

# SS16: X-ray diffraction and X-ray spectroscopy (mini-project)

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## Abstract

In this experiment, we study the X-ray emission lines production and verify Moseley's Law by measuring the energy of emission lines series in several metals. Then, we use spectroscopy to report on the composition of different samples: two semiconductors, several unlabelled alloys and international metal coins provided in the laboratory. We give results for the mass ratios of the unlabelled alloys. We also find that most coins are made up of either Ni-Cu or Cu-Zn alloys and expand on the reasons behind this choice.

## 1 Introduction

X-rays are an important experimental tool and have been for more than a 100 years now ever since their discovery by Wilhelm Röntgen. They are currently employed by both scientists, from scattering experiments in condensed matter to high-energy astrophysics, and citizens for medical scans etc. In this experiment, we first study the theoretical basis of X-ray production first developed by Moseley. We measure the energy of the  $K_{\alpha}$  and  $L_{\alpha}$  emission lines series of several samples of known elements with known atomic number  $Z$  to verify Moseley's Law. Having established the uniqueness of X-ray emission lines for a given  $Z$ , we use it to study the composition of several samples provided to us in the laboratory by measuring their emission spectra when exposed to a continuous X-ray source. We begin by independently confirming the composition of two semiconductor samples observed in the non-mini-project part of the experiment. Then, we report on the composition of some unlabelled metal alloys and the relative mass ratios of the samples. Finally, we report on the composition of an array of international coins provided in the laboratory and expand more on the reasoning for the mainly Ni-Cu-Zn composition.

## 2 Theory

We begin by introducing some of the background theory behind X-rays and their production.

### 2.1 X-ray atomic spectra

The emission spectra of atoms is due to energy transition of shell electrons from a higher energy level to a lower energy level. We are interested in X-rays specifically, which are due to transitions in the inner electron levels of high- $Z$  atoms. These are shielded from the outer electron layers and are mostly unaffected by the chemical structure of the sample i.e. by the surrounding atoms. Therefore, we can take an energy level of an electron to be  $E_n = -R(Z)/n^2$  where  $R(Z) = R_{\infty}(Z - b)^2$  is the modified Rydberg constant for a given  $Z$ ,  $b$  is some parameter depending on atom, and  $R_{\infty}$  is the hydrogen Rydberg constant. Then, the energy of an emitted photon by a transition from level  $n_i$  to  $n_f$  is given by:

$$\varepsilon = R(Z) \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right). \quad (1)$$

We can rewrite this at fixed  $n_i$ ,  $n_f$  (i.e. for a given line) as:

$$\sqrt{\varepsilon} = m \times Z + C, \quad (2)$$

where  $m, C$  are some constants. This relationship is known as ‘Moseley’s Law’.

The name convention of the energy levels of low- $n$  in X-ray notation is described in Table 1. The energy difference between different L, M levels is not so big, so if we have a low resolution detector we usually observe e.g. only one  $K_\alpha$  line.

Initial level	Final level	Siegbahn notation	IUPAC notation
K ( $1s_{1/2}$ )	L3 ( $2p_{3/2}$ )	$K_{\alpha 1}$	K-L3
	L2 ( $2p_{1/2}$ )	$K_{\alpha 2}$	K-L2
	M3 ( $3p_{3/2}$ )	$K_{\beta 1}$	K-M3
	M2 ( $3p_{1/2}$ )	$K_{\beta 3}$	K-M2
L3 ( $2p_{3/2}$ )	M5 ( $3d_{5/2}$ )	$L_{\alpha 1}$	L3-M5
	M4 ( $3d_{3/2}$ )	$L_{\alpha 2}$	L3-M4
	L2 ( $2p_{1/2}$ )	$M_{\beta 1}$	L2-M4
M5 ( $3d_{5/2}$ )	N7 ( $4f_{7/2}$ )	$M_{\alpha 1}$	M5-N7

Table 1: Table of the connection between Siegbahn and IUPAC notation. Energy levels in IUPAC are listed with atomic notation as well. Source: [1].

## 2.2 X-ray production

In practice, we produce X-rays by bombarding a sample of some material with high energy electrons or X-rays which removes one of the inner shell electrons from the sample atom. This produces a vacancy in the shell. The vacancy is filled by some electron of a higher  $n$  orbit (see Figure 1), and the fall of potential energy of the electron is compensated by an emitted X-ray (ignoring higher order effects like the *Auger effect*).

