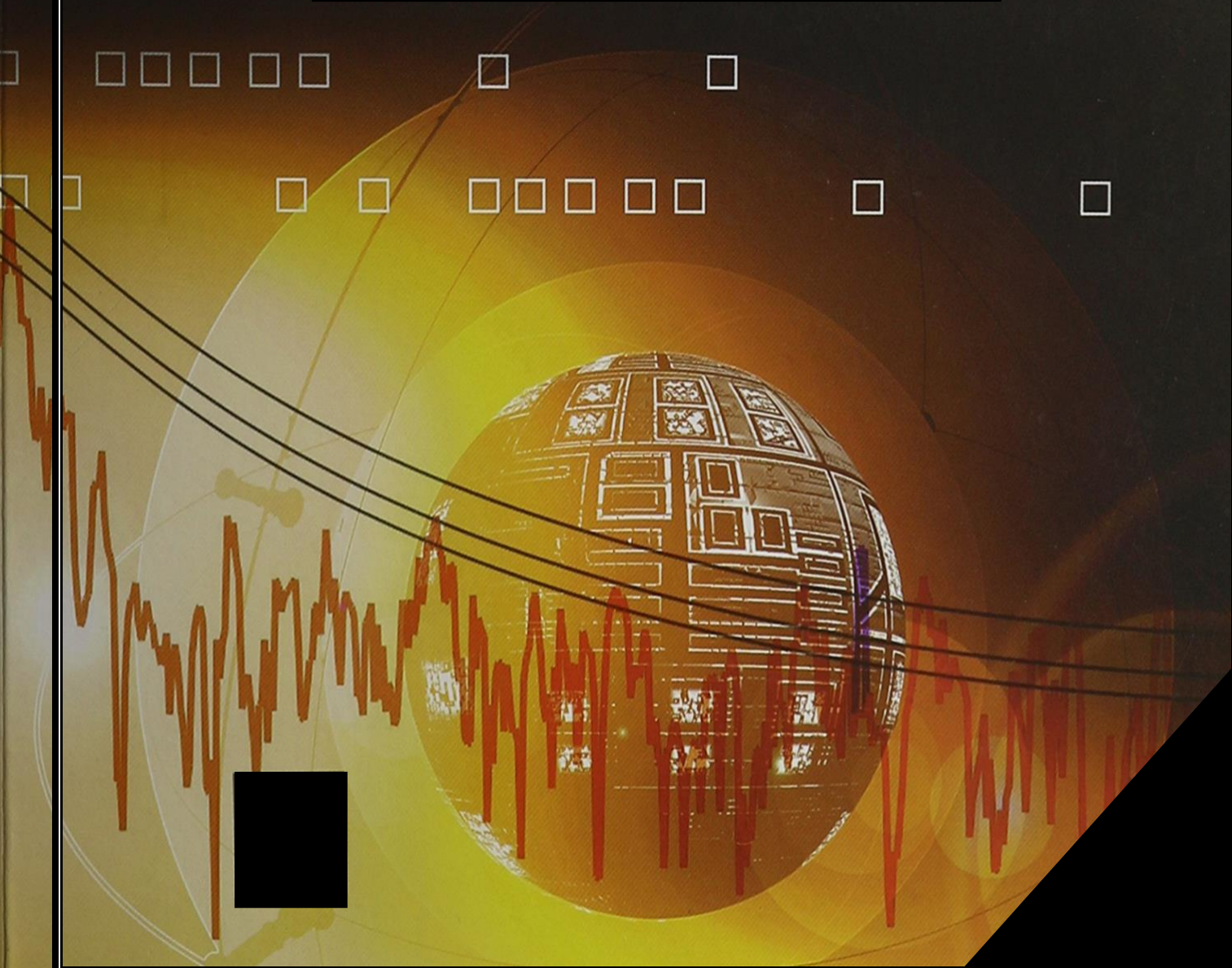


# INSTRUMENTAL ANALYSIS

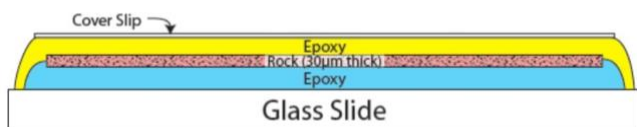
SHAAS N HAMDAN



## 1<sup>st</sup> Lab: Rock Thin Sections

- **Tools & instrument:**
  1. petrographic glass slides
  2. Cover slip & Epoxy (to put the cover)
  3. Diamond saw (cutting machine to cut rock slab)
  4. lap for grinding & a small warming plate
  5. coarse, medium, & fine carbide grit powder (about 400, 800, & 1200) to polished rock slab
  6. Automatic grinding machine to complete the polishing of the rock slab
  7. Microscope (To ensure the accuracy of work)
  8. Hot plat (Electric gas)
- thin section preparation is needed in order for samples to be examined microscopically in order to analyse the characteristics of the soil or rock
- This analysis is normally carried out using transmitted polarised light which creates a need for thin sections of known & exact thickness
- **Experience & steps**
  1. Cut the rock slab on the Diamond saw
  2. Start the polish by carbide on the grinding machine to make the surface smooth, and then use the glass disk and the carbide (400-600mm) & (800mm) to complete the polishing
  3. put slab on the Hot Plate with the slide to get off the pebbles from the slab
  4. While the rock slab is on the Hot Plate, put on it the Like Side to stick the slab on the slide
  5. put the slide on the slab by angle of 45°
  6. put the slide on the Automatic grinding machine to decrease the thickness of the slab
  7. Repeat the polish on the disk of the glass & look under the microscope to see the grains if it needs more polishing or not
  8. use the Epoxy to stick the cover

Thin sections: 0.03mm, 30µm



## 2<sup>nd</sup> Lab: Rock Staining

### I. Tools & instrument:

- The samples are cut & polished before staining, size is a personal preference, the only restriction being the ability to fit it within the containers being used for staining
- If the saw uses an **oil coolant**, wash off the excess oil from the slab with water

### Staining involves the use of 3 chemicals

<b>Hydrofluoric Acid (HF)</b>	To etch the polished surface, breaks bonds between K, Ca
<b>Amaranth</b> $C_{20}H_{11}N_2Na_3O_{10}S_3$	Powder to stain plagioclase on surface in a <b>red</b> color
<b>Sodium Cobaltinitrite</b>	To stain any K-feldspar on that surface a <b>yellow</b> color

- As Use HF: use resistant apron, gloves, & eye protection goggles when handling it
- 33HF/500ml water
- 20%Na<sub>3</sub>CO(NO<sub>2</sub>)<sub>6</sub> → 20g/100ml water

### III. Experience & steps

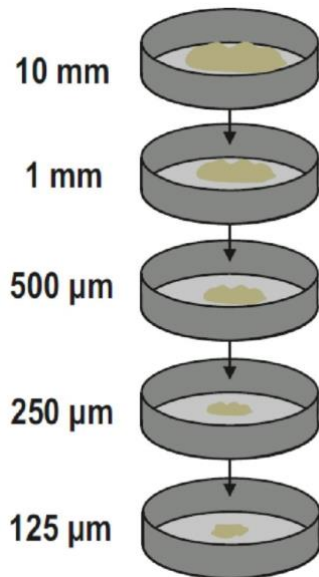
1. Dip polished face into the HF (1min), & then Rinse it (5-10 s)  
نعمل Polishing للصخر ثم نعرضه لحمض HF لمدة 3د (تعتمد المدة على حجم العينة) ونغسل الصخر جيدا بعد تعريضه للحمض
2. Dip the same face into the Amaranth solution for approximately 2-5 sec & then rinse it & you'll see that the plagioclase are staining in red color  
نأخذ العينة ونضعها في Amaranth وهي مادة عضوية تؤثر فقط على البلاجيوكليز من دقيقتين إلى ثم نغسلها والنتيجة سنرى مناطق تلونت في اللون الأحمر وهي بلورات ال plagioclase
3. Dip the same face of the slab in the same manner, in Sodium Cobalt nitrite for 1min, & then Wash the sample, The K-feldspar should be stained a yellow color  
بعد ان تجف العينة نغمسها في الصوديوم كوبالتنايتريت نغسل العينة ونلاحظ انه ظهر لون اصفر بها وهو صبغة الفلدسبار
4. Quartz & ferromagnesian will remain unstained & in their original color  
والمعدن الذي لا يتأثر بهذه الصبغات هو الكوارتز فيبقى لونه ابيض او سكري وايضا ال ferromagnesian والتي تبقى سوداء
5. Optional. protect it by spraying on a thin film of clear plastic



**Granite rocks**  
**Yellow is the K-feldspar staining by Na-Cobaltinitrite**  
**Red is the Plagioclase staining by Amaranth**  
 $C_{20}H_{11}N_2Na_3O_{10}S_3$   
 Gray & White is the quartz (don't stained)  
 Black is ferromagnesian minerals

