Fast and sensitive determination of transition metals in power industry waters using ion chromatography

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Introduction

Successful operation of a nuclear power plant (NPP) demands careful control of water chemistry as coolant systems, steam generator tubes, fuel cladding, piping, and other structural parts are subject to corrosion and crud deposition that can affect plant operation and radiation exposure during refueling downtime. Approximately 11% of the world's electricity is produced from nuclear energy.[1] Most of these NPPs are classified as pressurized water reactors (PWRs) or boiling water reactors (BWRs). A PWR has a primary cooling circuit where water flows as a liquid through the core of the reactor under high pressure and a secondary circuit that generates steam to drive the turbine and produce electricity. Boric acid, a neutron absorber, is added to the primary water to control core reactivity. A BWR is similar to a PWR, but uses only a primary circuit to boil water at a lower pressure to directly drive the turbine to produce electricity.

To minimize corrosion in PWRs, lithium hydroxide is added to the boron-containing primary water to raise the $pH_{300\,°C}$ to between 6.9 and 7.4.[3] Zinc injection into PWR water has been found to decrease primary water stress corrosion cracking and to suppress cobalt buildup on stainless steel surfaces where cobalt-60 is the principal contributor to out-of-core radiation fields.[4]

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Additionally, Ni-based alloys in steam generators used in PWRs can be oxidized by the primary water.[5]

In pure water, the BWR environment is oxidizing due to the radiolytic generation of species such as oxygen and hydrogen peroxide, increasing the propensity of metals to undergo intergranular stress corrosion cracking (IGSCC). Injecting hydrogen into the feedwater and adding noble metal suspensions promote recombination of hydrogen and oxidants on the metal surfaces, thus lowering IGSCC. Control of zinc, iron, copper, and other impurities in BWR final feedwater is highly dependent on the type of condensate polishing system in use.[6]

Two ion chromatography (IC) methods have been used to determine transition metals in power plant waters. Cation-exchange chromatography with nonsuppressed conductivity detection is a simple and direct technique for quantifying low-µg/L concentrations of selected transition metals.[7,8] However, to achieve low- or sub-µg/L detection limits for these transition metals requires the concentration of significant sample volumes, which may cause column overload due to the high concentration of lithium in PWR samples. The determination of transition metals can also be achieved by the formation of anionic complexes with a chromatographic eluent that contains pyridine-2,6-dicarboxylic acid (PDCA), separation of the complexed transition metals, postcolumn displacement of PDCA with 4-(2-pyridylazo)resorcinol (PAR), and absorbance detection at 530 nm.[9] This method provides broad selectivity for a variety of transition metals and yields sub-µg/L sensitivity.

This study describes the separation of iron (III), copper (II), nickel (II), and zinc (II) complexes with PDCA followed by postcolumn PAR reaction and absorbance detection at 530 nm. Surrogate samples include spiked deionized (DI) water (BWR surrogate) and spiked borated water containing lithium hydroxide with or without added zinc (PWR surrogates). Detection limits <0.1 µg/L were achieved after concentration of 4.7 mL of sample. The linearity, detection limits, precision, and accuracy of the method for determining the targeted transition metals at sub-µg/L concentrations in surrogate BWR and PWR samples are described.

Experimental
Equipment
- Thermo Scientific™ Dionex™ ICS-3000 Ion Chromatography System* including:

  – DP Dual Pump or SP Single Pump module

  – DC Detector/Chromatography module (single- or dual-temperature zone configuration) with high pressure, 6-port injector

- Thermo Scientific™ Dionex™ ICS Variable Wavelength Detector (VWD), single or multiple wavelength with tungsten lamp and 11 µL, 10 mm path length PEEK cell

- Thermo™ Scientific Dionex™ AS Autosampler with 5 mL sample syringe, 8.2 mL sample needle assembly, and 10 mL vials/tray

- Thermo Scientific™ Dionex™ PC10 Postcolumn Pneumatic Delivery Package, 2 mm including:

  – Pressurizable chamber

  – Postcolumn pneumatic controller

  – Reagent container

  – 125 µL Knitted reaction coil

  – Postcolumn reagent organizer

- Thermo Scientific™ Chromeleon™ Chromatography Data System (CDS) Software, version 6.8 or greater

- Helium or nitrogen; 4.5-grade (99.995%) or better, <5 ppm oxygen for eluent headspace and postcolumn reagent delivery

- Filter unit, 0.2 µm nylon

- Vacuum pump or equivalent, for degassing eluents

*Equivalent or improved results can be achieved using the Thermo Scientific Dionex ICS-5000⁺ system.

