Elemental Analysis

Archeological Chemistry Seminar

2023 AAS/ARAS Training Program

Techniques of Elemental Analysis

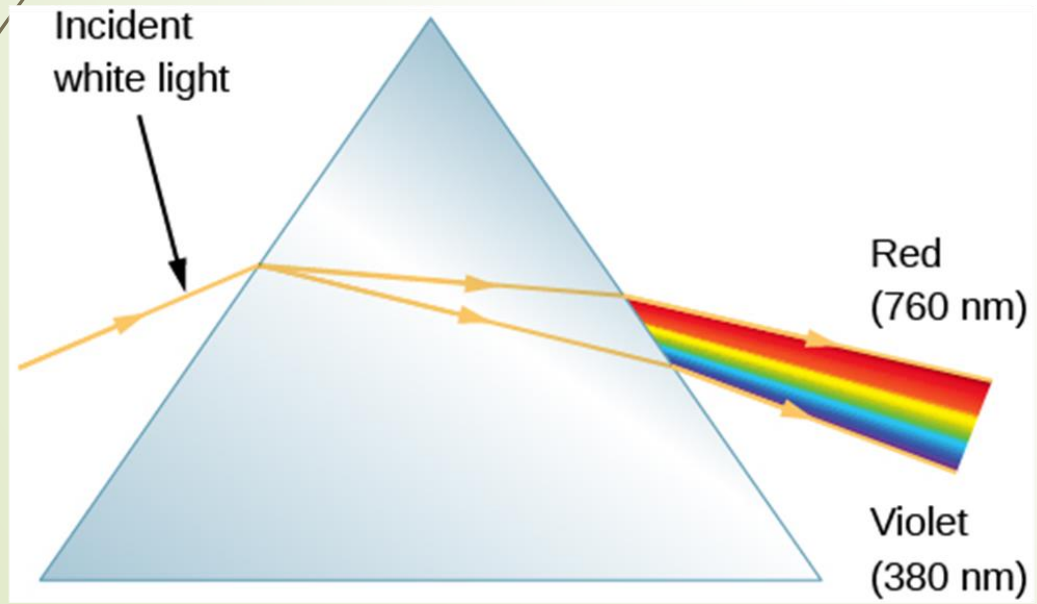
- Wet Chemical techniques
- Atomic Absorption Spectrophotometry (AAS)
- Optical Emission Spectroscopy (OES)
- Inductively Coupled Plasma (ICP)
- X-Ray Fluorescence (XRF)
- Laser Induced Breakdown Spectroscopy (LIBS)
- Neutron Activation Analysis (NAA)

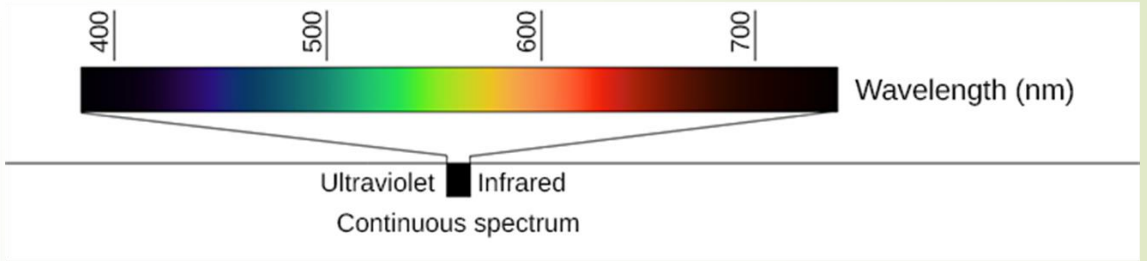
Wet Chemical techniques

- Usually involve isolating each element using a series of chemical reactions.
- Mostly used pre-1950
- Qualitative tests
  - Chemical tests indicating a color change, precipitant, etc…
    - Example: Cation Group Separation (i.e. Group I = Ag, Pb, Hg; Group IV = Ba, Sr, Ca)
  - Flame tests indicate the presence of metals by flame color
    - Example: Ca flame = orange; copper = blue
- Quantitative tests
  - Gravimetric Analysis
    - Measures the mass of a precipitant that has formed
  - Volumetric Analysis
    - Measures concentration of a dissolved substance

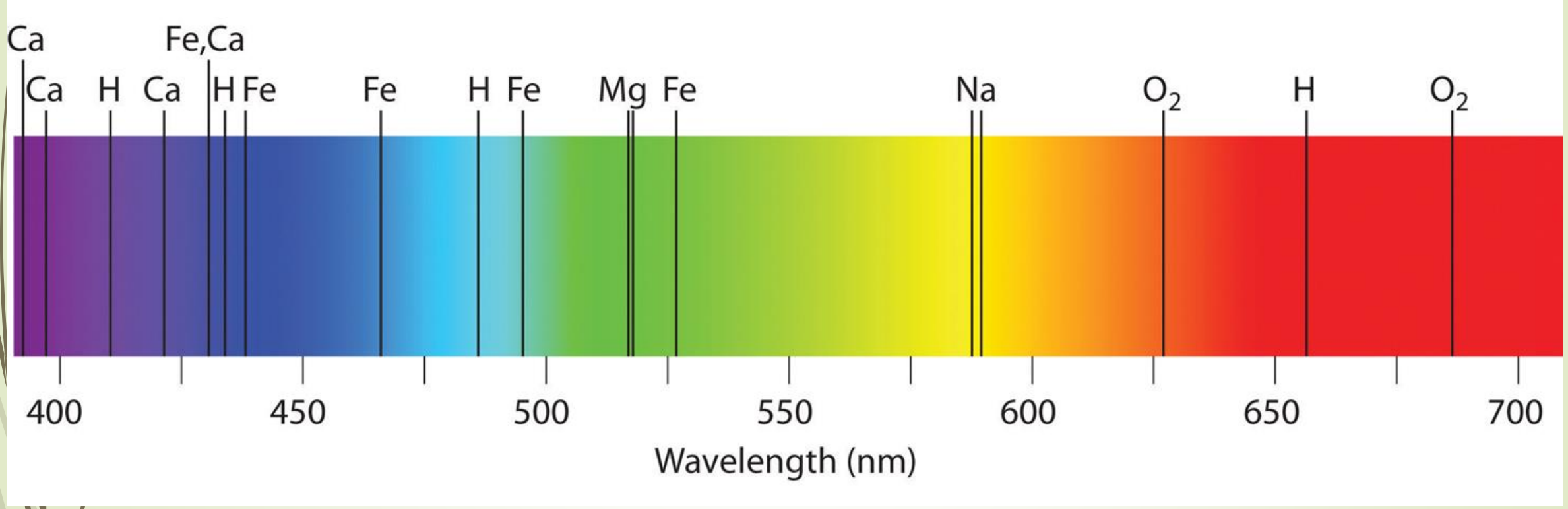
Properties of Light

- Reflection – when light bounces off an object
- Refraction – bending of light as it passes through an object
- Isaac Newton (1670) used a prism to break sunlight into a rainbow of colors
- The separated light is called a spectrum





