



# ICP / AAS comparison

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## ICP or AAS

- Introduction ICP
- Fundamental parts of ICP
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- Fundamental parts of AAS
- Analysis
- Comparison
- Applications



# Selection between ICP And AAS

□ ICP



□ AAS



# Important criteria

Selecting a technique requires the consideration of a variety of important criteria, including:

- **Detection limits**
- **Analytical working range**
- **Sample throughput**
- **Data quality**
- **Cost**
- **Interferences**
- **Ease-of-use**
- **Availability of proven methodology**

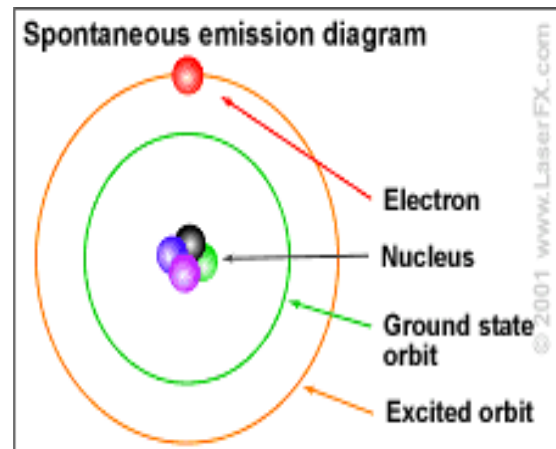


**ICP**

**Introduction**

# Emission

- Electrons in the element are excited.
- They jump to higher energy levels (excited state).
- As the electrons fall back down (ground state).
- Emitted(photon), the wavelength of which refers to the discrete lines of the emission spectrum.



# ICP - AES

## Inductively Coupled Plasma – Atomic Emission Spectroscopy (ICP-AES)

It is a multi-element analysis technique that will dissociate a sample into its constituent atoms and ions and exciting them to a higher energy level, Cause them to emit light at a characteristic wavelength , which will be analyzing



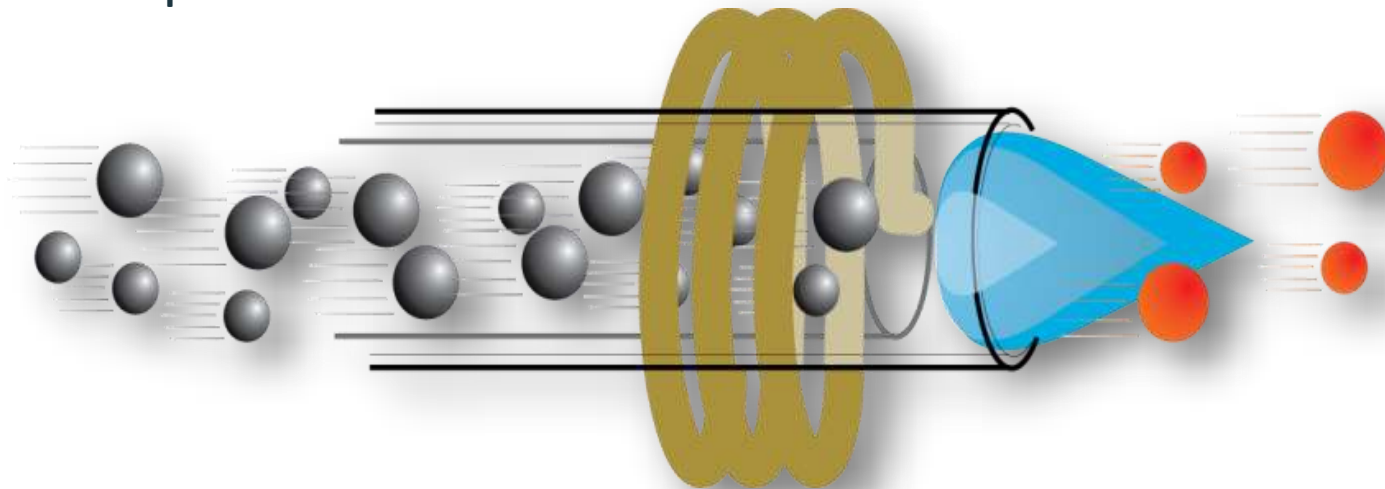
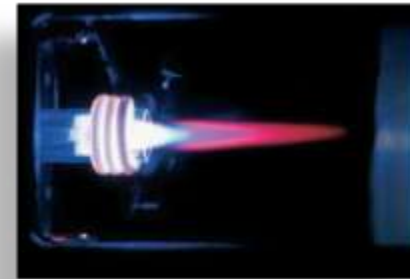
# Technique

1. The sample is nebulized and entrained in the flow of plasma support gas, which is typically Ar.
2. The plasma torch consists of concentric quartz tubes.
3. The inner tube contains the sample aerosol and Ar support gas and the outer tube contains flowing gas to keep the tubes cool.
4. A Radiofrequency (RF) generator produces an oscillating current in an induction coil that wraps around the tubes.
5. The induction coil creates an oscillating magnetic field, which produces an oscillating magnetic field, The magnetic field in turn sets up an oscillating current in the ions and electrons of the support gas (argon).
6. As the ions and electrons collide with other atoms in the support gas and temp increase.



# Plasma

- Gas in which a significant number of atoms are ionized (significant being >1%) Will interact with a magnetic field  
Inductive coupling between varying field and the plasma .



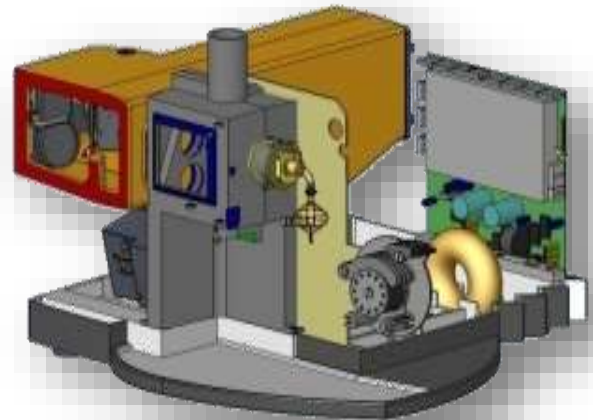
**ICP**

# Fundamental parts

# The functional parts of ICP

The iCAP 6000 spectrometer consists of several major components:

1. Sample introduction parts. Plasma torch.
2. Gas control.
3. Radio frequency power generator.
4. Optical system; Polychromator.
5. CID detector with thermoelectric cooling.



# 1. Sample introduction parts

- a. **Pump.**
- b. **Nebulizer.**
- c. **Spray chamber.**
- d. **Centre tube.**
- e. **Torch.**



## a. Peristaltic pump

- 4-channel 12-roller pump, with its unique drain sensor.
- The pump speed shall be computer controlled to provide programmable sample flows both during and between sample measurements .
- Included for the pump to be automatically switched into a standby mode upon instrument shutdown.



