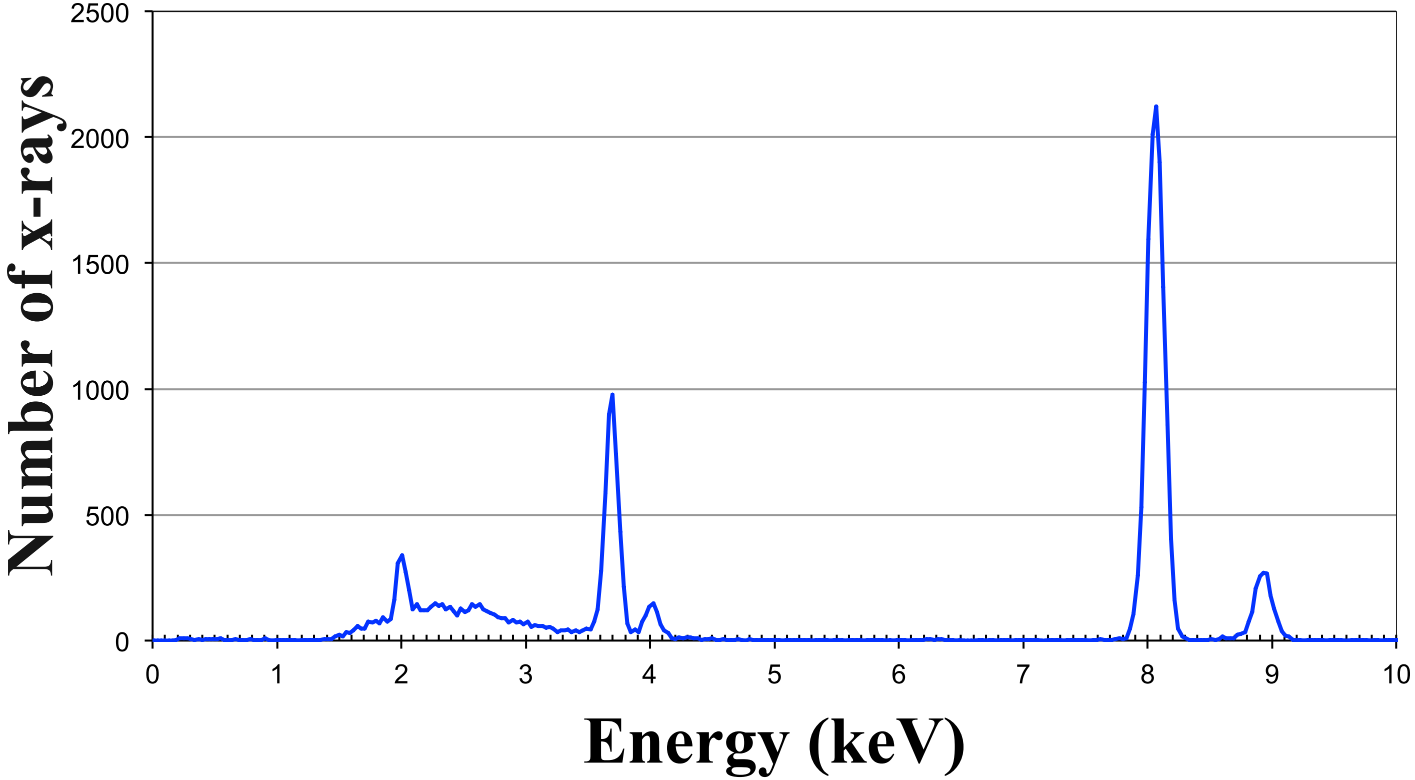
# *Calculations of Characteristic X-ray Energies and Wavelengths and the PIXE Spectrum*



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# 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.

