UC Berkeley College of Chemistry

Chemistry 105

Instrumental Methods in Analytical Chemistry

Inductively Coupled Plasma-Atomic Emission Spectroscopy

Short Report

Author:

Jonathan Melville

Lab Partners:

Jake Precht, Phuong Tran, and Jeremy Hsu

Graduate Student Instructors:

Richard Cooper & Daniel Mortensen

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1 Theory

ICP-AES, or Inductively Coupled Plasma-Atomic Emission Spectroscopy (also known as ICP-OES, Optical Emission Spectroscopy), is a type of emission spectroscopy that is often used to detect the presence of trace metals in a sample. Through the use of the eponymous Inductively Couple Plasma, an ICP-AES produces excited ions and atoms (by ionization in an intense electromagnetic field) that emit detectable amounts of light at characteristic wavelengths, with intensities proportional to the concentration of the ion. As indicated by the name, the spectra is measured and analyzed by an atomic emission spectrometer (AES) using concentration-intensity correlations that are similar to how the Beer-Lambert Law applies to AAS. ICP-AES is invaluable for its ability to record the spectra of multiple trace elements simultaneously, assuming they do not significantly overlap in characteristic wavelength, as well as the minimization of matrix effects due to the extreme nature of the plasma. If good wavelengths are chosen for the metals used, the amount of interference between spectra will be minimal; however, it is possible for interference effects to cause two spectra to overlap, wildly skewing readings. Nowadays, the presence of commercial ICP-AES software makes calculation of optimal wavelengths to minimize and account for overlap, through the use of proprietary software and interelement correction factors[1]. Like AAS, AES is widely used to measure the concentration or presence of trace elements in samples, and sees much modern use in environmental testing and protein analysis.

2 Results and Discussion

This section contains only tabulated results from the Appendix. Derivations can be found in Appendix A on page 5. Graphs can be found in Appendix B on page 9. Raw data can be found in Appendix C on page 13.

2.1 Results

2.1.1 Unknown Concentrations

	Concentration (ppb)			
Metal	**Brass-58**	**Pre-Rain Creek**	**Post-Rain Creek**	**Difference**
Iron	57.3940291081	49.8540606889	50.6463112024	0.7922505135
Zinc	60.7833747246	-0.5819309431	-0.4453814841	0.136549459
Nickel	10.2397539775	11.0803296422	11.7444576539	0.6641280117
Manganese	2.5480694188	1.7674494946	1.7157049908	-0.0517445038
Copper	798.5072809986	10.2752139061	9.5453224703	-0.7298914358
Chromium	-5.0852474686	-29.0073438581	10.750504919	39.7578487772

2.1.2 Brass-58 Percent Composition

Metal	**% Total**
Copper	79.9%
Zinc	6.08%
Iron	5.74%
Nickel	1.02%
Manganese	0.255%
Chromium	-0.509%
Total	92.5%

2.2 Discussion

Using our calibration curves, we were able to successfully create calibration curves with good fit and use them to calculate values for our unknown compositions that, if not correct, are eminently reasonable. However, this process was not without its flaws: it is apparent by looking at the raw data that a large majority of our calibration data had to be thrown out due to a complete lack of fitting that we can only assume is due to instrumental or operator error, though our "standard 3" contained valuable information. Moreover, we were unable to gather any significant data regarding the presence or absence of magnesium, and the abnormally high magnesium readings for our calibration curve only emphasize the anomalous fact that our unknown magnesium intensity values were so high that they were beyond the instrument's capability to detect. As a result of these anomalies, we were forced to discard our magnesium data. However, excepting this, our data is quite reasonable. Some of our values as calculated predict negative quantities of compounds, something that is obviously impossible, but these compounds are without exception already near-zero in concentration, and so they can be explained away as instrumental variation.

Looking first at our brass sample, we can see a clear abundance – almost 80% – of copper in the sample, something we might expect based on the general composition of brass as copper and zinc. In line with this reasoning, zinc is the next most abundant element in the sample, at about 6%. This number is comparatively small, and worryingly close to the next metal's % composition (Iron, 5.74%), but it is not outside the realm of plausibility. The total of all the percent compositions of the brass sample is 92.5% – not 100%, but this is to be expected considering that we are only looking at a limited subset of all metals and it is plausible that the alloy contains metals we did not test for.