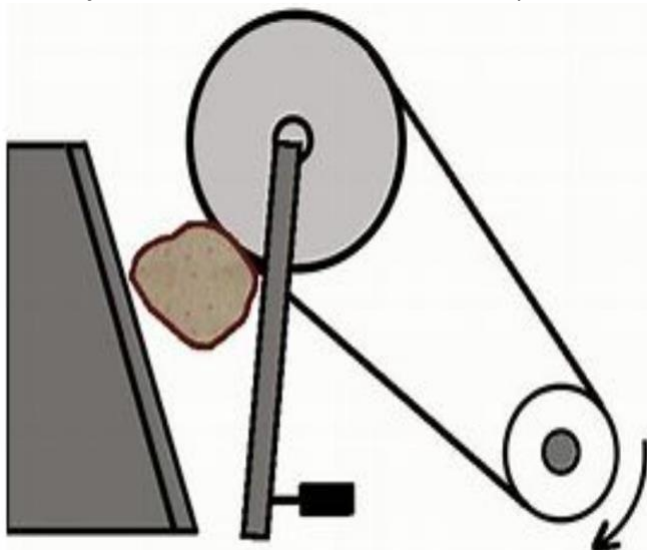
### 3<sup>rd</sup> Lab: Rock Preparation

- Preparation:** crush the rock into small species to separate the minerals (Eg. Hornblend, & plagioclase from Gabbroic Hornblendite rock)
- Decanting:** sample washing, after crushing the sample should be washed to remove dust
- sieving:** separate the sample into different size
- A separated mineral is required for optical study, X-ray diffraction, & chemical analysis
- The method of separation depends on amount of separated mineral & grain size of the mineral
- To separate minerals (sieves), grain size must be < 250µm because the grain of this size made up of one mineral (>250 may be > one mineral)



#### Tools & instrument:

- jaw crusher:** to crush builders into species



- Ring Mill:** to crush rock fragments into powder for wet chemical analysis or sand & silt size (less time) for separation
- Electrical grinding machine (the Agate mortar):** crush rock fragments into powder

#### Experimental Procedure:

- Use the jaw crusher to crush builders
- put these rock species into the Electrical grinding machine (the Agate mortar) or Ring Mill to crush it into a powder
- Put the crushed sample into the sieves to separate the sample into different size
- Decanting (washing) the crushed & sieved grains to remove dust

### 4<sup>th</sup> Lab: Mineral Separation

- Separation:** Separate minerals after crushing & sieving depending on the physical properties
- We can separate any mineral by 2 Ways:** magnetic separation & using Heavy liquids
- All minerals can be classified into 3 groups:

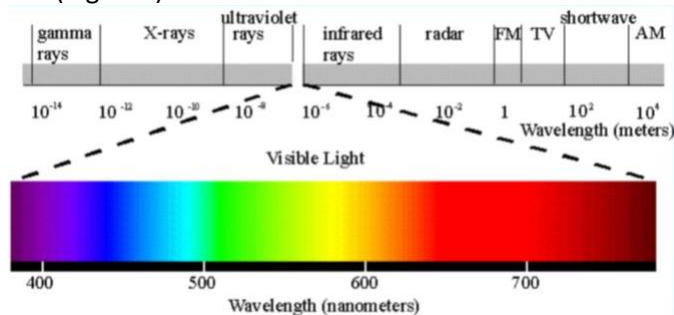
Group	Definition
Ferromagnetic	Have constant magnetic properties, regardless they are exposed to an external field
Diamagnetic (Repelled)	don't have magnetic properties unless it's exposed to an external field (repelled or attached to a magnetic field)
Paramagnetic (attached)	
Group	Separated using
Ferromagnetic	Hand-magnet
Diamagnetic	FIMS to separate it from para. & then using heavy liquids
Paramagnetic	FIMS

- The Frantz isodynamic magnetic separator FIMS:** incorporates an electromagnet with 2 elongate pole pieces arranged, space between the poles is much wider on one side than other
  - Mineral particles are introduced into the upper end of chute & slide toward the lower
  - At the lower end the particles are separated to 2 streams, higher & lower susceptibility
  - Metal with higher susceptibility move toward the side of the chute where the pole gap is narrow & magnetic flux greatest
  - **Side slope:** 20°, **Tilt:** 5° (low susceptibility) & 15° (moderate to high susceptibility)
  - The way in which mineral separate as they move along the length of chute depends on:
    - chute tilt, & slope & rate of feed to the chute
    - amperage applied to be electromagnet
- if we put minerals in a liquid, the mineral with more density than liquid will fall down

Common heavy liquids			
<b>Bromoform</b>	2.85 g/ml		
<b>Tetrabromoethane</b>	2.96 g/ml		
<b>Diiodomethane</b>	3.32 g/ml		
Granite Composition			
Para	I [A]	Dia	ρ[g/cm <sup>3</sup> ]
<b>Biotite</b>	0.8	Feldspar, Qz	< 3.0
<b>Monazite</b>	0.6	Apatite	3.1
		Zircon	4.56
0.4A	0.8A	1.5A	1.5A
Garnet	Biotite	Muscovite	Zircon
Ilmenite	Hornblende	Spinel	Rutile
Chromite	Hypersthene	Enstatite	Titanite
Chloritoid	Chlorite	Tourmaline	Apatite
Olivine	Augite	Zoisite	Corundum
	Actinolite	Diopside	Barite
	Staurolite	Tremolite	Fluorite
	Epidote		Sillimanite
			Kyanite

# 5<sup>th</sup> Lab: X-Ray diffraction for crystal structure

- discovered in 1895 by the German physicist **Wilhelm Conrad Röntgen** & were so named because their nature was unknown at the time
- X-RAY PROPERTIES** invisible, highly penetrating electromagnetic radiation of much shorter  $\lambda$  (higher  $f$ ) than VL

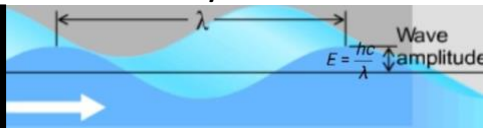


$\lambda = 10^{-8} - 10^{-11} \text{m}$  ( $f = 3 \times 10^{16} - 3 \times 10^{19} \text{Hz}$ )

- X-RAY ENERGY:** Electromagnetic radiation described as having packets of energy, photons
  - The energy of the photon is related to its frequency by the following formula:

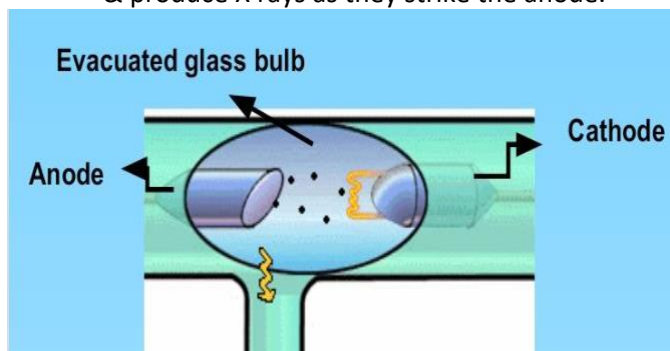
$$E = h\nu = hc/\lambda$$

$\lambda$  : wavelength  
 $\gamma$  : frequency  
 $c$  : speed of light



$\lambda_{\text{x-ray}} \approx 10^{-10} \approx 1 \text{\AA} \rightarrow E \approx 10^4 \text{eV}$

- PRODUCTION OF X-RAYS**
  - Visible light & X-ray photons are produced by the movement of electrons in atoms
  - e- occupy different E-levels, or orbitals
  - When e- drops to a lower orbital, it release some energy (extra energy in the form of a photon)
  - The energy level of the photon depends on how far the e- dropped between orbitals
- X-RAY TUBE**
  - X rays produced in a highly evacuated glass bulb (X-ray tube) that contains 2 electrodes-an anode made of platinum, tungsten, or another heavy metal of high melting point, & a cathode
  - When a high voltage is applied between the electrodes, streams of electrons (cathode rays) are accelerated from the cathode to the anode & produce X rays as they strike the anode.



- Generation of X-rays (K-Shell Knockout)**
  - Electrons in a higher orbital falls to the lower energy level, releasing its extra energy in the form of a photon. It's a big drop, so the photon has a high energy level; it is an X-ray photon

### How Atoms Emit Light

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- A collision with a moving particle excites the atom.
- This causes an electron to jump to a higher energy level.
- The electron falls back to its original energy level, releasing the extra energy in the form of a light photon.

