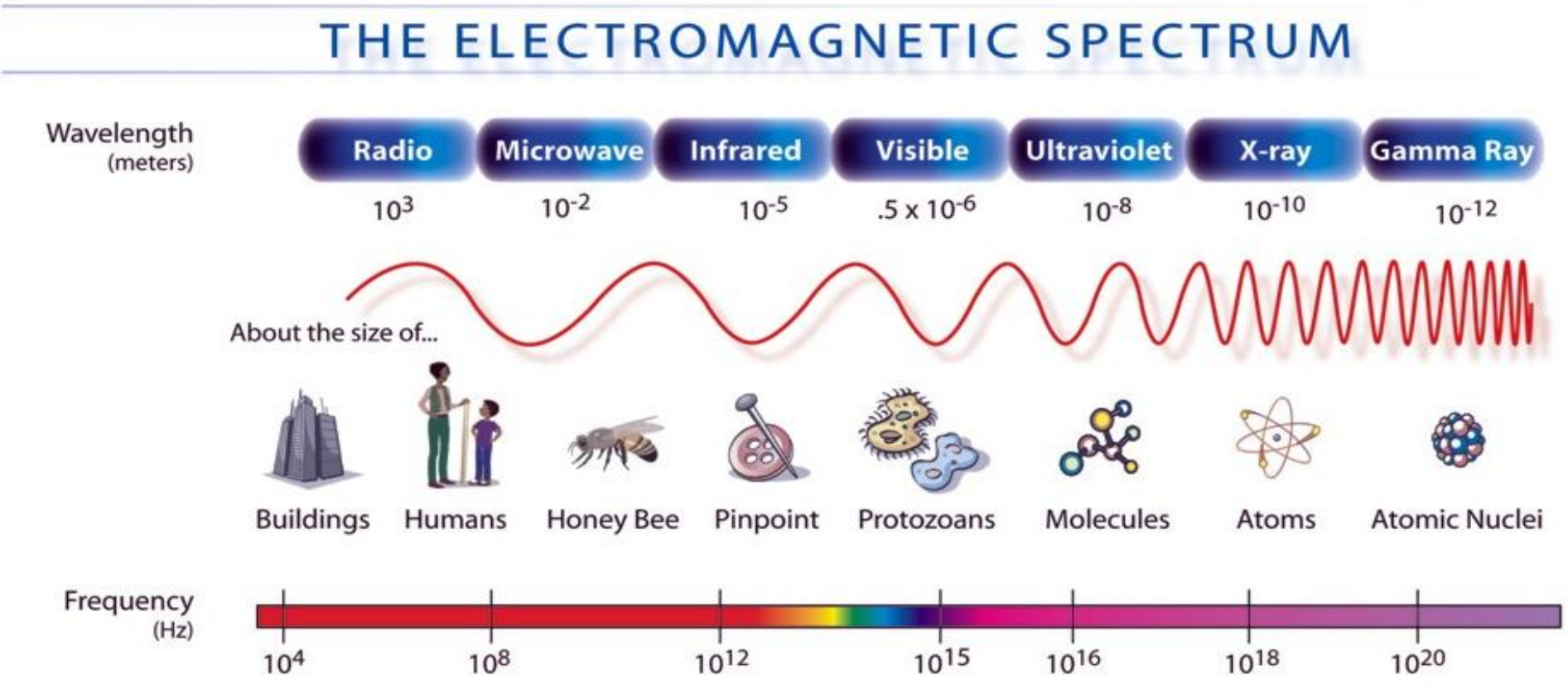
Materials Characterization Techniques II

Interaction of X-rays with materials and the associated techniques for materials characterization

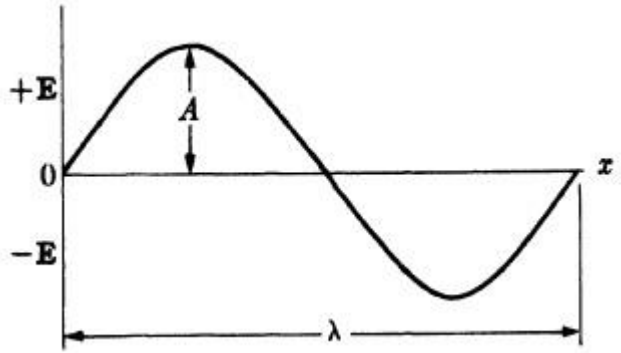
What are X-Rays?



- X-Rays are light... they can help you see
- They do all the things that light does when it encounters matter

What are X-Rays?

- Electromagnetic radiation, such as a beam of X-Rays, carries energy, and the rate of flow of this energy through unit area perpendicular to the direction of motion of the wave is called the intensity
- The average value of I is proportional to the square of the amplitude of the wave

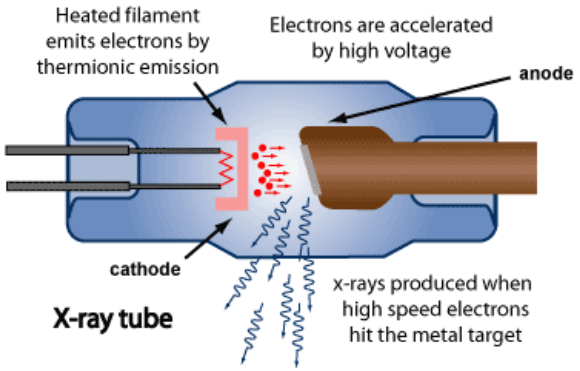


- X-Rays are also particles with energy called photons according to the Quantum theory

$$E = hv$$

How are X-Rays produced?

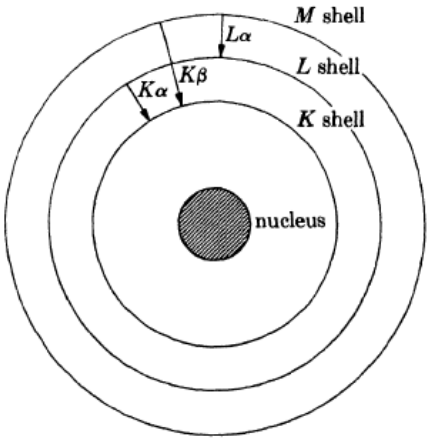
- X-Rays are produced when any electrically charged particle of sufficient kinetic energy is rapidly decelerated

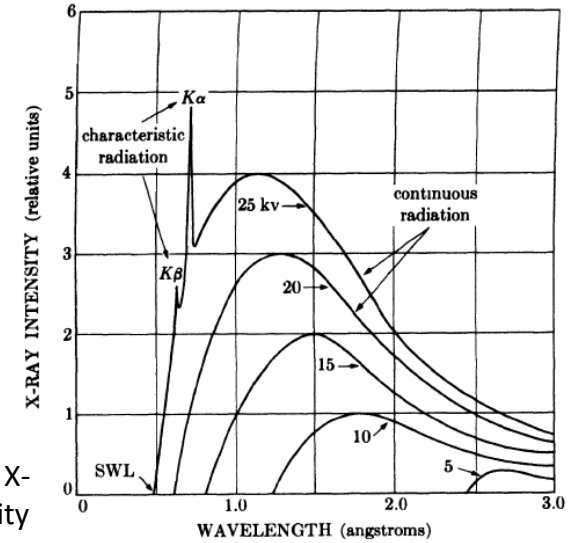


$$KE = eV = \frac{1}{2}mv^2$$

where e = 1.44 x 10^{-7} volts,
m = 9.11 x 10^{-28} g
$v = c/3$ for a tube voltage of
V = 30000 volts

- >99% of the energy is dissipated as heat around the X-Ray tube





Continuous X-Ray spectrum of molybdenum as a function of applied voltage

Figures adapted from Chapter 1 – Properties of X-Rays of ``Elements of X-Ray Diffraction`` by Cullity

Interaction of X-Rays with Matter

- X-Ray photons interact with the electrons in matter
- X-Rays can be:
  - attenuated
    - absorbed
    - fluoresced
    - incoherently scattered
  - coherently scattered
    - refracted
    - reflected
    - diffracted

$$I_x = I_0 e^{-(\mu/\rho)\rho x}$$

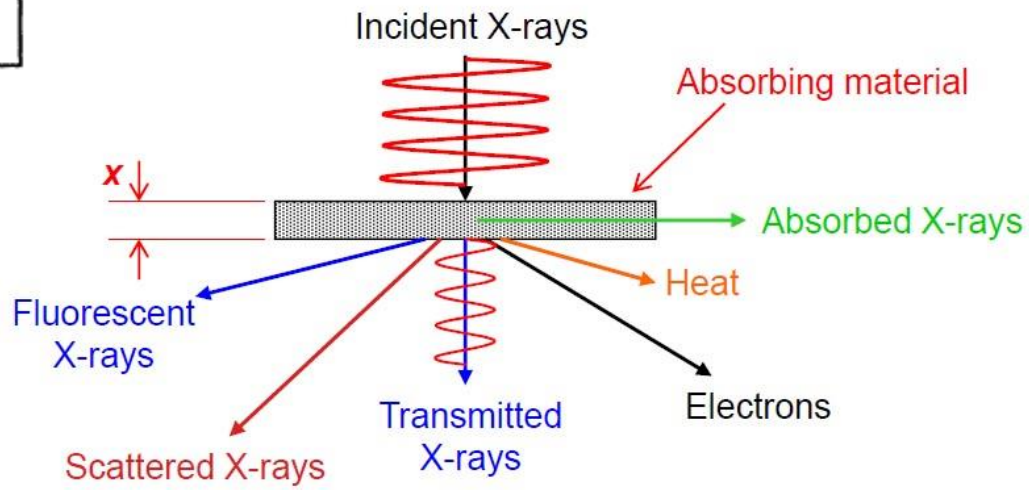
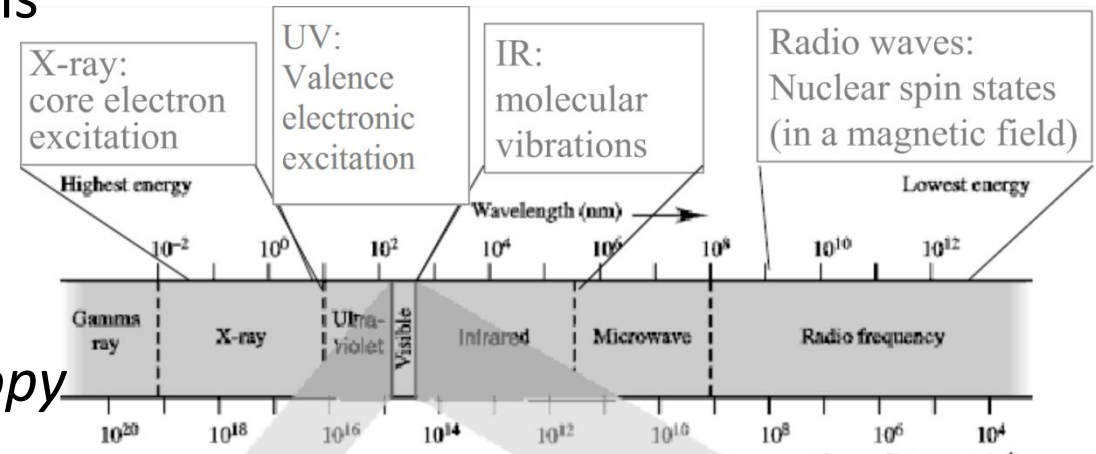


Figure adapted from Chapter 4 of Elements of X-Ray Diffraction by Cullity

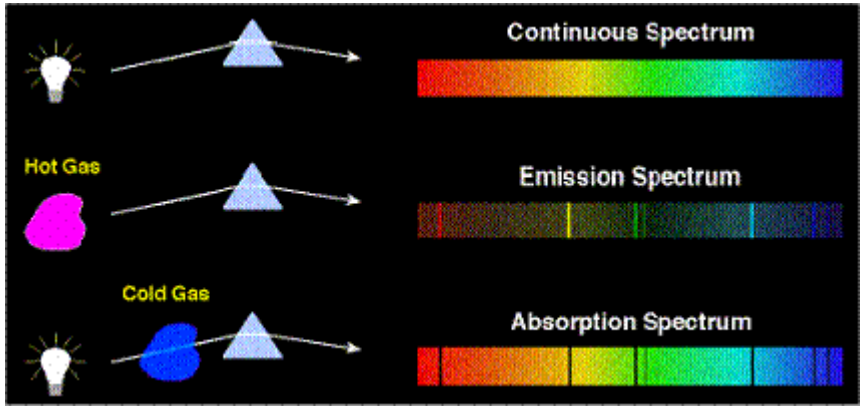
The change in X-Ray photons due to interaction with electrons can be used to discern information about the matter, *as in Spectroscopy*

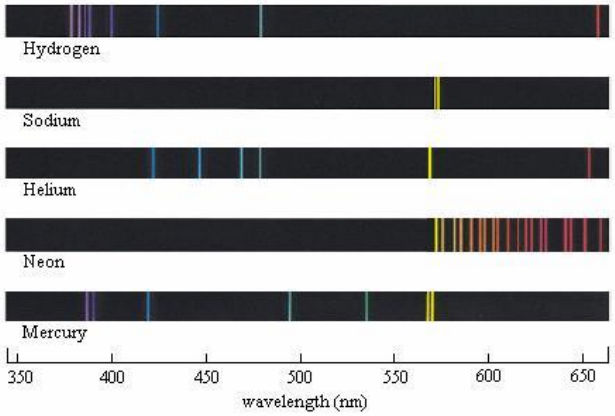


Spectroscopy

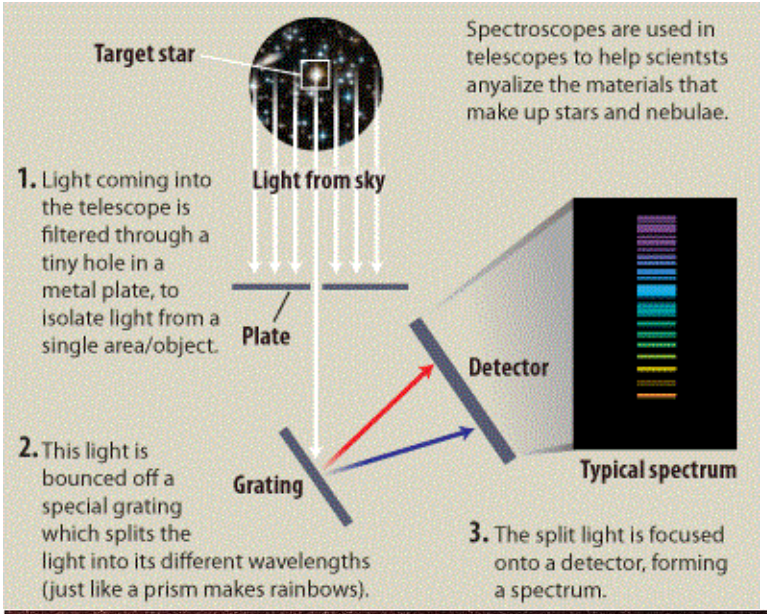
Spectroscope splits the light emitted by excited electrons into an emission spectrum. The spectrum consists of a series of lines; the color of these lines is specific to the wavelength which indicates the energy level of electron transitions

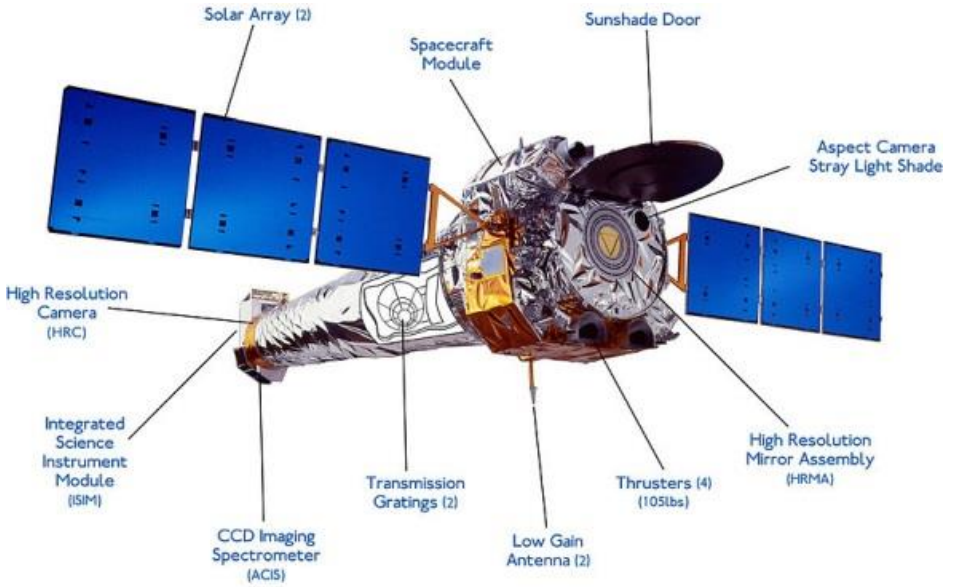
$$E = \frac{hc}{\lambda}$$

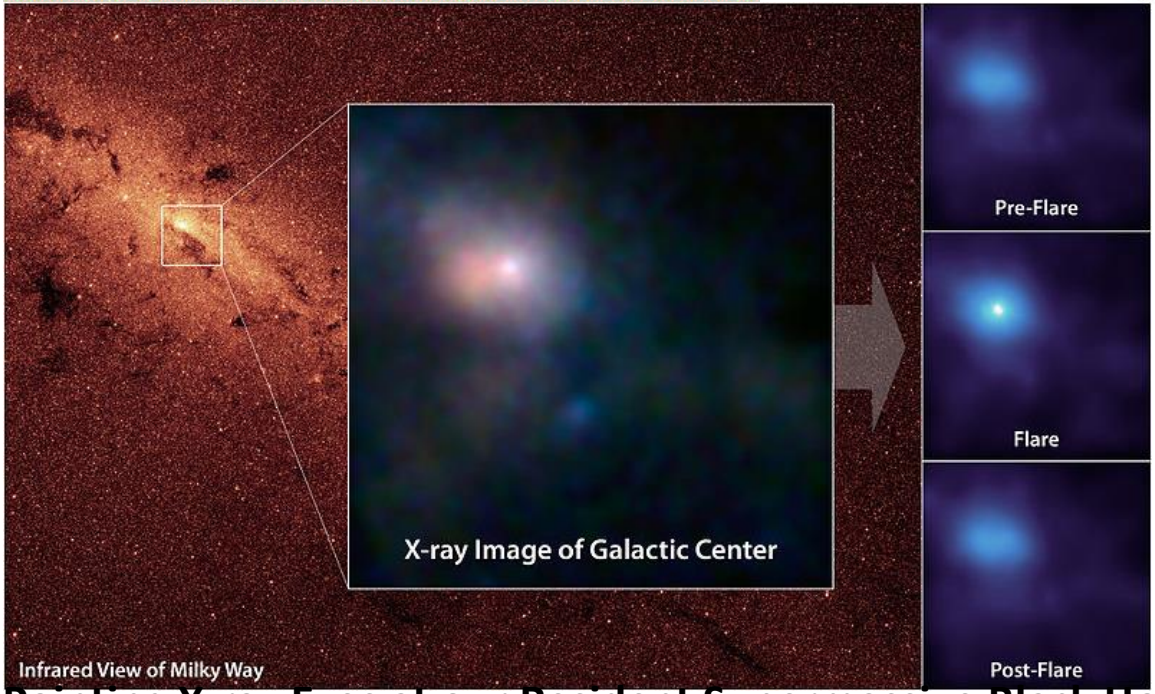




Spectroscopy in Space







In the main image, the brightest white dot is the hottest material located closest to the black hole. The time series at right shows a flare caught by NuSTAR over an observing period of two days in July; the middle panel shows the peak of the flare, when the black hole was consuming and heating matter to temperatures up to 100 million degrees Celsius.

The main image is composed of light seen at four different X-ray energies. Blue light represents energies of 10 to 30 kiloelectron volts (keV); green is 7 to 10 keV; and red is 3 to 7 keV. The time series shows light with energies of 3 to 30 keV. The background image of the central region of our Milky Way was taken at shorter infrared wavelengths by NASA's Spitzer Space Telescope.

Pointing X-ray Eyes at our Resident Supermassive Black Hole

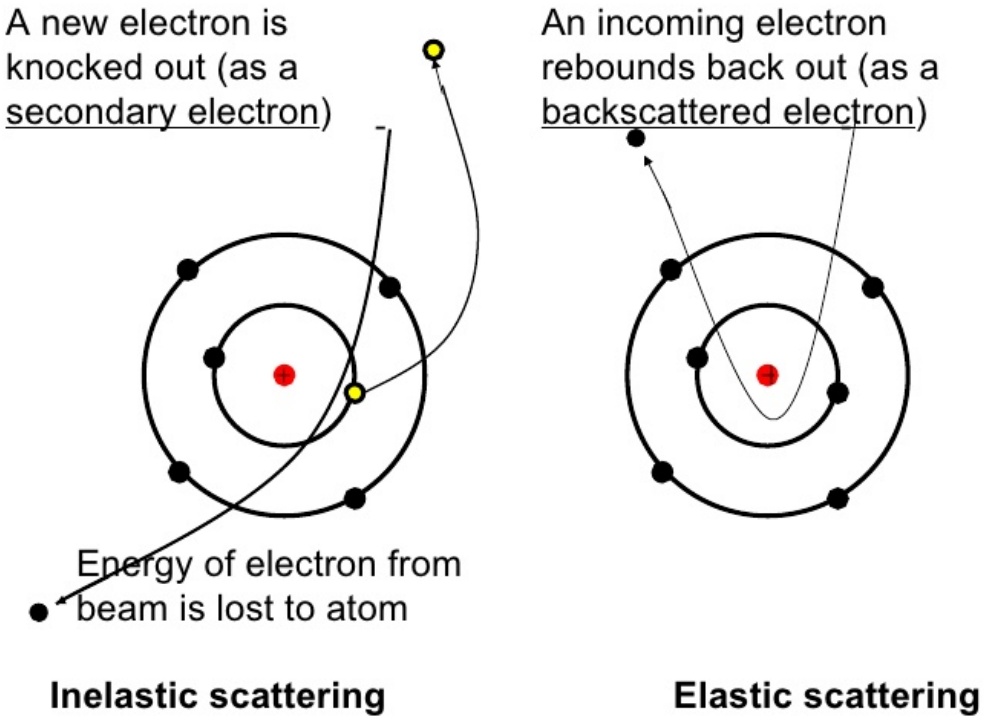
Material Characterization by Spectroscopy

Spectroscopic Techniques, Chemistry They Probe and Common Uses			
UV-vis	UV-vis region	bonding electrons	Quantitative analysis/Beer's Law
Atomic Absorption	UV-vis region	atomic transitions (val. e-)	Quantitative analysis Beer's Law
FT-IR	IR/Microwave	vibrations, rotations	Functional Group Analysis
Raman	IR/UV	vibrations	Functional Group Analysis/quant
FT-NMR	Radio waves	nuclear spin states	Structure determination
X-Ray Spectroscopy	X-rays	inner electrons, elemental	Elemental Analysis
X-Ray Crystallography	X-rays	3-D structure	3-D structure Anaylysis

- X-Ray crystallography: Determination of the wavelength of X-Ray radiation from a crystal with planes of known spacing by measuring the angle

Fundamentals of X-Ray interaction with matter

When an electron beam source such as a cathode ray tube generates electrons that hit a material, the energy in the electron is scattered both elastically and inelastically



All of the energy will eventually be reduced to the kinetic energy kT due to inelastic scattering

The electrons in the beam entering a crystalline material follow an irregular scattering path, losing energy as the path length in the crystal increases

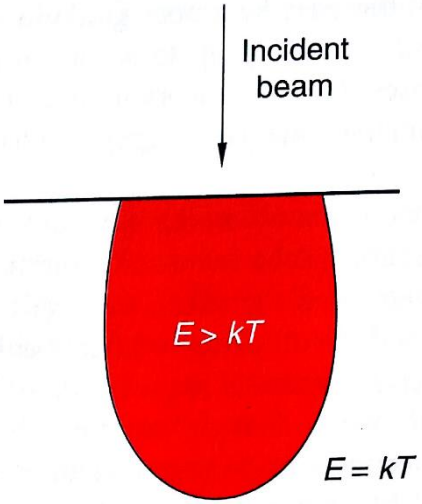
It is not possible to calculate the average trajectory for multiply scattered electrons

