

X-Ray Fluorescence (XRF) spectrometry for materials analysis and “discovering” the atomic number

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X-Rays were discovered in 1895 by the German scientist, Wilhelm Conrad Roentgen. This discovery opened doors for the development of X-Ray Fluorescence (XRF) spectroscopy which has now become a powerful and versatile technique for the analysis and characterization of materials. It distinguishes different elements present in a sample according to the characteristic X-ray energies emitted by them and helps in determining their respective concentrations.

In this experiment we will use XRF spectroscopy to analyze a sample’s elemental composition. From the characteristic X-ray energies, we will also verify Moseley’s Law which is a proof of the existence of a fundamental quantity, the *atomic number*. The atomic number increases in regular steps with an increase in the characteristic X-ray energy. We will use this relationship to find the Rydberg’s energy constant and screening coefficient for K_α X-rays.

KEYWORDS:

X-Ray Fluorescence (XRF) · Characteristic X-Rays · Bremsstrahlung Radiations · Moseley’s Law · Atomic number · Screening coefficient · Rydberg’s energy·

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1 Objectives

In this experiment we will,

1. differentiate between characteristic X-rays and Bremsstrahlung radiations,
2. use characteristic X-rays to identify elements,
3. acquire a spectrum, calibrate it and use it for qualitative (element identification) as well as quantitative (elemental concentration) analysis, and finally,
4. verify Moseley's law and the validity of an atomic number.

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2 Theoretical introduction

X-rays are part of the electromagnetic spectrum with energies ranging from 0.1 to 100 keV.

2.1 Production of X-rays

X-rays are produced by one of the three following mechanisms,

1. deceleration of high velocity electrons in the vicinity of a target nucleus,
2. atomic transitions between discrete energy levels, and
3. the radioactive decay of some atomic nuclei.

Each mechanism leads to a typical spectrum.

An **X-ray tube** is a commonly used device for the generation of X-rays by bombarding highly accelerated electrons on a heavy metal target. X-ray production in this manner results from the first two of the mechanisms listed above.

A schematic for producing X-rays is shown in Figure 1. Electrons are ejected thermally from a filament behind the cathode and accelerated towards the heavy metal anode by a high voltage (in kilovolts range). Upon hitting the target (anode), these fast electrons decelerate and lose energy in the form of high energy photons.

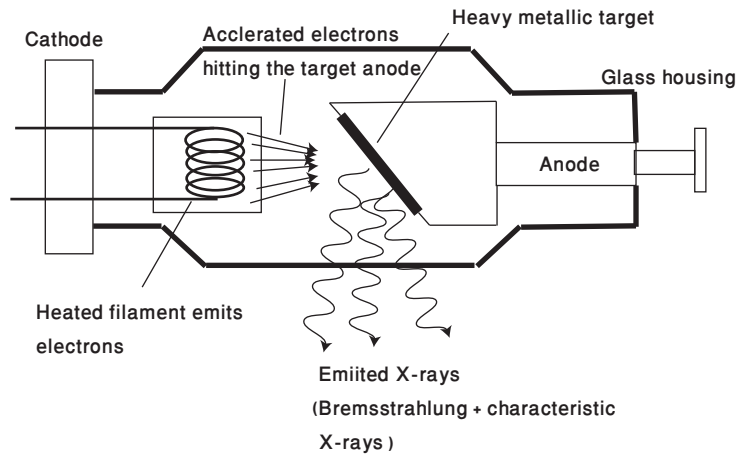


Figure 1: A simplified picture of an X-ray tube illustrating process of generating X-rays.

These photons are the X-rays, with precise value of energy depending on the kind of target used. The intensity of the X-rays produced is dependent on the number of electrons hitting the target (or tube current), which in turn depends on the temperature of the filament emitting the electrons. However, increasing the X-ray tube current at a constant X-ray tube voltage increases the X-ray intensity without affecting the energy distribution [1, 2].

The production of X-rays by two different atomic processes, the X-ray fluorescence and the bremsstrahlung radiation is discussed below.

2.2 X-ray fluorescence

X-ray fluorescence is the emission of characteristic or secondary X-rays from a material that has been excited by bombarding with high energy electrons, or other X-ray or γ -ray photons. If the incident particle has enough energy, it can knock out an orbital electron out of the inner shell of the target atom. To fill the vacancy, one of the electrons from the higher shells then jumps to the inner shell, emitting in the process, a photon with energy equal to the difference in binding energy of the two shells. The process is illustrated in Figure 2 (a).

The X-ray fluorescence produces an emission spectrum of X-rays at discrete energies. These emission spectral lines depend on the target element and hence are called characteristic or fluorescent X-rays. We can use these spectra to identify the elements by comparing the peak's energy with the element's binding energy [3].

Q 1. XRF can yield results only for elements with $Z > 16$ in air. Explain why the lighter elements cannot be analyzed?

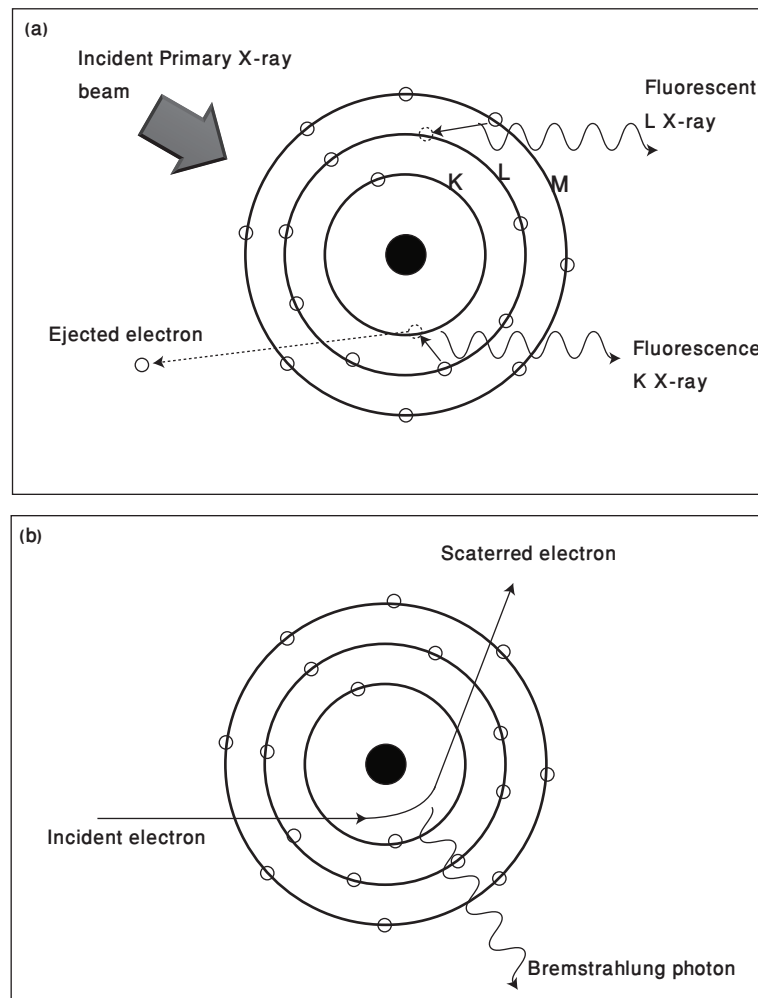


Figure 2: X-ray emission through (a) fluorescence and (b) bremsstrahlung radiation. (a) illustrates the characteristic emission of K and L X-rays as a result of electronic transition from L to K and M to L shells respectively, (b) shows a decelerating electron emitting bremsstrahlung X-rays.

2.3 Bremsstrahlung radiation

Bremsstrahlung is a German word for *braking radiation*. Accelerating charges give off electromagnetic radiation. In an X-ray tube, depicted in Figure 1, electrons travel from cathode with high speed towards the anode and penetrate the anode material. When these electrons pass in close proximity to the strong electric field of the nucleus, they get deflected and are decelerated by the attractive force from the nucleus, hence radiating X-rays, which are called braking or bremsstrahlung radiation. The production of these X-rays is illustrated in Figure 2 (b).