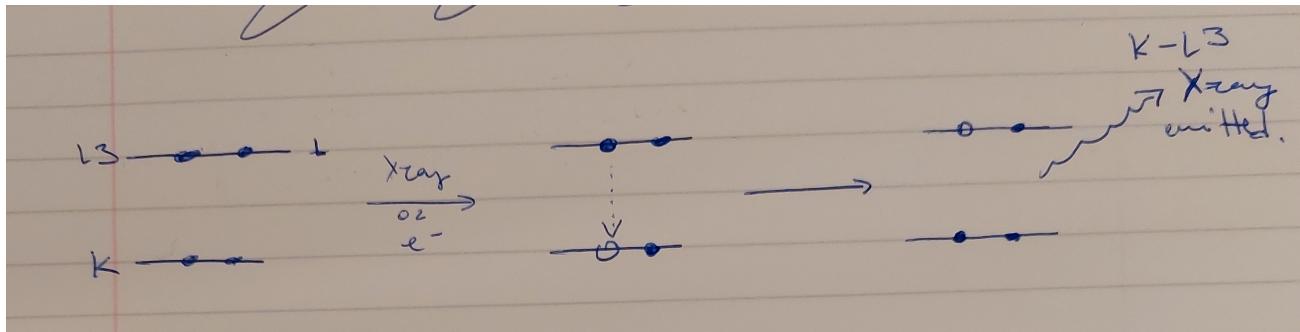


Figure 1: Schematic of the emission process for a K-L3 transition.

Usually, small laboratory X-ray tubes use an electron source. Because of that, we observe a continuum of X-ray radiation imposed on top of the emission lines. This radiation is called *bremsstrahlung* (“braking”) radiation. Its source is the interaction between decelerating electrons and stationary charges in the sample lattice. The maximal energy of a bremsstrahlung continuum is limited by the energy of the decelerating particle. If these are electrons accelerated by a potential difference  $V$ , then the maximal energy is given by:

$$\varepsilon_{\max} = eV. \quad (3)$$

Suppose we use one such continuous X-ray source for the production of X-rays from a sample. We will take the K-series as an example. To produce a vacancy, need an X-ray of energy  $\varepsilon_{\text{in}} = -E_1 = R(Z)$ , which will be provided by a collision with an electron with maximum energy  $\varepsilon_{\max}$  in the case of the X-ray source. The resultant energy of the emitted X-ray will be given by (1). Take for example the K-L transition. Its energy will therefore be (ignoring fine-structure):

$$\varepsilon_{\text{out}} = R(Z) \left( 1 - \frac{1}{2^2} \right). \quad (4)$$

A process like this one, in which  $\varepsilon_{\text{in}} \neq \varepsilon_{\text{out}}$ , is called *fluorescence*.

## 2.3 Composition analysis

As said above, the X-ray emission is relatively independent of the composition of the sample. We can use this fact to perform a composition analysis on a sample by exposing it to the continuous bremsstrahlung of a source; this will allow the different components to fluoresce. The signal will give us information not only *which* elements are present (given that the source is high enough to allow fluorescence), but their relative contribution — the intensity of the signal will depend only on the number density  $n$ . Suppose we measure the intensity of a two-metal alloy with the peaks in the  $K_\alpha$  line as  $I_a$  and  $I_b$ . This tells us that:

$$\frac{I_a}{I_b} = \frac{n_a}{n_b}, \quad (5)$$

where  $n_a$  and  $n_b$  are the number densities of materials a and b. From that, we could easily calculate percentage compositions for number densities or mass densities ( $\rho = n \times (\text{molar mass})$ ).

## 3 Experiment

Our experiment consists of the setup presented in Figure 2. First, we have an X-ray source with a molybdenum anode, which produces some characteristic  $K_\alpha$  X-rays that can be used for diffraction experiments (see the first part of [2]) and some continuous bremsstrahlung (see Section 2.2 for more details). These X-rays are focused through a circular aperture towards a target sample. The incident X-rays excite inner shell electrons, and the targets emit mostly in the characteristic X-rays of K,L, and M series. We detect these via an energy spectrometer that is sensitive in the region of our experiment. The setup parameters are: tube voltage  $V = 35$  kV, emission current 1 A, exposure time  $t = 100$  s. This, according to (3) and (4), allows us to produce, for example,  $K_\alpha$  X-rays with energy up to 26.25 keV from samples with atomic numbers up to at least 50, ignoring contribution of  $b$ .

