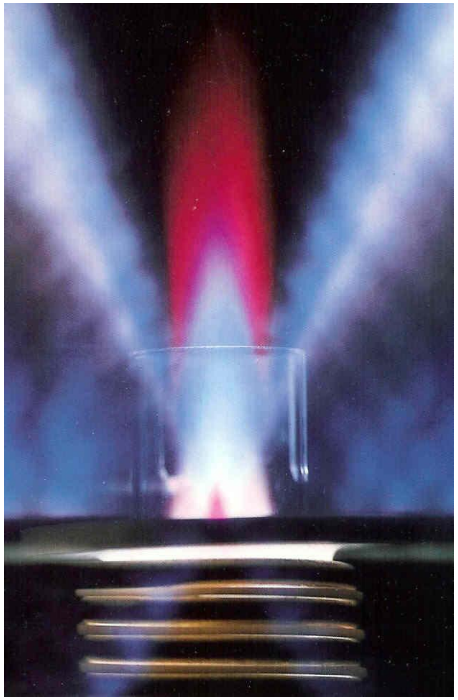
THE INDUCTIVELY COUPLED PLASMA
ICP

INDUCTIVELY COUPLED PLASMA – ICP

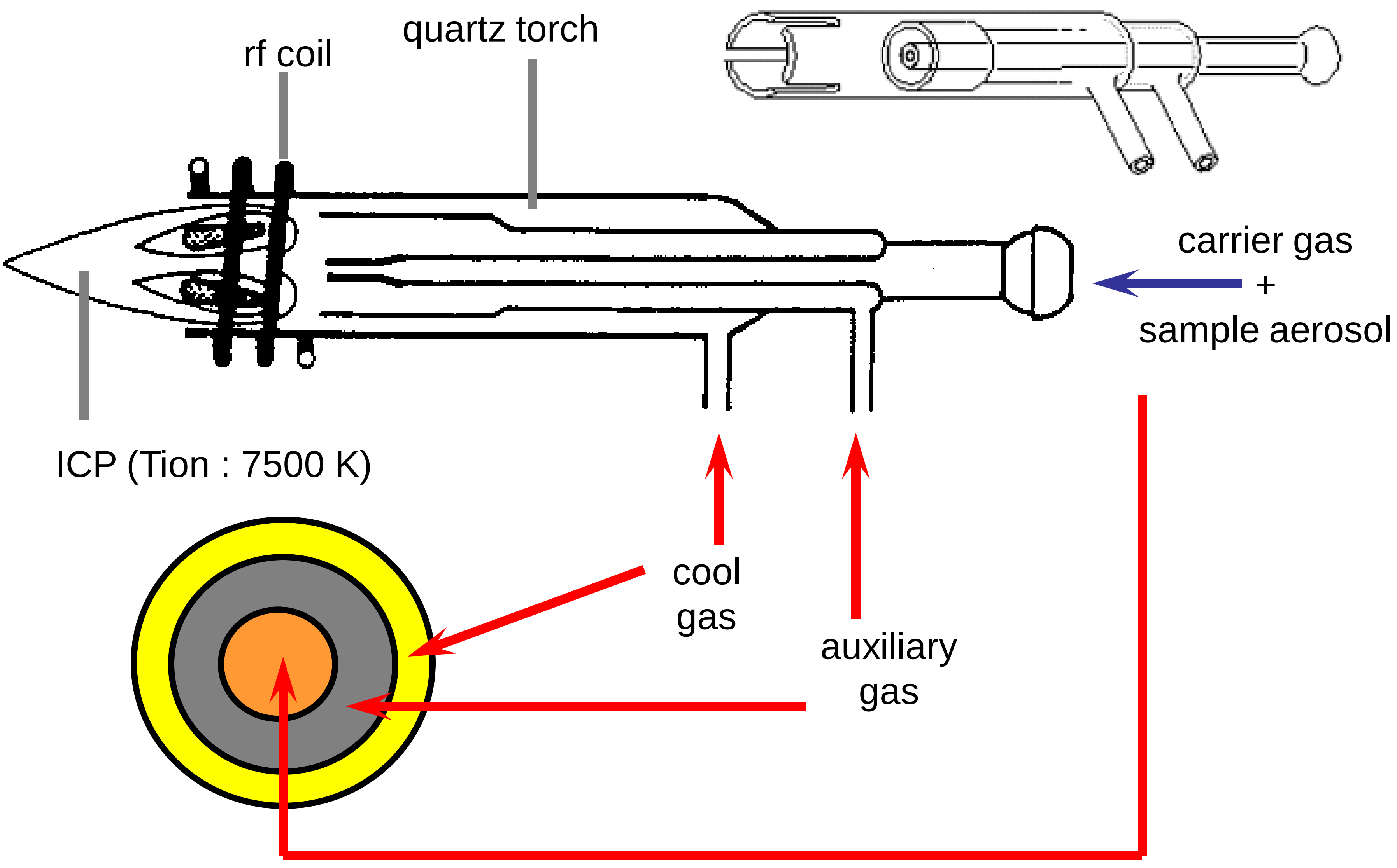
PLASMA =

GAS MIXTURE AT HIGH TEMPERATURE, CONTAINING MOLECULES, ATOMS, IONS AND ELECTRONS

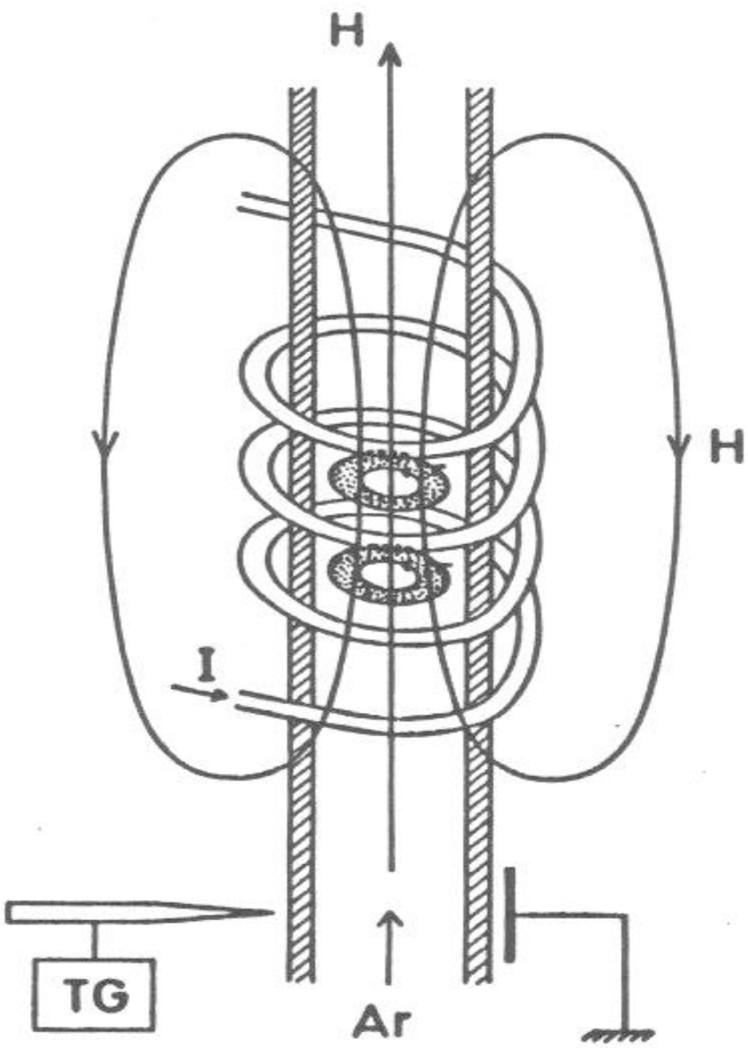
- ***Presence of charged particles***
  - ***Energy supply via induction***



PLASMA TORCH & ICP



FORMATION OF ICP & ANALYTE IONIZATION



rf current through Cu coil

time-dependent magnetic field

electrons accelerated in circular paths

collision with Ar atoms: ionization

seed electrons: spark (Tesla-generator)

analyte ionization

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

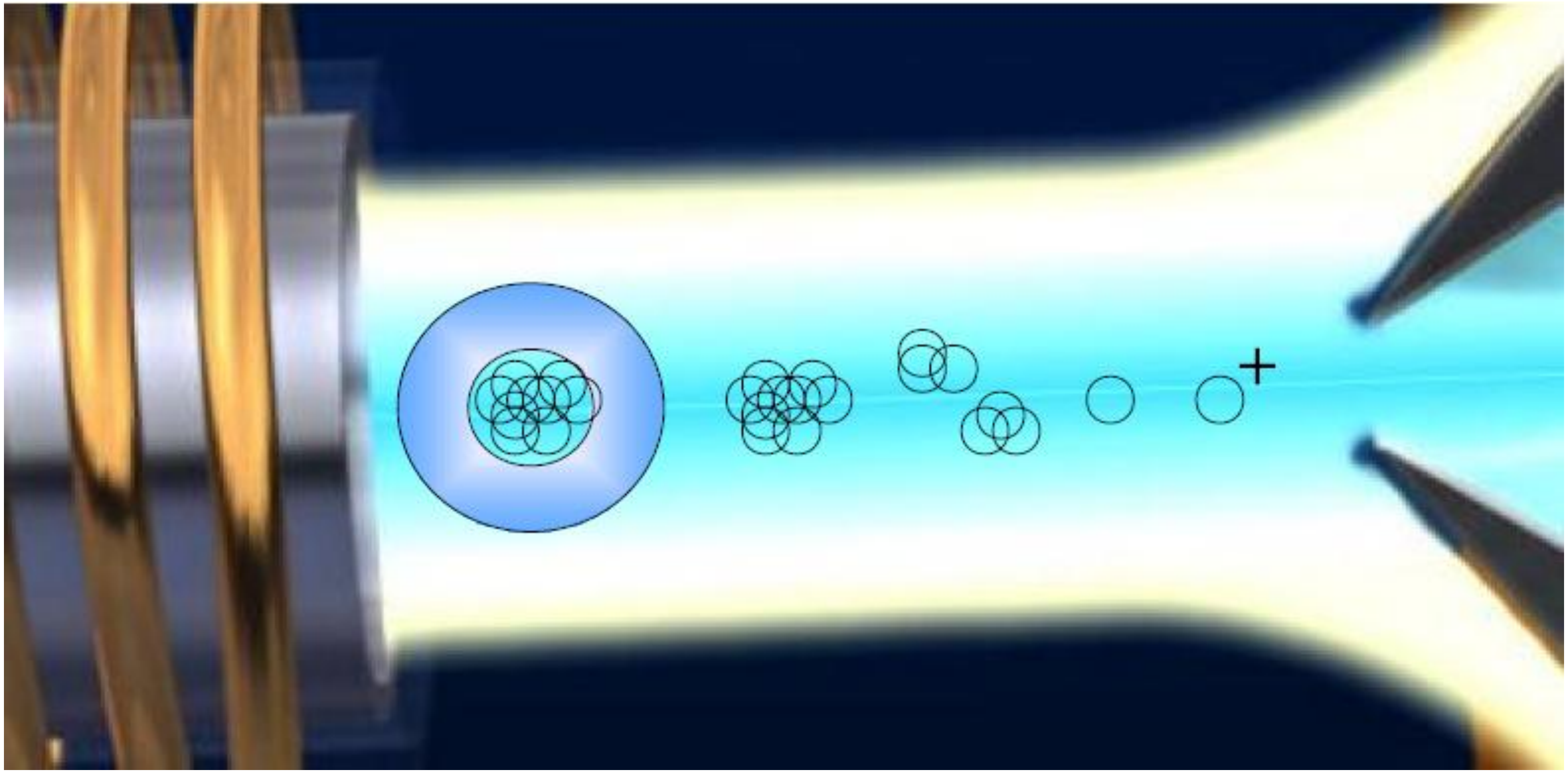
Penning ionization $Ar^* + M \rightarrow M^+ + Ar + e^-$

Rf frequency: 27.12 or 40.68 MHz

Quartz-controlled oscillator (27.12)

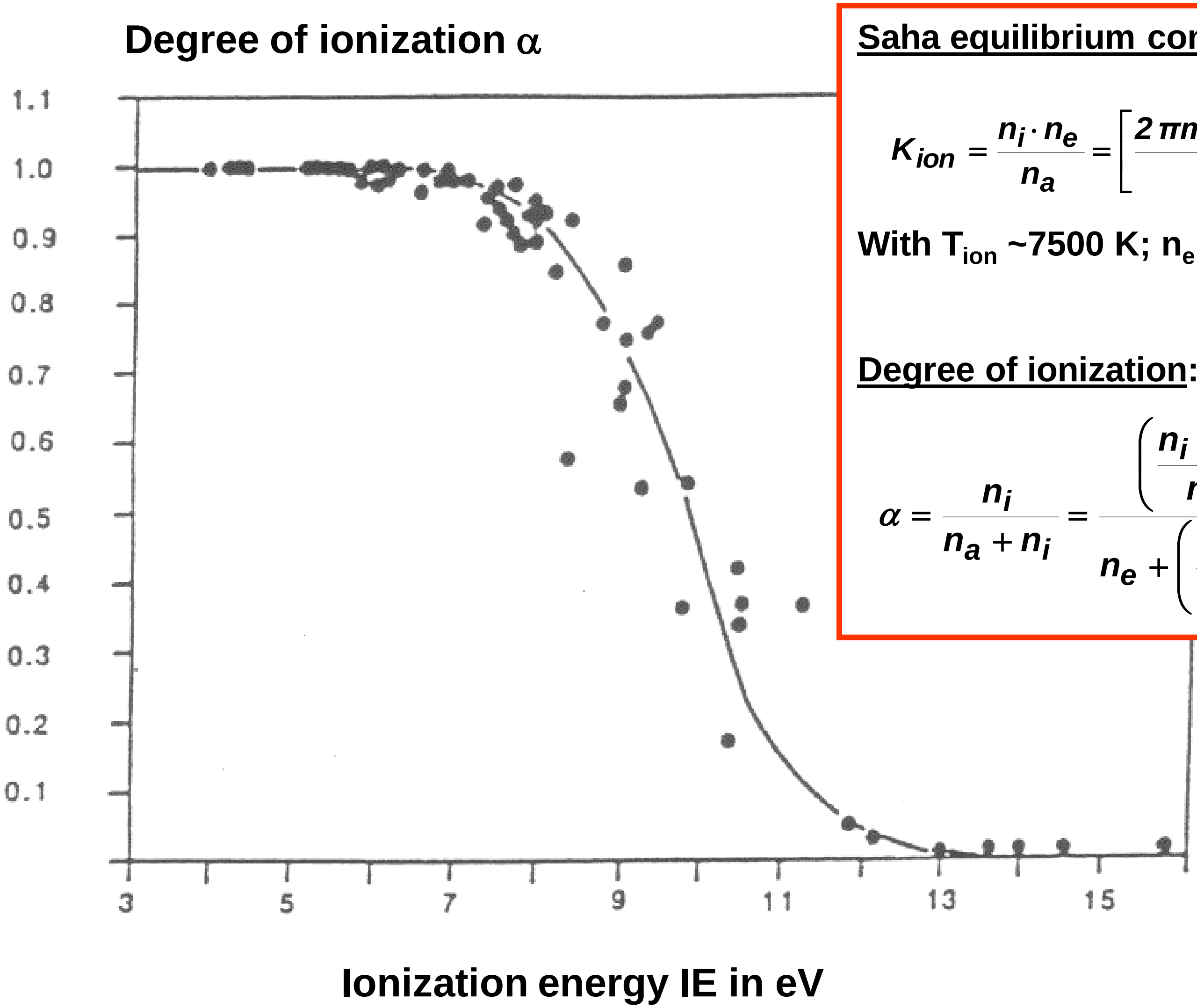
Free running generator (27.12 or 40.68)

PROCESSES IN THE ICP
SAMPLE INTRODUCTION VIA NEBULIZATION



Residence time of analyte in ICP: ~ ms

IONIZATION EFFICIENCY OF THE ICP



Saha equilibrium constant:

$$K_{ion} = \frac{n_i \cdot n_e}{n_a} = \left[\frac{2\pi m_e k T_{ion}}{h^2}\right]^{\frac{3}{2}} \cdot \frac{2Z_i}{Z_a} \cdot exp\left[-\frac{IE}{kT_{ion}}\right]$$

With T_{ion} ~7500 K; n_e ~ 10^{15} cm^{-3}

Degree of ionization:

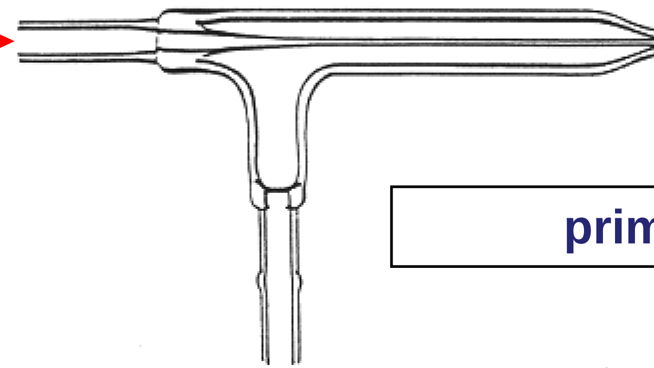
$$\alpha = \frac{n_i}{n_a + n_i} = \frac{\left(\frac{n_i \cdot n_e}{n_a}\right)}{n_e + \left(\frac{n_i \cdot n_e}{n_a}\right)} = \frac{K_{ion}}{n_e + K_{ion}}$$

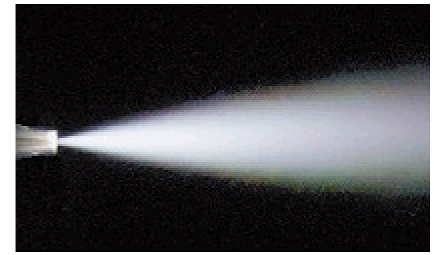
SAMPLE INTRODUCTION INTO THE ICP

- ***General***
  - ***Sample or representative part → ICP***
  - ***Convert sample into form transportable by Ar carrier gas***
- ***Standard sample introduction system***
  - ***Pneumatic nebulizer + spray chamber***
- ***Pneumatic nebulizer***
  - ***Conversion of sample solution into aerosol***
- ***Spray chamber***
  - ***Removal of larger droplets***
    - ***Avoid plasma overloading***
    - ***Warrant efficient atomization & ionization in ICP***

STANDARD SAMPLE INTRODUCTION SYSTEM
PNEUMATIC NEBULIZER & SPRAY CHAMBER

sample solution





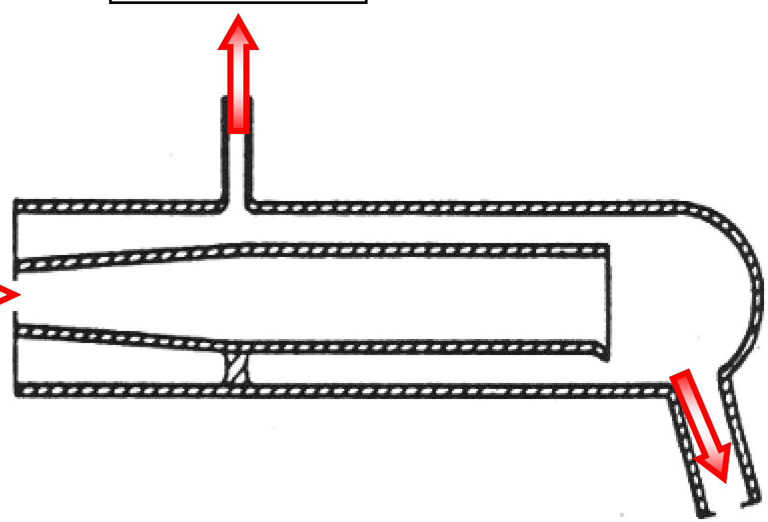
primary aerosol

1

2

to ICP

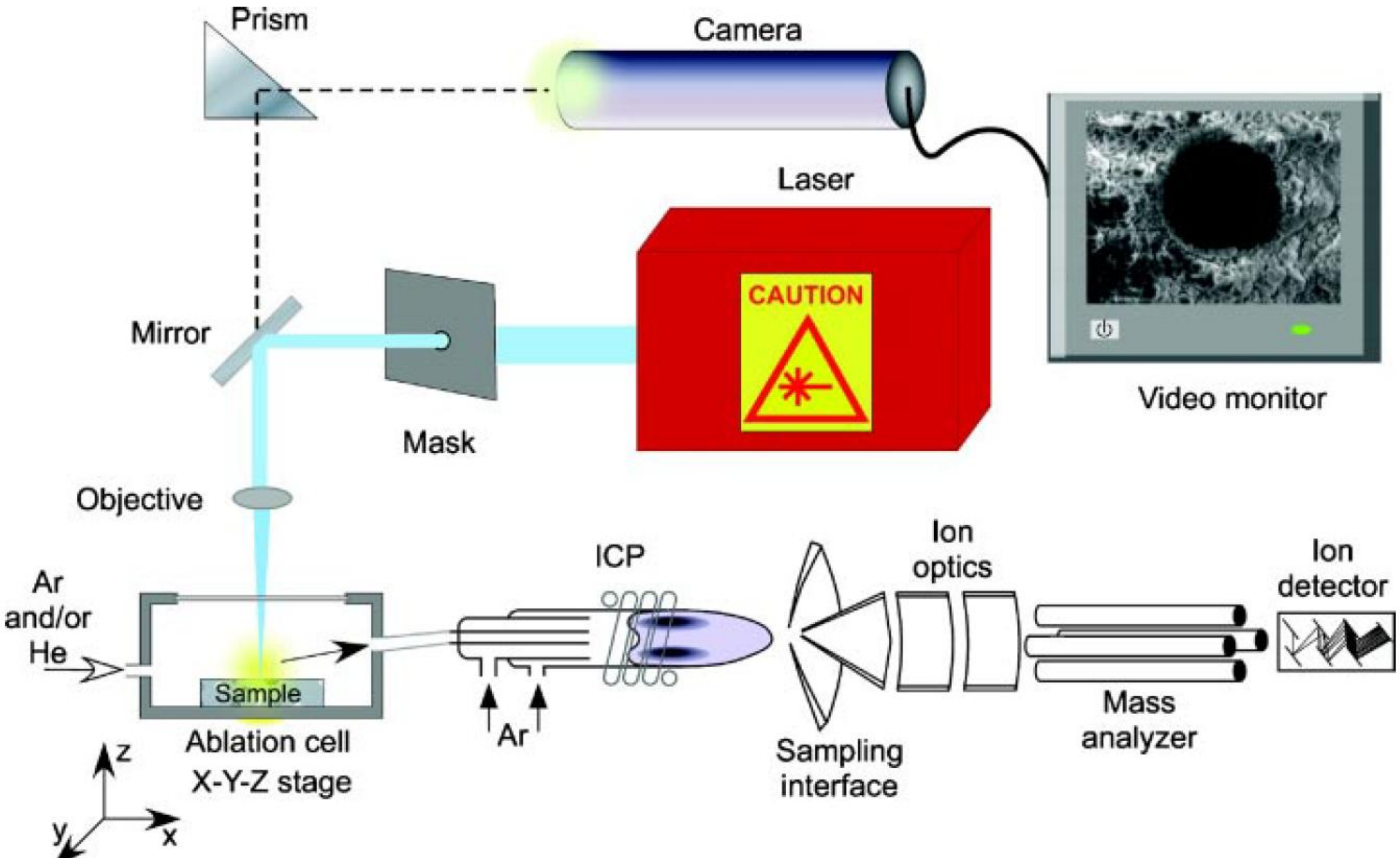
primary aerosol



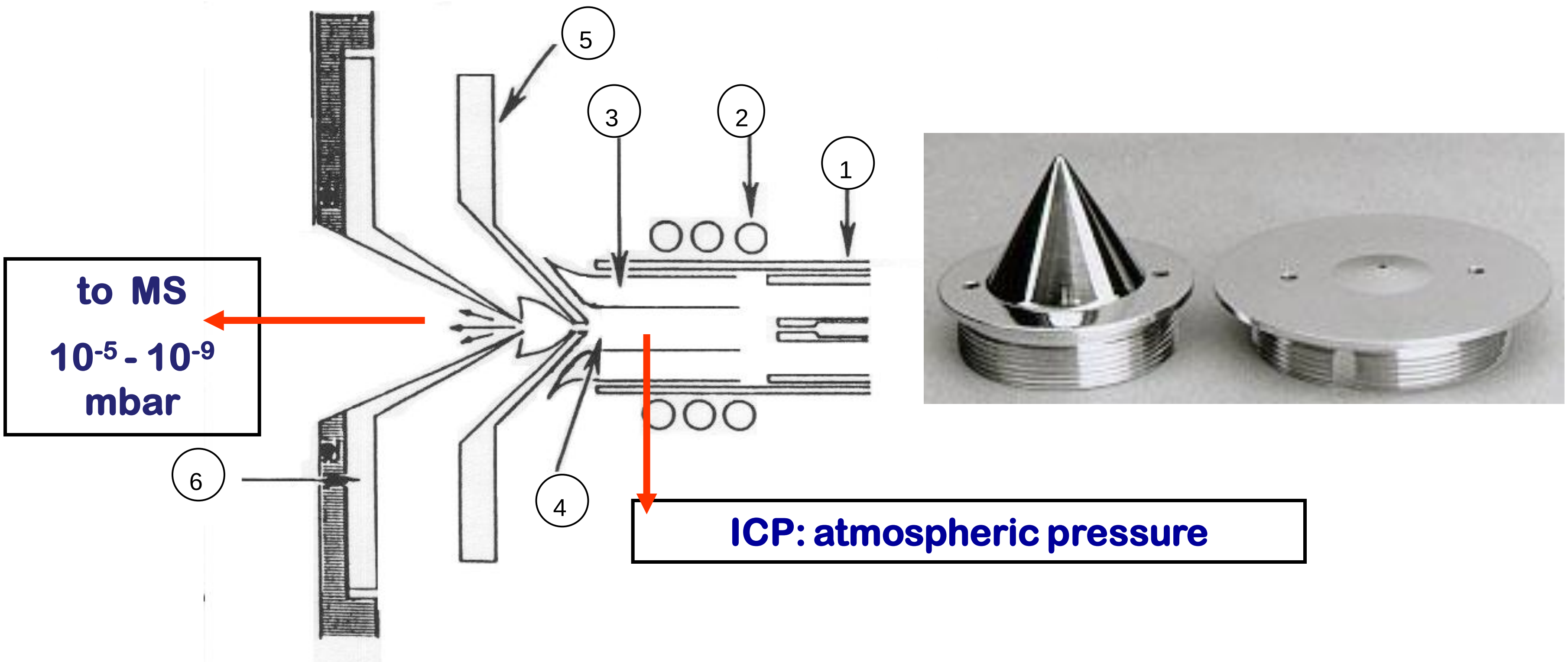
to waste

LASER ABLATION AS A MEANS OF SAMPLE INTRODUCTION

- ***Direct analysis of solid materials***
  - ***Conducting & non-conducting / Opaque & transparent***

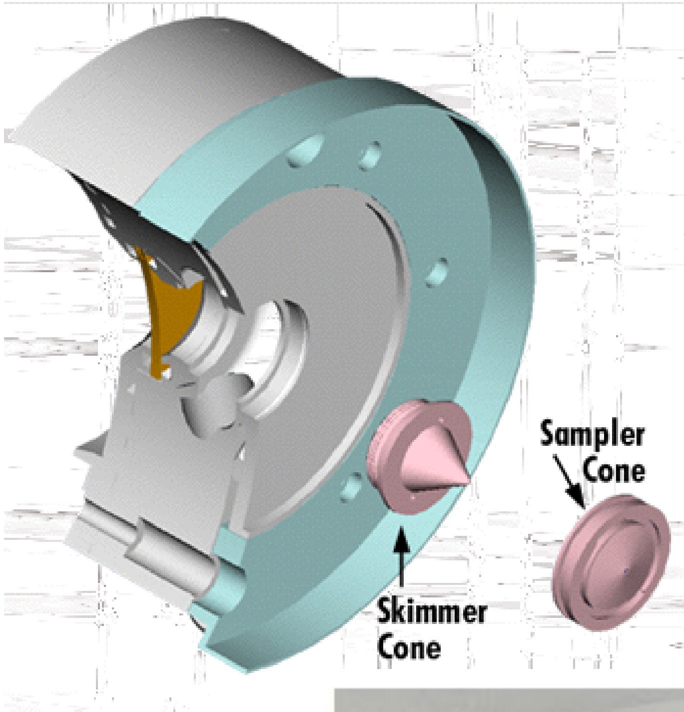


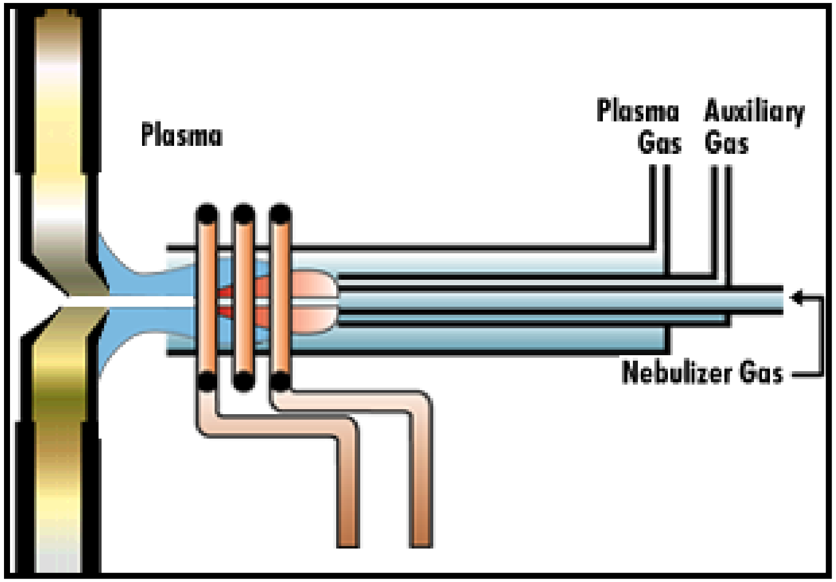
ION EXTRACTION FROM THE ICP



- *Sampling cone & skimmer, central aperture ~1 mm*
- *Expansion chamber (1 mbar) $\Rightarrow$ supersonic expansion of extracted gas*
  - *Composition of plasma gas is 'frozen'*
- *Central beam via skimmer aperture $\Rightarrow$ lens system & MS*

