Application Brief 106

Trace Anion Analysis Using Ion Chromatography with RFIC-ESP and an Electrolytic Water Purifier

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Introduction

The measurement of ng/L levels of anions in high-purity water is a challenging application. The Thermo Scientific™ Dionex™ ICS-3000 system utilizes the Thermo Scientific™ Dionex™ AutoPrep technique, which provides significant advantages in automating sample preparation and calibration for trace analysis. The Dionex AutoPrep technique utilizes the second pump in the Dionex ICS-3000 DP module to load samples and standards. The Dionex ICS-3000 DC module mounts a second 10-port valve and a 10 mL loop, which are necessary for this application.[1]

Eluent generation (EG) is an essential element in the successful application of this system to trace analysis due to its ability to generate extremely low-noise hydroxide eluent, which is very low in carbonate contamination. Additionally, the highly precise and reproducible gradients afforded by EG enhance chromatographic reproducibility, which aids in the determination of trace level analytes.

This application brief (AB) demonstrates the use of Reagent-Free™ Ion Chromatography with electrolytic sample preparation (RFIC-ESP™). The system provides power to the Thermo Scientific™ Dionex™ EWP Electrolytic Water Purifier, which in turn provides ultrapure water to load samples and standards, thus replacing the second pump used in the Dionex ICS-3000 system. In addition, the second valve is integrated into the Thermo Scientific™ Dionex™ ICS-2100 system to provide a compact, easy-to-operate system. The closed-cycle configuration enhances the baseline performance of the system and the removal of the loading pump reduces system complexity and cost. The Dionex ICS-2100 system is a fully capable RFIC-EG™ system that provides the same benefits of EG as described in the Dionex ICS-3000 system.

Instrumentation

- Dionex ICS-2100 system (P/N 069659)
- 10-port valve kit (P/N 069473)
- Calibrated loops kit (P/N 066342)
- Dionex Electrolytic Water Purifier (P/N 071553)
- Thermo Scientific™ Dionex™ IonPac™ AG18 (4 mm) and AS18 (4 mm) columns (P/N 060551 and P/N 060549)
- Thermo Scientific™ Dionex™ IonPac™ UTAC Ultratrace Anion Concentrator Cartridge (P/N 063079)

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Experimental Conditions

A Dionex ICS-2100 system was equipped with a two-position, 10-port valve in the auxiliary valve position, in addition to its standard six-port injection valve. A UTAC-LP1 concentrator column was installed in place of the sample loop on the six-port valve. As described above, the 10-port valve had a 10 µL loop installed as one sample loop, with the other loop being a 10 mL loop. Both loops were obtained from the calibrated loops kit (P/N 066342). The volume of water used to equilibrate the concentrator column to low-ionic strength before loading, and the water used to transfer the standards, was kept constant at 3.6 mL. This was added to the 10 mL transferred from the sample side and concentrated. Thus, a total of 13.6 mL of sample was concentrated.

The eluent was produced by eluent generation from a KOH cartridge, and a hydroxide gradient was used for the separation. A Dionex IonPac AG18 guard column and a Dionex IonPac AS18 analytical column were used to separate the constituent anions.

Chromatographic Conditions

System:	Dionex ICS-2100 Integrated IC system
Injection Volume:	10 µL (Standard) or 10 mL (Sample) + 3.6 mL transfer volume from electrolytic water purifier
Column:	Dionex AS18 separator, 4 mm, and AG18 guard, 4 mm
Column Temperature:	30 °C
Concentrator:	UTAC-LP1
Eluent:	KOH gradient 18 mM to 50 mM from 0 to 10 min 50 mM 10 to 18 min 18 mM at 18.1 min, hold to end, 24 min
Eluent Source:	Thermo Scientific™ Dionex™ EluGen™ II KOH cartridge on EGC-1
Eluent Flow Rate:	1.0 mL/min
Detection:	Thermo Scientific™ Dionex™ Suppressed conductivity (35 °C cell temp.)
Suppressor:	Thermo Scientific™ Dionex™ ASRS™ 300, 4 mm; operated at 99 mA
Electrolytic Water Purifier:	20 mA from Dionex ICS-2100 auxiliary power supply

Calibration

The 10 µL loop was used to measure a precise volume of diluted standard to the concentrator column. By repeatedly filling and dispensing the volume of the loop, multiple concentration levels were simulated. One, two, and four standard loop volumes were used to generate a standard curve. Loading the concentrator column with 13.6 mL of water (by controlling the time the column was in line with the load position of the valve), allows one to determine anion concentrations down to the low ng/L levels. The standards used are shown in Table 1.

