Determination of Trace Levels of Inorganic Anions in High-Purity Water Using Capillary Ion Chromatography

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One of the primary concerns in all power plants is to ensure the availability of high-purity water for the generation of ultrapure steam in the water–steam cycle of a power plant. Anions and organic acids should be monitored in raw water, demineralizer influent/effluent, process steam, boiler feed water, boiler blowdown water, high- and low-pressure steam condensate, and condensate polisher water. The measurement of trace levels of ionic impurities throughout the power generation process is critical for the identification and prevention of corrosive conditions in many power plant components. Corrosive ions should be minimized and continuously monitored. Control of corrosive impurities, such as strong acid anions, provides valuable information regarding the source of contamination, likely rates of contaminant buildup, and probable rates of corrosion, as well as timely data during the startup and shutdown of power plants.[1, 2]

Ion chromatography (IC) has become an important technique for monitoring water quality and for the determination of ionic species with respect to corrosive ions. Anions in the mg/L and µg/L levels can be analyzed with a large-volume (1–2 mL) direct-injection technique. For the determination of lower levels of ionic impurities (low µg/L or ng/L levels), sample preconcentration is necessary.[3] Typically, the analytes of interest are preconcentrated on a small precolumn in order to strip ions from a measured sample volume, which can range from 10–50 mL depending on the required detection limits.

The large volume of sample is typically delivered to the precolumn using a sample loading pump. However, care must be taken to avoid trace contamination resulting from the high-purity water coming into contact with the various pump components; also, the loading of the sample can take up to 50 min if 50 mL of sample is preconcentrated.

In capillary IC, everything is scaled down by a factor of 10 to 100 (Table 1).

Table 1. Parameters scaled down from analytical format to capillary.

	Analytical Format	Capillary Format
Column i.d.	4 mm	0.4 mm
Flow Rate	1.0 mL/min	10 µL/min
Injection Volume	40 mL	0.4 µL
Eluent Consumption/ Waste Generated	43.2 L/month	0.432 L/month
EGC Lifetime (75 mM)	28 days	18 months
Mass Detection Limits	7000 fg	70 fg

Converting IC methods from analytical to capillary scale provides the user with many advantages. One of the benefits is that the system can be left on and ready to run samples, without any need for continuous calibration. This mode of operation is unique to capillary IC and allows the consumption of only 15 mL of water a day, equating to 5.2 L a year. As a consequence, the waste generated is also dramatically reduced. The capillary eluent generation cartridge (EGC) producing the eluent lasts for 18 months under continuous operation mode, thereby reducing the overall cost of ownership.

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Scaling down the cross-sectional area of the column to 0.4 mm provides an increase in mass sensitivity by a factor of 100. For high-purity water analysis, where detection limits of sub-µg/L to ng/L are needed, a 0.4 mm column is highly beneficial and allows for a 200 µL injection on a capillary IC system rather than the equivalent to performing a 20 mL injection on an analytical system. The 200 µL injection volume can be injected onto a precolumn using a standard delivery device such as an autosampler, thereby eliminating cross contamination of the sample when it comes into contact with additional hardware like a sample loading pump. The ability to perform a direct injection onto a precolumn simplifies trace analysis and reduces overall analysis time. The sample loading time can be reduced by as much as 45 min when scaling down from 50 mL to 500 µL.

Figure 1 shows the determination of inorganic anions in high-purity water using a capillary Thermo Scientific™ Dionex™ IonPac™ AS15 anion-exchange column with suppressed conductivity detection. The separation is performed using a KOH gradient electrolytically generated from deionized water using an eluent generator. The sample (180 µL) is preconcentrated on a monolithic anion concentrator with an autosampler. Sample A is deionized water and Sample B is deionized water spiked with inorganic anions in the µg/L to ng/L concentration range. The chromatogram clearly demonstrates the high sensitivity and resolution achievable with capillary IC for the analysis of inorganic anions that are important to the power industry.

Capillary IC has taken mass sensitivity and ease-of-use to a whole new level for the power industry. It has simplified IC while simultaneously increasing the power and reproducibility of ion analysis. Capillary Reagent-Free™ IC (RFIC™) systems redefine IC.

Column:	Dionex IonPac AS15 column, 0.4 × 250 mm
Eluent Source:	EGC-KOH capillary
Eluent:	7 mM KOH (0 to 10 min), 7–32 mM KOH (10 to 16 min), 32–50 mM KOH (16 to 30 min), 50–65 mM (30 to 33 min), 7 mM KOH (33 to 38 min)
Flow Rate:	12 µL/min
Temperature:	30 °C
Concentrator:	Thermo Scientific Dionex IonSwift™ MAC-100
Inj. Volume:	180 µL
Detection:	Suppressed conductivity Thermo Scientific Dionex ACES™ Anion Capillary Electrolytic Suppressor

Samples: A: Deionized water
B: A + 0.5 µg/L fluoride; 2.5 µg/L chloride, nitrite, bromide, nitrate, and phosphate; 5.0 µg/L sulfate

Peaks:

	A	B
1. Fluoride	0.018	0.48 µg/L
2. Chloride	0.12	2.49
3. Nitrite	0.042	2.53
4. Carbonate	—	—
5. Sulfate	0.075	4.72
6. Bromide	—	2.36
7. Nitrate	0.15	2.58
8. Phosphate	—	2.15

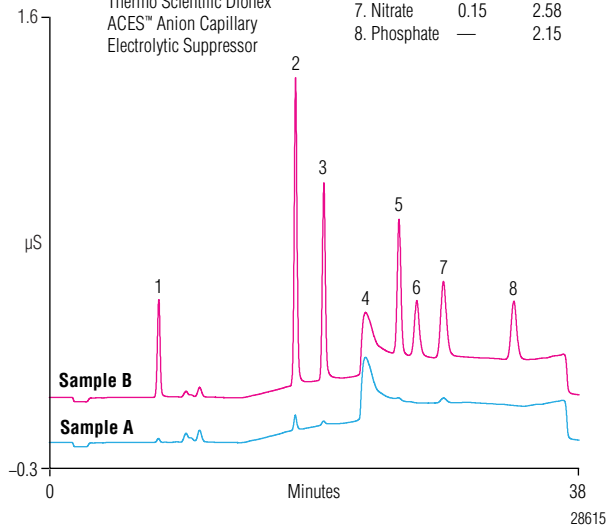

Figure 1. Analysis of trace anions in high-purity water with capillary ion chromatography.

References

1. *PWR Secondary Water Chemistry Guidelines;* Report TR-102134, Electric Power Research Institute: Palo Alto, CA, May 1993.
2. *Key Issues–Electricity Supply;* Nuclear Energy Institute: Washington, DC, 2007. Available at http://www.nei.org/keyissues/reliableandaffordableenergy/electricitysupply (2000, 15, 1479–1484, accessed April 4, 2011).
3. Weiss, J. *Ion Chromatography,* 2nd ed.; VCH: Weinheim, Germany, 1995, pp 360–367.

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