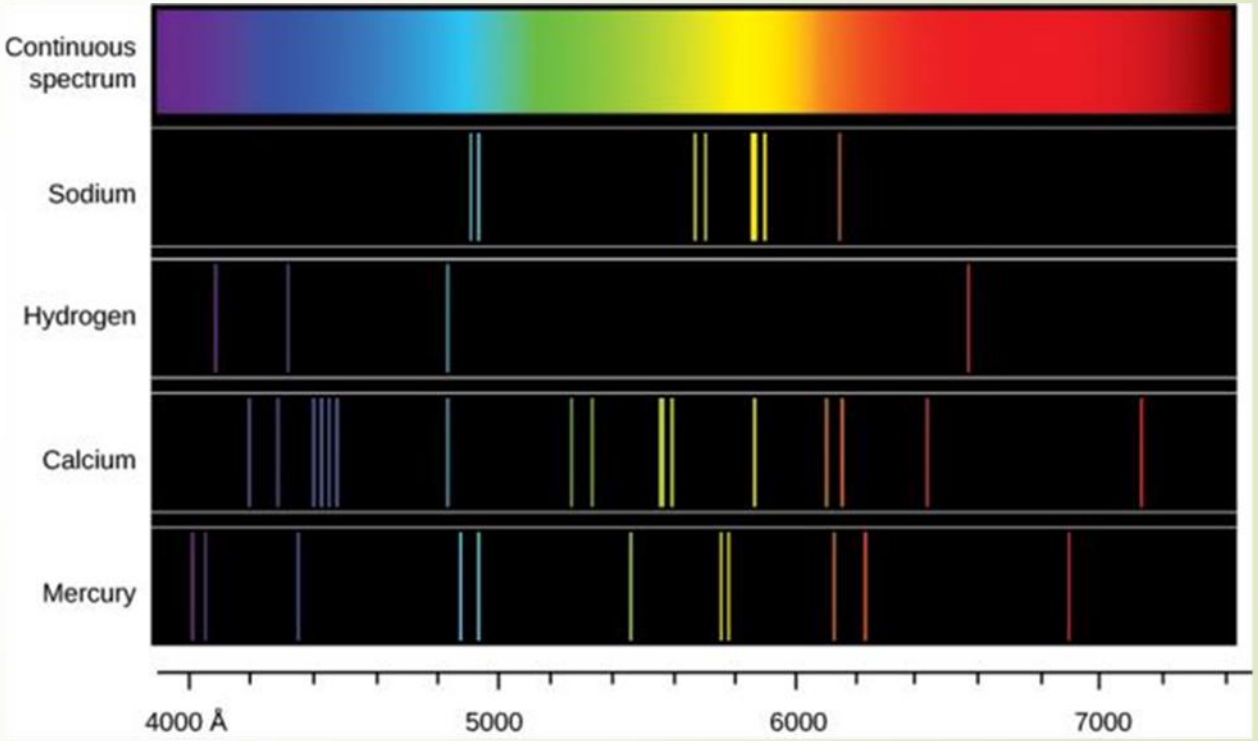
Sunlight Spectrum

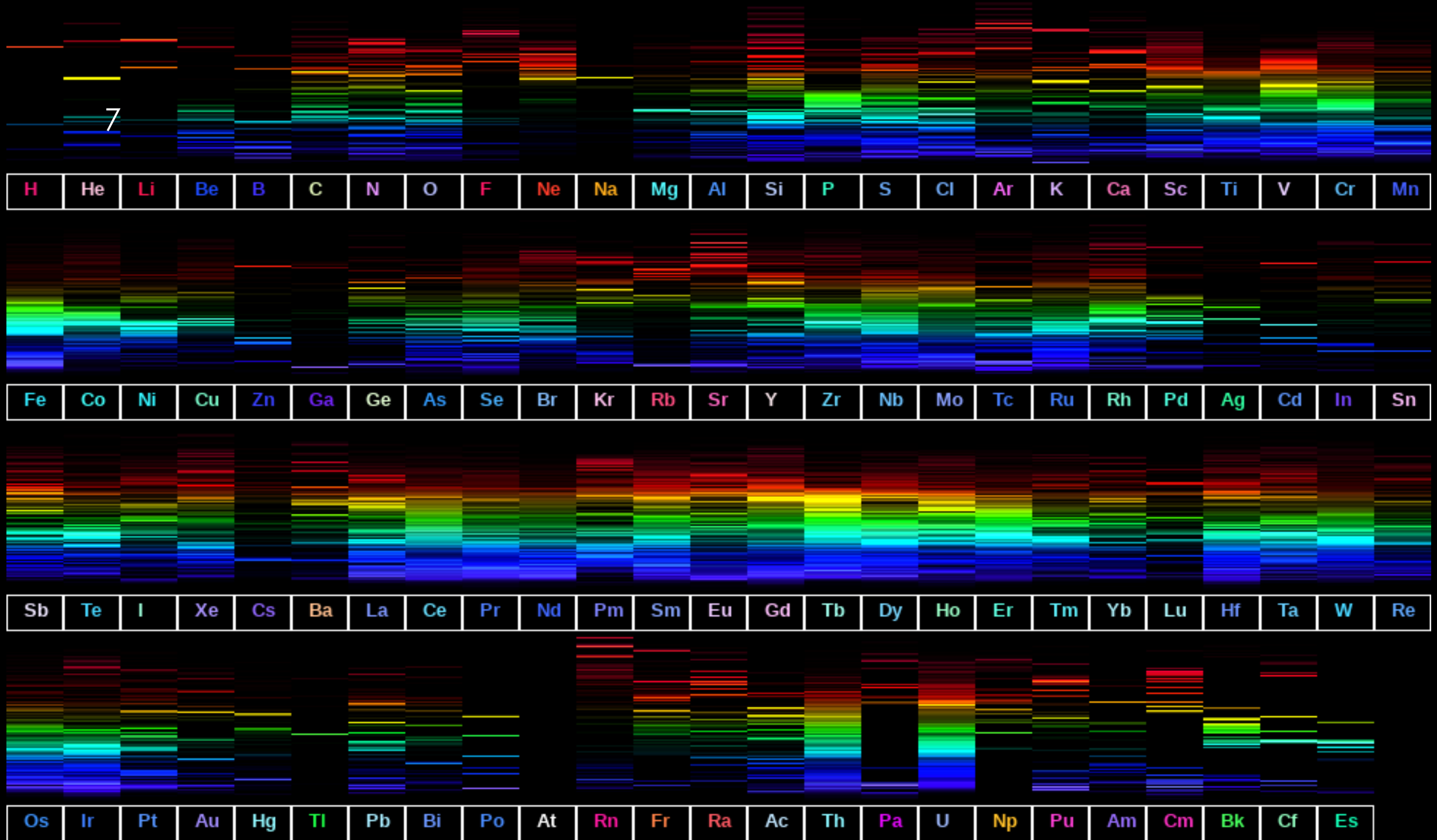


Spectral lines are the result of light absorption in the Sun's cooler photosphere.

Chemical Fingerprints

- Absorption lines and emission lines are indicative of chemical elements
- Each element has its own unique set of lines

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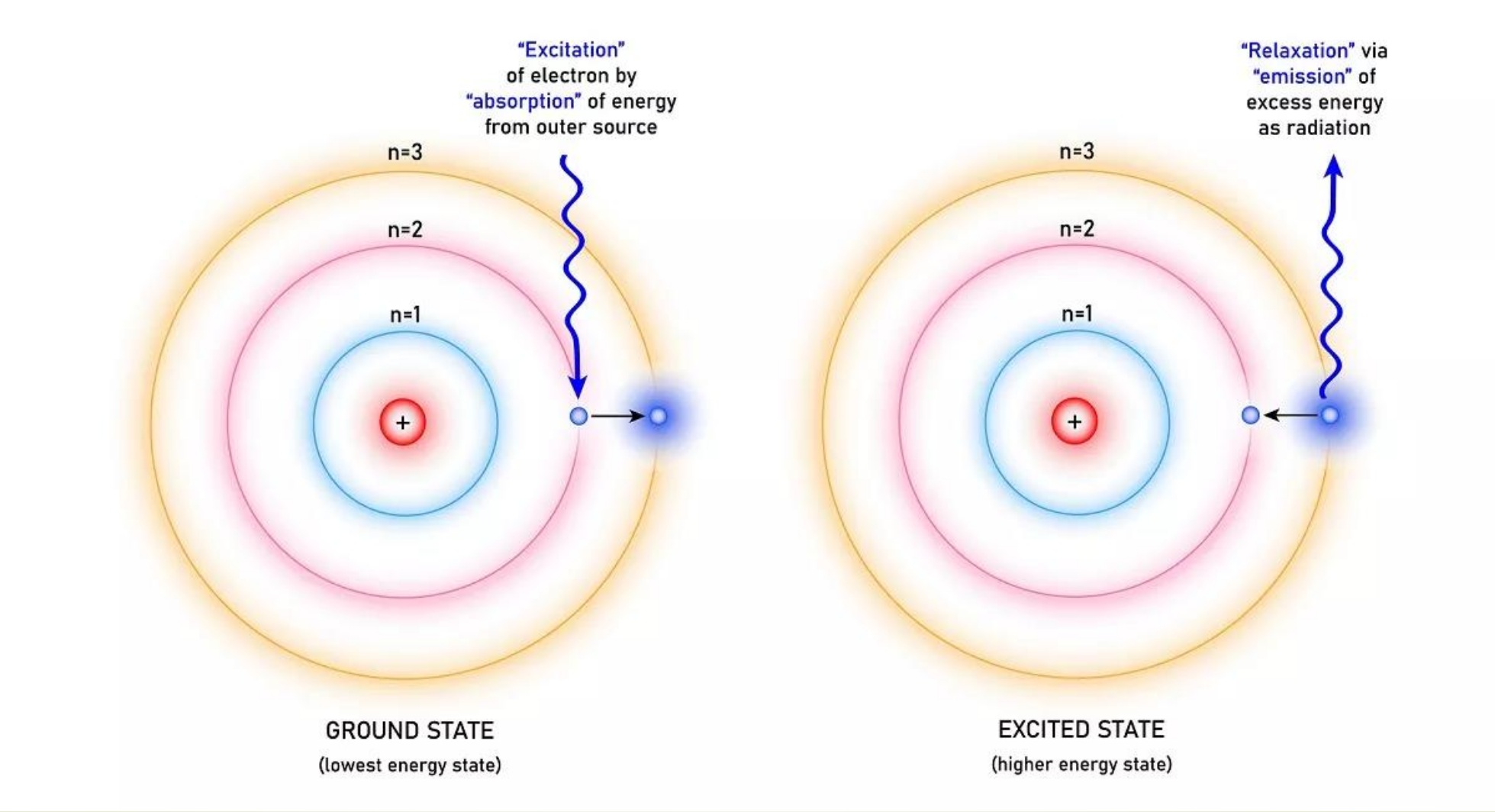
H He Li Be B C N O F Ne Na Mg Al Si P S Cl Ar K Ca Sc Ti V Cr Mn
Fe Co Ni Cu Zn Ga Ge As Se Br Kr Rb Sr Y Zr Nb Mo Tc Ru Rh Pd Ag Cd In Sn
Sb Te I Xe Cs Ba La Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu Hf Ta W Re
Os Ir Pt Au Hg Tl Pb Bi Po At Rn Fr Ra Ac Th Pa U Np Pu Am Cm Bk Cf Es

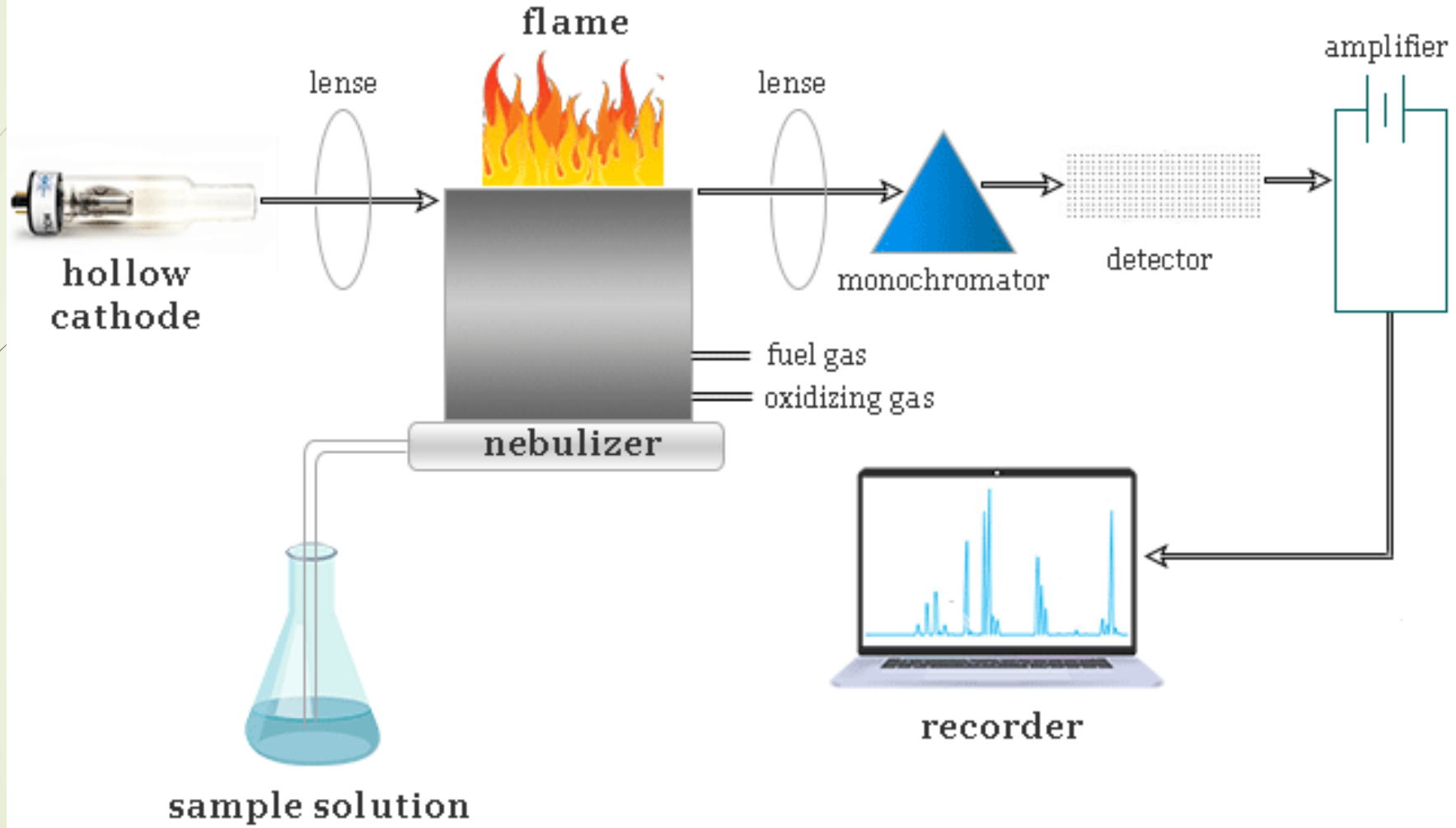
Excitation and De-Excitation of the Electron



