Evaluation of Potential Uses for a Hand Held Portable X-ray Fluorescence Spectrometer

Final Report
for
MLR-18-01

February 2018

Highway Division

IOWADOT

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8. ABSTRACT

One of the renewal projects under the Second Strategic Highway Research Program (SHRP 2) explored the potential for broad use of portable spectroscopic devices to fingerprint construction materials commonly used in transportation infrastructure. One of the instruments identified as having potential was a portable X-ray Fluorescence (XRF) instrument. In addition to the uses identified by the research project, there are some potential Iowa specific applications that are explored in this report. Testing was done on carbonate aggregates and stainless steel reinforcement. The conclusions are:

1. The handheld XRF was quick and easy to operate compared to the laboratory XRF. A technician with a few hours of training could perform tests on a wide variety of materials such as soils, rock, paint, plastics, and metals.
2. The handheld XRF with the metals library does very well at identifying the metal type. The flexibility to add additional element limits and metal types to the library is a useful feature for use on specialty alloys.
3. Once the handheld XRF was calibrated for carbonate aggregates, it was fairly accurate and repeatable on prepared samples of rock and powder. Curved or rough surfaces appeared to reduce the accuracy and repeatability.
4. The XRF fingerprint matching algorithm was unable to consistently match pebbles from the same sample. An enhanced algorithm using the full spectrum might produce better results. Some sample preparation might also improve the accuracy.

9. KEY WORDS

Portable XRF
Non-destructive testing
Carbonate Aggregate Chemistry

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DISCLAIMER

The contents of this report reflect the views of the author and do not necessarily reflect the official views or policy of the Iowa Department of Transportation. This report does not constitute a standard, specification or regulation.

IINTRODUCTION

One of the renewal projects under the Second Strategic Highway Research Program (SHRP 2) explored the potential for broad use of portable spectroscopic devices to fingerprint construction materials commonly used in transportation infrastructure. One of the instruments identified as having potential was a portable X-ray Fluorescence (XRF) instrument. In addition to the uses identified by the research project, there are some potential Iowa specific applications:

- Identification of the stainless steel reinforcing grade nondestructively on the job site. The DOT has recently been using stainless steel reinforcement in bridge elements subjected to high levels of moisture and chlorides. By controlling the chemistry of the stainless steel, the mill can produce steel that will meet the corrosion resistance requirements of ASTM A955. Several grades of corrosion resistant and plain stainless steel reinforcing bars are available.
- Identification of limestone aggregates nondestructively on the road, at the source, and in the laboratory. The DOT has been using a laboratory XRF to chemically analyze limestone aggregates for over 15 years. It involves crushing the aggregate, pulverizing it to a powder, and placing it into a sample cup in the XRF. The hand held XRF can be held up against rock core samples, larger pieces of aggregate, and aggregates in concrete or HMA. The scan from the hand held XRF could be compared to the extensive library of XRF results on file.
- Identification of chromium and lead in place on existing steel bridges. Currently the DOT takes bridge paint samples from about 100 bridges per year to check for lead or chromium in the paint layers.

OBJECTIVES

The objects of the study were to purchase a hand held XRF and evaluate its accuracy and feasibility as a field test for quick determination or identification of stainless steel, limestone aggregates, and heavy metals in bridge paint.

EVALUATION FOR XRF SELECTION

The initial step was to buy a handheld XRF. There are several manufacturers, each with a number of different models. The information from the manufacturers indicated that they could analyze metal alloys and heavy metals. Carbonate aggregates are a little more challenging since they are not homogeneous and the elements of interest are light atomic weights. Magnesium was the lightest element that was detectable with most of the units.

To evaluate the capability of each unit, stone samples were obtained that covered the elements of the greatest interest to the Iowa DOT geologists. The samples were divided up into several smaller rectangular samples approximately 40mm X 40mm X 10mm. The interested manufacturers were sent eight different stone samples and asked to test and send back the results and the samples. To aid them with their calibration, the chemical results on two of the samples were provided to them. Four manufacturers reported back results. The results from the Thermo Scientific Niton XL3t were the closest to the sample powder results on a Panalytical Axiosmax 4kW laboratory XRF calibrated for analyzing carbonate rock samples. The unit, including addition material libraries and test modes, was purchased for $39,005 in 2015. The unit is shown in Figure 1.

