

Title: Determination of elemental compositions of different samples by Energy Dispersive X-Ray Fluorescence (EDXRF)

Alan Yu*, and Haroon Chaudhry, Department of Chemistry and Chemical Biology, Rutgers, The State University of New Jersey, New Brunswick, New Jersey 08901.

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Submitted this time due to the XRF machine breaking down during our two weeks.

Abstract:

The purpose of this experiment was to determine the resolution of the energy-dispersive x-ray fluorescence device, Bruker S2 Ranger, and that was determined to be about 0.20153keV. This experiment also was to acknowledge the relationship between intensity (counts per second) with time and voltage in the Bruker S2 Ranger instrument to also determine the elemental compositions of samples. These samples include various coins, smeared lipstick on a white t-shirt, two suspect diamonds, BIC blue pen ink, an alloy, a stainless steel washer, and a green paint chip.

Keywords: energy-dispersive, x-ray fluorescence, composition, relationship, resolution, counts per second.

*To whom correspondence should be addressed.

I. Introduction

We used Energy Dispersive X-Ray Fluorescence (EDXRF) to determine the elemental compositions of a stainless steel washer, an alloy, a green paint chip, solder, different coins, pen ink, e-cigarette pods, and lipstick smeared on a white t-shirt. For my pre-laboratory report, Guo et al,¹ used x-ray fluorescence to determine if blending sewage sludge with “Zhundong coal” will alleviate the high demand in high-quality coal, which sources are depleting already. The first additional peer-reviewed article that I read was by Cámara et al,² where they used x-ray fluorescence to determine if novel manganese promoted inverse cerium oxide and copper oxide will catalyze better in a water-gas shift reaction. The second additional peer-reviewed article that I read was by Li et al,³ where they used x-ray fluorescence to determine the chemical compositions of the Cu/AlCeO catalyst they used for the hydrogenation.

Table 1. My refereed journal articles.

Corresponding Author	Date Submitted	Date Accepted	Samples	My reference number
Shuai Guo	June 5, 2019	September 12, 2019	Blends of Zhundong coal and sewage sludge	1
A. López Cámara	September 26, 2018	January 3, 2019	Catalytic samples of Cu and Ce in water-gas shift reactions	2
Shaoyong Li	July 23, 2018	January 4, 2019	Cu/AlCeO catalyzed hydrogenation of CO ₂ to methanol	3

From pages 595-600 from the textbook,⁴ the concept of x-ray fluorescence is explained. X-ray fluorescence occurs when an x-ray photon collides with an atom and the atom absorbs a photon. With enough energy, an inner shell, the K shell, electron can be knocked out which requires one of the higher shells, the L shell, electrons to lose energy to come down and replace that lost electron. The electron that comes down an energy level to another will emit a wavelength. The first equation the textbook yields is

$$E_{\text{X-RAY}} = \Phi_{\text{L}} - \Phi_{\text{K}} \quad (1)$$

where E is the energy that is equal to the energy difference between the two levels with Φ being a variable for the specific energy level's electron's energy. The next equation is brought back being

$$E = \frac{hc}{\lambda} \quad (2)$$

where h is Planck's constant, c is the speed of light, and λ is the wavelength. Using these two equations by setting them equal to each other yields

$$\Phi_L - \Phi_K = \frac{hc}{\lambda} \quad (3)$$

which tells us about the x-ray photon released from the L energy level to the K energy level.

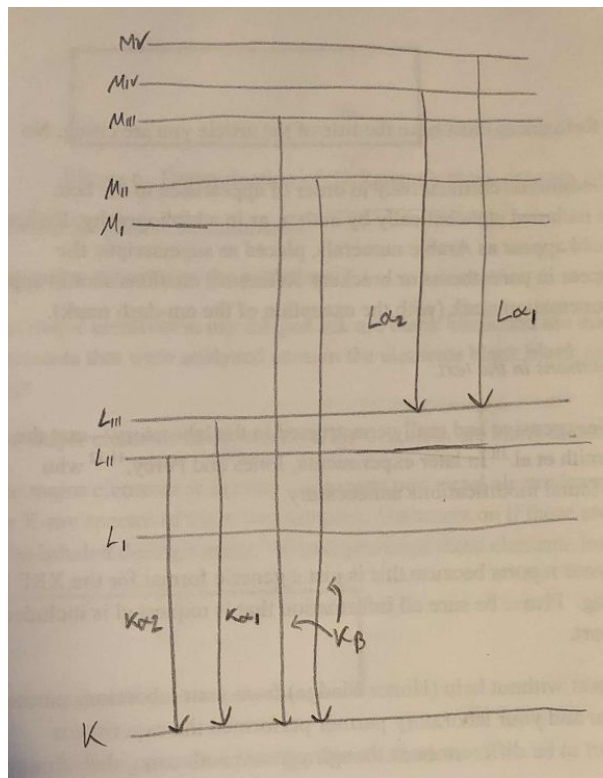


Figure 1. X-Ray energy level diagram.

