Nick Pekor
Dr. Michelle Ward
CHEM 1255
10/23/20

The Apple of my ICP – Determining the Amounts of Metals Present in Apples.

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

Nicholas T Pekor

Introduction

ICP-OES is a useful analytical technique for the detection of elements in samples. Because of this, ICP-OES is used in this experiment to determine the amount of calcium, magnesium, and potassium present in different apple samples. Outside of this experiment, ICP-OES has been used for multiple other experiments. Examples include using ICP-OES to determine the metal concentration inside of wild mushrooms found in Poland {1}, and analyzing the effects of photochemical formation of mercuric oxide {2}. Altogether, ICP-OES is useful for determining what elements are present in a sample, primarily metallic elements.

When a sample is loaded into an ICP-OES, it first goes through a process of nebulization. Nebulization involves the sample being converted into a fine aerosol. A fraction of the sample actually gets aerosolized, whereas the rest stays behind. The sample aerosol then gets taken to a plasma torch. The readings from the ICP-OES come from passing the samples through the plasma torch, which usually consists of argon. As the aerosol is passed through the plasma, the leftover liquid portion of the aerosol is vaporized, and splits the rest of the sample into its component atoms. The high temperature from the plasma atomizes all of the sample left, and excites the atoms. The excitation of the atoms result in electromagnetic radiation. A key idea of this is that each element has its own OES gradient. By analyzing what wavelengths are emitted from the sample, the ICP-OES can determine which atoms are present in the plasma. The wavelengths are picked up by the detector, and recorded by the ICP-OES.

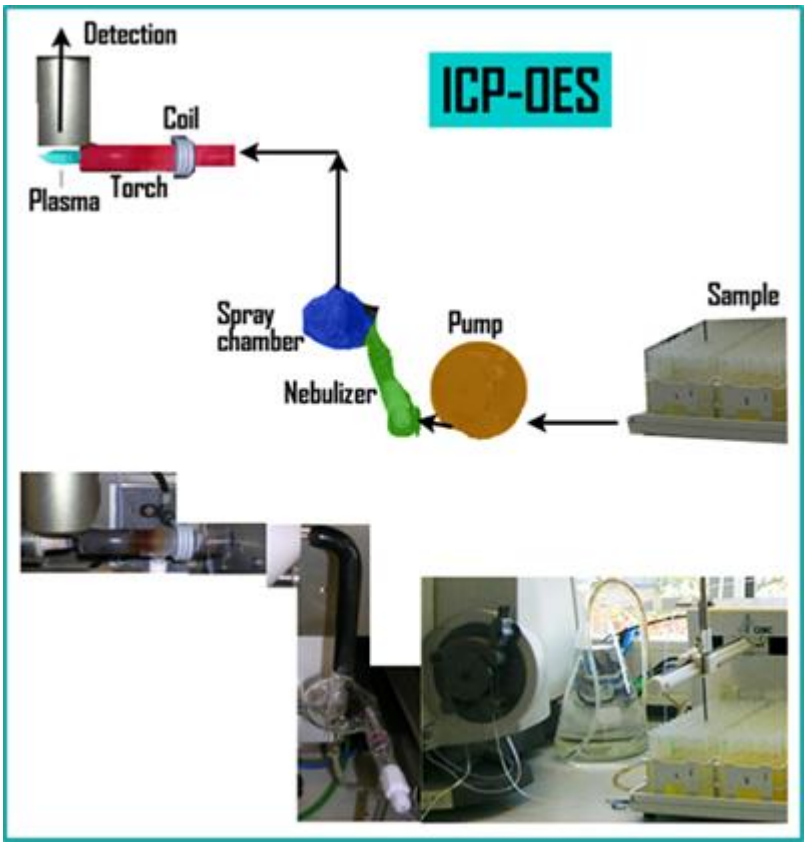

Figure 1 – Simple diagram of a standard ICP-OES. The sample is nebulized by the nebulizer, and formed into an aerosol in the spray chamber. The aerosol travels to the plasma, where it is excited {3}.

For this particular experiment, different solutions of differing concentrations of calcium, magnesium, and potassium were run through the ICP-OES. As the samples are pumped in, they reached the plasma torch present inside of the instrument. The plasma excited the three different ions present in the solution, which then gave off electromagnetic radiation of differing wavelengths corresponding to each of the elements present inside of the solution. Higher concentrations of a particular element will increase the value of the intensity reading received from the ICP-OES.

ICP-OES is useful for this experiment because of its ability to characterize different elements in the sample. ICP-OES is different from other instruments, like HPLC, FTIR, and GC, as ICP-OES focuses more on what elements are present, rather than what compounds are present. Considering that apples are a complex network of different cells, proteins, vitamins, and compounds, the readings from other instruments would likely come out extremely noisy, and leave significant data nearly indistinguishable from the rest of the data.

Experimental

Materials

The Assurance 1000 μg/mL Ca, 1000 μg/mL Mg, 1000 μg/mL K, and 1000 μg/mL Y ICP standard solutions were all purchased from SPEX Certiprep. The trace metal grade Nitric Acid was purchased from Fisher Chemical. The DIUF water was also purchased from Fisher Chemical. The apples used in the experiment were supplied by the University of Pittsburgh. All of the instrumentation, such as the 125 mL Pyrex beakers, the 100 mL volumetric flasks, the micropipettes, the filter papers, and the 0.22μm nylon syringe filters, were supplied by the University of Pittsburgh. The nitrogen, argon, and air, as well as the dilute nitric acid solution, were all provided by the University of Pittsburgh.

