MSEG 624

Practical Electron Microscopy

Lab 3: X-ray Energy Dispersive Spectroscopy

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Abstract

Operating parameters of the JEOL JSM-7400F SEM with Oxford INCA X-ray energy dispersive spectroscopy detector are investigated to surmise their impact on obtained spectra across three samples of differing elemental composition. The impact of a higher accelerating voltage as compared to a typical value for imaging is investigated to improve XEDS results. Lower and higher count rates are utilized to determine their impact on Full Width Half Maximum (FWHM) energy resolution. The effect of count rate on artifacts in identified elemental composition is also experimented.

Performed on: March 21, 2019   Submitted on: April 11, 2019

Introduction

X-ray energy dispersive spectroscopy (XEDS) is a technique that can be utilized in conjunction with SEM imaging to perform analysis of the elemental composition of a material sample. It utilizes the electron beam generated within the SEM for imaging to excite K (or other) shell electrons present within the sample and eject it from its shell. Another electron will then fill its place, emitting photons at an energy level that is characteristic to the element it comprises as it drops to the vacated energy shell. The energy level of these X-rays can then be measured to identify what element it originated from. The relative frequency of each finite energy level measured can be continuously tallied to produce a statistically sound analysis of the elemental composition of the sample – under the right conditions. As such it is important to identify the effects of settings and operational parameters on the results of XEDS analysis.

Experimental Methodology

In the experiments conducted, a copper grid sample placed on an aluminum foil substrate, a manganese sample, and a sample of unknown composition were all imaged under various operating parameters of the JEOL JSM-7400F SEM with Oxford INCA X-ray energy dispersive spectroscopy set up. Imaging reports and corresponding imaging parameters were recorded under these varying conditions, and were later used to draw evaluations of contrasting and comparable aspects of each instance considered. The provided procedure entitled *X-ray energy dispersive spectroscopy (XEDS) – spectral characterization, qualitative analysis, and quantitative analysis*[1] was followed with the aid and direction of laboratory Research Associate Dr. Zhao.

The samples were prepared for imaging beforehand, and placed into a sample holder. The sample was first placed into the sample exchange chamber, which was then closed and placed

under a vacuum of 9.63E-5 Pa. After the vacuum had reached and stabilized at this value, the sample was then properly exchanged into the specimen imaging chamber. The SEM began and the sample was positioned for imaging and focused by utilizing Low Mag, Quick View, and ACB (automatic contrast and brightness) settings options.

Section I

The accelerating voltage was first set to 30kV for XEDS imaging. It is worth noting that this value is significantly above the ~3kV typical value; this high accelerating voltage is set to be sufficient as to excite the K shell electrons present in the sample material. The working distance was set to 8mm, probe current to 8 nA, and the image was magnified to 5000x. The gun then needed to be properly aligned by increasing and decreasing the respective X and Y knobs until the image fully faded to black, then setting the alignment to the value in the middle of the range that produced an image.

The NCA software suite was then started to utilize the functionality of the X-ray detector. Set up was followed as prompted, and then probe current was increased until the desired counts/second (CPS) value of 2,000 was achieved. A spectrum was then acquired and a quantifying report was generated within the software (Appendix A, Report 1). The accelerating voltage was then changed to 5kV, and the probe current to 15nA for a CPS of 800. The gun had to be realigned, and the beam refocused, for these new conditions. A new spectrum was acquired at this altered set of conditions (Appendix A, Report 2).

Section II

Next, the Manganese was centered on the imaging stage at Low Mag setting, and a recognizable feature was identified for imaging. The accelerating voltage was reset to 30kV the

magnification returned to 5,000x, and the gun was realigned and refocused. In a similar fashion, the CPS was set to 1,000. A spectrum was then acquired to a Mn Kα peak height of 6,000 counts (Appendix A, Report 3). Another spectrum was then acquired to the same conditions, but with a CPS set to 5,000 (Appendix A, Report 4).

Section III

The unknown sample was then positioned in the center of the imaging stage to prepare for analysis. An image was configured at 5,000x magnification and 30kV accelerating voltage. Two spectra were then acquired at count rates of 1,000 and 5,000 CPS, respectively – for a set livetime of 200 seconds (Appendix A, Reports 5 and 6). The livetime settings, real runtimes, and the reported deadtimes were all recorded for both of the spectra and their respective count rates.

Results and Discussion

The results of *Section I* provide insight into how the applied accelerating voltage will impact XEDS analysis. When the accelerating voltage is set to 30kV, the results are somewhat typical of what one might expect, given the known materials comprising the sample (Appendix A, Report 1). Whereas when it is set to 5kV, a more extraneous composition is reported – with a clustered energy distribution (Appendix A, Report 2). The report generated from the 30kV accelerating voltage displays an expected Al and Cu composition (52.41 and 20.47 Wt% respectively), with levels of C and O also reported (24.03 and 3.09 Wt% respectively). The 5kV report was not able to generate an evaluation of respective weight or atomic percentages, it displayed a reported composition containing Al, Cl, C, Cu, and O.

