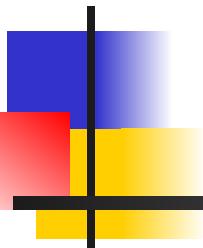


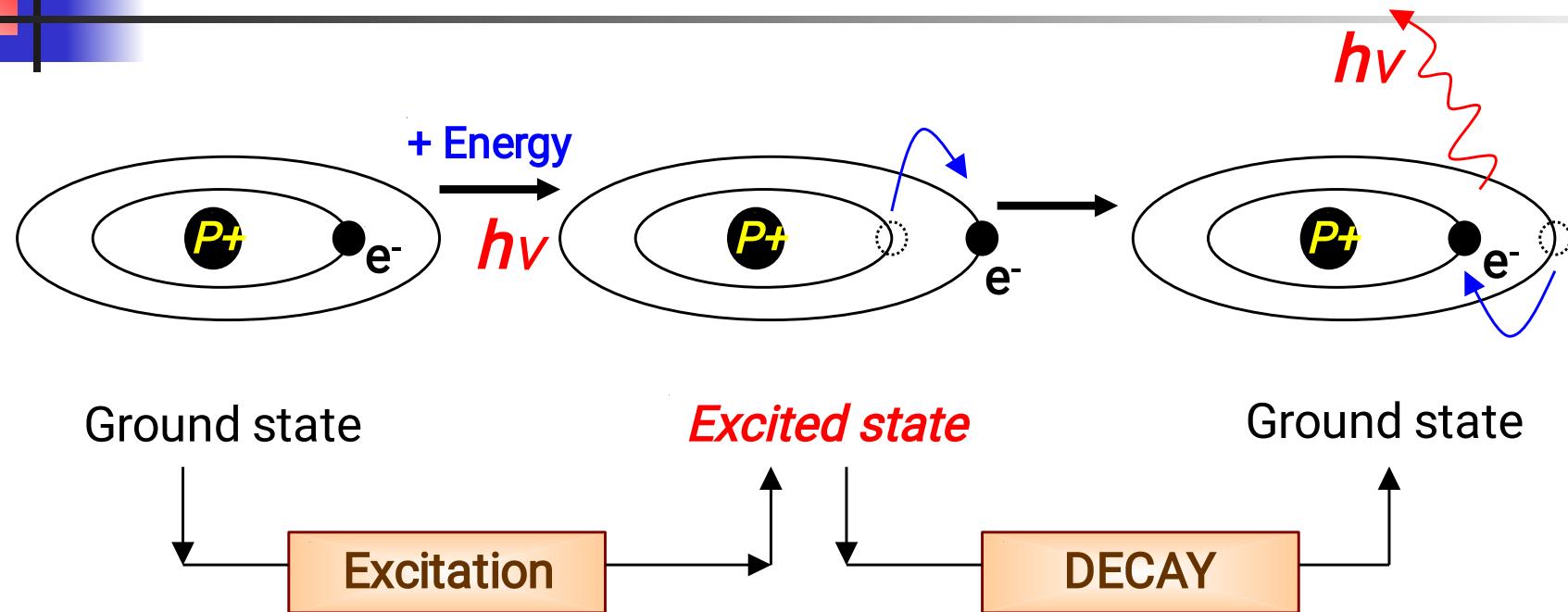
Basic Theory



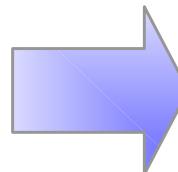
Atomic Absorption Spectroscopy

Mimi Wong

Bohr model of ATOM



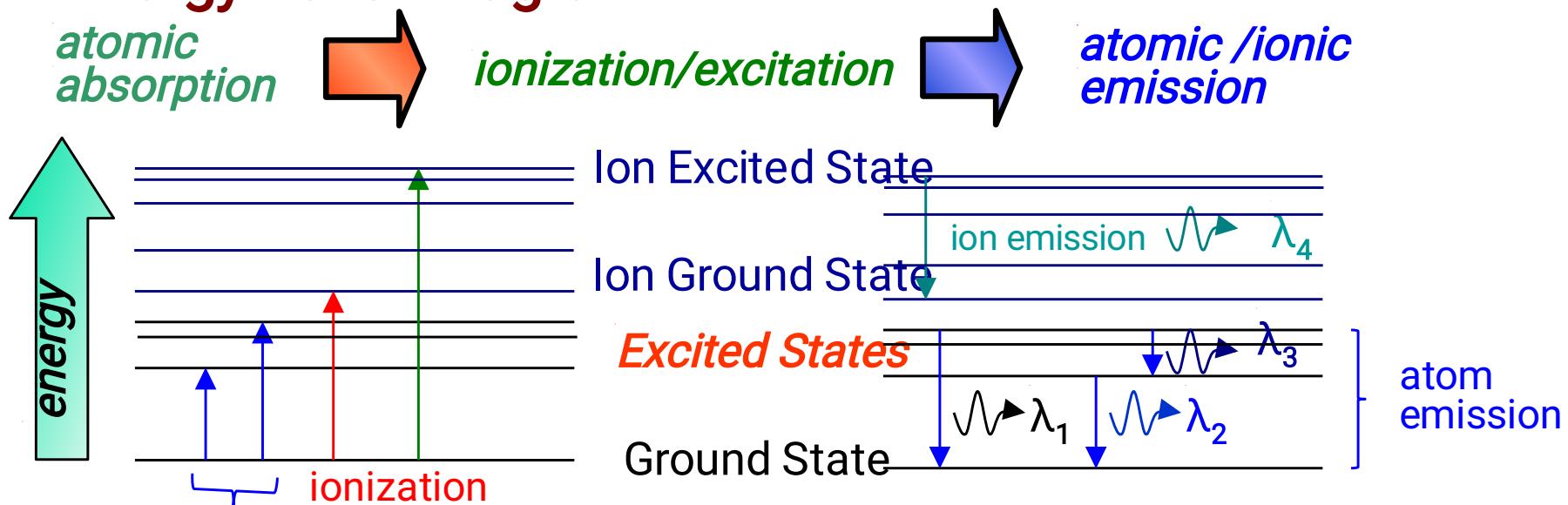
If higher energy is absorbed by the atom,
the electron can be completely
dissociated from the atom



Positively charged ion

Bohr model of ATOM

Energy Level Diagram



By Planck's equation:

$$E = h\nu$$

$$\text{and } \nu = c/\lambda$$

$$\therefore E = hc/\lambda$$

where, E = energy (or so-called **photon**)

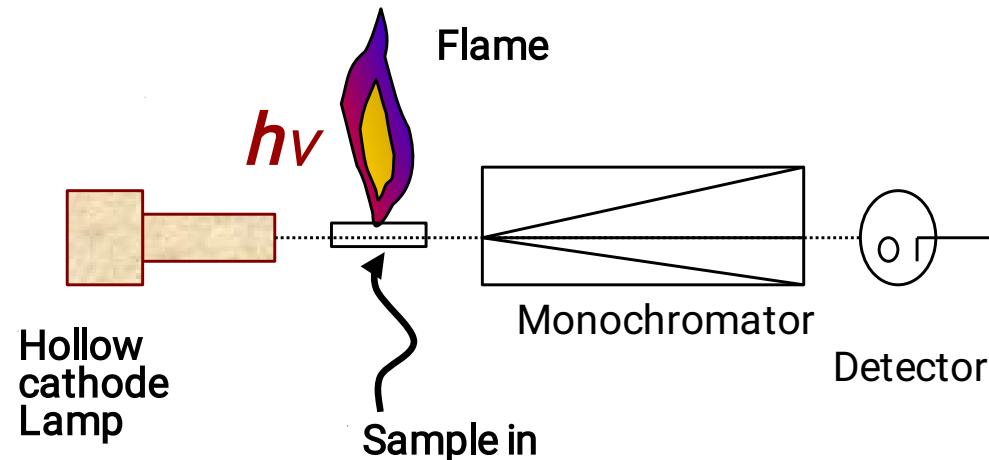
h = Planck's constant

ν = frequency

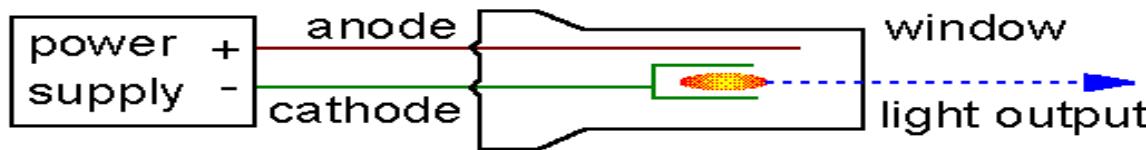
λ = wavelength

c = speed of light

Theory of AA



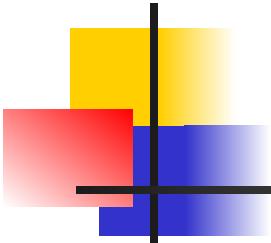
Light Source



Hollow Cathode Lamp (HCL)

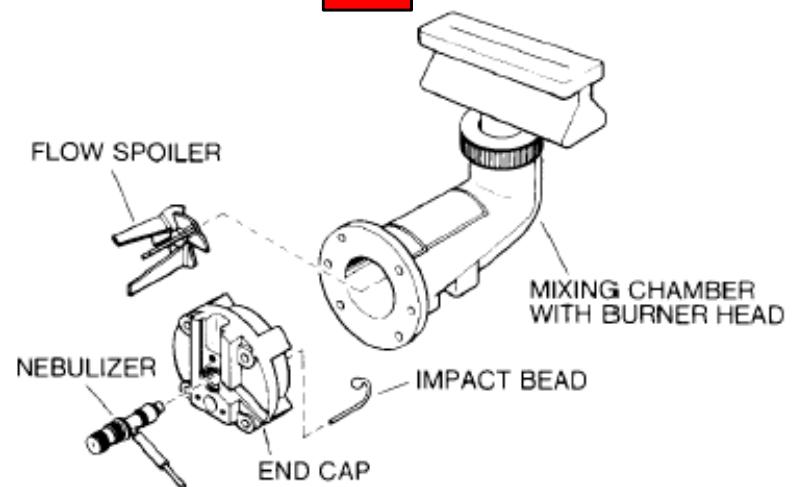
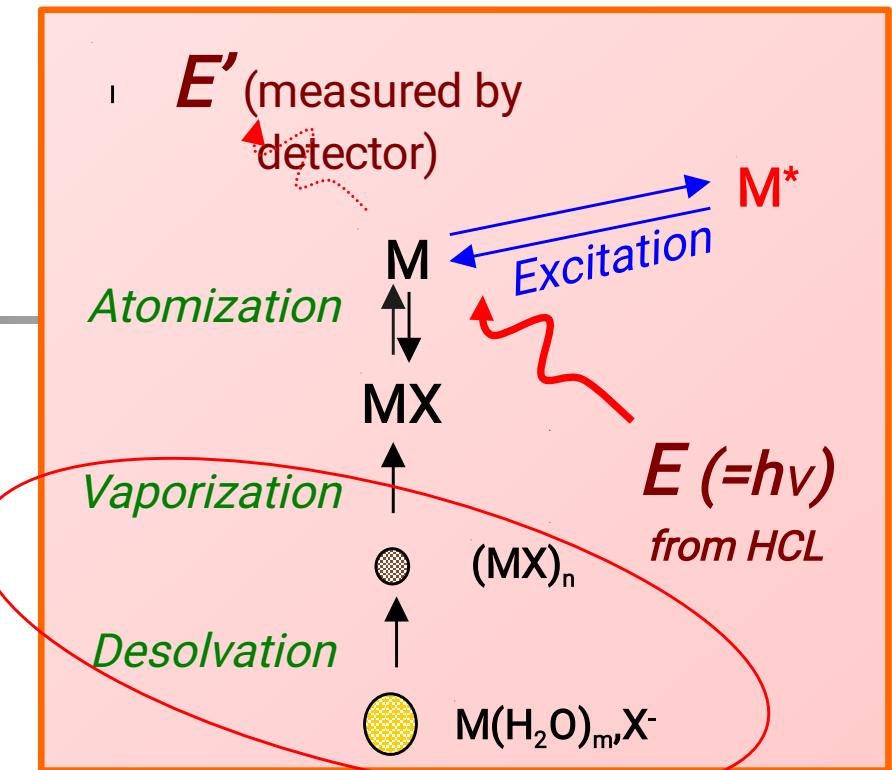
- are a type of discharge lamp that produce narrow emission from atomic species
- electric discharge ionizes rare gas atoms, which are accelerated into the cathode and sputter metal atoms into the gas phase. Collisions with gas atoms or electrons excite the metal atoms to higher energy levels, which decay to lower levels by emitting light

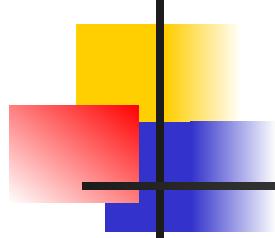
Atomizer



The analyte atoms be in the gas phase. Ions or atoms in a sample must undergo desolvation and vaporization in a high-temperature source

- FAAS: Air-Acetylene / Nitrous oxide-Acetylene → analyzes solution only
- GFAAS: electro-thermal furnace → accepts solution, slurries and solid samples

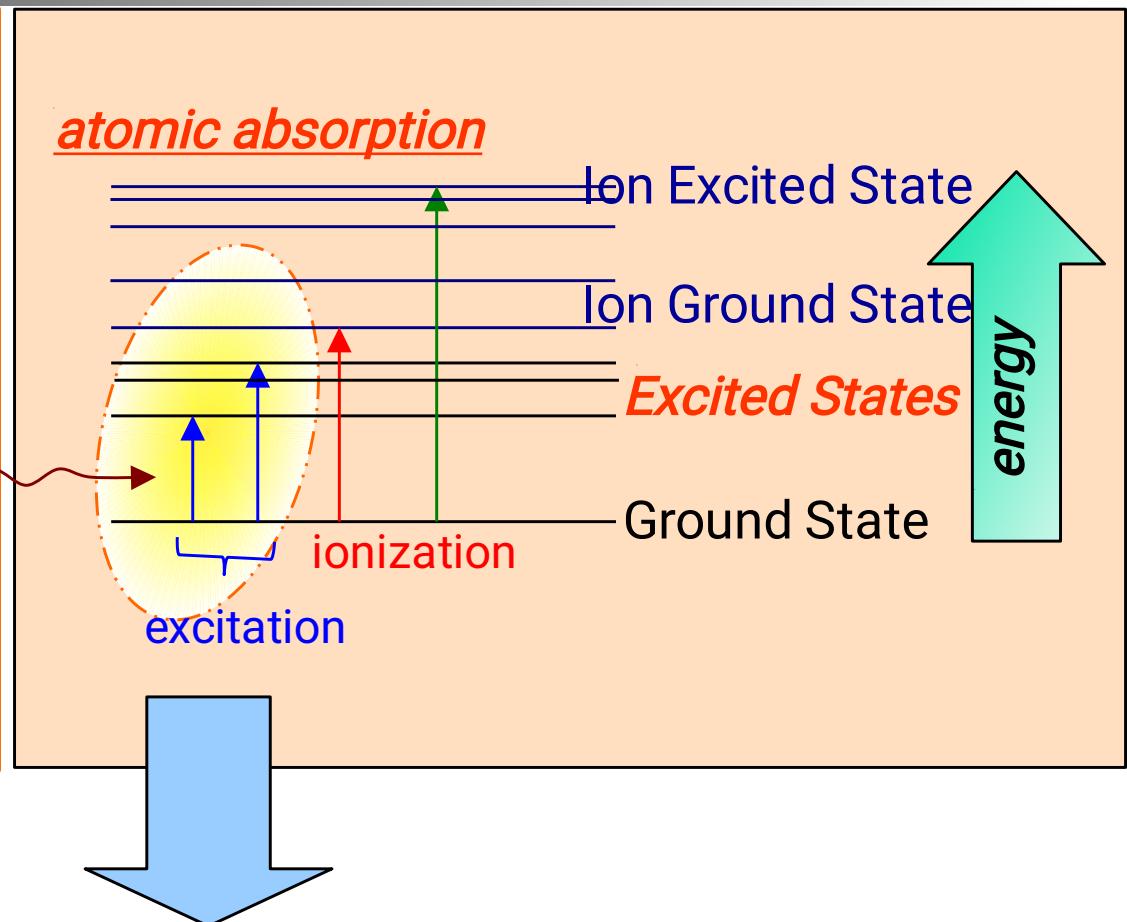
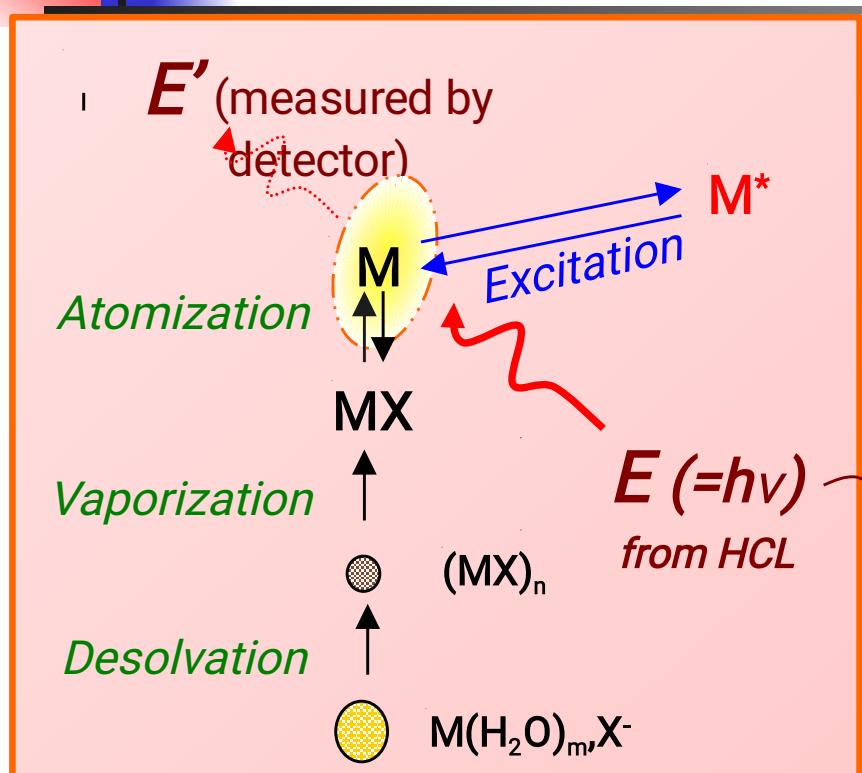




Advantages of GFAAS vs. FAAS

- much more efficient atomizer than flame
- can accept directly very small absolute quantities of sample
- provides a reducing environment for easily oxidized elements
 - samples are placed directly in the graphite furnace and the furnace is electrically heated in several steps to dry the sample, ash organic matter, and vaporize the analyte atoms

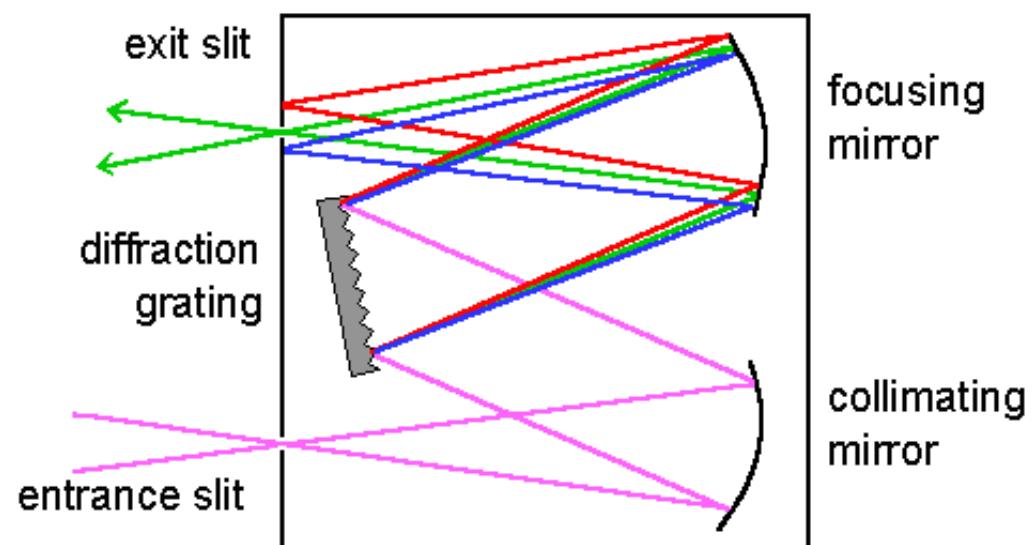
What happen inside atomizer



- Light (energy) from HCL is absorbed

Monochromator

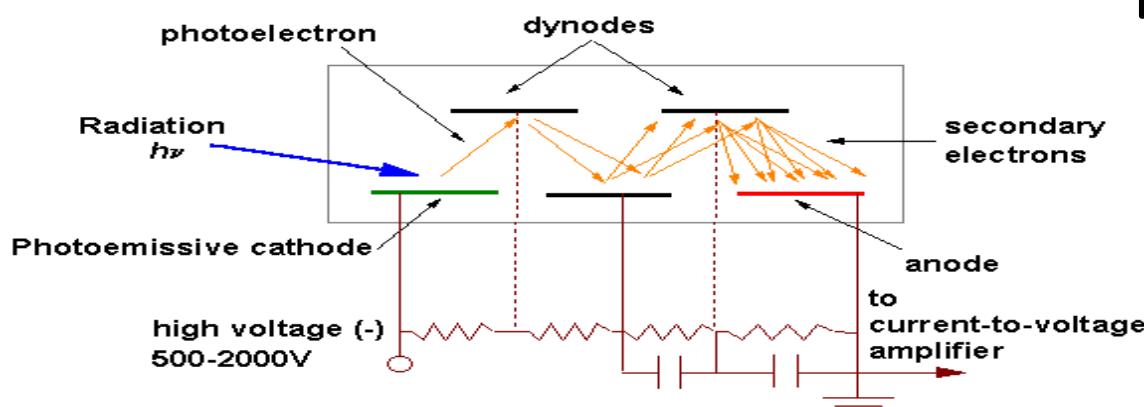
- consists of a diffraction grating (dispersing element), slits, and spherical mirrors. The light source emits a broad spectrum of radiation as represented by the multi-colored line from the lamp to the grating



Schematic of a Czerny-Turner monochromator

Detector

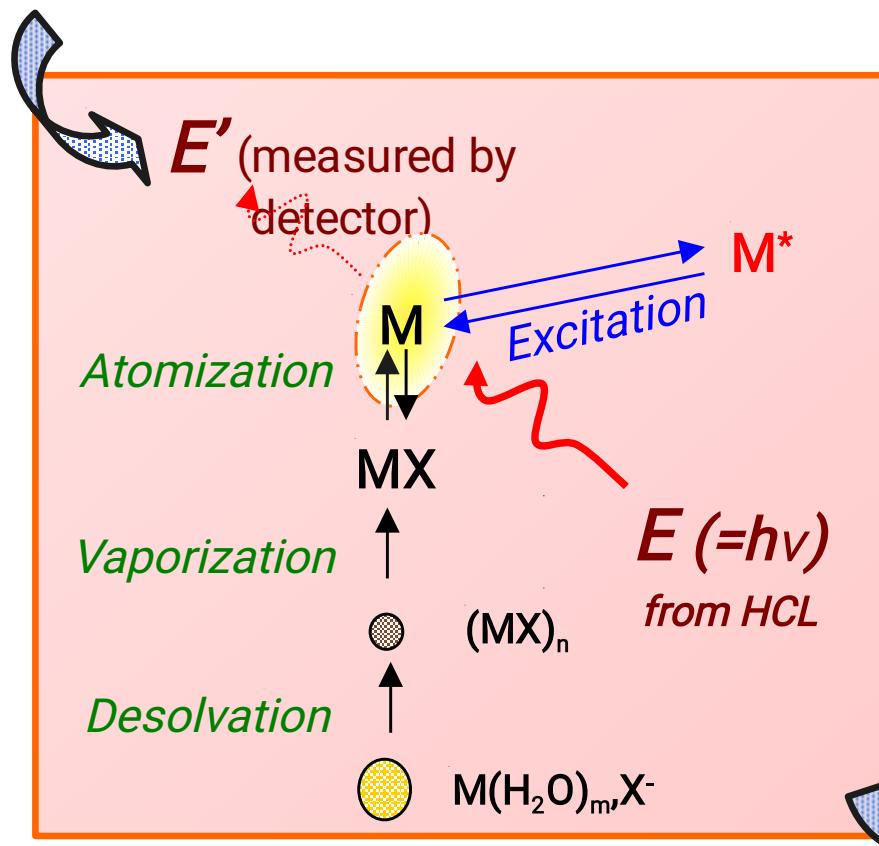
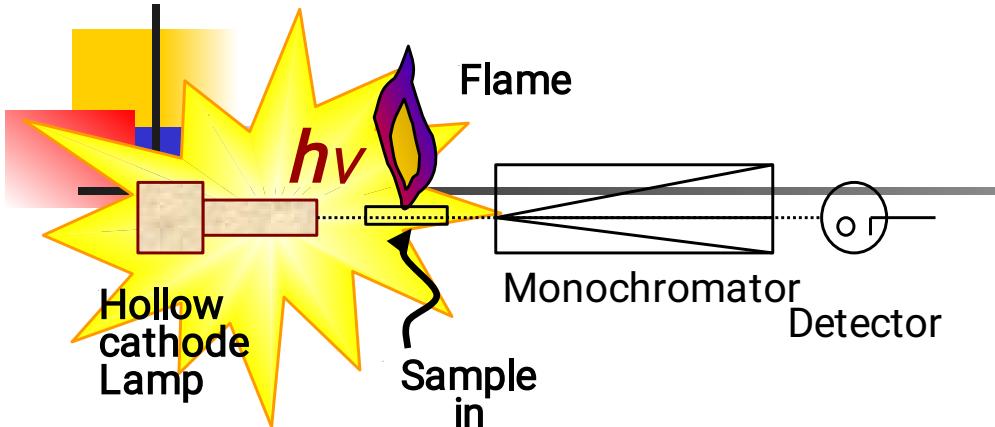
- convert photons to an electrical signal
- consists of a photocathode and a series of dynodes in an evacuated glass enclosure. When a photon of sufficient energy strikes the photocathode, it ejects a photoelectron due to the photoelectric effect



- The amplification depends on the number of dynodes and the accelerating voltage. This amplified electrical signal is collected at an anode at ground potential, which can be measured.

Schematic of a PMT

Summary



HCL emits unique energy which can only be absorbed by a particular element

→ *single element analysis*

By Beer's Law

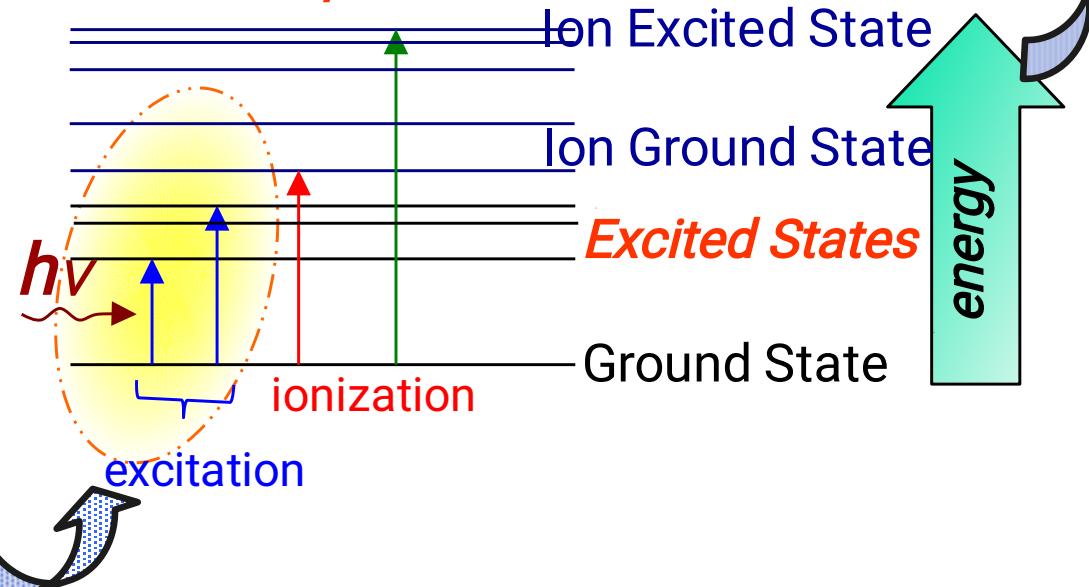
$$\Delta E = (E - E') = abc$$

$$\rightarrow c = \Delta E / ab$$

$$\rightarrow c \propto I$$

a = coefficient of absorption
 b = length of burner head
 c = element concentration
 I = intensity, $\propto \Delta E$

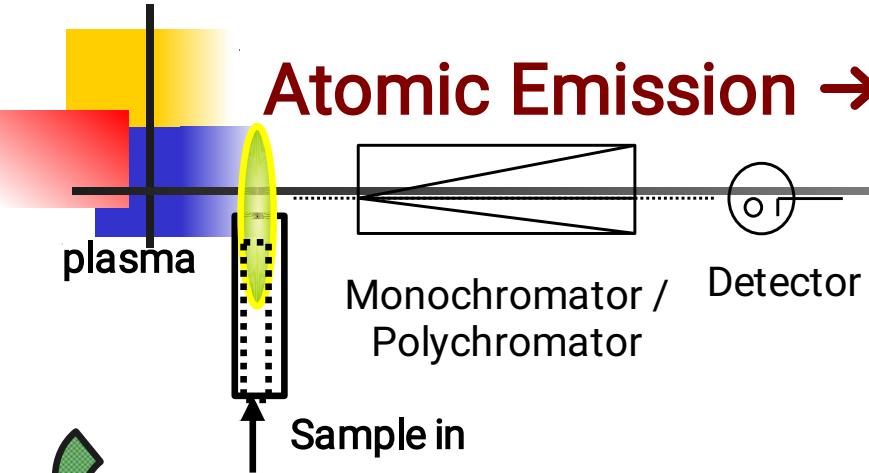
atomic absorption



Processes take place for a nebulized sample droplet in AA burner head

Theory of ICP-AES

Atomic Emission → ICP



Measure the emitted light during the excited atoms decay back to ground state

→ multiple element analysis

By Beer's Law

$$E_i = h\nu_i = \varepsilon bc$$

$$\rightarrow c = E_i / \varepsilon b$$

$$\rightarrow c \propto I_i$$

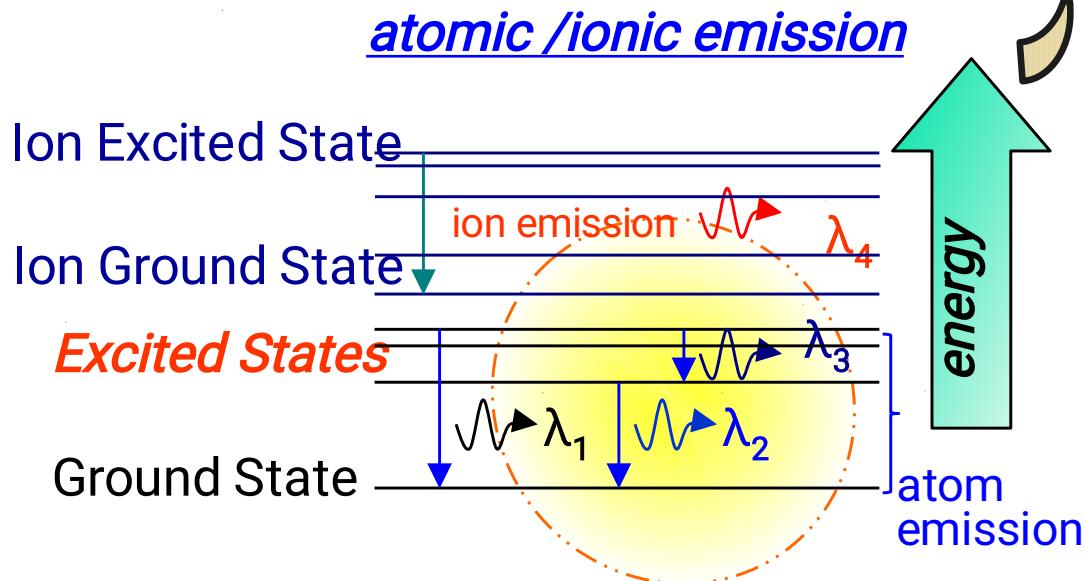
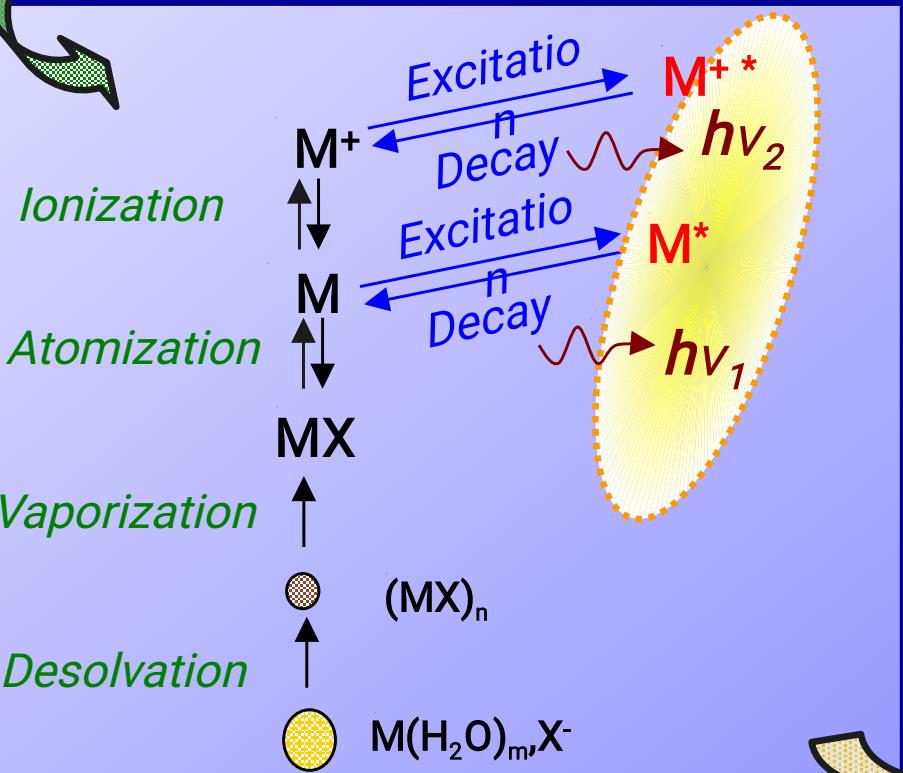
ε = coefficient of emission

b = length of burner head

c = element concentration

I_i = intensity, $\propto E_i$

$i = 1, 2, 3, 4, \dots, n$

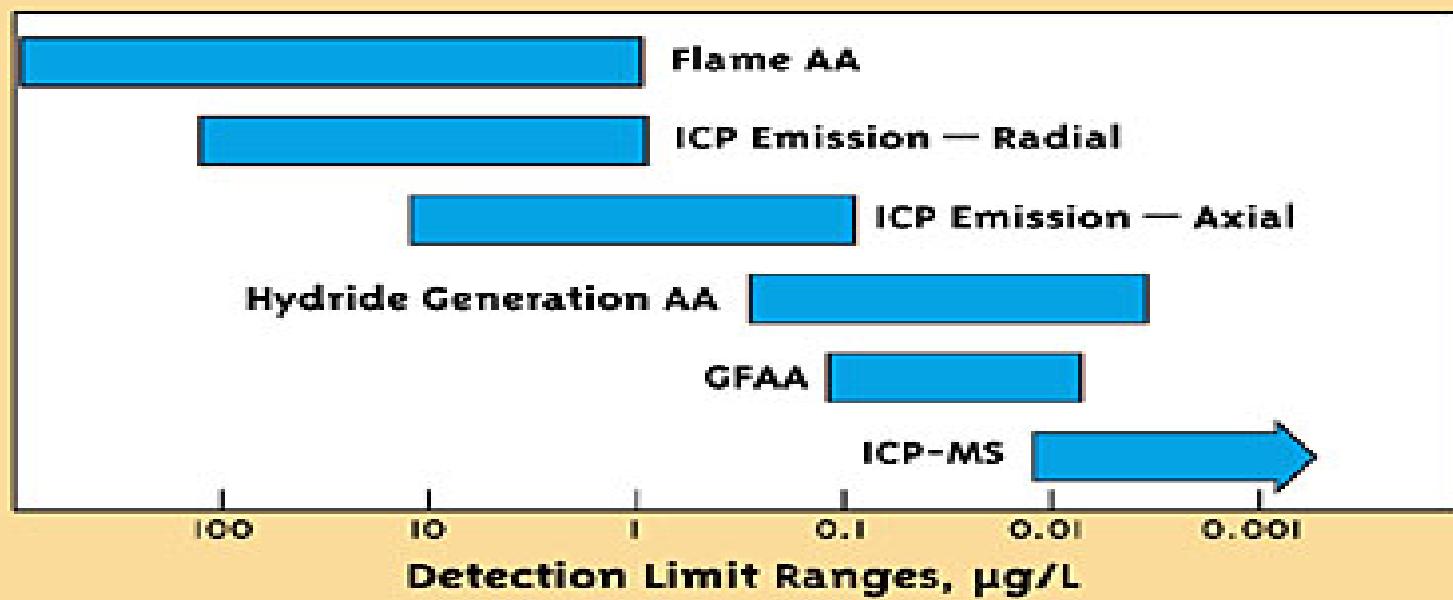


Processes take place for a nebulized sample droplet in ICP discharge

Detection Limits

Figure 2

Typical Detection Limit Ranges for the Major Atomic Spectroscopy Techniques



AA vs. ICP-AES : *Detection Limits*

	ICP-AES	Flame AAS	GFAAS
Level of measurement			
Detection Limit	Very good for most elements	Very good for some elements	Excellent for some elements
Typical Linear Dynamic Range	$10^5 - 10^6$ *	10^3	10^3
Precision			
short term	0.3 - 2 % **	0.1 - 1 %	1 - 5 %
long term (>4 hrs)	< 5 %		

