X-Ray Analysis

X-rays

- Originally discovered by Wilhelm Roetgen (1845-1923) in the nineteenth century, X-rays have become one of the most useful applications of spectroscopy in both science and medicine.

X-Ray Spectroscopy

- Emission
- Absorption
- Diffraction

X-ray spectroscopy is a common analytical technique with a broad range of applications, particularly in determining crystal structure and elemental analysis of solid samples.

Diffraction

wavelengths

0.1 => 25A

Diffraction

- Powder Pattern
  - qualitative analysis => ASTM database
  - isostructural

X-ray for Analytical Purposes

X-ray for Analytical Purposes generated by:

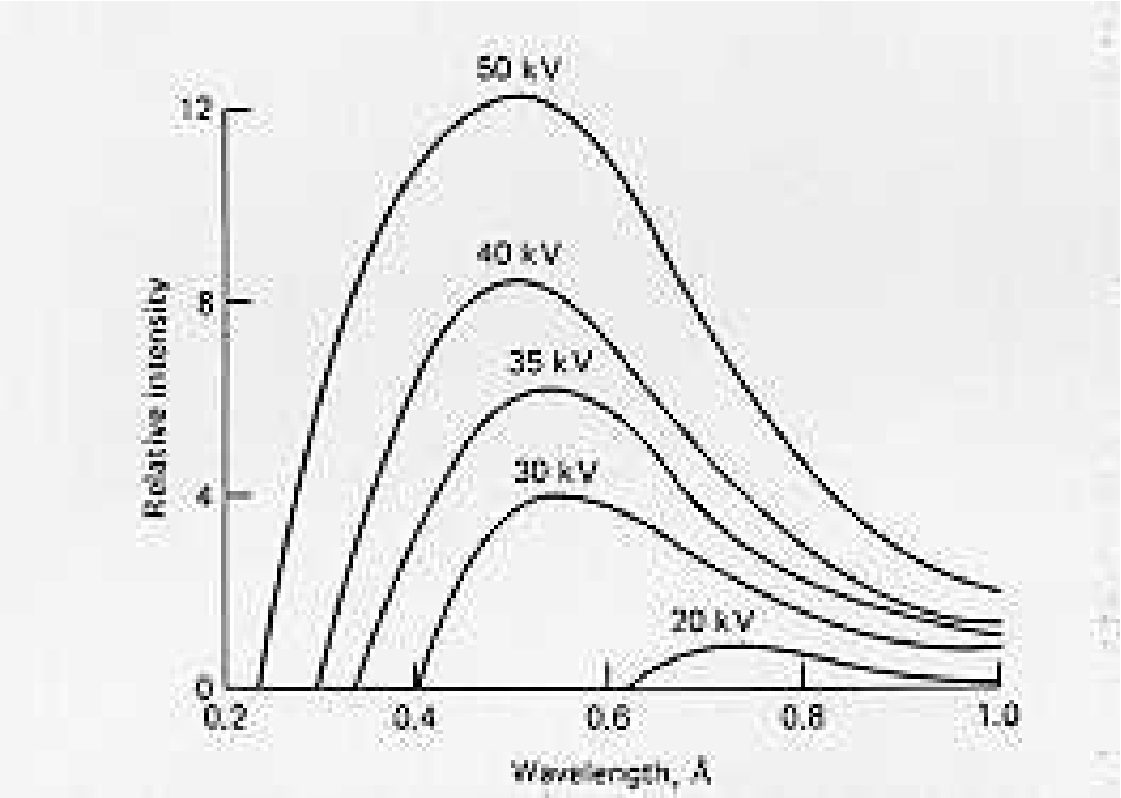
1. **bombardment of metal target by a beam of high energy electrons**
2. **exposure of a substance to a primary beam of X-rays in order to generate a secondary beam of fluorencent X-rays**
3. **radioactive source whose decay process results in X-ray emission**

Production of X-rays

- The electromagnetic radiation resulting from inner orbital electron transitions or deceleration of high-energy electrons is referred to as X-rays.
- X-ray tubes
- Radio active materials
- Synchrotron source

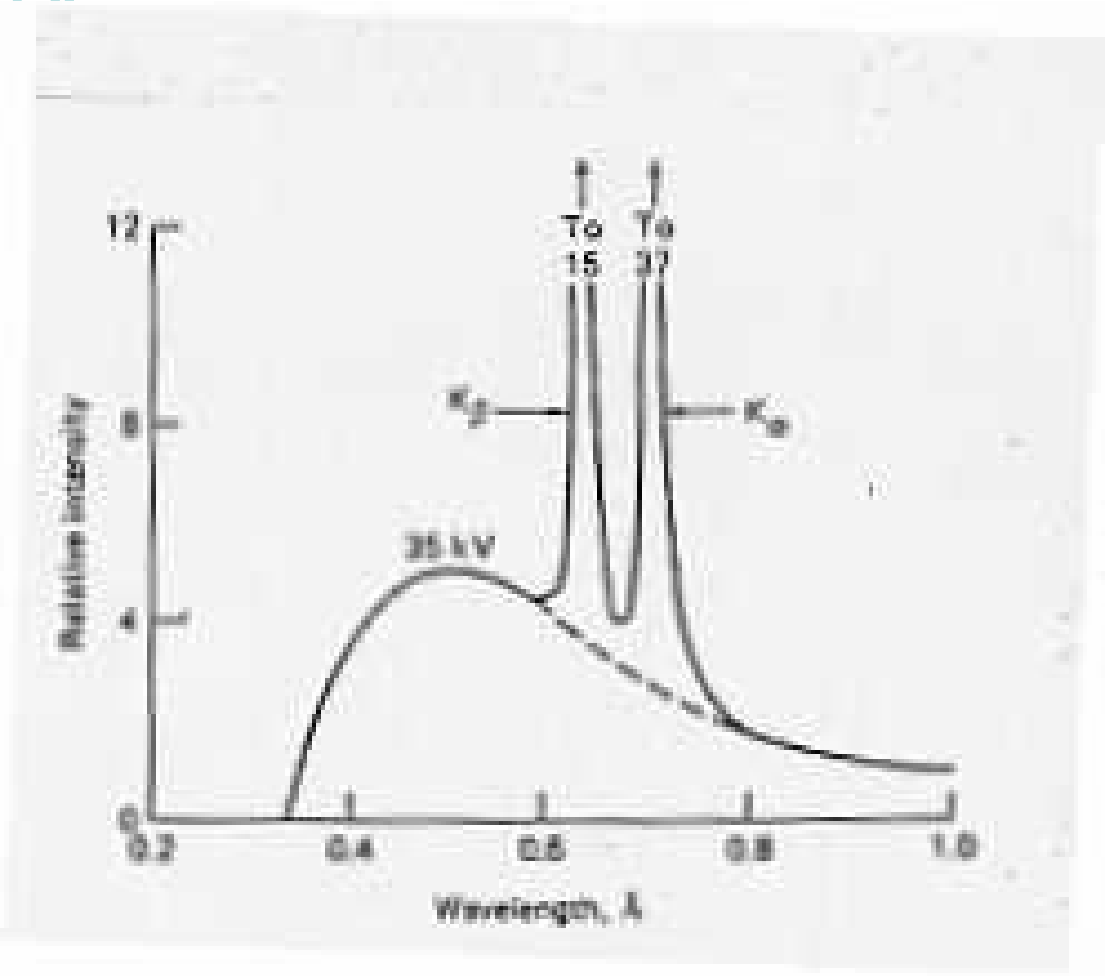
X-ray Tubes for Analytical Purposes

"Distribution of continuous radiation from an X-ray tube with a tungsten target. The numbers above the curves indicate the accelerating voltages."