This gives off a continuous distribution of radiation which becomes more intense and shifts toward higher frequencies when the energy of the bombarding electrons or the tube voltage (kV) is increased [4].

The bremsstrahlung spectrum can be described as follows.

An electrostatic field exists around the nucleus in which electrons experience the *braking* force. The nuclear field can be imagined as a target with the actual nucleus located in the center, as shown in Figure 3 (a). An electron striking anywhere within the target experiences a braking force and produces an X-ray photon. Now, the electrons striking closest to the center are subjected to the greatest force and lose the most energy to produce the highest energy photons while the electrons hitting the outer zones experience a weaker force and produce lower energy photons. The outer zones capture more electrons and create more photons. For this extremely simplified model, an X-ray energy spectrum is predicted to be like the one shown in Figure 3 (a).

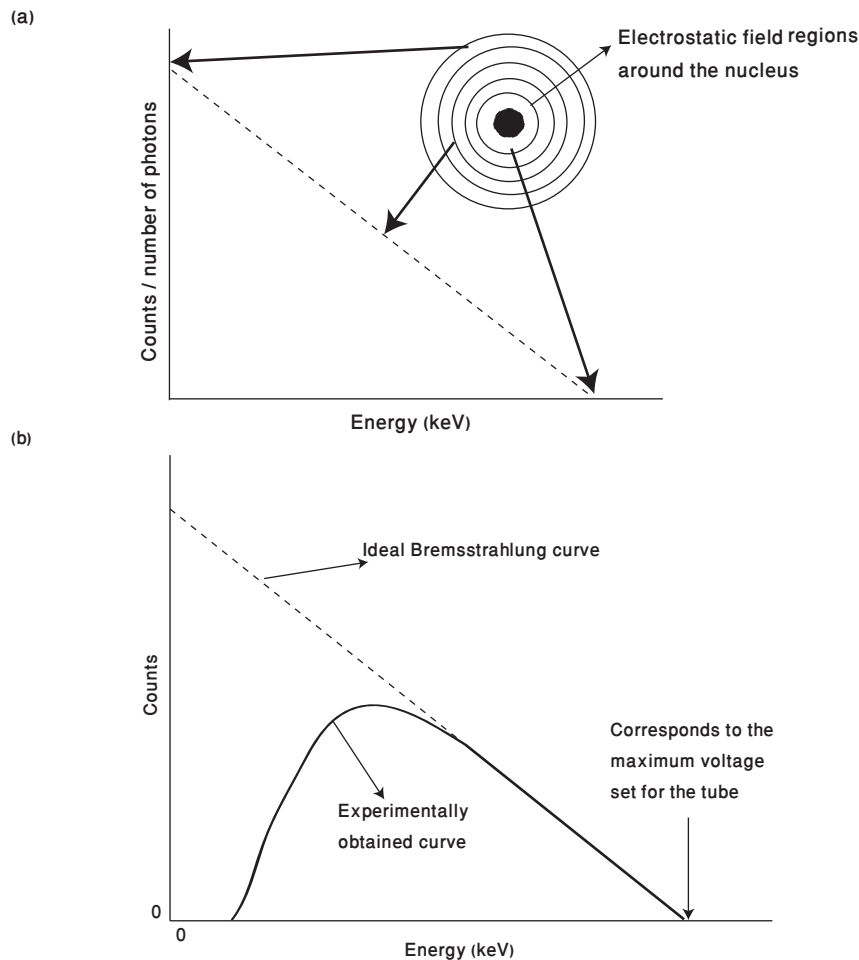


Figure 3: (a) A model for bremsstrahlung production and the associated X-ray photon energy spectrum, (b) an ideal bremsstrahlung curve shown as dashed line compared to the experimentally obtained solid curve.

Q 2. Discuss the bremsstrahlung curve and its shape. From Figure 3 (b), discuss the ideal and the experimentally obtained bremsstrahlung curves and comment on the reason for deviation from the ideal behavior.

The high-energy end of the bremsstrahlung spectrum is determined by the tube voltage (kV) which establishes the energy of the electrons as they reach the anode. Higher the tube voltage, greater would be the number and energies of electrons

striking the inner zones of nuclear force resulting in higher energy X-ray photons.

Q 3. In the spectra of Figure 4, distinguish between characteristic X-rays and bremsstrahlung radiation. Why is the Figure (b) more spread out along the energy scale as compared to (a)?

The tube voltage also influences the production of characteristic radiation. No characteristic radiation will be produced if the voltage is insufficient to overcome the binding energy of the K -shell electrons corresponding to a threshold voltage as shown in Figure 4 (a) and (b).

2.4 Detection of fluorescent X-rays

The detection of X-rays is based on various methods. The most commonly known methods in the past were photographic plates, Geiger counters and scintillators but from 1970 onwards, semiconductor detectors have been developed and used, using silicon or germanium as the detection elements. These detectors detect individual X-ray photons that are reacting with the detector material. Each individual photon is detected and then, over time, accumulated measurements make an accurate picture of the radiation coming from the source.

A PIN diode detector is today the most commonly used solid state X-ray detector. It consists of an intrinsic semiconductor region sandwiched between a p -type and n -type material, as shown in Figure 5. The X-ray photon enters the intrinsic region and causes an avalanche multiplication of charges and the reverse bias field sweeps the charges out of the region, resulting in a detectable and measurable current.

The mechanism of current production is illustrated in Figure 5. Each X-ray photon absorbed in the detector creates an electron-hole pair. The ejected electron will possess an amount of kinetic energy equal to the difference between energies of the incident photon and the band gap of the detecting material. This electron will collide with other atoms and will cause further ejection of charge carriers in the detector, producing an avalanche of charges. The migration of the electron and holes takes place under the influence of a voltage maintained between the p - and n -type faces of the detector, which constitutes a pulse of current. The pulses created are then amplified, recorded, and analyzed to determine the energy, number and identification of the elements.

The sensitivity of these detectors is increased by operating them at low temperatures which suppresses the random formation of charge carriers by thermal vibration [5].

2.5 Energy dispersive X-Ray fluorescence (EDXRF)

A schematic representation of an EDXRF spectrometer setup is shown in Figure 6. The setup of EDXRF instrumentation is quite simple, consisting of four basic components,

