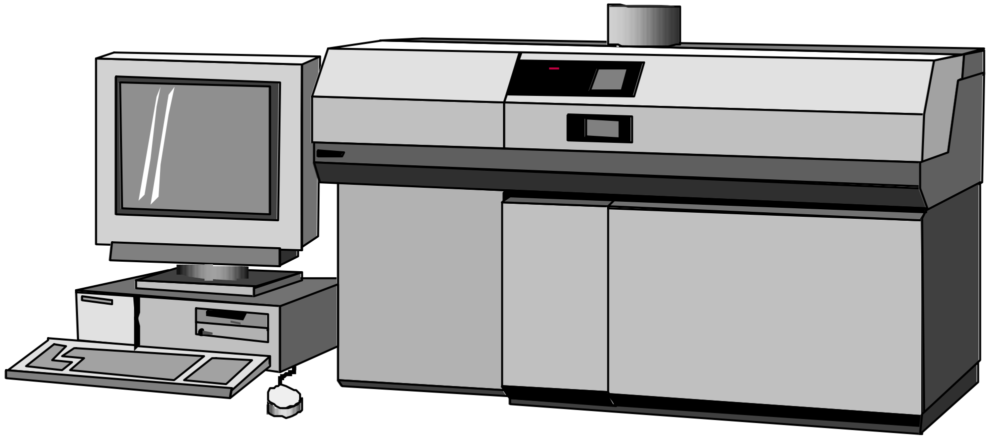
Introduction to ICP-MS



featuring the

Agilent Technologies 4500 Series

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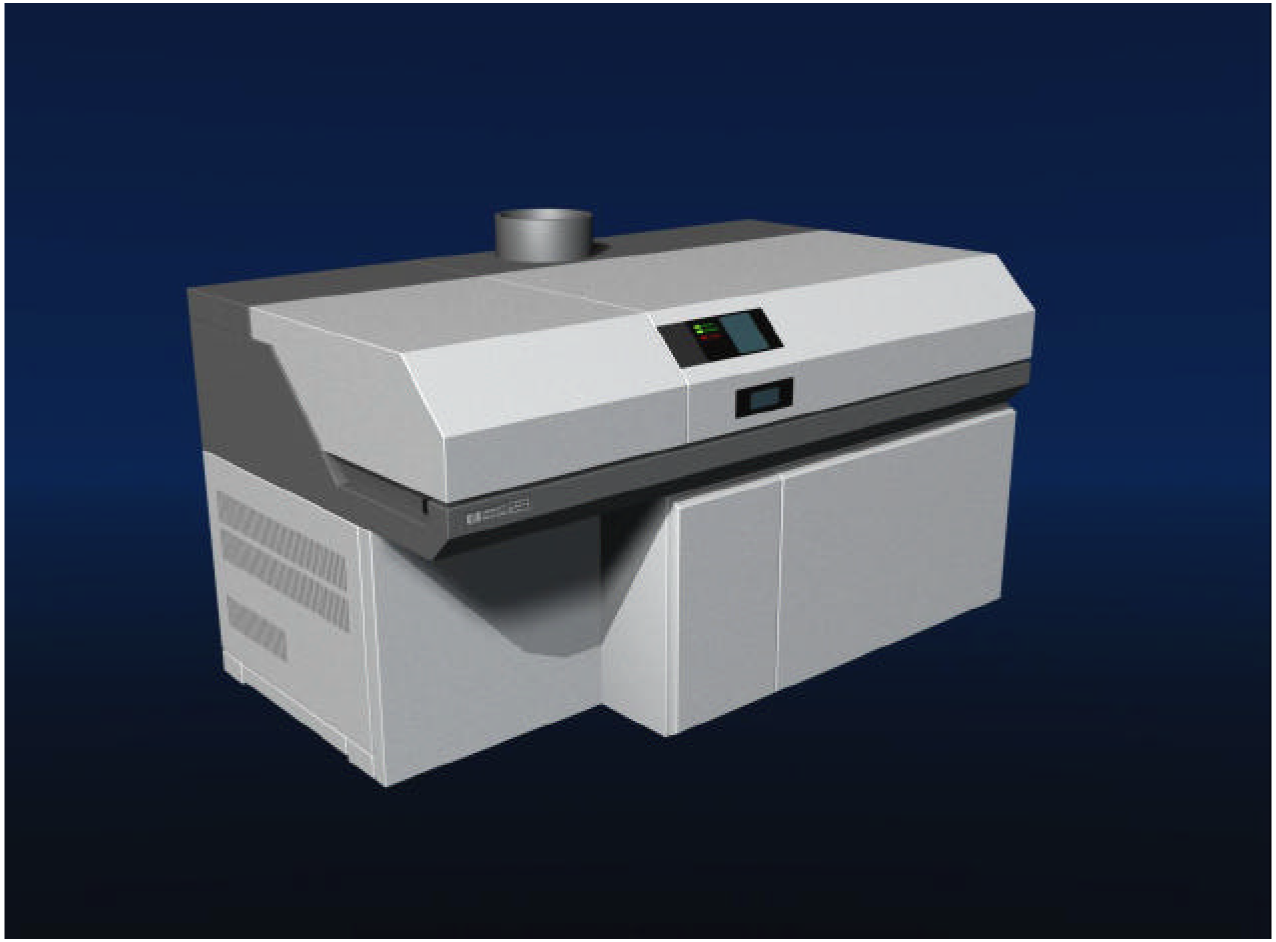
Agilent 4500 Series

Inductively Coupled Plasma Mass Spectrometer

- Independent* survey shows the Agilent 4500 to be the best selling ICP-MS world-wide
- Over 700 units sold 1994 - 1999

*Myers and Assoc. ICP-MS Market Study 1994-1998



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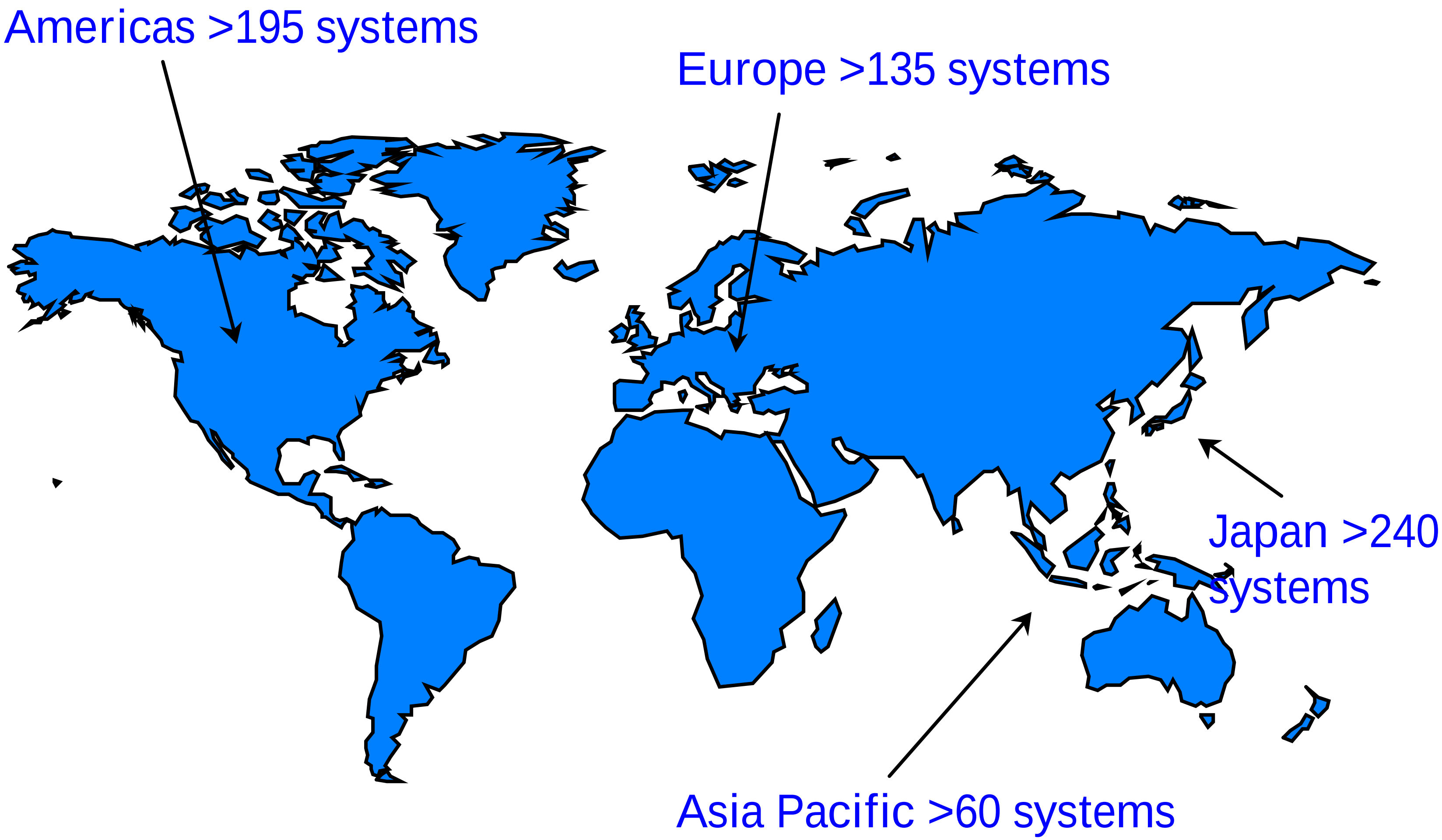
Agilent 4500 Series ICP-MS User Base



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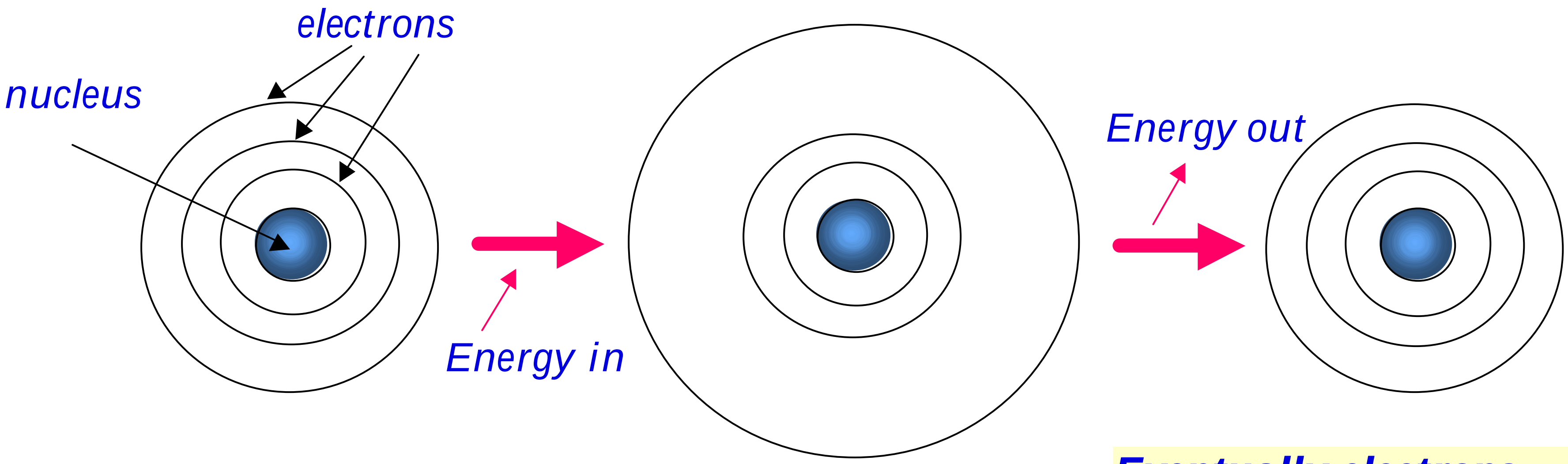
What is ICP-MS?

- An inorganic (elemental) analysis technique

- ICP - Inductively Coupled Plasma
  - high temperature ion source
- MS - Mass Spectrometer
  - quadrupole scanning spectrometer
  - as used in bench-top GC-MS
  - mass range from 7 to 250 amu (Li to U...)
  - separates all elements in rapid sequential scan
  - ions measured using dual mode detector
    - ppt to ppm levels
    - isotopic information available

Simple model of the atom



On absorbing the energy, the electrons in the outer shell move outwards to a different "orbit"

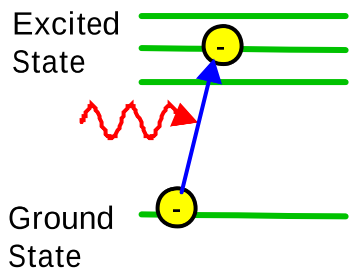
Eventually electrons return to their "ground state" and release the absorbed energy in the form of light. The wavelength (colour) of light is dependant on the change in "orbit"

The Atom

Atomic Spectrometry

Atomic Absorption

Light of specific wavelength from Hollow Cathode Lamp (HCL)

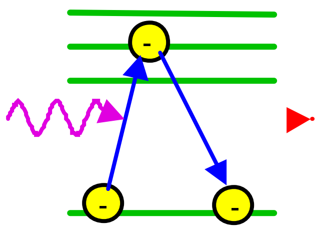


Light of specific characteristic wavelength is absorbed by promoting an electron to a higher energy level (excitation)

Light absorption is proportional to elemental concentration

Atomic Emission

Light and heat energy from high intensity source (flame or plasma)

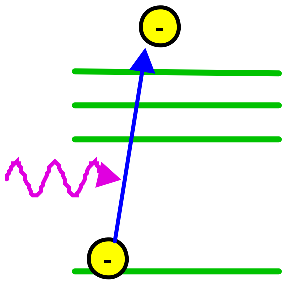


High energy (light and heat) promotes an electron to a higher energy level (excitation). Electron falls back and emits light at characteristic wavelength

Light emission is proportional to elemental concentration

Mass Spectrometry

Light and heat energy from high intensity source (plasma)

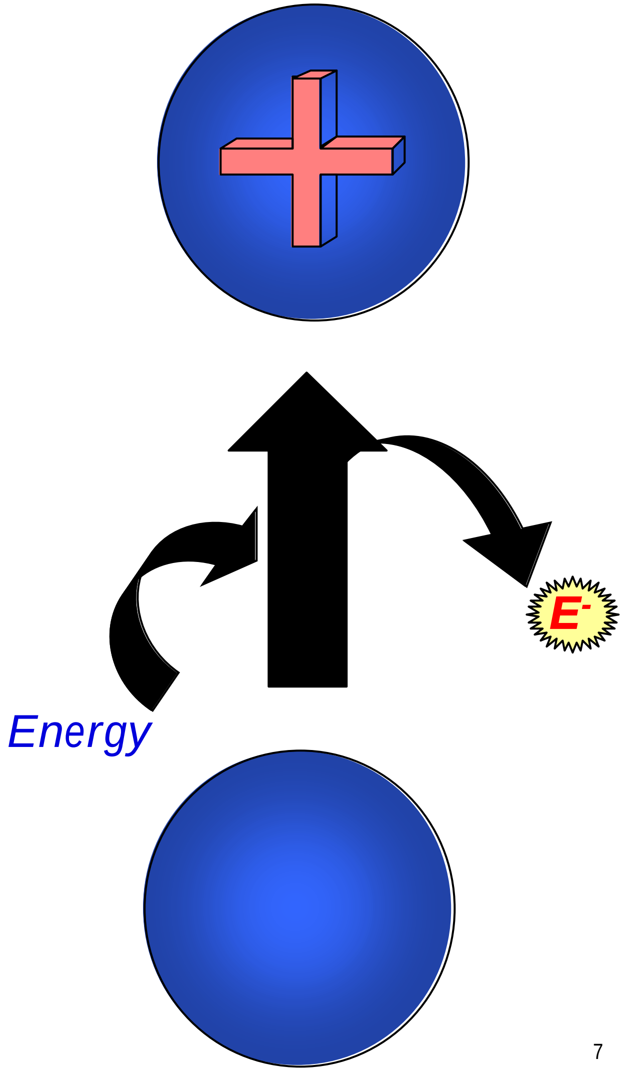


High energy (light and heat) ejects electron from shell (ionisation). Result is free electron and atom with positive charge (Ion)

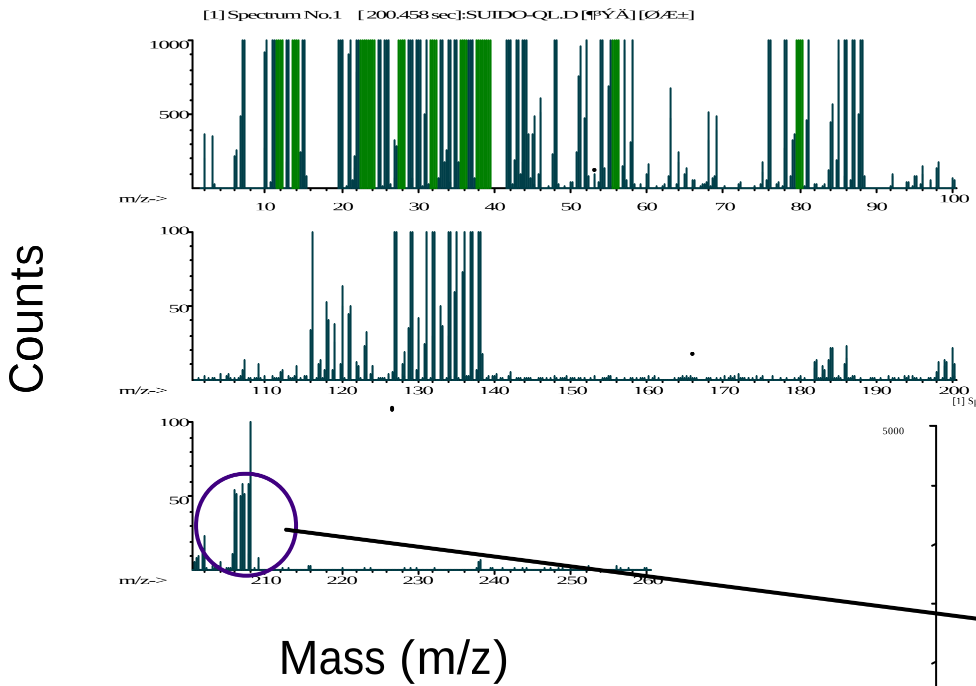
Ions are extracted and measured directly in mass spectrometer