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

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

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

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# The Characteristic X-ray Wavelengths

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

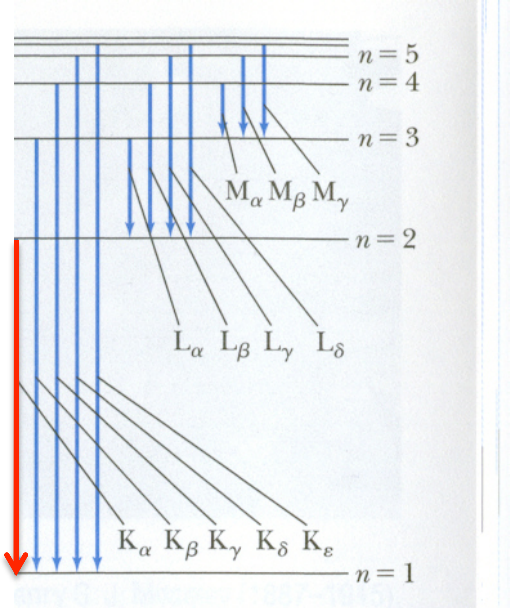
$$ {}^{64}_{29}Cu \longrightarrow $$ 64 nucleons {29 electrons, 29 protons, 35 neutrons}

- 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 $K_\alpha$ transition for copper and the difference in energy between these states is the energy of the emitted x-ray.

# 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 ($n = 1$).

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

The actual $K_\alpha$ energy is $8.04keV$ or about 7% of the true value.

Further, this corresponds to a wavelength of

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

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

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

Again, this is about 7% from the true value!! Hmm… not terrible

# *The Characteristic X-ray Wavelengths*

Comments:

- These energy/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

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

- Doing the math…

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

•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 $K_a$ transition in copper.

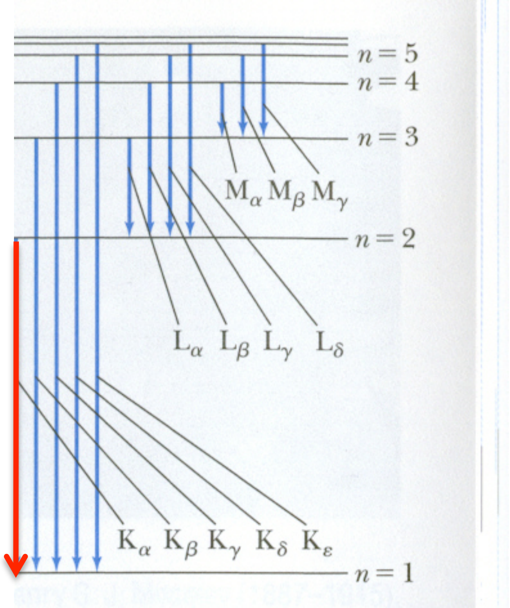
$$^{64}_{29}Cu \longrightarrow$$ 64 nucleons {29 electrons, 29 protons, 35 neutrons}

- 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.

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# 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 actual energy is 8040 $eV$ or about 0.8% of the true value.

This corresponds to a wavelength of

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

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

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

This is about 1% from the true value!!

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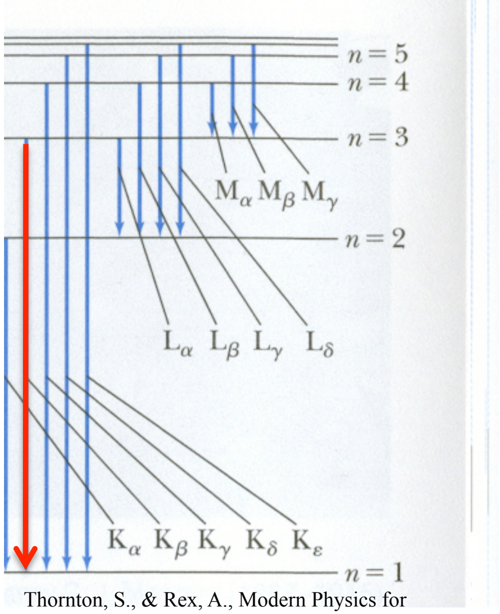
# More X-ray Wavelengths…

- What is the $K_b$ wavelength for Copper?

