

**Performance of the Thermo Scientific Niton XRF Analyzer: The Effects of Particle Size, Length of Analysis, Water, Organic Matter, and Soil Chemistry**

**Jennifer Lin**

**Abstract** Detecting changes in distributions of elements in soil with increasing depth, or the passage of time, can be important to assessing chemical weathering loss/gains, and ultimately the productivity of the soil. Generally, samples collected in the field are prepared for laboratory analysis using methods such as inductively coupled plasma spectroscopy or plasma mass spectroscopy. These methods are very reliable, and relatively routine, but modestly expensive and somewhat slow. Recently, several manufacturers have begun marketing portable x-ray fluorescence (XRF) analyzers, instruments that nondestructively quantify elemental concentrations by measuring characteristic fluorescence x-rays emitted by a sample. These instruments require only minor sample preparation, providing complete results within minutes. However, few studies have assessed how sample preparation affects measurements, or how accurate the XRF analyzer is relative to state of the art lab methods. Therefore, my research question was: How accurately and precisely does the instrument determine the elemental composition of a given sample when varying particle size, length of analysis, water content, organic matter content, and chemistry? Using a Thermo Scientific Niton XRF Analyzer, I tested these variables using soil samples from California and Chile and found that particle size, length of analysis, and soil chemistry did not significantly affect accuracy while water and organic matter content did. Precision of the instrument was generally high, though sometimes was low with short measurement times. Lastly, the instrument had high accuracy only for barium, calcium, potassium, strontium, and uranium. Therefore, it may need to be improved before it can be reliably used in fieldwork.

## Introduction

Soil serves a number of functions that play an important role in supporting life on Earth, such as providing a sink for water, heat, and chemicals, allowing plant growth, buffering potential pollutants, and being a medium for breaking down wastes (National Research Council 1993). As such, it is critical to improve and maintain soil quality so that the soil may effectively sustain ecosystems. Therefore, we must understand the processes underlying soil formation along with factors that affect its properties.

It is known that the atmosphere, biosphere, and hydrosphere transform the lithosphere, the Earth's crust and upper mantle, both physically and chemically (Spray and Moran 2006). This weathering process creates soils differing in texture, particle size, and chemical composition when different types of rocks are reduced to tinier particles, which then undergo chemical reactions by reacting with their surroundings (Bridges 1997). Much can be learned from observing the processes involved in weathering, such as global climate patterns and forces that influence topographic and soil alterations on Earth's surface (Huat *et al.* 2004). Geochemists engage in studying the chemical processes that form the distribution of elements in the Earth's crust and the ways in which it has naturally and anthropogenically changed over time (Walther 2005).

In field geochemistry, weathering profiles are often used for analyzing the effects of chemical weathering, which through the consumption of CO<sub>2</sub> influences global climate over geological time scales (Raymo *et al.* 1988). A weathering or soil profile is the vertical assemblage of weathered rock zones from the land surface to the unweathered parent rock (Senior and Mabbutt 1979). By constructing soil profiles in the same area over time, scientists are able to detect losses and gains in the elemental concentrations making up that soil distribution and use the data to determine the intensities of soil processes acting upon it while gaining a better understanding of soil profile character (Muir and Logan 1982).

Because weathering profiles are important for learning more about soil development and soil processes, they need to be examined in numerous locations in order to better understand the spatial pattern of soil distribution and their global impacts. In one recent study, Anderson *et al.* (2002) quantified mass gains and losses in a weathered profile to assess the time necessary for soil profile development and rate of mass loss in bedrock and soil. For their experiment, it was critical that they accurately measured the elemental concentrations in the rock and soil, so they

used a number of methods, including flame atomic adsorption spectrometry, X-ray fluorescence (XRF) spectrometry, and inductively coupled plasma-mass spectrometry (ICP-AES). A technique like ICP-AES is commonly used in geochemical labs because it can simultaneously identify and determine the concentrations of up to 40 elements with detection limits of parts per billion (Levinson 2001). Inductively coupled plasma spectroscopy (ICP-MS) is frequently used in labs as well since it can determine over 60 elements at very low concentration levels in a few seconds and provide isotope ratios (Robinson *et al.* 2005). Both of these methods require the dissolution and dilution of a sample in strong acid, making sample preparation an important (and time-consuming) part of the analysis (Nelms, 2005). On the other hand, XRF technology is not used as frequently in labs although it is useful because an XRF analyzer simply aims at a sample and quantifies the elemental concentrations by measuring characteristic fluorescence x-rays emitted by the sample (Kalnicky and Singhvi 2001).

XRF technology has been incorporated into handheld devices for on-site screening and instant turnaround analysis, thus making it easier and faster to gather data and refine equipmental designs. Despite its relatively recent development, portable XRF technology is viewed by the environmental community as an acceptable analytical approach for field applications. Most field portable XRF instrumentation has an elemental range that at most extends from potassium (atomic number 19) to uranium (number 92) (Kalnicky and Singhvi 2001), though the accuracy of readings may vary depending on the atomic number of the element, since these instruments more effectively quantify heavier elements (Thermo FS 2008, elect. comm.). Because of this, readings on elements commonly found in soils and rock (Mg, Al, Si, P, S, Cl) cannot be measured with the initial versions of the instrument. If it were able to give accurate readings on-site of these elements, this would be a revolutionary step in field geochemistry, as scientists could then trust measurements from portable XRF technology, allowing them to process data and assemble weathering loss/gain profiles each day. Furthermore, they could decrease the number of samples sent to the lab for analyses by using the XRF analyzer to help select the more important or more representative samples, thereby saving time and money.

There are still many studies that need to be done on the XRF analyzer before data gathered in the field should be published. To begin with, it is essential to evaluate the accuracy and precision of the analyzer, which are two distinct qualities. Precision requires the repetition of non-consecutive measurements to assess the degree of agreement between them while accuracy

measures the degree to which the measured values of the same material agree with the documented values of a Certified Reference Material (Kalnicky and Singhvi 2001). However, it should be noted that factors such as sample matrix, digestion/extraction methodology, and the laboratory conducting the analyses could greatly affect the comparison of XRF and lab data (Kalnicky and Singhvi 2001). I will test for both accuracy and precision in my experiments.

The main question for my study is: How accurately and precisely does an XRF analyzer determine the elemental composition of a given sample when the variables are particle size, length of analysis, water content, organic matter content and chemistry?

For particle size, I hypothesize that decreasing particle size will give more accurate results because the particles are more homogeneous, allowing the XRF analyzer to obtain measurements more representative of the sample. Next, I predict that increasing water content and organic matter content will decrease the accuracy of readings because water may dilute the concentrations while organic matter will reduce the mass of the sample and may contribute additional elements to the sample. In addition, I hypothesize that length of analysis has no effect on accuracy, as there is no apparent correlation. Lastly, I predict that differing chemistry of soil samples will affect accuracy of the results because some elements may respond differently in the presence of others by causing x-ray interferences, thereby skewing true representation of chemical composition. In regard to precision in these experiments, it is already known that precision improves as measurement time increases with this device, but there is a threshold where increased time no longer enhances precision (Thermo FS 2008, elect. comm.). Knowing that, I predict that particle size, water and organic matter content, and matrix type will not affect precision because precision seems to be linked more to the technology of the instrument rather than the material it is analyzing.

I will answer the study questions by conducting experiments in a lab using provided soil samples from California and Chile and a Thermo Scientific Niton XL3t XRF Analyzer. This analyzer is an upgraded model from Thermo Scientific Niton's previous models with shorter measurement times, increased precision, and lower detection limits (Thermo FS 2009, elect comm.). I hope that my findings will help determine whether the XRF Analyzer should actually be used in fieldwork, so that scientists can potentially save considerable amounts of time and money.

## Methods

To determine how accurately and precisely the XRF analyzer measures the elemental composition of a given sample when varying particle size, length of analysis, water content, organic matter content and chemistry, I tested all of these variables in a lab using the handheld Thermo Scientific NITON XL3t XRF analyzer. I used this specific analyzer because it is popular and available in the lab where I worked.

The samples I used came from the cities Hanford, Hesperia, and Fresno in California and the Atacama Desert in Chile, chosen because of their vastly differing chemistries, which vary in levels of sulfur, chlorine, and nitrates. Nine soil samples were used; five from Chile and four from California. These samples were divided into subsamples as needed by the experimental treatments.

To determine how well the instrument performed in relation to particle size, two treatments were used: coarse ground and fine ground. For coarse ground, I crushed the soil slightly with a mortar and pestle to particle sizes 1 mm in diameter or less, but did not homogenize it by mixing up the particles. Fine ground involved grinding and mixing particles until the particles were very fine and homogeneous. None of these samples was sieved. The treatments for water content were oven-dried, 5% water by weight added to dry soil, and 10% water by weight added to dry soil. For organic matter content, the treatments were 0%, 1%, and 10% organic matter (laboratory charcoal) in the sample. To determine the effect of length of analysis on accuracy, I had three different sampling times: 2 minutes, 3 minutes, and 6 minutes, which were set on the XRF analyzer and used for the powdered and coarse ground treatments mentioned above (Table 1).

Table 1. Analyses performed. All samples were fine ground, 0% organic matter, and 0% water unless otherwise stated.

Particle Size (Analyzed at each of 2, 3, and 6 minutes)	Water Content (Analyzed at 6 min)	Organic Matter Content (Analyzed at 6 min)
Coarse ground	0% water	0% Charcoal
Fine ground	5% water	1% Charcoal
	10% water	10% Charcoal

I repeated each treatment three times to account for variation. I placed the samples into testing cups, covering each using a polypropylene film, and then analyzed them one at a time. This took place in February from April 2009.

The data provided by the analyzer consisted of the concentrations of elements and their standard errors. The samples had previously been sent to ALS Laboratory Group, which determined their elemental concentrations using methods such as inductively coupled plasma spectroscopy and plasma mass spectroscopy. There was a small overlap in measured elements between the Niton analyzer and ALS measurements, leaving about twenty elements that could be used for data analysis comparisons. From the XRF data for these elements, I calculated both the average percentage errors under each treatment, taking the lab measurements as the true values, to assess accuracy and the coefficients of variation between replicates to show the precision of the Niton analyzer (See appendixes for full details). For organic matter and water, I took into account the lowered concentration of the sample due to adding these substances in my calculations.

I used sign tests to determine the significance of the effects of particle size, length of analysis, organic matter and water content. For particle size, I compared the root mean square (RMS) percentage error of fine ground samples to the RMS percentage error of coarse ground samples for each element at each analysis length (2, 3 and 6 minutes) whenever data were available. For length of analysis, I compared the RMS percentage errors of 2- and 3-minute sampling times, 2- and 6- minute sampling times, and 3- and 6-minute sampling times for each element, pooling fine ground and coarse ground samples. These sign tests for changes in percentage error were two-tailed because in each of these cases I did not know which of the pair of percentage errors would be higher. For organic matter, I compared the measured concentrations of the 1% organic matter samples to the 0% organic matter samples, and of the 10% OM samples to the 0% OM samples. For water content, I compared 5% water to dry, and 10% water to dry. These sign tests for changes in measured concentration were one-tailed, as I hypothesized that adding either organic matter or water would reduce the measurements of each element. I expect 5% of the sign tests to be significant due to random chance. Therefore, more than 5% of the test needs to be significant to be certain that there is an actual effect. Lastly, to compare the soils of Chile to those from California, I used the average percentage errors from each soil sample under optimal conditions (fine ground, 6-minute, no water, and no OM) and performed a Wilcoxon signed-rank test for each element. I used these non-parametric tests because small sample sizes meant that distributions of the relevant statistics could not be estimated. The level of significance used in all tests was 0.05. I performed all tests using the statistical program R.

