

Comparison of Off-peak vs. MAN vs. “Nth Point” background measurements

John Donovan, 09-03-2009

Comparison of methods

The following is an attempt to compare three methods (Off-peak, MAN and Nth Point) for background determination using both a homogeneous standard glass (NBS-K-411), a natural impact glass with a slight variability in composition and a volcanic (Marianas) glass with a somewhat larger variability in composition.

Compositional analyses were acquired on an electron microprobe equipped with 5 tunable wavelength dispersive spectrometers. Operating conditions were 40 degrees takeoff angle, and a beam energy of 15 keV. The beam current was 20 nA, and the beam diameter was 5 microns.

Elements were acquired using analyzing crystals LIF for Ca ka, Fe ka, LLIF for Ti ka, Mn ka, Cr ka, Ni ka, LIF for Ca ka, Fe ka, LLIF for Ti ka, Mn ka, Cr ka, Ni ka, LPET for Si ka, K ka, Cl ka, and TAP for P ka, Al ka, Mg ka, Na ka.

The counting time was 20 seconds for Mn ka, Cl ka, 30 seconds for Ti ka, 40 seconds for Al ka, Cr ka, Ni ka, Si ka, 80 seconds for Na ka, 90 seconds for Ca ka, K ka, 120 seconds for Fe ka, Mg ka, and 160 seconds for P ka.

The intensity data was corrected for Time Dependent Intensity (TDI) loss (or gain) using a self calibrated correction for Na ka, Si ka, Al ka, Ca ka, Cr ka.

The off peak counting time was 18 seconds for Ti ka, 20 seconds for Al ka, Si ka, Mn ka, Cr ka, Ni ka, Cl ka, 30 seconds for Fe ka, Ca ka, K ka, Mg ka, and 40 seconds for P ka, Na ka.

Off Peak correction method was LINEAR for Na ka, Si ka, K ka, Al ka, Mg ka, Ca ka, Ti ka, Mn ka, Fe ka, Cr ka, Ni ka, Cl ka, and EXPONENTIAL for P ka.

In this comparison all elements were measured using off-peak backgrounds, then the MAN backgrounds and Nth point background were calculated using the exact same on and off-peak intensity data for the comparison.

Off-peak backgrounds

Typically background is characterized in EPMA by measuring the x-ray intensities on either side of the analytical peak and interpolating the value underneath the x-ray peak. This interpolated intensity is then subtracted from the peak intensity to produce a background corrected net intensity for the element in question. Care must be taken to avoid interferences with the off-peak positions or other background artifacts or the interpolated background intensity will be inaccurate.

The net intensity thus obtained is then utilized in subsequent calculation to obtain quantitative analyses along with other corrections for deadtime, beam drift, standard drift and other compositionally dependent corrections such as peak overlap interferences and peak shape and/or shift effects along with the matrix correction itself.

Nth Point backgrounds

A related method utilized to save time, is the Nth Point background method which simply acquires an off-peak background measurement every “N” points. That is, one performs an off-peak background measurement on the first point of a set of data and then re-uses that off-peak measurement for subsequent data points, instead of explicitly measuring the off-peak background for all points in the data set.

Typically this would be utilized on major and minor elements, with the trace elements continuing to be measured using normal off-peak background measurements.

The downside to this method is that if the composition changes, the average Z of the material will change and according to Kramer's Law, the continuum intensity will change as well. Although the change will be proportional to the degree to which the average Z changes and therefore will be small for a small difference in composition. However if the change in background intensity is greater than the precision of the measurement, it will affect the accuracy of the analysis.

It is also conceivable that two or more elements with different atomic numbers could change inversely, resulting in a compositional change without a corresponding change in average atomic number. But that fortunate occurrence would not be known until the measurement has actually been performed, possibly requiring a re-measurement if the compositional change was significant, which might not be possible on samples of very small size and subject to beam damage (e.g., melt inclusions).

MAN backgrounds

Since Kramer's Law predicts that continuum should vary with average (or mean) atomic number (or Z-bar), assuming all other parameters such as beam current and spectrometer position remain constant, another set of methods has been utilized by several sources with varying degrees of robustness. The simplest of these methods was seen on early ARL instruments with fixed monochromators, by performing a single measurement performed at the on-peak position for an element on a material that was similar in average atomic number to the unknown in question, but not containing the element of interest. Obviously the accuracy of this technique depended not only on the similarity of average atomic number to the unknown in question, but was also, like the Nth Point technique, susceptible to changes in average atomic number due to changes in composition.

A more accurate variant of this average atomic number background method was developed at UC Berkeley to quantitatively correct for "on-peak" background by measuring a suite of standards (of known composition and therefore known average Z) with a range of average atomic numbers to cover the unknowns in question, which did not contain the element of interest.

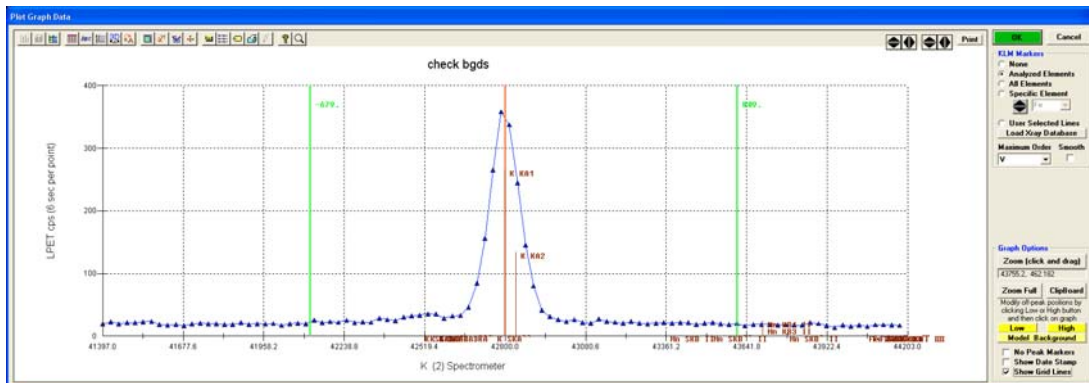
After correcting for differences in continuum absorption, such a calibration curve can accurately predict the continuum intensity in a wide variety of materials. The calculation of the actual continuum intensity for the unknown sample is performed during the matrix iteration as the composition is determined quantitatively.

Typically the accuracy of this method is equal to the precision of the Z-bar calibration curve which may be significantly better than a single off-peak measurement, since several on-peak measurements are averaged together for each of several standards during the MAN fit.

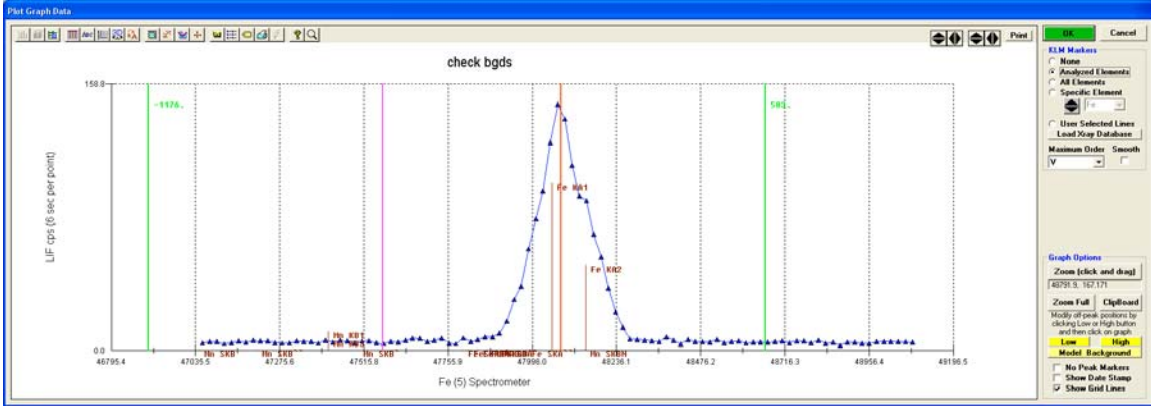
An additional advantage of these on-peak background methods is that there is no possibility of systematic errors due to off-peak interferences since no-off peak data is utilized at all, although like the Nth point method, it is usually applied to major and minor element concentrations only.

