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The Establishment of standard methods and experimental procedures for the prototypical ICP/TOF-MS using an ICP-AES

Senior Honors Thesis

by

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Abstract

The ICP-AES was used to develop a standard test method for the preparation of samples for analysis purposes, a method that could also be transposed onto the new prototypical ICP/TOF-MS. Whereas both of these instruments are analytical spectroscopic instruments and use the ICP's plasma as an energy source, the ICP/TOF-MS also has a mass spectrometer attached to it. This addition gives the instrument better reliability, accuracy, and precision in analysis as well as faster analysis time. Since the ICP-AES is a precursor of the ICP/TOF-MS, it can be used to develop a standard development method.

The experiment involved using a coal-ash sample called 1633b. This sample had certain certified values for its elements and its oxides. The sample was run with three different types of acids–hydrochloric, hydrofluoric, and aqua regia–as well as varying other parameters of the sample preparation procedures. Some of these parameter variations were the following: use of graphite crucibles, use of Teflon beakers, and the use of a mixed acid solution. After duplicates were run for each of the separate variations, the numbers obtained from the analysis of the prepared samples were compared with the certified numbers of 1633b. These comparisons gave the researcher the results on which he needed to base his experimental decisions.

From the comparisons, a conclusion was reached as to which method was preferred. Digesting the ash with an aqua regia acid solution was the best dissolving procedure. Secondly, the sample fused better when allowed to stay in the oven for only five minutes. Also, the molten material needed to be stirred and placed immediately into the dissolving acid. All of this was done in a new graphite crucible that could withstand the 1000°C that the method required.

Introduction

Analyses of materials are a large part of the world of chemistry, especially the world of analytical chemistry. Many methods exist as to how to analyze certain samples, and they all have their own unique physical and theoretical characteristics. These analyses include X-ray Fluorescence, Atomic Absorption, and Glow Discharge Spectroscopy. Some of these methods qualitatively determine the specific elements present in a sample and quantitatively determine the amount of these certain elements by a characteristic emission or property that the analytical instrument produces. However, these instruments utilize only one analytical technique each. The Inductively Coupled Plasma Time-of-Flight Mass Spectrometer (ICP/TOF-MS) incorporates the use of two different analytical techniques: inductively coupled plasma (ICP) and mass spectrometry (MS).

Of the analytical methods which focus on the qualitative aspects of samples, some do not also possess the ability to give quantitative data. In this study, an Inductively Coupled Plasma Atomic Emissions Spectrometer (ICP-AES) is utilized and is shown to have the capacity to do both quantitative and qualitative work. Because of the ICP-AES's similarity to the ICP/TOF-MS, the ICP-AES is used to develop a standard preparation method for the ICP/TOF-MS.

Analysis by way of atomic spectroscopy started in the field of atomic emissions. This field utilized a sample's ability to ionize into specific elemental ions, each of which emits certain wavelengths of light before being destroyed by heat. This idea originated in the nineteenth century with two men, Bunsen and Kirchoff, who founded the basics of atomic absorption and emissions by starting the sources out as flames.[1] Later researchers wanted to use electrically generated plasma discharges as the source instead of the flames.[1] These instruments typically used liquid argon, which would take the form of a gas through sublimation–the direct physical change of matter from liquid to gas. This gas would then be used by the instrument as support for the plasma in maintaining it and as a coolant for the torch that contained the mixture of plasma and sample.[2] Because the flame from the plasma would generally reach a temperature between 6000^0C and 1000^0C, the torch needed to be made of some sort of ionic character that could resist this incredible heat. Quartz was used as the torch, and a coil–called a Tesla coil[2]–was placed around it and was connected to the power generator.

In the case of an Inductively Coupled Plasma Atomic Emissions Spectrometer (ICP-AES), the power used to electrically generate the plasma discharge was radio frequency (RF).[2] This provided the instrument with the power to ignite the partially ionized plasma and create the incredible heat necessary to completely ionize the sample.

Complete ionization is the starting point for using inductively coupled plasma as an energy source. ICP as an energy source came to fruition with the use of the ICP-AES, which was introduced by Greenfield, and then Wendt and Fassell in the mid-1960s.[2] It was most commonly used for optical spectroscopy, but it soon came to be used analytically. Generally, liquid samples were the only samples that were being analyzed because injecting them into the system via a peristaltic pump was easy. However, new techniques developed, making it possible to analyze solids and slurries–solid samples mixed with water and soap.

ICP has long been a stable part of the analytical world. It has several unique characteristics that make it good for the analytical techniques that it utilizes. First and most important, it is a plasma--the fourth form of matter. It is neither gas, liquid, nor solid. It exists in its own state when it is ignited. Secondly, this plasma is inhomogeneous.[3] It is not the same flame completely throughout. Thus, repetitions of sample analysis are required, because it is generally assumed that the samples are not going to be the same throughout the plasma. The ICP as an energy source also has a toroidal shape.[3] This means that the ICP plasma has a shape that exists as a closed curve that is rotating about but not intersecting or containing an axis of its own.[4] This efficiently allows the instrument to introduce cold spray aerosols into the central channel of the plasma and analyze those aerosols more easily. This shape also gives the instrument low detection limits on elements and samples, wide linear dynamic ranges, as well as freedom from chemical, physical, and self-absorption interferences.[3]

From the introduction to the analysis of the sample, this instrument has specific characteristics that make it what it is. First of all, the sample is usually liquid and so is introduced through a tube via a peristaltic pump to the nebulizer. This apparatus is a specific glass piece that changes the sample from a liquid into a vapor by making the sample come out through a very small hole in the end of the nebulizer. This vapor is then sprayed into the spray chamber, another specific glass piece for this instrument. From here, it is sprayed into the inductively coupled plasma as small droplets, whereby it is finally atomized.[2] The atoms present in the sample are excited by the energetic species found in and produced by the plasma and emit specific light wavelengths characteristic of the distinctive elements found in the sample.[2] These light wavelengths are then allowed to enter the optical portion of the spectrometer. In here, the light bounces off several mirrors and contacts two different diffraction gradients before it hits the linear photo diode array (PDA).[2] This array consists of 1024 individual photo diodes called pixels.[2] There are many different wavelengths that are combined within this array, but only a few of them are really truly necessary. This is because certain elements emit characteristic wavelengths, and these are the wavelengths that are usually sought by the researcher. Thus, specific masks engineered with specific line lengths and gradients are used to determine only those elements that the researcher desires. However, some masks–called multi-element masks[2]–have the ability to analyze for several different elements at the same time.

Engineering the spectral lines of the masks is difficult. For one, the width of the gradients that light has to pass through on the mask has to be less than 10 picometers, because generally speaking, the spectral lines emitted by the ICP are less than 10 picometers. The spectral lines have to be determined by high resolution optics before the instrument is ever used.[3] These masks then help to determine the actual elements in the samples and are the qualitative measures of the sample. Also, the inhomogeneous nature of the plasma makes each reading different. Every time that the light passes through these gradients on the masks, the intensities are not the same. An average is used to determine the actual reading, which is the quantitative measure of the element in the sample. This can affect precision, but the average is generally accepted as a valid quantity.[3] These are the tools used to measure the sample qualitatively and quantitatively.

There are parameters also to be followed concerning the ICP: electron number densities, atom and ion emission intensities, number densities of analyte and argon species, and spectral line widths.[3] The higher temperatures and the higher analyte number densities give higher emissions intensities for the ionic species.[3] Simply put, if there are more ions of the element present, the intensity of the light emitted will be stronger. Thus, the quantitative numbers of the element will be much higher. Higher temperatures do this as well. However, the temperature's effect is all relative. It does increase the intensity, but it increases the intensity of all of the elements, not just the element that the researcher is testing. The percentage of that element does not necessarily increase, because the relative abundance of it is still the same. Electron number densities and high temperatures together tend to show the degree of ionization of the sample by the deviation from the local thermodynamic equilibrium (LTE).[3] It is also accepted that the ICP is a non-local thermodynamic equilibrium because of its inhomogeneous nature. Under steady conditions–the conditions of most ICP's–the species within them are regarded as constant.[3]

The most important parameter, though, is the spectral line width. This mainly concerns the effect that broadening has on the analysis. Most of this broadening is caused by electron impact within the plasma itself, which is called Lorentz Broadening.[3] Among other sources of this broadening, there is natural broadening from the Heisenberg Principle, or the Scattering Effect. The relative motion of the ionic species causes a shift in the wavelengths of the elements and the samples. This is called the Doppler Effect. Excited atoms hit ground-state atoms, causing Holtzman Broadening. Finally, Stark Broadening occurs when "Spectral lines from the plasma are broadened by the interaction between the emitting atoms and the local electric field generated by the surrounding ions and electrons."[3] All of this broadening tends to affect the qualitative as well as the quantitative measurements of the samples, because it skews the instrument's reading area. What this means is that broadening needs to be lessened. This is one of the main problems with simple atomic emissions spectroscopy, especially when one is using ICP as a source.

The ICP is only one of the analytical techniques that is used by the ICP/TOF-MS. In fact, it is only used as the ionizing source. The actual analysis is conducted by the mass spectrometry portion of the instrument. This is the place where the samples are determined and their images stored.

