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PART I: Analysis

Chapter 1

ANALYSIS OF SULFUR IN THE COPPER BASIN AND MUDDY RIVER SITES USING PORTABLE XRF INSTRUMENTATION

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ABSTRACT

The feasibility of using a portable analytical instrument, the Niton XRF XLt 500He, was tested as a technique for sulfur analysis of wet sediment or soil samples in the field. The effect of sample preparation on the precision and accuracy of sulfur determination was specifically evaluated. The Niton XRF XLt 500He uses X-ray fluorescence to detect different elements. This unit employs a helium purge to allow the analysis of elements lighter than potassium. Samples with sulfur varying from 0.3 to 2.0% were successfully measured with the instrument. The precision of the unit is excellent and the limit of detection can be extremely low with careful attention to sample preparation. The quantitation limit was estimated as 237 ppm sulfur.

Keywords: x-ray fluorescence, sulfur, sediment

1. PURPOSE OF THE STUDY

Experiments were conducted to determine to what accuracy and how precisely could sulfur be determined in sediments and soils using a portable Niton XRF Model XLt 500He. This unit has been modified by NITON Analyzers (Niton) to allow a flow of helium to displace the ambient air present in the instrument, especially in the areas of the sample and detector. Portable field analyzers using X-ray fluorescence are normally limited to the quantitative analysis of elements heavier than potassium, because air and moisture effectively scatter the weaker fluorescence from the lighter elements. Since helium does not appreciably scatter or absorb

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sulfur x-ray fluorescence, it was hoped that the helium purge method would allow better limits of detection and quantitation of sulfur in a portable analyzer.

2. INTRODUCTION

The presence of sulfur in soil can present potential risks of harm to human health and the environment. The Copper Basin, located near the junction of Tennessee, Georgia, and North Carolina and the Muddy River in Boston, Massachusetts both present significant levels of sulfur (S) in soils and sediments. The Copper Basin was once an active mining site and the elevated sulfur presence there is a result of pollution from mining activities. These elevated levels of sulfur can create high levels of acidity in water runoff, causing detrimental effects on the natural habitat and environment. The first step in the remediation of this site is a determination of the spatial extent of soils with greater than 2% sulfur, soils which are thought to have the greatest potential for acid mine drainage. XRF was used for the analysis of sulfur in the Copper Basin tailings. The Muddy River is the backbone of the Emerald Necklace, a historic landscape surrounding Boston, Massachusetts. Over the years, the Muddy River has accumulated large quantities of sediment consisting of decaying vegetation, sand from stormwater drains, and riverbank erosion. These sediments are contaminated with high levels of metals and petroleum hydrocarbons. The concentration of total sulfur in the sediment varies with location – roughly from 0.2% to 2%. Depending on the availability of oxygen in the sediments, sulfur can be generated as hydrogen sulfide under anoxic conditions, which is toxic to fish and when volatilized unpleasant to humans at extremely low concentrations in the air. Dredging of the river is planned for the near future and may release harmful levels of hydrogen sulfide into the air and water. The selection of a remediation strategy for the river that minimizes sulfur volatile emissions during sediment dredging operations could be guided by a sulfur analysis of Muddy River sediments. Portable XRF represents a convenient analytical option. Our study evaluates the suitability of the Niton XRF XLt 500He as a portable handheld instrument for sulfur quantitation.

Earlier studies conducted by A. Richter in 2005 (Richter, 2005) of tailings from the Copper Basin analyzed sulfur content with a portable XRF unit without a helium purge and showed promising results. Moist silty samples containing from 1 to 6% sulfur were analyzed with the aid of a special filter optimized for light elements. Calibration of the device was shown to be possible by taking into account the iron content of the sample, and a complex calibration was found to work with a number of different samples. However, the signal/noise was low, and the device offered the best performance for samples with high levels of sulfur. Improvements in the technology and the inclusion of a helium purge increased the signal/noise by a significant amount and promised analysis of samples with lower amounts of sulfur, such as sediments.

There are several well established methods for the analysis of total sulfur in soil, including combustion in an oxygen bomb (Parr, Bailey and Gehring, 1961) followed by analysis of the sulfate produced or alkaline oxidation followed by X-ray fluorescence (Tabatabai and Bremmer, 1970 and Perrott et al, 1991). However, XRF for sulfur analysis normally requires high vacuum pumps to eliminate the scattering effects of the air. These devices are not suited for portable use

due to the size of the instruments and the supporting operational requirements, such as power and vacuum pumps.

In this study, we compared the sulfur analyses obtained by the Niton XRF XLt 500He with the analyses of similar samples using the oxygen bomb method followed by sulfate analysis. Samples with certified sulfur concentrations were used for calibration. Sediment samples were run with and without the helium purge in the Niton XRF Model 500He in order to determine the degree of improvement in the signal detection attributable to helium's elimination of scattering by atmospheric gases.