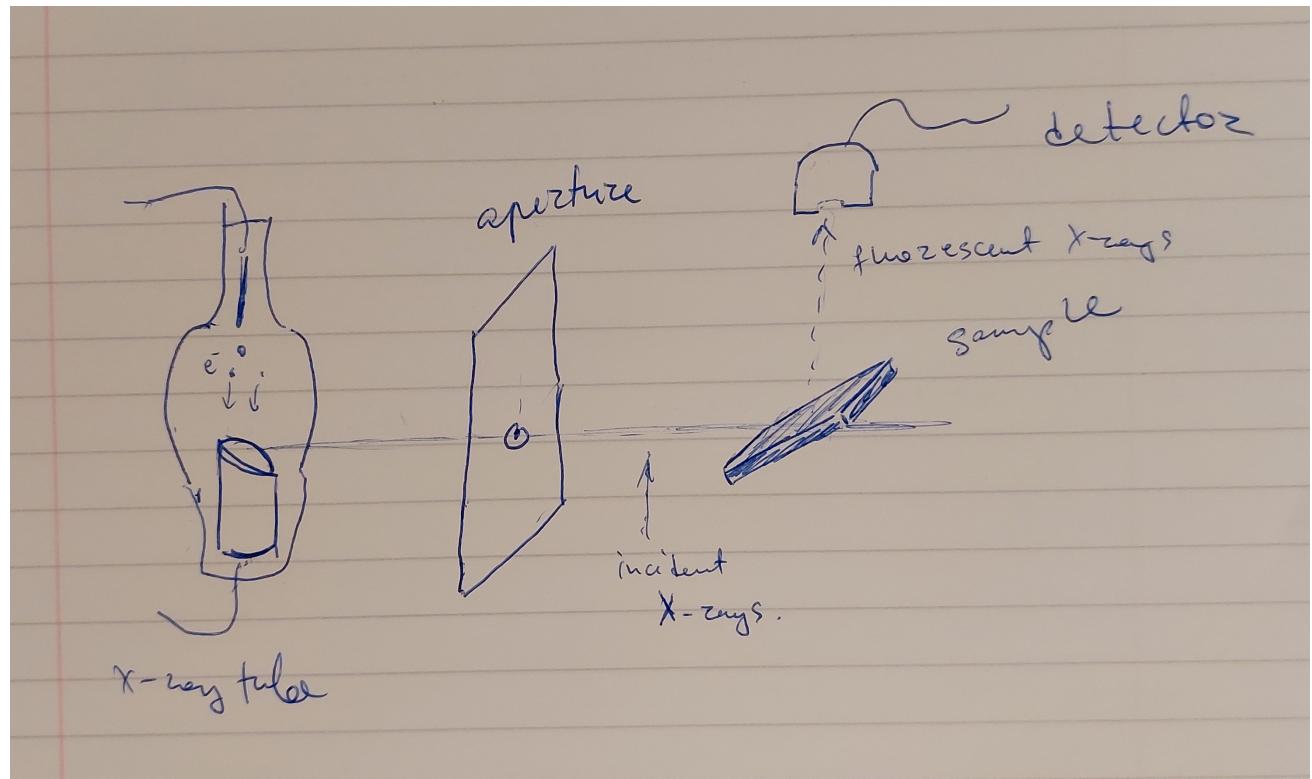


Figure 2: Diagram of the experimental setup. More info in the text of Section 3.

To operate the apparatus and extract data, we use the software provided by the labs *CASSY Lab 2*. The program has a built in database for the X-ray emission lines of most elements. It also allows for calculating a peak centre and fitting gaussian profiles with specified energy to find the intensity of emission lines. (expand on applicability since x-ray lines are asymmetrical.)

Before we can do any work that has to do with determining energies or referring to energy values from a database, need to set the scaling of the measurement apparatus. We will do so with two of the labelled provided samples - for Fe and Ag. These cover a wide range of values in the bremsstrahlung spectrum, so they are a good way to set the scaling. The particular lines which we use to calibrate are the Fe  $K_{\alpha}$  with  $E_{Fe} = 6.40 \text{ keV}$  and the Ag  $K_{\alpha}$  with  $E_{Ag} = 22.17 \text{ keV}$ . We also have to note the observational lower and upper limits, respectively 2 keV to 4 keV and  $\approx 35 \text{ keV}$ .

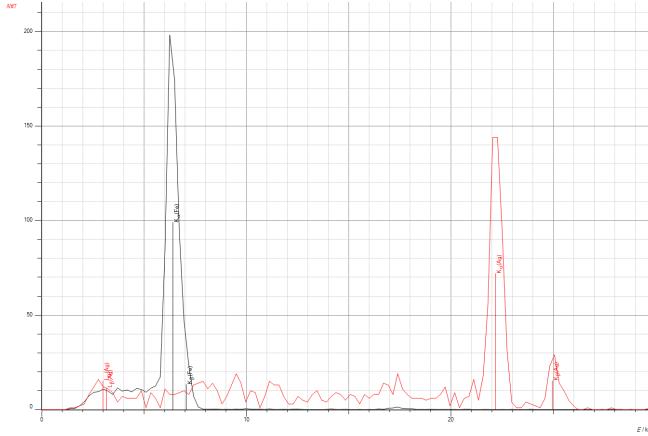


Figure 3: These are the Fe (black) and Ag (red) spectra used for calibration.

The first part of the experiment will test the validity of Moseley's Law with the help of several samples of known substances.

The second part and third part of the experiment will utilise our knowledge about X-rays to learn more about the composition of some samples provided for us, and about some metal coins from around the world.

## 4 Result and Analysis

### 4.1 Moseley's Law

We measure the line energy values from the labelled samples. These are mainly in two groups:

- those, whose  $K_{\alpha}$  lines lie in the observable range (excluding our two calibration points);
- those, whose  $L_{\alpha}$  lines lie in the observable range.