## b. Nebulizer

1. The sample solution after being sprayed by the nebulizer.
2. Entrained in argon as a fine mist.
3. Passes through the center channel of the torch and into the plasma.

Control of the nebulizer pressure, or flow, is either through the control software or via a manual adjustment.



## c. Cyclone spray chamber

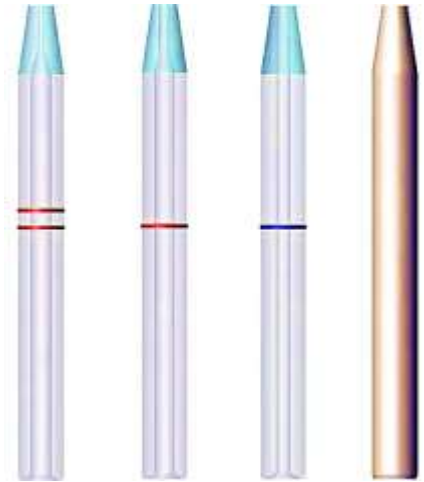
- Most samples are liquids that are pumped through a nebulizer to produce a fine spray.
- The large droplets are removed by a spray chamber and the small droplets then pass through to the plasma.



## d. Centre tube

### Types of Centre tube

1. 1.5mm quartz for aqueous solutions (single red ring).
2. 1.0mm quartz for organic solutions (double red ring).
3. 2.0mm quartz for high dissolved solids solutions  
(single blue ring, standard on Duo configurations).
4. 2.0mm Ceramic for HF solutions.





## e. Plasma torch

- The quartz torch surrounded by the copper induction coil.
- The copper coil is made from copper tubing and is kept cool by circulating water.
- RF energy is supplied to the coil which inductively heats the argon gas to approximately 10,000°C.
- At this temperature the gas turns into a plasma of positively charged atoms and electrons.
- The plasma is kept off the sides of the quartz torch by a separate flow of argon supplied tangentially to the inside torch.



## 2. Gas control

### iCAP 7200

- The nebulizer gas flow is manually controlled from 0 to 0.4 MPa.
- The auxiliary gas is controlled with precision restrictors with flows of 0, 0.5, 1.0 and 1.5 L/min. The coolant flow is fixed at 12 L/min.

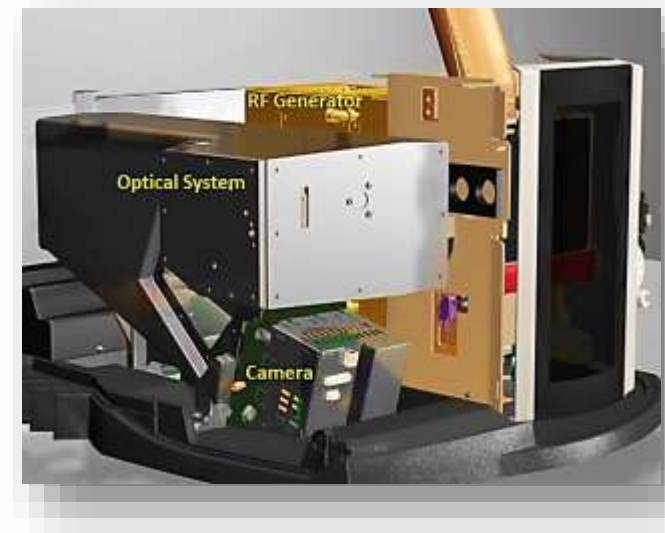
### iCAP 7400

- The nebulizer gas is computer controlled through an MFC with options from 0 - 1.5 L/min with increments of 0.1 L/min.
- The auxiliary gas is computer controlled through an MFC with options from 0 - 2 L/min in 0.1 L/min increments.
- The coolant flow is computer controlled through an MFC from 0 - 20 L/min.



### 3. Radio frequency RF power generator

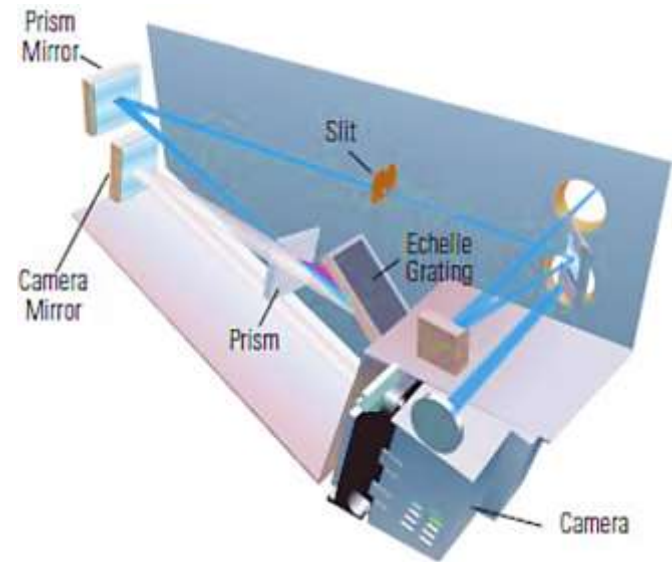
- Swing frequency impedance control.
- Frequency changes to match plasma load.
- Fast response, no complex matching networks.
- >78% Efficiency Ability to run even difficult organics e.g. methanol.
- Nominal Frequency: 27.12 M Hz.
- Full range of power control.
- 750-1600w Radial, 750-1350w Duo Optimum performance for all sample types.



# 4. Optical system

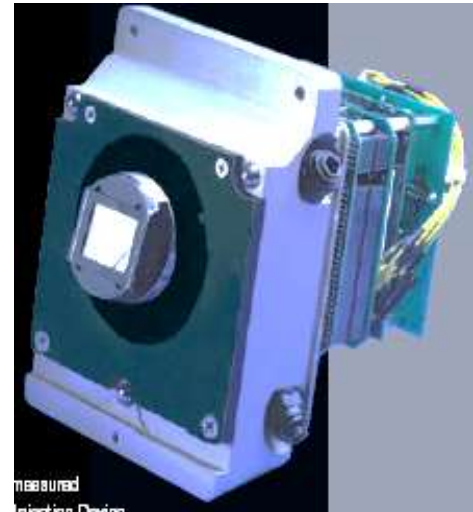
## Wavelength Range

- The instrument shall be able to operate over the range of 166.250 to 847.000 nm
- All elements must be represented by at least 3 sensitive and 3 secondary lines to satisfy the requirements of a wide range of sample types.
- An optical resolution of better than 0.007nm at 200nm, 0.014nm at 400nm and 0.021nm at 600nm.