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

- Recalling the energy level diagram for an atom, the $\mathrm{K}_\alpha$ 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*).

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

This corresponds to a wavelength of

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

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

The actual wavelength (measured in the laboratory) is 1.39x10$^{-10}$m.

This is about 5% from the true value!!

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

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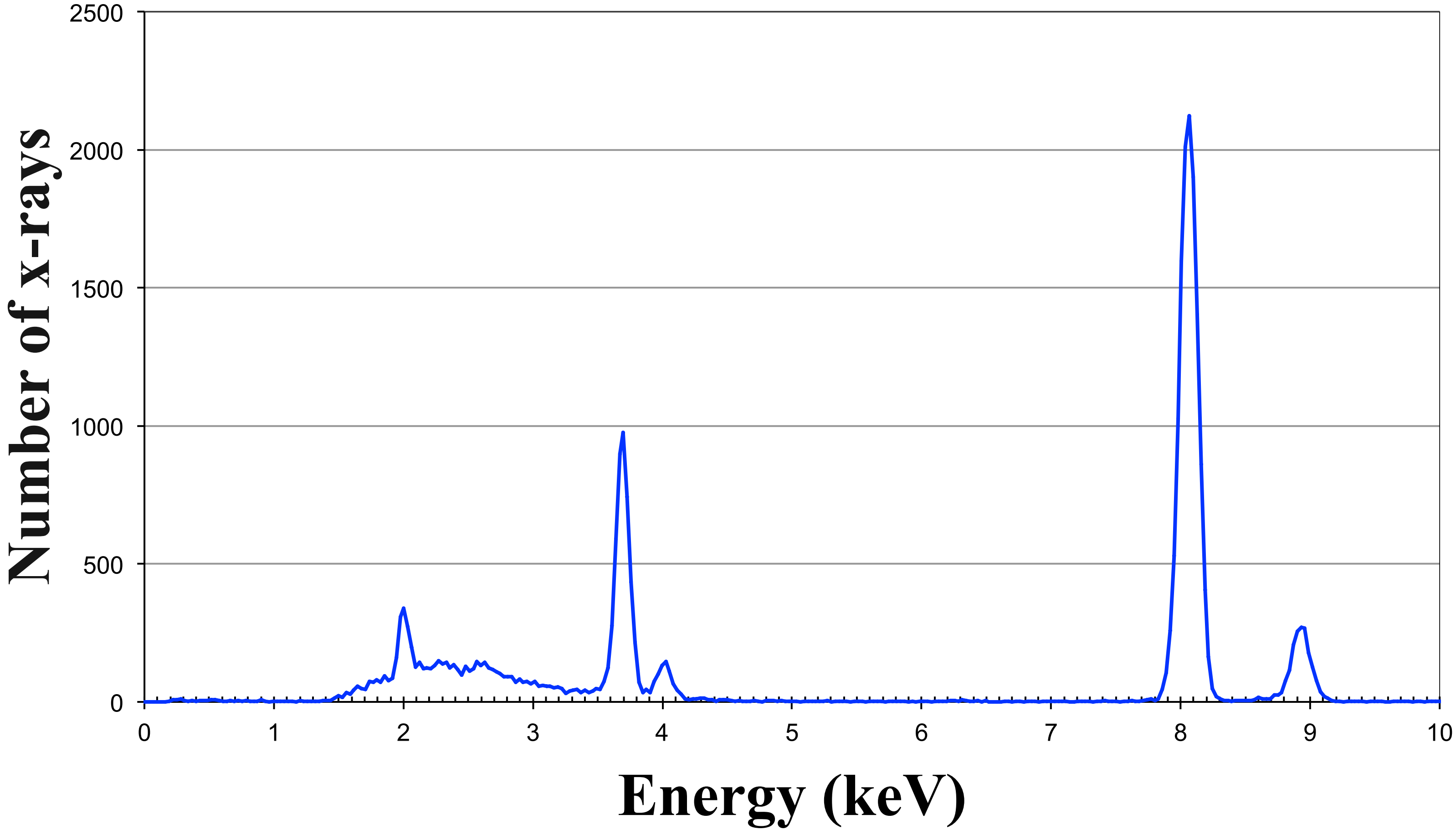
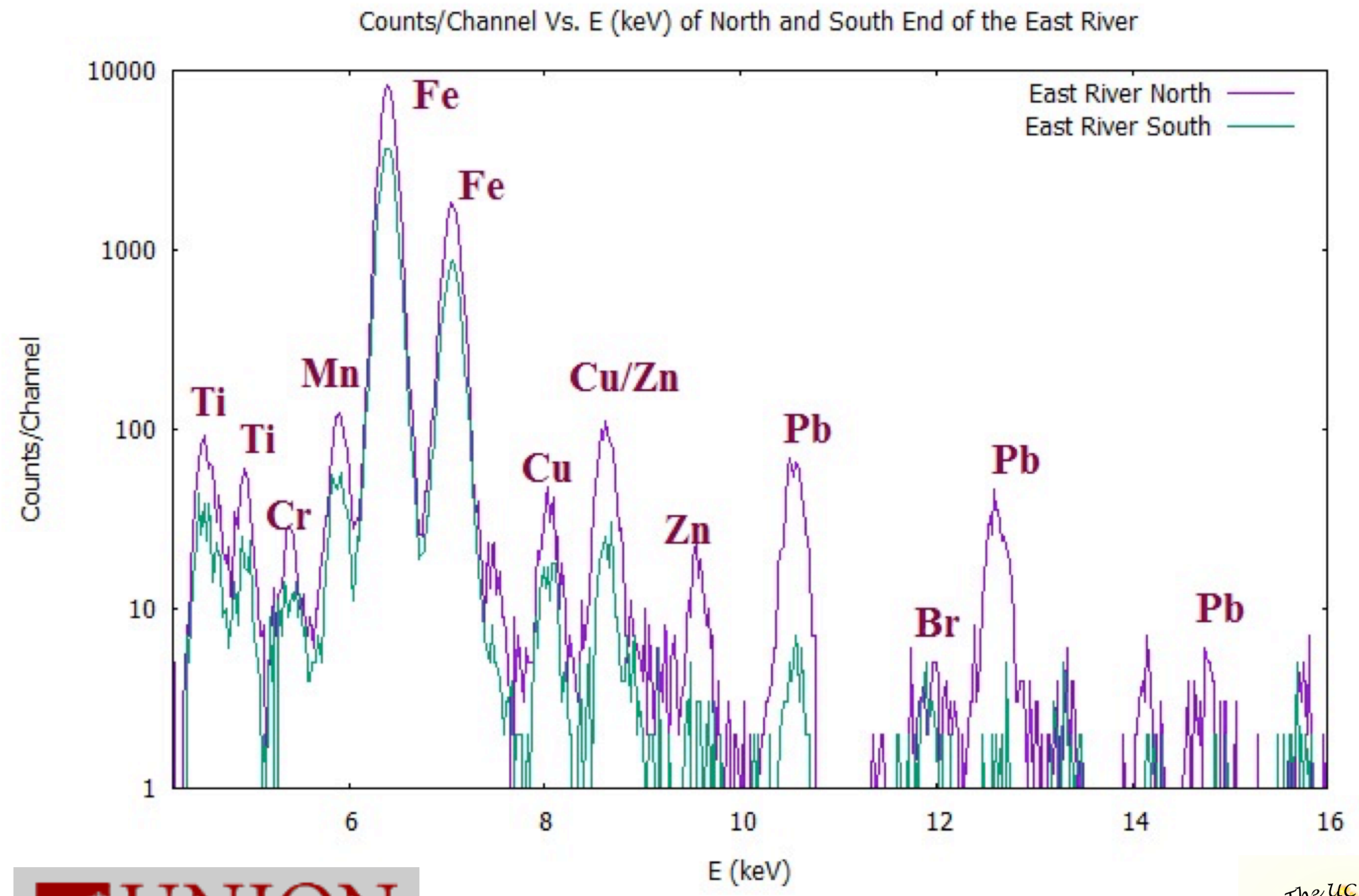
# Elemental Identification & the X-ray Energy Table