ION EXTRACTION FROM THE ICP





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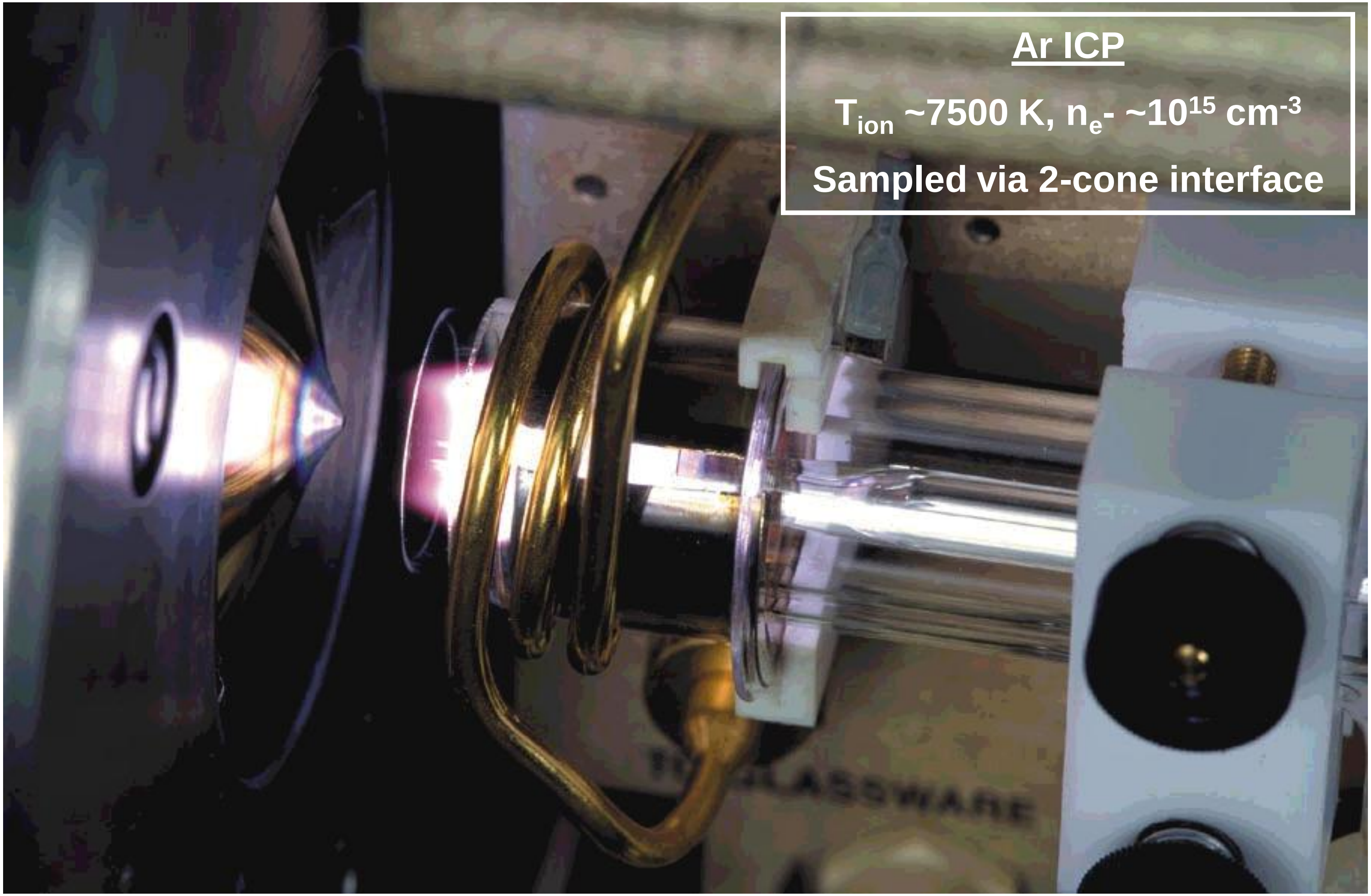
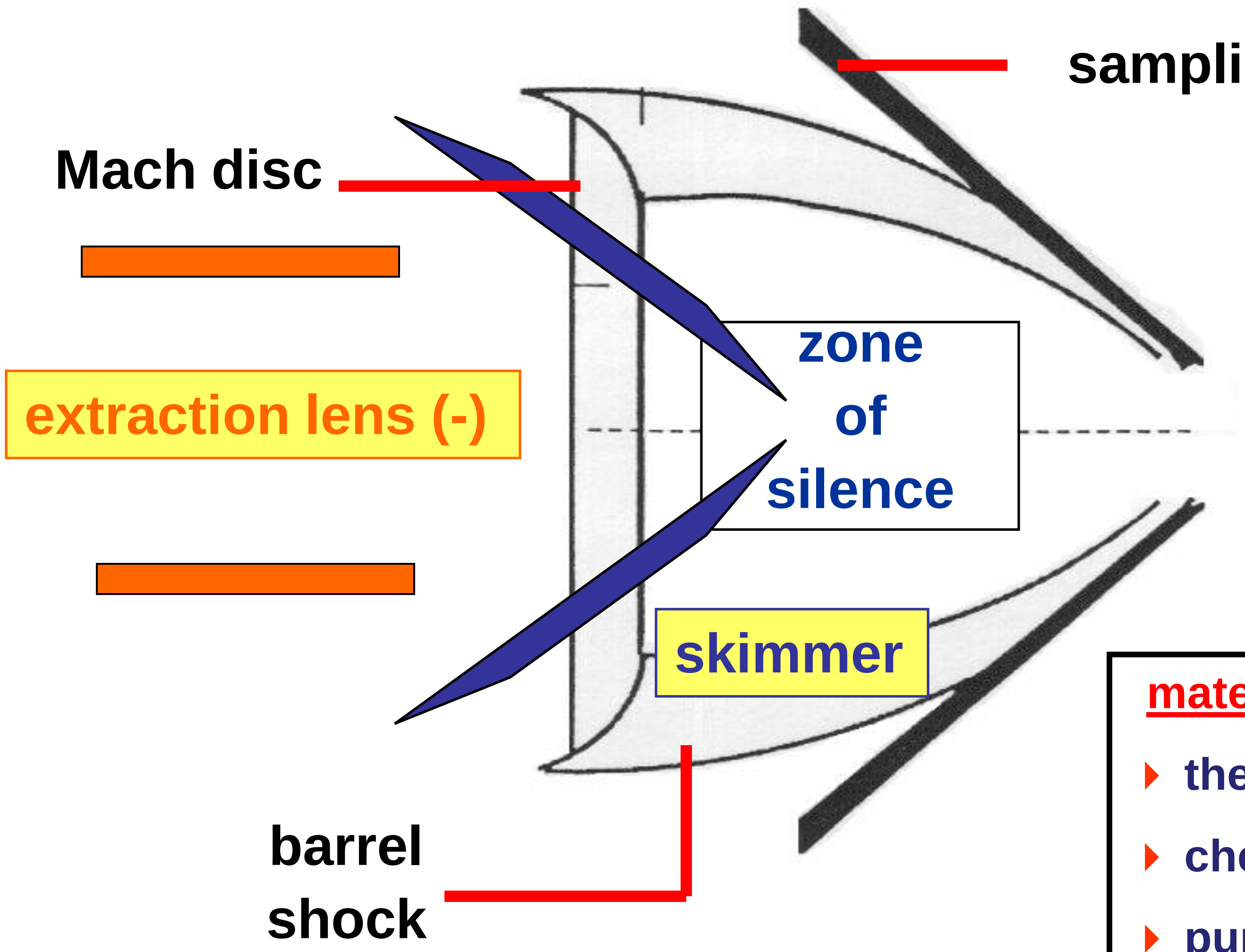
ION EXTRACTION FROM THE ICP



ION EXTRACTION FROM THE ICP



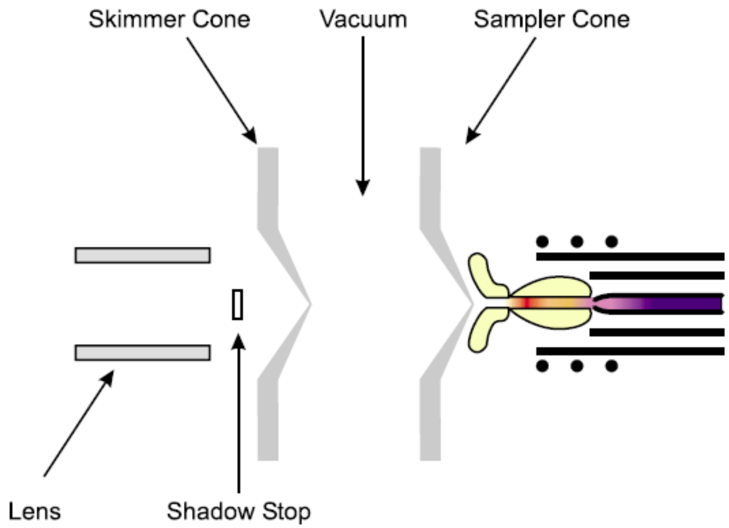
material cone & skimmer ?

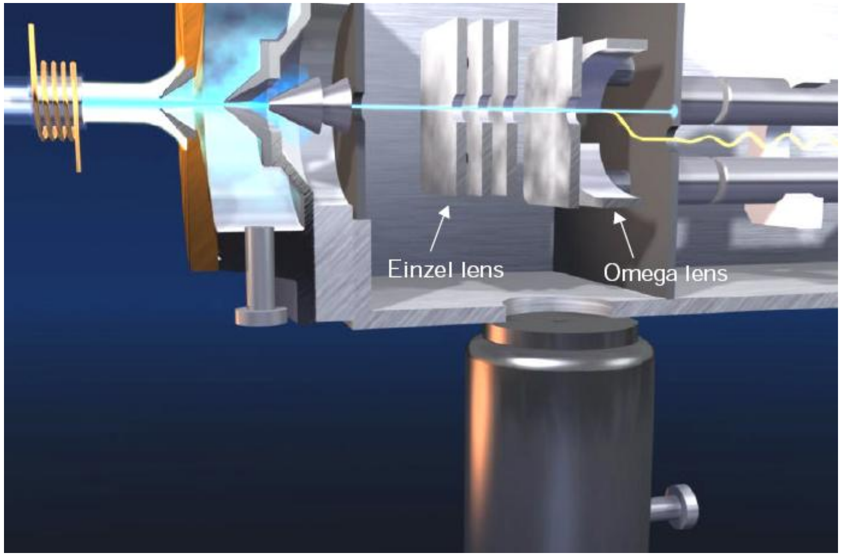
- thermal conductivity
- chemical inertness
- purchase price

Ni vs. Pt

LENS SYSTEM

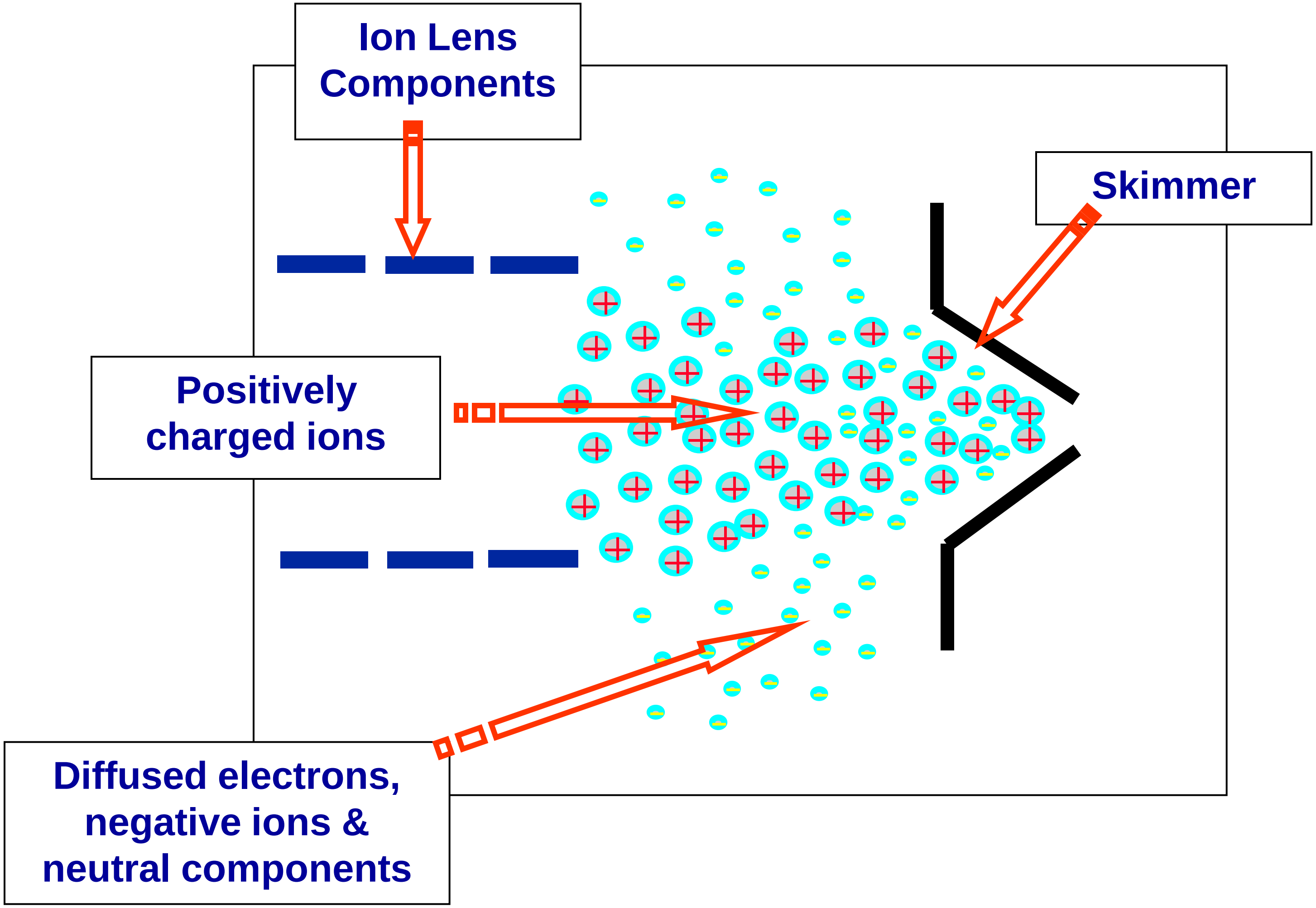
- *Set-up & complexity*
  - *from a single lens to complicated set-ups ...*





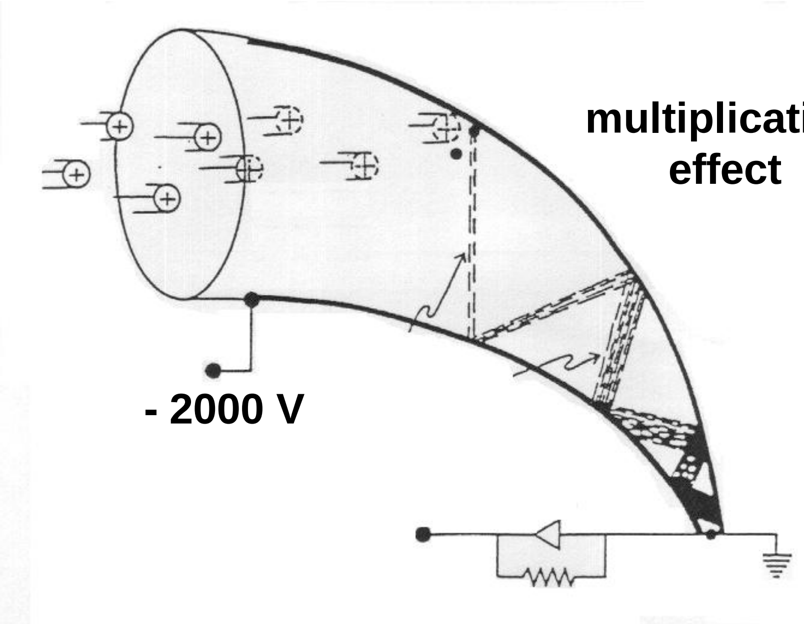
- *Goals?*
  - *Selection of positive ions*
  - *Efficient transport to & introduction into mass analyser*

SELECTION OF POSITIVE IONS IN THE LENS SYSTEM



ION DETECTION

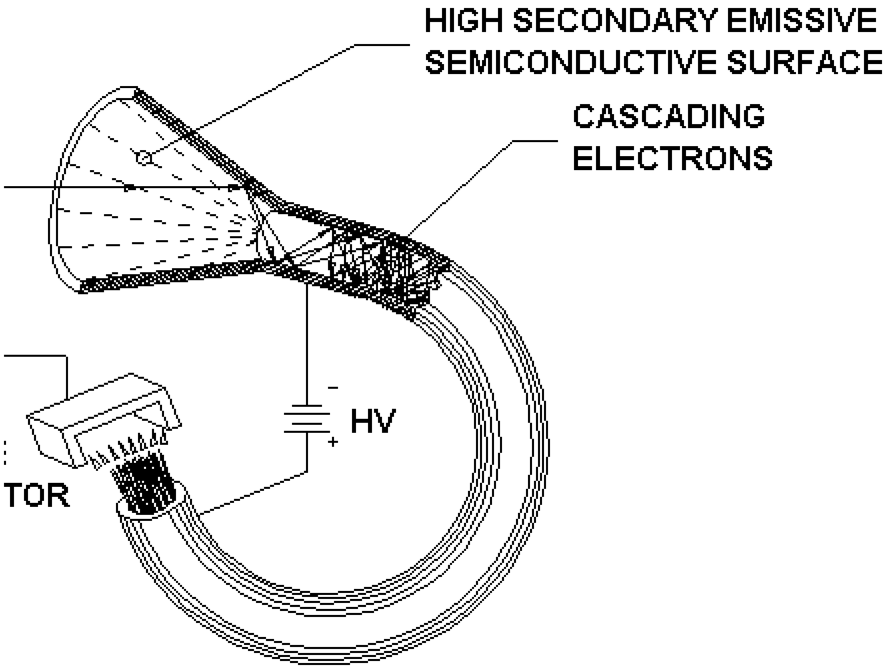
ION DETECTION
CONTINUOUS DYNODE ELECTRON MULTIPLIER



multiplication effect

- 2000 V

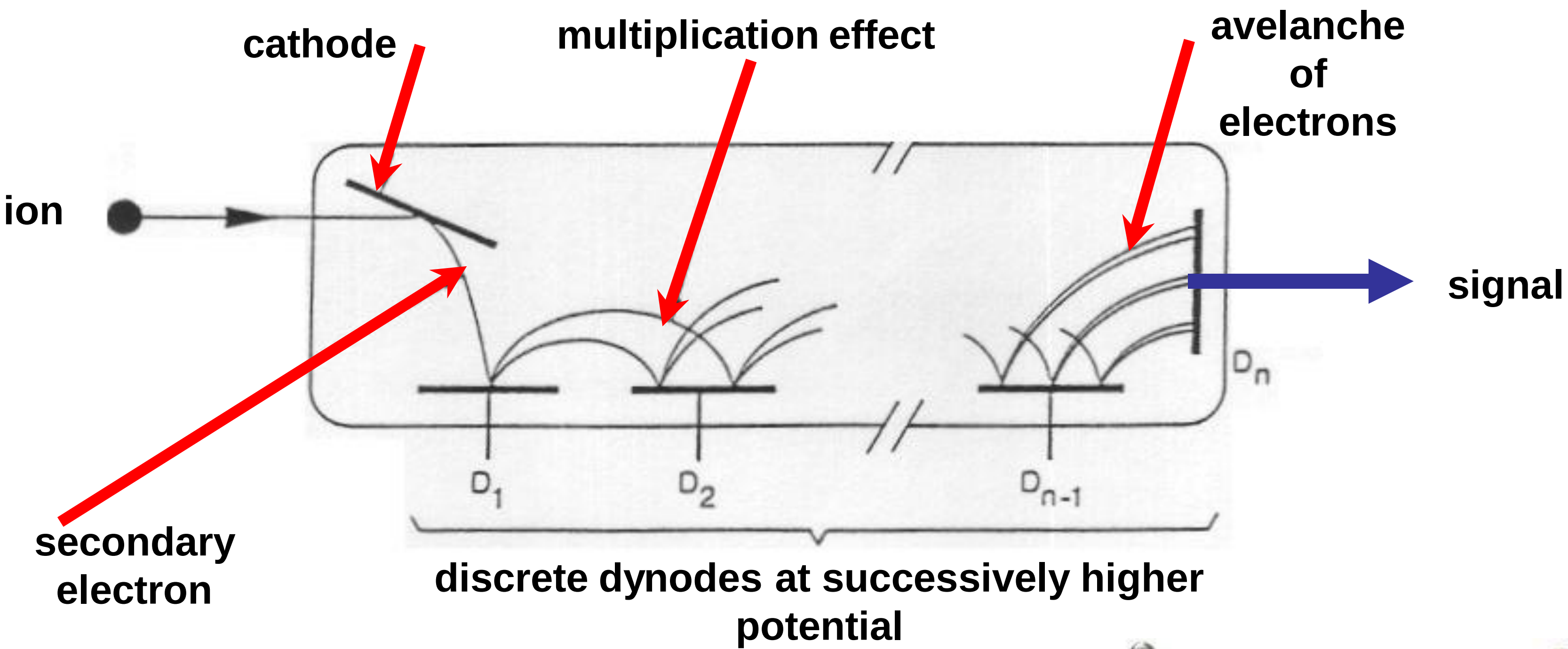
avelanche of electrons



multiplication factor: 10^7 - 10^8

pulse counting mode vs. analog mode

ION DETECTION
DISCRETE DYNODE ELECTRON MULTIPLIER



multiplication factor: 10^7 - 10^8

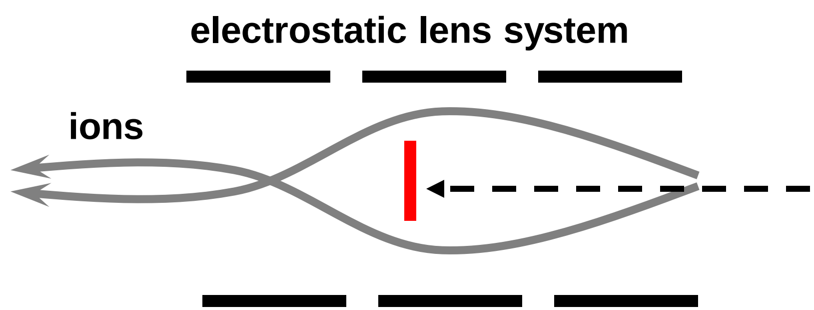
pulse counting mode vs. analog mode

ION DETECTION / ELECTRON MULTIPLIER

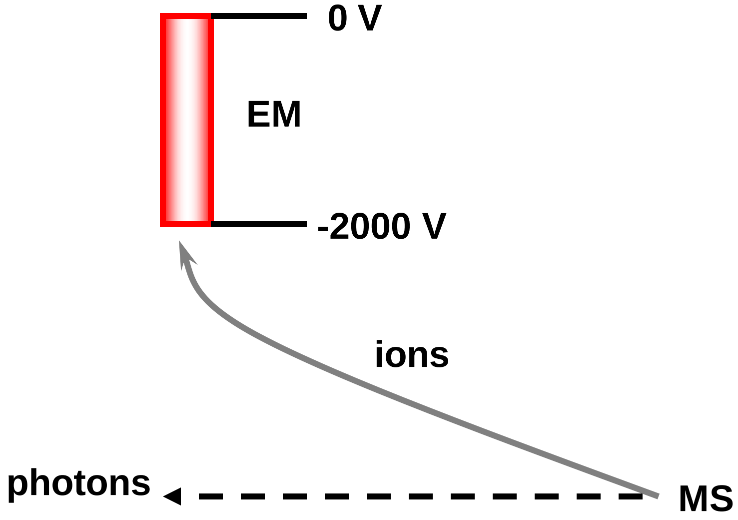
- ***Comparison of detector signal with threshold value***
  - ***Background < 0.1 count / s***
- ***Avoid photons reaching detector***
  - ***Photon stop in ion beam***
  - ***Detector mounted off-axis***
  - ***Ion lens system, quadrupole filter & detector off axis***
    - ***Omega-lens (Agilent)***
- ***Limited life-time (= consumable)***
  - ***1 - 2 years***
- ***Detector dead time***
  - ***Handling of one ion, no possibility to detect another one***
  - ***More pronounced effects at higher count rates***
  - ***Accurate isotope ratio determination requires correction***

PREVENTING PHOTONS FROM REACHING THE DETECTOR

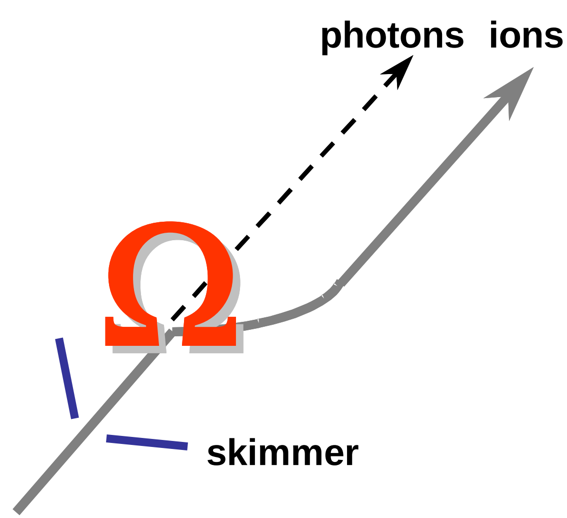
Various systems based on influence of electrostatic field on ion trajectory



Photon stop

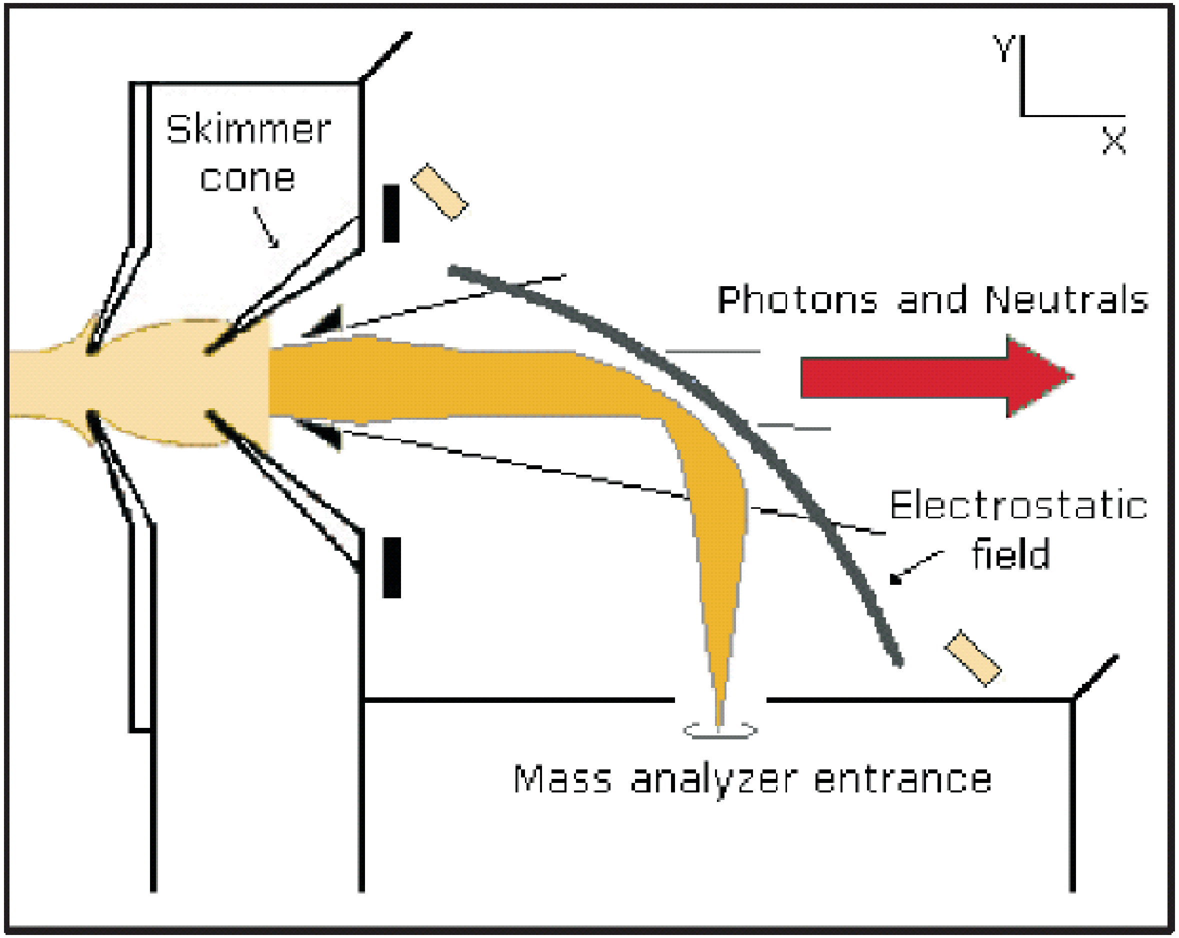


Off-axis detector



Omega lens

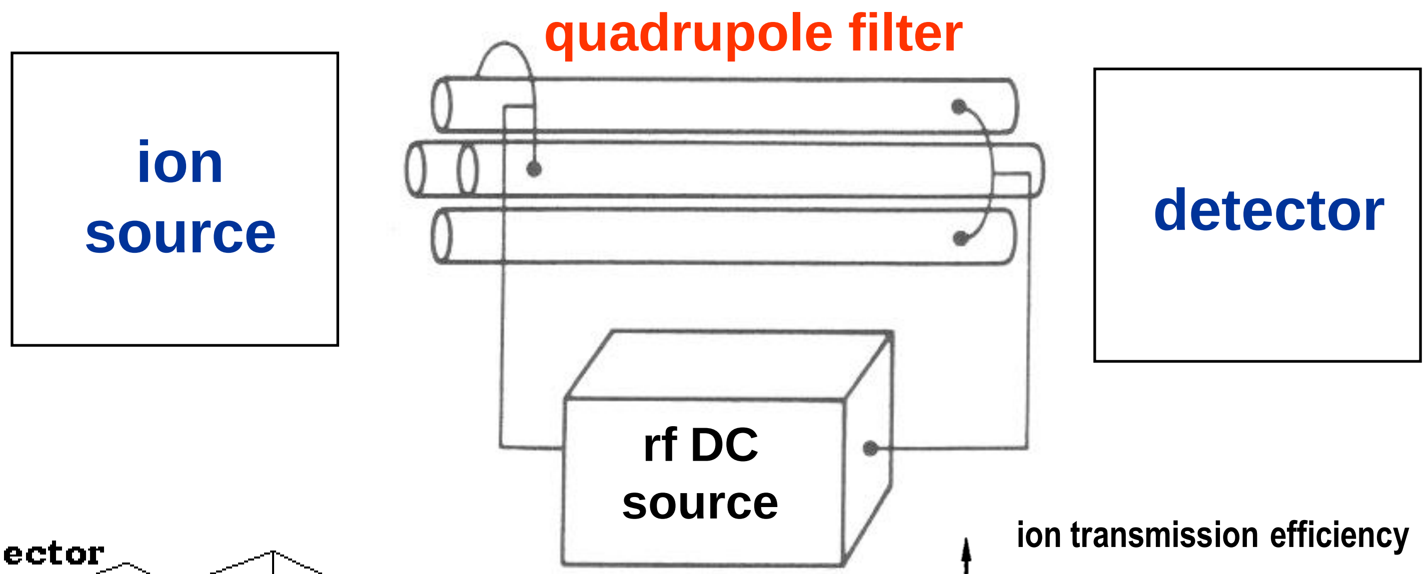
PREVENTING PHOTONS FROM REACHING THE DETECTOR

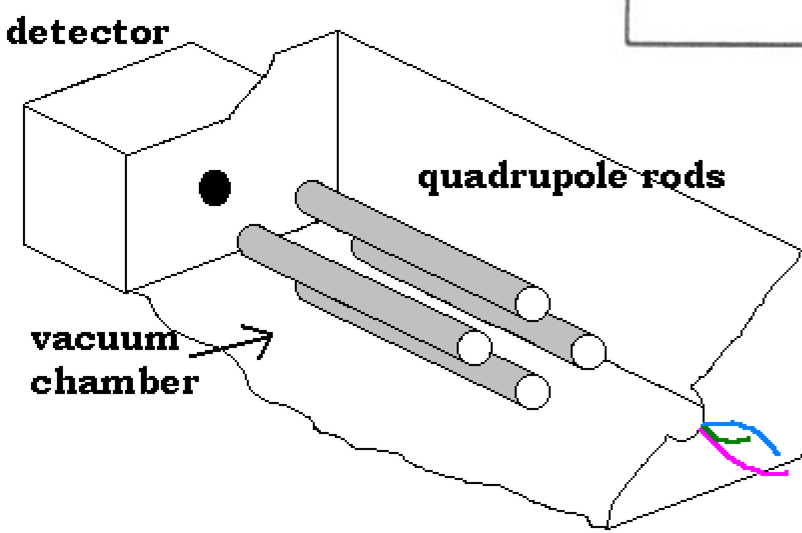


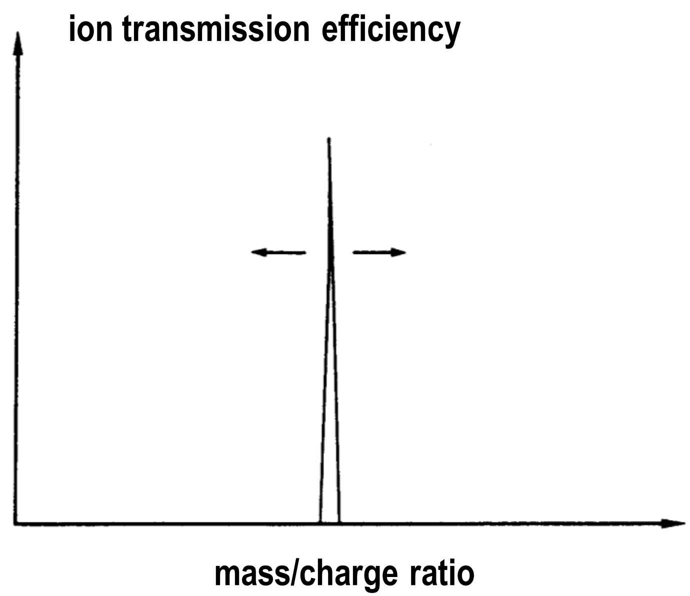
Ion mirror

THE MASS SPECTROMETER

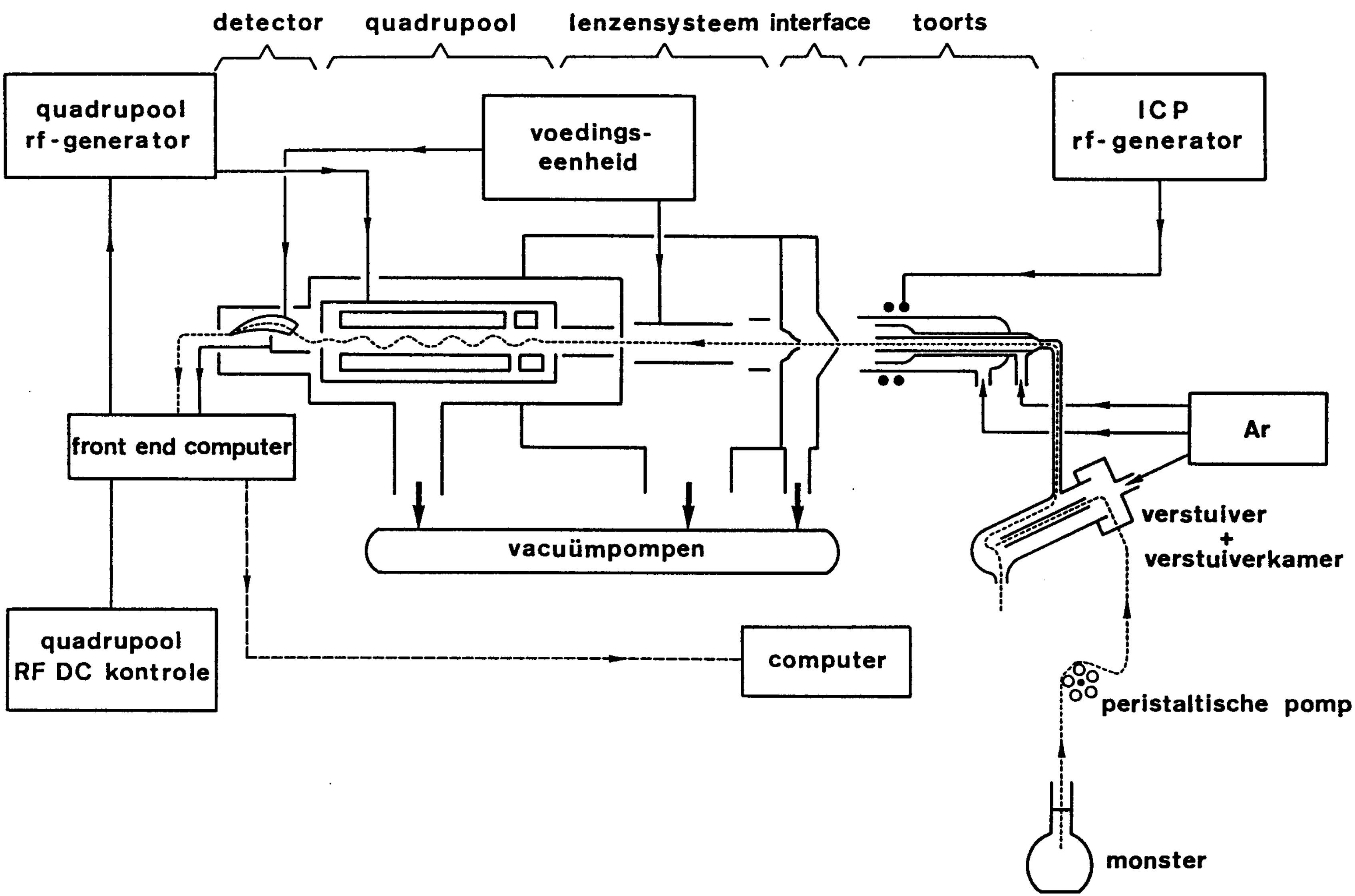
MASS ANALYSIS – THE QUADRUPOLE FILTER







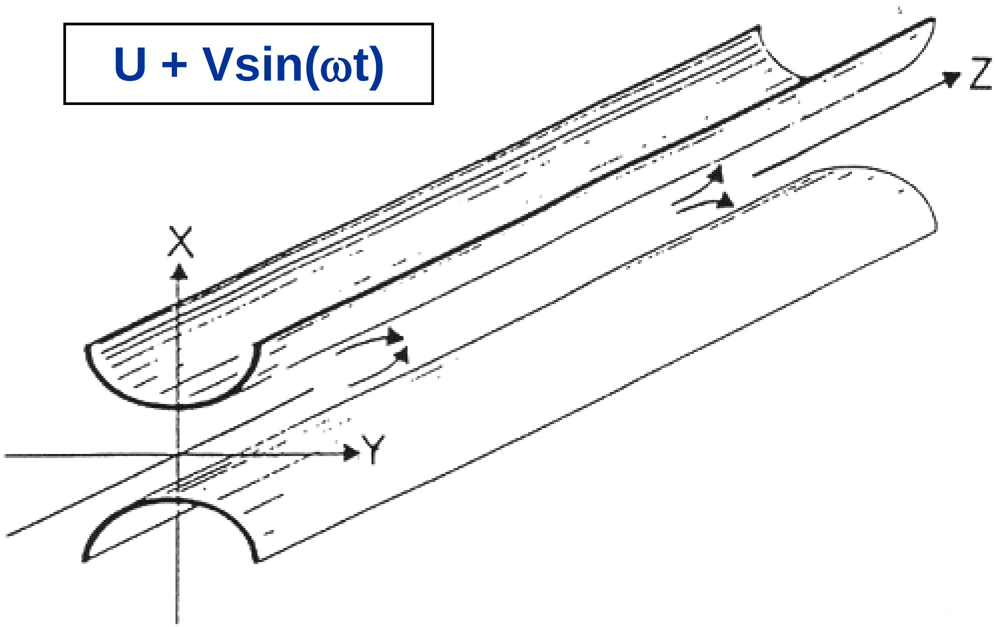
QUADRUPOLE-BASED ICP – MASS SPECTROMETRY



BASIC OPERATION PRINCIPLE OF QUADRUPOLE FILTER

separate evaluation of effect of
each pair of quadrupole rods on ion paths

U + Vsin(ωt)

