Understanding of XRF Technology and Clarification of its Application for RoHS Directives

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Abstract:

RoHS directives require screening and quantification of certain elements and compounds used in electronics components and parts.

X-ray Fluorescence (XRF) technology has emerged as an effective tool in the screening process of electronic components. XRF analyzers, bench top and portable, can determine the presence of concerned elements, but not compounds, in a relatively short period of time.

XRF technology is an established analytical method for elemental analyses. However, there are certain technical aspects that directly impact the RoHS application that may require further understanding of XRF principles. The quantitative determination of elements for compliance with RoHS directives could be compromised under certain conditions if the fundamental principles of XRF technology are not well understood and adhered to for this application.

The most influencing factor in XRF application for RoHS compliance is the ability of an XRF system to excite and induce characteristic x-rays of concerned elements without any interference that may result in either false negative or a false positive indication. Any false indication causes operational difficulties and has financial consequences. This factor is more pronounced in electronic components which are often composed of complex matrices and contain elements that could interfere directly with the characteristic x-rays of RoHS-concerned elements.

This paper provides an overview of XRF technology as it is applied to electronic components, the effectiveness and limitations of XRF methods as a screening, and the contributing factors in obtaining accurate measurements.

X-ray Fluorescence Spectrometry (XRF):

For over 50 years, XRF analysis has been a well established non-destructive analytical technique for elemental analysis (1). The basic physics of XRF spectrometry is based on energy transformation and transitions of electrons within an atom.

A neutral atom is composed of a certain number of electrons that equal the number of protons (Z) in its nucleus. These electrons, being in constant orbital motion, are bound to their atom by a specific amount of energy known as *Binding Energy* or *Ionization Energy*. This is the amount of energy that it is required to remove or eject an electron from its atom.

In the basic model of atomic structure, electrons are assigned to energy levels called shells or orbits. Each shell can accommodate a certain number of electrons with each possessing a specific amount of energy, angular momentum and direction of spin. These electron's parameters are referred to as quantum numbers (Pauli Exclusion Principle). The energy levels conventionally are referred to as K, L, M, N, O, etc. shells with K-shell electrons having the highest binding energy because of their close proximity to the nucleus of the atom.

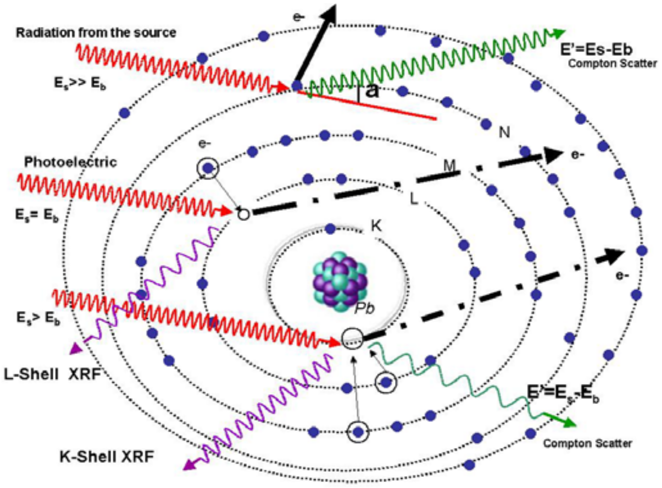

Figure 1 - XRF Process

The X-ray fluorescence process is initiated with the 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 a *characteristic x-ray* that is known as x-ray fluorescence. The energy of the characteristic x-ray is calculated by the formula:

$E = hC/\lambda = 12{,}936/\lambda$ Where:
h = Planck's constant, C = Speed of light, λ = Frequency, and E = Photon Energy

Table 1 - Photon Energies of Principle X-ray Spectral Lines of Selected Elements, keV

Cr	24	5.41	5.41	5.95	0.57	0.57	0.58		
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		
Ag	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
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
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

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

X-ray Fluorescence Analyzers:
Energy-Dispersive X-ray Fluorescence Analyzers, EDXRF, are generally used for RoHS application rather than Wavelength-Dispersive systems that utilize crystals for separation of spectral lines. With EDXRF, the detector receives the undispersed beam that includes all the x-ray fluorescence of the specimen elements and scatter radiations.