## Results

Of the 22 elements that were provided by both the ALS lab and the XRF analyzer, barium, cesium, lead, rubidium, strontium, thorium, zinc, and zirconium were consistently detected by the analyzer while the rest (As, Ca, Co, Cu, Fe, K, Mn, S, Sb, Sc, Sn, Te, Ti, U, and V) were occasionally above detection limits. In general, more elements were detected when the measurement time was six minutes. Looking at coefficients of variation (CVs), some elements, such as barium, calcium, iron, potassium, rubidium, and strontium, were often measured with high precision, with CVs under 0.1. Arsenic, cesium, copper, manganese, lead, antimony, sulfur, titanium, and vanadium were among the elements measured with fair precision (CVs between 0.1 and 0.3). Manganese, lead, tellurium, thorium, zinc, and zirconium were frequently measured with poor precision, with CVs over 0.3 (Table 2).

Table 2. Details for elements with poor precision. Measurement times were generally low (excluding water and organic matter samples). There are many more 10% H<sub>2</sub>O samples than 1% H<sub>2</sub>O samples. Also, there are more Pampas Limos 7 samples than the others. Lead, manganese, tellurium, thorium, zinc, and zirconium have at least four entries in the table. Particle size, water and organic matter content do not seem to affect precision.

Element	Soil Sample	Measurement time	Fine or coarse ground	OM or H <sub>2</sub> O	CV
Antimony	Hesperia 3	2 min	Fine		0.314
Arsenic	PL 7	3 min	Fine		0.514
Cesium	Hanford 2	2 min	Coarse		0.421
Cesium	PL 4	3 min	Fine		0.324
Copper	PL 7	3 min	Fine		0.357
Iron	PL 7	3 min	Fine		0.450
Iron	PL 7	2 min	Coarse		0.400
Lead	Hesperia 3	3 min	Fine		0.347
Lead	Fresno 9	2 min	Coarse		0.332
Lead	PL 5	3 min	Fine		0.426
Lead	PL 7	3 min	Coarse		0.306
Manganese	Hanford 8	3 min	Coarse		0.406
Manganese	PL 7	3 min	Fine		0.403
Manganese	PL 7	2 min	Coarse		0.513
Rubidium	PL 7	3 min	Fine		0.408
Rubidium	PL 7	2 min	Coarse		0.406
Scandium	PL 4	2 min	Fine		0.376
Scandium	PL 5	3 min	Fine		0.319
Strontium	PL 7	3 min	Fine		0.441
Strontium	PL 7	2 min	Coarse		0.346
Tellurium	Hesperia 3	6 min	Fine		0.356
Tellurium	PL 5	3 min	Fine		0.307
Tellurium	PL 7	6 min	Coarse		0.341
Thorium	Hanford 8	2 min	Coarse		0.610
Thorium	PL 7	6 min	Coarse		0.347
Tin	PL 9	6 min	Fine		0.362
Zinc	PL 1	2 min	Fine		0.527

Zinc	PL 7	3 min	Fine	0.927
Zinc	PL 7	2 min	Coarse	0.782
Zirconium	PL 1	2 min	Fine	0.452
Zirconium	PL 4	2 min	Coarse	0.462
Zirconium	PL 7	3 min	Fine	0.482
Zirconium	PL 7	6 min	Coarse	0.304
Arsenic	PL 9		H <sub>2</sub> O – 10%	0.344
Manganese	Fresno 9		H <sub>2</sub> O – 10%	0.384
Manganese	PL 7		H <sub>2</sub> O – 1%	0.350
Manganese	PL 9		H <sub>2</sub> O – 10%	0.316
Strontium	PL 5		H <sub>2</sub> O – 10%	0.633
Thorium	Hanford 8		H <sub>2</sub> O – 10%	0.333
Thorium	PL 4		H <sub>2</sub> O – 1%	0.340
Thorium	PL 5		H <sub>2</sub> O – 10%	0.489
Zinc	PL 9		H <sub>2</sub> O – 10%	0.428
Zirconium	PL 9		H <sub>2</sub> O – 10%	0.319
Antimony	PL 5		OM – 1%	0.300
Barium	Hanford 2		OM – 1%	0.327
Barium	Hanford 2		OM – 10%	0.389
Barium	Hesperia 3		OM – 1%	0.442
Barium	PL 4		OM – 10%	0.306
Cesium	PL 5		OM – 1%	0.403
Copper	Fresno 9		OM – 1%	0.342
Copper	PL 4		OM – 10%	0.320
Manganese	Fresno 9		OM – 10%	0.329
Tellurium	PL 4		OM – 1%	0.338
Thorium	PL 7		OM – 10%	0.368
Tin	PL 1		OM – 1%	0.337
Zinc	Hesperia 3		OM – 1%	0.401
Zinc	Fresno 9		OM – 1%	0.725
Zinc	Fresno 9		OM – 10%	0.638
Zinc	PL 4		OM – 10%	0.397
Zinc	PL 7		OM – 1%	0.316
Zinc	PL 9		OM – 10%	0.313

However, the mean of CVs across all elements and samples in the particle size treatments was 0.105, which suggests good precision. The mean for water treatments was 0.101, while for organic matter it was 0.122.

Next, under what I hypothesized to be the optimal set of conditions (6 minutes, fine-ground, no water, and no organic matter), I found large differences between the lab measurements and XRF measurements, as seen in Figure 1. Only five elements have percentages under 20%, which is the manufacturer's stated accuracy.



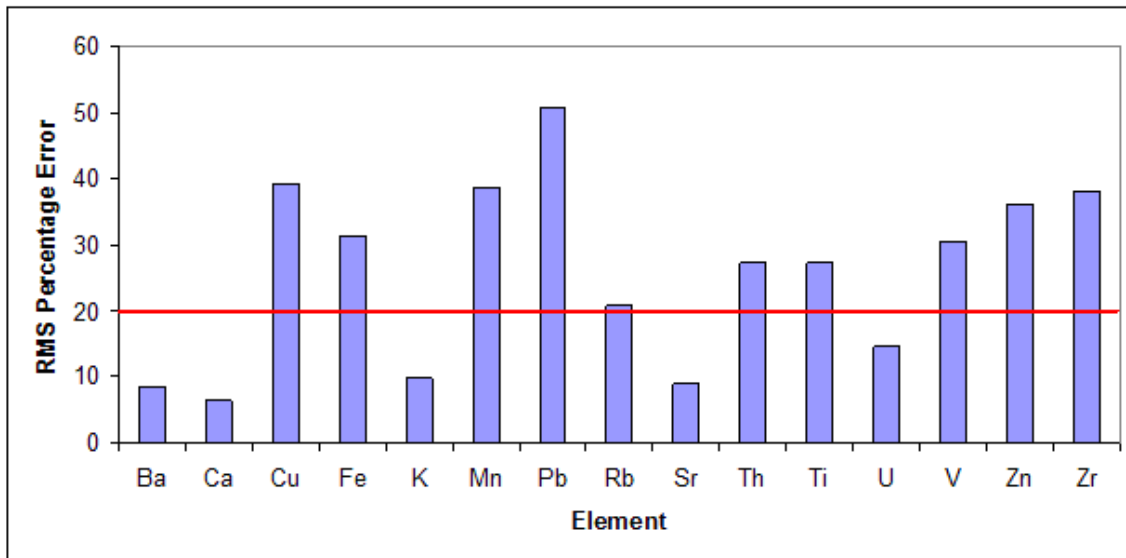


Figure 1. RMS percentage errors for the elements. Arsenic, cobalt, cesium, sulfur, antimony, tin, and tellurium were excluded because they had extremely large errors (104, 223, 1140, 1750, 2470, 1200, and 35600 respectively). The red line is the manufacturer's stated accuracy.

From my sign tests comparing fine ground and coarse ground particle sizes on the percentage of error, there were only two significant p-values (for rubidium and zinc) in the 6-minute comparison (Table 3).

Table 3. P-values from sign tests comparing particle size on the percentage of error. Elements with sample sizes less than 6 were excluded. Significant p-values have an asterisk next to them. Note that there are two significant p-values in the 6-minute section.

2 minutes			3 minutes			6 minutes		
Element	n	P-value	Element	n	P-value	Element	n	P-value
Barium	9	0.180	Barium	8	0.727	Barium	9	0.508
Cesium	7	0.125	Cesium	8	0.727	Cesium	9	1.00
Rubidium	9	0.508	Rubidium	9	0.508	Copper	7	1.00
Strontium	9	0.508	Strontium	9	0.508	Lead	9	0.508
Zinc	9	1.00	Thorium	6	0.219	Rubidium	9	0.00391*
Zirconium	9	1.00	Zinc	9	1.00	Strontium	9	1.00
			Zirconium	9	0.180	Thorium	9	1.00
						Vanadium	7	1.00
						Zinc	9	0.0391*
						Zirconium	8	0.727

My sign tests comparing analysis time on the percentage of error revealed one significant p-value for strontium in the 6- vs. 2-minute comparison and another for titanium in the 6- vs. 3-minute comparison (Table 4).

Table 4. P-values from sign tests comparing analysis time effects on the percentage of error. Both fine and coarse ground samples are included. Elements with sample sizes less than 6 were excluded. There is one significant p-value in the 6 vs. 2 minute comparison and one in the 6 vs. 3 minute comparison.

3 min vs. 2 min			6 min vs. 2 min			6 min vs. 3 min		
Element	n	P-value	Element	n	P-value	Element	n	P-value
Arsenic	9	0.508	Arsenic	10	1.00	Arsenic	9	1.00
Barium	16	0.210	Barium	17	0.143	Barium	17	1.00
Calcium	10	0.109	Calcium	10	0.754	Calcium	10	0.344
Cesium	15	0.607	Cesium	17	1.00	Cesium	16	1.00
Iron	10	0.754	Copper	13	1.00	Iron	10	0.754
Potassium	10	1.00	Iron	10	0.344	Potassium	10	1.00
Manganese	6	0.688	Potassium	10	0.754	Manganese	6	0.688
Lead	10	1.00	Manganese	6	1.00	Lead	11	1.00
Rubidium	18	1.00	Lead	13	1.00	Rubidium	18	0.815
Sulfur	7	0.125	Rubidium	18	0.815	Sulfur	6	0.219
Strontium	18	0.815	Sulfur	7	0.453	Strontium	18	0.815
Thorium	11	1.00	Strontium	18	0.0963*	Thorium	12	1.00
Titanium	10	0.215	Thorium	16	0.454	Titanium	10	0.0215*
Zinc	18	1.00	Titanium	10	0.344	Zinc	18	0.815
Zirconium	18	1.00	Zinc	18	0.238	Zirconium	18	0.815
			Zirconium	18	0.238			

From my sign tests comparing organic matter effects on the measured concentration, there were three significant p-values (for barium, rubidium and zirconium) in the 1% OM table and two significant p-values (for cesium and tellurium) in the 10% OM table (Table 5).

Table 5. P-values from sign tests comparing organic matter effects on the measured concentration. Elements with sample sizes less than 5 were excluded. There are three significant p-values in the 1% OM table and two in the 10% OM table.

1% Organic Matter			10% Organic Matter		
Element	n	P-value	Element	n	P-value
Arsenic	6	0.344	Arsenic	6	0.110
Barium	9	0.0196*	Barium	9	0.00196*
Calcium	9	>0.500	Calcium	9	>0.500
Cesium	7	>0.500	Cesium	7	0.00780*
Copper	9	0.500	Copper	9	>0.500
Iron	9	0.0900	Iron	9	>0.500
Potassium	9	>0.500	Potassium	9	>0.500
Manganese	7	0.0625	Manganese	7	>0.500
Lead	9	>0.500	Lead	9	>0.500
Rubidium	9	0.00196*	Rubidium	9	>0.500
Sulfur	5	>0.500	Sulfur	5	>0.500
Antimony	5	>0.500	Scandium	6	>0.500
Scandium	5	>0.500	Strontium	9	>0.500
Strontium	9	0.0900	Tellurium	5	0.0313*
Tellurium	5	>0.500	Thorium	9	>0.500
Thorium	9	0.254	Titanium	7	>0.500
Titanium	7	0.227	Vanadium	9	>0.500
Vanadium	9	>0.500	Zinc	9	>0.500
Zinc	9	>0.500	Zirconium	9	0.254
Zirconium	9	0.0196*			

In addition, some elements, usually cesium, antimony, tellurium, tin, and vanadium could not be detected when the organic matter content is increased.

