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Sampling Methodologies and Data Analysis Techniques for Geologic Materials Using Portable X-Ray Fluorescence (pXRF) Elemental Analysis

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This report represents work performed by the Wisconsin Geological and Natural History Survey and colleagues and is released to the open files in the interest of making the information readily available. This report has not been edited or reviewed for conformity with the Wisconsin Geological and Natural History Survey standards and nomenclature.

Sampling Methodologies and Data Analysis Techniques for Geologic Materials Using Portable X-Ray Fluorescence (pXRF) Elemental Analysis

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1. Introduction

The Wisconsin Geological and Natural History Survey (WGNHS), with partners at the Indiana and US geological surveys, has been developing methods for obtaining and interpreting the elemental composition of geological materials using a portable x-ray fluorescence (pXRF) elemental analyzer. This open-file report details the current WGNHS approach to pXRF analysis using a Thermo Fisher Scientific Niton XL3t GOLDD+ Handheld XRF analyzer, which was obtained in 2013. The details presented herein are likely also of interest for wider use outside of the WGNHS, and are separated into the following sections:

2. Instrument Safety and User Guidelines,
3. Sample Preparation of Geological Materials for pXRF Analysis,
4. Standards and Calibration,
5. Instrument Settings, Reporting Errors, Data Download and Backup,
6. Various Plotting Techniques for Data Interpretation, and,
7. pXRF versus ICP-MS: A Case Study of Sample Preparation and Analysis.

Prior to using the WGNHS pXRF, all users should read this report; additional recommended reading includes the instrument manual and Rowe et al. 2012.

In many applications, pXRF instruments provide a robust “first look” at a sample, which can be employed to refine the sampling strategy for more detailed, labor-intensive analysis. Handheld XRF units were originally developed for screening purposes, for example when surveying for precious metals, and have subsequently become more advanced to allow elemental analysis with increased precision and accuracy at lower detection limits. An x-ray fluorescence spectrometer is an instrument used for routine, relatively non-destructive chemical analysis. The pXRF may not be the appropriate instrument for obtaining highly-accurate and precise quantitative elemental composition of unknown samples, though this is in part determined by the questions at hand and the element(s) and concentrations considered. More robust techniques, such as ICP-MS (see case study below), may provide improved precision and accuracy for some elements at some concentrations. The primary limitation of the pXRF is the number of elements for which it is both precise and accurate. The handheld XRF is ideal for comparing the relative concentrations of elements within fine-grained samples, especially in sedimentary rocks, which typically have simple mineral composition. The scientific power of the pXRF is the speed at which it can collect precise and relatively accurate results at a comparatively low cost with minimal sample preparation. The pXRF provides percentage by weight for elements present in your samples; oxide-equivalents can be calculated using a conversion factor. The pXRF sometimes has difficulty detecting magnesium, and cannot detect elements lighter than it (see case study below).

2. Instrument Safety and User Guidelines

Before using any handheld XRF, familiarize yourself with all safety information!
WARNING –the WGNHS pXRF emits radiation when red lights are flashing

The portable X-ray fluorescence analyzer (pXRF) uses a directed x-ray radiation beam to analyze the elemental composition of materials. In order to minimize the chance of radiation exposure, and prolong the life of the pXRF, the WGNHS uses the instrument in a lead-lined test stand. The attached wrist strap must be used whenever the pXRF is not in the test stand. If the analyzer is dropped, the x-ray tube will likely break and the replacement cost is ~$7000.00. Because the pXRF cannot be used correctly without a fundamental understanding of the theoretical background and dangers of using the instrument, all student workers at WGNHS and external researchers must first receive safety and methods training by a WGNHS staff member. A refresher session is required if it has been more than 6 months since you used it last. The WGNHS strongly encourages using the pXRF analyzer only while mounted in its lead-lined test stand for both safety and to reduce the potential for damage to the instrument.

2a. pXRF Use by WGNHS and External Researchers

The WGNHS pXRF elemental analyzer is primarily used for in-house research. External collaborators with data requests that overlap with ongoing projects at the WGNHS may be trained to use the pXRF or may have samples run for them by WGNHS personnel. Collaborators will be asked to cover the cost of expendables and personnel time for training/running samples. Outside users will only have access to the pXRF at the discretion of the WGNHS; access can be revoked at any time for safety concerns. The WGNHS reserves the right to decline analysis of materials due to concerns of safety or data integrity.

Researchers at the WGNHS investigate a multitude of materials and elements, and therefore use different standards and calibrations in addition to varying the length of analysis to decrease error. For this reason, the recommended use of the pXRF is for researchers to sign-up to use the instrument for several days to a week at a time. This will allow each researcher to calibrate the instrument specifically for their study and then collect their data without the possibility of another researcher changing their preferred settings. The pXRF can be reserved through the WGNHS reservation system.

Actual costs will be determined after analysis is complete, but can be estimated as follows:

***Cost = Expendables + WGNHS Personnel Time**

Expendables = average cost is $0.35/sample
WGNHS Personnel Time = hourly salary ($15-40/hour**) + fringe for processing/running samples and/or training

*This formula can also be used for grant proposals.
**Typically 10-20 fully prepared samples can be run in 1 hour.

3. Preparation of Geological Materials for pXRF Analysis

The most common geological materials that are analyzed at WGNHS include hand samples, drill core, borehole cuttings (which sometimes include unlithified Quaternary deposits and/or soil from the upper portion of the borehole), and rock powders. The pXRF device requires enough material to cover the analyzer window. The following sections describe WGNHS standard preparation procedures, which are illustrated in Figures 1 and 2.

