

Quantitative Electron-Excited X-ray Microanalysis with Low Energy L-shell X-ray Peaks Measured with Energy Dispersive Spectrometry

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Abstract

Quantification of electron-excited X-ray spectra following the standards-based “k-ratio” (unknown/standard intensity) protocol with corrections for “matrix effects” (electron energy loss and backscattering, X-ray absorption, and secondary X-ray fluorescence) is a well-established method with a record of rigorous testing and extensive experience. Two recent studies by Gopon *et al* and Llovet *et al* have renewed interest in studying the accuracy of measurements made using L-shell X-ray lines. Gopon worked in the Fe – Si system and Llovet worked in the Ni – Si system. Both have reported unexpectedly large deviations in analytical accuracy when analyzing intermetallic compounds systems using the low photon energy Fe or Ni L-shell X-ray peaks with pure element standards and wavelength dispersive X-ray spectrometry. This study confirms those observations on the Ni intermetallic compounds using energy dispersive X-ray spectrometry, and extends the study of analysis with low photon energy L-shell peaks to a wide range of elements, Ti to Se. Within this range of elements, anomalies in analytical accuracy have been found for Fe, Co, and Ge in addition to Ni. For these elements, the use of compound standards instead of pure elements usually resulted in improved analytical accuracy. However, compound standards are not always better than elemental as is demonstrated with FeS using FeS₂ as a standard.

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Introduction

The basis for performing quantitative elemental microanalysis by electron-excited X-ray spectrometry is the standards-based intensity-ratio method with matrix (inter-element) corrections, as originated by Castaing [1, 2]. The so-called “k-ratio” is measured for the characteristic X-rays, I_{ch} , as corrected for the electron-excited continuum (bremsstrahlung) background, I_{cm} , for each element, i , present in the unknown and in a standard or suite of standards of known composition. The characteristic X-ray intensities for the unknown and standard are measured under identical conditions (beam energy, known beam current, spectrometer parameters (e.g., calibration), X-ray detector elevation angle and solid angle, etc.) and are corrected for instrumental measurement effects such as beam dose, detector deadtime (i.e., count rate effects), and any peak interferences from the characteristic X-rays of other elements present in the electron-excited volume of the unknown and standard. The k-ratio is thus:

$$k_z = \frac{I_{z,ch}(unknown)}{I_{z,ch}(standard)} \quad (1)$$

The suite of k-ratios for all elements in the electron-excited volume of the unknown can be converted into a corresponding suite of ratios of mass concentrations through the application of a series of calculated “matrix correction factors”. These factors consider the effects in both the unknown and the standard of: (1) beam electron energy loss and backscattering (the Z factor); (2) self-absorption of X-rays while propagating through each material (the A factor); and (3) the secondary fluorescence of X-rays that results from the photo-electric absorption of characteristic and continuum X-rays (the F and c factors). The relationship between k and C for each element is thus:

$$k_z = \frac{C_{z,unk} ZAFc_{z,unk}}{C_{z,std} ZAFc_{z,std}} \text{ for } z \in \text{element} \quad (2)$$

Iteration[3] is the process of finding the set of C_z which will produce computed k-ratios (Eq. 2) that match the measured k-ratios (Eq. 1). X-ray microanalysis is an implicit measurement model – it is not possible to invert the measurement equations to solve for the composition directly. Instead it is necessary to iteratively refine estimates of the composition until the estimated composition produces computed k-ratios that match the measured k-ratios within a tolerance.

Furthermore, iteration in X-ray microanalysis represents a set of coupled equations. It is only possible to solve them as a set. The matrix correction term for the element z ($ZAFc_{z,unk}$) depends upon all the elements in the unknown. This means that if there is an inaccuracy in one element, this adds additional inaccuracy in the other elements. In fact, there is a pernicious feedback loop that once the composition starts to deviate from a unity total, the result will be pushed towards further inaccuracy. This pernicious feedback can be mitigated by normalizing the mass fractions before computing the $ZAFc_{z,unk}$ term but it cannot be eliminated.

The Castaing standards-based method can achieve high accuracy results [2, 4, 5, 6, 7]. When tested against microscopically homogeneous materials of known composition that are suitably prepared to eliminate surface topography (ideally, polished to eliminate roughness to less than 50 nm), 95 % or more of analyses of major (mass concentration $C > 0.1$) and minor ($0.01 \leq C \leq 0.1$) elemental constituents fall within a relative deviation from expected value (RDEV) of ± 5 % [2]. The RDEV is defined as:

$$\text{RDEV} = ([\text{measured value} - \text{reference value}]/\text{reference value}) * 100 \% \quad (3)$$

An important aspect of this standards-based quantitative analysis method is that high accuracy measurements of an unknown with an arbitrary mix of elemental constituents requires only a simple

standards suite consisting of pure elements. For those elements that are reactive (e.g., Ca), gaseous (e.g., F), or degrade under electron bombardment (e.g., S), a stoichiometric compound that is stable under electron bombardment can be utilized, such as CaF₂, FeS₂, etc. The simplicity of the standards suite means that complex compositions can be analyzed without the need for a reference standard of similar multi-element composition to the unknown. Since it is in general difficult to achieve homogeneity on the microscopic scale with an arbitrary group of elements, which often separate into two or more phases of different composition, the simplicity of a standards suite consisting of pure elements and binary compounds provides great flexibility to the analyst when confronted with complex materials. If a microscopically homogeneous, multi-element material of known composition is available that is similar in composition to the unknown, it can be used as a standard with an expected improvement in analytical accuracy. The matrix correction factors are calculated relative to the compositions of the unknown (being determined iteratively) and the standard, and by minimizing the difference in composition by using a standard close in composition to the unknown, the matrix correction factors approach unity, minimizing the effects of uncertainties in the factors and improving accuracy[8].

