Atomic X-Ray Spectroscopy

Chapter 12

X-ray range → 10^{-5}Å to 100 Å
Used→ 0.1Å to 25 Å

Formation of X-Rays (emission)

- Produced by the deceleration of high-energy electrons.
- Electronic transition of electrons in the inner orbitals of atoms.

Formation of X-Rays (fluorescence)

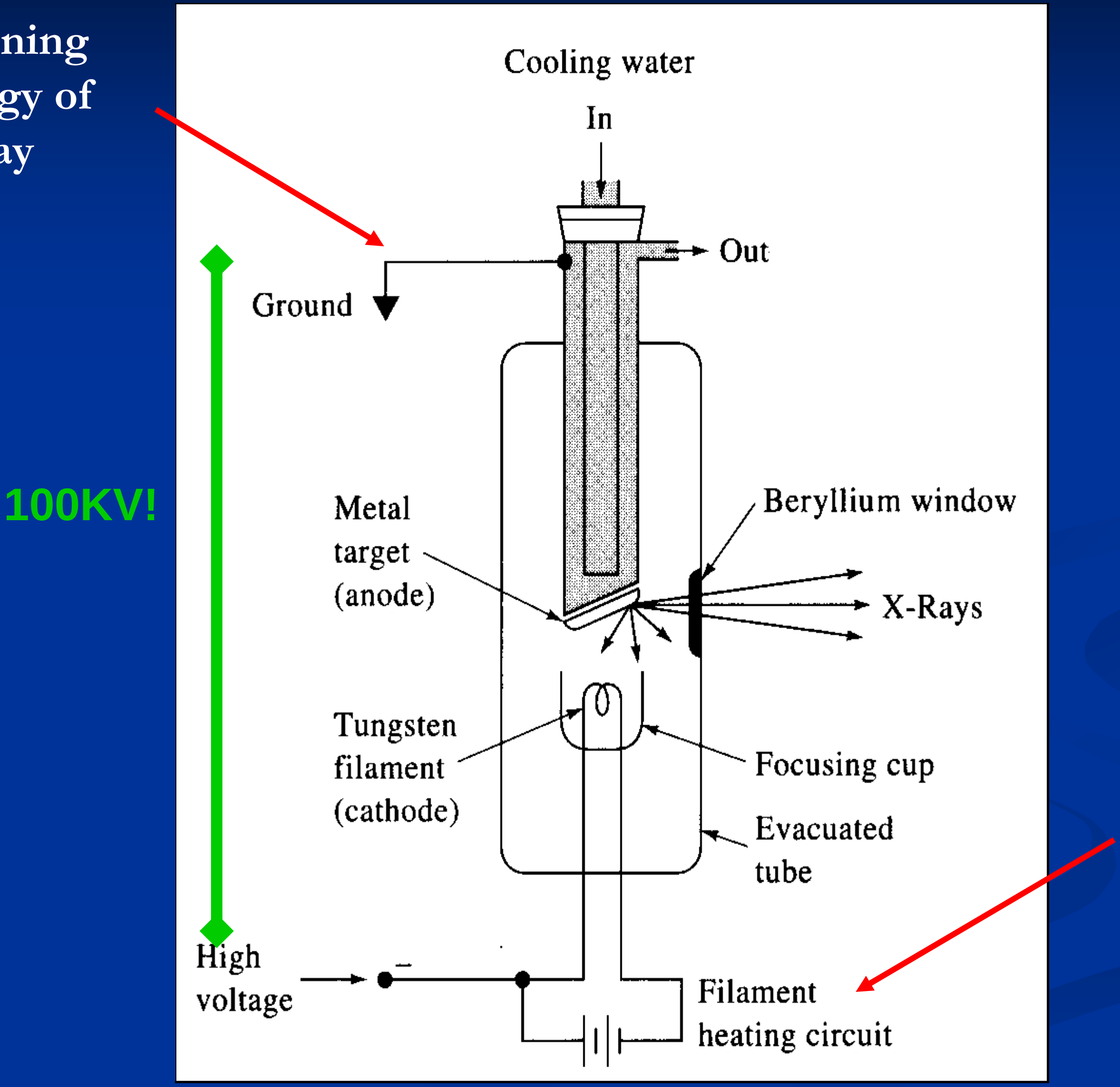
- Exposure of a substance to x-ray radiation → absorption and then → fluorescence
- Inner orbital electrons in K or L shells of metal atoms are knocked out! (big or small?)
- Outer shell electrons undergo transitions to the lower shells and give off high energy X-Rays

Formation of X-Rays (decay, synchroton)

- Radioactive decay → X-ray emission (common in medicine)
- Synchrotron source radiation (accelerated particles) very few of these available!

X-Ray Tube (electron beam sources)

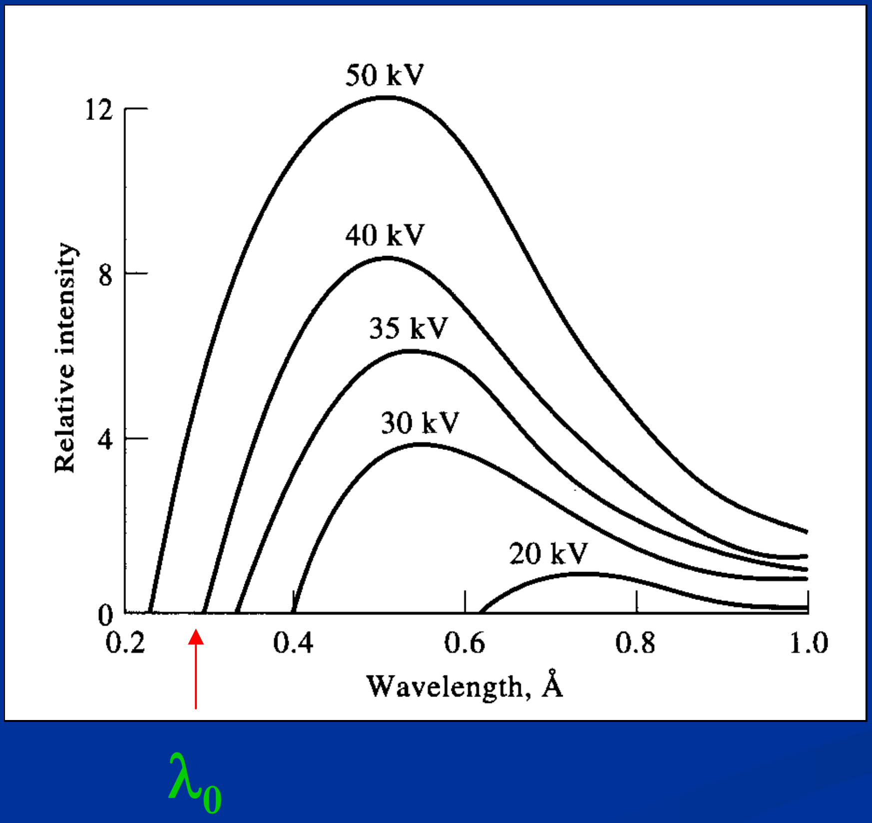
Determining the energy of the X-Ray



Controlling the intensity of X-Ray

X-ray tube emission

Continuum Spectra: *Results from Collisions between the electrons and the atoms of target materials*



