

Experiment 4

Energy-dispersive X-ray diffraction

X-ray fluorescence (XRF) and X-ray diffraction (XRD) may be used to determine the constituent elements and the crystalline structure of materials.

4.1 Introduction

X-ray fluorescence

XRF refers to the absorption of incident X-rays ($h\nu_0$) resulting in the production of a set of X-rays whose energies ($h\nu_j$) are characteristic of the absorber atom(s) (Z). The characteristic X-rays can therefore be used to identify the atom(s) present in the sample.

The incident X-ray photon ($h\nu_0$) undergoes a photoelectric interaction with a target atom (Z) resulting in the annihilation of the photon and ionization of the target atom. The energy equation is

$$K = h\nu_0 - B$$

where K is the kinetic energy of the photoelectron liberated from the atom and B is its binding energy to the atom. Subsequently, the ionized atom combines with an electron and undergoes a de-excitation to its electrically neutral ground state. X-ray photons, whose energies ($h\nu_j$) are characteristic of the target atom (Z), are produced in the de-excitation. An energy level diagram is shown in Fig. 4.1. Each level

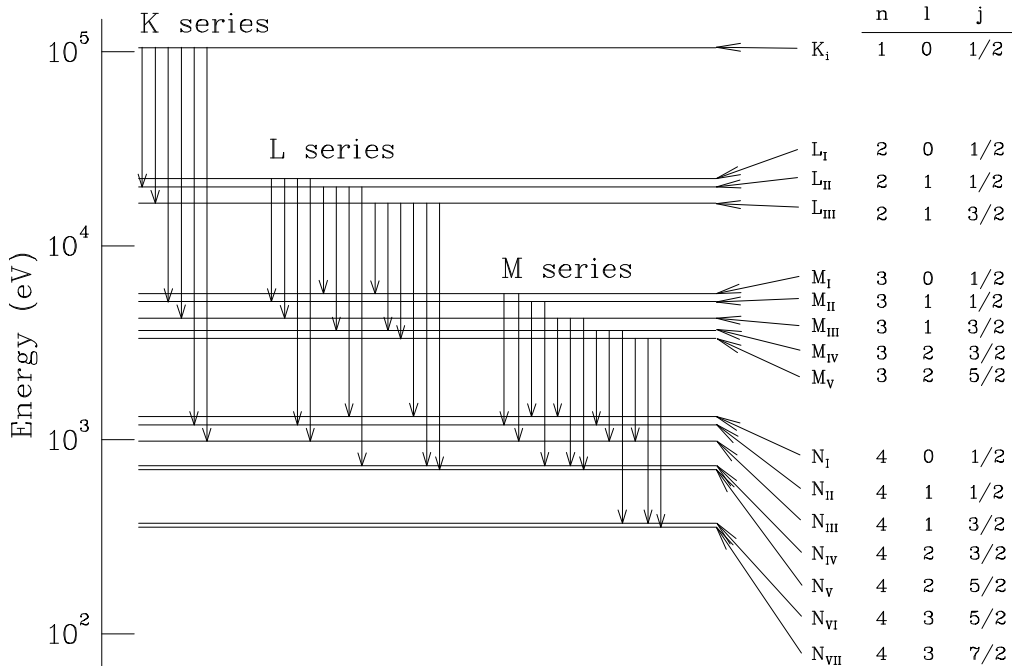


Figure 4.1: A schematic diagram of the X-ray energy levels

corresponds to the excitation of the atom when a single electron is missing from the otherwise full subshell (nlj). Zero energy corresponds to the ground state of the neutral atom. Level K , corresponds to the

binding energy (B_K) of an electron in the K shell. There are three closely spaced L -shell levels labelled L_I, L_{II}, L_{III} corresponding to slightly different L -shell electron binding energies. If

$$h\nu_0 > B_K$$

then all characteristic X-rays (K -series, L -series, *etc.*) are produced. If

$$B_L < h\nu_0 < B_K,$$

then the K -series X-rays are not produced.

