Quantitative Differentiation of Three Iron Oxides by EDS

John Konopka
Thermo Fisher Scientific

Precision in EDS analysis is dominated by the number of counts acquired. In principle, sufficient counts can be acquired to achieve any desired level of precision. Real world limits to count rate and counting time put a practical limit on the number of counts that can easily be acquired and systematic errors put a limit on achievable precision regardless of the number of counts acquired.

Conventional wisdom from the early years of microanalysis was that iron oxides could not be distinguished by EDS due to insufficient precision in the acquired spectra. At the time, beam current was often low, detectors provided small solid angles, SEM columns often provided only low take off angles. Windowless detectors used for soft X-ray analysis suffered from rapid contamination which made soft X-ray measurements highly unpredictable. All of this put a practical limit on the total counts which could be easily acquired in a spectrum and introduced systematic errors which resulted in poor precision and accuracy when measuring oxygen.

Newer SEMs provide high beam currents and high take-off angles, thin, one atmosphere x-ray windows make soft X-ray detection reliable, large area detectors provide high solid angles, and silicon drift detectors and digital pulse processors allow for counting rates at least an order of magnitude higher than was previously achievable. In principle, it should be possible to collect spectra with very high precision in less than about 100 seconds.

In this work different iron oxides were analyzed by direct measurement of both the Fe and O peaks. The goals being to verify that sufficient counts can be acquired to distinguish these materials and to demonstrate whether or not systematic errors will appear that interfere with this analysis.

Magnetite, hematite and (likely) goethite samples were mounted, polished and carbon coated then analyzed by EDS. Data was collected to provide from 100k to 1M counts in the Fe K alpha peak. In the first data set this was done by monitoring gross counts in the Fe K alpha peak. In the second data set this was done by monitoring a section of the background and stopping the acquisition when a set level was achieved. In this way the errors in the Fe and O peaks would be uncorrelated.

The system was calibrated to provide accurate results for some of the magnetite spectra by standardless correction methods and these corrections were applied to the

Spectra acquired from the remaining samples.

A subset of the results are listed in tables 1 and 2. The expected sd is calculated from the number of counts in a peak. The actual sd is calculated from the distribution of measured weight percents. The three materials are clearly distinct and the differences in measured compositions are much larger than the measured standard deviations. This is shown graphically in figure 1 which plots some results as histograms.
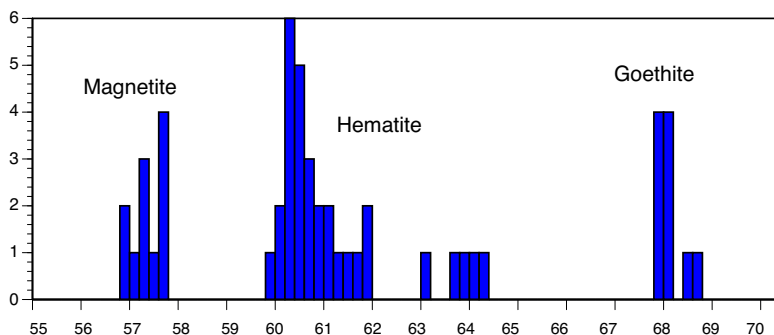
The conclusion is that well prepared samples of iron oxides can easily be distinguished reliably by EDS. The expected standard deviation predicted by the counts in individual peaks is much smaller than the precision measured for a group of spectra indicating significant contributions from systematic errors in these measurements. More work will be done to identify the sources of these errors and to see if they can be reduced.

Set #1	O wt%	Expected sd	Actual sd	Fe wt%	Expected sd	Actual sd	n
magnetite (1M)	27.74	0.029	0.231	71.86	0.068	0.221	11
hematite (1M)	31.62	0.031	0.112	68.32	0.064	0.135	11
goeth (350k)	38.103	0.052	0.293	60.57	0.096	0.369	10

Table 1. Data integrated by monitoring Fe K alpha peak. Peak iron counts in parens. 30mm² detector

Set #2	O wt%	Expected sd	Actual sd	Fe wt%	Expected sd	Actual sd	n
magnetite (1.35M)	27.74	0.025	0.227	72.35	0.062	0.228	5
hematite (1.35M)	30.31	0.026	0.349	69.69	0.060	0.349	10

Table 2. Data integrated by monitoring a region of the background. Peak iron counts in parens. 10mm² detector

Histogram of oxygen atomic percent values. This set of data was integrated to 350k counts in the Fe peak.

Nominal values	O wt%	Fe wt%	H wt%
magnetite	27.64	72.36	
hematite	30.06	69.94	
goethite	36.01	62.85	1.13