

Quantitative Electron-excited X-ray Microanalysis with Low Energy L-Peaks

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Quantitative electron-excited X-ray microanalysis following the standards-based intensity-ratio (“k-ratio”) method with matrix corrections, as originated by Castaing, is capable of achieving high accuracy results [1,2]. When tested against known homogeneous materials, 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 of ± 5 % (RDEV = $\{[\text{measured value} - \text{reference value}]/\text{reference value}\} * 100$ %) [3]. Achieving this accuracy requires only a simple standards suite that consists of pure elements, and for those elements that are reactive, e.g., Ca, gaseous, e.g., F, or degrade under electron bombardment, e.g., S, a stoichiometric compound can be utilized, e.g., CaF_2 , FeS_2 , etc. Because each constituent is measured against its own standard, the raw analytical total, which is the sum of all constituents including any such as O 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. Excursions outside this range may indicate a deviation in measurement conditions, the presence of a surface layer due to oxidation or contamination on the sample and/or standard, or for totals below unity, the additional possibility of an unmeasured constituent [4]. Thus, the report by Llovet et al. [5] of an unexpected and sharp departure of the analytical total from this range when analyzing a series of Ni-Si intermetallic compounds with the Ni L_3 - $M_{4,5}$ peak at 0.851 keV, as measured with wavelength dispersive spectrometry (WDS) against pure element standards, reveals a remarkable breakdown of standards-based analysis. This presentation examines the analysis of several materials representing a range of low energy L-family peaks from Fe (L_3 - $M_{4,5}$, 0.704 keV) to Se (L_3 - $M_{4,5}$, 1.379 keV) as measured with energy dispersive spectrometry (EDS) and quantified with NIST DTSA-II [6].

Table 1 presents EDS results for NiSi and NiSi₂, analyzed with pure Ni and Si as the peak fitting references and standards. Using the Ni L-family, extreme deviations from a unity analytical total are observed, with the deviation increasing as the beam energy (and overvoltage) increases. (Note that analyzing these same spectra with the Ni K-family resulted in analytical totals near unity and small RDEV values.) The analytical totals are so extreme that only by calculating normalized mass concentrations can the concentrations be sensibly compared for measurements at different beam energies. Even after normalization, the RDEVs of the normalized mass concentrations for Ni show such large deviations from the ideal composition as to greatly diminish the utility of the analytical results for practical applications. Similar behavior is found in Table 1 for analysis of alloys and stoichiometric compounds using the low energy L-family peaks for Fe, Co, and Ge when a pure element serves as the fitting reference and standard. However, as shown in Table 2, when the L-shell element of interest is analyzed with that element in a stoichiometric compound or a multi-element glass serving as the peak fitting reference and standard, the analytical totals are generally brought back into an acceptable range near unity and the RDEV values generally fall within ± 5 %, with a few exceptions. Note the magnitude of this effect: for example, for NiSi at 10 keV (overvoltage $U_{\text{NiL}} = 11.7$) the analytical total for L-family analysis with pure Ni is 1.607 with an RDEV of 11 % for Ni while with Al₃Ni the total is 1.015 with an RDEV of 0.9 %. For the systems examined in this study, the use of compound standards provides a huge improvement in the analytical total and the RDEV for analysis with the low energy L-family X-rays. The origin of the obvious

disconnection between the use of pure element standards and compound standards is the subject of continuing research.

Table 1 Analysis of various materials using the L-family and pure elements as peak fitting references and standards

Analyzed material	Peak Fitting Reference	Standard	L-3 energy	Beam energy (keV)	L-overvoltage	Analytical total	RDEV (norm mass conc) L
NiSi	Ni	Ni	0.853	15	17.6	2.229	34 %
NiSi	Ni	Ni	0.853	10	11.7	1.607	11 %
NiSi	Ni	Ni	0.853	5	5.9	1.186	6.7 %
NiSi ₂	Ni	Ni	0.853	15	17.6	3.327	31 %
NiSi ₂	Ni	Ni	0.853	10	11.7	1.687	25 %
NiSi ₂	Ni	Ni	0.853	5	5.9	1.169	16 %

FeAl ₃	Fe	Fe	0.708	20	28.2	1.294	4.7 %
FeAl ₃	Fe	Fe	0.708	15	21.2	1.198	6.6 %
FeAl ₃	Fe	Fe	0.708	10	14.1	1.128	8.5 %
Co-Ta alloy	Co	Co	0.779	15	19.3	1.555	8.8 %
Co-Ta alloy	Co	Co	0.779	10	12.8	1.406	9.0 %
Co-Ta alloy	Co	Co	0.779	5	6.4	1.207	5.8 %
GeTe	Ge	Ge	1.217	20	16.4	0.8373	-30 %
GeTe	Ge	Ge	1.217	15	12.3	0.9073	-19 %
GeTe	Ge	Ge	1.217	10	8.2	0.9595	-10 %

Table 2 Analysis of various materials using the L-family and mixtures as peak fitting references and standards

Analyzed material	Peak Fitting Reference	Standard	L-3 energy	Beam energy (keV)	L-overvoltage	Analytical total	RDEV (norm mass conc) L
NiSi	Al ₃ Ni	Al ₃ Ni	0.853	15	17.6	1.087	1.2 %
NiSi	Al ₃ Ni	Al ₃ Ni	0.853	10	11.7	1.015	0.9 %
NiSi	Al ₃ Ni	Al ₃ Ni	0.853	5	5.9	1.014	0.32 %
NiSi ₂	Al ₃ Ni	Al ₃ Ni	0.853	15	17.6	1.097	9.9 %
NiSi ₂	Al ₃ Ni	Al ₃ Ni	0.853	10	11.7	1.040	7.3 %
NiSi ₂	Al ₃ Ni	Al ₃ Ni	0.853	5	5.9	1.018	5.6 %
			0.708	20	28.2	1.043	-1.9 %

FeAl ₃	FeS ₂	FeS ₂					
FeAl ₃	FeS ₂	FeS ₂	0.708	15	21.2	1.011	-2.4 %
FeAl ₃	FeS ₂	FeS ₂	0.708	10	14.1	0.9874	-3.4 %
Co-Ta alloy	Co-W alloy	Co-W alloy	0.779	15	19.3	1.016	-1.6 %
Co-Ta alloy	Co-W alloy	Co-W alloy	0.779	10	12.8	1.009	0.22 %
Co-Ta alloy	Co-W alloy	Co-W alloy	0.779	5	6.4	1.034	-3.0 %
GeTe	Ge	SRM1872	1.217	20	16.4	1.011	-3.1 %
GeTe	Ge	SRM1872	1.217	15	12.3	1.028	-0.09 %
GeTe	Ge	SRM1872	1.217	10	8.2	1.015	-1.7 %

References

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