Atomic Absorption Spectrometry (AAS)

- Developed in 1950s
- Comes in two forms:
  - Flame atomizer
  - Graphite furnace
- Samples must be dissolved into a solution and then aspirated into the flame/furnace
- Flame/furnace temperature:
  - 2200-3000°C

Atomic absorption spectroscopy



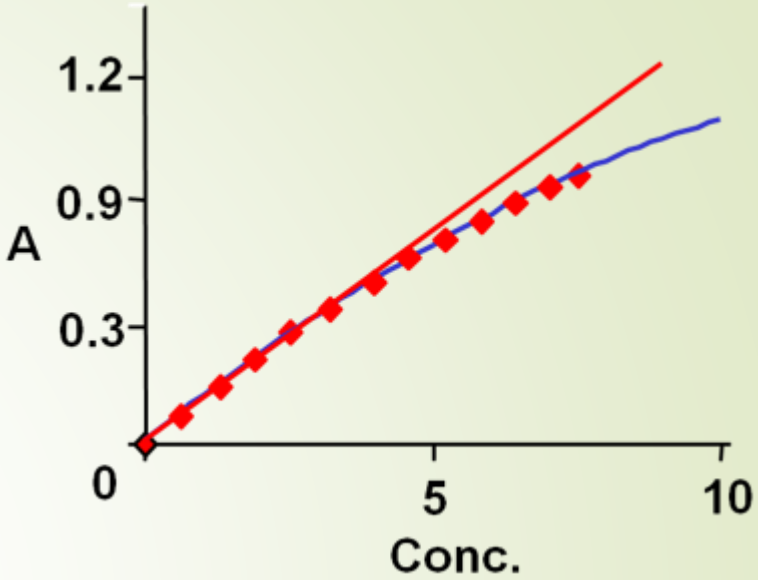
AAS Principles

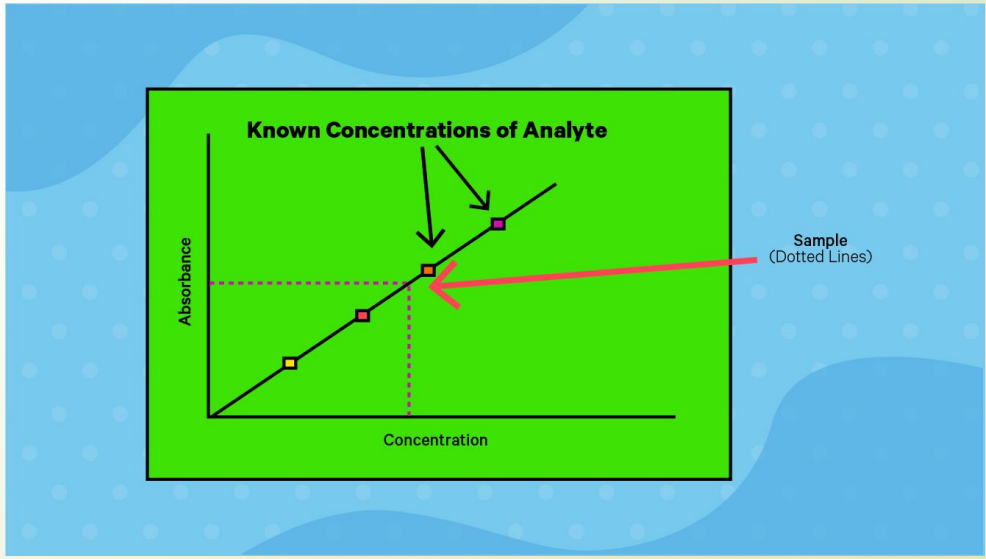
- A hollow-cathode Lamp (HCL) must be selected to match the element of interest
- Excitation of the tube produces emission lines only for that element
- Flame/furnace atomizes the sample
- If element is present, it will absorb the wavelength emitted by the HCL
- Decrease in signal is proportional to its concentration in the vapor

Hollow-cathode lamps for analysis of Sr and Ba

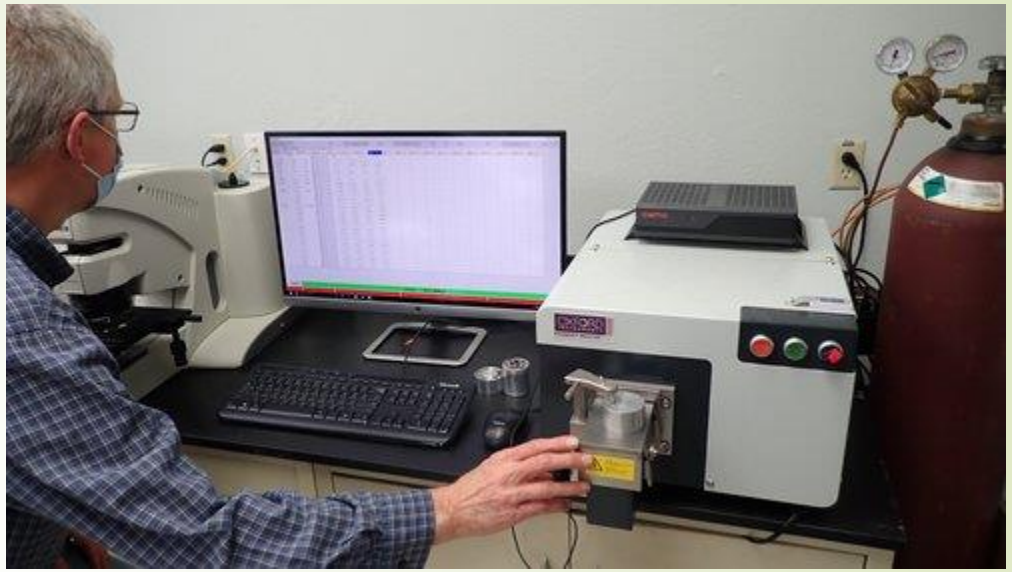
Analysis Technique

- As for most all techniques, comparison of a sample's signal to that of standards is required.
  - Ideally, samples are measured in the linear region of the standards.
- Can measure most metals
- Suffers from:
  - calibration drift
  - reproducibility
- Detection limits are typically between 1-100 ppm (mg/kg)

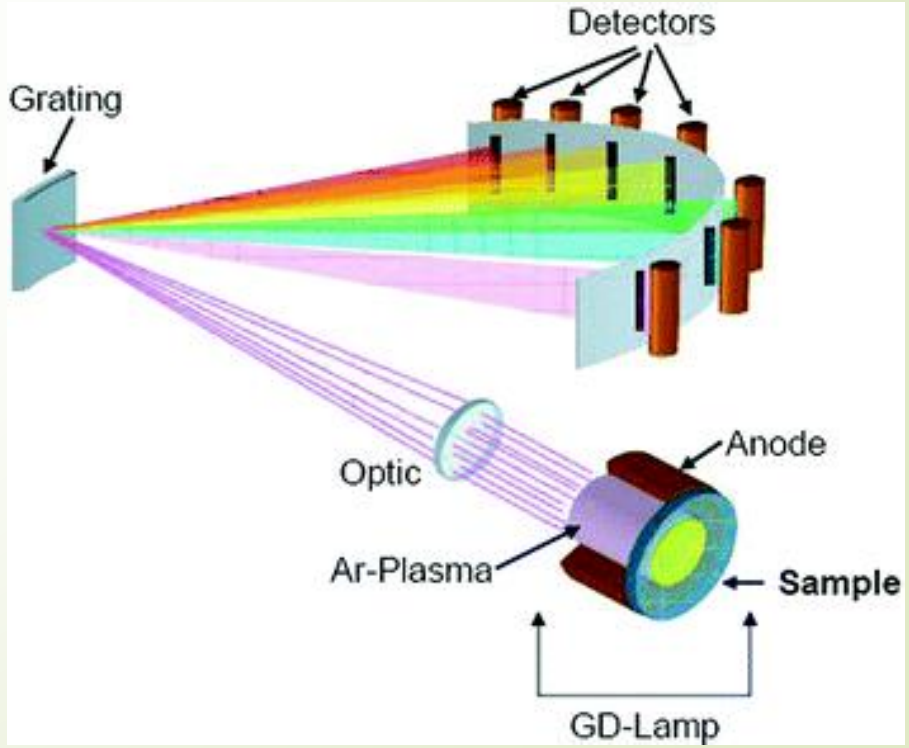




Optical Emission Spectroscopy (OES)



- Standard method of analysis for archeological materials from 1950-1980
  - Pottery, obsidian, faience, and metals
- Samples are volatilized by an electric spark
  - Causes sample to atomize and emit light
- Light spectrum is focused onto a diffraction grating
  - Grating separates wavelengths (colors)
  - Each wavelength is measured separately by photomultiplier tubes
- Disadvantages:
  - Reproducibility is a challenge
  - Originally used photographic film



Photomultiplier Tubes

- Used to dramatically increase weak signals in analytical instruments
- Incoming photon (signal) passes through a window and strikes a metal surface
- An electron is ejected and accelerated toward another positively charged plate
- Upon striking metal plate, multiple electrons are ejected and again accelerated toward another plate
- The repeated process exponentially increases electrical signal