X-ray diffraction

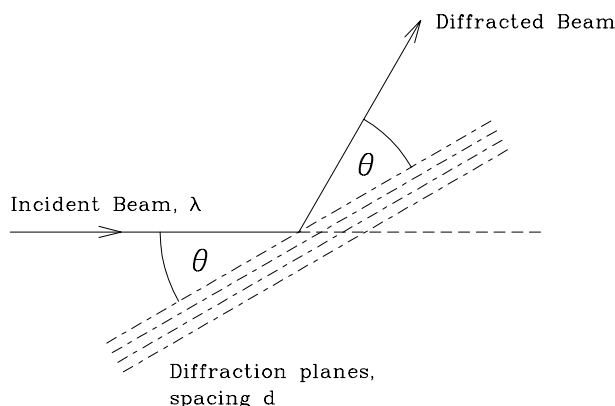


Figure 4.2: Geometry of X-ray diffraction

X-ray diffraction is used extensively to determine the structure of crystalline and also of non-crystalline and amorphous materials. For crystalline materials, the direction θ and wavelength λ of the diffracted beam are related by Bragg's Law; with reference to Fig. 4.2, this is

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

where n is the order of diffraction from crystalline lattice planes of spacing d . The equation may be rewritten as

$$2d_n \sin \theta = \lambda \quad (4.1)$$

where $d_n = d/n$ and the equation now represents first order diffraction from planes d/n . Using

Bragg's Law, a measurement of θ and λ for a diffracted beam enables the spacing d_n to be determined. For cubic lattices,

$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \quad (4.2)$$

where a is the side length of the cubic lattice cell (the lattice constant), and h, k and l are the Miller indices of the lattice planes.

4.2 The apparatus

An overview of the apparatus is shown in Fig. 4.3. The incident beam produced by the X-ray machine has its intensity continuously distributed over a range of X-ray photon energy up to a maximum value eV , where V is the voltage of the X-ray tube. This voltage accelerates a beam of electrons that is directed vertically upward to strike a Cu target; the impact generates X-rays that exit the head atop the X-ray machine horizontally through a thin collimator tube as a narrow focused beam. The front panel controls enable the user to set the value of the voltage that determines the energy of the X-ray photons, the operating current that determines the intensity of the beam (number of photons per second), and two independent controls that need to be set to open for the X-ray beam to emerge: setting the port to open allows the beam of electrons to hit the Cu target and to generate the X-rays, and setting the shutter to open allows the generated X-ray to emerge through the collimator. The initial turnkey switch automatically starts the cooling water flow through the X-ray tube; this should be visually verified before operating the X-ray machine, and one should wait for the water to run cold before turning the switch to off.

The incident beam strikes a crystalline powder sample that is mounted using a dual-sided tape to a sample holder atop a large cylindrical enclosure, seen in Fig 4.4. The enclosure contains two narrow