The results of the 30kV analysis appear reasonable and provide weight and atomic percentages, whereas the 5kV report appears to have issues present in its analysis. The elemental composition and relative weight percentages seem accountable, as the Al and Cu composition of the sample are expected, the O reported to be present can be attributed to an AlO_3 layer present on the aluminum foil, and the C seen can be explained as sample contamination. The samples being investigated in this study have been used for many years in succession, and may have had carbon tape applied to them for imaging purposes. These intelligible origins of the reported elemental composition contrast that of the 5kV spectrum plot. The 5kV spectrum contains significant levels of Cl, as reported, with no readily intelligible potential sources of a Cl composition. It is also important to note that the peaks as well as the overall energy distribution seen in the 5kV spectrum are both significantly lower, and it eliminates higher energy peaks seen in the 30kV spectrum plot. This likely occurred because a 5kV applied accelerating voltage is too low to sufficiently induce characteristic dispersive Kα X-rays. This is evidenced by the low peak counts clustered to lower energy levels, with noise and false positives.

The reports generated in *Section II* give proximate compositional results for the Mn sample. They both display a largely Mn composition (79.53 and 82.96 Wt% for 1000 and 5000 CPS respectively), as well as C levels around 13 Wt% and O levels around 6 Wt% (Appendix A, Report 3, 4). These results give further credence to the prior claim of carbon and oxidation contamination of the samples. The resolution of the Oxford INCA X-ray detector was estimated by calculating Full Width at Half Maximum (FWHM) averaged over the major peaks for both 1,000 and 5,000 CPS. For 1,000 CPS, the FWHM is linearly interpolated to be 0.14213 for the 5.9keV Mn peak and 0.15701 for the 6.5keV Mn peak; these values are averaged to a FWHM of 0.14957 keV. The data utilized in these calculations are displayed below in Figs. 1, 2, and 3.
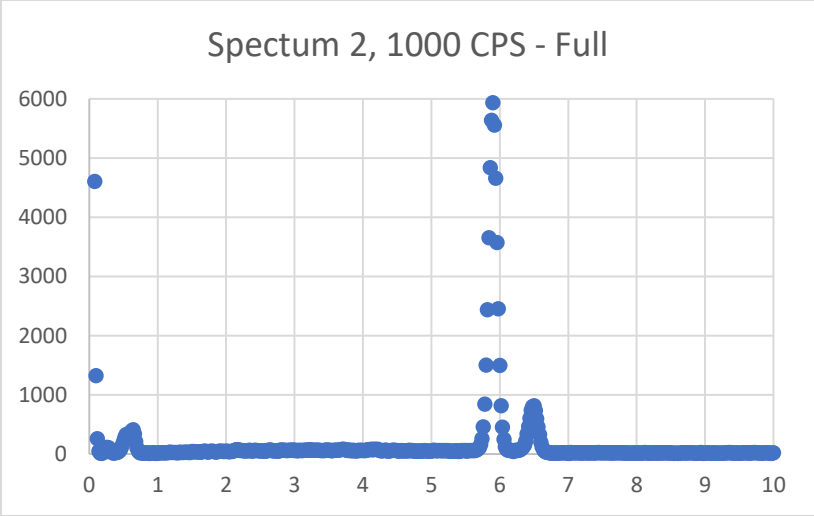
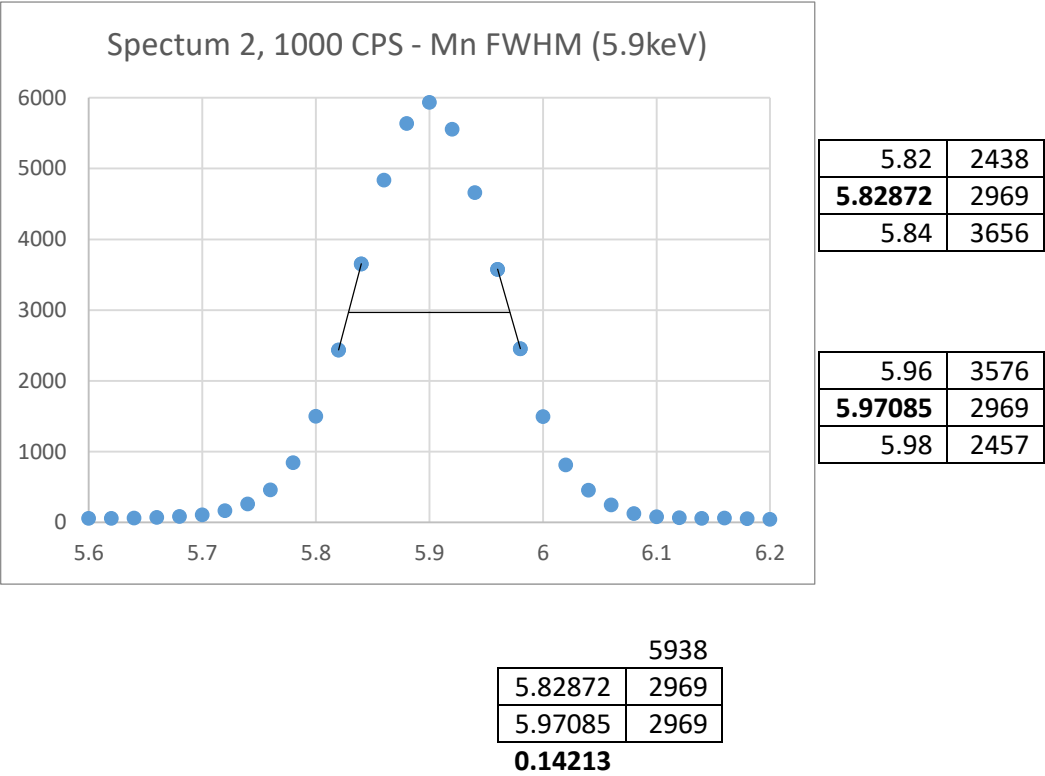*Fig. 1:* 1000 CPS Spectrum 2 data exported and plotted in Excel.