Off-peak Method Details

Off-peak background positions are selected after acquiring a scan over the region of the peak position. A scan for K Ka is shown here:



No obvious off-peak interferences are noted, except for a possible 2nd order interference from Mn Kb3 which would be a very low intensity interference. Another example is for Fe Ka, which required the low off-peak position to be moved to avoid the Mn Kb1 peak as shown here:



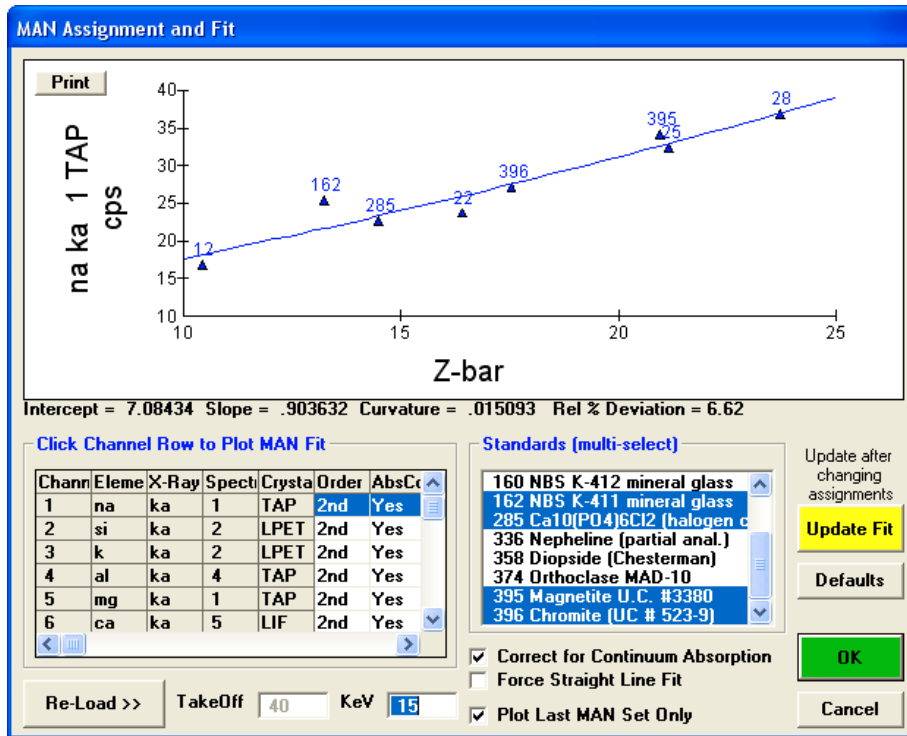
The original Fe low off-peak position is shown in purple and the new (current) position is shown in green. Similar considerations are followed for the remaining elements.

Off-peak intensity intensities were calculated automatically for all elements as is typically done in EPMA.

MAN Method Details

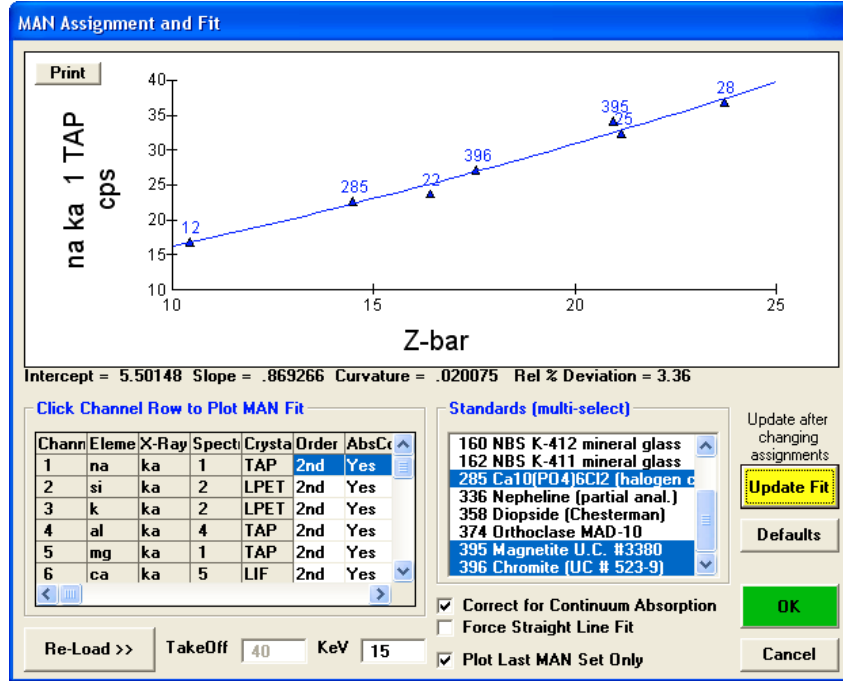
The MAN method is based on the measurement of the on-peak intensities in a numbers of standards that cover a range of average atomic number, but that do not contain the element of interest. The intensities must be corrected for continuum absorption which varies based on the composition of the standards.

The following plot shows the continuum corrected intensities for Na Ka in materials that ostensibly do not contain Na.

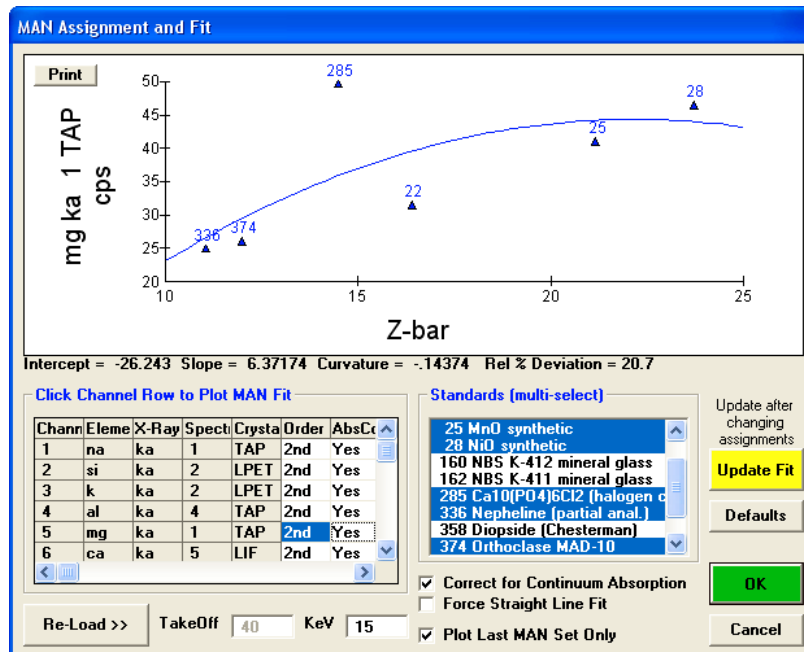


However, due to contamination and/or on-peak interferences from other elements, an elevated intensity might be observed. Since background is defined as the lowest intensity which can be measured, intensities that are demonstrably contaminated or interfered with can be removed from the MAN fit.