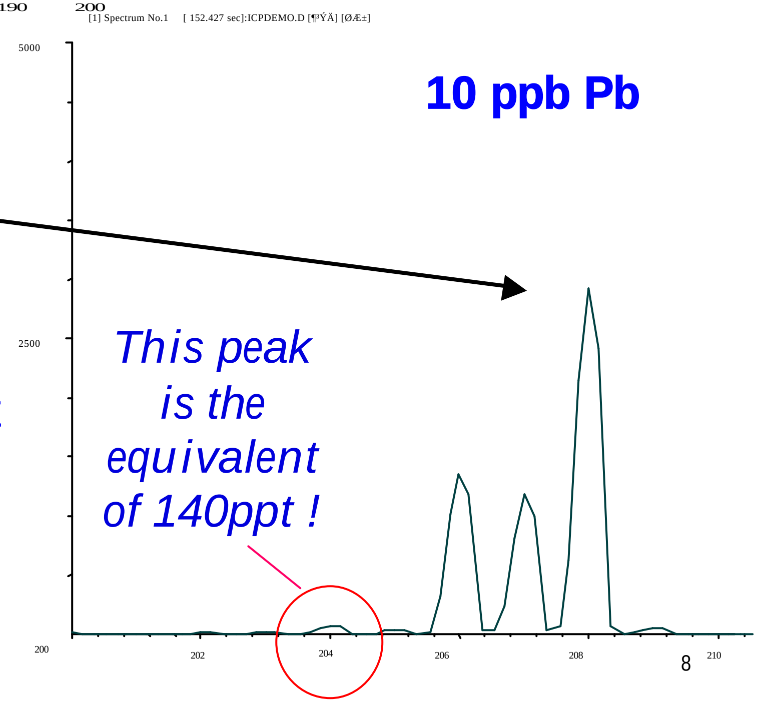
It's all about IONS

- The source in ICP-MS is responsible for producing POSITIVELY CHARGED IONS ($IONS^+$)
- $IONS^+$ will be attracted to negatively charged particles and fields
- $IONS^+$ will be repelled away from positively charged particles and fields



Typical ICP-MS Full Mass Spectrum





Spectral simplicity is a key ICP-MS benefit over optical inorganic techniques

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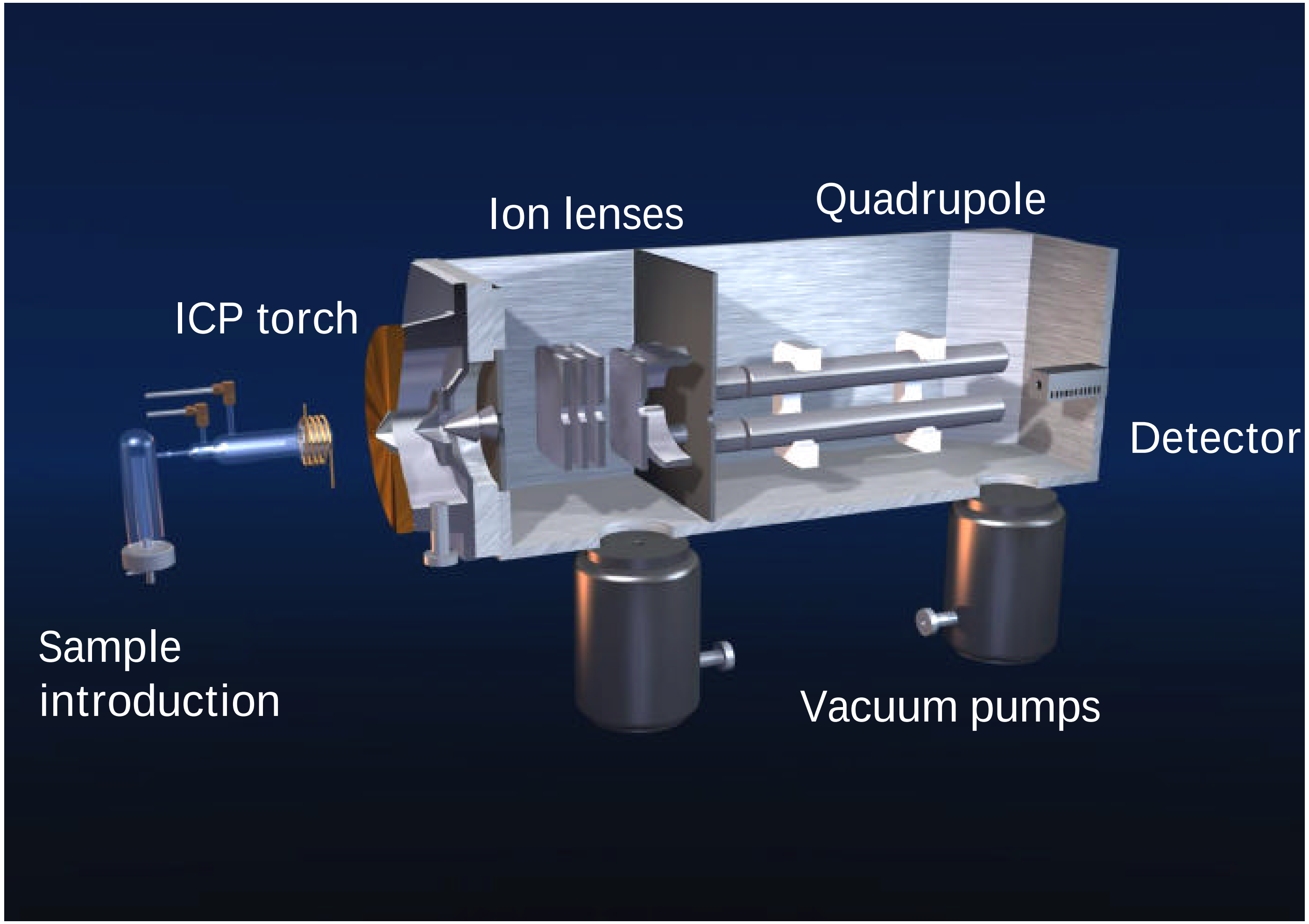
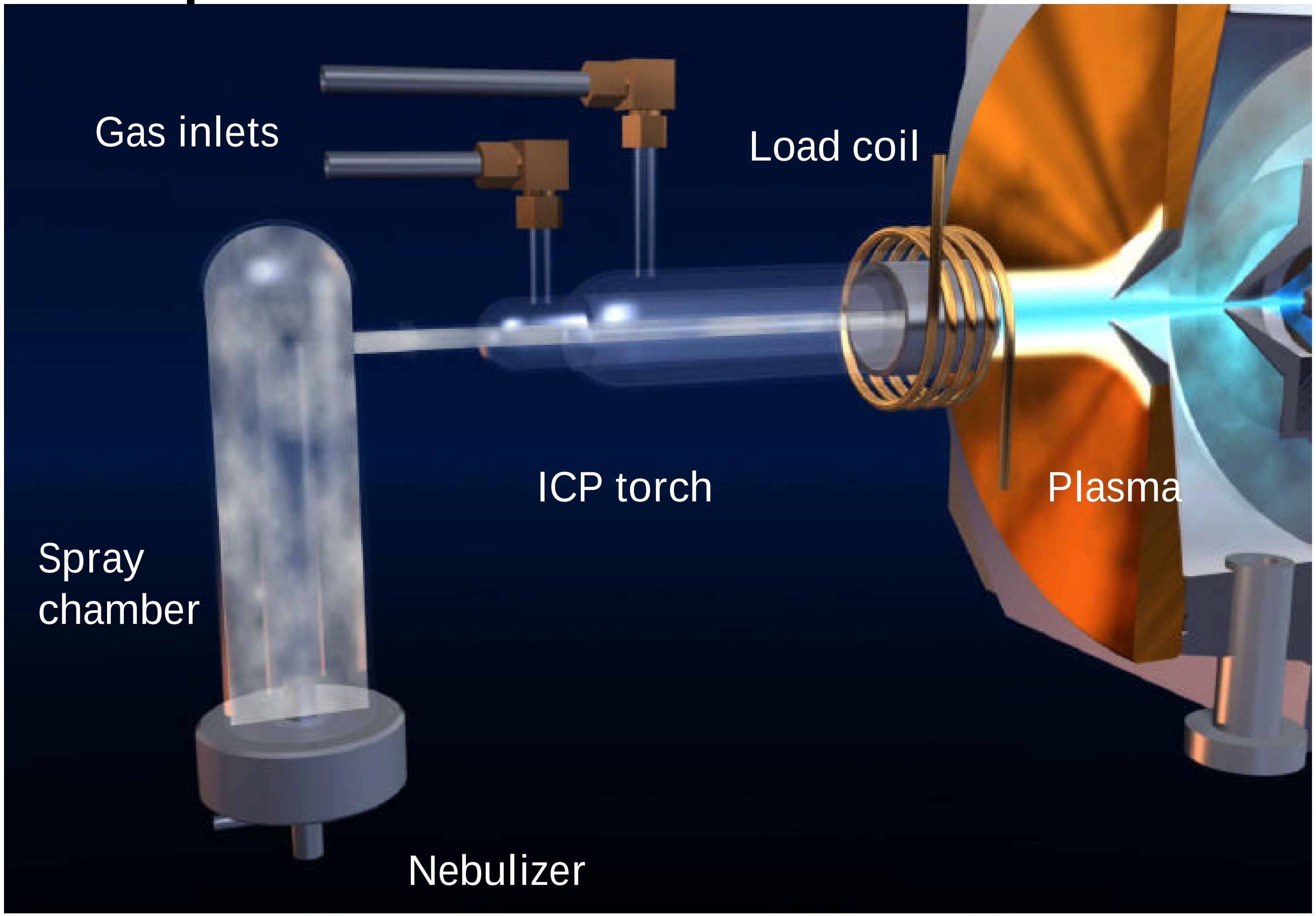
Agilent 4500 Series System Diagram

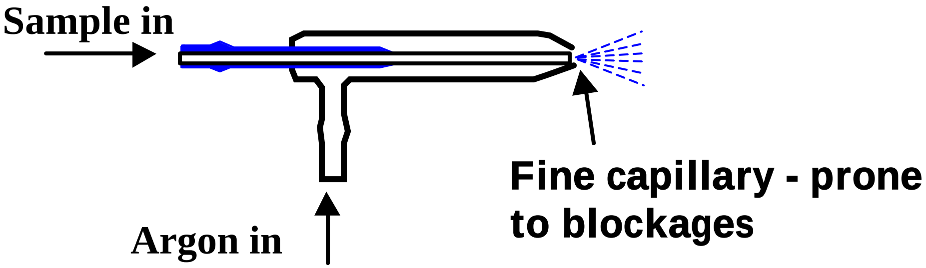


Sample Introduction

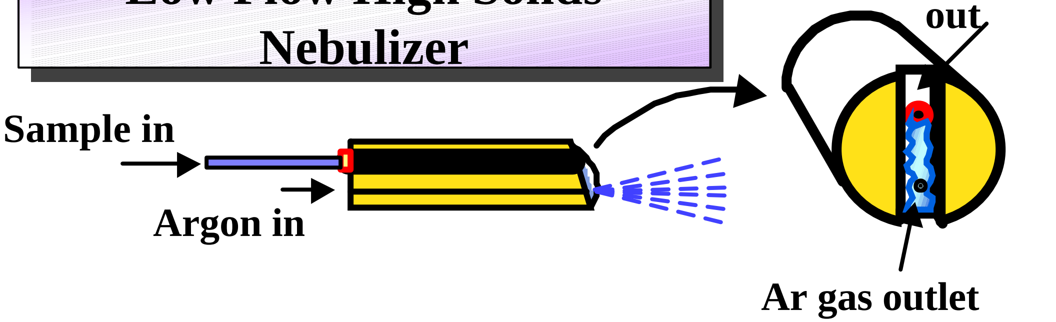


Available Nebulizers

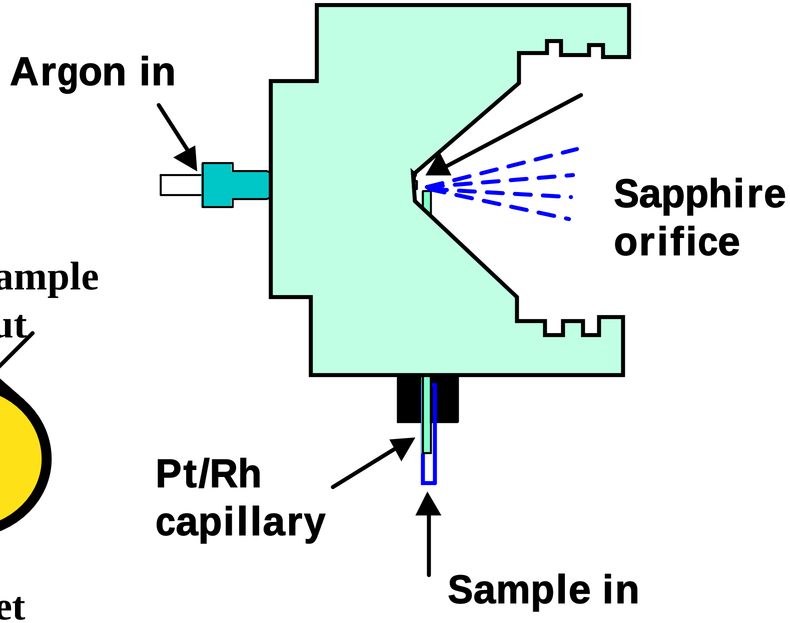
Concentric Nebulizer



Low Flow High Solids Nebulizer



Cross-flow Nebulizer



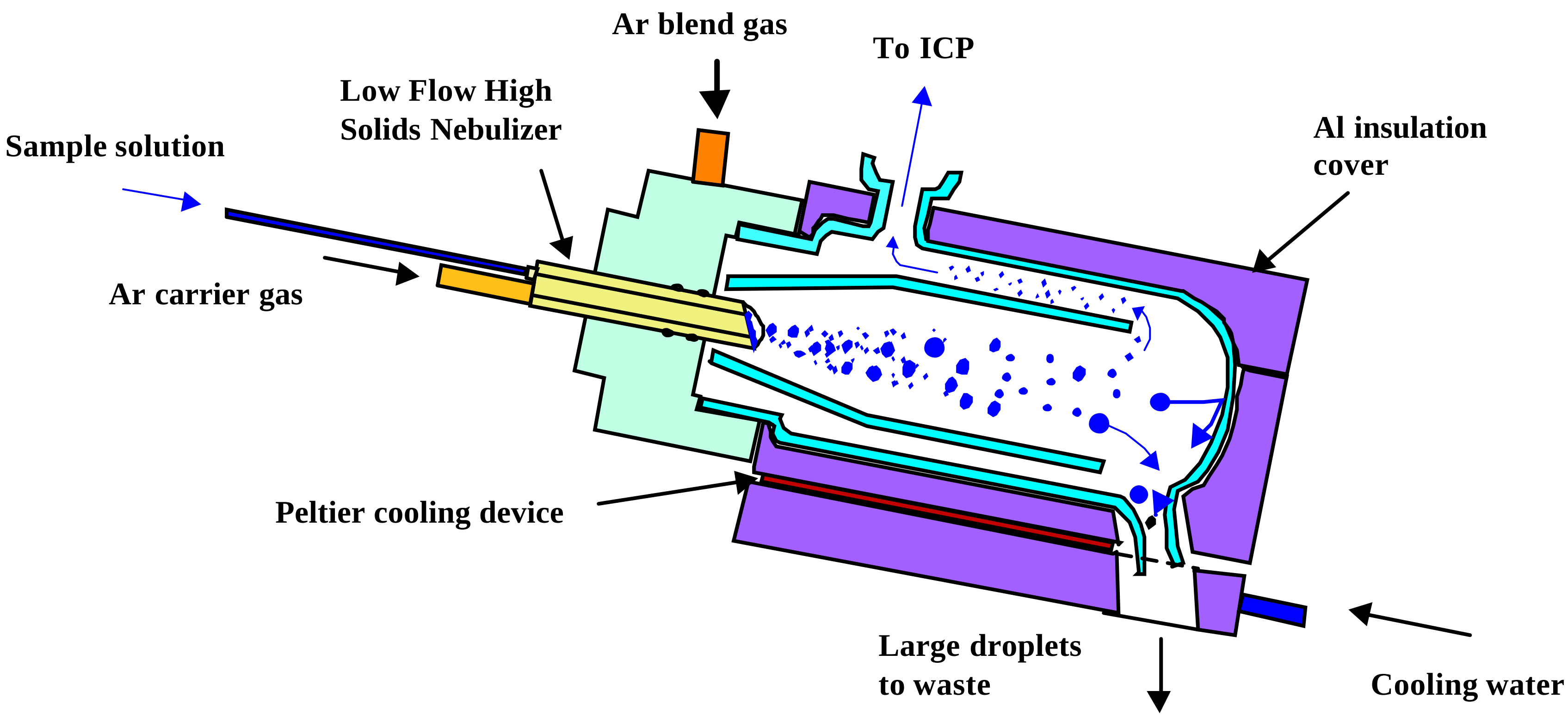
Your Application will Dictate Which Nebulizer to Use

- Different applications mean different nebulizers
  - Low Flow High Solids
    - environmental/geological/foods etc
  - Concentric
    - high precision close to detection limit
      - isotope ratio measurements - semiconductor materials
  - X-Flow
    - good precision, low flow, resistant to HF
      - HF analysis, VPD, geological samples
- **THE KEY IS TO HAVE THE FLEXIBILITY OF BEING ABLE TO CHOOSE**

