X-ray Fluorescence Analysis of Lead in Tin Plating Using Theoretical Intensity of Scattered X-rays
- Analysis of RoHS Regulated Elements by Energy Dispersive X-ray Fluorescence Spectrometer (EDX) -

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Abstract

RoHS regulated elements, such as cadmium and lead, are analyzed by energy dispersive X-ray fluorescence spectrometer (EDX). However, the quantitative values obtained by this method are affected by the thickness when the sample is a thin film, such as plating. Therefore, we measured the film thickness in an attempt to correct the quantitative values.

The sample was a tin-plated copper resistor terminal. The calibration curve method was used for lead concentration, and the fundamental parameter (FP) method was used for tin thickness. The measurement of lead yielded a quantitative value of 313.4 ppm, and the measurement of tin obtained a plating thickness of 9.1 µm.

A thickness correction factor was calculated from the tin plating thickness, giving a final quantitative value of 272.7 ppm for lead. A measurement was performed using an energy dispersive micro X-ray fluorescence spectrometer (µEDX) that is unaffected by the sample shape. The resulting 269 ppm quantitative value for lead approximately matched the EDX quantitative value.

Other samples, such as a display terminal, diode terminal, and washer, were also measured using the same method. In all cases, the EDX and µEDX quantitative values approximately matched, proving the validity of this method.

Keywords: X-ray fluorescence analysis, Theoretical intensity, Scattered X-rays, RoHS, RoHS regulated elements, EDX (energy dispersive X-ray fluorescence spectrometer)

1. Introduction

The European Union (EU) issued the RoHS Directive to restrict the use of hazardous substances contained in televisions, computers, and other electrical and electronic devices. The directive identifies six hazardous substances, cadmium (Cd), lead (Pb), mercury (Hg), hexavalent chromium (Cr(VI)), polybrominated biphenyls (PBB), and polybrominated diphenyl ethers (PBDE) and specifies a maximum allowable concentration of 100 ppm for cadmium and 1000 ppm for lead, mercury, hexavalent chromium, PBB, and PBDE.

Considering the huge number of electrical and electronic devices that need to be analyzed or evaluated, including all their constituent parts, it is extremely important that screening analysis methods are quick and easy. Currently, energy dispersive X-ray fluorescence spectrometer (EDX) systems are primarily used for screening analysis, with a large number of reports already available.[1),2),3),4)]

However, recently there have been reports of problems with quantitative values being lower than actual when analyzing thin films, such as plating.

Therefore, to resolve the problem, the authors investigated using correction factors to correct the quantitation values based on film thickness. The film thickness correction factors were calculated using the newly developed theoretical intensity of scattered X-rays. This process is described below.

2. Analysis Procedure

The typical procedure for analysis using a Shimadzu EDX-720 energy dispersive X-ray fluorescence spectrometer is shown in Figure 1.

First the instrument is started and calibrated by quantitating standard samples. Next, unknown samples must be pretreated appropriately, such as by layering thin samples, bundling wire rods, or separating composites into constituent materials.

Quantitative analysis is performed using the calibration curve method. Actual samples often have irregular shapes, such as screws and electrical terminals, making shape correction based on scattered X-rays essential. In this case, RhKa Rayleigh scattering or other such scattered X-rays are used.

If all quantitated values are below their respective lower control limit values, then the sample is considered compliant with the RoHS Directive and the process is finished, but if the concentration of even one element is greater than or equal to the control value, then qualitative analysis is additionally required. If the corresponding element is not detected at that point, then the prior quantitation value is assumed to be a false positive due to X-rays from other elements and the sample is considered compliant with RoHS. If the corresponding element is detected at that point, then the prior quantitation value is assumed to be valid and a final determination is made by measuring the sample precisely using an ICP (Inductively coupled plasma) or other system, after correcting for film thickness, as necessary. Shimadzu Corporation specifies the control limit value for lead to be 600 ppm. This value was calculated by referring to the IEC 62321 Annex D[5)], in spite of the 1000 ppm maximum concentration allowed by RoHS.

