DIONEX
Part of Thermo Fisher Scientific

Application Note 286

Determination of Trace Copper, Nickel, and Zinc in Boiling Water Reactors Using Nonsuppressed Conductivity Detection

INTRODUCTION

Currently, more than 440 commercial nuclear power plants operate worldwide in 30 countries, providing ~14% of the global electricity demand.[1] The U.S. is the world's largest producer of nuclear power, with 104 nuclear power plants operating in 31 states, generating ~20% of the country's electricity and >30% of the total global nuclear generation of electricity.[2] The United Nations predicts a growth in the world population from 6.6 billion in 2007 to 8.2 billion by 2030; therefore, demand for energy is also expected to significantly increase over this same period.[3] The most dramatic increase in demand is expected in Asia with an average of 4.7% per year to 2030, while the demand in the U.S. is expected to increase at a lower rate of ~1% per year to 2035, according to a conservative estimate by the U.S. Department of Energy.[3,4]

There are two common types of nuclear reactors: the most popular reactor for generating electricity is the pressurized water reactor (PWR), which is installed in ~60% of the nuclear power plants worldwide. This design is distinguished by having a primary cooling circuit that flows through the core of the reactor at very high pressure and a secondary circuit where steam is generated to drive the turbine. The next most common reactor is known as a boiling water reactor (BWR), which is installed in ~20% of the nuclear power plants worldwide. The design of a BWR is similar to the PWR, except only a single circuit exists where the water is maintained at a lower pressure to allow the water to boil at approximately 285 °C.[5]

According to the Electric Power Research Institute, BWR components are susceptible to damage caused by intergranular stress corrosion cracking (IGSCC) and other types of corrosion.[6] This can cost the plant billions of dollars due to extended outages, replacement and repair of components, and it can also mean increased radiation exposure. Therefore, every nuclear power plant must maintain strict control of its water chemistry by periodically monitoring for ionic impurities to minimize IGSCC, this helps maintain the long-term integrity of the reactor and reactor coolant system.

Corrosion products are present as impurities in the feedwater, condensate, and reactor coolant as ionic, colloidal, or oxide forms. Common corrosion products typically monitored at various sites within the plant include iron, copper, nickel, zinc, chromium, and cobalt. More than 80% of BWR plants analyze for iron, nickel, copper, and zinc in reactor water, and nearly all the BWR plants determine these metals in feedwater. Copper and zinc are reportedly more significant in plants containing brass or other copper-alloy condenser tubes. In addition, zinc is also an additive used in many plants to control the shutdown radiation dose rate. Nickel and chromium are corrosion products in BWRs from stainless steel piping.[7] Reliable analytical methods must be used by the individual nuclear power plants to minimize maintenance costs and related expenses associated with corrosion products.

Ion chromatography (IC) is a well established, accepted technique used in the nuclear power industry for the determination of trace concentrations of transition metals and other corrosive ions. The best selectivity and sensitivity for achieving low to sub-µg/L detection limits for transition metals can be obtained by separating anionic complexes of the metals using pyridine-2,6-dicarboxylic acid (PDCA) included in the eluent, followed by postcolumn reaction with 4-(2-pyridilazo) resorcinol (PAR) and absorbance detection at 530 nm. This approach was successfully used to determine trace concentrations of iron, copper, nickel, and zinc in BWR and PWR matrices.[8]

Alternately, cation-exchange chromatography with nonsuppressed conductivity detection can be used to determine selected transition metals. This technique has been used to determine low-µg/L concentrations of nickel and zinc in PWR matrices containing boric acid and lithium hydroxide for pH adjustment (see Dionex Application Note 250.[9]) However, this method is not suitable for determination of iron due to the lack of specificity for the different oxidation states; therefore, the authors recommend the procedure described in Dionex Application Note 277.[8] Although nonsuppressed conductivity does not provide equivalent sensitivity and selectivity for transition metals relative to a postcolumn reaction with visible detection, it does provide a direct and simple approach for this determination and is therefore suitable for use in some power plants, depending on their analysis requirements.

The work shown here describes the determination of trace concentrations of copper, nickel, and zinc in a BWR matrix (i.e., deionized water) by cation-exchange chromatography using a 2 mm Thermo Scientific Dionex IonPac™ SCS 1 column and nonsuppressed conductivity detection. A Thermo Scientific Dionex Ultralow Pressure Trace Cation Concentrator (TCC-ULP1) column is used to concentrate 8 mL of sample, which enables detection limits of <0.2 µg/L for copper, nickel, and zinc. The linearity, detection limits, and precision of the method for determining the target transition metals in a BWR sample are discussed.