$E_e = E'_e + h\nu$

At λ_o, $E'_e = 0$

$h\nu_0 = hc/\lambda_o = Ve$

V: accelerating voltage

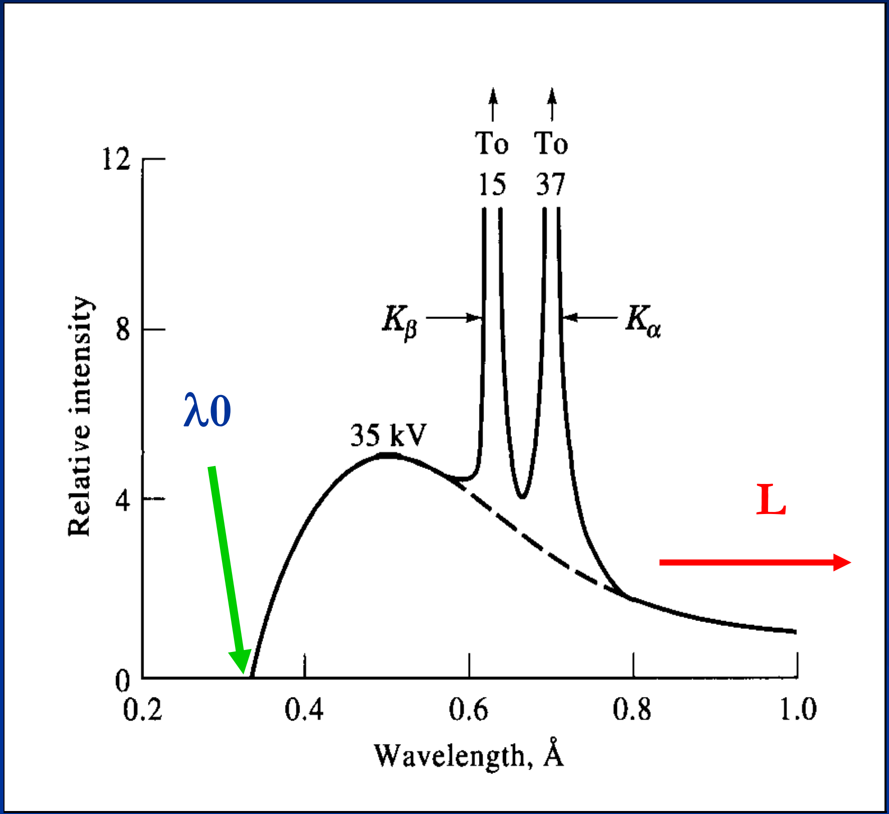
e: charge on e^-

$\lambda_0 = 12{,}398/V$

Duane-Hunt Law

- Independent of material
- Related to acceleration voltage → E

Line spectra is possible!



Line Spectrum of a Molybdenum target

From electron transitions involving inner shells