A second benefit of standards-based analysis is the utility of the raw analytical total. Because each constituent is measured against its own standard under controlled analytical conditions, the raw analytical total, which is the sum of all constituents including any such as oxygen that may be calculated by the method of assumed stoichiometry, provides a useful internal quality measure. The analytical total typically falls in the range 0.98 to 1.02 mass fraction, and the range 0.95 – 1.05 captures at least 95% of analyses. Excursions outside this range may arise from several factors: (1) deviation in instrument measurement conditions such as beam current drift; (2) the presence of a surface layer on the sample and/or standard due to oxidation or other surface reactions; (3) contamination deposited on the sample and/or standard; (4) surface topography such as a scratch or pit; and (5) for an analytical total that falls below unity, the additional possibility of an unmeasured elemental constituent [2].

Thus, the reports by Gopon *et al.* [9] and Llovet *et al.* [10] of an unexpected and sharp departure of the analytical total from this range reveals a remarkable breakdown of standards-based analysis. Llovet *et al.* observed analytical totals greater than 1.2 (120 weight percent) at $E_0 = 6$ keV which gives an overvoltage $U_0 = 7.0$ for the Ni L₃ edge, where the overvoltage is defined as:

$$U_0 = (E_0/E_c) \quad (4)$$

E_0 is the incident beam energy and E_c is the excitation energy for the X-ray shell being measured. Moreover, large RDEV values were observed for the raw concentrations of Ni measured with the low energy L-shell X-ray but not for the corresponding concentration calculated for Si, which was measured with the K-shell X-ray. Unacceptably larger RDEV values persisted even after normalization was applied or conversion to atomic fractions. These deviations from conventional analytical experience were so severe as to render the results nearly useless. Llovet *et al.* [10] noted that the analytical total and RDEV problems may arise because the close proximity of the measured L-peaks to the L-shell absorption edges makes the calculation of mass absorption coefficients (MAC), which are critical to accurate calculation of the mass absorption factor, difficult. Indeed, when the Ni L₃-M₁ (Ni L ℓ) X-ray peak is used for analysis, which is a minor L-family member that is well separated from the L-edges and which can be measured by WDS because of its high spectral resolution, the analytical total and RDEV value are found to be reasonable.

In fact, Gopon and Llovet's work has brought new focus on a problem which was identified and then overlooked for decades. Pouchou [11] observed in 1996 similar issues with the Ni L-lines in the Ni-Al system. He measured the effective mass absorption coefficient for Ni L₃-M₅ changed from nominally 3300 cm²/g to 2304 cm²/g for NiAl and 2850 cm²/g for Ni₃Al.

This work examines the low energy L-shell analysis problem using energy dispersive X-ray spectrometry (EDS) rather than WDS. Several materials are analyzed that represent a range of low energy L-family peaks from Ti (L_3 - $M_{4,5}$, 0.452 keV) to Se (L_3 - $M_{4,5}$, 1.379 keV).

It is worthwhile to note that, for these elements, the full range of L-family lines arising from vacancies in the L_3 , L_2 and L_1 sub-shells and being filled by electrons from the M- and N-families of sub-shells are sufficiently close in energy that the peaks interfere when measured using a traditional energy dispersive detector. As a result, when the reference spectra are fit to the unknown spectra, the full range of L-family lines are fit as a single entity. The resulting k-ratio is a composite of the k-ratios for each individual line. When the matrix correction is performed, the matrix correction factor is a line-weight fraction weighed composite of the matrix correction factors for each line. In some cases, the matrix correction factor can differ by a factor of 2 or more when two characteristic X-ray lines are located on opposite sides of a strong absorption edge as often happens with lines resulting from L_2 and L_3 vacancies. This is distinctly different from a wavelength dispersive analysis in which only a very narrow range of energies is measured corresponding to one or a small number of characteristic X-rays with almost identical energy.

Materials and Methods

Materials examined include stoichiometric compounds procured from commercial vendors, microanalysis test materials of independently determined bulk composition and demonstrated micro-homogeneity, NIST reference materials, and specific materials synthesized such as an Ni-Si alloy with a composition selected to contain the stoichiometric phases NiSi and NiSi₂.

Electron-excited X-ray spectrometry was performed using two platforms: (1) a JEOL 8500F thermal field emission electron probe microanalyzer with a Bruker Quantax XFlash 6|30 silicon drift detector and (2) a TESCAN thermal field emission scanning electron microscope equipped with four 30 mm² Pulsetor Torrent silicon drift detectors.

EDS spectra were collected using Bruker Esprit software on the JEOL 8500F platform and exported in the ISO/EMSA standard [12] spectral format for subsequent quantitative processing with the NIST DTSA-II software [13]. For the TESCAN platform, EDS spectra were collected with Pulsetor SDDs and the NIST DTSA-II software [14] with the SEMantics extension [15], which was also used to process the spectra. For each measurement condition in this study, a sufficient electron dose was utilized so that the total spectrum count, integrated from a threshold of 0.1 keV to the incident beam energy, E_0 , exceeded 3 million counts, as listed in the tables of results.

