

X-Ray fluorescence

Benjamin Topper

Lab Partner : Clayton S. Ohair

Spring 2007 – Dr Hoffmann

Abstract

X-ray fluorescence is the induced release of x-ray energy photons by an unknown material hit by incident radiation. In this experiment we used a radioactive ^{109}Cd source to fluoresce samples with unknown atomic makeup ; a cooled intrinsic germanium solid-state X-ray detector is used to measure the X-ray energy spectrum. Each element having a unique x-ray spectrum, we can therefore determine the atomic composition of the unknown material.

Introduction

The goal of our experiment is to determine the atomic composition of unknown materials, using x-ray spectroscopy.

X-rays were discovered in 1895 by Rontgen : he discovered a new kind of radiation that could penetrate objects (we have all seen the x-ray picture of his wife's hand, which is one of the first x-ray image ever made). X-rays are a form of electromagnetic radiation with a wavelength in the range of 10 to 0.01 nanometers, corresponding to frequencies in the range of 10^{12} - 10^{15} hertz.

The X-rays emitted by the Cadmium source will hit the unknown material. If the energy is sufficient, some electrons in the atoms of the unknown material will get excited and emit their own photons, which energy is typical for each atom. We say that the unknown material fluoresces. These photons will then reach the detector, hitting some electrons there that will create a small electric current. This is what we are able to detect and quantify. As photons from different atoms are emitted with different energies, they will induce different electric currents. Therefore, by calibrating the detector (in fact, the computer) appropriately, we can get the photon energy spectrum back.

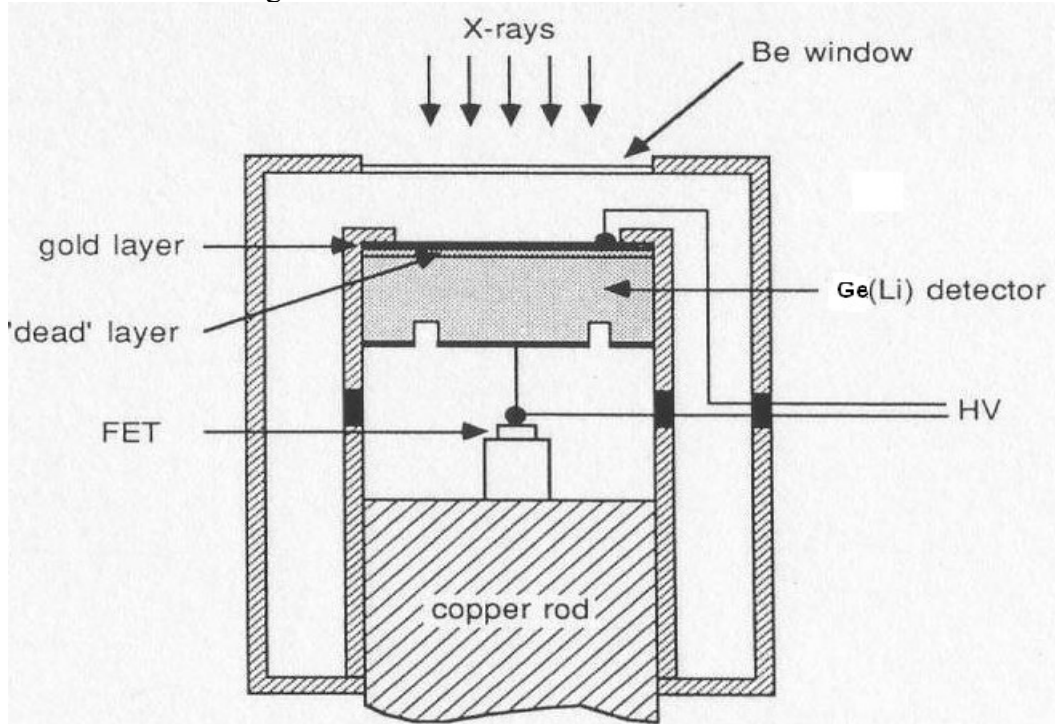
I. Experimental Procedure

Equipment used

Germanium Detector+Pre-amp

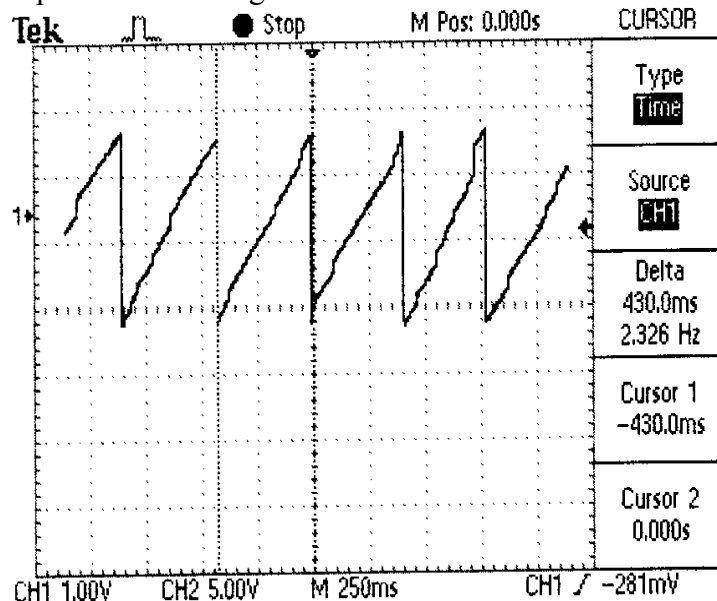
This is the most important piece of the apparatus. We should describe it carefully to understand exactly how the experiment works. Moreover how the detector exactly works doesn't seem to be explicitly shown in any previous lab report.

Here is a schematic drawing of a Ge(Li) detector, like the one from Princeton Gamma Tech we used -slightly modified from its original version- :



After hitting the backing plate, the x-ray photons enter the detector through the very thin Be window (be careful never touching it ! It breaks very easily) and will hit some electrons from the Ge(Li) crystal, that now become "free electrons".

