

Dispersive X-Ray Fluorescence Measurement of Trace Zinc Contamination on Lab Benches (XRF)

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I submit this laboratory report as an original document. I assert that all ideas and discussion of data contained herein are my own work, unless otherwise referenced.

ABSTRACT

The traces of Zn on lab benches can be measured qualitatively and quantitatively via x-ray fluorescence (XRF) method. The peak at 8.639 keV of the fluorescence intensity versus energy spectrum signified the counts per second (CPS) of Zn in the sample, which will be used to compute the quantitative measurement of Zn with calibration approach. 3 standard solutions were prepared from a 1000 ppm Zn stock solution, by diluting 1.0, 2.5, and 5.0 mL of the stock solution in a 10-mL volumetric flask, resulting in 100, 250, and 500 ppm of standard solution respectively. A calibration curve equation, $CPS = (0.139 \pm 0.036) \frac{cps}{ppm} - (18.83 \pm 11.86) cps$, with an R^2 -value of 0.937 was obtained. The CPS of the unknown sample was averaged and corrected to be 9.17 ± 3.06 cps. From the calibration curve, the concentration of Zn in the unknown was found to be 200.83 ± 102.17 ppm, equivalent to 20.02 ± 10.19 μ g of Zn. the micropipette was calibrated for 100 μ L of distilled water, resulted in 99.9 ± 1.3 μ L volume pipetted.

INTRODUCTION

Traces of materials can be analyzed easily, but contamination will make it more difficult to do so. One of the common techniques to control the contamination in the laboratory is by performing a wipe test. Both the surface of the laboratory and the instruments/tools should be tested for contamination. The typical method of analyzing the samples is by digesting the wipes in acid with inductively coupled plasma mass spectrometry (ICPMS).

One of the very common contaminant substances on the surface of the lab bench is zinc. Wipe test can be performed to detect the presence of these traces. A rapid measurement can be employed instead of the ICPMS by using the x-ray fluorescence (XRF) method to qualitatively and quantitatively measure the zinc contaminant.

The theoretical understanding of the XRF phenomenon comes from defining the atomic structure. For the element Zn, let the second ($n = 2$) electron shell be denoted as K, and the $n = 3$ be denoted as L.¹ When there is an electron vacancy in K shell, filling of electron from L shell into K shell will emit photons with characteristic energy/wavelength, which is called the K_{α} spectrum line. The K_{α} of Zn is 8.639 keV.

PROCEDURE ²

Three standard solutions were prepared by diluting 1.0, 2.5, and 5.0 mL of 1000 ppm stock solution of Zn in 10.0 mL volumetric flasks each, resulting in standard concentration of 100, 250, and 500 ppm respectively. Three towel rounds were prepared and 100 μ L of each standard solution were added onto the center of the towel rounds. They were dried in the oven for 5 minutes. Another two towel rounds were prepared and they were wetted with about 100 μ L of distilled water. Each of the two towel rounds was used to wipe the surface of the lab bench and was left to dry in the oven for 5 minutes. The concentration of Zn on the lab bench was determined through a calibration approach.

After the towel rounds were left to cool down, they were loaded into the spectrometer and the spectrum under the same spectral conditions were measured. For Zn, the K_{α} line occurred at 8.639 keV, which should be the guidance for measuring the CPS of Zn. The XRF cells were assembled by cutting small squares of mylar film and securing them to the bottom of the cells. It was ensured that the films were not contaminated with the dust from the lab bench, towel rounds, and the hands. The counts per second (CPS) of Zn were recorded for each towel round, and three replicates measurements were taken for each sample.

A blank measurement was performed by using an unexposed towel round. The unexposed towel round was wetted with 100 μ L of distilled water, dried in the oven for 5 minutes, and left to cool down prior to taking its spectrum and the value of CPS of Zn.

The micropipette was calibrated to deliver 100 μ L of distilled water. An empty bottle and cap were weighted and the first addition of 100 μ L of distilled water was made. The bottle and cap were reweighed. The addition of distilled water and mass measurement were done for 10 times and the average volume of water transferred was calculated.