The basic blocks of an EDXRF system are a radiation source, collimators, a detector, electronics modules, a CPU module, and a display mechanism. The combination of these blocks will provide the resulting data for analysis of a specimen.

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 spectra lines that can overlap each other and cause *interference* in both qualitative and quantitative analysis. The spectral line data along with their corresponding intensities are then compared to the *Calibration* parameters previously stored in the XRF CPU for quantification and eventual output to display.

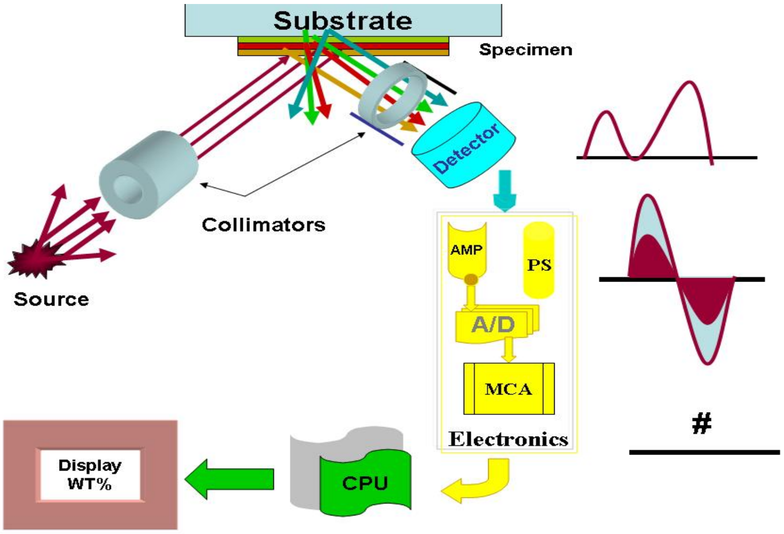

Figure2 - XRF System Diagram

In addition to the creation of characteristic x-rays of the composing elements, irradiation of a sample creates multiples of scattering effects. These scattered x-rays also appear in the resulting spectrum and contribute to the complexity of the analysis. The most dominant scattering phenomenon is the *Modified Scatter* also known as the *Compton Effect*. In Compton Scatter, the incident x-ray photons collide with outer shell electrons which are loosely bounded. In this collision, an incident x-ray photon looses some of its energy and is deflected at a different angle from incident. The resulting x-ray with lower energy continues in its new path until its next interaction with another electron which can further result in another scattering event or cause x-ray florescence. Furthermore, the radiation beam from the sample can cause x-ray fluorescence in the detector's material by ejecting its electrons. This phenomenon known as *Escape Peaks*, which will also appear in the spectrum and should be considered when it coincides with the spectral line of the analyzing elements.

XRF Building Blocks and Their Function:

Source:
The external force/energy required for excitation of an atom and ejection of its electrons is supplied by either an X-ray tube or a radioisotope source in an XRF system. The source provides energy/force in the form of gamma or x-rays to excite the specimen elements and cause fluorescence of characteristic x-rays by ejecting the inner shell electrons.

X-ray tubes provide a continuous x-ray spectrum where both the energy and the output intensity are adjustable. The output energy and intensity of an x-ray tube are functions of applied high voltage and amperage to its filament respectively.

Considerations for choosing x-ray tubes are target material, focal spot, power, filtration of undesired low energy x-rays, and heat removal which all influence the production of characteristic x-rays and the resulting spectrum in XRF analysis.

Radioisotopes are generally used for their physical size and their ability to provide gamma or x-ray photons with specific energy that come from their natural decay. A radioisotope, unlike an x-ray tube, can not be turned off and its energy is not adjustable.

