

The Good, the Bad and the Ugly Regarding RoHS Testing

Choosing a competent laboratory

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Q: Why do companies send samples to an independent laboratory?

A: To get unbiased, useful information about the samples.

It's really that simple. What's not so simple to know is whether the information you receive is trustworthy. More often than not, when you receive information that gives your sample a passing grade, you are less likely to question it. Conversely, when you receive information that your sample fails, you are more likely to question it. Why should that be so? In either case, the information could be wrong. As a matter of fact, an incorrect passing grade could be much more detrimental to your company than an incorrect failing grade.

In the case of RoHS testing, the result of an incorrect passing grade for your sample could cost your company millions in damages. Think about it: your sample was tested by a laboratory and the results were in compliance with RoHS requirements, but in reality the product was not in compliance. If your company is cited for an infraction by EU officials, will the due diligence defense work for you? On the one hand, you should be able to produce a document that shows the laboratory results for your product and perhaps no further action will be pursued; or, you may go to court and be able to recoup losses from the lab. But if word gets out to the media that your product contains hazardous substances above the legal limit, your brand and/or company name could suffer irreparable damage. How much is that worth to you? I submit that it's worth making sure that your lab is competent to do the testing you need.

The information that follows is intended as guidance to help you decide if the information you receive from a laboratory is trustworthy.

- **Material testing is not the same as environmental testing.**

Many labs misapply EPA methods to RoHS testing. EPA methods are often developed for testing water, air, soil, or sludge samples and they are often extraction methods as opposed to full dissolution methods. Most EPA methods are not suited for analysis of materials found in electrical and electronic equipment. Demand proof from your lab that they can analyze the materials they are testing, or better yet, send in a

sample of known composition to check their accuracy. Such materials are available from reference materials suppliers.

Testing a sample made up of plastic, ceramic, glass, and/or metal using a method designed for analysis of water is akin to following a recipe for making spaghetti and meatballs but using the ingredients for chocolate cake. The method must match the material, just as you need the proper ingredients to make spaghetti and meatballs and the proper directions to make chocolate cake.

- **Question the results if they always come back as “not detected”.**

There are many reasons why a substance is not detected in a sample. The obvious reason is it's not there. But don't be fooled: just because the result says “not detected” does not mean that the substance isn't there. It may be that the test method was incapable of detecting the substance within the material being tested. This is often the case when a method designed for analyzing one material is used to test a very different material. For example, a method used to determine PCBs in soil is not likely applicable to metal or plastic. The solvent used for extracting the PCBs from soil may not be capable of extracting PCBs from plastic, and there is no reason to test for PCBs within a metal (they cannot be present in metal). You have to ask yourself why labs test for organic substances in metal samples; I can tell you that organic substances are not present within a metal without having to test at all. Such testing is a waste of time and money, and besides, there is no way to validate a test used to determine the presence of something that cannot be present. That is called “proving the negative”; for example, prove to me that invisible pink unicorns do not exist. Can you do it? Should you do it? If you think so, I have truckloads of invisible pink unicorns to sell you.

One company I know sent a sample of plastic they knew contained deca-BDE to a laboratory in Asia for analysis of PBBs and PBDEs. The results came back “not detected” for all congeners of PBBs and PBDEs, including deca-BDE. You do not have to believe me; you can try it yourself. Take some old samples you know contain hazardous substances and send them to your current lab without warning them. If the lab detects the presence of the hazardous substances and they report reasonable results, great. If not, you know what you need to do: stop sending samples to that lab.

- **Check the laboratory's accreditations.**

While accreditation to recognized laboratory standards such as ISO 17025 does not mean that a lab's results are automatically correct, it does mean that they have been audited. Pay particular attention to the scope of accreditation; it will tell you what type of testing the lab is accredited to do.

