Ion Sources

Some characteristics of ion sources (especially in high precision work):

- It should have high efficiency in generating ions of the element of interest (or a range of elements).
- All of the ions should have the same energy.
- It should produce an ion beam with low divergence.
- The ions should be the same charge (preferably +1 for positive ions or -1 for negative ions) so we separate by mass and not m/q.
- The ion beam should be stable.
- The ion beam should have isotopic ratios the same as the sample.

Thermal Ionization MS

- Advantages
  - Extremely Stable
  - Generally less prone to isotopic fractionation effects than other sources
  - Thermalized ions (narrow energy range)
- Disadvantages
  - Complicated sample preparation
  - Incomplete isotope (elemental) coverage
    - » Inconsistent positive or negative ionization efficiencies across periodic table

Inductively Coupled Plasma MS

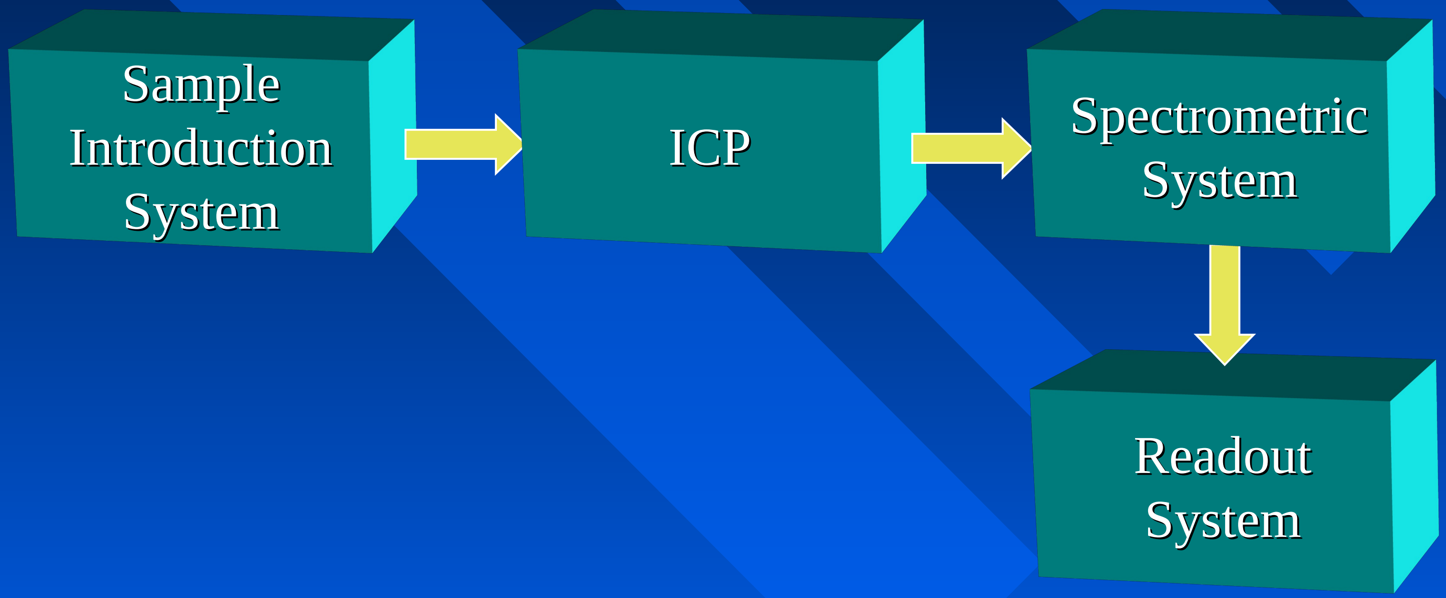
- Advantages
  - High sensitivity
  - Nearly complete isotope coverage
  - Liquid, solid or gas samples
  - Short analysis times
  - Less "art"

- Disadvantages
  - Isobaric interferences
  - Relatively noisy
  - Wide ion energy spread
  - Inefficient
  - Spectral complexity

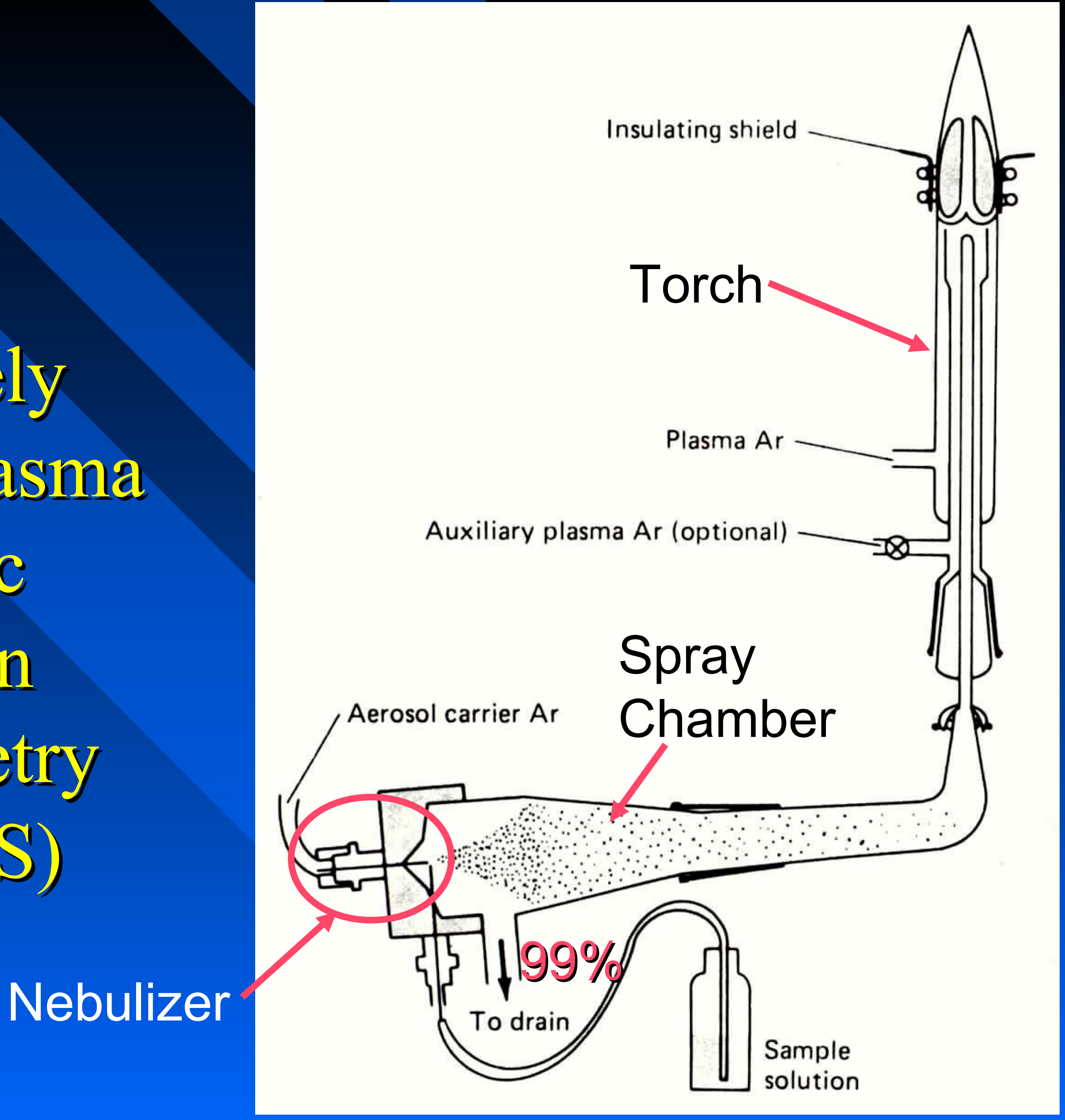
So what is the ICP?

- What equipment does it require?
- How does it operate?
- What are its features?
- How does it work with MS?

Basic ICP Instrument



Inductively Coupled Plasma - Atomic Emission Spectrometry (ICP-AES)



Types of ICP Nebulizers

- Concentric pneumatic
- Cross-flow pneumatic
- Ultrasonic (high sensitivity)
- High-solids (V-groove, Babington, etc.)
- .....

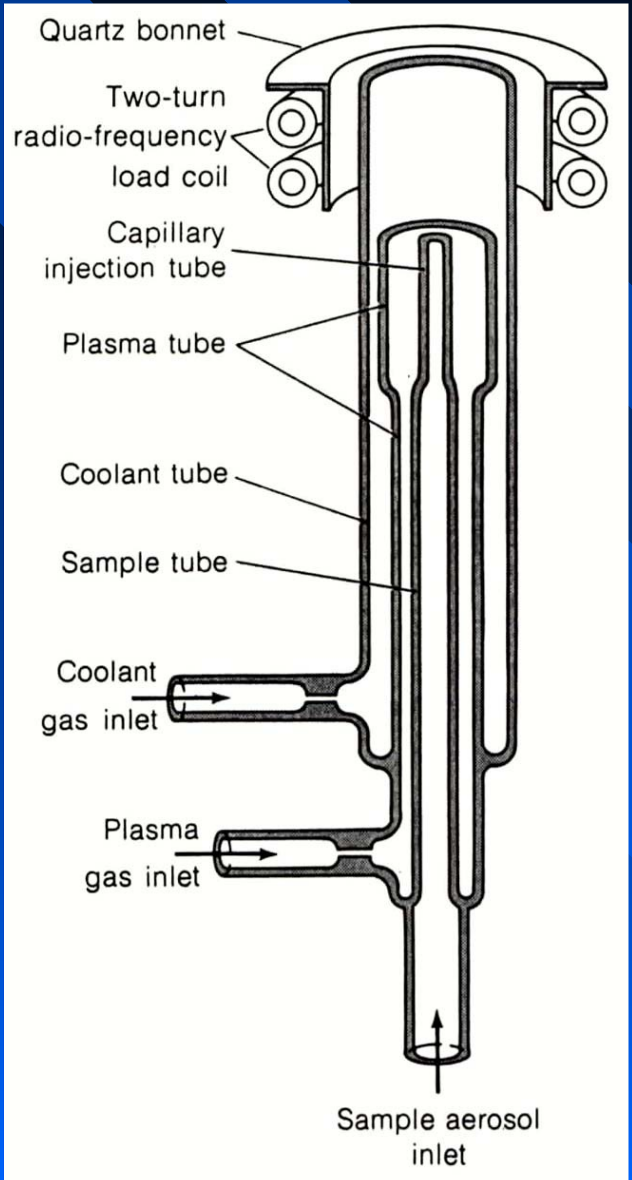
Types of ICP Spray Chambers

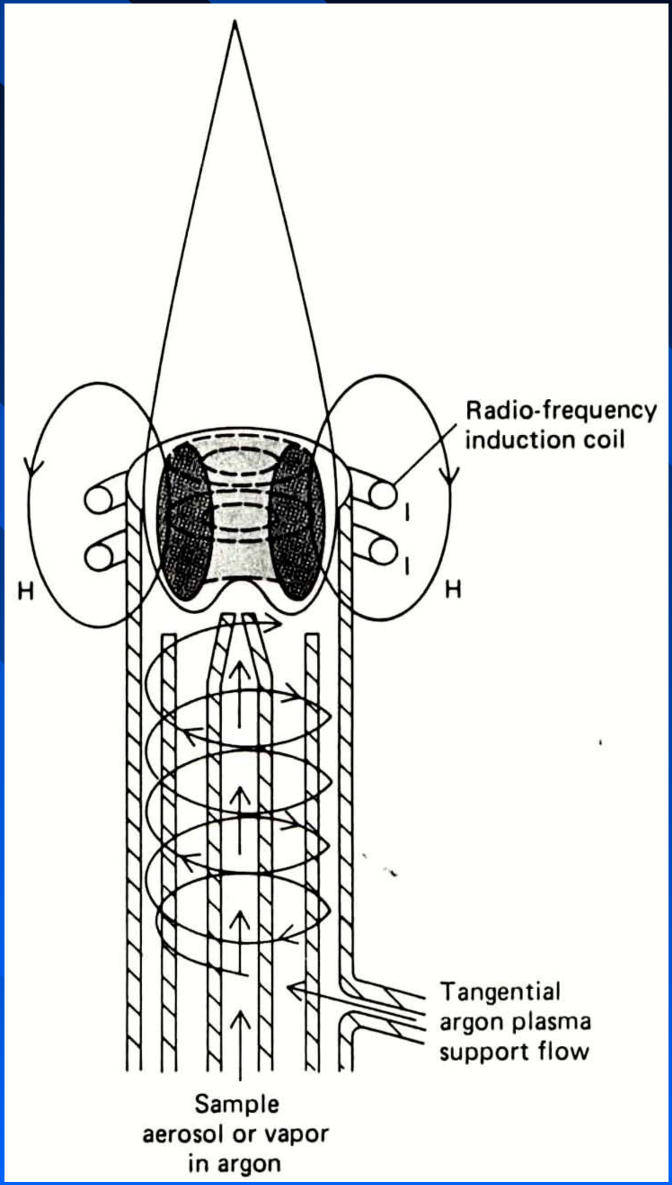
- Scott-type
- High-efficiency
- Cyclonic
- Desolvating
- …..

