Company Logo

K. N. Toosi University of Technology

Faculty of Materials Science and Engineering

Advanced Methods of Materials Analysis

Fourth Session

(X-Ray Interaction with the Material)

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X-Ray Interaction with the Material

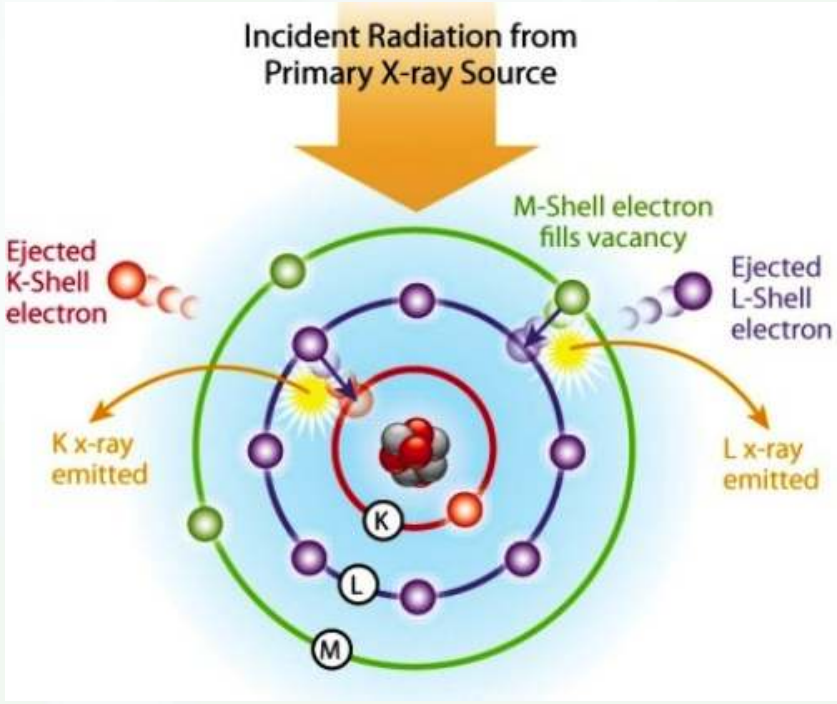
The impact of X-rays on the sample creates various effects that are used to identify and analyze materials. The most important signals received by the interaction are as follows:

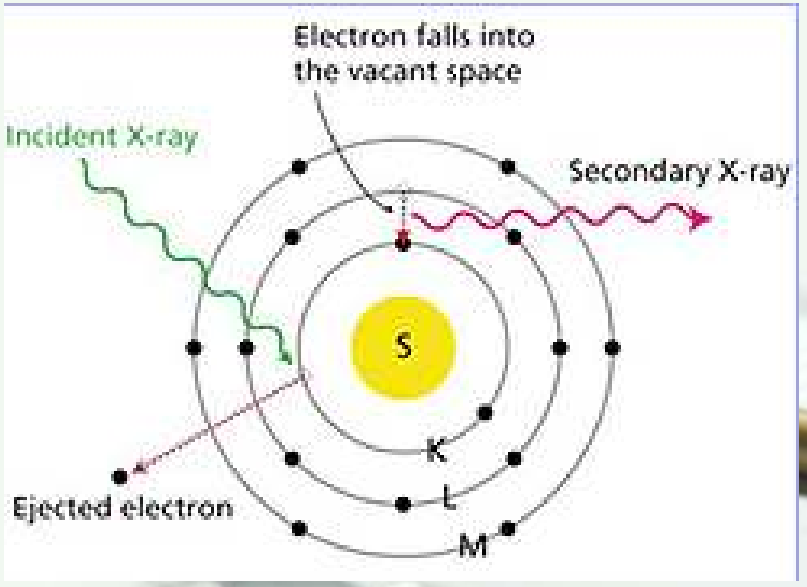
- ✓ Special fluorescence radiation (X-ray fluorescence, XRF)
- ✓ Electron
- ✓ Scattering
- ✓ Adsorption in material
- ✓ Pass through material
- ✓ Heat production

X-Ray Interaction with the Material

X-Ray Fluorescence (XRF)

As a result of the X-ray hitting the sample, the electrons in the atomic orbits are removed and the replacement of these electrons from the upper orbits produces a characteristic X-ray of fluorescence.

