X-ray Fluorescence and Moseley's Law

1. Background

1.1 Ordering of the periodic table

The 19th century saw many efforts to arrange the elements in a sensible order. The chemist John Dalton prepared one of the first tables of the elements in 1803, ordering them by increasing atomic weight. In the following decades it was recognized that groups of elements like lithium, sodium and potassium shared similar chemical properties, suggesting the presence of recurring patterns of chemical behavior. Using this concept, Dmitri Mendeleev developed around 1870 what is now known as the periodic table. Elements were placed in order in the periodic table, largely according to their atomic weight, and numbered consecutively, although no physical meaning was attached to these "atomic numbers". But this scheme had some puzzling anomalies, one of which was the ordering of nickel and cobalt; cobalt has higher atomic weight (58.93) than nickel (58.69), but its chemical properties suggest that it should precede nickel in the periodic table. This anomaly and others (atomic weight of argon is greater than that of potassium, same for tellurium and iodine) were gradually leading to the realization that the significant parameter in terms of ordering the periodic table was not atomic weight but rather the number of electrons and therefore the number of positive charges in the atom. A definitive resolution of these anomalies would await the X-ray measurements of H. G. Moseley.

In 1897 J. J. Thomson discovered the electron and established its discrete nature. The atomic model built on this discovery (the so-called raisin-pudding model) was one with positive charge distributed continuously throughout the atom with the electrons located at equilibrium positions in the atom, about which they oscillated when perturbed. Ernest Rutherford's alpha particle scattering measurements put this model to rest, as they demonstrated that the positively charged part of the atom consisted of a small, dense core, later termed the nucleus. In 1913 Niels Bohr, working in Rutherford's laboratory in Manchester, England, proposed a theory of the atom which combined Rutherford's results with the concept of quantized radiation developed by Planck and Einstein. In Bohr's model, the electron moves about the nucleus in a circular orbit, the attractive force resulting from the Coulomb interaction between the negatively charged electron and a nucleus with equal and opposite charge. The key breakthrough in Bohr's model was the quantization of electron angular momentum. Using this model, Bohr was able to derive the formula for wavelength λ of the light for the various transitions (also known as lines) in hydrogen-like spectra,

$$1/\lambda = R[1/n_f^2 - 1/n_i^2]Z^2 .$$

The integers n_i and n_f represent the angular momentum (units of $\hbar$) of the initial and final states of the electron, and Z is an integer, known as the atomic number, representing the units of charge in the nucleus. R is the Rydberg constant; $R_\infty = me^4/4\pi c\hbar^3$, where m and e are the electron mass and charge, respectively, with the subscript denoting that this formula applies to an infinitely heavy nucleus. For a nucleus of finite mass M, the electron's mass m must be replaced by its reduced mass, $mM/(m + M)$.

Not only did the Bohr model accurately describe the spectrum of the hydrogen atom where $Z = 1$, but also for the singly ionized helium atom where one electron orbits a nucleus with $Z = 2$. The success of the Bohr formula with the hydrogen and helium atoms suggested that it may also apply to transitions in heavier elements. If this proved to be the case, one would be able to order such transitions as a function of Z, thus providing an unambiguous means of ordering the elements in the periodic table.

The stage is now set for Moseley's measurements. It was already known that atoms of a given element emitted X-rays at well defined, characteristic energies. Armed with the new Bohr model, Moseley set about to measure the characteristic energies for a number of different elements, and to correlate the X-ray energy for a given element with the atomic number, Z, of that element.

Moseley's measurements were spectacularly successful. In the words of Robert Millikan (of Millikan oil drop/electron charge fame):

> "In a research which is destined to rank as one of the dozen most brilliant in conception, skillful in execution, and illuminating in results in the history of science, a young man twenty-six years old threw open the windows through which we could glimpse the sub-atomic world with a definiteness and certainty never dreamed of before."

Moseley's life was cut tragically short – he was killed at age 27 fighting for the British in World War I.

