

**Guidelines for
Measuring Anionic
Contamination of
Printed Circuit Boards
(PCB) & Circuit
Assemblies (PCA)
using
Ion Chromatography**

L Zou, A Brewin and C Hunt

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Guidelines for Measuring Anionic Contamination of Printed Circuit Boards (PCB) and Circuit Assemblies (PCA) using Ion Chromatography

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Abstract

This document provides the procedure to identify the level of anionic contamination residues on printed circuit boards (PCBs) and circuit assemblies (PCAs) using Ion Chromatography (IC). Recommendations for test parameter settings and sample preparation to optimise the IC system performance, are provided. Specific issues relevant to testing PCBs and PCAs (resin content in the flux, and solvent fraction in the extract solution), are discussed. Details are given on achieving robust and stable IC measurements when rosin is present in the extract samples, based on prefiltering. A chemical selective disposable cartridge is used to remove rosin from the sample stage, and an in-line trap column is used to prevent contamination of the analytical column. Since the use of a 75% IPA solution (as recommended in IPC TM650 2.3.28) causes background shift, the use of a low IPA content extraction solution is also strongly recommended, in order to eliminate rosin dissolved in the test samples.

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1 Introduction

Achieving high reliability is increasingly the key issue in today's electronic industry. A major factor influencing reliability is the cleanliness of the printed circuit boards (PCBs) and assemblies (PCAs) themselves, in which mobile ionic residual contamination from various processing steps may lead to an electromigration risk, via dendritic growth and subsequent reliability issues. Therefore board cleanliness is very important. There are several analytical techniques that may be used to identify residues, but one that is finding widespread acceptance is ion chromatography (IC). This decision is based on the relevance of the information provided and the cost for routine testing. The extraction method is relevant to the use environment, and the sensitivity of IC to relevant residues is excellent. Hence IC provides a unique capability for identifying and quantifying individual ions for a given contamination issue, and hence for trouble-shooting failures. For PCAs that are subjected to a number of production and cleaning process, identification of specific ions can aid in correcting the root cause of problems. In consequence, IC is now regarded as a valuable tool for process contamination and process monitoring.

Ion chromatography provides quantitative anion identification, but to apply the technique reliably to electronic boards certain aspects of the technique need to be optimised. A suitable analytical column must be selected, and test parameter settings derived, to achieve the optimum anion separation from the circuit board extract solution. The extract solution itself must be efficient at extracting the residues, but not so powerful that it dissolves the PCA structure. A typical extract solution is a mixture of iso-propyl alcohol (IPA) and water, usually with 75% IPA.

It is common for residues to contain flux contamination, and in particular resins, which this work has shown to be problematical. Although rosin, a natural resin, has been a constituent of fluxes for a long time (historically at levels up to 25%), today it is more typically at a level of a few per cent, and found in many formulations. Rosin is a natural product and varies from batch to batch, containing mainly three weak carboxylic acids, abietic, neoabietic and dehydroabietic acid. It is removed from the board when IPA is used in the extract solution, but when the extract solution is injected into the IC, in which the eluent is KOH, the rosin is likely to be deposited from solution. Since rosin is a hydrophobic material with near zero solubility in water, within the IC system it will readily bond to the active sites of the analytical column, reducing anion exchange sites and leading to unstable anion retention time. This will result in peak identification problems and lost anion resolution.

The existing IPC TM650 2.3.28 standard specifies the use of a 75% IPA solution as the extract solution, and that was the initial basis for the work done here. Avoiding

rosin in the extract solution can be achieved by either of two procedures; (i) at the sample stage by passing the extract solution through a chemical selective cartridge, or (ii) after injection into the IC, by passing the solution through an inline trap column before the analytical column. Tests have shown that after removing the rosin correct anion levels are measured. An alternative extract solution with a low IPA content, 10%, was also evaluated. It is shown here that this solution eliminates rosin dissolution into the extraction solution, but can still retain good extraction efficiency for the anions of interest.

This document details the equipment, test conditions, parameter settings, and sample preparation for optimum IC analysis of extracts from PCBs and PCAs.

2 Ion Chromatography

Ion chromatography is a form of liquid chromatography. The technique is based on analytical separation of ions from a solution, by passing the solution over a specialised column material. The simplest ion chromatograph system comprises a sample injection system, a pump, an analytical column, a suppressor and a detector, as shown in Figure 1.

The analysis begins with a portion of the sample injected into the IC system, mixing with the eluent and then passed to the analytical column. The analytical column separates the ions of interest in the sample into narrow bands within the stream of the eluent. Thus, by the time the sample leaves the analytical column, dissimilar ions are separated and leave the analytical column at different times. The eluent then sweeps these groups of ions into the suppressor device. This device electrolytically transforms the eluent into pure water to be swept along to the conductivity detector, so removing interfering ions. The detection of the ions is based on their conductivity relative to the water eluent.

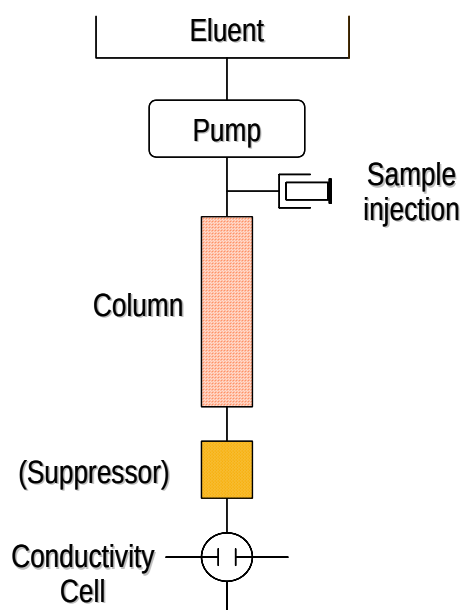


Figure 1: Diagram of ion chromatography system

3 Equipments and materials

3.1 Equipment

1. Ion Chromatograph capable of anion detection of better than 50 ppb
2. Water bath capable of sustaining a constant temperature of $80 \pm 2^{\circ}\text{C}$.