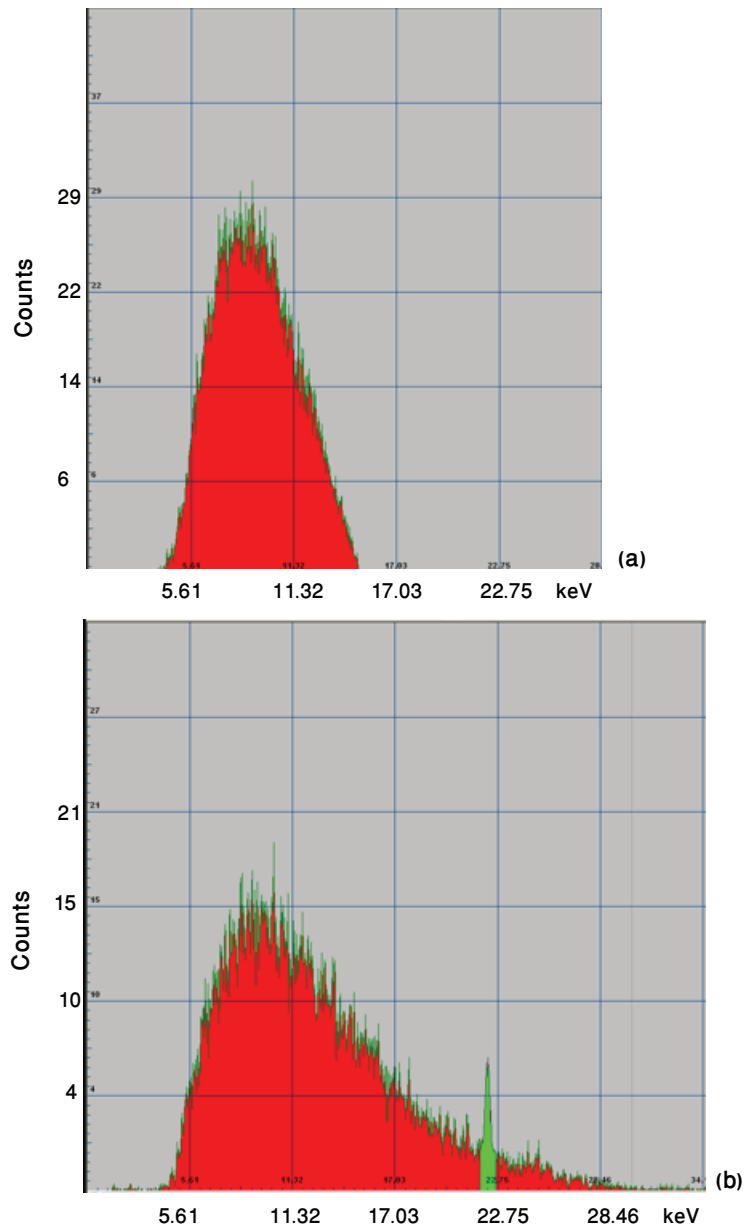


Figure 4: Mini-X, X-ray tube output Spectrum with Ag as target anode (a) at 15 kV and 2 μA . Clearly the tube voltage is insufficient to overcome the binding energy K -shell electrons and produce Ag K_{α} X-rays; (b) at 30 kV and 2 μA , the spectrum shows a triangular bremsstrahlung continuous spectrum along with a distinguished characteristic X-ray peak of silver near 22 keV

- excitation source,
- sample,
- detector, and
- data collection and analyzing system.

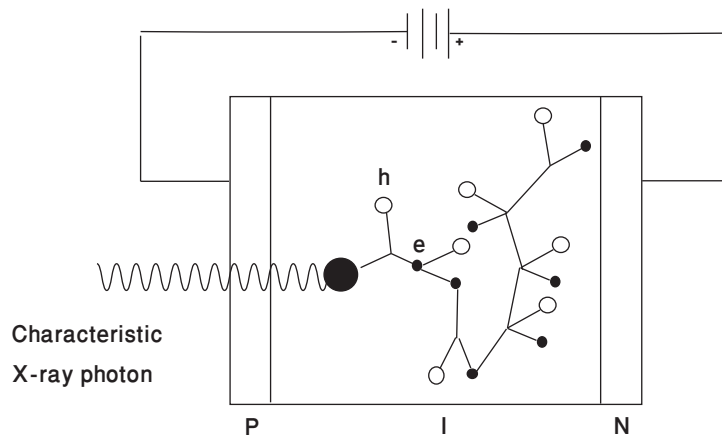


Figure 5: A PIN diode detector. The characteristic photon produces a single electron hole pair, if the electron produced has got enough energy, the charge keeps on multiplying by collisions; e and h represent electrons and holes respectively.

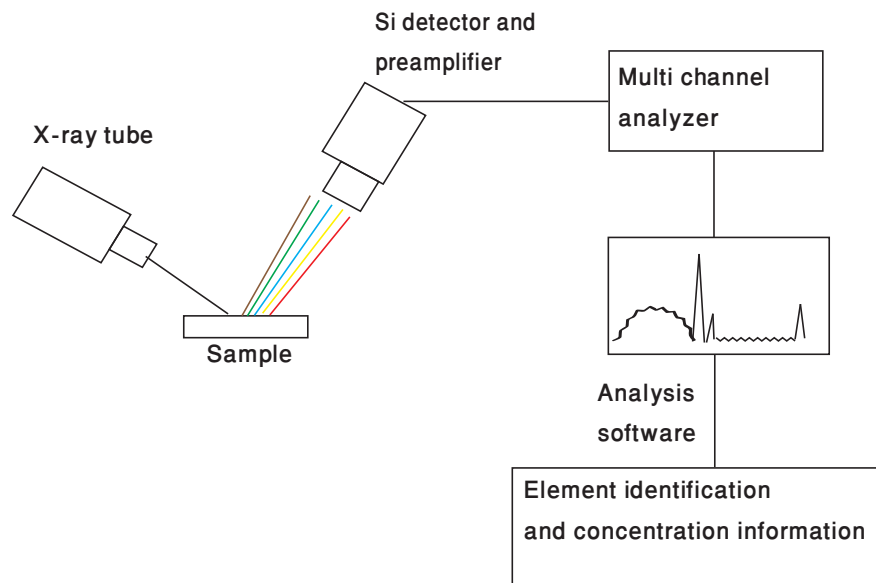


Figure 6: The schematic of an EDXRF Spectrometer. The X-rays from the source irradiate the sample, characteristic X-rays are detected by the Si detector, the multi channel analyzer separates different elemental peaks and the analysis software gives the final list of elements and their concentrations.

The EDXRF spectrometer helps plotting the relative abundances (in terms of intensities) of characteristic X-rays versus their energy. The characteristic X-rays generated strikes the detector element (in this case Silicon), creating an electron hole pair, which produces a charge pulse proportional to the energy of the X-ray. This charged pulse is converted to a voltage pulse by a charge sensitive preamplifier. A multi channel analyzer (MCA), is then used to analyze these pulses and sort them according to their voltages. This data is then sent to the computer interface, where it is displayed as the spectrum of the X-ray irradiated sample. The spectrum is further processed to identify elements and quantitatively analyzed to find the

respective concentrations in a sample [6].

Q 4. What is a wave dispersive X-ray fluorescence spectrometer? What is the difference between EDXRF and WDXRF and advantages of using one over the other [7]?

2.6 Moseley's Law

The power of XRF analysis was first realized by Henry Moseley in 1912, seventeen years after Wilhelm Roentgen had discovered the X-ray.

2.6.1 How atoms got their atomic numbers

Mendeleev's periodic table of the elements was a significant advance in chemistry, reflecting the similarities in the chemical properties of the elements and their periodic recurrence with an increase in the atomic mass. For over 40 years, the atomic mass was a useful guide for scientists, but it provided no explanation for the periodicity of properties of the elements. During the early decades of the twentieth century dramatic advances in physics revealed the structure of atoms and uncovered the physical basis of the periodic table. The atomic number was explained as the number that specifies the position of an atom in the periodic table and is the number of positive charges in the atomic nucleus.

The basis was laid in 1911 when Rutherford discovered the atom's nuclear core after which Bohr in 1913 showed that the nuclear charge Ze determines the scale of the energy states of an atom. In the same year, Moseley measured the wavelengths of X-rays emitted by many different kinds of atoms and showed that each chemical element is uniquely identified by its nuclear charge. In other words, the nuclear charge number Z specifies the position of an element in the periodic table and is, therefore, the same as the atomic number which is the serial number of the element in the periodic table. Hence the properties of X-ray line spectra were the basis of Moseley's discovery, and this is how elements got their atomic numbers !

2.6.2 X-ray line spectra

In 1905, a decade after Roentgen discovered X-rays, the British physicist Charles Barkla found that a target struck by a beam of high energy X-rays (primary/incident beam) emitted secondary X-rays distinctly different in behavior from those in the incident beam. He discovered that the secondary X-rays emitted by a target are unique to the chemical element the target is made of, so he called them characteristic X-rays, and pointed out that they could be used to identify the target material.