5.82	2438
5.82872	2969
5.84	3656

5.96	3576
5.97085	2969
5.98	2457

	5938
5.82872	2969
5.97085	2969
0.14213	

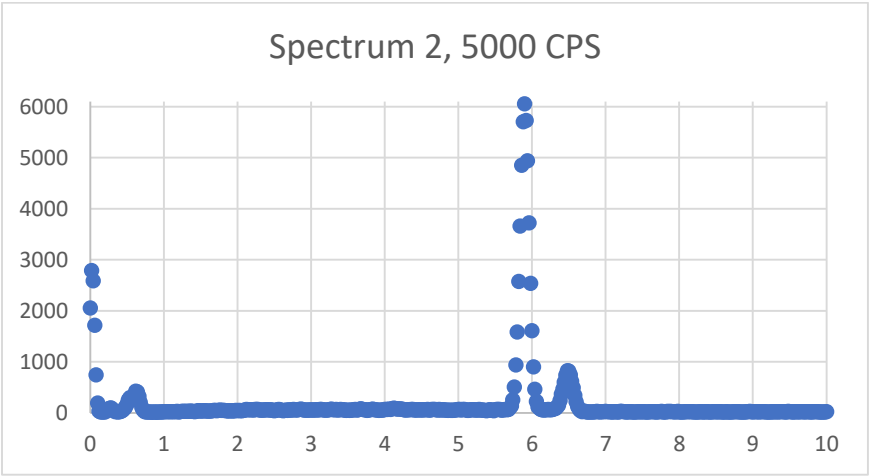*Fig. 2:* FWHM is calculated for the isolated 1000 CPS 5.9keV Mn peak from exported data.

6.4	341
6.41079	409.5
6.42	468

6.56	461
6.5678	409.5
6.58	329

	819
6.41079	409.5
6.5678	409.5
	0.15701
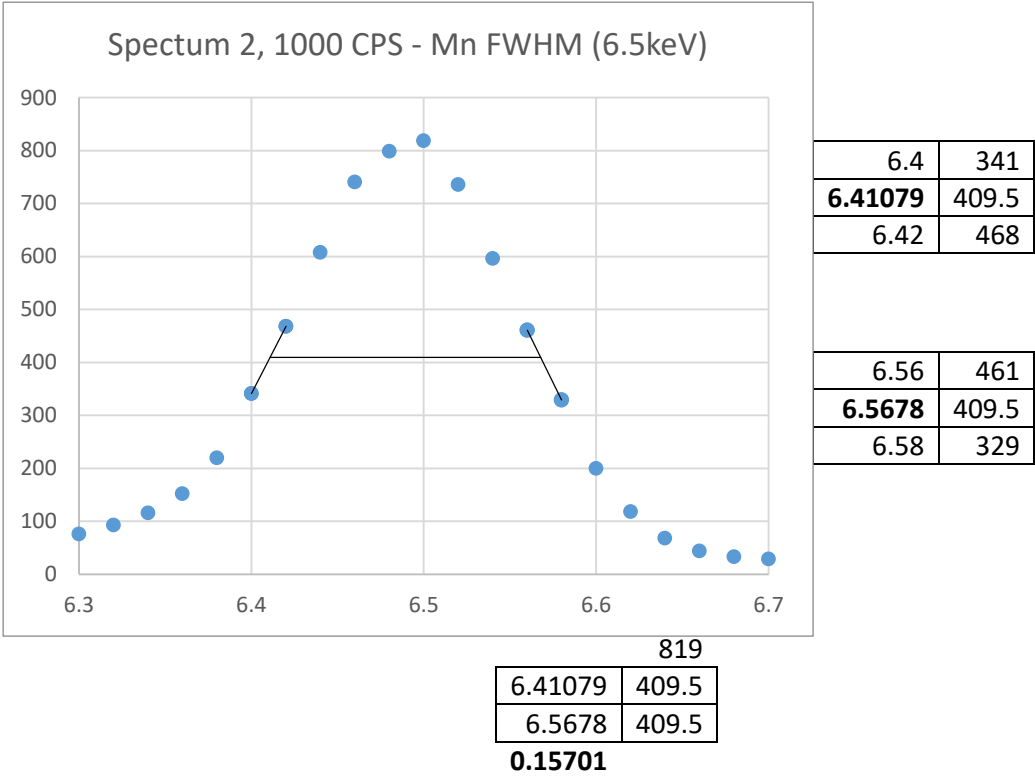
Fig. 3: FWHM is calculated for the isolated 1000 CPS 6.5keV Mn peak from exported data.