The Inductively Coupled Plasma

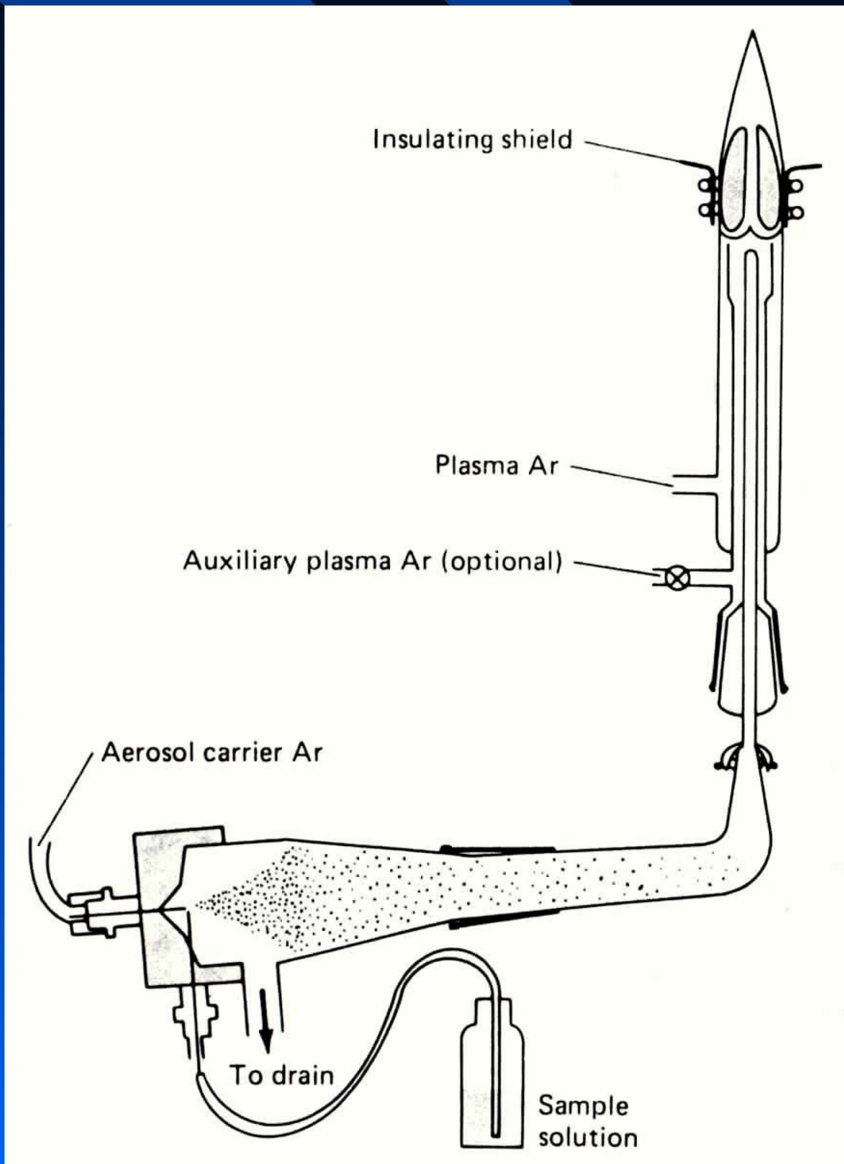
- A plasma is a hot, partially ionized gas.
- The ICP is an argon-based, radio frequency plasma.
- The input rf frequency is either 27 or 40 MHz at powers from 1 to 2 kW.
- The plasma is formed and contained in a three tube quartz touch.
- The temperature in the central analyte channel ranges from about 6000 to 8000° K.
- At these temperatures most elements are largely atomized and ionized