Barkla had, infact, discovered a new means of chemical analysis. From his measurements of the absorption of X-rays Barkla found that an anode emits two distinctly

different types of characteristic X-rays, a more penetrating type (shorter wavelengths, higher energy) that he called K radiation or K X-rays, and a more easily absorbed type (longer wavelengths, lower energy) that he called L radiation. These emissions are called X-ray lines because they are analogous to the spectral lines in the visible light spectra of atoms and are a unique fingerprint of the emitter atom [8].

2.6.3 Mathematical formulation of Moseley's law

Moseley studied X-ray line spectra and discovered a simple relationship that allowed him to predict the frequencies (energies) of X-rays for any element and to see that the charge of the atomic nucleus is the property that gives an atom its identity. Moseley after studying the X-ray line spectra in detail found that the most intense short wavelength line in the characteristic X-ray spectrum from a particular target element, called the K_α line, varied smoothly with that element's atomic number Z .

From Bohrs theory of atomic structure, something you have already studied in your Modern Physics class, the energy of an electron in its orbit n is given by,

$$\begin{aligned} E_n &= -hc \frac{R_\infty Z^2}{n^2}, \\ &= -\frac{R_\infty Z^2}{n^2}, \end{aligned} \quad (1)$$

where h is Planck's constant, c is the velocity of light, $R_\infty = 1.097 \times 10^7 \text{ m}^{-1}$ is the Rydberg constant for an infinitely heavy nucleus, $R_{E\infty} = hcR_\infty = 13.06 \text{ eV}$ is Rydberg energy, Z is the nuclear charge, and n is the principal quantum number used to designate energy levels.

The emission of radiation from the atom, according to Bohr, is due to the transition of the atom from an initial higher energy state E_i to a final lower energy state E_f , and the frequency ν of the emitted radiation is given by the condition,

$$E_i - E_f = h\nu.$$

Now, a K_α X-ray emission is due to transfer of an L -shell ($n = 2$) electron to the K -shell ($n = 1$), where a vacancy has been created by irradiating the atom with incident X-rays prior to the transition. Hence the energy of the K_α photon is, using (1),

$$\begin{aligned} E_{K_\alpha} &= -R_\infty Z^2 \left(\frac{1}{2^2} - \frac{1}{1^2} \right), \\ &= \frac{3R_\infty Z^2}{4}, \end{aligned} \quad (2)$$

which shows that the energy of characteristic K_α X-rays is proportional to square of the nuclear charge. In the X-ray notation, the subscript α refers to the transitions

of electrons from L to K shell. A K_β X-ray is emitted when electron jumps from an M ($n = 3$) to the K shell.

Moseley, who was studying K_α X-ray spectra at the same time as Bohr, used this expression, but modified Z to $Z - 1$ to fit to his experimental data. Thus, Moseley's relationship was,

$$E_{K_\alpha} = \frac{3R_{E\infty}(Z - 1)^2}{4}. \quad (3)$$

The above equation is usually referred to as Moseley's law [9].

2.6.4 Effective nuclear charge and the screening effect

Moseley used $Z - 1$ instead of Z in (3) which is attributed to the fact that the electron is not only attracted to the nuclear charge $+Ze$ but is also repelled by other electrons. Within a few years, this very idea had become commonplace in the understanding of the multielectron atom, the true nuclear charge Z could be replaced by an effective charge given by

$$Z_{\text{eff}} = Z - \zeta, \quad (4)$$

where ζ was called the screening constant [10, 11]: neighboring electrons "screen" or "shield" the nuclear attraction. Thus, (3) could be modified to state that the energy of an electron in a multi electron atom could be given approximately by,

$$E_{K_\alpha} = \frac{3R_{\infty}Z_{\text{eff}}^2}{4}. \quad (5)$$

Q 5. Explain what does the screening factor indicate? Is there a way to determine this factor experimentally?

3 Experimental Apparatus

Amptek's XRF kit available and setup in our laboratory, is a package designed to help the user quickly begin doing elemental analysis via X-ray fluorescence. Once this kit is assembled and the software configured and calibrated, one can begin doing simple analyses. The XRF kit consists of the following parts:

- **XR100 CR detector** with Si-PIN diode, to collect the X-rays reflecting off the sample,
- **Mini-X USB controlled X-ray tube**, being used as an X-ray source,
- **PX4 digital pulse processor** is a pulse processor as well as a multi-channel analyzer (MCA); in terms of counts, it distributes the detected X-rays over its physical channels with respect to their energy, also working as the interface between the detector and the computer,

- **XRF mounting plate** on which the X-ray source and detector are mounted according to the guiding sketch imprinted on it, and

Be careful: Be very careful when handling the XR100 Si detector; the window of the detector is brittle and can be damaged beyond repair by mishandling. Also, touching the detector may interfere with its thermoelectric cooling system [13].

Safety Note: Before turning the X-ray source ON, make sure that the brass-aluminium radiation shield is properly in place, to avoid exposure to radiation. Also be careful in placing the shield, making sure that it does not bump into the outer windows of the X-ray source tube or detector [15].

Q 6. How does the Si detector measures the energy of the X-ray photon?

3.1 Standard materials used in the experiment

We will use three kinds of standard reference samples in our experiment.

3.1.1 Stainless steel (SS-316)

The composition of the stainless steel alloy is given in the following table.

<i>Cr</i>	<i>Mn</i>	<i>Fe</i>	<i>Ni</i>	<i>Cu</i>	<i>Mo</i>
18.45	1.63	65.19	12.18	0.17	2.38

Table 1: Elemental composition (wt %age) of Amptek's stainless steel standard sample [12].

3.1.2 Chromium copper alloy (IARM-158B)

The composition of the chromium copper alloy is given in the following table.

<i>Cr</i>	<i>Ag</i>	<i>Al</i>	<i>Fe</i>	<i>Mn</i>	<i>Ni</i>	<i>Pb</i>	<i>Si</i>	<i>Sn</i>
0.85	0.01	0.002	0.09	0.019	0.32	0.01	0.02	0.01
<i>Zn</i>	<i>Cu</i>	<i>As</i>	<i>C</i>	<i>Co</i>	<i>P</i>	<i>S</i>	<i>Sb</i>	<i>O</i>
0.014	98.5	0.001	0.002	0.002	0.005	0.003	0.002	0.005

Table 2: Elemental composition (wt %age) of chromium copper standard sample, obtained from Brammer [16].

3.1.3 Silicon brass alloy (31X-WSB7)

The composition of the silicon brass alloy is given in the following table.

<i>Si</i>	<i>Zn</i>	<i>Cu</i>	<i>Al</i>	<i>Pb</i>	<i>Fe</i>	<i>Mn</i>	<i>Ni</i>
4.25	7.581	72.74	3.87	0.025	1.95	03.39	3.03
<i>P</i>	<i>Sb</i>	<i>Sn</i>	<i>As</i>	<i>Bi</i>	<i>Cd</i>	<i>Co</i>	<i>Cr</i>
0.188	0.636	1.93	0.103	0.190	0.007	0.012	0.014

Table 3: Elemental composition (wt %age) of Si-brass standard sample, obtained from Brammer [16].

4 Experiment 1: Elemental analysis

In the first experiment, we will learn how to analyze a material sample to find its constituent elements and determine their relative concentrations. We will start off by obtaining the spectral data of a stainless steel sample (SS-316). Data will be acquired and analyzed using two softwares, ADMCA 2.0 and XRS-FP.

The assembly of the apparatus and its various components is shown in Figure 9. One should make sure that the PX4, X-ray tube and the detector are all connected with the computer interface. The equipment manuals [12, 13, 15] should be consulted for proper procedures and precautions.

The spectrum processing and concentration analysis carried out with the aid of the two softwares ADMCA and XRS-FP, is illustrated as a flow chart in Figure 8.

