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1.0 Introduction

The use of portable X-Ray Fluorescence (pXRF) spectrometers for geochemical analysis has become increasingly more popular over the past decade. These instruments have proven to be a cost- and time-effective alternative to traditional wet chemistry techniques, and provide near instant results for interpretation, with minimal sample preparation (Rouillon and Taylor, 2016; Schneider et al., 2016; Young et al., 2016). At the Geological Survey of Canada (GSC), the Groundwater Geoscience Program has used a pXRF to successfully characterize sediment samples obtained from boreholes in order to obtain chemostratigraphy of aquitards and aquifers in the Oak Ridges Moraine of southern Ontario (Knight et al., 2016a-e, 2015a), the Ottawa Valley near Kinburn Ontario (Knight et al., 2012), Nanaimo Lowlands of B.C. (Knight et al., 2015b), and the Spiritwood Valley, southern Manitoba (Plourde et al., 2012). Data obtained by use of the pXRF and the analysis of the results, complements data and results obtained through surface geophysics (Oldenburger et al., 2016, Pugin, 2016, Pullan et al.,2013) downhole geophysics (Crow et al., 2014, 2013, 2012), micropaleontology results, and pore water geochemistry (Medioli et al., 2012; Hinton et al., 2015).

Operating parameters of the pXRF have also been investigated in order to determine the best analysis methods – including dwell time (Knight et al., 2012; Hall et al., 2014), water content and grain size (Zhu et al., 2011; MacLachlan et al., 2015; Bertrand et al., 2015). A comparison of pXRF data collected from in situ diamicton core with samples processed to <63 μm was carried out by Plourde et al (2012). They determined that a grain size of <63 μm was optimal for the characterization of glacial derived materials as there was too much variability in the original diamicton sample probably due to pebbles and large grain size changes at or near the core sample surface. Bertrand et al. (2015) and MacLachlan et al. (2015) investigated the influence of grain size on elemental concentrations by comparing ITRAX XRF scanning with ICP-AES and traditional XRF methods. Bertrand et al. (2015) concluded that grain size variations only affected a limited number of elements and for those elements the effect of grain size was small for size ranges of 10 μm to upwards of 20 μm. MacLachlan et al.(2015) also concluded that changes in grain size only affected a limited number of elements and that a threshold of 25 wt % > 6 μm in grain size had to be reached before significant changes occurred in return concentrations.

The Geological Survey of Canada commonly processed sediment samples to <63 μm which reflects the silt and clay size fraction. The Ontario Geological Survey (OGS) processes sediment samples (diamictons) to <74 μm for standard Chittick determinations, resulting in the inclusion of a very-fine sand component to the silt and clay size fraction. Both scientific institutes have considerable numbers of surface sediment samples and borehole samples collected throughout southern Ontario. Reprocessing the <74 μm samples to obtain the <63 μm size fraction would have been time consuming, costly, and commonly beyond the project budget of both organizations therefore this study was undertaken to determine if sediment samples obtained from these two (2) size fractions could be compiled into a continuous dataset. Preliminary findings were presented as part of a pXRF data quality control poster at the Geological Society of America conference in 2016 (Landon-Browne et al., 2016).

This paper presents the findings of a comparative study on the geochemistry of <74 μm and <63 μm sediment samples. This research provides support for integration of two datasets on the respective samples sizes for a chemostratigraphic framework of Southern Ontario.

2.0 Sample preparation and analytical methods

For this study, twenty eight (28) unconsolidated sediment samples were processed at the OGS in Sudbury to isolate the <74 μm fraction, and delivered to the GSC in Ottawa. A split of the sample was sent to the GSC sedimentology laboratory to obtain the <63 μm size fraction. The amount of sediment in the 11 μm window between <74 μm and <63 μm ranged in increments from 1.68% to 16.72% (Table 1). The processed sediment samples were placed in 2 cm by 5 cm plastic vials. Prior to analysis the open end of the vial was covered with a 4μm thick Chemplex® Prolene® Thin-Film to seal the sample from the pXRF detector.

Table 1: Identification of samples used in this study and the percent of sediment in the each sample between <74 μm and <63 μm.