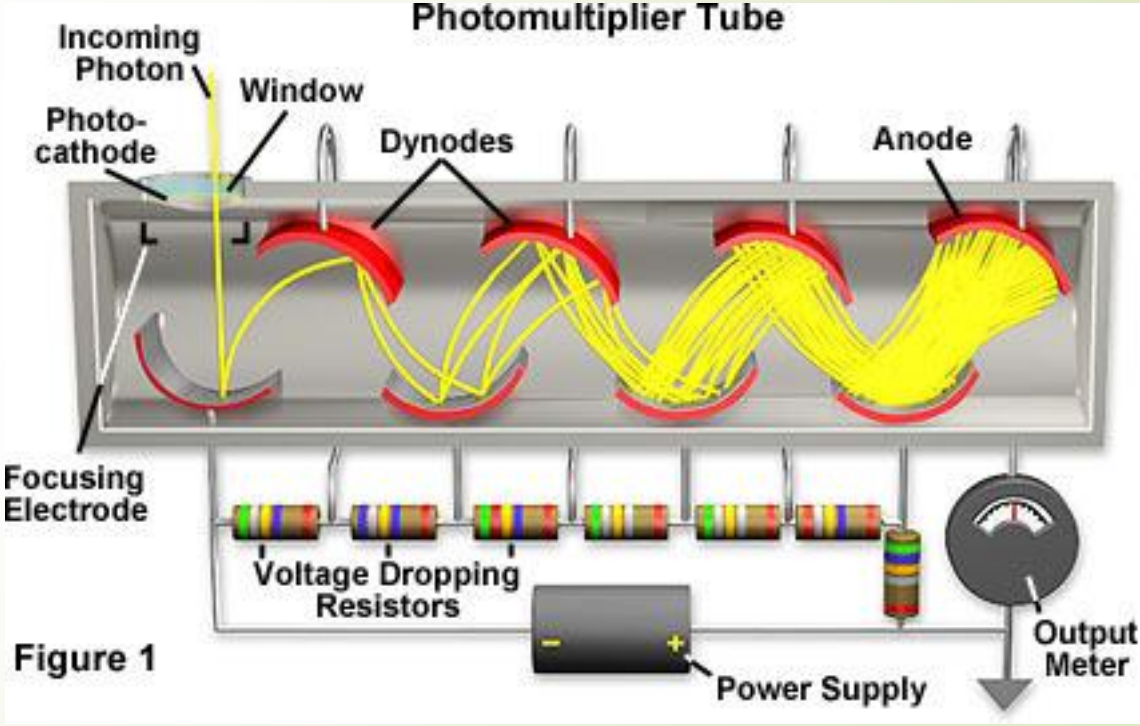
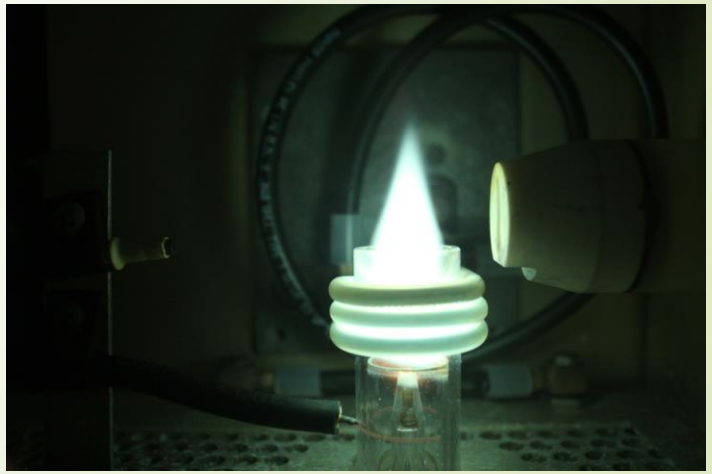


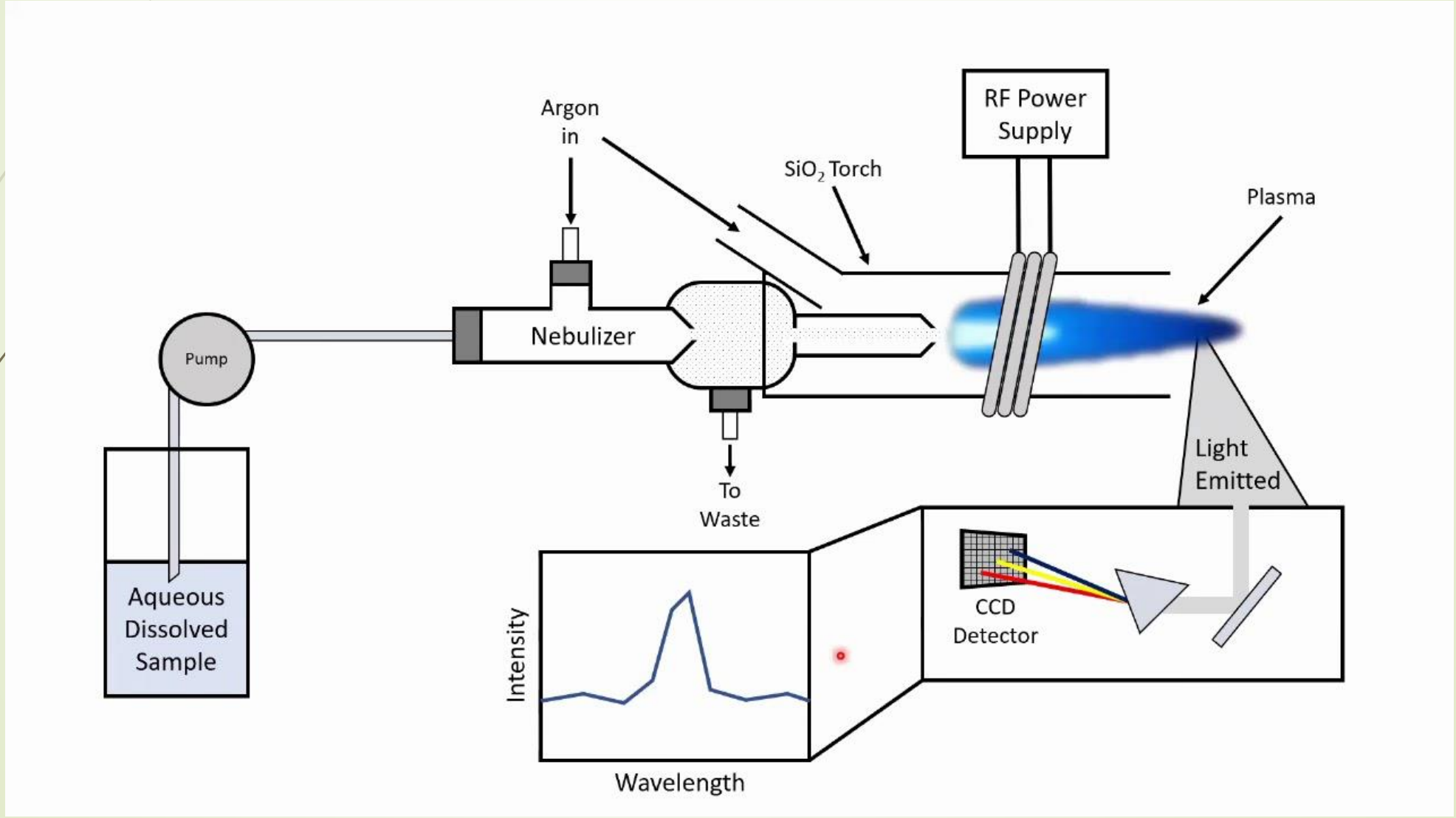
Figure 1

Inductively Coupled Plasma (ICP)

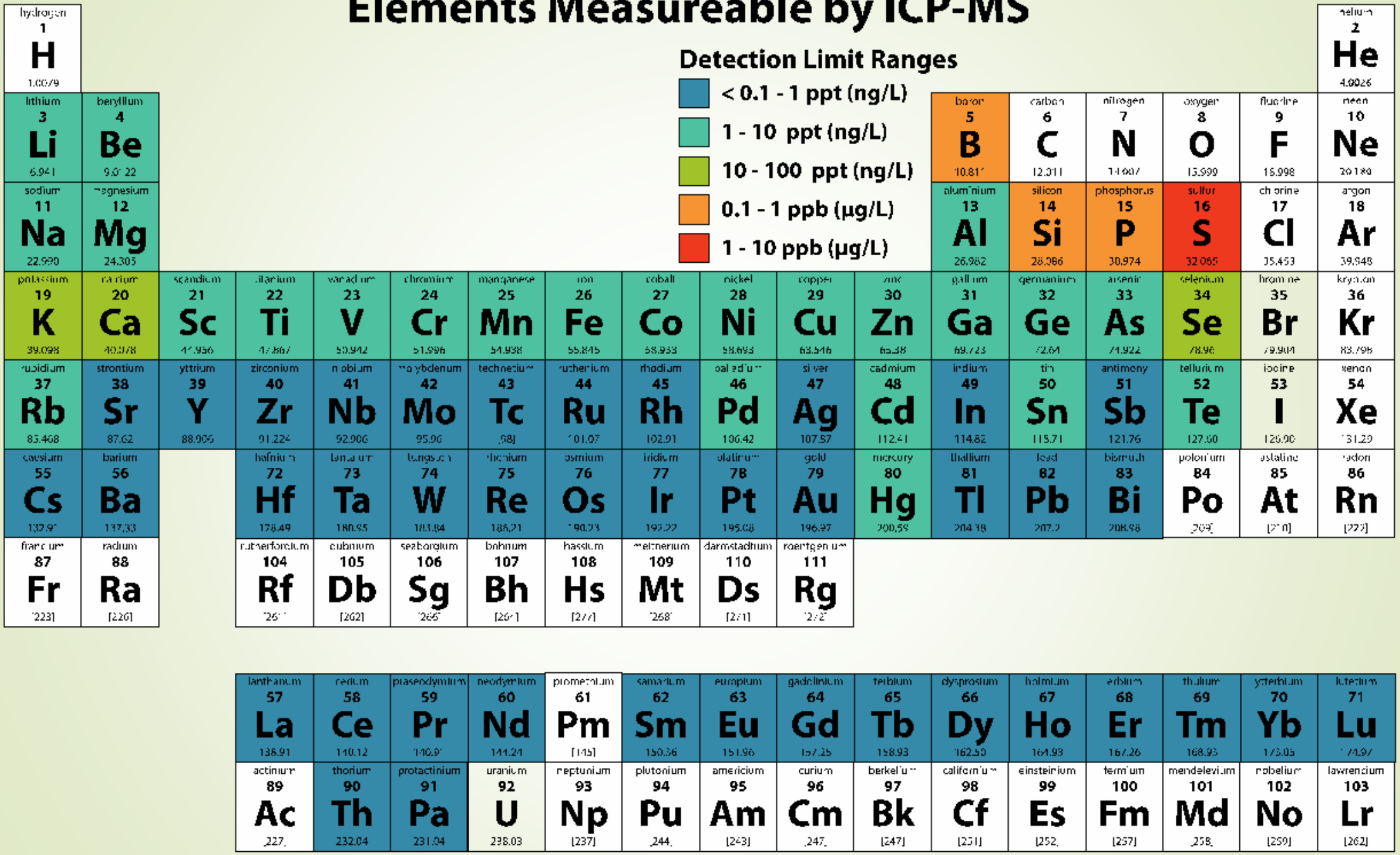
- Popular, modern technique for elemental analysis
- Similar to atomic absorption technique operated in emission mode
- Samples are injected into a stream of argon gas
- Argon is heated to 8000-10,000°C by alternating radio-frequency field carried by copper coils.
- Ionized elements oscillate in the RF field, frictional heating raises temps to final state
- Samples can be analyzed by ICP-OES upon deexcitation
- Samples can be analyzed by ICP-MS due to their charged nature
- Superb detection limits



