Use of EDXRF for RoHS Compliance Screening in PCBA Manufacturing

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Abstract

With the enactment of the European Union (EU) ROHS Directive 2002/95/EC (Ref.1), certain electrical and electronic products that are manufactured in or exported to the European Union have restrictions on the use of Lead, Mercury, Cadmium, Hexavalent Chromium, Polybrominated Biphenyl (PBB) and Polybrominated Diphenyl Ethers (PBDE).

EDXRF (Energy Dispersive X-ray Fluorescence) is one of the methods that can be used for screening of RoHS materials. EDXRF has the advantage of simple or no sample preparation as well as being non-destructive with a relatively short testing time. However, it has disadvantages such as matrix interference combined with the fact that for most electronic devices, it is difficult or impossible to perform the analysis on homogeneous areas without overlapping other materials on the device. Thus the 'screening' results need to be carefully analyzed or verified.

This paper describes the work done on the testing of European Union ROHS 5 of 6 (lead in solder exemption) and ROHS 6 of 6 components and solders with EDXRF equipment (both desktop and handheld). It identifies the various uses and constraints of EDXRF equipment.

Introduction

There are a number of spectrographic and wet chemical analysis techniques that give reasonably accurate and repeatable results for most RoHS elements. Some of these can also determine the valence state of chromium and confirm the bromine compound as either PBB or PBDE. Unfortunately most of these methods are destructive, requiring either physical grinding of the samples, chemical digestion or both. Most require a dedicated chemist with a full wet chemical analysis laboratory and a considerable amount of time and cost. This is not a popular choice for most electronic manufacturers that wish to have some method for in-house RoHS screening of components.

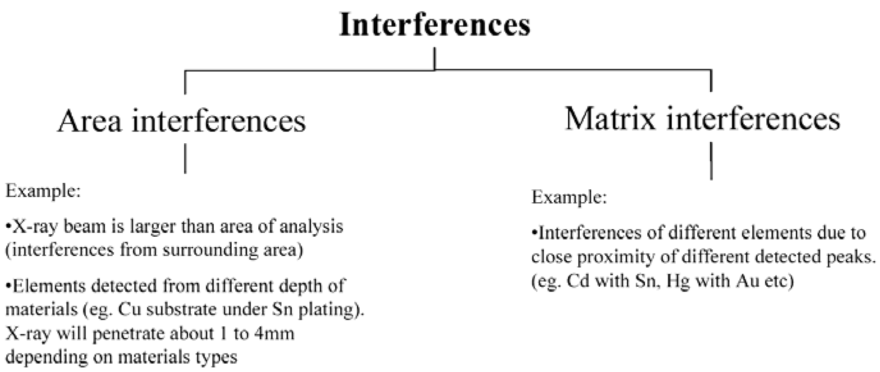
Qualitative screening employing X-ray fluorescence spectrometric analysis (EDXRF) is non destructive, with minimum or no sample preparation required. Compared to other analytical procedures, this test method offers high throughput and wide ranges of measured concentrations. The equipment is in most cases less expensive than that required for alternative methods. It is for the most part non-destructive and can be operated by people of varying technical backgrounds. There are no chemicals required and risk of X-ray exposure to personnel is minimal provided that simple safety guidelines are followed. External analytical services are only typically required to confirm the presence of Cr VI or PBB / PBDE if Cr or Br levels are over the RoHS limits (>0.1wt %).

The basic EDXRF equipment constitutes an X-ray source, which can be either an isotope or X-ray tube (current driven). It also consists of an EDX detector incorporated into a system of analyzers and processors. The most common X-ray source presently in the market is X-ray tube. These sources are typically safer due to better control of radiation. The size of the X-ray beams is controlled using collimators (mono-capillary tube or poly-capillary tubes). There are several detector types available in the market, for example: SiLi SSD (solid state devices), SSD (Silicon Strip Detector) and PIN diode detectors.

The two basic EDXRF configurations are the handheld and desktop models. The models chosen for this work use X-ray tube sources. The spot size for the hand held unit is approximately 10 mm^2. The collimators (spot size) for the bench top model are 0.05 to 1.2 mm^2.

X-ray Fluorescence Spectrometry (EDXRF) faces several technical constraints when used for RoHS applications. These constraints cause poorer accuracy of the results. The main constraint of the equipment is interference from the sample.

There are two main types of interferences, which will cause result uncertainty. These are area and matrix interferences. These are described in Figure 1.



Interferences

Area interferences

Example:

- X-ray beam is larger than area of analysis (interferences from surrounding area)
- Elements detected from different depth of materials (eg. Cu substrate under Sn plating). X-ray will penetrate about 1 to 4mm depending on materials types

Matrix interferences

Example:

- Interferences of different elements due to close proximity of different detected peaks. (eg. Cd with Sn, Hg with Au etc)

Figure 1 - Interferences of EDXRF

Components are made of many different types of homogeneous materials (Figure 2). These cannot be broken down into individual materials unless destructive method is used. The EDXRF, depending on the equipment type, will suffer from different types of area interference.

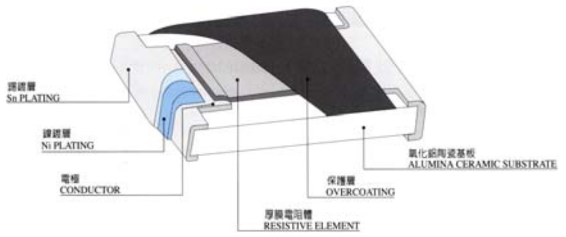


Figure 2 - Common materials in a typical resistor

Handheld EDXRF suffers from area interference when testing small components, as the X-ray probe of the equipment is much bigger than the area of interest (Figure 3). This causes emission from the whole component instead of just the area of interest (area interference) It is therefore difficult to interpret content of individual homogeneous materials.

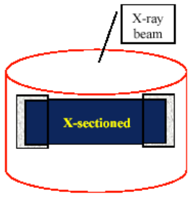


Figure 3 - Area interference of handheld EDXRF

Desktop EDXRF has a relatively small X-ray spot size that makes the desktop EDXRF system ideal for small, homogeneous samples. It can also analyze solder joints if there are no area constraints. For most electronic devices it is difficult or impossible to perform the analysis on homogeneous areas without overlapping other materials on the device. With the small spot size of the desktop system, the equipment does not have interference from the area unlike the handheld. However, as these are X-ray equipment, the X-ray spot will penetrate a certain depth and result in depth interference (Figure 4). This occurs when the elements underneath the materials of interest (i.e. under-plating) are also detected. The system, similar to the handheld, will treat the two materials as though they are homogeneous and give a single composition. This can generate error in the data, as most electronic components are not homogeneous within the depth of the detector window.

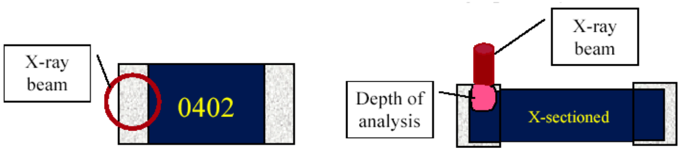


Figure 4 - Area and depth interferences

The scenario on the left (Figure 4) occurs when an X-ray analysis beam is larger than the interested region (plating). Interference will come from the component body.

For example; $Pb_{total}=Pb_{plating} + Pb_{body}$

The scenario on the right (Figure 4) will inevitably occur when we analyze plating materials. The fluorescence X-ray will be emitted from the plating on top (i.e. Sn) and from the underlying substrate (i.e. Cu) depending on the depth of X-ray penetration.

For example: $Pb_{total}= Pb_{plating}+Pb_{Cu\ substrate} + Pb_{Ni\ Substrate}$.

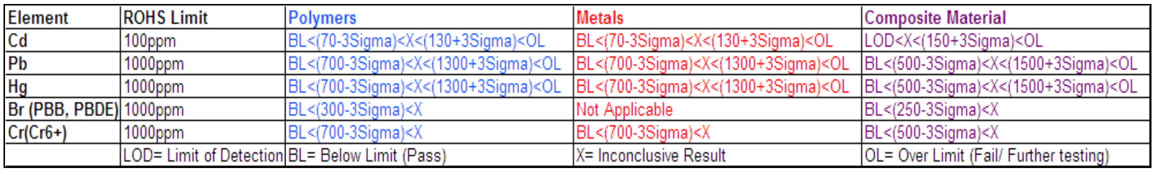
It is impossible at the present moment, to identify the contribution of the interested elements from each of the different materials. (Penetration is about 1 to 4mm depending on materials type and density of materials).