Remarks:

For comparing the typical ICP-AES, FAAS and GFAAS in the market

* Can reach to 10^8 with range extension

** precision improves with the use of internal standards

AA vs. ICP-AES : ☰

Matrix & Interferences

	ICP-AES	Flame AAS	GFAAS
<i>Interferences</i>			
Spectral	common	almost none	few
Chemical (matrix)	almost none	many	many
Ionization	minimal	some	minimal
Dissolved solids (max tolerable conc)	2 - 30 %	0.5 - 3 %	> 20 %
Semi-quantitative analysis	yes & easy	no	no

Remarks:

For comparing the typical ICP-AES, FAAS and GFAAS in the market

* Can reach to 10^8 with range extension

** precision improves with the use of internal standards

AA vs. ICP-AES : *Speed & Cost*

	ICP-AES	Flame AAS	GFAAS
No. of elements	> 75	> 68	> 50
Sample throughput	5-30 elements /min/sample	15 sec/elements /sample	4 min/elements /sample
Sample Usage	high	Very high	Very low
Routine operation	easy	easy	easy
Method development	skill required	easy	skill required
Unattended operation	yes	no	yes
Combustible gases	no	yes	no
Hollow Cathode Lamp / Electrodeless Discharge Lamp (EDL)	no	yes	yes
Capital cost	high	low	medium/high
Sample running cost	affordable	low	high

Remarks:

For comparing the typical ICP-AES, FAAS and GFAAS in the market

Interference & Solutions

Technique	Type of Interference	Method of Compensation
Flame AAS	Ionization	Ionization buffers
	Chemical	Releasing agent or nitrous oxide-acetylene flame
	Physical	Dilution, matrix matching, or method of additions
GFAAS	Physical and chemical	Standard Temperature Platform Furnace (STPF) conditions, standard additions
	Molecular absorption	Zeeman or continuum source background correction
	Spectral	Zeeman background correction
ICP-OES	Spectral	Background correction or the use of alternate analytical lines
	Matrix	Internal standardization
ICP-MS	Spectral	Interelement correction (IEC), use of alternate masses, higher resolution systems or reaction/collision cell technology
	Matrix	Internal standardization

Application

- Choosing a Technique for the Determination of Copper in an Electroplating Bath

Criteria	Flame AAS	Single-Element GFAAS	Multi-Element GFAAS	Radial/Axial ICP-OES	ICP-MS
Detection limits	✓	✓	✓	✓	✓
Accuracy/precision	✓	✓	✓	✓	✓
Concentration range	✓			✓	✓
Sample volume	✓	✓	✓	✓	✓
Elements per sample	✓	✓	✓	✓	✓
Sample throughput	✓	✓	✓	✓	✓
Purchase price	✓				

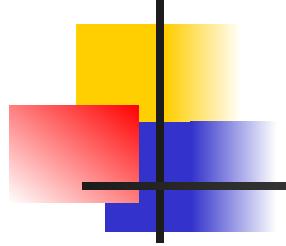
Application

- Choosing a Technique for the Determination of Lead and Cadmium in Blood

Criteria	Flame AAS	Single-Element GFAAS	Multi-Element GFAAS	Radial/Axial ICP-OES	ICP-MS
Detection limits	□	✓	✓	□	✓
Accuracy/precision	□	✓	✓	□	✓
Concentration range	□	✓		□	✓
Sample volume	□	✓	✓	□	□
Elements per sample	□		✓	✓	✓
Sample throughput	□	✓	✓	✓	✓
Operator expertise	✓	✓	✓	✓	
Purchase price	✓	✓	✓		

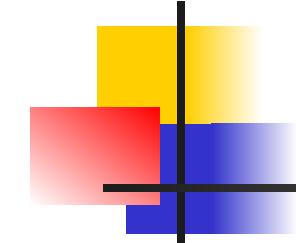
Source: Choosing The Right Trace Element Technique, R. Thomas, Today's Chemist at Work, Vol 8, No. 10, 42-48

Other Applications



- Pb poisoning : detection of Zn and Pb in human hair
- Se and Hg analysis in sea food, such as fish tissue, mussels, oyster & etc.

Advantages of AA over ICP-AES



1. Wide dynamic range

1. measure from ppm to sub-ppb levels (FAAS + GFAAS)

2. Low running cost

1. Gas supply : Acetylene vs. Argon
2. Labour skill : Less in AAS
3. Training time : Less in AAS
4. Method development time : Less in AAS
5. Maintenance : Less in AAS

3. Spectral Interference → “Zero”

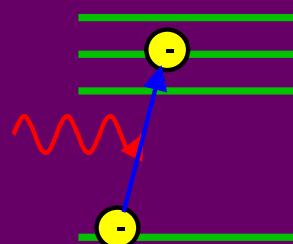


• ICP-OES - Inductively Coupled Plasma Optical Emission Spectrometry
=
Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES)

Atomic spectrometry

Atomic Absorption

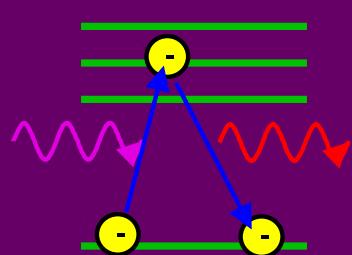
Light of specific wavelength from Hollow Cathode Lamp (HCL)



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

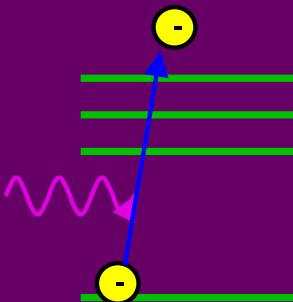
Light and heat energy from high intensity source (flame or plasma)



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

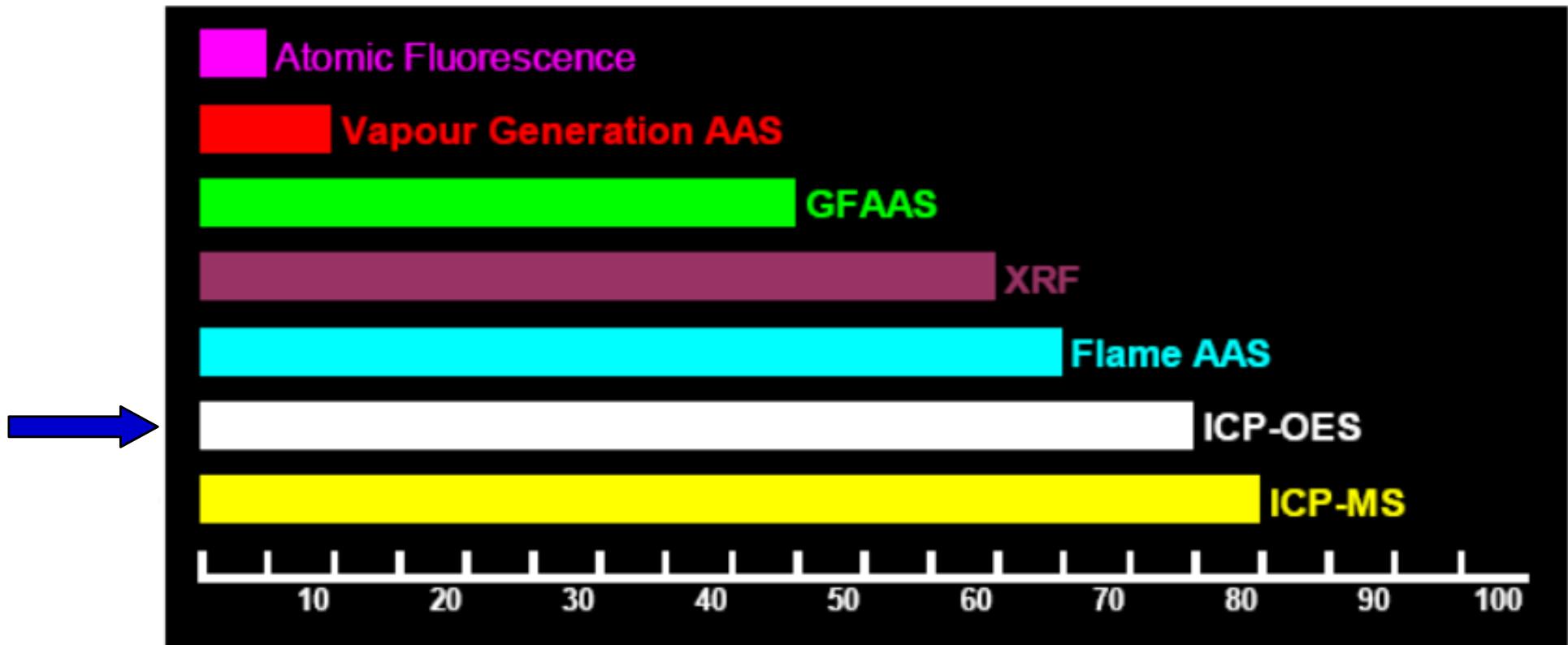
Mass Spectrometry

Light and heat energy from high intensity source (plasma)

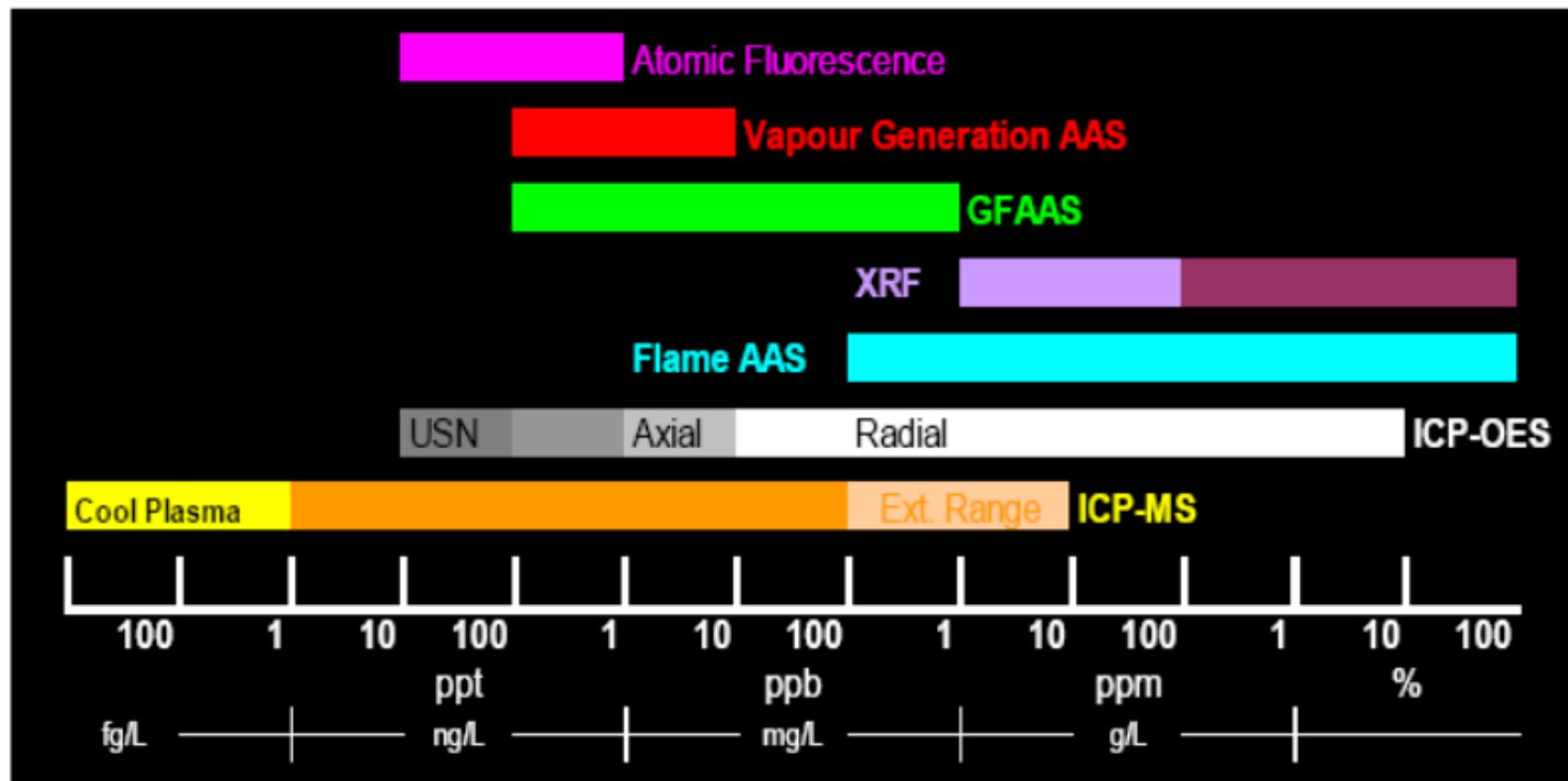


High energy (light and heat) ejects electron from shell (ionization). Result is free electron and atom with positive charge (Ion)
Ions are extracted and measured directly in mass spectrometer

Number of Applicable Elements



Relative Sensitivities and Dynamic Ranges



Characteristics of instruments

	ICP-MS	ICP-AES	GF-AAS
Detection	mass	emission	absorbance
Merit	high sensitivity multielement	multielement	high sensitivity
Demerit	damage from high salinity	relatively low sensitivity	monoelement
Ranges	< ppt ~ 100 ppb	0.1 ppb ~ 10 ppm	1 ppb ~ 100 ppb

Introduction to ICP-AES

- Atomization Emission Sources
 - Flame – still used for metal atoms
 - Electric Spark and Arc
 - Direct current Plasmas
 - Microwave Induced Plasma
 - **Inductively Coupled Plasma – the most important technique**
- Advantages of plasma
 - Simultaneous multi-element Analysis – saves sample amount
 - Some non-metal determination (Cl, Br, I, and S)
 - Concentration range of several decades (wide range)
 - Enable high resolution
- Disadvantages of plasma
 - very complex Spectra - hundreds to thousands of lines
 - Expensive optical components
 - Expensive instruments, highly trained personnel required

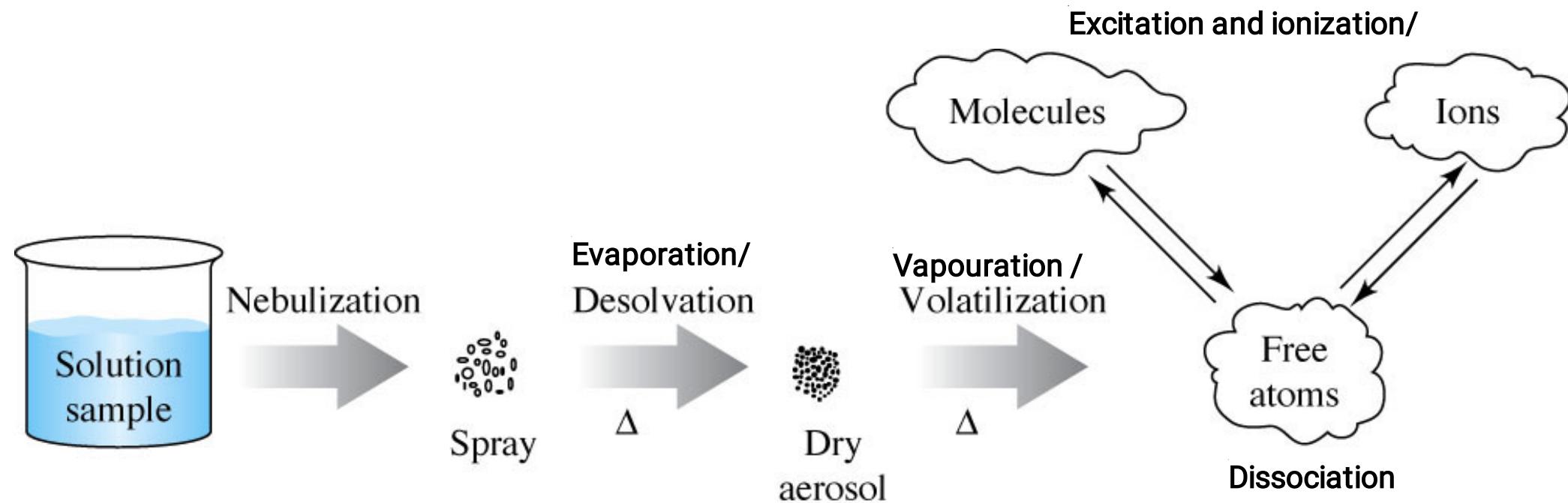


Atomization ☰

- Need to break sample into atoms to observe atomic spectra

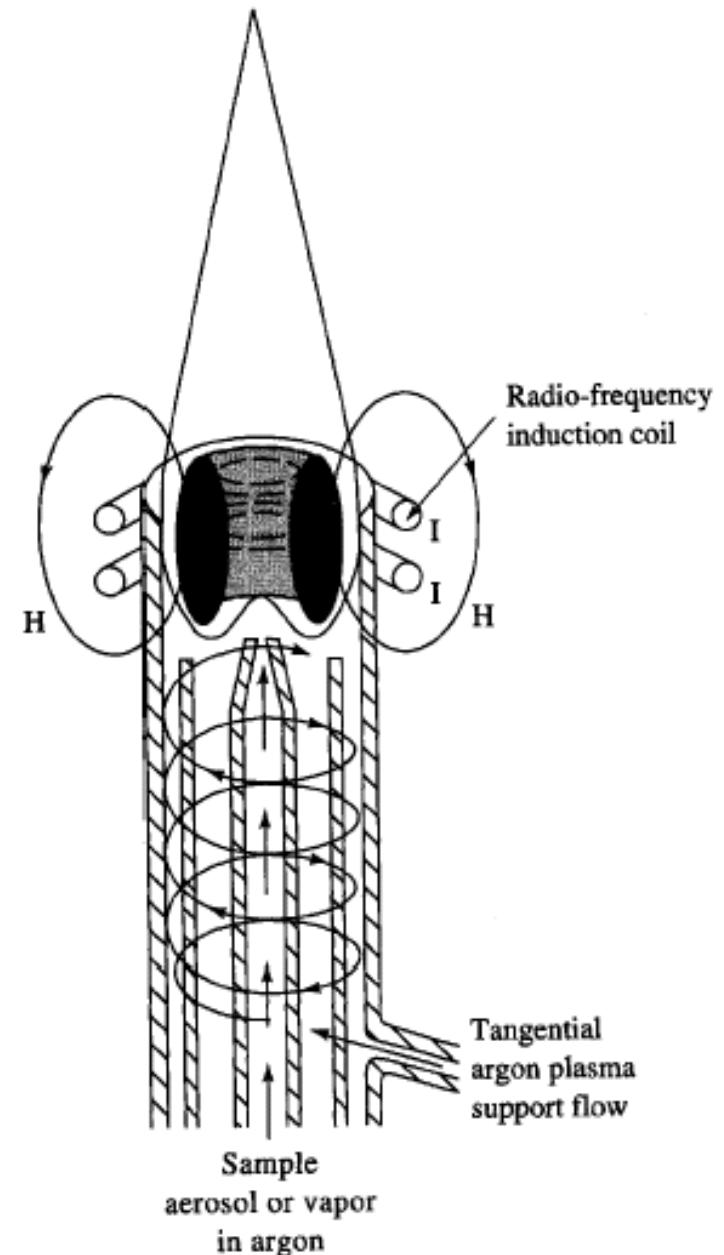
ii. Basic steps:

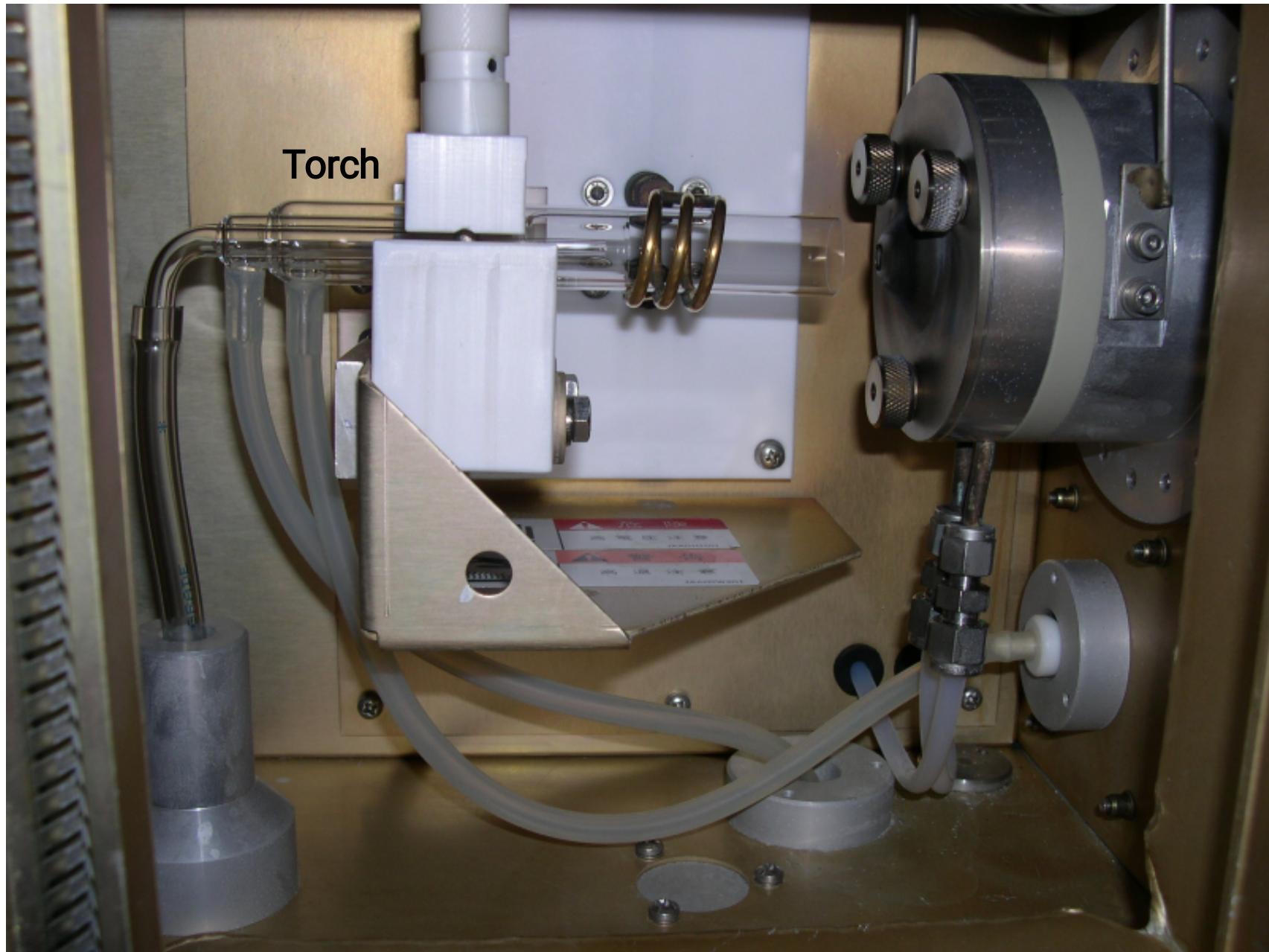
- a) nebulization – solution sample, get into fine droplets by spraying through thin nozzle
- b) desolvation - heat droplets to evaporate off solvent just leaving analyte and other matrix compounds
- c) volatilization – convert solid analyte/matrix particles into gas phase
- d) dissociation – break-up molecules in gas phase into atoms.
- e) excitation and ionization – with light, heat, etc. for spectra measurement. ->cause the atoms to become charged

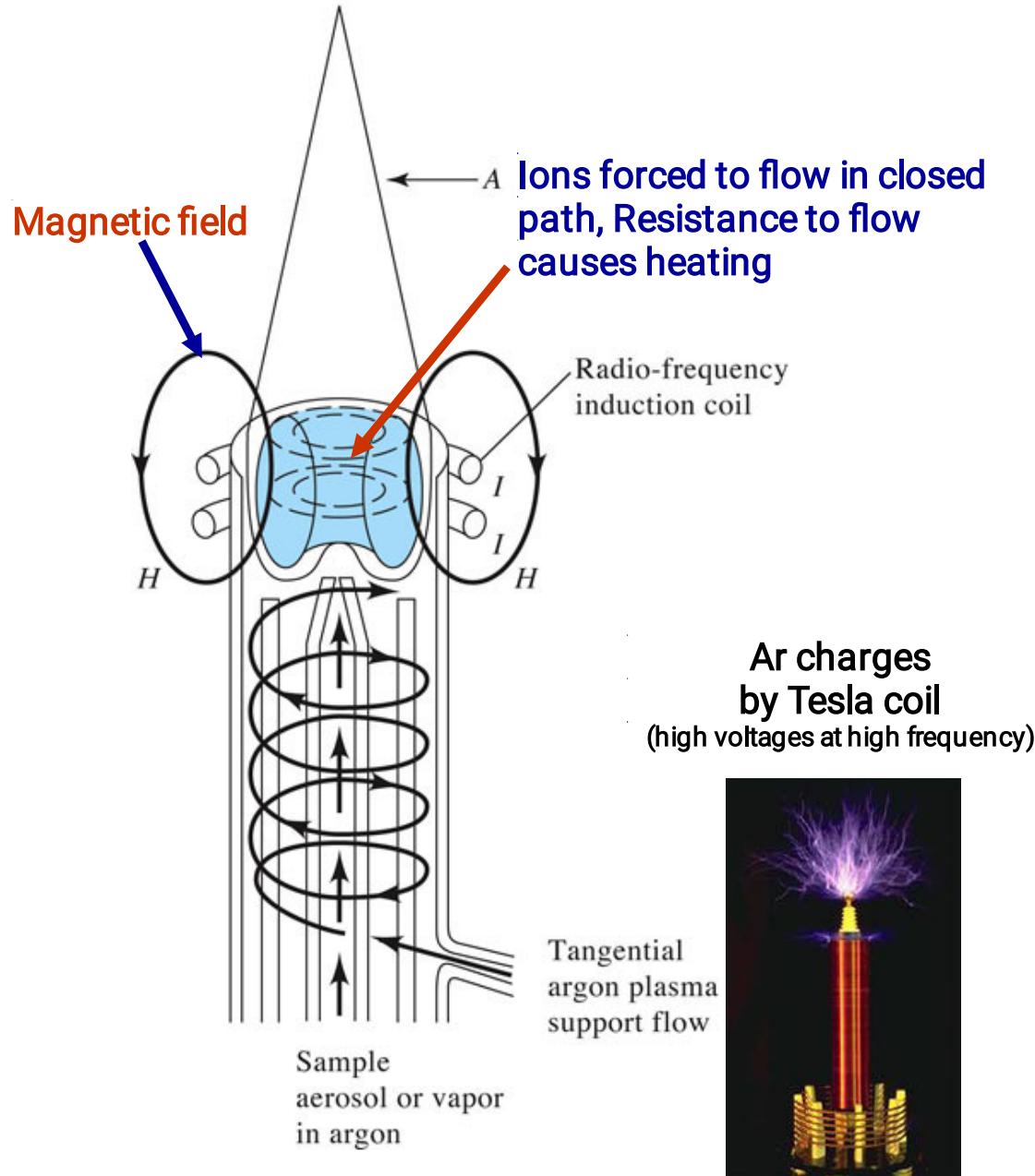


Inductively Coupled Plasma

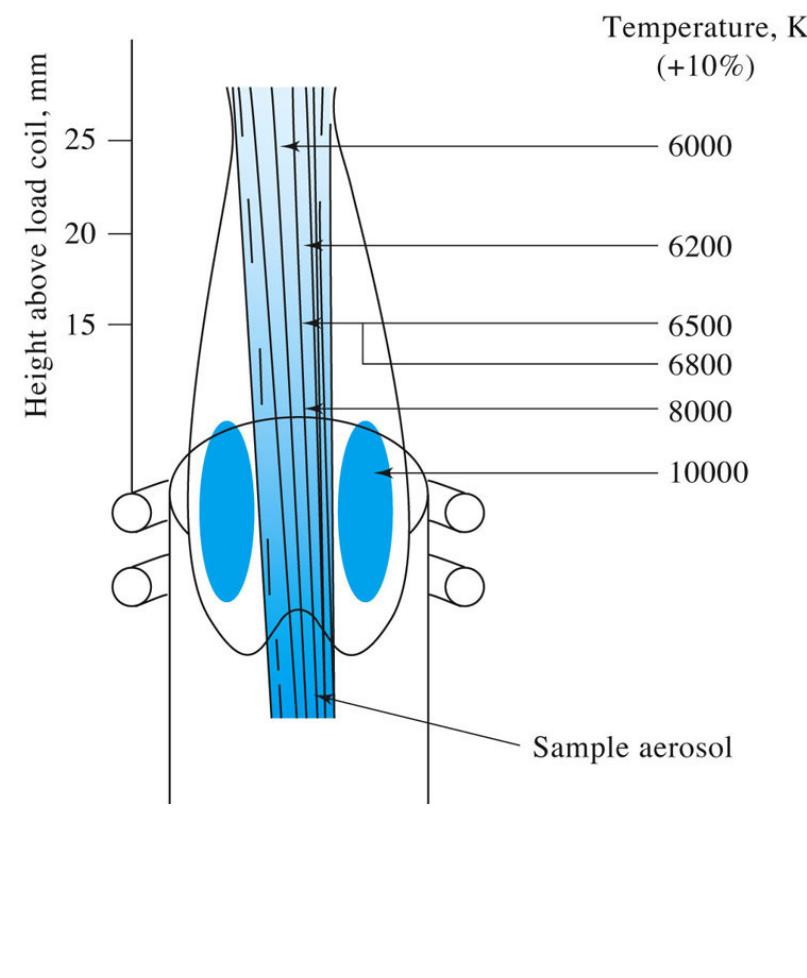
- **Inductively Coupled Plasma (ICP)**
 - Plasma generated in a device called a Ar cools outer tube, defines plasma shape
 - Rapid tangential flow of argon cools outer quartz and centers plasma
 - Rate of Argon Consumption 5 - 20 L/Min
 - Radio frequency (RF) generator 27 or 41 MHz up to 2 kW
 - **Tesla coil** produces initiation spark





