

SOLVENT EXTRACTION MATRIX SELECTION AND ITS POTENTIAL AFFECTS ON CLEANLINESS TEST RESULTS

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ABSTRACT

Ion Chromatography (IC) is the predominant instrument used in the determination of overall cleanliness of printed circuit boards (PCB) and assemblies (PCA) in the medical device industry. Cleanliness testing should be one of many steps in your quality assurance process and its importance is critical as a first step in predicting overall product reliability.

Cleanliness requirements used by our medical product-based customers will be presented and discussed as well as compared to those requirements present in the non-medical product based industry.

Most customers develop specifications for cleanliness testing on their own, but as a common thread, most of them reference the use of IPC-TM-650, method 2.3.28A – “Ionic Analysis of Circuit Boards, Ion Chromatography Method” as the testing procedure. Whether known or not, other ion chromatography-based cleanliness test methods are available for use, specifically those from Delphi Automotive Systems and the US military. Although major differences are not present when comparing the methods, one striking difference is present: the solvent extraction matrix.

Overall, DI water and isopropyl alcohol / DI water solutions appear to be the matrices of choice. But why? And more importantly, which is the “best” matrix to choose? And does it really matter which matrix is chosen?

This presentation covers an internal study focused on determining the affects, if any, of the solvent extract matrix selection on the cleanliness results of a given sample. Additional relevant topics will also be addressed and discussed. Specifically, if differences are present, do these differences show any trends between the different matrices that may help in explaining why one matrix should be used instead of another? And also, should the products’ end use have any determining factor in which matrix is selected?

Key words: Ion Chromatography, IC, cleanliness, PCB, PCA

INTRODUCTION

The use of Ion Chromatography (IC) as an analytical tool in the qualification of a printed circuit assembly process is in increasing demand. As the importance of cleanliness increases with changes in raw materials, fluxes, solders, etc.,

more specialized testing equipment is needed to help decipher problems when they arise. New chemistries are constantly being developed and printed circuit assemblies, due to their applications, are changing in size and shape. Specifically, as circuit trace and component spacings become tighter and tighter, surface cleanliness becomes exponentially more critical.

Currently, industry specifications include cleanliness testing of some variety as part of most regimented qualification processes. For years, this testing was highlighted by bulk conductivity readings of a “solvent extract” of the assembly under test (specifically IPC-TM-650, method 2.3.25, also known as the “ROSE” Test). As time has passed, more information than a simple conductivity measurement is needed. With that, IC provides that information.

IC can be used as a failure analysis tool such that the measurement of specific ion concentrations can help in determining the origin of a detected contaminant or even suggest possible root causes for observed “failure” related issues. IC test methods are now available industry-wide, as well as from individual customers, that address the many different printed circuit board / assembly sectors. IPC, Delphi Automotive Systems, and the US Military, along with others, have all developed IC test methods and in some cases requirements that address everything from bare printed circuit boards to populated printed circuit assemblies to housing materials to surface mount adhesives.

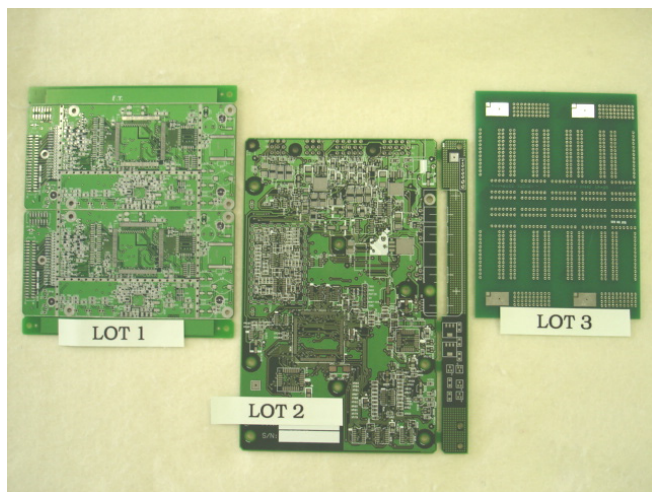
With all of these different IC test methods and different sample types, the one striking variation in each of the procedures is the solvent extract matrix used in the specific sample preparations. Deionized (DI) water and isopropyl alcohol (IPA) / DI water solutions appear to be the matrices of choice. For this study, we focused on determining if there is any affect on the cleanliness results of a sample based on extract matrix selection. Additionally, if differences are present, which we expect, do the differences show any trends between the different matrices? These trends could be in respect to a specific ion, overall ionic conductivity, etc.

