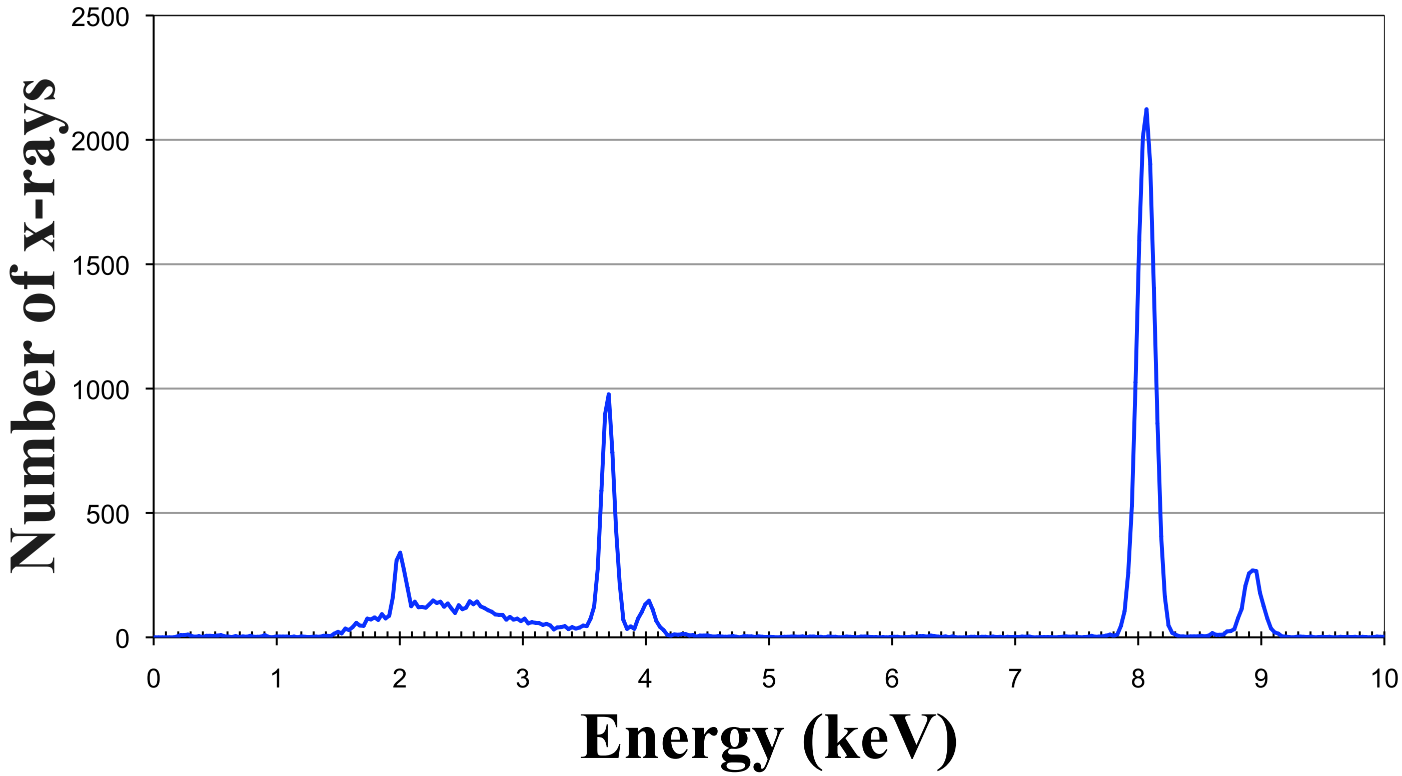
Calculations of Characteristic X-ray Energies and Wavelengths and the PIXE Spectrum



The Characteristic X-ray Wavelengths

- **Electronic transitions within inner shells of heavier atoms are accompanied by large energy transfers.**
- **The inner electrons of high *Z* elements are bound tightly to the atom, since they see essentially the entire nuclear charge.**
- **First let's make do a small calculation in order to simplify or lives when we calculate the energies of the orbits.**

$$E_n = -\frac{Z^2 m e^4}{2(4\pi\varepsilon_0)^2 n^2 \hbar^2} = -\left(\frac{m e^4}{2(4\pi\varepsilon_0)^2 \hbar^2}\right)\frac{Z^2}{n^2}$$

$$= -\left[\frac{(9.11\times10^{-31}\,kg)(1.6\times10^{-19}\,C)^4}{32\pi^2\left(8.85\times10^{-12}\,\frac{C^2}{Nm^2}\right)^2\left(\frac{6.63\times10^{-34}\,Js}{2\pi}\right)^2}\times\frac{1eV}{1.6\times10^{-19}\,J}\right]\frac{Z^2}{n^2}$$

$$= -(13.57\,eV)\frac{Z^2}{n^2}$$

The Characteristic X-ray Wavelengths

- Let's calculate the lowest energy, or longest expected x-ray wavelengths for the element copper.