Regardless of the type, a source must have enough energy to excite an atom by ejecting its electrons to cause x-ray fluorescence. If the energy of the source is less than the binding energy of the desired electron in a certain element, that source is not capable of inducing x-ray fluorescence of preferred energy. For example, production of Cd K-shell characteristic x-rays requires at least 26.72 keV of energy where 88.00 keV of energy is needed for inducing K-shell characteristic x-rays of Pb. This means that a 40 keV x-ray tube is capable of inducing K-shell x-rays of Cd but not of Pb. Therefore, a 40 keV x-ray tube can only generate L-shell x-rays of Pb at 10.5, 12.6 and 14.7 keV (Table 1).

Collimation:

Collimation is the combination of the source focal spot and apertures that radiation travels from the source to the samples and from the sample to the detector. An XRF system's collimator defines the exposure area of a sample and also can be designed to control the depth of interrogation of a sample. Effective collimation can simplify the spectrum by reducing the scattering radiation (Compton Effect) that originate from interaction of the source photons with the lighter elements in a matrix.

Detector:

A detector serves as medium of exchange for various radiation energies coming from the sample as result of x-ray fluorescence or scattering events. Effectiveness of a detector which is its ability to stop the radiation of desired energy is a function of its material of composition and thickness. A radiation photon can only be accounted for if it is stopped within the detecting medium and induce an electrical signal. Because the absorption of radiation is a function of atomic density, the detector material is chosen based on the application and the energy of the desired characteristic x-rays.

Generally, XRF systems with low energy x-ray tubes utilize a solid state detector such as Si Pin Diodes and XRF systems with high energy output such as those with radioisotopes use a CdTe, CZT, HgI, or similar detectors.

Electronics:

Electronics for an XRF system are combinations of power supplies, pre-amplifiers, amplifiers, filters, converters, scaler, mutichannel analyzer, memory, and other necessary components for converting a detector's pulses to a recognizable data format.

There are many considerations in design of XRF electronics that influence the stability, speed, and quality of data. The eventual output of an XRF electronics is a spectrum that represents the spectral lines for all specimen's characteristic x-rays of elements present along with scattering effects such as Compton, and escape peaks (Figure 3) as a function of energy.

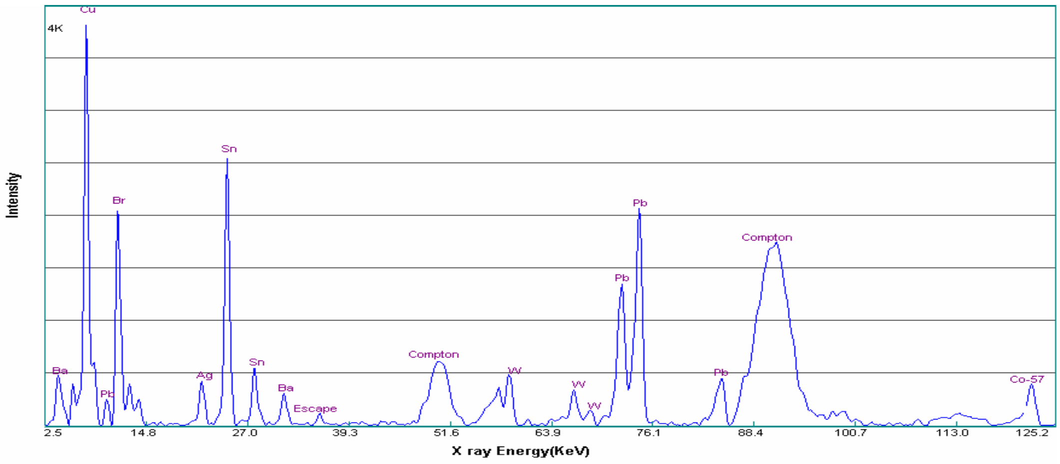

Figure 3 - Characteristic x-rays of a component from a Co-57 Source

Central Processing Unit (CPU):

The CPU, central processing unit, is the brain of an XRF system. This is where data reduction techniques, analytical algorithms, stability corrections, calibration data, safety interlocks, and other operation protocols are stored and executed. The effectiveness of an XRF in performing its intended application depends on the CPU's capability and its level of sophistication.

