Comparison of Testing Methods for Residues on Electronic Hardware

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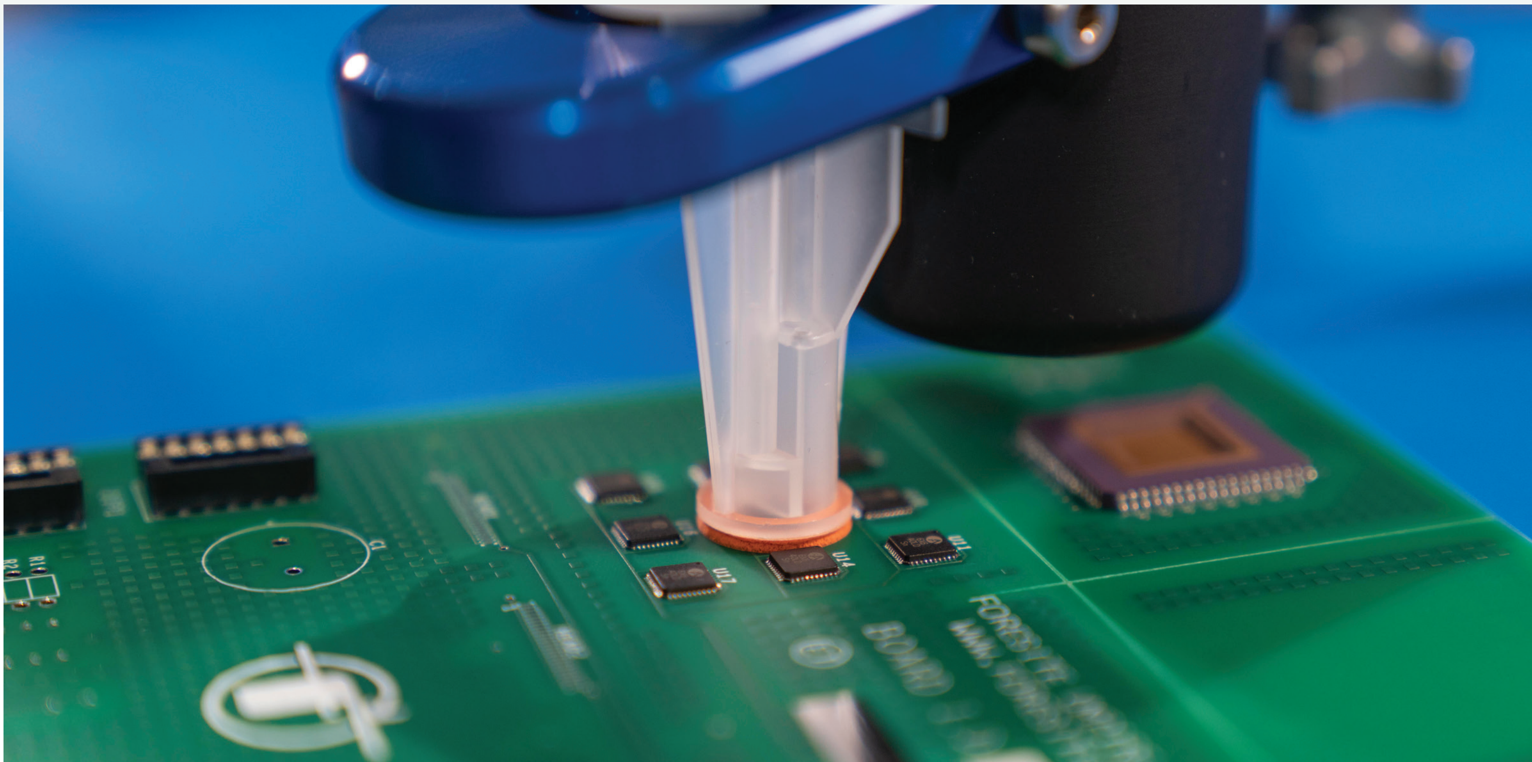

Comparison of Testing Methods

In this white paper, we discuss the pros and cons of five analytical techniques when applied to residue analysis on electronic assemblies. We evaluate the following for their application and limitations for analyzing both visible and invisible residues:

