chem 5390

Advanced X-ray Analysis

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Department of Chemistry

Advance X-Ray Diffraction

Lecture: TTh 8:00 a.m. – 9:20 p.m. CHEM 253 and CHEM 271

Instructor: Dr. Teresa D. Golden

Office hours: 10:30 - 11:30 p.m. MW, CHEM 279, 565-2888, tgolden@unt.edu

Advance X-Ray Diffraction

Reading:

X-ray Diffraction Procedures for Polycrystalline and Amorphous Materials, H.P. Klug and L.E. Alexander, Wiley, 1974, ISBN 0-471-49369-4

Elements of X-ray Diffraction, B.D. Cullity and S.R. Stock, Prentice Hall, 3rd edition, 2001, ISBN 0-201-61091-4

X-ray Diffraction, C. Suryanarayana and M. Norton, 1998, ISBN 0-306-45744-X

Introduction to X-ray Powder Diffractometry, R. Jenkins and R. Synder, John Wiley & Sons, 1996, 0-471-51339-3

Advance X-Ray Diffraction

Exams:

There will be exams, homework assignments, a research project and a final exam. Dates for each exam will be announced in class.

The final will be Tuesday, December 7th, 8:00 - 10:00 a.m.

Project:

The research project can include the student's graduate research related to x-ray analysis or an assigned topic. Abstract for research topic is due September 30th. Outline due October 26th. Research Paper due December 2nd, 2021.

Advance X-Ray Diffraction

Lecture Topics: CHEM 253

I. Production and Properties of X-rays
II. Basic Crystallography
III. Diffraction Theory
IV. Instrumentation for X-ray Diffraction
V. Crystallographic Databases
VI. Qualitative Analysis
VII. Quantitative Analysis

Advance X-Ray Diffraction

Lab Topics: CHEM 271

Lab 1: Safety, Sample Prep and Instrument Operation (Powder)

Lab 2: Crystal Structure Determination - Cubic (Powder)

Lab 3a: Crystal Structure Determination - Hexagonal (Powder)

Lab 3b: Basic Instrument Operation (Single-Crystal)

Lab 4: Determination of Precise Lattice Parameters (Powder)

Lab 5: Determination of Crystallite Size and Strain (Powder)

Lab 6a: Intro to Software, ICDD JCPDS jPowd, Rietveld (Powder)

Lab 6b: Intro to Software, Databases (Single Crystal)

Lab 7: Open Research Project

History of X-rays

A. Discovery of X-rays

Wilhelm Röntgen discovered x-rays on November 8th, 1895 in Wurzburg Germany.

While experimenting with Crookes tubes, he noticed that some BaPtCN material smeared on thin cardboard and covered with black paper a distance away began to glow.

History of X-rays

Discovery of X-rays

History of X-rays

Discovery of X-rays

Soon he noticed other objects, i.e., wood, books, and metal sheets were penetrated by x-rays.

He then x-rayed his wife's hand and noticed the flesh was transparent but the bones were opaque.

History of X-rays

Discovery of X-rays

In 1901, Wilhelm Röntgen won the Nobel prize in Physics for his discovery.

History of X-rays

Following Röntgen discovery, 3 major branches of science have developed using this radiation.

- ❖ X-ray radiography (function of average atomic number and density of matter)
  - Diagnostic methods – medical and industrial - relies on the relationship between density of materials and absorption of x-rays.
- ❖ X-ray crystallography (structure analysis)
  - Single crystal and Powder - relies on the dual wave/particle nature of x-rays to discover information about the structure of crystalline materials.
- ❖ X-ray spectroscopy (elemental analysis)
  - Fluorescence - relies on characteristic secondary radiation emitted by materials when excited by a high-energy x-ray source and is used primarily to determine amounts of particular elements in materials.

History of X-rays

X-ray radiography

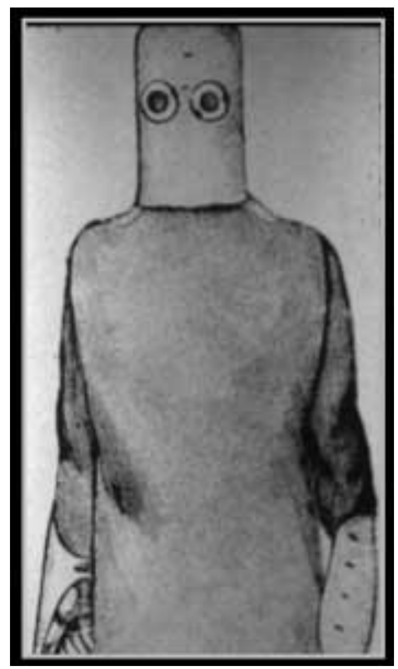
In 1896, the public started to x-ray objects, people, animals, etc… not realizing the health effects.

Herbert Jackson of King's College began developing tubes to focus x-rays in 1896.

That same year Thomas Edison began experimenting with x-ray "lamps" but abandoned the research when his assistant became sick and died.