RESULTS AND DISCUSSION

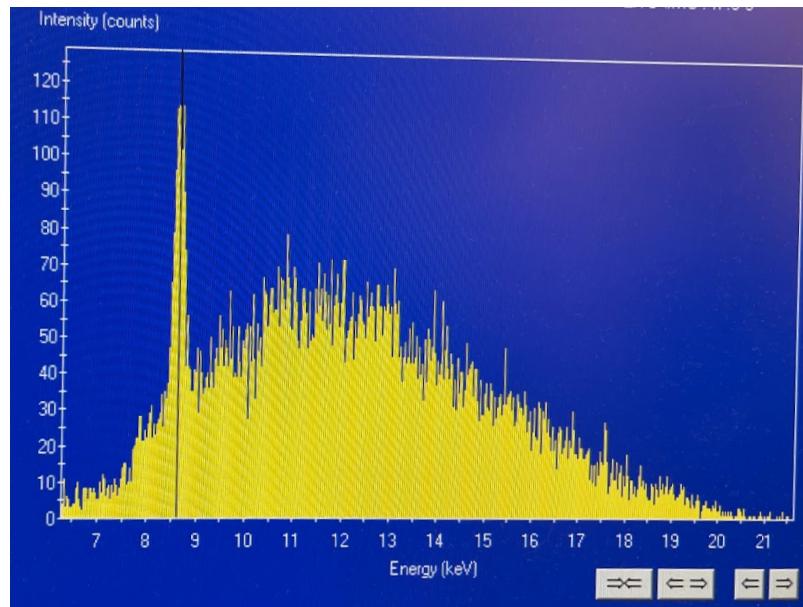


Figure 1. XRF plot of 500 ppm standard solution.

Figure 1 above showed the fluorescence intensity versus energy of 500 ppm standard solution of Zn. The highest peak occurred at 8.639 keV, which was the same as the value of K_{α} of Zn. Obviously, this indicated the presence of Zn in the sample measured. This was used as the baseline to detect any presence of Zn in the unknown samples. The rest of the peaks were less significant than the peak of Zn and would be ignored. The XRF plots for other standard solutions and the rest of the replicates produced the same observation and were not included under discussion and could be found in **Appendix** under *Supplemental Figures and Tables*.

Table 1. Calibration data for Zn standard.

Concentration of Zn (ppm)	^a CPS _{corrected}
100	0.33
250	7.67
500	54.00

^a CPS_{average sample} - CPS_{average blank}, CPS_{average blank} = 65.67

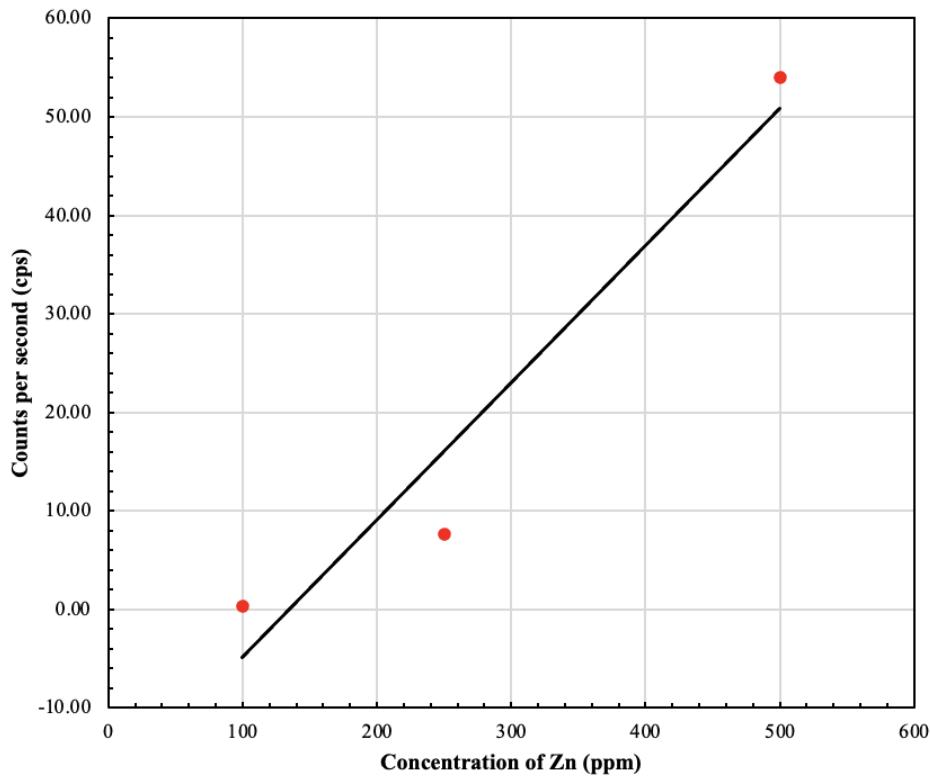


Figure 2. Calibration plot of Zn standard solution.

To quantitate the amount of Zn on the lab benches, calibration method was used by preparing 3 standard solutions with varying concentration, by ensuring that the concentration in the unknown sample encompassed within the calibration plot. The corrected CPS measurement of standard solutions as tabulated in **Table 1** were plotted in **Figure 2** as shown above. The CPS of standards were corrected with the blank's CPS to correct for any possible traces in the mylar film and the unwetted and unexposed towel prior to taking measurement. The calibration line in **Figure 2** followed the following **Eq. 1**, with an R^2 -value of 0.937.

$$CPS = (0.139 \pm 0.036) \frac{cps}{ppm} - (18.83 \pm 11.86) cps \quad \text{Eq. 1}$$

The measurement of two unknown samples were collected and corrected to be 7.00 and 11.33 cps. Taking the average of the two resulted in 9.17 ± 3.06 cps. Using this value and uncertainty, plugging into **Eq. 1** would yield a concentration of 200.83 ± 102.17 ppm, which was equivalent to 20.02 ± 10.19 μg of Zn.