We expect to see a straight line fit for the two groups of lines. The scaling constant  $m$  depends purely on the line we are observing, i.e. on the  $n_i, n_f$  for the given line. We can predict the ratio of the constants for the two series. Following (1) and Moseley's law, we get:

$$m_K \propto \left(1 - \frac{1}{2^2}\right)^{1/2} = \sqrt{\frac{3}{4}}, \quad m_L \propto \left(\frac{1}{2^2} - \frac{1}{3^2}\right)^{1/2} = \sqrt{\frac{5}{36}} \Rightarrow \frac{m_K}{m_L} = \sqrt{\frac{27}{5}}. \quad (6)$$

Results presented in Figure 4.

We see that these both follow our expectations - have good fits to the model. We can deduce that our description of X-ray emission works sufficiently well for our purposes (given experimental accuracy etc), so we can proceed to use X-ray K and L series lines as a signature of a given element in spectral analysis.

Also, can calculate ratio from given values:

$$\text{predicted: } \frac{m_K}{m_L} = \sqrt{\frac{27}{5}} = 2.324, \quad \text{observed: } \frac{m_K}{m_L} = \frac{0.1026}{0.0411} = 2.496. \quad (7)$$

Agreement is not so good, but we have not taken into account many other effects like change of energy due to being in a state  $l \neq 0$  etc. So, not too bad.

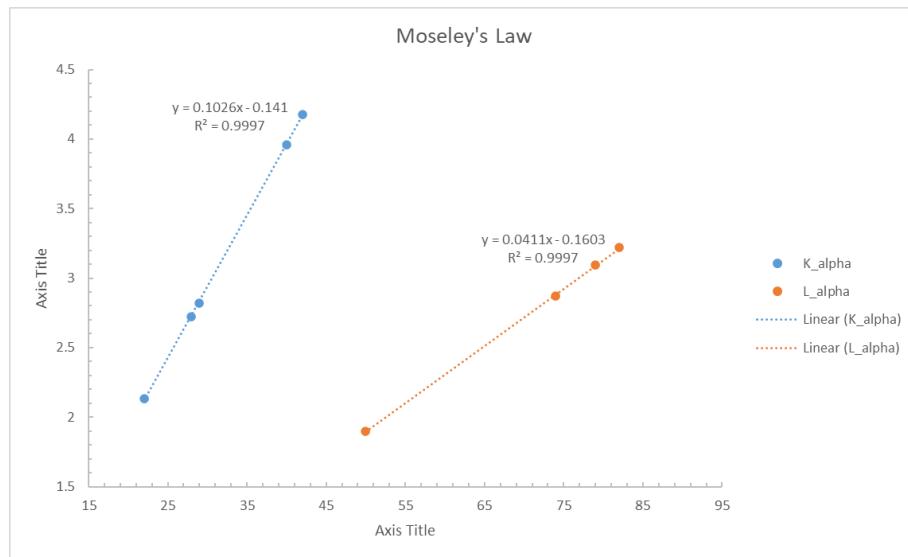


Figure 4:  $\text{sqrt}(\text{energy})$  vs Z number for given samples: [list samples](#). produce better final figures.

## 4.2 Provided alloys and semiconductors

Now, can move to the analysis of samples. We will use fluorescence to determine the composition of the semiconductors from the non-MP part and of some unlabelled samples that are provided in the physics lab.

### 4.2.1 Semiconductors

The semiconductors are part of the non-MP experiment, where we determined their structure by determination of the lattice constant. Here, we provide an independent confirmation of our previous results.

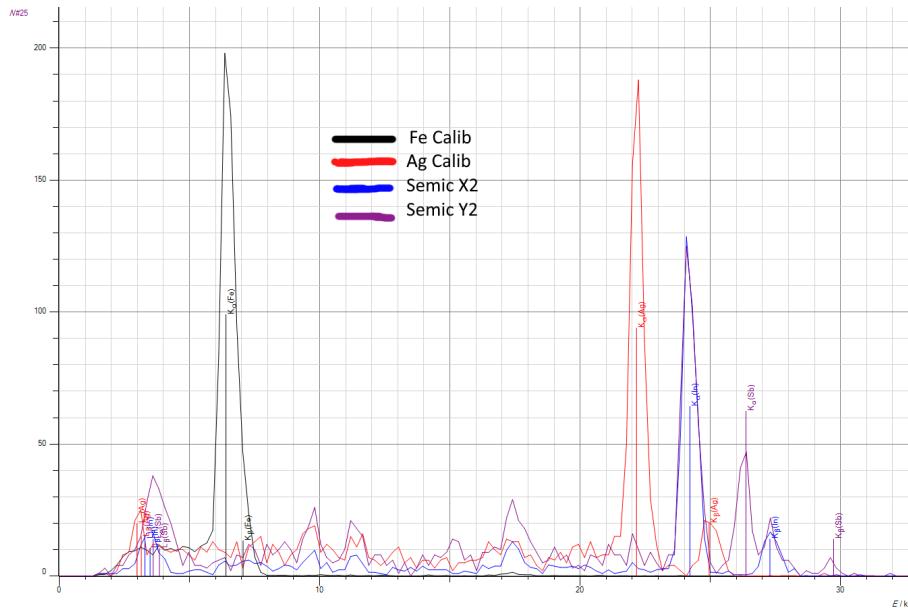


Figure 5: Fluorescence spectra of the Fe, Ag calibration and semiconductors labelled as X2 and Y2 in sample boxes provided. We see that X2 and Y2 show traces of In, and Y2 shows additionally traces of Sb. [prob should go to appendix?](#)