1. **FTIR** (Fourier Transform Infrared Spectroscopy)
2. **SEM/EDX** (Scanning Electron Microscopy/Electron Dispersive X-ray)
3. **XRF** (X-ray Fluorescence)
4. **Ion Chromatography** (Localized, steam extraction/electrical testing)
5. **ROSE** (Product immersion/bulk resistivity testing)

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Terry Munson is the founder and president of Foresite, Inc. Terry has extensive experience with how cleanliness issues are affecting product reliability for electronic hardware. He is the primary developer of ion chromatography analysis for use in the electronics manufacturing industry and is an active member in the IPC. Mr. Munson's insights have been seen in various industry trade publications, some of which are available in the Resources section of our website – he is a frequent presenter at electronics industry conferences.

Comparison of Testing Methods

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FTIR – Fourier Transform Infrared Spectroscopy

In its simplest form, Fourier Transform Infrared Spectroscopy (FTIR) consists of two mirrors located at a right angle to each other and oriented perpendicularly, with a beam splitter placed at the vertex of the right angle and oriented at a 45° angle relative to the two mirrors. Radiation incident on the beam splitter from one of the two “ports” is then divided into two parts, each of which propagates down one of the two arms and is reflected off one of the mirrors. The two beams are then recombined and transmitted out the other port. When the position of one mirror is continuously varied along the axis of the corresponding arm, an interference pattern is swept out as the two phase-shifted beams interfere with each other.

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FTIR provides specific information about chemical bonding and molecular structures, making it useful for analyzing organic materials and certain inorganic materials. Chemical bonds vibrate at characteristic frequencies, and when exposed to infrared radiation, they absorb the radiation at frequencies that match their vibration modes. Measuring the radiation absorption as a function of frequency produces a spectrum that can be used to identify functional groups and compounds.

FTIR Applications and Limitations

- Identifying the molecular structure of organic compounds for contamination analysis;
- Identification of organic particles, powders, films, and liquids (material identification);
- A large sample library of materials is available to match material signatures for identification of unknown residues or contaminants.

FTIR is a qualitative analytical technique and does not provide any information regarding elemental content nor quantify ionic content of a sample.

Figure 1: FTIR Diagram

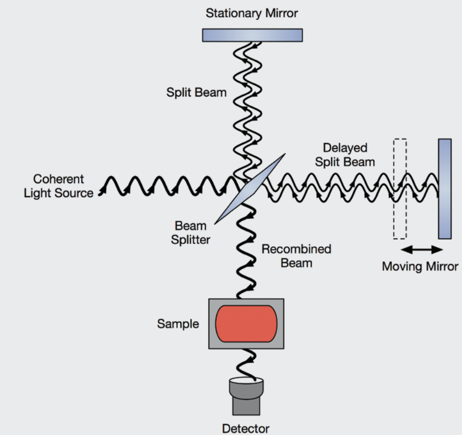
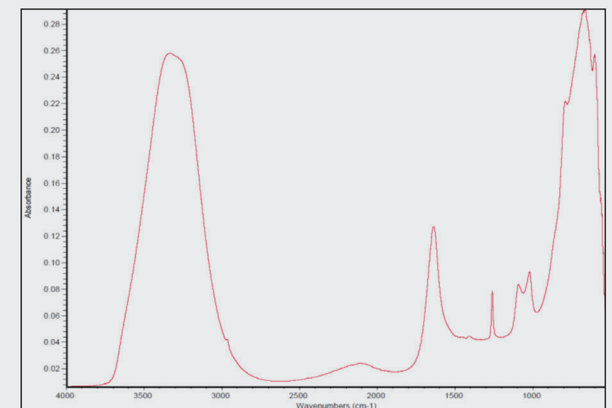


Figure 2: FTIR Spectra



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SEM/EDX – Scanning Electron Microscope

Scanning Electron Microscope – There are four primary components of the EDX setup:

