Incorporating X-ray Fluorescence into Undergraduate Chemistry Curriculum

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Purpose

X-ray fluorescence (XRF) is an analytical technique rarely taught to undergraduate chemistry students. Elemental XRF analysis methods provide advantages over other analytical methods including non-destructive sample analysis as well as multi element analysis. The technological improvements to the source x-ray tubes and detectors have made it feasible to incorporate fairly inexpensive, small bench-top XRF instruments into an undergraduate laboratory course.[1] Using an Amptek Exp-1 XRF instrument, an experimental procedure of metal alloys is being designed for delivery to undergraduate students at Washington State University.

Advantages of XRF[2]

- Quasi non-destructive elemental analysis
- Little to no sample preparation
- Small sample amounts
- Simultaneous elemental analysis for elements Mg to U
- Rapid analysis time
- Trace elemental analysis in the ppm range

Benefits to Students

- Broaden scope of instrumentation
- Allow comparison of XRF to other analytical methods
- Experience with radiation producing instruments in a controlled environment
- Highlight a method which operates under fluorescence not absorbance
- Direct analysis of solid state samples

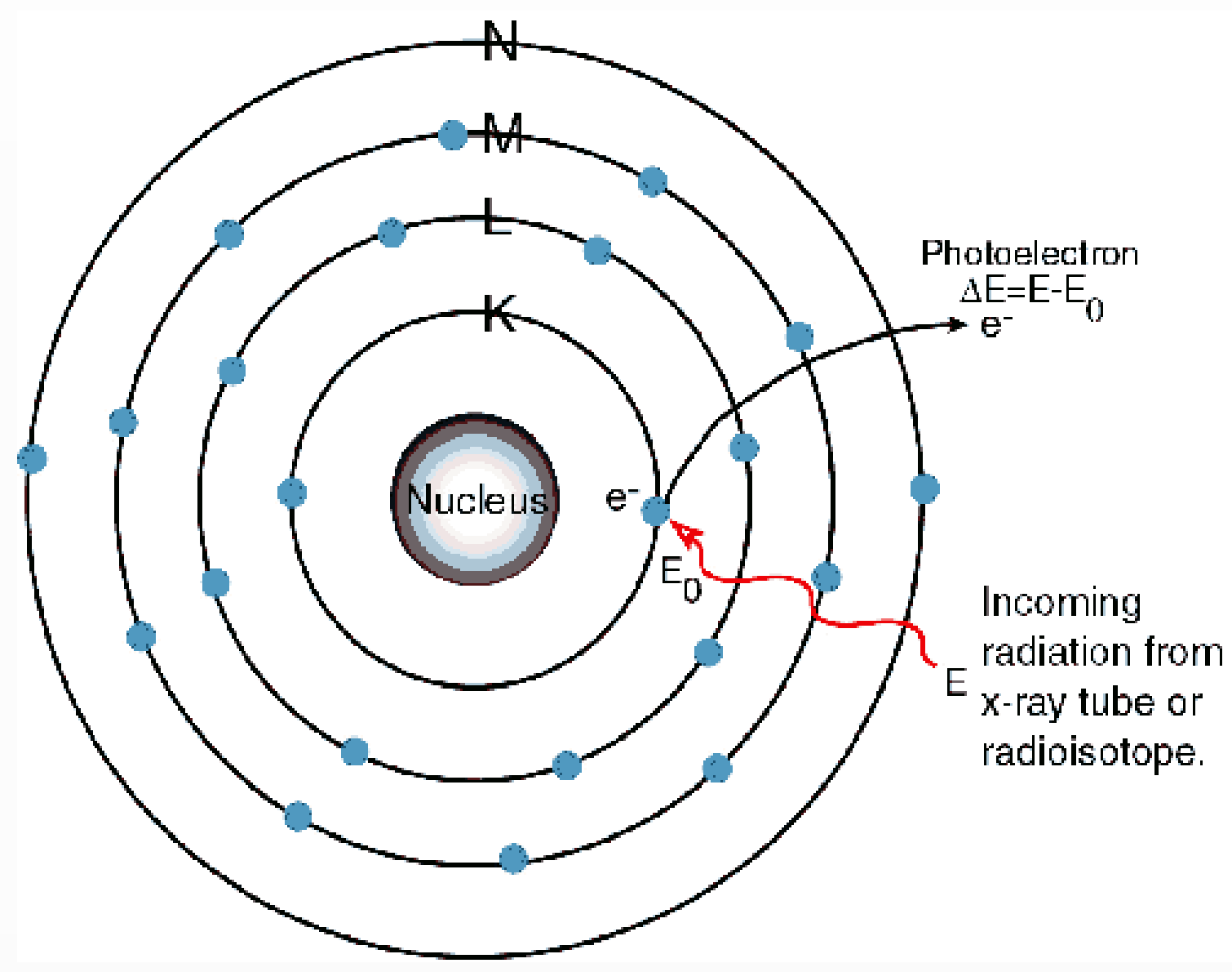
References

[1]. Palmer, P. T., Energy-Dispersive X-ray Fluorescence Spectrometry: A Long Overdue Addition to the Chemistry Curriculum. *Journal of Chemical Education* **2011,** *88* (7), 868-872.

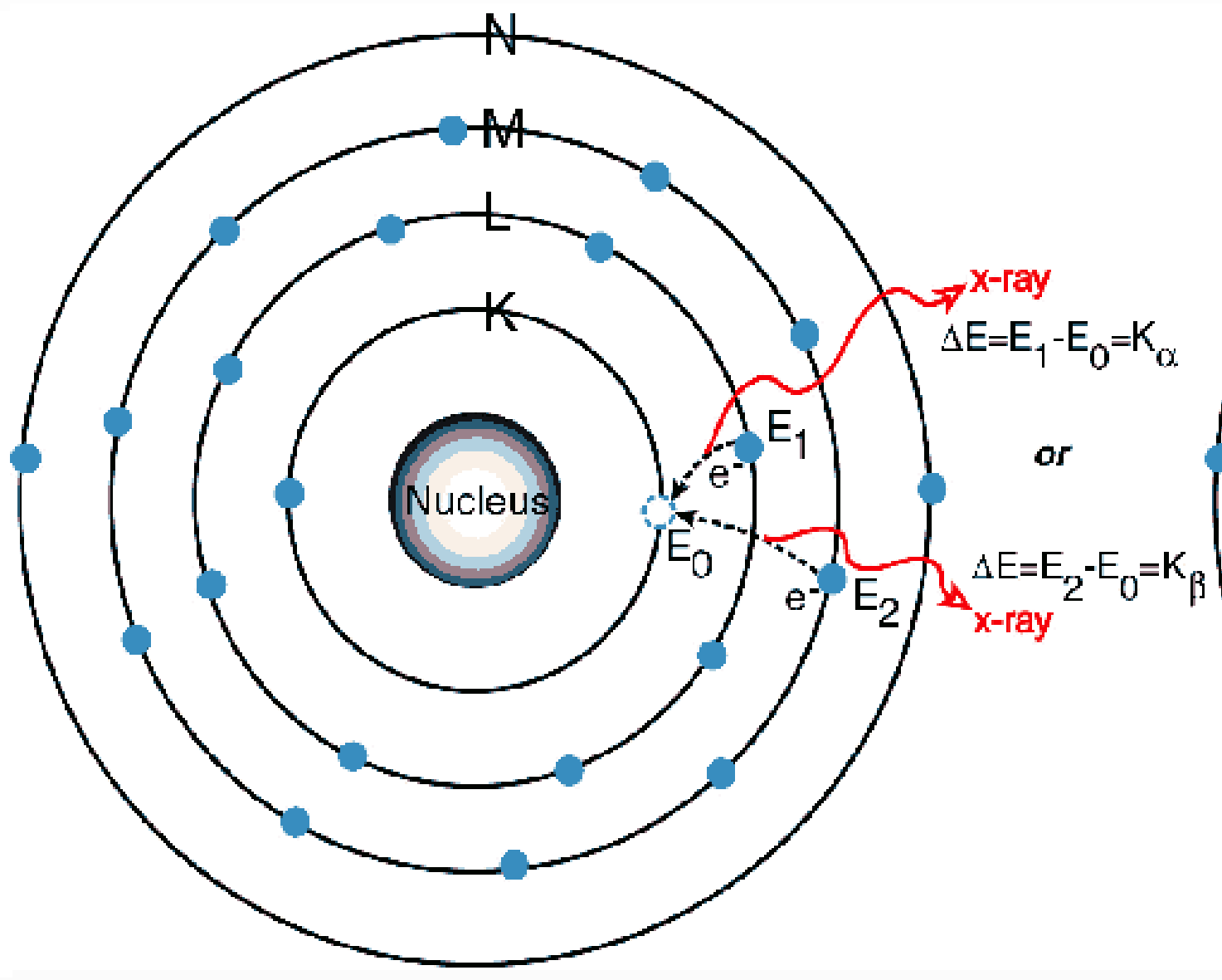
[2]. Finch, L. E.; Hillyer, M. M.; Leopold, M. C., Quantitative Analysis of Heavy Metals in Children's Toys and Jewelry: A Multi-Instrument, Multitechnique Exercise in Analytical. Chemistry and Public Health. *Journal of Chemical Education* **2015,** *92* (5), 849-854.

