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Abstract

For optimal results manufactures of pXRF spectrometers recommend analyses of samples that meet the criteria of infinite thickness, which for unconsolidated sediments is approximately 25 mm in thickness and compacted to ensure there are no air gaps.

To quantify individual elemental response and the theoretical required infinite sample thickness Certified Reference Materials (CRM's) Till 1 to 4, ranging in thickness from 1 to 40 mm, were analysed in Soil and Mining mode.

Results show a relationship between filters used to process data and sample thickness. For samples less than infinite thickness, pXRF analyses often returned results that were substantially greater than, or less than, results returned from samples of infinite thickness. For these samples post data collection correction factors can be applied to adjust results for greater accuracy.

1.0 Introduction

The application of portable X-Ray Fluorescence (pXRF) spectrometers for geochemical analysis has seen increasing use over the past decade. These instruments have proven to be cost- and time-effective alternative to traditional laboratory based analytical techniques, and provide near instant results for interpretation, with minimal sample preparation (Rouillon and Taylor, 2016; Schneider et al., 2016; Young et al., 2016). A Thermo Scientific Niton pXRF has been used to successfully characterize the elemental composition of sediment samples obtained from boreholes in the Ottawa Valley near Kinburn Ontario (Knight et al., 2012), the Spiritwood Valley, southern Manitoba (Plourde et al., 2012), the Nanaimo Lowlands of B.C. (Knight et al., 2015b) and the Oak Ridges Moraine of southern Ontario (Knight et al., 2015a, 2016a-e) and for mineral resource field study in the Northwest Territories (Kjarsgaard et al., 2014; Plourde et al., 2013).

Operating parameters of the pXRF have been investigated in order to refine the analytical protocol and minimize operator, environmental, and instrumental variance in the results; e.g. including dwell time (Knight et al., 2013; Hall et al., 2014), and water content and grain size (Zhu et al., 2011; MacLachlan et al., 2015; Bertrand et al., 2015). Studies by Plourde et al. (2012) determined that a grain size of <0.063 mm (silt + clay size fraction) was optimal for the geochemical characterization of glaciogenic sediments as significantly courser size fractions returned results with increasing variance when compared to data from laboratory based geochemical analyses using digestive methods. Manufactures of pXRF spectrometers recommend that best results are obtained if the sample is of infinite thickness, which is approximately 25 mm for standard pXRF cups, and compacted to ensure there are no air gaps, (NITON, 2010). However, there are instances when limited quantities of clay-silt (mud) sized material are recovered from samples. For these samples, pXRF analyses returned results for some elements that were substantially greater than, or less than, results returned from samples of infinite thickness. Preliminary work on sample thickness influence on elemental analysis was presented at CANQUA 2015 (Knight et al., 2015c) and GSA 2016 (Landon-Browne et al., 2017).

The objective of this report is to document the effect of variable sample thickness on pXRF results for unconsolidated sediment. The relationship between individual elemental response and the theoretical required infinite sample thickness was investigated using Certified Reference Materials (CRM's) Till 1 to 4 ranging in thickness from 1 to 40 mm. Approximately 6200 analyses were carried out in Soil and Mining mode.

2.0 Theory of Infinite Thickness

Portable XRF spectrometry is a surface to near-surface analytical technique that uses an energy source higher than the binding energy of electrons from the inner shells of atoms causing electrons to be displaced. When an electron from an outer shell fills the vacancy of an inner shell there is a loss of energy. The lost energy "fluorescence process" is characteristic to each element and occurs in a fraction of a second. In this regard, pXRF analysis employs the well understood principles of quantitative analysis by energy dispersive spectrometry (EDS) in spot mode on a scanning electron microscope (SEM) or electron probe micro analyzer (EMP). These focused electron incident beam techniques are explained in Reed (1993, 2005).

The spectrometer comprises an X-ray beam (emitted by interaction of an electron beam with an anode), a silicon-drifted detector (SDD), and an amplifier combined with a multi-beam analyzer to provide elemental abundances of the material being analysed. When the electron beam makes contact with the anode it creates a cloud of radiation that is directed towards the window where the sample is located (Keith Grattan, pers. comm. NITON Thermo Scientific) resulting in a primary X-ray penetration depth (PD). This depth differs from the escape depth or critical penetration depth (CPD) that is defined by the thickness of the samples that will account for 99% of the returned fluorescence.

Each element in the Periodic Table has electron orbitals of characteristic energy. When elements are subjected to radiation an inner shell electron is ejected and replaced by an outer shell electron. There are limited number of ways for this to happen; L → K transition, called a Kα; M → K transition, called a K β; M → L transition, called a Lα. Each of these transitions releases a fluorescent photon with a characteristic energy equal to the difference of the energy from the initial to final orbital electron. The resulting fluorescent radiation can be analyzed by sorting the energies of the photons (energy-dispersive analysis) or by separating the wavelengths of the radiation (wavelength –dispersive analysis).

