

Light Element Analysis by Portable XRF in Mining Applications

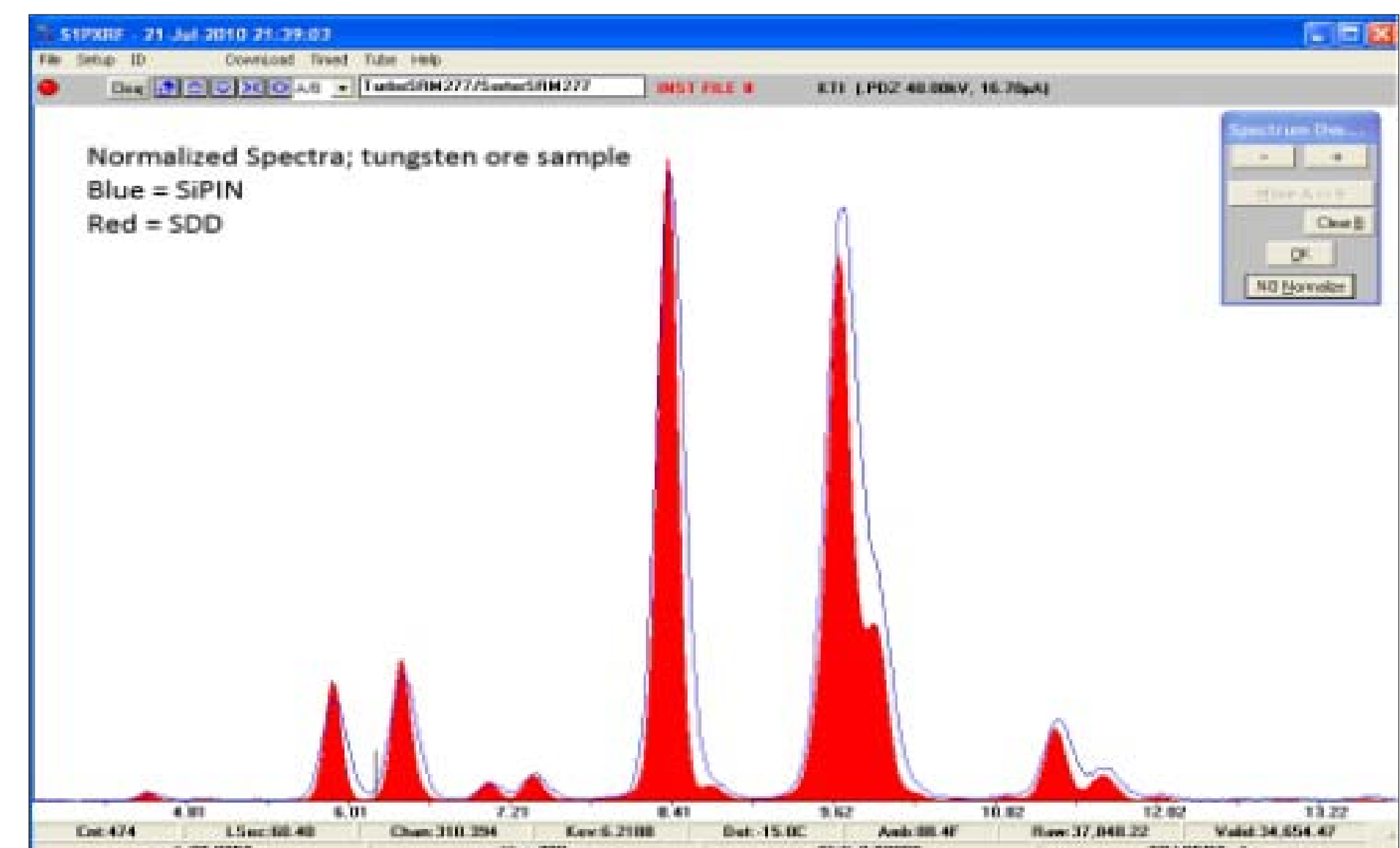
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Introduction

In recent years, portable XRF has become an accepted technique for field analysis in mining applications. With the introduction of instruments based on Silicon Drift Detector technology, measurement of light mineral elements such as Al, Si, and S are now possible. This provides the ability to analyze more of the sample matrix than previously was possible.

