Monitoring for Trace Anion Contamination in the Extracts of Electronic Components

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Dionex ICS-2500, Anions, Contamination, Electronic Components, Ion Chromatography

Introduction

Ion chromatography (IC) is the method of choice for the analysis of ionic contamination on electronic components. When present with moisture, some anions—particularly chloride and sulfate—form dilute concentrations of mineral acids and cause corrosion.[1] IC has been successfully applied to the determination of ionic contamination on printed circuit boards,[2,3] semiconductor wafers,[4,5] and disk drive components.[6,7] This application note focuses on the determination of ionic contamination of disk drive components, but the extraction procedure and analytical method can be applied to other electronic devices.

Modern disk drives have very close head-to-disk interfaces, making component cleanliness critical to drive performance and reliability. Anions are one of the possible contaminants of drive components. Ionic contamination can come from several sources: packaging materials, human contact, assembly environment, aqueous rinse solutions, solvents, adhesives, and lubricants. A comprehensive anion analysis of drive components prior to manufacturing can significantly reduce the incidence of corrosion and head-to-disk interface failures. The anions most routinely monitored are fluoride, chloride, bromide, nitrate, sulfate, and phosphate.[8] Acetate, formate, acrylate, methacrylate, benzoate, and oxalate are also of interest.

High-volume direct injection[9] and preconcentration[10] are the two methods used to increase IC sensitivity to the parts-per-billion (ppb) levels and lower. This application note describes the use of these approaches to determine trace anion contaminants in extracts of disk drive components.

Equipment

Thermo Scientific™ Dionex™ ICS-2500 IC system consisting of:

- GS50 Gradient pump
- CD25A Conductivity detector
- LC30 Chromatography enclosure equipped with Thermo Scientific™ Rheodyne™ Model 9126 injector PEEK, rearloading (P/N 057001)

- Thermo Scientific™ Dionex™ IonPac™ AS17 analytical column, 2 × 250 mm (P/N 055683)
- Dionex IonPac AG17 guard column, 2 × 50 mm (P/N 055685)
- 300 cm of green 0.75 mm (0.030 in.) PEEK tubing to make a 1000 µL sample loop, optional
- Dionex IonPac TAC-LP1 concentrator column, 4 × 35 mm (P/N 46026), optional
- Thermo Scientific™ Dionex™ ASRS™ ULTRA Suppressor, 2 mm (P/N 053947)
- Thermo Scientific™ Dionex™ AS40 Autosampler with 5 mL vials using caps without filters
- Thermo Scientific™ Dionex™ EG50 Eluent Generator with Thermo Scientific™ Dionex™ EluGen™ EGC II KOH cartridge (P/N 060585)

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- Thermo Scientific™ Dionex™ CR-ATC Continuously Regenerated Anion Trap Column (P/N 060477)
- Thermo Scientific™ Dionex™ Chromeleon™ chromatography workstation
- Upchurch Scientific™ plastic tubing cutter (Upchurch P/N A-327 or Thermo Scientific P/N 49584)
- Thermo Scientific™ Nalgene™ 60 mL polymethylpentene (PMP) container for extractions
- Vacuum oven, lab-line model 3625 or equivalent (VWR P/N 52433-474)

Reagents and Standards

Deionized (DI)water, Type I reagent-grade, 18 MΩ cm resistance

ACS reagent-grade materials for preparing anion standards (VWR or other)

Fluoride standard 1000 mg/L, 100 mL (Thermo Scientific P/N 037158)

Chloride standard 1000 mg/L, 100 mL (Thermo Scientific P/N 037159)

Sulfate standard 1000 mg/L, 100 mL (Thermo Scientific P/N 037160)

Nitrate standard 1000 mg/L, 100 mL (Thermo Scientific P/N 056497)

Phosphate standard 1000 mg/L, 100 mL (Ultra Scientific, VWR P/N ULICC-005)

Bromide standard 1000 mg/L, 100 mL (Ultra Scientific, VWR P/N ULICC-001)

CONDITIONS	
Eluent:	Potassium hydroxide (Dionex EG50 as the source)
Temperature:	30 °C
Dionex EG50 Offset Volume:	0 mL
Eluent Flow Rate:	0.5 mL/min
Detection:	Suppressed conductivity, Dionex ASRS ULTRA recycle mode
Dionex ASRS Current Setting:	50–100* mA
Expected Background Conductivity:	1 µS (40 mM KOH)
Expected System Backpressure:	15.2–16.6 MPa (2200–2400 psi)
Sample Volume:	1 mL for direct injection method or 5 mL for preconcentration method

* 50 mA is the low range for these conditions. The data shown in this application note was run at 100 mA.