Instrumentation

The ICP-OES used in the experiment was the Perkin Elmer Optima 7000 DV OES. The gas pressures supplied from the gas tanks were set to about 50 psi for nitrogen, about 100 psi for argon, and about 60 for air. The WinLab32 Instrument Control program was used to set the parameters of the ICP-OES. A premade file named apple.acp was loaded to set the parameters of the instrument. With the file loaded, the source equilibration delay was set to 15 seconds, the sample flow rate was set to 1.00 mL/min, and the washing step was set to run between sample measurements, to run at a rate of 1.50 mL/min for 30 seconds. The concentration data for the apple samples and the standard solutions were added manually into the program. The program also had preloaded plasma control parameters, such as the gas flow rate. The plasma gas flow rate was set at 15 L/min, the auxiliary gas flow rate was set at 0.2 L/min, and the nebulizer gas flow rate was set at 0.65 L/min. The RF power of the plasma control was set to 1300 W, and the pump flow rate was set to 1.50 mL/min. Before the samples were run through the ICP-OES, the instrument was flushed with a premade dilute nitric acid solution for about 15 minutes, and then flushed with DIUF water for about 20 minutes. After the samples were run through the ICP-OES, the same was repeated.

Procedure

For this experiment, eight apple samples needed to be made. To start, an organic apple was taken, and pieces were cut off of it, making sure there was no peel on the pieces. Each piece should weigh around 1 gram. For the pieces cut, two pieces weighed 1.0516 grams, and two other pieces weighed 1.0324 grams. The process is repeated with a nonorganic apple; four pieces were cut from the apple, with no peel, and weighed. For the nonorganic apple pieces, two weighed 0.9323 grams, and two weighed 1.1367 grams. Each individual apple piece was then placed in their own 150 mL Pyrex beaker.

Next, half of the samples need to be spiked with ion stock solutions. First, four of the apple sample beakers were gathered, the two samples weighing 1.0324 grams, and the two samples weighing 1.1367 grams. To all of these beakers, 0.010 mL of the 1000 μg/mL Ca and Mg standards, and 0.20 mL of the 1000 μg/mL K standard were added.

All eight of the sample beakers are taken to a fume hood. 10 and 15 mL aliquots of 65% HNO_3 is then added to each of the samples, as the samples are heated up on a hot plate. Acid is added repeatedly to the samples until everything in the beaker has fully dissolved. As this was happening, an empty beaker was put through the same process, adding amounts of 65% HNO_3 and heated thoroughly. This ninth beaker is meant to account for any error that may occur from ions falling out of solution. Once all of the samples dissolved, they are left to cool. Once cool, they are filtered thoroughly by passing the solutions through a filter paper, and then a 0.22μm nylon syringe filter.

The filtrate is then placed into a 100 mL volumetric flask, and diluted to the mark with DIUF water. By the end, there were eight different volumetric flasks, eight with their own apple sample, and with the blank. This completes the production of the apple samples.

The standards need to be produced next. For this, 10 mL of both the 1000 μg/mL Ca and Mg stock solution were added to a 100 mL volumetric flask, and diluted to the mark with DIUF water. 5 mL of this solution was then pipetted into another 100 mL volumetric flask, where 10 mL of the 1000 μg/mL K stock solution was added, and diluted to the mark with DIUF water. From this resulting solution, various amounts of the solution was pipetted into four different reaction flasks to produce solutions C, D, E, and F. For solution C, 5 mL was pipetted, D 10 mL, E 15 mL, and 5 20 mL. These four volumetric flasks were then all diluted to the mark with DIUF water. The resulting ion concentrations are shown in **Table 2**.

Each of the standards and samples are run through the ICP-OES twice, once using the digested blank as the blank sample and the 1000 μg/mL Y stock solution as the internal standard, and once using DIUF water as the blank sample and the 1000 μg/mL Y stock solution as the internal standard.

Results

The following masses are the masses of each apple sample used in the experiment.

Table 1 – Masses of each apple piece used in the experiment, and the amounts of solvent used to create the apple samples.

Sample	Mass (g)	Volume (mL)
Normal	1.0516	100
Normal Spiked	1.0324	100
Organic	0.9323	100
Organic Spiked	1.1367	100

The raw data received from the ICP-OES is listed at the end of the lab report. The two tables directly below is meant to put the data necessary for calculations into a much neater set of tables.

Table 2 – Concentrations and Intensities of the Samples for each ion for the DIUF Blank Trial.

Sample	Ca [] (mg/L)	Mg [](mg/L)	K [](mg/L)	Ca I (C/s)	Mg I (C/s)	K I (C/s)
Blank	0	0	0	155617.4	62920.8	-2953.9
c	0.25	0.25	5	349014.8	482953.1	6076824.2
d	0.50	0.50	10.0	668796.7	995859.0	10734898.2
e	0.750	0.750	15.0	896863.0	1478273.0	17240470.5
f	1.00	1.00	20	1317143.1	1969171.1	23072747.6
Normal	0.882	0.341	10.70	1132107.5	670714.2	12224872.3
Normal Spiked	1.410	0.527	12.74	1805145.2	1039364.5	14564636.1
Organic	0.905	0.419	9.684	1161975.7	825439.8	11062696.1
Organic Spiked	1.423	0.654	13.88	1821805.6	1288969.7	15869241.2

Table 3 – Concentrations and Intensities of the Samples for each ion for the Digested Blank Trial. Standard C was excluded from this trial, as the ICP-OES did not give data that should be expected. The cells marked by "???" signify that no values were received, and will instead be calculated later on in the lab.