Quantification with NIST DTSA-II proceeds in two stages: (1) peak fitting to extract the k-ratios for unknown and standards relative to references and (2) calculation of matrix correction factors to convert the measured k-ratios into mass concentrations. NIST DTSA-II uses the filter-fit linear least squares (FF-LLS) peak fitting method [16] to extract k-ratios. When processing EDS spectra, it is important to understand the distinction between a “peak fitting reference” and a “standard”. Our goal is to compare the intensity from the unknown to the intensity from a standard for a specific family of lines for a particular element. For electron-excited X-ray microanalysis, a “standard” is a material of known composition which is also homogeneous on a microscopic scale so that the same composition is sampled no matter where the beam is placed. However, peak fitting by FF-LLS can only proceed by fitting clean peak shapes free of interfering elements to the standard or unknown. The algorithm needs to know the shape of the collection of peaks independently for each element in the fit. A “peak shape reference” is a spectrum that can serve as this clear view. Many EDS quantitative software packages use modeled spectra as their peak shape reference but DTSA-II uses measured spectra because they represent higher fidelity representations of the peak shape leading to better accuracy. Pure element spectra can always act as references. Compounds can sometimes act as references for a specific set of an element’s lines if no other element in the compound has

characteristic lines near the element-of-interest's lines. (The precise definition of "near" depends on the resolution of the detector but is approximately the full-width half-maximum (FWHM) at the X-ray energy.) The "peak shape reference" will be fit to both the unknown and the standard producing two intermediary k-ratios, $k_{unk/ref}$ and $k_{std/ref}$. The k-ratio of the unknown relative to the standard is

$$k_{unk/std} = \frac{k_{unk/ref}}{k_{std/ref}} \quad (5)$$

Sometimes the standard spectrum has a clean, interference free representation of a family of peaks for the element of interest. In this case, the standard can be fit directly to the unknown and $k_{std/ref} = 1$. It can be helpful to think of a peak shape reference as a transfer standard to transfer the intensity information from the standard to allow comparison with the unknown.

An example of a material which could be used as a standard but is not suitable as a peak shape reference for the peak family including the Pb M₅-M₇ is PbS where the S K-family and the Pb M-family mutually interfere. To extract the intensity of the Pb M-family, a peak shape reference will be necessary for both the S K-family (like FeS₂) and Pb M-family (like pure Pb). However, PbS could act as a peak shape reference for the Pb L-family as there are no interferences between S and the Pb L-family. Note that a peak reference can be measured from material for which the composition is not accurately known, as long as that material 1) satisfies the interference-free requirement; and 2) has the element of interest in sufficient abundance to produce a high intensity peak or peak family.

Results and Discussion

Tables 1–20 present results for analysis with low energy L-family peaks of stoichiometric compounds and alloys for elements ranging from Ti to Se (with the exception of Mn for which a suitable binary sample containing Mn as a major constituent ($C > 0.1$) was not available). In all cases, there is an analysis with a pure element serving as the peak fitting reference and standard for the element measured with the low energy L-shell peak family. For most of these materials, analyses using the corresponding higher energy K-shell X-rays using pure element standards are also reported for comparison to the L-shell analyses. Additionally, for those examples where the pure element reference/standard produced anomalous results (i.e., where the analytical total deviates significantly from unity and/or there are large RDEV values), analyses are presented using stoichiometric compounds or known alloys as the peak fitting references and standards.

For each beam energy and analysis condition the following information is provided: (1) the raw analytical total; (2) the RDEV values for the raw and normalized mass concentrations, and (3) for those materials of known stoichiometry, the RDEV values for the atomic concentrations; (4) the overall uncertainty budget estimated with NIST DTSA-II[17] for the normalized mass concentration; (5) the relative standard deviation of the normalized mass concentration for multiple replicate measurements (three to seven); and (6) the mean integrated spectral count from a threshold energy of 0.1 keV to the incident beam energy, E_0 , to serve as a measure of the statistical quality of the EDS spectra (note that the counting statistics of the measured peak for the unknown and standard comprise a component of the DTSA-II uncertainty budget).

Summary of Analysis with Pure Element References/Standards

Ni - Si intermetallic compounds (Table 9)

NiSi

At a beam energy of 6 keV, EDS analysis of NiSi using the Ni L-shell and Si K-shell X-ray peaks with pure elements as peak references and standards gives an analytical total of 1.19 with RDEV values (raw mass concentration) of 0.06% for Si and 28% for Ni, which is similar to the results reported using WDS measurements reported by Llovet et al. [10]. Note that as the beam energy is further reduced, the analytical total and RDEV values decrease for analysis with the Ni L-shell X-rays, but even at the lowest beam energy used, $E_0 = 3$ keV, the analytical total is 1.12 with RDEV values of 6.7% for Si and 15% for Ni.

Increasing the beam energy results in larger RDEV values for Ni L-family analysis. At a beam energy of 15 keV, analysis using the Ni and Si K-shell X-ray peaks with pure elements as peak references and standards gives an analytical total of 0.9902 and RDEV values (raw mass concentration) of -0.23% for Si and -1.3% for Ni (after conversion to atomic concentrations, the RDEV values are 0.56% for Si and -0.56% for Ni). Analyzing these same 15 keV spectra using the Ni L-shell and Si K-shell X-ray peaks with pure elements as peak references and standards gives an analytical total of 1.45 with RDEV values (raw mass concentration) of 4.3% for Si and 65% for Ni.

NiSi₂

For the stoichiometric compound NiSi₂, similar trends are found. At $E_0 = 6$ keV, the analytical total is 1.17 with RDEV values (for the raw mass concentrations) of -4.0% for Si and 37% for Ni. At $E_0 = 3$ keV, the analytical total is 1.13 with RDEV values (for the raw mass concentrations) of 3.9% for Si and 21% for Ni.

Ni – Al intermetallic compounds (Table 10)

NiAl₃ and Ni₂Al₃

The anomalous analytical results found for analysis with the Ni L-shell are not unique to the Ni-Si system. Similar anomalies are observed for the Ni – Al intermetallic compounds NiAl₃ and Ni₂Al₃, presented in Table 10, with large deviations observed in the analytical total (at $E_0 = 6$ keV, 1.16 for NiAl₃ and 1.18 for Ni₂Al₃) and in the corresponding RDEV values for the raw mass concentrations: NiAl₃ (Al = 3.5%; Ni = 34%) and Ni₂Al₃ (Al = 5.7%; Ni = 27%).