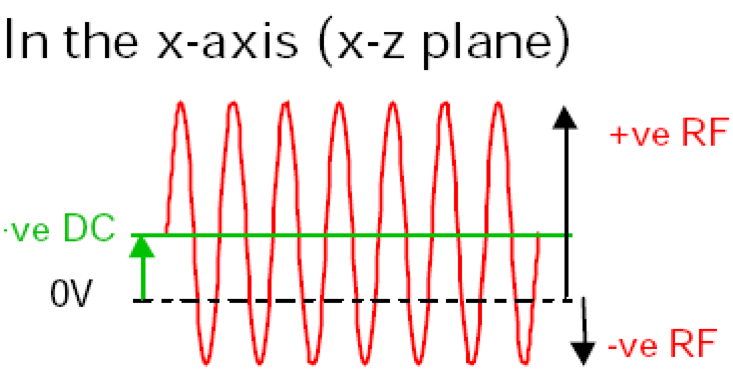


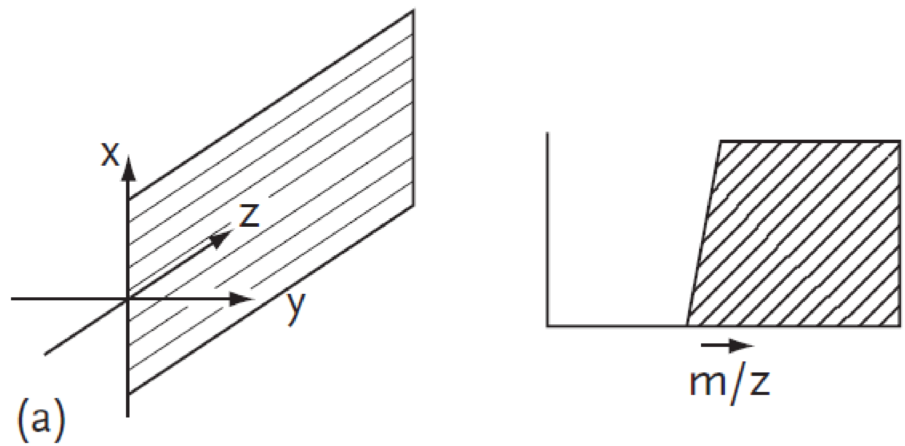
Electrode potential XZ vs. YZ
equal magnitude, different polarity

- ***Quadrupole rods***
  - ***DC component***
  - ***AC (rf) component***
- ***Instable path ?***
  - ***Magnitude actual negative potential***
  - ***frequency of AC component***
  - ***Position of ion***
  - ***Velocity of ion***
  - ***Mass-to-charge ratio of ion***
- ***Heavy ions***
  - ***Average (DC) potential***
- ***Lighter ions***
  - ***Motion corrected by AC field***

BASIC OPERATION PRINCIPLE OF QUADRUPOLE FILTER

- ***XZ-plane***
  - ***DC component : +***
    - ***Sufficiently heavy ions only undergo focusing effect (DC)***
    - ***Path of lighter ions affected by AC-field***



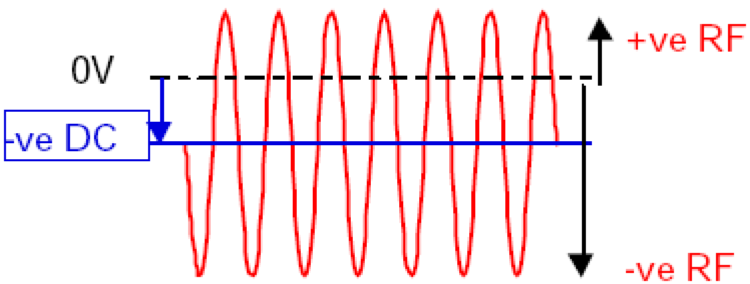


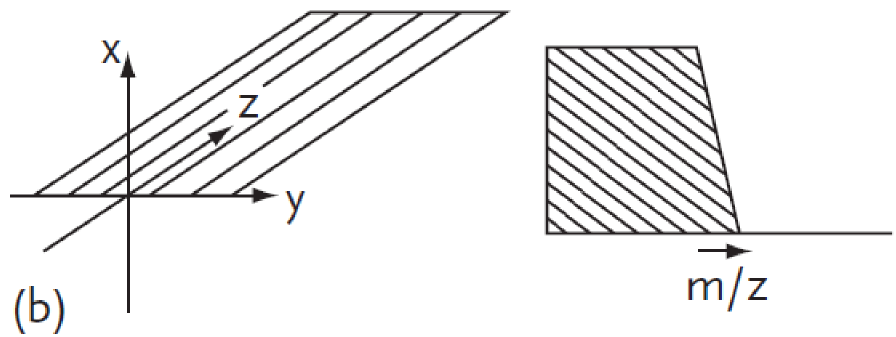
High mass filter

BASIC OPERATION PRINCIPLE OF QUADRUPOLE FILTER

- ***YZ-plane***
  - ***DC component : -***
    - ***Sufficiently heavy ions only undergo defocusing effect (DC)***
  - ***Path of lighter ions affected by AC-field***

In the y-axis (y-z plane)

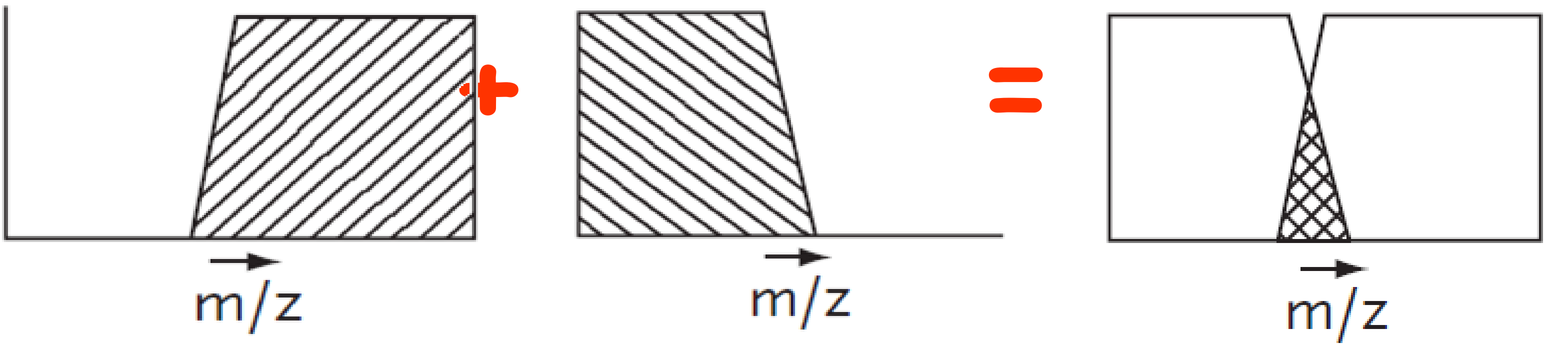




Low mass filter

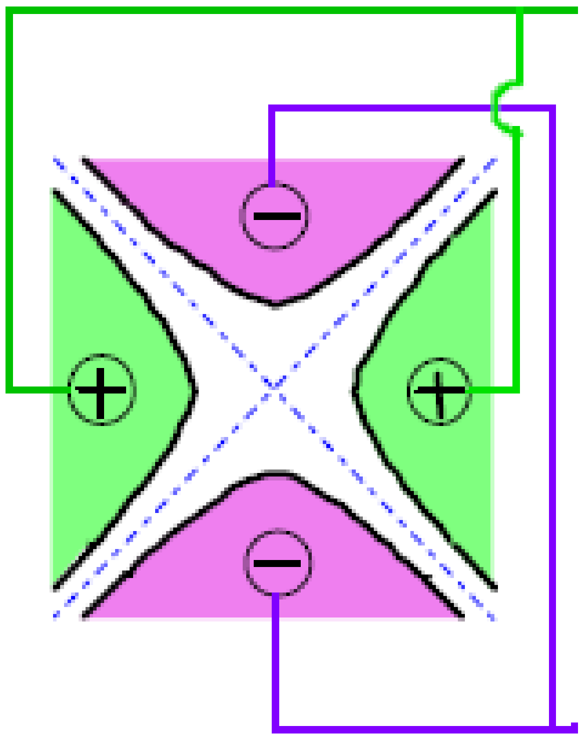
Basic operation principle of quadrupole filter

high mass filter + low mass filter = bandpass mass filter



- ***Advantages***
  - ***High scanning speed***
  - ***Can be used at relatively high pressures***
  - ***Instrumental simplicity & low purchase price***
- ***Disadvantages***
  - ***Low mass resolution (R)***
    - ***Ions only separated if $\Delta m \geq 1/2$ u***
- ***Data acquisition modes***
  - ***Spectral scanning vs. peak hopping / peak jumping***

BASIC OPERATION PRINCIPLE OF QUADRUPOLE FILTER



SPECTRAL INTERFERENCES IN QUADRUPOLE-BASED ICP-MS

- ***Disadvantage of quadrupole filter***
  - ***Low mass resolution (R)***
    - ***Ions separated if $\Delta m \geq 1/2$ u***
    - ***Otherwise: overlap of ion signals (spectral interferences)***

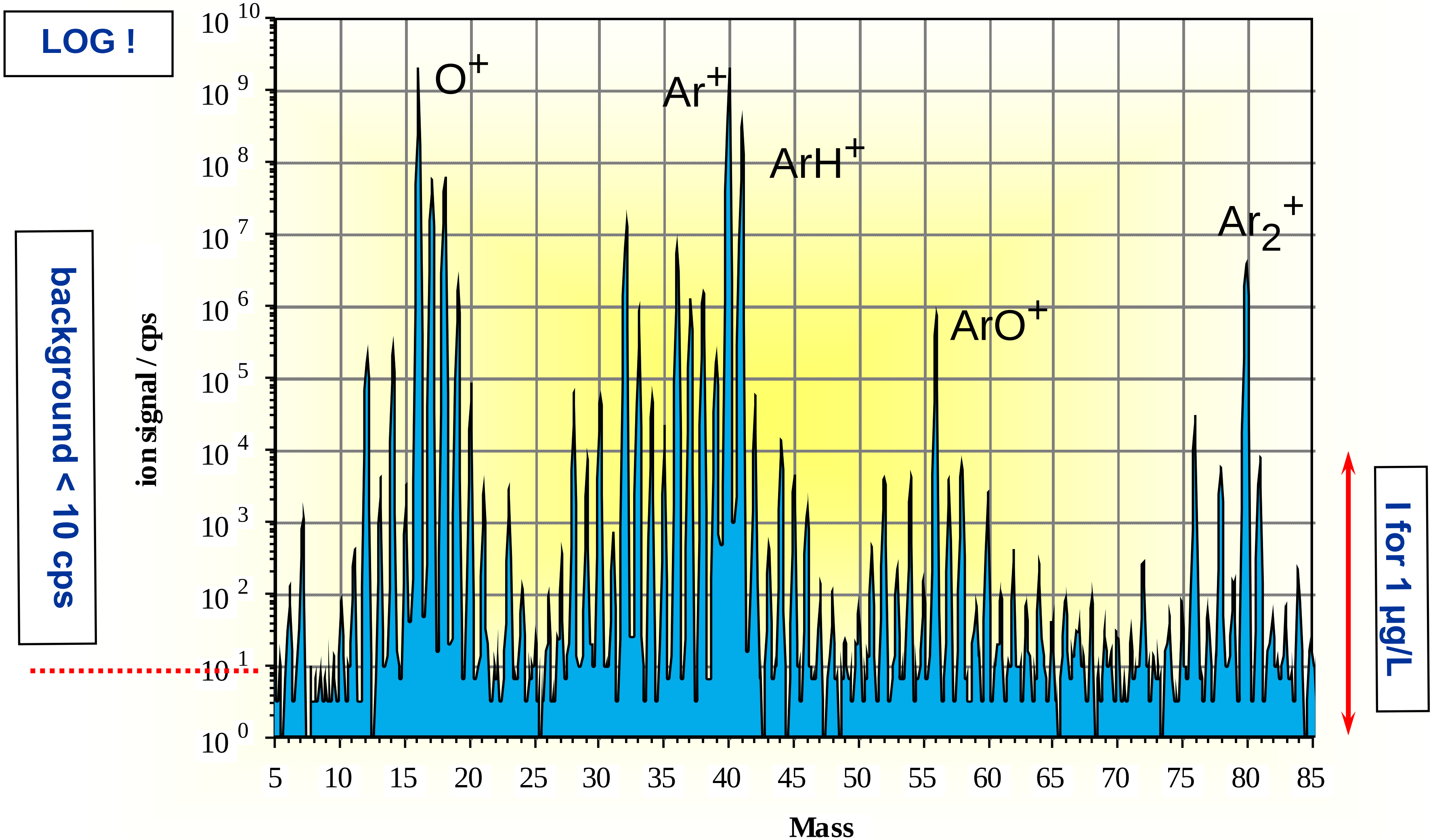
- ***Overlap of signals of isobaric nuclides***
  - ***Not problematic***
    - ***For every element (except In): one isotope interference-free***

- ***Polyatomic ions & doubly charged ions***
  - ***Spectral overlap of ions showing the same <u>nominal</u> m/z ratio***

TYPES OF POLYATOMIC IONS IN ICP-MS

- ***Ar-containing ions***
  - ***Ar introduced in ICP at ~ 20 L/min***
  - ***Ar^+ and Ar_2^+***
  - ***Ar + elements from solvent, surrounding air and/or matrix***
    - ***ArO^+, $ArOH^+$, ArN^+, ArC^+, $ArCl^+$, $ArNa^+$, …***

ICP-MS BACKGROUND SPECTRUM
FOR HIGH-PURITY WATER



ICP-MS BACKGROUND SPECTRUM FOR HIGH-PURITY WATER

Mass	Molecular ion	Interferes with
28	N_2^+	Si
29	N_2H^+	Si
30	NO^+	Si
31	NOH^+	P
32	O_2^+	S
33	O_2H^+	S
39	$^{38}ArH^+$	K
40	$^{40}Ar^+$	Ca
41	$^{40}ArH^+$	Ca
44	CO_2^+	Ca
54	$^{40}ArN^+$	Fe, Cr
55	$^{40}ArNH^+$	Mn
56	$^{40}ArO^+$	Fe
57	$^{40}ArOH^+$	Fe
76	$^{40}Ar^{36}Ar^+$	Se
78	$^{40}Ar^{38}Ar^+$	Se
80	$^{40}Ar_2^+$	Se

TYPES OF POLYATOMIC IONS IN ICP-MS

- ***Ar-containing ions***
  - ***Ar introduced in ICP at ~ 20 L/min***
  - ***Ar^+ and Ar_2^+***
  - ***Ar + elements from solvent, surrounding air and/or matrix***
    - ***ArO^+, $ArOH^+$, ArN^+, ArC^+, $ArCl^+$, $ArNa^+$, …***
- ***Oxide & hydroxide ions***
  - ***MO^+ (m/z + 16) and MOH^+ (m/z + 17)***
  - ***MO^+/M^+ determined by M-O bond strength***
  - ***Usually $MO^+/M^+ > MOH^+/M^+$***
  - ***Optimization of instrument settings $MO^+/M^+ \leq 0.05$ (5%)***
  - ***Still problematic if $m/z(M_1O^+) = m/z(M_2^+)$ and $c(M_1) >> c(M_2)$***
  - ***Formed in ICP : low t° in neighbourhood of vaporizing droplets***
- ***Other molecular ions***
  - ***SO_2^+, SO_2H^+, $SiCl^+$, ...***

DOUBLY-CHARGED IONS IN ICP-MS

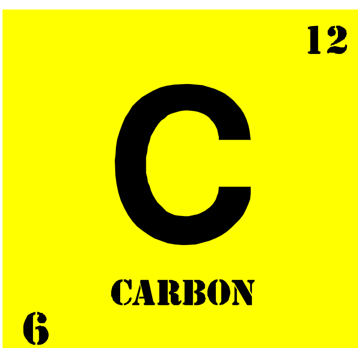
- ***Doubly charged ions***
  - ***M^{2+} (m/z ÷ 2)***
  - ***M^{2+}/M^{+} determined by ($IP_2 - IP_1$)***
  - ***Optimization of instrument settings $M^{2+}/M^{+} \leq 0.05$ (5%)***
  - ***Still problematic if $m/z(M_1^{2+}) = m/z(M_2^{+})$ and $c(M_1) >> c(M_2)$***
  - ***if m/z of M_1 = uneven $\Rightarrow M_1^{2+}$ is no problem***
    - ***M_1^{2+} signal at non-integral m/z***
    - ***Quadrupole filter shows sufficient resolution***
  - ***Formed in ICP***

SOME IMPORTANT SPECTRAL INTERFERENCES DUE TO THE PRESENCE OF CHLORINE

Matrix Element	Mass	Molecular ion	Interferes with
Chlorine (Cl)	51	$^{35}ClO^+$	V
e.g. HCl, $HClO_4$	52	$^{35}ClOH^+$	Cr
Cl^-, ClO_4^-	53	$^{37}ClO^+$	Cr
	54	$^{37}ClOH^+$	Cr, Fe
	75	$^{40}Ar^{35}Cl^+$	As

SOME IMPORTANT SPECTRAL INTERFERENCES DUE TO THE PRESENCE OF CARBON

Matrix Element	Mass	Molecular ion	Interferes with
Carbon (C)	24	C_2^+	Mg
e.g. organics, CO_2,	25	C_2H^+, $^{12}C\,^{13}C^+$	Mg
$CO_3^=$	26	CN^+	Mg
	28	CO^+	Si
	44	CO_2^+	Ca
	45	CO_2H^+, $^{13}CO_2^+$	Sc
	52	ArC^+	Cr
	...		



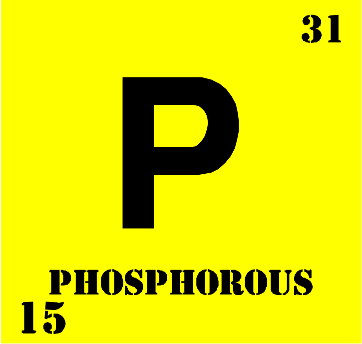
SOME IMPORTANT SPECTRAL INTERFERENCES DUE TO THE PRESENCE OF SULPHUR

Matrix Element	Mass	Molecular ion	Interferes with
Sulfur (S)	48	$^{32}SO^+$	Ti
e.g. H_2SO_4, $SO_4^=$	49	$^{32}SOH^+$	Ti
	50	$^{34}SO^+$	Ti, V
	51	$^{34}SOH^+$	V
	64	$^{32}S_2^+$, $^{32}SO_2^+$	Zn
	70	$^{38}Ar^{32}S^+$	Ge
	72	$^{40}Ar^{32}S^+$, $^{38}Ar^{34}S^+$	Ge
	74	$^{40}Ar^{34}S^+$	Ge
	...		

32
S
SULPHUR
16

SOME IMPORTANT SPECTRAL INTERFERENCES DUE TO THE PRESENCE OF PHOSPHORUS

Matrix Element	Mass	Molecular ion	Interferes with
Phosphorus (P)	47	PO^+	Ti
e.g. H_3PO_4, PO_4^{3-}	48	POH^+	Ti
	63	PO_2^+	Cu
	71	ArP^+	Ge
	...		

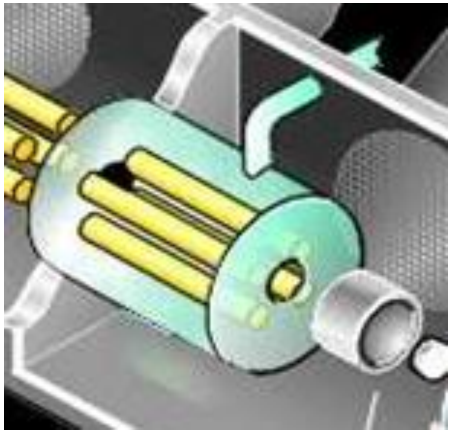


SPECTRAL INTERFERENCES IN ICP-MS

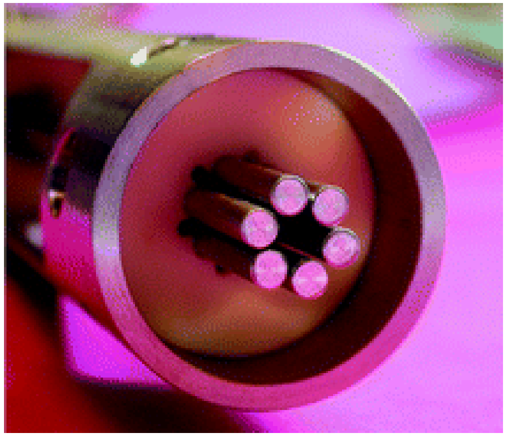
COLLISION/REACTION CELLS

- ***Multipole assembly with (2n + 2) rods:***
  - ***Quadrupole***
  - ***Hexapole***
  - ***Octopole***

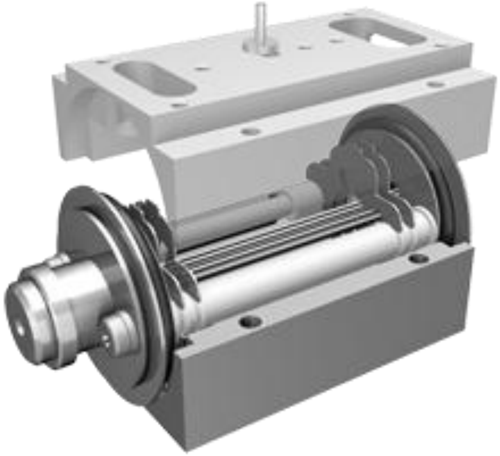
Quadrupole cell
Perkin Elmer



Hexapole cell
Thermo Scientific
Xseries II

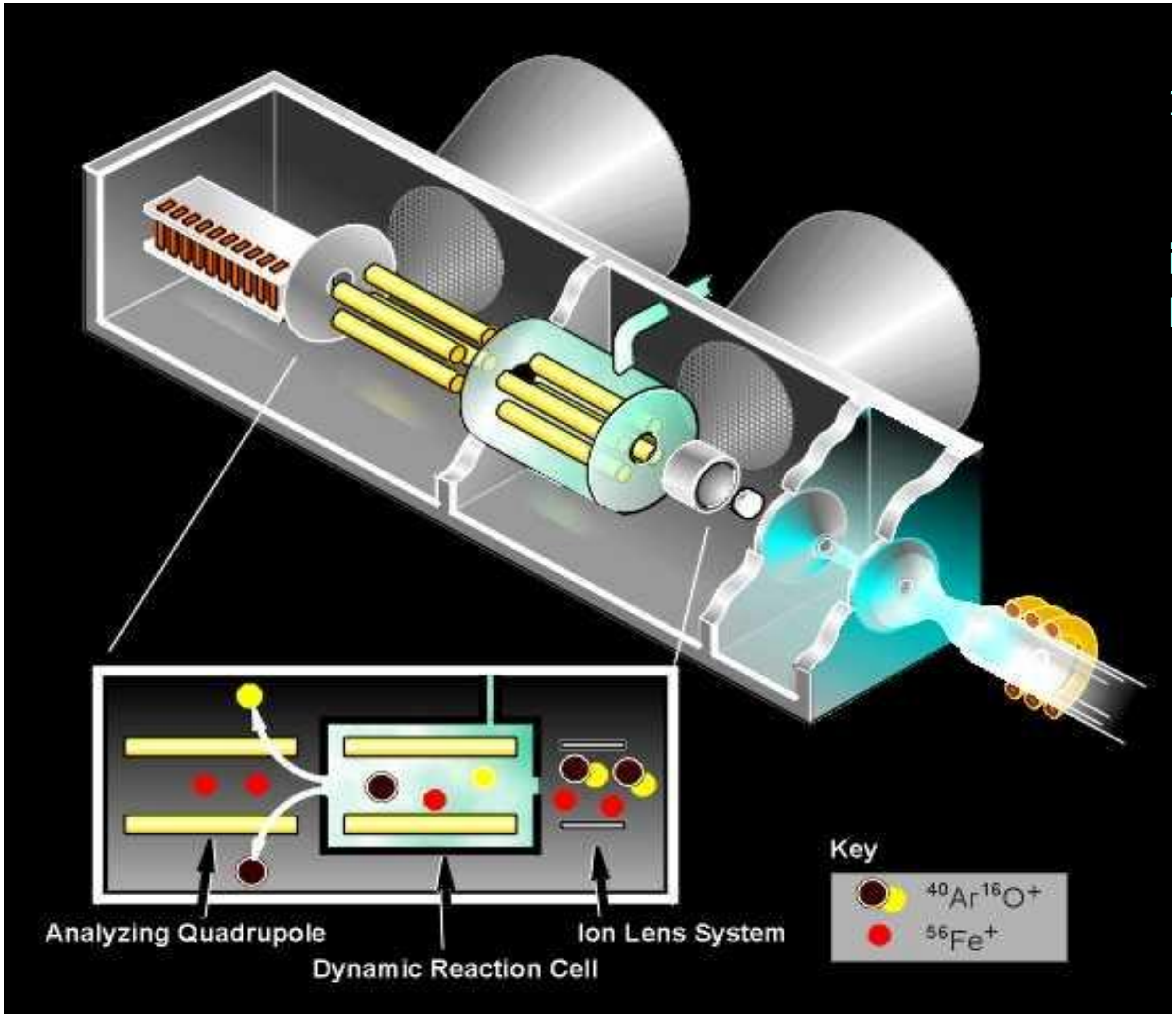


Octopole cell
Agilent Technologies



USE OF A COLLISION/REACTION CELL IN QUADRUPOLE-BASED ICP-MS: GENERAL CONCEPT

- ***Analyte & interfering ions in / analyte ions out***



DIFFERENCES BETWEEN DIFFERENT TYPES OF COLLISION/REACTION CELLS?