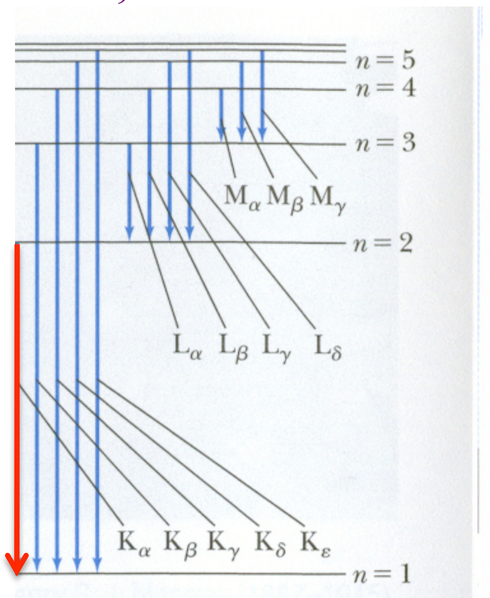
$$^{64}_{29}Cu \longrightarrow$$ 64 nucleons {29 electrons, 29 protons, 35 neutrons}

- The energy of an inner shell electron is given by *Z = 29*, and *n = 1*.

$$E_1 = -(13.57eV)\frac{Z^2}{n_{lower}^2} = -(13.57eV)\frac{(29)^2}{(1)^2} = -11412.4eV$$

- The energy of an outer shell electron is given by *Z = 29*, and *n = 2*.

$$E_2 = -(13.57eV)\frac{Z^2}{n_{upper}^2} = -(13.57eV)\frac{(29)^2}{(2)^2} = -2853.1eV$$



Thornton, S., & Rex, A., Modern Physics for Scientists and Engineers, 3rd Ed., Thomas Brooks Cole 151(2006).

- This is the transition of an electron from the *n = 2* state to the *n = 1* state, or an electronic transition from the L-shell to the K-shell.

- This transition is called the K_α transition for copper and the difference in energy between these states is the energy of the emitted x-ray.

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The Characteristic X-ray Wavelengths

The energy of the emitted photon is the difference in energy between the upper state ($n = 2$) and the lower state ($n = 1$).

$$\Delta E = E_{upper} - E_{lower} = -2853.1eV - \left(-11412.4eV\right) = 8559.3eV$$

This corresponds to a wavelength of

$$\Delta E = \frac{hc}{\Delta\lambda}$$

$$\Delta\lambda = \frac{hc}{\Delta E} = \frac{\left(6.63\times10^{-34}Js\times\frac{1eV}{1.6\times10^{-19}J}\right)3\times10^{8}\,\frac{m}{s}}{8559.3eV} = 1.45\times10^{-10}m$$

The actual wavelength (measured in the laboratory) is $1.54x10^{-10}m$.

This is about 70% from the true value!! Hmm…

The Characteristic X-ray Wavelengths

Comments:

- These wavelengths are calculated based on a hydrogen-like atom using the Bohr model of the atom.
- This means that there is a single electron that transitions.
- The problem with heavy or high Z atoms is that they are rarely single electron atoms.
- So do we live with this or can we fix our results and theory?
- I guess we have to fix the theory since it doesn't give the expected results.

Modifications to the Bohr Theory

- To start, in multi-electron atoms the higher orbital electrons are partially screened from the nucleus.

- In other words they don't see the full nuclear charge of the nucleus.

- The net charge an electron say in the *L*-shell sees is Ze^- due to the nucleus *minus* e^- due to the one electron in the *K*-shell (one was ejected.)

- Now, this is only the *L* to K-shell transitions. Further modifications are needed from *M* to *L*-shell transitions, for example.