The theory of X-ray fluorescence has been described previously (Jenkins, 1999). The X-ray sulfur fluorescence occurs from 2.2 to 2.4 keV and is relatively free from interference attributable to fluorescence from other elements or to excitation lines from the source.



Figure 1. The Niton XLt 500 He system with sample stand, analyzer, and Helium purge.

The Thermo Fisher Scientific Niton XLt 500He system uses the helium purge technique in a portable, handheld format. The analyzer has a sealed measurement head which is purged at 150 mL/min with pure helium to remove air from the X-ray analysis path. This allows the light element X-rays to pass through and reach the X-ray detector. The analyzer has factory calibration for various common applications using certified reference material. The factory calibration can be modified, if necessary, by the user to improve the accuracy for a particular type of material being analyzed. The analyzer uses a 40 Kev miniaturized X-ray tube and can determine, using K shell radiation, elements Mg to Ba and L shell radiation for elements Cs to U.

The XRF signal can be significantly influenced by the preparative technique (Pasmore et al, 2005 and Shesky, 1997). For the most precise work, drying the sample to eliminate water followed by grinding and sieving to 120 mesh is recommended (Niton). The advantages of this

procedure are: representativeness of the sample is excellent since homogeneity is achieved, intimate contact and flatness of the sample will produce the highest and most reproducible fluorescence, and the sample concentration reported will not be diluted by water content, which must be separately determined. Our study evaluated the effect of water on the sulfur analysis, since it is not always convenient to dry the sample in the field. We studied whether water content presented additional unique analytical problems in the analysis of the lighter elements with the Niton XRF Model 500He compared to the analysis of the heavier elements.

Elements heavier than potassium are excited by x-rays in the 5 to 40 keV range. One can estimate the penetration distance, $x = 46000/\mu \cdot \rho$, where x is the distance traveled for 99% absorption, μ is the mass absorption coefficient and ρ is the density. The X-ray excitation of heavier elements penetrates a couple of mm into the sample, and the fluorescence readily passes back through a thickness of the sample before being detected. However X-rays used to excite the lighter elements, like sulfur, are only 5 keV and thus will only pass only a few microns into the sample. The resulting X-ray fluorescence will also emerge from only the top few microns of the sample. In recognition of the “weak” penetration of x-rays involved in the analysis of lighter elements, sediment samples were prepared with a thinner sample covering – 4 micron thick clear polypropylene cover. This thin cover protects the source and detector from the sediment sample. The cover also is used in the preparation of the sample “cup” which provides a clear “window” covering for the soil. In comparison a clear 6 micron Mylar cover is recommended (Niton) for analysis of the heavier elements.

Several experiments were conducted to determine what factors influence the accuracy of the sulfur analysis using the portable XRF XLt 500He. Certified soil and sediment standards containing a range of total sulfur content (0.3% to 2%) typically found in sediments were analyzed. Indeed, sediment samples collected from two different locations in the Muddy River were found to have sulfur at the extremes of the calibration range.

2.1 The Effect of Water Content on Sulfur Determination

Experiments were conducted to determine the effects of water content in soil and sample preparative techniques on the determination of sulfur in soil and sediment samples. The effect of significant water content in sediment samples and the effect of particle size homogeneity were studied. Four sample preparative methods were studied to determine the effect on the resulting analytical results. Table 1 summarizes the different Sediment Methods described above.

Table 1. Summary of Sediment Sample Preparation

Summary of Sediment Sample Preparation

	Dried?	Ground?	Water
Method 1	Yes	yes	Added to dry sample
Method 2	Yes	No	Added to dry sample
Method 3	No	No	Dried to differing degrees
Method 4	No	No	Excess water blotted

2.2 The Effect of Water Content on Other Elements

Samples prepared by the methods shown in Table 1 were also analyzed for other “light” elements as well as for iron, a typical “heavier” element found in sediments to determine if the conclusions based on Sulfur data could be generalized to other elements.

2.3 The Benefit of Helium for Sulfur Analysis

Samples were analyzed for sulfur with and without helium flow in order to determine the benefit (i.e., an expected increase in signal to noise) based on the reduction of fluorescence scatter from air due to the use of a helium “purge”.

2.4 Accuracy of Sulfur Analysis

In order to determine the accuracy of the sulfur analysis, identical samples were analyzed using an alternate method for the determination of total sulfur to compare to the results obtained with XRF. Thus the “oxygen bomb” method (described as modified below) is relatively inexpensive and has been used for many years for the successful determination of sulfur in a variety of materials. One of the goals of this paper is the comparison of the accuracy and precision of sulfur concentrations in soils determined by the two methods.