1. The beam source;
2. The X-ray detector;
3. The pulse processor;
4. The analyzer.

A number of free-standing EDX systems exist. However, EDX systems are most commonly found on scanning electron microscopes (SEM-EDX) and electron microprobes. Scanning electron microscopes are equipped with a cathode and magnetic lenses to create and focus a beam of electrons, and since the 1960s they have been equipped with elemental analysis capabilities. A detector is used to convert X-ray energy into voltage signals; this information is sent to a pulse processor, which measures the signals and passes them to an analyzer for data display and analysis. (from Wikipedia)

Energy Dispersive X-ray Spectroscopy (EDS, EDX or EDXRF) is an analytical technique used for the elemental analysis or chemical characterization of a sample. As a type of spectroscopy, it relies on the investigation of a sample through interactions between electromagnetic radiation and matter, analyzing x-rays emitted by the matter in response to being hit with charged particles. Its characterization capabilities are due in large part to the fundamental principle that each element has a unique atomic structure allowing x-rays that are characteristic of an element's atomic structure to be identified uniquely from each other. (from Wikipedia)

Figure 3: Amray 3200 SEM

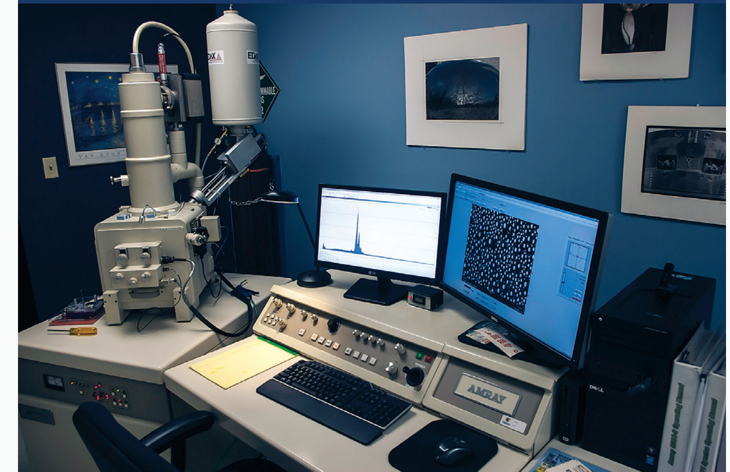
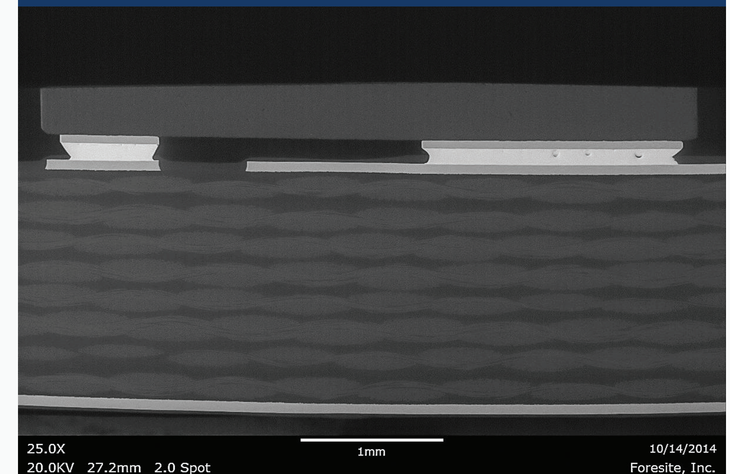


Figure 4: SEM Image of SMT LED at 25x



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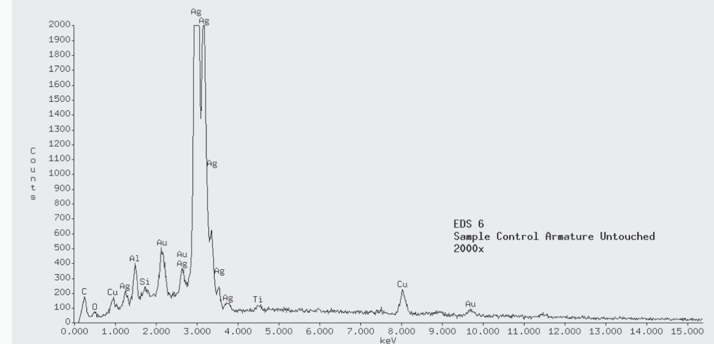
SEM/EDX Applications and Limitations

