Ion Chromatography

How DfR Can Help You Control Ion Contamination

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Background

The ionic cleanliness of printed circuit board (PCB) and printed circuit assembly (PCA) surfaces is important in electronics manufacturing and affects reliability of the product. The electronics industry has been interested in how ionic cleanliness correlates with corrosion, electrochemical migration, dendritic growth, and subsequent open circuits or leakage current during testing and in the field.

The most prominent, initial method for cleanliness evaluation is resistivity of solvent extract (ROSE) that measured the conductivity of a solution after flowing it over a surface of interest. A major disadvantage of this technique was its inability to detect specific ionic species generating conductivity.

Ion chromatography (IC) has become an important technique for the evaluation of ionic cleanliness. This technique, which detects individual ions, allows quicker trouble-shooting of contamination sources and better predictions about the detrimental effects of each ionic species by themselves. Ion chromatography is a form of high-performance liquid chromatography (HPLC) and works with aqueous sample solutions. It is able to measure concentrations of major anions, such as chloride and bromide, as well as major cations such as sodium, ammonium, and potassium in the parts-per-billion (ppb) and low parts-per-million (PPM) range. Concentrations of weak organic acids (WOAs) can also be measured through IC.

IC uses ion exchange columns in which the analyte interacts with a stationary packed resin. The resin is a polymer with charged chemical groups, or side chains, covalently bound to its backbone. In an anion column, anions in the analyte are attracted to positively charged groups on the resin. Sample solutions are injected into the column and pass through it under pressure from an eluent. The eluent is a liquid that pushes the analyte through the column, and which contains ions that compete with the analyte helping to separate the individual ions. The separation power is based on many factors including the eluent used, ionization equilibrium (pKa), physical size of each ion, and the resin type and charged group density within the resin. A conductivity detector generates a peak on the chromatogram for each species after it leaves the column. Columns and systems are customized and optimized for specific applications and specific ions and groups of ions.

DfR uses three separate columns and systems to detect anions, cations, and weak organic acids. Cations and anions have a minimum detection limit of 50-100ppb (50-100µg/L). Weak organic acids are more difficult to detect because of their lower conductivity values and therefore have a higher detection limit of 100-500ppb (100-500µg/L), depending on the specific acid.

Sample Preparation

IPC-TM-650, method 2.3.28, revision B as of November 2012, is the generic test procedure for PCBs and PCAs. Method 2.3.28.2 is similar but tailored to PCBs.

DfR Solutions uses an extraction process based on IPC-TM-650, method 2.3.28. During receipt and all subsequent processing, appropriate contamination control precautions including gloves are used. Samples are visually inspected and then subjected to the ion extraction process.

The specific steps are as follows:

1. The samples are placed into clean, KAPAK-brand heat-sealable polyester film bags.
2. A measured mixture of 18.2MΩ•cm de-ionized water (75% by volume) and semiconductor grade isopropanol (25% by volume) is poured into each bag and the bags sealed.
3. The bags are suspended in an 80°C ± 2°C water bath to allow dissolution of surface ionic contaminants into the extraction solution. The samples are entirely immersed in the extraction solution when the bags are suspended in the water bath.
4. After one hour +5 minutes, -0 minutes, the bags are removed from the water bath, gently shaken to mix the solutions, opened, and the samples removed from the bags.
5. About 10mL of each extraction solution is poured into ion chromatography vials.

One sample blank is prepared from the same extraction mixture and is prepared using the same steps as the actual sample. This sample blank contains nothing except the extraction liquid. It provides a measurement of background levels of ions from any of the materials used and processes performed.

The following solutions are then analyzed using a Metrohm modular ion chromatography system:
An 18.2MΩ•cm de-ionized water blank from the de-ionized water source
A four point calibration with NIST-traceable standard ion solutions
Sample blank
Sample extraction solutions

Ion chromatography measures the concentrations of each ion in the standard ion solution in ppm w/v using the calibration samples. The concentrations of ions in the sample blank are subtracted from their respective ion concentrations measured in the sample extractions. These resulting concentrations are converted to µg/in2. The basic conversion equation is below. A PCB or PCBA surface area is calculated by multiplying length by width, adding and subtracting areas outside of the square, multiplying by two for both faces, and adding 10% for components when applicable.

$$\frac{ion\ weight\ (\mu g)}{sample\ surface\ area\ (in^2)} = \frac{IC\ concentration\ \left(ppm = {}^{\mu g}/_{mL}\right) \times volume\ of\ extract\ (mL)}{sample\ surface\ area\ (in^2)}$$

Contamination Levels

Based on prior experience with field issues of electronics with contamination, DfR Solutions has developed a set of recommended levels for some anionic species on printed circuit board assemblies, presented below. These levels are especially applicable to uniformly applied contamination. The levels are divided into two categories: upper control limits, and maximum levels. The upper control limits are recommended maximum average levels for benign environments. The maximum levels are recommended maximums for all samples. A buffer between the upper control limits and maximum levels allows manufacturing variations in the amounts of contamination left.