3.2 Materials

1. Clean room gloves.
2. KAPAC (available from 3M) plastic bags, or other ion-free equivalent bags.
3. Deionised water with a resistivity of at least 18.0 megohm-centimetre, and electronic grade or better 2-Propanol (IPA)
4. HPLC or IC grade chemicals for compounds or anions of interest, suitable for creating a series of calibration standards (specified in Section 4.1)
5. 125 ml high-density polyethylene containers.
6. OnGuard II RP disposable cartridge and 5 ml plastic syringe.

4 Standard solution and test sample preparation

4.1 Preparation of standard solution

4.1.1 Stock anion standard solution

For analysis of PCB/PCA residues it is recommended that a 10 anion calibration solution is used, and contains:

- Fluoride
- Acetate
- Formate
- Chloride
- Bromide
- Nitrate
- Adipic
- Succinic
- Sulphate
- Phosphate

Fluoride, chloride, bromide, nitrate, sulphate and phosphate are available as 1000 ppm anion standard solutions from commercial sources, such as Fishers. When commercial standards are unavailable, 1000 ppm standards can be prepared by dissolving the appropriate amounts of corresponding mass for the target analytes in 1000 ml of deionised water according to Table 1. Then 100 ml final volume of 1000 ppm stock standard can be kept in 125 ml high-density polyethylene containers. Concentrated standards are stable for at least six months when stored at 4°C.

**Table 1: Amounts of compounds used to prepare
1000 ml of 1000 ppm anion standards**

Anion	Compound	Mass (g)
Acetate	Sodium acetate ($\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$)	2.31
Formate	Sodium formate (HCOONa)	1.51
Adipic	Adipic acid ($\text{C}_6\text{H}_{10}\text{O}_4$)	1.01
Succinic	Succinic acid ($\text{C}_4\text{H}_6\text{O}_4$)	1.01

4.1.2 Composite standard Solution

Composite standards at lower analyte concentration are diluted from the 1000 ppm standard stock solution. By dilution, low concentration standards can be prepared at 0.1, 0.5, 1.0, 2.5 and 5.0 µg/ml for use as system calibration solutions. Low concentration standards should be disposed of after one month.

4.2 PCB extraction

1.a.1. 4.2.1 Extraction solution

Prepare 10/90 v/v IPA / DI water extract solution. According to the experimental results in Appendix 2, 10% IPA extraction solution is strongly recommended as the extract solution for use with PCBs. The current IPC standard recommends a 75% IPA extract solution which has been shown to dissolve rosin. The use of 10% IPA extract solution minimises rosin dissolution, yet still retains a high extraction efficiency for the anions of interest from electronic boards. The use of 10% IPA also does not distort the IC baseline as much, an important factor when looking at low levels of anions with a weak strength. Using a 10% IPA solution obviates the need to pre-filter and the removal of rosin prior to injection into the IC.

1.a.2. 4.2.2 Extraction procedure

1. Place the boards individually into the bags specified in Section 3.2. If the bag being used is significantly larger than the PCB/PCA then it should be effectively reduced in size using a heat-sealer. The bag should be sized to fit the board with about 5 cm excess on each side to minimize extraction solution, with 10 cm at the top to allow for air expansion when the bag is heated.
2. Add a known volume of the extraction solution to the bag, covering the PCB/PCA. As a guide use 0.5 ml/cm² of surface area.
3. Heat-seal all sample bags and place the bags in an 80 ± 2 °C water bath for 60 ± 5 min.
4. Remove the bags from water bath and shake them vigorously for ten seconds to mix the contents. Allow the solution within the bag to cool to ambient temperature before opening.
5. Record the surface area of PCB (length × width × 2). As a general rule for PCAs, the surface area is calculated as: (length × width × 2) + 10% (to allow for components).

4.3 Test sample preparation

If the test sample is 10% IPA solution, the sample can be analysed directly using the IC system. If the test sample is a 75% IPA solution, the sample needs to be treated to remove possible rosin. Use a OnGuard II RP disposable cartridge (or similar) to remove the risk of rosin contamination, to ensure stable IC performance. A syringe and OnGuard II RP disposable cartridge are shown in Figure 4 for flushing through of the sample. This procedure is assessed in Appendix 3.



Figure 4: OnGuard II RP disposable cartridge

Sample treatment procedure:

1. Prepare the OnGuard II RP by flushing with 10 ml methanol (the 5 ml syringe is satisfactory for this). This will wet the cartridge material, activating the surface for the most efficient extraction of rosin.
2. Flush the cartridge with 10 ml DI water to remove trace ionic contaminants from the cartridge
3. Syringe the sample through the cartridge at a flow rate of less than 4 ml/min for the best sorption process. Use sufficient volume to inject into the IC.
4. Always discard the first 6 ml of the sample, and then inject the sample into the IC.
5. The optimum performance of the cartridge is achieved when it is used in a vertical orientation.

5 Ion Chromatography measurements

5.1 Test Condition and parameter settings

The test parameters of the IC equipment need to be selected to give good peak separation for the anions in the calibration solution, and an acceptable analysis time. The IC system should be calibrated or checked in line with the manufacturer's recommendations. On a daily basis the IC should be checked at a single concentration; if the result of the check is outside the 95% confidence interval then the instrument should be recalibrated.

The conditions used in this work are given in Appendix A. Figure 5 presents an IC spectrum for the standard 10 anions solution. In this example an eluent profile has been used, as shown by the dashed blue line.

It is recommended to use a test temperature of 30 °C.