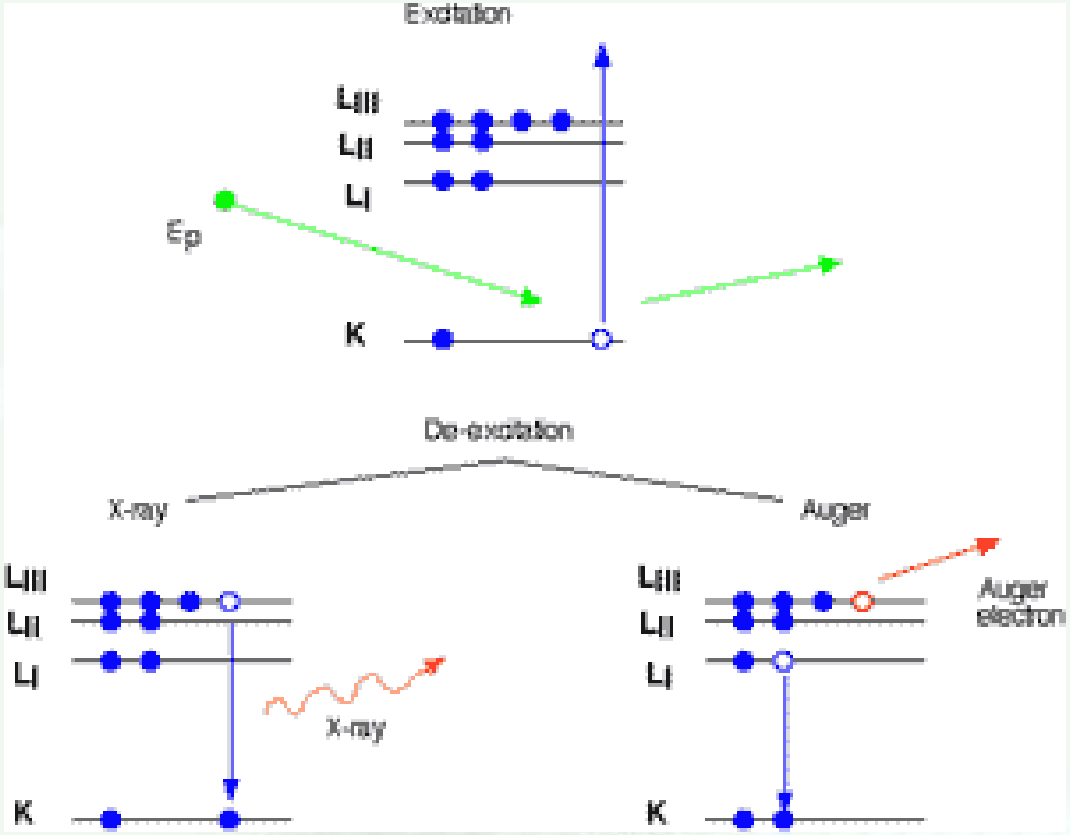




X-Ray Interaction with the Material

Electron

The electrons emitted by the special X-rays produced inside the atom are called Auger electrons.



X-Ray Interaction with the Material

Scattering

Coherent Scattering

If the bonding electrons oscillate strongly and X-rays are emitted at the same wavelength of the incident beam (radiation), we have coherent scattering.

Incoherent Scattering

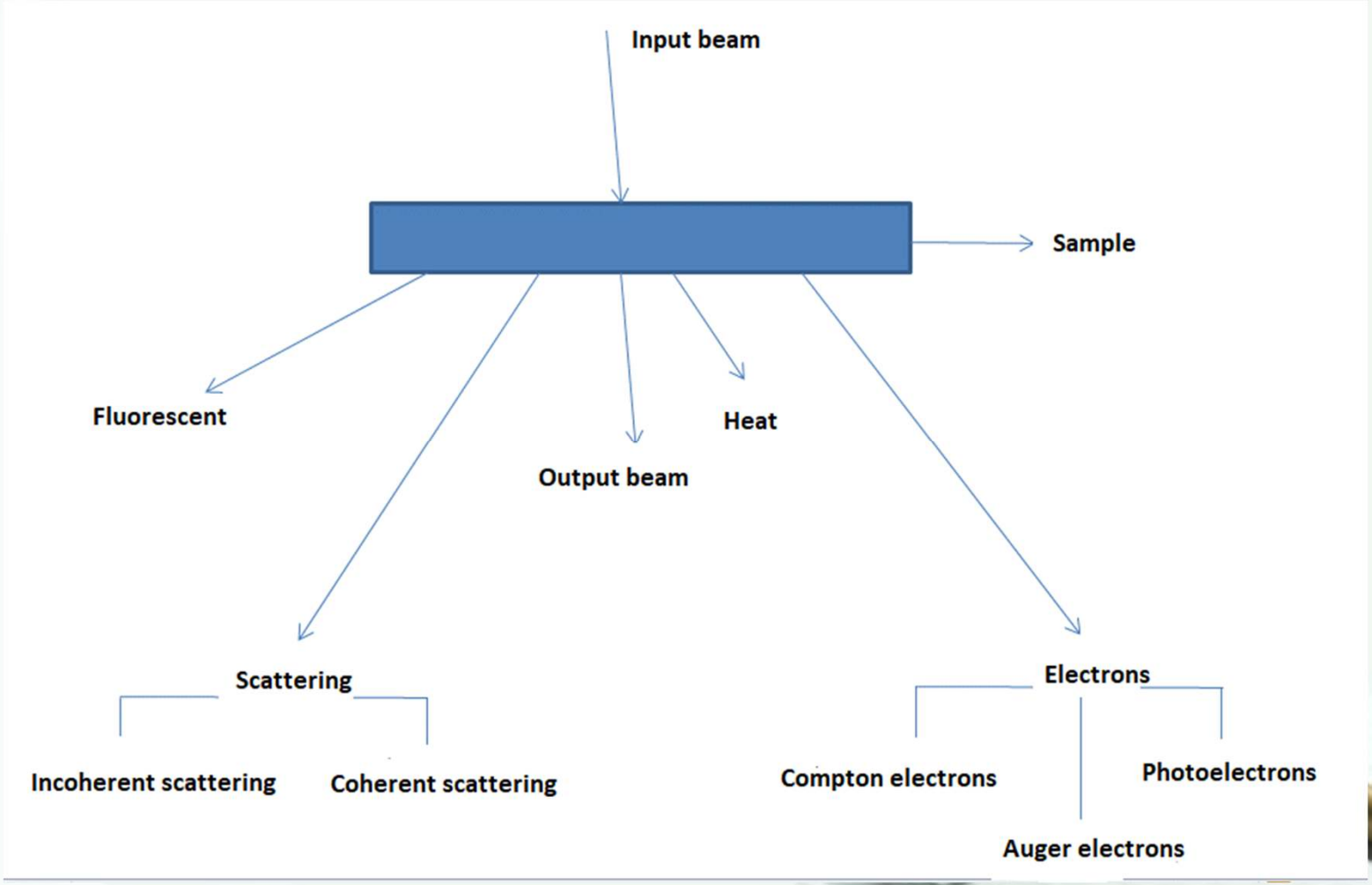
If the bonding electrons, which are less strong, scatter part of the radiation beam and increase its wavelength slightly (depending on the scattering angle), we have an incoherent scattering.

