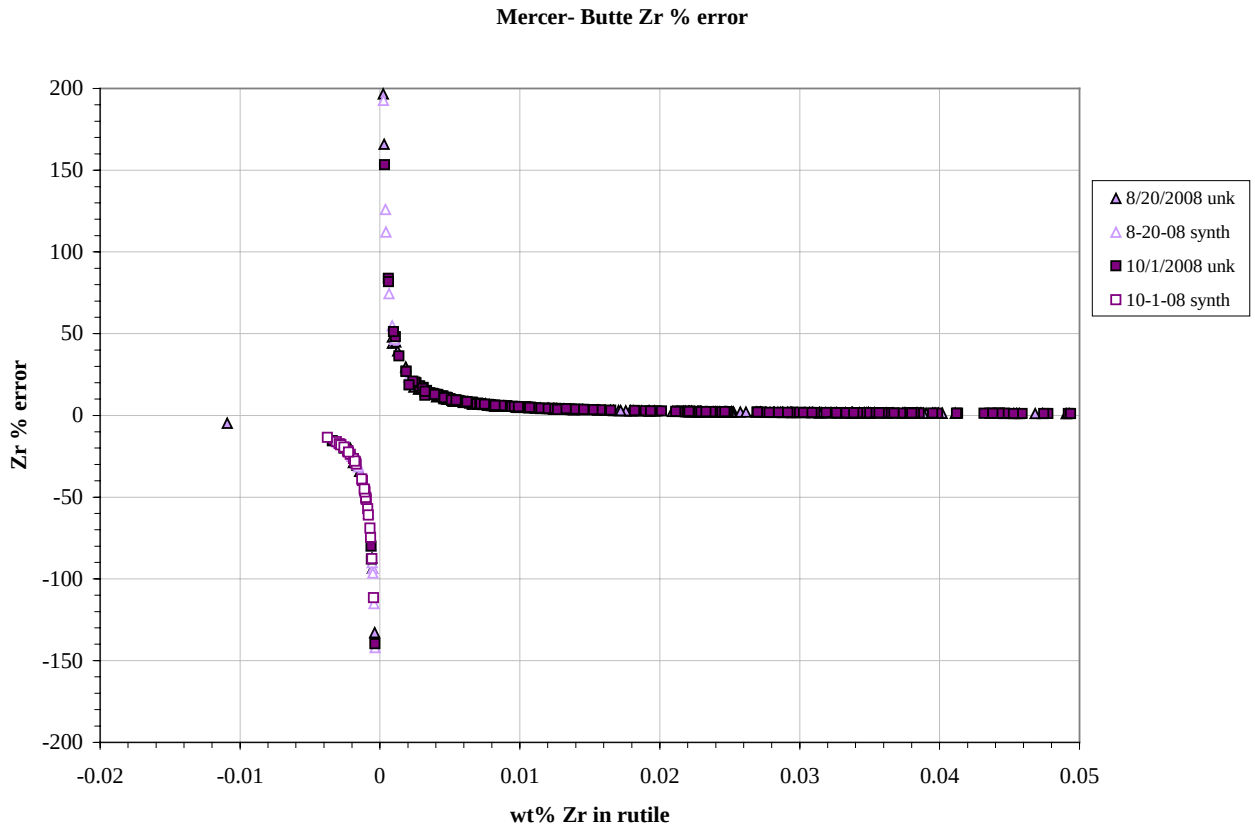
Trace Element Analysis of Rutile, Effects of intensity corrections on the analytical sensitivity calculations

When performing minor and especially trace element analyses, one must perform significant corrections to the x-ray intensities to correct for various spectral and sample artifacts such as interferences, peak shape changes, time dependent intensity, continuum artifacts and other accuracy corrections.

However, if analytical sensitivity calculations utilize the measured peak and background intensities rather than the accuracy corrected intensities, a significant error in the calculation will be introduced especially as the peak intensity is adjusted to be similar to the background intensity.