EQUIPMENT

Thermo Scientific Dionex ICS-2100 system* including:
  Single isocratic pump
  Vacuum degasser
  High-pressure 6-port valve
  Column heater enclosure
  Conductivity cell

Thermo Scientific Dionex AS Autosampler with 10 mL syringe (P/N 055068), 8.2 mL sampling needle assembly (P/N 061267), and 10 mL vials/tray

Dionex IonPac Mixer, 500 µL (P/N 079971) for low-noise operation

Thermo Scientific Dionex Chromeleon™ Chromatography Data System (CDS) software, 7.1

**Any Thermo Scientific Dionex system with temperature control can be used for this application, including the ICS-1100, 1600, 3000, or 5000.*

REAGENTS AND STANDARDS

Deionized (DI) water, Type I reagent grade, 18.2 MΩ-cm resistivity or better

Combined Six Cation Standard II, 100 mL (P/N 057590)

Zinc sulfate monohydrate, ≥99.9% trace metals basis (Sigma-Aldrich P/N 307491)

Nickel sulfate hexahydrate, crystalline/certified ACS (Fisher Scientific P/N N-73)

Copper (II) sulfate pentahydrate, ACS grade (98.0–102.0%), (J.T. Baker, VWR P/N JT1841-1)

Oxalic acid dihydrate, ACS reagent, ≥99.5% (Fluka P/N 75700)

Methanesulfonic acid, >99% (P/N 033478)

CONDITIONS

Columns: Dionex IonPac SCS 1 Analytical, 2 × 250 mm (P/N 079808)
Dionex IonPac SCG 1 Guard, 2 × 50 mm (P/N 079810)
Eluent: 2 mM MSA/0.5 mM Oxalic acid
Flow Rate: 0.25 mL/min
Sample Volume: 8 mL
Temperature: 30 °C
Conc. Column: Dionex IonPac TCC-ULP1, 5 × 23 (P/N 063783)
Detection: Nonsuppressed conductivity
Background: ~900 µS
Noise: ~5–7 nS peak-to-peak
Backpressure: ~2100 psi
Run Time: 35 min

PREPARATION OF SOLUTIONS AND REAGENTS

Oxalic Acid Eluent Stock Solution, 50 mM

To prepare a 50 mM oxalic acid solution, add 6.303 g of oxalic acid dihydrate to a 1 L polypropylene volumetric flask and bring to volume with DI water. Invert the solution several times to mix, then store at room temperature in a designated location until needed.

Eluent Solution

Prepare 1.0 N methanesulfonic acid (MSA) stock solution by adding 96.10 g MSA, >99% to a 1 L volumetric flask containing ~500 mL of DI water. Bring to volume and mix thoroughly. The authors recommend initially preparing 3 mM MSA eluent to reproduce the quality assurance (QA) chromatogram supplied with the column. To prepare 3 mM MSA, add 3 mL 1.0 N MSA to a 1 L volumetric flask containing ~500 mL of degassed DI water. Bring to volume and mix thoroughly. To prepare the eluent solution used to determine the metals in this application (2 mM MSA/0.5 mM oxalic acid), combine 2 mL 1.0 N MSA and 10 mL 50 mM oxalic acid in a 1L volumetric flask containing ~500 mL degassed DI water. Bring to volume with degassed DI water and mix thoroughly. Store the eluent under ~5–10 psi of head pressure with an inert gas in a plastic eluent bottle.

Zinc Standard Solution, 1000 mg/L

Dissolve 0.2744 g zinc sulfate monohydrate in 100 mL DI water. Store this solution at 4 °C when not in use.

Nickel Standard Solution, 1000 mg/L

Dissolve 0.4478 g nickel sulfate hexahydrate in 100 mL DI water. Store this solution at 4 °C when not in use.

Copper Standard Solution, 1000 mg/L

Dissolve 0.3929 g copper sulfate pentahydrate in 100 mL of DI water. Store this solution at 4 °C when not in use.