As these electrons have an electric charge, they will be "swept out" by the high voltage (1.50kV) we are applying to it. The detector therefore acts like a small capacitor as it can easily be shown when looking on an oscilloscope how the voltage evolves in the detector :



Seesaw shape- this is what we get on the oscilloscope

A positive slope shows that electrons are being "swept out". Once the potential difference becomes big enough, the capacitor "discharges" (falling slope) and the information is sent to the pre-amplifier. That's why we need the inhibitor to act every 1ms to send reset pulses with 10microsecond shaping time constant, to let enough time for the detector to "charge" and "discharge" completely.

Also, as the information is a very small voltage, it has to be immediately pre-amplified ; that's why the pre-amp is immediately fixed on the detector : if there were long wires between them, the information would never get through.

The germanium detector has to be kept very cool -using liquid nitrogen- because if it isn't, it starts heating up very quickly and can get destroyed fast.



Picture of the detector and the pre-amp.

Bias supply

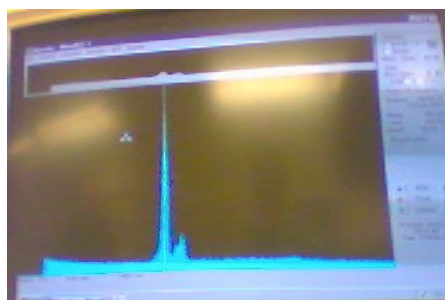


This is the 1.50kV bias supply. It applies the bias to the germanium detector to sweep out the electrons and create the small electric current we want (after amplification).

Amplifier

Once the signal is preamplified, we can safely send it to the Ortec amplifier. The signal coming out of the amplifier can now be read on a computer.

Computer



This is a picture of the software, Maestro, we use to get the data. You can then export the graphs on winplot to work on them on another computer, as the one attached to the experiment is pretty old (running on windows 95).

Liquid Nitrogen

The liquid nitrogen is used to cool the detector. Please use the gloves when filling the dewar, liquid nitrogen is at 77K and therefore every object in contact with it get very cold !

Experimental Setup and Procedure

a) Initial Setup (setting and connections, testing the detector)

Follow very carefully all the steps on the "Operation Instructions" of the Princeton Gamma-Tech detector.

Some of the steps are not exactly correct ; for example step 3 tells you that you should -12V for the preamplifiers output. It turns out that the experimental value we get is -10V. Anyway, following all the steps should make you understand a little better how the componenets are connected to each other.

Step 5 tells you not to raise the detector bias at a rate higher than 100V/s. You should therefore also be careful afterwards not to turn the bias off without taking care : first lower smoothly the voltage from 1.50kV to 0.05kV, then you can turn it off safely.

b) Cooling

Before starting the experiment, you have to fill the Dewar with liquid nitrogen (~77K) and allow the detector to cool for approximately 4 hours. If properly concealed and maintained the Dewar can stay cool for 9 days.

We actually performed the experiment : taking datas just after refill and 5 days after refill. We did not notice any influence. This is very likely due to the fact that 9days is a very safe estimation, the real time before it really isn't cool any more is more likely to be around 30 days (a factor of 3 for saftey).

Why do we want to cool the detector ? For two reasons.

First because we want to reduce the noise due to thermal excitation of electrons. But we also cool it because that kind of detectors have a tendancy to heat up very quickly Therefore if we don't keep it at a very low tempreature, not only the background noise may be too high high and may not allow us to get any valuable experimental data, but we could also break the detector.

c) Calibration

To calibrate the detector, we use the weak cadmium source.

Place carefully the cadmium source in front of the detector, put the amplifier on gain 100. You should then be able to see the 88keV peak on the extreme right.

The most useful gain are gain 200 and 500 as they let you collect accurate energy measurements for respectively for th ~25keV and ~10keV, which is where most of the "common" elements peak (as we will see later the 13.4keV was actually never explained in previous labs).

As we quickly found out, the calibration is not accurate over all the energy spectrum.

Let say we are using gain 200 ; the cadmium self-fluorescing peaks will be exactly in the center of the window, as with this gain the energy ranges from 0 to ~50keV.

Calibrating the first cadmium peak at 23.2keV (its exact value), we quickly find out that the further we are from where we calibrated, the less accurate the measurements are. For example if we had done the calibration on the 23.2keV peak, and we want to look for copper, the 8.1keV copper peak will not be at 8.1keV, but will be slightly shifted.

Next section will show a table to allow us estimate that shiftin. All the results will be given after correction.

d) Experiments and uncertainties

Gain 200

$$E(\text{corrected}) = E(\text{measured}) + (E(\text{calibration}) - E(\text{measured}))/10$$

For example for a calibration at 23.2keV, the 13.4keV peak will appear at 12.31keV.

Gain 500

$$E(\text{corrected}) = E(\text{measured}) + (E(\text{calibration}) - E(\text{measured}))/9.4 + 0.05$$

Gain 1000

$$E(\text{corrected}) = E(\text{measured}) + (E(\text{calibration}) - E(\text{measured}))/8 + 0.02$$

All the data are given with the corrected values (the mathematical formulas stated above were already applied to our raw results).

II. Experimental Data & Data Analysis

Here are shown some of our most interesting experimental results.

After studying material which composition was already known, my lab partner and I decided to bring our own (unknown) materials to analyze them. Our goal was to bring some objects which we didn't know what they were made of, fluoresce them and find out their composition.

From our first experiments, we understood that it would be almost impossible to detect any element lighter than Aluminium (atomic mass 13) ; but apart from this constraint, we could bring anything we wanted.

Peak energy indicates the energy, in keV, of the peak after correction. Different atoms have peaks at different energies, so by comparing those values to the theoretical ones we can determine the compositions of the studied materials - this is why this experiment is interesting !
See references for more details on the theory.

FWHM gives an estimate of the absolute experimental uncertainty ($E = E(\text{corrected}) \pm \text{FWHM}$)

Intensity means number of counts. As we did not let all experiments run for the same number of counts, they cannot immediately be compared one with the other. The number of counts can however immediately be used to estimate the relative intensity of the peaks.