Zn is commonly found in the earth's crust, and the releases to the environment are common and very significant. The abundance of Zn as contaminant comes from the industrial sources which includes the electroplating, smelting and ore processing, and drainage from both active and inactive mining operations. About 1.9% of the estimated total environmental releases of Zn comes from domestic manufacturing and processing facilities.³ Emissions of Zn to air are due to windborne soil particles and forest fires. Apart from air emission, Zn could also be emitted into water. Zn are found in the earth's crust, where soluble compounds of zinc can be

formed and released into water. For water emission, one of the ways to reduce Zn contamination is by implementing “Biochar” as a filtration medium. It is a versatile and affordable filtration material which is effectively filtering out Zn or unwanted traces of materials in water. Another way to mitigate Zn in water is through coated bare or corroded galvanized roofing.⁴

XRF is affected by the changes in the sample matrix. It is necessary to let the sample dry in the oven prior to taking the XRF spectra because the measurement relies on the volume of solution sample used. It showed the best performance for volume ranging from 5 to 10 mL.⁵ The wipe sample required only 100 µL of distilled water, which will pose a disadvantage to XRF measurement due to low sensitivity to the sample matrix.

The presence of 2 peaks for Zn is due to the different oxidation state of Zn. It should be possible to use both peaks for the analysis of the contamination rather than considering only one peak as it could holistically consider all types of Zn and more accurately measure the contamination of Zn in the unknown sample.

Gloves are not a good idea to perform the experiment in quantitatively measuring the traces of Zn. A study done by Garçon et al. found that gloves can contain up to 17 mg of Zn.⁶ If gloves were worn during the experiment, there will be cross contamination of Zn onto the sample, thus inaccurately measuring the contaminants in the unknown sample.

The micropipette was calibrated for 100 µL of distilled water. The actual volume pipetted, after averaging 10 volume of water pipetted, resulted in 9.9 ± 1.3 µL of volume actually pipetted. The actual volume pipetted should be taken into account in any dilution factor calculations to ensure the accuracy of the concentrations made, if there is any. It is important to calibrate the micropipette as it involves the mechanism of a spring, which will wear out with time if the spring is constantly compressed upon pipetting.

CONCLUSIONS

There is always contamination of materials in the laboratory. The contamination can be both quantitatively and qualitatively measured through inductively coupled plasma mass spectrometry. However, an easier method is to employ a wipe test with calibration curve approach to determine the concentration of desired traces in the unknown sample. At a K_{α} spectral line of 8.639 keV, the fluorescence intensity of Zn in terms of counts per second of Zn could be measured. Zn contamination can spread through air and water, coming from smelting, ore processing, mining operations, electroplating, and soluble Zn compounds eluted into water streams.

REFERENCES

- ¹ X-ray fluorescence - university of Georgia.
http://cais.uga.edu/wp-content/uploads/2019/01/XRF_Background.pdf (accessed Nov 5, 2021).
- ² Cruz, F. *CHEM438 Instrumental Methods Laboratory - Dispersive X-Ray Fluorescence Measurement of Trace Zinc Contamination on Lab Benches lab*; University of Delaware: Newark, Delaware, 2018; pp 1-6.
- ³ 6. potential for human exposure. <https://www.atsdr.cdc.gov/toxprofiles/tp60-c6.pdf> (accessed Nov 5, 2021).
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<https://portofpt.com/preventing-zinc-pollution-in-stormwater/> (accessed Nov 5, 2021).
- ⁵ What is X-ray fluorescence (XRF).
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- ⁶ Garçon, M.; Sauzéat, L.; Carlson, R. W.; Shirey, S. B.; Simon, M.; Balter, V.; Boyet, M. Nitrile, Latex, Neoprene and Vinyl Gloves: A Primary Source of Contamination for Trace Element and Zn Isotopic Analyses in Geological and Biological Samples. *Geostandards and Geoanalytical Research* **2017**, *41* (3), 367–380.

APPENDICES

Lab Notebook

23			
Exp. No.	Experiment/Subject	Date	
7	CHM438 (XRF)	10/25/2024	
Name	Lab Partner	Locker/ Desk No.	Course & Section No.
Mohd Fayed	Justin M Thank		021L
<p><u>PRF LAB Questions</u></p> <p>1. Electrons from the atoms get ionized from the absorption of X-rays of sufficient energy. Removing the e^- from inner shell of atom will cause the e^- from the outer shell to fall and fill the vacancy. e^- excess energy emission is the X-ray. Every element has different electronic energy levels, so the signature is different for each element.</p> <p>2. $6.4 \text{ keV} \left(\frac{1000 \text{ eV}}{1 \text{ keV}} \right) \left(\frac{1.602 \times 10^{-19} \text{ J}}{1 \text{ eV}} \right) \left(\frac{1}{6.63 \times 10^{-34} \text{ Js}} \right) = 1.546 \times 10^{18} \text{ s}^{-1}$</p> $\lambda = \frac{c}{\nu} = \frac{2.998 \times 10^8 \text{ m/s}}{1.546 \times 10^{18} \text{ Hz}} = 1.937 \times 10^{-10} \text{ m} = \frac{1 \text{ nm}}{10^{-9} \text{ m}} = 0.194 \text{ nm}$			
Signature	Date	Witness/TA	Date
THE HAYDEN-MCNEIL STUDENT LAB NOTEBOOK		Note: Insert Divider Under Copy Sheet Before Writing	