Mass spectrometry (MS) is different from all of the other forms of analytical techniques in that it does not involve irradiating a molecule at its ground-state energy level and then measuring the amount of radiation that is absorbed. The mass spectrometer simply ionizes the molecules and measures the ions.[5] Specifically, it measures the mass-to-charge ratio. However, the one aspect that cannot go unnoticed about MS is that it is destructive, much like the ICP. Once the sample is introduced into the system, it cannot come back. However much is used for the analysis is however much is lost. This is because the mass spectrometer changes the form of the sample to its ions. Generically speaking, the molecules fragment into their cations and electrons according to the following reaction:

$$M \rightarrow M^{+} + e^{-}$$

Molecules do typically fragment like this, but specific compounds and elements have specific fragmentation patterns which may look different. These fragmentation patterns give way to fragmentation pathways that show a spectrum of the masses of the different fragments of the compound.[5]

A molecule or compound fragments because the mass spectrometer ionizes the compound by use of an ion source. There is a wide range of ion sources that can be used, especially with a mass spectrometer. An ICP is a logical choice, and it is the one that is used in this research. Sometimes, even with the ICP, the ionization is not complete because some of the ionized material does not have enough internal energy to make it to the ionized state.[5] It just simply reverts back to the sample.

Ion repeller plates are located after the ion source and direct the molecules that have ionized toward the accelerator plates located on the other side of the chamber. These accelerator plates contain a high potential. The ions flow by as the plates increase the kinetic energy of the ions and, thereby, their velocity. From there, more magnets force the molecules to bend or travel through a sector of a circle designed for the instrument. After this travel, the ions reach the detector, which simply measures the velocity of the ions as they travel by the mass analyzer. The mass is determined from the measured velocity through the following simple physical kinetics equation:

$$KE = \frac{1}{2} mv^2$$

Since the kinetic energy is constant for all ions present because of the accelerator plates, and the velocities are determined by the mass analyzer, the only variable in the equation is the mass. This is calculated mathematically by the computer, and then the masses are placed on the spectrum for the specific sample.

These mass spectra are very characteristic of each sample. There are four main factors that help to determine the specific fragmentation pathways of the sample: strengths of bonds, stability of fragmentation products, internal energy of fragmenting ion, and the time interval between ion formation and ion detection.[5] The most intense peak on these characteristic spectra is usually the base peak, or the fragment most frequently made by the compound when ionized. All compounds have typical base peaks as well as typical fragmentation patterns, a situation which explains why it is easy to tell qualitatively what the sample is from a mass spectrometer, as soon as one learns how to discern the fragmentation patterns.

The typical mass analyzer used for a mass spectrometer is a quadrapole mass analyzer[6], which is especially used for plasma source mass spectroscopy. The major drawback concerning this analyzer is that it can only read one mass at a time. Therefore, most of the analyte is wasted, and the sensitivity and sample throughput are reduced.[6] The way to counter this problem is to implement a mass spectrograph, which is the coupling of a mass spectrometer with an array detector.[6] This improvement allows for analysis of all of the sample at a faster speed and with better sensitivity. However, the mass spectrometer is not necessary. Two quadrapoles can be connected to an ICP, the combination of the two constituting an ICP-AES. This gives better sensitivity and a quicker pace, but it does still lose part of the sample because of the plasma beam.[6]

All of these connections have the ability to be connected to an ICP. That is why the trend in analytical chemistry began to move toward combining the two techniques. The ICP provides high ionization with low detection limits[3] while mass spectrometry provides very respectable and accurate data of the samples as well as typical qualitative characteristics of specific samples.

The combination of the ICP and the mass spectrometer led to the development and the onset of the ICP-MS. The positive viewpoint of the combination of these two instruments is that it provides better detection limits via the ICP with less background noise via the mass spectrometer.[6] This form is also very handy because it is much simpler than the atomic emissions spectroscopy. ICP-MS provides less chance for overlap of data while still enabling the instrument to maintain very low detection limits.[7] The ICP allows for trace-element analysis, analysis of very rare elements that are not found in abundance but are only found in the smallest traces in samples. The complications only arise while the molecular ions are forming.[7] The ICP is a good source for ionization, but the transition from the ICP to the MS can sometimes be tricky, leading to these complications. The ICP-MS is also known as a versatile instrument because it has the ability to analyze several different types of samples.[8] It can analyze liquid and solid as well as the slurry samples, much like the ICP-AES. Because of its use of the MS, it is a much more stable instrument and provides better and more accurate data because the calibration of the ICP-MS is much simpler.[8]

During the time of ionization, there are some variables that need to be watched. They are the forward power (voltage), gas flows (including injector flow rate), and mass spectrum input ion-optic voltages. If not monitored correctly, they can cause considerable background noise and overlap.[7] The gas flows influence the number and distribution of particles in the aerosol that make their way to the nebulizer. In turn, the gas flows influence the number of particles that make their way to the plasma torch itself.[8]

After ionization, the ions enter into the mass spectrometer and are analyzed by a quadrapole mass analyzer. It is only a scanning monochromator; that is, it scans for one element at a time, but it is still very accurate.[7] On the quadrapole analyzer, there are two cones, the sampler cone and the skimmer.[7] These help to constitute the scanning monochromator, which will scan the whole spectrum of the sample.

As with the ICP-AES, overlap and background noise can still occur with the ICP-MS. It is a mass spectrometer, so the overlapping will be much less. The overlapping will occur between naturally occurring isotopes and background materials. Chemicals found in the background are usually the digesting acid of the sample preparation method. Typically, this is nitric acid (HNO_3). It is chosen because its background noise is similar to the background noise of water, and so it typically does not show a lot of interference with the sample's spectrum.[7]

Because it is obvious that the ICP-MS is a much more efficient and accurate analytical instrument than the ICP-AES, the trend is starting to shift even more toward the ICP-MS. A prototypical type of ICP-MS is the ICP/TOF-MS, which requires the use of a Time-of-Flight Chamber within the mass spectrometer itself. This Time-of-Flight Chamber is a major improvement over the scanning monochromator that is present in the typical ICP-MS.

It has been shown that most mass analyzers utilize quadrapole scanners. The Time-of-Flight Chamber is much faster than this scanning technique ever could be. It has a much higher ion throughput than the quadrapole mass analyzers, and it provides a complete spectrum for each extraction of the sample made instead of simply one at a time.[9] These high ion transmissions are extracted in one pulsed event by the ICP/TOF-MS,[10] which also provides a higher resolution because it makes a recording of the spectra every second. There are literally thousands of masses that are present and recorded each and every second. Because there is so much more information collected here as compared to the quadrapole analyzer, the information is more precise and accurate. This leads to the very high sensitivity present in the Time-of-Flight Chamber. There are actually thousands of spectra taken, recorded, and stored every second because the distance between the masses is a nanosecond or less.[9] This means that the readouts must be fast to be able to keep up with the uptake of the information by the computer. There is one major complaint with this Time-of-Flight Chamber. Since it has to operate on a pulse and the

ICP operates on a continuous beam, there is some transmission efficiency and sensitivity lost.[9] The ICP/TOF-MS is not truly as simultaneous as it seems, and it is not good for analyzing samples with varying signals.[6] Yet, it is about as close to being simultaneous as an instrument can be and still provide very good data. All in all, the spectral acquisition of the Time-of-Flight Chamber exceeds that of the quadrapole mass analyzer by about two to three orders of magnitude.[10]

The data given by the ICP/TOF-MS is very complete and accurate. It produces a spectrum of all the elements--not just one at a time--giving complete ion throughput because the entire analog signal at the detector is recorded. Typically, the starting velocities of all of the masses are roughly equal.[10] Since kinetic energy has been proven by the previously cited equation to be mass-dependent, the time at the analyzer is recorded, and so the discrepancy between the two times (starting and finishing) is used to determine the velocities. From there, the masses are determined. Then, the spectrum is presented. Resolution and sensitivity of the molecules and the instrument depend on the time spread between certain molecules of the same mass contacting the detector. If there is any overlap of this time spread and any other mass's time spread, then the resolution is inadequate.[9]

One other advantage that the ICP/TOF-MS possesses that the quadrapole mass analyzers do not possess is a structural one. Because the ICP/TOF-MS can be aligned directly or perpendicularly to the beam of ions[9], these analyzers may be constructed in many different ways instead of in the long, rectangular box pattern that takes up a lot of horizontal space. Quadrapole mass analyzers have to be lined up directly to the ion beam, or else they cannot analyze anything at all. It is true that the quadrapoles have more sensitivity than the ICP/TOF-MS, but one of the two structural types of the ICP/TOF-MS can rival this sensitivity, namely the perpendicular type.[9] In fact, this type of ICP/TOF-MS is about three thousand times greater in sensitivity than the other form.[9] This is due to the fact that the on-line ICP/TOF-MS takes small samples of the plasma beam in short periods of time, while the perpendicular version can sample a larger percentage of the beam in its pulse since it is filled with the continuous beam of the ICP before it makes its extraction.[9]

Conclusions have been made and they tend to favor the ICP/TOF-MS, because it provides one with a greater degree of sensitivity while also providing one with great accuracy and complete ionization. It is the promising final development of these types of analytical techniques. "With a fast data-acquisition system and a right-angle geometry, the TOFMS should be able to sample nearly 50% of the continuous ion beam generated from the ICP."[9]

Materials and Methods

The sample to be used in the ICP preparation is a reference sample that comes from the national standards association–National Institute of Standards (NIST)–which has already determined the percentages of elements within this specific reference sample named 1633b. Therefore, one can calibrate the ICP with this standard by analyzing the reference standard for specific elements. The numbers acquired in the analysis can then be compared to NIST's reference values for the standard, which is the basis of this experiment.

