

Elemental Analysis of Sedimentary Rocks: Method Development in WD-XRF Analysis and Further Comparison of the Method to hXRF Practices

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Summary

X-ray Fluorescence Spectrometry (XRF) is a precise and powerful technique in elemental analysis which is commonly used for a vast range of materials in industry. However, the accuracy of the results greatly depends on the sample preparation of the solids prior to the analysis. In general, geological specimens are heterogeneous and proper quantitative analysis without suitable sample preparation and homogenization is unlikely. There are two common types of sample preparations known as Fusion Bead (FB) and Pressed-Pellet (PP) methods. Each of these techniques has its own inherent limitations and strengths. In this paper we present an improved PP method in which the common problems of PP method known as particle size and mineralogical effects are resolved or minimized. Acceptable calibration lines with correlation coefficients (over 0.99, except for S with 0.98) for Na, Mg, Al, Si, P, S, K, Ca, Ti, Fe, V, Cr, Mn, Fe, Rb, Sr, Zr and Ba show the strength of the linear relationship between analysis data (XRF PP method) and reference data (XRF FB method and ICP-MS). The calibration lines of some of the critical elements were compared with recently published results obtained by a handheld XRF on some volcanic basalt specimens.

Introduction

X-ray fluorescence (XRF) spectroscopy has become a common tool to generate quantitative inorganic geochemical results and to obtain chemo-stratigraphic information. Two main configurations of XRF include Energy Dispersive (ED) and Wavelength Dispersive (WD). WD-XRF is known for its lower detection limit and higher energy resolution compared with ED-XRF which is mainly used in the handheld instrument (hXRF) for rapid analysis. Therefore, WD-XRF produces more accurate results on elemental analysis in general (Fitton 1997). Although the specimens can be analyzed without any sample preparation on the drill core and flat rock surface for rapid analyses and further chemostratigraphic characterization using hXRF, results should be used for qualitative or at best semi-quantitative purposes with a high degree of caution. hXRF potentially suffers from several limitations which can compromise its analytical accuracy to a significant degree: (1) heterogeneity of geological specimens, especially in the sedimentary rocks (2) sample analyzing depth for light elements (3) non-uniform particle size and particle size greater than the analytical depth (4) X-ray absorption under air environment and (5) low energy X-rays detection limits (Young et. al 2016). Therefore, it is important to consider the limitation and capabilities of this instrument and shouldn't be considered as a quantitative tool. However, hXRF is employed to generate data for plot correlation ratios and/or estimation of the normative mineralogy, to obtain general information about the geochemical signatures of the reservoir formations, etc. For geological specimens (for instance unconventional reservoirs such as Montney/Duvernay), an accurate and representative result

requires a proper method of sample preparation prior to exposure of a sample to X-rays due to heterogenic nature regardless of any subsequent spectroscopic analysis method.

Two common methods of sample preparations for XRF are Fusion Bead (FB) and Pressed Pellet (PP) techniques. FB provides a complete homogenous glass sample for analysis and eliminates the mineralogical and particle size effects, which provides the best accuracy and reproducibility. In the FB method, however, volatile constituents (such as F, S, Cl, Br) and trace elements can evaporate and escape from the sample to some extent due to the high fusion temperature (1000-1200°C). Moreover, dilution of the sample with a borate flux affects the lower detection limit of the trace elements. The PP method on the other hand is relatively simpler, sample preparation is minimal and it does not compromise the analysis of volatile elements. In addition, the detection limit of analysis is lower because little to no dilution is involved. However, the PP method suffers from so-called mineralogical and grain-size effects. The mineralogical effect occurs due to the difference in elemental position in the matrix, caused by the difference in oxidation state and coordination of a specific atom in different matrices. Non-uniform or larger particles (compared to the analytical depth) can introduce errors in an analysis. This phenomenon is more prominent in lighter elements such as Si and Al due to their shallow analyzing depths (Willis et al. 2014). In this study, we took a holistic approach to establish an accurate, rapid and simple sample preparation method by using matrix-specific standards to analyze sedimentary formations such as the Montney Formation. In-house standards were prepared from actual reservoir samples, characterized and used to establish the calibration lines. Using in-house standards instead of certified reference materials (CRMs) enabled us to control the particle size range by suitable pulverization conditions, and mineralogical control over selected standards obtained by XRD. The accurate elemental analyses of the specimens have been measured by FB analysis and/or analysis by ICP (MS or OES). Sulphur concentrations for in-house standards were determined by a Leco Sulphur analyzer.