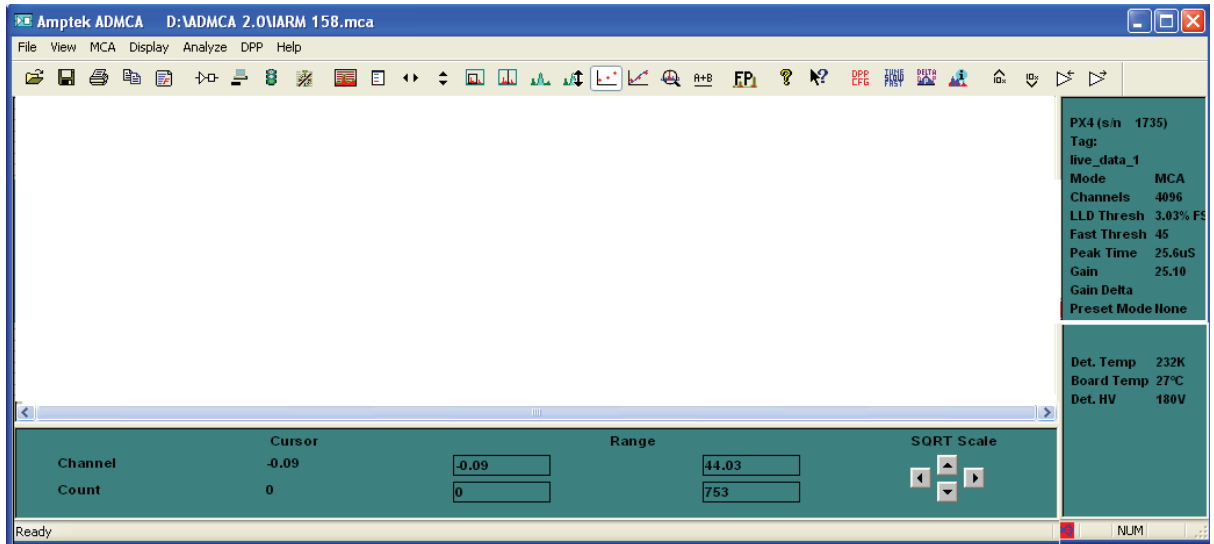
Never switch the X-ray source ON without the shielding in place. Do not expose yourself to direct or reflected X-rays. Do not touch the X-ray tube when it is switched ON.

Do not touch the Be window of the detector. Be very careful while placing and mounting the detector, any sudden movement or the slightest mechanical shock can damage the detector.

4.1 Acquiring spectrum in ADMCA

The ADMCA program [17] is the main display and acquisition software. It is a Windows software package that provides data acquisition, display, and control for Amptek's signal processor PX4. It also calibrates the hardware by assigning energy values to its channels, so that an energy spectrum of the sample can be visualized.

(a)



(b)

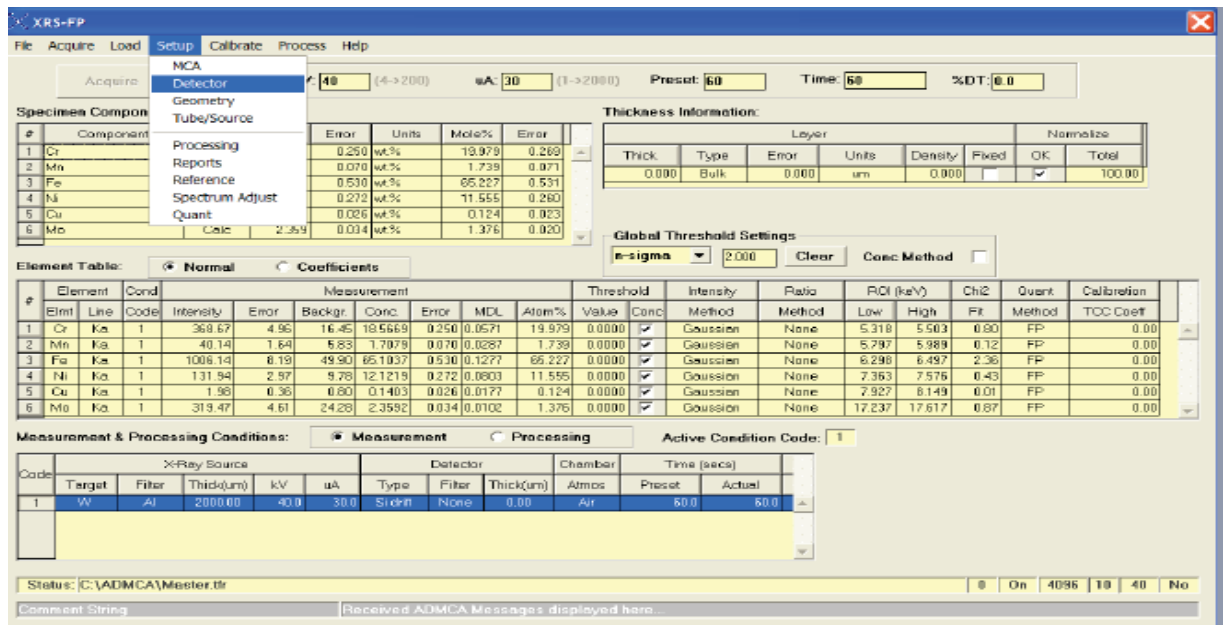


Figure 7: Screenshots of (a) ADMCA software for elemental identification, and (b) XRS-FP concentration analysis software.

4.1.1 ADMCA Features

- full control of the hardware features available in the connected hardware (PX4 and detector),
- live display of the spectrum. Capable of displaying and calibrating up to 8142 channels of the MCA,
- spectral calibration and qualitative analysis, and
- an active link to the XRF-FP Quantitative Analysis Software Package.

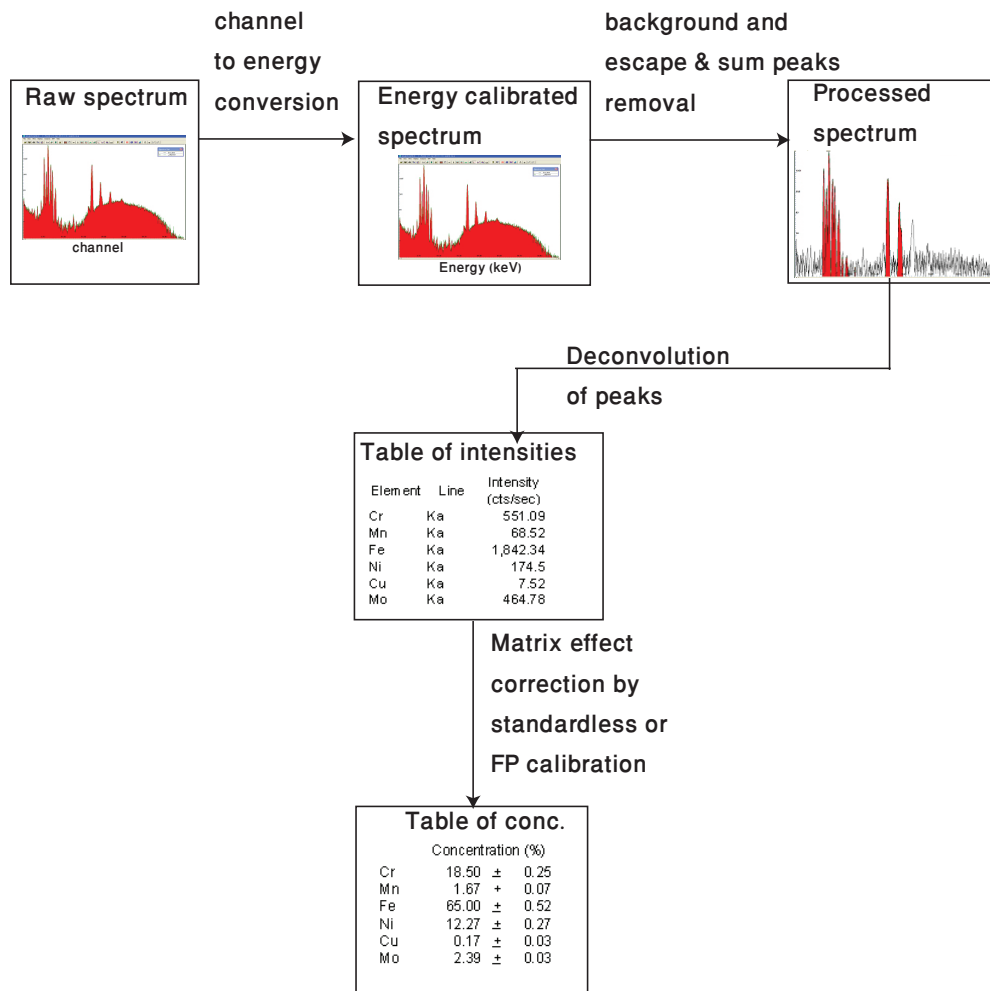


Figure 8: Spectrum processing and concentration analysis steps carried out by the ADMCA and XRS-FP softwares. The first two steps are performed by ADMCA and the remaining ones by XRS-FP software.