XRF Application and RoHS Compliance Considerations:

Based on the August 19, 2005 Publication, EU's RoHS directives, unless is an exempted application, restricts the levels of lead (Pb), mercury (Hg), chromium hexavalent (Cr VI), polybrominated biphenyls (PBB), and polybrominated diphenyl Ethers (BPDE) to less than 0.1%, and cadmium (Cd) to less than 0.01% by weight in homogenous materials.

British DTI RoHS Enforcement Guidance Document (3) and IEC ACEA ad hoc Working Group recommended Procedures for Determination of Levels of Regulated Substances (4) cite the use of XRF technique for the Screening Process.

The ad hoc Working Group document explains both qualitative and quantitative Screening by XRF spectrometry in detail. This document outlines the basic underlying principals and explains some of the limitations for all suggested analytical methods for RoHS compliance.

Implementation of RoHS directives by using analytical techniques has been challenging due to several factors. The challenges are not limited to the Screening process (5); they also include Verification laboratory methods (6).

The contributing factors to the challenges of implementing RoHS directives originate from the directives' non-technical nature, electronic materials' compositions and variability in size, and implementation of the screening process through XRF and laboratory methods.

RoHS directives definition of "homogenous material" and what classifies as a "homogenous constituent layers" is too vague especially in cases of components with multi-layer coatings such as Ni/Cu plated brass parts.

The other difficulty is RoHS directives implied determination of restricted substances quantities in "weight percent", and calculation of nonexempt portions from the "exempted portions" by analytical methods.

The fact is that electronic components are anything but homogenous in size or composition. To complicate the matter further, "exempt" and "nonexempt" restricted elements might be present in the same component. For example a chip resistor may contain Pb from of lead-oxide passivation glass, which is exempt along with Pb from termination which is not exempt.

Application of XRF for RoHS Screening:

The challenges experienced in both the XRF screening process and confirming laboratory verifications have been outlined in several articles (5, 6, and 7). Some of these difficulties are due to material matrix, and size, and some to the application of analytical methods.

A successful screening process using an XRF system requires recognition of parameters that influence the measurements, limitations due to the technology and material, and applicability of the method for intended purpose.

Some of the challenges surrounding the XRF screening and parameters that influence it are:

Measurement of Compounds:

XRF is an analytical technique for measurement of elements. For example, XRF can establish the presence or absence of Br and Cr regardless of their chemical compositions. However, XRF cannot make a distinction between Cr^{+6}, Cr^{+3} and other forms of Cr compounds such as $CaCr0_4$, CNa_2Cr0_4 , etc. The same holds for bromine compounds.

Standard Samples:

An XRF system is a *comparative technique* for elemental analysis. This means, an XRF requires a set of calibration standards in order to perform its quantitative measurements. Representative standards containing exact elemental compositions with relative concentrations of the analyzing matrix are essential for accurate quantification in XRF application

The existing samples being offered as standards are mostly polymer base materials with known concentration of certain elements. These samples do not necessarily make representative standards due to their matrix composition and absence of other elements that would otherwise be present in electronic components.

For example, one set of samples being offered for RoHS application contains all RoHS elements at two concentration levels along with a blank. In the real word, Br always is accompanied by Sb as a flame retardant which would cause internal absorption influencing the Br characteristic x-rays as shown in Figure 4. . The same holds for Cr which is always present for RoHS application with other metals such as Fe. Another example is the absence of Sn from all samples being offered for RoHS application. Sn is a major constituent of electronic process and its absorption and enhancement effects must be characterized for accurate measurements especially at low concentration of Pb, Hg, and Cd.