The ICP Torch and Plasma

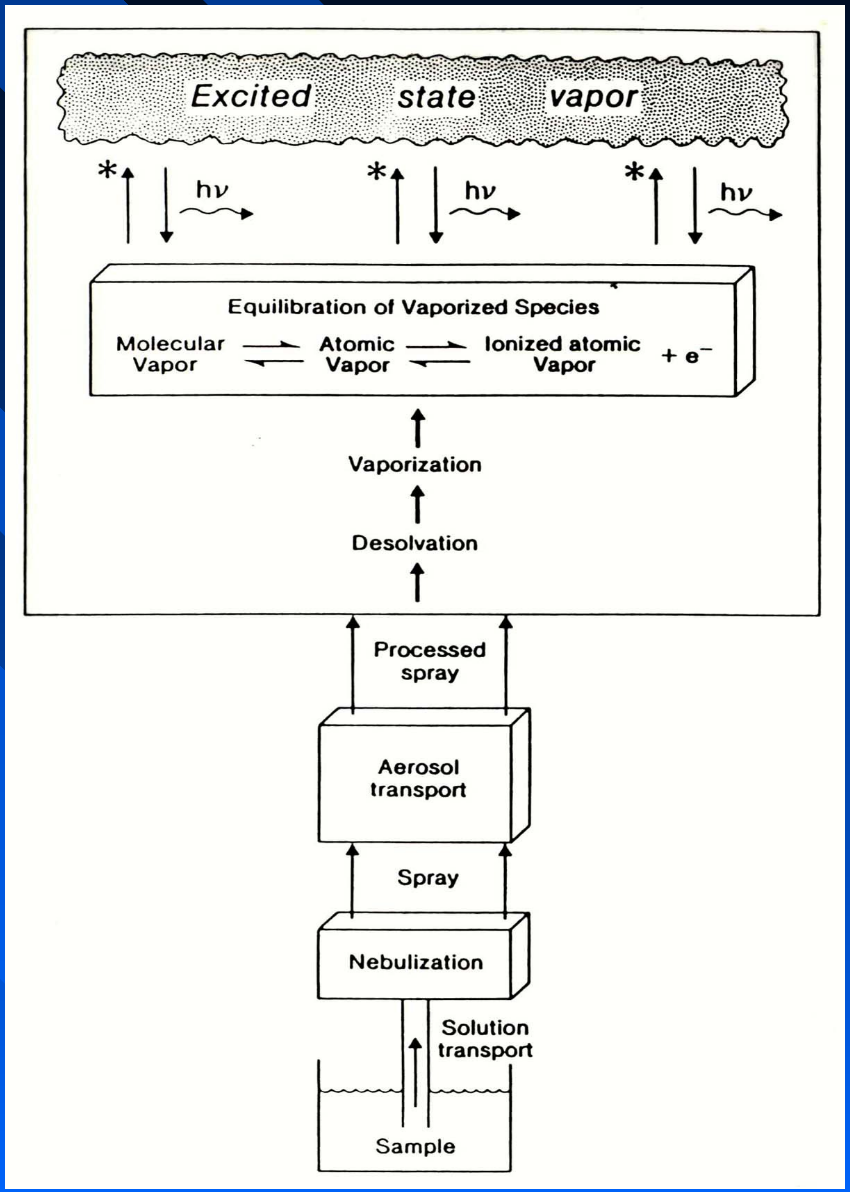




THE STEPS

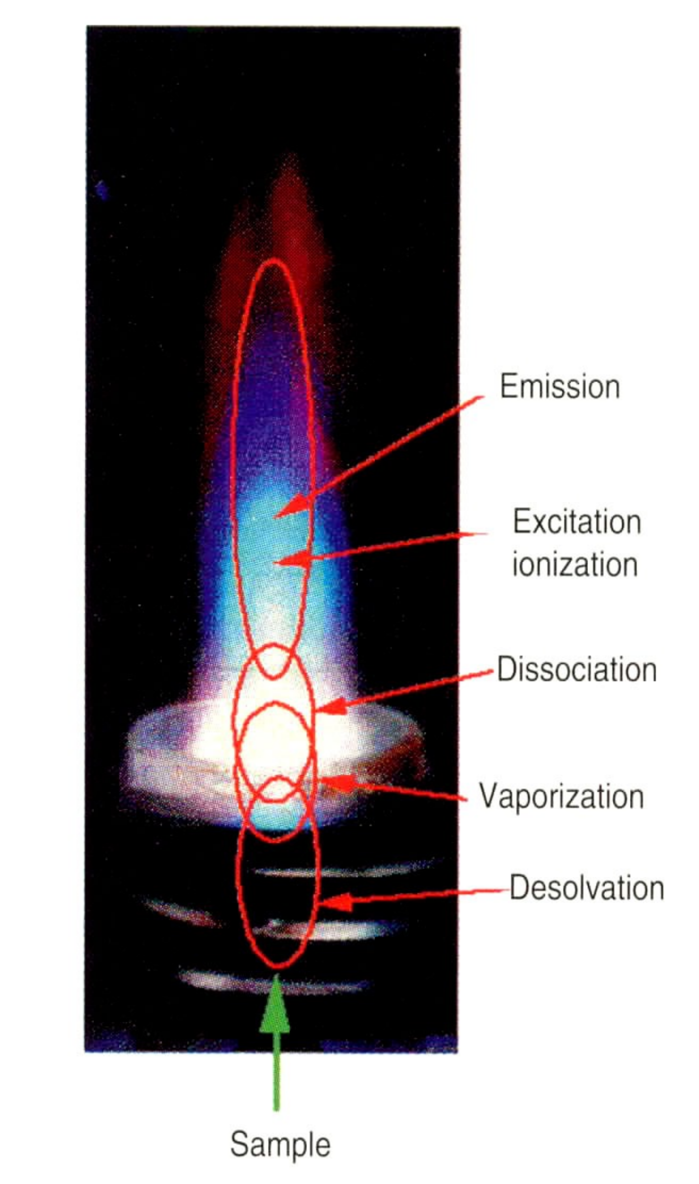


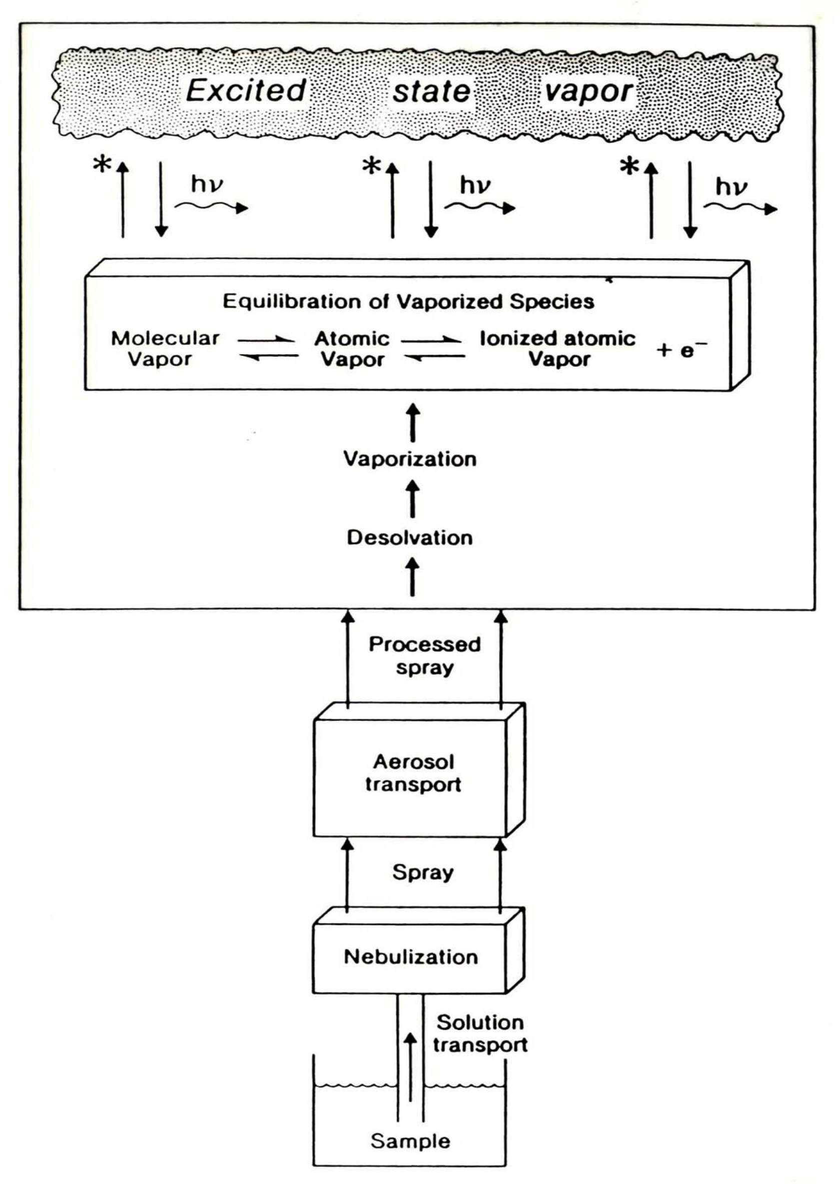
Insulating shield
Plasma Ar
Auxiliary plasma Ar (optional)
Aerosol carrier Ar
To drain
Sample solution



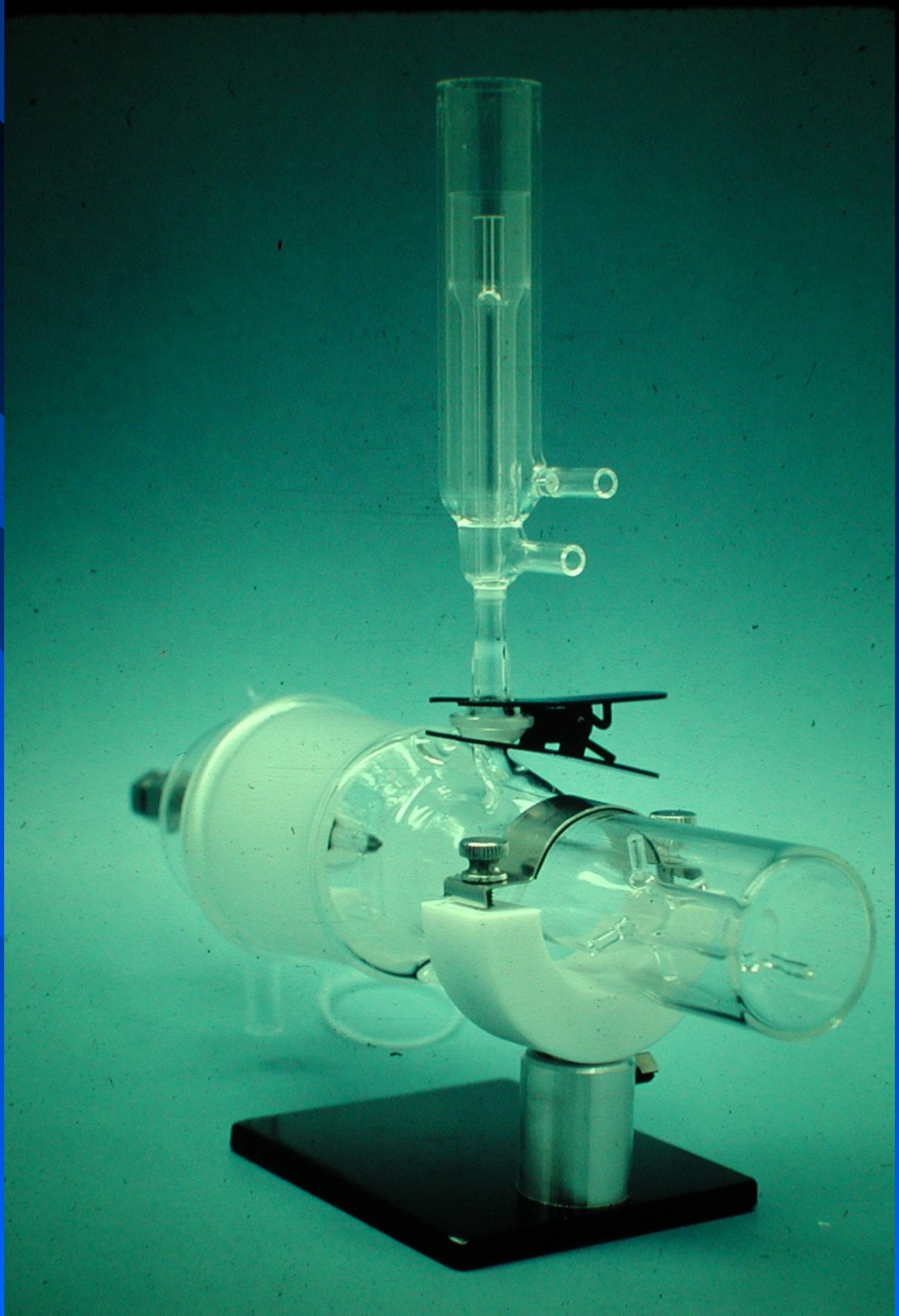
Excited state vapor
*
hν
Equilibration of Vaporized Species
Molecular Vapor
Atomic Vapor
Ionized atomic Vapor
+ e⁻
Vaporization
Desolvation
Processed spray
Aerosol transport
Spray
Nebulization
Solution transport
Sample

THE STEPS

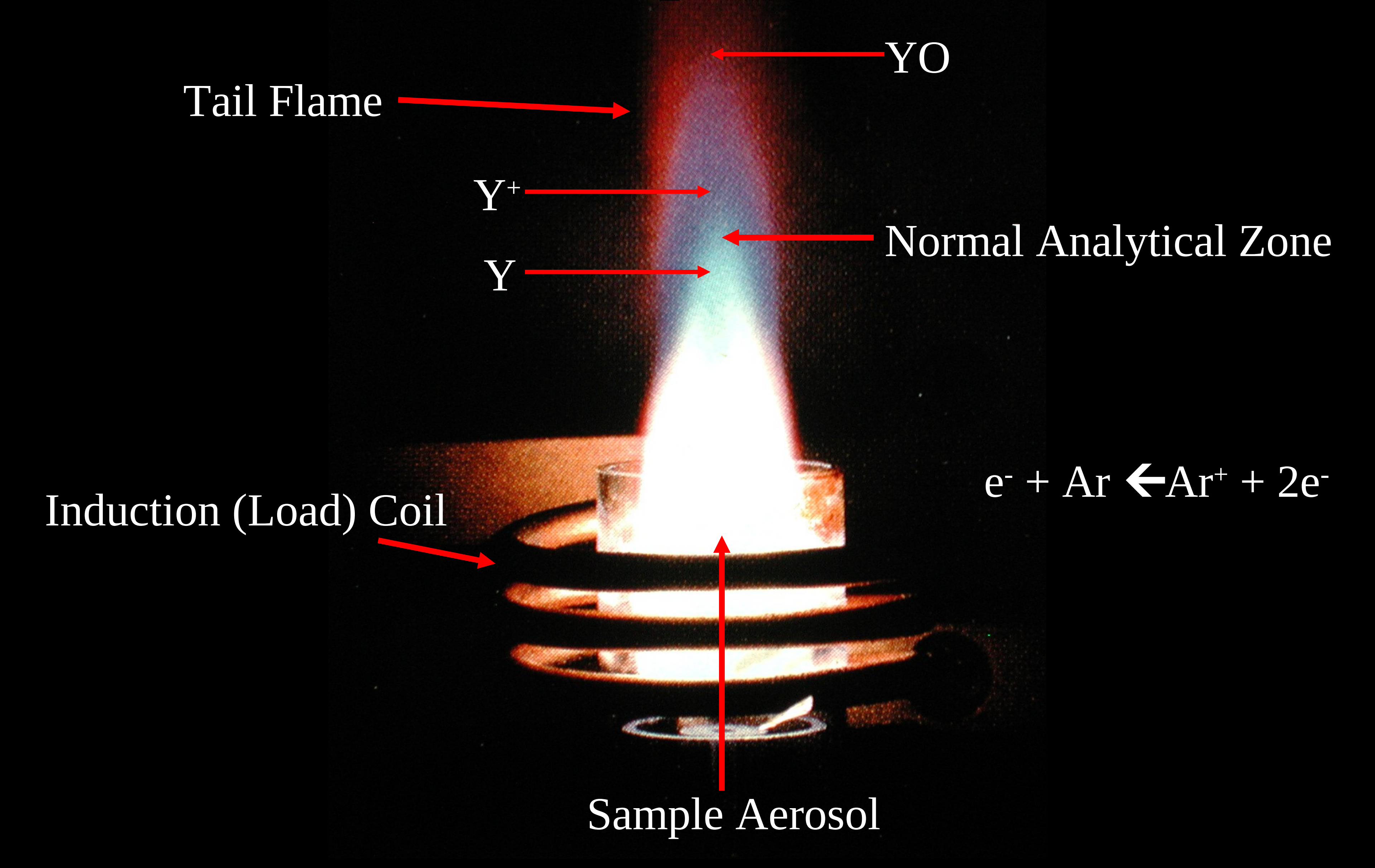

Emission
Excitation
ionization
Dissociation
Vaporization
Desolvation
Sample


Excited state vapor
*
hν
Equilibration of Vaporized Species
Molecular Vapor
Atomic Vapor
Ionized atomic Vapor
+ e⁻
Vaporization
Desolvation
Processed spray
Aerosol transport
Spray
Nebulization
Solution transport
Sample