Exp. No.	7	Experiment/Subject	CHEM 438 (XRF)	Date	10/28/2024
Name	Abdul Fayeed	Lab Partner	Justin M Thanh	Locker/ Desk No.	Course & Section No. 04L

Objective

The purpose of this lab is to determine the trace of Zn contamination on lab benches via dispersive x-ray fluorescence measurement.

Introduction

A wipe test is performed to collect the sample of zinc on the lab benches. As opposed to the acid digestion method, x-ray fluorescence will be done instead to identify the contaminants and quantitate the zinc.

Procedure

- Get trained on the use of X-ray Spectrometer.
- Assemble the XRF cells. (Be careful not to overstretch and tear the mylar film)
- Make 6 sample cells. Don't contaminate the film.
- Set up the experiment in the software.
- Analyze the wipe sample through qualitative and quantitative measurement.

Qualitative

- Use high tube voltage and do survey scan
- Identify and label the peaks.
- Adjust voltage, filters, and current to produce a clear spectrum.
Label appropriately.

calibration with pipette

Number	mass (g)	empty. (of the fast bottle)
0	16.4811	
1	16.5779	
2	16.6761	
3	16.7777	
4	16.8775	
5	16.9771	
6	17.0774	
7	17.1777	
8	17.2779	
9	17.3774	
10	17.4771	

Zn K_α line : 8.639 keV

-2x : -17.278 keV

Signature	Date 10/25/2024	Witness/TA	Date
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Exp. No.	7	Experiment/Subject	CHM 438 (XRF)	Date	10/25/2021
Name	Abdul Fayed	Lab Partner	Jasmin N. Thank	Locker/ Desk No.	Course & Section No. G21C

- Quantitative
1. Make standard solution of Zn from 1000 ppm stock (~10mL of Zn stock adds an appropriate mass of Zn to 100mL).
 2. Make 6 towel rounds. Cut out circles of lab w/ scissors.
 3. Use one of the 3-ply rounds, lightly wet w/ 100 μL distilled water, and wipe the entire surface of lab bench. Expose the surface evenly.
 4. Dry the towel in oven for 5 minutes. Cool down then measure the spectrum.
 5. Repeat the wipe sample by using a second 3-ply towel round.
 6. Throw away & use the other 4 3-ply rounds to make the calibration curve by adding aliquots of Zn with the micropipette.
 7. Aim to hit span the range (lying above and below the estimated wipe value).
 8. Dry the circles in oven in labeled beaker for 5 minutes. Cool down then measure the spectrum.
 9. Record the cps (counts/ $\frac{sec}{min}$)
 10. Measure the blanks: unexposed towel round and mylar films.
 11. Calibrate micropipette by weighing empty bottle and cap (± 0.1 mg) and add 100 μL of water, then reweigh and recap and reweigh. Repeat 10 times. Repeat 10 times.

Sample	conc. Zn (ppm)	K _{a1} (ev)	K _{a2} (ev)	K _{a3} (ev)
Blank				
Unk. 1				
Unk. 2				
Stand. 1	50 (0.5ml)			
Stand. 2	100 (1ml)			
Stand. 3	250 (2.5ml)			
Stand. 4	500 (5ml) (10mLdil)			

conclusions:

X-ray fluorescence can be used to detect the trace of Zn and both quantitatively and qualitatively measure the trace.