2.5 Calibration of the Niton XRF XLt 500He

Standard sediments samples, with known and certified composition were used for calibration of the Niton XRF XLt 500He. Data for all experiments consisted of counts (of X-ray fluorescence) detected per second. Additional experiments were conducted to quantify the signal to noise ratio (S/N) as a function of total signal acquisition time. For the Studies (A) – (C), total acquisition times were kept constant nominally at 240 seconds for Sulfur and other “light” elements, and 60 seconds for the “heavier” elements. Filtration and x-ray tube operating conditions are set up in the instrument to individually optimize excitation of the light and heavy elements in order to maximize the signal to noise ratio. Different sediment and soil “standards” containing certified levels of sulfur were used to calibrate the Niton XRF XLt 500He. Table 2 shows the fluorescence level in counts per second (cps) for different concentrations of sulfur. These data were used to create calibration curves. Different calibration curves were used to best match the actual sulfur concentration present in the sediments tested. The two ranges of sulfur found in the sediments best matched the calibration curves in the range of 0 to 0.3% (low) or 0 to 3.0% (high) as shown in Figures 2 and 3.

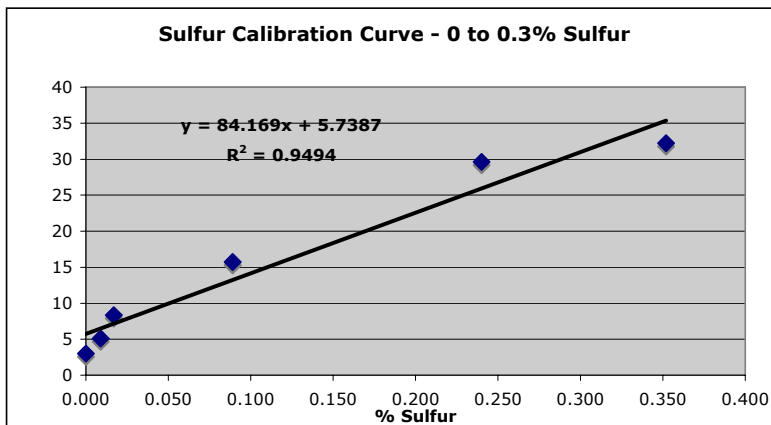


Figure 2. XRF calibration at low sulfur concentrations

Table 2. Certified Standards used for Calibration of XRF

Sample	S cert. %	S cps
99.999% Silica	0.00	2.99
NCS DC73308	0.01	5.09
NCS DC73309	0.02	8.33
NIST2709	0.09	15.71
NIST2710	0.24	29.59
NIST 1646a	0.35	32.23
NIST 2684b	3.08	484.78

2.6 The Effect of Sampling Time on Signal/Noise

As predicted by statistical considerations, the standard deviation of the sulfur signal decreases as the sampling time is increased. Figure 4 shows the expected relationship between the standard deviation and the inverse square root of the sampling time. (It is assumed that the total sample excitation is directly proportional to the sampling time for constant excitation power.

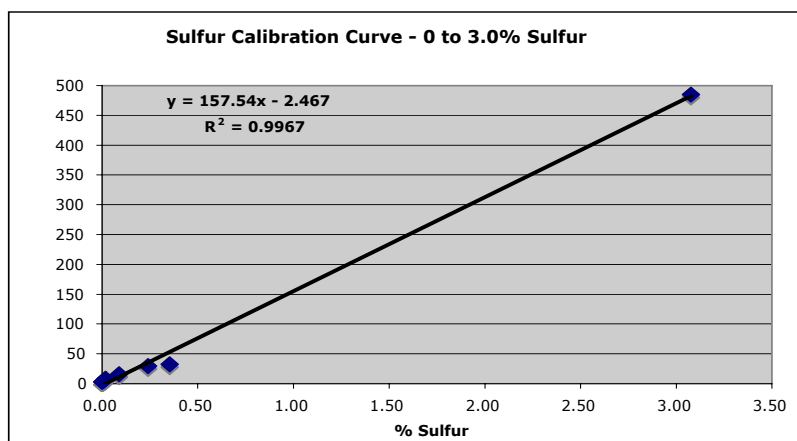


Figure 3. XRF calibration at high sulfur concentrations

The non-zero intercept indicates that there is a significant contribution to the standard deviation of the sulfur signal that does not arise from stochastic events involved in excitation of or fluorescence from sulfur in the sample. While data collection for longer times does improve the signal to noise ratio, a significant component of noise remains even at longer measurement times. The portability of the XRF XLt 500He permits data collection in the field. In field situations, measurements at shorter times allow a large area to be screened in a relatively short period of time. In this case, it may be more important to have data from many samples with a larger standard deviation, than data from fewer samples that have a smaller standard deviation. In general, we found that collecting fluorescence data with the XRF XLt 500He for a period of four minutes improves the S/N by a factor of two over data measured for only 30 seconds. Only additional slight improvement in S/N can be realized by data measurements longer than 4 or five minutes.