1. SEM/EDX is excellent at identifying pure elements, but can detect only gross high levels of ionic elements. The EDX scan to the right is of a contact brush on a motor showing carbon, oxygen, copper, silver, aluminum (part of the detector), silica and gold (sputter coating to prevent charging of the sample), but it does not show the chloride and succinic acid from a water soluble flux that were present.
2. The SEM/EDX analysis provides relative elemental composition information. EDX uses a single electron beam to excite the sample, which will burn through a thin film of organic and/or ionic residues on the surface of the sample. Scanning electron microscopes are limited in the size of sample that can be placed in the chamber; therefore SEM/EDX is potentially a destructive test in that a PCBA or other object of interest may need to be cut to size, sputter coated, or otherwise prepared for testing. An additional limitation lies in the fact that thin film materials, such as chloride and sulfate, can be volatilized under sublimation, carried away in the vacuum and not detected.

Figure 5: SEM/EDX Analysis



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XRF – X-Ray Fluorescence

The X-ray fluorescence principle is depicted in Figure 6. An inner shell electron is excited by an incident photon in the X-ray region. During the de-excitation process, an electron is moving from a higher energy level to fill the vacancy. The energy difference between the two shells appears as an X-ray, emitted by the atom. The X-ray spectrum acquired during the above process reveals a number of characteristic peaks. The energy of the peaks leads to the identification of the elements present in the sample (qualitative analysis), while the peak intensity provides the relevant or absolute elemental concentration (semi-quantitative or quantitative analysis). A typical XRF spectroscopy arrangement (Figure 6) includes a source of primary radiation (usually a radioisotope or an X-ray tube) and equipment for detecting the secondary X-ray. (from Wikipedia)

XRF Applications and Limitations

1. XRF is a quick, non-destructive analytical technique used to determine the elemental makeup of a material. Since it uses X-rays to excite electrons in the test sample, it can be used to measure plating thicknesses, but is not well suited to thin film metals and organic and ionic materials.

2. XRF can identify ionic residues in heavy concentrations; the photo of dendritic growth to the right was caused by partially heat-activated, no-clean flux (succinic, maleic and glutaric acids) and HASL flux (chloride). XRF is not able to determine the contaminants, only the metals and flame retardant (organobromide).