My sign tests comparing water effects on the measured concentration revealed four significant p-values (for barium, cesium, potassium, and scandium) in the 5% water table and two significant p-values (for calcium, potassium, manganese, scandium, titanium, and vanadium) in the 10% water table (Table 6).

Table 6. P-values from sign tests comparing water effects on the measured concentration. Elements with sample sizes less than 5 were excluded. There are four significant p-values in the 5% water table and six in the 10% water table.

5% Water			10% Water		
Element	n	P-value	Element	n	P-value
Arsenic	6	0.344	Arsenic	6	>0.500
Barium	9	0.0196*	Barium	9	0.0900
Calcium	9	0.254	Calcium	9	0.0196*
Cesium	8	0.0352*	Cesium	8	0.364
Copper	8	>0.500	Copper	8	>0.500
Iron	9	0.500	Iron	9	0.0900
Potassium	9	0.0196*	Potassium	9	0.00196*
Manganese	7	0.227	Manganese	7	0.00780*
Lead	9	0.254	Lead	9	0.500
Rubidium	9	>0.500	Rubidium	9	>0.500
Sulfur	7	0.227	Antimony	7	>0.500
Antimony	6	0.344	Scandium	6	0.0157*
Scandium	5	0.0313*	Tin	5	0.188
Strontium	9	>0.500	Strontium	9	>0.500
Tellurium	6	0.110	Tellurium	6	0.344
Thorium	9	>0.500	Thorium	9	>0.500
Titanium	9	0.0900	Titanium	9	0.0196*
Vanadium	7	0.227	Vanadium	7	0.00780*
Zinc	9	>0.500	Zinc	9	0.500
Zirconium	9	0.09	Zirconium	9	0.254

Lastly, the Wilcoxon signed-rank test revealed only one significant p-value and that was for rubidium (Table 7). Elements with sample sizes lower than 7 were excluded.

Table 7. P-values from a Wilcoxon signed-rank test comparing average percentage errors from CA to those from Chile. Sample size was 9 for all elements. There is only one significant p-value.

Element	P-value
Barium	0.4127
Cesium	0.5556
Lead	0.5556
Rubidium	0.01587*
Strontium	0.7302
Thorium	0.7302
Zinc	0.1111
Zirconium	0.5556

## Discussion

Precision of the instrument overall was decently high when averaged across all treatments and elements. Some elements were measured with very poor precision, particularly during low measurement times, suggesting that measurement time affects precision (Table 2). Next, it appears that the XRF instrument is not very accurate for most elements as only barium, calcium, potassium, strontium, and uranium had average percentage errors under 20% (Figure 1). Because the p-values from the sign tests were largely insignificant, particle size, measurement time, and soil chemistry did not have a significant impact on accuracy (Tables 3-4). However, increasing the length of analysis did allow greater detection of elements (Appendix I). Organic matter content and water did have a significant effect on the results, as there was a large percentage of significant p-values (Tables 5-6).

My first hypothesis predicted that smaller particles would yield more accurate results because they are more homogeneous. Only two p-values were significant from the sign tests, so particle size does not significantly affect accuracy (Table 3). Furthermore, it is unknown why barium, calcium, potassium, strontium, and uranium have the highest accuracy and arsenic, cobalt, cesium, sulfur, antimony, tin, and tellurium the least (Figure 1). From the periodic table, barium, calcium, and strontium are alkaline earth metals, potassium is an alkali metal, and uranium is an actinide. This contrasts with those with poor precision; sulfur is an other nonmetal, antimony and tellurium are metalloids, tin is an other metal, and cesium is an alkali metal. It is possible that it

is more difficult for the XRF analyzer to measure the concentrations of nonmetals, metalloids, and other metals.

Next, I hypothesized that the length of analysis would have no effect on accuracy, as there is no apparent correlation. We found a majority of insignificant p-values, which supports my hypothesis (Table 4). However, it was not correct in the sense that increasing the measurement time tended to introduce more elements to the readings that the lab also detected in the sample. This is important for samples near the detection limit as a longer analysis time provides a lower detection limit (Kalnicky and Singhvi 2001). Therefore, it is important to use a longer measurement time, preferably six minutes or longer.

Furthermore, I expected that increasing water content and organic matter content would decrease the accuracy of readings because water might dilute the concentrations while organic matter might add other elements to the sample while decreasing concentrations. Due to the high percentage of significant p-values in my tests, these substances did significantly affect measurements, though more so for water than for organic matter (Tables 5-6). For organic matter content, the charcoal was finer than the soil particles and became fully integrated in the sample, thereby making it harder for the instrument to analyze the soil properly. This was confirmed by the fact that the concentrations became negative and that some elements could not be detected after organic matter was added. For water content, the observed decrease in concentrations supports my hypothesis as well. Kalnicky and Singhvi (2001) came to the result that moisture has an effect on accuracy, but they concluded that the overall error might be small when the water content is around 5-20%, but much larger when the content is greater than 20%. My findings suggest that even at 5%, the error is large enough that the soils should be dried before analysis.

I predicted that differing chemistry of soil samples would affect accuracy of the results because some elements might respond differently in the presence of other elements by causing certain interferences. There was only one insignificant p-value, so soil chemistry did not affect accuracy (Table 7). This suggests that elements do not act very differently in soils, despite varying soil chemistries.

Lastly, I hypothesized that precision would not be affected by particle size, water and organic matter content, and matrix type because precision is linked more to the technology of the instrument rather than the material it is analyzing. This was generally observed when the

coefficients of variation were averaged over all variables and areas, equaling 10-12%. However, there were some elements that had very poor precision, particularly during low measurement times, suggesting that length of analysis had the most influence on precision (Table 2). My finding that having a larger measurement time increases precision supports the findings by Thermo Fisher Scientific Inc. However, I also found that some elements, especially lead, manganese, tellurium, thorium, zinc, and zirconium, were measured with poor precision more often than were others. Looking at a periodic table, their atomic numbers are scattered and groups are varied. From my data, their concentrations greatly differed as well. Therefore, I do not see why these elements in particular had worse precision. Next, I noticed that there were many more 10% water samples than 1% water samples, though overall, their CVs were not much different from those of dry samples. Lastly, Pampas Limos 7 had more entries in Table 2 than did the other soil samples. It is unknown why this particular soil sample had worse precision. I know that it differs from the other Chilean samples in the concentrations of sodium nitrate and sodium chloride, though this would suggest that Pampas Limos 9 should also have had poor precision (assuming precision is linked to soil chemistry).

The instrument could provide only a small number of elemental concentrations that the lab group also provided since the device requires that the concentration of an element be above a certain detection limit (It differs for each element) for it to be measured. This greatly affected my results because had the instrument been able to measure more elements, the overlap of measured elements between the lab and the XRF analyzer would have been larger. This would have given me more p-values to look at and would have been especially helpful in my sign tests for particle size and soil chemistry, which involved only a dozen elements or less. My results could have definitely improved if there were more repetitions since three is very minimal. My experiments might include some confounding factors, however. For instance, settling might have occurred in the samples stored in XRF cups when left alone for a period and evaporation might have occurred in the water samples, which would influence results (Kalnicky and Singhvi 2001). Perhaps there were some days when the instrument was not performing optimally, which could explain the arbitrary poor precision in the Pampas Limos 7 measurements.

Furthermore, it may not have been that the XRF analyzer was faulty, but that it needed to be calibrated differently. Kalnicky and Singhi (2001) discovered that sample matrix effects and sample morphology are some factors that possibly influence XRF response and should be

considered when calibrating the instrument. I only used the default calibration setting and this may have influenced my results when I performed my treatments on the samples.

For future research, I would suggest testing other XRF devices as well and having more labs to analyze the soil. The lab I used might have disregarded some elements that the analyzer detected. I would also suggest looking into the performance of the helium purge system that comes with this XRF analyzer model because it allows one to measure light elements such as magnesium, aluminum, silicon, and phosphorus, which other models are not capable of detecting (Thermo FS 2008, elect comm). This device is quite new and geochemists have not used it to determine how field conditions (like those I tested) may influence sample data.

Based on my current conclusions, it would be important for a user of this Thermo Scientific Niton XRF analyzer to know which elements actually matter for their purposes so that they can determine whether using the analyzer or a geochemical lab is the more appropriate or smarter choice. My results indicate that the analyzer would be dependable for barium, calcium, potassium, strontium, uranium and possibly rubidium. One should also increase the measurement time to at least 6 minutes in order to measure more elements and then make sure the amounts of water and organic matter are minimal.

In response to my research question, particle size, length of analysis and soil chemistry do not affect accuracy of measurements while interferences with water and organic matter do. This analyzer is suitable for only a handful of elements, so the lab would still be preferable for such soil analyses. Therefore, the instrument either needs to be calibrated differently or needs to be improved before it can be used reliably in fieldwork.

### **Acknowledgements**

I would like to thank my advisors Simona Balan and Professor Ronald Amundson for providing me with guidance and support for understanding the experimental designs, methods, and data analysis and for allowing me to use their equipment to complete my study. I would also like to thank the ES 196 instructors, especially Tim De Chant and Shelly Cole, and fellow ES students for giving me advice and support throughout the year.

**References Cited**

- Anderson, S.P., W.E. Dietrich, and G.H. Brimhall Jr. 2002. Weathering profiles, mass-balance analysis, and rates of solute loss: Linkages between weathering and erosion in a small, steep catchment. *GSA Bulletin* 114: 1143-1158.
- Bridges, E.M. 1997. *World soils*. Cambridge University Press, Cambridge, UK. 176 pp.
- Huat, B.B.K., G.S. Sew, and F.H. Ali. 2004. *Tropical Residuals Soils Engineering*. Taylor & Francis, London. 260 pp.
- Kalnicky, D.J. and R. Singhvi. 2001. Field portable XRF analysis of environmental samples. *Journal of Hazardous Materials* 83: 93-122.
- Levinson, R. 2001. *More modern chemical techniques*. Royal Society of Chemistry. 184 pp.
- Muir, J.W. and J. Logan. 1982. Eluvial/illuvial coefficients of major elements and the corresponding losses and gains in three soil profiles. *Journal of Soil Science* 33: 295-308.
- National Research Council (U.S.) Committee on Long-Range Soil and Water Conservation. 1993. *Soil and water quality: an agenda for agriculture*. National Academies Press. 516 pp.
- Nelms, S. 2005. *Inductively coupled plasma mass spectrometry handbook*. Wiley-Blackwell. 485 pp.
- Raymo, M.E., W.F. Ruddiman, and P.N. Froelich. 1988. Influence of late Cenozoic mountain building on ocean geochemical cycles. *Geology* 16: 649-653.
- Robinson, J.W., E.M.S. Frame, and G.M. Frame. 2005. *Undergraduate instrumental analysis*. CRC Press. 1079 pp.
- Senior, B.R. and J.A. Mabbutt. 1979. A proposed method of defining deeply weathered rock units based on regional geological mapping in southwest Queensland. *Journal of the Geological Society of Australia* 26: 237-254.
- Spray, S.L. and M.D. Moran. 2006. *Tropical deforestation*. Rowman & Littlefield. 195 pp.
- Thermo Fisher Scientific Inc. 2008. Thermo Scientific NITON XL3t. <http://www.niton.com/Portable-XRF-Technology/literature.aspx> > Niton XL3t Spec Sheet, accessed January 31, 2009.
- Thermo Fisher Scientific Inc. 2008. The XL3t XRF analyzer. <http://www.niton.com/NITON-Analyzers-Products/xl3t.aspx>, accessed April 25, 2009.
- Walther, J.V. 2005. *Essentials of geochemistry*. Jones & Bartlett Publishers, Massachusetts. 704 pp.



