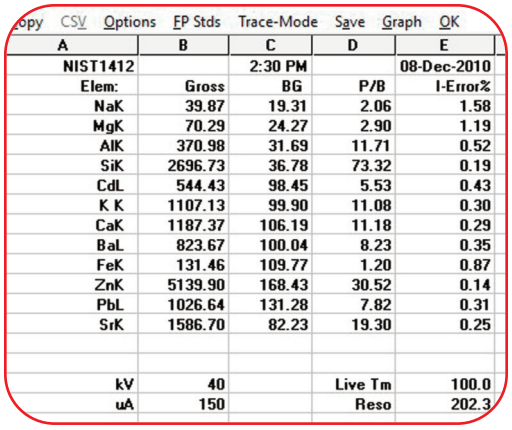
Spectral Background Fitting and Peak Noise Statistics

X-ray Fluorescence (XRF) background fitting can be done in a variety of ways including fully mathematical methods and fully manual methods. Manual methods allow the user to define side bands around the peaks of interest and can be quite effective in certain applications. Mathematical methods can be effective in separating the background component from the characteristic XRF signal peaks. However, depending on the sample matrix, there can be regions of the background that are not well-behaved, resulting in some small overfit or underfit. For trace elemental analysis, no matter the background fitting method, there will always be some noise associated with peak fitting and the question becomes "when is an XRF peak a peak?".

EDAX has provided some tools in its XRF software to assist with addressing this question. In the output of spectral intensity or quantification calculations, there is a column labeled "I-Error %" (Figure 1).



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A	B	C	D	E
NIST1412		2:30 PM		08-Dec-2010
Elem:	Gross	BG	P/B	I-Error%
NaK	39.87	19.31	2.06	1.58
MgK	70.29	24.27	2.90	1.19
AlK	370.98	31.69	11.71	0.52
SiK	2696.73	36.78	73.32	0.19
CdL	544.43	98.45	5.53	0.43
K K	1107.13	99.90	11.08	0.30
CaK	1187.37	106.19	11.18	0.29
BaL	823.67	100.04	8.23	0.35
FeK	131.46	109.77	1.20	0.87
ZnK	5139.90	168.43	30.52	0.14
PbL	1026.64	131.28	7.82	0.31
SrK	1586.70	82.23	19.30	0.25
kV	40		Live Tm	100.0
uA	150		Reso	202.3

Figure 1. Orbis Vision software Intensity Results.

The I-Error % is the relative error ratioing the calculated peak's standard deviation to the peak intensity. For a Gross Region of Interest (ROI) peak, where the peak is simply the summation of all the X-ray events within a defined ROI, the relative error can be calculated as follows:

I-Error% = 100 * (Gross CPS)$^{0.5}$ / (Gross CPS) / (Live Time)$^{0.5}$
= 100 * {Standard Deviation) / {Gross CPS}
where CPS is X-ray Counts per Second

For Net peak intensities where the background is fitted and the background intensity is subtracted from the Gross ROI intensity, the relative peak error is:

I-Error% = 100 * (Net CPS + Bkg CPS)$^{0.5}$ / (Net CPS) / (Live Time)$^{0.5}$
= 100 * {Standard Deviation} / {Net CPS}

The I-Error%, being equal to one relative standard deviation, is useful in determining if the user is making a measurement with acceptable statistical significance.

Acceptable peak statistics may vary depending on the quality of the background and the ability of the background fitting routine to fit the background reliably. There are cases where automated background fitting routines have trouble fitting a spectral background that does not vary smoothly, leading to underfit or overfit. In these cases, it may be beneficial to switch to a manual background fit, employ a primary-beam filter, or use the quantification threshold function. A quantification threshold allows the user to assign an intensity threshold below which the Orbis Vision software will remove the elemental peak from quantification calculations.

In the Orbis Vision software, the quantification threshold functions are set in the Quantification Parameter Table, which is accessed from the "Setup" options under "Edit Table". There are two different thresholds shown in columns "Sigma" and "Thres.Cts", with default settings of 6 and 0, respectively. The Sigma parameter is used in a statistical threshold defined in the following equation:

$$N_{Threshold} = \sigma \times \sqrt{2 \times \frac{Bkg}{Live\ Time}}$$

where:

σ = sigma factor (column I in Edit Parameters Table), set to 6 as default

Bkg = background [CPS]

Live Time = Live Time of the measurement [s]

$N_{Threshold}$ = Statistical Intensity Threshold [CPS]

This statistical threshold accounts for statistical noise in the background. The Threshold Counts is simply a value in CPS to take account of when the background is under fit and an erroneous peak intensity is generated as a result.

If the Threshold CPS is set to zero, then the routine will use the statistical threshold, otherwise it will use the Threshold CPS setting. Elements with peak intensities below the applicable threshold will be reported as "< MDL" in the quantitative results. In any given application, some initial measurements need to be made to determine the appropriate values for intensity errors in accessing the statistical significance of a peak or for the thresholding factors.