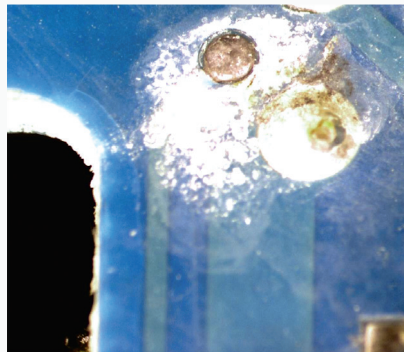


Figure 6: The Principle of XRF and the Typical XRF Detection Arrangement

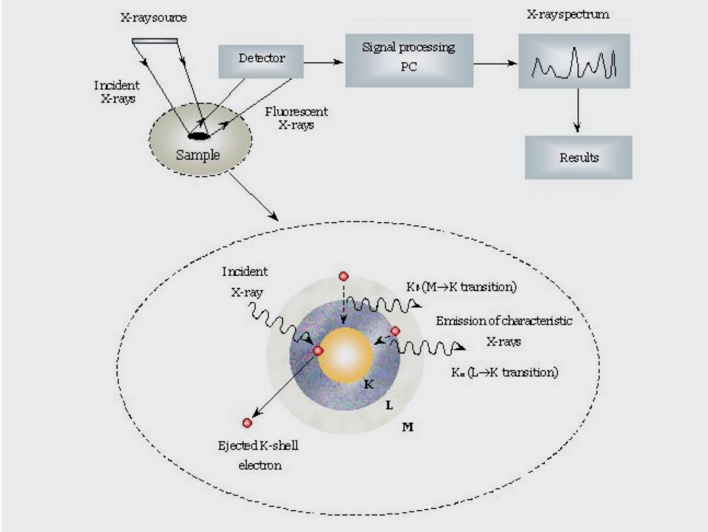
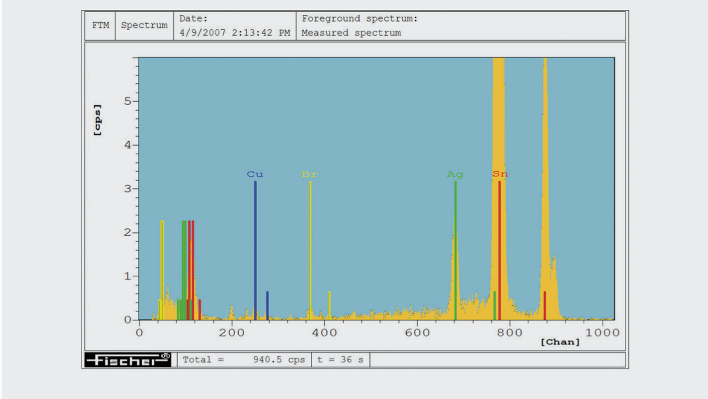


Figure 7: XRF Detects copper, bromide, silver and tin on Dendrite Short



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HPLC – Ion Chromatography

High-performance Liquid Chromatography (or High-pressure Liquid Chromatography, HPLC) is a form of column chromatography used frequently in biochemistry and analytical chemistry to separate, identify, and quantify ionic and organic compounds. HPLC utilizes a column that holds chromatographic packing material (stationary phase), a pump that moves the mobile phase(s) through the column, and a detector that shows the retention times of the molecules. Retention time varies depending on the interactions between the stationary phase, the molecules being analyzed, and the eluent used with a conductivity or UV-Vis detector.

(from Wikipedia)

Ion-exchange Chromatography (or Ion Chromatography) is a process that allows the separation of ions and polar molecules based on the charge properties of the molecules. It can be used for almost any kind of charged molecule including large proteins, small nucleotides and amino acids. The solution to be injected is usually called a *sample*, and the individually separated components are called *analytes*. It is often used in protein purification, water analysis, and quality control. In electronics analysis the critical step is to get the ionic residue into a solution for analysis. Traditional bag extractions are limited to extracting large areas of the board and components when failures and residue areas are typically localized in nature.

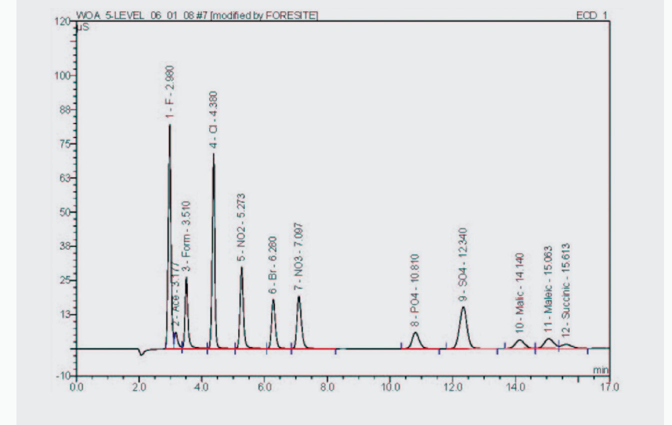
C3 (Critical Cleanliness Control)® is a localized extraction system that allows for ionic and organic residues to be solubilized under normal humidity exposure and voltage conditions in a specific component location.

Dionex - Ion Chromatography Applications and Limitations

Foresite uses Dionex AS22 anion and CS12A cation column technology with a 5 level calibration ranging from 0.1 ppb to 100 ppm. Repeatability R^2 = is 0.9998 with a 100 µL injection loop. DI water for the system is triple-polished 18.2 MΩ with less than 0.05 ppb of detectable ionics. The bicarbonate/carbonate eluent is optimized for the 17 minute elution run time.