It is advised to explore the available control and configuration options in the software by going through its drop-down menus and buttons on the menu bar. ADMCA allows you to choose peaks as Regions-of-interest (ROIs) and specify the respective energies they correspond to.

4.1.2 Procedure

1. Mount the stainless steel standard sample (SS-316) in the sample holder inside the shielding enclosure as shown in Figure 10.
2. Switch ON the PX4 by pressing its power button, until you hear it beep twice.
3. Launch ADMCA. Click *ConnecttoPX4* when prompted by the software. If properly connected to PX4, ADMCA will show a green USB connection sign

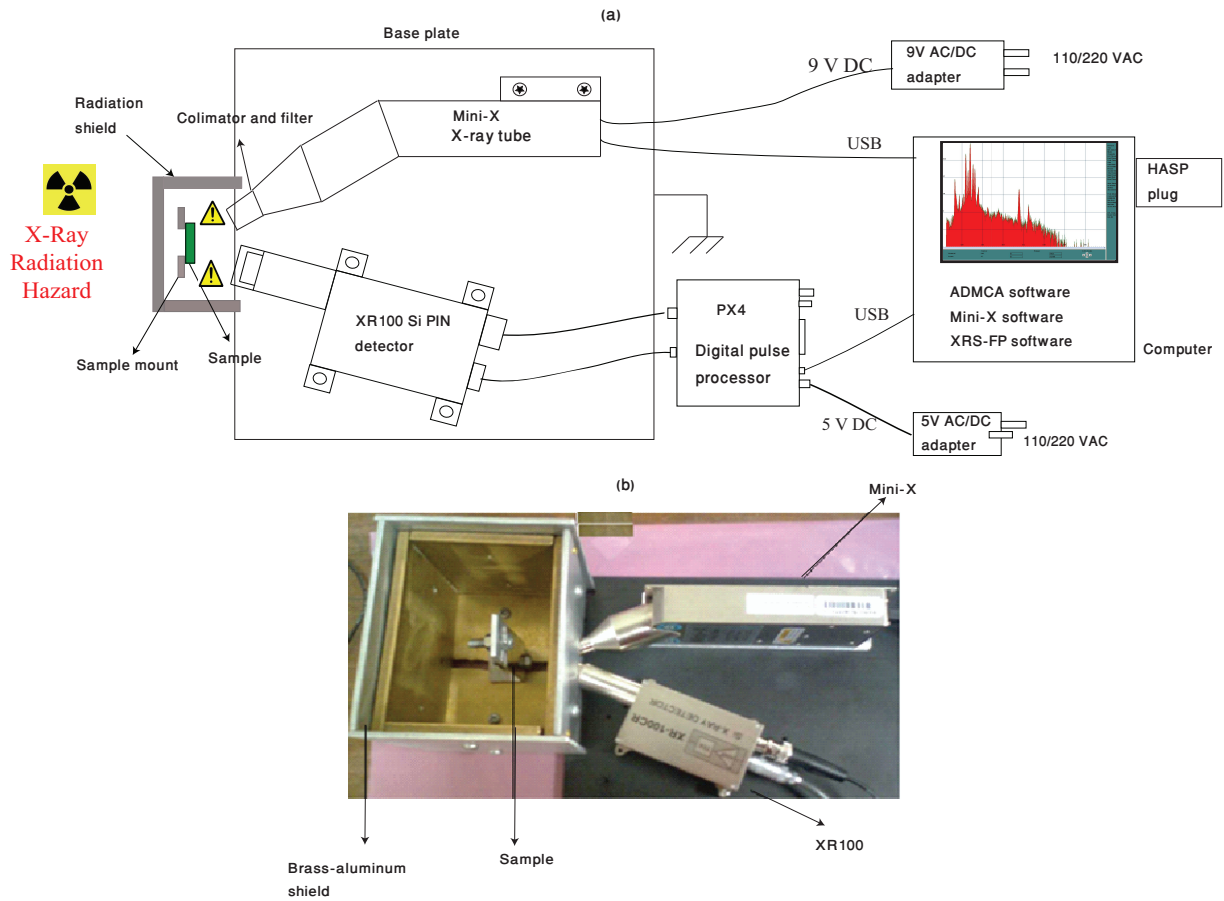


Figure 9: (a) Diagram of EDXRF spectrometer components connected to computer for spectral data acquisition and concentration analysis, (b) X-ray tube and Si detector mounted on the base plate to irradiate the sample material. The brass-aluminum box positioned to shield the experimenter from incident as well as reflected X-rays.

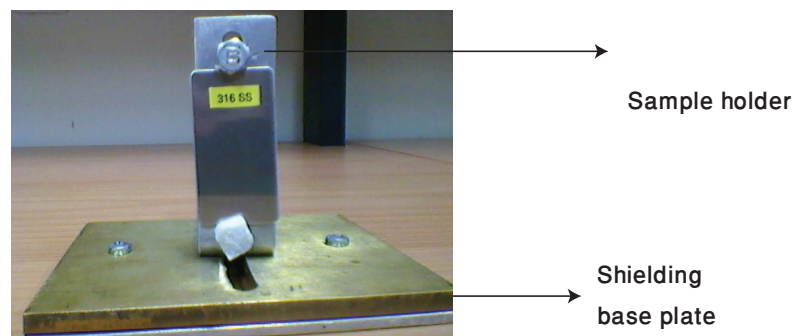


Figure 10: Stainless steel sample mounted on the sample holder.

in the lower right corner. Also check if the green LED in PX4's power button is blinking, as it indicates acquisition. If yes, stop acquisition.

4. Make sure that the safety interlock is plugged in carefully at the back of the Mini-X tube as shown in Figure 11(a). Plug the adapter into AC mains.

5. Start the Mini-X controller software and click the *Switchonthetube* button. In a couple of seconds, the software should indicate that Mini-X control is ready.
6. Set the voltage to 30 kV and current to 30 μA and turn on the source by clicking the *HV ON* button, as shown in Figure 11(b). A periodic beep sound indicates that the tube is emitting X-rays.
7. Now start acquisition in ADMCA and observe the spectrum as it gradually builds in the display window. Stop acquisition when counts exceed 50,000. (Number of counts can be seen in the right panel of ADMCA.)
8. Stop the X-ray source by clicking the *HV OFF* button in Mini-X control window and plug out its adapter. (**Make sure the source tube is never turned ON when you are not acquiring a spectrum.**)
9. Save the acquired spectrum with a suitable name, for example *steel.mca*. Do not exit ADMCA yet, as you will be calibrating your spectrum next.

Q 7. On the spectrum *steel.mca* identify the characteristic peaks. Use the X-ray Chart [21] to identify peaks of Fe, Cr, and Mo.

4.1.3 Spectrum calibration

The spectrum saved in the last section shows only counts corresponding to different channels of the MCA. To assign energy values to those channels is termed as calibration. We can perform calibration by using a sample of known composition, in this case steel (SS-316), whose elemental composition and respective concentrations are provided in Table 1. For accurate calibration, at least two peaks from the spectrum should be identified.

