



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)



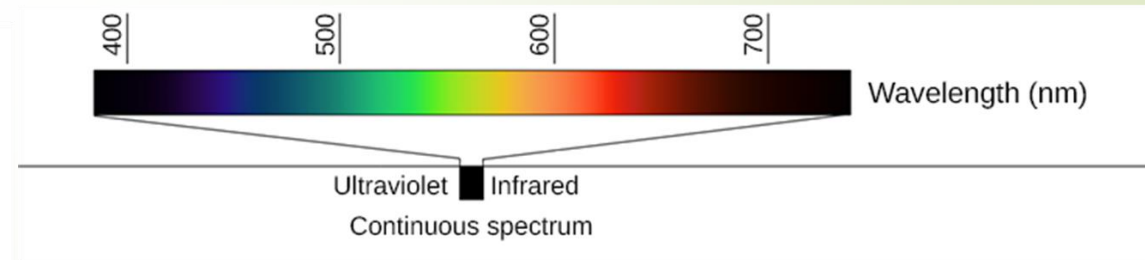
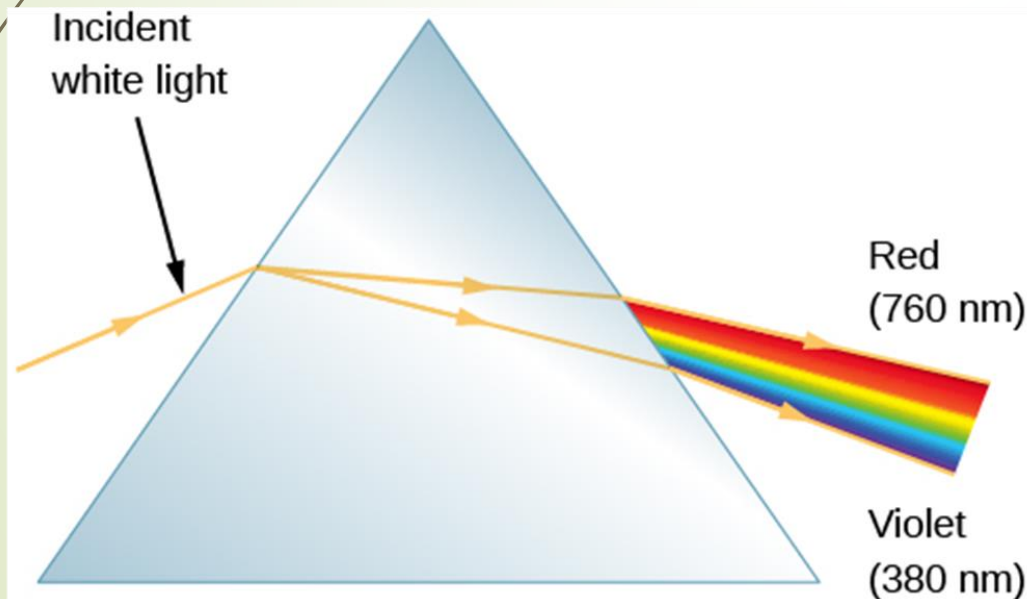
Wet Chemical techniques

- 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

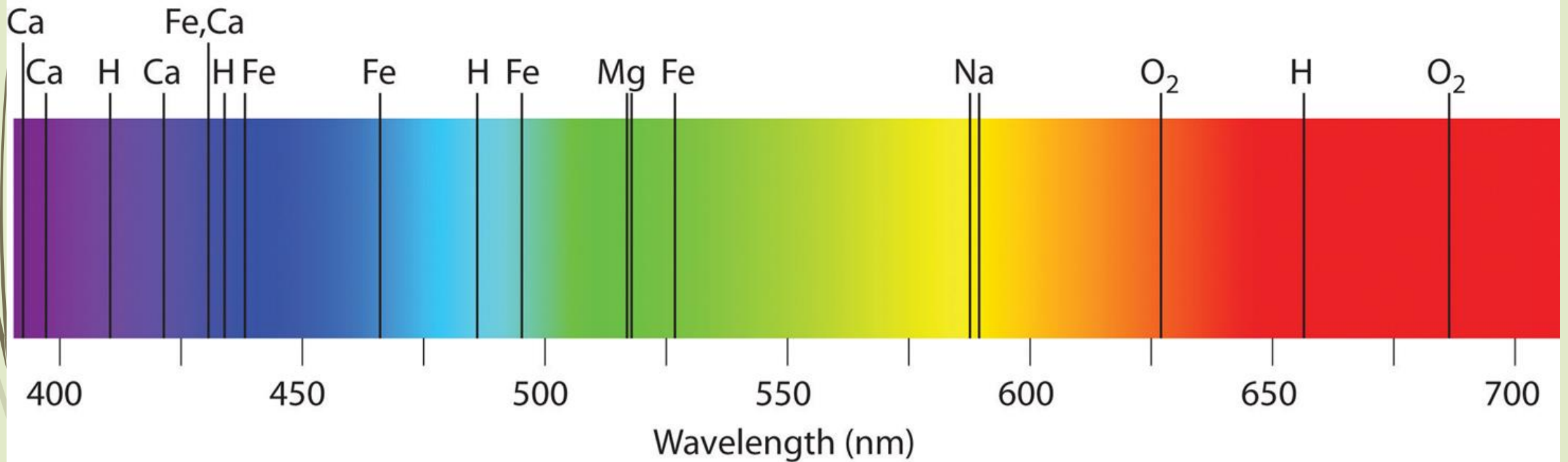


Properties of Light

- 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



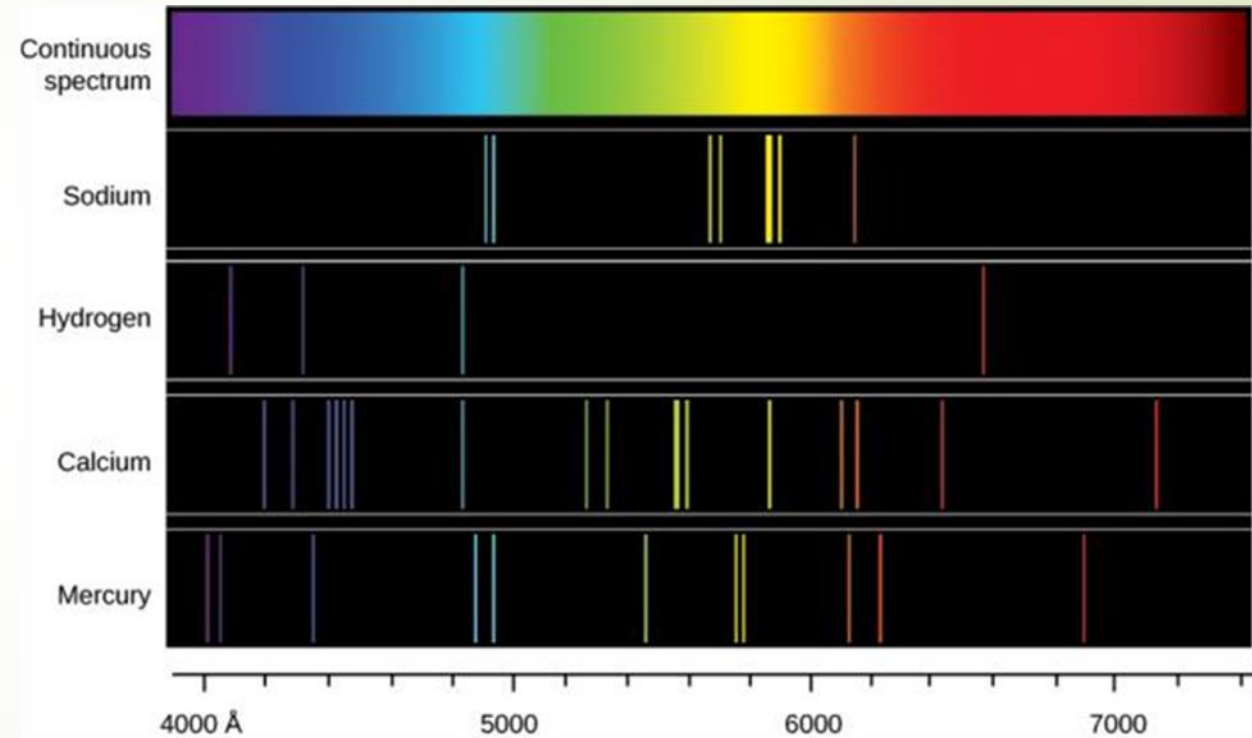
Sunlight Spectrum



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

Chemical Fingerprints

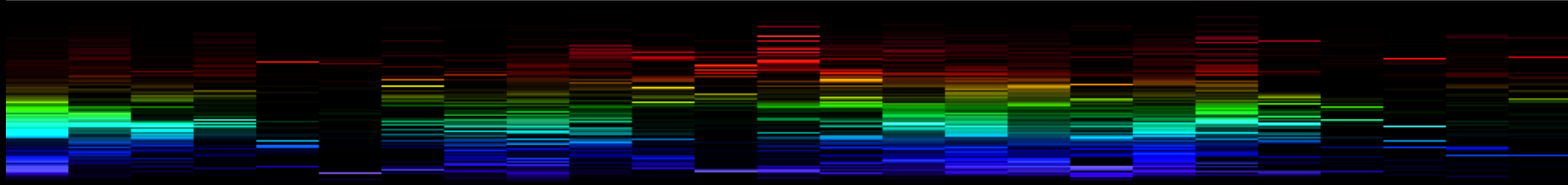
- Absorption lines and emission lines are indicative of chemical elements
- Each element has its own unique set of lines