This poster presents a brief summary of portable XRF, demonstrates some of the technical challenges in measuring geologic standards, discusses levels of sample preparation required, and shows data taken on both standards and real field samples with a Bruker S1Turbo^{SD} LE equipped with the Light Element Mining calibration.

General



Silicon Drift Detectors (SDD) allow measurement at up to ten times the count rates of conventional SiPIN detectors. SDD detectors also improve the resolution available to the handheld user from ~200eV to ~145eV. This enables lower detection limits and shortens measurement times.

Category	Laboratory XRF	Portable XRF
Sample Preparation	Significant sample preparation is required. Usually fused beads or pressed pellets for powders. Large XRF equipment must be used in a controlled and equipped laboratory.	Minimal sample preparation required, depending on accuracy needs. Usually powders in sample cups (see EPA 6200).
Location	The laboratory environment allows greater excitation power, use of high vacuum, multiple monochromators, and other improvements that often allow very low detection limits.	Instruments are used in the field, often with batteries. Samples can be measured in-situ, without the need to transport offsite.
Limit of Detection	Detection limits are generally higher than for laboratory equipment, especially for lower-Z elements, which have short penetration depths in the samples and in air.	Detection limits are generally lower than for laboratory equipment, especially for lower-Z elements, which have short penetration depths in the samples and in air.
Accuracy	Careful sample preparation allows high accuracy because of homogeneity. This accuracy can be particularly important at low levels.	The amount of sample preparation is related to the accuracy obtained. Varying levels of accuracy are acceptable for different applications, ranging from semiquantitative to quantitative.
Turnaround time	Turnaround time is often long because of transportation to the laboratory and time needed for adequate sample preparation.	Turnaround time is very short because of minimal sample preparation and no need for sample transport.
Training	Generally, well-trained, skilled laboratory technicians are required to run the equipment and prepare samples.	Normally less training and laboratory skill is needed to use the portable equipment and to prepare the samples.
Cost	The initial cost of the equipment is higher than for a portable device. Also, the sample transfer and preparation, and the maintenance of a laboratory can add to the cost of measurement.	The initial cost of the equipment is lower, as are sample preparation and transportation costs. When accuracy is important, often the lowest overall cost is for a laboratory analyzer to be used in conjunction with the portable device. The majority of samples are measured in the field by the portable analyzer and the laboratory analyzer is used to verify the accuracy of the portable device, requiring only a fraction of the samples to be sent and prepared for laboratory analysis.

Technical Challenges

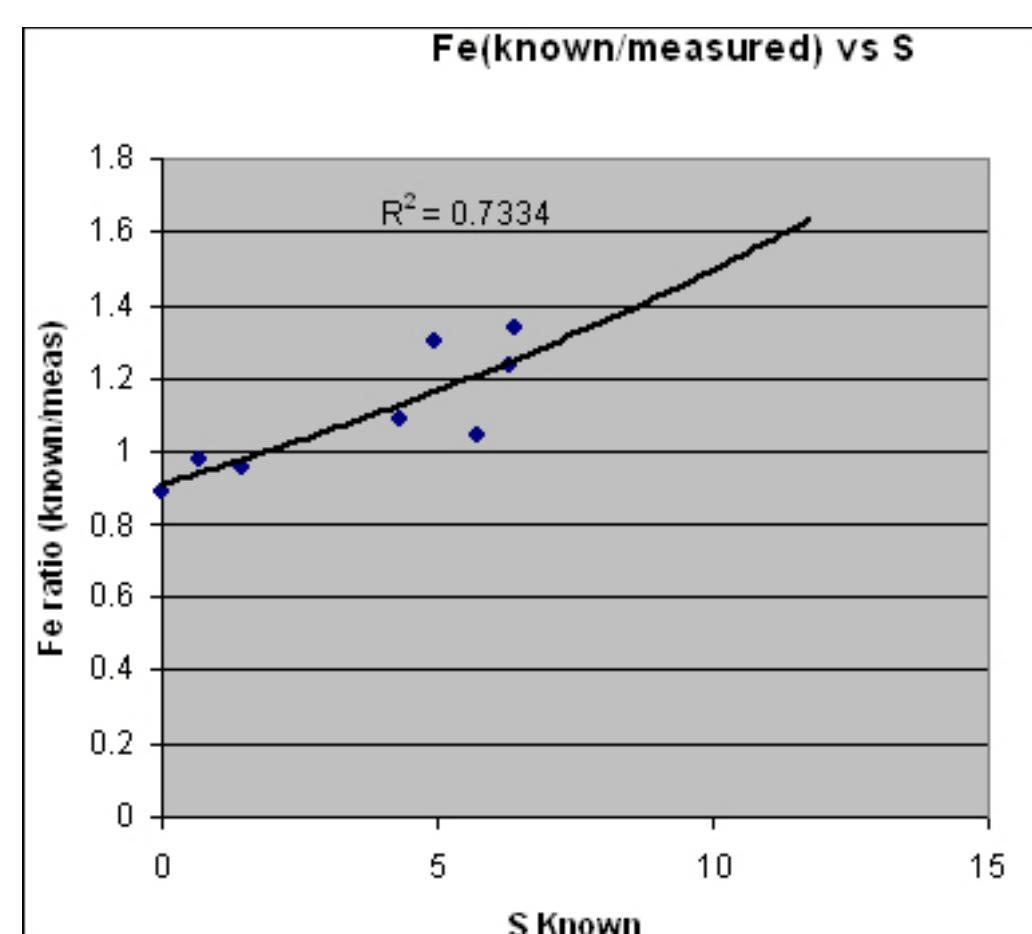
Penetration Depths of Various Elements in SiO₂ and Air