Pump Program Method 1: 1 mL Direct Injection

Time (min)	Flow (mL/min)	DI H_2O (%)	Valve	Dionex EG50 Conc (mM)	Comments
–5.00	0.50	100	Load	0.3	0.30 mM KOH
–2.4	0.50	100	Load	0.3	Load loop, Dionex AS40 on
–0.1	0.50	100	Load	0.3	Dionex AS40 off
0.00	0.50	100	Inject	0.3	Inject, 0.3 mM KOH
6.00	0.50	100	Inject	1.0	1.0 mM KOH
19.00	0.50	100	Inject	10.0	10 mM KOH
19.20	0.50	100	Inject	10.0	10 mM KOH
35.80	0.50	100	Load	40.0	40 mM KOH

Pump Program Method 2: Preconcentrate 5 mL on a TAC-LP1

Time (min)	Flow (mL/min)	DI H_2O (%)	Valve	Dionex EG50 Conc (mM)	Comments
–9.00	0.50	100	Inject	0.3	0.3 mM KOH
–6.5	0.50	100	Load	0.3	Load TAC-LP1, Dionex AS40 on
–0.1	0.50	100	Load	0.3	Dionex AS40 off
0.00	0.50	100	Inject	0.3	Inject, 0.3 mM KOH
6.00	0.50	100	Inject	0.3	0.3 mM KOH
8.00	0.50	100	Inject	1.0	1.0 mM KOH
19.00	0.50	100	Inject	10.0	10 mM KOH
19.20	0.50	100	Inject	10.0	10 mM KOH
35.80	0.50	100	Inject	40.0	40 mM KOH

Preparation of Solutions and Reagents

Standard Solutions

Stock Anion Standard Solution (1000 mg/L)

Several of the analytes of interest are available as 1000 mg/L anion standard solutions from Thermo Fisher Scientific or other commercial sources. When commercial standards are unavailable, 1000 mg/L standards can be prepared by dissolving the appropriate amounts of the corresponding mass for the target analytes in 1000 mL of deionized water according to Table 1. We recommend making a 100 mL final volume of 1000 mg/L stock standards in 125 mL high-density polyethylene (HDPE) containers. Concentrated standards are stable for at least one month when stored at 4 °C.

Composite Standard Solution

Composite standards at lower analyte concentrations are prepared from the 1000 mg/L standards above. Select a range similar to the expected analyte concentrations in the samples. Take aliquots from this dilute standard to make working standards at the low-µg/L (parts per billion or ppb) down to the high-ng/L (parts per trillion or ppt) range. Dilute stock standards at the low-mg/L (parts per million or ppm) levels should be prepared fresh weekly. Working standards at the low µg/L (ppb) range should be made fresh daily. Acetate and formate are best calibrated separately, rather than in a mixed standard, because of the instability of these analytes.

Table 1. Amounts of compounds used to prepare 1 L of 1000 mg/L anion standards.

Anion	Compound	Mass (g)
Fluoride	Sodium fluoride (NaF)	2.210
Acetate	Sodium acetate ($CH_3COONa·3H_2O$)	2.305
Formate	Sodium formate (HCOONa)	1.511
Acrylate	Sodium acrylate ($H_2C=CHCO_2Na$)	1.324
Methacrylate	Sodium methacrylate ($H_2C=C(CH_3)CO_2Na$)	1.270
Chloride	Sodium chloride (NaCl)	1.648
Nitrite	Sodium nitrite ($NaNO_2$)	1.499
Bromide	Sodium bromide (NaBr)	1.288
Nitrate	Sodium nitrate ($NaNO_3$)	1.371
Benzoate	Sodium benzoate ($C_6H_5CO_2Na$)	1.190
Sulfate	Sodium sulfate (Na_2SO_4)	1.479
Oxalate	Sodium oxalate ($Na_2C_2O_4$)	1.522
Phthalate	Phthalic acid ($C_6H_4–1,2(CO_2H)_2$)	1.000
Phosphate	Potassium phosphate, monobasic (KH_2PO_4)	1.433

System Preparation and Setup

This section describes the procedures for the initial installation and start-up of the Dionex ASRS ULTRA, Dionex EGC II KOH EluGen cartridge, and Dionex CR-ATC. Prepare the Dionex ASRS according to the *Quickstart Instructions for the Dionex ASRS ULTRA* (Document No. 031368). Install the Dionex EGC II OH EluGen cartridge according to the instructions in the *Operator's Manual for the Dionex EG50 Eluent Generator System* (Document Number 031908). Install the Dionex CR-ATC between the Dionex EGC II KOH cartridge and the Degas Module in the Dionex EG50 according to the *Operator's Manual for the Continuously Regenerated Anion Trap Column* (Document Number 031910-01).