Resolution of the collected data is dependent on the ability of the manufacture's proprietary software to separate different energy levels and to minimize spectral interferences. Regardless of the manufacture all pXRF instruments use filter settings to differentiate analysed elements by reducing these interferences and minimizing the effects of energy peak overlaps. These filters utilize a combination of voltage, current, and a series of plates placed between the X-ray tube and the sample to isolate specific regions of the energy spectrum. For the pXRF used in this study the filter positions, except in light element mode which is blank, consist of a stacked foil that is placed between the X-ray tube and the sample to focus specific regions of the spectra and to improve the detected signal. The filters reduce the X-ray intensity that reaches the sample by eliminating X-rays that are not producing a meaningful signal and are thus contributing to background noise that reduces the precision of the result and increase the detection limit for the element being detected. Variable X-ray kV intensities and filters are pre-set by the manufacture to increase accuracy and precision while maximizing the efficiency of elemental detection. A combination of filters and data processing algorithms (modes) are factory-calibrated for specific materials and expected concentrations being analyzed. For geological materials several modes are common between manufacturers. These include a "Test All Geo mode/Geochem mode", or a similar name used for unknown expected concentrations, as well as 'Soil' and 'Mining' mode where expected concentrations are known. Soil mode utilizes Compton normalization signal processing algorithm based on measured results of a certified standard versus the Compton peak produced from incoherent backscatter radiation. Soil Mode is used for element concentrations expected to occur with <1%, and includes elements that are often defined as trace elements. Mining mode is selected to detect elements expected to exceed 1% concentration (major elements). This mode utilizes 'Fundamental Parameters', an algorithm that applies X-ray physics to correct for overlapping peaks and matrix differences. Mining Mode can be configured to target specific elements, often Cu/Zn or Ta/Hf. Portable XRF spectrometry of elements lighter than magnesium (Mg) are difficult due to absorption of their X-rays by air (Adams et al., 2020); however; some manufacturers such as Bruker and Olympus are reporting in their newest instruments concentrations for sodium (Na).

For optimal precision and accuracy samples must have sufficient thickness to be infinite in terms of X-ray penetration. This infinite thickness corresponds to the thickness of samples where the analyzer returns a result that will not change if a thicker sample is analysed. Stiko (2009) outlines the complexity of trying to determine quantitative results for samples of less than infinite thickness and notes that as a sample

becomes thinner, there is less matrix affect. Compacting an unconsolidated sample may provide an increase in density at the sample surface, and interface with the X-ray beam. In theory the denser the sample, the less thickness of material is required for infinite thickness. Temporary storage of unconsolidated sediment samples of mixed grain size will undergo granular convection partially differentiating sand, silt and clay. For these samples re-homogenization of the sediment prior to analyses is crucial to the characterization of the bulk composition, especially for light elements (Huntley, 2012)

3.0 Sample preparation and analytical methods

To investigate the effects of variable sample thickness using pXRF spectrometry, four CANMET certified reference materials (CRM's), Till-1 through Till-4 were analysed multiple times with various thickness. These samples were collected by Geological Survey of Canada, and have become global reference materials for exploration and environmental studies (Lynch, 1996). The four standards Till 1–4 were collected from Canadian glacial sediments near Lanark ON, Sisson Brook, NB, Cobalt, ON, and the O'Brien Mine in the Abitibi region of Quebec, respectively. Till-4 was modified to incorporate molybdenite bearing soil from near Gatineau, Quebec (Lynch 1996). Till-1 and Till-3 are soil samples, whereas Till-2 and Till-4 represent glacial derived till. These samples cover a broad range of elemental concentrations and are representative of glacial derived materials sourced from several different bedrock types within Canada. Their reference values are listed in Table 1.

3.1 Sample Preparation
The reference material samples were placed in 2 by 5 cm plastic vials with increasing increments of 0.3 g of sample, which corresponds to an increase of 1 mm in thickness. Samples were not compacted. Weights and corresponding incremental increases in thickness are listed in Table 2. Prior to analysis the opening of the vial was covered with a 4μm thick Chemplex® Prolene® Thin-Film held in place with an elastic band (Fig. 1).

3.2 Sample Analysis
Data acquisition was carried out using a Thermo Scientific Niton portable XL3t GOLDD XRF spectrometer, equipped with a Cygnet 50kV, 2 watt silver anode X-ray tube, and an XL3 25mm^2 silicon drift detector (SDD) with 180,000 counts per second throughput. The pXRF is mounted in a closed system test stand, as displayed in Figure 2.

