DIONEX

Application Brief 106

Trace Anion Analysis Using an ICS-2100 System with RFIC-ESP and an Electrolytic Water Purifier

INTRODUCTION

The measurement of ng/L levels of anions in high-purity water is a challenging application. The Dionex ICS-3000 system utilizes the AutoPrep technique, which provides significant advantages in automating sample preparation and calibration for trace analysis. The AutoPrep technique utilizes the second pump in the ICS-3000 DP module to load samples and standards. The 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 Electrolytic Water Purifier (EWP) and the EWP in turn provides ultrapure water to load samples and standards, thus replacing the second pump used in the ICS-3000 system. In addition, the second valve is integrated into the 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 ICS-2100 is a fully capable RFIC-EG™system which provides the same benefits of EG as described in the ICS-3000 system.

INSTRUMENTATION

Dionex ICS-2100 (P/N 069659)

10-port valve kit (P/N 069473)

Calibrated loops kit (P/N 066342)

Electrolytic Water Purifier (P/N 071553)

IonPac® AG18 (4 mm) and AS18 (4 mm) column (P/N 060551 and P/N 060549)

UTAC-LP1 Concentrator Cartridge (P/N 063079)

EXPERIMENTAL CONDITIONS

An ICS-2100 system was equipped with a 2-position, 10-port valve in the auxiliary valve position, in addition to its standard 6-port injection valve. An UTAC-LP1 concentrator column was installed in place of the sample loop on the 6-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. An IonPac AG18 guard column and an IonPac AS18 analytical column were used to separate the constituent anions.

Table 1. Chromatographic Conditions	
System	**ICS-2100**
Injection Volume	10 µL (Standard) or 10 mL (Sample) + 3.6 mL transfer volume from electrolytic water purifier
Column	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	EluGen® II KOH cartridge on EGC-1
Eluent Flow Rate	1.0 mL/min
Detection	Suppressed conductivity (35 °C cell temp.)
Suppressor	ASRS® 300, 4 mm; operated at 99 mA
Electrolytic Water Purifier	20 mA from 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 2.

Table 2. 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

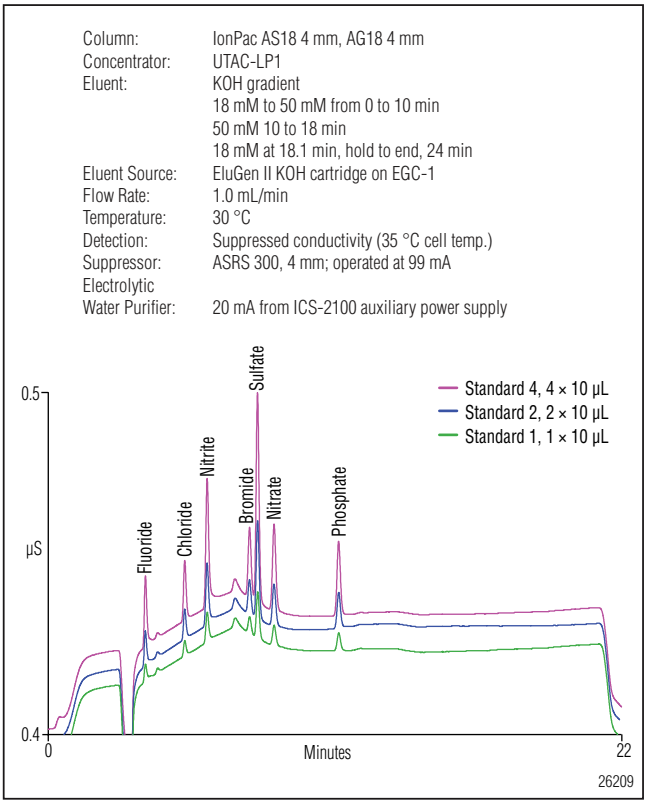

Figure 1. Standard levels overlaid.

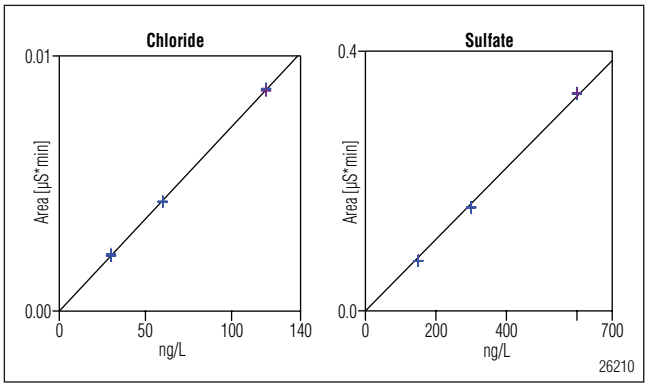

Figure 2. Calibration plots for chloride and sulfate (5 replicates per level).