OGS Project	OGS Sample Number	OGS Geologist	GSC Sample Number	% of sediment between 74 and 63 microns
GRS-14	LP-MW-01-10-019	Marich	2	1.68
GRS-14	LP-MW-24-10-008	Marich	3	3.88
GRS-14	LP-MW-17-10-072	Marich	1	4.42
MRD-324	SS-12-06-53	Bajc	25	4.47
GRS-14	LP-MW-21-10-043	Marich	5	4.66
MRD-324	SS-12-07-34	Bajc	26	5.92
MRD-303-PSA	34-BH24-OF-2009	Burt	10	5.93
MRD-303-PSA	35-BH01-OF-2008	Burt	8	5.94
MRD-303-PSA	18-BH29-OF-2009	Burt	15	5.98
MRD-303-PSA	65-BH22-OF-2009	Burt	7	6
MRD-303-PSA	24-BH30-OF-2009	Burt	17	6
GRS-14	LP-MW-21-10-046	Marich	6	6.01
MRD-303-PSA	30-BH25-OF-2009	Burt	9	6.04
MRD-303-PSA	24-BH25-OF-2009	Burt	11	6.14
MRD-303-PSA	10-BH31-OF-2009	Burt	18	6.27
MRD-303-PSA	16-BH29-OF-2009	Burt	14	6.32
MRD-303-PSA	29-BH25-OF-2009	Burt	12	6.48
MRD-303-PSA	24-BH29-OF-2009	Burt	16	6.59
MRD-324	SS-12-08-25	Bajc	27	7.41
GRS-14	LP-MW-24-10-015	Marich	4	8.22
MRD-324	SS-13-01-39	Bajc	19	9.4
MRD-324	SS-13-02-03	Bajc	20	10.01
MRD-303-PSA	05-BH07-OF-2008	Burt	13	11.4
MRD-324	SS-13-02-52	Bajc	28	12.16
MRD-324	SS-13-02-27	Bajc	21	12.4
MRD-324	SS-13-02-31	Bajc	22	12.77
MRD-324	SS-13-03-33	Bajc	23	15.07
MRD-324	SS-13-03-50	Bajc	24	16.72

Data acquisition was carried out using a Thermo Scientific Niton Portable XL3t GOLDD XRF spectrometer, equipped with a Cygnet 50kV, 2watt silver anode X-Ray tube, and an XL3 25mm^2 silicon drift detector (SDD) with 180,000 counts per second throughput. The pXRF was mounted in a closed system test stand, as displayed in Figure 1. The complete set of the twenty eight samples was analysed in soil mode 3 times followed by analyses in Mining Cu/Zn mode 3 times.

Soil mode is recommended for elements expected to occur in concentrations of <1%. This mode uses Compton normalization that utilizes built in standards to which samples are normalized to the Compton peak. Mining mode is recommended for elements expected to occur in concentrations of >1% and uses fundamental parameters where factory built in calibration programs measure the detectors response to the elemental composition of the sample and corrects for overlapping peaks. In soil mode a 60 second dwell time was used for each of three filters. In Mining Mode, a 45 second dwell time was used for each of the 4 filters. Filter parameters are: Main (50 kV @ 40 µA max), Low (20 kV @ 100 µA max), High (50 kV @ 40 µA max) and Light (8 kV @ 250 µA max). The limit of detection and filter used for each element that is detectable in soil mode are listed in Table 2 and in Table 3 for Mining Mode.