Figure 8: Ion Chromatography System

Figure 9: Test results



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ROSE Testing

Foresite uses an Aqueous Technologies Zero-Ion G3 Ionic Contamination Tester for ROSE testing per IPC TM-650 2.3.25. The Windows PC-based control system captures all relevant testing data and automatically calculates NaCl/ square equivalence (per military and IPC specifications). The combination of test board submersion and immersion spraying creates an environment whereby the soluble contamination is extracted and measured.

Foresite also uses the 1978 Omega Meter 600R system for general process ionic analysis. A 750 ppm solution from Alpha Metals (now Specialty Coating) is used for validation. ROSE (resistivity of solvent extraction) is an early ’70s screening method that uses a large tank of IPA/DI water (75%/25%) at room temperature to solubilize ionic residues from the surface of a sample. The conductivity of the test solution is measured and this value is used to determine the amount of residue removed from the sample. These systems were developed when about 30% of flux in use (wave solder flux primarily) was rosin with amine hydrochloride activators. Current no-clean and water soluble fluxes react differently and only about 20% of the residues are brought into solution with a 15 minute extraction.

The IPC-TR-583 report written in 1996 indicated that these tools are difficult to correlate and that a calculation factor to correlate results from different test systems does not exist. This system works on the principle that a large tank of solution (10,000 to 150,000 mL) is needed to cover the entire board and that the surface area of every component and connector are calculated into a value used to express the surface contamination in µg/in^2 of NaCl equivalent (this is not a measure of Na+ or Cl- ions, but rather a scale of 1 – 20 defined by the conductivity of the 750 ppm salt standard). This tool is a gross measure of general surface ionics and as such should only be used as a process trend tool and not a predictor of field performance. The Mil spec. pass/fail criterion of 14 µg/in^2 of NaCl equivalent for the 600R is now mainly used to meet old contractual requirements. No new test method has been adopted into IPC J-STD-001 (Mil standards were disband and adopted by the IPC in 2000). Many companies have established C3 and ion chromatography limits as performance indicators and process control tools.

Limitations of the method include dilution when relatively small test samples are submerged in the large volume of solution. This can lead to minute conductivity changes in the test solution that cannot be accurately measured. Subsequently, false positive test results could be observed when a dirty but very small board is tested. These systems are also inherently sensitive to environmental CO_2, which is absorbed into the system, reacts to become carbonate, and is very detectable with these systems. The Omega Meter is also prone to “deadband” issues in which the solution is cleaned to a resistivity level that exceeds the measurable range of the resistivity probe in the system. In this case, much of the contamination present will not be measured before the resistivity drops to a measurable range.

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Example: Investigation of a Dendrite Short

This investigation uses five investigative techniques to analyze the conditions at the site of the short circuit. Each tool provides information used to determine the root cause of the failure.

FTIR analysis shows only the conformal coating signature below the dendrite.

SEM/EDX analysis indicates the presence of carbon, oxygen and copper.

XRF analysis indicates the presence of copper and bromide.

ROSE testing (Omega Meter 600R) indicated that the total board cleanliness from production sampling was 4.3 µg/in^2 (0.69 µg/cm^2); well below any cleanliness requirements published by IPC or the military.

C3 and IC analysis indicate that the residue was corrosive with a C3 leakage event at 23 seconds, and the chemical makeup of the residue from the via and top surface of the coated assembly was high in sulfate at 5.34 µg/in^2 and 231.11 µg/in^2 of WOA (succinic + malic acids). The opposite side of the assembly is next to a selective solder location and flux overspray allowed flux to migrate to the other side and into the via holes. The sulfate residue most likely originated from the etch process prior to OSP.

The root cause of this dendrite short over top of the conformal coating was a thick layer of flux that was not exposed to the selective solder heating. This buildup of partially heat- activated flux absorbed environmental moisture over a three month period in the field (office environment), completing the three conditions necessary for a dendrite to form.