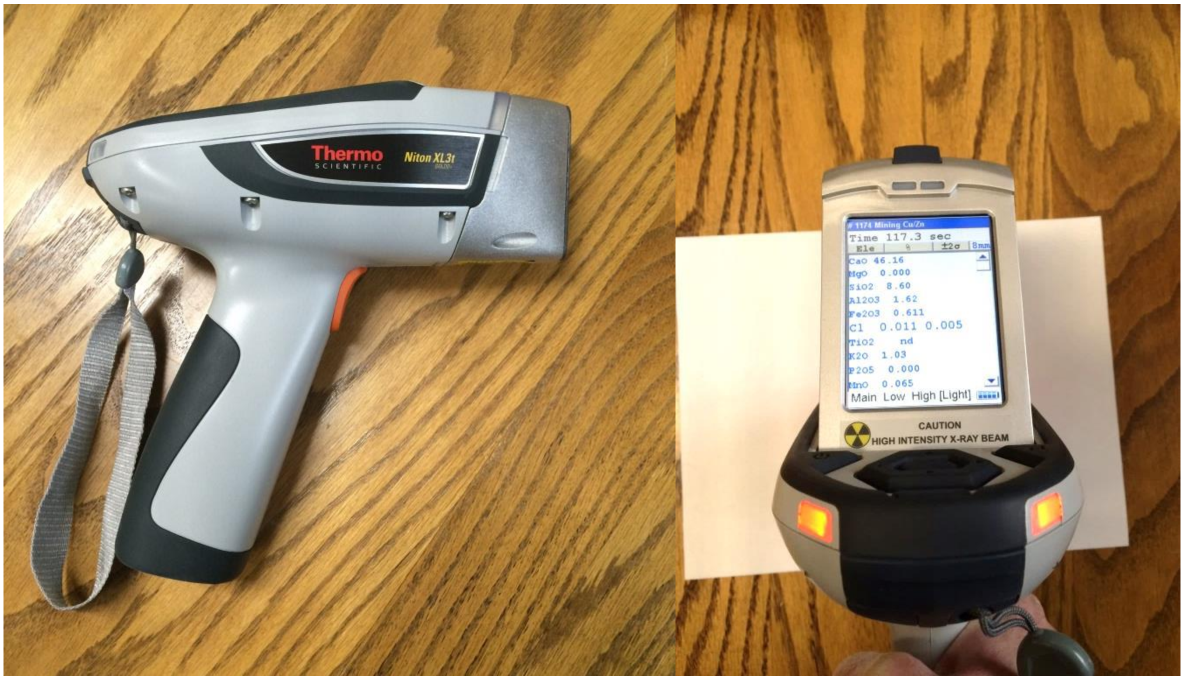


FIGURE 1 Hand held portable XRF used for the study.

EVALUATION ON STAINLESS STEEL REINFORCEMENT

The Iowa DOT has been using corrosion resistant stainless steel reinforcement (ASTM A955) in bridges at locations where high chloride concentrations are expected. The grades allowed in Iowa are:

S24100 (XM-28)
S31653 (316LN)
S31803
S32304 (2304)

The XRF has a metals library and an element matching feature that tries to match the chemistry of the test sample to its library of known metal grades. Additional grades of metal can be added as needed by an authorized user.

Table 1. is a list of projects that had stainless steel reinforcement. The certified mill test reports on all projects indicated a S24100 type of stainless steel. On four projects, the XRF indicated S32304 as the type. The difference in type was confirmed by checking the magnetic properties. The reinforcement supplier does carry both grades and after bringing the issue to their attention, they produced the certified mill test reports for the S32304 type bars. The certified mill test report is the DOT’s method for ensuring that the material supplied meets the specifications and the Buy America requirements.

Several girders for a bridge project in Sioux City (BRFIMX-029-6(246)134—14-97) were fabricated with special ASTM A1010 stainless steel that included a more restrictive chromium level. The existing library record for the A1010 was copied and the chromium level changed. Samples were easily checked using the handheld XRF on cleaned samples of the steel. A weld was checked and the materials were a match E309 for filler wire which would be an acceptable grade according to the specifications.

TABLE 1 Project samples of stainless steel reinforcement checked with the handheld XRF.

IMN-080-3(189)122--0E-77
BRF-92-1(64)--38-78
NHSX-100-1(46)--3H-57
NHSX-020-9(204)--3H-28
BRFN-061-2(89)--39-29
BRM-0155(685)--8N-85
IM-NHS-080-1(388)2--03-78
BRFN-148-3(32)--39-15
BRFN-069-5(98)--39-85
BRFN-063-5(52)--39-86
BRF-065-3(74)—38-91

EVALUATION ON AGGREGATES

The first step in the aggregate testing evaluation was to perform a calibration. The Iowa DOT has been using a 4kW Panalytical Axiosmax XRF to determine the elements of importance for aggregate source approvals and specification compliance. The hand held XRF would be used on solid particles of aggregate, but the results still need to be calibrated back to the Axiosmax results on powder samples.

Initial Carbonate Aggregate Calibration

Initial calibrations were developed using both pressed pellets and powder samples that covered the range of elements. The samples were first analyzed in the Axiosmax. Thirty-one millimeter pellets were made using 6.25 grams of sample, 1.25 grams of binding agent, 0.5 grams of boric acid, and pressed at 15 tons of pressure for 30 seconds. The results of the calibrations are in appendix A and Table 2. The results for both the powder and pellets calibration samples were very consistent for all the elements of interest.
To check which calibration best matched results on rock samples, the eight relatively homogeneous rock samples used in the selection evaluation process were used. A portion of each rock sample was crushed and powdered for testing in the Axiosmax. The oxides and elements in order of importance are: Al_2O_3, MgO, CaO, SrO, S, Cl, and Fe_2O_3. The rock sample surfaces were tested in five different locations and averaged to try to reduce the impact of the non-homogeneity. With the exception of Mg, the powder calibration sample results matched closely to the rock sample results. To establish a Mg calibration, the results of one set of the rock samples were used. The results for the oxides and elements of importance are show in Appendix B.

TABLE 2 Initial Handheld XRF element calibrations from powder samples.

Element	Range	Slope	Intercept
Sr	Main	1.1595	-0.0012
Fe	Main	0.8972	0.0515
Mn	Main	0.9881	0.0121
Ti	Main	0.9294	-0.0124
Ti	Low	0.9294	-0.0124
Ca	Low	0.8270	-0.1480
K	Low	1.0482	-0.0201
Al	Light	0.9165	-0.0164
Si	Light	0.9897	0.0100
Cl	Light	0.9722	0.0029
S	Light	0.8054	-0.0434
Mg*	Light	1.5340	0.0000

*Calibration based off of solid samples testing.