Connect the columns and suppressor in the IC system by using the red 0.005 in. (0.125 mm) or yellow 0.003 in (0.075 mm) PEEK tubing. Keep the lengths of connecting tubing as short as possible to minimize the system void volume and ensure efficient 2 mm column operation. Carefully use an Upchurch Scientific plastic tubing cutter to ensure that the surfaces of the tubing cuts have straight, smooth surfaces. Irregularity on the surface of a tubing end can result in unwanted additional dead volume.

For the direct injection method, make a 1000 µL sample loop by cutting a 220 cm portion of the green 0.030 in. (0.75 mm) i.d. PEEK tubing. The volume of a loop can be verified by measuring the weight difference between the sample loop filled with deionized water and the empty loop. The inside diameter of the PEEK tubing can vary by as much as 20%.

For the preconcentration method, connect the TAC-LP1 concentrator column to the Rheodyne valve as shown in Figure 1. Align the direction of the column by pointing the arrow on the label of the Dionex TAC-LP1 from Port 1 to Port 4.

It is critical to minimize the effect of band broadening when using a preconcentration technique. To minimize the dead volume that causes band broadening, use the smallest length possible of red 0.005 in (0.125 mm) PEEK tubing between the outlet of the TAC-LP1 and Port 4.

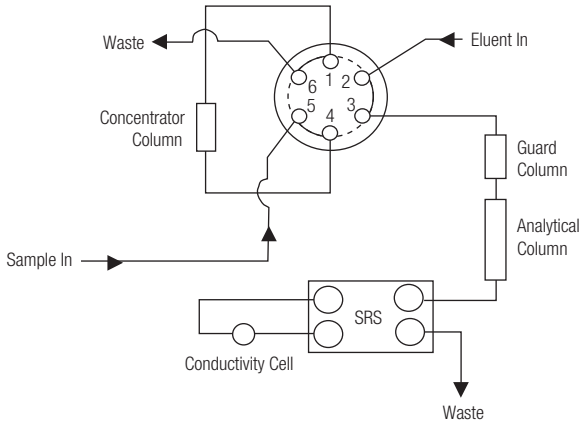

Figure 1. Loading the concentrator column.

System Operation

Fill the eluent container with degassed, high-purity, deionized water. Turn on the gradient pump to begin the flow of eluent through the system. If the system backpressure is below 14 MPa (2000 psi), a length of yellow PEEK 0.003 in. (0.075 mm) tubing should be added between the outlet of the degas assembly in the Dionex EG50 and the inlet of the injection valve. For optimal Dionex EG50 performance, maintain a system backpressure of 15.2–16.6 MPa (2200–2400 psi). Confirm that there are no leaks in the chromatographic pathway. For more information, see the *Operator's Manual for the Dionex EG50 Eluent Generator System* (Document Number 031908).

Using Chromeleon CDS, turn on the Dionex EG50 to deliver the highest eluent concentration required by the method. Allow the LC30 oven to stabilize at 30 °C. Determine the status of the system by measuring the short-term noise. In a representative 1 min level portion of the chromatogram, a peak-to-peak measurement should be less than 10 nS. It may take 12 h or more for the system to equilibrate to a stable background conductivity for trace analysis. We recommend running the system overnight to equilibrate for use the following day.

For method 2, select "Concentrator" as the "Injection Type" on the front panel of the Dionex AS40 Autosampler. This selection configures the autosampler to load at 1 mL/min against a concentrator backpressure between 345 and 690 kPa (50 and 100 psi). The "Bleed On" will be set automatically when the "Injection Type" is set to "Concentrator". This setting prevents air from accidentally being forced through the concentrator column and ensures that an accurate, reproducible volume is loaded for each injection. Select the "Proportional" sampling mode to deliver a sample aliquot equal to the fill volume of the 5 mL vial. For more information on the operation of the autosampler, see the *Operator's Manual for the Dionex AS40 Automated Sampler* (Document Number 034970).

Sample Loading

Load the sample into either the sample loop or concentrator column with a Dionex AS40 Autosampler using the 5 mL vials. For analysis of samples containing target anions at µg/L concentration levels, the probability of contamination during sample collection and storage is high. Extraction and standard containers, as well as autosampler vials and caps, should be cleaned prior to use. ***Use only Dionex AS40 sample vial caps without filters when performing low-level analyses.*** The following procedure should be used in the collection, storage, and analysis of µg/L-level samples and standards.