If the sample is a thin film, quantitation values are affected by the film thickness. Therefore, quantitation values must be corrected for film thickness. Currently, quantitation values for lead are only subject to film thickness correction if the quantitated value exceeds 300 ppm, which is half the control value.
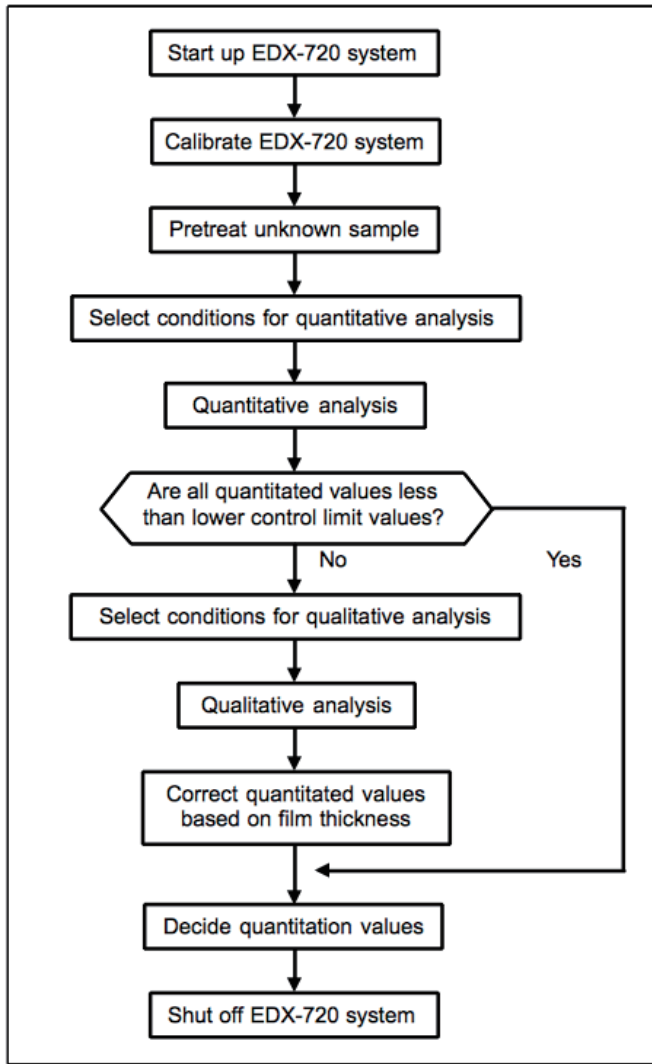
Fig. 1 Analytical procedure by the EDX-720

3. Analysis of Lead in Resistor Terminals

As a specific measurement example, film thickness correction was used for the analysis of lead in the tin-plating surface of resistor terminals. The key steps of the procedure include pretreatment, confirming constituent elements by qualitative analysis, deciding conditions for quantitative analysis including for shape correction, quantitating lead, measuring the tin-plating thickness, and correcting the lead quantitation value based on the film thickness.

3.1 Sample Pretreatment

The resistor terminals (lead wires) were cut into pieces a few millimeters long and secured in the EDX-720 analysis chamber. Fig. 2 shows photographs of the entire resistor and cut sections of the resistor terminals, and a cross sectional diagram of the tin plating on the pure copper lead wire.

(a) Resistor   (b) Resistor terminal   (c) Cross section of terminal
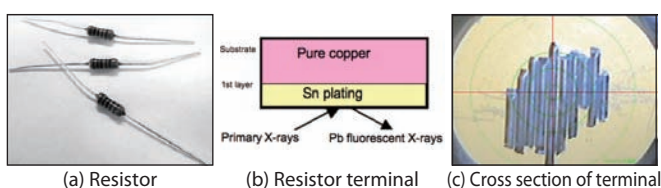
Fig. 2 Sample (resistor)

3.2 Qualitative Analysis

Fig. 3 shows the results from qualitatively analyzing the resistor terminals to confirm the constituent elements. These results indicate that large amounts of tin and copper and trace amounts of lead were detected.