History of X-rays

By 1910, x-ray operators started to wear protective clothing and using shielding on equipment. (Lead)



History of X-rays

X-ray Therapy

Around 1913, medical doctors began using x-rays to treat ringworm and other ailments.

History of X-rays

History of X-rays

The nature of these x-rays however took many years to uncover.

- Röntgen tried unsuccessfully to produce interference effects with x-rays (i.e. visible light and law of optics).

- Thomson and Rutherford's experiments showed x-rays behaved as waves with very small wavelength.

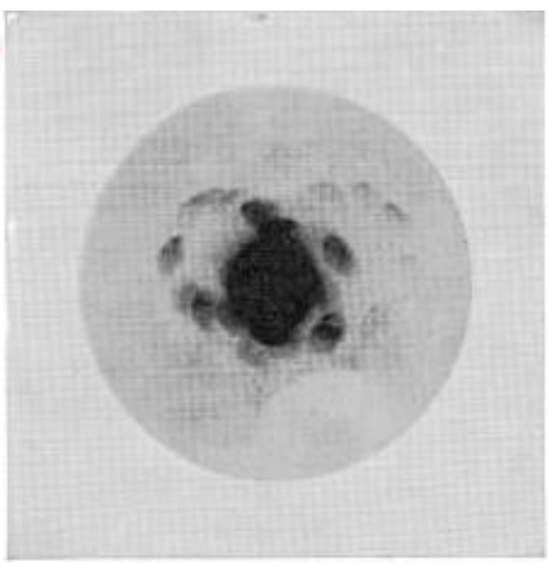
- Bragg's experiments interjected the particle theory. In 1912 suggested a theory was needed to explain both waves and particles.

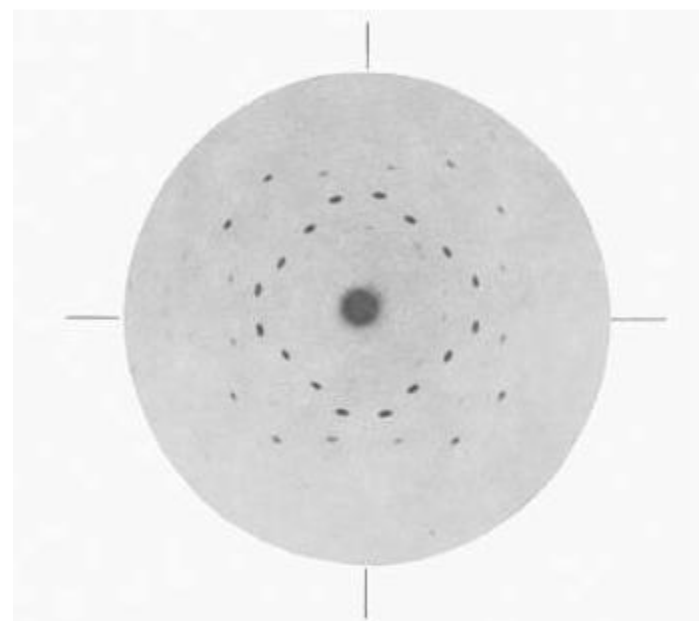
History of X-rays

Crystallography

In 1912 M. von Laue and P. Knipping obtained the first diffraction pattern of a crystal using X-rays.

Awarded Nobel prize in 1914.





History of X-rays

Important for Calculations

In 1914, the father and son team of English physicists, William Henry Bragg and William Lawrence Bragg determined the atomic structure of a simple inorganic substance, salt (NaCl), and deciphered the mathematical relationships between crystal structure and the associated diffraction pattern.