Extraction with PMP Containers:

1. Rinse the sample container and cap 3–5 times with deionized water. Fill the container until it overflows, cap securely, and soak for at least 4 h.
2. Empty the container and refill it with deionized water and cap securely. Soak the container for an additional 24 h before sample collection.
3. Empty the container and rinse it twice with deionized water.
4. Add the disk drive part into the extraction vessel.
5. Fill the container with 20 mL of deionized water.
6. Heat the sealed container containing the part and-deionized water for 85 °C in an oven for 1 h.
7. Remove the container from the oven and allow ~1 h for the container to cool to room temperature.

Loading Samples in the Autosampler Vials:

1. Rinse the vials and caps 3–5 times with deionized water. Place the vials and caps in a large precleaned container and soak for 4 h in deionized water.
2. Drain or empty the container and refill it with deionized water. Soak the caps and vials for an additional 24 h before use.
3. Fill the 5 mL vial with the standard, sample, or blank.
4. Insert the cap into the vial with the insertion tool (Thermo Scientific P/N 037987) and load into the sample cassette.

Results and Discussion

Choice of System Components

The microbore format, chosen for the analytical columns and suppressor, has several advantages. There is a fourfold increase in mass sensitivity for the microbore (2 mm) over the standard bore (4 mm) format with no change in concentration sensitivity. The increased mass sensitivity allows smaller sample volumes to be concentrated, and therefore reduces the time per analysis. The microbore format also uses less eluent and produces less eluent waste.

The Dionex EG50 Eluent Generator enhances IC performance for the determination of anions at trace levels.[11] This device electrolytically produces high-purity, carbonate-free KOH eluents using deionized water as the carrier stream. Gradient separations with carbonate-free hydroxide eluents have negligible baseline shifts, lower background conductivity, and are highly precise. The results include better retention time reproducibility and improved signal-to-noise ratios.

The Dionex CR-ATC is used to remove trace anionic contaminants in the eluent. This high-pressure, electrolytically regenerated trap column device operates continuously without the need for off-line regeneration. This device further minimizes baseline drift during gradient operation. A high-capacity anion trap column (ATC-HC), Thermo Scientific P/N 059604, can be used in place of the Dionex CR-ATC. The ATC-HC is placed between the outlet of the gradient pump and the inlet of the Dionex EluGen cartridge. However, the ATC-HC will not deliver the fast start-up time achieved with the Dionex CR-ATC. Also, the ATC-HC requires periodic regeneration.

The Dionex IonPac AS17 column provides the best selectivity for the analytes of interest to the electronics industry: common inorganic anions, low-molecular-weight organic acids, acrylate, methacrylate, benzoate, and phthalate. The other anion-exchange columns evaluated for this method did not adequately resolve the target analytes. For instance, the Dionex IonPac AS15 5 µm column has very good resolution for the weakly retained organic acids such as acetate, glycolate, and formate from fluoride.[12] However, several target analytes are not well resolved using the Dionex AS15 5 µm column, such as acrylate, chloride, carbonate, benzoate, and methacrylate.[13] The Dionex ASRS ULTRA delivers low background and noise for sensitivity at trace levels. The use of the DS-3 conductivity cell minimizes the effects of cell drift and temperature fluctuations.

Columns: Dionex IonPac AG17 and AS17, 2 mm
Eluent: Potassium hydroxide:
0.3 mM from 0 to 6 min
0.3–1.0 mM from 6 to 8 min
1–10 mM from 8 to 19 min
10–40 mM from 19 to 35 min
Eluent Source: Dionex EG50
Temperature: 30 °C
Flow: 0.5 mL/min
Injection: A. 1 mL direct injection
B. 5 mL preconcentrated with the Dionex IonPac TAC-LP1
Detection: Suppressed conductivity, Dionex ASRS ULTRA, recycle mode

Peaks:		A µg/L	B µg/L
1.	Fluoride	N.D.	0.10
2.	Acetate	1.7	4.6
3.	Formate	3.0	9.5
4.	Acrylate	0.68	N.D.
5.	Methacrylate	N.D.	N.D.
6.	Chloride	0.28	0.75
7.	Nitrite	0.16	1.2
8.	Bromide	N.D.	N.D.
9.	Nitrate	0.10	0.10
10.	Benzoate	0.42	0.85
11.	Carbonate	–	–
12.	Sulfate	0.64	0.30
13.	Oxalate	N.D.	N.D.
14.	Phthalate	N.D.	N.D.
15.	Phosphate	N.D.	N.D.