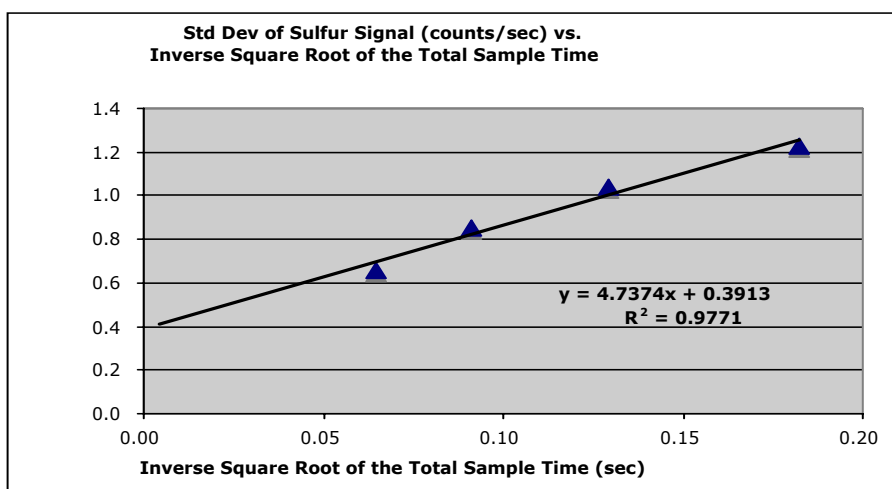


Figure 4. Standard deviation of sulfur fluorescence as a function of the inverse square root of the total sample time

3. RESULTS

3.1 The Effect of Water Content on Sulfur Determination

3.1.1 Sediment Method 1

Sediment samples were placed in an oven overnight at 60°C to dry completely, then ground with a mortar and pestle and passed through a 120 mesh screen. The effect of water on the analysis was studied by adding organic-free water to the dried sample and then thoroughly mixing the dried sediment and water. Sediment samples were prepared with water varying from 0 to 50% w/w. Figure 5 was based on XRF data of shallow sediments in a portion of the Muddy

River with approximately 0.30% sulfur. A linear trend of decrease in sulfur x-ray fluorescence with increase in water concentration is consistent with a simple dilution of the sediment with added water; the sulfur fluorescence is practically halved (44% decrease) as the sample is diluted to about 50% with added water.

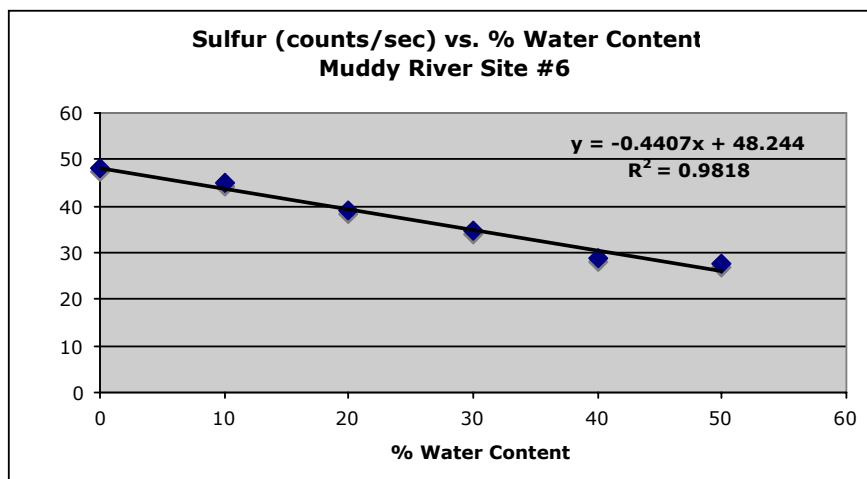


Figure 5. Sulfur (cps) versus water content for Method 1

3.1.2 Sediment Method 2

Sediment samples were placed in oven at 60°C overnight to dry completely, and then they were simply forced through a coarse screen (approximately 60 mesh) in order to remove stones, sticks, and leaf fragments. The effect of water on the analysis was studied by adding organic-free water to the dried sample. Comparison of the results from Method 1 and Method 2 show how important particle size and homogeneity is for sulfur analysis of