These two scattering occur simultaneously and in all directions.

X-Ray Interaction with the Material

- ✓ In addition to the electrons, fluorescence, and X-ray scattering, part of the X-ray is absorbed by the material, part is passed through material, and in addition heat is generated.
- ✓ Among these, fluorescence and coherent rays are most used in material analysis. Fluorescence beams are used for elemental analysis of materials and coherent beams are used to identify the type of phases and the crystal structure of materials.

X-Ray Interaction with the Material



X-Ray Interaction with the Material

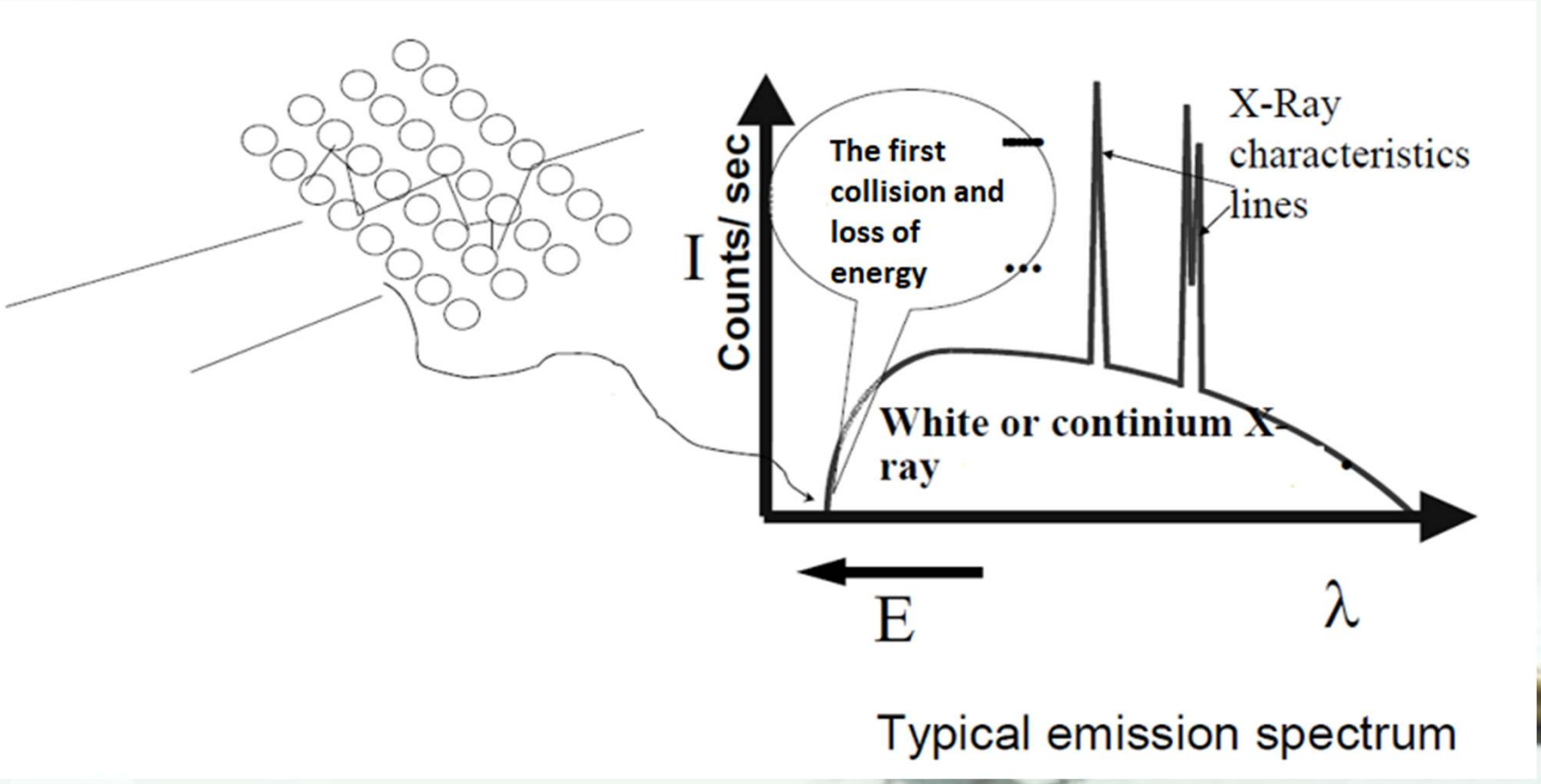
X-Ray Absorption

Some of the X-rays emitted to the sample or X-rays created by electron transfer can be absorbed by other atoms.

- ✓ **Actual Absorption**: Due to electron transfer (characteristic radiation)
- ✓ **Scattering:** Due to the scattering of rays in different directions due to hit with electrons (continuous or white rays).