- **Atomic number >23**
- **2 line series K and L**
- **$E_K > E_L$**

- **Atomic number < 23**
- **K only**

A minimum acceleration voltage is required for

A minimum acceleration voltage required for each element increases with atomic number

Line spectra

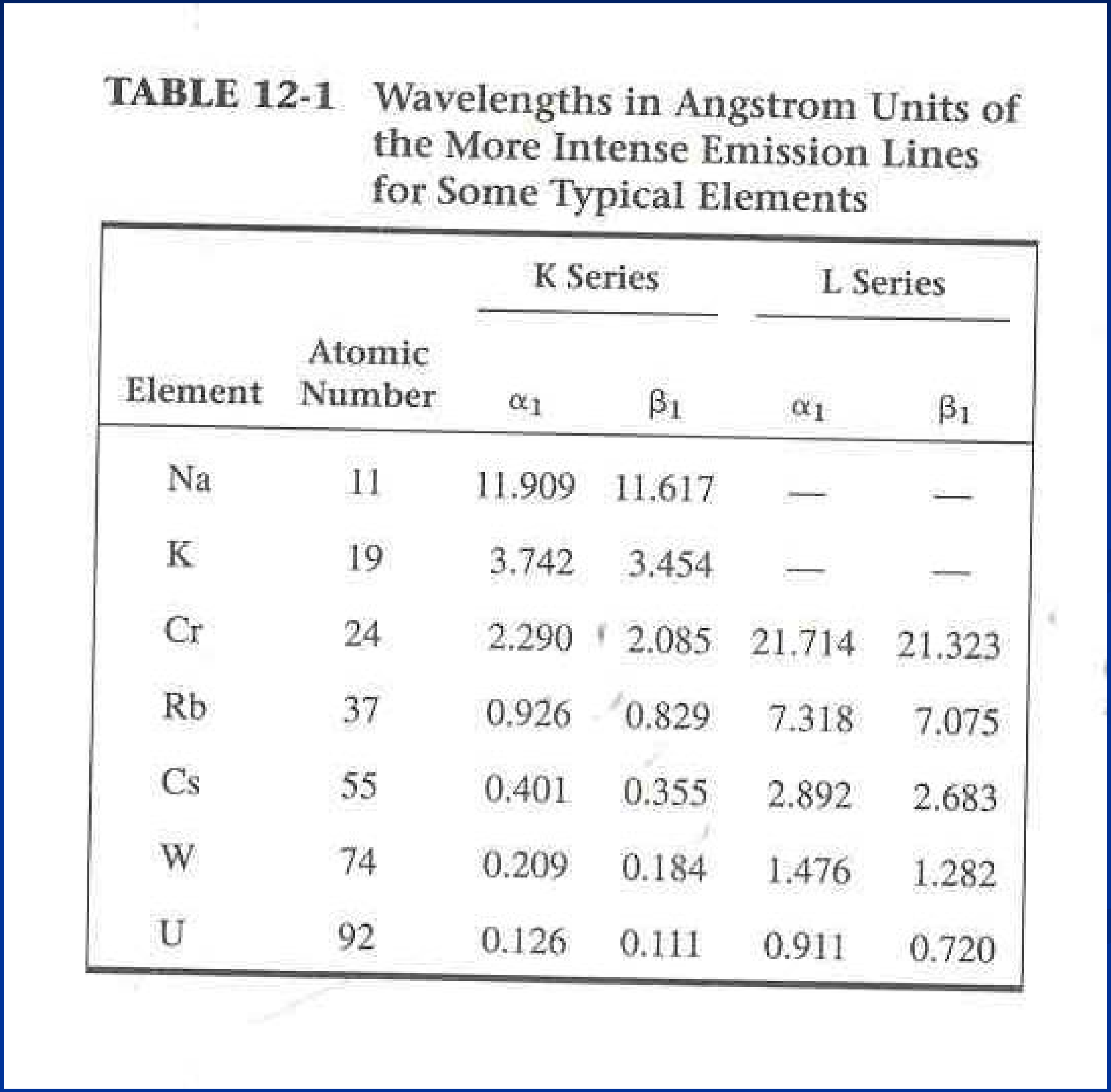
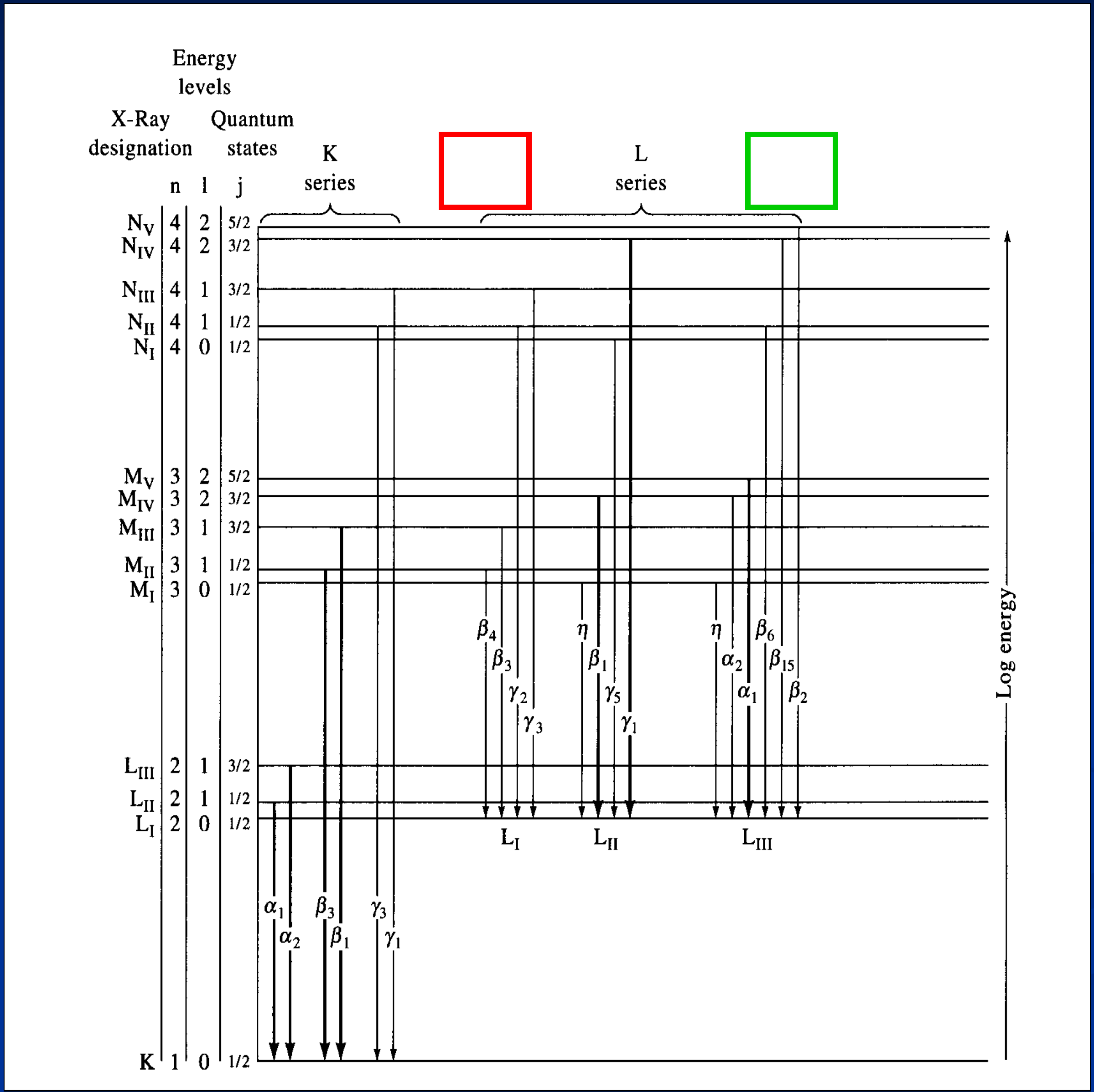