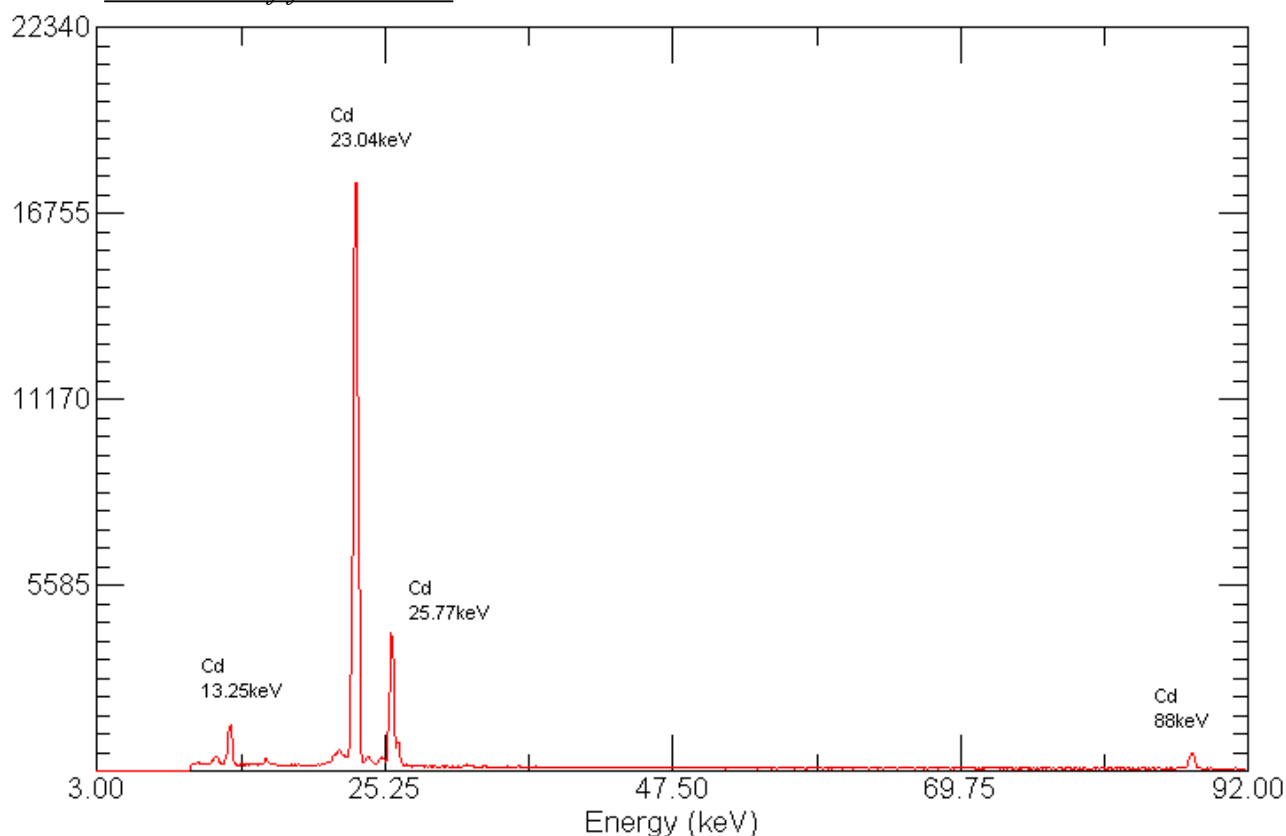
Suspected element shows which element we suspect this peak to be.

Theoretical peak is the theoretical value of the peak energy for this element. This allows us to compare our experiment with theoretical predictions from quantum mechanics. Next to the value is indicated the kind of emission line. **K-alpha** emission or absorption lines result when an electron transitions from the innermost "K" shell (principal quantum number 1), to a 2p orbital of the second or "L" shell (with principal energy quantum number 2). The line is actually a doublet - which we think we were able to detect for lead-, with slightly different energies depending on spin-orbit interaction energy between the electron spin and the orbital momentum of the 2p orbital. **K-beta** is for the transition from the higher energy level of the K-layer.

Auger is a phenomenon in which the emission of an electron from an atom causes the emission of a second electron.

See references for more details on the theory.

Cadmium self-fluorescence



Gain : 100 - No backing

Interesting Peaks :

Peak energy	FWMH	Intensity	Suspected element	Theoretical peak	%
13.25	0.38	149	Cd	18 Auger	30%
23.04	0.40	1861	Cd	23.2 K- α	0.7%
25.77	0.30	452	Cd	26.2 K- β	0.7%
88.0	0.20	154	Cd	88.0	-

Analysis

Our first discovery was to see that cadmium self fluoresces, which means that after one atom emits the 88.0keV, it bounces on some other cadmium atoms that are going to fluoresce.

Therefore, we see the 23.2 and 26.2 peaks, as well as the 88.0keV peak.

Why do we see a 13.3 peak ? We had a lot of trouble finding an explanation for this peak. Even though it is in every report and on the x-ray spectrum website we used to compare our graphs (see references), there was no explanation for this peak.