II. Experimental

Equipment: Bruker S2 Ranger (Madison, WI) with Palladium X-Ray tube and XFlash SDD detector, plastic XRF cups, Kapton XRF sample cup film.

Reagent (standards): Solder wire

Briefly describe what you did:

There were two weeks to the EDXRF experiment. Week one was the basics and understanding how the machine operated. Five total tests were run that included the Background, Alloy, Resolution, Time Trial, and Solder Test which is described below. Week two was the application of Week 1 into real samples to determine the compositions and authenticities. Samples that were run were different types of coins, types of pens, two suspect diamonds, two e-cigarette pods, and lipstick from a suspect's white T-shirt. These tests are also described below.

Week 1

Experiment 1. Background Test.

A blank cup was run without any yellow Kapton film under the application “Pen Ink” that ran for 10 minutes at 40kV, 300μA.

Experiment 2. Alloy Test.

A blank cup with yellow Kapton film ran under the application “Alloy test two volts” which had 20kV and 40kV X-ray tube voltages.

Experiment 3. Resolution Test.

A stainless steel washer was run under the application “Chem 348 coins” where this will be used to determine the resolution of the machine.

Experiment 4. Time Trial Test.

A green paint card was run using the application “Time Trials 4 runs” where the machine analyzes the sample under 60, 120, 240, and 300 seconds.

Experiment 5. Solder ID Test.

A small length of solder was run under the application “Chem 348 coins”.

Week 2

Experiment 6. Identification of elements in different coins.

Four different coins (quarter, penny, dime, and nickel), ran under the application “Chem 348 coins”.

Experiment 7. Identification of elements in student’s pen ink.

Both lab partners had their pen ink scribbled on Whatman filter paper and ran under the application “Pen Ink”.

Experiment 8. Determination of the authenticity of two suspect diamonds.

Two suspect diamonds were already prepared in the machine and were run under the application “Chem 348 coins”.

Experiment 9. Identification of elements in two e-cigarette pods.

Two sample e-cigarette pods were prepared (Juil and Eonsmoke) and were run under the application “Chem 348 coins”.

Experiment 10. Identification of elements in lipstick from suspect’s white T-shirt.

Sample was run under the application “Pen Ink”.

III. Results and Discussions

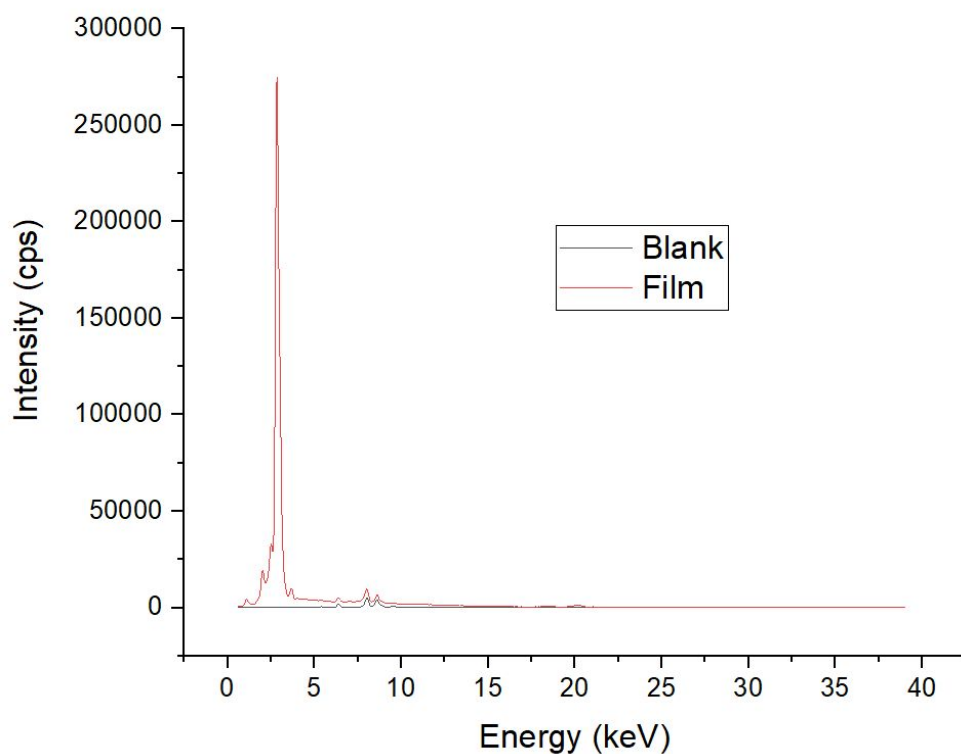


Figure 2. Background stacked X-ray spectra. From this plot, it can be concluded that there is a very strong palladium L- α peak at 2.847keV which is from the palladium x-ray tube.