How XRF Operates

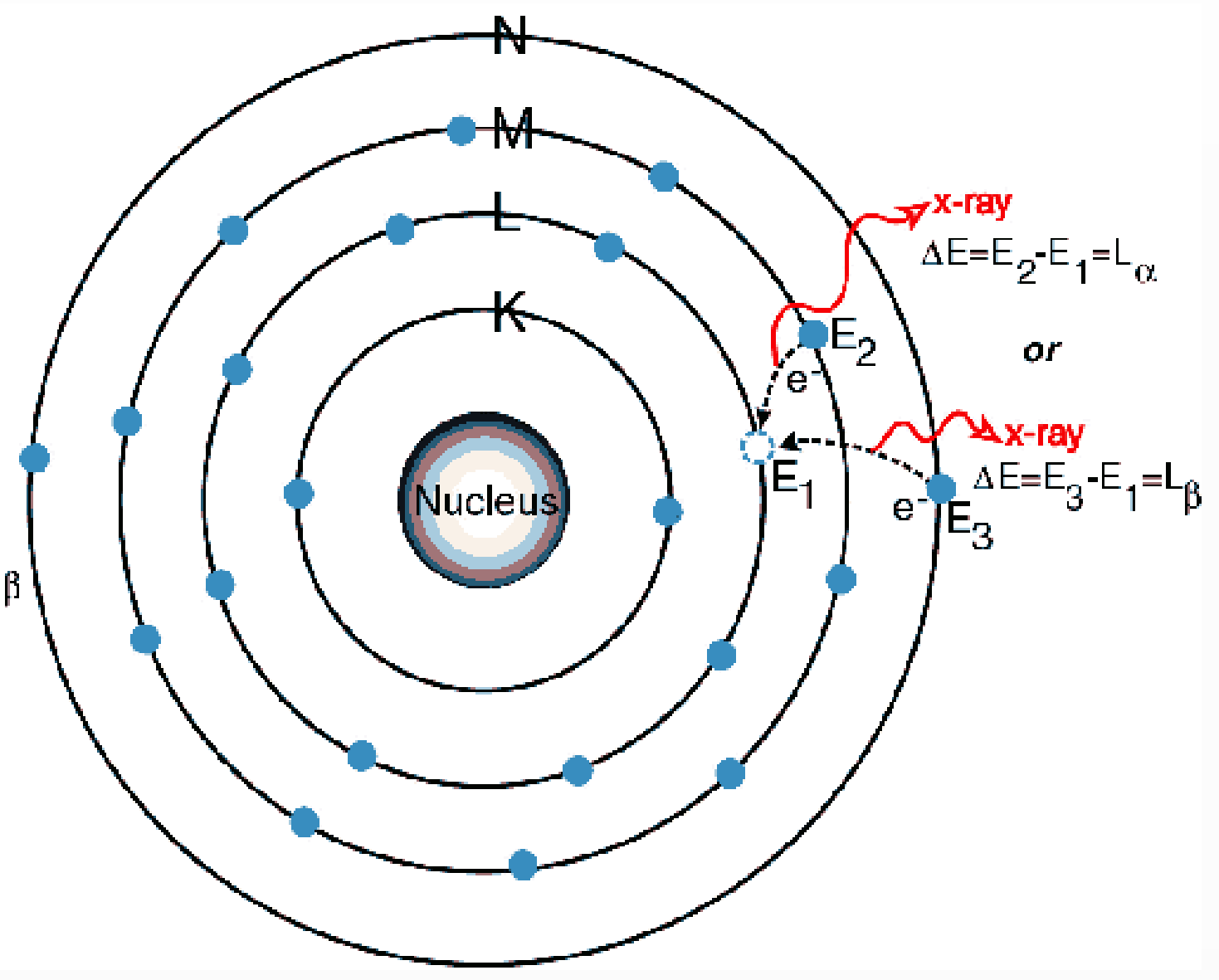
An x-ray produced by a source, an x-ray tube in this case, impinges on a sample and ejects an electron from an inner orbital of the atom. Due to the vacant hole produced the atom is unstable. To revert back to a lower potential an electron from an outer orbital transfers to fill the vacant hole. The energy difference between the initial and final points of the transferred electron is observed as the emission of an x-ray photon signal by the detector.