- Therefore the net charge is $(Z - 1)e^-$

- The potential energy is thus $$V_n = -\frac{(Z-1)e^2}{4\pi\varepsilon_0 r_n}$$

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Modifications to the Bohr Theory

- The energy of the orbit is given as

$$E_n' = \frac{1}{2}mv_n^2 + V_n = \frac{1}{2}m\left(\frac{(Z-1)e^2}{4\pi\varepsilon_0 n\hbar}\right)^2 - \frac{(Z-1)e^2}{4\pi\varepsilon_0 \dfrac{4\pi\varepsilon_0 n^2\hbar^2}{m(Z-1)e^2}}$$

- Doing the math…

$$E_n = -\frac{(Z-1)^2 me^4}{2(4\pi\varepsilon_0)^2 n^2\hbar^2}$$

•This is the modified Bohr theory to take into account screening of the outer shell electrons by the inner shell electrons.

- How do our calculations look now? Did we do any better?

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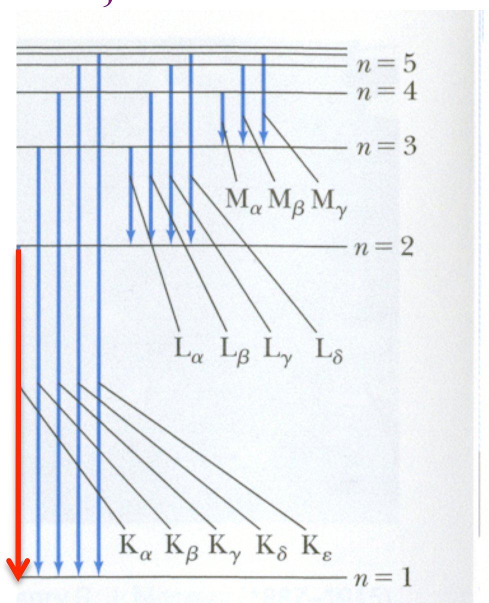
Modifications to the Bohr Theory and the new X-ray Wavelengths

- Let's recalculate the expected x-ray energy and wavelength for the K_α transition in copper.

$${}^{64}_{29}Cu \longrightarrow$$ 64 nucleons {29 electrons, 29 protons, 35 neutrons}



- The energy of an inner shell electron is given by $Z = 29$, and $n = 1$.

$$E_1 = -(13.57eV)\frac{(Z-1)^2}{n_{lower}^2} = -(13.57eV)\frac{(28)^2}{(1)^2} = -10638.9eV$$

- The energy of an outer shell electron is given by $Z = 29$, and $n = 2$.

$$E_2 = -(13.57eV)\frac{(Z-1)^2}{n_{upper}^2} = -(13.57eV)\frac{(28)^2}{(2)^2} = -2659.7eV$$

- This is the transition of an electron from the $n = 2$ state to the $n = 1$ state, or an electronic transition from the L-shell to the K-shell including screening.

Modifications to the Bohr Theory and the new X-ray Wavelengths

The energy of the emitted photon is the difference in energy between the upper state ($n = 2$) and the lower state ($n = 1$).

$$\Delta E = E_{upper} - E_{lower} = -2659.7eV - \left(-10638.9eV\right) = 7979.2eV$$

This corresponds to a wavelength of

$$\Delta E = \frac{hc}{\Delta\lambda}$$

$$\Delta\lambda = \frac{hc}{\Delta E} = \frac{\left(6.63\times10^{-34}Js\times\frac{1eV}{1.6\times10^{-19}J}\right)3\times10^{8}\,\frac{m}{s}}{7979.2eV} = 1.56\times10^{-10}m$$

The actual wavelength (measured in the laboratory) is $1.54x10^{-10}m$.

This is about 1.2% from the true value!!

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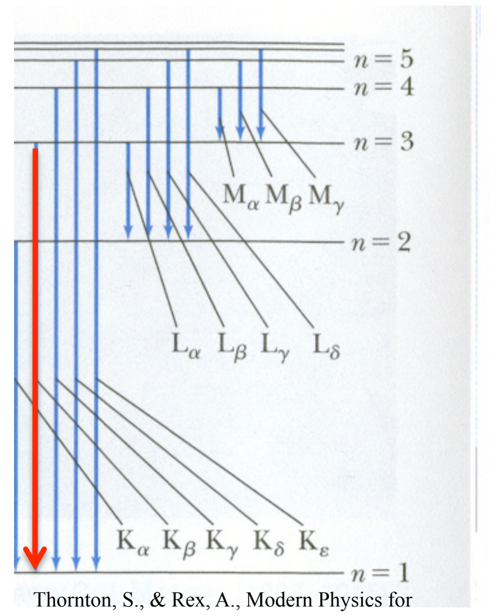
More X-ray Wavelengths…

- What is the K_β wavelength for Copper?