After concluding that the substrate material was pure copper and the lead was contained in the tin-plating material, the sample was further investigated.
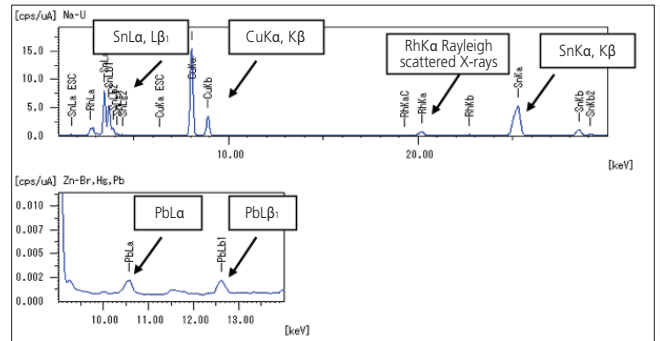

Fig. 3 Results of qualitative analysis of resistor terminal

Table 1 Analytical conditions for lead and tin

Instrument	EDX-720 energy dispersive X-ray fluorescence spectrometer	
Purpose	To quantitate lead	To measure tin-plating thickness
Elements, spectra	PbLβ$_1$	SnKα
X-ray tube	Rh target	
X-ray tube voltage and current	50 kV with automatically controlled current	
Collimators	10 mm diameter	
Filters	Yes	No
Detector	Si (Li) semiconductor detector	
Integration time	300 sec	100 sec
Atmosphere	Air	
Shape correction	RhKα Rayleigh scattered X-rays	
Quantitative analysis	Calibration curve method	Fundamental parameter (FP) method
Standard samples	Six MBH (74X series) solder samples	One pure tin and pure copper sample each

3.3 Analytical Conditions for Lead and Tin

Analytical conditions for lead (quantitative analysis) and tin (film thickness measurement) are indicated in Table 1.

3.4 Quantitative Analysis of Lead

Lead was quantitated by correcting for shape based on X-ray scattering and the calibration curve method.

3.4.1 Calibration Curve for PbLβ$_1$

MBH solder samples (in bulk form) were used as the standard sample. The calibration curve shown in Fig. 4 was prepared based on the intensity ratio of PbLβ$_1$ and scattered X-rays. The horizontal axis indicates the lead concentration (ppm) and the vertical axis indicates the measured intensity ratio of PbLβ$_1$ and RhKα Rayleigh scattering. RhKα Rayleigh scattering was used as the scattered X-rays. The calibration curve is expressed by the following equation.
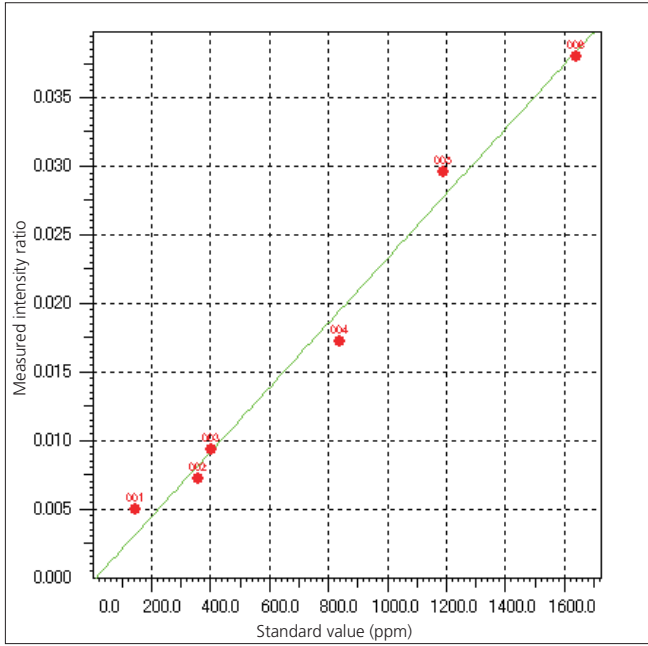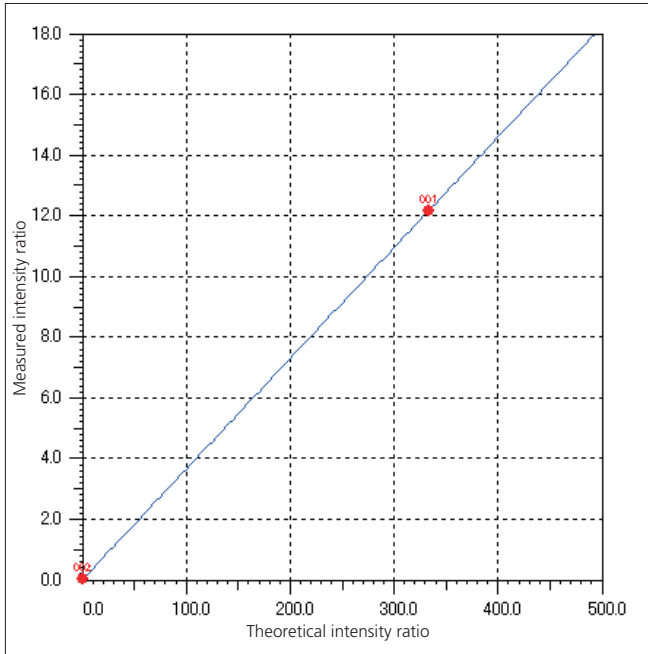
Fig. 4 Calibration curve for PbLβ1