Table 2 summarizes the counting statistics for the four different time trials and the corresponding peak area of the two most intense element X-rays analyzed. It can be seen that as time increases, the peak area (in counts per second) increases. This shows a direct relationship between intensity and time.

STDEV = standard deviation and is equal to the square root of element peak area.

Table 2. Counting statistics for the four different time trials.

Time (seconds)	Peak Area of Zinc	STDEV area	Peak Area of Titanium	STDEV area
60	4295	65.54	4234	65.07
120	8558	92.51	8415	91.73
240	17061	130.62	16815	129.67

300	21225	145.69	20852	144.40
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Figure 3 shows the stack plot of the counting statistics

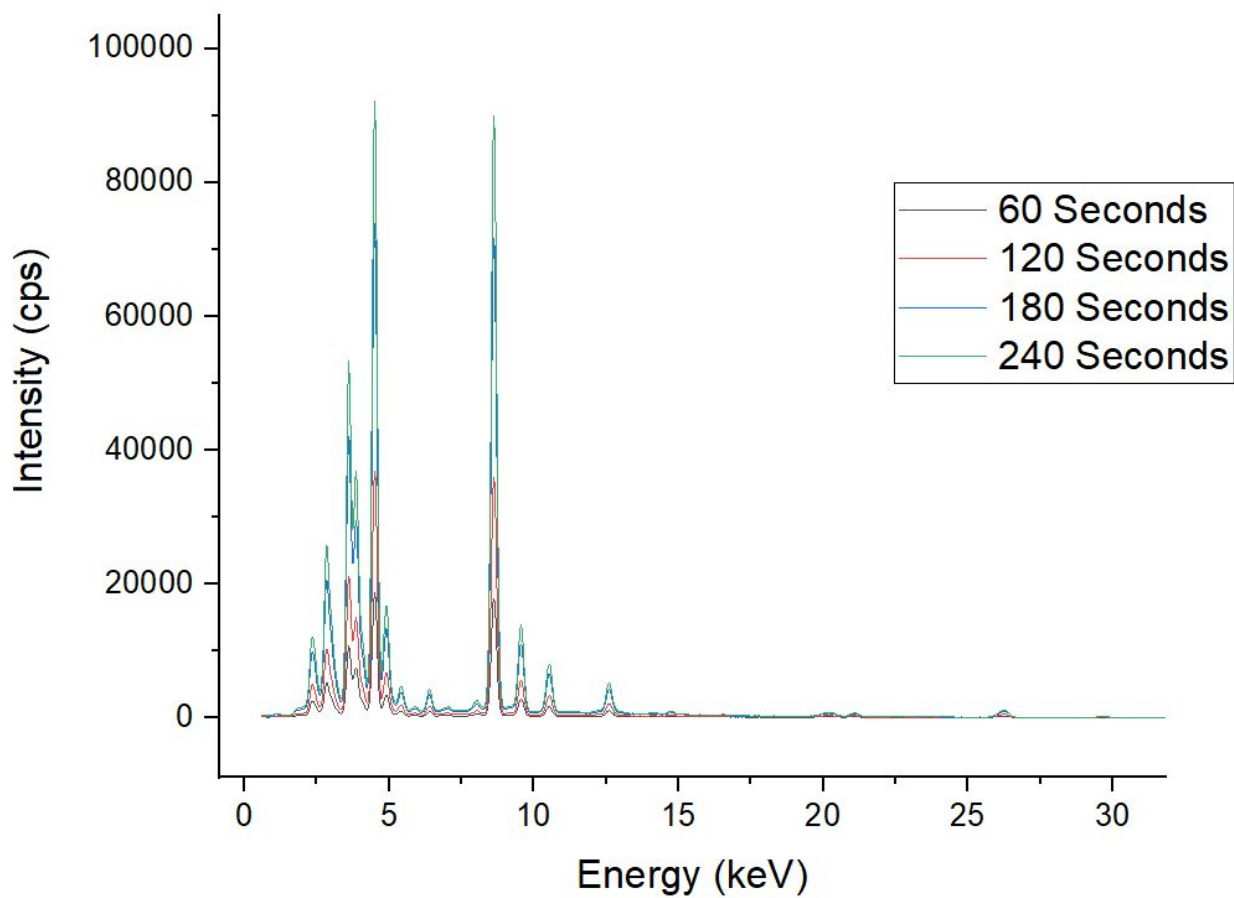


Figure 3. X-ray spectra of counting statistics.

Figure 4 shows plot of time vs STDEV for element Zinc.