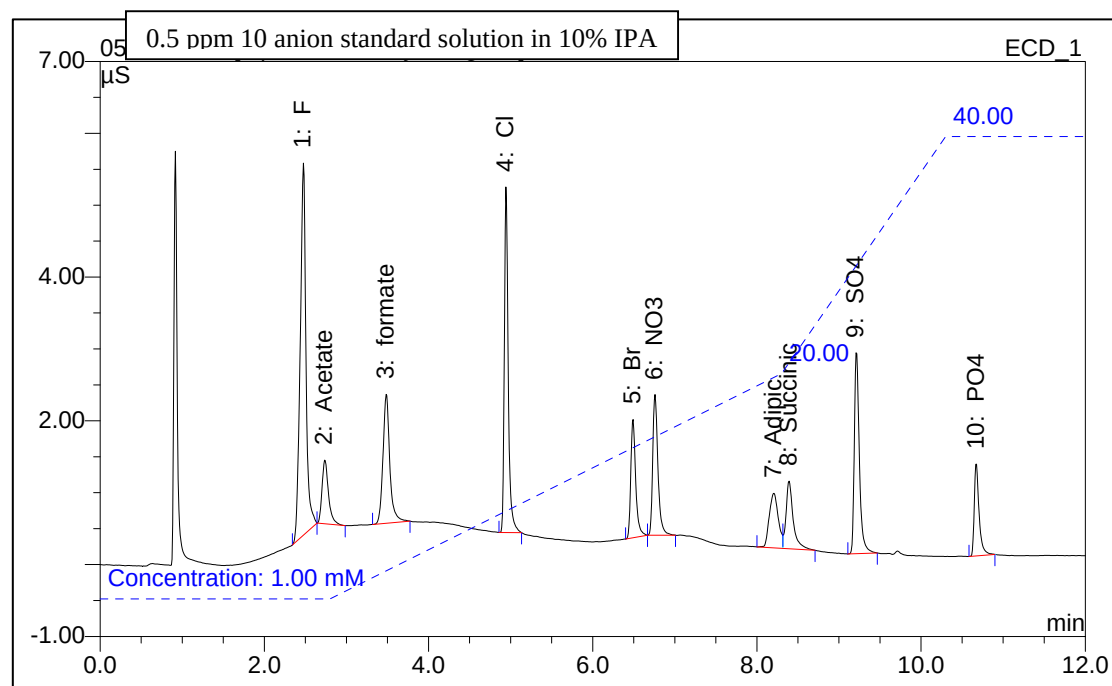


Figure 5: IC spectrum for 0.5 ppm 10 anions standard solution in 10% IPA.
The eluent profile is shown as the blue dashed line

5.2 IC system calibration and validation

1. Ensure the machine provides a stable reading with repeated runs of the check solution (recommend 0.5ppm solution). If the machine is not used everyday then it may need to be preconditioned by running the eluent at a high concentration.
2. After the system is stable, compare the results of the 10 anion standard solution to the calibration values. If the concentrations of the anions are outside the 95% confidence probability, then the system needs to be calibrated.
3. If a calibration is required prepare standard solutions containing the 10 anions, at five concentration levels, 0.1ppm to 5ppm (specified in Section 4.1.2). The IPA concentration in the standard solutions should be the same as the extract test sample.
4. Calibrate the IC using the standard solutions and the manufacturer's procedure.
5. After calibration, run a check using 1ppm standard solution to validate the calibration curve. If the validation measurement falls within the 95% confidence probability, the IC calibration is satisfactory. Otherwise the calibration needs to be repeated.

5.3 Test procedure

1. Check the IC is within calibration, see Section 5.2
2. Follow the manufacturer's instructions to inject the test sample.
3. The test sample results should be within the calibration range, otherwise take one of the following actions
 - a. Make and analyse additional standards, and recalibrate the system using new standard solutions.
 - b. Dilute the test sample with the same IPA/water solution used in the extract solution, and calculate the dilution factor A:

$$A = \text{Sample volume after dilution} / \text{Sample volume before dilution}$$

6 Reporting Results

The following information should be reported:

1. The IC equipment used, with any modifications
2. Details of the calibration
3. The extract solution
4. The extraction method
5. Values from the IC typically reported in µg/ml.
6. Analysis of extracts from PCB/PCA usually expressed as µg anion per square centimetre based on the extraction volume and the calculated sample surface area:

$$\mu\text{g}/\text{cm}^2 = [\text{Dilution factor (A)}] \times [\mu\text{g}/\text{ml} \times \text{extraction solution volume (ml)}] / [\text{sample surface area (cm}^2\text{)}]$$

Appendix A: Investigation of a trap column

The most important part in the IC system is the analytical column, which separates anions due to their different size, polarity, ionic strength, and affinity to the stationary phase, or column material. Hence anions are dispersed in the column according to the above factors and emerge at different times, the length of time in the column being known as the anion retention time. Anion retention time is the parameter used for identification. For a good IC system anion retention time should be stable. However when test samples contain rosin, anion retention times will decrease gradually. To achieve robust and stable anion retention times, any rosin needs to be removed before it reaches the analytical column. To achieve this a trap column can be used.

In this work a trap column was evaluated with a Dionex IC 25 system consisting of IonPak AS17 analytical column, IonPak AG17 guard column, EG40 eluent generator, CR-ATC continuously regenerated anion trap column, ASRS Ultra suppressor (2mm). Figure A.1 shows a diagram of the IC system. An NG1 trap column, as shown in Figure A.2, can be connected in front of AG17 guard column to trap the rosin after sample injection, protect the analytic column from rosin contamination, and improve the stability of anion retention time. The system used contained an eluent generator that could assess the KOH profile with time. This was selected since the retention times of certain anions are unacceptably long. By increasing the eluent concentration these retention times can be brought down to less than 12 minutes.

The test procedure used for this IC equipment is detailed below, and should be followed after a calibration or validation, according to Section 5.2:

1. Apply 5-20 psi head pressure to Dionex IC 25 system using a He cylinder.
2. Turn on Dionex IC 25 system, LC25 Chromatograph oven, EG40 eluent generator and IC 25 Ion chromatograph.
3. Open the prime valve, and prime the GS 40 gradient pump for 10 seconds, then close the prime valve, and turn on the pump.
4. Set the eluent concentration at 40mM, ASRS current at 100 mA, and oven temperature at 30°C to equilibrate the system until the background conductivity is stable and less than 1.2 μ S. If the system is used every day 45 mins equilibration time should be enough. If the system has not been used for more than two days, 90 mins equilibration time will be needed to achieve the stable IC performance.
5. Check the system pressure is between 1800-2500 psi, and the system is on flow rate control mode.
6. The test sample results should be within the calibration range. If not, take one of the following actions
 - a. Make and analyse additional standards, and recalibrate the system using new standard solutions.

