

THE EFFECTIVENESS OF 75% IPA/25% DI EXTRACTION SOLUTION ON NO-CLEAN FLUX RESIDUES

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ABSTRACT

Two of the three primary cleanliness test methods for PCBs, Resistance Of Solvent Extract (ROSE) and Ion Chromatography (IC), rely on the assumption that all ionic contamination on a PCB will be soluble in a solution of 75% isopropyl alcohol (IPA) 25% De-ionized water (DI). This assumption is made in the most critical step of an analytical procedure, the extraction step. If this extraction step is not functional or even optimal, then no instruments further down the logical path can correct for poor extraction and you will not know the actual contamination levels on the PCBA. This is why, in many analytical textbooks, extraction studies are covered in the first few chapters, as poor extraction efficiency is the death of an analytical method.

Considering the importance of the extraction step, and that two-thirds of the primary cleanliness assessment methods rely upon the same extraction solution, one would assume that there would be studies that demonstrate the appropriateness of the 75% IPC/25% DI extract solution. Studies showing the relevance of this extract for rosin-based fluxes that were popular in the 1970s have currently existed, but no such studies on newer materials exist on No-Clean fluxes. This is a troublesome fact for the industry as a whole, as subject matter experts agree that the current extraction solution and procedure is unlikely to be efficient with common materials now. However, no studies as to the relevance of the 75% IPA/25% DI extraction studies currently exist. In fact, the solubility of the specific ions tested for in the IC analysis in 75% IPA/25% DI is not only unknown in the industry, but literature searches for this data have yielded nothing. This paper attempts to begin to rectify this situation and promote open discussions on the future of ionic cleanliness test methods.

This study is broken into two parts, first a review of the solubility of some critical ions in different ratios of IPA/DI and at different temperatures. As noted above, despite using this extraction solvent for decades, this essential piece of information is missing. The second is to look at the influence of extraction time on several fluxes under the current standard. Prior work conducted by this team,

indicated that there was a statistically significant increase in the concentration of extracted ions with a 3-hour extraction vs. the standard 1-hour extraction. Due to sample and time constraints, this relationship was not explored further. In this study, we will repeat that study but with more samples, and additional extraction times to determine if this trend is essential or not.

Key words: Ionic Cleanliness; Solubility; Cleaning; Reliability

INTRODUCTION

The continuous challenge in the electronics industry is to keep up with the demand for smaller, faster, and more reliable electronics. This places great strains on both the manufacture and the manufacturers of those electronics. The strain on manufacturing the electronics comes from every direction. Environmental regulations have removed lead from the majority of electronics, forcing materials changes; packages have become smaller with more voltage requirements; complex devices are expected to work reliably for years under harsh environments that a decade ago it would be unimaginable to a circuit designer. These examples and many more combine to create a multitude of challenges.

This rapid development of manufacturing and reliability challenges is juxtaposed with the slow pace of new test method development. Resistance Of Solvent Extract (ROSE) testing is the de facto ionic contamination testing method, primarily because it was developed in the 1970s, when PCBs were becoming more common in military and other high-reliability applications. Briefly, in the ROSE method, a PCB to be tested is submerged in a solution of 75% isopropanol or IPA (but more properly propan-2-ol) and 25% DI water. The change in the resistance of the solution is monitored. As ionic materials dissolve into solution, the resistance of the solution decreases, indicating that there is ionic contamination. This dip in resistance is then converted into the mass of sodium chloride per unit area that would be expected to produce an equivalent dip in the resistance of the solution. Traditionally this is expressed as micrograms of sodium chloride equivalent per square

centimeter ($\mu\text{g NaCl eq. /cm}^2$). Shortly after ROSE's development, the United States Department of Defense decided that a value of $1.56 \mu\text{g NaCl eq. /cm}^2$ was to be used as a criterion for product acceptance; meaning if a particular assembly that was below this value, it would be acceptable for field use.

Relevant to the current work is the decision to use the extraction solution of 75%/25% IPA/DI water. This decision was made because the vast majority of solder fluxes on the market were rosin based, and therefore highly soluble in IPA. This is because the major constituent of rosin is abietic acid, and is highly soluble in IPA¹. The true systematic name for abietic acid is abieta-7,13-dien-18-oic acid (CAS Number 514-10-3) and it is shown as Figure 1². It is commonly cited as virtually insoluble in water, but it does exhibit some solubility in water³. It is also known to be highly soluble in various organic solvents, although exact numbers are hard to come by^{2,4,5}. Once dissolved into solution abietic acid can ionize into an electrically conductive species that can be measured by resistance. This is what characterizes abietic acid as what our industry calls, Weak Organic Acids (WOAs). The degree to which the ionization occurs is highly dependent on pH, but will cause a change in resistance none the less.