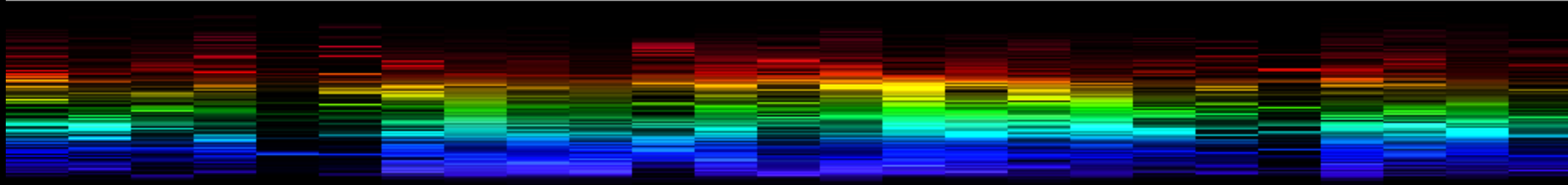
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H	He	Li	Be	B	C	N	O	F	Ne	Na	Mg	Al	Si	P	S	Cl	Ar	K	Ca	Sc	Ti	V	Cr	Mn
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Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn
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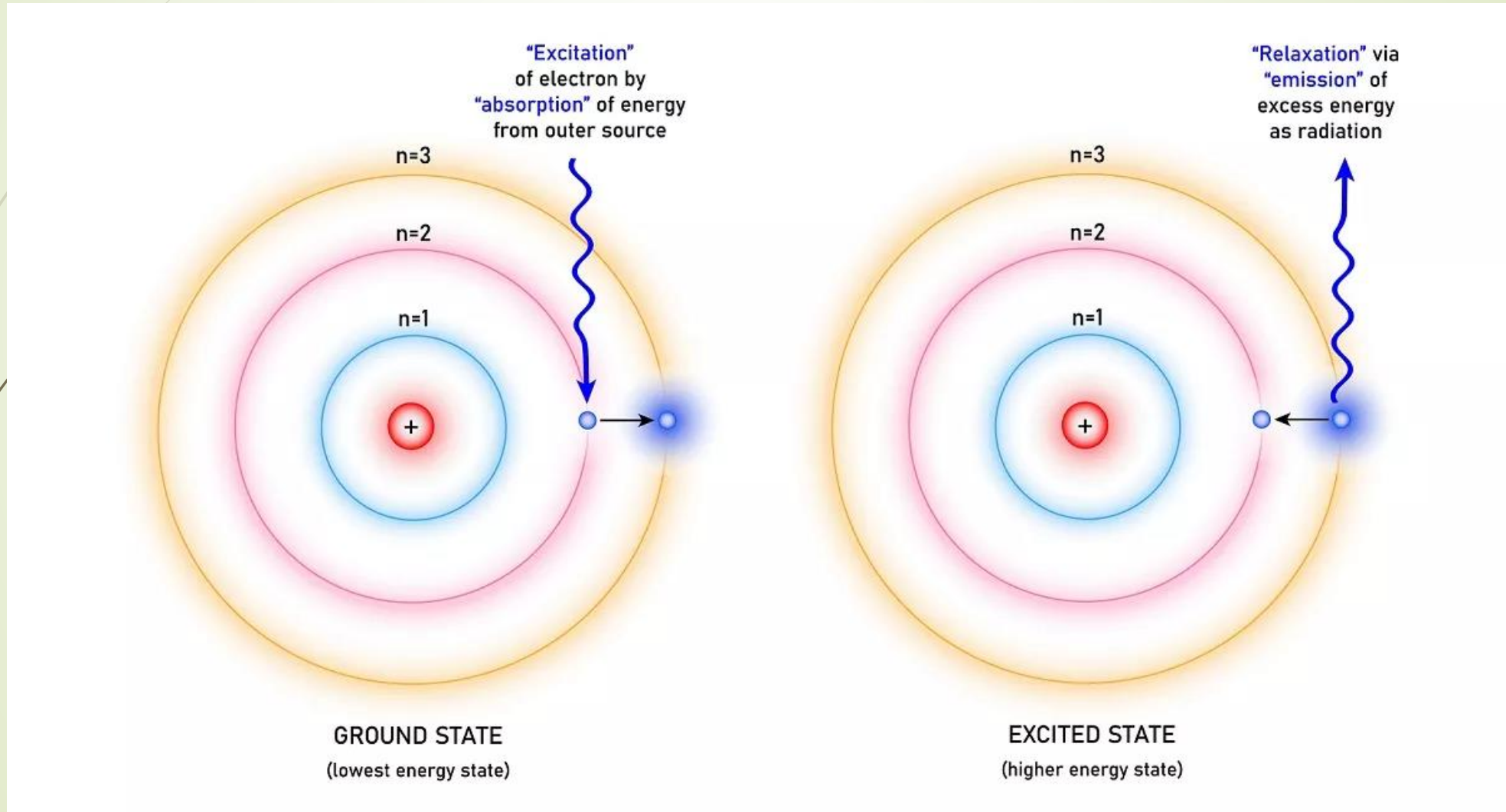


Sb	Te	I	Xe	Cs	Ba	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Hf	Ta	W	Re
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Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn	Fr	Ra	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es
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Excitation and De-Excitation of the Electron



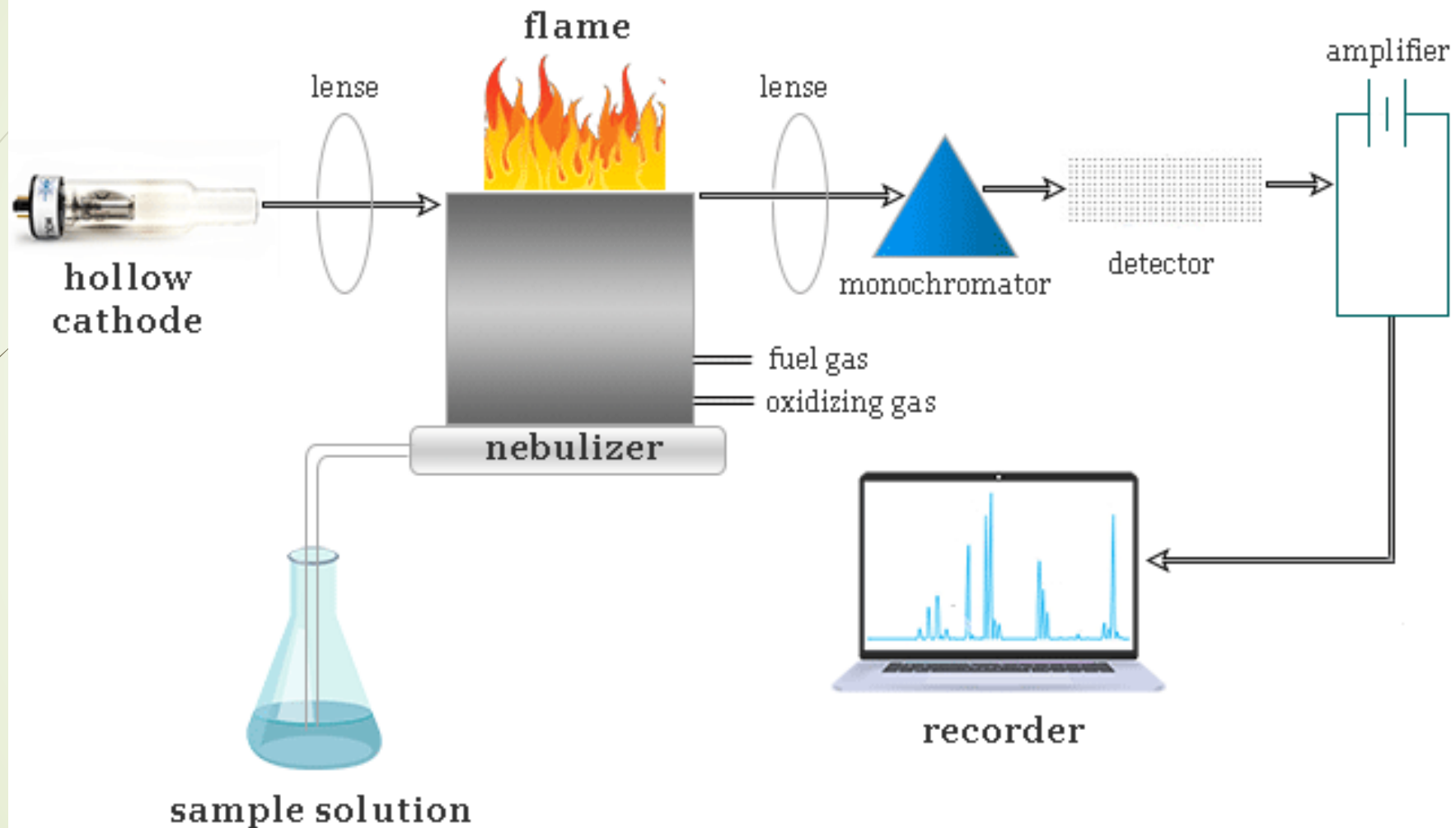
Atomic Absorption Spectrometry (AAS)