TABLE 12-1 Wavelengths in Angstrom Units of the More Intense Emission Lines for Some Typical Elements

Element	Atomic Number	K Series		L Series	
		α_1	β_1	α_1	β_1
Na	11	11.909	11.617	—	—
K	19	3.742	3.454	—	—
Cr	24	2.290	2.085	21.714	21.323
Rb	37	0.926	0.829	7.318	7.075
Cs	55	0.401	0.355	2.892	2.683
W	74	0.209	0.184	1.476	1.282
U	92	0.126	0.111	0.911	0.720

Electron Transitions → X-Rays



Question: which K series appear at short wavelength between W and Cr?

- Which K series appear at short wavelength between W and Cr?
- Which K series appear at short wavelength between metal W and W oxide (W is a heavy element)?

Radioactive sources are more common

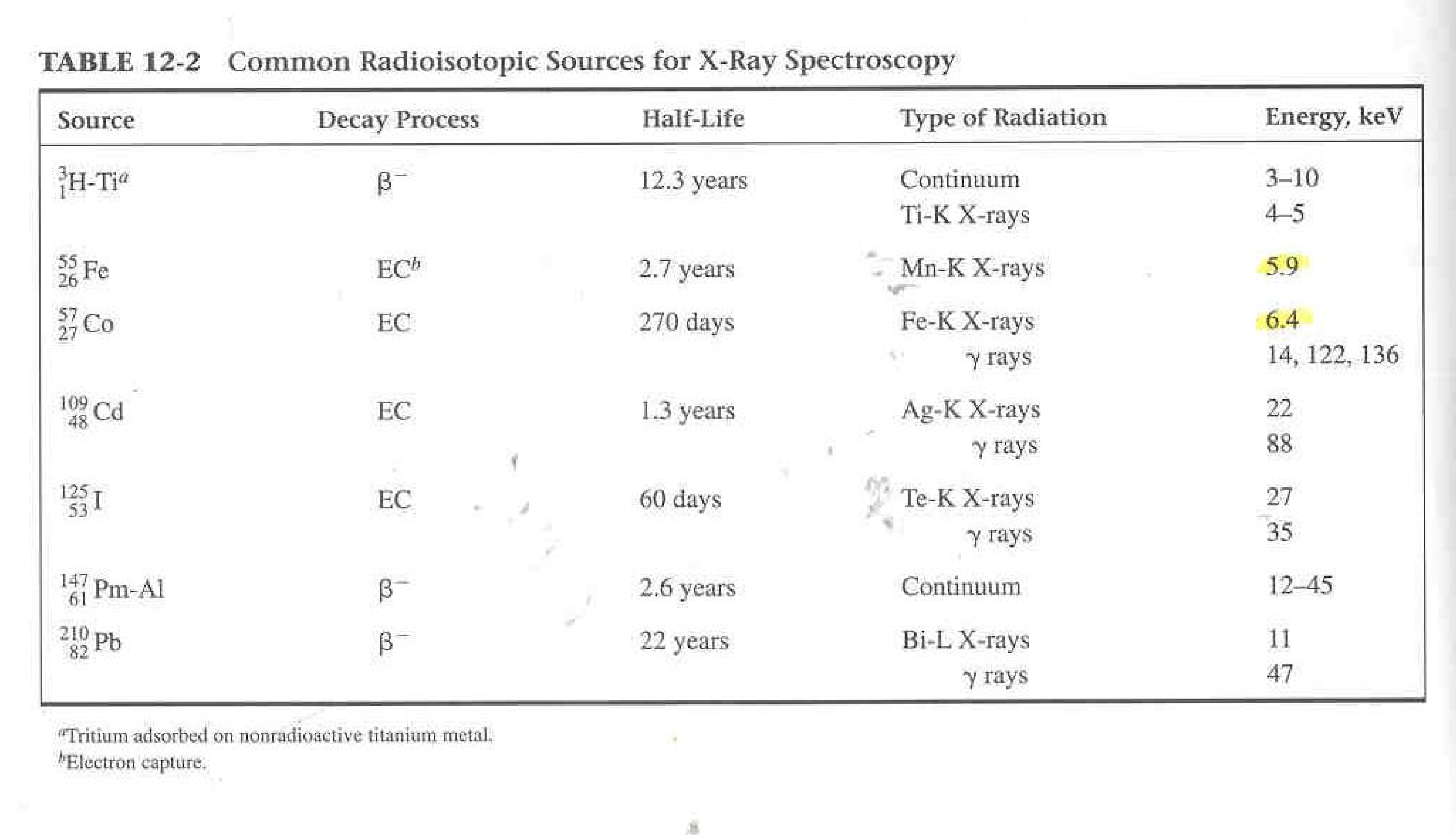


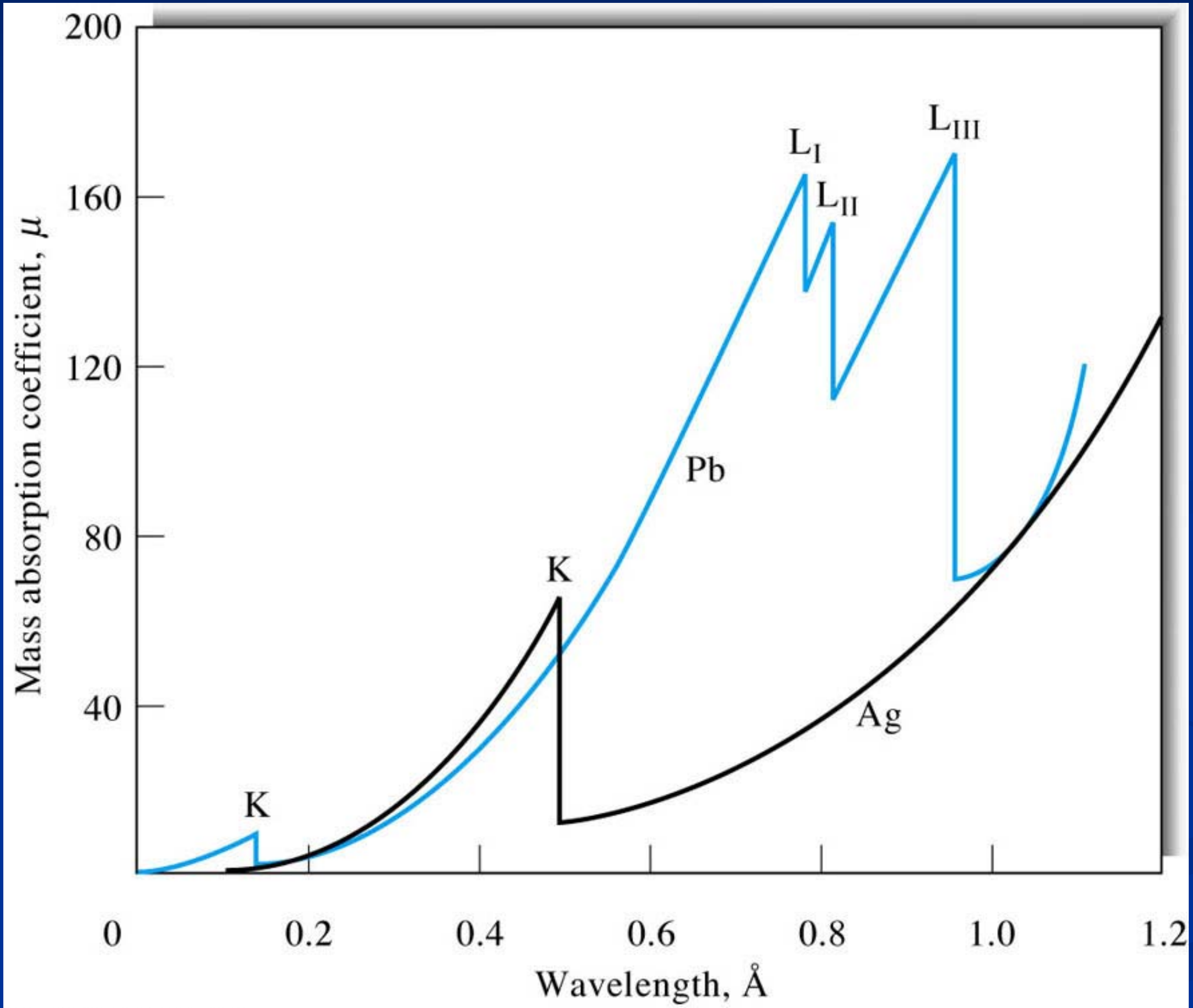
TABLE 12-2 Common Radioisotopic Sources for X-Ray Spectroscopy

Source	Decay Process	Half-Life	Type of Radiation	Energy, keV
$^{3}_{1}$H-Ti[a]	β^-	12.3 years	Continuum	3–10
			Ti-K X-rays	4–5
$^{55}_{26}$Fe	EC[b]	2.7 years	Mn-K X-rays	5.9
$^{57}_{27}$Co	EC	270 days	Fe-K X-rays	6.4
			γ rays	14, 122, 136
$^{109}_{48}$Cd	EC	1.3 years	Ag-K X-rays	22
			γ rays	88
$^{125}_{53}$I	EC	60 days	Te-K X-rays	27
			γ rays	35
$^{147}_{61}$Pm-Al	β^-	2.6 years	Continuum	12–45
$^{210}_{82}$Pb	β^-	22 years	Bi-L X-rays	11
			γ rays	47

[a] Tritium adsorbed on nonradioactive titanium metal.

[b] Electron capture.

X-ray absorption



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$\text{Ln } P_0/P = \mu X$

μ is the linear absorption coefficient is characteristic of the Element and # of atoms in the path of the beam.