We see that semiconductor Y2 shows traces of In and Sb, a group III and V elements respectively. This is a very common structure for semiconductors, so this is reassuring ([expand?](#)). In addition, this confirms our result from the first part of the practical, where we arrived at the conclusion that the semiconductor is an InSb via lattice diffraction. We can measure intensities of the  $K_\alpha$  lines for both,

and calculate the ratios:

$$\frac{n_{\text{In}}}{n_{\text{Sb}}} = \frac{I_{\text{In}}}{I_{\text{Sb}}} = \frac{122.5}{42.8} \approx 2.86 \Rightarrow p_{\text{In}} = \frac{n_{\text{In}}}{n_{\text{In}} + n_{\text{Sb}}} = 74\% \quad p_{\text{Sb}} = 26\% \quad (8)$$

For sample X2, we see a trace of In only. Checking with our result from the diffraction analysis, we see that the dopant is P (phosphorus). The characteristic X-rays of P in K-series (most energetic ones) have energies around 2 keV, which is around our detection limit of about 2 keV to 4 keV. This highlights one of the shortcomings of our method: it is limited in detecting only those elements, which have X-ray emission lines in the range of the bremsstrahlung and the range of operation of the detector.

#### 4.2.2 Unlabelled alloys

The lab has two boxes of unlabelled metallic samples - alloys of different metals. We can determine their composition and ratios by using Section 2.3. Result is presented in Table 2.

sample	element	line	intensity	Kalpha/Kbeta	nA/nB	prop	by mass
b1-1	Cr	Kalpha	381.9	5.55	0.42	0.30	0.28
b1-1	Cr	Kbeta	68.8				
b1-1	Fe	Kalpha	903.1	4.14		0.70	0.72
b1-1	Fe	Kbeta	218.2				
b1-2	Cu	Kalpha	2110.2	6.14	1.78	0.64	0.69
b1-2	Cu	Kbeta	343.9				
b1-2	Zn	Kalpha	1182.9	17.09		0.36	0.31
b1-2	Zn	Kbeta	69.2				
b1-3	Cu	Kalpha	3947.9	14.33	1.27	0.56	0.61
b1-3	Cu	Kbeta	275.5				
b1-3	Zn	Kalpha	3119.6	16.51		0.44	0.39
b1-3	Zn	Kbeta	188.9				
b2-a	unusable						
b2-b	unusable						
b2-c	Fe	Kalpha	1351.9	3.74	2.06	0.67	0.69
b2-c	Fe	Kbeta	361.8				
b2-c	Zn	Kalpha	655.6	8.57		0.33	0.31
b2-c	Zn	Kbeta	76.5				
b2-d	Fe	Kalpha	1443.6	3.92	3.42	0.77	0.79
b2-d	Fe	Kbeta	368.1				
b2-d	Zn	Kalpha	421.9	9.74		0.23	0.21
b2-d	Zn	Kbeta	43.3				
b2-e	unusable						
b2-f	Fe	Kalpha	1443.3	3.89	2.56	0.72	0.74
b2-f	Fe	Kbeta	371.5				
b2-f	Zn	Kalpha	563.9	9.37		0.28	0.26
b2-f	Zn	Kbeta	60.2				

Table 2: Table of the fitted intensities in alloy samples. Some of the measurements made had signal comparable with the background due to a human error during data acquisition; included here for completeness. **add a column with line energy, improve siunitx for number formatting, prob delete the unusable ones**

We can first check for consistency of the fits by looking at the ratios of intensities for  $K_\alpha$  and  $K_\beta$ , which should be approximately the same for all samples as it depends on the structure of the individual atom. Samples b2-c,d,f have close values for both the Fe and Zn lines. Since these two elements do

not overlap in the spectrum (as seen in Figure A3), these ratios should be close to the true ratio. We would expect to observe similar ratios in the other samples for Fe and Zn.

For sample b1-1, the Fe ratio is a little above 4, so we can say that the fit was pretty good. For samples b1-2,3, the Zn ratio is twice the one measured above. The fit here is pretty poor since Cu and Zn are respectively  $Z = 29$  and  $Z = 30$ . Their spectra overlap by a lot (as seen in Figure A2) — the  $K_\alpha$  of Zn is between  $K_\alpha$  and  $K_\beta$  of Cu. This, combined with the low resolution of our detector, makes it pretty difficult to fit here. Nevertheless, the  $K_\alpha$  lines are much stronger, so we can still try to extract the composition of the alloys.

Alloy composition is usually presented by mass in practical applications. These results are in the last column of Table 2.

### 4.3 International coins

The lab has a box of various coins from around the world, the content of which we can again interpret using our fluorescence method, similar to the analysis in Section 4.2.2.

