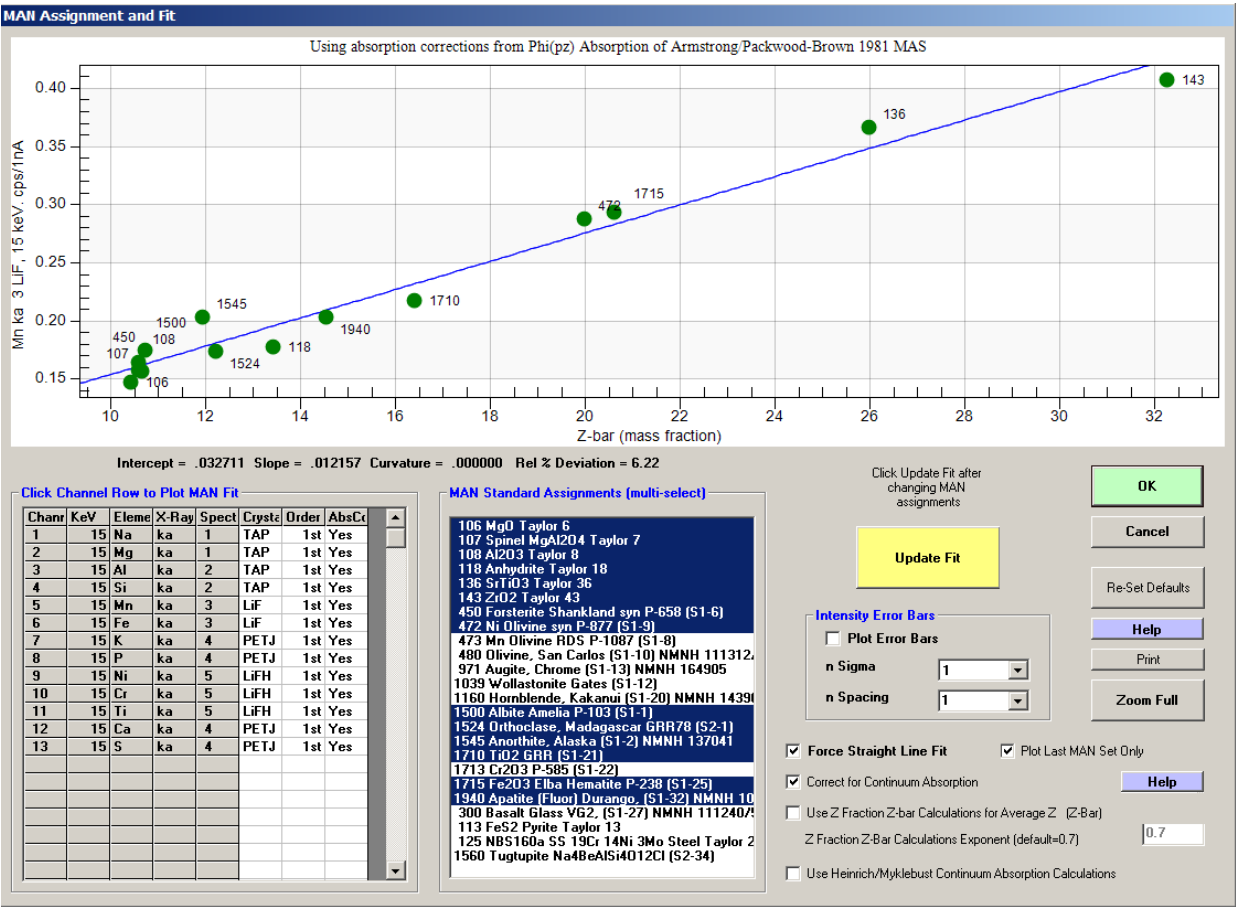