Table 1. Standard concentrations (µg/L).

Peak	Ret. Time (min)	Standard 10 µL	Standard 2 × 10 µL	Standard 4 × 10 µL
Fluoride	3.7	20	40	80
Chloride	5.2	30	60	120
Nitrite	6.1	100	200	400
Bromide	7.7	100	200	400
Sulfate	8.0	150	300	600
Nitrate	8.6	100	200	400
Phosphate	11.2	150	300	600

Column: Dionex IonPac AS18 4 mm, AG18 4 mm
Concentrator: UTAC-LP1
Eluent: KOH gradient
18 mM to 50 mM from 0 to 10 min
50 mM 10 to 18 min
18 mM at 18.1 min, hold to end, 24 min
Eluent Source: Dionex EluGen II KOH cartridge on EGC-1
Flow Rate: 1.0 mL/min
Temperature: 30 °C
Detection: Suppressed conductivity (35 °C cell temp.)
Suppressor: Dionex ASRS 300, 4 mm; operated at 99 mA
Electrolytic Water Purifier: 20 mA from Dionex ICS-2100 auxiliary power supply

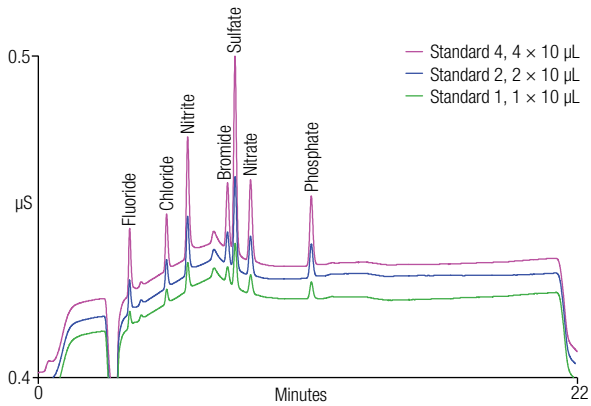

Figure 1. Standard levels overlaid.

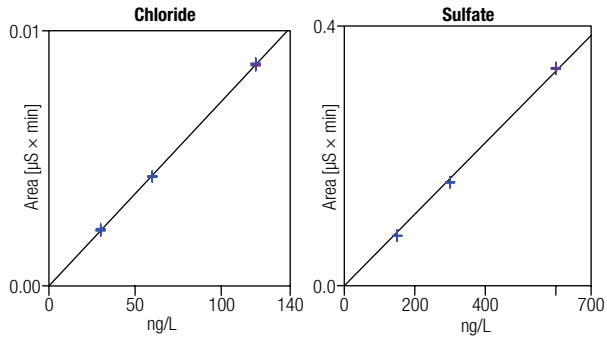

Figure 2. Calibration plots for chloride and sulfate (five replicates per level).

Table 2. Calibration report.

Peak Name	Ret.Time (min)	Calibration Type	Points	Coeff. of Det.
Fluoride	3.7	Lin	15	0.99077
Chloride	5.2	Lin	15	0.99348
Nitrite	6.1	Lin	15	0.99692
Bromide	7.7	Lin	15	0.99910
Sulfate	8.0	Lin	15	0.99301
Nitrate	8.6	Lin	15	0.99272
Phosphate	11.2	Lin	15	0.94801

Results

EWP Performance Verification

The functionality of the Dionex EWP was tested by comparing results with and without the water purifier in the eluent stream. The water purifier was removed from the eluent stream and the effluent of the detector cell was directly concentrated on the UTAC column and injected. As shown in Figure 3, the water purifier is effective at removing nearly all the background ions. This demonstrates the capability of the Dionex EWP to produce very low backgrounds of the common anions. Only fluoride, chloride, and sulfate can be detected under these conditions at levels above the limit of quantification. Unquantified levels of contaminants with retention times of formate and acetate were also detected.

Table 3. Background anion concentrations after Dionex EWP treatment.