Spray Chamber

Agilent 4500 uses Peltier device to chill spray chamber

- thermoelectric - so fast and accurate
- no messy outboard tubes and chillers

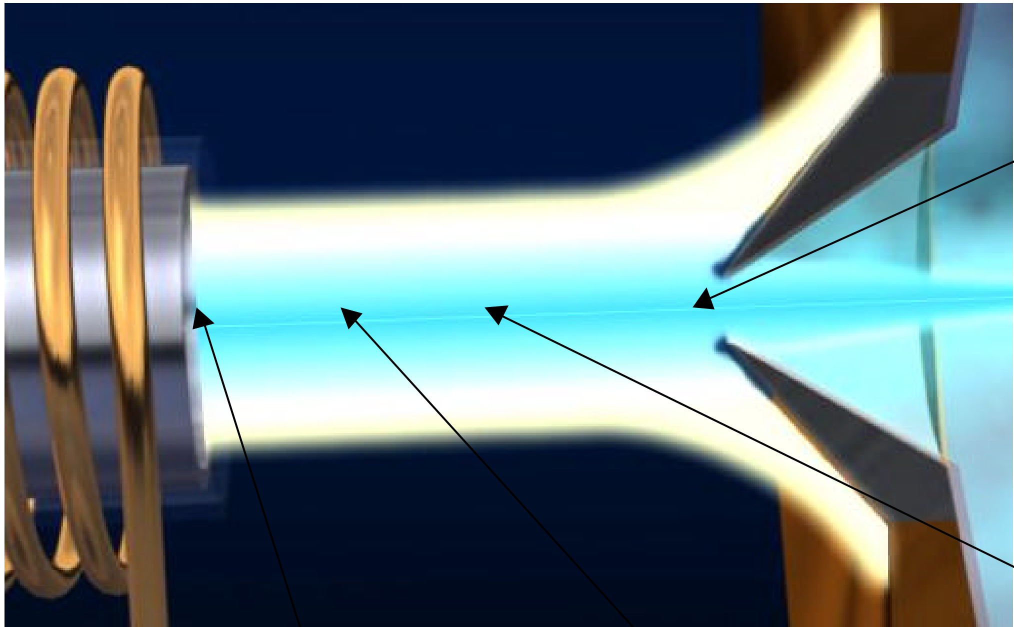


Simplified Model of Plasma

Hottest part of plasma ~ 8000K

Sample channel is at ~6000K

Residence time is a few milliseconds



By sample cone, analytes present as M+ ions

Highest M+ population should correspond to lowest polyatomic population

Aerosol is Dried

Particles are decomposed and dissociated

Atoms are formed and then ionized

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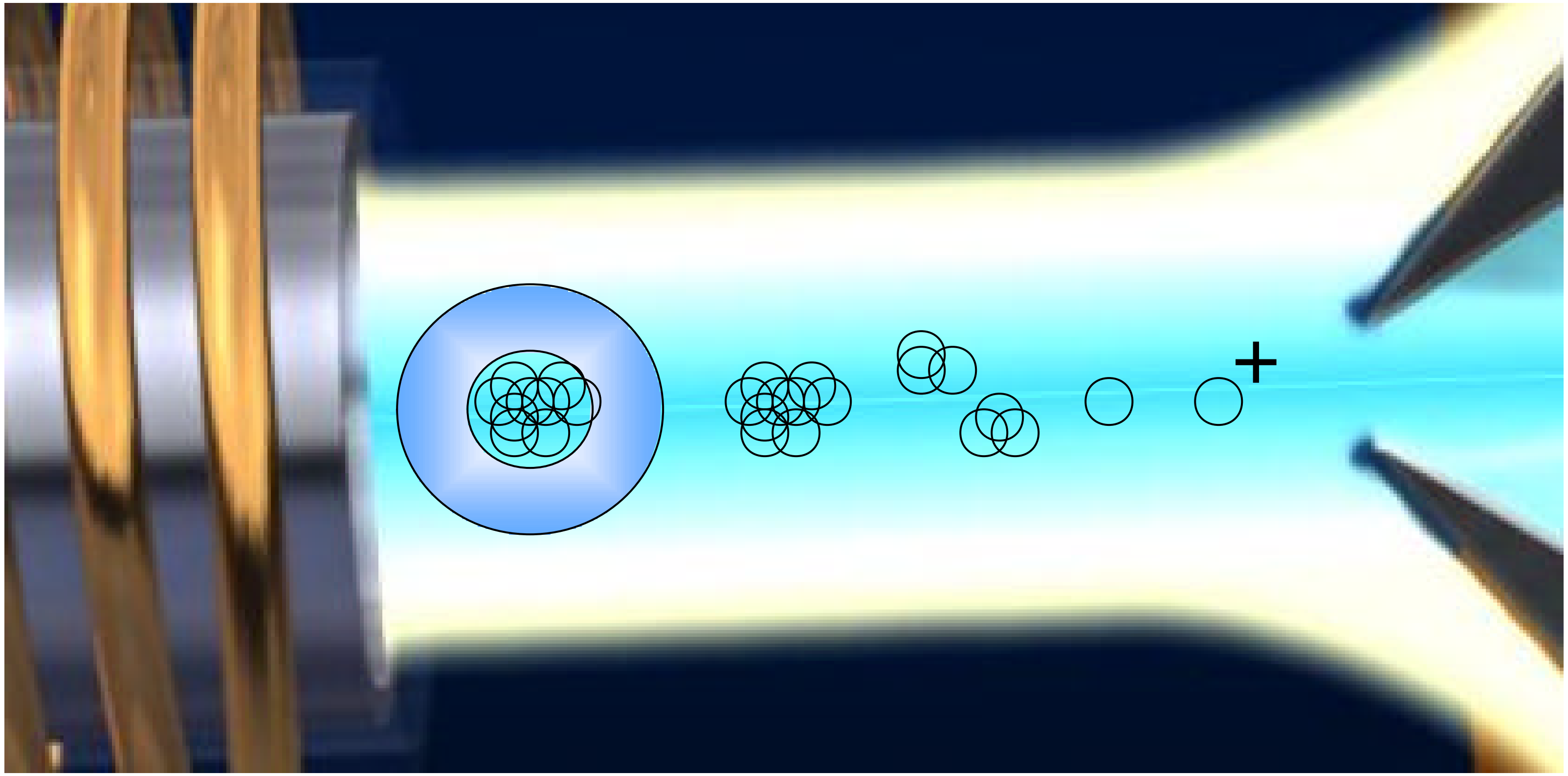
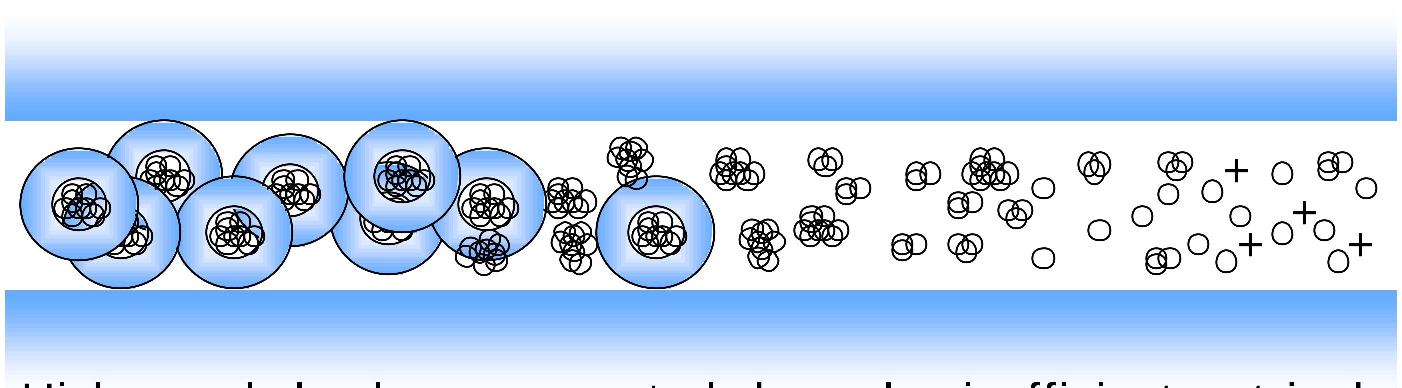
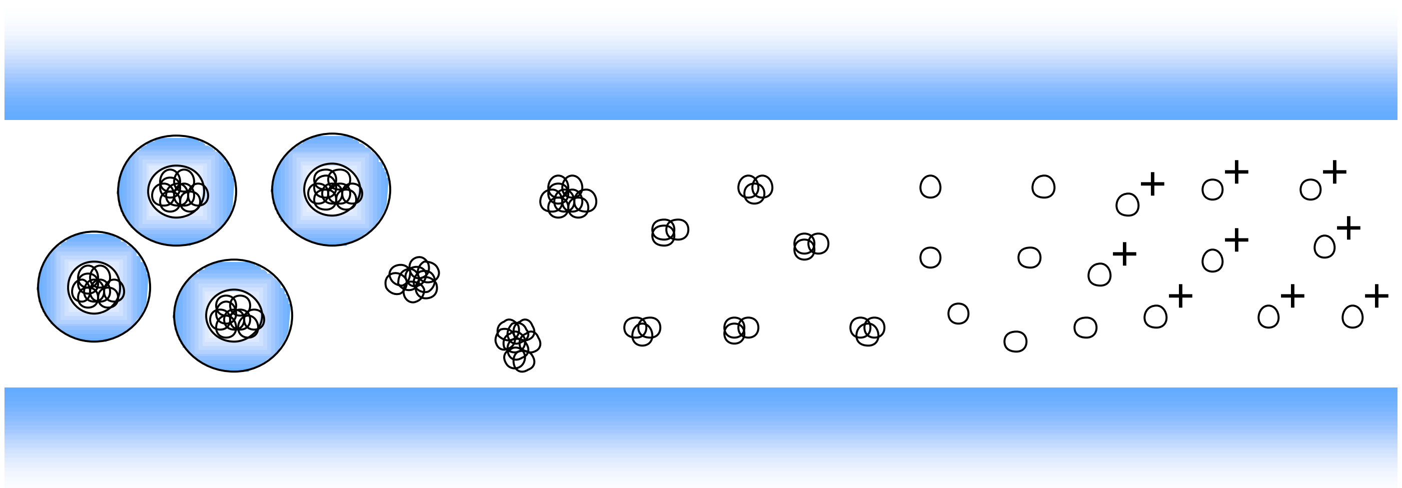
Sample Decomposition



Comparison of Plasma Cooling



High sample load, narrow central channel -> inefficient matrix decomposition



Low sample load, wide central channel -> efficient matrix decomposition

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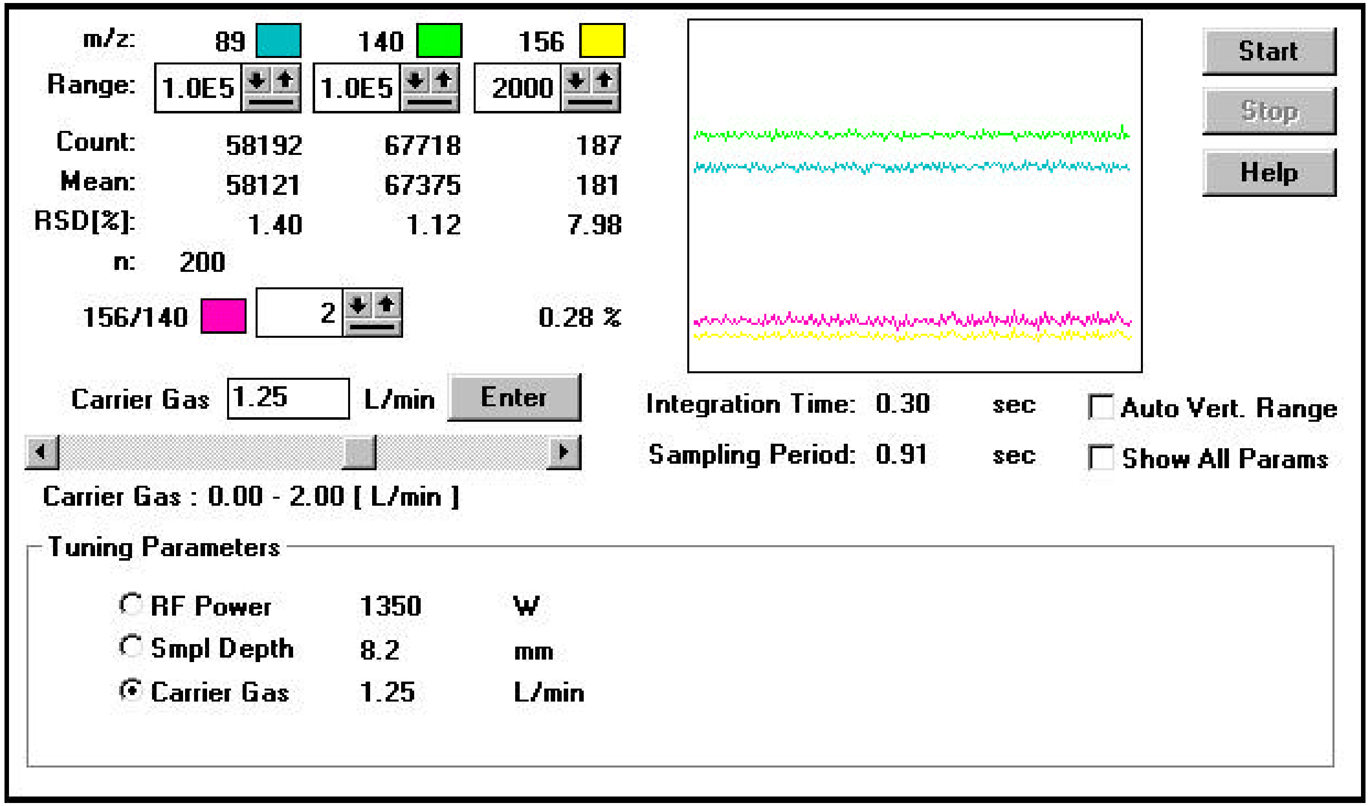
Low Oxide Level, Characteristic of the Agilent 4500



- Plasma conditions normal
- CeO/Ce ratio (worst- case) <0.3%
- Typical ICP-MS CeO/Ce ratio is 2% to 3%

Benefits of Efficient Matrix Decomposition

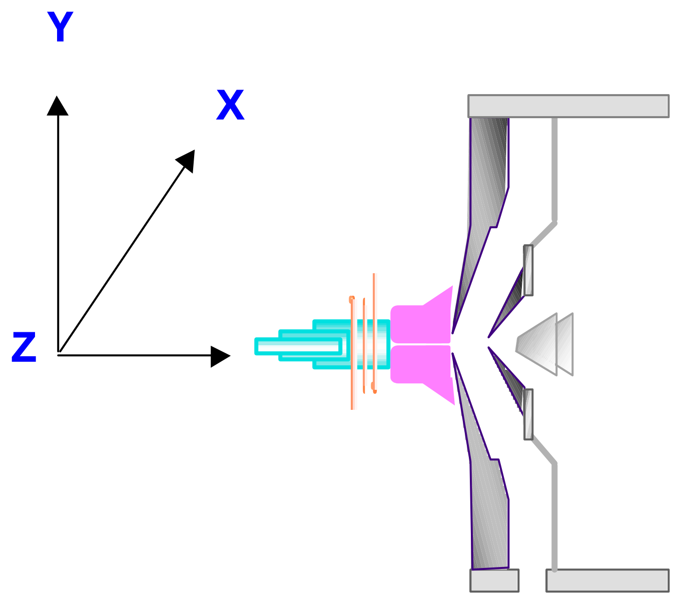
- Low oxide interference levels
  - usually measured by using “worst-case” indicator CeO/Ce
- Low matrix deposition on sample and skimmer cones
- Low polyatomic levels (eg Cl-based and S-based)
- Low matrix transfer into high-vacuum area
  - reduced requirement to remove and clean ion lenses
- Better tolerance to matrix changes

RF Generator

- 27 MHz RF supply
  - industry standard frequency for ICP-MS
- 1.6 kW
  - solid state - means no power tubes to replace
  - high power for flexibility
- Designed specifically for ICP-MS
  - not an "off the shelf" solution
- Fast and precise matching circuit
  - a.k.a torchbox
  - automatic
  - allows rapid switching from aqueous to organics
    - useful in LC applications

Agilent 4500 Series Automated Torch Positioning - Practical Benefits

- X-Y Optimization
  - cool plasma conditions require more precise torch positioning - narrow analyte channel
    - X-Y adjustable to 0.1mm
- Z optimisation (sampling depth)
  - ability to optimise sampling depth is critical to cool plasma analysis
    - at optimal sampling depth - **ALL** interferences are minimised
- Ease of use
  - automated positioning avoids manual adjustment with gloved hands
  - XY autotuning increases productivity



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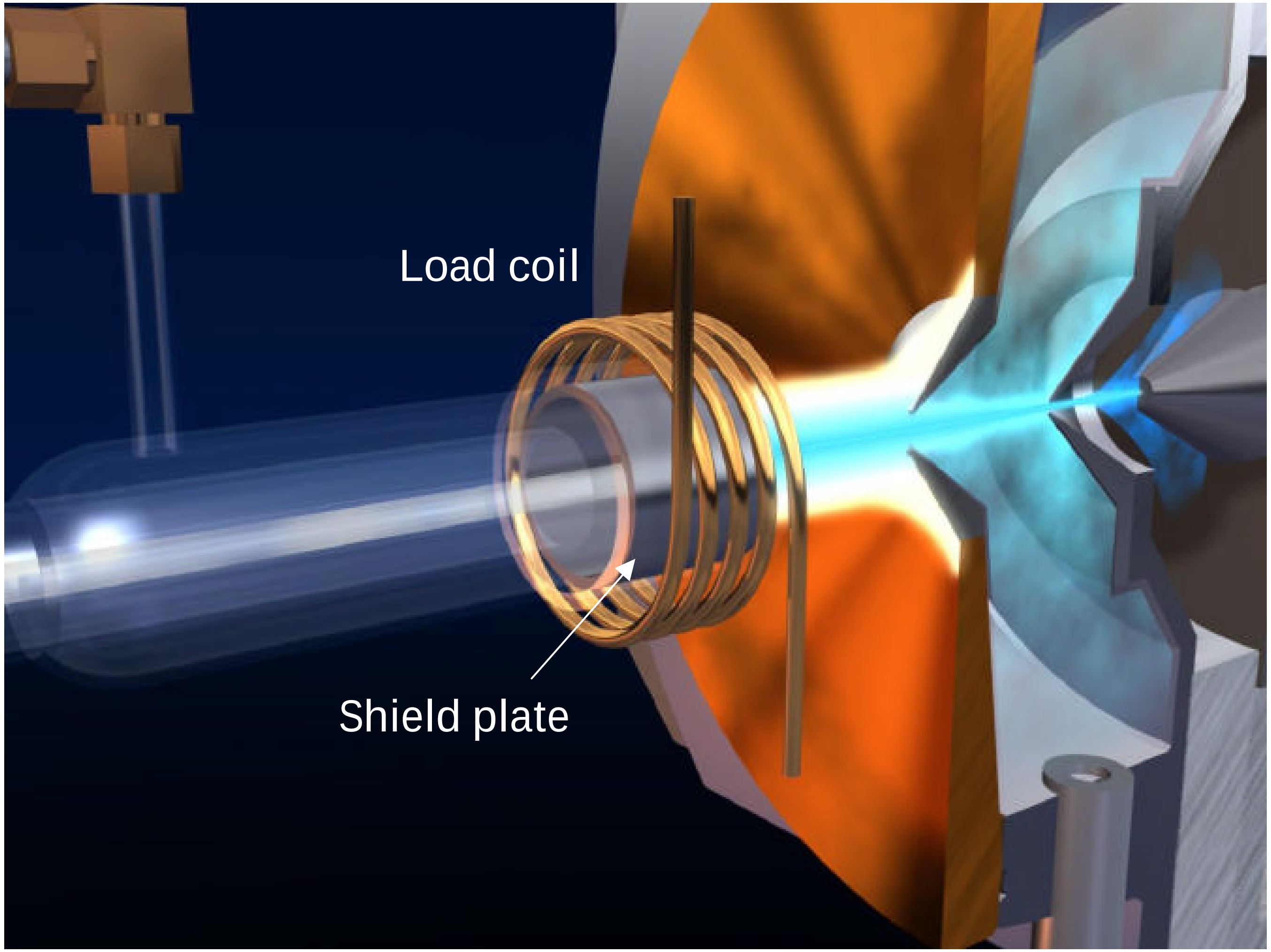
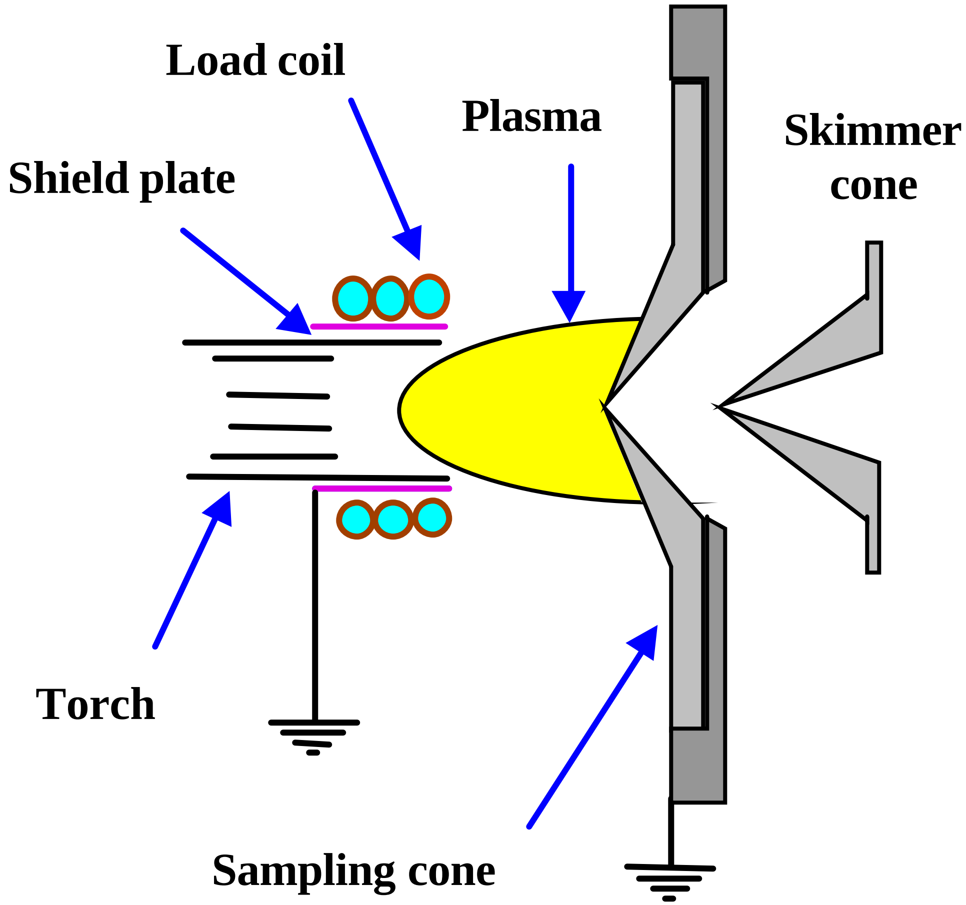
Shield Torch System