Data was collected in Soil and Mining Cu/Zn modes. In soil mode a 60 second dwell time for each of the three filters (low, medium and high) was used. In Mining Mode, a 45 second dwell time was used for each of the 4 filters (low, medium, high, and light). The limit of detection (LOD) and filter used for each element that is detectable in Soil mode are listed in Table 3 and in Table 4 for Mining Mode. After approximately 10 analyses the test stand was cleaned with compressed air and gently whipped with Kim-wipes®.

Two analytical protocols were implemented. The initial protocol analysed Till-1 and Till-3 for sample thickness ranging from 1-20 mm, 3 times. Results showed that for some elements infinite thickness had not been achieved. The protocol was revised to analyze each sample from thickness 21-40 mm 3 times and append the resulting data to the original protocol 1 dataset. Examination of this data resulted in

reanalysis using a second protocol where samples ranging from 1-7 mm where analysed 50 times and samples ranging from 8 – 40 mm where analysed 10 times.

Figure 1: Samples of Till-1 in plastic vials, covered by Chemplex® Prolene®film secured with an elastic band. Samples range from 1 mm thickness (on the left), to 20 mm thickness (on the right). Photograph by A.R.R. Landon-Browne. NRCan photo 2020-937.
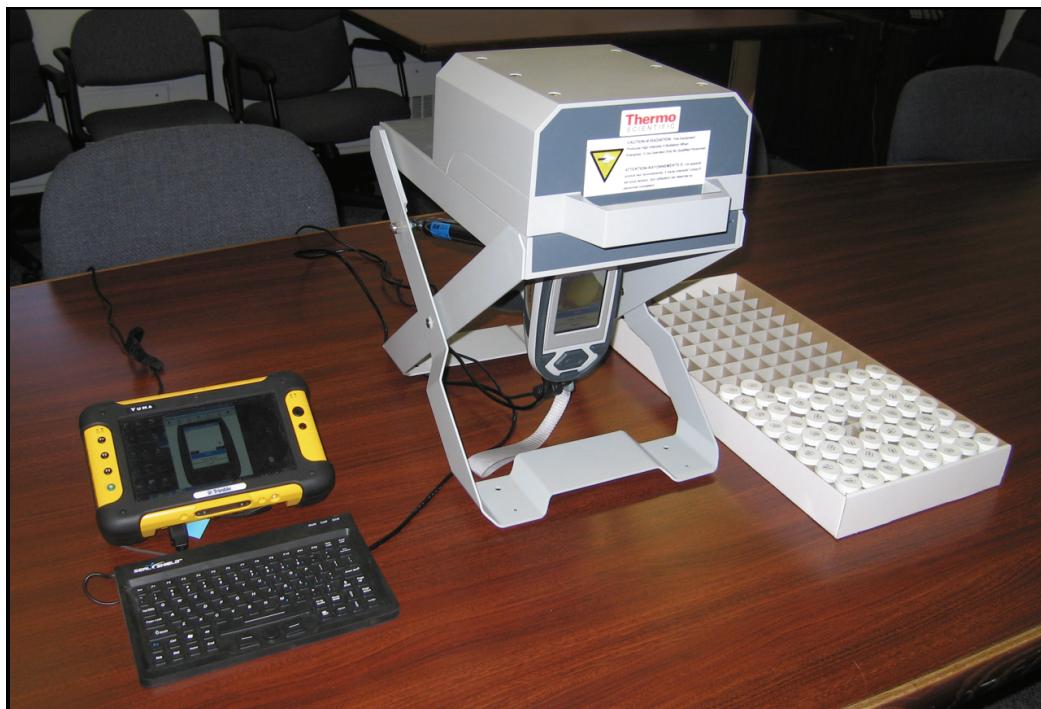
Figure 2. Bench mounted (closed system), pXRF operated via portable computer, with vials of Till-1 and Till-3 samples of vary thickness in a box on the right hand side of the photo. Photograph by R.D. Knight. NRCan photo 2020-926.

3.3 Reproducibility and Precision of Standards

The Chemplex® Prolene®film that separates the samples from the spectrometer may contain trace amounts of Ca, P, Fe, Zn, Cu, Zr, Ti and Al. These elements are not listed as known impurities and most likely represent internal detector "noise". For Soil mode an empty vial with Chemplex® Prolene®film was analysed 3 times to determine impurities and the effect of having no sample material in the vial on the returned results. A stack of several mm of Chemplex® Prolene®film was analysed 5 times to verify the reported impurities and to determine any new impurities in the film. Information on precision, accuracy, instrument drift, dwell time optimization, and calibration of pXRF spectrometry of reference materials including Till-1, Till-4, and TCA 8010 are discussed in Knight et al. (2013).