No	Country	Denomination	Ni	Cu	Zn	Other
3	United Kingdom	50p old	yes	yes	no	no
4	United Kingdom	50p new	yes	yes	no	no
5	United Kingdom	20p new	yes	yes	no	no
6	United Kingdom	10p old	yes	yes	no	no
7	United Kingdom	10p new	yes	no	no	no
8	United Kingdom	2p new	no	yes	no	no
9	Singapore	1 dollar old	yes	yes	no	no
10	Singapore	50c old	yes	yes	no	no
11	Singapore	20c new	yes	no	no	no
12	Bulgaria	50 stotinki	yes	yes	yes	no
13	Bulgaria	5 stotinki	no	yes	no	no
14	European Union	50c	no	yes	yes	no
15	European Union	2c old	no	yes	no	no
16	European Union	2c new	no	yes	no	no
17	Romania	10 bani	yes	no	no	no
18	Norway	1 krone	yes	yes	no	no
19	Switzerland	20 centim	yes	yes	no	no
20	Sweden	1 krona	yes	yes	no	no
21	Japan	1 yen	no	no	no	no
22	Hong Kong	10c	no	yes	yes	no
23	Uganda	200 schillings	yes	yes	no	no
24	USA	25c	yes	yes	no	no
25	USA	1c	no	yes	yes	no
26	Canada	25c	yes	yes	no	Fe?
27	Brazil	5 centavos	no	yes	no	no

Table 3: Table of metal composition for a selection of international coins.

When looking at plots of the spectra, we see that almost all coins are made predominantly out of Ni, Cu, and Zn with  $Z = 28$  to  $30$  respectively. The spectra are overlapping, so similarly to the b1-2,3 samples in Section 4.2.2, we cannot really fit the samples well for all  $\alpha, \beta$  lines. Nevertheless, we can still determine if one of the three elements is present. Additionally, we note down any additional features of the spectra that are of interest. The results can be summarised in Table 3. Two exceptions to the general rule are obvious - the 1 Yen and 25c Canadian coins. We can compare our results with the information from the institutions that issue these coins.

The official information lists the 1 Yen coin to be made of 100% aluminium (citation needed). The  $K_\alpha$  line for aluminium is at 1.49 keV, out of the range of our setup. This is the reason we do not see

any signal in our spectrum.

The official information informs us that the 25c canadian coin is a 94% steel core with 6% Ni-Cu plating ([citation needed](#)). When we look at the spectrum, however, the strength of the Fe line is much less than the Ni and Cu. This is due to the fact that the X-rays do not penetrate deep into the coin. If a thick enough coating is applied, we could even fully shield the steel core. In fact, several coins on our list follow this pattern, e.g. the new 2p and 10p coins.

#### 4.3.1 Why Ni,Cu,Zn?

One obvious question that comes up from these results is why are alloys of Ni, Cu, and Zn the choice? There are several properties of these alloys that make them preferable for coin minting.

Historically, coins were most often made from gold, silver, and copper, with their value determined by the value of the metal in the coin. With the inflation of prices, however, the metal in the coins gradually became more expensive than their monetary value. There was a need for new materials to be implemented while keeping many of the familiar and useful properties of old coins.

Firstly, there are visual considerations of the coins. Ni-Cu and Cu-Zn alloys can have varying colours depending on the ratio of elements used. Ni-Cu are usually silver in appearance, while Cu-Zn alloys are usually golden in appearance, with small amounts of other additives sometimes present, like in the case of the *nordic gold* alloy used for the make of the 50 euro cent coin.

Secondly, the cost considerations required some inexpensive materials to be used so that mass production is practical and coins are not produced at a loss. Due to inflation, this has also led to the change of coin composition throughout the years. One example is the UK 10p coin. While the old coin was made from pure Ni25Cu75, the new coin is made from 94% steel clad in 6% Ni. The method of implementing a cheaper core while using Ni,Cu,Zn for an outer layer also keeps the appearance the same or similar, which is one of the reasons for the approach.

Thirdly, the minting of the coins includes making the alloys and producing the coins with intricate detailing on their surfaces. The alloying of the specific ratios required by the specifications can be a difficult task outside of the specialised large scale industrial complexes. The three metals also allow for the detailing on different designs — their alloys have been used to produce detailing by artisans for centuries (millennia?). Both of these specifics make the production of good counterfeit coins more difficult, which brings more security to the currency.

Finally, these alloys are very practical for everyday use. Coins, in their daily use, are exposed to the elements and physical wear. These alloys are very resistant to rusting (although Ni-Cu are often subject to formation of *patina*) and have high durability against physical stresses like bending, stretching etc. This is another reason for the cladding method — this gives them resistance against the elements and the physical toughness also helps preserve the detailing on the surface.

#### 4.3.2 Cost-based analysis of coins.

This is a potential direction to investigate. Main idea — calculate the “value” of a coin via its weight+official composition to see if anything interesting appears (coins worth more than their value, similar value for all coins etc.)