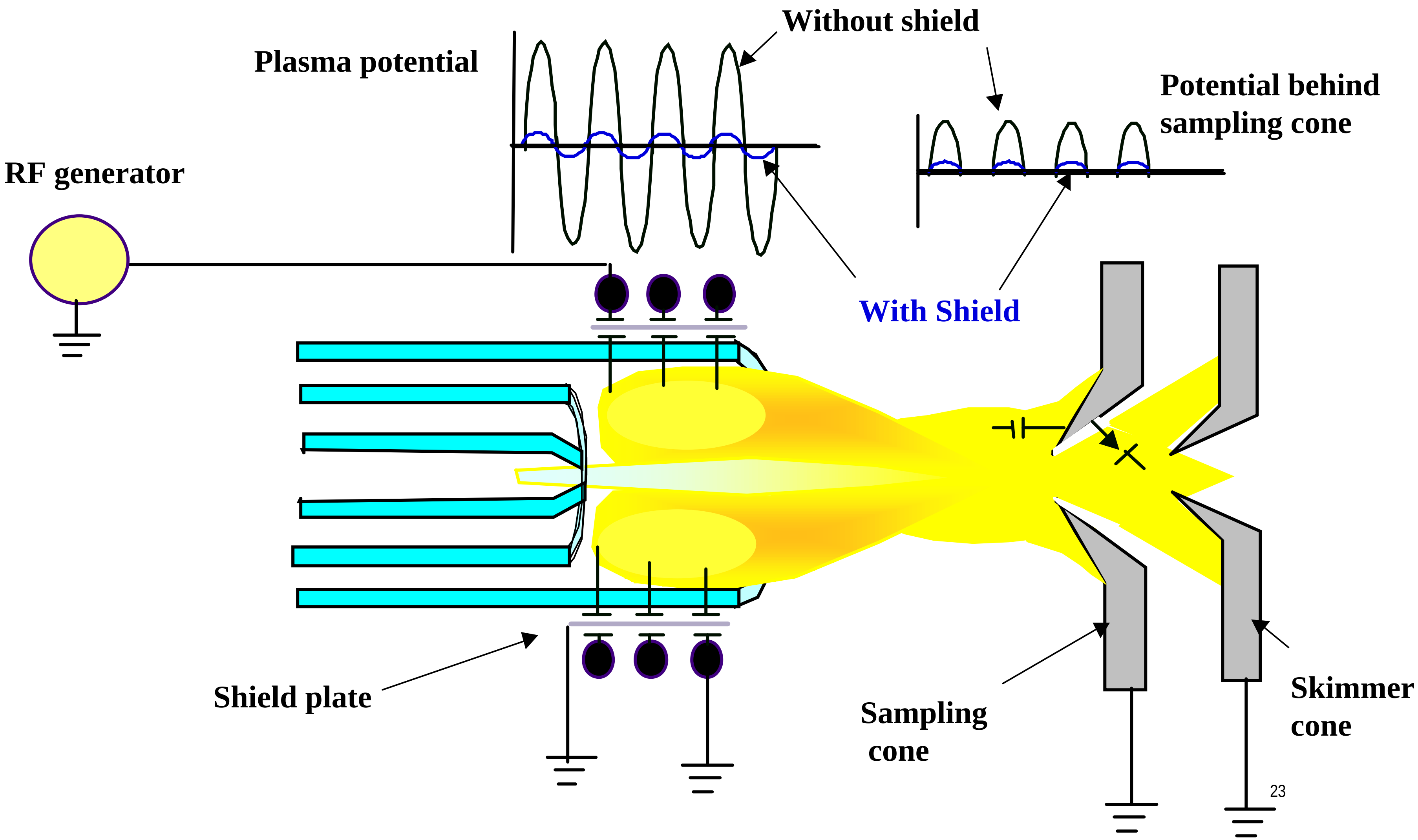


Principles of the Shield Torch System

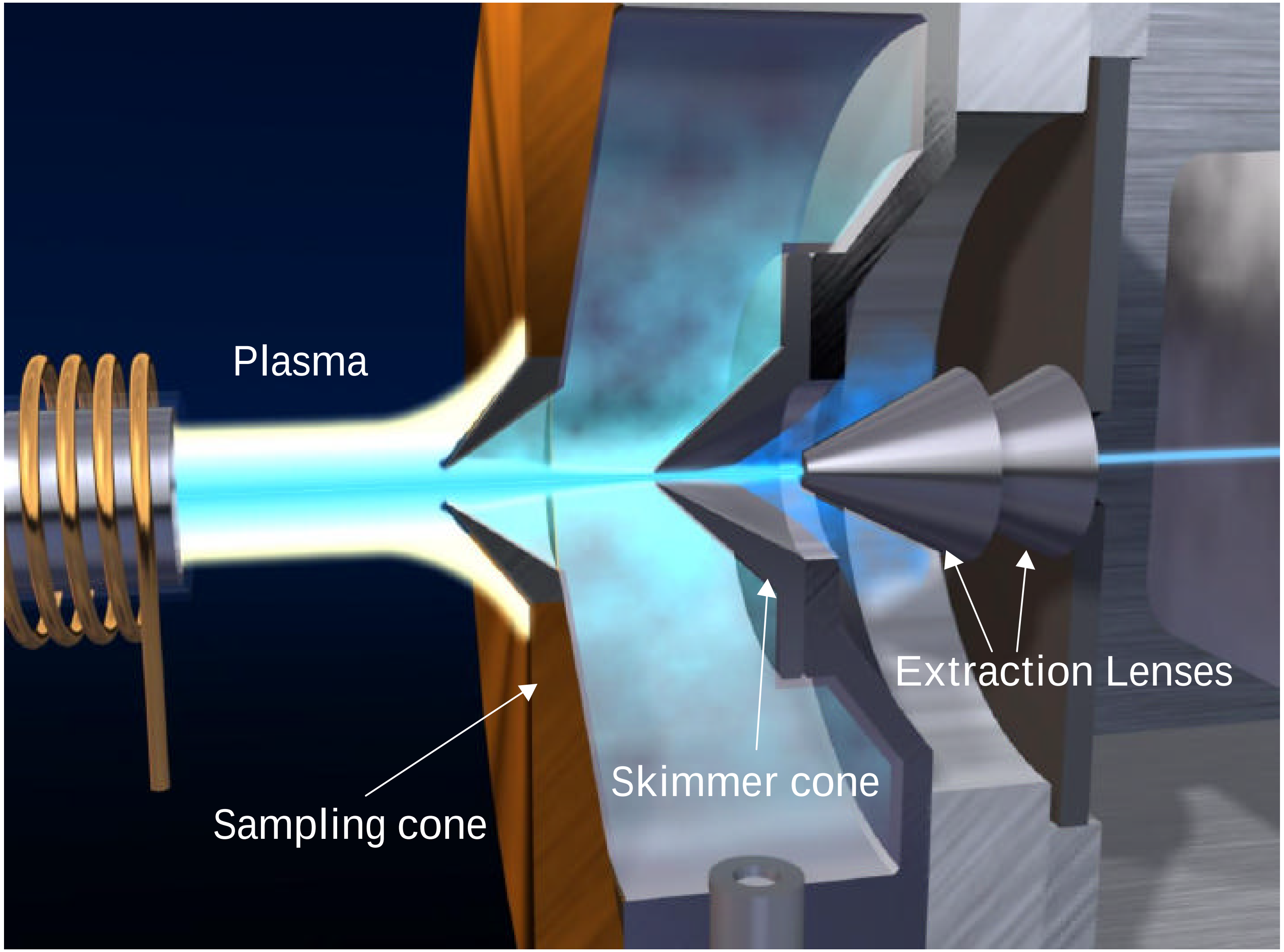
- The shield plate reduces capacitive coupling between the load coil and the plasma
- The ShieldTorch system eliminates secondary discharge behind the sampling cone
- Patented in Japan by Yokogawa/Agilent
  - virtually eliminates Ar based molecular species
  - allowed, for the first time, ppt determination of Ca, K and Fe by quadrupole ICP-MS



Electrical Model of Plasma and Interface



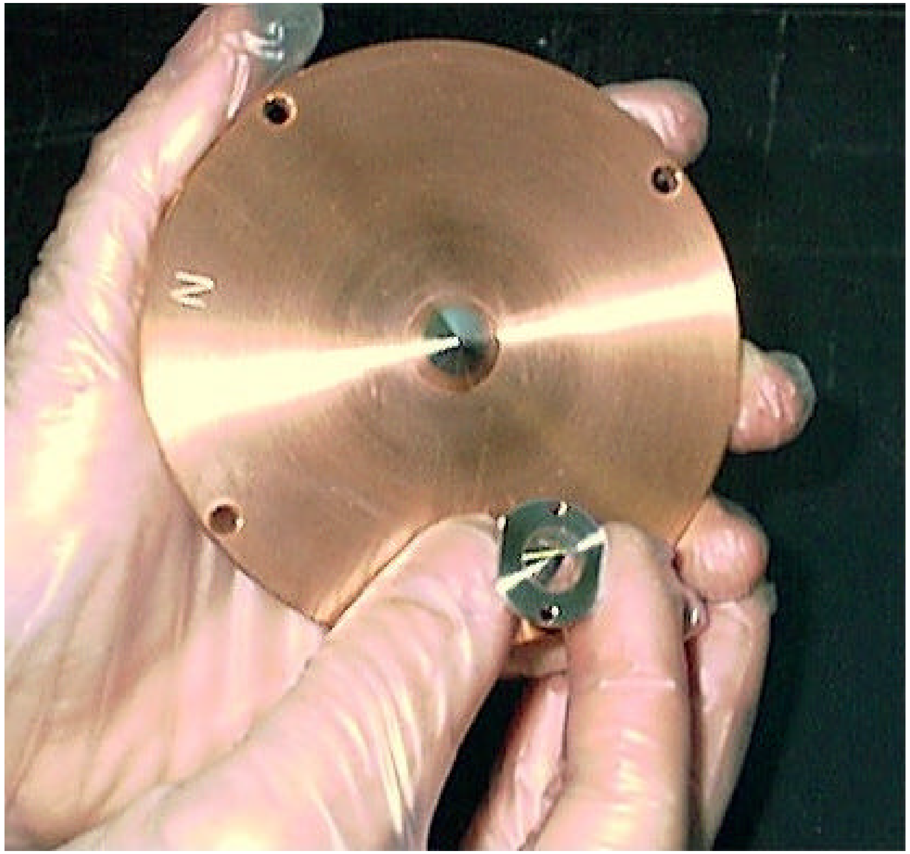
The Sampling Interface



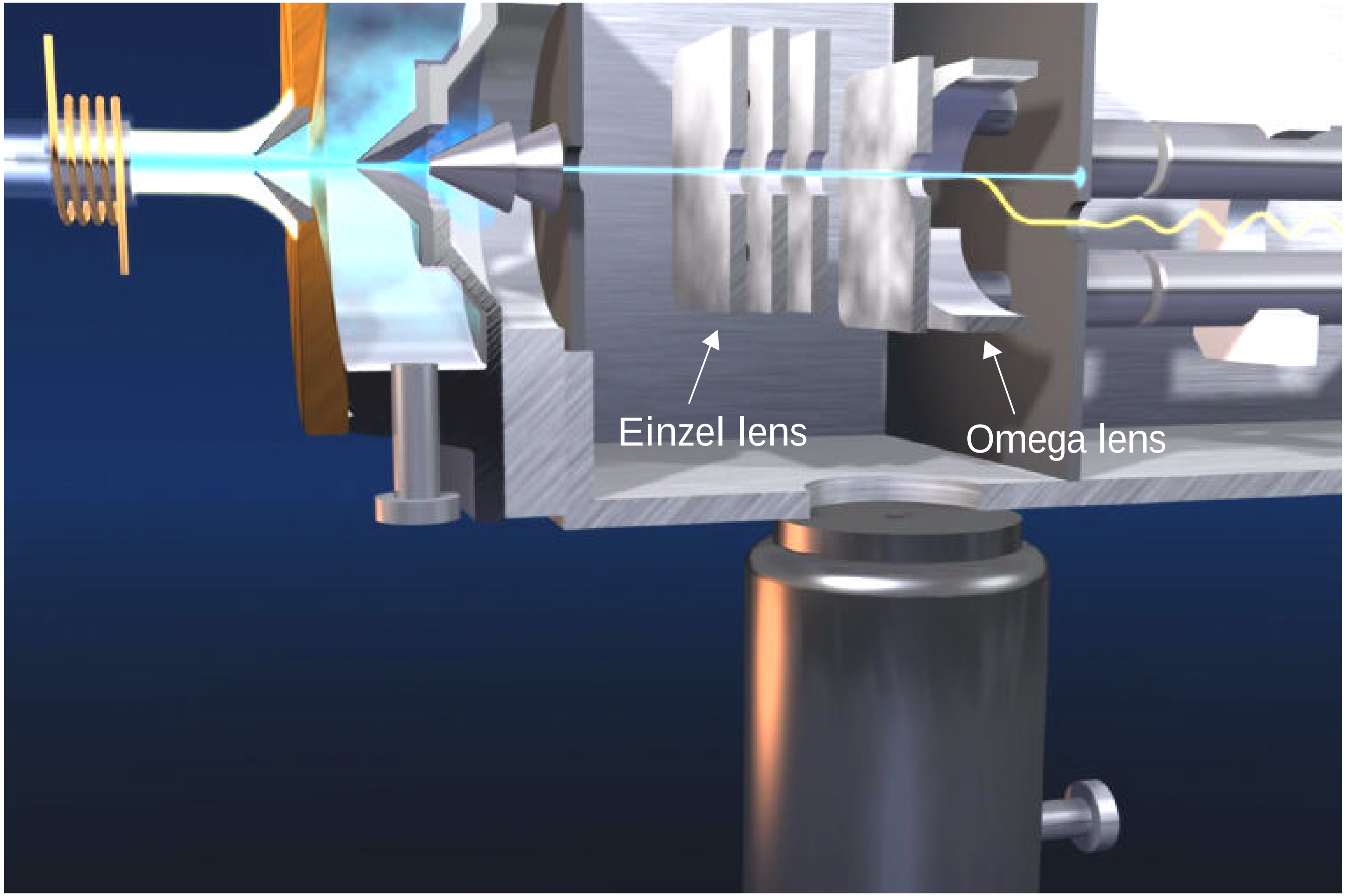
The Sampling Interface

- **Sample cone**
  - 1.0 mm orifice
  - acute angle resists clogging
  - Cu outer
  - Ni inner
  - Excellent thermal conductivity
    - ➔extends the life of the cone
- **Skimmer cone**
  - Ni standard
    - ➔0.4 mm diameter orifice
    - ➔runs "hot” to burn off salt deposits
    - ➔virtually impossible to clog

- Pt options for both sampler and skimmer



The Ion Lenses



Ion Lenses - function

- Detector must be screened from Plasma
  - plasma is an intense source of photons and neutrals
  - electron multiplier is photon/neutral sensitive
- Common approach is to place a metal disc in the neutral path
  - "Photon Stop" or "Shadow Stop"
  - ions must be defocused around the disc and then re-focused on the other side
- A more advanced approach is to use an off axis lens system

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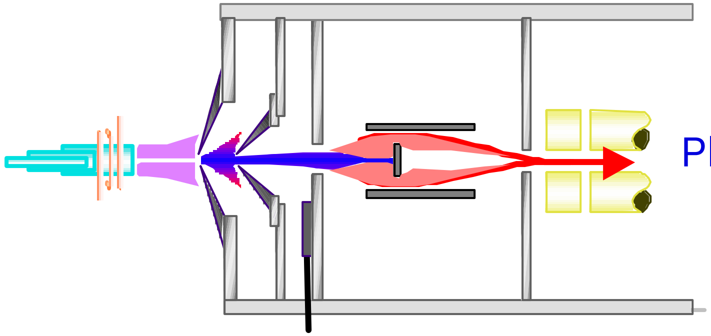
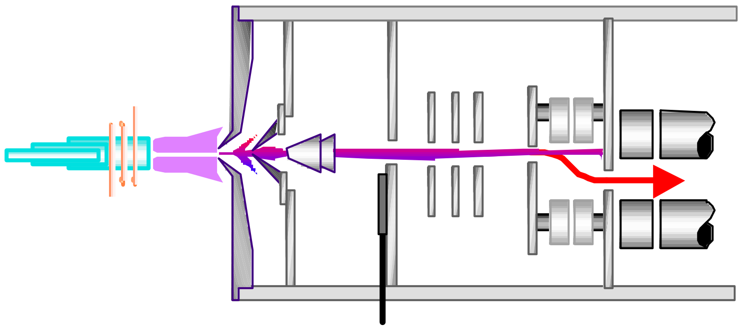
Different types of lens systems