- **Grinding up parts and components prior to testing for RoHS substances is technically worthless.**

Frankly, it shouldn't be necessary to discuss this subject, but there are so many labs out there grinding up complex parts prior to testing, it has to be addressed. Take a look at the picture of a cross-section of a multi-layer capacitor given in Figure 1 below. The picture ought to be self-explanatory: in a chip capacitor, there are both exempt and non-exempt applications of lead. The exempt application is the lead oxide (PbO) in ceramic; the non-exempt applications are the solder and the nickel (neither may contain lead above 0.1% by weight). If the chip

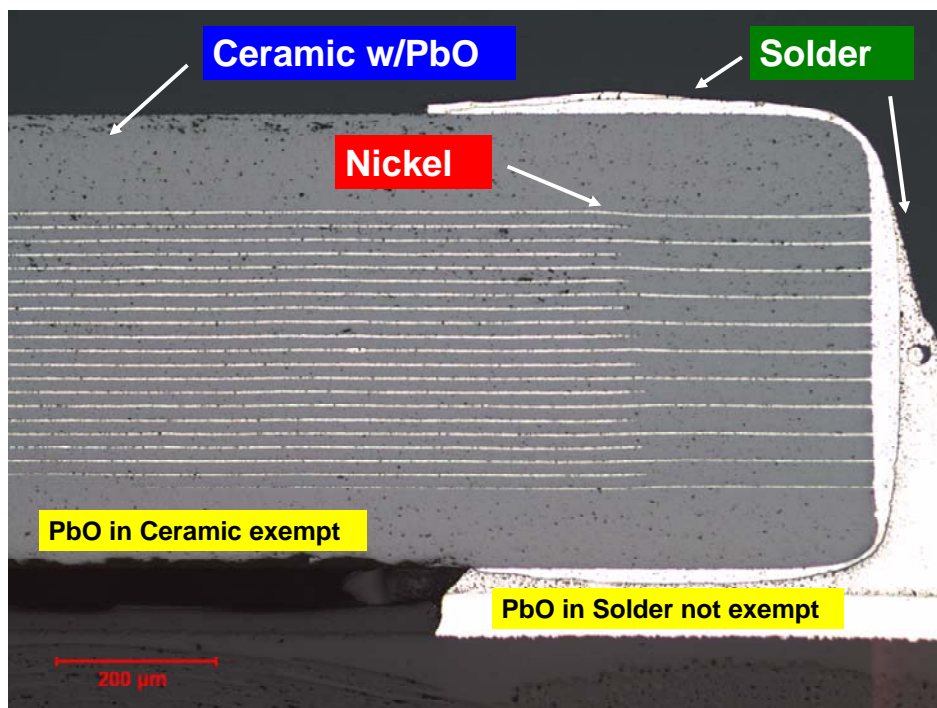


Figure 1: Cross-section of a multi-layer chip capacitor.

capacitor is ground up prior to testing, the total lead concentration of the chip capacitor is the result after testing. Since the lead from the exempt ceramic layer may have been mixed with lead from the solder or the nickel layer, nothing may be said concerning whether the chip capacitor complies or does not comply with RoHS requirements. If the lead only came from the ceramic layer, the chip capacitor would comply; if the lead came from the solder or from the nickel layer, the chip capacitor may not comply. Given the test result, there is no way to determine the concentration of lead in the solder. Because the sample was ground up, there is no way to assess compliance based solely on the test result.

A chip capacitor is a relatively simple example, since there are only three materials present: ceramic, nickel and solder. As the complexity of a sample increases, the argument made above only gets stronger. So if a populated printed

circuit board is ground up prior to testing for RoHS substances, what can be said of compliance to RoHS requirements based on the test results? The answer is: nothing.

Dilution is another issue regarding grinding up samples prior to testing for RoHS substances. The RoHS requirements are that “homogeneous materials” in certain electrical and electronic equipment shall not contain more than 0.1% by weight lead, mercury, hexavalent chromium, PBB and PBDE and not more than 0.01% by weight cadmium. Again, there are exemptions, but let’s consider a non-exempt application. Let’s say a certain printed circuit board has on it 1 gram of tin lead solder containing 37% lead and let’s pretend that the solder is the only source of lead on the printed circuit board. Let’s say the mass of the total printed circuit board is one pound, or about 454 grams. We can calculate what the result for total lead should be: $[(0.37 \times 1 \text{ g})/454 \text{ g}] \times 100 = 0.081\%$ by weight. If the board was ground up prior to testing, the result for lead would receive a passing grade, whereas the solder used would fail to meet RoHS requirements. An EU representative told me that they will not grind up samples prior to testing, so it seems likely they would test the solder and find 37% lead. So dilution is certainly an issue associated with grinding up complex parts.