3a. Hand Samples

When possible, preference is to analyze the cut face of a rock slabbed with a water-cooled rock saw. Lithologies such as friable sandstone, common in the Wisconsin Cambrian succession, sometimes make slabbing difficult. Similarly, slabbing of salt materials using a water-cooled saw is possible if the saw can be modified for use with minimal water. Use of organic liquids for keeping the saw cooled should also work, as long as the elemental composition of the liquid is light (for example carbon, hydrogen, and oxygen) and therefore undetectable to the pXRF. Slabbed rock faces provide a flat, stable surface for pXRF analysis and ensure that the sample is as close to the analyzer as possible and does not rock and/or roll during pXRF analysis. Hand samples can also be powdered and analyzed in vials (see below).

3b. Drill Core

Similar to hand samples, a slabbed core face is preferred, but not essential. Always make sure the area to be analyzed is clean; a common contaminant on drill core is drilling mud or rock saw residue (sand paper is a preferred means to rapidly clean small surfaces for analysis). The rounded, outer surface of core works well too, and we have successfully analyzed the outer surface of various core diameters (HQ, NQ, and AX). To avoid rolling of whole (un-slabbed) core samples, use props such as modeling clay or Styrofoam wedges and blocks, the latter is preferred as it is made of elements that the pXRF analyzer cannot detect. Core samples can also be powered and analyzed in vials (see below).

3c. Borehole Cuttings

Borehole cuttings can be analyzed quickly and efficiently. If cuttings are in a plastic vial, remove the cap and use a small rubber band (type used for dental braces) to secure a piece of XRF thin film (typically 4 μm-thick polypropylene or similar) across the vial top. Turn vial over so cuttings rest on film and place vial upside-down on pXRF stage. Use a new film for each sample. If cuttings are in a glass vial, you should consider transferring them to a plastic vial or sample holder because the pXRF may read the silicon of the glass vial. Cuttings stored in envelopes will also need to be transferred into a plastic vial or sample holder. Both rock powder (below) and borehole cuttings can be compressed in a sample holder to create a flatter surface, though this may not be ideal if you do not want to alter the borehole cuttings grain size and there is not enough material to sub-sample. If a sample vial opening is too small and falls within the sample analysis window, transfer material to a plastic vial or sample holder (see below) with a wider mouth; many plastics are made completely of light elements that are not identifiable by the pXRF analyzer.

3d. Rock Powders

Rock powders can be made using a mortar and pestle, a ball-mill, or drilled from rock samples using a masonry bit. Be sure to mix the sample well to homogenize the material. We have found that the easiest and quickest way to create rock powders is to drill the rock using a tungsten carbide drill bit (hardness = ~9 on Mohs scale) on a drill press or a Dremel tool. It is recommended to drill a shallow pilot hole and discard initial powder to guarantee minimal contamination (i.e., weathered rock surfaces or drilling mud left on core) and clean the drill bit between samples using compressed air and disposable wipes. Other cleaning techniques include washing the bit in a weak HCl acid bath, sonifier, and alcohol (to decrease drying time). This type of sampling easily creates rock powder (collected on weigh paper) and allows removal of discrete portions of the rock, limited only by drill bit width. Similar to cuttings above, the powder can be placed directly in a plastic vial and analyzed using thin-film secured by a rubber band.

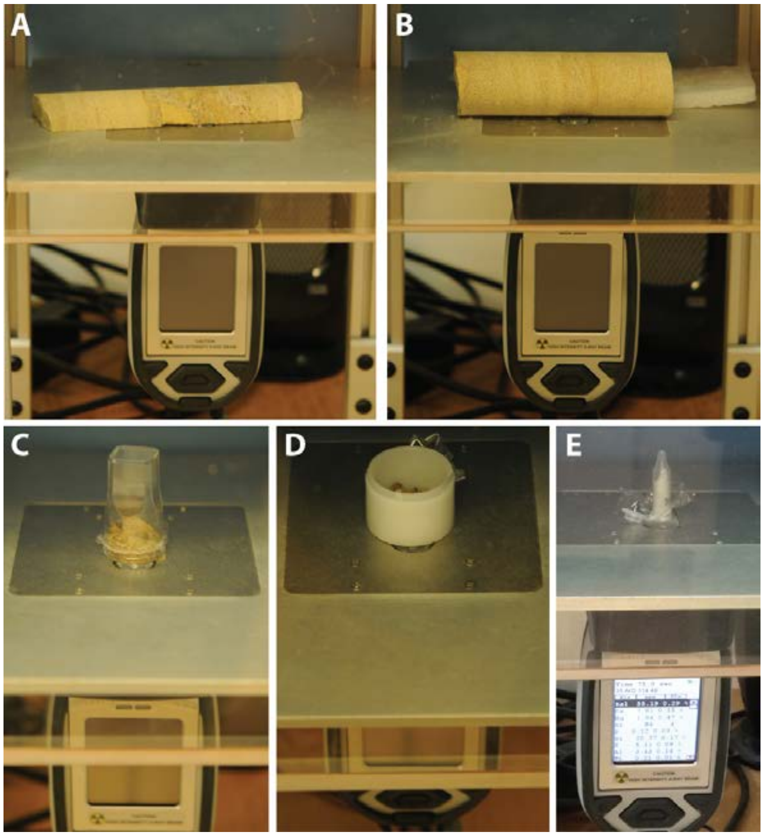
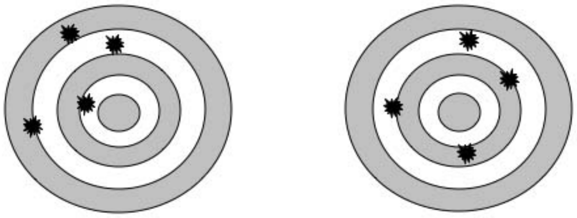


Figure 1: Geologic materials on the pXRF sample stage (for a scale reference, the pXRF data screen is ~7x5cm). (A) slabbed core, (B) unslabbed core, note use of Styrofoam to keep the core from rolling, (C) cuttings in a sample vial with polypropylene film secured over the vial mouth with a rubber band, (D) cuttings in a pXRF sample holder from the instrument manufacturer, (E) rock powder in a small vial with polypropylene film secured with a rubber band across the mouth of the vial.