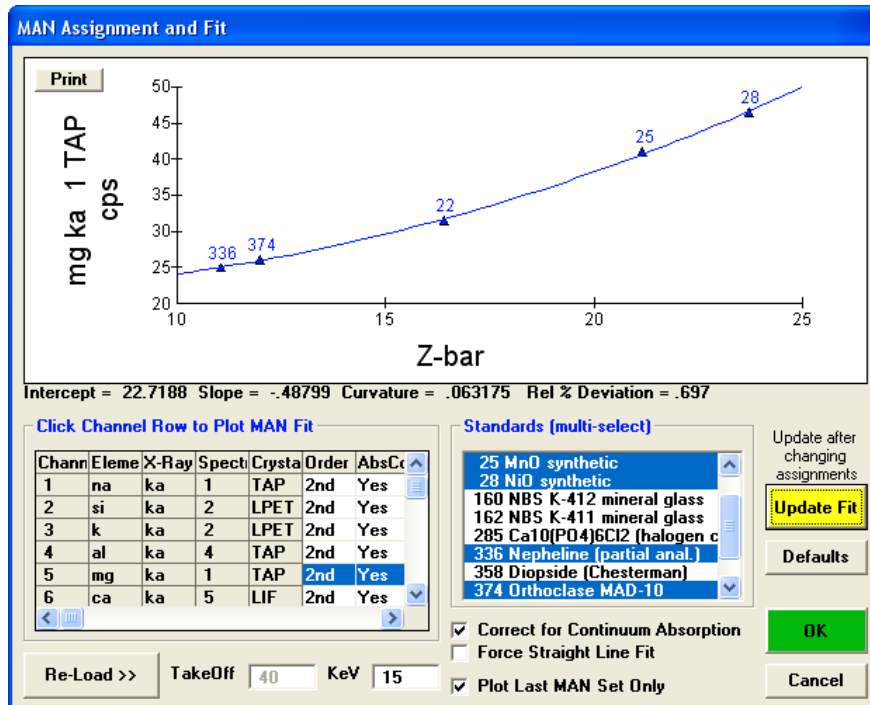
Since it is known that the 162 (NBS K-411) glass standard does contain a trace amount of Na, it was removed resulting in the following MAN fit:



Incidentally the elevated Na intensity in the 162 glass corresponds to an off-peak measured concentration of approximately 250 PPM of Na. The MAN calibration curve for Mg is shown below, which includes a well known interference of 2nd order Ca Kb on Mg.



This is corrected by deselecting the offending standard and updating the fit as shown here:



Note that the standards shown do not contain the element of interest so the on-peak measurement characterizes the continuum intensity accurately for a large range of compositions assuming that the proper range of Z-bar is utilized (see below). Once the MAN fits have been checked for each element in which it is desired to perform the MAN fit on, the process is complete and the software automatically performs all calculations using on-peak intensities only, for any composition within the Z-bar range.

MAN intensities were calculated by instructing the program to ignore the off-peak intensities and utilize only the on-peak intensities for all calculations.

Note that as is typically the case for Nth Point background measurements, only major and minor elements are usually selected for the MAN background fitting.

Nth Point Method Details

The Nth point test was performed by taking the off-peak intensities from the first measured point in each sample and then applying that off-peak intensity correction to all subsequent points in the sample.

```
For i% = 1 To sample(1).Datarows%      ' all data points
For j% = 1 To sample(1).LastElm%      ' all elements
```

```
If sample(1).Type% = 2 Then          ' only unknown samples
sample(1).HiPeakCounts!(i%, j%) = sample(1).HiPeakCounts!(1, j%) ' set to first point
sample(1).LoPeakCounts!(i%, j%) = sample(1).LoPeakCounts!(1, j%) ' set to first point
End If
```

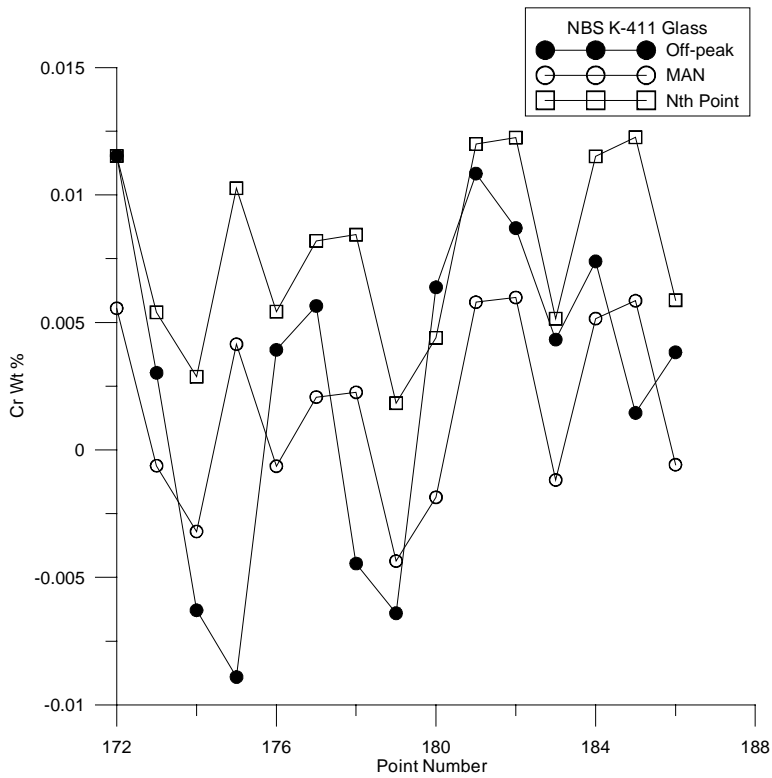
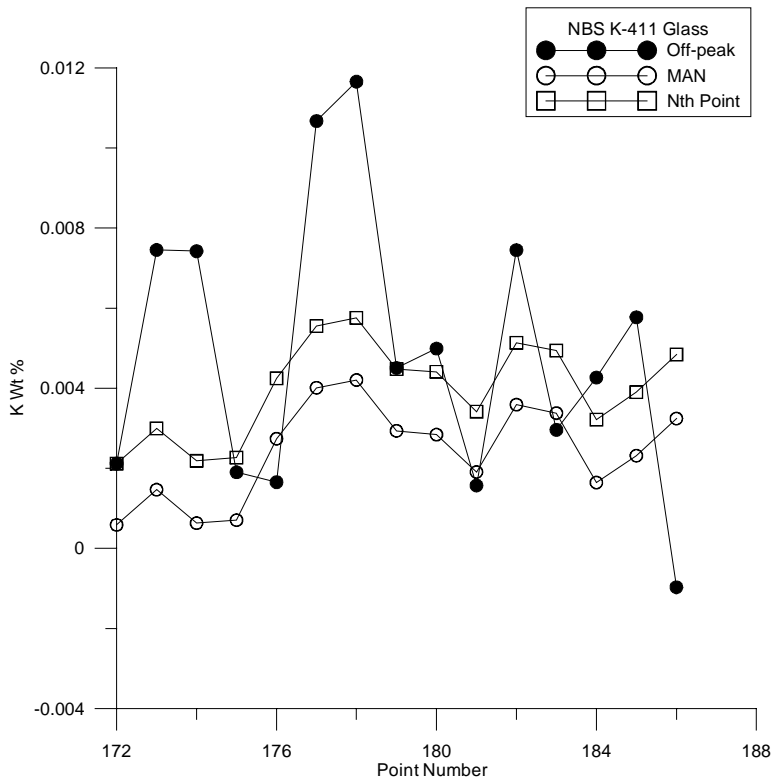
```
Next j%
Next i%
```

Comparison on homogeneous glass standard (NBS K-411) for minor and trace elements

The general composition (using all off-peak measurements) for this NBS K-411 glass is shown here:

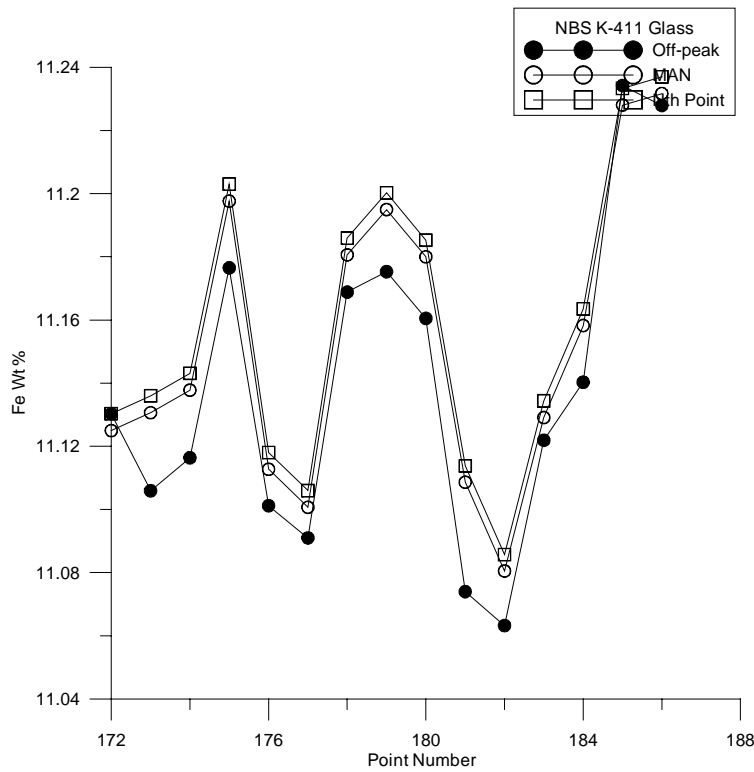
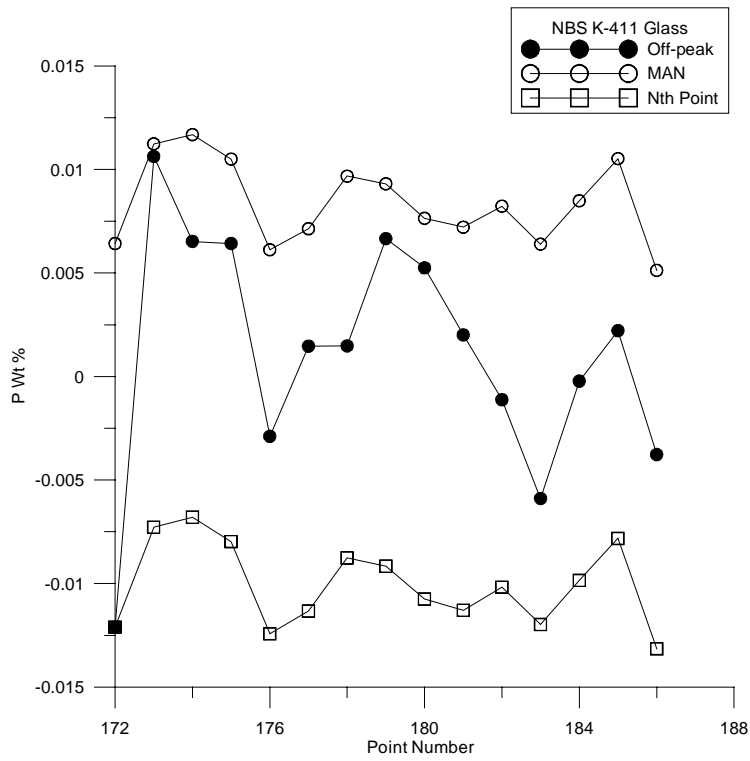
ELEM:	Na2O	SiO2	K2O	Al2O3	MgO	CaO	TiO2	MnO	FeO	P2O5	Cr2O3	NiO	Cl	SUM
172	.02457	54.3487	.00255	.01651	14.5646	15.0320	-.02732	.10725	14.3191	-.02773	.01686	-.00961	.00389	99.4906
173	.03371	54.1678	.00898	.03384	14.6439	14.9154	-.00150	.12004	14.2877	.02435	.00442	.01611	.01153	99.3836
174	.03016	54.3127	.00894	.04460	14.5443	14.9736	.00777	.15500	14.3012	.01496	-.00919	.05964	.00465	99.5672
175	.02878	54.3222	.00229	.03000	14.5694	14.8502	.00956	.13737	14.3785	.01473	-.01302	.05258	.00042	99.5029
176	.02685	54.3224	.00199	.02922	14.5471	14.7672	-.01942	.15593	14.2816	-.00663	.00573	.02940	.00840	99.2679
177	.02157	54.3761	.01285	.04817	14.5511	15.0695	.02181	.11403	14.2685	.00336	.00825	.01074	.00715	99.6315
178	.02917	54.4881	.01404	.03226	14.6022	14.9958	-.02121	.13289	14.3686	.00338	-.00652	.04266	.00525	99.8055
179	.03282	54.1881	.00543	.04818	14.6519	14.8253	-.00836	.10442	14.3770	.01526	-.00937	.03645	.00130	99.3882
180	.03081	54.3600	.00601	.01952	14.5708	15.0191	-.01225	.12691	14.3579	.01203	.00932	.02402	.00561	99.6486
181	.02766	54.4328	.00189	.04438	14.5296	14.8754	.00299	.11823	14.2466	.00461	.01584	-.00452	-.00211	99.4140
182	.02135	54.3248	.00897	.04341	14.5606	15.1122	-.00448	.14434	14.2328	-.00258	.01272	.03898	.00718	99.6187
183	.02735	54.3576	.00356	.03627	14.4900	15.0267	.01673	.12594	14.3083	-.01348	.00632	.02656	.00670	99.5371
184	.01172	54.3387	.00514	.02191	14.5326	15.1021	.00837	.12217	14.3319	-.00050	.01081	-.00367	-.00057	99.6009
185	.01804	54.2679	.00695	.03347	14.5607	14.8411	.01075	.12225	14.4528	.00508	.00212	.02910	-.00184	99.4688
186	.03354	54.4203	-.00116	.03550	14.5788	15.1229	-.00806	.12718	14.4446	-.00865	.00560	-.01101	.00344	99.8622
AVER:	.02654	54.3352	.00589	.03448	14.5665	14.9686	-.00164	.12760	14.3305	.00255	.00399	.02250	.00407	99.5458
SDEV:	.00617	.08379	.00427	.01006	.04164	.11528	.01450	.01535	.06590	.01326	.00942	.02239	.00397	
SERR:	.00159	.02163	.00110	.00260	.01075	.02977	.00374	.00396	.01701	.00342	.00243	.00578	.00103	
%RSD:	23.2	.2	72.5	29.2	.3	.8	-882.6	12.0	.5	520.6	235.9	99.5	97.6	

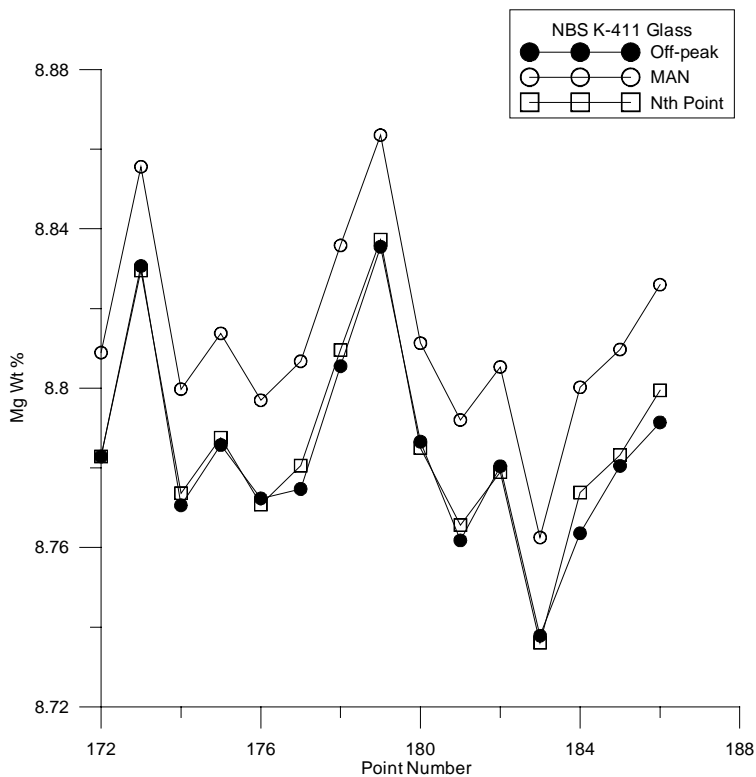
The following graphs compare several elements on the homogeneous standard glass using the three methods.