The same calculations were conducted for the spectrum generated using 5000 CPS. These calculations gave a FWHM of 0.14328 for the 5.9keV Mn peak and 0.16173 for the 6.5keV Mn peak; these values are averaged to a FWHM of 0.15251 keV. The data utilized in these calculations are shown below in Figs. 4, 5, and 6.

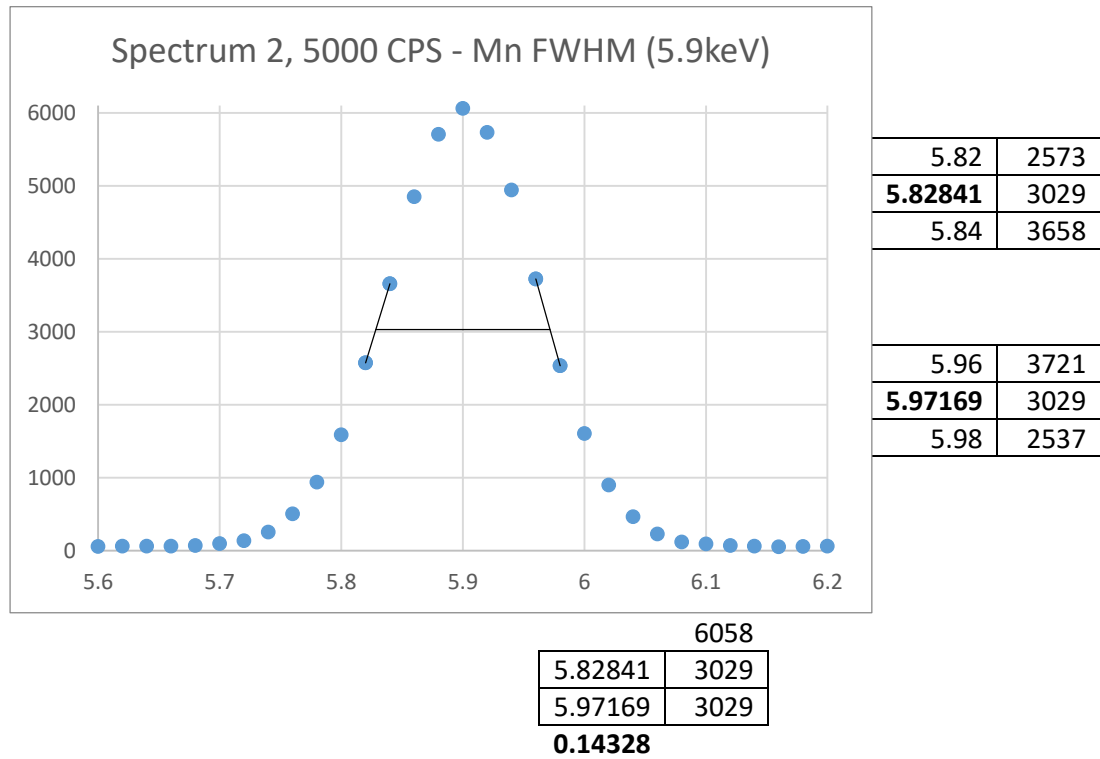***Fig. 4:*** 5000 CPS Spectrum 2 data exported and plotted in Excel.

5.82	2573
5.82841	3029
5.84	3658

5.96	3721
5.97169	3029
5.98	2537

6058

5.82841	3029
5.97169	3029
0.14328	

Fig. 5: FWHM is calculated for the isolated 5000 CPS 5.9keV Mn peak from exported data.