Intermediate Working Standard

Prepare a 20 mg/L combined intermediate solution for copper, nickel, and zinc by adding 400 µL from each of the 1000 mg/L metal stock solutions to a 20 mL scintillation vial. Then add 4 mL 1.0 N MSA followed by 14.80 g DI water. Prepare a secondary intermediate standard by diluting the primary intermediate standard 1:100 to prepare a combined 200 µg/L each of Cu, Ni, and Zn. Store this solution at 4 °C when not in use.

Working Standard Solutions

The working standards for Cu, Ni, and Zn were prepared in the range of 0.25 to 5.0 µg/L by adding the appropriate volumes of the 200 µg/L secondary intermediate standard solution to a 100 mL volumetric flask, then bringing with DI water. These standards were shown to be stable during the duration of this study when stored at 4 °C when not in use. However, if the quality control check standards deviate from an acceptable range, prepare a fresh standard from the stock solution.

SAMPLE

A DI water matrix was used to simulate a BWR sample in a nuclear power plant. The sample was prepared using the same procedure as for the working standards. The accuracy and precision of the method for determining trace concentrations of metals in a simulated BWR sample was evaluated by spiking the sample with 0.5 µg/L each of Cu, Ni, and Zn.

SYSTEM PREPARATION AND CONFIGURATION

The system configuration and preparation for the work shown here are described for the Dionex ICS-2100 system for determination of nonsuppressed cations.

Configure the IC system by installing the 2 × 50 mm Dionex IonPac SCG 1 and 2 × 250 mm Dionex IonPac SCS 1 columns in the column compartment. Connect the outlet of the analytical column directly to the inlet of the conductivity detector and the outlet of the detector to a waste line. To reproduce the QA chromatogram supplied with the analytical column, install a 6 µL sample loop on the injection valve. A Dionex IonPac mixer is required for use with the Dionex IonPac SCS 1 column to reduce the effects of small temperature fluctuations or pump pulsations, and thereby reduce background noise. Install the mixer before the eluent inlet of the injection valve. To invert the signal polarity to obtain positive analyte peaks, open the Instrument Configuration screen in the Dionex Chromeleon CDS and double-click *ICS-2100* system under the *Instrument*. Then select the *Signal panel* and double-click *ED1*. In the *ED1* panel, change the *Factor* from 1.000 to –1.000. Repeat this process for the ED_1_Total signal channel.

Install and configure the AS autosampler. This method requires configuration of the Dionex AS autosampler in Sample mode to concentrate using the AS front panel (under System Parameters). The Concentrate Sample mode allows the Dionex AS autosampler to deliver sample to a low-pressure concentrator column at a maximum pressure of 100 psi. Because this application requires large sample injection volumes, a sample syringe size of 10 mL must be installed. To accommodate the larger volume, an 8.2 mL sampling needle assembly is required for operation.

Reproducing the QA chromatogram supplied with the column is highly recommended. For best results equilibrate the columns with 3 mM MSA for ≥60 min to ensure the lowest background signal. A system equilibrated with 3 mM MSA has a typical background signal of <1100 µS and peak-to-peak noise of <10 nS. Analyze a DI water blank first to ensure that no peaks elute at the same retention time as the cations of interest. Prepare a 100× dilution of the Dionex Six Cation Standard II and make a 6 µL full-loop injection. Confirm that the resulting chromatogram is similar to the QA chromatogram supplied with the column.

Install a 5 × 23 mm TCC-ULP1 concentrator in place of the sample loop using black PEEK™ tubing with the direction of sample loading opposite the direction of analytical flow. Next, equilibrate the columns with 2 mM MSA/0.5 mM oxalic acid for at least 90 min (preferably overnight.) A system equilibrated with this eluent has a typical background signal of ~900 µS and peak-to-peak noise of approximately 5–10 nS. Inject 8 mL of a 0.5 µg/L standard of copper, nickel, and zinc. The column is equilibrated when duplicate injections of the standard produce identical retention times.

RESULTS AND DISCUSSION

The work shown describes the determination of trace concentrations of copper, nickel, and zinc using the Dionex IonPac SCS 1 column (2 × 250 mm) with nonsuppressed conductivity detection. This column is a 4.5 µm silica-based poly(butadiene-maleic acid) copolymer column functionalized with carboxylic acids specifically designed for use with nonsuppressed conductivity detection. Dionex Application Notes 158 and 250 demonstrate the ability to directly detect µg/L to mg/L concentrations of selected transition metals in samples typically encountered in BWR and PWR nuclear power plants using this column and detection technique.[9] This study demonstrates that this approach also can be used to determine sub-µg/L concentrations of copper, nickel, and zinc in BWR samples following further optimization to the method parameters.