Signature	Date	Witness/TA	Date
	10/25/2021		

Supplemental Figures and Tables

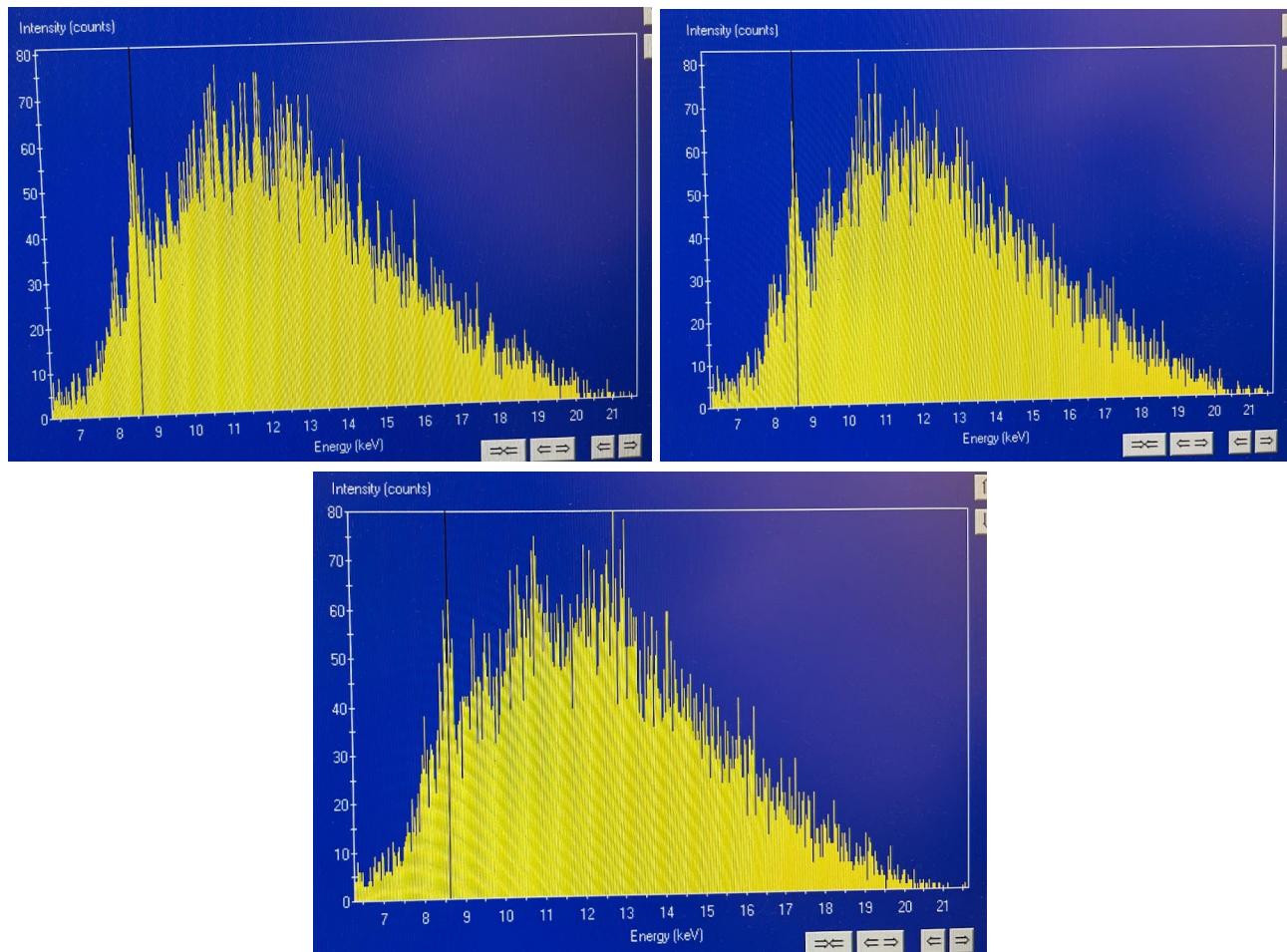


Figure A. XRF plot of 100 ppm standard solution of three replicates.

Table A. Replicates data of the CPS for 100 ppm standard solution.