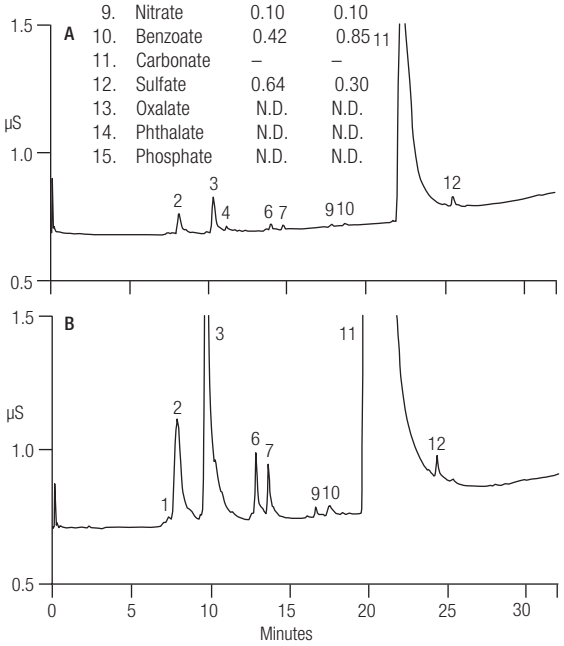

Figure 2. Deionized water extract system blanks.

Columns: Dionex IonPac AG17 and AS17, 2 mm
Eluent: Potassium hydroxide:
0.3 mM from 0 to 6 min
0.3–1.0 mM from 6 to 8 min
1–10 mM from 8 to 19 min
10–40 mM from 19 to 35 min
Eluent Source: Dionex EG50
Temperature: 30 °C
Flow: 0.5 mL/min
Injection: A. 1 mL direct injection
B. 5 mL preconcentrated with the Dionex IonPac TAC-LP1
Detection: Suppressed conductivity, Dionex ASRS ULTRA, recycle mode

Peaks:		A µg/L	B µg/L
1.	Fluoride	1.1	1.2
2.	Acetat	1.4	4.8
3.	Formate	1.5	6.6
4.	Acrylate	3.1	1.9
5.	Methacrylate	1.5	2.1
6.	Chloride	1.6	2.6
7.	Nitrite	1.3	3.1
8.	Bromide	0.7	1.0
9.	Nitrate	0.9	1.3
10.	Benzoate	5.6	10
11.	Carbonate	–	–
12.	Sulfate	3.1	3.8
13.	Oxalate	2.3	2.4
14.	Phthalate	3.6	5.6
15.	Phosphate	2.9	4.1

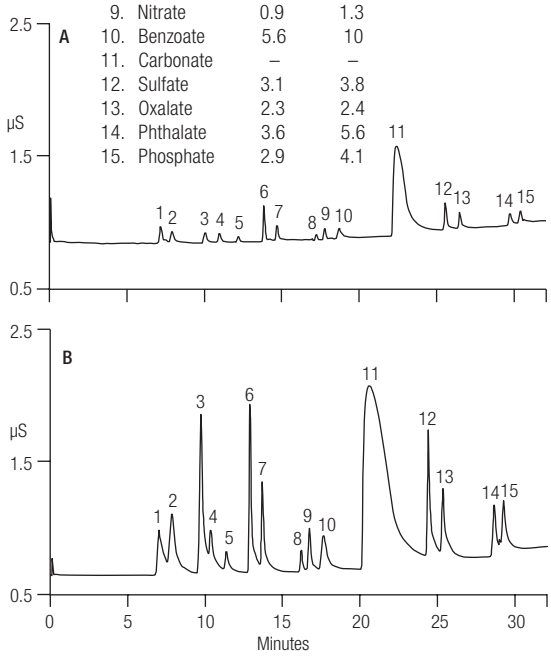

Figure 3. Trace anion standard analyses.

Method Performance

To achieve sensitivity at trace levels, we designed two methods: direct injection of 1 mL of sample and preconcentration of 5 mL of sample on a TAC-LP1. A method blank was established by subjecting 20 mL of deionized water to all the steps of the extraction procedure. The average concentration for each of the analytes of interest was calculated from seven replicate method blanks. Most analytes were detected below 1 ppb, except acetate and formate. Typical relative standards of deviation (RSDs) for the contaminant anions in the blank can range from 20–60%, because each sample makes contact with a different extraction vessel and autosampler vial. These average anion concentrations in the method blank were subtracted from the values measured in the extracts of the parts. Figure 2 shows the representative method deionized water blanks for both approaches. Determining a blank establishes a starting point above which tracelevel anion determinations can be made.

