Standards-Based pXRF Analysis
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Portable XRF (pXRF) provides rapid, non-destructive elemental analysis of materials down to the ppm level. The Imaging and Chemical Analysis Laboratory at Montana State University uses a ThermoFisher Scientific Nitoin XL3t GOLDD+ XRF analyzer (https://www.thermofisher.com/order/catalog/product/XL3TGOLDDPLUS).

- pXRF can provide **rapid, semi-quantitative analyses** for reconnaissance compositional surveys;
- However, **results can be improved by careful sample preparation** and **use of certified standards to obtain quantitative analyses.**
- Note that **light elements cannot be detected**, and typically Mg is the lightest element that can be analyzed. The pXRF uses an energy dispersive spectrometer (EDS), and there are simply physical limits to the detection of elements using this type of detector.
- Detection limits: "pXRF is now a **routine analytical method for elements with medium to high atomic mass (K to Pb, and Th and U,**) at concentrations between a few mg/kg and a few %.... The lower analytical limits (or limits of detection, LOD) vary with tube and detector specification and analyser geometry, but also with sample matrix composition. Higher abundance of heavier major elements, especially iron, negatively affects trace element detection. The best instruments are now capable of **LOD in the 5 to 100 mg/kg range for elements with Z between 19 (K) and 68 (Pb).** LOD vary between elements with emission lines and possible interferences". (Bruno Lemiere. A Review of pXRF (Field Portable X-ray Fluorescence) Applications for Applied Geochemistry. Journal of Geochemical Exploration, 2018, 10.1016/j.gexplo.2018.02.006.
- In addition to minerals, metals and ceramics, pXRF can be used to identify trace element content of plant materials, the composition of soluble elements in waters, testing of commercial products, paint chips, and much more.
- Other factors that may impact quality of data include:
    - **Sample geometry** is important (flat surfaces are best compared to irregular shapes of materials "as received");
    - **Sample homogeneity** is important to consider as the "nugget effect" may produce unreliable analyses if discrete domains are enriched or depleted of elements due to concentration in a disbursed phase;
    - **Matrix effects** that impact secondary X-ray yield may be important, e.g., organic material in soil matrix may diminish the signal (see Ravansari and Lemke, 2018) and steps should be taken to "clean up" the sample before analysis.

Typical Applications:

The pXRF has very broad application in Earth, environmental, materials science research such as:

- Mineral exploration, to identify ore and "pathfinder" elements in rocks and core;
- Environmental science; documenting presence of toxic metals;
    - e.g., soil analysis for toxic trace elements
- Food products; identifying presence of toxic metals;
- Materials testing; confirming composition of metals, alloys, ceramics and identification of any contaminating components;
- Art restoration and forensics; using trace materials to confirm provenance….
- And much more.