X-ray for Analytical Purposes

"Line spectrum for a tube with a molybdenum target"



X-ray for Analytical Purposes

Short wavelength limit of continuum
function of accelerating voltage, not
metal

$\lambda_o = 12{,}398/V$
where V => volts

X-ray for Analytical Purposes

2 series of lines for all metals z > 23
K & L series

1 series of lines for all metals z < 23
K series

line spectrum: min accelerating V to produce increases with Z

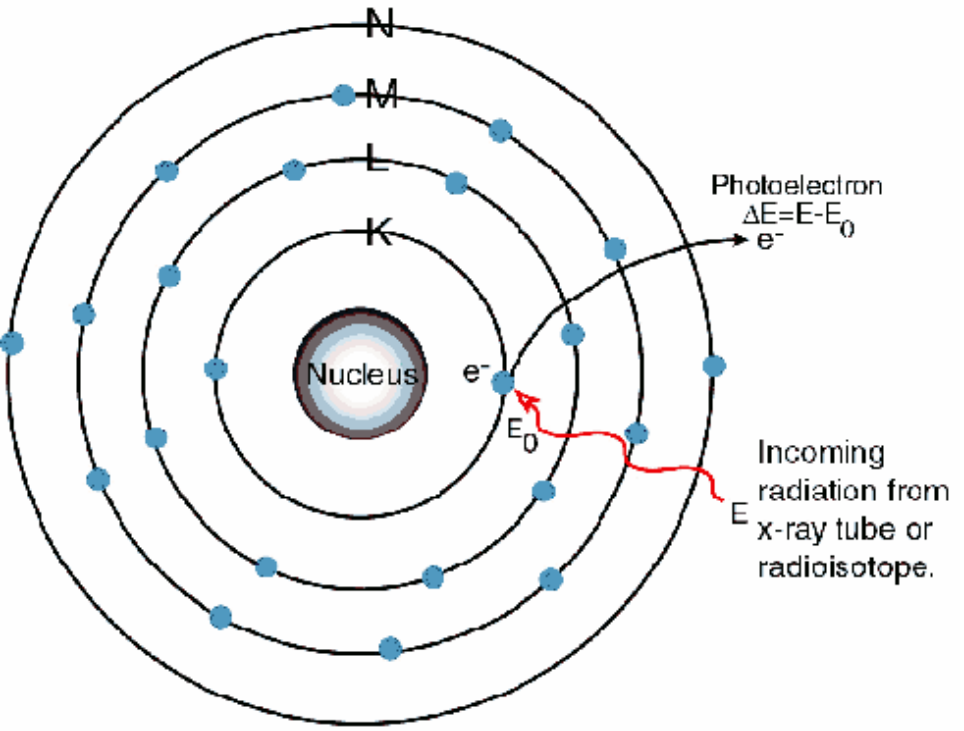
X-ray Fluorescence Spectroscopy-

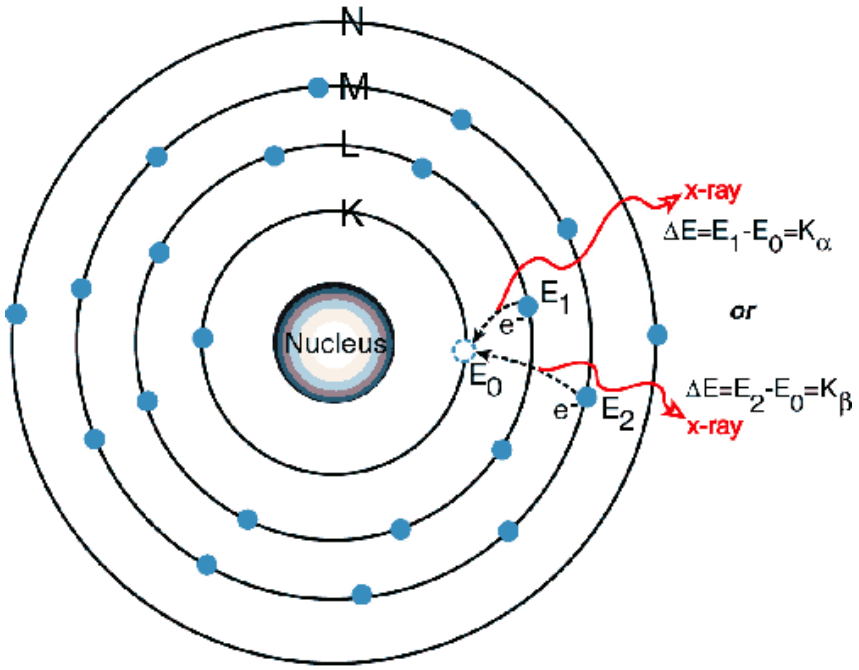
- X-ray fluorescence is a spectroscopic method that is commonly used for solids in which secondary x-ray emission is generated by excitation of a sample with x-rays. The x-rays eject inner-shell electrons. Outer-shell electrons take their place and emit photons in the process. The wavelength of the photons depends on the energy difference between the outer-shell and inner-shell electron orbitals. The amount of x-ray fluorescence is very sample dependent and quatitative analysis requires calibration with standards that are similar to the sample matrix.

XRF Instrumentation

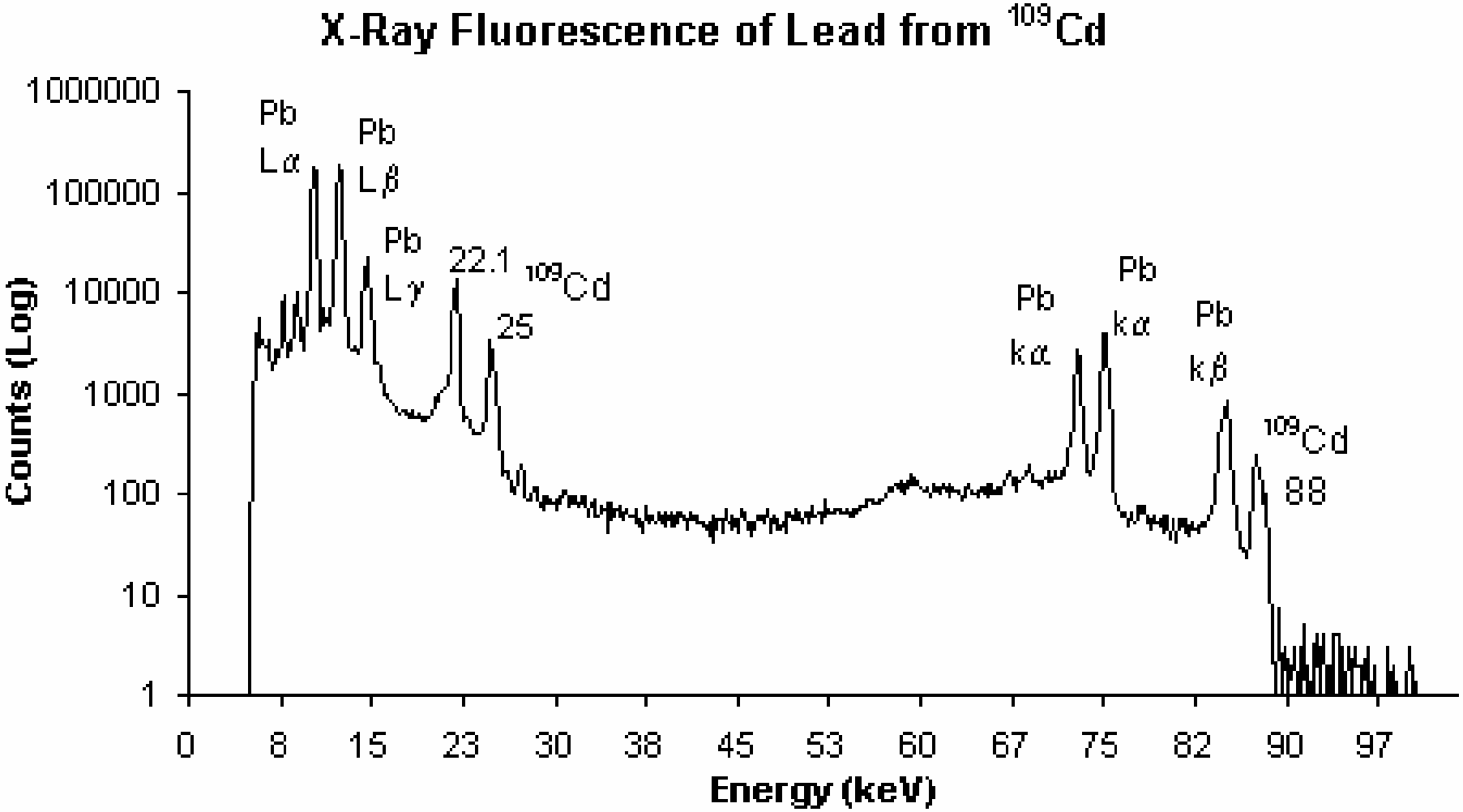
- Solid samples are usually powdered and pressed into a wafer or fused in a borate glass. The sample is then placed in the sample chamber of an XRF spectrometer, and irradiated with a primary X-ray beam. The X-ray fluorescence is recorded with either an X-ray detector after wavelength dispersion or with an energy-dispersive detector.