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

where n is an integer

λ is the wavelength of the x-rays

d is the interplanar spacing in the specimen

θ is the diffraction angle

Bragg Equation

History of X-rays

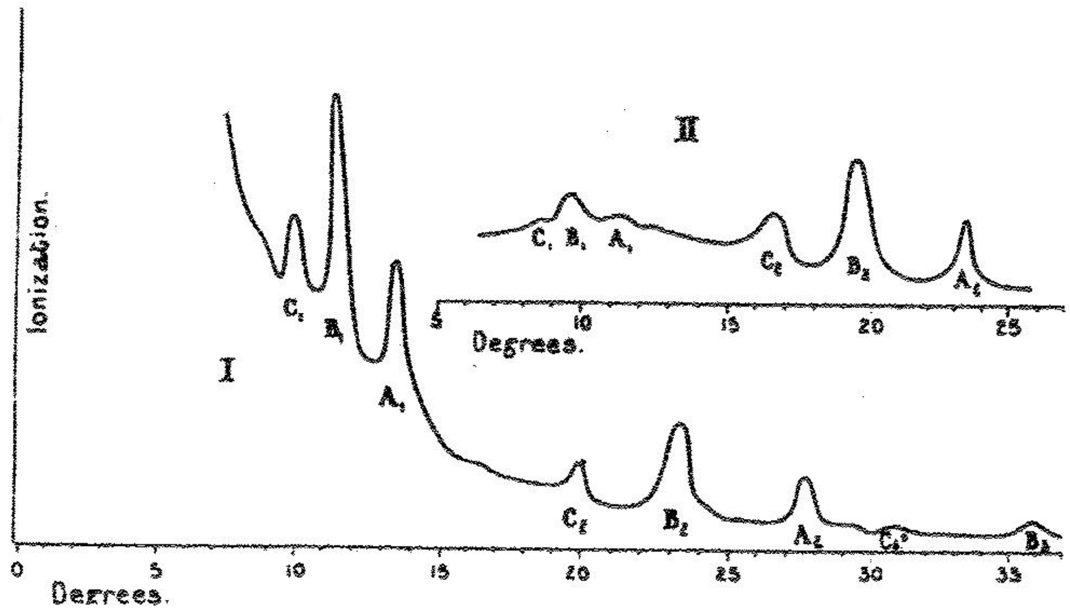


Figure 6. *Diffractograms produced by W.H. and W.L. Bragg with sodium chloride crystals. I: diffractogram obtained with a crystal cleaved along the (100) planes, II: diffractogram obtained with a crystal cleaved along the (111) planes*

History of X-rays

Crystallography

First x-ray powder diffractometer was developed in 1935 by LeGalley – gave poor intensities.

In 1945 – Parrish and Gordon developed a Geiger-counter instrument.

Phillips Company (now PANalytical) produced the first commercial instrument in 1947.

History of X-rays

Crystallography

Rosalind Franklin collected X-ray diffraction data on Na salt of DNA.
In 1953, the structure of DNA was solved by J. Watson, a biologist, and F. Crick, a physicist, thanks to the use of X-rays.

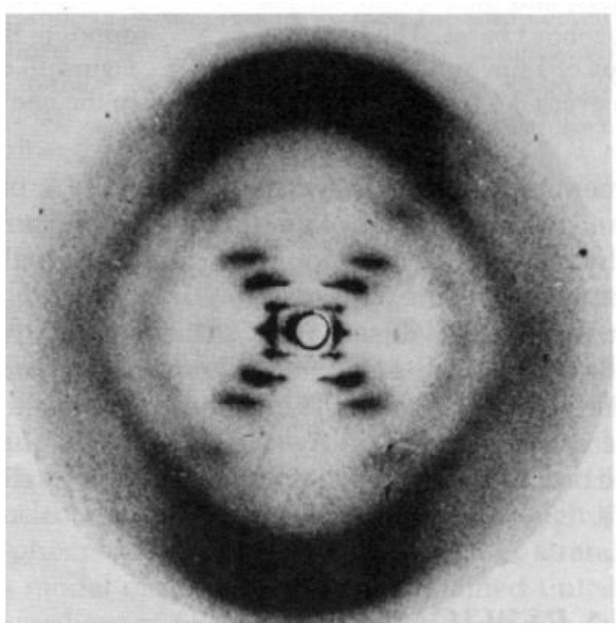
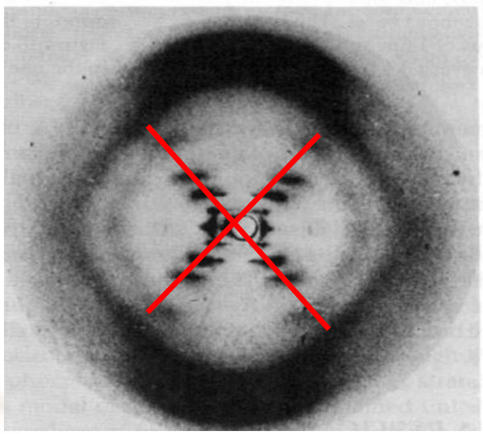


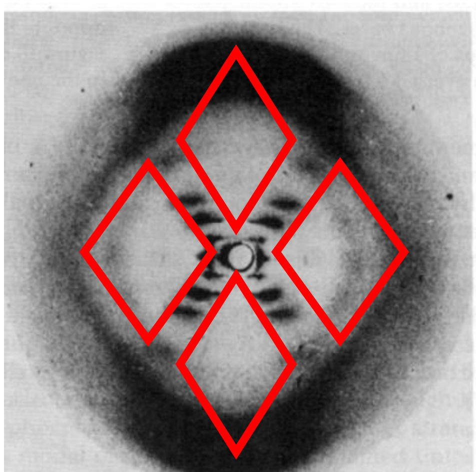
Photo 51- The x-ray diffraction image that allowed Watson and Crick to solve the structure of DNA