Consumables
- Thermo Scientific™ Dionex™ IonPac™ CG5A column, 2 × 50 mm

- Dionex IonPac CS5A column, 2 × 250 mm

- Thermo Scientific™ Dionex™ IonPac™ TCC-2 Trace Cation Concentrator, 3 × 35 mm

Reagents and standards

Reagents

- Deionized water, 18 MΩ·cm resistance or higher

- Thermo Scientific™ Dionex™ MetPac™ reagent: pyridine-2,6-dicarboxylic acid (PDCA), 5× concentrate

- 4-(2-Pyridylazo) resorcinol (PAR), monosodium salt

- Dionex MetPac PAR Postcolumn Diluent

- Boric acid, ACS reagent-grade or better

- Lithium hydroxide, monohydrate, ACS reagent-grade

- Nitric acid, ULTREX™ II

Standards

- Iron Reference Solution, 1,000 ppm ± 1%

- Copper Reference Solution, 1,000 ppm ± 1%

- Nickel Reference Solution, 1,000 ppm ± 1%

- Zinc Reference Solution, 1,000 ppm ± 1%

Conditions

Columns:	Dionex IonPac CG5A, 2 × 50 mm Dionex IonPac CS5A, 2 × 250 mm
Eluent:	7.0 mM Pyridine-2,6-dicarboxylic acid (PDCA) 66 mM Potassium hydroxide 5.6 mM Potassium sulfate 74 mM Formic acid
Flow Rate:	0.3 mL/min
Concentrator:	Dionex IonPac TCC-2
Vol. Conc.:	4.7 mL
Column Temp.:	30 °C
Postcolumn:	0.24 mM 4-(2-Pyridylazo) resorcinol (PAR) 1.0 M 2-Dimethylaminoethanol 0.50 M Ammonium hydroxide 0.30 M Sodium bicarbonate
PCR Flow Rate:	0.15 mL/min (40–60 psi)
PC Mixer:	125 µL Knitted reaction coil, 2 mm
Detection:	Absorbance at 530 nm
Noise:	~0.12 mAU/min
Backpressure:	2150 psi
Run Time:	20 min

Preparation of reagents and standards

Best practices for cleaning reagent/sample containers

It is essential to use high-quality water of high resistivity (18 MΩ·cm) containing as little dissolved carbon dioxide, metal-containing impurities, organics, microorganisms, and particulate matter larger than 0.2 µm as possible. Prior sparging and filtration through a 0.2 µm porosity nylon filter under vacuum is recommended to remove particulates and reduce dissolved air. Keep the eluent solution blanketed under 34–55 kPa (5–8 psi) of helium or nitrogen at all times to reduce contamination from carbon dioxide gas and other contaminants.

Do not use glass containers. Rinse high-density polyethylene bottles used for standards and samples solutions and polystyrene autosampler vials at least three times with filtered DI water, soak overnight in 10 mM high-purity nitric acid, and rinse again before use. Rinse autosampler septa, soak overnight, and rinse again before use. Avoid contact with the inside surface of all eluent and reagent containers. Handle containers with vinyl or nitrile disposable gloves that have been rinsed with DI water and air dried.

Eluent and postcolumn solutions

Prepare 1 L of PDCA eluent by diluting 200 mL or 204 g of the MetPac PDCA Eluent Concentrate with 800 mL of degassed, DI water. For the postcolumn PAR reagent solution, accurately weigh 0.060 g of PAR into 1,000 mL of MetPac PAR Postcolumn Reagent Diluent.

Nitric acid solution (1.0 M)

Add 63.0 g of concentrated nitric acid (15.8 M) to a 1 L volumetric flask containing ~500 mL of DI water. Dilute to the mark and mix thoroughly. Use this solution to acidify both BWR and PWR surrogate samples.

Intermediate working standards

Prepare 100 g of 1.00 mg/L iron (III), copper (II), nickel (II), and zinc (II) intermediate solutions by diluting 0.100 g of the respective 1000 mg/L reference solutions and 0.20 g of 1 M nitric acid to 100 g with DI water in a 125 mL HDPE bottle. Store these solutions at 4 °C when not in use.