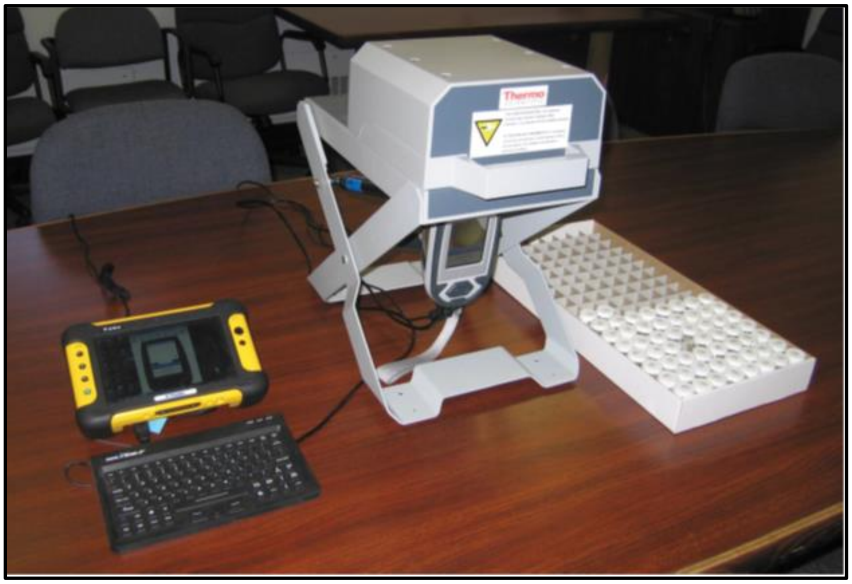

Figure 1. Bench mounted, closed system, pXRF operated via computer, with samples in a box on the right hand side of the photo.

Table 2: Soil mode limit of detection (LOD) and filter used to detect elements. A/S – Application Specific, N/A- Not Applicable, as provided by Themo Scientific (2016).

Element	**Filter**	**LOD**
Ag	High	A/S
As	Main	7
Au	Main	9
Ba	High	45
Ca	Low	N/A
Cd	High	12
Co	Main	90
Cr	Low	22
Cs	High	35
Cu	Main	13
Fe	Main	N/A
Hg	Main	9
K	Low	150
Mn	Main	50
Mo	Main	3
Ni	Main	30

Element	**Filter**	**LOD**
Pb	Main	8
Pd	High	12
Rb	Main	3
S	Low	275
Sb	High	20
Se	Main	4
Sn	High	20
Sr	Main	3
Te	High	35
Th	Main	4
Ti	Low	60
U	Main	4
V	Low	25
W	Main	30
Zn	Main	10
Zr	Main	4

Table 3: Mining mode limit of detection (LOD) and filter used to detect elements. Blank LOD's represent unknown values.

Element	Filter	LOD
Ag	High	A/S
Al	Light	1000
As	Main	5
Bal	Main	
Ba	High	40
Ca	Low	N/A
Ce	High	
Cl	Light	80
Fe	Main	N/A
K	Low	N/A
La	High	
Mg	Light	6000
Mn	Main	65

Element	Filter	LOD
Nb	Main	3
Nd	High	
P	Light	400
Pb	Main	10
Pr	High	
Rb	Main	3
S	Light	90
Si	Light	N/A
Sr	Main	3
Th	Main	
Ti	Main	20
Zn	Main	15
Zr	Main	3

2.1 Reproducibility and Precision of Standards

At the beginning, the end, and after every 10 sample analyses, a Teflon blank and an SiO_2 blank were analysed to determine the cleanliness of the pXRF window and sample stand environment. After approximately 10 analyses the operating environment (test stand) was purged with compressed air and wiped clean. The Teflon blank and SiO_2 blank, return different values in Soil and mining Mode with far more elements being detected at trace amounts in Mining Mode. Till-4 and TCA 8010 (an internal GSC standard) where analyzed at the beginning and at the end of every analytical session as well after every 10 analyses. We recommend that the Chemplex Prolene thin-film be replaced on a regular basis as it becomes contaminated due to static attracting dust in the operating environment. A study into the precision, accuracy, instrument drift, dwell time optimization and calibration of pXRF spectrometry for reference materials including Till-4 and TCA 8010 is available from Knight et al. (2013). Summary statistics for standard reference materials Till-4 and TCA 8010 are listed in Appendix A for both size fractions.

4.0 Results

A total of 336 analyses were carried out on the twenty eight samples and 183 analyses of reference materials and blank standards. Results are listed in the pXRF results data table in Microsoft Excel format and as 4 individual comma delimitated files for the two size fractions of unconsolidated sediment samples and the analysed reference materials. A graphical display of the data is presented as x-y scattergrams in .pdf format comparing the elemental concentrations for <74 μm data to <63 μm data. The graphs are displayed in order of best fit for the top left corner to worst fit in the bottom of the .pdf figure.