X-ray Fluorescence Spectroscopy- XRF

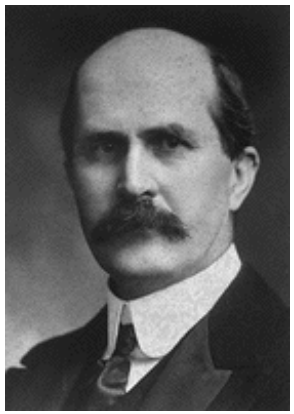




XRF Spectrum



History of Diffraction

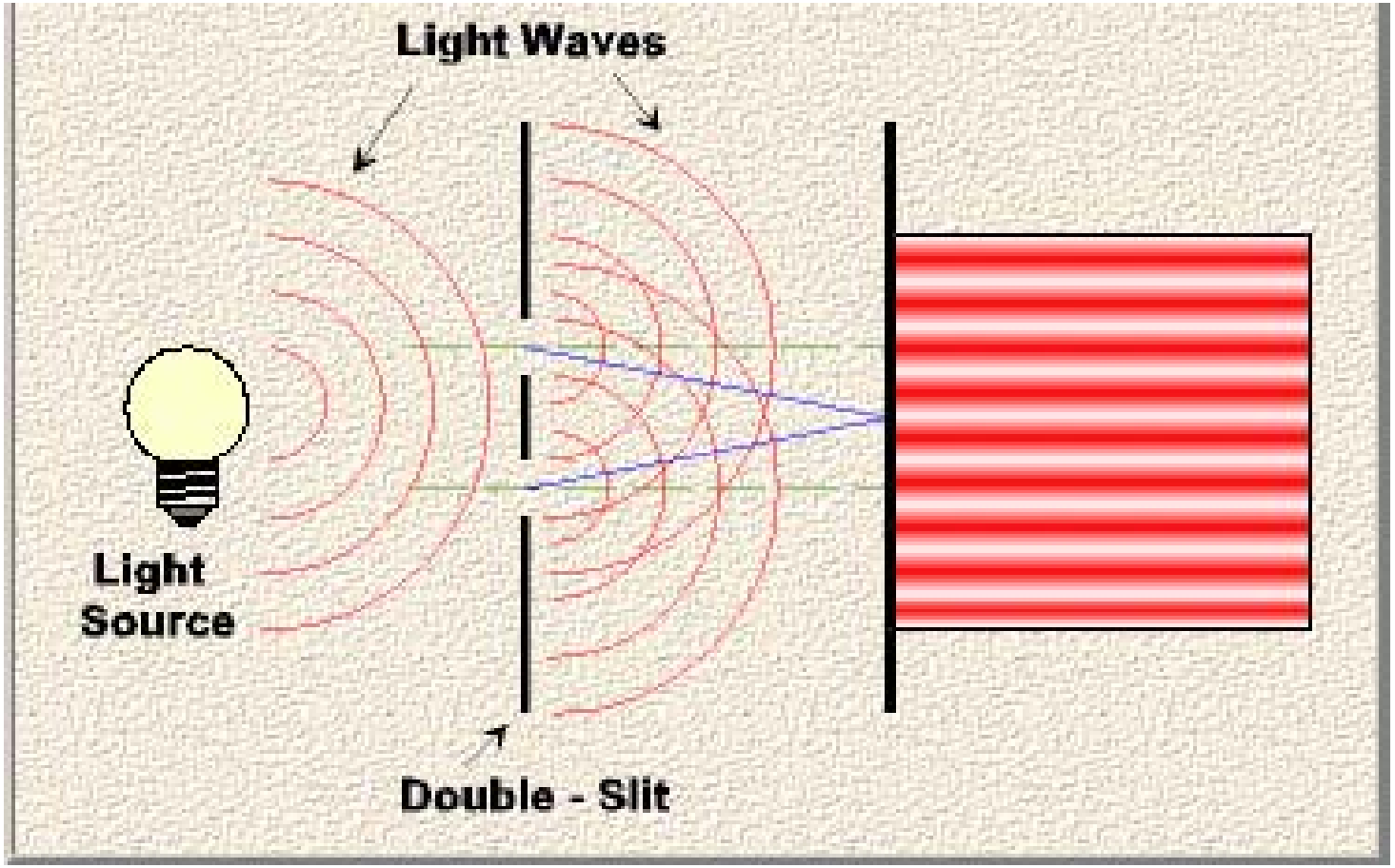


William Bragg and his son Lawrence

X-ray Diffraction

- William Bragg and his son Lawrence in 1913-1914 founded the analysis of crystal structure by means of X-rays. If the fundamental discovery of the wave aspect of X-rays, as evidenced by their diffraction in crystals, was due to von Laue and his collaborators, it is equally true that the use of X-rays as an instrument for the systematic revelation of the way in which crystals are built was entirely due to the Braggs.

How Diffraction Works



Diffraction of X-Rays

Bragg's Law

when AP + PC = $n\lambda$ scattered radiation will be "in phase"

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

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

Diffraction of X-Rays

Bragg's Law "Diffraction of X-rays by a crystal."