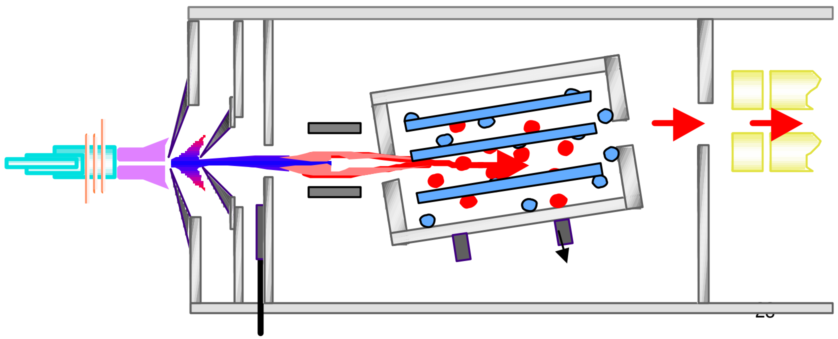


Photon/Shadow/”Neutral” Stop System

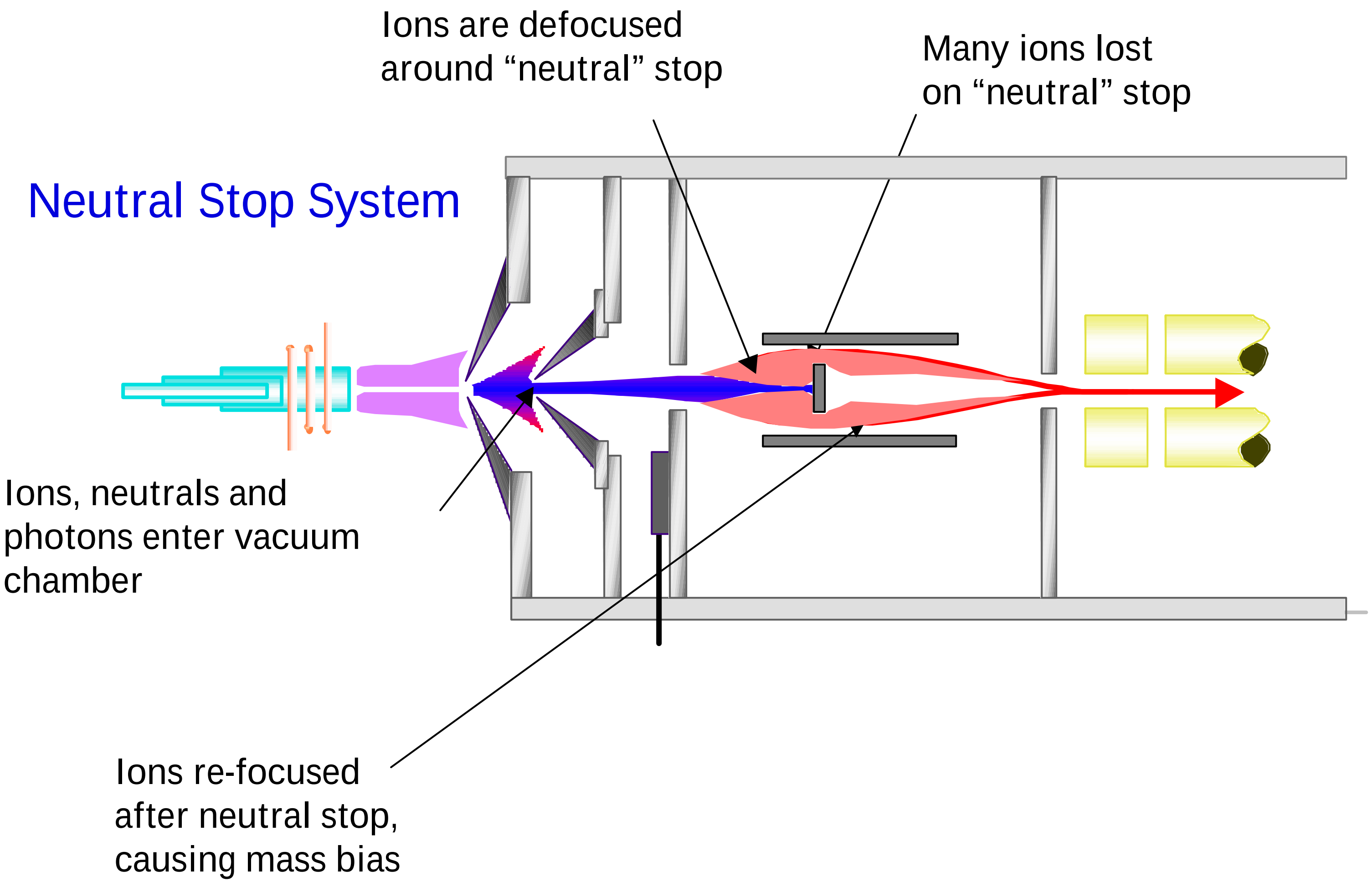
Off-Axis System



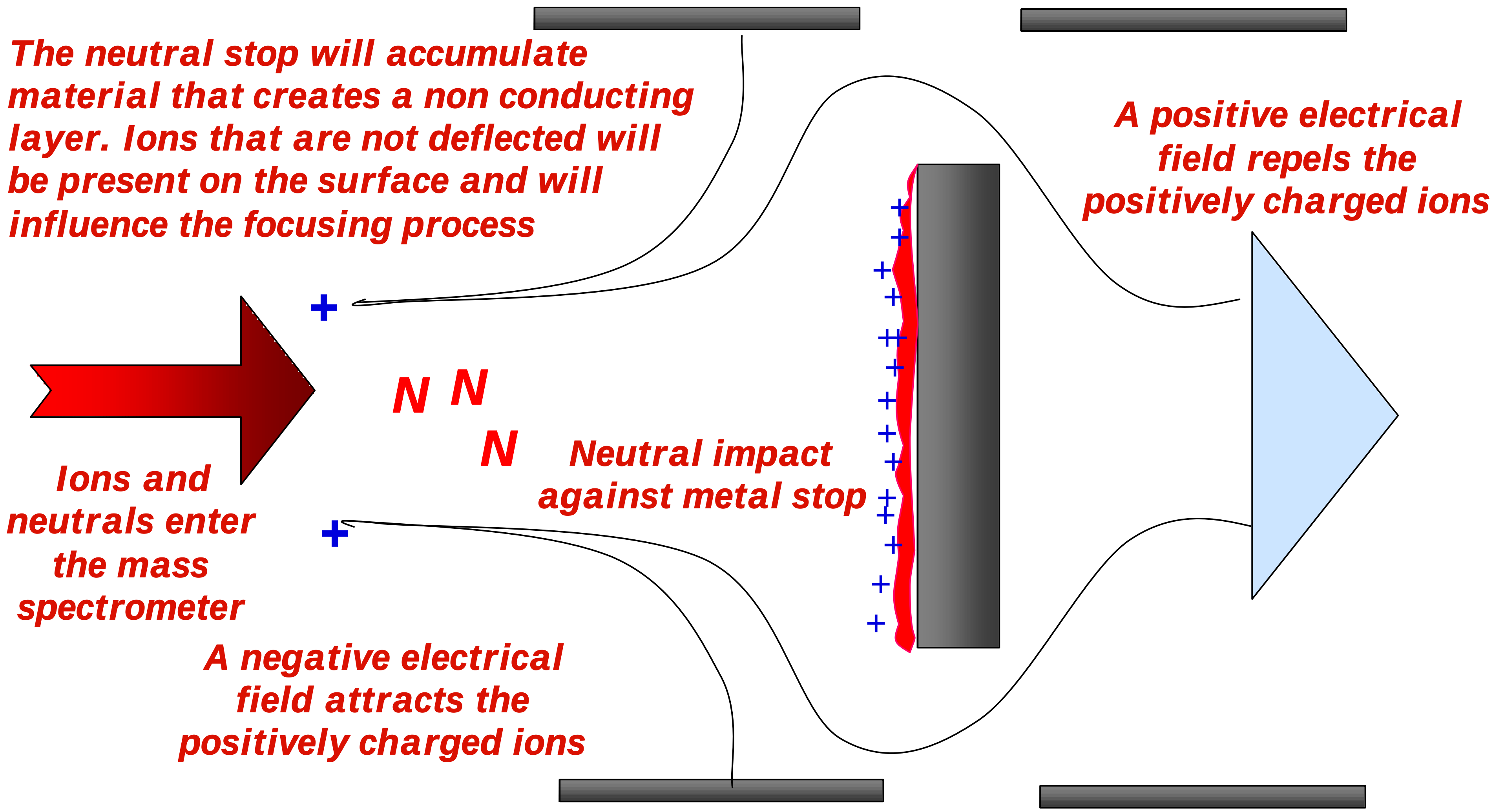
Collision cell



“Neutral” Stop lens system

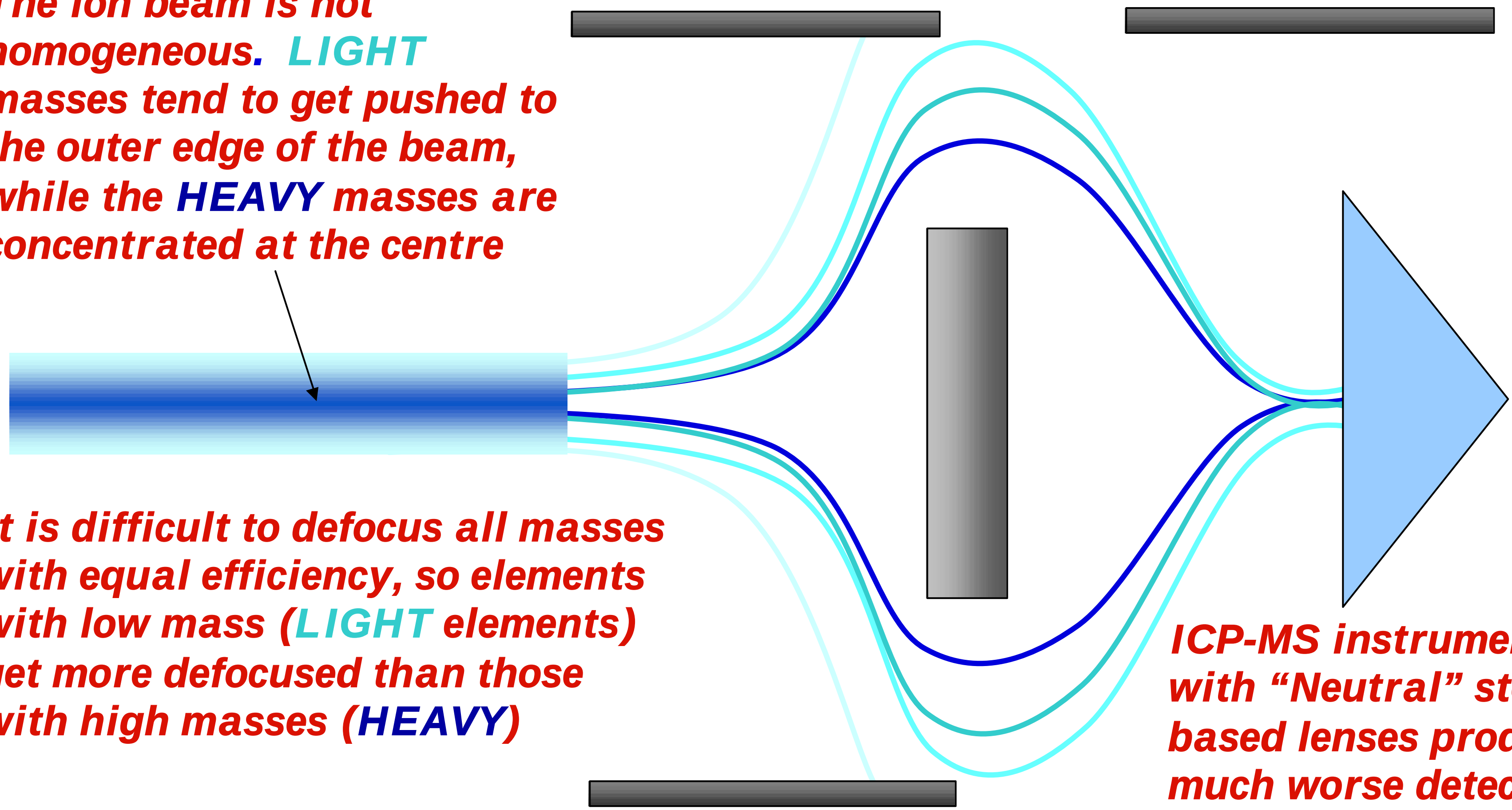


Neutral Stop based lens design



Neutral Stop based lens design

The ion beam is not homogeneous. LIGHT masses tend to get pushed to the outer edge of the beam, while the HEAVY masses are concentrated at the centre



It is difficult to defocus all masses with equal efficiency, so elements with low mass (LIGHT elements) get more defocused than those with high masses (HEAVY)

ICP-MS instruments with "Neutral" stop based lenses produce much worse detection limits for low mass elements

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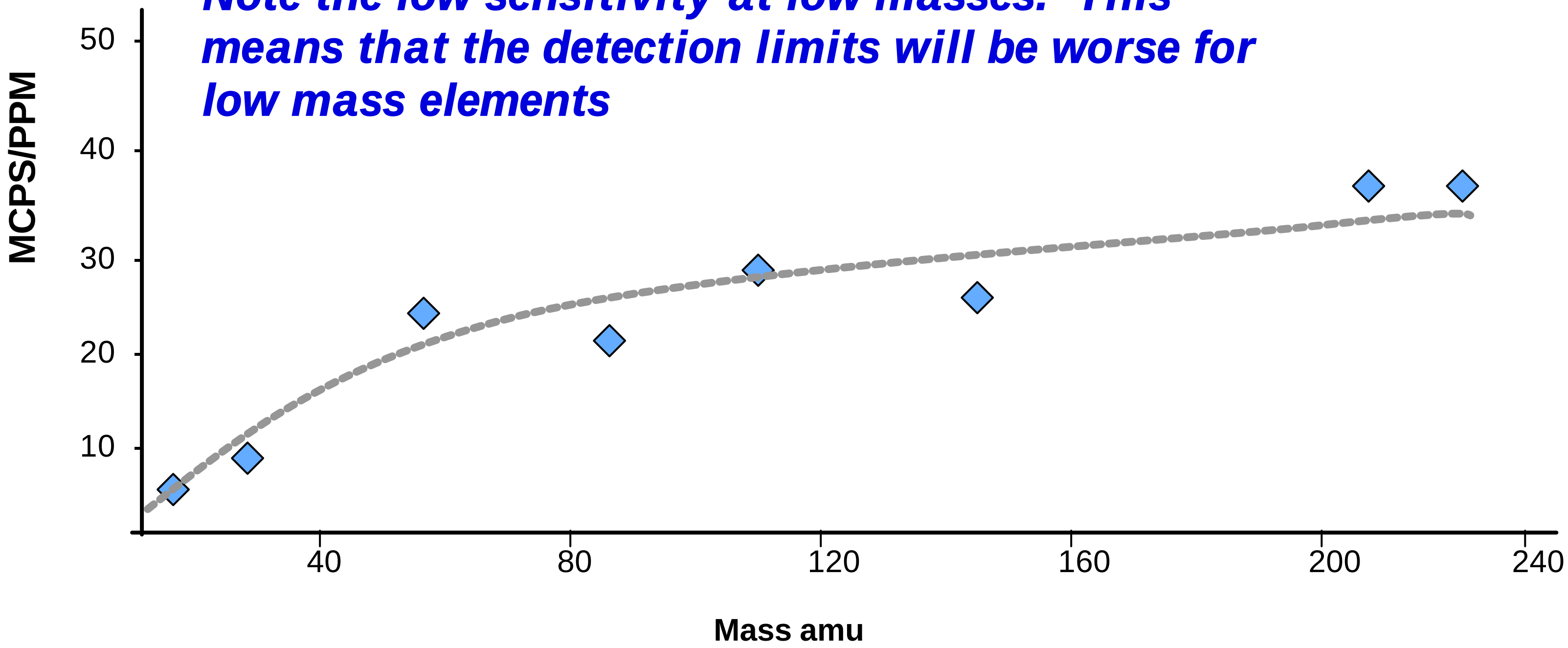
Mass Response curve - “Neutral” stop

This is a typical mass response from an instrument with a “neutral” stop
Note the low sensitivity at low masses. This means that the detection limits will be worse for low mass elements



“Neutral” Stops

- Can charge up when contaminated
  - leads to signal instability (drift) when “dirty”
  - require frequent cleaning
- Induce mass bias effects
  - lead to significantly lower sensitivity at low mass than high
    - semiquantitative measurements less accurate
    - can lead to problems with interference correction
    - gives false low measurements of “doubly charged” species

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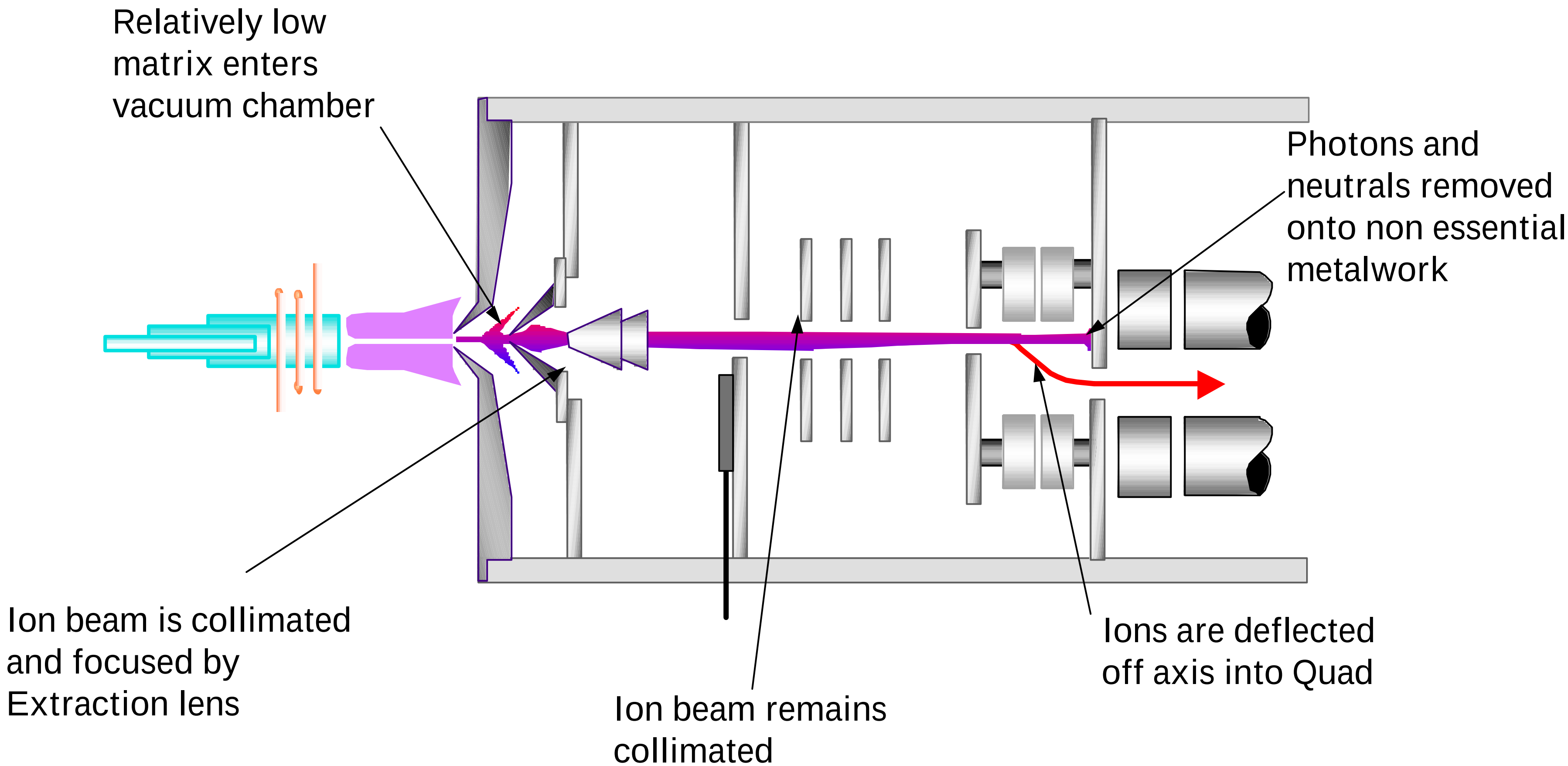
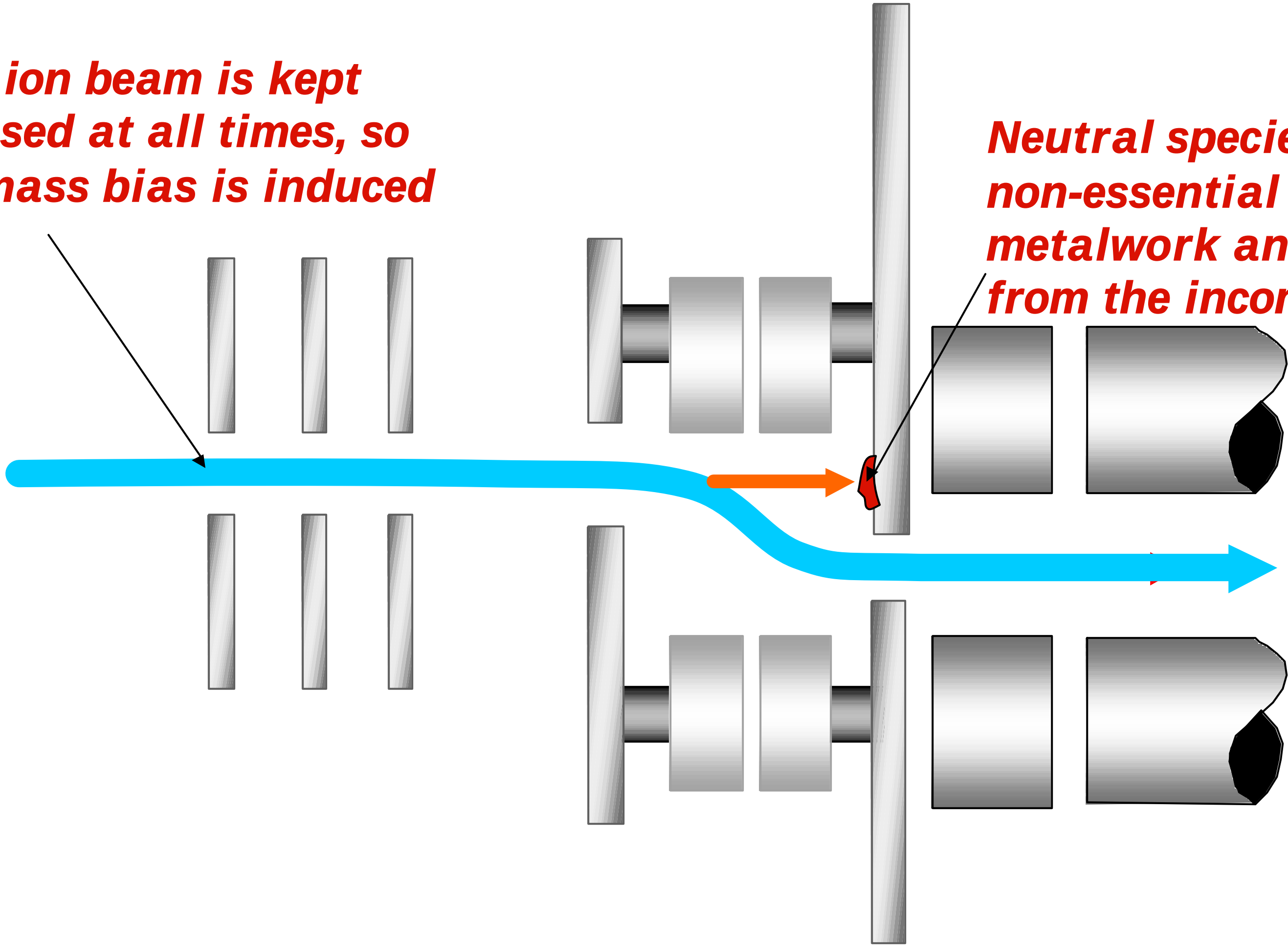
Omega lens - off axis system



