

XRF- A Reality Check

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The requirement for non-destructive material screening

The Restriction of Hazardous Substances (RoHS) regulations of the European Union, and similar regulations being enacted around the world, require the virtual elimination of lead (Pb), mercury (Hg), cadmium (Cd), hexavalent chromium (Cr6), polybrominated biphenyls (PBB) or polybrominated diphenyl ethers (PBDE) from electronic products. Allowable concentration levels in any homogeneous material contained within a product are extremely low: 0.01% for Cd and 0.1% for other substances by weight. The most significant issue affecting the practical validation of RoHS compliance in the day-to-day assembly environment is ensuring that no restricted substances, especially tin-lead (SnPb) materials, have inadvertently entered into the production stream. This is particularly important because many suppliers are still shipping both compliant and non-compliant materials and most assembly facilities are producing both SnPb and lead-free products, thus having both sets of materials in the same facility.

The foundation of an in-house screening program is the validation of all incoming materials. This captures any supplier or shipping errors and establishes the accuracy of the in-house inventory system. It may be desirable to perform additional checks after materials have been installed on assembly machines to catch logistical errors in internal handling. Screening of completed assemblies between compliant and totally SnPb units is possible by inspecting any typical solder joint. In cases where there is foreknowledge of the possibility of non-compliance of specific components or materials, these might also be inspected. However, it is impractical to inspect each individual subcomponent in a final assembly for compliance, which emphasizes the advantages of incoming component validation.

Speed and accuracy are vital for any test utilized for the screening process. Screening tests should be easy to set up and perform and should provide rapid results, ideally within a few minutes, to minimize cost and loss of productivity. For incoming inspection, and to a lesser degree in-process confirmations, it is highly desirable to perform validation sampling without removing components from their packaging.

X-ray fluorescence spectrometry

XRF analysis has been a well established, non-destructive analytical technique for elemental analysis for over 50 years. It is used in applications in a number of other industries and is now becoming a potentially vital part of the electronic assembly process.

The x-ray fluorescence process is initiated with ejection of an inner shell electron by an external force/energy that creates an electron vacancy. This vacancy is filled by transition of an outer shell electron of the atom. The difference in the binding energies of the two electrons results in creation of *characteristic x-rays* that are known as x-ray fluorescence.