As a coal ash sample, 1633b is a coal sample that has been heated to an exceedingly high temperature. This sample, like other coal-ash samples, is collected from the inside of a combustor after it has had the enormous heat of the combustion process occur and has transformed the original coal samples into this ash sample. Thus, an ash sample like 1633b tends to be different from a coal sample, because it has no carbon and very little sulfur. This is because the exceptional heat has degraded all of the carbonaceous material within the original coal sample and most of the sulfur.

NIST is a society that makes the standards and standard test methods for the analysis of materials in the analytical chemistry world, so their reference standards are the best choice to use in the calibration of new instrumentation, like the ICP/TOF-MS or the ICP-AES. Because 1633b is a reference sample made and calibrated by NIST, it can be used in experimental method development such as this experiment.

Once a bottle of 1633b has been obtained, the researcher proceeds into discovering the best way to prepare these samples for analysis. The first step in all of this is to ash the samples. The correct way to do this is via the American Society for Testing and Materials (ASTM) method, numbered D3682[11], which involves taking the sample, whether it is an ash sample or not, and grinding it to pass through a 250-micrometer sieve. The sample is then spread over a porcelain or quartz dish and placed in a cold muffle furnace. The temperature for the furnace is then set at 500°C. The furnace is to reach this temperature in one hour, after which it is turned up to 750°C. The sample is allowed to sit in the furnace at this temperature for two hours. This is to ensure that all of the carbonaceous material in the sample has been destroyed. The sample is then taken out of the furnace and allowed to cool. Once this has been accomplished, the sample is ground again and passed through a 75-micrometer sieve. The amount of sample that passes through the sieve is placed back into the furnace at 750°C for one hour. After this final heating, the sample is placed into a plastic sample bottle.[11]

The next step is the questionable part of the whole experiment. This is the point at which the sample is dissolved and prepared as a liquid sample so that the ICP can analyze it. There are many different variations of the dissolution procedure that can be used for these samples, and the object of this whole experiment is to determine which variation is the best. Before this can begin, though, all of the apparatus needed in the dissolving process must be cleaned with 5 + 95 nitric acid (five parts nitric acid, 95 parts water) and then rinsed with reagent-grade water. Also, the apparatus needs to be handled with tongs so as not to contaminate it with the oils of the hands.

Contamination is a major problem in ICP analysis, so these steps are very necessary in order to avoid as much of the contamination as possible. Apparatuses needed in all of the different variations of dissolution procedures include the following: graphite crucibles, stirrer/hot plates, teflon beakers, glass beakers, watchglasses, glass flasks, plastic sample bottles, specific acids, mixed acid solutions, a mortar, a pestle, and an accurate balance.

The first method used to dissolve the sample involves the use of hydrofluoric acid and aqua regia. Aqua regia is an acid that contains one part nitric acid, three parts hydrochloric acid, and one part water. It is a potent acid that is used to dissolve samples very completely. One takes 0.1000 +/- 0.0001g of the sample and places it into a teflon beaker, adding 5 mL of each of the acids and heating the sample to dryness. Next, he adds water and heats the sample to dryness once more. After this, the sides of the teflon beaker are rinsed off with water, and the rinse water is collected in a glass beaker. Then, one dilutes to 100 mL the sample obtained from rinsing the teflon beaker. The sample is now fully prepared from this method. The problem with this method of dissolution is that there is a lot of loss due to evaporation, but luckily there is no loss due to the actual preparation of the sample.

The second method is similar to the first in that it involves the use of a mixed-acid dissolution. The sample is placed into a 250 mL polycarbonate bottle with an o-ring seal and a screw cap. This bottle should be able to withstand up to 130°C as well as the pressure developed during digestion. One adds 0.1000 +/- 0.0001 g of sample and the mixed acid used to digest the sample into this bottle. The mixed acid solution used in this variation is a 70-part hydrochloric acid and a 30-part hydrofluoric acid mixture. Five mL of this mixed acid solution are added to the sample in the bottle, and 2.0 mL of nitric acid are then added. The bottle is then placed into a steam or hot water bath, or an oven for two hours to heat at 130°C. After two hours, one removes the bottle from the heating apparatus and adds 93.0 mL of 1.5% boric acid (H_3B0_3) to the sample. The bottle is then placed back into the heat source and heated for another hour. After cooling down, the sample is now fully prepared for analysis by the ICP. Once again, this style of preparation loses a lot of the sample through silica precipitation, but there is less loss due to evaporation and transfer.

The final variation involves the use of the lithium tetraborate pellet once again. The same amount of sample and lithium tetraborate are added and mixed together as before, but this time, they are placed into a conical-bottomed graphite crucible. The crucible is then placed into the furnace and heated to 1000°C. It is allowed to heat for fifteen minutes, and then it is taken out of the oven as a scalding, molten, glass-like ball. While it is still hot, it is poured into a beaker where 50 mL of a diluted aqua regia solution (one part nitric acid, three parts hydrochloric acid, and 46 parts water) has been poured. The meeting of the hot glass ball and the acid produces a tremendous release of energy, causing the ball to break very easily, allowing it to dissolve much more fully. This rids the process of the precipitation of the silica, because the sample in the beaker is immediately transferred to a stirrer/hot plate and heated. Also, the aqua regia is a good acid for fully dissolving the silicon within a sample. The sample is then covered with a watchglass, in order to stifle any evaporation problems. Once the sample is obviously dissolved, it is transferred to a flask and diluted to 100 mL. This solution is then filtered and the final sample placed into a plastic bottle for storage. The reasoning behind placing the sample in plastic bottles is so that the acids that are within the sample will not dissolve any of the glass of the flask and make the sample inherit any extra silicon. Problems with this method are that there is still some evaporation loss as well as loss due to transfers, but this variation has proved to be the most consistent with ideal sample preparation for the ICP.

Within this last method of preparation, there are variations. The first one involves the acids that can be used to dissolve the pellet. One can use 5% hydrochloric acid (HCl) or 5% nitric acid (HNO_3). The second modification has the heating time in the oven being varied between 5, 10, and 15 minutes. Also, there is the test of whether or not pouring the pellet out as a hot, molten ball is better than letting it cool before placing it in the digesting acid. Finally, the last variation involves stirring the molten ball directly after heating or not stirring it.

These are the three typical preparation procedures applicable to ICP analysis that are capable of fully dissolving the sample. Once this reference standards has been dissolved and fully prepared, the next step is to make the ICP elemental standards for the calibration of the specific ICP method. There needs to be a low standard (presumably 10 parts per million) and a high standard (presumably 100 parts per million) for each element in question. All of the elements in question can be combined into three solutions–low, middle, and high–whereby all of the elements can be analyzed and calibrated at once. This is because the ICP/TOF-MS has the ability to run about thirty different elements all at the same time, and the ICP-AES has the capability to analyze up to six elements at a time. The two points, the high and the low, make a straight calibration line for the instrument for each element so that the numbers acquired by the analysis can be believed and used.

The typical elements analyzed by the ICP-AES are aluminum (Al), barium (Ba), calcium (Ca), iron (Fe), magnesium (Mg), manganese (Mn), phosphorous (P), potassium (K), silicon (Si), sodium (Na), strontium (Sr), sulfur (S), and titanium (Ti). These elements are usually about 90 to

95% of the total elemental components of materials, not including carbon. The analysis of these elements thus proves very successful for the ICP, because it gives the instrument the ability to analyze the entire sample, and therefore provide a very good quantitative analysis. Carbon is not prevalent here, as explained above in the ashing procedures. It is burned off by the excessive heat. Sulfur is not necessarily a question in most labs either, because most labs contain some type of automated sulfur analyzer that analyzes for sulfur, thereby reducing the workload of the ICP. These analyzers generally do not require any preparation whatsoever. The ashing procedures burn most of the sulfur and all of the carbonaceous materials off so that the researcher can analyze the other elements in the sample much more easily, giving him a better representation of the entire sample. The only other two elements that are not analyzed for by the ICP-AES in this experiment are barium and strontium, because they are trace elements that do not constitute a great deal of the sample's elemental percentages and are hard to detect using the ICP-AES.

Each element also has its own specific wavelengths of light where the ICP expects the intensities of certain elements to be located. These wavelengths are measured in nanometers (nm). If the intensities of these samples are not at these wavelengths, then there is a problem with the ICP more than likely.

Element	Wavelength(nm)
Aluminum	396.152, 256.80, 308.215, 309.271
Barium	455.403, 493.41, 233.53
Calcium	317.93, 315.887, 364.44, 422.67
Iron	259.940, 271.44, 238.204
Magnesium	279.553, 279.08, 285.21, 277.983
Manganese	257.610, 294.92, 293.31, 293.93
Phosphorous	178.287, 214.900
Potassium	766.491, 769.896
Silicon	212.412, 288.16, 251.611
Sodium	588.995, 589.592
Strontium	421.55
Sulfur	180.73, 182.04, 182.62
Titanium	337.280, 350.50, 334.941

Each specific element is calibrated by the standards prepared for the ICP, not a reference coal-ash standard. The ICP elemental standards involve the use of standard elemental solutions that are diluted so as to have the right amount of parts per million to fit the amount the experiment calls for, such as 10 or 100 parts per million (ppm). These low and high standards fit a calibration curve when analyzed by the instrument. Once this curve is established, the samples, 1633b, can be analyzed. The value for the standard is then determined by measuring the intensity of the sample's reading and comparing it to the calibration that has been established by the two ICP elemental standards. Wherever the intensity of the signal fits on the curve determines the amount of parts per million for the sample and gives the quantitative results for the reference standard.