Inductively Couple Plasma



Elements Measureable by ICP-MS



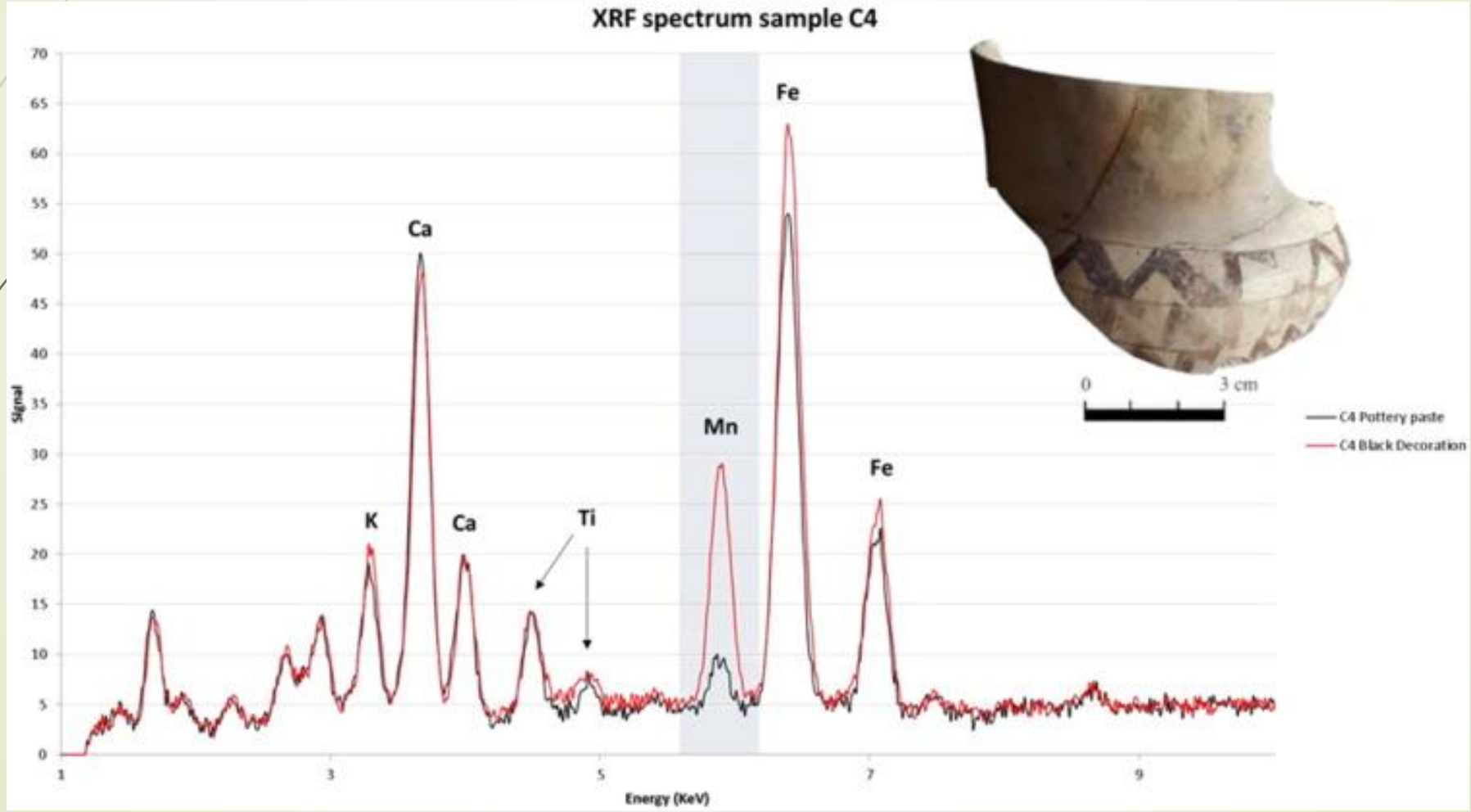
X-Ray Fluorescence (XRF)

- XRF is the emission of secondary x-rays from a material that has been excited by bombardment of primary, high-energy x-rays
- Common tool for rapid elemental analysis
  - Used for metals, ceramics, glass, and building materials
  - Geochemistry, forensic science, metallurgy, archeology, and art objects
- Measures composition of surface layer only (0.1-2 mm)
  - Bulk analysis requires homogenization of sample
- Inner shell electrons absorb primary x-ray and is excited to higher energy levels
  - De-excitation gives off characteristic secondary x-rays indicative of element

XRF of Pottery

XRF Lab – Field Museum

Analysis of Serra d'Alto *figuline* pottery (Matera, Italy):



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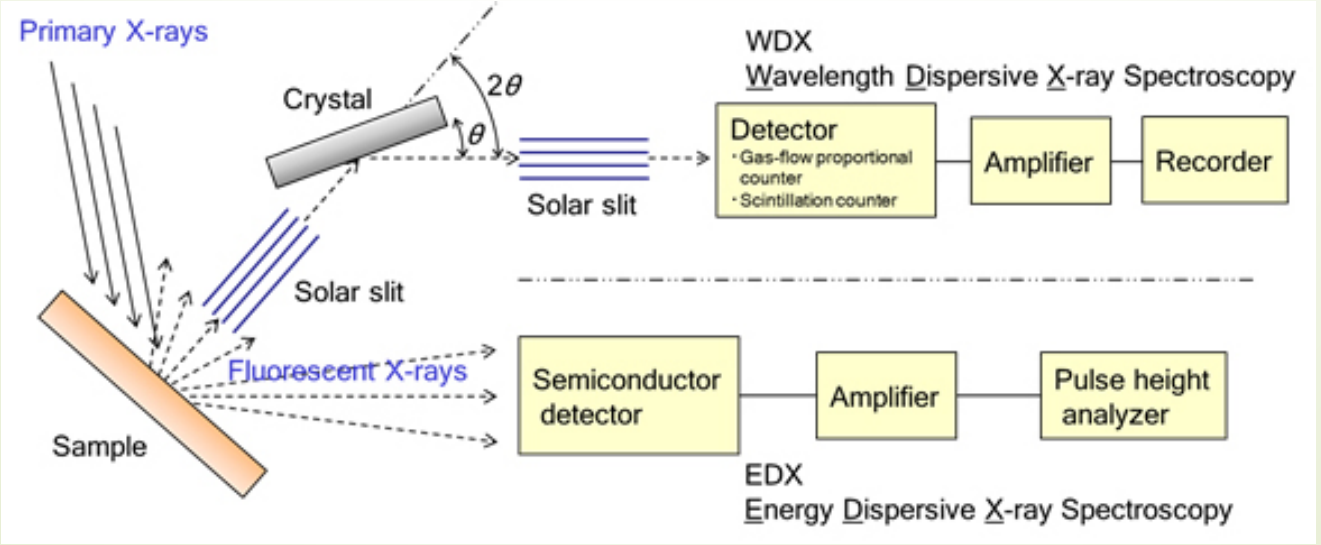
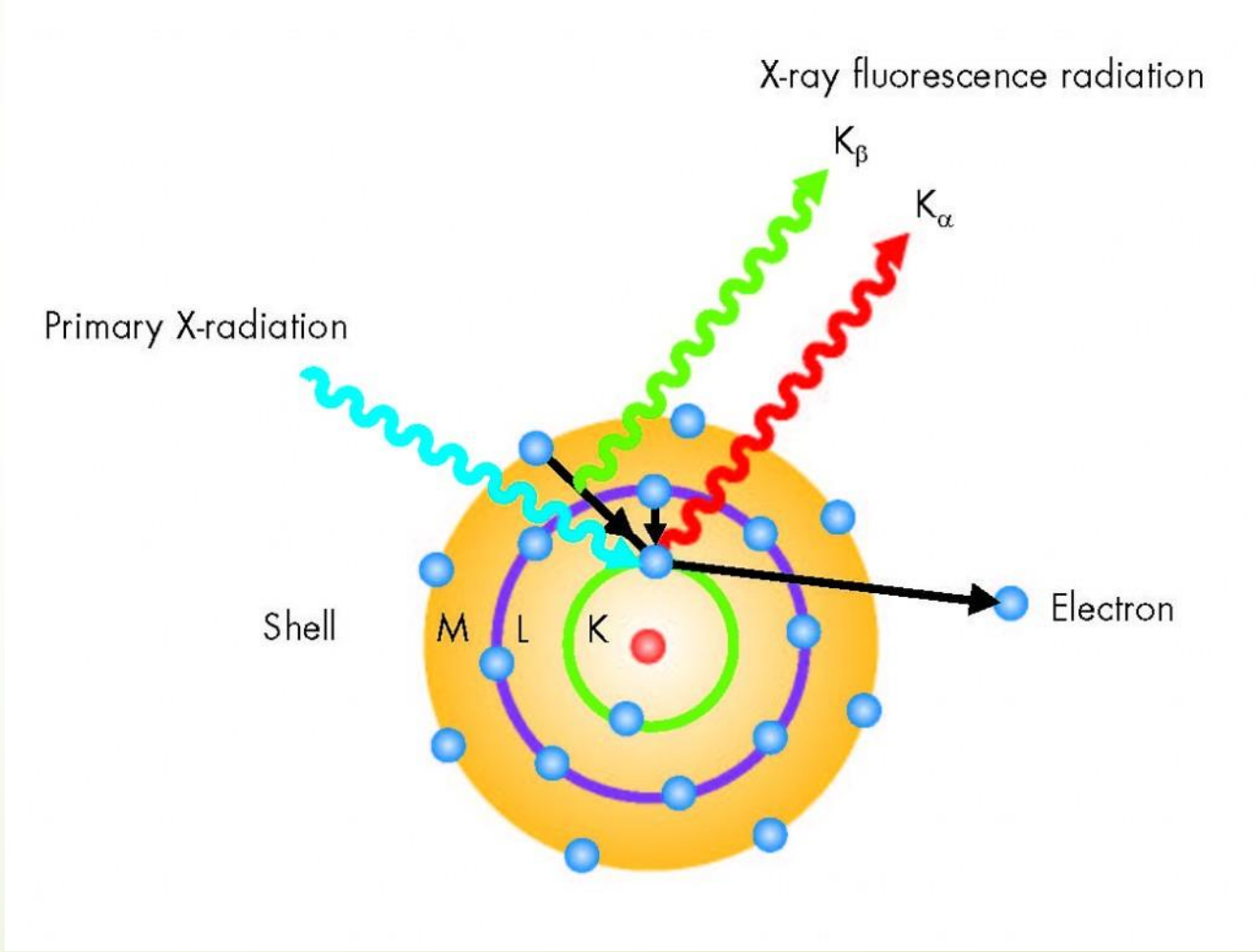
XRF Types

- XRF analysis can be performed two ways:
  - Wavelength Dispersive XRF
    - Secondary x-rays sorted by wavelength
  - Energy Dispersive XRF
    - Secondary x-rays sorted by energy



Where do the Secondary X-rays come from?