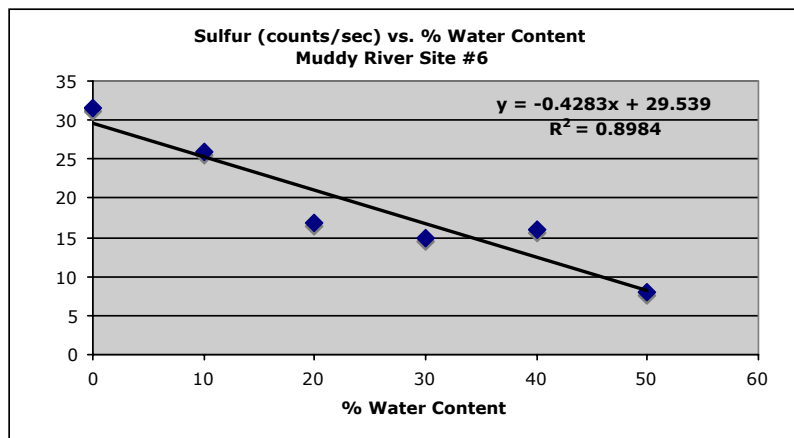


Figure 6. Sulfur (cps) versus water content for Method 2

sediment samples. While both methods show a dilution effect as water is added to the dried sediment, the effect is much larger for the coarsely sieved sediment; the sulfur fluorescence has decreased 76% with the addition of 50% water by weight in Method 2, much more than with Method 1. Note in **Figure 6** that R^2 for Method 2 is significantly poorer than for Method 1, probably due the greater homogeneity of the samples created with Method 2. In addition, the number of counts decreased overall for the sample created with Method 2. The coarseness and irregularity of the front surface of the Method 2 sample creates greater scattering at angles not captured by the fluorescence detector.

3.1.3 Sediment Method 3

Wet sediment samples were passed through a coarse screen (approximately 60 mesh) to remove bulky particles, then put in an oven at 60°C for different lengths of time to obtain samples of different water content. In this case, no water was added to the analyzed

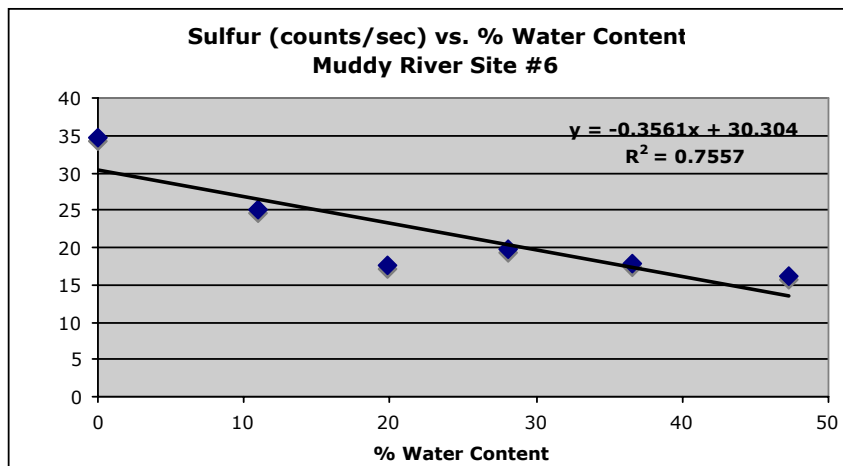


Figure 7. Sulfur (cps) versus water content for Method 3

sediment as was the case for Methods 1 and 2. Method 3 is a closer representation of natural samples. Figure 7 shows that the linear regression for Method 3 fits the data less well than in Method 1 or Method 2. Method 3 produces samples that are possibly more heterogeneous than the previous methods that may be the cause of greater scatter in the graph. The overall quantitation extrapolated to zero % water content is similar to that of Method 2 – only 60% of the “dry” quantitation extrapolation using Method 1.

Methods 1 – 3 were also used to evaluate the sediment in a different section of the Muddy River. While Site #6 sediment could be characterized as sandy with low levels of organic matter, Site #3 sediment appeared to contain high levels organic matter and petroleum compounds (approximately 1,700 ppm extractable petroleum hydrocarbons). Upon analysis, Site #3 had approximately 2% sulfur – considerably higher sulfur than at Site #6. However, the conclusions about the effect of water content on sulfur analysis were the same for either Site.

Figure 8 shows the effect of sample preparation for the different methods on the precision and accuracy for Muddy River Site #3.

3.1.4 Sediment Method 4

This method for sample preparation and analysis was a simulation of a very simple procedure that potentially could be used in the field. Wet sediment samples were passed through a coarse screen (approximately 60 mesh) to remove bulky particles, then simply blotted for about 30 seconds with a paper towel to remove water as much water as possible. Each sample was then assembled in a measurement cup with the sediment still in contact with the paper towel. Five replicate samples were prepared and sulfur counts/sec (cps) recorded normally with the Niton XLt 500He (Filter 2 for 240 seconds). The mean sulfur cps was 109.1 with a standard deviation of 7.8 cps. This sulfur content is only 53% of the sulfur content of the “dry” sample determined by Method 1. The results of this test indicate that Method 4 can give reproducible sulfur content based on wet weight, but will naturally report a sulfur content lower than that of a thoroughly dried sample.