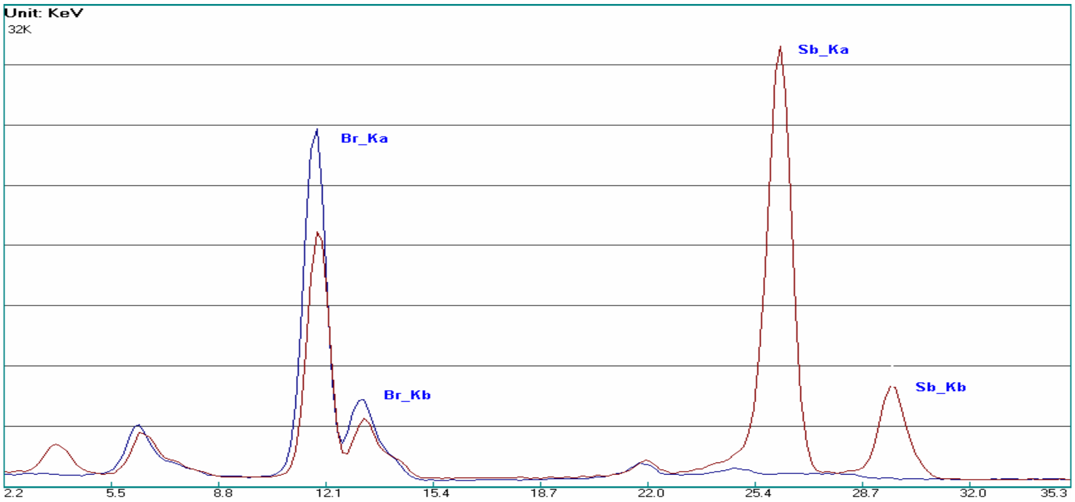

Figure 4 - Comparison of Br concentration in presence and absence of Sb

In the absence of representative calibration standards, XRF systems resort to Fundamental Parameter (FP) techniques to correct for a specimen's self enhancement and self absorption effects due to the presence of other elements that are not represented in calibration standards. FP method requires homogenous distribution, total knowledge of elements present, and infinitely thick specimen for proper modeling. Also, the use of FP method is time consuming and requires a trained analyst in many cases.

In some XRF systems, multiple calibration routines have to be chosen by the operator and the same sample must be analyzed several times for complete quantification.

False Negative and False Positive Indications:

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 or false positive indication. This is a function of an XRF's source, either an x-ray tube or a radioisotope, having enough energy to penetrate the material's surface and induce characteristic x-rays of desired elements. A false indication can occur generally under two conditions in RoHS application when:

1. The desired element's radiation signature, characteristic x-rays, is masked by other elements present in the specimen. Most electronic components use a combination of Br and Sb compounds along with Ba on occasion as flame retardants. Both Sb and Ba are effective absorbers of x-rays especially at lower energies (L-Shell) for RoHS elements. Additionally, Sn, Au, Ta, Bi, Pt, and many other heavy elements are common in electronic materials and processes. These elements are also strong radiation absorbers and easily mask L-shell characteristic x-rays of Pb, Hg, and Cd which can result in false negative readings when restricted elements are present.

2. Characteristic K-shell x-rays of interfering elements present in high concentrations overlap the L-shell characteristic x-rays of RoHS substances causing a convoluted spectrum, making the identification of a desired element impossible in some cases. For example, elements such as Arsenic (As), Selenium (Se), Bromine (Br), Germanium ((Ge), and Zinc (Zn) produce K-shell characteristic x-ray (Table 1) spectral lines (peaks) in the same range as L-shell x-rays of Hg, Pb, and Au. A large concentration of these elements requires sophisticated algorithms to clearly identify the presence of Pb and Hg especially when dealing with low concentrations in a sample. False positive indication can also occur when a large concentration of Sb is misidentified as Cd in materials such as insulating wires.