Figure 2: Pictures of prepared cuttings materials (A, B) and rock powder (C).

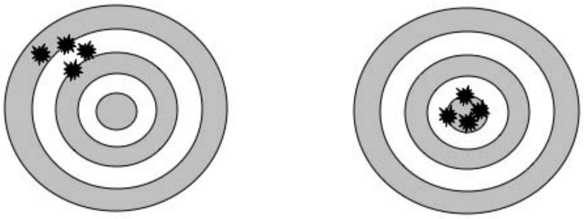
4. Standards and Calibration

Depending on the question at hand, calibration of the instrument may be recommended. Calibrating the instrument may improve the accuracy of your data, i.e., how close the collected values are to the actual (true) value. Precision, a.k.a. reproducibility, is the degree to which repeated analysis of a given sample or standard yields the same value. The difference between accuracy and precision is shown in Figure 3. When data is being collected from a variety of different lithologies, the default internal calibration may be the most appropriate. If data are being collected from a single lithology (i.e., shale) then the user may want to identify a series of standards of the same lithology that possess a range of concentrations for the elements of interest so that calibration factors can be calculated (see, for example, Rowe et al. 2012, and Section 7 of this report). The matrix (lithology) of the material analyzed can result in different interpretations by the pXRF algorithms used to determine elemental concentrations.



Not Accurate
Not Precise

Accurate
Not Precise



Not Accurate
Precise

Accurate
Precise

Figure 3: Accuracy versus Precision (taken from noaa.gov)

In the default setting, the pXRF is calibrated to a piece of metal of known composition located within the unit itself. It is possible to improve the accuracy of the data using element-specific calibration factors prior or following analysis. Please note that not every element is found in the suite of standards currently held by the WGNHS (Appendix 1). Depending on the element(s) of interest to the investigator and the material being analyzed, the investigator may need to find (or make) an appropriate set of standards that contains these elements. Additionally, because the pXRF software analyzes the spectra of fluorescence to determine elemental composition, and some elements/minerals have overlapping spectra, it is important to choose standards of similar material to the samples which will be analyzed (Rowe et al., 2012). A 'standard' will need to be measured by multiple analytical techniques (e.g., ICP-MS and pressed-pellet XRF) so that the accepted values for the standard are as close to the true composition as possible. The pXRF manual provides detailed information on the calculation of calibration factors and their input in the pXRF analyzer (see pg. 575 of the manual; also Rowe et al. 2012).

Instrument precision and accuracy must be monitored by routine analysis of standards. It is regular operating protocol to analyze standards before and during data collection sessions. Regular comparison of the values obtained for various elements from the standards allows for determination of precision - this will vary for each element at different concentrations. Standards should be run at the beginning and end of a session, as well as intermittently while collecting data; the frequency is up to the user depending on how confident they want to be in the instruments precision and the user's tolerance for drift and noise. Elemental composition is specific to each standard therefore it is requisite to choose an appropriate set of standards that reflect the composition of the samples under investigation. If the instrument appears to be drifting or the data appears noisy for an element of interest during repeated measurement of standards, the user will have to decide whether the sample data will need to be re-collected given the question being asked. The user should also be familiar with uncertainty, or the margin of error, for the data collected using the pXRF which is reported as 2-sigma; a fourfold increase of measurement time should lead to a twofold reduction of imprecision error (see Appendix B of the manual, pg. 196).

The WGNHS routinely uses the following five standards. USGS and NIST standards have been pressed into pucks; the Thermo Scientific Standard is loosely compacted material in a pXRF sample cup with thin film.

a) USGS Brush Creek Shale, SBC-1
   http://crustal.usgs.gov/geochemical_reference_standards/pdfs/SBC-1.pdf
b) USGS Devonian Ohio Shale, SDO-1
   http://crustal.usgs.gov/geochemical_reference_standards/pdfs/ohioshale.pdf
c) USGS Carbonatite, COQ-1
   http://crustal.usgs.gov/geochemical_reference_standards/pdfs/carbon.pdf
d) NIST Standard Reference Material 1d, Argillaceous Limestone, SRM-1d
   https://nemo.nist.gov/m-srmors/certificates/1D.pdf
e) Thermo Scientific Blank 180-647 SiO_2
   Part of Thermo Scientific Soil/Mining QC Reference Sample Set

Appendix 1 contains pXRF data collected from the five standards listed above (both before and after the analysis performed for the case study detailed below in section 7). These data and plots are presented for the most basic determination of calibration factors for a variety of elements in varying lithologies; note that the standards presented do not allow calibration of all elements (further discussion in Section 7). A lithological unit-specific example of calibration factor determination is presented in the case study below (section 7 of this report, Appendix 5). Below, we present example plots for characterizing whether the instrument is precise, drifting, or producing noisy data (Fig. 4).