- ***Hexapole & octopole cell***
  - ***Guide ions from point a to point b***
- ***Quadrupole cell***
  - ***Guides ions from point a to point b***
  - ***Can be used as a mass filter***

$\Rightarrow$ ***Slightly different ways of application***

Perkin Elmer dynamic reaction cell – DRC

- ***Typical use: highly reactive gases***
  - ***Determination of Fe***
    - $^{40}Ar^{16}O^{+} + NH_3 \rightarrow {}^{40}Ar^{16}O + NH_3^{+}$
    - $^{56}Fe^{+} + NH_3 \rightarrow$ ***NO reaction***

    charge transfer to reaction gas
  - ***Determination of Fe***
    - $^{40}Ar^{16}O^{+} + CO \rightarrow {}^{40}Ar^{+} + CO_2$
    - $^{56}Fe^{+} + CO \rightarrow$ ***NO reaction***

    atom transfer to reaction gas
  - ***Determination of Pd***
    - $^{90}ZrO^{+} + O_2 \rightarrow {}^{90}ZrO_2^{+}$
    - $^{106}Pd^{+} + O_2 \rightarrow$ ***NO reaction***

    atom transfer from reaction gas
  - ***Determination of S***
    - $^{32}S^{+} + O_2 \rightarrow {}^{32}SO^{+} + O$
    - $^{16}O_2^{+} + O_2 \rightarrow$ ***NO reaction***

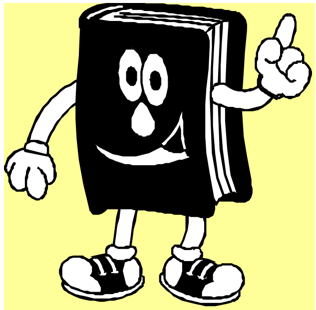
    atom transfer from reaction gas

PERKIN ELMER DYNAMIC REACTION CELL – DRC
THEORETICAL CONSIDERATIONS

- ***Reaction is thermodynamically allowed ($\Delta G < 0$)***
  - ***~ exothermic reaction ($\Delta H < 0$)***
  - ***ion-molecule reaction MAY proceed***
  - ***is usually fast***

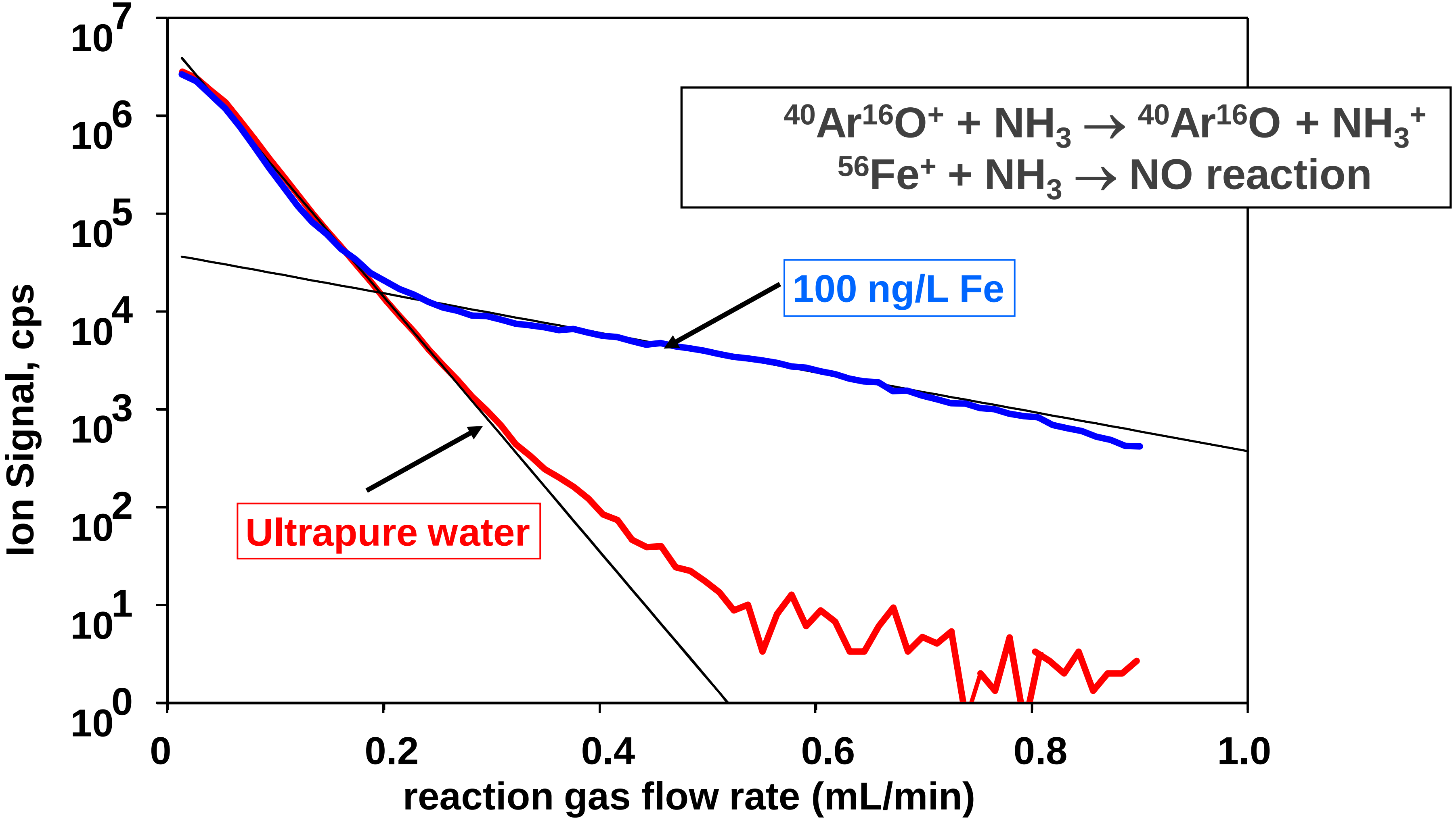
- ***Reaction is thermodynamically not allowed ($\Delta G > 0$)***
  - ***~ endothermic reaction ($\Delta H > 0$)***
  - ***ion-molecule reaction will not proceed***
  - ***no energy is being supplied***

- ***Consultation of thermodynamic / kinetic data***

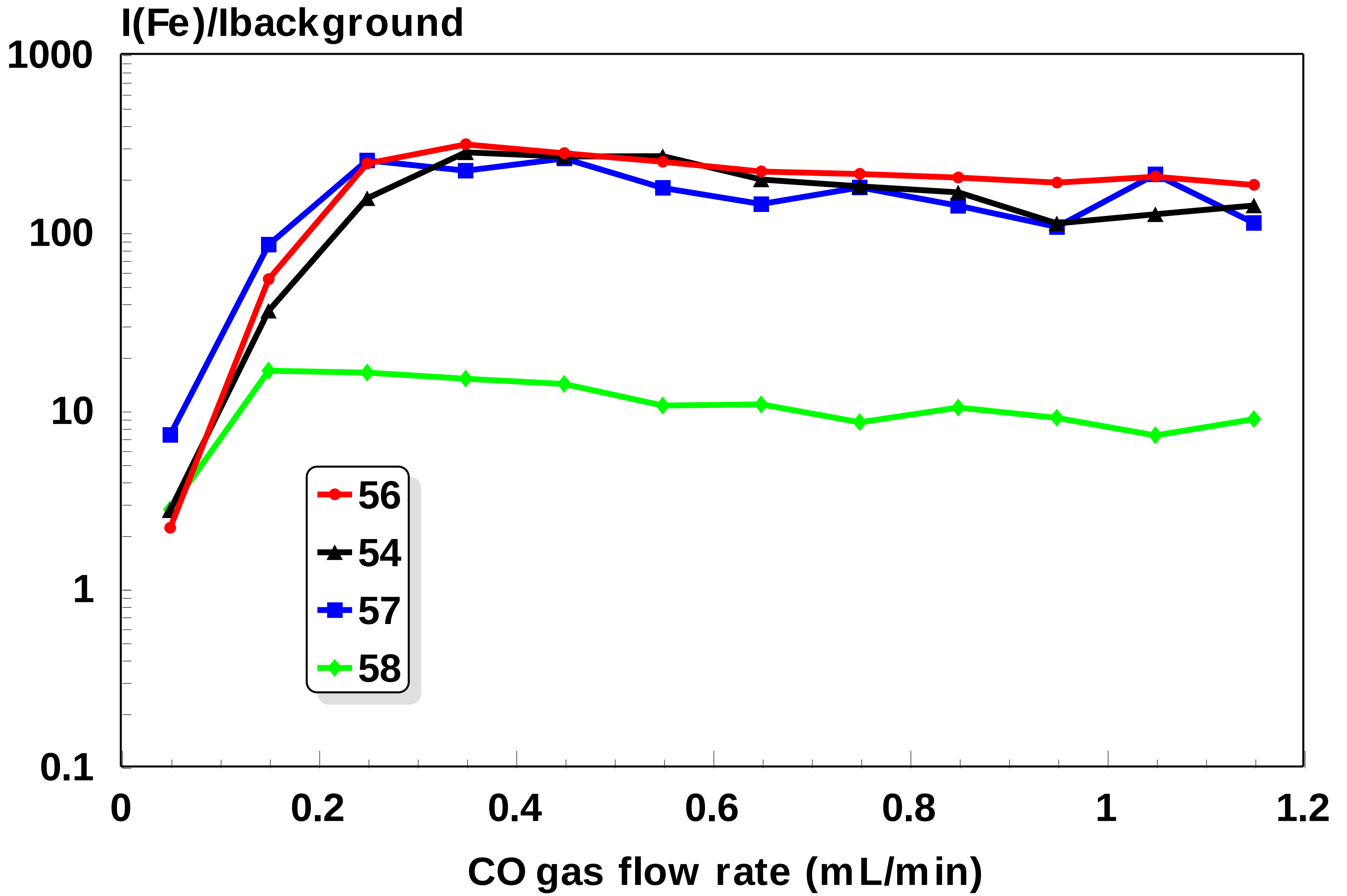


PERKIN ELMER DYNAMIC REACTION CELL – DRC
OPTIMIZATION OF REACTION GAS FLOW RATE

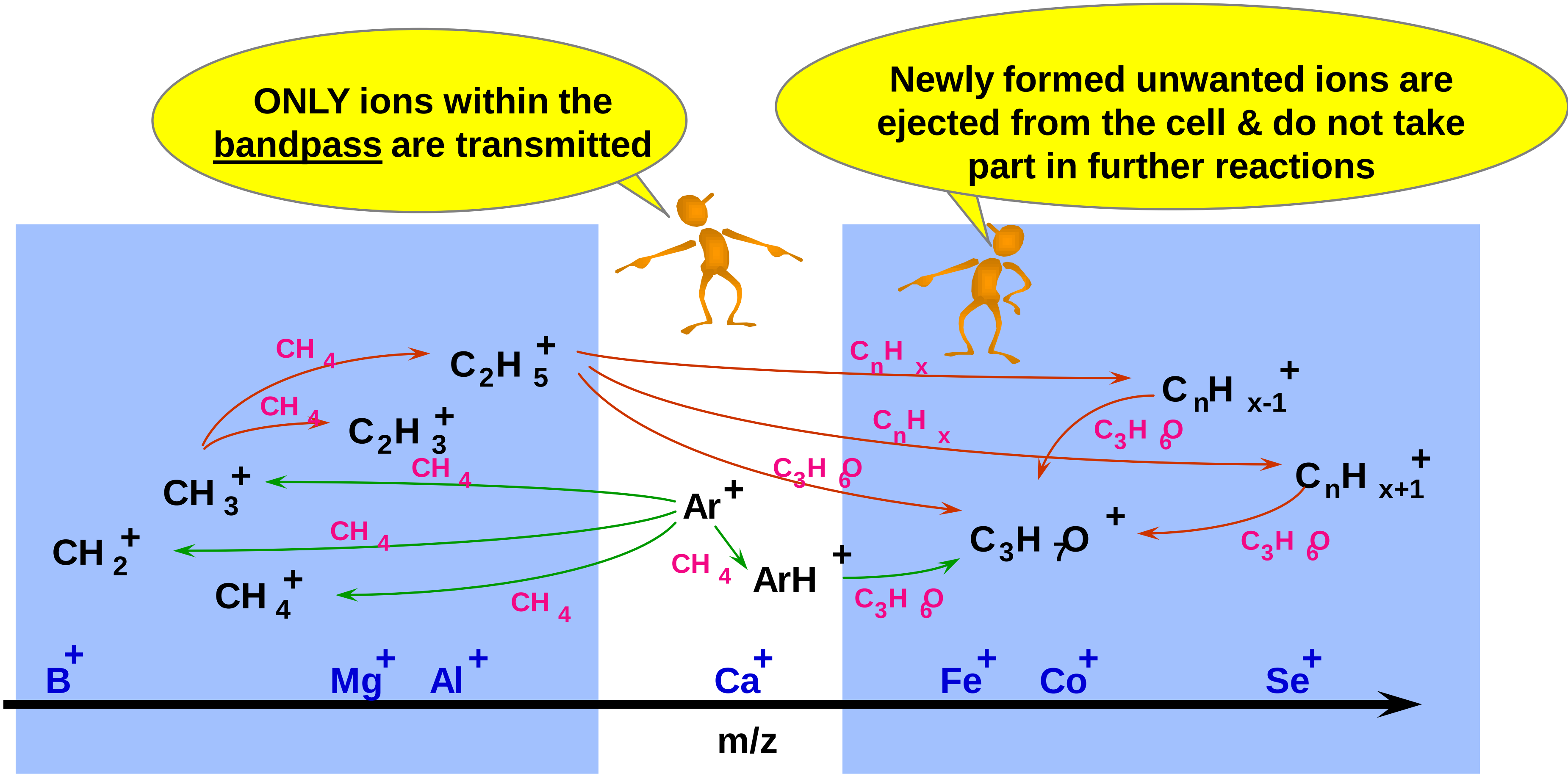
interference-free determination of Fe



PERKIN ELMER DYNAMIC REACTION CELL – DRC
OPTIMIZATION OF REACTION GAS FLOW RATE



SIDE REACTIONS WHEN USING REACTIVE GASES ? TACKLED BY USING QUADRUPOLE AS MASS FILTER



- Bandpass can be shifted in synchronicity with the mass analyzer

Figure from Scott Tanner / Sciex

SIDE REACTIONS WHEN USING REACTIVE GASES ?
TACKLED BY KINETIC ENERGY DISCRIMINATION

- ***Ions produced inside the hexapole / octopole cell***
  - ***Velocity ~ 0***

- ***Ions extracted from ICP***
  - ***Higher velocity***

$\Rightarrow$ ***selection of ions according to their velocity or E_{kin}***

  - ***Accomplished via decelerating potential = energy filter***
  - ***'Kinetic energy discrimination'***

BACKGROUND SPECTRUM WITH / WITHOUT H_2/HE PRESSURIZED HEXAPOLE COLLISION CELL

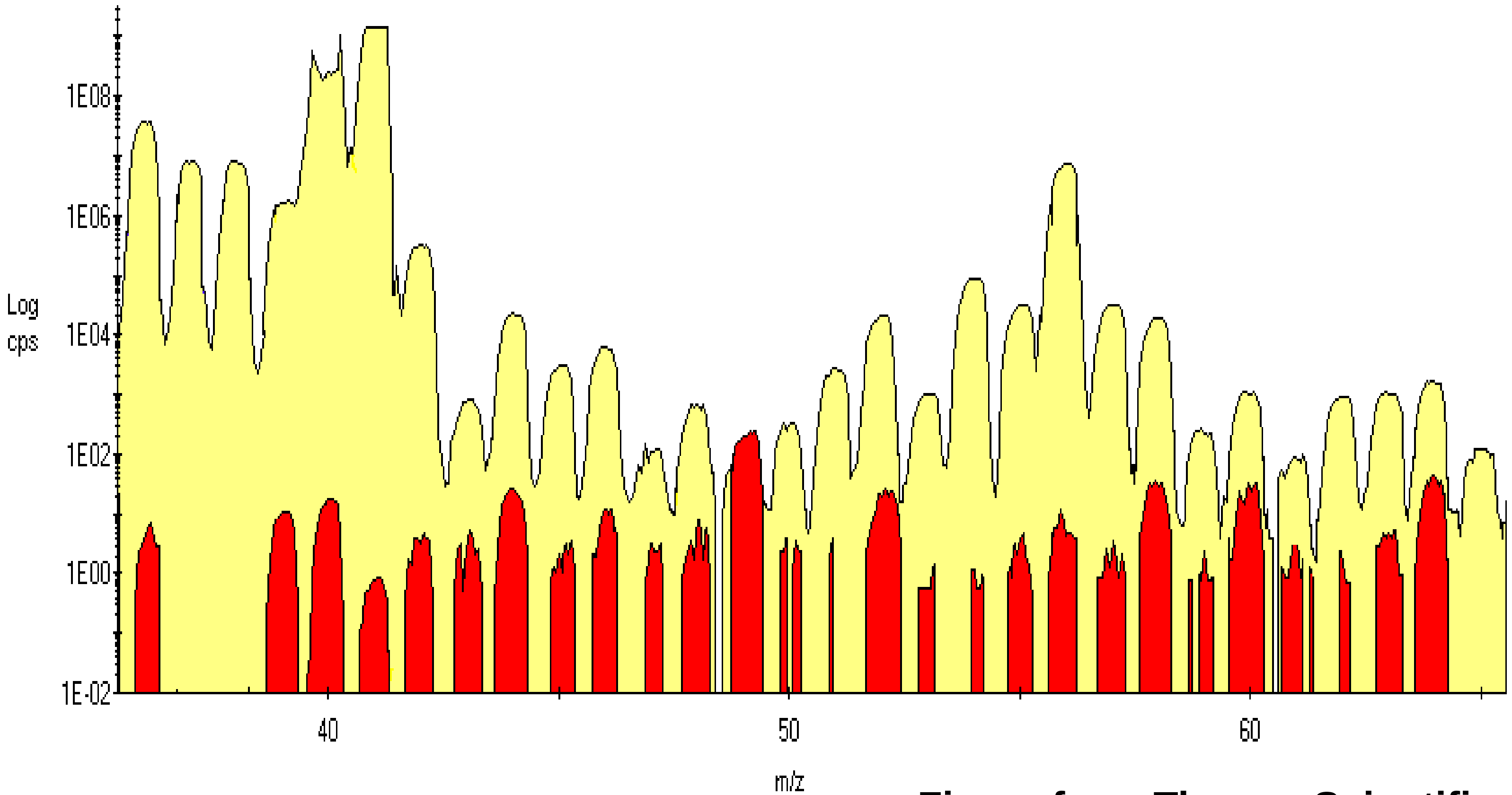


Figure from Thermo Scientific

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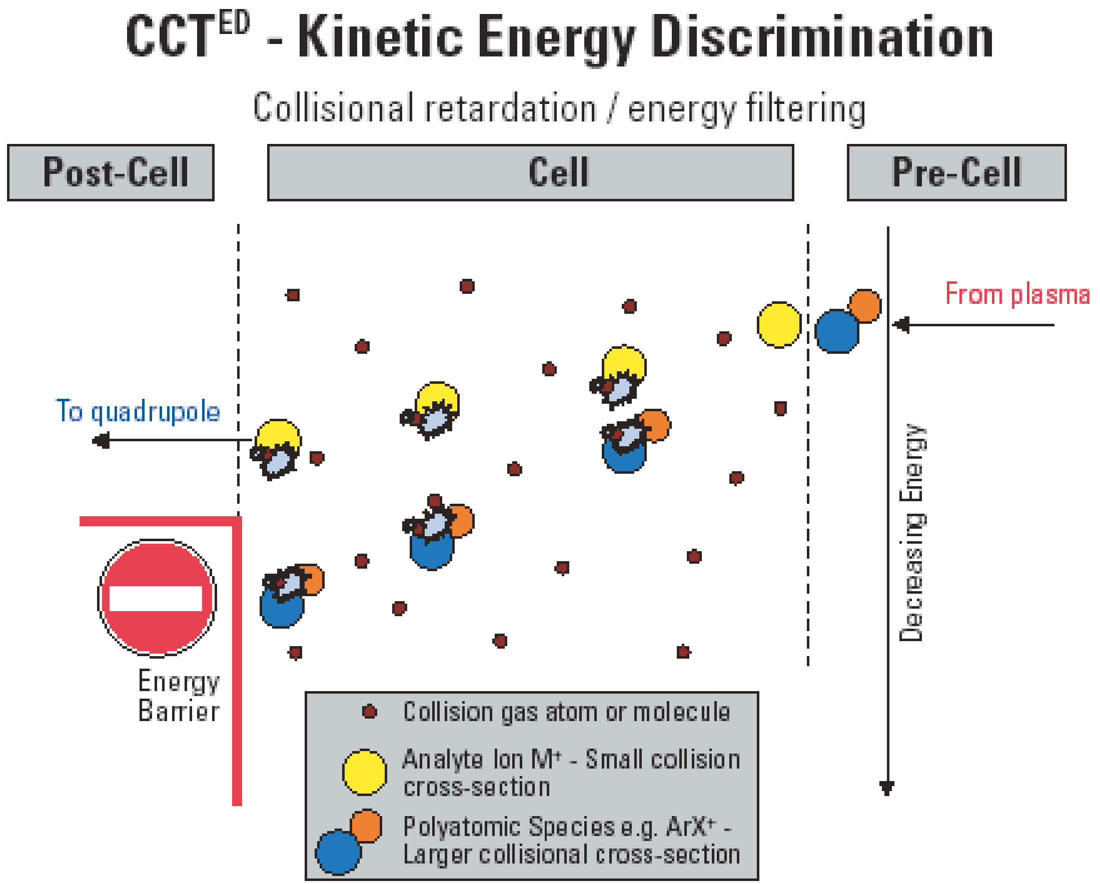
ALTERNATIVE USE OF KINETIC ENERGY DISCRIMNATION USE OF INERT GAS (HELIUM) ONLY

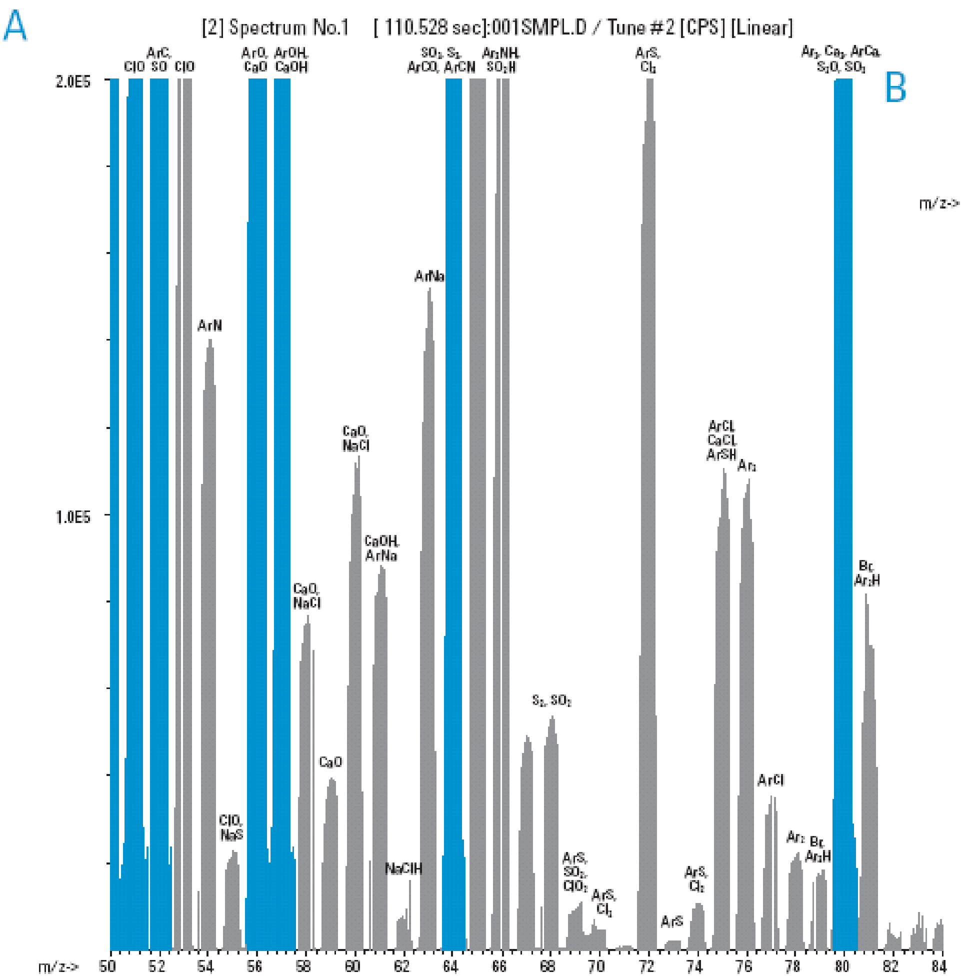


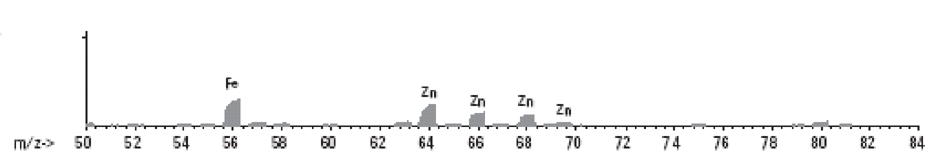
- ***Molecular ions are larger and thus, undergo more collisions***
  - ***Loose more E_{kin} than atomic ions***
- ***Energy barrier selectively discriminates against molecular ions***

BACKGROUND SPECTRUM WITH / WITHOUT HE-ONLY PRESSURIZED OCTOPOLE COLLISION CELL

With empty octopole cell

Octopole cell with He





Figures from Agilent's ICP-MS primer

PRESENT-DAY QUADRUPOLE-BASED ICP-MS INSTRUMENTS

- ***Agilent 7700***
  - ***Octopole Collision reaction cell***
  - ***Preferred modus of operation***
    - ***Use of He as inert collision gas & kinetic energy discrimination***

PRESENT-DAY QUADRUPOLE-BASED ICP-MS INSTRUMENTS

- ***Perkin Elmer Nexion***
  - ***Quadrupole reaction cell***
  - ***Preferred modus of operation***
    - ***Use of He as inert collision gas & kinetic energy discrimination***
    - ***Use of reaction gases for selective ion-molecule reaction***

Perkin-Elmer NexION
Universal cell technology

- ***Use as Q-based reaction cell with mass filtering capabilities***

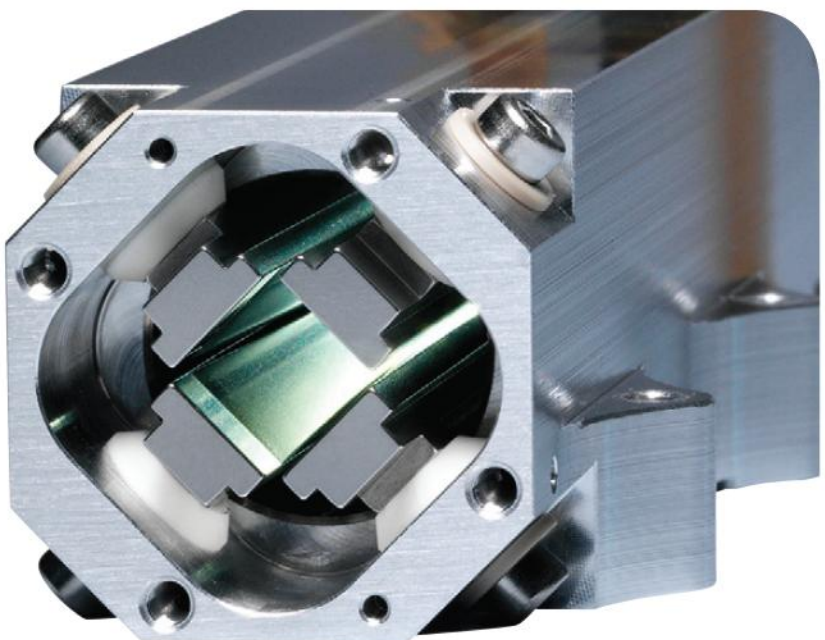
and

- ***Use as collision cell with kinetic energy discrimination***

Figure from Perkin Elmer

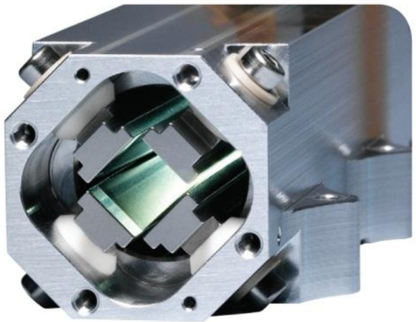
PRESENT-DAY QUADRUPOLE-BASED ICP-MS INSTRUMENTS

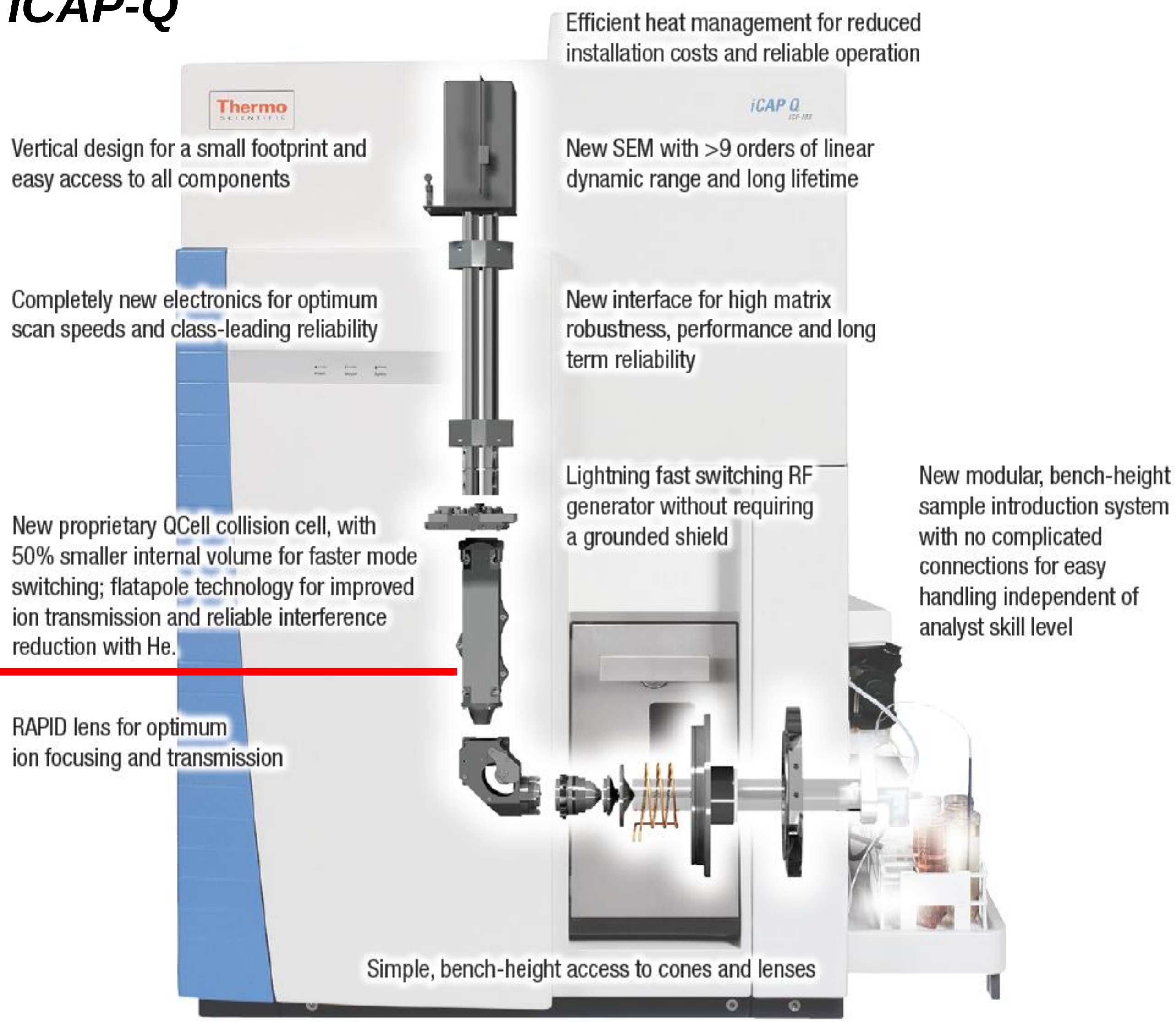
- ***ThermoScientific ICAP-Q***
  - ***Flatapole reaction cell***
  - ***Preferred modus of operation***
    - ***Use of He as inert collision gas & kinetic energy discrimination***
    - ***Use of reaction gases for selective ion-molecule reaction***