The use of the “standard” 75% IPA in DI water extract solution dates back to the 1960’s. This solution was chosen by the US Military, and later IPC, for their cleanliness-based test methods due to its ability to solublize the residues of fluxes, which were used in that time period.

METHODOLOGY

For the study, three (3) lots of bare printed circuit boards (see Photograph 1) were obtained from three (3) different printed circuit board manufacturers.

- Lot 1 = 76.6 sq. in. – solder mask coated
- Lot 2 = 94.0 sq. in. – solder mask coated
- Lot 3 = 52.2 sq. in. – non-solder mask coated



Photograph 1. Representative overview of individual printed circuit board specimens

From these lots, five (5) PCB specimens were tested via IC after sample extraction using three (3) different extract matrices: DI water, 10% isopropyl alcohol in DI water (10% IPA), and 75% isopropyl alcohol in DI water (75% IPA). The IC extraction procedure placed each PCB specimen along with an appropriate amount of extract solution (approximately 1.0 – 1.3 mL solution per square inch of board area) into an individual ion-free bag that was then heat sealed and placed into a water bath at 80°C for 1 hour (per IPC-TM-650, method 2.3.28A).

In addition to the extract solutions obtained from the three (3) different extract matrices listed above, a set of rinse solutions was obtained by using one (1) of the same matrices, the 75% IPA matrix, but in a different preparation technique.

This set of rinse solutions was obtained by performing the “ROSE” test, “solvent extract” method – IPC-TM-650, method 2.3.25, on a group of five (5) PCB specimens from each of the three (3) lots.

All of the extract and rinse solutions collected were then analyzed both by IC as well as in the traditional manner through a Bulk Conductivity Analysis.

For the IC analysis, the extract and rinse solutions and appropriate “blanks” were analyzed for specific ion content using a Dionex DX-500 Ion Chromatograph (see Photograph 2) with an AS11 column for anion analysis and

a CS12A column for cation analysis. A five-level calibration for both anions and cations was performed. Samples were run through a 175-microliter sample loop in a sodium hydroxide eluent with self-regenerating suppression for anion analysis and through a 200-microliter sample loop in a methane sulfonic acid eluent with self-regenerating suppression for cation analysis. A conductivity detector was then used to measure the ionic activity for each sample.



Photograph 2. Overview of Ion Chromatography instrumentation

With the ion chromatograph, ionic data for seven (7) anions, five (5) weak organic acid (WOA) anions, and six (6) cations was obtained for each of the solutions. Specifically, these ionic species were as follows:

Table 1. Measured ionic species

Anions	WOA Anions	Cations
Fluoride	Acetate	Lithium
Chloride	Formate	Sodium
Nitrite	MSA	Ammonium
Bromide	Adipate	Potassium
Nitrate	Succinate	Magnesium
Sulfate		Calcium
Phosphate		

For the Bulk Conductivity Analysis, the extract and rinse solutions and appropriate “blanks” were analyzed for total ion content using an Omega CDB-410 conductivity meter (see Photograph 3) with a conductivity cell having a cell constant of 0.98 cm⁻¹.