- b. Dilute the test sample with the same IPA/water solution used in the extract solution, and calculate the dilution factor A:

$$A = \text{Sample volume after dilution} / \text{Sample volume before dilution}$$

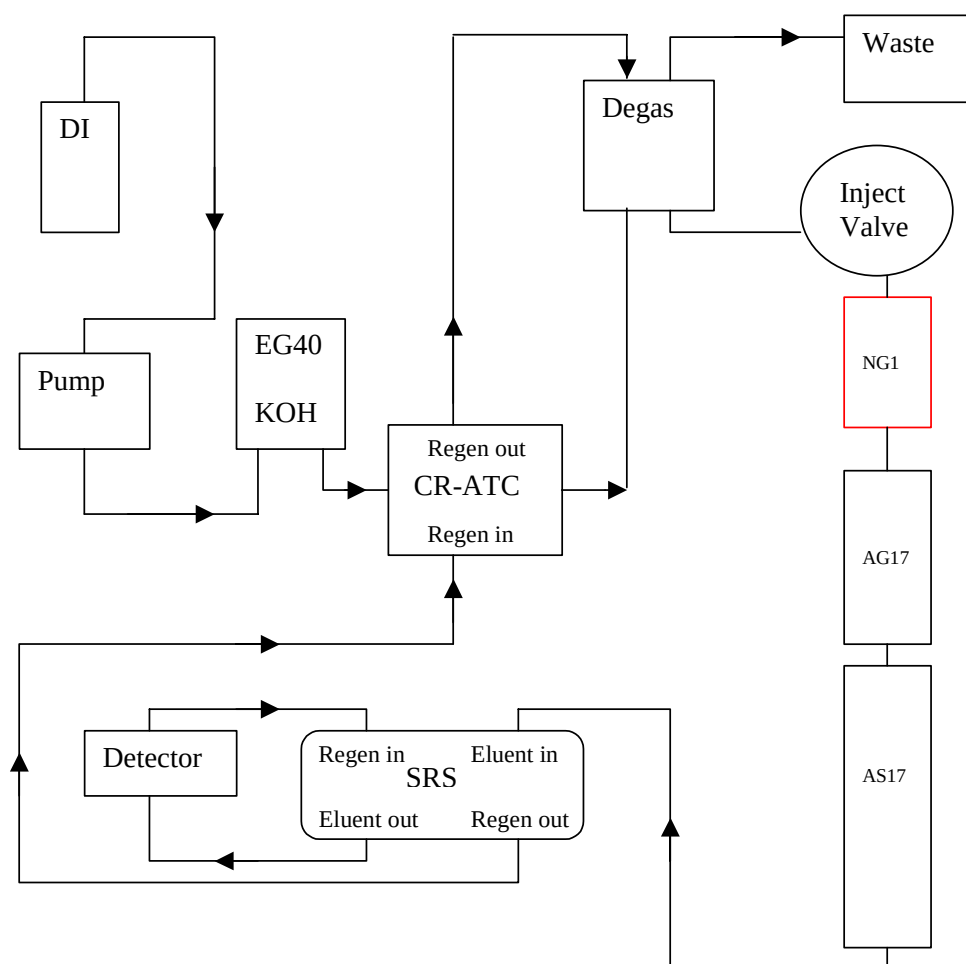


Figure A.1: Diagram of IC system

The parameters used for the flowing tests are as follows:

Test time:	12 mins	
Equilibration time	10 mins	
Eluent concentration during equilibration	40 mM	
Temperature:	30 °C	
Eluent flow rate:	0.5 ml/min	
SRS current:	100 mA	
Sample volume:	25 µl	
Eluent concentration with time:	Time (min)	Concentration (mM)
(Prior to test condition system)	-10	40
(Reduce concentration prior to	-9.9	1
sample injection)	0	1
	2	1
	7.5	20
	9.5	40
	12	40

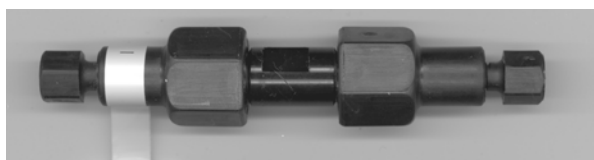


Figure A:2: NG1 in line trap column

An NG1 trap column has a very high selectivity for hydrophobic substances, especially for unsaturated or aromatic substances. It is compatible with the IPA solvent and stable over a pH range of 0-14. The NG1 trap column was installed before the guard column. Figure A.3 demonstrates that without the NG1 trap column, the anion peaks shift after three high concentration rosin sample injections. However, it is clear from Figure A.4, that the anion peaks are very stable with the NG1 in line.

This implies that the NG1 column will trap rosin after sample injection, prevent the column being poisoned with rosin, and hence improve anion retention time stability. However, the NG1 column does delay anion peaks, and broadens early peaks, as shown in Figure A.5. This may decrease resolutions for peaks which are very close. Figures A.6 and A.7 show the results obtained using a10 anion standard solution. With NG1 in line fluoride and acetate peaks can only be partially resolved, but

without the NG1 in the system these two peaks can be completely resolved. Hence with NG1 in line the peak resolution may be compromised.