Looking next at our creek sample, we can notice several reassuring trends. A majority of the metals tested for have near-identical concentrations before and after rainfall, something that is not outside the realm of belief considering that we do not know for sure the effects of rainfall on metal content. By comparing to experimentally-determined metal concentrations on the North Fork of Strawberry Creek, as measured during a 2006 water quality report[3], we can determine that our measurements, though not identical, are of the same order of magnitude as the report's values. We would not expect to see identical values in two different areas of the creek eight years apart, but it is reassuring to see that our calculations are of the same order of magnitude that we could reasonably expect a creek to have. For example, our concentration of iron is about 50 ppb, in line with the report's 34 ppb, and our value of about 10 ppb for copper is not dissimilar from the report's measurement of 4.0 ppb. There is the issue of our pre-rainfall chromium concentration, which is illogically low at -29 ppb, something we are unable to explain outside of experimental or instrumental error – it's possible that this is due to interelement interference that was not accounted for by the software. It is worth pointing out that the water quality report shows a chromium concentration of < 1 ppb, and while -29 ppb is certainly nonsensical we may be justified in simply rounding the concentration up to around 0 ppb.

Though there is no easy quantitative way to determine and circumvent the presence of interelement interferences, this problem is neatly solved by the preexistence of interelement interference tables which can be used to determine characteristic wavelengths for metals that do not appear on the spectra of other elements. Many commercial ICP/OES software algorithms, including Perkin-Elmers MSF (Multi-component Spectral Fitting), and Varian/Agilents FACT (Fast Automated Curve-fitting Technique) automatically perform interference correction, or it can be calculated using interelement correction factors[1].

2.3 Accuracy and Error

All in all, our data is a mixed bag. Many of our calibration curves were worthless, failing to produce positive correlations at all, and had to be binned. However, the calibration curve used for the majority of our calculations is exceptionally clean, with R^2 values that are strictly greater than 0.999. However, our unknown samples did not come out so neatly, and while many of our final concentrations are plausible there are several that are not. Additionally, unknown errors in our instrumental method led to the loss of our magnesium intensity data for our unknowns, a mysterious occurrence considering that the Mg data was apparently too high for the detector to read yet none of our samples should have contained such significant quantities of magnesium. Despite all of these setbacks, however, we still acquired final data values that we deemed acceptable.

References

[1] *ICP/OES Interference Maxims* [Online]; Wisconsin Department of Natural Resources. http://dnr.wi.gov/regulations/labcert/documents/ICP-OES_Interference_correction.pdf (accessed Mar 29, 2014).

[2] *Optima 7000 DV ICP-OES Manual*; Perkin-Elmer Informatics. http://www.perkinelmer.com/Content/relatedmaterials/productnotes/prd_optima-7000dv-icp-oes.pdf (accessed March 25, 2014).

[3] *University of California, Berkeley Strawberry Creek Water Quality 2006 Status Report* [Online]; UC Berkeley Office of Environmental Health and Safety. http://strawberrycreek.berkeley.edu/naturalhistory/documents/SC2006WQStatuspdf10.02.2006.pd (accessed Mar 19, 2014).

A Calculations

A.1 Detection Limits

Detection limits for this machine (Perkin-Elmer Optima 7000 DV ICP-AES) vary by element and were obtained from the product manual[2]. Detection limits for magnesium were not available, unfortunately, but luckily our samples contained an excess of magnesium, saturating the detector and rendering it unable to give a reading (so not knowing this doesn't effect our results). However, this does mean that we were unable to determine the magnesium values in our creekwater samples.

Element	**Wavelength** (nm)	**Det. Lim.** (ppb)
Cr	267.716	0.25
Cu	224.700	0.9
Fe	259.939	0.2
Mn	257.610	0.03
Ni	231.604	0.4

A.2 Calibration Standards

A.2.1 Masses

This section deals with the specific salts we used to create our calibration samples, and the calculation of the precise concentrations of the metal ions in the solutions of these salts.