X is sample thickness

$\text{Ln } P_0/P = \mu_M \eta X$

η is density of the sample

μ_M is mass absorption coefficient

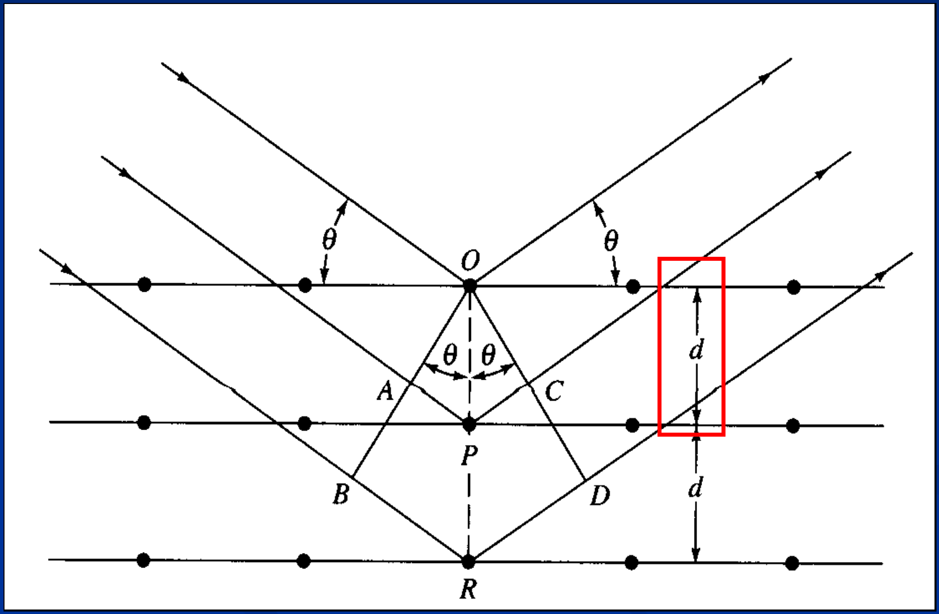
Bragg's Law of Diffraction
light scattering by lattice of atoms!

$$AP + PC = n\lambda$$

$$AP = PC = d\sin\theta$$

$$n\lambda = 2d\sin\theta$$

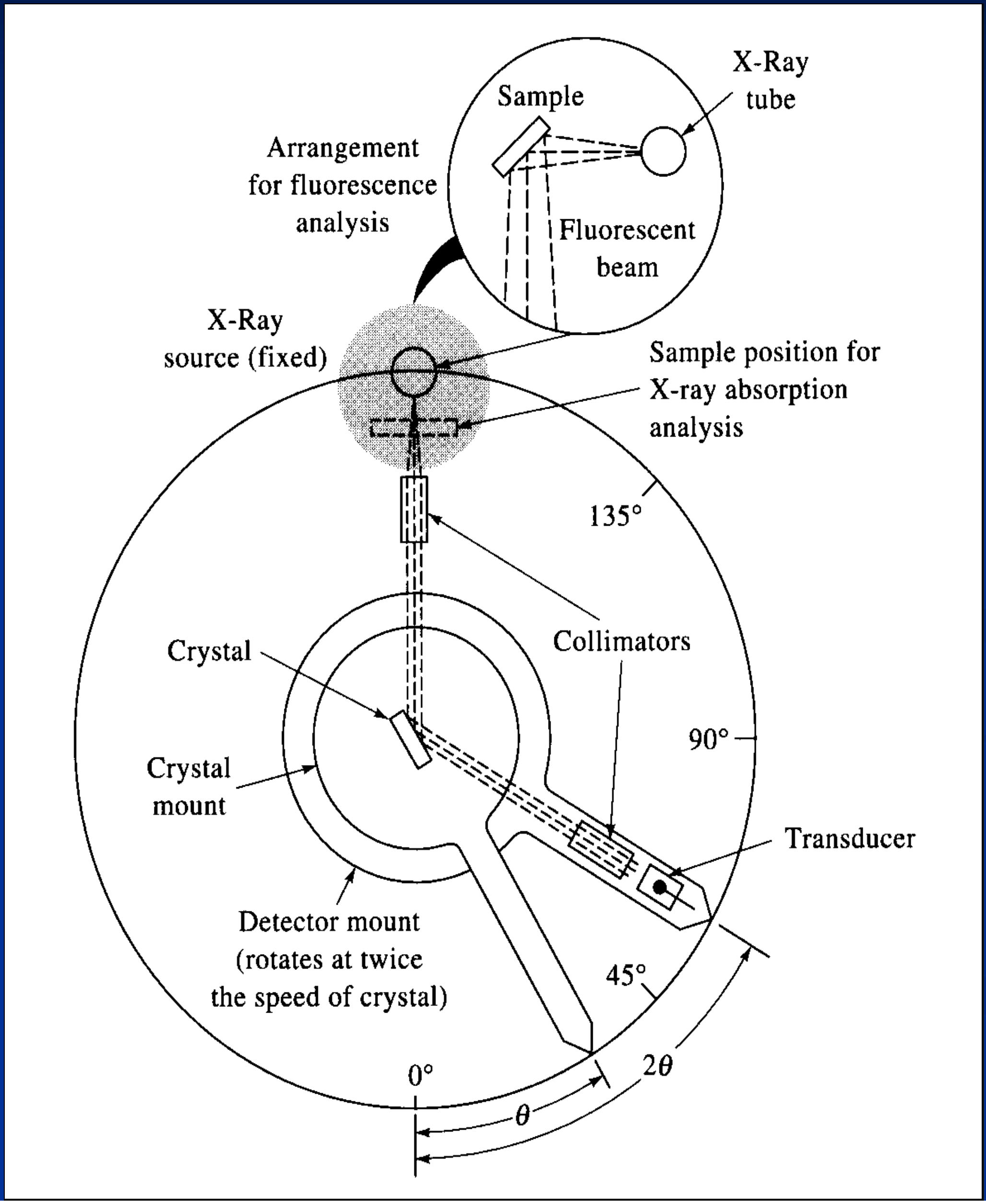
$$\sin\theta = \frac{n\lambda}{2d}$$



Constructive interference only at angles proportional to λ and d!

If λ is known and θ can be measured then you can calculate d!
If d is known and θ can be measured then you can calculate λ!

X-Ray Monochromator (diffractometer?)