- ▶ 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

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AAS Principles

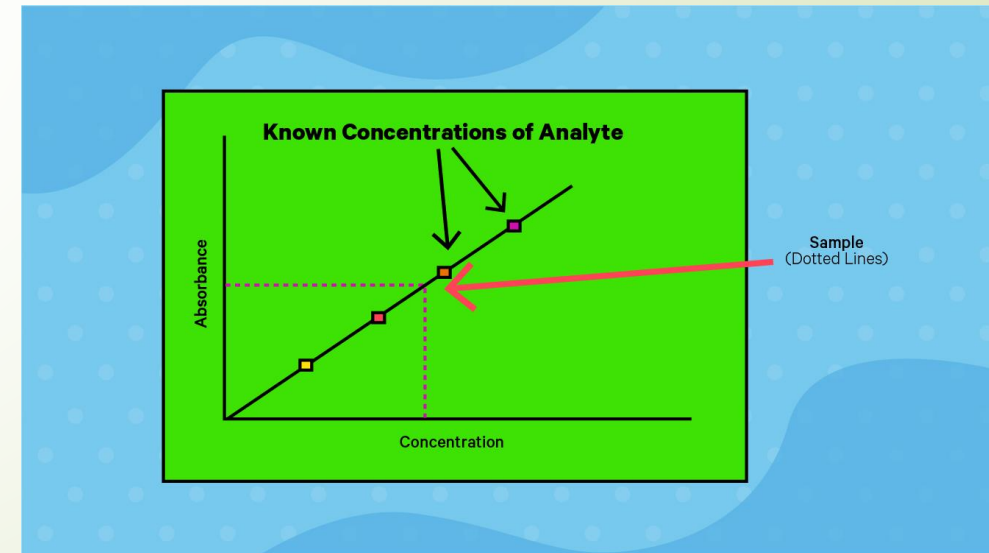
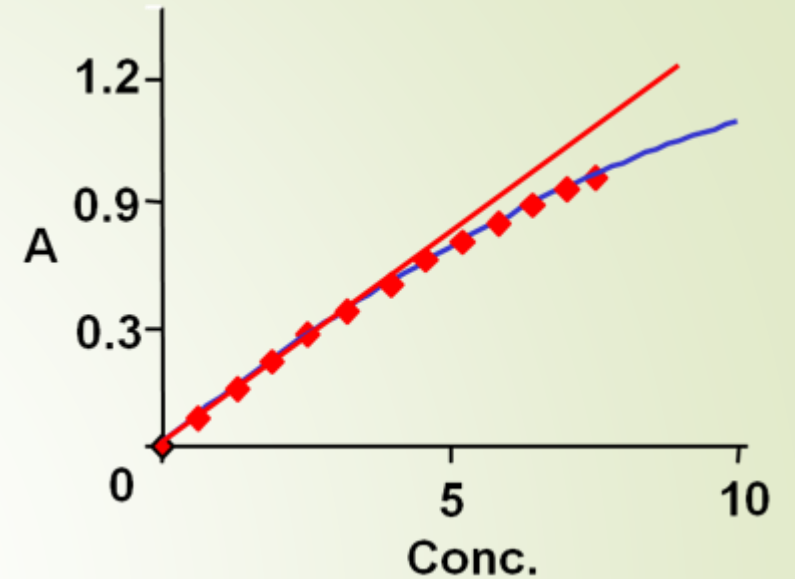
- ▶ A hollow-cathode Lamp (HCL) must be selected to match the element of interest
- ▶ Excitation of the tube produces emission lines only for that element
- ▶ Flame/furnace atomizes the sample
- ▶ If element is present, it will absorb the wavelength emitted by the HCL
- ▶ Decrease in signal is proportional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



Hollow-cathode lamps for analysis of Sr and Ba

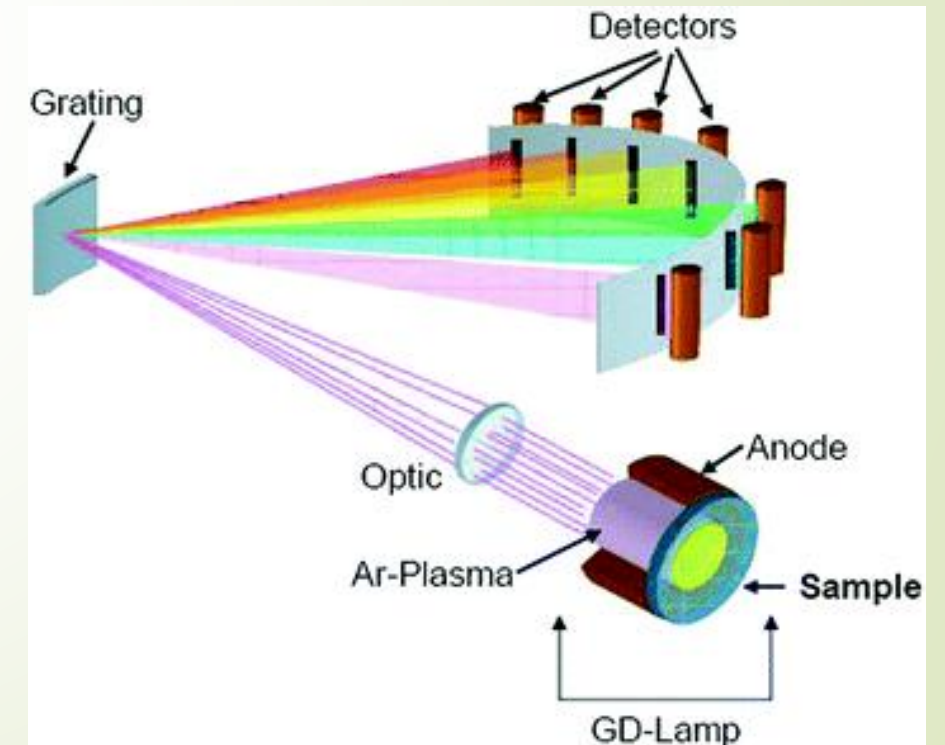
Analysis Technique

- ▶ 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)



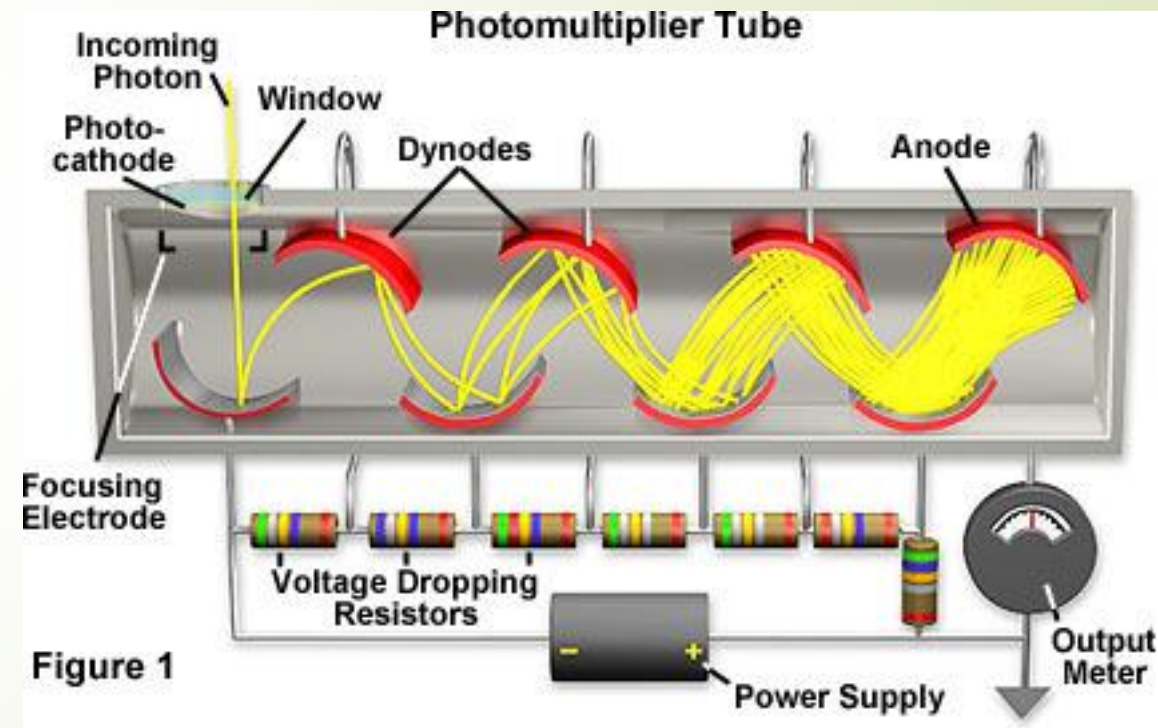
Optical Emission Spectroscopy (OES)