## Appendixes

### Appendix I – Average Percentage Errors

Tables 8-16. Average percentage errors for soil samples of varying particle sizes and lengths of analysis.

#### Hanford 2, CA

Element	Fine Ground 2 min	Fine Ground 3 min	Fine Ground 6 min	Coarse Ground 2 min	Coarse Ground 3 min	Coarse Ground 6 min
Barium	-2.35	-1.55	-5.32	-7.38	-9.71	-9.91
Cesium	1280	1290	1210	826	907	933
Copper		51.2	77.3		63.4	107
Lead	14.6	23	9.52	-0.07	13.2	5.87
Rubidium	-4.36	-6.02	-6.33	-4.25	-3.21	-5.18
Strontium	15.9	14.5	13.7	12.7	15.2	12
Thorium	19.3	40	27.5	47	31	60.8
Vanadium						41.8
Zinc	-19.4	-21.9	-11.1	-10.1	-14.8	-11.5
Zirconium	19.6	0.27	12.2	3.23	9.53	4.14

#### Hanford 8, CA

Element	Fine Ground 2 min	Fine Ground 3 min	Fine Ground 6 min	Coarse Ground 2 min	Coarse Ground 3 min	Coarse Ground 6 min
Barium	-2.79	-5.15	-4.57	-2.15	-0.37	-0.57
Cesium	1630	1340	1390	1450	1570	1620
Lead	5.22	-1.73	-1.96	-4.37	-2.37	-7.76
Rubidium	-8.46	-10.2	-9.07	-7.13	-9.69	-7.25
Tin					1720	1790
Strontium	11.5	10.3	9.5	8.51	7.52	8.8
Thorium	5.67	21.8	21.3	76.6	11.8	45.2
Vanadium						38.2
Zinc	-33.2	-22.1	-24.3	-29.8	-20	-21.5
Zirconium	37.9	38.2	42	31.7	23.8	16.7

#### Hesperia 3, CA

Element	Fine Ground 2 min	Fine Ground 3 min	Fine Ground 6 min	Coarse Ground 2 min	Coarse Ground 3 min	Coarse Ground 6 min
Barium	0.0587	-2.31	-3.15	-6.25	-7.75	-9.98
Cesium	1700	1700	1580	1280	1330	1390
Lead	-19.4	-1.75	1.5	4	5.37	11.9
Rubidium	-8.03	-8.17	-8.2	-8.27	-7.43	-7.99
Tin			624			602
Strontium	7.41	7.54	5.4	9.45	8.3	8.96
Thorium	31.8	38.9	21.4	11.3	17.4	16.7
Vanadium			36.2			24.4
Zinc	-16.7	-23	-27.9	-22.6	-23.4	-27
Zirconium	4.01	5.58	1.56	13.5	17.1	15.1

## Fresno 9, CA

Element	Fine Ground 2 min	Fine Ground 3 min	Fine Ground 6 min	Coarse Ground 2 min	Coarse Ground 3 min	Coarse Ground 6 min
Barium	-12.1	-9.24	-7.4	-7.85	-2.06	-4.1
Cesium	1200	1060	1270	1110	1400	1160
Copper		163	65.1		116	100
Lead	71.8	59.7	76.5	105	88.8	73.7
Rubidium	-8	-3.6	-3.32	0.292	-0.699	-2.15
Strontium	2.46	5.88	5.29	3.32	4.47	4.18
Thorium	38.9	27.5	20.2	16.4	22.1	26.4
Uranium	51.1	47.2	43.6	20.3	9.7	22.4
Vanadium			21.7			18.4
Zinc	-28.9	-18.2	-21.7	-29.3	-19.3	-20.6
Zirconium	28.3	24.3	26.7	28.6	36.6	35.5

## Pampas Limos 1, Chile

Element	Fine Ground 2 min	Fine Ground 3 min	Fine Ground 6 min	Coarse Ground 2 min	Coarse Ground 3 min	Coarse Ground 6 min
Arsenic	16.2	27.5	32.9	20.4	26.4	19.7
Barium	-19.8	-15.7	-15.6	-16.9	-12.1	-18.6
Calcium	-13.1	-8.01	0.804	-8.09	-3.76	-0.886
Cobalt			670			
Cesium	274	228	206	237	234	254
Copper	51.1	47.6	48.6	31.2	48.2	39.4
Iron	-31.6	-32.9	-30.7	-33.6	-35.9	-35.6
Potassium	-2.54	5.57	12.3	-2.78	6.12	12.4
Manganese	-51.2	-54	-53.1	-55.6	-52.9	-52.7
Lead	22.5	26	13.9	-5.11	8.1	11.2
Rubidium	-19.1	-14.8	-15	-15.3	-16.5	-14.3
Sulfur						1790
Tin						420
Strontium	-5.03	-2.67	-1.1	-2.64	1.51	-10.2
Thorium	34.1	25.4	27.3	32.8	35.4	20.2
Titanium	-19.5	-15.8	-16.3	-18.5	-6.79	-4.07
Vanadium			13.9	-3.96	4.51	10.2
Zinc	-9.76	-34.9	-39.4	-46.2	-38.2	-36.7
Zirconium	90.9	53.6	67.8	23.3	54	55.6

## Pampas Limos 4, Chile

Element	Fine Ground 2 min	Fine Ground 3 min	Fine Ground 6 min	Coarse Ground 2 min	Coarse Ground 3 min	Coarse Ground 6 min
Arsenic	-21	-5.53	4.1	-0.65	3.7	-4.67
Barium	-16.8	-0.0143	6.79	-7.86	-5.82	-7.25
Calcium	-2.64	4.29	11.2	-3.01	4.03	11
Cesium		1040	1120	1230	1220	1070
Copper			8.68			34.9
Iron	-53.2	-52.2	-49.1	-52.1	-52.4	-52.1
Potassium	-26.1	-19.1	-17.7	-18.4	-13	-9.79
Lead			-46.6			-25
Rubidium	-44.2	-44	-43.7	-44.7	-45.2	-42.7
Sulfur	2330	2560	2710	2300	2460	
Antimony			3580			-99.5
Tin			1980			1590
Strontium	-21.3	-20.4	-17.1	-14.6	-22.1	-18.5
Tellurium			8260			7970
Thorium		13.8	3.6			-2.18
Titanium	-57.5	-50.9	-47.7	-56.5	-52	-50.1
Vanadium			-49.5			-60.9
Zinc	-50.6	-49.5	-60.8	-62.8	-59.3	-57.1
Zirconium	-21.2	-14.8	-18.4	2.06	-25.5	-28.6

## Pampas Limos 5, Chile

Element	Fine Ground 2 min	Fine Ground 3 min	Fine Ground 6 min	Coarse Ground 2 min	Coarse Ground 3 min	Coarse Ground 6 min
Arsenic	79.6	87.4	93.4	80.5	83.2	71.4
Barium	3.56	2.48	-1.56	2.56	0.199	13.2
Calcium	-13.5	-7.18	-3.15	-18	-12.1	-8.56
Cesium	938	678	703	944	945	1040
Copper		-1.1	19.3		39.5	18.3
Iron	-46.4	-46.8	-41.7	-44.8	-43.7	-43
Potassium	-11.8	-3.46	0.00355	-3.98	3.06	7.74
Lead		22.5	-1			33.8
Rubidium	-33.6	-32.1	-32.7	-28.8	-25.9	-29.1
Sulfur	2210	2340	2460	2050	2210	
Antimony	4650		2560		4000	4090
Selenium						326
Tin		1810	1820		1990	2330
Strontium	6.21	6.99	1.34	-0.902	0.29	-6.68
Tellurium	25200	18400	18700		26600	25000
Thorium		-15.4	10	40.6	12.2	5.42
Titanium	-53.1	-50.6	-41.2	-53.5	-47.2	-45.7
Vanadium			-51.4		-52.9	-56.5
Zinc	-55	-55.8	-57	-47.8	-48.7	-51.7
Zirconium	-19.2	-17	-19.3	-8.81	-5.29	-4.46

## Pampas Limos 7, Chile

Element	Fine Ground 2 min	Fine Ground 3 min	Fine Ground 6 min	Coarse Ground 2 min	Coarse Ground 3 min	Coarse Ground 6 min
Arsenic	313	168	238		242	234
Barium	-1.29		-5.51		-2.75	-12.8
Calcium	3.8	-0.304	14.9	-10.4	1.08	7.74
Cesium	1530		1280		1360	1300
Copper		-7.08	5.24			14.8
Iron	-46.4	-60.8	-48.4	-51.5	-42.1	-46
Potassium	-11.8	-13.7	1.92	-16.5	-0.339	4.61
Manganese	-75.1	-78.9	-72.1	-80.1	-67.8	-71.6
Lead	76.4		114		119	96
Rubidium	14.9	-10.4	15.3	-11.8	9.99	14.6
Sulfur	2620	2470	2880			2650
Antimony	7280		4220		6980	4570
Tin			2120		1770	1860
Strontium	313	-23.3	-5.75	-23.3	7.79	-2.51
Tellurium	-1.29		40800			41900
Thorium	3.8		60.6		39.6	77.4
Titanium	1530	-51.8	-36.3	-44	-35.3	-35.4
Vanadium			-15.2		3.82	-19.6
Zinc	-51.1	61.3	-29.7	50.6	-24.8	-24.7
Zirconium	-11	4.99	71.3	21.7	49.8	89.4

## Pampas Limos 9, Chile

Element	Fine Ground 2 min	Fine Ground 3 min	Fine Ground 6 min	Coarse Ground 2 min	Coarse Ground 3 min	Coarse Ground 6 min
Arsenic	166	194	175	182	176	186
Barium	10.4	22.1	14.1	4.68	1.41	3.17
Calcium	-14.5	-0.562	-0.415	-25.1	-19.3	-15.2
Cesium	801	913	885	767	908	665
Copper	-31.8	-37.4	-28.9		-17	-25
Iron	-34.7	-37.2	-37.9	-36.4	-27.3	-34.4
Potassium	5.44	13	19.9	11.6	17.8	27.7
Manganese	-66.9	-65.9	-74.1	-68.5	-61.8	-67.2
Lead		-31	-44			-39.3
Rubidium	-13.7	-15.7	-14	-16.2	-19.2	-12.4
Sulfur	2080	2430	2420	1780	1880	1980
Antimony		3910	4230			2720
Tin		1030	864			867
Strontium	1.72	16.4	6.67	8.65	13.8	13.9
Tellurium			96600			87000
Thorium		9.16	8.32		8.8	15.7
Titanium	-33.8	-47	-33.9	-49.4	-35	-42.7
Vanadium		-27.3	-32.9	-30.8	-7.64	-2.89
Zinc	-20.3	-20.4	-20.8	-18.4	-11.3	-17.6
Zirconium	-6.23	-2.39	-5.02	-12.9	-17.4	-17.5

Tables 17-25. Average percentage errors for samples of varying organic matter content for each area.