Fig. 5 Sensitivity curve for SnKα

$$W_{Pb} = a \frac{M_{f,PbL\beta_1}}{M_{s,RhK\alpha R}} + b \qquad (1)$$

Where W is the concentration (ppm), M is the measured intensity (cps/μA), f is the fluorescent X-rays, s is the scattered X-rays, RhKαR is the RhKα Rayleigh scattering, a is the slope of the calibration curve (ppm), and b is the intercept (ppm). Theoretically, b should be zero, but it is used to correct for slight measurement errors.

3.4.2 Quantitative Analysis of Lead

The resistor terminals were quantitated using the calibration curve in Fig. 4 That resulted in a quantitated value of 313.4 ppm for lead.

Since the value exceeded 300 ppm, which is half the lower control value for lead, it required measurement of the tin-plating thickness according to the procedure in Figure 1 and correcting the quantitation value based on film thickness.

3.5 Tin-Plating Thickness Measurement

The tin-plating thickness was measured for shape correction based on the fundamental parameters (FP) method using X-ray scattering.

3.5.1 SnKa Sensitivity Curve

Pure tin and pure copper (both in bulk form) were measured as standard samples. The sensitivity curve obtained based on the intensity ratio of SnKα and scattered X-rays is shown in Fig. 5 The vertical axis indicates the measured intensity ratio between SnKα and RhKα Rayleigh scattering and the horizontal axis indicates the theoretical value of the same ratio. RhKα Rayleigh scattering was used as the scattered X-rays. The sensitivity curve is expressed by the following equation.

$$\frac{M_{f,SnK\alpha}}{M_{s,RhK\alpha R}} = c \frac{T_{f,SnK\alpha}}{T_{s,RhK\alpha R}} + d \qquad (2)$$

Where T is the theoretical intensity (au), c is the slope of the sensitivity curve, and d is the intercept. Just as in equation (1), d is used to correct for slight measurement errors.
Theoretical intensity, T, was calculated from the sample area density m (g/cm²) and concentration of elements W (%), based on the following equation.[6),7),8)] The sample thickness t (μm) can be determined by dividing area density m by sample density ρ (g/cm³).

$$T = f(m, W) \qquad (3)$$
$$t = m/\rho \qquad (4)$$

For bulk samples, the sample thickness t and area density m are infinite, but for thin films, they have a fixed value. However, by using theoretical intensity T, the same equation can be used to express both bulk and thin film samples. In other words, a bulk standard sample can be used to quantitate unknown thin film samples. This is a major advantage of the FP method, unlike the calibration curve method, which requires using separate equations for bulk and thin film samples.