Photograph 3. Overview of Conductivity Meter

RESULTS AND INTERPRETATION

For the “extracted” samples a few trends are visible in the data obtained. Even though the analyzed PCB specimens do not necessarily have the same process history, for example, two (2) of the three (3) board types used in the analysis are solder mask coated while the third is not, the processing amongst an individual group is the same. Sample history / processing is an important issue when analyzing the results of cleanliness testing but truly only when one is trying to determine where a certain ionic species is originating. For this study, or any other similar study, the processing is not much of an issue except that it may shed some light on any chemistry / solubility issues that might be present.

The following figures, in graphical form, summarize the IC data obtained. In the figure below it is obvious that the ionic contamination levels present on each lot of specimens varies greatly.

For instance, Lot 3 would appear graphically to suggest the presence of a lesser amount of contamination in respect to the other lots, however upon closer examination of the data, one can see that there is actually more contamination present if not biased by the scaling of the graphs. For Lots 1 and 2, the maximum amount detected for any one specific species failed to exceed 6.00 µg/sq. in and 3.00 µg/sq. in, respectively, however for Lot 3, numerous species were actually detected above both of these maximum levels.

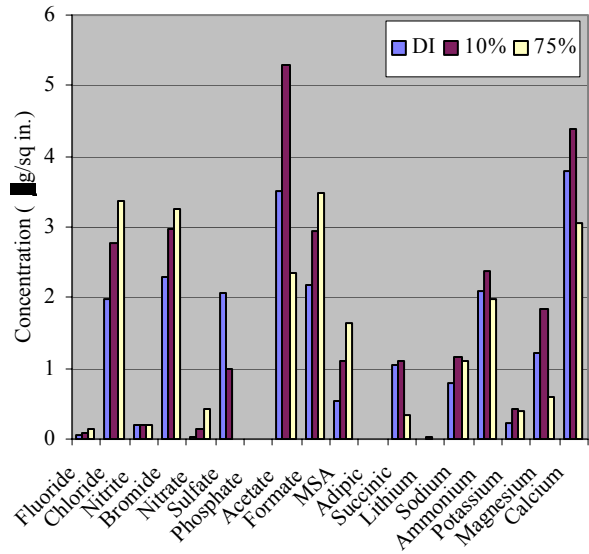


Figure 1. Lot 1 IC Results

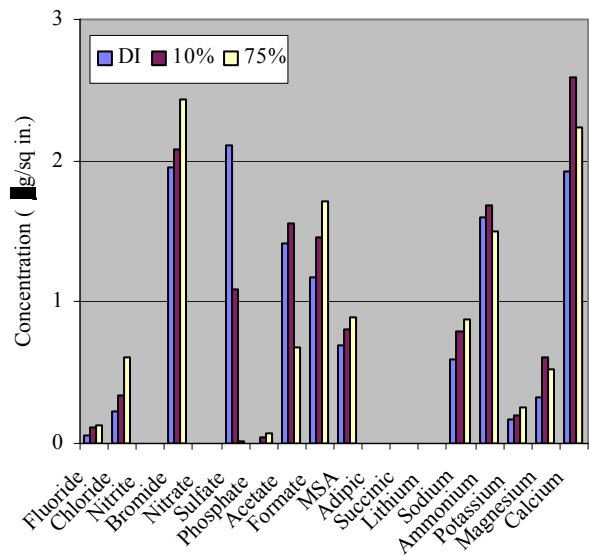


Figure 2. Lot 2 IC Results

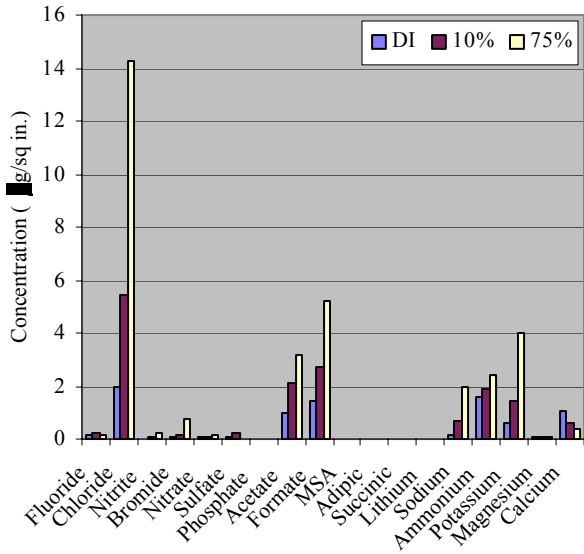


Figure 3. Lot 3 IC Results

While it is possible that some trends may be obscured by the sample type and sample processing history described above, a few trends are still evident and are pertinent.