Element	Air (cm)	Silica (microns)
Ba	0.049	0.1
C	0.428	0.5
O	0.147	2.1
Ni	0.595	3.1
Mg	0.898	5.1
Si	2.46	12.4
Ti	40.1	47.3
Fe	115.6	128
As	517	544
Zr	1601	1765
Sn	4552	6577

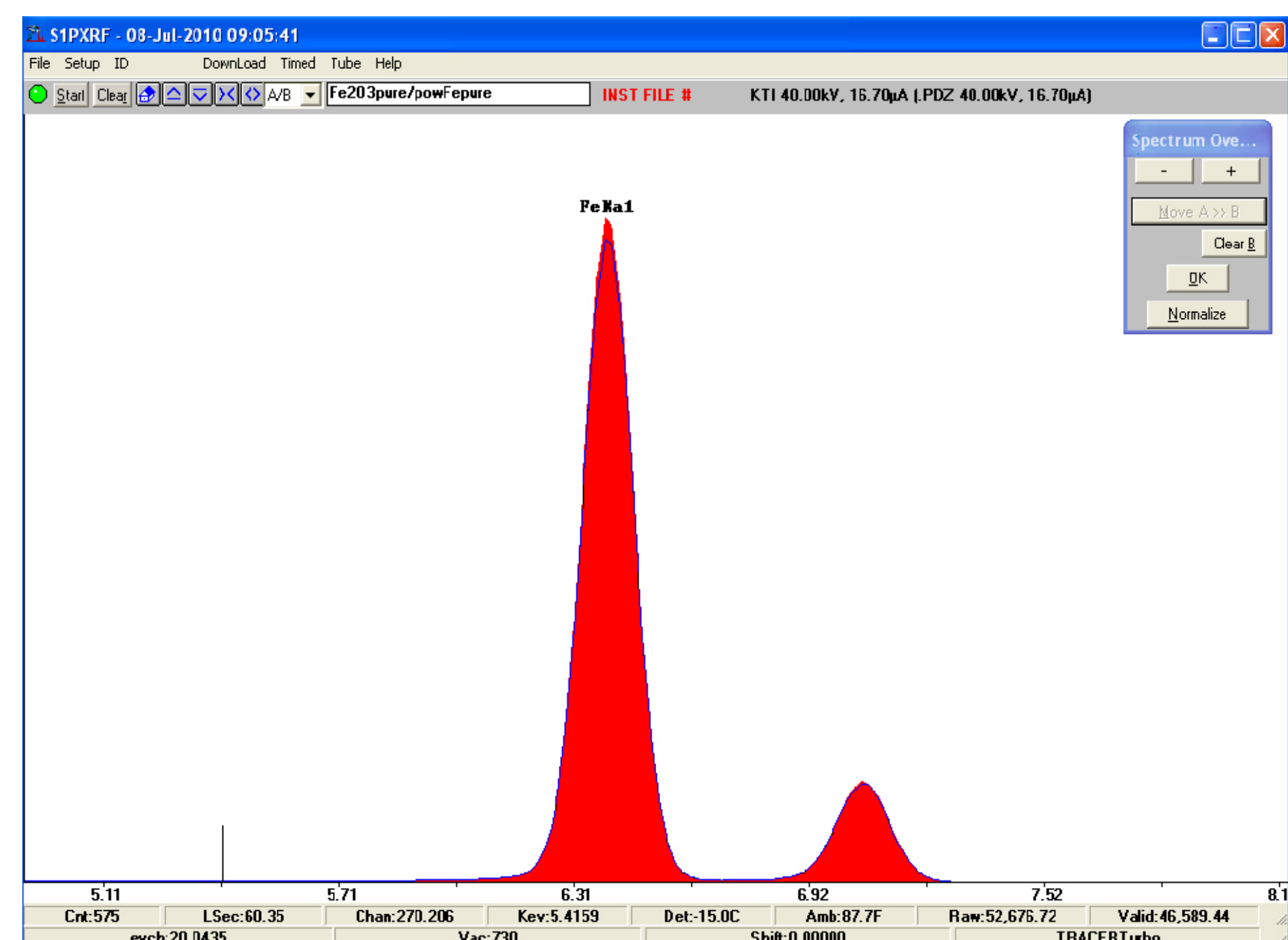
Average density of air = 0.0012g/cm³
Density of SiO₂ = 2.6g/cm³
Depths are for 90% absorption of the Ka1 line for each element