By measuring the wavelength associated with a particular line (now designated K_α), from the spectrum of each element, Moseley established that the lines from a large number of elements obeyed the relation

$$1/\lambda = C(Z-\sigma)^2 .$$

This relation is now known as Moseley's Law. C and σ are constants with $C \approx R$ (Rydberg constant) and $\sigma \sim 1$. σ is known as the screening constant. The connection between this formula and the Bohr formula is that $1/\lambda \sim Z^2$ in both cases. A plot representing Moseley's data is shown in Fig. 1. The data can be interpreted as resulting from an electron transitioning from an initial state with $n = 2$ to a final state with $n = 1$, with one other electron screening the nucleus, thus reducing the effective nuclear
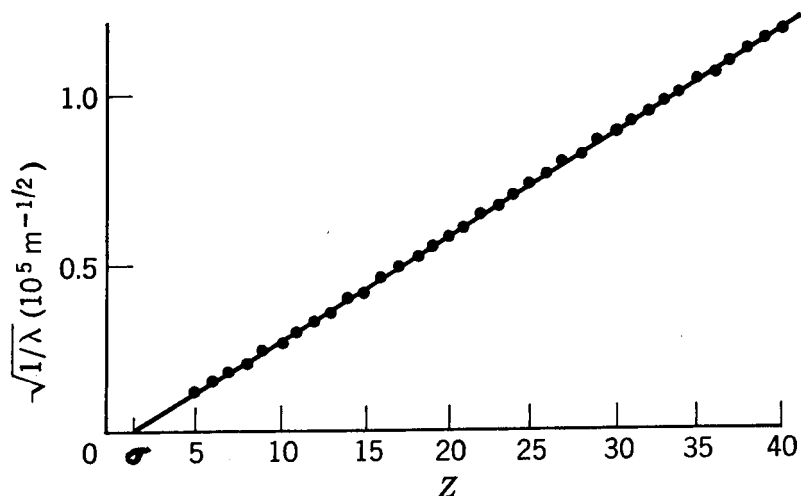

Fig. 1. Moseley's data. The line represents a fit to data using Moseley's Law.

charge to $Z - 1$. An understanding of why the nucleus is screened by only one electron for the K_α lines would await the development of quantum mechanics in the 1920's.

Moseley's work provided an unambiguous means for ordering of the elements in the periodic table – according to atomic number Z. His work helped resolve several outstanding problems with the table: the above mentioned anomalies with heavier elements preceding lighter elements; the assignment of $Z = 44$ to ruthenium, implying that the element $Z = 43$ (technetium, which has no stable isotopes and must be synthesized in a nuclear reactor or particle accelerator) was as yet undiscovered; and the prediction of other as yet undiscovered elements at $Z = 61$, 72 and 75 [1].

With each element emitting X-rays at unique energies, X-ray analysis has become a powerful tool for analyzing chemical composition. X-ray analysis is used to determine the elements present in biological, environmental and geological samples. Fig. 2. shows the X-ray spectrum from a water pollution sample, with channel number on the x-axis being proportional to X-ray energy, and the y axis showing the intensity of the detected X-rays. An X-ray detector very similar to the one you will use in this experiment was used on the Mars Sojourner Rover to analyze the composition of Martian rocks and soil. A spectrum obtained on this mission is available in the laboratory.

As an aside, X-ray energy is obtained from wavelength by multiplying $1/\lambda$ by hc where h is Planck's constant and c is the speed of light; remember $E = $ energy $= h\nu$ and $\nu = c/\lambda$.
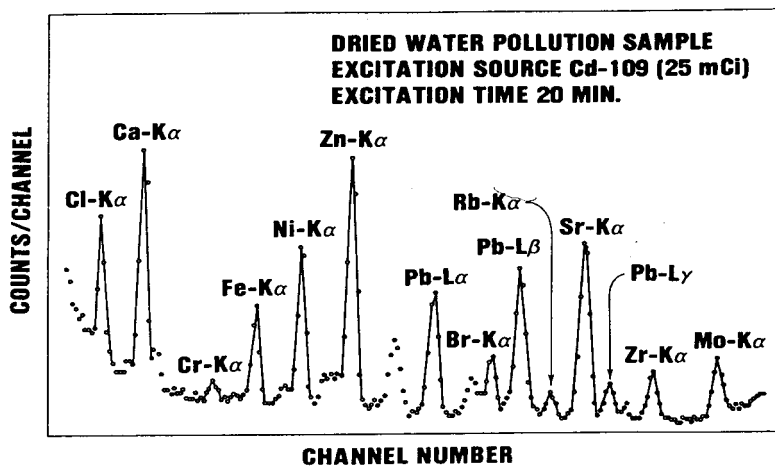

Fig. 2. X-ray spectrum of a water pollution sample.