$$\sin\theta = \frac{n\lambda}{2d}$$

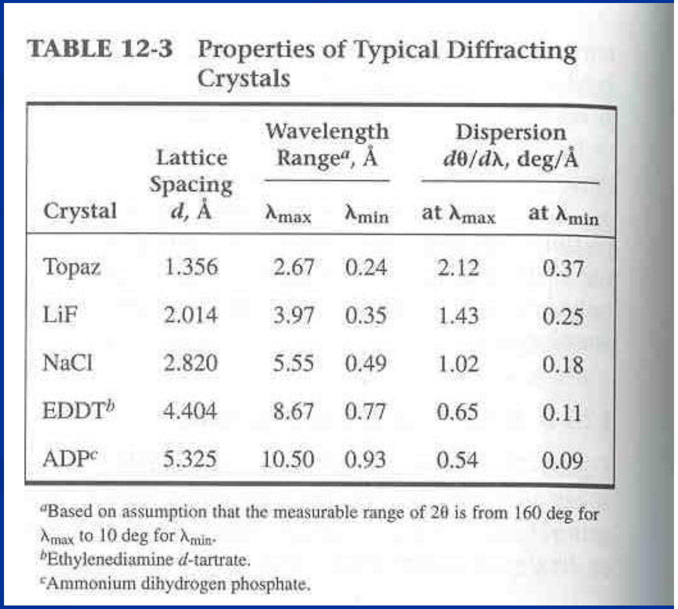


TABLE 12-3 Properties of Typical Diffracting Crystals

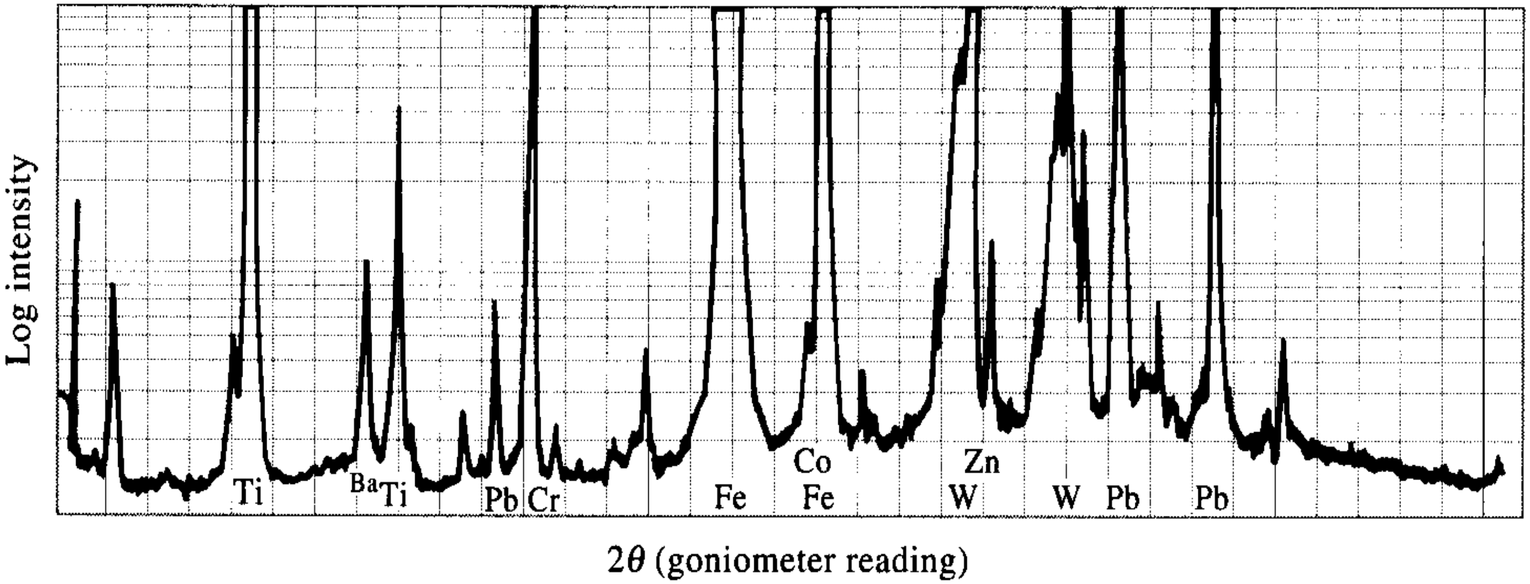
Crystal	Lattice Spacing d, Å	Wavelength Range[a], Å λ_{max}	Wavelength Range[a], Å λ_{min}	Dispersion $d\theta/d\lambda$, deg/Å at λ_{max}	Dispersion $d\theta/d\lambda$, deg/Å at λ_{min}
Topaz	1.356	2.67	0.24	2.12	0.37
LiF	2.014	3.97	0.35	1.43	0.25
NaCl	2.820	5.55	0.49	1.02	0.18
EDDT[b]	4.404	8.67	0.77	0.65	0.11
ADP[c]	5.325	10.50	0.93	0.54	0.09

[a] Based on assumption that the measurable range of 2θ is from 160 deg for λ_{max} to 10 deg for λ_{min}.

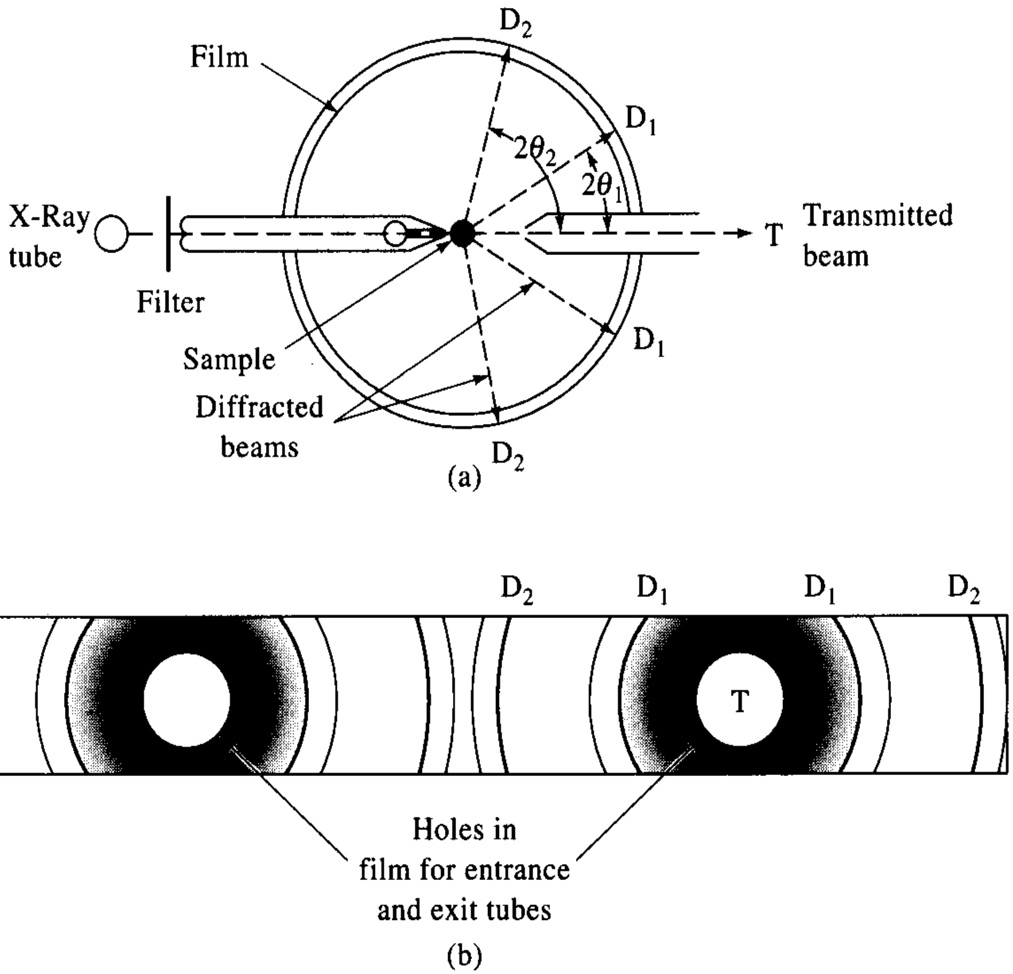
[b] Ethylenediamine *d*-tartrate.

[c] Ammonium dihydrogen phosphate.