Precision on Carbonate Aggregate Samples

For the precision testing, five separate sets of the eight rock samples used in the selection evaluation process were measured. The rock sample surfaces were tested in five different locations and averaged to try to reduce the impact of the non-homogeneity. The 40 average results were analyzed for each oxide and element of interest. Table 3 shows the results of that analysis.

TABLE 3 Variation of the Handheld XRF on five separate sets of eight rock samples

Oxide/Element	Avg. Standard Deviation	Avg. Coefficient of Variation
Al_2O_3*	0.077	27
MgO*	1.004	31
CaO	0.467	1
SrO	0.0002	2
S*	0.050	28
Cl*	0.004	42
Fe_2O_3	0.051	11
SiO_2*	0.254	15
K_2O	0.025	21
MnO	0.003	7

* HH XRF Light Filter

Testing the Spectral Fingerprint Mode

The Thermo XRF has a spectral fingerprint feature that allows the user to create a library of known materials. The user can then run an unknown material in the fingerprint mode and the unit will look for a match to the known materials in the XRF library. The spectral fingerprint feature would allow technicians in the field to use the XRF to do comparisons on project samples. Without the spectral fingerprint feature, comparing individual elements and their percentages would be tedious and prone to errors. In the current XRF model, the spectral fingerprinting uses only the main filter and misses characterizing the lighter elements. To test the fingerprint feature, the eight rock samples from the earlier evaluation and calibration efforts were used. One set was used to create the library of known samples. Five other sets were used as unknowns to test the feature. The match fingerprint mode was able to match 100% of the time. Encouraged by these results, further testing was done.

The second fingerprinting trial was with carbonate aggregate pebbles from different sources around the state. Nineteen different samples of ¾" X ½" size aggregate were used. Because of the non-homogenous nature of the rock ledges represented in the samples, three to six pebbles were selected from each sample based on their differences in texture and color. Running the teach fingerprint function resulted in a library of 101 pebbles representing the 19 different sources. Five separate pebbles were then selected from each sample for the matching. Out of the 95 tests, only 41% had a match to the correct source. In total eight sources were identified correctly, seven were misidentified, and four had no consistent matches. Figure 2 is a plot of spectrums from two pebbles from different source that resulted in a close match.

A third attempt at fingerprinting was tried. This time the fingerprint library only consisted of 4 sources with 20 fingerprints. Running different pebbles from the same samples resulted in 61% of pebbles matching and three out of the four sources correctly identified. The fourth source was misidentified.

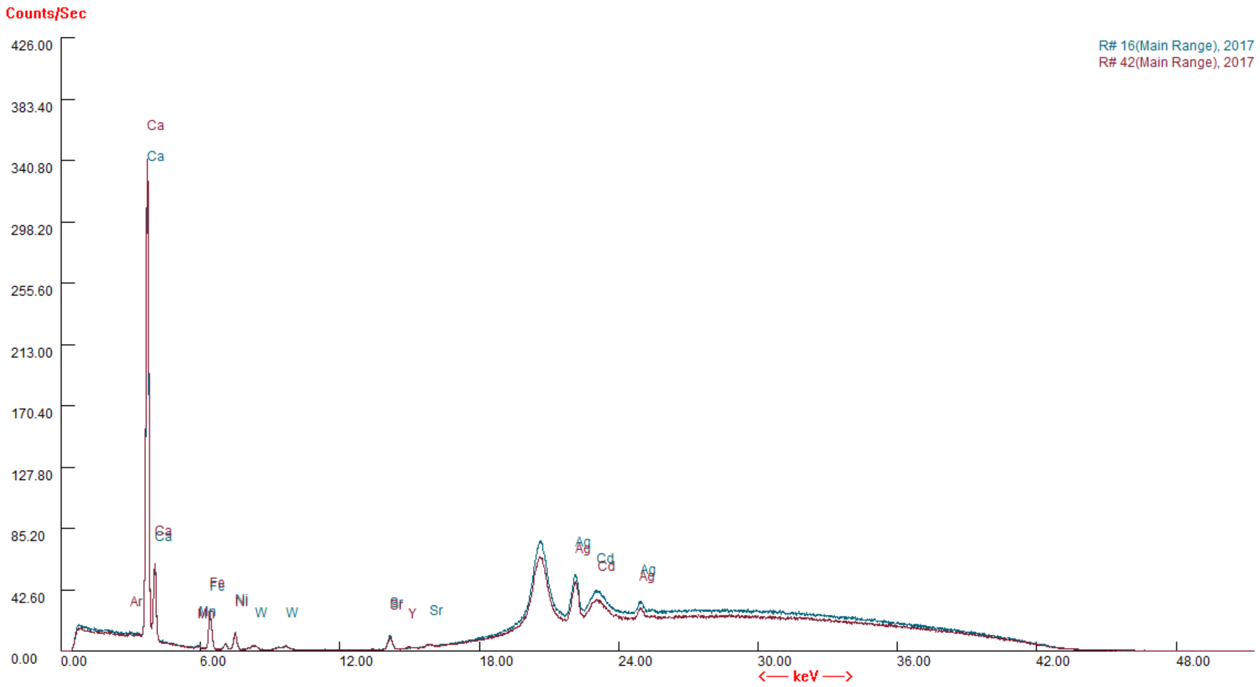


FIGURE 2 Comparison of spectrum from two different aggregate sources.

