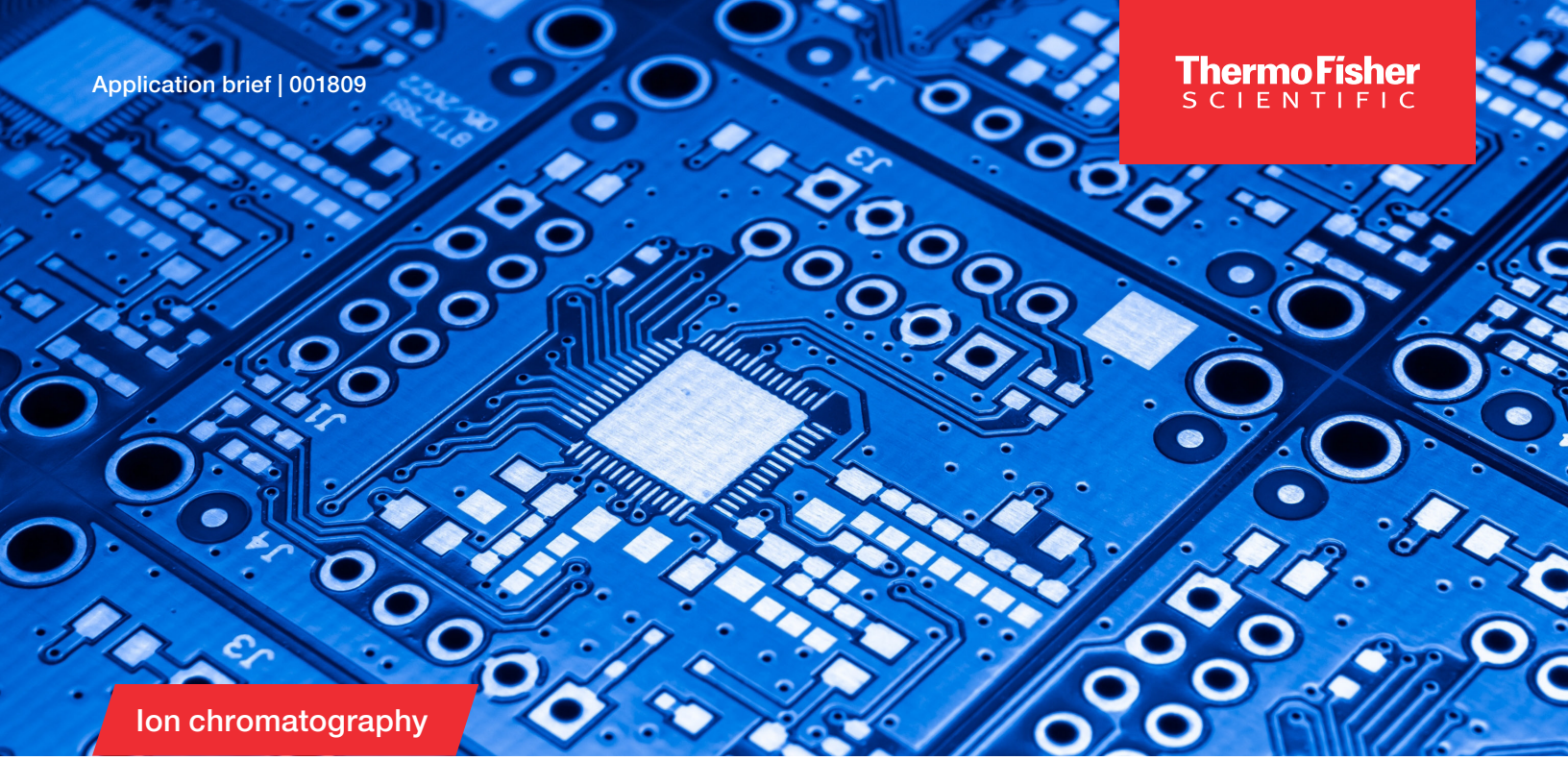

Application brief | 001809

Ion chromatography

Improved determinations of residual anions and organic acids to evaluate printed circuit board cleanliness