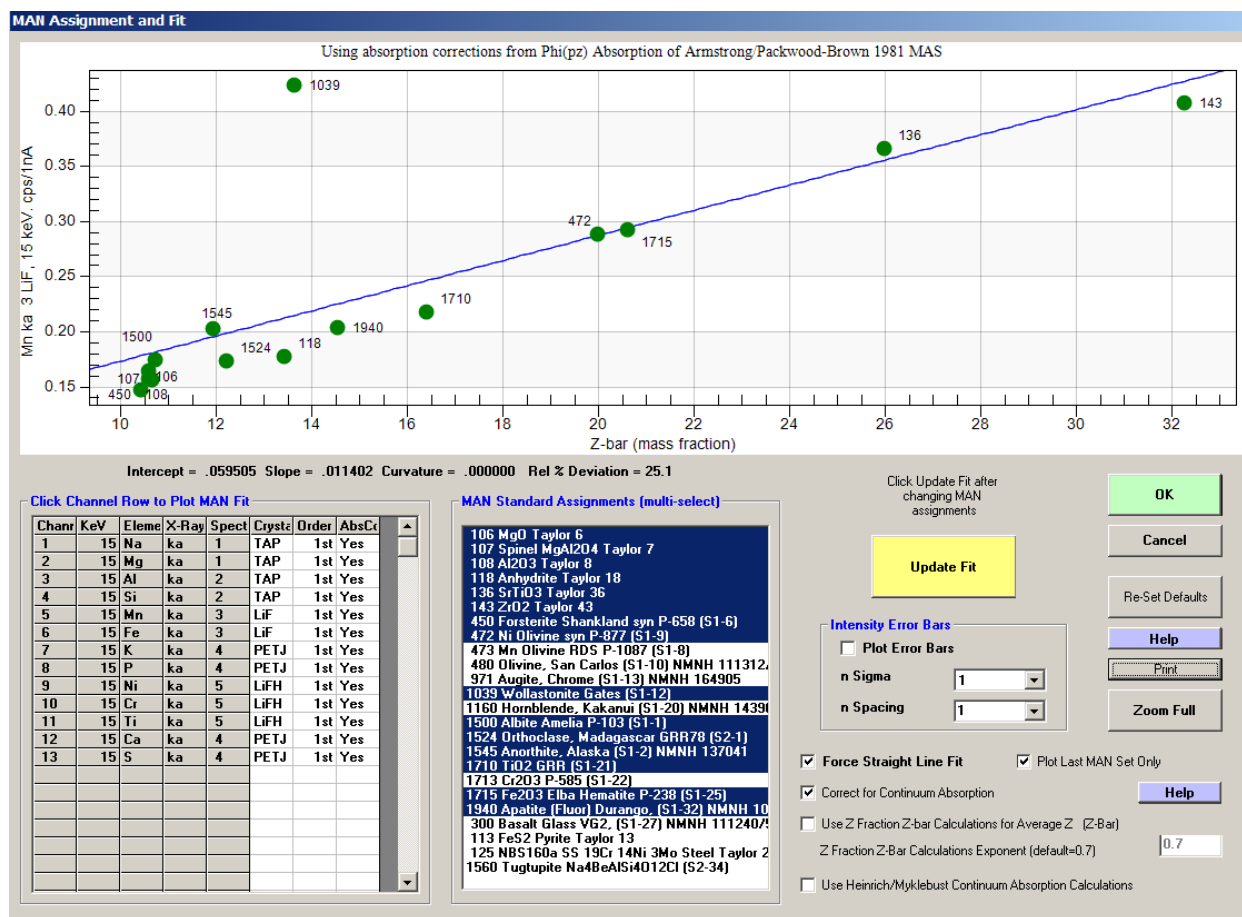


