

Using a Reagent-Free ion chromatography system to monitor trace anion contamination in the extracts of electronic components

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Introduction

Thermo Scientific Application Note 153 (AN153) showed that ion chromatography (IC) successfully determines low $\mu\text{g/L}$ and, for some analytes, high ng/L anions in extracts of electronic components.¹ Keeping the anionic contamination of electronic components low can reduce the incidence of component failure. The IC method in AN153 separated 14 inorganic anions and organic acids on a Thermo Scientific™ Dionex™ IonPac™ AS17 column set after either a 1 mL direct injection or a 5 mL sample preconcentration. In this application update a hydroxide gradient program similar to, but faster than, the program used in AN153 separates a new set of 14 anions. This set of anions differed from the original set by the replacement of nitrite and phthalate with 2-ethylhexanoate and citrate. 2-Ethylhexanoate is the byproduct of an adhesive sometimes used in the disk drive industry. We have also incorporated the recently introduced Carbonate Removal Device (CRD). The CRD removes most of the carbonate from a 1 mL sample injection allowing a more reliable quantification of sulfate, oxalate, and other anions eluting just after carbonate.²

Experimental

Equipment

- Thermo Scientific™ Dionex™ ICS-3000* system consisting of:
 - DP Dual Pump
 - EG Eluent Generator with CR-ATC and Thermo Scientific™ Dionex™ EluGen™ EGC-KOH cartridge
 - CRD (Carbonate Removal Device) (P/N 62983)
 - DC Detector/Chromatography compartment
- Thermo Scientific™ Chromeleon™ 6.7 Chromatography Management Software

* Equivalent or improved results can be achieved using any Thermo Scientific™ Dionex™ Reagent-Free™ Ion Chromatography (RFIC™) system. An autosampler was not used for the work presented in this application update, but either a Thermo Scientific™ Dionex™ AS40 Autosampler or a Thermo Scientific™ Dionex™ AS Autosampler can be used as long as the proper precautions are taken to produce a clean blank. For these precautions, see the Sample Loading and the Precautions sections of Application Note 153.¹

Reagent and standards

- Deionized water (DI), Type I reagent grade, 18.2 MΩ·cm resistivity
- Sodium fluoride (NaF)
- Sodium acetate anhydrous (C₂H₃O₂Na)
- Formic acid (CH₂O₂)
- Acrylic acid (C₃H₄O₂)
- Methacrylic acid (C₄H₆O₂)
- Sodium chloride (NaCl)
- Potassium bromide (KBr)
- Sodium nitrate (NaNO₃)
- Benzoic acid (C₇H₆O₂)
- Sodium sulfate (Na₂SO₄)
- Oxalic acid (C₂H₂O₄)

- Potassium dihydrogen phosphate (KH₂PO₄)
- Citric acid (C₆H₈O₇)
- 2-ethylhexanoic acid (C₈H₁₆O₂)

All compounds were ACS reagent grade or better and obtained from reliable sources. 2-Ethylhexanoic acid was purchased from Fluka Biochemika, Milwaukee, WI.

Conditions

Column: Thermo Scientific™ Dionex™ IonPac™ AS17, 4 × 250 mm

Guard: Thermo Scientific™ Dionex™ IonPac™ AG17, 4 × 50 mm

Eluent: Dionex EGC-KOH cartridge

Gradient: 0.3 mM isocratic to 7 min;
gradient to 15 mM at 20 min;
gradient to 40 mM at 25 min;
isocratic to 26.9 min;
step change to 0.3 mM at 27 min

<i>Time (min)</i>	<i>Concentration (mM)</i>
-7.0	0.3
0.0	0.3
7.0	0.3
20.0	15
25.0	40
26.9	40
27.0	0.3

Flow Rate: 1 mL/min

Temperature: 30°C

Sample Loop: 25 µL

Detection: Suppressed conductivity,
Thermo Scientific™ Dionex™ ASRS™
ULTRA II in external water mode with CRD

Preparation of solutions and reagents

Eluent

The KOH eluent is prepared automatically by pumping DI water through the Eluent Generator equipped with a Dionex EGC-KOH cartridge.

Standard solutions

Stock standards

Prepare 1,000 mg/L standards for each of the anions in DI water. Standards should be prepared from the highest purity compounds available (i.e., ACS reagent grade or better). Table 1 provides the amounts needed to prepare 100 mL of each standard. Concentrated standards are stable for at least one month when stored at 4°C.