## 5 Conclusions

In this experiment, we first study the theoretical basis of X-ray production first developed by Moseley. We measure the energy of the  $K_{\alpha}$  and  $L_{\alpha}$  emission lines series of several samples of known elements with known atomic number  $Z = 22$  to  $40$  and  $50$  to  $82$  respectively. We find that there exists a linear relationship between the square root of the energy and number  $Z$  like predicted by Moseley’s law. Having established the uniqueness of X-ray emission lines for a given  $Z$ , we use it to study the composition of several samples provided to us in the laboratory by measuring their emission spectra when exposed to the continuous X-ray source. For the semiconductors, we observe traces of In in sample X2 and traces of In and Sb, which confirms the independently derived results from the non-mini-project. We

also note the observational limitations of our setup, since the dopant of X2 was not observed — P has a  $K_{\alpha}$  of energy below the observational limit.

Then, we report on the composition of some unlabelled metal alloys and the relative mass ratios of the samples. We measure these by performing gaussian fits using the built-in capabilities of the acquisition software. We also go through some analysis to confirm our observations are self-consistent by comparing the ratios of  $K_{\alpha}/K_{\beta}$  for the same elements in different samples.

Finally, we report on the composition of an array of international coins provided in the laboratory. We discover that most have signs of Ni, Cu, and Zn in their spectra predominantly. While it is difficult to exactly extract intensities of the lines since they overlap, we report on the presence of either element in the coins in addition to any other element seen in the spectra. We discuss some seemingly anomalous results, like the 1 Yen and 25c canadian coins, which turn out to be 100% aluminium and Ni-Cu clad steel. We conclude with an explanation for the frequency of use of these three metals, as well as the need to produce steel-core coins.

## References

- [1] R. Jenkins, R. Manne, R. Robin, and C. Senemaud. Nomenclature, symbols, units and their usage in spectrochemical analysis - VIII. nomenclature system for x-ray spectroscopy (recommendations 1991). *Pure and Applied Chemistry*, 63(5):735–746, jan 1991.
- [2] Oxford Physics. *X-ray diffraction*. Oxford Physics, October 2010.

## Appendix A Energy spectra plots

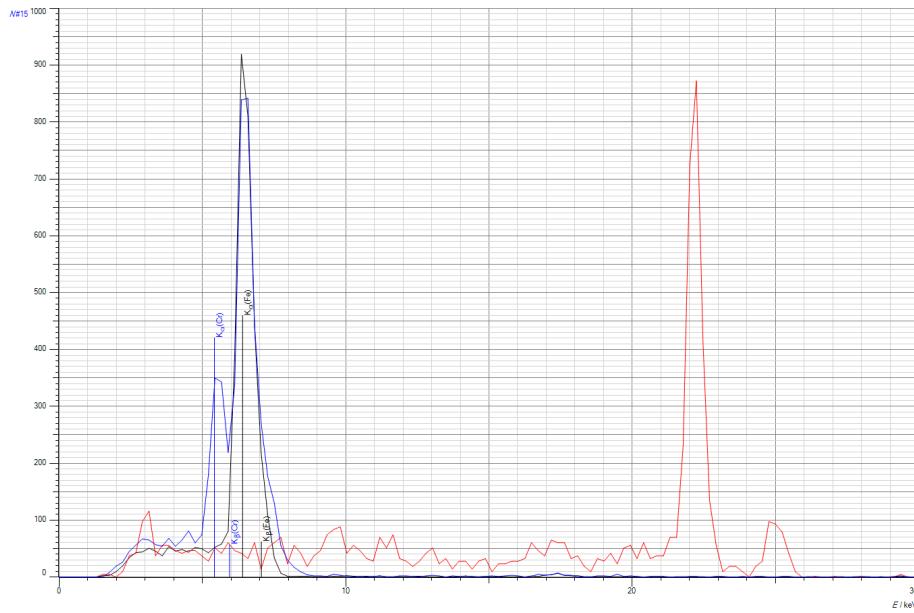


Figure A1: Spectrum of sample b1-1. Calibration spectra of Fe and Ag in black and red respectively. It can be seen that the sample consists of Fe and Cr, and their spectra overlap. This presents a difficulty in fitting emission lines.