All EDXRF systems are also subjected to matrix interference. Matrix interference, also known as spectral interference, is the prime influencing factor when testing RoHS elements. Each element usually generates 3 to 4 different energy peaks (in KeV), out of which, the strongest intensity peak (major peak) is used to quantify the elements. Interference occurs when the energy peak, which is used to identify one element is very close to another element. For example, Pb (lead) is sometimes detected when there is the presence of As (Arsenic). This occurs as the major peak of As ($K_{\alpha 1}$: 10.53KeV) lies closely to the major peak (energy) of Pb ($L_{\alpha 1}$: 10.55KeV). Thus the minor peak of Pb has to be used to quantify the element. The lower peak energy from the minor peak of Pb results in a higher standard error. Some other interferences, which are identified during the evaluation or reported in IEC TC 111 Working Group (WG3) (Ref. 2) are:

i) Cadmium: Interference possibly from bromine, lead, tin, antimony
ii) Lead: Interference possibly from bromine, arsenic
iii) Mercury: Interference possibly from bromine, lead, indium, gold, tin
iv) Chromium: Interference possibly from chlorine, zinc
v) Bromine: Interferences possibly with iron, lead

Due to the uncertainty of results caused by the interferences, acceptance criterion for RoHS have to be modified for interpretation of EDXRF results. Recommendations are given in the document of IEC TC111 WG 3' (Ref: 2). The recommendations include an 'uncertainty' factor and margin of safety (Table 1).

Table 1 - Acceptance criterion recommended by IEC



Element	ROHS Limit	Polymers	Metals	Composite Material
Cd	100ppm	BL<(70-3Sigma)<X<(130+3Sigma)<OL	BL<(70-3Sigma)<X<(130+3Sigma)<OL	LOD<X<(150+3Sigma)<OL
Pb	1000ppm	BL<(700-3Sigma)<X<(1300+3Sigma)<OL	BL<(700-3Sigma)<X<(1300+3Sigma)<OL	BL<(500-3Sigma)<X<(1500+3Sigma)<OL
Hg	1000ppm	BL<(700-3Sigma)<X<(1300+3Sigma)<OL	BL<(700-3Sigma)<X<(1300+3Sigma)<OL	BL<(500-3Sigma)<X<(1500+3Sigma)<OL
Br (PBB, PBDE)	1000ppm	BL<(300-3Sigma)<X	Not Applicable	BL<(250-3Sigma)<X
Cr(Cr6+)	1000ppm	BL<(700-3Sigma)<X	BL<(700-3Sigma)<X	BL<(500-3Sigma)<X
	LOD= Limit of Detection	BL= Below Limit (Pass)	X= Inconclusive Result	OL= Over Limit (Fail/ Further testing)

The limits include a safety margin of 30% for polymers and metals samples, and 50% for composite materials. Results from EDXRF that are below the limit (BL) are considered as 'Pass' and results that are above the limit (OL) is considered as 'Fail'. Results that are in between the two limits are considered as 'Inconclusive' (X).

The term "3Sigma" expresses the repeatability of the analyzer, where σ is the standard deviation of the results obtained from a sample with content of the regulated substances near the limits of interest.

The project evaluates different manufacturer's hand held and desktop equipment to study the general technology and capability. It was carried out using statistical Measurement System Analysis.
Subsequent work involves studying the constraint of the equipment and applicability in analyzing different types of samples.

Experimental Design and Procedures

Phase 1: Equipment assessment / Gage Repeatability and Reproducibility study

The project included the evaluation of eight desktop EDXRF systems from four equipment suppliers and three handheld systems from three different equipment suppliers. The desktop units had two series, a high series and a low series with the former having more design features and/or a smaller X-ray analysis beam size.

Two Measurement System Analysis (MSA) methods were used to evaluate the equipment: Gage Repeatability and Reproducibility (GR&R), and Gage Bias and Linearity. The GR&R test used Certified Reference Materials (CRM) with the relevant RoHS elements in concentrations close to the Maximum Concentration Value (MCV) defined by the EU RoHS legislation. The Gage bias and linearity used samples of Sn3Ag0.5Cu solder, doped with various concentrations of lead.

The test methods for the GR&R are described as follows:

i) Select one standard sample from the standard calibration set. The selected sample should have a composition close to the RoHS MCV (0.1wt% for lead, bromine, chromium, mercury, and 0.01wt% for Cadmium).
ii) Five readings are taken with the sample. For each reading, the sample should be removed from the sample table and replaced before the next reading.
iii) Repeat the above tests on three different days.
iv) The test time per sample is 30 sec. for the handheld and 300 sec. for the desktop.
v) The X-ray beam diameter is 0.1mm for high series desktop EDXRF and 1mm for low series desktop EDXRF. There are no restrictions on the beam diameter for the handheld EDXRF (fixed beam size).

The test method for the Gage Bias and Linearity are described as follows:
i) Five solder samples of increasing lead content were tested (0.03%, 0.06%, 0.1%, 0.24%, 0.38wt %). The solder was fabricated by the solder suppliers and tested initially using Inductively Coupled Plasma Spectroscopy (ICPS).
ii) Three readings were taken per solder sample.

The acquisition time was 30 seconds per reading for handheld and 300 seconds per reading for desktop.

Phase 2: Application testing for components

Application of the EDXRF for different types of components was studied. Common tin-lead and lead-free components were tested and the lead (Pb) coating concentrations from the component terminals were recorded.

The tested samples involved in this experiment covered area array, lead-frame, lead-less devices, and chip components. Both tin-lead and lead-free versions for each component type were tested. lead-free components (other than BGA and CSP) were hand dipped with 1% lead to test the equipment for a low-level sensitivity of lead as typically lead containing lead-frame coated components contain 5 to 15wt% lead.

The test matrix was designed as follows: three samples for each component type, three replications for each component type, two operators, and two orientations. The 1% lead samples were separated and tested as a different lot. The orientations for these samples were based on the highest lead values given from the tin-lead containing samples. Sn-3%bismuth coated SOIC devices were used to check for the possibility of interference of bismuth over the detection of lead. The lead-free BGA/CSP samples were Tin-Silver-Copper (SAC). The lead-free lead-frame/lead-less/chip samples were pure tin coated unless otherwise specified (Table 2).

Table 2 - Materials and experiment matrix

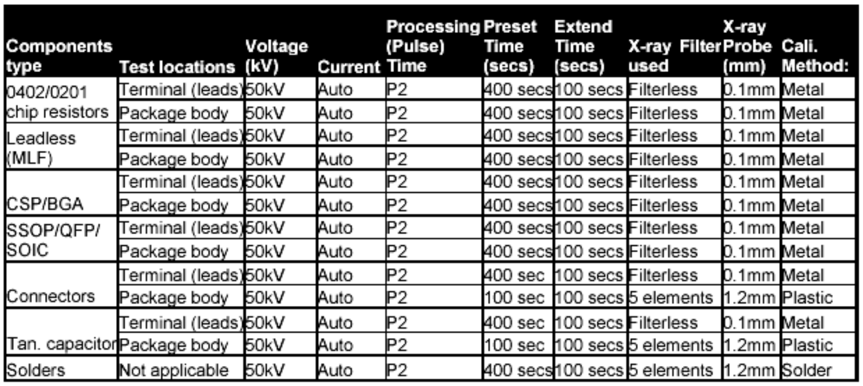
Item #	Component Type	Descriptions	ROHS Element	Concentration (%)	sub Qty	Test Qty	Repetition	Orientations/placement	Oper
1	CSP	0.5 mm pitch CSP	Pb	37%	18	3	3	1	2
2	CSP	0.5 mm pitch CSP	-	SAC	18	3	3	1	2
3	BGA	1.27 mm pitch BGA	Pb	37%	18	3	3	1	2
4	BGA	1.27 mm pitch BGA	-	SAC	18	3	3	1	2
5	Lead frame	0.4 mm pitch QFP 256	Pb	15%	36	3	3	2	2
6	Lead frame	0.4 mm pitch QFP 256	Pb	1%	36	3	3	2	2
7	Lead frame	0.4 mm pitch QFP 256	-	LF	36	3	3	2	2
8	Lead frame	SSOP	Pb	15%	36	3	3	2	2
9	Lead frame	SSOP	Pb	1%	36	3	3	2	2
10	Lead frame	SSOP	-	LF	36	3	3	2	2
11	Lead frame	SOIC	-	Sn2~4 %Bi	36	3	3	2	2
12	Leadless	0.5 mm pitch MLF	Pb	Between 5 and 15%	18	3	3	1	2
13	Leadless	0.5 mm pitch MLF	Pb	1%	18	3	3	1	2
14	Leadless	0.5 mm pitch MLF	-	Pure Sn	18	3	3	1	2
15	Chip	0201	Pb	Between 5 and 15%	36	3	3	2	2
16	Chip	0201	Pb	1%	36	3	3	2	2
17	Chip	0201	-	LF	36	3	3	2	2
18	Chip	0402	Pb	Between 5 and 15%	36	3	3	2	2
19	Chip	0402	Pb	1%	36	3	3	2	2
20	Chip	0402	-	LF	36	3	3	2	2
21	Chip	Tantalum	Pb	Between 5 and 15%	36	3	3	2	2
22	Chip	Tantalum	Pb	1%	36	3	3	2	2
23	Chip	Tantalum	-	LF	36	3	3	2	2

The experiment used a 3 factor, 2 level general factorial design of experiment. The objective was to identify the significant factors, which would influence the results obtained by the EDXRF and evaluate the equipment on their applicability in testing component exterior terminations.