History of X-rays

Crystallography



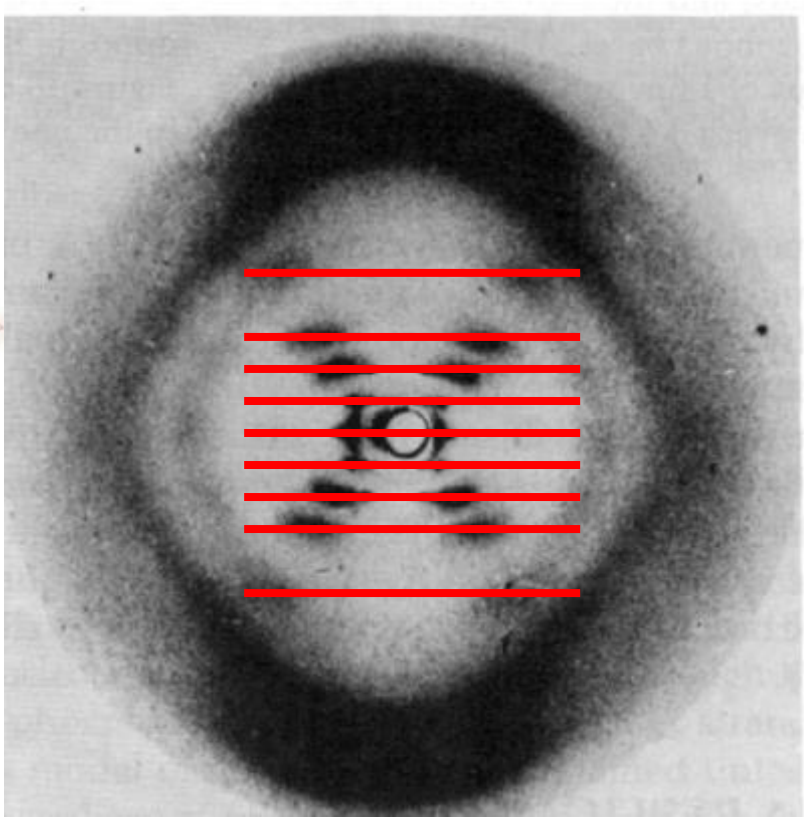
"X" pattern characteristic of helix



Diamond shapes indicate long, extended molecules

History of X-rays

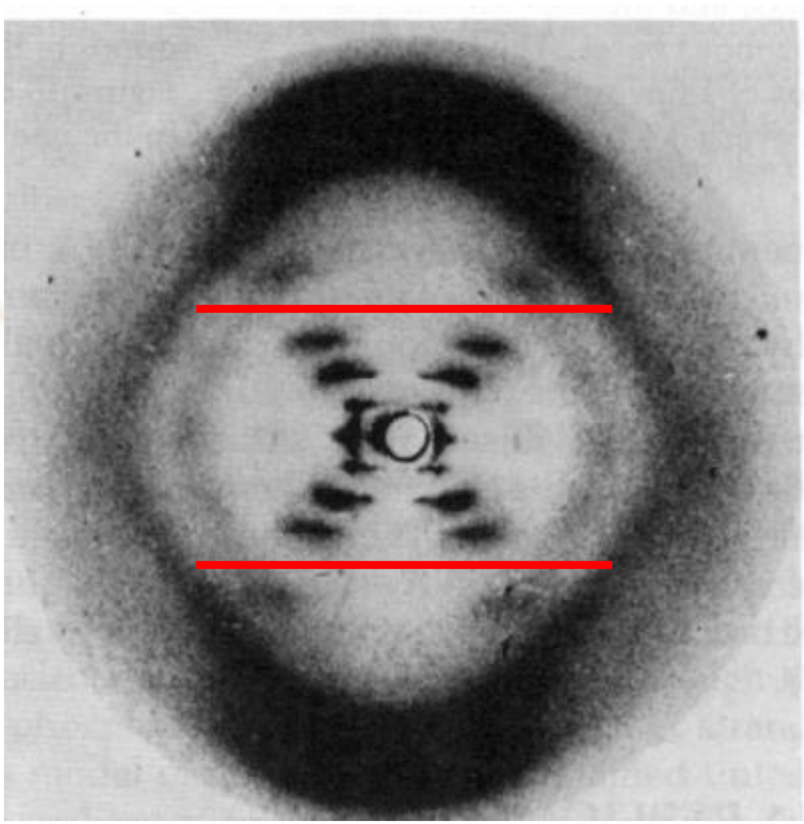
Crystallography