Metal Salt	**Salt** (mg)	**Salt** ($\frac{g}{mol}$)	**Metal** ($\frac{g}{mol}$)	**Metal** (mmol)	**Metal** (mg)
$Ni(NO_3)_2 \cdot 6\ H_2O$	183.66	290.795	58.693	0.63158	37.0695
Mn	62.22	54.938	54.938	1.133	62.220
$MgSO_4$	261.2	120.37	24.305	2.170	52.741
Cu	53.300	63.546	63.546	0.839	53.300
Zn	52.990	65.38	65.38	0.810	52.990
$CrCl_3 \cdot 6\ H_2O$	277.09	266.45	51.996	1.040	54.072
$FeSO_4 \cdot 7\ H_2O$	265.45	278.01	55.845	0.954	53.322

A.2.2 Concentrations

All solutions were prepared to a volume of 50.00 mL, then serially diluted a thousandfold down to an initial concentration of approximately 1000 ppb. This initial solution was diluted by a factor of half, then half again, then by two-fifths, producing calibration concentrations of approximately 500, 250, and 100 ppb. Precise concentration values vary from this figure, as the initial amount of salt added was not exact.

	Concentration (ppb)			
Metal [Salt]	**Initial**	**Dilution 1**	**Dilution 2**	**Dilution 3**
$Ni(NO_3)_2 \cdot 6\ H_2O$	741.390	370.695	185.347	74.139
Mn	1244.4	622.2	311.1	124.44
$MgSO_4$	1054.825	527.412	263.706	105.483
Cu	1066	533	266.5	106.6
Zn	1059.8	529.9	264.95	105.98
$CrCl_3 \cdot 6\ H_2O$	1081.448	540.724	270.362	108.145
$FeSO_4 \cdot 7\ H_2O$	1066.440	533.220	266.610	106.644

A.2.3 Graphs and Curve-fitting

By plotting the concentrations of each metal against the intensity of the measurement (intensity data can be found in Appendix C on page 13), we can create very good fits that allow us to extrapolate or interpolate the concentration of each metal in our unknown sample. Because of the wide variation in intensities, each metal has been given its own graph to allow for greater readability. For brevity, the graphs have been placed in Appendix B on page 9, while a summarized table of regression data is provided here for further calculation.

Metal	Slope	Intercept	R^2
Nickel	92.672	-836.761	0.99944
Manganese	2917.194	-6252.767	0.99996
Magnesium	10248.772	1002551.090	0.99321
Copper	1259.992	20111.762	0.99999
Zinc	265.998	-1500.619	0.99987
Chromium	375.684	35554.204	0.99942
Iron	568.193	-27081.210	0.99977

A.2.4 Calculating Unknown Concentrations

By taking the individual intensities of each element in our unknown samples (Brass 58, pre-rainfall creekwater, and post-rainfall creekwater) and putting them through the appropriate inverse functions ($y = mx + b \rightarrow x = \frac{y-b}{m}$), we can easily derive the concentrations of specific elements in our sample.

	Concentration (ppb)			
Metal	**Brass-58**	**Pre-Rain Creek**	**Post-Rain Creek**	**Difference**
Iron	57.3940291081	49.8540606889	50.6463112024	0.7922505135
Zinc	60.7833747246	-0.5819309431	-0.4453814841	0.136549459
Nickel	10.2397539775	11.0803296422	11.7444576539	0.6641280117
Manganese	2.5480694188	1.7674494946	1.7157049908	-0.0517445038
Copper	798.5072809986	10.2752139061	9.5453224703	-0.7298914358
Chromium	-5.0852474686	-29.0073438581	10.750504919	39.7578487772
Magnesium	N/A	N/A	N/A	N/A