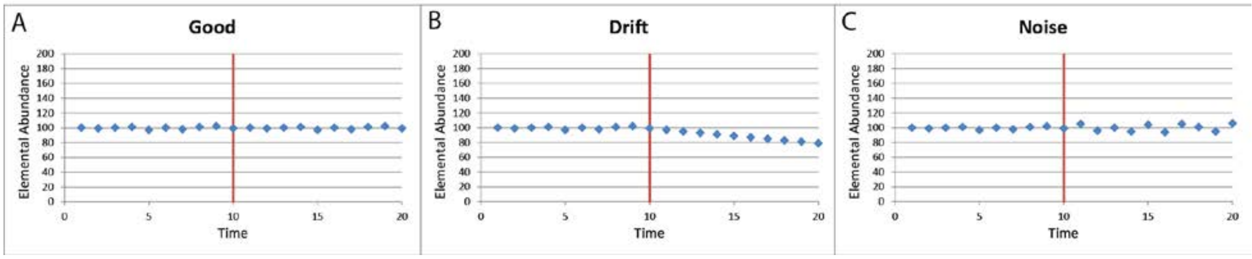


Figure 4: Examples of how elemental abundance data from before and after Time = 10 can be used to judge A) good data, B) instrument drift, and C) noisy data.

5. Instrument Settings, Reporting Errors, Data Download and Backup

Detailed directions for setting up the WGNHS pXRF, dealing with errors, downloading data and backing up the instrument are available in Appendix 2. The WGNHS Analysis form, used to keep track of users, instrument use, and errors encountered, is available as Appendix 3.

6. Plotting Techniques for Data Interpretation

The plotting techniques detailed in Appendix 2 were developed by the WGNHS to characterize sample elemental composition, and by proxy, mineralogic and quantitative lithologic variability within stratigraphic successions. These may or may not be ideal for you depending on your preferences; examples are given for plotting in both Excel 2011 and Excel 2013 on a Windows OS. An example of plotted pXRF data for a core drilled and analyzed by the WGNHS is shown in Figure 5 below. Note that the relative changes in elemental concentrations through the core are useful for identifying lithostratigraphic unit boundaries and describing unit characteristics; for example, the Elk Mound Group is a quartz-dominated sandstone (elevated uniform silicon) with minimal to minor clay (low potassium and aluminum) and minimal carbonate cement (low to no calcium and magnesium). We have also included an additional template in Appendix 4 focused on subsurface data.

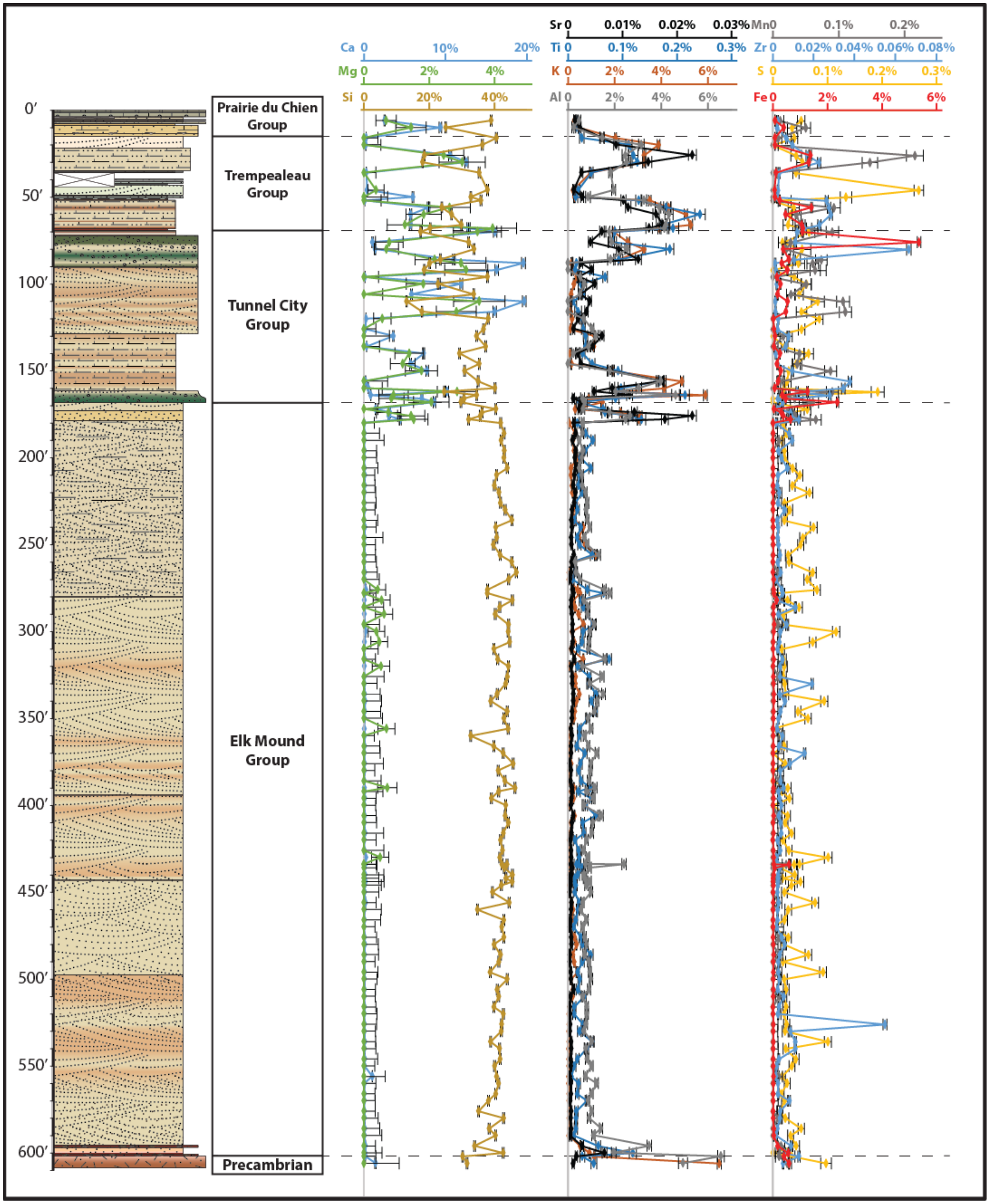


Figure 5: Elemental profiles collected using pXRF from the WGNHS Triemstra Quarry core (WID = 11005900).