X-Ray Interaction with the Material

Emission Spectrum



Typical emission spectrum

Diffractometry Method

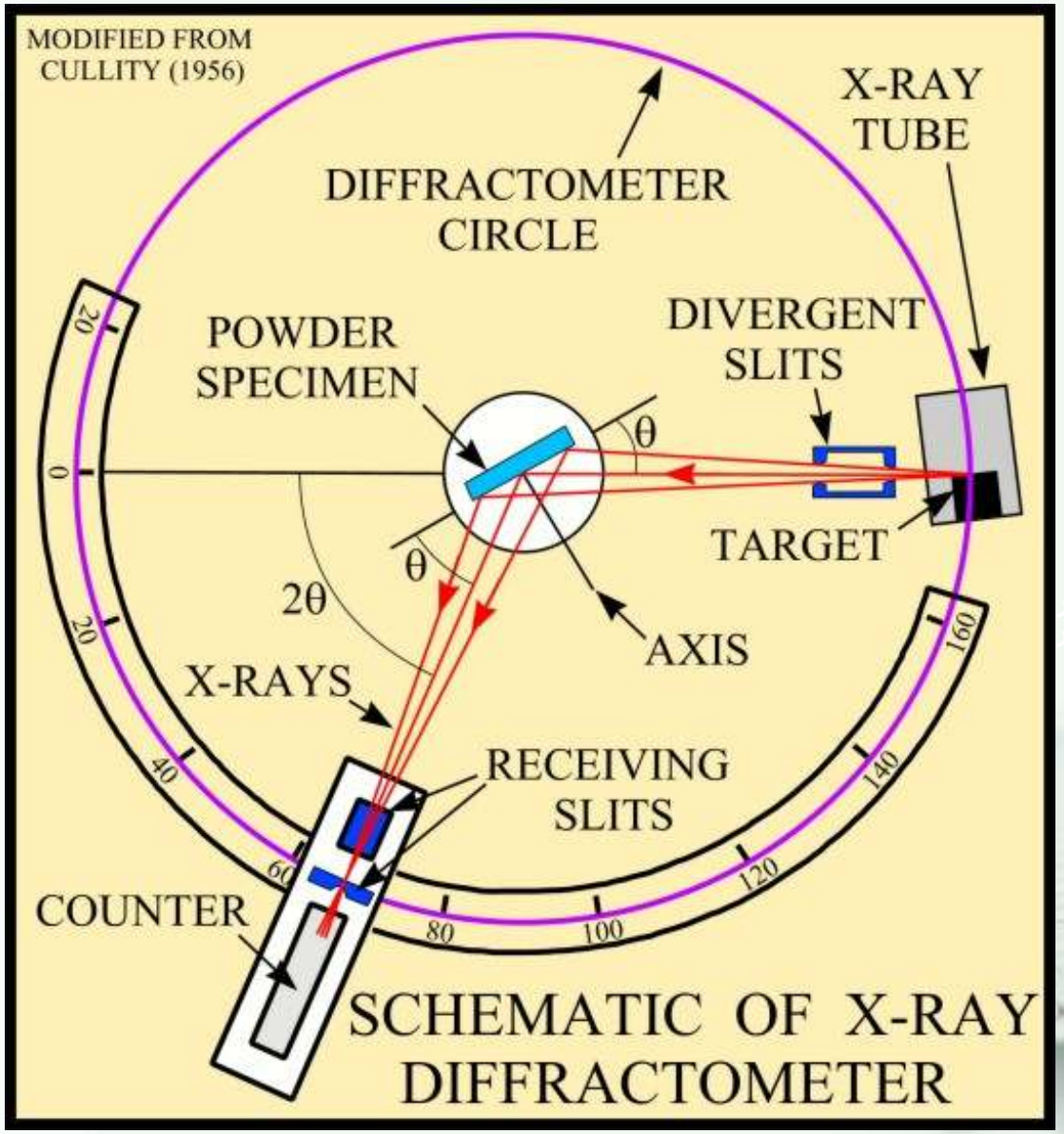
Diffractometer Measurements

- ✓ Diffractometry is another method for calculating the distances of crystal planes. In this method, a counter is used to detect diffraction beams. The counter may work based on the ionization of the gas or the fluorescence property of a material due to X-ray impact.
- ✓ The conventional gas type counter is the Geiger Counter, which works based on the ionization of the gas inside it due to the impact of rays with gas.

Diffractometry Method

- ✓ The gas is ionized and the ions move between the electrodes. The released electrons are absorbed towards the anode and the gas ions are absorbed towards the cathode.
- ✓ By connecting the anode and cathode to an external current, if the gas ionizes, which is the moment the beam hits the counter, more current will pass through the anode and cathode. The counter is usually mounted on a platform and moves in a circle.

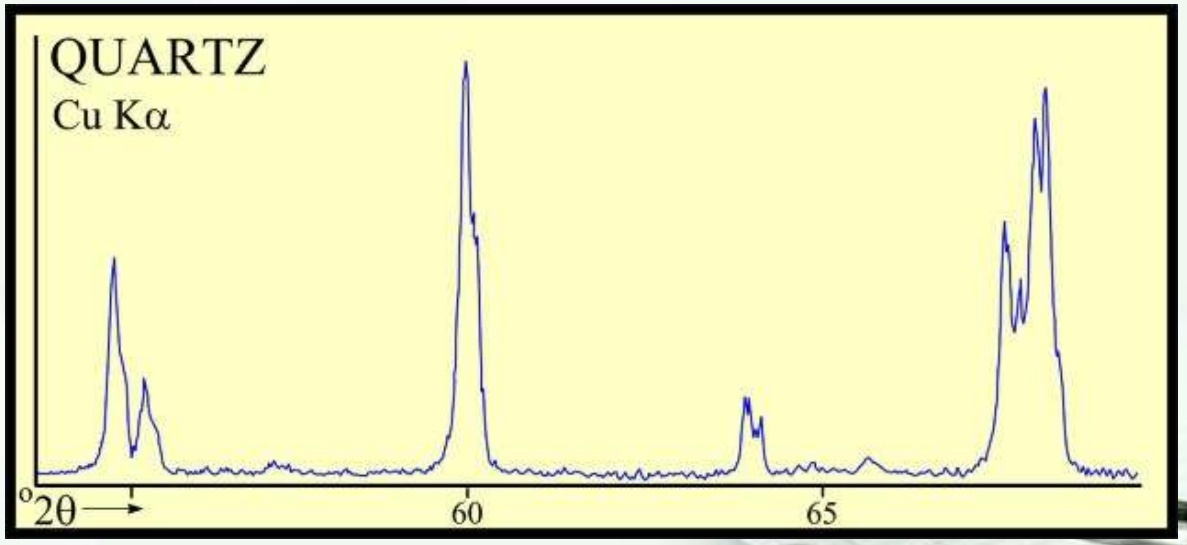
Diffractometry Method



How the Diffractometer Works?