Working standard solutions

Prepare working standards containing the four transition metals in the concentration range of 0.1 to 10 µg/L by adding the appropriate weights of intermediate working standard solutions and 0.20 g of 1 M nitric acid to 100 g with DI water in a 125 mL HDPE bottle. Store these solutions at 4 °C when not in use.

Sample preparation

BWR surrogate samples

Prepare BWR surrogate samples for spike recovery and precision studies in the same manner as working standard solutions preparation. Spike recoveries from BWR surrogates use two sets of transition metal concentrations: 0.2 µg/L Fe, Cu, Zn, and 0.4 µg/L Ni; and 0.8 µg/L Fe, Cu, Zn, and 1.0 µg/L Ni. Retention time and peak area precision studies use two sets of transition metal concentrations: 0.2 µg/L Fe, Cu, Zn, and 0.4 µg/L Ni; and 1.0 µg/L Fe, Cu, Zn, and 2.0 µg/L Ni.

PWR surrogate samples

To prepare a 1,000 mg/L lithium stock solution, add 0.6046 g lithium hydroxide monohydrate to a 125 mL HDPE bottle and dilute to 100 g with DI water. Store this solution at 4 °C when not in use.

In this study, PWR surrogates are composed of the following boron/lithium concentrations: 1,000 mg/L boron + 1.8 mg/L lithium, 2,000 mg/L boron + 3.8 mg/L lithium, and 2,500 mg/L boron + 5.0 mg/L lithium. Evaluate surrogate matrices (with and without 15 µg/L zinc added) for analyte recovery and precision. Use the weights of boric acid, 1,000 mg/L lithium stock solution, and 1.00 mg/L zinc intermediate working standard shown in Table 1 to prepare these surrogate matrices. Agitate each surrogate matrix solution to completely dissolve the boric acid. Spike recoveries from all six PWR surrogate matrices use two sets of transition metal concentrations: 0.2 µg/L Fe(III), Cu, Zn, and 0.4 µg/L Ni; and 0.8 µg/L Fe(III), Cu, Zn, and 1.0 µg/L Ni. Retention time and peak area precision studies use 0.2 µg/L Fe(III), Cu, Zn, and 0.4 µg/L Ni concentrations in 2,500 mg/L boron + 5.0 mg/L lithium matrix with and without 15 µg/L zinc.

System preparation and configuration

To minimize absorbance detector noise and drift, use an IC system that has a temperature-controlled compartment to house both the column set, mixing tee, and knitted reaction coil. To minimize peak broadening, house the thermostatted items in the same compartment (i.e., the Dionex ICS-3000 system upper DC compartment). To minimize pump fluctuations, install green PEEK (0.030 in. i.d.) tubing (e.g., 10 m) between the eluent pump and injector. In this study, eluent pressure fluctuations were reduced to ~0.3% peak-to-peak by performing this step. Install the Dionex IonPac TCC-2 concentrator on the 6-port injector in place of the sample loop. Sample loading occurs with a flow direction opposite to the flow direction indicated on the concentrator. Improper concentrator installation will result in chromatographic peak broadening. Condition the concentrator with eluent while the injector is in the Inject position. Install the Dionex IonPac CG5A/CS5A column set and condition with the effluent going to waste. Attach the column to the mixing tee, plug one port on the tee, and attach one end of the knitted reaction coil to the third port on the tee. Connect the other end of the knitted reaction coil to the absorbance detector cell inlet. Attach a short piece of red PEEK (0.005 in. i.d.) tubing to the cell output followed by a PEEK union and green PEEK

Table 1. Amounts of boric acid, lithium hydroxide, and zinc used to prepare 500 g of PWR surrogate matrices.

Matrix Composition (mg/L)	Mass Boric Acid (g)	Mass Lithium Hydroxide Solution* (g)	Mass Zinc Solution** (g)
1,000 B + 1.8 Li	2.861	1.000	None
1,000 B + 1.8 Li + 0.015 Zn	2.861	1.000	7.5
2,000 B + 3.8 Li	5.722	2.000	None
2,000 B + 3.8 Li + 0.015 Zn	5.722	2.000	7.5
2,500 B + 5.0 Li	7.153	2.500	None
2,500 B + 5.0 Li + 0.015 Zn	7.153	2.500	7.5

*1,000 mg/L lithium stock solution
**1.00 mg/L zinc intermediate working standard

tubing to waste. Turn on the visible lamp in the detector to allow sufficient time for the lamp's output to stabilize. The baseline noise at 530 nm, without introducing PAR postcolumn reagent, must be 10 µAU or less.