7. pXRF versus ICP-MS: A Case Study of Sample Preparation and Analysis

In this case study, we compare data collected using pXRF with data collected from the same samples using ICP-MS (see Appendix 5 and Table 1).

7a. Methods and Materials:

The WGNHS routinely collects pXRF data on core and hand samples in order to quantify rock composition. Typically, these analyses are done on slabbed core or hand sample surfaces, but are also collected on the outside surface of rock core and powdered rock samples. From an extensive pXRF dataset from rock surfaces, we identified a suite of samples representing a range of elemental concentrations from south-central and west-central Wisconsin that span the Tunnel City Group – Wonewoc Formation boundary; this suite was powdered for additional analyses. This boundary was chosen because these units are dominated by two different lithologies that are common in Wisconsin and presumably have different matrix properties. The Wonewoc is a quartz-dominated sandstone with iron-oxide and sulfide cements, and the Tunnel City is a shaly, dolomite-cemented glauconitic sandstone with iron-oxide and sulfide cements.

The suite of 59 samples comes from cores (56000829 WGNHS Belisle Quarry, 62000166 WGNHS Arcadia Quarry, 11005900 WGNHS Triemstra), well cuttings (32000107 Arbor Hills), and hand samples (Granddad Bluff, La Crosse, WI). Samples powders were drilled using a tungsten carbide bit on a drill press. For pXRF, powders were analyzed in vials fitted with a 4 μm (0.16 mil) polypropylene thin film (see sample preparation methods above, Section 3). pXRF analyses of both rock and powdered samples was run for a total of 75 seconds (15 seconds Main filter, 30 seconds Light filter, 15 seconds Low filter, and 15 seconds High filter). ICP-MS analysis was performed by ALS Global (ME-MS61L Super Trace Lowest DL 4A package) at their Reno, NV laboratory in June 2016.

Accuracy as described herein was determined visually by how well the pXRF data matched the ICP-MS data at varying elemental concentrations. Calibration potential was determined by inspecting the r-squared values of the cross-plots of powdered samples analyzed by ICP-MS and pXRF. The calibrations determined did not use the rock surface pXRF data because we could not be certain that the rock surface analysis was performed in the same spot that was sampled for powder and subsequently analyzed by ICP-MS.

7b. Results:

Results of the pXRF and ICP-MS analyses are presented in Appendix 5, and summarized in Table 1 below. It should be noted that this comparison of pXRF and ICP-MS data is for the run times used; longer run times may increase pXRF accuracy and/or precision at certain concentrations and decrease the need for, or improve, calibration factors.

Table 1: Summary of analysis of standards (see Appendix 1) and comparison between ICP-MS and pXRF data (see Appendix 5).
For standards (far right column), 0 = no data, 1 = reproducible, and 2 = not reproducible but in most cases the value was relatively similar.
For elemental ranges analyzed, * denotes the presence of values below the LOD.
Green, yellow, and red indicate degree of accuracy and potential for calibration from better to worse, respectively.

