Options for Quantitative Analysis of Light Elements by SEM/EDS

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Key Words

EDS, Light Elements, Oxidation, Quantitative Analysis, SEM, X-ray

Introduction

The title of this document provokes two immediate questions: what are light elements and why is their treatment different from that of other elements when it comes to quantitative analysis?

Light elements refer to those with atomic number (Z) less than about 11. There is no official cutoff for what is a light element. One consideration is that up until about 1990 most energy dispersive spectroscopy (EDS) detectors used entrance windows made of beryllium that were about 8 microns thick. This window would not transmit X-rays for elements with Z less than 11. Light elements are treated differently because the X-rays they generate can be very difficult to measure reliably, if they can be detected at all.

As the atomic number is reduced, it becomes increasingly difficult to ionize an atom, and the ionized atom produced is less likely to generate an X-ray which results in a weaker signal from the light elements. Light element atoms produce longer wavelength X-rays. These are much more easily absorbed within the sample than shorter wavelength X-rays. Much of the weak signal that is produced will be trapped within the sample itself. As a result of this absorption, most X-rays from light elements that reach the detector come from near the surface of the sample, which means light element analysis is more strongly affected by sample contamination or coatings applied to samples to prevent charging.



The sum of these effects is that light elements can be difficult or impossible to measure and the X-ray intensities measured from these elements are more often subject to systematic errors than are intensities measured from heavier elements. All of these effects become much stronger as the atomic number is reduced.

Carbon is a special case. Carbon often accumulates as a contaminant on the surface of a sample in an electron microscope. This makes it very difficult to measure carbon reliably because one doesn't know if the carbon signal arises from the sample itself or from the contamination deposited during analysis.

There are four options for quantifying light elements.

- Direct analysis
- Calculation by stoichiometry
- Element by difference
- Fixed concentration



Direct Analysis

The simplest action to take is to simply treat light elements like all other elements. No special options are selected in the software. With modern silicon drift detectors and digital pulse processors, good measurements can be made of many light elements. This approach can work well for elements as light as carbon or boron. Greater care is required to ensure that the sample is flat and clean. Even more than usual it is important to confirm the credibility of an analysis by comparison with analyses of similar materials. This method is particularly useful for analyzing oxides of materials, which may exist in multiple oxide states or which are not fully oxidized.

Figure 1 shows a result for the analyses of an iron oxide, hematite, that was analyzed by directly measuring the iron and oxygen peaks, using a scanning electron microscope (SEM) and the Thermo Scientific[™] NORAN[™] System 7 X-ray microanalysis system.

Element Setup	Analysi	s Setup	Compare Information			
Quant Results	Processing	P&S Selec	t Analysis Automation			
Wed Jul 17 18:03:41 2013 Filter Fit Chi-squared value: 144.711 Errors:+/-1 Sigma Correction Method: Proza (Phi-Rho-Z) Acc.Voltage: 15.0 kV Take Off Angle: 35.0 deg						
Element Net	Element	Wt.% Error	Atom %			
OK 1159	161 30.09	+/-0.10	60.03			
Fe K 966	04 69.91	+/-0.41	39.97			
Total	100.00		100.00			

Figure 1: Quantitative results for iron and oxygen in a hematite sample in which both the iron and oxygen peaks were measured directly

When measuring light element peaks directly, it is important to consider not only sample preparation but analysis conditions and the stability of the sample under the beam, and the amount of carbon contamination being generated. It is beyond the scope of this document to detail these considerations and their remedies.

A direct analysis may be performed with or without standards.

Calculation by Stoichiometry

Stoichiometry refers to the branch of chemistry involving reactions of optimum amounts of material reacting to completion such that there is neither any excess nor deficit of any reagent. For example, if silicon is reacted with oxygen, we expect that the relative numbers of atoms reacted will be in the ratio of one to two resulting in silicon dioxide or SiO₂.

Stoichiometry in microanalysis calculates the concentration of a light element based on the measured concentrations of the heavy elements in a sample and their known stoichiometric relationships to the light element.