# 5. Charge injection device CID

- **New CID86 chip (Charge Injection Device).**
- **Allows free choice of wavelengths from 166 to 847 nm.**
- **More stable, lower noise.**
- **With the ability to measure transient signals.**
- **Thermoelectric cooling by a triple stage peltier.**
- **Reduce dark current and background noise resulting in enhanced detection limits.**

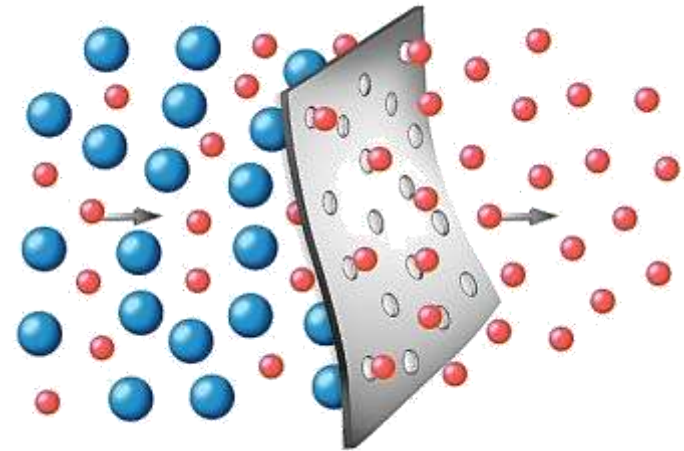


**AAS**

# **Introduction**

# Absorption

- The process whereby the intensity of a beam of electromagnetic radiation is attenuated in passing through a material medium by conversion of the energy of the radiation to an equivalent amount of energy appearing within the medium.



# Atomic Absorption Spectrometer AAS

AAS is an analytical technique used to measure a wide range of elements concentration in samples, where the free atoms of the sprayed element solution absorbed the radiation of the Hollow cathode lamp of the

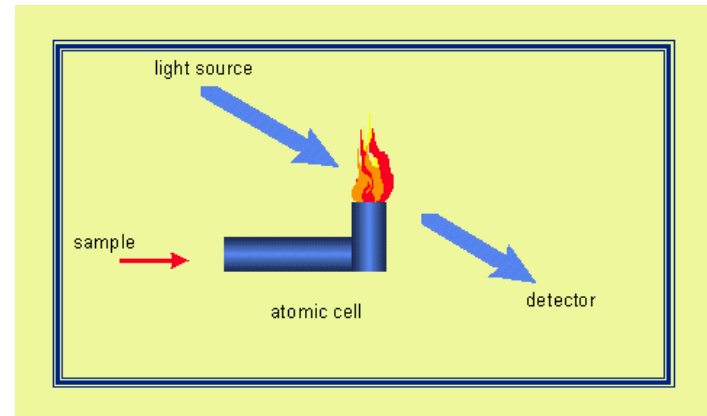
*analyzed element.*





# Technique

- The sample is weighed and then dissolved.
- The resulting solution is sprayed into the flame and atomized.
- Light of a suitable wavelength for a particular element is shone through the flame.
- Some of this light is absorbed by the atoms of the sample.
- The amount of light absorbed is proportional to the concentration of the element .

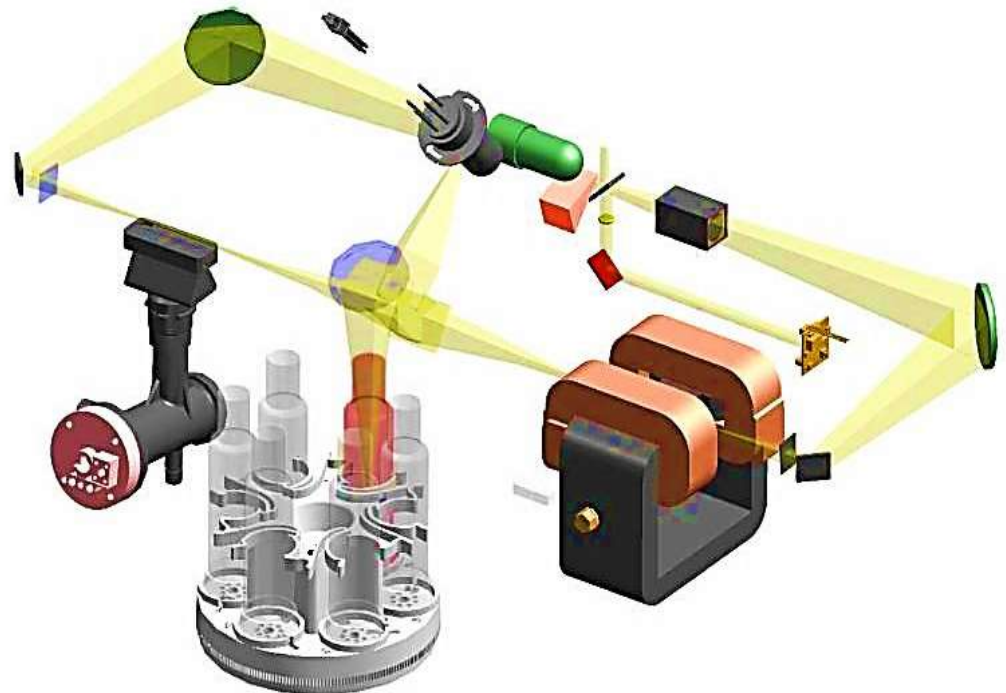


**AAS**

**Fundamental parts**

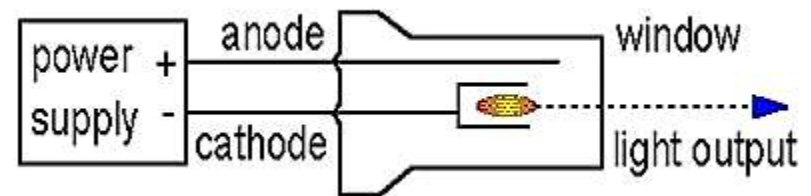
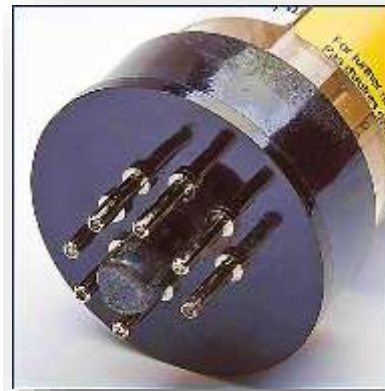
# AA main parts

1. Lamp
2. Atomizer
3. Monochromator
4. Photomultiplier tube
5. Optical system
6. Automatic gas control



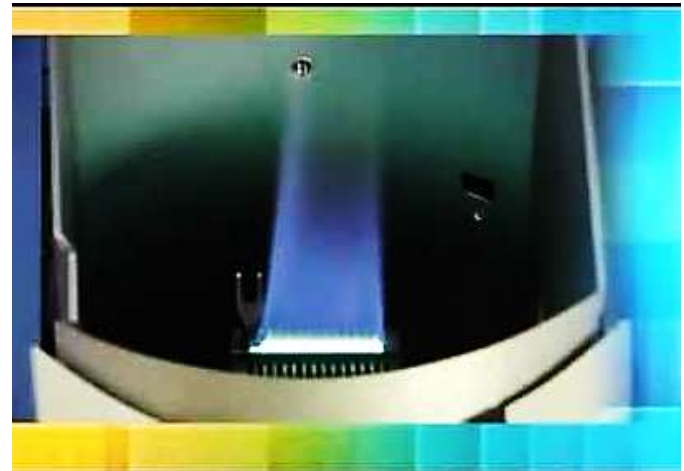
# 1. Lamps

- Hollow Cathode Lamps (HCLs) are high intensity, stable light sources that emit the element specific spectral lines required for Atomic Absorption spectrometry.
- Provide a constant intense beam of analytical light.
- There are Coded or uncoded lamps.