PRESENT-DAY QUADRUPOLE-BASED ICP-MS INSTRUMENTS

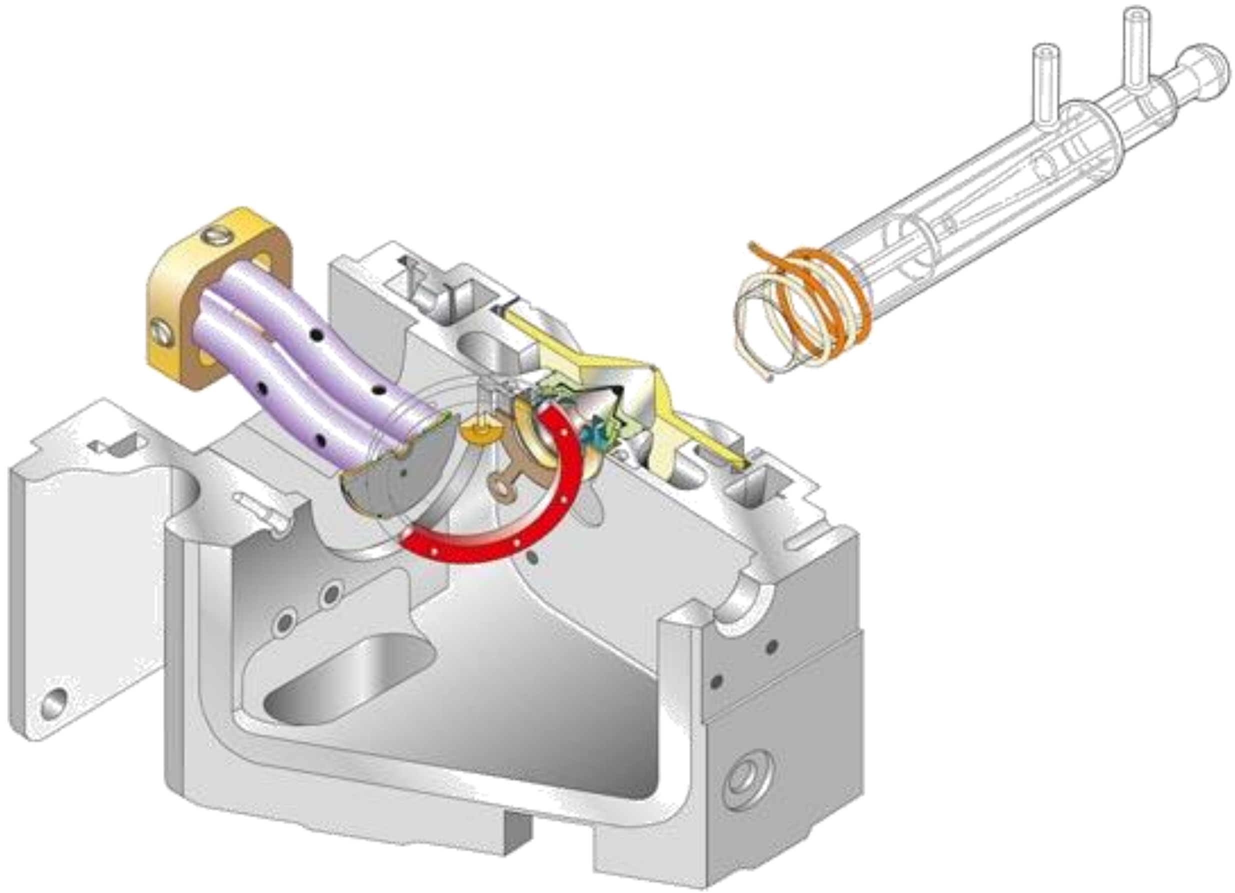
- ***ThermoScientific ICAP-Q***





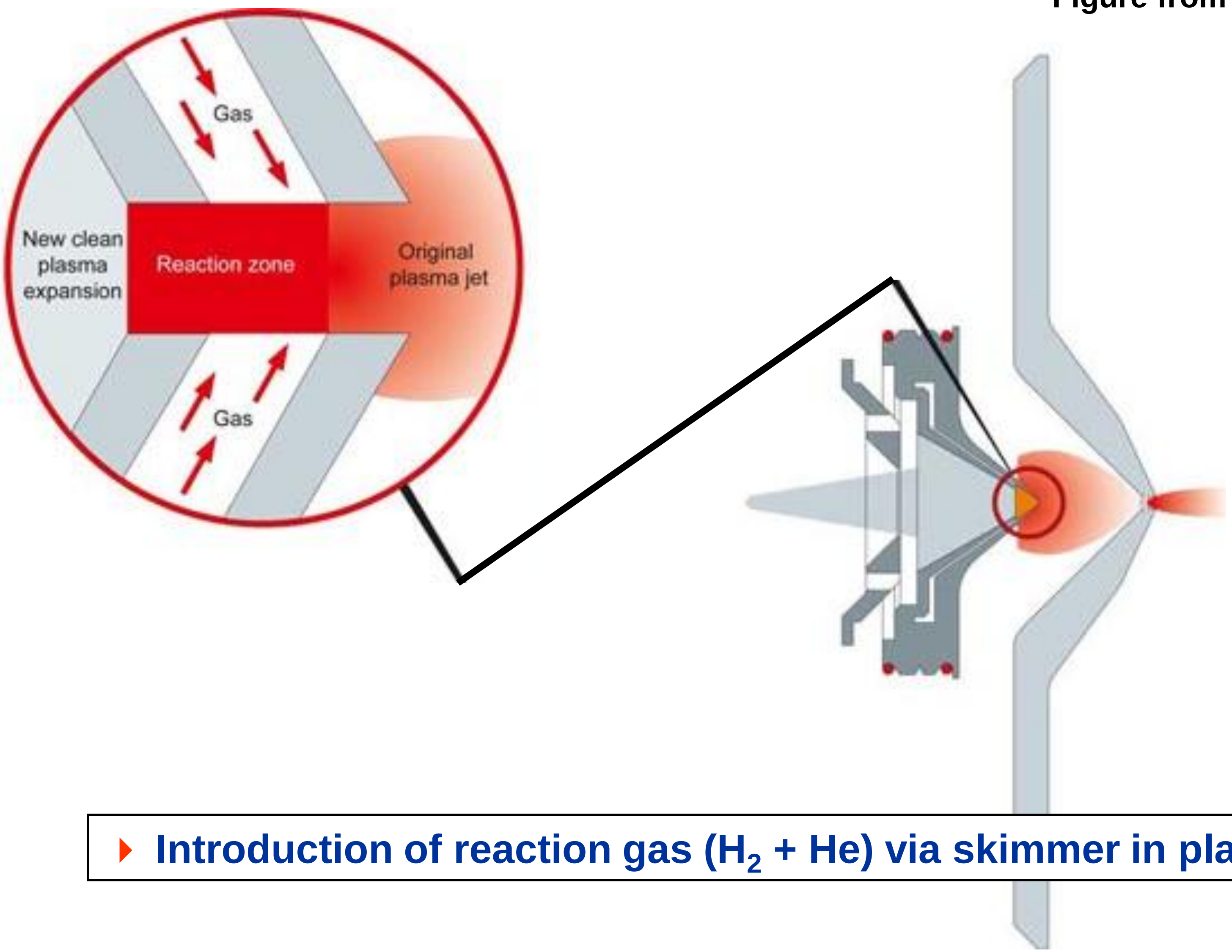
PRESENT-DAY QUADRUPOLE-BASED ICP-MS INSTRUMENTS

- ***Bruker Aurora M80***



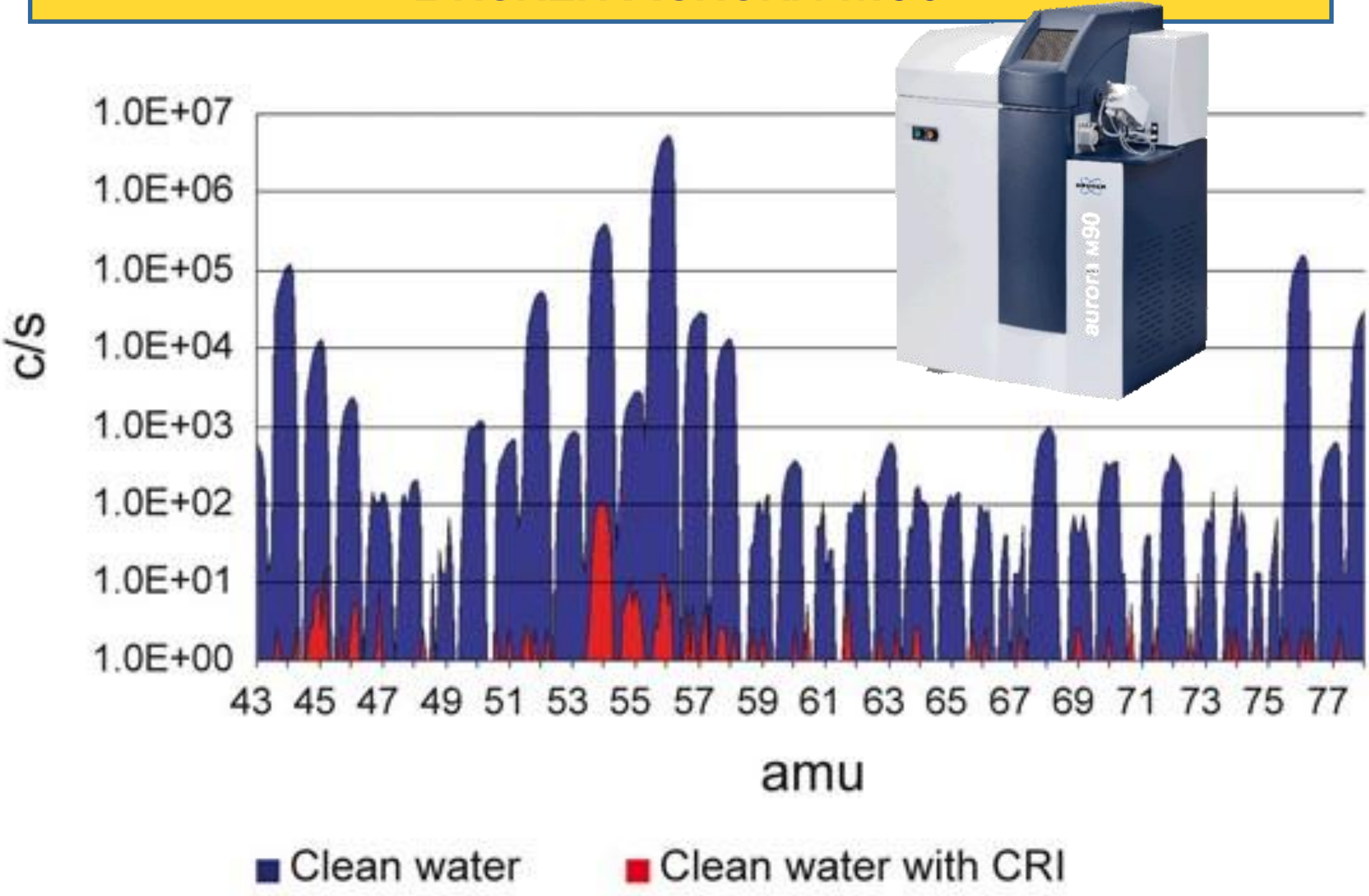
COLLISION/REACTION INTERFACE – CRI
BRUKER AURORA M90

Figure from Bruker website



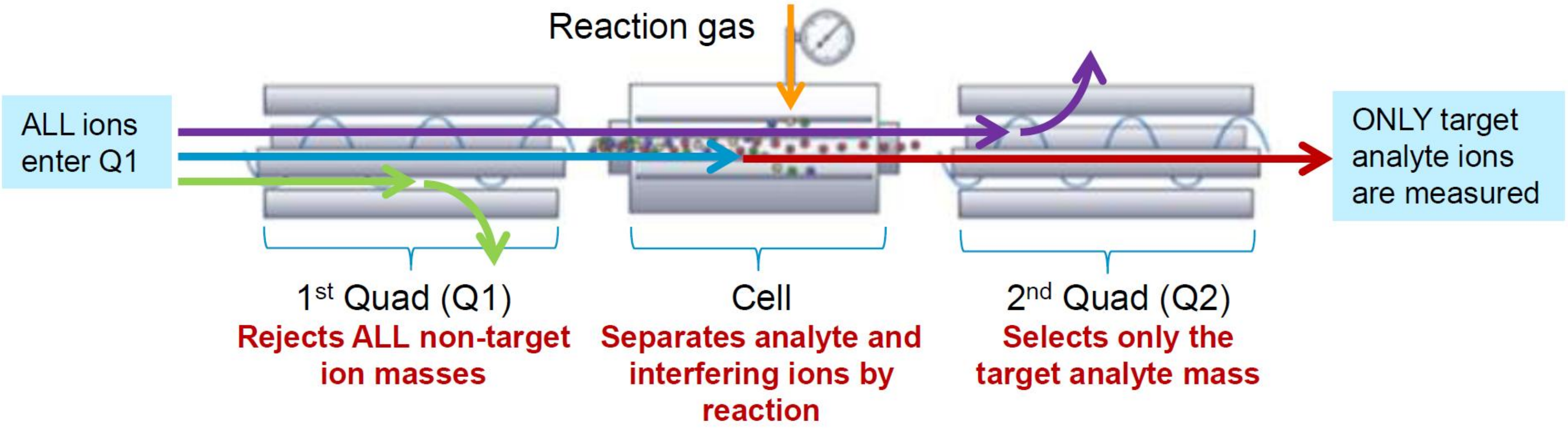
- Introduction of reaction gas (H_2 + He) via skimmer in plasmajet

COLLISION/REACTION INTERFACE – CRI
BRUKER AURORA M90



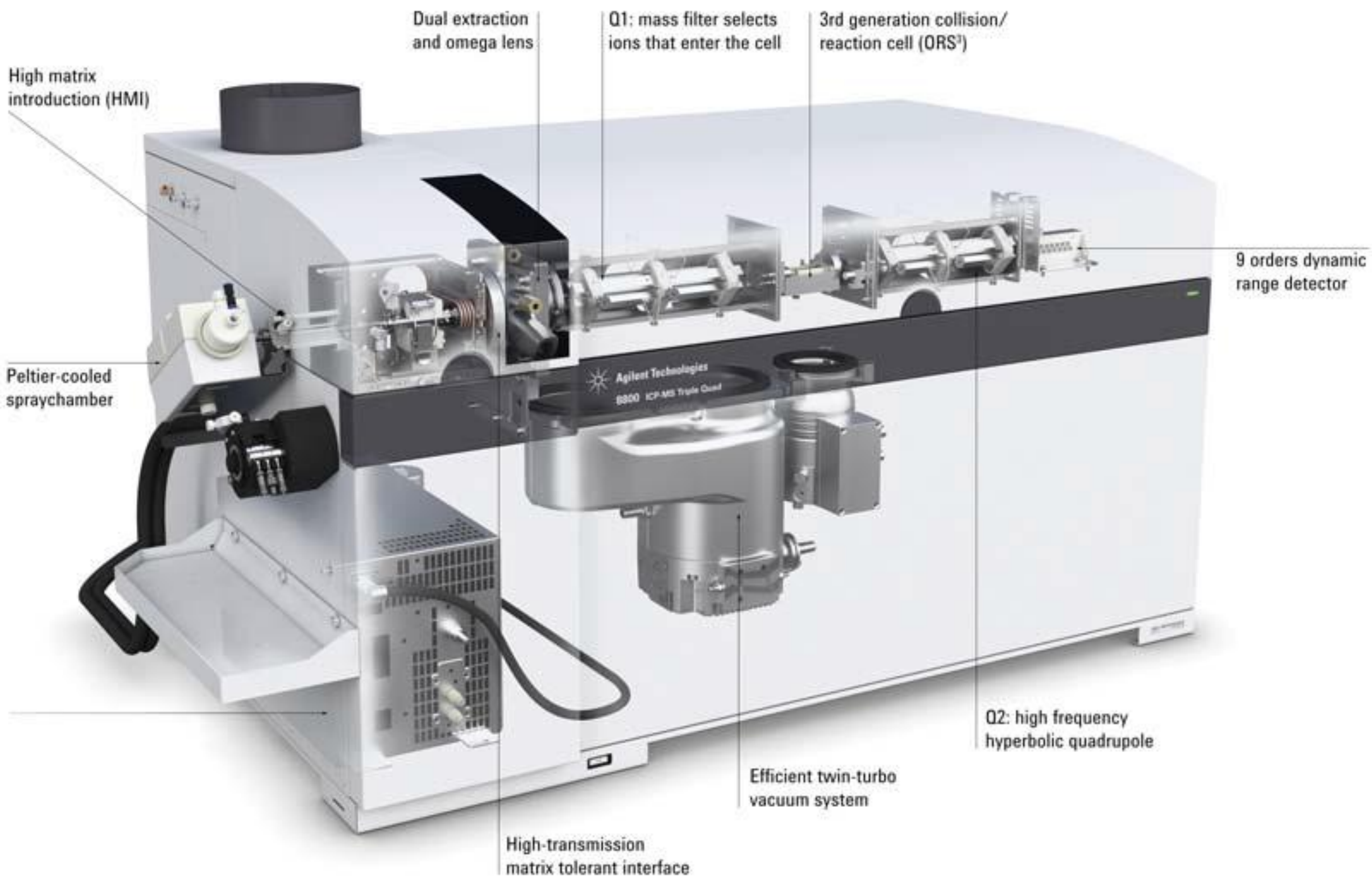
ICP-MS/MS or ICP-QQQ

- ***Agilent 8800***
  - ***Introduced in 2012***
  - ***Quadrupole filter 1 / Octopole reaction cell / Quadrupole filter 2***
    - ***Double mass selection*** (with "Double" underlined)



PRESENT-DAY QUADRUPOLE-BASED ICP-MS INSTRUMENTS

- **_Agilent 8800 ICP-QQQ_**
  - **_Superior tool for avoiding spectral overlap_**



SECTOR FIELD ICP-MS
(HIGH RESOLUTION ICP-MS)

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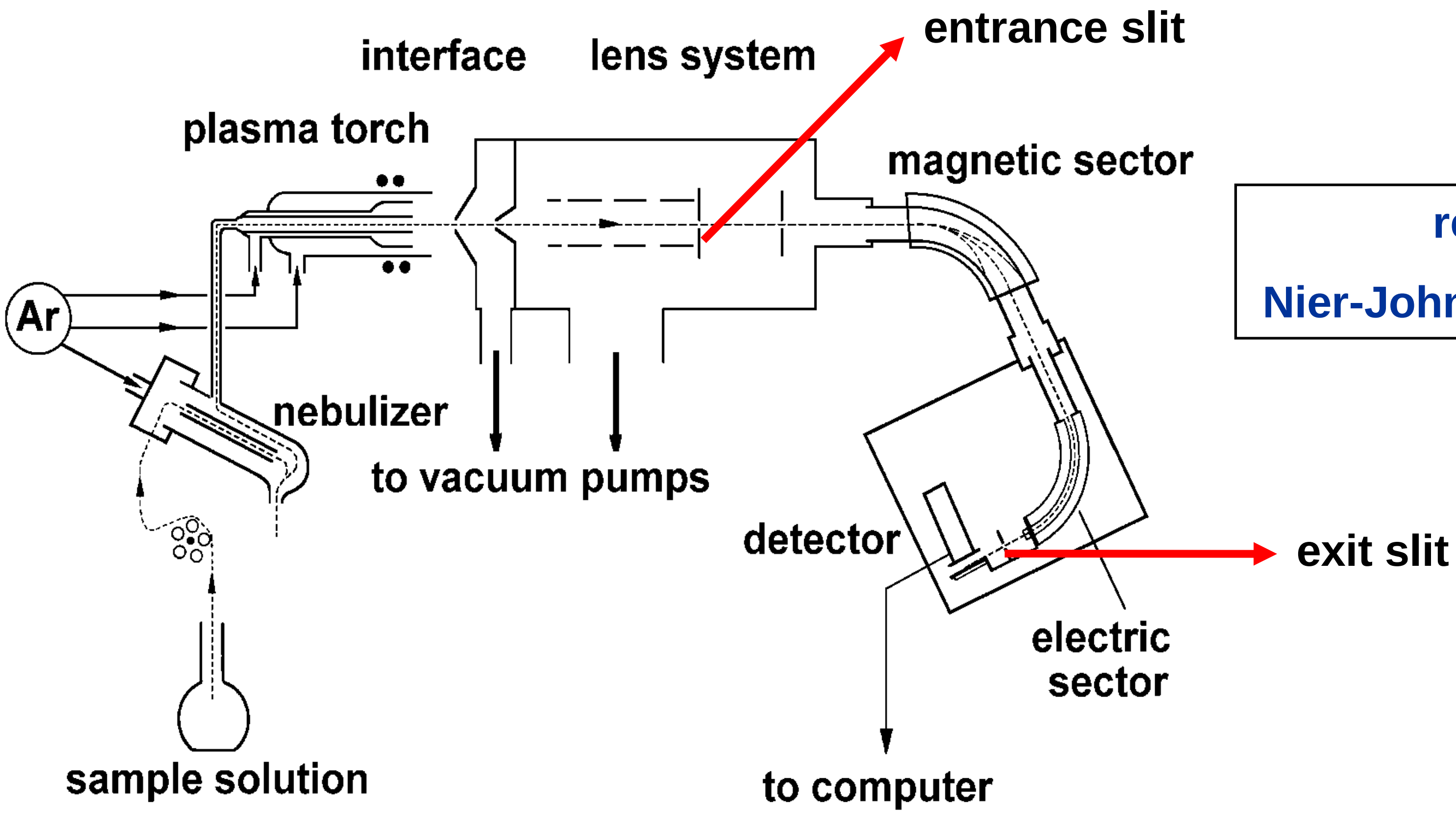
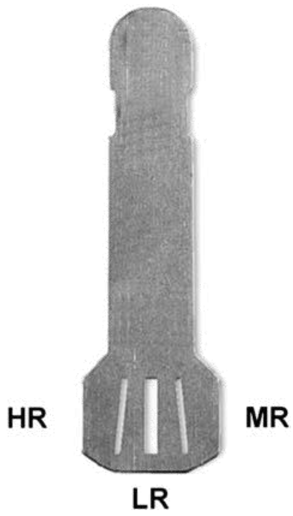
SECTOR FIELD ICP-MS



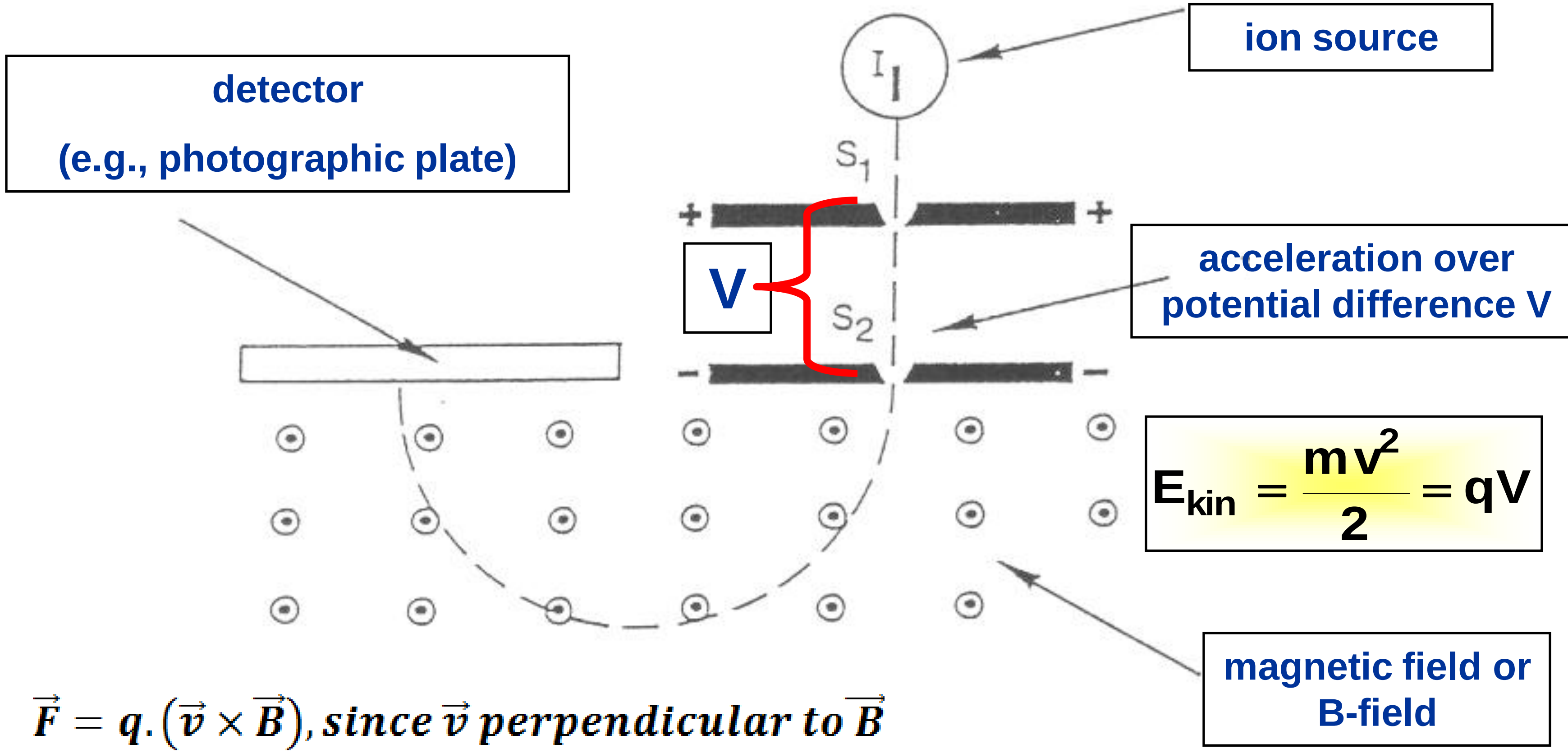
reverse

Nier-Johnson geometry

selection of mass resolution setting R = 300, 4000 or 10000



SEPARATION OF IONS IN A MAGNETIC SECTOR



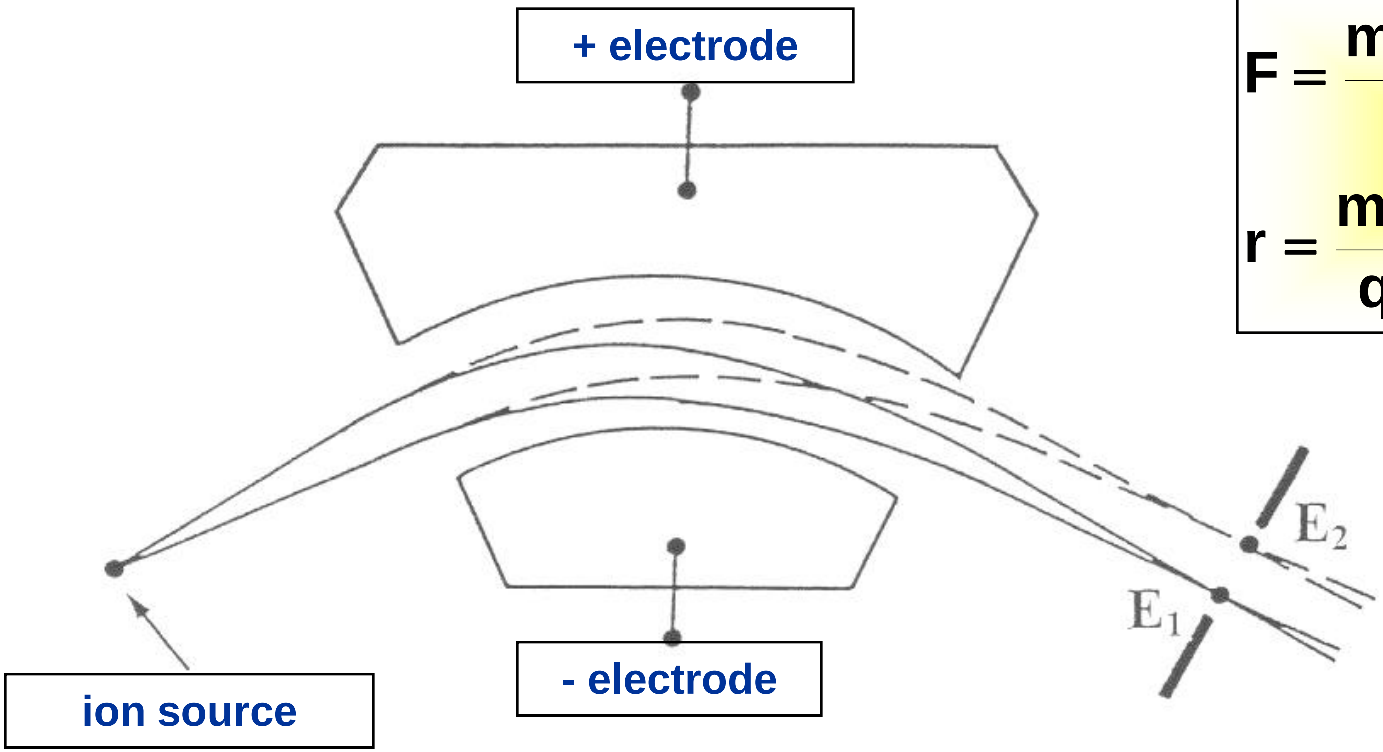
$$E_{kin} = \frac{mv^2}{2} = qV$$

$$\vec{F} = q.(\vec{v} \times \vec{B}), since\ \vec{v}\ perpendicular\ to\ \vec{B}$$

$$F = \frac{mv^2}{r} = qvB\ (Lorent\ force)$$

$$r = \frac{mv}{qB} = \frac{\sqrt{2Vm}}{\sqrt{qB}}$$

USE OF AN ELECTROSTATIC SECTOR AS ENERGY FILTER

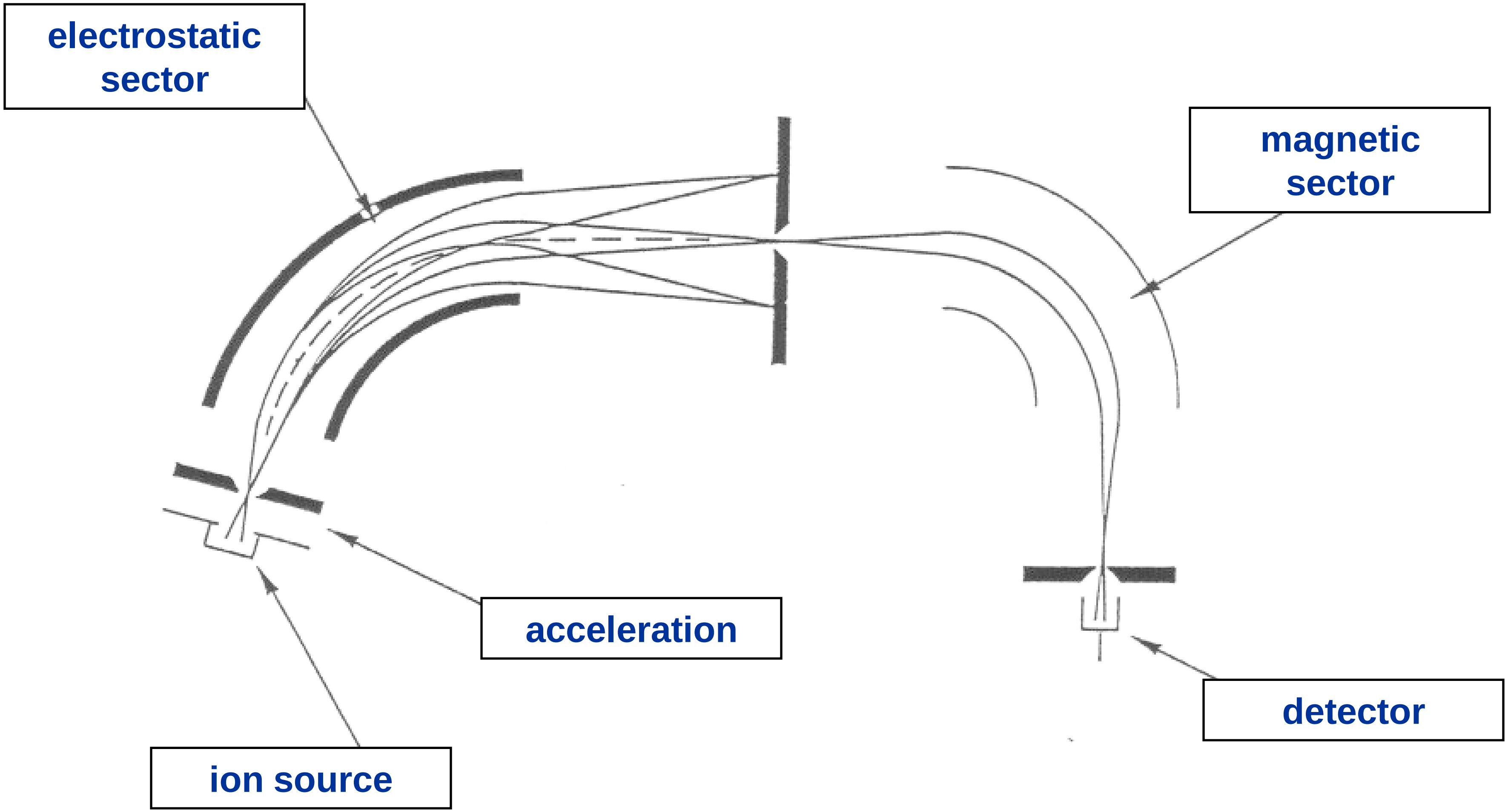


$$F = \frac{mv^2}{r} = qE$$

$$r = \frac{mv^2}{qE} = \frac{2E_{kin}}{qE}$$

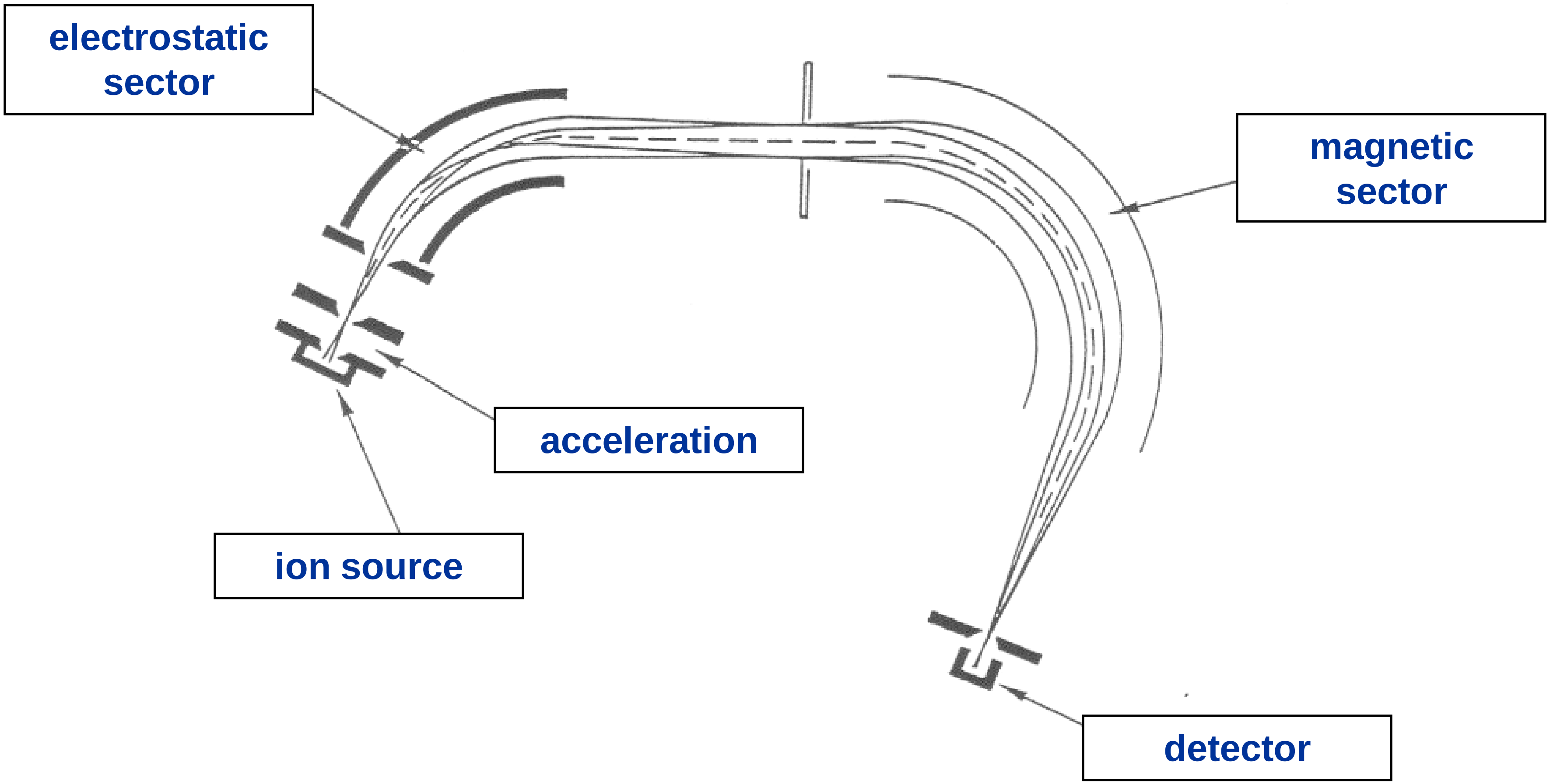
energy filtering leads to improved mass resolution