Sample	Ca [] (mg/L)	Mg [](mg/L)	K [](mg/L)	Ca I (C/s)	Mg I (C/s)	K I (C/s)
Blank	0	0	0	-982844.4	161036.6	2957759.8
d	0.50	0.50	10.0	-159624.1	903485.1	8100458.4

e	0.750	0.750	15.0	90001.9	1423946.8	14724574.8
f	1.00	1.00	20	518357.7	1977797.8	21282041.5
Normal	???	???	???	327561.1	579902.8	9503851.2
Normal Spiked	???	???	???	927869.8	921457.1	11677327.2
Organic	???	???	???	353023.6	734991.8	8346558.2
Organic Spiked	???	???	???	987210.8	1201472.6	13044355.2

The concentrations of ions in the standard are entered into the ICP-OES before the sample is run. As the data is run through the ICP-OES, the intensities of the standard solutions are outputted. After this, the apple samples are run through the machine as well, outputting the signal intensities of the samples. By comparing the standards' concentrations and intensities to the apple samples intensity, the ICP-OES is able to predict the concentrations of the ions present in the apple samples. The plots below show the runs of the DIUF blank samples for all ions. The trendline is only fit to the standard samples, so as to clearly show how close the predicted results found by the ICP-OES are to what is to be expected.

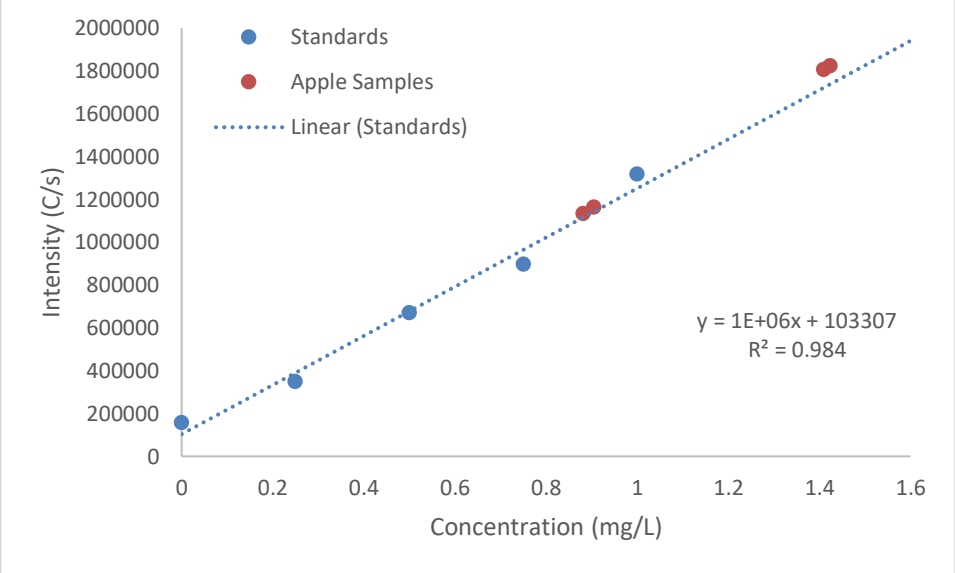

Figure 2 – Calibration curve for Ca^{2+} readings for the DIUF Blank trial. The values used for the curve are listed on **Table 2**. The x-axis corresponds to the concentrations of the Ca^{2+}, shown in the second column, and the y-axis corresponds to the intensity of the signal for Ca^{2+}, shown in the fifth column.

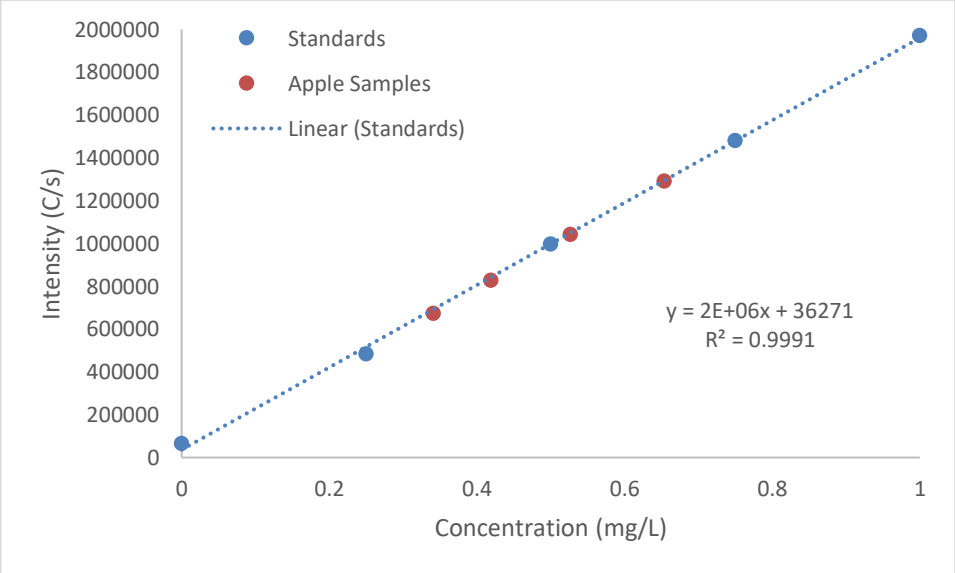

Figure 3 – Calibration curve for Mg^{2+} readings for the DIUF Blank trial. The values used for the curve are listed on **Table 2**. The x-axis corresponds to the concentrations of the Mg^{2+}, shown in the third column, and the y-axis corresponds to the intensity of the signal for Mg^{2+}, shown in the sixth column.

