

Which XRF Line Series to Use?

The direct analysis range of benchtop Energy Dispersive X-ray Fluorescence (ED-XRF) Analyzers using 50 kV X-ray tubes generally runs from Na to Bk. Portions of this elemental range generate two sets of X-ray line series, which can be measured and used for analysis. These nominal elemental ranges are Zn to Ba generating L and K series and Nd to Bk generating M and L series. The question often comes up as to which line series is the best to use and the answer is always, “It depends on the situation”. One should consider a number of factors including line intensity (which includes excitation and detection efficiency), line overlaps and interferences, and matrix absorption effects.

In general, the higher energy lines are preferred. The number of possible electron transitions producing the X-ray signal is lower for the higher energy line series (i.e. K vs L), which means the K α lines are more intense than the L α lines and the potential for line overlap is lower for the higher energy K lines. This can often be a relatively simple exercise of comparing the line intensities and peak-to-background ratios to determine which X-ray line series provides the best precision without spectral overlaps.

There are certain times when the lower energy line series can be more useful. For example, when measuring the thickness of thin metallic coating layers, where “thin” is characterized by the signal absorption of the layer being measured versus the energy of the X-ray signal, the lower energy line series is more sensitive to change in layer thickness. Hence, a small change in “thin” layer thickness evokes a greater change in lower energy signal intensity compared to the higher energy line series. However, the lower energy line series will obviously saturate at a lower thickness limit than the higher energy line series.

The analysis of more complicated sample structures is another instance where one should also consider the use of the lower energy line series. In one case, a customer wanted to measure the Sn coating thickness on an electrical component. Results using the Sn(L) and Sn(K) lines were not similar (Table 1) even when the quantitative models were calibrated with the same type standard. The reason was that the sample component was coated on both sides of the substrate and the substrate was an Al alloy about 0.8 mm thick. The substrate could only absorb about 30% of the Sn(K) fluorescence generated from the opposing surface while it would absorb essentially 100% of the Sn(L) fluorescence. Once the coating was removed from one side of the electrical component to test this hypothesis, the Sn(L) and Sn(K) measurements fell into the same range (Table 2). The measurement of the underlying Ni-alloy layer thickness was now consistent because the result of the Ni thickness, which had the same Ni signal intensity in either case, depended on the calculated value of the Sn layer above it.

There is a website (http://henke.lbl.gov/optical_constants/filter2.html) that calculates the absorption characteristics of a sample matrix, which can be used to verify the probe depth of XRF. The probe depth depends on the matrix absorption characteristics, as well as the X-ray signal line energy.

This website calculator can accept input of multi-element sample matrix formulae and density (it also calculates theoretical density in lieu of manual input) and outputs transmission/absorption characteristics from 1 to 30 keV with a resolution of up to 500 intervals.

Sn(L) on Ni(ZnCu) on Al base				Sn(K) on Ni(ZnCu) on Al base				
Layer	Element	Thickness (μm)	Composition (wt%)	Measurement Position	Layer	Element	Thickness (μm)	Composition (wt%)
1	Sn	1.44	100.0	Eyelet Side	1	Sn	2.52	100.0
2	Ni	1.26	86.9		2	Ni	1.98	87.5
2	Cu		2.2		2	Cu		2.1
2	Zn		10.9		2	Zn		10.4
Base	Al		99.7		Base	Al		99.7
	Fe		0.3			Fe		0.3

Table 1. Initial coating thickness measurements on the electrical contact surface comparing measurements made with Sn(L) and Sn(K) lines.

Sn(L) on Ni(ZnCu) on Al base				Sn(K) on Ni(ZnCu) on Al base				
Layer	Element	Thickness (μm)	Composition (wt%)	Measurement Position	Layer	Element	Thickness (μm)	Composition (wt%)
1	Sn	1.58	100.0	Eyelet Side	1	Sn	1.47	100.0
2	Ni	1.27	86.7		2	Ni	1.21	86.6
2	Cu		2.2		2	Cu		2.2
2	Zn		11.1		2	Zn		11.2
Base	Al		99.7		Base	Al		99.7
	Fe		0.3			Fe		0.3

Table 2. Comparison of coating measurements using Sn(L) and Sn(K) after coating on the opposing side of the electrical contact was removed by polishing.