- Incoming primary x-rays are generated by bombarding certain metals (W or Mo) with electrons
- Primary x-rays will be either scattered or absorbed
- Absorbed x-rays eject inner-shell electrons from the atom
  - Atom replaces ejected electron with outer shell electrons

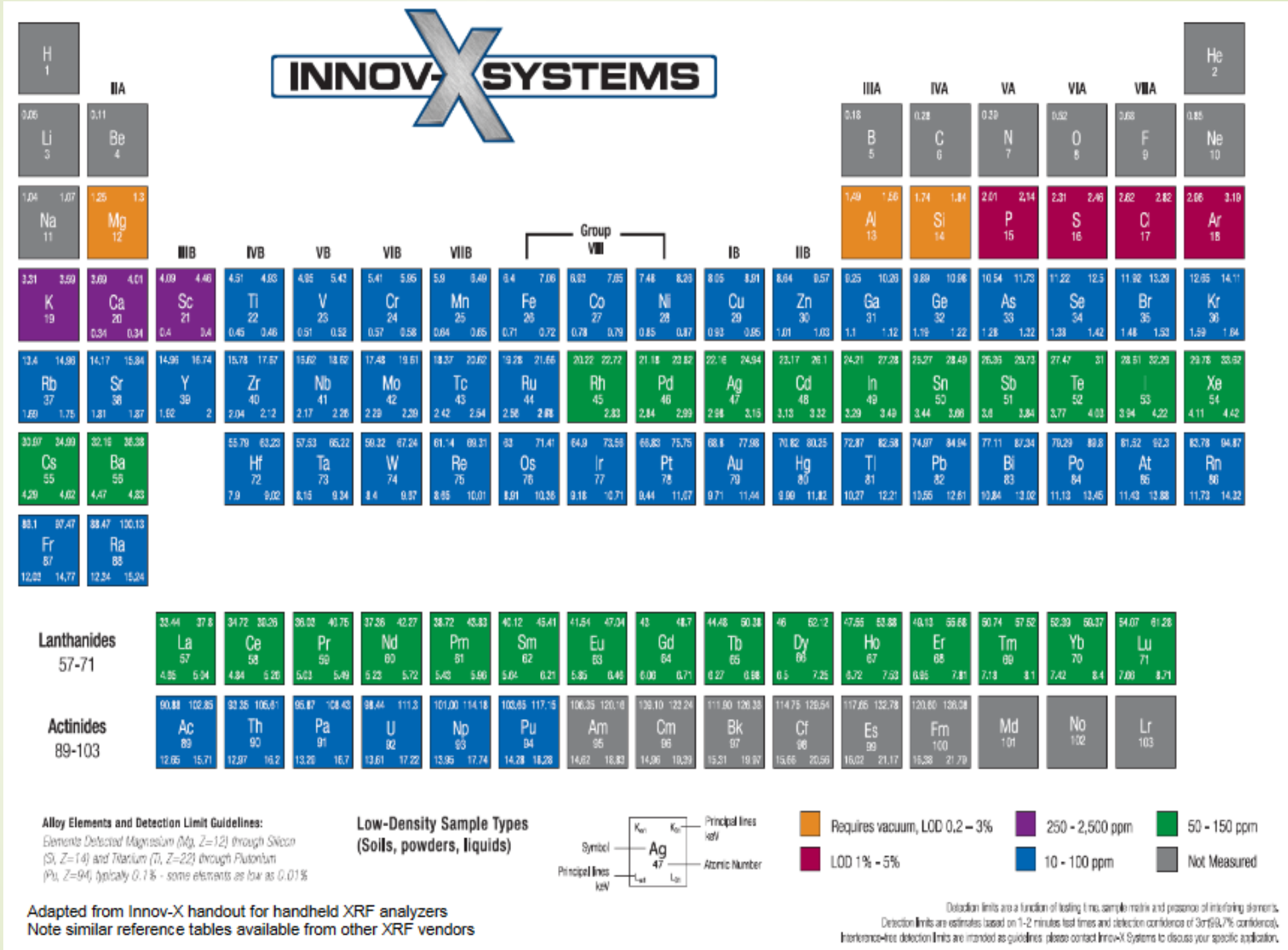


Laboratory (XRF) and Portable XRF (pXRF) Analyzers

XRF and pXRF Considerations

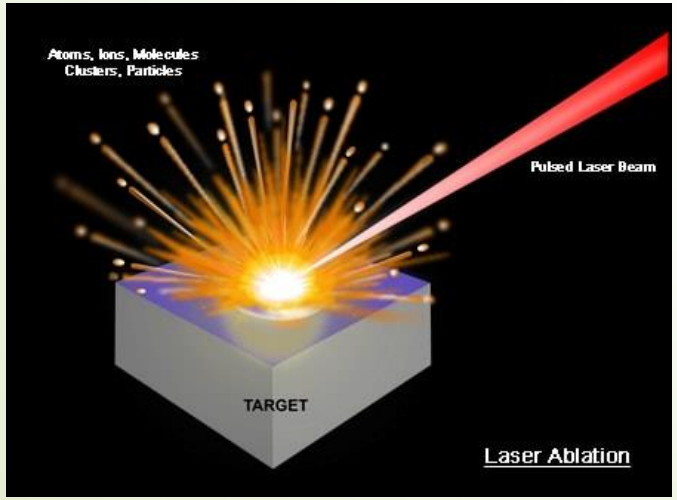
- Convenient for use with solid samples (surface analysis only)
- Sensitive to matrix composition
  - Requires experienced operator
- WDXRF (0.1 wt%) has better limits of detection than EDXRF (0.2-1 wt%) for the major light elements
  - Na, Mg, Al, Si….
- For trace elements, limits of detection are comparable (3-20 ppm)
  - Ni, Cu, Zn, Ga, Rb, Sr, Y, Zr, Nb, Pb, Th, and U
- pXRF should be considered as semi-quantitative without careful sample prep and matrix correction
- Lots of bad data being published based on pXRF
  - "decades of protocol developed for laboratory XRF analysis is completely ignored" Shackley 2010

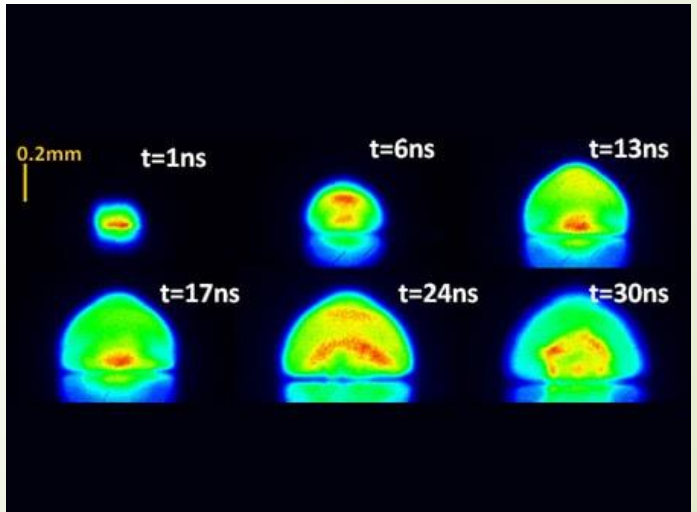
XRF Elements & Approximate Detection Limits

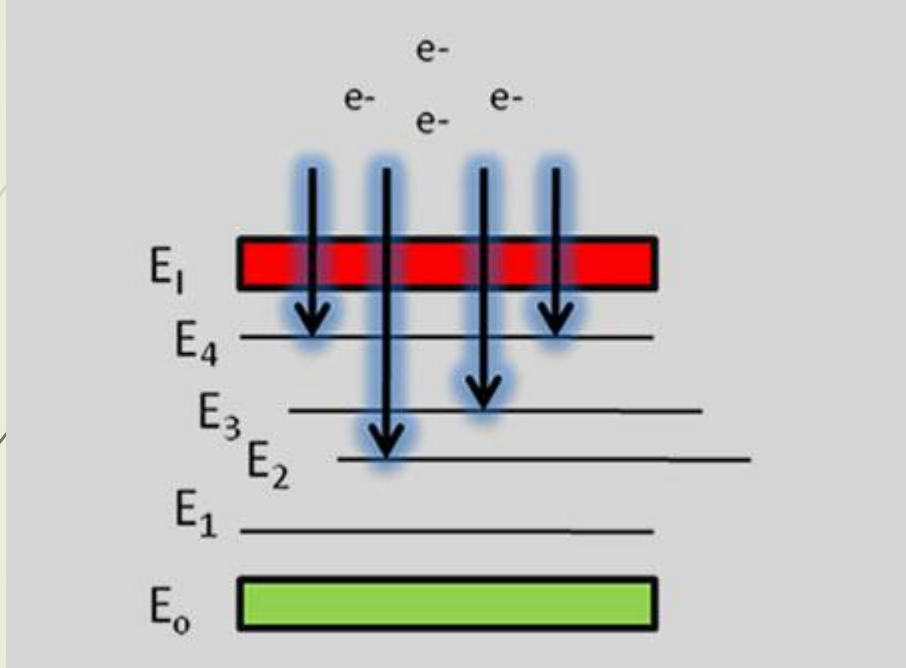


Laser Induced Breakdown Spectroscopy

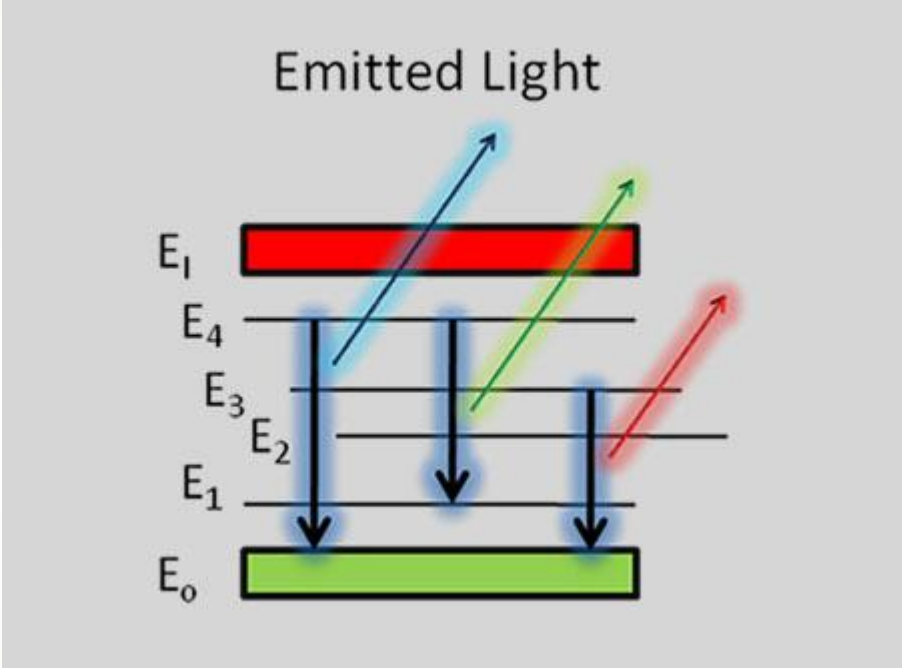
- A rapid chemical analysis technique that uses a short laser pulse to create a micro-plasma on the sample surface
- Focused laser pulse (10 ns) can vaporize surface spots (<1mm^2) to temperatures greater than 30,000°C
- Cooling plasma allows excited electrons to fall to lower energy levels, giving off characteristic wavelengths of light.