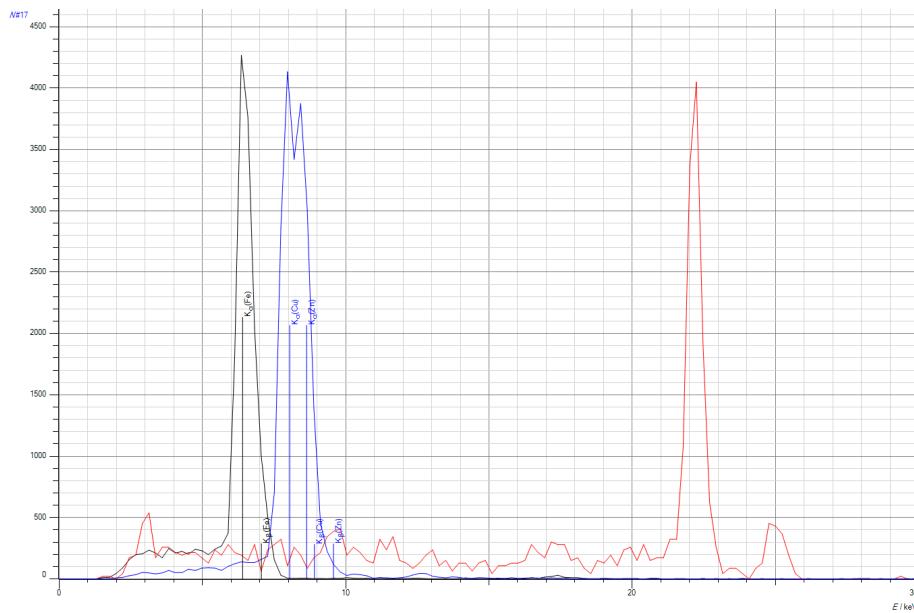


Figure A2: Spectrum of sample b1-3. Calibration spectra of Fe and Ag in black and red respectively. It can be seen that the sample consists of Cu and Zn, and their spectra overlap significantly. This presents a difficulty in fitting emission lines.

## Appendix B Extracted intensity data

Add data here as tables, refer to it when needed.

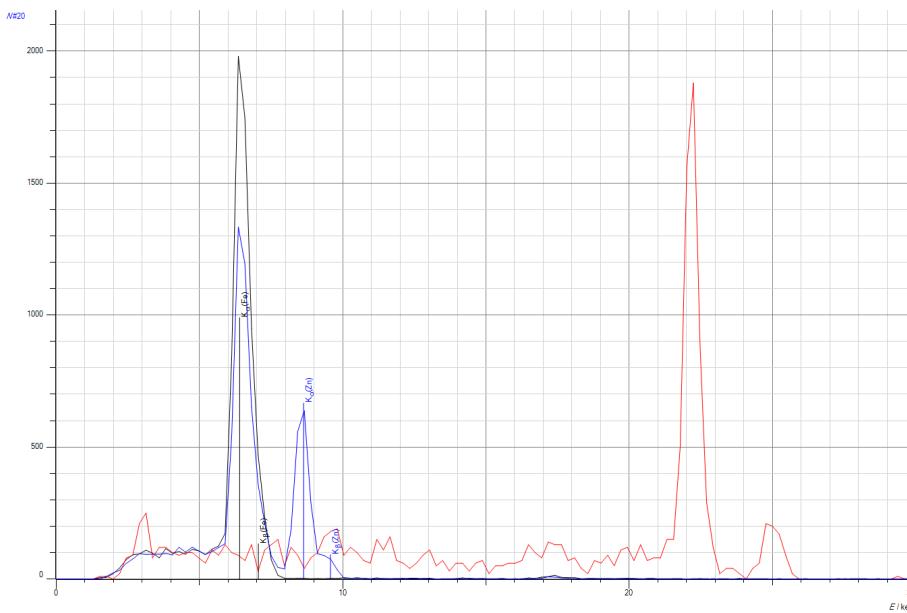


Figure A3: Spectrum of sample b2-c. Calibration spectra of Fe and Ag in black and red respectively. It can be seen that the sample consists of Fe and Zn, and their spectra do not overlap.

No	Country	Denomination	Ni, %	Cu, %	Zn, %	Other, %	Weight, g
3	United Kingdom	50p old	25	75	0	0	
4	United Kingdom	50p new	25	75	0	0	
5	United Kingdom	20p new	16	84	0	0	
6	United Kingdom	10p old	25	75	0	0	
7	United Kingdom	10p new	6	0	0	mild Steel - 94	
8	United Kingdom	2p new	0	6	0	mild Steel - 94	
9	Singapore	1 dollar old	2	92	0	Al - 6	8.05+-0.20
10	Singapore	50c old	25	75	0	0	8.56+-0.20
11	Singapore	20c new	?	0	0	steel - ?	6.56+-0.28
12	Bulgaria	50 stotinki	10			0	5
13	Bulgaria	5 stotinki				steel - ?	3.5
14	European Union	50c	0	89	5	Al - 5, Sn -1	7.8
15	European Union	2c old		x		0	3.06
16	European Union	2c new		x		0	3.06
17	Romania	10 bani	?	0	0	steel - ?	4
18	Norway	1 krone	25	75	0	0	4.35
19	Switzerland	20 centim	25	75	0	0	4
20	Sweden	1 krona	25	75	0	0	
21	Japan	1 yen	0	0	0	al-100	1
22	Hong Kong	10c				0	1.85
23	Uganda	200 schillings	~30	~70	0	0	8.5
24	USA	25c				0	
25	USA	1c	0	2.5	97.5	0	2.5
26	Canada	25c	2.2	3.8	0	Steel AISI 1006 - 94	4.4
27	Brazil	5 centavos	0			0	

Table B1: Table of official info about the international coins. Notable are the coins with predominantly steel composition with a coating of one of the three main elements. CITATIONS