6.4	368
6.40909	413
6.42	467

6.56	492
6.57082	413
6.58	346

826

6.40909	413
6.57082	413
0.16173	
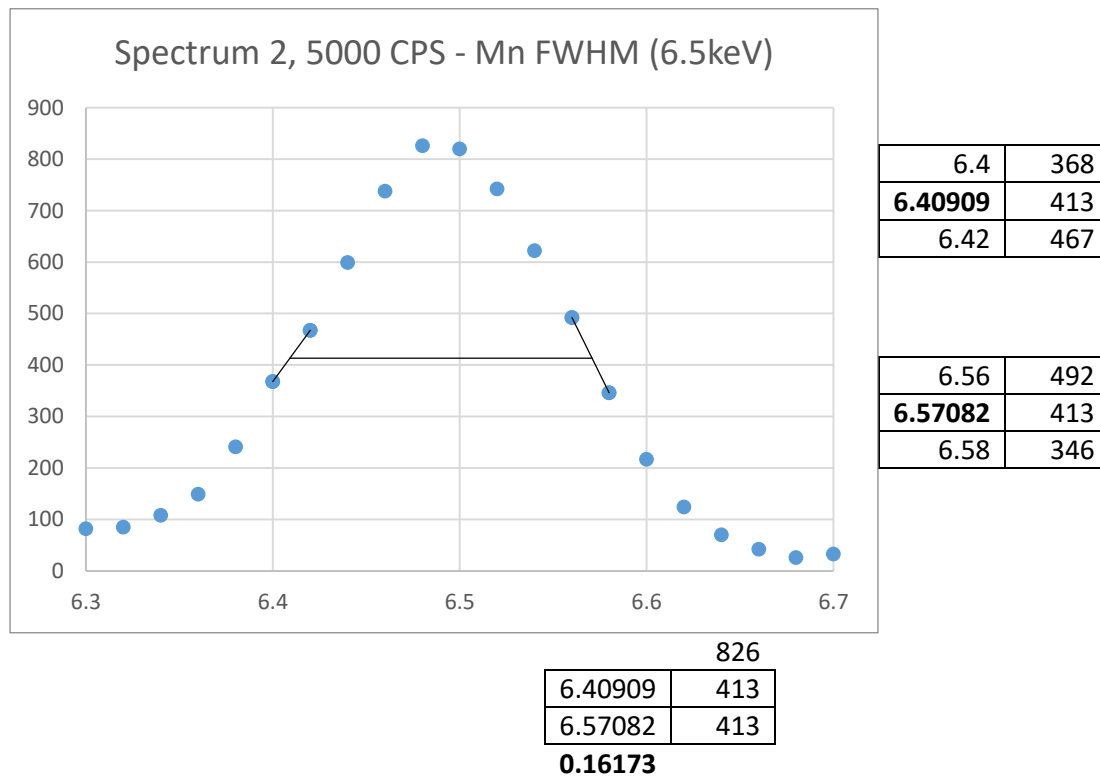
Fig. 6: FWHM is calculated for the isolated 5000 CPS 6.5keV Mn peak from exported data.

The results of *Section III* will guide analysis of elemental composition for a sample of unknown material, and contribute insight into choice of optimal analysis conditions.

CPS	Livetime (s)	Runtime (s)	Deadtime
1000	200	107	5%
5000	200	130	22%

Table 1: Set Livetime, Software Deadtime, and recorded Runtime are tabulated.

The livetimes for both CPS settings were set to 200 at the direction of Dr. Zhao, as the 100 second livetime that is specified in the provided procedure would not have been sufficient to achieve 6000 counts over the runtime. The software also provided a calculated deadtime for each run – both of which are reported above in *Table 1*, along with the set livetime and real runtime of each count rate. From the spectra plots generated for each count rate, the real runtime that may be expected from a given count rate and end count total were far less than the real runtimes required. For the 1000 CPS run, to reach 6000 counts one may expect it to take just 6 seconds; for the 5000 CPS run, one may expect it to take 1.2 seconds to reach 6000 counts. Instead, it requires 107 and 130 seconds, respectively. I inquired about this large discrepancy during this experiment, and Dr. Zhao was unsure of the underlying reason, himself. Dr. Zhao stated he has previously asked about the source of such a discrepancy, but has not received concrete reasoning.

As such, what may be said to be the *effective* deadtime can be calculated as the percent difference of this discrepancy. This value is found to be 179% for 1000 CPS and 196% for 5000 CPS. This is at a clear disparity from the 5% and 22% deadtimes calculated by the software. It is, however, interesting to note that the difference between effective deadtimes and the difference between the calculated deadtimes are the same, at 15%. So the effective deadtimes can be seen to be at a consistent 174% greater than their respective calculated deadtimes. Further study would be required to verify whether this is a trend, and to then draw conclusions on the matter.

At 1000 CPS, three elements were identified to comprise the unknown sample – Ti, Nb, and Al (at 46.54, 42.48, and 10.98 Wt% respectively). At 5000 CPS, these elements were again identified to comprise the unknown sample (at 38.24, 34.71, and 8.88 Wt% respectively), but there were also 5 other elements identified – C, O, Os, V, and Fe (at 10.65, 6.07, 0.82, 0.34, and 0.30 Wt% respectively). These additional 5 elements are identified as artifacts. The weight percentages of Ti, Nb, and Al remain in the same *relative* composition to each other between the two count rates (~110:100:39).

The additional 5 elements emerge in the 5000 CPS spectrum, while the relative composition remains the same among Ti, Nb, and Al – suggesting that if both 1000 and 5000 CPS spectra do in fact identify the comprising elements, they are Ti, Nb, and Al while the remaining elements identified in the 5000 CPS spectrum are artifacts. Further study would be required to put any weight behind this claim, as two spectra (with 5/8 identified elements in one being alleged artifacts) are hardly definitive. As only Ti, Nb, and Al are said to be the comprising elements of the unknown sample, the other elements are excluded and the average composition is found to be 44.18 Wt% Ti, 40.16 Wt% Nb, and 15.66 Wt% Al.

Summary

The JEOL JSM-7400F SEM Oxford INCA X-ray energy dispersive spectroscopy detector was implemented to learn how to utilize its functions in identifying elemental composition of a sample. A high (~30kV) accelerating voltage is determined to improve results in XEDS by exciting a sufficient portion of the K shell electrons present in the sample material.

