RoHS Substance Measurements in Complex Products

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Abstract

With the wide breadth of component types used in complex electronic equipment, implementation of the European Union Restriction of Hazardous Substances 2011/65/EU/ (RoHS) is a challenge. A low volume, very high mix, manufacturer of complex equipment has tens of thousands of purchased part numbers that encompass a wide range of part types including low risk common off-the-shelf parts from robust suppliers to higher risk specialty parts at niche suppliers. One expectation of the directive is that higher risk items and process materials are measured for the restricted substances. The use of a basic handheld x-ray fluorescence instrument provides a relatively fast and inexpensive way to detect restricted substances. However, interpretation of the results must be done with perspective and judgment. The results and learnings from a physical assessment program using X-ray fluorescence (XRF) analysis are discussed. Substance measurement anomalies can occur due to sample heterogeneity and interference with XRF signal generation and detection. False readings of Hg in Au and Cd in Sn are the result of known measurement artifacts, and can be identified with examination of the spectrum. Melted solder samples can give inaccurate concentration of lead due to segregation and segmentation within the sample during cooling. Plastic parts can be at risk of Cd and Pb non-compliance from pigment or plasticizers. Inaccurate measurements can result from extraneous material in the sample window. Techniques are given for measuring contamination at soldering stations, identifying SnPb or SAC solder use when the sample contains extraneous material, and tips for containing and securing samples for analysis.

Keywords: X-ray fluorescence spectrometry, XRF, restricted materials in electronics, RoHS

Introduction

The EU RoHS directive restricts Lead (Pb), Mercury (Hg), Cadmium (Cd), Hexavalent Chromium (Cr^{+6}), Polybrominated Biphenyls (PBB), and Polybrominated Diphenyl Ether (PBDE) in electronic equipment to a maximum in homogeneous materials of 1000 ppm for all but Cd, which is limited to 100 ppm. There are a range of items in electronics with obvious low or high risk levels of RoHS non-compliance. Common parts from suppliers that have been supplying RoHS compliant components to the consumer industry are low risk. We see two challenges with the other part types. Specialty parts from suppliers that have limited to no customers in the European Union are high risk, especially if there are soldering operations or high-risk materials involved. Measurement techniques are the other challenge. Precision techniques, such as ICP-OES, are high cost and time-consuming, and are destructive because physical samples need to be taken and processed to yield suitable analytes. Simple methods like consumer-oriented chemical swabs for lead are not accurate and prone to interference by substances present on the surfaces analyzed. Handheld X-ray fluorescence (HHXRF) equipment gives reasonable accuracy at a low cost for facilities desiring internal audit capability. HHXRF analysis is well suited for verifying process compliance, such as detection of gross violations involving the use of SnPb instead of SAC solder, or the use of incorrect material or alloy against specification. Non-destructive *in situ* analysis provides quantitative results quickly and produces records that can justify the correct call and course of action as needed.

HHXRF detects most of the restricted materials likely to be present in electronics. For Pb, Hg and Cd, the XRF provides sufficient indication of presence or absence of the substances to make a determination of a part's compliance status. XRF is not useful for measuring the restricted flame retardants PBB and PBDE – bromine is found in many other unrestricted compounds. HHXRF cannot differentiate between hexavalent chromium, which is restricted, and trivalent or metallic chromium, which are allowed. It measures the total of the chromium element that is present.

Basics of XRF Measurement

In XRF measurement, x-rays from the instrument knock out inner shell electrons in the atoms of the sample, such as in the K orbital. See Figure 1. An outer shell electron, such as in the L orbital, drops down to fill each vacancy. The energy difference from this orbital change results in the emission of an x-ray. Each element emits x-rays with characteristic energy levels, allowing identification. From these energy levels and the number of x-rays per second for all of the materials in the sample, the XRF instrument uses algorithms to calculate the concentration of each element. The x-ray energy is represented in a spectrum of energy level in kV versus counts per second. Each element produces x-rays at least two energy levels for each orbital. The characteristic alpha x-ray comes from the next higher shell and the beta x-ray comes from 2 shells higher. For the K shell, these are represented as K_α and K_β or Ka and Kb. Each element typically has only one inner shell with the right level of excitation from the XRF to eject an electron, and will show either two K orbital energy signals or two L orbital energy signals in the spectrum. More information on XRF science and measurement accuracy can be found in other publications [1] [2] [3] [4].

Figure 1: Graphic Showing XRF Analyzer and Atom from the Sample.
Image used with permission from Olympus

HHXRF analyzes all the material in front of the 10 mm diameter analyzing window, see Figure 2, and only the surface, to a depth that depends on the density of the sample. In dense metallic samples, the depth is approximately 1 mm or less. For plastic samples, the depth is as much as 15 mm. The best results are from samples that are of homogeneous material, flat, large enough to cover the window, and thick enough to appear infinite in depth.

Figure 2: XRF Analyzer in the Test Stand, Used for Increased Safety, and the Analyzer Window

Many XRF analyzers use more than one excitation condition (i.e. "Beams"). This allows the analyzer to generate spectra that will optimally energize the sample to induce fluorescence for a variety of elements and matrix types. The result is better analytical confidence over a wider range of samples and sample types.

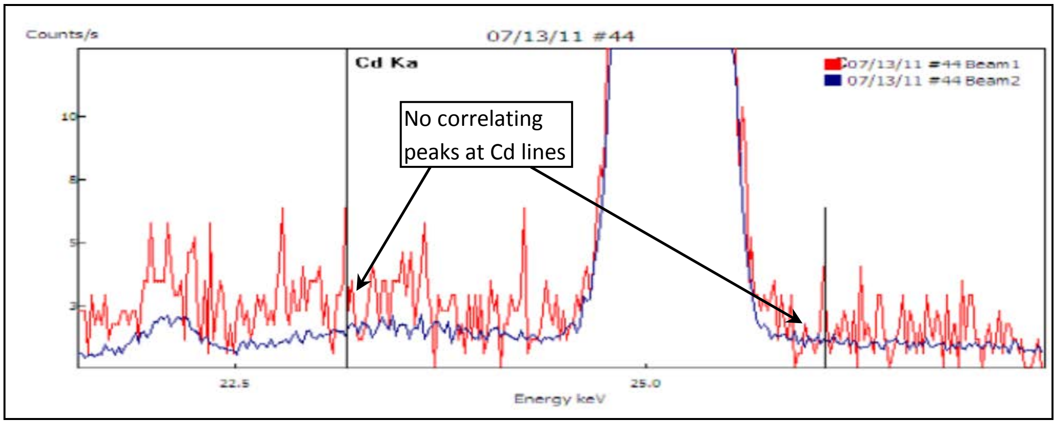
There are a few well known spectral effects that should be considered. Pile up peaks (a.k.a. Sum peaks) result from when two x-rays enter the detector at the same time. The analyzer reads these as one x-ray with the sum of the energy of the two x-rays. Escape peaks result from the excitation and subsequent fluorescence of the silicon in the detector. The detector records the expected energy minus that of the created silicon x-ray.

The substance concentration measurement in a basic handheld XRF analyzer is limited in commercial use by the nature of the sample. Samples of interest for RoHS analysis are rarely homogenous or flat. The non-destructive and rapid nature of XRF testing still makes it a useful compliance screening technique. Violations are usually glaringly obvious with violations measured at a few percent versus a compliance threshold of 1000 ppm. Homogeneous substances with measurements greater than 700 ppm Pb need closer scrutiny before making a determination of compliance. For heterogeneous substances, such as PCB finishes or metal parts with plating layers, the measurements must be analyzed using perspective and judgment that takes into account the effect of the homogeneous layer content in relation to the total material being measured.

Mistaken Identity

The XRF gives a report with a substance concentration in parts per million or percent, yet it is not a tool that gives Yes or No answers. The results require interpretation within the context of the item being analyzed to understand the meaning of the number. Experience and familiarity with the particular XRF model and material being analyzed are essential towards meaningful and satisfactory assessment conclusion. There are overlapping energy peaks, and especially with the affordable handheld XRF guns, the x-ray counts can be assigned to the incorrect element. It is always good practice to inspect the spectrum when presented with unexpected results. We provide some examples of false positive element detection, where one or both of the energy levels lack correlation with the energy spectrum.

Figure 3 shows the spectrum for a tin-plated high frequency coaxial cable in which the data showed 900 ppm of cadmium. Because any Cd that is present would logically be expected in the metal jacket or plating, the alloy calibration displayed as Beam 2 in Figure 3 will be the best indicator of the substance. The results from the polymer calibration is shown in red and is not used in the measurement calculation. The alloy calibration, in blue, does not show correlation with the Cd energy levels. Our conclusion is that Cd is not present in this sample. The presence of Cd at the concentrations indicated by the software was not supported by observed spectra. The only observed peak in the Cd region was the expected escape peak from the Sn K_α line, which was more visible using a log scale, shown in Figure 4. It was hypothesized that the XRF algorithm used wasn't properly accounting for them, thus leading to a false reading of Cd. This was later confirmed following a consultation with the analyzer's manufacturer and a subsequent reprocessing of the spectra using an updated algorithm provided by them to correct for this. The lack of alignment of energy level for the element reported with the center of a peak and absence of signal at the K_β energy line are indications that measurement is false.



No correlating peaks at Cd lines

Figure 3: XRF Spectrum Showing Location of Cd K-shell Energy Levels and Lack of Signal in Alloy Beam 2, in Blue

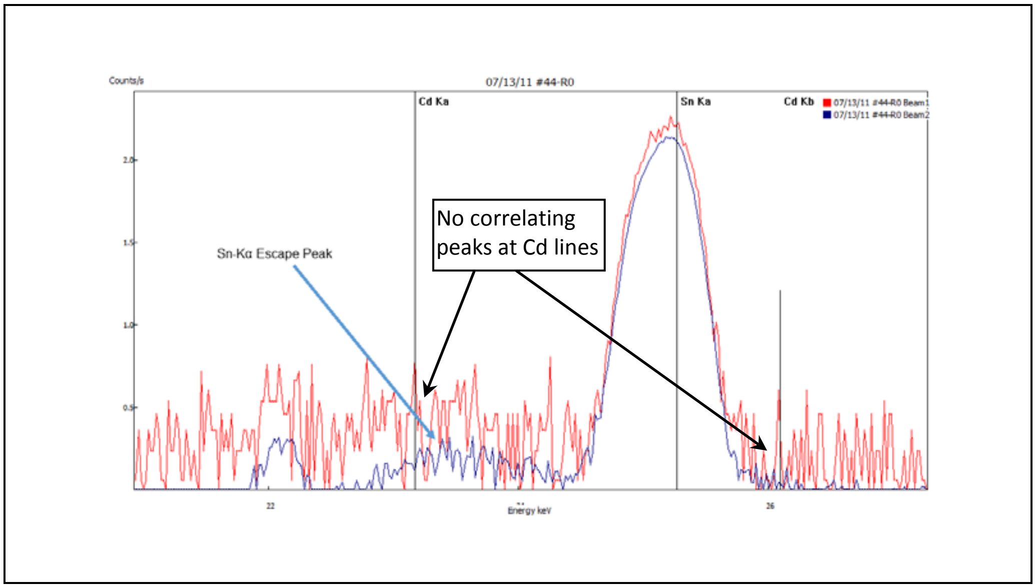


Figure 4: Sn K$_\alpha$ Escape Peak Offset from Cd K$_\alpha$ Line Shown in Log Scale.

With gold plated parts, Hg can be erroneously detected. In each of the cases where Hg readings have been reported on a gold plated part, see example in Figure 5, analysis of the spectrum showed a lack of correlation with one of the Hg energy levels – L$_\beta$ does not align with the center of the peak – and there is no correlation with L$_\alpha$. We have confirmed the lack of Hg with ICP-OES measurements.

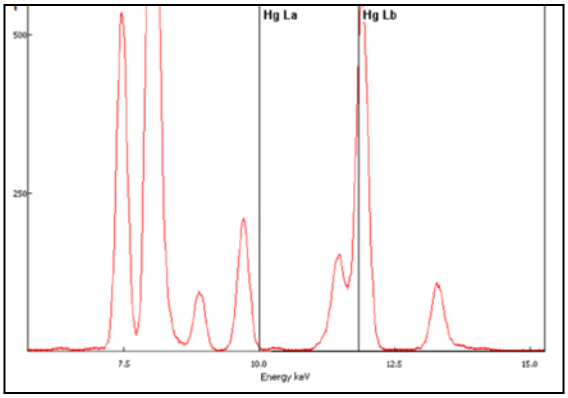


Figure 5: XRF Spectrum Showing Location of Hg L-shell Energy Levels and Lack of Alignment with Peaks. Hg was Measured at 2100 ppm.

