

Exploring the Limits of EDS Microanalysis for Rare Earth Element Analyses

Nicholas W.M. Ritchie¹ and Heather A. Lowers²

¹ Microscopy and Microanalysis Research Group, NIST, Gaithersburg, MD.

² Central Minerals and Environmental Resources Science Center, U.S. Geological Survey, Denver, CO.

In 1973, Reed suggested that energy dispersive spectrometers (EDS) could perform quantitative measurements much as the wavelength-dispersive detector (WDS) has been doing for decades [1]. Despite poor energy resolution of early detectors and controversies over fitting models [2] quantitative measurements with EDS have been performed over many decades and are not new. However, new improvements in detector and electronics technology have allowed for accuracy and precision, even in the presence of severe peak interferences, that rivals WDS. Materials of known concentration were analyzed to demonstrate the improvements in accuracy, precision, and detection of trace quantities of REE.

Four Drake and Weill engineered rare earth element containing glasses called REE1, REE2, REE3 and REE4 [3] and two REE containing minerals were examined for this study. The data were collected on a TESCAN MIRA3 equipped with four independent 30mm² PulseTor SDDs. The beam energy was 20keV and the probe current was 0.9nA. The probe current was remeasured between spectra and the spectra from the four independent SDD were combined into a single spectrum for quantification using NIST DTSA-II [4]. Standards were collected from an SPI Rare Earth Phosphate standard block. Five replicates of each standard were collected for 60.0 s each and combined into a single 300s standard spectrum. The spectra for each element were combined with the necessary references into a standard bundle to facilitate quantification. Many of the standards also required a reference to resolve interference of the REE M-lines with either the P K or the O K lines with GdP₅O₁₄ serving as the P K peak-shape reference and MgO serving as the O K peak shape reference. In addition, the research glass K411 (NIST Standard Reference Material 470) was used as a standard for Si and Ca, and pure Al for Al. For comparison, the research glass K412 was used as a standard for Si, Al, Ca and O. Oxygen was computed using stoichiometric assumptions. Nine or ten 600 seconds spectra were collected from a randomly selected set of points on each unknown.

An example of a spectrum from glass REE1 and the residual generated during the quantification is shown in Figure 1. The marker lines for O, Si, Al, Ca, Nd, Sm, Yb, and Lu reveal the complexity of the REE L-line structure. The residual under the REE L-lines is seen to be particularly smooth and structureless because of the high quality unknown and standard spectra. The fit under the Ca K lines has a small but unexplained structure and the fit under the Al K (1.48keV), Si K(1.74keV), and REE M-lines shows additional structure but remains fairly clean. This residual suggests that other elements haven't been overlooked and that reliable k-ratios are achieved. Similar analyses were performed on monazite and xenotime minerals. The results are given in Table 1.

The data in Table 1 suggests EDS of REE is accurate and precise at the 0.3% mass fraction level and above. Detection limits are challenged due to the background continuum present in EDS analysis. Further improvements may be possible through better deconvolution, higher throughput, or longer count times.

References:

- [1] Reed S J B and Ware N G, X-ray Spectrometry **2** (1973), p. 69.
- [2] Schamber F H, A modification of the linear least-squares fitting method which provides continuum suppression (Ann Arbor Science Publishers) (1977), p 241.
- [3] Drake M and Weill D, Chemical Geology **10** (1972), p. 79.
- [4] Newbury D E and Ritchie N W, Journal of Materials Science **50** (2015), p. 493.