A lower count rate is seen to marginally improve energy resolution in the FWHM of the peaks in the spectrum obtained, as well as minimize artifacts across the two spectra investigated.

Acknowledgements

Thank you to Dr. Ni and Dr. Zhao for teaching me this material and providing lab space in which to conduct these experiments.

References

[1] Ni, Chaoying, "*X-ray energy dispersive spectroscopy (XEDS) – spectral characterization, qualitative analysis, and quantitative analysis*," MSEG624 Practical Electron Microscopy, University of Delaware, Spring 2019.
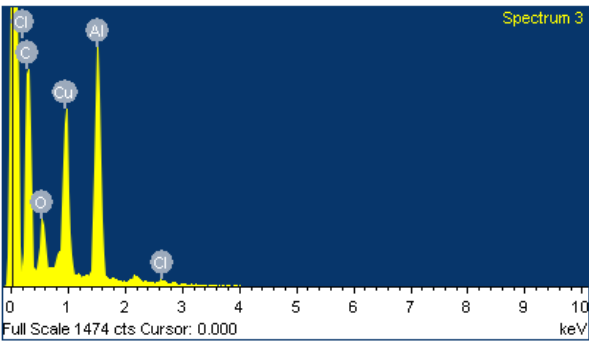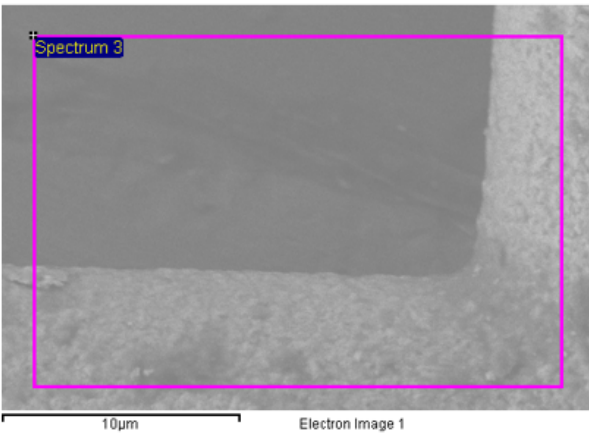
Appendix A

Spectrum processing :

Peak possibly omitted : 6.350 keV

Processing option : All elements analyzed (Normalised)

Number of iterations = 7

Standard :

C   CaCO3   1-Jun-1999 12:00 AM

O   SiO2   1-Jun-1999 12:00 AM

Al   Al2O3   1-Jun-1999 12:00 AM

Cu   Cu   1-Jun-1999 12:00 AM

Element	Weight%	Atomic%
C K	24.03	44.88
O K	3.09	4.33
Al K	52.41	43.57
Cu K	20.47	7.22
Totals	100.00	
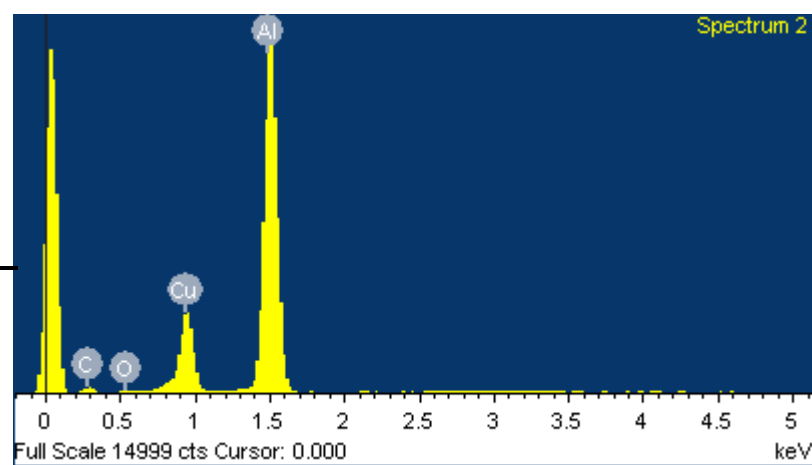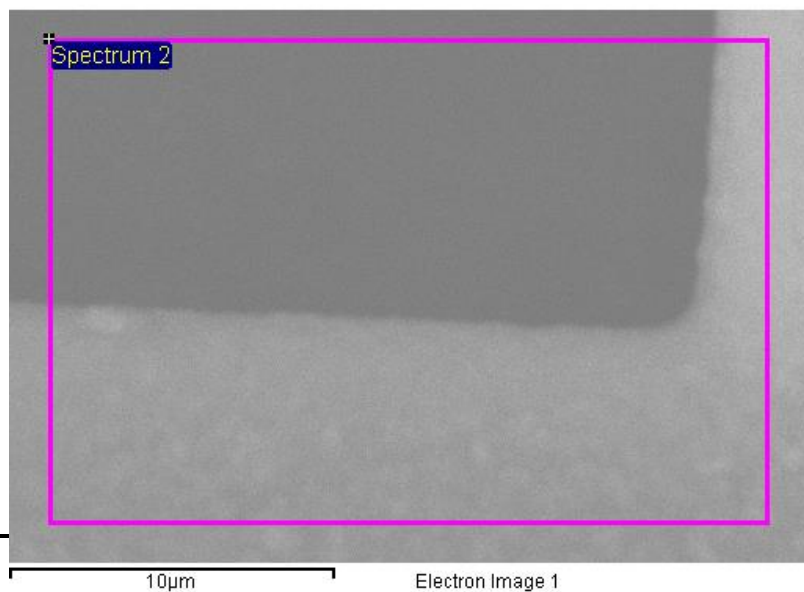
Report 1: 5000x copper grid sample spectrum obtained at 30kV, 8mm WD, and 2,000 CPS.