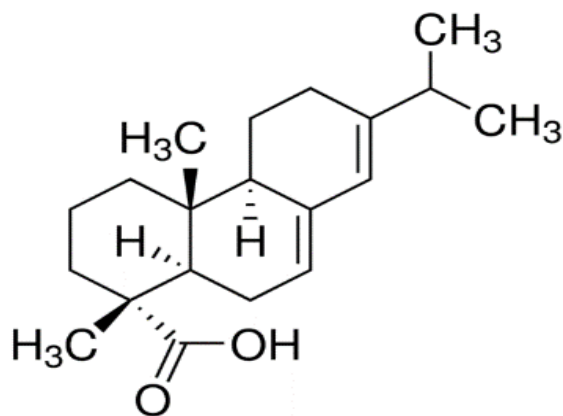


Figure 1. Abietic Structure [1]

As time progressed newer fluxes entered the market which were not based on rosin, namely Water Soluble (WS), sometimes called “water wash flux”, and No Clean (NC) or “low residue flux.” There are a multitude of reasons why these fluxes came onto the market, and why they necessitated different WOAs but those are beyond the scope of this paper. The flux manufacturers turned towards a different type of organic acid, linear dicarboxylic acids. Dicarboxylic acids are organic molecules which have two carboxylic acid groups and linear dicarboxylic acids are simply the dicarboxylic acid derivatives of straight chain hydrocarbons. The exact identities of the dicarboxylic acids used are considered proprietary, but there are a series of dicarboxylic acids that have been reported in the literature such as: adipic acid, succinic acid, glutaric acid, malic acid^{6,7}, and more recently pimelic acid⁸. Table 1 shows the structure of these acids⁹. The important thing to note from

the structures in Table 1 is that they are substantially different from that of abietic acid, and as a result, they all have some degree of solubility in water.

Table 1. Common Dicarboxylic Acids [9]

Number of carbons (straight)	Common name	Formula
C2	Oxalic acid (ethanedioic acid)	HOCCOOH
C3	Malonic acid (propanedioic acid)	HOOCCH ₂ COOH
C4	Succinic acid (butanedioic acid)	HOOC(CH ₂) ₂ COOH
C5	Glutaric acid (pentanedioic acid)	HOOC(CH ₂) ₃ COOH
C6	Adipic acid (hexanedioic acid)	HOOC(CH ₂) ₄ COOH
C7	Pimelic acid (heptanedioic acid)	HOOC(CH ₂) ₅ COOH
C8	Suberic acid (octanedioic acid)	HOOC(CH ₂) ₆ COOH
C9	Azelaic acid (nonanedioic acid)	HOOC(CH ₂) ₇ COOH
C10	Sebacic acid (decanedioic acid)	HOOC(CH ₂) ₈ COOH

One additional consideration is that the WOAs can react. One known chemical reaction that they undergo is acid-base reactions. In this reaction, WOAs react with a base, such as an amine activator, metals, or other bases that are present. These result in the formation of a salt. Typically organic salts are more soluble in water than organic solvents; in fact this property is a common way to purify WOAs¹⁰. It is suspected by the authors that these WOA salts are capable of causing current leakage paths, or even ECM. This is because these salts, when dissolve results in the formation of an electrolyte solution.

During this time a new cleanliness assessment method was introduced to the industry in the form of Ion Chromatography (IC). IC is an analytical technique from the liquid chromatography family and can be used to identify and quantify ionic species in solution. A small portion of a liquid sample (typical volume ~25 μL) is injected into a moving fluid called an eluent. The eluent carries the sample to an analytical column. This column consists of very fine particles coated with an ionic compound. This coating attracts the ions of interest, slowing them down. The degree of this slowing depends on a number of factors, but the ultimate goal is to slow each ion of interest down enough that they travel as discrete bands in the plumbing of the instrument. This causes the ions to be removed, by the eluent, from the column at different times. The eluent exiting the column passes through a conductivity cell, where the conductivity is continuously measured. When these bands of ions pass through the detector a large peak forms from the ion. The size of the peak is

proportional to the amount of ions present and the time from injection it takes to appear is characteristic (but not conclusive) of different ions¹¹. Despite these changes, no changes to the extraction solvent was made. It was assumed that the WOAs of Table 1 would be equally soluble in 75%/25% IPA/DI water as abietic acid is. An informal survey within the industry revealed that no one knew the answer to the question “What *is* the solubility of common WOAs in IPA/DI water mixtures?” This is a critical question as for detecting ions via conductivity, which is used in both ROSE and IC, they must be dissolved in solution.