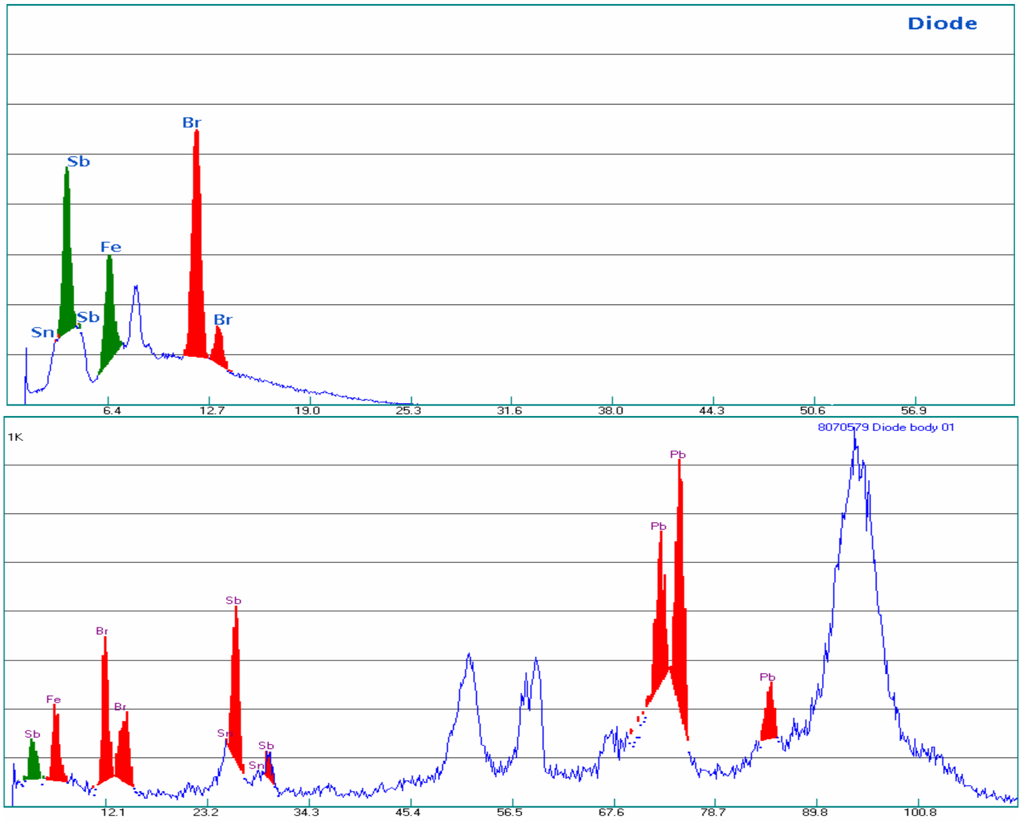

Figure 5- X-ray Spectra created from a low energy X-ray tube and a radioisotope

XRF systems with K-shell excitation capability for all RoHS elements have been proven to be more effective in identifying restricted substances especially Pb, Hg, and Cd in many types of components because of their ability to induce both K-Shell and L-shell spectral energy patterns of these elements. The XRF screening process is improved and simplified by utilizing higher (source) energy levels that induce fluorescence of the K-shell x-rays in elements in particular Pb and Hg reducing potential for false negative results which can be obtained by surface measurements using low energy x-ray tube XRF systems.

The K-Shell x-ray systems, due to their penetrating feature, are capable of providing qualitative data for presence or absence of RoHS substances through packaging material without needing to disturb packaging seals. As first line screening, materials such as BGA trays in vacuum packs, electrostatic bags containing components, and solder paste jars encapsulated under nitrogen can be monitored in incoming QC effectively.

Figure 5 shows the comparison of XRF spectra for a diode inspected with a 40 keV (top) and 122 keV (bottom) X-ray source. The analysis of the 40 keV spectrum identified large concentrations of Br but no Pb (L-shell) at energy levels between 10-14 keV. Using the higher energy source, the resulting spectrum displays the K-Shell peaks between 72.8 to85 keV with no obstructions.

Weight percent calculations:

Quantitative analysis of an element by XRF technique is based on the intensity, counts per unit time, of characteristic x-rays of that element detected by the system. The characteristic x-ray intensity, count rate, is a function of the number of atoms of that element present in the specimen. Therefore, XRF accounts for the absolute amount of atoms present in a measurement area in mg/cm^2 unit that is also referred to as *area-density*. The thicker a sample, in a homogeneous matrix, the larger the number of atoms hence, the greater the characteristic count rate for a given atom.

The weight percent calculations (wt%, PPM) from the laboratory techniques provide a relative ratio of a desired element as a function of total weight of the specimen analyzed by the method which is not affected by the materials thickness.

XRF analyses for bulk sample measurements such as Pb in Pb/Sn solder compositions are straight forward and highly accurate due to existence of suitable standards and sample size. XRF analyzers use mathematical models to provide wt%

calculations by correcting for variations in thickness, density, and variations of the composition of a specimen from the standard calibration samples for quantitative analysis.

