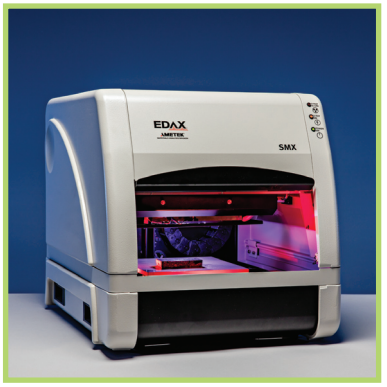
Analysis of Pb-Free Solder and Solder Films with XLNCE SMX-BEN XRF Analyzer

Materials Challenge

Pb-free solders became prominent in electronics manufacturing with the advent of the European RoHS/ELV regulations. X-ray fluorescence spectrometry (XRF) is a non-destructive, non-contact atomic spectrometry, which is ideal for measuring the composition of major, minor and trace components in Pb-free solders as well as the thickness of solder films. The RoHS directive limits the concentration of Pb in solder to less than 1000 ppm. The formulation of Sn-based Pb-free solders use several other alloying elements, including Ni, Cu, Bi, Ag, In and Sb, at minor and trace levels often in the range of 1000 to 5000 ppm to optimize solder characteristics. XRF spectrometry is easily capable of measuring Pb to the RoHS directive and these other solder alloying elements for quality control and failure analysis.

SMX-BEN Instrument

The SMX-BEN XRF analyzer is a benchtop instrument equipped with a 50 kV, 50W X-ray tube; 6 programmable collimator sizes and 5 programmable primary beam filters. Analysis is done in an air atmosphere.



The XLNCE SMX-BEN XRF Analyzer

SMX-BEN Measurements

Three standards were measured with composition and thickness described in Table 1. Each standard sample was about 5 mm in diameter, mounted to a 2-pinhole metal frame.

Standard #	Sn (wt%)	Ag (wt%)	Cu (wt%)	Pb (PPM)*	Thickness (µm) **
1	96.17	3.1	0.61	1220	"infinite"
2	97.1	2.4	0.5	NR	10.97
3	97.2	2.4	0.4	NR	18.99

* NR indicates Not Reported
** Infinite indicates the samples were bulk samples with respect to XRF measurement depth

Table 1: composition and thickness of PB-free solder samples measured.

Samples measurements were made under the following conditions:

- 47 kV, 0.960 mA
- 30 seconds measuring time
- 2 mm collimator

Quantification was done using physical computer modeling known as "Fundamental Parameters"(FP). The FP quantitative method, which is commonly known as the "No Standards" method, can be calibrated with a variety of "standards" including a single, pure element, e.g. Cu, up to matching type standards for best accuracy. The method's name "No Standards" derives from the fact that type standards are not a requirement to get quantitative information albeit with lower accuracy. In the measurements in this application note, the accuracy of measurements will be compared between a calibration using matching pure, bulk elements of Sn, Cu, Ag and Pb, which are inexpensive and readily available, and a calibration using a type standard, i.e. standard #2.

Results

Samples #1 and #3 were measured 30 times to obtain measurement statistics. In Table 2, results are shown where the FP calibration was done with pure, bulk elements, i.e. Sn, Ag, Cu and Pb. This is commonly done when type standards are not readily available and the limits on accuracy can be loosened.

Standard#		Sn (wt%)	Ag (wt%)	Cu (wt%)	Pb (PPM)	Thickness (µm)
1	Mean	96.52	3.04	0.35	899.62	
	Max	96.59	3.12	0.38	1077.37	
	Min	96.44	2.97	0.33	767.11	
	Std. Dev.	0.033	0.031	0.011	57.129	
	RSD %	0.03%	1.02%	3.20%	6.35%	
3	Mean	97.06	2.91	0.03		14.67
	Max	97.14	3.03	0.03		14.86
	Min	96.94	2.83	0.03		14.46
	Std. Dev.	0.042	0.042	0.001		0.099
	RSD %	0.04%	1.44%	3.24%		0.67%

Table 2: Statistics on 30 repeat measurements using pure, infinite elements for calibration of the FP quantification method.

In these types of calculations, the composition is typically normalized to 100 wt%. Errors tend to affect the accuracy on trace elements, i.e. elements with less than 1 wt%, more heavily due to the low concentrations of the traces. Interestingly, this quantification on sample #1 would indicate that the sample would be flagged for further testing as typical RoHS XRF testing protocols flag samples with XRF results exceeding 700 PPM for Pb for further testing. To improve the repeatability, the measuring time can be increased. A factor of 4 increase in measurement time, i.e. measuring for only 2 minutes, would improve precision by a factor of 2.

Table 3 shows the results for these same 30 measurements using type standards for calibration of the FP method. Type standards can either be purchased from commercial vendors for typical quality control problems and regulatory issues or can be made in-house by validating standards through destructive testing.

Standard#		Sn (wt%)	Ag (wt%)	Cu (wt%)	Pb (PPM)	Thick-ness (µm)
1	Mean	96.11	3.16	0.61	1278.82	
	Max	96.18	3.22	0.64	1445.06	
	Min	96.05	3.11	0.58	1125.82	
	Std. Dev.	0.036	0.030	0.016	83.037	
	RSD %	0.04%	0.94%	2.66%	6.49%	
3	Mean	97.20	2.40	0.40		18.94
	Max	97.27	2.47	0.42		19.34
	Min	97.11	2.33	0.37		18.67
	Std. Dev.	0.038	0.035	0.012		0.123
	RSD %	0.04%	1.44%	2.96%		0.65%

Table 3: Statistics on 30 repeat measurements using type standards for calibration of the FP quantification method.

Accuracy on the trace elements is now much improved and the thickness measurement accuracy is also greatly enhanced by using a type standard in the range of 10 µm thick. Use of a single type thickness standard will calibrate the FP quantification with high accuracy for a limited range of thickness. Generally, thicker layers are harder to accurately calculate using FP methods because errors in the physical modeling tend to accrue over the thicker layer. A thick, single type standard can correct these errors, but then use of this single, thick type standard calibration model will adversely affect the results for thinner layer measurements. In cases where thickness measurements are required over a "thin" to "thick" range, where thin and thick are defined by the absorptive properties of the materials to be measured and the energy of the available XRF signal peaks, it is best to have a few type thickness standards available which cover the range of thickness to be measured. The FP quantification routine used by the XLNCE SMX family of XRF instruments has several linear and non-linear correction functions available to calculate the internal calibration coefficients as a function of coating thickness. So, if a thickness range of coating standards is available, the FP quantification can be calibrated such that calibration coefficients are also a function of the coating thickness being measured. This provides superior accuracy in thickness/composition measurements over a much broader range of thickness and composition from a single calibration model.

Recommended EDAX Solution

The XLNCE SMX-BEN XRF elemental analyzer is capable of non-destructive, non-contact measurements to determine layer thickness and composition as well as bulk sample compositional analysis. The SMX-BEN can be used to measure Pb traces in Pb-free solder for RoHS compliance as well Pb content in Pb containing solders for high reliability uses, such as military and aviation. Furthermore, this unit is well-suited for measuring the composition of other minor and trace alloying elements commonly used in Pb-free solders, such as Ni, Cu, Bi, Ag, In and Sb. The SMX-BEN unit can be used for quality control in the laboratory as well as process control measurements with software having operator, supervisor and maintenance access levels to ensure that the right job is done at the right time.