NiT_i (Table 11)

Analysis of NiTi with the Ti K-family and Ni L-family from pure element standards is presented in Table 11. At $E_0 = 15$ keV the analytical total is 1.225 with RDEV values (raw mass concentrations) of 1% for Ti and 40% for Ni.

NiO (Table 12)

Compared to the other Ni-containing materials analyzed for this study, analysis of NiO does not show the extremes of deviation in the analytical total and RDEV values. At a beam energy of 15 keV, which corresponds to an overvoltage of 17.6 for the Ni L₃ ionization edge, the analytical total is 1.052 and the RDEV (raw mass concentration value) for Ni is 4.9% relative.

Ti – Se

Table 21 provides an overall summary of the results from Tables 1–20 for analysis at $E_0 = 15$ keV using low photon energy L-shell X-ray peaks with pure elements serving as the peak reference and standard. For L-shell analysis of elements lower in atomic number than nickel (28), reasonable analytical totals and modest RDEV values are found for titanium (TiSi₂); vanadium (V₃Si and V₅Si₃); chromium (50Cr-50Fe alloy, with Fe analyzed with the Fe K-shell X-rays as well as when analyzed with the L-family for both Cr and Fe); iron (Fe₂O₃ and 50Cr-50Fe alloy, with Cr analyzed with the Cr K-shell X-rays as well as when

analyzed with the L-family for both Cr and Fe). Anomalous analytical totals and large RDEV values are found for iron in FeAl_3 , Fe_2Al_5 , FeS , and FeS_2 , and cobalt in Co-Ta and Co-W alloys.

For elements above nickel in atomic number, the analytical totals and RDEV values at $E_0 = 15$ keV are well behaved for copper (Cu_2O , CuO , CuS and CuAu SRM alloys) and zinc (ZnS). For gallium, analysis of GaP gives a low total (0.9479) and RDEV (raw mass concentrations) of -4.5% for Ga and -6.7% for P, but after conversion to atomic concentrations the RDEV values are 1.2% for Ga and -1.2% for P. Germanium is an exception to this trend: analysis of GeTe gives a total of 0.9355 with most of the deviation occurring in Ge (raw mass concentration RDEV = -21% relative) compared to Te (raw mass concentration RDEV = 1.6% relative). For heavier elements, e.g., As, Se, and beyond, analysis with L-shell X-rays from pure element standards does not reveal significant anomalies in the analytical total and the RDEV values.

Summary of Analysis with Compound References/Standards

Table 22 provides an overall summary of the results from Tables 1–20 for analysis at $E_0 = 15$ keV using stoichiometric compounds and alloys as the L-shell peak reference and standard for those materials in Table 21 that showed anomalous analytical totals and large RDEV values when using pure elements as the peak reference and standard for the L-family. For all materials tested except for FeS , discussed further below, the use of compound standards yielded analytical totals much closer to unity and significantly reduced the RDEV values for the raw mass concentrations. In nearly all cases, normalization of the mass concentrations or normalization by conversion to atom concentrations resulted in RDEV values below 5% relative.

The standard matters much more than the peak fitting reference

After fitting the designated peak or peak family to extract the characteristic X-ray intensities, DTSA-II constructs the “peak fitting residual spectrum” which reveals the intensity that remains in each channel under the fitted peak(s) after removing the characteristic intensity in the k-ratio scaled reference spectrum. The peak fitting residual spectra for the Ni L-family region for NiSi with various peak reference spectra (derived from Ni, NiAl_3 , NiTi, and NiSi_2) are shown in Figure 1. The different peak reference spectra result in variations in the peak fitting residual spectra that indicate there are differences in the relative heights of the L-family absorption edges in each material relative to NiSi. While these variations appear dramatic with the expanded intensity scales shown in Figures 1(a) to 1(e), when the intensity scale is chosen to show the entire Ni L-family peak structure in Figure 1(f), the variation in the background of the peak fitting residual spectra is seen to be much less significant. Quantitatively, the net Ni L-family intensity after subtracting each residual fitting spectrum from the original spectrum changes by 6% from the lowest background (fitting reference from NiTi) to the highest background (fitting reference from pure Ni). Similar results are shown for GeTe in Figure 2, which compares the fitting of the Ge L-family using Ge and SRM 1872 as the peak fitting references.

While the analytical results are relatively insensitive to the peak shape reference, the choice of the standard has a strong effect on the accuracy. Table 9 presents the analysis of NiSi at $E_0 = 10$ keV with pure Ni as peak reference and standard, which gives the analytical total = 1.321 and Ni RDEV = 47% (raw mass concentration). When NiAl_3 is used as the peak fitting reference and Ni is the standard, the results are similar: the analytical total = 1.328 and the Ni RDEV = 48% (raw mass concentration). When NiAl_3 is used as the peak reference and standard, the analytical total is 1.0109 and the Ni RDEV = 2.0% (raw mass concentration = 0.6896). Choosing Ni as the peak reference and NiAl_3 as the standard gives virtually the same results: the analytical total = 1.0110 and the Ni RDEV = 2.0% (raw mass concentration = 0.6897).

Similar results are found for GeTe, as presented in Table 18. For analysis at $E_0 = 20$ keV, the use of Ge as the peak reference and standard for Ge L-family analysis gives the analytical total = 0.9074 and Ge RDEV = -28% (raw mass concentration = 0.2616), while the use of SRM 1872 (O-Ge-Pb glass K453) for the peak reference and standard for the Ge L-family gives the analytical total = 1.021 and Ge RDEV = 1.2% (raw mass concentration = 0.3673). Using SRM 1872 as the peak fitting reference and Ge as the standard gives the analytical total = 0.9120 and Ge RDEV = -27% (raw mass concentration = 0.2659). Using Ge as the peak fitting reference and SRM 1872 as the standard gives the analytical total = 1.022 and Ge RDEV = 1.3% (raw mass concentration = 0.3675).