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Data/Graph: S. Chalise & S. LaBrake

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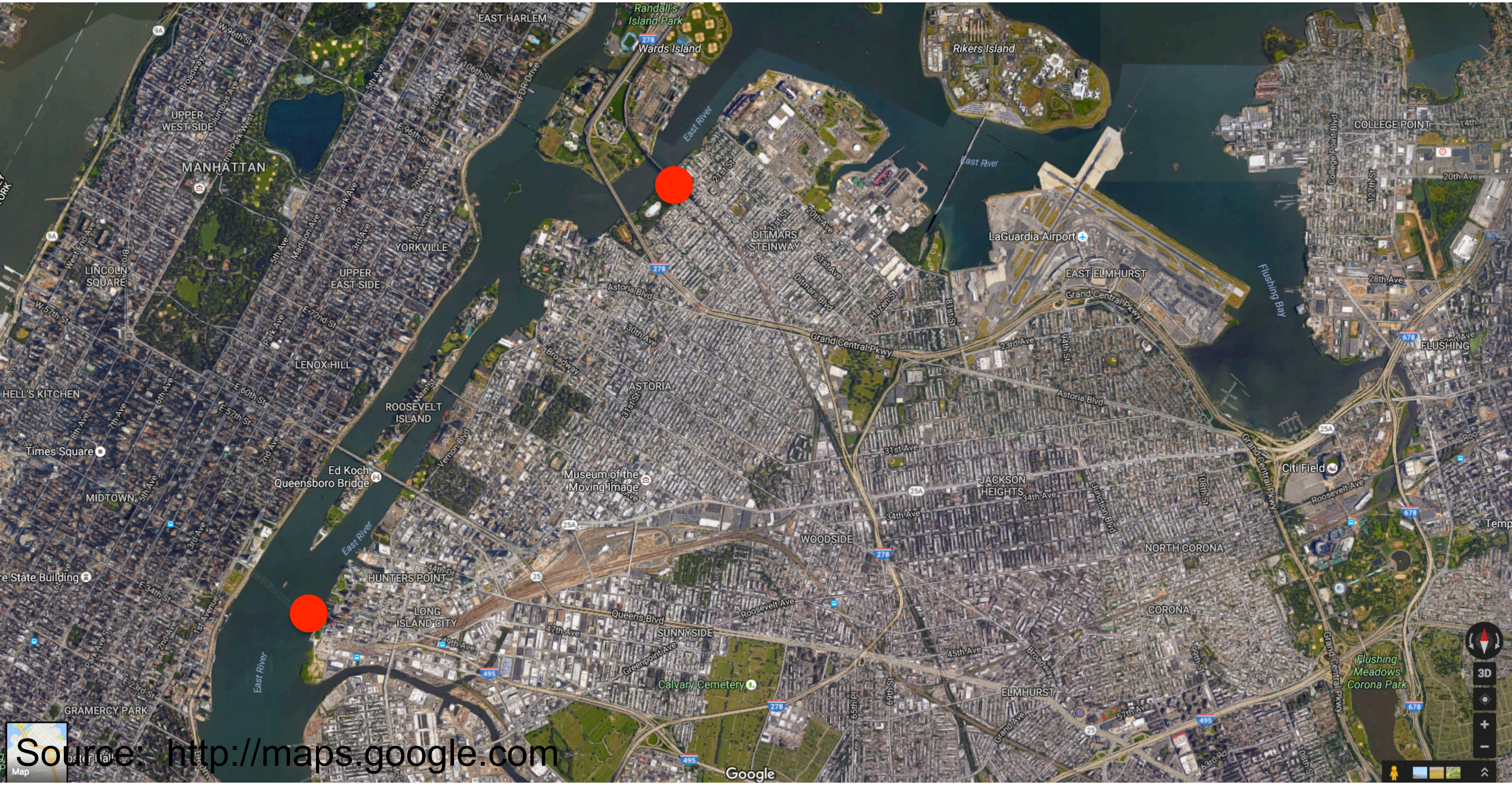
# Queens, New York