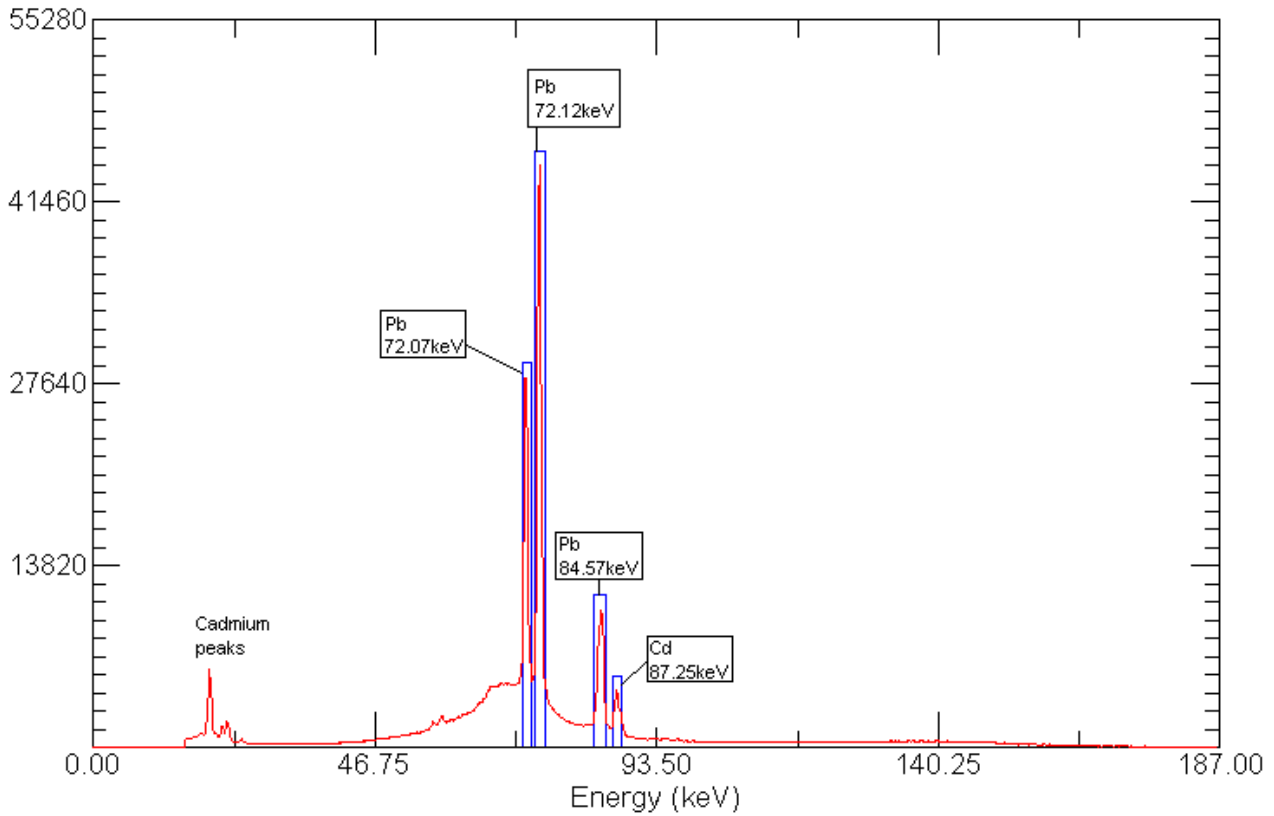
It turns out that this peak may very likely be an Auger peak, ie the emission of a secondary electron caused by a first electronic-emission.

The theoretical value for the Auger peak for Cadmium is around 18keV. Our experiment therefore doesn't seem very accurate.

We think we may have found a theoretical argument to explain the lack of accuracy for this peak (30% out of range !). In the Jenkins book (see references), it is shown that the presence of intermolecular binding can shift peaks to lower energies. We therefore thought that Cadmium can be in some molecular form, very likely with silver, like for example SilverCadmiumOxide.

The presence of Silver peaks can even be inferred on this graph (at 22 and 25keV).

Lead



Gain : 50

Interesting Peaks :

Peak energy	FWMH	Intensity	Suspected element	Theoretical peak	%
~25	-	-	Cadmium peaks	23.2-26.2	-
72.07	0.54	28092	Pb (Lead)	72.8 K-α1	1%
72.12	0.54	44029	Pb (Lead)	74.95 K-α2	3.9%
84.57	0.89	10457	Pb (Lead)	84.92 K-β	0.5%
87.25	0.49	4287	Cd (Cadmium)	88.0	0.9%

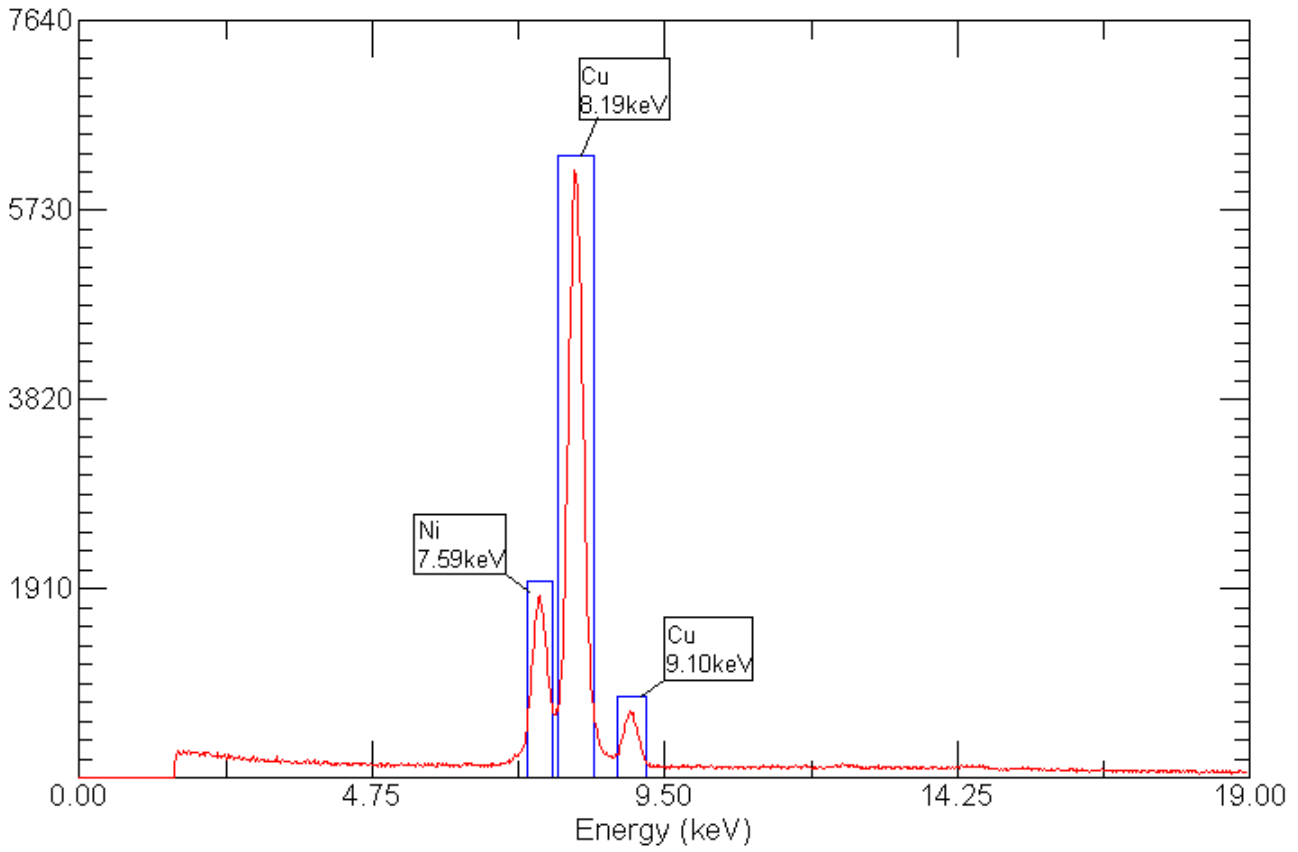
Analysis

This experiment showed what we expected : lead and cadmium.