- ▶ 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



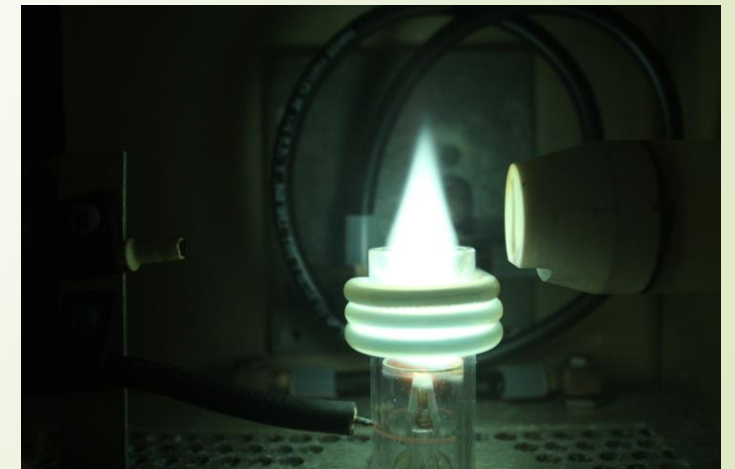
Photomultiplier Tubes

- 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

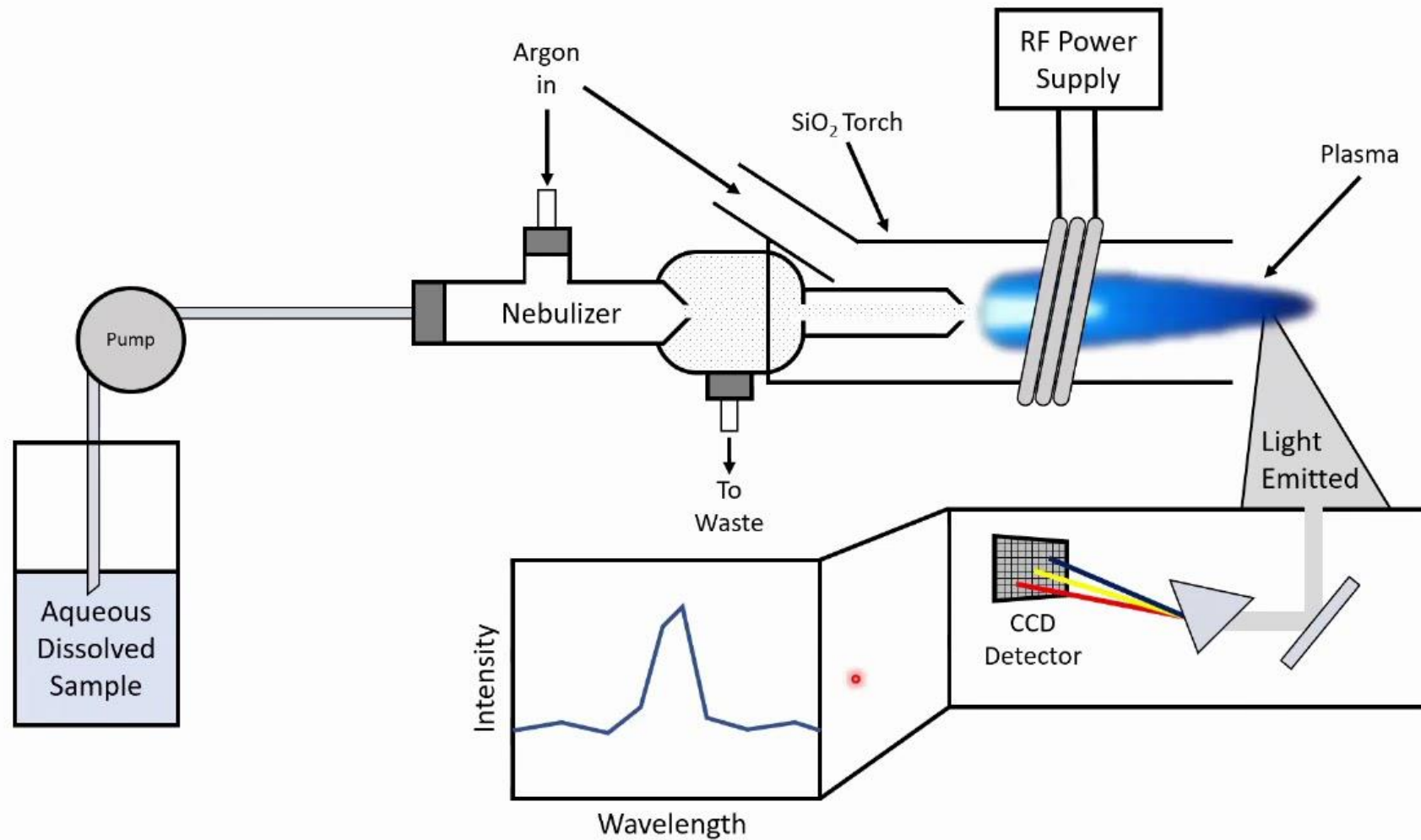


Inductively Coupled Plasma (ICP)

- 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

Elements Measureable by ICP-MS																	
hydrogen 1 H 1.0079															helium 2 He 4.0026		
lithium 3 Li 6.941	beryllium 4 Be 9.0122																
sodium 11 Na 22.990	magnesium 12 Mg 24.305																
potassium 19 K 39.098	calcium 20 Ca 40.078	scandium 21 Sc 44.956	titanium 22 Ti 47.867	vanadium 23 V 50.942	chromium 24 Cr 51.996	manganese 25 Mn 54.938	iron 26 Fe 55.845	cobalt 27 Co 58.933	nickel 28 Ni 58.693	copper 29 Cu 63.546	zinc 30 Zn 65.38	gallium 31 Ga 69.723	germanium 32 Ge 72.64	arsenic 33 As 74.922	selenium 34 Se 78.96	bromine 35 Br 79.904	krypton 36 Kr 83.796
rubidium 37 Rb 85.468	strontium 38 Sr 87.62	yttrium 39 Y 88.906	zirconium 40 Zr 91.224	niobium 41 Nb 92.906	molybdenum 42 Mo 95.96	technetium 43 Tc [98]	ruthenium 44 Ru 101.07	rhodium 45 Rh 102.91	palladium 46 Pd 106.42	silver 47 Ag 107.87	cadmium 48 Cd 112.41	indium 49 In 114.82	tin 50 Sn 118.71	antimony 51 Sb 121.76	tellurium 52 Te 127.60	iodine 53 I 126.90	xenon 54 Xe 131.29
caesium 55 Cs 132.91	barium 56 Ba 137.33	hafnium 72 Hf 178.49		tantalum 73 Ta 180.95	tungsten 74 W 183.84	rhenium 75 Re 186.21	osmium 76 Os 190.23	iridium 77 Ir 192.22	platinum 78 Pt 195.08	gold 79 Au 196.97	mercury 80 Hg 200.59	thallium 81 Tl 204.38	lead 82 Pb 207.2	bismuth 83 Bi 208.98	polonium 84 Po [209]	astatine 85 At [210]	radon 86 Rn [222]
francium 87 Fr [223]	radium 88 Ra [226]	rutherfordium 104 Rf [261]		dubnium 105 Db [262]	seaborgium 106 Sg [266]	bohrium 107 Bh [267]	hassium 108 Hs [277]	meitnerium 109 Mt [268]	darmstadtium 110 Ds [271]	roentgenium 111 Rg [272]							