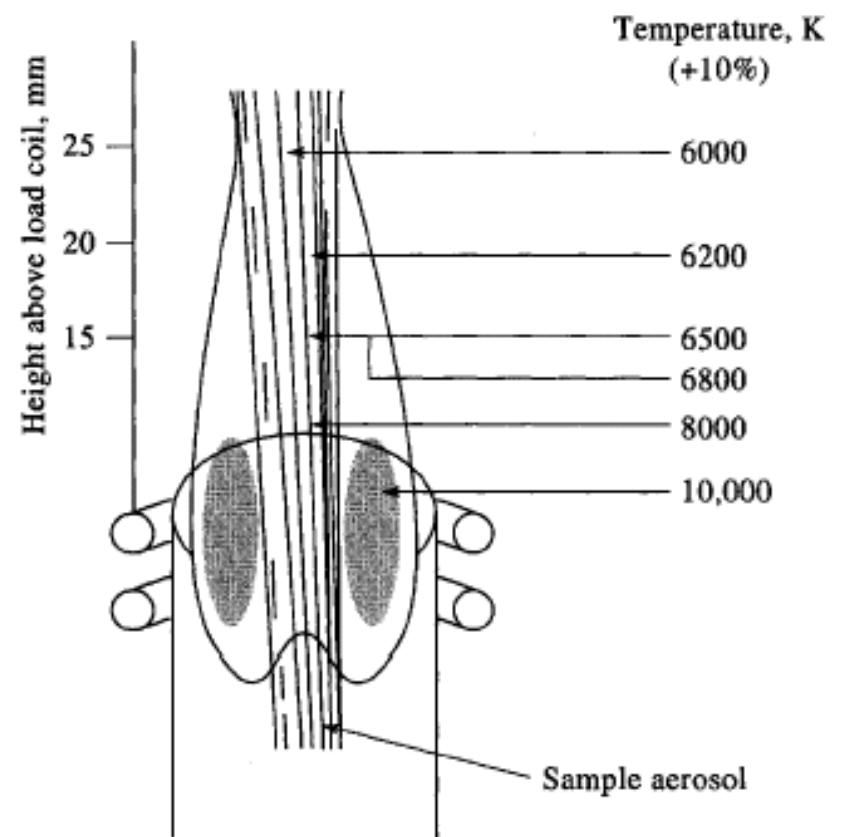


Temperature Regions in Plasma Torch



Plasma characteristics

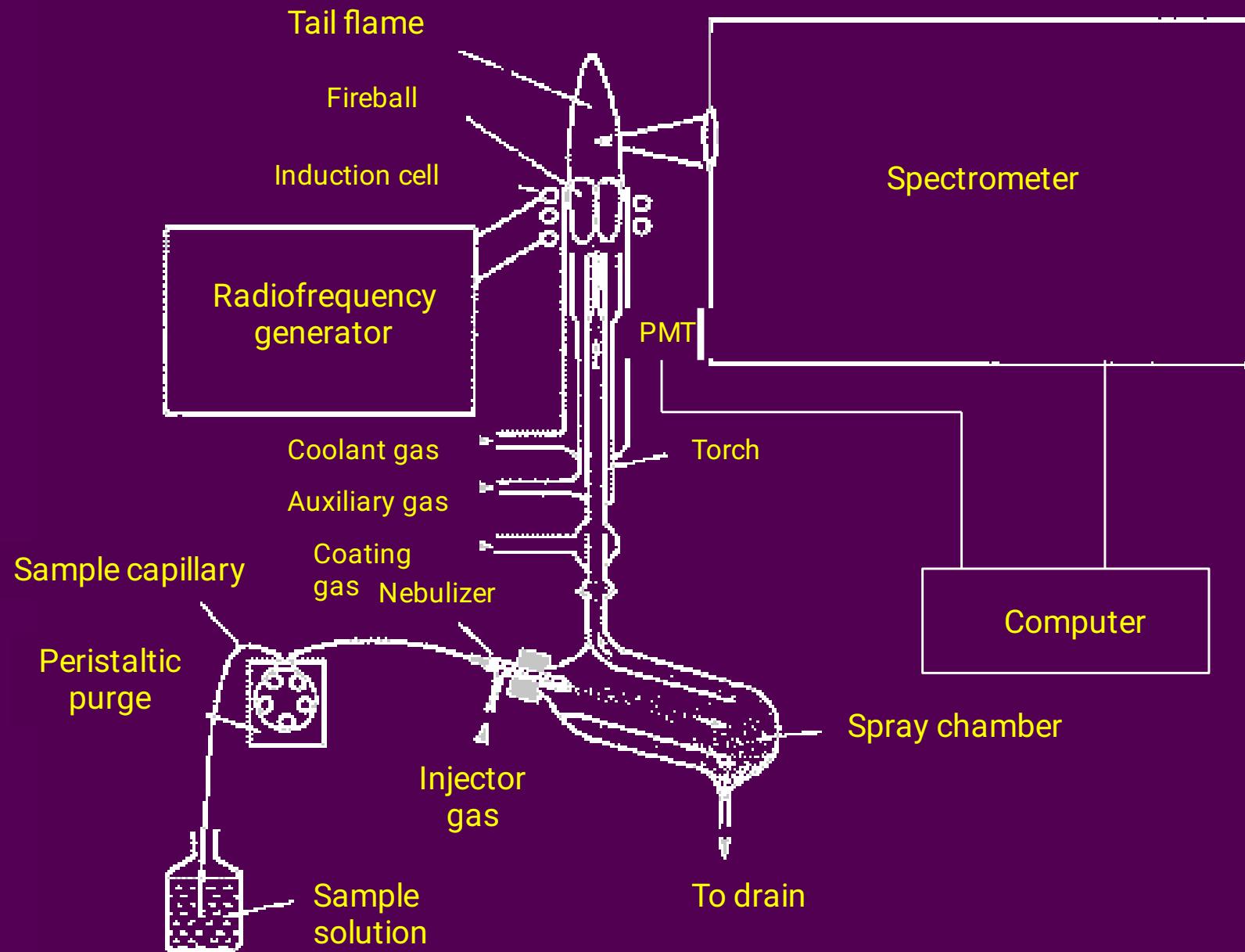
- Hotter than flame (10,000 K) - more complete atomization/excitation
- Atomized in "inert" atmosphere
- Ionization interference due to high density of e- is very small
- Sample atoms reside in plasma for ~2 msec
- Plasma chemically inert, little oxide formation
- Temperature profile quite stable and uniform.



Instrumentation of ICP-AES



- Radio Frequency (RF) Generator
- Sample Introduction System
- Torch
- Spectrometer (Polychromators)
- Detector



Schematic diagram of ICP-AES instrument

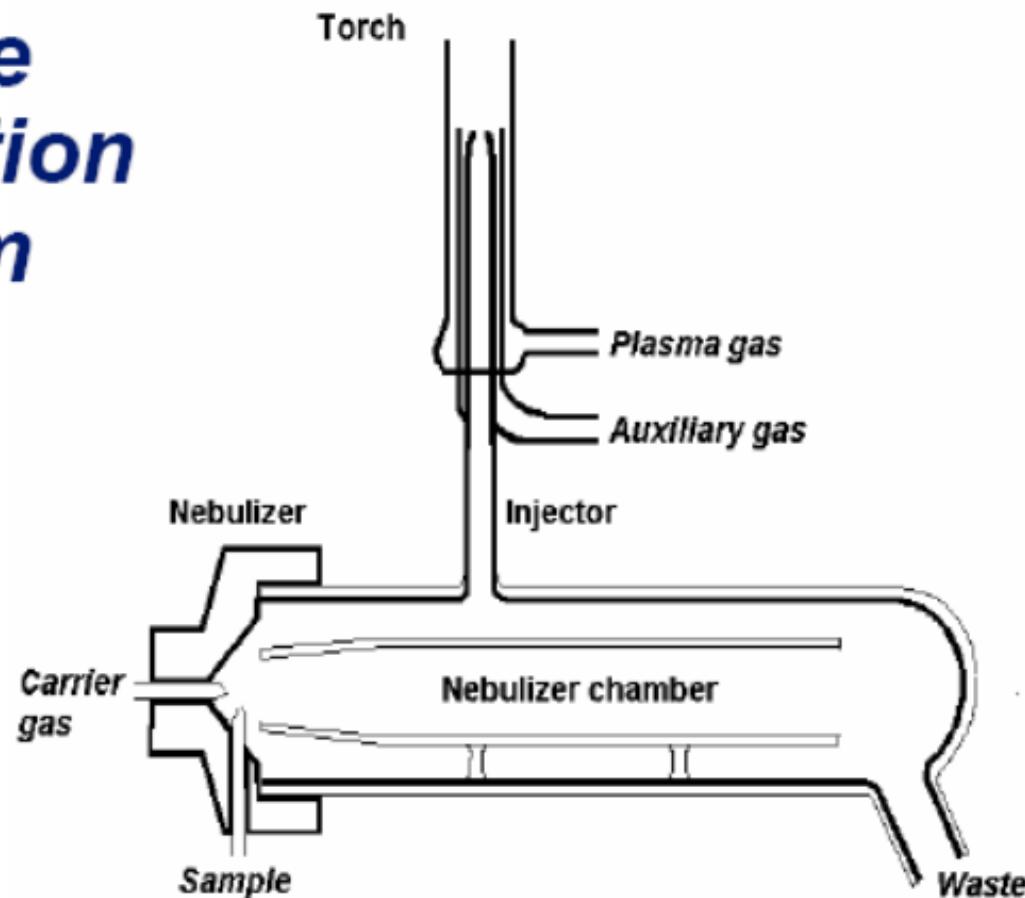
A. RF Generator

Radio-Frequency (RF) Generator is a device that is used to provide the power required for the generation and sustaining of the plasma discharge.

The power required for ICP-AES measurements ranges between 600 and 2500 W

B. Sample Introduction System

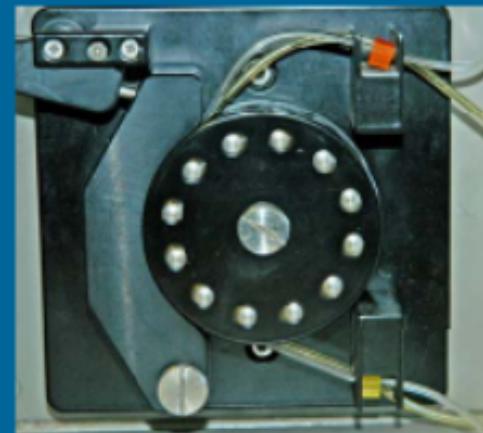
ICP-OES: Sample Introduction System



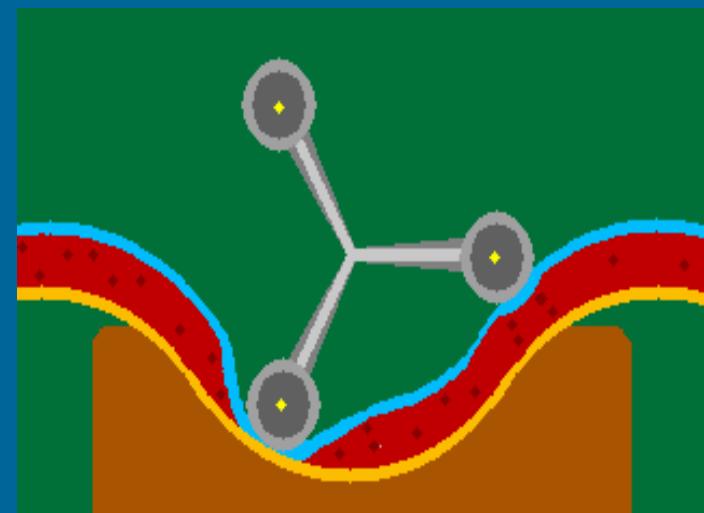
(1) Peristaltic Pump

Sample Introduction

- Solution is drawn up by means of a peristaltic pump
- Solution is turned into a fine aerosol by a nebulizer
- Aerosol is introduced into a plasma which excites the atomic species in the aerosol



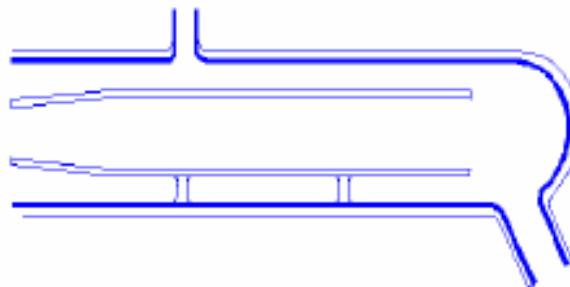
Peristaltic Pump



(2) Spray Chamber

☒ Scott chamber

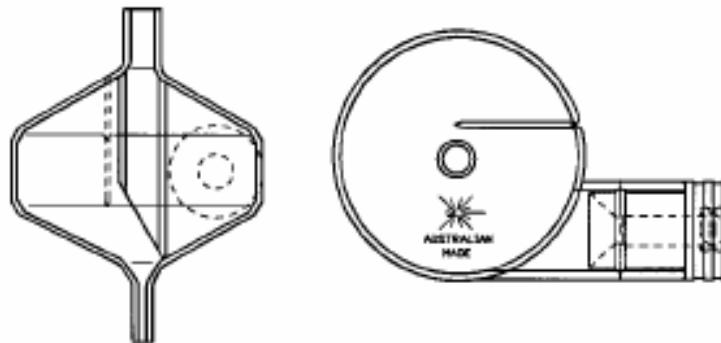
- traditional equipment
- large volume



(source: Perkin Elmer)

☒ Cyclonic chamber

- ☒ more aerosol
- ☒ smaller volume
- ☒ better wash out



(source: Glass Expansion)

Why we need Spray Chambers?

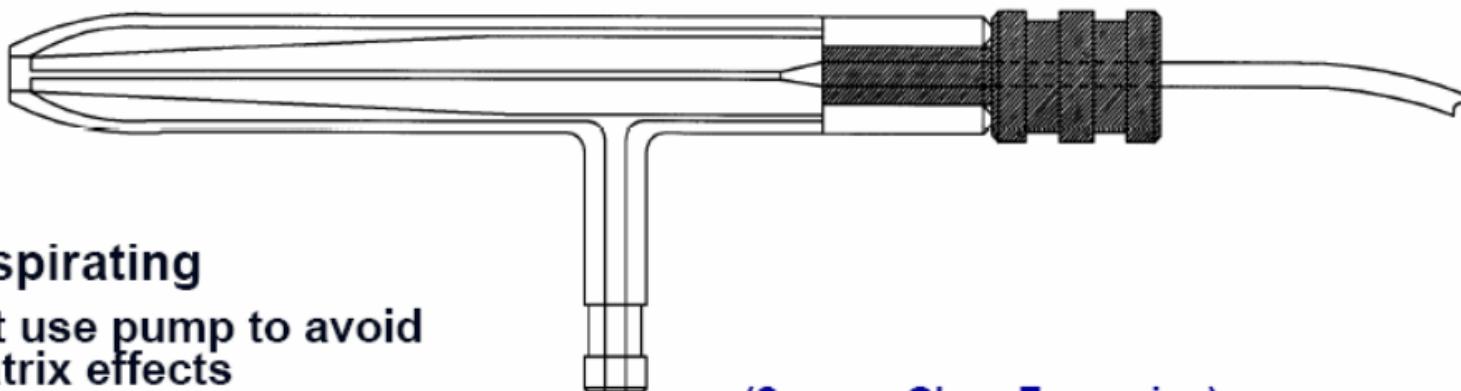
- ☒ Separation of small droplets from large ones
 - small droplets to the plasma
 - large droplets to the drain
- ☒ Compensate pulsation of the pump

(3) Nebulizer

☒ Transform a liquid sample into an aerosol

- direct introduction of a liquid would extinguish plasma
- two types of nebulizers are commonly used
 - (a) pneumatic nebulizers
 - (b) ultrasonic nebulizers
- mostly use of a peristaltic pump to transport
 - (a) sample to the nebulizers
 - (b) aerosol to the plasma

ICP-OES: Concentric (Meinhard) Nebulizer

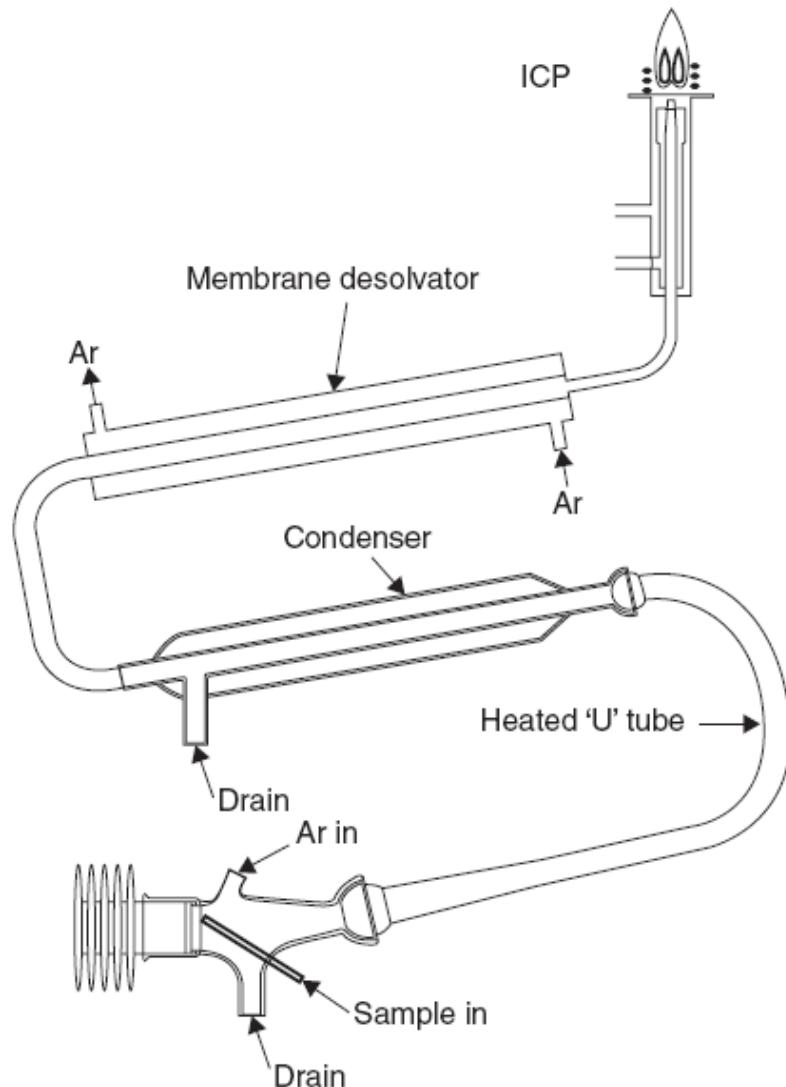


- **Self aspirating**
 - but use pump to avoid matrix effects
- **Clogs easily**
 - Filter sample before aspirating
 - Only for dilute solutions
 - ◆ Type A: use only for clean solutions
 - ◆ Type C: for high salt content
 - ◆ Type K: same as type C but with smoothed surfaces
- **Insert for cyclonic spray chamber**

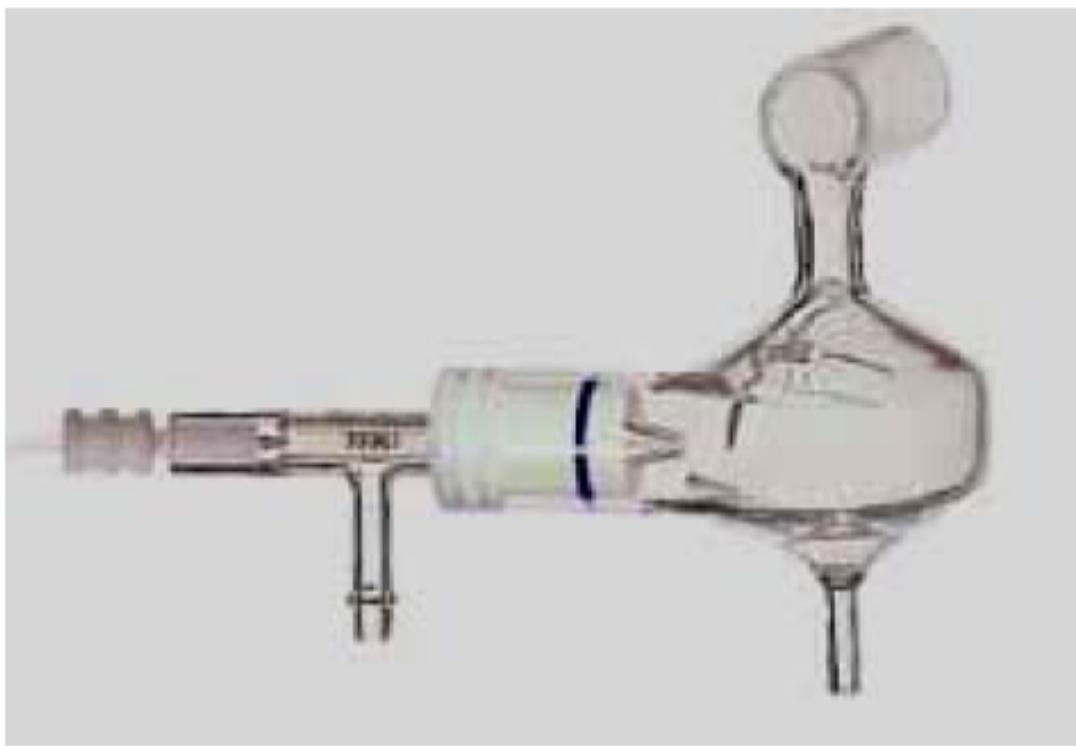
(Source: Glass Expansion)

Ultrasonic Nebulizer (USN)

- ultrasonic oscillations of a quartz plate (1.4 MHz)
 - very small droplets
 - high efficiency (~10-15 %)
 - but: high mass in the plasma
 - sample flow rate 1-3 L/min
- reducing solvent by vaporization and condensation
 - ICP OES: dry aerosol increases interferences
 - ICP-MS prefers dry aerosol to reduce interferences of oxide ions

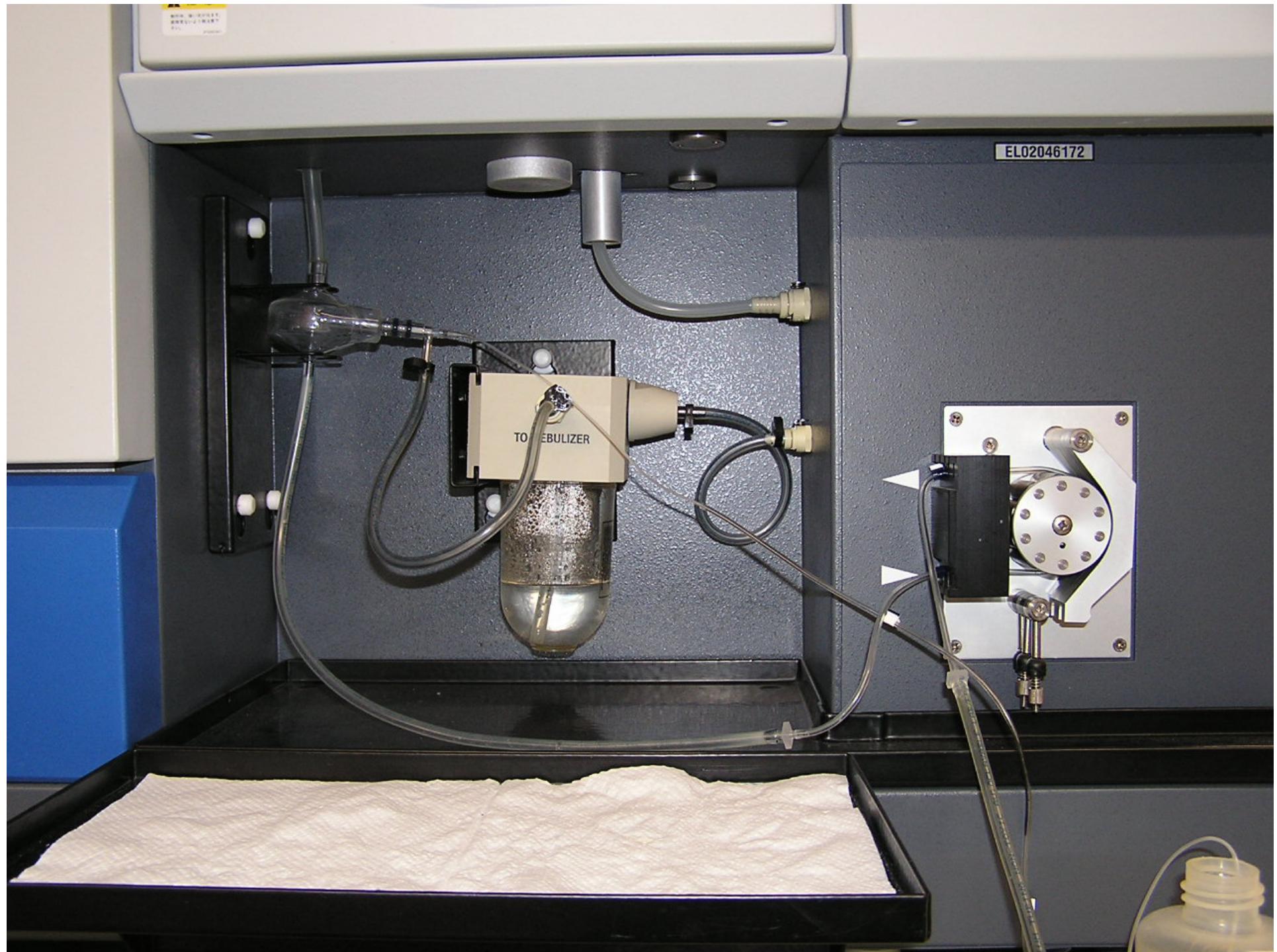


Concentric Nebulizer with Cyclonic Chamber

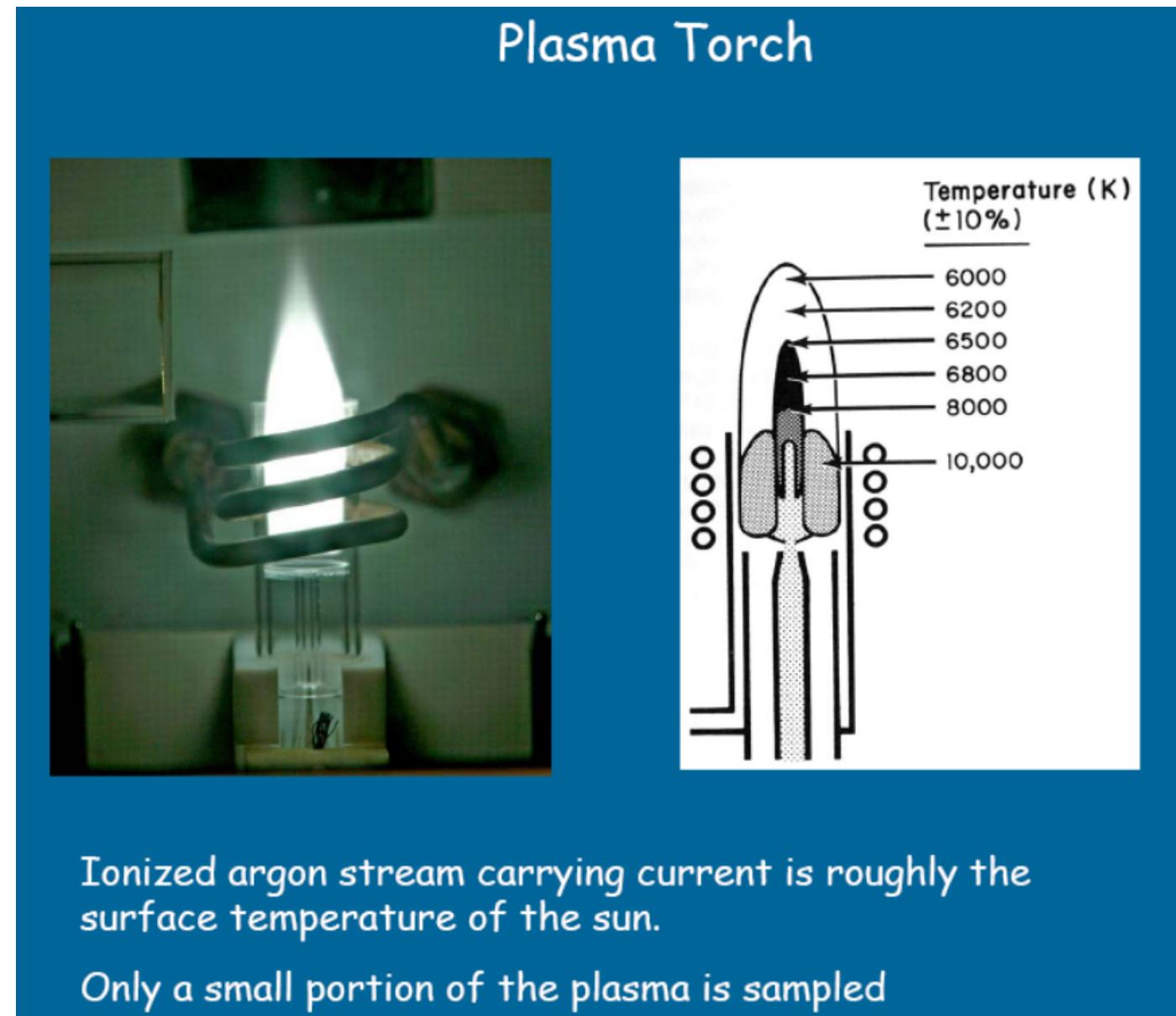
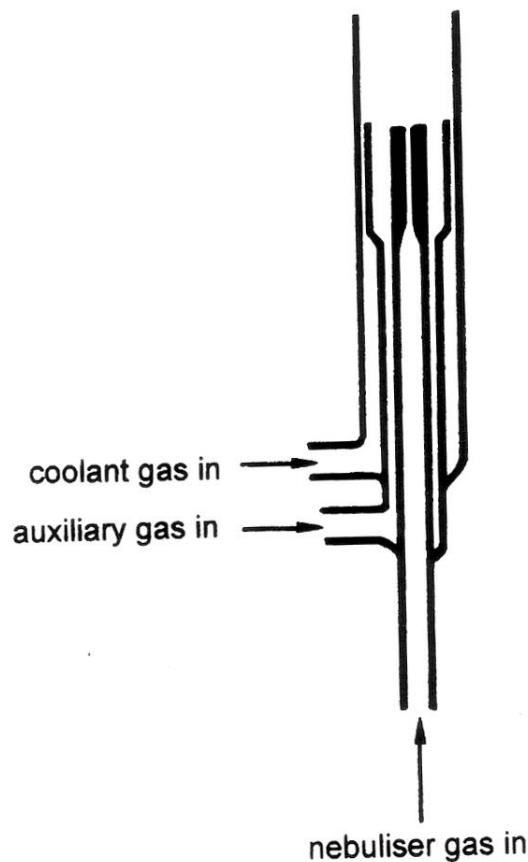


(Source: Glass Expansion)

- better detection limits than cross-flow
- low concentrations with concentric nebulizer (clogging)
- excellent combination for noble metals (glass), drinking water, etc.
- good wash out behavior



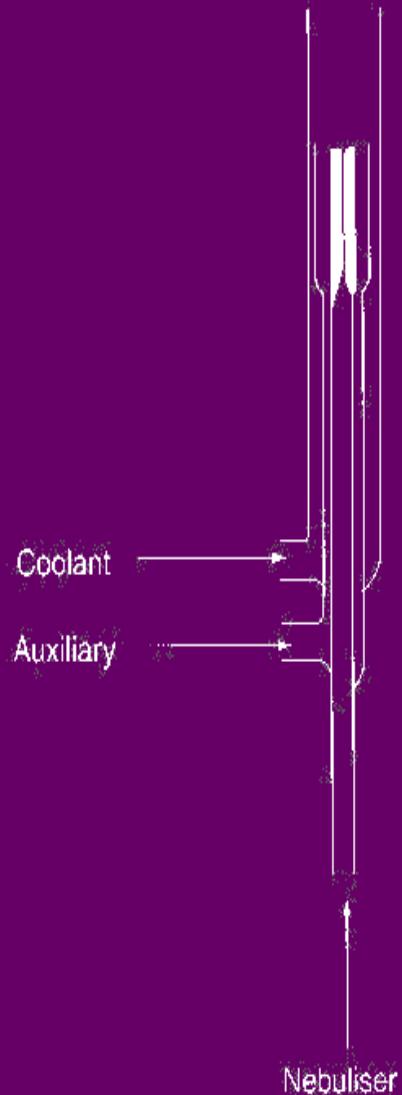
Torch



Plasma Torches

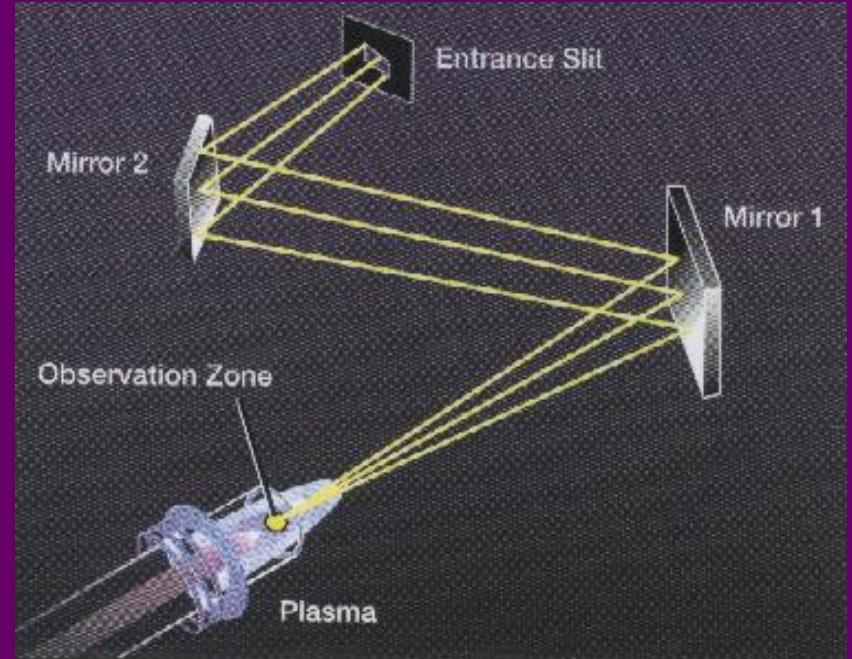
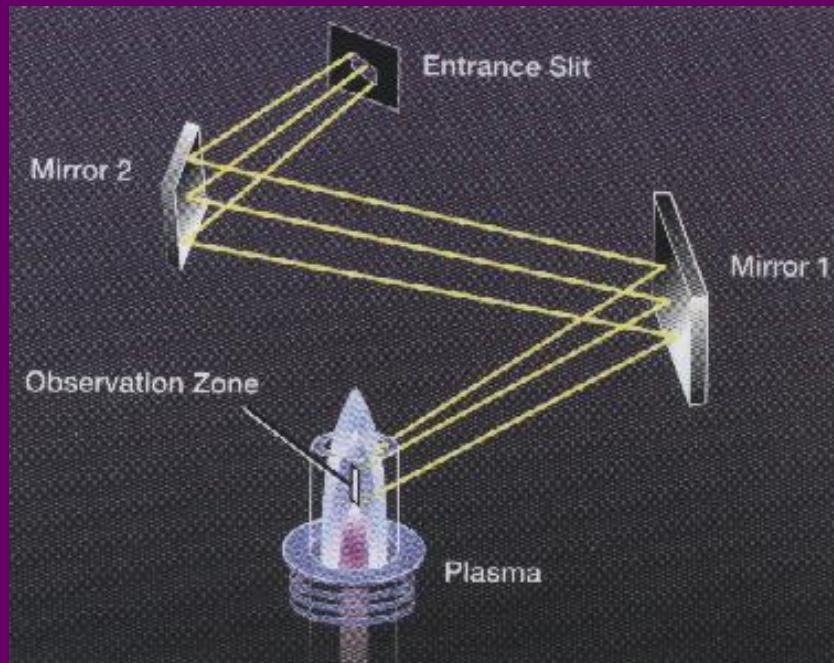
The plasma torch consists of three concentric quartz tubes through which the gas (normally argon) flows:

- The **outer tube** contains the coolant gas flow, which spirally flows tangentially through the torch at a high velocity. This assists in cooling the torch and hence prevents damage.
- The **middle tube** contains the auxiliary gas flow to keep the plasma discharge away from the auxiliary and nebulizer tubes
- The **innermost tube** has the nebulizer gas flow which carries the sample aerosol to the plasma.