For example, when analyzing a sample of albite, NaAlSi₃O₈, the heavier elements are Na, Al and Si. These have the known oxides Na₂O, Al₂O₃ and SiO₂. So if we assume that all of the heavier elements are fully oxidized then we can calculate the amount of oxygen present just by measuring the heavier elements.

Figure 2 shows an example of this kind of analysis. The symbol "S" next to the weight percent result for oxygen indicates that the oxygen result was based on a calculation and not a measurement.

Element Set	up Analysis Se	etup Compare I	nformation Q	uant Results F	Processing P&S	Select Analys	sis Automation	
Mon Nov 03 13:05:38 2008 Filter Fit Chi-squared value: 17.219 Errors:+/-1 Sigma Correction Method: Proza (Phi-Rho-Z) Acc.Voltage: 10.0 kV Take Off Angle: 35.0 deg								
Element Line OK NaK AIK SiK CaK Total	Net Counts 241481 66172 87740 238220 978	Element Wt & 48.80S 8.47 10.37 32.03 0.34 100.00	Wt.% Error +/-0.05 +/-0.06 +/-0.14 +/-0.03	Atom % 61.60 7.44 7.76 23.03 0.17 100.00	Compnd Formula Al203 Si02 Ca0	Compnd Wt.% 11.42 19.59 68.52 0.47 100.00	Num. of Cations 0.967 1.008 2.991 0.022 4.988	

Figure 2: Quantitative result for an albite sample in which oxygen was calculated by stoichiometry

Many elements can exist in more than one oxidation state. To choose which oxidation state of an element to use in an analysis, click once on that element's symbol in the Element Setup periodic table, then click the Advanced button just below the periodic table. In the Advanced Element dialog (Figure 3), choose the desired compound to use for that element and close the window. Options are provided for oxides, borides, carbides and nitrides when available.

Figure 3 shows an example choosing FeO as the compound to use in calculating an oxygen result from the iron composition.

Advanced Element				
Quantification of Weight % Calculated By difference Fixed %	Compound Formula Fe2O3 Fe3O4 Fe8 Fe82 Fe82 Fe3C Fe4N			
Use Derivative References Quant Data Source EDS Is Ratio Element	Use Compound			

Figure 3: Advanced pane showing how to choose the Compound Formula for an element. In this case FeO is selected for iron. Note that the option By Difference is greyed out as the system is not currently configured for analysis with standards.

To use this feature select the checkbox "Use compounds for all elements" under the Analysis Setup tab (see Figure 4). In special cases it may be desirable to only calculate an element by stoichiometry for selected elements and not all elements. In this case, do not check the "Use compounds for all elements" option. Instead, as seen in Figure 3, check the "Use Compound" option only for the desired elements.

Stoichiometry, also called compound analysis, can only be used when there are two or more heavier elements in the sample. For example, when analyzing iron oxide this method cannot tell us the oxidation state, it will only report the oxidation state we set in the periodic table. For single element oxides or cases where there are mixed oxide states, use either the direct method or element by difference.

An advantage of using stoichiometry is that it can be used both with the standardless quantitative method and in analysis with standards.

Element Setup Analysis Setup	Compare Information Quant Results Processing Analysis Automation
Ident Sensitivity (1-100)	20 Uvervoltage: 1.5 Y
Quant Fit Method	Filter Without Standards
Correction Method	Proza (Phi-Rho-Z)
Number Oxygen Atoms	0 Use Compounds For All Elements
TEM Thickness (nm)	Use Matrix Correction
TEM Density (g/cc)	
Match	
Match Cutoffs (eV):	Low 0 High 10000
Max. Number of Match I	Results: 5
Chi-square Cutoff:	100
Match Database: FeN	

Figure 4: Analysis Setup pane showing the option to Use Compounds for All Elements. In this view the option is selected.