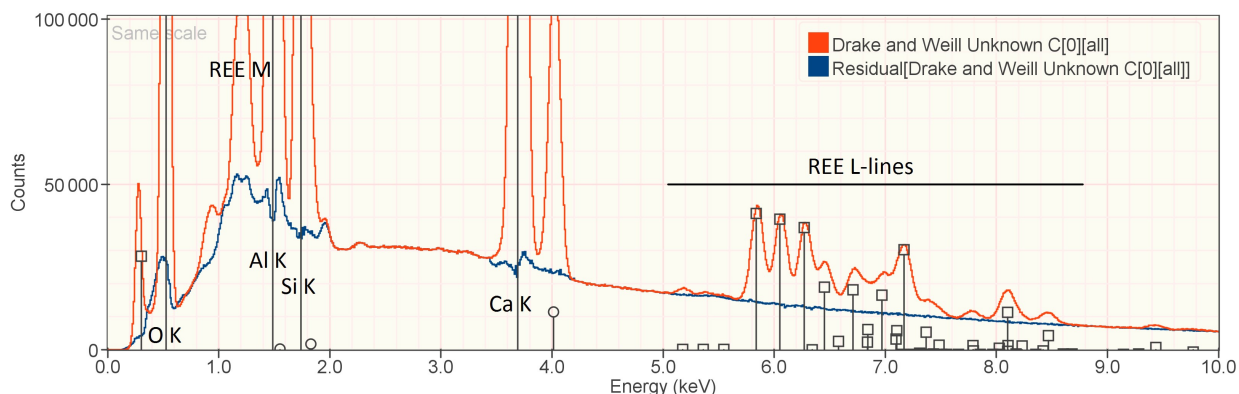


Figure 1. A raw spectrum from Drake and Weill glass REE1 and residual generated during quantification.

	REE1		REE2		REE3		REE4		BS1		NAM	
	Avg (n=10)	REDEV	Avg (n=9)	REDEV	Avg (n=10)	REDEV	Avg (n=10)	REDEV	Avg (n=10)	REDEV	Avg (n=10)	REDEV
O	39.04	2.70%	38.34	0.20%	38.67	-0.60%	39.65	0.60%	32.8	-	27.35	-
Al	17.4	7.70%	16.21	0.00%	16.48	1.40%	17.64	3.90%	-	-	-	-
Si	12.2	-3.20%	12.7	0.40%	12.15	-4.30%	12.86	-2.80%	0.06	-	0.88	-
P	-	-	-	-	-	-	-	-	14.97	-	11.51	-
Ca	18.38	2.20%	17.97	-0.40%	18.07	-0.20%	19	0.50%	-	-	0.59	-
As	-	-	-	-	-	-	-	-	4.7	-	-	-
Y	-	-	-	-	3.26	1.50%	-	-	34.7	-	1.41	-
La	-	-	-	-	3.72	1.90%	-	-	-	-	8	6%
Ce	-	-	-	-	3.4	-0.50%	-	-	-	-	20.53	3%
Pr	-	-	-	-	3.85	1.60%	-	-	-	-	2.66	8%
Nd	-	-	3.8	4.10%	-	-	-	-	0.12	-29%	9.61	6%
Sm	-	-	3.82	4.00%	-	-	-	-	0.42	-26%	3.25	9%
Eu	3.88	2.10%	-	-	-	-	-	-	0.2	-14%	-	-100%
Gd	3.93	1.60%	-	-	-	-	-	-	2.57	-10%	2.19	2%
Tb	3.83	1.30%	-	-	-	-	-	-	0.73	-2%	0.42	69%
Dy	-	-	-	-	-	-	3.93	3.30%	5.73	1%	0.91	2%
Ho	-	-	-	-	-	-	3.99	3.50%	1.06	-11%	0.04	-56%
Er	-	-	-	-	-	-	3.9	2.30%	3.47	6%	0.25	83%
Tm	3.8	-0.40%	3.83	2.50%	-	-	-	-	0.44	2%	0	-100%
Yb	-	-	-	-	-	-	-	-	2.19	-2%	0.04	-25%
Lu	-	-	3.72	-0.80%	-	-	-	-	0.19	-16%	-	-100%
Pb	-	-	-	-	-	-	-	-	-	-	0.18	-26%
Th	-	-	-	-	-	-	-	-	0.08	-73%	11.57	14%
U	-	-	-	-	-	-	-	-	0.01	-74%	0.34	169%

Table 1. Average analysis of REE containing materials and the % relative deviation from the accepted value.