The analysis of the samples by the ICP-AES produces qualitative and quantitative results and is the final step in the procedures of analyzing the samples. Once this final step has been accomplished, the data accumulated from the analysis of the reference standards is compared against its known concentrations, which come along with the standards and are provided by NIST. If the data for the reference standards is within the given error range of each element, then the ICP has been calibrated and the method is successful in determining the elements in a given sample. However, if it does not fall within the error range, then the method is deemed unsuccessful and must be either corrected or not used anymore. This error range is used to compare the different variations within methods and the different methods themselves to see which is a better preparation procedure.

For each method and variation, there were duplicates run for each sample. The first method, which involved the dissolution of the sample in a teflon beaker with hydrofluoric acid, had a blank prepared containing only the acid and water. The weights of the two duplicates prepared for this method were the following:

1633B #1: 0.3031 g

1633B #2: 0.3015 g

The second method involved the use of a mixed-acid solution and polycarbonate bottles to dissolve the sample. A blank was also prepared by this method that had no sample in it, only lithium tetraborate. The weights of the two duplicates that were prepared were the following:

1633B #1: 0.1001 g

1633B #2: 0.1000 g

The third method involved the dissolution of a glass-like pellet by certain acids with specific variations in the preparation. The first two variations were combined to show which acid and which oven time worked best in the preparation method. A blank was prepared along with the duplicates of each acid and contained only lithium tetraborate, no sample.

	5% HCl	5% HNO_3	Aqua Regia
5 min. #1	0.0999 g	0.1002 g	0.1002 g
5 min. #2	0.1002 g	0.1003 g	0.0996 g
10 min. #1	0.1004 g	0.1004 g	0.0998 g
10 min. #2	0.1001 g	0.1000 g	0.1002 g
10 min. #3	N/A	N/A	0.1000 g
15 min. #1	0.1000 g	0.0996 g	0.1000 g
15 min. #2	0.1003 g	0.0999 g	0.0995 g

Another variation involved stirring or not stirring the sample after it was taken out of the oven. There were blanks prepared consisting of only lithium tetraborate for the stir variation and the non-stir variation. The weights were the following:

1633B #1 Stir: 0.0998 g
1633B #1 Non Stir: 0.0996 g
1633B #2 Stir: 0.0997 g
1633B #2 Non Stir: 0.1002 g

A different variation involved whether the pellet was placed into the digesting acid immediately after it was taken out of the oven as a "hot pellet" or if it was allowed to cool to room temperature before being placed into the acid as a "cold pellet." There were, of course, blanks prepared of both kinds. The weights of the samples were the following:

1633B #1 Hot: 0.0998 g
1633B #1 Cold: 0.1002 g
1633B #2 Hot: 0.1001 g
1633B #2 Cold: 0.1001 g

The final variation involved using the graphite crucibles, some of which were new, unused crucibles and others which were used crucibles. This was to test if the preparation method could be replicated with reused graphite crucibles instead of new crucibles each time. Economically speaking, this would be very handy. They were also blanks prepared with these samples, and the weights of the samples were the following:

1633B #1 New: 0.0997 g
1633B #1 Old: 0.0997 g
1633B #2 New: 0.1004 g
1633B #2 Old: 0.0999 g

The final piece of equipment was the actual instrument, the ICP-AES. This instrument was used because this experiment is a developmental experiment. The ICP-AES was more easily acquired and has the ability to provide the researcher with the same data as the ICP/TOF-MS. The data needed only to be very general to indicate the general trends of the different preparation procedures. Therefore, the best method of preparation should easily stand out against the rest.

Results

After each stage, the results of that stage were examined to see how well that form of preparation worked and to compare it to the results of the previous stage or stages. Changes were then made in the preparation methods to optimize the results of the next stages in order to find the best method possible for dissolution. These changes were necessary because the later preparation stages were all dependent on the results of the preceding stages. Therefore, after comparing the numbers of the preceding stages, a decision was made regarding which part of that stage was a better way to prepare the samples. Once this decision was made, the experiment progressed to the next stage. This decision was implemented to prepare the samples in the next stage if the two successive stages were testing for the same type of procedure. If the two successive stages were testing different facets of the sample preparation, then the results were used for the stages dependent upon results for that facet of the sample preparation.

The first results examined involved the use of the three different types of acids in dissolving the samples: 5% nitric acid, 5% hydrochloric acid, and aqua regia. Another parameter other than the dissolution of the samples with three different acids was added to these samples. This parameter was the variability of the heating time for the fusion of the lithium tetraborate pellet. Three different heating times of the samples at 1000^{0}C in the oven were used: 5, 10, and 15 minutes. Each acid had three different sets of samples assigned to its preparation, one set for each separate heating time. Duplicates were run of each acid at each of the three heating times. Each set consisted of two duplicates and a blank that was prepared for each time and each acid. There were a total of nine samples for each acid in this first part of the preparation study.

What was analyzed in the numbers was the recovery percentage of the sample, 1633b. The researcher wanted the recovery to be somewhere within the 95-100% range so that there could be complete confidence in the method as well as the instrument.

At first, the samples were analyzed, and their values were given in ppm (Table 1). From there, the numbers in ppm were put through a formula tthat produced their elemental percentages. The formula was the following:

$$[C - B/D] \times D \times V/W \times 100\%$$

C was the concentration of the sample given in parts per million. B was the concentration of the blank given in parts per million. D represented the dilution factor of the sample. This meant that if a sample had to be diluted to 1/10 of its original concentration to fit into the calibration range, then the dilution factor would be ten. However, if the sample were analyzed before being diluted, then the dilution factor would be one. This dilution factor had a lot of significance, especially regarding how much the blank took away from the sample concentration. V stood for the volume of the sample, which was always 0.1 L. W stood for the weight of the sample as measured in milligrams. This formula gave the percentages of each element by a final multiplication of 100%. Once these numbers were obtained, they were converted into their oxide forms by specific oxidation conversion figures:

Element x Conversion Factor = Oxide

$Al \times 1.890 = Al_2O_3$

$Fe \times 1.430 = Fe_2O_3$

$Mg \times 1.658 = MgO$

$Na \times 1.348 = Na_2O$

$Si \times 2.139 = SiO_2$

$Ca \times 1.400 = CaO$

$K \times 1.205 = K_2O$

$Mn \times 1.582 = MnO_2$

$P \times 2.292 = P_2O_5$

$Ti \times 1.668 = TiO_2$

The oxide numbers were calculated for each specific stage and duplicate. Once this was accomplished, the oxides for one specific sample were added together to see how close this sum came to the 95-100% recovery that the researcher sought. This was done for each sample to show comparisons between successive stages and later stages as well. The only strange thing was that the oxide numbers in almost all cases seemed to be within the recovery range that the researcher wanted, but some of the numbers did not compare to the elemental percentages of the 1633b reference standard. This non-comparison was the reason that the numbers had to be scrutinized to see if each samples's recovery was true, or if the recovery was too high because of other contaminating influences. This contamination factor was weighed in the researcher's mind when discerning whether or not that particular form of method preparation was good.

Table 1. Elemental values of ashes in parts per million (ppm)

	Al	Ca	Fe	K	Mg	Mn	Na	P	Si	Ti
Aqua Regia 5 min. #1	14.77*	15.85	75.85	1.18*	6.33	6.76	0.94	2.96	23.87*	7.87
Aqua Regia 5 min. #2	15.04*	15.63	76.5	1.27*	6.2	7.26	1.19	3	24.03*	7.81
Aqua Regia 10 min. #1	15.15*	15.48	77.59	1.36*	6.24	7.49	0.99	2.71	24.28*	7.89
Aqua Regia 10 min. #2	12.65*	13.19	66.27	1.23*	5.27	6.43	1.11	2.3	20.46*	6.67
Aqua Regia 10 min. #3	15.37*	14.94	73.38	1.38*	6.05	7.39	1.23	2.42	23.83*	7.7
Aqua Regia 15 min. #1	15.11*	14.51	73.27	1.37*	5.92	7.37	0.94	2.15	23.42*	7.68
Aqua Regia 15 min. #2	15.41*	14.69	71.89	1.48*	5.93	7.72	1.1	1.92	23.69*	7.54
5% HNO3 5 min. #1	13.22*	16.63	78.34	2.37*	5.52	7.46	3.27	5.23	23.41*	7.39
5% HNO3 5 min. #2	13.52*	16.67	80.65	2.53*	5.61	7.87	3.4	5.71	23.91*	7.64
5% HNO3 10 min. #1	13.36*	16.88	77.87	2.69*	5.72	8.02	3.56	4.63	23.6*	7.68
5% HNO3 10 min. #2	13.54*	17.29	82.58	2.73*	5.74	8.55	3.47	4.34	24.01*	7.55
5% HNO3 15 min. #1	13.91*	16.95	82.91	2.84*	5.71	8.34	3.34	4.83	24.37*	7.67
5% HNO3 15 min. #2	13.75*	17.31	82.94	2.9*	5.79	8.14	3.41	4.3	24.59*	7.6
5% HCl 5 min. #1	11.81*	15.32	75.33	2.31*	5.12	0.14	3.76	6.66	22.54*	7.64
5% HCl 5 min. #2	11.19*	15.03	76.53	2.52*	5.12	0.14	3.98	6.43	22.23*	7.55
5% HCl 10 min. #1	11.09*	15.43	75.79	2.55*	5.25	0.14	3.51	6.32	22.31*	7.57
5% HCl 10 min. #2	10.93*	21.69	80.13	2.71*	5.41	0.14	4.2	6.56	22.31*	7.8

Table 1 (Cont.)