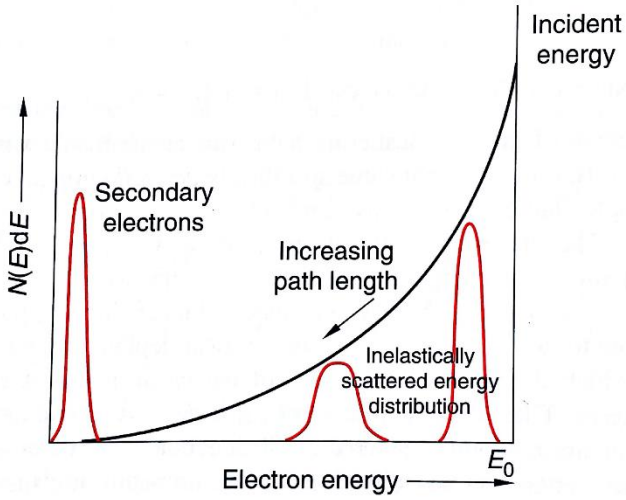
However it is possible to define and measure two critical depths, the diffusion depth x_D and the penetration depth X_R

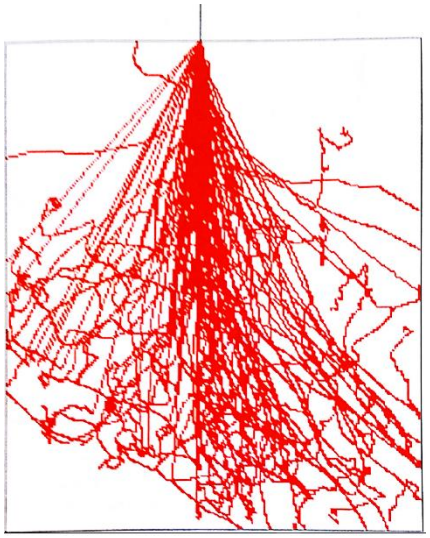
The diffusion depth is the depth beyond which the incident electrons are randomly scattered in any direction

The penetration depth is the depth at which the electron energy is reduced to the thermal energy kT

An envelope of material bounded by the penetration depth can be observed using detection techniques such as electron microscopy or x-ray fluorescent spectroscopy

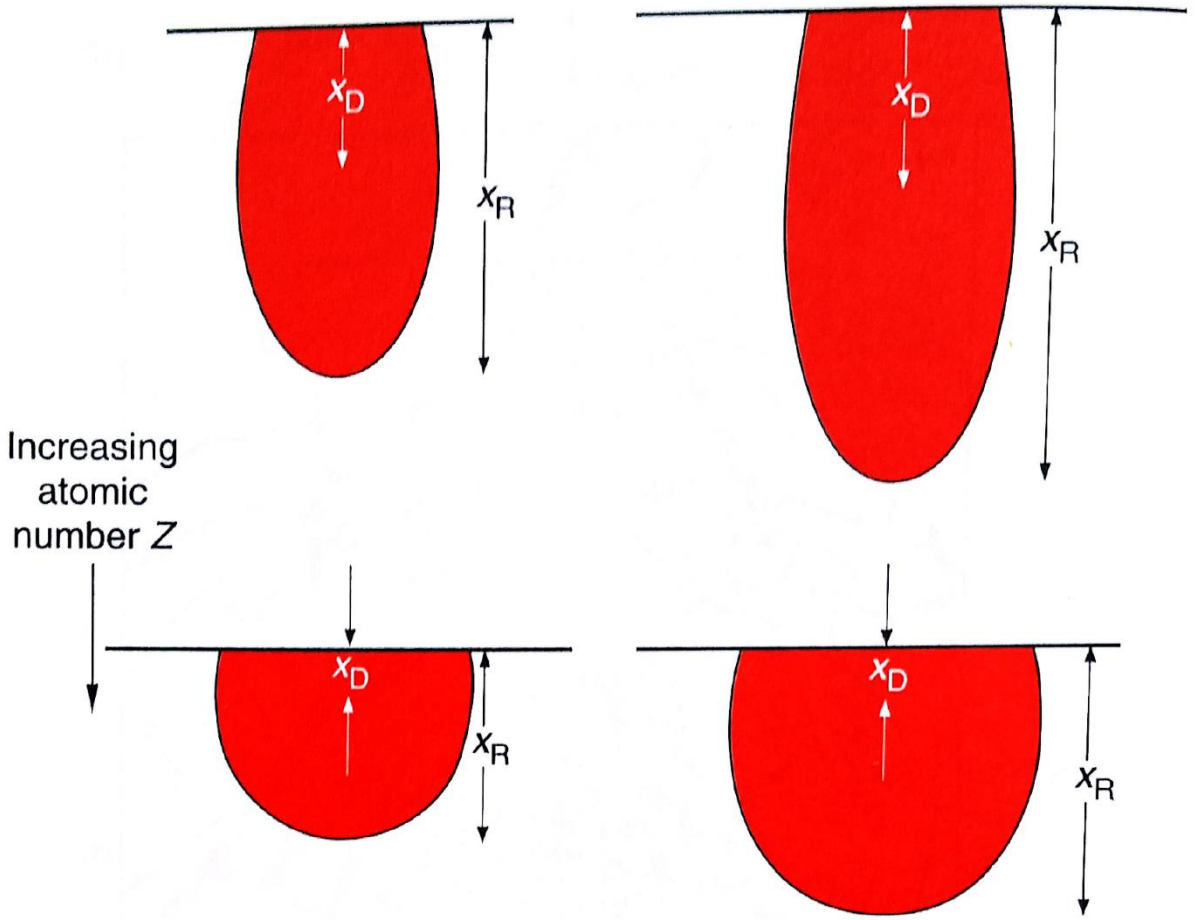






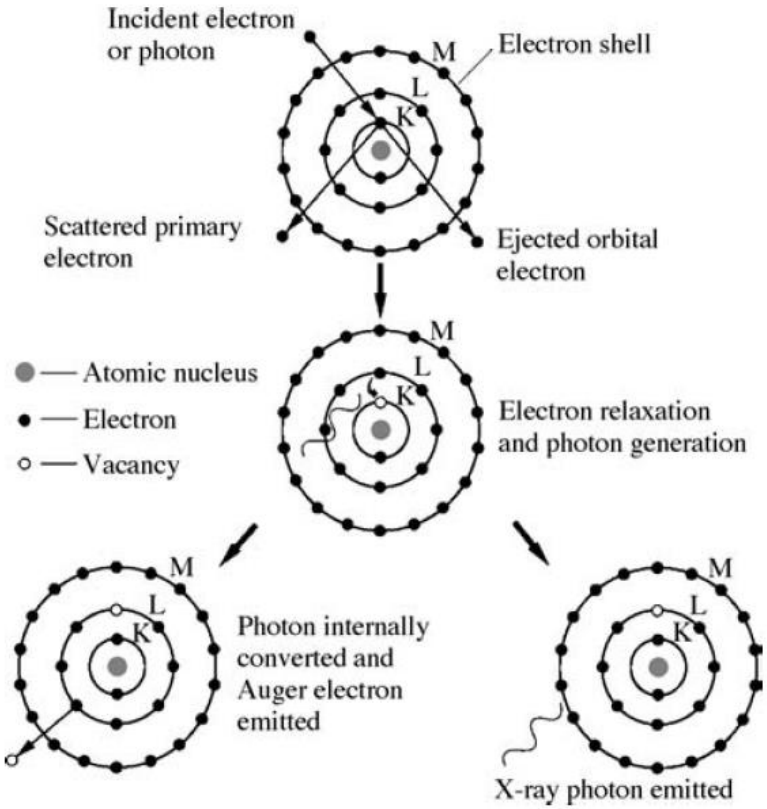
Both x_D and x_R decrease with increasing atomic number Z and decreasing incident beam energy E_o

The shape of the envelope of scattered paths changes markedly with the atomic number, because the lateral spread of the beam is roughly proportional to the difference X_D-X_R while X_R is less sensitive to Z than X_D



It is possible to ionize an atom in the specimen hit by a beam of electrons, if the incident electron energy exceeds the energy required to eject an electron from the atom

Ionization of the atom occurs by an inelastic scattering event which raises the energy of the atom above the ground state by an amount equal to the ionization energy.



All such transitions are accompanied by the emission of a photon

If an electron from one of the inner shells of the atom is hit by the incident beam, then the resulting photon will have an energy in the X-ray region of the spectrum

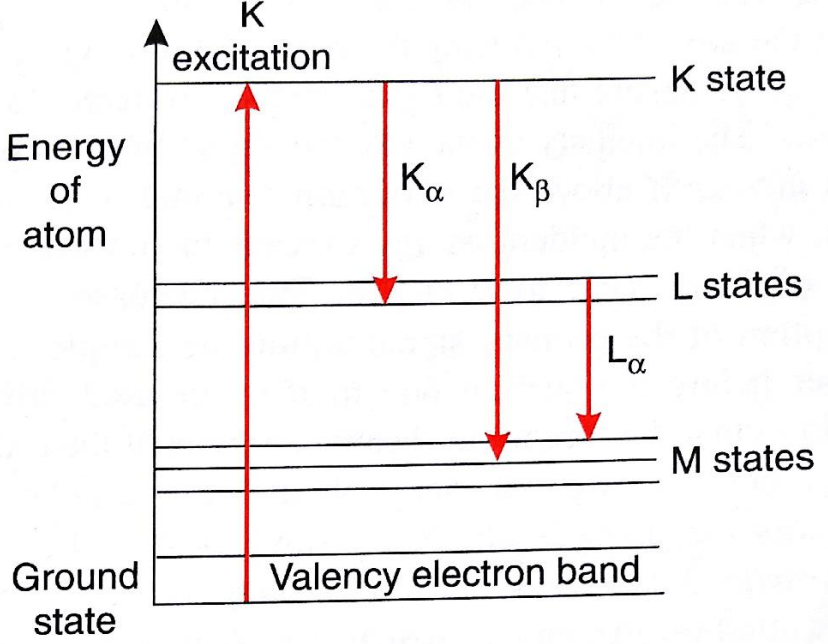
In general decay of an atom from the excited state takes place in more than one stage, with the emission of several photons of different wavelengths, each corresponding to a transition of the excited atom back towards the ground state

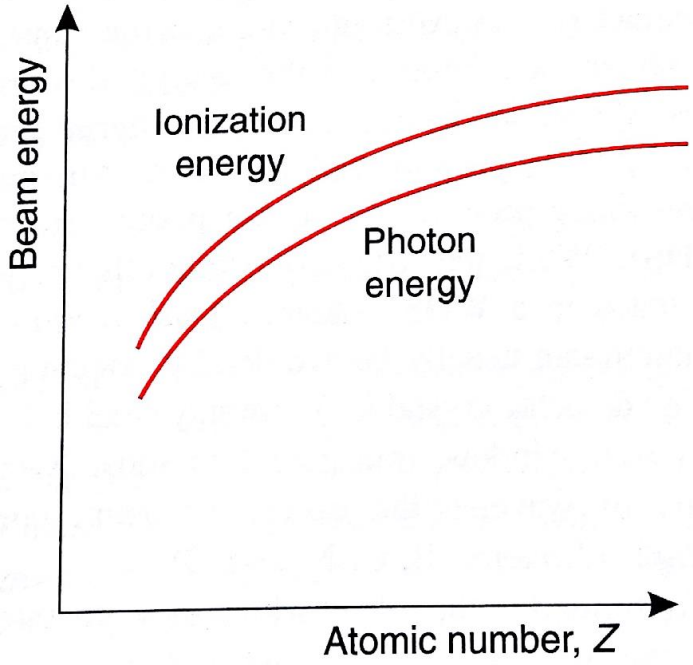
The energy lost by the incident electron must exceed the threshold energy for the ionization state

The energy of most energetic photon which can be emitted in response will always be less than the threshold for ionization

Consider a particular inner shell of electrons (innermost K-shell)

The ionization energy for electrons occupying this shell must increase with increasing atomic number because the inner-shell electrons are more deeply embedded in the atom for the higher atomic numbers





The X-ray spectrum generated when an electron beam hits a solid target contains all wavelengths starting from the minimum wavelength derived from the following relationship

$$\lambda = \frac{hc}{eV}$$

where h is the Planck constant, c is the speed of light, e is the charge on the electron and V is the accelerating voltage applied to the electron beam

Recall that X-rays are most practically generated by accelerating a beam of electrons on to a pure metal target contained in a vacuum tube

The high energy electrons eject ground-state electrons from the atoms of the target material, creating holes in the inner shells, and X-rays with different wavelengths are emitted during the refilling of these ground states

If all of the incident electron energy were converted into a photon, the frequency v would be given by the quantum relationship:

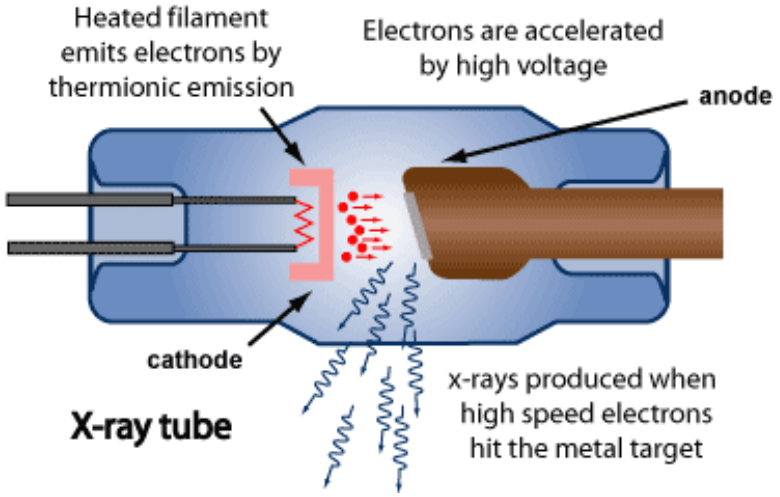
$$E = eV = h\nu = h\frac{c}{\lambda}$$

The condition that all of the energy of the exciting electron is used to create a photon sets an upper limit on the frequency of the X-rays generated and a lower limit on the X-ray wavelength. The above relationship lead to an inverse dependence of this minimum wavelength on the accelerating voltage of the X-ray tube:

$$\lambda_{min} = 1.243/V$$

where λ is in nanometers and V is in kilovolts

X-ray production:



$$E = eV = h\nu = \frac{hc}{\lambda}$$

$$F_{\max} = \frac{hc}{\lambda_{\min}} = \frac{1}{2}m\left[v^*\right]^2 = e_e V$$

$$\lambda_{\min} = \boxed{\lambda_{SWL}} = \frac{hc}{e_e V} = \frac{(6.626\times10^{-34})(3\times10^{8})}{(1.6022\times10^{-19})V} \cong \boxed{\frac{12.43}{V}\ (\text{Å})}$$

(kV)

$$\lambda_{min} = 1.243/V$$

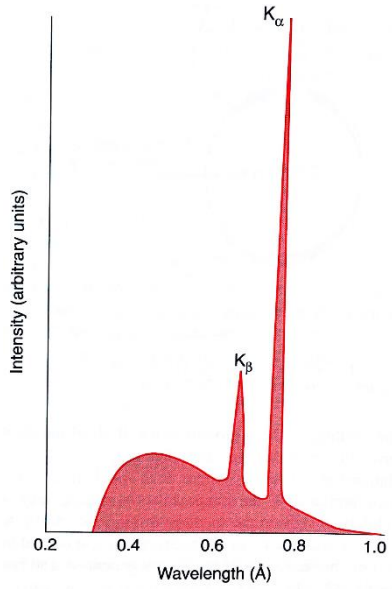
Above this minimum wavelength there is a continuous spread of X-ray wavelengths for the scattered photons generated by the incident beam

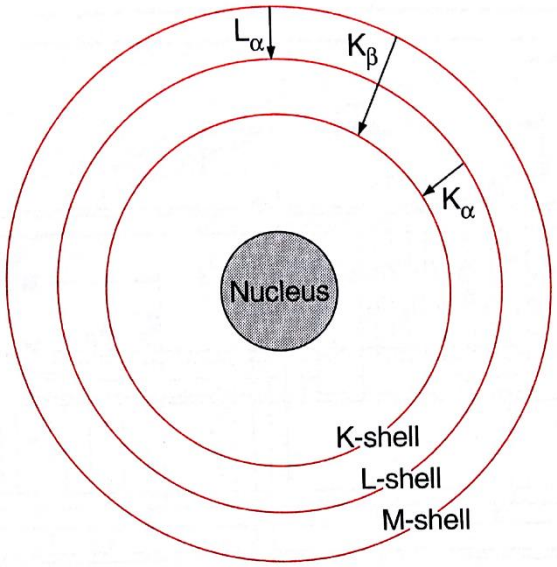
The intensity of the X-ray photon increases with incident electron energy, beam current and the atomic number of the target (the density of electrons in the target material)

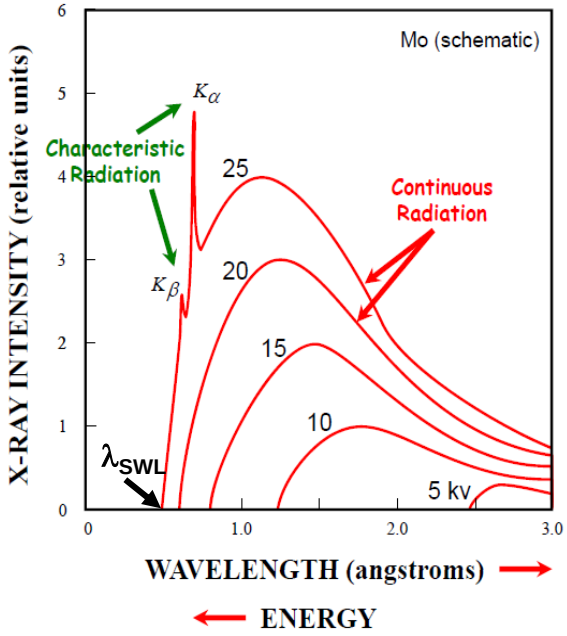
This continuous distribution of photon energies and wavelengths in the X-rays emitted from the target is called white radiation

White radiation is characteristic of only pure target metals as presence of other atoms in the path of the scattered X-rays will result in absorption of some of the wavelength photons

Superimposed on the continuous spectrum of white radiation are a very narrow and intense peaks that are called the characteristic radiation



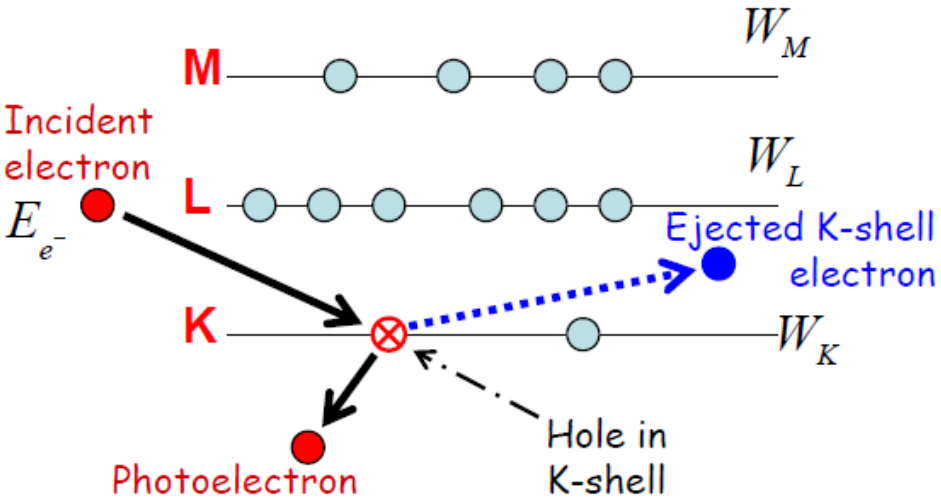


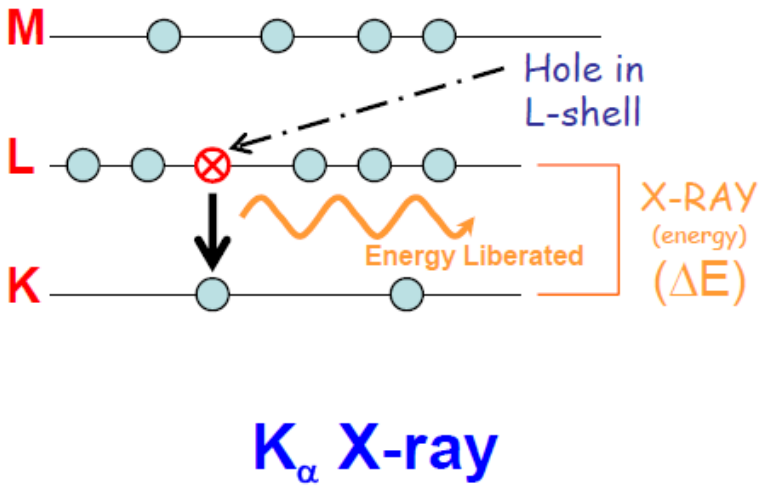


A characteristic peak corresponds to the energy released when the hole in an inner electron shell is filled by an electron from a higher energy shell of the same atom

The removal of an electron from the K-shell excites the atom to an energy state E_K and if the hole in the K-shell is then filled by an electron from the L-shell, the energy of the atom will decay to E_L

The decrease in the energy (E_K-E_L) will appear as an X-ray photon of fixed wavelength which contributes to the K_α line of the characteristic target spectrum

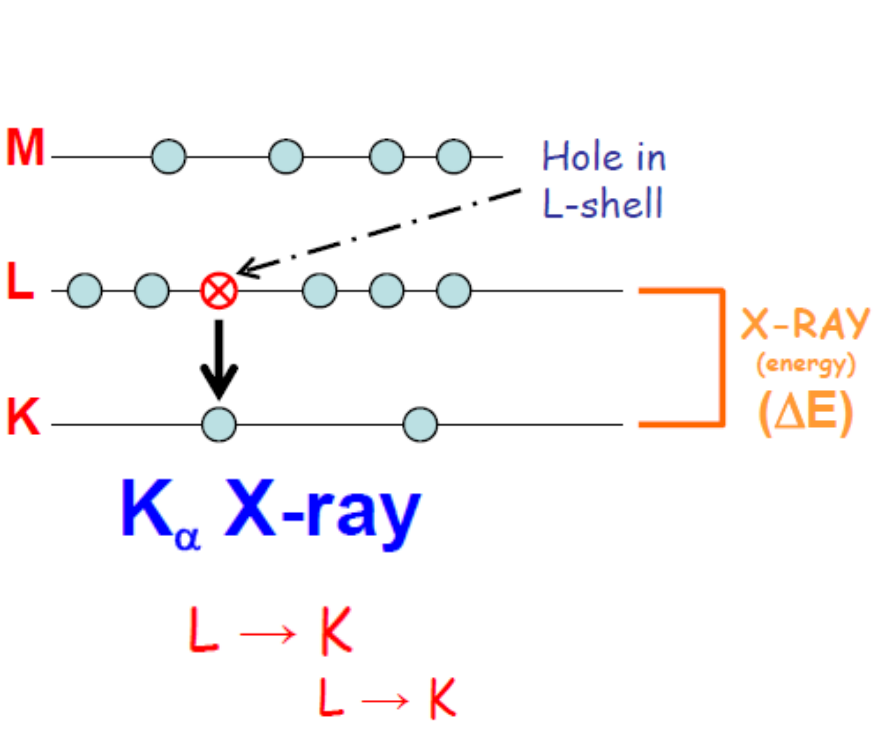


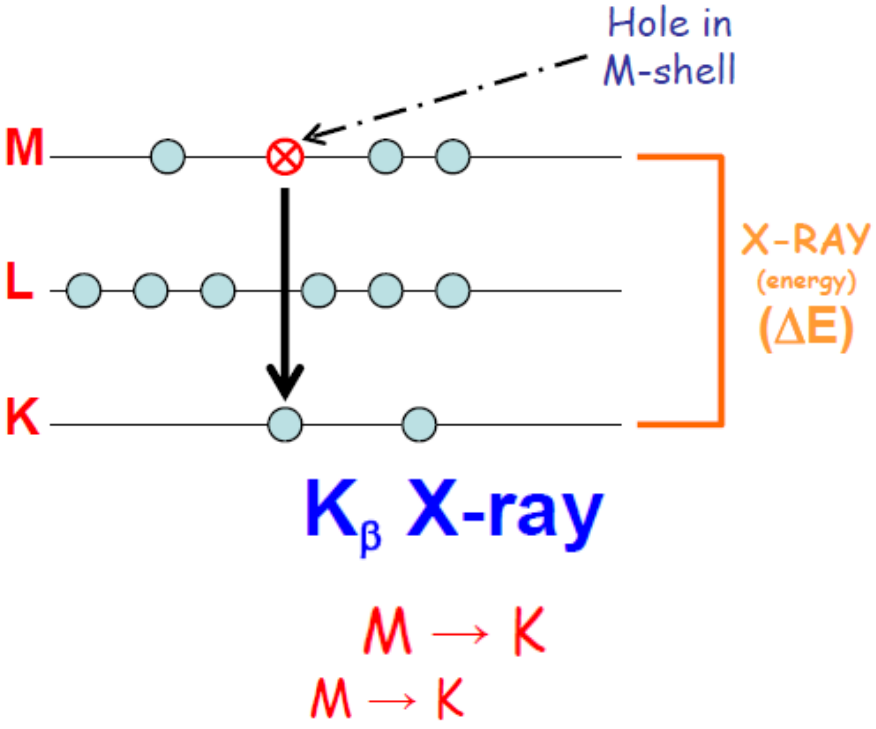


Filling the hole in the K-shell with an electron from the M-shell reduces the energy state of the atom E_M, leading to a K_β photon and a second line in the K-shell spectrum.