3.5.2 Tin-Plating Thickness Measurement

The resistor terminals were quantitated using the sensitivity curve created in Fig. 5 This resulted in a tin-plating thickness of 9.1 μm.

3.6 Lead Quantitation Value Corrected for Film Thickness

The lead quantitation value of 313.4 ppm was corrected by multiplying it by a film thickness correction factor of 0.87 for a tin-plating thickness of 9.1 μm (refer to Table 2), resulting in a corrected lead quantitation value WPb of 272.7 ppm.

The method used to calculate the film thickness correction factor is described below.

4. Film Thickness Correction Factor

Assume the concentration of lead in tin plating W_{Pb} is expressed as W'_{Pb}, due to the effects of the plating thickness. The difference between these is caused by quantitating the unknown thin film sample using the calibration curve for the bulk standard sample. The film thickness correction factor k is defined as follows.

$$k = W_{Pb} / W'_{Pb} \qquad (5)$$

Substituting equation (1) into (5) and ignoring the negligible intercept b results in equation (6).

$$k = \left(\frac{M_{f, PbL\beta_1}}{M_{s, RhK\alpha R}} \right) \Big/ \left(\frac{M'_{f, PbL\beta_1}}{M'_{s, RhK\alpha R}} \right) \qquad (6)$$

In this case, M represents the bulk measurement intensity and M' the thin film measurement intensity. Substituting equation (2) into (6) and ignoring intercept b, as before, results in the following.

$$k = \left(\frac{T_{f, PbL\beta_1}}{T_{s, RhK\alpha R}} \right) \Big/ \left(\frac{T'_{f, PbL\beta_1}}{T'_{s, RhK\alpha R}} \right) \qquad (7)$$

T represents the bulk theoretical intensity and T' the thin film theoretical intensity. Based on equation (7), the thin film correction factor k can be calculated from the theoretical intensity of fluorescent X-rays and scattered X-rays in bulk and thin film samples.

The same method can be used to determine the thin film correction factors for nickel or zinc plating, or for quantitating cadmium or chromium. These factors are summarized in Table 2. Note that the factors for cadmium and chromium in tin plating are omitted. This is due to a lack of suitable standard samples, which prevents obtaining accurate quantitation values using the calibration curve method. Thin film correction is performed by simply multiplying quantitation values by the thin film correction factor. Some of the factors are less than 1.0, which is caused by differences in the transmittance of fluorescent and scattered X-rays in thin films (in this case a plating layer), but such factors may be used just as they are.

Table 2 Thickness correction factors for the EDX-720

Platings	Ni			Zn			Sn
Substrates	Cu[*]			Fe[*]			Cu
Elements	Cd	Pb	Cr	Cd	Pb	Cr	Pb
Spectra	CdKα	PbLα	CrKα	CdKα	PbLα	CrKα	PbLβ_1
Film thickness (µm)	Correction factors						
1.0	29.7	3.98	4.55	44.7	5.95	6.73	3.35
1.5	20.1	2.83	3.18	29.8	4.18	4.71	2.40
2.0	15.2	2.26	2.51	22.3	3.29	3.71	1.92
2.5	12.3	1.93	2.11	17.9	2.77	3.10	1.64
3.0	10.4	1.70	1.84	14.9	2.42	2.70	1.45
3.5	8.99	1.55	1.66	12.8	2.18	2.42	1.32
4.0	7.94	1.44	1.53	11.2	1.99	2.20	1.22
4.5	7.14	1.35	1.43	9.95	1.85	2.04	1.14
5.0	6.49	1.28	1.35	8.97	1.74	1.91	1.09
6.0	5.53	1.19	1.23	7.49	1.58	1.72	1.00
7.0	4.83	1.13	1.16	6.44	1.47	1.58	0.94
8.0	4.31	1.08	1.10	5.66	1.39	1.49	0.90
9.0	3.91	1.05	1.07	5.05	1.33	1.41	0.87
10.0	3.58	1.03	1.04	4.56	1.28	1.35	0.85
15.0	2.61	0.99	0.98	3.13	1.15	1.19	0.80
20.0	2.13	0.99	0.97	2.44	1.10	1.12	0.80