Table 3. Calibration Report				
Peak Name	**Ret.Time (min)**	**Cal. 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 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 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 4. Background Anion Concentrations After EWP Treatment

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

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 an EWP.

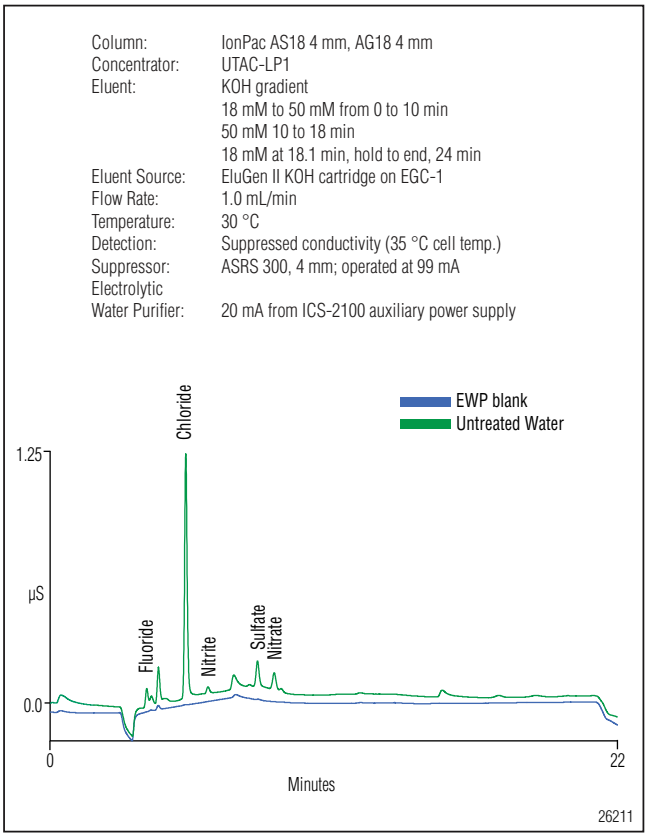

Figure 3. Untreated water (eluent after the detector) compared to EWP processed water.

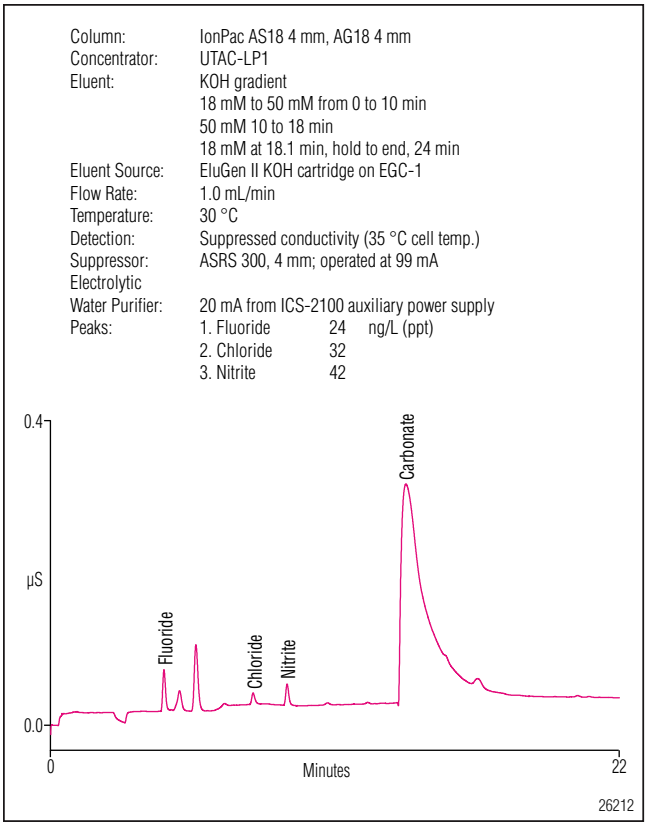

Figure 4. Chromatogram of ultrahigh-purity water.

CONCLUSION

Trace anion quantification is demonstrated using an ICS-2100 system with an integrated, auxiliary, 10-port valve, and an Electrolytic Water Purifier. The low backgrounds generated when using the 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*. Doc. No. 065180-01, Sunnyvale, CA, 2008.

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LPN 2322 PDF,10/09