Since the residual energy of the atom is lower in the E_M state than it is in the E_L state, this photon has a higher energy so that the wavelength of the K_β line is less than that of the K_α line

Further decay of the energy of the excited atom from the E_L and E_M states will result in the generation of L and M characteristic radiation of much longer wavelengths

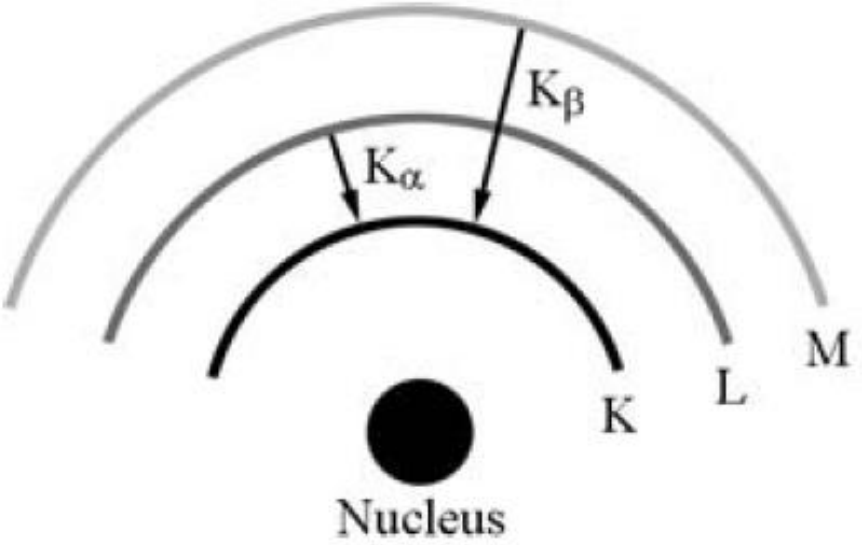


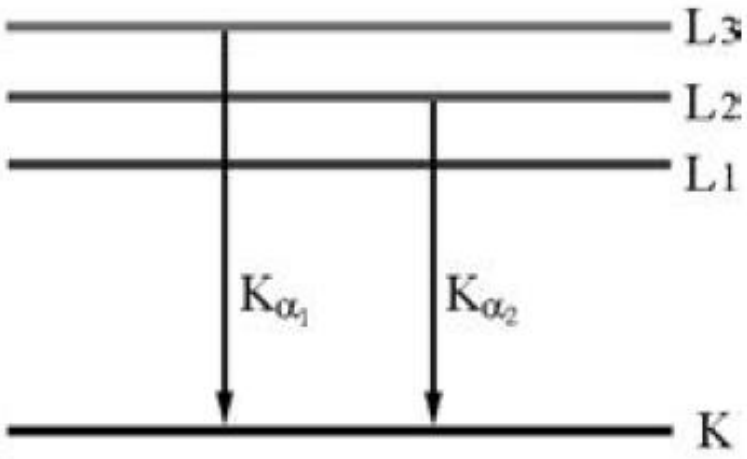


K_a line contains two characteristic lines K_{a1} ve K_{a2}. This occurs because of three sub-shells of L shell L_1, L_2 and L_3 only two of which L_2 and L_3 can donate electrons. K_{a1}, K_{a2} and K_b are the three strong characteristic lines that are used in X-ray diffraction. The difference between the wavelengths of K_{a1}, K_{a2} are very small so that they are often considered as one

Characteristic lines of copper:

$$\lambda_{K\alpha_1} = 0.15406\,\text{nm} \qquad \lambda_{K\alpha_2} = 0.15444\,\text{nm} \qquad \lambda_{K\beta} = 0.13922\,\text{nm}$$





$K_{\alpha 1}$ and $K_{\alpha 2}$ characteristic emissions are called the K_{α} pair

K_a pair is used as the monochromatic X-ray emission in X-ray diffraction

Wavelengths of the characteristic lines of common anode target materials:

Anode Material	Atomic Number	$K\alpha$(nm)	Critical Excitation Potential (keV)	Optimum Voltage (kV)
Cr	24	0.22291	5.99	40
Fe	26	0.1937	7.11	40
Cu	29	0.1542	8.98	45
Mo	42	0.0710	20.00	80

There are many alternative options for the origin of a donor electron to fill a hole in the L and M shells so that the characteristic L and M spectra consists of several closely spaced lines

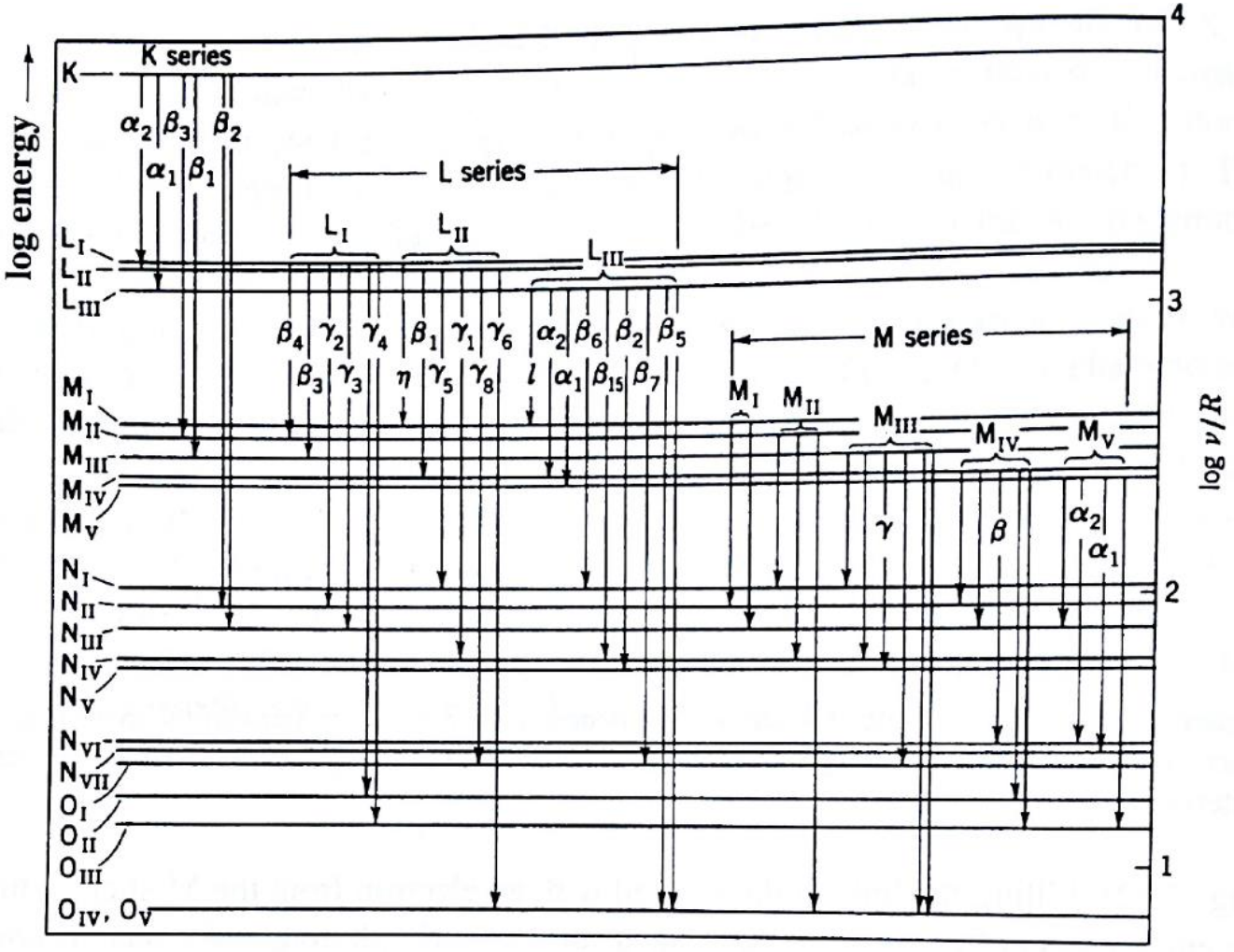
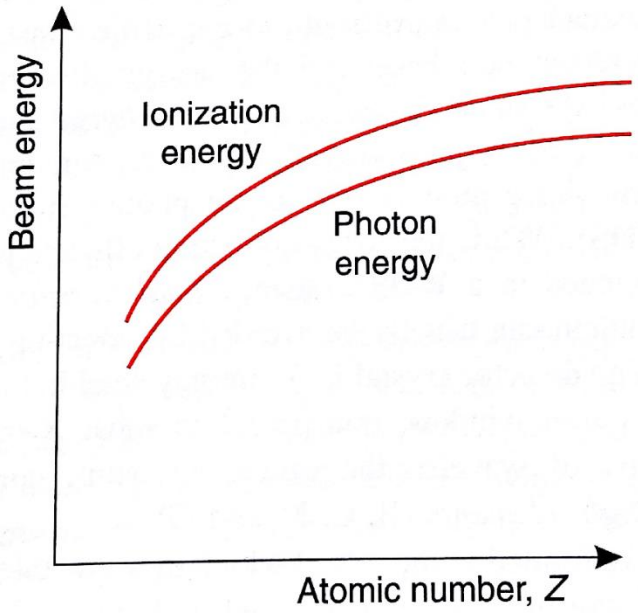


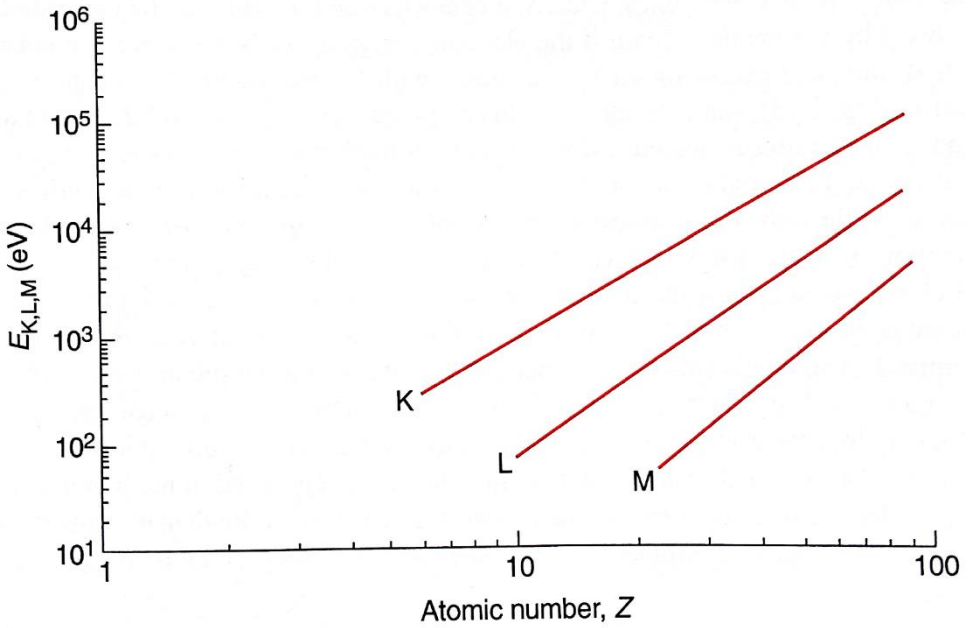
Figure 2.14 The atomic energy levels and characteristic X-ray spectrum for a uranium atom. After Barratt and Massalski, *Structure of Metals*, 3rd revised edition, with permission from Pergamon Press

A characteristic line can only be generated in the target by the incident beam if its energy exceeds the excitation energy for that line

The excitation energy increases with the atomic number of the target material since the electrons in any given shell are more tightly bound to a higher atomic number radius

The low atomic number elements can only give K-lines while only the heaviest elements have M and N-lines in their spectra





Properties of characteristic X-ray emissions

The energy of the characteristic emission is the difference between energies of two electrons: the scattered and the donated electrons

For example the energy of the K_α emission equals the difference between energies of electrons in the K shell and L shell

This energy difference varies with atomic number of the target material

Therefore it is possible to identify the target material element based on the energy (wavelength) of the emitted characteristic lines

Moseley rule defines the relationship between the wavelength of characteristic X-rays and the atomic number (Z) of the target element

$$\lambda = \frac{B}{(Z - \sigma)^2}$$

where B and σ are constants that depend on the properties of the shells

There are many possible alternatives of donor electrons for a hole created in the inner K shell of an atom by an inelastic scattering.

Possibilities are limited and this energy transition of an excited atom is governed by the **selection rule**:

Each electron in an atom is defined with 4 quantum numbers: n, l, m_l and m_s

- Principal quantum number (n) defines the electron shell or energy level of an atom

E.g. K shell is n=1, L shell is n=2, M shell is n=3

- Angular quantum number (l) describes the subshells and gives the magnitude of the orbital angular momentum

The value of l ranges from 0 to n-1. In chemistry l=0 is s orbital, l=1 is p orbital, l=2 is d orbital

- Magnetic quantum number (m) describes the orbital within that subshell and ranges between –l and +l

E.g. The s subshell (l=0) contains only one orbital and the m of an electron in an s orbital is 0. The p subshell (l=1) contains three orbitals so the m of an electron in a p orbital is either -1, 0, 1. The d subshell (l=2) contains five orbitals with m values of -2, -1, 0, 1, 2

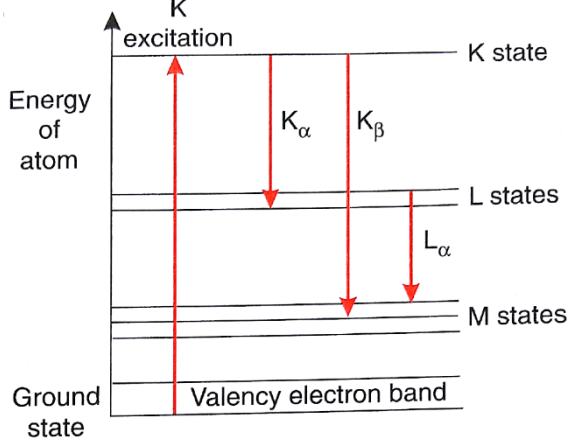
- Spin projection quantum number (m_s) describes the spin angular momentum (s) of the electron within an orbital and gives the projection of the spin angular momentum. The values range from –s to s

E.g. –s, -s+1, -s+2,…,s-2, s-1, s

An electron has spin number s=1/2 so m_s will be either +1/2 referring to spin up or -1/2, referring to spin down. Each electron in any orbital must have different quantum numbers because of the Pauli exclusion principle, therefore an orbital never contains more than two electrons

Quantum numbers of electrons in K, L and M shells are as follows. The total momentum value (J) is the sum of $+m_l$ and $+m_s$

Shell (Electrons)	n	l	m	s	Orbitals	J
K (2)	1	0	0	$\pm\frac{1}{2}$	1s	$\frac{1}{2}$
L (8)	2	0	0	$\pm\frac{1}{2}$	2s	$\frac{1}{2}$
	2	1	1	$\pm\frac{1}{2}$		
	2	1	0	$\pm\frac{1}{2}$	2p	$\frac{1}{2}; \frac{3}{2}$
	2	1	−1	$\pm\frac{1}{2}$		
M (18)	3	0	0	$\pm\frac{1}{2}$	3s	$\frac{1}{2}$
	3	1	1	$\pm\frac{1}{2}$		
	3	1	1	$\pm\frac{1}{2}$	3p	$\frac{1}{2}; \frac{3}{2}$
	3	1	−1	$\pm\frac{1}{2}$		
	3	2	2	$\pm\frac{1}{2}$		
	3	2	1	$\pm\frac{1}{2}$		
	3	2	0	$\pm\frac{1}{2}$	3d	$\frac{3}{2}; \frac{5}{2}$
	3	2	−1	$\pm\frac{1}{2}$		
	3	2	−2	$\pm\frac{1}{2}$		



Selection rule

Selection rules for electron transition between two shells are:

1. The change in n must be at least 1 **($\Delta n>1$)**
2. l must change by at least 1 **($\Delta l_{min}=\pm1$)**
3. J must change by either 0 or 1 **($\Delta J=\pm1$ or 0)**

Transition of an electron from subshell L_1 to shell K is forbidden according to the selection rule as the **$\Delta l\neq0$**

Transitions to K shell from L shell is limited to only L_2 and L_3 electrons and these transitions generate the $K_{\alpha2}$ and $K_{\alpha1}$ emissions respectively

The possible electron transitions to K, L and M shells are shown below

The Siegbahn notation is used to describe the characteristic X-ray emission: An English letter followed by a Greek letter and a number

$K\alpha_1$	$L_3 \rightarrow K$	$L\gamma_1$	$N_4 \rightarrow L_2$
$K\beta_1$	$M_3 \rightarrow K$	$M\alpha_1$	$N_7 \rightarrow M_5$
$L\alpha_1$	$M_5 \rightarrow L_3$	$M\beta$	$N_6 \rightarrow M_4$
$L\beta_1$	$N_3 \rightarrow L_3$		

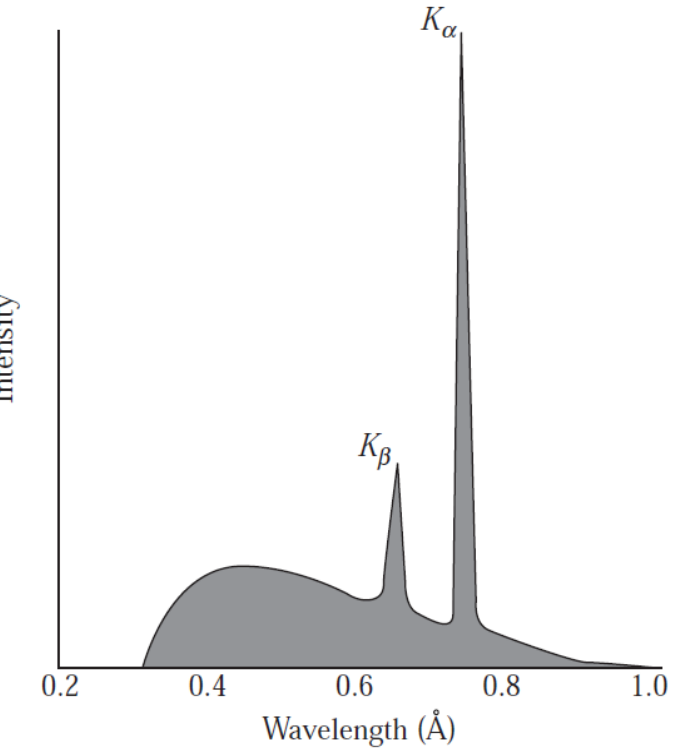
The intensity of characteristic emissions are ordered as $\alpha > \beta > \gamma$

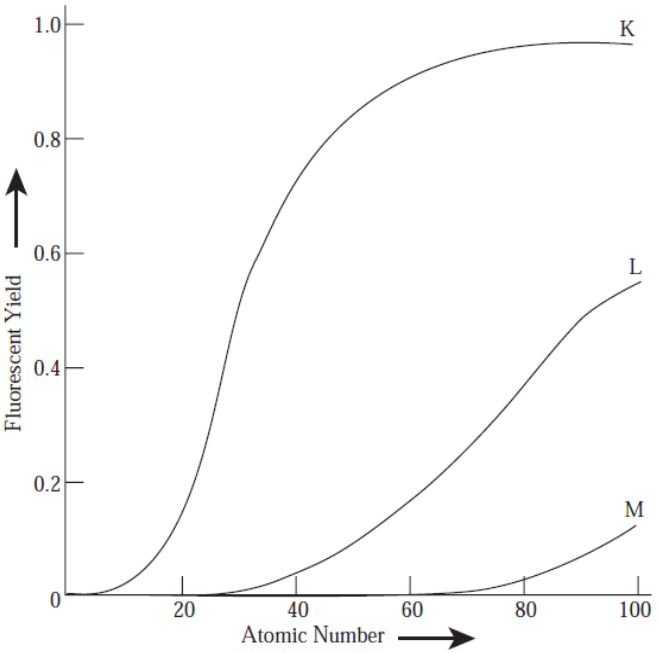
The potential of an atom to produce X-ray photons depends on the atomic size and the energy of the incident electrons or photons that are inelastically scattered

When a hole in the inner shell is filled by an electron, there are two possible outcomes: emission of high energy photon or emission of an Auger electron

In any case the energy given off as photon or electron can scatter another electron from the K, L and M shells

The secondary scatter of electron is called fluorescence. Fluorescence yield is a parameter of the target material and measures the relative activity of x-ray emissions





Fluorescence yield varies with the atomic number of the target material

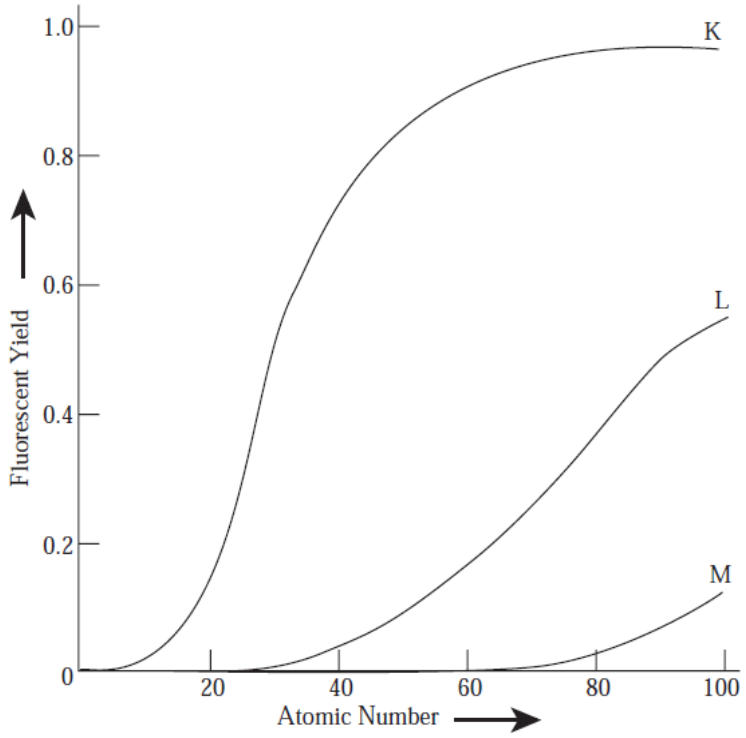
Fluorescence yield for an atom with atomic number lower than 4 (Be) is zero

Fluorescence yield for an oxygen atom (8) is 0.005

In general fluorescence yield increases with atomic number

Therefore identification of elements with low atomic number in X-ray spectroscopy is not possible due to the structural disadvantage

X-rays generated by scattering an inner electron (K series) produce more fluorescence due to higher energy



Fluorescence yields for excitation of the K, L, and M shells of some elements

Atomic number	Element	ω_k	ω_L	ω_M
4	Be	0.00045	–	–
5	B	0.00101	–	–
6	C	0.00198	–	–
7	N	0.00351	–	–
8	O	0.00579	–	–
9	F	0.00901	–	–
10	Ne	0.0134	–	–
11	Na	0.0192	–	–
12	Mg	0.0265	–	–
...	...	...	...	...
19	K	0.138	–	–
20	Ca	0.163	0.00067	–
21	Sc	0.190	0.00092	–
22	Ti	0.219	0.00124	–
23	V	0.249	0.00163	–
24	Cr	0.281	0.0021	–
...	...	...	...	...
56	Ba	0.900	0.126	–
57	La	0.906	0.135	0.00111
58	Ce	0.911	0.144	0.00115
59	Pr	0.915	0.153	0.00120
...	...	...	...	...