## 2. Atomizers

- **Metal in the sample must undergo desolation and vaporization in a high-temperature source such as a flame or graphite furnace to be free atoms.**
- **Destroy any analyte ions and breakdown complexes**  
**Create atoms (the elemental form) of the element of interest.**



# Type of atomizers

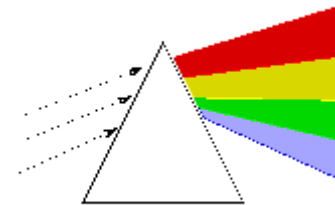
The main function is to generate a free atoms

1. Flame
2. Graphite
3. Hydride System



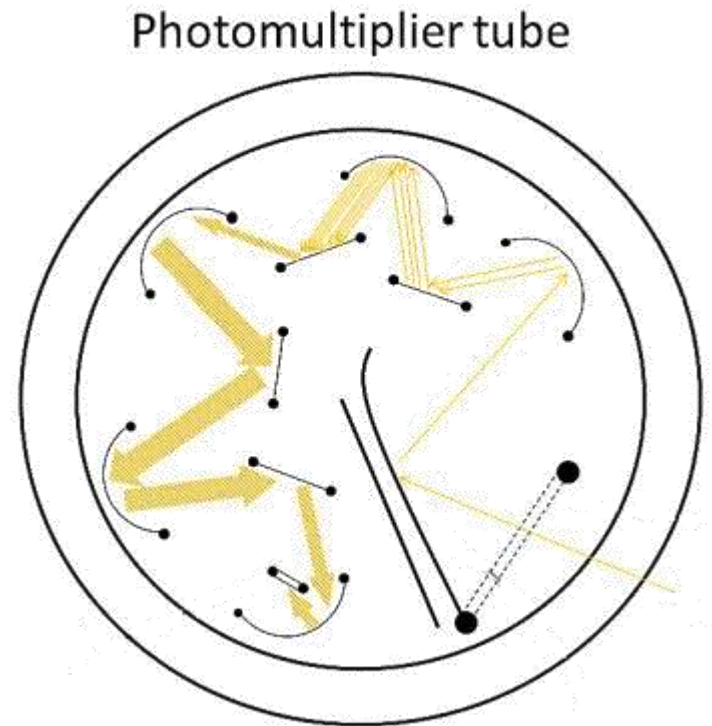
# 3. Monochromator

- A monochromator is an optical device that transmits a mechanically selectable narrow band of wavelengths of light .
- Echelle monochromator provides automatic wavelength and band pass set-up.
- The high energy Quad Line background correction system corrects for up to 2A of background with less than 2 % error, and is fitted as standard to all instruments.



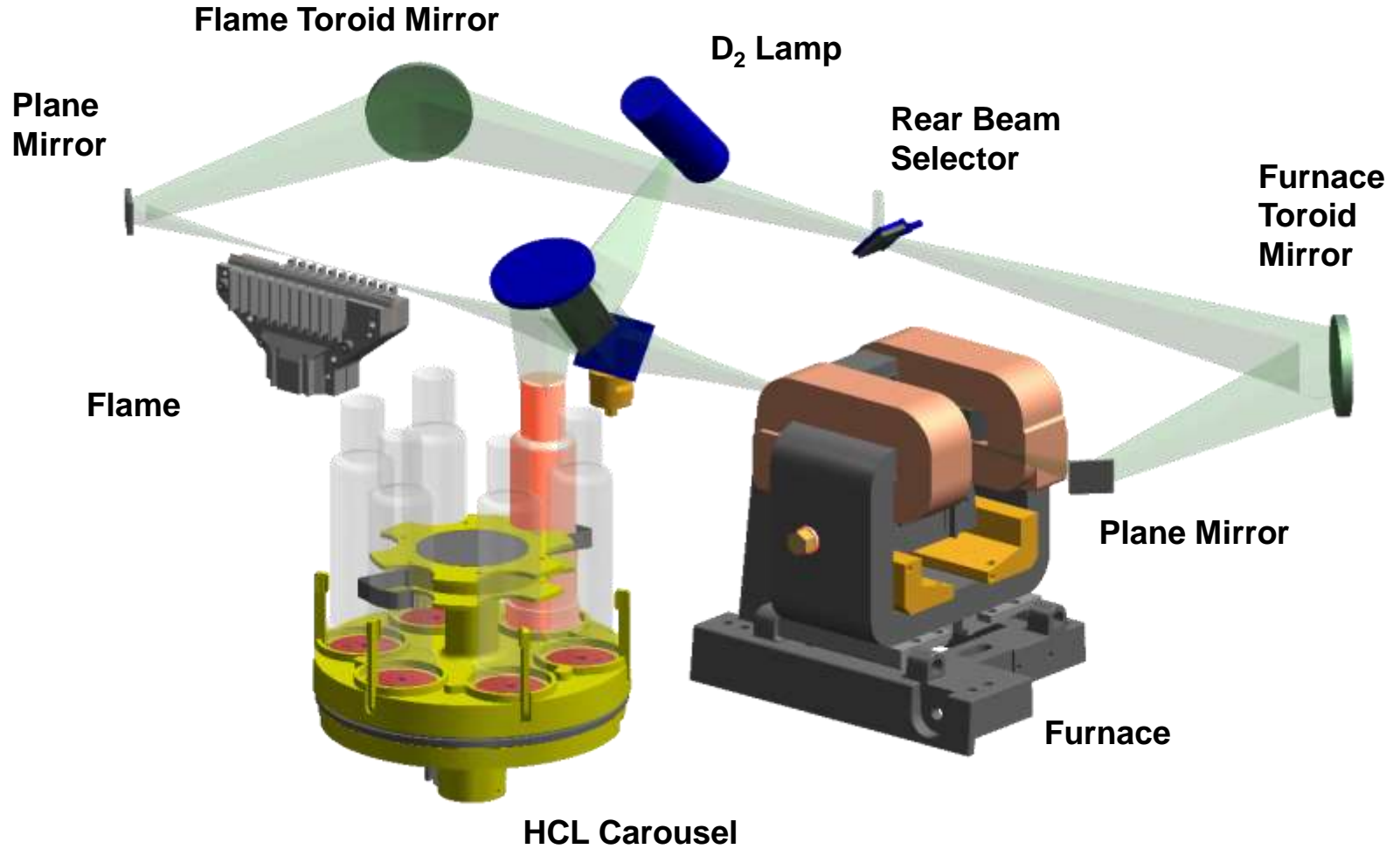
# 4. Photo multiplier tube PMT “Detector”

- The PMT change the incidence photons into electrical signal.
- As the detector the PMT determines the intensity of photons of the analytical line exiting the monochromator.