The handheld EDXRF used the designated mode for metallic samples and a test time of 60secs per location.

The test locations and parameters for the desktop EDXRF are shown in Table 3 with Fundamental Parameters (FPM) for metal areas or ceramic areas and Plastics Mode for plastic.

Table 3 - Test location and parameters for desktop EDXRF



Components type	Test locations	Voltage (kV)	Current	Processing (Pulse) Time	Preset Time (secs)	Extend Time (secs)	X-ray Filter used	X-ray Probe (mm)	Cali. Method:
0402/0201 chip resistors	Terminal (leads)	50kV	Auto	P2	400 secs	100 secs	Filterless	0.1mm	Metal
	Package body	50kV	Auto	P2	400 secs	100 secs	Filterless	0.1mm	Metal
Leadless (MLF)	Terminal (leads)	50kV	Auto	P2	400 secs	100 secs	Filterless	0.1mm	Metal
	Package body	50kV	Auto	P2	400 secs	100 secs	Filterless	0.1mm	Metal
CSP/BGA	Terminal (leads)	50kV	Auto	P2	400 secs	100 secs	Filterless	0.1mm	Metal
	Package body	50kV	Auto	P2	400 secs	100 secs	Filterless	0.1mm	Metal
SSOP/QFP/ SOIC	Terminal (leads)	50kV	Auto	P2	400 secs	100 secs	Filterless	0.1mm	Metal
	Package body	50kV	Auto	P2	400 secs	100 secs	Filterless	0.1mm	Metal
Connectors	Terminal (leads)	50kV	Auto	P2	400 sec	100 secs	Filterless	0.1mm	Metal
	Package body	50kV	Auto	P2	100 sec	100 secs	5 elements	1.2mm	Plastic
Tan. capacitor	Terminal (leads)	50kV	Auto	P2	400 sec	100 secs	Filterless	0.1mm	Metal
	Package body	50kV	Auto	P2	100 sec	100 secs	5 elements	1.2mm	Plastic
Solders	Not applicable	50kV	Auto	P2	400 secs	100 secs	5 elements	1.2mm	Solder

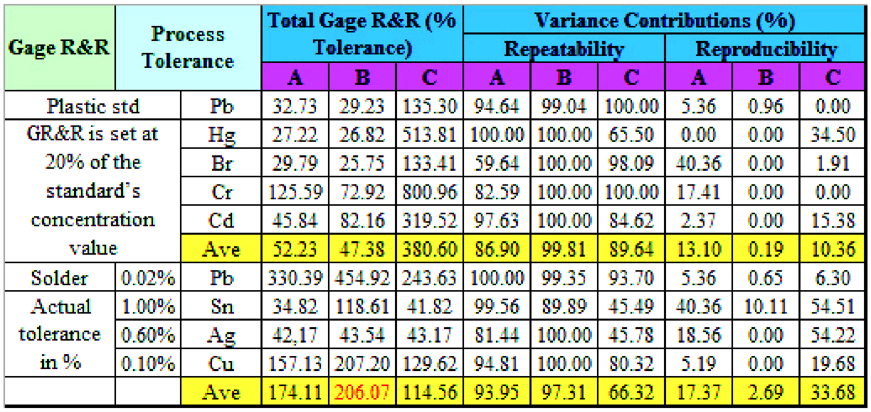
Results and Discussion

Phase 1: Handheld EDXRF

The GR&R was carried out for each element on each type of equipment. 10% of the elements' concentration was used as the tolerance for the polymer standards (with a total of 20% for upper and lower tolerance). This was standardized for the different equipment suppliers.

The results of the GR&R for handheld EDXRF are summarized in Table 4 for equipment Suppliers A, B, and C:

Table 4 - Gage Repeatability and Reproducibility studies of handheld EDXRF



Gage R&R	Process Tolerance		Total Gage R&R (% Tolerance)			Variance Contributions (%)					
						Repeatability			Reproducibility		
			A	B	C	A	B	C	A	B	C
Plastic std		Pb	32.73	29.23	135.30	94.64	99.04	100.00	5.36	0.96	0.00
GR&R is set at 20% of the standard's concentration value		Hg	27.22	26.82	513.81	100.00	100.00	65.50	0.00	0.00	34.50
		Br	29.79	25.75	133.41	59.64	100.00	98.09	40.36	0.00	1.91
		Cr	125.59	72.92	800.96	82.59	100.00	100.00	17.41	0.00	0.00
		Cd	45.84	82.16	319.52	97.63	100.00	84.62	2.37	0.00	15.38
		Ave	52.23	47.38	380.60	86.90	99.81	89.64	13.10	0.19	10.36
Solder	0.02%	Pb	330.39	454.92	243.63	100.00	99.35	93.70	5.36	0.65	6.30
Actual tolerance in %	1.00%	Sn	34.82	118.61	41.82	99.56	89.89	45.49	40.36	10.11	54.51
	0.60%	Ag	42,17	43.54	43.17	81.44	100.00	45.78	18.56	0.00	54.22
	0.10%	Cu	157.13	207.20	129.62	94.81	100.00	80.32	5.19	0.00	19.68
		Ave	174.11	206.07	114.56	93.95	97.31	66.32	17.37	2.69	33.68

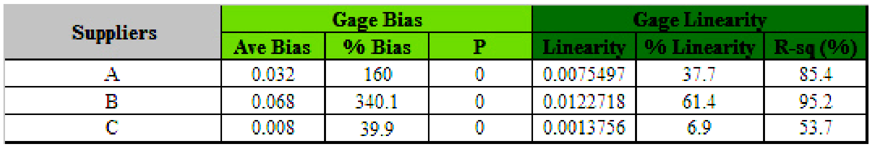
Generally, it can be observed that most of the tools are unable to achieve the desired 20% or less tolerance for GR&R, as is typically required for equipment to be capable for a process. The experiment showed that the variances are largely due to the poor repeatability of the readings based on equipment constraints.

From the Gage R&R results for the polymer standards, equipment supplier C shows the worst performance among the different sets (average % tolerance of 380%). The poor results are largely contributed by chromium (800%). Equipment supplier C did not have a filter for chromium (it actually did not have any filters) and as such, was unable to filter out noise to give a good signal to noise ratio. This resulted in the poor chromium reading. The other handheld EDXRF equipment also performed poorly for chromium and this was due to the fact that Chromium is a light element and is sensitive to noise and interference. For the solder samples, supplier B showed poor results. Lead and copper largely contributed to the variance for the solder samples. Equipment supplier A showed better overall results for the GR&R test (polymer and solder samples). Supplier C showed good results for the solder samples.

Gage bias studied the differences of the readings from the actual value of the sample. A large difference would show a high bias, which would signify poorer accuracy. Gage bias could be positive or negative depending on if the readings were higher or lower than the actual value of the sample. Gage linearity studied the deviation of the readings from the actual sample's value with increasing concentration. If the readings did not increase linearly with increasing concentration for the actual sample value, gage linearity would be poor. Ideally, linearity should be small in absolute value relative to the master part measurements. R-sq shows the proportion of the variation in the average bias that is related linearly with the master part measurements. If the R-value is not close to 1 (<0.8 or 80%), the relationship is not linear and linearity cannot be assessed with a non-linearity problem potentially existing.