COMBINATION OF ELECTROSTATIC AND MAGNETIC SECTOR



high mass resolution / huge loss in transmission efficiency

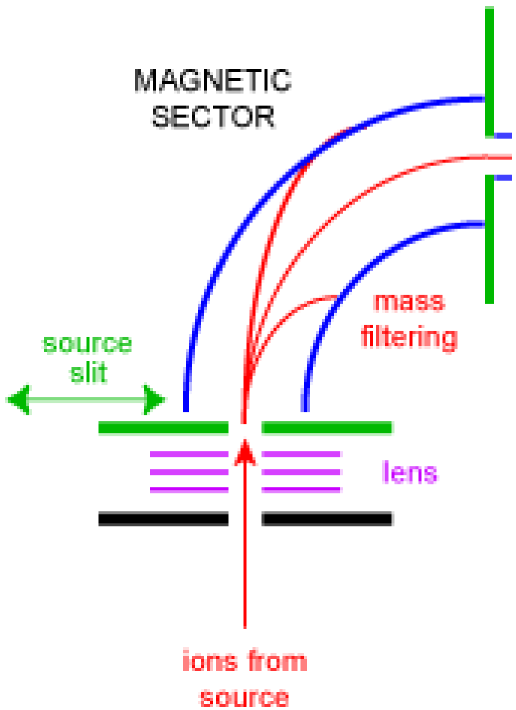
DOUBLE-FOCUSING SET-UP
NIER-JOHNSON GEOMETRY



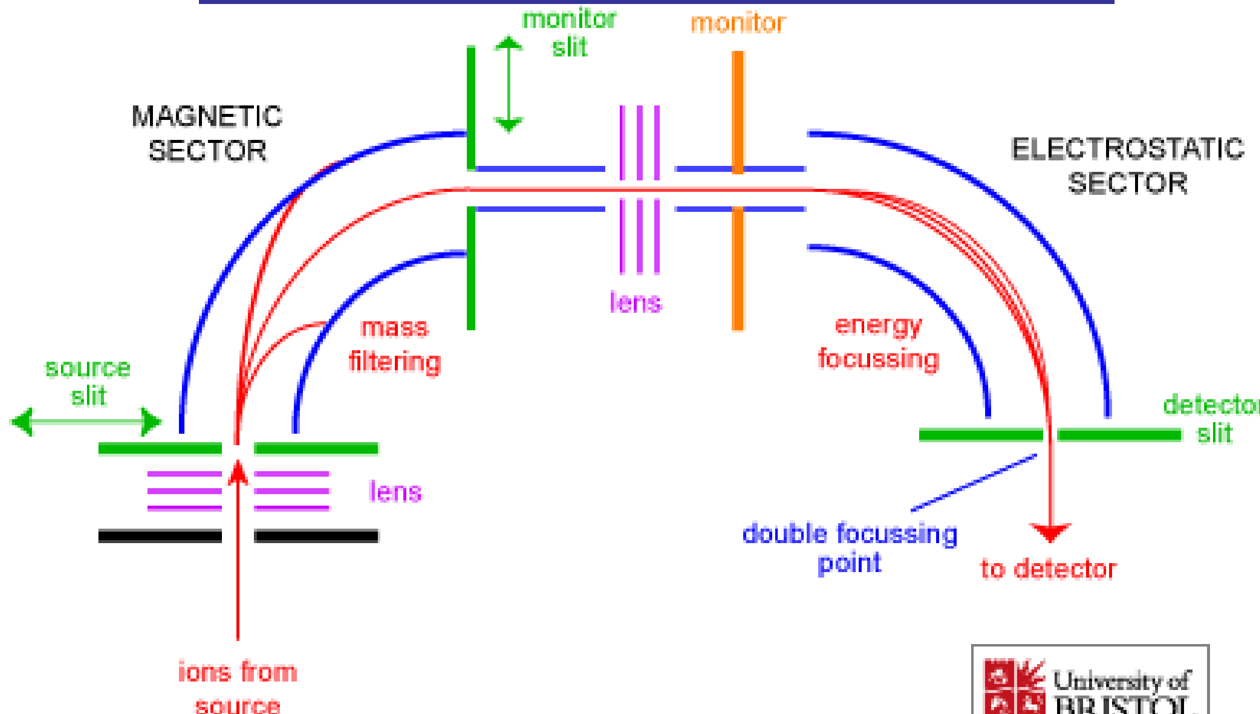
high mass resolution / limited loss in transmission efficiency

DOUBLE-FOCUSING SECTOR FIELD MS OF REVERSE NIER-JOHNSON GEOMETRY

Mass analysis in a magnetic sector



Double-focusing sector field MS of reverse Nier-Johnson geometry

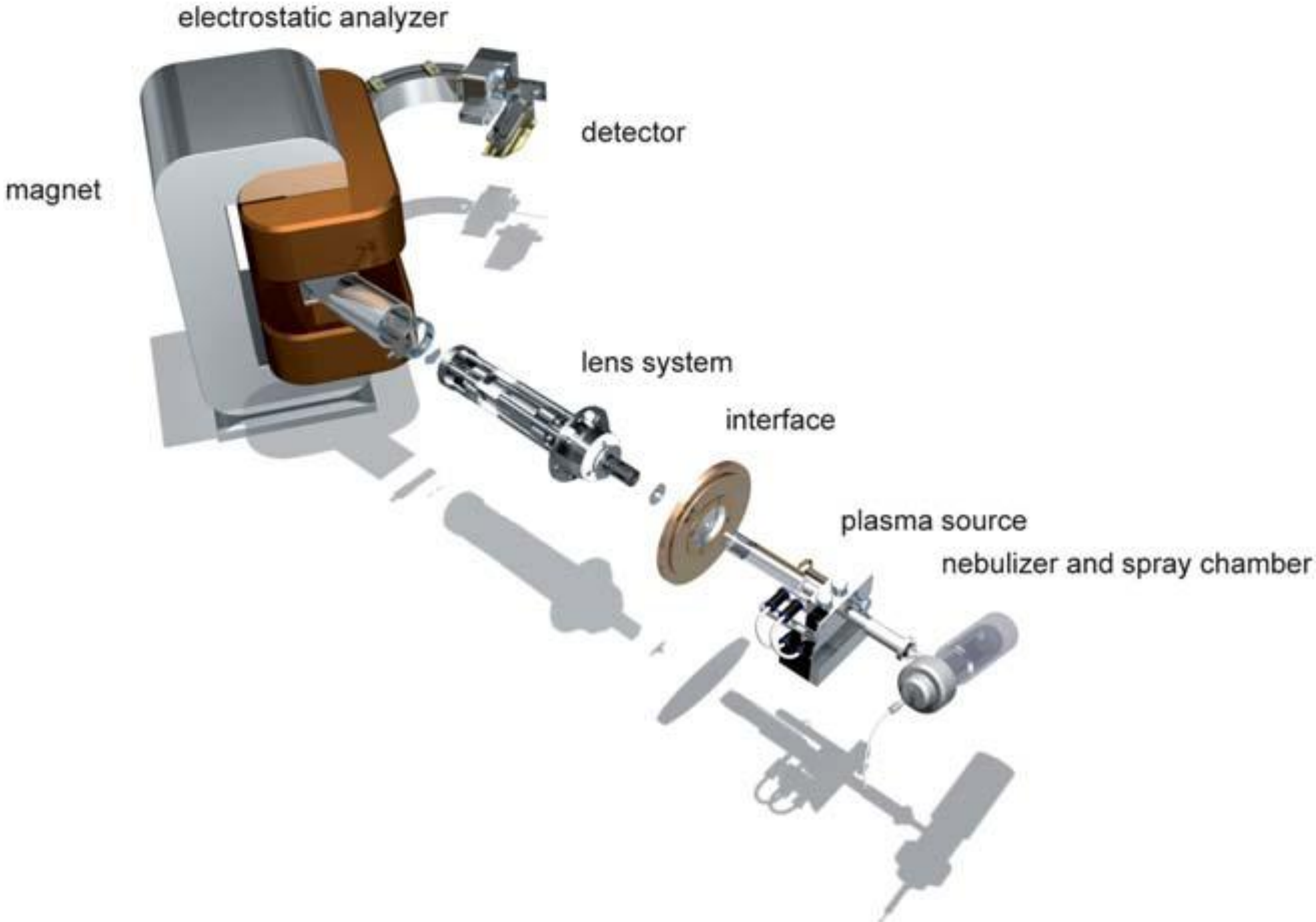


University of BRISTOL

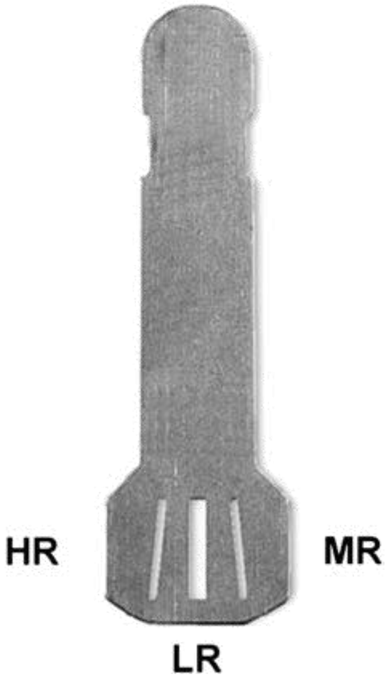
Reverse Nier-Johnson geometry

- Major clean-up of ion beam
- Improved background & abundance sensitivity

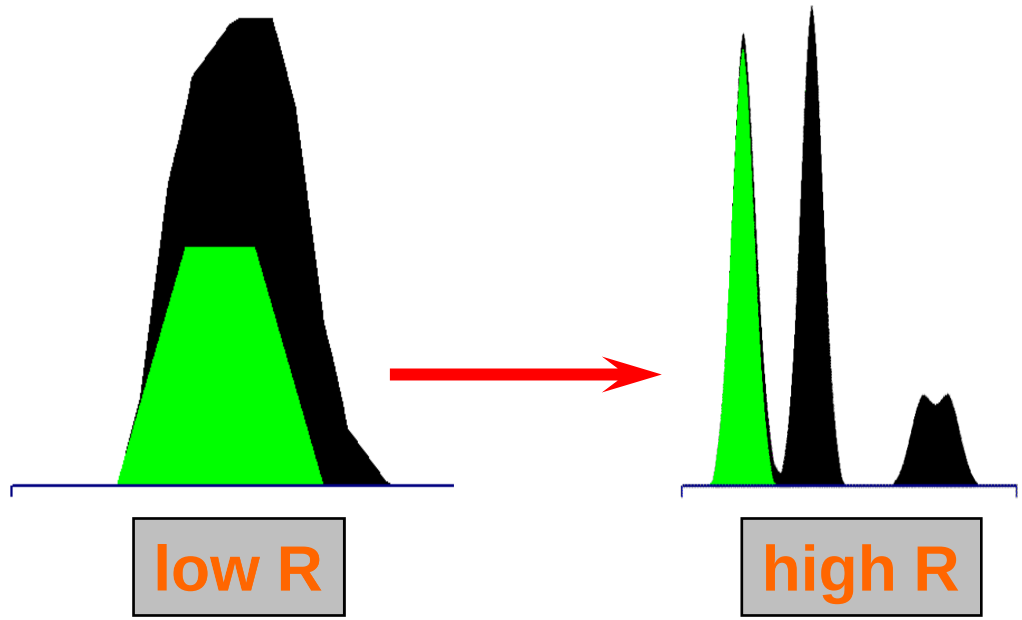
SECTOR FIELD ICP-MS



SECTOR FIELD ICP-MS
'HIGH RESOLUTION' ICP-MS

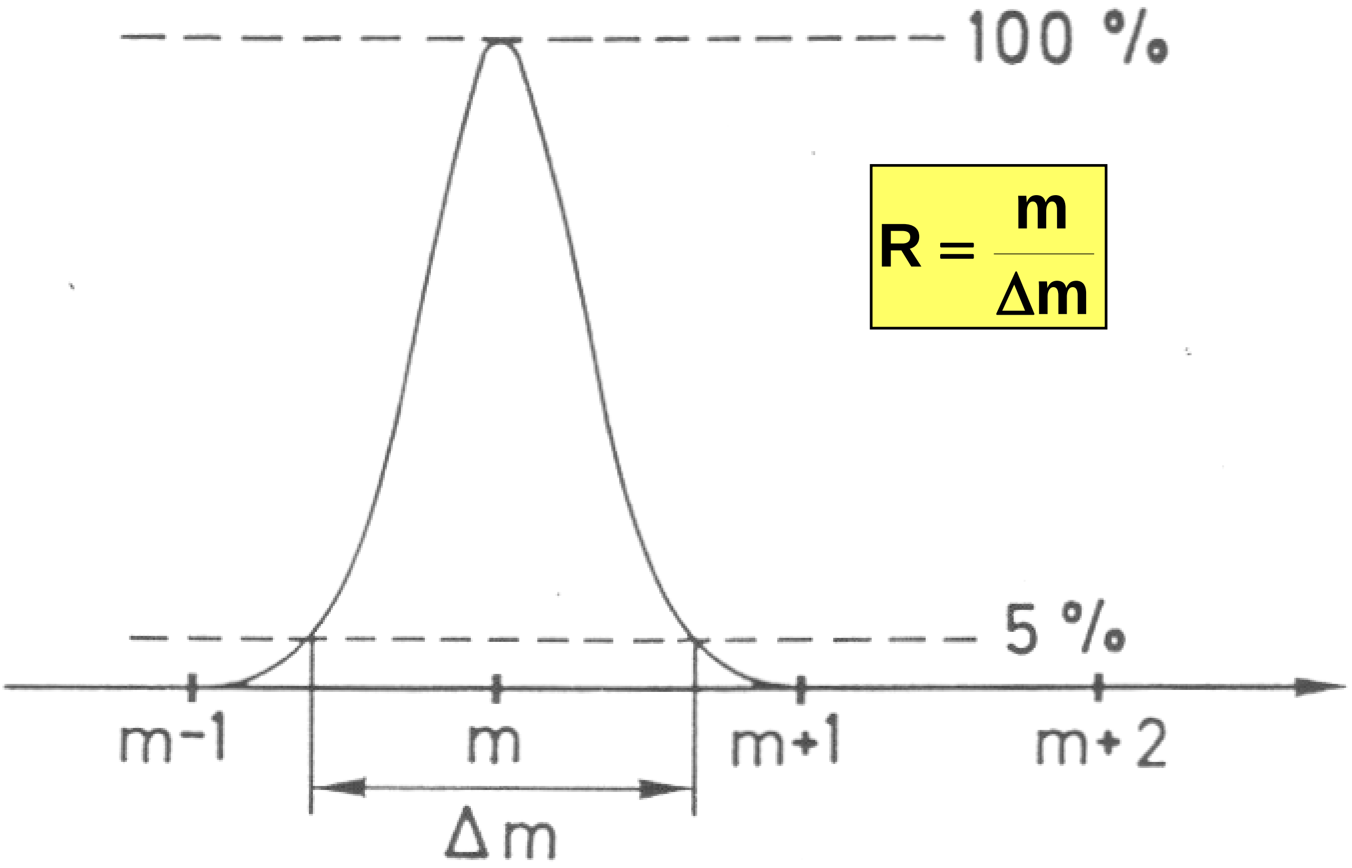


3 pre-defined R-settings
300, 4000, 10000



DEFINITION OF MASS RESOLUTION – 1

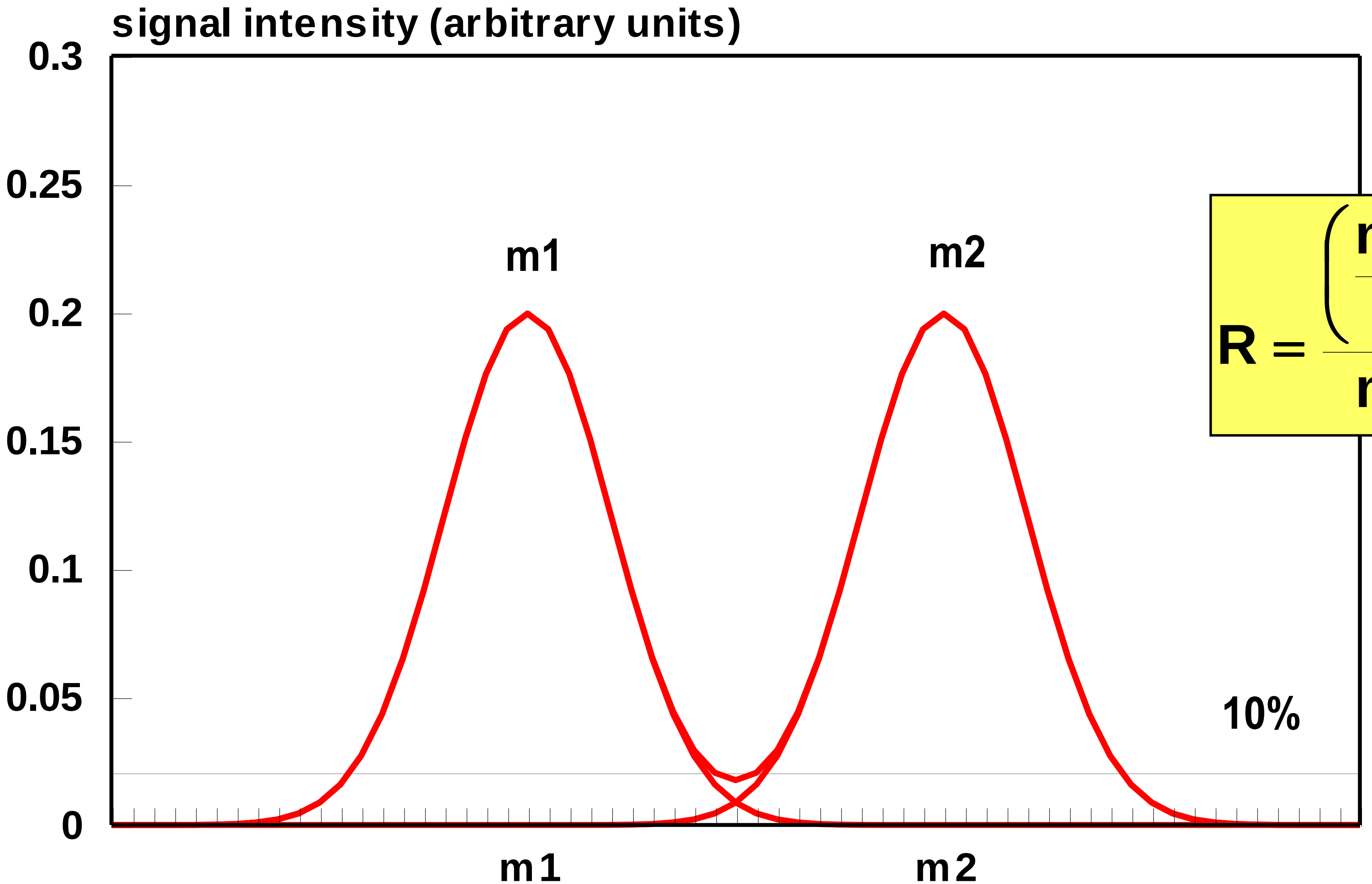
- ***used for calculation of instrumental R***



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

DEFINITION OF MASS RESOLUTION – 2
10% VALLEY DEFINITION

- ***Calculation of mass resolution that is required***

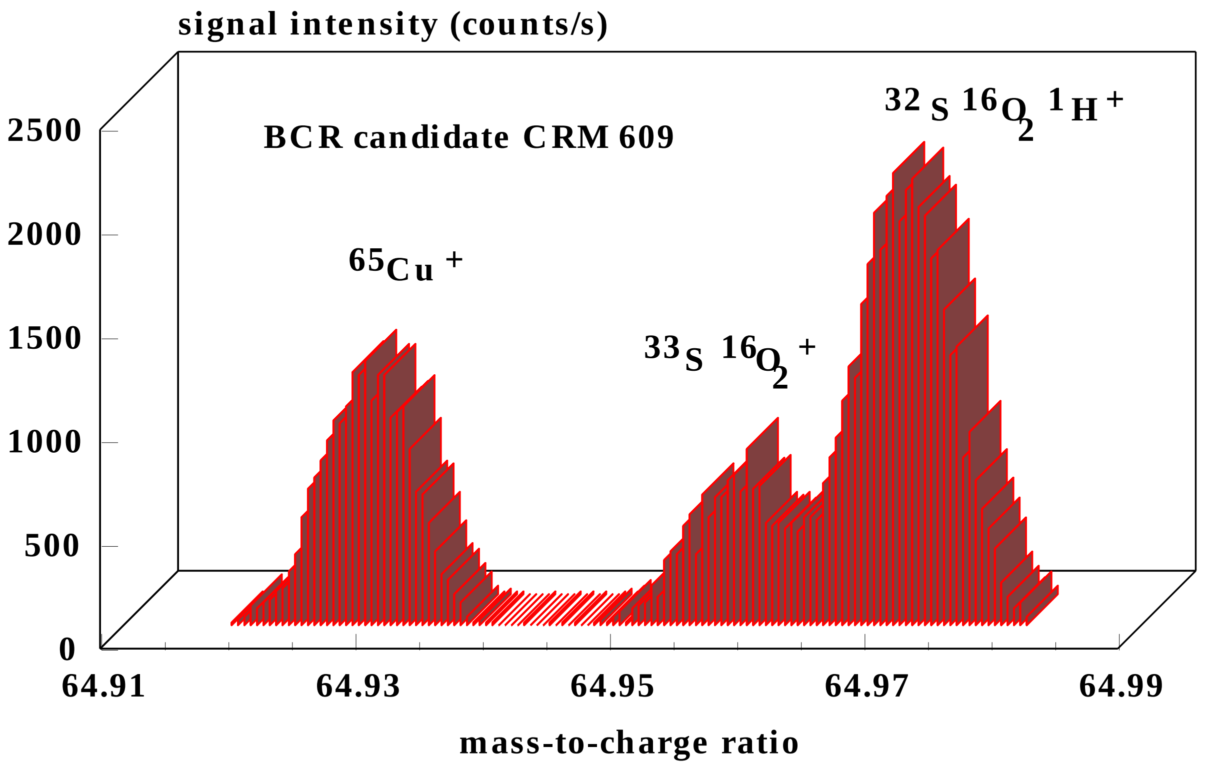


$$R = \frac{\left(\frac{m_1 + m_2}{2}\right)}{m_2 - m_1}$$

SECTOR FIELD ICP-MS
'HIGH RESOLUTION' ICP-MS

Determination of Cu in groundwater

At low R: overlap of $^{63}Cu^+$ and $^{40}Ar^{23}Na^+$, is $^{65}Cu^+$ interference-free?



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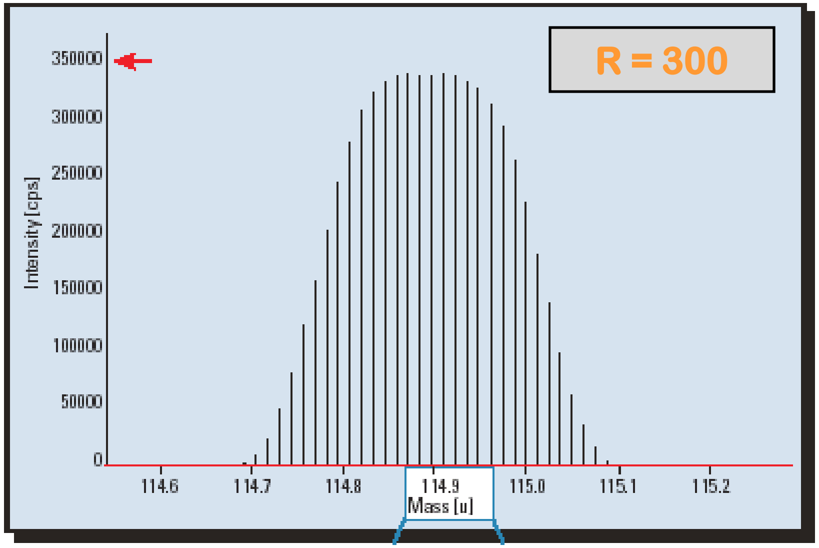
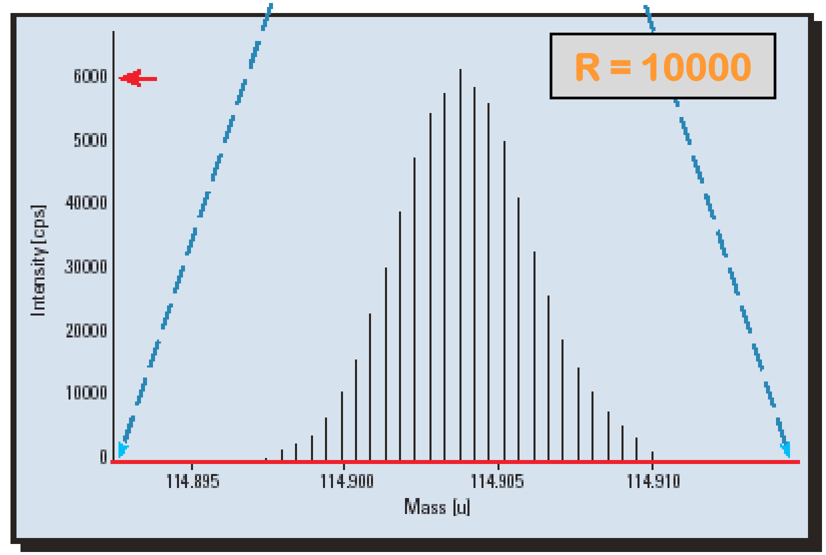
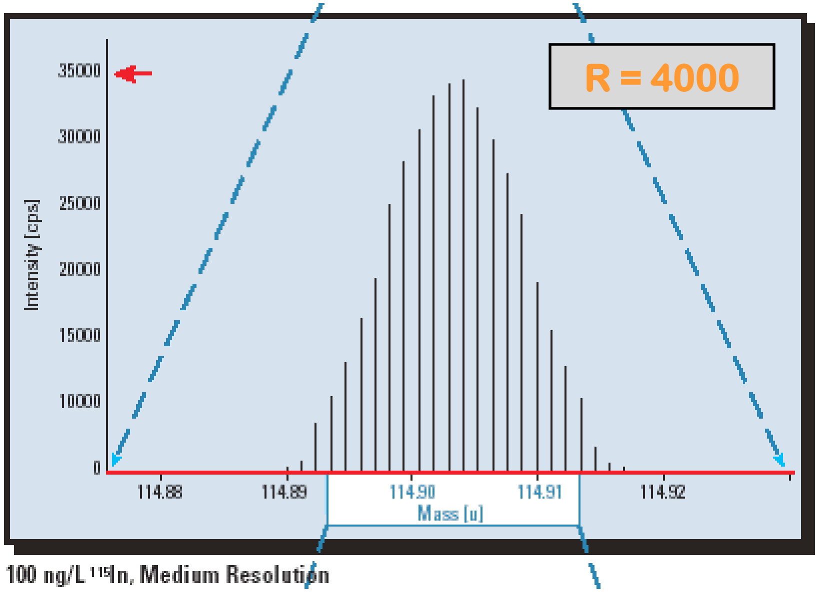
EFFECT OF MASS RESOLUTION SETTING ON SIGNAL INTENSITY



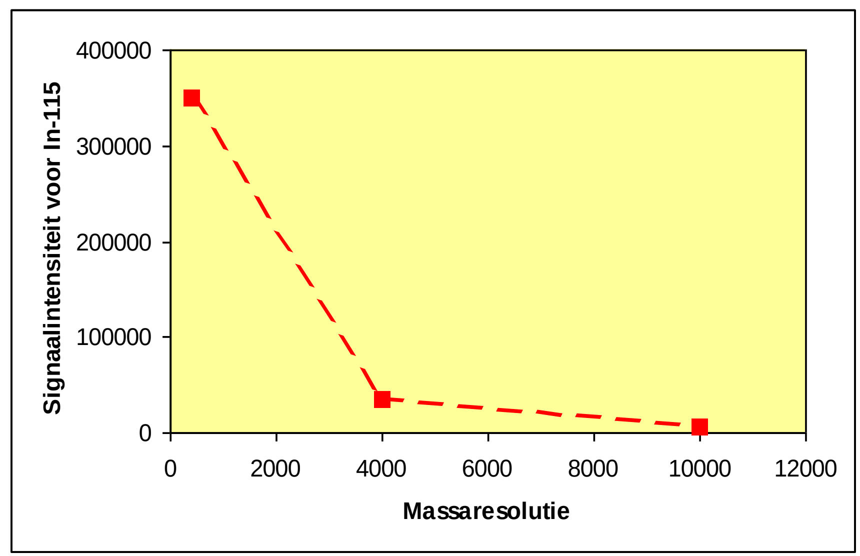
100 ng/L ^{115}In, Low Resolution



100 ng/L ^{115}In, High Resolution



100 ng/L ^{115}In, Medium Resolution



PRESENT-DAY SECTOR FIELD ICP-MS INSTRUMENTS OFFERING HIGH MASS RESOLUTION

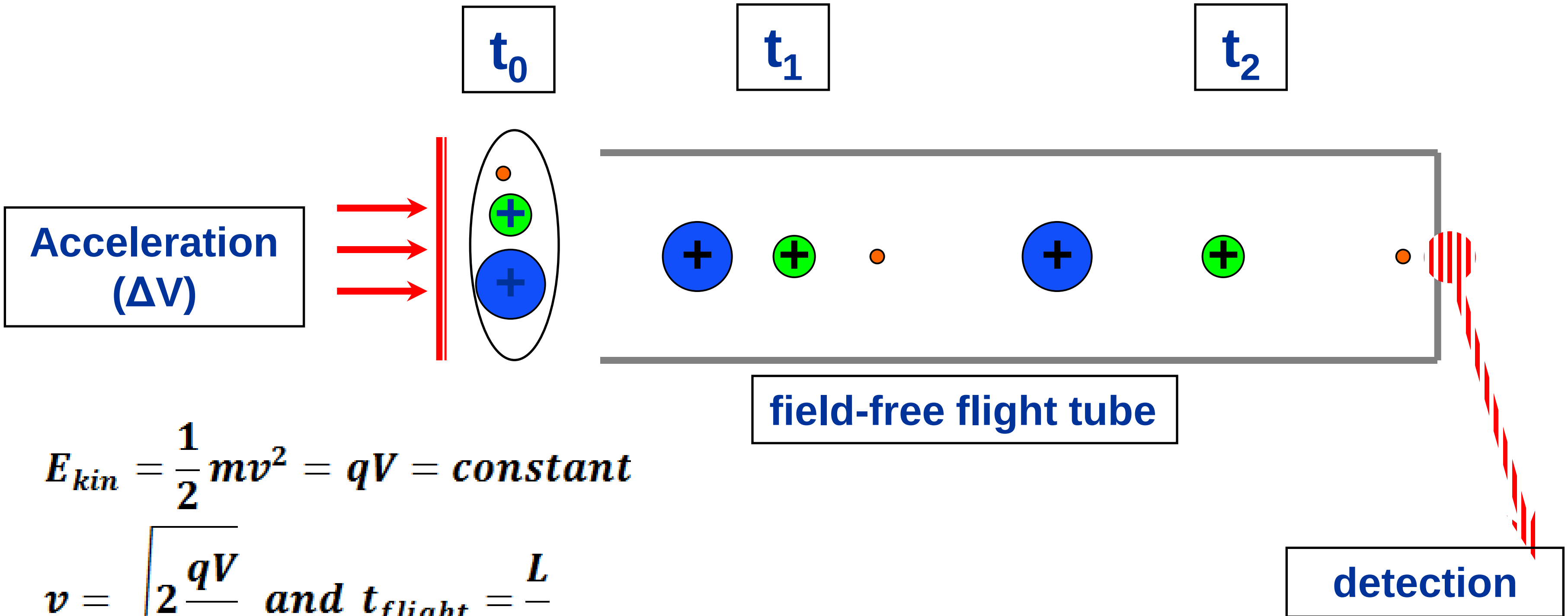
- ***Thermo Scientific Element 2 / Element XR***