1.2 Designations of the various X-rays

Moseley selected out one particular line, or energy, from the spectrum of each element to make the plot in Fig. 1. This is to say that there are more than one X-ray line associated with each element. This can be understood in terms of electrons transitioning between the various inner shells within the atom. Each shell is designated by a quantum number n, and an associated letter; $n = 1$, the innermost shell, is known as the K shell, $n = 2$ is known as the L shell, $n = 3$ is known as the M shell, and so on. Fig. 3 shows the possibilities for various transitions (vertical scale not linear – closer to logarithmic). The open arrows pointing upward represent electron transitions from the $n = 1$, $n = 2$, etc. levels to the cross-hatched region known as the continuum, where electrons are no longer bound to the atom. Such a transition results in a vacancy in the electron shell structure. The vacancy is filled when an electron

from an higher lying shell (higher means greater n) transitions to a lower lying shell, accompanied by the emission of a characteristic X-ray. All transitions to the K shell are known as K lines, with the transition from the L shell known as the K_α line, from the M shell as the K_β line, and so on. Transitions to the L shell are known as L lines, and transitions to the M shell are known as M lines. The K lines are clearly more energetic than the L lines, and the L lines more energetic than the M lines.
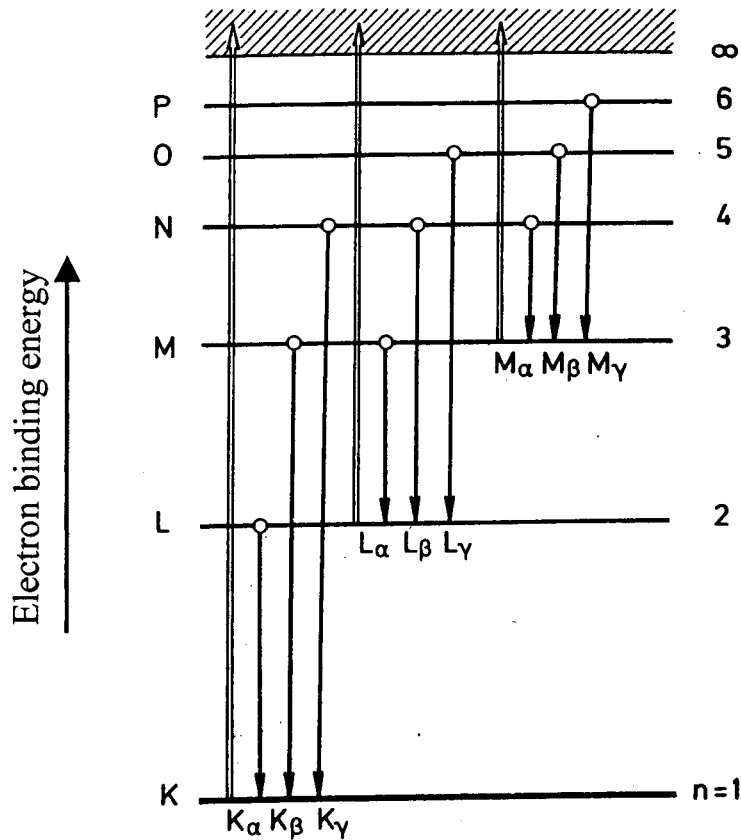

Fig.3. Diagram of K, L, M,… shell energy levels and identification of the various X-ray lines.