Viewing position of plasma

- The plasma generated in an ICP can be viewed by the spectrometer, side-on or end-on. These viewing positions are called **radial** and **axial** viewing, respectively



Radial: light emitted from analyte has to pass only a short distance in plasma
i.e. less chance of self absorption

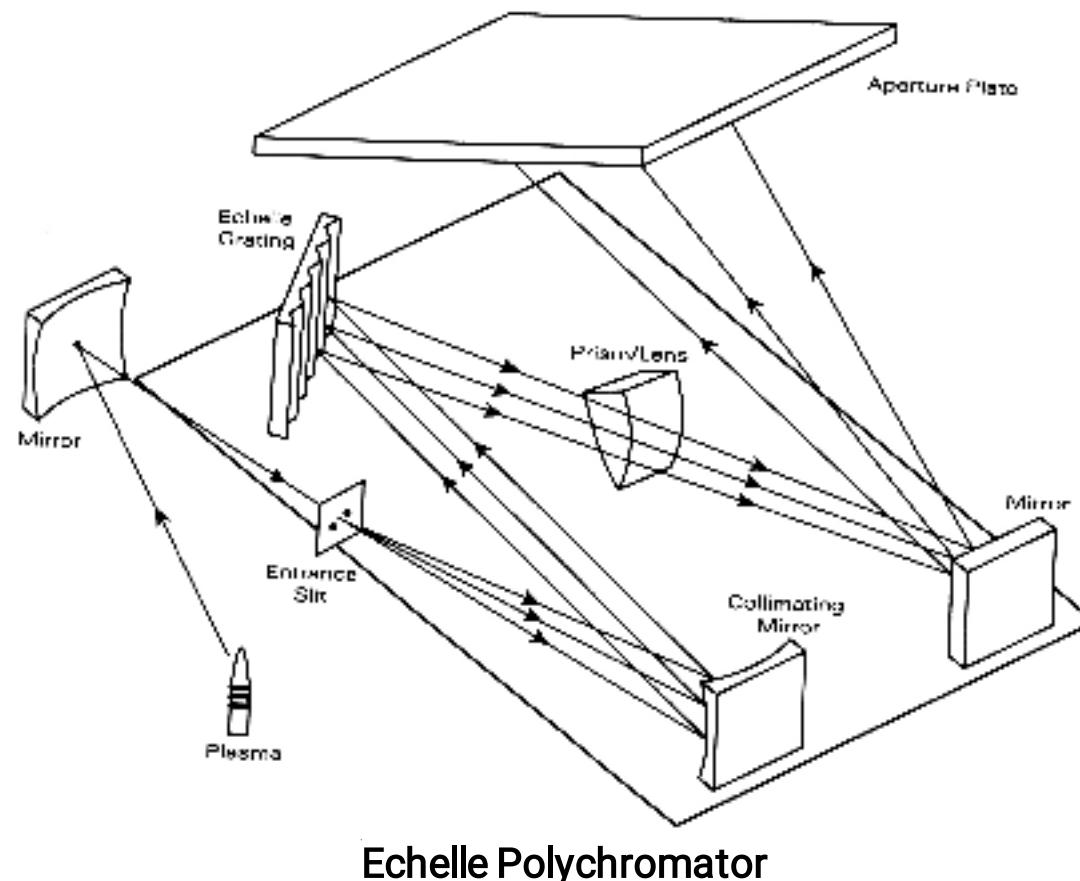
Axial: better collection efficiency of emitted light
i.e. improved sensitivity

4. Spectrometer (Polychromator)

The role of a spectrometer is to isolate the analytical wavelengths of interest from the light emitted by the plasma source.

The advantage of polychromators is:

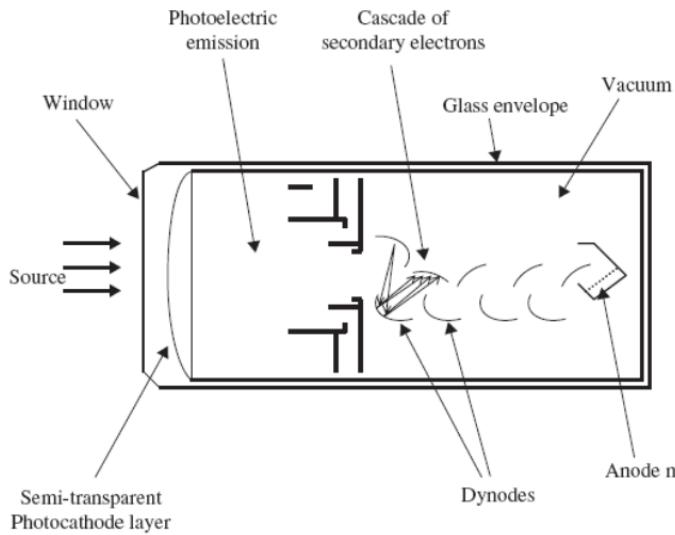
- capable of determining several analytes simultaneously.
- high sample throughput
- lower running cost



5. Detectors

- Commonly used detectors:
 - Photomultiplier tubes (PMT)
 - Solid-state detectors:
 - Charge-coupled devices (CCD) – arrays detector
 - Silicon photodiodes with thousands of individual elements
 - Very sensitive, very well-suited to echelle grating polychromators, very fast

Photomultiplier tubes (PMT)

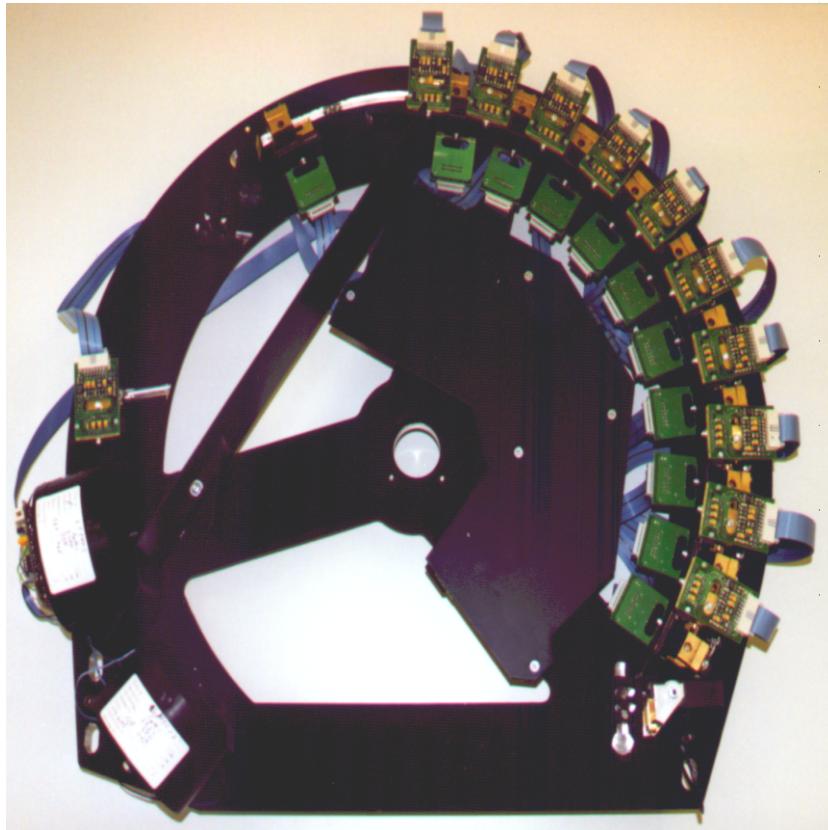


Schematic diagram of an end-on PMT

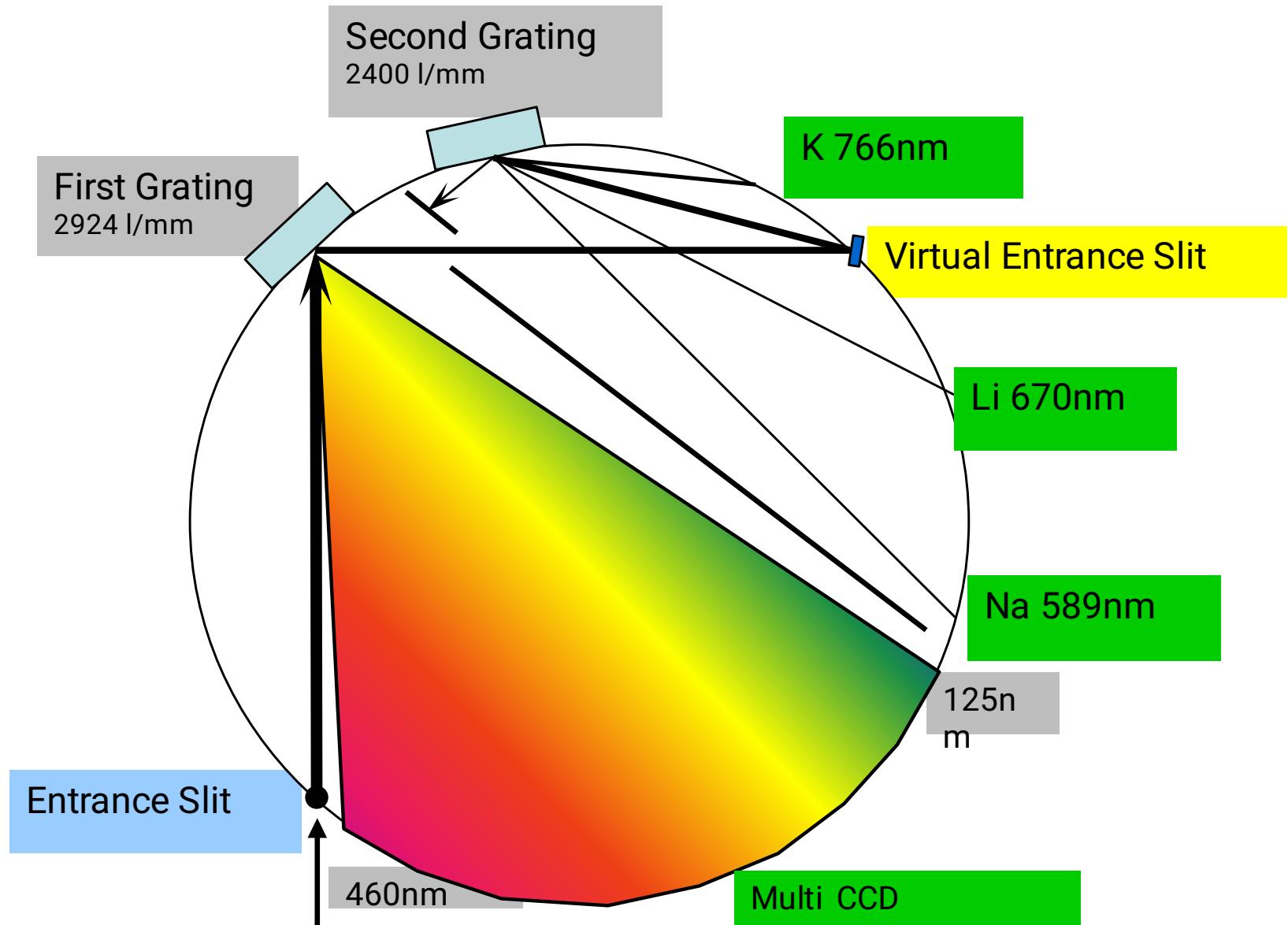
PMT consists of a photo-sensitive cathode and a series of dynodes, which are set at successively more positive potentials until an anode is reached. Light comes from the plasma, passes through the transparent casing of the multiplier and strikes cathode. This then emits electrons, which are accelerated down the dynode chain. Each time an electron impacts with a dynode, a number of secondary electrons are emitted.

CCD

Examples of the wavelength ranges covered by individual CCD chips:



- Chip 1 127,000 - 142,125 nm
- Chip 2 141,285 - 160,681 nm
- Chip 3 160,040 - 179,618 nm
- Chip 4 178,704 - 198,477 nm
- Chip 5 197,023 - 216,947 nm
- Chip 6 215,903 - 235,897 nm
- Chip 7 234,792 - 254,788 nm



Detection Limits of ICP-OES

- Typical detection limits (Varian Vista MPX):
- Considerations include the number of emission lines, spectral overlap
- Linearity can span several orders of magnitude.

Element	Wavelength (nm)	Detection Limit axial (ug/L)	Detection limit radial (ug/L)
Ag	328.068	0.5	1
Al	396.152	0.9	4
As	188.98	3	12
As	193.696	4	11
Ba	233.527	0.1	0.7
Ba	455.403	0.03	0.15
Ba	455.403	0.03	0.15
Be	313.107	0.05	0.15
Ca	396.847	0.01	0.3
Ca	317.933	0.8	6.5
Cd	214.439	0.2	0.5
Co	238.892	0.4	1.2
Cr	267.716	0.5	1
Cu	327.395	0.9	1.5
Fe	238.204	0.3	0.9
K	766.491	0.3	4
Li	670.783	0.06	1
Mg	279.55	0.05	0.1
Mg	279.8	1.5	10
Mn	257.61	0.1	0.133
Mo	202.03	0.5	2
Na	589.59	0.2	1.5
Ni	231.6	0.7	2.1
P	177.43	4	2.5
Pb	220.35	1.5	8
Rb	780.03	1	5
S	181.972	4	13
Sb	206.83	3	16
Se	196.03	4	16
Sr	407.77	0.02	0.1
Sn	189.93	2	8
Tl	336.12	0.5	1
Tl	190.79	2	13
V	292.4	0.7	2
Zn	213.86	0.2	0.8

Sampling and sample preparation

Are the samples representative of what you are trying to measure?

Will any elements volatilize during sample preparation?

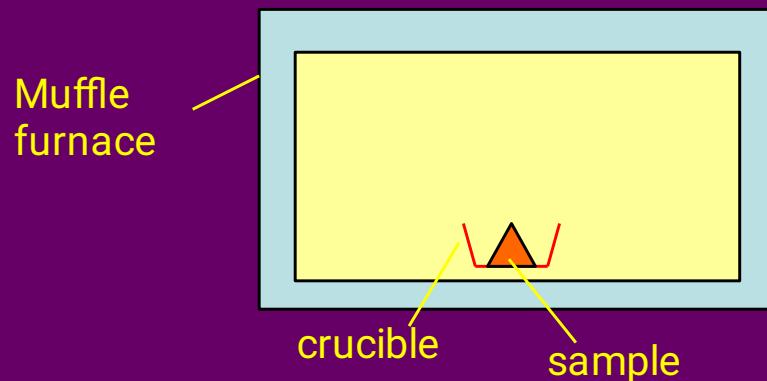
How much contamination can the sample tolerate during preparation?

Sample preparation

- For many applications, the sample analyzed by ICP-AES will not be in a suitable form. In order to transform solid samples into suitable form, sample pre-treatment is required.
- The pre-treatment method used will depend on the nature of the sample and the element which are to be determined.
- Those methods commonly used are:
 - Dry-ash,
 - Acid digestion,
 - Fusion,
 - Solubilization
 - Microwave digestion.

Analysis using ICP – Sample preparation

Dry Ashing



- Dry at 105 -100 °C
- Ash at 200-800 °C
- Dissolve the ashed sample in acids, usually HCl, H_2SO_4 , HNO_3 and HCl/ HNO_3

Preparation is simple and widely applicable but sample losses through volatilization and retention

Acid Digestion

Use of strongly oxidizing mineral acid, such as HNO_3 , HF, H_2SO_4 and HClO_4 to oxidize the resistant components, with gentle heat.

It can be carried out in closed or open reaction systems. Closed systems minimize the losses in volatilization.

Acid Digestion

Sample is allowed to dissolve in an acid mix.

Sample is typically heated to speed dissolution.

Advantages:

Most direct dissolution, minimizing possible introduction of contaminants

Usually best for metals

Disadvantages:

Ineffective against geological and ceramics, especially if Si is to be determined

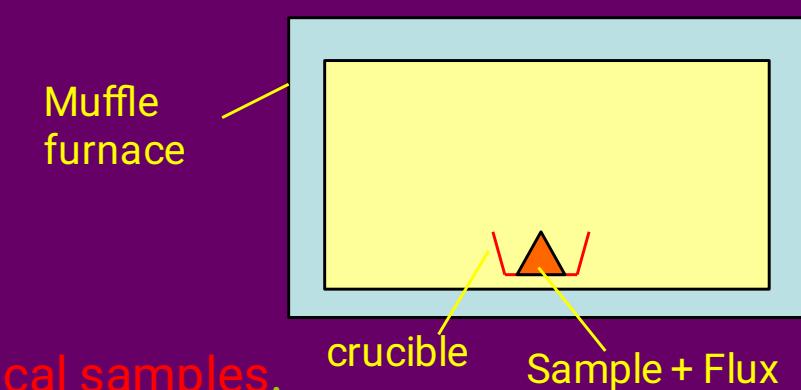
Can be time consuming

Analysis using ICP – Sample preparation

Salt Fusion

- Sample is mixed in a platinum crucible with a flux which attacks all the major rock-forming silicates.
- Fused in a furnace.
- Cooled to room temperature.
- Dissolved in HNO_3 .

Fusion methods are commonly used with geological samples.



Salt Fusion

Sample is mixed with lithium metaborate in a 1:9 ratio

Mix is melted at 900C and dissolved in a nitric acid solution

Advantages:

Attacks geological and most ceramics

Provides a high concentration salt environment which dampens any intersample matrix differences.

Disadvantages:

Easily volatilized elements cannot be determined

High metal contents may prove difficult

Analysis using ICP – Sample preparation

Microwave digestion

Microwave sample preparation uses microwave power to heat several samples at once, which can speed up a digestion processes.



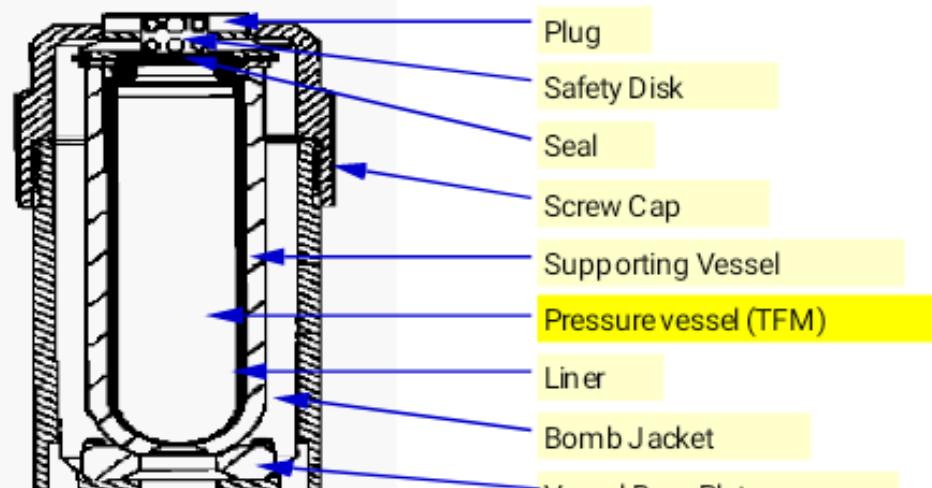
Advantages: improved detection limits, low acid concentration and a reduced need for dry ashing or fusion.

Reaction pressure, temperature and time are computer controlled

Preparation of Solid Sample

Acid digestion

apparatus: microwave system



Microwave sample preparation system

MULTIWAVE (Anton Paar GmbH)



Analysis using ICP – Sample preparation

Microwave digestion

USEPA method 3051: MICROWAVE ASSISTED ACID DIGESTION OF SEDIMENTS, SLUDGES, SOILS, AND OILS

- Digestion vessels carefully acid washed and rinsed with water before use.
- Sample up to 0.5 g and 10 ml of concentrated HNO_3 are placed in microwave vessel. (For soils, sediments, and sludge use no more than 0.50 g. For oils use no more than 0.25 g.)
- Sample vessel equipped with a single-port cap and a pressure relief valve.
- The vessels are capped and heated by a suitable laboratory microwave unit.
- The vessel contents are filtered, centrifuged, or allowed to settle and then diluted to volume and analyzed.



Microwave Digestion

Sample is allowed under controlled temperature and pressure conditions in a pressure vessel.

Advantages:

Effective for a wide range of materials, especially those containing organics

Direct method of dissolution, minimizing introduction of contaminants

Disadvantages:

Time consuming method development

Labor intensive

Typical applications of ICP-AES/ICP-MS

- Natural Waters
- Saline Brines
- Geological Materials
- Ceramics and glasses
- Coals and Paper Products
- Leachates

ICP/AES INTERFERENCES

Spectral Interferences

Physical Interferences

Chemical Interferences

Memory Effect

- **Spectral interferences:**

- caused by background emission from continuous or recombination phenomena,
- stray light from the line emission of high concentration elements,
- **overlap of a spectral line from another element,**
- or unresolved overlap of molecular band spectra.

- **Corrections**

- Background emission and stray light compensated for by subtracting background emission determined by measurements adjacent to the analyte wavelength peak.
- Correction factors can be applied if interference is well characterized
- Inter-element corrections will vary for the same emission line among instruments because of differences in resolution, as determined by the grating, the entrance and exit slit widths, and by the order of dispersion.

Spectral Interference

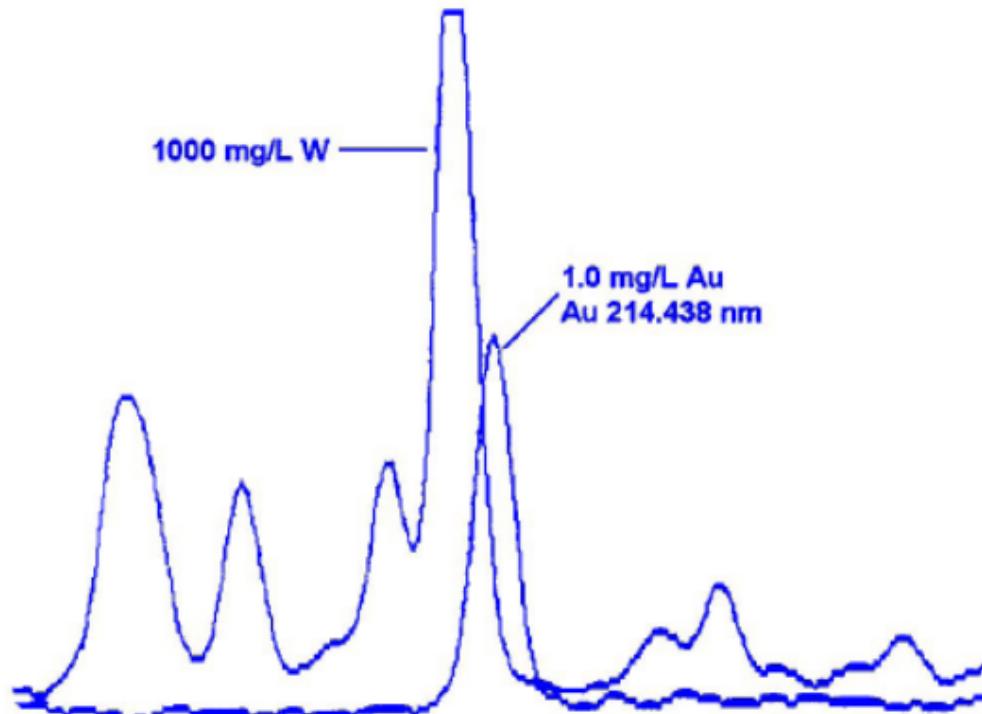


Figure 4-10. Tungsten matrix spectrum causing a complex background shift at the gold 267.595 nm line.

Some elemental lines may interfere with others.

Best solution is to find another spectral line.

Samples should be scanned for possible problems

The Example for Choosing Wavelength in ICP-AES

Element wavelength (nm)	Element wavelength (nm)
Ag 328.068	S 180.731
As 188.979	Sb 206.833
Ba 233.527	Sc 361.384
Be 313.042	Sn 189.926
Bi 223.061	Sr 421.552
Cd 226.502	Th 283.730
Ce 394.275	U 409.014
Co 228.616	V 311.071
Cr 283.563	W 239.709
Cu 324.754	Y 371.030
Ga 294.364	Zn 213.856
La 408.672	Zr 343.823
Li 670.784	
Mo 313.259	
Nb 269.706	
Nd 417.732	
Ni 231.604	
Pb 220.353	

Analytical line selection

For Ag, As, Bi, Cu, Ga, Li, Ni, Pb, Sc, Th, Zn and Zr the primary line was chosen to eliminate possible interferences.

Ba: the 233.527 nm line was chosen because the 455.403 nm and the 493.409 nm lines were too sensitive.

Be: the 313.042 nm line was chosen because the 234.861 nm has an Fe interference which causes wing overlap.

Cd: the 226.502 nm line was chosen for its maximum sensitivity and minimal spectral interferences.

Ce: the 394.275 nm line was chosen for its maximum sensitivity and minimal spectral interference.

Co: the 238.892 nm line has a nearby Fe line. The 228.616 nm line was used.

Cr: the 283.563 nm line was chosen for its maximum sensitivity and minimal spectral interference.

La: the 379.478 nm line has an Fe interference. The 333.749 nm has Fe, Mg and Ti interference. The 408.672 nm line was used.

Mo: the 313.259 nm line was chosen for its maximum sensitivity and minimal spectral interference.

Nb: the 309.418 nm line has a nearby OH band and a direct V overlap. The 269.706 nm line was used.

Nd: the 417.732 nm line was chosen for its maximum sensitivity and minimal spectral interference.

Sb: the 217.581 nm line has an Fe line which causes an elevated background. The 206.833 nm line was used.

Sr: the primary 407.771 nm line was too sensitive and therefore the 421.551 nm line was used.

U: The 263.533 nm and the 385.958 nm lines had interferences from the major elements. The 409.014 nm line was chosen for its maximum sensitivity and minimal spectral interference.

V: the 311.071 nm line was chosen for its maximum sensitivity and minimal spectral interference.

W: the 239.709 nm line was chosen for its maximum sensitivity and minimal spectral interference.

Physical interferences

- Cause
 - effects associated with the sample nebulization and transport processes.
 - Changes in viscosity and surface tension can cause significant inaccuracies,
 - especially in samples containing high dissolved solids
 - or high acid concentrations.
 - Salt build up at the tip of the nebulizer, affecting aerosol flow rate and nebulization.
- Reduction
 - by diluting the sample
 - or by using a peristaltic pump,
 - by using an internal standard
 - or by using a high solids nebulizer.

Physical interferences

Instrumental Drift

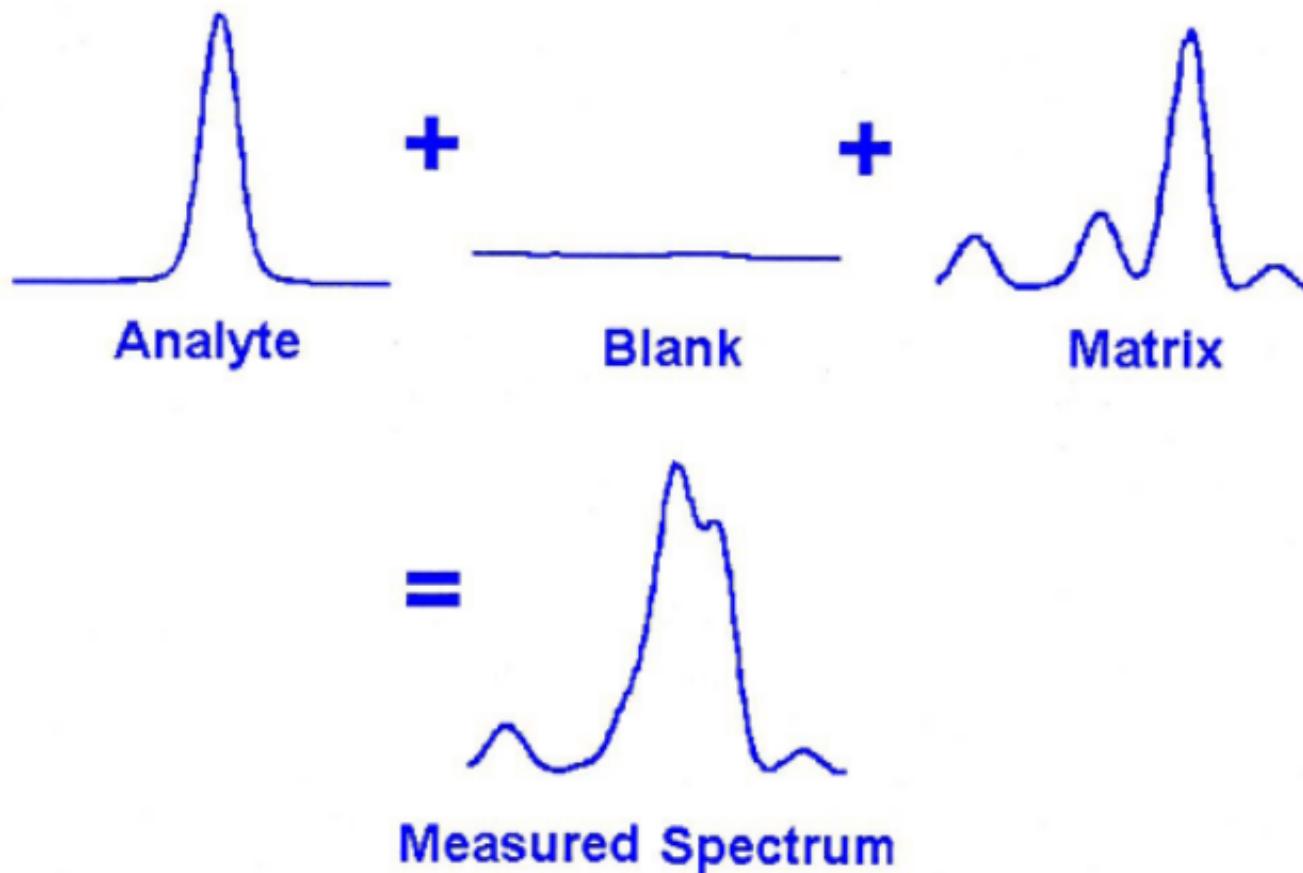
Instrument reading can drift over a period of time due to physical changes in the optical system, or the configuration of the plasma.

Standards need to be run at the beginning and end of each run in order to estimate and correct for this drift.

Wavelength calibration

- **Chemical interferences:**
 - include molecular compound formation
 - Normally, this effect is not significant with the ICP technique.
 - Chemical interferences are highly dependent on matrix type and the specific analyte element.

Combined Effects



Compensation : (a) matrix of standards should be closely matched with that of the samples (matrix-matched calibration)
(b) Matrix removal

Memory interferences:

- When analytes in a previous sample contribute to the signals measured in a new sample.
- Memory effects can result
 - from sample deposition on the uptake tubing to the nebulizer
 - from the build up of sample material in the plasma torch and spray chamber.
- The site where these effects occur is dependent on the element and can be minimized
 - by flushing the system with a rinse blank between samples.
- ***High salt concentrations*** can cause analyte signal suppressions and confuse interference tests.