Validation of a test method is also a key to knowing whether results are trustworthy. There is no way to know whether a test method is valid unless it can be shown to produce reliable results. One thing certified reference materials are used for is to validate test methods. While it is possible to develop certified reference materials with known concentrations of substances within individual materials, it is not feasible to do so for all the possible configurations of electrical and electronic components which may be ground up prior to testing. That means there is no way to prove (or disprove) the validity of test results when complex samples are ground up prior to testing. So grinding up samples prior to testing is not a reliable method.

Contamination of samples is a real concern regarding grinding up complex components prior to testing. Plastics and solders are low melting point materials, so the friction caused in a knife-cutter can cause these materials to smear on the cutting surfaces. Simply brushing the surfaces of the blades will not remove these materials; see Figures 2 and 3 for pictures showing a knife-cutter interior after grinding a printed circuit board. If hard materials such as steel are put through the knife-cutter, these also cause damage to the blades. See Figure 4. Guess where the damaged parts of the blades went? They went into the sample, of course.

See Figures 5, 6, and 7 for pictures of a circuit board and the “homogenized” sample after going through a knife-cutter and 1 millimeter screen. While further grinding is possible using liquid nitrogen and an ultra-centrifugal mill, that picture shows what most labs use as a “homogeneous material” for testing. As you can see, the sample is anything but homogeneous. No wonder our clients have reported inconsistencies in results: the sample is inconsistent.

With all the problems associated with grinding complex samples prior to analysis, do you think such testing is useful? I do not.

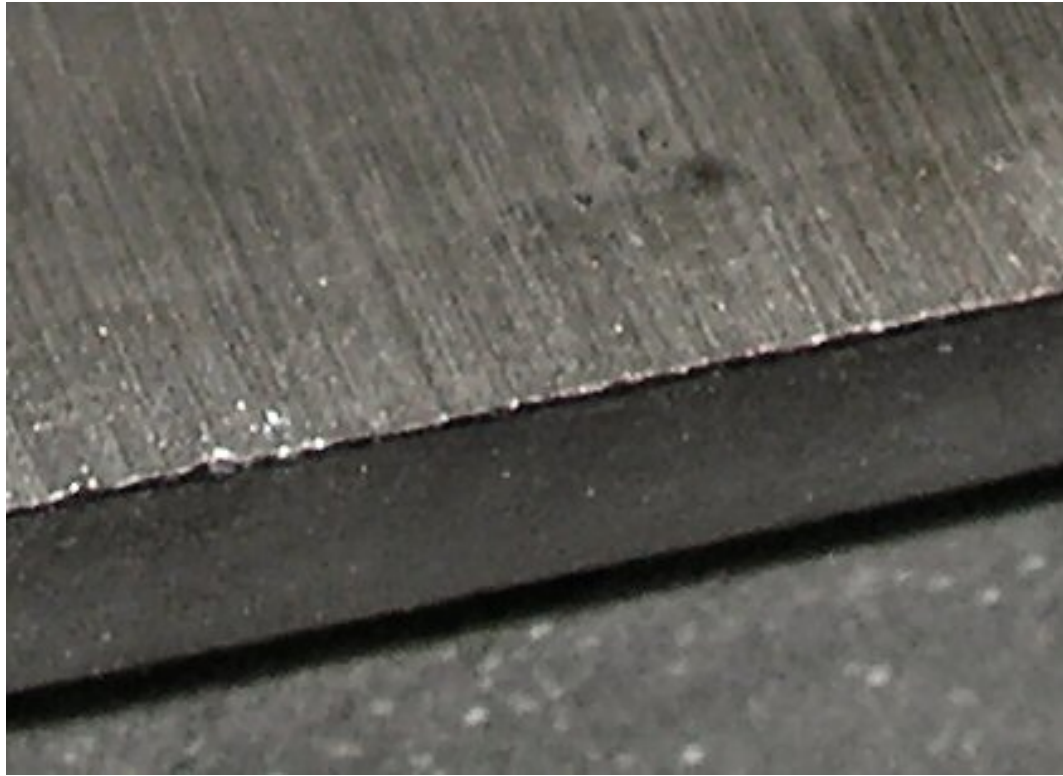


Figure 2: Interior of a knife-cutter after grinding printed circuit board. Note smeared material in the grooves.