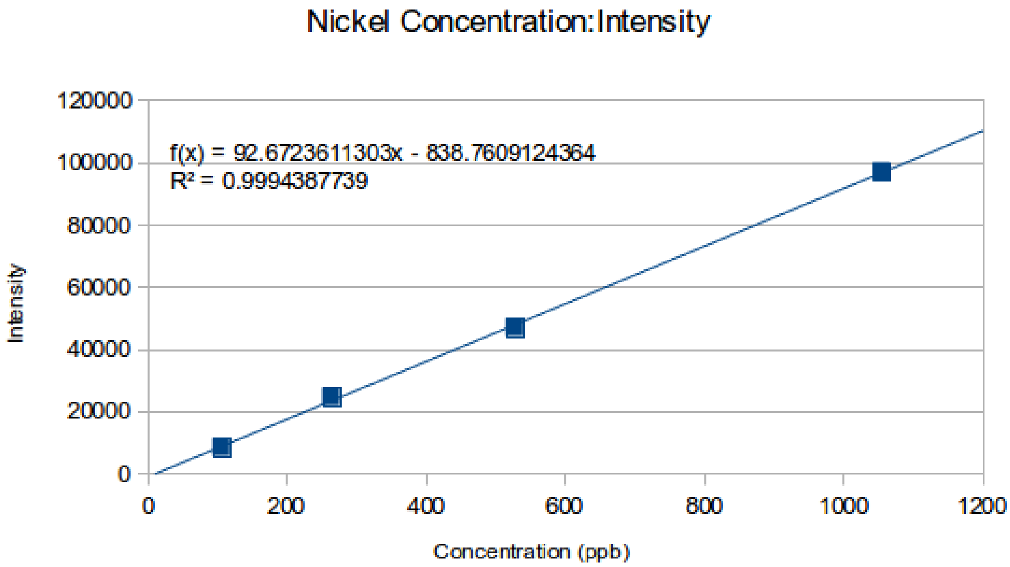
A.2.5 Calculating Brass Percent Composition

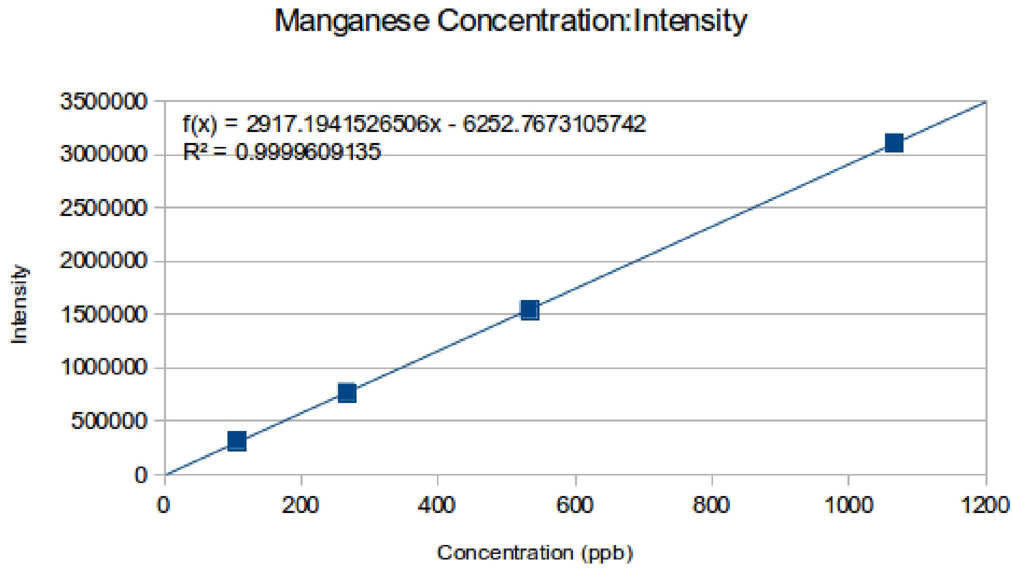
Based on a dilution factor of 1×10^6 times from the pure metal to the AES solution, we can determine the percentage composition of the brass-58 alloy as follows:

Metal	**% Total**
Copper	79.9%
Zinc	6.08%
Iron	5.74%
Nickel	1.02%
Manganese	0.255%
Chromium	-0.509%
Total	92.5%