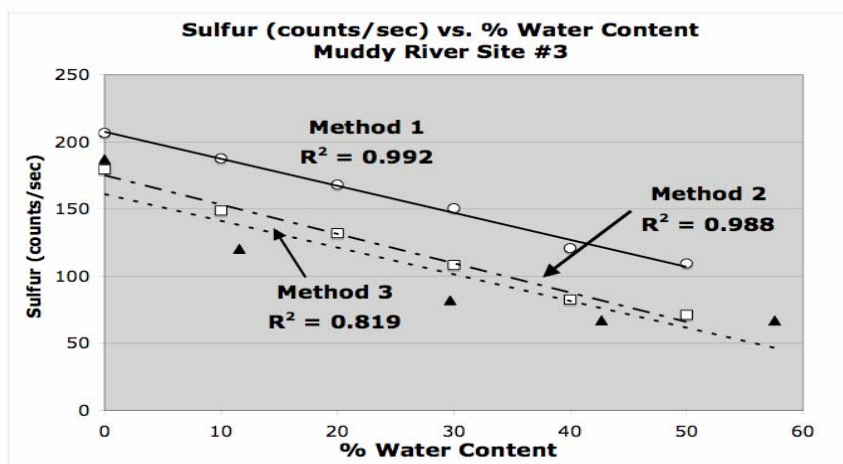


Figure 8. Effect of sample preparation on precision and accuracy – Site #3

3.2 The Effect of Water Content on Other Elements

The effect of water content in the sediment on the counts was studied for a number of different elements. Figure 10 shows the ratio of the counts per second on a sample with a certain water content compared to a thoroughly dried sample using Method 1. The “dilution” effect of water on the dry (maximum) signal varied with the element. While the X-ray fluorescence from iron only decreased 23% when the sample contained 50% water, aluminum, silicon, and phosphorus and sulfur X-ray fluorescence decreased approximately 50% with a dilution of 50% by water. The background fluorescence for all elements was assumed to be zero for each element, but in reality, there are background counts/sec that must be subtracted for each

element for the most accurate work. The different background levels may account for the apparent differences in the effect of water. For the most accurate research, it is important to characterize the background and the “dilution” effect of water content for the samples of each element.

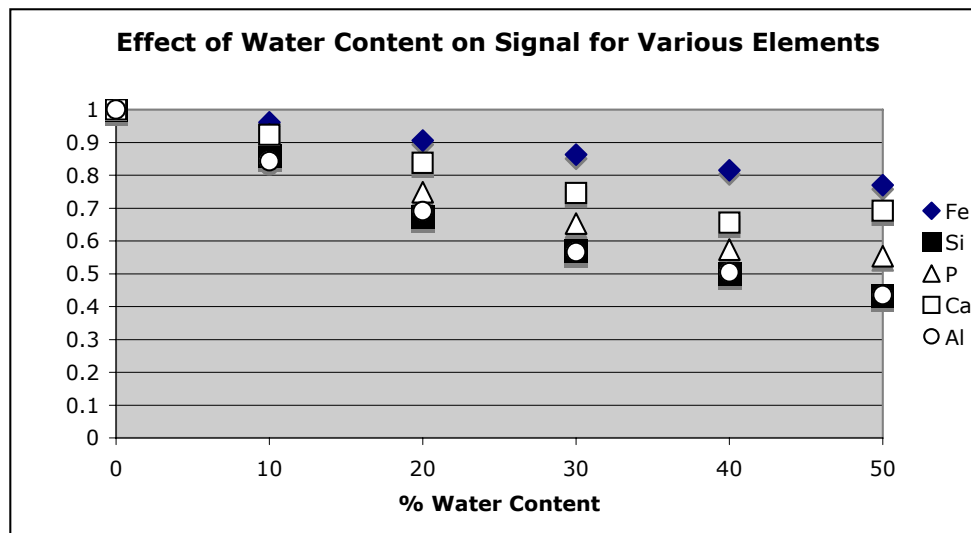


Figure 9. Effect of water content on x-ray fluorescence for elements other than sulfur

3.3 The Benefit of Helium for Sulfur Analysis

The effect of the helium on S/N was determined by calculating the relative standard deviation (RSD in parts per thousand, ppt) for a sediment standard with a low concentration of sulfur, NIST 1646a with 0.35% Sulfur. The RSD for the sample with helium was 19.9 ppt, compared to an RSD of 28.3 ppt when the helium was not used, a 30% improvement in RSD that is attributable to the helium purge.

3.4 Accuracy of Sulfur Analysis

There are several methods to analyze sulfur and sulfate resulting from the oxidation of sulfur (Eaton and Franson, 2005). The sulfur analytical methods used in this investigation are described in this section. In order to determine the accuracy of the portable XRF device, sulfur determinations using the Niton XLt 500He (X-Ray fluorescence) were compared to results using the “oxygen bomb” method. While the XRF method reports the concentration of sulfur directly to the user in a single step, the oxygen bomb method first requires combustion of the sample and subsequent analysis of the combustion residue as described below in order to determine the sulfur concentration in the original sediment sample.