## Hanford 2

Element	0% OM	1% OM	10% OM
Barium	-5.32	-18.8	-29.6
Cesium	1210		
Copper	77.3	26.1	97.2
Lead	9.52	2.13	15.7
Rubidium	-6.33	-6.56	1.24
Strontium	13.7	9.31	17.5
Thorium	27.5	54.6	54.8
Zinc	-11.1	-11	-2.62
Zirconium	12.2	10.2	12.1

## Hanford 8

Element	0% OM	1% OM	10% OM
Barium	-4.57	-4.67	-37
Cesium	1390	1490	
Copper		73.4	109
Lead	-1.96	3.19	-11.9
Rubidium	-9.07	-11.6	-7.78
Strontium		1720	
Thorium	9.5	8.73	11.4
Zinc	21.3	10.1	11.1
Zirconium	-24.3	-23.8	-23.7

## Hesperia 3

Element	0% OM	1% OM	10% OM
Barium	-3.15	-27.9	-43.7
Cesium	1580		
Copper		122	
Lead	1.5	-10.5	18.3
Rubidium	-8.2	-14.4	-7.93
Tin	624		
Strontium	5.4	1.4	12.8
Thorium	21.4	18.4	45.1
Vanadium	36.2		
Zinc	-27.9	-9.62	-30.3
Zirconium	1.56	-9.53	8.59

## Fresno 9

Element	0% OM	1% OM	10% OM
Barium	-7.4		
Cesium	1270		
Copper	65.1	74.9	83.7
Lead	76.5	33.1	42.3
Rubidium	-3.32	-21.7	-20.3
Strontium	5.29	-8.97	-10.2
Thorium	20.2	19.9	30.5
Uranium	43.6	42	41.6
Vanadium	21.7	25.2	
Zinc	-21.7	46.3	41
Zirconium	26.7	4.67	17.4

## Pampas Limos 1

Element	0% OM	1% OM	10% OM
Arsenic	32.9	34.1	34.4
Barium	-15.6	-13.2	-16.1
Calcium	0.804	-1.68	4.62
Cobalt	670		
Cesium	206	363	188
Copper	48.6	41.1	28
Iron	-30.7	-26.5	-28.2
Potassium	12.3	13	9.73
Manganese	-53.1	-47.6	-42.1
Lead	13.9	6.33	19.7
Rubidium	-15	-19.2	-18
Antimony		1610	
Tin		462	
Strontium	-1.1	-6.6	8.27
Tellurium		27500	
Thorium	27.3	19.7	42.9
Titanium	-16.3	-7.25	-6.8
Vanadium	13.9	19.2	34.4
Zinc	-39.4	-35.8	-39.7
Zirconium	67.8	58	40.9

## Pampas Limos 4

Element	0% OM	1% OM	10% OM
Arsenic	4.1	-7.46	-11.3
Barium	6.79	4.88	-30.3
Calcium	11.2	18	20.6
Cesium	1120	1210	
Copper	8.68	4.81	18.9
Iron	-49.1	-55.5	-53.1
Potassium	-17.7	-16.7	-11.1
Lead	-46.6	-39.1	-30.8
Rubidium	-43.7	-44.4	-41.9
Sulfur	2710	2860	2790
Antimony	3580	4500	
Tin	1980	1960	
Strontium	-17.1	-23.8	-9.89
Tellurium	8260	7960	
Thorium	3.6	6.37	
Titanium	-47.7	-55	-48.6
Vanadium	-49.5		-56.4
Zinc	-60.8	-55.6	-43.2
Zirconium	-18.4	-23.3	-21

## Pampas Limos 5

Element	0% OM	1% OM	10% OM
Arsenic	93.4	78.6	90.6
Barium	-1.56	-4.9	-14.1
Calcium	-3.15	2.19	-2.57
Cobalt			619
Cesium	703	813	563
Copper	19.3	19.8	27.1
Iron	-41.7	-49.4	-38.4
Potassium	0.00355	3.6	9.4
Lead	-1	5.12	27.3
Rubidium	-32.7	-33.2	-24.1
Sulfur	2460	2650	2360
Antimony	2560	3930	
Tin	1820		
Strontium	1.34	-9.16	3.33
Tellurium	18700		
Thorium	10	37.6	19.6
Titanium	-41.2	-45.1	-38
Vanadium	-51.4	-59.7	-55.2
Zinc	-57	-48.9	-50.4
Zirconium	-19.3	-27.7	-16.9

## Pampas Limos 7

Element	0% OM	1% OM	10% OM
Arsenic	238	197	229
Barium	-5.51	-16.7	-16.1
Calcium	14.9	29.2	15.2
Cesium	1280	!	953
Copper	5.24	9.84	8.65
Iron	-48.4	-50.1	-36.8
Potassium	1.92	5.91	5.05
Manganese	-72.1	-77.2	-64
Lead	114	118	102
Rubidium	15.3	2.92	12.8
Sulfur	2880	3360	2710
Antimony	4220		
Tin	2120		
Strontium	-5.75	-5.3	-10.6
Tellurium	40800		28100
Thorium	60.6	42.3	23.3
Titanium	-36.3	-38.8	-17.8
Vanadium	-15.2	4.88	30.7
Zinc	-29.7	-15.7	-26.3
Zirconium	71.3	76	99.6

## Pampas Limos 9

Element	0% OM	1% OM	10% OM
Arsenic	175	168	151
Barium	14.1	10.9	
Calcium	-0.415	9.91	5.91
Cesium	885	882	
Copper	-28.9	-21.2	-21.9
Iron	-37.9	-44.5	-41.7
Potassium	19.9	19.7	22.2
Manganese	-74.1	-77.2	-72.4
Lead	-44	-41.3	-33.8
Rubidium	-14	-14.9	-24
Sulfur	2420	2690	2430
Antimony	4230		
Tin	864	982	
Strontium	6.67	27.1	11.8
Tellurium	96600	150000	
Thorium	8.32	0.61	-2.89
Titanium	-33.9	-51.5	-39.1
Vanadium	-32.9	-28.8	0.751
Zinc	-20.8	-29.2	3.24
Zirconium	-5.02	-24.4	-21.1

Tables 26-34. Average percentage errors for samples of varying water content for each area.

## Hanford 2

Element	0% H <sub>2</sub> O	5% H <sub>2</sub> O	10% H <sub>2</sub> O
Barium	-5.32	-32.4	-22
Cesium	1210		
Copper	77.3	80.1	87.9
Lead	9.52	9.39	17.1
Rubidium	-6.33	-2.89	0.546
Strontium	13.7	18.3	25.3
Thorium	27.5	29	50.7
Zinc	-11.1	-3.8	-8.54
Zirconium	12.2	21.6	8.05

## Hanford 8

Element	0% H <sub>2</sub> O	5% H <sub>2</sub> O	10% H <sub>2</sub> O
Barium	-4.57	-23.6	-19.3
Cesium	1390	505	973
Copper		99.4	
Lead	-1.96	-8.92	1.2
Rubidium	-9.07	-11.3	-8.77
Strontium	9.5	9.51	11.4
Thorium	21.3	24.3	51
Zinc	-24.3	-32.1	-29.5
Zirconium	42	8.92	32.5

## Hesperia 3

Element	0% H <sub>2</sub> O	5% H <sub>2</sub> O	10% H <sub>2</sub> O
Barium	-3.15	-30	-30.8
Cesium	1580		
Copper		175	
Lead	1.5	12.2	14.4
Rubidium	-8.2	-8.98	-6.9
Tin	624		
Strontium	5.4	7.78	11.4
Thorium	21.4	42.5	61.6
Vanadium	36.2		
Zinc	-27.9	-20.4	-25.9
Zirconium	1.56	14.8	16

## Fresno 9

Element	0% H <sub>2</sub> O	5% H <sub>2</sub> O	10% H <sub>2</sub> O
Barium	-7.4	-14.7	-20.4
Cesium	1270		
Copper	65.1		
Lead	76.5	67.9	52.3
Rubidium	-3.32	-4.51	-0.285
Strontium	5.29	6.64	5.44
Thorium	20.2	46.9	22.3
Uranium	43.6	38.4	31.9
Vanadium	21.7	19.4	18.9
Zinc	-21.7	-17.3	-17.9
Zirconium	26.7	32.4	36.5

## Pampas Limos 1

Element	0% H <sub>2</sub> O	5% H <sub>2</sub> O	10% H <sub>2</sub> O
Arsenic	32.9	38.5	43.3
Barium	-15.6	-30.8	-23.5
Calcium	0.804	-12.4	-16.6
Cobalt	670		
Cesium	206	142	214
Copper	48.6	43.3	24
Iron	-30.7	-34	-34.3
Potassium	12.3	2.32	-6.31
Manganese	-53.1	-56.9	-54.5
Lead	13.9	9.52	-0.3
Rubidium	-15	-16	-13.8
Strontium	-1.1	-9.08	-9.71
Thorium	27.3	69.8	40.9
Titanium	-16.3	-14.4	-15.2
Vanadium	13.9	-2.67	-4.2
Zinc	-39.4	-35.9	-38.9
Zirconium	67.8	56.7	49.6

## Pampas Limos 4

Element	0% H <sub>2</sub> O	5% H <sub>2</sub> O	10% H <sub>2</sub> O
Arsenic	4.1	0.263	6.39
Barium	6.79	-12	-13.7
Calcium	11.2	12.7	4.33
Cesium	1120	912	756
Copper	8.68	33.7	24.8
Iron	-49.1	-47.9	-53
Potassium	-17.7	-16.8	-27.6
Lead	-46.6	-50	-35.1
Rubidium	-43.7	-40.9	-43.5
Sulfur	2710	2710	2490
Antimony	3580	3360	
Tin	1980		
Strontium	-17.1	-17.5	-21.3
Tellurium	8260		
Thorium	3.6	4.91	2.27
Titanium	-47.7	-48.7	-58.7
Vanadium	-49.5		
Zinc	-60.8	-57.4	-64.5
Zirconium	-18.4	-28.1	-11.9

## Pampas Limos 5

Element	0% H <sub>2</sub> O	5% H <sub>2</sub> O	10% H <sub>2</sub> O
Arsenic	93.4	71.8	90.4
Barium	-1.56	5.85	-1.13
Calcium	-3.15	4.27	-1.42
Cesium	703	833	911
Copper	19.3	11.5	3.4
Iron	-41.7	-47	-49.6
Potassium	0.00355	-2.97	-18.7
Lead	-1	2.18	-16.7
Rubidium	-32.7	-34.2	-29.1
Sulfur	2460	2780	2620
Antimony	2560	3030	
Tin	1820	1660	1720
Strontium	1.34	-15.5	81.3
Tellurium	18700	15000	18600
Thorium	10	2.48	30.4
Titanium	-41.2	-46	-57.5
Vanadium	-51.4	-53.6	
Zinc	-57	-51.3	-57.3
Zirconium	-19.3	-28.3	-28.4

## Pampas Limos 7

Element	0% H <sub>2</sub> O	5% H <sub>2</sub> O	10% H <sub>2</sub> O
Arsenic	238	223	244
Barium	-5.51	-15.4	-12.5
Calcium	14.9	4.47	1.89
Cesium	1280	1100	1250
Copper	5.24	3.26	-16.9
Iron	-48.4	-40	-52
Potassium	1.92	-11.1	-3.16
Manganese	-72.1	-66.3	-80.5
Lead	114	96.9	90.5
Rubidium	15.3	7.05	10.9
Sulfur	2880	2650	2470
Antimony	4220	3880	
Tin	2120		1510
Strontium	-5.75	-2.36	-6.24
Tellurium	40800		41300
Thorium	60.6	52.6	25.9
Titanium	-36.3	-38.2	-39.4
Vanadium	-15.2	11.1	-24.5
Zinc	-29.7	-27.1	-30.2
Zirconium	71.3	47.8	73.5

## Pampas Limos 9

Element	0% H <sub>2</sub> O	5% H <sub>2</sub> O	10% H <sub>2</sub> O
Arsenic	175	204	170
Barium	14.1	1.9	
Calcium	-0.415	-11.1	-16.7
Cesium	885	638	
Copper	-28.9	-30.8	-38.2
Iron	-37.9	-32.8	-43.5
Potassium	19.9	12.8	2.54
Manganese	-74.1	-59.6	-76.2
Lead	-44	-34.7	-48.6
Rubidium	-14	-13.8	-19.5
Sulfur	2420	2250	2100
Antimony	4230		
Tin	864	672	
Strontium	6.67	8.66	-0.948
Tellurium	96600	89900	
Thorium	8.32	33.9	-7.78
Titanium	-33.9	-31.2	-47.5
Vanadium	-32.9	-22.6	-36.4
Zinc	-20.8	-27.3	1.95
Zirconium	-5.02	-12.7	-15.7



Tables 35-43. Average percentage errors for 1% and 10% OM when compared to 0% OM concentration values for each area.