Within a given series of lines, K for example, the α line will clearly have less energy than the β line, and the β line less energy than the γ line. Many of the lines have sub-levels resulting from spin-orbit coupling and from screening effects [2]. These various levels are denoted by numerical subscripts, e.g. $K_{\alpha 1}$, $K_{\alpha 2}$. The energy differences between these sublevels are quite small for the lower Z elements. For iron ($Z = 26$) the $K_{\alpha 1}$ and $K_{\alpha 2}$ energies are 6.403 and 6.390 keV, respectively. This energy difference is too small to be resolved by our detector. At higher Z, the energy differences become appreciable; for lead, the $K_{\alpha 1}$ and $K_{\alpha 2}$ energies are 74.957 and 72.794 keV, respectively. This splitting into sublevels is known as the "fine structure" of X-ray spectra.

In general the K_α line is the most prominent feature of an X-ray spectrum. The K_β line will typically have 10–15% of the intensity of the K_α line for $Z \leq 30$, with the intensity ratio increasing to about 30% for the higher Z elements. A spectrum showing the K_α and K_β lines for a manganese target is shown in Fig. 4. For lower Z elements, identifying the K lines is usually the easiest way to determine the composition of a target; the L lines for these elements have very little energy and may not be detected efficiently by the detector, if detected at all. At higher X-ray energies the detector efficiency drops off

so much (see attached efficiency curve for our detector) that the K lines for the higher Z elements will be hard to see. In this case, it may be easier to identify a high Z target by looking for the lower energy L lines.
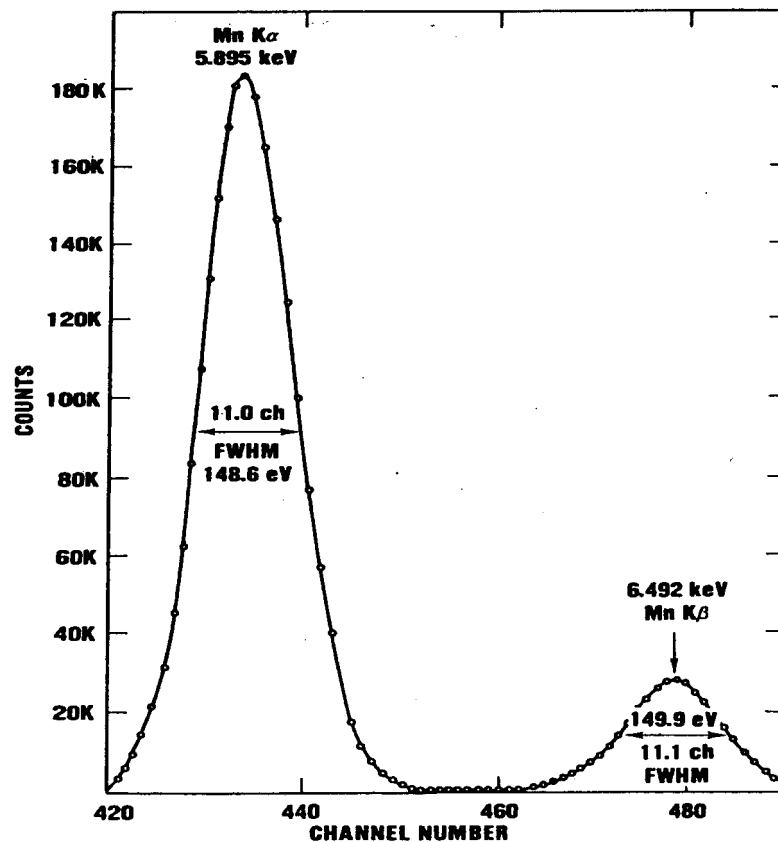
Fig. 4. X-ray spectrum from a manganese target.