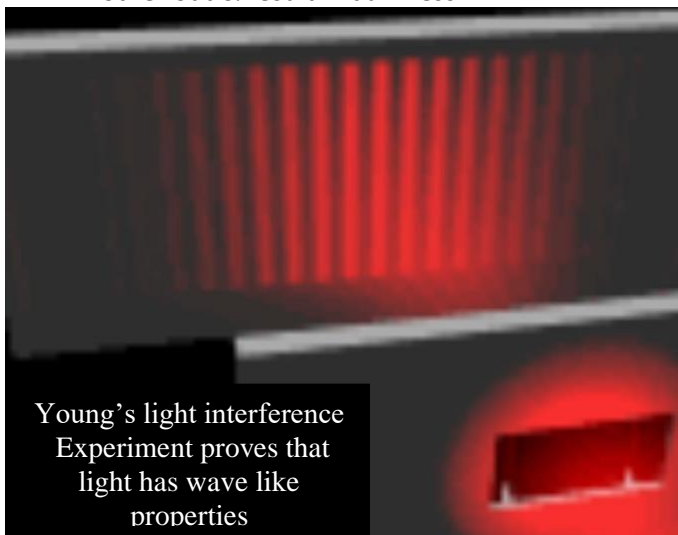
**Light Photon**

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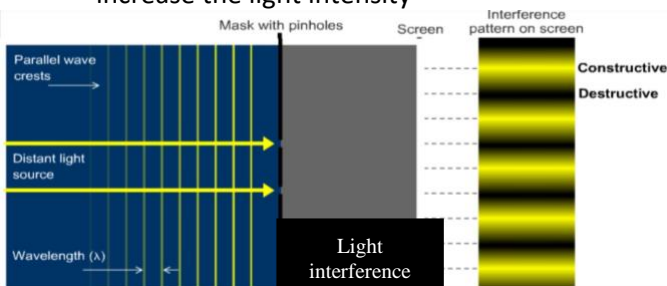
The free e- collides with the tungsten atom, knocking e- out of a lower orbital. A higher orbital e- fills the empty position, releasing its excess energy as a photon

- Absorption of X-rays**
  - A larger atom is more likely to absorb X-ray because larger atoms have greater energy differences between orbitals (energy level more closely matches the energy of photon)
  - Smaller atoms, where the e- orbitals are separated by relatively low jumps in energy, are less likely to absorb X-ray photons
  - The soft tissue in your body is composed of smaller atoms, & so does not absorb X-ray photons particularly well. Ca (in bones) are much larger, so they are absorb X-ray
- Diffraction:** wave phenomenon in which the apparent bending & spreading of waves when they meet an obstruction

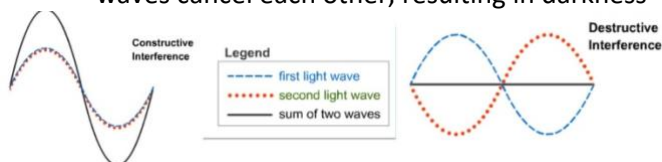
- Diffraction occurs with EMR such as light & radio waves, & in sound waves & water waves
- Ex. double-slit diffraction, that's why firstly we remember light diffraction
- **LIGHT DIFFRACTION:** caused by light bending around the edge of an object
  - The interference pattern of bright & dark lines from the diffraction experiment explained by the additive nature of waves
  - wave peaks add together to make brighter light, or a peak & a trough will cancel each other out & result in darkness



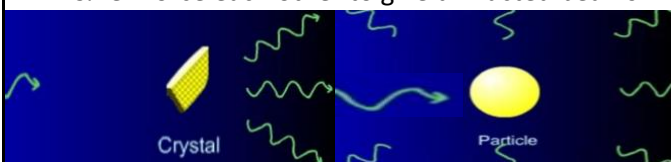
- **Constructive & Destructive Waves**
  - **Constructive interference** is the result of synchronized light waves that add together to increase the light intensity



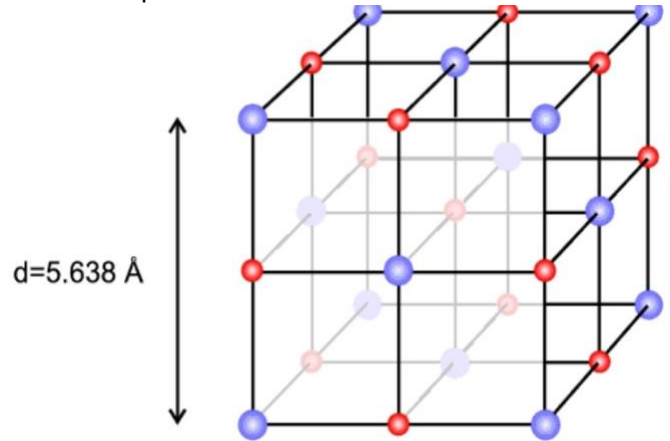
- **Destructive interference:** results when 2 light waves cancel each other, resulting in darkness



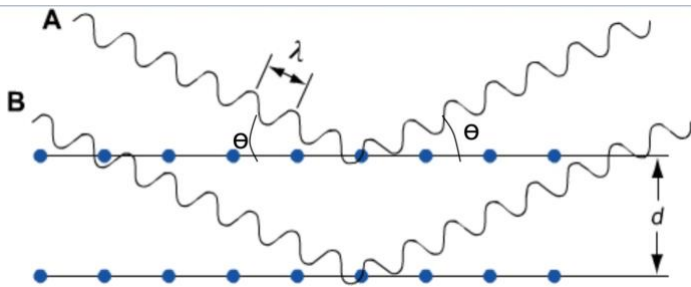
- **Single particle:** To understand diffraction we have to consider what happens when a wave interacts with a single particle. The particle scatters the incident beam uniformly in all directions
- **Solid material:** If we consider a crystalline material, scattered beams add together in a few directions & reinforce each other to give diffracted beams



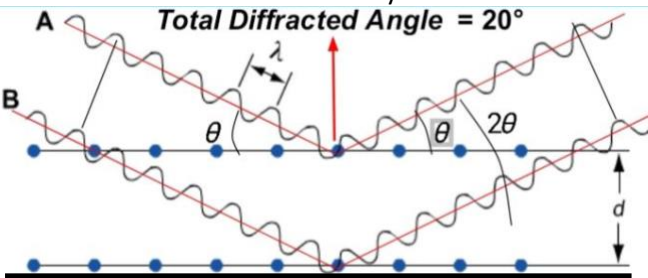
- **Diffraction of Waves by Crystals**
  - The structure of crystal determined by studying the diffraction pattern of a beam of radiation incident on the crystal
  - Beam diffraction in a certain specific directions
  - By measuring the directions of the diffraction & the corresponding intensities, one obtains information concerning the crystal structure responsible for diffraction



- **X-RAY CRYSTALLOGRAPHY:** technique in crystallography in which the pattern produced by the diffraction of x-rays via closely spaced lattice of atoms in a crystal is recorded & then analyzed to reveal the nature of that lattice
- X-Ray Diffraction XRD
  - W. L. Bragg presented a simple explanation of the diffracted beams from a crystal.
  - The Bragg derivation is simple but convincing only since it reproduces the correct result
  - W.H. Bragg & his son W.L. Bragg developed a relationship to explain why the cleavage faces of crystals appear to reflect X-ray beams at certain  $\theta$  of incidence, & This observation is an example of X-ray wave interference "analysis of crystal structure by means of X-rays"
- **Bragg Equation:** identifies angles of the incident radiation relative to the lattice planes for which diffraction peaks occurs
  - Bragg derived the condition for constructive interference of the X-rays scattered from a set of parallel lattice planes
  - W.L. Bragg considered crystals to be made up of parallel planes of atoms. Incident waves are reflected specularly from parallel planes of atoms in the crystal, with each plane is reflecting only a very small fraction of the radiation, like a lightly silvered mirror
  - The diffracted beams are found to occur as the reflections from planes interfere constructively
  - We treat elastic scattering, in which the energy of X-ray is not changed on reflection
  - In mirror like reflection the angle of incidence is equal to the angle of reflection

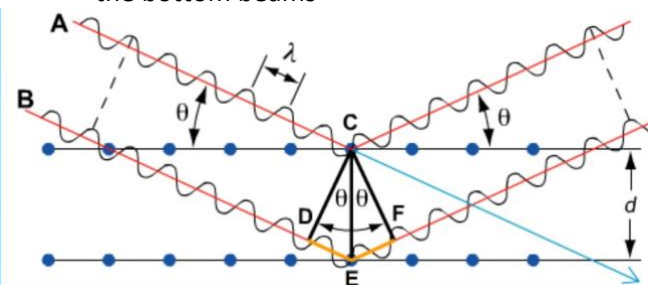


- When the X-rays strike a layer of a crystal, some of them will be reflected
- We are interested in X-rays that are in-phase with one another, X-rays that add together in x-ray diffraction analysis in-phase before they are reflected & after they reflected



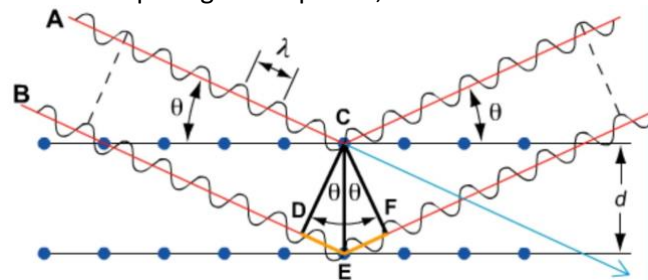
θ: Incident angle, θ: Reflected angle, λ: Wavelength of X-ray