Source: http://maps.google.com

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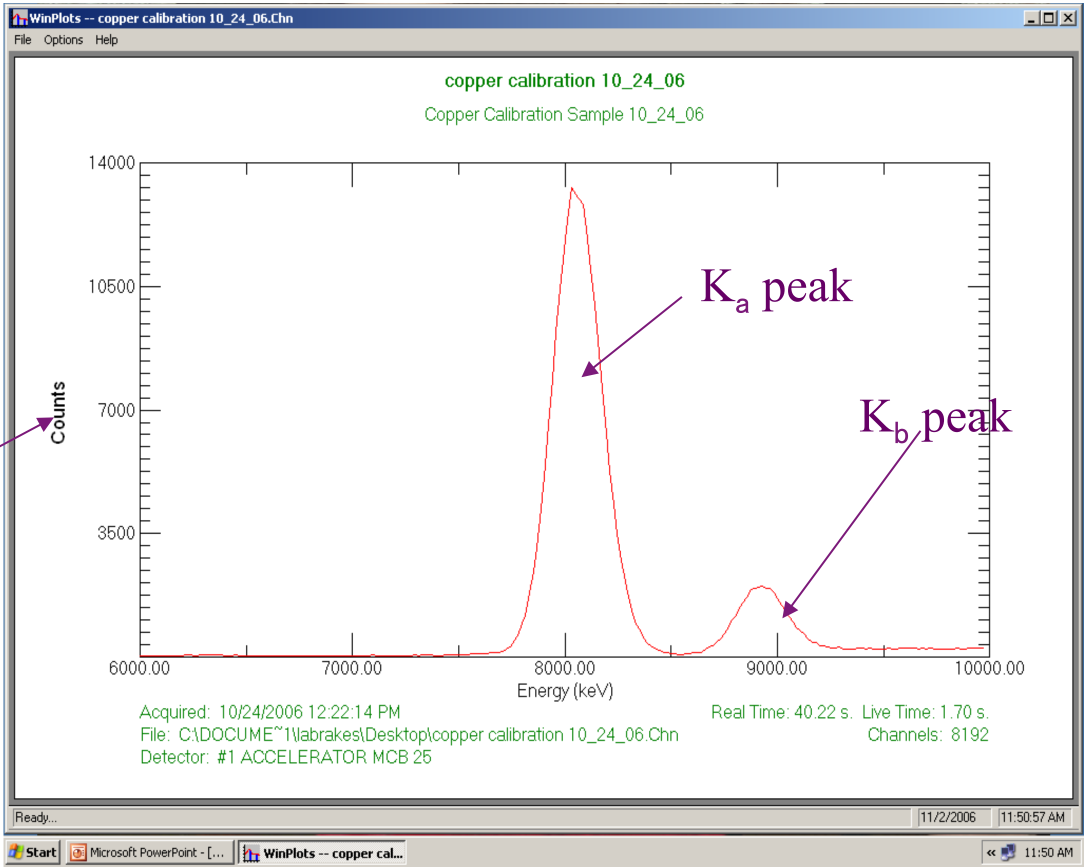
# Conclusions

- **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?**

# *The X-ray Spectrum of Copper*

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



copper calibration 10_24_06

Copper Calibration Sample 10_24_06

Acquired: 10/24/2006 12:22:14 PM

File: C:\DOCUME~1\labrakes\Desktop\copper calibration 10_24_06.Chn

Detector: #1 ACCELERATOR MCB 25

Real Time: 40.22 s. Live Time: 1.70 s.

