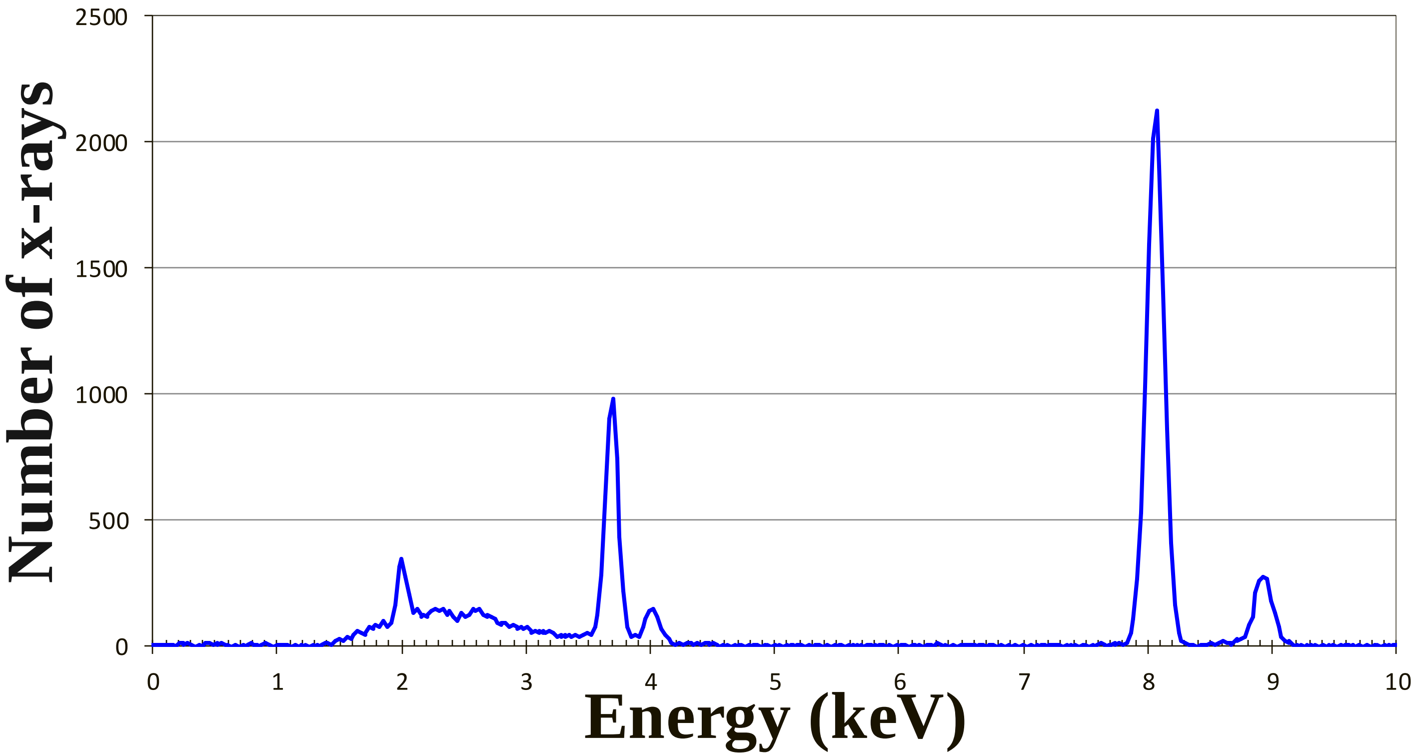
Determining the Elemental Target Make-up From The PIXE Spectrum



The Characteristic X-ray Energies & Elemental Identification

- Electronic transitions within inner shells of atoms are accompanied by large energy transfers. Therefore, we need the high energy proton beam to eject these bound electrons.
- First let's do a small calculation to simplify our lives when we calculate the energies of the orbits.

The energy of an electron in any state (orbital) is given by the sum of the electron's kinetic ($K = \frac{1}{2}mv^2$) and electric potential energies ($U = \frac{1}{4\pi\varepsilon_0}\frac{Q_1 Q_2}{r}$).

$$E_n = K + U = \frac{1}{2}mv_n^2 + \frac{1}{4\pi\varepsilon_0}\frac{(Ze)(-e)}{r_n}$$

The speed (v) of the electron in an orbital and its distance (r) from the nucleus are quantized, meaning that they have only certain allowed energies given by:

$$v_n = \frac{Ze^2}{4\pi\varepsilon_0 n\hbar} \qquad r_n = \frac{4\pi\varepsilon_0 n^2\hbar^2}{mZe^2}$$

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

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

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

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The Characteristic X-ray Energies & Elemental Identification

$$\Delta E = E_{upper} - E_{lower}$$

$$\Delta E = -(13.6eV)Z^2\left(\frac{1}{n_{upper}^2} - \frac{1}{n_{lower}^2}\right)$$

The lowest energy/highest probability transition, K_α:

$n_{upper} = 2;\quad n_{lower} = 1$

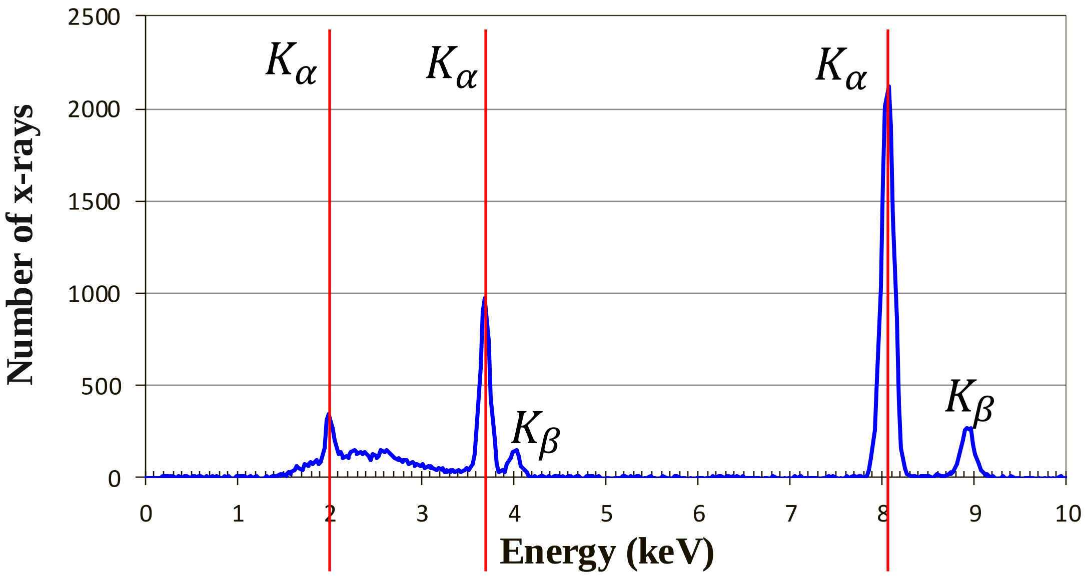
The main metal on the standard:

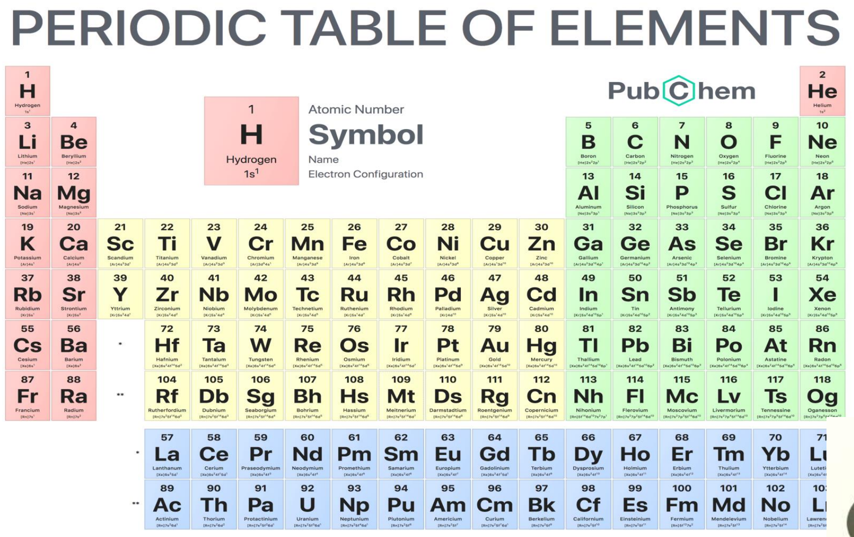
$$\Delta E = 8050eV = -(13.6eV)Z^2\left(\frac{1}{2^2} - \frac{1}{1}\right) \rightarrow Z = 28 \rightarrow Ni$$

The impurities:

$$\Delta E = 2000eV = -(13.6eV)Z^2\left(\frac{1}{2^2} - \frac{1}{1}\right) \rightarrow Z = 14 \rightarrow Si$$

$$\Delta E = 3700eV = -(13.6eV)Z^2\left(\frac{1}{2^2} - \frac{1}{1}\right) \rightarrow Z = 19 \rightarrow K$$





https://pubchem.ncbi.nlm.nih.gov/periodic-table/

The Characteristic X-ray Energies & Elemental Identification

$$\Delta E = E_{upper} - E_{lower}$$

$$\Delta E = -(13.6eV)Z^2\left(\frac{1}{n_{upper}^2} - \frac{1}{n_{lower}^2}\right)$$

The higher energy/lower probability transition, K_β:

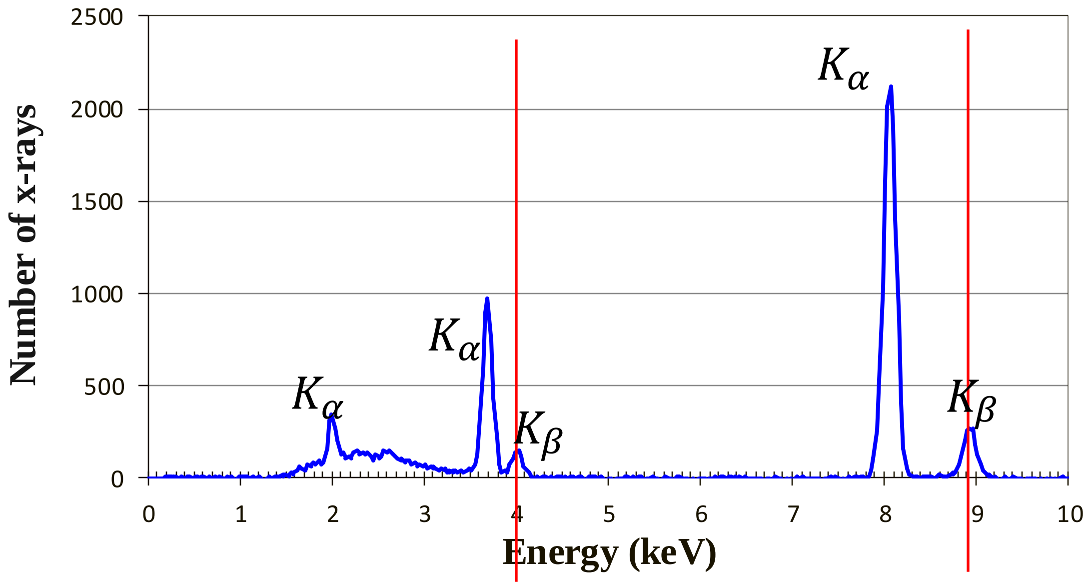
$n_{upper} = 3; \quad n_{lower} = 1$

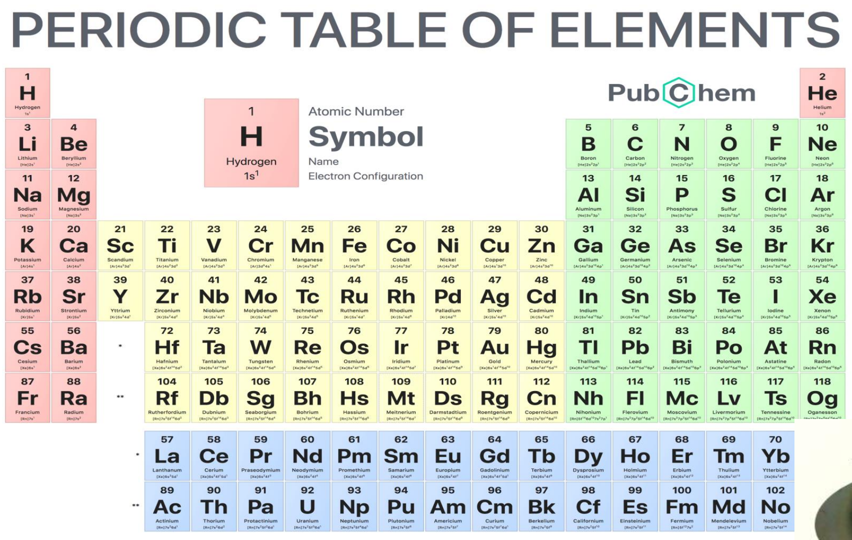
The main metal on the standard:

$$\Delta E = 8950eV = -(13.6eV)Z^2\left(\frac{1}{3^2} - \frac{1}{1}\right) \rightarrow Z = 27.2 \rightarrow Ni/Co$$

The impurities:

$$\Delta E = 4000eV = -(13.6eV)Z^2\left(\frac{1}{3^2} - \frac{1}{1}\right) \rightarrow Z = 18.2 \rightarrow K/Ar$$