The 2 mm column format was chosen for this application to increase mass sensitivity, thereby reducing the sample volume needed to achieve the required detection limits of the target metal ions. This column format requires a lower analytical flow rate than the standard 4 mm column, thereby reducing eluent consumption and waste. An eluent containing 2 mM MSA and 0.5 mM oxalic acid was previously determined to be optimum for separating common cations and most transition metals on the Dionex IonPac SCS 1 column.[9] This eluent was determined to be suitable for this application, which allowed the separation of copper from the void volume while resolving nickel and zinc from other common cations. The oxalic acid concentration chosen for this study is considerably lower than previous application documents and therefore increases the retention times of calcium and magnesium. Although these analytes were not of particular interest in this application, it is possible that they may be in the sample.

Therefore, the run time can be either extended from 30 to 40 min to allow these alkaline earth metals to elute from the column or data acquisition can be stopped at 35 min, which is before the elution time of calcium (if present in the sample) but it will not interfere due to the additional time required to load the large sample volume. Calcium elutes during the sample loading cycle.

Method Performance

It is important to establish a DI water blank by injecting 8 mL on the concentrator column to verify that no peaks elute at the retention times of the analytes of interest. To obtain a representative blank, prepare the DI water blank using the same set of containers and other components used to prepare the samples. As shown in Figure 1, trace concentrations of sodium and ammonium, which did not interfere with the target metals, were detected in the water blank. Calibration curves from 0.25–5.0 µg/L for zinc and 0.5–5.0 µg/L for copper and nickel were prepared in DI water from the 200 µg/L combined standard solution.

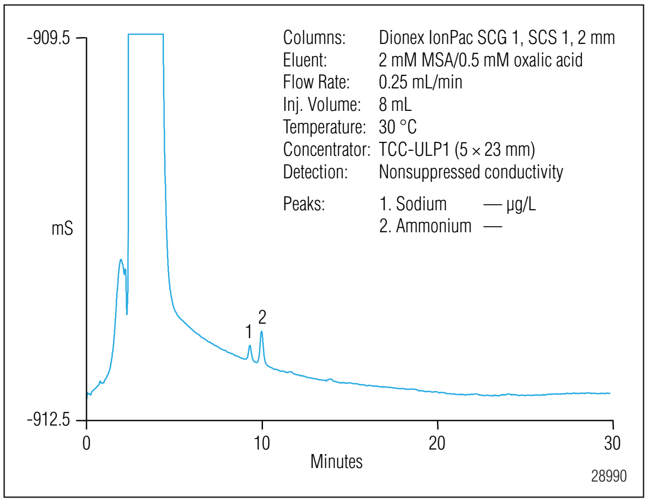

Figure 1. Representative chromatogram of a deionized water blank.

The limits of detection (LODs) and limits of quantification (LOQs) were determined by first measuring the peak-to-peak noise from the DI water blank injection. The typical baseline noise using the conditions described in this study was ~5–7 nS. The calculated LODs for copper, nickel, and zinc were 0.14, 0.12, and 0.054 µg/L, respectively, based on 3× the signal-to-noise ratio (S/N). The calculated LOQs for copper, nickel, and zinc were 0.45, 0.40, and 0.18 µg/L, respectively, based on 10× the S/N. This demonstrates the capability of quantifying sub-µg/L concentrations of the target transition metals when concentrating an 8 mL sample combined with using a 2 mm Dionex IonPac SCS 1 column and nonsuppressed conductivity detection.

If greater sensitivity is required, a larger volume of BWR coolant water (e.g., 20 mL) can be concentrated. However, this cannot be accomplished with the Dionex AS autosampler because an independent sample loading pump is required. If an independent pump is used, be sure the pump does not contribute background contamination for the ions of interest. Table 1 summarizes the calibration data, LODs, and LOQs for copper, nickel, and zinc. Figure 2 shows a representative chromatogram of a 0.5 µg/L copper, nickel, and zinc standard using the Dionex IonPac SCS 1 column with an eluent of 2 mM MSA and 0.5 mM oxalic acid.