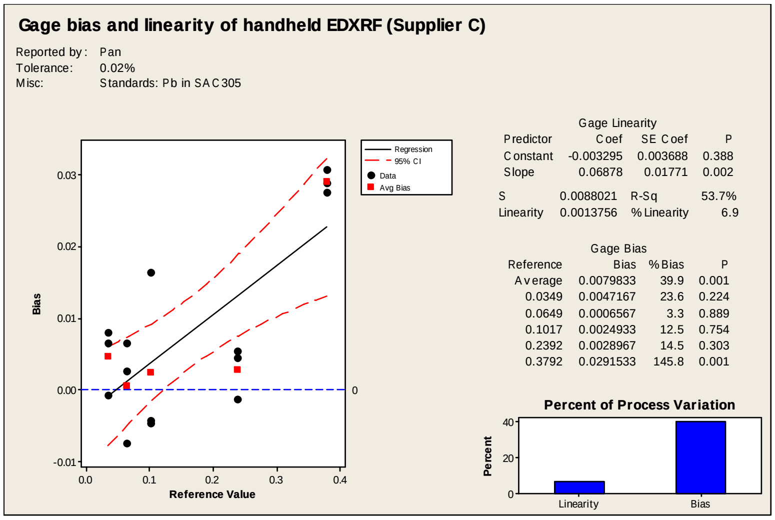
The results for the handheld EDXRF are summarized in Table 5

Table 5 - Gage bias and linearity studies of handheld EDXRF



Suppliers	Gage Bias			Gage Linearity		
	Ave Bias	% Bias	P	Linearity	% Linearity	R-sq (%)
A	0.032	160	0	0.0075497	37.7	85.4
B	0.068	340.1	0	0.0122718	61.4	95.2
C	0.008	39.9	0	0.0013756	6.9	53.7

Supplier C showed the best result in both the Gage bias and linearity, however, poor R-sq was observed (53.7%). The poor R-sq value of supplier C showed a wide variation of readings though the average readings showed good average linearity (0.00138). This was also demonstrated by the higher process variation as shown in Figure 5, which would result in low % bias and % linearity (% bias is bias/process variation).



Gage Linearity

Predictor	Coef	SE Coef	P
Constant	-0.003295	0.003688	0.388
Slope	0.06878	0.01771	0.002

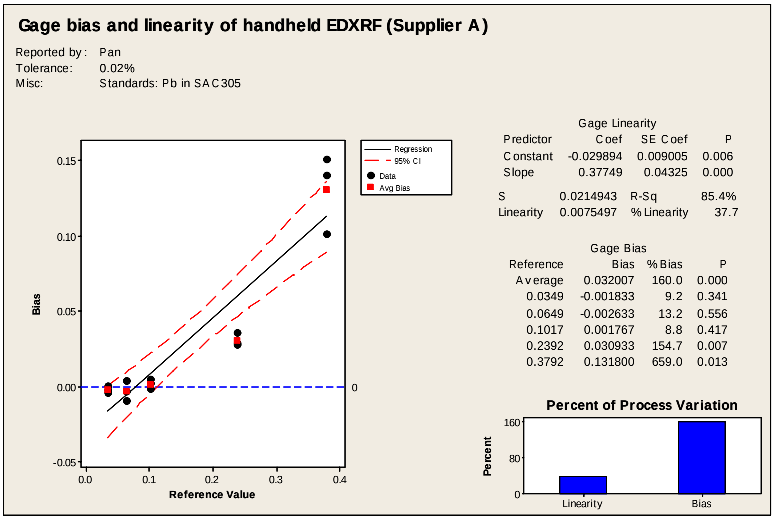
S	0.0088021	R-Sq	53.7%
Linearity	0.0013756	% Linearity	6.9

Gage Bias

Reference	Bias	% Bias	P
Average	0.0079833	39.9	0.001
0.0349	0.0047167	23.6	0.224
0.0649	0.0006567	3.3	0.889
0.1017	0.0024933	12.5	0.754
0.2392	0.0028967	14.5	0.303
0.3792	0.0291533	145.8	0.001

Figure 5 - Gage bias and linearity of handheld Supplier C

Supplier A showed reasonable bias (0.032) and linearity (0.0075) with a better linear fit than supplier C (R-Sq 85.4%) (Figure 6). Supplier B showed the poorest bias (0.068) and linearity (0.0122), but better linear fitting is observed (R-sq: 95.2%).



Gage Linearity

Predictor	Coef	SE Coef	P
Constant	-0.029894	0.009005	0.006
Slope	0.37749	0.04325	0.000

S	0.0214943	R-Sq	85.4%
Linearity	0.0075497	% Linearity	37.7

Gage Bias

Reference	Bias	% Bias	P
Average	0.032007	160.0	0.000
0.0349	-0.001833	9.2	0.341
0.0649	-0.002633	13.2	0.556
0.1017	0.001767	8.8	0.417
0.2392	0.030933	154.7	0.007
0.3792	0.131800	659.0	0.013

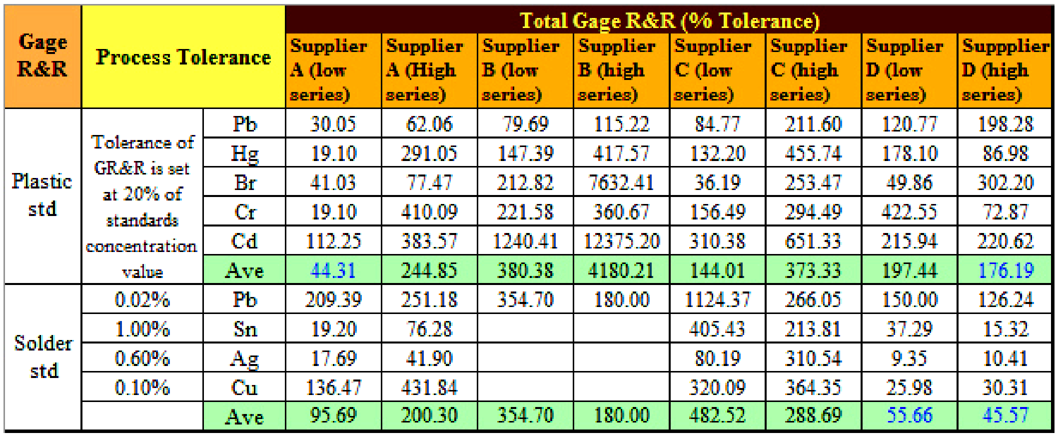
Figure 6 - Gage bias and linearity of handheld Supplier A

As the test was carried out on Pb in solder materials, only the Fundamental Parameters mode was used for the test (rather than an empirical calibration). The results show handheld Supplier C had good Fundamental Parameters.

Phase1: Desktop EDXRF

Gage R&R was carried out using similar statistical analysis as the handheld EDXRF. The tests were carried out using a 1mm beam diameter for the low series EDXRF and a 0.1 beam diameter for the high series EDXRF, except for one of the suppliers, which only had a 0.05mm beam diameter. The tests were carried out for 300 seconds per reading. 5 readings were taken per set. Three separate sets were obtained (in three different days). The tests were carried out with polymer and solder samples. The tolerances set for the polymer samples were 20% of the element concentration.

Table 6 - Gage Repeatability and Reproducibility studies of desktop EDXRF



Gage R&R	Process Tolerance		Total Gage R&R (% Tolerance)							
			Supplier A (low series)	Supplier A (High series)	Supplier B (low series)	Supplier B (high series)	Supplier C (low series)	Supplier C (high series)	Supplier D (low series)	Suppplier D (high series)
Plastic std	Tolerance of GR&R is set at 20% of standards concentration value	Pb	30.05	62.06	79.69	115.22	84.77	211.60	120.77	198.28
		Hg	19.10	291.05	147.39	417.57	132.20	455.74	178.10	86.98
		Br	41.03	77.47	212.82	7632.41	36.19	253.47	49.86	302.20
		Cr	19.10	410.09	221.58	360.67	156.49	294.49	422.55	72.87
		Cd	112.25	383.57	1240.41	12375.20	310.38	651.33	215.94	220.62
		Ave	44.31	244.85	380.38	4180.21	144.01	373.33	197.44	176.19
Solder std	0.02%	Pb	209.39	251.18	354.70	180.00	1124.37	266.05	150.00	126.24
	1.00%	Sn	19.20	76.28			405.43	213.81	37.29	15.32
	0.60%	Ag	17.69	41.90			80.19	310.54	9.35	10.41
	0.10%	Cu	136.47	431.84			320.09	364.35	25.98	30.31
		Ave	95.69	200.30	354.70	180.00	482.52	288.69	55.66	45.57

Desktop supplier B was not able to provide the solder sample readings for tin, silver and copper during the evaluation due to some equipment constraints.