The Omega Lens - off axis system

The ion beam is kept focused at all times, so no mass bias is induced

Neutral species impact on a non-essential piece of the metalwork and are kept away from the incoming ion beam



Mass Response curves

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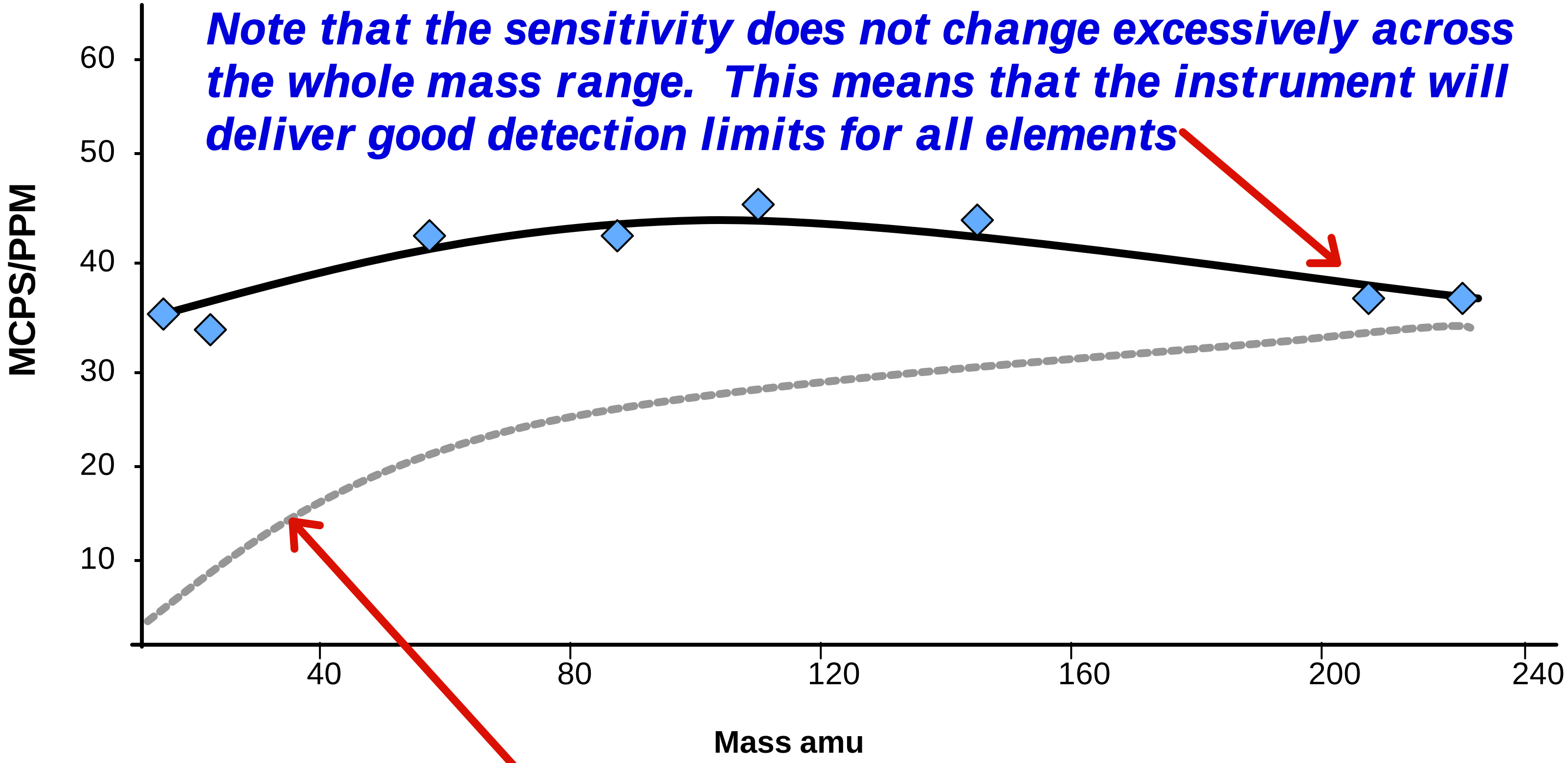
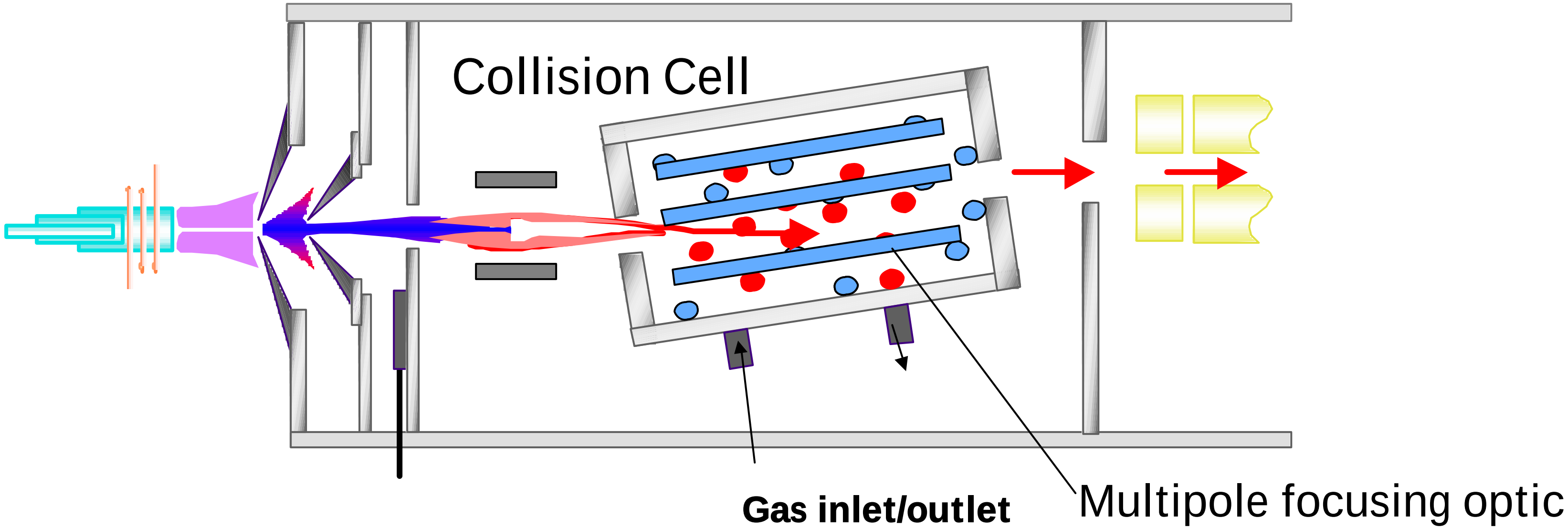
This is the mass response from a default tuned Agilent 4500. Note that the sensitivity does not change excessively across the whole mass range. This means that the instrument will deliver good detection limits for all elements



This is the typical mass response from an instrument with a "neutral" stop. Note the low sensitivity at low masses. This means that the detection limits will be worse for low mass elements

Principle of Collision Technology



- A simple lens accelerates ions and neutrals into the cell
- Molecular species collide (hit) gas atoms/molecules
  - are broken up
- Not good for “complicated” matrices

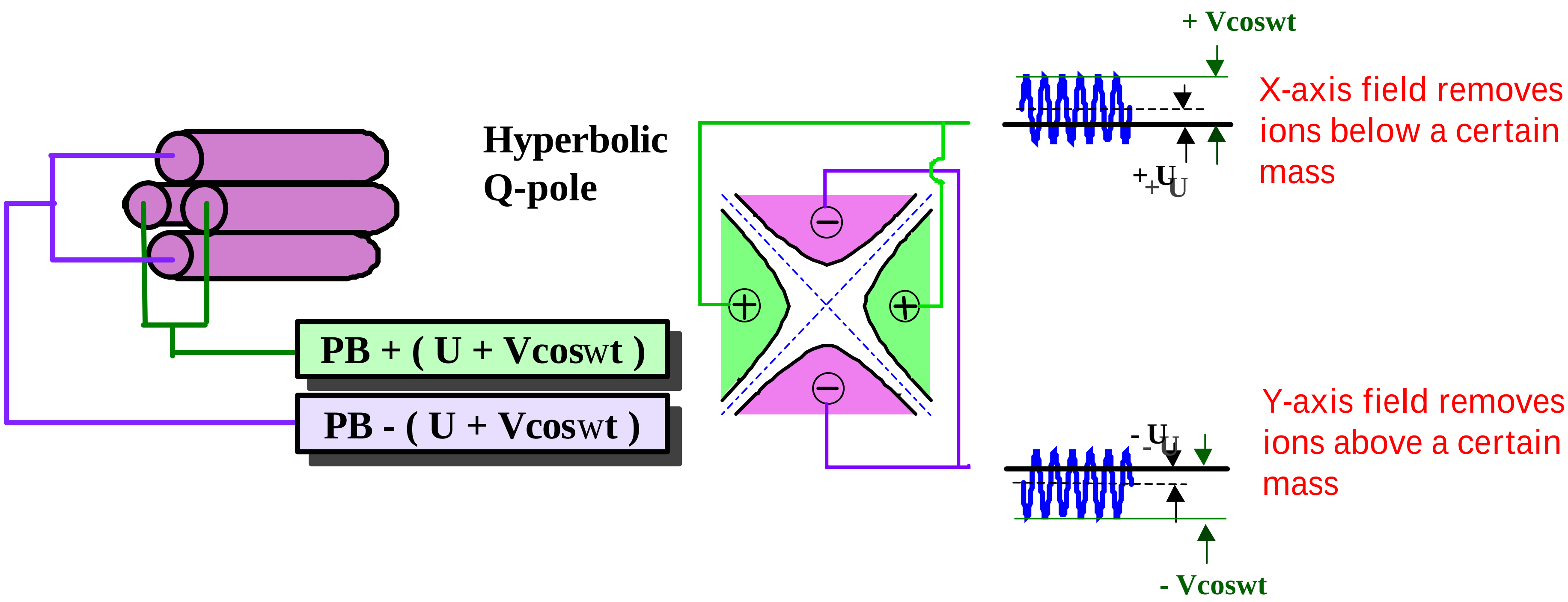
Quadrupole

- Agilent 4500 Series quadrupole rods have true hyperbolic cross-section
  - only ICP-MS with hyperbolic rods
  - improved abundance sensitivity
- Pre-filter
  - improved mass filter function
- 3.0MHz RF drive
  - fastest in any ICP-MS
  - excellent transmission
  - excellent resolution

Quadrupole Mass Spectrometer

- Quadrupole is precisely aligned square array of 2 pairs of rods
- Ions travel down the length of the central space between the rods and are filtered according to mass
- REQUIREMENTS -
- Good vacuum (low pressure) ->low scattering -> less peak spreading
- Ions should be subjected to a large number of RF cycles - efficient filtering
  - function of rod length and quadrupole RF frequency
- RF field should be hyperbolic, ideally from hyperbolic rods
  - round rods are cheaper to manufacture - hyperbolic field is only partially simulated using electronics

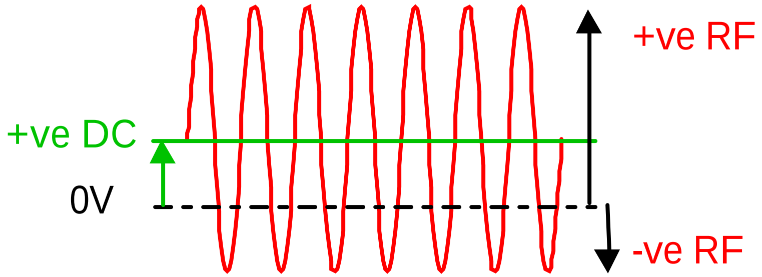
Quadrupole Theory



For a given combination of RF and DC voltages, the quadrupole only lets ions of a specific mass pass through to the detector.
(In fact, quadrupole filter works on mass/charge ratio, not mass)

How the Quadrupole Works

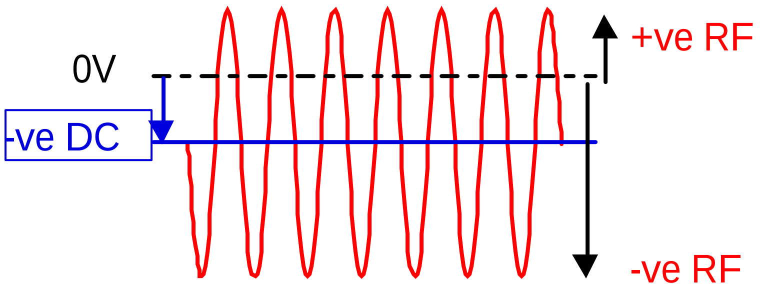
In the x-axis (x-z plane)



Overall +ve field repels ions from rods towards stable central trajectories. However, -ve swing of RF causes ions to oscillate. Lighter ions have less momentum and so oscillate more leading to unstable trajectories.