4.0 Results

A total of ~6200 analyses were carried out in Soil and Mining mode. Results are organized in two folders: Research Protocol 1 and Research Protocol 2.

Research Protocol 1 contains two subfolders, one for sample analyses from 1 to 20 mm in sample thickness and a second folder for with data appended for sample thickness ranging from 21 to 40 mm. Data are presented in excel format workbooks for Soil and Mining mode each containing a worksheet for Till-1 and Till-3 data. Summary data are graphically represented for Soil and Mining mode in a single .pdf file. For Research Protocol 1 the precision of data obtained from 3 analyses was not acceptable as occasionally one of the three results would be an outlier, especially for sample thickness <8 mm where concentrations where exponentially higher or lower than results obtained for sample thickness of > 8 mm. Results are similar to those obtained from Research Protocol 2, however due to the small sample population used to obtain a mean they are not discussed.

Research Protocol 2 contains Excel workbooks for Till-1 to 4 for both Soil and Mining mode. Each workbook contains multiple worksheets including raw data obtained from the pXRF, a summary data sheet, and data obtained from analyses of samples ranging in thicknesses from 1-40 mm. Summary data are graphically represented in .pdf file Graphs Till-1 to 4.pdf. Regression lines equations superimposed on the data graphs, lists of r^2 coefficient of determination, analytical filter, and descriptive regression equation style are presented in Appendix Research Protocol 2 – Equations.docx.

Elements are correlated to a regression line that is generally based on the filter type used to obtain data for each element. Three trends are loosely observed as samples increase in thickness; linear, positive exponential (most common), and negative exponential (Fig. 3). Soil mode elements detected on the Low filter generally follow a linear trend, with some elements displaying a positive exponential trend for sample thickness of 1-2 mm. Elements detected on the Main filter follow a positive exponential trend with high concentrations from 1 mm decreasing to ~7 mm in sample thickness and generally remaining consistent from 7 mm to 40 mm in sample thickness. High filter elements in Soil mode (Ba) are generally not detected at sample thicknesses below 5 mm and follow an exponential trend with increasing concentration correlated with increasing sample thickness (Fig. 3).

In Mining mode, elements are detected using the Light, Low and Main filters display similar positive exponential trends as those for the Low and Main filters in Soil mode. At thicknesses >7 mm consistent (precise) concentrations are observed, but may not correspond to the recommended value (Fig. 4). Elements collected with the Low and Main filters in Mining mode return concentrations similar to the

recommended value when the sample thickness is >5-7 mm. For the High filter, Ba displays a similar negative exponential trend in Mining mode as in Soil mode, however the concentration levels return precise results at a thickness of 15-20 mm and greater, as opposed to 20-25 mm and greater in Soil mode, depending on the CRM being analyzed. Linear regression was observed for High filter La, Nd, and Zr where concentration increased with increasing sample thickness.

4.1 Minimal sample thickness and thin sample correction

Minimal sample thickness is determined based on a regression formula and applies to the thickness when the regression line reaches horizontal: i.e. the sample analysis concentration does not vary with increasing sample thickness. Examples of minimum sample thickness for Till 1 to 4 analysed during this study in Soil mode and Mining mode to acquire a concentration that will not vary greatly if sample thickness was increased are shown in Table 5.

For samples that contain less material (thinner) than listed in Table 5, a correction factor can be applied to adjust the thin sample value to a more accurate value. In order to acquire a correction factor, elemental concentrations are determined for a reference material similar in composition and thickness to the research project sample being analysed. This thin reference sample should be analysed a minimum of three times and preferably more to obtain an average result without the influence of analytical outliers. The concentration of the infinite thick reference sample is divided by the average concentration of the thin reference sample. Analyzing a reference sample of infinite thickness during the collection of data insures that similar operating environments exist and eliminates any chance of instrument drift when compared to similar reference concentrations collected during previous studies. The resulting number is used as the calibration factor to adjust the thin sample concentration to a thickness corrected value corresponding to a sample of infinite thickness.

$$Calibration\ factor(x) = \frac{infinite\ thickness\ concentration(SRM)}{thin\ concentration\ (SRM)}$$

$$thickness\ corrected\ value\ concentration\ (TCV) = (x) * thin\ study\ sample\ concentration(y)$$

For example, samples of infinite thickness for Fe obtained from Till 1 (9-40 mm) during this study have a mean concentration of 42785 ppm that corresponds to the horizontal component of the regression line Shown in the graph file – Graphs Till-1 to 4.pdf. For a CRM at a thickness of 1 mm Fe is analysed 50 times during the same session at an average value of 76945 ppm (see Till-1 - Soil Mode.xls). For this example a hypothetical analyses of a 1 mm thick sample from a suit of similar matrix to the CRM results in a value of 77255 ppm. Applied to the equation above results in:

$$\frac{42785}{76945} = 0.56\ (callibration\ factor)$$

$$0.56 * 77255 = 43263\ thickness\ corrected\ value\ (TCV)$$

This value of 43263 is the adjusted concentration corrected to an infinite thickness for the sample.