Detection Limit Ranges

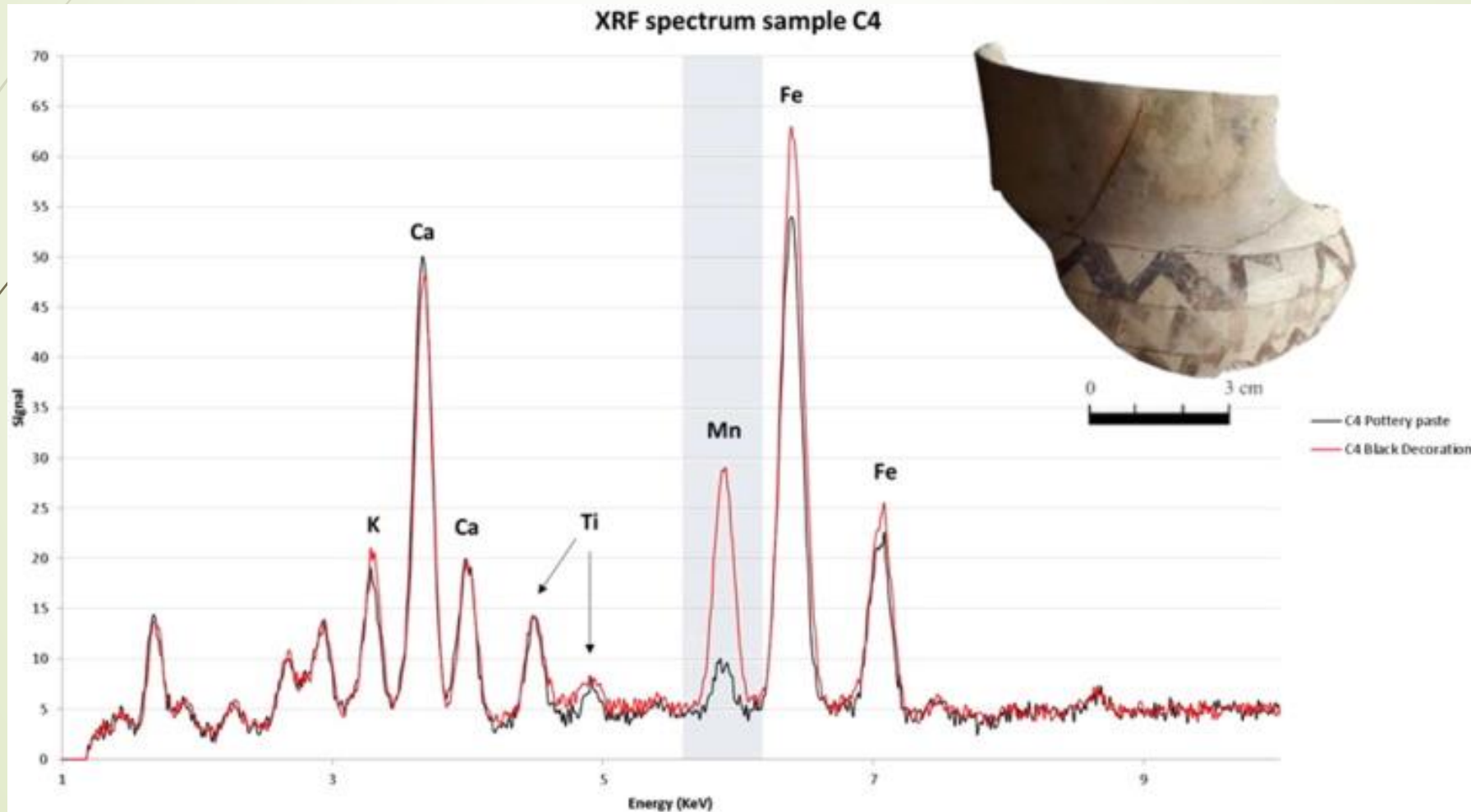
- < 0.1 - 1 ppt (ng/L)
- 1 - 10 ppt (ng/L)
- 10 - 100 ppt (ng/L)
- 0.1 - 1 ppb (µg/L)
- 1 - 10 ppb (µg/L)

lanthanum 57 La 138.91	cerium 58 Ce 140.12	praseodymium 59 Pr 140.91	neodymium 60 Nd 144.24	promethium 61 Pm [145]	samarium 62 Sm 150.36	europium 63 Eu 151.96	gadolinium 64 Gd 157.25	terbium 65 Tb 158.93	dysprosium 66 Dy 162.50	holmium 67 Ho 164.93	erbium 68 Er 167.26	thulium 69 Tm 168.93	ytterbium 70 Yb 173.05	lutetium 71 Lu 174.97
actinium 89 Ac [227]	thorium 90 Th 232.04	protactinium 91 Pa 231.04	uranium 92 U 238.03	neptunium 93 Np [237]	plutonium 94 Pu [244]	americium 95 Am [243]	curium 96 Cm [247]	berkelium 97 Bk [247]	californium 98 Cf [251]	einsteinium 99 Es [252]	fermium 100 Fm [257]	mendelevium 101 Md [258]	nobelium 102 No [259]	lawrencium 103 Lr [262]

X-Ray Fluorescence (XRF)

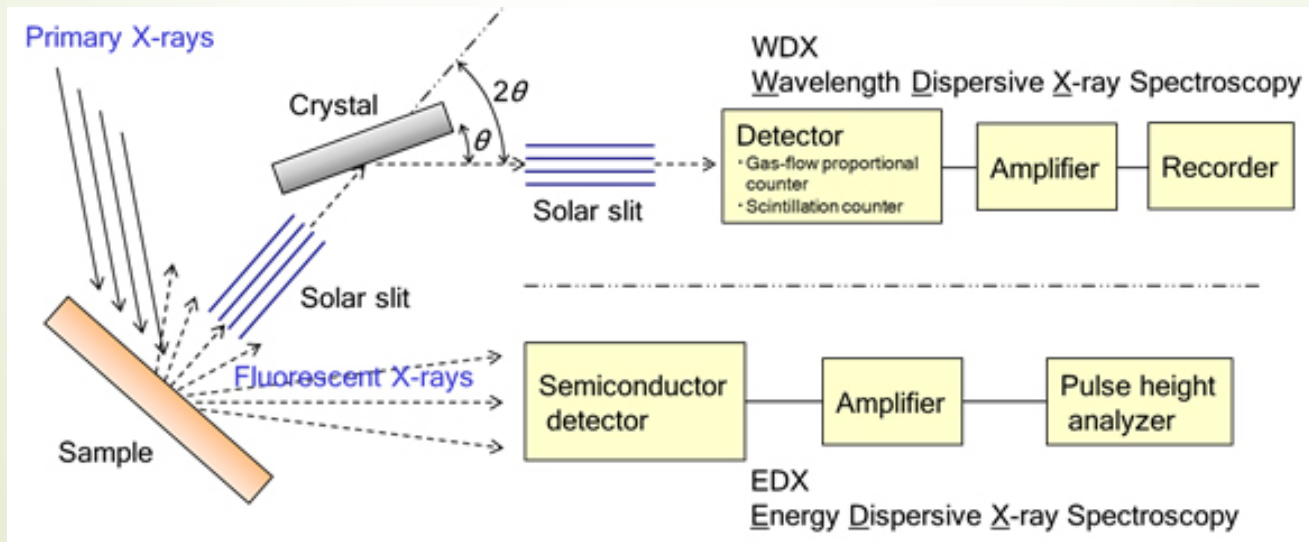
- ▶ XRF is the emission of secondary x-rays from a material that has been excited by bombardment of primary, high-energy x-rays
- ▶ Common tool for rapid elemental analysis
 - ▶ Used for metals, ceramics, glass, and building materials
 - ▶ Geochemistry, forensic science, metallurgy, archeology, and art 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