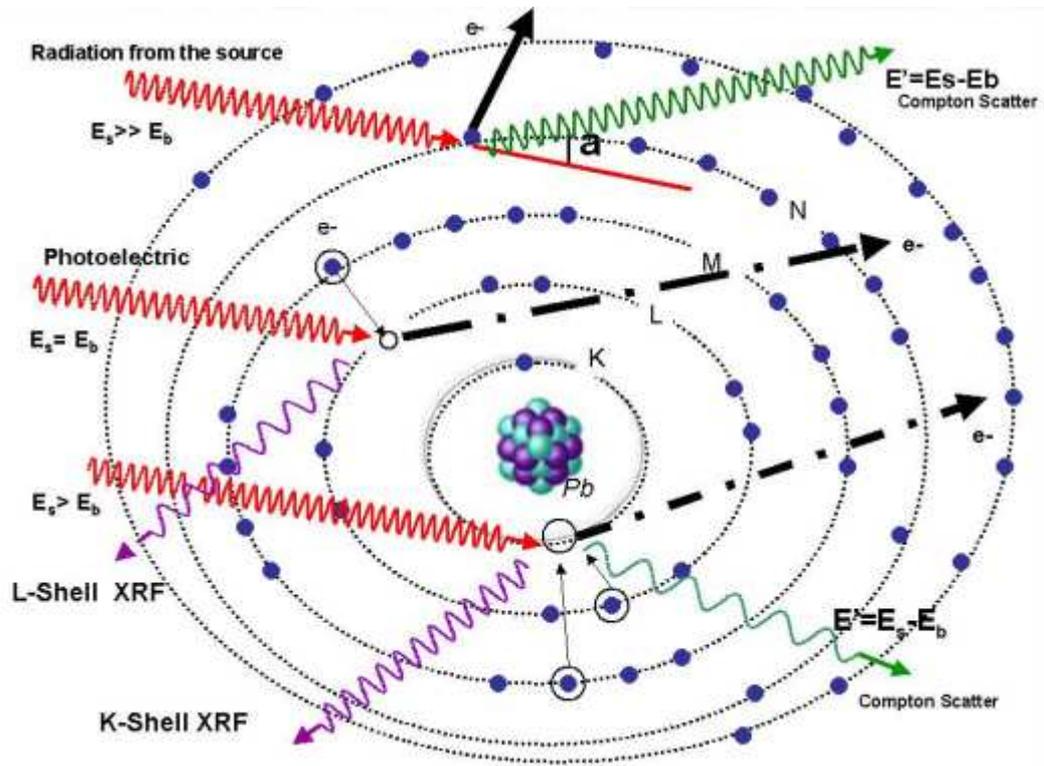


Figure 1: XRF process

It is the absorbed radiation energy of the source by the atom that causes its rise to an *excited* state. The ejection of electrons and subsequent characteristic x-ray photons allows the atom to discharge the absorbed energy, *fluoresce*, and return to its ground/normal state. Because each atom has a unique energy pattern, with its electrons having distinct quantum numbers, resulting characteristic x-rays (*Table 1*) are also unique with specific frequency and act as fingerprints of elements in XRF analysis.

Characteristic X-Ray Energies (keV)									
Element	Mass	KAlpha	KBeta1	KBeta2	LAlpha1	LAlpha2	LBeta1	LBeta2	LGamma
Be	4	0.11							
Cr	24	5.41	5.41	5.95	0.57	0.57	0.58		
Mn	25	5.90	5.89	6.49	0.64	0.64	0.65		
Fe	26	6.40	6.39	7.06	0.71	0.71	0.72		
Co	27	6.93	6.92	7.65	0.78	0.78	0.79		
Ni	28	7.48	7.46	8.26	0.85	0.85	0.87		
Cu	29	8.05	8.03	8.91	0.93	0.93	0.95		
Zn	30	8.64	8.62	9.57	1.01	1.01	1.03		
As	33	10.54	10.51	11.73	1.28	1.28	1.32		
Se	34	11.22	11.18	12.50	1.38	1.38	1.42		
Br	35	11.92	11.88	13.29	1.48	1.48	1.53		
Zr	40	15.78	15.69	17.67	2.04	2.04	2.12	2.22	2.30
Mo	42	17.49	17.37	19.61	2.29	2.29	2.40	2.52	2.62
Aq	47	22.16	21.99	24.94	2.98	2.98	3.15	3.35	3.52
Cd	48	23.17	22.98	26.10	3.13	3.13	3.32	3.53	3.72
In	49	24.21	24.00	27.28	3.29	3.28	3.49	3.71	3.92
Sn	50	25.27	25.04	28.49	3.44	3.44	3.66	3.90	4.13
Sb	51	26.36	26.11	29.73	3.60	3.60	3.84	4.10	4.35
Te	52	27.47	27.20	31.00	3.77	3.76	4.03	4.30	4.57
I	53	28.61	28.32	32.29	3.94	3.93	4.22	4.51	4.80
Ba	56	32.19	31.82	36.38	4.47	4.45	4.83	5.16	5.53
Ta	73	57.53	56.28	65.22	8.15	8.09	9.34	9.65	10.90
W	74	59.32	57.98	67.24	8.40	8.34	9.67	9.96	11.29
Pt	78	66.83	65.11	75.75	9.44	9.36	11.07	11.25	12.94
Au	79	68.80	66.99	77.98	9.71	9.63	11.44	11.58	13.38
Hg	80	70.82	68.90	80.25	9.99	9.90	11.82	11.92	13.83
Pb	82	74.97	72.80	84.94	10.55	10.45	12.61	12.62	14.76
Bi	83	77.11	74.81	87.34	10.84	10.73	13.02	12.98	15.25

Table 1: Photon energies of principle x-ray spectral lines of selected elements

The basic blocks of an energy-dispersive x-ray fluorescence (EDXRF) system are source, collimator, detector, electronics, CPU and display mechanism. The combination of these blocks, which require sophisticated design considerations, provides the resulting data for analyses of a specimen.

For RoHS applications, EDXRF analyzers are generally used rather than wavelength-dispersive systems that utilize crystals for separation of spectral lines. In EDXRF, the detector receives the undispersed beam that includes all the x-ray fluorescence of the specimen elements and scatter radiations.