Testing on Rock Cores

The Iowa DOT routinely receives rock cores from quarries when the producers are exploring areas before opening them up for production. These cores are examined for depth of ledges and quality of the ledge material. Seven cores samples were selected from cores received by the laboratory. Short sections were taken from the core and sliced in half vertically. One half was used for testing with the handheld XRF and the other half was crushed and powered for testing in the Axiosmax XRF. The results are in Table 4. In most cases, the handheld results matched relatively well with the Axiosmax results on the powder samples. Not surprising the handheld results on the flat surface were more consistent and closer to the Axiosmax results than those on the curve side.

TABLE 4 XRF results on rock core samples.

Oxide/Element	Instrument/ Sample Type	Percentage							AAD (a)	r^2 (b)
		Core 1	Core 2	Core 3	Core 4	Core 5	Core 6	Core 7		
CaO	H-H XRF curved side	50.1	29.0	52.8	35.6	40.2	38.0	40.3	2.45	0.96
	H-H XRF flat side	51.1	28.9	53.3	36.0	40.8	38.7	41.3	2.13	0.97
	Axiosmax XRF powder	50.6	30.3	52.4	39.3	44.3	41.4	44.0		
MgO	H-H XRF curved side	2.41	14.30	1.63	8.76	4.29	8.48	6.16	1.97	0.91
	H-H XRF flat side	1.47	16.29	1.43	9.12	6.21	8.98	5.01	1.83	0.92
	Axiosmax XRF powder	1.76	20.43	0.38	7.15	3.64	7.57	3.62		
SiO2	H-H XRF curved side	5.64	4.11	4.22	10.19	10.91	6.49	10.27	1.05	0.97
	H-H XRF flat side	2.11	1.18	2.77	9.34	10.34	5.38	9.45	0.85	0.97
	Axiosmax XRF powder	3.47	2.28	2.23	10.59	10.49	6.57	9.80		
Al2O3	H-H XRF curved side	1.30	0.51	0.87	2.19	2.54	1.19	2.05	0.54	0.84
	H-H XRF flat side	0.28	0.20	0.36	1.72	1.98	0.79	1.81	0.13	0.97
	Axiosmax XRF powder	0.16	0.17	0.11	1.84	1.90	0.99	1.71		
Fe2O3	H-H XRF curved side	0.249	0.458	0.225	0.668	0.739	0.406	0.698	0.062	0.97
	H-H XRF flat side	0.167	0.411	0.174	0.617	0.807	0.465	0.658	0.048	0.98
	Axiosmax XRF powder	0.164	0.455	0.112	0.654	0.881	0.435	0.744		
Cl	H-H XRF curved side	0.064	0.110	0.077	0.027	0.025	0.024	0.020	0.020	0.42
	H-H XRF flat side	0.072	0.053	0.097	0.022	0.022	0.026	0.018	0.015	0.91
	Axiosmax XRF powder	0.044	0.033	0.051	0.026	0.018	0.030	0.019		
S	H-H XRF curved side	0.829	0.353	0.228	1.505	2.565	1.070	0.608	0.806	0.65
	H-H XRF flat side	0.054	0.063	0.073	0.260	0.591	0.293	0.447	0.040	0.98
	Axiosmax XRF powder	0.060	0.024	0.029	0.254	0.556	0.208	0.384		
K2O	H-H XRF curved side	0.086	0.055	0.069	0.688	0.934	0.386	0.870	0.043	1.00
	H-H XRF flat side	0.013	0.010	0.025	0.669	0.947	0.360	0.855	0.043	1.00
	Axiosmax XRF powder	0.038	0.032	0.037	0.770	0.991	0.420	0.894		
SrO	H-H XRF curved side	0.011	0.004	0.012	0.021	0.054	0.016	0.052	0.003	1.00
	H-H XRF flat side	0.010	0.004	0.012	0.021	0.054	0.016	0.054	0.002	1.00
	Axiosmax XRF powder	0.009	0.001	0.010	0.021	0.059	0.017	0.058		
MnO	H-H XRF curved side	0.086	0.055	0.069	0.121	0.093	0.124	0.086	0.026	0.90
	H-H XRF flat side	0.013	0.010	0.025	0.124	0.087	0.131	0.088	0.020	0.92
	Axiosmax XRF powder	0.038	0.032	0.037	0.106	0.064	0.114	0.064		
	(a) Average Absolute Deviation from the Handheld to Axiosmax									
	(b) Coefficient of Determination from the linear correlation between the Handheld and the Axiosmax									

EVALUATION ON BRIDGE PAINT

A thorough evaluation of the unit was not done on bridge paint because of time constraints. The Minnesota DOT does have a procedure for using a handheld XRF for testing their steel bridge coatings for lead and chromium prior to painting contracts.

DISCUSSION

The handheld XRF was very effective at identifying metal types. The only surface preparation required was removing any mill scale or rust. The handheld XRF also did well on carbonate aggregate samples when they were ground to a flat surface or crushed to powder prior to testing. Not surprising the handheld was less accurate on rough surfaces and on light elements of low concentrations.

The fingerprinting of carbonate aggregates without sample preparation was not successful. There are several possible reasons for this.