Both methods begin with a 5 min equilibration at an eluent concentration of 0.3 mM potassium hydroxide. This dilute eluent is used to elute weakly retained ions such as fluoride, acetate, and formate. A linear gradient to a higher KOH concentration is used to separate more strongly retained ions such as sulfate and phosphate. The chromatographic baseline shift during the gradient is typically less than 200 nS when using the Dionex EG50. A much larger shift in background conductivity would have been observed with manually prepared eluents.[14] The separations are performed at 30 °C to provide the best retention time reproducibility during trace analysis. Figure 3 shows a trace anion standard analyzed by each method.

Columns: Dionex IonPac AG17 and AS17, 2 mm
Eluent: Potassium hydroxide:
0.3 mM from 0 to 6 min
0.3 to 1.0 mM from 6 to 8 min
1 to 10 mM from 8 to 19 min
10 to 40 mM from 19 to 35 min
Eluent Source: Dionex EG50
Temperature: 30 °C
Flow: 0.5 mL/min
Injection: A. 1 mL direct injection
B. 5 mL preconcentrated with the Dionex IonPac TAC-LP1
Detection: Suppressed conductivity, Dionex ASRS ULTRA, recycle mode

Peaks:		A µg/L	B µg/L
1.	Sulfate	3.1	3.8
2.	Oxalate	2.3	2.4

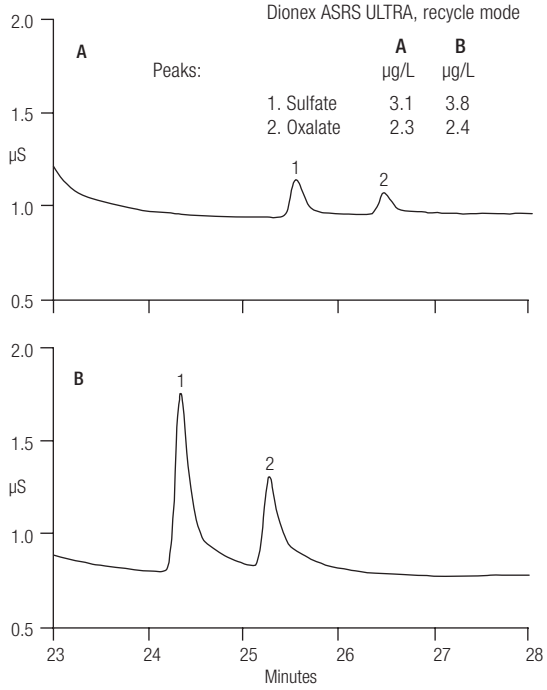

Figure 4. Comparison of direct injection and preconcentration with the Dionex IonPac AS17.

Differences in the chromatographic performance result from the direct injection and preconcentration methods. To illustrate this difference, Figure 4 shows a separation of a sulfate and oxalate. A greater response is observed with the preconcentration technique than with direct injection. This response is expected because the 5 mL preconcentration technique loads five times more sample than the 1 mL direct injection technique. Also, observe that the two analytes elute ~1.2 minutes later for the direct injection compared to preconcentration. This timing difference occurs because of the additional time required for the 1 mL sample volume to pass through the void volume of the analytical column set. In the preconcentration method, the sample is loaded off-line onto the Dionex IonPac TAC-LP1, requiring 6 min. The peaks are more efficient for the direct injection method because less band broadening occurs when loading sample directly on the analytical column, compared to loading onto a concentrator column.

Columns: Dionex IonPac AG17 and AS17, 2 mm
Eluent: Potassium hydroxide:
0.3 mM from 0 to 6 min; 0.3 to 1.0 mM from 6 to 8 min;
1 to 10 mM from 8 to 19 min; 10 to 40 mM from 19 to 35 min
Eluent Source: Dionex EG50
Temperature: 30 °C
Flow: 0.5 mL/min
Injection: A. 1 mL direct injection
B. 5 mL preconcentrated with the Dionex IonPac TAC-LP1
Detection: Suppressed conductivity, Dionex ASRS ULTRA, recycle mode

Peaks:		A µg/L	B µg/L
1.	Unidentified	–	–
2.	Fluoride	1.2	2.2
3.	Acetate	4.7	6.7
4.	Formate	4.6	8.8
5.	Acrylate	0.31	–
6.	Methacrylate	0.15	–
7.	Chloride	1.1	1.4
8.	Nitrite	0.10	0.85
9.	Bromide	0.14	0.24
10.	Nitrate	0.21	0.29
11.	Benzoate	0.56	0.83
12.	Carbonate	–	–
13.	Sulfate	0.27	0.22
14.	Oxalate	N.D.	N.D.
15.	Phthalate	N.D.	N.D.
16.	Phosphate	N.D.	N.D.
17.	Unidentified	–	–