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Keywords

Dionex IonPac AS11-HC column, semiconductor, IPC-TM-650 Method, PCBs

Goal

To demonstrate two techniques to improve resolution for determining specific anionic contamination on the surface of printed circuit boards (PCBs) per the IPC-TM-650 Method

Introduction

Organic acid and inorganic residues from solder flux and other manufacturing processes can cause soft and hard failures in the printed circuit board (PCB), as previously discussed in Thermo Scientific Application Note 1163: Determination of anions on the surface of printed circuit boards by IPC-TM-650 Method 2.3.28 using HPIC.[1] Therefore, the PCB industry monitors the cleanliness of populated PCBs using the IPC™ Test Method IPC-TM-650 to assure board cleanliness and prevent failures associated with residual contamination.[2] These organic acids of interest are primarily dicarboxylic acids, which are challenging to resolve due to their similar chemical structures. Application Note 1163 (AN1163) provides an analytical method using the Thermo Scientific™ Dionex™ IonPac™ AS11-HC-4µm column for this analysis.

This application brief, using a 2 mm i.d. Thermo Scientific™ Dionex™ IonPac™ AS11-HC column with 9 µm resin, demonstrates two techniques to modify the column selectivity to improve resolution. Method A uses a hydroxide separation at 20 °C, which resolves the organic acids, except succinate and malate, within 38 min. Method B uses the hydroxide separation reported in AN1163 but with a modified methanol gradient to partially resolve or fully resolve the target organic acids within 60 min.

Experimental

Equipment

- Thermo Scientific™ Dionex™ ICS-6000 HPIC™ system
  - Dual Pump DP module, isocratic configuration (P/N 22181-6009) with pump_1 to deliver DI water for eluent generation and pump_2 to deliver DI water as suppressor regenerant
  - Eluent Generator EG module (P/N 22181-60019)
  - Detector Chromatography DC module with two 6-port injection valves (P/N 22181-600499)
  - CD Conductivity Detector (P/N 079829)
- Thermo Scientific™ Dionex™ AS-AP Autosampler (P/N 079656) includes:
  - 100 µL syringe (syringe P/N 074305)
  - Three 19-position sample trays for 10 mL vials (P/N 074938)
- Three 8-position sample trays for 10 mL vials (P/N 069877) typically used for standards

Reagents

- ASTM Type 1 deionized water (DI water) with 18 MΩ·cm resistivity[3]
- Fisher Scientific™ reagents
  - Adipic acid, 99%, P/N AC102815000, (CAS 124-04-9)
  - Methanesulfonic acid, 98%, P/N AC432970050 (CAS 75-75-2)
  - Methanol, Optima™ LC/MS grade, P/N A456-500 (CAS 67-56-1)
  - Phthalic acid, 99%, P/N AC131072500 (CAS 88-99-3)
  - Sodium acetate, trihydrate, P/N AAA131840I, (CAS 127-09-3)
  - Sodium formate, 99%, P/N AC148230051 (CAS 141-53-7)
  - L-Glutamic acid, monosodium salt, P/N AAJ6342414 (CAS 142-47-2)
  - D-(+) Malic acid, 98%, P/N AAA1168814 (CAS 636-61-3)
  - Sodium succinate, heptahydrate, 99%, P/N AA4198330 (CAS 6106-21-4)
  - Thermo Scientific™ Seven Anion Standard II, 100 mL, P/N NC1145568 (contains fluoride, chloride, nitrite, nitrate, bromide, phosphate, and sulfate)

Alternatives for the Seven Anion Standard II:

- Sodium bromide, ACS Reagent, P/N AC212675000 (CAS 7647-15-6)
- Sodium fluoride, 99%, P/N AAA1301930 (CAS 7681-49-4)
- Sodium sulfate, anhydrous, P/N AAA198900I (CAS 7757-82-6)
- Sodium chloride, crystalline certified ACS grade, P/N S271-500 (CAS 7647-14-5)
- Sodium nitrate, P/N S343-3 (CAS 7631-99-4)
- Sodium nitrite, crystalline, ACS certified, P/N S347-3 (CAS 7632-00-0)
- Sodium phosphate, dibasic, monohydrate, P/N S375-500 (CAS 7558-79-4)

Software

- Thermo Scientific™ Chromeleon™ Chromatography Data System (CDS) software, Chromeleon 7 version 3

Consumables

Table 1. Consumables list for the Dionex ICS-6000 system

Product name	Description	P/N
Thermo Scientific™ Dionex™ IC PEEK Viper™ fitting tubing assembly kit	Dionex IC Viper fitting assembly kit for the Dionex ICS-6000 HPIC dual microbore system with CD	302965
Thermo Scientific™ Dionex™ EGC 500 KOH Eluent Generator cartridge	Anion eluent generator cartridge for HPIC high pressure systems	075778
Thermo Scientific™ Dionex™ CR-ATC 600 Electrolytic trap column	Continuously regenerated anion trap column	088662
Thermo Scientific™ Dionex™ HP EG Degasser kit	Analytical EG kit with degasser module and tubing	075522
Thermo Scientific™ Dionex™ ADRS 600 suppressor	Suppressor for 2 mm anion columns	088667CMD
Thermo Scientific™ Dionex™ IonPac™ AG11-HC guard column	Anion guard column, 2 × 50 mm	052963
Thermo Scientific™ Dionex™ IonPac™ AS11-HC analytical column	Anion analytical column, 2 × 250 mm	052961
10 mL sample vial kit	10 mL sample vials for Dionex AS-AP autosampler	055058

Ion chromatography conditions

Method A:

KOH gradient, eluent pump	1 mM KOH (-5 to 9 min), 1–14 mM (9 to 16 min), 14 mM (16 to 23 min), 14–85 mM (23 to 30 min), 85 mM (30 to 32 min), 1 mM (32 min)
Eluent source	Dionex EGC-500 KOH eluent generator cartridge, Dionex CR-ATC 600 trap column, Dionex HP EG degas module
Injection volume	5 µL
Flow rate	0.38 mL/min
Column temp.	20 °C
Detection temp.	20 °C
Detection	Suppressed conductivity, ADRS 600 suppressor, external water mode by pump 2 @ 0.38 mL/min, 57 mA
Conductance background	<0.5 µS/cm
System backpressure	~2,600 (100 psi = 689.5 kPa) with 800 psi backpressure tubing
Run time	38 min

Method B:

Proportioning pump 1	A: DI water for eluent generation B: Methanol
KOH gradient, pump 1	1 mM KOH (-5 to 17 min), 1–15 mM (17 to 24 min), 15 mM (24 to 35.3 min), 15–60 mM (35.3 to 54.6 min), 1 mM (54.61 min)
Eluent source	Dionex EGC-500 KOH eluent generator cartridge, Dionex CR-ATC 600 trap column, Dionex HP EG degas module
Methanol gradient, pump 1	2% (-5 to 24 min), 2–10% (24 to 29 min), 10–15% (29 to 51 min), 15–2% (51 to 54.6 min), 2% (54.6 to 55 min)
Injection volume	5 µL
Flow rate	0.38 mL/min
Column temp.	30 °C
Detection temp.	20 °C
Detection	Suppressed conductivity, ADRS 600 suppressor, external water mode (DI) by pump 2 @ 0.38 mL/min, 57 mA
System backpressure	2,400–3,000 psi
Conductance background	~0.5 µS/cm
Run time	60 min

Standard and sample preparation

Use only ASTM Type I deionized water (DI) I water for preparations.