Calibration curves of ICP-AES

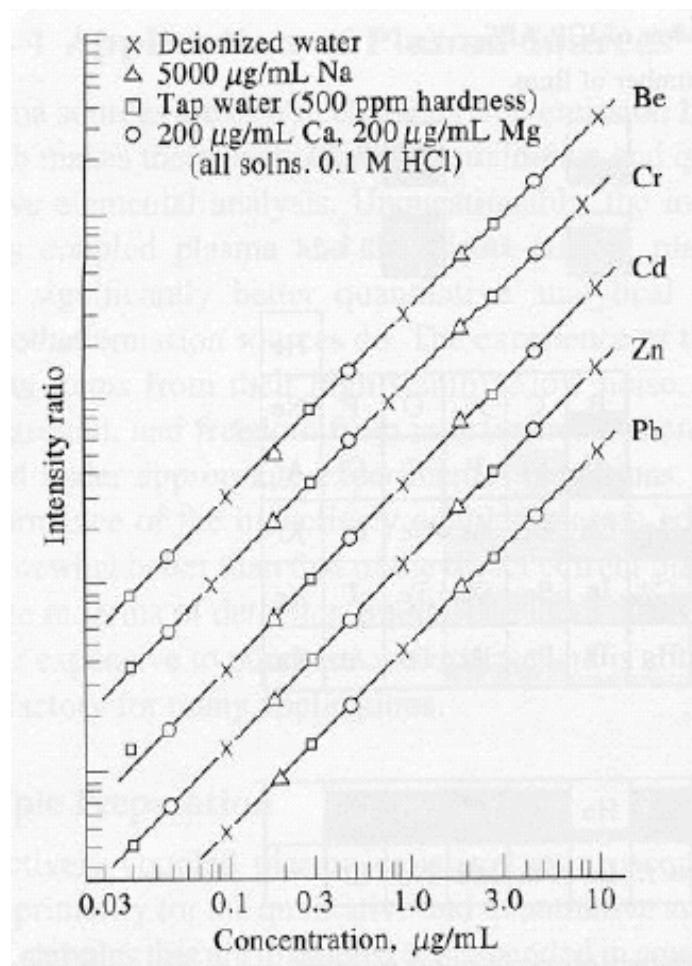


TABLE 10-2 Effect of Standardization Frequency on Precision of ICP Data*

Frequency of Recalibration, hr	Relative Standard Deviation, %			
	10^1 to 10^2	10^2 to 10^3	10^3 to 10^4	10^4 to 10^5
0.5	3-7	1-3	1-2	1.5-2
2	5-10	2-6	1.5-2.5	2-3
8	8-15	3-10	3-7	4-8

*Data from: R. M. Barnes, in *Applications of Inductively Coupled Plasmas to Emission Spectroscopy*, R. M. Barnes, Ed., p. 16. Philadelphia: The Franklin Institute Press, 1978. With permission.

TABLE 10-3 Comparison of Detection Limits for Several Atomic Spectral Methods*

Method	Number of Elements Detected at Concentrations of				
	<1 ppb	1-10 ppb	11-100 ppb	101-500 ppb	>500 ppb
Inductively coupled plasma emission	9	32	14	6	0
Flame atomic emission	4	12	19	6	19
Flame atomic fluorescence	4	14	16	4	6
Flame atomic absorption	1	14	25	3	14

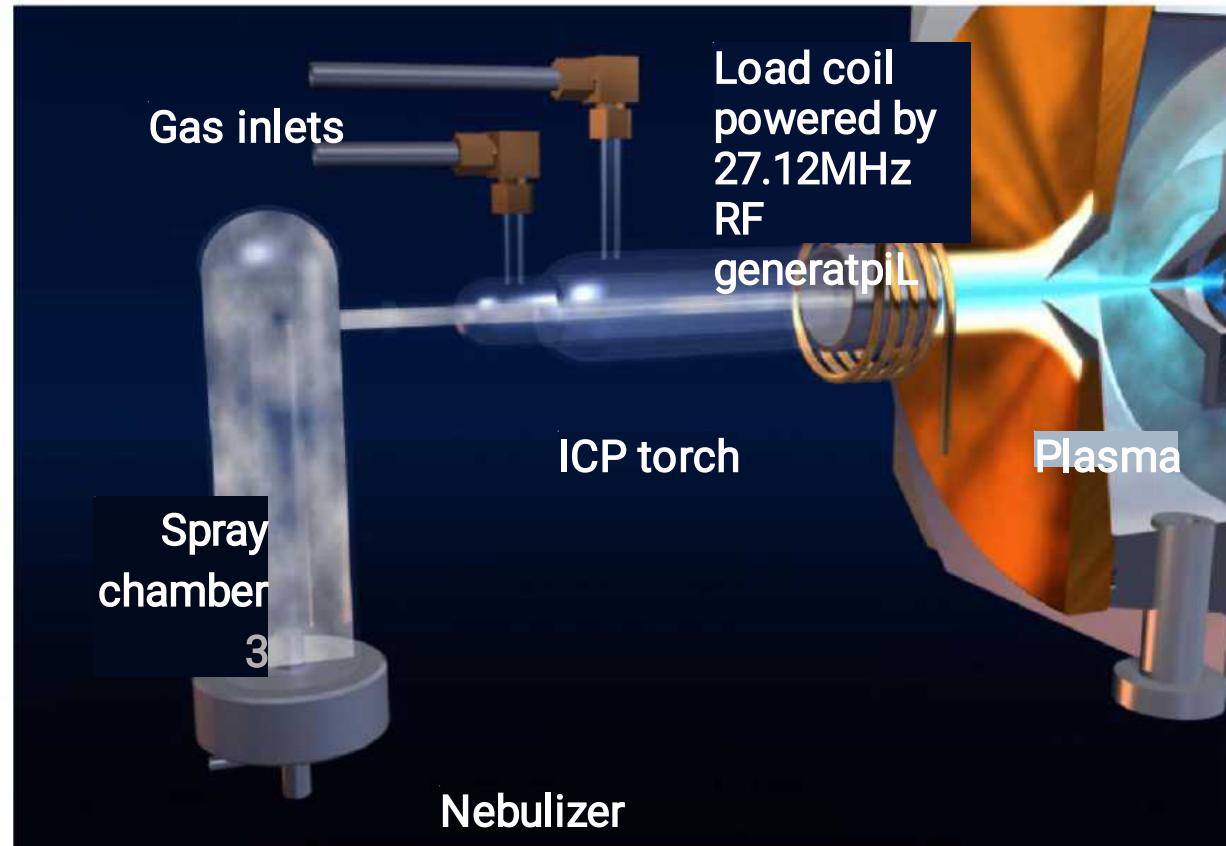
*Detection limits correspond to a signal that is twice as great as the standard deviation for the background noise. Data abstracted with permission from V. A. Fassel and R. N. Kniseley, *Anal. Chem.*, 1974, 46(13), 1111A. Copyright 1974 American Chemical Society.

Strengths of ICP-AES

- Can detect most cations and some anions
- Detection Limits down to parts per trillion for some elements
- Rapid simultaneous determination of selected elements
- Selective determination of other elements in sequential mode
- Good linear range - up to hundreds of ppms for alkalis
- Suitable for routine analyses of multiple samples
- Dependable work horse type of instrument

Weaknesses of ICP-AES

- Not effective for low levels of alkalis (less than 1-5 ppm)
- subject to matrix problems
- suitable standards required on every run
- Only elemental data is provided - no direct structural information
- Does not provide, in most cases, parts per billion or parts per trillion data - Go to ICP-MS



AAS, ICP-AES, ICP-MS

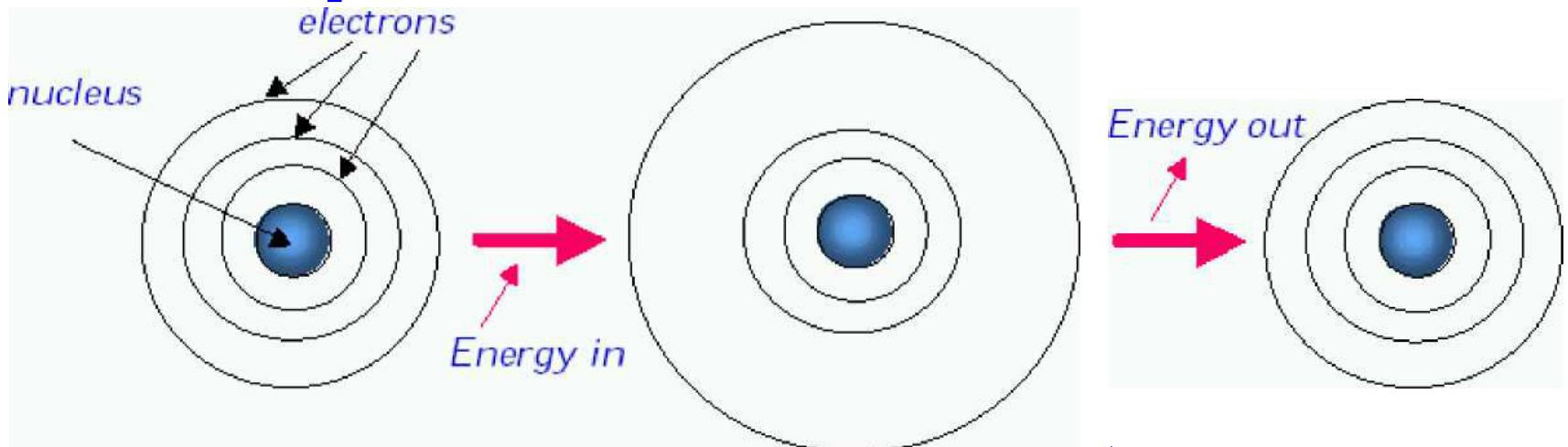
Akhmad Sabarudin

Analytical Techniques for Elemental Analysis

- AAS - Atomic Absorption Spectrometry
- ICP-OES - Inductively Coupled Plasma Optical Emission Spectrometry

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

Simple Model of the Atom



The Atom

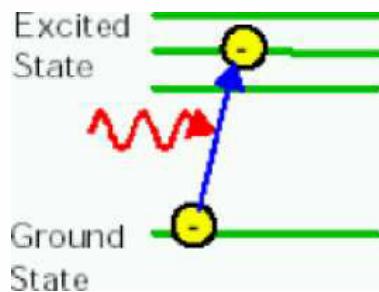
On absorbing the energy, the electrons in the outer shell move outwards to a different "orbit"

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"

Atomic Spectroscopy

Atomic Absorption

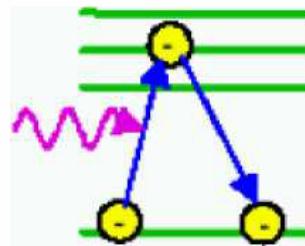
Light of specific wavelength from Hollow Cathode Lamp (HCL)



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

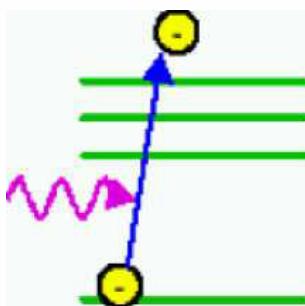
Light and heat energy from high intensity source (flame or plasma)



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

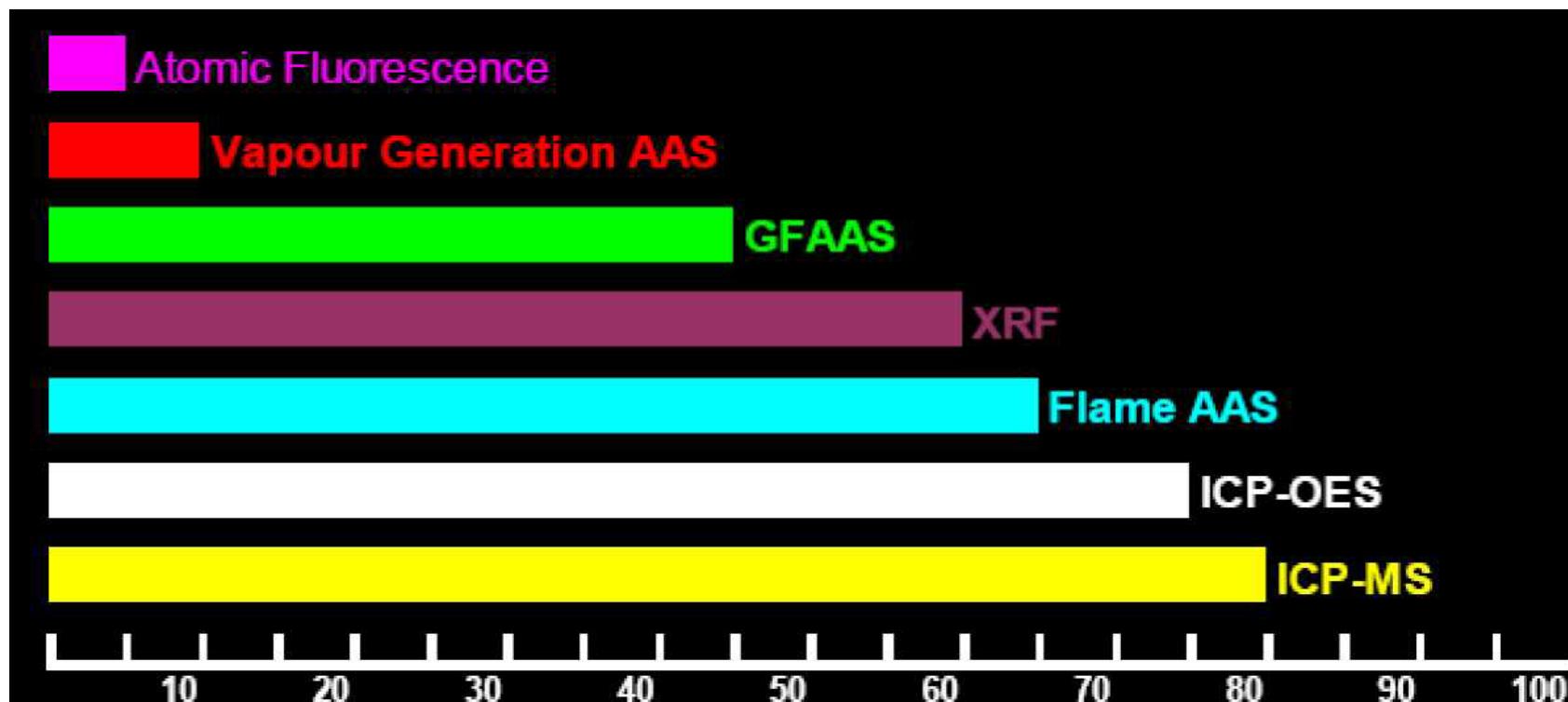
Mass Spectrometry

Light and heat energy from high intensity source (plasma)

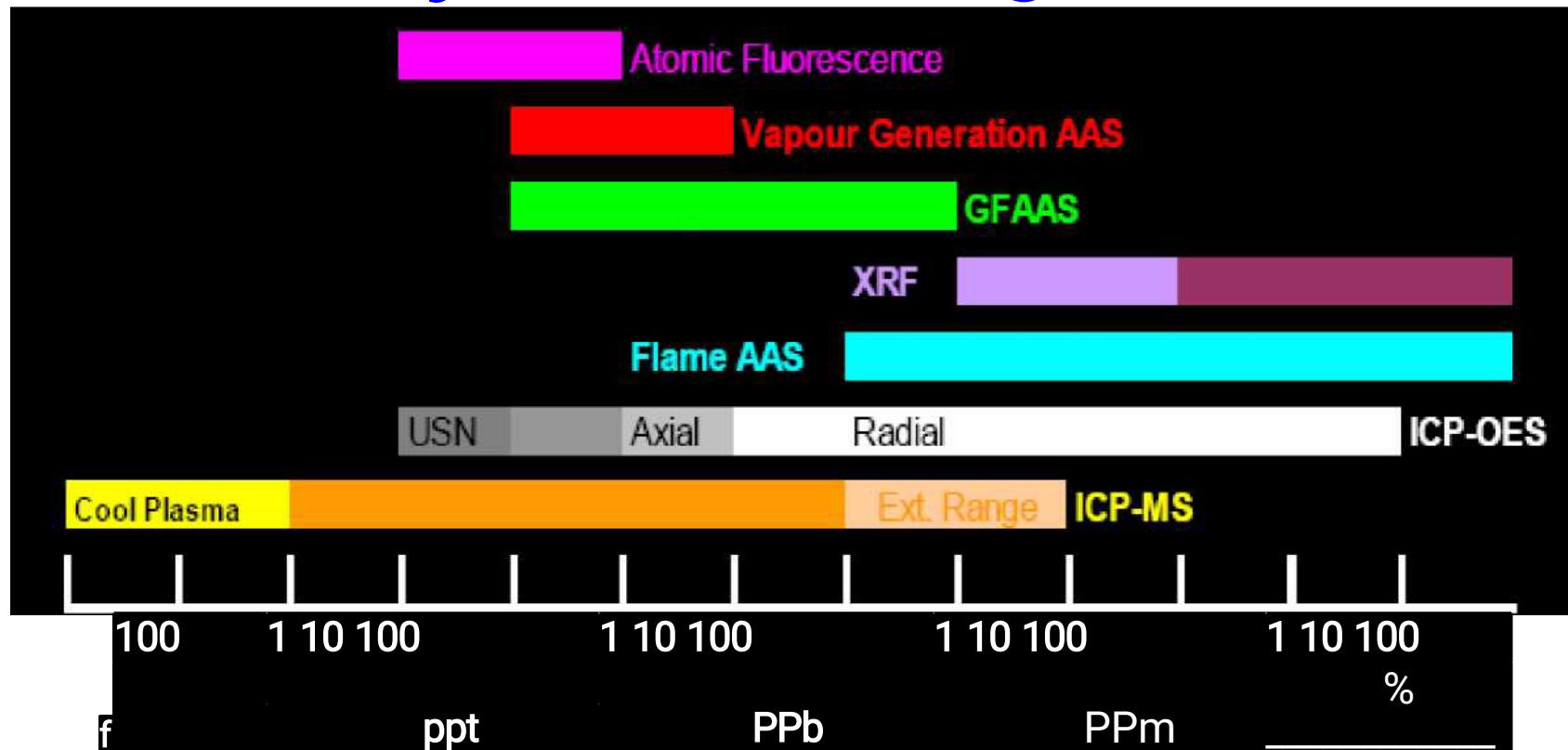


High energy (light and heat) ejects electron from shell (ionisation). Result is free electron and with positive charge (ion)
Ions are extracted and measured directly in spectrometer

Number of Applicable Elements



Relative Sensitivities and Dynamic Ranges



LOD of each method

ICP-MS

1 ppm

100 ppb

10 ppb

1 ppb

100 ppt

10 ppt

1 ppt

Ca

Br Fe P B Cr
Na Cd Pb Cu
Zn Mg Co Mo
REEs Cs U

ICP-AES

B		
U	Pd Sn	
Al	As	Se
Pb	Ni	Sb
Cr	B	Fe
Cd	Cu	Li
Zn	Ti	Ag
Be	Bi	Sr
Ca	Mn Mg	
Ba		

GF-AAS

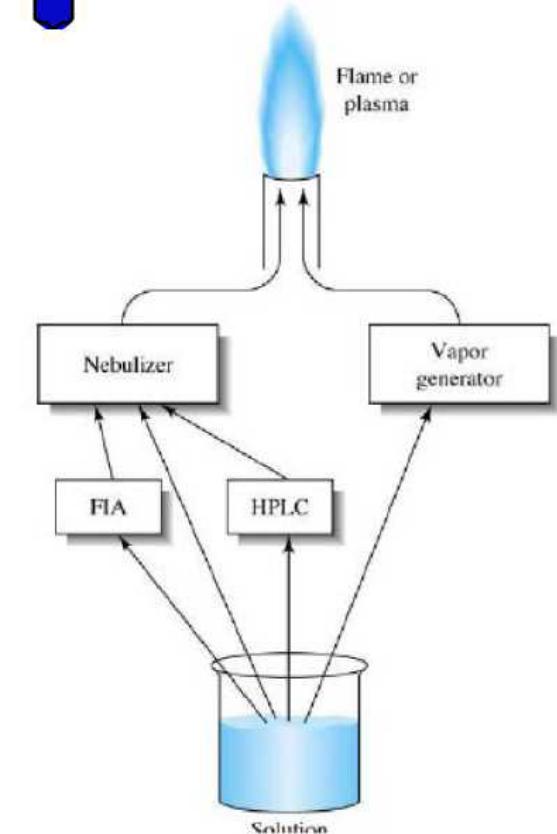
Hg		
Ti	Se	
As	Sn	V
Ni	Sb	Tl
Ba	Ca	Pb
Co	As	Cu
Al	Cr	Mn
Cd	Mg	Ag
Zn		

LOD : Limit of Detection

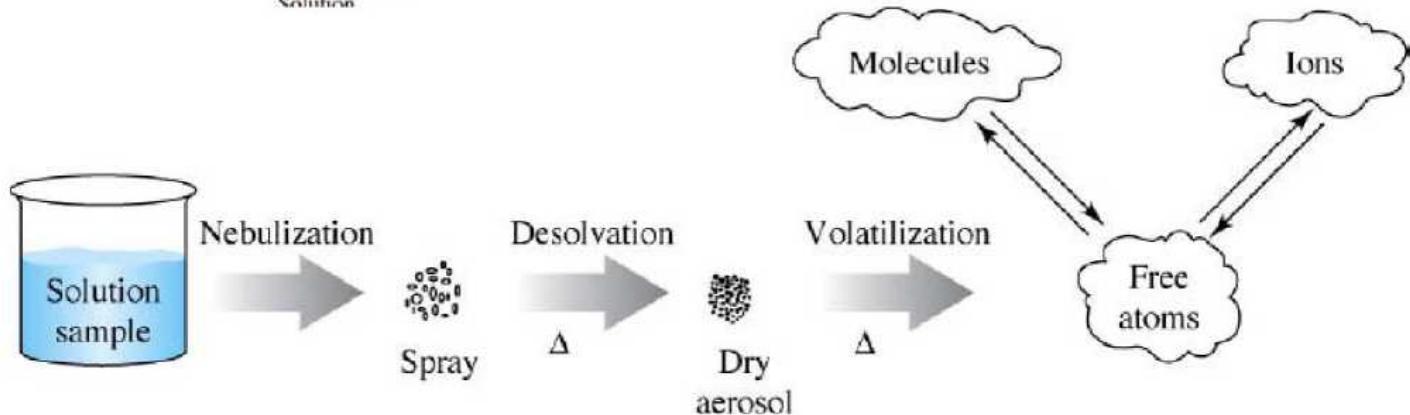
Characteristics of instruments

	ICP-MS	ICP-AES	GF-AAS
Detection	mass	emission	absorbance
Merit	high sensitivity	multielement	high sensitivity
	multielement		selective
Demerit	damage from high salinity	relatively low sensitivity	monoelement
Ranges	1 ppt ~ 100 ppb	0.1 ppb ~ 10 ppm	1 ppb ~ 100 ppb

Atomization in AAS, ICP-AES, ICP-MS

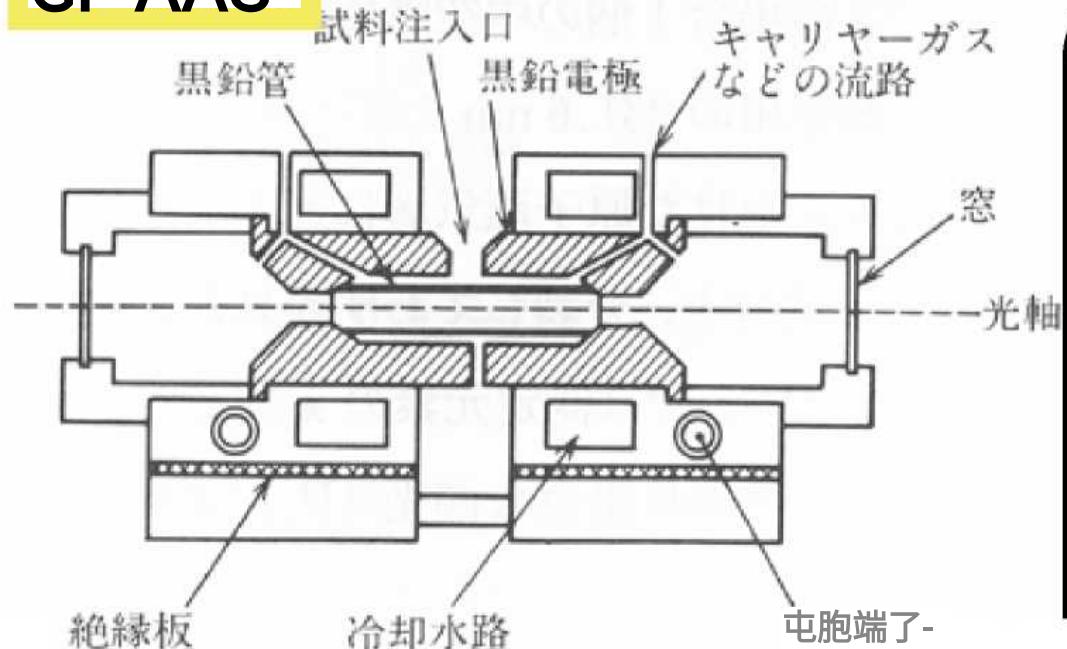


Processes leading to atoms, molecules, and ions with continuous sample introduction into a plasma or flame

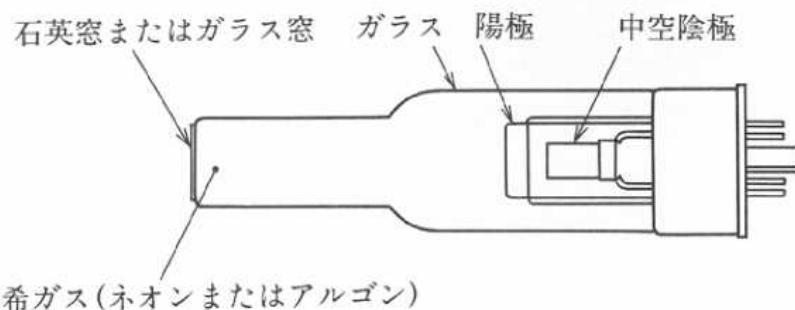


GF-AAS

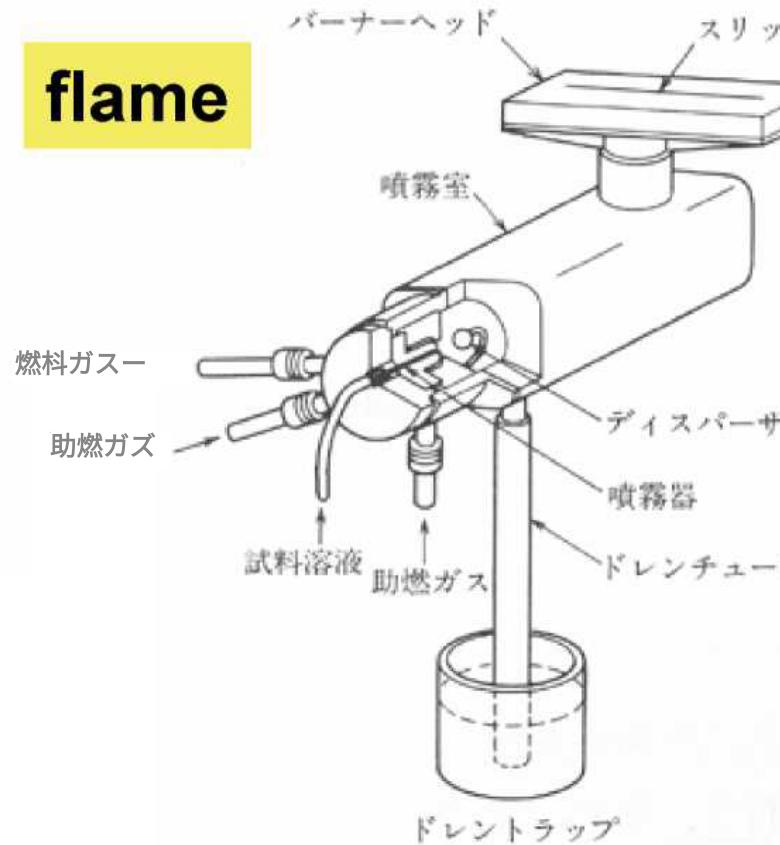
AAS



graphite tube (黒鉛炉)



flame

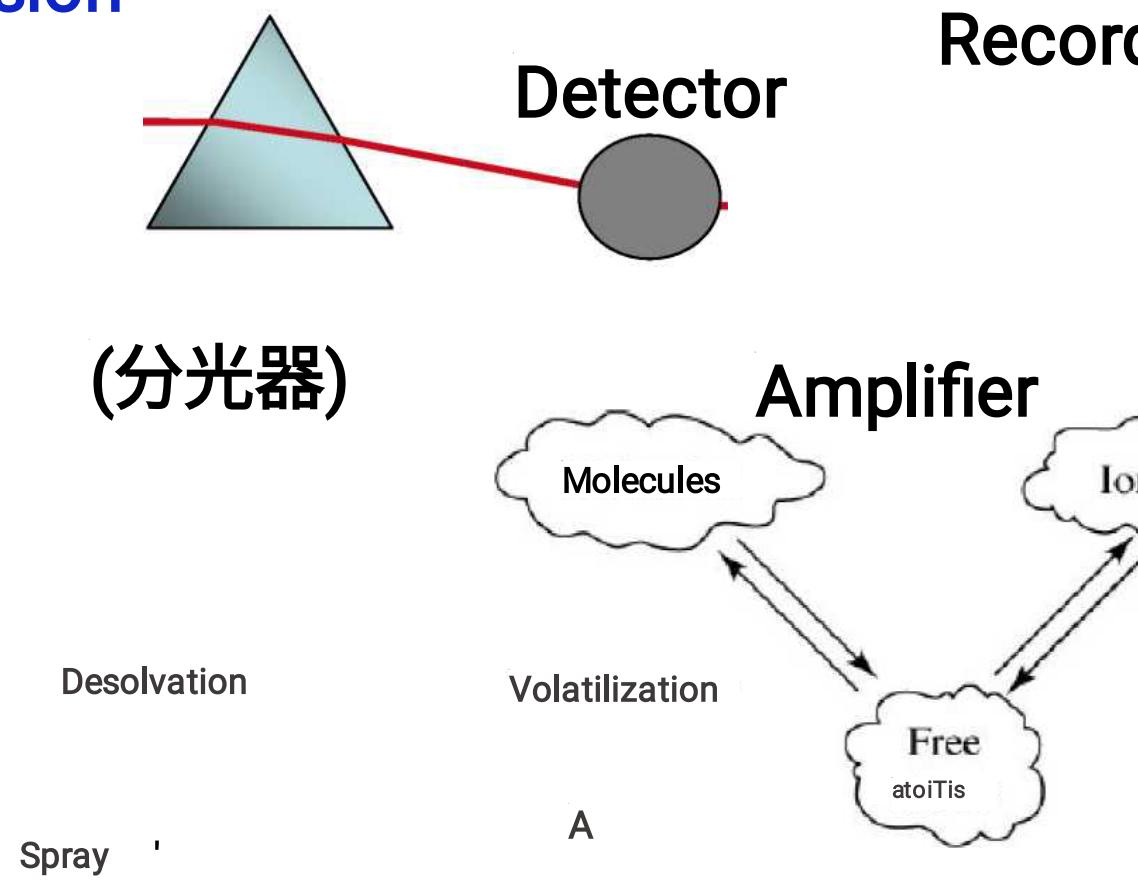
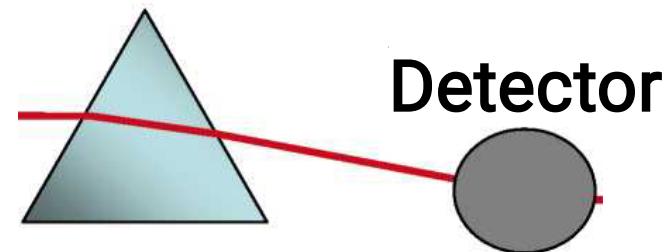
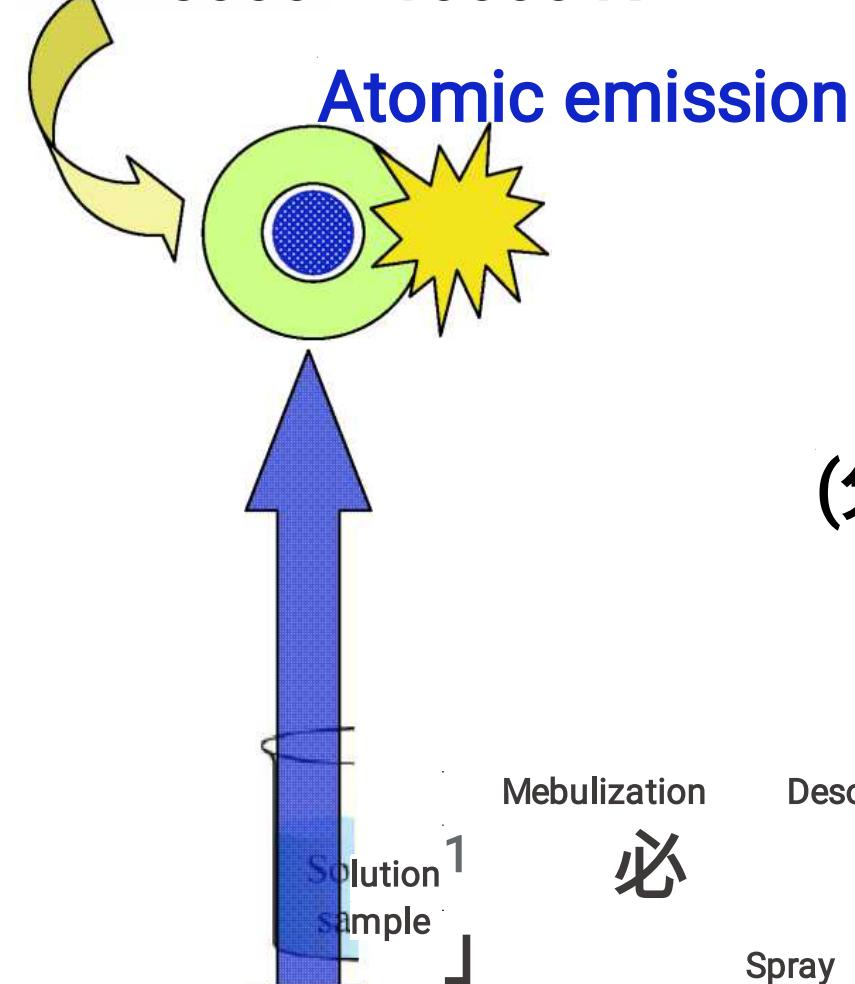


J.