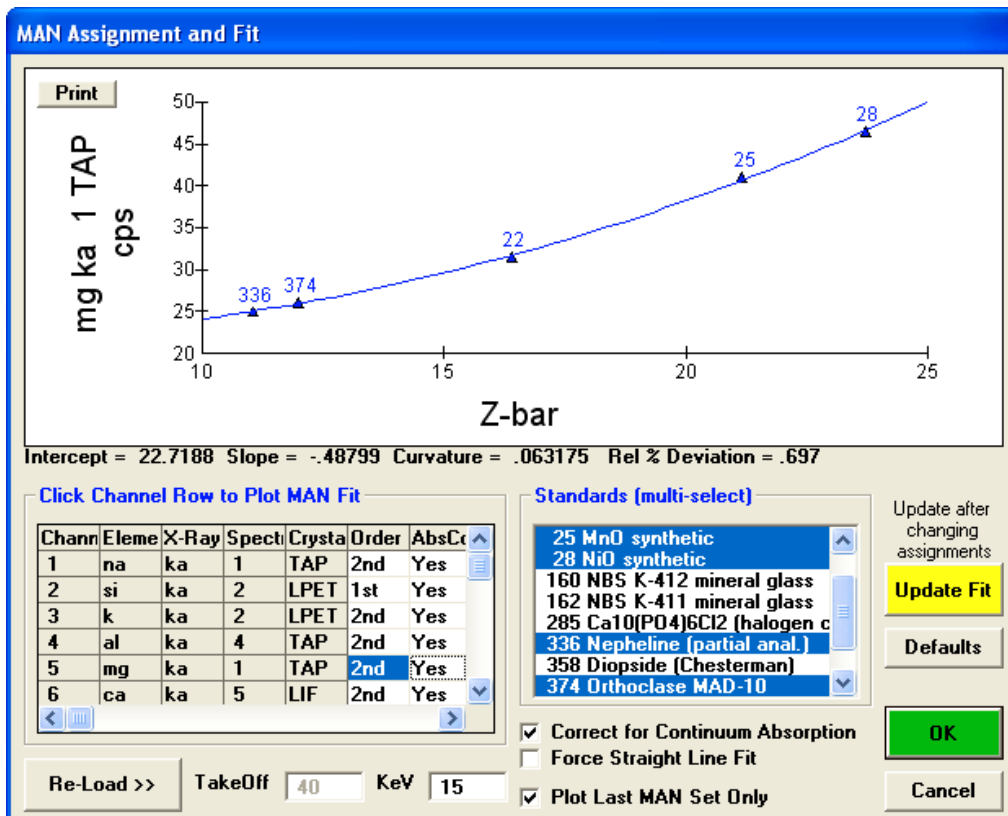
Note the greater variation in the off-peak measurements due to the combined statistical variation of both the on-peak and off-peak measurements. Note also that since the MAN intensity is essentially a constant

background intensity (for a given constant composition), the MAN and Nth Point method give very similar plots, essentially reflecting only the variation in the on-peak intensities.





In this graph of Mg the MAN results are slightly high (~250 PPM) apparently because no low Z-bar standard was measured such as SiO₂ or Al₂O₃ for fitting Mg Ka as seen in the MAN fit (shown above and again here):

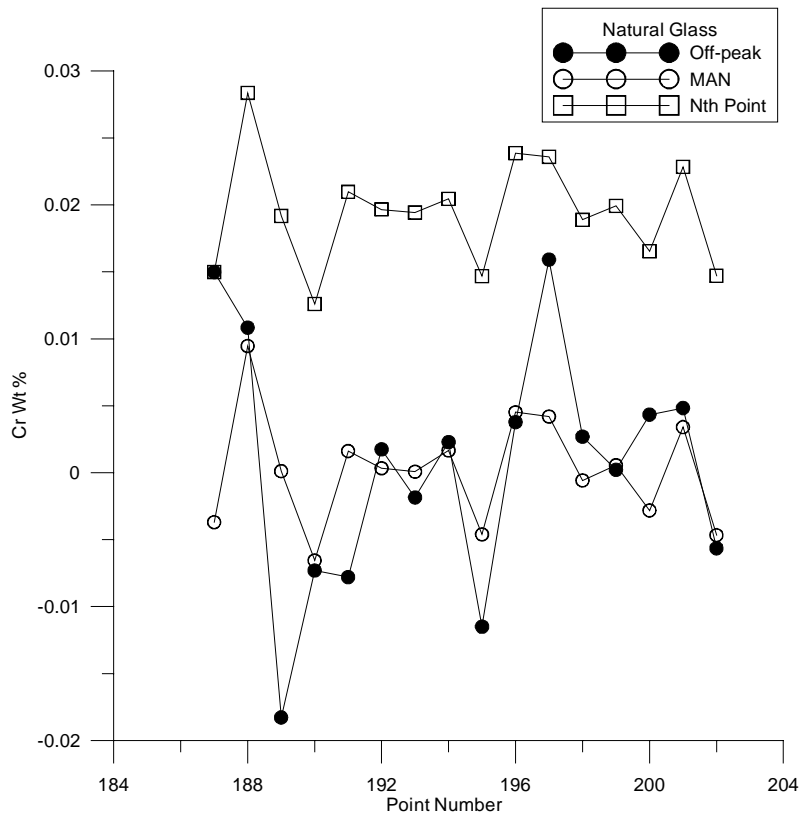
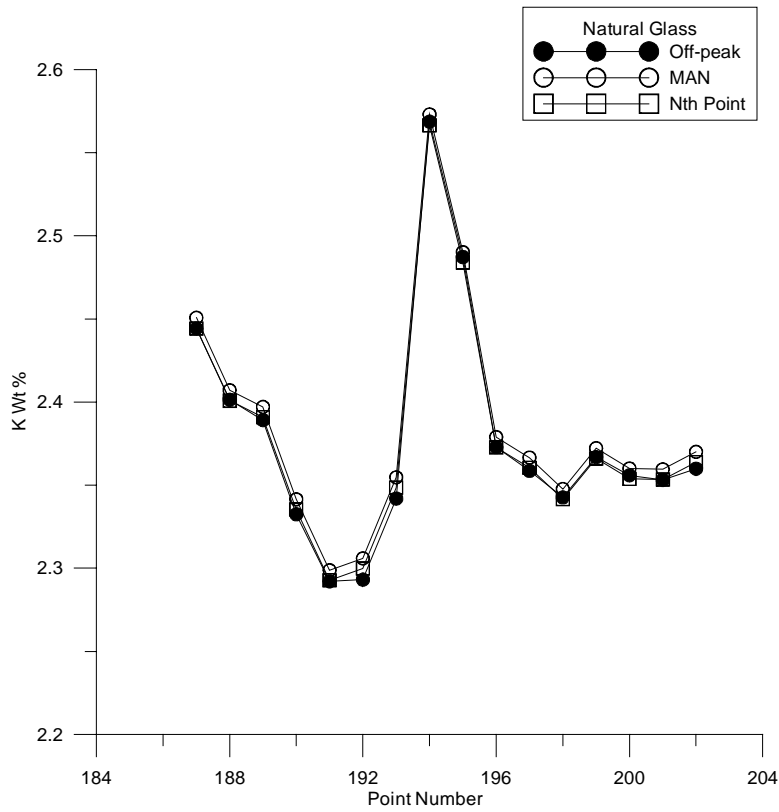