An oxygen bomb (Model 1108 Oxygen Combustion Bomb, Parr Instrument Company, 211 Fifty-Third Street, Moline, Illinois 61265 USA) was used to oxidize the sediment samples and the combustion methodology described (Parr Instrument Company) was followed closely, except

as noted below. In this method, one gram of the sediment was exactly weighed and finely ground to make a pellet with a compression press (Model 2811 Parr Pellet Press). The pellet was reweighed before placing it in contact with a wire fuse and then placed into the stainless steel bomb. One to five milliliters of organic-free water was added to the bomb before final assembly in order to provide a “sink” for the conversion of oxidized sulfur as SO_2 into sulfate as sulfuric acid. After assembly, pure oxygen was admitted up to a pressure of 30 atmospheres in order to provide sufficient oxygen for complete combustion of the pellet. The fuse was ignited with the application of an electric current that in turn initiates the combustion of the pellet. The sulfur is then oxidized to sulfate, which is recovered quantitatively by washing the residue from the spent bomb. Depending on the concentration of sulfur in the sample, 250 mL to 500 mL of organic-free water was used for rinsing the stainless steel bomb after combustion. The washings containing the sulfate were analyzed using both the turbidity method (Hach, 2004) to quantitate sulfur, or using ICP - AES. The ICP - AES analysis was performed by VHG labs, Inc., 276 Abby Road, Manchester, New Hampshire.

Initial tests with calibration sediment sample 1646a in pelletized form showed evidence of incomplete combustion. Since the calibration sediment standard had a low percentage of organic content, it was thought that the bomb did not completely ignite due to insufficient heat. Upon the recommendation of Parr, Inc., a couple of drops of mineral oil were added to the pellet before ignition. However, based on observations of the pellet after combustion, and based on the recorded temperature rise in the calorimeter, mineral oil was rejected as an ignition aid. Instead, naphthalene was selected as an ignition aid for two reasons. Naphthalene has a high heat of combustion, 9.62 kcal/gram (Atkins, 2006), which can be obtained with high purity, and it contributes no sulfur to the residue and washings. Blanks consisting of approximately 0.9 gram of naphthalene with no sediment were combusted in the oxygen bomb and analyzed for sulfur; the blanks yielded no detectable sulfate as analyzed by the turbidity method. However, a small and variable amount of sulfur was detected with the combustion of the naphthalene blank in the washings when analyzed by ICP-AES; this blank was used to correct the sulfur values for the baseline tests summarized in Table 2, below. It was found that consistent combustion based on a consistent increase in the calorimeter temperature and by visual observations of the residue was achieved with one gram sample pellets prepared from a mixture of sediment and naphthalene in a 2:1 w/w ratio. Based on these results, naphthalene was selected as a combustion aide and added to all standard and sediment samples for oxygen bomb combustion.

The sulfur concentration in the original sediment sample was calculated based on the sulfate concentration of the washings from the oxygen bomb combustion. The procedure for sulfate determination from bomb washings described by Parr Instrument Company was modified. Parr’s procedure specifies boiling the residue and washings from the spent oxygen bomb in a platinum crucible with hydrochloric acid before analysis of the sulfate. While this step was not performed, satisfactory results were obtained based on the results from calibration standards. Upon combustion in oxygen, it is assumed that one mole of sulfur produces one mole of sulfate, and one mg of sulfur produces three mg of sulfate. Two methods were used to determine the sulfate concentration in the bomb washings.

The turbidity method for sulfate (Eaton and Franson, 2005) is based on the decrease in light transmission due to the formation of a fine dispersion of a precipitate of barium sulfate when a test sample containing sulfate is added to barium chloride. The turbidity determination is usually

regarded as semi-quantitative, since the amount of the decrease in light transmission due to light scattering from the barium sulfate precipitate is sensitive to several factors: other constituents in the unknown solution, the specific conditions of precipitation – such as agitation and temperature, and the elapsed time between the beginning of the analysis and the final light transmission reading. Turbidity measurements were performed using the Hach DR/890 Colorimeter following the procedures described for the Sulfa Ver 4 Method (Procedures Manual, 2005, Ed.7). Best results were achieved using the “user calibration mode” calibrating between 10 and 50 mg/L sulfate. Samples with concentrations greater than 50 mg/L sulfate were diluted so that the resulting concentrations fell within the calibrated range of concentrations. Hach reports the precision of the sulfate turbidity test as +/- 3 mg/L. The user calibration curve prepared with 8 standard sulfate solutions gave a R2 goodness of fit value of 0.946. It was essential to prepare a new calibration curve for each lot of barium chloride ampules used in the Hach turbidity analytical method.

Samples of bomb washings were also analyzed by ICP - AES (Inductively Coupled Plasma – Atomic Emission Spectroscopy). Table 2 compares the results of sulfur determinations in the washings for five replicate bomb combustion experiments comparing the results from the turbidity and the ICP - AES methods for sulfate (and thus sulfur). The original sample was a certified sediment standard “1646a” with 0.352% +/- 0.004% sulfur. Based on this test of five samples, the standard deviation of the turbidity method is 0.0074%, while the standard deviation of the ICP - AES is smaller, at 0.0046%. The turbidity method is biased 18% low, while the ICP - AES method is biased 15% low. Both methods appear to be biased low. Possibilities for this bias may be due to the modification and simplification of the oxygen bomb procedure used for this work. The residue digestion described (Parr) with concentrated hydrochloric acid in a platinum crucible was not conducted for our experiments. The turbidity method may have an additional negative bias due to settling or agglomeration of the barium sulfate produced in the method.