Ejection of inner electron



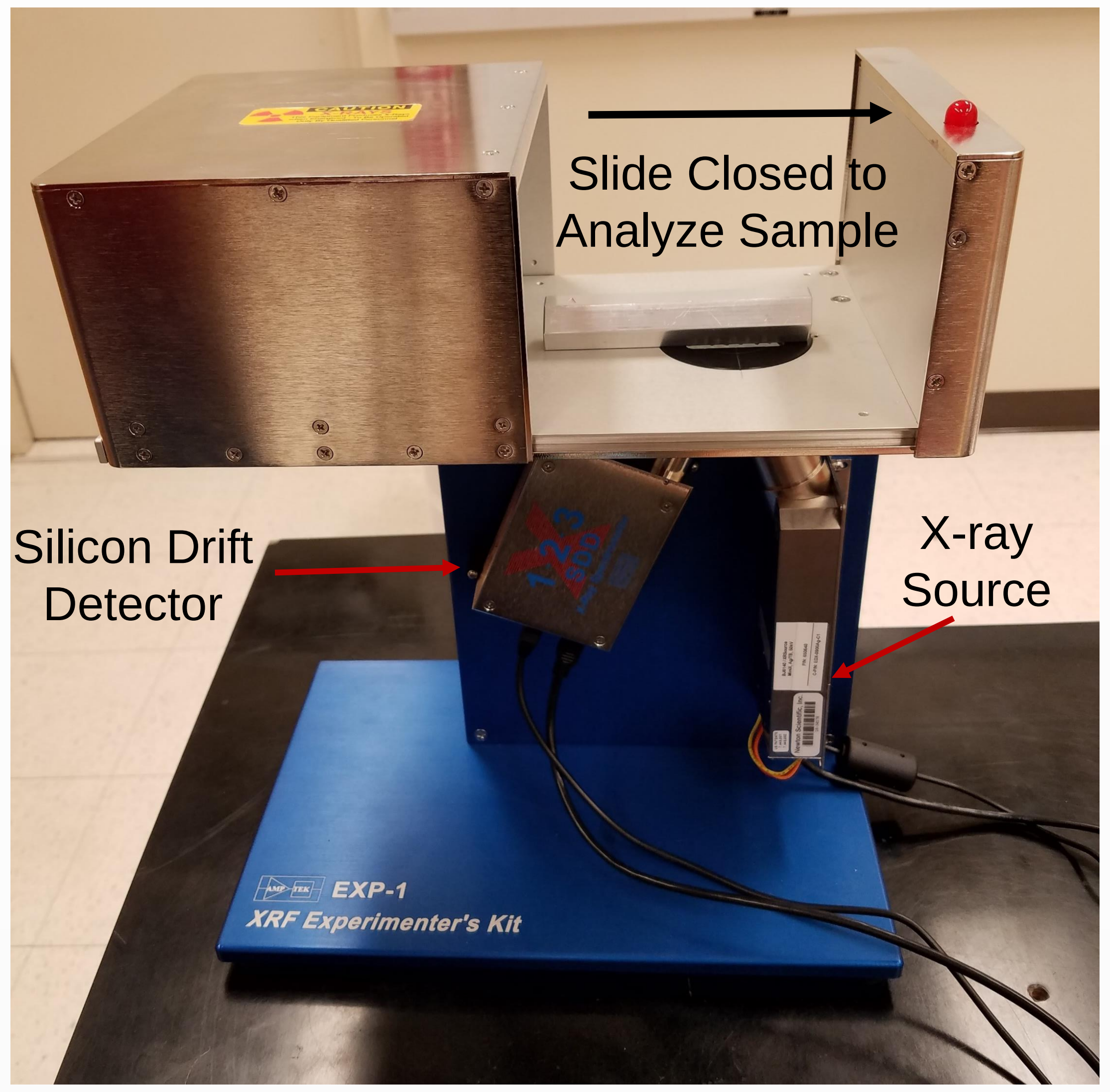
K-Line emissions



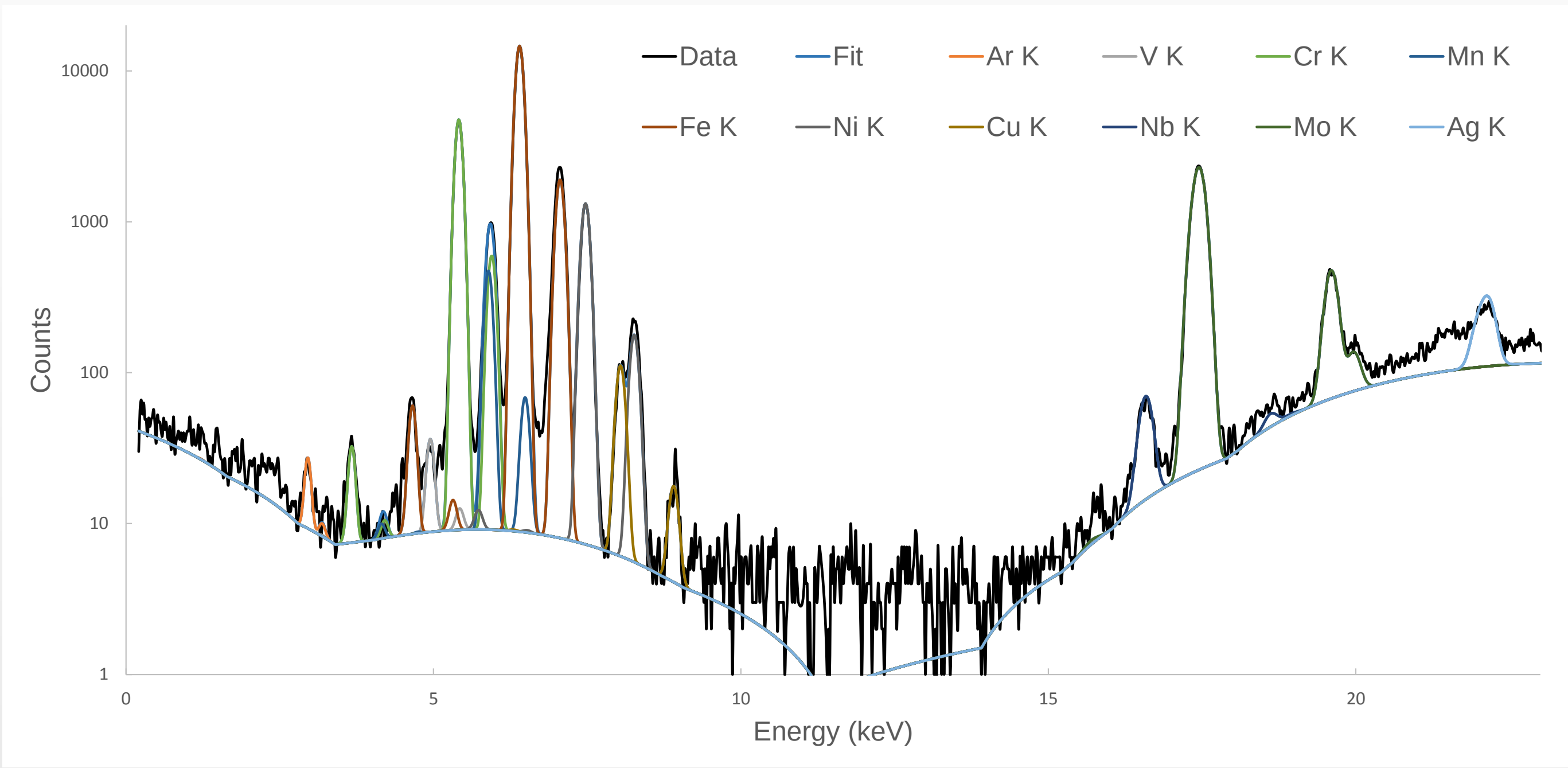
L-Line emissions

*http://amptek.com/xrf/

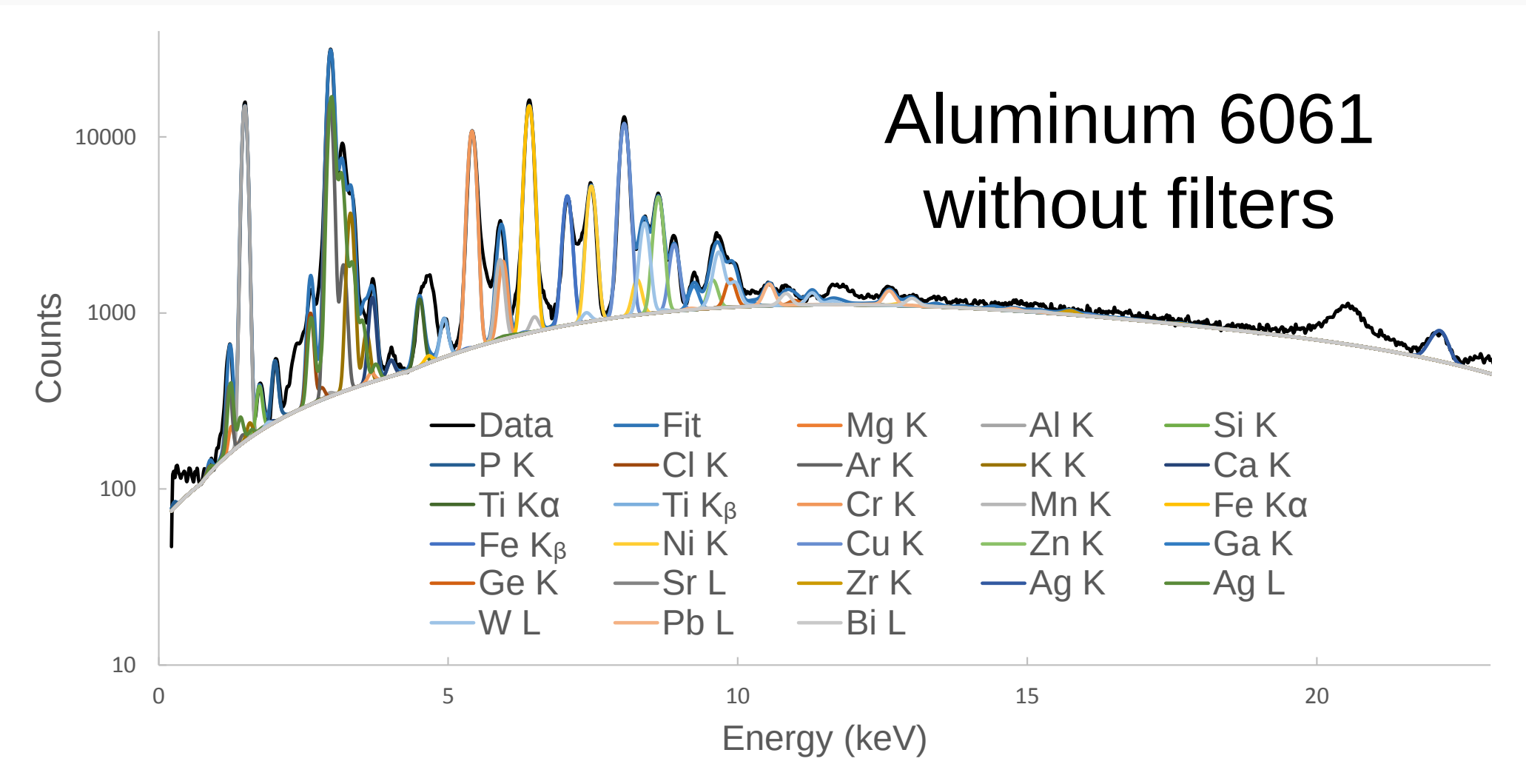
Instrument Setup

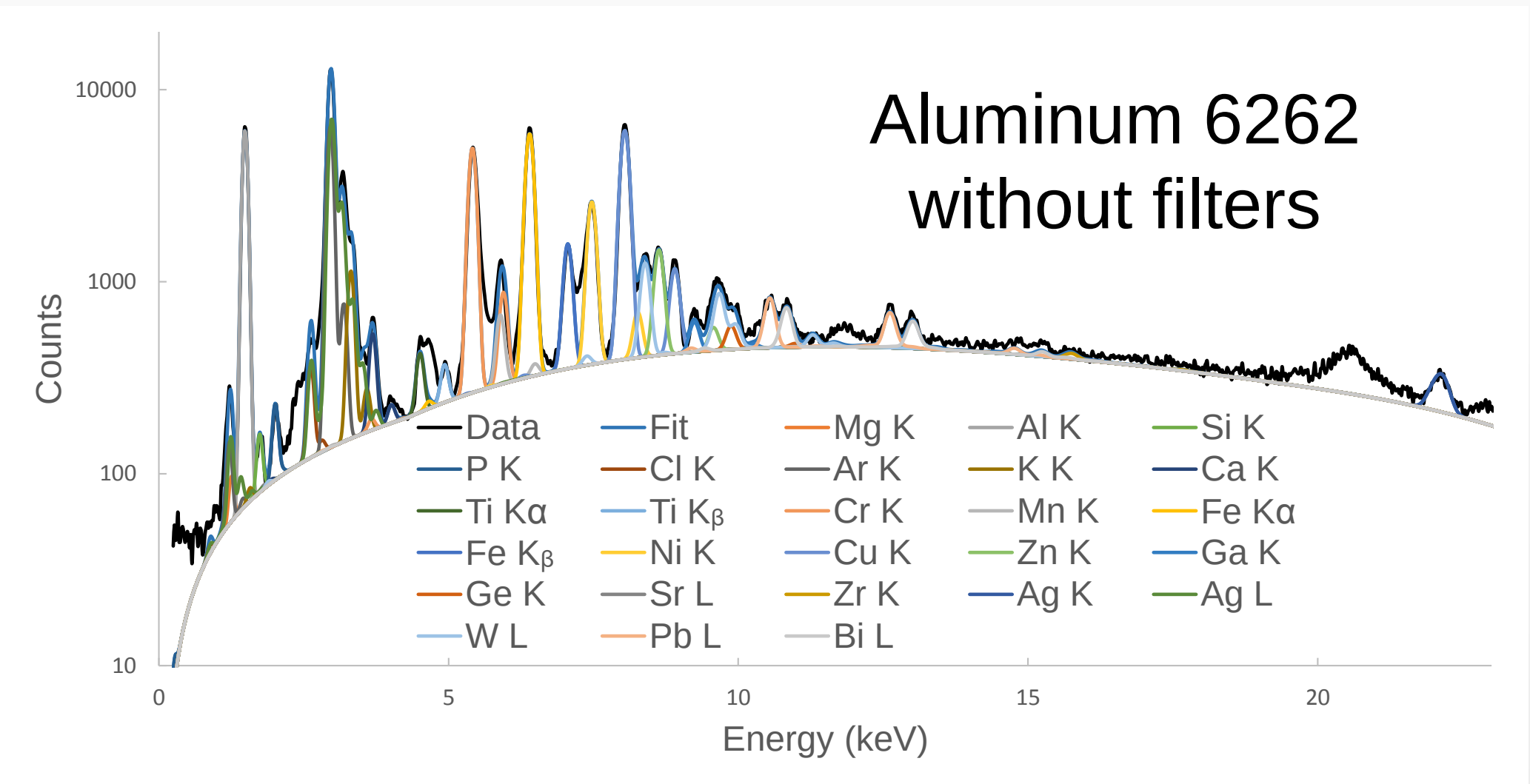


Experimental



Stainless Steel SS316 with Al/W filters





Metal samples were placed in the XRF instrument and analyzed. Using the characteristic energies of the electron transitions the elemental peaks were assigned. Aluminum and tungsten filters were employed