Comparison of WDS and EDS Rare Earth Element Analysis

H. A. Lowers[1] and P. K. Carpenter[2]

[1]Central Minerals and Environmental Resources Science Center, U.S. Geological Survey, Denver, CO 80225 USA
[2]Department of Earth and Planetary Sciences, Washington University, Saint Louis, MO 63130 USA

Demand for rare earth elements (REE) is on the rise as more uses for these materials are found in the technology and energy sectors. Electron microscopy coupled with wavelength-dispersive spectroscopy (WDS) and energy-dispersive spectroscopy (EDS) analysis allows in situ analysis of REE containing minerals from prospective mineral deposits to help determine its potential as an economic resource. The analysis of REE minerals is complicated due to on- and off-peak interferences, background selection, availability of standards, and the number of elements present to analyze. We set out to compare standards and standardless based EDS to WDS to determine the best option in terms of time of analysis, accuracy, and element detection, to test EDS detector performance for REE analysis, and to evaluate the standard materials used for REE quantitative analysis.

Standards-based EDS analyses were acquired at 15 kV, 50 nA probe current, 20 micron defocused beam diameter, and 200-600 seconds live count time on a JEOL 8200 electron microprobe with a 10 mm^2 e2v Gresham silicon drift detector at Washington University. WDS analyses with off-peak and mean atomic number (MAN) background corrections were also acquired on the same instrument utilizing the same operating conditions. Natural and synthetic mineral standards, Edinburgh REE glasses [1], Roeder REE glasses [2], Drake and Weill REE glasses [3], and Smithsonian REE orthophosphates [4] were used for calibration and accuracy checks for both EDS and WDS analysis. The Edinburgh REE glasses and Smithsonian orthophosphates contain a single rare earth element in a Ca-Al-Si-O matrix and PO$_4$ matrix, respectively. The Drake and Weill REE glasses contain multiple REEs, usually four, which were chosen to reduce to the number of peak interferences on the WDS spectrometer.

A comparison of the measured k-ratio (k-measured) on the unknown using a multielement standard to the theoretically calculated k-ratio (k-calculated) has been used as a nonbiased method for evaluating the accuracy of the analysis. K-calculated is obtained by division of the elemental k-ratio for each secondary standard by the elemental k-ratio for the primary standard using k-ratio values calculated using the Armstrong $\Phi(\rho z)$ of the CalcZAF program [5]. The ratio k measured/k calculated is plotted versus elemental weight percent in figure 1. A value of one on these plots represents perfect agreement between the measured and observed values regardless of element concentration.

The EDS data presented in Figure 1 indicate excellent agreement with the Drake and Weill REE standards but an overestimation of the measurement for the Edinburgh glasses due to pulse-pileup peaks in the REE L-family range which are not corrected for on the EDS system used. A wide dispersion of the ratio for the ~1 and ~0.1 wt% Roeder REE glasses indicates decreased accuracy by EDS at low concentrations but also possible errors in the accepted values for the REE in these trace element glasses. The accurate measurement of REE by EDS thus requires accurate removal of pulse-pileup artifacts and long count times for precise measurement at low concentrations.

The off-peak background-corrected WDS data presented in Figure 1 reveals reasonable agreement among the standards with the exception of Ce, Er, and Tm in the Edinburgh REE glasses and the low level Roeder glasses. These inconsistencies suggest an error in the accepted element concentrations of these materials. The error in measurement of Tb in the Drake and Weill glass is due to an off-peak

interference (Eu) and is eliminated with the MAN background correction (fig. 1). This k-ratio evaluation method allows inspection of data, reveals background placement issues, and possible problems with standard compositions regardless of the matrix correction scheme used.