Element By Difference

As with stoichiometry, this method does not measure the light element directly but derives its concentration from the composition of the other elements in the sample. In this case, the heavier elements are analyzed using standards and when the result is less than 100%, the missing mass is assigned to the designated light element.

To use this method, the beam current must be measured and standards must be used. This gives the system the information needed to detect the missing mass.

To select this method, click once on the symbol of the designated light element in the Element Setup periodic table, and then click on the Advanced button below the periodic table. In the window that appears click the "By difference" option. (This option will be greyed out and cannot be selected unless the system is currently configured to perform quantitative analysis with standards.)

Figure 5 shows this option being set for boron. Figure 6 shows a quantitative result where boron was calculated by difference. The symbol "D" next to the weight percent result indicates that this element was calculated by difference.

Advanced Element					
Quantification of Weight % Calculated By difference Fixed X	Compound Formula B2O B4C BN				
Use Derivative References Quant Data Source EDS Is Ratio Element	Use Compound				

Figure 5: Advanced pane showing the option By Difference selected

Element Set	tup 🛛 Analysis Se	etup Compare I	nformation	Quant Results	Processing
Tue Mar 19 Filter Fit Wit Correction M Acc.Voltage) 22:22:11 2013 th Standards – C Method: Proza (I e: 15.0 kV Take	hi-squared value Phi-Rho-Z) 9 Off Angle: 30.0	e: 80.381 E deg	rrors:+/-1 Sigma	
Element Line BK SiK FeK CoK NiK	Net Counts 1038 19024 214731 75559 241410	Element Wt.% 2.86D 0.95 28.06 13.64 54.48	Wt.% Error +/-0.02 +/-0.14 +/-0.16 +/-0.25	Atom % 13.50 1.73 25.63 11.80 47.33	
Total		100.00		100.00	

Figure 6: Quantitative result for which the value for boron was determined by the Difference method

Fixed Concentration

In this method we simply tell the system how much of the designated element is present. This provides no new information. However, as explained below it can be important to account for all elements in an analysis. This is most often used when a very light element is present at a low level where small errors in the weight percent will not greatly affect the total results. In such cases, the Fixed method may be a better approach than ignoring the light element altogether.

Figure 7 shows this option set for boron. As before, to set this value, click once on the element's symbol, then click on the Advanced button below the periodic table. Figure 8 shows a result using the fixed amount of boron. The symbol "F" next to the weight percent result for boron indicates that this result is a fixed value and not a result derived from measured data.

Regardless of which method is used, it is important to account for light elements in an analysis even if they cannot be observed by the detector in use. X-ray microanalysis involves a number of strongly nonlinear physical effects. When the NORAN System 7 software conducts a calculation to derive a quantitative result from a spectrum, it makes corrections for all of these effects, many of which involve each element affecting the calculation of results for the other elements in the sample.

When we tell the system to include some amount of a light element, even if it is not measured directly, the software includes the effects of the light elements on the other elements in the ZAF or Phi-Rho-Z calculations.

Advanced Element	
Quantification of Weight % Calculated By difference Fixed 3.00 %	Compound Formula B2O B4C BN
☑ Use Derivative References [Use Compound
Quant Data Source EDS	Close

Figure 7: Advanced pane showing the value of boron set to the fixed value of 3.00%

[Element Setup	Analysis Setup	Compare Info	ormation	Quant Results	Processing		
	Tue Mar 19 22:25:26 2013 Filter Fit Chi-squared value: 80.381 Errors:+/-1 Sigma Correction Method: Proza (Phi-Rho-Z) Acc.Voltage: 15.0 kV Take Off Angle: 30.0 deg							
	Element Line	Net Counts	Element Wt %	Wt.% Error	Atom %			
	BK	1038	3.00F		14.09			
	SiK	19024	0.89	+/-0.02	1.61			
	Fer Co K	214731 75559	27.94	+/-0.14	25.40 11.70			
	NiK	241410	54.59	+/-0.26	47.20			
	Total		100.00		100.00			

Figure 8: Quantitative result in which the value of boron was set to the fixed value of 3.00%

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