Lesson learned: Always verify that peaks for both characteristic x-rays of the element shell are present. If one of the element's characteristic x-ray energy level does not correlate with a peak in the spectrum -- either the peak is missing or off center -- it is likely that the element is not actually present.

Missing Lead

One of the important process materials to measure is the solder used in manufacturing or rework. The often-used Sn3.0Ag0.5Cu "Pb-free" SAC305 solder contains 200-500 ppm of Pb, and is specified at 700 ppm maximum. A typical measurement technique for solder paste is to dispense an amount onto a printed circuit board and run it through the reflow oven. The melted button of solder is then cleaned and measured. Solder wire used in hand-soldering or rework is wound into a tight bundle for measurement, creating a contoured sample. Due to concerns about the effect of surface contours in the solder wire bundle on the accuracy of the measurement, several samples of a known high-Pb SAC solder, with an assay of 980 ppm, were measured multiple times to determine measurement variation. The solder wire bundles were then placed in a small vapor phase reflow oven, which melted the samples into a solder "button". The theory was that the flat, smoother surface of the button would produce more consistent results. The surprising results show that the flat surface of the button measured at less than 70% of the Pb concentration than was in the bundled solder wire; see figure 6.

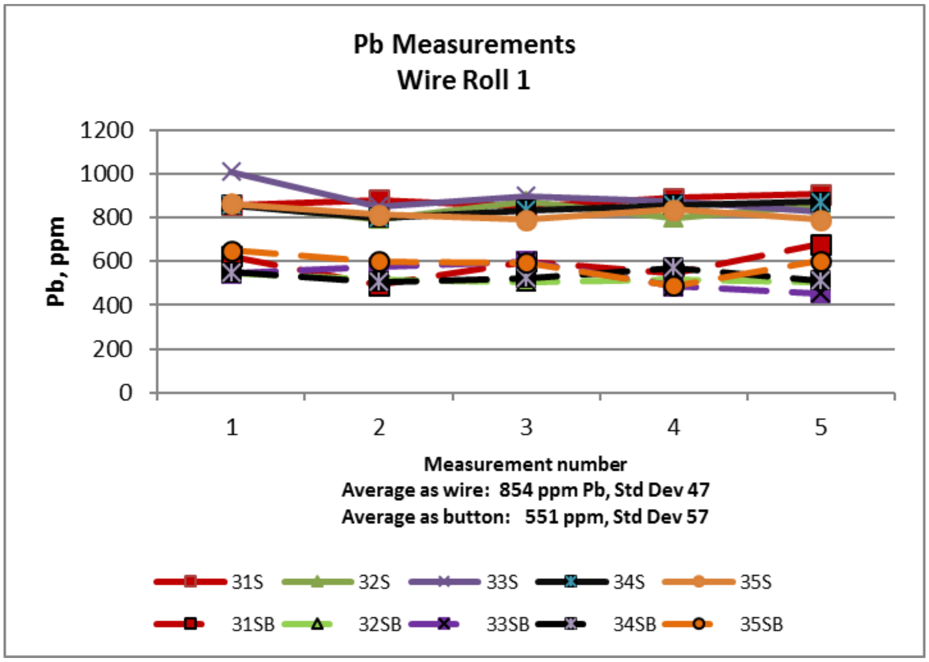


Figure 6: The difference in Pb Measurement for a Bundle of Solder Wire versus the Flat Bottom-side of the Melted Sample. Solder is SAC305 with Assay of 980 ppm Pb.

Measurements taken of the top, curved, surface of the solder button showed other differences in Pb concentration. For the above samples, the top of the button measured about the same as the wire bundle. For other samples, the measurement depended on the cooling method, as illustrated in Figure 7.

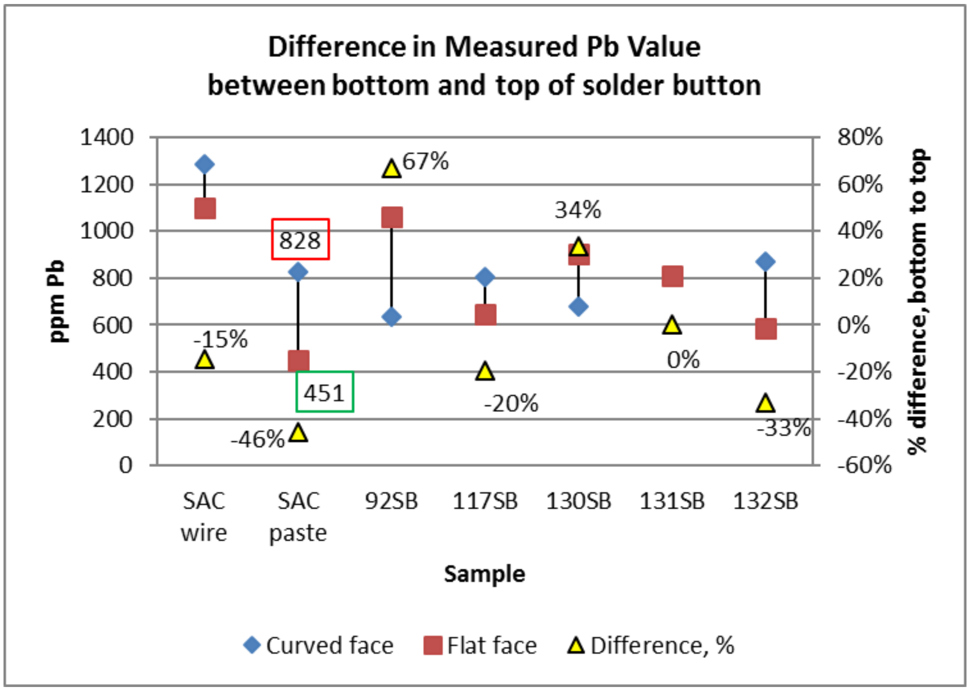


Figure 7: Measurements of Top and Bottom of Solder Buttons.

Variation in the difference between topside and bottom-side measurements of the samples is shown in Figure 7. Samples 31SB through 35SB, 92SB and "SAC wire", were melted in a small vapor phase oven which cooled the sample slowly, with faster cooling on the top of the sample than the bottom. Samples 130-132SB, shown in Figure 8, were made from wire bundles heated on a hot plate. Samples 117SB and 132SB were moved to a hot aluminum plate and cooled slowly. Sample 132SB was additionally air-cooled on top to simulate a convection oven cooling section. These samples show lower Pb on the slow-cooled side of the sample. Sample 130SB was lowered into cold water to cool it quickly. The bottom contacted the water first, so cooled first. In this sample, the bottom has a higher Pb content than the top. Sample 131SB has a form that looks like it was flowing while cooling. This sample shows no difference between top and bottom. Sample 92SB is atypical, showing lower Pb concentration on the top than on the bottom. This was a combination of SAC and SnPb wire. The "SAC paste" sample was solder paste dispensed onto a blank printed circuit board (PCB) and run through a convection oven. The blowers at the end of the oven would have cooled the top quickly while the bottom of the sample likely cooled more slowly as the PCB cooled. Note that the bottom-side measurement at 451 ppm Pb would be acceptable but the topside measurement of 828 ppm Pb would raise concerns and a review of the assay or additional measurement would be pursued. The suppressed Pb measurement could lead to a false indication of compliance.

Figure 8: Solder Buttons from Melted Bundles of Solder Wire (bundle example on left).

Our theory is that the slow-cooled portion of the button exterior will become enriched with Sn since it solidifies at a higher temperature. The composition at the fast-cooled exterior of the sample contains a more representative concentration at the surface. Samples 130-132SB were cross-sectioned vertically and analyzed to look for segregation of the Sn or concentration of the Pb in the interior. There was no clear evidence of either. The cross-section of sample 132SB in Figure 9 shows differences in microstructure between the slow-cooled bottom and faster-cooled top. However, no difference in Sn distribution could be visually observed and the low concentration of Pb could not be mapped. ICP-OES is being pursued to make accurate measurements of the Pb content.

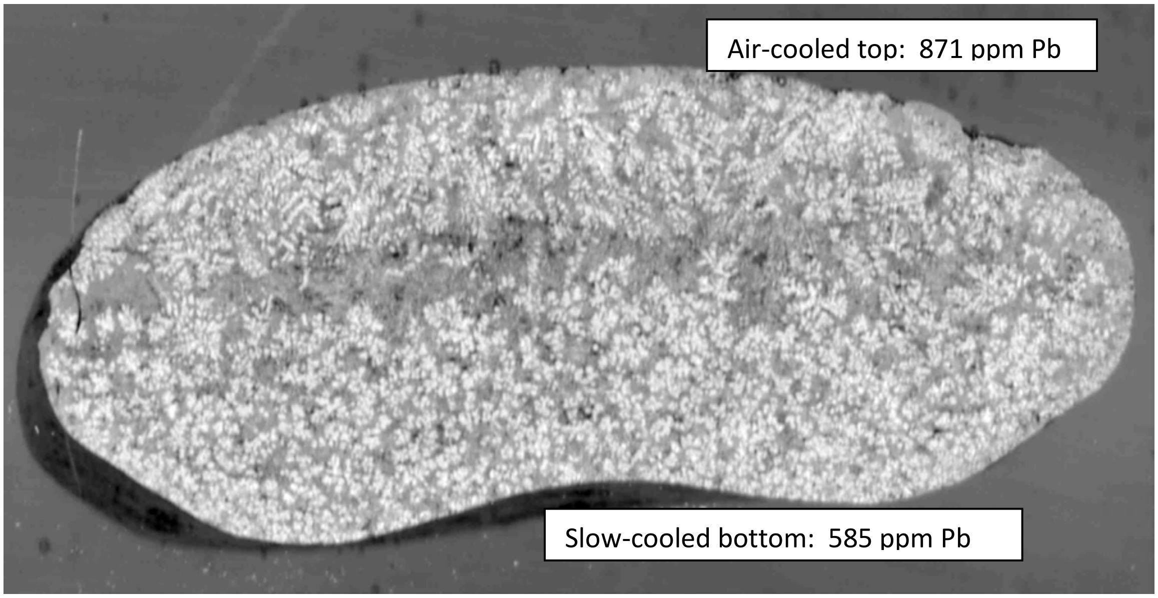


Figure 9: Cross-section of Sample 132SB

Sample 117SB was potted, then ground and polished from each side to remove the surface layers, Figure 10 and Table 1. In this sample, the original solder button measured 645 ppm Pb on the bottom and 803 ppm Pb on the top. After a thin polish on each side, the measurement increased slightly on the bottom. On the top, the sample had epoxy in the measurement area, diluting the measurement (see next topic for explanation). After 1 mm of material was removed from each side of the 4 mm thick sample, the measurements became closer to each other but had not converged. This shows that contamination levels measured are impacted by surface effects.

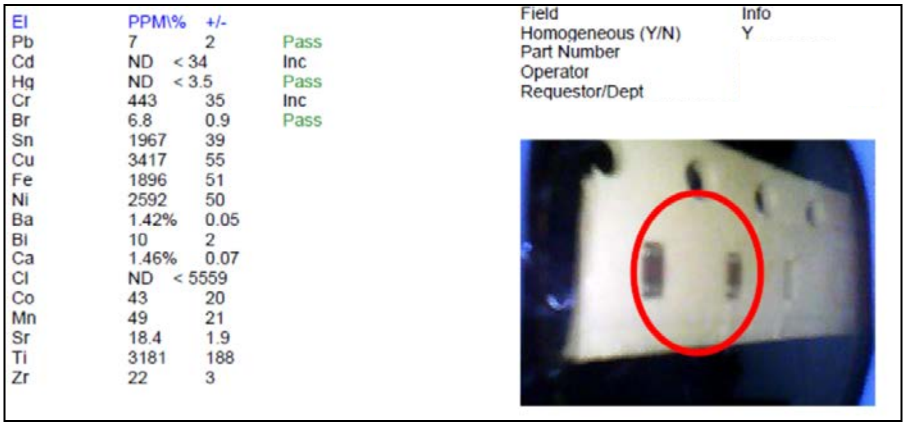
Figure 10: Polished Solder Button

Table 1: Results of Exterior Removal on Sample 117SB

ppm Pb	**Original measurement**	**Thin surface polish**	**~1mm removed from surface**
Top	803	149 (epoxy in analysis area)	988
Bottom	645	789	897

Lessons learned: Cooling of molten solder can affect surface concentrations. Measure both top and bottom of melted samples before making a determination. If possible, slice off the outer layer and measure the internal portion of the sample, reducing the chance of measuring a segregated layer. Measure solder wire without melting it.