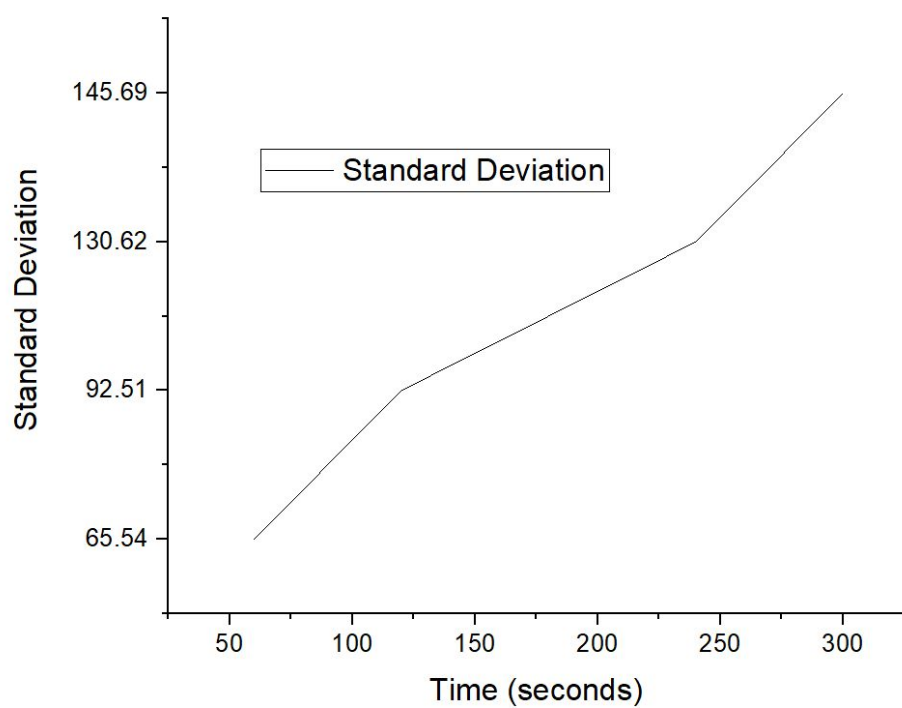


Figure 4. Time vs STDEV for element Zinc.

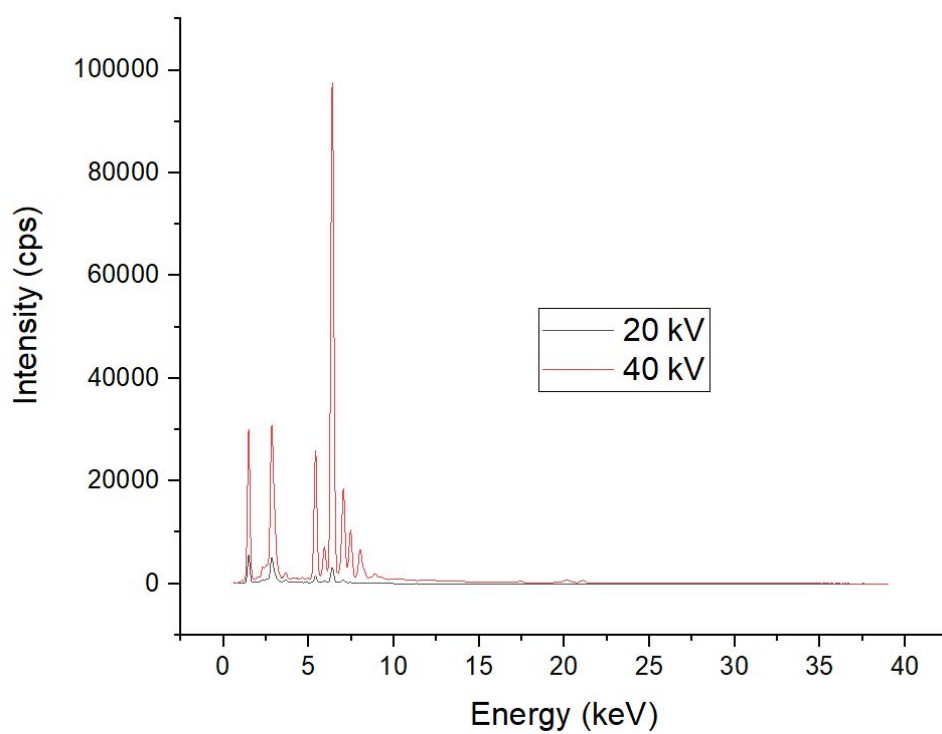


Figure 5. Compared x-ray spectra collected at 20kV and 40kV of measured alloy.

Table 3 compares the elements (3 most intense) detected at the two different voltages

Table 3. Different Voltage comparisons of the 3 most intense element peaks.

Voltage (kV)	Iron	Aluminum	Chromium
20	~3,000keV Intensity	~5,500keV Intensity	~1,500keV Intensity
40	~100,000keV Intensity	~30,000keV Intensity	~22,000keV Intensity

Figure 6 shows the fitting of the 6.40keV (Fe) peak to determine the resolution which was determined to be 0.20153keV at 6.40keV (Fe).