A typical emission energy spectrum covers energies between 0.2 and 20 keV

Note that **Au**$K_{\alpha 1}$ = 66,99 keV while **Au**$L_{\alpha 1}$ and **Au**$M\alpha_1$ energies are 9,713 and 2,123 keV respectively

So **Au**$K_{\alpha 1}$ line will not appear in the emission spectrum

Heavy elements are identified by X-ray spectroscopy according to their L and M characteristic lines which have lower energy compared to K lines

Emission spectrum of heavy elements are therefore quite complicated as there appear multiple L and M characteristic lines

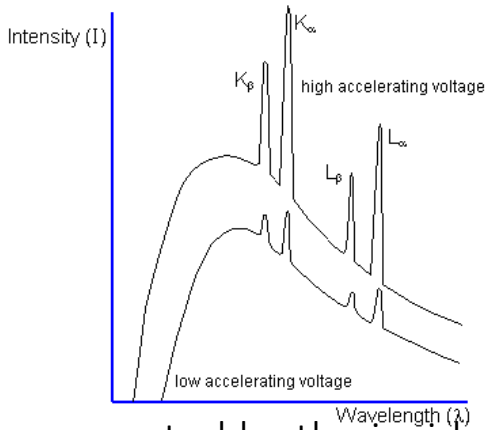
On the other hand emission spectrum of elements with atomic number less than 20 (Ca) have only characteristic emissions originating from K shells

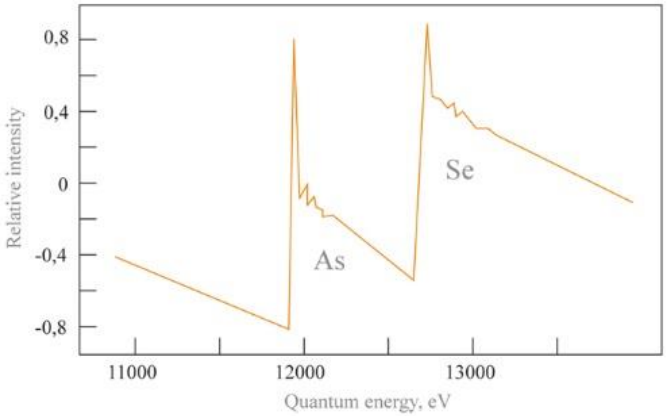
The fluorescence yield of elements with low atomic number is low and identification with X-ray spectroscopy is harder

Atomic number	Element	$K\alpha_1$		$L\alpha_1$		$M\alpha_1$	
		λ (Å)	E (keV)	λ (Å)	E (keV)	λ (Å)	E (keV)
4	Be	114	0.109	–	–	–	–
5	B	67.6	0.183	–	–	–	–
6	C	44.7	0.277	–	–	–	–
7	N	31.6	0.392	–	–	–	–
8	O	23.62	0.525	–	–	–	–
9	F	18.32	0.677	–	–	–	–
10	Ne	14.61	0.849	–	–	–	–
11	Na	11.91	1.041	–	–	–	–
12	Mg	9.89	1.254	–	–	–	–
13	Al	8.339	1.487	–	–	–	–
14	Si	7.125	1.740	–	–	–	–
15	P	6.157	2.014	–	–	–	–
16	S	5.372	2.308	–	–	–	–
17	Cl	4.728	2.622	–	–	–	–
…	…	…	…	…	…	…	…
19	K	3.741	3.314	–	–	–	–
20	Ca	3.358	3.692	36.33	0.341	–	–
21	Sc	3.031	4.091	31.35	0.395	–	–
22	Ti	2.749	4.511	27.42	0.452	–	–
23	V	2.504	4.952	24.25	0.511	–	–
24	Cr	2.290	5.415	21.64	0.573	–	–
25	Mn	2.102	5.899	19.45	0.637	–	–
26	Fe	1.936	6.404	17.59	0.705	–	–
27	Co	1.789	6.930	15.97	0.776	–	–
28	Ni	1.658	7.478	14.56	0.852	–	–
29	Cu	1.541	8.048	13.34	0.930	–	–
30	Zn	1.435	8.639	12.25	1.012	–	–
…	…	…	…	…	…	…	…
45	Rh	0.6133	20.13	4.597	2.697	–	–
46	Pd	0.5854	21.18	4.368	2.839	–	–
47	Ag	0.5594	22.16	4.154	2.984	–	–
						–	–
56	Ba	0.3851	32.19	2.776	4.466	–	–
57	La	0.3707	33.44	2.666	4.651	14.88	0.833
58	Ce	0.3571	34.72	2.562	4.840	14.04	0.883
59	Pr	0.3441	36.03	2.463	5.034	13.34	0.929
…	…	…	…	…	…	…	…
78	Pt	0.1855	66.83	1.313	9.442	6.047	2.051
79	Au	0.1851	66.99	1.276	9.713	5.840	2.123
80	Hg	0.1751	70.82	1.241	9.989	5.645	2.196

The wavelengths of the characteristic lines which are emitted constitute a fingerprint for the elements present in the solid hit by the electron beam and provide a powerful method of identifying the chemical constituents and their distribution in X-ray fluorescence spectroscopy and energy dispersive X-ray spectroscopy

The characteristic lines that appear in the x-ray emission spectrum are groups of lines rather than a single line and there may be overlap between the lines emitted by one chemical constituent and those emitted by another in the sample





X-rays generated by the incident electron beam also have an absorption spectrum, since X-ray photons have a probability of exciting atoms to higher-energy states.

A K photon from a higher-atomic number element will have a sufficient energy to excite an atom of lower atomic number element to the K state by absorption of the photon

The excited atom will decay back towards the ground state, generating a new, lower energy photon that is characteristic of this atom in a process termed X-ray fluorescence

Both emission and absorption spectra produced by both electrons and x-rays can be used to derive information on the chemical composition of the sample

If elastic scattering of the X-rays dominate the interaction with a sample, it should be ensured that their intensity are not lost due to inelastic scattering processes

A monochromatic X-ray beam traversing a thin sample in the x direction loses intensity I at the rate:

$$dI/dx = -\mu I$$

where μ is the linear absorption coefficient for the X-rays

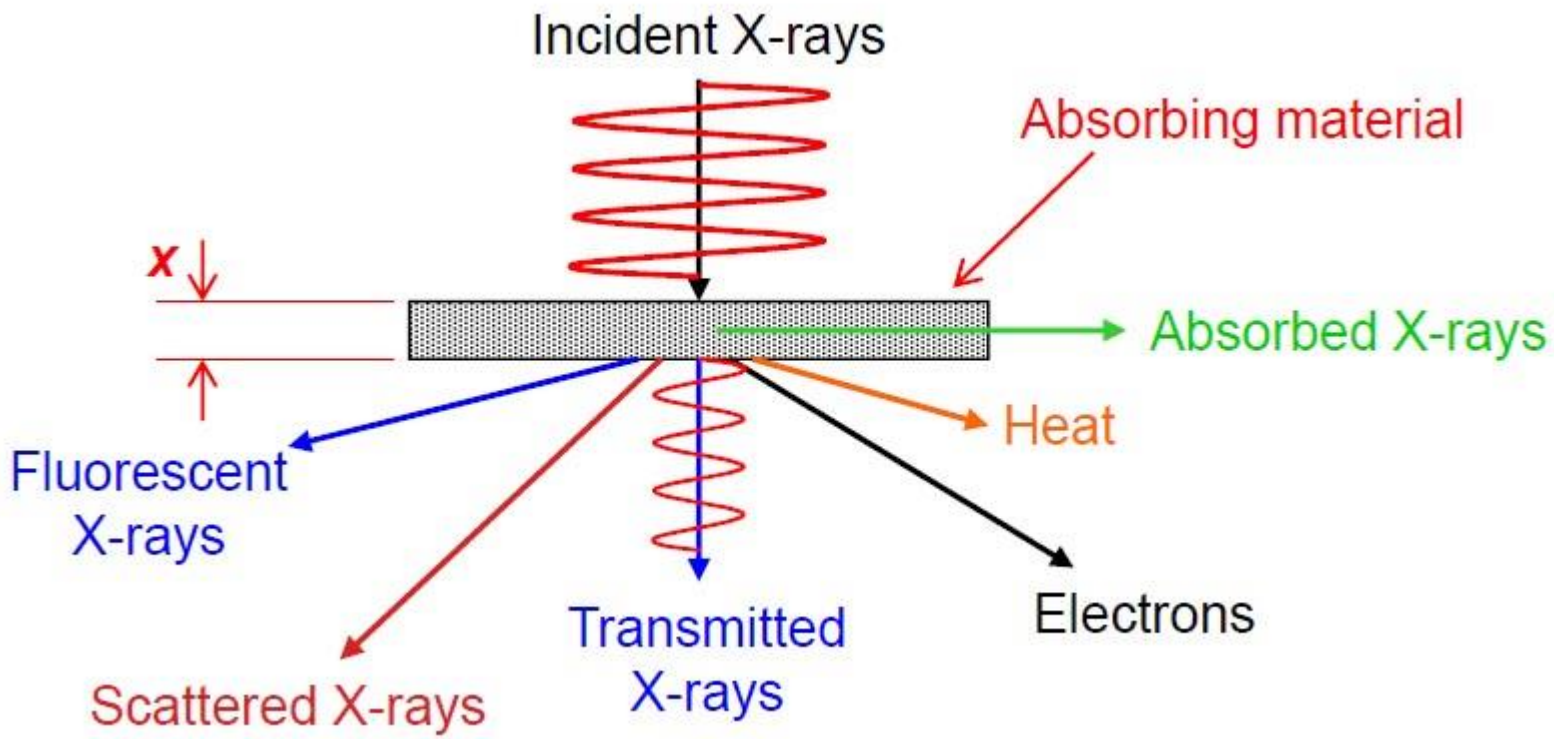
The tabulated values in the literature are generally for the mass absorption coefficient μ/ρ where ρ is the density, rather than the linear absorption coefficient

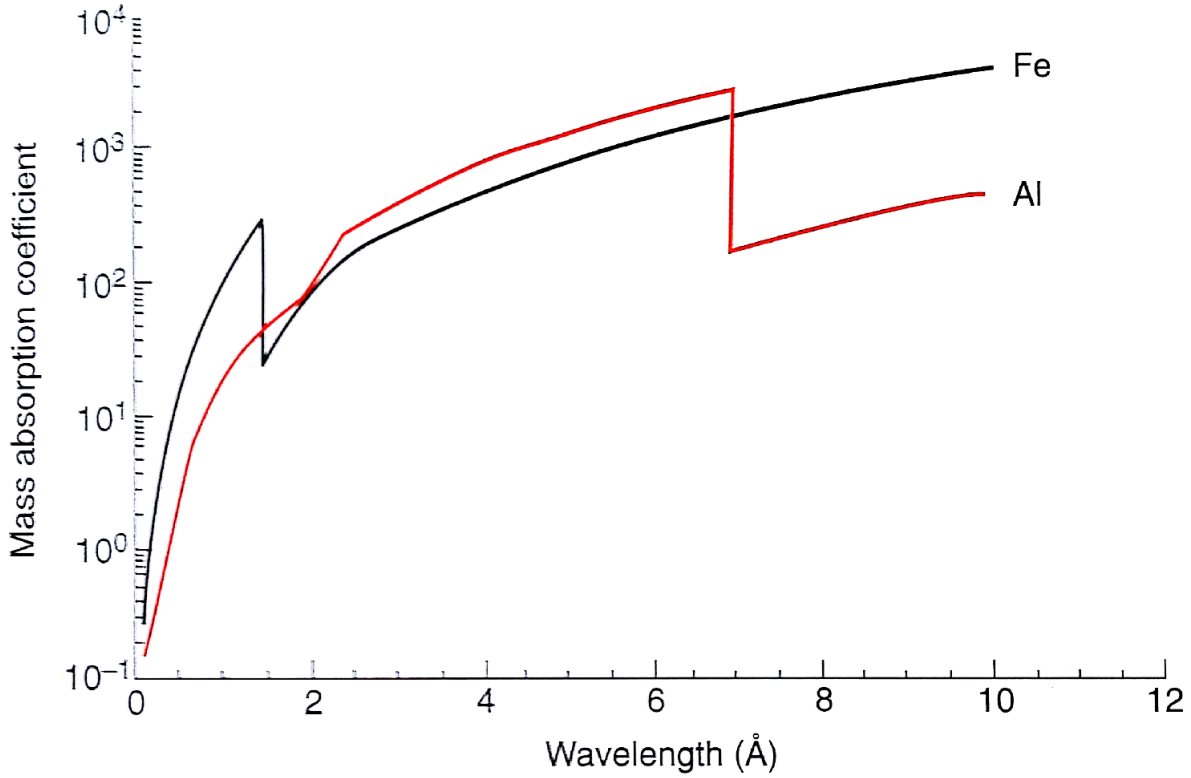
The transmitted intensity is given by the following equation

$$\frac{I}{I_o} = exp\left(-\frac{\mu}{\rho}\rho x\right)$$

In order to produce monochromatic K_α emission, continuous X-ray spectrum and the other characteristic lines should be absorbed by a filter

X-ray filter material absorbs the part of the X-ray spectrum with wavelengths greater than the K_α line





Of the two metals for which mass absorption coefficients are given, the lower-density aluminum has the lower linear absorption coefficient at any wavelength

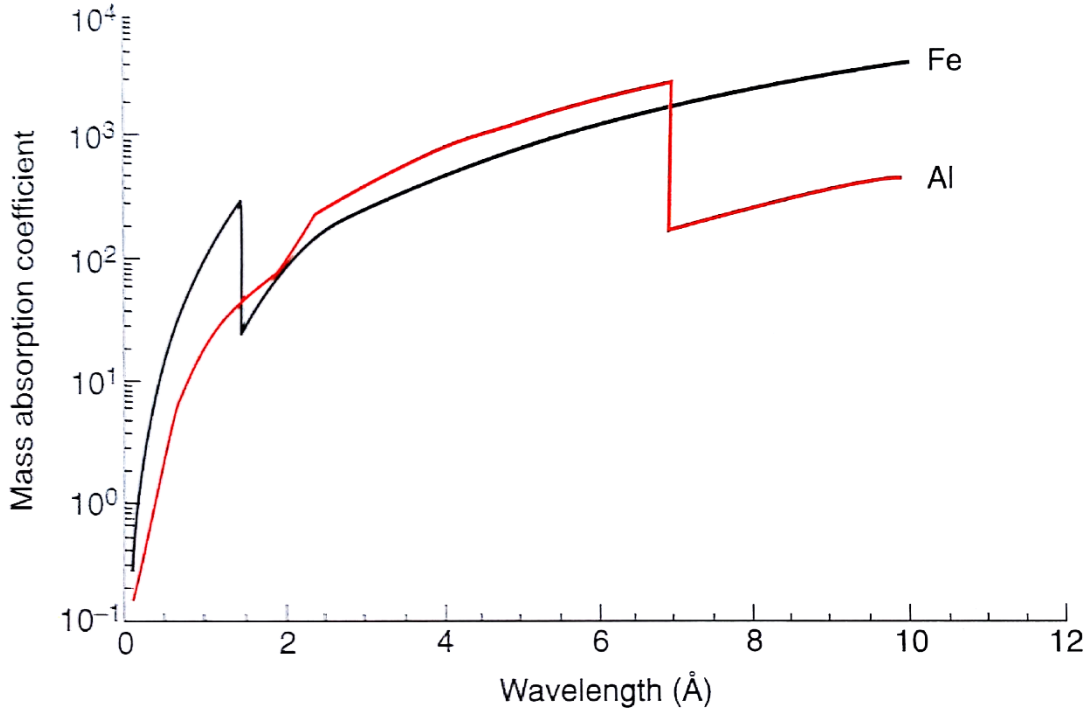
All materials show a general increase in the mass absorption coefficient with wavelength, with a sequence of step discontinuities called absorption edges

Absorption edges correspond to the wavelengths at which the incident X-ray photon possesses sufficient energy to eject an inner-shell electron in the specimen

In a way the absorption edges are the X-ray equivalents of the minimum ionization energies

For X-ray diffraction measurements fluorescent radiation should be avoided and absorption of the incident beam should be minimized

An anode material is selected which has a characteristic radiation with a wavelength close to the minimum, but on the long wavelength side of the absorption edge in the specimen



For example – To analyze the structure of steels and iron alloys (E_{FeK}= 7.109 keV, λ= 0.17433 nm)

CoK_α radiation (λ= 0.1789 nm) is suitable as it lies to the long wavelength side of the K_{Fe} edge and will give sharp diffraction patterns from steel which are free of background fluorescence

CuK_α radiation (λ= 0.154 nm) is not suitable as it has enough energy to excite the atoms of steel for X-ray fluorescence

The CoK_α radiation will be absorbed by iron and aluminum at different rates

The mass absorption coefficients for iron is 46 and 67.8 for aluminum

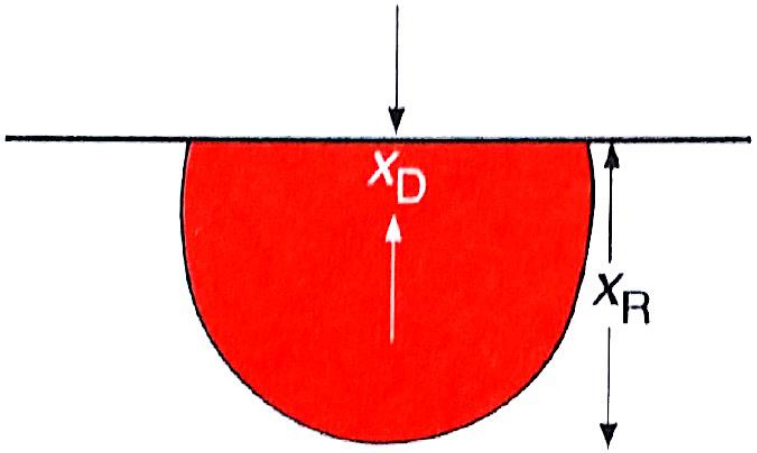
The density of iron is 7.88 g/cc and 2.7 g/cc for aluminum

The thickness of the sample which will reduce the intensity of the incident beam to 1/e of its initial intensity are calculated as

$\frac{1}{\exp(1)} = exp(-46 * 7.88x), x = 27.6\ \mu m$ for iron

$\frac{1}{\exp(1)} = exp(-67.8 * 2.7x), x = 54.6\ \mu m$ for aluminum

These values determine the thickness of the samples which provide signal for X-ray diffraction when CoK_α radiation is used



X-ray absorption depth for Lead and concrete as a function of X-ray energy

Energy (KeV)	Lead (mm)	Concrete (mm)
50	0.06	4.32
70	0.18	12.70
100	0.27	15.10
150	0.30	22.32
200	0.52	25.00
250	0.88	28.00
300	1.47	31.21
400	2.50	33.00
1000	7.90	44.45
2000	9.98	62.23

X-ray diffraction experiments require either monochromatic or white radiation

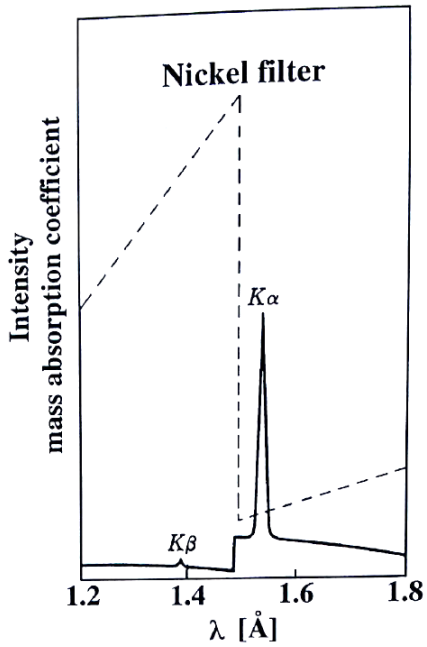
Monochromatic radiation is generated by exciting K-radiation from a pure metal target and then filtering it by a foil which strongly absorbs the β-component of the K-radiation without any appreciable reduction of the intensity of the α-component

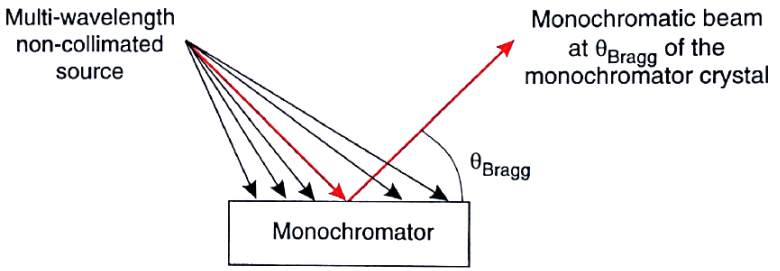
The filter material should have an absorption edge that falls exactly between the K_α and K_β wavelengths

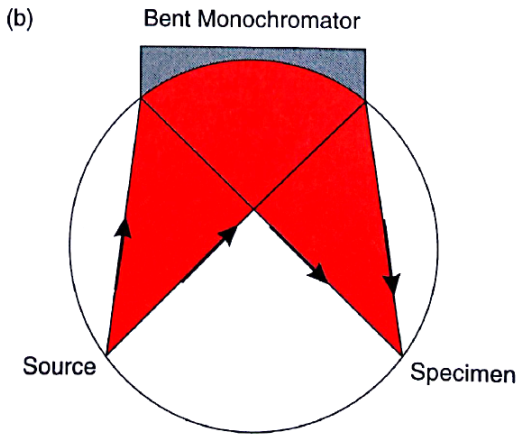
For example a nickel filter is used ($E_{NiK\beta}$= 0.1488 nm) with a copper target ($E_{CuK\beta}$= 0.138) which transmits the CuK_α beam (0.154 nm) but not the K_β

A better selection of a monochromatic beam can be achieved by exciting a second material by the scattered X-rays, a single crystal oriented to diffract at the characteristic K_α peak. This monochromatic diffracted beam can be used as the source of radiation for the specimen to be analyzed

In addition this monochromatic crystal can be bent into an arc of circle to focus a diffracted beam to a line at the specimen position