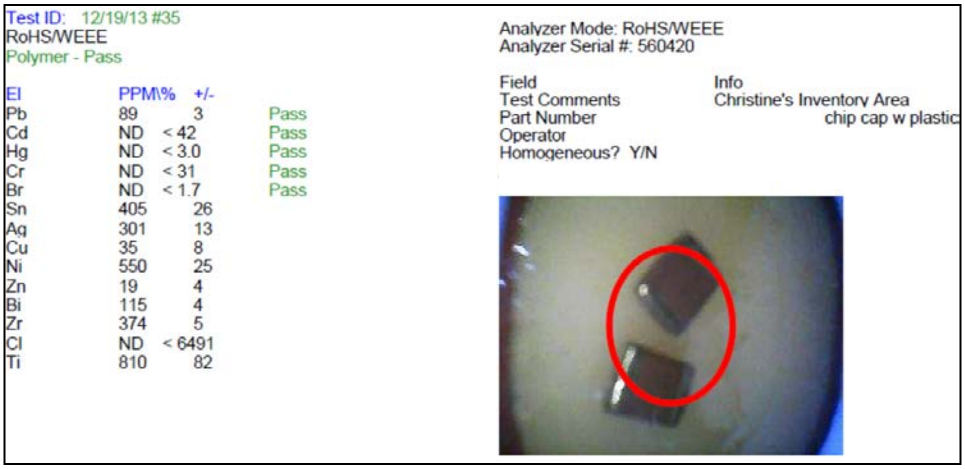
Another circumstance where the Pb measurement is suppressed and may be misinterpreted is when there is extra material in the sample. This dilutes the calculated concentration of Pb. Figure 11 shows a capacitor with a level of Pb well below the maximum concentration level of 1000 ppm. This component is in the carrier tape, however. Figure 12 shows another component with plastic included in the sample window. This measurement is also well below the maximum concentration level for Pb. When the plastic backing is removed from the sample, in Figure 13, the Pb concentration is measured at 1.2% -- well above the limit. While this concentration is allowed per RoHS exemption Annex IV-40, this illustrates the dilution of the Pb reading. Samples should have all packaging and extraneous material removed, and measured without any material within several inches of the sample.



El	PPM\%	+/-	
Pb	7	2	Pass
Cd	ND	< 34	Inc
Hg	ND	< 3.5	Pass
Cr	443	35	Inc
Br	6.8	0.9	Pass
Sn	1967	39	
Cu	3417	55	
Fe	1896	51	
Ni	2592	50	
Ba	1.42%	0.05	
Bi	10	2	
Ca	1.46%	0.07	
Cl	ND	< 5559	
Co	43	20	
Mn	49	21	
Sr	18.4	1.9	
Ti	3181	188	
Zr	22	3	

Field	Info
Homogeneous (Y/N)	Y
Part Number	
Operator	
Requestor/Dept	

Figure 11: Low Pb Reading, 7 ppm, in this Capacitor with Carrier Tape Included in the Sample.



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Test ID:  12/19/13 #35                                  Analyzer Mode: RoHS/WEEE
RoHS/WEEE                                               Analyzer Serial #: 560420
Polymer - Pass
                                                        Field                  Info
El          PPM\%   +/-                                 Test Comments          Christine's Inventory Area
Pb          89       3         Pass                     Part Number                 chip cap w plastic
Cd          ND    < 42         Pass                     Operator
Hg          ND    < 3.0        Pass                     Homogeneous?  Y/N
Cr          ND    < 31         Pass
Br          ND    < 1.7        Pass
Sn          405      26
Ag          301      13
Cu          35       8
Ni          550      25
Zn          19       4
Bi          115      4
Zr          374      5
Cl          ND    < 6491
Ti          810      82
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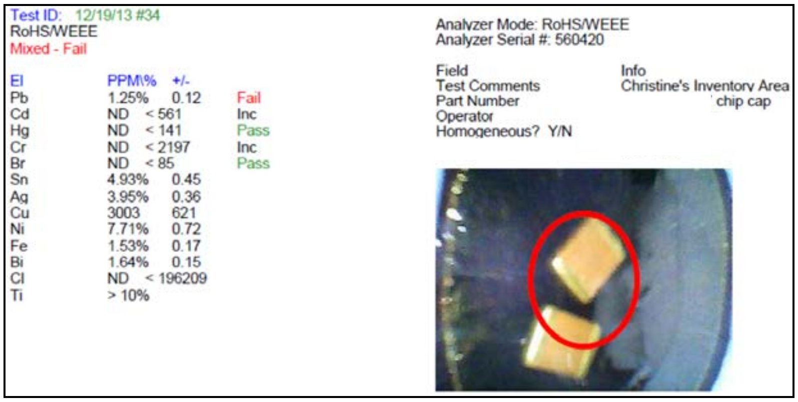
Figure 12: Low Measurement of 89 ppm Pb Would be RoHS Compliant Without Exemptions. This Measurement Includes Plastic Material Behind the Components.