4.1 Soil Mode

Seventeen elements (As, Ba, Ca, Cr, Cu, Fe, K, Mn, Ni, Pb, Rb, S, Sr, Ti, V, Zn and Zr) display little to no change between the analytical results of both size fractions. A selection of elements comparing the <63 μm size fraction to the <74 μm size fraction is displayed in figure 2. For Ca, Fe, Sr and Ti any difference between the results for the 2 size fractions is well within the percent error listed in the data table. Some elements such as Cu, as displayed in figure 2, have a poor comparison between the 2 size fractions, however, it should be noted that the concentrations are near the detection limit where precision becomes an issue.

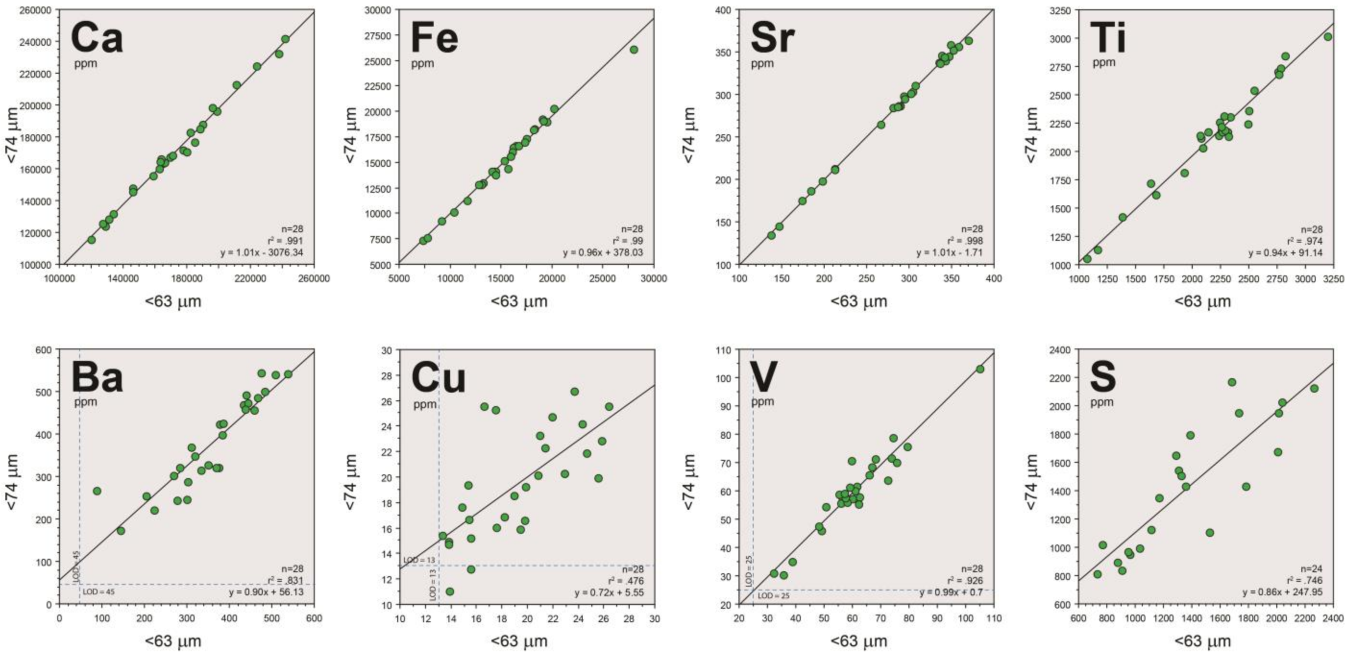

Figure 2. Comparison of <63 μm size fraction with <74 μm size fraction in Soil Mode. Black line represents the regression line. Dashed blue lines represent to limit of detection.

4.2 Mining Mode

In mining mode four filters are used to detect elements, light, low, main and high. Light elements are from Mg – Cl. The remaining three filters detect the same elements as Soil Mode.