- The difference in the distances traveled is related to distance between adjacent layers
- Connecting the 2 beams with perpendicular lines shows the difference between the top & the bottom beams



The line CE is equivalent To the distance between The two layers (d)  
DE = d sin θ

- The length DE is the same as EF, so the total distance traveled by the bottom wave is expressed by:  $DE = d \sin \theta \rightarrow DE + EF = 2d \sin \theta$
- So,  $n\lambda = 2d \sin \theta$  (Bragg law)
- d: spacing of the planes, n: order of diffraction



- **Bragg Law:** Constructive interference of the radiation from successive planes occurs as the path difference is an integral number of λ
- Bragg reflection can only occur for  $\lambda (n\lambda < 2d)$
- we cannot use VLT. Because No diffraction occur as above condition isn't satisfied

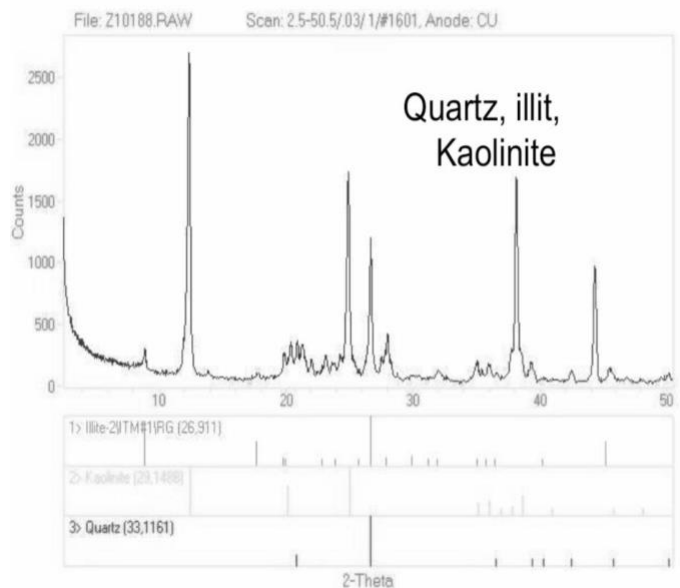
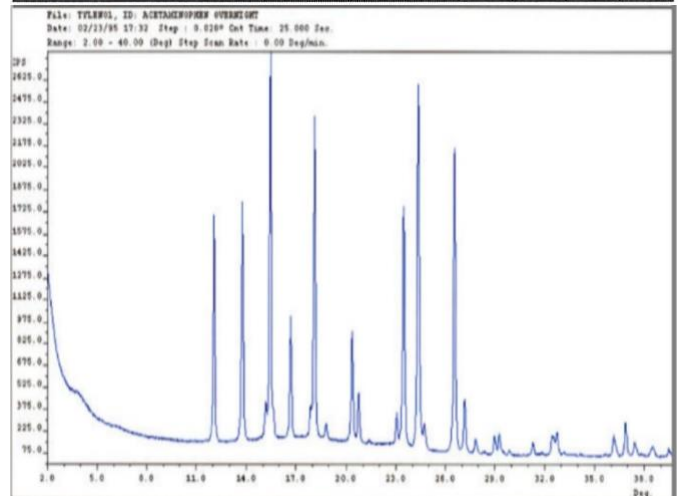
- The diffracted beams (reflections) from any set of lattice planes can only occur at particular angles predicted by the Bragg law

- **Diffraction maximum (diffractograph)**

- Coherent scattering from a single plane is not sufficient to obtain a diffraction maximum. It is also necessary that successive planes should scatter in phase
- This will be the case if the path difference for scattering off 2 adjacent planes is an integral number of λ

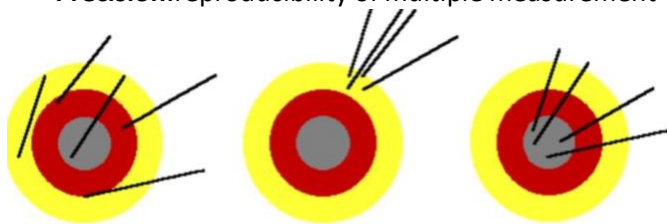
5-0490 MINOR CORRECTION

d	3.34	4.26	1.82	4.26	SiO <sub>2</sub>	★		
I/I <sub>1</sub>	100	35	17	35	SILICON OXIDE	QUARTZ, LOW		
Rad. CuKα <sub>1</sub>	λ 1.5404	Filter Ni	d Å	I/I <sub>1</sub>	hkl	d Å	I/I <sub>1</sub>	hkl
Dia.	Cut off	Coll	3.343	35	100	1.228	2	220
I/I <sub>1</sub> , G.C. DIFFRACTOMETER	d corr. abs?		2.458	100	101	1.1997	5	213
Ref. SWANSON AND FUYAT, NBS CIRCULAR 539, VOL. III (1953)			2.282	12	110	1.1973	2	221
Sys. HEXAGONAL	S.G. D <sub>3h</sub> <sup>2</sup> - P3 <sub>1</sub> 21		2.237	6	111	1.1802	4	310
a <sub>1</sub> 4.913	a <sub>2</sub> 5.405	A	2.128	9	200	1.1530	2	311
α	β	γ	1.980	6	201	1.1408	<1	204
			1.817	17	112	1.1144	<1	303
Ref. IBID.			1.801	<1	003	1.0816	4	312
	nβ 1.5448	nγ 1.533	1.672	7	202	1.0636	1	400
2V	D <sub>2</sub> 2.647	mp	1.659	3	103	1.0477	2	105
Ref. IBID.		Color	1.608	<1	210	1.0437	2	401
			1.541	15	211	1.0346	2	214
Sample from Lake Toxaway, N.C. Spect. Anal.:			1.453	3	113	1.0149	2	223
<0.01% Al; <0.001% Ca,Cu,Fe,Mg.			1.418	<1	300	0.9896	2	402,115
X-ray pattern at 25°C			1.382	7	212	.9872	2	313
			1.375	11	203	.9781	<1	304
			1.372	9	301	.9762	1	320
			1.288	3	104	.9607	2	321
			3-0427, 3-0444					
REPLACES 1-0649, 2-0458, 2-0459, 2-0471, 3-0419			1.256	4	302	.9285	<1	410



# 6<sup>th</sup> Lab: X Ray Fluorescent (elemental analysis)

- Accuracy:** is how close a result to the true value
  - Determining the accuracy of a measurement usually requires calibration of the analytical method with a known standard
- Standards:** Materials containing a known concentration of an analyte
  - They provide reference to determine unknown concentration & calibrate analytical instrument
- Precision:** reproducibility of multiple measurement



good accuracy  
poor precision

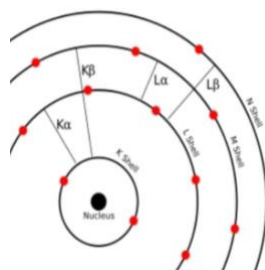
poor accuracy  
good precision

good accuracy  
good precision

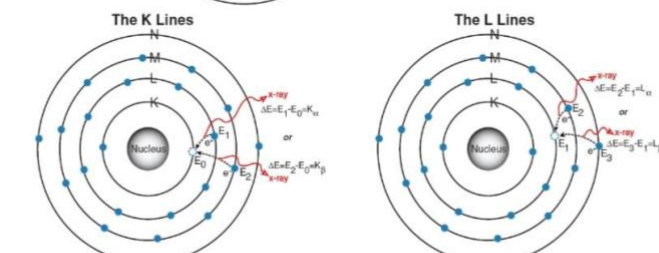
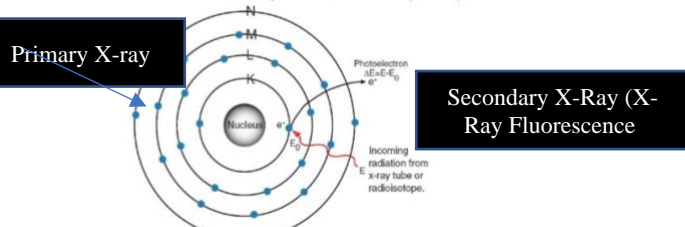
- described by the standard deviation, standard error, or confidence interval

- X-ray fluorescence:** emission of characteristic secondary X-rays (fluorescent) from a material that excited by bombarding with high-energy X-ray or  $\gamma$ 
  - used for **elemental & chemical analysis** (in the investigation of metals, glass, ceramics, & building materials), research in geochemistry, forensic science, & archaeology

- Electronic orbitals:** Each element has electronic orbitals of characteristic energy. Following removal of inner e<sup>-</sup> by an energetic photon provided by a primary radiation source, an electron from an outer shell drops into its place

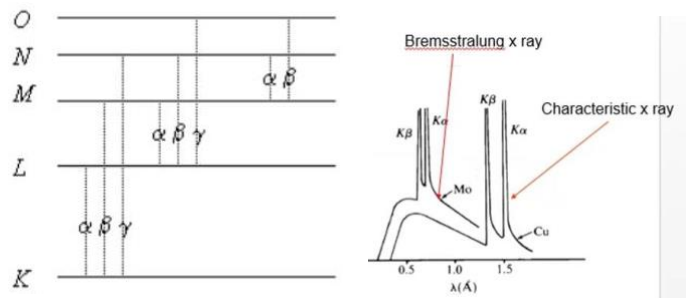


The X-Ray Fluorescence Process  
Example: Titanium Atom (Ti = 22)



2) An electron from the L or M shell "jumps in" to fill the vacancy. In the process, it emits a characteristic x-ray unique to this element and in turn, produces a vacancy in the L or M shell.