1.3 How X-rays are generated

X-rays are photons with energy in the range of approximately 1 keV to 100 keV with corresponding wavelengths of approximately 1 nm to .01 nm. As mentioned previously, an X-ray results when an electron transitions between inner shells of an atom. For such a transition to occur, there must be a vacancy in one of the inner shells to which an electron can transition . How is such a vacancy created? There are three different ways: bombardment of the target with fast electrons; irradiation of the target with energetic photons, and by radioactive decay. In the first two cases, the particle striking the target must have sufficient energy to overcome the binding energy of the ejected electron. With electron bombardment, a sufficiently energetic electron striking the target can eject an inner shell electron from a target atom, thus creating the vacancy; this is how X-rays are generated in medical and dental X-ray machines. In the second case, an inner shell electron is also ejected, but this time by a sufficiently energetic photon. In the third case, a "parent" nucleus changes from Z to $Z-1$ by capturing an electron from the innermost (K) shell, thus leaving a vacancy in the electron shell structure of the "daughter" atom. (This mode of radioactive decay is known as electron capture.)

5

In our apparatus, X-rays are produced by bombarding a target with energetic photons. These photons result from the radioactive decay of ^{57}Co to ^{57}Fe by electron capture. After the decay, the daughter ^{57}Fe nucleus is left in an excited state, and it decays to the ground state by emitting photons with energy of 122 keV and 14 keV (and sometimes a single photon with energy 136 keV). Photons such as these which originate in the nucleus are called gamma rays. The ^{57}Fe atom also emits an X-ray as the K shell vacancy in the ^{57}Fe atom is filled.

References

1. R. Eisberg and R. Resnick, *Quantum Physics of Atoms, Molecules, Solids, Nuclei and Particles*, 2d ed., Wiley, New York, 1985, p. 342.

2. H. Haken and H. Wolf, *The Physics of Atoms and Quanta*, Springer, New York, 1996, pp. 314.

2. The Experiment

2.1 Required exercises

The primary goal of this experiment is to verify Moseley's Law. X-ray spectra from known samples will be used for the verification and to calibrate the energy scale of the detector. With the energy calibration established, the system is then used to establish the identity of several unknown samples. Detailed procedure for operating the system follows in Part 3.

The known samples, in order of increasing *Z*, are:

Cl	$Z = 17$	(in the form of NaCl)
Ti	22	
Cr	24	
Fe	26	
Ni	28	
Cu	29	
Zn	30	
Ag	47	
Cd	48	
Sn	50	
Gd	64	

Identify the K_α lines from the known samples and plot $(1/\lambda)^{1/2}$ vs. *Z*. A table of X-ray energies is attached to this write-up. From the slope and intercept determine values for the constants *C* and σ:

$$1/\lambda = C(Z-\sigma)^2 \,,$$

where σ is known as the screening constant. How close is σ to 1? How would you argue for a value different from 1?

State your result for C in terms of the Rydberg constant, $R = me^4/4\pi c\hbar^3$, where m and e are the mass and charge of the electron, respectively. In practical units, $R = 1.0974 \cdot 10^7$ m^{-1}. Approximately what fraction of R is C? How do you explain this?

Acquire an X-ray spectrum for 3 or 4 of the unknown targets. Identify the element(s) in each target from the acquired spectrum.

2.2 Optional exercises

1. Acquire an X-ray spectrum for a number of the higher Z ($Z \geq 47$) elements and identify the Lα lines. Plot $(1/\lambda)^{1/2}$ vs. Z and obtain the slope and intercept as you did for the K$_\alpha$ lines. Interpret the values you derive for the slope and intercept, again in terms of the Rydberg constant R and the number of electrons screening the nucleus for the L$_\alpha$ lines.

2. Run the apparatus for 30-60 minutes (or longer, if possible) without a target and try to identify the x-rays in the background which are superimposed on any data you obtain with a given target.

3. Apparatus and Procedure

3.1 General Comments

This apparatus consists of a ^{57}Co radioactive source (same source as in the Mossbauer Experiment), a set of targets of different elements, and an Amptek XR-100CR semiconductor detector. This detector measures the X-ray energy directly, in contrast to Moseley's method of measuring X-ray wavelength. The advantage of a detector like ours is the compact size and ease of operation. However, for resolving closely spaced lines in an X-ray spectrum, wavelength measurement remains the standard.