It is relatively easy to find the solubility of most WOAs in water. It is somewhat more difficult, but still possible, to find the solubility of WOAs in common solvents, such as IPA. What is virtually impossible to find in literature is the solubility of WOAs in a mixed solvent system. Many complex factors and interactions govern solubility. These factors are not additive nor linear. A literature review found only a few cases where the solubility of abietic acid or any dicarboxylic acids of interest were measured^{12,13}. Generally, this was under conditions that were not similar to those in industry. It was with this stumbling block the solubility was to be investigated

METHODS

1.) Gravimetric:

To assess the solubility of abietic acid, glutaric acid, malic acid, succinic acid, and sodium succinate saturated solutions of each were prepared in the solvent systems indicated in Table 2. To do this each acid was obtained from Sigma Aldrich and was used without any further purification. Next the acids were placed in 250 mL jars with a magnetic stir bar and a quantity of the chosen solvent. The jars were sealed and vigorously stirred at room temperature (20-25°C) for at least one week. A substantial excess of acid was used to ensure that solubility was reached, as indicated by a large amount of undissolved acid. Next each solution was transferred into four pre-weighed vials using a syringe and a 5 µm membrane filter to remove any suspended solids. The

weight of all vials were recorded. The vials were then placed in a dry bath at 110 °C until they reached a constant weight, indicating dryness. For all weights an analytical balance with an accuracy of ±0.0001 g was used.

Table 2. Solvent Systems

IPA (%V)	DI (%V)
0%	100%
10%	90%
50%	50%
75%	25%
100%	0%

2.) Ion Chromatography:

A parallel study was undertaken to approach the issue for the other direction, namely looking at changes in ion concentration as a function of extraction solvent, as measured by IC. A total of twenty-five boards were printed with an industry standard NC solder paste. The boards were reflowed, without populating the QFN components, in a standard reflow profile. After reflow, boards were randomly assigned an extraction solution from Table 2. A total of five boards were used for each solvent tested. Each board was extracted individually per IPC-TM-650 2.3.28 (80° C for 1 hour). The extraction volume was held constant for all boards. Twelve of the samples were analyzed immediately by Laboratory A, who produced the boards. Thirteen of the samples were sent to Laboratory B for analysis.

RESULTS

Gravimetric

The results of the gravimetric method is presented as Figure 2. The plots show all four replicates plotted for each IPA concentration as well as a LOESS fit, with standard error shown.

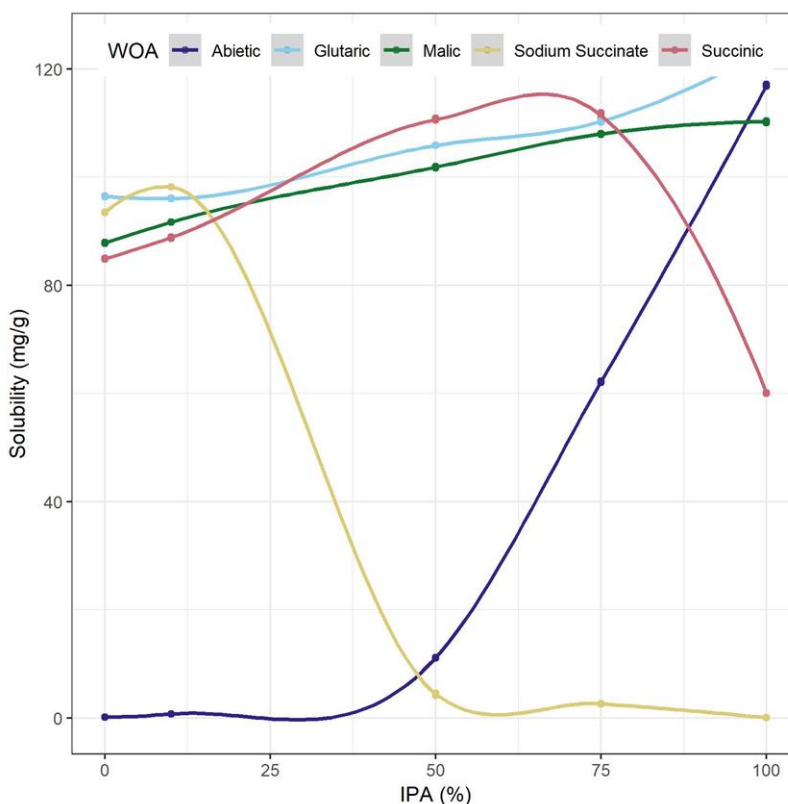


Figure 2. Gravimetric Results

Ion Chromatography

Due to instrument errors, the full data set is not available at the time of writing. Preliminary data is available and discussed, along with future work. IC results for the total WOA extracted from each board is presented only, to protect proprietary information. This is presented as Figure 3.