- The matching algorithm uses only the spectrum from the main filter which does not include all the elements present.
- The samples and even the pebbles within the sample are not homogeneous. This heterogeneous make-up may prevent them from successful fingerprinting when compared against large libraries.
- The pebble surfaces were very rough.
- With the exception of calcium, magnesium, and silicon; there is relatively little difference chemically with most approved sources used in Iowa.

Thermo Fisher Scientific representatives have indicated that they are developing a new algorithm for fingerprinting that will use the full spectrum. When this is available it has the potential for more accurate matching of aggregate sources.

The handheld XRF worked well as a quick non-destructive method to characterize core samples. It could help the geologists in evaluating and selecting samples for further destructive quality testing.

CONCLUSIONS AND RECOMMENDATIONS

The following can be concluded from the testing conducted:

1. The handheld XRF was quick and easy to operate compared to the laboratory XRF. A technician with a few hours of training could perform tests on a wide variety of materials such as soils, rock, paint, plastics, and metals.
2. The handheld XRF with the metals library does very well at identifying the metal type. The flexibility to add additional element limits and metal types to the library is a useful feature for use on specialty alloys.
3. Once the handheld XRF was calibrated for carbonate aggregates, it was fairly accurate and repeatable on prepared samples of rock and powder. Curved or rough surfaces appeared to reduce the accuracy and repeatability.
4. The XRF fingerprint matching algorithm was unable to consistently match pebbles from the same sample. An enhanced algorithm using the full spectrum might produce better results. Some sample preparation might also improve the accuracy.

RECOMMENDATIONS

Based on this study, the following recommendations are suggested:

1. When a new version of the fingerprinting algorithm with the full spectrum is released, the experiment with pebble matching should be repeated.
2. Add the XRF testing to the Laboratory SOP for stainless steel item testing.

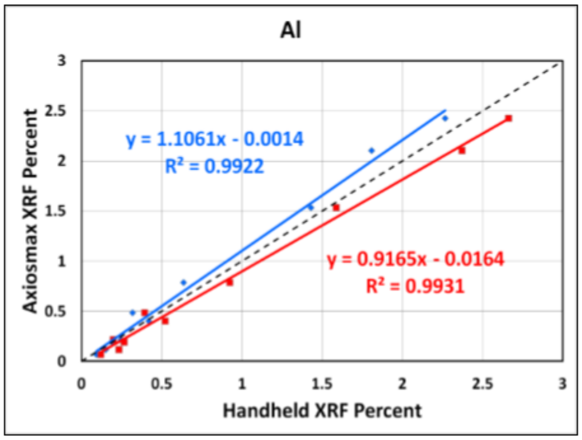
ACKNOWLEDGEMENT

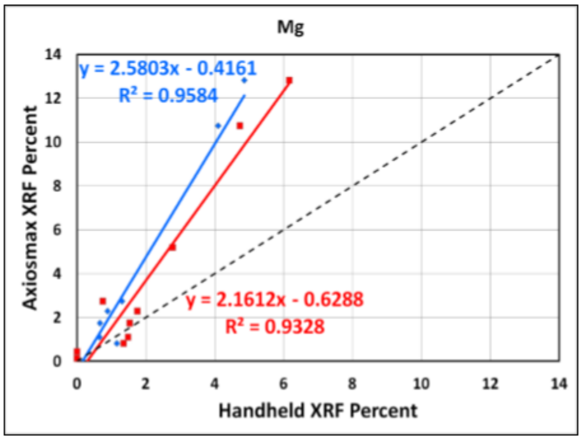
The author wishes to extend appreciation to Michelle Barger, Ricardo Corona, Bob Dawson, Neal Tieck, and Ryan Vashaw for their help on the calibration and testing.