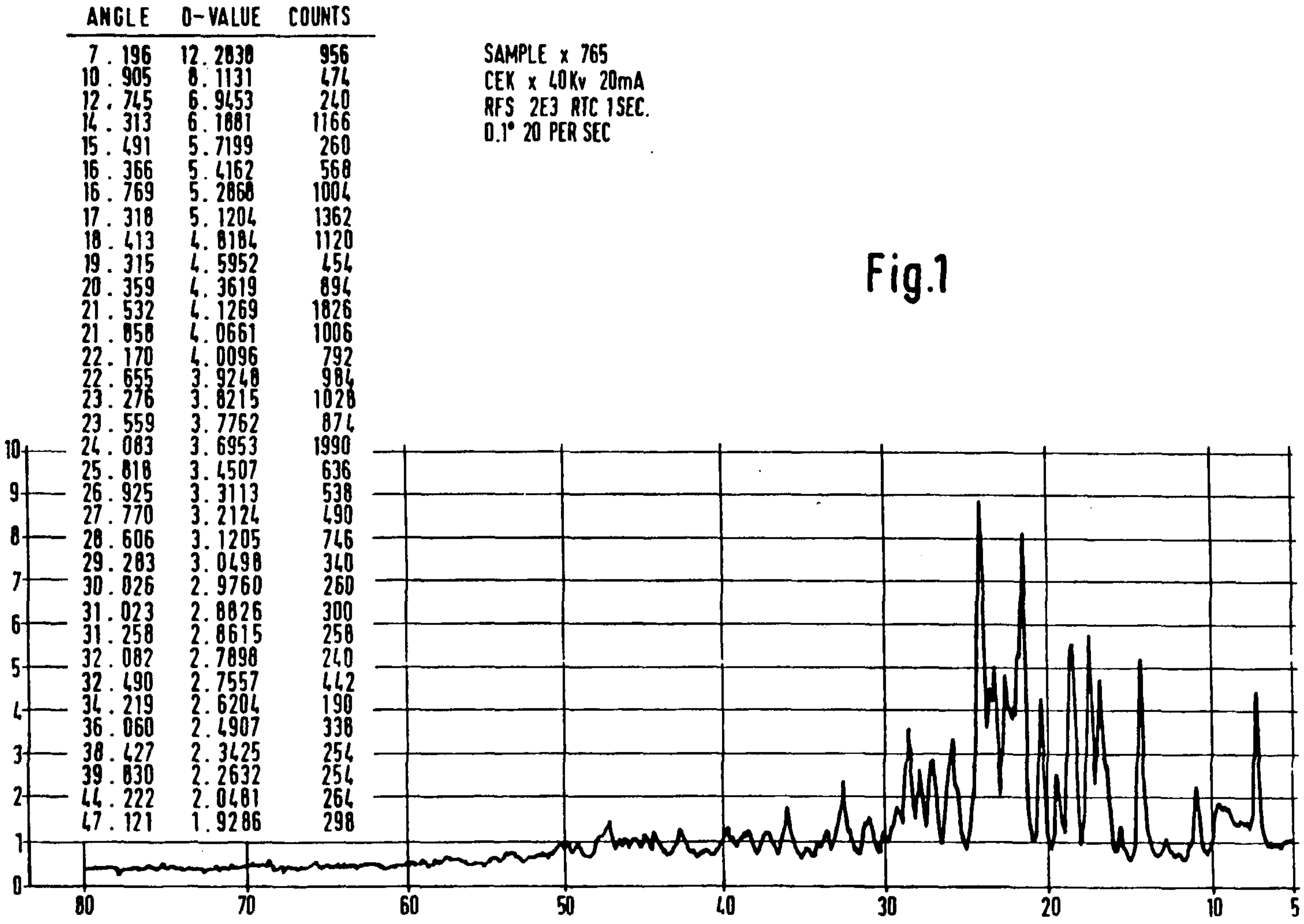
X-Ray Diffraction Spectrum



Debye-Scherrer Powder Diffractometer (Camera)



X-Ray Spectra of Polymorph 1



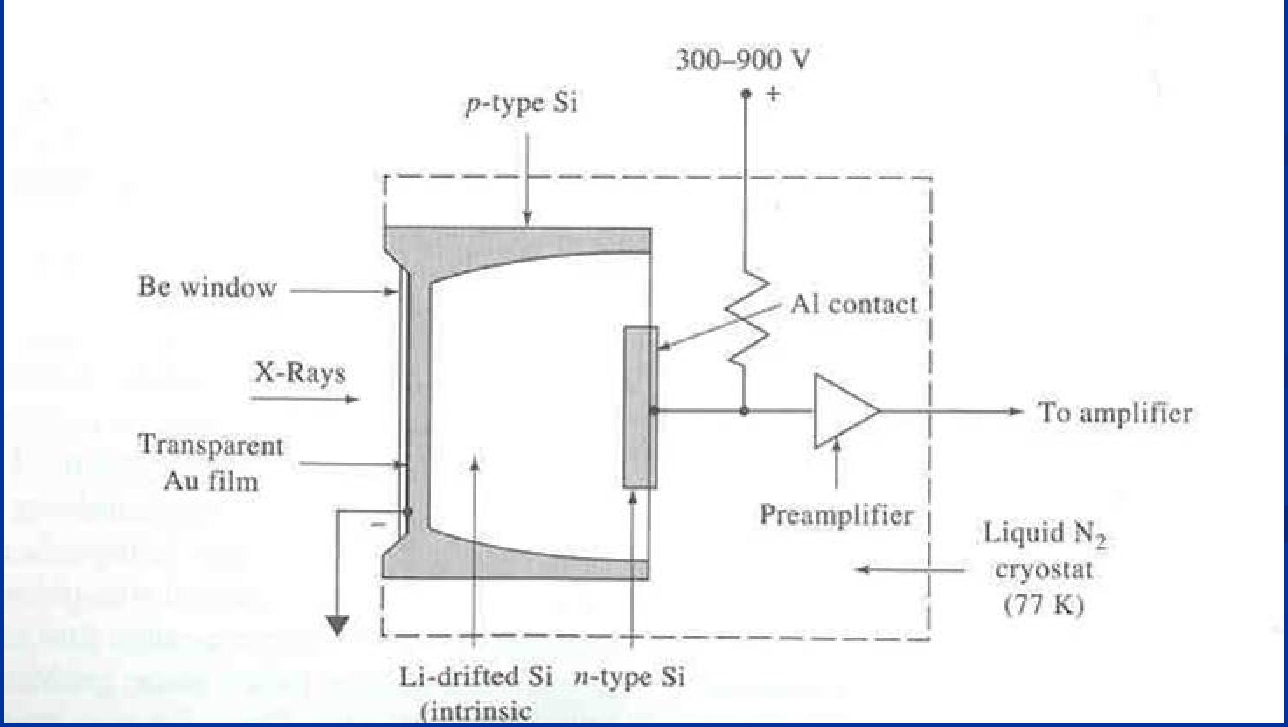
ANGLE	D-VALUE	COUNTS
7.196	12.2838	956
10.905	8.1131	474
12,745	6.9453	240
14.313	6.1881	1166
15.491	5.7199	260
16.366	5.4162	568
16.769	5.2868	1004
17.318	5.1204	1362
18.413	4.8184	1120
19.315	4.5952	454
20.359	4.3619	894
21.532	4.1269	1826
21.858	4.0661	1006
22.170	4.0096	792
22.655	3.9248	984
23.276	3.8215	1028
23.559	3.7762	874
24.083	3.6953	1990
25.818	3.4507	636
26.925	3.3113	538
27.770	3.2124	490
28.606	3.1205	746
29.283	3.0498	340
30.026	2.9760	260
31.023	2.8826	300
31.258	2.8615	258
32.082	2.7898	240
32.490	2.7557	442
34.219	2.6204	190
36.060	2.4907	338
38.427	2.3425	254
39.830	2.2632	254
44.222	2.0481	264
47.121	1.9286	298