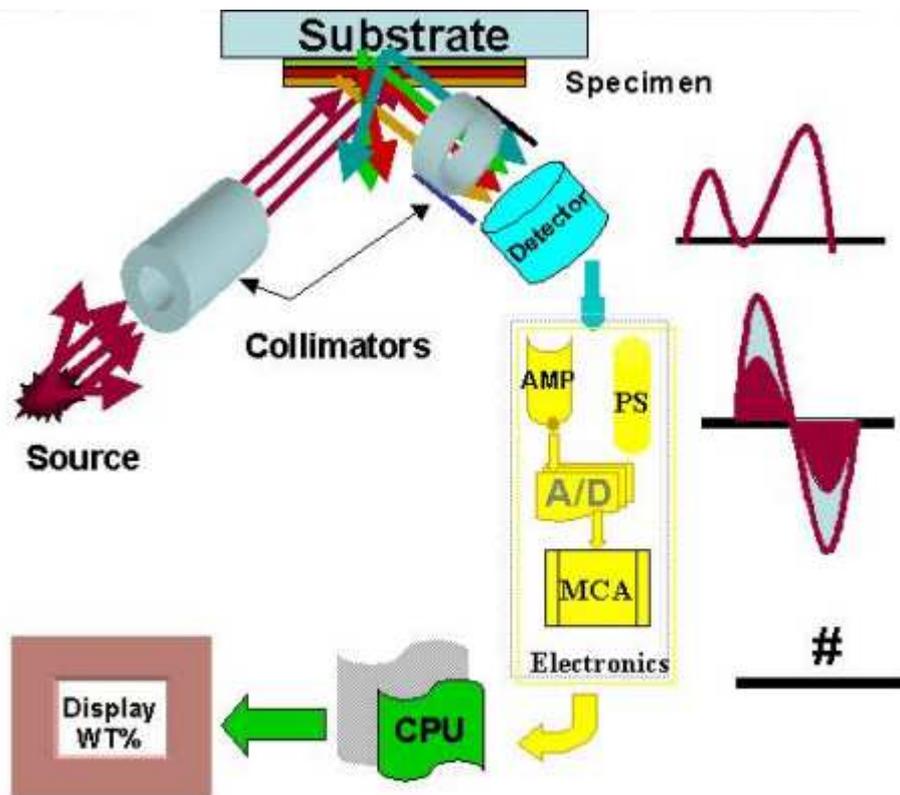


Figure 2: XRF system diagram

The resulting data from an XRF analyzer are a series of identified energy lines associated with elemental composition of the specimen, the basis of *qualitative analysis*, with corresponding relative intensities as a function of their concentrations, which is the basis of *quantitative analysis*. A sample composed of several elements yields multiple spectral lines that can overlap each other and cause interference in both qualitative and quantitative examination. The spectral line data along with their corresponding intensities are then compared to the *calibration* parameters previously stored in XRF CPU for quantification and eventual output to display.

The proper application of XRF in the PCB assembly process

The most fundamental function of an XRF analyzer in the screening process is its ability to clearly identify the presence of a desired element, thus eliminating the possibility of a false negative. This is a function of an XRF's source being either an x-ray tube or a radioisotope. The source must produce x-ray or gamma-ray photons with higher energy than the binding energy of the electrons in the desired atom to cause characteristic x-ray fluorescence.

The XRF analyzers that are being used for RoHS application range from portable and benchtop to large-scale laboratory systems. These XRF systems have unique capabilities for their intended functions but limitations for broad applications. Thus, only a few of the systems offered to the PCB assembly industry are ideal and others are functionally limited for the task at hand.

Even in their incoming, un-assembled state, most components utilized in electronic assembly do not consist of single, homogeneous materials. The RoHS directive requires that all 'homogeneous materials' contained within an electronic product be compliant (i.e., lead free). This has been further defined to include the plating on component leads and PCB pads. XRF technique has been proven to be very effective in identifying restricted substances, especially

Pb, Hg and Cd, in many types of components because of its ability to identify the spectral energy patterns of these elements within a variety of matrices used in electronics.

This technique can be greatly expanded and simplified by utilizing higher (source) energy levels that induce fluoresce of the K-shell x-rays of the elements, in particular lead and mercury atoms. The lower energy, L-shell, x-ray energies for Pb and Hg lie between 9.9 and 14.8 KeV. Many other elements commonly present in electronic materials such as arsenic (As), selenium (Se), bromine (Br), germanium (Ge) and zinc (Zn) produce characteristic x-ray spectral lines (peaks) in the same range. In contrast, K-shell energies for Pb and Hg are much higher, 68.9 to 85 KeV, and suffer no interference from either As, Se or Br.

Figure 3 shows the comparison of XRF spectra for a diode inspected with a 40 KeV (top) and a 122 KeV (bottom) XRF source. The analysis of the 40 KeV spectra identified large concentrations of Br but no Pb (L-shell) at energy levels 10 to 14 KeV. Using the higher energy source, the resulting spectrum displays the K-shell peaks between 70 and 75 KeV with no obstructions. Clearly, this higher energy (K-shell) spectrum makes it much easier to identify Pb in the presence of Br, leading to a much more robust validation process.