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



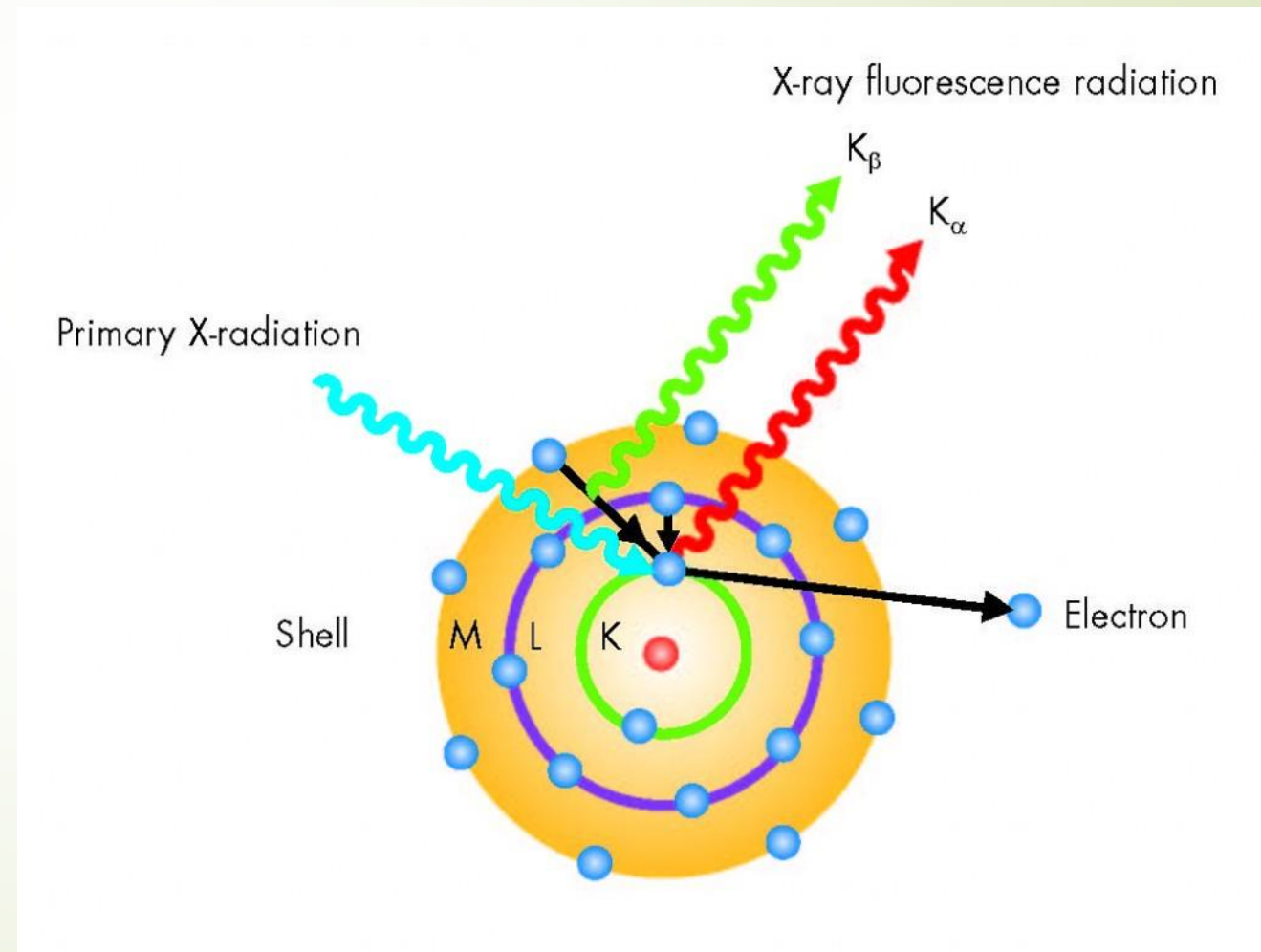
XRF Types

- ▶ 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



H 1	IIA																He 2																		
0.05 Li 3	0.11 Be 4											0.18 B 5	0.28 C 6	0.39 N 7	0.92 O 8	0.69 F 9	0.85 Ne 10																		
1.04 Na 11	1.25 Mg 12											1.49 Al 13	1.56 Si 14	2.01 P 15	2.34 S 16	2.31 Cl 17	2.46 Ar 18	2.62 K 19	2.82 Ca 20	2.66 Sc 21	3.19 Ti 22														
		III B	IV B	V B	V I B	V II B	Group VIII			IB	II B																								
3.51 K 19	3.69 Ca 20	4.01 Sc 21	4.09 Ti 22	4.46 V 23	4.51 Cr 24	4.83 Mn 25	4.95 Fe 26	5.43 Co 27	5.41 Ni 28	5.95 Cu 29	5.9 Zn 30	6.49 Ga 31	6.49 Ge 32	6.81 As 33	6.81 Se 34	6.81 Br 35	6.81 Kr 36	6.81 Rb 37	6.81 Sr 38	6.81 Y 39	6.81 Zr 40	6.81 Nb 41	6.81 Mo 42	6.81 Tc 43	6.81 Ru 44	6.81 Rh 45	6.81 Pd 46	6.81 Ag 47	6.81 Cd 48	6.81 In 49	6.81 Sn 50	6.81 Sb 51	6.81 Te 52	6.81 I 53	6.81 Xe 54
13.4 Rb 37	14.89 Sr 38	14.17 Y 39	15.84 Zr 40	14.96 Nb 41	16.74 Mo 42	15.73 Tc 43	17.57 Ru 44	15.62 Rh 45	18.62 Pd 46	17.48 Ag 47	19.61 Cd 48	18.37 In 49	20.62 Sn 50	19.28 Sb 51	22.72 Te 52	21.18 I 53	23.82 Xe 54	22.16 Cs 55	24.94 Ba 56	22.17 La 57	26.1 Ce 58	24.21 Pr 59	27.28 Nd 60	25.27 Pm 61	28.49 Sm 62	26.36 Eu 63	29.73 Gd 64	27.47 Tb 65	31 Dy 66	28.51 Ho 67	32.29 Er 68	29.78 Tm 69	33.62 Yb 70	30.78 Lu 71	
33.07 Cs 55	34.09 Ba 56	32.16 La 57	36.38 Ce 58	33.44 Pr 59	37.8 Nd 60	34.72 Pm 61	38.26 Sm 62	36.02 Eu 63	40.76 Gd 64	37.26 Tb 65	42.27 Dy 66	38.72 Ho 67	45.83 Er 68	40.12 Tm 69	45.41 Yb 70	41.54 Lu 71	47.04 Hf 72	43 Ta 73	48.7 W 74	44.8 Re 75	50.38 Os 76	46 Ir 77	53.88 Pt 78	48.13 Au 79	55.68 Hg 80	50.74 Tl 81	57.62 Pb 82	53.88 Bi 83	62.39 Po 84	59.74 At 85	60.37 Rn 86	54.07 Fr 87	61.28 Ra 88		
4.29 Fr 87	4.02 Ra 88	4.67 Ac 89	4.83 Th 90	4.96 Pa 91	5.04 U 92	5.03 Np 93	5.49 Pu 94	5.23 Am 95	5.72 Cm 96	5.43 Bk 97	5.96 Cf 98	5.04 Es 99	5.85 Fm 100	6.00 Md 101	6.71 No 102	6.07 Lr 103	6.81 104	6.81 105	6.81 106	6.81 107	6.81 108	6.81 109	6.81 110	6.81 111	6.81 112	6.81 113	6.81 114	6.81 115	6.81 116	6.81 117	6.81 118	6.81 119	6.81 120		

XRF Elements & Approximate Detection Limits

Lanthanides 57-71	33.44 La 57	37.8 Ce 58	34.72 Pr 59	38.26 Nd 60	36.02 Pm 61	40.76 Sm 62	37.26 Eu 63	42.27 Gd 64	38.72 Tb 65	45.83 Dy 66	40.12 Ho 67	45.41 Er 68	41.54 Tm 69	47.04 Yb 70	43 Lu 71
Actinides 89-103	4.29 Ac 89	4.02 Th 90	4.67 Pa 91	4.83 U 92	4.96 Np 93	5.04 Pu 94	5.03 Am 95	5.49 Cm 96	5.23 Bk 97	5.72 Cf 98	5.43 Es 99	5.96 Fm 100	6.00 Md 101	6.71 No 102	6.07 Lr 103

Alloy Elements and Detection Limit Guidelines:
 Elements Detected Magnesium (Mg, Z=12) through Silicon (Si, Z=14) and Titanium (Ti, Z=22) through Plutonium (Pu, Z=94) typically 0.1% - some elements as low as 0.01%

Low-Density Sample Types (Soils, powders, liquids)



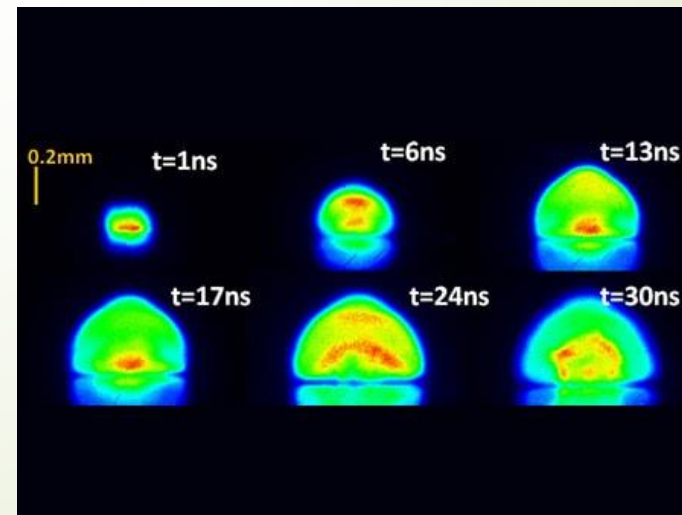
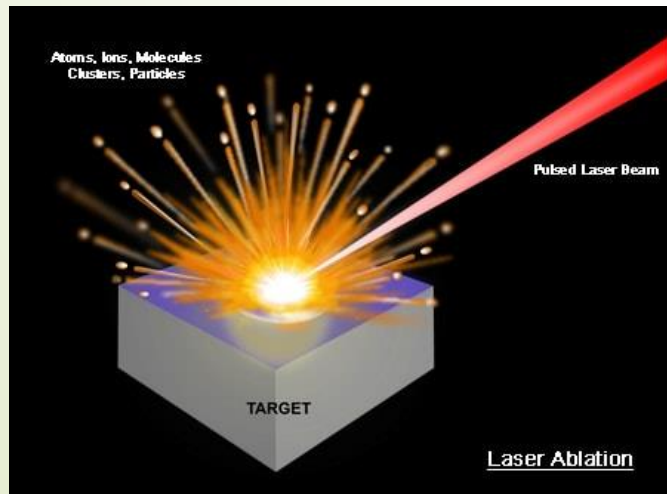
- Requires vacuum, LOD 0.2 - 3%
- LOD 1% - 5%
- 250 - 2,500 ppm
- 10 - 100 ppm
- 50 - 150 ppm
- Not Measured