- The concentrations of chloride, bromide, nitrate, formate, and MSA increase with increasing IPA concentration in the matrix, while the concentration of sulfate decreases to zero with an increasing concentration of IPA (see Figure 4)

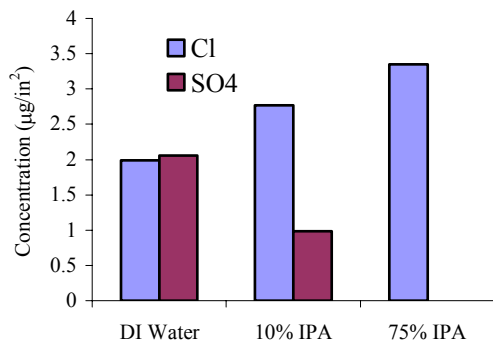


Figure 4. Representative Results for Chloride (Cl) and Sulfate (SO₄) by Extract Matrix

- There is, in one-way or another, always “fluctuation” in the ionic concentrations (µg of ion / sq in.) detected
- For most of the cation species, the ionic concentration values typically increase from the DI water matrix to the 10% IPA matrix and then either hold steady for the 75% IPA matrix or decrease back down towards the DI water matrix value

For the remaining ions, some trends can be observed within a particular sample group, however these trends do not hold across every group. As an example, for most of the cation species, the ionic concentration values typically increase from the DI water matrix to the 10% IPA matrix and then either hold steady for the 75% IPA matrix or decrease back down towards the DI water matrix value. In these cases, the trend may be that there is no “true” trend as might also be the case with some of the remaining ionic species.

As an additional analysis of interest, the specific ion results obtained from the “ROSE” rinse solutions, in comparison to the matrix specific results, suggests that the “ROSE” sample preparation procedure in almost every instance, fails to extract similar ionic levels from the same samples. Even from a bulk conductivity standpoint, the ultimate result in the “ROSE” test methodology, the IC extracts had significantly higher conductivity readings, 2 to 4 orders of magnitude in some cases, than that of the “ROSE” rinse solutions. Also, for the IC extracts, the bulk conductivity readings increased with decreasing amounts of IPA in the matrix.

DISCUSSION AND FUTURE STUDY

Ionic cleanliness level requirements vary depending on the industry in which the products are used. The industry issue is critical due to the reliability desired. The tables below summarize some of the requirements. None of these requirements are industry-wide; individual corporations have specified each set of requirements.

Table 2. Cleanliness Requirements, µg/sq in. – Medical

Ions	Bare PCB	Components, Bare PCB, PCA
Fluoride		---
Chloride		< 3.0
Nitrite		---
Bromide	Each < 0.52	< 6.0
Nitrate		< 4.0
Sulfate		< 4.0
Phosphate		< 4.0
Acetate		< 4.0
Formate		< 4.0
MSA	None specified	< 2.0
Adipate		
Succinate		< 30.0
Lithium		---
Sodium		< 4.0
Ammonium	Each < 1.00	< 4.0
Potassium		< 4.0
Magnesium		---
Calcium		---
Total Anions	< 1.61	---
Total WOA	< 5.00	---
Total Cations	< 3.20	---

Table 3. Cleanliness Requirements, $\mu\text{g}/\text{sq in.}$ – Non-Medical

Ions	Automotive – HASL PCB	Automotive – OSP PCB	Automotive – Ni/Au PCB
Chloride	< 4.84	< 4.84	< 4.84
Bromide	< 6.45	< 6.45	< 6.45
Na + K	< 12.90	< 25.81	< 12.90
Fluoride			
Chloride			
Bromide			
Nitrate			
Nitrite			
Sulfate			
Phosphate	Total	Total	Total
Sodium	< 24.52	< 38.06	< 24.52
Potassium			
Lithium			
Ammonium			
Magnesium			
Calcium			