to reduce background in a region of interest while resulting in lower count rates.

Quantitative Results

	Expected Ranges		Amptek Exp-1		Total Reflection XRF	
Element	**6262 [wt%]**	**2024 [wt%]**	**6262 [wt%]**	**2024 [wt%]**	**6262 [wt%]**	**2024 [wt%]**
Mg	0.8 - 1.2	1.2 - 1.8	5.49(.13)			
Al	94.6 - 97.8	93.5	92.6(.2)	91.8(.3)	98(5)	86(3)
Si	0.4 - 0.8	0.5 max	0.6(.1)	0.05(.09)		
Ti	0.15 max	0.15 max	0.065(.013)	0.09(.03)	0.027(.005)	0.024(.006)
Cr	0.04 - 0.14	0.1 max	0.38(.03)	0.5(.2)	0.062(.005)	0.012(.002)
Mn	0.15 max	0.3 - 0.9	0.015(.004)	0.97(.02)	0.077(.008)	0.87(.02)
Fe	0.7 max	0.5 max	0.293(.009)	0.441(.007)	0.360(.011)	0.223(.015)
Cu	0.15 - 0.4	3.8 - 4.9	0.143(.002)	5.44(.10)	0.330(.012)	5.08(.13)
Zn	0.25 max	0.25 max	0.029(.001)	0.091(.005)	0.096(.003)	0.080(.004)
Pb	0.4 - 0.7		0.028(.001)	0.013(.003)	0.038(.002)	0.003(.001)
Bi	0.4 - 0.7		0.015(.001)	0.011(.002)	0.031(.002)	

*() denotes standard deviation, red is outside expected range

Quantitative results for the Amptek measurements of aluminum alloys were determined by the fundamental parameters method (FP). Fundamental parameters include the geometry of the instrument and energy of the x-ray. Total reflection XRF (TXRF) results were determined using digestion and a Sc internal standard. Amptek results for Al, Pb, and Bi were lower than expected while Mg and Cr were higher. Results from TXRF differed from the Amptek for elements Ti, Cr, Fe, and Pb.

Conclusions

The XRF spectra produced by the instrument allows for qualitative identification of the composition of the metal alloy samples. This can be implemented easily in the Curriculum. The FP quantitative results showed that the concentration of several elements were not in the expected ranges. Especially, Cr resulted in a 170 % difference from expected values. Using an external calibration may provide more accurate results. The current software used to provide fitting of the spectra and the FP quantification is difficult to work with and provides inconsistent results. Improvements to the software should be main goal to better enable student use.

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