5% HCl 15 min. #1	10.43*	17.14	77.53	2.86*	5.26	0.13	3.79	6.06	21.83*	7.55
5% HCl 15 min. #2	10.7*	16.18	80.76	2.99*	5.39	0.13	4.27	6.27	22.48*	7.67
Hot Pellet #1	13.97*	14.96	74.55	2.16*	5.1	0.13	4.04	7.67	23.13*	7.67
Hot Pellet #2	13.76*	14.08	70.16	2.16*	4.9	0.13	3.83	7.59	22.64*	7.43
Cold Pellet #1	14.59*	14.21	71.72	2.34*	4.97	0.04	3.58	7.76	23.21*	7.66
Cold Pellet #2	14.82*	13.64	69.53	2.33*	4.88	0.13	3.97	7.94	23.26*	7.7
New Graphite #1	14.71*	13.33	71.39	1.97*	4.79	0.16	4.02	6.83	21.55*	7.31
New Graphite #2	15.37*	12.75	66.5	1.54*	4.62	0.18	3.7	7.06	22.27*	7.32
Used Graphite #1	14.83*	13.12	65.38	0.75*	4.58	0.19	2.6	6.99	22.77*	7.26
Used Graphite #2	15.59*	15	76.01	7.89*	5.07	0.23	1.28	6.91	24*	8
Stir #1	14*	16.75	75.01	2.48*	5.39	0.25	3.03	6.81	21.13*	7.14
Stir #2	12.96*	16.91	75.39	3*	5.29	0.22	2.1	7.11	20.57*	6.77
Not Stir #1	12.78*	17.12	74.18	3.15*	5.23	0.17	1.36	7.72	19.64*	6.77
Not Stir #2	13.31*	17.05	73.97	3.61*	5.25	0.08	1.57	7.44	20.51*	6.64
Mixed Acid #1	19.63*	13.9	72.75	0.92*	8.59	0.19	2.42*	8.15	77.23*	7.27
Mixed Acid #2	18.5*	20.03	100.1	2.07*	9.45	0.12	3.83*	9.69	56.28*	9.39
Teflon #1	32.84*	19.22	12.65*	1.72*	7.62	0.36	5.76	2.38*	11.91*	1.64*
Teflon #2	34.96*	19.68	13.46*	1.76*	6.91	0.32	5.42	2.25*	94.74	1.69*

*denotes that the sample numbers used were 1:10 dilution numbers

As was stated, the first two parameters of the study, the acid and the time, were tested in the same step. The numbers for this part of the experiment (Tables 2, 4, and 6) are the percentages of each metal found in the samples as compared to the true 1633b elemental values as certified by NIST. This table also gives the relative error between the sample's elemental percentage and the certified values. The data in tables 3, 5, and 7 lists the oxide percentages found in the samples and compares the data to the true 1633b oxide values, which were produced by taking the NIST certified values and multiplying them by their elemental conversion factors. At the bottom of each column is the sum of the percentages of the oxides found in the sample; this number is the number the researcher was hoping would be somewhere within the 95-100% confidence range.

Table 2. Elemental percentages of Aqua Regia Samples

	True 1633b	5 min. #1	5 min. #2	10 min. #1	10 min. #2	10 min. #3	15 min. #1	15 min. #2
Al	15.05	14.74	15.1	15.18	12.63	15.37	15.11	15.49
Rel. Error		2.06	-0.33	-0.86	16.08	-2.13	-0.4	-2.92
Ca	1.51	1.44	1.42	1.14	0.91	1.08	1.36	1.38
Rel. Error		4.64	5.96	24.5	39.74	28.48	9.93	8.61
Fe	7.78	7.55	7.66	7.72	6.56	7.29	7.3	7.19
Rel. Error		2.96	1.54	0.77	15.68	6.3	6.17	7.58
K	1.95	1.18	1.28	1.35	0.91	1.36	1.34	1.45
Rel. Error		39.49	34.36	30.77	53.33	30.26	31.28	25.64
Mg	0.482	0.63	0.62	0.62	0.52	0.6	0.59	0.6
Rel. Error		-30.71	-28.63	-28.63	-7.88	-24.48	-22.41	-24.48
Mn	0.013	0.003	0.003	0.003	0.003	0.003	0.003	0.003
Rel. Error		76.92	76.92	76.92	76.92	76.92	76.92	76.92
Na	0.201	0.1	0.12	0.1	0.11	0.13	0.1	0.11
Rel. Error		50.25	40.3	50.25	45.27	35.32	50.25	45.27
P	0.23	0.28	0.29	0.26	0.22	0.23	0.19	0.17
Rel. Error		-21.74	-26.09	-13.04	4.35	0	17.39	26.09
Si	23.02	23.72	24.03	24.22	20.31	23.72	23.31	23.7
Rel. Error		-3.04	-4.39	-5.21	11.77	-3.04	-1.26	-2.95
Ti	0.791	0.78	0.78	0.79	0.66	0.76	0.76	0.75
Rel. Error		1.39	1.39	0.13	16.56	3.92	3.92	5.18

Table 3. Oxide percentages of Aqua Regia Samples

	TRUE 1633b	5 min. #1	5 min. #2	10 min. #1	10 min. #2	10 min. #3	15 min. #1	15 min. #2
Al	28.44	27.85	28.54	28.69	23.87	29.04	28.56	29.27
Rel. Error		2.074543	-0.35162	-0.87904	16.06892	-2.1097	-0.42194	-2.91842
Ca	2.11	2.01	1.99	1.59	1.27	1.52	1.9	1.94
Rel. Error		4.739336	5.687204	24.64455	39.81043	27.96209	9.952607	8.056872
Fe	11.13	10.8	10.96	11.04	9.38	10.42	10.43	10.29
Rel. Error		2.96496	1.527403	0.808625	15.72327	6.379155	6.289308	7.54717
K	2.35	1.42	1.54	1.62	1.1	1.64	1.61	1.75
Rel. Error		39.57447	34.46809	31.06383	53.19149	30.21277	31.48936	25.53191
Mg	0.8	1.05	1.03	1.02	0.86	0.99	0.98	0.99
Rel. Error		-31.25	-28.75	-27.5	-7.5	-23.75	-22.5	-23.75
Mn	0.021	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Rel. Error		52.38095	52.38095	52.38095	52.38095	52.38095	52.38095	52.38095
Na	0.27	0.14	0.17	0.14	0.15	0.18	0.14	0.16
Rel. Error		48.14815	37.03704	48.14815	44.44444	33.33333	48.14815	40.74074
P	0.53	0.65	0.66	0.6	0.5	0.53	0.45	0.4
Rel. Error		-22.6415	-24.5283	-13.2075	5.660377	0	15.09434	24.5283
Si	49.24	50.73	51.4	51.8	43.44	50.74	49.86	50.69
Rel. Error		-3.026	-4.38668	-5.19903	11.77904	-3.0463	-1.25914	-2.94476
Ti	1.32	1.3	1.3	1.31	1.1	1.28	1.28	1.26
Rel. Error		1.515152	1.515152	0.757576	16.66667	3.030303	3.030303	4.545455
Oxide Sum		95.95	97.6	97.82	81.68	96.33	95.21	96.73

Table 4. Elemental percentages of 5% HNO_3 Samples

	True	5 min.	5 min.	10 min.	10 min.	15 min.	15 min.
	1633b	#1	#2	#1	#2	#1	#2
Al	15.05	13.19	13.48	13.3	13.54	13.97	13.76
Rel. Error		12.36	10.43	11.63	10.03	7.18	8.57
Ca	1.51	1.58	1.58	1.6	1.64	1.55	1.58
Rel. Error		-4.64	-4.64	-5.96	-8.61	-2.65	-4.64
Fe	7.78	7.82	8.04	7.76	8.26	8.32	8.3
Rel. Error		-0.51	-3.34	0.26	-6.17	-6.94	-6.68
K	1.95	2.34	2.5	2.62	2.67	2.75	2.8
Rel. Error		-20	-28.21	-34.36	-36.92	-41.03	-43.59
Mg	0.482	0.54	0.55	0.56	0.57	0.56	0.56
Rel. Error		-12.03	-14.11	-16.18	-18.26	-16.18	-16.18
Mn	0.013	0.003	0.003	0.003	0.003	0.003	0.003
Rel. Error		76.92	76.92	76.92	76.92	76.92	76.92
Na	0.201	0.23	0.24	0.22	0.21	0.18	0.19
Rel. Error		-14.43	-19.4	-9.45	-4.48	10.45	5.47
P	0.23	0.46	0.51	0.39	0.37	0.44	0.38
Rel. Error		-100	-121.74	-69.57	-60.87	-91.3	-65.22
Si	23.02	23.27	23.74	23.4	23.9	24.36	24.51
Rel. Error		-1.09	-3.13	-1.65	-3.82	-5.82	-6.47
Ti	0.791	0.73	0.76	0.76	0.75	0.76	0.76
Rel. Error		7.71	3.92	3.92	5.18	3.92	3.92