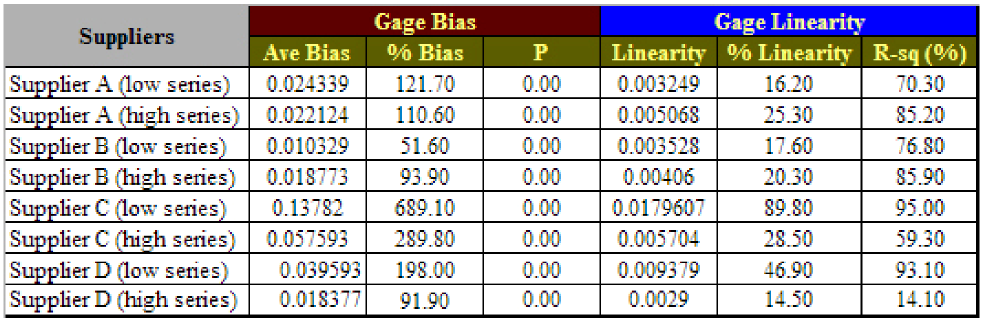
Most of the elements analyzed were unable to obtain a GR&R % of less than 20%. Most of the equipment showed weaknesses in chromium and cadmium analysis, these being the 'light' elements (low atomic mass) and low concentration elements respectively. Poor GR&R was also observed for lead in solder materials due to the tight tolerances. Generally, the GR&R was better for the low series than the high series due to the difference in beam diameter. The low-end series used beam diameters, which were 10 times bigger than the high series. The test was conducted using the same test time of 300seconds for both. This timing may not have been optimized for GR&R but was sufficient to do a comparison of the different equipment types.

Among the low-end series desktop EDXRF equipment, Supplier A (low end series) showed better GR&R for the polymer samples. For the high-end series desktop, Supplier D showed better GR&R for polymer samples. Supplier D showed better GR&R for the solder samples. The solder sample GR&R for Supplier B could not be determined due to insufficient information/ equipment constraints.

Gage bias and linearity was conducted using the solder samples of different Pb contents (0.03%, 0.06%, 0.1%, 0.24%, 0.38%). The solder was provided by the solder supplier and tested using ICPS. Three readings were obtained per solder using an analysis time of 300secs. A 1mm beam diameter was use for the low series and 0.1mm beam diameter used for the high series.

The results for the gage bias and linearity are summarized in Table 7:

Table 7 - Gage bias and linearity studies of desktop EDXRF



Suppliers	Gage Bias			Gage Linearity		
	Ave Bias	% Bias	P	Linearity	% Linearity	R-sq (%)
Supplier A (low series)	0.024339	121.70	0.00	0.003249	16.20	70.30
Supplier A (high series)	0.022124	110.60	0.00	0.005068	25.30	85.20
Supplier B (low series)	0.010329	51.60	0.00	0.003528	17.60	76.80
Supplier B (high series)	0.018773	93.90	0.00	0.00406	20.30	85.90
Supplier C (low series)	0.13782	689.10	0.00	0.0179607	89.80	95.00
Supplier C (high series)	0.057593	289.80	0.00	0.005704	28.50	59.30
Supplier D (low series)	0.039593	198.00	0.00	0.009379	46.90	93.10
Supplier D (high series)	0.018377	91.90	0.00	0.0029	14.50	14.10

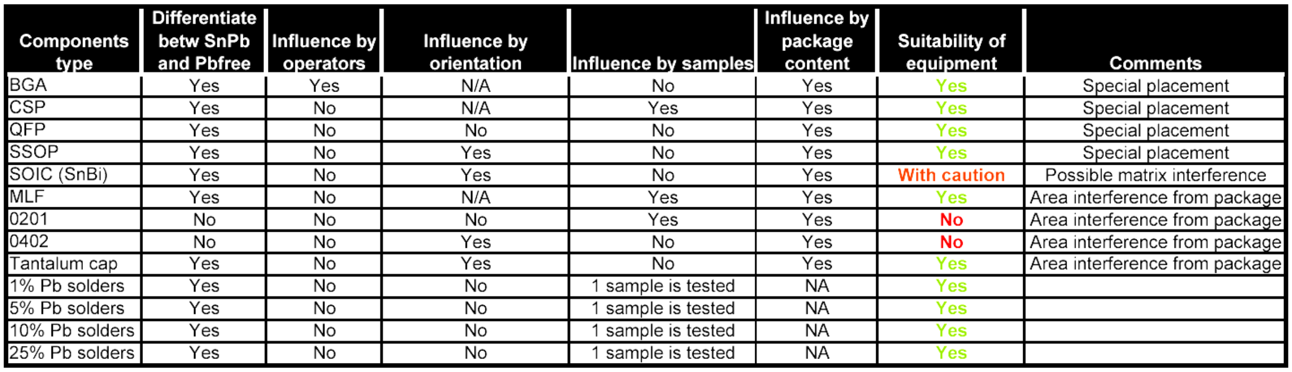
For the low-end series desktop EDXRF equipment Supplier B showed the best average bias (0.0103) and Supplier A showed the best gage linearity (0.00325). For the high-end series desktop EDXRF, Supplier D (0.1mm) has the best average gage bias (0.0184) and linearity (0.0029). This showed that Supplier D had good Fundamental Parameters (the test was conducted using the FP method on the solder). However, it should be noted that Supplier D had very poor R-sq value of 14.1% and low % linearity at 14.5%.

Besides the Measurement System Analysis that was carried out on the handheld and desktop EDXRF equipment, other consideration for the selection of the equipment includes equipment's ease of use, software user interface, equipment's hardware design, reliability, supplier development roadmap, price and applicability. These factors are not covered in this paper. After consideration of the various criteria, supplier A was chosen for the handheld EDXRF and supplier A for the high-end series of desktop EDXRF. The low-end series of desktop EDXRF was not selected due to limitations in their application. The selected EDXRF equipments were included in the phase 2 of the project for process evaluation and optimization.

Phase 2: Handheld EDXRF

The experiment was carried using the DOE as described in Table 2. Test data was analyzed using ANOVA with results in Table 8.

Table 8 - Results summary for Phase 2 analysis (Handheld EDXRF)



Components type	Differentiate betw SnPb and Pbfree	Influence by operators	Influence by orientation	Influence by samples	Influence by package content	Suitability of equipment	Comments
BGA	Yes	Yes	N/A	No	Yes	Yes	Special placement
CSP	Yes	No	N/A	Yes	Yes	Yes	Special placement
QFP	Yes	No	No	No	Yes	Yes	Special placement
SSOP	Yes	No	Yes	No	Yes	Yes	Special placement
SOIC (SnBi)	Yes	No	Yes	No	Yes	With caution	Possible matrix interference
MLF	Yes	No	N/A	Yes	Yes	Yes	Area interference from package
0201	No	No	No	Yes	Yes	No	Area interference from package
0402	No	No	Yes	No	Yes	No	Area interference from package
Tantalum cap	Yes	No	Yes	No	Yes	Yes	Area interference from package
1% Pb solders	Yes	No	No	1 sample is tested	NA	Yes	
5% Pb solders	Yes	No	No	1 sample is tested	NA	Yes	
10% Pb solders	Yes	No	No	1 sample is tested	NA	Yes	
25% Pb solders	Yes	No	No	1 sample is tested	NA	Yes	

Based on a 95% confidence level, the factor with P-Value less than 0.05 is considered as a significant factor that may influence the final results which is designated by 'Yes' in Table 8(Columns 2 to 5). P-Values higher than 0.05 are considered as an insignificant factor in the experiment and are designated by 'No' in Table 8 (Columns 2 to 5).

The summary Table 8 shows that the handheld can be used to qualify most of the components except for surface mount chip components of 0201 and 0402. Caution needs to be exercised when testing bismuth containing coating materials due to matrix interference. Qualitative analysis includes the ability to differentiate the tin-lead and lead free components.

For BGA components, the operators influenced the results of the sample testing. Some of the components were tested with different component orientation, and almost all components except 0201 chip resistors were influence by the test orientation of the components. Influence by samples represents the part-to-part differences of the components. For CSP, MLF and 0201, the compositional difference of each individual sample was greater than the repeatability of the test equipment. This caused inconsistent results to be obtained.

All the samples besides solder materials suffered from area interferences, as the parts were not homogeneous and the large analysis window of the handheld EDXRF proved impossible to isolate the specific area of interest, such as plating, on the small components.