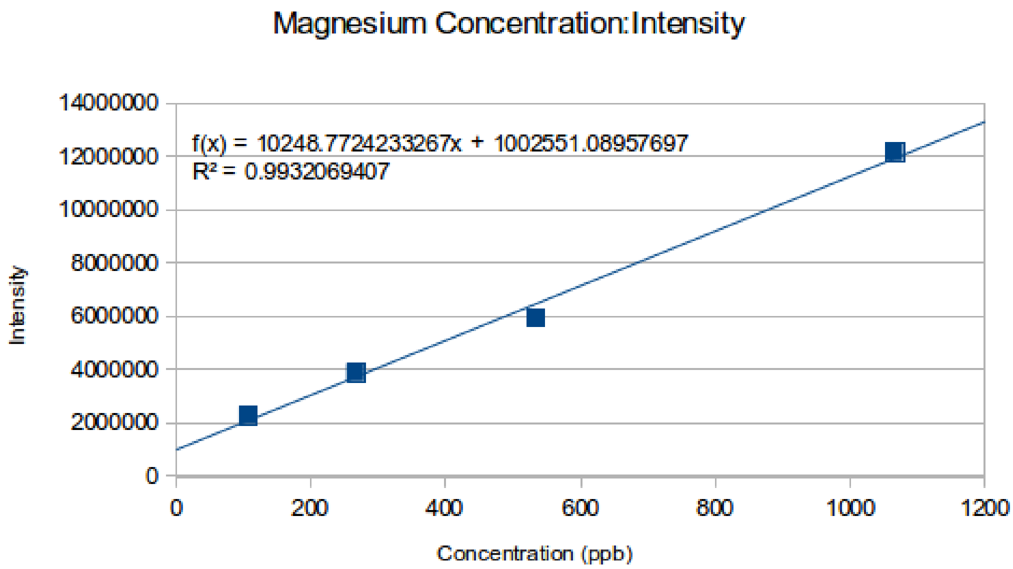
A similar composition breakdown can be created in an identical fashion for the creekwater unknowns, though of course since creekwater is not composed of pure metal absolute concentration is more valuable than % composition, and since the creekwater was not diluted like the brass-58 sample further calculations are unnecessary.