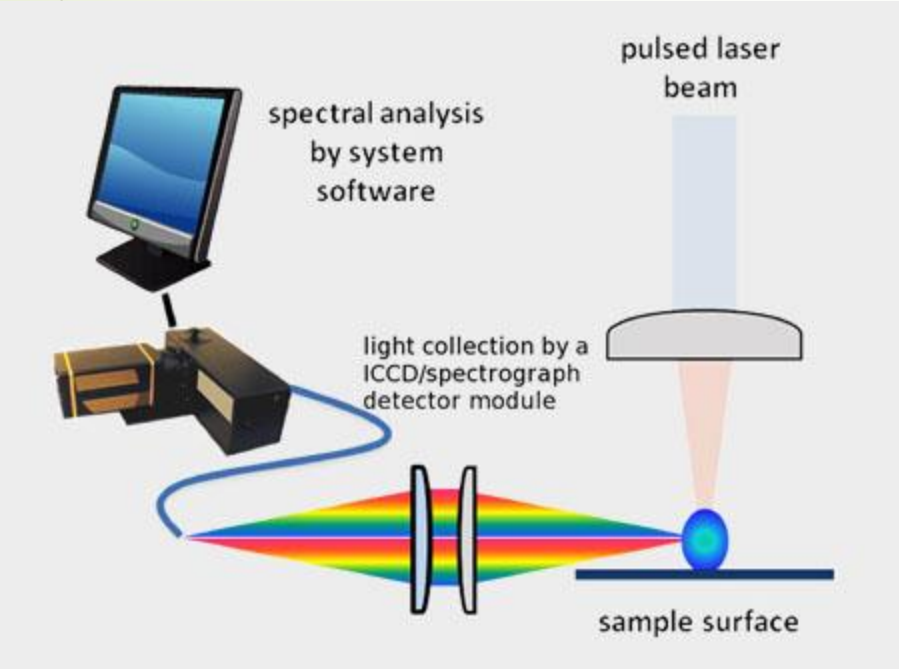




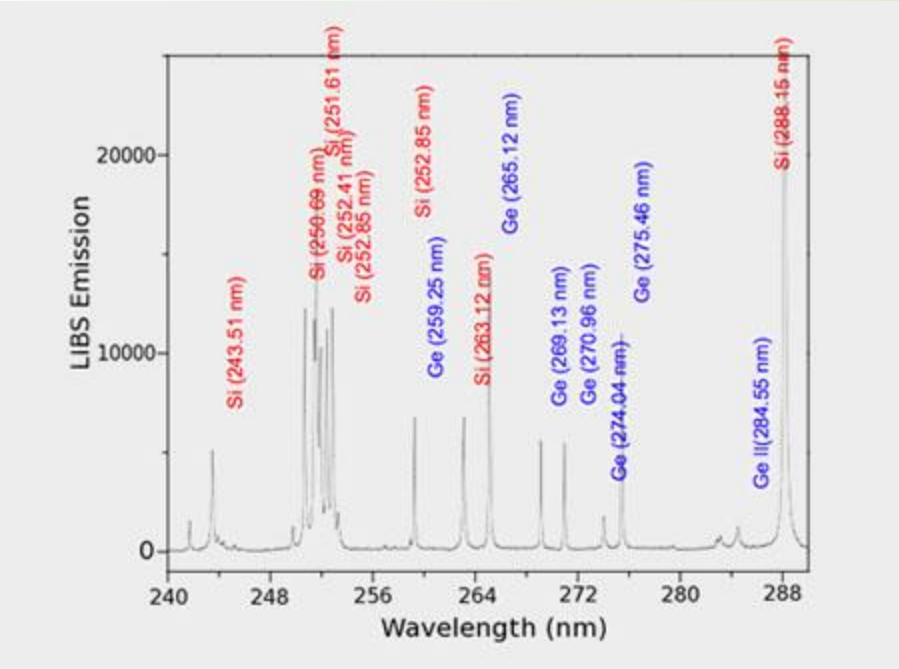
Emission of continuum light during early stage (< 200 ~ 300 nsec) of plasma cooling process.



Emission of discrete atomic lines at later times (> 1 μsec).

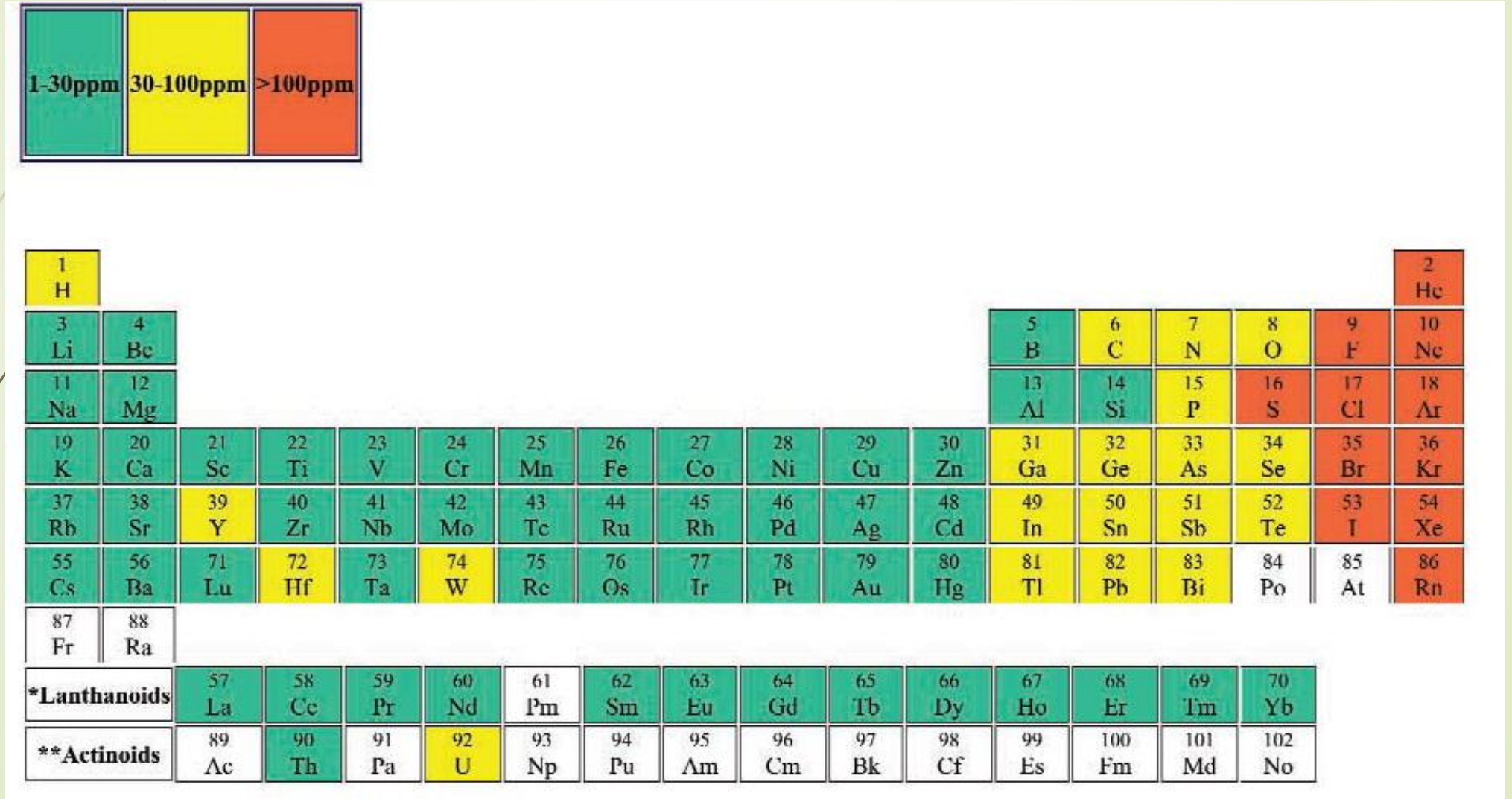


Emitted light collection by a set of optical lens and optical fiber.



Display of LIBS spectra and their subsequent analysis by the instrument software for both qualitative and quantitative elemental analysis

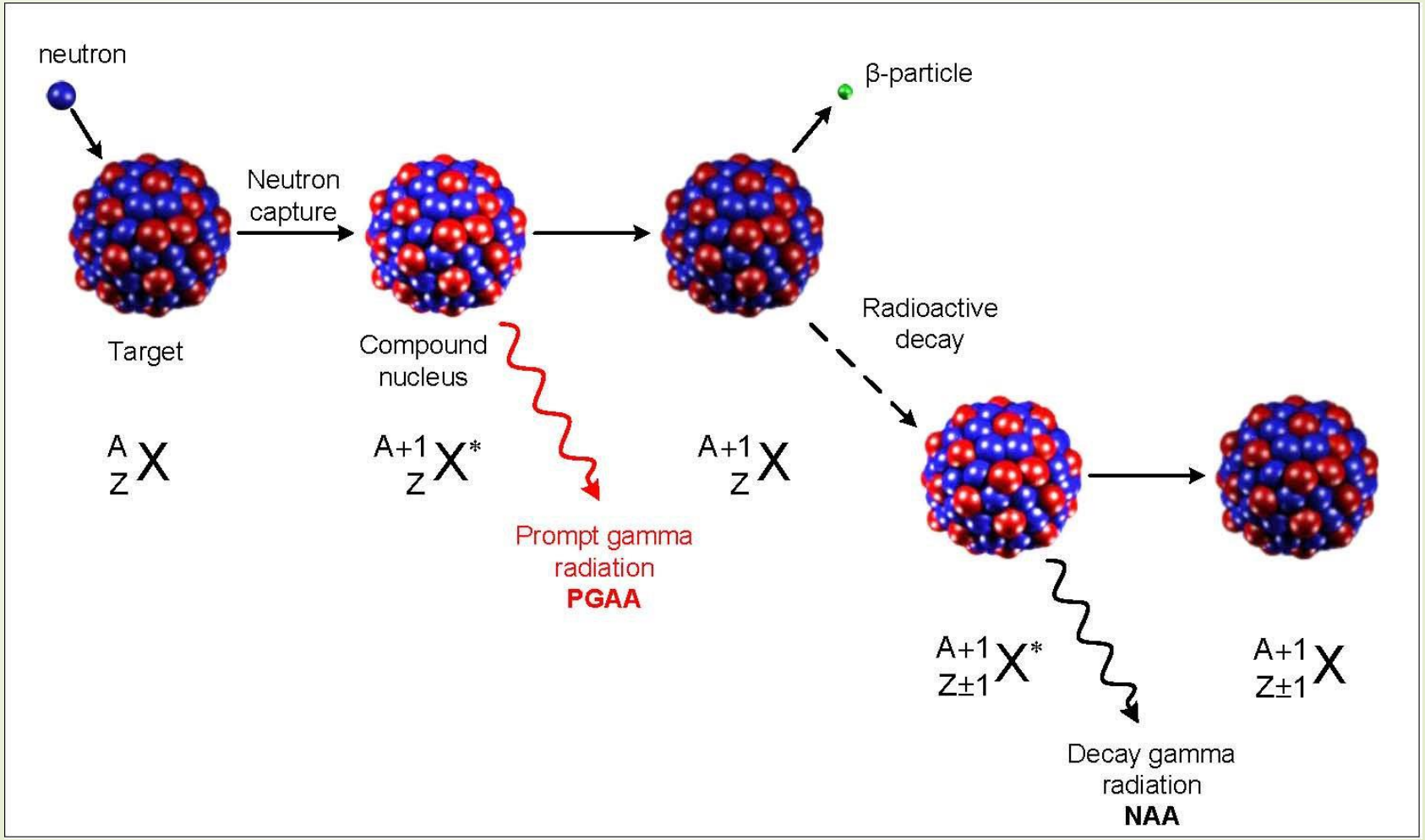
LIBS Detection Limits



Neutron Activation Analysis (NAA)