Sixteen elements (Al, Ba, Ca, Fe, K, Mg, Mn, Nb, Nd, Pb, Si, Sr, Ti, Th, Zn and Zr) display little to no change between the analytical results of both size fractions. A selection of elements comparing the <63 μm size fraction to the <74 μm size fraction is displayed in figure 3. The top row of elements (Ca, Fe, Sr, Ti) are displayed in the same order as in figure 2 for Soil Mode. Note that the precision for Ti is poorer in Mining Mode than in Soil Mode. K in the lower row of graphs on figure 3 displays excellent correlation between grain sizes. The remaining 3 elements (Si, Al, Mg) on the lower row in figure 3 are only detected in Mining Mode using the light filter. Comparison of size fractions is excellent for both Si and Al however Mg displays a greater degree of scatter between the 2 size fractions.

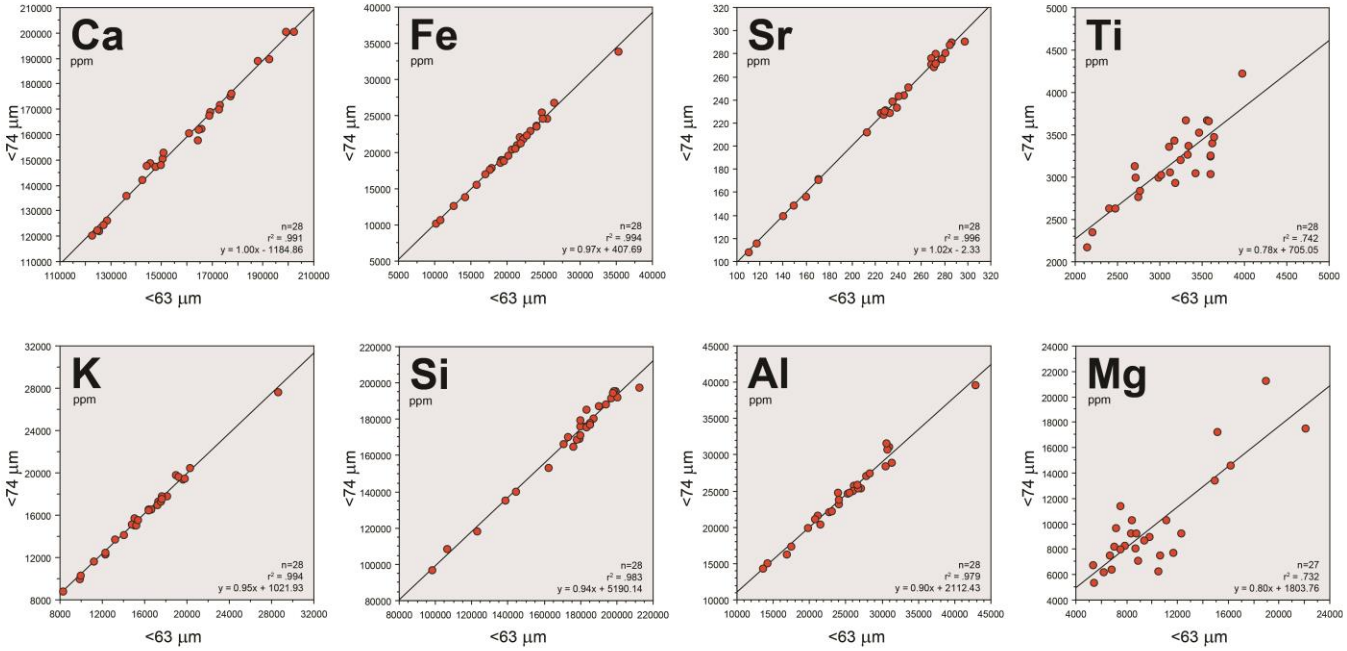

Figure 3. Comparison of <63 µm size fraction with <74 µm size fraction in Mining Mode. Black line represents the regression line. All elements are above the detection limit.

5.0 Conclusions

From the investigation of twenty eight samples of unconsolidated sediments, we conclude that the minor grain size difference between <74 µm and <63 µm has little affect on the elemental concentrations determined by pXRF analyses in both Soil and Mining Mode. These conclusions are similar to those from investigations of Bertrand et al. (2015) and MacLachlan et al. (2015) on the influence of grain size changes on elemental concentrations. Thus reprocessing the <74 µm samples to obtain the <63 µm size fraction is not warranted and will not affect the concentrations returned by pXRF analyses. As a result, analyses obtained from these 2 size fractions can be combined into a single dataset.