I think it is helpful to also have an example of how the k-ratio and composition are calculated in a microprobe analysis. Here are two parts.

It is important to remember that the k-ratio is  $k = (P-B)_{\text{smp}} / (P-B)_{\text{std}}$  and we mean the peak and background intensities measured on both the sample and standard. For conventional measurement this means driving the WDS to the peak, then to each background position, counting, and fitting a  $y=mx+b$  fit to the background points to obtain the background under the peak. This is done for the U and Th measurements. For almost all other measurements we use the MAN background method where we measure the intensity at the peak position in a suite of standards known to not contain that element (this is a background measurement in effect). When this is plotted up it looks like the two following graphs, one for Mn in standards not containing Mn, and a second where I have enabled the plotting of Mn in our wollastonite standard which contains 0.1 wt% MnO. This shows that the MAN background is good for measurements down to about 100-200ppm. For measurement using the MAN method, we initially measure P+B, then calculate the initial estimate of the composition, use that to determine the background from the MAN fits for all elements (each has it's own MAN fit), then use that background to calculate P-B and proceed with normal calculation of k-ratio and the analysis. This is done each time we click on the Analyze button and it is transparent to the user.



Now with measurement at Mn peak including wollastonite, standard number 1039:



I interpret the distance from background to 0.1 wt% to indicate the ability to discriminate a concentration of 100-200 ppm from the background and hence a visual estimate of the detection limit. We use the full formal DL calculations for measurements of either background method.

For how a k-ratio is calculated, here is the example using Cr2O3 as the primary standard and calculation of the Cr content in the Smithsonian Cr-augite standard (the Cr2O3 is our Cr primary standard and the Cr-augite standard is included in current runs as a true secondary standard).

It is important to understand that all intensities are calculated to a pure element basis and the generated intensity in the scattering volume is calculated and to which the ZAF corrections are applied; this is done for both sample and standard and is done on demand when we click on the Analyze button.

I am using the CalcZAF program to generate these numbers to simplify the output, here is the composition, k-ratio, and ZAF data for the Cr2O3 standard (essentially pure Cr2O3 but has a small amount of Fe):

ELEMENT	ABSCOR	FLUCOR	ZEDCOR	ZAFCOR	STP-POW	BKS-COR	F(x) u	E <sub>c</sub>	E <sub>o</sub> /E <sub>c</sub>	MACs
Cr ka	.9961	.9998	1.0720	1.0677	1.1039	.9711	.9837	5.9900	2.5042	68.4406
O ka	1.4171	.9921	.8727	1.2270	.8164	1.0690	.4945	.5317	28.2114	2529.93
Fe ka	1.0542	1.0000	1.0775	1.1359	1.1142	.9671	.9340	7.1120	2.1091	309.128

ELEMENT	K-RAW	K-VALUE	ELEMWT%	OXIDWT%	ATOMIC%	FORMULA	KILOVOL
Cr ka	.00000	.63952	68.283	99.800	39.909	1.994	15.00
O			31.609	.063	60.037	3.000	
Fe ka	.00000	.00088	.100	.129	.054	.003	15.00
TOTAL:			99.992	99.992	100.000	4.997	

The calculated k-ratio for Cr in Cr2O3 relative to pure Cr metal is 0.63952. This means the emitted x-ray intensity for Cr K-alpha from Cr2O3 at 15kV and 40 degree x-ray takeoff angle is 63.952 % or fractional 0.63952 of the intensity emitted from pure Cr metal under the same conditions. The ZAF factor is 1.0677 and that is calculated using the software; it is the multiplicative combination of the Z (1.0720) A (~1) and F (also ~1) factors. From  $C = k * ZAF$ ,  $k_{\text{purel}} = C / ZAF = 0.68283 / 1.0677 = 0.63952$ . All concentrations are on a weight fraction basis until converted to wt% or oxide wt% or atomic %.