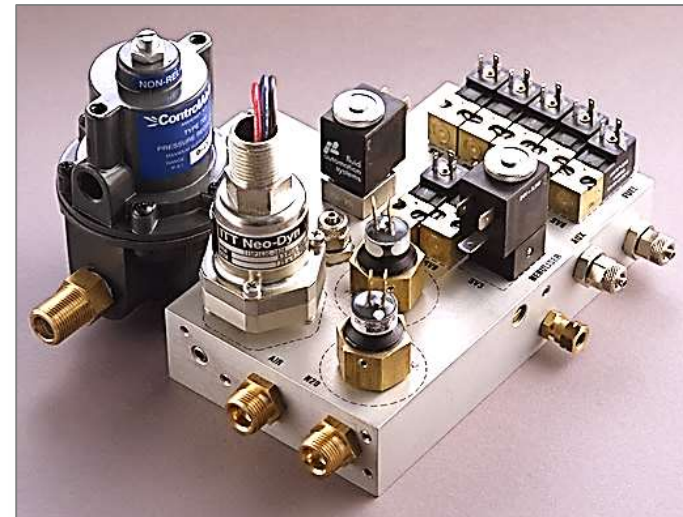


# 5. Optical System



# 6. Automatic Gas Control

- Full safety monitoring facilities and safe shutdown.
- Completely enclosed “kitchen” area.
- Automatic binary flow gas control system for superb reliability and reproducibility.



# AAS Techniques

# 1. Flame Atomic Absorption FAAS

- Flame atomic absorption spectrometry, either an air/acetylene or a nitrous oxide/acetylene flame is used to evaporate the solvent and dissociate the sample into its component atoms
- Flame limits the excitation temperature reached by a sample to a maximum of approximately 2600°C (with the N<sub>2</sub>O/acetylene flame). )



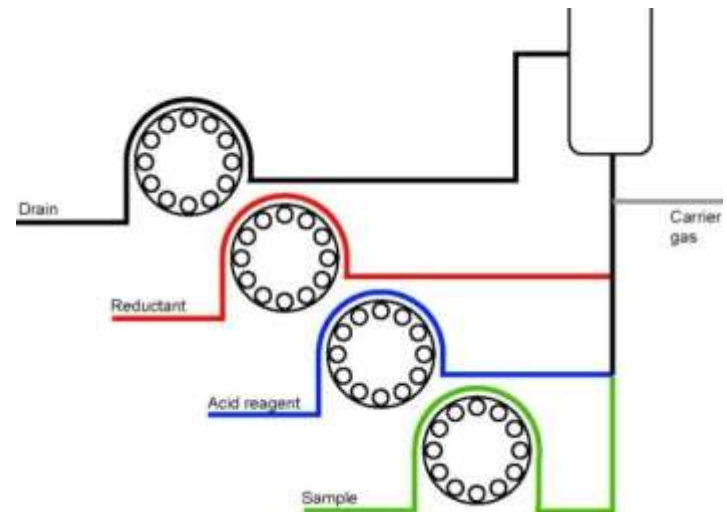
## 2. Furnace atomic Absorption GFAAS

- **Electrothermal atomization (ETA) is a technique for improving the sensitivity and limit-of-detection (1000 times) for atomic absorption measurements.**
- **A small amount of sample is placed inside a hollow graphite tube.**
- **This is resistively-heated in a temperature program to remove liquid, burn off organics, atomize the residuals to form a plume of free metal vapor, detect the metals and finally clean the tube.**



# 3. Hydride Atomic Absorption HSAAS

- Parts per billion sensitivities for a number of environmentally important elements are not attainable by conventional flame atomic absorption spectrometry and alternative techniques have to be used.
- Hydride generation AAS is applicable to mercury and the arsenic group elements.



The elements that can be determined with the VP100 are those that can form gaseous hydrides, or in the case of mercury, a mono-atomic vapor.



# Analysis

ICP & AAS

# Sample preparation

**Microwave digestion is the best solution for samples preparation.**

- **Short digestion times. Minutes, not hours**
- **No loss of volatile elements. Complete recovery of Hg, As, Cd etc.**
- **No acid fumes. Improved laboratory working conditions.**
- **No sample contamination from the environment.**
- **No cross contamination.**
- **Low blanks, as minimal quantities of acids are used.**





# Standards preparation

- AAS, By using standards from single-element primary standards,
- ICP, Multi-element primary standards,  
And/or a combination of single-element and multi-element primary standards.
- It is a widely accepted practice to use NIST SRMs (standard reference materials) to validate various kinds of laboratory operations.



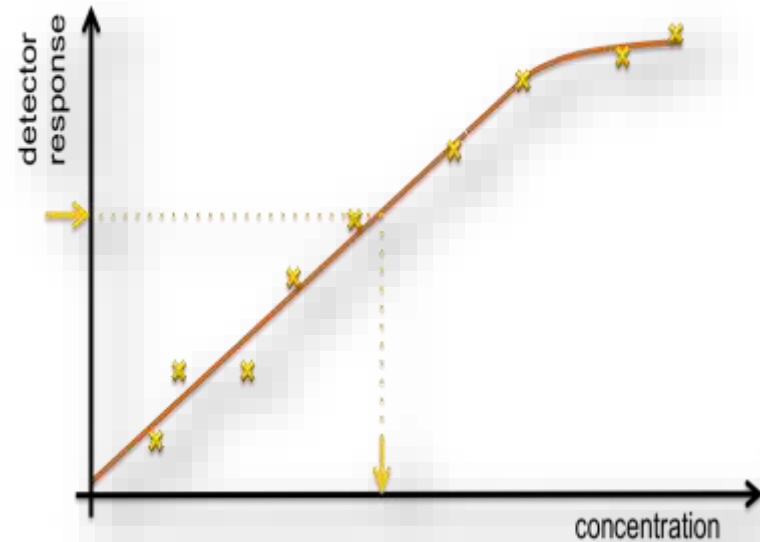
# Water & chemicals

- Forget about grids.
- But, All types of acids, water and other used chemicals should be free of the required elements.