## Hanford 2

Element	APE for 1% OM	APE for 10% OM
Barium	-15.1	-33.1
Calcium	-6.92	-9.3
Cesium	-0.534	-10.6
Copper	-29.6	0.141
Iron	-2.09	-5.12
Potassium	-7.15	-10.2
Manganese	-25.4	-17.1
Lead	-7.68	-4.94
Rubidium	-1.25	-2.73
Antimony	-1.69	-12.2
Strontium	-4.8	-6.99
Tellurium	-21.3	-20.8
Thorium	20.1	9.32
Vanadium	6.06	3.2
Zinc	-0.944	-1.42
Zirconium	-2.76	-10.1

## Hanford 8

Element	APE for 1% OM	APE for 10% OM
Barium	-1.11	-40.6
Calcium	2.82	-11.2
Cesium	5.61	-71.8
Copper	-12.5	-4.1
Iron	3.99	-9.34
Potassium	-0.0461	-9.61
Manganese	-5.89	-32.7
Lead	4.2	-19.1
Rubidium	-3.76	-8.72
Scandium	5.17	-1.83
Strontium	-1.7	-8.4
Thorium	-10.2	-17.6
Vanadium	16.4	21.8
Zinc	-0.393	-9.3
Zirconium	-11.9	-18.4

## Hesperia 3

Element	APE for 1% OM	APE for 10% OM
Barium	-26.3	-47.7
Calcium	-8.72	-13
Copper	-17.2	-17.6
Iron	-4.96	-14.3
Potassium	-10.7	-14.6
Manganese	-34.2	-41.7
Lead	-12.7	4.86
Rubidium	-7.66	-9.73
Strontium	-4.76	-3.67
Thorium	-3.44	7.63
Titanium	-5.39	-8.23
Vanadium	-14.4	-3.74
Zinc	24.2	-13
Zirconium	-11.8	-3.76

## Fresno 9

Element	APE for 1% OM	APE for 10% OM
Arsenic	4.71	-23.5
Barium	-11.7	-55.8
Calcium	13.4	4.92
Copper	4.88	0.147
Iron	-17.8	-22.9
Potassium	-8.88	-15.5
Manganese	-26.8	-45.2
Lead	-25.3	-27.4
Rubidium	-19.8	-25.8
Strontium	-14.4	-23.3
Thorium	-1.24	-2.3
Titanium	-0.966	-11.1
Uranium	-2.07	-11.3
Vanadium	1.8	-6.36
Zinc	85	62.1
Zirconium	-18.2	-16.5

Pampas Limos 1

Element	APE for 1% OM	APE for 10% OM
Arsenic	-0.101	-8.94
Barium	1.8	-10.6
Calcium	-3.44	-6.6
Cesium	49.6	-15.3
Copper	-6	-22.5
Iron	5.04	-6.78
Potassium	-0.357	-12.1
Manganese	10.7	11.2
Nickel	5.07	-12.9
Lead	-7.59	-5.45
Rubidium	-5.87	-13.2
Sulfur	-35.7	16.5
Antimony	46	-0.218
Scandium	54.6	29.5
Strontium	-6.5	-1.47
Tellurium	9.6	-18.2
Thorium	-6.96	0.977
Titanium	9.77	0.265
Vanadium	3.59	6.14
Zinc	4.9	-10.5
Zirconium	-6.79	-24.5

Pampas Limos 4

Element	APE for 1% OM	APE for 10% OM
Arsenic	-12	-23.3
Barium	-2.78	-41.2
Calcium	5.06	-2.47
Cesium	5.87	-45
Copper	-4.52	-1.56
Iron	-13.4	-17
Potassium	0.137	-2.75
Lead	12.9	16.6
Rubidium	-2.33	-7.28
Sulfur	4.48	-7.28
Antimony	23.6	-22.7
Scandium	-7.45	-8.54
Selenium	1.59	-23.1
Strontium	-9.02	-2.21
Tellurium	-4.55	-36
Thorium	1.65	-24.9
Titanium	-14.8	-11.5
Vanadium	-31.7	-22.3
Zinc	12.2	30.5
Zirconium	-6.89	-12.9

Pampas Limos 5

Element	APE for 1% OM	APE for 10% OM
Arsenic	-8.59	-11.3
Barium	-4.37	-21.5
Calcium	4.46	-9.46
Cesium	12.5	-25.7
Copper	-0.599	-4.08
Iron	-14.1	-4.87
Potassium	2.56	-1.55
Lead	5.12	15.7
Rubidium	-1.86	1.4
Sulfur	6.33	-13.8
Antimony	49.8	-15.8
Scandium	-8.95	-10.7
Selenium	13.1	-25
Tin	-19.5	-36.2
Strontium	-11.3	-8.23
Tellurium	26.3	-45.1
Thorium	23.8	-2.21
Titanium	-7.52	-5.18
Vanadium	-17.9	-17
Zinc	17.8	3.99
Zirconium	-11.4	-7.3

Pampas Limos 7

Element	APE for 1% OM	APE for 10% OM
Arsenic	-13	-12.4
Barium	-12.8	-20.1
Calcium	11.3	-9.75
Cesium	9.52	-31.4
Copper	3.33	-7.08
Iron	-4.28	10.3
Potassium	2.87	-7.24
Manganese	-19.3	16
Lead	0.556	-15.1
Rubidium	-11.6	-11.9
Sulfur	14.8	-15.2
Antimony	3.36	-24.3
Scandium	9.77	-6.87
Tin	2.36	-48.9
Strontium	-0.531	-14.7
Tellurium	10	-38
Thorium	-12.3	-30.9
Titanium	-4.79	16.3
Vanadium	22.4	38.6
Zinc	18.7	-5.67
Zirconium	1.72	4.9

## Pampas Limos 9

Element	APE for 1% OM	APE for 10% OM
Arsenic	-3.48	-17.9
Barium	-3.72	-36.8
Calcium	9.26	-4.29
Cesium	-1.28	-69
Copper	9.72	-1.15
Iron	-11.6	-15.6
Potassium	-1.18	-8.24
Manganese	-13.1	-4.11
Lead	3.75	6.48
Rubidium	-2.07	-20.5
Sulfur	9.69	-9.52
Scandium	11.5	-8.32
Strontium	18	-5.7
Thorium	-8.05	-19.3
Titanium	-27.3	-17.1
Vanadium	5.04	35.1
Zinc	-11.5	17.3
Zirconium	-21.2	-25.3

Tables 44-52. Average percentage errors for 5% and 10% water when compared to 0% water concentration values for each area.

## Hanford 2

Element	APE for 5% H <sub>2</sub> O	APE for 10% H <sub>2</sub> O
Barium	-41.1	-26.6
Cesium	-15.4	-28.4
Copper	-2.49	7.39
Iron	-7.1	-7.01
Potassium	-19.8	-34.1
Manganese	-25.4	-34.1
Lead	-6.82	3.31
Rubidium	-2.9	-0.944
Strontium	-5.42	2.09
Thorium	-5.4	11.8
Titanium	-14.5	-32.7
Zinc	6.9	-3.7
Zirconium	7.69	-13.7

## Hanford 8

Element	APE for 5% H <sub>2</sub> O	APE for 10% H <sub>2</sub> O
Barium	-23.5	-26.1
Calcium	-31.6	-26.6
Cesium	-60.1	-39.9
Copper	-11.1	7.46
Iron	-5.44	-14.4
Potassium	-32.8	-26.4
Manganese	-40.8	-41.1
Lead	-7	1.56
Rubidium	-4.35	-7.37
Antimony	-31.8	7
Scandium	-29.4	-26.8
Strontium	-2.96	-5.69
Thorium	-0.879	16
Titanium	-30.6	-28.7
Zinc	-5.86	-22.2
Zirconium	-21.3	-13.6

## Hesperia 3

Element	APE for 5% H <sub>2</sub> O	APE for 10% H <sub>2</sub> O
Barium	-29.9	-34.1
Calcium	-25.2	-34.8
Cesium	-70.3	-64
Iron	-7.34	-10.4
Potassium	-27.7	-31.9
Manganese	-49.5	-43.6
Lead	-1.97	9.2
Rubidium	-4.28	-7.66
Antimony	-17.5	-22.6
Strontium	-0.791	-1.78
Tellurium	-19.1	-30.8
Thorium	20.2	22
Titanium	-28.1	-34.8
Uranium	-0.935	20
Vanadium	-12.5	-38.7
Zinc	-5.86	-22.2
Zirconium	-21.3	-13.6

## Fresno 9

Element	APE for 5% H <sub>2</sub> O	APE for 10% H <sub>2</sub> O
Arsenic	-25.7	-27.9
Barium	-12.5	-22.6
Calcium	-0.229	-24.4
Cesium	-50.9	-58.4
Copper	26.7	4.98
Iron	-4.61	-8.01
Potassium	-6.31	-24.2
Manganese	-23.9	-36.9
Lead	-9.61	-22.4
Rubidium	-6.17	-7.18
Strontium	-3.78	-9.87
Thorium	16.2	-8.37
Titanium	-7.77	-23.4
Uranium	-8.44	-17.3
Vanadium	-6.79	-12.1
Zinc	0.365	-5.62
Zirconium	-0.656	-3

## Pampas Limos 1

Element	APE for 5% H <sub>2</sub> O	APE for 10% H <sub>2</sub> O
Arsenic	-0.99	-2.92
Barium	-22.1	-18.5
Calcium	-17.4	-25.5
Cobalt	5.98	-11.2
Cesium	-25	-7.81
Copper	-8.41	-24.9
Iron	-9.45	-14.6
Potassium	-13.5	-24.9
Manganese	-12.6	-12.7
Lead	-8.67	-21.2
Rubidium	-6.07	-8.7
Antimony	-3.75	19
Scandium	8.81	-26.6
Tin	-12.6	-14.9
Strontium	-12.7	-17.8
Tellurium	-24.7	-20.8
Thorium	26.7	-0.395
Titanium	-2.84	-8.72
Vanadium	-18.8	-24.3
Zinc	0.541	-9.13
Zirconium	-11.3	-19.8

## Pampas Limos 4

Element	APE for 5% H <sub>2</sub> O	APE for 10% H <sub>2</sub> O
Arsenic	-8.5	-8.02
Barium	-21.7	-27.3
Calcium	-3.77	-15.6
Cesium	-21.3	-36.9
Copper	16.9	3.33
Iron	-2.65	-16.8
Potassium	-3.92	-20.9
Lead	-11.2	9.36
Rubidium	-0.299	-9.83
Sulfur	-4.76	-17.1
Antimony	-10.8	-15.7
Scandium	-14.8	-27.1
Selenium	-12.9	-13.6
Tin	-40.7	-36.7
Strontium	-5.49	-14.6
Tellurium	-25.1	-35.1
Thorium	-3.79	-11.2
Titanium	-6.8	-28.9
Vanadium	-18.3	-24.5
Zinc	3.37	-18.4
Zirconium	-16.3	-2.8

## Pampas Limos 5

Element	APE for 5% H <sub>2</sub> O	APE for 10% H <sub>2</sub> O
Arsenic	-15.6	-11.4
Barium	2.15	-9.61
Calcium	2.28	-8.39
Cesium	10.3	13.3
Copper	-11.2	-22
Iron	-13.6	-22.2
Potassium	-7.83	-26.9
Lead	-1.95	-24.3
Rubidium	-7.12	-5.19
Sulfur	6.79	-4.44
Antimony	11.8	-5.96
Scandium	3.07	-16.6
Selenium	-13.7	-22.8
Tin	-13.1	-15
Strontium	-20.8	61
Tellurium	-23.7	-10.3
Thorium	-11.5	6.68
Titanium	-12.8	-34.9
Vanadium	-9.3	-34.2
Zinc	7.68	-10.6
Zirconium	-15.5	-20.1