We can choose two elements, Fe (at 6.40 keV) and Mo (at 17.48 keV), to be our references, as they are reasonably apart on the energy scale. Furthermore, both the Fe and Mo peaks are easy to identify, former due to its tallness compared to the other peaks and the latter due to its horizontal separation from the main chunk of the spectrum.

Now perform the following steps to complete the calibration.

- From the ADMCA menu bar, click the *Define ROI* button. Click on the start and end points of the desired peaks on the horizontal axis, one by one. A list of selected regions will show in a dialog box, showing the *start* and *end* values for each ROI. Also the ROIs should turn turquoise.
- Click the *Calibrate* button on the menu bar. Clicking on ROIs will show their start and end points in the *Calibrate* dialog box. Click the *Centroid* button to select the centroid of the peak, and enter the energy value corresponding to the selected ROI (e.g., 6.4 for Fe). Click the *Add* button and repeat for the other ROI. This procedure is illustrated in Figure 12.

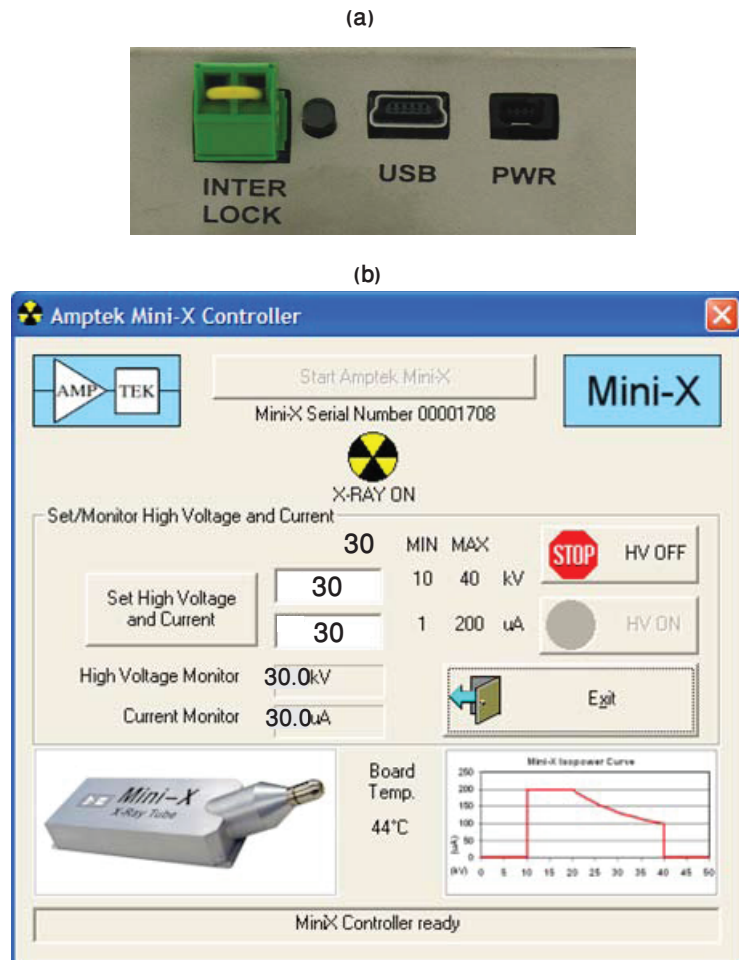


Figure 11: (a) Safety plug inserted to complete the circuit for high voltage production in the tube, (b) USB controlled Mini-X's software window to send the final command to allow the X-ray emission.

- In the *Units* box, choose the appropriate units and click *OK*.
- Clicking the *Enable calibration* button on the menu bar will convert the horizontal axis to energy units, finally showing the intensity versus energy spectrum for the sample.
- Save the calibrated spectrum file with an appropriate name. Also, opening *Preferences* from *View* menu, specify the file path and file name and check the box for loading this calibrated spectrum every time, the ADMCA is run [17].

Our software and hardware has now been calibrated with the energy scale. Once the spectrum has been calibrated, a qualitative analysis can be carried out by importing libraries for K_{α} , K_{β} , L_{α} or L_{β} lines from the “Analyze” menu. A typical result of the analysis is shown in Figure 13.

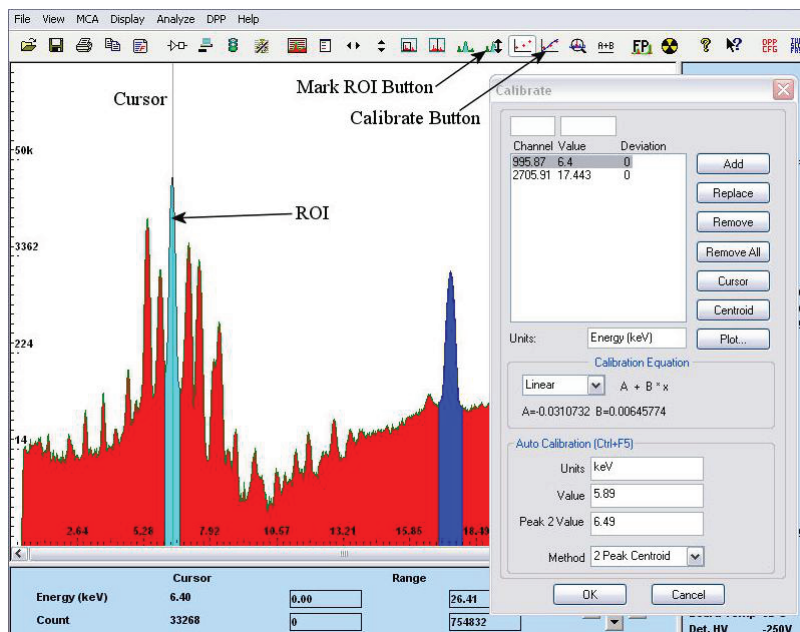


Figure 12: The ADMCA display window showing the calibration dialog box.

4.2 Quantitative analysis with XRS-FP

To run *quantitative analysis*, the spectrum acquired and saved in ADMCA has to be opened in the software named XRS-FP, a quantitative analysis software [18, 19] package for X-ray fluorescence. It processes the raw X-ray spectral data from Amptek's detector, signal processing electronics and ADMCA spectrum to obtain the elemental *peak intensities* and the elemental *concentrations*.

XRS-FP does spectrum processing, requiring as input the parameters which describe the spectrometer itself (e.g. type, area, and thickness of the detector, the distance between the tube and the sample, etc.) and parameters which control the processing. Prior to running the analysis, appropriate the settings in the *Setup* menu should be entered. Figure 7 (b) captures a screenshot of XRS-FP window.