# Calibration

- **Optical absorption spectrometry is a comparative technique in which the signals by solutions of known concentrations used to generate a calibration curve is compared to the signals of unknown samples to generate results.**





# Comparison

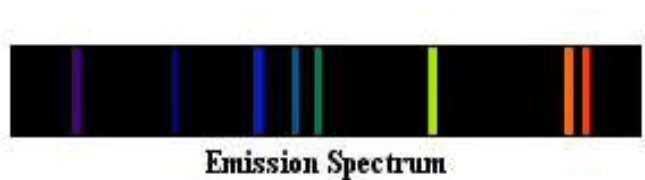


# Theory of Technique

## ICP-AES

### Emission

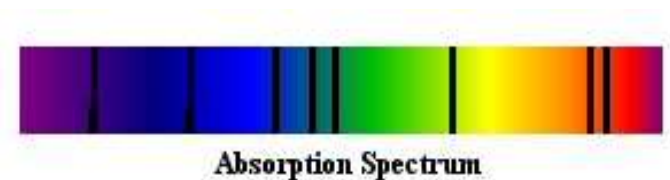
- Is the process that creates a photon and takes the atom or molecule in an excited state back to the ground state.
- Many interference



## AAS

### Absorption

- Is the process that consumes a photon and puts the atom or molecule in an excited state.
- Few interference



# Samples Throughput

## ICP-AES

- All elements in the sample can be analyzed in the same time, multi elements analysis.
- Prepare 3-5 points for calibration for all the required elements.
- Short time for standards preparation.
- Consume less glass ware.
- One report for all results.

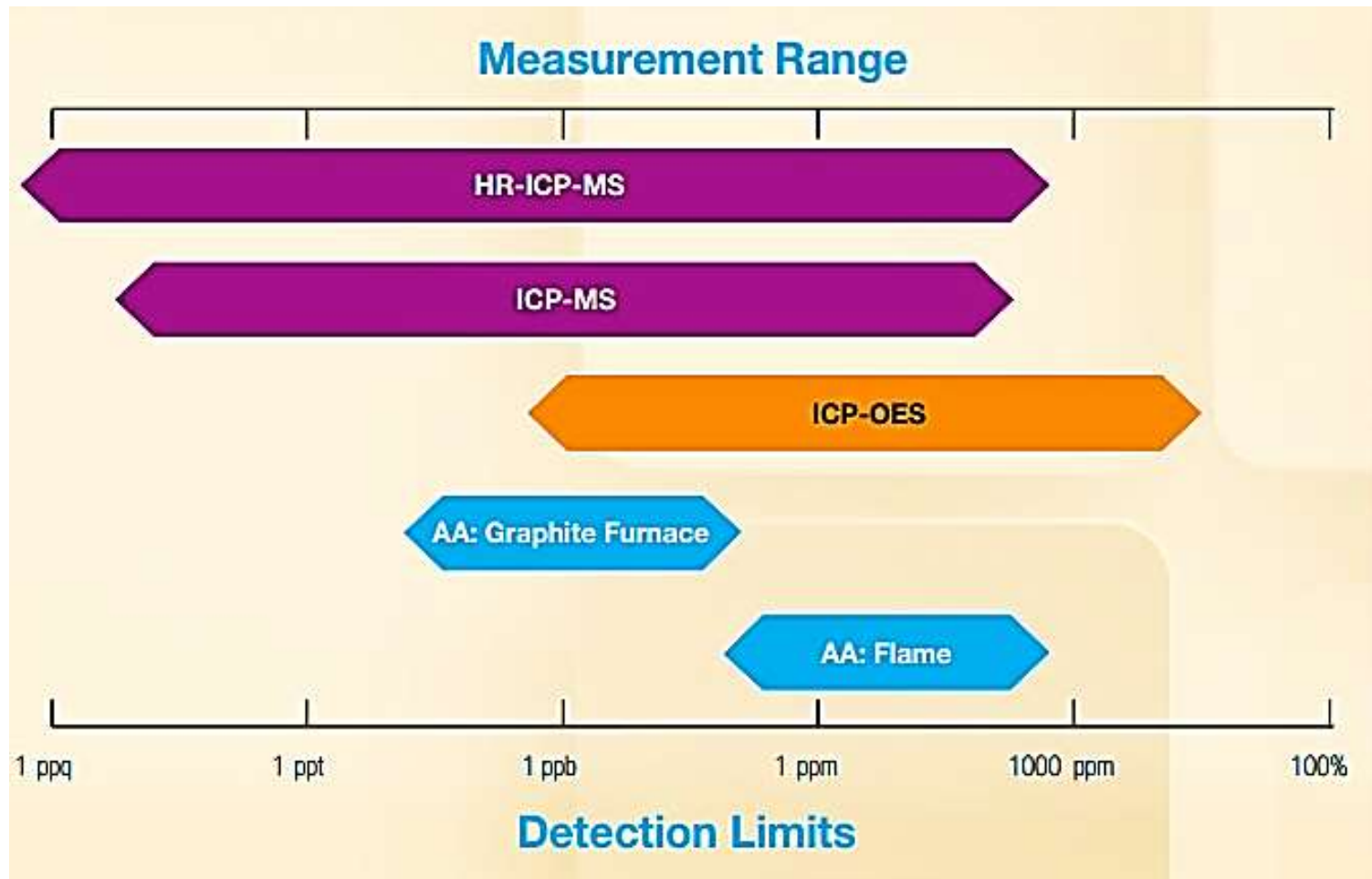
## AAS

- Element by element, single element analysis.
- Prepare 3-5 points for calibration for each elements.
- Long time for standards preparation.
- Consume a lot of glass ware.
- One report for each element.