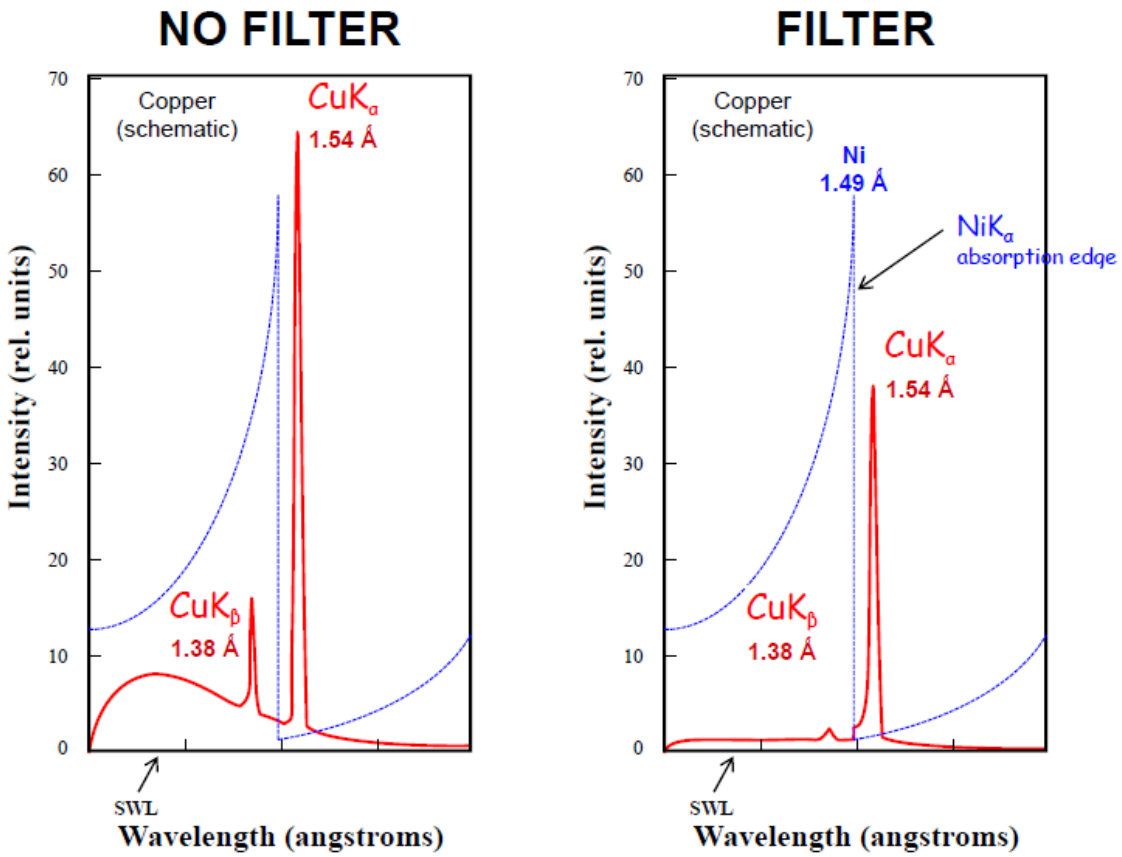




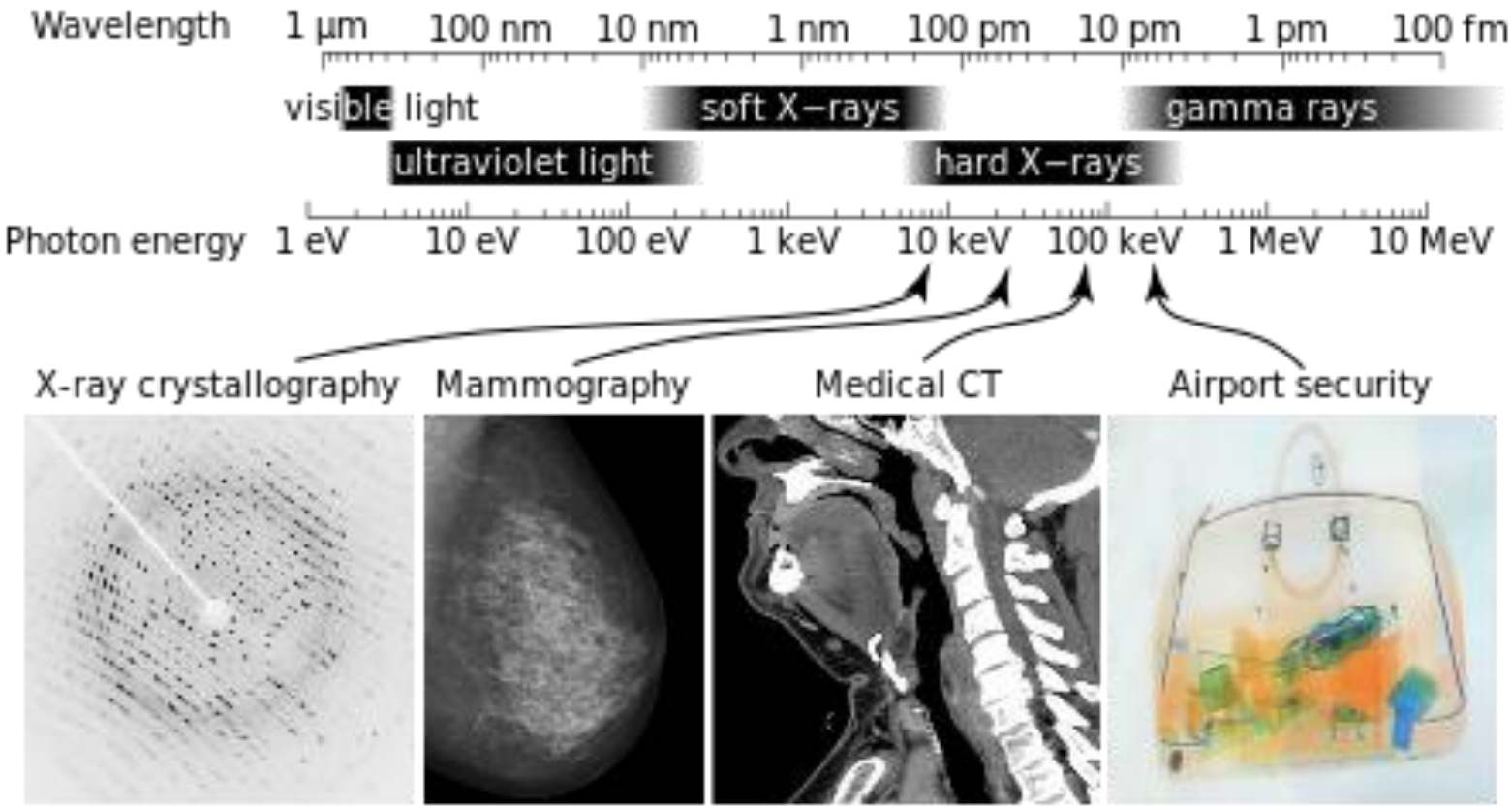
X-ray filtration mechanism

A filter material is chosen that has an absorption edge close to the K_α line of the target, at a smaller wavelength

Nickel absorbs radiation around the K_β line and the photons that are emitted at lower wavelengths



Applications of X-rays absorption at various wavelengths



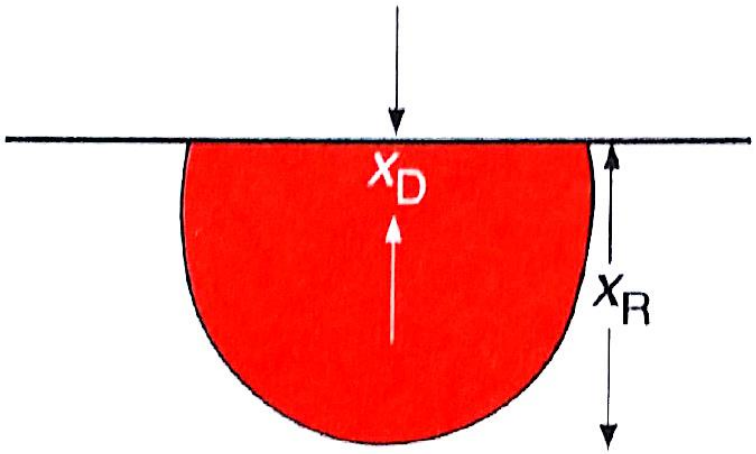
The X-ray signal generated from a focused electron beam comes from a volume of the sample material, defined by the envelope of electron energies which exceed the energy required to excite the characteristic radiation of interest

This volume shrinks as the beam voltage is reduced

The intensity of the emitted signal first increases as the electron beam energy is increased above the minimum required to excite the characteristic signal

Signal intensity increases until the beam energy reaches about 4x the minimum excitation energy.

With further increase in the beam energy, signal intensity decreases due to an increased absorption of the primary signal within the sample since the signal now originates deeper below the surface (high diffusion depth)



The optimum beam energy is of the order of four times the excitation energy for the shortest characteristic X-ray wavelength to be detected

The efficiency of the generation of characteristic X-rays is very low as the generated X-rays are emitted at all angles and most of them are absorbed in the sample

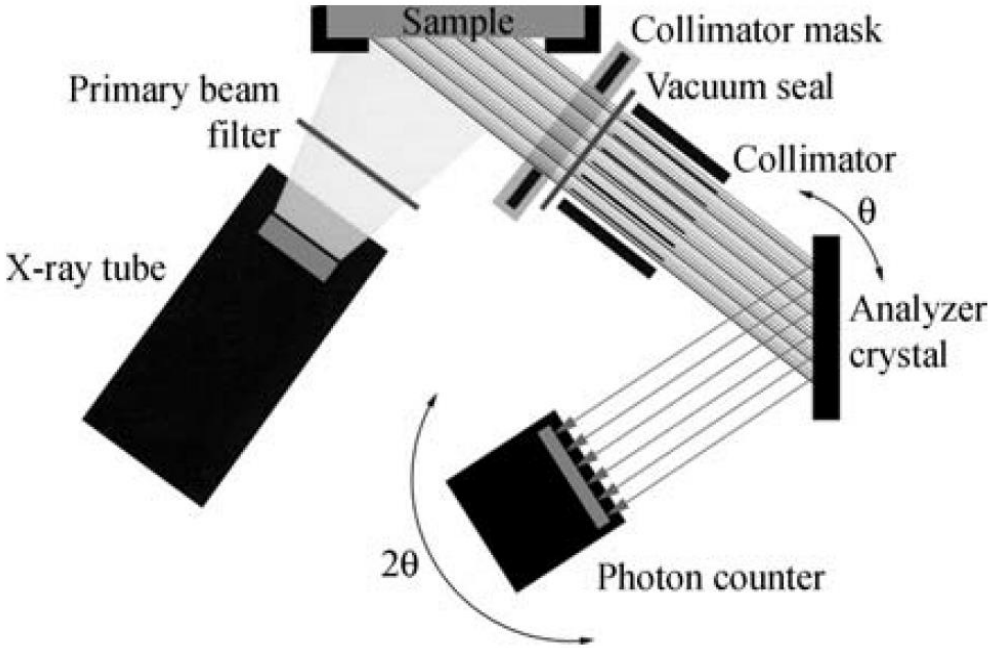
X-ray collection is also inefficient. Collection is done by a solid state detector

Solid state detectors are based on the energy discrimination capability of a cryogenically cooled semiconductor crystal

The charge generated in the detector by each absorbed photon is proportional to the photon energy, leading to a detectable current pulse proportional to the photon energy

This method is termed an energy-dispersive spectrometer (EDS)

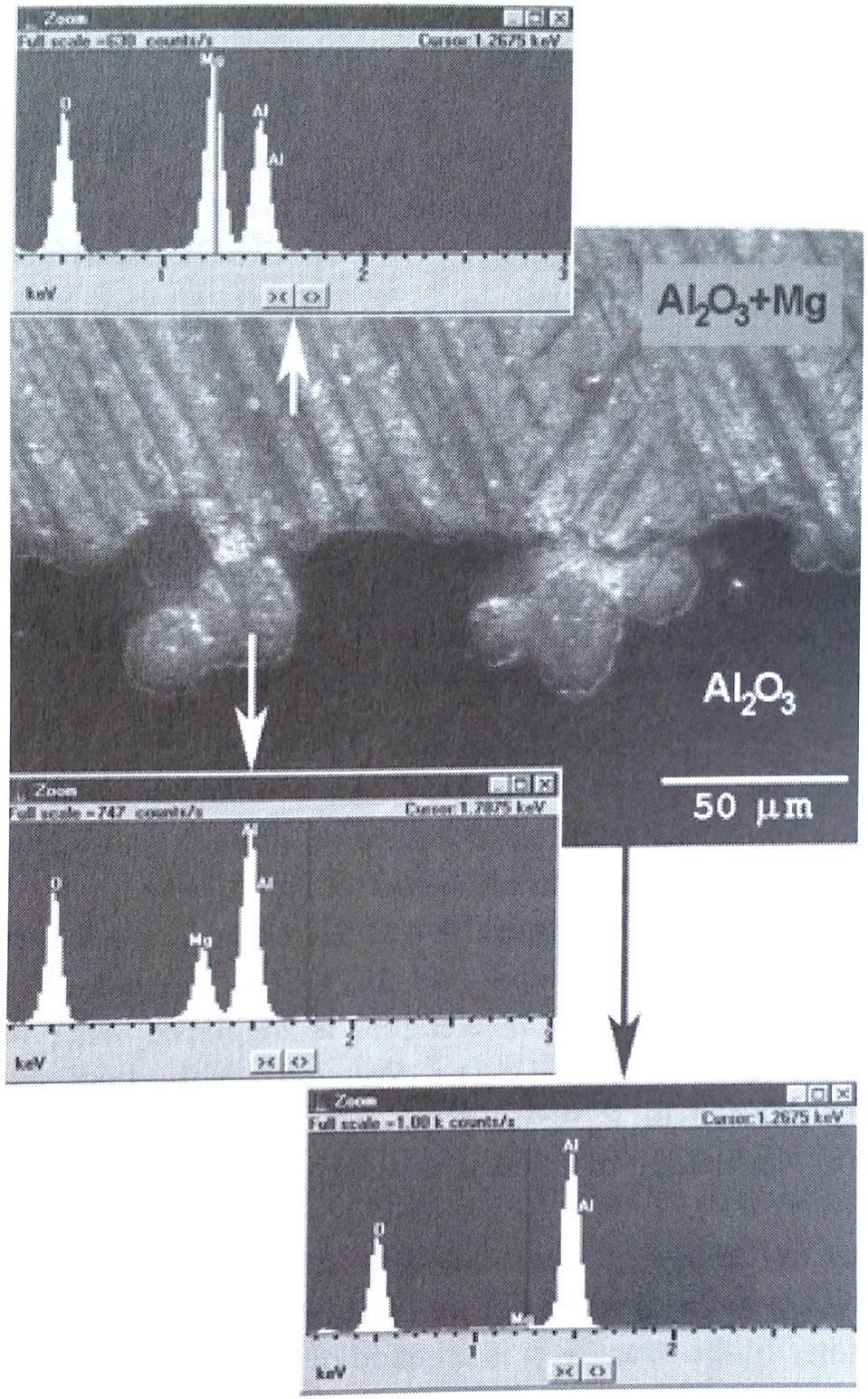
Although X-ray collection efficiency is low, signal overlap is frequently encountered. This problem can be avoided by selecting alternative characteristic emission lines



The X-ray signals may be displayed in three distinct modes:

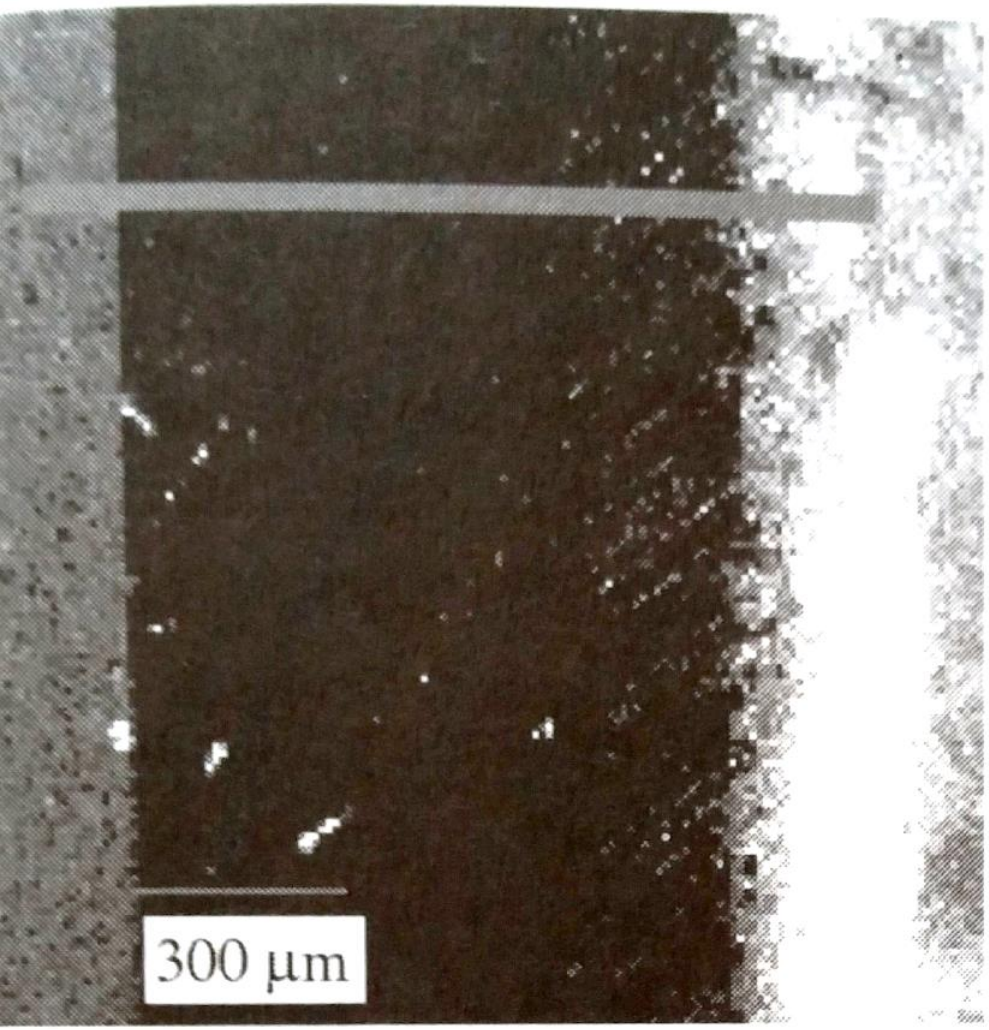
As a spectrum, in order to identify the elements present from their characteristic fingerprints. Such a spectrum may be collected with the beam stationary at a specific location on the sample surface (point analysis) or while the beam is scanned over a selected area.

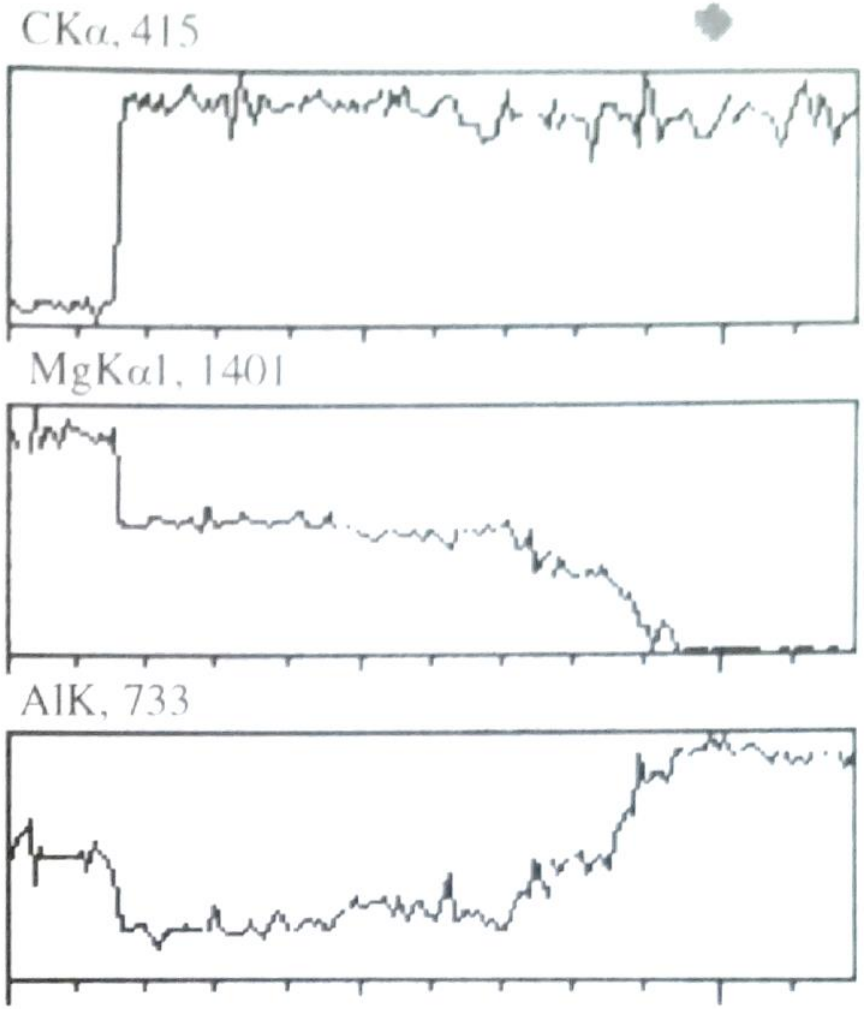
Typical collection times required to ensure detection of all elements are of the order of 100 seconds using a scanning electron microscope



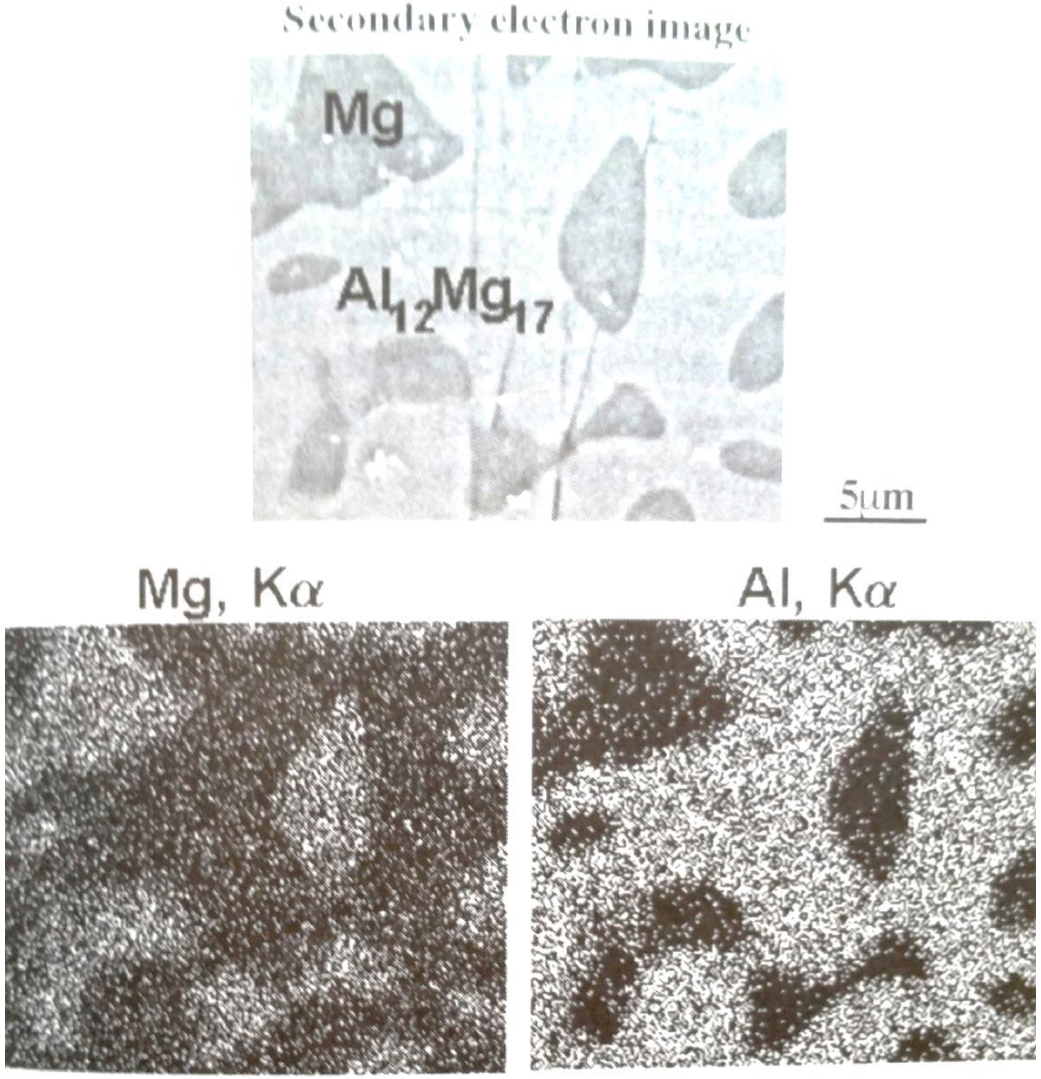
As a line-scan, in which the beam is traversed across a selected region of the sample and the rate of detection for one or more selected characteristic X-ray wavelengths is displayed as a function of the position of the beam.