Table 1. Linearity, LODs, and LOQs for Copper, Nickel, and Zinc in Deionized Water

Analyte	Range (µg/L)	Coeff. of Determination (r^2)	RSD	LOD[a] (µg/L)	LOQ[b] (µg/L)
Copper	0.5–5.0	0.9991	3.26	0.14	0.45
Nickel	0.5–5.0	0.9997	1.56	0.12	0.40
Zinc	0.25–5.0	0.9994	2.48	0.054	0.18

[a] S/N = 3

[b] S/N = 10

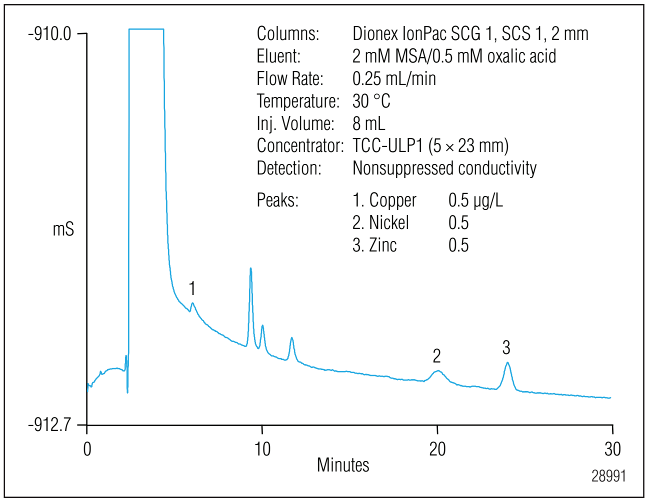

Figure 2. Separation of 0.5 µg/L each of copper, nickel, and zinc in deionized water.

Method performance was evaluated by spiking a DI water matrix with 0.5 µg/L each of copper, nickel, and zinc and performing eight replicate injections each day over three days. Figure 3 shows an overlay of eight replicate injections of the target metals. The recoveries for these metals over this period ranged from 92.2–99.4%, which indicates the accuracy of the method for determining sub-µg/L concentrations of the target metals in BWR samples.

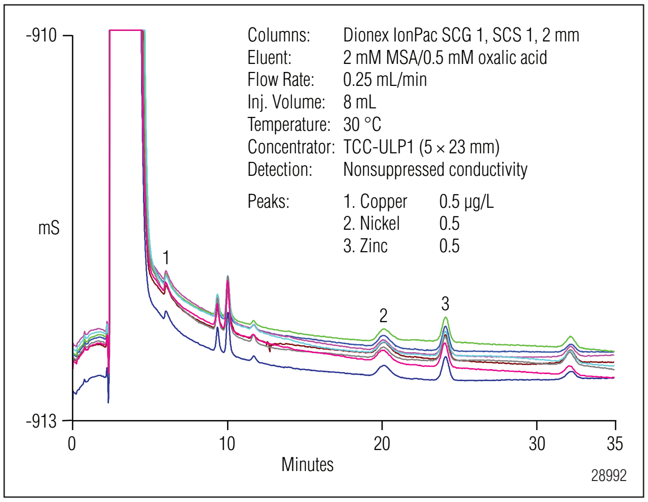

Figure 3. Overlay of eight replicate injections of 0.5 µg/L each of copper, nickel, and zinc in deionized water (i.e., simulated BWR water).

Method precision was also evaluated over the three days by calculating the retention time and peak area relative standard deviations (RSDs) from the replicate injections for each day. Table 2 summarizes the between-day retention time and peak area RSDs for each of the target metals. The intraday retention time RSDs for copper, nickel, and zinc ranged from 0.16–0.48, 0.21–0.40, and 0.05–0.17, respectively. The intraday peak area RSDs for the target metals ranged from 2.5–5.8 %, but the precision for most metals was within 3–4% during the three-day study.