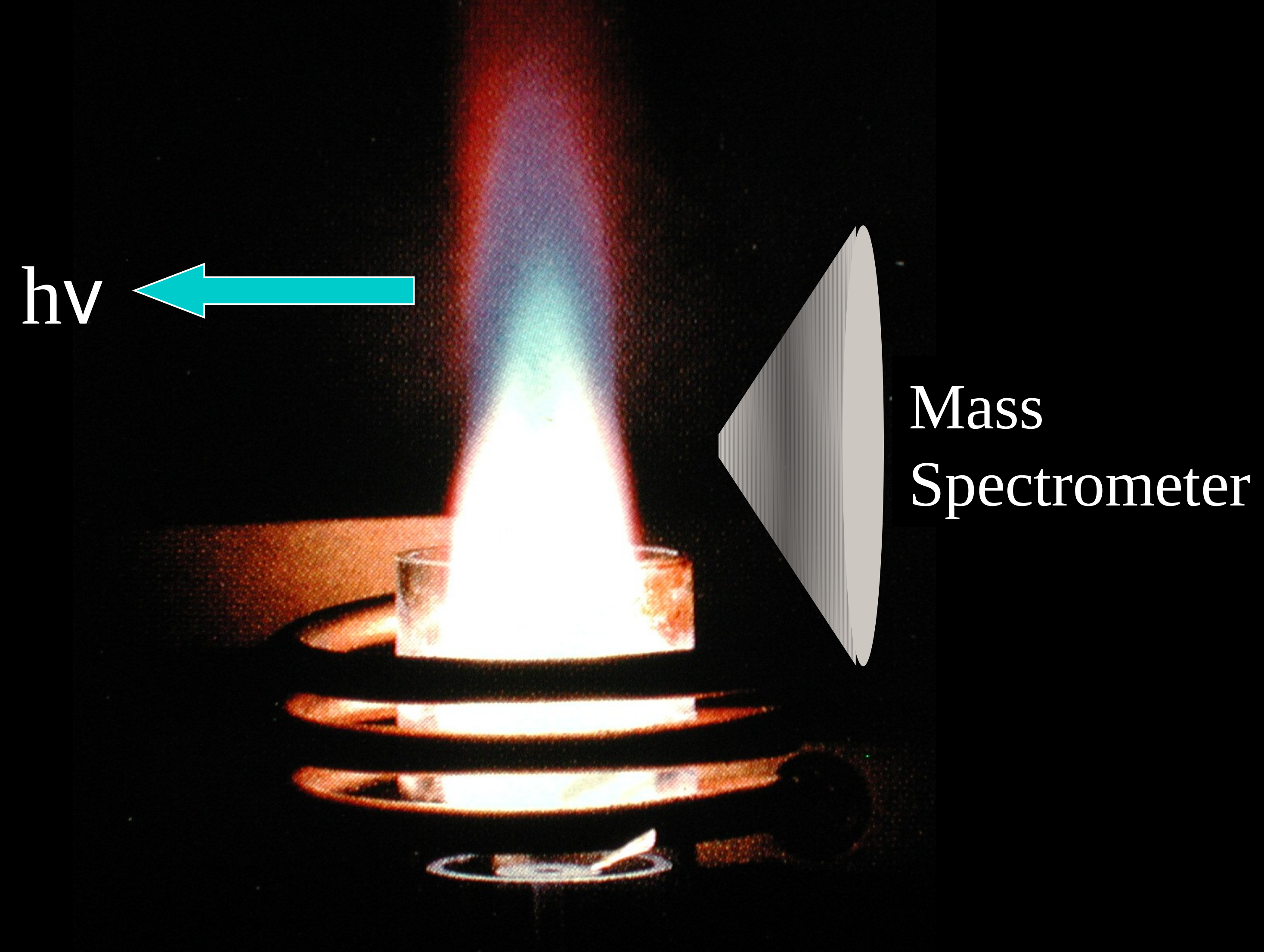
ICP torch, nebulizer, spray chamber



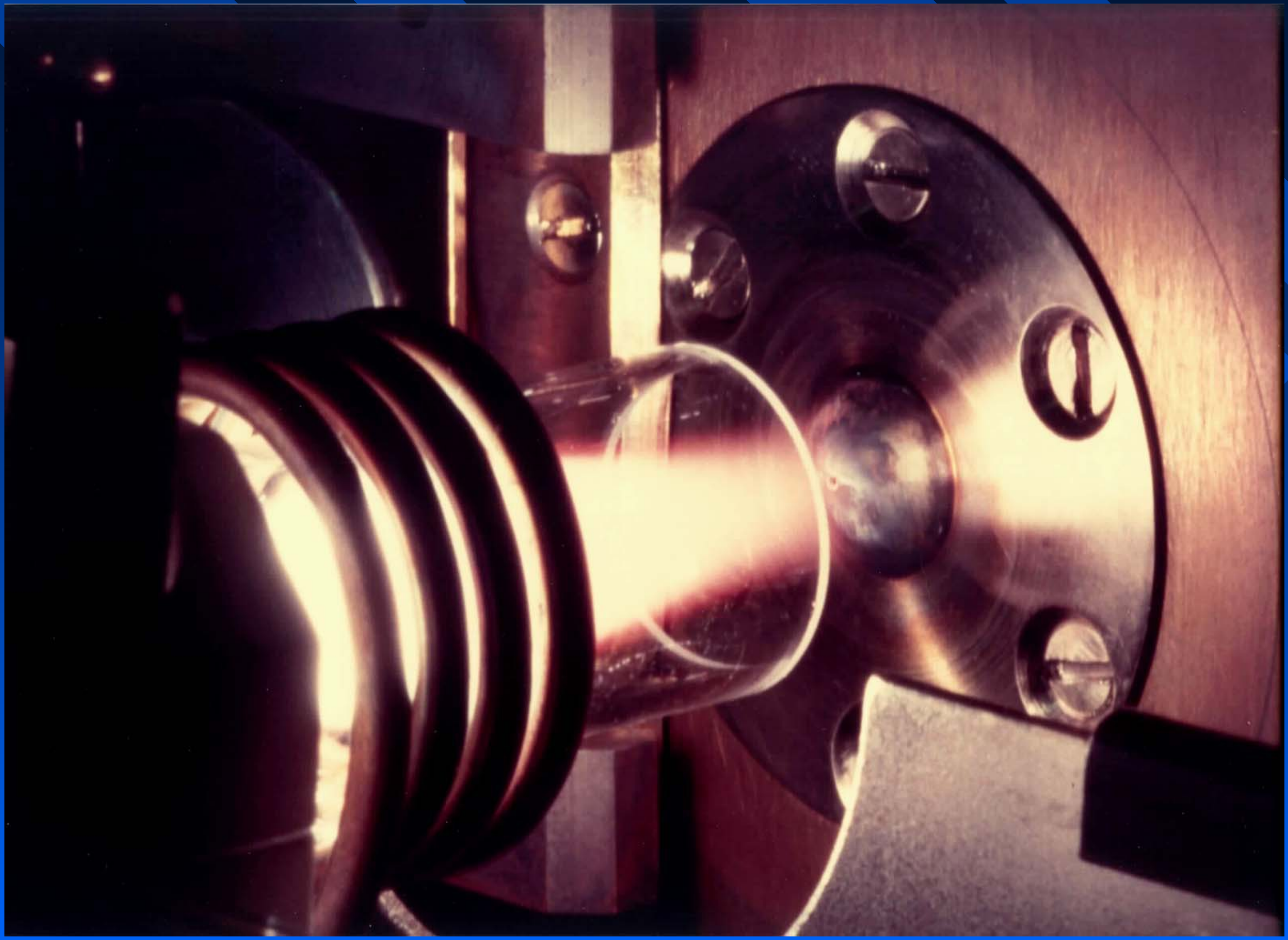
Inductively Coupled Plasma (ICP)

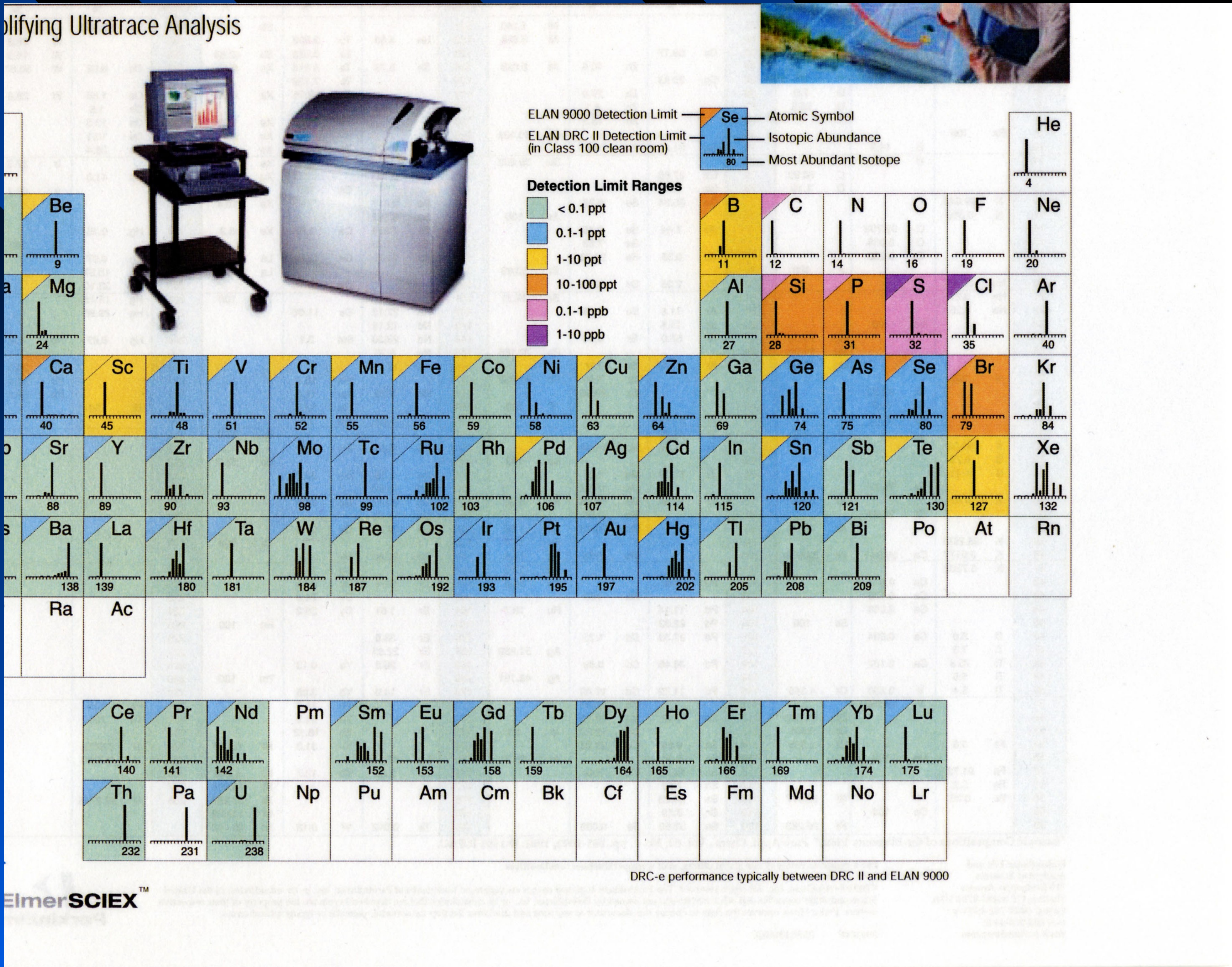


Inductively Coupled Plasma (ICP)