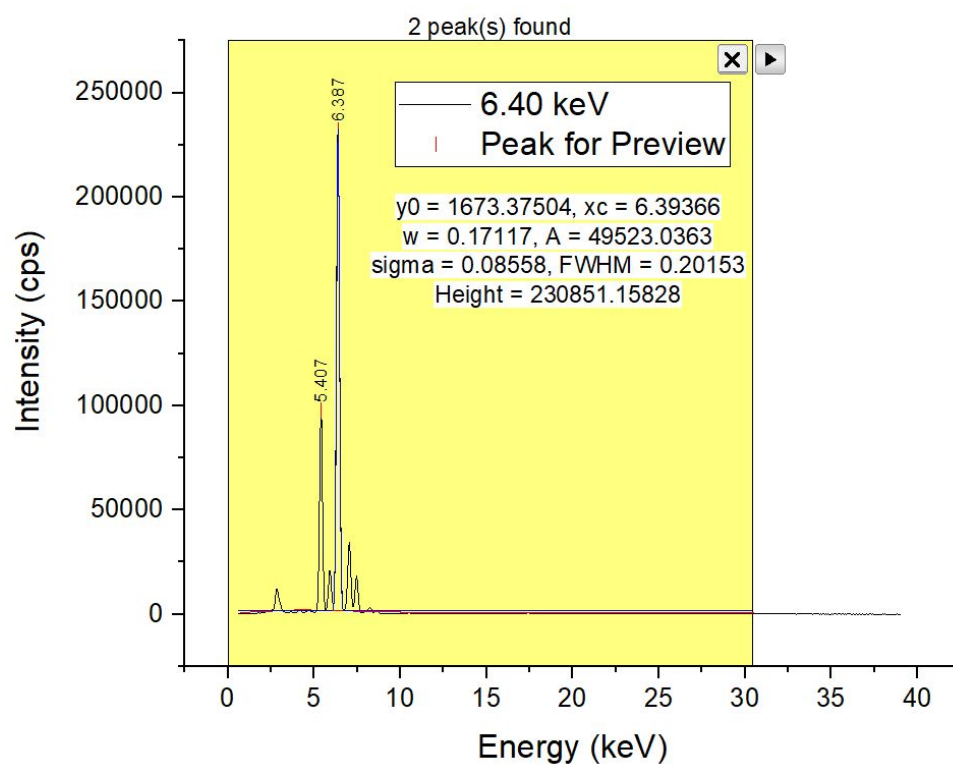


Figure 6. Determination of S2 Ranger's blank detector's resolution using a stainless steel washer.

Element identification summaries.

The major elements in the solder are tin and copper.

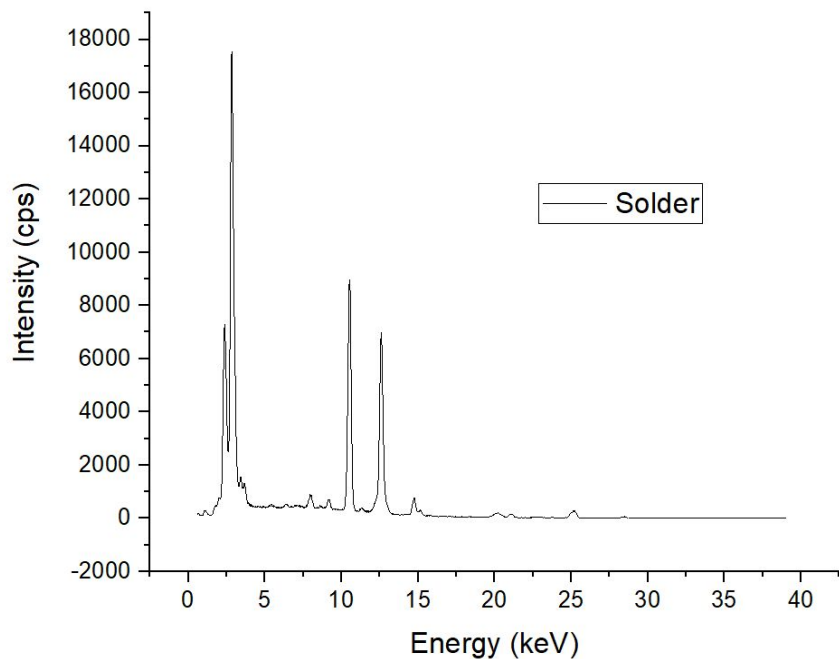


Figure 7. X-ray spectra of solder.

The major elements in my ink pen ink are chromium and copper and is due to it being a ballpoint pen and having potential trace elements when creating the object.