B Graphs

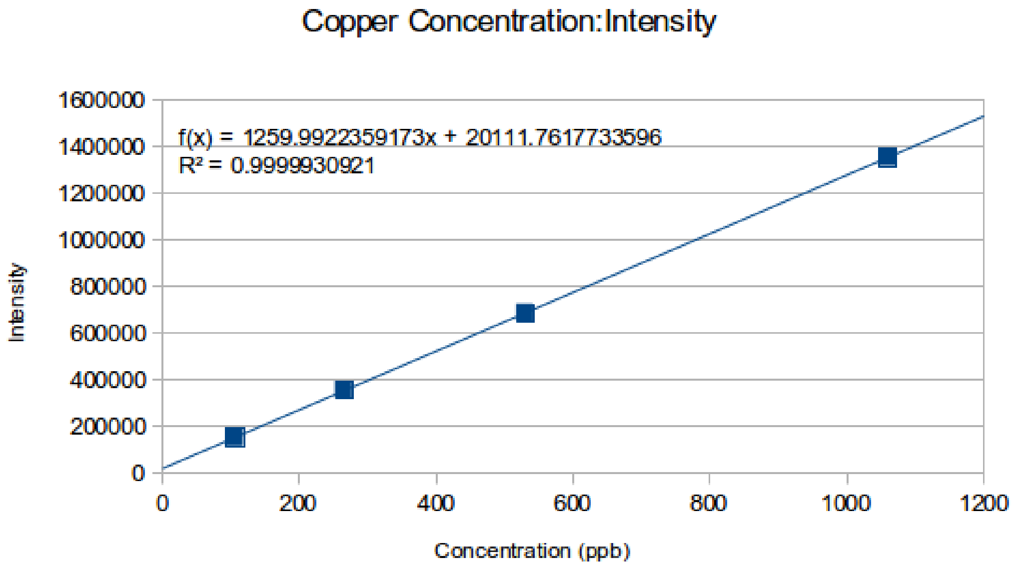


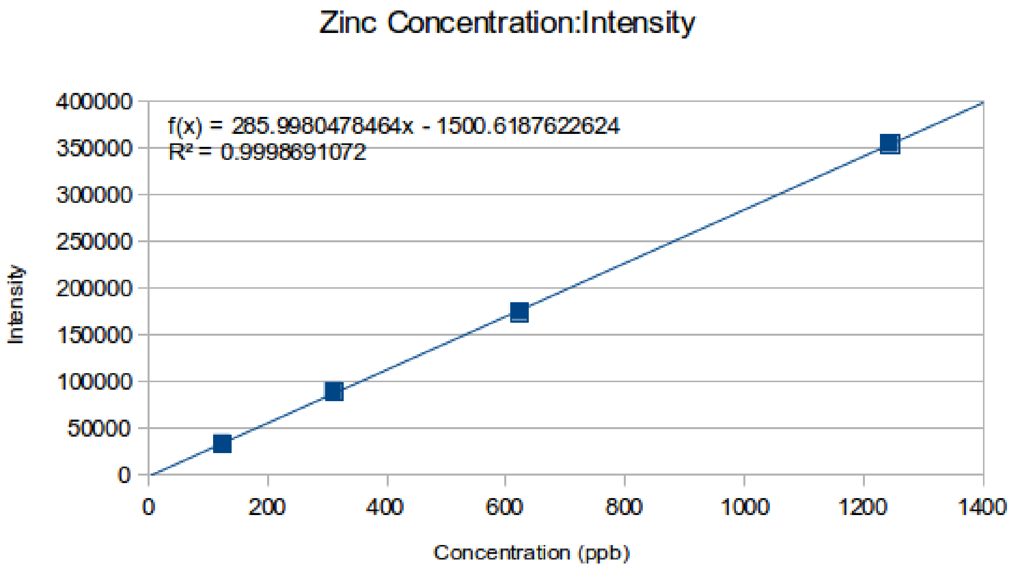


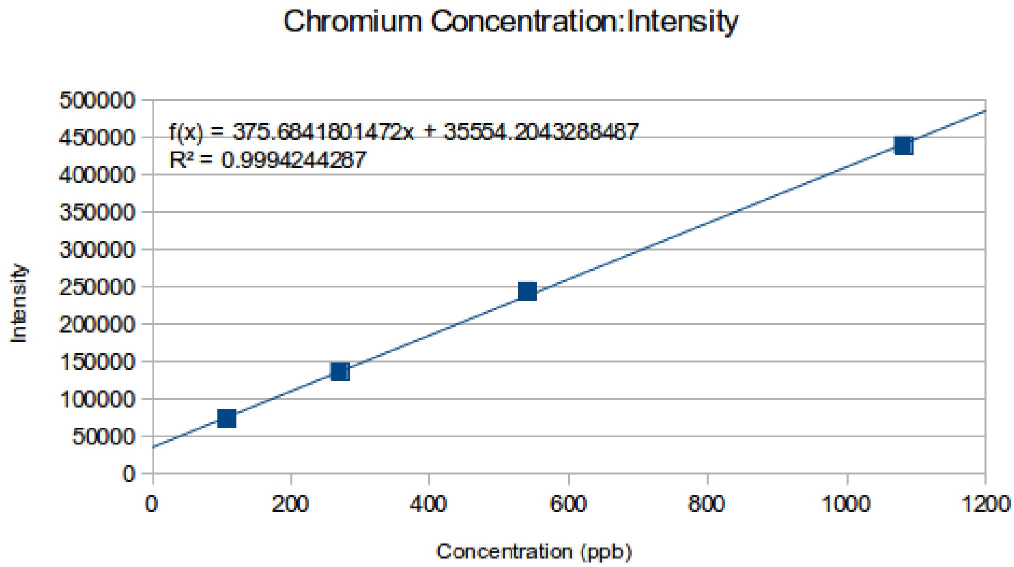
Manganese Concentration:Intensity
f(x) = 2917.1941526506x - 6252.7673105742
R² = 0.9999609135
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
Intensity
0
200
400
600
800
1000
1200
Concentration (ppb)

