Analysis of Circuit Boards and Electrical Connectors for RoHS/WEEE Regulated Elements Using XRF

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Introduction

Manufacturers and suppliers of electronic and electrical products to member states within the EU must comply with RoHS (Restriction of Hazardous Substances) and WEEE (Waste from Electrical and Electronic Equipment) regulations. Six materials are restricted under these directives: lead (Pb), mercury (Hg), cadmium (Cd), hexavalent chromium (Cr VI), polybrominated biphenyls (PBB) and polybrominated diphenyl ethers (PBDE). Maximum allowable concentrations of these materials are 1000ppm, with the exception of cadmium, which is restricted to a maximum of 100ppm.

X-ray fluorescence (XRF) spectroscopy is widely used for elemental analysis to determine whether components and equipment meet the RoHS/WEEE requirements. Small, handheld XRF instruments are routinely used for checking various locations on a component or piece of equipment to determine whether that item is in compliance. However, concentrations of elements vary depending on the exact location of the measurement and an item may pass or fail based on a measurement that is not truly representative of the entire component. Therefore, analyses of electronic components as received (heterogeneous) and ground (homogeneous) samples were compared to determine whether use of the "spot checking" method on electronic components is accurate in determining concentrations of restricted elements.

XRF Analysis

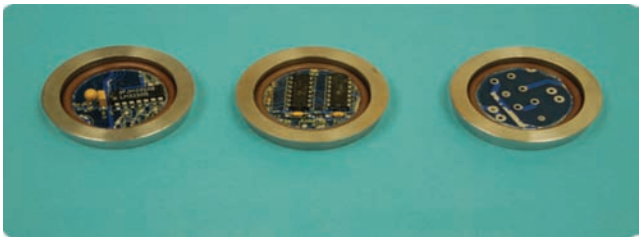
A Bruker S2 Ranger bench-top ED-XRF instrument was used for analysis, in an effort to mimic the direct-reader handheld systems. Calibration curves were created using polyethylene standards spiked with known concentrations of RoHS/WEEE elements. Samples were analyzed by XRF for bromine, cadmium, chromium, lead, and mercury using a semi-quantitative program designed for analysis of these elements.

Experiment 1 – XRF Analysis of a Non-Compliant Circuit Board

Procedure

Three circular samples, with 40mm diameter, were cut from different locations on a circuit board known to be non-compliant with RoHS/WEEE regulations, as shown in Figure 1. Both the front and back sides of the samples were analyzed by XRF.

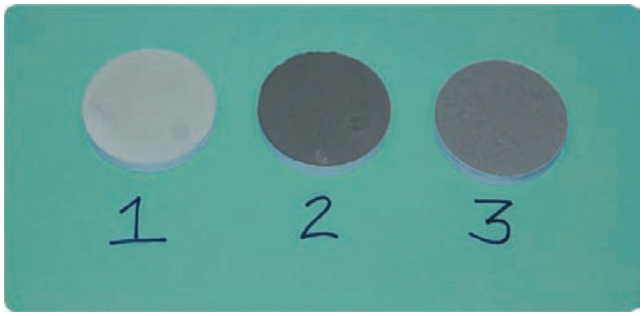
Figure 1- Discs cut from circuit board



Next, the samples were cut into small pieces and all copper items were removed. Each sample was placed into a chromium-free vial and submerged in liquid nitrogen for 20 min. Samples were then ground on a SPEX SamplePrep 6770 Freezer/Mill for 3 cycles, each of 2 min. in duration, at 10Hz, using a 15 min. pre-cool segment prior to grinding and 2 min. cooling segments between cycles. Following this treatment, unground material was removed from the powdered sample and submerged again in liquid nitrogen for 20 min. This material was then returned to the Freezer/Mill for additional grinding.

Ground samples were pressed into pellets measuring 40 mm in diameter (Figure 1) by layering the sample material onto a base of boric acid and pressing at 30 tons on a SPEX SamplePrep 3630 X-Press. These pellets were then analyzed by XRF, as before.

Figure 2 - Samples after grinding and pressing on a boric acid base



Results

Results for both procedures are shown below in Table 1 and are displayed graphically in Figures 3-5. The elements cadmium and mercury were not detected in any of the samples prior to or after grinding and therefore are not shown in the table. Bromine levels exceeded RoHS/WEEE limits for all samples. However, by switching to non-brominated flame retardants in the manufacture of circuit boards, this obstacle could be overcome.

The results for chromium and lead are more interesting. While chromium was not detected in any of the samples prior to grinding, it was found in samples 1 and 2 after they were ground and pressed into pellets. In particular, sample 2 was found to contain 1166ppm of chromium, which exceeds the RoHS/WEEE maximum limit of 1000ppm. Lead levels were measured within the acceptable range in the cut disc samples, but the results increased significantly in samples 1 and 2 after grinding and both samples then failed to meet RoHS/WEEE requirements.