5.0 Discussion

For unconsolidated dry sediment samples pXRF manufactures emphasize that in order to obtain best results, sediments should be compacted in a 25 mm tall by 30 mm diameter plastic cup to ensure there are no air gaps and that the sample is densely packed. In order to reduce sample preparation time, and cost, we have successfully used the method of placing unconsolidated sieved sediment samples in 50 mm tall and 20 mm in diameter plastic vials opened on one end and covered with 4μm thick Chemplex® Prolene® Thin-Film. Samples analyzed during this study were prepared as described in section 3.1. The closed nature of this container does not allow for the sample to be compacted and thus there is more air in the sample (less dense) than recommended by the manufacturer of the pXRF.

Using this method the analysis of increasing amounts of sample thickness (mass) demonstrates that there is a relationship between the amount (thickness) of sample being analysed, the element being analysed, and the returned elemental concentration. For light elements such as K and Ca the penetration depth of the X-ray is microns but for heavier elements such as Ba the depth of X-ray penetration increases to millimeters. For most elements 2 grams of sample are required to obtain a thickness of 7 mm in the plastic vials which is a sufficient amount of sample to return consistent results for most elements (excluding Ba). However we recommend that a thickness of 40 mm is needed in order to be able to acquire a complete suite of element data (including Ba; Table 5). For samples that are less than "infinite thickness" the data can be post corrected to obtain a more accurate result that compares to a sample of infinite thickness.

6.0 Summary

A total of ~6200 analyses were carried out in Soil and Mining mode on forty samples obtained for each of CRM Till-1 to 4. Sample thickness varied from 1 to 40 mm to assess the required thickness necessary for each element to meet infinite sample thickness. For sample thickness of 1 to 7 mm each thickness was analyzed 50 times. For sample thickness > 7 mm analysis was replicated 10 times. Thickness > 7 mm generally returned consistent analysis for all elements in both Soil and Mining modes except Ba, Ni and U with additional Mining mode elements of Ag and Nd.