*Shaded cells are elements that have a path length too short to be measured using portable XRF.

The mineralogy of pyrite causes the reported iron to progressively diverge from its expected value with increasing sulfur content. The correlation is imperfect because of other contributing factors, but a definite trend is observable in Fe attenuation as the S content increases.



The SDD detector allows measurement of sulfur, so to correct for this effect, a Type Standardization (TS) can be done for a given S concentration. For widely varying sulfur values, TS curves can be plotted for a series of sulfur concentrations and a post-processing calculation can correct results for the mineralogy of pyrite.



Although there is a 30% difference in weight percent iron between Fe and Fe₂O₃, the density difference between the two samples affects the measured volume, yielding nearly identical spectra. This and other issues create challenges in designing calibrations to quantitatively determine elemental concentration in unknown matrices.

Sample Preparation



Typical measurement according to EPA6200 section 11.3 (shown below). As stated in 11.3, semi-quantitative or "screening" data can be taken using this method.



Typical configuration after sample preparation according to EPA6200 sections 11.4 – 11.6. For quantitative analysis where not all major elements can be measured, it is very important to have the correct distance between detector and sample, as well as the proper film over the sample cup.

6200 - 19 Revision 0 February 2007

11.3 For in situ analysis, remove any large or nonrepresentative debris from the soil surface before analysis. This debris includes rocks, pebbles, leaves, vegetation, roots, and concrete. Also, the soil surface must be as smooth as possible so that the probe window will have good contact with the surface. This may require some leveling of the surface with a stainless-steel trowel. During the study conducted to provide example performance data for this method, this modest amount of sample preparation was found to take less than 5 min per sample location. The last requirement is that the soil or sediment not be saturated with water. Manufacturers state that their FPXRF instruments will perform adequately for soils with moisture contents of 5 to 20 percent but will not perform well for saturated soils, especially if ponded water exists on the surface. Another recommended technique for in situ analysis is to tamp the soil to increase soil density and compactness for better repeatability and representativeness. This condition is especially important for heavy element analysis, such as barium. Source count times for in situ analysis usually range from 30 to 120 seconds, but source count times will vary among instruments and depending on the desired method sensitivity. Due to the heterogeneous nature of the soil sample, in situ analysis can provide only "screening" type data.