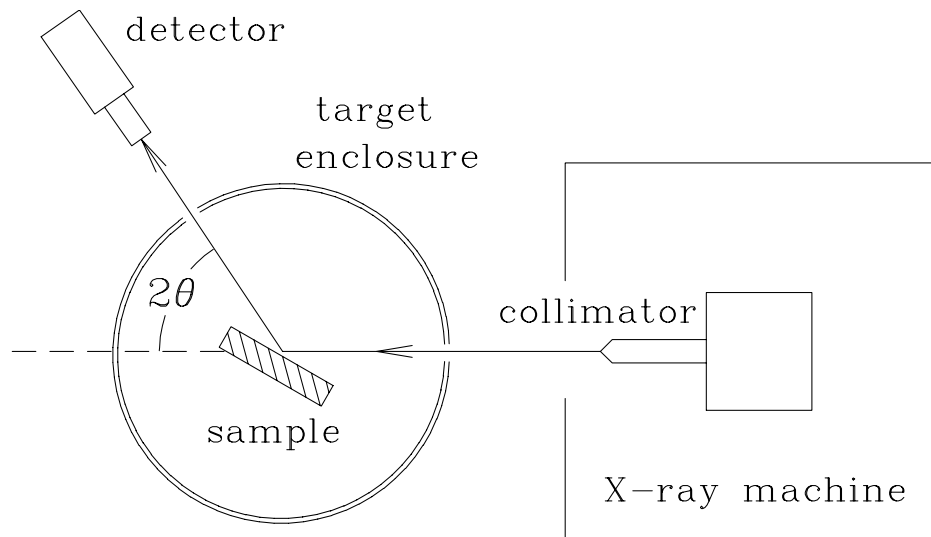
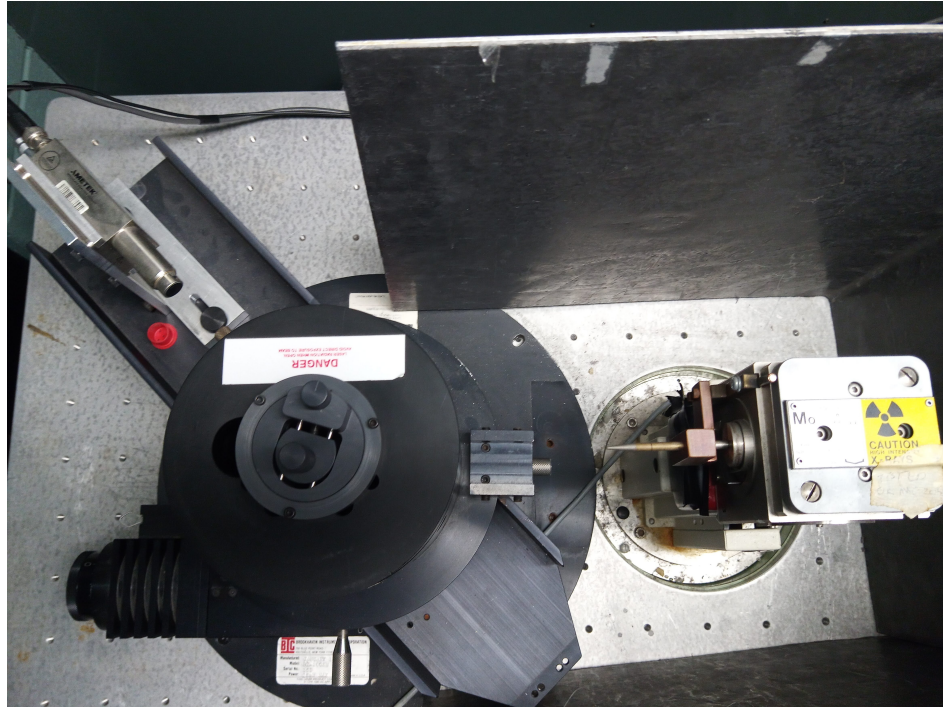


Figure 4.3: A top view (lid removed) and a schematic diagram of the X-ray apparatus.

openings for the incident and the scattered beams as well as two positioning control knobs that allow changes to the orientation and the forward displacement of the sample holder. These controls allow the user to optimize for maximum intensity at the detector; usually this is done on a known sample with a strong signal. As the samples are replaced it is desirable to place the front surface of the sample into the exact same position, so different samples may be placed on spacers, to keep the overall thickness approximately constant.

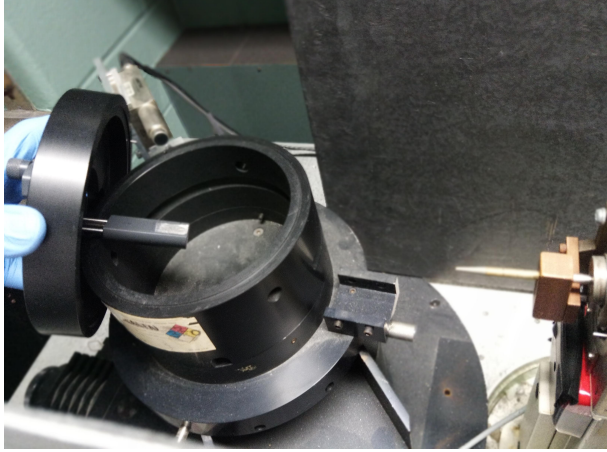


Figure 4.4: The target enclosure with its lid lifted. The sample holder is suspended from the lid of the enclosure. Two knobs on top control the vertical position and the forward displacement of the target attached to the lower end of the sample holder.

Fig. 4.5 is identical to that experiment and will not be described here. Note also that the scripts developed to analyze the data from that experiment will be usable for this experiment with only minor modifications.



Figure 4.6: The solid-state detector.