Properly calculated analytical errors should all fall on a smooth curve regardless of concentration:



The secondary curve in the lower left are negative concentrations (unavoidable when attempting to measure concentrations that are close to zero).

The form of the analytical sensitivity calculation often takes the form of:

$$\varepsilon_{P-B} = \frac{\sqrt{\frac{N_P}{t_P^2} + \frac{N_B}{t_B^2}}}{\left(\frac{N_P}{t_P} - \frac{N_B}{t_B}\right)}$$

Where : N_P is the total peak counts

N_B is the total background counts

t_P is the peak count time

t_B is the background count time

From "Scanning Electron Microscopy and X-Ray Microanalysis" by Goldstein, et. al. (Plenum Press, 1992 ed., 1981) p. 432 – 436.

In the following example, neither an interference nor "blank" correction is applied to the measured intensities and the composition and analytical sensitivities are calculated as:

ELEM:	Zr	Zr	Fe	Ta	Nb	W	SUM
XRAY:	(la)	(la)	(ka)	(ma)	(la)	(la)	
1388	.02721	.00000	2.48450	.04709	2.05769	.77572	100.000
1389	.03717	.00000	1.73062	.09594	1.39664	1.13171	100.000
1390	.03480	.00000	5.37609	.07497	1.22065	1.71276	100.000
1391	.03874	.00000	1.68135	.04556	.90801	1.62877	100.000
1392	.02842	.00000	2.15875	.05588	.71476	2.45537	100.000
1393	.01120	.00000	1.55285	.03876	.31754	.93811	100.000
AVER:	.02959	.00000	2.49736	**.05970**	1.10255	1.44041	100.000
SDEV:	.01013	.00000	1.45243	.02172	.60286	.62116	
SERR:	.00414	.00000	.59295	.00887	.24612	.25359	
%RSD:	34.2	.5	58.2	36.4	54.7	43.1	
STDS:	257	257	395	573	541	574	
ZCOR:	1.1607	1.1607	1.1325	1.2505	1.1308	1.5525	
KRAW:	.00061	.00000	.03257	.00048	.00982	.00933	
PKBG:	1.27593	.00000	14.2067	1.17394	7.68654	2.19645	

Percent Analytical Relative Error (One Sigma, Single Line):

ELEM:	Zr	Zr	Fe	Ta	Nb	W
1388	2.0	.0	.2	3.8	.3	.9
1389	1.5	.0	.2	1.9	.4	.7
1390	1.6	.0	.1	2.4	.4	.5
1391	1.4	.0	.2	3.9	.5	.5
1392	1.9	.0	.2	3.2	.6	.4
1393	4.7	.0	.2	4.5	1.1	.8
AVER:	2.2	.0	.2	**3.3**	.6	.6
SDEV:	1.2	.0	.0	1.0	.3	.2
SERR:	.5	.0	.0	.4	.1	.1

Note that the Ta concentration is 0.05970 wt. % and the analytical sensitivity is calculated at 3.3 % relative error. The next example shows the effect when the interference correction is applied (Fe and W interfere with Ta):