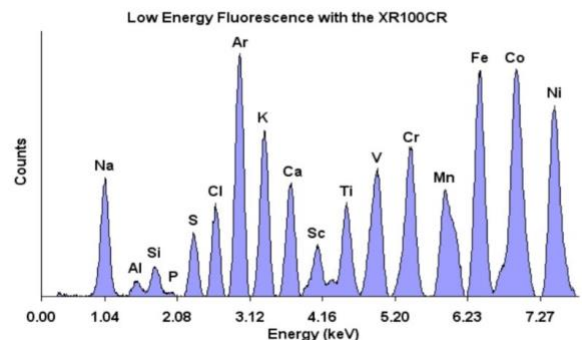
3) When a vacancy is created in the L shell by either the primary excitation x-ray or by the previous event, an electron from the M or N shell "jumps in" to occupy the vacancy. In this process, it emits a characteristic x-ray unique to this element and in turn, produces a vacancy in the M or N shell.



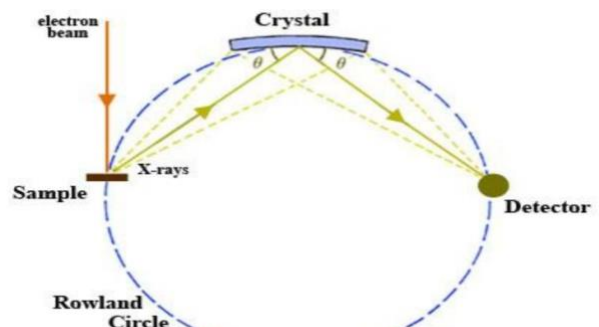
- In XRF spectrometer:** X-ray photons are counted & their corresponding energies (keV) are measured. The resultant data set is displayed as a spectrum
- Moseley's law:** relationship between atomic number (Z) & energy of emission lines for each specific X-ray line series (the K $\alpha$  line or the L $\beta$  line)
 
$$E = a(z-s)^2$$

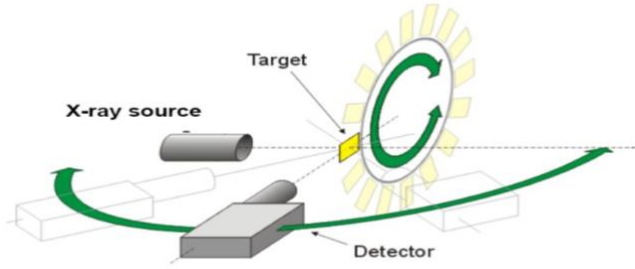
Energy = constant (atomic# - constant of line series)

- Moseley's law indicates that element's spectral lines are smooth function of the atomic number
- The spectral lines for elements with **low atomic number (light) occur at lower energies**
- The peak energies & spectral group patterns provide for **qualitative identification**



- XRF is well-suited for investigation (advantages)
  - bulk chemical analyzes of major element
  - bulk chemical analyzes of trace elements
  - detection limits for trace elements are typically on the order of a few parts per million (ppm)
- Limitations (disadvantages)**
  - depending on  $\lambda$  & intensity of incident x-ray
  - Limited in ability to precisely & accurately measure abundances of element with  $Z < 11$
  - cannot distinguish variations among isotopes
  - cannot distinguish ions of the same element in different valence states

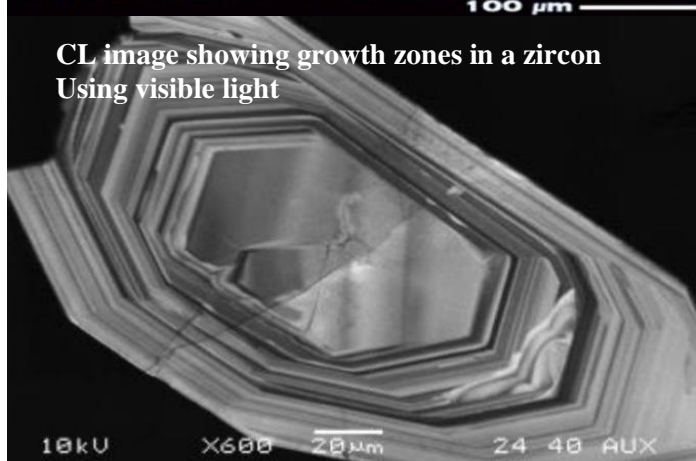
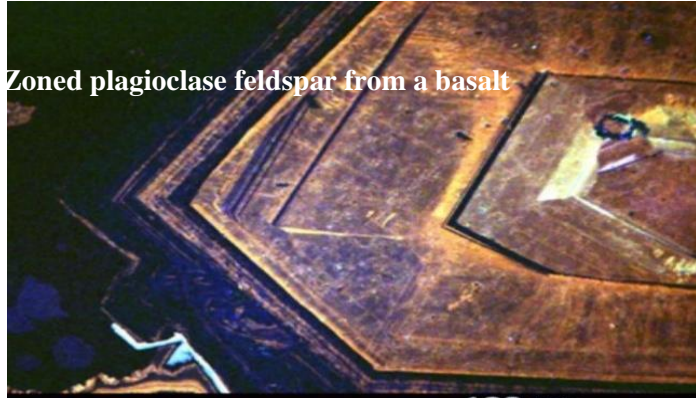




### Generation of Characteristic X-Rays

- Characteristic X-rays generated when an energetic beam of electrons interacts with the inner shell electrons by inelastic scattering with enough energy to excite inner shell electrons to outer shell orbitals, leaving inner-shell vacancies
- As outer-shell electrons fall to the various inner shell orbitals, characteristic amounts of energy are generated that are a function of the target element & the type of orbital decay
- Much of the energy is emitted from the atom or internally absorbed & knock out another outer shell electron (Auger electron) with additional energy emissions

الفرق بين coating & curving هو في الكونتج ابقاء جميع المظاهر المورفولوجية واضحة

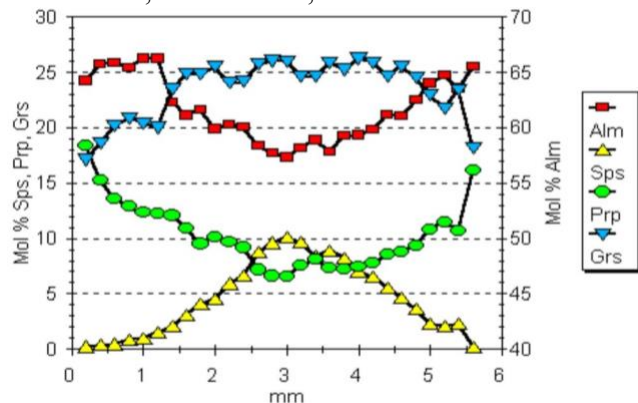


	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	H Hydrogen 1.008																	He Helium 4.002602
2	Li Lithium 6.94	Be Beryllium 9.012182											B Boron 10.811	C Carbon 12.011	N Nitrogen 14.007	O Oxygen 15.999	F Fluorine 18.998	Ne Neon 20.180
3	Na Sodium 22.98976928	Mg Magnesium 24.304											Al Aluminum 26.9815385	Si Silicon 28.0855	P Phosphorus 30.973761998	S Sulfur 32.06	Cl Chlorine 35.45	Ar Argon 39.948
4	K Potassium 39.0983	Ca Calcium 40.078	Sc Scandium 44.955912	Ti Titanium 47.88	V Vanadium 50.9415	Cr Chromium 51.9961	Mn Manganese 54.938044	Fe Iron 55.845	Co Cobalt 58.933194	Ni Nickel 58.6934	Cu Copper 63.546	Zn Zinc 65.38	Ga Gallium 69.723	Ge Germanium 72.630	As Arsenic 74.9216	Se Selenium 78.9718	Br Bromine 79.904	Kr Krypton 83.798
5	Rb Rubidium 85.4678	Sr Strontium 87.62	Y Yttrium 88.90584	Zr Zirconium 91.224	Nb Niobium 92.90638	Mo Molybdenum 95.94	Tc Technetium 98	Ru Ruthenium 101.07	Rh Rhodium 102.9055	Pd Palladium 106.42	Ag Silver 107.8682	Cd Cadmium 112.411	In Indium 114.818	Sn Tin 118.710	Sb Antimony 121.757	Te Tellurium 127.6	I Iodine 126.905	Xe Xenon 131.29
6	Cs Cesium 132.90545196	Ba Barium 137.327	57-71	Hf Hafnium 178.49	Ta Tantalum 180.94788	W Tungsten 183.84	Re Rhenium 186.207	Os Osmium 190.23	Ir Iridium 192.222	Pt Platinum 195.084	Au Gold 196.966569	Hg Mercury 200.59	Tl Thallium 204.38	Pb Lead 207.2	Bi Bismuth 208.9804	Po Polonium 209	At Astatine 210	Rn Radon 222
7	Fr Francium 223	Ra Radium 226	89-103	Rf Rutherfordium 261	Db Dubnium 262	Sg Seaborgium 263	Bh Bohrium 264	Hs Hassium 265	Mt Meitnerium 266	Ds Darmstadtium 267	Rg Roentgenium 268	Cn Copernicium 269	Nh Nihonium 270	Fl Flerovium 271	Mc Moscovium 272	Lv Livermorium 273	Ts Tennessine 274	Og Oganesson 274