Table 5. Oxide percentages of 5% HNO_3 Samples

	TRUE	5 min.	5 min.	10 min.	10 min.	15 min.	15 min.
	1633b	#1	#2	#1	#2	#1	#2
Al	28.44	24.94	25.47	25.15	25.59	26.4	26.01
Rel. Error		12.30661	10.44304	11.56821	10.0211	7.172996	8.544304
Ca	2.11	2.21	2.21	2.24	2.3	2.17	2.22
Rel. Error		-4.73934	-4.73934	-6.16114	-9.00474	-2.8436	-5.21327
Fe	11.13	11.18	11.5	11.09	11.81	11.9	11.87
Rel. Error		-0.44924	-3.32435	0.359389	-6.10961	-6.91824	-6.6487
K	2.35	2.82	3.02	3.16	3.21	3.31	3.38
Rel. Error		-20	-28.5106	-34.4681	-36.5957	-40.8511	-43.8298
Mg	0.8	0.9	0.91	0.93	0.94	0.93	0.93
Rel. Error		-12.5	-13.75	-16.25	-17.5	-16.25	-16.25
Mn	0.021	0.01	0.01	0.01	0.01	0.01	0.01
Rel. Error		52.38095	52.38095	52.38095	52.38095	52.38095	52.38095
Na	0.27	0.31	0.32	0.3	0.29	0.25	0.26
Rel. Error		-14.8148	-18.5185	-11.1111	-7.40741	7.407407	3.703704
P	0.53	1.06	1.17	0.9	0.84	1	0.88
Rel. Error		-100	-120.755	-69.8113	-58.4906	-88.6792	-66.0377
Si	49.24	49.78	50.78	50.05	51.13	52.11	52.42
Rel. Error		-1.09667	-3.12754	-1.645	-3.83834	-5.82859	-6.45816
Ti	1.32	1.22	1.26	1.27	1.25	1.28	1.26
Rel. Error		7.575758	4.545455	3.787879	5.30303	3.030303	4.545455
Oxide Sum		94.42	96.65	95.1	97.37	99.36	99.22

Table 6. Elemental percentages of 5% HCl Samples

	True 1633b	5 min. #1	5 min. #2	10 min. #1	10 min. #2	15 min. #1	15 min. #2
Al	15.05	11.82	11.17	11.04	10.92	10.43	10.67
Rel. Error		21.46	25.78	26.64	27.44	30.7	29.1
Ca	1.51	1.43	1.4	1.41	2.04	1.56	1.46
Rel. Error		5.3	7.28	6.62	-35.1	-3.31	3.31
Fe	7.78	7.54	7.64	7.55	0.8	7.74	8.04
Rel. Error		3.08	1.8	2.96	-2.83	0.51	-3.34
K	1.95	2.31	2.5	2.5	2.67	2.8	2.92
Rel. Error		-18.46	-28.21	-28.21	-36.92	-43.59	-49.74
Mg	0.482	0.51	0.5	0.52	0.53	0.52	0.53
Rel. Error		-5.81	-3.73	-7.88	-9.96	-7.88	-9.96
Mn	0.013	0.003	0.003	0.003	0.003	0.003	0.003
Rel. Error		76.92	76.92	76.92	76.92	76.92	76.92
Na	0.201	0.27	0.29	0.23	0.3	0.27	0.32
Rel. Error		-34.33	-44.28	-14.43	-49.25	-34.33	-59.2
P	0.23	0.61	0.59	0.58	0.61	0.6	0.61
Rel. Error		-165.22	-156.52	-152.17	-165.22	-160.87	-165.22
Si	23.02	22.44	22.08	22.12	22.19	21.75	22.33
Rel. Error		2.52	4.08	3.91	3.61	5.52	3
Ti	0.791	0.76	0.75	0.75	0.78	0.76	0.77
Rel. Error		3.92	5.18	5.18	1.39	3.92	2.65

Table 7. Oxide percentages of 5% HCl Samples

	TRUE 1633b	5 min. #1	5 min. #2	10 min. #1	10 min. #2	15 min. #1	15 min. #2
Al	28.44	22.34	21.11	20.87	20.64	19.71	20.16
Rel. Error		21.44866	25.77356	26.61744	27.42616	30.6962	29.11392
Ca	2.11	2	1.96	1.98	2.86	2.18	2.04
Rel. Error		5.21327	7.109005	6.161137	-35.545	-3.31754	3.317536
Fe	11.13	10.78	10.92	10.8	11.45	11.07	11.5
Rel. Error		3.144654	1.886792	2.96496	-2.87511	0.539084	-3.32435
K	2.35	2.78	3.01	3.01	3.21	3.38	3.52
Rel. Error		-18.2979	-28.0851	-28.0851	-36.5957	-43.8298	-49.7872
Mg	0.8	0.84	0.83	0.86	0.89	0.86	0.88
Rel. Error		-5	-3.75	-7.5	-11.25	-7.5	-10
Mn	0.021	0.01	0.01	0.01	0.01	0.01	0.01
Rel. Error		52.38095	52.38095	52.38095	52.38095	52.38095	52.38095
Na	0.27	0.37	0.4	0.31	0.41	0.37	0.43
Rel. Error		-37.037	-48.1481	-14.8148	-51.8519	-37.037	-59.2593
P	0.53	1.4	1.36	1.34	1.4	1.37	1.41
Rel. Error		-164.151	-156.604	-152.83	-164.151	-158.491	-166.038
Si	49.24	48.02	47.22	47.32	47.45	46.52	47.77
Rel. Error		2.47766	4.102356	3.899269	3.635256	5.523964	2.985378
Ti	1.32	1.28	1.26	1.26	1.3	1.26	1.28
Rel. Error		3.030303	4.545455	4.545455	1.515152	4.545455	3.030303
Oxide Sum		89.8	88.08	97.75	89.61	86.71	88.99

From this data, the first thing that could be ascertained was that 5% HCl at any time–5, 10, or 15 minutes–could not be used as the dissolving acid, because the sum of the oxides of the samples did not even reach 90% at any time or duplicate. Normally, this would not be that significant, but the other acids had recoveries that were higher each time, which showed that 5% HCl was not the acid to be used. Therefore, the choice was between 5% nitric acid and aqua regia as dissolving acids. Both gave reliable and consistent recovery percentages, but the nitric acid numbers had higher degrees of error in the elemental percentages of silicon and aluminum. Because the elemental percentages were multiplied by a conversion factor, these relative errors were magnified in the oxide percentages as indicated in tables 3, 5, and 7. These strong errors were very prevalent in the nitric acid samples' numbers at all times for aluminum and silicon. Also evident was that there were errors for aluminum and silicon among the numbers when using aqua regia as the dissolving agent, but these errors did not occur every time as they did in the hydrochloric acid samples. From this data, aqua regia was selected to be the acid of choice in the dissolution of the samples.

To decide between the different times among the aqua regia numbers, the researcher had to be a little bit more meticulous. The samples that were in the oven for ten minutes were ruled out immediately, because unlike the other two times, they consistently had a high error for calcium. This decision was not made because of difficulty with the second sample at ten minutes. Actually, some of it was lost in a transfer process during the preparation. Therefore, another sample (#3) was prepared. This third sample still had the obvious calcium error that the other two samples possessed, so it was evident that ten minutes was not a good time for the fusing of the lithium tetraborate pellet. The distinction between the five and fifteen-minute samples was a little less obvious. Both of them had only slight errors among the main four elements (aluminum, calcium, iron, and silicon), but the fifteen-minute samples had a greater absolute error than did the five-minute samples for these main four elements. This difference led to the final realization that it would be better for the researcher to dissolve the samples with aqua regia and fuse them with lithium tetraborate in an oven for five minutes. This conclusion was to be used for the rest of the experiment whenever it was necessary to utilize this type of procedure.

In the progression of this experiment, the next step was to test the pellet as hot or cold. A hot pellet was one that was taken out of the oven while still in its molten state and immediately dissolved in the acid. A cold pellet was one that was allowed to cool to room temperature before being placed into the dissolving acid. The elemental data for the hot and cold pellets and the comparison to the true 1633b certified elemental values is shown in table 8. The values of the oxides found in the samples of the hot and cold pellets is compared to the certified oxide values of 1633b in table 9.

From the elemental data, it is seen that both the hot and the cold pellets have disadvantages. The hot pellets have a higher aluminum relative error and a slightly higher silicon error when compared to the cold pellets, but neither of these offsets the deficiencies of the cold pellets in calcium and iron. It is true that the second duplicate of the hot pellet has a high error for calcium, but this does not occur consistently. For example, the first duplicate does not show the high error in calcium. The difference between the relative errors of these samples favors the hot pellet, enabling the researcher to conclude that the pellets were to be dissolved immediately after they were taken out of the oven so that could be dissolved as hot pellets for the rest of the fusion study of the experiment.