Stock organic acid standards, 1,000 mg/L, were prepared in DI water by dissolving 100 mg of the reagent acid, adjusted for assay, with DI water into a 100 mL volumetric flask. Similarly, 100 mg of the organic acid salt reagent, adjusted for assay and molecular weight ratio of the salt to the anion, were dissolved in 100 mL of DI water. Individual 10 mg/L standards were prepared by diluting 1 mL of the 1,000 mg/L with 99 mL of DI water. The individual standards were used to confirm the retention time of each organic acid.

A combined 10 mg/L organic acid and 10-fold diluted seven anion standard was prepared by pipetting 1 mL each of 1,000 mg/L stock standard, and 10 mL of the Dionex Combined Seven Anion II standard into a 100 mL HDPE bottle. DI water was added to a total weight of 100 g. The combined standard was used to demonstrate the resolution of the select organic acids and inorganic anions after the method development.

Instrument setup and installation

Install and set up the Dionex ICS-6000 HPIC system as described in AN1163 for the Dionex ICS-5000+ HPIC system.[1] In PCB extractions, 75 to 90% isopropyl alcohol is used to extract the PCB contaminants. It is therefore recommended that the suppressor is installed in external water mode to maintain suppressor robustness. Condition and hydrate the consumables as discussed in AN1163.

Results and discussion

Methods A and B demonstrate the impact of reducing the separation temperature or adding a methanol gradient on column selectivity. Method A was optimized on a 2 mm i.d. Dionex IonPac AS11-HC column using the starting conditions listed in AN1163 without methanol, taking advantage of selectivity changes at 20 °C, and further optimizing the gradient to reduce the run time. Figure 1 shows the final conditions. All organic acids and inorganic anions of interest are fully resolved except succinate and malate (Peaks 8–9). Succinate and malate have some resolution, but it is unlikely they could be quantified accurately with this separation.

Method A

Columns:	Dionex IonPac AG11-HC guard, Dionex IonPac AG11-HC analytical, 2 mm i.d.
Eluent source:	Dionex EGC-500 KOH cartridge, Dionex CR-ATC 600 trap column, Dionex high pressure degasser
KOH gradient:	1 mM KOH (-5 to 9 min), 1–14 mM (9 to 16 min), 14 mM (16 to 23 min), 14–85 mM (23 to 30 min), 85 mM (30 to 32 min), 1 mM (32 min)
Methanol gradient:	none
Flow rate:	0.38 mL/min
Injection volume:	5 µL
Column temp.:	20 °C
Detector oven temp.:	20 °C
Detection:	Suppressed conductivity, Dionex ADRS 600, 2 mm, external water mode by pump 2 @ 0.38 mL/min, 57 mA
System pressure:	2,600 psi (with ~800 psi backpressure tubing between trap column and injection valve)
Run time:	38 min

Peaks:	mg/L		mg/L
1. Fluoride	2	9. Malate	10
2. Acetate	10	10. Carbonate	10
3. Formate	10	11. Bromide	10
4. Methanesulfonic acid	10	12. Nitrate	—
5. Chloride	10	13. Sulfate	10
6. Nitrite	10	14. Phosphate	20
7. Adipate	10	15. Phthalate	10
8. Succinate	10		

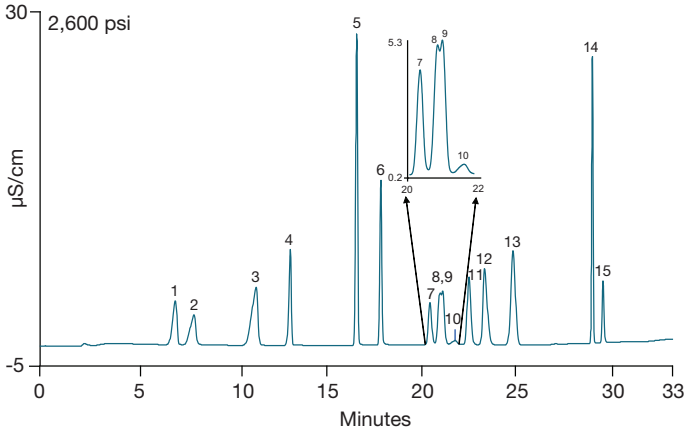

Figure 1. Separation of nine organic acids and seven inorganic anions within 38 min on a 2 mm i.d. Dionex IonPac AS11-HC column using a 20 °C column temperature