- **Samples & standards:** The net intensity of the characteristic X-ray peak is proportional to the mass concentration of that element in the specimen
  - **quantitative analysis relies on comparing the specimen with standard of the element**
  - The standards are natural or synthetic materials with accurately known composition, either because they pure stoichiometric compound, or analyzed carefully by other techniques
  - **Spot analysis, Profile analysis, Map analysis**
  - $Al_2Si_3O_{12}$  Pyrope  $Mg_3$ , Almandine  $Fe_3$ , Spessartin  $Mn_3$ , Grossular  $Ca_3$ , Andradite  $Ca_3Fe_2Si_3O_{12}$



### Chemical Analysis

- Reading chemical data
  - $SiO_2$ ,  $Al_2O_3$ ,  $Fe_2O_3$ ,  $TiO_2$ ,  $Cr_2O_3$ ,  $FeO$ ,  $MnO$ ,  $MgO$ ,  $CaO$ ,  $BaO$ ,  $Na_2O$ ,  $K_2O$ ,  $F$ ,  $Cl$
  - The unit of wt% is  $gram_{oxide} / gram_{mineral}$
- **Methods of analysis (major elements)**
  - **Wet chemical:** chemistry class stuff
  - **Electron probe:** fairly common, moderately easy, microscopic, highly precise & accurate
  - **SEM EDS:** here in building, easy, fairly precise & accurate, microscopic
  - **XRF (X-ray fluorescence):** whole-rock chemistry, very common, very easy
  - **Others:** both whole-rock, & microanalysis
- **Mineral Formulas**
  - minerals must have a well-defined composition
  - The composition range of a mineral expressed by a general chemical formula
  - formulas for different minerals are written with different numbers of oxygen's, because elements or groups will turn out to be integers
- To Calculate a mineral formula from the mineral analysis we're given (the feldspar analysis which contain 8O)
  - general formula:  $(Ca, Na, K)(Fe, Al, Si)_4O_8$
  - Step 1: Moles of oxide
  - Step 2: Normalize Oxygens
  - Step 3: Calculate Cations
  - Step 4: Allocate cations to sites



يستخدم به thin section ويجب عمل polishing له وان يكون flat بسبب ان الاشعة يجب ان تنعكس وتعود لل detector فاذا كان هناك تعرجات يحدث لها تشوه، ويجب عمل coating في الكربون C لانه تحليل كيميائي لا يغطي بالمعادن ولان ال X-ray لا يستطيع تحليل العناصر اقل من 11 ولان الكربون موصل للتيار الكهربائي

الهدف منه هو تحليل كيميائي بمناطق صغيرة

الفرق الرئيسي بطرق التحليل الكيميائي Wavelength-dispersive spectrometry, Energy-dispersive spectrometry

### Step 1 - Moles of oxide

	A	B	C
oxide	weight percent (g oxide / g mineral)	Molecular weight (g oxide / mol oxide)	A / B (mol oxide / g mineral)
$SiO_2$	57.8	60.084	0.96
$Al_2O_3$	25.5	101.961	0.25
$CaO$	8.09	56.079	0.14
$Na_2O$	6.61	61.9756	0.11
$K_2O$	0.52	94.196	0.01
<b>Total</b>	<b>98.52</b>		

### Step 2 - Normalize O<sub>2</sub>

	C	D	E
oxide	A / B (mol oxide / g mineral)	O per oxide (mol O / mol oxide)	C * D (mol O / g mineral)
$SiO_2$	0.96	2	1.924
$Al_2O_3$	0.25	3	0.750
$CaO$	0.14	1	0.144
$Na_2O$	0.11	1	0.107
$K_2O$	0.01	1	0.006
<b>Total</b>			<b>2.931</b>

### Step 3 - Calculate Cations

	C	F	G	H
oxide	A / B (mol oxide / g mineral)	$C * 8 / \Sigma E$ (mol oxide / mol mineral)	$X^+$ per oxide (mol cation / mol oxide)	F * G (mol cation / mol mineral)
$SiO_2$	0.96	2.626	1	2.626
$Al_2O_3$	0.25	0.683	2	1.365
$CaO$	0.14	0.394	1	0.394
$Na_2O$	0.11	0.291	2	0.582
$K_2O$	0.01	0.015	2	0.030
<b>Total</b>				<b>4.998</b>

# 9<sup>th</sup> Lab: Spectroscopy

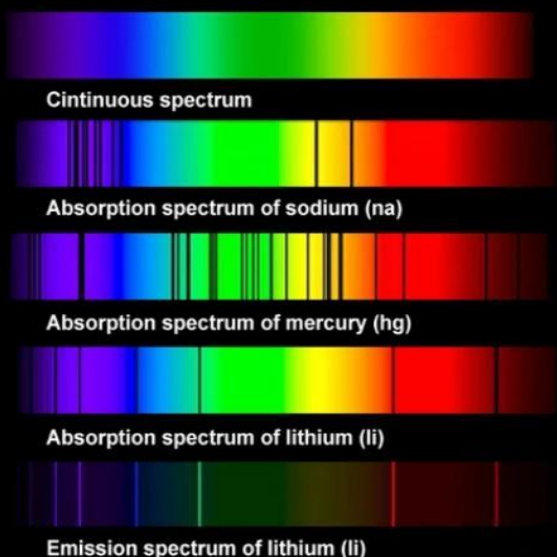
## Atomic Absorption Spectroscopy (AAS) (elemental analysis such as XRF)

- Spectroscopy:** use of the absorption, emission, or scattering of EM radiation to qualitatively or quantitatively study matter or physical processes depending on the distances between energy levels
- The matter can be atoms, molecules, atomic or molecular ions, or solids
- The interaction of radiation with matter can cause redirection of the radiation & transitions between the energy levels of the atoms or molecules

Spectroscopy	Transition	Transfer energy
<b>Absorption</b>	From lower to higher level	From radiation field to absorber
<b>Emission</b>	From higher to lower level	From the emitter to radiation field
<b>Nonradiative decay</b>	From higher to lower level	No radiation is emitted
<b>Scattering</b>	Redirection of light due to its interaction with matter	May not include emission (may have a different $\lambda$ compared to light incident sample)

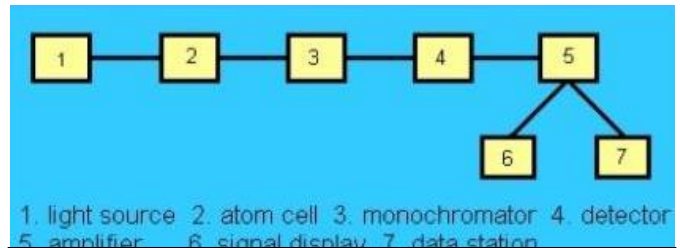
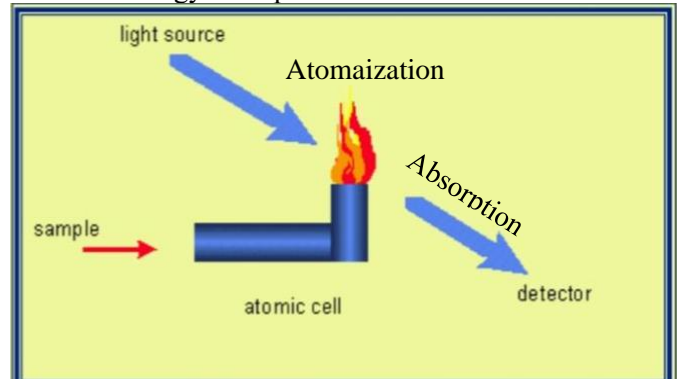
the type of transition that can occur when a photon in these spectral ranges interacts with matter  
\*for energy levels split by a magnetic field