An unexpected and curious counter example: Can FeS and FeS₂ serve as standards for each other?

As listed in Table 6, over the beam energy range from 20 keV to 5 keV, analysis of FeS₂ and FeS using the Fe L-family peaks from pure Fe results in analytical totals that deviate significantly from unity with large RDEV values for Fe in both FeS₂ and FeS. The interesting exception to this trend is that of FeS analyzed at 5 keV where the analytical total is 1.013 and the RDEV value (raw mass concentration) is less than 2% relative. Analysis of FeS₂ with compound standards, FeAl₃ or Fe - Cr alloy, produces reasonable analytical totals and low RDEV values over the full range of beam energy, but analysis of FeS using the same compound standards does not produce reasonable analytical totals and RDEV values, even at 5 keV.

It seems reasonable to ask, can FeS and FeS₂ serve as standards for each other? Based on the 70-year history of quantitative electron-excited X-ray microanalysis following the standards-based k-ratio (matrix corrections) protocol, this question would seem to be absurd! Surely two binary materials as similar in composition as FeS and FeS₂ should be able to serve as standards for each other. Indeed, as listed in Table 23, when using the Fe K-L_{2,3} (Fe K α) peak for analysis, FeS and FeS₂ are excellent mutual standards: the analytical totals are close to unity and the RDEV (raw mass concentration) are consistently under 1 percent relative over the energy range from 20 keV down to 10 keV. However, when iron is analyzed using the Fe L-family with FeS₂ and FeS serving as mutual standards over the beam energy range from 20 keV down to 5 keV, both FeS₂ and FeS show anomalous analytical totals and large RDEV values: analytical totals from 1.231 – 1.137 and RDEV ranging from 47% – 27% for Fe in FeS₂ and analytical totals ranging from 0.7803 – 0.8660 and RDEV ranging from -33% – -20% for Fe in FeS, even as the beam energy is reduced to 5 keV.

What does visual inspection of the original and fitting-residual spectra for FeS and FeS₂ reveal? Figure 3 shows FeS and FeS₂ spectra measured at a beam energy of 15 keV for the same dose. The Fe K-L_{2,3} (Fe K α) peak and the S K-family peaks scale in a fashion consistent with the stoichiometric formulae, Figures 3(a) and 3(b). However, the Fe L-family does not scale in a consistent fashion, Figures 3(c) and 3(d). For spectra collected under the same dose conditions, the Fe L-family intensity for the Fe L₃-M_{4,5} (Fe L α,β) peaks after fitting with elemental Fe as the reference differ by less than 2% (FeS = 3,239,000 counts; FeS₂ = 3,302,000 counts; FeS₂/FeS = 1.019) despite the significant change in Fe concentration in FeS and FeS₂. As listed in Table 24, the DTSA-II results, including the ZAF factors, for these spectra produce similar k-ratios (relative to Fe: 0.4322 for FeS and 0.4405 for FeS₂) and thus similar concentration values for Fe (0.5215 for FeS and 0.5420 for FeS₂), which yields large RDEV values for both compounds (-18% for FeS and 16% for FeS₂).

Inspection of the Fe L-family peaks in the expanded spectra shown in Figure 3(d) shows significant differences in the shape of the family, particularly in the relative intensities of the Fe L₃-M₁ (L ℓ) peak in the FeS and FeS₂ spectra. There may be several reasons for these changes in the Fe L-family X-rays between two such similar materials. (1) Mass absorption coefficients: As noted by in the Llovet et al. [10] study of Ni-Si compounds, calculating accurate mass absorption coefficients near absorption edges is problematic; The assumption of a mass concentration-based additive model for calculating the mass

absorption coefficient of a compound, which works well for high energy photons, may fail for low photon energies. (2) “Chemical effects” involving changes in the valence level electrons are possible with the energy of the Fe L-photons at approximately 700 eV, leading to modifications in the Coster-Kronig and Auger yields. The emission of fewer X-rays and more Auger electrons could explain why the FeS spectrum is similar to FeS₂. If this were the case, it would seem that the largest effect must be Auger yields changing since the integrated area is changing along with the peak shape.

Summary

Quantitative electron beam X-ray microanalysis performed with energy dispersive spectrometry for elements analyzed with low photon energy L-shell X-ray peaks can show anomalous analytical totals and large RDEV values for certain materials.

(1) The analysis excursions previously reported for Ni-Si intermetallic compounds with WDS analysis have been confirmed for EDS analysis and also found for Ni-Al intermetallic compounds and NiTi.

(2) Similar excursions occur for some elements, e.g., Fe, Co, Ni, and Ge, but within set of materials available for this study, not all combinations of elements produced the excursions for a given element. Thus, for Ni-containing compounds, excursions were observed for Ni-Si, Ni-Al, and NiTi intermetallic compounds but not for NiO. Similarly, elemental Fe was satisfactory for Fe₂O₃ but gave poorer accuracy for FeAl₃ and Fe₂Al₅.

(3) For the limited range of materials tested, elemental standards gave reasonable analytical totals over the beam energy range from 5 keV to 20 keV despite high overvoltage for the L-family X-ray: TiSi₂, V₃Si and V₅Si₃, Fe₂O₃, 50Cr-50Fe alloy, NiO, Cu₂O, CuO, CuS, Cu-Au alloys, ZnS, GaP, As₂Te₃, and CdSe.

(4) For most cases where an elemental standard for L-family analysis proved unsatisfactory, it was found that a compound standard produced much better accuracy in both the analytical total and the RDEV values, even at high overvoltage. Among the suite of materials analyzed, FeS was found to be an unexpected exception to this observation since compound standards were found to be satisfactory for FeS₂.