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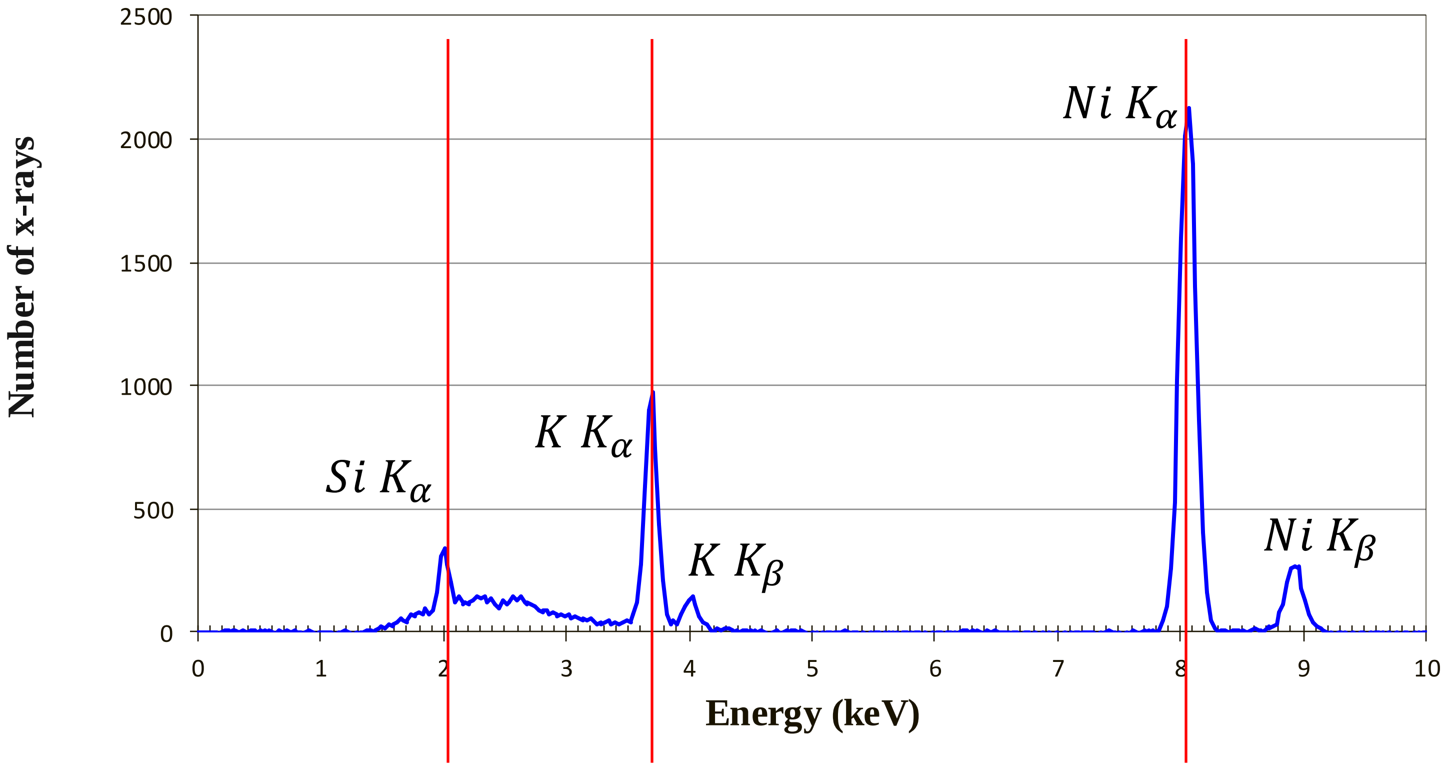
The Characteristic X-ray Energies & Elemental Identification



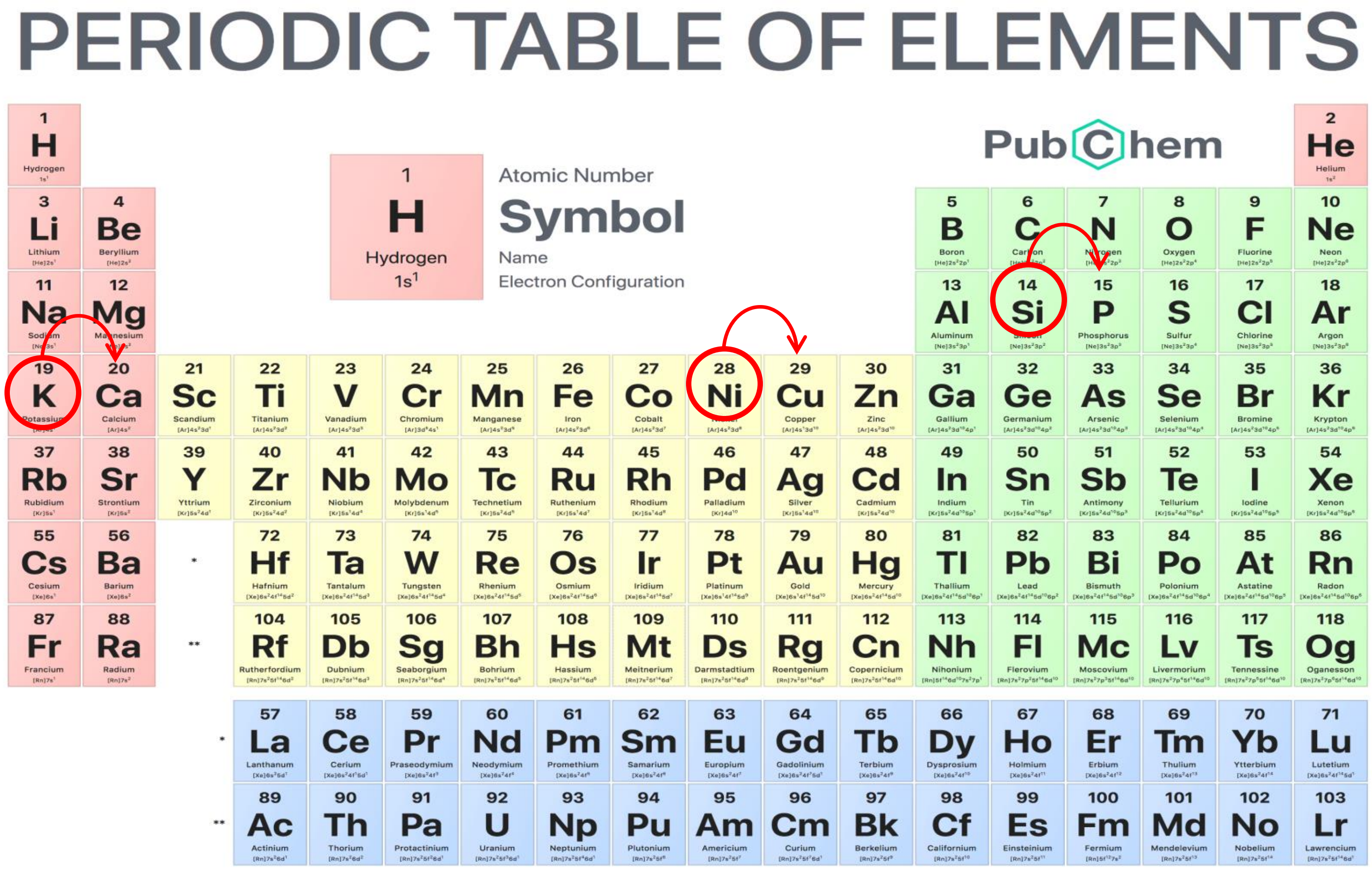
We've identified the elements present in the standard.

The problem, however, is that the main element is not nickel but copper.

Which means that the impurities probably are not correct either.

Why is that?

The Characteristic X-ray Energies & Elemental Identification



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It seems like we're *one off* from nickel to get copper.

Maybe we're *one off* from the others as well.

Maybe the impurities are not Si and K, but rather P and Ca.

How do we fix this?

Note adding one, while it may work, is not really satisfying without a reason.

The Characteristic X-ray Energies & Elemental Identification

- The energy formula ($\Delta E = E_{upper} - E_{lower}$) seems ok.
- ΔE is what ΔE is!! The data are what we see on the graph. So that's probably not the problem.
- What if the expression for the energy of an electron in any given state in the atom is not correct?
- The $n = 1$ state is the $1s$-orbital. In the $1s$ orbital there are two electrons. We ejected one but there is still one left.
- The transitioning electron from say the $n = 2$ state does not simply see the full nuclear charge (Ze) but rather the one electron left in the $n = 1$ state tries to repel the transitioning electron.
- Thus, maybe the charge that the transitioning electron sees is $Z_{eff}e = Ze - e = (Z - 1)e$.