The spectrum $I(E)$, *i.e.* the number of photons detected as a function of photon energy, consists of a series of relatively narrow peaks superimposed on a smoothly varying background. The peaks arise from

- X-rays fluoresced from the target atoms,
- X-rays diffracted from the crystal lattice.

The position of the peak on the MCA energy scale is a measure of the corresponding photon energy.

Energy Dispersive X-ray Diffraction

In this apparatus, the diffraction is observed by measuring $I(E)$ while keeping θ constant. Bragg's Law may be rewritten in terms of the diffracted beam photon energy, E , as

$$2d_n \sin \theta = \lambda = \frac{hc}{E} \quad (4.3)$$

or

$$E_{hkl} = \frac{hc}{2 \sin \theta} \times \frac{1}{d_{hkl}}. \quad (4.4)$$

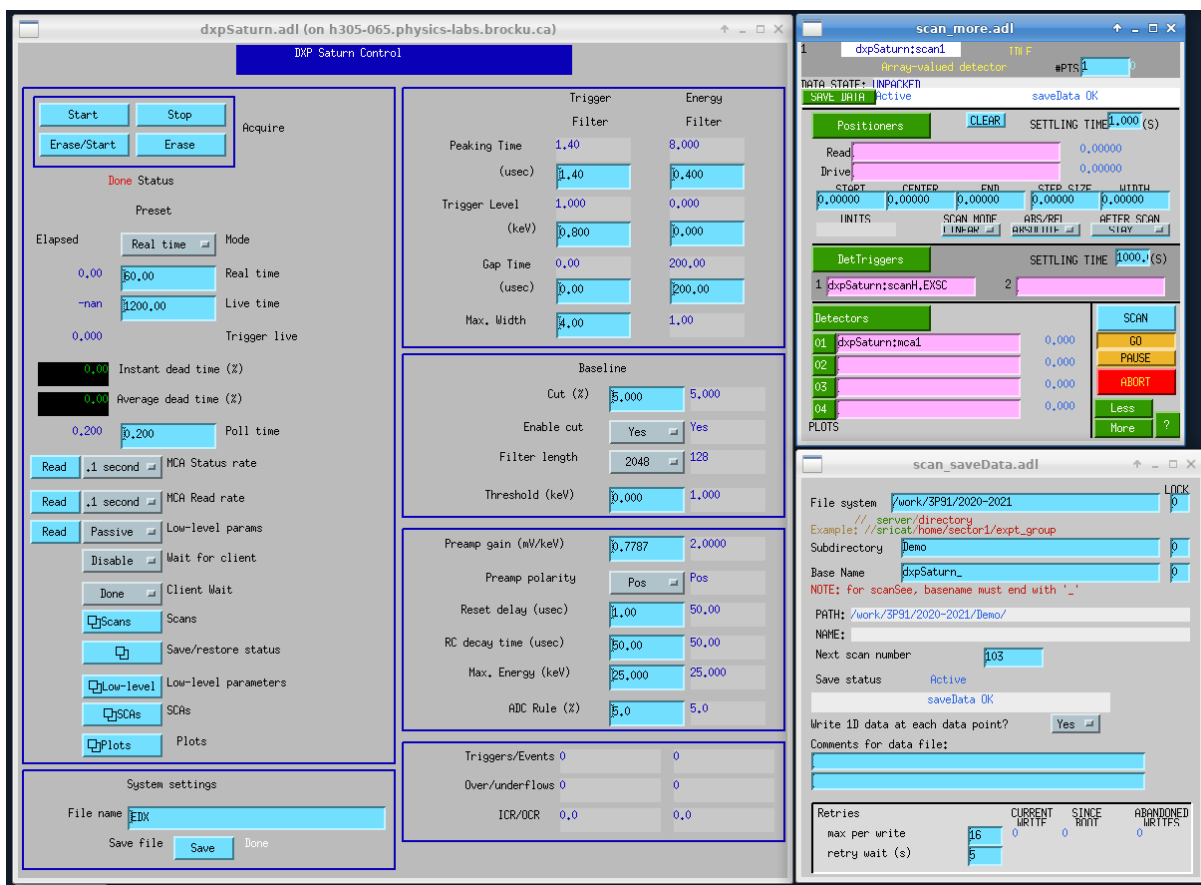


Figure 4.5: The EPICS software interface. MCA display is found under the button "Plots".