Method Development

The specimens required for calibration and method evaluation were obtained from the Montney Formation in western Alberta and northeastern British Columbia. Core samples were pulverized with a Tungsten carbide grinding mill and pressed with an automatic pressing instrument under optimized conditions. The Montney is composed of interbedded fine-grained sandstone, siltstone and shale units with varying amounts of dolomitization. This variation in lithology makes it an ideal material to use as a standard. By using these specimens, we were able to achieve a dynamic range of major and trace elements. The mineralogy is primarily composed of Quartz, Feldspars, Calcite and Dolomite, with varying amounts of clays and minor amounts of apatite, pyrite and siderite. The particle size range of pulverized samples was monitored and controlled using a Laser Diffraction Particle Size (LD-PSD) Analyzer. To generate the calibration lines for elements, seven samples were used as secondary standards to develop a sufficiently wider range of major, minor (Na, Mg, Al, Si, P, S, K, Ca, Ti, Fe) and trace elements (V, Cr, Mn, Fe, Rb, Sr, Zr, Ba) using PP sample preparation. This calibration method can be modified to add more elements of interest.

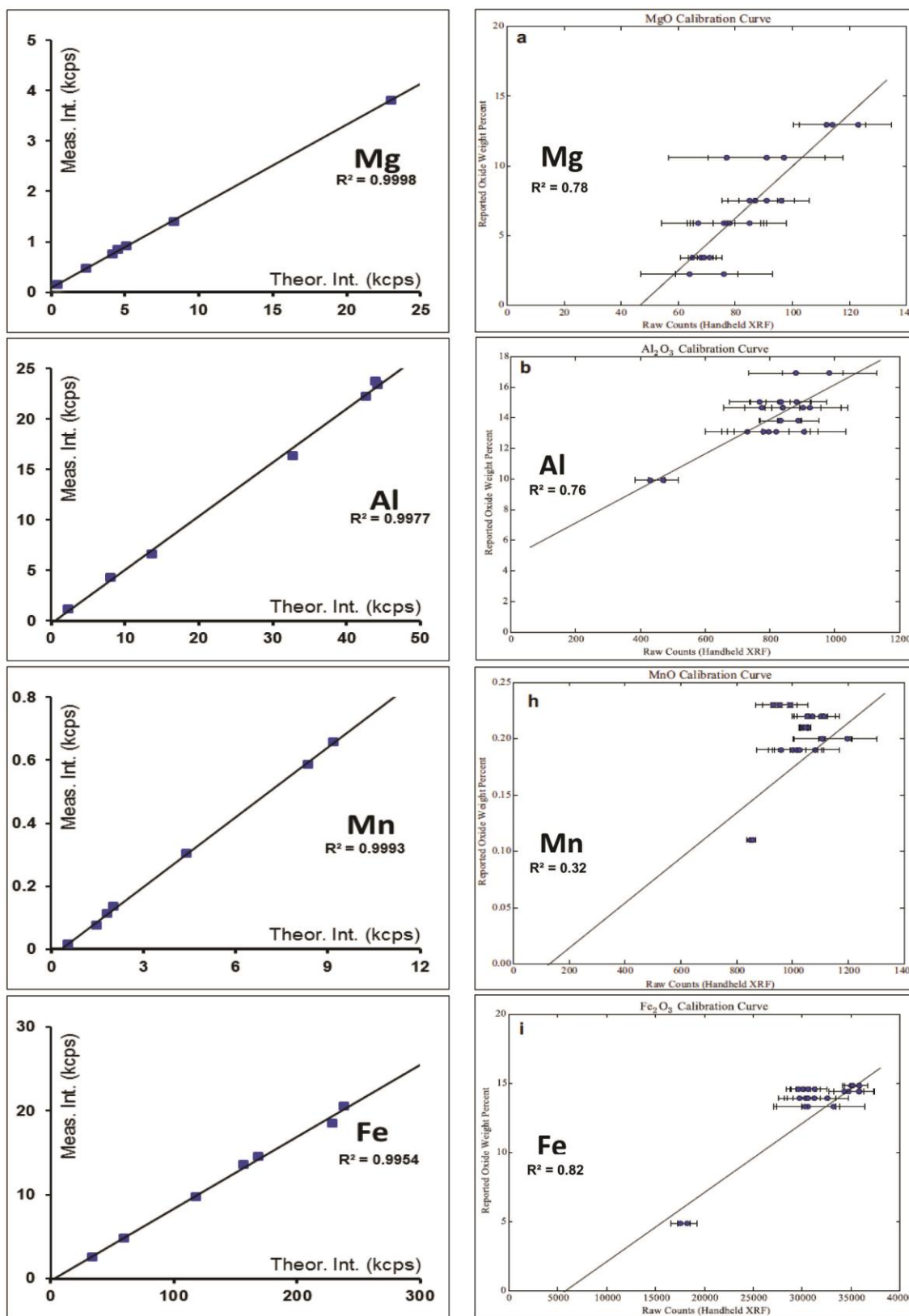


Figure 1: comparison of calibration method (left) Benchtop WD-XRF with PP samples, (right) hXRF by Young et al.