*Even if the substrate for the nickel plating is changed from copper to iron or the substrate for the zinc plating is changed from iron to copper, the corresponding change in the thin film correction factor is minimal. Therefore, these factors can be used for either iron or copper substrates.

5. Quantitative Analysis of Other Samples

In addition to the resistor terminals, the lead was quantitated in terminals from several other electronic parts as well. Fig. 6 shows photographs of these parts, including the resistors described above, and diagrams of their cross sections. Quantitative analysis results are indicated in Table 3.

To verify results, the samples were also quantitated using a µEDX-1200 energy dispersive micro X-ray fluorescence spectrometer. This spectrometer analyzes a 50-µm diameter area, so shape effects are minimal. This resulted in µEDX-1200 values that were approximately the same as values obtained after film thickness correction, which confirms that the film thickness correction method discussed in this article is valid.

(a) Resistor   (b) Display   (c) Diode   (d) Washer

Tin-plated copper   Tin-plated copper   Tin/nickel-plated copper   Zinc-plated steel

(e) Connector   (f) IC   (g) Resistor   (h) Spark killer

Tin/nickel-plated copper   Tin-plated copper   Tin-plated copper   Nickel-phosphorus -plated copper
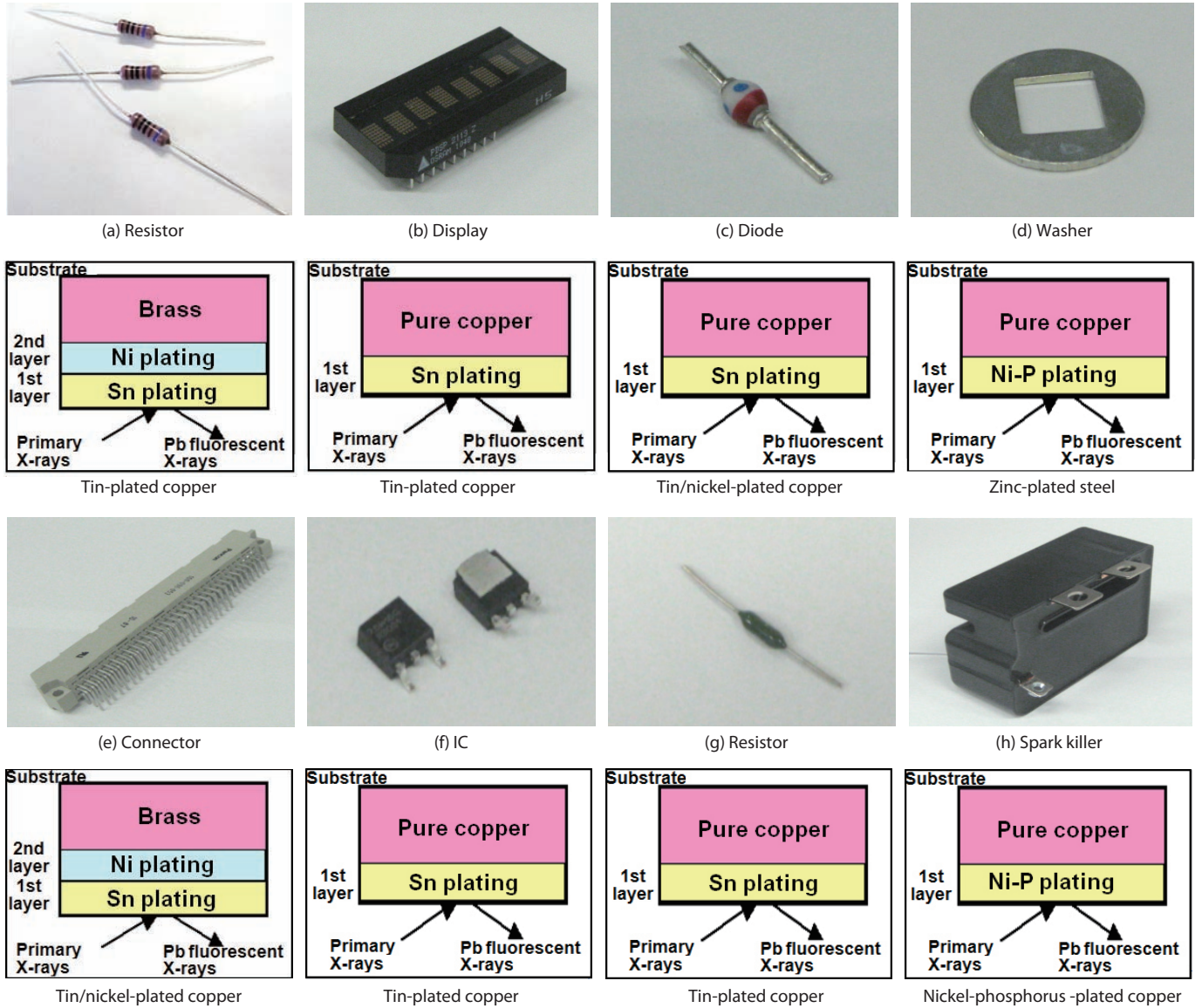
Fig. 6 Electrical parts