References

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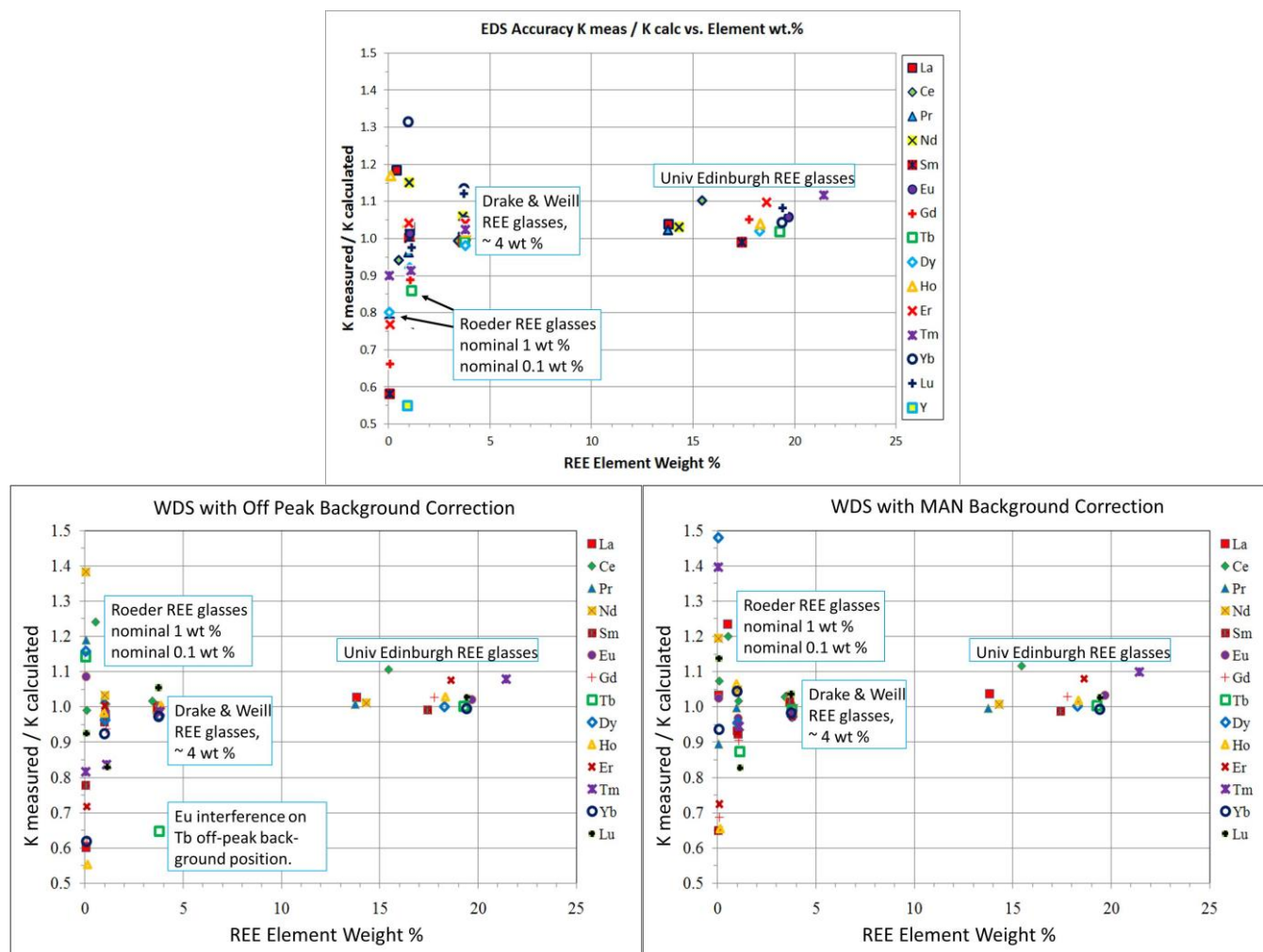[5] http://probesoftware.com/Technical.html

Figure 1. K-ratio comparisons of REE elements calibrated relative to USNM REE orthophosphates using EDS (top), WDS with off-peak background correction (left) and WDS with MAN background correction (right).