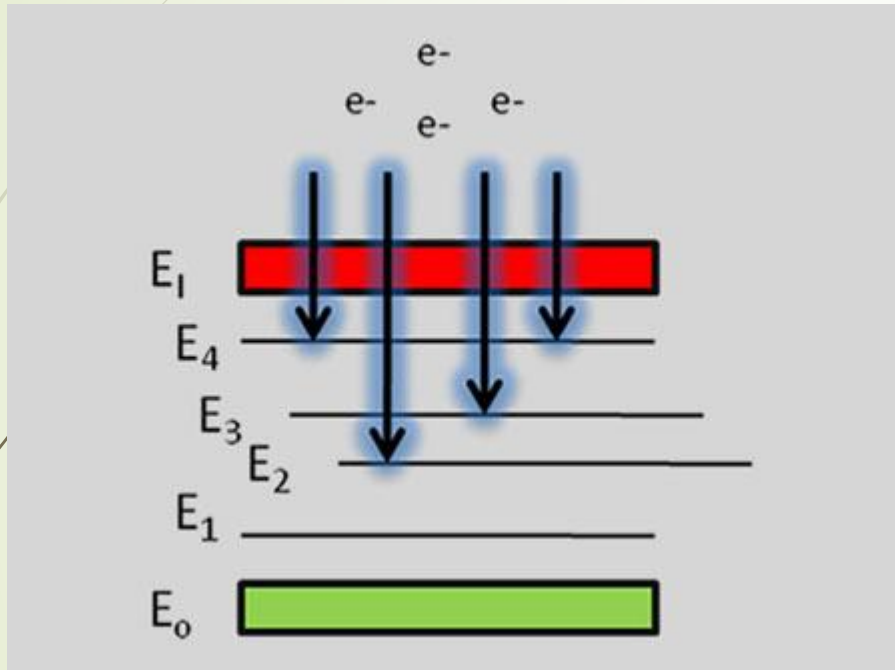
Adapted from Innov-X handout for handheld XRF analyzers
 Note similar reference tables available from other XRF vendors

Detection limits are a function of testing time, sample matrix and presence of interfering elements.
 Detection limits are estimates based on 1-2 minutes test times and detection confidence of 3σ(99.7% confidence).
 Interference-free detection limits are intended as guidelines, please contact Innov-X Systems to discuss your specific application.

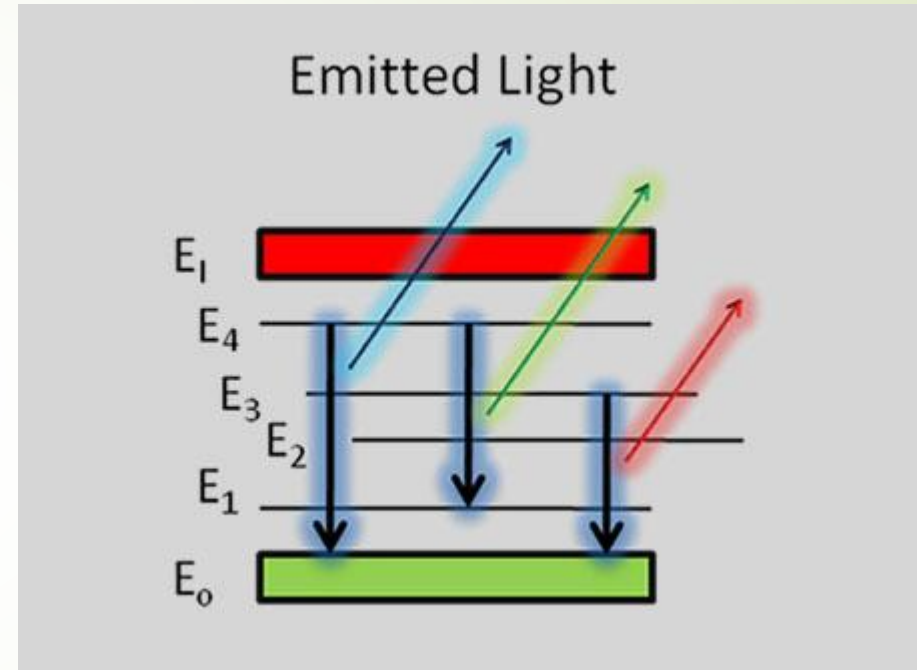
Laser Induced Breakdown Spectroscopy

- ▶ 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 ($<1\text{ mm}^2$) to temperatures greater than $30,000^\circ\text{C}$
- ▶ Cooling plasma allows excited electrons to fall to lower energy levels, giving off characteristic wavelengths of light.

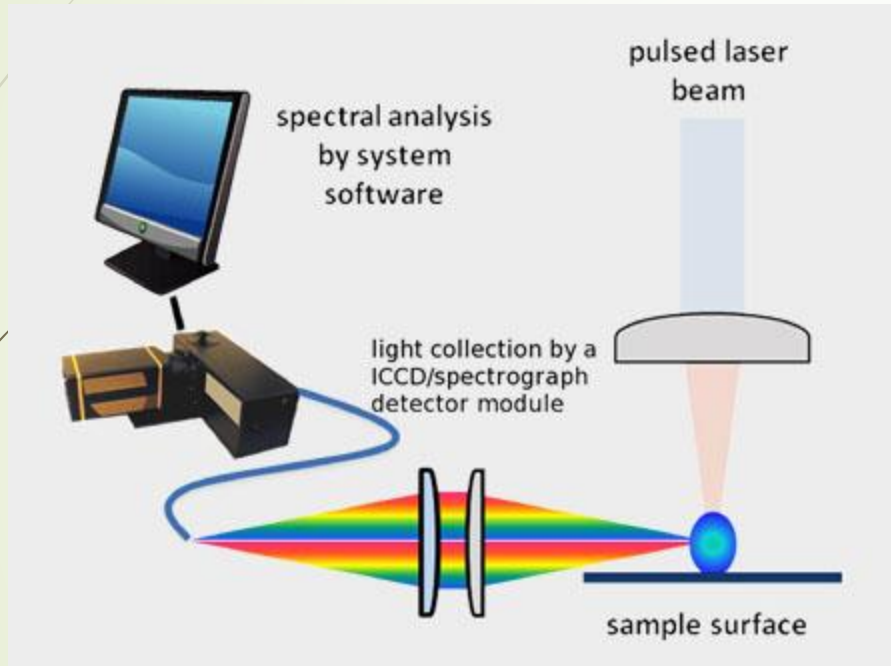




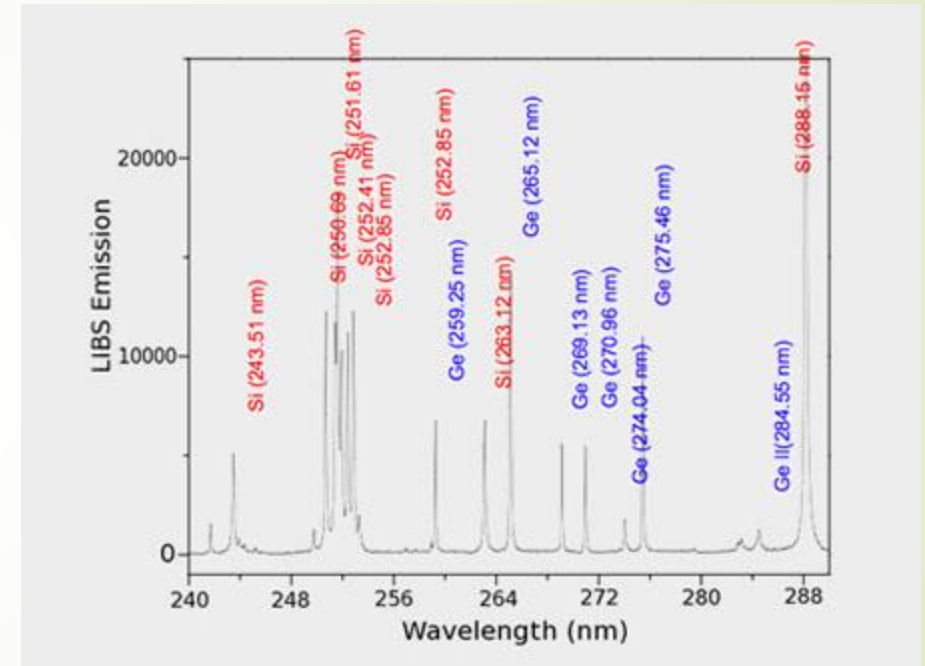
Emission of continuum light during early stage ($< 200 \sim 300$ nsec) of plasma cooling process.



Emission of discrete atomic lines at later times ($> 1 \mu\text{sec}$).