Comparison on natural impact glass for minor and trace elements

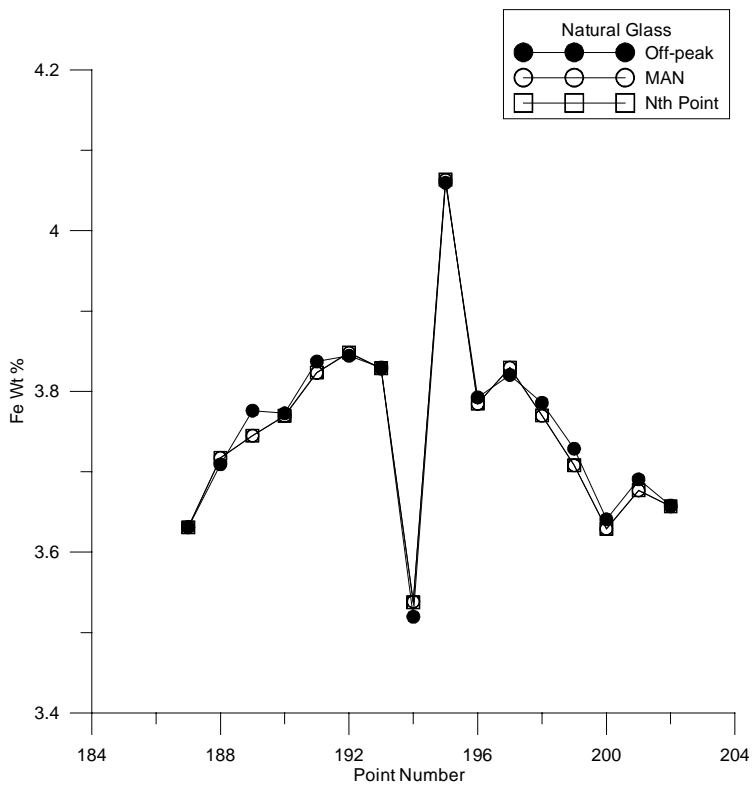
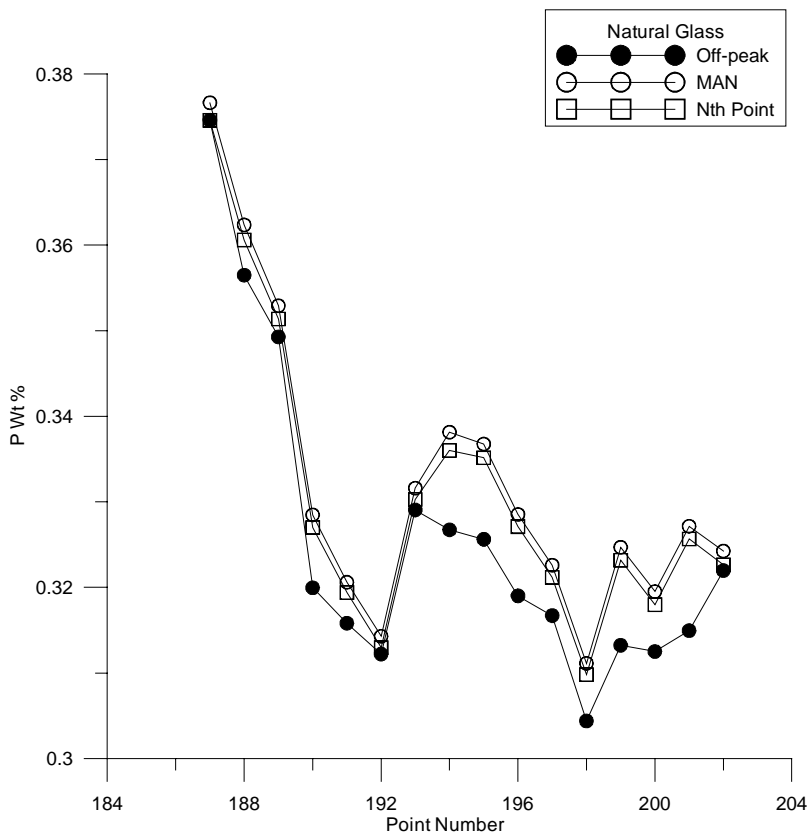
The general composition (using all off-peak measurements) for this natural impact glass is shown here:

ELEM:	Na2O	SiO2	K2O	Al2O3	MgO	CaO	TiO2	MnO	FeO	P2O5	Cr2O3	NiO	Cl	SUM
187	4.31497	57.1994	2.94430	9.45497	.69272	15.1591	.88371	.15219	4.67110	.85832	.02190	.00736	1.53021	97.5450
188	4.30530	56.9537	2.89258	9.29977	.67314	15.5715	.83410	.15361	4.77184	.81685	.01583	.00368	1.54162	97.4856
189	4.42648	56.6722	2.87789	9.24139	.66534	15.9864	.83232	.12079	4.85778	.80032	-.02672	-.01640	1.55008	97.6382
190	4.41194	56.6940	2.80959	9.15413	.63565	16.2270	.80671	.17250	4.85353	.73312	-.01069	.01442	1.54207	97.6960
191	4.50532	56.3621	2.76107	9.11796	.60184	16.5900	.80437	.16235	4.93654	.72365	-.01140	.02543	1.58254	97.8047
192	4.46002	56.3683	2.76225	9.13950	.59039	16.3803	.77610	.15510	4.94561	.71536	.00254	.00170	1.55359	97.5002
193	4.36442	56.6469	2.82102	9.26136	.54607	16.4432	.75389	.15031	4.92689	.75397	-.00271	-.01781	1.54317	97.8425
194	4.31968	57.1436	3.09412	9.76946	.55293	15.0602	.65455	.13503	4.52792	.74866	.00334	.00848	1.54986	97.2181
195	4.21006	57.1039	2.99601	9.73727	.56616	15.4280	.79254	.11512	5.22252	.74611	-.01681	-.01018	1.52651	98.0728
196	4.30661	57.0100	2.85825	9.30470	.57965	16.2955	.80065	.15163	4.87903	.73097	.00552	-.00226	1.56307	98.1307
197	4.18713	56.9338	2.84112	9.27783	.62166	16.2700	.82555	.14548	4.91499	.72568	.02326	-.00961	1.50433	97.9217
198	4.32387	56.7947	2.82187	9.44012	.67721	16.6280	.82117	.16608	4.87044	.69745	.00392	.01583	1.51273	98.4320
199	4.26236	56.3800	2.85107	9.42974	.70396	16.1015	.78238	.15124	4.79681	.71773	.00032	-.00593	1.49429	97.3282
200	4.10709	56.7704	2.83789	9.39474	.70197	16.2854	.79136	.13861	4.68389	.71607	.00633	.01639	1.48400	97.5993
201	4.09179	56.5734	2.83460	9.37028	.71446	16.1527	.73747	.14767	4.74788	.72165	.00706	.01611	1.55700	97.3207
202	4.13653	56.7939	2.84264	9.40767	.71872	15.9649	.77252	.12716	4.70609	.73774	-.00825	.00933	1.55420	97.4124
AVER:	4.29585	56.7750	2.86539	9.36255	.64012	16.0340	.79184	.14656	4.83205	.74648	.00084	.00353	1.53683	97.6843
SDEV:	.12408	.27123	.08488	.18630	.06074	.48265	.05051	.01580	.15602	.04290	.01349	.01287	.02657	
SERR:	.03102	.06781	.02122	.04657	.01519	.12066	.01263	.00395	.03900	.01073	.00337	.00322	.00664	
%RSD:	2.9	.5	3.0	2.0	9.5	3.0	6.4	10.8	3.2	5.7	1606.2	364.4	1.7	