Table 8. Elemental percentages of Hot and Cold Pellets

	True 1633b	Hot #1	Hot #2	Cold #1	Cold #2
Al	15.05	13.99	13.75	14.56	14.8
Rel. Error		7.04	8.64	3.26	1.66
Ca	1.51	1.4	1.3	1.31	1.25
Rel. Error		7.28	13.91	13.25	17.22
Fe	7.78	7.47	7.01	7.16	6.95
Rel. Error		3.98	9.9	7.97	10.67
K	1.95	2.16	2.16	2.31	2.3
Rel. Error		-10.77	-10.77	-18.46	-17.95
Mg	0.482	0.5	0.48	0.48	0.47
Rel. Error		-3.73	0.41	0.41	2.49
Mn	0.013	0.003	0.003	0.003	0.003
Rel. Error		76.92	76.92	76.92	76.92
Na	0.201	0.21	0.19	0.14	0.17
Rel. Error		-4.48	5.47	30.35	15.42
P	0.23	0.75	0.74	0.76	0.78
Rel. Error		-226.09	-221.74	-230.43	-239.13
Si	23.02	23.01	22.44	2.3	23.07
Rel. Error		0.04	2.52	0.09	-0.22
Ti	0.791	0.77	0.74	0.76	0.77
Rel. Error		2.65	6.45	3.92	2.65

Table 9. Oxide percentages of Hot and Cold Pellets

	TRUE 1633b	Hot #1	Hot #2	Cold #1	Cold #2
Al	28.44	26.45	25.98	27.53	20.64
Rel. Error		6.997187	8.649789	3.199719	27.42616
Ca	2.11	1.96	1.83	1.83	27.98
Rel. Error		7.109005	13.27014	13.27014	-1226.07
Fe	11.13	10.68	10.02	10.24	1.75
Rel. Error		4.043127	9.973046	7.996406	84.27673
K	2.35	2.6	2.6	2.78	9.93
Rel. Error		-10.6383	-10.6383	-18.2979	-322.553
Mg	0.8	0.83	0.79	0.8	2.77
Rel. Error		-3.75	1.25	0	-246.25
Mn	0.021	0.01	0.01	0.01	0.79
Rel. Error		52.38095	52.38095	52.38095	-3661.9
Na	0.27	0.29	0.26	0.18	0.23
Rel. Error		-7.40741	3.703704	33.33333	14.81481
P	0.53	1.73	1.7	1.74	1.78
Rel. Error		-226.415	-220.755	-228.302	-235.849
Si	49.24	49.22	48.01	49.2	49.35
Rel. Error		0.040617	2.497969	0.081235	-0.2234
Ti	1.32	1.28	1.24	1.27	1.28
Rel. Error		3.030303	6.060606	3.787879	3.030303
Oxide Sum		95.03	92.43	95.57	95.86

The next step in the development of a standard preparation method was to determine whether a new graphite crucible was better for fusion of the pellet or if one could use a crucible that had already been used at least once. The researcher then prepared a set of two samples and a blank for each type of crucible, one set using the new graphite crucibles and the other set incorporating the use of used graphite crucibles.

Table 10 is the data for the elemental percentages of the samples and the comparison of this data to the certified elemental values of 1633b. When looking at table 10, the reader should notice some strange occurrences. Almost everyone knows that the use of new equipment is always preferable to the use of used equipment. The numbers for the elemental percentages in table 10 for the new and used crucibles show that the used crucibles gave as good if not better numbers than the new crucibles. This was definitely very strange. Most of the discrepancies involved calcium, but it was evident that the second sample of the used graphite crucibles did not have a problem with any of the elements specifically. This error was even more prevalent in the oxides of the samples, which are shown along with their recovery sums and the certified oxide percentages of 1633b in table 11. In fact, the recovery percentage of the oxides of the second sample of the used crucibles shown in table 11 exceeded the recovery of the other runs by about 5% each. This was definitely very strange and suggested that the used crucibles should be used. However, because these results were not definitively consistent with the other used crucible sample, it could not be positively determined if the used crucibles were better for a fusion method or not.

Table 10. Elemental percentages of New and Used Graphite

	True 1633b	New #1	New #2	Used #1	Used #2
Al	15.05	14.52	15.07	14.61	15.35
Rel. Error		3.52	-0.13	2.92	-1.99
Ca	1.51	1.3	1.23	1.3	1.49
Rel. Error		13.91	18.54	13.91	1.32
Fe	7.78	7.16	6.62	6.56	7.61
Rel. Error		7.97	14.91	15.68	2.19
K	1.95	1.21	1.53	1.37	0.79
Rel. Error		37.95	21.54	29.74	59.49
Mg	0.482	0.48	0.46	0.46	0.51
Rel. Error		0.41	4.56	4.56	-5.81
Mn	0.013	0.003	0.003	0.003	0.003
Rel. Error		76.92	76.92	76.92	76.92
Na	0.201	0.24	0.205	0.13	0.0001
Rel. Error		-19.4	-1.99	35.32	99.95
P	0.23	0.68	0.7	0.69	0.69
Rel. Error		-195.65	-204.35	-20	-20
Si	23.02	21.56	22.12	22.74	23.93
Rel. Error		6.34	3.91	1.22	-3.95
Ti	0.791	0.73	0.73	0.72	0.8
Rel. Error		7.71	7.71	8.98	-1.14

Table 11. Oxide percentages of New and Used Graphite

	TRUE 1633b	New #1	New #2	Used #1	Used #2
Al	28.44	27.45	28.49	27.62	29
Rel. Error		3.481013	-0.17581	2.883263	-1.96906
Ca	2.11	1.82	1.72	1.82	2.08
Rel. Error		13.74408	18.48341	13.74408	1.421801
Fe	11.13	10.24	9.47	9.38	10.88
Rel. Error		7.996406	14.91465	15.72327	2.246181
K	2.35	2.38	1.85	1.65	0.95
Rel. Error		-1.2766	21.2766	29.78723	59.57447
Mg	0.8	0.79	0.76	0.76	0.84
Rel. Error		1.25	5	5	-5
Mn	0.021	0.01	0.01	0.01	0.01
Rel. Error		52.38095	52.38095	52.38095	52.38095
Na	0.27	0.32	0.28	0.17	0
Rel. Error		-18.5185	-3.7037	37.03704	100
P	0.53	1.56	1.6	1.59	1.57
Rel. Error		-194.34	-201.887	-200	-196.226
Si	49.24	46.11	47.31	48.64	51.18
Rel. Error		6.356621	3.919578	1.218522	-3.93989
Ti	1.32	1.22	1.21	1.21	1.33
Rel. Error		7.575758	8.333333	8.333333	-0.75758
Oxide Sum		91.88	92.68	92.85	97.84

From experience, it has been known by the researcher that the new graphite crucibles give much better results. Given the inconsistency of the used graphite crucible numbers, the researcher decided to go ahead and continue to use the new crucibles in the later stages of the experiment.

Stirring the samples was next in line to be studied in the developmental procedures. This stirring was actually a misnomer. This action was more of a swirling motion, whereby tongs were used to remove the samples from the oven and the crucible was swirled around while still hot. This stirred the sample within the crucible so that ideally more of the sample would be retained in the acid and recovered in the final dissolution procedure.

The question revolved around whether or not the samples needed to be stirred. The data in tables 12 and 13 are the elemental and oxide numbers for the samples for stirring and not stirring as compared to the respective certified values for 1633b. As was shown by this data, neither type of samples had remarkable recovery. However, since both types of samples were low in recovery, this discrepancy suggests that there was some type of instrumental error involving the ICP-AES. When compared to each other, the stirred samples not only had on average a higher recovery, but they also deviated less from the elemental percentages found in 1633b. The samples that were not stirred typically had higher errors involving aluminum and silicon. Even though the stirred samples did have relatively high errors involving these elements, the samples that were not stirred were shown to have less recovery. It was also evident that these recovery numbers when compared to the recoveries of some of the samples prepared in earlier stages of the experiment were low. However, because the consistency of this meager quantity, an instrumental error was suggested by the numbers.

Table 12. Elemental percentages for Stir and Not Stir

	True 1633b	Stir #1	Stir #2	Not Stir #1	Not Stir #2
Al	15.05	14.01	12.98	12.82	13.28
Rel. Error		6.91	13.75	14.82	11.76
Ca	1.51	1.55	1.57	1.62	1.6
Rel. Error		-2.65	-3.97	-7.28	-5.96
Fe	7.78	7.46	7.5	7.39	7.33
Rel. Error		4.11	3.6	5.01	5.78
K	1.95	2.46	2.99	2.98	3.42
Rel. Error		-26.15	-53.33	-52.82	-75.38
Mg	0.482	0.53	0.52	0.51	0.51
Rel. Error		-9.96	-7.88	-5.81	-5.81
Mn	0.013	0.003	0.003	0.003	0.01
Rel. Error		76.92	76.92	76.92	23.08
Na	0.201	0.13	0.04	0.11	0.13
Rel. Error		35.32	80.1	45.27	35.32
P	0.23	0.68	0.71	0.77	0.74
Rel. Error		-195.65	-208.7	-234.78	-221.74
Si	23.02	21.12	20.58	19.66	20.41
Rel. Error		8.25	10.6	14.6	11.34
Ti	0.791	0.7	0.67	0.97	0.65
Rel. Error		11.5	15.3	-22.63	17.83

Table 13. Oxide percentages for Stir and Not Stir

	TRUE 1633b	Stir #1	Stir #2	Not Stir #1	Not Stir #2
Al	28.44	26.48	24.54	24.23	25.09
Rel. Error		6.891702	13.71308	14.80309	11.77918
Ca	2.11	2.17	2.19	2.27	2.24
Rel. Error		-2.8436	-3.79147	-7.58294	-6.16114
Fe	11.13	10.66	10.73	10.57	10.48
Rel. Error		4.222821	3.59389	5.031447	5.840072
K	2.35	2.96	3.6	3.59	4.13
Rel. Error		-25.9574	-53.1915	-52.766	-75.7447
Mg	0.8	0.87	0.86	0.85	0.85
Rel. Error		-8.75	-7.5	-6.25	-6.25
Mn	0.021	0.01	0.01	0.02	0.01
Rel. Error		52.38095	52.38095	4.761905	52.38095
Na	0.27	0.18	0.06	0.15	0.19
Rel. Error		33.33333	77.77778	44.44444	29.62963
P	0.53	1.56	1.63	1.78	1.7
Rel. Error		-194.34	-207.547	-235.849	-220.755
Si	49.24	45.18	44.01	42.04	43.65
Rel. Error		8.245329	10.62145	14.62226	11.35256
Ti	1.32	1.18	1.11	1.62	1.09
Rel. Error		10.60606	15.90909	-22.7273	17.42424
Oxide Sum		91.25	88.74	87.12	89.43

After all of this data was tabulated and recorded, the researcher came to the conclusion that stirring the sample was much better for the samples when preparing them. It was only a slight advantage, but all advantages had to be taken when working with the sensitive analytical instruments and specific elemental reference standards.