PRESENT-DAY SECTOR FIELD ICP-MS INSTRUMENTS OFFERING HIGH MASS RESOLUTION

- ***Nu Instruments AttoM***

OTHER TYPES OF ICP-MS INSTRUMENTATION

TIME-OF-FLIGHT (TOF) ANALYZER



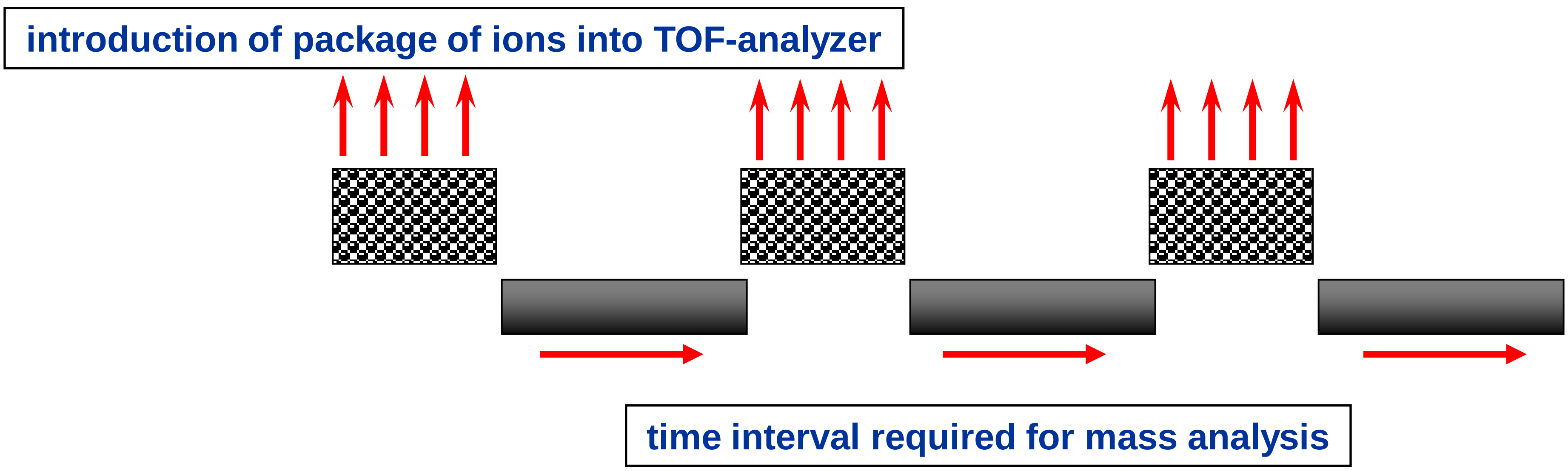
$$E_{kin} = \frac{1}{2}mv^2 = qV = constant$$

$$v = \sqrt{2\frac{qV}{m}} \quad and \quad t_{flight} = \frac{L}{v}$$

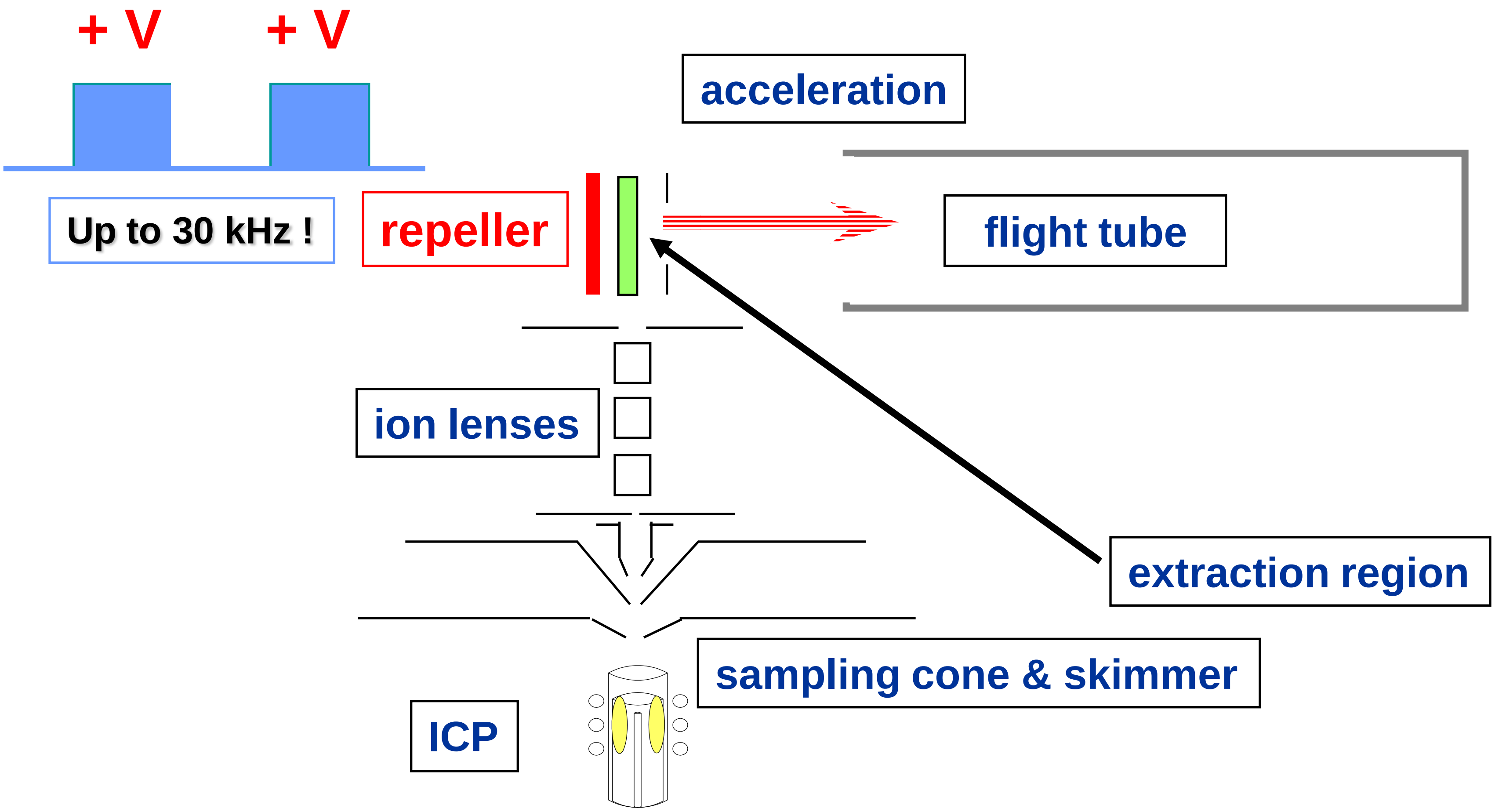
$$t_{flight} = \frac{L\sqrt{m}}{\sqrt{2qV}}$$

USE OF TOF-ANALYZER IN ICP-MS

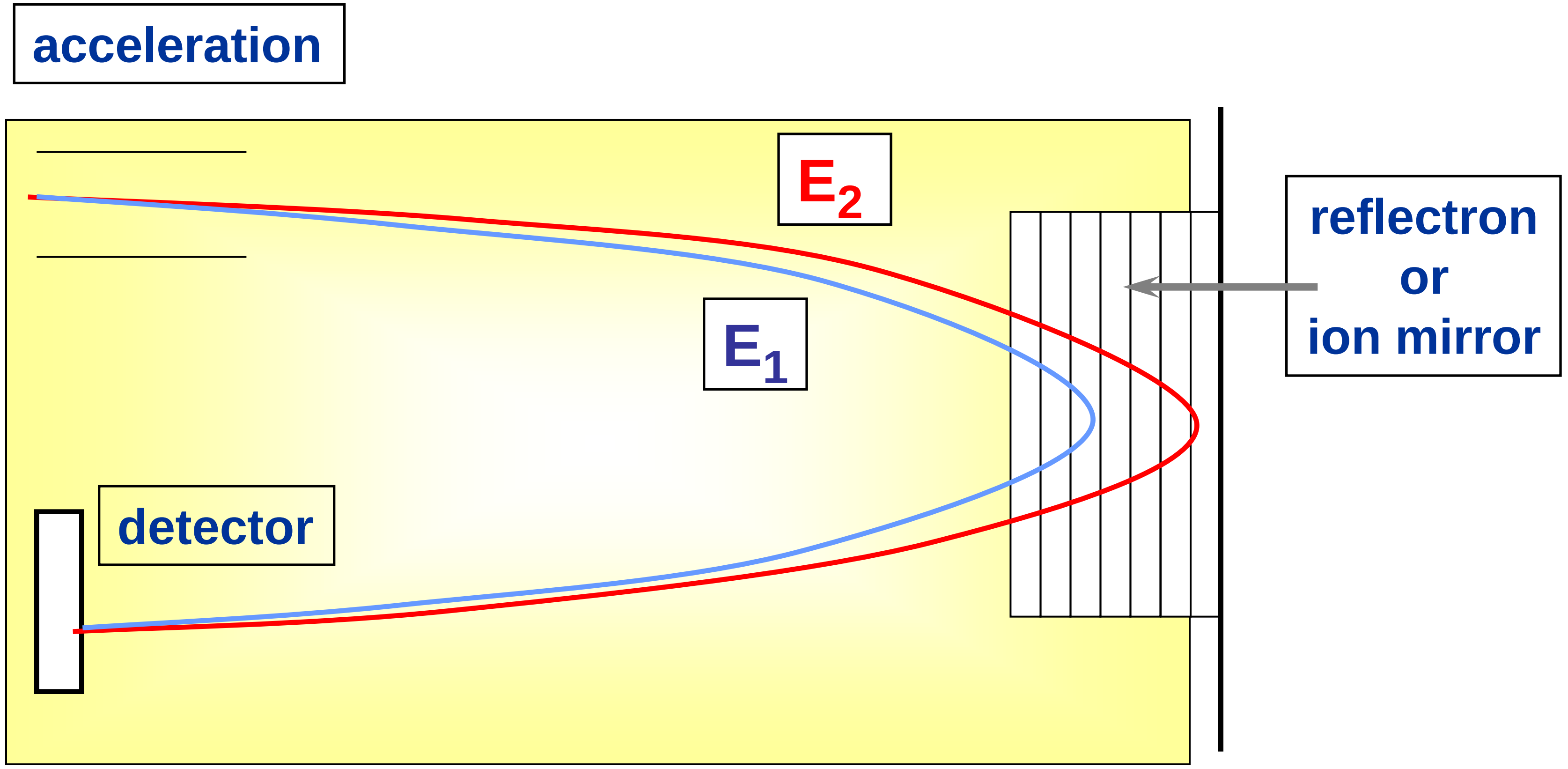
- ***Ions have to be introduced pulse-wise (no continuous introduction)***
  - ***Otherwise: simultaneous arrival at detector of***
    - ***heavy ion introduced at t & lighter ion introduced at t + Δt***
    - ***ICP = continuous ion source***
  - ***beam modulation required***



ORTHOGONAL ACCELERATION AS A MEANS OF BEAM MODULATION



USE OF ION MIRROR (REFLECTRON) IN TOF-ICP-MS TO IMPROVE MASS RESOLUTION

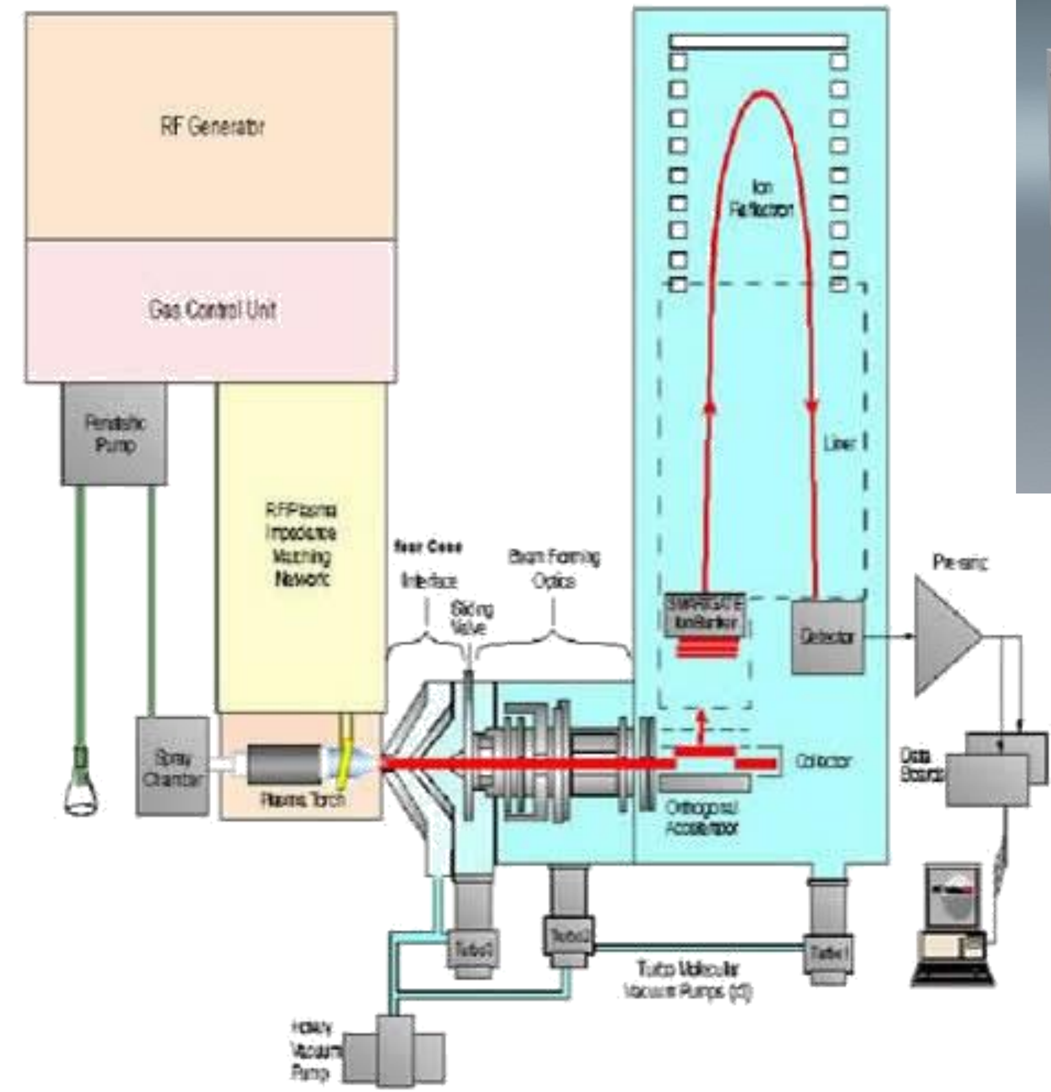


ion, mass m, E_2

ion, mass m, E_1

$E_2 > E_1$

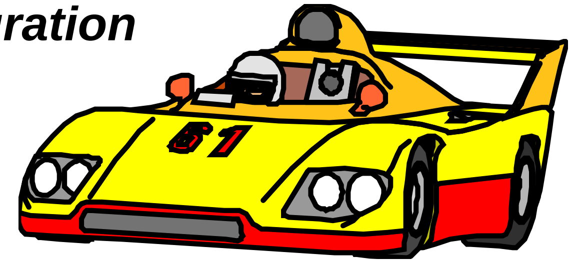
ORTHOGONAL ACCELERATION AS A MEANS OF BEAM MODULATION



GBC OptiMass 9500
ICP-TOF-MS

FIGURES OF MERIT OF TOF-ICP-MS

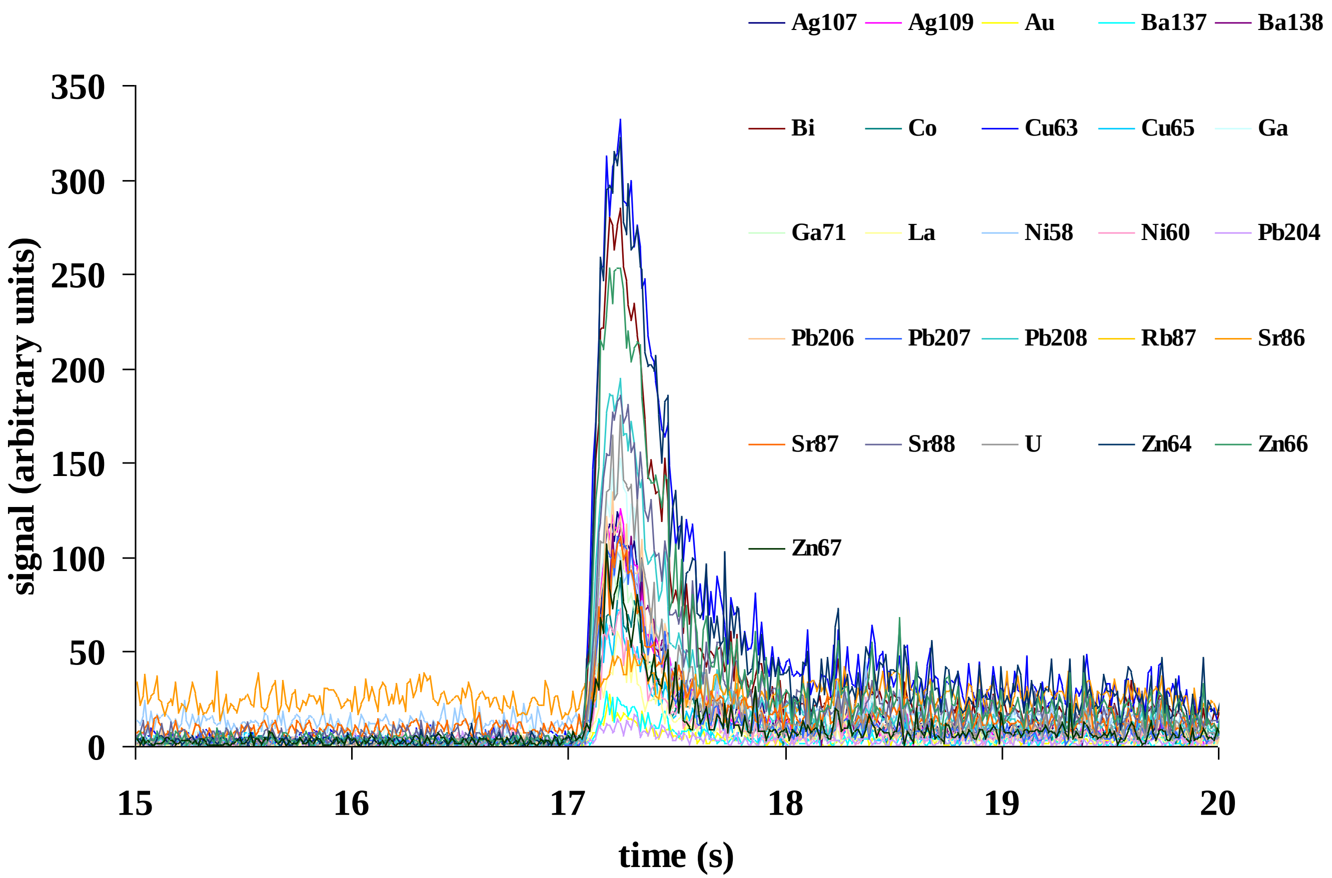
- *Simultaneous handling of ions extracted from ICP*
- *Fast + pronounced multi-element capabilities*
  - *up to 30,000 full mass spectra per second*
  - *well-suited for transient signals with short duration*
    - *ETV-ICP-MS*
    - *LA-ICP-MS*
    - *GC-ICP-MS*



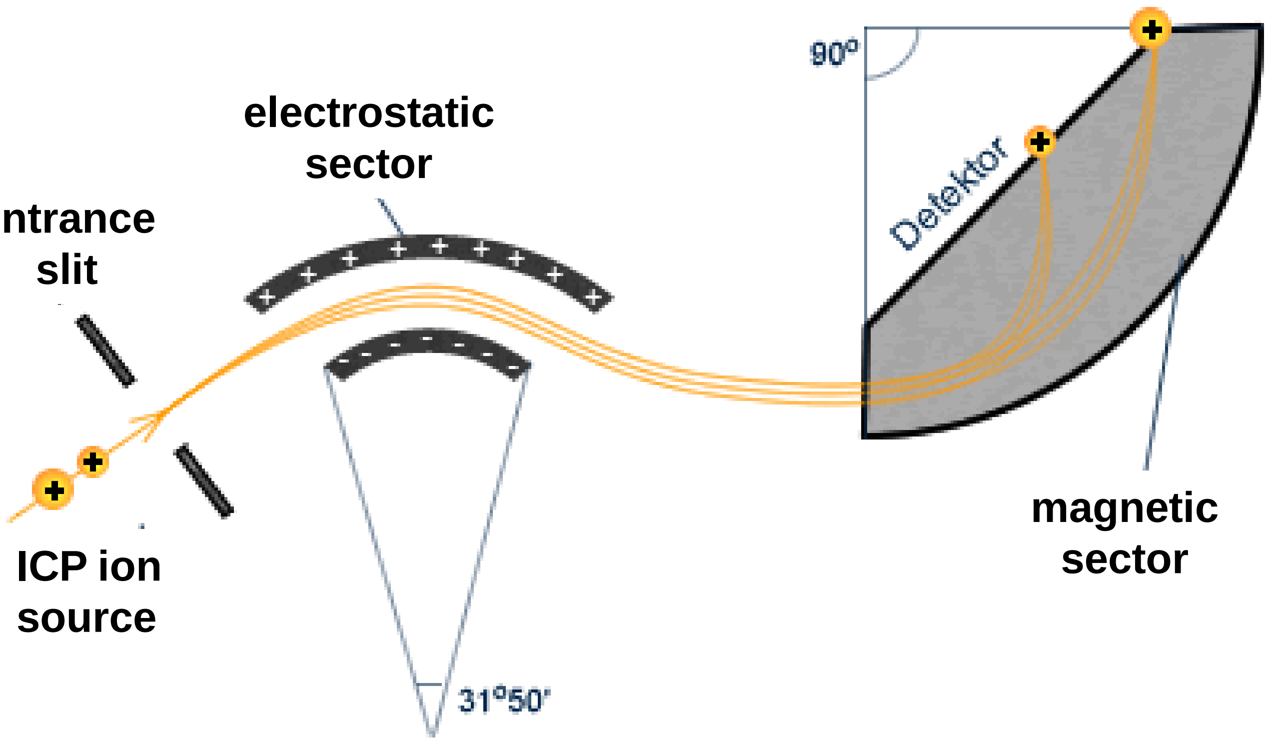
- *Sensitivity & LODs*
  - *inferior to ICP-QMS*
- *Other figures of merit*
  - *Unit mass resolution or better*
  - *similar to ICP-QMS in many ways*
- *No commercial success (so far) …*

FIGURES OF MERIT OF TOF-ICP-MS

- ***Most promising for LA-ICP-MS applications***
  - ***e.g., single-shot analysis of NIST SRM 612 glass (FWHM = 0.30 s)***



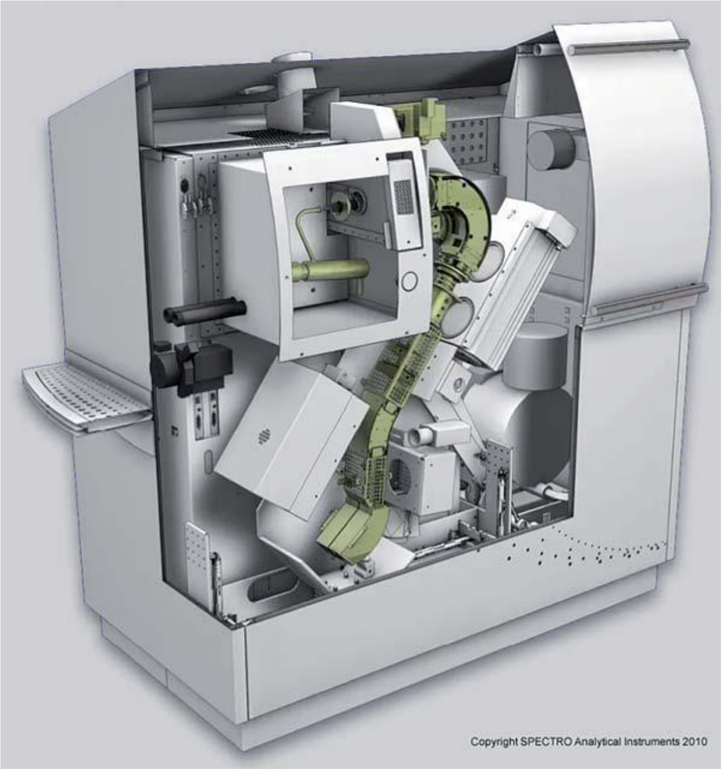
DOUBLE-FOCUSING SECTOR FIELD MS OF MATTAUCH-HERZOG GEOMETRY



- *All ion beams focused in one focal plane*
  - *Detector with 4800 miniaturized semi-conductor based detectors*
  - *Simultaneous monitoring of entire elemental mass spectrum (Li to U)*