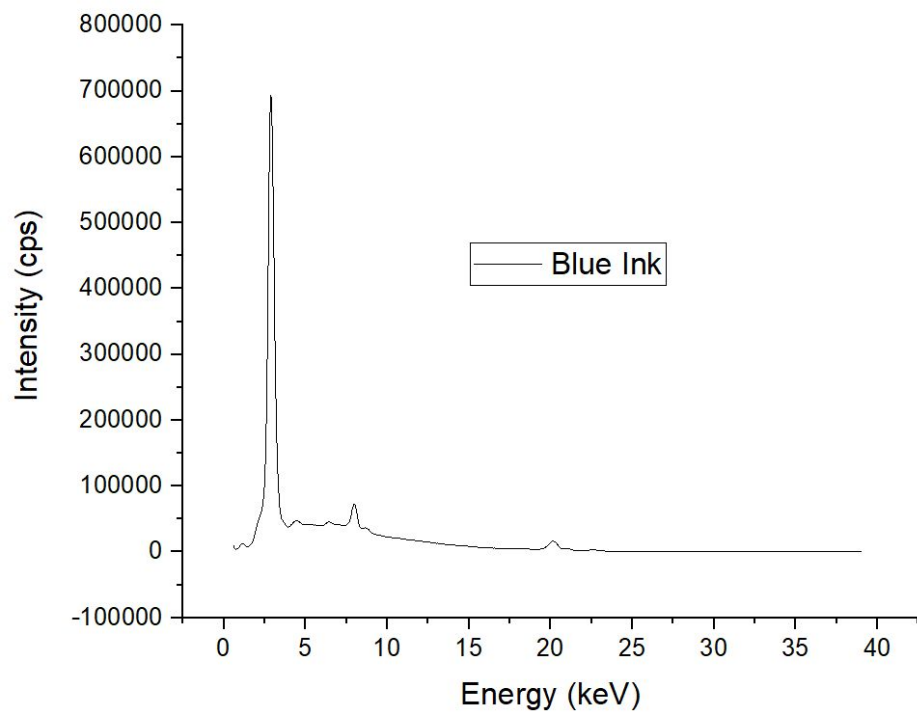


Figure 8. X-ray spectra of my BIC blue ink pen.

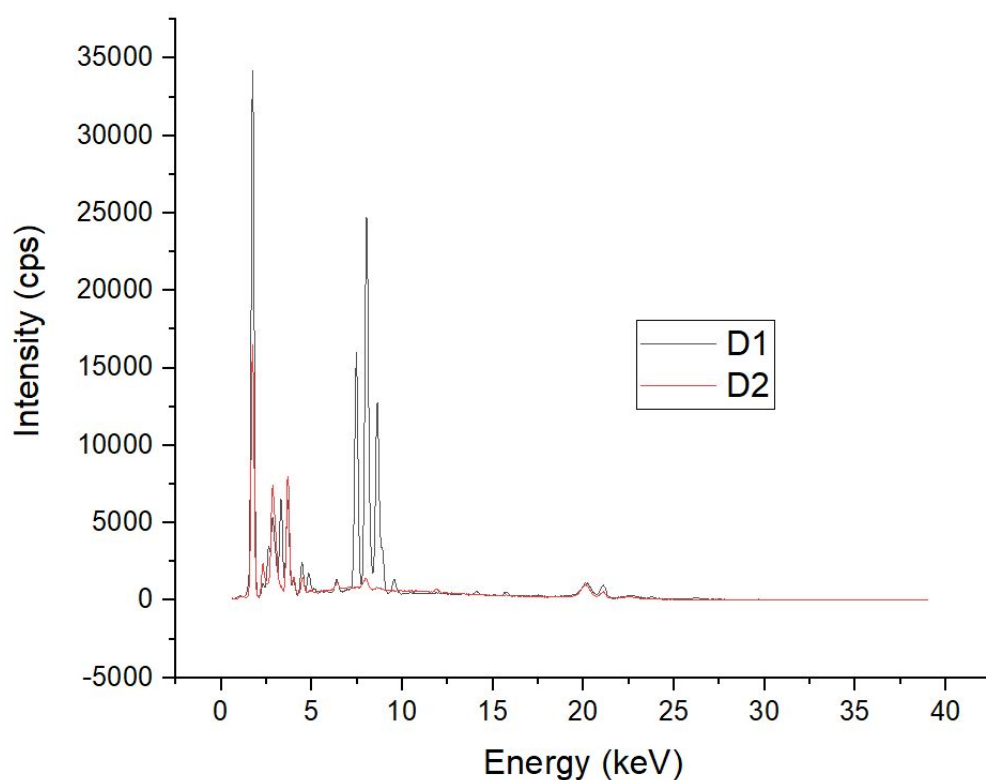


Figure 9. X-ray spectra of the two suspect diamonds.

The two suspect diamonds that were analyzed contain the elements silicon, titanium, and calcium. This means that these diamonds have been falsified.