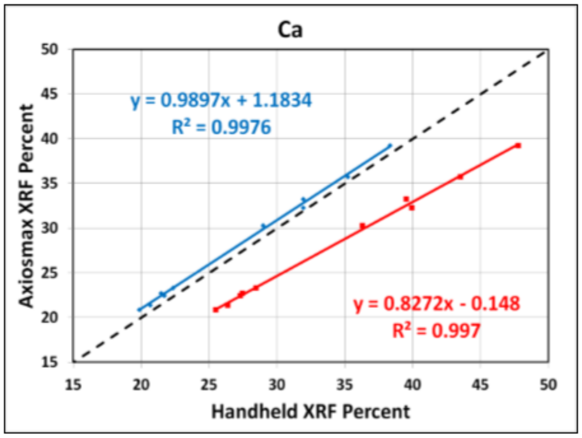
Appendix A

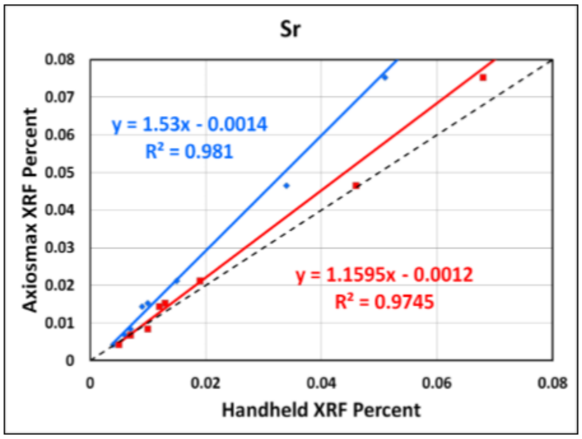
Calibration Results

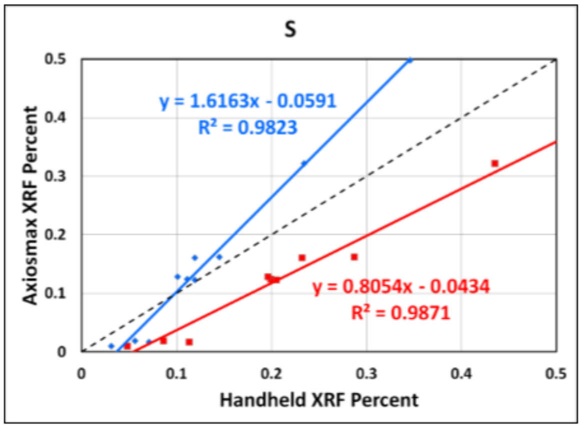
Calibration of Handheld XRF to the Panalytical XRF with Pressed Pellets and Powder Samples