Filter (Run Time)		Wonewoc Notes	Wonewoc elemental ranges analyzed	Tunnel City Notes	Tunnel City elemental ranges analyzed	Rock Surface vs Powder	Standards
Mining Mode Light (30s)	🟩 **Al**	pXRF is accurate or overestimates concentration, calibration possible.	ICP-MS 0.04 - 5.27% pXRF$_{powd}$ 0.14 - 4.37% pXRF$_{rock}$ 0.07 - 4.99%	pXRF is accurate or underestimates concentration, calibration possible.	ICP-MS 0.08 - 8.10% pXRF$_{powd}$ 0.14 - 6.24% pXRF$_{rock}$ 0.16 - 6.33%	rock is similar, but noisy	180-647^{0} SRM-1D^{1} SBC-1^{2} COQ-1^{1} SDO-1^{2}
Mining Mode Main (15s) Soils Mode Main (15s)	🟩 **As**	pXRF is accurate or overestimates concentration, though limited data due to pXRF LOD. LOD is ~8ppm.	ICP-MS 0.08 - 8.21ppm pXRF$_{powd}$ 7.59 - 9.04ppm* pXRF$_{rock}$ 9.64 - 47.69ppm*	pXRF is accurate or overestimates concentration, calibration possible, LOD is ~7ppm.	ICP-MS 0.81 - 547.00ppm pXRF$_{powd}$ 6.82 - 428.89ppm* pXRF$_{rock}$ 7.10 - 620.89ppm*	rock is similar or overestimates	180-647^{0} SRM-1D^{0} SBC-1^{1} COQ-1^{0} SDO-1^{1}
Mining Mode Low (15s) Soils Mode Low (15s)	🟩 **Ca**	pXRF is accurate or overestimates concentration, calibration possible.	ICP-MS 0.01 - 2.85% pXRF$_{powd}$ 0.01 - 5.05% pXRF$_{rock}$ 0.03 - 3.45%	pXRF is accurate or overestimates concentration, calibration possible.	ICP-MS 0.06 - 18.65% pXRF$_{powd}$ 0.09 - 24.53% pXRF$_{rock}$ 0.18 - 24.04%	rock is similar, but noisy	180-647^{0} SRM-1D^{1} SBC-1^{1} COQ-1^{1} SDO-1^{1}
Mining Mode Main (15s) Mining Mode High (15s) Soils Mode High (15s)	🟥 **Cd**	pXRF overestimates concentration, calibration not possible. LOD ~12ppm.	ICP-MS 0.006 - 0.03ppm* pXRF$_{powd}$ 12.46 - 15.97ppm* pXRF$_{rock}$ 12.79 - 25.97ppm*	pXRF overestimates concentration, calibration not possible. LOD ~12ppm.	ICP-MS 0.005 - 3.70ppm* pXRF$_{powd}$ 12.87 - 20.95ppm* pXRF$_{rock}$ 15.07 - 27.33ppm*	similar values	180-647^{0} SRM-1D^{1} SBC-1^{1} COQ-1^{0} SDO-1^{0}
Mining Mode Main (15s) Soils Mode Main (15s)	🟨 **Co**	pXRF is accurate, though limited data due to pXRF LOD. LOD ~50ppm.	ICP-MS 0.39 - 34.60ppm pXRF$_{powd}$ 48.13 - 63.68ppm* pXRF$_{rock}$ 143.42 - 252.80ppm*	no data due to pXRF LOD.	ICP-MS 3.48 - 100.00ppm pXRF$_{powd}$ ------------ ppm* pXRF$_{rock}$ 315.52 - 15673.35ppm*	rock overestimates	180-647^{0} SRM-1D^{0} SBC-1^{0} COQ-1^{0} SDO-1^{0}
Mining Mode Main (15s) Mining Mode Low (15s) Soils Mode Low (15s)	🟨 **Cr**	pXRF overestimates concentration, calibration may be possible. ICP-MS has large 2-sigma.	ICP-MS 0.90 - 38.90ppm pXRF$_{powd}$ 50.64 - 128.89ppm* pXRF$_{rock}$ 56.65 - 278.04ppm*	pXRF overestimates concentration, calibration not possible. ICP-MS has large 2-sigma.	ICP-MS 2.40 - 90.60ppm pXRF$_{powd}$ 64.82 - 182.58ppm* pXRF$_{rock}$ 63.73 - 238.35ppm*	similar values	180-647^{0} SRM-1D^{0} SBC-1^{1} COQ-1^{0} SDO-1^{1}
Mining Mode Main (15s) Soils Mode Main (15s)	🟥 **Cu**	pXRF data is limited due to pXRF LOD.	ICP-MS 0.86 - 645.00ppm pXRF$_{powd}$ 26.06 - 358.57ppm* pXRF$_{rock}$ 25.07 - 126.57ppm*	pXRF data is noisy, calibration not possible.	ICP-MS 1.01 - 269.00ppm pXRF$_{powd}$ 22.43 - 184.73ppm* pXRF$_{rock}$ 25.15 - 80.04ppm*	pXRF data limited	180-647^{0} SRM-1D^{0} SBC-1^{1} COQ-1^{0} SDO-1^{1}
Mining Mode Main (15s) Soils Mode Main (15s)	🟩 **Fe**	pXRF is accurate.	ICP-MS 0.01 - 4.76% pXRF$_{powd}$ 0.01 - 5.25% pXRF$_{rock}$ 0.01 - 11.32%	pXRF is accurate.	ICP-MS 0.60 - 18.30% pXRF$_{powd}$ 0.39 - 20.44% pXRF$_{rock}$ 0.32 - 28.33%	rock is similar or overestimates	180-647^{0} SRM-1D^{1} SBC-1^{1} COQ-1^{1} SDO-1^{1}
Mining Mode Low (15s) Soils Mode Low (15s)	🟩 **K**	pXRF is accurate or overestimates, calibration possible.	ICP-MS 0.02 - 5.60% pXRF$_{powd}$ 0.03 - 6.11% pXRF$_{rock}$ 0.03 - 6.28%*	pXRF accurate or overestimates for concentrations <=~4%, calibration possible; not possible for >~4%.	ICP-MS 0.07 - 5.43% pXRF$_{powd}$ 0.08 - 9.35% pXRF$_{rock}$ 0.02 - 9.08%	rock is similar or underestimates	180-647^{0} SRM-1D^{1} SBC-1^{1} COQ-1^{1} SDO-1^{1}
Mining Mode Light (30s)	🟩 **Mg**	pXRF is relatively accurate, though limited data due to pXRF LOD.	ICP-MS 0.01 - 1.14%* pXRF$_{powd}$ 0.31 - 1.48%* pXRF$_{rock}$ 0.26 - 0.75%*	pXRF is accurate or underestimates concentration, calibration possible.	ICP-MS 0.02 - 11.05% pXRF$_{powd}$ 0.44 - 6.95%* pXRF$_{rock}$ 0.47 - 9.24%*	rock is similar or overestimates	180-647^{0} SRM-1D^{0} SBC-1^{2} COQ-1^{0} SDO-1^{2}
Mining Mode Main (15s) Soils Mode Main (15s)	🟩 **Mn**	pXRF is accurate.	ICP-MS 1.40 - 3790.00ppm pXRF$_{powd}$ 73.58 - 4023.68ppm* pXRF$_{rock}$ 79.67 - 3898.10ppm*	pXRF is accurate for concentrations <=~1000ppm, noisy above that, calibration possible.	ICP-MS 24.7 - 2630.00ppm pXRF$_{powd}$ 79.24 - 2574.50ppm* pXRF$_{rock}$ 0.10 - 2678.67ppm*	rock is similar, but noisy	180-647^{0} SRM-1D^{1} SBC-1^{1} COQ-1^{1} SDO-1^{1}
