

INTRODUCTION

A portable X-Ray Fluorescence spectrometer (pXRF) has been utilized in multiple projects to characterize the geochemistry of a suite of elements and provides results similar to fusion and 4-acid methods. The pXRF analyses can provide near-instantaneous elemental composition of sediments, with minimal sample preparation and at low cost. However, questions persist regarding data precision and accuracy.

To provide a normalized sample grain-size, volume, and to minimize nugget effects in glacially-derived sediments, samples are dried and sieved to < 0.063 mm (silt + clay) prior to analysis. To ensure quality control, a number of Certified Reference Materials (CRM) and Standard Reference Materials (SRM) are analyzed with each project, and comparisons made with previously published results. For further quality control, a sub-suite of sediment samples are analyzed by ICP-MS/ES after lithium borate fusion and multi-acid digestions.

To date, this research supports the application of pXRF for the characterization of major and trace elements in glacial-derived sediments. We have found that pXRF provides reliable data for 14 elements, and can be used as a screening tool to select subsets of samples for traditional laboratory analytical methods. While routine collection of geochemical data by laboratory methods can be beyond the scope and budget of many programs, pXRF analyses can be used as an alternative analytical

Does the size fraction matter?

Major grain size variation

In Situ (drill core) Processed (<0.063 mm)





Spiritwood val

jeneity of in situ samples in this mud and pebble rich diamicton indicates that the field application of pXRF on unsieved samples will likely result in highly variable analytical results. Not only will pebbles under the surface influence analysis, but sand size particles will have significant effects on the analysis. For this reason pXRF spectrometry will not provide accurate results when pebbles and variable grain sizes are present in the sample being analysed.

Clay / Silt

Sand

Pebble

Shale clast

Granite clast

Removal of size fractions >0.063 mm provide quality data that assist in the interpretation of both visual core logging and downhole



The bivariate plots displayed above show that an increase in fine sand content from <0.063 mm to <0.074 mm obtained from glacial derived sediment of southern Ontario does not affect the results obtained using a pXRF as long as the concnetrations are well above the detection limit.

pXRF protocol for successful data acquisition relies on the assumption that the sample being analysed has an "infinite thickness". Infinite thickness corresponds to the thickness of a sample where the analyzer returns a result that will not change if the sample was thicker. Samples of less than infinite thickness will in many instances return results that are not precise.

The recommended depth of a sediment sample sieved to <0.063 mm to obtain a consistent (precise) concentration for elements being tested in Soil mode is listed in Table 1. Blank depths indicate that the returned result was not impacted by the thickness of the sample; however for most elements post data collection to correct for poor accuracy would be beneficial.



of data above this "minimum" dwell time should optimum dwell time becomes a highly important factor for both a timely and cost effective procedure in which analytical precision is not compromised. For an element present at low concentration levels, increasing the dwell time results in greater number of counts and should improve analytical precision.



lines represent the recommended value. Dashed vertical lines represent time gaps in analyses when the pXRF was shut down for <1 hour. Solid vertical lines represent a break in analyses > 24 hours. Large blue dots represent the data point while the smaller red dots represent $\pm 2\sigma$.



For elements that normally display a high degree of presicion, battery charge has no effect on the quality of the data.

Quality Control of pXRF Spectrometry

Ayesha R.R. Landon-Browne, Ross D. Knight, Bruce A. Kjarsgaard, and Hazen A.J. Russell

Till -1 Till -3

4mm

Table 1

How much sample do I need?





fairly consistent with increasing sample thickness include Ca. Cr. K. Ti and V. Flements ecreases with increasing thickness until infinite thickness is achieved (generally >6mm), include As, Cu : Of this group Mn has the lowest X-ray intensity and is determined using the Ka1 6.10keV line while Zr has the highest X-ray intensity and is determined using the Ka1 15.98 keV line. Ba was the only element detected where concentrations continue to increase until 20 -25mm of sample thickness is achieved. Barium is detected using the High filter and the Ka1 line of 32.70 keV.

Our results indicate that thicker samples provide a higher degree of compaction (increasing density) at the sample surface interface with the X-ray beam, allowing for more X-ray beam sediment interaction which provides more consistent results.