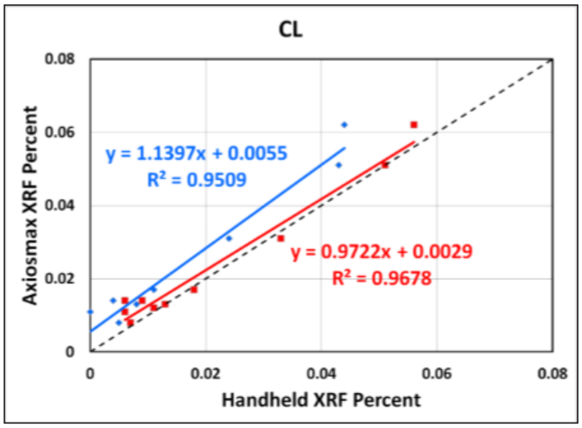






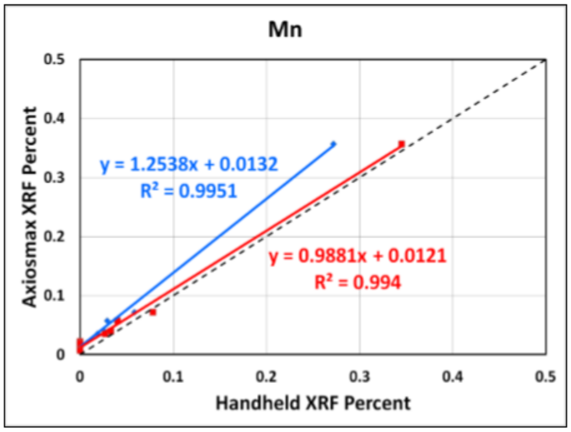


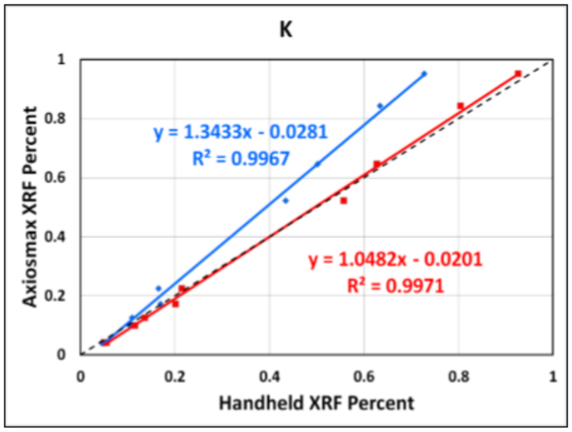


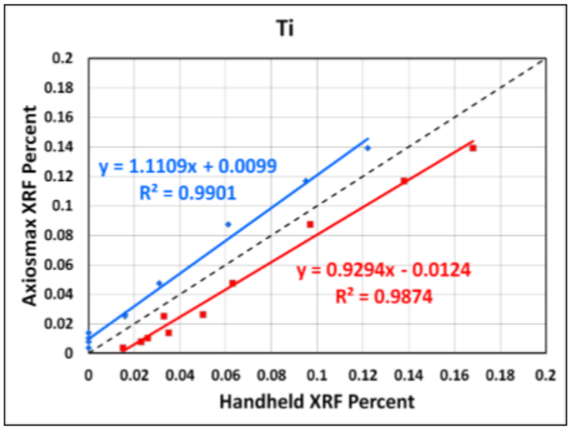


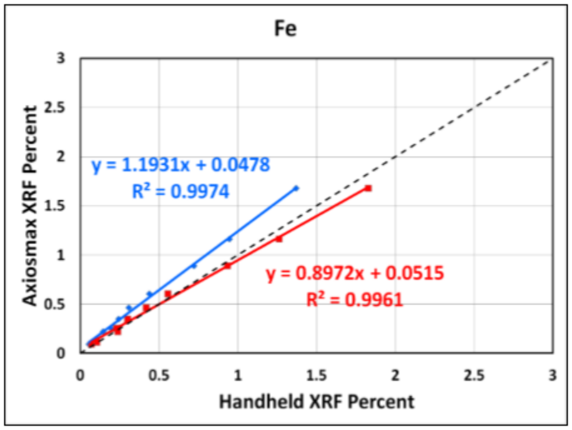
◆ Pellet

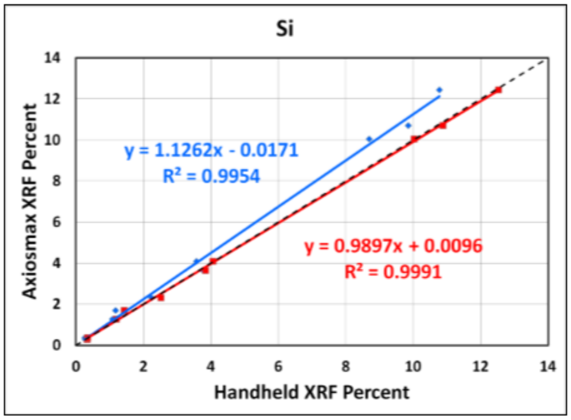
🟥 Powder











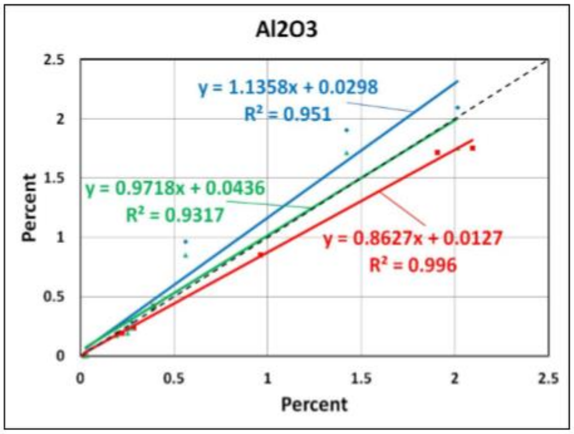
◆ Pellet

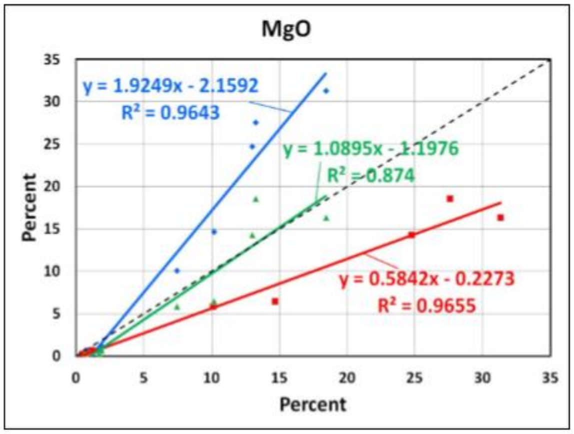
🟥 Powder

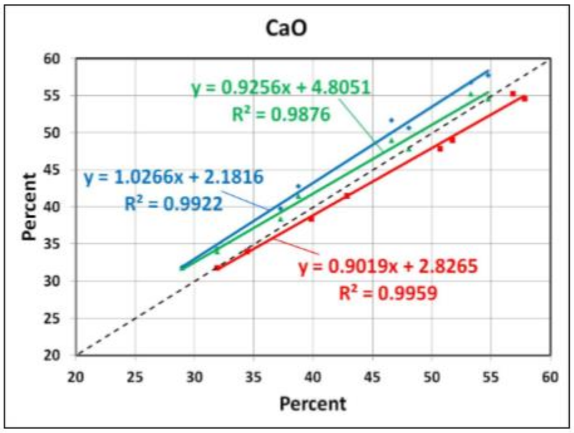
Appendix B

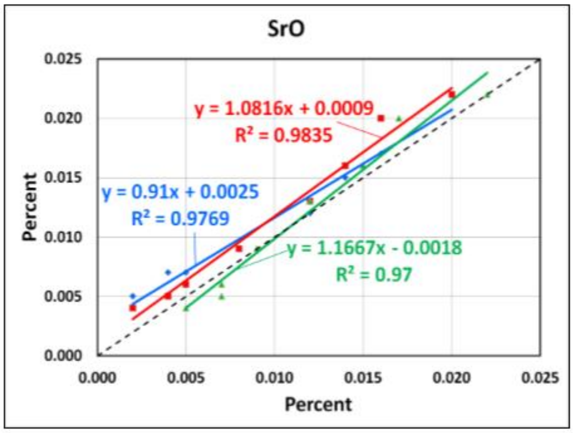
Comparison of Handheld XRF to the Panlytical Axiosmax XRF

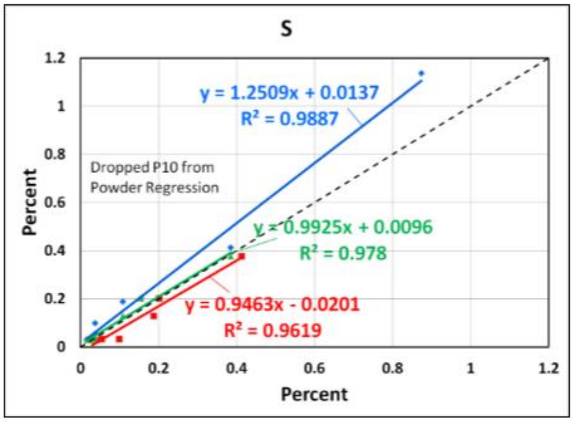
Handheld XRF (HH)to the Panalytical XRF (AM) with Solids and Powder Samples