CPS₁	CPS₂	CPS₃	CPS_{average}	CPS_{corrected}
62.00	66.00	70.00	66.00	0.33

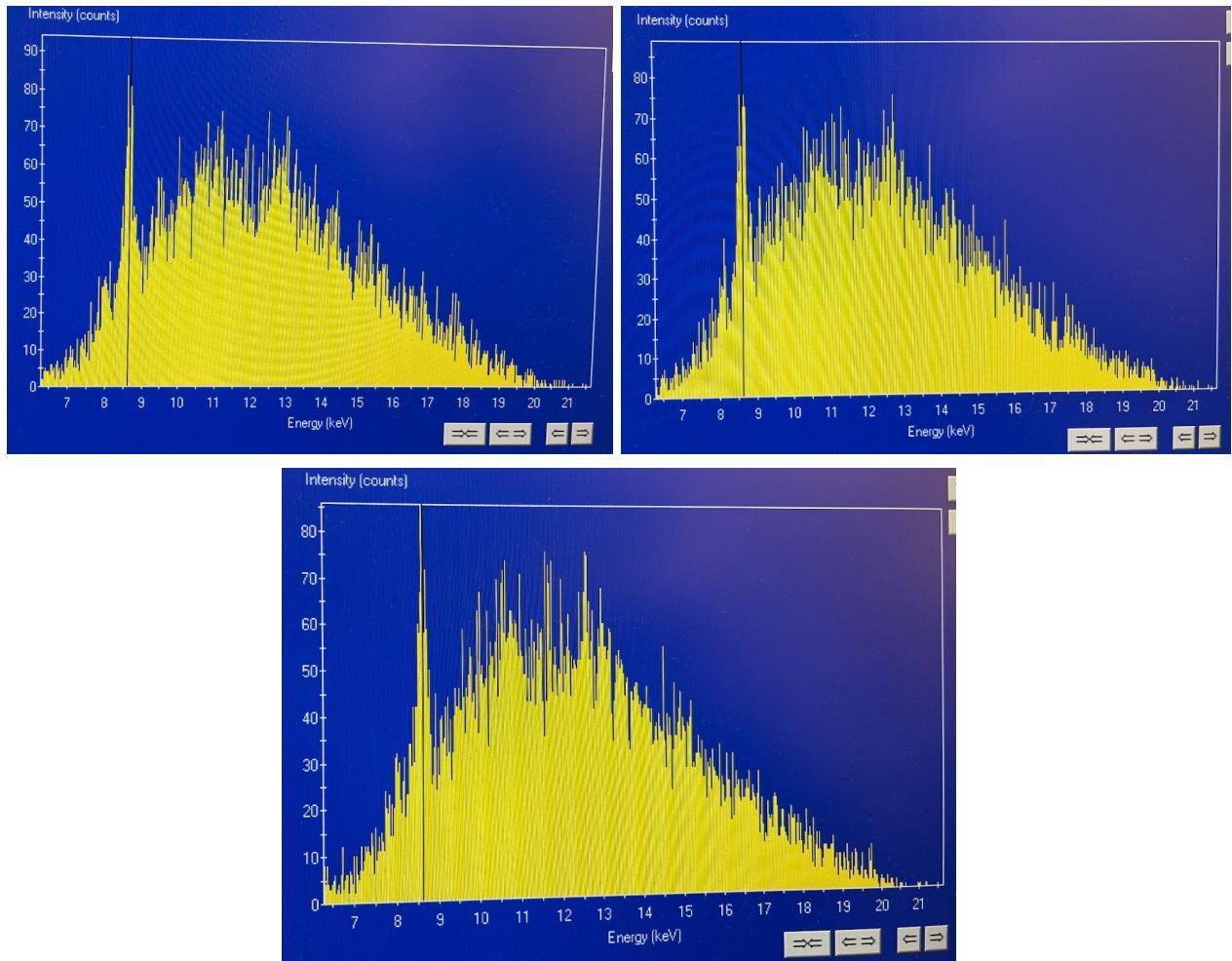


Figure B. XRF plot of 250 ppm standard solution of three replicates.

Table B. Replicates data of the CPS for 250 ppm standard solution.