The test involving the stirring of the samples was the last to be done involving the lithium tetraborate pellets. From there, the researcher had to test different forms of preparation that did not involve the fusion of a lithium tetraborate pellet. The first of the two was the process of a mixed-acid digestion.

This digestion involved the use of a mixture of hydrofluoric and hydrochloric acids in a polycarbonate bottle. A blank and two samples of 1633b were prepared using this technique. The only comparable numbers other than the typical certified elemental and oxide percentages that could be used against these samples were the numbers from all of the samples from the previous steps involving the use of a lithium tetraborate pellet. Table 14 shows the elemental percentages of the mixed-acid digestion samples and 1633b and the relative errors between them. This table also indicates that the mixed-acid digestion samples' numbers were so far out of reach of the desired numbers that they were not worth considering. Table 15 shows oxides of the samples and 1633b and presents the fact that their recovery was above 170% for each case. Any person with a scientific mind knows that one cannot create something out of nothing. Supposedly, this procedure produced excessive amounts of silicon and magnesium. The other elements were also generally high when compared to certified 1633b values, but they were overshadowed by the outrageously high numbers for silicon. The only explanation that this researcher could put forth was that in the transfer of the sample from the polycarbonate bottles to the glass flasks for filtration and dilution, the hydrofluoric acid in the samples digested some of the glass and left it in the sample. The abundance of silicon in glass could account for the massive amounts of silicon that were found in the sample percentages. The researcher decided that this was not a wise method of preparation to pursue and decided that this method not be used any more. After all, this method created matter that was not there, contradicting the Law of the Conservation of Matter, which states that matter can neither be destroyed nor created.

Table 14. Elemental percentages for Mixed Acid Samples

	True 1633b	Mixed #1	Mixed #2
Al	15.05	16.84	15.73
Rel. Error		-11.89	-4.52
Ca	1.51	1.39	0.2
Rel. Error		7.95	-32.45
Fe	7.78	7.27	10.01
Rel. Error		6.56	-28.66
K	1.95	1.41	2.04
Rel. Error		27.69	-4.62
Mg	0.482	0.83	0.91
Rel. Error		-72.2	-88.8
Mn	0.013	0.02	0.01
Rel. Error		-53.85	23.08
Na	0.201	0.78	2.23
Rel. Error		-288.06	-1009.45
P	0.23	0.76	0.92
Rel. Error		-230.43	-30
Si	23.02	74.12	53.24
Rel. Error		-221.98	-131.28
Ti	0.791	0.71	0.92
Rel. Error		10.24	-16.31

Table 15. Oxide percentages for Mixed Acid Samples

	TRUE 1633b	Mixed #1	Mixed #2
Al	28.44	31.83	29.74
Rel. Error		-11.9198	-4.57103
Ca	2.11	1.94	2.8
Rel. Error		8.056872	-32.7014
Fe	11.13	10.39	14.31
Rel. Error		6.648697	-28.5714
K	2.35	1.7	2.46
Rel. Error		27.65957	-4.68085
Mg	0.8	1.37	1.51
Rel. Error		-71.25	-88.75
Mn	0.021	0.03	0.02
Rel. Error		-42.8571	4.761905
Na	0.27	1.05	3.01
Rel. Error		-288.889	-1014.81
P	0.53	1.74	2.1
Rel. Error		-228.302	-296.226
Si	49.24	158.55	113.89
Rel. Error		-221.994	-131.296
Ti	1.32	1.18	1.54
Rel. Error		10.60606	-16.6667
Oxide Sum		209.79	171.39

The final preparation stage that was included within this experiment involved the use of Teflon beakers, aqua regia, and hydrofluoric acid. While these samples were being dissolved in the Teflon beakers by the aqua regia and the hydrofluoric acid, the researcher noted that the samples were not dissolving very well. In fact, there was a great deal of residue left over in the beaker after both heatings and dissolutions of the samples.

This lack of dissolving was very evident in the numbers that were obtained from the analysis of these samples. As is seen in tables 16 and 17, not only were the elemental percentages extremely low as compared to 1633b, but so were the sums of the oxides for each sample. In fact, none of the samples' recoveries reached 40%, which was well below the 95-100% recovery range that the researcher sought. Therefore, it was with no hesitation that this method was also dismissed from any further inquiry.

Table 16. Elemental percentages for Teflon Samples

	True 1633b	Teflon #1	Teflon #2
Al	15.05	10.79	11.51
Rel. Error		28.31	23.52
Ca	1.51	0.58	0.59
Rel. Error		61.59	60.93
Fe	7.78	4.56	4.41
Rel. Error		41.39	43.32
K	1.95	0.57	0.58
Rel. Error		70.77	70.26
Mg	0.482	0.24	0.22
Rel. Error		50.21	54.36
Mn	0.013	0.006	0.005
Rel. Error		53.85	61.54
Na	0.201	0.17	0.16
Rel. Error		15.42	20.4
P	0.23	0.78	0.74
Rel. Error		-239.13	-221.74
Si	23.02	3.63	2.82
Rel. Error		84.23	87.75
Ti	0.791	0.54	0.55
Rel. Error		31.73	30.47

Table 17. Oxide percentages for Teflon Samples

	TRUE 1633b	Teflon #1	Teflon #2
Al	28.44	20.38	21.76
Rel. Error		28.34037	23.48805
Ca	2.11	0.81	0.83
Rel. Error		61.61137	60.66351
Fe	11.13	6.51	6.3
Rel. Error		41.50943	43.39623
K	2.35	0.69	0.7
Rel. Error		70.6383	70.21277
Mg	0.8	0.4	0.37
Rel. Error		50	53.75
Mn	0.021	0.01	0.01
Rel. Error		52.38095	52.38095
Na	0.27	0.24	0.22
Rel. Error		11.11111	18.51852
P	0.53	1.78	1.69
Rel. Error		-235.849	-218.868
Si	49.24	7.75	6.04
Rel. Error		84.26076	87.73355
Ti	1.32	0.9	0.93
Rel. Error		31.81818	29.54545
Oxide Sum		39.47	38.84

Discussion

As was evident from the results, preparation by use of any other method than the fusion of the lithium tetraborate pellet proved fruitless and could not withstand the scrutiny of the researcher's hope for a 95-100% recovery. Only the fused pellets provided this high confidence range of recovery.

It was true that the recovery numbers lessened each successive stage of the experiment, but this fault can be attributed to instrumental error. The ICP-AES did not continue running throughout the experiment. In fact, it was down sometimes for weeks because of electrical malfunction. When the researcher would begin work on the samples again, there would be a noted difference in the recoveries after the malfunctions as compared to before the malfunctions. This would seem to be a problem, but because the lessening was so consistent, the different stages that needed to be compared–such as stirred and not stirred–were easily compared. Their numbers each had the same lessening effect caused by the instrumental error, which eliminated all biases and errors between the immediately comparable number (e.g. stir and not stir). This process of bias elimination stood for all of the different stages that could be compared.

Out of all of this comparison, a final fusion method did come into being. The method involved the use of a lithium tetraborate pellet, so the sample has to be weighed out to 0.1000 +/-

0.0005 g and placed into a new graphite crucible. The researcher decided that there was just a slight advantage in using the new graphite crucibles, but this advantage was well worth taking. The sample then needs to be covered up as always with 0.4000 +/- 0.0005 g of lithium tetraborate and thoroughly mixed with a spatula to ensure that all of the sample will be fused in the heating process. Next, the sample is placed into the oven at 1000^0C for five minutes. Upon the termination of this time period, the sample is taken out and the graphite crucible swirled with tongs while the sample is still in the molten state. After the swirling is completed, the sample is immediately placed into a beaker with a magnetic stirring bar and 50 mL of acid composed of 2 mL of nitric acid, 6 mL of hydrochloric acid, and 46 mL of deionized water. This beaker then has a watchglass placed atop it so that no materials can escape the beaker, thereby helping the recovery. The beaker is then placed onto a hot plate that heats and stirs the sample for about five minutes or less if the sample dissolves rather quickly. Once the sample has cooled to room temperature, it is poured into a flask and diluted to 100 mL with deionized water. After this, it is filtered through a #1 analytical filter and placed into a plastic bottle for storage. From there, it is ready to be analyzed.

This method is the final method to be used and will be the method used when beginning the work on the ICP/TOF-MS. It should provide similar results to those of the ICP-AES, because both of the instruments are similarly based analytically if one takes out the fact that the ICP/TOF-MS has a mass spectrometer added to it.

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