Three trends are loosely observed as samples increase in thickness; linear, positive exponential (most common), and negative exponential. With care samples analysed that are less than infinite thickness can be post corrected to compensate for poor precision.
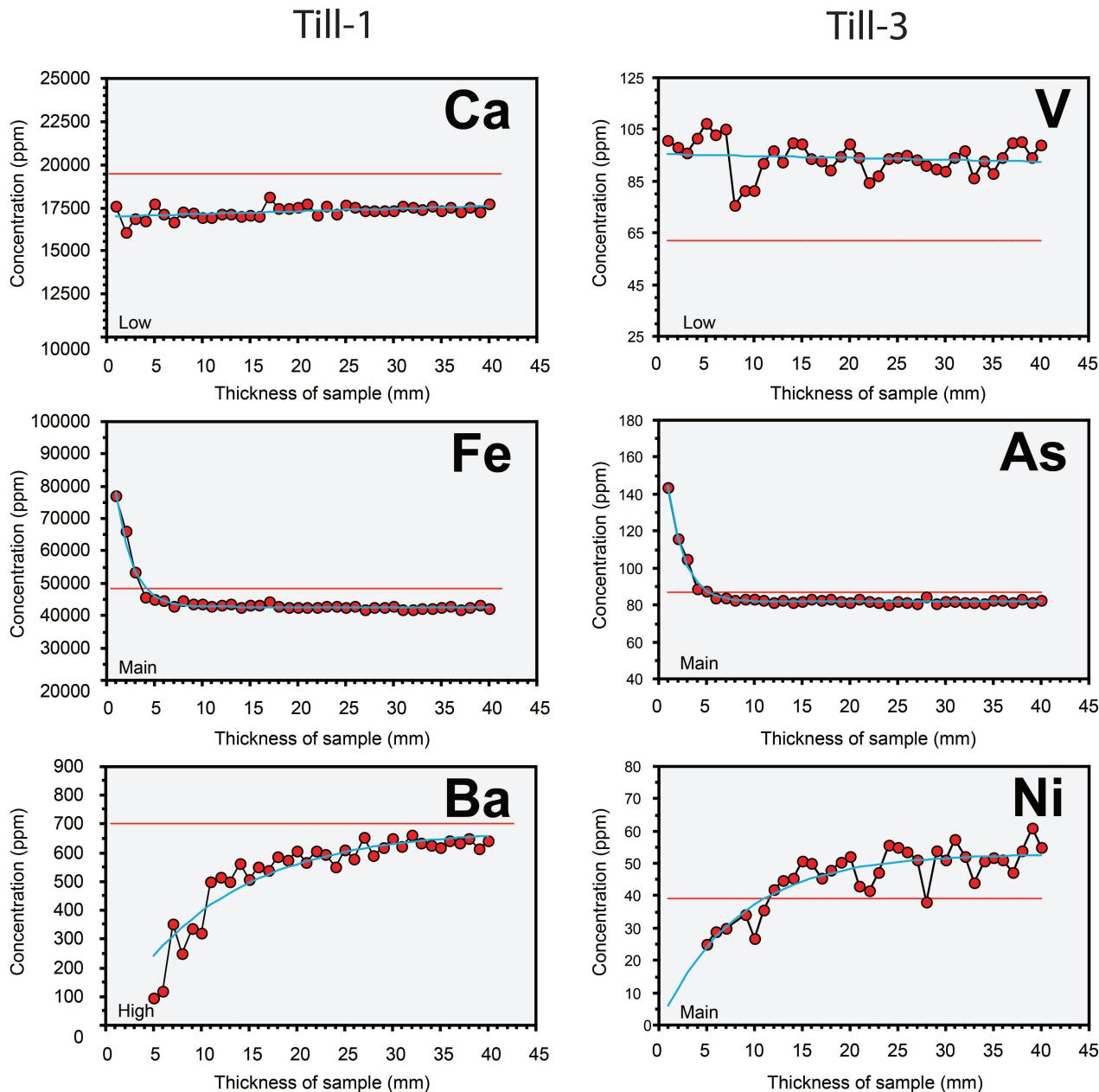
Figure 3: Soil mode trends for Till-1 and Till-3 that are typical for the low, main, and high filters. Red dots represent the average of ~50 analyses for each sample thickness from 1-8 mm and ~10 analyses for sample thickness from 9-40 mm. Red horizontal line depicts the recommended elemental concentration as determined by Lynch (1996). The blue line represents the regression equations presented in Research Protocol 2- Equations.docx Till-1 and Till-3 Soil mode.
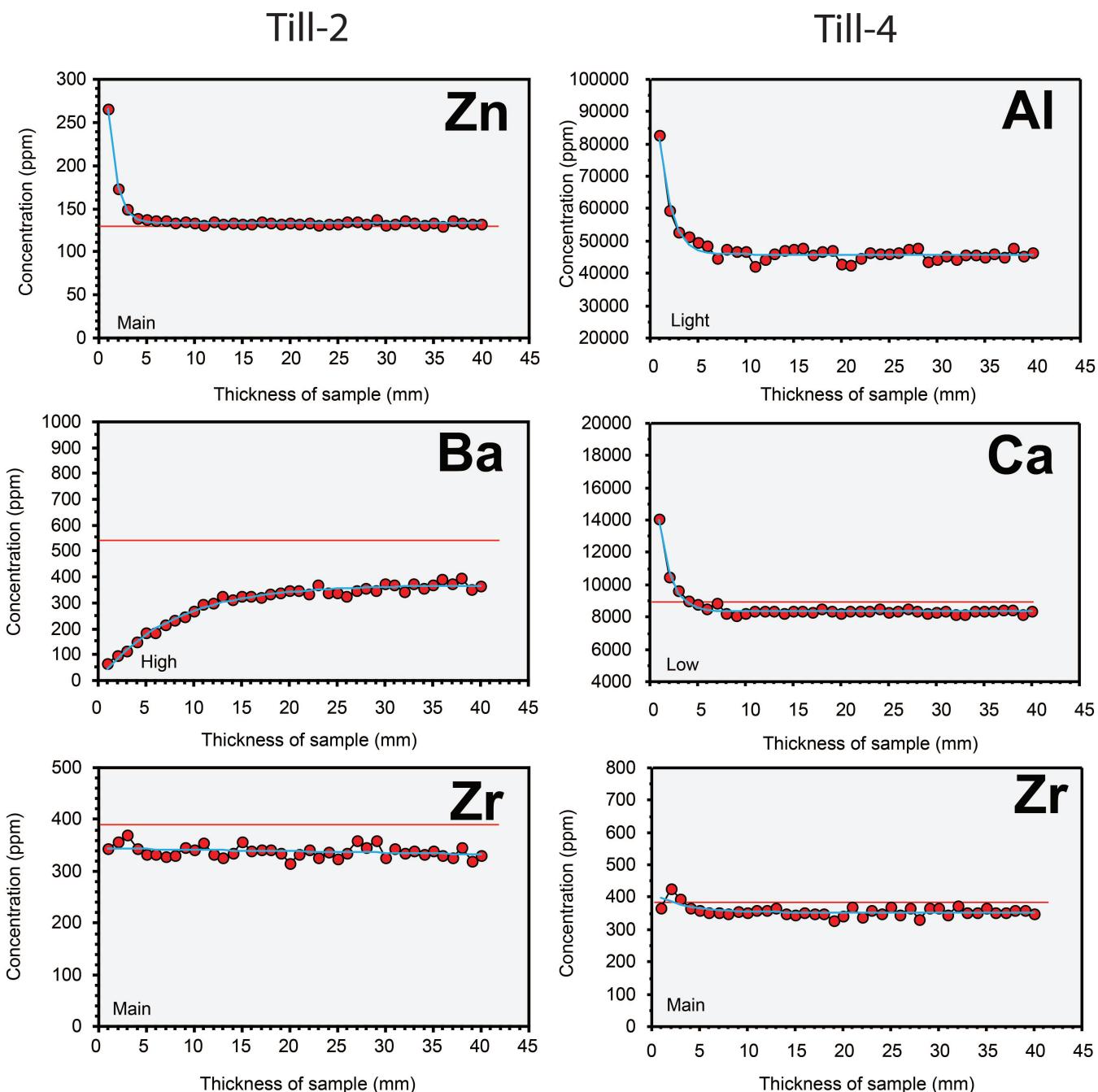
Figure 4: Mining mode trends for Till-2 and Till-4 that are typical for the light, low, main, and high filters. Red dots represent the average of ~50 analyses for each sample thickness from 1-8 mm and ~10 analyses for sample thickness from 9-40 mm. Red horizontal line depicts the recommended elemental concentration as determined by Lynch (1996). The blue line represents the regression equations presented in Research Protocol 2- Equations.docx Till-2 and Till-4 Mining mode.