Light source
hollow cathode lamp (中空陰極ランプ)

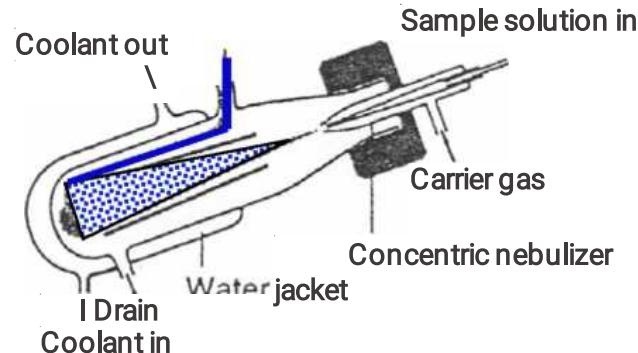
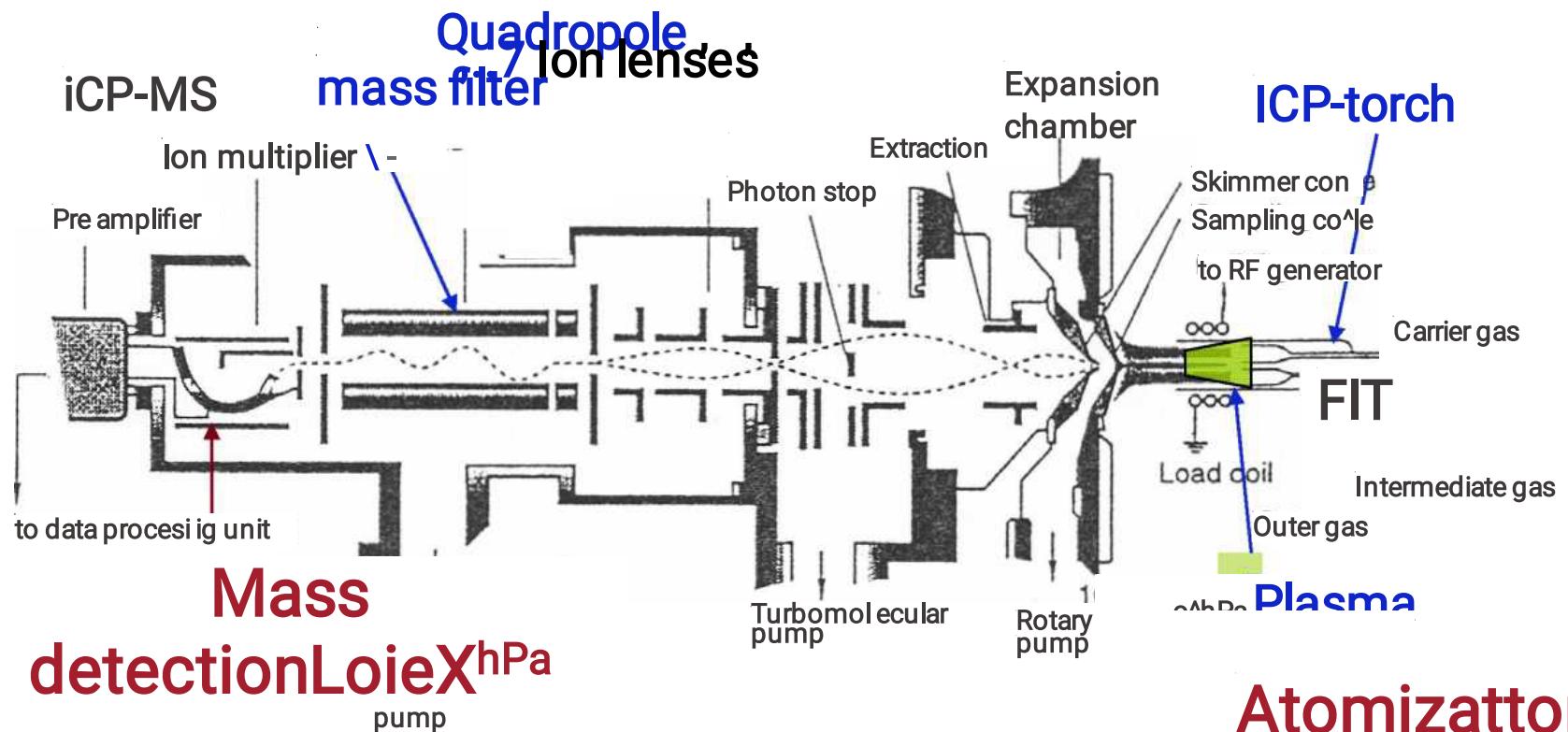
ICP-AES

Ar plasma (heating)
5000~10000 K



Sample ■ - solution:aqueous soln.

ICP-MS



Introduction to ICPM

What can ICP-MS do?

What can be measured:

- Almost all elements (Li-U) + radionuclides (only H,He,Ar, Ne, F cannot be measured)

How to measure:

- Elements are ionized, ions are filtered my mass (m/z), and ions are counted

What concentration:

- From ppm to ppt level in solution
- 1 ppm (part per million) = 1×10^{-6} Kg/L (= 1ng/L)
- 1 ppb (part per billion) = 1×10^{-9} Kg/L (= 1 ng/L)
- Ppt (part per trillion) = 1×10^{-12} Kg/L (= 1 ng/L)
- 1 ppq (part per quadrillion) = 1×10^{-15} Kg/L (= 1 pg/L)

Advantages of ICP-MS

- Excellent detection limits
 - low ppb - ppt for all elements
- Wide elemental coverage -
from
Li-U "
 - over 70 elements measurable
- High throughput
 - all elements determined simultaneously
 - 20 element nin/3 replicates/
 - Washout in 3 minutes
- Wide dynamic range
 - linear over 9 orders
- Powerful semi-quantitative analysis
 - no standards needed
- Isotopic analysis
 - isotope ratios
 - isotope dilution
- Routine technique
 - many users run systems overnight
- Small size
 - saves lab space
 - mobile installations

Applications

Trace contaminants in environmental samples

Semi-conductor reagents

Precious group elements

Radioactive contamination

Clinical analysis of trace elements

Lead and aluminium in food

Trace elements in foels - oil. coal. crudes

F inger-printing gold bars

Geological histoiy

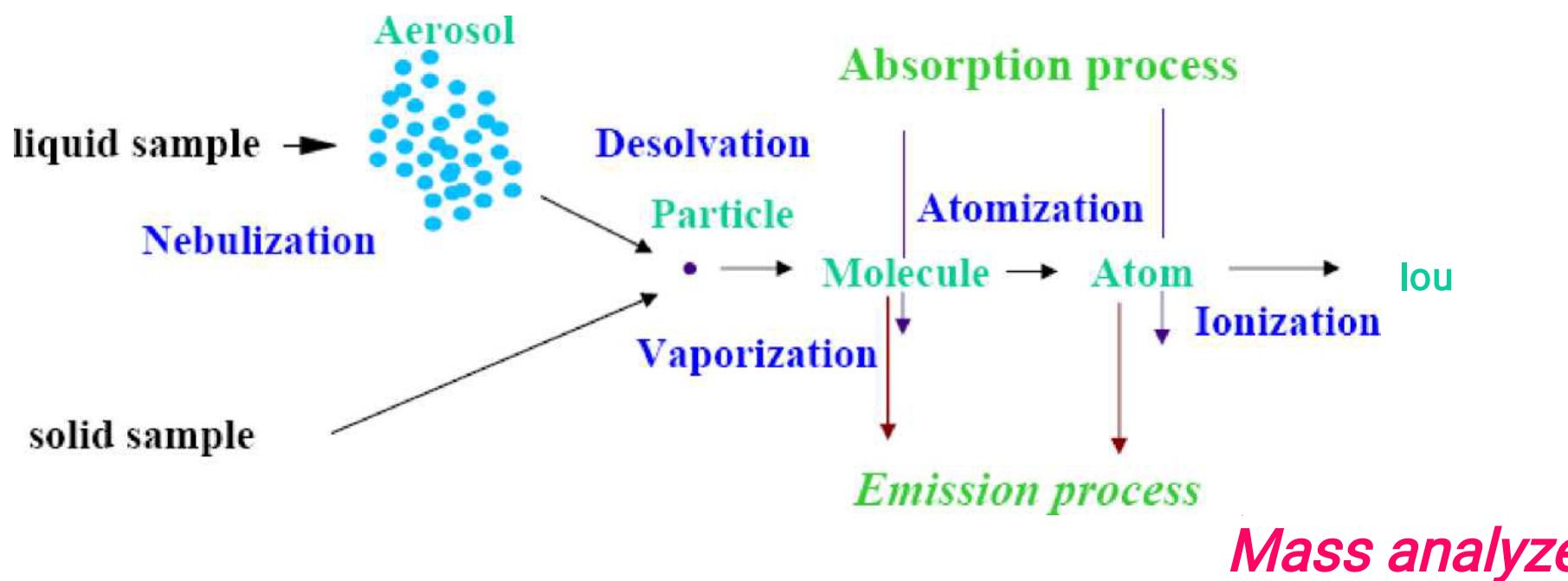
Forensic analysis - gunpowder residues, forgeiy

What is ICP-MS?

- Inorganic (elemental) analysis technique.
- ICP - Inductively Coupled Plasma
 - high temperature ion source
 - MS - Mass Spectrometer
 - quadrupole scanning spectrometer
 - mass range from 2 to 260 amu (Li to U...)
 - separates all elements in rapid sequential scan
 - ions measured using dual mode detector
 - ppt to ppm levels
 - isotopic information available

Processes in ICP Prior to MS Measurement

Nebulization Desolvation Vaporization Atomization Ionization



The Purpose of the Plasma

Ionization : Electron Loss (IC^AMS)

$|M|^{+} 4- e^{-}$

Excitation : Emission (iGP-OES)

t

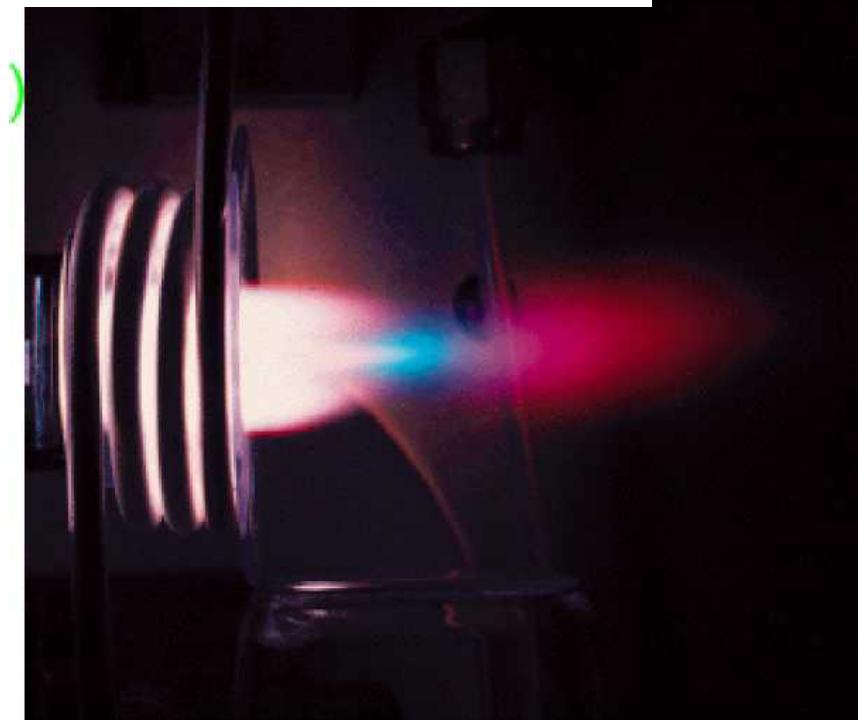
Atomization : Dissociation

t

Vaporization : Particles to gas

t

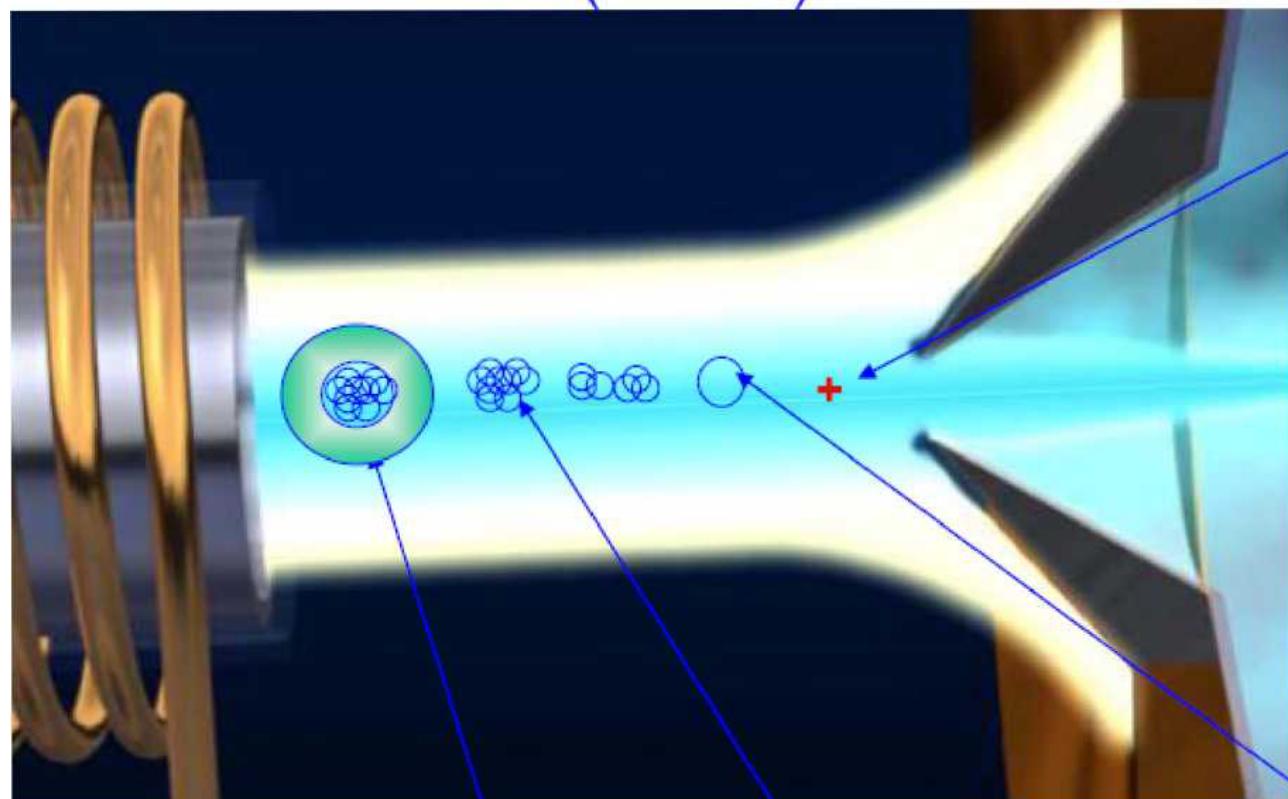
Desolvation : Drying Droplets



Sample Ionization in the Plasma

..... \rightarrow_f Sample channel

Residence time is a few milliseconds



Aerosol is Dried Particles are decomposed and dissociated

By sample cone, analytes present as M^+ ions

Highest M^+ population should correspond to the lowest polyatomic population

Atoms are formed and then ionised

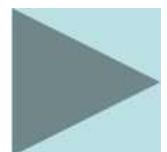
Interferences

• Spectroscopic interferences

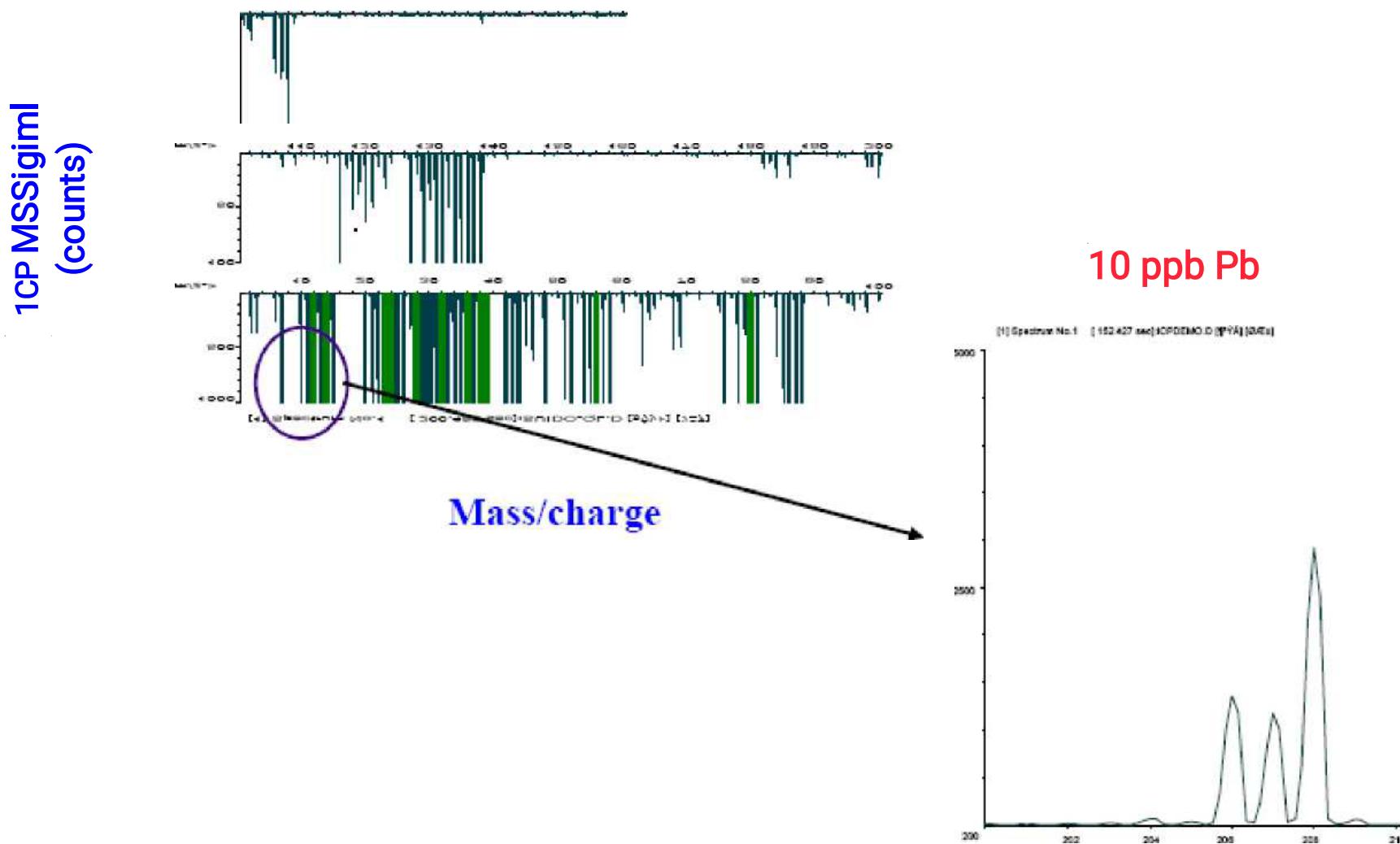
- $^{40}\text{Ar}^+$, $^{40}\text{Ca}^+$ determination of Ca using the next abundant isotope $^{44}\text{Ca}^+$ (2.1%).
- $^{58}\text{Ni}^+$, $^{58}\text{Fe}^+$ determination of Fe using $^{56}\text{Fe}^+$ isotope; correction can be made using the known natural abundance ratio of the isotopes.
- Polyatomic or adduct ions
- Formed from interactions between species in the plasma and species in the matrix or the atmosphere.
- Largely found at m/z values of <82.
- OH_2^+ (wZ : 18), O_2^+ (w^z 32), AlH^+ (w/Zz 40), ArO^+ (56), ArAr^+ (ni/z 80)
- Doubly charged ions
- e.g., Ar^{2+} ($//z/r$ 20).
- Refractory oxide ions
- Oxides and hydroxides could be formed from the analyte itself, the matrix components, the solvent, and the plasma gases.
- MO^* , MOH^* (M: analyte or matrix element).

Non-spectroscopic interferences

-Matrix effects

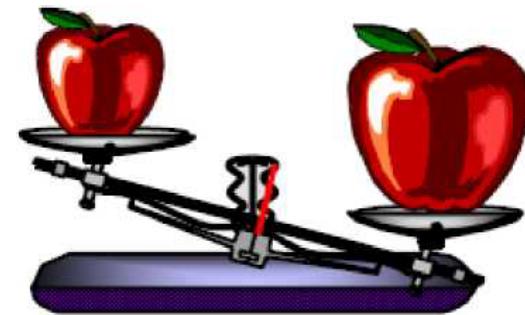


Typical ICP-MS Full Mass Spectrum



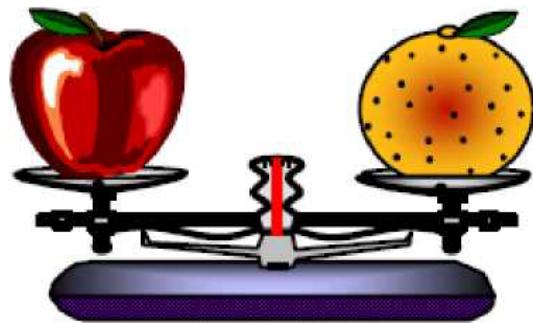
Isotopes and Isobars

Atomic number (number of protons) is the same, but number of neutrons is different (e.g. Pb204 & Pb 208) Chemical characteristics are same, but physical properties are different.



Isotopes

Isotopes Atomic number is different, but atomic weight is almost identical so species appear at same mass (e.g. Pb204 & Hg208). Chemical characteristics are different, but physical properties are similar.

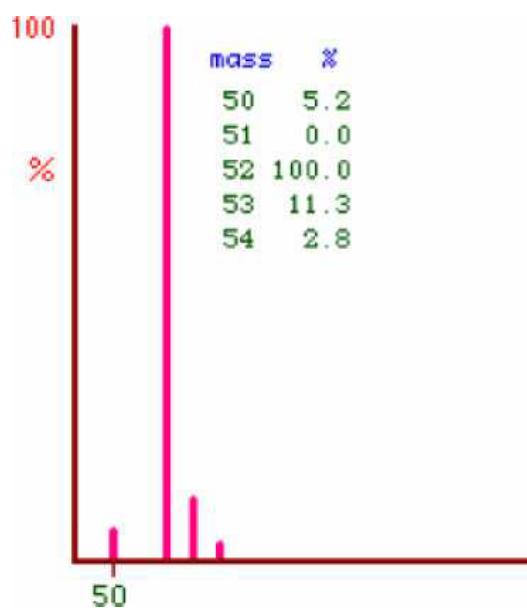


Isobars

Atomic structure of chromium isotopes

Web Elements

Isotope pattern of chromium



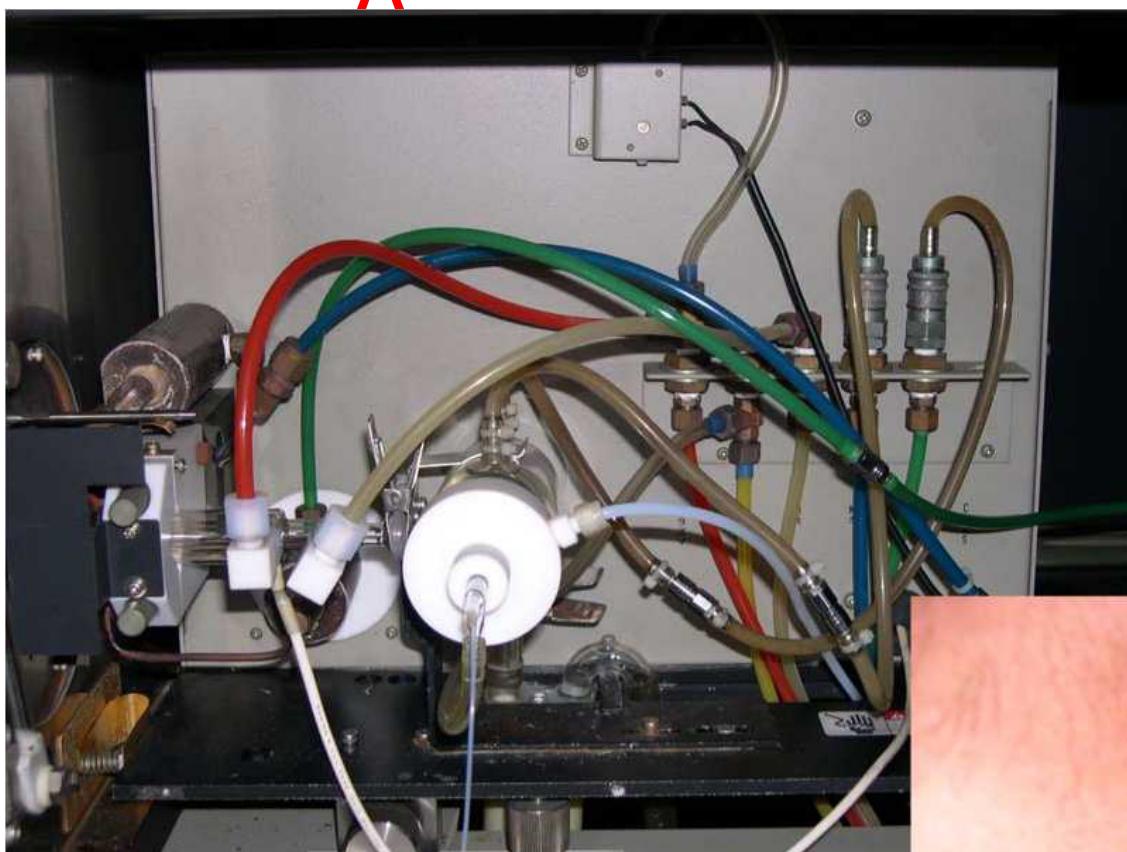
	^{60}Cr	^{62}Cr	^{63}Cr	^{64}Cr
Number of protons (p^+)	24	24	24	24
Number of electrons (e^-)	24	24	24	24
Number of neutrons (n)	26	28	29	30
Atomic mass ($p^+ + n$)	50	52	53	54
Atomic number (p^+)	24	24	24	24
Natural abundance	4.35%	83.79%	9.50%	2.37%

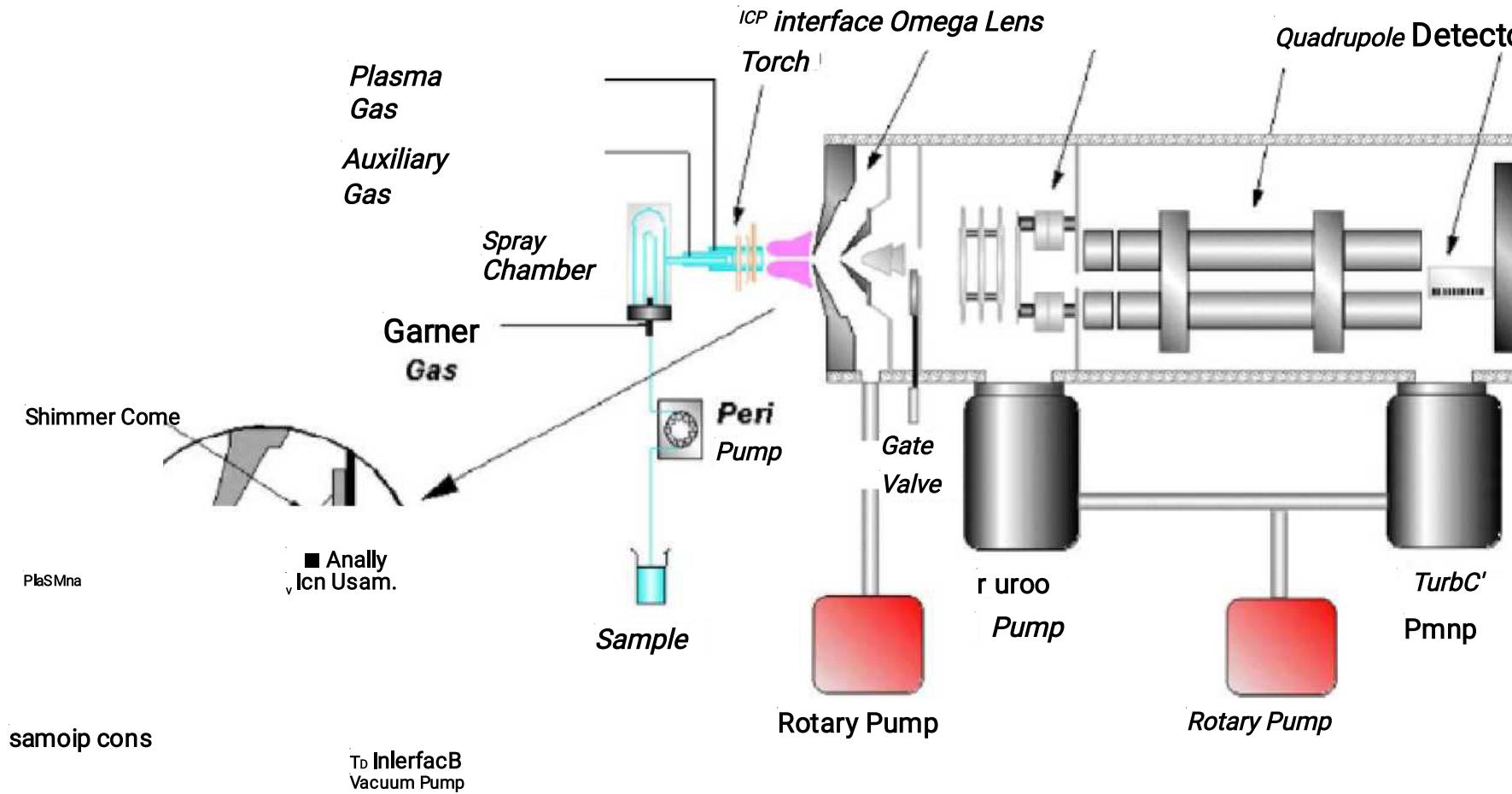
- Nominal atomic weight 51.996*
- * Calculated using the formulae $0.6917n + 0.3083/7 + p^+$ (referenced to the atomic weight of carbon)

Schematics Design (Instrumentation)

- Sample Introduction
- ICP (Inductively Coupled Plasma)
- Interface
- Ion Lens System
- Mass Filter
- Detector
- Vacuum System
- Control & Measurement Electronics







What is ICP-MS ?