The XR-100CR detector is optimized to detect photons in the energy range of 1 to 30 keV. The efficiency of the detector drops off rapidly at higher energies (see attached efficiency curve). The output of the XR-100CR detector is conditioned and amplified, and then sent to a mulitchannel analyzer (MCA). This device plots number of counts on the y axis vs. energy, in the form of channel number, on the x axis. A typical plot of the MCA output will look something like the plots in Figs. 2 and 4.

Caution: the radioactive source, target and detector are all located inside a lead lined box with a hinged lid. The lead lining provides sufficient shielding so that it is safe to be around the closed box for long periods of time. An additional layer of lead inside the box covers the source so as to reduce exposure when the box is open, as when changing targets. The source strength (posted inside box) is sufficient that it is prudent to minimize the increased exposure when the lid is open. **Open the lid of the box only as necessary to change or remove targets. Be sure to keep the lid closed at all other times.**

3.2 The XR-100CR Detector

The XR-100CR semiconductor detector consists of a piece of silicon 300 μm thick. One side of the silicon (anode) is doped with an excess of p-type impurities, and the opposite side (cathode) with an excess of n-type impurities, resulting in the formation of a p-n junction, just as in a conventional diode. Within the silicon, electrons from the n-type region diffuse across the junction toward the p-type region, and holes from the p-type region diffuse across the junction toward the n-type region. This net migration of charge results in the development of a voltage across the p-n junction, and the formation of a region in which there are no free charge carriers. This region is called the depletion region, and the electric field due to the charge migration reaches a maximum within this region. When electron-hole pairs are created in this region, the electric field acts to sweep the electrons and holes in opposite directions, resulting in a net current through the diode. Since the effect of incident radiation is to create electron-hole pairs in the silicon (one pair for every 3.62 eV of energy in the incident photon), the integral of the current pulse resulting from a photon impinging on the detector will be a measure of that photon's energy. The integral of the current pulse is in turn amplified to produce a shaped output pulse, the (peak) amplitude of which is proportional to the collected charge, and therefore incident photon energy.

The depletion region is clearly the key part of the detector, as electron-hole pairs formed there will move in opposite directions and contribute to the desired energy measurement. Increasing the width of this region increases the probability that the incident radiation will be stopped there and its energy deposited within the region. In order to increase the width of the depletion region, an external bias potential is applied across the detector, with the positive side connected to the cathode, and the negative side connected to the anode. (Note: this bias is applied in the opposite sense of a forward bias, and hence is termed a reverse bias.) The effect of the reverse bias is to pull electrons remaining in the n-type region and holes remaining in the p-type region even further from the p-n junction, resulting in a wider depletion region. In the absence of an external bias, the depletion region is typically some 10's of μm wide, whereas with the bias applied, the depletion region can encompass almost the entire body of the silicon detector. The external bias also acts to increase the strength of the electric field in the depletion region, resulting in increased charge collection efficiency as electrons and holes are less likely to experience recombination or trapping when they are swept out of the region more rapidly.

Electron-hole pairs are also generated by thermal excitations in the silicon. Pairs so generated will add noise to energy measurements and degrade the resolution of the detector. In order to reduce the thermal generation of electron-hole pairs, the detector is cooled to approximately 250 K. The cooling is accomplished with a thermoelectric heat pump.

A natural question arises at this point: how linear is the XR-100CR detector? It turns out that semiconductor detectors are in general very linear, and the manufacturer of the XR-100CR quotes a linearity of .1% over the 1 to 30 keV design range of this device.

To protect the XR-100CR detector it is covered by a beryllium window. To pass lower energy X-rays (several keV), this window must be very thin. The window on our detector is .001" thick. Such a thin window is, of course, very fragile, and being made of Be, also very brittle. **<u>Any contact with the window can easily damage it.</u>** In order to help protect the window, the red plastic cap (with a hole in the end) must be left in place at all times.

3.3 Procedure: preliminary setup

Now is a good time to turn on the MCA and XR-100CR amplifier/power supply if you have not already done so. The power switch for the amplifier/power supply is at the back of the unit on the left side. The RTD (Rise Time Discriminator) should be on (switch up). Also turn on the dmm. The dmm current reading in μA indicates the detector temperature in Kelvins. Typical operating current is 248 ± 2 μA.