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

1-30ppm	30-100ppm	>100ppm
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1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	71 Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra																
*Lanthanoids	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb			
**Actinoids	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No			

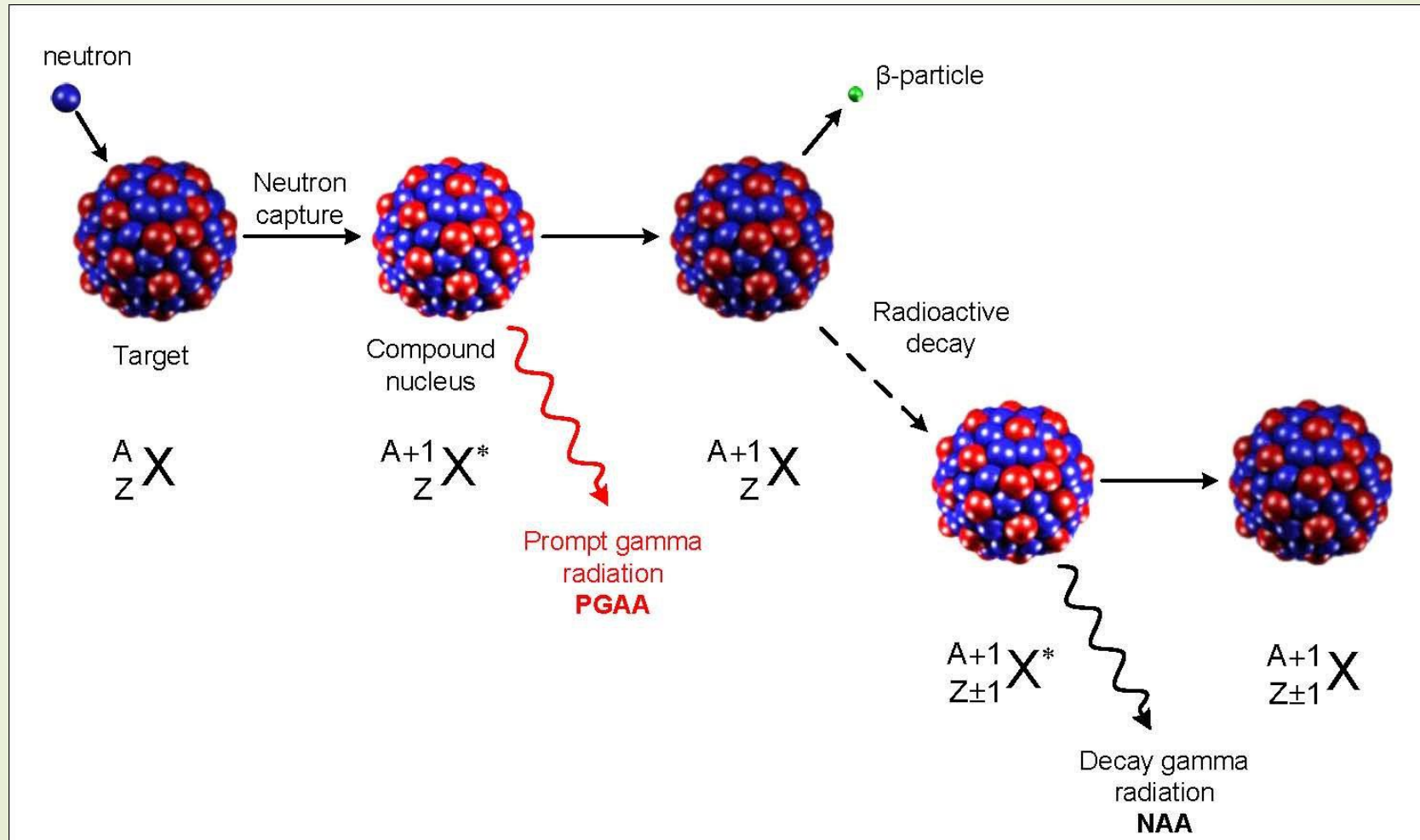
Neutron Activation Analysis (NAA)

- ▶ 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

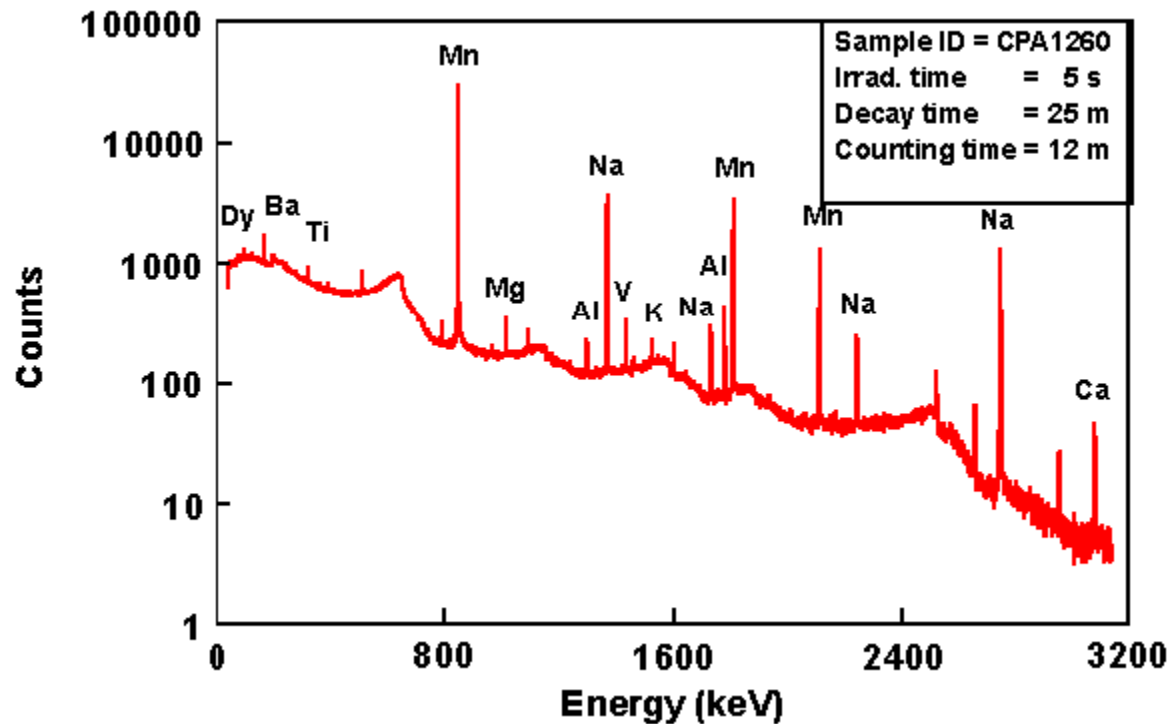
(Also includes accelerators)

- ▶ 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)

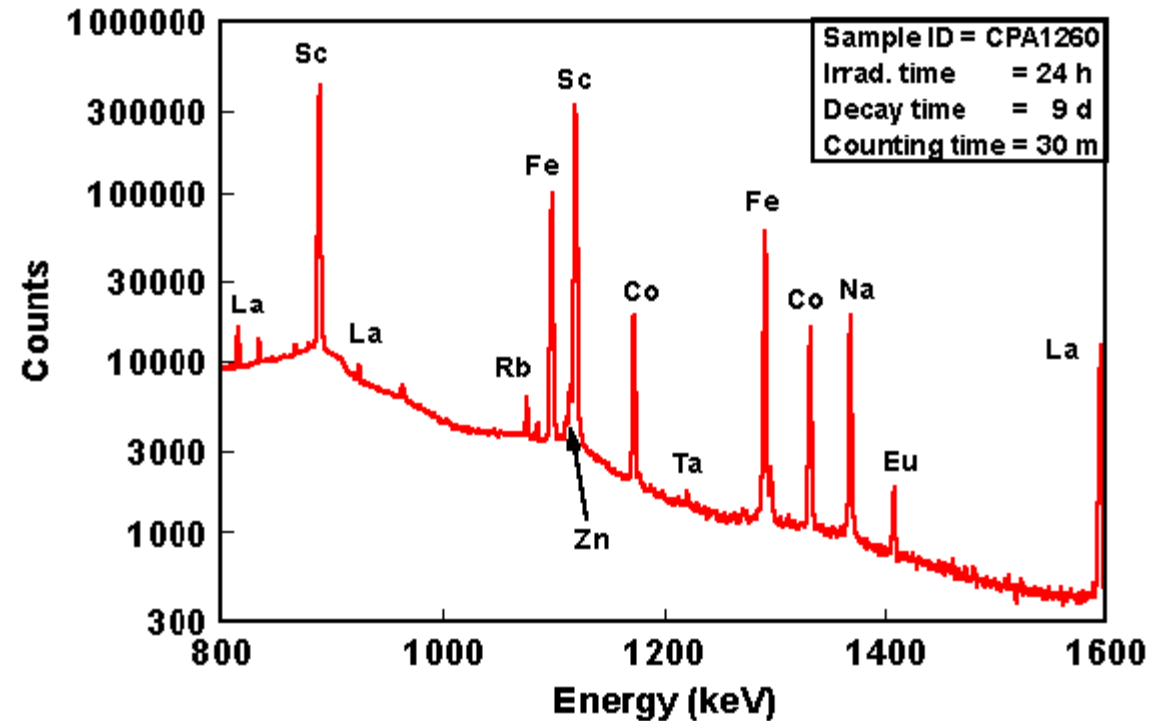
Measurement of the Radioactivity



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 detector.

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

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

Image References

slide #

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