- Samples are irradiated by neutrons
  - Three ways: nuclear reactor, accelerator, nuclide source
- Elements capture neutrons and become radioactive
  - Radioactive elements then emit beta particles and gamma rays
- Gamma ray energies are unique to each element and measured by gamma ray detector
- Advantages are:
  - Up to 70 elements can be measured simultaneously
  - Extremely low detection limits, ppt to ppb
  - Highly precise (reproducible)
  - Only requires milligrams of sample

Inside the Nuclear Reactor
(Also includes accelerators)

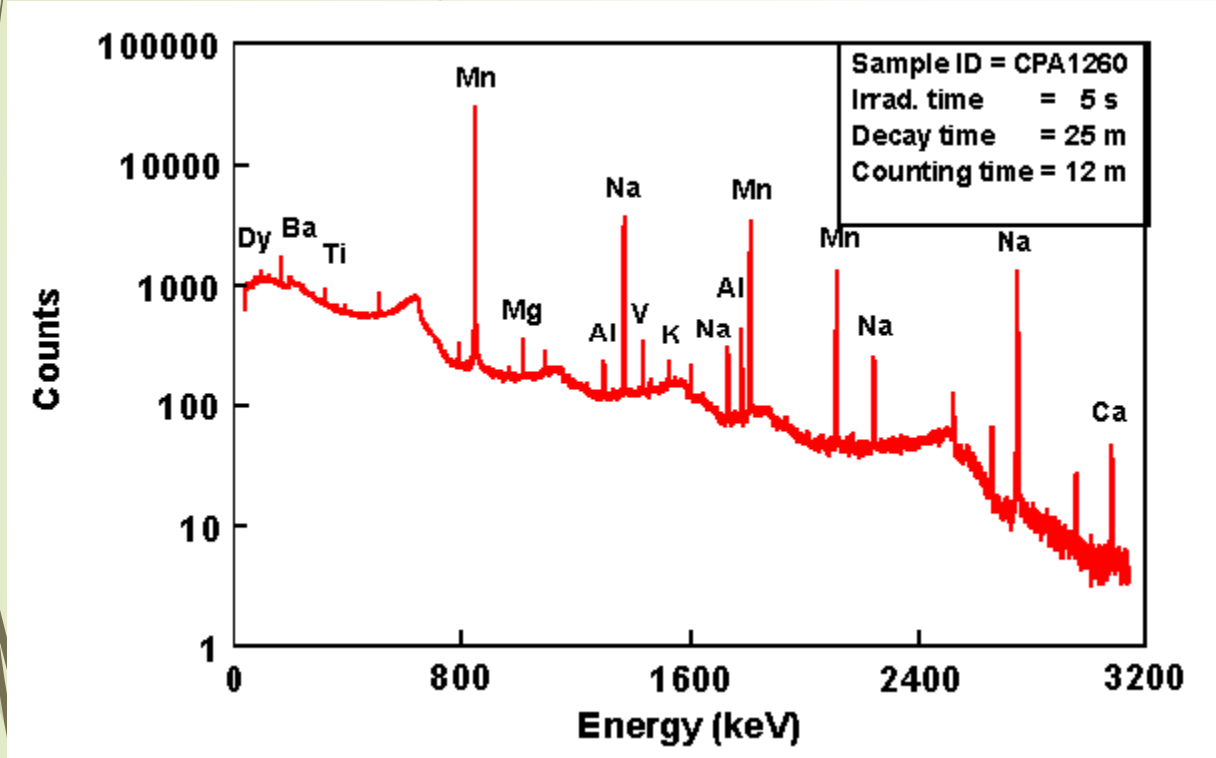


Inside the Nuclear Reactor – II
(Also includes accelerators)

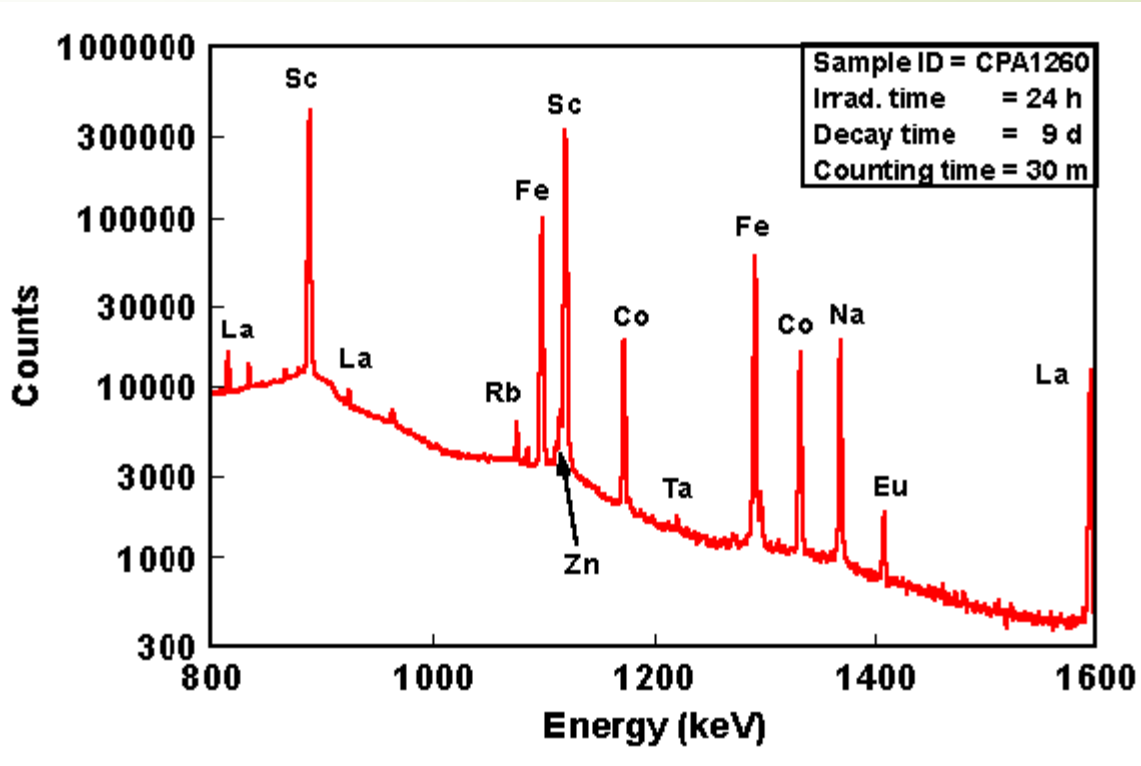
- Samples (e.g. soil, pottery) are ground to a fine powder
  - Placed in polyethylene or quartz tubes
  - Tubes placed in spinning wheel to irradiate all samples equally
  - Neutron flux must have energies of approximately 0.04 MeV
    - Moderators (wax, water, heavy water) can be used to slow neutrons
  - Neutrons lose energy through collisions until they reach thermal equilibrium
    - "Thermal Neutrons"
  - Samples capture neutrons in their nucleus and become neutron-rich
    - And also radioactive
- After samples are removed from neutron source, they remain radioactive for weeks
  - Measured by scintillation detectors (e.g. NaI)

Measurement of the Radioactivity

NAA Results from MURR



Gamma-ray spectrum showing several short-lived elements measured in a sample of pottery irradiated for 5 seconds, decayed for 25 minutes, and counted for 12 minutes with an HPGe detector.



Gamma-ray spectrum from 800 to 1600 keV showing medium- and long-lived elements measured in a sample of pottery irradiated for 24 hours, decayed for 9 days, and counted for 30 minutes on a HPGe dectector.

Which technique is better?

- There is no one 'best' technique.
- The most appropriate technique depends on:
  - Availability of technique
  - Accuracy and precision considerations
  - Physical state of sample to be analyzed (solid, liquid, gas)
  - Matrix of sample (soil, pottery, pigment, etc…), interfering elements
  - Detection limit(s)
  - Destructive vs. non-destructive analysis
  - Cost of analysis

Comparison of Techniques

Technique	Strengths	Limitations	Applications	System
Flame AAS – Flame Atomic Absorption Spectroscopy	Very easy-to-use Widely accepted Reference method in many fields Wide application range	Low sensitivity Sequential analysis Use of flammable gas	Ideal for laboratories analyzing many samples for up to six elements and for the determination of concentrations in ppm level	**AA-7000F**
GFAAS – Graphite Furnace Atomic Absorption Spectroscopy	Inexpensive Low detection limits Wide application range Unatteneded operation	Limited analytical working range Sample throughput limited in comparison to flame AAS or ICP-OES	Ideal for laboratories analyzing many samples for up to six elements at low detection limits with typical concentrations in ppb level	**AA-7000G + GFA-7000**
ICP-OES – Inductively Coupled Plasma Optical Emission Spectroscopy	Fast analytical speed Simultaneous multi-element analysis Highest sample throughput Widest analytical range Good documentation Wide application range Unatteneded operation Qualitative and quantitative analysis	Higher initial investment	Ideal for laboratories doing multi-element analysis on a large number of samples in ppm to ppb level	**ICPE-9000**
ED-XRF – Energy Dispersive X-ray Fluorescence Spectroscopy	Easy-to-use Non destructive analysis Fast screening No need for sample pretreatment	Lower precision at low concentration levels	Ideal for laboratories doing fast analysis in the upper ppm to % level with no sample preparation	**EDX-720P/800P**

Image References

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