Here hkl are the Miller indices of the planes which produce diffraction of photons of energy E_{hkl} . For a particular value of the diffraction angle θ (the detector is positioned at a fixed angle 2θ relative to the incident beam) diffraction from planes with different d_{hkl} values produce diffraction peaks at energies E_{hkl} , given by Eq. 2.1. Diffraction peak energies E_{hkl} are a function of θ (Eq. 2.1); XRF characteristic peak energies are independent of θ . In addition, the diffraction peak intensities are normally much weaker than those produced by the characteristic X-rays fluoresced from the target. Either of the above features may be used to differentiate characteristic X-ray fluorescence and diffraction features in the spectrum.

4.3 Measurement checklist

CAUTION

The instructor will demonstrate the operation of the X-ray machine, the solid-state photon detector and the multichannel analyser. Under no circumstances is the apparatus to be operated prior to instruction. Under no circumstances are adjustments to be made to the target arrangement with the X-ray beam on. The X-ray beam is a radiation hazard. Lead-lined enclosure should always be in place whenever the X-ray beam is on. Radiation exposure badges must be worn by the operator. Failure to maintain radiation safety protocols will result in an immediate involuntary withdrawal from the course.

The objective is to identify the constituent elements (using XRF) of unknown powdered samples. To do that, a series of samples with known XRF energies must be used to first calibrate the MCA energy scale.

Operating the X-ray machine



Figure 4.7: The front-panel controls of the X-Ray machine.

1. Verify that the HV control is set at zero and use the turnkey to turn the machine on. Verify that the cooling water is flowing freely into the drain.
2. Slowly turn up the voltage and current settings to the operational values. The machine is normally operated at a tube voltage of 20–30 kV and a current of up to a maximum of about 15 mA. These values are not at all critical; this voltage range provides an incident X-ray beam spectrum which is reasonably well-matched to that required for both XRF and XRD, and the current setting produces the intensity of the beam that keeps the spectrum acquisition times reasonably short, 30–300 s.

- Align the target. Note that it may be well-aligned by the previous experimenter, so you may want to skip this step initially, and check the strength of the signal from a well-known sample first, but be sure to be able to perform this step if necessary.

Note: The X-ray beam port and shutter must both be *CLOSED* and the X-ray tube high voltage turned OFF prior to making any beam/target alignment changes. This is **mandatory**.

Alignment (*X-ray HV OFF; beam port and shutter CLOSED*): position, visually, a calibration target into the X-ray beam path (which is determined by the axis of the X-ray beam collimator) and set the solid-state detector rotatable platform somewhere in the range $2\theta = 45^\circ\text{--}60^\circ$ relative to the incident X-ray beam path. Check visually, but carefully, that the X-ray beam path strikes the target surface centrally and also that the target surface can be seen by the Si detector. A laser pointer may be useful here. It is not necessary to set a precise value of 2θ ; knowing the approximate value (\pm a few degrees) may be helpful in identifying features of the diffraction spectrum.

Energy Calibration

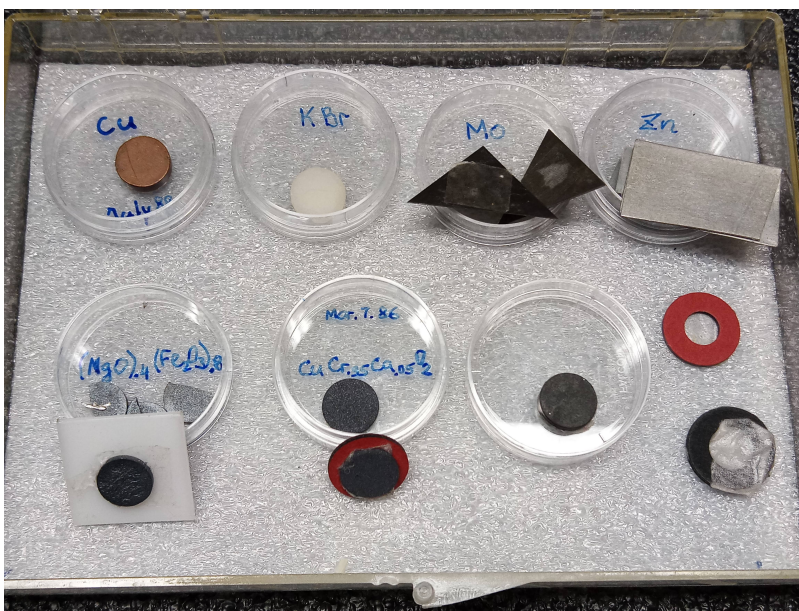


Figure 4.8: A typical sample kit. Note the mounting supports under some of the samples, and extras at lower right.