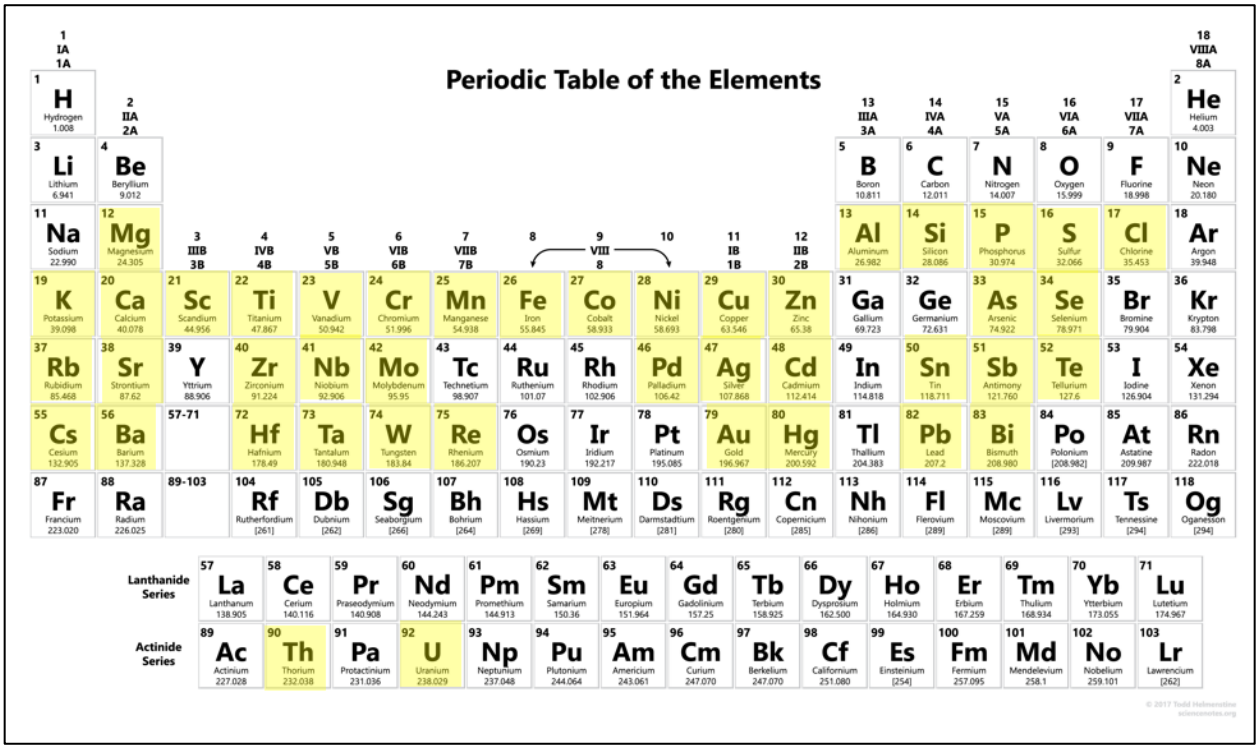
Modes of Analysis

The pXRF can be used in a wide variety of settings, from remote field sites to controlled laboratory experiments. **pXRF produces ionizing radiation and it is essential that users are trained in the safe operation of this instrument and have completed the CITI X-ray Safety Course.** The following modes of analysis may be used:

- "**Point and shoot**"—The pXRF may be used at remote settings for *in situ* analysis. It's often difficult to hold the gun at a uniform distance and orientation to the measured material, and it may be necessary to build a jig to help support the weight of the instrument. The instrument will be placed on (near) the material of interest such as a rock outcrop, machined part, art or archeological artifact, etc. to obtain the analysis. This will give a rapid reconnaissance of the composition of a material, **but quantitative analysis is not possible.** Results provide a good guide about what elements are present, and can be used for further in detail sampling due to heterogeneous mineral grains, and morphologic irregularities. Analyses should be interpreted as order of magnitude (e.g., 10s or 100s of ppm) or for relative abundances of elements present.
- **Field Preparation—**samples may be homogenized by milling (even using a mortar and pestle) to make a uniform sample that can be spread out and flattened for analysis; this improves data for elemental abundances and ratios.
- **Lab Preparation—**material is milled, dried, homogenized and sieved to uniform grain size; these powders can be placed in the dedicated Teflon cups for analysis. In some cases, samples may need to be "cleaned up" to remove e.g., organic compound, rinsed in a weak acid to remove calcite overgrowth cements, possibly to do some sort of gravimetric or hydraulic separation to increase abundances of detrital minerals, or to concentrate clays, etc, Use of the pXRF gun in the dedicated analyzing stand is recommended to maintain fixed orientation of the pXRF instrument and for safety to shield from X-rays. **This will produce the best quantitative analytical results.**

- As both major and trace elements may be of interest, it is best to **select the Test GEO All Analytical Suite**, which will be used in the data reduction procedures below.

This is a list of elements that can routinely be analyzed with the pXRF:



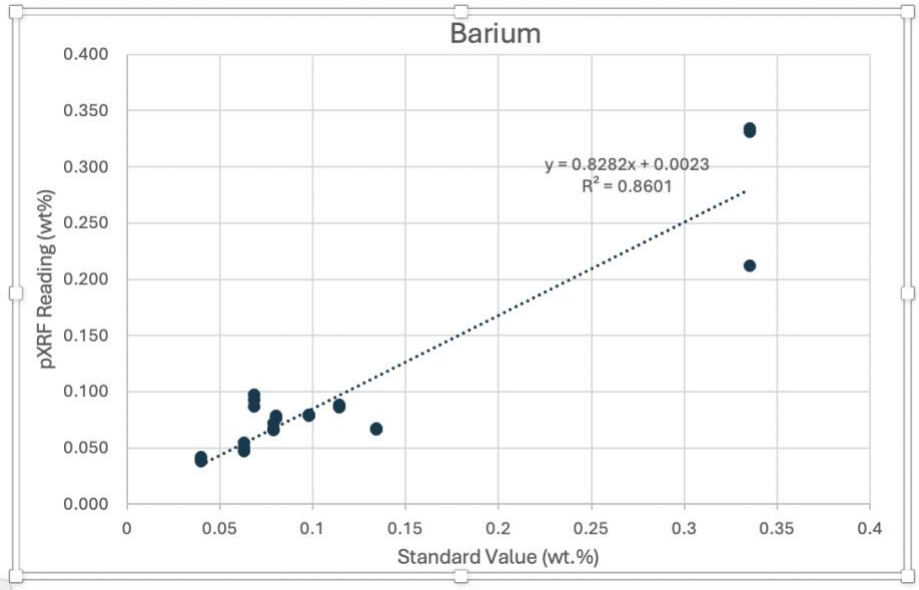
Quantitative Analysis

pXRF can produce rapid, reliable qualitative analyses for many types of materials, and for some applications these results may be sufficient to answer research questions. However, **be aware of the limitations of this method**, particularly the inability to measure light elements (e.g., Na, F). It is also difficult to resolve peak overlaps in the X-ray spectrum. So if a complete analysis is needed, e.g., whole rock geochemical analyses, use the pXRF data as a guide and obtain additional data using related methods such as wavelength dispersive XRF or laser ablation Optical Emission Spectroscopy (OES) Inductively Coupled Mass Spectrometry (ICPMS) for materials that have been dissolved or Laser Ablation (LA) ICPMS for analytical spots on solid materials. **pXRF data can be improved by using standards-based analysis for quantitative results** (below).

Standards-Based pXRF Quantitative Analysis:

- ICAL has obtained numerous standards from credentialed sources (NIST, USGS) that are representative of common natural materials (rocks, soils) and these cover the range of elements expected to occur in Nature.
    - AGV-2, andesite, USGS
    - SBC-1, Brush Creek Shale, USGS
    - BCR-2, Columbia River Basalt, USGS
    - GSP-2, Granodiorite Silver Plume, USGS
    - NOD-P-1, Manganese Nodule, USGS
    - SARM, USGS
    - SDC-1
    - NIST 2709A
    - RCRA 180-661
    - Till-4
    - NIST 2780
    - SiO2 180-647
- **A calibration curve must be determined for each element of interest**. Refer to the **Excel spreadsheet: Standard_Testing_472015**.
- **The first tab, Standards Data, is a compilation of the certified values for elements present in each of the standards used by ICAL**. This compilation is meant as an aid to determine the best standards to use if you want to calibrate for additional elements.
- **There are numerous tabs with the certified compositions for each of the standards available in ICAL**.
- **A selection of standards should be used to create a working calibration curve for each element of interest.**
    - **Try to select a range of compositions to obtain the best calibration over a range of compositions**.
    - **Apply the linear regression function in Excel to obtain the equation for the calibration curve**. Enter the measured value into the equation and determine the corrected value for each element.
- **I recommend obtaining duplicate analyses (at least 3) to check for reproducibility, precision and accuracy**. Relative errors are reported in the data output, and these uncertainties can be carried through subsequent calculations.
- **It is probably a good idea to run one or two standards as unknowns to also check for accuracy of data**; but if standards are run as unknowns these should not be included in the calibration curve.
- **There is a tab for each element of interes**t where a calibration curve has been determined using a best-fit regression curve relating the known elemental concentration from standards (X) and the measured concentration of that element (Y) from the pXRF.

- **To correct the measured values, simply solve Y = mX+B:** Where X is the corrected concentration; Y is the measured concentration from pXRF, m is the slope from the regression curve and B is the intercept.
- **Elements that currently have standardization curves** developed include: **Barium, Strontium, Aluminum, Arsenic, Nickel, Copper, Iron, Zinc, Phosphorous, Niobium, Vanadium, Calcium, Potassium, Manganese, Silica, Lead, Thorium, Titanium, Zirconium.**
- **NOTE: It is recommended that these calibrations should be updated for each major project**. The instrument is fairly stable but count rates can vary as the intensity of X-rays may degrade over time as the X-ray tube fatigues. New standard data can easily be inserted into the spreadsheets for any specific elements of interest.
- **If calibration curves are needed for additional elements, select the appropriate standards for each element. Try to select standards that have high and low concentrations to get the best fit of the regression curve**. The element concentrations are compiled in a single tab on the spreadsheet titled **Standard Data** for easy comparison and selection.
    - **Note: a) many of the elements will not be detectable** with the EDS detector on the pXRF, and b) many of the elements (e.g, REEs) may be at concentrations below the detection limits of the instrument.
    - **Acquire analyses of the chosen standards for elements of interest**. Obtain at least 3 measurements just to check for precision, accuracy and reproducibility.
    - In Excel, **plot the standard composition (wt% or PPM) on the X-axis vs. the measured concentrations from the pXRF readout on the Y-axis**.
    - **Calculate the regression curve from these data. Here is an example of the last calibration for Ba.**



- Here is a table of the most recent calibration data with regression parameters for each element. These correction factors can then be applied uniformly to numerous samples as large datasets acquired by the pXRF (see description of Post_Processing XRF below).