Table 1. Certified elemental concentrations and standard deviations for Till-1 to 4 (Lynch, 1996). Concentrations for Al, Mg, and Si are calculated from oxide weight percentages. Only elements detected by the pXRF are included in this table. C = concentration; σ = one standard deviation.

| Element	Till-1		Till-2		Till-3		Till-4	
	C (ppm)	σ (ppm)	C (ppm)	σ (ppm)	C (ppm)	σ (ppm)	C (ppm)	σ (ppm)
As	18	1	26	2	87	4	111	6
Al	72505		85000		64567		76000	
Ba	702	59	540	56	489	36	395	37
Ca	19440	715	9077	500	18797	715	8934	357
Cr	65	6	74	8	123	14	53	10
Cu	47	4	150	10	22	5	237	17
Fe	48100	2200	38400	1700	27800	1200	39700	1900
K	18429	830	25486	996	20090	830	26980	996
La	28	2	44	4	21	2	41	4
Mg	13000		11000		10300		7600	
Mn	1420	75	780	28	520	39	490	30
Mo	2	1	14	2	2	1	16	2
Ni	24	4	32	3	39	7	17	3
P	930	60	750	80	490	40	880	50
Pb	22	3	31	3	26	3	50	4
Rb	44	6	143	12	55	7	161	15
S	<500	-	<500	-	<500	-	800	100
Sb	7.8	0.5	0.8	0.1	0.9	0.1	1	0.1
Si	284673				323003			
Sr	291	10	144	18	300	12	109	11
Th	5.6	0.5	18.4	1.4	4.6	0.4	17.4	1.4
Ti	5990	210	5300	19	2910	90	4840	130
U	2.2	0.3	5.7	0.4	2.1	0.2	5.0	0.5
V	99	10	77	10	62	6	67	7
Y	38	4	40	4	17	3	33	3
Zn	98	10	130	8	56	6	70	7
Zr	502	58	390	39	230	24	385	34

Table 2: Sample mass and corresponding thickness in mm.