The wt% calculations become challenging when more than one source of a restricted element is present at the location which is being analyzed. For example, a PCB that contains Au/Cu/Pb in its through holes can be populated by a component with leads containing Sn/Pb mixture. Soldering this component with Sn/Ag/Pb paste will further add to the concentration of Pb content in that solder joint. Should a representative wt% measurement of Pb at this joint be reflective of only the surface Pb content in solder, Pb content in solder and the leads, or total Pb concentration from all sources? In other words, wt% of "what" shall be calculated?

Another example of wt% calculation difficulty is when both exempt and non-exempt mixtures of the same element are present within a component. An XRF analysis of such a component can only provide the total amount of Pb concentration which would be comparable with laboratory methods that also provide the total concentration due to sample grinding and digestion.

Measurement Area and Component Size:

The present XRF systems for RoHS application offer measurement areas that vary from less than 1 mm^2 to over 100 mm^2 . The most efficient area for RoHS application will be debated for years to come and it is application dependent.

The consideration for a measurement area is dependent on the nature of the application and practicality of use. Measurement of a very small area could result in a gross miscalculation of a substance's concentration in cases where the matrix in not uniform. For example, in a non-eutectic solder mixture where Pb rich and starved areas can be formed a very small measure area may not provide the best representation of the overall concentrations.

A measurement area that is to large is not accommodating to component analysis and can falsely include elemental concentration of surrounding components such as other parts on a PCB.

Regardless of the focal spot size of an XRF system, measurements should be performed on components, parts, and assemblies that are equal or smaller than the system's measurement area. Otherwise, expectations of accurate measurements such as in this case shown in Figure 6 are unreasonable and not achievable.

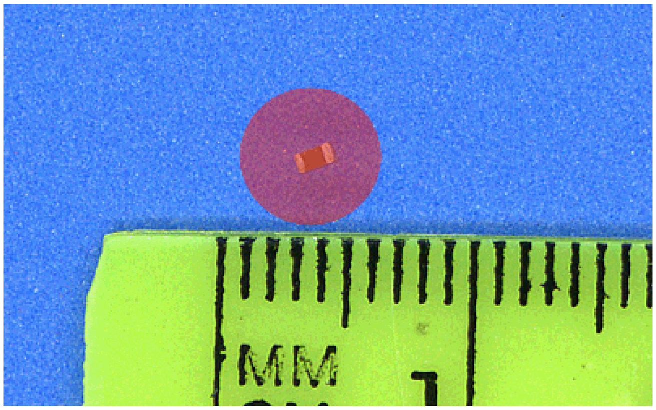

Figure 6 - Measurement of a component that is smaller than the XRF beam size

The Reality of the Screening Process:

The facts are that:

- RoHS directives are technically challenged
- Electronic materials are not homogenous in composition, shape, or size
- There is no perfect data that can be obtained easily by XRF or laboratory methods
- There is an expectation for the screening process that may not be realistically achievable by the technical capabilities of analytical instrumentations
- Percent calculations by weight are relative values and do not provide an indication for the total amount of prohibited substances

The good news is:

- The majority of electronic materials either contain the prohibited substances in a few percent levels or are below the RoHS limits making a timely screening process feasible and practical using XRF systems
- XRF is a powerful tool that can be very effective in the validation of both the absence and presence of RoHS restricted elements when used correctly
- Understanding the limitations and capabilities of a particular XRF system will enhance its application for the Screening process
- Not all XRF systems are created equal and vary drastically in capability, ease of use, time of measurement, cost, and applicability for RoHS directives
- High energy XRF systems are more effective for qualification/quantification and reducing false indications especially in complex materials
- Incoming QC is the most appropriate place for implementing the Screening process
- Some XRF systems can be programmed for quantification of complex components by the users based on the lab results for future comparison of the same parts
- If a similar sample preparation method proposed for adaptation by IEC global RoHS test standards are utilized for XRF screening, XRF will provide a very accurate results for non-homogenous materials and components with complex shapes or SMT component assemblies at any concentration

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