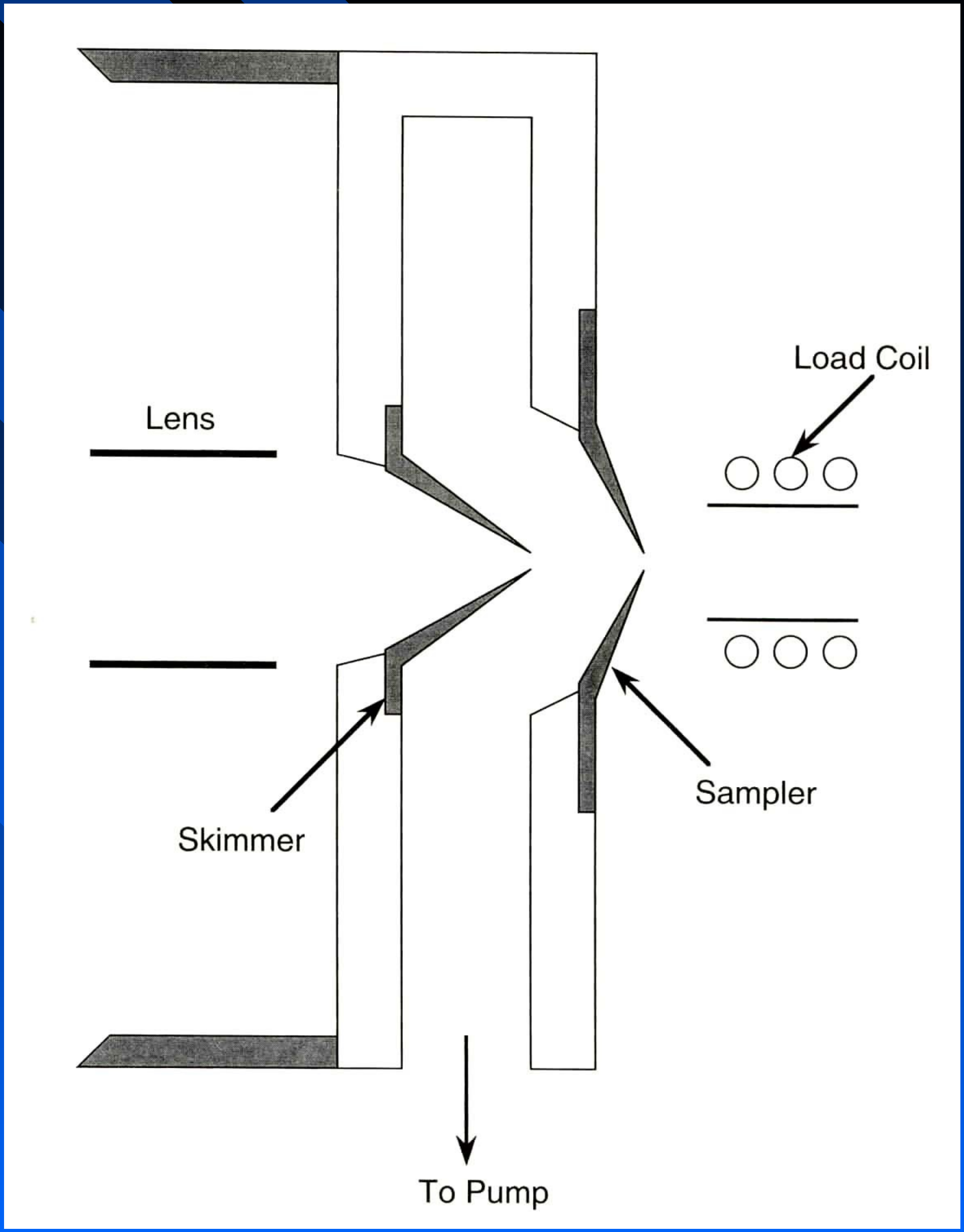


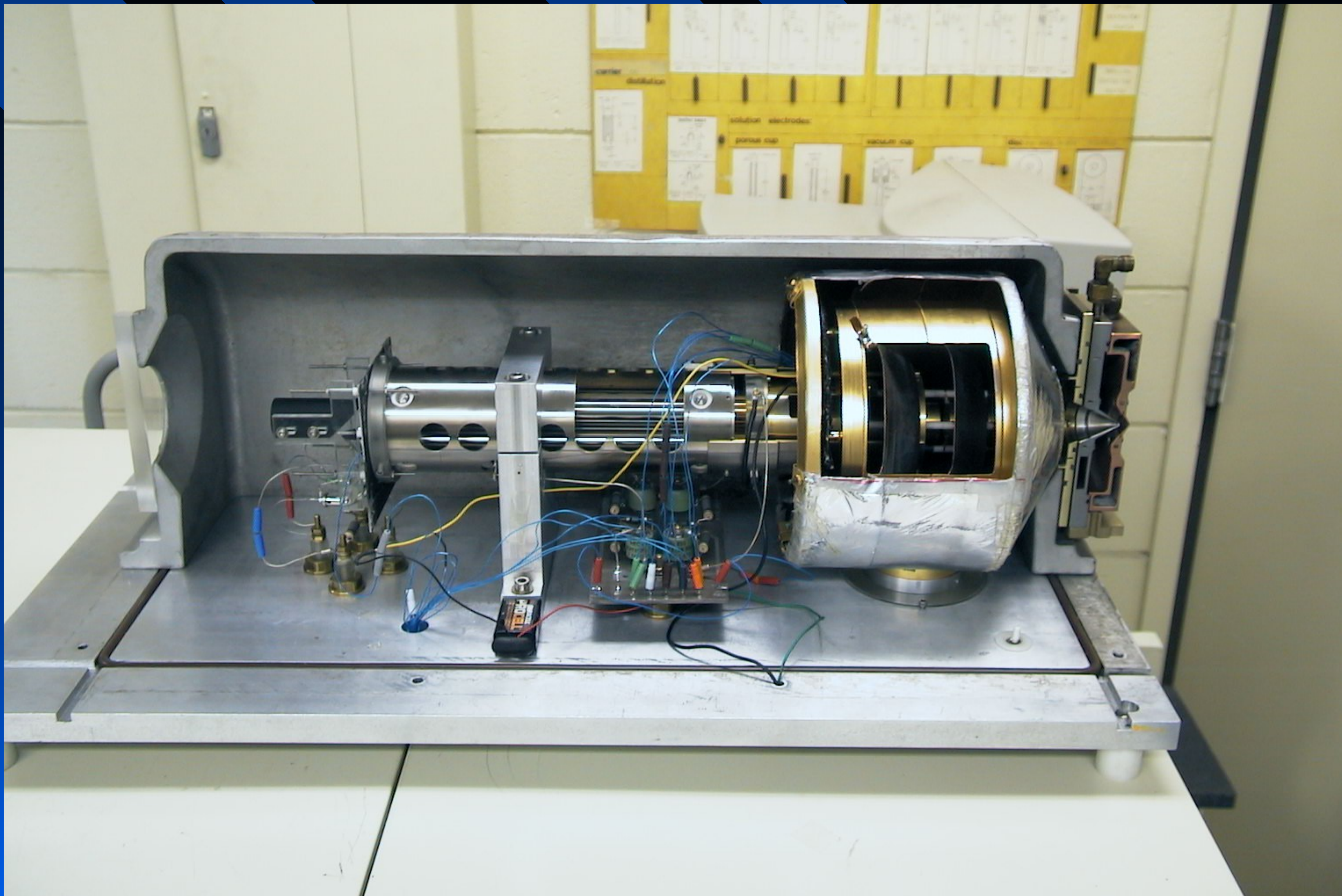
Inductively Coupled Plasma - Mass Spectrometry