6.0 Acknowledgements

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Appendix A

Summary statistics Till-4 and TCA 8010

A1a. Summary statistics of TCA8010 by pXRF spectrometry (mining mode), <0.063 mm size fraction.

	Recommended Value (ppm)	Count	Mean (ppm)	%error	Std Dev (ppm	%RSD	Minimum (ppm)	Maximum (ppm)
As	111	12	141	27.3	3.34	2.36	136	145
Ba	395	12	385	-2.4	16.13	4.19	365	419
Ca	8934	12	8487	-5.0	240	2.82	8153	8774
Fe	39700	12	40983	3.2	336	0.82	40346	41401
K	26980	12	25963	-3.8	386	1.48	25028	26479
Mn	490	8	310	-36.7	38.37	12.38	256	382
Pb	50	12	51	1.4	2.55	5.02	48	56
Rb	161	12	80	-50.2	0.91	1.13	79	81
S	800	12	1495	86.8	104.94	7.02	1342	1711
Sr	109	12	85	-22.4	1.49	1.76	82	87
Th	17.4	12	23.6	35.8	2.71	11.47	17.2	27.1
Ti	4840	12	4215	-12.9	223.44	5.30	3831	4596
Zn	70	12	70.32	0.5	3.75	5.33	63	75
Zr	385	12	342	-11.2	9.13	2.67	332	364

A1b. Summary statistics for SRM Till-4 by pXRF spectrometry for (mining mode), <0.063 mm size fraction.

	Recommended Value (ppm)	Count	Mean (ppm)	%error	Std Dev (ppm	%RSD	Minimum (ppm)	Maximum (ppm)
As	5.45	11	7.82	43.5	1.09	13.99	5.37	9.49
Ba	549	12	494	-10.0	16.76	3.39	461	516
Ca	15509	12	14316	-7.7	476.54	3.33	13593	15124
Fe	20290	12	20075	-1.1	395.81	1.97	19273	20559
K	19094	12	18422	-3.5	365.55	1.98	17536	18930
Pb	12.2	12	9.56	-21.6	1.26	13.18	7.9	11.7
Rb	53.6	12	26.2	-51.1	0.47	1.81	25.4	27.3
Sr	310	12	218	-29.7	1.81	0.83	215	222
Th	5.1	11	13.10	156.9	2.79	21.26	9.2	17.8
Ti	2578	11	2292	-11.1	154	6.72	2071	2548
Zn	31.9	12	40.7	27.5	11.39	28.01	24.9	56.6
Zr	272	12	246	-9.7	20.96	8.53	215	274

A2a. Summary statistics of SRM TCA8010 by pXRF spectrometry (soil mode), <0.063 mm size fraction.

	Recommended Value (ppm)	Count	Mean (ppm)	%error	Std Dev (ppm)	%RSD	Minimum (ppm)	Maximum (ppm)
As	5.45	10	6.57	20.5	1.18	18.02	4.57	8.31
Ba	549	10	701	27.7	17.50	2.50	669	726
Ca	15509	10	13781	-11.1	165.03	1.20	13408	13989
Cd	0.11	7	9.05	8123.4	0.76	8.38	8.01	10.23
Cr	48.4	10	15.7	-67.6	3.98	25.39	8.1	21.2
Cs	1	10	54	5268.9	2.57	4.80	50	58
Cu	28	10	29	5.1	3.36	11.43	22	35
Fe	20290	10	14480	-28.6	431.48	2.98	13609	15161
K	19094	10	16771	-12.2	220.42	1.31	16380	17028
Mn	310	10	296	-4.4	10.53	3.55	282	310
Ni	17.2	10	64.8	276.7	7.34	11.33	54.1	79.5
Rb	53.6	10	48.9	-8.7	0.82	1.68	47.6	50.5
Sb	2.3	10	18.2	689.0	2.41	13.26	14.0	21.5
Sn	0.6	10	9.2	1433.5	0.96	10.43	7.9	11.0
Sr	310	10	268	-13.4	2.70	1.01	264	272
Te	0.02	10	76.19	380860	6.62	8.69	60.9	86.8
Th	5.1	10	3.5	-30.9	0.61	17.18	2.5	4.6
Ti	2578	10	2439	-5.4	90.26	3.70	2302	2549
U	1.1	8	6.6	500.5	1.62	24.59	4.6	8.5
V	49	10	76.3	55.6	7.64	10.02	58.5	85.4
Zn	31.9	10	39.4	23.4	8.64	21.95	30.0	49.6
Zr	272	10	315	15.7	20.22	6.42	275	335