Element	Slope	B Intercept	R^2
Barium	0.8282	0.0023	0.8601
Strontium	0.9286	0.0005	0.9987
Aluminum	0.8838	0.0941	0.9765
Arsenic	0.7642	0.0018	0.9255
Nickel	0.8006	0.0029	0.9949
Copper	0.7877	0.0008	0.9955
Iron	1.0064	0.0191	0.9899
Zinc	0.7546	0.0027	0.9811
Phosphorous	1.1024	0.034	0.9031
Niobium	1.1186	-0.0003	0.9128
Vanadium	0.814	0.006	0.9782
Calcium	1.0829	-0.0252	0.9963
Potassium	0.8444	0.2938	0.9805
Manganese	1.0943	-0.0314	0.9983
Silica	1.0259	0.2307	0.9679
Lead	1.0708	-0.0014	0.9609
Thorium	1.104	-0.0005	0.9948
Titanium	0.9113	0.0419	0.9841
Zirconium	1.476	-0.0096	0.956

pXRF Post Processing

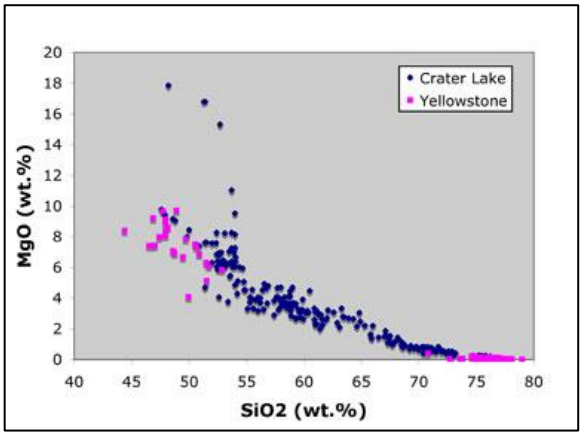
Once the calibration curves are created for each element of interest, these correction factors can be applied to entire pXRF datasets. This can be done in the **Excel spreadsheet Post_Processing_pXRF_3242015_A_v2 file**. From this spreadsheet instructions:
"DISCLAIMER: This spreadsheet is designed to work in conjuction with Standard_Testing_Sheet_3242015.xlsx and the GEO TEST ALL analysis suite on the Thermo Niton pXRF. The equations in this sheet are derived from plotting the standard values in weight % (X-axis) against the Thermo Niton pXRF readings in weight % (Y-axis). The standard readings from the Thermo Niton pXRF should be resampled reguarly and equations updated to account for any skew in accuracy or precision on the device. **Update of readings should be used to update linear regression analysis in the Stand_Testing_3242015.xlsx and updated to the respective date.** This post-processing

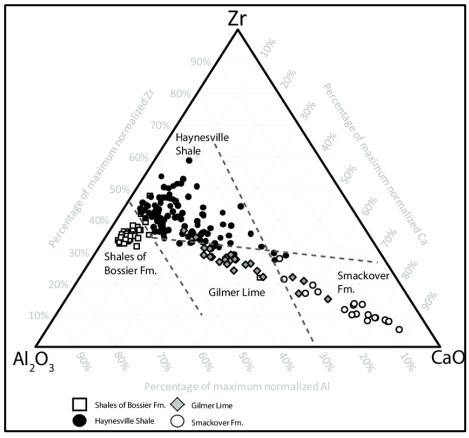
is considered a minimum threshold for reporting quantitative results. Publishing of data post-processed in this spreadsheet is at the user's risk. Careful examination of any quantitative analysis should be conducted to verify results. Equations pre-loaded within this spreadsheet should only be used with Montana State University's Thermo Niton pXRF.