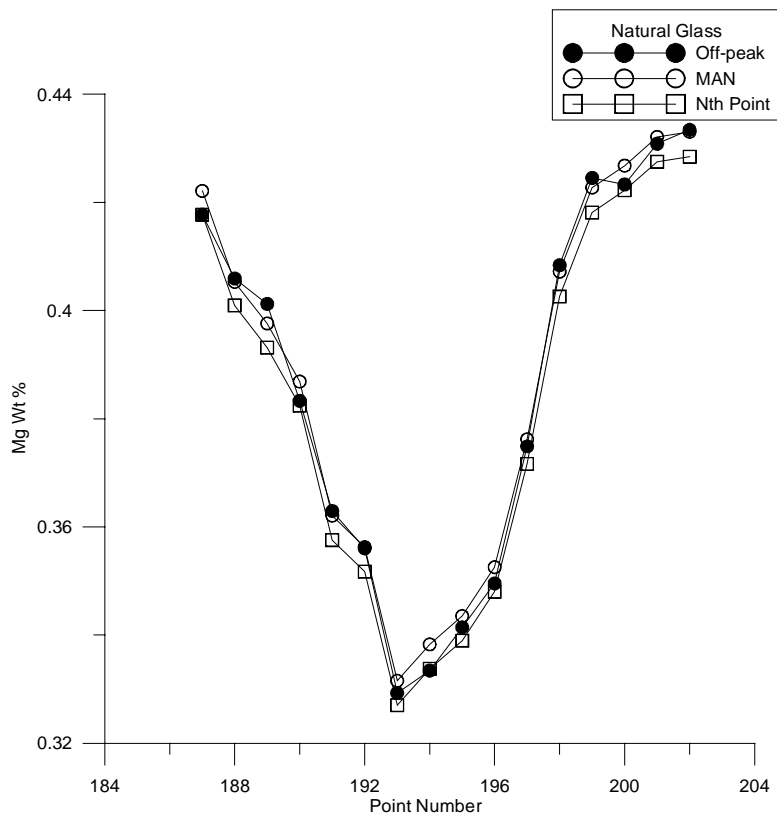
K, Cr, P, Fe and Mg Concentration Plots for the natural impact glass



The MAN fit seems to do a slightly better job than the Nth point method, but clearly at these concentrations one would always measure the off-peak intensities for all data points.



Amazingly the MAN and Nth Point data plot almost on top of each other (the values are different only in the third decimal place).

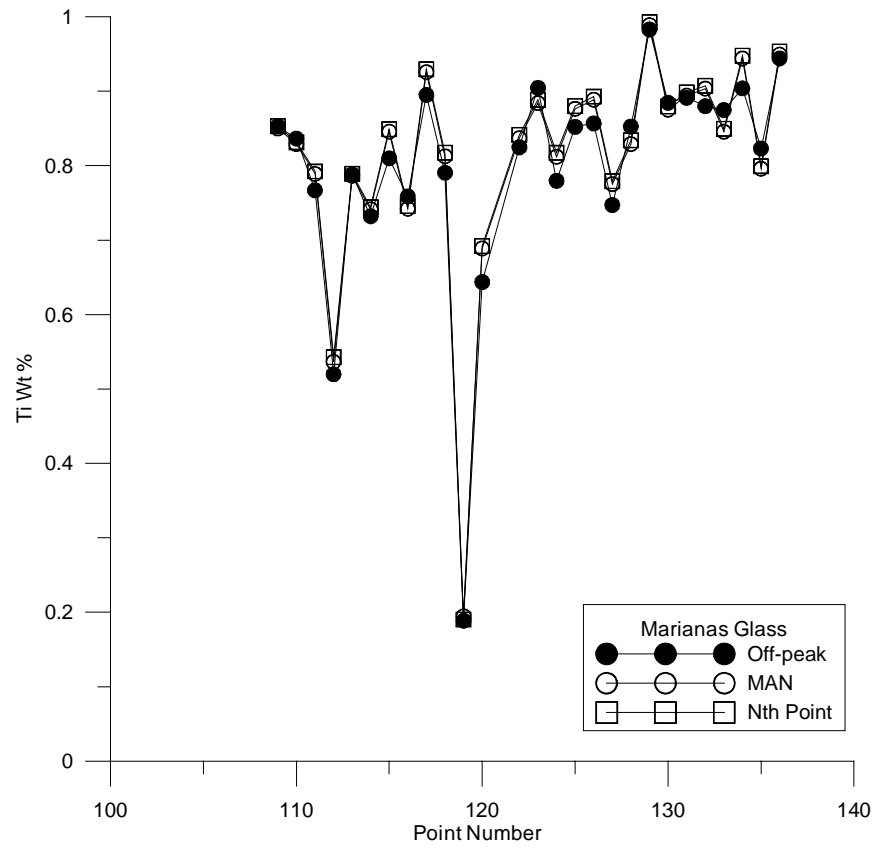


Comparison on volcanic glass for minor and trace elements

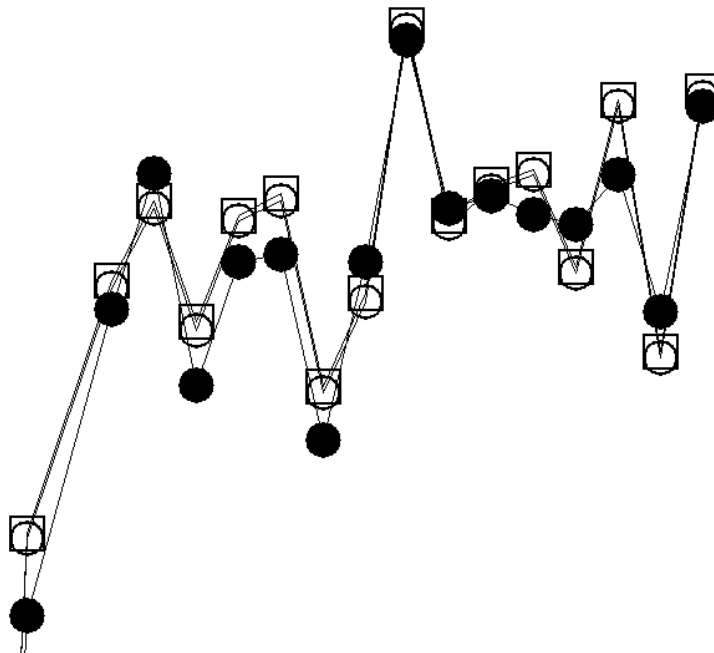
The general composition (using all off-peak measurements) for this volcanic glass is shown here:

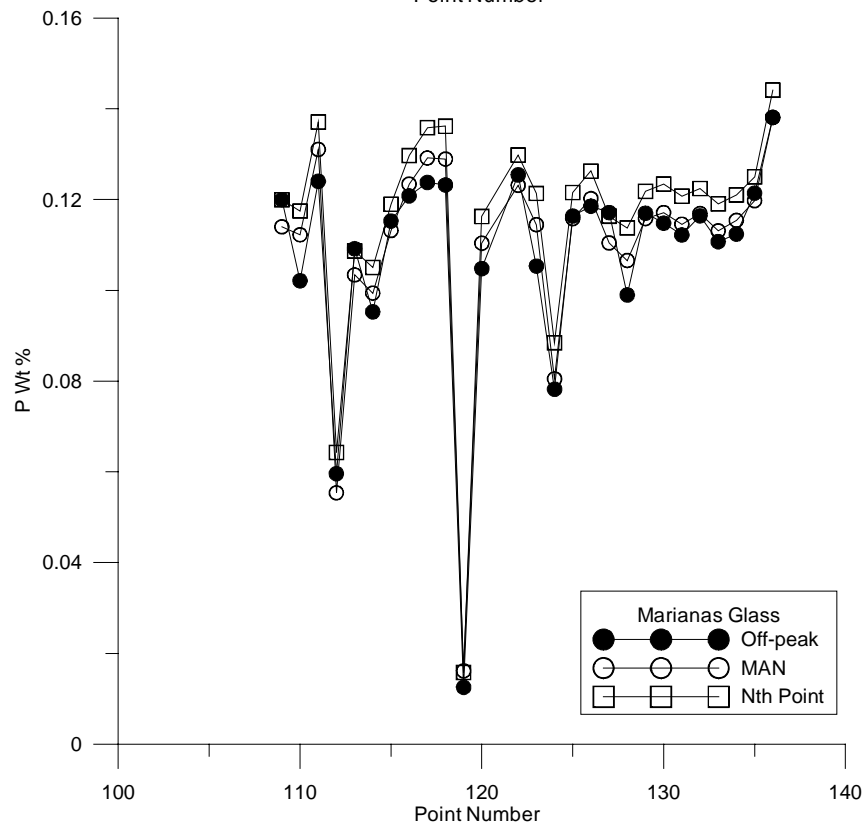
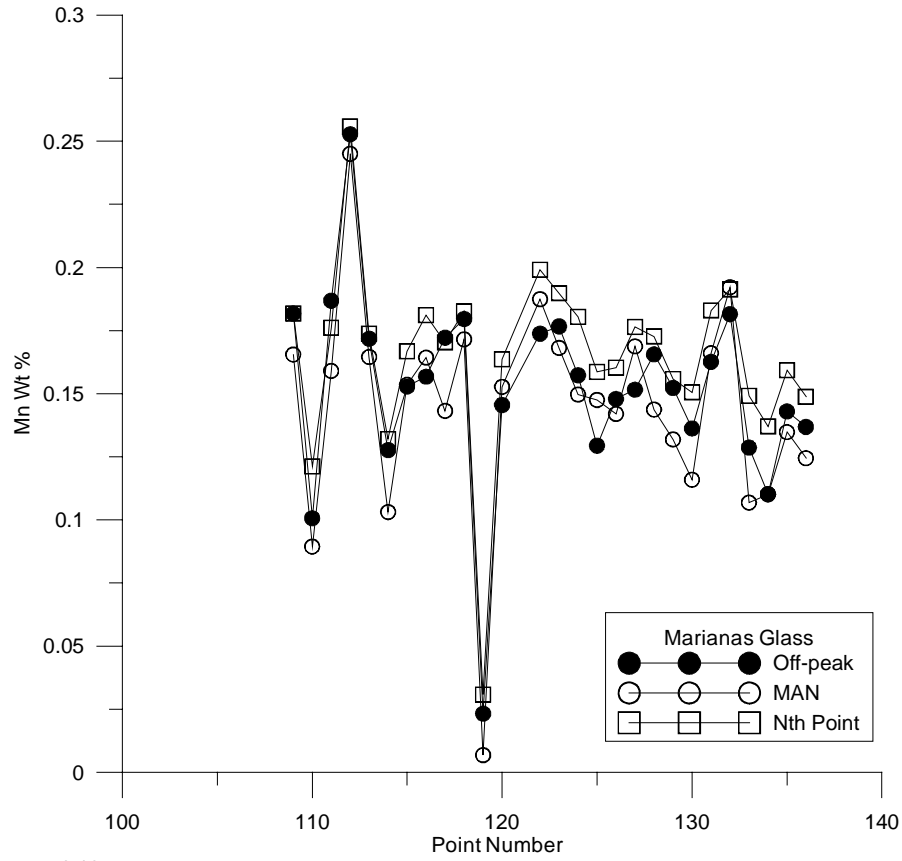
ELEM:	Na2O	K2O	Al2O3	MgO	FeO	TiO2	MnO	P2O5	SiO2	CaO	NiO	F	S	Cl	SUM
109	2.952	1.260	16.370	3.706	10.199	1.423	.235	.275	56.390	7.689	-.048	.010	-.002	.251	100.650
110	3.198	1.006	16.110	3.502	9.639	1.395	.130	.234	57.186	7.517	-.033	.031	.012	.250	100.107
111	3.049	1.419	16.088	3.358	9.957	1.279	.241	.284	55.431	7.169	.001	.026	.007	.463	98.657
112	1.185	.622	9.778	10.479	11.072	.867	.326	.137	51.302	11.543	-.008	.027	.011	.200	97.483
113	3.742	1.083	17.884	3.018	9.551	1.315	.222	.250	56.539	7.856	.005	-.002	.013	.351	101.749
114	3.400	1.427	17.687	3.296	8.683	1.221	.165	.218	56.215	7.757	.012	.071	.073	1.892	101.662
115	2.795	1.411	16.646	3.283	9.550	1.351	.197	.264	56.736	6.587	-.024	.018	.037	1.493	99.999
116	3.393	1.309	16.418	3.419	9.523	1.265	.202	.277	55.231	6.846	-.001	-.026	.089	2.152	99.623
117	2.020	1.412	16.191	3.277	9.820	1.493	.222	.284	56.501	6.939	.033	.062	.052	1.967	99.802
118	2.255	1.501	16.532	2.657	10.484	1.318	.232	.282	56.240	5.954	.023	.142	.098	2.778	99.811
119	4.395	.292	29.778	.726	2.447	.315	.030	.029	53.678	11.391	-.050	-.050	.020	.279	103.237
120	3.308	1.265	17.703	3.348	8.713	1.074	.188	.240	55.157	8.041	.013	.103	.094	1.965	100.724
122	2.901	1.341	16.109	3.477	10.041	1.376	.224	.287	55.674	7.095	-.015	.022	.055	1.816	99.985
123	3.101	1.455	15.883	3.279	9.805	1.509	.228	.241	55.698	6.663	.020	.106	.098	2.637	100.084
124	1.589	.999	11.175	8.079	9.589	1.300	.203	.179	55.580	12.286	-.019	.081	.046	.856	101.716
125	3.379	1.317	16.068	3.488	9.794	1.421	.167	.267	55.942	7.157	.012	.078	.028	.667	99.603
126	2.977	1.354	15.915	3.336	10.323	1.429	.191	.272	56.199	6.984	-.029	.070	.029	.672	99.540
127	3.309	1.214	16.079	3.417	10.054	1.246	.196	.268	56.373	7.041	.016	.014	.037	1.082	100.097
128	1.495	1.337	16.547	3.290	10.261	1.422	.214	.227	56.142	7.360	.014	.051	.094	2.201	100.136
129	2.403	1.530	16.591	3.099	9.148	1.640	.197	.268	56.867	6.935	-.040	.018	.068	1.990	100.257
130	3.005	1.318	16.200	3.433	9.925	1.475	.176	.263	55.610	6.934	.015	-.030	.047	1.617	99.634
131	3.273	1.470	16.002	3.476	9.937	1.487	.210	.257	55.291	7.116	.014	.038	.039	1.062	99.417
132	3.266	1.353	15.919	3.491	9.776	1.468	.234	.267	56.247	7.204	.052	.026	.010	.404	99.615
133	2.944	1.345	16.228	3.340	10.241	1.459	.166	.254	56.894	7.000	.026	.054	.026	.962	100.699
134	2.929	1.418	15.689	3.452	9.680	1.508	.142	.258	55.808	7.238	-.027	-.010	.015	.329	98.360
135	3.335	1.367	15.927	3.495	9.679	1.373	.185	.278	56.484	7.194	-.022	.018	.008	.349	99.584
136	2.779	1.278	15.112	3.372	10.092	1.575	.177	.316	56.052	7.564	-.001	.062	.010	.381	98.659
AVER:	2.903	1.263	16.394	3.689	9.555	1.333	.196	.247	55.832	7.669	-.002	.038	.041	1.151	100.033
SDEV:	.700	.271	3.160	1.731	1.504	.256	.050	.056	1.147	1.532	.026	.044	.032	.827	
SERR:	.135	.052	.608	.333	.289	.049	.010	.011	.221	.295	.005	.008	.006	.159	
%RSD:	24.1	21.4	19.3	46.9	15.7	19.2	25.6	22.7	2.1	20.0	-1109.1	117.5	78.0	71.9	

Ti, Mn and P Concentration Plots for the volcanic glass



To see how small the difference in the MAN and Nth Point methods are one really needs to zoom in on them as shown here:





Only at very low concentrations in a somewhat inhomogeneous material does the Nth Point begin to show systematic errors compared to MAN.

Conclusion

The MAN and Nth Point data are very similar especially in the homogeneous glass standard although the Nth Point method performed better than the MAN method for Mg ka in the glass standard due to the lack of a suitable standard for MAN calibration in the low Z-bar end of the fit range (an SiO₂ standard could have been used to avoid this).

The MAN method performed about the same or only slightly better than the Nth Point method for trace elements in the impact glass. Only in the somewhat more variable volcanic glass did the MAN perform slightly better than the Nth Point method and then only at concentrations where one would normally perform off-peak measurements on all points anyway.

The Nth Point method is surprisingly accurate in almost all situations except at concentrations below 0.1% where the composition varies somewhat but has the advantage of being very simple to use.