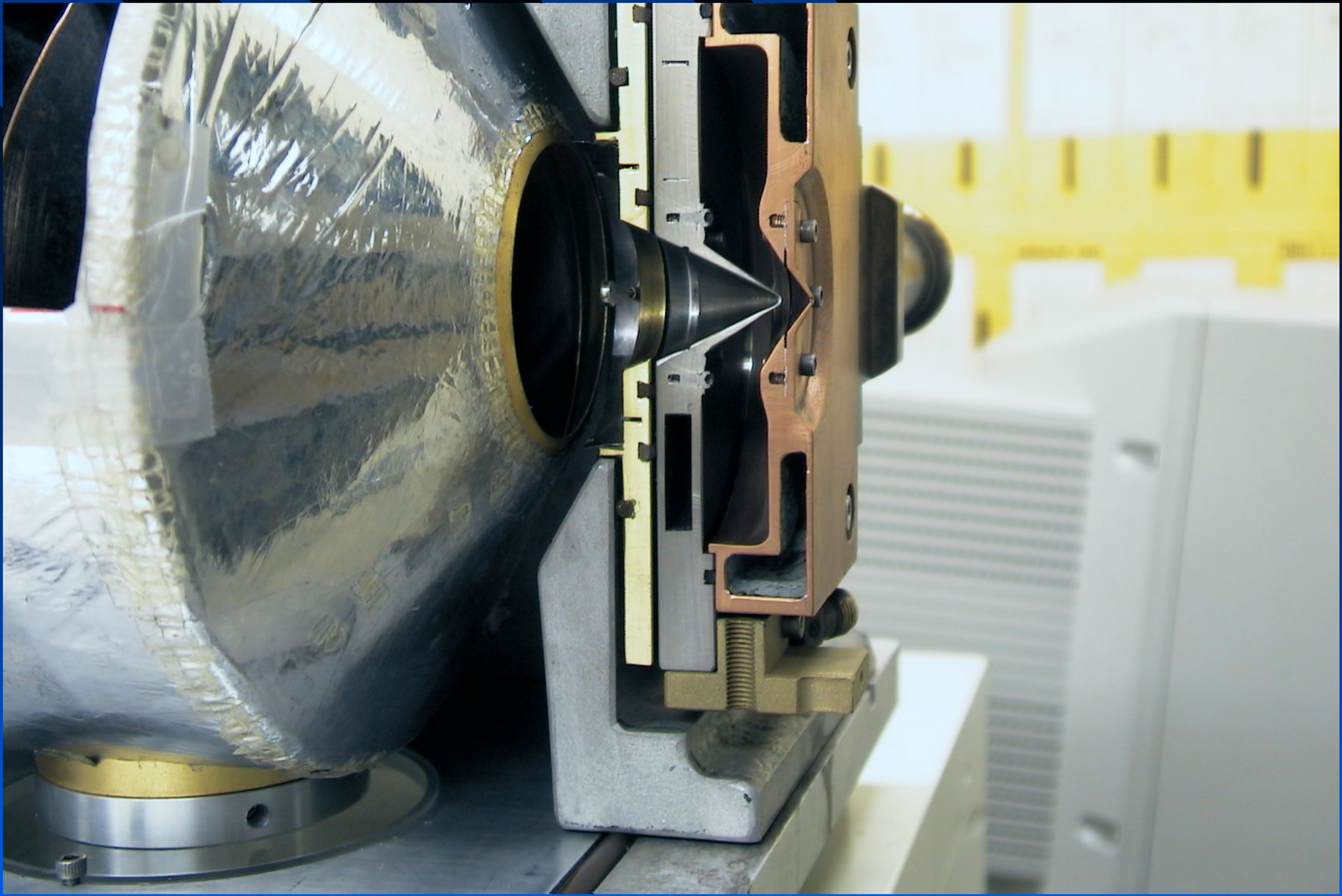


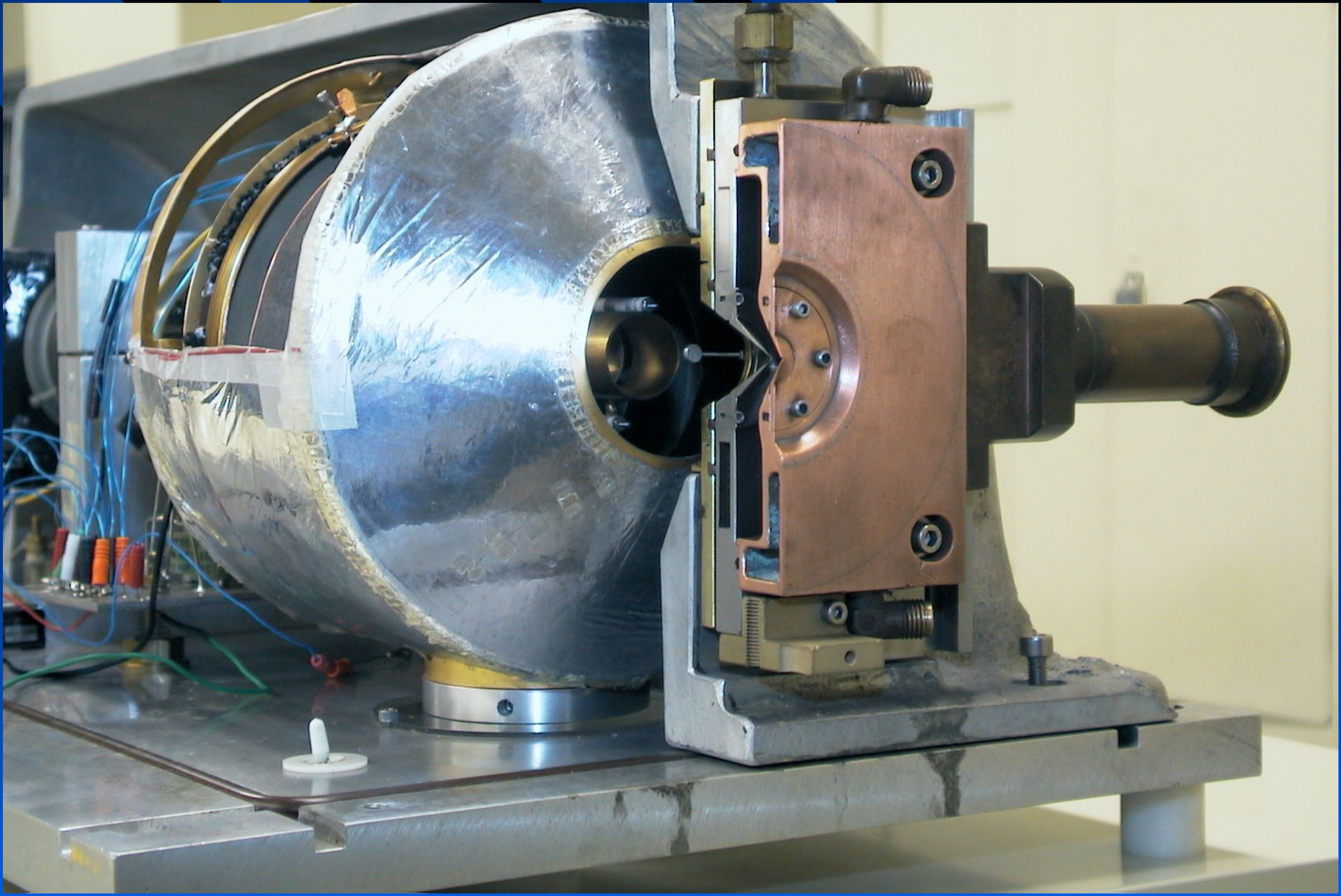

plifying Ultratrace Analysis
ELAN 9000 Detection Limit
ELAN DRC II Detection Limit (in Class 100 clean room)
Atomic Symbol
Isotopic Abundance
Most Abundant Isotope
Se
80
Detection Limit Ranges
< 0.1 ppt
0.1-1 ppt
1-10 ppt
10-100 ppt
0.1-1 ppb
1-10 ppb
He 4
Be 9
B 11 C 12 N 14 O 16 F 19 Ne 20
Mg 24
Al 27 Si 28 P 31 S 32 Cl 35 Ar 40
Ca 40 Sc 45 Ti 48 V 51 Cr 52 Mn 55 Fe 56 Co 59 Ni 58 Cu 63 Zn 64 Ga 69 Ge 74 As 75 Se 80 Br 79 Kr 84
Sr 88 Y 89 Zr 90 Nb 93 Mo 98 Tc 99 Ru 102 Rh 103 Pd 106 Ag 107 Cd 114 In 115 Sn 120 Sb 121 Te 130 I 127 Xe 132
Ba 138 La 139 Hf 180 Ta 181 W 184 Re 187 Os 192 Ir 193 Pt 195 Au 197 Hg 202 Tl 205 Pb 208 Bi 209 Po At Rn
Ra Ac
Ce 140 Pr 141 Nd 142 Pm Sm 152 Eu 153 Gd 158 Tb 159 Dy 164 Ho 165 Er 166 Tm 169 Yb 174 Lu 175
Th 232 Pa 231 U 238 Np Pu Am Cm Bk Cf Es Fm Md No Lr
DRC-e performance typically between DRC II and ELAN 9000
ElmerSCIEX™