Smear spacing reveals distance between repeating structures

History of X-rays

Crystallography



Missing smears indicate interference from second helix

History of X-rays

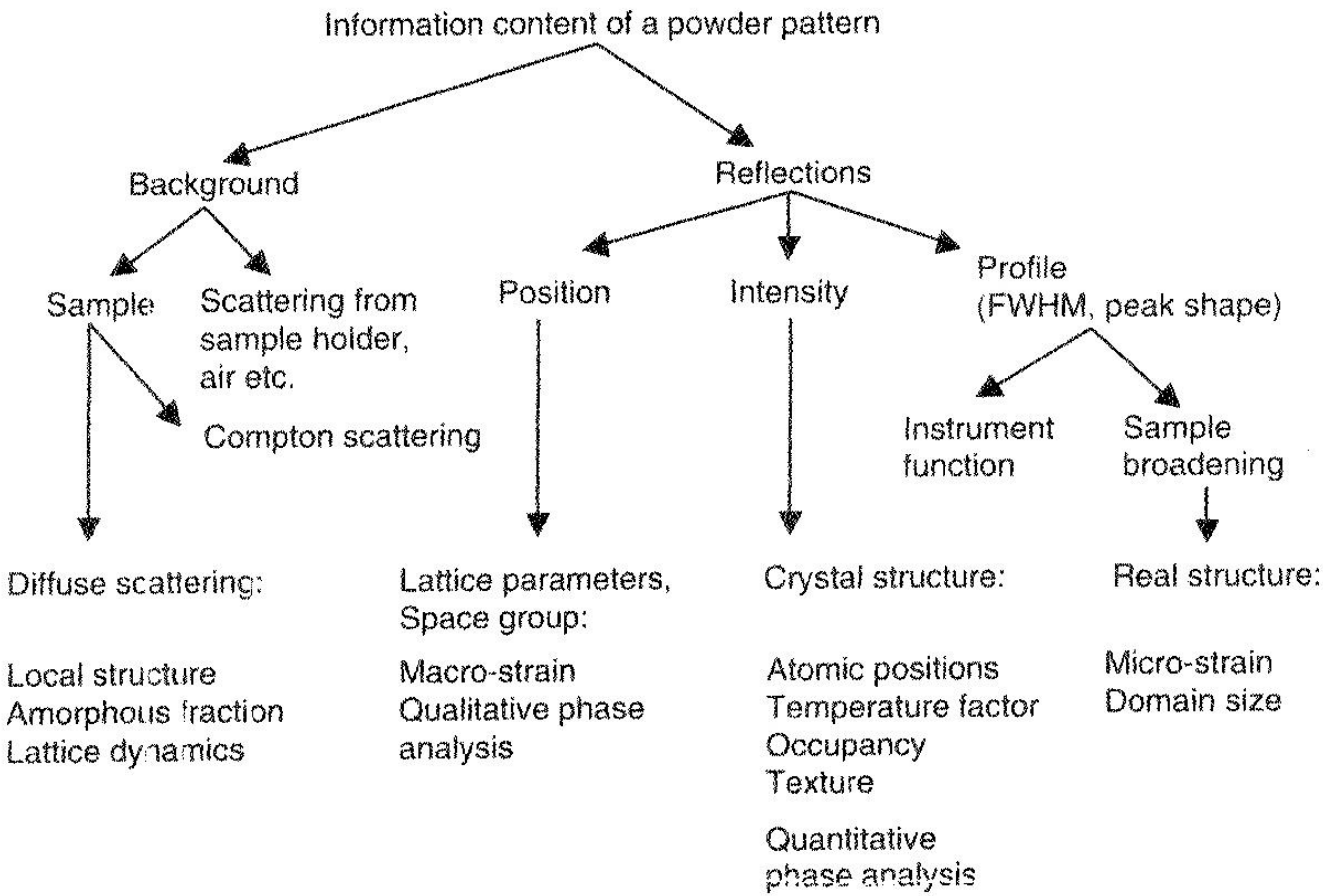


Figure 1 General information content of a powder diffraction pattern.