Figure 3: Another interior area of a knife-cutter after grinding printed circuit board. Note smeared material and nicks and scratches.

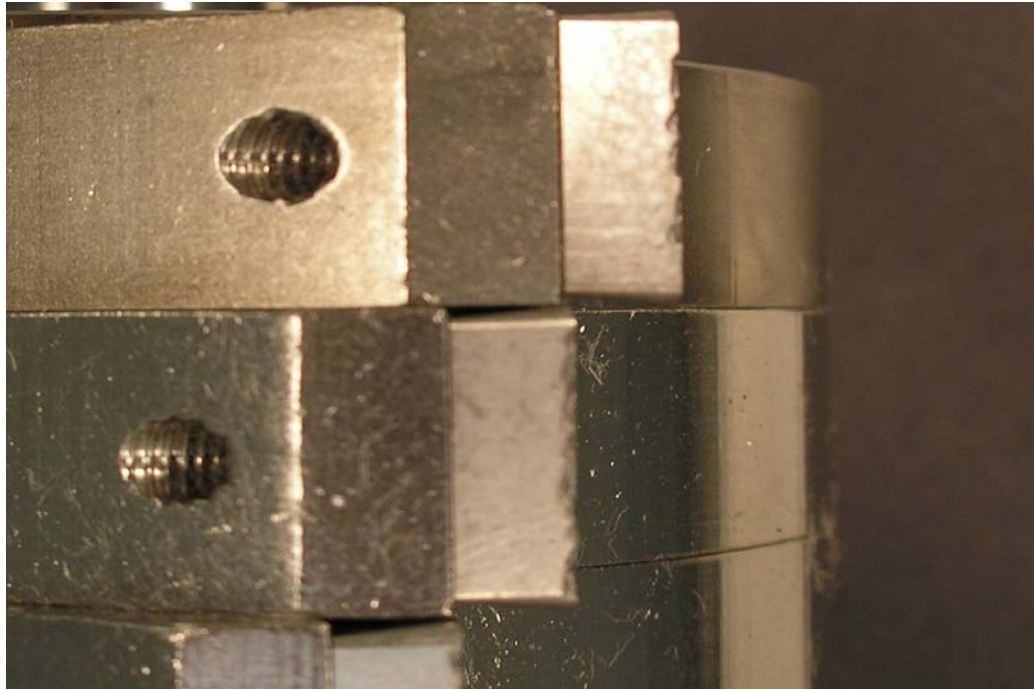


Figure 4: Blades of knife-cutter after grinding electronic samples. Note chipped edges.

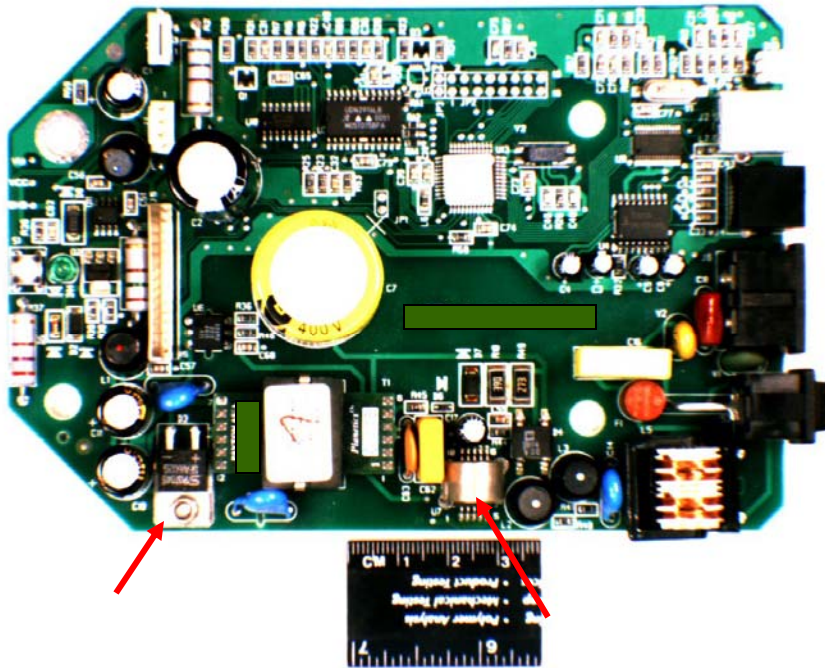


Figure 5: Typical circuit board to be ground prior to testing. Note that the two metallic pieces toward the bottom of the image were removed before grinding.