Diffractometry Method

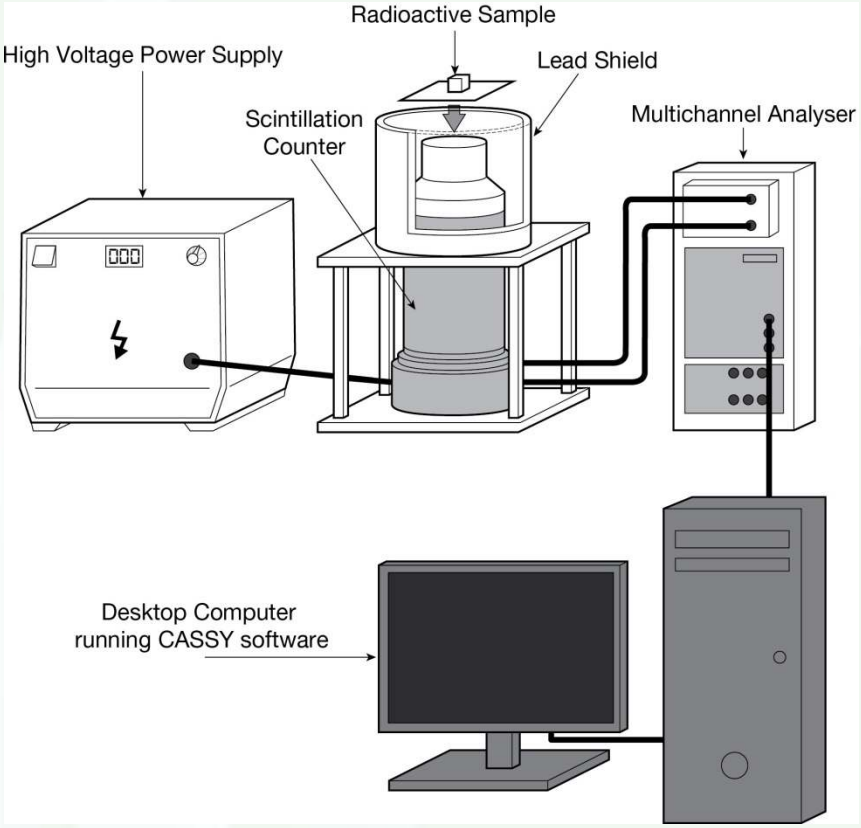
Whenever we draw the angular changes of the counter in terms of its anode and cathode current, the following curve is obtained.

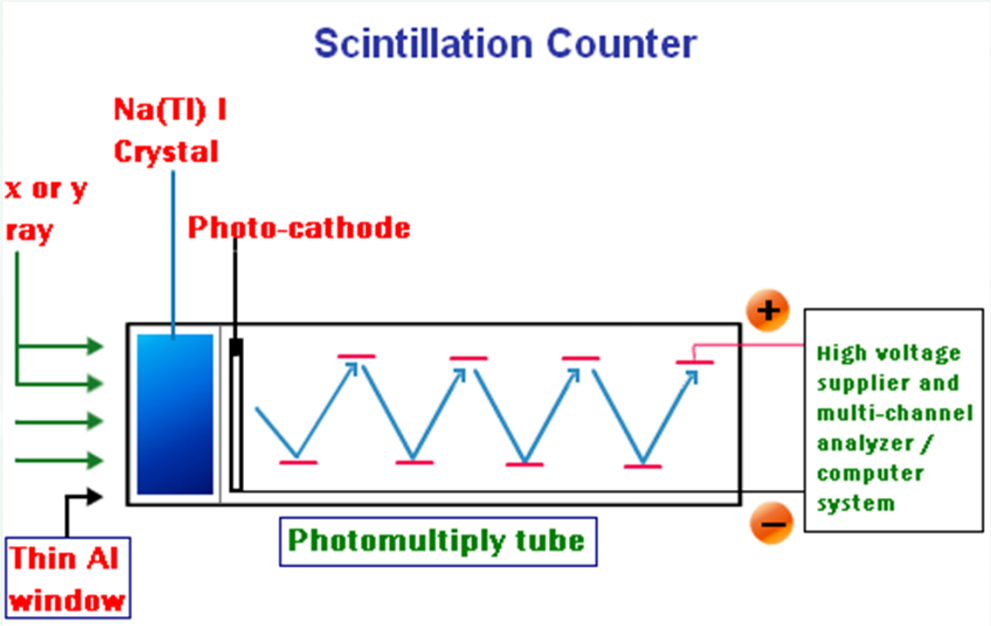


Diffractometry Method

- ✓ In places where there are peaks in the curve, are related to the diffraction, and the same places are the lines in the Debaye Scherrer photographic film.
- ✓ By measuring 2θ from the location of the peaks, the value of d can be calculated using Bragg's law. Instead of Geiger counter, you can use scintillation counter, which works with fluorescent materials due to X-ray impact, and get the same curves.

Diffractometry Method





Diffractometry Method

- ✓ In the diffractometer method, the sample is powdered and a tablet is prepared from it. The sample rotates at the same time as the counter rotates, and its rotation speed is generally half the rotation speed of the counter.
- ✓ In this case, the angle between the main path of the ray and the surface of the powder is always equal to the angle of the radius of diffraction with the surface of the powder.

Diffractometry Method

- ✓ **The accuracy of diffractometry method in determining d is much higher than the Debye Scherrer method due to the accurate calculation of 2θ (accuracy of one thousandth of an angstrom vs. one hundredth).**

How to Find the Composition of Materials

Hanawalt Method

By measuring the amount of 2θ, the amount of d as well as the type of material can be determined. To do this, you can use pre-calculated graphs or tables that represent variations 2θ by d based on Bragg's law. From the numbers that are calculated as d, it is necessary to first select the three numbers related to the most colorful film lines in the Debye Scherrer method or the largest three curved peaks in the diffractometry method, and then refer to the pre-prepared tables.