The major elements in the smeared lipstick cloth are silicon, iron, titanium, and copper.

The major elements in the two e-cigarettes pod metal electrodes are iron, nickel, chromium, zinc, copper and silicon. Figure 10 shows the X-ray spectra of these two samples. Chromium and silicon can be inhaled and are considered toxic to the lungs.

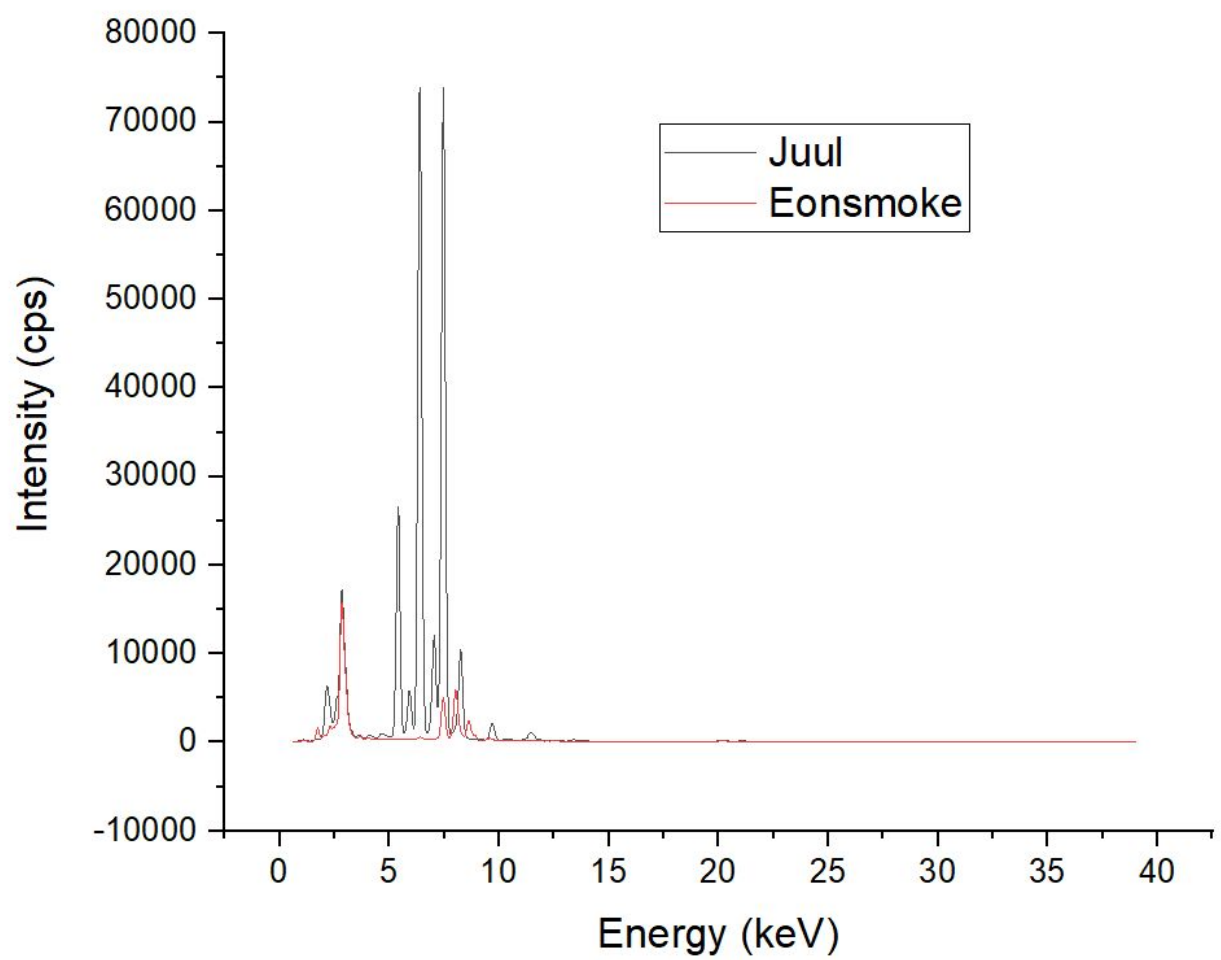


Figure 10. X-ray spectra of e-cigarette electrodes.