Special placement is required for the BGA components due to the presence of high lead solders within the package. The high Pb solders within the package have an EU RoHS exemption. The lead solder usually lies close to the center of the package (flip chip solder interconnects). To reduce the area interference of the lead in the package, the solder balls should be analyzed near to the side of the component as shown in Figure 6. The dashed horizontal line in Figure 6 is the 0.1wt% lead limit.

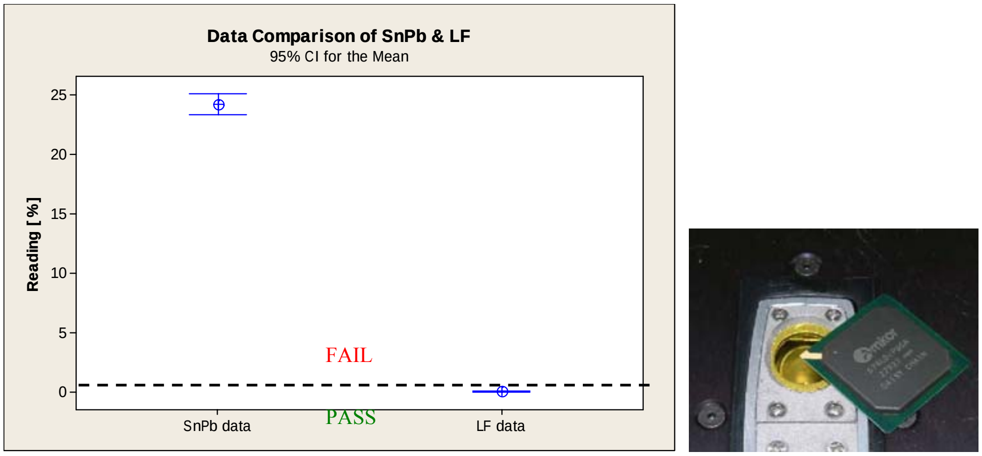


Figure 6 - Handheld EDXRF analysis of BGA

Care should be taken on the component placement. More training would be needed for the operator as this appeared to be a significant factor, which may influence the readings.

No lead was detected in the package body of the CSP (Figure 7) and the leadless component, which was tested with the whole component at the center of the window.

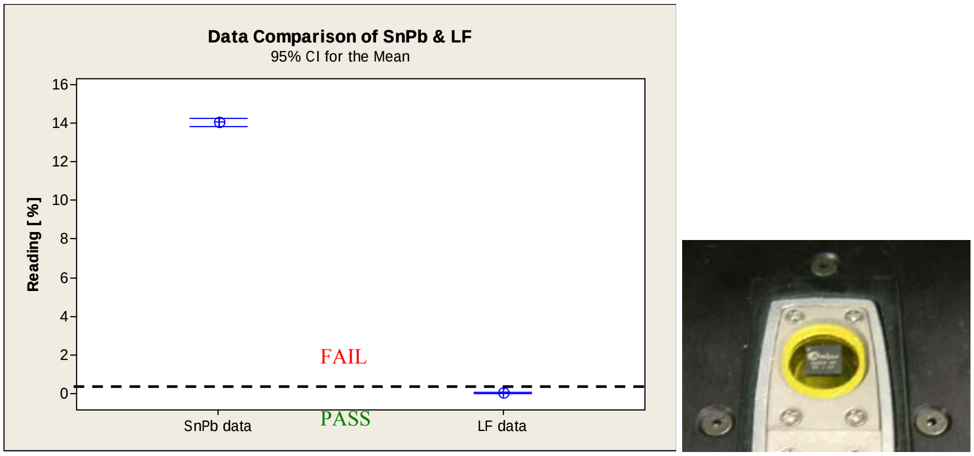


Figure 7 - Handheld EDXRF analysis of CSP

QFP could be placed either horizontally or vertically. However, considering the alignment with the SSOP, all the lead-frame devices would be recommended to stand vertically when the test stand method mode was applied. This reduced the area interference from the package body, which was also found to contain Pb under the EU RoHS exemption (Figure 8).

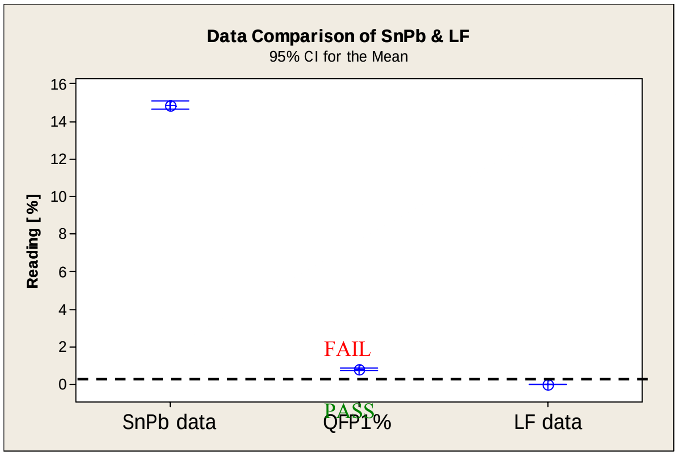


Figure 8 - Handheld EDXRF analysis of QFP

Plastic clips were used as a fixture to hold the component samples vertically. It should be noted that metal materials should not be used as the holder or this could create misleading readings. For any devices smaller than the inspection window, the component would be put in the center of the window.

Component to component variation (influence of samples) was found on 0201R, MLF and CSP components.

The handheld EDXRF was unable to differentiate the tin-lead and lead free surface mount resistors (Figure 9). This was due to the presence of lead oxide on the package body of the resistors, which was covered by a EU RoHS exemption. The area interference resulted in high levels of lead detected on the lead free resistors.

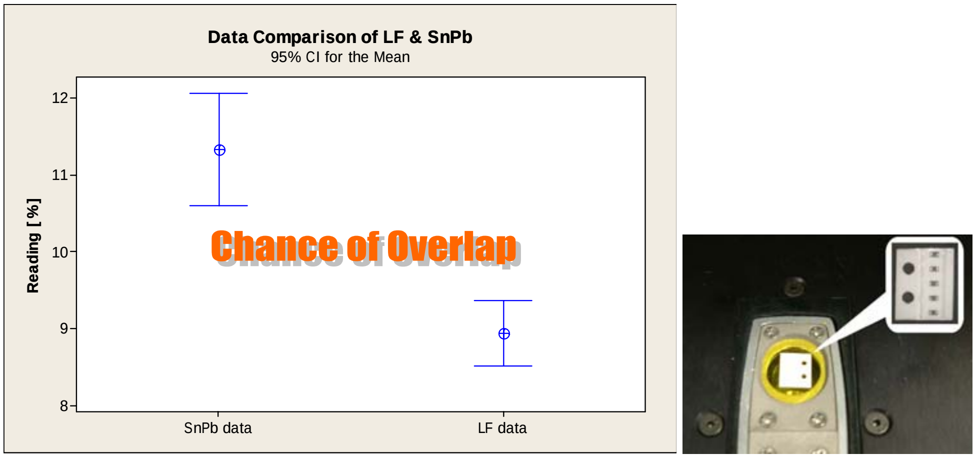


Figure 9 - Handheld EDXRF analysis of chip components

The current test method was not applicable to test chip resistors because of the misleading readings contributed by the lead oxide in the component body. Chip capacitors and chip inductors have no lead-oxide in the component body so there would be no issues. Figure 10 shows results for a pure tin tantalum (pass), a 1wt% lead coated tantalum (fail) and a 5 to 15wt% lead coated tantalum (fail).

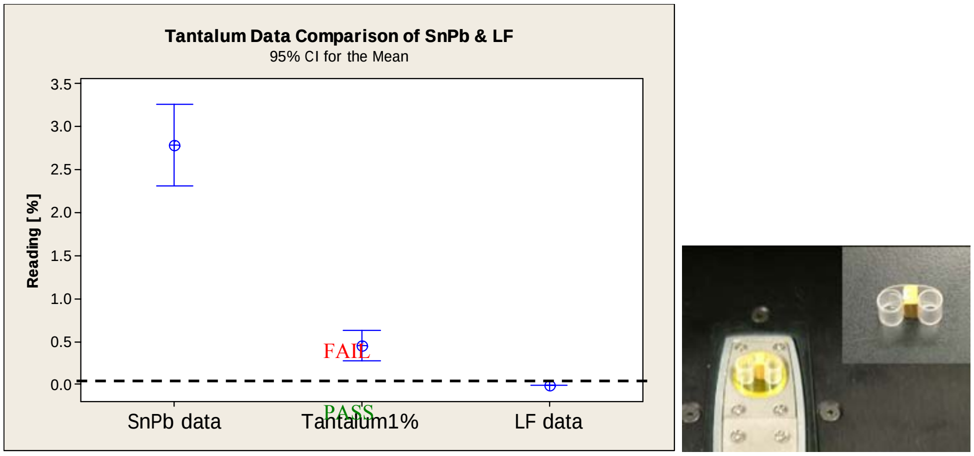


Figure 10 - Handheld EDXRF analysis of tantalum capacitor

The equipment was suitable to test solder materials with solder containing higher concentrations of lead showing higher variance in lead readings. The equipment is able to differentiate the different concentration of lead content.