CPS ₁	CPS ₂	CPS ₃	CPS _{average}	CPS _{corrected}
87.00	74.00	59.00	73.33	7.67

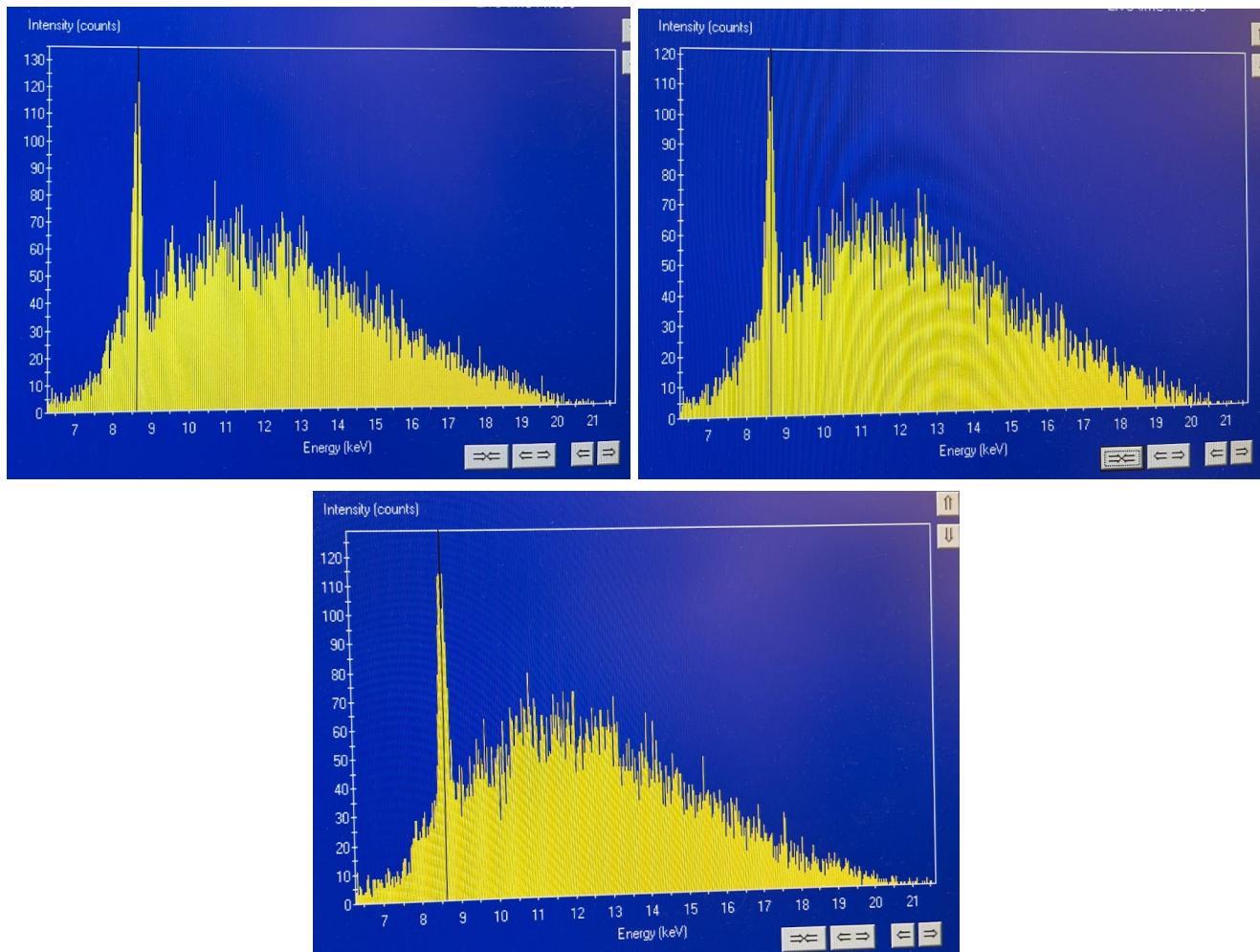


Figure C. XRF plot of 500 ppm standard solution of three replicates.

Table C. Replicates data of the CPS for 500 ppm standard solution.

CPS ₁	CPS ₂	CPS ₃	CPS _{average}	CPS _{corrected}
128.00	122.00	109.00	119.67	54.00

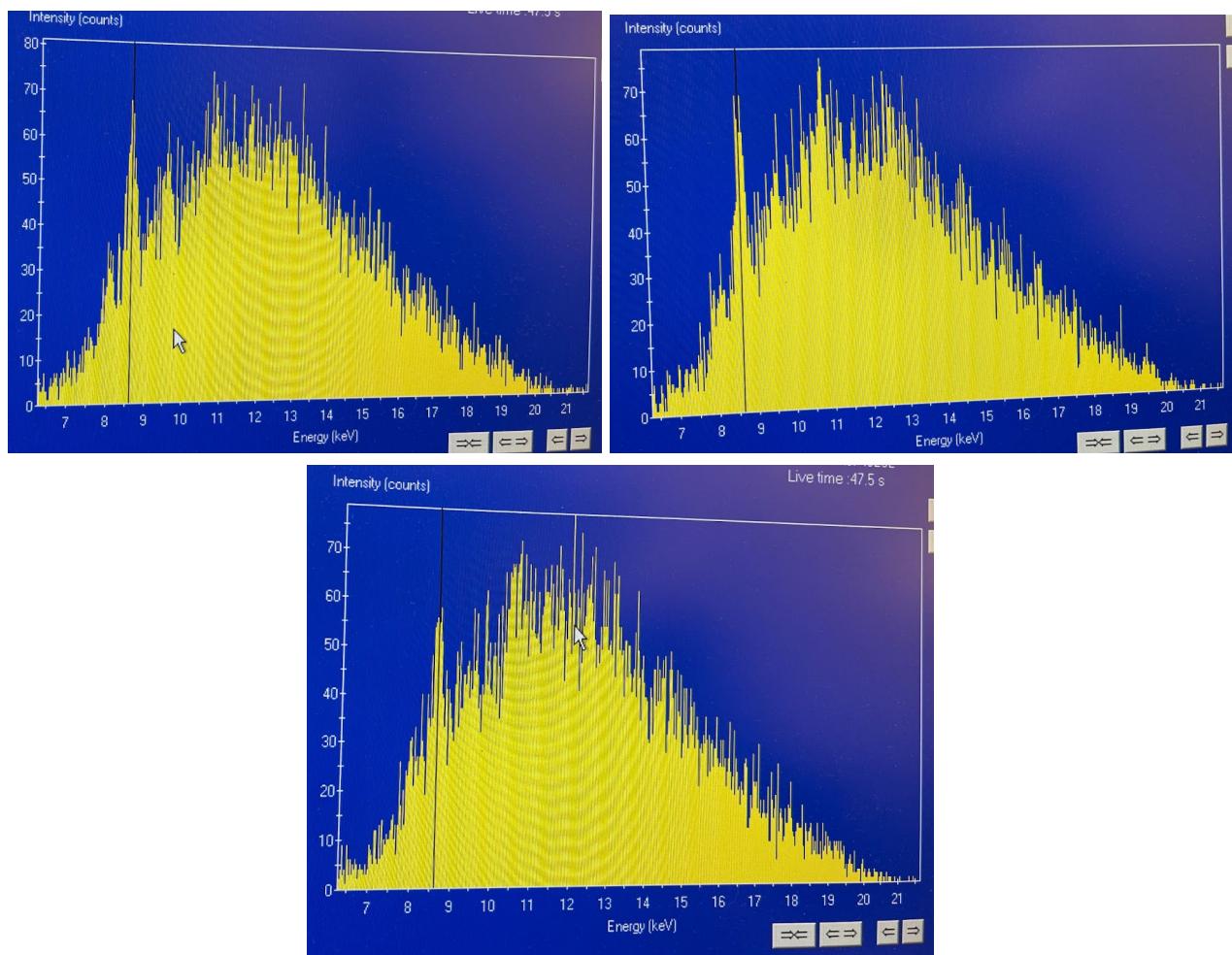


Figure D. XRF plot of blank sample of three replicates.