Light ions lost

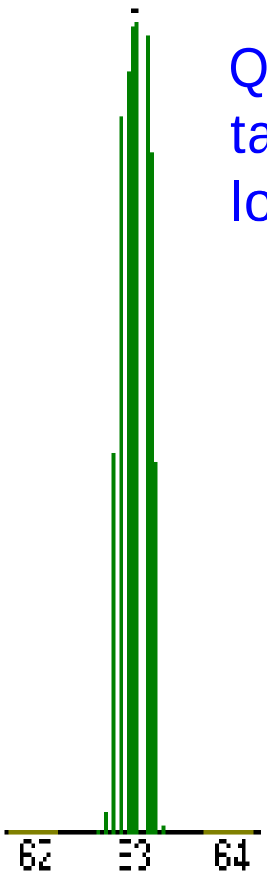
In the y-axis (y-z plane)



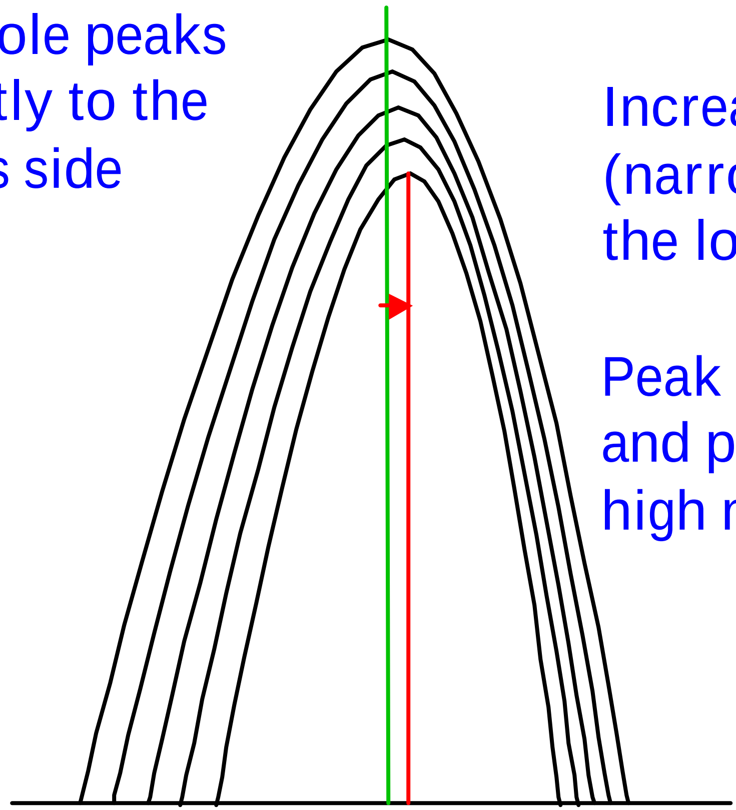
Overall -ve field attracts ions away from central stable trajectory. However, +ve swing of RF causes ions to be repelled from rods. Heavier ions have more momentum and so cannot be repelled to stable central trajectories

Heavy ions lost

Peak Shape and Resolution



Quadrupole peaks tail slightly to the low mass side

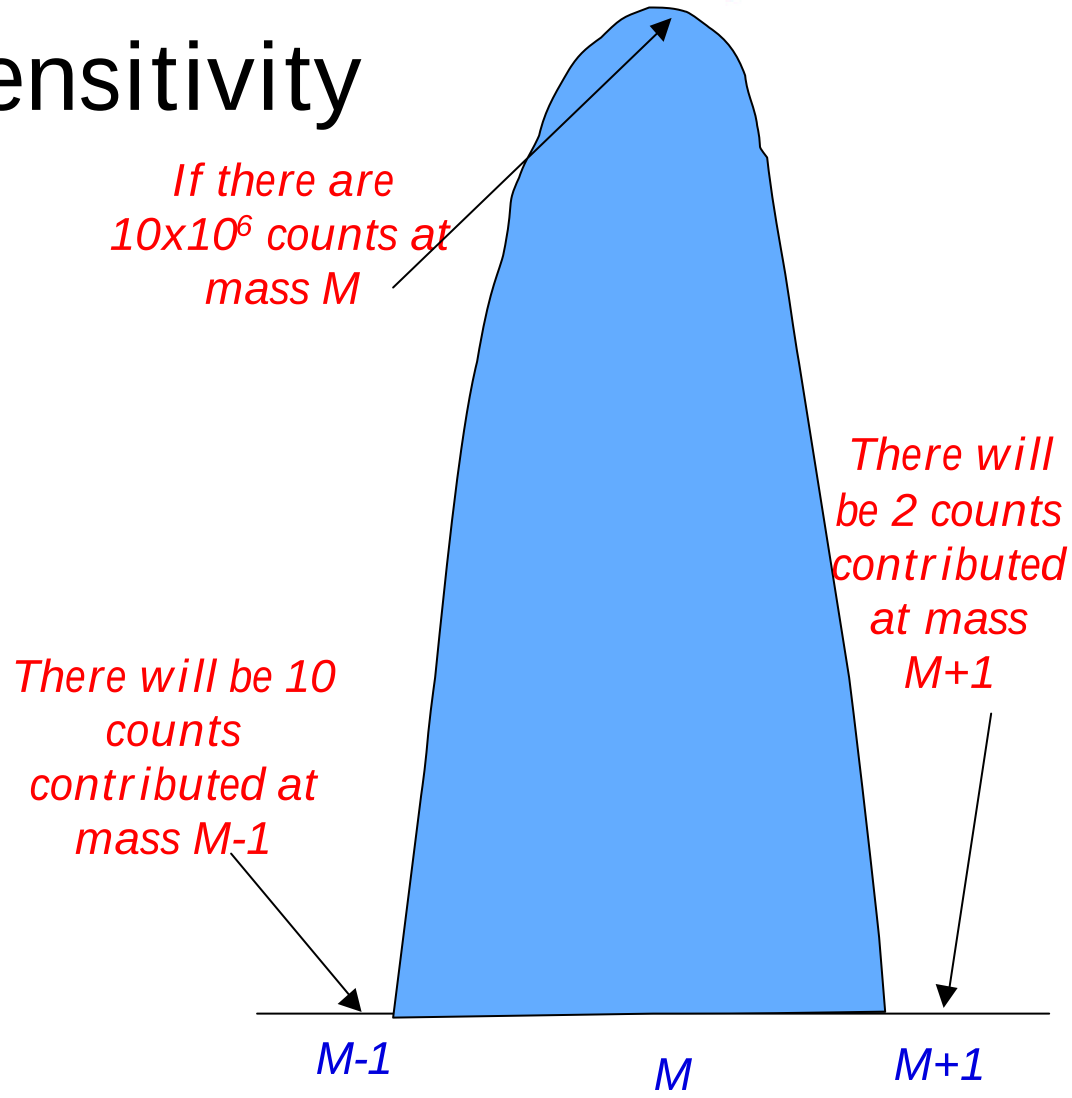


Increasing the Resolution (narrower peaks) affects the low mass side more.

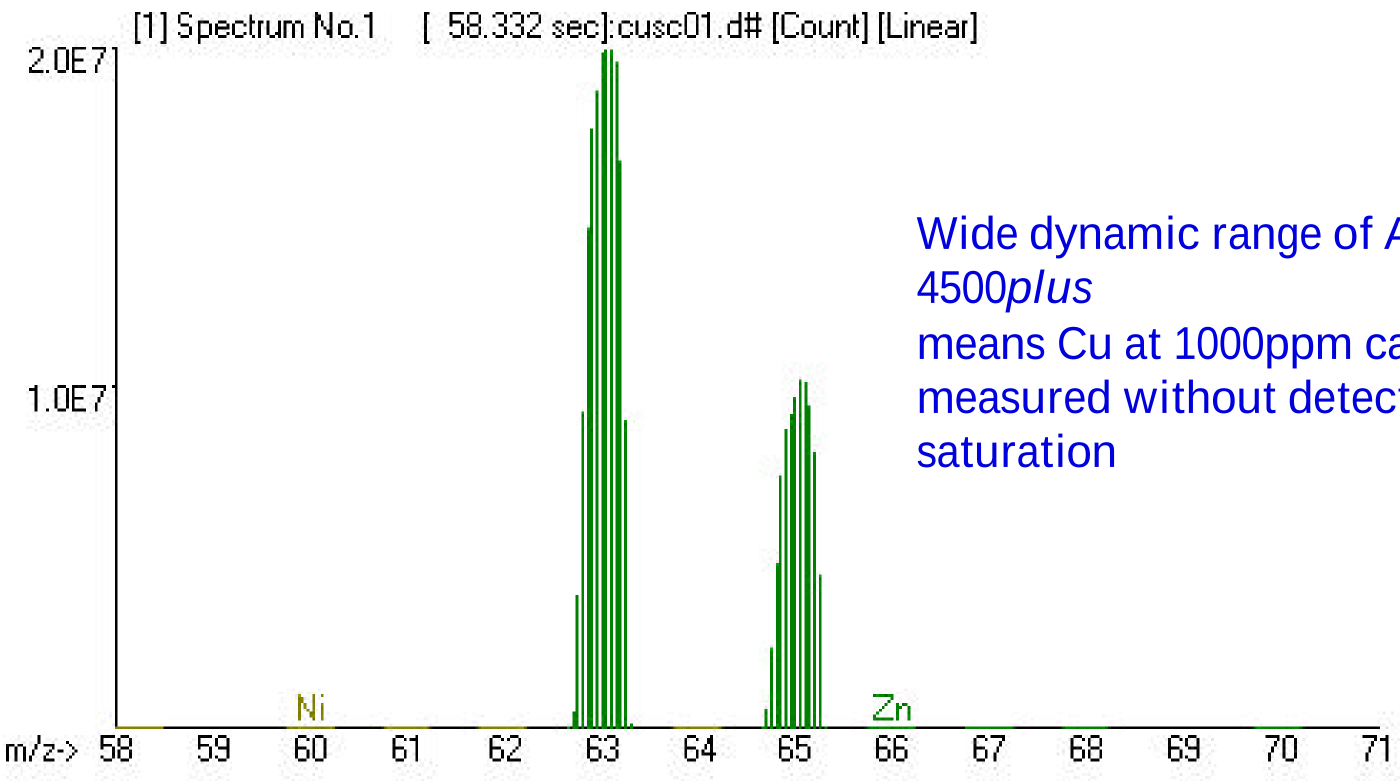
Peak height is reduced and peak center shifts to high mass side.

Abundance sensitivity

- Is a measure of peak symmetry
  - usually quoted as two numbers
    - low mass
    - high mass
- Is a measure of how much of a signal in mass M appears one mass below (M-1) and one mass above (M+1)
- For instance
  - 1×10^{-6} low mass
  - 2×10^{-7} high mass

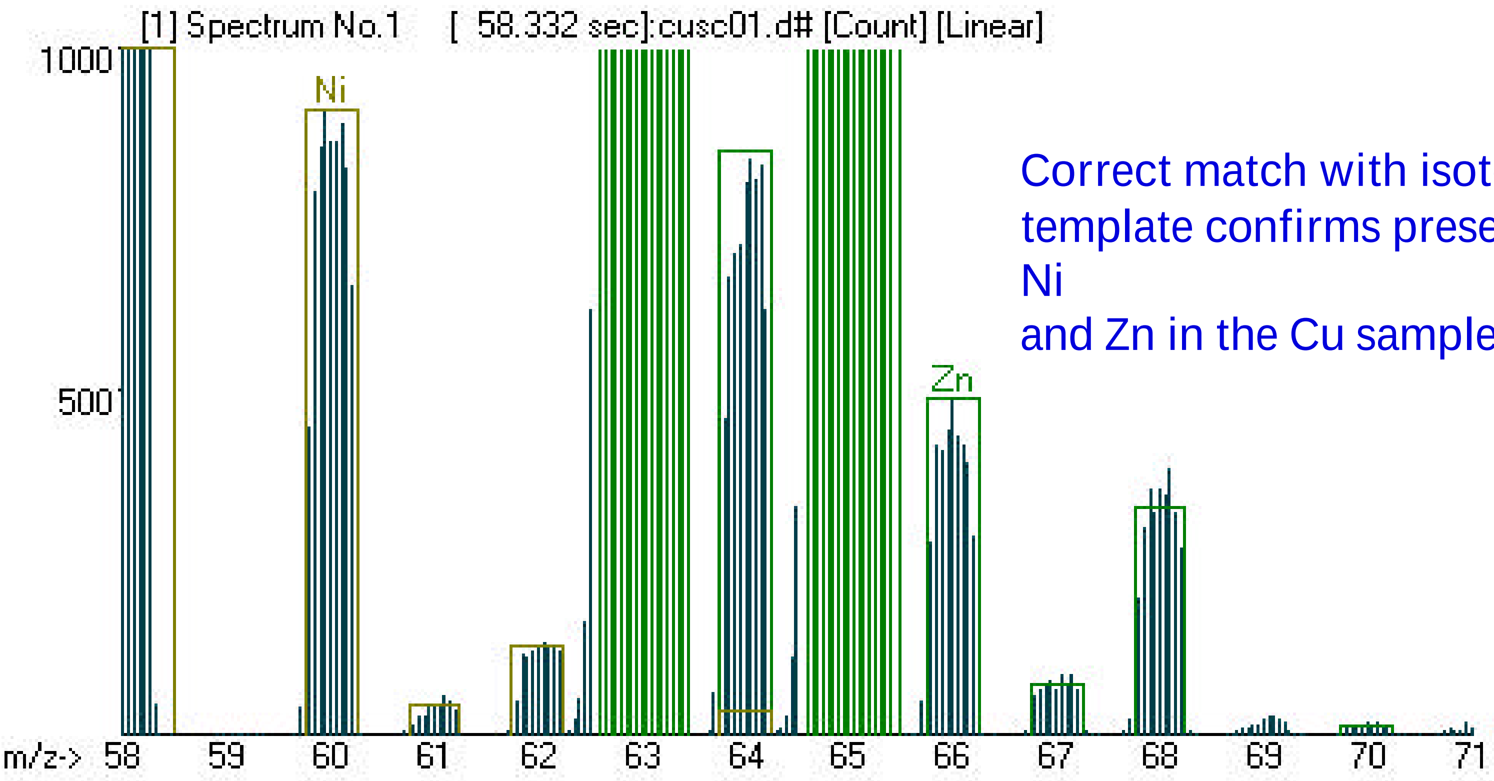


Spectrum of 0.1% (1000ppm) Solution of High-Purity Copper



Wide dynamic range of Agilent 4500*plus*
means Cu at 1000ppm can be measured without detector saturation

Expanded Scale Showing Trace Impurities at 0.01% Relative to Cu (100ppb in Soln)



Correct match with isotopic template confirms presence of Ni
and Zn in the Cu sample

Excellent abundance sensitivity ensures Cu peaks are completely resolved from trace Ni and Zn at 62,64, 66

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Vacuum System

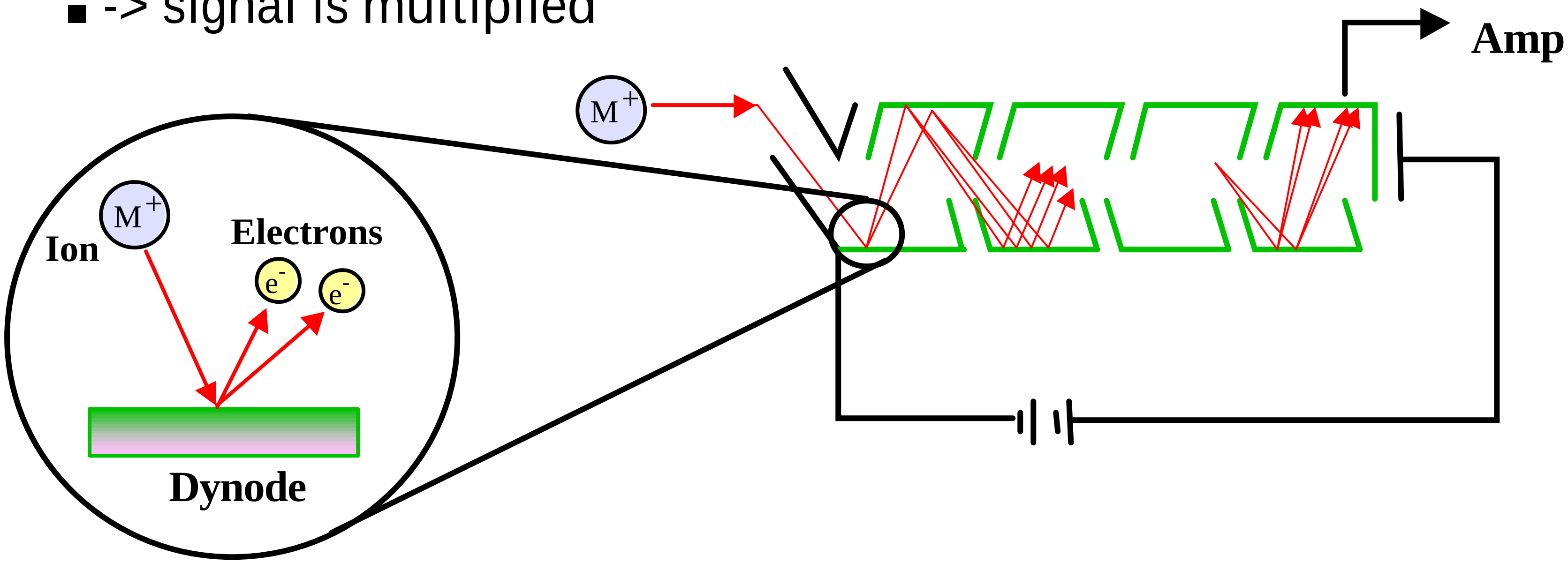
- Interface
  - 18 cu.m/hour rotary pump
    - typical operating pressure 0.1 torr
- Intermediate chamber
  - 250 L/sec turbomolecular pump
    - typical operating pressure 10-4 torr
- Analyser/detector chamber
  - 70 L/sec turbomolecular pump
    - typical operating pressure 10-6 torr
- Good vacuum means
  - lower noise
  - improved abundance sensitivity

“But Most Users Want to Analyse ppt to 10's of ppm”

- Two approaches
  - defocus the ion beam when a "high" signal is measured
    - loss of data
    - dynamic range only 6 orders - max conc ~1ppm
  - operate the detector in a sensitive (pulse counting) and low gain (analogue) mode
    - no loss of data up to max conc
    - dynamic range extended to 8 orders
    - max conc 100ppm
    - can be extended to 1000ppm by lens adjustment

The Detector

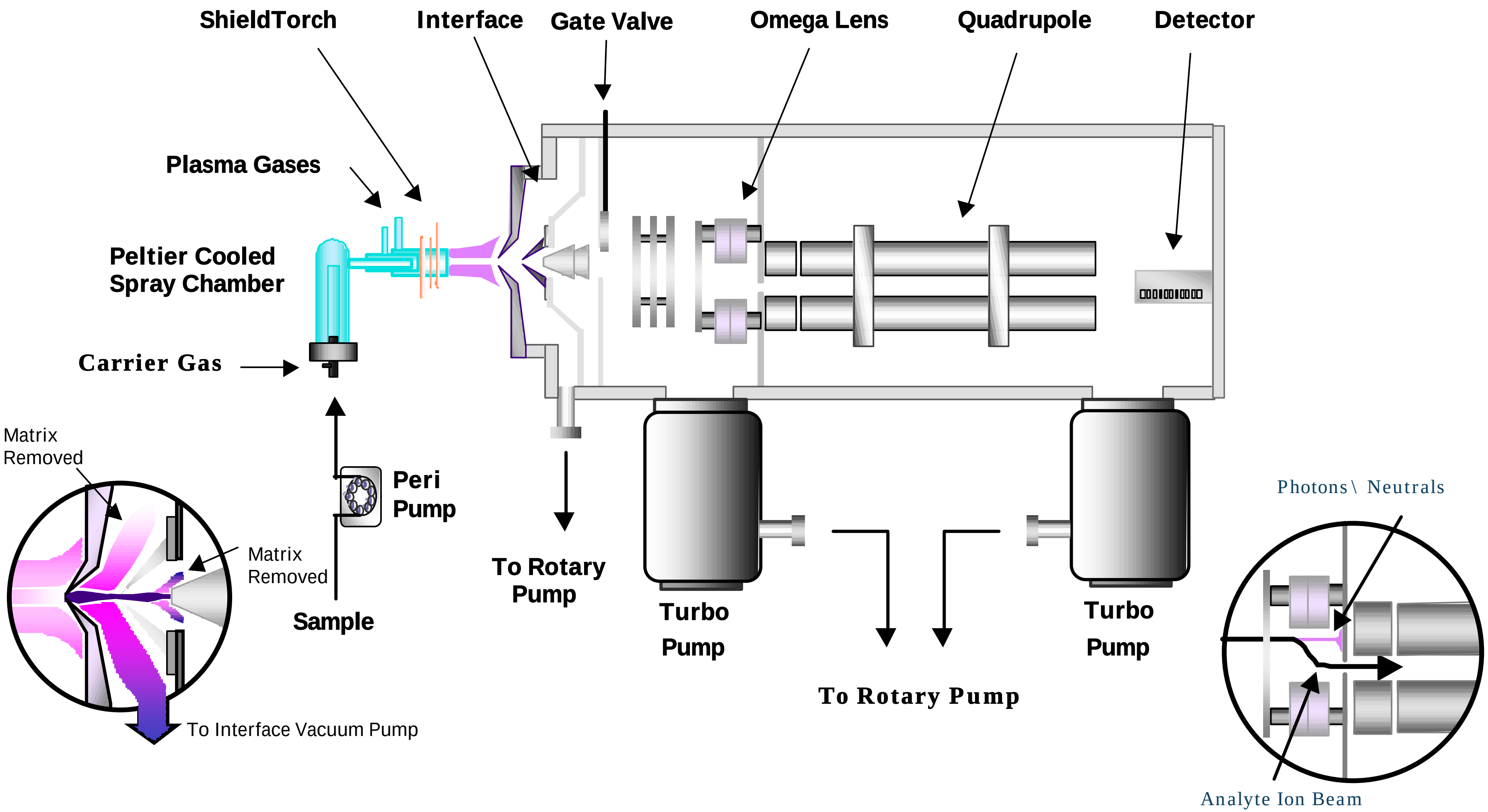
- Electron multiplier
  - the Agilent 4500 Series features a discrete dynode detector (ETP)
    - each dynode gives "cascade" of electrons
    - -> signal is multiplied