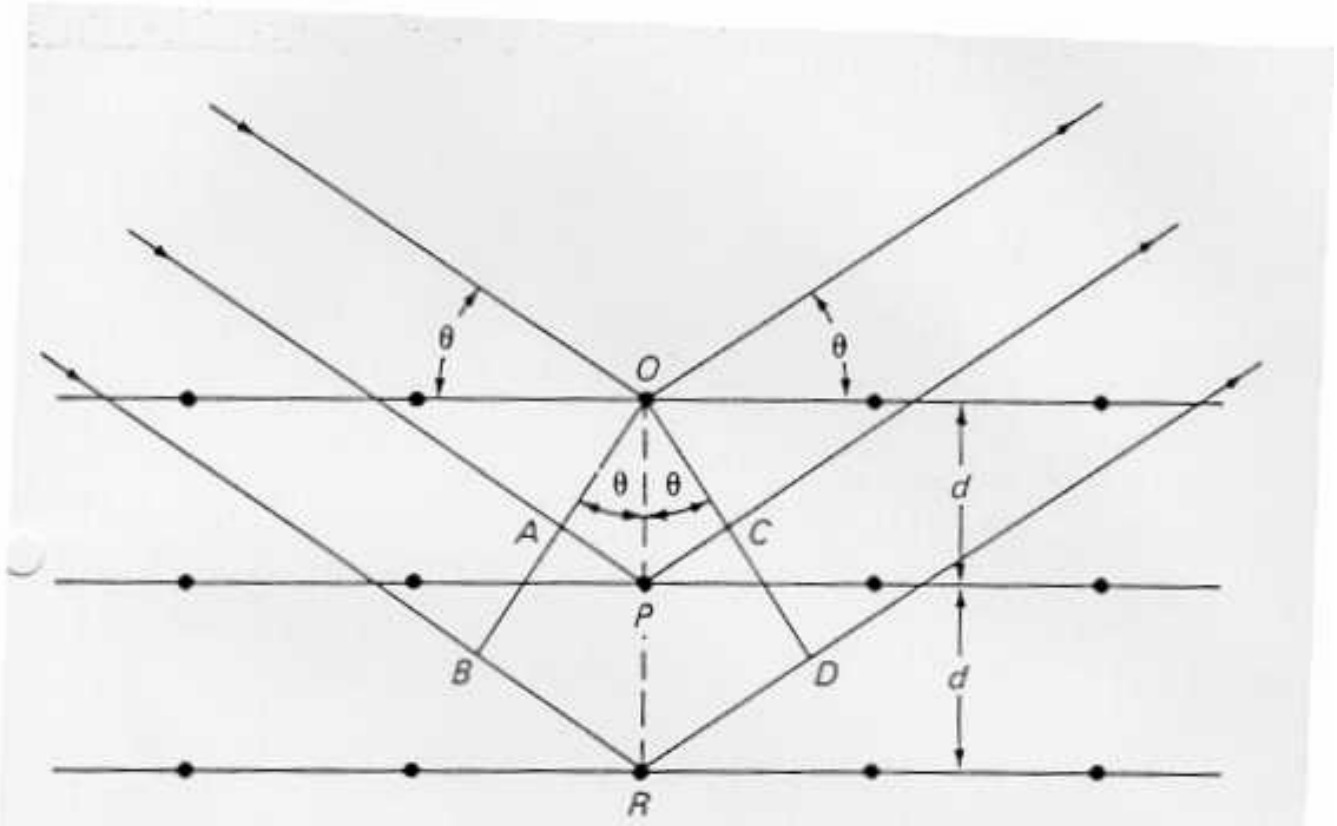


FIGURE 15–6 Diffraction of X-rays by a crystal.

Instrument Components

5 basic components

1. source
2. device for restricting wavelength range
3. sample holder
4. radiation detector
5. signal processor and readout

Sources

"Schematic of an X-ray tube."

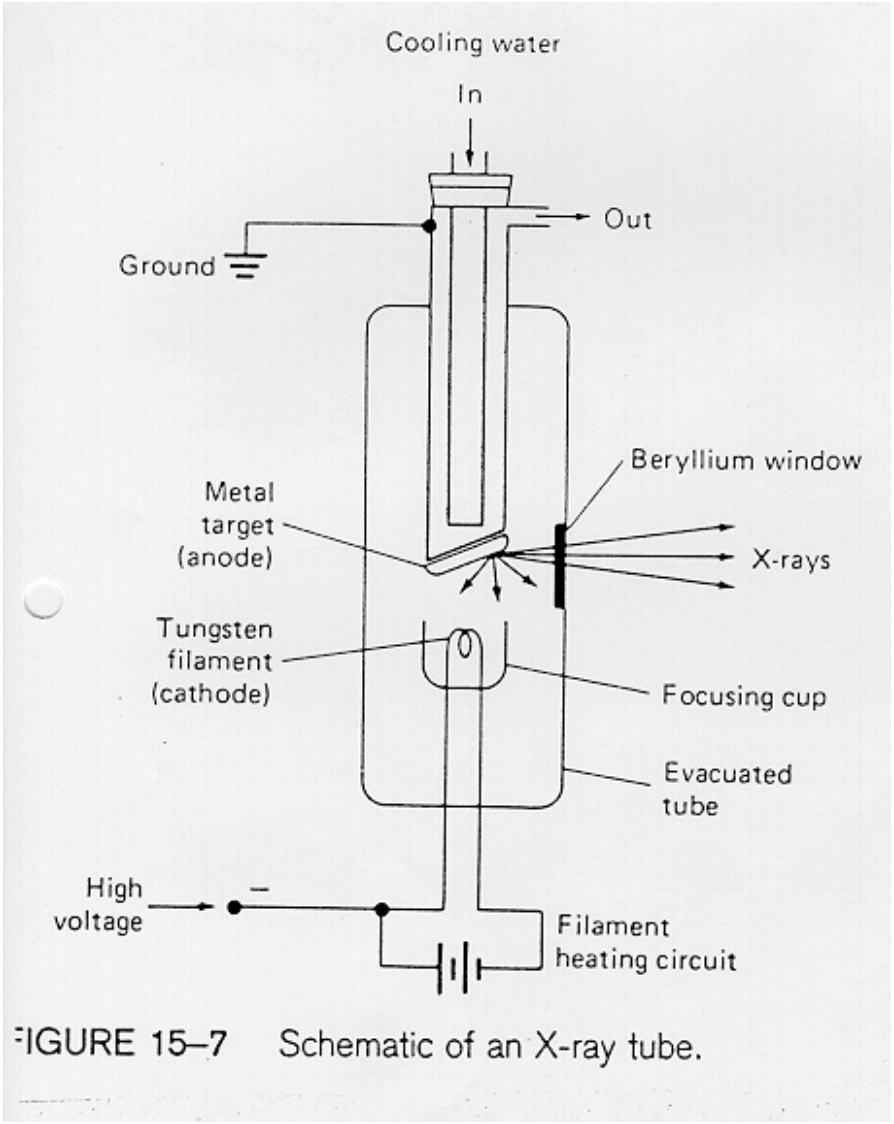


FIGURE 15–7 Schematic of an X-ray tube.

“Monochromator”

Device for restricting wavelength range

- **filter => thin metal, element to the left in the Periodic Table**
- **collimators & slits**

X-ray Monochromator

"An X-ray monochromator and detector. Note the angle of the detector with respect to the beam (2Θ) is twice that of the crystal face. For absorption analysis, the source is an X-ray tube, and the sample is located in the beam as shown. For emission work, the sample becomes a fluorescent source of X-rays as shown in the inset."

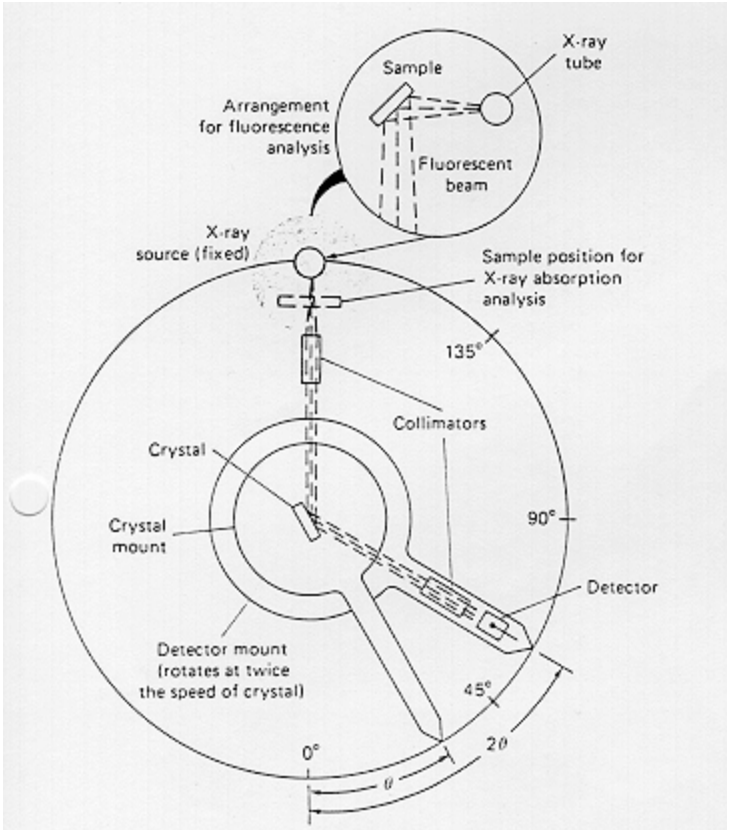
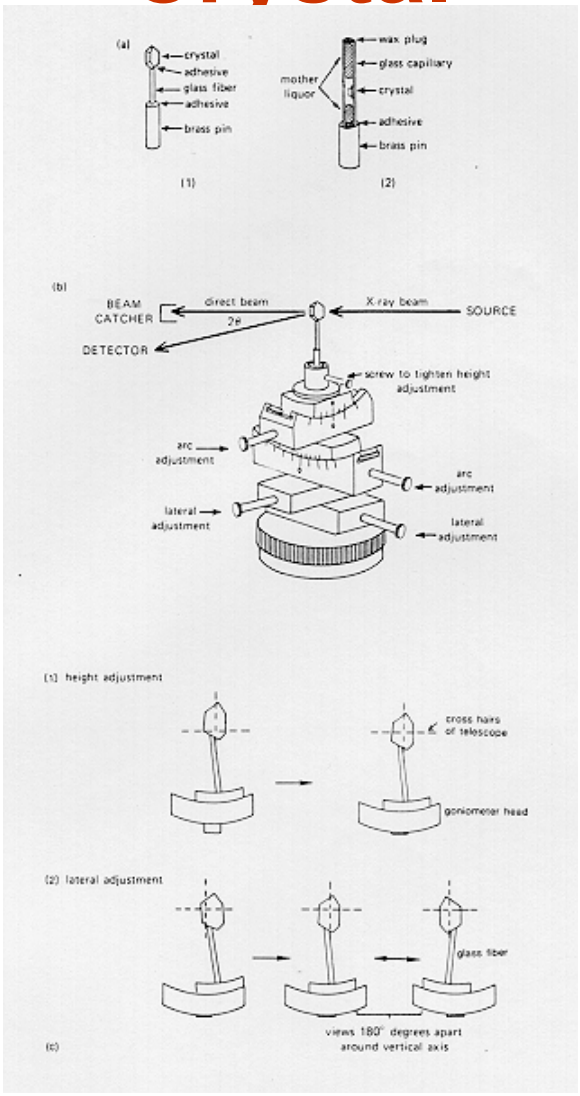