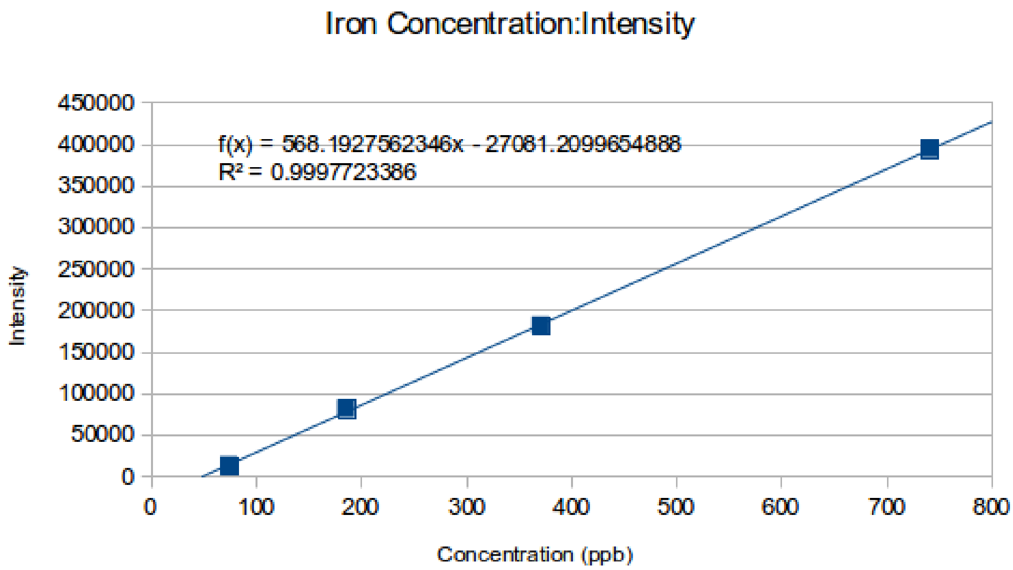


Magnesium Concentration:Intensity
f(x) = 10248.7724233267x + 1002551.08957697
R² = 0.9932069407
14000000
12000000
10000000
8000000
6000000
4000000
2000000
0
Intensity
0
200
400
600
800
1000
1200
Concentration (ppb)


Copper Concentration:Intensity
f(x) = 1259.9922359173x + 20111.7617733596
R² = 0.9999930921
Intensity
Concentration (ppb)
1600000
1400000
1200000
1000000
800000
600000
400000
200000
0
0
200
400
600
800
1000
1200


Zinc Concentration:Intensity
f(x) = 285.9980478464x - 1500.6187622624
R² = 0.9998691072
Intensity
Concentration (ppb)
400000
350000
300000
250000
200000
150000
100000
50000
0
0
200
400
600
800
1000
1200
1400


Chromium Concentration:Intensity
f(x) = 375.6841801472x + 35554.2043288487
R² = 0.9994244287
Intensity
500000
450000
400000
350000
300000
250000
200000
150000
100000
50000
0
0
200
400
600
800
1000
1200
Concentration (ppb)


Iron Concentration:Intensity
f(x) = 568.1927562346x - 27081.2099654888
R² = 0.9997723386
Intensity
450000
400000
350000
300000
250000
200000
150000
100000
50000
0
0
100
200
300
400
500
600
700
800
Concentration (ppb)

C Raw Data

Sample ID	Elem	Wavelength	Int (Corr)
1000 ppb brass std.	Fe	259.939	53562.97356
1000 ppb brass std.	Zn	213.857	350455.3171
1000 ppb brass std.	Cu	324.752	727346.4845
1000 ppb brass std.	Cr	283.563	371458.5782
1000 ppb brass std.	Mg	279.553	13011258.27
500 ppb brass std.	Fe	259.939	1951111.54
500 ppb brass std.	Zn	213.857	212155.8309
500 ppb brass std.	Cu	324.752	669912.1389
500 ppb brass std.	Cr	283.563	571276.7991
500 ppb brass std.	Mg	279.553	6273275.127
100 ppb brass std.	Fe	259.939	101024.1545
100 ppb brass std.	Zn	213.857	41424.21525
100 ppb brass std.	Cu	324.752	92673.36258
100 ppb brass std.	Cr	283.563	55431.62597
100 ppb brass std.	Mg	279.553	1333372.371
1000 ppb creek std.	Fe	259.939	584086.5927
1000 ppb creek std.	Zn	213.857	357603.8548
1000 ppb creek std.	Ni	341.476	98466.77701
1000 ppb creek std.	Mn	257.61	3283494.973
1000 ppb creek std.	Cu	324.752	1261947.342
500 ppb creek std.	Fe	259.939	2584402.889
500 ppb creek std.	Zn	213.857	24059.20028
500 ppb creek std.	Ni	341.476	408.0885826
500 ppb creek std.	Mn	257.61	3541.554524
500 ppb creek std.	Cu	324.752	-18918.11446
250 ppb creek std.	Fe	259.939	71770.81809