2. The smallest droplets pass through the spray chamber and into the ion source - the plasma

4. Ions are extracted from the plasma by extraction lenses in the interface region

6. Ion lenses focus and collimate the ions. The Omega lens bends the ion beam off-axis to prevent photons from striking the detector

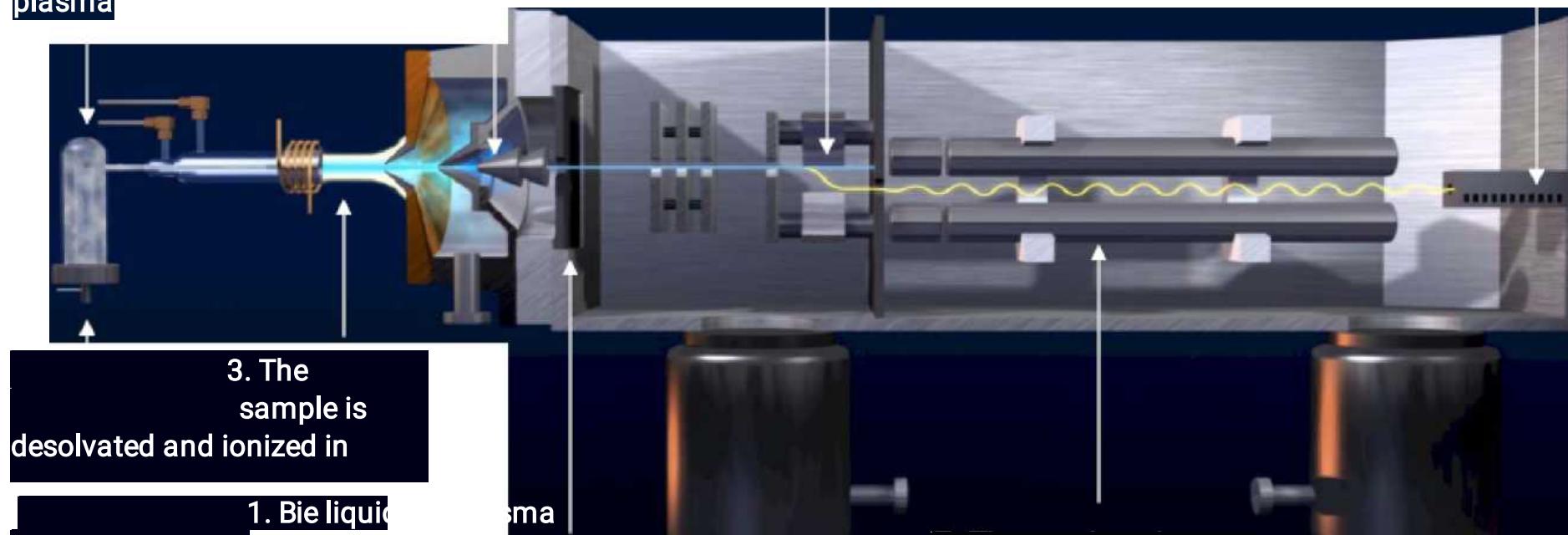
B. Ions are measured by a discrete dynode detector providing 9 orders of linear dynamic range

3. The sample is desolvated and ionized in

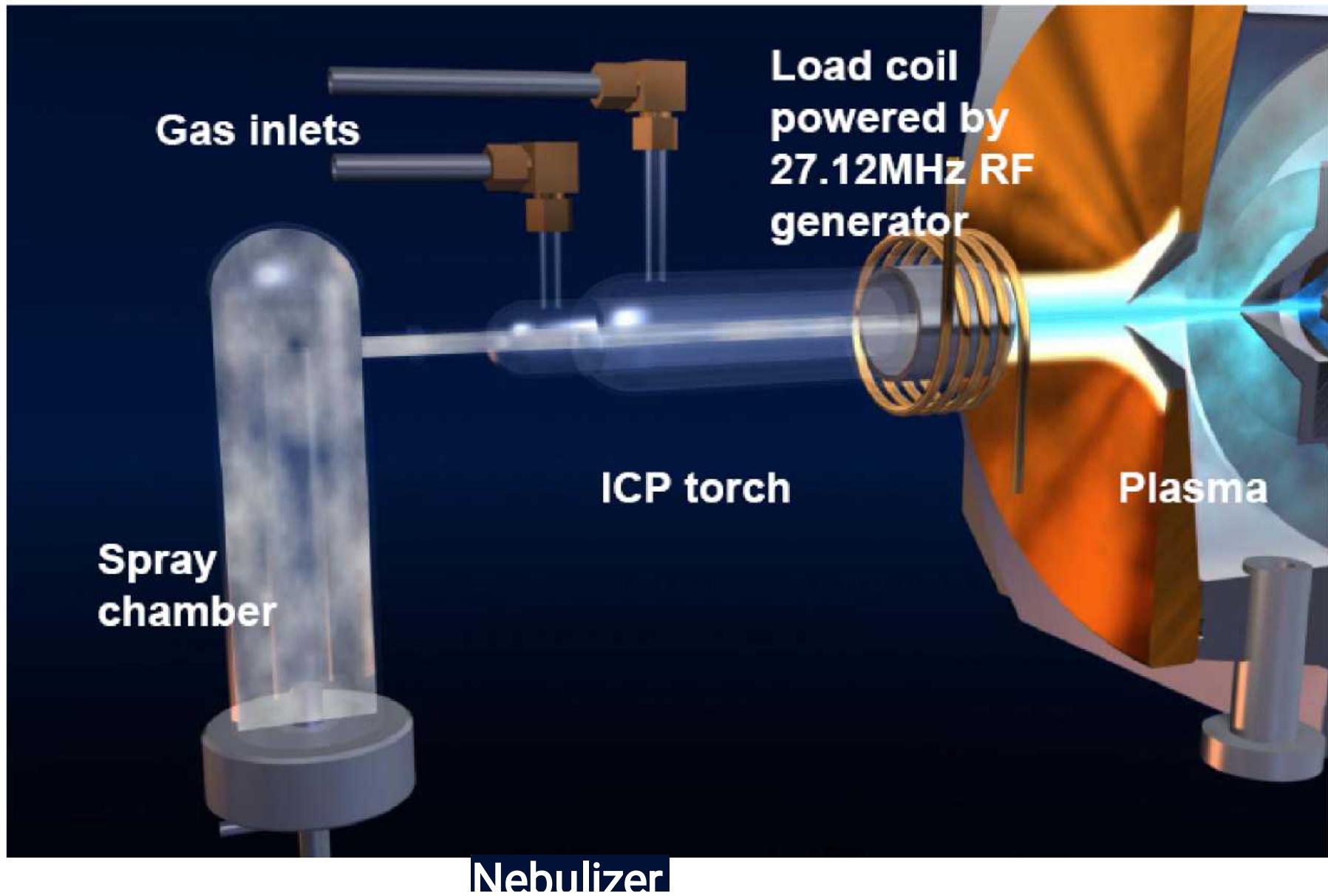
1. The sample is mixed with argon gas by the nebulizer to

5. An isolation valve separates the high vacuum region (spectrometer) from the sample introduction area to facilitate maintenance

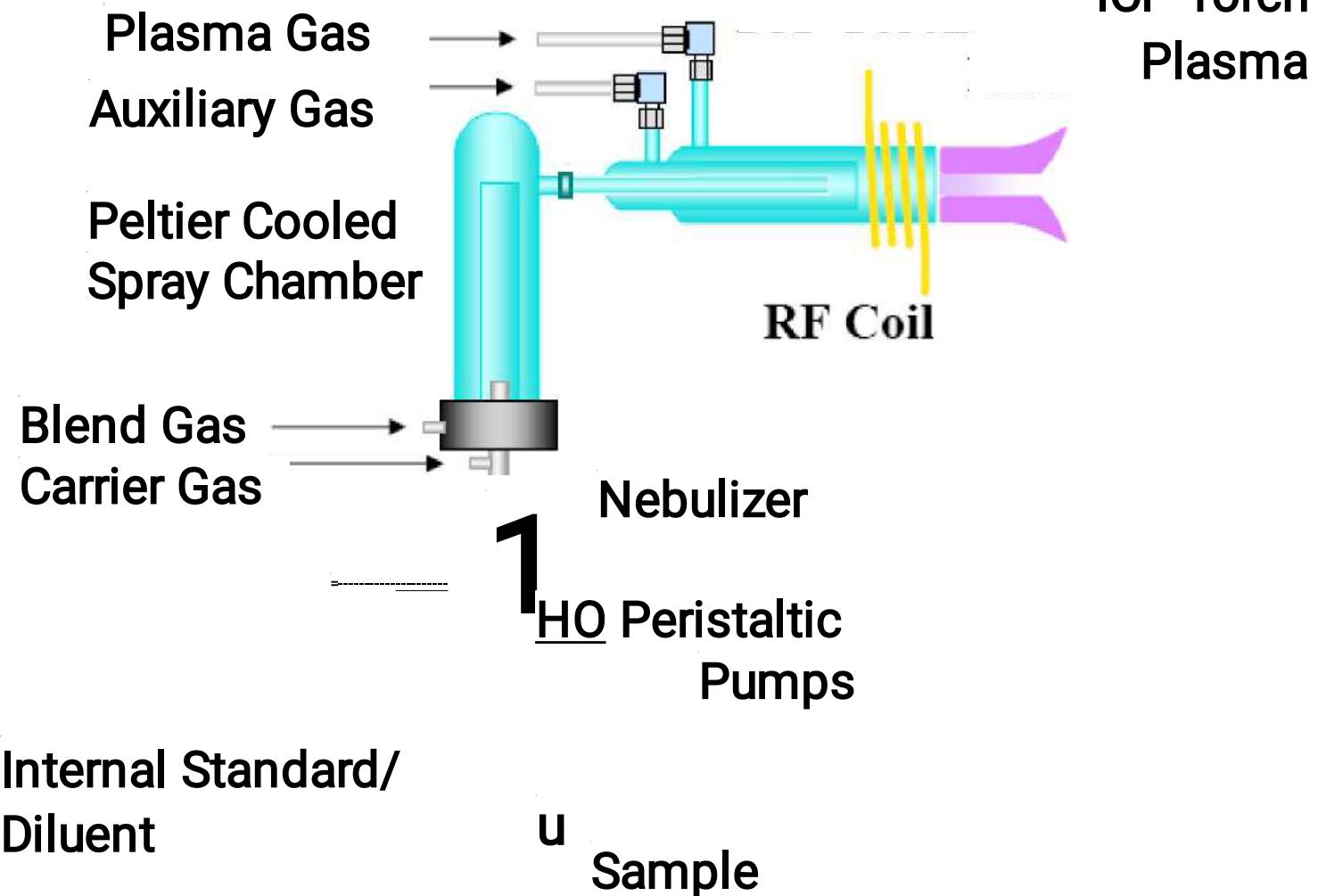
7. The quadrupole mass spectrometer separates ions based on their mass to charge ratio. The selected ions continue on to the detector



Sample Introduction

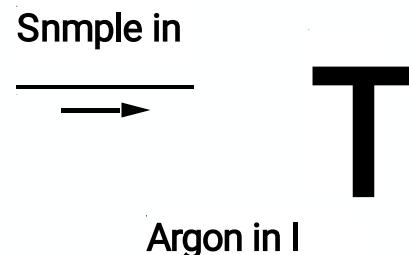


Sample Introduction System

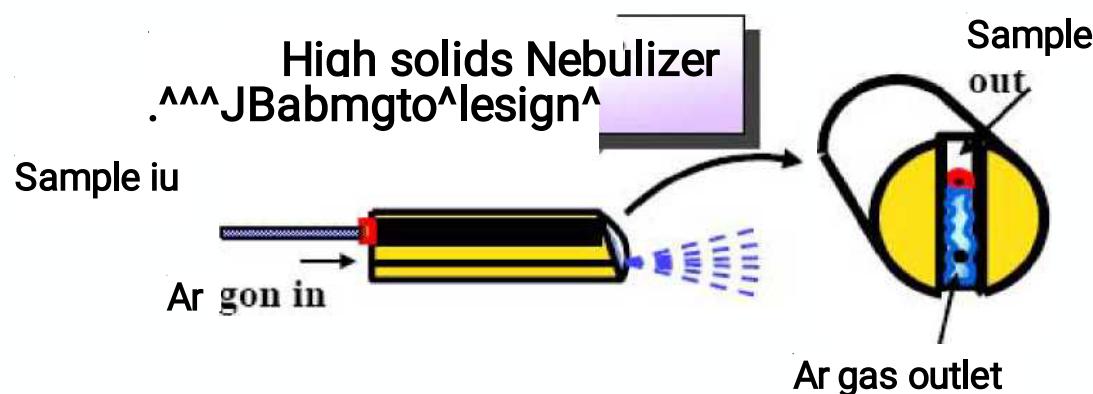


Typical Nebulizer

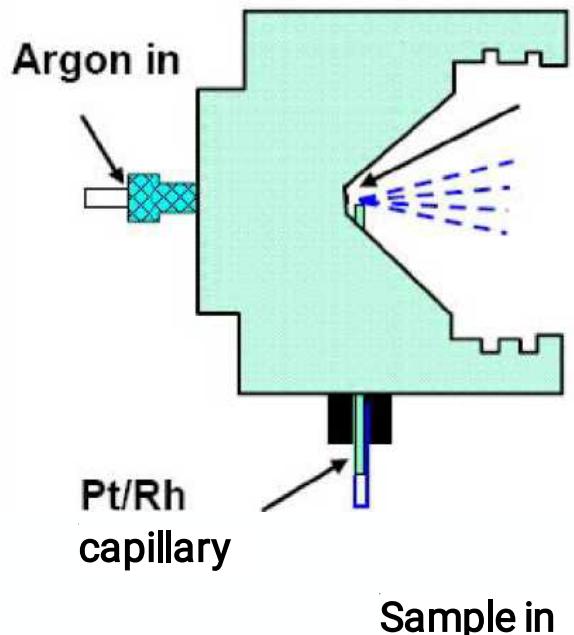
Concentric Nebulizer



Fine capillary - prone to blockages



Cross-flow Nebulizer



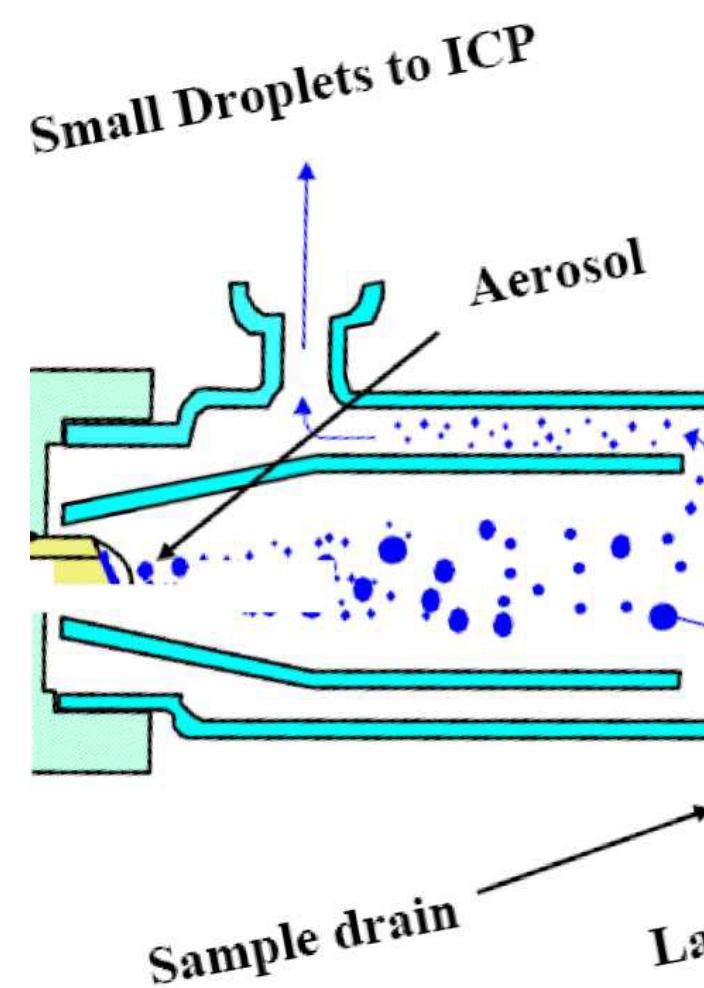
bet - DouUe ?aSS

CaR^{be}
wica\ SPva%_{CO}tvWe

Sample solution (High solids type)



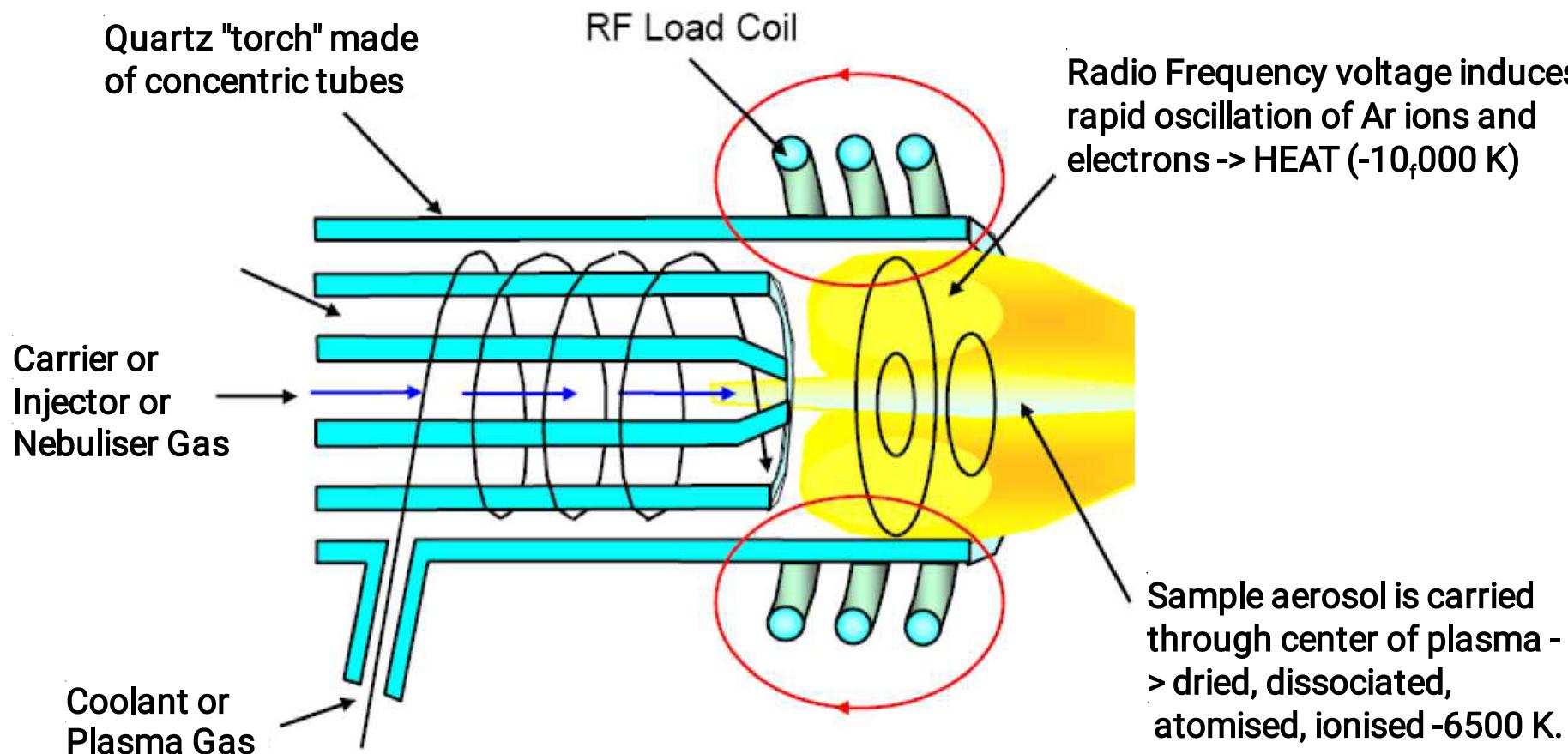
Ar carrier gas



Effect of Spray Chamber Cooling by Peltier Device

- Controls water vapor loading on plasma
- Decreased water load increases plasma temperature
 - Higher plasma temperature:
 - Improves ionization efficiency -> higher signal gives better matrix decomposition.
 - Decreased water load decreases polyatomic interferences
 - ArO, ArOH
 - Metal oxides (eg CaO interference on Fe, Ni, Co)*
 - Constant temperature improves signal stability

The Inductively-Coupled Plasma



Inductively-Coupled Plasma

Plasma is electrical discharge, not chemical flame:

- Ar gas used.
- Plasma at atmospheric pressure -> very high temperature (a low pressure plasma is a fluorescent lamp).
- Plasma is generated through inductive coupling of free electrons with rapidly oscillating magnetic field (27 MHz).
- Energy is transferred collisionally to argon molecules.
- Plasma is contained in gas flow in a quartz tube (torch).
- Sample aerosol is carried through the center of the plasma.
- Proximity to 10,000° C plasma causes dissociation, atomization and ionization.
- Ions are extracted into the spectrometer.

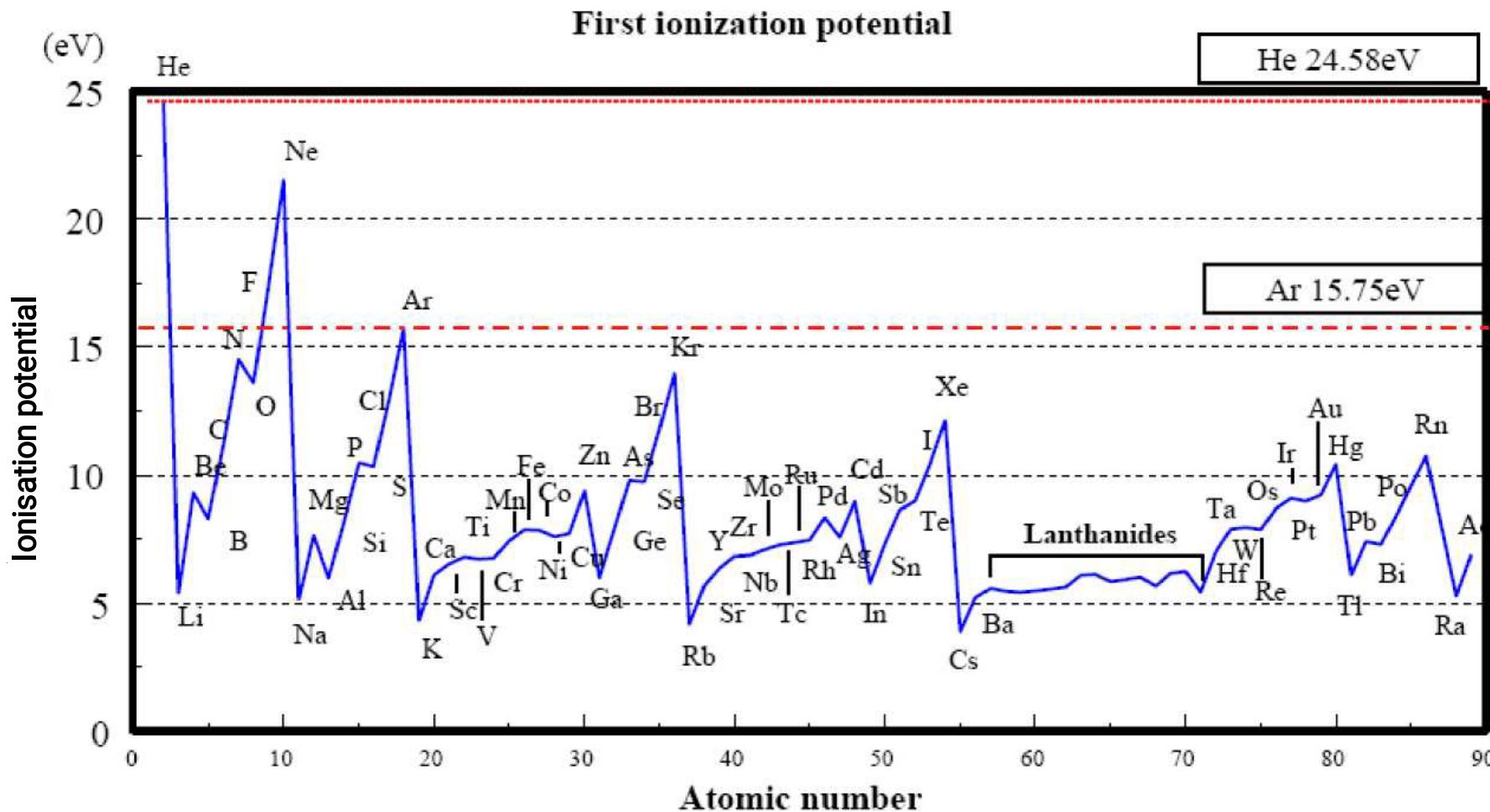
Why Use Argon Plasma?

- Ar is inert
- Ar is relatively inexpensive!
- Ar is easily obtained at very high purity

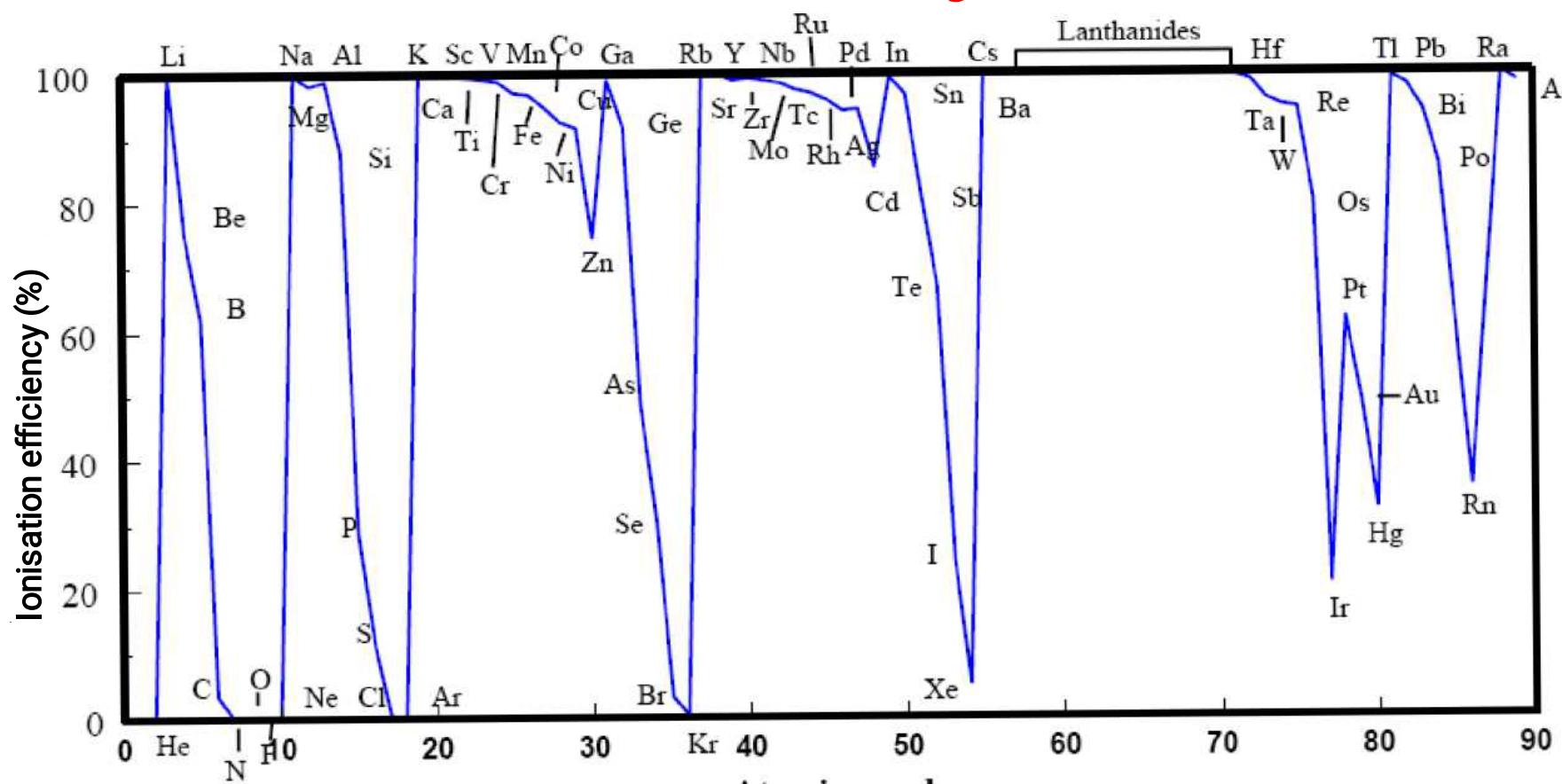
MOST IMPORTANTLY

- Ar has a 1st ionization potential of 15.75 electron volts (eV):
 - Higher than the 1st ionization potential of most other elements (except He, F, Ne) and,
 - Lower than the 2nd ionization potential of most other elements (except Ca, Sr, Ba, etc J.)
- Since the plasma ionization environment is defined by the Ar. most analyte elements are efficiently singly charged*

Ionization Potential of Elements



Ionization Efficiency of Elements



Electron temperature: 6680 K
Electron density: $1.47 \times 10^{14} \text{ cm}^{-3}$

Key Points about ICP-MS

- ICP-MS is a very high sensitivity elemental analyzer and chromatographic detector
- ICP-MS couples the ionization efficiency of Inductively-Coupled Argon Plasma with the detection capability of the quadrupole mass spectrometer
- ICP-MS can measure almost the entire periodic table at ppt to percent levels
- ICP-MS can provide isotopic information unlike other atomic spectroscopic techniques
- ICP-MS is fast, typical sample analysis time is under 5 minutes

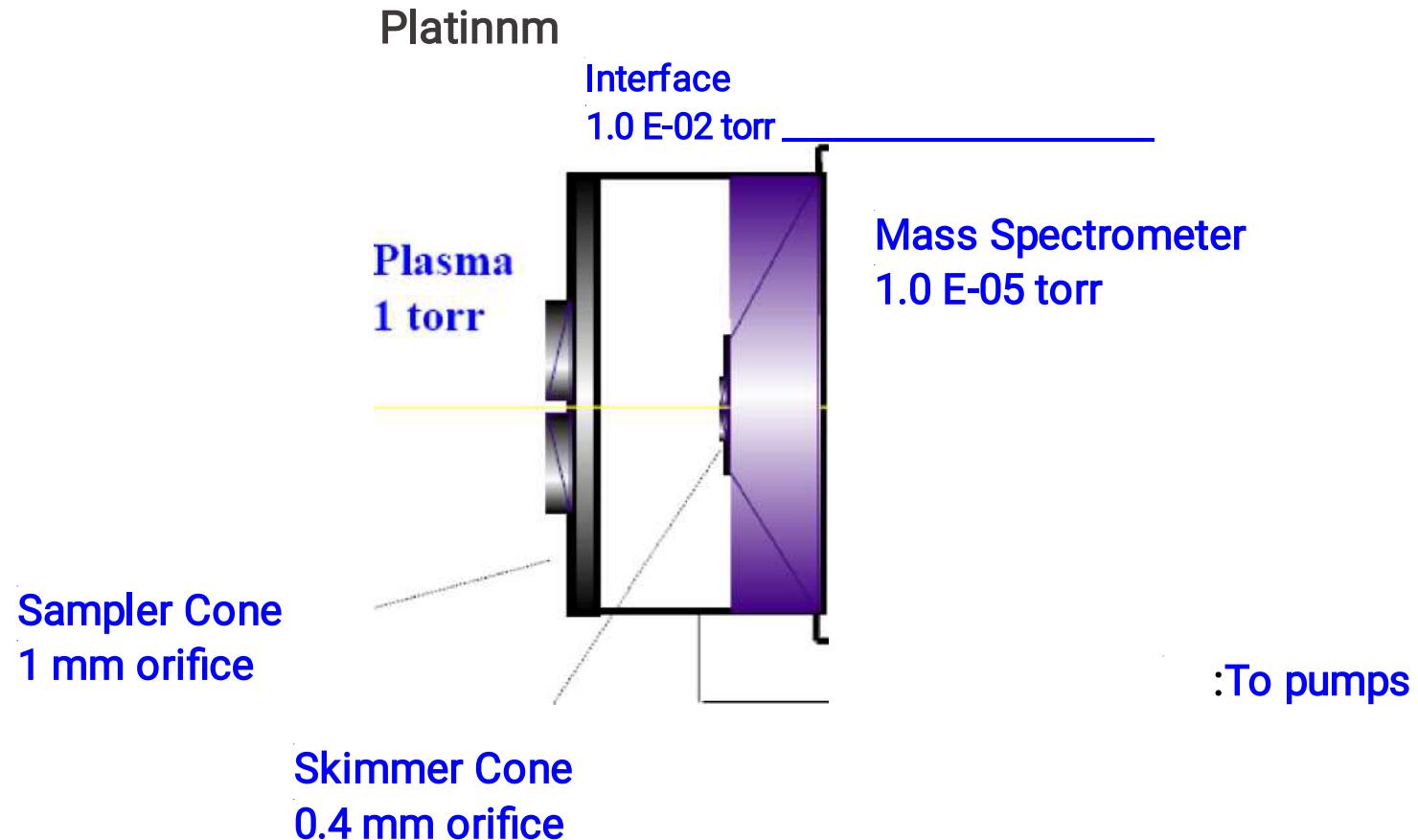
Interface

n Sampling cone

n Skimmer cone

Allows introduction of ions into the vacuum chamber

Material : Nickel



The Electrostatic Lenses

Ions, photons and neutrals all enter the spectrometer through the interface

the detector is sensitive to photons/neutrals, as well as ions Ions are charged particles

can be deflected using electric fields
Photons travel in straight lines

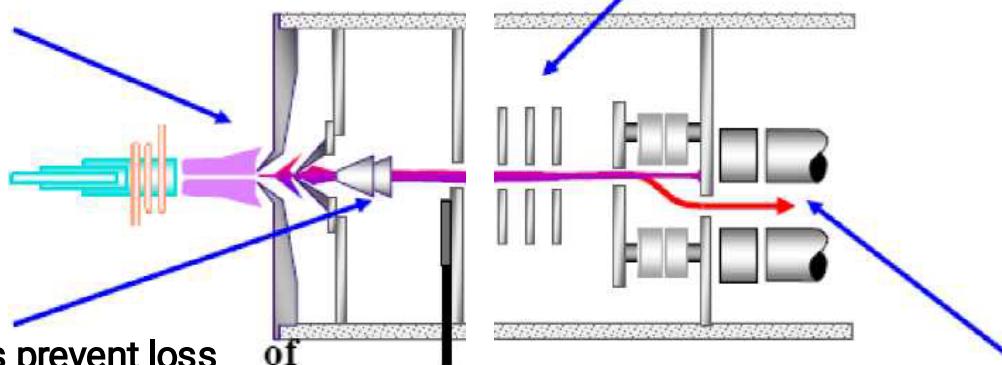
If ions can be deflected off-axis, they will be separated from non-charged species (photons/neutrals)

must ensure that mass bias is not introduced when ions are deflected

High Transmission Off-Axis System

Lower sample uptake rate (0.3mL/min), larger injector tube (2.5mm), higher temp plasma (27MHz), variable sample depth & small cone orifices (1.0/0.4mm) - efficient matrix deposition

Compound ion lenses - efficient focusing, high transmission across the mass range



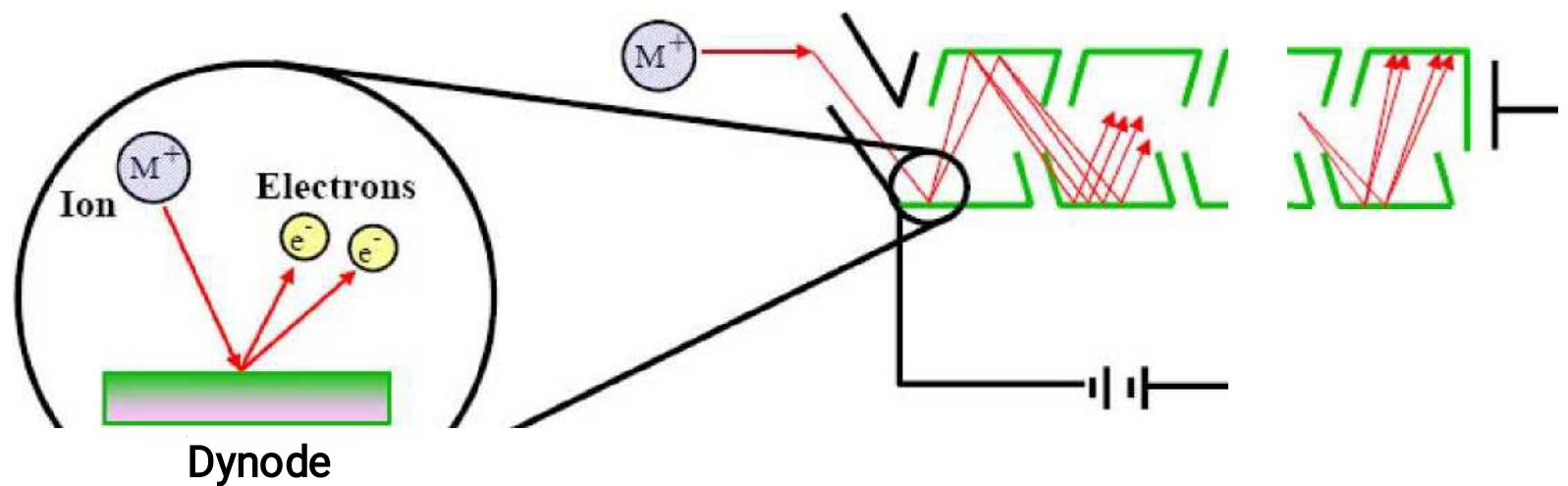
Dual extraction lenses prevent loss of low mass ions exit from interface. Also serve to protect main ion lenses by trapping sample matrix.