(5) FeS and FeS₂ cannot serve as mutual standards when analysis is attempted with the Fe L-family, producing large deviations from unity in the analytical total and large RDEV values over the beam energy range tested, 5 keV – 20 keV. While other binary compound standards, e.g., FeAl₃ and Fe-Cr alloy, are suitable for FeS₂, these materials are not satisfactory standards for FeS.

Analytical Strategy for Low Photon Energy L-family X-ray Peaks

Based upon the observations of this study, the following analytical strategy is recommended:

1. If analytical conditions permit, the use of the K-shell X-ray peak(s) for an element, even at low overvoltage, is more likely to yield accurate analytical results than the use of the corresponding low photon energy L-family peaks, especially if only pure elements are available as standards.
2. If a beam energy must be used that only allows analysis with an element’s low photon energy L-family peaks, then inspection of the raw analytical total for significant deviations from unity can provide an indication of possible excursions in the RDEV values for that element.
3. For those materials tested in this study, when the use of a pure element for the L-family standard produced poor accuracy, the use of a compound standard containing the element of interest has been found to significantly improve the analytical results for the analytical total and the RDEV (raw mass concentration) for that element. FeS proved to be an exception to this observation on the utility of compound standards, and of course there may be other materials that show this unexpected effect.

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Table Captions

Table 1	TiSi ₂ (standards Ti, Si)
Table 2	V ₃ Si and V ₅ Si ₃ (standards: V, Si)
Table 3	50Cr-50Fe alloy (standards: Cr, Fe)
Table 4	Fe ₂ O ₃ (standards: MgO, Fe)
Table 5	FeAl ₃ and Fe ₂ Al ₅ (standards: Al, Fe, FeS ₂)
Table 6	FeS ₂ and FeS (standards: CuS, Fe, FeAl ₃ , 50Cr-50Fe alloy)
Table 7	Co - Ta alloy (standards: Co, Ta, Co-W alloy)
Table 8	Co - W alloy (standards: Co, W, Co - Ta alloy)
Table 9	NiSi and NiSi ₂ (standards: Si, Ni, NiTi, NiAl ₃)
Table 10	NiAl ₃ and Ni ₂ Al ₃ (standards: Al Ni, NiSi, NiTi)
Table 11	NiTi (standards: Ti, Ni, TiSi ₂ , NiAl ₃ , Ni ₂ Al ₃)
Table 12	NiO (standards: Ni, MgO)
Table 13	Cu ₂ O and CuO (standards: Cu, MgO)
Table 14	CuS (standards: Cu, FeS ₂)
Table 15	Cu-Au NIST SRM 482 Alloys (standards: Cu, Au)
Table 16	ZnS (standards: Zn, FeS ₂)
Table 17	GaP (standards: Ga, GaSb, Ca ₅ (PO ₄) ₃ F)
Table 18	GeTe (standards: Ge, Te, NIST SRM 1872 Ge-Pb-O glass)
Table 19	As ₂ Te ₃ (standards: As, Te, GaAs)
Table 20	CdSe (standards: Cd, Se)
Table 21	Summary of Analysis at E ₀ = 15 keV with Elemental Standards for L-shell X-rays
Table 22	Summary of Analysis at E ₀ = 15 keV with Compound Standards for L-shell X-rays
Table 23	Analysis of FeS and FeS ₂ serving as mutual standards
Table 24	DTSA-II Analysis at E ₀ = 15 keV of FeS and FeS ₂

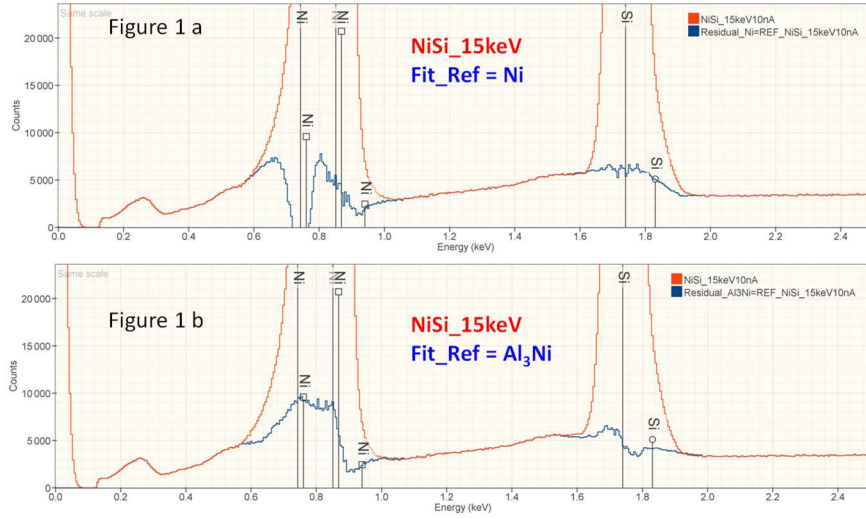


Figure 1: NiSi at $E_0 = 15$ keV: (a) original spectrum and peak fitting residual with elemental Ni as the peak fitting reference; (b) original spectrum and peak fitting residual with Al_3Ni as the peak fitting reference.