Table 2. Comparison of % S for Turbidity Method and ICP – AES with Modified Oxygen Bomb Method

	Turbidity	ICP
	0.2923	0.306
	0.2959	0.299
	0.2966	0.304
	0.2818	0.297
	0.2818	0.295
	0.2897	0.300
Std Deviation	0.0074	0.0047
Bias	-18%	-15%

Table 3 compares the sulfur analyses carried out by different methods. The known % for sulfur is given (if known). Two XRF results are given in the Table: “low S” based on a calibration with standards from 0 to 0.35% sulfur and “high S” based on calibration with standards from 0 to 3.076% sulfur. The analysis based on the oxygen bomb method use the ICP analysis of the bomb combustion products to determine the sulfur %. Sample 1646a is a standard sample with a certified sulfur percentage of 0.352%. The Sediment samples (Sed#3

and Sed#6) have unknown true sulfur values, and the bomb and XRF analyses were conducted on dried and ground samples. Sediment #3 was analyzed to have a sulfur concentration of 1.85%, while the XRF analyses varied from 2.56% to 1.41% based on which calibration graph was used. The “high S” calibration was more appropriate, since Sediment #3 had a concentration of sulfur of 1.85%. On the other hand, the “low S” calibration graph was used for Sediment #6 since it had a sulfur concentration of 0.415% as determined with the oxygen bomb method.

Table 3.

Comparison of Sulfur Analyses (w/w%)

Sample	True Value	XRF <i>low S</i>	XRF <i>high S</i>	Bomb*
1646a	0.352	0.315	0.22	0.327
Sed #3	unknown	2.56	1.41	1.85
Sed #6	unknown	0.504	0.322	0.415

*Sulfur based on ICP analysis of bomb combustion product

4. DISCUSSION AND CONCLUSIONS

The effect of water on the analysis of sulfur with the Niton XRF XLt 500He appears to be linear; that is, the sulfur XRF signal decreases linearly with the water content, apparently due to simple dilution of the sample with water. Highest precision and the best accuracy is achieved by the sample preparative technique recommended by Niton: the sample should be dried and ground to pass through a 120 mesh sieve. An increase in water content leads to a decrease in the detected sulfur fluorescence signal (a dilution effect resulting in decreased accuracy) and an increase in the variance of the fluorescence (decreased precision). The coarse screening (greater than 60 mesh) of the dried or wet sample results in a decrease of about one-third of the sulfur fluorescence even with dried samples. Table 4 summarizes the results of the experiments with samples of different % water content.

Table 4.

Effect of Water Content on S (cps) and Regression

	Site #3 1.8 % S		Site #6 0.4% S	
	R ²	S (cps)	R ²	S (cps)
Method 1	0.992	221.4	0.982	48.2
Method 2	0.989	175.0	0.898	29.5
Method 3	0.818	152.2	0.786	30.3

The effect of dilution by water for other elements showed the same qualitative linear decrease in fluorescence with increase in water content; however, the slope of the regression varied with the element.

Helium increased the S/N by 30% for sulfur, leading to greater sensitivity. The limit of detection is a measure of the sensitivity of the analytic method and its determination has been described (Harris, 2007). The limit of detection is defined as the three times the standard deviation of a blank sample divided by the slope of a calibration curve for that sample. For this determination a silica standard certified as 99.999% pure was used as the blank. In the case of XRF analysis of sulfur, the limit of detection is 0.0071% or 71 ppm. The quantitation limit is defined as ten times the standard deviation of a blank sample divided by the slope of a calibration curve, or 0.0237% or 237 ppm. Since many sediments contain 0.20% to 2.0% sulfur, the sensitivity of the portable XRF method is adequate for most investigations. It should be noted that the detection limits used samples that were dried and sieved to pass 120 mesh. The limits of detection for sulfur in samples without the most careful preparation will be higher.

For the most accurate and precise work, it is essential that samples are dried, ground, and sieved (as recommended) to achieve a fine degree of homogeneity. In addition, if the highest accuracy is required for sulfur determination, a calibration curve must be constructed with a number of different standards with sulfur content approximately that of the unknown.

The Niton XRF XLt 500He can be used for semiquantitative sulfur analysis (+/- 20%) portably in the field with wet sediment samples. It is recommended that one remove as much water from the samples as possible in the field before taking measurements, and then correcting for the water content in the samples, which can be determined at a later time. A handheld XRF device has been shown to be a versatile and easy to use analytical method for a number of metals and non-metals. Use of the helium purge extends the utility of the device by permitting the analysis not only of the heavy metals but also of elements that could not previously be analyzed in the field with a hand-held unit. The precision of the unit is excellent, and the limit of detection can be quite low with proper sample preparation.

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