11.4 For intrusive analysis of surface or sediment, it is recommended that a sample be collected from a 4- by 4-inch square that is 1 inch deep. This will produce a soil sample of approximately 375 g or 250 cm³, which is enough soil to fill an 8-ounce jar. However, the exact dimensions and sample depth should take into consideration the heterogeneous deposition of contaminants and will ultimately depend on the desired project-specific data quality objectives. The sample should be homogenized, dried, and ground before analysis. The sample can be homogenized before or after drying. The homogenization technique to be used after drying is discussed in Sec. 4.2. If the sample is homogenized before drying, it should be thoroughly mixed in a beaker or similar container, or if the sample is moist and has a high clay content, it can be kneaded in a plastic bag. One way to monitor homogenization when the sample is kneaded in a plastic bag is to add sodium fluorescein dye to the sample. After the moist sample has been homogenized, it is examined under an ultraviolet light to assess the distribution of sodium fluorescein throughout the sample. If the fluorescent dye is evenly distributed in the sample, homogenization is considered complete; if the dye is not evenly distributed, mixing should continue until the sample has been thoroughly homogenized. During the study conducted to provide data for this method, the time necessary for homogenization procedure using the fluorescein dye ranged from 3 to 5 min per sample. As demonstrated in Secs. 13.5 and 13.7, homogenization has the greatest impact on the reduction of sampling variability. It produces little or no contamination. Often, the direct analysis through the plastic bag is possible without the more labor intensive steps of drying, grinding, and sieving given in Secs. 11.5 and 11.6. Of course, to achieve the best data quality possible all four steps should be followed.

11.5 Once the soil or sediment sample has been homogenized, it should be dried. This can be accomplished with a toaster oven or convection oven. A small aliquot of the sample (20 to 50 g) is placed in a suitable container for drying. The sample should be dried for 2 to 4 hr in the convection or toaster oven at a temperature not greater than 150 EC. Samples may also be air dried under ambient temperature conditions using a 10- to 20-g portion. Regardless of what drying mechanism is used, the drying process is considered complete when a constant sample weight can be obtained. Care should be taken to avoid sample cross-contamination and these measures can be evaluated by including an appropriate method blank sample along with any sample preparation process.

CAUTION: Microwave drying is not a recommended procedure. Field studies have shown that microwave drying can increase variability between the FPXRF data and confirmatory analysis. High levels of metals in a sample can cause arcing in the microwave oven, and sometimes slag forms in the sample. Microwave oven drying can also melt plastic containers used to hold the sample.

11.6 The homogenized dried sample material should be ground with a mortar and pestle and passed through a 60-mesh sieve to achieve a uniform particle size. Sample grinding should continue until at least 90 percent of the original sample passes through the sieve. The grinding step normally takes an average of 10 min per sample. An aliquot of the sieved sample should then be placed in a 31.0-mm polyethylene sample cup (or equivalent) for analysis. The sample cup should be one-half to three-quarters full at a minimum. The sample cup should be covered with a 2.5 µm Mylar (or equivalent) film for analysis. The rest of the soil sample should be placed in a jar, labeled, and archived for possible confirmation analysis. All equipment including the mortar, pestle, and sieves must be thoroughly cleaned so that any cross contamination is below the established lower limit of detection of the procedure or DOQs of the analysis. If all recommended sample preparation steps are followed, there is a high probability the desired laboratory data quality may be obtained.

Results

Element	Known	Averages			Standard Deviations		
		30 sec	90 sec	180 sec	30 sec	90 sec	180 sec
Al ₂ O ₃	11.188	11.09	11.32	11.90	0.916	0.436	0.283
SiO ₂	66.243	60.05	59.71	61.13	0.866	0.346	0.573
K ₂ O	2.604	2.88	2.85	2.88	0.035	0.053	0.046
CaO	1.350	1.26	1.26	1.26	0.043	0.014	0.018
TiO ₂	0.519	0.52	0.50	0.51	0.014	0.019	0.012
MnO	0.276	0.35	0.34	0.33	0.016	0.012	0.006
Fe ₂ O ₃	6.178	7.26	7.04	6.88	0.333	0.235	0.114
Cu	0.342	0.41	0.39	0.38	0.026	0.018	0.006
Zn	0.418	0.50	0.48	0.46	0.029	0.021	0.008
As	0.154	0.15	0.15	0.16	0.008	0.007	0.003
Sr	0.026	0.03	0.03	0.03	0.000	0.000	0.000
Pb	0.552	0.62	0.60	0.56	0.041	0.027	0.009