FIGURE 15–9 An X-ray monochromator and detector. Note that the angle of the detector with respect to the beam (2θ) is twice that of the crystal face. For absorption analysis, the source is an X-ray tube and the sample is located in the beam as shown. For emission work, the sample becomes a fluorescent source of X-rays as shown in the insert.

Sample Holder

- as crystal moves θ, detector moves 2θ
- goniometer head for single crystal
- cup for powder sample

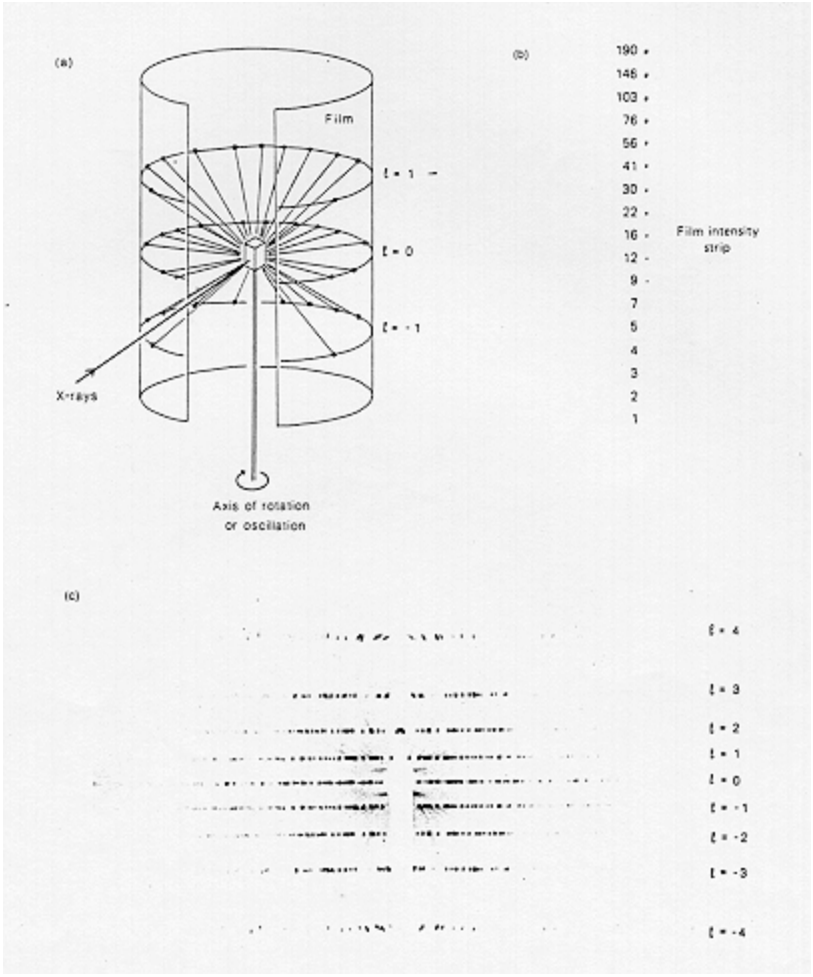
Goniometer Head for Single Crystal



Radiation Detector

- **X-ray film**
  - **now used mainly for unit cell dimension and space group determinations**
    - Precession camera
    - Weissenburg