Figure 6: Ground up printed circuit board, no magnification.



Figure 7: Close up of ground circuit board. Note wires and bits of components.
Is this homogeneous?

- **Watch out for bad science and false claims**

Several laboratories claim to be able to identify and quantify all the substances listed on materials declarations such as Sony SS-00259 or Motorola 12G02897W18. I submit that those claims are bad science, false, misguided or all of the above. How do I know? First, let's take a look at how one laboratory said they tested for PBB and PBDE congeners: the lab listed US EPA methods 8081A, 8270C, 3540C and 3550B. The titles for and scopes of those methods are as follows:

8081A – Title: Organochlorine Pesticides by Gas Chromatography; Scope: “pesticides in extracts from solid and liquid matrices”

8270C – Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS); Scope: “solid waste matrices, soil, air sampling media and water”/ tetra-bromo diphenyl ether (tetraBDE)

3540C – Soxhlet Extraction; Scope: “solids such as soils, sludges and wastes”

3550B – Title: Ultrasonic Extraction; Scope: “solids such as soils, sludges and wastes”

Notice that there is no mention of metal, plastic, ceramic or glass in the scopes of these methods? The methods are applicable to air, soil, and water for the most part. Only one of the listed methods contained a PBB or PBDE in its scope, and that was 8270C (tetraBDE). None of the other methods even mention PBB or PBDE. Note also that there are two sample preparation methods listed: soxhlet extraction and ultrasonic extraction. Which one of those methods was used to prepare the samples? Were both methods used? Unlikely. Method 8081A used to cover analysis of both pesticides and PCBs, but now it only covers pesticides, so we know that is an incorrect reference. Method 8081A now states that PCBs should be analyzed by method 8082. OK, so maybe the lab made a mistake. Let's look at the title and scope of method 8082:

8082 – Title: Polychlorinated Biphenyls (PCBs) by Gas Chromatography;
Scope: “used to determine the concentrations of polychlorinated biphenyls as Arochlors or as individual PCB congeners in extracts from solid and aqueous matrices”

There are some interesting sections within EPA method 8082; in Section 3 on interferences, subsection 3.3 states that “interferences by phthalate esters introduced during sample preparation can pose a major problem in PCB determinations”. Subsection 3.3.1 goes on to say that “common flexible plastics contain varying amounts of phthalate esters which are easily extracted or leached from such materials during laboratory operations. Interferences from phthalate esters can best be minimized by avoiding contact with any plastic materials and checking all solvents and reagents for phthalate contamination.” It looks as if EPA 8082 says that flexible plastic samples are to be avoided when analyzing PCBs. And remember: we aren't talking about PBBs or PBDEs – method 8082 is for PCBs.

OK, so now I have to ask which method was used to determine PBBs and PBDEs; was it EPA 8270C or EPA 8082 or both? Since the only part of electrical or electronic products that contain PBDEs are plastics, is method 8082 applicable to analysis of electronic samples? The answer must be no. So we are left with method 8270C. Is that method applicable to analysis of PBBs and PBDEs? In section 1.4, EPA 8270C says “In most cases, Method 8270C is not appropriate for the quantitation of multicomponent analytes, e.g., Arochlors, Toxaphene, Chlordane, etc., because of limited sensitivity for those analytes.” Looks like EPA Method 8270C is out for quantitative analysis of PCBs, which might mean it is not useful for quantifying PBBs or PBDEs. So which method was actually used? There is no real way to know, barring direct answers from the laboratory.

After all that, the kicker is that the sample analyzed by that lab was made of inorganic materials: steel, ceramic, and copper. Go figure. So that lab analyzed inorganic materials for PBBs and PBDEs using methods for analysis of soil, air and water. Furthermore, the methods referenced were applicable to PCBs (or pesticides!) and one was known to be negatively impacted by plastic containing phthalates, and the other method says it isn't appropriate for quantifying PCBs. Makes you scratch your head, doesn't it?