Type of Radiation	Frequency Range (Hz)	$\lambda$ Range(m)	Type of Transition
gamma	$10^{20}$ - $10^{24}$	<1p	nuclear
X-rays	$10^{17}$ - $10^{20}$	1n-1p	inner electron
ultraviolet	$10^{15}$ - $10^{17}$	400n -1n	outer electron
visible	$(4-7.5) \times 10^{14}$	750nm-400nm	
near-infrared	$(1-4) \times 10^{14}$	2.5 $\mu$ m-750nm	outer electron molecular vibrations
infrared	$10^{13}$ - $10^{14}$	25 $\mu$ m - 2.5 $\mu$ m	molecular vibrations
microwaves	$3 \times (10^{11}-10^{13})$	1mm - 25 $\mu$ m	molecular rotations, electron spin
radio waves	$<3 \times 10^{11}$	>1mm	nuclear spin flips*



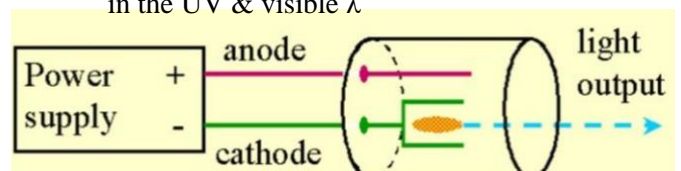
لكل عنصر  $\lambda$  محدد يمتصه من VL بسبب ابعاد المدارات  
Absorption spectrum, Depending on energy levels

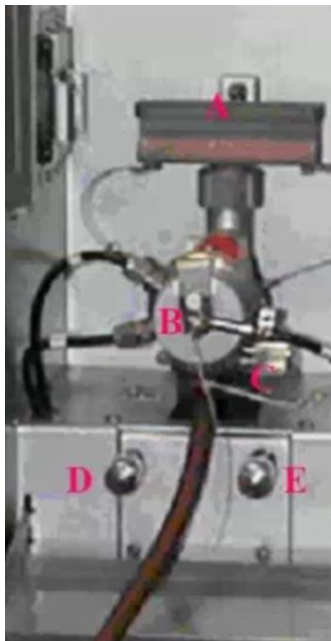
- Atomic absorption** measures the amount of energy (in form of photons of light, & change in  $\lambda$ ) absorbed by the sample
  - a detector measures the  $\lambda$  of light transmitted by the sample (after  $\lambda$ ) compares to the  $\lambda$ , (before  $\lambda$ ) which originally passed through the sample
  - A signal processor then integrates the changes in  $\lambda$ , which appear in the readout as peaks of energy absorption at discrete  $\lambda$



The function of fire is change the liquid into ions  
لكل عنصر light source خاص فيه  
نضع العينة في ال atom cell في ال  
بعض العناصر لها طول موجي متساوي تقريبا فنستخدم ال  
monochromator ليعمل عمليات انعكاس متعددة للضوء ونتيجة  
هذه العمليات يفصل بين هذه العناصر

- To provide element specific  $\lambda$ , a light beam from a lamp whose cathode is made of the element being determined is passed via the flame من الكاثود مصنوع من نفس العنصر الذي يجري له تحليل ليعطي نفس الطول الموجي)
- Photonmultiplier (detector):** A device can detect the amount of reduction of the light intensity due to absorption by the analyte which directly related to the amount of the element in the sample
- Cathode lamp:**
  - The **hollow cathode lamp (HCL)** uses a cathode made of the element of interest with a low internal pressure of an inert gas
  - The light is emitted directionally via the lamp's window, a window made of a glass transparent in the UV & visible  $\lambda$





## Atomic Cell

### A. Burner

تخرج منه ال flame باستخدام غازين الاستلين والاكسجين

### B. Nebulizer

يجعل العينة رذاذ

### C. Rotational Adjust Knob

### D. Horizontal Adjust Knob

### E. Vertical Adjust Knob

## Flame Atomizers

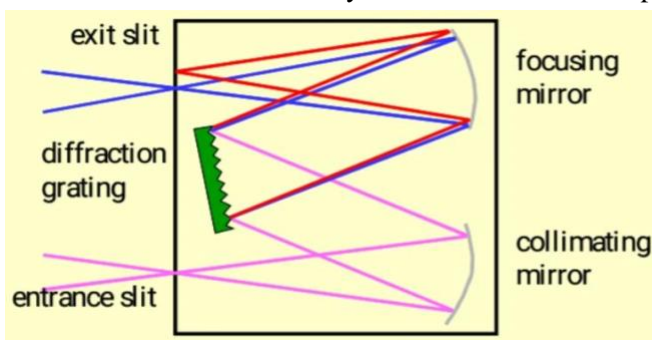
- A typical atomizer is a concentric tube nebulizer with a laminar flow burner
- The aerosol, which uses the oxidizer flow, is mixed with the fuel & passes a series of baffles which remove the larger mist & only passes the finer solution droplets
- The removal of the coarse mist means most of the sample is drained from the mixing chamber
- The aerosol-oxidant-fuel mixture are then combusted in a slotted burner that provides a flame from 5 - 10 cm in length
- Laminar flow burner provides quiet reproducible flame with a long path length

## Types of Flames: Several fuel & oxidant employed in flame spectroscopy depending on T needed

- 1700 - 2400°C: various **fuel** when air (**oxidant**) only easily decomposed samples are atomized
- Most common is oxygen or nitrous oxide (**oxidant**) with **fuel** Acetylene (2500 - 3100°C)

Fuel	Oxidant	T(100°C)	Velocity(cm/s)
Gas	Air	17 - 19	39 - 43
Gas	O <sub>2</sub>	27 - 28	370 - 390
H <sub>2</sub>	Air	20 - 21	300 - 440
H <sub>2</sub>	O <sub>2</sub>	25.5 - 27	900 - 1400
Acetylene	Air	21 - 24	158 - 266
Acetylene	O <sub>2</sub>	30.5 - 31.5	1100 - 2480
Acetylene	Nitrous	26 - 28	285

- **Monochromator:** important device, separate the spectral line of interest from others spectral lines with different  $\lambda$  emitted by the hollow-cathode lamp



- The desired spectral line is chosen with the preferred  $\lambda$  & bandwidth by an appropriate monochromator's setting named grating
- A grating is a reflective surface, scored either mechanically or holographically with parallel grooves that designed for different  $\lambda$  regions
- most of the instruments are equipped with 2 gratings with the goal to cover a  $\lambda$  range 189 - 851nm which is used in atomic absorption
- **consists of** the diffraction grating (dispersing element), slits, & spherical mirrors

- **Beer-Lambert Law:** linear relationship between absorbance & concentration of absorbing species  
مقدار الامتصاص للاشعة يتناسب تناسب طردي مع تركيز العنصر

$$A = a(\lambda) * b * c = \epsilon * b * c$$

measured absorbance = ( $\lambda$ -dependent absorptivity coefficient) \* (path length) \* (analyte concentration)

$$T = I / I_0$$

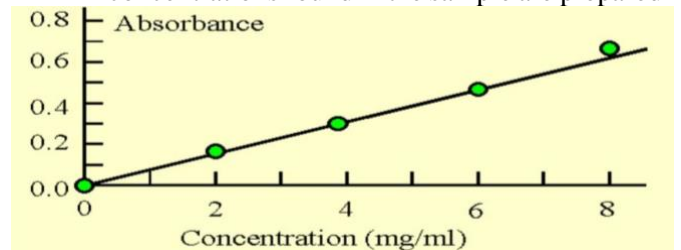
Transmittance = light intensity after / initial intensity

$$A = -\log T = -\log (I / I_0)$$

- **Calibration Curves:** Atomic absorption follow Beer's law with absorbance being directly proportional to concentration

يستخدم لتحويل ال **concentration** ل **intensity of absorption** قبل ان نبدأ بعملية القياس نستخدم مجموعة **standards** تحتوي تركيز محدد معروف ثم نقيس ال absorption لهم ثم نعملهم **best line** ثم نحال ال unknown ونقيس ال absorption ونحدد نقطة ونقرأ تركيزها لهذا فأنها عملية تحتاج وقت كثير فال XRF تستخدم أكثر منها

- departures from linearity are often encountered, & it is foolhardy to perform an atomic absorption analysis without experimentally determining whether a linear relationship exist
- A calibration curve that covers the range of concentrations found in the sample are prepared



- Linear regression uses the method of least squares to determine the best linear equation to describe a set of x & y data points
- The method of least squares minimizes the sum of the square of the residuals – the difference between a measured data point & hypothetical point on a line
- Residual squared, +ve & -ve value don't cancel
- Spreadsheets will often have built-in regression functions to find the best line for a set of data
- A common application of linear regression in analytical chemistry is to determine the best linear equation for calibration data to generate a calibration or working curve
- concentration of analyte in a sample can then be determined by comparing a measurement of the unknown to the calibration curve
- Linear Regression Equations