Weissenburg



Weissenburg

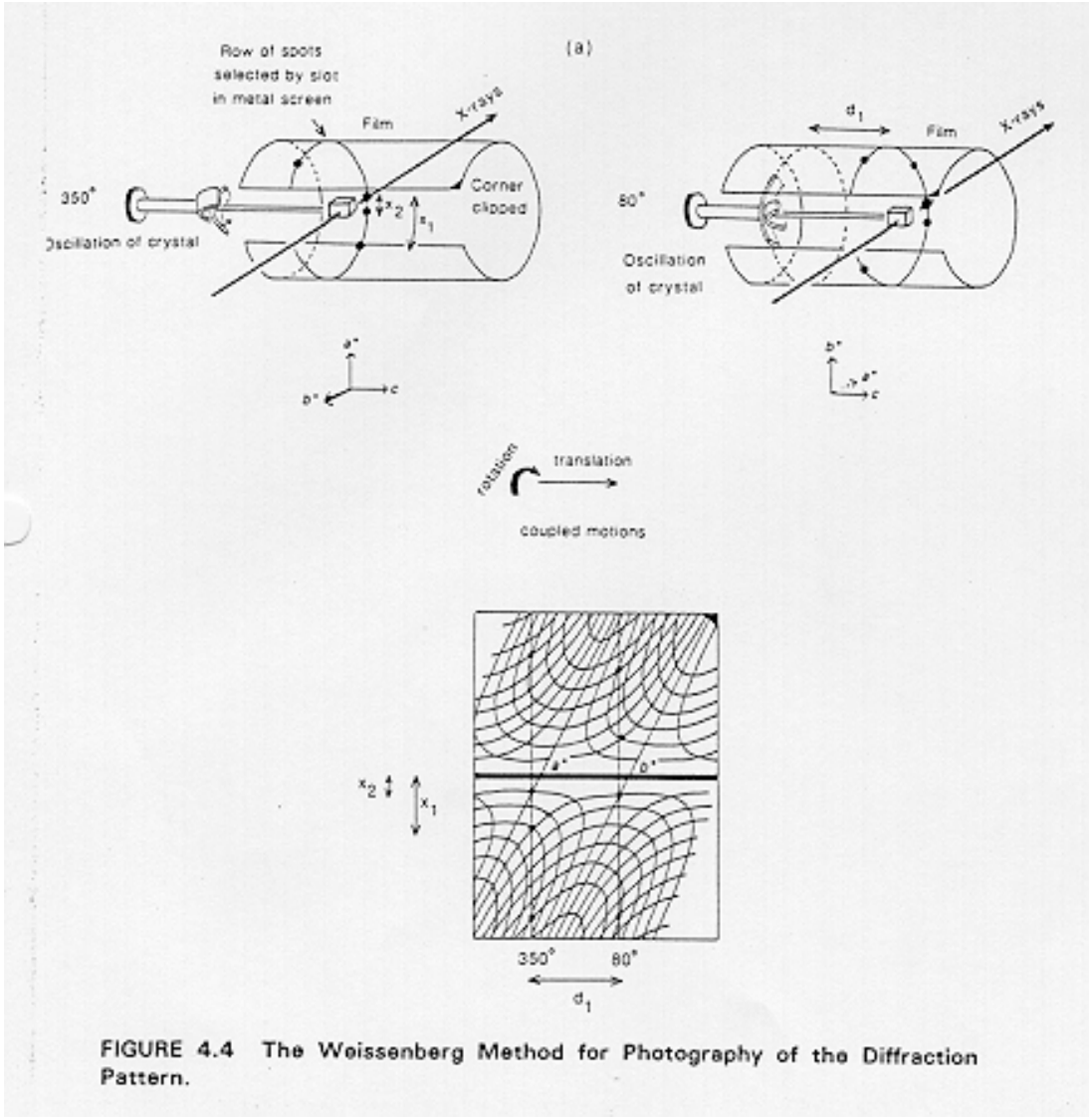
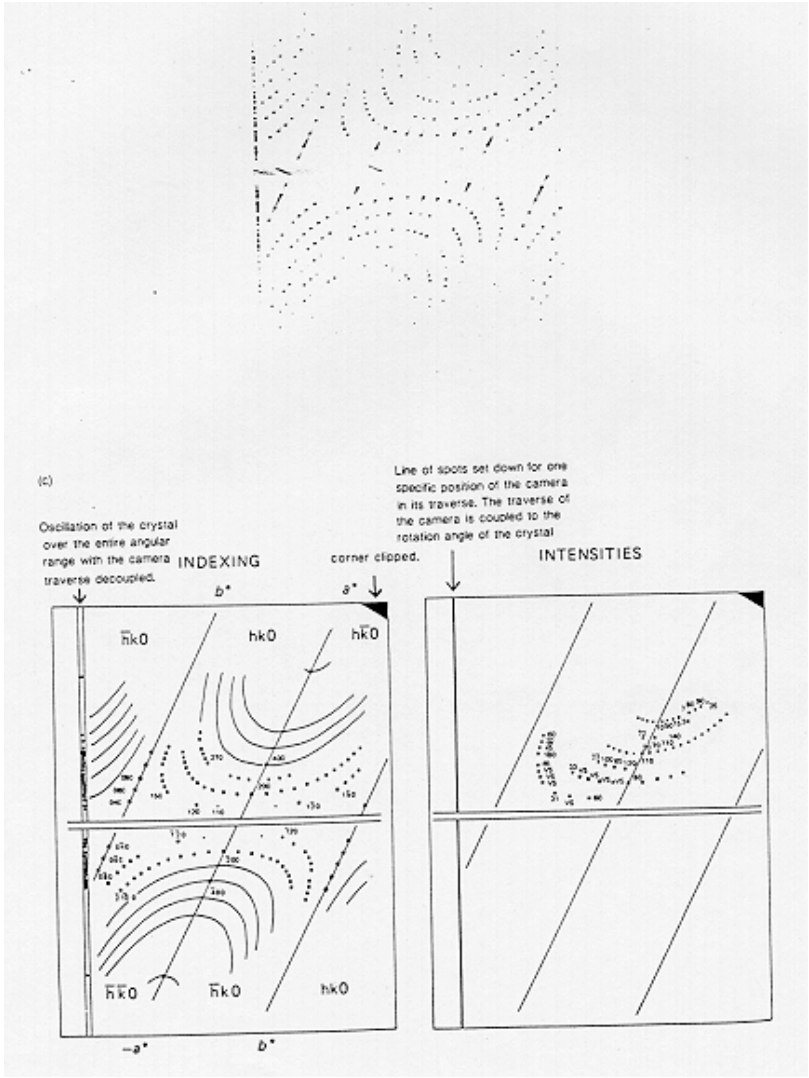


FIGURE 4.4 The Weissenberg Method for Photography of the Diffraction Pattern.

Weissenburg



Radiation Detector

Electrical Detectors

1. gas filled detectors
   - gas is ionized by X-rays, conducts
2. scintillation counters
   - X-rays strike phosphrs which give off light
     - originally => counted flasks
     - now => photomultiplier tube used to detect light

Radiation Detector

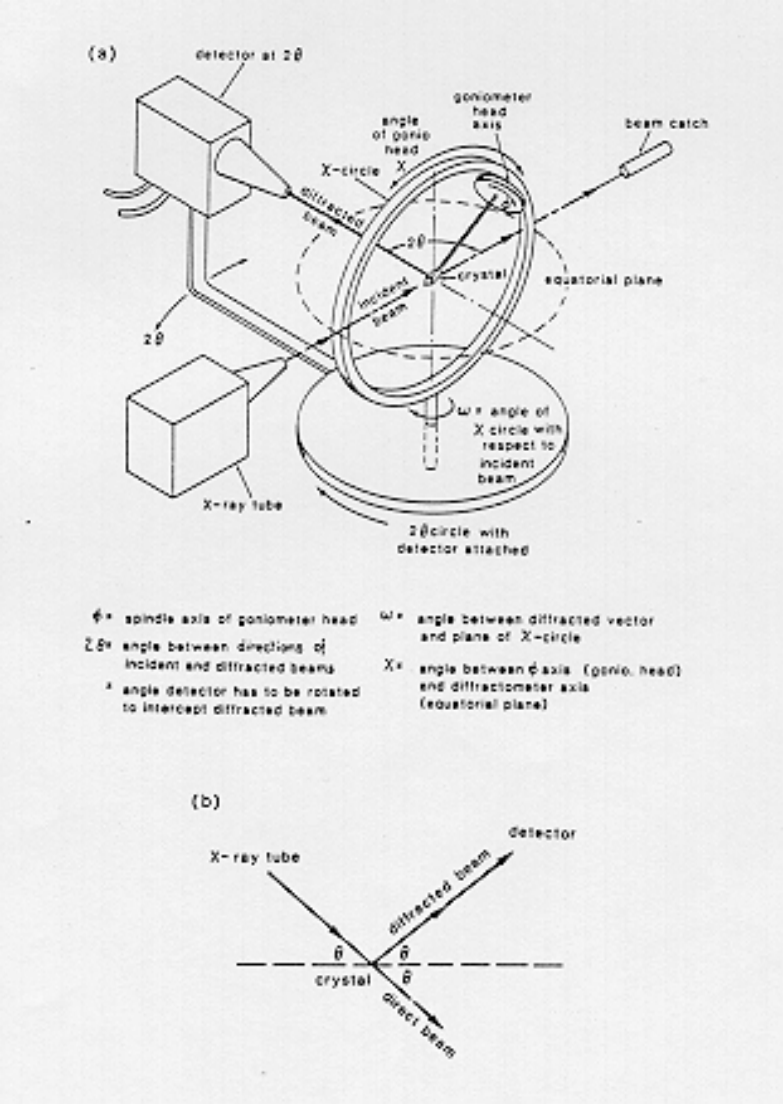
Electrical Detectors

3. semiconductor detectors
   - lithium drifted silicon detectors
   - charge-coupled device (CCD)

Signal processor & Readout devices

- high speed computer

Automatic Diffractometer



X-ray Diffraction

Information provided by X-ray diffraction:

1. Declare that structures are isostructural.
2. Identify unknowns
3. Determine crystal structure

Isostructural

- Use powder pattern
- measure Bragg angle, θ
- calculate d spacing
- match d spacing with known structure

TABLE VII

LATTICE SPACINGS OF METAL SQUARATES IN Å

M(III)(OH)(C_4O_4) $\cdot 3H_2O$ (2)	V(III)(OH)(C_4O_4) $\cdot 3H_2O$	V(III)(OH)(C_4O_4) $\cdot 2H_2O$	V(III)(OH)(C_4O_4)
7.72	7.72	7.57	
6.76	6.61		6.65
6.40	6.37	6.28	
6.16	6.18		
5.75	5.72	5.70	5.51
5.19	5.17	5.17	5.04
4.56	(4.53)		
4.25	4.24	4.23	
3.95	3.96	3.95	3.93
3.70	3.70	3.66	
3.43	3.44	3.41	3.28
3.25	3.23	3.22	
3.13	3.14	3.12	
3.04	3.03	3.03	
2.84	2.84	2.82	
2.74	2.76	2.73	
2.68	2.66	2.66	
2.58	2.58	2.57	2.54
2.48	(2.49) (2.46)	2.48	2.45
2.41	2.39	2.40	
2.29	2.29	2.29	
2.16	2.15	2.15	