- **The Element Equation tab is a compilation of the correction factors for each element** obtained from the Standard Testing Spread Sheet.
- **The Raw Data tab are the analytical data for samples, as downloaded from the pXRF and the DMSNT software.** Copy your analyzed data set into this tab.
- **The Processed Data tab applies the Element Equation to the raw data.** Read the corrected values in the red columns. Note there are replicate analyses so you can calculate average and S.D. if this is needed.
    - **If you have determined correction factors for additional elements of interest, these can be added to the Element Equation tab, and create a new column of corrected data for that element.** Use the following relationship for the new element and correction factors:

[[(Raw Data New Element Cell #)/10000) – (Element intercept)]/Element Slope]*10000

- **Corrected data can be tabulated from the Processed Data tab.** You should
    - **Check all data—**do the numbers make sense in the context of your sample (e.g., rock type, geochemical environment, composition of experimental components, related literature)?
    - **Are there anomalies or outliers?** From your duplicate analytical runs, are there one or more anomalous reading(s)? Is this an artifact of sample heterogeneity, perhaps incomplete homogenization of samples in powders,…?
    - **Represent your data on graphs:** simple X-Y diagrams are easily prepared in Excel. Geochemical data are also commonly presented as normalized Ternary Diagrams, and many geochemical plotting programs will have superposed compositional fields based on empirical geochemical data. Numerous Geochemical Plotting Programs can be accessed at: https://serc.carleton.edu/NAGTWorkshops/petrology/plot_programs.html





References: Representative Articles That Demonstrate pXRF Methods and Products

These are representative articles that describe pXRF instrumentation, calibration, analysis, and applications to the types of research commonly done at ICAL on mineral exploration, environmental characterization and remediation, soils and agricultural crops, archeological samples, etc. There is a wealth of information in the literature of pXRF applications to all kinds of basic and applied research.

Arenas-Islas, D., Huerta-Diaz, M.A., Norzagaray-López, C.O., Mejia-Piña, K.G., Valdivieso-Ojeda, J.A., Otero, X.L. and Arcega-Cabrera, F., 2019. Calibration of portable X-ray fluorescence equipment for the geochemical analysis of carbonate matrices. *Sedimentary geology*, *391*, p.105517.
https://d1wqtxts1xzle7.cloudfront.net/91443053/j.sedgeo.2019.10551720220923-1-1uoc46k-libre.pdf?1663947190=&response-content-disposition=inline%3B+filename%3DCalibration_of_portable_X_ray_fluorescen.pdf&Expires=1718747086&Signature=DfkBuWrjI3QdHK-XtCNULlwv2XPvLKEhjYp20NdY1rN5dpV6fe1F30KwYUKET0U-KGDlqanPzxa4J4Zv4QiN3~cIOfkvVm1MgF~DbX0ZEnU0HxgXt2LqI0AgvDYdKd2jd7EJc9DNK-7jPZ3VCj3GqgIDnkSUUv6AHfmk6Y-iNSjAETnDV8WOyy6J3YJgnasiY8jdWaaOXzNzowjiQW7ccG0ASdHUaKCBbPg1HYTIBoF~wLNsNY8znBc1qq5KzsFHxY7CjtOxgsPP2~AcjmffkqMHQoUjpPoIUj4pE9izA3kyOl5ptHeitO~ygWf3u7ZtFkLa9QvmZoArR7L5zm6x1Q__&Key-Pair-Id=APKAJLOHF5GGSLRBV4ZA

Bachofer, S.J., 2008. Sampling the soils around a residence containing lead-based paints: An X-ray fluorescence experiment. *Journal of chemical education*, *85*(7), p.980.
https://pubs.acs.org/doi/pdf/10.1021/ed085p980?casa_token=9nYxOzlHFZ0AAAAA:1IESMRpEg7-Exl5V8sBMfK8nMQQKyG0vEwqMFrsgjCMUhA4OtosVpK55icEpdOiKmokGfCL0NOExhOA

N. W. Brand, C. J. Brand; Performance comparison of portable XRF instruments. *Geochemistry: Exploration, Environment, Analysis* 2014;; 14 (2): 125–138. doi: https://doi.org/10.1144/geochem2012-172
https://pubs.geoscienceworld.org/geea/article/14/2/125/129003/Performance-comparison-of-portable-XRF-instruments?casa_token=LB5-nRNdltYAAAAA%3aG8OmRQcU6sbeAFV-LFUGvX7L7gXWYI_PjQ4H6qQ99XnbIksoNVnvzfX30NBnYbsgpYljiqM