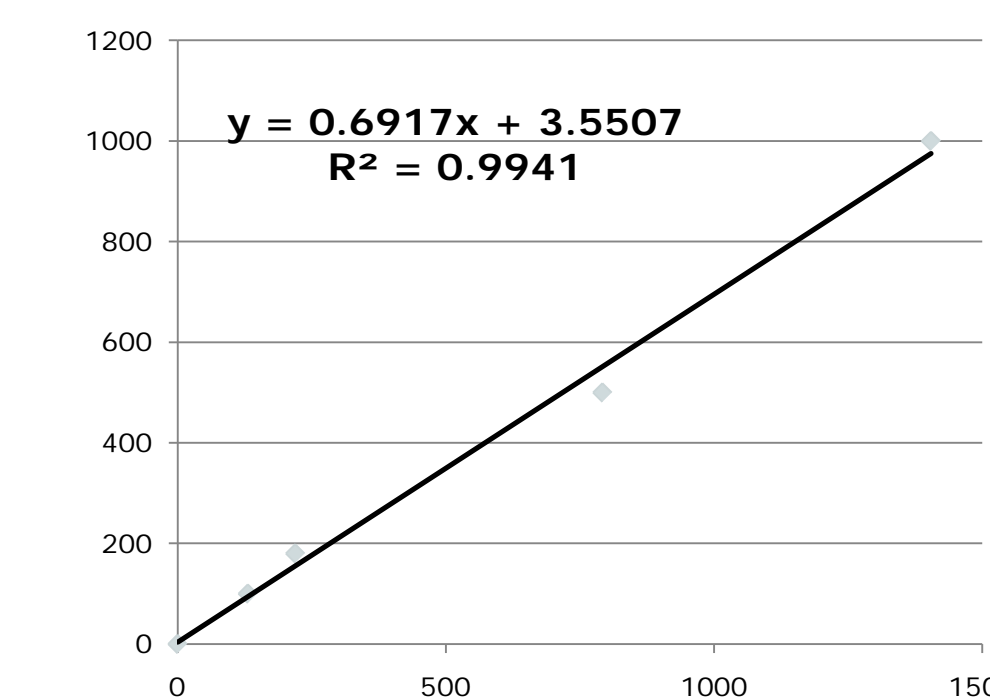
Measurements of varying times on SRM2710a, which was moved and/or shaken between assays. As seen for Al, Si, Mn, Fe, Cu, Zn, and Pb, longer assay time normally leads to improved accuracy. Precision often, but not always, improves with longer assay time.

Element	LLD (ppm) Mining LE	LLD (ppm) Mining
MgO	11000	NA
Al ₂ O ₃	2000	NA
SiO ₂	1700*	NA
P ₂ O ₅	200	NA
S	50	NA
K ₂ O	65	NA
CaO	70	400
TiO ₂	39	200
V ₂ O ₅	36	150
Cr ₂ O ₃	25	65
MnO	17	33
Fe ₂ O ₃	23	25
Co ₃ O ₄	20	30
NiO	25	15
CuO	20	7
ZnO	7	7
As ₂ O ₃	20	6
Se	12	3
Rb	11	4
Sr	11	5
ZrO ₂	24	7
Nb ₂ O ₅	-35	8
MoO ₃	41	10
Rh	NA	18*
Pd	NA	30*
Ag	NA	8*
Cd	NA	27
SnO ₂	-200	197*
Sb ₂ O ₃	-200	55
CaO ₂	-90	246
H ₂ O	-60	80*
Ta ₂ O ₅	-50	60*
W ₂ O ₃	33	18
Pt	NA	15*
Au	NA	57
Hg	30	13
PO ₄	49	12
Bi	35	10
U	NA	15