Very good precision on that experiment, verly likely due to the large number of counts.

Nickel coin

I put this experiment in the "known" one because I was expecting to find almost only nickel (as it is called a "nickel coin")... but in fact we didn't only find nickel.



Gain : 500

Interesting Peaks :

Peak energy	FWMH	Intensity	Suspected element	Theoretical peak	%
7.59	0.20	1836	Ni	7.47 K- α	1.6%
8.19	0.25	6107	Cu	8.1 K- α	1.1%
9.10	0.24	664	Cu	9.0 K- β	1.1%

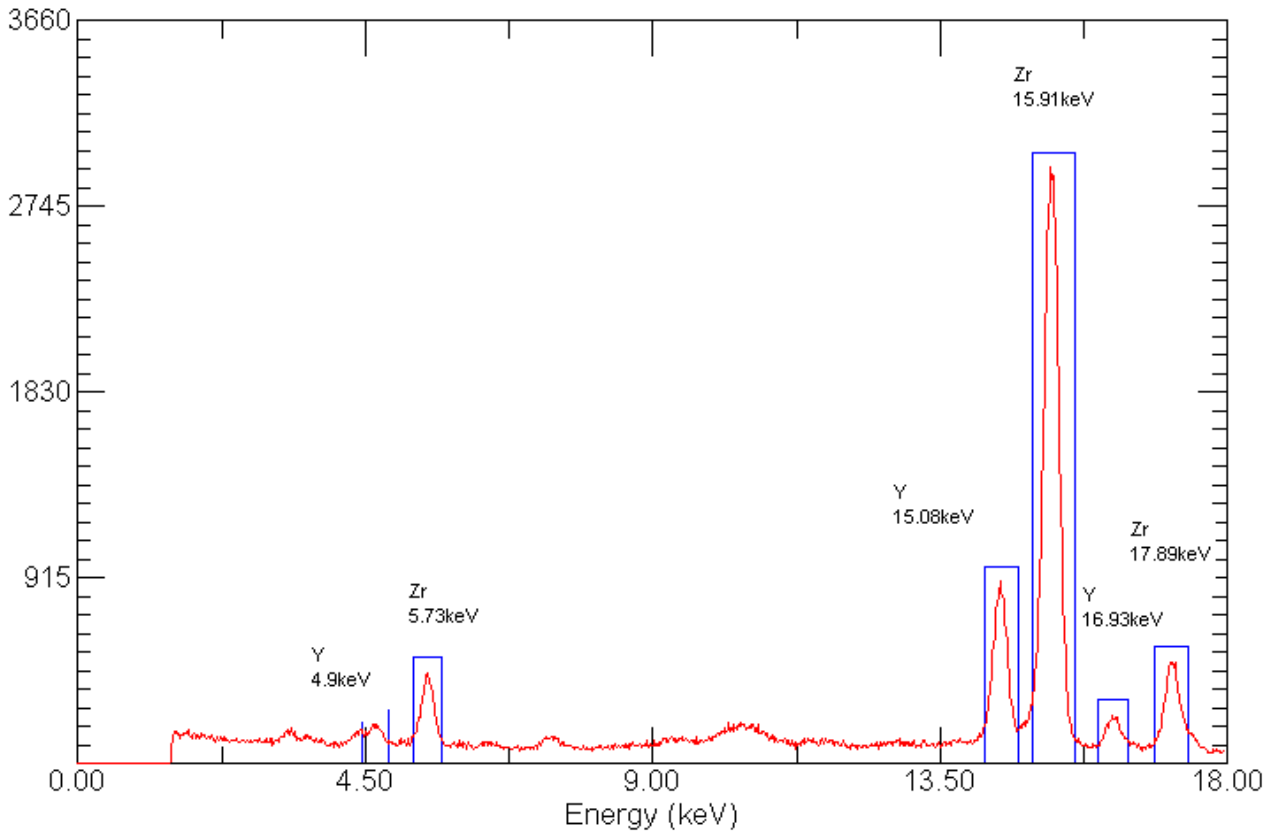
Analysis

This experiment shows that what is commonly called a "nickel coin" is in fact made up of Copper and Nickel.

Unknown n°1 : Diamond ?

My lab partner brought an object he had found : it looked like a real diamond, but we were both pretty sure it was a fake one. However we had no idea what a fake diamond was made of !

Here is the result of that experiment :



Gain : 500

Interesting Peaks :