Spectrum processing :

Peak possibly omitted : 6.350 keV

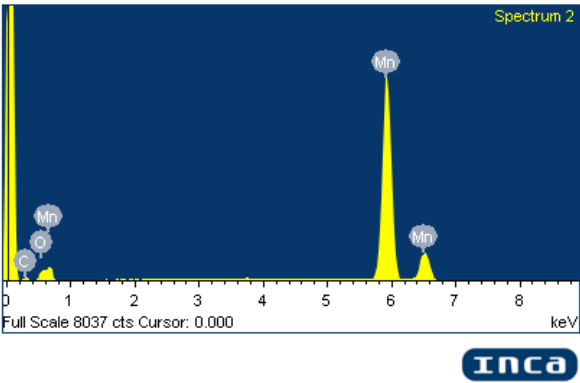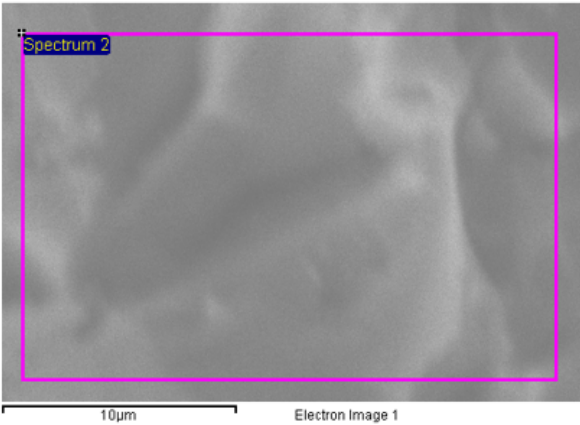Processing option : All elements analyzed (Normalised)

Number of iterations = 7

Standard :

Element	Weight%	Atomic%
Totals	.00	

Comment:

Report 2: 5000x copper grid sample spectrum obtained at 5kV, 8mm WD, and 800 CPS.

Spectrum processing :

Peak possibly omitted : 2.160 keV

Processing option : All elements analyzed (Normalised)

Number of iterations = 5

Standard :

C   CaCO3   1-Jun-1999 12:00 AM

O   SiO2   1-Jun-1999 12:00 AM

Mn   Mn   1-Jun-1999 12:00 AM

Element	Weight%	Atomic%
C K	13.87	38.30
O K	6.60	13.68
Mn K	79.53	48.02
Totals	100.00	

Comment:

Report 3: 5000x Mn sample spectrum obtained at 30kV, 8mm WD, and 1,000 CPS.

Spectrum processing :

No peaks omitted

Processing option : All elements analyzed (Normalised)
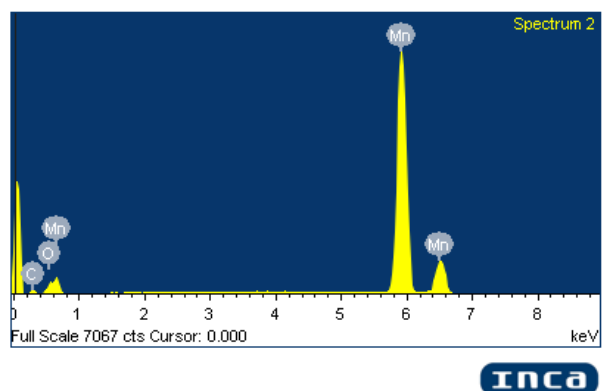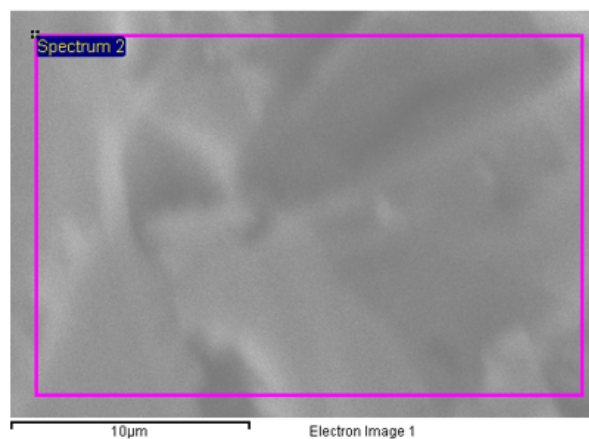
Number of iterations = 5

Standard :

C   CaCO3   1-Jun-1999 12:00 AM

O   SiO2   1-Jun-1999 12:00 AM

Mn   Mn   1-Jun-1999 12:00 AM

Element	Weight%	Atomic%
C K	12.38	36.39
O K	4.66	10.29
Mn K	82.96	53.32
Totals	100.00	

Comment:

Report 4: 5000x Mn sample spectrum obtained at 30kV, 8mm WD, and 5,000 CPS.