How to Find the Composition of Materials

Hanawalt Method

	3.39 – 3.32 (±.02)									File No.	I/Ic
i	3.38_9	8.58_X	3.04_9	4.11_8	3.18_8	1.69_7	2.65_6	1.88_5	$(Mg,Fe)_2Al_4Si_5O_{18}$/Cordierite, ferroan	9– 472	
	3.33_X	6.72_9	3.19_8	8.09_7	3.28_7	5.18_4	3.10_4	4.30_4	$C_{19}H_{19}N_7O_6$	29–1716	0.20
i	3.31_8	6.40_X	6.10_8	3.85_5	2.77_5	6.70_4	3.48_4	2.64_4	$C_{12}H_8Cl_6$	17–1054	
	3.38_9	6.13_X	8.66_9	3.20_9	3.29_5	9.70_3	4.57_3	3.46_3	$C_{11}H_{11}N_3 \cdot HCl$	28–1749	
i	3.34_X	5.93_2	5.19_1	3.77_1	3.65_1	3.51_1	2.94_1	1.67_1	$C_4H_8N_2O_2$	26–1863	3.30
	3.37_X	5.85_8	3.86_8	3.72_7	3.52_7	3.03_7	2.70_7	7.72_6	$C_6H_9N_3O_2 \cdot HCl$	5– 459	
*	3.31_8	5.73_X	3.43_7	3.59_6	3.19_5	4.36_4	4.19_3	3.27_2	$C_6H_5NO_2$	30–1845	1.00
	3.30_X	5.44_7	5.63_5	3.24_4	4.97_3	6.58_3	4.58_2	3.15_2	$(NH_4)_4P_2O_7$	20– 102	
	3.38_X	5.30_X	3.49_X	5.90_5	3.67_5	3.26_5	3.18_5	2.99_5	$KH_3P_2O_7$	15– 509	
	3.35_X	5.21_8	4.86_8	4.33_8	4.04_8	3.90_8	3.55_8	2.73_8	β-$C_9H_{11}NO_2$	22–1874	
i	3.40_X	5.01_9	3.09_7	4.10_4	3.00_4	4.03_3	6.74_2	3.45_2	$C_3H_6N_6$	24–1654	1.10
*	3.30_X	4.76_6	4.18_6	5.73_5	2.92_3	3.98_3	2.38_2	3.35_2	$C_8H_6O_4$	37–1919	
	3.31_X	4.71_8	3.50_5	5.56_3	3.84_3	3.03_3	7.02_2	2.30_2	$C_6H_5NO_2 \cdot HCl$	29–1827	
*	3.39_X	4.48_5	3.43_5	3.01_5	4.09_4	2.98_4	2.78_4	3.18_3	$NaHSO_4$	25– 833	
	3.34_9	4.42_X	10.1_9	1.48_9	2.56_8	1.68_8	1.28_7	1.23_7	$Al_2Si_2O_5(OH)_4 \cdot 2H_2O$/Halloysite-10A	9– 451	
i	3.40_9	4.38_X	2.88_7	5.76_4	2.61_4	4.09_4	2.76_4	1.76_3	V_2O_5/Shcherbinaite, syn	9– 387	1.60
*	3.33_X	4.30_5	2.82_5	6.08_2	4.72_2	1.71_1	3.52_1	2.15_1	$(NH_4)_2Ca_2(SO_4)_3$	22–1037	2.30
i	3.37_X	4.28_3	1.84_2	1.55_1	2.47_1	2.31_1	1.39_1	2.14_1	$AlPO_4$/Berlinite, syn	10– 423	
*	3.34_X	4.26_2	1.82_1	1.54_1	2.46_1	2.28_1	1.37_1	1.38_1	SiO_2/Quartz, low, syn	33–1161	3.60