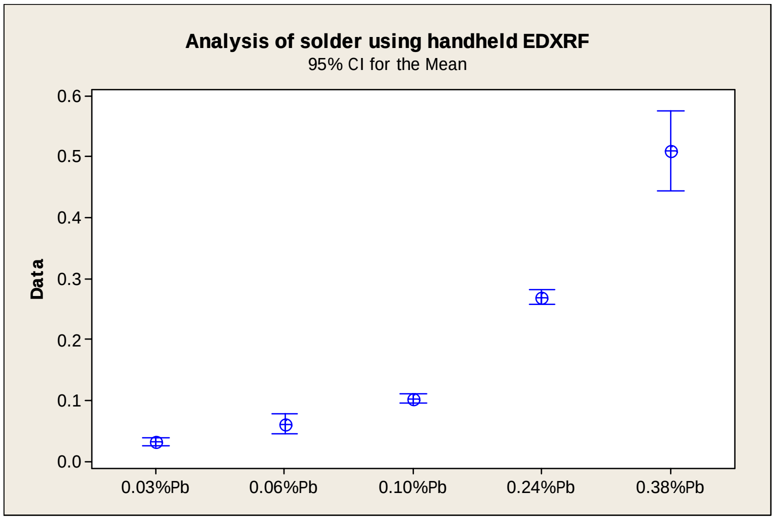


Figure 11 - Handheld EDXRF analysis of solders

Due to the matrix interference of cadmium and chromium with tin, the value of the RoHS elements may be artificially high (> RoHS Maximum Concentration Limits). The results for the handheld for various lead concentrations in tin-silver-copper solder are shown in Figure 11.

Phase 2: Desktop EDXRF

The experiment was carried out similar for desktop EDXRF.

Table 9 - Result summary of Phase 2 analysis (Desktop EDXRF)

Components type	Differentiate betw SnPb and Pbfree	Influence by operators	Influence by orientation	Influence by samples	Influence by package content	Suitability of equipment	Comments
BGA	Yes	No	No	Yes	No	Yes	
CSP	Yes	No	No	No	No	Yes	
QFP	Yes	No	No	No	No	Yes	
SSOP	Yes	No	No	No	No	Yes	Possible matrix interference
SOIC (SnBi)	No	No	No	No	No	With caution	Possible matrix interference
MLF	Yes	No	No	No	No	Yes	
0201	Inconclusive	Yes	No	No	Yes	With caution	Area interference from package
0402	Inconclusive	Yes	No	No	Yes	With caution	Area interference from package
Tantalum cap	Yes	No	No	Yes	No	Yes	
1% Pb solders	Yes	No	Influence by location	1 sample is tested	NA	Yes	Solder is not homogeneous
5% Pb solders	Yes	Yes	Influence by location	1 sample is tested	NA	Yes	Solder is not homogeneous
10% Pb solders	Yes	No	Influence by location	1 sample is tested	NA	Yes	Solder is not homogeneous
25% Pb solders	Yes	No	Influence by location	1 sample is tested	NA	Yes	Solder is not homogeneous

Table 9 gives the results for the desktop EDXRF summarizing the use of the equipment in differentiating tin-lead and lead free parts.

The desktop EDXRF was able to correctly identify most of the components except for SOIC with bismuth and the surface mount resistors. The SOIC with bismuth suffers from matrix interference with lead. Lead would be falsely identified with the presence of bismuth. Caution would need to be exercised when testing bismuth containing coated materials.

The desktop EDXRF had reduced area interference due to its smaller analysis probe. But when testing the plating of small components such as 0402 and below, some area interference would still occur depending on the placement of the analysis spot. The operators would influence this. Results for the tantalum capacitor are shown in Figure 12.

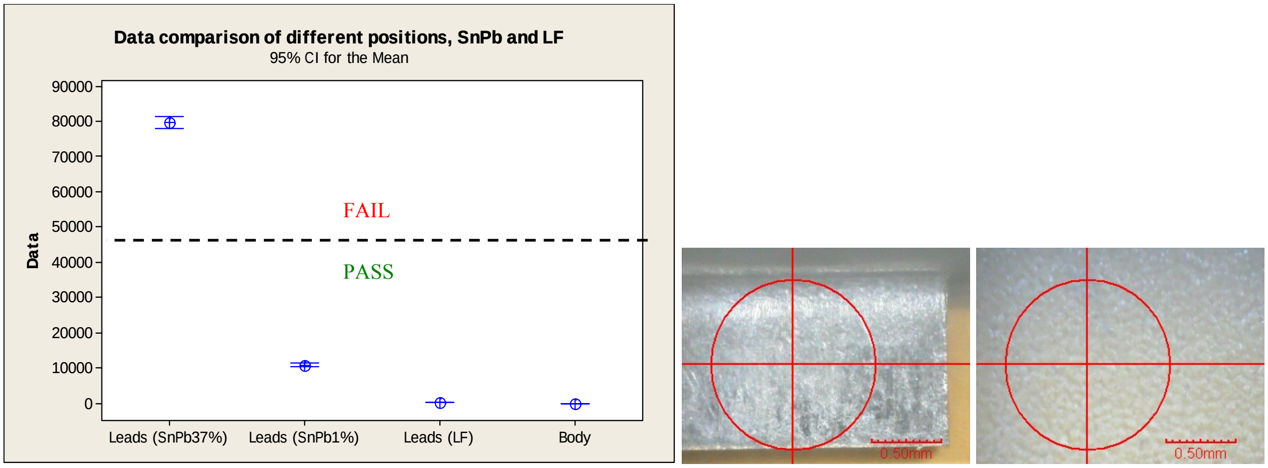


Figure 12 - Desktop EDXRF analysis of tantalum capacitor

Area interferences were observed for chip resistors (Figure 13), which had lead in the package material. When area interference was suspected, the component terminal should be tested at a different position (closer to the edge)

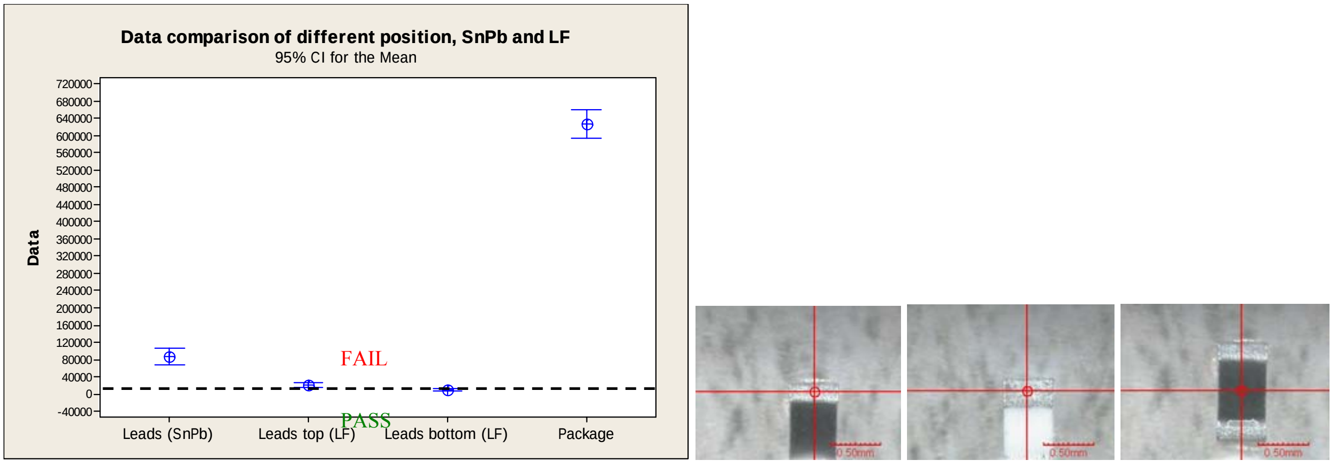


Figure 13 - Desktop EDXRF analysis of resistor

Correct positioning of the analysis spot, which should be far from the package body, would result in reduced area interference and better results.