The output pulses from the XR-100CR detector amplifier are positive-going, 0-8 volts peak amplitude. For a given energy incident photon, the amplitude of the output pulse will depend on the amplifier gain setting. The gain is set with the 10-turn potentiometer, and can be varied from 0 to 10.00 units (number in window is the integer, number on dial the fraction). Setting the gain involves a trade-off between the maximum energy you want to detect and the ability to resolve closely spaced lines. The lower the gain, the higher the energy you will be able to detect, but the energy scale will be more compressed and the more difficult it will be to resolve closely spaced lines. At maximum gain, the sensitivity is around 1 volt of output pulse amplitude per keV of incident photon energy. More precisely, with the gain set at 1.00, the detector creates pulses with heights of 1 volt per ≅8.4 keV of photon energy.

Before acquiring any spectra, choose an upper bound on the X-ray energy you wish to measure, and set the XR-100CR amplifier gain accordingly. Once this gain is set, it is a good idea to lock the 10-turn potentiometer with the small black lock lever to the right of the dial. As a practical matter, the highest Z target available in the lab that will yield a spectrum in a reasonable amount of time is gadolinium, with $K_{\alpha 1}$ energy = 42.98 keV. With this number in mind, you also want to have a reasonable amount of "headroom", or signal above this maximum value so that you can resolve the highest energy. A good choice is to use 50 keV as a maximum energy, and to set the gain so that you get peak heights of about 7.5 volts with this energy. To record a 50 keV photon so that it has a pulse height of about 7.5 volts, a proportional argument gives

$$\frac{\text{Gain} = 1.0}{1\,\text{V}/8.4\,\text{keV}} = \frac{\text{Gain} = x}{7.5\,\text{V}/50\,\text{keV}} \quad \Rightarrow \quad x = 1.26$$

The amplifier output is connected to the input of a computer-based high speed data acquisition card. A LabVIEW application is used to perform the data acquisition and create a pulse-height histogram from the input pulse waveforms. The user of the program may select the resolution of the histogram, i.e., the number of bins, along with other parameters. The resulting data sets can also be analyzed to find peak locations and widths in terms of the pulse height voltages.

Start the LabVIEW application according to the instructions from the TA or lab manager. A variety of parameter choices will produce a reasonable spectrum, but experience shows that the following settings are a good place to start:

Low level disc	300 mV
Hysteresis	50 mV
Digitizer vertical range	10 V
Digitizer sample rate	20.00 MHz
Digitizer record length	8000 points
Histogram update	5 cycles
Histogram bins	1000
Histogram minimum	0 V
Histogram maximum	7.9 to 8.0 V*

* If too many counts show up at the 8 volt max, back the histogram maximum off a bit to 7.9 V.

3.4 Acquiring a Spectrum

Before placing any targets in the lead lined box, the TA, Professor or lab manager will go over the hardware arrangement inside the box with you. Again, it is prudent to minimize the time that the lid is open so as to minimize radiation exposure. After going over the hardware arrangement inside the box, place a target (Fe is a good one to start with) in the holder and close the lid.

Start the LabVIEW application "LabVIEW Pulse Height Analyzer" whose icon should be on the desktop. Then click on the arrow button at the upper left corner of the application window. When it starts, the program will load the most recent data set. First, you should clear any old data by clicking on the CLEAR button. Then start data acquisition by clicking on the TAKE DATA button. After a short delay you should see the blue dots of the histogram graph appear.   Let the data taking run until you can see clear peaks appear, and then a bit more until the spectrum is well established.

After you stop the data acquisition (how should be obvious), it is a good idea to save the data set with the SAVE DATA button and to print out the entire spectrum with the PRINT DATA button. Then you can use the ANALYZE DATA dialog box to fit a Gaussian peak shape to the important peaks. Detailed instructions for using the pulse height analyzer and analysis feature are available under the SHOW INSTRUCTIONS buttons.

As you acquire spectra for the different elements, make a rough graph of energy vs. pulse height for the *K* lines. (Consult the attached energy tables to find the energies for the lines of interest.) This graph may help you identify the unknown samples.