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The Characteristic X-ray Energies & Elemental Identification

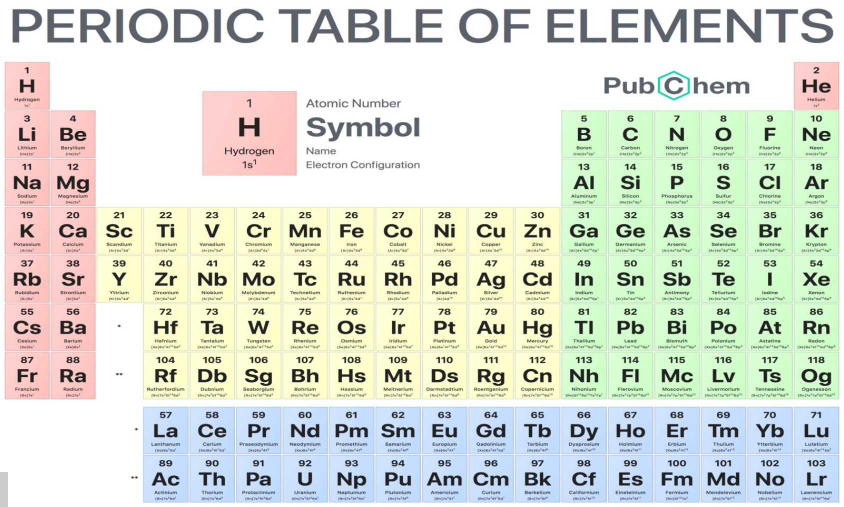
$$E_{old} = -\left(\frac{me^4}{2(4\pi\varepsilon_0\hbar)^2}\right)\frac{Z^2}{n^2} \rightarrow E_{new} = -\left(\frac{me^4}{2(4\pi\varepsilon_0\hbar)^2}\right)\frac{(Z-1)^2}{n^2} = -(13.6eV)\frac{(Z-1)^2}{n^2}$$

$$\Delta E = E_{upper} - E_{lower}$$

$$\Delta E = -(13.6eV)(Z-1)^2\left(\frac{1}{n_{upper}^2} - \frac{1}{n_{lower}^2}\right)$$

The lowest energy/highest probability transition, K_α:

$$n_{upper} = 2; \quad n_{lower} = 1$$



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The main metal on the standard

$$\Delta E = 8050eV = -(13.6eV)(Z-1)^2\left(\frac{1}{2^2} - \frac{1}{1}\right) \rightarrow Z = 29 \rightarrow Cu$$

The impurities:

$$\Delta E = 2000eV = -(13.6eV)(Z-1)^2\left(\frac{1}{2^2} - \frac{1}{1}\right) \rightarrow Z = 15 \rightarrow P$$

$$\Delta E = 3700eV = -(13.6eV)(Z-1)^2\left(\frac{1}{2^2} - \frac{1}{1}\right) \rightarrow Z = 20 \rightarrow Ca$$

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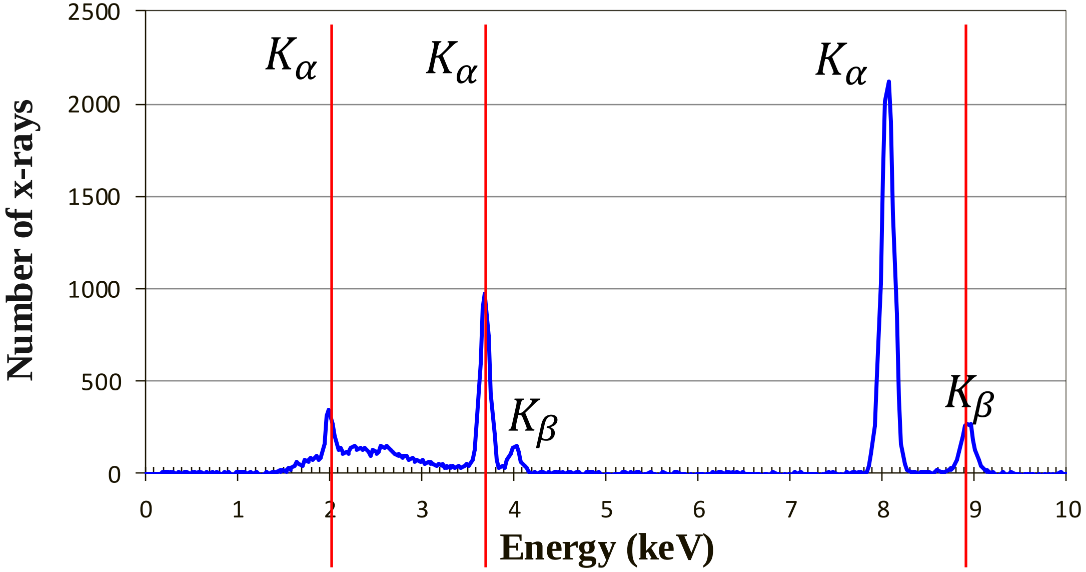
The Characteristic X-ray Energies & Elemental Identification

$$\Delta E = E_{upper} - E_{lower}$$

$$\Delta E = -(13.6eV)(Z-1)^2\left(\frac{1}{n_{upper}^2} - \frac{1}{n_{lower}^2}\right)$$



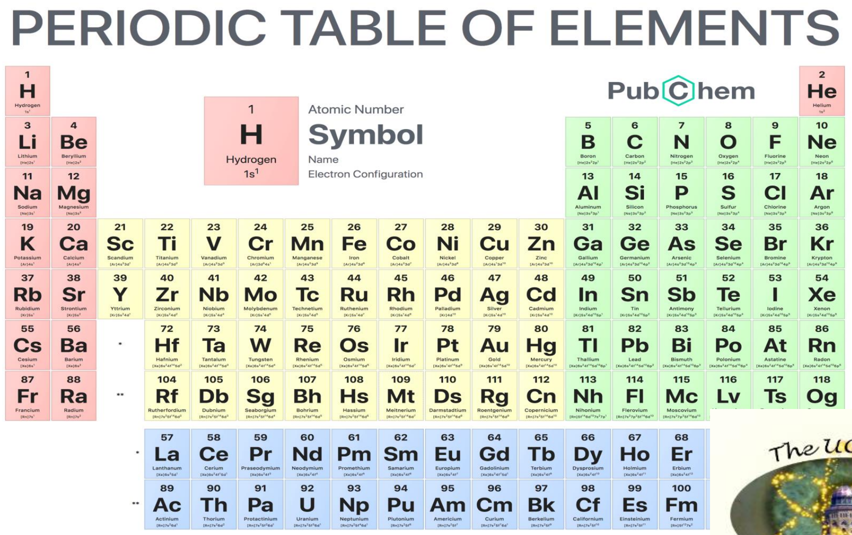
The higher energy/lower probability transition, K_β:

$n_{upper} = 3; \quad n_{lower} = 1$

The main metal on the standard:

$$\Delta E = 8950eV = -(13.6eV)(Z-1)^2\left(\frac{1}{3^2} - \frac{1}{1}\right) \rightarrow Z = 28.2 \rightarrow Ni/Cu$$

Notice we are still off a little. The K_β transitions should also be corrected. It's not as simple to do as the K_α transitions.