You've heard about the problems with RoHS testing, but what are the solutions?

1. Clear guidance on what constitutes a “homogeneous material” is required.

The only definitions and guidance we have for “homogeneous material” today comes from the European Commission in their “Frequently Asked Questions” document. The information in that document is useful, but it still leaves several questions unanswered. In addition, the European Commission states on the bottom of each page of that document that the information given is “Not Legally Binding”. The explanation from the European Commission concerning the legal uncertainty of their guidance is that only the European Court of Justice may make legal determinations concerning interpretations of the Commission’s definitions. That leaves the guidance open to considerable interpretation, which in turn causes confusion and often contradictory ideas concerning what constitutes a “homogeneous material”. In my informed opinion, this fluid situation was purposely created by lobbyists for some of the most powerful multi-national electronics companies.

But why? My answer is that the more any law is open to interpretation, the less likely it is that any charge of violation of the law will stand up in court. And “homogeneous materials” are the basis of conformance with RoHS requirements. If it is difficult to understand what constitutes a “homogeneous material” and the European Commission’s definitions are “Not Legally Binding”, then any prosecution based on a perceived infraction is difficult at best. The advantage lies with the defense. This takes the teeth out of the RoHS Directive, at least where the large multi-national corporations are concerned. They can afford enormous court costs and can buy the best legal defense available. But the fact of the matter is that such a situation only benefits the large multi-nationals. Small companies cannot afford the costs of litigation. Those small companies would benefit from a clear, unambiguous definition of “homogeneous material”, since it would be easier for them to assess their products’ compliance with RoHS requirements and thus easier for them to avoid being charged with an infraction of the law.

In my opinion, it is a priority for governments to pressure the European Commission for clear, legally binding definitions of “homogeneous material”, if only to protect the interests of the small and medium enterprises (SMEs). Those companies do not have easy access to government through lobbyists as do the multi-nationals. Therefore, the governments must represent the SMEs. Perhaps it would be possible to get a preliminary ruling on the definition of “homogeneous material” from the European Court of Justice. That would be very helpful to not only the SMEs but also to the laboratories testing samples for compliance with RoHS requirements.

2. Getting resolution to the “homogeneous materials” issues will take time. What should be done in the meantime?

We need to come up with some practical ways of going about conformity assessment given the current information. If we take the European Commission's guidance as the best available definition of "homogeneous material", we can begin to find ways to deal with compliance issues. There are some fairly clear examples of homogeneous materials: individual types of metals, plastics, ceramics, glass, alloys, paper, and resins. If you think about it, practically any material falls under the scope of the RoHS Directive, since clocks and lamps can be made from rocks, wood and any other solid material you could imagine. This should act as guidance for the analyst: the best samples for analysis are individual homogeneous materials, whether those materials are available separately or need to be separated from parts or assemblies. Clients submitting samples to laboratories should try to send materials as opposed to complex parts or assemblies

As samples become more complex, that is, as they become more difficult to separate into individual homogeneous materials, adjustments in analytical tactics have to be made. A good example is a plated metal sample. According to the European Commission's guidance, plating and coatings are considered "homogeneous materials" which can, "in principle", be separated from the substrate using mechanical means. This is somewhat problematic for a chemical analyst, because the typical means of separating plating or coatings from metal substrates is through chemical separation. ASTM B 767 and ASTM A90 are good references for how this may be accomplished. It is difficult to mechanically separate most coatings and plating from metal substrates without getting at least some of the substrate included in the sample. Chemical separation of plating or coatings from substrates should be utilized where possible.

Mechanical or chemical separation of plating and coatings is not always practical or possible. Certain types of plating over certain types of substrates pose chemical separation problems and thin or multiple plating layers cannot be mechanically separated. There are some analytical techniques that can be employed with quantitative results in some instances. For example, consider a single thin plating layer over a metal substrate that cannot be removed cleanly by mechanical means and cannot be chemically separated. A portion of the sample including both plating and substrate may be dissolved and analyzed and compared to an analysis of the base metal only. If elements are found in the combined sample and are not found in the base metal sample, they may be attributed to the plating layer. The plating layer mass can be estimated and the concentration of the elements in the plating layer can then be calculated. If there is a significant difference between concentrations found in the combined and base metal samples, calculations may be made for each material. If the concentrations found in both samples are about the same, it is likely that the elements are found only in the base metal.