Extended Dynamic Range

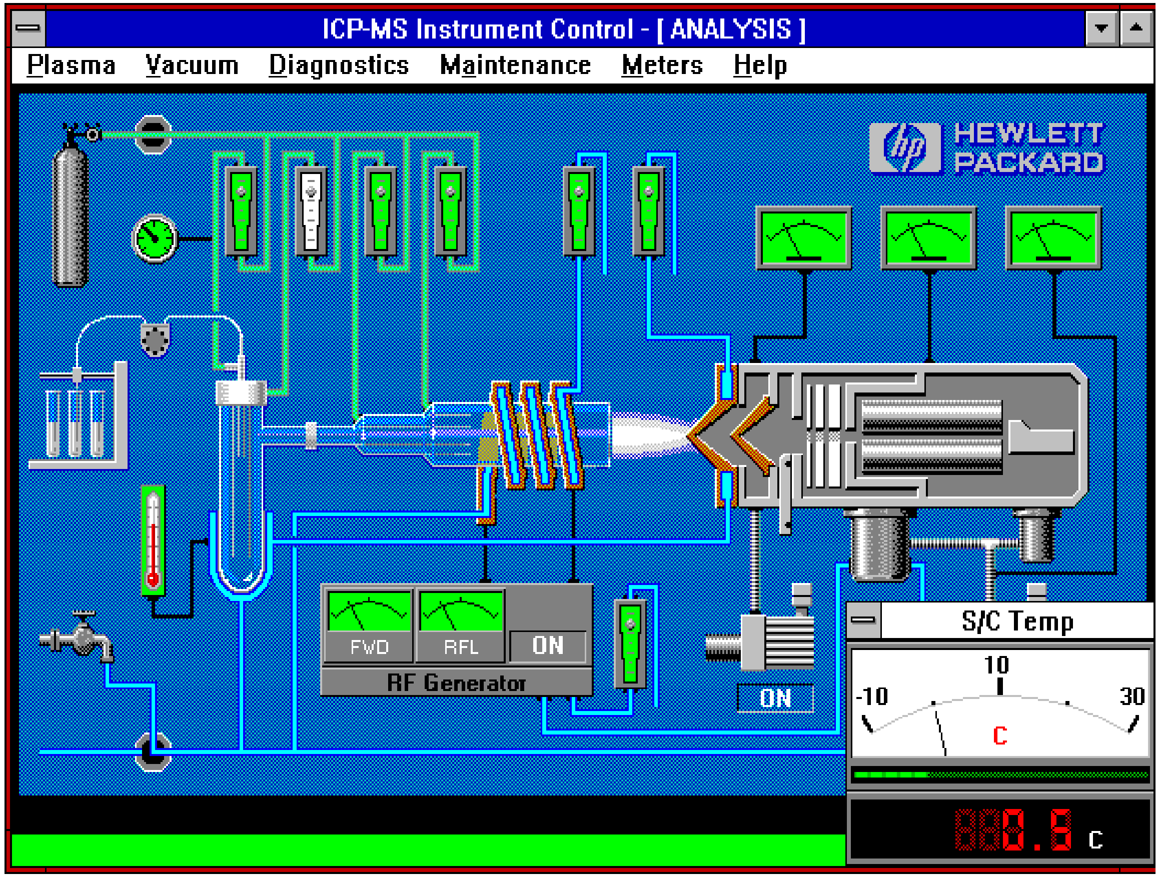
- Detector range is extended using analog mode in addition to conventional pulse counting mode
- Linear dynamic range extends from <1ppt to >100ppm
- Detector pre-scan (1 sec) identifies any matrix peaks and select the appropriate mode for each mass -
  - pulse count
  - analog
  - skip mass completely
- Both modes are analyses within the same acquisition - data is measured using a single, linear calibration
- Fast, automated detector voltage setting and calibration is performed in seconds

Agilent 4500 Series ICP-MS Schematic



Powerful Software Control

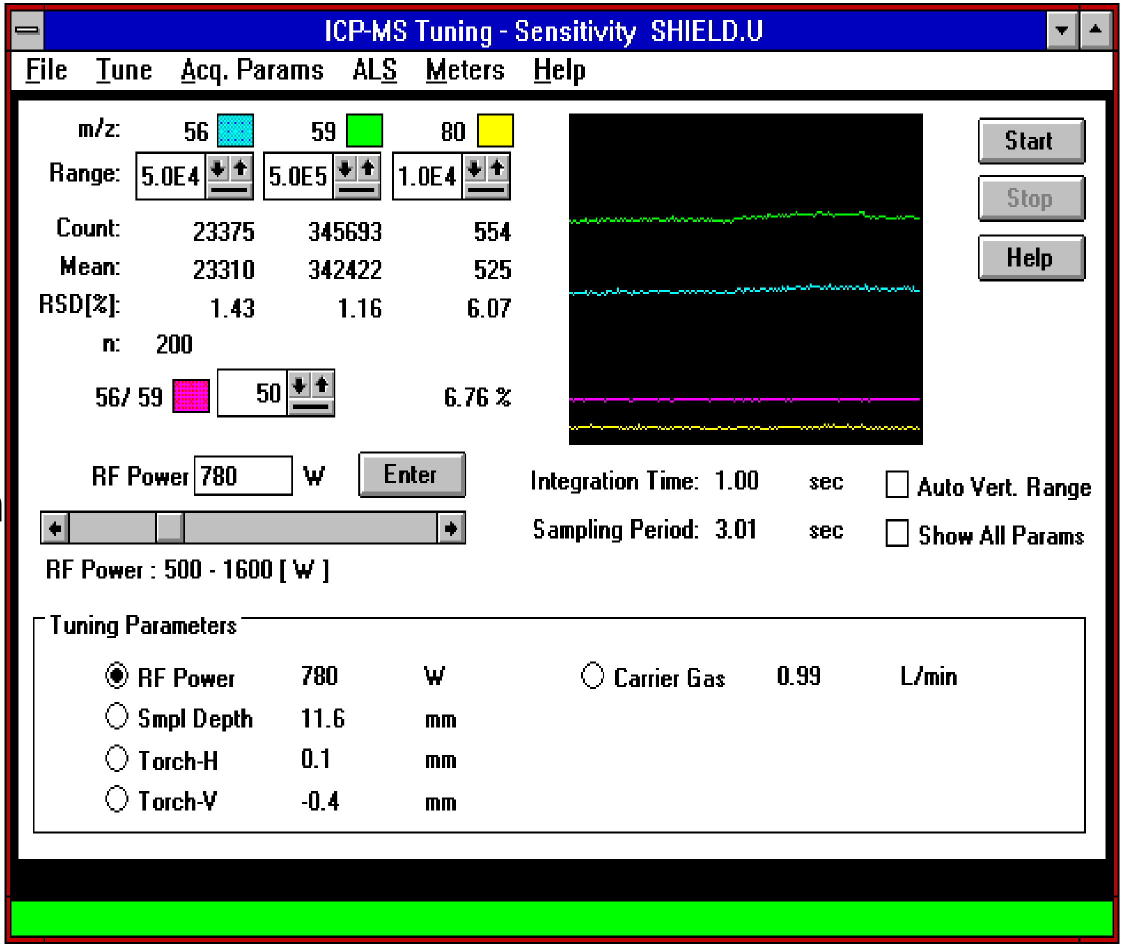
- Auto system startup and shutdown
- All parameters controlled via the datastation
  - carrier gas flows
  - peristaltic pumps
  - spray chamber temperature
  - plasma position
  - ion lenses
  - quadrupole
  - detector



***All** existing Agilent 4500 systems can be made Year 2000 compliant*

Automating Instrument Tuning

- Instrument tuning
  - plasma position automatically optimized
  - real time signal display
  - automatic peak resolution display
  - all system calibration routines automated
  - all tuning parameters can be saved and archived with data
  - automatic tune report generator

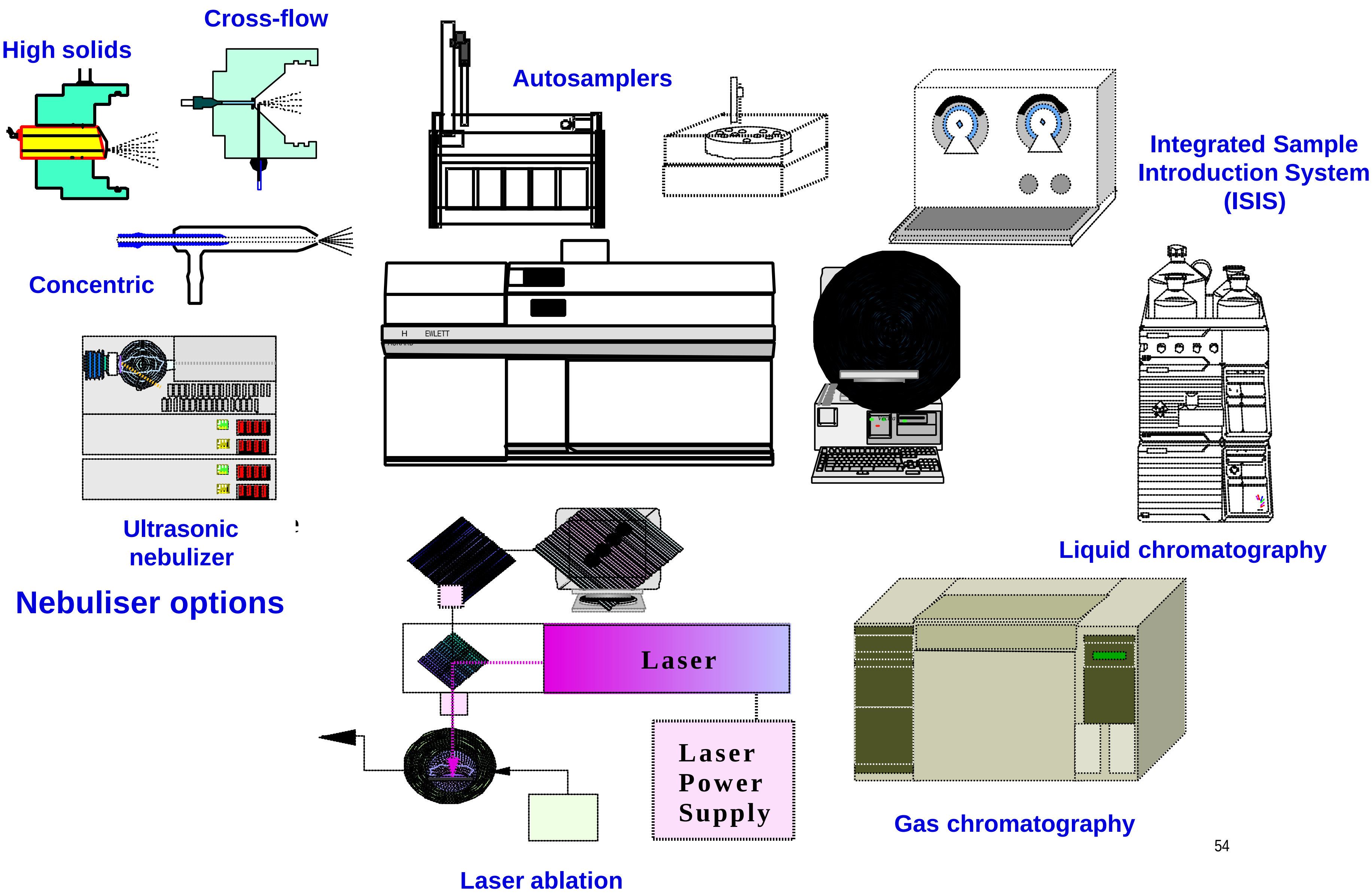


Intelligent AutoTuning

- Comprehensive AutoTune systems automate instrument setup
  - plasma position
    - torch controlled by stepper motors in all 3 planes
  - mass calibration/resolution
  - full system autotune - lenses/plasma conditions are optimized for -
    - high sensitivity across the mass range
    - low oxides
    - low doubly charged ions
    - low background
  - detector setup
- A tune report can be generated at the end of the process

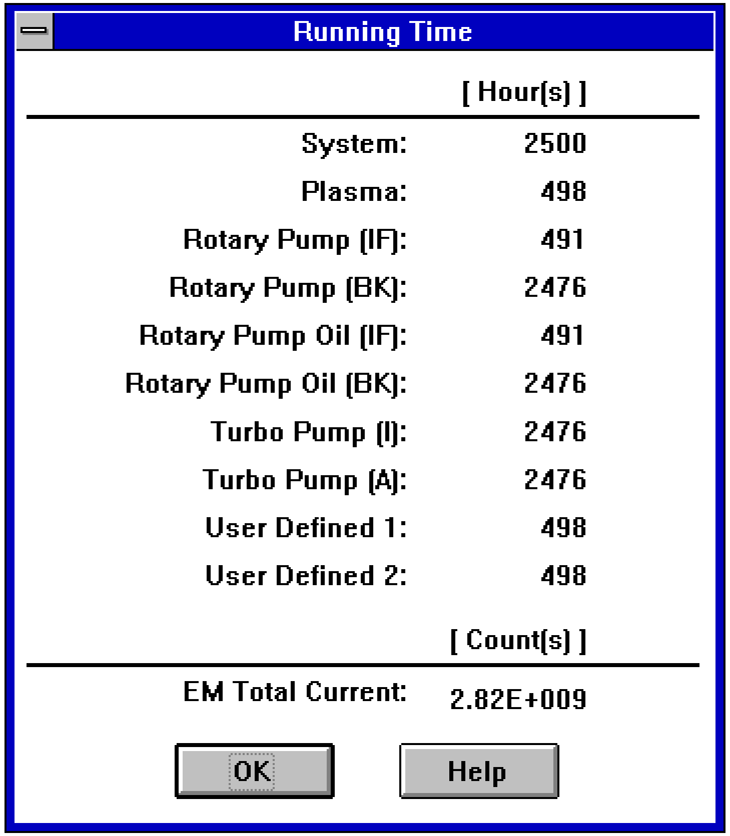
Agilent Technologies
Innovating the HP Way

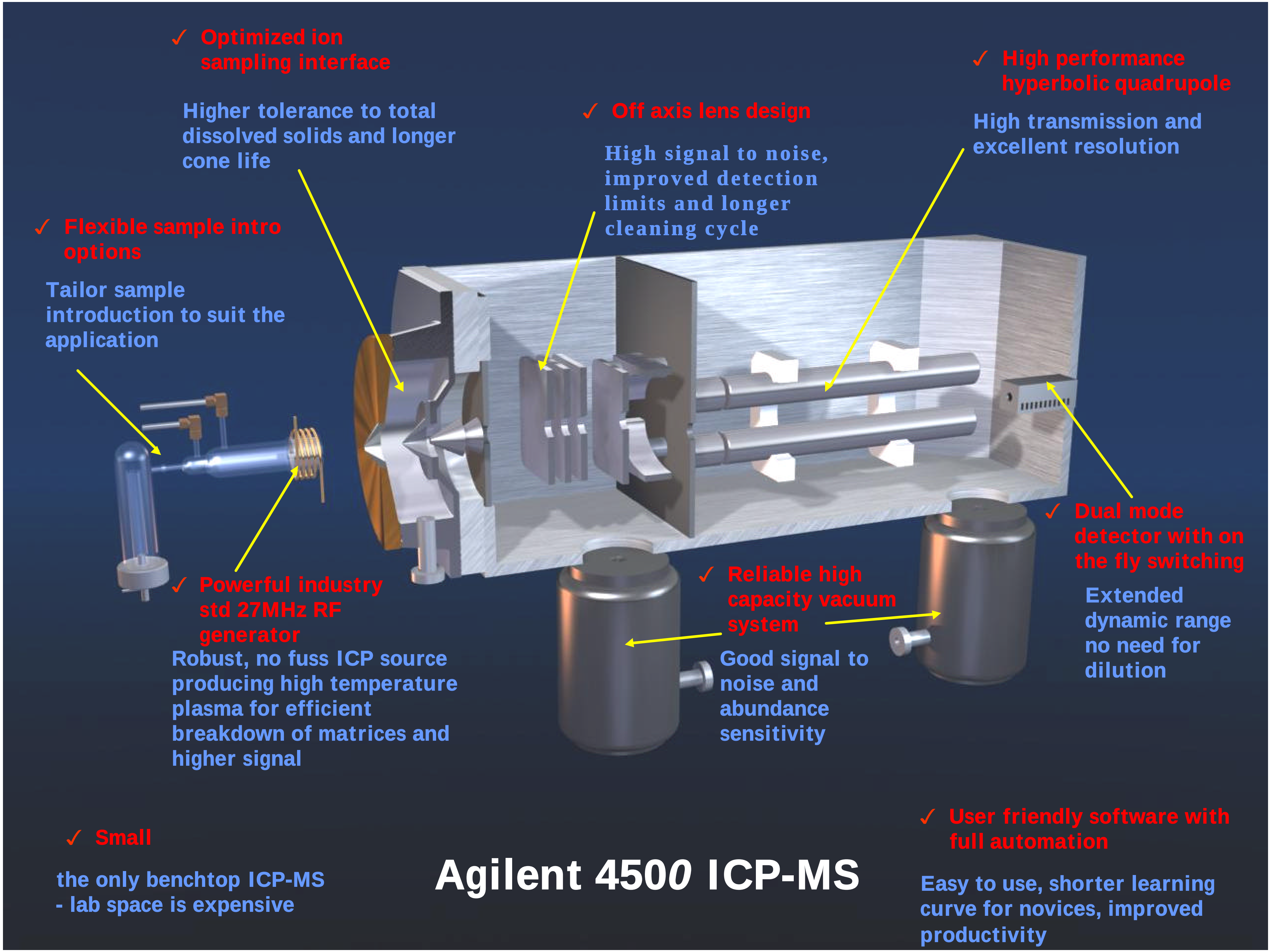
Sample Introduction Options



Agilent 4500 Series summary

- Low maintenance
  - fast change sample inlet system
  - runtime log predicts routine maintenance
  - solid state RF generation
  - maintenance free turbo pumps
- Minimum downtime
- Agilent corporate design standard: <2 failures/year (~98% uptime)
- Remote diagnostics
- Local hardware/applications support
- Phone/modem support




✓ Optimized ion sampling interface
Higher tolerance to total dissolved solids and longer cone life
✓ Off axis lens design
High signal to noise, improved detection limits and longer cleaning cycle
✓ High performance hyperbolic quadrupole
High transmission and excellent resolution
✓ Flexible sample intro options
Tailor sample introduction to suit the application
✓ Powerful industry std 27MHz RF generator
Robust, no fuss ICP source producing high temperature plasma for efficient breakdown of matrices and higher signal
✓ Reliable high capacity vacuum system
Good signal to noise and abundance sensitivity
✓ Dual mode detector with on the fly switching
Extended dynamic range no need for dilution
✓ Small
the only benchtop ICP-MS - lab space is expensive
Agilent 4500 ICP-MS
✓ User friendly software with full automation
Easy to use, shorter learning curve for novices, improved productivity