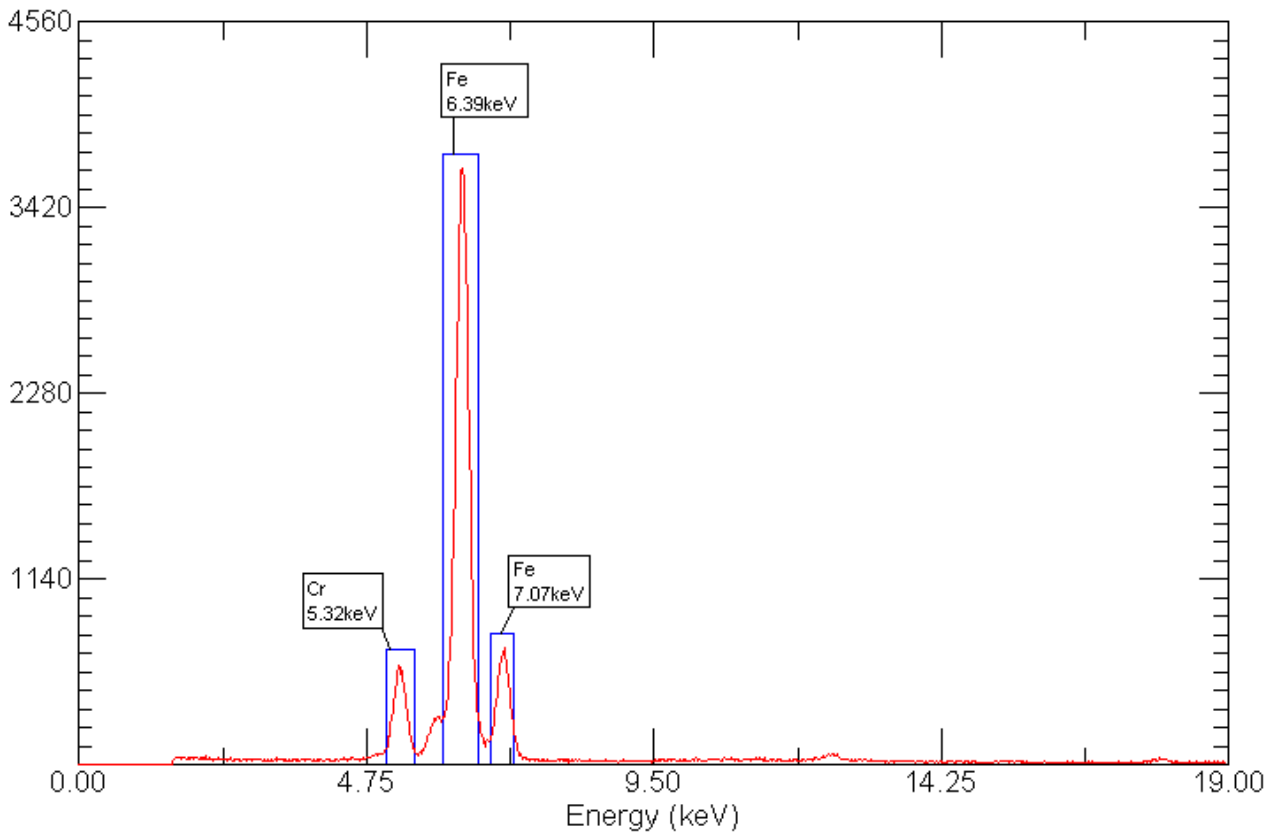
Peak energy	FWMH	Intensity	Suspected element	Theoretical peak	%
4.9	0.18	168	Y (Yttrium)	5.1	4%
5.73	0.23	426	Zr (Zirconium)	6.0	4.7%
15.08	0.23	900	Y (Yttrium)	15.0 K-α	0.6%
15.91	0.27	2941	Zr (Zirconium)	15.8 K-α	0.7%
16.93	0.24	226	Y (Yttrium)	16.7 K-β	1.4%
17.89	0.22	500	Zr (Zirconium)	17.7 K-β	1.1%

Analysis

This was a very interesting and challenging experiment as it was our first one with no clue on what we were looking for. It turned out to be pretty easy to label the Yttrium and the Zirconium, so then to look on the internet if fake diamonds were made up with those elements. It turns out that they are.

Very good precision on that experiment except for low energy peaks, as expected (it is almost out of our detection range).

Unknown n°2 : Spoon



Gain : 500

Interesting Peaks :

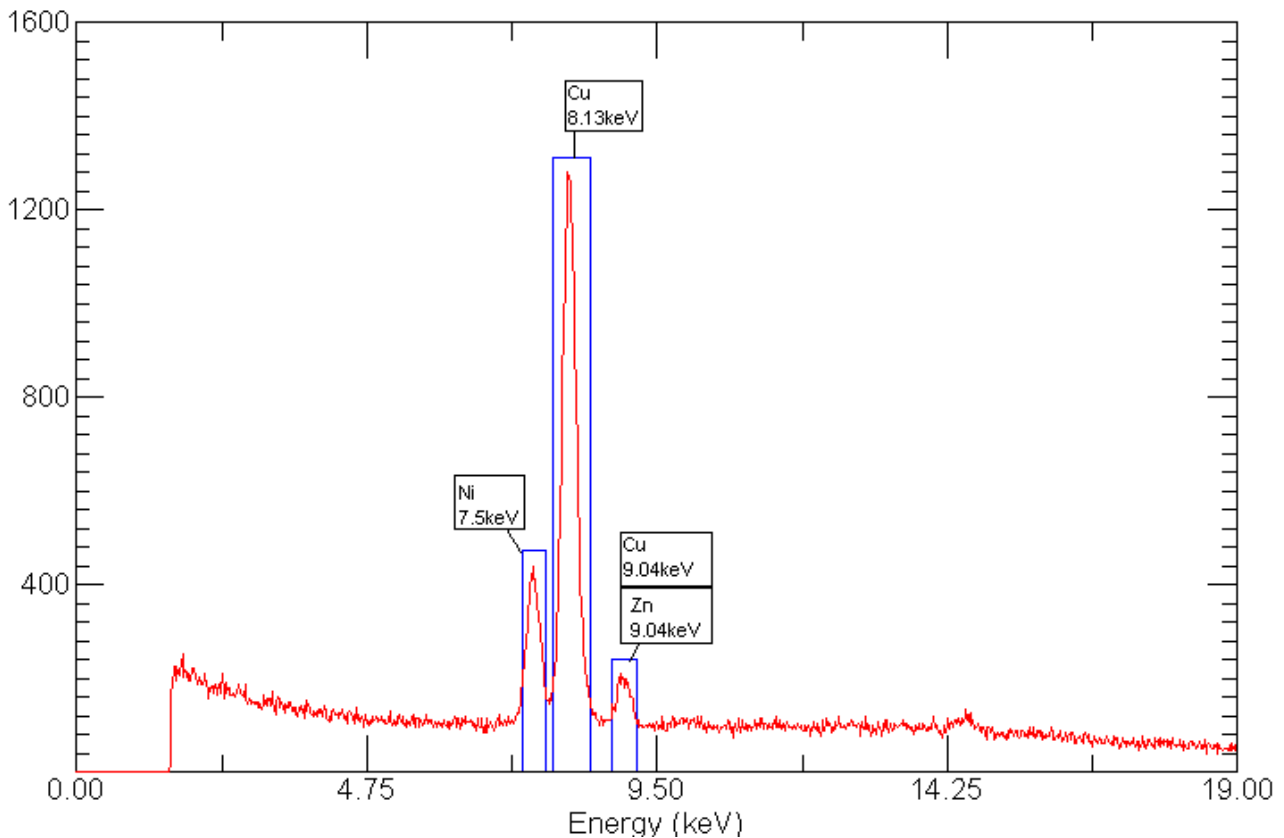
Peak energy	FWMH	Intensity	Suspected element	Theoretical peak	%
5.32	0.21	599	Cr	5.4 K- α	1.5%
6.39	0.22	3657	Fe	6.4 K- α	0.15%
7.07	0.20	681	Fe	7.1 K- β	0.42%