The number of counts for each characteristic wavelength of interest is displayed for each position of the beam





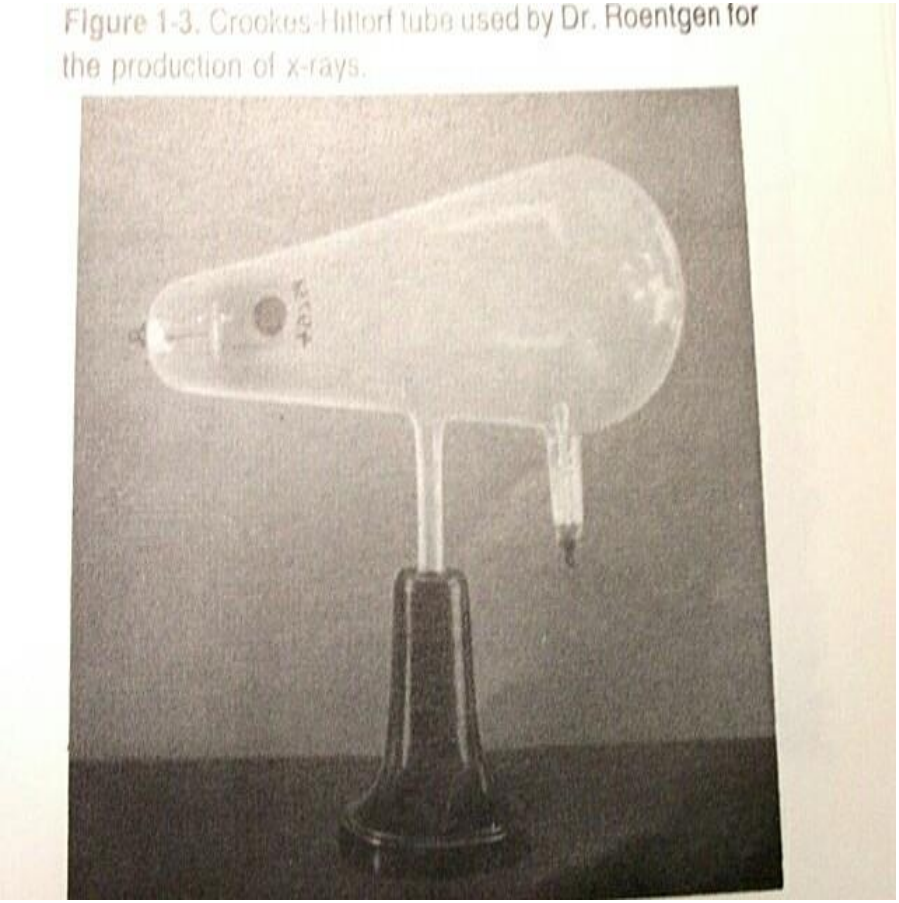
As an X-ray dot image or elemental map in which each characteristic photon detected is recorded as a white dot in a position on the screen corresponding to the coordinates of the beam as it is scanned over a selected area of the specimen surface. More than one element with a range of wavelengths may be detected simultaneously



X-ray tube

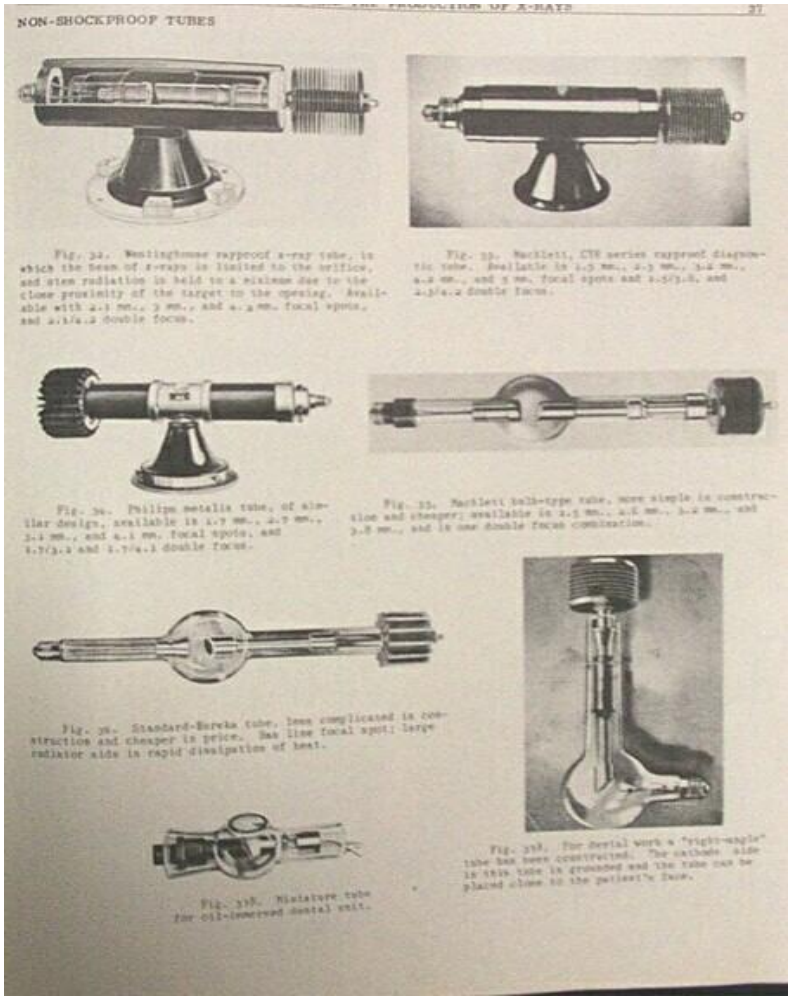
The X-Ray Tube Development

- Dr. Roentgen used a Crookes-Hittorf tube to make the first x-ray image.
- There was no shielding so x-rays were emitted in all directions.



The X-Ray Tube Development

- This is the variety of tube designs available in 1948.
- The Coolidge tube, the first to use a heated filament to obtain electrons is still available.



The X-Ray Tube Development

- Two major hazards plagued early radiography.
  - Excessive radiation exposure
  - Electric Shock
- Moderns tubes are designed to overcome these problems
- The modern tube is based on the Coolidge tube

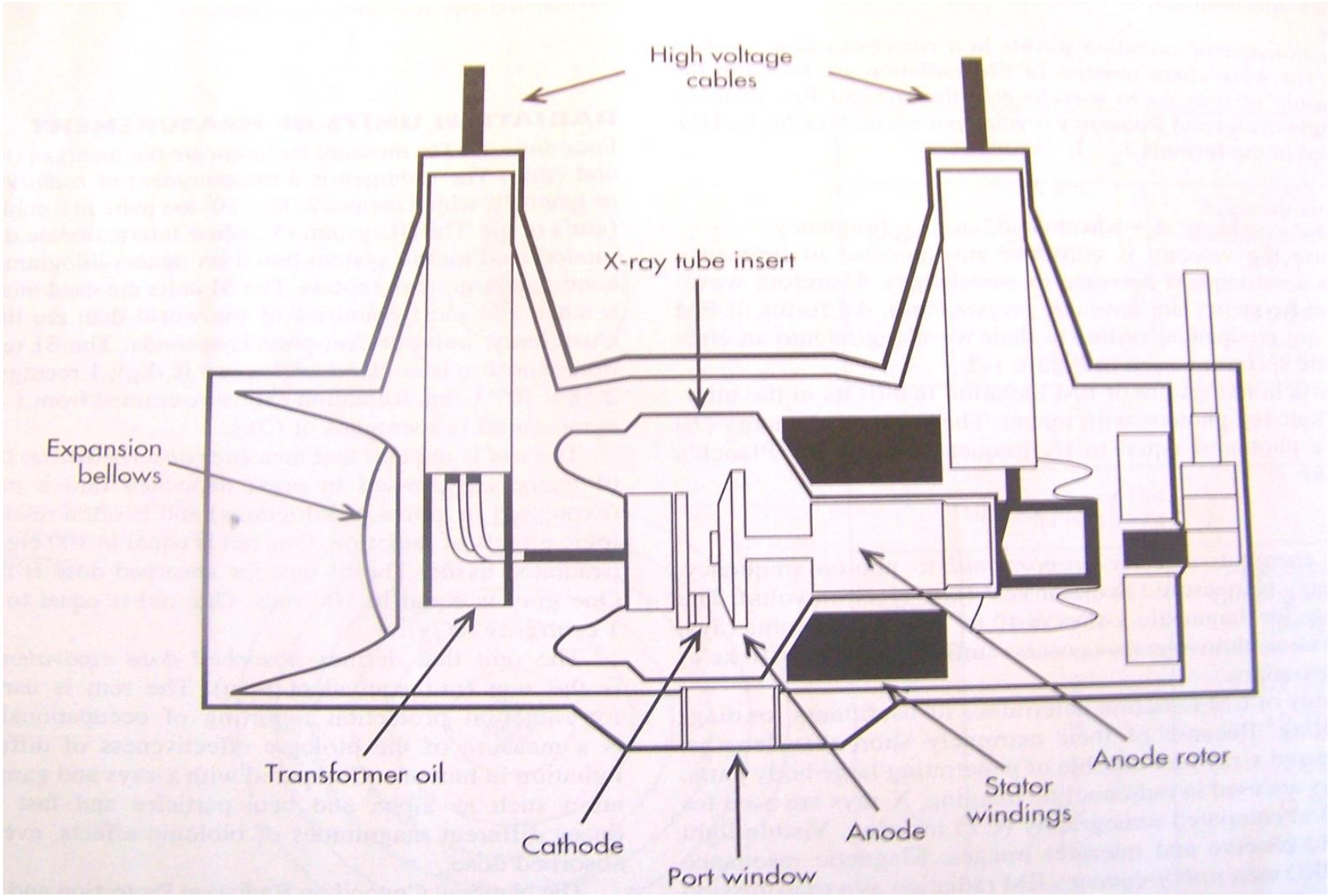
The X-Ray Tube Development

- This is a modern rotating anode x-ray tube.
- It is encased completely in a metal protective housing.
- The housing provide electrical and radiation safety

The Modern X-ray Tube

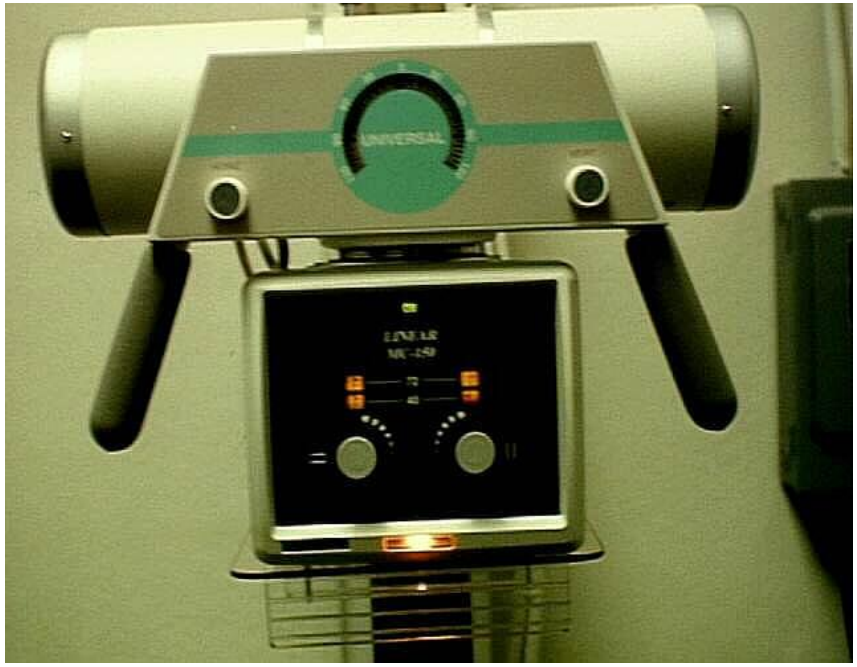
- There are two principle parts:
  - The rotating anode
  - The cathode
- Any tube that has two electrodes is called a diode.
- Inside the tube is a high vacuum

Parts of the X-ray Tube



Protective Housing

- The tube is housed in a lead lined metal protective housing.
- The x-ray photons are generated isotropically or in all directions.
- The housing is designed to limit the beam to window.



Protective Housing-leakage radiation

- The housing is designed to minimize the radiation outside the port
- The tube can not have more than 100 mR at 1 m (26 μ C/kg) / Hour when operated at its maximum output.

Protective Housing – prevent damage

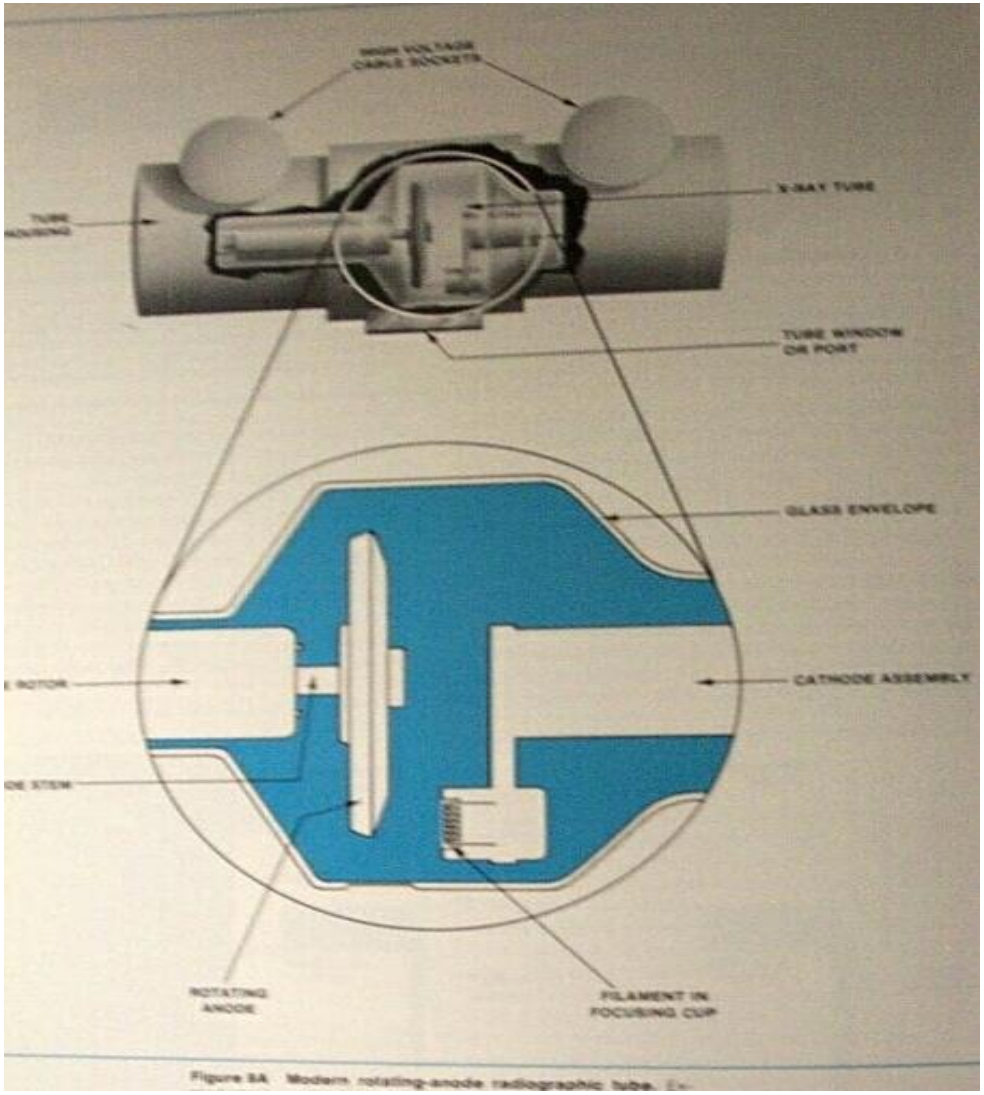
- The housing also provide mechanical support and protection from damage.
- On some tubes, the housing also contains oil that provides more insulation and a thermal cushion.
- Never hold the tube during an exposure.
- Never use the cables or terminals as handles.

Protective Housing- supply of high voltage

- The housing incorporates specially designed high voltage receptacles to protect against electrical shock.
- Some housing have a fan for cooling.

The X-Ray Tube Glass Envelope

- The glass envelope is made of Pyrex to withstand the tremendous heat produced during x-ray.
- The window is a 5 cm square with a thin section of glass where the useful beam is emitted.



The Cathode

- The cathode is the negative side of the tube and contains two primary parts:
- The filaments
- The focusing cup

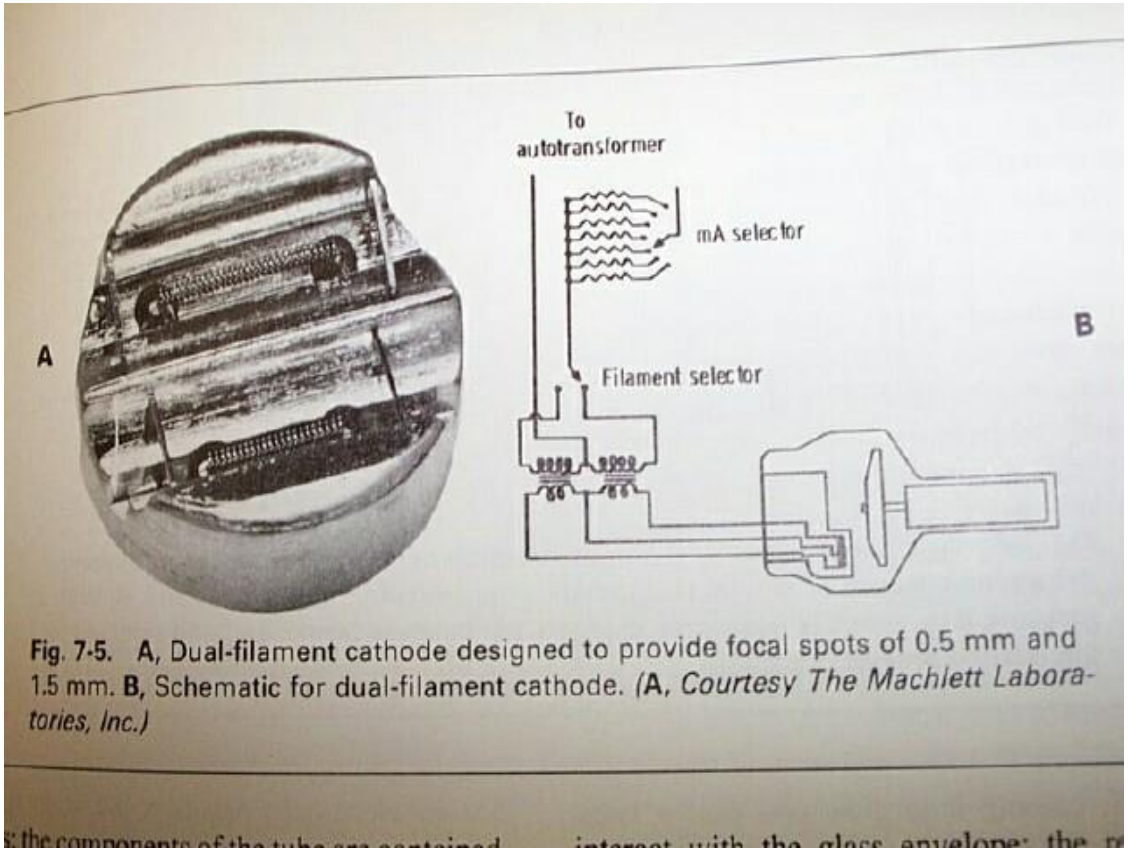
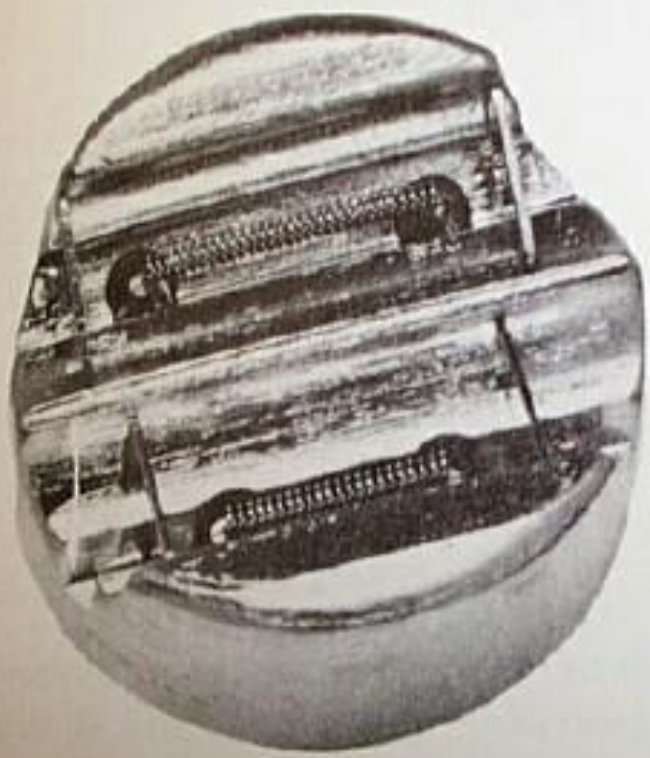


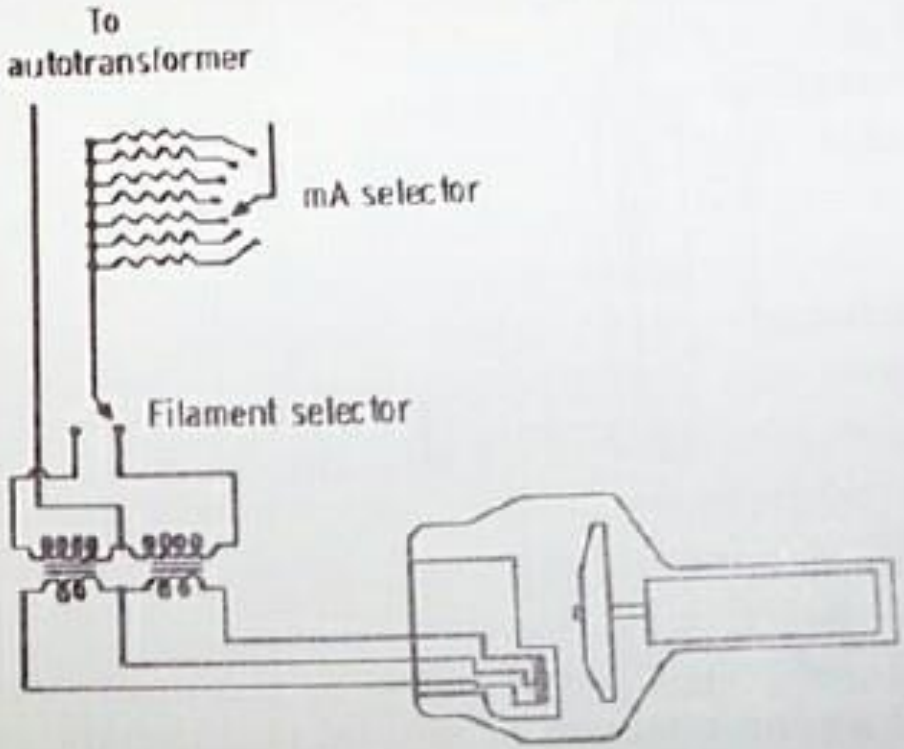
Fig. 7-5. **A**, Dual-filament cathode designed to provide focal spots of 0.5 mm and 1.5 mm. **B**, Schematic for dual-filament cathode. *(**A**, Courtesy The Machlett Laboratories, Inc.)*

The Filaments

- Most tube have two filaments which provide a large focal area and a small focal area
- Two foci provide the choice of quick exposures or high resolution.
- The filaments are made of thoriated tungsten.



A



B

Fig. 7-5. **A**, Dual-filament cathode designed to provide focal spots of 0.5 mm and 1.5 mm. **B**, Schematic for dual-filament cathode. *(**A**, Courtesy The Machlett Laboratories, Inc.)*

The Filaments

- Tungsten is used in x-ray tube filaments because of it’s
  - High melting point of 3410°C.
  - Comparaivelly Low work function (emits electrons at lower temperatures)
  - High tensile strength
  - Flexibility to be turned to a thin spiral
- Electrons are produced by thermionic emission when a 4 A or higher current is applied.