Matrix interference was observed for Sn-3bismuth alloy (Figure 14) since the energy level of bismuth and lead was very close (10.55keV and 10.73keV for lead and bismuth respectively). Other common matrix interferences included cadmium and mercury, which occurred with tin and gold respectively.

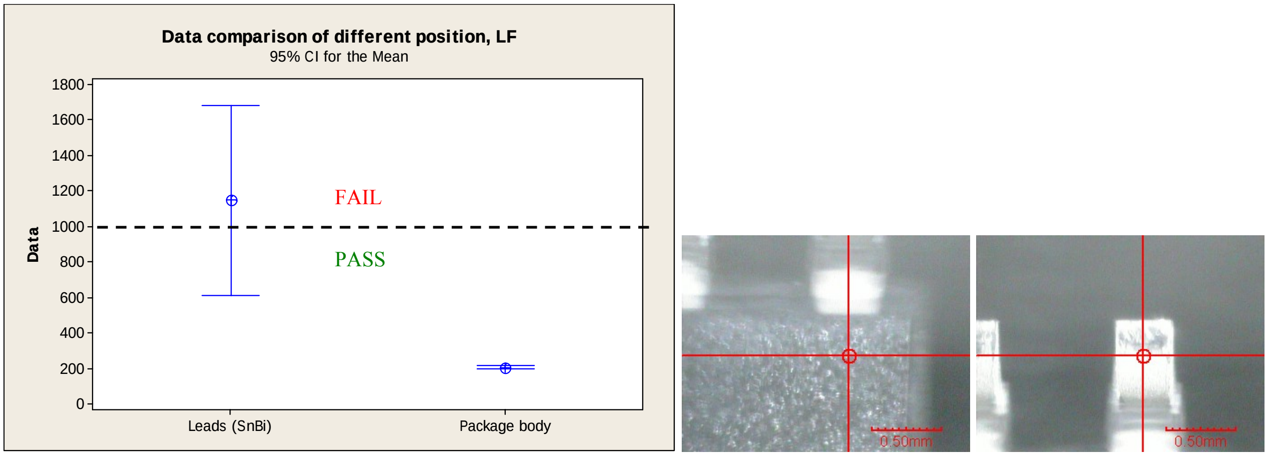


Figure 14 - Desktop EDXRF analysis of SOIC

Unlike the handheld EDXRF, desktop EDXRF had minimum area interference except for the surface mount resistors. But matrix interference was more obvious as the analysis focused on the plating materials which, due to the high concentration of tin, gold, silver or other metals, suffered from matrix interference.

The equipment was suitable to test solder materials, and was able to differentiate the lead content in the different tin3.0silver0.5copper samples (Figure 15).

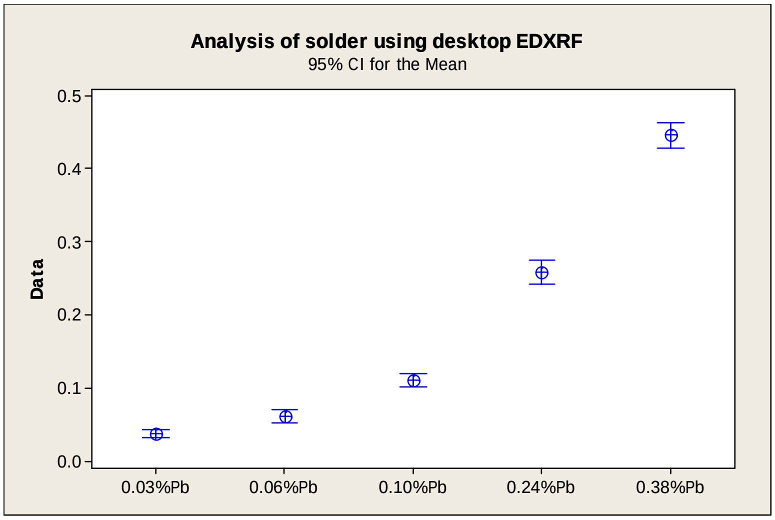


Figure 15 - Desktop EDXRF analysis of solders

Due to the finer X-ray spot size of the equipment (1.2mm), the analysis was sensitive to non-homogeneity of the solder sample. Testing at different locations gave slightly different results since the solder sample was not homogeneous, resulted from solder solidification segregation. This was demonstrated by a X-ray map generated by the desktop EDXRF (Figure 16)

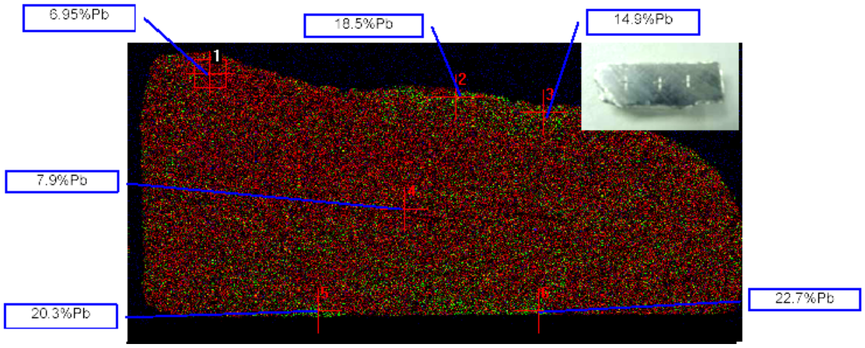


Figure 16 - Segregation of lead in solder materials

The red dots represent tin and the green dots represent lead. The above sample was a cross-sectioned solder sample cast into the shape of a medallion. The bottom, flat portion was in contact with the mold during the casting. The sample should contain an average of about 10wt% lead. But as observed, the sample was highly non-homogeneous with large portions of the sample with minimum traces of Pb and others with high concentrations of lead. Thus analysis using small spot sizes may result in inaccurate or inconsistent readings of lead in solder. The issue occurred when testing large solder masses and may be reduced with solder joints.

The solder samples also suffered from matrix interference of cadmium with tin, with the value of the RoHS element being detected to be high (> RoHS Maximum Concentration Limit). Chromium with a high standard error would also be detected due to the high concentration of tin. Filters for chromium and cadmium were available for the desktop EDXRF, which would help to reduce the interference.

Conclusions

The study showed that all of the evaluated equipment had limitations with accuracy and repeatability. Gage R&R, Gage linearity, and R-sq values were not optimum for any of the supplier equipment. The selected equipment was still subject to error from factors such as placement, orientation, and operators. Area and matrix interference added additional sources of error.

With all of these considerations, sufficient confidence for both of these tool types could be achieved for the purpose of an in-house screening tool. Using this work as a guide to optimize the tests for each component type would serve to improve results. Other than confirmation of chromium and bromine chemical states, external referee testing could be minimized.

Future Work

This project covered a range of components, which are common in the electronics industry. While they represent a reasonable variety of interconnects and package types, there are many other non-common, new type of materials or designs, which were not evaluated in this project. As more experiments are carried out on different component types, more information will be available and presented.

The EU RoHS legislation determines the compliance of the product level. While information is being gathered for the bulk material and at the component level, there are still limited work and recommendations for product assembly level. The IEC draft standard recommends destructive test on assemblies (Ref. 3). Destructive tests may result in large costs incurred if a large number of samples are required. There would also be uncertainty in the method to use and the level of accuracy. There would be the possibility of using EDXRF in non-destructive screening of assemblies. Experiments should be carried out to determine the level of accuracy and the best method for the analysis. Locations on an assembly could have limited access for the EDXRF equipment (limits on working distance). The actual size of the board that can be tested would also be a limitation for the desktop EDXRF equipment.

Acknowledgements

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References

(1) European Union Directive 2002/95/EC, Restriction of the use of certain hazardous substances in electrical and electronic equipment, 27 January 2003.

(2) IEC TC 111 WG 3, 'Procedures for the Determination of Levels of Regulated Substances (Lead, Mercury, Hexavalent Chromium, Polybrominated Biphenyls, Polybrominated Biphenyl Ether) in Electro-technical Products', draft 05 May 2006.

(3) IEC TC 111 PT 3, 'Procedures for the Sample disjointment related to the determination of the regulation of Six Regulated Substances (Lead, Mercury, Hexavalent Chromium, Polybrominated Biphenyls, Polybrominated Biphenyl Ether) in Electro-technical Products', draft version 1.0, 19 October 2006.