250 ppb creek std.	Zn	213.857	86209.27897
250 ppb creek std.	Ni	341.476	22331.0908
250 ppb creek std.	Mn	257.61	701104.7696
250 ppb creek std.	Cu	324.752	-6642.393715
100 ppb creek std.	Fe	259.939	114768.3646
100 ppb creek std.	Zn	213.857	51194.35715
100 ppb creek std.	Ni	341.476	136333.8881
100 ppb creek std.	Mn	257.61	603083.6916
100 ppb creek std.	Cu	324.752	50992.65963
Brass 58	Fe	259.939	9506.242361
Brass 58	Zn	213.857	20258.8005
Brass 58	Ni	341.476	-88.83286601
Brass 58	Mn	257.61	1551.540778
Brass 58	Cu	324.752	-19286.60787
Brass 58	Cr	283.563	-28524.36487
Brass 58	Mg	279.553	-13989.41236
Pre Rain Creek	Fe	259.939	413.5290421
Pre Rain Creek	Zn	213.857	1446.663662
Pre Rain Creek	Ni	341.476	-63.71230508
Pre Rain Creek	Mn	257.61	1453.407284
Pre Rain Creek	Cu	324.752	-22150.50774
Pre Rain Creek	Cr	283.563	-27999.17551
Pre Rain Creek	Mg	279.553	34425.24012
Post Rain Creek	Fe	259.939	2567.677028
Post Rain Creek	Zn	213.857	1421.788384
Post Rain Creek	Ni	341.476	-86.07095416
Post Rain Creek	Mn	257.61	1440.924438
Post Rain Creek	Cu	324.752	-22131.4051

Post Rain Creek	Cr	283.563	-27042.73665
Post Rain Creek	Mg	279.553	4439.796171
1000 ppb std 3	Fe	259.939	394438.2914
1000 ppb std 3	Zn	213.857	354864.5174
1000 ppb std 3	Ni	341.476	97165.61924
1000 ppb std 3	Mn	257.61	3107903.083
1000 ppb std 3	Cu	324.752	1355719.205
1000 ppb std 3	Cr	283.563	439457.3669
1000 ppb std 3	Mg	279.553	12145232.71
500 ppb std 3	Fe	259.939	181651.4753
500 ppb std 3	Zn	213.857	174652.6958
500 ppb std 3	Ni	341.476	47045.24541
500 ppb std 3	Mn	257.61	1540296.514
500 ppb std 3	Cu	324.752	686492.1173
500 ppb std 3	Cr	283.563	244347.1294
500 ppb std 3	Mg	279.553	5934200.923
250 ppb std 3	Fe	259.939	81680.22402
250 ppb std 3	Zn	213.857	89444.17021
250 ppb std 3	Ni	341.476	24738.99611
250 ppb std 3	Mn	257.61	766792.045
250 ppb std 3	Cu	324.752	355779.4225
250 ppb std 3	Cr	283.563	136334.5832
250 ppb std 3	Mg	279.553	3878993.738
100 ppb std 3	Fe	259.939	13222.49232
100 ppb std 3	Zn	213.857	33443.68741
100 ppb std 3	Ni	341.476	8538.423244
100 ppb std 3	Mn	257.61	312995.8772
100 ppb std 3	Cu	324.752	152834.8798

100 ppb std 3	Cr	283.563	73701.54913
100 ppb std 3	Mg	279.553	2271731.809
Brass 58	Fe	259.939	5529.675581
Brass 58	Zn	213.857	14667.63711
Brass 58	Ni	341.476	112.1774806
Brass 58	Mn	257.61	1180.44582
Brass 58	Cu	324.752	1026224.548
Brass 58	Cr	283.563	33643.75789
Brass 58	Mg	279.553	N/A
Pre Rain Creek	Fe	259.939	1245.518305
Pre Rain Creek	Zn	213.857	-1655.411467
Pre Rain Creek	Ni	341.476	190.0753086
Pre Rain Creek	Mn	257.61	-1096.773939
Pre Rain Creek	Cu	324.752	33058.44932
Pre Rain Creek	Cr	283.563	24656.60903
Pre Rain Creek	Mg	279.553	N/A
Post Rain Creek	Fe	259.939	1695.669501
Post Rain Creek	Zn	213.857	-1619.089584
Post Rain Creek	Ni	341.476	251.6213797
Post Rain Creek	Mn	257.61	-1247.722695
Post Rain Creek	Cu	324.752	32138.79195
Post Rain Creek	Cr	283.563	39592.99669
Post Rain Creek	Mg	279.553	N/A