A2b. Summary statistics of Till-4 by pXRF spectrometry (soil mode), <0.063 mm size fraction.

	Recommended Value (ppm)	Count	Mean (ppm)	%error	Std Dev (ppm)	%RSD	Minimum (ppm)	Maximum (ppm)
As	111	10	104	-6.3	2.35	2.26	100	109
Ba	395	10	460	16.6	18.59	4.04	442	503
Ca	8934	10	7974	-10.7	85.14	1.07	7876	8112
Cr	53	10	21	-60.8	1.61	7.74	19	24
Cu	237	10	216	-8.8	5.83	2.69	207	224
K	26980	10	23788	-11.8	185.54	0.78	23488	24061
Mn	490	10	434	-11.5	16.88	3.89	413	457
Mo	16	10	17	8.7	1.74	10.03	14	20
Ni	17	10	57	237.6	7.73	13.47	43	66
Pb	50	10	43	-14.3	1.92	4.47	38	45
Rb	161	10	151	-6.0	1.53	1.01	149	153
S	800	10	714	-10.8	94.05	13.18	536	810
Sr	109	10	105	-3.6	0.76	0.73	104	106
Th	17.4	10	42.1	141.7	1.51	3.60	39.5	44.1
Ti	4840	10	4641	-4.1	43.30	0.93	4555	4690
U	5	10	13	157.2	3.91	30.37	7	18
V	67	10	122	81.6	9.54	7.84	100	132
W	204	10	174	-14.9	5.41	3.12	165	183
Zn	70	10	66	-5.8	4.08	6.18	59	72
Zr	385	10	440	14.4	11.21	2.55	420	455

A3a. Summary statistics of SRM TCA 8010 by pXRF spectrometry (mining mode), <0.074 mm size fraction

	Recommended Value (ppm)	Count	Mean (ppm)	%error	Std Dev (ppm)	%RSD	Minimum (ppm)	Maximum (ppm)
As	5.45	10	7.71	-41.5	1.58	20.47	5.75	10.9
Ba	549	11	505	8.0	14.73	2.91	485	529
Ca	15509	11	14170	8.6	313.33	2.21	13492	14525
Fe	20290	11	19978	1.5	447.75	2.24	19146	20591
K	19094	11	18227	4.5	314.18	1.72	17734	18697
Pb	12.2	11	10.1	17.3	1.76	17.44	7.4	13.7
Rb	53.6	11	26.3	51.0	0.58	2.22	25.1	27.2
Sr	310	11	219	29.3	1.40	0.64	216	221
Th	5.1	11	13.3	-161.2	3.14	23.57	8.6	19.0
Ti	2578	7	2365	8.2	217.16	9.18	2149	2653
Zn	31.9	11	38.4	-20.4	9.52	24.79	27.3	51.3
Zr	272	11	246	9.5	20.10	8.16	215	283

A3b. Summary statistics of SRM Till-4 by pXRF spectrometry (mining mode), <0.074 mm size fraction

	Recommended Value (ppm)	Count	Mean (ppm)	%error	Std Dev (ppm)	%RSD	Minimum (ppm)	Maximum (ppm)
As	111	11	141	27.4	5.23	3.70	134	152
Ba	395	11	394	-0.2	20.13	5.11	354	427
Ca	8934	11	8500	-4.9	126.00	1.48	8324	8713
Fe	39700	11	40842	2.9	159.76	0.39	40582	41155
K	26980	11	26091	-3.3	278.09	1.07	25776	26638
Mn	490	9	289	-41.1	17.50	6.06	257	314
Pb	50	11	50	0.1	2.75	5.50	46	55
Rb	161	11	80	-50.3	1.19	1.48	78	82
S	800	11	1429	78.6	73.90	5.17	1318	1537
Sr	109	11	85	-21.7	0.91	1.07	84	87
Th	17.4	11	24.8	42.2	3.22	13.01	20.1	31.3
Ti	4840	11	4145	-14.4	310.03	7.48	3826	4927
Zn	70	11	69	-1.7	3.43	4.98	64	74
Zr	385	11	351	-8.9	13.15	3.75	332	370