History of X-rays

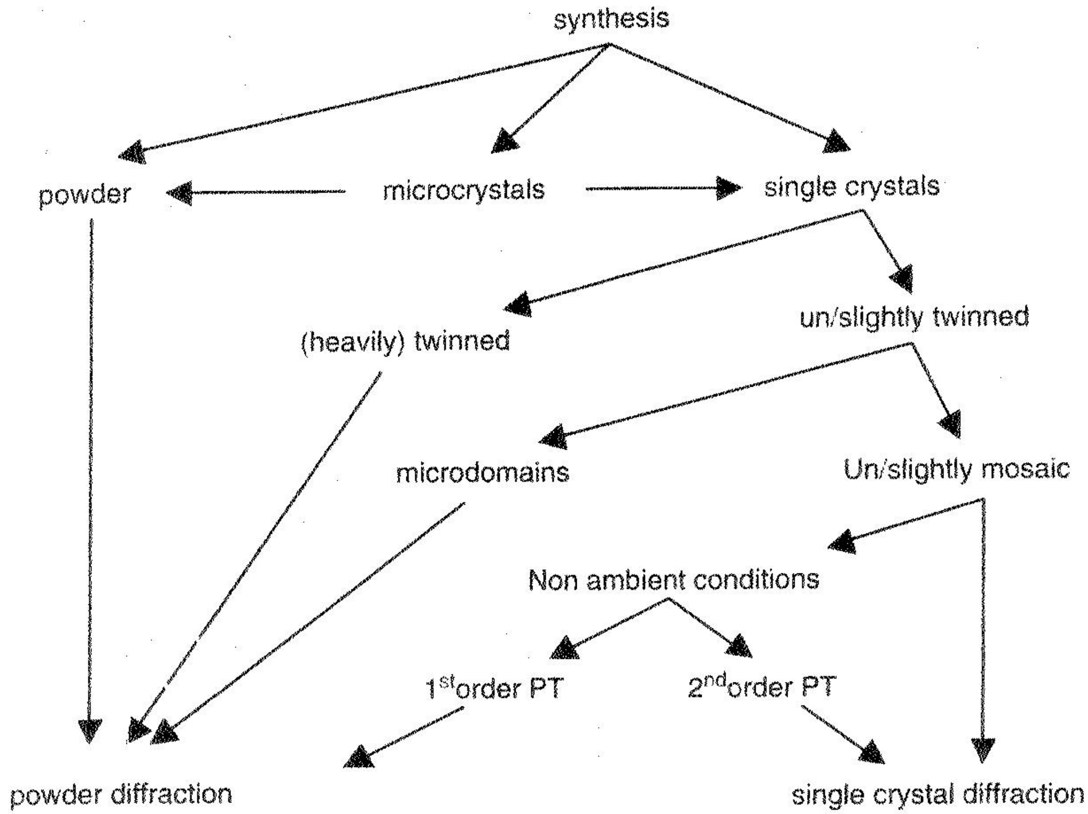
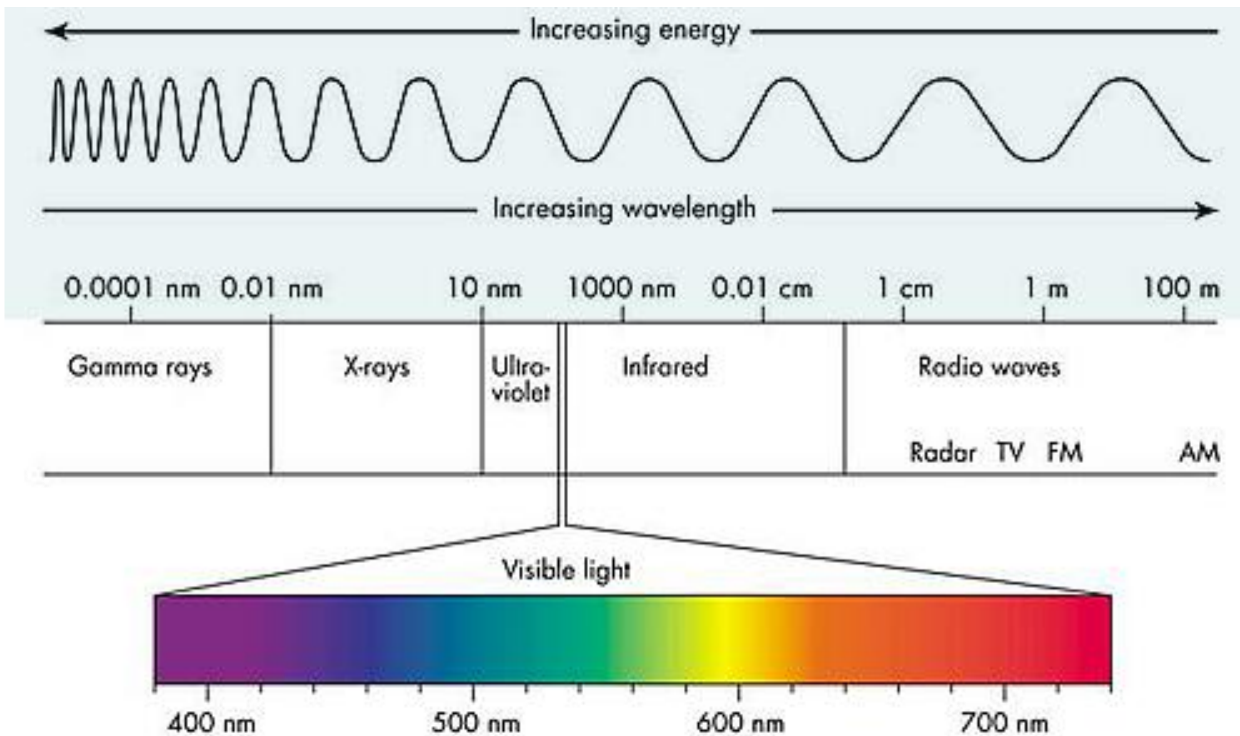


Figure 2 Illustration of the relationship between the domains of applicability of the powder and single-crystal methods in the area of structure solution.