Analysis

Very straightforward analysis of a Castilian's cafeteria spoon. It turns out to be made up with Chrome and Iron, which is called stainless steel and is used for kitchen tools.

Again a very good accuracy on the results except at very low energy.

Unknown n°3 : 1Euro



Gain : 500

Interesting Peaks :

Peak energy	FWMH	Intensity	Suspected element	Theoretical peak	%
7.5	0.22	410	Ni	7.47 K- α	0.4%
8.13	0.24	1259	Cu	8.1 K- α	0.4%
9.04	0.22	185	Cu	9.0 K- β	0.5%
9.04	0.22	185	Zn	8.7 K- α	1%

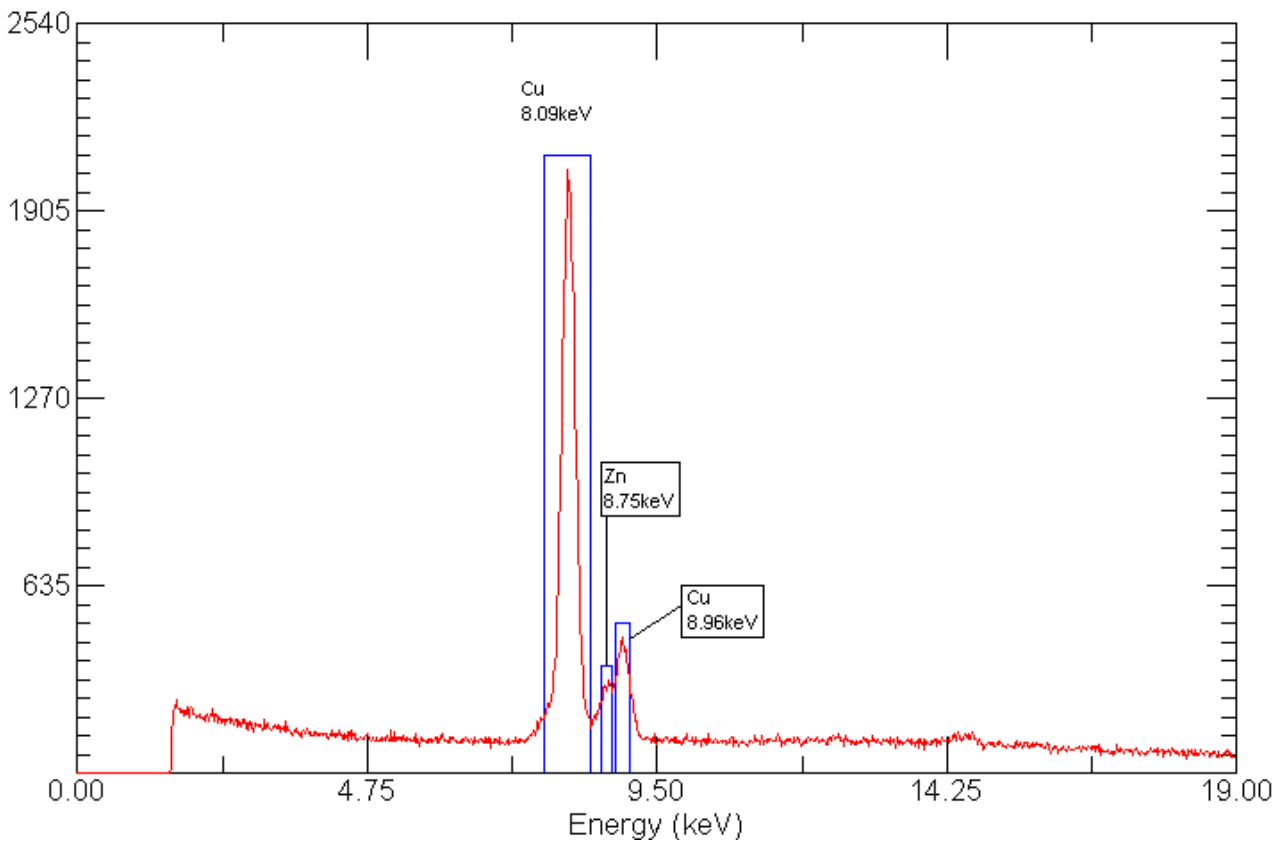
Analysis

As all the other students that had done experiments had been analysing US coins, we decided to analyse European ones !

The composition of 1euro coin was easily found on the internet, and confirmed our experimental result.

Notice that two peaks seem to be overlapping, due to the lack of resolution of the detector. However we should have been able to get a better result if we had let the experiment run for a longer time.