As sample sizes become small and the samples become more complex, separation of "homogeneous materials" is not feasible from either a cost or functional perspective (or both). The best solution to this problem is to obtain the materials from which the samples were made and analyze those materials. This is often not practical due to the inaccessibility of the materials. Still, there are many companies out there who desire to have their

small, complex components evaluated to RoHS requirements. Gross deviations from MCVs may be determined within homogeneous materials in these samples via a variety of micro-analysis techniques, but it is important to realize that those techniques are limited in resolution and thus quantitative ability. It is highly unlikely that any currently available techniques used for analysis of materials in situ are able to accurately determine values near the MCVs for RoHS substances. The best that can be achieved at this time are evaluations based on gross deviations from the MCVs, i.e. extremely high values may be determined on a semi-quantitative basis.

3. How are hexavalent chromium concentrations in chromate conversion coatings evaluated?

Hexavalent chromium in chromate conversion coatings cannot be determined in weight percent. There are several reasons, the best of which is that chromate conversion coatings are extremely thin and cannot be mechanically disjointed from the substrate without incorporating substrate metal into the sample. See Figure 8 below. Typical weigh-strip-weigh methods will not work for determination of total chromate conversion coating mass, because the mass of the coating is so small that extremely sensitive balances would be required.

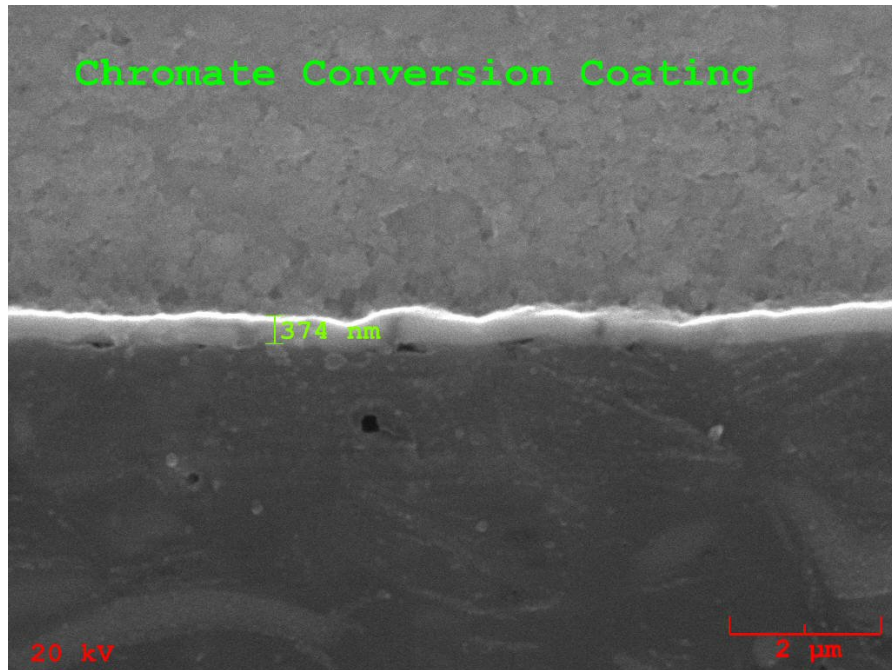


Figure 8: Cross-section of an aluminum panel coated with a yellow dichromate conversion coating. The aluminum substrate is at the top of the photo. Note that the chromate coating is only 374 nanometers in thickness.

The industry and international standard for measuring hexavalent chromium in chromate conversion coatings over metals is the ISO 3613 water extraction-diphenylcarbazine test. Those who have been using the EPA

3060A test using an alkali/water extraction should be aware that the alkali can attack aluminum, zinc, iron and cadmium substrates and cause turbidity in the test solutions, which can interfere with UV-VIS readings. EPA 3060A should not be used for analysis of hexavalent chromium in chromate conversion coatings.