Sample #	Mass of Sample (g)	Thickness of Sample (mm)	Sample #	Mass of Sample (g)	Thickness of Sample (mm)
Sample - 1	0.3	1	Sample -21	6.3	21
Sample - 2	0.6	2	Sample -22	6.6	22
Sample - 3	0.9	3	Sample -23	6.9	23
Sample - 4	1.2	4	Sample -24	7.2	24
Sample - 5	1.5	5	Sample -25	7.5	25
Sample - 6	1.8	6	Sample -26	7.8	26
Sample - 7	2.1	7	Sample -27	8.1	27
Sample - 8	2.4	8	Sample -28	8.4	28
Sample - 9	2.7	9	Sample -29	8.7	29
Sample - 10	3.0	10	Sample -30	9.0	30
Sample - 11	3.3	11	Sample -31	9.3	31
Sample - 12	3.6	12	Sample -32	9.6	32
Sample - 13	3.9	13	Sample -33	9.9	33
Sample - 14	4.2	14	Sample -34	10.2	34
Sample - 15	4.5	15	Sample -35	10.5	35
Sample - 16	4.8	16	Sample -36	10.8	36
Sample - 17	5.1	17	Sample -37	11.1	37
Sample - 18	5.4	18	Sample -38	11.4	38
Sample - 19	5.7	19	Sample -39	11.7	39
Sample - 20	6.0	20	Sample -40	12.0	40

Table 3: Soil mode limit of detection (LOD) and filter (Niton 2010).

Element	Filter	LOD (ppm)	Element	Filter	LOD (ppm)
Ag	High	A/S	Pd	High	12
As	Main	7	Rb	Main	3
Au	Main	9	S	Low	275
Ba	High	45	Sb	High	20
Ca	Low	N/A	Sc	Low	75
Cd	High	12	Se	Main	4
Co	Main	90	Sn	High	20
Cr	Low	22	Sr	Main	3
Cs	High	35	Te	High	35
Cu	Main	13	Th	Main	4
Fe	Main	N/A	Ti	Low	60
Hg	Main	9	U	Main	4
K	Low	150	V	Low	25
Mn	Main	50	W	Main	30
Mo	Main	3	Zn	Main	10
Ni	Main	30	Zr	Main	4
Pb	Main	8			

Table 4: Mining mode limit of detection (LOD) and filter (Niton 2010).

Element	Filter	LOD (ppm)
Ag	High	A/S
Al	Light	1000
As	Main	5
Au	Main	20
Bal	Main	-
Ba	High	40
Bi	Main	5
Ca	Low	N/A
Cd	High	10
Ce	High	-
Cl	Light	80
Co	Main	100
Cr	Main	30
Cr	Low	30
Cu	Main	15
Fe	Main	N/A
K	Low	N/A
La	High	-
Mg	Light	6000
Mn	Main	65
Mo	Main	3
Nb	Main	3

Element	Filter	LOD (ppm)
Nd	High	-
Ni	Main	30
P	Light	400
Pb	Main	10
Pr	High	-
Rb	Main	3
S	Light	90
Sb	High	-
Se	Main	3
Si	Light	N/A
Sn	High	3
Sr	Main	3
Th	Main	-
Ti	Main	20
Ti	Low	20
U	Main	-
V	Main	20
V	Low	20
W	Main	-
Y	Main	-
Zn	Main	15
Zr	Main	3

Table 5: Approximate thickness in millimeters of samples Till-1 to 4 required to obtain a consistent reading (infinite thickness) in Soil and Mining mode.

Element	Till-1		Till-2		Till-3		Till-4	
	Soil mode	Mining mode	Soil mode	Mining mode	Soil mode	Mining mode	Soil mode	Mining mode
Ag	-	-	-	18	-	12	-	10
Al	-	4	-	6	-	4	-	7
As	5	4	6	5	5	6	6	5
Ba	25	12	25	15	25	20	25	15
Ca	3	4	6	4	2	5	1	6
Cr	3	-	3	-	3	-	3	-
Cu	7	3	5	5	8	-	5	5
Fe	7	4	7	7	6	6	6	6
K	5	4	6	6	8	6	4	5
La	-	11	-	22	-	2	-	-
Mg	-	3	-	5	-	3	-	5
Mn	5	4	5	5	7	3	13	3
Nb	-	4	-	5	-	5	-	6
Nd	-	12	-	26	-	18	-	20
Ni	27	-	15	-	19	-	14	-
P	-	2	-	1	-	8	-	9
Pb	6	4	7	5	6	5	5	5
Rb	7	6	7	5	8	5	5	5
S	1	3	1	4	1	3	1	7
Sc	1	-	1	-	1	-	1	-
Si	-	5	-	6	-	5	-	6
Sr	7	10	8	5	9	5	6	6
Th	1	-	5	6	4	9	4	8
Ti	8	3	1	4	8	5	1	4
U	10	3	16	7	8	4	12	8
V	10	-	1	-	2	-	1	-
Y	-	7	-	6	-	7	-	5
Zn	4	4	6	5	8	4	3	3
Zr	5	1	5	1	6	4	3	6

7.0 Acknowledgements

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9.0 List of Appendices

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