## Pampas Limos 7

Element	APE for 5% H <sub>2</sub> O	APE for 10% H <sub>2</sub> O
Arsenic	-9.4	-8.59
Barium	-15	-16.7
Calcium	-13.6	-20.2
Cesium	-17.6	-12
Copper	-6.79	-28.9
Iron	10.5	-16.3
Potassium	-17.1	-14.5
Manganese	14.6	-37.2
Lead	-12.6	-19.9
Rubidium	-11.8	-13.4
Sulfur	-12.3	-22.3
Antimony	-12.4	17.1
Scandium	-21.3	-18.6
Tin	-25.3	-34.8
Strontium	-1.59	-10.5
Tellurium	13.8	-8.83
Thorium	-9.74	-29.5
Titanium	-7.7	-14.3
Vanadium	24.4	-19.9
Zinc	-1.49	-10.7
Zirconium	-18	-8.85

## Pampas Limos 9

Element	APE for 5% H <sub>2</sub> O	APE for 10% H <sub>2</sub> O
Arsenic	4.79	-11.8
Barium	-15.1	-9.44
Calcium	-15.2	-24.7
Cesium	-28.7	-3.99
Copper	-7.55	-21.8
Iron	2.75	-18.1
Potassium	-10.6	-23
Manganese	48	-17.4
Lead	10.9	-17.3
Rubidium	-4.75	-15.7
Sulfur	-11.5	-21.4
Antimony	-34.7	-10.6
Scandium	-22.5	-36.2
Tin	-24	4.11
Strontium	-3.23	-16.4
Tellurium	-11.5	42.4
Thorium	17.4	-23.4
Titanium	-1.14	-28.5
Vanadium	9.48	-14.7
Zinc	-12.8	15.8
Zirconium	-12.7	-20.1

## Appendix II – Coefficients of Variation

Tables 53-61. Coefficients of variation for fine and coarse ground samples for elements that the instrument consistently found in each repetition (Has no relation to lab data). Mean of all CVs across all areas is 0.105.

## Hanford 2

Element	Fine Ground 2 min	Fine Ground 3 min	Fine Ground 6 min	Coarse Ground 2 min	Coarse Ground 3 min	Coarse Ground 6 min
Barium	0.028	0.044	0.016	0.065	0.007	0.060
Calcium	0.011	0.078	0.069	0.018	0.072	0.065
Cesium	0.118	0.178	0.130	0.421	0.034	0.202
Copper			0.103			0.023
Iron	0.021	0.015	0.042	0.040	0.034	0.085
Potassium	0.036	0.081	0.078	0.010	0.095	0.083
Manganese	0.053	0.246	0.167	0.037	0.196	0.102
Lead	0.113	0.140	0.100	0.162	0.099	0.125
Rubidium	0.025	0.017	0.026	0.075	0.078	0.040
Strontium	0.026	0.023	0.009	0.036	0.012	0.012
Tellurium	0.097					
Thorium	0.251	0.127	0.060	0.078	0.265	0.026
Titanium	0.024		0.111	0.025		0.052
Vanadium						0.216
Zinc	0.027	0.014	0.120	0.031	0.055	0.063
Zirconium	0.042	0.078	0.171	0.048	0.163	0.077
<i>Mean</i>	0.062	0.087	0.086	0.080	0.093	0.082

## Hanford 8

Element	Fine Ground 2 min	Fine Ground 3 min	Fine Ground 6 min	Coarse Ground 2 min	Coarse Ground 3 min	Coarse Ground 6 min
Barium	0.012	0.032	0.029	0.022	0.019	0.037
Calcium	0.017	0.070	0.071	0.011	0.009	0.019
Cesium	0.205	0.111	0.032	0.065	0.043	0.060
Iron	0.032	0.024	0.015	0.012	0.034	0.045
Potassium	0.020	0.112	0.093	0.025	0.017	0.014
Manganese	0.260	0.016	0.089	0.183	0.406	0.189
Lead	0.166	0.174	0.017	0.016	0.157	0.041
Rubidium	0.071	0.036	0.024	0.031	0.059	0.039
Antimony			0.218		0.207	0.149
Scandium						0.114
Tin			0.063		0.090	0.106
Strontium	0.021	0.029	0.011	0.020	0.012	0.014
Tellurium		0.197	0.197		0.170	0.115
Thorium	0.062	0.066	0.152	0.610	0.118	0.342
Titanium	0.047	0.084	0.057	0.047	0.015	0.041
Vanadium						0.145
Zinc	0.183	0.101	0.048	0.066	0.036	0.040
Zirconium	0.078	0.043	0.110	0.122	0.096	0.072
<i>Mean</i>	0.090	0.078	0.077	0.095	0.093	0.088

## Hesperia 3

Element	Fine Ground 2 min	Fine Ground 3 min	Fine Ground 6 min	Coarse Ground 2 min	Coarse Ground 3 min	Coarse Ground 6 min
Barium	0.038	0.068	0.024	0.043	0.055	0.030
Calcium	0.016	0.008	0.028	0.034	0.012	0.039
Cesium	0.161	0.160	0.063	0.244	0.152	0.029
Iron	0.032	0.039	0.037	0.020	0.030	0.025
Potassium	0.019	0.014	0.056	0.024	0.009	0.044
Manganese	0.273	0.205	0.096	0.106	0.161	0.127
Lead	0.227	0.347	0.057	0.148	0.246	0.029
Rubidium	0.029	0.029	0.026	0.039	0.021	0.023
Antimony	0.314		0.076			0.293
Tin			0.245			0.025
Strontium	0.019	0.006	0.014	0.019	0.023	0.010
Tellurium		0.162	0.356			0.027
Thorium	0.166	0.190	0.201	0.023	0.049	0.046
Titanium	0.010	0.008	0.034	0.053	0.056	0.074
Vanadium			0.245			0.185
Zinc	0.108	0.050	0.100	0.082	0.101	0.088
Zirconium	0.020	0.021	0.030	0.058	0.067	0.053
Mean	0.102	0.093	0.099	0.069	0.076	0.068

## Fresno 9

Element	Fine Ground 2 min	Fine Ground 3 min	Fine Ground 6 min	Coarse Ground 2 min	Coarse Ground 3 min	Coarse Ground 6 min
Barium	0.052	0.037	0.030	0.125	0.032	0.067
Calcium	0.047	0.034	0.050	0.021	0.021	0.011
Cesium	0.052	0.223	0.187	0.132	0.025	0.072
Copper		0.291	0.184		0.015	0.242
Iron	0.059	0.025	0.029	0.015	0.026	0.006
Potassium	0.033	0.022	0.013	0.025	0.029	0.013
Manganese	0.218	0.223	0.114		0.169	0.092
Lead	0.190	0.061	0.056	0.332	0.244	0.043
Rubidium	0.066	0.045	0.029	0.026	0.021	0.022
Antimony						0.087
Strontium	0.050	0.020	0.017	0.026	0.003	0.014
Thorium	0.103	0.193	0.133	0.172	0.041	0.064
Titanium	0.026	0.028	0.048	0.046	0.063	0.015
Uranium	0.153	0.072	0.188	0.282	0.093	0.122
Vanadium			0.074			0.069
Zinc	0.288	0.063	0.040	0.103	0.037	0.107
Zirconium	0.015	0.034	0.038	0.102	0.059	0.025
Mean	0.096	0.091	0.077	0.108	0.059	0.063

## Pampas Limos 1

Element	Fine Ground 2 min	Fine Ground 3 min	Fine Ground 6 min	Coarse Ground 2 min	Coarse Ground 3 min	Coarse Ground 6 min
Arsenic	0.176	0.057	0.031	0.229	0.072	0.085
Barium	0.132	0.025	0.023	0.050	0.116	0.052
Calcium	0.028	0.023	0.011	0.052	0.034	0.041
Cobalt			0.058			
Cesium	0.294	0.161	0.146	0.125	0.203	0.264
Copper	0.259	0.124	0.054	0.130	0.243	0.161
Iron	0.102	0.029	0.034	0.052	0.150	0.147
Potassium	0.011	0.006	0.009	0.030	0.025	0.044
Manganese	0.072	0.167	0.028	0.217	0.110	0.151
Lead	0.122	0.070	0.024	0.009	0.268	0.049
Rubidium	0.087	0.042	0.029	0.007	0.068	0.089
Sulfur						0.166
Scandium		0.340	0.252			0.213
Tin						0.194
Strontium	0.074	0.064	0.024	0.103	0.241	0.062
Thorium	0.257	0.230	0.113	0.149	0.172	0.029
Titanium	0.017	0.018	0.038	0.021	0.149	0.114
Vanadium			0.068	0.056	0.108	0.170
Zinc	0.527	0.067	0.113	0.116	0.217	0.194
Zirconium	0.452	0.071	0.097	0.032	0.218	0.270
Mean	0.174	0.093	0.064	0.086	0.149	0.131

## Pampas Limos 4

Element	Fine Ground 2 min	Fine Ground 3 min	Fine Ground 6 min	Coarse Ground 2 min	Coarse Ground 3 min	Coarse Ground 6 min
Arsenic	0.207	0.063	0.007	0.062	0.101	0.096
Barium	0.212	0.141	0.009	0.073	0.094	0.023
Calcium	0.010	0.005	0.007	0.018	0.013	0.019
Cesium		0.324	0.110	0.199	0.205	0.056
Copper			0.104			0.132
Iron	0.081	0.065	0.011	0.060	0.025	0.032
Potassium	0.052	0.016	0.017	0.019	0.010	0.014
Lead			0.106			0.204
Rubidium	0.047	0.013	0.021	0.113	0.124	0.026
Sulfur	0.010	0.018	0.016	0.021	0.015	0.035
Antimony			0.232			0.196
Scandium	0.376	0.103	0.078	0.268	0.202	0.058
Tin			0.146			0.092
Strontium	0.090	0.070	0.043	0.118	0.008	0.062
Tellurium			0.052			0.086
Thorium		0.197	0.063			0.143
Titanium	0.089	0.121	0.035	0.056	0.107	0.063
Vanadium			0.185			0.172
Zinc	0.291	0.276	0.128	0.108	0.114	0.085
Zirconium	0.096	0.150	0.107	0.462	0.047	0.042
Mean	0.130	0.111	0.074	0.121	0.082	0.082



## Pampas Limos 5

Element	Fine Ground 2 min	Fine Ground 3 min	Fine Ground 6 min	Coarse Ground 2 min	Coarse Ground 3 min	Coarse Ground 6 min
Arsenic	0.126	0.115	0.048	0.132	0.145	0.020
Barium	0.108	0.007	0.043	0.160	0.037	0.068
Calcium	0.008	0.004	0.034	0.033	0.055	0.048
Cesium	0.092	0.175	0.092	0.027	0.083	0.072
Copper		0.148	0.054		0.138	0.171
Iron	0.079	0.049	0.114	0.042	0.010	0.087
Potassium	0.045	0.017	0.016	0.006	0.005	0.019
Lead		0.426	0.073			
Rubidium	0.102	0.009	0.036	0.051	0.065	0.022
Sulfur	0.013	0.026	0.061	0.048	0.058	0.066
Antimony	0.105		0.048		0.252	0.298
Scandium		0.319	0.083	0.184	0.138	0.051
Selenium						0.134
Tin		0.177	0.046		0.197	0.142
Strontium	0.083	0.087	0.045	0.147	0.221	0.211
Tellurium	0.112	0.307	0.129		0.128	0.189
Thorium		0.026	0.180	0.090	0.149	0.125
Titanium	0.051	0.074	0.064	0.038	0.086	0.144
Vanadium			0.087		0.124	0.059
Zinc	0.228	0.131	0.020	0.128	0.024	0.017
Zirconium	0.005	0.126	0.056	0.172	0.183	0.175
Mean	0.083	0.123	0.066	0.090	0.110	0.106