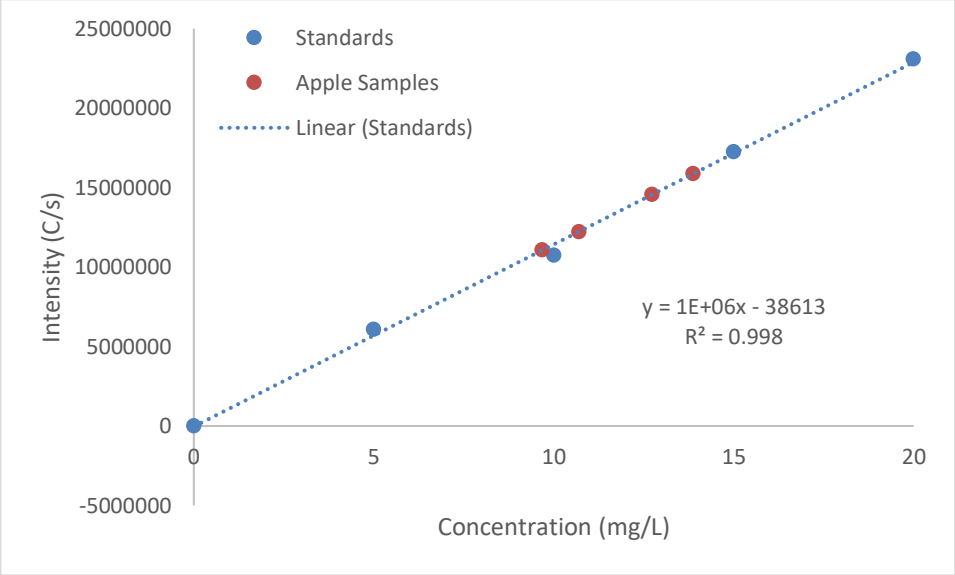

Figure 4 – Calibration curve for K^{+} readings for the DIUF Blank trial. The values used for the curve are listed on **Table 2**. The x-axis corresponds to the concentrations of the K^{+}, shown in the fourth column, and the y-axis corresponds to the intensity of the signal for K^{+}, shown in the seventh column.

For the digested samples trial, the ICP-OES did not predict the concentrations of the apple samples. Instead, a calibration curve received from the standards' values must be used to directly calculate the concentrations. This is done through standard linear regression, through the equation.

$$x = \frac{y - b}{m}$$

$$x_{Digested_{Normal_{Ca^{2+}}}} = \frac{327561.1\ \frac{C}{s} - \left(-963053\ \frac{C}{s}\right)}{1474712.377\ \frac{\text{L}}{\text{mg}}} = 0.875\ \frac{\text{mg}}{\text{L}} \quad [1]$$

x is the concentration of the sample, y is the intensity of the sample, b is the y-intercept of the trendline, and m is the slope of the trendline. By plugging in the intensity of the sample and the parameters of the trendline, the concentration of the apple samples can be calculated.

The apple samples' values are shown on the plots below, showing that the calculated values lie directly on the trendline. Again, the trendline received only corresponds to the standard sample readings.

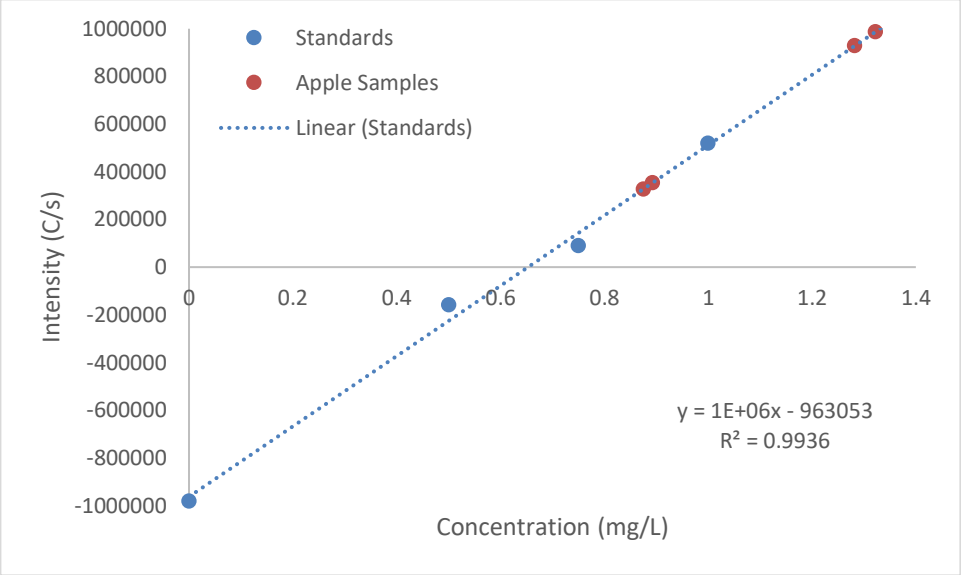

Figure 5 – Calibration curve for Ca^{2+} readings for the Digested Blank trial. The values used for the curve are listed on **Table 3**. The x-axis corresponds to the concentrations of the Ca^{2+}, shown in the second column, and the y-axis corresponds to the intensity of the signal for Ca^{2+}, shown in the fifth column.