Table 1. Mass of compounds used to prepare 100 ml of 1,000 mg/L anion standards

Anion	Compound	Amount (g)
Fluoride	Sodium Fluoride	0.2210
Acetate	Sodium Acetate	0.1389
Formate	Formic Acid	0.1022
Acrylate	Acrylic Acid	0.1014
Methacrylate	Methacrylic Acid	0.1011
Chloride	Sodium Chloride	0.1646
2-Ethylhexanoate	2-Ethylhexanoic Acid	0.1006
Bromide	Potassium Bromide	0.1487
Nitrate	Sodium Nitrate	0.1370
Benzoate	Benzoic Acid	0.1008
Sulfate	Sodium Sulfate	0.1479
Oxalate	Oxalic Acid	0.1008
Phosphate	Potassium Dihydrogen Phosphate	0.1432
Citrate	Citric Acid	0.1005

System preparation and setup

Application Note 153 provides a thorough discussion of the system preparation and setup used in this application update. See Technical Note 62 for instructions describing CRD installation.²

Results and discussion

To separate the 14 anion set of fluoride, acetate, formate, acrylate, methacrylate, chloride, 2-ethylhexanoate, bromide, nitrate, benzoate, sulfate, oxalate, phosphate, and citrate, we evaluated the Dionex IonPac AS17 separation used in AN153 and the Dionex IonPac AS15 separation used in Application Update 142.³ Both columns use hydroxide eluent gradients making them ideally suited for use with an RFIC system. This allows the most sensitive and reproducible analyses with the additional benefit of removing the time and possible errors associated with manual eluent preparation. We found that the Dionex IonPac AS17 column offered the

fastest analysis and best resolution for this set of 14 anions. If glycolate must be determined, consider using the Dionex IonPac AS15 column.

Figure 1 shows the separation of a standard mixture of the 14 anions at 0.188 (fluoride) to 1.88 (2-ethylhexanoate) mg/L concentrations on an AS17 column set.

2-Ethylhexanoate elutes just before bromide at 13.8 min and citrate is the last anion to elute. This method is about six minutes faster than the method described in AN153. To achieve this time savings, one short gradient ramp was eliminated and the other gradient ramps were made steeper. These faster conditions may not completely resolve nitrite from chloride or phthalate.

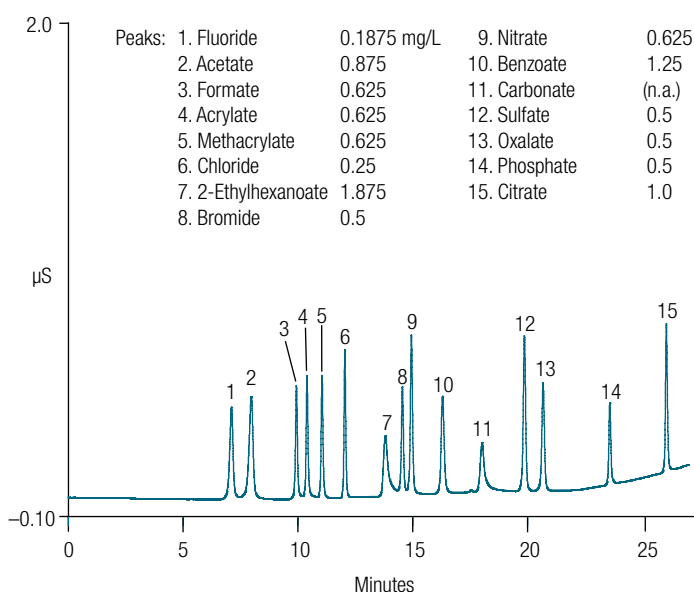


Figure 1. Separation of a mixed anion and organic acid standard.

Tables 2 and 3 show the standards used for method calibration and the calibration results. The method reported here uses a 25 µL injection volume. For determining lower concentrations of contaminating anions, up to 1 mL of sample can be used and the system should be calibrated with lower concentration standards using the same injection volume as the sample, as described in AN153. Despite using only a 25 µL injection volume, this method has good sensitivity as shown in the chromatogram of the MDL standard (Figure 2) and the results of the MDL determination (Table 4). The excellent sensitivity can be attributed to the RFIC system.

Table 2. Standard concentrations for method calibration.

Analyte	Level 1 (mg/L)	Level 2 (mg/L)	Level 3 (mg/L)
Fluoride	0.094	0.188	0.375
Acetate	0.438	0.875	1.750
Formate	0.313	0.625	1.250
Acrylate	0.313	0.625	1.250
Methacrylate	0.313	0.625	1.250
Chloride	0.125	0.250	0.500
2-Ethylhexanoate	0.938	1.875	3.750
Bromide	0.250	0.500	1.000
Nitrate	0.313	0.625	1.250
Bezoate	0.625	1.250	2.500
Sulfate	0.250	0.500	1.000
Oxalate	0.250	0.500	1.000
Phosphate	0.250	0.500	1.000
Citrate	0.500	1.000	2.000

Table 3. Method calibration results as reported by Chromeleon software.