# Test Bank

One of these elements Can't be detected by XRF

1. **Carbon**
2. Potassium
3. Iron
4. Calcium

XRD is a method used to identify substances due to:

1. chemical composition
2. **Structure**
3. Density

Device separate equal  $\lambda$  of different elements in AAS

1. detector
2. nebulizer
3. hurner
4. **Monochometer**

A wave phenomenon in which the apparent bending & spreading of waves when they meet an obstruction

1. Reflection
2. Refraction
3. **Diffraction**
4. Interference

Minerals that slightly repelled by a magnetic field:

1. paramagnetic
2. **diamagnetic**
3. Ferromagnetic

Minerals that slightly attached by a magnetic field:

1. **paramagnetic**
2. diamagnetic
3. ferromagnetic

Qz & Fs separated from minerals using

1. **bromofom**
2. Iodoform
3. acetone
4. Ethanol

Staining for granites is done by using sodium cobalt nitrite, alkali-feldspar color changes into:

1. Red
2. **Yellow**
3. White
4. Orange

In X-ray tube anode made of these metals except:

1. Copper (Cu)
2. Tungsten (W)
3. Rhodium (Rh)
4. **Al**

Hint. Heavy metal with high melting point  
*Platinum, Tungsten*

The standard thin section of rocks thickness

1. 0.3mm
2. 0.003mm
3. **0.03mm**
4. 3.0mm

Materials containing a known concentration & used to build calibration curve in instrument analysis

1. Chemicals
2. Buffer
3. **Standard**
4. Indicator

Method to distinguish between amorphous & crystalline silica? 2 techniques

1. **XRD**: can detect crystalline compounds  $\rightarrow$  SiO<sub>2</sub>
2. **XRF**: amorphous (Si & O atoms concentration)

Before magnetic separation of minerals, sample are treated by hand magnet. Why? will clog the Frantz separator (instrument used to separate minerals)

Function of the crystal in Spectrometers of XRF?

عندما تصطدم ال primary X-ray بالعينة يخرج منها احد الالكترونات ويحل مكانه e من مستوى طاقة اعلى، وفرق الطاقة يُسُغ على هيئة x-ray تسمى XRF ولان لكل عنصر له characteristic X-ray فان كل  $\lambda$  للأشعة المنبعثة يحدث له تداخل وانعكاس عند  $\theta$  معينة، اذا تم عكس هذه الاشعة مباشرة لل detector ستكون نسبة الخطأ كبيرة لذا يتم تمريرها ل crystal تتميز باحتوائها **constant d spacing** وتتحرك بحركة دائرية، وحركتها هذه تعمل على فصل ال x-ray المختلفة بحيث يتمكن ال detector من قياسها كل على حدى (لانها تدور فعند كل  $\theta$  بمحيط دورانها **تعكس  $\lambda$  محدد** لعنصر محدد وعندما تتحرك تتغير  $\theta$  فتعكس  $\lambda$  لعنصر اخر وباقي الاطول يحدث لها تداخل هدام...)

How would you know that thin sections are still thick? **Using microscopic**

Give names of essential materials & machines needed to make thin section?

1. **Glass slides, Cover slip, & Epoxy**
2. **Diamond saw (cutting machine for rock slab)**
3. **Coarse, medium, & fine carbide grit powder (400, 800, & 1200) to polished rock slab**
4. **Automatic grinding machine for polishing**
5. **Lap for grinding & a small warming plate**
6. **Microscope (To ensure the accuracy)**
7. **Hot plat (Electric gas)**

What is the Diffraction: **wave phenomenon in which the apparent bending & spreading of waves as they meet an obstruction, can be occurs with EMW such as light & radio waves, & in sound & water waves**

What is the difference between coating & covering? **The coating is just a thin cover on the sample to keep the details clear**

Why minerals show several characteristics peaks on the diffractograph? **The diffracted beam (reflection) from any set of lattice planes can only occur at particular angles ( $2\theta$ ) predicted by the Bragg law**

Instruments used to distinguish among isotopes of an element **TIMS XRF, TMS & SIMS**

Instrument used to distinguish ions of the same element in different valence states **wet chemical analysis or Mossbauer spectroscopy**

X ray cannot analysis atoms with atomic number  $Z < 11$  why? **Larger atoms have greater energy differences between orbitals (energy level more closely matches the energy of photon), & in Smaller the electron orbitals are separated by low jumps in energy, are less likely to absorb X-ray photons**

SEM magnification 1000,000 times LM why? **Because Resolution limited by  $\lambda$  (LM work with VL)**

In contrast to visible light electron rays can give images with magnification up to 600.000X, why? **Because it's works with x-ray  $\lambda$**

In SEM samples coated by gold, while for chemical analysis EPMA samples coated by carbon, Why?

**الذهب اكثر قدرة لانتاج secondary ray لصنع صورة imaging يستخدم الكربون لانه خفيف ( $Z < 11$ ) ولانه موصل للتيار الكهربائي ولو كان عنصر اقل سيحدث له تحليل وليس للعينة**

Difference between quantitative & qualitative analysis? **Quantitative is the amount (concentration) of an atoms & qualitative is the type (e.g. Minerals, Crystals) of a given materials**

# important information

- XRD are used to identify crystalline substrate & XRF for noncrystalline substance
- In SEM samples coated by gold, & for chemical analysis in EPMA samples coated by carbon
- Diagram represents the interaction between radiation &  $\lambda$
- Quantitative analysis (amount of an atoms): Microprobe analysis or Electron probe microanalyzer (EPMA), Atomic Absorption Spectroscopy (AAS), XRF
- Qualitative analysis (crystal structure): Atomic Absorption Spectroscopy (AAS), or XRD

WDS (Wavelength-dispersive spectrometry)	EDS (Energy-dispersive spectrometry)
--	--------------------------------------

By $\lambda$ , using a diffracting crystal to isolate the characteristic X-ray peaks	By energy using a solid-state detector that discriminates between the energies of incoming photons
High spectral resolution (element clearly resolved)	Low spectral resolution (deconvolute overlapping peaks)
Higher peak/background (better detection limits)	Lower peak/background (lower precision)
Sequential measurement of peaks, slower	Simultaneous collection of whole spectrum, rapid
Specimen flat & in focus	Insensitive to specimen geometry
Delicate moving parts	No moving parts, & Less expensive
Expensive to buy مثال XRF لكن حجمه صغير	الفرق بينه وبين WDS هو انه يعطي التحليل لكل العناصر مرة واحدة

### Staining involves the use of 3 chemicals

<b>Hydrofluoric Acid (HF)</b>	To etch the polished surface, breaks bonds between K, Ca
<b>Amaranth</b> $C_{20}H_{11}N_2Na_3O_{10}S_3$	Powder to stain plagioclase on surface in a <b>red</b> color
<b>Sodium Cobaltinitrite</b>	To stain any K-feldspar on that surface a <b>yellow</b> color

Group	Definition
Ferromagnetic	Have constant magnetic properties, regardless they are exposed to an external field
Diamagnetic (Repelled)	don't have magnetic properties unless it's exposed to an external field (repelled or attached to a magnetic field)
Paramagnetic (attached)	
Group	Separated using
Ferromagnetic	Hand-magnet
Diamagnetic	FIMS to separate it from para. & then using heavy liquids
Paramagnetic	FIMS

### Common heavy liquids

<b>Bromoform</b>	2.85 g/ml
<b>Tetrabromoethane</b>	2.96 g/ml
<b>Diiodomethane</b>	3.32 g/ml

### Granite Composition

Para	I [A]	Dia	$\rho$ [g/cm <sup>3</sup> ]
<b>Biotite</b>	0.8	Feldspar, Qz	< 3.0
<b>Monazite</b>	0.6	Apatite	3.1
		Zircon	4.56
0.4A	0.8A	1.5A	1.5A
Garnet	Biotite	Muscovite	Zircon
Ilmenite	Hornblende	Spinel	Rutile
Chromite	Hypersthene	Enstatite	Titanite
Chloritoid	Chlorite	Tourmaline	Apatite
Olivine	Augite	Zoisite	Corundum
	Actinolite	Diopside	Barite
	Staurolite	Tremolite	Fluorite
	Epidote		Sillimanite
			Kyanite

Rays	Function
Back-scattered	Different phases
Secondary (SR)	External Morphology (Texture) Imaging, & Zooming High-resolution composition maps
XRD	Crystal Structure (mineralogical)
XRF	Chemical analysis (amorphous, oxides, or elemental analysis)
WDS	Such XRF (elemental analysis)
EDS	Intensity at same time
Electron probe micro-analyzer (EPMA)	Quantitative: chemical analysis such as SEM but at small scales Internal compositional structures
Atomic Absorption Spectroscopy (AAS)	Elemental analysis such as XRF Quantitative or Qualitative analysis
Cathodoluminescence (VL)	Internal structure (Gold coating)
CL	Composition, lattice structure, superimposed strain or damage