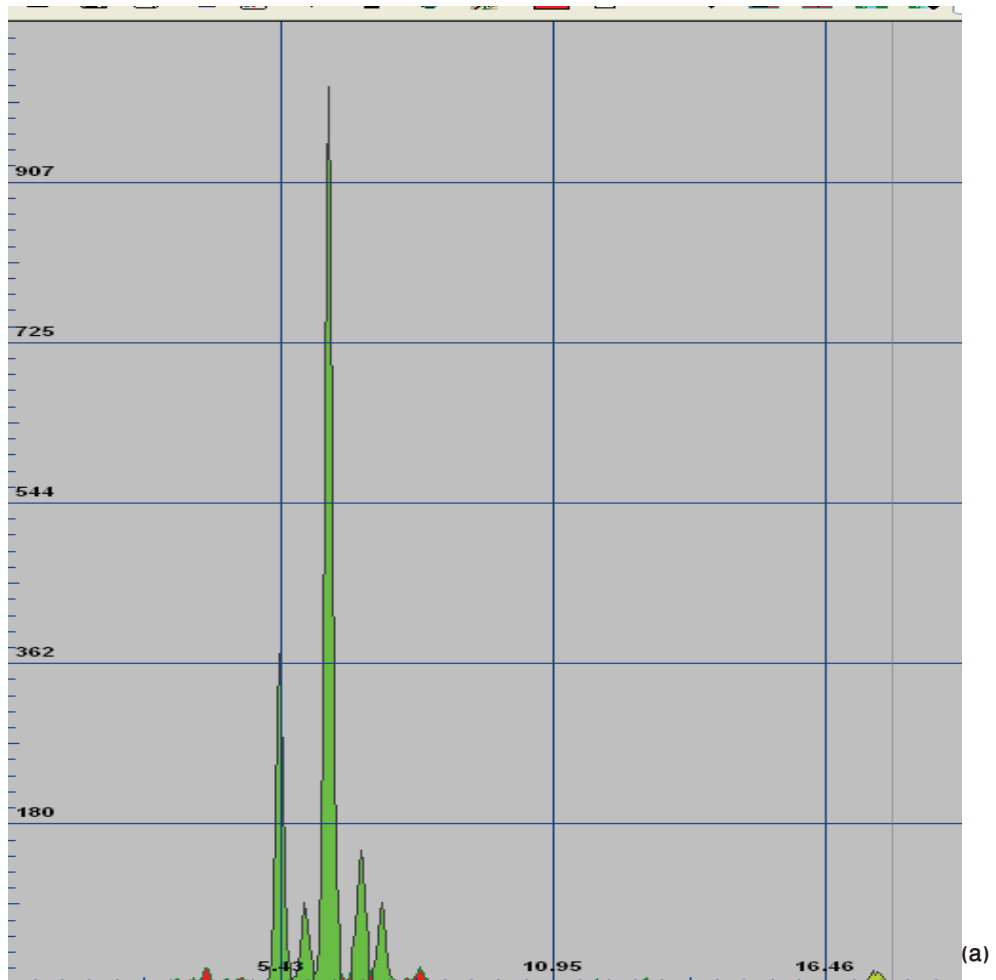
Before starting this section, students are strongly encouraged to refer to the XRS-FP guide [19, 20] to have a detailed information of these parameters and their effects on the analysis.

Q 8. What are sum peaks, escape peaks and background peaks [20]? Why is it important to remove these peaks?

4.2.1 Spectrum processing in XRS-FP

An XRF spectrum consists of characteristic peaks superimposed on a background (bremsstrahlung radiation and detector effects). Spectrum is processed to effectively extract the signal (net peak intensity) from the noise (the background peaks).

XRS-FP carries out the following processes to arrive at a table of elemental con-



D:\ADMCA 2.0\U-steel.mca 02/01/2011 15:47:24

Regions of Interest Details

Start	End	FWHM (N)	Net Area	Gross Area	Centroid (N)	Uncertainty	Status	Element
5.11	5.57	0.149	5836	6256	5.39	1.40	GOOD	Ka1-Cr
5.69	6.03	0.112	993	1535	5.91	4.59	GOOD	Ka1-Mn
6.11	6.57	0.155	15988	17395	6.38	0.86	GOOD	Ka1-Fe
6.88	7.15	0.135	1558	2518	7.04	3.79	GOOD	Ka1-Co
7.30	7.69	0.136	1236	1603	7.47	3.59	GOOD	Ka1-Ni
17.24	17.78	0.050	359	432	17.47	6.27	GOOD	Ka1-Mo

(b)

Figure 13: (a) Output from ADMCA: Region of interest defined for the six selected green peaks, (b) ROI detail, showing the initial and final positions for the each peak, the centroids and the elements whose X-ray line exists at that centroid value.

centrations.

- **Spectrum smoothing:** Smoothing of the spectrum is the first step in spectral processing. This operation typically performs a Gaussian smooth of each channel in the spectrum, for the specified number of times.
- **Si escape peak removal:** Escape peaks result from fluorescence inside the detector material (Si), due to which a fraction of the parent characteristic

X-ray gets lost as Si- K_{α} escape photons, with an energy of 1.75 keV. This energy loss has to be accounted for before proceeding to final analysis.

- **Sum peak removal:** When two X-ray photons arrive quicker than the PX4 hardware allows, the corresponding counts bear energy that is the sum of the two photons. Such *coincidences* are to be filtered out to get a precise result.
- **Background removal:** The background arises primarily from bremsstrahlung X-ray continuum from an X-ray tube whose shape depends on the anode atomic number and incident electron-beam energy. Only after subtracting the background from the acquired spectrum can a true spectral representation of the sample be obtained.
- **Deconvolution:** Finally, to calculate the net peak intensities, the spectrum is reconstructed as a sum of separate peaks by assigning them corresponding areas. This process is called deconvolution (the reverse of convolution).

4.2.2 Procedure

1. After connecting the HASP plug available with the XRF unit to the USB port of the computer, launch XRS-FP.
2. Choose *Expert mode* to open the XRS-FP main window. The table on top left should be showing a list of elements.
3. From the *Load* dropdown menu, select *Spectrum*, which should import the acquired spectrum from ADMCA.
4. Next from the XRS-FP *Set up* menu, specify the parameters defining the detector and X-ray tube types, the thickness of the detector's window, the filters used in the X-ray tube and the geometry of the arrangement of source, sample and detector. This information can be taken from XRF manuals [15, 17].
5. In the *Thickness Information* table, define sample to be in *Bulk* mode and check the *Normalize* option to 100 in order to get weight percentages of elements.
6. Enter the voltage and current values used for the X-ray tube into the *Measuring & Processing conditions* table.
7. Process the spectrum by choosing *Spectrum* \gg *All* from the *Process* menu.
8. Finally, click *Analyze* in the *Process* menu. This should return you the percentage concentrations of elements.

Q 9. Obtain a spectrum of the Cu film provided and using the ADMCA and XRS-FP softwares, perform the complete concentration analysis for the metal.

Q 10. Run a complete ADMCA and XRS-FP standard analysis for the Chromium alloy IARM-158B as done for steel. Find the calibration coefficients for all the elements of the alloy and their concentrations.

5 Experiment 2: Verification of Moseley's law

In this experiment we verify Moseley's Law as well as calculate the screening constant ζ for K_α X-rays. In order to have enough elements for the verification of the Moseley's law, We will be using the following three known samples for the purpose:

- stainless steel SS-316,
- chromium copper (IARM 158B),
- silicon brass (31X WSB7).

Always use gloves when handling these samples and place them in the desiccator after use.

5.1 Procedure

1. Place all the standard samples SS-316, IARM-158B and 31XWSB7, one by one, on the mount inside the shielding enclosure.
2. Acquire their respective spectra in ADMCA. (The spectrum should already be calibrated if you have specified the path and filename of the calibration file.)
3. Save the spectra with appropriate names.
4. Using the *ROIDetail* option in ADMCA the respective energy values for various elements can be seen.
5. Use MATLAB to plot a graph between the atomic number and peak energies obtained.
6. Linearize the graph to obtain values for its slope and intercept.

Moseley's law (3) is expressed as

$$E_{K_\alpha} = \frac{3R_\infty(Z - \zeta)^2}{4},$$

which can be linearized by taking square root of both sides:

$$\sqrt{E_{K_\alpha}} = \sqrt{\frac{3R_{E\infty}}{4}} Z - \sqrt{\frac{3R_{E\infty}}{4}} \zeta,$$

which resembles the equation of a straight line. From the slope and the intercept of this line, Rydberg's energy (R_∞) and scattering factor (ζ) can be calculated.

Q 11. Plot the graph of your values and discuss your results. Does your result verify Moseley's Law?

Q 12. Use your graph to calculate the value of the Rydberg's constant and scattering factor. How close is your value to the theoretical value of $R_\infty = 13.60$ eV?

Q 13. Calculate the uncertainty in your calculated values of R_∞ and ζ .