## Pampas Limos 7

Element	Fine Ground 2 min	Fine Ground 3 min	Fine Ground 6 min	Coarse Ground 2 min	Coarse Ground 3 min	Coarse Ground 6 min
Arsenic	0.107	0.514	0.046		0.127	0.080
Barium	0.042		0.052		0.118	0.024
Calcium	0.013	0.145	0.047	0.121	0.030	0.018
Cesium	0.124		0.111		0.124	0.177
Copper		0.357	0.097			0.187
Iron	0.067	0.450	0.049	0.400	0.045	0.040
Potassium	0.026	0.168	0.030	0.080	0.014	0.011
Manganese	0.209	0.403	0.174	0.513	0.261	0.053
Lead	0.153		0.104		0.306	0.143
Rubidium	0.071	0.408	0.048	0.406	0.056	0.039
Sulfur	0.005	0.155	0.068	0.125	0.014	0.016
Antimony	0.267		0.230		0.048	0.233
Scandium			0.052		0.204	0.067
Tin			0.148		0.183	0.135
Strontium	0.102	0.441	0.090	0.346	0.144	0.050
Tellurium	0.161		0.173			0.341
Thorium	0.146		0.076		0.038	0.347
Titanium	0.068	0.187	0.127	0.061	0.041	0.019
Vanadium			0.222		0.256	0.148
Zinc	0.059	0.927	0.128	0.782	0.060	0.112

Zirconium	0.167	0.482	0.190	0.223	0.228	0.304
Mean	0.105	0.386	0.108	0.306	0.121	0.121

## Pampas Limos 9

Element	Fine Ground 2 min	Fine Ground 3 min	Fine Ground 6 min	Coarse Ground 2 min	Coarse Ground 3 min	Coarse Ground 6 min
Arsenic	0.107	0.123	0.085	0.144	0.065	0.109
Barium	0.078	0.152	0.019	0.061	0.172	0.062
Calcium	0.057	0.044	0.035	0.026	0.027	0.014
Cesium	0.255	0.079	0.049	0.129	0.211	0.215
Copper	0.192	0.058	0.088		0.100	0.106
Iron	0.086	0.007	0.039	0.034	0.095	0.014
Potassium	0.027	0.027	0.024	0.046	0.043	0.022
Manganese	0.127	0.046	0.124	0.205	0.081	0.041
Lead		0.088	0.078			0.216
Rubidium	0.080	0.090	0.057	0.082	0.008	0.057
Sulfur	0.057	0.033	0.021	0.048	0.053	0.022
Antimony		0.260	0.120			0.163
Scandium	0.263	0.267	0.051	0.284	0.145	0.128
Tin		0.295	0.362			0.295
Strontium	0.072	0.117	0.016	0.029	0.030	0.076
Tellurium			0.173			0.240
Thorium		0.228	0.131		0.073	0.094
Titanium	0.212	0.069	0.168	0.079	0.136	0.022
Vanadium		0.146	0.180	0.097	0.168	0.065
Zinc	0.130	0.096	0.079	0.116	0.086	0.011
Zirconium	0.203	0.100	0.145	0.050	0.050	0.014
Mean	0.130	0.116	0.097	0.095	0.091	0.095

Tables 62-63. Coefficients of variation for organic matter samples for elements that the instrument consistently found in each repetition (Has no relation to lab data). Mean of CVs across all areas is 0.122.

Element	Hanford 2		Hanford 8		Hesperia 3		Fresno 9	
	1% OM	10% OM	1% OM	10% OM	1% OM	10% OM	1% OM	10% OM
Barium	0.327	0.389	0.014	0.078	0.442	0.036		
Calcium	0.068	0.108	0.088	0.059	0.081	0.078	0.042	0.030
Copper	0.201	0.138	0.058	0.259	0.173		0.342	0.089
Iron	0.017	0.025	0.069	0.051	0.016	0.012	0.243	0.221
Potassium	0.095	0.146	0.105	0.082	0.105	0.098	0.042	0.048
Manganese	0.038	0.150	0.073	0.134	0.182	0.232	0.273	0.329
Lead	0.118	0.037	0.110	0.101	0.092	0.140	0.172	0.203
Rubidium	0.068	0.058	0.012	0.024	0.106	0.019	0.246	0.234
Antimony			0.163					
Scandium		0.078						
Tin			0.152					

Strontium	0.036	0.050	0.015	0.027	0.086	0.015	0.258	0.226
Tellurium			0.088					
Thorium	0.158	0.289	0.037	0.223	0.060	0.131	0.243	0.247
Titanium	0.049	0.073	0.046	0.021	0.107	0.049	0.158	0.040
Uranium							0.248	0.155
Vanadium			0.097		0.103	0.070	0.196	
Zinc	0.027	0.103	0.029	0.053	0.401	0.079	0.725	0.638
Zirconium	0.167	0.177	0.072	0.118	0.051	0.091	0.242	0.298
<i>Mean</i>	0.105	0.130	0.072	0.095	0.143	0.081	0.245	0.212

Element	Pampas Limos 1		PL 4		PL 5		PL 7		PL 9	
	1% OM	10% OM	1% OM	10% OM	1% OM	10% OM	1% OM	10% OM	1% OM	10% OM
Arsenic	0.098	0.056	0.123	0.139	0.084	0.041	0.166	0.035	0.108	0.157
Barium	0.060	0.081	0.017	0.306	0.245	0.029	0.212	0.013	0.095	
Calcium	0.048	0.053	0.016	0.029	0.002	0.019	0.035	0.019	0.032	0.005
Cobalt						0.138				
Cesium	0.059	0.265	0.146		0.403	0.176		0.173	0.179	
Copper	0.174	0.034	0.149	0.320	0.220	0.054	0.263	0.240	0.116	0.109
Iron	0.031	0.022	0.030	0.074	0.116	0.146	0.106	0.038	0.068	0.098
Potassium	0.009	0.003	0.009	0.037	0.026	0.030	0.013	0.029	0.003	0.017
Manganese	0.042	0.011					0.190	0.007	0.084	0.078
Lead	0.070	0.056	0.174	0.088	0.172	0.178	0.224	0.111	0.094	0.167
Rubidium	0.008	0.008	0.034	0.096	0.050	0.043	0.038	0.028	0.031	0.151
Sulfur			0.016	0.029	0.013	0.026	0.030	0.023	0.020	0.024
Antimony	0.088		0.252	0.130	0.300					
Scandium	0.154	0.027	0.103		0.094	0.183	0.124	0.086	0.176	0.185
Tin	0.337		0.174	0.135					0.176	
Strontium	0.016	0.101	0.028		0.072	0.083	0.141	0.020	0.036	0.003
Tellurium	0.051		0.338					0.158	0.214	
Thorium	0.092	0.106	0.223		0.266	0.076	0.198	0.368	0.205	0.345
Titanium	0.052	0.061	0.050	0.092	0.151	0.235	0.016	0.033	0.045	0.051
Vanadium	0.206	0.088		0.252	0.072	0.147	0.154	0.277	0.080	0.065
Zinc	0.091	0.015	0.071	0.397	0.151	0.110	0.316	0.027	0.082	0.313
Zirconium	0.139	0.095	0.049	0.096	0.195	0.020	0.261	0.185	0.052	0.254
<i>Mean</i>	0.091	0.064	0.105	0.148	0.146	0.096	0.146	0.098	0.095	0.126

Tables 64-65. Coefficients of variation for water samples for elements that the instrument consistently found in each repetition (Has no relation to lab data). Mean of coefficients of variation across all areas is 0.101.

Element	Hanford 2		Hanford 8		Hesperia 3		Fresno 9	
	1% OM	10% OM	1% OM	10% OM	1% OM	10% OM	1% OM	10% OM
Barium	0.244	0.032	0.015	0.046	0.072	0.095	0.117	0.160
Calcium	0.043	0.017	0.049	0.006	0.026	0.016	0.012	0.064
Cesium			0.194	0.137				

Copper	0.031	0.204	0.163		0.155				
Iron	0.057	0.047	0.027	0.030	0.078	0.055	0.044	0.059	
Potassium	0.055	0.011	0.012	0.041	0.019	0.060	0.037	0.018	
Manganese	0.125	0.192	0.047	0.121	0.298	0.117	0.189	0.384	
Lead	0.032	0.117	0.081	0.191	0.109	0.129	0.067	0.164	
Rubidium	0.074	0.052	0.064	0.051	0.030	0.019	0.050	0.069	
Antimony			0.077						
Strontium	0.094	0.046	0.039	0.049	0.038	0.056	0.052	0.061	
Tellurium									
Thorium	0.025	0.151	0.047	0.333	0.166	0.071	0.063	0.085	
Titanium	0.061	0.040	0.051	0.045	0.033	0.023	0.055	0.047	
Uranium							0.144	0.137	
Vanadium							0.056	0.095	
Zinc	0.070	0.060	0.175	0.108	0.032	0.180	0.067	0.019	
Zirconium	0.251	0.017	0.149	0.060	0.134	0.021	0.062	0.131	
<i>Mean</i>	0.089	0.076	0.079	0.094	0.091	0.070	0.072	0.107	

Element	Pampas Limos 1		PL 4		PL 5		PL 7		PL 9	
	1% OM	10% OM	1% OM	10% OM	1% OM	10% OM	1% OM	10% OM	1% OM	10% OM
Arsenic	0.141	0.204	0.052	0.117	0.081	0.050	0.048	0.125	0.086	0.344
Barium	0.083	0.012	0.043	0.144	0.113	0.052	0.034	0.047	0.083	
Calcium	0.043	0.064	0.004	0.031	0.010	0.020	0.036	0.023	0.053	0.005
Cesium	0.154	0.090	0.077	0.144	0.116	0.121	0.180	0.149	0.130	
Copper	0.026	0.211	0.043	0.218	0.267	0.246	0.093	0.149	0.152	0.233
Iron	0.021	0.030	0.016	0.028	0.033	0.037	0.068	0.129	0.037	0.167
Potassium	0.008	0.022	0.030	0.012	0.010	0.033	0.015	0.032	0.010	0.032
Manganese	0.059	0.179					0.350	0.223	0.025	0.316
Lead	0.073	0.059	0.065	0.161	0.250	0.245	0.176	0.128	0.250	0.198
Rubidium	0.086	0.038	0.064	0.035	0.065	0.044	0.091	0.053	0.082	0.245
Sulfur			0.015	0.037	0.009	0.020	0.027	0.031	0.084	0.037
Antimony			0.299		0.193		0.273			
Scandium	0.246	0.034	0.089	0.196	0.106	0.099	0.115	0.107	0.046	0.102
Tin					0.201	0.042		0.148	0.257	
Strontium	0.028	0.038	0.105	0.057	0.038	0.633	0.105	0.009	0.046	0.056
Tellurium					0.261	0.229		0.206	0.239	
Thorium	0.156	0.152	0.340	0.081	0.118	0.489	0.074	0.192	0.081	0.257
Titanium	0.050	0.119	0.008	0.028	0.136	0.094	0.092	0.090	0.102	0.060
Vanadium	0.110	0.066			0.181		0.083	0.275	0.026	0.187
Zinc	0.121	0.047	0.140	0.206	0.055	0.010	0.085	0.066	0.020	0.428
Zirconium	0.110	0.163	0.062	0.200	0.037	0.127	0.092	0.151	0.092	0.319
<i>Mean</i>	0.089	0.090	0.085	0.106	0.114	0.144	0.107	0.117	0.095	0.187