ICP-MS Interface Cones

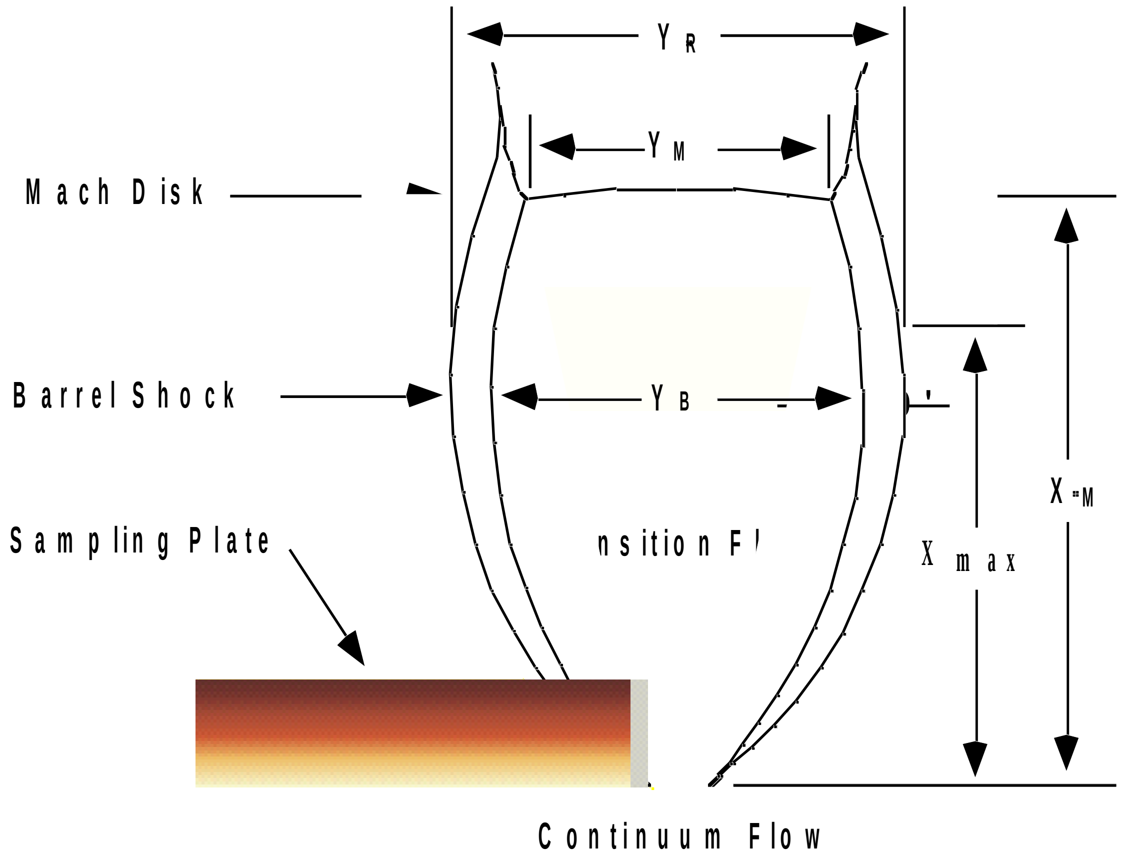








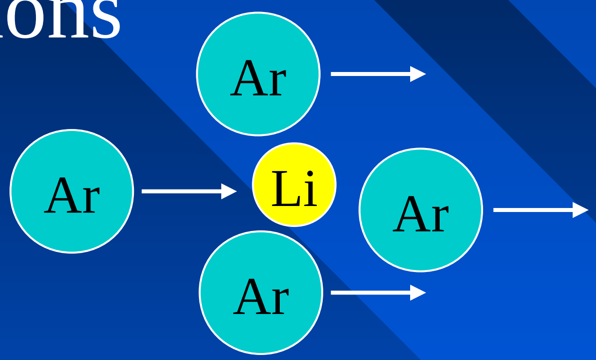
Supersonic Expansion



Consequences of Expansion

$$KE_{Ar} = \frac{5}{2}kT$$

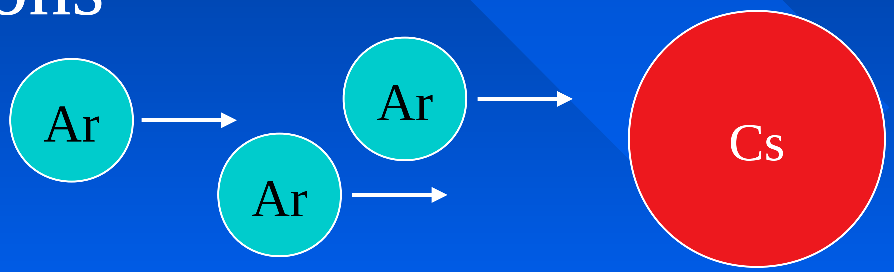
Small ions



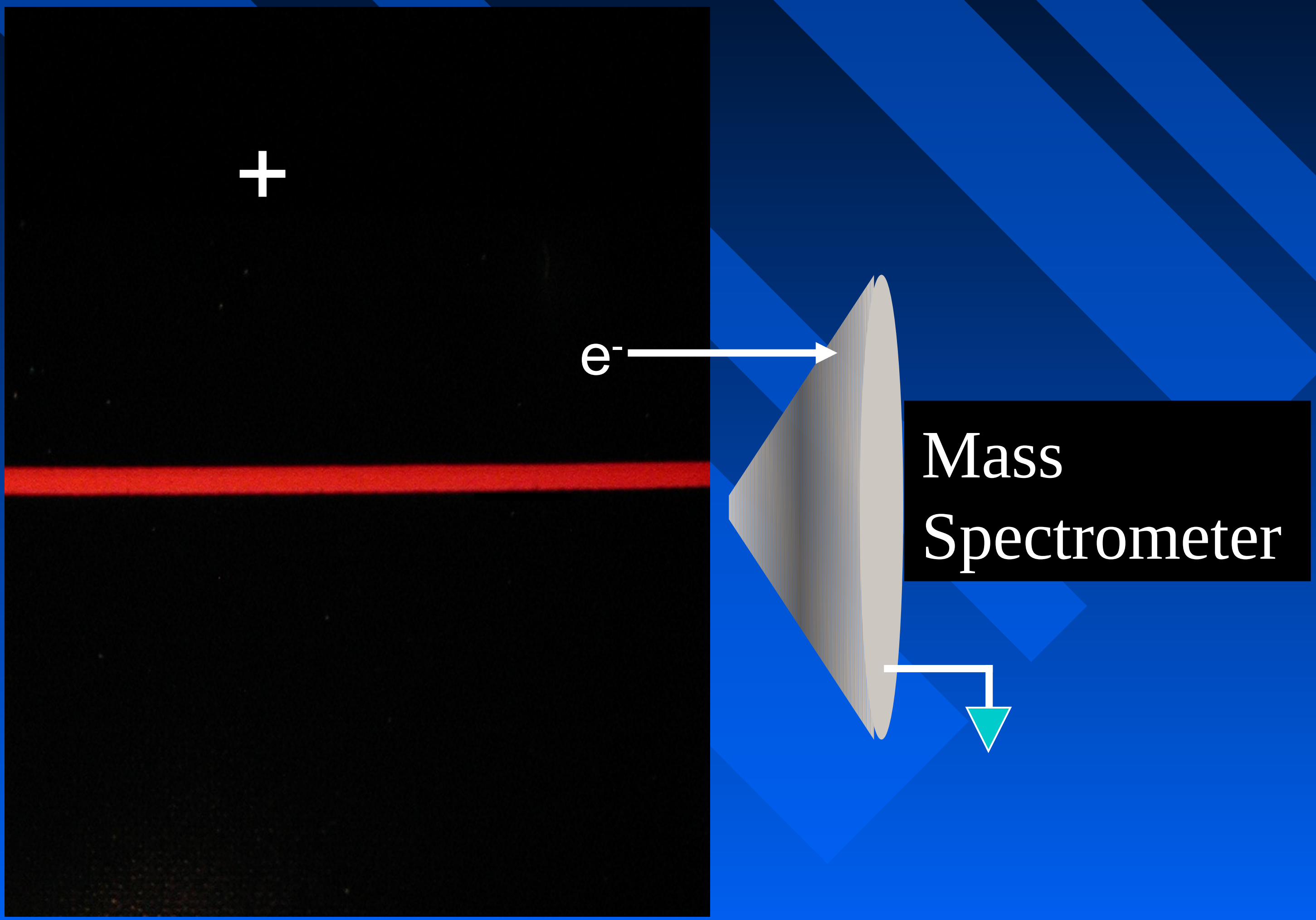
KE = 0.5 MV^2

So $KE_{M^+} = kM^+$

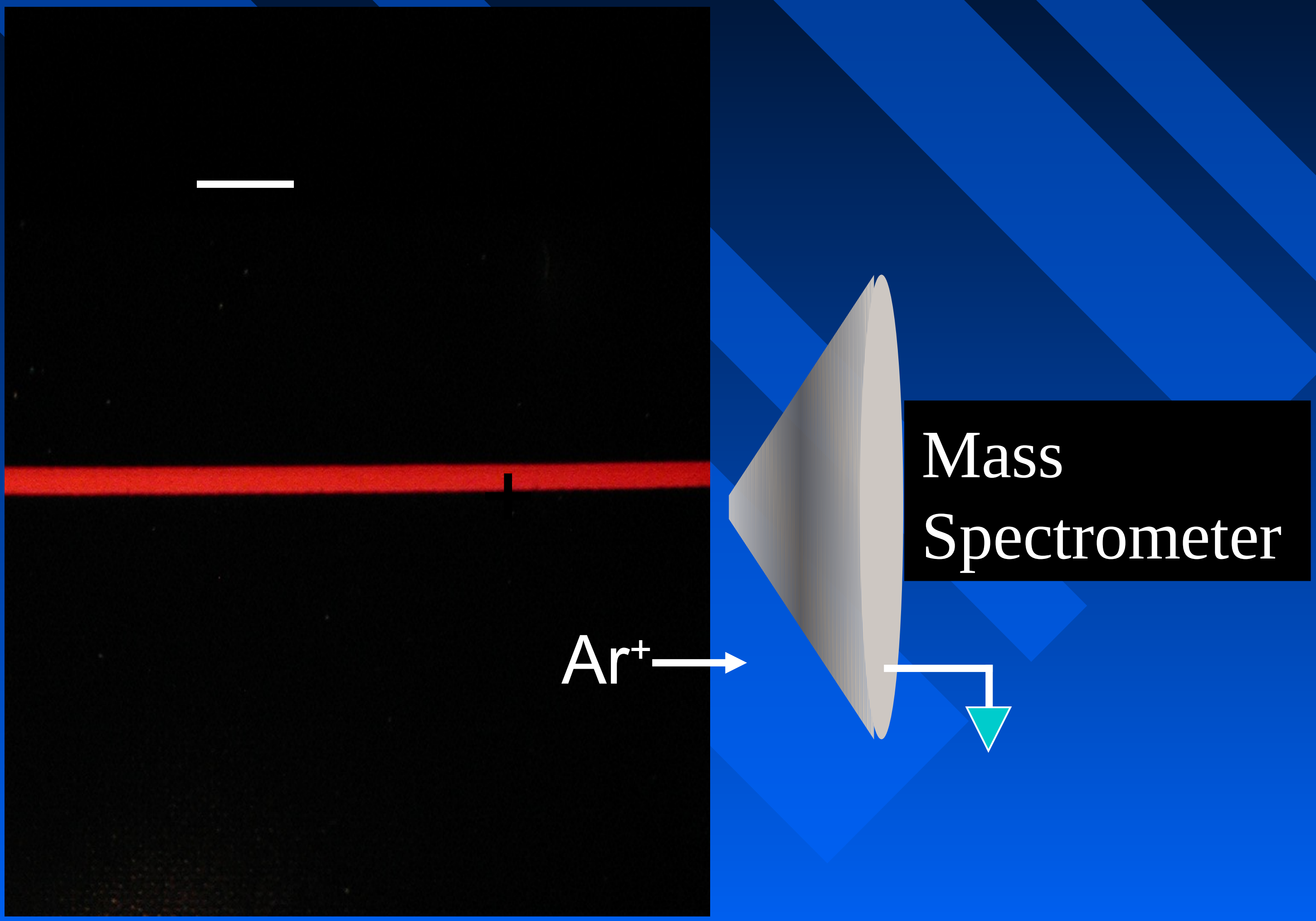
Large ions



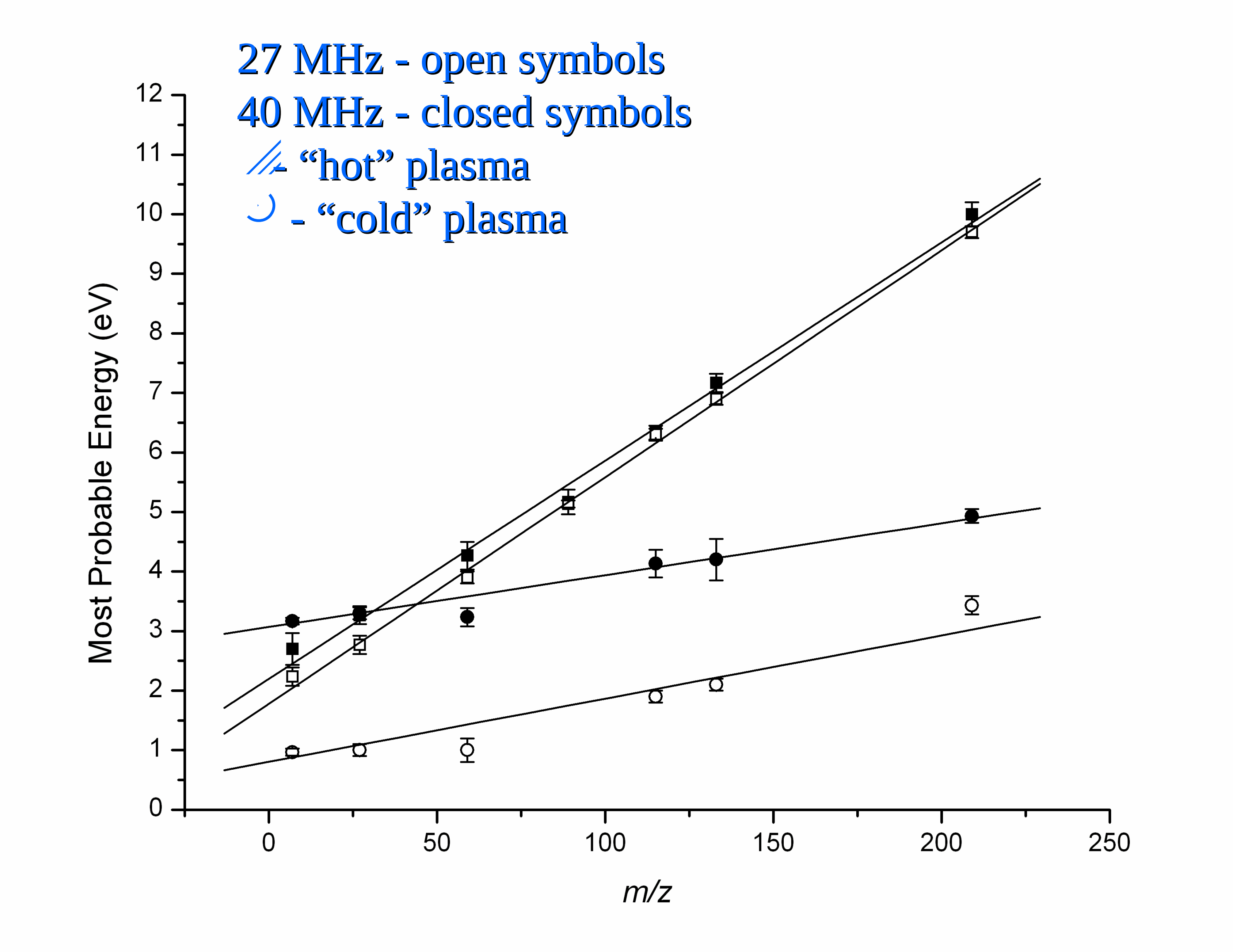
Plasma Offset (Rectification)



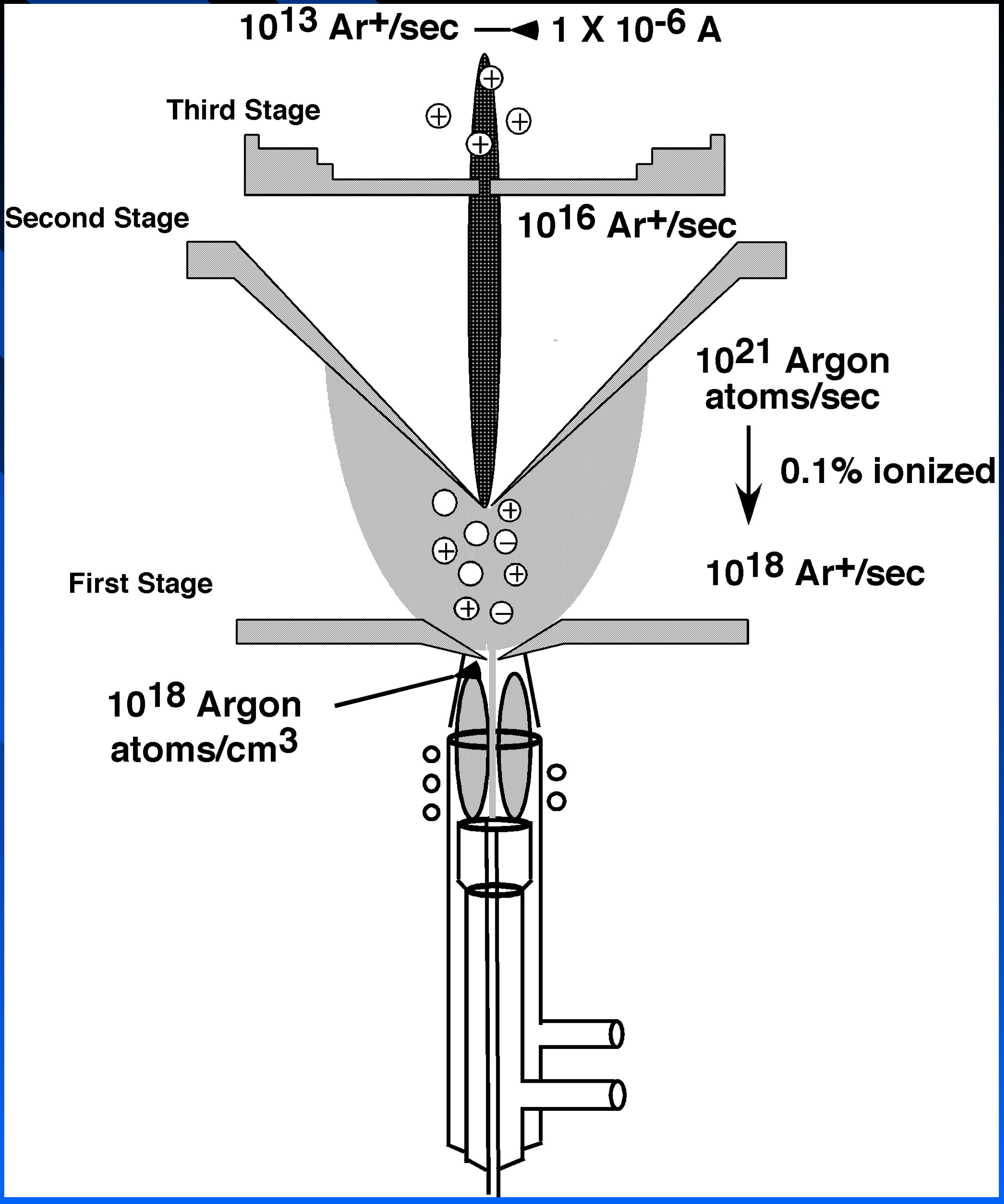
Plasma Offset (Rectification)