What dwell time should I use?



For many studies the optimal analytical dwell time ranges from 30 – 40 seconds.



Does battery life affect the returned result?

The bivariate plots below display data aquired by pXRF compared with data obtained by lithium borate fusion (orange dots) and 4-acid (blue dots) digestions with ICP ES/MS analysis for sediments obtained from 2 boreholes located in southern Ontario and processed to < 0.063 mm. The green dashed line represents the 1:1 relationship. The black line represents a linear regression determined by the least squares approach.



pXRF spectrometry the good, the not so good, the ugly

Comparing the analyses of 689 samples of sediments sieved to <0.063 mm with a pXRF and lithium borate fusion digestion and ICP ES/MS analysis we conclude that 9 elements return excellent results, 5 elements return good results, and 4 elements return poor results. Elements that are not detected (12) may be the result of samples not containing that element in sufficient concentration to be above the detection limit. This may also hold true for Ni and Mo, while Sc has an overlap with Ca and should not be identified with the pXRF.



pXRF vs Fusion and 4-acid methods

Data correction for accuracy

Data correction or calibrations are typically carried out: 1) pre-collection, by entering a calibration slope and intercept into the pXRF spectrometer or; 2) post-collection, by correcting data based on analyses of standards. For the diagrams below the original raw data point for Fe in Till-1,-2, and -3 is represented by blue dots while the smaller red dots represent $\pm 2\sigma$. After post analysis correction based on a regression line obtained from CRM's the same data points are plotted as green and yellow dots. In general, calibration is not necessary for all



For groundwater studies, the collection of sediment geochemistry data is often beyond the scope, and budget of many programs, and is generally not included as a part of routine data collection. Portable X-ray fluorescent spectrometry has proven to be a successful tool to characterize the chemostratigraphy of glacially derived sediments, as well as improving the interpretation of downhole geophysics, micropaleontology results, and pore water geochemistry. Data collected from this method has now become a routine part of borehole studies within the Groundwater Geoscience Program at the Geological Survey of Canada.



50 100 150

4 - Acid

4 - Acid

50 100 150 200 250

4 - Acid

20 30 40 50

0 50 100 150 200 250 300 350 400 450 500 \$

4 - Acid

4 - Acid

The variation in concentration of some elements (e.g. Ca, Fe, Rb, V) between the Thorncliffe and the overlving Newmarket Till indicate that the silt and clay size fraction (procliffe Formation was not incorporated into the matrix of the Newmarket Till



Core geochemistry trends suggest that provenance of the core sediment was relatively consistent and depositional processes did not partition sediment to impart a highly variable geochemical signal between stratigraphic units. For Ca the concentrations obtained by pXRF spectrometry mimic the % carbon content for all units.

Calcium data collected from the Queensville borehole would improve in accuracy by post collection calibration. Cu is close to the detection limit and thus displays poor precision and accuracy. Elements that contain sufficient concentrations to be determined by soil mode gennerally do not need correction. The graphs below display how correction of the Ca data

produces both precise and accurate results.



Groundwater Geoscience Program - Geological Survey of Canada

pXRF spectrometer drift: variable projects and analytical time gaps



From 2009 to 2016 approximately 7000 analyses have been carried out on CRM/SRM as part of eleven different projects. For each analytical session a Teflon blank, silica blank, and a suit of standards are analyzed at the start and finish of each session, and after every ten samples. The box and whisker diagrams plotted below display the variation in Ca and Zr values obtained from Till-4. Data for individual projects is represented by a box and whisker diagram. The two mustard coloured box and whisker plots on the left side of the diagram are the same samples measured by the same instrument but with a different X-ray tube. The large variation in the light blue box and whisker plot for Ca may be the result of several operators for the pXRF during a particular project.





pXRF spectrometer drift within and between projects



results between projects can vary substantially however variation within each project is, for many elements acceptable. Notice that occasionally there are outliers that most likely represent erroneous data.

Although there is drift from project to project, for most elements there is very little drift within a project - demonstrating that samples from a given project should be analysed in as short a time frame as possible



Canada