Analyte	r ²	%Coeff. Det.	Offset	Slope
Fluoride	99.99	99.9899	-0.006	0.4714
Acetate	99.99	99.9899	-0.0006	0.1237
Formate	99.995	99.9954	-0.0032	0.0977
Acrylate	100	99.9999	-0.0019	0.0968
Methacrylate	99.995	99.9948	-0.0003	0.0968
Chloride	99.993	99.9931	-0.0038	0.2873
2-Ethylhexanoate	99.712	99.7117	-0.0089	0.0313
Bromide	99.996	99.9945	-0.0023	0.1177
Nitrate	99.995	99.9945	-0.0058	0.1548
Benzoate	100	100	-0.0032	0.0663
Sulfate	99.988	99.9882	-0.0064	0.2183
Oxalate	99.992	99.9925	-0.0029	0.1585
Phosphate	99.967	99.9672	-0.003	0.0965
Citrate	99.996	99.9958	0.0002	0.0746

Peaks:	1. Fluoride	1.0 µg/L	12. Benzoate	5.0
	2. Acetate	5.0	13. Unknown	-
	3. Formate	3.0	14. Carbonate	n.a.
	4. Acrylate	5.0	15. Unknown	-
	5. Methacrylate	5.0	16. Unknown	-
	6. Chloride	0.75	17. Sulfate	2.5
	7. Unknown	-	18. Oxalate	2.5
	8. 2-Ethylhexanoate	10.0	19. Phosphate	5.0
	9. Bromide	3.0	20. Unknown	-
	10. Nitrate	2.5	21. Unknown	-
	11. Unknown	-	22. Citrate	0.5

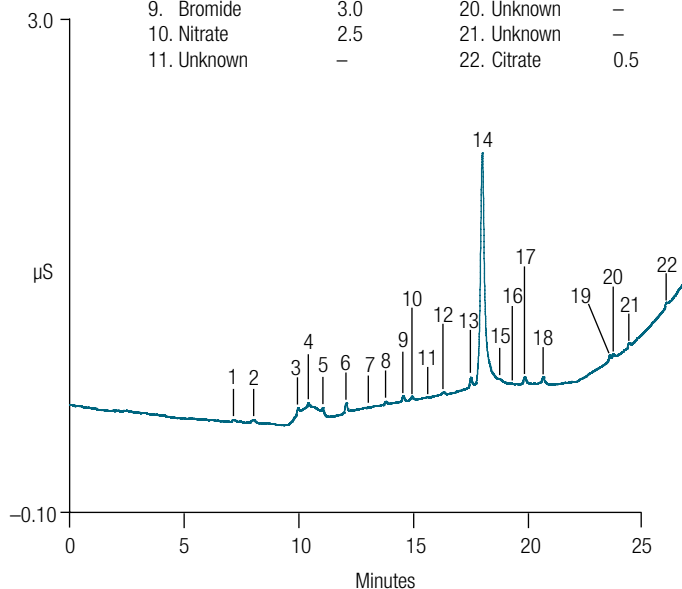


Figure 2. Separation of a low concentration mixed anion and organic acid standard.

Table 4. Determination of MDLs for 14 anions.

Analyte	Concentration (µg/L)	RSD (%)	MDL (µg/L)
Fluoride	1.0	15.4	0.48
Acetate	5.0	16.0	2.5
Formate	3.0	23.5	2.2
Acrylate	5.0	23.9	3.7
Methacrylate	5.0	16.4	2.6
Chloride	0.75	17.8	0.42
2-Ethylhexanoate	10.0	12.5	3.9
Bromide	3.0	16.3	1.5
Nitrate	2.5	12.1	0.95
Bezoate	5.0	20.5	3.2
Sulfate	2.5	17.9	1.4
Oxalate	2.5	19.1	1.5
Phosphate	5.0	17.3	2.7
Citrate	2.5	17.5	1.4

Summary

An RFIC system equipped with a Dionex IonPac AS17 column separated anions and organic acids in high-purity water. This method can be used to determine fluoride, acetate, formate, acrylate, methacrylate, chloride, 2-ethylhexanoate, bromide, nitrate, benzoate, sulfate, oxalate, phosphate, and citrate in the water extracts of electronic components.

Precautions

For a successful trace-level anion determination, contamination must be minimized. Please see the Precautions section of Application Note 153 for advice on minimizing contamination.

References

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