Identify Unknowns

- use powder pattern
- measure Bragg angle, θ
- calculate d spacing
- match d spacing with ASTM data

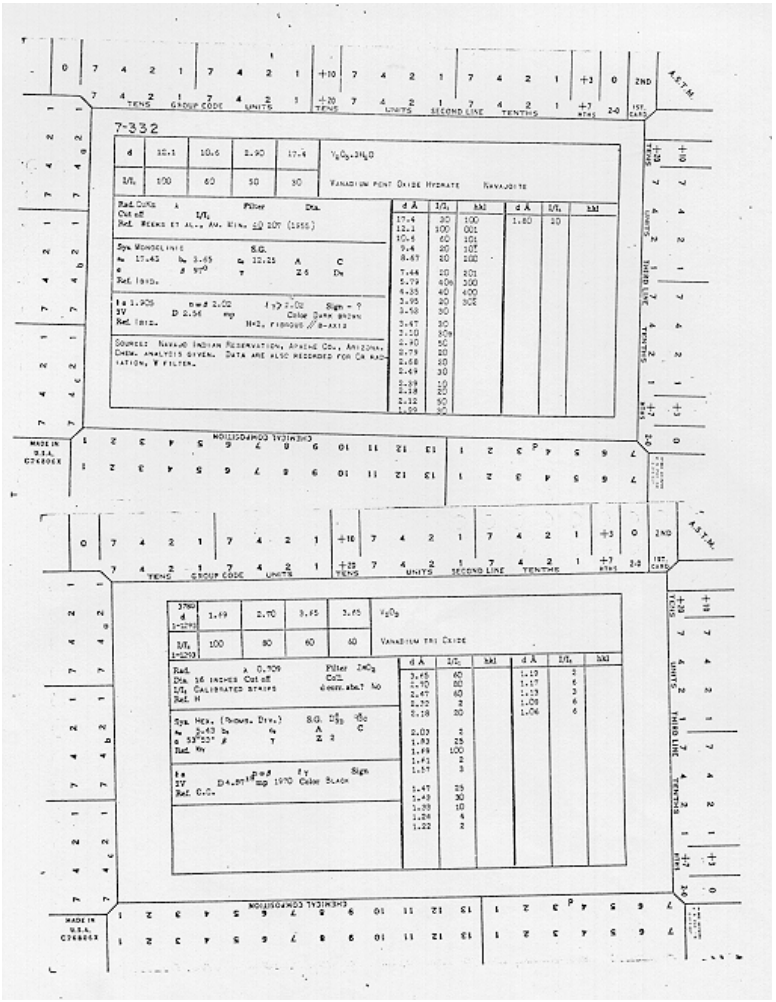
Data Sheet for Powder Data

End of run # 4162

2θ angle	θ	sin θ	d	ASTM card # 1-1293
24.3	12.2 (12°12')	0.21132	3.65	3.65
32.95	16.48 (16°29')	0.28374	2.71	2.70
36.2	18.1 (18°6')	0.31068	2.48	2.47
41.25	20.63 (20°38')	0.35239	2.19	2.18
49.85	24.98 (24°59')	0.42235	1.83	1.83
54.0	27.0 (27°0')	0.45399	1.70	1.69
63.3	31.7 (31°42')	0.52547	1.46	1.47
65.25	32.63 (32°38')	0.53926	1.43	1.43

V_2O_3

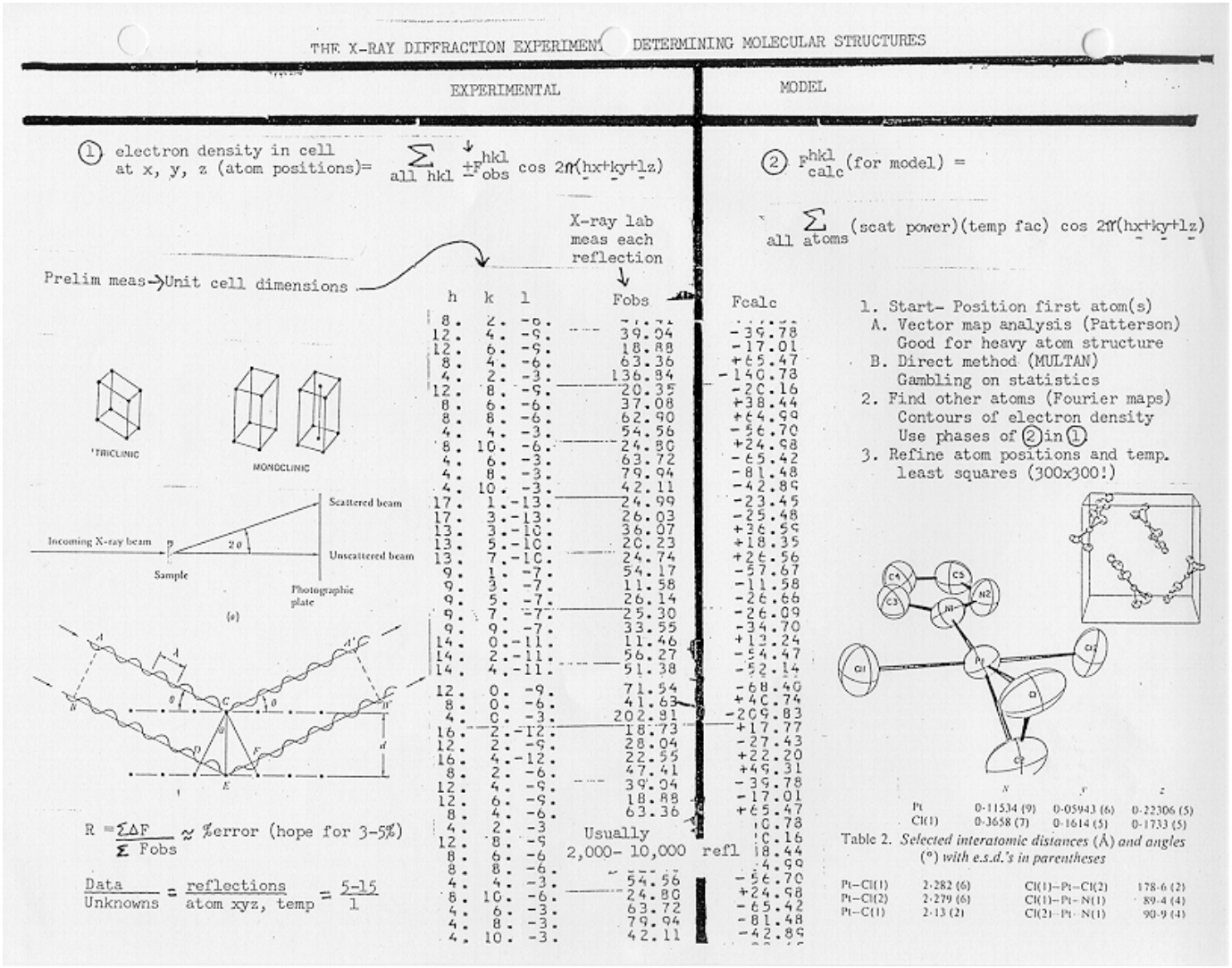
ASTM Data Base



Determine Crystal Structure

- use single crystal data
- calculate d spacing, unit cell dimensions
- index reflections
- propose structure
- match calculated data to experimental data