Mining Mode Main (15s) Soils Mode Main (15s)	🟨 **Mo**	pXRF data is limited due to pXRF LOD. LOD ~5ppm.	ICP-MS 0.06 - 3.18ppm pXRF$_{powd}$ 4.67 - 9.68ppm* pXRF$_{rock}$ 5.56 - 23.65ppm*	pXRF data is limited due to pXRF LOD. LOD ~5ppm.	ICP-MS 0.04 - 5.47ppm pXRF$_{powd}$ 5.28 - 5.44ppm* pXRF$_{rock}$ 6.28 - 32.99ppm*	pXRF data limited	180-647^{0} SRM-1D^{0} SBC-1^{0} COQ-1^{0} SDO-1^{1}
Mining Mode Main (15s) Soils Mode Main (15s)	🟥 **Ni**	pXRF overestimates concentration, calibration not possible. LOD ~37ppm.	ICP-MS 0.54 - 16.5ppm pXRF$_{powd}$ 39.71 - 81.52ppm* pXRF$_{rock}$ 37.98 - 246.15ppm*	pXRF overestimates concentration in almost all cases, calibration not possible. LOD ~37ppm.	ICP-MS 2.55 - 158.00ppm pXRF$_{powd}$ 37.97 - 138.91ppm* pXRF$_{rock}$ 58.59 - 1102.22ppm*	rock overestimates	180-647^{0} SRM-1D^{1} SBC-1^{1} COQ-1^{1} SDO-1^{1}
Mining Mode Light (30s)	🟩 **P**	pXRF overestimates concentration, calibration possible. LOD ~0.04%.	ICP-MS 0.001 - 0.336% pXRF$_{powd}$ 0.07 - 0.95%* pXRF$_{rock}$ 0.04 - 2.04%*	pXRF data is noisy, calibration not possible. LOD ~0.04%.	ICP-MS 0.02 - >1.0% pXRF$_{powd}$ 0.03 - 3.37%* pXRF$_{rock}$ 0.03 - 12.64%*	rock is similar or overestimates	180-647^{0} SRM-1D^{0} SBC-1^{1} COQ-1^{1} SDO-1^{1}
Mining Mode Main (15s) Soils Mode Main (15s)	🟩 **Pb**	pXRF accurate within error. LOD ~7ppm.	ICP-MS 0.37 - 42.50ppm pXRF$_{powd}$ 7.28 - 39.82ppm* pXRF$_{rock}$ 8.67 - 49.44ppm*	pXRF accurate within error. LOD ~7ppm.	ICP-MS 0.84 - 49.6ppm pXRF$_{powd}$ 7.56 - 36.67ppm* pXRF$_{rock}$ 8.42 - 49.18ppm*	similar values	180-647^{0} SRM-1D^{0} SBC-1^{1} COQ-1^{0} SDO-1^{1}
Mining Mode Light (30s) Soils Mode Low (15s)	🟩 **S**	pXRF is accurate or overestimates concentration, calibration possible.	ICP-MS 0.01 - 5.23%* pXRF$_{powd}$ 0.008 - 6.40%* pXRF$_{rock}$ 0.10 - 22.42%*	pXRF is accurate or overestimates concentration, calibration possible.	ICP-MS 0.01 - >10.0%* pXRF$_{powd}$ 0.016 - 13.11%* pXRF$_{rock}$ 0.01 - 33.22%*	rock is similar or overestimates	180-647^{0} SRM-1D^{2} SBC-1^{2} COQ-1^{0} SDO-1^{2}
Mining Mode Light (30s)	🟩 **Si**	No ICP-MS data available.	No ICP-MS data available.	No ICP-MS data available.	No ICP-MS data available.	No ICP-MS data available.	180-647^{2} SRM-1D^{2} SBC-1^{2} COQ-1^{2} SDO-1^{2}
Mining Mode Main (15s) Soils Mode Main (15s)	🟩 **Sr**	pXRF is accurate or underestimates concentration, calibration possible.	ICP-MS 5.14 - 262.00ppm pXRF$_{powd}$ 5.46 - 222.71ppm pXRF$_{rock}$ 4.77 - 255.11ppm	pXRF is accurate or underestimates concentration, calibration possible.	ICP-MS 11.65 - 612.00ppm pXRF$_{powd}$ 11.22 - 509.89ppm pXRF$_{rock}$ 7.32 - 589.22ppm	similar values, though rock is noisier	180-647^{0} SRM-1D^{1} SBC-1^{1} COQ-1^{1} SDO-1^{1}
Soils Mode Main (15s)	🟨 **Th**	pXRF accurate within error, though limited data due to pXRF LOD. LOD ~5ppm.	ICP-MS 0.55 - 10.20ppm pXRF$_{powd}$ 4.93 - 8.67ppm* pXRF$_{rock}$ 5.97 - 8.03ppm*	pXRF accurate within error, though limited data due to pXRF LOD. LOD ~6ppm.	ICP-MS 0.94 - 11.15ppm pXRF$_{powd}$ 5.50 - 12.33ppm* pXRF$_{rock}$ 7.29 - 11.16ppm*	similar values	180-647^{0} SRM-1D^{0} SBC-1^{0} COQ-1^{0} SDO-1^{0}
Mining Mode Main (15s) Mining Mode Low (15s) Soils Mode Low (15s)	🟩 **Ti**	pXRF is accurate or overestimates concentration, calibration possible. LOD ~70ppm.	ICP-MS 60.00 - 1930.00ppm pXRF$_{powd}$ 147.37 - 2153.76ppm pXRF$_{rock}$ 77.88 - 4841.03ppm*	pXRF is accurate or overestimates concentration, calibration possible. LOD ~180ppm.	ICP-MS 70.00 - 3580.00ppm pXRF$_{powd}$ 182.96 - 4074.24ppm* pXRF$_{rock}$ 182.91 - 3497.15ppm*	rock is similar, but noisy	180-647^{0} SRM-1D^{1} SBC-1^{1} COQ-1^{0} SDO-1^{1}
Mining Mode Main (15s) Mining Mode Low (15s) Soils Mode Low (15s)	🟩 **V**	pXRF overestimates concentration, calibration possible. LOD ~20ppm.	ICP-MS 0.80 - 62.60ppm pXRF$_{powd}$ 18.83 - 104.87ppm* pXRF$_{rock}$ 23.69 - 107.93ppm*	pXRF overestimates concentration, calibration not possible. LOD ~30ppm.	ICP-MS 2.40 - 113.00ppm pXRF$_{powd}$ 32.70 - 168.52ppm* pXRF$_{rock}$ 27.5 - 276.48ppm*	similar values	180-647^{0} SRM-1D^{0} SBC-1^{1} COQ-1^{1} SDO-1^{1}
Mining Mode Main (15s) Soils Mode Main (15s)	🟩 **Zn**	pXRF accurate within error. LOD ~13ppm.	ICP-MS 0.60 - 13.5ppm pXRF$_{powd}$ 15.07 - 20.33ppm* pXRF$_{rock}$ 13.26 - 953.76ppm*	pXRF accurate within error for concentrations <~40ppm. LOD ~12ppm.	ICP-MS 1.40 - 4860.00ppm pXRF$_{powd}$ 12.68 - 3543.19ppm* pXRF$_{rock}$ 13.69 - 2686.44ppm*	similar values	180-647^{0} SRM-1D^{1} SBC-1^{1} COQ-1^{1} SDO-1^{1}
Mining Mode Main (15s) Soils Mode Main (15s)	🟩 **Zr**	pXRF is accurate or overestimates concentration, calibration possible.	ICP-MS 3.90 - 261.00ppm pXRF$_{powd}$ 18.51 - 1440.68ppm pXRF$_{rock}$ 8.71 - 3384.34ppm	pXRF is accurate or overestimates concentration, calibration possible.	ICP-MS 1.40 - 276.00ppm pXRF$_{powd}$ 18.19 - 412.82ppm pXRF$_{rock}$ 14.76 - 448.78ppm	similar values	180-647^{0} SRM-1D^{0} SBC-1^{1} COQ-1^{2} SDO-1^{1}