Ion	Amount (ng/L)
Fluoride	2
Chloride	3
Sulfate	5

Column:	Dionex IonPac AS18 4 mm, AG18 4 mm
Concentrator:	UTAC-LP1
Eluent:	KOH gradient 18 mM to 50 mM from 0 to 10 min 50 mM 10 to 18 min 18 mM at 18.1 min, hold to end, 24 min
Eluent Source:	Dionex EluGen II KOH cartridge on EGC-1
Flow Rate:	1.0 mL/min
Temperature:	30 °C
Detection:	Suppressed conductivity (35 °C cell temp.)
Suppressor:	Dionex ASRS 300, 4 mm; operated at 99 mA
Electrolytic Water Purifier:	20 mA from Dionex ICS-2100 auxiliary power supply

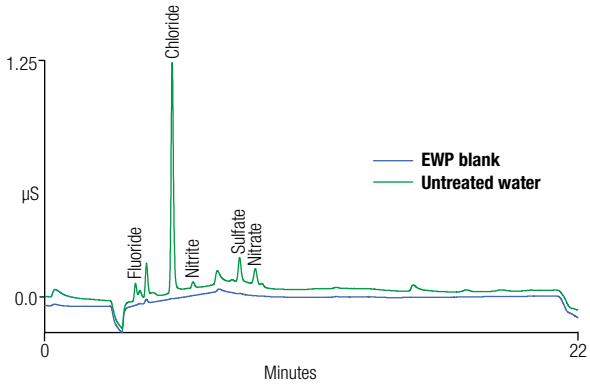

Figure 3. Untreated water (eluent after the detector) compared to EWP processed water.

An example of the analysis of an ultrahigh-purity water sample is shown in Figure 4. This is typical of the results that can be expected from this type of analysis. Minimum detection limits of less than a ng/L are possible using this technique with the closed loop configuration afforded by the use of a Dionex EWP.

Column:	Dionex IonPac AS18 4 mm, AG18 4 mm		
Concentrator:	UTAC-LP1		
Eluent:	KOH gradient, 18 mM to 50 mM from 0 to 10 min 50 mM 10 to 18 min, 18 mM at 18.1 min, hold to end, 24 min		
Eluent Source:	Dionex EluGen II KOH cartridge on EGC-1		
Flow Rate:	1.0 mL/min		
Temperature:	30 °C		
Detection:	Suppressed conductivity (35 °C cell temp.)		
Suppressor:	Dionex ASRS 300, 4 mm; operated at 99 mA		
Electrolytic Water Purifier:	20 mA from Dionex ICS-2100 auxiliary power supply		
Peaks:	1. Fluoride	24	ng/L (ppt)
	2. Chloride	32	
	3. Nitrite	42	

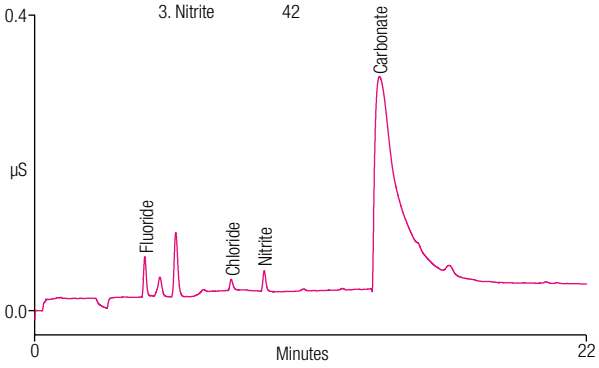

Figure 4. Chromatogram of ultrahigh-purity water.

Conclusion

Trace anion quantification is demonstrated using a Dionex ICS-2100 system with an integrated, auxiliary, 10-port valve, and an Electrolytic Water Purifier. The low backgrounds generated when using the Dionex EWP along with eluent generation and high-performance ion chromatography, all work together to provide sub ng/L minimum detection limits. The system represents a low-cost solution for the ultratrace analysis of anions and cations. Determination of ions at these low levels is necessary to characterize the impurities in the high-purity water being produced by the semiconductor manufacturing industry.

References

1. Dionex Corporation. *AutoPrep User's Guide.* Sunnyvale, CA, 2008. [Online] http://www.thermoscientific.com/content/dam/tfs/ATG/CMD/CMD%20Documents/Product%20Manuals%20&%20Specifications/Chromatography/Chromatography%20Sample%20Preparation%20Equipment/Man-065180-AutoPrep-Man065180-EN.pdf (accessed Feb. 11, 2016).

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