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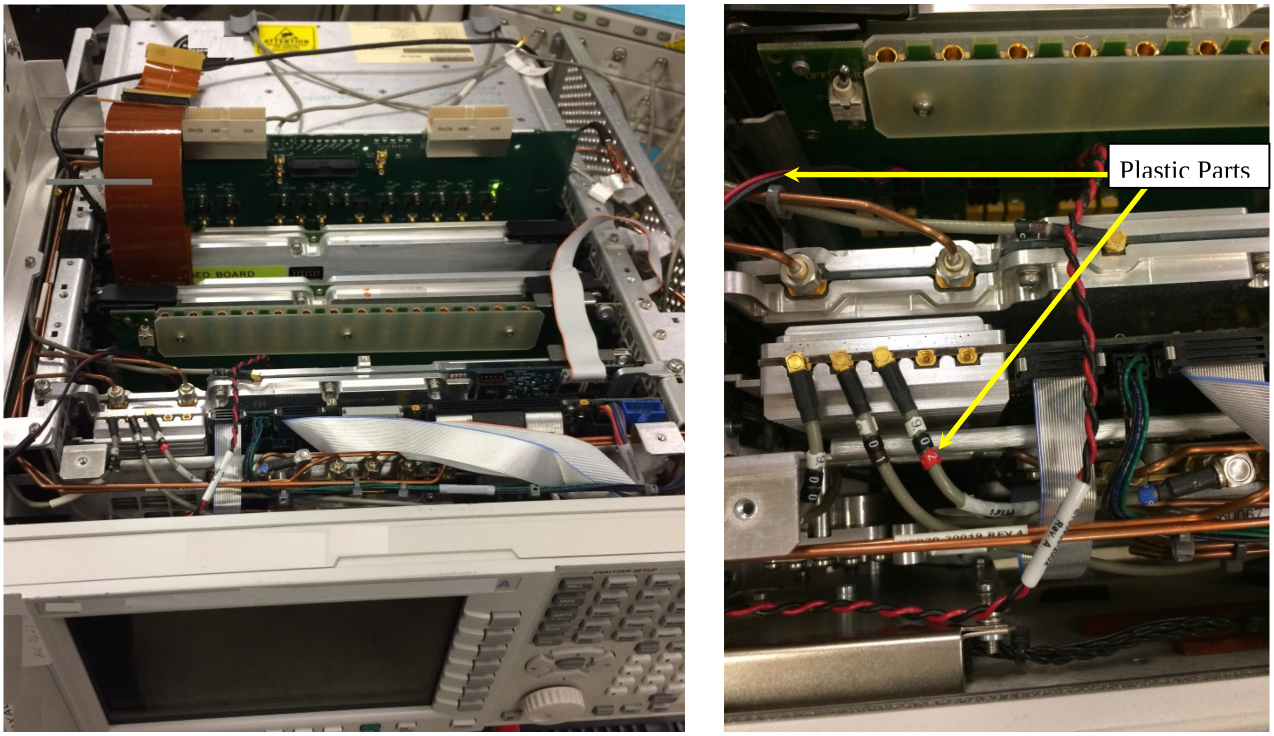
Test ID:  12/19/13 #34                                  Analyzer Mode: RoHS/WEEE
RoHS/WEEE                                               Analyzer Serial #: 560420
Mixed - Fail
                                                        Field                  Info
El          PPM\%   +/-                                 Test Comments          Christine's Inventory Area
Pb          1.25%    0.12      Fail                     Part Number                 chip cap
Cd          ND    < 561        Inc                      Operator
Hg          ND    < 141        Pass                     Homogeneous?  Y/N
Cr          ND    < 2197       Inc
Br          ND    < 85         Pass
Sn          4.93%    0.45
Ag          3.95%    0.36
Cu          3003     621
Ni          7.71%    0.72
Fe          1.53%    0.17
Bi          1.64%    0.15
Cl          ND    < 196209
Ti          > 10%
```

Figure 13: Measurement of 1.25% Pb on the Same Component as in Figure 10 Indicates Either a Non-compliant Component or a Component with an Allowed Exemption for Pb in Capacitors.

Lesson learned: Remove extra material from the sample analysis area. Have only the sample and an x-ray neutral holder in the analysis window.

Beware the Plastic Parts

In a complex product, as in Figure 14, with thousands of parts and part numbers, complex printed circuit assemblies and microcircuits, common and specialty cables, the most frequent source of restricted substances are the plastic jackets on wires, the colorful clips that identify the cables, and the protective covers for sensitive external connectors.



14a 14b

Figure 14: a) Example Test and Measurement Product (in this case used as a test bed), Showing Multiple Printed Circuit Assemblies and Cable Types.
b) Close-up View of Product Interior. Restricted Substances Have Been Found in Cable Markers and Plastic Coatings on Wire

The plastic contains pigment to give the needed colors, and these pigments may contain Cd or Pb. Yellow and red – and colors that contain these pigments, such as orange, green and purple – are most likely to contain Cd. Plasticizers may contain Pb and can be found with any color. When recycled plastic is used, this may contain these substances. Examples of plastic cable markers and the protective rubber caps that are similar to those used on external connectors on the final product are shown in Figure 15. XRF measurements of these items are shown in Figures 16 and 17. Molded plastic housings are another potential source for Cd and Pb.

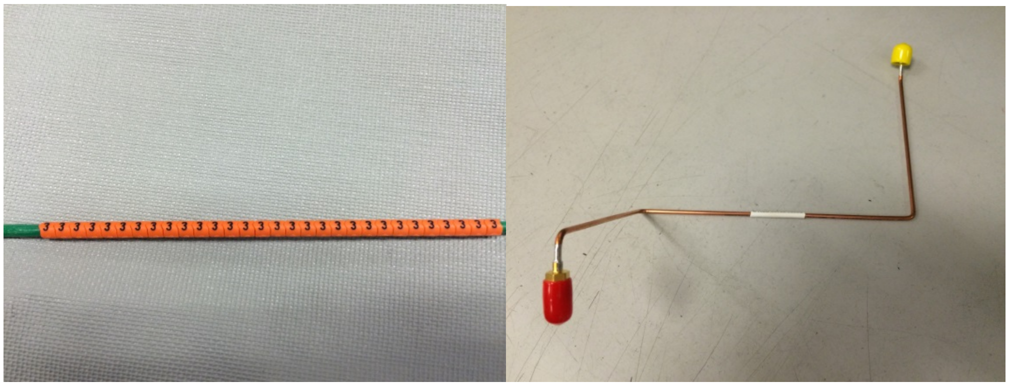
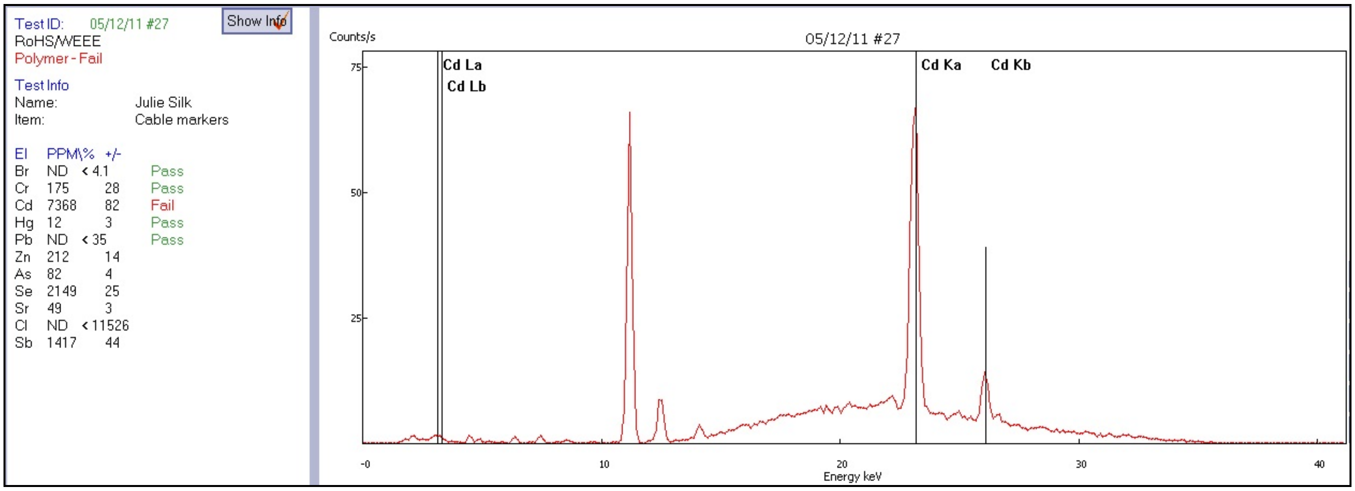


Figure 15: Plastic Cable Markers, RF Cable with Protective Rubber Caps



Test ID: 05/12/11 #27
RoHS/WEEE
Polymer - Fail

Test Info
Name: Julie Silk
Item: Cable markers

El	PPM\%	+/-	
Br	ND	< 4.1	Pass
Cr	175	28	Pass
Cd	7368	82	Fail
Hg	12	3	Pass
Pb	ND	< 35	Pass
Zn	212	14	
As	82	4	
Se	2149	25	
Sr	49	3	
Cl	ND	< 11526	
Sb	1417	44	

Figure 16: Results showing Cd in Markers Used to Identify Cables.

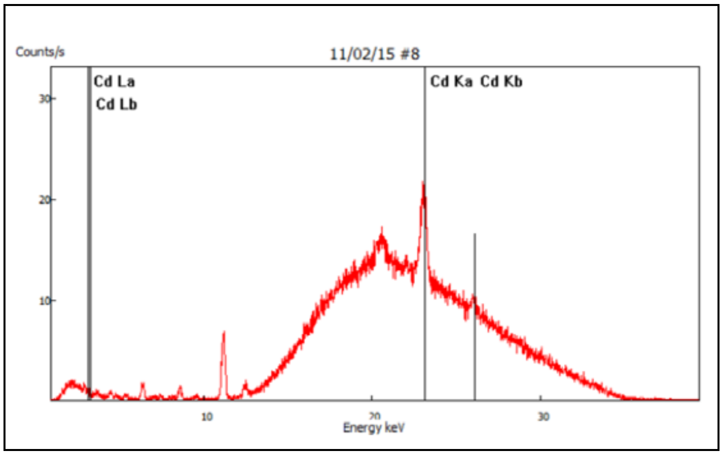


Figure 17: Results Showing Cd in Red Rubber Cap Used as a Protective Cover for Connectors

Lesson learned: Pay attention to the seemingly insignificant parts that are part of the final product. Plastic parts have pigments, additives, plasticizers and perhaps recycled material that can contain restricted substances.

Helpful Techniques

Measurement of soldering or rework stations is an important part of the continued compliance assessment in production areas. Borrowing a production soldering iron tip to use for troubleshooting at an engineer's bench where SnPb solder was still being used, was a frequent cause of rework station contamination early in our transition to RoHS compliance. Evidence of contamination can be found on the soldering iron tips and in debris under the tip-cleaning sponge or on the work surface. The tip of a soldering iron is difficult to measure due to the curved geometry and length of the tip. The XRF gun works best when the sample is flat and dead center perpendicular to the aperture of the XRF. The preferred alignment is impossible with the solder iron tip in the test stand, and it is very difficult to get the tip in the center, or keep it there when the test stand lid is closed.

A technique involving analysis of solder drops run off from tips, Figure 18, was found to give consistent and useful indications of solder type used. Test data shows that solder drop test samples can reliably indicate previous use of tin-lead solder prior to the test by picking up residual Pb from impervious surfaces.

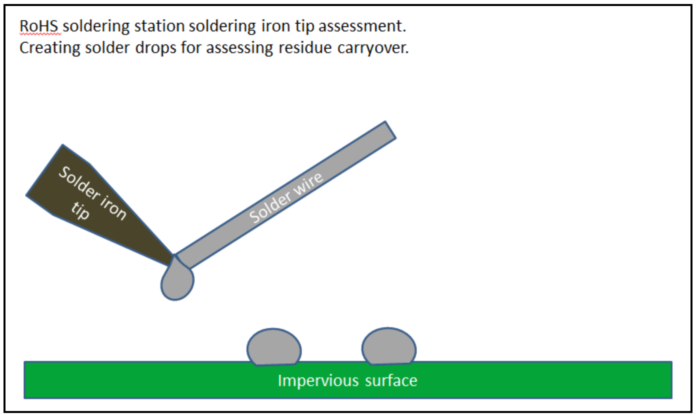