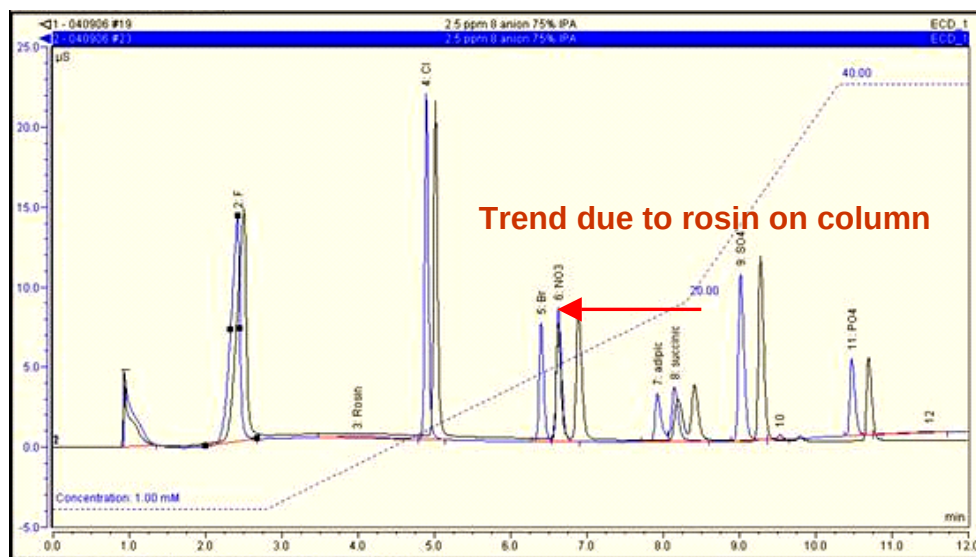


Figure A.3: Spectra for the eight anion solutions before and after high concentration rosin sample injections without NG1 in line

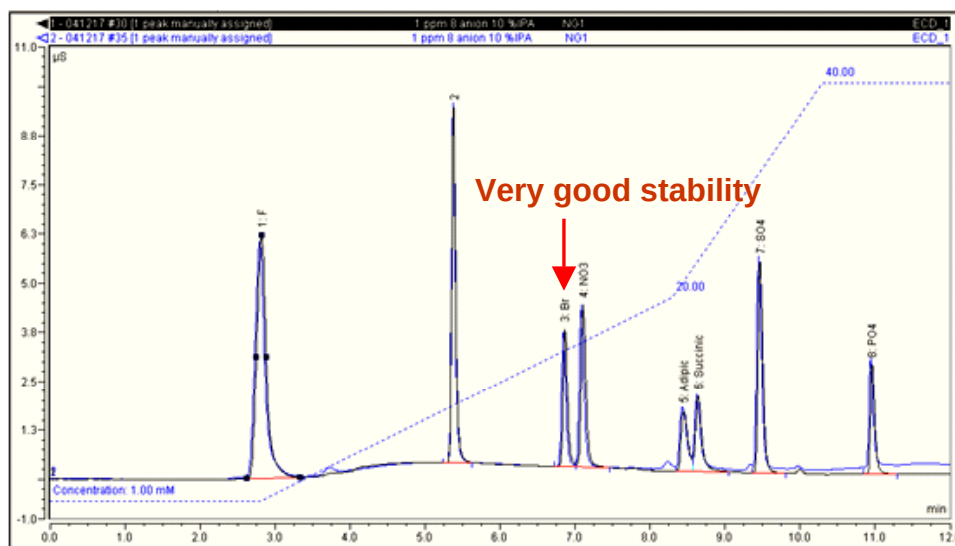


Figure A.4: Spectra for the eight-anion solutions before and after high concentration rosin sample injections with NG1 trap in line