Channels: 8192

11/2/2006 11:50:57 AM

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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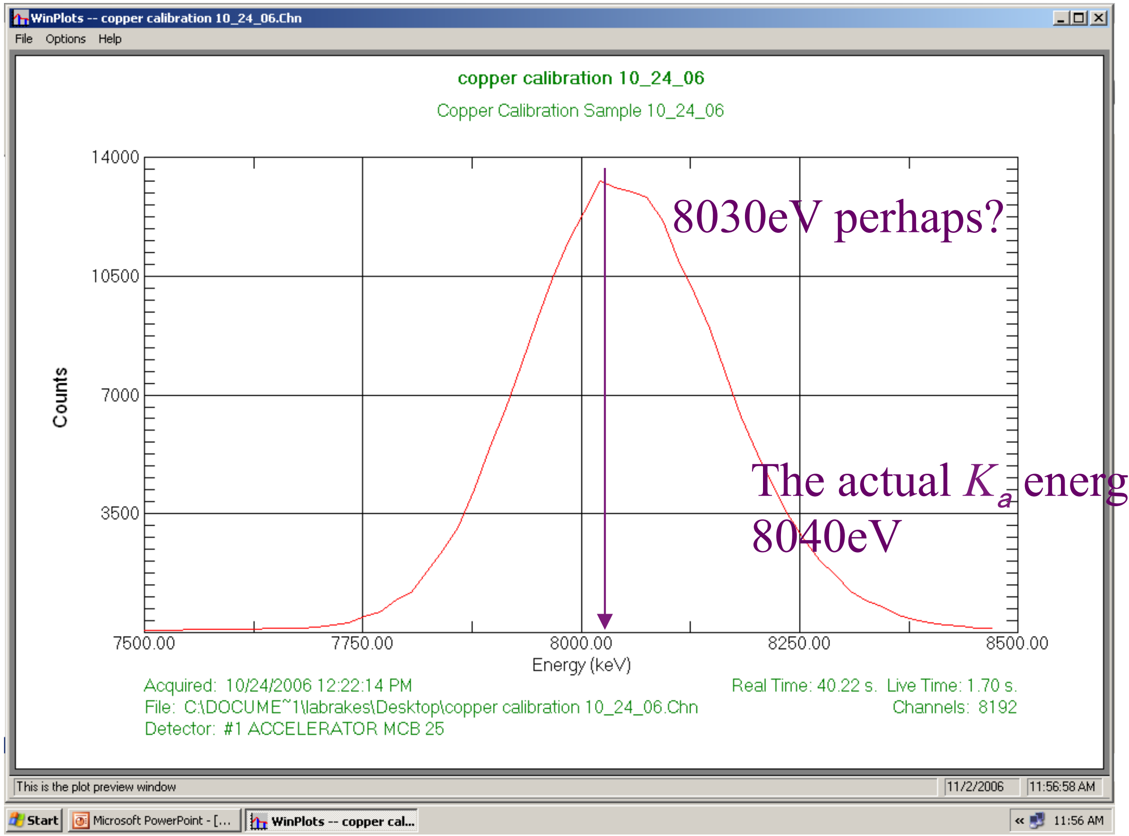
# *The X-ray Spectrum of Copper*

**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.**



WinPlots -- copper calibration 10_24_06.Chn

copper calibration 10_24_06

Copper Calibration Sample 10_24_06

Acquired: 10/24/2006 12:22:14 PM

File: C:\DOCUME~1\labrakes\Desktop\copper calibration 10_24_06.Chn

Detector: #1 ACCELERATOR MCB 25

Real Time: 40.22 s. Live Time: 1.70 s.