7c. Discussion:

Comparison of rock surface (core and hand sample) pXRF values to both powdered rock pXRF and ICP-MS data should be done with the caveat that the rock powders were sampled from both the surface, and below it, and therefore may contain material not analyzed on the rock surface using pXRF. The rocks, due to small-scale features like burrows and non-uniform cements, as well as spatially-variable oxidation, are heterolithic over the scale of the pXRF analysis window. Additionally, the rock surface analyses were undertaken in some cases months before the powders were drilled; while we drilled powder from the same core depth, the sample would not have been the exact same spot on the core surface that was initially analyzed.

It should also be noted that grain size and mineralogy may cause differences in the concentrations measured by ICP-MS and pXRF on the rock powders analyzed. Rock powders collected using a drill bit can be relatively coarse depending on lithology and degree of cementation. In ICP-MS, the sample is fully digested which would minimize the effects of grain size and mineralogy relative to the pXRF analysis of loosely packed rock powders in a vial. Future studies of sandstones could incorporate comparison of pXRF to energy-dispersive XRF analysis of pressed pellets to further test the effects of grain size (see Rowe et al. 2012 for a study of mudstone).

As summarized in Table 1, a variety of elements elements are accurate and/or can be calibrated using the pXRF for at least one of the lithologies (Tunnel City and/or Wonewoc) studied at the settings reported. Trace elements studied that are problematic may require further analysis at longer run times to better understand pXRF accuracy; some calibrations are not possible because there is not enough data (too many analyses indicated values less than the limit of detection). Furthermore, the limit of detection appears to be unit specific (Table 1). Comparison of pXRF data collected from rock surfaces and powdered rock are fairly similar based on visual inspection (Table 1). Rock surface pXRF data are, in general, noisier than powdered pXRF data. This has been observed in other WGNHS studies (Zambito unpublished data on the Devonian Milwaukee Formation). One explanation for this is that the drilling process used for powdering the rock materials is creating a more homogenous and lithologically ‘averaged’ sample for rocks that are heterolithic, though one cannot rule out the more common interpretation that grain size and mineralogic variability are playing a role in the differences observed. pXRF calibrations determined for the Wonewoc Formation may be appropriate for litholologically similar units like the St. Peter, Jordan, and Mount Simon sandstones. pXRF calibrations determined for the Tunnel City Group may be appropriate for the Eau Claire Formation.

7c. Conclusions:

Based on the standards analyzed, the pXRF produces reproducible data for a majority of elements and standards; values that were not reproduced within two standard deviations were nonetheless relatively similar with only a few exceptions. The calibrations provided may be of use when analyzing a given type of rock material for the first time; for the Wonewoc and Tunnel City, and possibly other analogous Paleozoic rock units in Wisconsin, the case study calibrations are likely more appropriate. Based on the samples and analyses of the case study the accuracy of the pXRF, and our ability to calibrate for inaccurate readings, is specific to the Wonewoc and Tunnel City. This is most likely due to matrix effects that are a result of the different dominant lithologies in the units. Additionally, limits of detection for some elements are different in these two rock units.

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9. References

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Appendix 5: Tunnel City – Wonewoc Methods and Calibration Case Study