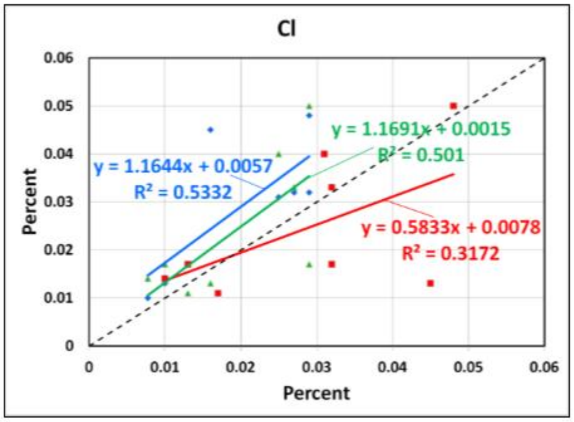








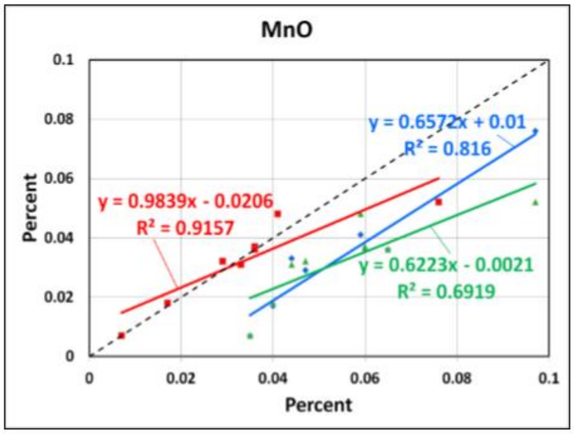


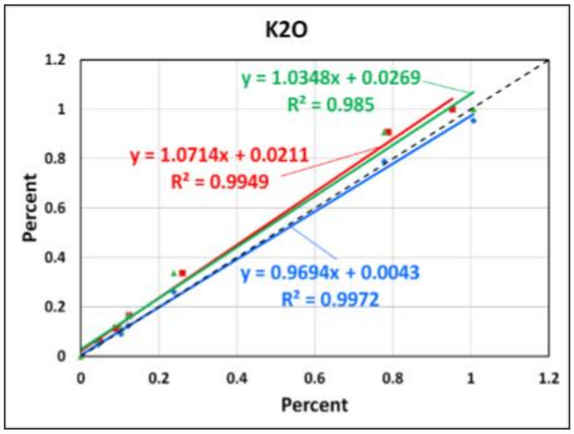


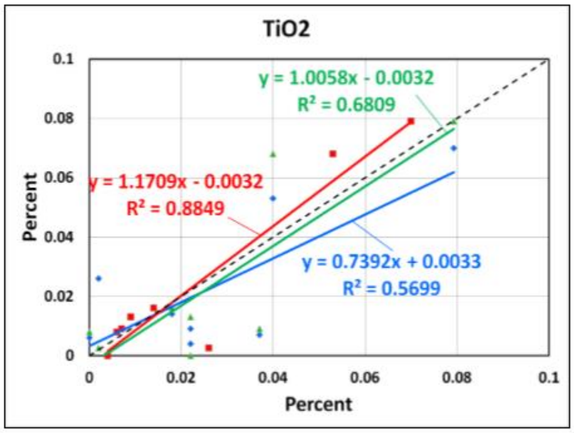
◆ HH Rock Coupon (X axis) to AM Rock Coupon (Y axis)

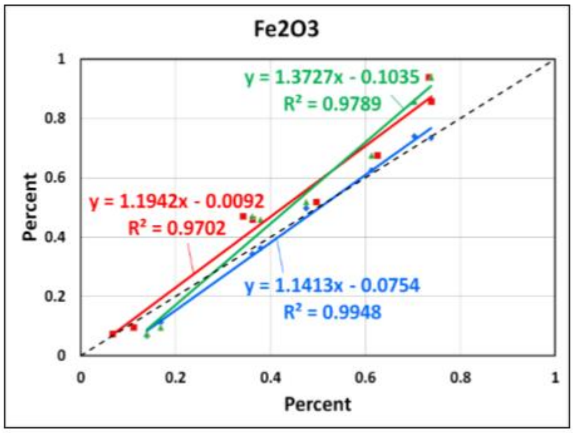
■ AM Rock Coupon (X axis) to AM Powder (Y axis)

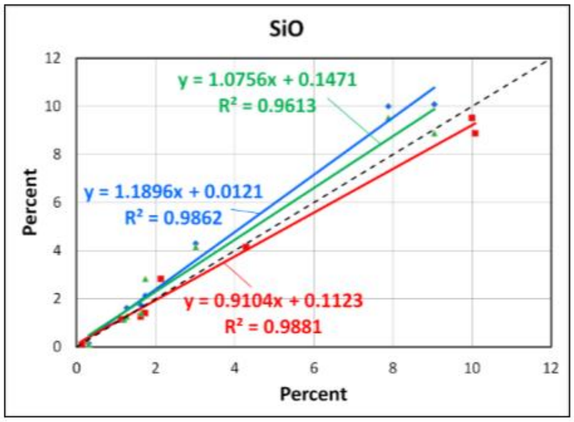
▲ HH Rock Coupon (X axis) to AM Powder (Y axis)











◆ HH Rock Coupon (X axis) to AM Rock Coupon (Y axis)

■ AM Rock Coupon (X axis) to AM Powder (Y axis)

▲ HH Rock Coupon (X axis) to AM Powder (Y axis)