If we take the measured k-ratio for Cr in the Cr-augite standard from the current microprobe run, that value is  $k_{\text{raw}} = (P-B)_{\text{Cr-augite}} / (P-B)_{\text{Cr2O3}}$  which needs to be converted to  $k_{\text{purel}}$  for the ZAF correction. The intensities (background corrected) are 3.28 cps/nA for the Cr-augite and 424.21 cps/nA for the Cr2O3 standard. So  $k_{\text{raw}} = 3.28 / 424.21 = 0.0077$  and the units cancel. This means the emitted x-ray intensity for Cr from the Cr augite is 0.77 % relative to the Cr2O3 standard; it is a small number just like the U Th measurements. To calculate the weight percent Cr in the augite, we take the k-ratio and multiply it by the ZAF factor which is 1.1789 and also by the correction factor to convert from Cr2O3 to pure Cr 0.63952 and again by 100% to convert to element wt%:  $k_{\text{raw}} * ZAF * CF * 100 = 0.007732 * 1.1789 * 0.63952 * 100 = 0.583 \text{ wt\% Cr}$ . The accepted value for Cr in Cr augite is 0.582 and so the measured concentration relative to the accepted value is  $0.5829 / 0.582 = 1.0016$  and that is excellent accuracy (you may see some roundoff differences if you duplicate these calculations). Here is the printout from the Probe for EPMA software for the analysis of the Cr-augite used for this example. The intensities

are UNCT, the unknown count rate in cps/nA, STCT, the intensity on the Cr2O3 std, KRAW, ZCOR which is the total ZAF correction, and STKF which is the intensity from the working standard relative to a pure element reference. I have chosen the most simple example that also includes a trace element. At the bottom is the CalcZAF output for the Cr-augite for comparison.

St 971 Set 1 Augite, Chrome (Si-13) NMNH 164905, Results in Elemental Weight Percents

ELEM:	Na	Mg	Al	Si	Mn	Fe	K	P	Ni	Cr	Ti	Ca	S	O	
TYPE:	ANAL	ANAL	ANAL	ANAL	ANAL	ANAL	ANAL	ANAL	ANAL	ANAL	ANAL	ANAL	ANAL	CALC	
BGDS:	MAN	MAN	MAN	MAN	MAN	MAN	MAN	MAN	MAN	MAN	MAN	MAN	MAN		
TIME:	45.00	45.00	45.00	45.00	45.00	45.00	20.00	20.00	25.00	25.00	25.00	20.00	15.00	---	
BEAM:	25.02	25.02	25.02	25.02	25.02	25.02	25.02	25.02	25.02	25.02	25.02	25.02	25.02	---	
ELEM:	Na	Mg	Al	Si	Mn	Fe	K	P	Ni	Cr	Ti	Ca	S	O	SUM
24	.62228	10.3170	3.96948	23.4294	.09488	3.62938	-.00066	.00160	.03358	.58322	.28975	12.3578	-.00039	43.7070	99.0343
AVER:	.62228	10.3170	3.96948	23.4294	.09488	3.62938	-.00066	.00160	.03358	.58322	.28975	12.3578	-.00039	43.707	99.0343
SDEV:	.00000	.00000	.00000	.00000	.00000	.00000	.00000	.00000	.00000	.00000	.00000	.00000	.00000	.000	.00000
SERR:	.00000	.00000	.00000	.00000	.00000	.00000	.00000	.00000	.00000	.00000	.00000	.00000	.00000	.00000	
%RSD:	.00000	.00000	.00000	.00000	.00000	.00000	.00000	.00000	.00000	.00000	.00000	.00000	.00000	.00000	
PUBL:	.62300	10.4440	4.25000	23.5960	.09300	3.66100	n.a.	n.a.	n.a.	.58200	.30600	12.3640	n.a.	44.2410	100.160
%VAR:	-.12	-1.22	-6.60	-.71	2.02	-.86	---	---	---	.21	-5.31	-.05	---	-1.21	
DIFF:	-.00072	-.12702	-.28052	-.16663	.00188	-.03162	---	---	---	.00122	-.01625	-.00619	---	-.53402	
STDS:	1500	450	1545	1039	473	1715	1524	1940	472	1713	1710	1039	113	---	
STKF:	.0502	.2597	.1501	.2064	.4924	.6548	.1102	.1570	.5146	.6395	.5548	.3185	.5062	---	
STCT:	48.13	408.03	300.59	452.56	105.53	160.09	96.65	72.80	393.98	424.21	255.59	289.98	296.02	---	
UNKF:	.0032	.0698	.0277	.1830	.0008	.0305	.0000	.0000	.0003	.0049	.0024	.1137	.0000	---	
UNCT:	3.09	109.68	55.50	401.13	.17	7.45	-.01	.01	.22	3.28	1.12	103.55	.00	---	
UNBG:	.57	1.08	1.90	3.98	.20	.26	.60	.10	1.84	.65	.32	.84	.18	---	
ZCOR:	1.9307	1.4778	1.4318	1.2806	1.2101	1.1908	1.0929	1.4013	1.1826	1.1789	1.1936	1.0865	1.2452	---	
KRAW:	.06421	.26879	.18465	.88636	.00159	.04655	-.00005	.00007	.00055	.00774	.00438	.35711	-.00001	---	
PKBG:	6.42132	102.904	30.2107	101.746	1.84472	30.1192	.99123	1.05058	1.11841	6.07556	4.48414	124.518	.98964	---	