Photons and neutrals removed - ions are deflected off axis into quadrupole with minimal mass bias

High transmission - sensitivity maintained with less sample loading on system - lower sample uptake, small interface orifices and larger diameter torch injector. Results in much less frequent ion lens cleaning and extended interface rotary pump oil lifetime.

The Detector

Electron multiplier
discrete dynode detector (ETP)
each dynode gives "cascade" of
electrons -> signal is multiplied



Collision Unit

- Inert Gas (H_2 , He, Xe, NH_3) is added to Ion clusters
 - Inert Gas reacts with the molecular interferent
- ${}^3\text{S}\text{ArH} + \text{H}_2 \rightarrow \text{H}_3 + \text{Ar}$
- But not the analyte ion
- ${}^{39}\text{K} + \text{H}_2 \rightarrow {}^{39}\text{K} + \text{H}_2$
 - (no reaction)
- Collision Reaction Cell then 'mass filters' the ion of interest from the byproducts of reaction

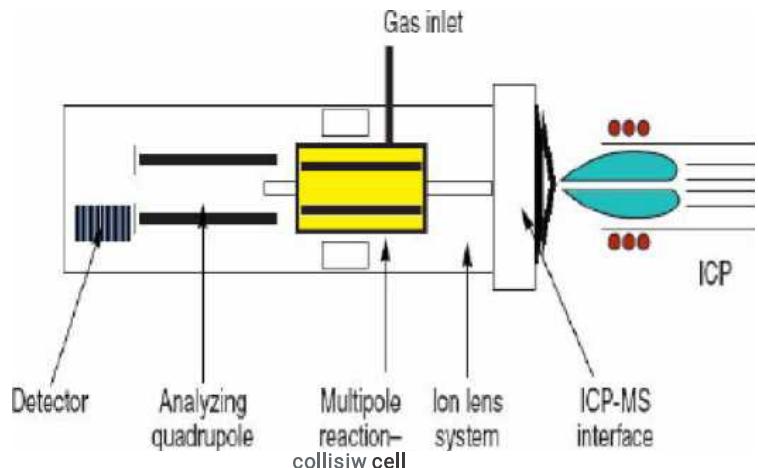
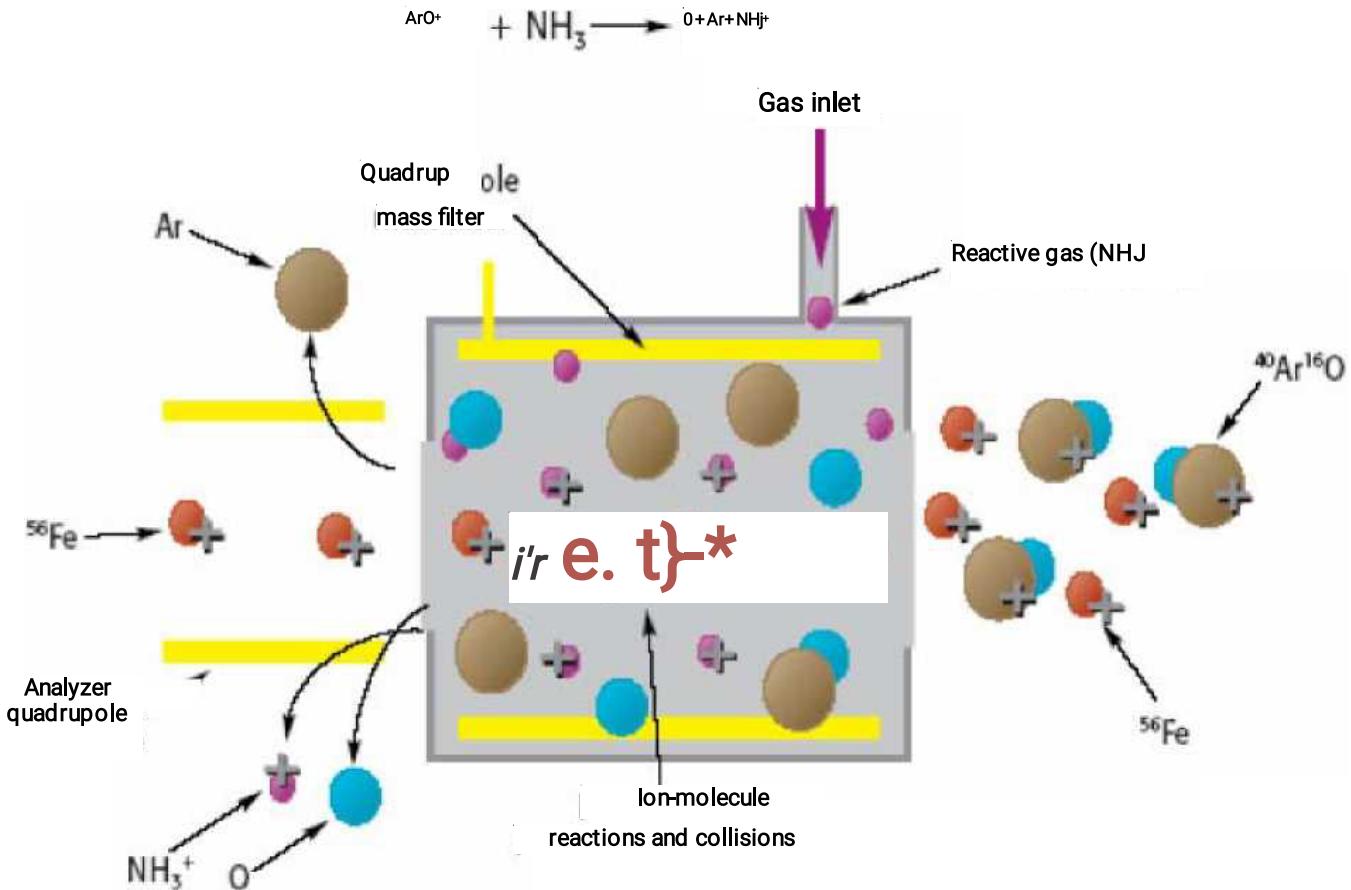


Figure 1. Layout of a typical collision/reaction cell instrument.



Elimination of the ArO interference with a dynamic reaction cell.

Applications of ICP-MS

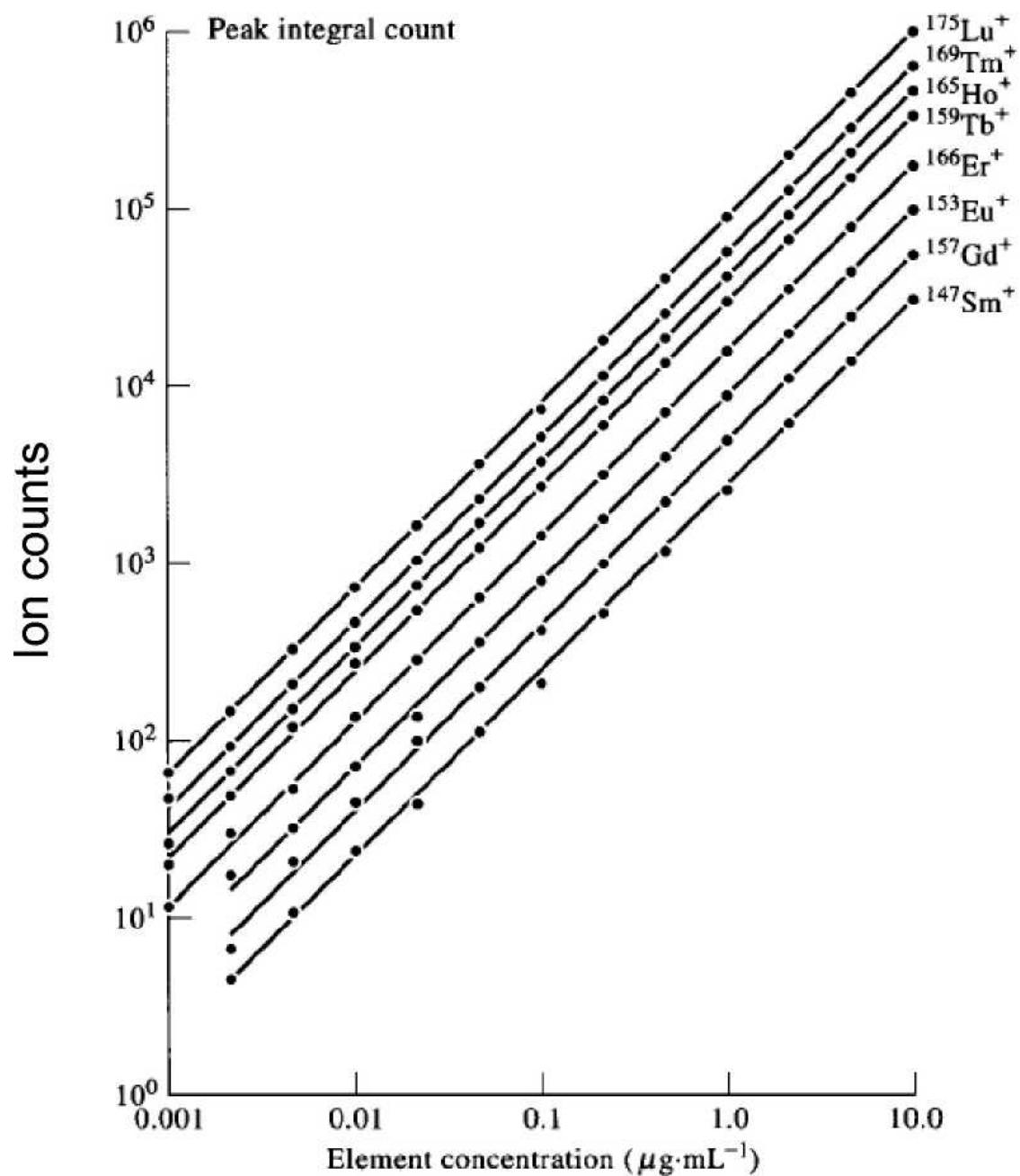
Qualitative and Semi-quantitative Analysis

1. Easily be adapted to multi-element analysis.
2. The semi-quantitative analysis for one or more of the components in a mixture can be achieved by comparing the peak intensity to the one with known concentration.

Quantitative Analysis

1. Use a set of calibration standards for preparing a calibration curve. The linear relationship between peak count and concentration can be 4 to 6 orders of concentration.
2. Internal standard: an element that is absent from the samples and that has an atomic mass and ionization potential near those of the analytes (hadium and rodium are often used as IS since they are infrequently found naturally in samples).
3. Isotope dilution method may be employed for more accurate quantitative analysis, (addition of a known quantity of a standard solution that is enriched in one of the isotopes.)

Isotope Ratio Measurements



ICPMS calibration
curves for several
rare earth
elements.

Application of ICP-MS (Some examples)

Table 2 Analytical results for trace elements in several nitric acids by ICP-MS

Element	m/z	Supplier A		Supplier B	
		Ultra ^a /	Trace ^b /	Anal ^c /	Extra ^d /
		ng mL ⁻¹	ng mL ⁻¹	ng mL ⁻¹	ng mL ⁻¹
Li	7	0.000	0.000	0.001	0.001
Be	9	0.000	0.000	0.000	0.000
Na	11	0.57	1.72	1.16	0.82
Mg	23	0.026	0.077	0.094	0.47
	24	0.073	0.061	0.066	0.28
Al	27	0.027	0.017	0.012	0.031
K	39	0.033	0.36	0.34	0.63
Ca	43	0.66	1.19	0.88	0.78
Sc	45	0.002	0.001	0.003	0.002
Ti	49	0.03	0.07	0.03	0.02
V	51	0.15	0.096	0.17	0.087
Cr	52	0.018	0.12	0.036	0.036
Mn	55	0.050	0.064	0.060	0.24
Fe	57	0.001	0.075	0.043	0.048
Co	59	0.004	0.003	0.015	0.005
Ni	60	0.039	0.061	0.033	0.127
Cu	63	0.24	1.33	0.12	0.32
Zn	66	0.21	0.11	0.14	0.18
Ga	69	0.007	0.005	0.007	0.006
Ge	74	0.000	0.002	0.001	0.001
As	75	0.013	0.012	0.007	0.006
Se	82	0.028	0.006	0.048	0.004
Rb	85	0.006	0.003	0.004	0.002
Sr	88	0.003	0.003	0.004	0.021
Y	89	0.007	0.011	0.011	0.007
Zr	90	0.001	0.002	0.001	0.001
Nb	93	0.005	0.000	0.005	0.001
Mo	98	1.08	5.82	41.7	1.09
Ru	102	0.002	0.000	0.004	0.000
Rh	103	0.001	0.000	0.000	0.000
Pd	106	0.008	0.006	0.044	0.008
Ag	107	0.11	0.089	408.7	0.17
Cd	114	0.019	0.071	0.53	0.015
In	115	0.001	0.001	0.002	0.003
Sn	118	0.023	0.036	0.031	0.059
Sb	121	0.003	0.005	0.010	0.010
Te	130	0.012	0.058	0.47	0.015
Cs	133	0.000	0.000	0.001	0.000
Ba	138	0.012	0.015	0.014	0.027
La	139	0.005	0.048	0.078	0.29
Ce	140	0.12	0.31	3.99	0.12
Pr	141	0.008	0.14	0.061	0.000
Nd	146	0.000	0.058	4.05	0.000
Eu	151	0.001	0.002	0.008	0.010
Sm	152	0.001	0.000	0.010	0.010
Gd	157	0.000	0.002	0.013	0.008
Tb	159	0.005	0.005	0.020	0.002
Dy	163	0.000	0.000	0.042	0.000
Ho	165	0.000	0.011	0.000	0.000
Er	167	0.000	0.000	0.000	0.000
Tm	169	0.002	0.002	0.006	0.002
Yb	174	0.000	0.000	0.000	0.000
Lu	175	0.000	0.000	0.004	0.004
	180	0.001	0.000	0.000	0.004
	181	0.000	0.000	0.000	0.000
	184	0.000	0.000	0.26	0.039
	195	0.001	0.007	0.010	0.002
Au	197	0.003	0.009	0.008	0.023
Hg	202	0.000	0.000	2.4	0.014
Tl	205	0.000	0.000	0.009	0.000
Pb	209	0.003	0.011	0.008	0.056

Synthesis of cross-linked chitosan possessing JV-methyl-D-glucamine moiety (CCTS-NMDG) for adsorption/concentration of boron in water samples and its accurate measurement by ICP-MS and ICP-AES

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Abstract

A chitosan resin derivatized with α -methyl-D-glucamine (CCTS-NMDG) was synthesized by using a cross-linked chitosan (CCTS) as base material. The α -methyl-D-glucamine (NMDG) moiety was attached to the amino group of CCTS through the amine of chloromethyl oxime. The adsorption behavior of 59 elements on the synthesized resin was systematically examined by using the resin packed in a mini-column, passing water samples through it and measuring the adsorbed elements in eluates by ICP-MS. The CCTS-NMDG resin shows high ability in boron sorption with the capacity of $0.61 \text{ mmol mL}^{-1}$ ($=2.1 \text{ mmol g}^{-1}$). The sorption kinetics of this resin was faster than that of the commercially available resins. Other advantages of the synthesized resin are: (1) quantitative collection of boron at neutral pH regions; (2) complete removal of large amounts of matrices; (3) no loss of efficiency over prolonged usage; (4) effective collection of boron in wide range concentration using a mini column containing 1 mL resin; (5) complete elution of boron with 1 mol L $^{-1}$ nitric acid. The resin was applied to the collection concentration of boron in water samples. Boron in tap water and river water was found to be in the range of $6-8 \text{ \mu g L}^{-1}$. The limit of detection (LOD) of boron after pretreatment with CCTS-NMDG resin and measurement by ICP-MS was $0.07 \text{ \mu g L}^{-1}$ and the limit of quantification (LOQ) was $0.14 \text{ \mu g L}^{-1}$ when the volume of each sample and eluent was 10 mL.

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Synthesis of chitosan resin possessing 3,4-diamino benzoic acid moiety for the collection/concentration of arsenic and selenium in water samples and their measurement by inductively coupled plasma-mass spectrometry

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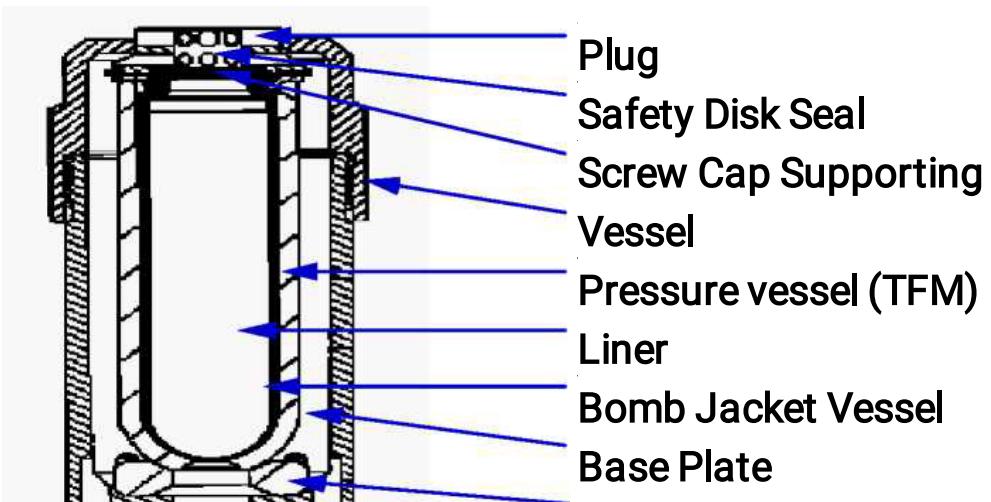
Abstract

A chitosan resin functionalized with 3,4-diamino benzoic acid (CCTS-DBA resin) was newly synthesized by using a cross-linked chitosan (CCTS) as base material. The adsorption behavior of trace amounts of elements on the CCTS-DBA resin was examined by the pretreatment with a mini-column and measurement of the elements by inductively coupled plasma-Mass spectrometry (ICP-MS). Arsenic(V) could be retained on the CCTS-DBA resin at pH 3 as an oxoanion of $H_2AsO_4^-$. Selenium(VI) is strongly adsorbed at pH 2 and pH 3 as an oxoanion of SeO_4^{2-} , while selenium(IV) as $HSeO_3^-$ is adsorbed on the resin at pH 3. The sorption capacities are 82, 64, and 88 mg g⁻¹ resin for As(V), Se(IV), and Se(VI), respectively. The effect of common anions and cations on the adsorption of As(V), Se(IV), and Se(VI) were studied: there was no interference from such anionic matrices as chloride, sulfate, phosphate, and nitrate up to 20 ppm, as well as from such artificial river water matrices as Na, K, Mg, and Ca after passing samples through the mini-column containing the resin. The CCTS-DBA resin was applied to the collection of arsenic and selenium species in bottled drinking water, tap water, and river water.

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Solid samples

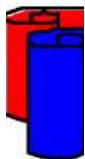
Acid digestion apparatus: microwave system



Microwave sample preparation system
MULTIWAVE (Anton Paar GmbH)

Analytical results of peach leaves

Element	Mass number	Measured value (mg/Kg)	Certified value (mg/Kg)
La	139	8.99	(9)
Ce	140	9.88	(10)
Pr	141	1.21	
Nd	146	6.76	(7)
Sm	147	0.926	(1)
Eu	151	0.142	(0.17)
Gd	157	1.15	(1)
Tb	159	0.0890	
Dy	163	0.305	
Ho	165	0.0553	
Er	167	0.170	
Tm	169	0.0143	
Yb	172	0.112	
Lu	175	0.0117	



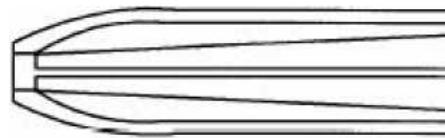
Analytical results for REEs in NIES No.2 sediment sample

Element	m/z	Direct ^{*1}		Column ^{*1}		(Mg g ⁻¹)	(Mg g ⁻¹)
		(ng g ⁻¹)	g	(M g ⁻¹)	g		
Y	89	11.7	0.19	10.4	1.3	0.53	9.45
La	139	8.06	0.25	7.21	0.90	0.04	7.06
Ce	140	14.2	0.79	13.5	1.7	0.69	13.2
Pr	141	1.66	0.07	1.63	0.22	0.03	1.69
Nd	146	6.72	0.20	6.15	0.87	0.18	6.02
Sm	147	1.30	0.02	1.17	0.16	0.03	1.19
Eu	151	0.43	0.01	0.43	0.05	0.01	0.48
Gd	157	1.27	0.01	1.25	0.23	0.03	1.21
Tb	159	0.20	0.00	0.19	0.09	0.02	0.20
Dy	163	1.31	0.04	1.21	0.17	0.03	1.23
Ho	165	0.29	0.00	0.29	0.05	0.01	0.32
Er	167	0.81	0.06	0.76	0.10	0.03	0.81
Tm	169	0.11	0.01	0.10	0.03	0.01	0.12
Yb	172	0.80	0.03	0.79	0.12	0.03	0.80
Lu	175	0.11	0.01	0.11	0.03	0.01	0.10

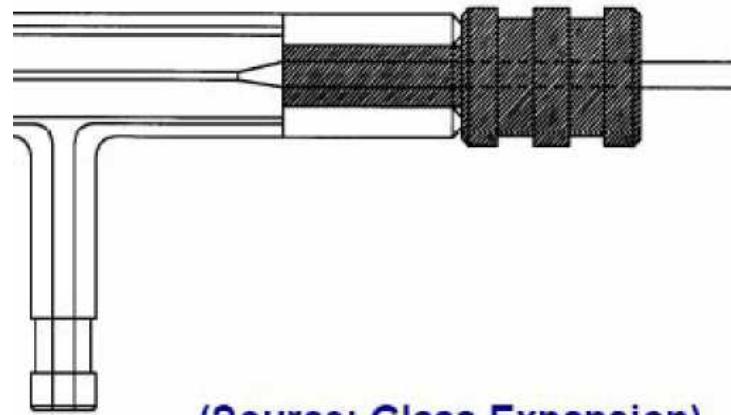
*1 : 0.2 g sample with **HNO₃ (5 ml) + HF (1 ml)** (2500-fold dilution, n=3).

*2 : 0.2 g sample with **HNO₃ (5 ml) + HF (1 ml) + HCl (1 ml)** (2500-fold dilution)

ICP-OES: Concentric (Meinhard) Nebulizer



Self aspirating
■ but use pump to avoid
matrix effects Clogs easily

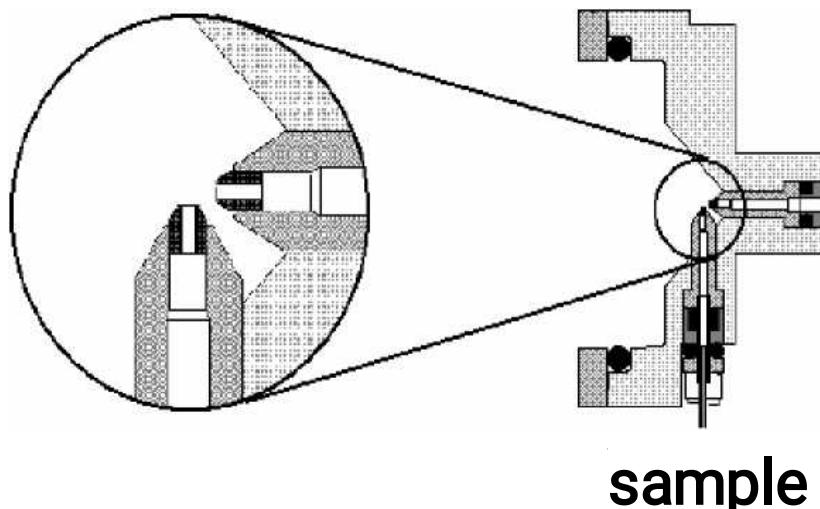


(Source: Glass Expansion)

- Filter sample before aspirating
- Only for dilute solutions
- ◆ Type A: use only for clean solutions
- ◆ Type C: for high salt content
- ◆ Type K: same as type C but with smoothed surfaces

- Insert for cyclonic spray chamber

Cross Flow Nebulizer



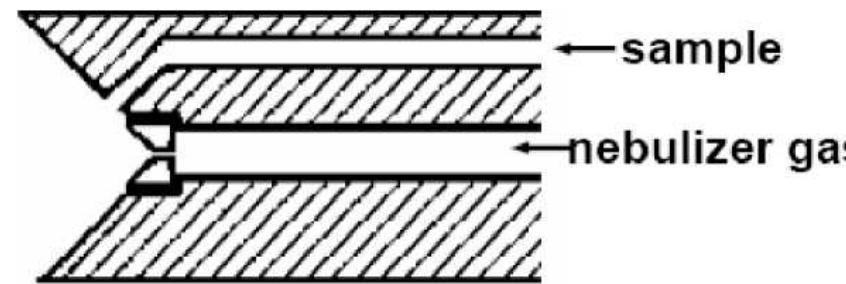
- universal nebulizer
- suitable for most matrices
 - high concentrations, Ar even small particles
- resistant against HF

■ PEEK
■ Aluminum oxide

- good detection limits
- used in combination with Scott spray chamber

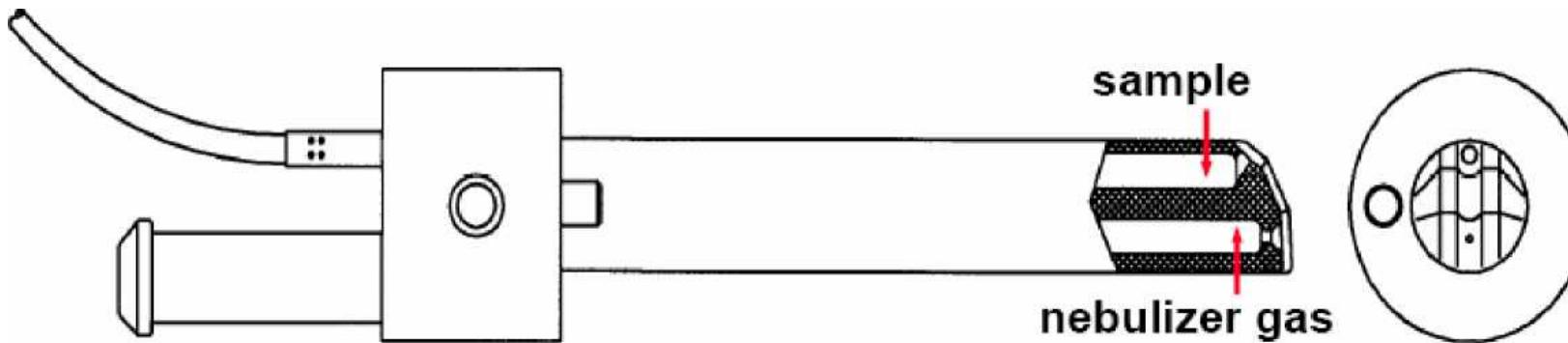
Sharp (ConeSpray)-Nebulizer

- high matrix concentrations
- small particles
- best reproducibility with higher pump rates (2 to 4 mL/min); good results also with 1 mL/min
- Insert for cyclonic nebulizer chamber



The orifice of the nebulizer gas nozzle is formed like a symmetric crater

ICP-OES: V-groove Nebulizer

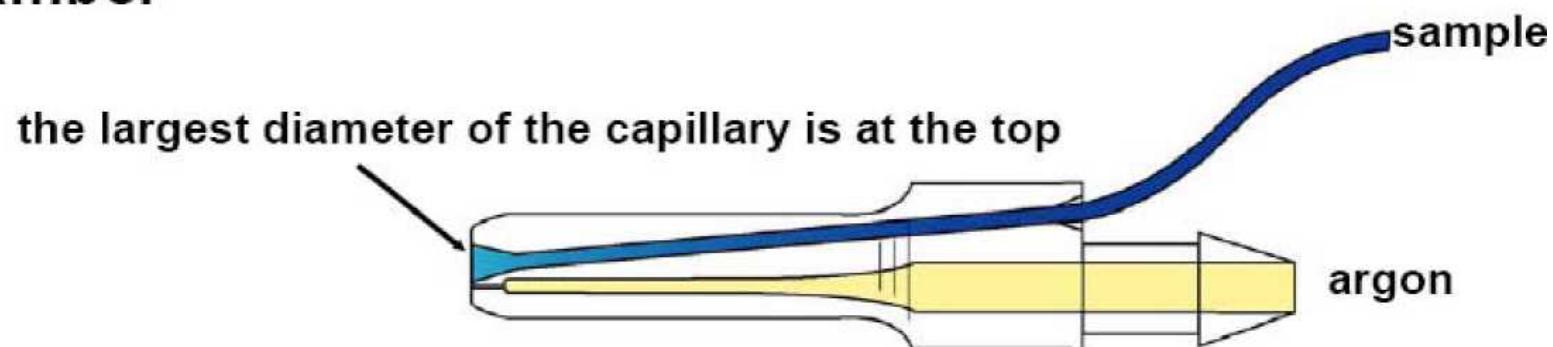


(Source: Glass Expansion)

- for high load of dissolved content
- for small particles
- best reproducibility with higher pump rate
 - however, difference in performance is negligible
- insert for cyclonic spray chamber

Burgener Nebulizer

- for high matrix concentrations
- for small particles
- insert for cyclonic spray chamber



(source: Thermo Elemental)

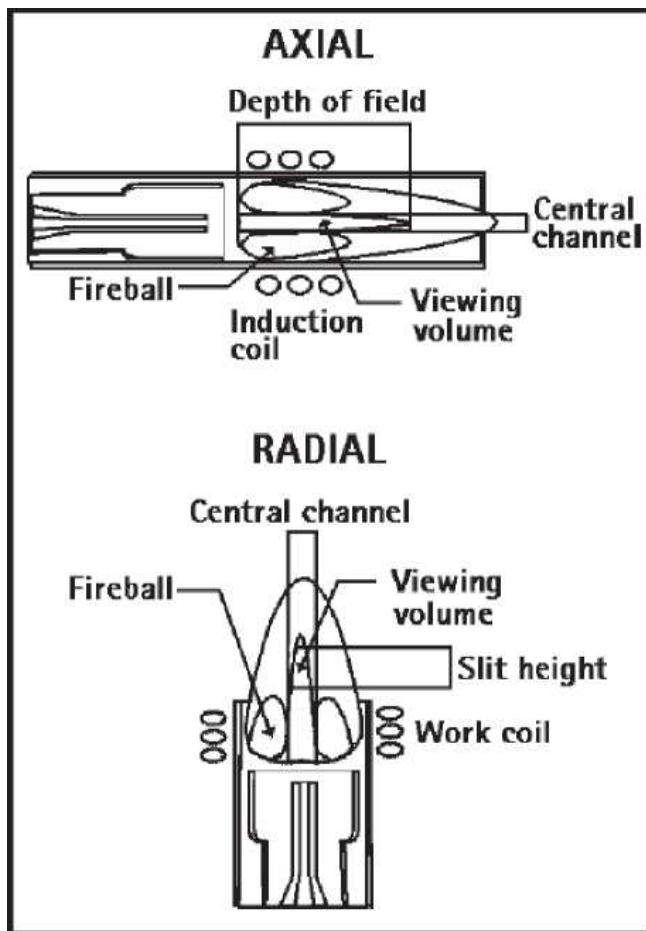


Figure 1. Schematic diagram of radial and axially viewed plasma systems, note the three concentric tubes of the torches, the vertical orientation and side viewing of the 'radial' torch and the horizontal orientation and end-on viewing of the 'axial' torch.

Element	Wavelength [nm)	3cr Detection Limits		Improvement Factor
		Vista-PRO Radial [ug/L]	Vista-PRO Axial [ug/L]	
Ag	328.068	1	0.3	3.3
AJ	167.016	0.9	0.2	4.5
As	191.979	5	1.5	3.3
Au	267.595	5	1.0	5
B	249.773	0.6	0.1	6
Ba	455.403	0.15	0.03	5
Be	234.861	0.05	0.01	5
Bi	223.061	6	2	3
Ca	396.847	0.06	0.01	6
Cd	214.436	0.6	0.05	12
Ce	418.660	2	2	1
Ca	235.892	1	0.2	5
Cr	267.116	0.9	0.15	6
Cu	327.396	1	0.3	3.3
Fe	259.940	0.8	0.1	a
K	766.490	+	0.3	13.3
U	670.784	1	0.06	16.7
Mg	279.553	0.04	0.01	4
Mn	257.610	0.08	0.03	27
Mo	202.030	2	0.5	4
Na	549.592	2	0.15	13.3
Ni	231.604	1.4	0.3	4.7
P	177.432	5	2	2.5
Pb	220.353	5	0.6	6.3
S	191.971	10	5	2
Sb	231.147	5	2	2.5
Se	196.026	6	2	3
Si	251.611	2.2	1.4	1.6
Sr	407.771	0.05	0.01	5
T	334.941	0.2	0.1	2
T	190.790	6	2	3
V	292.402	0.7	0.2	3.5
W	207.911	3.5	2	1.6
Zn	213.856	0.8	0.2	4
Zr	343.623	0.9	0.3	3

Table 1 Comparison of 3cr detection limits for mdHg and neatly/ie wed Vista-