Table 3 Results of quantitative analysis for electrical part terminals

Instruments	Samples	(a) Resistor terminal	(b) Display terminal	(c) Diode terminal	(d) Washer
	Materials	Tin-plated copper	Tin-plated copper	Tin/nickel-plated copper[*1]	Zinc-plated steel
EDX	Lead quantitation value (ppm)	313	342	477	195
	Plating thickness (μm)	9.1	6.2	7.3	7.0
	Correction factor	0.87	1.00	0.94	1.47
	Corrected lead quantitation value (ppm)	273	342	448	287
μEDX[*3]	Plating thickness (μm)	8.7	6.9	7.7	7.8
	Lead quantitation value (ppm)	269	332	480	318

Instruments	Samples	(e) Connector terminal	(f) IC terminal	(g) Resistor terminal	(h) Spark killer terminal
	Materials	Tin/nickel-plated brass[*2]	Tin-plated copper	Tin-plated copper	Nickel-phosphorus -plated copper
EDX	Lead quantitation value (ppm)	594	266	723	212
	Plating thickness (μm)	5.4	6.2	12.9	3.4
	Correction factor	1.09	1.00	0.80	1.55
	Corrected lead quantitation value (ppm)	648	266	578	329
μEDX[*3]	Plating thickness (μm)	6.0	6.6	12.7	2.9
	Lead quantitation value (ppm)	614	290	634	314

(*1) The first layer of tin plating was analyzed.
(*2) The first layer of tin plating was analyzed. The brass substrate was already confirmed not to contain lead.
(*3) Analyses of micro areas are prone to variability due to material segregation. Therefore, each sample was analyzed in 10 locations or more and the resulting values were averaged.

6. Summary

The authors previously reported[9] that there was a new FP method available for shape correction that can be applied to simultaneously quantitate constituent elements and the thickness of thin films on irregularly shaped samples, such as screws and terminals. Using this FP method eliminates the need for thin film correction.

However, to efficiently analyze a wide variety of samples for RoHS analysis, bulk and thin film samples are directly quantitated using bulk calibration curves and then only samples with a problem are reanalyzed.

The subject method was developed to make it possible to perform RoHS analysis both accurately and efficiently by measuring the thickness of such thin films and correcting the quantitated values based on the film thickness. Therefore, this technique can be utilized as an effective means of using EDX for RoHS analysis along with other analytical methods reported previously.[4]

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