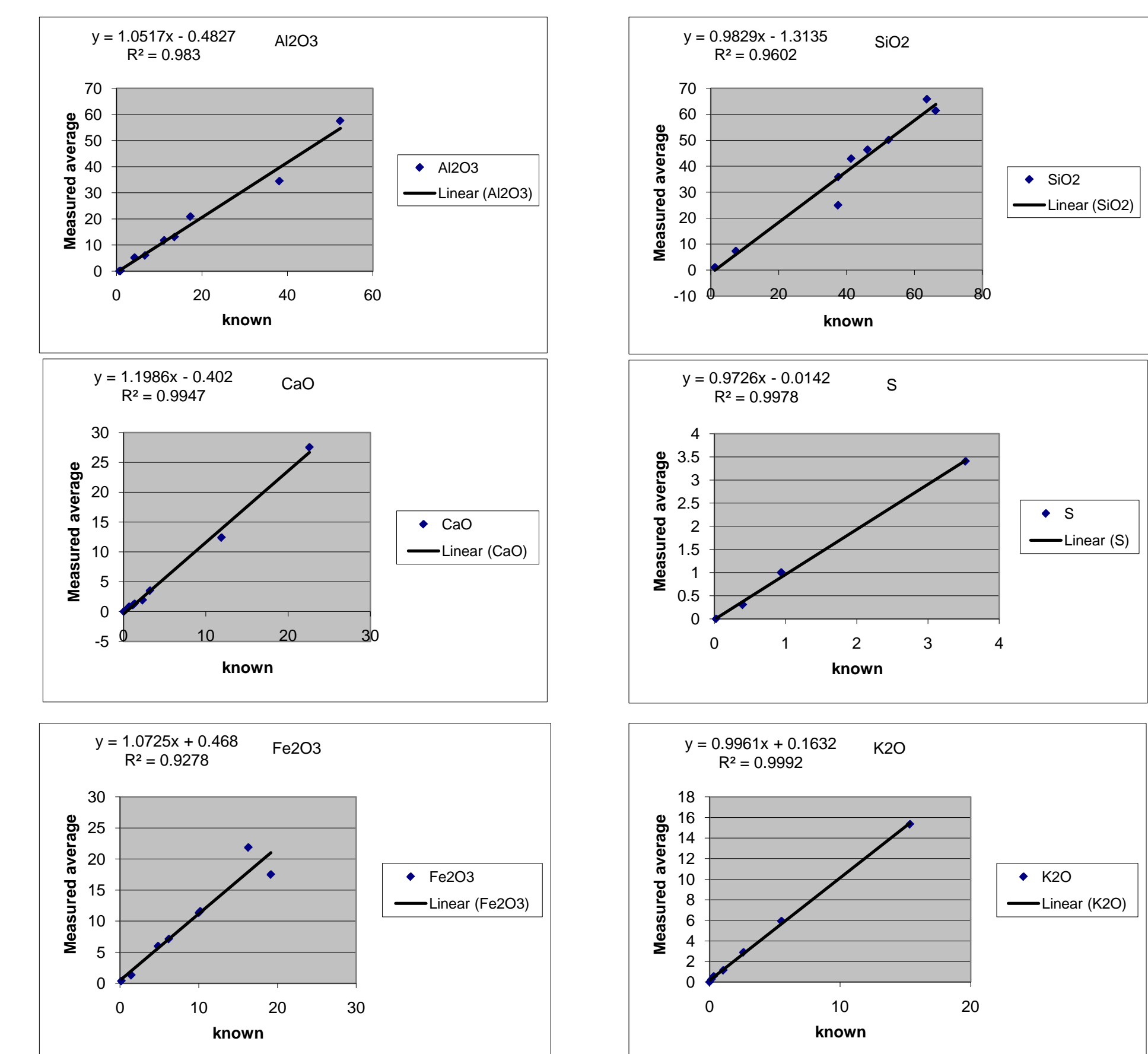
LLD (or LOD) values are calculated from background variability of an instrument, taking into account only counting statistics. At this limit, 95% of the times an element is seen, it is certain to be present. However, for a sample with a known element concentration at the LLD, statistically it is only expected to be seen 50% of the time. Additionally, errors introduced during the calibration process (mainly peak overlaps) and inhomogeneity of the measured sample are not included in calculation of the LLD. Therefore, a more realistic limit for quantitatively measuring an element can be estimated from the reported precision for an element near its low end (in a matrix similar to that to be measured) and from the homogeneity of the sample to be measured.