St 971 Set 1 Augite, Chrome (Si-13) NMNH 164905, Results Based on 6 Atoms of o

ELEM:	Na	Mg	Al	Si	Mn	Fe	K	P	Ni	Cr	Ti	Ca	S	O	SUM
24	.05945	.93235	.32313	1.83228	.00379	.14274	-.00004	.00011	.00126	.02464	.01329	.67723	-.00003	6.00000	10.0102

CalcZAF output for Smithsonian Cr-augite standard using accepted analysis (wet chemistry). The largest component of the ZAF correction is due to x-ray absorption, here is for Na and least for Fe as these are the lowest energy and highest energy x-rays.

ELEMENT	ABSCOR	FLUCOR	ZEDCOR	ZAFCOR	STP-POW	BKS-COR	F(x)u	Ec	Eo/Ec	MACs
Na ka	1.8808	.9928	1.0325	1.9281	1.0246	1.0077	.4475	1.0730	13.9795	3202.87
Mg ka	1.4745	.9916	1.0096	1.4762	1.0093	1.0003	.5876	1.3050	11.4943	1999.22
Al ka	1.3935	.9850	1.0427	1.4312	1.0503	.9927	.6368	1.5600	9.6154	1689.52
Si ka	1.2654	.9985	1.0150	1.2824	1.0301	.9853	.7157	1.8390	8.1566	1236.54
Ca ka	1.0333	.9974	1.0544	1.0866	1.1073	.9522	.9319	4.0390	3.7138	275.740
Ti ka	1.0323	.9949	1.1621	1.1935	1.2274	.9468	.9416	4.9670	3.0199	247.056
Cr ka	1.0144	.9894	1.1746	1.1789	1.2439	.9443	.9660	5.9900	2.5042	149.845
Mn ka	1.0082	.9991	1.2015	1.2102	1.2725	.9442	.9746	6.5390	2.2939	114.990
Fe ka	1.0052	1.0000	1.1849	1.1910	1.2541	.9448	.9795	7.1120	2.1091	96.0898
O ka	2.7910	.9992	.9532	2.6582	.9285	1.0266	.2511	.5317	28.2114	6264.80

ELEMENT	K-RAW	K-VALUE	ELEMWT%	OXIDWT%	ATOMIC%	FORMULA	KILOVOL
Na ka	.00000	.00323	.623	.840	.587	.059	15.00
Mg ka	.00000	.02075	10.444	17.319	9.315	.932	15.00
Al ka	.00000	.02970	4.250	8.030	3.415	.342	15.00
Si ka	.00000	.18400	23.596	50.480	18.213	1.823	15.00
Ca ka	.00000	.11379	12.364	17.300	6.688	.669	15.00
Ti ka	.00000	.00256	.306	.510	.138	.014	15.00
Cr ka	.00000	.00494	.582	.851	.243	.024	15.00
Mn ka	.00000	.00077	.093	.120	.037	.004	15.00
Fe ka	.00000	.03074	3.661	4.710	1.421	.142	15.00
O			44.241	.000	59.943	6.000	
TOTAL:			100.160	100.160	100.000	10.010	