The units given by ISO 3613 are $\mu\text{g}/\text{cm}^2$, not weight percent. Those units cannot be compared or reconciled without an accurate total mass of the chromate conversion coating. As stated above, obtaining a total mass for chromate coatings is not feasible. So the correct units are $\mu\text{g}/\text{cm}^2$. In support of that statement, General Motors Worldwide Standard GMW3059 gives a maximum allowable concentration of $0.1 \mu\text{g}/\text{cm}^2$, even though the EU End-of-Life Vehicle Directive (ELV) gives a maximum concentration value of 0.1% by weight. The European Commission and their experts should have known that they had the incorrect units for measuring hexavalent chromium in chromate conversion coatings, because ISO 3613 says so.

The best means of evaluating whether or not the hexavalent chromium concentration in a chromate conversion coating is acceptable is to follow the ISO 3613 water extraction procedure and obtain results in $\mu\text{g}/\text{cm}^2$ and then compare the result to the stated GMW3059 limit of $0.1 \mu\text{g}/\text{cm}^2$. If the result is greater than $0.1 \mu\text{g}/\text{cm}^2$, the sample would be considered unacceptable for General Motors' use, so perhaps this is a good gauge of whether a sample is compliant with RoHS requirements. We cannot make a definitive statement concerning compliance, however, since the units stipulated by the EU are percent by weight. Until the Europeans either tell us how to measure hexavalent chromium in chromate conversion coatings in weight percent, give us an exemption for chromate conversion coatings or they change the units of measure to $\mu\text{g}/\text{cm}^2$, we cannot evaluate metal products for compliance to RoHS requirements.

4. How should the concentration of a brominated flame retardant be measured in a sample and how can we tell which brominated flame retardant was added?

First of all, There is only one reason to add a flame retardant to a material: to keep it from burning. If a material is not flammable under normal conditions, it is not likely that a brominated flame retardant has been added. For example, steel is not flammable under normal conditions, so there is no reason why a brominated flame retardant would have been added. Secondly, even if you tried to add a brominated flame retardant to steel during the production process, it would not survive the production temperatures (1650°C) - it would decompose and would vaporize as a variety of gases.

It is really only necessary to test organic-based samples for brominated flame retardants. IMR Test Labs analyzes such samples using an oxygen-bomb combustion / ion chromatography method. This technique results in an accurate result for total bromine within the sample, but does not tell which species of brominated flame retardant is present. If we find a high bromine concentration, we suggest that the client ask their vendor which brominated flame retardant was added to the material. As of January 2006, several

brominated flame retardants such as deca-BDE and TBBP-A were exempt from the RoHS restrictions.

See discussions concerning analysis of PBB and PBDE on pages 2, 8 and 9 of this document.

5. How do you test for hexavalent chromium within materials?

The type of material should first be identified. For example, if the sample is a metal of any kind, the chromium within the metal is not considered to be in the hexavalent state, but the ground, or zero state. It only makes sense to test the surface of metals for hexavalent chromium and then only if a chromate conversion coating or other coating containing hexavalent chromium was applied (such as paint, for example). If there is a coating on the metal which can be cleanly separated from the substrate, that coating may be tested for hexavalent chromium. For paint samples, there is an international standard test method for determination of hexavalent chromium given in ISO 3856/5. That method may be modified for use in analysis of plastic samples, but we will need some certified reference materials to be able to prove such methods work well.

For organic materials, there is a relatively simple, cost effective means of determining whether samples comply with RoHS requirements for hexavalent chromium. The samples are tested for total chromium via ICP-AES or other viable method, just as the samples are tested for lead and cadmium. If the total chromium concentration in the material is less than 0.1% by weight, the hexavalent chromium concentration cannot be greater than the total chromium concentration and thus the sample complies for hexavalent chromium. Other methods such as ISO 3856/5 have to be employed if the total chromium concentration is greater than 0.1% by weight. Indicators that an organic sample may contain hexavalent chromium include colors such as red, orange, green, and yellow. Any plastic samples having those colors should be evaluated for compliance to RoHS requirements.

Conclusions:

Choosing a competent laboratory for testing products for compliance to RoHS requirements is not easy. The underlying problems are that there are few standard test methods available for quantifying RoHS substances in all the material types used to manufacture electrical and electronic equipment and there is not currently an accreditation program for laboratories claiming to be able to assess products for conformance. It is hoped that the information given in this document will help industry to understand the analytical problems associated with RoHS and thus will help companies make more informed decisions about the test data they are receiving from laboratories.