Printed circuit board fabrication can leave process residues that tend to be spread relatively evenly across surfaces. IPC's original contamination specification of 10µg/in^2 equivalent NaCl applied to bare printed circuit board manufacturing. Assembly processes will introduce flux residues from soldering. A key difference between this type of contamination and PCB fabrication contamination is localization. Flux residues can be concentrated around solder joints or under components. Because the IPC method is to extract contaminants from an entire PCB or PCBA, and calls for the extracted contamination to be divided by the entire surface area of the board, the levels of flux residues measured may be much lower than actual levels in concentrated areas.

DfR has noted contamination-related failures on boards where the full board had weak organic acid levels measured below DfR's recommended levels. In these cases, visible flux residues are common, typically around solder joints and under components. Interpretation of these recommended levels should account for the possibility of localized residues.

Contaminant	Upper Control Limit (µg/in^2)	Maximum Level (µg/in^2)
Bromide (Br^-)	10	15
Chloride (Cl^-)	2	4
Fluoride (F^-)	1	2
Nitrate(NO_3^-)	4	6
Nitrite (NO_2^-)	4	6
Phosphate (PO_4^{3-})	4	6
Sulfate (SO_4^{2-})	4	6
Total Weak Organic Acids	50	100

Printed Circuit Board Assembly Failures

Excessive contamination on PCBAs is often associated with failures from decreased resistance between conductors that are designed to be electrically insulated. The decrease in resistance and consequent increase in leakage current can be from electrochemical migration (ECM), conductive anodic filament (CAF), or a conductive electrolyte spanning the conductors. As the spacing between conductors decreases with advancing technology, the levels of contamination and especially localized contamination that result in failures are also decreasing.

ECM is a surface process. There are four steps involved in the classical formation of ECM: creation of a pathway between two conductors, electro-dissolution of metal, ionic migration, and electro-deposition. The creation of a path is usually moisture adsorbing or condensing on the surface. The next step requires a metal anode that oxidizes and dissolves forming ions. Once dissolved, metal ions will migrate to and deposit on the cathode. The deposited metal can grow to completely span the conductors or at least decrease the effective conductor spacing. Leakage current may be present during this process, even before a full metal bridge and electrical short.

CAF typically refers to the same process as ECM but within the laminate between internal copper layers or plated through holes. The pathway that CAF follows is often voids, resin starvation, delamination, or drill damage around plated through holes.

In the electronics industry, tin, lead, copper, and silver are the most common metals involved in ECM and CAF. Some metals such as gold and certain steels are usually significantly more resistant to electrochemical oxidation.

However, all that is needed for a leakage current is a conductive pathway, regardless of whether metals are oxidizing and migrating, and regardless of their rates of oxidation and migration. Some leakage current will be passed through any liquid medium with dissolved ionic contamination spanning conductors under bias.

Excessive contamination can also result in failures from increased resistance. The typical mechanism is corrosion of conductors. Conductive metals are attacked by corrosive contamination and form inert or insoluble species. As the conductor volume is reduced, resistance increases.

Specific Contaminants

Some contaminants can lower the relative humidity threshold for water to adsorb to the PCB surfaces. These hygroscopic chemicals may themselves increase the electrical conductivity of a solution.

Extensive case studies have shown that halide ions, primarily chlorine and bromine ions tend to be the most harmful contaminants on a µg/in^2 level comparison.

Chloride

Sources of chloride include an aqueous wash process using water that has not been fully deionized. Reliance on the cleanliness of municipal water can result in intermittent contamination issues because water treatment plants may not tightly control levels of some ions. This is especially true in countries other than the US. Another source of chloride is from handling with bare skin, in particular while in warm, humid environments where sweat on the skin is more likely. Residues of some flux chemistries that are not halide-free may also contain chloride.

Bromide

For epoxy-glass laminate, surface bromide levels typically fall within the range of 0 to 7 µg/in^2, depending upon the amount of flame retardant added by the panel and pre-preg manufacturer. Exposure to reflow conditions tends to increase the porosity of the laminate and solder mask and increases the level of bromide extracted from the sample. With several exposures to reflow conditions, bromide can reach levels as high as 10-12 µg/in^2. Bromide levels less than 10 µg/in^2 are not typically considered detrimental on organic printed circuit boards. However, levels between 10 µg/in^2 and 15 µg/in^2 may increase the risk for failures if attributable to corrosive flux residues. Levels above 15 µg/in^2 should be considered a significant risk of failures, especially if attributable to corrosive flux residues.

Cations

By themselves, cations are not considered a reliability risk unless present in relatively high quantities. In addition, they do not participate in the same chemistries that anions do. Therefore, DfR does not have recommended levels. Cations are sometimes useful in determining sources of the more detrimental anions. Calcium and magnesium are often detected when aqueous wash has not been properly deionized. Sodium, potassium, and ammonium are often used as counter ions to active anion ingredients in cleaning chemistries, various processing chemistries, and fluxes. Sodium may also be introduced by handling with bare skin.

Weak Organic Acids (WOAs)

WOA levels from flux can vary greatly. They are commonly found in liquid wave flux and solder paste fluxes. Levels can vary depending on the liquid delivery method (e.g. foam and spray) and for solder pastes, the preheat and reflow dynamics. Low-solids (no-clean) fluxes typically use WOAs as their primary active ingredients. The amount of detected WOAs is often proportional to the amount of residual flux. Bare printed circuit boards typically do not have WOA residues, but HASL processes typically use strong fluxes that must be thoroughly cleaned afterward, and may be detectable if not properly removed.