SAMPLE x 765
CEK x 40Kv 20mA
RFS 2E3 RTC 1SEC.
0.1° 2θ PER SEC

Fig.1

X-Ray detectors

- Geiger tube: formation of ions and electrons from an inert gas kept at 1200-1600V
- Phosphors (Scintillation counters): fluorescence of ZnS when hit by a particle
- Semicoductor detectors based on a modified diode



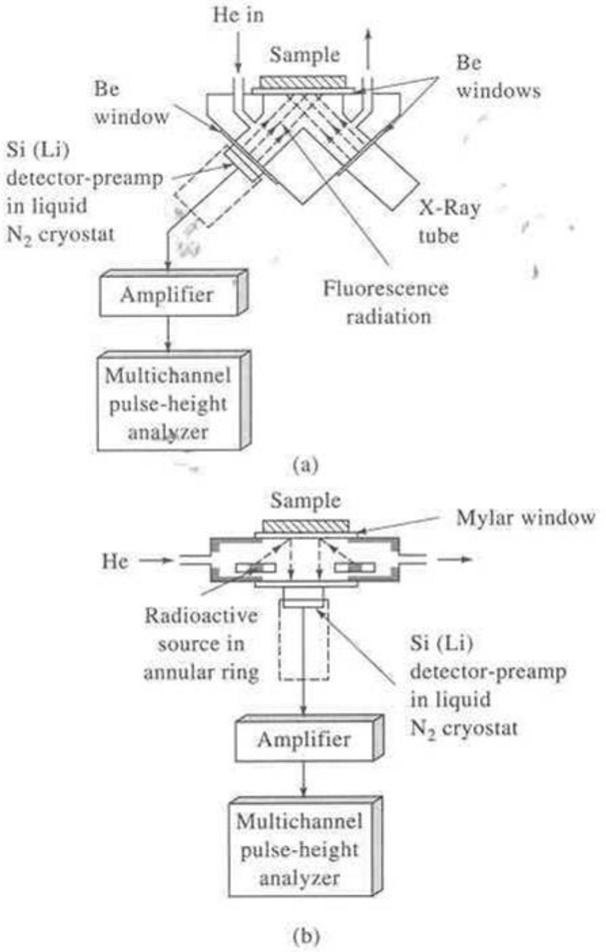


Figure 12-14 Energy dispersive X-ray fluorescence spectrometer. Excitation by X-rays from (a) an X-ray tube and (b) a radioactive substance.

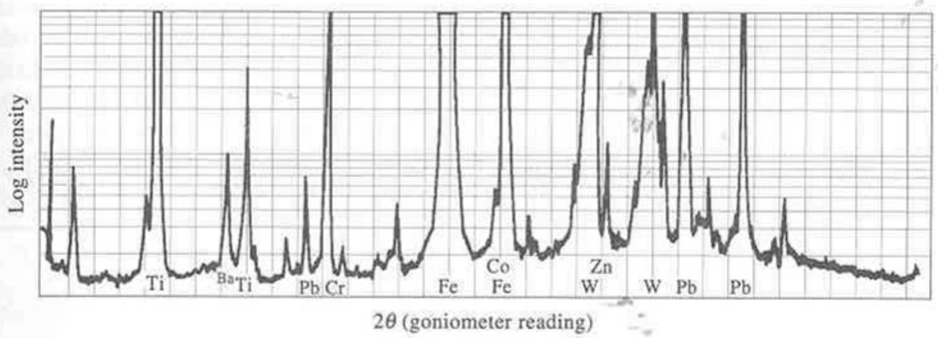


Figure 12-16 X-Ray fluorescence spectrum for a genuine bank note recorded with a wavelength dispersive spectrometer. *(Taken from H. A. Liebhafsky, H. G. Pfeiffer, E. H. Winslow, and P. D. Zeman,* X-Ray Absorption and Emission in Analytical Chemistry, *p. 163. New York: Wiley, 1960. Reprinted by permission of John Wiley & Sons, Inc.)*

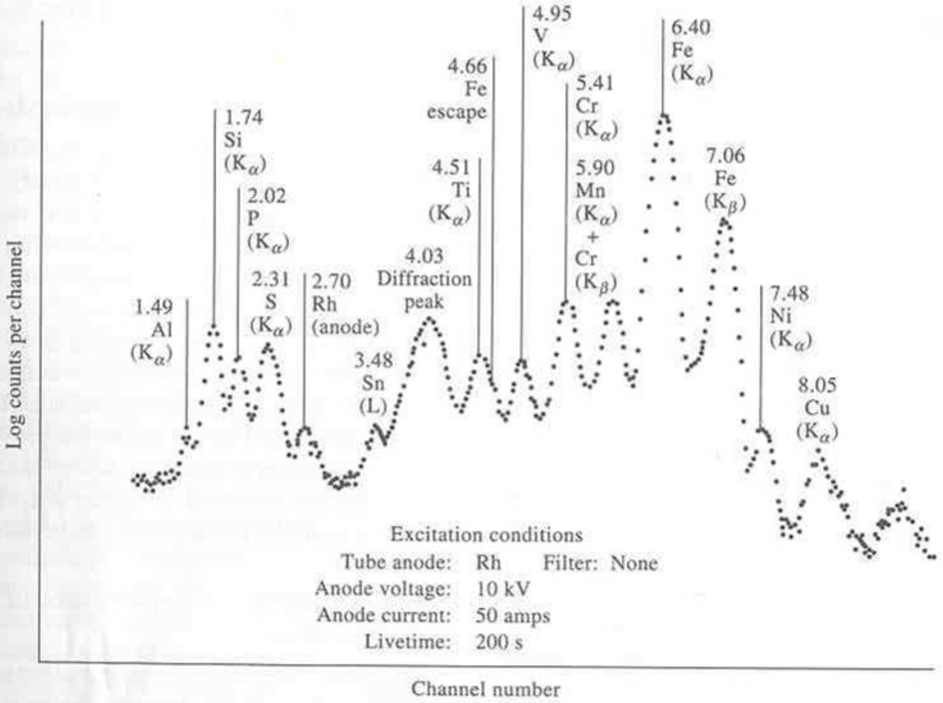


Figure 12-17 Spectrum of an iron sample obtained with an energy dispersive instrument with an Rh anode X-ray tube source. The numbers above the peaks are energies in keV. *(Reprinted with permission from J. A. Cooper, Amer. Lab.,* **1976**, *8(11), 44. Copyright 1976 by International Scientific Communications, Inc.)*