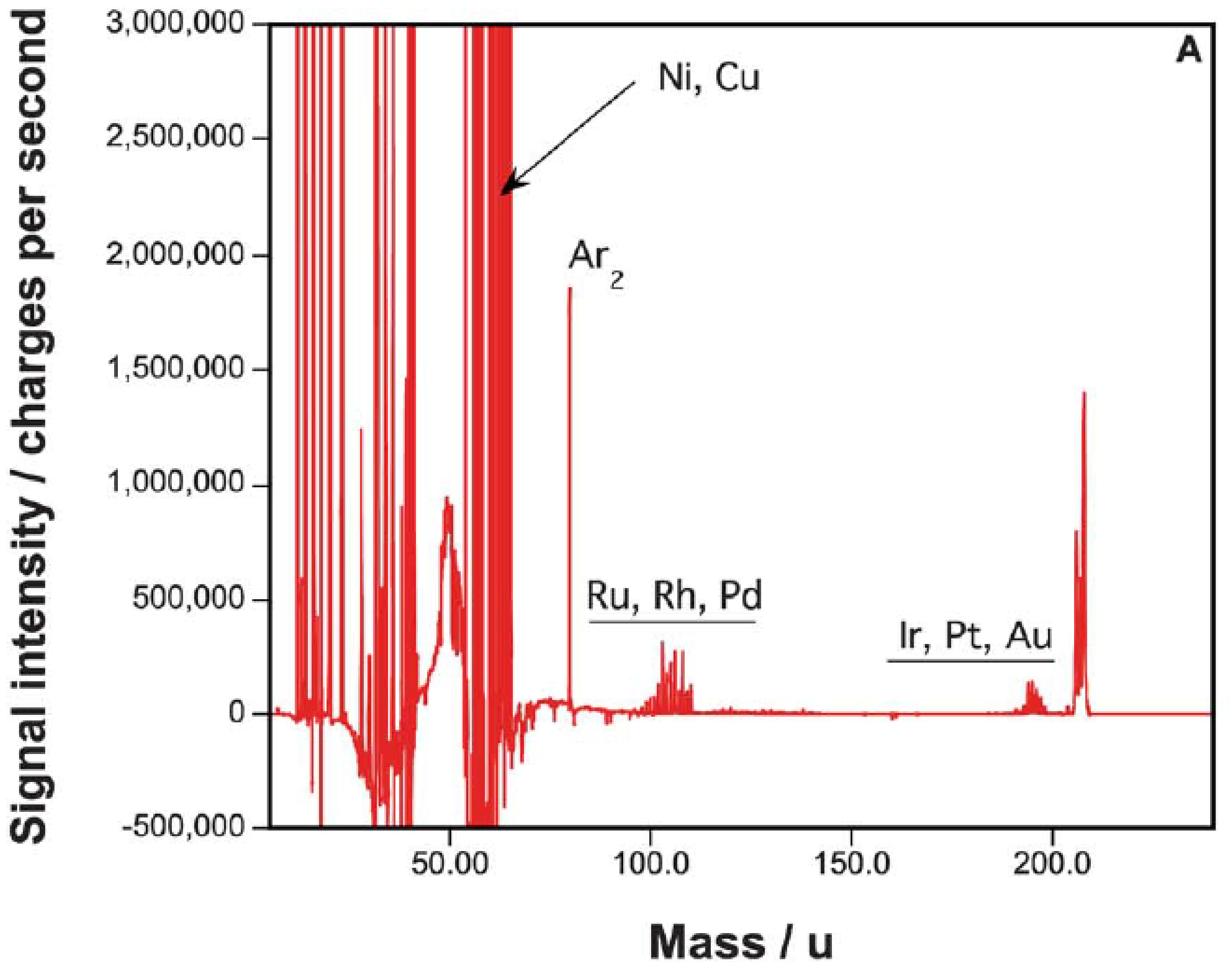
DOUBLE-FOCUSING SECTOR FIELD MS OF MATTAUCH-HERZOG GEOMETRY

- ***Introduced commercially @ Pittcon-2010 by Spectro***



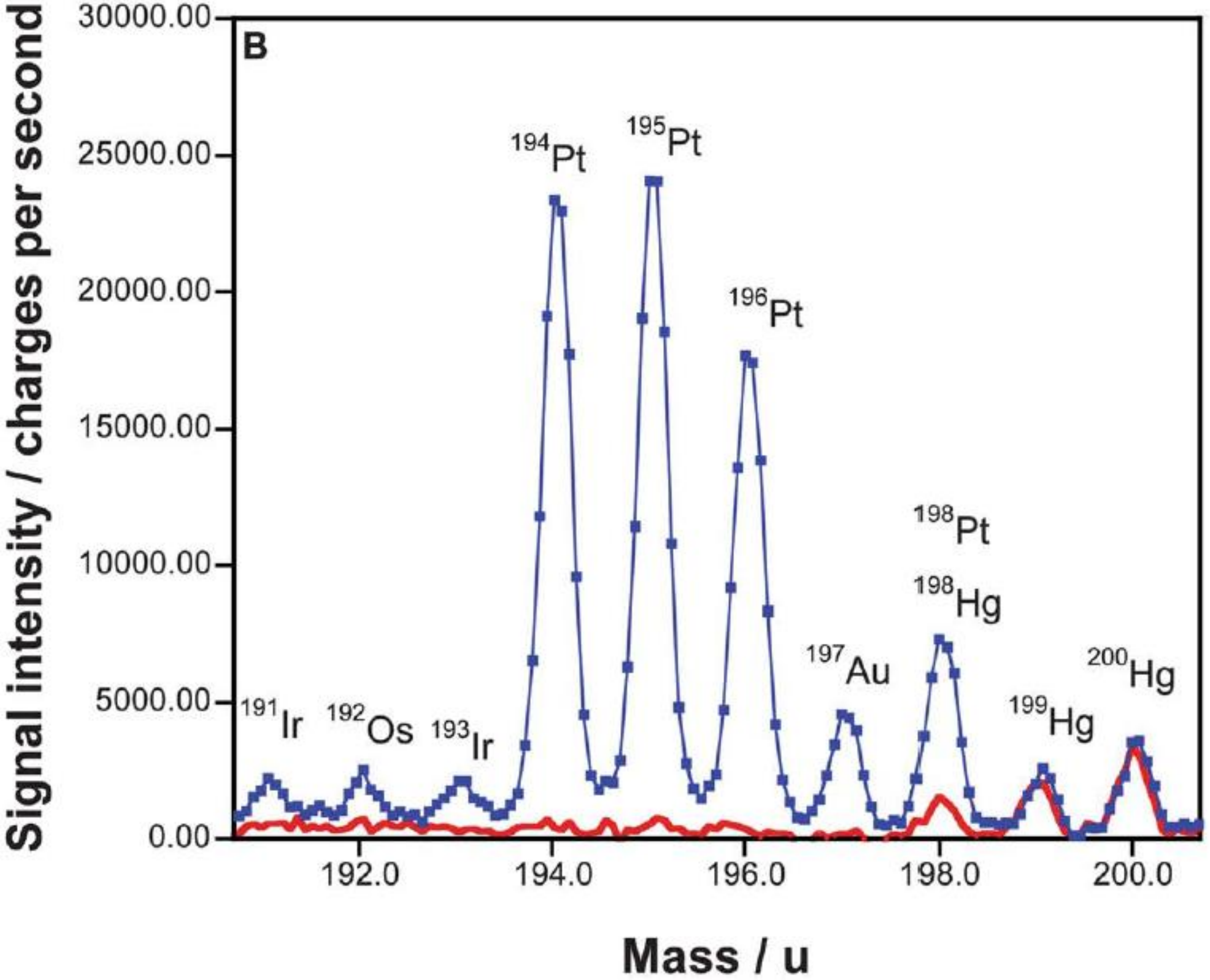
DOUBLE-FOCUSING SECTOR FIELD MS OF MATTAUCH-HERZOG GEOMETRY

- ***Simultaneous monitoring of entire elemental mass spectrum***

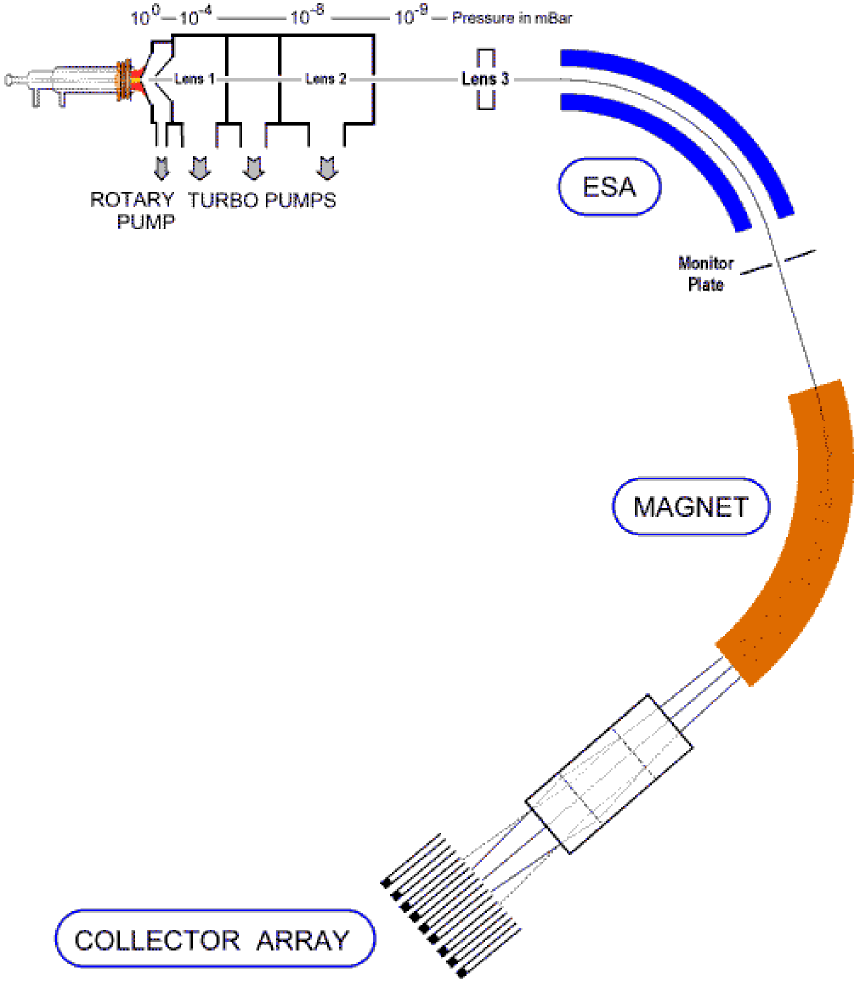


DOUBLE-FOCUSING SECTOR FIELD MS OF MATTAUCH-HERZOG GEOMETRY

- ***Simultaneous monitoring of entire elemental mass spectrum***



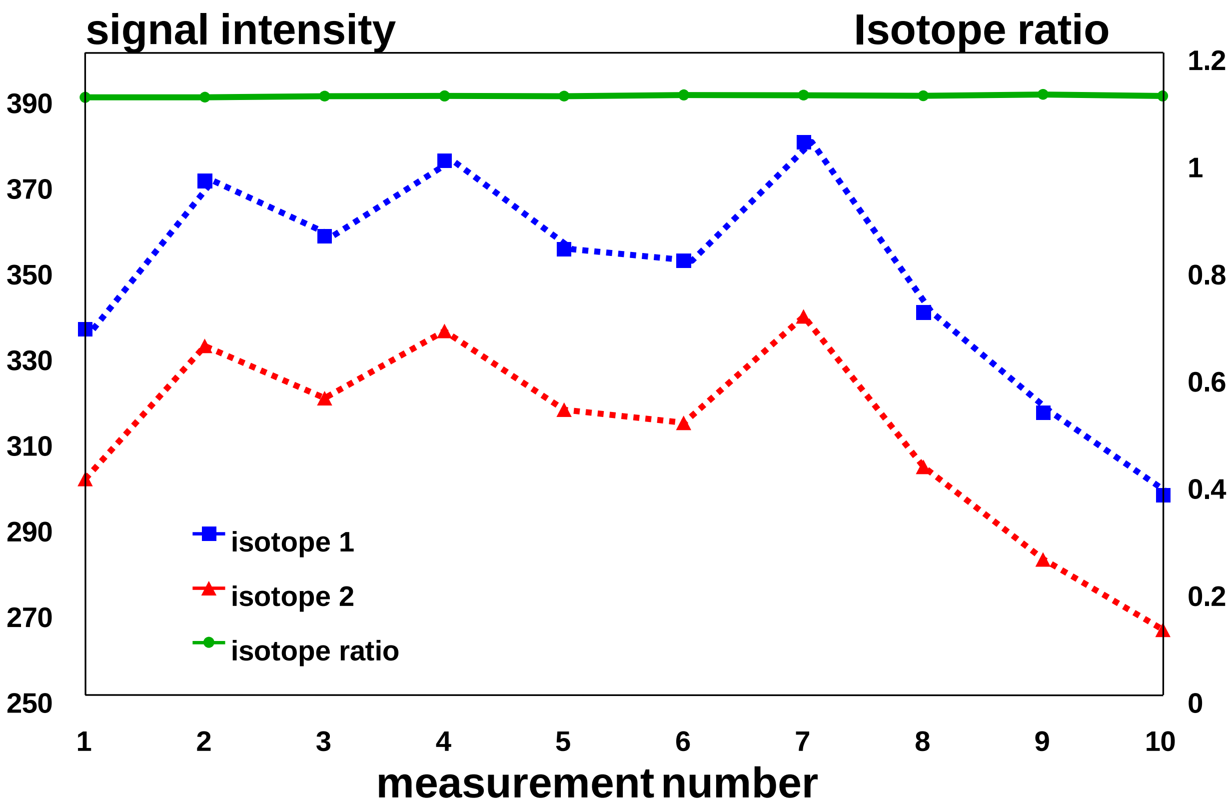
MULTI-COLLECTOR ICP-MS
A DEDICATED TOOL FOR ISOTOPIC ANALYSIS



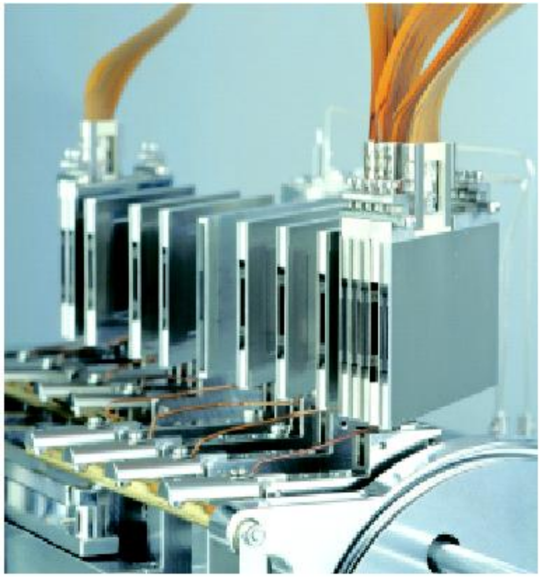
Isotope ratio precision:

down to 0,002 % RSD !

ARRAY OF FARADAY COLLECTORS: SIMULTANEOUS MONITORING OF ION SIGNAL INTENSITIES



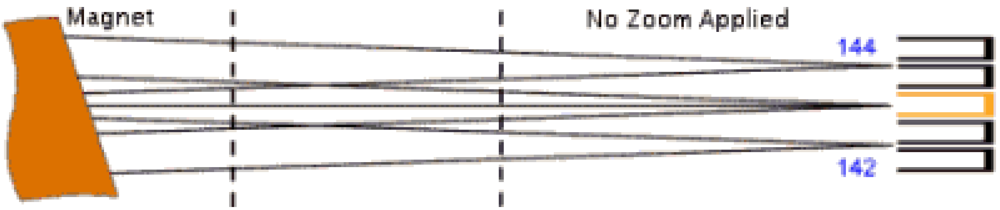
Isotope ratio precision: down to 0,002 % RSD !



- ***Simultaneous monitoring:***
  - ***Automatic correction for signal instability & signal drift***
  - ***Higher isotope ratio precision***
- ***With ICP-MS instrument equipped with only one detector:***
  - ***Mimicked by fast 'hopping'***

ION BEAMS → FARADAY COLLECTORS ?

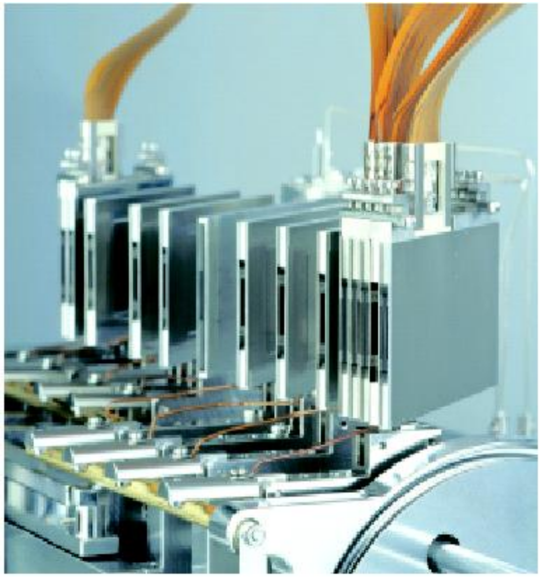
Zoom optics



The ion beams are steered into the appropriate collectors by applying suitable voltages on the zoom "optics" (= electrostatic lenses).

Moveable detectors

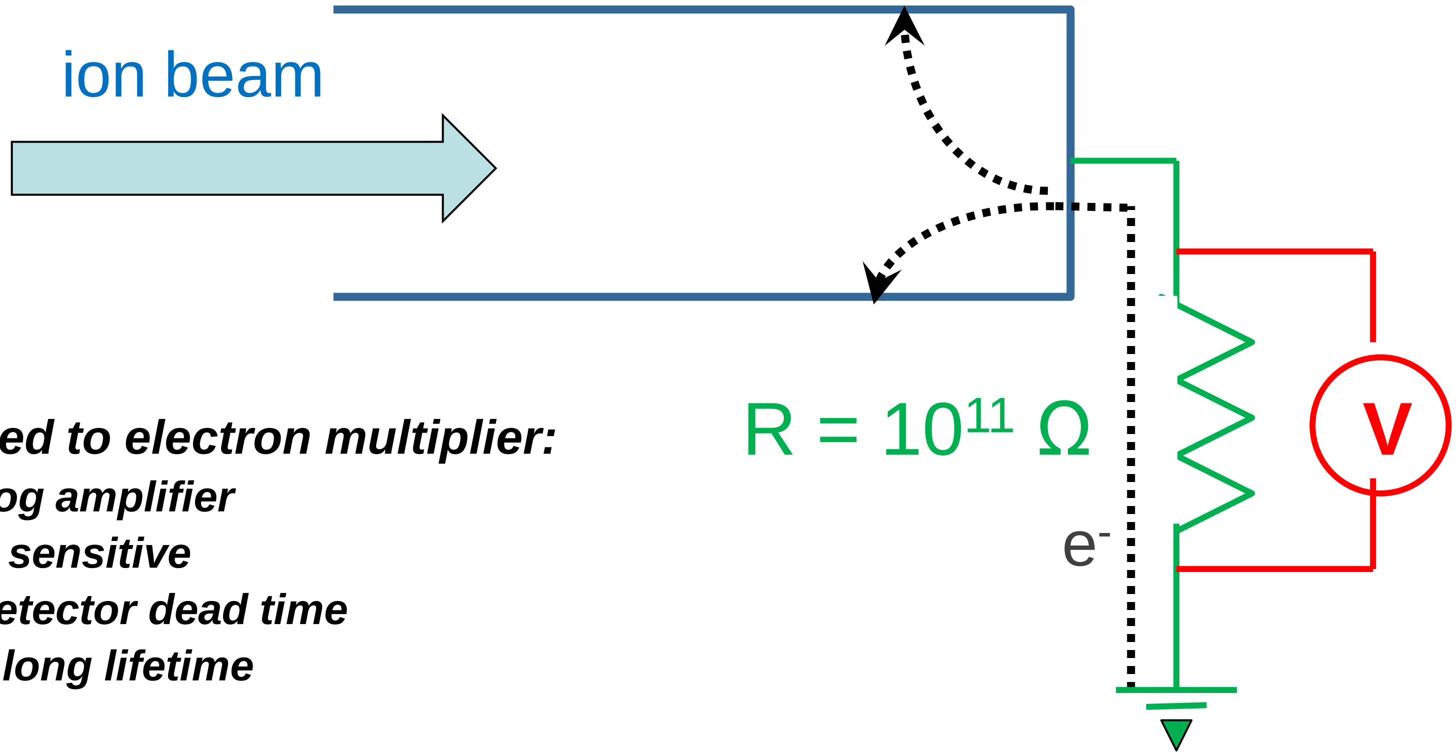
(motorized)



The position of the Faraday collectors can be optimised with respect to the respective ion beams

Or a combination of both …

FARADAY COLLECTOR – OPERATING PRINCIPLE



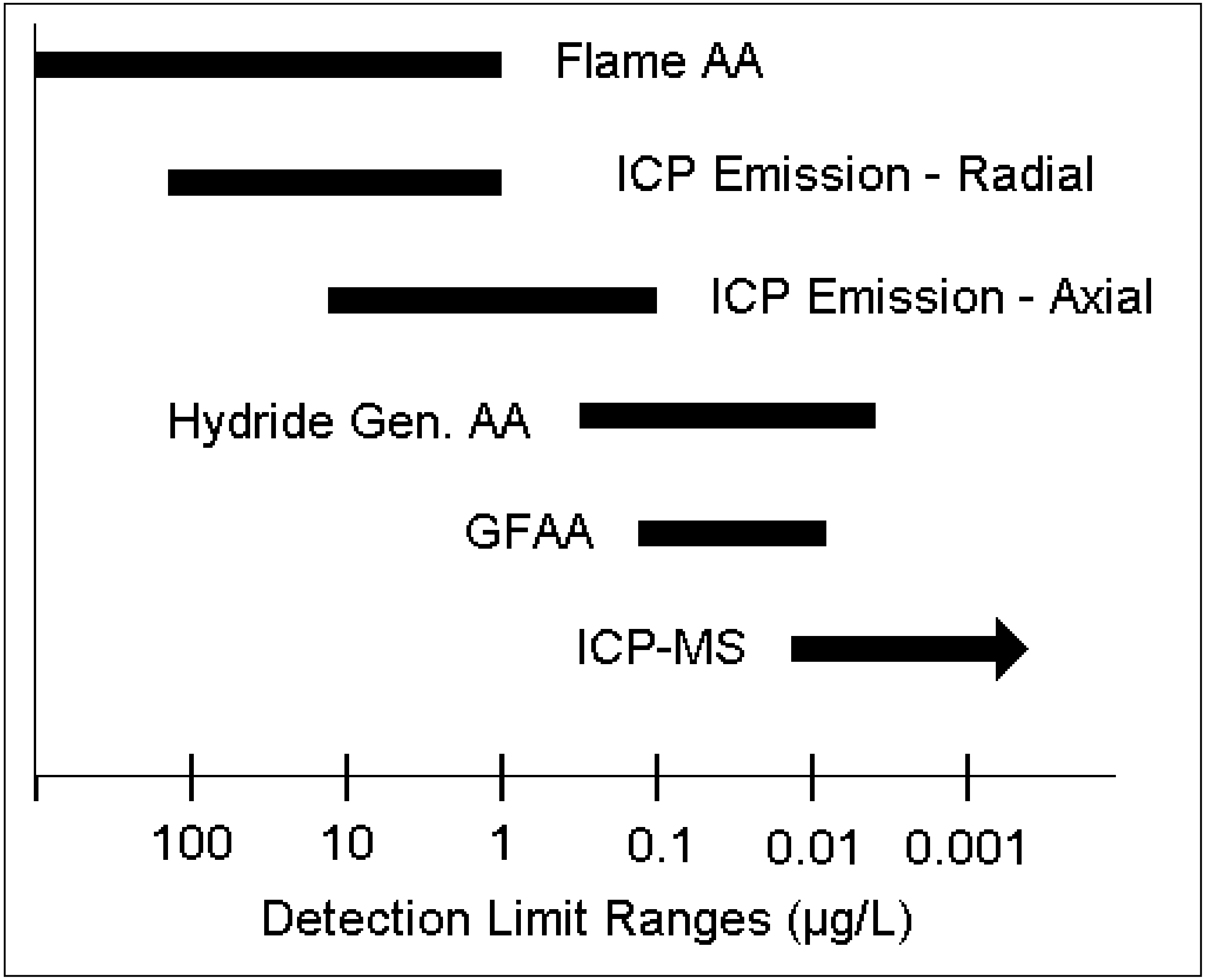
- ***Compared to electron multiplier:***
  - ***Analog amplifier***
  - ***Less sensitive***
  - ***No detector dead time***
  - ***Very long lifetime***

ICP-MS
FIGURES OF MERIT

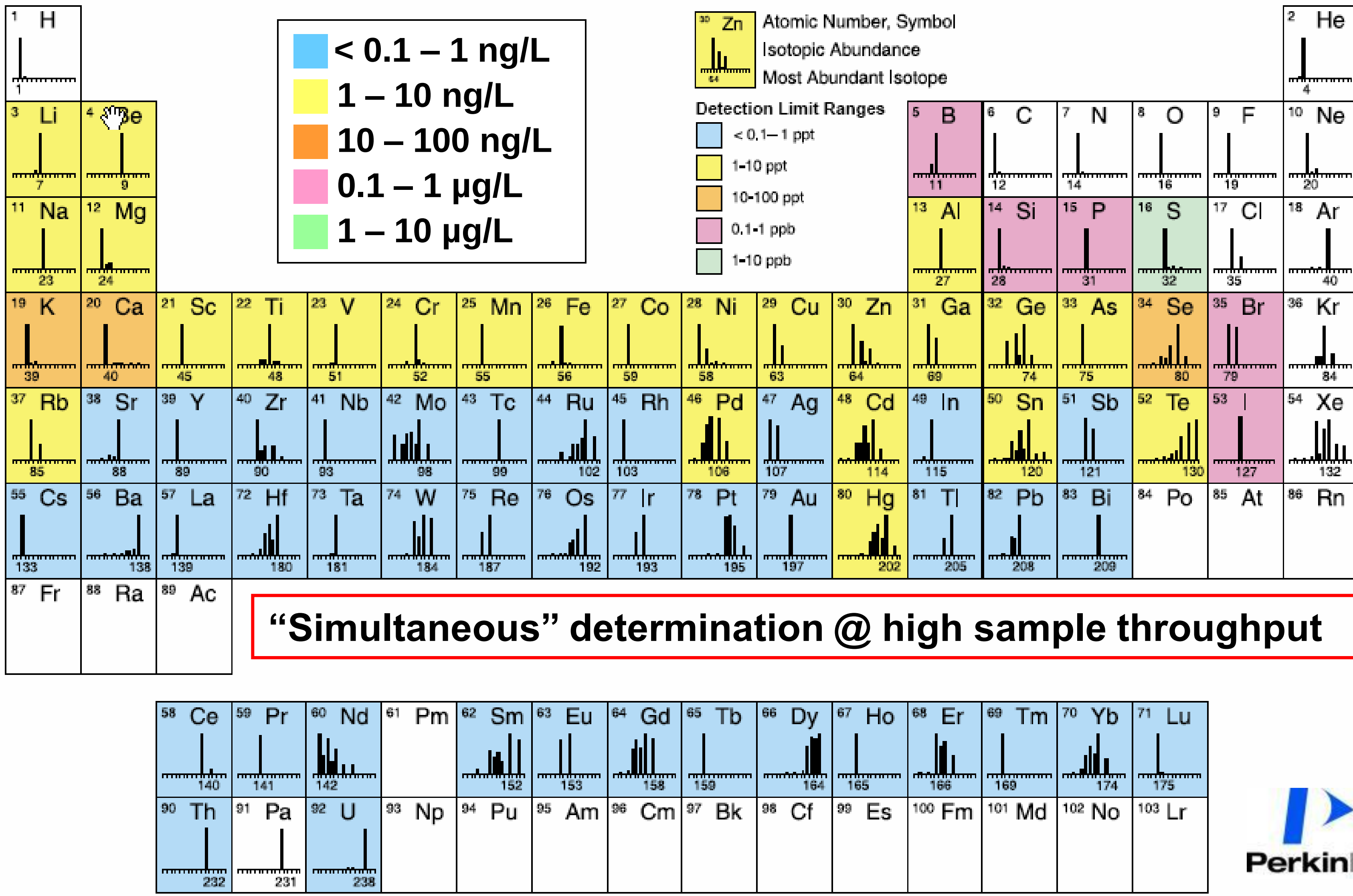
UNIVERSITEIT GENT

FIGURES OF MERIT OF ICP-MS
LIMITS OF DETECTION - LODS

- ***Lowest detection limits attainable***

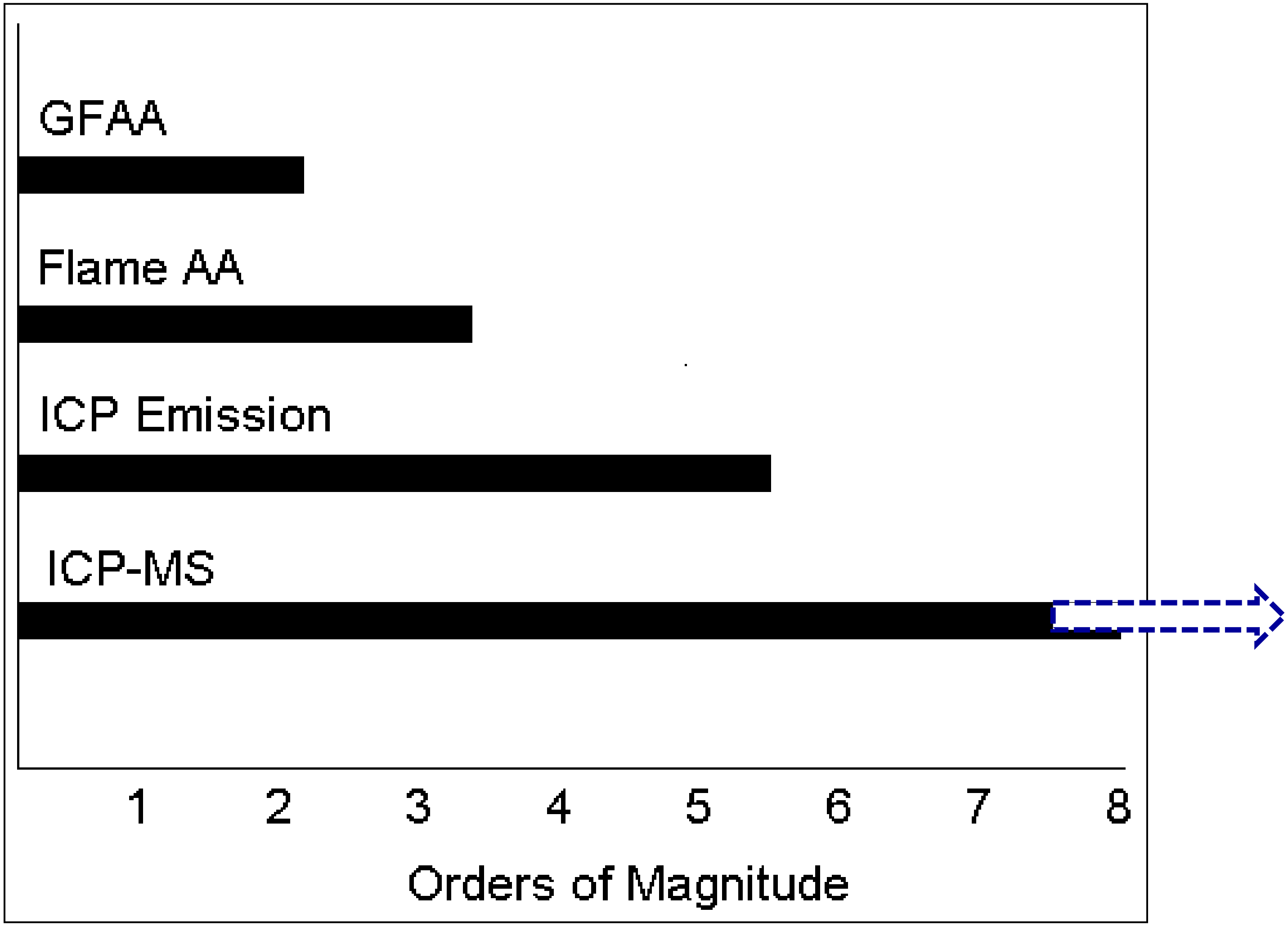


QUADRUPOLE-BASED ICP-MS
LIMITS OF DETECTION – LODS



PerkinElmer

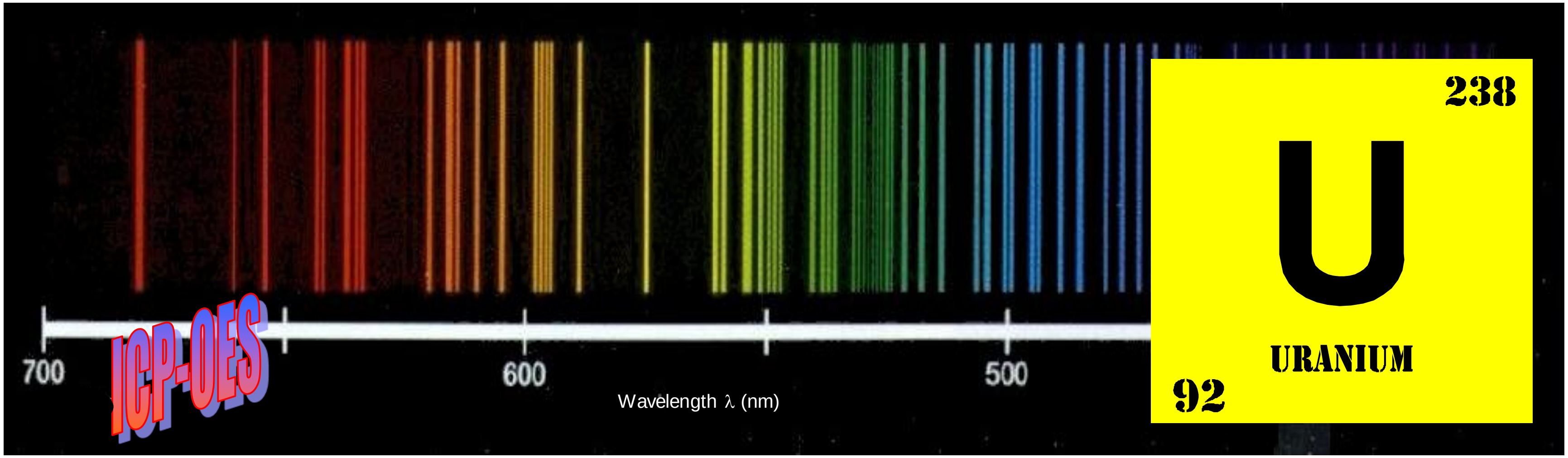
Figures of merit of ICP-MS
Linear dynamic range

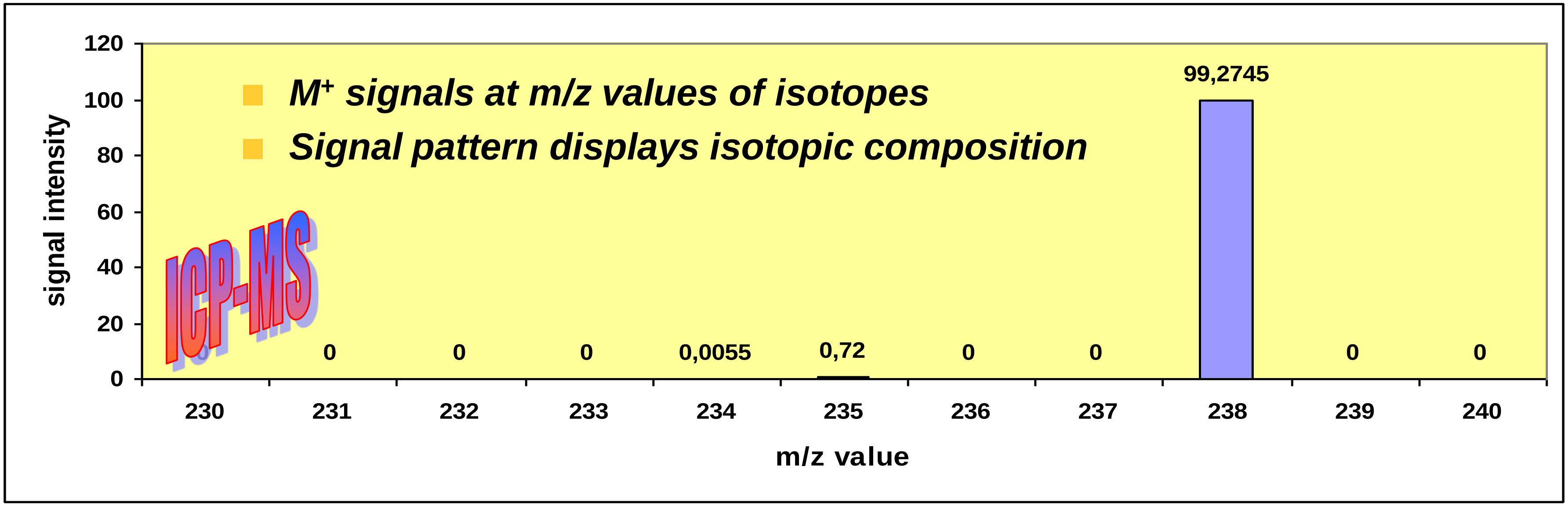


Dual mode electron multiplier (pulse counting vs. analog mode)

ADVANTAGES OF ICP-MS

RELATIVELY SIMPLE MASS SPECTRA

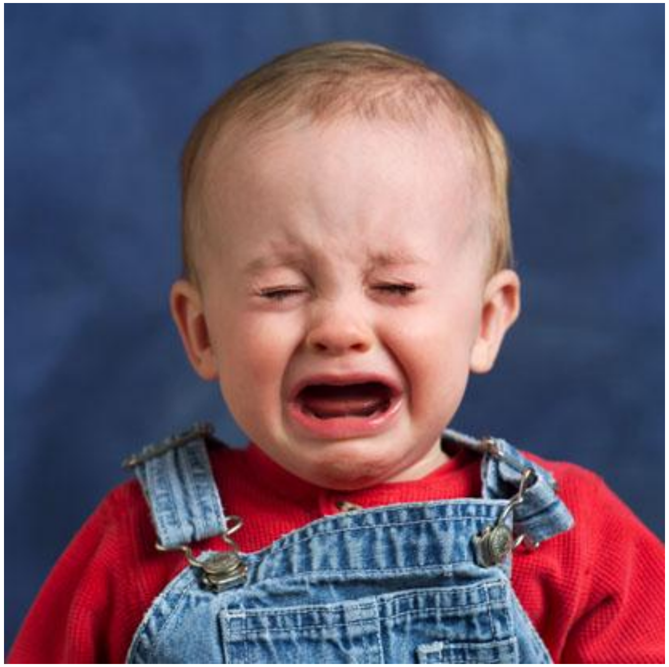




ADVANTAGES OF ICP-MS

- ***Low limits of detection***
- ***Multi-element capabilities***
- ***Wide linear dynamic range***
- ***High sample throughput***
- ***Relatively simple spectra***
- ***Ease of combination with***
  - ***Alternative sample introduction systems***
  - ***Chromatographic separation techniques***
- ***Ability to obtain isotopic information***

DISDVANTAGES OF ICP-MS



- **Purchase price**
  - **Quadrupole-based ICP-MS ~ 150,000 €**
  - **Sector field ICP-MS ~ 350,000 €**
  - **Multi-collector ICP-MS ~ 600.000 €**
- **Costs of operation**
  - **High purity Ar gas (20 L/min)**
  - **Consumables**
- **Spectral interferences**
  - **Collision/reaction cell in ICP-QMS**
  - **High mass resolution in ICP-SFMS**
  - **No solution in**
    - **TOF-ICP-MS**
    - **Mattauch-Herzog ICP-MS**

DISDVANTAGES OF ICP-MS
OPERATING COSTS (PER YEAR IN US $)

Technique	Gases	Power	Supplies	Total
Flame AA	2500	200	1300	4000
Furnace AA	200	400	5000	5600
ICP-OES	3500	1000	2300	6800
ICP-MS	3500	1000	11000	15500

Calculated taking into account an average of 4 hrs of operation / day = 1000 hrs / year