o	3.36_X	4.23_X	3.57_7	5.27_4	3.72_4	4.04_4	3.97_3	7.19_2	$C_6H_8N_2O_2S$	30–1944	
*	3.35_X	4.22_9	3.25_7	4.43_6	3.67_5	6.22_4	2.89_4	3.55_3	$C_6H_4N_2O_4$	37–1915	
i	3.32_X	4.22_X	5.28_8	4.97_8	3.52_8	3.48_8	2.65_8	2.41_8	$C_6H_{14}N_4O_2 \cdot HCl$	25–1541	
i	3.35_8	3.88_X	3.73_8	3.54_8	2.91_7	2.52_7	2.32_7	1.92_5	$C_5H_9NO_4 \cdot HCl$	25–1925	
*	3.39_X	3.87_9	3.29_8	2.36_6	3.01_5	2.04_4	1.99_4	2.41_3	$HgSO_4$	31– 867	
*	3.41_9	3.84_X	3.52_9	3.26_9	3.87_7	3.03_7	2.74_3	2.37_3	$KHSO_4$/Mercallite, syn	11– 649	
*	3.31_X	3.77_8	4.22_7	3.24_7	3.29_6	2.99_5	3.47_5	2.90_3	$KAlSi_3O_8$/Orthoclase	31– 966	
*	3.36_8	3.52_X	7.69_X	6.16_5	3.84_4	3.14_1	3.79_1	3.09_1	$C_6H_4(CO)_2C_6H_4$/Hoelite, syn	28–2002	
*	3.35_X	3.50_7	5.04_6	3.56_6	4.00_5	3.15_5	5.58_4	2.48_3	$(NH_4)_2S_2O_8$	31– 69	
*	3.36_X	3.47_7	6.52_6	2.59_6	3.02_6	3.28_5	3.56_5	2.61_4	$BaAl_2Si_2O_8$/Celsian, syn	38–1450	
*	3.36_X	3.47_7	6.52_6	2.59_6	3.02_6	3.28_5	3.56_5	2.61_4	$BaAl_2Si_2O_8$/Celsian, syn	38–1450	
*	3.30_X	3.47_9	3.66_9	4.87_5	3.06_3	3.03_3	2.88_3	2.86_3	$K_2Cr_2O_7$/Lopezite, syn	27– 380	0.63
	3.33_X	3.46_6	3.79_5	3.26_5	3.01_5	2.58_5	2.91_3	2.77_3	$(K,Ba)(Si,Al)_4O_8$/Orthoclase, barian	19– 3	
*	3.38_X	3.45_7	3.44_7	2.28_6	6.30_4	2.22_3	2.75_3	5.07_3	KPO_3\Potassium metaphosphate	35– 819	
i	3.39_X	3.43_X	2.21_6	5.39_5	2.54_5	2.69_4	1.52_4	2.12_3	$Al_6Si_2O_{13}$/Mullite, syn	15– 776	
	3.39_X	3.41_9	2.31_4	2.84_3	3.82_2	2.14_2	2.03_2	2.00_2	$NaBF_4$/Ferruccite, syn	11– 671	
	3.41_9	3.39_X	2.31_4	2.84_3	3.82_2	2.14_2	2.03_2	2.00_2	$NaBF_4$/Ferruccite, syn	11– 671	
i	3.38_X	3.39_8	2.53_8	3.11_7	2.29_6	3.57_4	2.41_4	2.37_4	Gd_2S_3	20–1056	
i	3.39_8	3.38_X	2.53_8	3.11_7	2.29_6	3.57_4	2.41_4	2.37_4	Gd_2S_3	20–1056	
*	3.30_X	3.29_X	4.76_6	4.18_6	5.73_5	2.92_3	3.98_3	2.38_2	$C_8H_6O_4$	37–1919	
*	3.33_X	3.28_8	2.97_7	3.83_4	2.36_4	2.34_4	2.35_3	2.21_3	$CdSO_4$	14– 352	