Focusing Cup

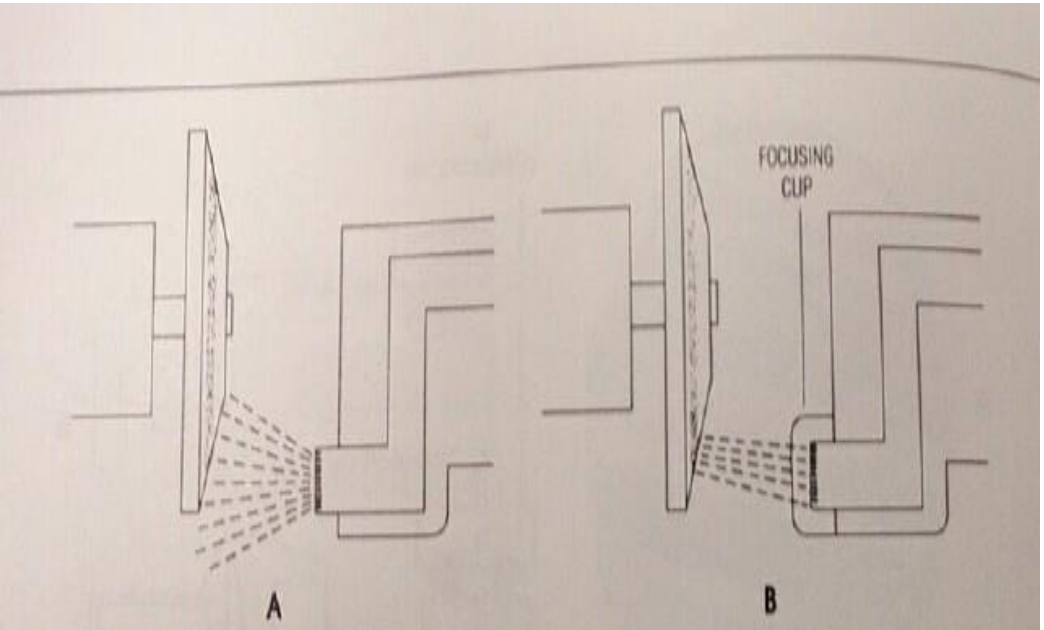


Fig. 7-6. A, Without a focusing cup, the electron beam would be spread beyond the anode because of mutual electrostatic repulsion among the electrons. B, With a focusing cup, which is negatively charged, the beam is condensed and directed to the desired area of the anode.

- This is made of nickel and it houses the filaments
- The focusing cup has a negative charge so that it can condense the electron beam to a small area of the anode.

Filament Current

- The current that flows through the Filament is called the filament current
- This is resulted from applying a low voltage across the filament
- When the x-ray machine is turned on, a low current flows through the filament to warm it and prepare it for the big heat necessary for x-ray production.

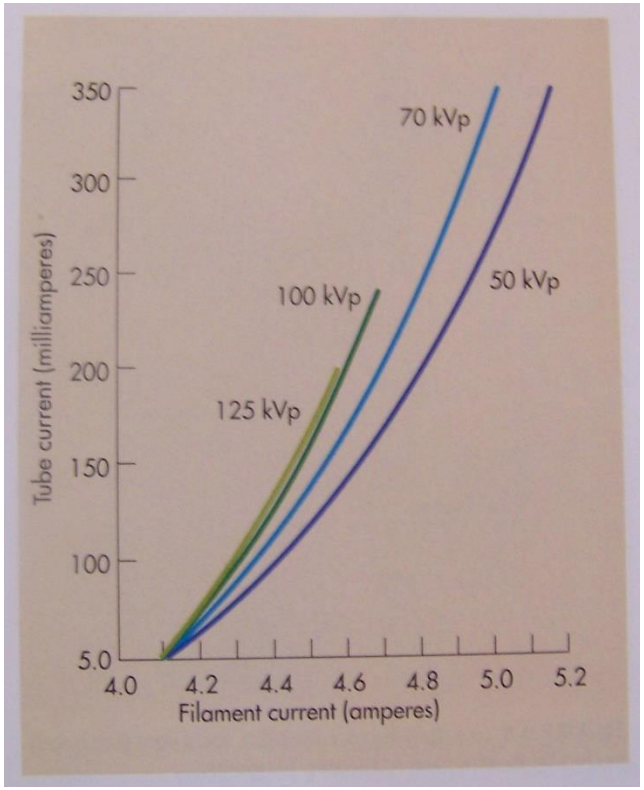
Filament Current

- When the machine is ‘stand by’, the filament is not hot enough for thermionic emission.
- So, it is boosted to a higher value just before the exposure
- Once the current is high enough for thermionic emission electrons are emitted from the filament

X-ray tube current

- This is the current that flows across the x-ray tube (flowing electrons from filament to anode)
- This is resulted when the high potential difference (kV) is applied across the tube & if emitted electrons are available at the filament

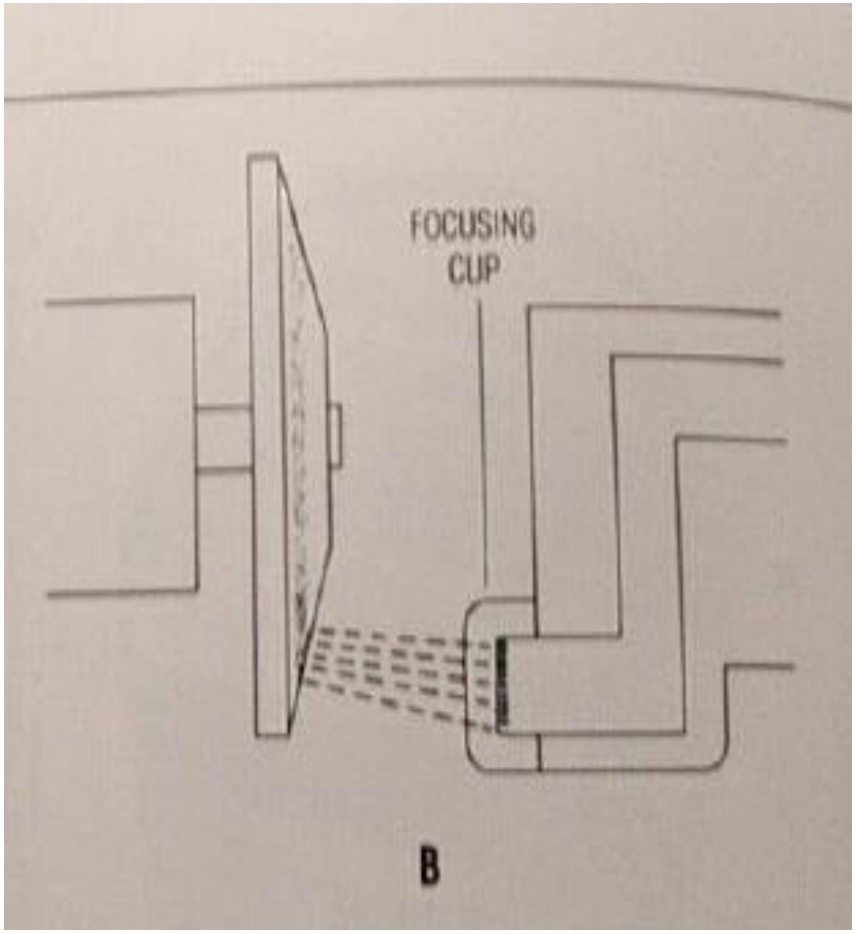
Filament Current & Tube Current



- The x-ray tube current is adjusted by controlling the filament current.
- A small rise in filament current will result in a large rise in tube current.
- The relationship between tube and filament current is dependent upon the tube voltage.

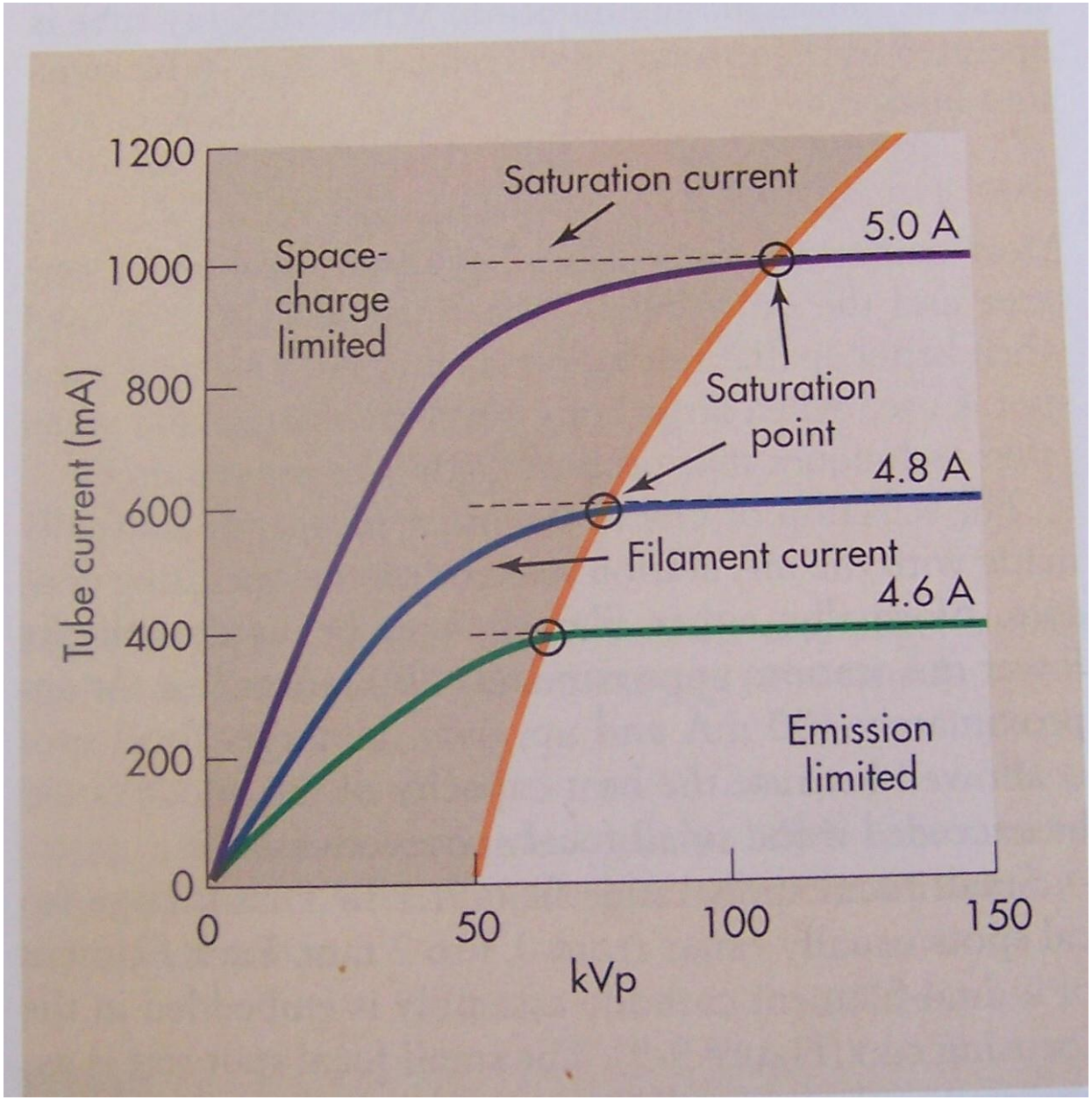
Space Charge

- When emitted by the filament, the electrons form a cloud near the filament momentarily before being accelerated to the anode. This is called a **space charge.**



Space Charge Effect

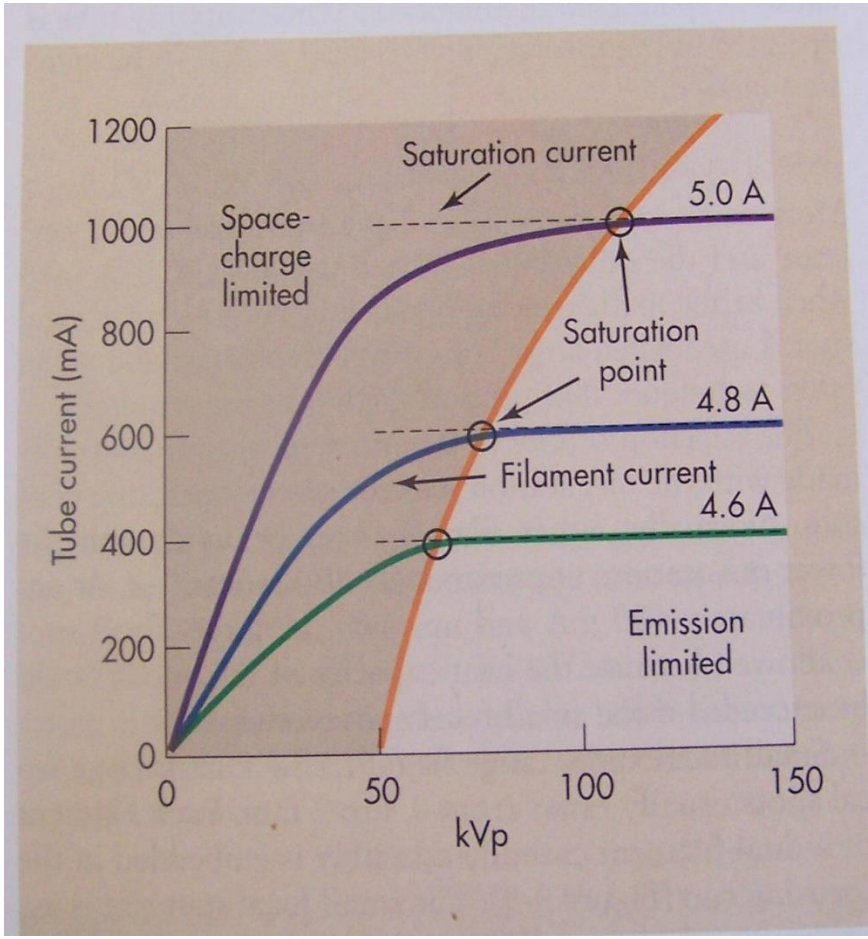
- It prevents further emission of electrons and hence limit the tube current for a particular anode voltage (kV).
- Because of that the tube current (mA) increases when the anode voltage (kV) is increased
- This is against the basic requirement in radiography ; which requires independent varaition of kV and mA



- At very high mA and very low kVp, the thermionic emission can be space charge limited.

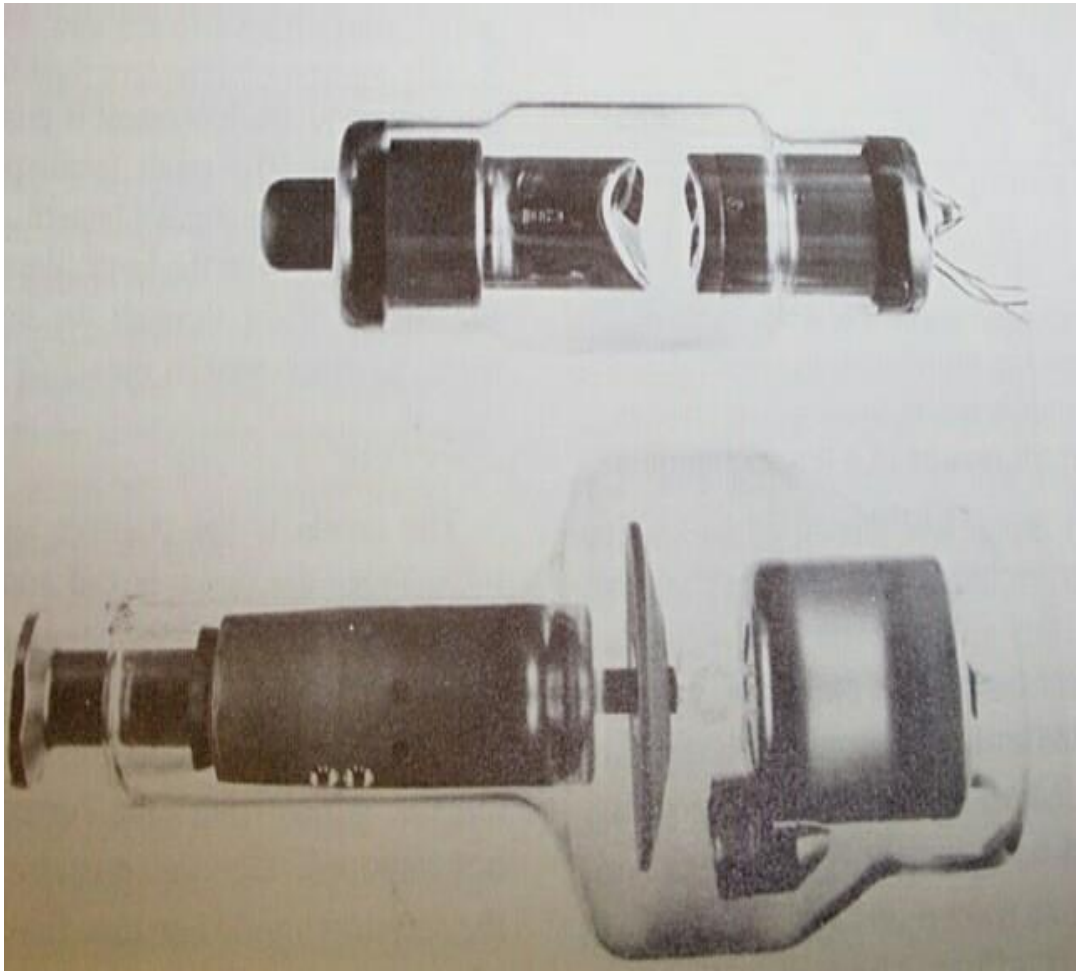
Saturation Current

- The highest tube current for a given filament current is called the saturation current
- After saturation the tube current is independent of the kV
- Above 1000 mA space charge limited exposure can be a major problem.



The Anode

- The anode is the positive side of the tube.
- X-ray tubes are classified by the type of anode:
  - Stationary (top)
  - Rotating (bottom)



The Stationary Anode

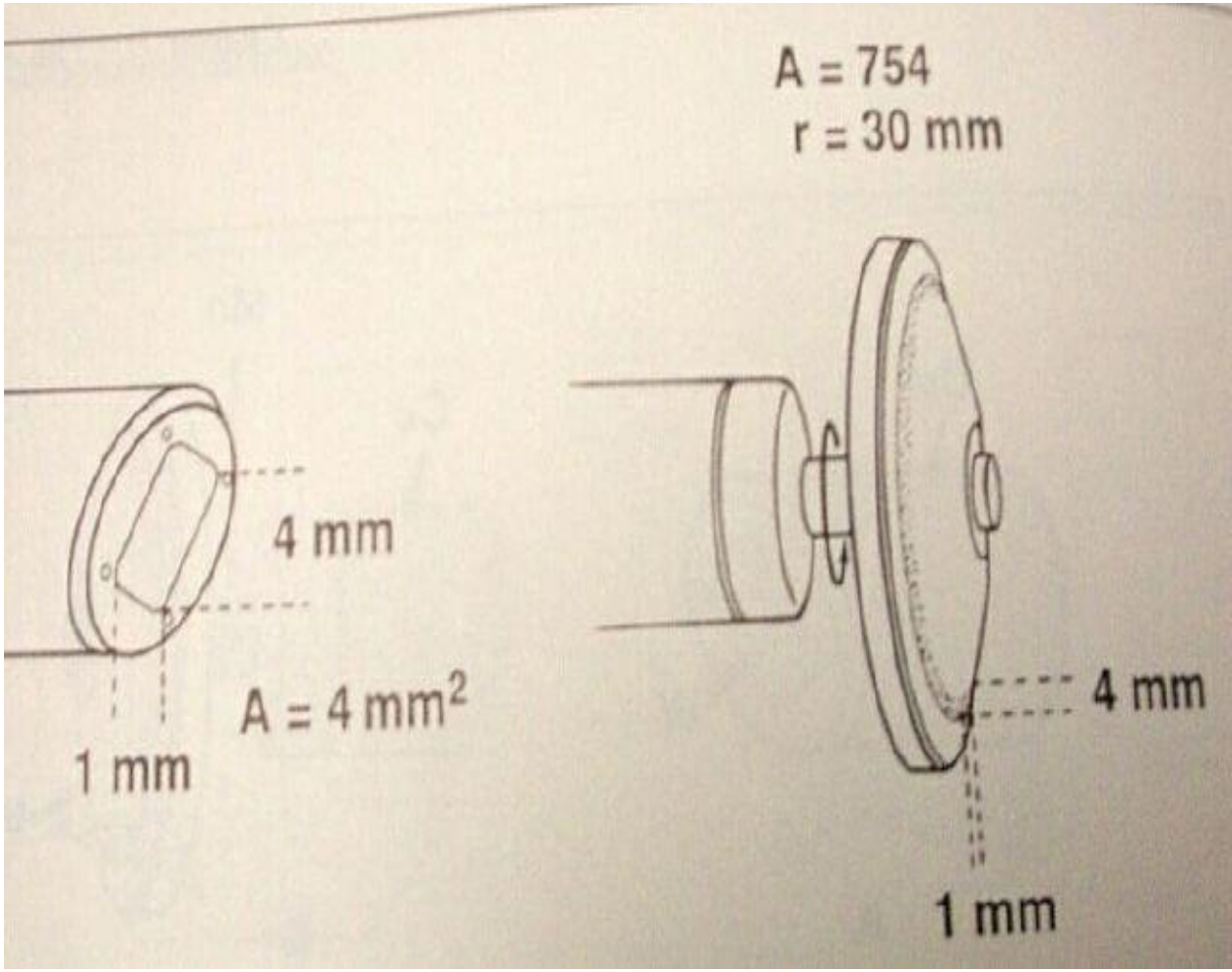
- Stationary anodes are used in dental x-ray and some portable x-ray machine where high tube current and power are not required.
- Tube output is low
  - 80kv
  - 15 mA
  - Long exposure times over 100ms
- Larger focal spots –low resolution
- Heat is confined to a small area

The Rotating Anode

- The Rotating Anodes are used for all the other applications where high tube out put and high tube rationgs are required
  - 125 – 150 kVp
  - 25 – 1200 mA
  - Short exposure times upto less than 1ms
- Smaller focal spots with high ratings – high resolution

The Rotating Anode

- The rotating anode allows the electron beam to interact with a much larger apparent target area.
- The heat is not confined to a small area.

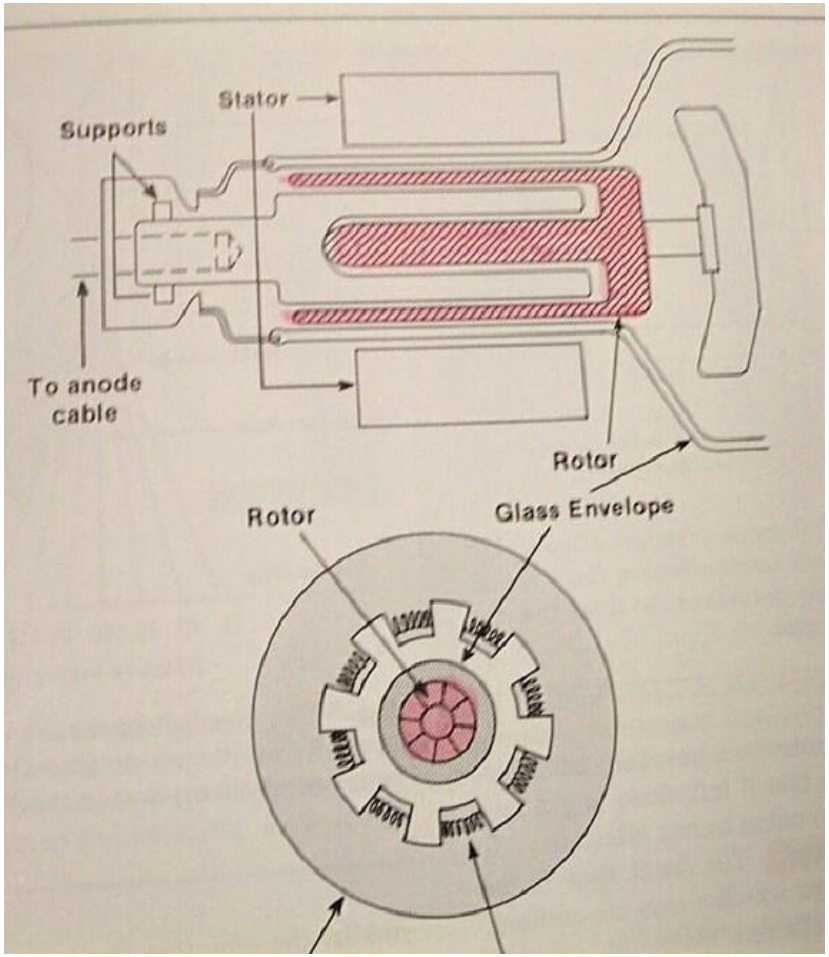


The functions of Rotating Anode

- The anode serves three major functions:
  - Receives the electrons emitted from the cathode.
  - It is a electrical conductor.
  - Mechanical support for the target.

