

How to Get the Most Out of Orbis Micro-XRF Measurements with Multiple Acquisition Conditions

Introduction

Micro X-ray Fluorescence (Micro-XRF) is a versatile, non-destructive elemental analysis technique providing qualitative and quantitative elemental composition analysis, as well as thickness and composition measurements on coated samples. For benchtop micro-XRF systems, the elemental measurement range typically runs from Na to Bk. Within this range, measurements can be further optimized by using specific acquisition conditions for certain ranges of the elemental spectrum. For example, in this application note, primary beam filters were used while maintaining constant tube excitation conditions. Primary beam filters are typically pure, thin metal foils used to condition the primary excitation beam.

Filtering

The benefits of filtering are:

- Improved Peak-to-Background (P:B) ratios by reducing background scatter
- Elimination of overlapping tube characteristic lines and Bragg diffraction peaks
- Elimination of sum peaks by suppressing the intensity of the parent peaks

Filtering typically optimizes the acquisition conditions over a limited range of the spectrum. So, the overall spectral analysis may benefit from acquiring the spectrum using more than one filtering condition. Of course, the time for each measurement condition can be varied as well depending on the LOD requirements for the elements of interest to accommodate the overall, allotted measuring time.

Examples

One example of this type of analysis was described in an Insight Application Note: *Discriminating Glass Fragments Using Micro-XRF Spectrometry with Poly-Capillary Optics* distributed in 2015 (EDAX Insight Vol. 13 No. 4) describing the forensic comparison of glass fragments. In this analysis, elemental ratios are used to determine if fragments from unknown glass sources are consistent with glass fragments from

a known source (e.g. the window at a crime scene). Specific filtering conditions were used to remove characteristic tube line overlaps (i.e. to observe Cl K and S K without the overlap of Rh L scatter) and to eliminate sum peaks generated by Si K and Ca K lines. A filter was also employed to improve P:B for trace Pb, which was used to distinguish bottle glass. In this example, the goal was not to do a full quantitative analysis but rather compare and distinguish fragments using characteristic elemental ratios.

Full quantitative analysis of glass is also important as glass composition often affects the performance parameters of specialty glasses, such as high strength glasses. In this case, three acquisition conditions were used to measure the light elements from Na to Si; S to Ca; and Ti to Zr. SRM 1831, which is a soda lime glass, was used as a standard to calibrate all three acquisition conditions. A calibration standard of some type is required for each acquisition condition. This can be a high purity element, oxide or other compound “pseudo” standard(s) or it can be a compositional type standard(s). Elements found in the unknown, which are not found in the calibration setup standards, will be quantified based on interpolation or extrapolation from the calibrated elements. Calibration results for SRM 1831 are shown in the Table 1.

Filter	Component	Measured	Reported	Relative Error
0	Na ₂ O	13.32	13.32	-0.02%
0	MgO	3.51	3.51	-0.02%
0	Al ₂ O ₃	1.21	1.21	-0.02%
0	SiO ₂	73.06	73.08	-0.02%
1	SO ₃	0.250	0.250	-0.02%
1	K ₂ O	0.330	0.330	-0.02%
1	CaO	8.20	8.20	-0.02%
2	TiO ₂	0.019	0.019	-0.02%
2	Fe ₂ O ₃	0.087	0.087	-0.09%
2	SrO	0.010	0.011	-0.38%
2	ZrO ₂	0.0037	0.0059	-36.93%
2	MnO	0.0014	0.0019	-29.11%

Table 1. Results for SRM 1831 Soda Lime Glass calibration standard.

Filter	Component	SRM 620 Soda Lime (Measured)	Rel. Error	SRM 93A Borosilicate (Measured)	Rel. Error	FGS 2 Float Glass (Measured)	Rel. Error
0	Na ₂ O	14.06	-2.3%	4.27	7.2%	14.61	7.9%
0	MgO	2.63	-28.8%	0.080	1501.5%	4.12	6.0%
0	Al ₂ O ₃	1.64	-8.7%	2.03	-11.0%	1.01	-27.5%
0	SiO ₂	73.69	2.2%	80.82	0.0%	70.17	-2.2%
1	SO ₃	0.187	-33.1%	0.00	NR	0.02	NR
1	Cl			0.12	101.4%		
1	K ₂ O	0.414	1.0%	0.03	131.6%	0.63	14.3%
1	CaO	7.21	1.4%	0.02	84.7%	8.81	6.2%
2	TiO ₂	0.015	-17.8%	0.01	-14.4%	0.056	3.0%
2	BaO					0.036	61.2%
2	MnO					0.03	7.4%
2	Fe ₂ O ₃	0.043	-1.0%	0.03	-2.6%	0.43	16.2%
2	Rb ₂ O					0.0040	3.5%
2	SrO	0.031	NR	0.001	NR	0.030	-0.5%
2	ZrO ₂	0.0180	NR	0.028	-32.8%	0.025	-17.8%
2	As ₂ O ₃	0.0626	11.8%				
ND	B ₂ O ₃			12.56			

Table 2. Results for three standard glasses using the SRM 1831 calibration. "NR" indicates there is no reported value for this element in the certification. Total measuring time was five minutes.

From the results in Table 1, we can see that the method is working as we are measuring the glass standard against itself. Also, ZrO₂ and MnO, highlighted in green, were not entered into the calibration. So, we can see what type of accuracy to expect for oxide traces when we are interpolating or extrapolating the calibrations under more ideal circumstances.

In Table 2, measurement results are shown for other NIST glass standards. SRM 620 is another soda lime glass. FGS 2 is a float glass which is simply soda lime glass formulated for flat glass applications, i.e. windows. Soda lime glass also has a somewhat different formulation for bottle glass. Finally, SRM 93A is a borosilicate glass with a significantly different composition to the soda lime glass. Results for elements highlighted in green are interpolated/extrapolated from the elements in the SRM 1831 calibration. Errors for the soda lime and float glass are consistent with what is observed for the MnO and ZrO₂ shown in Table 1. Note that the error level of some elements may be related more to line fitting, particularly of overlapping peaks, than the calibration itself. This is probably true of the BaO result in FGS 2. Overall, the errors in the borosilicate glass seem to be a bit higher than those for the other glasses. This may be related to a difference in glass matrix or simply that

many of the observed elements in SRM 93A are at lower trace levels. The MgO is below the limit of detection and the error here is related to background and peak fitting noise.

Conclusion

Primary beam filters can be used to remove various spectral interferences to get a more reliable value for the affected peak intensities. In the examples discussed here, the Rh L scatter peak could be filtered to better analyze S and Cl; sum peaks which could interfere with K, Mn and other potential traces found in these glasses were suppressed by filtering; and the P:B for trace Pb was improved by filtering which allowed for distinguishing bottle glass fragments. Full spectral analysis and quantification using multiple acquisition conditions is done in a stand-alone software routine, which can be ordered from EDAX.