Element 1	Ni
SLOPE	0.6917
OFFSET	3.5507
CORR	99.7%

Reference values	S1 Meas. Results	Adjusted S1 Result
0	0	3.55
100	131.1	94.24
180	219.45	155.35
500	792.17	551.53
1000	1404.84	975.33

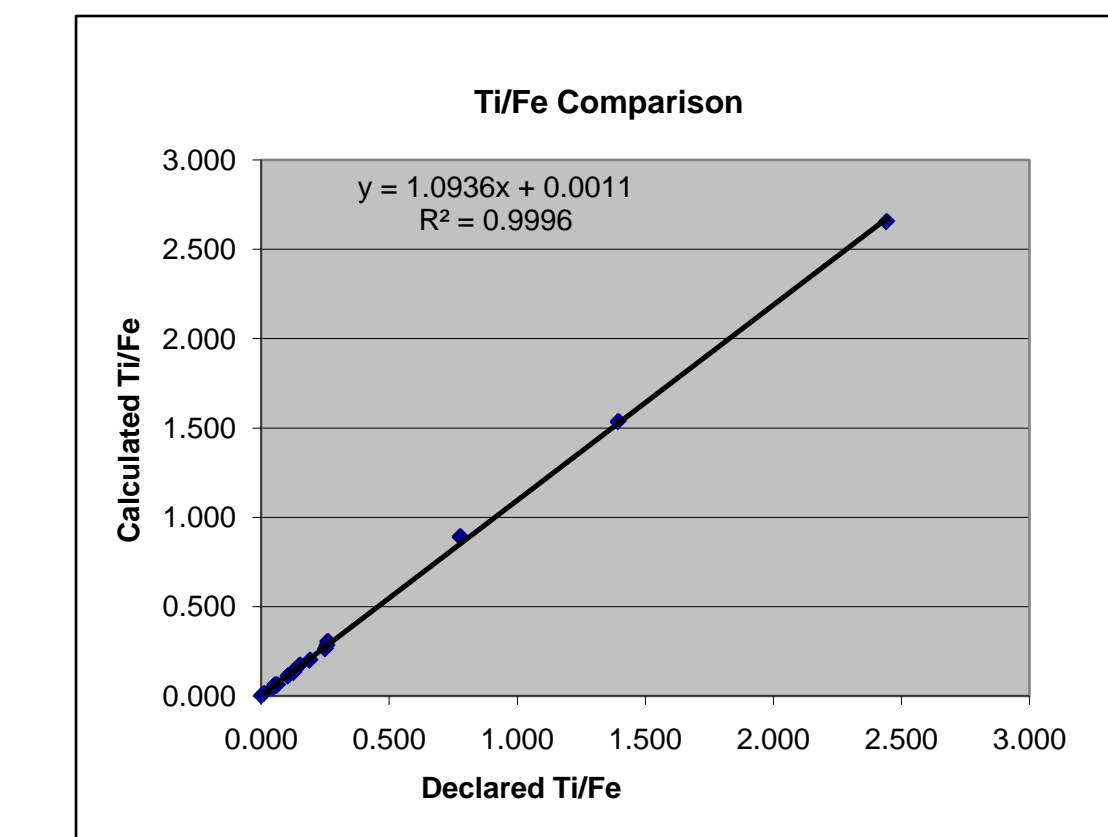


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Using the Mining LE calibration, five 30-second assays were taken of nine standards. The averages of these shots were plotted against accepted values. Accuracy and linearity of the light element calibration for geologic materials are shown for six elements.

The standards used were: SARM2, SARM3, BCS204a, SRM2710, BCS301, BCS395, AMIS124, UM-1, GXR-5



An important application in titanium mining is to identify titaniferous oxide classes by the Ti/Fe ratio. These data were taken from field samples at the USGS. Portable XRF can expedite the measurement process by giving good results with minimal sample preparation.

Conclusion

Although significant technical challenges exist in the measurement of mining, soil, and other geologic samples with portable XRF, good results can be achieved if valid assumptions are made. Often "good enough" results can be achieved for less demanding applications when very little is known about the sample matrix. Portable XRF provides a flexible measurement technique that can be tailored to create optimum performance for a given project, based on the balance between required accuracy/precision and the information available about the sample matrix composition.