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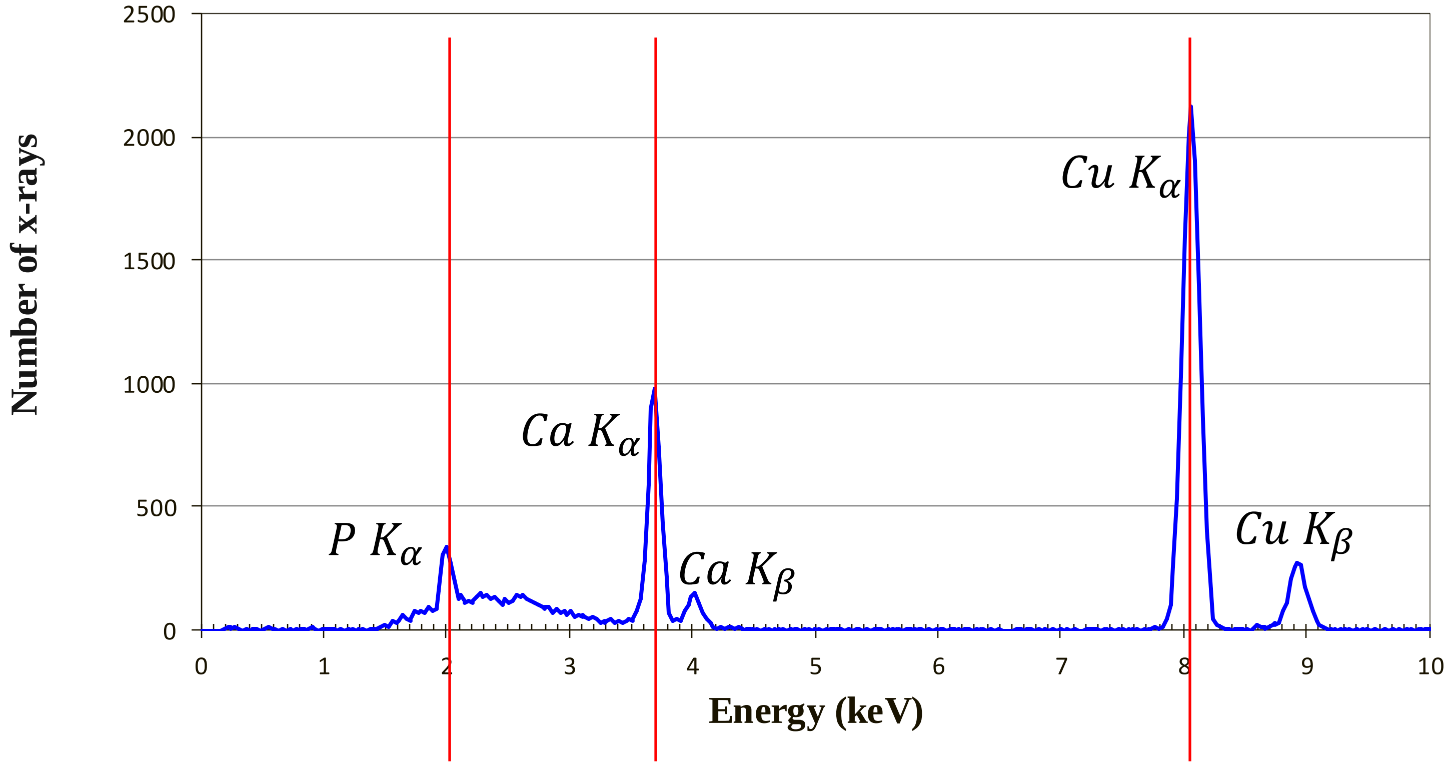
The Characteristic X-ray Energies & Elemental Identification



The single element standards are used to calibrate the energy scale so that we can run a real sample.

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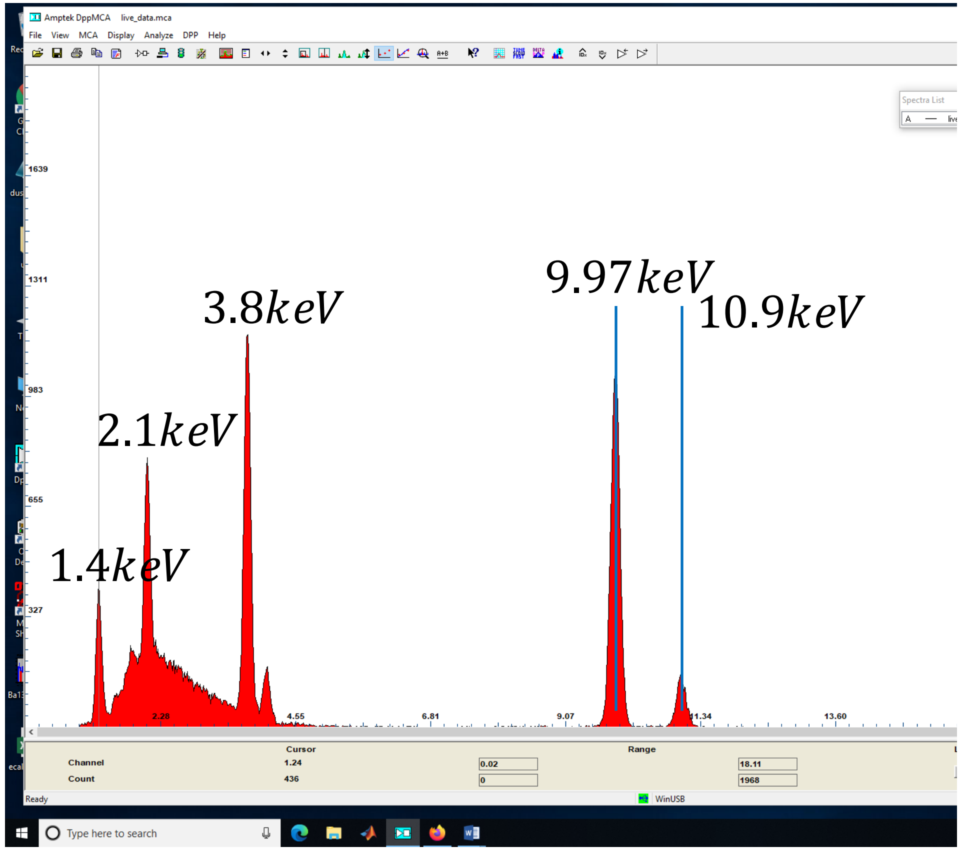
The X-Ray Energy Table For Elemental Identification