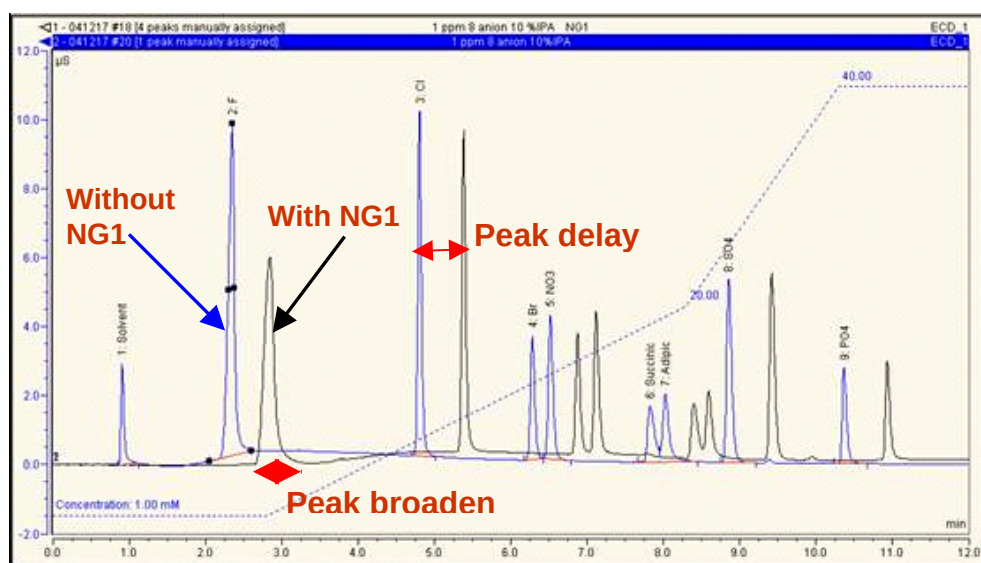


Figure A.5: Eight anion spectrums with and without NG1 in line

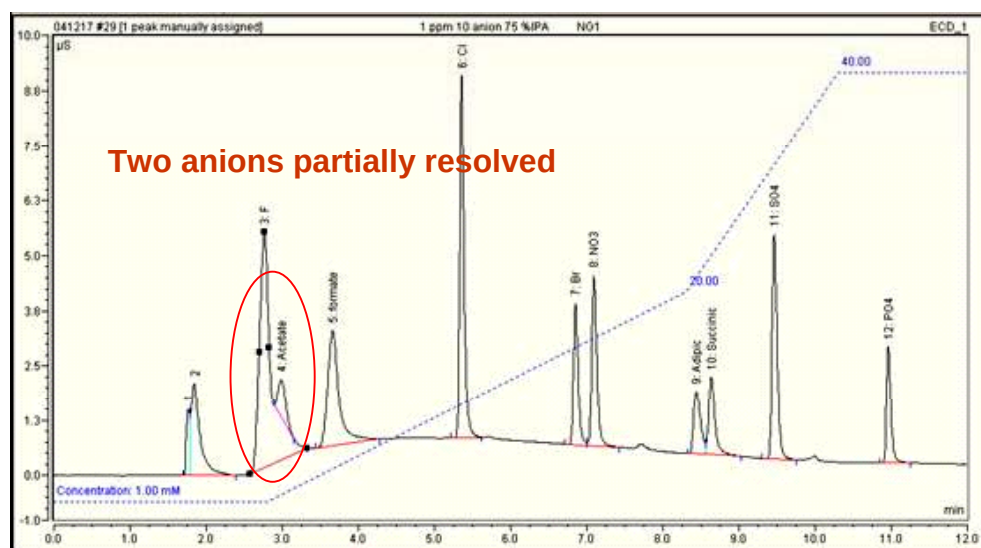


Figure A.6: Ten anion spectrums with NG1 in line showing partially resolved peaks

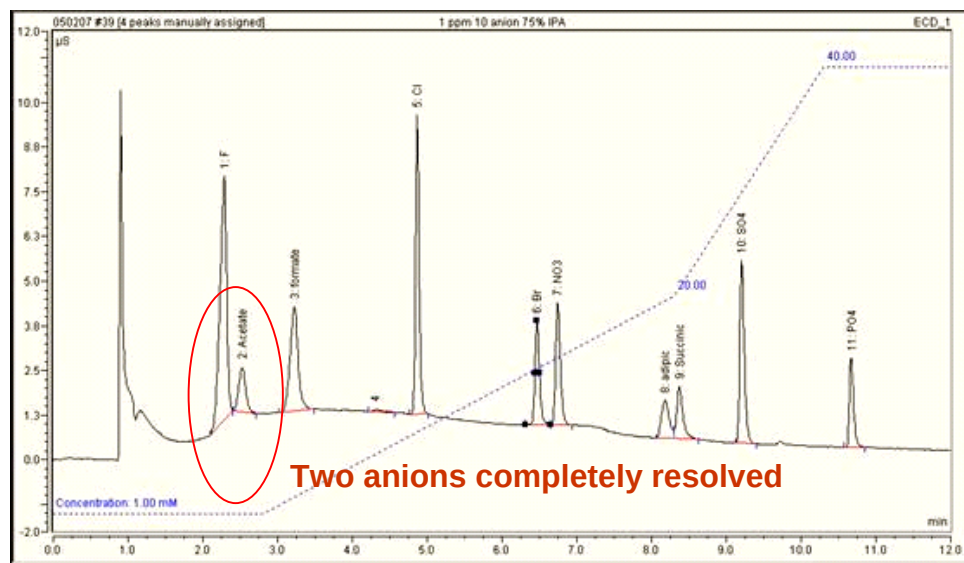


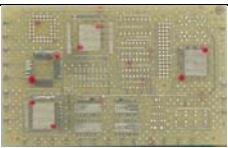
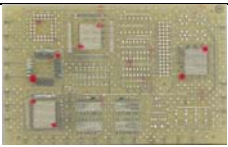
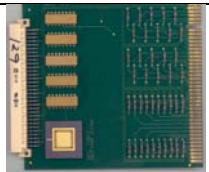
Figure A.7: 10 anion spectrums without NG1 in line, showing resolved peaks

Appendix B: Study of a low IPA content extraction solution

In Appendix A the effect of rosin contaminating the column and extending anion retention time in an unstable way was discussed. A simple solution to this problem would be to eliminate rosin from the extraction samples. Rosin is a hydrophobic material, and by lowering the IPA content in the extract solution, the concentration of rosin in the solution could be potentially reduced. Hence a 10% IPA extraction solution was selected and the results compared with those from the previous 75% solution. When using the 75% solution, the ion trap was employed, but the ion trap was absent when using the 10% solution.

The details of five different assemblies are listed in Table 1.

Table 1: Assembly details

Board	Code	Size	Process	Flux
	A	16 x 10	Wave	35% rosin flux
	A	16 x 10	Wave	603 flux
	B	10.5 x 12.5	Reflow + Wave	Unknown
	C	10.5 x 5.0	Reflow + Wave	Unknown
	D	26.5 12.5	Reflow + Wave	Unknown

Board A was prepared using only wave soldering and a rosin flux and a weak organic acid flux. There were no components but four 20 x 20 mm square glasses were pre-

assembled using a thermal adhesive with 150-180 μm glass balls. This not only simulated component stand-off, but also acted as potential traps for flux. Boards B, C and D were assembled using both reflow and wave soldering. Boards B and D were NPL test boards with different flux technologies. Board C was a commercial power supply product. With these five different assemblies the surface contamination was extracted using both 10% and 75 % IPA solutions. The extracts were analysed using the IC system for the 10 anions of interest. The anion concentrations from two extractions for the assemblies are compared in Figure B.1. which clearly demonstrates that there was no significant difference between results using the two extract solutions.