Figure 18: Creating Solder Drops

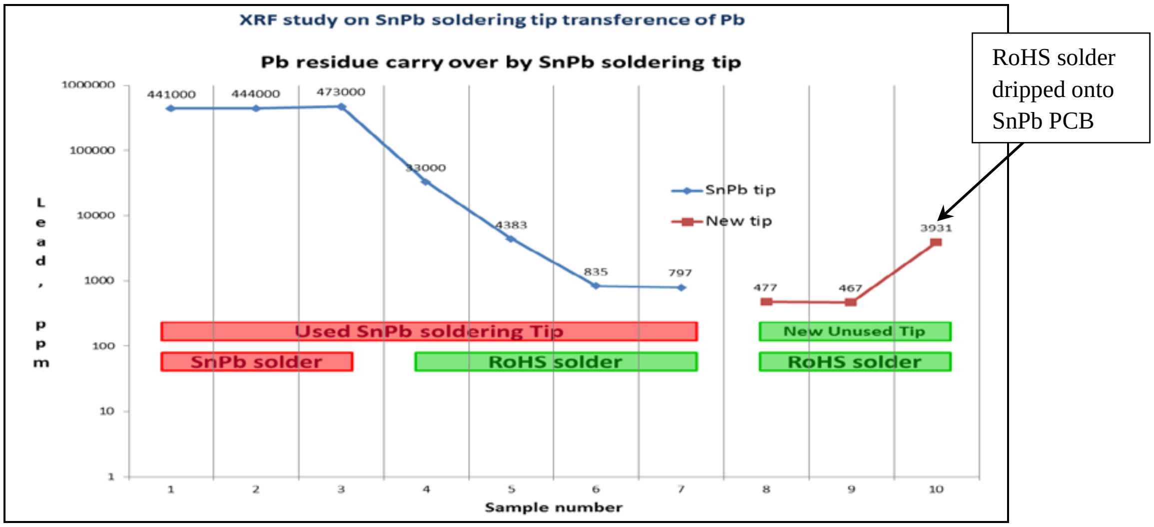
For example, to verify if a manual soldering station has been using SnPb solder, solder drops created with Pb-free solder melted and run off the soldering tip may be quickly analyzed and conclusions drawn without having to shut down the station and cool off the soldering iron for analysis. If indeed SnPb solder had been used just prior to the test, sufficient Pb residue will be present within the Pb-free solder drop to register an unmistakable Pb peak within the XRF spectrum. The Sn:Pb and Sn:Ag ratio provides some indication on the extent of SnPb solder as part of the makeup of the sample and by inference the degree of SnPb contamination. For example, an increasing or stable Sn:Pb ratio over time could be indicative of continued compliance to Pb free process control whereas a decreasing Sn:Pb ratio could be indicative of surreptitious use of SnPb solder and lapses in process control. Ag:Sn ratio of SAC solder tends toward the expected range of 3-4% and provides reliable indication of the presence of SAC solder as well as baseline value for quantifying SnPb. Sn:Pb ratios are also useful indicators in cases involving extraneous material, such as components in carrier tapes. Even through absolute Pb concentrations measured may be well below the 1000 ppm threshold, Sn:Pb ratios of 4:1 or lower may be indicative of Sn:Pb solder masked by the presence of the extraneous material to give a lower average Pb concentration.

Solder drops also provide useful insight into the effects of running fresh solder over SnPb contaminated solder tips, as illustrated in Figure 19. As an aside to verifying the presence of Pb, test results show that residual Pb diminishes almost exponentially when soldering iron used with SnPb were subsequently switched to Pb-free solder without any cleaning of the soldering iron tip in between the switching of solder material. Generally, residual Pb in solder drops obtained from tips subjected to prior use of SnPb drops off to well below the 1000 ppm limit by the 3rd subsequent solder drop after switching to Pb-free solder. This does not imply efficacy in cleansing or diluting off Pb from used soldering tip by running Pb-free solder over it a couple of times, but rather demonstrates the transient concentration of residual Pb and the risks of contaminating subsequent solder joints in the event of suspected isolated SnPb use.

Tests were also carried out whereby a SAC305 solder drop was

a) dripped onto SnPb reflowed PCB surface
b) dripped over a small detached piece of SnPb finished chip termination

Upon XRF analysis, both samples showed the presence of Pb, demonstrating the sensitivity of the method towards detecting fugitive and residual Pb from SnPb processes.

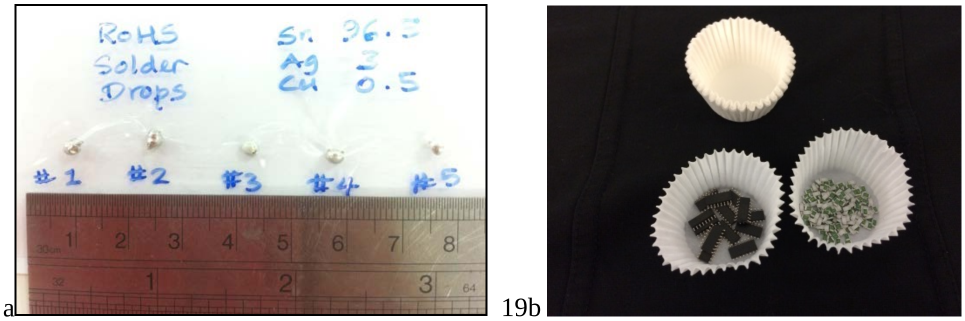


RoHS solder dripped onto SnPb PCB

Figure 19: Results of Solder Drop Study: Dilution of SnPb with RoHS Solder, Contamination of RoHS Tip with SnPb on PCB.

Direct measurements on a printed circuit assembly (PCA) are made difficult by the presence of components. It is often not practical to measure the termination finish on a component that is soldered on a board, for instance, as it is impossible to get the sample or area of interest near enough to the XRF measurement window on an densely packed assembly. Through-hole component leads and sharp edges are particularly risky as they can puncture the protective membrane covering the XRF aperture. The area of analysis is also rather large compared to the items or areas of interest; anything within the 10mm diameter measurement area will be analyzed and elemental compositions amalgamated by element. Collimators may be helpful to focus the beam into a tight spot at the expense of reduced measurement signal strength. Components can be clipped off the board and measured, or better yet measured before loading. To measure the type of solder used for each process, it is best to use a location where solder is applied but there are no components. For instance, a location where a surface mount component is located but not loaded will contain solder from the paste applied in the stencil process. A soldered bottom-side test pad is a good indicator of the alloy used in the wave solder process. In these tests, the analyzer will typically need to be used outside the test stand, so additional safety precautions are necessary. The other factor in measuring on a printed circuit assembly is the spot size and depth of the XRF measurement. The reading will show the restricted substance averaged out over all the material in the measurement window to a depth well beyond the metallization layers. An indication of the solder alloy used can be calculated by the ratio of tin to other metals. Typically used SAC305 solder will show a ratio of tin to silver of ~30:1. Eutectic tin-lead will show a ratio of about 2 parts tin to 1 part lead.