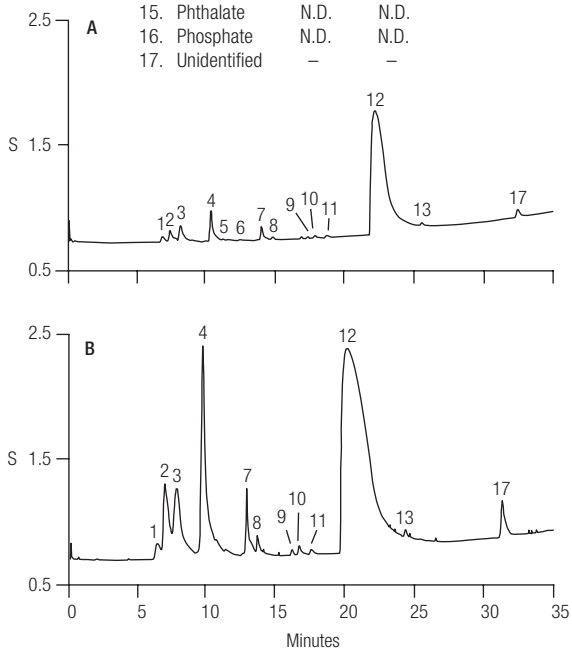

Figure 5. Analysis of deionized water extract from a disk drive spacer.

An extract solution of a disk drive spacer was evalu-ated with both methods. The spacer is fabricated from an aluminum alloy and is used as a spacer between disks. The part was soaked for 1 h in 20 mL of deionized water at 85 °C. Three 5 mL aliquots from the extract solution were loaded into the autosampler for IC analysis. Figure 5 shows representative chromatograms by both methods for the analysis of the disk drive spacer extract. The reported concentration values have not been corrected for the method blank. The anions of interest were detected below 10 µg/L. Two peaks are labeled as “unidentified”.

Columns: Dionex IonPac AG17 and AS17, 2 mm
Eluent: Potassium hydroxide:
0.3 mM from 0 to 6 min
0.3–1.0 mM from 6 to 8 min
1–10 mM from 8 to 19 min
10–40 mM from 19 to 35 min
Eluent Source: Dionex EG50
Temperature: 30 °C
Flow: 0.5 mL/min
Injection: A. 1 mL direct injection
B. 5 mL preconcentrated with the Dionex IonPac TAC-LP1
Detection: Suppressed conductivity, Dionex ASRS ULTRA, recycle mode

Peaks:		A µg/L	B µg/L
1.	Fluoride	1.8	2.0
2.	Acetate	3.1	7.7
3.	Formate	6.2	13.
4.	Acrylate	1.3	1.0
5.	Methacrylate	N.D.	0.065
6.	Chloride	4.3	5.4
7.	Nitrite	0.10	1.0
8.	Bromide	N.D.	N.D.
9.	Nitrate	0.70	0.90
10.	Benzoate	0.36	0.60
11.	Carbonate	-	-
12.	Unidentified	-	-
13.	Sulfate	1.5	1.7
14.	Oxalate	46.	46.
15.	Phthalate	0.86	1.0
16.	Phosphate	4.0	5.0

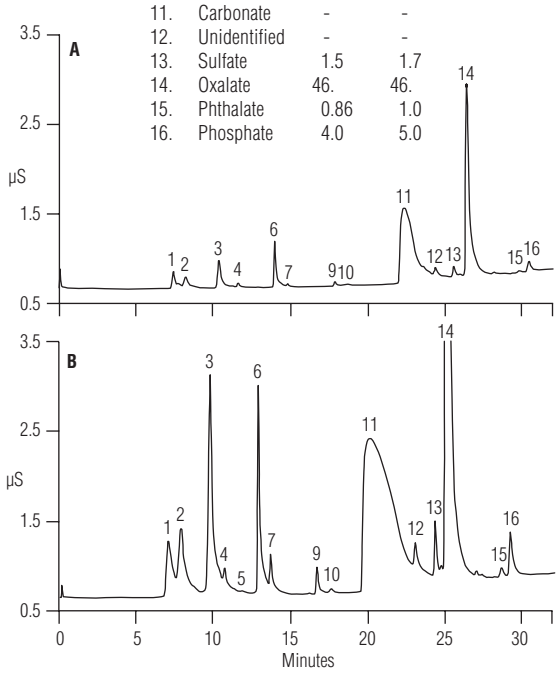

Figure 6. Analysis of deionized water extract from a disk drive clamp.