Spectrum processing :

No peaks omitted

Processing option : All elements analyzed (Normalised)
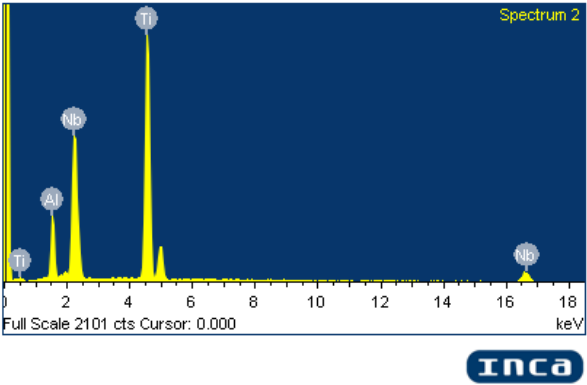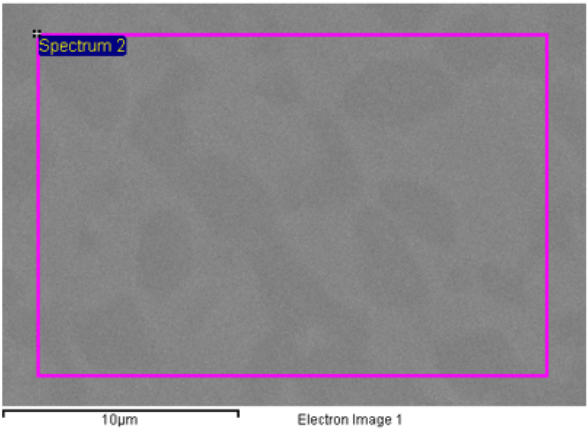
Number of iterations = 5

Standard :

Al   Al2O3   1-Jun-1999 12:00 AM

Ti   Ti   1-Jun-1999 12:00 AM

Nb   Nb   1-Jun-1999 12:00 AM

Element	Weight%	Atomic%
Al K	10.98	22.17
Ti K	46.54	52.92
Nb L	42.48	24.90
Totals	100.00	

Comment:

10µm   Electron Image 1

Spectrum 2

Full Scale 2101 cts Cursor: 0.000   keV

INCA

Report 5: 5000x unknown sample spectrum obtained at 5kV, 8mm WD, and 8,000 CPS.

Spectrum processing :

No peaks omitted

Processing option : All elements analyzed (Normalised)

Number of iterations = 6

Standard :

C CaCO3 1-Jun-1999 12:00 AM

O SiO2 1-Jun-1999 12:00 AM

Al Al2O3 1-Jun-1999 12:00 AM

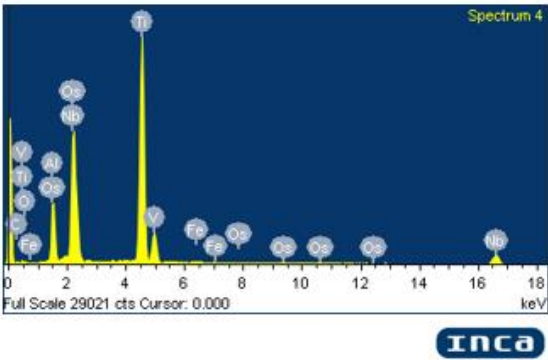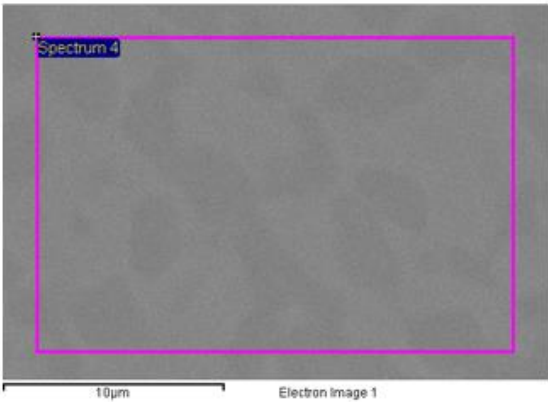Ti Ti 1-Jun-1999 12:00 AM

V V 1-Jun-1999 12:00 AM

Fe Fe 1-Jun-1999 12:00 AM

Nb Nb 1-Jun-1999 12:00 AM

Os Not defined 1-Jun-1999 12:00 AM

Element	Weight%	Atomic%
C K	10.65	31.85

Comment:

	Weight%	Atomic%
O K	6.07	13.63
Al K	8.88	11.83
Ti K	38.24	28.68
V K	0.34	0.24
Fe K	0.30	0.19
Nb L	34.71	13.42
Os M	0.82	0.15
Totals	100.00	

Report 6: 5000x unknown sample spectrum obtained at 5kV, 8mm WD, and 8,000 CPS.

Supplemental

All files used and supplementary material can be found at:

https://github.com/zswain/MSEG624