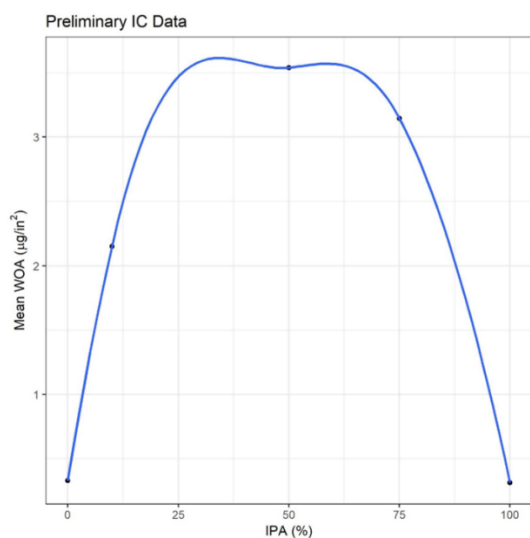


Figure 3. Preliminary IC Results

INFERENCES

The results of these findings would seem to have practical impacts on measuring the reliability of PCBAs. The gravimetric results indicate that more “modern” WOAs are soluble in pure water about as much as they are in IPA. However, if the WOA forms a salt with a base, the trend is the opposite. These salts would still be capable of electrochemical migration and to serve as a leakage path for current. The IC data shows a different picture, however. The maximum extraction appears to be around 50%/50% IPA/DI water. This indicates that it is possible that ROSE and IC under report contamination, as there could be more ions present than are soluble under a different concentration of IPA. It is suspected that a non-extraction based technique such as SIR may have an advantage over ROSE or IC.

CONCLUSIONS

Gravimetric

At the present time, there is not enough data in literature to confirm the gravimetric findings, so additional work will be needed. The WOA with the most available solubility data from reputable sources is succinic acid. The solubility in pure DI water ranges from 77 mg/mL¹⁴ to 83 mg/mL¹⁵. Our reported value was 84.8 ± 0.06^9 mg/mL, which is in good agreement. However, the solubility in IPA and/or IPA + water is not readily available. The solubility of succinic acid in similar alcohols is 57 mg/mL for ethanol, and 158 mg/mL for methanol¹⁴. Our value for pure IPA was 60.0 ± 0.02^4 mg/mL, which seems plausible. The data for malic acid and glutaric acid is suspect, as our values are substantially less than those found in the literature.

While there is a lack of solid data in literature for the solubility of the WOAs in solvent mixtures, the trends do match what might be expected. Abietic acid needs a critical amount of organic solvent to begin to be solubilized. While not discussed in this paper sodium succinate was expected to follow an opposite trend than the other materials, as it is a salt, as salts tend to have less solubility in organic solvents than their acid counterparts. The flux reactions should generate different salts of WOAs, which would be less detectable, but equally as harmful as their parent acid compounds.

Ion Chromatography

The IC data is interesting but does not have enough of a sample size to draw any firm conclusions. What is clear from the data is that the solubility of all of the WOAs is not linear with IPA concentration, for this particular solder flux. It appears that, for the flux studied, there is an optimum IPA concentration, which *may* be located around 50% IPA 50% DI water. This indicates that the commonly used 75% IPA 25% DI water system may not be optimal.

FURTHER WORK

The findings of this study are interesting and warrant further investigation. To better refine the gravimetric data for the WOAs understudy a complimentary solubility determination method will be used. Top contenders for this method are titrations, ultraviolet-visible spectroscopy (UV-VIS), laser solubility determination, or a synthetic method^{16,17}. These methods have potential for being much more sensitive than the gravimetric method. The UV-VIS method is currently being explored. In addition to additional experimental work for the solubility of WOA in mixed solvent systems, a theoretical approach using Hansen Solubility Parameters is being undertaken¹⁸. In addition to improving the data as a function of IPA concentration, the temperature dependence of the solubility is of critical importance.

The IC work is being continued as well. Currently, additional IC samples are being run at Laboratory B. This work will be updated and expanded to additional fluxes. The specific flux used is suspected to be a substantial factor in the amount of extractable WOA ions.

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