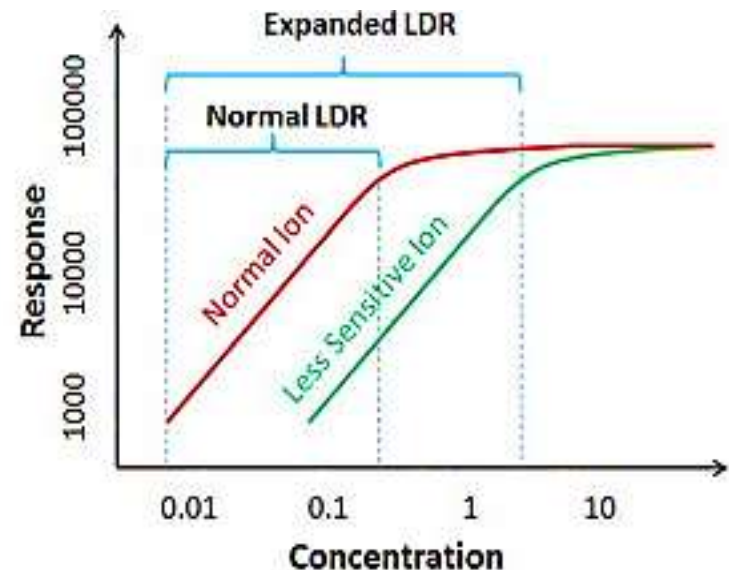
# Detection limits



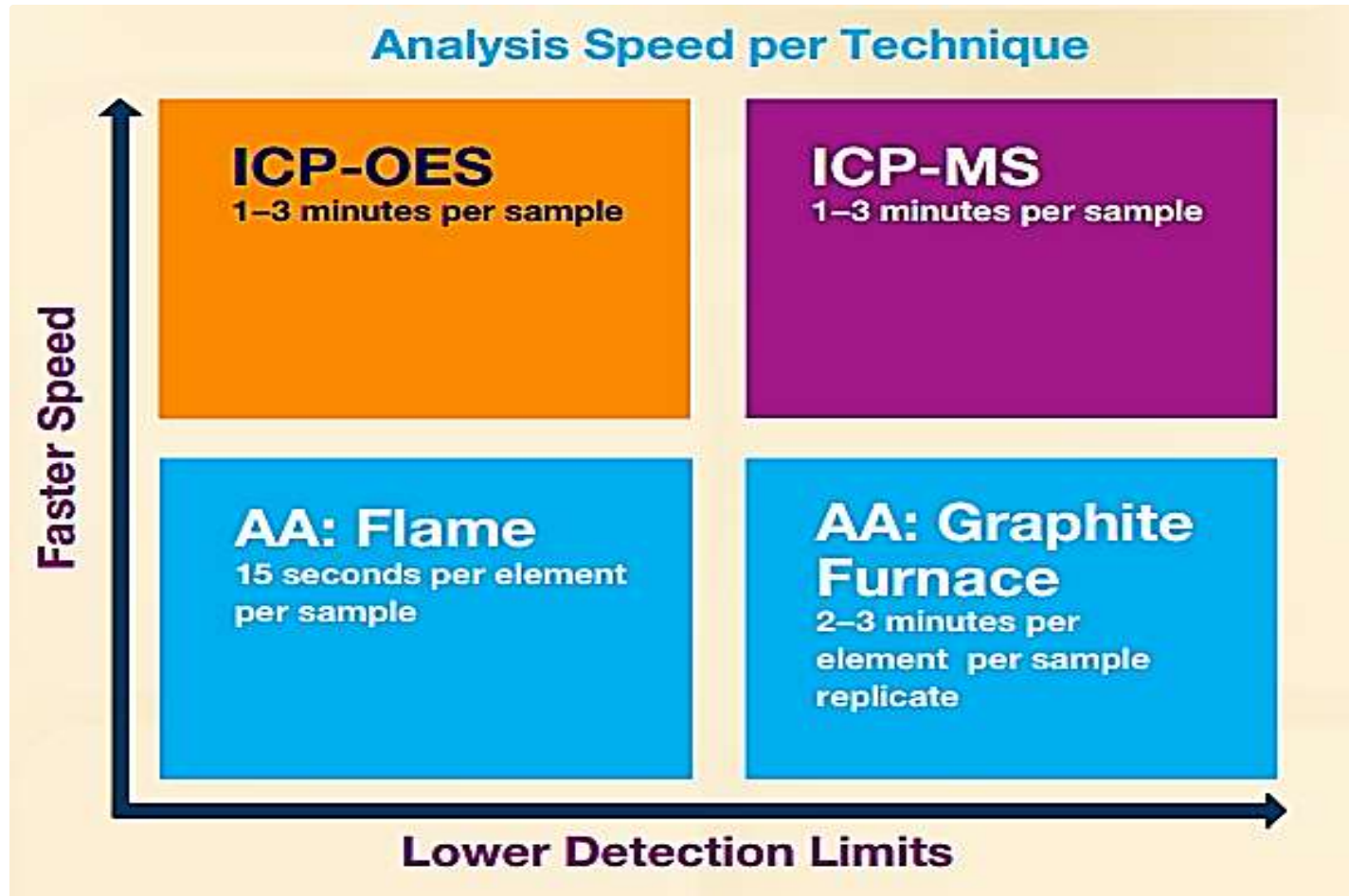


# Linear Dynamic Range.

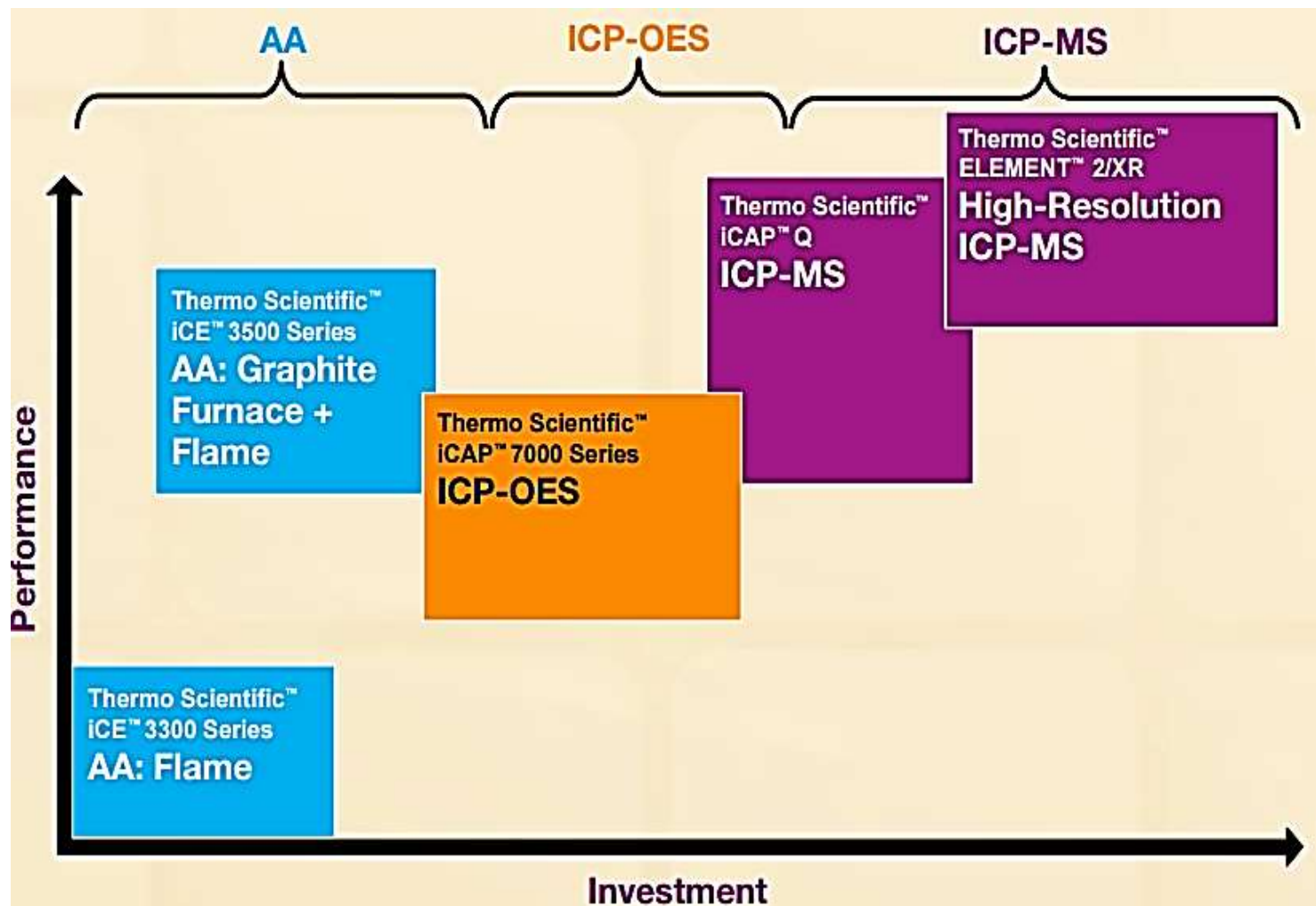
- The large linear dynamic range for ICP of about  $10^5$ .
- For example, copper can be measured at the 324.75 nm wavelength from its detection limit of about 0.002 ppm to over 200 ppm. In ICP, extrapolation of two point calibrations can be accurately used to achieve orders of magnitude above the top standard.
- This compares to a linear dynamic range of typically  $10^3$  for AAS