A4a. Summary statistics of SRM TCA8010 by pXRF spectrometry (soil mode), <0.074 mm size fraction

	Recommended Value (ppm)	Count	Mean (ppm)	%error	Std Dev (ppm)	%RSD	Minimum (ppm)	Maximum (ppm)
As	5.45	12	6.32	15.9	0.98	15.51	4.79	8.0
Ba	549	12	702	27.8	18.87	2.69	665	729
Ca	15509	12	13775	-11.2	183.77	1.33	13469	14071
Cd	0.11	8	9.77	8780.7	1.82	18.62	7.52	12.76
Cr	48.4	10	13.6	-71.8	3.63	26.63	7.5	19.9
Cs	1	12	52	5124.4	3.12	5.96	46	58
Cu	28	12	29	4.1	4.00	13.71	23	35
Fe	20290	12	14583	-28.1	179.33	1.23	14359	14845
K	19094	12	16671	-12.7	233.83	1.40	16350	17069
Mn	310	12	305	-1.5	18.99	6.22	270	336
Ni	17.2	12	60.0	248.9	7.74	12.90	49.7	76.5
Rb	53.6	12	49.1	-8.4	0.87	1.77	47.1	50.7
Sb	2.3	12	17.8	675.4	3.55	19.90	13.1	23.3
Sn	0.6	8	10.0	1559.6	2.55	25.61	7.5	15.5
Sr	310	12	268	-13.5	1.89	0.70	264	271
Te	0.02	12	76.61	382945.8	5.62	7.34	66.65	85.96
Th	5.1	12	3.6	-30.2	0.63	17.76	2.3	4.6
Ti	2578	12	2244	-13.0	55.76	2.48	2147	2372
U	1.1	10	6.1	457.5	0.95	15.54	4.4	7.7
V	49	12	75	52.5	6.79	9.08	65	83
Zn	31.9	12	36	11.8	6.97	19.55	27.5	47.8
Zr	272	12	326	19.8	17.47	5.36	298	356

A4b. Summary statistics of Till-4 by pXRF spectrometry (soil mode), <0.074 mm size fraction

	Recommended Value (ppm)	Count	Mean (ppm)	%error	Std Dev (ppm)	%RSD	Minimum (ppm)	Maximum (ppm)
As	111	12	103	-7.0	2.66	2.57	99	108
Ba	395	12	461	16.6	14.73	3.20	443	485
Ca	8934	12	7924	-11.3	118.63	1.50	7654	8074
Cr	53	12	22	-58.1	2.37	10.68	19	27
Cu	237	12	214	-9.9	4.10	1.92	208	224
Fe	39700	12	33219	-16.3	237.51	0.71	32972	33698
K	26980	12	23723	-12.1	320.58	1.35	23175	24348
Mn	490	12	445	-9.2	20.95	4.71	406	489
Mo	16	12	18	9.9	1.79	10.19	15	21
Ni	17	12	58	240.1	12.39	21.43	44	77
Pb	50	12	42	-15.9	1.57	3.73	40	45
Rb	161	12	152	-5.6	1.54	1.01	149	154
S	800	12	642	-19.7	98.78	15.38	446	764
Sr	109	12	106	-3.0	0.82	0.78	104	107
Th	17.4	12	42.2	142.7	1.84	4.36	39	45
Ti	4840	12	4626	-4.4	65.58	1.42	4455	4706
U	5	12	14	170.3	4.53	33.55	6	20
V	67	12	123	82.9	11.65	9.50	102	139
W	204	12	175	-14.0	10.14	5.78	163	195
Zn	70	12	67	-4.8	3.79	5.68	60	72
Zr	385	12	435	12.9	10.05	2.31	418	450