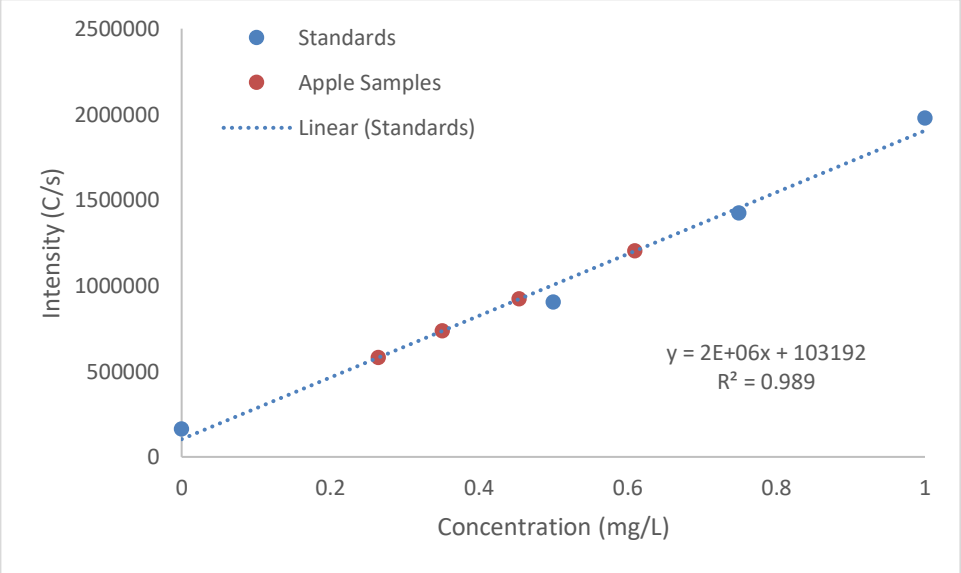

Figure 6 – Calibration curve for Mg^{2+} readings for the Digested Blank trial. The values used for the curve are listed on **Table 3**. The x-axis corresponds to the concentrations of the Mg^{2+}, shown in the third column, and the y-axis corresponds to the intensity of the signal for Mg^{2+}, shown in the sixth column.

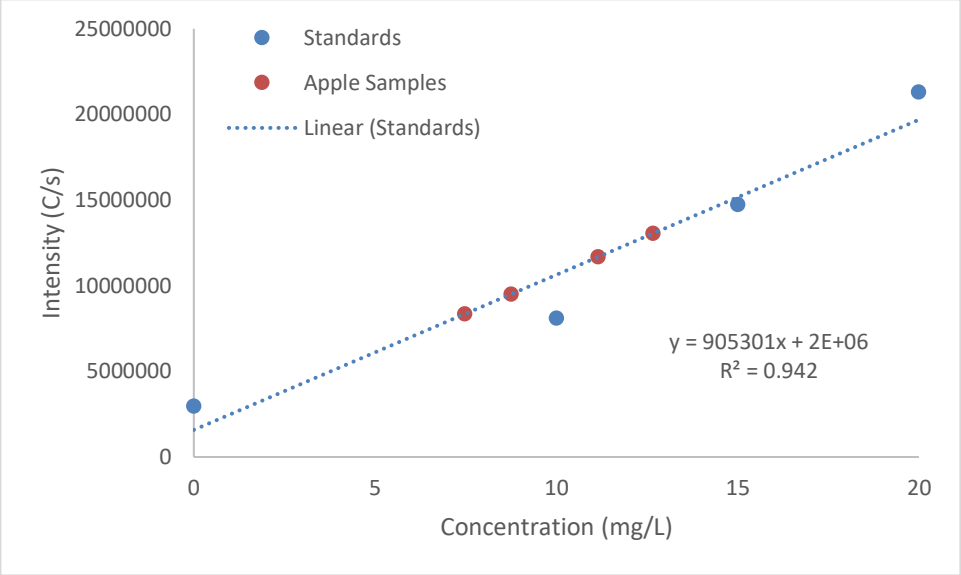

Figure 7 – Calibration curve for K^+ readings for the Digested Blank trial. The values used for the curve are listed on **Table 3**. The x-axis corresponds to the concentrations of the K^+, shown in the fourth column, and the y-axis corresponds to the intensity of the signal for K^+, shown in the seventh column.

Table 4 – Calculated Concentrations for the Apple Samples for the Digested Blank Trial. This data fills in the cells labeled by "???" in **Table 3**.

Sample	Ca [] (mg/L)	Mg [] (mg/L)	K [](mg/L)
Normal	0.875163	0.264611	8.75
Normal Spiked	1.282232	0.454199	11.15
Organic	0.892429	0.350697	7.47
Organic Spiked	1.322471	0.609629	12.66

It is important to realize that the concentrations received from the ICP-OES or calculated through **Calculation [1]** do not mimic the actual concentrations of the apple itself. This is because the apple samples were diluted before they were run through the ICP-OES. To account for this, the following calculation is used.

$$C_{Apple} = \frac{V_{Dilution}}{m_{Apple}} \cdot C_{Reading} \qquad [2]$$

$$C_{DIUF\,Normal\,Ca^{2+}} = \frac{100\text{ mL}}{1.0516\text{ g}} \cdot 0.882\ \frac{\text{mg}}{\text{L}} = 83.9\ \frac{\text{mL}\cdot\text{mg}}{\text{g}\cdot\text{L}} \rightarrow 83.9\ \frac{\text{mg}}{\text{kg}}$$

C_{Apple} is the concentration of the particular ion present in the apple piece that was weighed out. $V_{Dilution}$ is the amount of solvent added to the apple piece to dilute it. m_{Apple} is the mass of the apple piece, and $C_{Reading}$ is the concentration of the particular ion in the apple sample run through the ICP-OES. **Calculation [2]** is used for every ion in every sample to determine the amounts of the ions in the apple pieces.