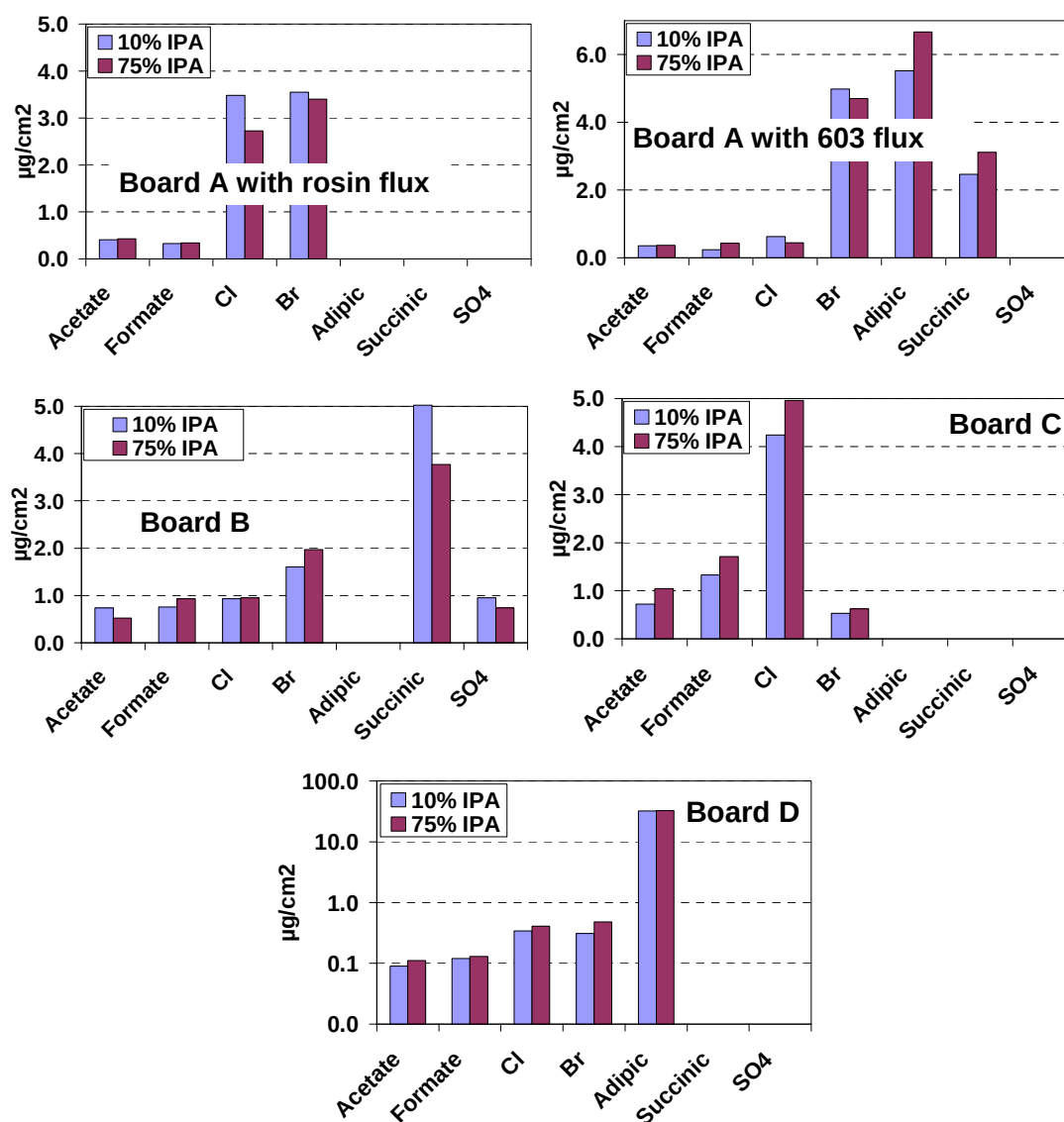


Figure B.1: Anion concentrations between 10% IPA and 75% IPA extractions for five assemblies

These results suggest that the 10% IPA solution has a similar dissolution power to the 75% IPA solution for these electronic boards.

There is a further advantage to using a 10% IPA solution rather than a 75% IPA extract solution, i.e. a flattening of the IC base-line, as shown in Figure B.3. Although the column chemistry is nominally compatible with the 75% solution there is clearly an effect on the instrument when using this solution. With the 75% IPA solution the baseline increases, and this sometimes makes anion quantification difficult.

The two extractions for board A with rosin flux were also analysed using HPLC technique to measure the rosin concentration in these two extractions. Because rosin is a mixture of materials, concentrations of the three main components were measured. The results are plotted in Figure 2. From Figure 2 we can clearly see that using 75% IPA extraction solution from board A shows very significantly higher rosin levels (about 800 ppm/cm²), but using 10% IPA extraction solution to extract same board, the rosin level on the board is below 1ppm/cm². This means that solubility of rosin in 10% IPA is negligible.

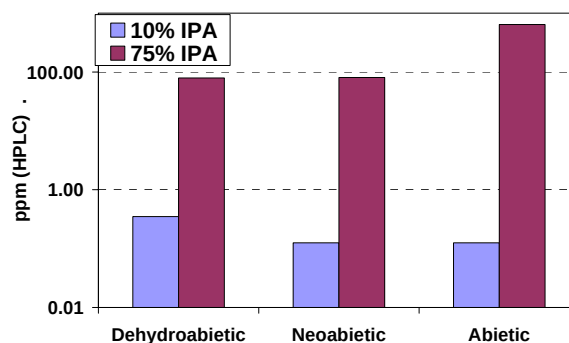


Figure B.2: HPLC analysis for two extract solutions, 10% and 75% IPA, from board A manufactured with rosin flux, showing the three main rosin components.