Production and Properties of X-rays

B. Properties of X-rays



Production and Properties of X-rays

B. Properties of X-rays

Hazards

X-Ray Absorption in Human Tissue

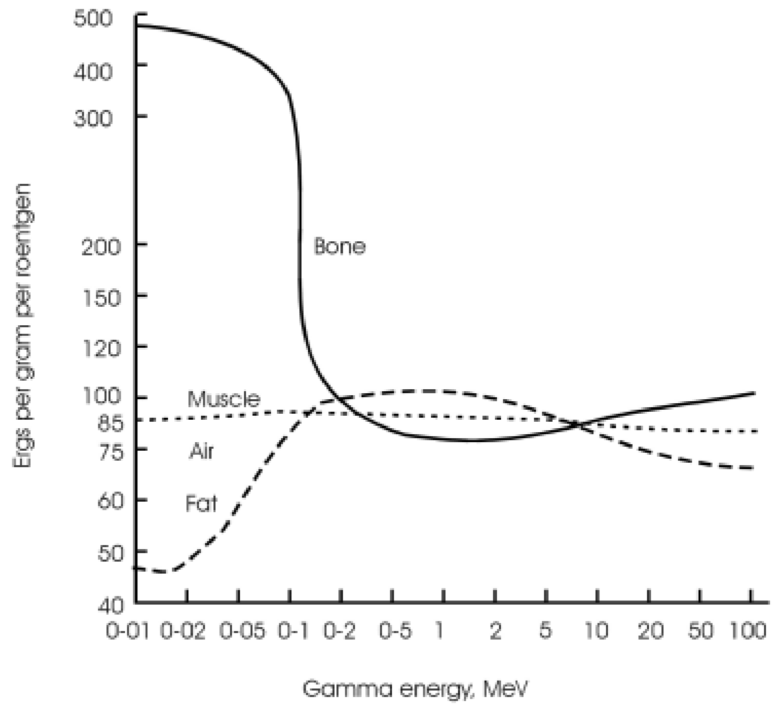
When X-ray photons interact with matter -- human tissue in this discussion -- some of the photons are absorbed by the tissue. Many analytical x-ray machines produce X-rays up to 50 or 60 kV. Over this energy range, bone absorbs roughly five times the energy that muscle absorbs and about ten times that of fat. This is significant since the hands are mainly muscle and bone. They are therefore more susceptible to X-ray injury.

Production and Properties of X-rays

Properties of X-rays

Hazards

The figure shows the absorption characteristics for bone, muscle, and fat, as a function of the gamma (or X-ray) energy.



Energy absorption per roentgen of various tissues.
(From O. Glasser, *Medical Physics*, Vol. II)

Production and Properties of X-rays

Properties of X-rays

Hazards

Injuries

Injuries are generally characterized by the clinical symptoms manifested (burns, swelling, and so on), and the estimated dose. There are short-term and long-term injuries.

Short-Term Injuries

Short-term injuries are generally manifested by soreness, reddening of the skin, swelling, inflammation, and tissue breakdown characteristic of second and third degree burns. Most often these signs do not begin until several days after the accident.

Production and Properties of X-rays

Hazards

Figure 1 shows the fingers of an accident victim about 1 month after his exposure, and Figure 2 was taken 3½ months after exposure.

Production and Properties of X-rays

Hazards

Long-Term Injuries

Many long term injuries are due to the progression of short-term damage. Despite initial treatment of the injury, the tissue may be damaged beyond recovery, sometimes necessitating the removal of the damaged tissue (such as a finger). Cancer and cataracts, in the case of eye exposure, are also considered potential (latent) long-term injuries.

Production and Properties of X-rays

Hazards

Dose Definitions

"Absorbed dose" of any ionizing radiation is the energy imparted to matter by ionizing particles per unit mass of irradiated material at the place of interest. The unit of radiation absorbed dose is the "rad." 1 rad is 100 erg/gram.

"RBE dose" is equal numerically to the product of the absorbed dose in rads and an agreed factor RBE (relative biological effectiveness) whose values for ICRP (International Commission on Radiological Protection). The "rem" (roentgen equivalent [in] man) is the unit of RBE dose.

Production and Properties of X-rays

Hazards

Dose Limits

Maximum Permissible Dose Equivalent for Occupational Exposure

Dose to whole body	**5 rem per year**
Skin of whole body	**50 rem per year**
Hands	**50 rem per year**
Pregnant women (with respect to fetus)	**0.5 rems in gestation period**

[Note that average background radiation in U.S. is 0.36 rem per year.]

Production and Properties of X-rays

Hazards

Sample Dose Calculation

If a hand were covering that window and the X-rays were totally absorbed in the hand in a column of flesh and bones 30 mm tall and 101 mm^2 in cross-section area, then 3.0 cm^3 or ~3.0 gram would receive the dose.

The dose received by the irradiated portion of the hand would be (2.1 x E8 erg/sec)/(3.0 gram) or 7.1 E7 erg/gram or about 7.1 E5 rems for every second of exposure!

Compared to 75 rems per year maximum allowed occupational exposure to the hands, this is about 9500 times the annual dose limit to the hand every second!

Production and Properties of X-rays

Hazards

Minimizing Exposure

How can exposure to radiation be minimized?

There are four physical factors that affect the exposure level in a "radiation field"

1. **Distance**
2. **Time**
3. **Shielding**
4. **Output factors (kV, mA)**

- **Exposure varies as the inverse square of the distance (assuming a point source, as from scattering)**
- **Exposure increases linearly with time**
- **Exposure is inversely exponential with the thickness of shielding.**
- **Exposure increases linearly with current (mA) and as the square of the potential (kV).**

Production and Properties of X-rays

Hazards

Dosimetry

An operator of analytical x-ray equipment is provided with an extremity monitoring device and any person coming in contact with equipment capable of exposing a major portion of the body shall be required to wear a whole-body monitoring device. Such devices are referred to as dosimeters. These portable devices are capable of measuring and registering the total accumulated exposure to ionizing radiation.