SPEX SamplePrep 6770 Freezer/Mill

Figure 3 - Bromine (ppm)

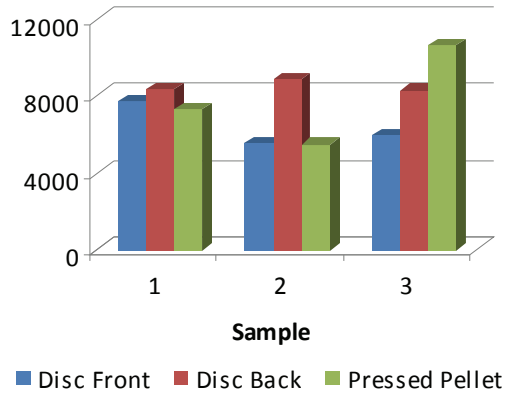


Figure 4 - Chromium (ppm)

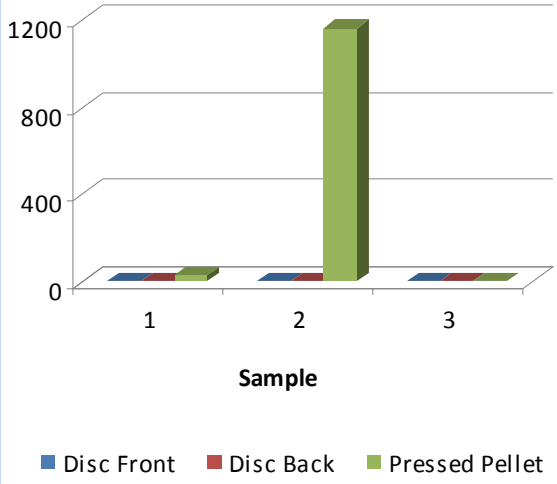


Figure 5 - Lead (ppm)

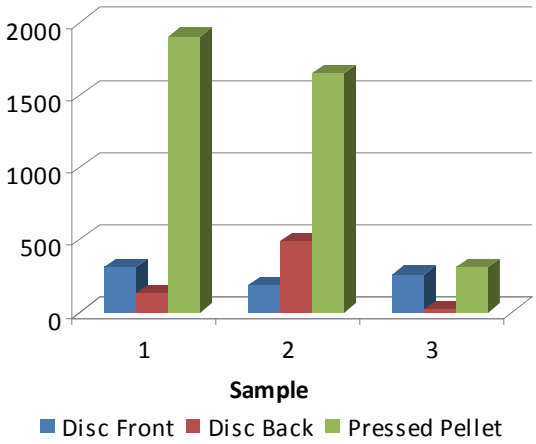


Table 1 – Concentration of RoHS/WEEE Elements in Samples of Non-Compliant Circuit Board (ppm)

	Bromine			Chromium			Lead		
Sample	Front	Back	Pellet	Front	Back	Pellet	Front	Back	Pellet
1	7,726	8,323	7,287	0	0	32	305	128	1,903
2	5,521	8,853	5,504	0	0	1166	181	485	1,654
3	5,941	8,305	10,626	0	0	0	261	525	308

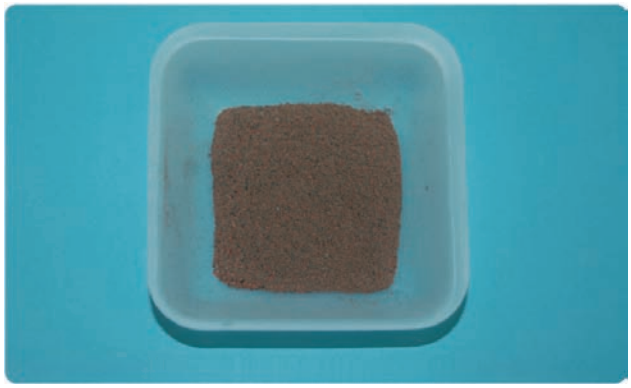
Experiment 2 – XRF Analysis of Non-Compliant Circuit Board Connectors and Components

Procedure

The connectors and components were removed from RoHS/WEEE non-compliant circuit boards, sorted by type (Figure 6), placed into 40mm sample cups covered with Mylar® film, and analyzed by XRF. The samples were then ground in the 6770 Freezer/Mill, using the same protocol as described previously, and analyzed a second time as loose powders.