Ion Energies Depend on Mass



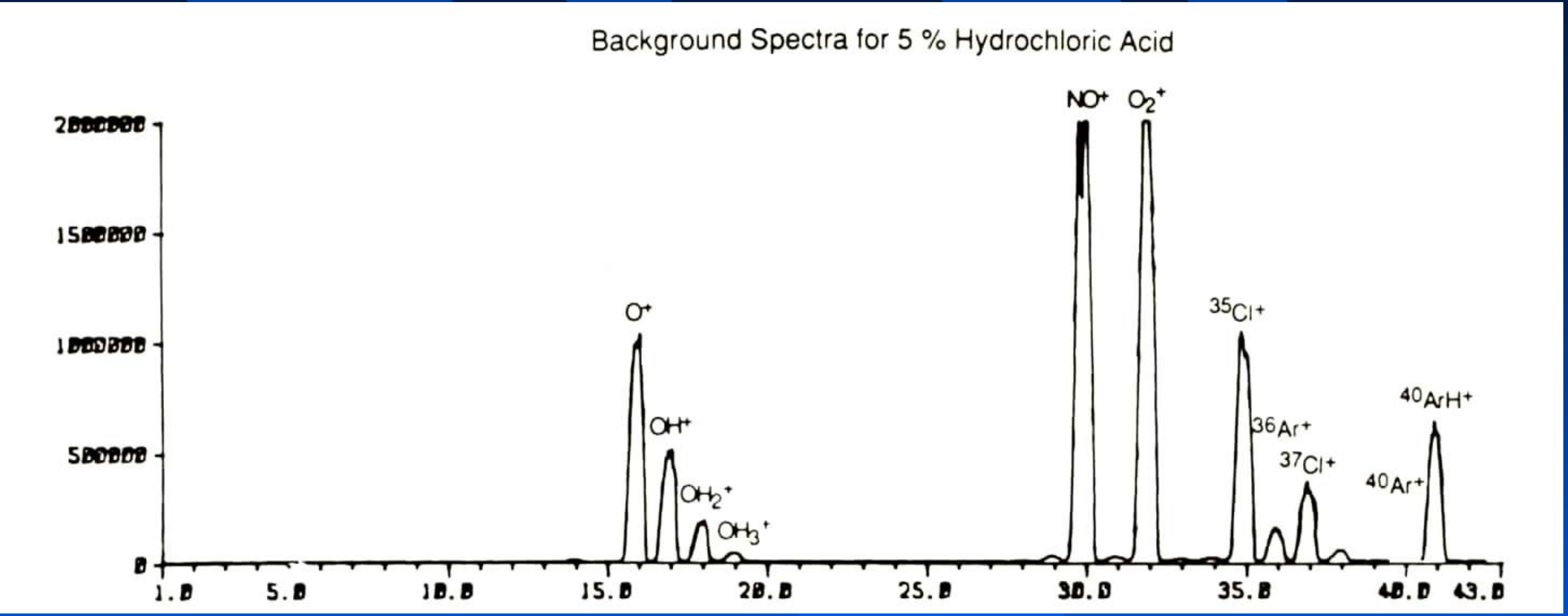
Ion Currents in ICP-MS



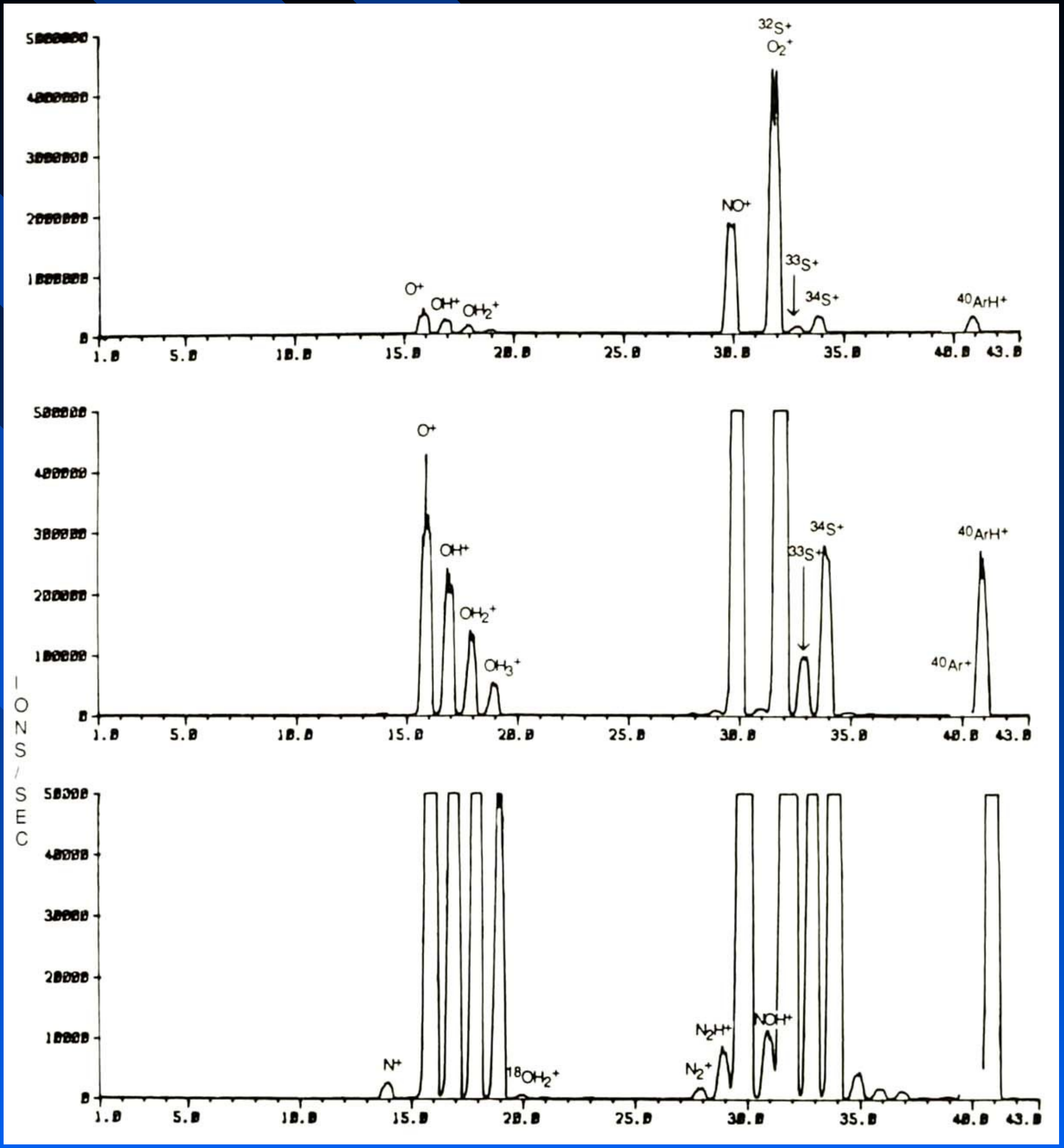
Spectral Characteristics of ICP-MS

- Basic Background Species
  - argon, water, and air.
  - N_2^+, Ar^+, ArO^+, Ar_2^+
- Interelement Spectral Overlaps
  - isobaric overlaps.
  - element oxides and hydroxides.
- Matrix Induced Spectral Overlaps
  - chlorine and sulfur based species.
  - ClO^+, SO_2^+
- Argon - Matrix Related Species
  - $ArNa^+$, $ArCl^+$

ICP-MS Background: 5% HCl



ICP-MS Background: 5% H_2SO_4



Oxide and Hydroxide Species

- Problems Caused by Oxides
  - spectral interferences.
  - can result in the implementation of inappropriate isobaric corrections.
- Oxides Formed From
  - plasma gases.
  - air entrainment.
  - sample solvent.
  - matrix components of the sample.
  - the sought-for-elements in the sample.

Variables Affecting Oxide Levels

- Oxide Levels Depend On:
  - injector gas flow rate.
  - foward power.
  - sampler - skimmer spacing.
  - sampler orfice size.
  - plasma gas composition.
  - aerosol processing.
  - solvent load.
  - oxygen level.

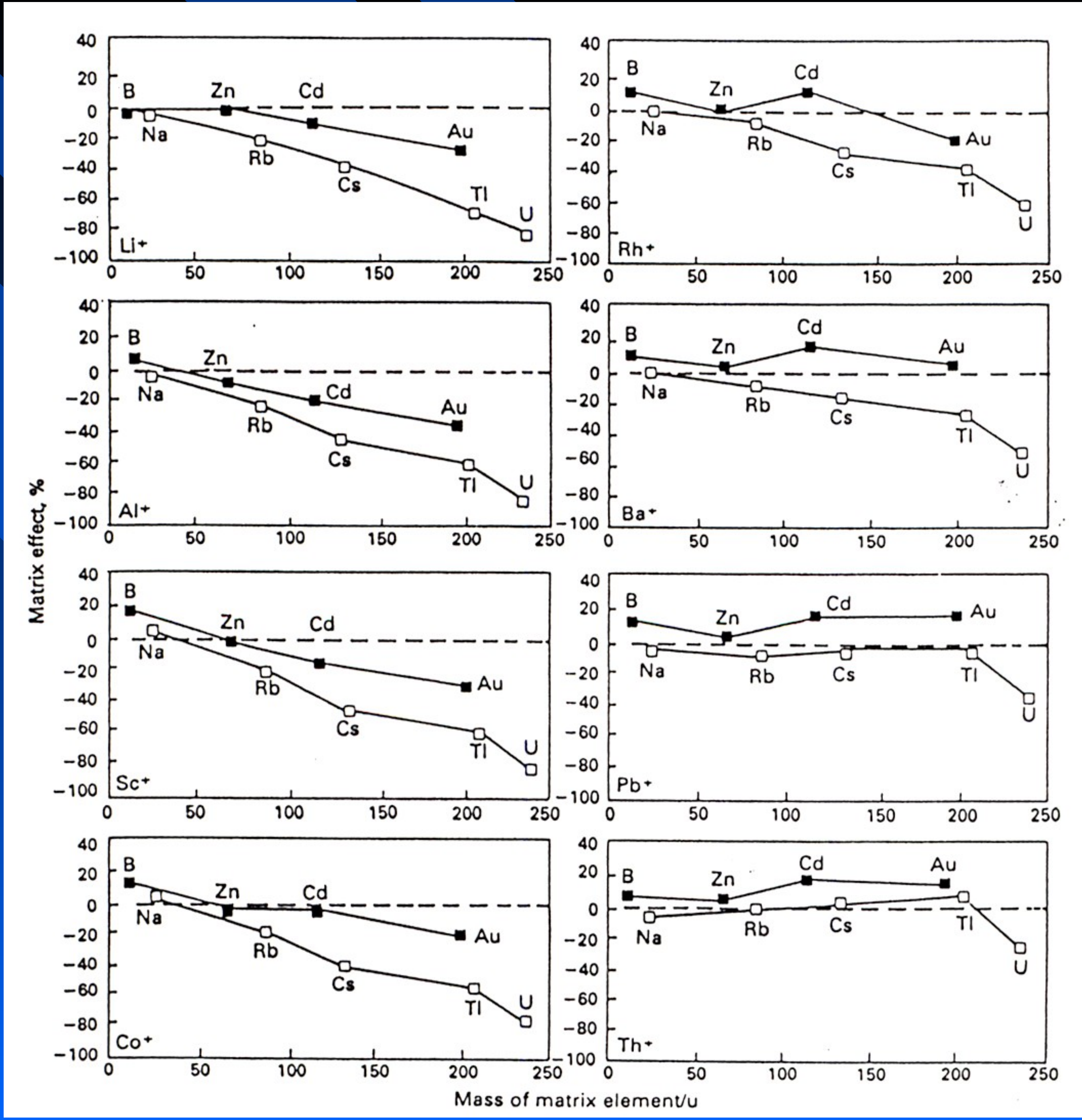
All these experimental variables can be used, to some extent, to control oxide levels in ICP-MS.

Matrix Induced Signal Changes

A high concentration of a concomitant:

- generally, suppression of the analyte signal is observed.
- the suppression is more serious with heavier matrix elements.
- light analytes are more seriously affected.
- the effects may be minimized by:
  - reducing the nebulizer flow rate.
  - using an internal standard.
  - using dilute solutions.

Matrix Effects in ICP-MS



ICP-MS Options for Isotope Ratios

- Multi-collector sector-field spectrometer
  - Offered by Thermo (Neptune), GV, and Nu
  - Isotope-ratio precision ~0.002% rsd (20 ppm)
- Time-of-flight mass spectrometer
  - Leco & GBC
  - Isotope-ratio precision ~0.05% rsd analog
  - Isotope-ratio precision ~0.01% rsd counting
- Array-detector sector field
  - Not yet commercially available
  - Isotope-ratio precision ~0.007% rsd

Thermo Neptune MC-ICP-MS

Nu Instruments MC-ICP-MS

Leco Renaissance ICP-TOFMS

GBC Optimass ICP-TOFMS