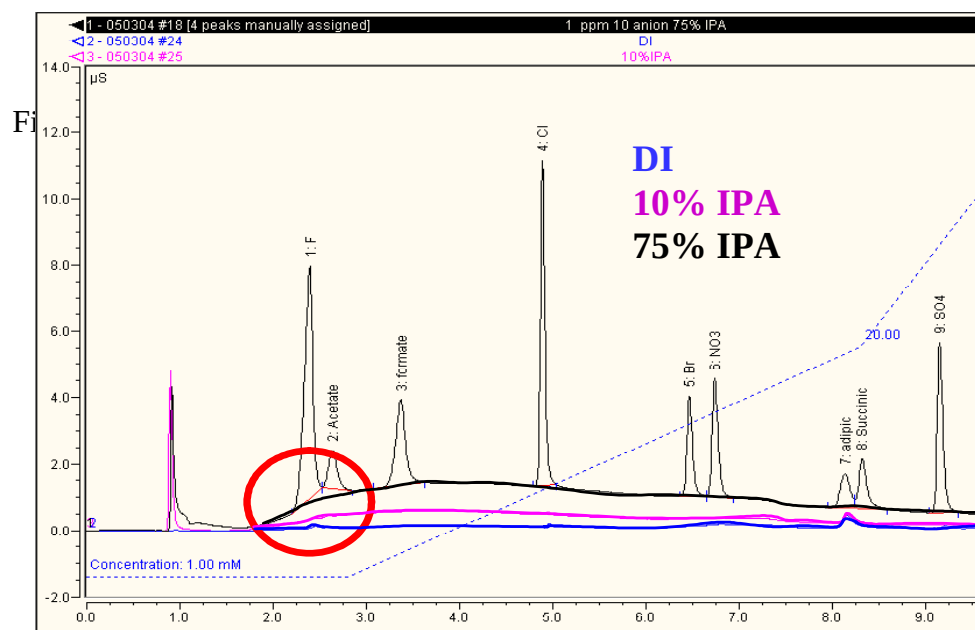


Figure B.3: IC base-line comparison for different IPA extraction solutions

Appendix C: Assessment of a chemical selective cartridge

An external trap (an OnGuard II RP cartridge) was evaluated for removing rosin from a 75% IPA extraction solution. The cartridge has the same function as NG1 trap column, but the capacity is much less than the column, and is disposed of after each test sample. The cartridge should remove rosin from the test sample, hence protecting the IC system and ensuring the correct performance.

Samples with a range of rosin concentrations in a 75% IPA solution were prepared, and then passed through the cartridge using a syringe. These samples were then analysed using HPLC to measure the concentration of the three main components (abietic, neoabietic and dehydro-abietic acid), in the solution before and after treatment. The results are compared in Figure C.1, and clearly show the concentration increasing in line with the added rosin. The results for the filtered solutions indicate that all three rosin components are well below the 1 ppm, even for the sample with the 1000ppm rosin. This low rosin level in the sample is acceptable for IC systems. A level of 1000ppm rosin should cover the highest rosin residue level extracted from today's print circuit assembly. Hence the cartridge method is eminently suitable for removing rosin from extract solutions, even when heavy flux residues are present on test assemblies.

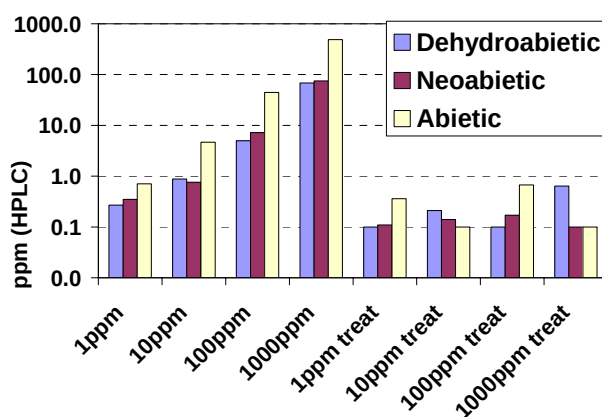


Figure C.1: The concentrations of the three main components using HPLC of rosin at different concentrations before and after filtering using an OnGuard II RP cartridge

Although the above results demonstrated the use of the cartridge for removing rosin, they raised the question of the effect on the other anions of interest? Hence an additional trial was performed to address this aspect. Three standard solutions in 75% IPA solution with rosin levels at, 0, 10 and 1000 ppm rosin were prepared, passed

through the cartridges, and then analysed using the IC. Figure C.2 presents a comparison of anion concentrations in the samples with and without treatment. The measured levels of anions before and after filtering treatment were very similar, even with 1000 ppm rosin in the sample, demonstrating that the cartridge successfully removed rosin from the sample, while not effecting the anions of interest.

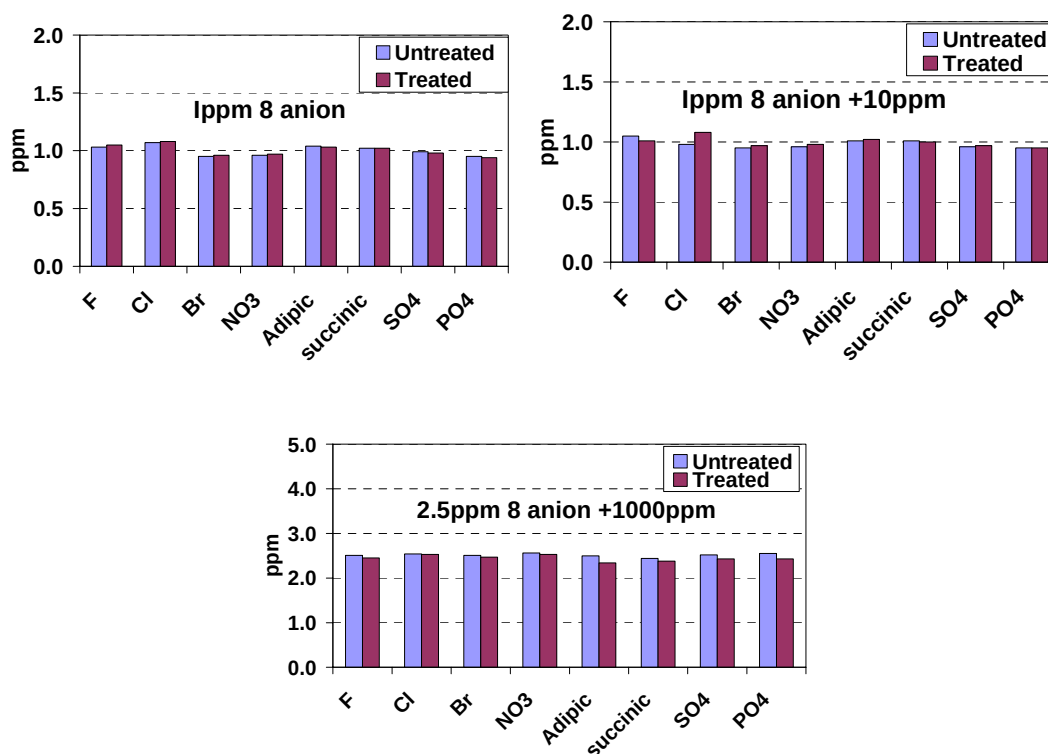


Figure C.2: Eight anion concentrations by IC in treated and untreated standard samples with rosin