# Analysis speed



# Costs



# Easy to use

- **FAAS** systems are usually very easy to set up and run. They are capable of some degree of automation but should not be run unattended, due to the flammable gas risk.
- **GFAAS** systems are somewhat more difficult to set up because of the accuracy of sample injection required to achieve the best results. Also.
- **ICP-AES** systems are easy to set up and have to be adjusted relatively infrequently. If there are major spectral interferences, method development can be complicated.

Easy!



**FAAS, ICP-AES then GFAAS**



# Precision

Item	FAAS	GFAAS	ICP-AES
Short term	0.1-1.0%	0.5-5%	0.1-2%
Long term	2-beam 1-2% 1-beam < 10%	1-10% (tube lifetime)	1-5%

Accurate  
Precise

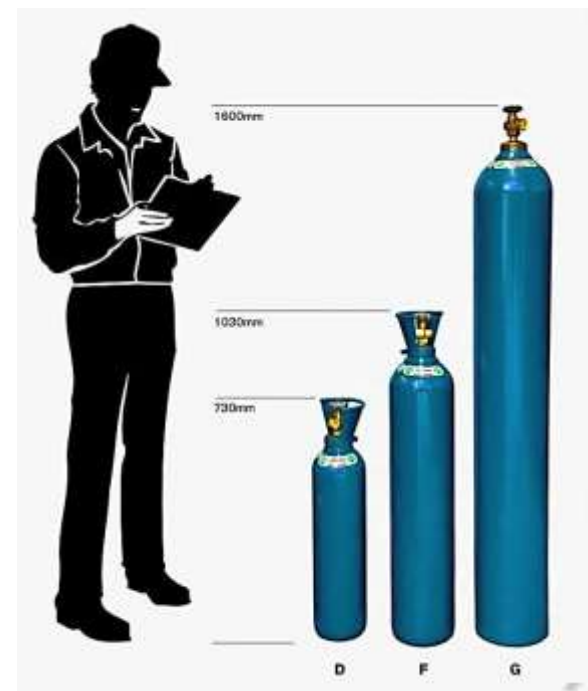


# Interferences

Item	FAAS	GFAAS	ICP-AES
Spectral	Very few	Very few	Many
Chemical "Matrix"	Many	Very many	Very few
Physical "Matrix"	Some	Very few	Very few

# Argon consumption for ICP

- G size mixed argon gas cylinder contains 8.7 cubic meters of gas (8700 Liters).
- The cylinder dimensions are 163cm high x 27cm diameter.
- Average rate of 20 L / min.
- The cylinder will be enough for more than 7 hours.
- More than 200 samples will analyzed using one cylinder.
- Note: ( 1 L liquid = 781 L gas ) Argon



# Hollow cathode lamps for AAS

**A required lamp For every element will analyzed.**

- If your lamp need to analyze 20 elements you will buy 20 lamps.
- Hollow cathode lamps are gas discharge devices in which the discharge is highly constrained within the cathode of a specific metal.
- HCL has to change with a new one after time depending on the frequent usage.





# Applications

ICP & AAS

# Applications

1. **Environmental Analyses Applications**
2. **Petrochemical Analyses**
3. **Metallurgical analyses**
4. **Geological analyses**
5. **Foodstuffs analyses**
6. **And more.**



# Environmental

1. Waters – potable, natural, effluent, wastewaters, sea and coastal waters
2. Soils – soils, sediments, foliage, biota, contaminated land, landfill sites
3. Sludge's – solid and digested waste
4. Air – chimney exhaust filters, air filters of contaminated sites, dusts



# Petrochemical

1. Specifically oils & greases,
2. Additives, pigments, intermediates
3. Petrochemical applications at refineries, wear metal analysis for industrial fleets, heavy industry by-products
4. Paints and inks



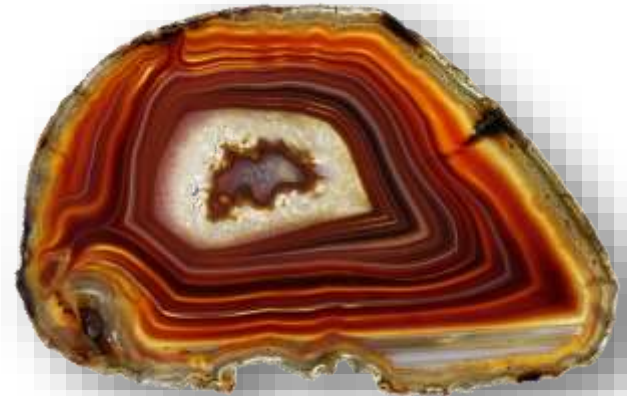
# Metallurgical

- **Steels and Alloys**
- **Precious metals – PGMs**
- **Bulk Materials – bronzes and brasses**
- **Traces – contaminants.**



# Geological

- **Rock samples, sediments, slags, ceramics, cements**
- **Survey work, quality control, raw material screening**
- **Robust**
- **Matrix tolerant**
- **Stability**
- **Detection limits (traces)**



# Foodstuffs

- **Bulk materials, raw and finished products in food production**
- **Trace analysis of micronutrients**
- **Toxins - contamination of land and sea**
- **Animal feed**
- **Crop analysis**