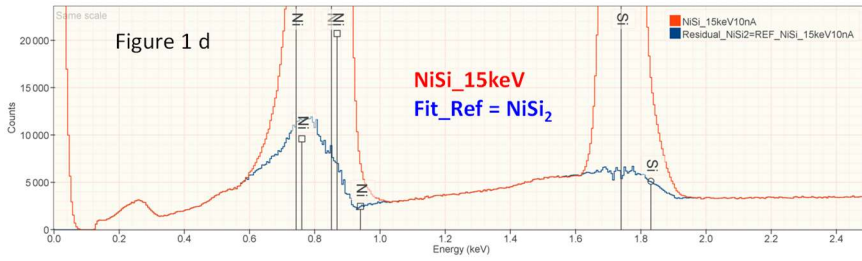
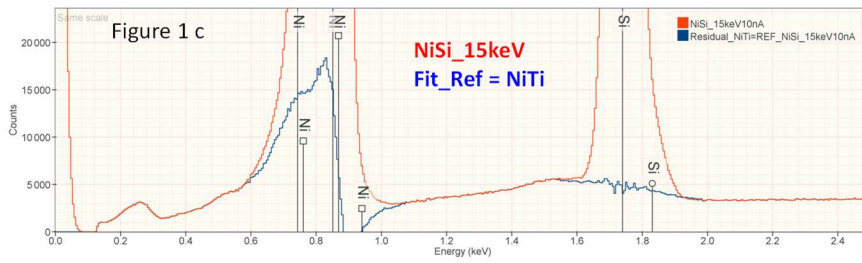


Figure 1: NiSi at $E_0 = 15$ keV: (c) original spectrum and peak fitting residual with NiTi as the peak fitting reference; (b) original spectrum and peak fitting residual with NiSi₂ as the peak fitting reference.

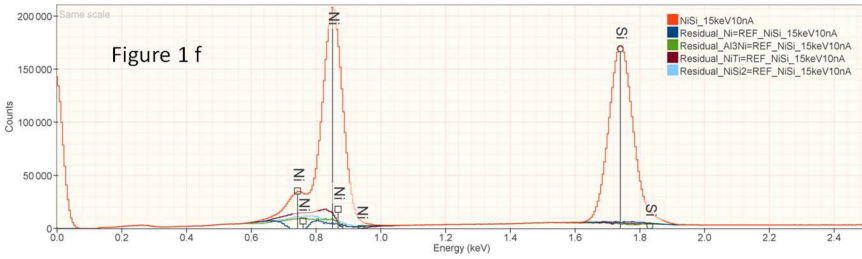
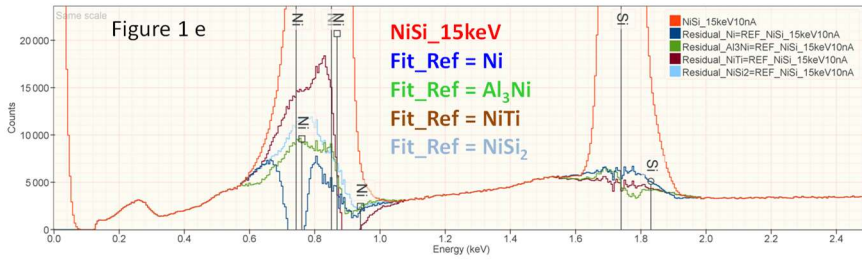


Figure 1: NiSi at $E_0 = 15$ keV: (e) original spectrum and peak fitting residuals with Ni, Al₃Ni, NiTi and NiSi₂ as the peak fitting references; (f) same as 1(e) but using the Ni L-family to define the vertical scale.

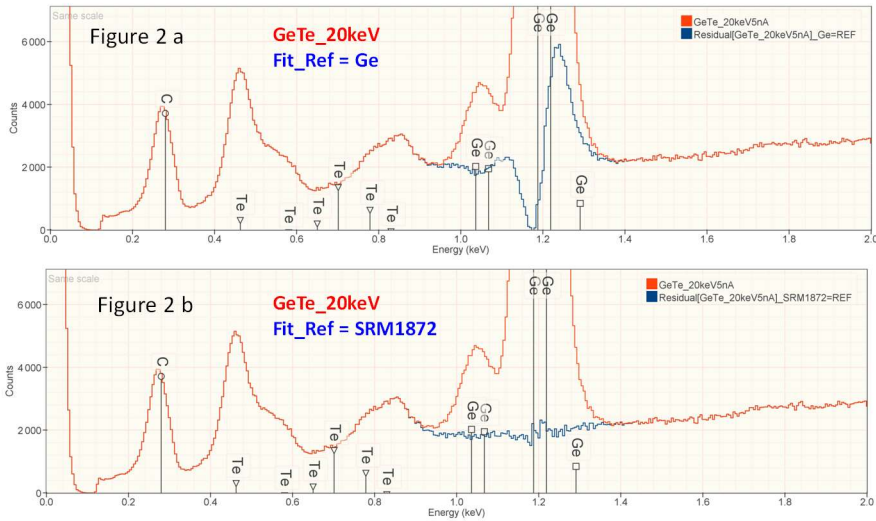


Figure 2: GeTe at $E_0 = 20$ keV: (a) original spectrum and peak fitting residual with Ge as the peak fitting reference; (b) original spectrum and peak fitting residual with Ge in SRM 1872 (O-Ge-Pb glass) as the peak fitting reference.

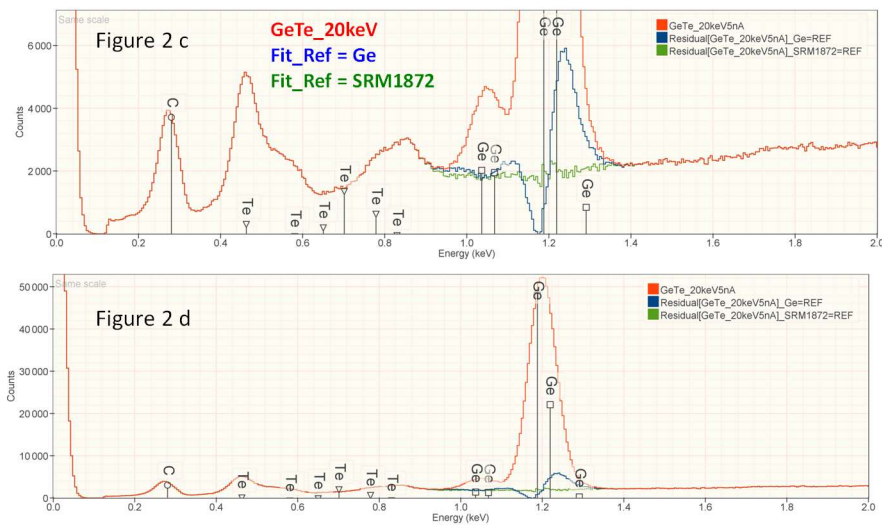


Figure 2: GeTe at $E_0 = 20$ keV: (c) original spectrum and peak fitting residuals with Ge and with Ge in SRM 1872 (O-Ge-Pb glass) as the peak fitting references; (d) same as 2(c) but with the Ge L-family peak used to define the vertical scale.