While specialized sample containers can be purchased to hold small items, the important criteria are invisibility to the XRF and flatness to the sample window. Recent use of SnPb solder at workstations can be identified using cellophane tape application over the test area to pick up loose debris and directly analyzing these. Even tiny specks barely visible to unaided vision will turn up clearly in the resultant spectrum. Cellophane or ESD-safe polyimide tape is also useful for holding debris from under the sponge used to clean tips and other small parts, and allow easy maneuvering of the sample and target area to align with the ideal XRF focal point. When the parts will be used after testing, the paper liners used for mini-cupcakes work great to hold the sample. These liners are invisible to x-rays and also protect the XRF window from damage from sharp components. The downside is that the sample cannot be seen in the image. New holders should be tested with a known or assayed sample with and without the holder to identify any effect.



19 a

19b

Figure 19. a) Solder Drops Held in Place with Cellophane Tape for XRF Analysis; b) Paper Mini-cupcake Liners

Summary and Conclusions

A handheld XRF analyzer can provide sufficient accuracy and information to expediently evaluate materials, parts, components and even solder joints for compliance or violation of EU RoHS substance restrictions. The data requires perspective and experiential judgment to circumvent misinterpretation of measurement artifacts and unrealistic expectations that could easily lead to unnecessary expenditure of effort based on erroneous conclusions. We offer the following guidance for interpretation of XRF measurements:

- Always verify that peaks for both characteristic x-rays of the element shell are present. If one of the element's characteristic x-ray energy level does not correlate with a peak in the spectrum -- either the peak is missing or off center -- it is likely that the element is not actually present.
- Cooling of molten solder can affect surface concentrations. Measure both top and bottom of melted samples. If possible, slice off the outer layer and measure the internal portion of the sample, reducing the chance of measuring a segregated layer.
- It is not necessary to melt solder wire to get a good measurement.
- Remove extra material from the sample whenever possible and use only the sample and an x-ray neutral holder in the analysis window.
- If this is not possible, use material dissection to the homogeneous material or engineering judgment
- Pay attention to seemingly insignificant parts. Plastic parts have pigments, additives, plasticizers and perhaps recycled material that can contain restricted substances.
- To assess soldering or rework stations or associated processes for contamination, measure solder drops from the soldering iron tips, debris from work surfaces, soldering iron tip holders.
- Sample holders such as cellophane, ESD-safe polyimide tape and mini-cupcake liners provide good mounting surfaces for small items and allow easy maneuvering of the sample within the test stand.

Acknowledgements

Dillon McDowell, Ted Shields and Mary Wu of Olympus-OSSA provided contributions on basic XRF measurement and the science behind mistaken identity of elements.
Tom Kaminska and Randall Spagnola of Keysight Technologies provided input and review.
The entire Keysight Technologies (and previously Agilent Technologies) XRF users group contributed over the years.
Michelle Curtis of CDI Corporation provided solder button surface removal and analysis.
Karen Miles of Materials & Processes Solutions provided the solder button vertical cross-section and analysis

References

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RoHS Substance Measurements in Complex Products

Julie Silk

Soon-Tatt Cheah

Keysight Technologies

Contents

- Industrial Monitoring and Control Products
- X-ray Fluorescence (XRF) Measurements
- Examples and Guidance
  - Mistaken Identity
  - Missing Lead
  - Surprising Culprits
  - Soldering and Rework Station Measurements
  - Cheap and Easy Sample Holders

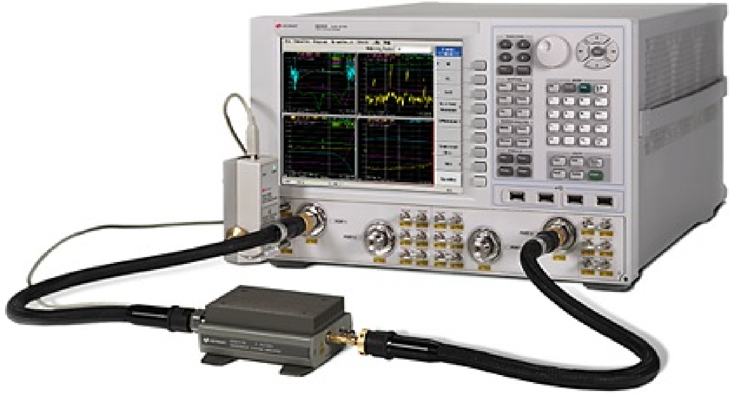
EU RoHS

- The European Union's Restriction of Hazardous Substances directive of 2011 put test and measurement equipment in scope, with an effective date of July 22, 2017.
  - Test equipment is EU RoHS category 9 Industrial Monitoring and Control equipment
- EU RoHS restricts 6 substances (so far) to a maximum concentration level in homogeneous substances:

Pb: Lead to 1000 ppm
Hg: Mercury to 1000 ppm
Cd: Cadmium to 100 ppm
Cr: Hexavalent chromium to 1000 ppm
PBB and PBDE: water-soluble brominated flame retardants to 1000 ppm

Test Equipment: It’s Complicated

- Products are complex, with many different part numbers and part types. The products have a long production life.
- The company has thousands of products converted. Some were originally designed in the 1980’s.
- The company had extra time to convert because of this complexity and the expectation for high reliability.

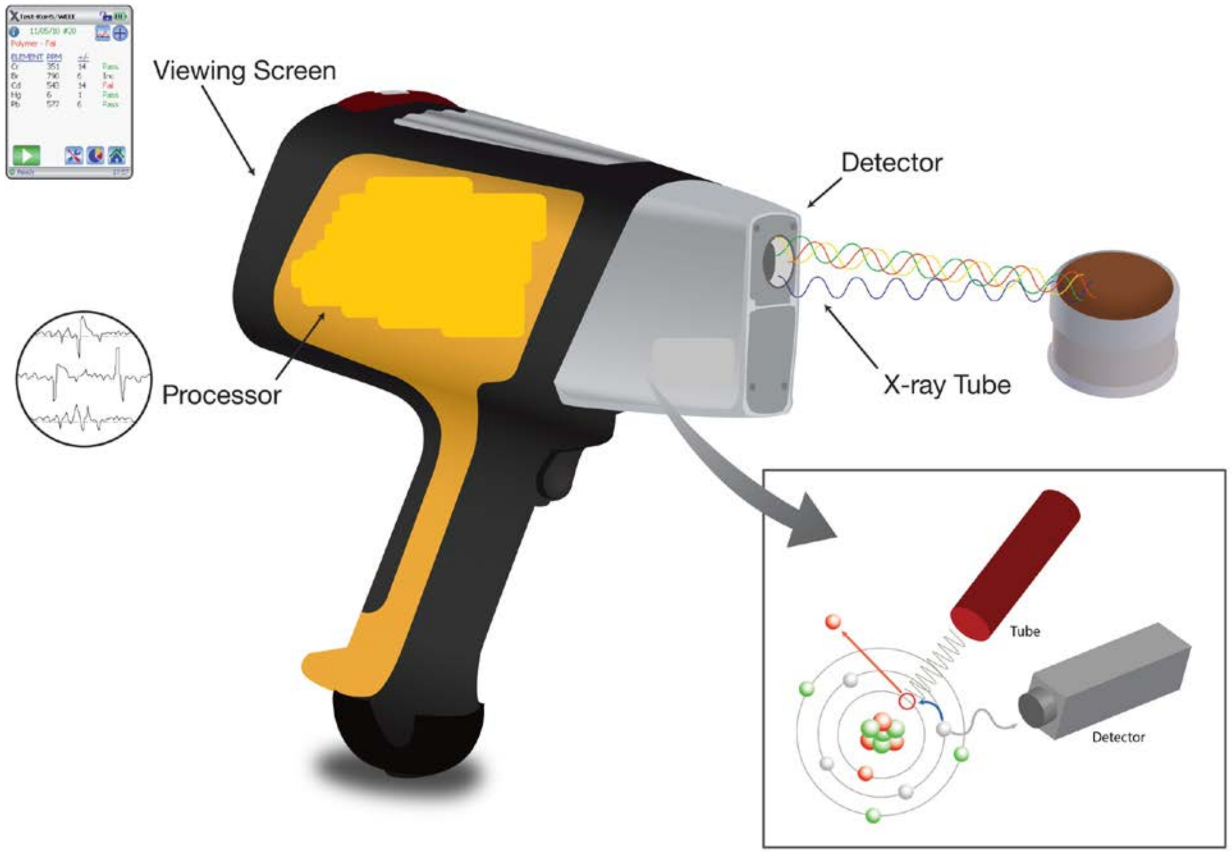


RoHS Substances Measurable with XRF

- Handheld X-Ray Fluorescence (HHXRF or XRF) works best for measuring Pb, Hg and Cd of the RoHS substances.
- Bromine is in unrestricted compounds, and the XRF cannot distinguish these.
- Chromium is also present in unrestricted forms, such as metallic and trivalent chromium.
- Other techniques are expensive (ICP-OES) or inaccurate (consumer Lead swabs)

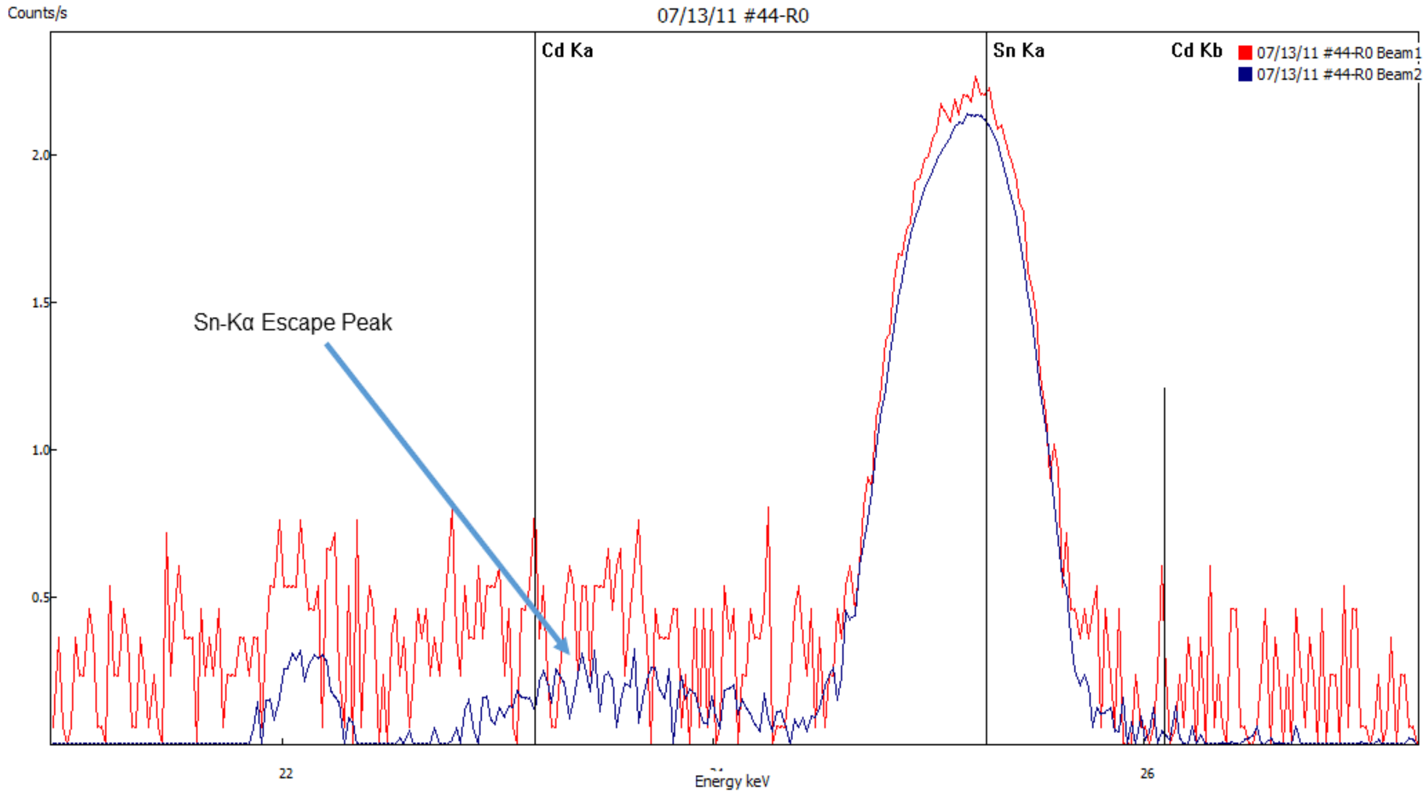
XRF Basics

- When an x-ray with the right energy hits the sample, an electron is removed from an inner shell. Each atom will produce characteristic x-rays as this vacancy is filled.
- The element can be identified and concentration calculated.
- Accuracy is in the range of +/- 30%



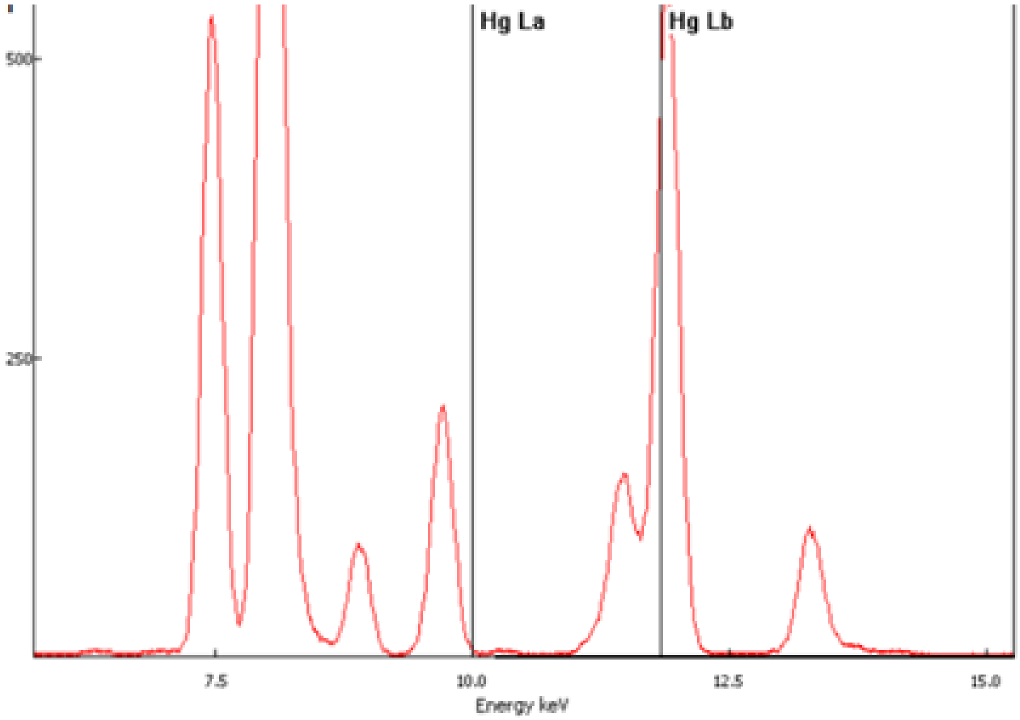
Misidentification: Escape Peaks

- Escape Peaks are a known artifact from the excitation of Si in the detector. The detector records the difference between the expected energy and the created Si x-ray
- They can be misidentified as a different element
- In this example, the Tin K-alpha (Ka or K_α) escape peak was identified as Cd with a measurement of 900 ppm



Misidentification: Overlap

- Hg has characteristic energy levels that partially overlap Au peaks
- Hg was measured at 2100 ppm in this gold-plated example.
- Peaks must be found at both energy levels to confirm presence Without this correlation, we conclude no Hg is present.
- This was confirmed with ICP-OES.

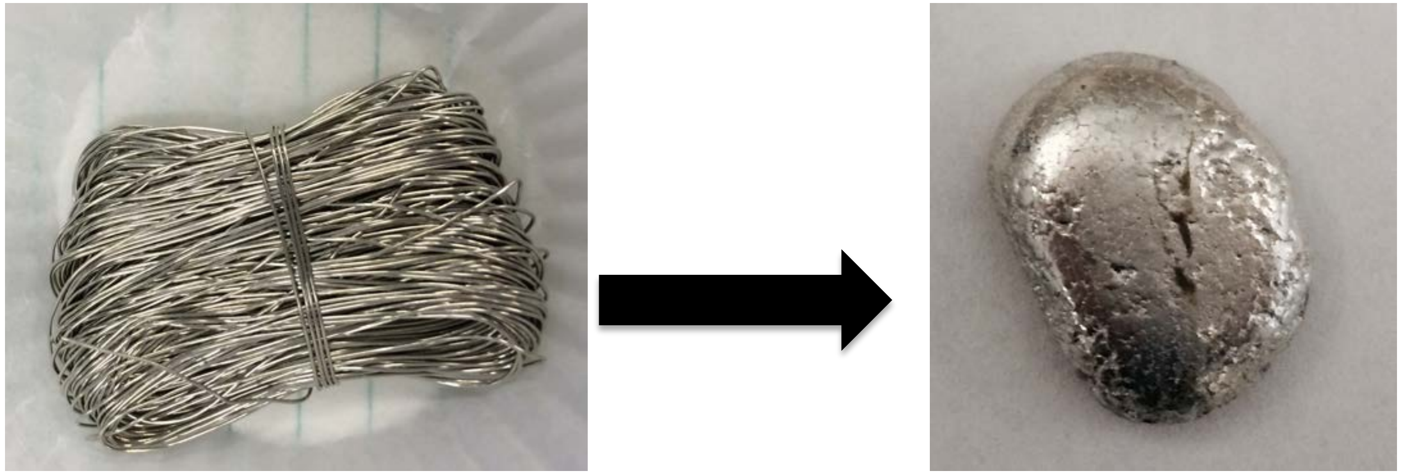


Lesson learned

- Always verify that peaks for both characteristic x-rays of the element shell are present.
- If one of the element’s characteristic x-ray energy levels does not correlate with a peak in the spectrum -- the peak is missing or off center -- it is likely that the element is not actually present.

Solder Measurements

- The perfect XRF sample is homogeneous, flat and “infinitely” thick.
- “Pb-free” SAC305 solder typically contains ~400 ppm Pb. Spec is 700 ppm max.
- Melted solder paste or a sample from a solder pot has a flat bottom.
- Solder wire bundles are not flat. If melted, the measurement would be more consistent and accurate. ... we thought

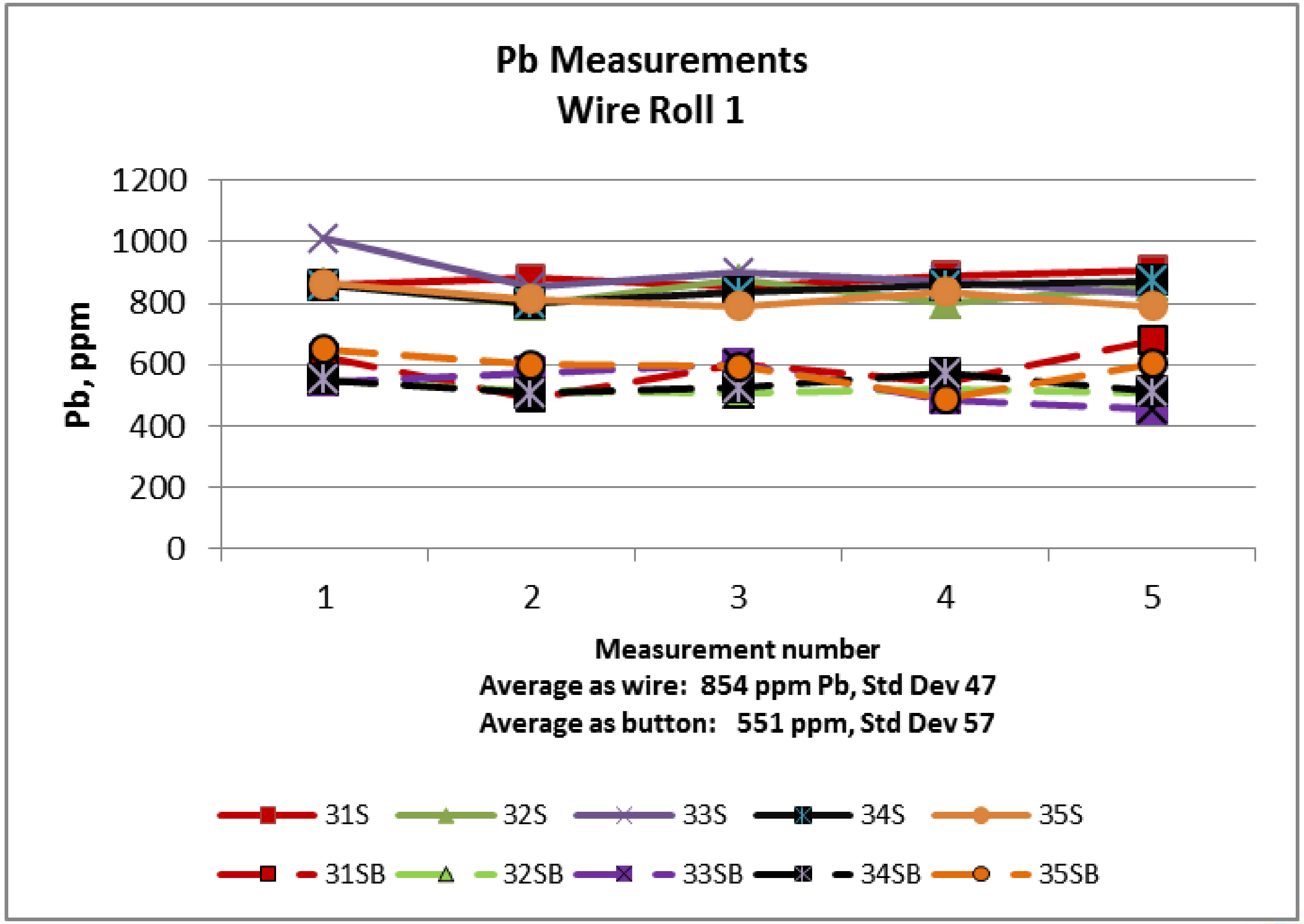


Missing Lead

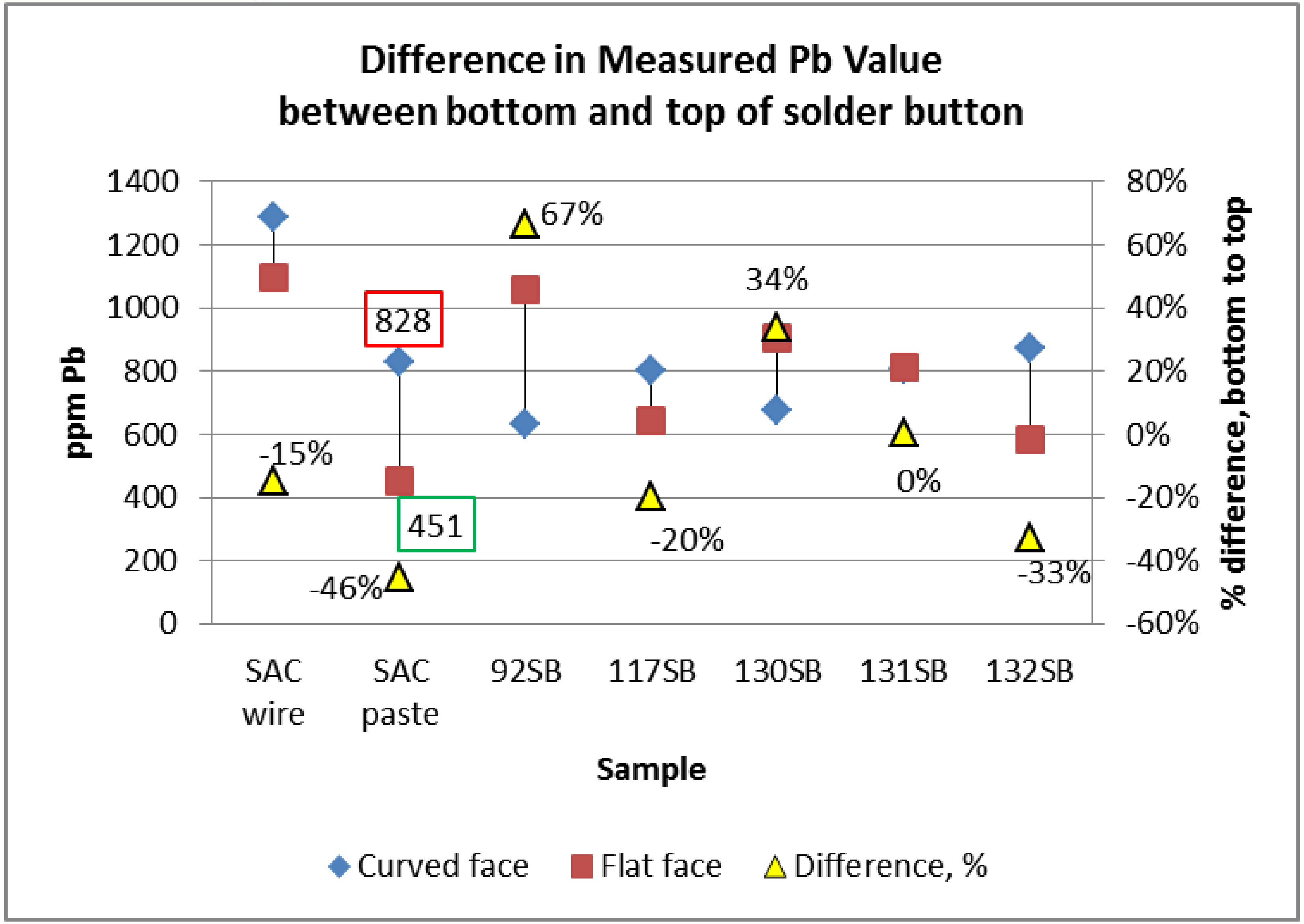
- Pb measurement dropped from 854 ppm on the wire to 551 ppm for the solder “buttons”
- Why?

Note: this is a known high-Pb SAC305 sample with 980 ppm Pb assay.

A similar result is found on samples with Pb in the typical 400 ppm range.



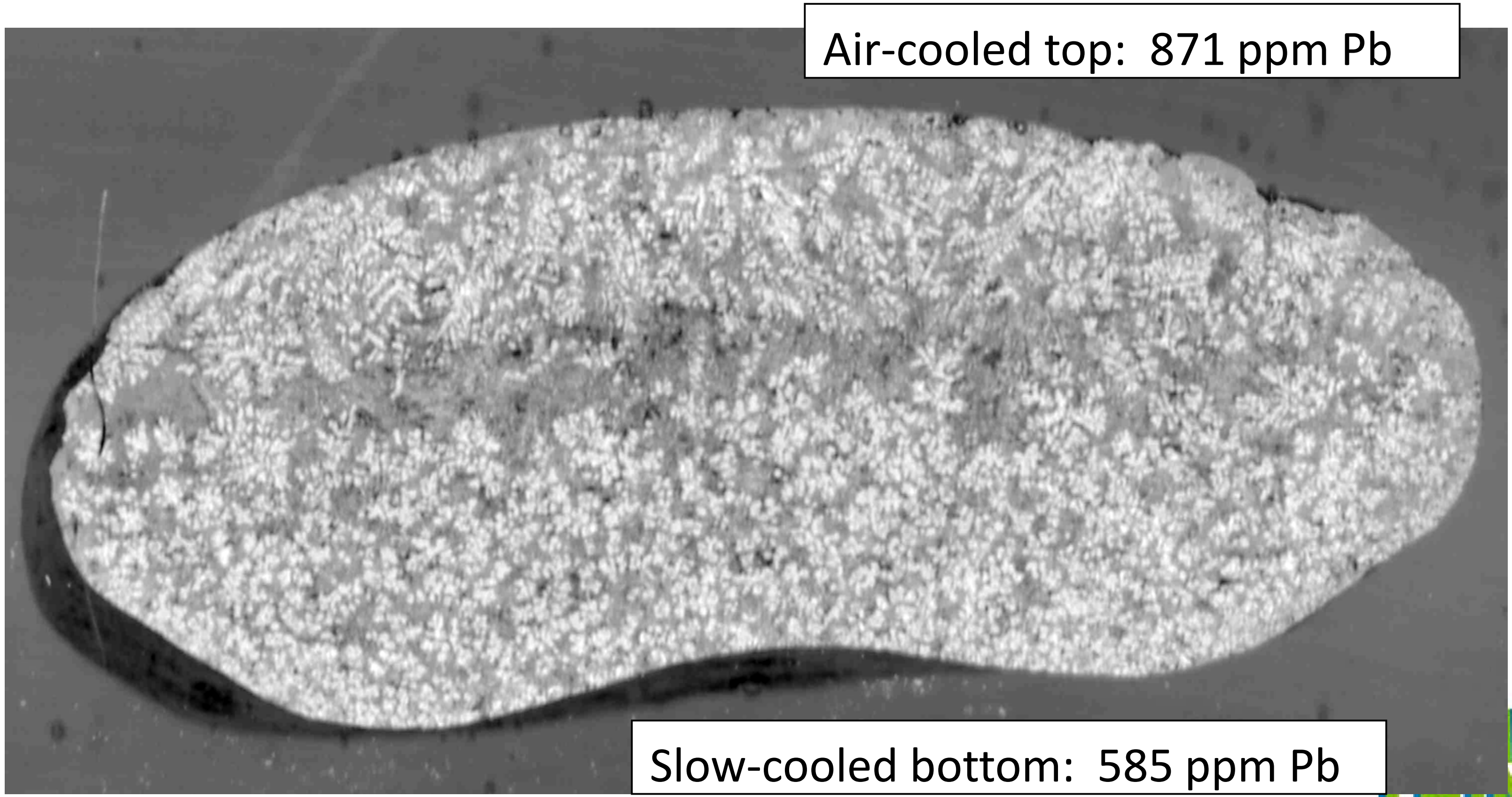
Solder Button: Top versus Bottom



- There was a wide variation in top versus bottom measurements in samples
- We suspect Sn segregation at the slow-cooled surfaces
- For a sample of melted SAC paste, the bottomside measurement is ok at below 500 ppm, the topside at over 800 ppm could be over the limit

Vertical Cross-section

- Microstructure did not show obvious differences in Sn concentration top to bottom
- Pb concentration is too low for EDS mapping



Air-cooled top: 871 ppm Pb

Slow-cooled bottom: 585 ppm Pb

Removal of Outer Surface

- On a solder button that showed a difference between top and bottom Pb measurement, the outer surfaces were polished until 1 mm of material was removed from each side.
- Note the change in Pb measurement, indicating the impact of surface effects on the contamination reading. Note: wire bundle measured 800 ppm with HHXRF, with assay of 980 ppm.

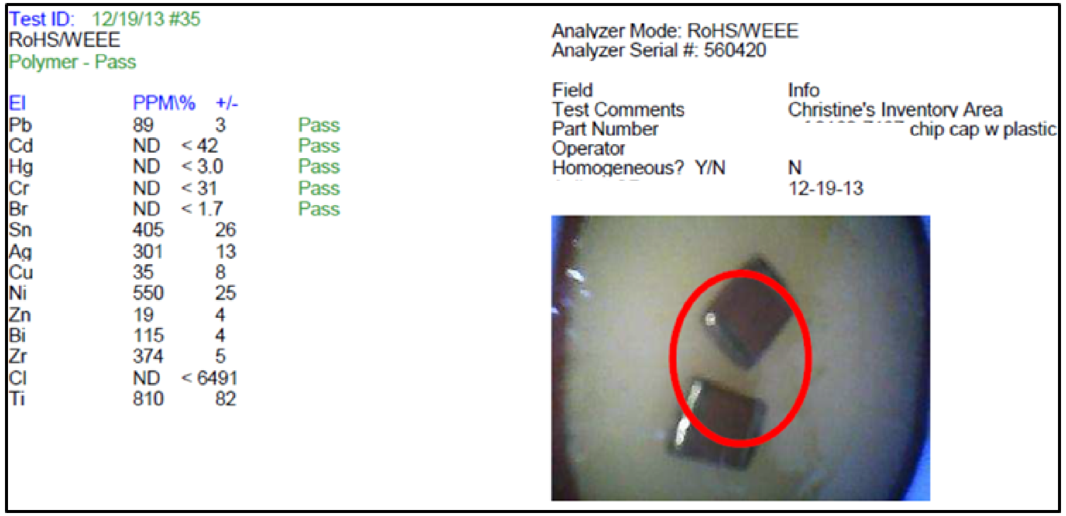
ppm Pb	Original measurement	Thin surface polish	~1mm removed from surface
Top	803	149 (epoxy in analysis area)	988
Bottom	645	789	897

Lesson learned

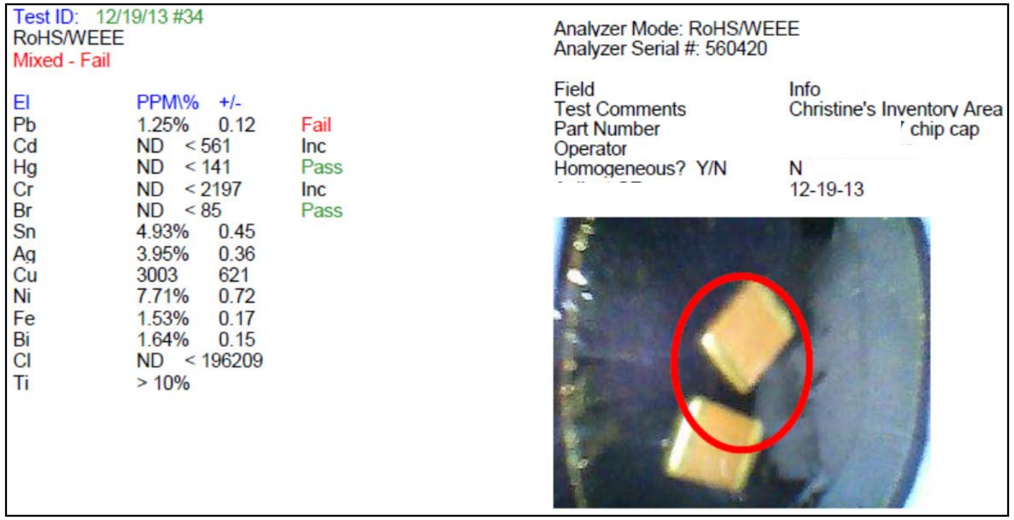
- Measure both top and bottom of melted samples. If possible, slice off the outer layer and measure the internal portion of the sample, reducing the chance of measuring a segregated layer.
- To measure solder wire, there is no need to melt it

Pb Dilution

- The XRF measures all material in the window and to a depth dependent on the material
- When extraneous materials are in the analysis area, the measurement will be diluted by this material.