$1.4keV \rightarrow Al\ K_\alpha$

$2.1keV \rightarrow P\ K_\alpha$

$3.8keV \rightarrow Ca\ K_\alpha$

$9.97keV \rightarrow Ge\ K_\alpha$

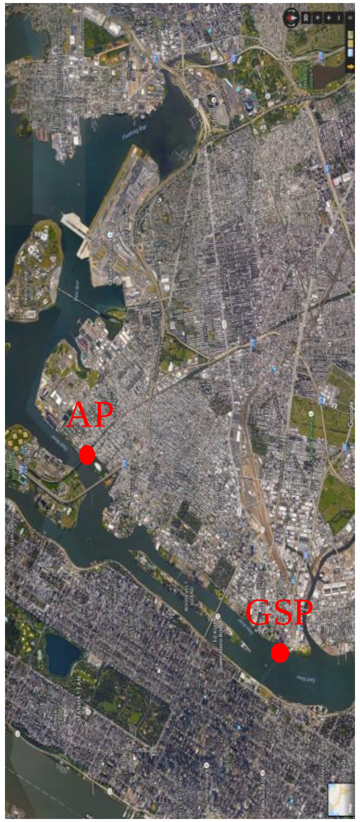
$10.9keV \rightarrow Ge\ K_\beta$

Characteristic X-Ray Energies

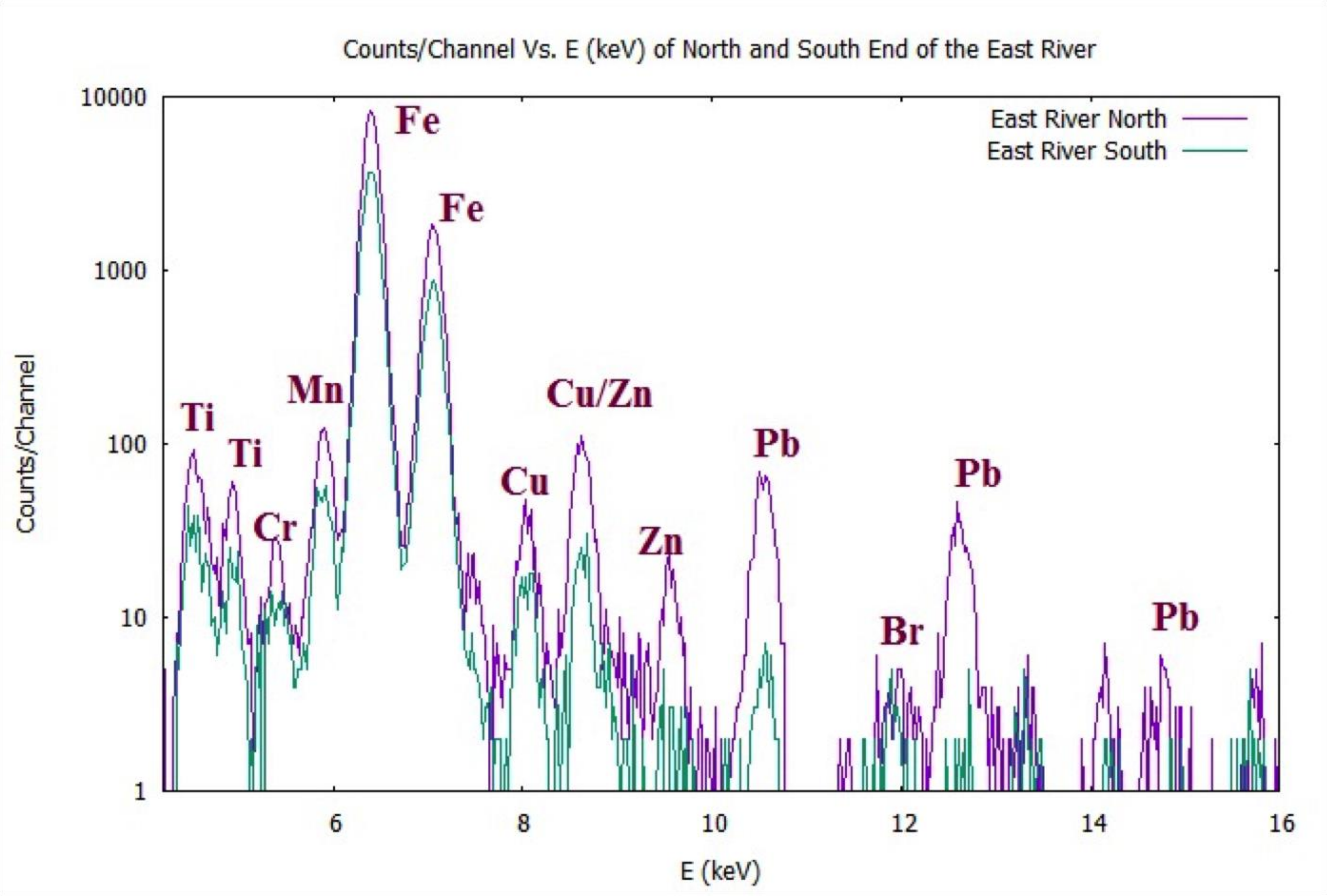
(X-ray Energies in keV)

Z	Element	Ka1	Ka2	Kb1	La1	La2	Lb1	Lb2	Lg1
3	Li	0.0543							
4	Be	0.1085							
S	B	0.1833							
6	C	0.277							
7	N	0.3924							
8	O	0.5249							
9	F	0.6768							
10	Ne	0.8486	0.8486						
11	Na	1.04098	1.04098	1.0711					
12	Mg	1.25360	1.25360	1.3022					
13	Al	1.48670	1.48627	1.55745					
14	Si	1.73998	1.73938	1.83594					
15	P	2.0137	2.0127	2.1391					
16	S	2.30784	2.30664	2.46404					
17	Cl	2.62239	2.62078	2.8156					
18	Ar	2.95770	2.95563	3.1905					
19	K	3.3138	3.3111	3.5896					
20	Ca	3.69168	3.68809	4.0127	0.3413	0.3413	0.3449		
21	Sc	4.0906	4.0861	4.4605	0.3954	0.3954	0.3996		
22	Ti	4.51084	4.50486	4.93181	0.4522	0.4522	0.4584		
23	V	4.95220	4.94464	5.42729	0.5113	0.5113	0.5192		
24	Cr	5.41472	5.405509	5.94671	0.5728	0.5728	0.5828		
25	Mn	5.89875	5.88765	6.49045	0.6374	0.6374	0.6488		
26	Fe	6.40384	6.39084	7.05798	0.7050	0.7050	0.7185		
27	Co	6.93032	6.91530	7.64943	0.7762	0.7762	0.7914		
28	Ni	7.47815	7.46089	8.26466	0.8515	0.8515	0.8688		
29	Cu	8.04778	8.02783	8.90529	0.9297	0.9297	0.9498		
30	Zn	8.63886	8.61578	9.5720	1.0117	1.0117	1.0347		
31	Ga	9.25174	9.22482	10.2642	1.09792	1.09792	1.1248		
32	Ge	9.88642	9.85532	10.9821	1.18800	1.18800	1.2185		
33	As	10.54372	10.50799	11.7262	1.2820	1.2820	1.3170		
34	Se	11.2224	11.1814	12.4959	1.37910	1.37910	1.41923		

Environmental Pollution Along the East River in Queens, New York



Google map showing the two locations that were originally taken; one sample was taken in Astoria Park and the other 3 miles south in Gantry State Park.

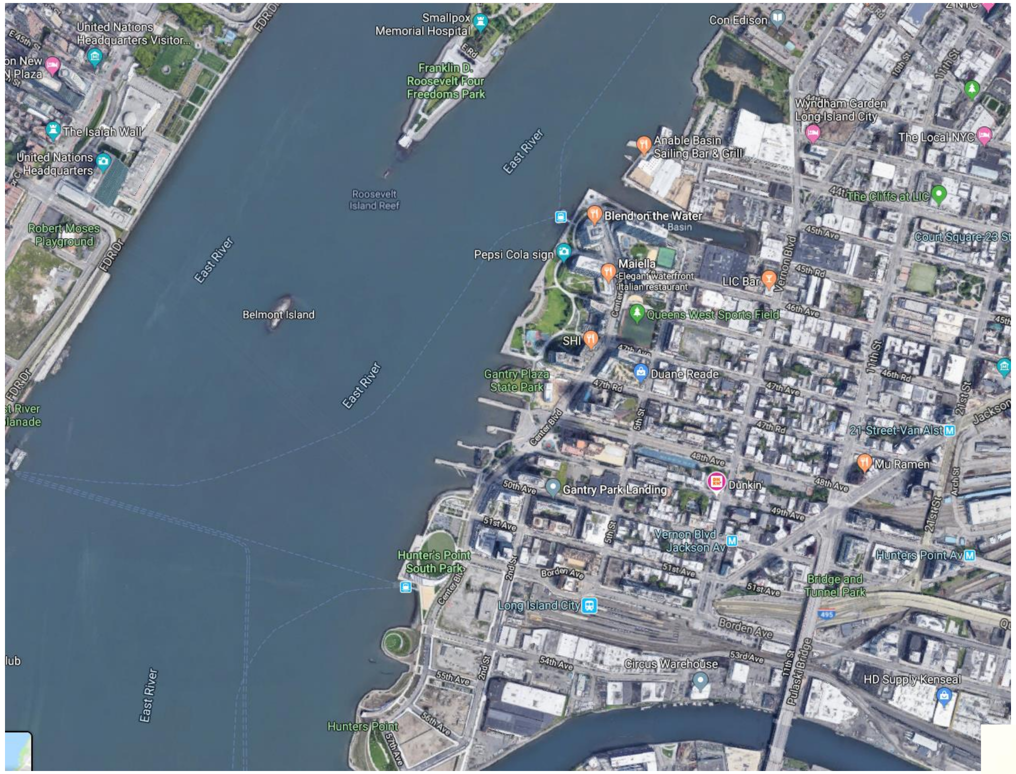


PIXE spectra on the soil samples taken from each park. What do you notice?