Single Crystal X-ray Analysis



Electron Density Data

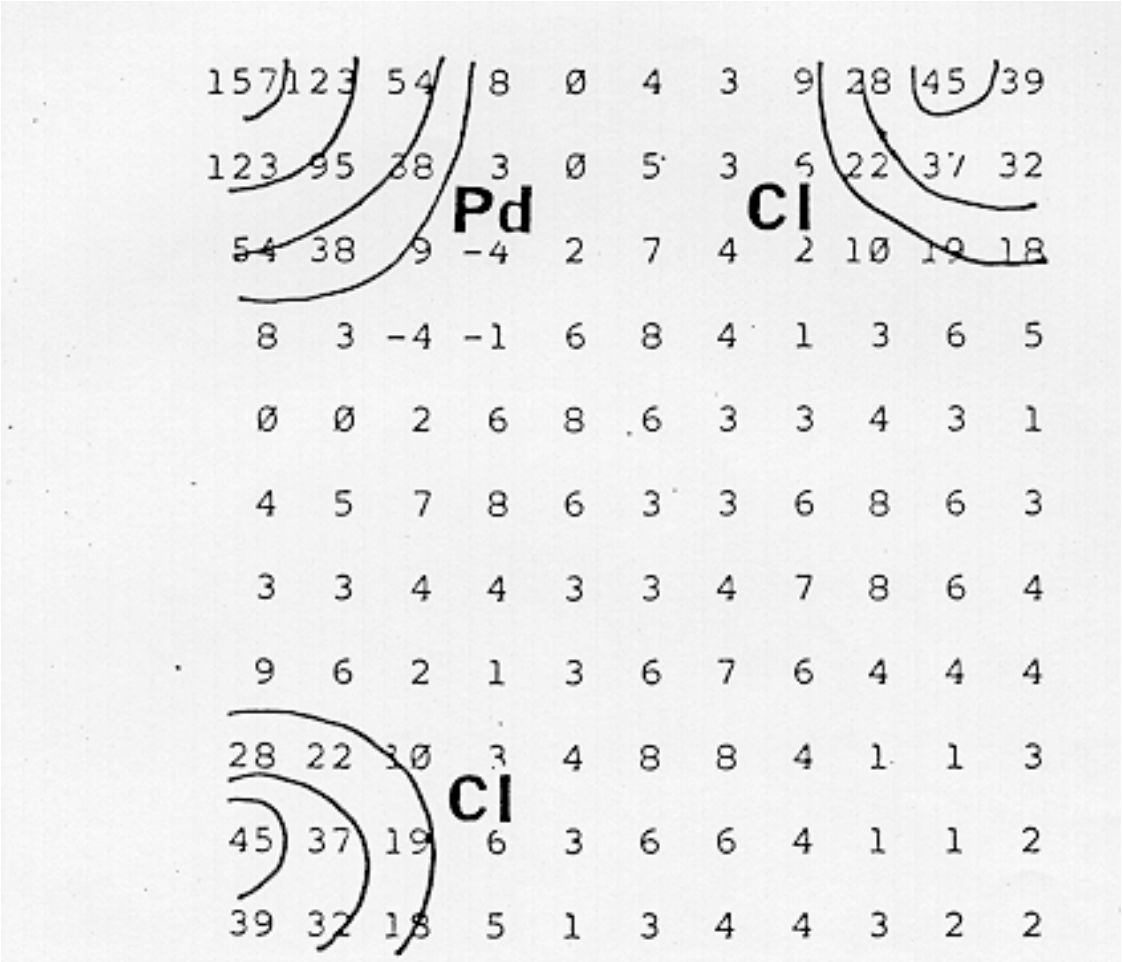
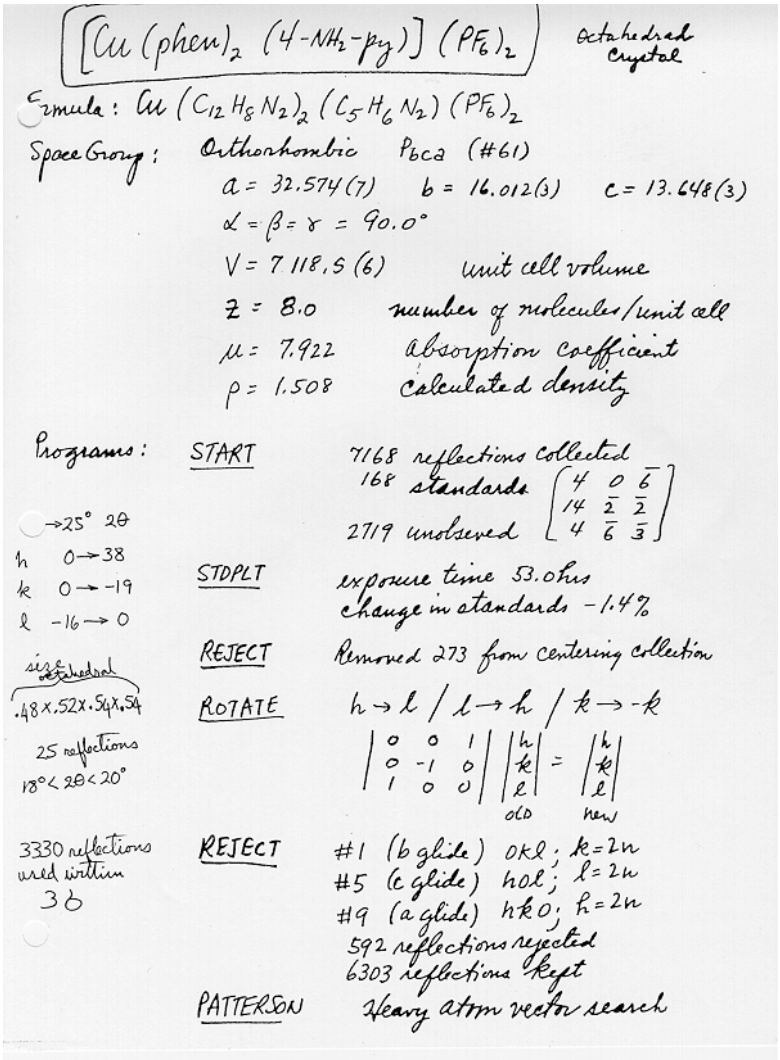


Figure 2. Section of electron density map showing Pd and Cl atoms.

Single Crystal X-ray Analysis



$[Cu(phen)_2(4\text{-}NH_2\text{-}pz)](PF_6)_2$ — octahedral crystal

Formula: $Cu(C_{12}H_8N_2)_2(C_5H_6N_2)(PF_6)_2$

Space Group: Orthorhombic P_{bca} (#61)

$a = 32.574(7)$ $b = 16.012(3)$ $c = 13.648(3)$

$\alpha = \beta = \gamma = 90.0°$

$V = 7118.5(6)$ unit cell volume

$Z = 8.0$ number of molecules/unit cell

$\mu = 7.922$ absorption coefficient

$\rho = 1.508$ calculated density

Programs:

START
- 7168 reflections collected
- 168 standards $\begin{bmatrix} 4 & 0 & \bar{6} \\ 14 & \bar{2} & \bar{2} \\ 4 & \bar{6} & \bar{3} \end{bmatrix}$
- 2719 unobserved

$\rightarrow 25°$ 2θ

h $0 \rightarrow 38$

k $0 \rightarrow -19$

l $-16 \rightarrow 0$

STDPLT
- exposure time 53.0 hrs
- change in standards −1.4%

size octahedral

.48 × .52 × .54 × .54

REJECT — Removed 273 from centering collection

25 reflections

$18° < 2\theta < 20°$

ROTATE — $h \rightarrow l$ / $l \rightarrow h$ / $k \rightarrow -k$

$$\begin{vmatrix} 0 & 0 & 1 \\ 0 & -1 & 0 \\ 1 & 0 & 0 \end{vmatrix} \begin{vmatrix} h \\ k \\ l \end{vmatrix}_{old} = \begin{vmatrix} h \\ k \\ l \end{vmatrix}_{new}$$

3330 reflections used within 3θ

REJECT
- #1 (b glide) $0kl$; $k = 2n$
- #5 (c glide) $h0l$; $l = 2n$
- #9 (a glide) $hk0$; $h = 2n$
- 592 reflections rejected
- 6303 reflections kept

PATTERSON — Heavy atom vector search

Trans-Bisbisulfitetetraaminеruthenium(II)