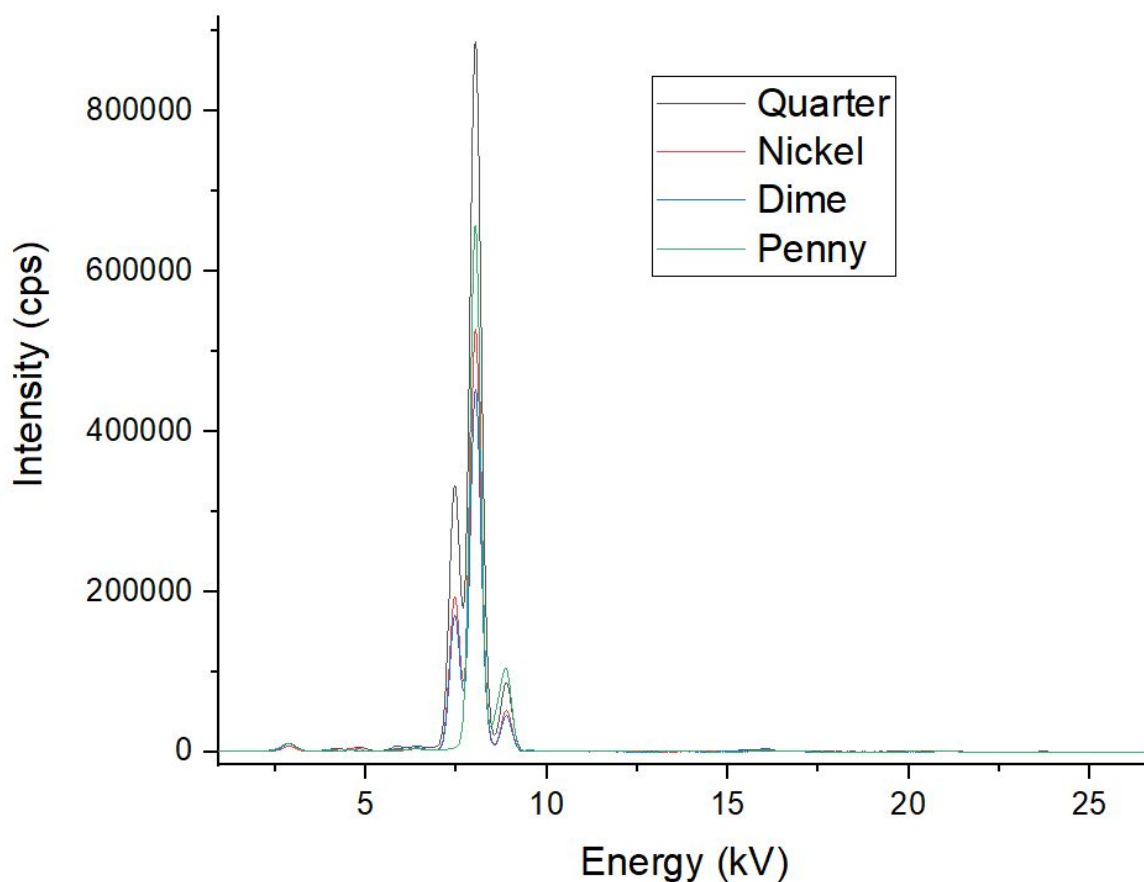


Figure 11. X-ray spectra of coins 1(Quarter), 2(Nickel), 3(Dime), and 4(Penny).

From this, the major elements in the quarter are copper and nickel, the nickel has copper and nickel, the dime has copper and nickel, and the penny has only copper.

IV. Conclusions

Using x-ray fluorescence, the resolution of the instrument was found to be 0.20153keV. A direct relationship was also found between the intensity (counts per second) and time with voltage. For multielement analysis, this instrument is capable of it, but peaks will be devoured by other peaks that are larger than it. In cases like this, a gaussian peak estimation could be used for peaks that are still visible, rather than peaks that get absorbed by the other peaks.

For elemental analysis, solder was found to contain tin and copper. The pen contained chromium and copper. The diamonds contained silicon, titanium, and calcium which leads to them being falsified. The smeared lipstick cloth contained silicon, iron, titanium, and copper. The two e-cigarettes pod metal electrodes contained iron, nickel, chromium, zinc, copper and silicon. It can be said that both chromium and silicon can be inhaled and are considered toxic to

the lungs. For the coins, the quarter, nickel, and dime has copper and nickel, but for the penny, it only had copper.

V. References

1. Shuai Guo, Qiyao Yang, Honglin Liang, Deyong Che, Hongpeng Liu, and Baizhong Sun, Effect of blending sewage sludge with coal on combustion and ash slagging behavior. RSC Adv., 2019, 9, 29482-29492.
2. A. López Cámara, V. Cortés Corberán, A. Martínez-Arias, L. Barrio, R.Si, J.C. Hanson, and J.A.Rodríguez, Novel manganese-promoted inverse CeO₂/CuO catalyst: In situ characterization and activity for the water-gas shift reaction. Catalysis Today, Vol. 339 (2020).
3. Shaozhong Li, Limin Guo, and Tatsumi Ishihara, Hydrogenation of CO₂ to methanol over Cu/AlCeO catalyst. Catalysis Today, Vol, 339 (2020).
4. Undergraduate Instrumental Analysis, James W. Robinson, Eileen M. Skelly Frame, George M. Frame II, CRC Press, 2014, 7th edn.