While it is possible to filter the lower energy spectrum more carefully to separate the L-shell peak for Pb, there is a certain degree of impracticality as this would require careful calibration and an accurate knowledge of the concentrations of all of the interfering or masking elements, thus adding a great deal of complexity and time to the process. Because of these effects, the lower energy spectra (L-shell) are much less flexible for inspecting a wide range of component types where *masking elements* such as Br and Sb may exist in varying combinations and concentrations. In all cases, it is necessary to identify all the materials (matrix) within the sample area/volume to ensure accurate separation of the (possible) spectral peaks associated with each element. K-shell methodology accomplishes this accurately and efficiently.

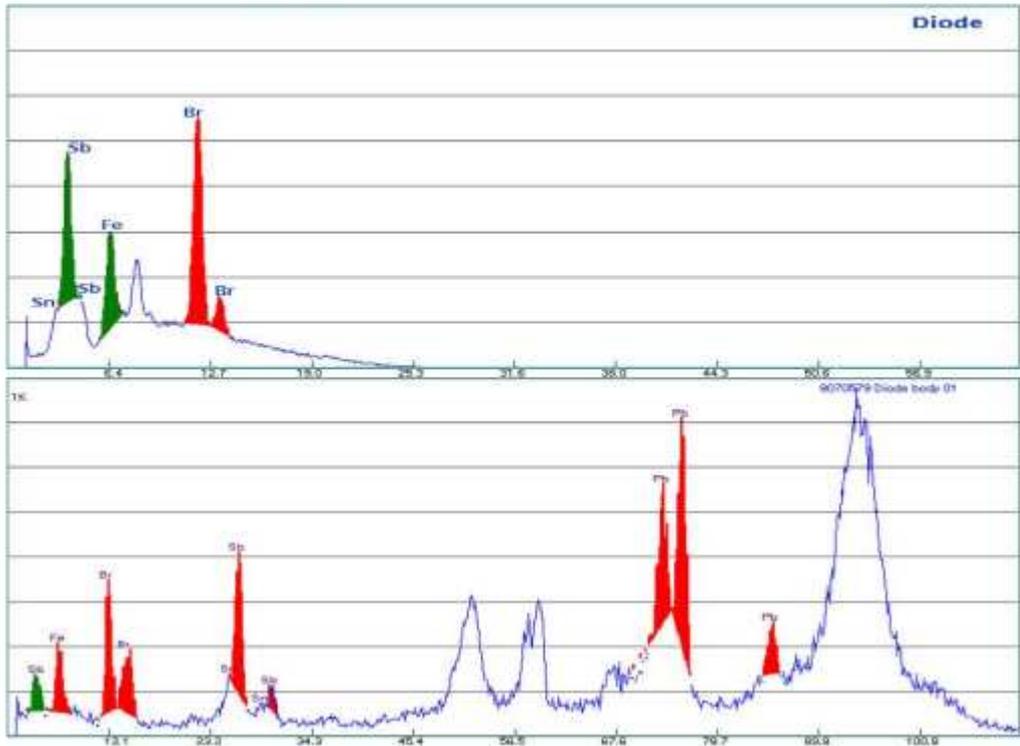


Figure 3: Spectral energy comparison

It is important to note that regardless of the energy band, XRF is a comparative technique and it requires representative calibration standards. Also, it should be understood that XRF's measured intensity of spectral lines, quantification, is a function of number of atoms present in an absolute term per unit area measured. Accordingly, weight percent calculations are relative terms and a function of the number of atoms present and the weight of the specimen.

Conclusion

The need for screening incoming materials and monitoring the assembly process against intrusion of non-RoHS (EU, China, Korea, California and others, no doubt, to come) directive compliant materials is essential and it must be done in an efficient, non-destructive, yet accurate way. XRF is a powerful tool that can be very effective in the validation of both the absence and presence of certain RoHS-restricted elements (Cr, Br, Pb, Hg and Cd). XRF presents an elemental analysis, and while it can not quantitatively measure compounds and, therefore, does not provide actual chemical composition, the qualitative data provided by XRF are a pre-requisite for such measurements. In an XRF application, the presence of a spectral line of an element is essential for its recognition; qualitative analysis. Therefore, the XRF source must have enough energy to remove electrons of the desired atom for production of characteristic x-ray spectral lines. An isotope-based XRF for inducing higher energy, K-shell, x-rays is a more effective method for this application. K-shell x-rays having higher energies than L-shell are less likely to be absorbed by the specimen's matrix, reducing false negative possibilities. Hence, the most appropriate system for the PCB assembler is a K-shell system if accurate, fast and reliable material elemental monitoring is desired