Method B followed the conditions in AN1163 using a 2 mm i.d. Dionex AS11-HC column, but the methanol gradient was optimized to improve resolution. Figure 2 shows the final conditions. Adipate (Peak 8), nitrate (Peak 9), succinate (Peak 10), and malate (Peak 11) are not fully resolved.

Method B

Columns:	Dionex IonPac AG11-HC guard, Dionex IonPac AS11-HC analytical, 2 mm i.d.
Pump 1 proportioning:	A: DI water for eluent generation B: Methanol for methanol gradient
Eluent source:	Dionex EGC-500 KOH cartridge, Dionex CR-ATC 600 trap column, Dionex high pressure degasser
KOH gradient:	1 mM (-5 to 17 min), 1–15 mM (17–24 min), 15 mM (24–35.3 min), 15–60 mM (35.3 to 54.6 min), 1 mM (54.61–55 min)
Methanol gradient:	2% (-5 to 24 min), 2–10% (24 to 29 min), 10–15% (29 to 51 min), 15–2% (51 to 54.6 min), 2% (54.6 to 55 min)
Flow rate:	0.38 mL/min
Injection volume:	5 µL
Column temp.:	30 °C
Detector oven temp.:	20 °C
Detection:	Suppressed conductivity, Dionex ADRS 600, 2 mm, external water mode by pump 2 @ 0.38 mL/min, 57 mA
System pressure:	~2,100 (measured without backpressure tubing.) ~2,400 psi with 300 psi backpressure tubing
Run time:	60 min

Peaks:	mg/L		mg/L
1. Fluoride	2	9. Nitrate	10
2. Acetate	10	10. Succinate	10
3. Formate	10	11. Malate	10
4. Methanesulfonic acid	10	12. Carbonate	—
5. Chloride	10	13. Sulfate	10
6. Nitrite	10	14. Phosphate	20
7. Bromide	10	15. Phthalate	10
8. Adipate	10		

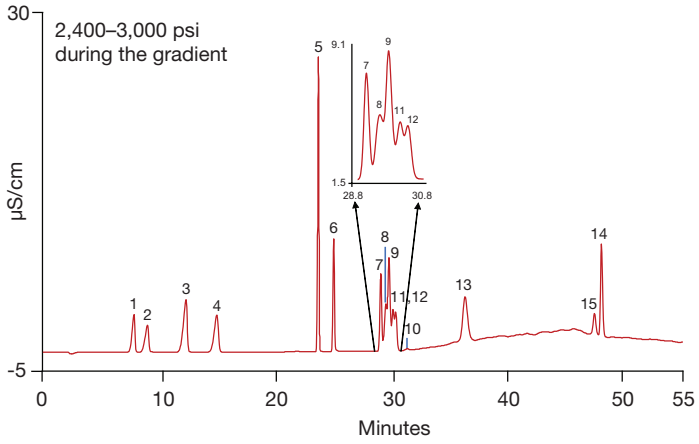

Figure 2. Separation of nine organic acids and seven inorganic anions on a Dionex IonPac AS11-HC column using methanol in the eluent

Conclusion

This application brief presented two methods for the determination of organic acids and inorganic anions needed in the PCB industry, per the IPC-TM-650 Method. These methods are alternatives to the method presented in AN1163. Compared to that method, both methods had reduced system pressure but some loss of resolution. The resolution of these two methods may be sufficient for the analytical goals of the PCB industry laboratory.

References

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