$^{64}_{29}Cu \longrightarrow$ 64 nucleons {29 electrons, 29 protons, 35 neutrons}

- Recalling the energy level diagram for an atom, the K_β transition is from the $n = 3$ state to the $n = 1$ state.



Thornton, S., & Rex, A., Modern Physics for Scientists and Engineers, 3rd Ed., Thomas Brooks Cole 151(2006).

- The energies of the upper and lower states are thus

$$E_1 = -(13.57eV)\frac{(Z-1)^2}{n_{lower}^2} = -(13.57eV)\frac{(28)^2}{(1)^2} = -10638.9eV$$

$$E_2 = -(13.57eV)\frac{(Z-1)^2}{n_{upper}^2} = -(13.57eV)\frac{(28)^2}{(3)^2} = -1182.1eV$$

More X-ray Wavelengths…

The energy of the emitted photon is the difference in energy between the upper state ($n = 3$) and the lower state ($n = 1$).

$$\Delta E = E_{upper} - E_{lower} = -1182.1eV - (-10638.9eV) = 9456.8eV$$

This corresponds to a wavelength of

$$\Delta E = \frac{hc}{\Delta\lambda}$$

$$\Delta\lambda = \frac{hc}{\Delta E} = \frac{\left(6.63\times10^{-34}Js\times\frac{1eV}{1.6\times10^{-19}J}\right)3\times10^{8}\,\frac{m}{s}}{9456.8eV} = 1.32\times10^{-10}m$$

The actual wavelength (measured in the laboratory) is $1.39\text{x}10^{-10}$m.

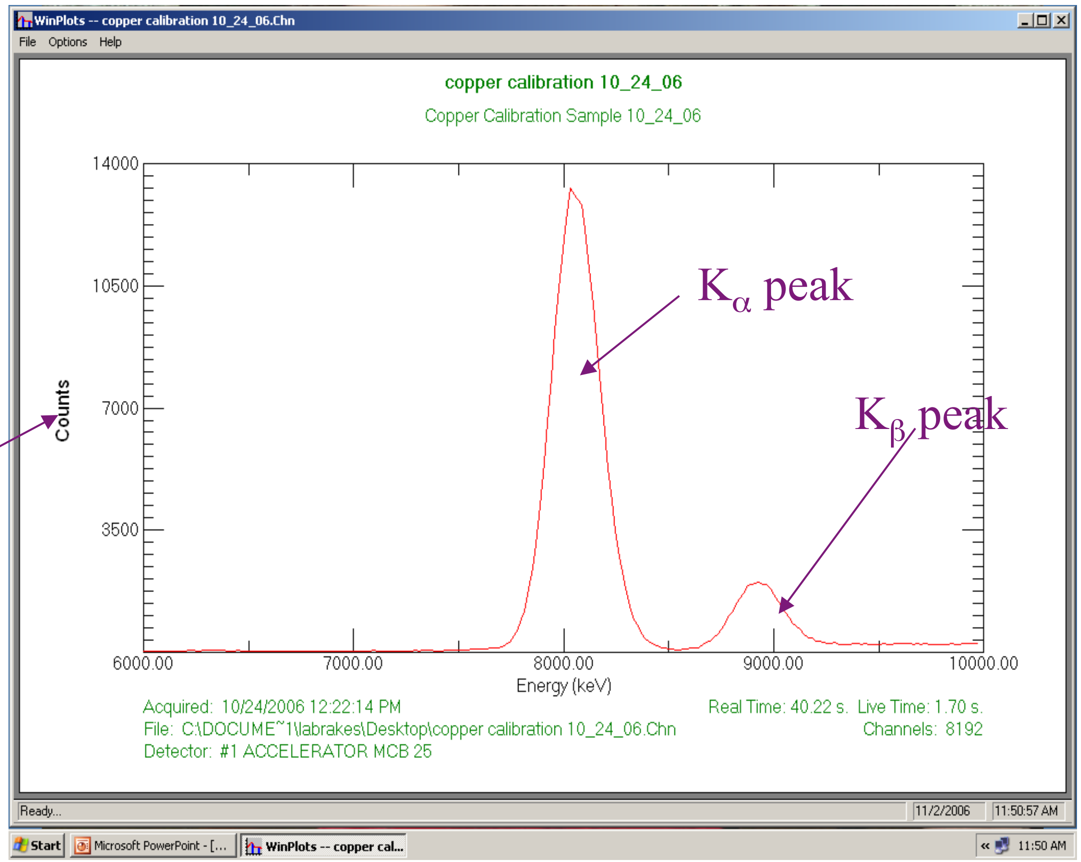
This is about 5.3% from the true value!!