Production and Properties of X-rays

Hazards

Dosimetry

At the University of North Texas, thermoluminescent dosimeters (TLDs) in the form of ring badges and optically stimulated luminescence (OSL) whole-body badges may be issued to operators of analytical x-ray equipment. Thermoluminescent dosimeters contain crystalline materials (for example, CaF_2 with a Mn impurity or LF) that emit light if they are heated after having been exposed to radiation. The whole body badges contain a thin layer of aluminum oxide. After use, the aluminum oxide is stimulated with a laser light and the luminescence is measured. The amount of luminescence is proportional to the amount of radiation exposure.

Production and Properties of X-rays

Hazards

Dosimetry

Remember that dosimetry badges are to be worn only for work related to research and not for "checking" dental or medical doses.

The badges/rings are to be worn at all times when operating, or in the vicinity of, the analytical x-ray equipment. They should be stored in a location away from the equipment (and heat sources) to avoid exposure to the badges when they are not being worn. These badges are issued by, and returned to, the UNT Radiation Safety Office via the authorized user who supervises the worker.

Production and Properties of X-rays

Hazards

Equipment

The X-ray equipment manufactured today is much safer than that made before the 1970s. Major advances have been in the areas of:

- **interlocks**
- **enclosures**
- **shutters**
- **failsafe warning lights**
- **remote and computer controls**

The sealed X-ray tubes and the mechanical goniometers are basically unchanged.

Production and Properties of X-rays

Hazards

Equipment - Interlocks

Interlocks are a set of switches in a series, where EVERY switch must be closed in order for the X-rays to be generated and/or for a shutter to be opened. These switches are connected to doors, panels, and collimators, which if opened or removed, would create a radiation hazard for the user.

If any switch is opened while the X-rays are on or the shutter is open, the X-ray generator will immediately shut off and/or the shutter will close.

Production and Properties of X-rays

Hazards

Equipment - Enclosures

Enclosures are boxes, some having a transparent window, which contain the X-ray instruments so that stray or scattered X-rays do not escape into the room. Enclosures, along with interlocks, also prevent people from encountering the direct X-ray beam.

Equipment - Shutters

Shutters open and close a path for the X-ray beam. When a shutter is properly functioning and closed, no X-rays can pass beyond the shutter.

Production and Properties of X-rays

Hazards

Equipment - Warning Lights, Failsafe

Lights are used to indicate that the X-ray generator is turned on and that a shutter is open. These lights are 'failsafe' so that in the event of a lamp failure (e.g., broken filament) the X-ray generator will NOT turn on and the shutter will NOT open (and, in fact, if on or open, will shut off or close in the event of a lamp failure). Also, the X-ray generator will not turn back on nor the shutter open again without the user first taking action to do so.

Production and Properties of X-rays

Hazards

Equipment - Remote and Computer Controls

Remote and computer controls of X-ray instruments are major safety advances in that the user need not be anywhere near the instrument to operate it. Enclosures, interlocks and warning lights serve to prevent possible radiation exposure to anyone in the vicinity of the instrument.

Equipment - Safety Over-Rides

Any mechanical or electrical system can, by deliberate action, be made unsafe (e.g., using a key to over-ride the interlock system, using jumper wires to bridge an open switch, and/or mechanically opening or removing something). Such actions are reserved for service personnel in the repair or alignment of the instrument. Such actions should NEVER be done by users.

Production and Properties of X-rays

Hazards

Equipment - Repairs

Users are NEVER to attempt repairs or make non-trivial adjustments to instruments. If there is a problem, inform the instrument supervisor. Depending on the severity of the problem, in the absence of the supervisor, users should label the instrument as "down" and power it off. For lesser problems, if deemed safe to do so, label it and walk away.

If users encounter an instrument being repaired, stay back and do not touch it!

Production and Properties of X-rays

Hazards

Normal Operating Procedures

'Normal Operating Procedures' mean operating procedures for conducting suitable for analytical purposes with shielding and barriers in place. These do not include maintenance but do include routine alignment procedures. Routine and emergency radiation safety considerations are part of these procedures.

Normal operating procedures shall be written and available to all analytical x-ray equipment workers.

Production and Properties of X-rays

Hazards

One of the major causes of X-ray accidents has been taking short cuts in attempts to complete work more quickly. Most of these involved defeating interlocks, or modifications to the instruments, but still one must think through every task and procedure to recognize and avoid hazards.

Work smart!

Assignment

- Read W. L. Bragg's Nobel Lecture "The diffraction of X-rays by crystals" at class website under "Assignment 1"

http://chemistry.unt.edu/~tgolden/courses/course_downloadsFall18.html