Channels: 8192

This is the plot preview window

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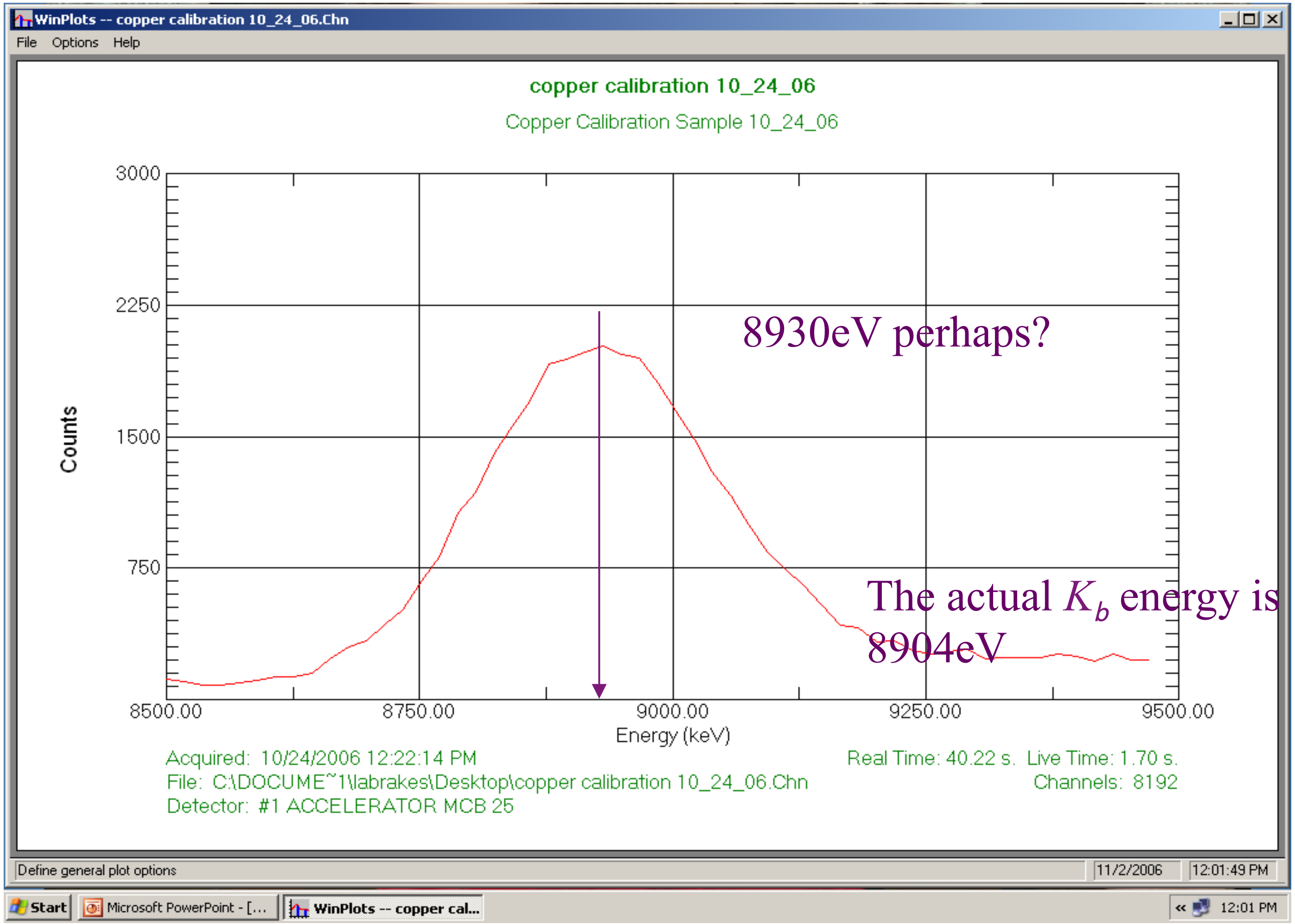
8030eV perhaps?

The actual $K_a$ energy is 8040eV

# *The X-ray Spectrum of Copper*



copper calibration 10_24_06

Copper Calibration Sample 10_24_06

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Detector: #1 ACCELERATOR MCB 25

Real Time: 40.22 s. Live Time: 1.70 s.

Channels: 8192

Define general plot options

11/2/2006

12:01:49 PM

8930eV perhaps?

The actual $K_b$ energy is 8904eV