Table 5 – Concentrations of Ions in Apple Pieces for DIUF Blank Trial

Sample	Ca [] (mg/kg)	Mg [] (mg/kg)	K [] (mg/kg)
Normal	83.87219	32.42678	1017.497
Normal Spiked	136.575	51.04611	1234.018

Organic	97.07176	44.94262	1038.721
Organic Spiked	125.1869	57.53497	1221.079

Table 6 – Concentrations of Ions in Apple Pieces for Digested Blank Trial

Sample	Ca [] (mg/kg)	Mg [] (mg/kg)	K [] (mg/kg)
Normal	83.22206	25.16269	832.1595
Normal Spiked	124.1991	43.99452	1080.184
Organic	95.7234	37.61633	801.5272
Organic Spiked	116.343	53.6315	1113.913

Discussion

Tables 5-6 show the final expected concentrations of the ions present in the apples, measured by different methods through the ICP-OES. The first method used a blank standard that consisted only of DIUF water, and the second method used a blank standard consisting of a "digested" solution, which was in reality nitric acid that was boiled, filtered, and diluted. Looking at the data shown in **Tables 5-6**, there is a clear shift in values for the concentrations of ions in the apple solutions. The shift is most noticeable for the K concentration values, as a difference of over 100 mg/kg is observed for all the samples. This shift shows that the data received from the ICP-OES is not necessarily accurate nor precise. For future, it would be advised to perform multiple runs with the same blank. By performing more runs and finding the average values, the results calculated should be much more favorable.

Despite the disparaging values, the overall trend of the concentrations remains constant between the two methods. Comparing the concentrations of ions between the normal and organic samples, a majority of the readings showed that the organic samples tend to have a higher ion concentration. Likewise, spiking the sample always resulted in an increase to the concentration of the ions, when compared to the unspiked samples.

The calcium concentrations shown from the results clearly indicate that the apples have already been soaked in a $CaCl_2$ solution. This is because the expected concentration of apples should be between 10-50 mg/kg. For all apple samples, the concentration of calcium is much higher than what is to be expected. It is safe to assume that the apples were previously soaked in $CaCl_2$ before being bought, as the $CaCl_2$ helps preserve the apples. The calcium concentrations overall indicate that the apples are safe to store, without the need for any $CaCl_2$. The magnesium and potassium concentrations are in the range to be expected from apples. Naturally, apples tend to have magnesium concentrations ranging from 25-50 mg/kg, and potassium concentrations ranging from 500-1500 mg/kg. The concentrations received mirror these ranges and show that the concentrations of magnesium and potassium were not altered before being analyzed.

References

Jerzy Falandysz; Katarzyna Szymczyk; Hideki Ichihashi; Leszek Bielawski; Magdalena Gucia; Aneta Frankowska; Shin-Ichi Yamasaki; ICP/MS and ICP/AES elemental analysis (38 elements) of edible wild mushrooms growing in Poland. Food Additives & Contaminants **2001.** *Volume 12*. https://www.tandfonline.com/doi/pdf/10.1080/02652030119625?needAccess=true (accessed 10 23,2020)

Evan J. Granite; Henry W. Pennline; James S. Hoffman; Effects of Photochemical Formation of Mercuric Oxide. I&EC **1999**. *Volume 38*. https://pubs.acs.org/doi/pdf/10.1021/ie9904495 (accessed 10 23,2020)

Radboud University. https://www.ru.nl/science/gi/facilities-activities/elemental-analysis/icp-oes/ (accessed 10 23, 2020)

ICP-OES Readings on following pages

Mean Data

ID: Calib Blank Seq. No.: 1 A/S Pos:

Sample Qty: g Prep. Vol.: Dilution: : Date: 2020/09/29 15:30:09

Analyte	Corr. Intensity	Conc (Calib)	Std. Dev.	Calib Units	Conc (Sample)	Std. Dev.	Sample Units	RSD
Y 371.029	921,134.5	[0.00]	7,308.49	mg/L				0.79 %
Ca 317.933	155,617.4	[0.00]	1,688.64	mg/L				1.09 %
Mg 285.213	62,920.8	[0.00]	672.38	mg/L				1.07 %
K 766.490	-2,953.9	[0.00]	1,258.39	mg/L				42.60 %

Mean Data

ID: c Seq. No.: 2 A/S Pos:

Sample Qty: g Prep. Vol.: Dilution: : Date: 2020/09/29 15:33:33

Analyte	Corr. Intensity	Conc (Calib)	Std. Dev.	Calib Units	Conc (Sample)	Std. Dev.	Sample Units	RSD
Y 371.029	948,389.8		22,614.38					2.38 %
Ca 317.933	349,014.8	[0.25]	10,891.72	mg/L				3.12 %
Mg 285.213	482,953.1	[0.25]	22,013.60	mg/L				4.56 %
K 766.490	6,076,824.2	[5]	236,573.74	mg/L				3.89 %

Mean Data

ID: d Seq. No.: 3 A/S Pos:

Sample Qty: g Prep. Vol.: Dilution: : Date: 2020/09/29 15:40:54

Analyte	Corr. Intensity	Conc (Calib)	Std. Dev.	Calib Units	Conc (Sample)	Std. Dev.	Sample Units	RSD
Y 371.029	940,244.8		8,056.90					0.86 %
Ca 317.933	668,796.7	[0.50]	1,197.27	mg/L				0.18 %
Mg 285.213	995,859.0	[0.50]	5,778.59	mg/L				0.58 %
K 766.490	10,734,898.2	[10.0]	106,845.04	mg/L				1.00 %

Mean Data

ID: e Seq. No.: 4 A/S Pos:

Sample Qty: g Prep. Vol.: Dilution: : Date: 2020/09/29 15:46:23

Analyte	Corr. Intensity	Conc (Calib)	Std. Dev.	Calib Units	Conc (Sample)	Std. Dev.	Sample Units	RSD
Y 371.029	940,849.1		15,763.50					1.68 %
Ca 317.933	896,863.0	[0.750]	31,131.98	mg/L				3.47 %
Mg 285.213	1,478,273.0	[0.750]	18,720.81	mg/L				1.27 %
K 766.490	17,240,470.5	[15.0]	500,703.39	mg/L				2.90 %