The Rotating Anode

- The Anode must also be a good thermal conductor.
- When the electron beam strikes the anode more than 99% of the kinetic energy is converted to heat.



The Target

- Tungsten-rhenium is used as the target for the electron beam.
- Tungsten is used for three reasons
  - High atomic number
  - Heat conductivity
  - High melting point

  Rhenium is used to increase the surface properties to minimise the pitting and cracking of the target

The Rotating Anode - speed

- When the exposure button is depressed, current is applied to the tube that produces a magnetic field that starts the rotation of the anode.
- The rotor is the rotating part of an electromagnetic induction motor.
- It spins at 3000/3400 rpm.
- High speed anodes spin at 9,000/10,000 rpm.

Breaking The Rotating Anode

- When the anode is spinning at the correct speed, the exposure can be made.
- After the exposure is completed, it slows by reversing the motor.
- This is necessary to avoid excessive wear and tear of the bearings

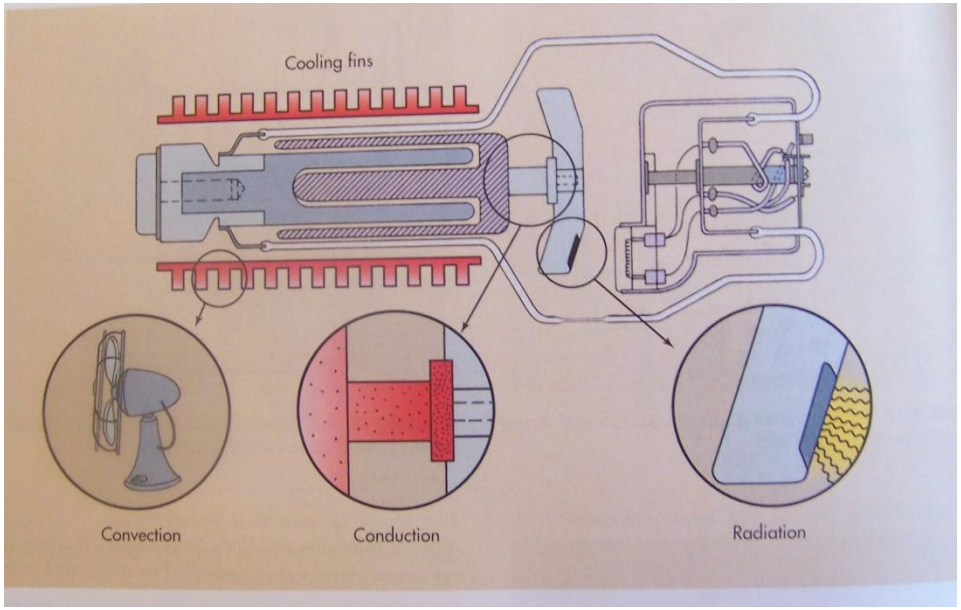
Dissipation of heat from the target

- Even with the anode rotating, some melting occurs.
- The heat must be rapidly dissipated from the target.
- Molybdenum and copper are used to rapidly transfer the heat from the target.
- The anode dissipates heat by radiating towards the glass envelop

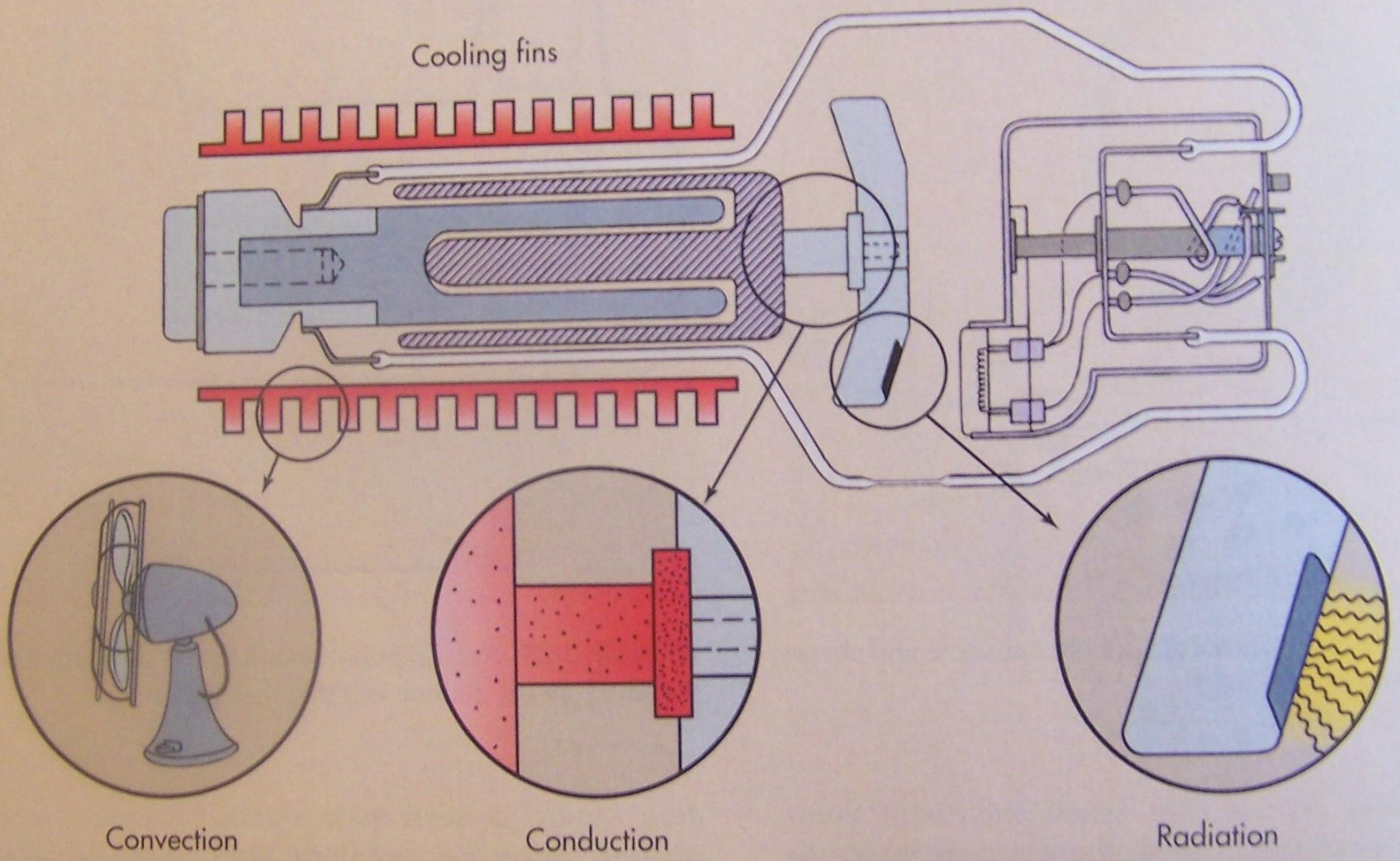
The anode stem

- The anode stem is made from molybdenum
- It is made appropriately thin as to minimize the heat conduction towards the rotor

Tube cooling



- The x-ray tube uses all three forms of cooling.
  - Radiation
  - Conduction
  - Convection


Cooling fins
Convection
Conduction
Radiation

Radiation Safety for X-ray Diffraction

Overview of Issue:

- Exposure types
  - Short-term high-dose
  - Long-term low-dose
- Invisible, odorless colorless; most exposures undetectable
- Lab users must understand radiation safety issues and pass an exam to use lab
- Safeguards present in lab do not substitute for knowledge and following safe procedures

Radiation Safety Tutorial Resources

- NDT (Nondestructive Testing Resource Center) Radiation Safety Tutorial (Comprehensive and Excellent)
  (http://www.ndt-ed.org/EducationResources/CommunityCollege/RadiationSafety/cc_rad-safety_index.htm)
- Summary article by Jenkins and Haas (1973)
- NBS Handbook 111 (1977) guide

Interaction of X-rays with Matter

Radiation interacts with matter by transfer of energy. Main processes are:

- Absorption (energy transferred)
- Scattering (energy redirected)

Absorption is of most concern in x-ray interaction with tissues

Energy Transfer:

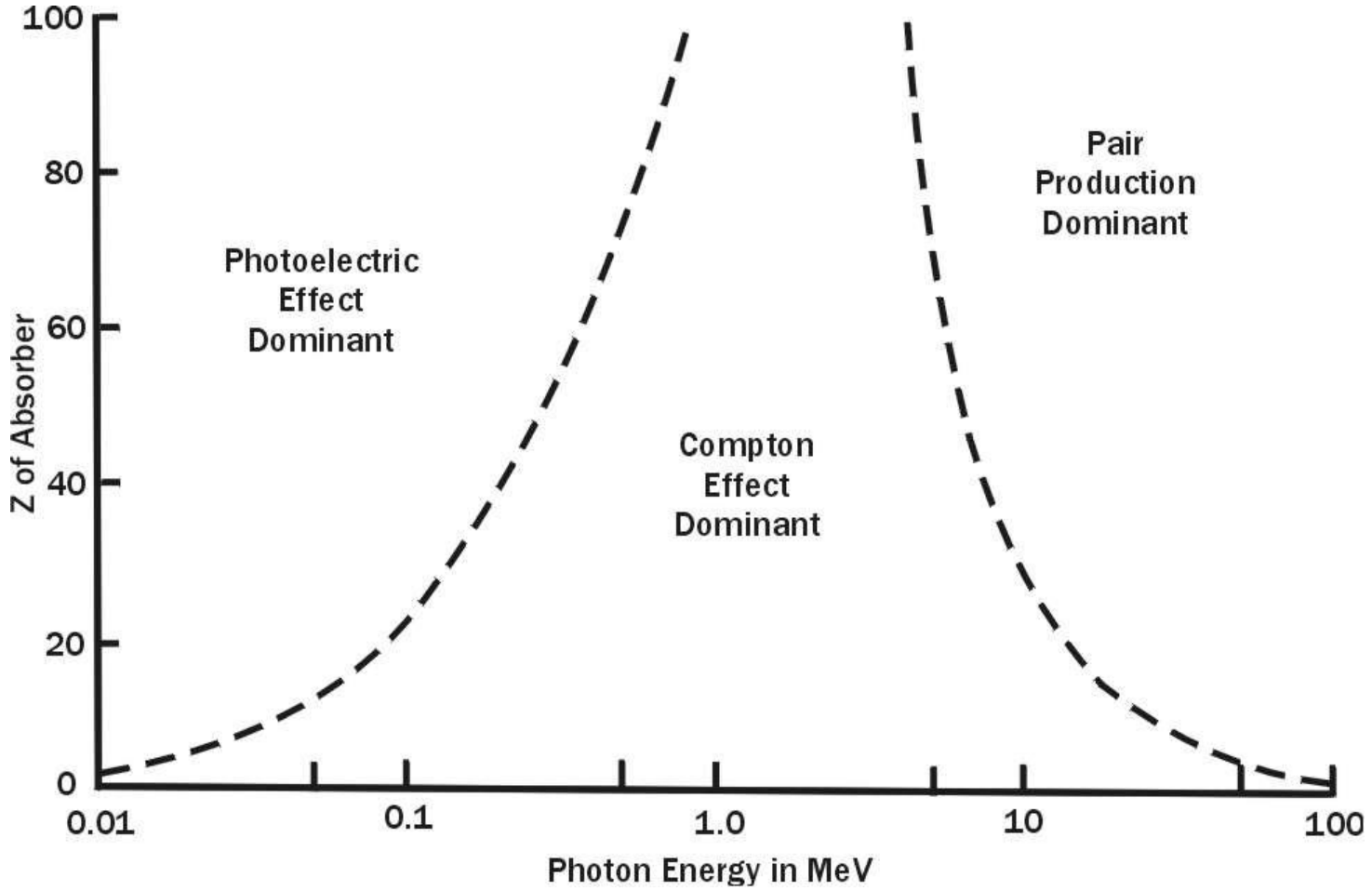
Multiple reactions with orbital shell electrons until all energy is spent

- Highest potential for damage to target.

Some of incoming x-ray energy is transferred to target

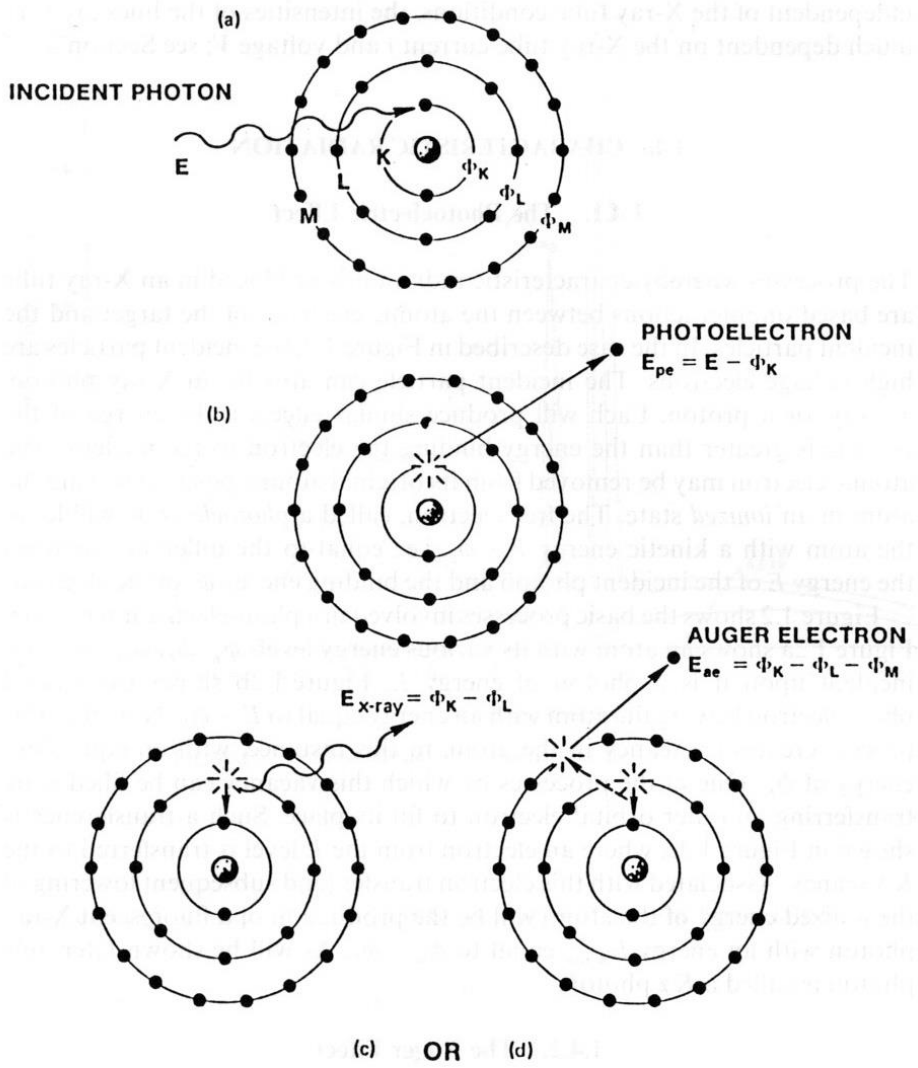
- Typical result is release of heat and a rise in temperature

Three processes are dominant in the production of ionizing radiation: Photoelectric effect, Compton scattering, and Pair production. Which effect dominates is related to the atomic weight of the target material and the energy of the "producing" radiation.



At XRD energies (~10 keV or ~0.01 MeV), the photoelectric effect is dominant

Photoelectric (PE) absorption of x-rays occurs when the x-ray photon is absorbed resulting in the ejection of electrons from the atom.



An incident x-ray photon interacts with an inner-shell orbital electron, dislodging it and producing a photoelectron.

An outer shell electron moves to fill the vacancy, producing a characteristic x-ray.

The photoelectron may escape the atom or interact with an outer shell electron producing lower energy Auger electron

Interactions continue until all energy is dissipated

Photoelectron interaction with the target atom is described by the following equation:

$$KE = E_x - P$$

Where

- KE is the kinetic energy of the photoelectron
- E_x is the energy of the incident X-ray photon
- P is the energy required to remove the electron or its binding energy in the atom

As regards interaction with matter (particularly living tissue), all of these interactions can result in atomic and molecular damage and heat.

- **Compton Effect**
  - Also called “incoherent scattering”
  - Occurs when an X-ray photon ejects an electron and scatters a lower energy X-ray photon from the atom
  - Occurs between 100 keV and 10 Mev; not significant at energies involved in XRD
- **Pair Production**
  - Produces an electron and positron with annihilation of the X-ray photon
  - Occurs with X-ray photons exceeding 2 MeV
  - Does not occur at energies involved in XRD

Other Radiation Effects

While other effects are minor as regards to radiation damage effects and safety, they can be significant in other aspects of radiation science.

- **Thomson Scattering** (a.k.a Rayleigh, coherent or classical scattering) is what makes X-ray diffraction possible
- **Photodisintegration** occurs when the X-ray photon is captured by the nucleus with the ejection of a particle at high energy from the nucleus. This high-energy process is intrinsic to nuclear fission reactions

Measurement of Radiation Dose

- **Roentgen (R)** is a unit of radiation exposure. It is the amount of radiation that generates 2.58 x 10^{-4} coulombs per kilogram of air (at STP).
- The **RAD (Roentgen-Absorbed Dose)** is the amount of radiation that will deposit 0.01 Joules of energy in a kg of material. One R is about .87 RAD in air, 0.93 RAD in tissue and 0.97 RAD in bone
- The **REM (Roentgen-Equivalent Mean)** is the absorbed dose in RADSs multiplied by a weighting factor for the type of radiation. For x-rays the factor is 1, thus 1RAD = 1REM.

The SI unit for the RAD is the **gray** equivalent to 100 RAD.
The SI unit for the REM is the **sievert**, equivalent to 100 REM.

Dosages are commonly expressed in R/hr or mR/hr. Received dosages are expressed as REM or mREM over a specified period of exposure time (hr, day, year, etc.).

Background Radiation

Below are estimates of natural and man-made background radiation at sea level at middle latitudes. The total averages 400 – 500 mREM/yr

- **Natural Sources (300 mREM):** "Natural" background radiation consists of radiation from cosmic radiation, terrestrial radiation, internal radionuclides, and inhaled radon.
- **Occupational Sources (0.9 mREM):** According to NCRP Report No. 93, the average dose for workers that were actually exposed to radiation in 1980 was approximately 230 mREM.
- **The Nuclear Fuel Cycle (0.05 mREM):** Each step in the nuclear fuel cycle can produce radioactive effluents in the air or water.
- **Consumer Products (5-13 mREM):** The estimated annual dose from some commonly-used consumer products such as cigarettes (1.5 pack/day, 8,000 mREM) and smoke detectors (1 mREM) contribute to total annual dose.
- **Miscellaneous Environmental Sources (0.6 mREM):** A few environmental sources of background radiation are not included in the above categories.
- **Medical Sources (53 mREM):** The two contributors to the radiation dose from medical sources are diagnostic x-rays and nuclear medicine. Of the estimated 53 mREM dose received annually, approximately 39 mREM comes from diagnostic x-rays.

Maximum Permissible Dose Equivalents for Radiation Workers (New Mexico and University of New Mexico)

	NM State Annual Limits		UNM Action Levels	
	(rem)	(Sievert)	Quarterly (mrem)	Monthly (mrem)
Total Effective Dose Equivalent (TEDE)	5	0.05	600	200
DDE + CDE (any organ)	50	0.5	6,000	2,000
Eye	15	0.15	1,800	600
Skin/Extremity	50	0.5	60,000	2,000
Minor (under 18)	10% of above		10% of above	
Fetus	0.5	0.005	n/a	25
Permitted maximum annual dosage to general public from UNM sources	0.1	0.001	n/a	n/a

Notes:
TEDE=DDE + CEDE
DDE: Deep dose equivalent, external whole body, tissue depth of 1 cm
CEDE: Committed Effective Dose Equivalent, sum of organ dose times organ weighting factor
CDE: Committed Dose Equivalent, internal to organs from uptake of radioactive material
For Minors, dose limits are 10% of adult dose, and radiation work is not permitted

Occupational Exposure

- In terms of absolute energy content, 1 RAD is not a lot (i.e., ~ 0.01 joule absorbed/kg).
- The main risks associated exposure to analytical X-rays are
  - **High Intensity Exposures:** Skin burns and lesions and possible damage to eye tissue
  - **Long-term chronic Exposures:** Possible chromosomal damage and long term risk of skin cancer
- Goal of all Radiation Safety practice is **ALARA** – As Low as Reasonably Achievable

Long-term Effects of Radiation Exposure

Long-term effects are usually related to increased risk of cancer, summarized in the table below:

Disease	Additional Cases per 100,000 (with one-time 10 REM dose) *
Adult leukemia	95
Cancer of digestive system	230
Cancer of respiratory system	170

* Source: Biological Effects of Ionizing Radiation V (BEIR V) Committee

- Radiation-induced life shortening (supported by animal experiments) suggests accelerated aging may result in the loss of a few days of life as a result of each REM of exposure
- Genetic Effects of radiation fall into two general categories
  - **Effect on individuals:** Can change DNA and create mutation but long term effects not well understood. Biological repair mechanisms may reduce importance.
  - **Effect of offspring:** Exposure to a fetus *in utero* can have profound effects on developing organs resulting in severe birth defects. For this reason pregnant women should avoid any non-background exposures

Bioeffects on Surface tissues

- Because of the low energy (~8 keV for Cu) of analytical x-rays, most energy will be absorbed by skin or other exposed tissue
- The threshold of skin damage is usually around 300 R resulting in reddening of the skin (erythema)
- Longer exposures can produce more intense erythema (i.e., “sunburn”) and temporary hair loss
- Eye tissue is particularly sensitive – if working where diffracted beams could be present, eye protection should be worn

Radiation Sources in X-Ray Diffraction Laboratories

- The **primary beam** from the X-ray tube tower can deliver as much as 400,000 R/minute
- After collimation and filtration about 5,000 – 50,000 R/min reaches the sample.
- The **diffracted beam**, radiating in all directions from a sample, can be as much as 80 R/hr.
- Exposure of any part of the body to the primary beam will deliver hundreds of times the maximum permissible yearly dose in a fraction of a second
- An hour of exposure to the diffracted beam can result in a year's worth of permissible exposure.
- Malfunctioning HV Power supplies can be a source of radiation and it is important that these devices be well shielded from workers

Measures taken to Reduce Risk of Exposure in the Laboratory

- Complete enclosure of source and diffractometer whenever possible.
- Spring-loaded fail safe shutters on the X-ray primary beam.
- Fail-safe interlocks installed on the housing.
- A fail-safe indicator light in the shutter-opening circuit.
- Seal all openings in the housing with lead tape.
- Periodic checks of the system for leakage at normal operating conditions using properly calibrated survey equipment. There is no required interval for this, but it must be requested if the following conditions exist:
  - Prior to the receipt of new equipment
  - Prior to a change in the arrangement, number , or type of local components in the system
  - Prior to any maintenance requiring the disassembly or removal of a local component in the system
  - Anytime a visual inspection of the system reveals an abnormal condition.
- High-voltage power supplies, if not functioning properly, can be the source of X-rays. It is important that the HV voltage multipliers and other circuitry be properly shielded to eliminate this as a possible radiation source.

The Three Principles of Radiation Protection

⬇Decrease **Time** of exposure in field of radiation

⬆Increase **Distance** from a source of radiation. Intensity decreases as the inverse square of the distance.

⬆Increase **Shielding** around radiation sources

Causes of XRD Lab Accidents

1. Poor equipment configuration, e.g. unused beam ports not covered
2. Manipulation of equipment when energized, e.g., adjustment of samples or alignment of cameras when x-ray beam is on.
3. Equipment failure, e.g., shutter failure, warning light failure
4. Inadequate training or violation of procedure, e.g., incorrect use of equipment, overriding interlocks.

In our lab with the equipment we have and how it is set up, 1, 2, and 3 are very unlikely.

#4 is always possible and is ultimately up to **you**.

Requirements for Analytical X-ray Laboratories

- No persons will be allowed to use analytical X-ray equipment until authorized in writing by the Radiation Safety Office
- No individuals under 18 years of age may use or assist in the use of analytical X-ray equipment
- Operating procedures shall be written and available to users and inspectors of analytical X-ray equipment
- No person shall bypass a safety device without written authorization from the Radiation Safety Office.
- The Radiation Safety Office must be promptly notified whenever exposure is suspected.