Table 4. Cleanliness Requirements, $\mu\text{g}/\text{sq in.}$ – Non-Medical

Ions	Automotive – PCB’s Any Finish	PCA’s
Fluoride	---	< 3.0
Chloride	< 8.0	< 6.0
Nitrite	---	---
Bromide	< 15.0	< 10.0
Nitrate	---	< 7.0
Sulfate	---	< 10.0
Phosphate	---	< 7.0
Acetate	---	
Formate	---	
MSA	---	< 300.0
Adipate	---	
Succinate	---	
Lithium	---	---
Sodium	---	---
Ammonium	---	---
Potassium	---	---
Magnesium	---	---
Calcium	---	---

Of interest in regards to the requirement tables above, the values listed in Tables 2 and 4 are based on a sample extraction using the 75% IPA extract matrix, while the values listed in Table 3 are based on a sample extraction using the 10% IPA extract matrix.

When applying the requirements from Table 2, for the medical industry, to the values obtained for the test specimens the importance of extract matrix selection is clearly evident.

For example, when comparing the chloride requirements specified in Table 2 above to the chloride levels detected for each lot of specimens analyzed, both “passing” and “failing” levels were found.

When using the “< 0.52 $\mu\text{g}/\text{sq in.}$ ” requirement, the specimens extracted with the DI water and 10% IPA matrices for Lot 2 would meet the requirement, while the remaining lot / matrix combinations would not meet the requirement.

When using the “< 3.0 $\mu\text{g}/\text{sq in.}$ ” requirement, the pass / fail determinations are a little more complicated. For Lot 1, the specimens extracted with the DI water and 10% IPA matrices would meet the requirement. For Lot 2, all of the specimens would meet the requirement. For Lot 3, only the specimens extracted with the DI water matrix would meet the requirement.

This exact scenario is the reason why extraction matrix selection is critical.

In respect to the analysis performed on the “ROSE” rinse solutions, virtually no anion content was detected with very little cation content either. The specific ion results simply suggest that the extraction procedure for the normal IC test methods is more successful at removing ionic species from the surface of a given specimen. Even from a bulk conductivity standpoint, the solutions prepared from the “ROSE” test methodology are 1,000 to 10,000 times lower than the IC test methodology.

Whether the procedure is “better” is up for debate, but from a cleanliness standpoint, the “ROSE” test does not appear to give a completely accurate account of the ionic material present or more specifically, the “ROSE” sample preparation procedure appears to only remove a small portion of the ions that are removed by any IC procedure / extraction matrix combination.

There is a strong correlation between the IC and Bulk Conductivity results, however one must first realize some key characteristics of conductivity-based measurements – for example...

- 5 ppm of chloride in a DI water only matrix will not conduct the same as 5 ppm of chloride in an IPA / DI water matrix
- 5 ppm of chloride in a DI water only matrix will not conduct the same as 5 ppm of bromide in a DI water only matrix

The figures below compare the relationship between the summations of the ionic species detected by IC in the various extraction solutions to the bulk conductivity of those same extraction solutions.

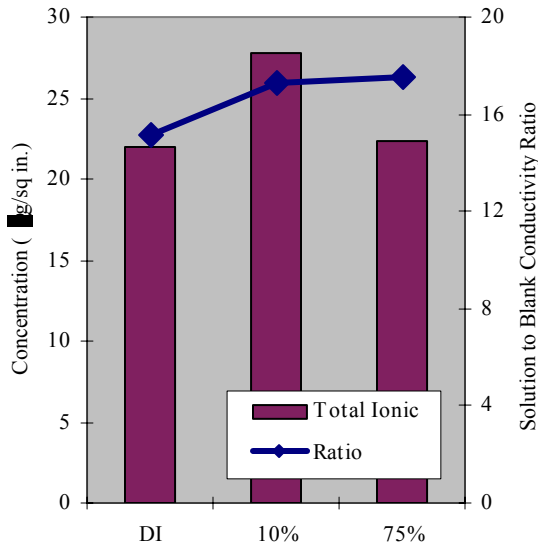


Figure 5. Comparison of Total Ionic Concentration to Bulk Conductivity Results for Lot 1