Unknown n°4 : 50cents-euro



Gain : 500

Interesting Peaks :

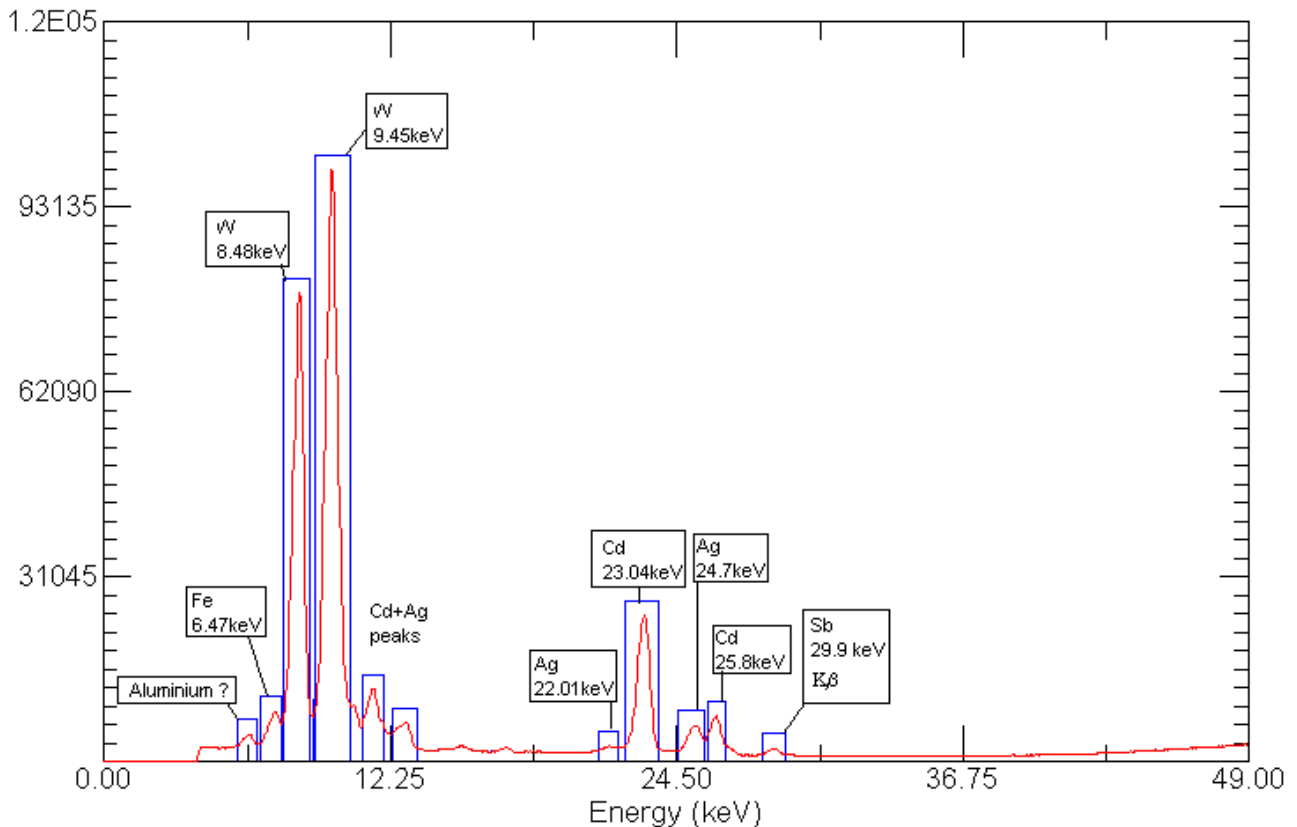
Peak energy	FWMH	Intensity	Suspected element	Theoretical peak	%
8.09	0.24	1962	Cu	8.1 K- α	0.1%
8.75	0.05	300	Zn	8.7 K- α	0.6%
8.96	0.14	436	Cu	9.0 K- β	0.45%

Analysis

Again here two peaks are almost overlapping.

The composition of the 50cents-euro was also found on the internet and confirmed our experiment.

Unknow n°5 : Backing plate



Gain : 500

Interesting Peaks :

Peak energy	FWMH	Intensity	Suspected element	Theoretical peak	%
~2	-	5 121	Aluminium ?	1.55 K-β	4%
6.47	0.05	10 530	Fe (Iron)	6.6 K-α	2.0%
8.48	0.28	86 300	W (Tungsten)	8.4 K-α	0.95%
9.45	0.35	100 000	W (Tungsten)	9.7 K-β	2.6%
~13	-	-	Ag + Cd peaks	~13 Auger	-
22.01	-	3 091	Ag (Silver)	22.2 K-α	1%
23.04	0.22	25 043	Cd (Cadmium)	23.2 K-α	1%
24.7	0.22	4 500	Ag (Silver)	25.0 K-β	1.1%
25.8	0.14	6 542	Cd (Cadmium)	26.2 K-β	2%
29.9	0-	2 987	Sb (Antimony)	29.9 K-β	-

Analysis

The backing plate was removed during the other experiments to avoid this noise.

Analysing that backing plate was very challenging as we only had very little idea of what it could be made of.

It turns out to be made of Tungsten (W), Iron(Fe) and Antimony (Sb). There could be some Aluminium too but that peak is definitely out of range and we really can't tell if it's just background noise or an acutal peak.

Silver and Cadmium are due to cadmium self-fluorescence.

Conclusion

Those experiments show that X-ray fluorescence is a very straightforward and accurate way to find the composition of any element, if it's made up with any element heavier than aluminium. However overlapping peaks can sometimes cause trouble to tell which element is present for sure.

Some ways to improve this experiment could be to take more counts during for each experiment. I cannot think of any mean that could enable us to reach lower energies. Articles on that subject seem to say that Aluminium is a lower limit for that kind of detectors. Therefore the only way to find lower-mass elements would be to get a new kind of detector !

Bibliography

I. Internet ressources

a) Websites

X-Ray transitions energy database

<http://physics.nist.gov/PhysRefData/XrayTrans/Html/search.html>

X-ray Spectrum of Elements on the Periodic Table

<http://ie.lbl.gov/xray/mainpage.htm>

Wikipedia

http://en.wikipedia.org/wiki/X-ray_fluorescence

http://en.wikipedia.org/wiki/Auger_electron

<http://en.wikipedia.org/wiki/K-alpha>

Informations about x-ray fluorescence

<http://www.learnxrf.com/>

b) PDF documents

MIT document on x-ray physics

<http://ocw.mit.edu/NR/rdonlyres/Physics/8-13-14Fall-2004-Spring-2005/54D1D468-43EF-4228-B53E-6AA080C341C0/0/jlexp31.pdf>

Short description of how x-ray fluorescence works

<http://www.amptek.com/pdf/xrf.pdf>

II. Books

The book I mostly used

X-ray Fluorescence Spectrometry, **Jenkins, R.**

Some other useful informations :

Principles and Practice of X-ray Spectrometric Analysis, **Bertin, E. P.**

And of course the other lab reports !