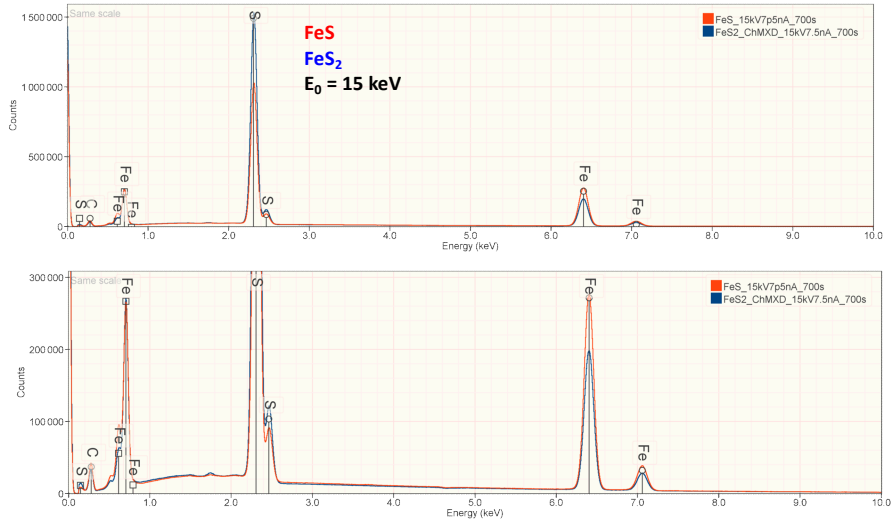


Figure 3. FeS and FeS₂ measured at E₀ = 15 keV (a) Photon energy range 0 – 10 keV, full intensity scale; (b) intensity scale expanded to show Fe K-family and Fe L-family.

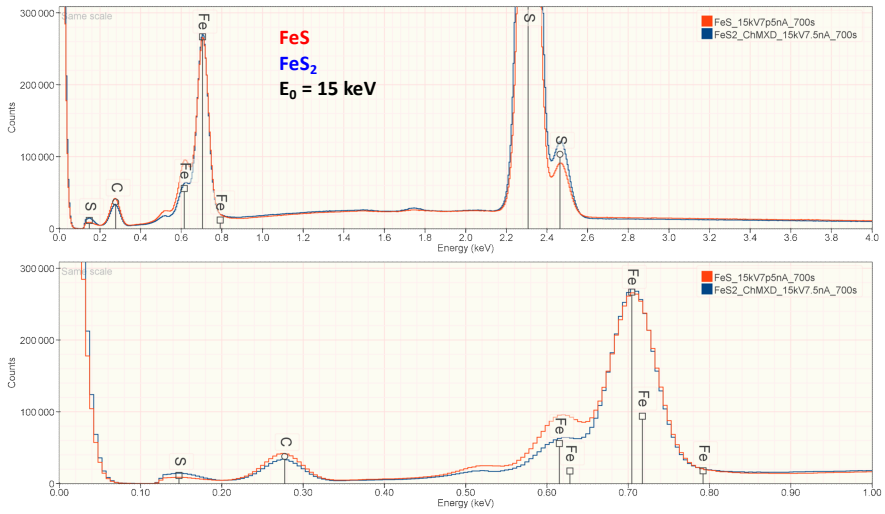


Figure 3. FeS and FeS₂ measured at E₀ = 15 keV (c) Photon energy range 0 – 4 keV, expanded intensity scale; (d) photon energy range 0 – 1 keV, expanded intensity scale to show the Fe L-family.

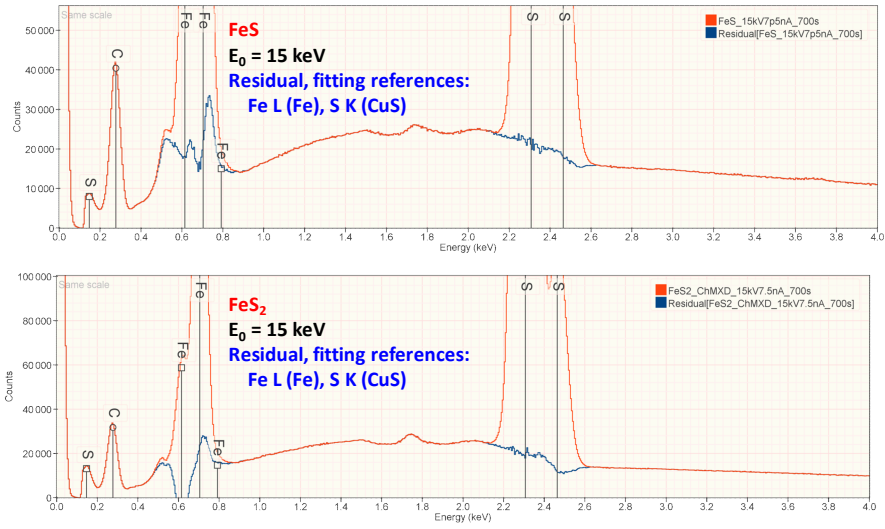


Figure 4. FeS and FeS₂ measured at $E_0 = 15$ keV showing the residual spectra after peak fitting with the reference for the Fe L-family derived from elemental Fe (S K-family reference from CuS).