Source: http://maps.google.com
Data/Graph: S. Chalise & S. LaBrake

Environmental Pollution Along the East River in Queens, New York

On the left, Astoria State Park along the East River in North Queens.



On the right, Gantry Plaza State Park along the East River in South Queens.

Source: http://maps.google.com

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Environmental Pollution Along the East River in Queens, New York

- Hell Gate Bridge is a 1000' railroad bridge built in 1916.
- Painted originally with Hell Gate Red, a lead-based paint.
- Sandblasted and repainted around 1990 with a non-lead-based paint.
- Is the bridge the source of the lead?

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Photo: S. LaBrake

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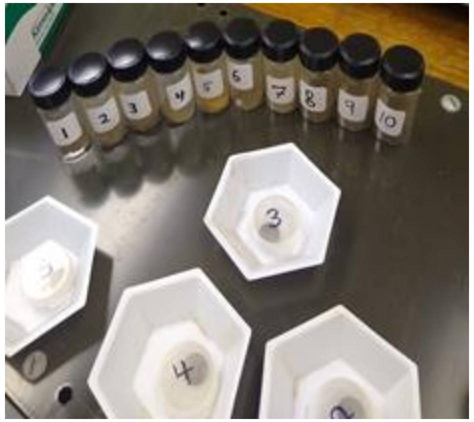
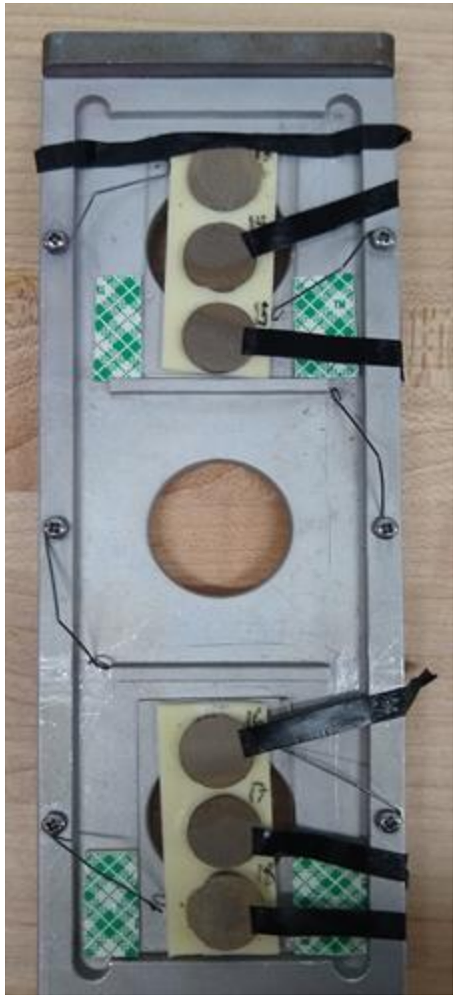
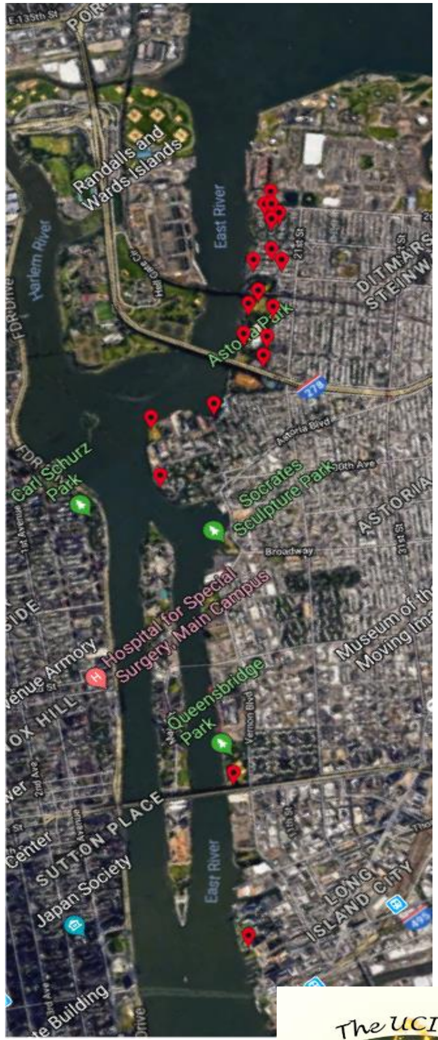
Environmental Pollution Along the East River in Queens, New York



- We've taken 20 samples along the east river from Astoria to Gantry State park in 2018 – 2019.
- In the summer of 2019, we took 20 more samples surrounding the Hell Gate Bridge.
- Above are the soil samples from summer 2019 and on the right the soil pellets mounted on the target ladder.



On the right, a Google map showing the 20 sampling locations between Astoria State Park and Gantry Plaza State Park.



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Source: http://maps.google.com