Mean Data

ID: f Seq. No.: 5 A/S Pos:

Sample Qty: g Prep. Vol.: Dilution: : Date: 2020/09/29 15:50:06

Analyte	Corr. Intensity	Conc (Calib)	Std. Dev.	Calib Units	Conc (Sample)	Std. Dev.	Sample Units	RSD
Y 371.029	956,374.7		5,397.14					0.56 %
Ca 317.933	1,317,143.1	[1.00]	8,196.17	mg/L				0.62 %
Mg 285.213	1,969,171.1	[1.00]	6,958.02	mg/L				0.35 %
K 766.490	23,072,747.6	[20]	171,192.08	mg/L				0.74 %

Mean Data

ID: normal Seq. No.: 6 A/S Pos:

Sample Qty: g Prep. Vol.: Dilution: : Date: 2020/09/29 15:54:00

Analyte	Corr. Intensity	Conc (Calib)	Std. Dev.	Calib Units	Conc (Sample)	Std. Dev.	Sample Units	RSD
Y 371.029	933,936.2						mg/L	%
Ca 317.933	1,132,107.5	0.882	0.0065	mg/L	0.882	0.0065	mg/L	0.74 %
Mg 285.213	670,714.2	0.341	0.0014	mg/L	0.341	0.0014	mg/L	0.41 %
K 766.490	12,224,872.3	10.70	0.198	mg/L	10.70	0.198	mg/L	1.85 %

Mean Data

ID: normal spiked **Seq. No.:** 7 **A/S Pos:**

Sample Qty: g **Prep. Vol.:** **Dilution:** : **Date:** 2020/09/29 15:57:23

Analyte	Corr. Intensity	Conc (Calib)	Std. Dev.	Calib Units	Conc (Sample)	Std. Dev.	Sample Units	RSD
Y 371.029	921,873.9						mg/L	%
Ca 317.933	1,805,145.2	1.410	0.0152	mg/L	1.410	0.0152	mg/L	1.08 %
Mg 285.213	1,039,364.5	0.527	0.0089	mg/L	0.527	0.0089	mg/L	1.69 %
K 766.490	14,564,636.1	12.74	0.257	mg/L	12.74	0.257	mg/L	2.02 %

Mean Data

ID: organic **Seq. No.:** 8 **A/S Pos:**

Sample Qty: g **Prep. Vol.:** **Dilution:** : **Date:** 2020/09/29 16:02:06

Analyte	Corr. Intensity	Conc (Calib)	Std. Dev.	Calib Units	Conc (Sample)	Std. Dev.	Sample Units	RSD
Y 371.029	959,575.3						mg/L	%
Ca 317.933	1,161,975.7	0.905	0.0154	mg/L	0.905	0.0154	mg/L	1.70 %
Mg 285.213	825,439.8	0.419	0.0092	mg/L	0.419	0.0092	mg/L	2.20 %
K 766.490	11,062,696.1	9.684	0.0514	mg/L	9.684	0.0514	mg/L	0.53 %

Mean Data

ID: organic spiked **Seq. No.:** 9 **A/S Pos:**

Sample Qty: g **Prep. Vol.:** **Dilution:** : **Date:** 2020/09/29 16:06:27

Analyte	Corr. Intensity	Conc (Calib)	Std. Dev.	Calib Units	Conc (Sample)	Std. Dev.	Sample Units	RSD
Y 371.029	943,731.5						mg/L	%
Ca 317.933	1,821,805.6	1.423	0.0033	mg/L	1.423	0.0033	mg/L	0.23 %
Mg 285.213	1,288,969.7	0.654	0.0063	mg/L	0.654	0.0063	mg/L	0.96 %
K 766.490	15,869,241.2	13.88	0.181	mg/L	13.88	0.181	mg/L	1.31 %

Mean Data

ID: Calib Blank **Seq. No.:** 1 **A/S Pos:**

Sample Qty: g **Prep. Vol.:** **Dilution:** : **Date:** 2020/09/29 16:26:08

Analyte	Corr. Intensity	Conc (Calib)	Std. Dev.	Calib Units	Conc (Sample)	Std. Dev.	Sample Units	RSD
Y 371.029	942,804.8	[0.00]	6,665.37	mg/L				0.71 %
Ca 317.933	982,844.4	[0.00]	25,378.53	mg/L				2.58 %
Mg 285.213	161,036.6	[0.00]	1,716.67	mg/L				1.07 %
K 766.490	2,957,759.8	[0.00]	29,341.14	mg/L				0.99 %

Mean Data

ID: c **Seq. No.:** 2 **A/S Pos:**

Sample Qty: g **Prep. Vol.:** **Dilution:** : **Date:** 2020/09/29 16:28:48

Analyte	Corr. Intensity	Conc (Calib)	Std. Dev.	Calib Units	Conc (Sample)	Std. Dev.	Sample Units	RSD
Y 371.029	10,431.3		1,256.87					12.05 %
Ca 317.933	79,424,459.6	[0.25]	8,948,955.52	mg/L				11.27 %
2020/09/29 16:29:28	Standard intensity and concentration values are not in the same order.							
Mg 285.213	89,743,255.0	[0.25]	11,418,577.39	mg/L				12.72 %
2020/09/29 16:29:28	Standard intensity and concentration values are not in the same order.							
K 766.490	1,135,944,406.5	[5]	37,562,958.49	mg/L				12.11 %
2020/09/29 16:29:28	Standard intensity and concentration values are not in the same order.							