How to Find the Composition of Materials

Hanawalt Method

- ✓ The Hanawalt method is a method of finding the type of crystal.
- ✓ This method uses a book of the same name.
- ✓ The chemical formula of all possible crystals is given in this book and 8 important lines (d) are given from each.
- ✓ It is based on the most colorful three lines of Debye Scherrer film or the longest three peaks of the diffractometry curve, and the first three columns are printed in more colorful.

How to Find the Composition of Materials

- ✓ The indexes of the numbers show the intensity of the diffraction (colorful), where 10 (x) is the most colored line and 1 is the least colored line, and they are placed as an index along with distance between the crystal plates (d).
- ✓ To identify the composition of the test material by having the distances of the crystal planes (d), we determine the three full-color lines or the longest three curved peaks. Then we select the most colored line (the longest curved peak) and find a part in the book where these numbers are within that part (two numbers written above page) that in fact the numbers in the first column of the table are in the same range.

How to Find the Composition of Materials

- ✓ Then in the second column, which is in descending order, we match the second full line, then the third line and then the remaining 5 lines to determine the composition of the material by matching 8 numbers.
- ✓ In some cases, there is a discrepancy between the calculated number and the book, which is related to the test method. The error is generally between 0.01% and 0.001% angstrom.

The complete information of each item in this card is as follows:

How to Find the Composition of Materials

- ✓ On the right side of the table is a column called File No. There is a number for each compound that is actually the card number of that compound (ASTM card).

- ✓ The complete information of each item in this card is as follows:

d values, intensities, type of radiation (copper, iron, cobalt, etc.), radiation wavelength, type of filter, crystal structure, size a, b and c, size of angles in the crystal, allowable planes, specific gravity, melting point and the color of the material.

How to Find the Composition of Materials

- ✓ If there are multiple compounds in the sample, after identifying the first compound, the extra lines remain in the list that belong to another material. In this case, the previous method is also performed for the second compound.
- ✓ If a line is common to two or more elements or, for example, when three colorful lines do not belong to one element but belong to two or more elements, we must determine the material by trial and error, of course, today special software and equipment X-ray diffraction devices do this.