An extract of a disk clamp was also analyzed as shown in Figure 6. This component is fabricated from 300-series stainless steel and is used to secure the disk to the spindle. Higher anion levels were detected in the extract solution of the clamp than from the spacer, especially oxalate which was measured at 46 µg/L. The source of this contaminant is the oxalic acid used for cleaning this part.

Table 2. Target anions and their concentrations in calibration standards.

Anion	Levels		
	1	2	3
Fluoride	1.0	3.0	10
Acetate	1.5	5.0	15
Formate	0.6	2.0	6.0
Acrylate	1.0	3.0	10
Methacrylate	0.3	1.0	3.0
Chloride	1.0	3.0	10
Nitrite	1.0	3.0	10
Bromide	0.3	1.0	3.0
Nitrate	0.3	1.0	3.0
Benzoate	1.5	5.0	15
Sulfate	1.0	3.0	10
Oxalate	1.0	3.0	10
Phthalate	1.5	5.0	15
Phosphate	1.5	5.0	15

Calibration curves were obtained using standards prepared in deionized water. Table 2 lists the analyte concentrations in the calibration standards. Three replicate injections were used at each concentration level. Results for the anions of interest yielded a linear response with coefficients of determination (r^2) greater than 0.98. To accurately determine the area of a peak at trace levels, it may be necessary to manually draw the baselines using tools in the Chromeleon CDS software. Keep in mind that the lowest quantifiable analyte concentration is generally three to five times greater than the lowest detectable concentration.[15]

Table 3. MDLs for analysis of deionized water extracts of disk drive components.

Anion	1 mL Direct Injection MDL,* µg/L	5 mL TAC-LP1 MDL,* µg/L Preconcentration
Fluoride	0.08	0.024
Acetate	0.16	0.072
Formate	0.17	0.038
Acrylate	0.45	0.12
Methacrylate	0.35	0.11
Chloride	0.05	0.014
Nitrite	0.10	0.031
Bromide	0.16	0.043
Nitrate	0.11	0.028
Benzoate	0.71	0.27
Sulfate	0.13	0.028
Oxalate	0.17	0.035
Phthalate	0.37	0.10
Phosphate	0.28	0.076

*Calculated based on three times signal-to-noise

Table 3 summarizes the method detection limits (MDLs) for the target analytes that were calculated for both methods. MDLs were calculated based on three times the signal-to-noise ratio. The 5 mL preconcentration method has the most sensitivity, but requires an additional concentrator column, more sample, and more time to load the sample. Conversely, the 1 mL direct injection method has good sensitivity without the need for a preconcentration column.

The following calculations are used to determine the weight of the anionic contaminants per unit area.[16] The level in the blank is subtracted from that found in the sample:

$$C_s - C_b = C_{s-b} \qquad \text{(equation 1)}$$

where C_s is the concentration in the sample, C_b is the concentration in the blank, and C_{s-b} is the blank-corrected concentration for the sample in nanograms per milliliter (ng/mL). To calculate the total weight in nanograms of the ionic species extracted, the extract volume is multiplied by the volume injected:

$$(C_{s-b}\ \text{ng/mL}) \times (20\ \text{mL extracted}) = W \qquad \text{(equation 2)}$$

where W is the weight of the extracted ion in nano-grams. The weight is referenced to the area of the part with the following equation:

$$W/A = X \qquad \text{(equation 3)}$$

where A is the area of the part in cm^2 and X is the weight per unit area in ng/cm^2.

Precautious

When performing trace analysis, special care must be taken to minimize contamination. Use only the highest quality deionized water. The sources of trace-level contamination are numerous. To minimize contamination, wear disposable, powder-free polyvinyl chloride (PVC) gloves. After putting them on, rinse with deionized water and air dry. Do not dry with paper towels. All containers should be dedicated for this analysis and copiously rinsed with 18 MΩ cm deionized water before use. Exercise caution when handling anything that could have contact with the blank, samples, or standards. The various components in the chromatographic flow path (eluent containers, injector, pump, valves, tubing, columns, suppressor, and conductivity cell) are all potential sources of contamination. Take care when switching from a system setup that previously handled significant concentrations of anions. Rinse with high-purity water to reduce residual contamination. If unexpected broad peaks appear in the chromatogram, it may be necessary to modify the gradient. These peaks can result from retained species of previous injections. Confirm this possibility by using an eluent concentration higher than the ending concentration of the gradient. It is best to run with this higher concentration for 15 min after all peaks of interest have eluted. To confirm that the column has been cleaned of retained species, rerun a sample to observe the quality of the separation.

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