Table 2. Retention Time and Peak Area Precisions for Copper, Nickel, and Zinc Spiked into Deionized Water

Analyte	Amount Added (µg/L)	N[a]	Avg. Retention Time (min)	Retention Time RSD	Peak Area RSD
Copper	0.5	24	6.0	0.38	4.56
Nickel	0.5	24	20.1	0.35	4.09
Zinc	0.5	24	24.1	0.11	3.42

[a] Eight replicates each day over three days

This was not surprising, considering that copper and nickel were evaluated at concentrations near the calculated LOQs. However, the results demonstrated that nonsuppressed conductivity detection is a feasible alternative to colorimetric detection for determining sub-µg/L concentrations of copper, nickel, and zinc in BWR sample matrices. To determine iron(III), copper, and zinc at concentrations <0.1 µg/L and nickel at concentrations <0.2 µg/L, use the method described in Dionex Application Note 277.[8]

CONCLUSION

A cation-exchange chromatography method combined with nonsuppressed conductivity detection is shown here for the determination of sub-µg/L concentrations of copper, nickel, and zinc in a simulated BWR sample. This method eliminates the time and expense associated with preparing a PAR postcolumn reagent for this determination and, therefore, further enhances its ease-of-use. Use of the silica-based Dionex IonPac SCS 1 column, combined with a low MSA eluent concentration with oxalic acid as an effective complexing agent, enables the separation of these metals from common cations that may be present in BWR matrices. Excellent recoveries demonstrated during the study indicate the method is accurate for determining low concentrations of the target metals in BWR samples. In addition, the method demonstrates good linearity for the evaluated concentration range, and sub-µg/L LODs and LOQs that are applicable to the nuclear power industry.

REFERENCES

1. World Nuclear Association, *Nuclear Power in the World Today,* London, UK, 2011. http://www.world-nuclear.org/info/inf01.html. Updated February 2011. (Accessed Aug 2, 2011.)
2. World Nuclear Association, *Nuclear Power in the USA,* London, UK, 2011. http://www.world-nuclear.org/info/inf41.html. Updated March 2011. (Accessed Aug 2, 2011.)
3. World Nuclear Association, *World Energy Needs and Nuclear Power,* London, UK, 2011. http://www.world-nuclear.org/info/inf16.html. Updated December 2010. (Accessed Aug 2, 2011.)
4. Nuclear Energy Institute, *Key Issues: Electricity Supply,* Washington, DC, 2011. http://www.nei.org/keyissues/reliableandaffordableenergy/electricitysupply. (Accessed Aug 2, 2011.)
5. World Nuclear Association, *Nuclear Power Reactors,* London, UK, 2011. http://www.world-nuclear.org/info/inf32.html. Updated March 2011. (Accessed Aug 2, 2011.)
6. Electric Power Research Institute, *BWRVIP–BWR Vessel and Internals Project: BWR Water Chemistry Guidelines–2004 Revision,* Palo Alto, CA, 2004.
7. Electric Power Research Institute, *Chemistry Monitoring and Control for Fuel Reliability,* Palo Alto, CA, 2004.
8. Dionex Corporation, *Determination of Transition Metals in Power Industry Waters Using Ion Chromatography.* Application Note 277, LPN 2816, 2011, Sunnyvale, CA.
9. Dionex Corporation, *Determination of Trace Nickel and Zinc in Borated Power Plant Waters Containing Lithium Hydroxide Using Nonsuppressed Conductivity Detection.* Application Note 250, LPN 2532, 2010, Sunnyvale, CA.

SUPPLIERS

VWR International, 1310 Goshen Parkway, West Chester, PA, 19380, U.S.A., Tel: 1-800-932-5000. www.vwr.com

Sigma-Aldrich, PO Box 14508, St. Louis, MO, 63178, U.S.A., Tel: 1-800-325-3010. www.sigma-aldrich.com

Speed • Simplicity • Solutions

DIONEX

Dionex Products
1228 Titan Way
P.O. Box 3603
Sunnyvale, CA
94088-3603
(408) 737-0700

North America
U.S./Canada (847) 295-7500

South America
Brazil (55) 11 3731 5140

Europe
Austria (43) 1 616 51 25 Benelux (31) 20 683 9768 (32) 3 353 4294
Denmark (45) 36 36 90 90 France (33) 1 39 30 01 10 Germany (49) 6126 991 0
Ireland (353) 1 644 0064 Italy (39) 02 51 62 1267 Sweden (46) 8 473 3380
Switzerland (41) 62 205 9966 United Kingdom (44) 1276 691722

Asia Pacific
Australia (61) 2 9420 5233 China (852) 2428 3282 India (91) 22 2764 2735
Japan (81) 6 6885 1213 Korea (82) 2 2653 2580 Singapore (65) 6289 1190
Taiwan (886) 2 8751 6655

www.thermoscientific.com/dionex

LPN 2918-03 PDF 03/16