The purpose of this study was to quantify commonly occurring major elements in sedimentary environments by the PP method, thereby reducing the mineralogical and particle size effects. Linear calibration plots for some of the elements are shown in Figure 1 accompanied by the correlation coefficients (R^2). The calibration lines of the same elements acquired by the hXRF analyzer in a very recent publication (Young et al. 2016) were inserted for the precision comparison. The comparison clearly shows the definite superiority of data points in the PP method and WD- XRF analyzer. Very strong correlation with minimum 0.99 R^2 values (except for S with 0.98) is obtained for almost all the elements. This can only be achieved with (1) the excellent sample preparation technique, (2) reliable configuration of the benchtop WD-XRF, (3) advanced Fundamental Parameter algorithm (FP) of the instrument to correct the overlap and inter-element effects in matrix and (4) the proficiency of the analyst to generate accurate and precise results. WDXRF also detects Na, which is undetectable by hXRF analyzers due to the low X-ray power limitations. Identifying Na is important in sedimentary rocks as it indicates the presence of Na-feldspar, certain clays (Na-Montmorillonite) and halite. Furthermore, this method gives reliable results for S which hXRF is incapable due to matrix effects (Rowe et al. 2012) or FB method due to the volatility of S at high temperatures. Calibration plots of Na and S are shown in Figure 2.

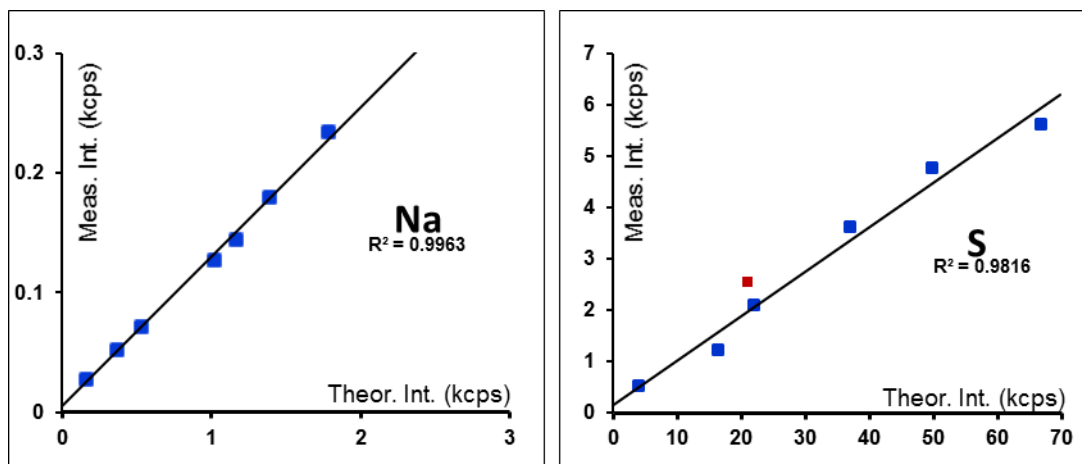


Figure 2: Calibration line of Na and S obtained by WD-XRF analyzer on PP samples. Red data point was excluded from the S line.

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