Figure 10: Dendrite between Vias

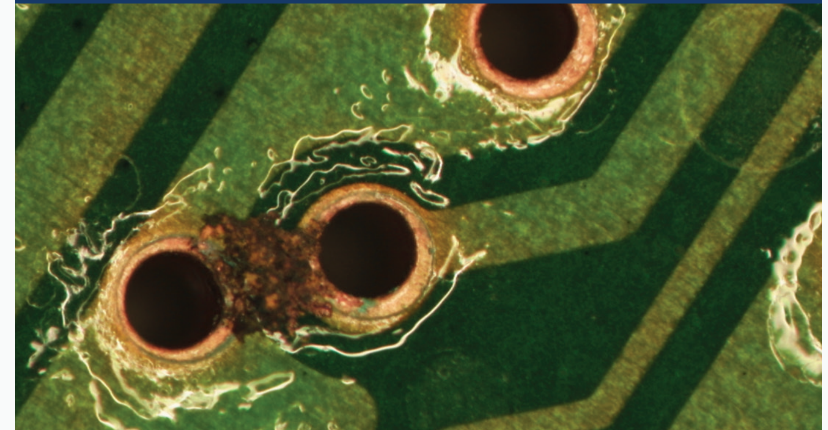
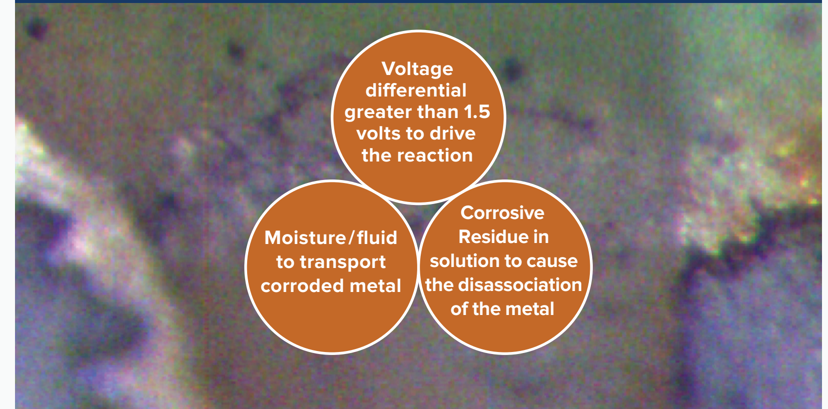


Figure 11: Three Conditions Necessary for a Dendrite to Form



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Conclusion

The tools used for analysis of residue-related electronics assembly failure analysis are varied and each is capable of providing useful data. Just as important as understanding the capability of each method is understanding the limitations.

In analyzing the dendrite growth failure, SEM/EDX gave us the confirmation that the copper alone corroded and the large level of carbon and oxygen came from another source. SEM/EDX also indicated the lack of chloride or sulfate residue. The FTIR results indicated that the dendrite was in and above the conformal coating. The XRF results confirmed that the copper alone is corroded and the normal bromide signature allows us to understand that this was a brominated flame retardant fabricated bare board. The ROSE testing indicates acceptable levels of cleanliness for the total board even though the board had a dendrite short and electrical failure. The C3 and IC indicate that the high WOA and marginal level of sulfate came from the process and not an external source of contamination (i.e. coffee, tap water or carbonated soda) and that the flux residue is corrosive as indicated by the C3 results.

The corrective action is to optimize cleaning prior to the OSP process and to heat activate the flux after the selective soldering process by exposing the flux to post-soldering heating (cure oven with a 150°C set point for 30 seconds) to complete the no-clean flux activation.

Other uses for these analytical tools include lot-to-lot comparison of samples using FTIR. SEM/EDX is well suited to analyzing a metal surface for tin whiskers or looking at the grain boundaries and intermetallic formation of a solder joint. XRF is ideal for non-destructive elemental analysis of metal or plastic materials or to screen for RoHS compliance. If we want to determine the amount of residue present on a corrosion site (or even a location that shows no dendrite but is shorting due to stray voltage) we use the C3 and IC system to determine if the residues are corrosive and which ionic/organic residues are present.

Foresite, Inc. is the industry expert at solving reliability and residue problems. We're eager to help you improve your product. Contact us for details.

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