Mean Data

ID: d **Seq. No.:** 3 **A/S Pos:**

Sample Qty: g **Prep. Vol.:** **Dilution:** : **Date:** 2020/09/29 16:32:13

Analyte	Corr. Intensity	Conc (Calib)	Std. Dev.	Calib Units	Conc (Sample)	Std. Dev.	Sample Units	RSD
Y 371.029	932,848.0		8,429.69					0.90 %
Ca 317.933	-150,624.1	[0.50]	3,455.38	mg/L				2.29 %
2020/09/29 16:32:52	Standard intensity and concentration values are not in the same order.							
Mg 285.213	903,485.1	[0.50]	26,490.44	mg/L				2.93 %
2020/09/29 16:32:52	Standard intensity and concentration values are not in the same order.							
K 766.490	8,100,458.4	[10.0]	114,205.00	mg/L				1.41 %
2020/09/29 16:32:52	Standard intensity and concentration values are not in the same order.							

Mean Data

ID: e **Seq. No.:** 4 **A/S Pos:**

Sample Qty: g **Prep. Vol.:** **Dilution:** : **Date:** 2020/09/29 16:35:13

Analyte	Corr. Intensity	Conc (Calib)	Std. Dev.	Calib Units	Conc (Sample)	Std. Dev.	Sample Units	RSD
Y 371.029	923,274.3		7,506.66					0.81 %
Ca 317.933	90,001.9	[0.750]	12,824.26	mg/L				14.25 %
2020/09/29 16:35:54	Standard intensity and concentration values are not in the same order.							
Mg 285.213	1,423,946.8	[0.750]	33,850.51	mg/L				2.38 %
2020/09/29 16:35:54	Standard intensity and concentration values are not in the same order.							
K 766.490	14,724,574.8	[15.0]	173,433.84	mg/L				1.18 %
2020/09/29 16:35:54	Standard intensity and concentration values are not in the same order.							

Mean Data

ID: f **Seq. No.:** 5 **A/S Pos:**

Sample Qty: g **Prep. Vol.:** **Dilution:** : **Date:** 2020/09/29 16:38:32

Analyte	Corr. Intensity	Conc (Calib)	Std. Dev.	Calib Units	Conc (Sample)	Std. Dev.	Sample Units	RSD
Y 371.029	913,498.0		6,032.46					0.66 %
Ca 317.933	518,357.7	[1.00]	19,916.04	mg/L				3.84 %
2020/09/29 16:39:13	Standard intensity and concentration values are not in the same order.							
Mg 285.213	1,977,797.8	[1.00]	43,874.90	mg/L				2.22 %
2020/09/29 16:39:13	Standard intensity and concentration values are not in the same order.							
K 766.490	21,282,041.5	[20]	86,179.58	mg/L				0.40 %
2020/09/29 16:39:13	Standard intensity and concentration values are not in the same order.							

Mean Data

ID: normal **Seq. No.:** 6 **A/S Pos:**

Sample Qty: g **Prep. Vol.:** **Dilution:** : **Date:** 2020/09/29 16:41:11

Analyte	Corr. Intensity	Conc (Calib)	Std. Dev.	Calib Units	Conc (Sample)	Std. Dev.	Sample Units	RSD
Y 371.029	936,528.5						mg/L	%
Ca 317.933	327,561.1	0.000	0.0000	mg/L	0.000	0.0000	mg/L	0.00 %
Mg 285.213	579,902.8	0.000	0.0000	mg/L	0.000	0.0000	mg/L	0.00 %
K 766.490	9,503,851.2	0.000	0.0000	mg/L	0.000	0.0000	mg/L	0.00 %

Mean Data

ID: normal spiked **Seq. No.:** 7 **A/S Pos:**

Sample Qty: g **Prep. Vol.:** **Dilution:** : **Date:** 2020/09/29 16:44:00

Analyte	Corr. Intensity	Conc (Calib)	Std. Dev.	Calib Units	Conc (Sample)	Std. Dev.	Sample Units	RSD
Y 371.029	930,635.9						mg/L	%
Ca 317.933	927,869.8	0.000	0.0000	mg/L	0.000	0.0000	mg/L	0.00 %
Mg 285.213	921,457.1	0.000	0.0000	mg/L	0.000	0.0000	mg/L	0.00 %
K 766.490	11,677,327.2	0.000	0.0000	mg/L	0.000	0.0000	mg/L	0.00 %

Mean Data

ID: organic **Seq. No.:** 8 **A/S Pos:**

Sample Qty: g **Prep. Vol.:** **Dilution:** : **Date:** 2020/09/29 16:46:58

Analyte	Corr. Intensity	Conc (Calib)	Std. Dev.	Calib Units	Conc (Sample)	Std. Dev.	Sample Units	RSD
Y 371.029	930,929.5						mg/L	%
Ca 317.933	353,023.6	0.000	0.0000	mg/L	0.000	0.0000	mg/L	0.00 %
Mg 285.213	734,991.8	0.000	0.0000	mg/L	0.000	0.0000	mg/L	0.00 %
K 766.490	8,346,558.2	0.000	0.0000	mg/L	0.000	0.0000	mg/L	0.00 %

Mean Data

ID: organic spiked **Seq. No.:** 9 **A/S Pos:**

Sample Qty: g **Prep. Vol.:** **Dilution:** : **Date:** 2020/09/29 16:50:08

Analyte	Corr. Intensity	Conc (Calib)	Std. Dev.	Calib Units	Conc (Sample)	Std. Dev.	Sample Units	RSD
Y 371.029	939,943.6						mg/L	%
Ca 317.933	987,210.8	0.000	0.0000	mg/L	0.000	0.0000	mg/L	0.00 %
Mg 285.213	1,201,472.6	0.000	0.0000	mg/L	0.000	0.0000	mg/L	0.00 %
K 766.490	13,044,355.2	0.000	0.0000	mg/L	0.000	0.0000	mg/L	0.00 %