These energies are actually tabulated and in practice look up the element based on the transition energies observed on a calibrated x-ray spectrum

The X-ray Spectrum of Copper

This is a typical *PIXE* plot that shows the x-ray spectrum of copper.

Number of x rays detected



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This sample was run on our accelerator and calibrated using a set of standards.

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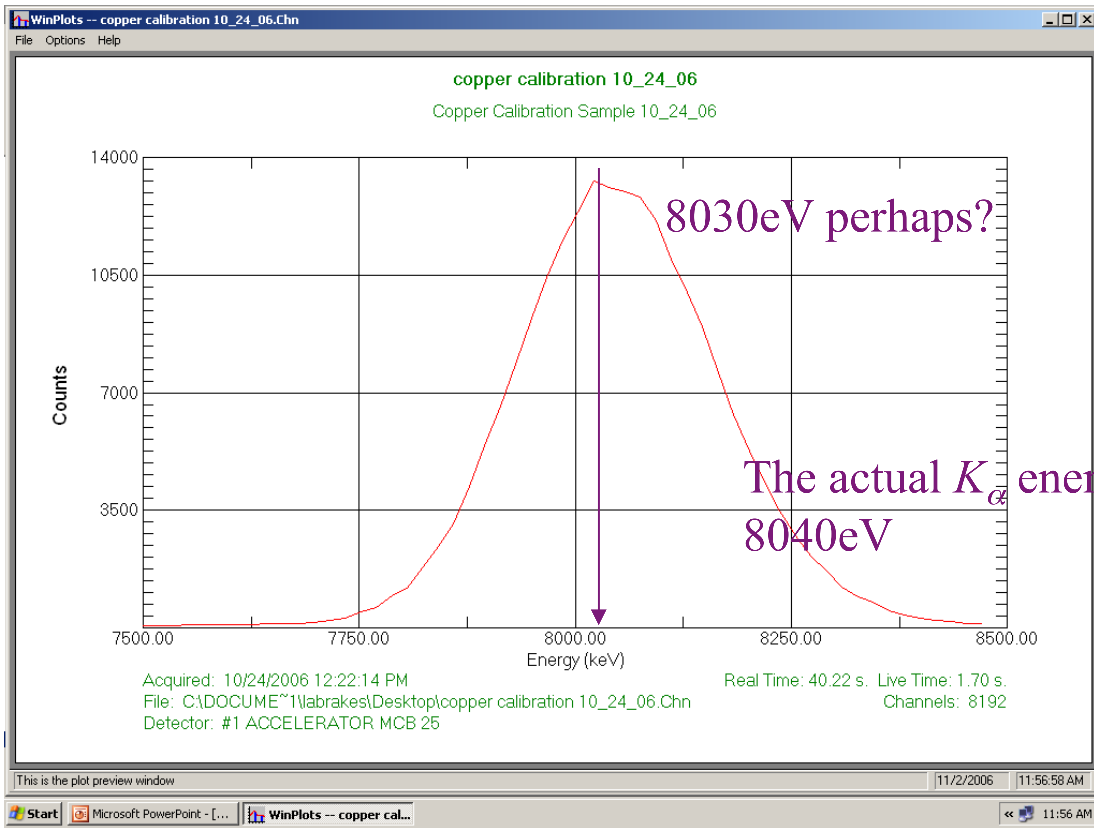
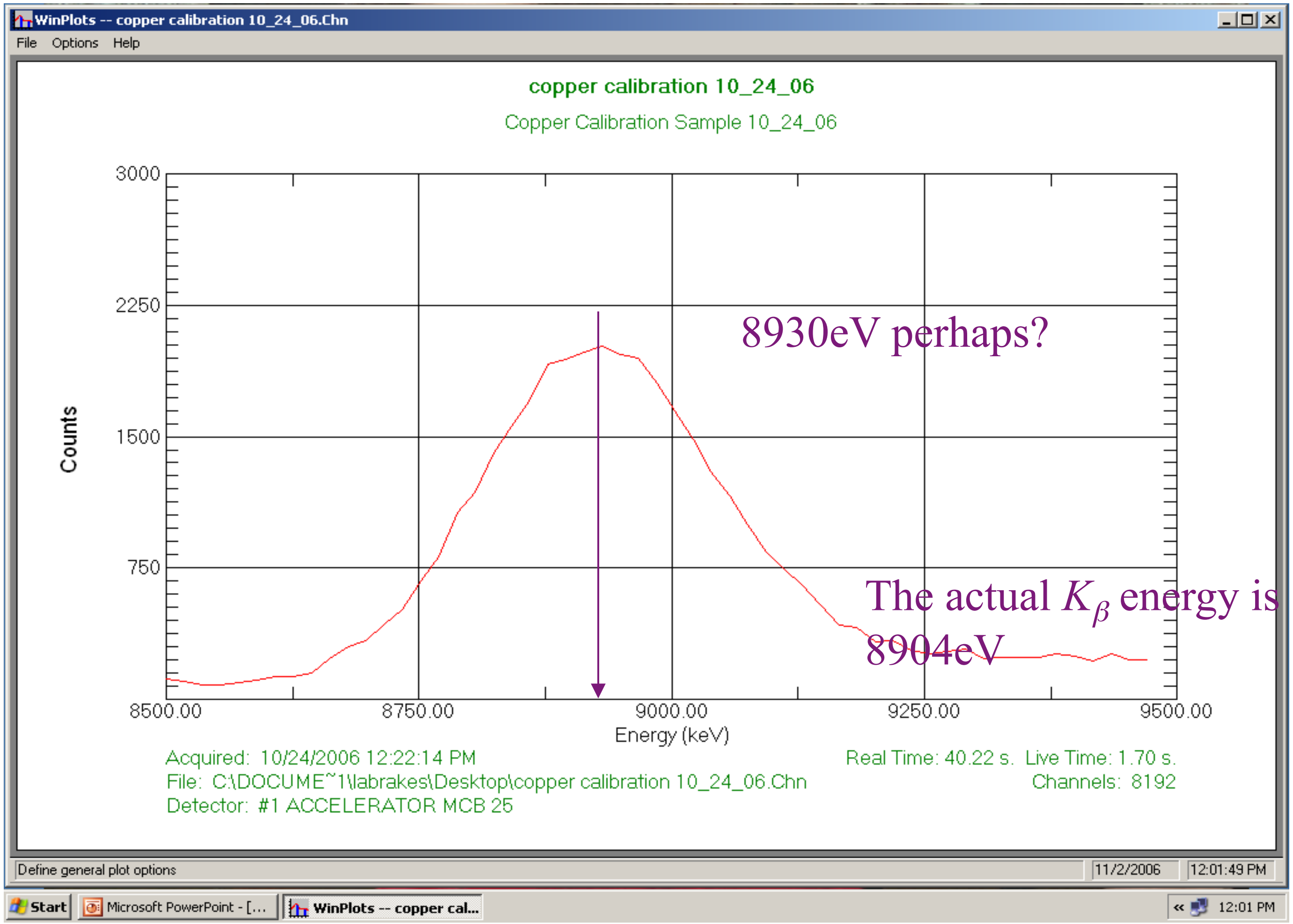
The X-ray Spectrum of Copper

Here we will read off the peak energies and compare those experimentally determined peak energies with the energies of the transitions that we just calculated.



The X-ray Spectrum of Copper



Conclusions

•So, we can calculate the x-ray transition energies to a fairly high degree of accuracy.

•There are lots of other effects we haven't looked at, absorption of x-ray, attenuation of x-rays, failure to produce an x-ray (Auger electrons)…

•Screened Bohr model seems to work well to describe the transitions.

•X-ray energies for K-series transitions scale with $(Z - 1)^2$.

•L-series x-rays are more complicated how do we describe them?

•Further, how much of the elements are present?

•What are the environmental sources of the elements you found?

•What is the chemical identity of the elements – what are the elements bonded too?

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