Figure 6 – Connectors and Components from non-compliant circuit board

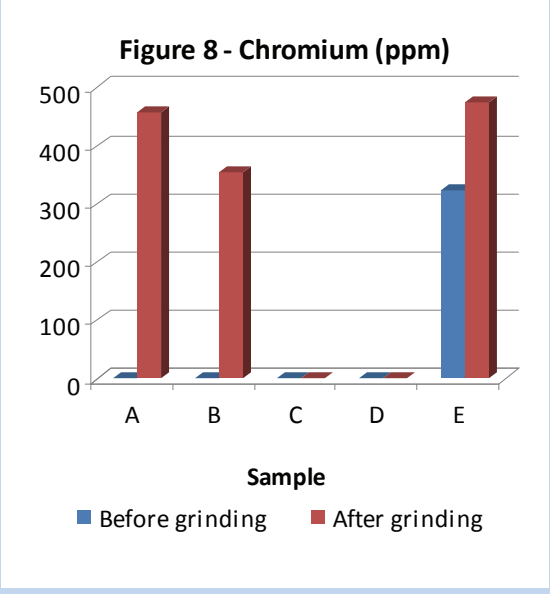
Figure 7 – Sample C after grinding

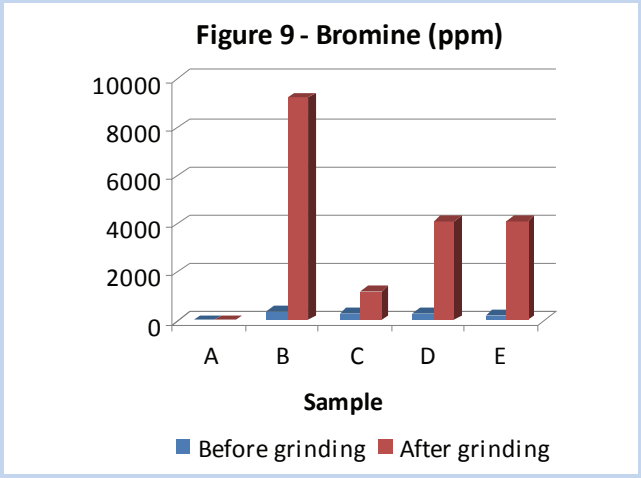


Results

Results for the materials prior to and after grinding are compared in Table 2 and shown in Figures 8-10. As in Experiment 1, mercury was not detected in any of the samples. Since sample E was a metal, the presence of chromium was not surprising. Interestingly, cadmium was detected in sample E before grinding, but not after. This indicates that the analysis of the loose, whole connectors occurred at a location where cadmium was present. However, after grinding, the sample was homogenized and the cadmium level must have been so low as to be undetectable. Sample E was found to consist of 98% iron, with small amounts of titanium, vanadium, manganese, selenium, tin, antimony, and tellurium, in addition to the chromium, cadmium, and lead shown below.

Bromine concentrations increased dramatically for samples B-E after grinding, putting all beyond acceptable RoHS/WEEE limits. Lead levels increased in all cases, but significantly for samples B-E. Sample D just met RoHS/WEEE limits for lead prior to grinding, but failed by a wide margin after grinding.





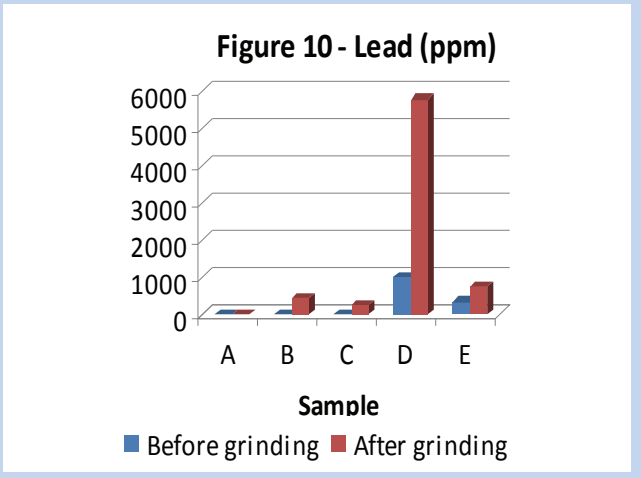


Table 2 – Concentration of RoHS/WEEE Elements in Samples of Non-Compliant Connectors and Components (ppm) Before and After Grinding

	Chromium		Cadmium		Bromine		Lead	
Sample	Before	After	Before	After	Before	After	Before	After
A	0	458	0	0	6	13	0	11
B	0	326	0	0	368	9,246	10	443
C	0	0	0	0	278	1,208	11	230
D	0	0	0	0	316	4,124	969	5,790
E	323	474	42	0	210	4,147	338	767

Conclusions

Overall, the data indicate that the method of sample preparation and the location of sample selection on the circuit board greatly influence the XRF results. Concentrations of metals, as determined by XRF, were generally much higher for a homogenized sample than for a heterogeneous sample from a circuit board or connectors. Spot checking various locations on a board with a handheld XRF instrument is more likely to give results that meet RoHS/WEEE requirements, while processing a section of the board to obtain a more homogeneous sample is more likely to yield results which exceed RoHS/WEEE limits. However, a homogeneous sample is more representative of the overall composition and analysis of such a sample gives results that are likely to indicate more accurately the true concentrations of restricted substances.

Special Thanks to Bruker AXS, Inc

Bruker S2 Ranger ED-XRF

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