ELEM:	Zr	Zr	Fe	Ta	Nb	W	SUM
XRAY:	(la)	(la)	(ka)	(ma)	(la)	(la)	
1388	.02204	.00000	2.48456	.04237	2.05765	.77574	100.000
1389	.02963	.00000	1.73068	.09015	1.39661	1.13175	100.000
1390	.02339	.00000	5.37640	.06462	1.22060	1.71286	100.000
1391	.02789	.00000	1.68143	.03769	.90798	1.62885	100.000

```
  1392  .01206  .00000 2.15890  .04423  .71473 2.45554 100.000
  1393  .00495  .00000 1.55289  .03389  .31753  .93813 100.000

AVER:   .01999  .00000 2.49748  .05216 1.10252 1.44048 100.000
SDEV:   .00959  .00000 1.45253  .02145  .60285  .62122
SERR:   .00392  .00000  .59299  .00876  .24611  .25361
%RSD:     48.0      .5    58.2    41.1    54.7    43.1
STDS:      257     257     395     573     541     574

ZCOR:  1.1607  1.1607  1.1325  1.2506  1.1308  1.5526
KRAW:   .00041  .00000  .03257  .00042  .00982  .00933
PKBG:  1.18655  .00000 14.2067 1.15189 7.68654 2.19645
INT%:   -35.57    ----    ----  -13.42    ----    ----

Percent Analytical Relative Error (One Sigma, Single Line):

ELEM:       Zr      Zr      Fe      Ta      Nb       W
  1388     2.5      .0      .2     4.2      .3      .9
  1389     1.8      .0      .2     2.0      .4      .7
  1390     2.3      .0      .1     2.8      .4      .5
  1391     1.9      .0      .2     4.6      .5      .5
  1392     4.4      .0      .2     4.0      .6      .4
  1393    10.4      .0      .2     5.1     1.1      .8

AVER:      3.9      .0      .2     3.8      .6      .6
SDEV:      3.3      .0      .0     1.2      .3      .2
SERR:      1.4      .0      .0      .5      .1      .1
```

With the Ta composition now at 0.05216 wt. %, the analytical error is now 3.8 %, which is a small increase in the right direction since the Ta intensity has decreased by some 13 %. The last example shows the effect when the "blank" correction is applied to the peak intensities.

```
ELEM:       Zr      Zr      Fe      Ta      Nb       W   SUM
XRAY:     (la)    (la)    (ka)    (ma)    (la)    (la)
  1388  .02330  .00000 2.48485  .01082 2.05731  .77582 100.000
  1389  .03089  .00000 1.73088  .05860 1.39638 1.13187 100.000
  1390  .02465  .00000 5.37701  .03307 1.22040 1.71304 100.000
  1391  .02915  .00000 1.68162  .00614  .90783 1.62903 100.000
  1392  .01332  .00000 2.15914  .01267  .71461 2.45581 100.000
  1393  .00622  .00000 1.55307  .00234  .31748  .93823 100.000

AVER:   .02126  .00000 2.49776  .02061 1.10234 1.44063 100.000
SDEV:   .00959  .00000 1.45269  .02145  .60275  .62129
SERR:   .00392  .00000  .59306  .00876  .24607  .25364
%RSD:     45.1      .5    58.2   104.1    54.7    43.1
STDS:      257     257     395     573     541     574

ZCOR:  1.1604  1.1604  1.1327  1.2507  1.1306  1.5528
KRAW:   .00044  .00000  .03257  .00017  .00982  .00933
PKBG:  1.19835  .00000 14.2067 1.05964 7.68654 2.19645
INT%:   -35.58    ----    ----  -13.42    ----    ----
BLNK#:     131     131    ----     131    ----    ----
BLNKL: .000000 .000000    ---- .000000    ----    ----
BLNKV: -.00127 .000000    ---- .031558    ----    ----

Percent Analytical Relative Error (One Sigma, Single Line):
```

ELEM:	Zr	Zr	Fe	Ta	Nb	W
1388	2.3	.0	.2	16.3	.3	.9
1389	1.8	.0	.2	3.1	.4	.7
1390	2.2	.0	.1	5.4	.4	.5
1391	1.9	.0	.2	27.9	.5	.5
1392	4.0	.0	.2	13.6	.6	.4
1393	8.3	.0	.2	72.4	1.1	.8
AVER:	3.4	.0	.2	**23.1**	.6	.6
SDEV:	2.5	.0	.0	25.7	.3	.2
SERR:	1.0	.0	.0	10.5	.1	.1

Due to the large "blank" correction the Ta concentration has decreased to 0.02061 wt. % and the analytical error is now 23.2 %. As expected the analytical error is approaching 100% as the concentration approaches the detection limit

John Donovan
Director, MicroAnalytical Facility
CAMCOR, University of Oregon