Bruno Lemiere. A Review of pXRF (Field Portable X-ray Fluorescence) Applications for Applied Geochemistry. Journal of Geochemical Exploration, 2018, DOI: 10.1016/j.gexplo.2018.02.006. https://brgm.hal.science/hal-01740950

Hall, G.E., Bonham-Carter, G.F. and Buchar, A., 2014. Evaluation of portable X-ray fluorescence (pXRF) in exploration and mining: Phase 1, control reference materials. *Geochemistry: Exploration, Environment, Analysis*, *14*(2), pp.99-123.
https://www.lyellcollection.org/doi/pdf/10.1144/geochem2013-241

Hu, W., Huang, B., Weindorf, D.C. and Chen, Y., 2014. Metals analysis of agricultural soils via portable X-ray fluorescence spectrometry. *Bulletin of environmental contamination and toxicology*, *92*, pp.420-426. https://link.springer.com/article/10.1007/s00128-014-1236-3

Hunt, A.M. and Speakman, R.J., 2015. Portable XRF analysis of archaeological sediments and ceramics. *Journal of Archaeological Science*, *53*, pp.626-638.
https://d1wqtxts1xzle7.cloudfront.net/35925652/YJASC4271_proof-libre.pdf?1418405713=&response-content-disposition=inline%3B+filename%3DPortable_XRF_analysis_of_archaeological.pdf&Expires=1718747367&Signature=atu5SB49SpcevQmnYYXg-qf6xLfMI1QnZpq5s1HTtkFmjERwjPsgYxaIwUfMH4Gh~12pgKUhk-3IpQtmGjuxz8jB7csnkW6D07DfUVGGtl8lU35wQ9XBJmz4cqoA0d-SAPWjG1pZWWLXe8PyyLxfegcONUdu8gQlSlSqanHpd7AgXV9IehwHItDTnDGofbH0lcoyf~qS2qqfvcNBSUwjrvq7jCWht-os-TYVgR034uYhbj025HdVrMjFmDJT~j76zSW7dVBmK0sfVvlHcCXmzrkBQJbCrFP5X1Yz-0vkU56PaEqmauhjkICI0TMhtiwmklCrEqBbLwX64RT9NGBX7w__&Key-Pair-Id=APKAJLOHF5GGSLRBV4ZA

Kenna, T.C., Nitsche, F.O., Herron, M.M., Mailloux, B.J., Peteet, D., Sritrairat, S., Sands, E. and Baumgarten, J., 2011. Evaluation and calibration of a Field Portable X-Ray Fluorescence spectrometer for quantitative analysis of siliciclastic soils and sediments. *Journal of Analytical Atomic Spectrometry*, *26*(2), pp.395-405.
https://pubs.rsc.org/en/content/articlehtml/2011/ja/c0ja00133c?casa_token=6uh3YxwGp4cAAAAA:xiGbAtVkwfD-RORsjNhHn3tlSiWkdSHAzV3afji5KlKfda2VBtY0L-5catU_nQ1O3JE4X6uuMQNnpw

Ravansari, R. and Lemke, L.D., 2018. Portable X-ray fluorescence trace metal measurement in organic rich soils: pXRF response as a function of organic matter fraction. *Geoderma*, *319*, pp.175-184.
https://www.sciencedirect.com/science/article/pii/S001670611732026

Richards, M.J., 2019. Realising the potential of portable XRF for the geochemical classification of volcanic rock types. *Journal of archaeological science*, *105*, pp.31-45.
https://www.sciencedirect.com/science/article/abs/pii/S0305440318305193

Rouillon, M. and Taylor, M.P., 2016. Can field portable X-ray fluorescence (pXRF) produce high quality data for application in environmental contamination research?. *Environmental*

Pollution, *214*, pp.255-264.
https://www.sciencedirect.com/science/article/abs/pii/S0269749116302366

U.S. Environmental Protection Agency Method 6200, FIELD PORTABLE X-RAY FLUORESCENCE SPECTROMETRY FOR THE DETERMINATION OF ELEMENTAL CONCENTRATIONS IN SOIL AND SEDIMENT
https://www.epa.gov/sites/default/files/2015-12/documents/6200.pdf

Zhou, S., Wang, J., Wang, W. and Liao, S., 2023. Evaluation of Portable X-ray Fluorescence Analysis and Its Applicability As a Tool in Geochemical Exploration. *Minerals*, *13*(2), p.166.
https://www.mdpi.com/2075-163X/13/2/166