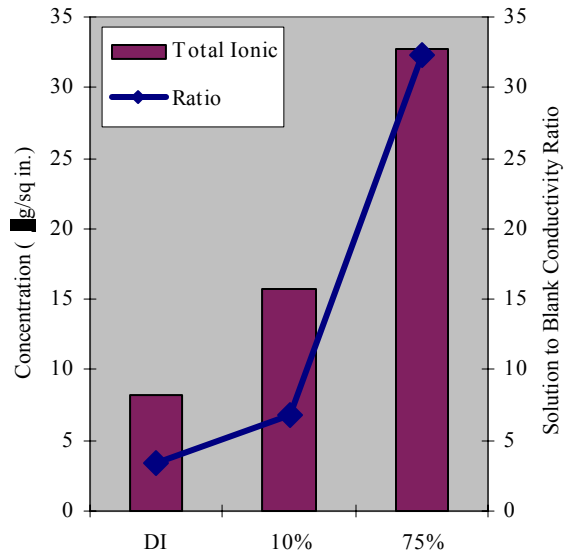


Figure 7. Comparison of Total Ionic Concentration to Bulk Conductivity Results for Lot 3

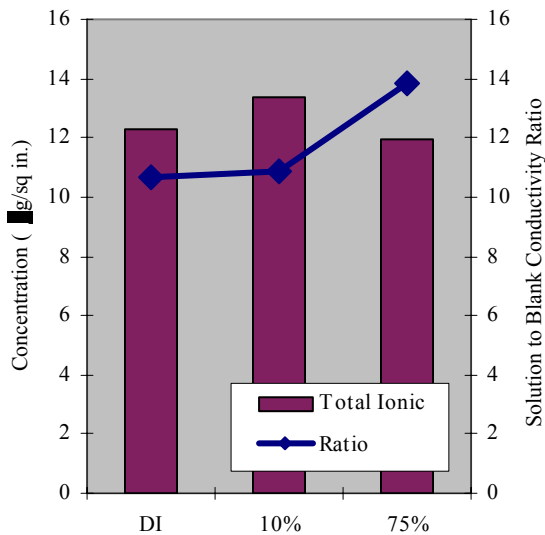


Figure 6. Comparison of Total Ionic Concentration to Bulk Conductivity Results for Lot 2

Studying the results of the experiment, we developed one plausible theory, that being – deionized water removes all soluble ions from the surface of the boards and that the addition of IPA only aids in the extraction of ions from within the sample.

This observation is most evident in the testing of the non-solder mask coated specimens, Lot 3, from the fact that for each of the ionic species detected, the actual levels found were significantly higher than for either the Lot 1 or Lot 2 specimens.

Additionally, in the case of sulfate, a greater concentration of IPA in the extraction matrix appears to reduce the solubility of the ion.

Considering that the real-world concern of ionic contamination is its mobility in the presence of moisture, it is logical that testing with DI water only is potentially a more realistic choice than testing with an IPA-containing matrix.

We hope to prove this theory with additional testing. We will repeat the above detailed experiment on materials that are impervious, or relatively impervious, to internal extraction with IPA. We will use materials such as metal, plastic, and possibly glass.

However, until our theory is proved or disproved, it is obvious that IC results using differing matrices cannot be correlated. It is plausible that samples would produce a “passing” ionic cleanliness result based on the extract matrix called out in a particular test method or specification while the same samples would produce a “failing” result using a different extraction matrix – or vice versa.