For the calibration, use samples of Zn, Mo and KBr, others as available. Fig. 4.8 shows a typical sample set made available for this experiment. Be sure to not mix up the samples when replacing them in their respective containers. Some of the samples are of very high purity or may be fragile, be sure to wear gloves and handle the samples with care. For fragile samples, always pre-mount them using mounting supports (washers, teflon sheet pieces), do not mount or peel off the samples directly from the sample holder.

- Spectrum acquisition (*X-ray HV ON; beam port and shutter OPEN*): acquire a “smooth”-looking spectrum in which the peaks are clearly defined, that is the peak locations can be determined by inspection to ± 1 channel number. The XRF lines due to the main elements in the layer are normally significantly stronger than any diffraction lines.

When the accumulation is completed, set the beam port and shutter to *OFF*. In addition, set *HV OFF* before changing the sample.

- Record the channel number n for each of the XRF peaks and identify the peaks with the characteristic energies E_n corresponding to the known elements in the calibration target. You may use plotting

and fitting software to refine your values. A copy of the “X-ray Data Booklet” is made available, use it to supply the true energies of the identified peaks, and establish a calibration relation

$$E_n = a \times n + b$$

with the calibration constants a and b . This calibration can be used throughout the experiment, providing the gain of the detector amplifier and the configuration settings of the MCA remain unchanged. Using the calibration, the energies of XRF and diffraction peaks obtained subsequently in the spectra of other materials may be determined.

6. Diffraction peaks: using the value of d that corresponds to the highest intensity in the calibration samples and an estimated value of 2θ , calculate E_{hkl} values from Eq. 4.4, thus establishing the energy where a diffraction peak might be located. Inspect the $I(E)$ spectrum for such (weak) peaks. If one (or more) are found, change 2θ (by a few degrees) and re-acquire the spectrum to verify that, indeed, the peak energy shifts, *i.e.* is a function of θ .

Analysis of powder samples

7. Alignment (*X-ray HV OFF; X-ray beam port and shutter CLOSED*): install the powdered crystalline target and repeat the beam-target-detector alignment described in step 3.
8. Spectrum acquisition (*X-ray HV ON, X-ray beam port and shutter OPEN*): acquire a spectrum; strong XRF lines and (possibly) much weaker diffraction lines should be visible. Change the detector angle by a few degrees and repeat the accumulation; compare with the previous spectrum. The diffraction peaks shift position in the spectrum, the XRF peaks do not. After this provisional classification into XRF and diffraction lines, keep the detector angle fixed and accumulate until a “smooth” spectrum is obtained. A “smooth” spectrum is a very qualitative term which simply means that the centres of the peaks of interest may be determined by visual inspection to approximately ± 1 channel.
9. Shutdown: when the data acquisition has been completed, close the X-ray beam port and shutter, turn the X-ray current and HV OFF, dial voltage and current controls down to zero, wait for the cooling water to run cold, and turn off the X-ray machine.

Data Analysis

10. Determine the energies of the XRF and diffraction peaks (if any).
11. Using the characteristic X-ray energy tables (see the *X-Ray Data Booklet*), identify the elements in the powder samples. Several samples are provided, some with an expected composition specified and one “unknown”. Verify the presence of the elements in samples of known composition, and determine the composition of the unknown sample.

References

- *X-Ray Data Booklet*, Center for X-Ray Optics and Advanced Light Source, Lawrence Berkeley National Laboratory, University of California, Berkeley, CA. 2009. A copy is available at the console of the X-ray spectrometer.
- EPICS software has a home here: <https://epics-controls.org/>, and the technical documentation for the XIA Saturn driver for EPICS, by Mark Rivers at U. Chicago is here: <https://www.physics.brocku.ca/Courses/3P91/References/MCA/>.