```
Test ID:   12/19/13 #35                         Analyzer Mode: RoHS/WEEE
RoHS/WEEE                                       Analyzer Serial #: 560420
Polymer - Pass
                                                Field                  Info
El          PPM\%   +/-                         Test Comments          Christine's Inventory Area
Pb          89         3        Pass            Part Number            [redacted] chip cap w plastic
Cd          ND    < 42          Pass            Operator
Hg          ND    < 3.0         Pass            Homogeneous?  Y/N      N
Cr          ND    < 31          Pass            [redacted]             12-19-13
Br          ND    < 1.7         Pass
Sn          405       26
Ag          301       13
Cu          35         8
Ni          550       25
Zn          19         4
Bi          115        4
Zr          374        5
Cl          ND    < 6491
Ti          810       82
```



```
Test ID:   12/19/13 #34                         Analyzer Mode: RoHS/WEEE
RoHS/WEEE                                       Analyzer Serial #: 560420
Mixed - Fail
                                                Field                  Info
El          PPM\%   +/-                         Test Comments          Christine's Inventory Area
Pb          1.25%    0.12       Fail            Part Number            [redacted] chip cap
Cd          ND    < 561         Inc             Operator
Hg          ND    < 141         Pass            Homogeneous?  Y/N      N
Cr          ND    < 2197        Inc             [redacted]             12-19-13
Br          ND    < 85          Pass
Sn          4.93%    0.45
Ag          3.95%    0.36
Cu          3003     621
Ni          7.71%    0.72
Fe          1.53%    0.17
Bi          1.64%    0.15
Cl          ND    < 196209
Ti          > 10%
```

Parts with plastic similar to carrier tape behind them
89 ppm Pb: looks great!

Parts without extra material
1.25% Pb: not great!

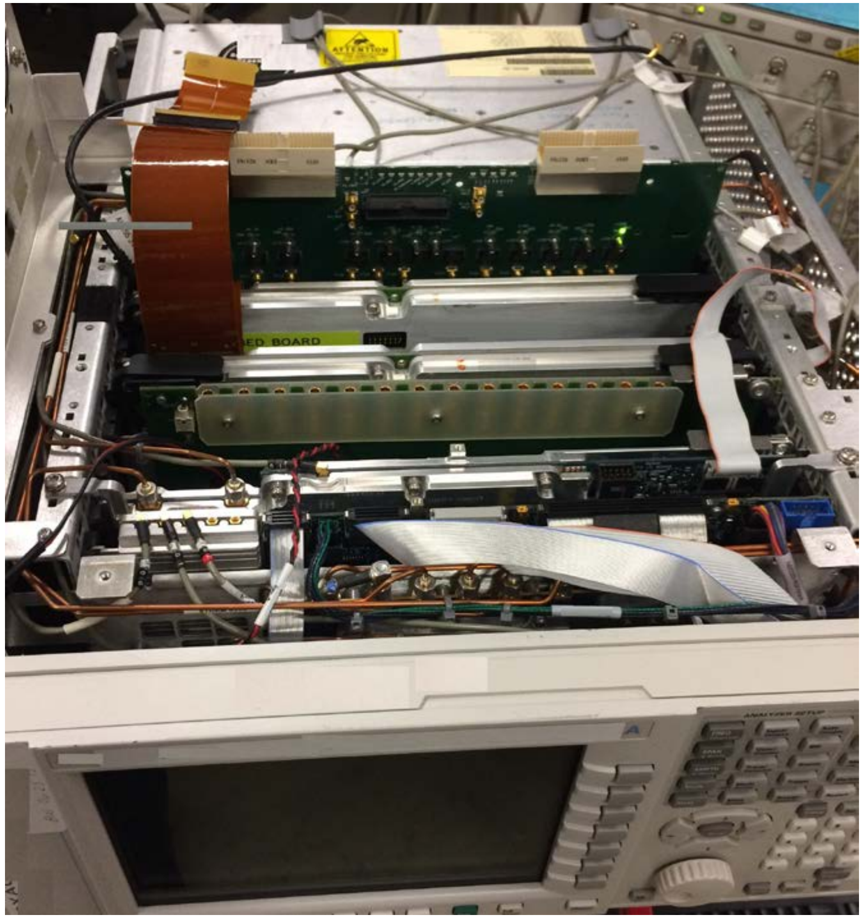
Note: these parts are acceptable per
RoHS Exemption Annex IV-40

Lesson learned

- Remove extra material from the sample analysis area whenever possible and use only the sample and an x-ray neutral holder in the analysis window.
- If this is not possible, use material dissection to the homogeneous material or engineering judgment

In Complex Products

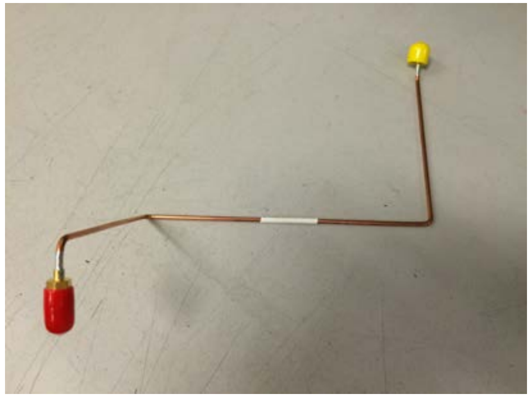
- An example test and measurement product shows the complexity inside. Many PCAs, lots of cables. Specialty parts for high precision and microwave frequencies.
- Which of these part types give us the most trouble?

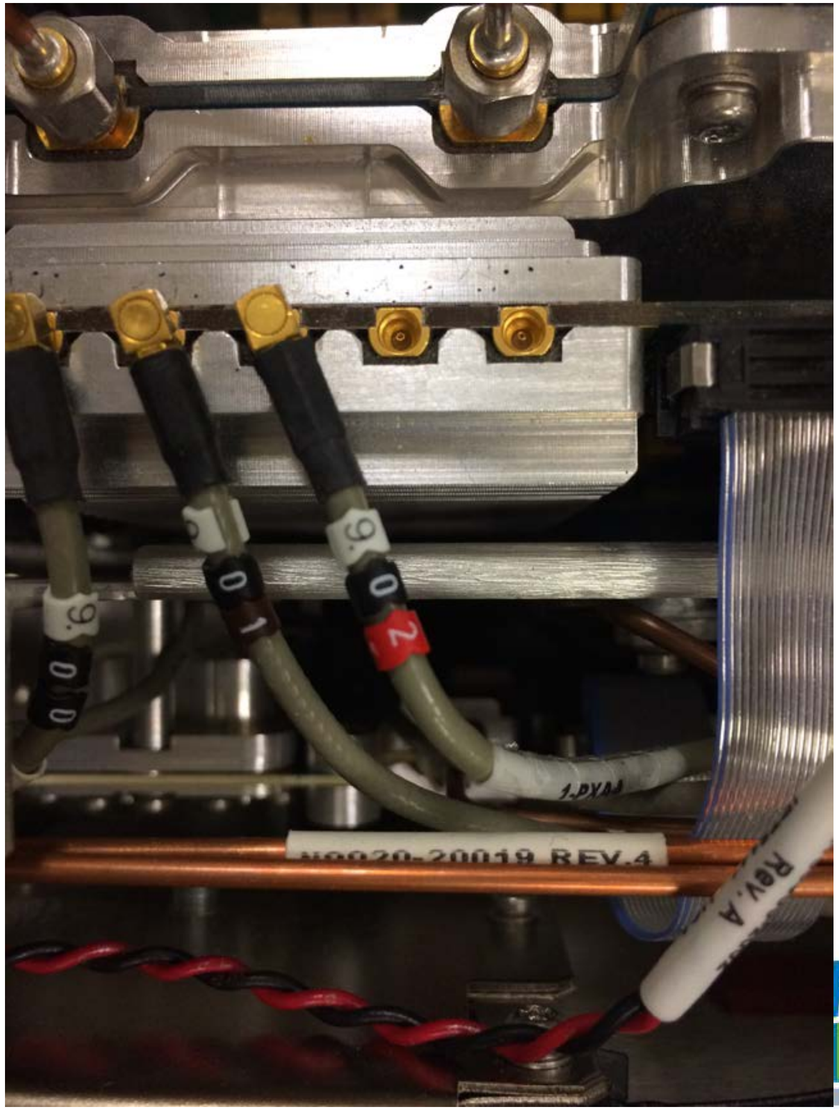


The Trivial Parts Can Bite You

Plastics: Cd in red and yellow pigment, Pb in plasticizers, contaminated recycled plastic found in low-tech parts:

- coatings on wires
- molded housings
- rubber covers for connectors
- cable markers





Lesson learned

- Pay attention to seemingly insignificant parts. Plastic parts have pigments, additives, plasticizers and perhaps recycled material that can contain restricted substances.

Solder / Rework Station Assessment

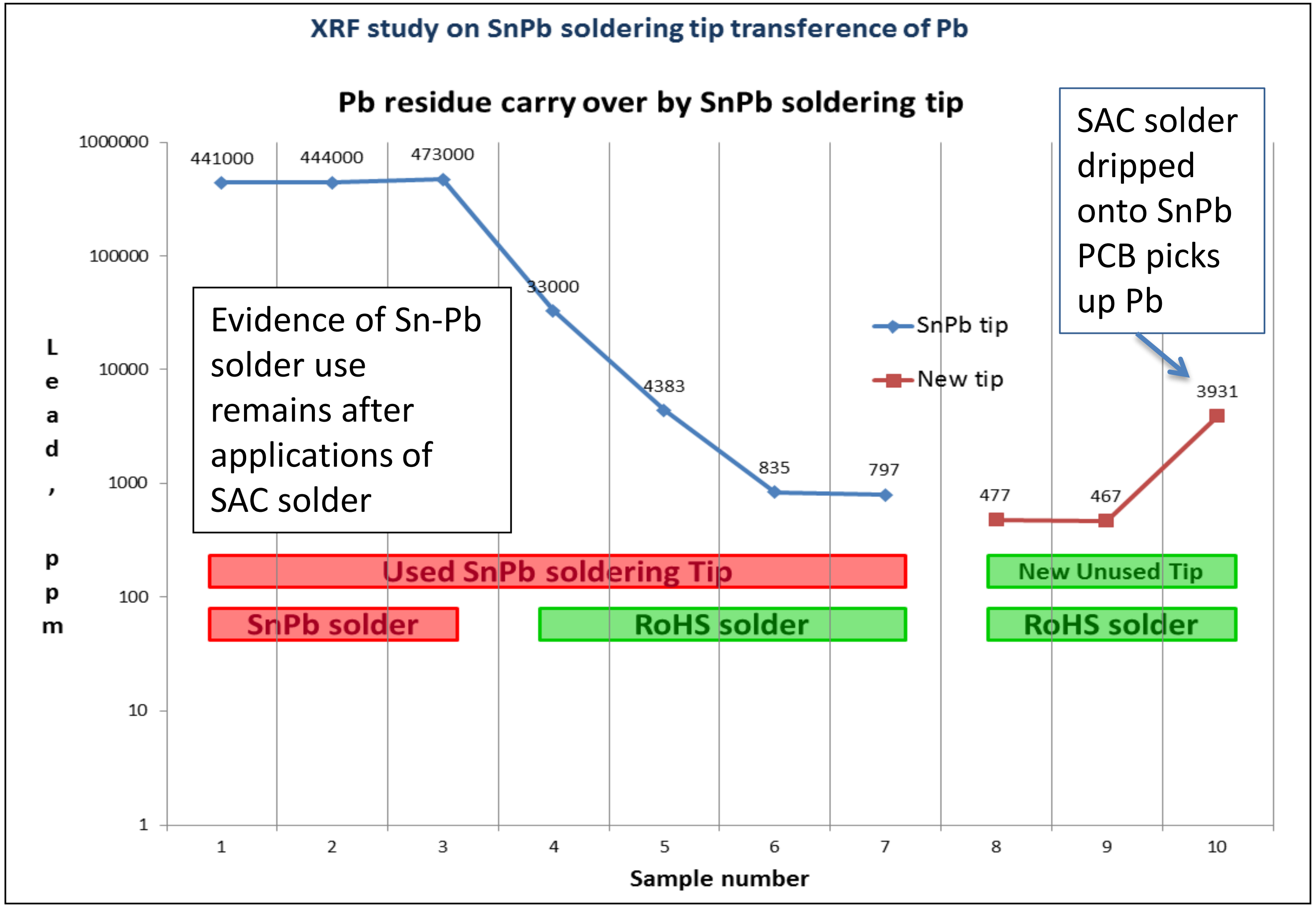
Cross-contamination at rework stations was a big issue early in our transition. Assessment at the solder station involves measuring

- Solder tips via solder drops
- Debris from the bench or soldering iron holder
- Tin-Lead ratio analysis of mixed materials

Solder Station Debris

- Because of our long transition and long-life older products, we have a mix of solder requirements.
- Pb-free solder and rework stations should be segregated from SnPb rework stations.
- Debris on the solder station work surface or in the solder iron holder are good locations to find evidence of cross-contamination.

Solder Drops



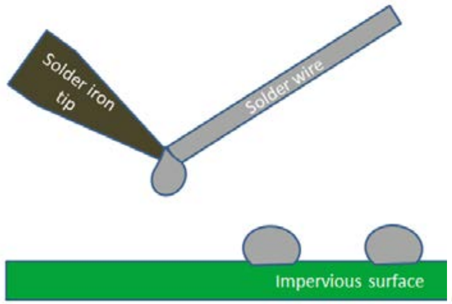
XRF study on SnPb soldering tip transference of Pb

Pb residue carry over by SnPb soldering tip

Evidence of Sn-Pb solder use remains after applications of SAC solder

SAC solder dripped onto SnPb PCB picks up Pb

- Soldering iron tips are difficult to measure in the test stand used for increased safety.
- Creating solder drops to measure contamination works well.



Tin-Lead Ratio

- In a sample with lots of extra material in addition to the item you want to measure, such as a printed circuit board or assembly, an indication of the solder type used can be determined using the ratio of elements in the solder:
  - SAC solder is ~30:1 Sn to Ag, with Pb in the ppm range. If this ratio exists, and without other sources of either element, the solder used was likely Pb-free.
  - Eutectic Sn-Pb solder has a ratio of ~2:1 Sn to Pb. Example:
    When Pb measures 1%, if the Sn is around 2%, Sn-Pb was used. With other materials contributing, this ratio can range quite widely and still indicate Sn-Pb in one of the plating layers.

Sample containment

- Specialized containers can be purchased for holding small samples
- Cellophane or ESD-safe polyimide tape can easily and securely capture these small items. It's nearly free, easy to maneuver in the test stand and convenient to (properly) dispose of when done.
- Paper liners can be used to hold parts that will be used later.

Lessons learned

- To assess soldering or rework stations or associated processes for contamination, measure solder drops from the soldering iron tips, debris from work surfaces and soldering iron tip holders.
- Consider tin-lead or tin-silver ratios to determine solder type that was used
- Sample holders such as cellophane, ESD-safe polyimide tape and paper mini-cupcake liners provide good mounting surfaces for small items and allow easy maneuvering of the sample within the test stand.

Summary

A handheld XRF analyzer can provide sufficient accuracy and information to expediently evaluate materials, parts, components and even solder joints for compliance or violation of EU RoHS substance restrictions.

The data requires perspective and experiential judgment to account for measurement artifacts, avoid misinterpretation and prevent unrealistic expectations that could easily lead to erroneous conclusions and unnecessary expenditure of effort.

Guidance Summary

- Verify peaks for both characteristic x-rays of the element shell are present in the spectrum.
- Cooling of molten solder can affect surface concentrations. Measure both top and bottom of melted samples or slice off the outer layer and measure the interior.
- Remove extra material from the sample analysis area whenever possible.
- If this is not possible, use material dissection to the homogeneous material or engineering judgment
- Pay attention to plastic parts.
- To assess soldering stations, measure solder drops from the soldering iron tips, debris from work surfaces and soldering iron tip holders.
- Consider tin-lead and tin-silver ratios to determine the solder type that was used
- Simple sample holders provide good mounting surfaces for small items.

Acknowledgements

- Dillon McDowell, Ted Shields and Mary Wu of Olympus NDT
- Tom Kaminska, Randall Spagnola and the rest of the Keysight Technologies (and previously Agilent) XRF Users Group
- Michelle Curtis of CDI Corporation
- Karen Miles of Materials & Processes Solutions