Table D. Replicates data of the CPS for the blank sample.

CPS ₁	CPS ₂	CPS ₃	CPS _{average}
65.00	62.00	70.00	65.67

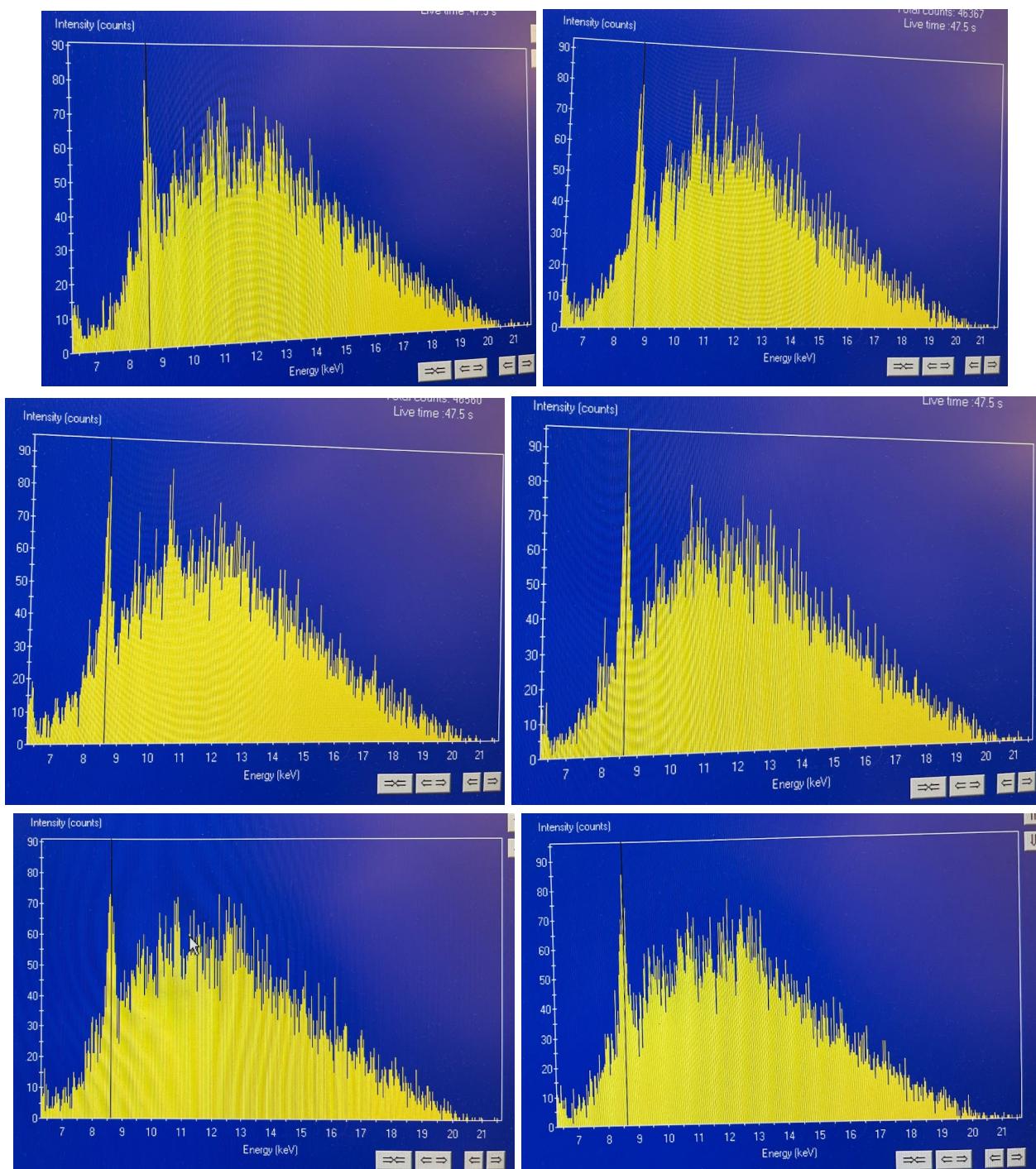


Figure E. XRF plot of 2 unknown samples with three replicates each.

Table C. Replicates data of the CPS for 500 ppm standard solution.

Sample	CPS ₁	CPS ₂	CPS ₃	CPS _{average}	CPS _{corrected}
1	72.00	74.00	72.00	72.67	7.00
2	69.00	77.00	85.00	77.00	11.33