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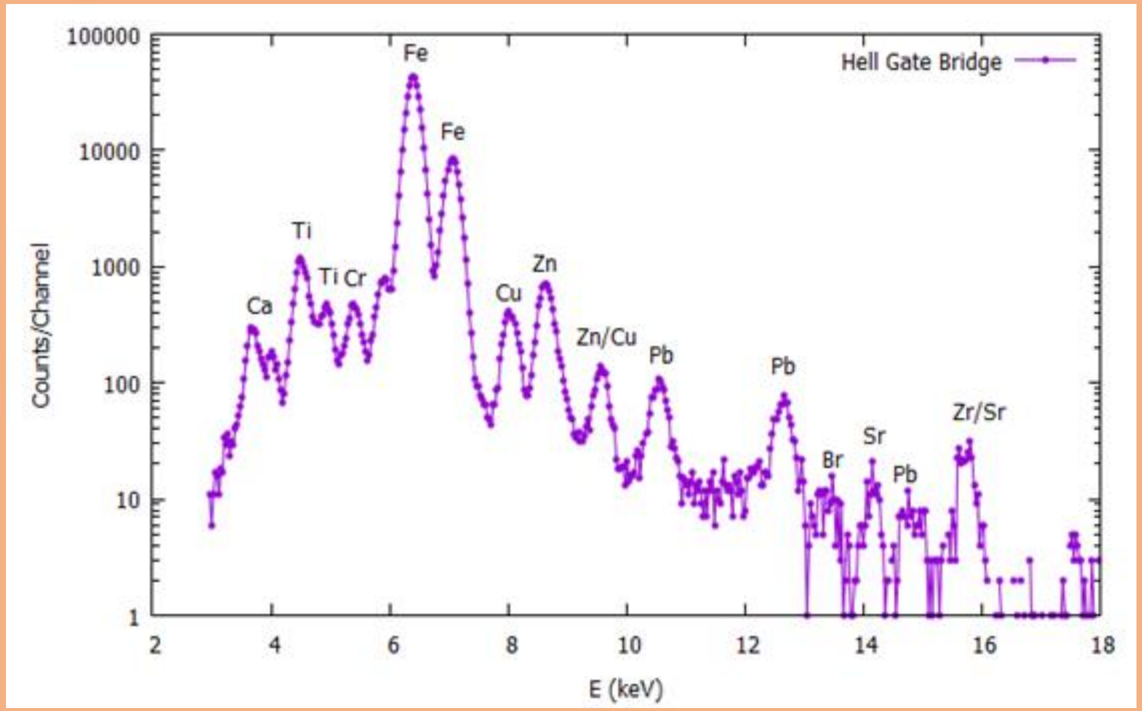
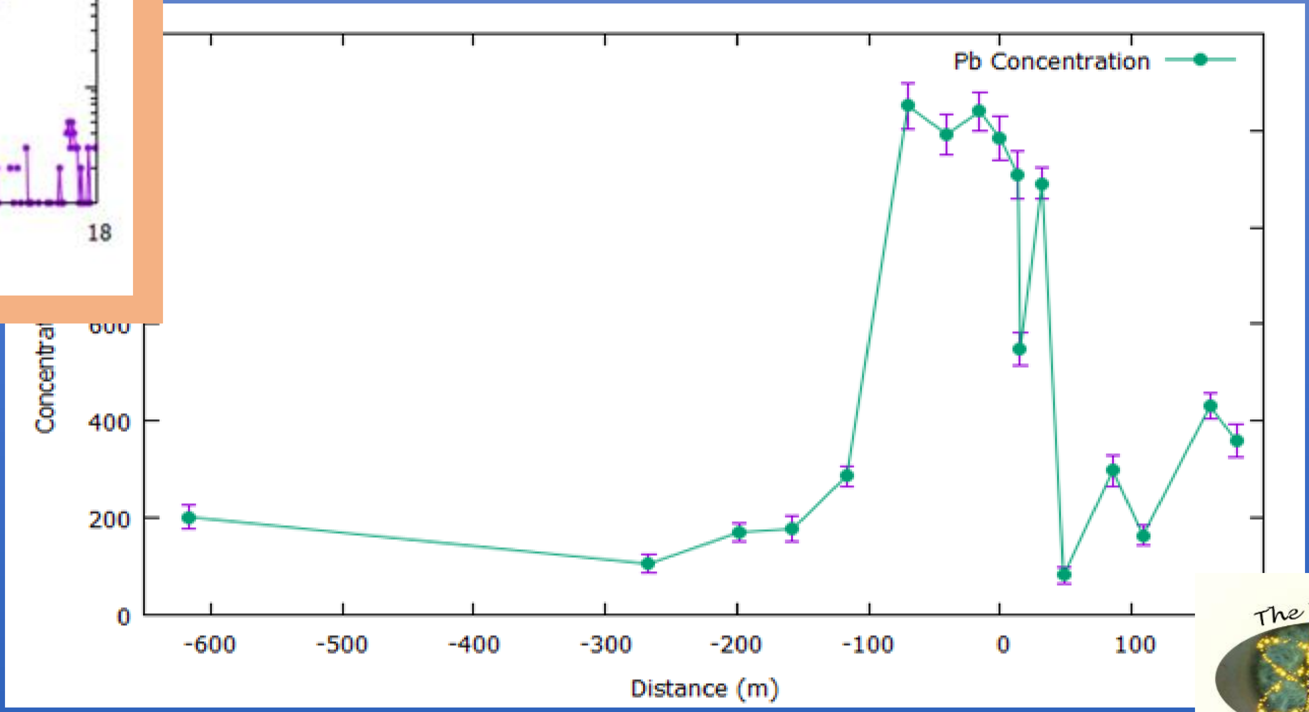
Environmental Pollution Along the East River in Queens, New York



On the left, a typical PIXE spectrum for a soil sample taken near the Hell Gate Bridge, in Astoria, Queens, NY.



On the right, a plot of the lead concentration around the Hell Gate Bridge, in Astoria, Queens, NY.

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Data/Graph: M. Villaneuve & S. LaBrake

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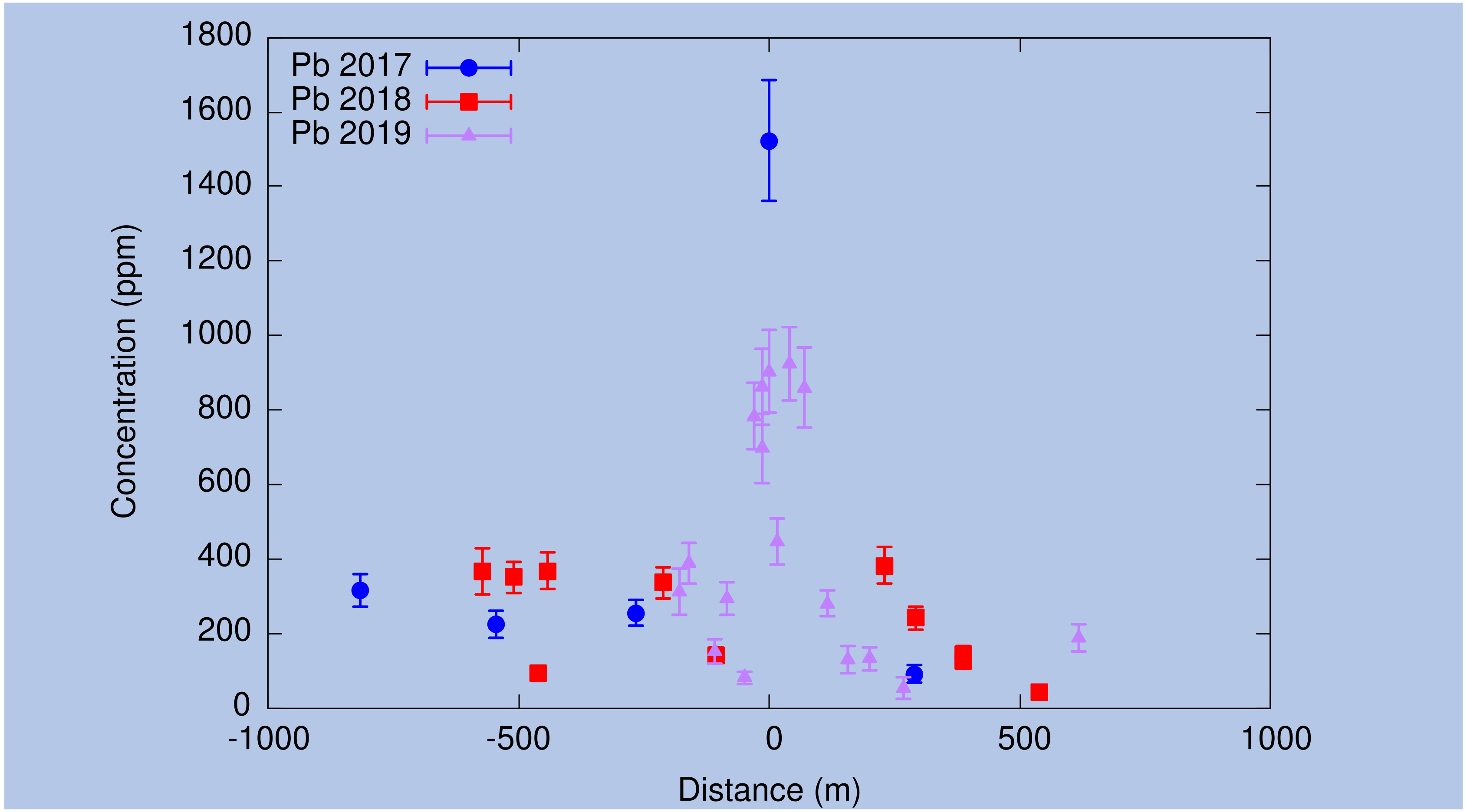
Environmental Pollution Along the East River in Queens, New York



A plot of the lead concentration of samples taken around the Hell Gate Bridge as a function of distance from the bridge. The bridge is taken at zero and north of the bridge is taken as positive.

Conclusions

- So, we can calculate the x-ray transition energies to a 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?