Attach a source of high-purity nitrogen or helium capable of supplying up to 80 psi to the Dionex PC10 postcolumn delivery system. Connect green PEEK tubing from the Dionex PC10 outlet, fill the 1 L postcolumn reagent container with PAR reagent, seal the reservoir cap, and briefly flush the reservoir outlet line to waste with low pressure. While the PDCA eluent flow is on, remove the mixing tee plug and quickly attach the green PEEK tubing from the reservoir. Increase the gas pressure on the Dionex PC10 system to deliver PAR postcolumn reagent. Set the pressure on the Dionex PC10 system by monitoring the total postcolumn flow (eluent + PAR reagent) gravimetrically by collecting waste from the absorbance cell outlet line. The total flow rate should be 0.45 mL/min. Adjust the length of red PEEK cell outlet tubing so that the correct flow rate is achieved with the Dionex PC10 pneumatic pressure between 40–60 psi. Lock the pressure regulator setting and use the vent toggle valve to stop PAR reagent flow when replacing PAR reagent. Important: to prevent the Dionex PC10 outlet line from clogging (and subsequent PAR reagent flow decrease), flush the Dionex PC10 outlet line with PAR diluent before adding fresh PAR reagent. After venting the Dionex PC10 pressure, replace the PAR reagent container with PAR diluent and reseal the reservoir cap. Quickly disconnect the PAR reagent line from the mixing tee (plugging the port), direct the PAR reagent line to waste, and switch on the Dionex PC10 toggle valve to deliver 10–20 mL of PAR diluent to waste. After venting the pneumatic pressure, reassemble the Dionex PC10 system with PAR reagent, reconnect the reservoir outlet line to the mixing tee, and turn on the pneumatic pressure. Check the total flow rate gravimetrically and adjust the pneumatic pressure as needed.

Install and configure the Dionex AS Autosampler. This method requires the configuration of the autosampler sample mode to Concentrate using the Dionex AS autosampler front panel (under System Parameters). The Concentrate sample mode allows the autosampler to deliver sample to a low-pressure concentrator at a maximum pressure of 100 psi. Because this application requires large sample injection volumes, a sample syringe size of 5 mL must be installed. To accommodate the larger volume, an 8.2 mL sampling needle assembly is required for operation.

Results and discussion
Linearity, limits of detection/quantification
This study focused on method performance of IC with postcolumn derivatization and absorbance detection for determining iron (III), copper (II), nickel (II), and zinc (II) in surrogate NPP waters. The limit of detection (LOD) and limit of quantification (LOQ) estimates were assessed by measuring peak-to-peak noise in blank injections and converting these noise measurements to estimated analyte concentrations using calibration standards prepared in DI water. The LOD and LOQ were calculated from noise in the system blank using data from a chromatogram generated without injecting the DI water concentrate into the column (Figure 1, Trace A). The baseline noise, calculated between 5–10 min (the RT window of the four target analytes) from 1 min increments, was ~0.14 mAU (n = 5). The calculated LODs for the targeted transition metals were based on 3× the signal-to-noise ratio (S/N), whereas the LOQs were based on 10× the S/N (Table 2). Data for the DI water blank (Figure 1, Trace B) show iron (III) concentrations at the LOQ and zinc (II) at the LOD. These results demonstrate the capability of IC with postcolumn derivatization and absorbance detection to easily achieve <0.1 µg/L LODs of the target analytes when concentrating 4.7 mL of sample.

Columns:	Dionex IonPac CG5A/CS5A, 2 mm
Eluent:	7.0 mM Pyridine-2,6-dicarboxylic acid (PDCA)
	66 mM Potassium hydroxide
	5.6 mM Potassium sulfate
	7.4 mM Formic acid
Eluent Flow Rate:	0.30 mL/min
Concentrator:	Dionex IonPac TCC-2
Vol. Concentrated:	4.7 mL
Temperature:	30 °C
Postcolumn:	0.24 mM 4-(2-Pyridylazo) resorcinol (PAR)
	1.0 M 2-Dimethylaminoethanol
	0.50 M Ammonium hydroxide
	0.30 M Sodium bicarbonate
PCR Flow Rate:	0.15 mL/min
Detection:	Absorbance at 530 nm

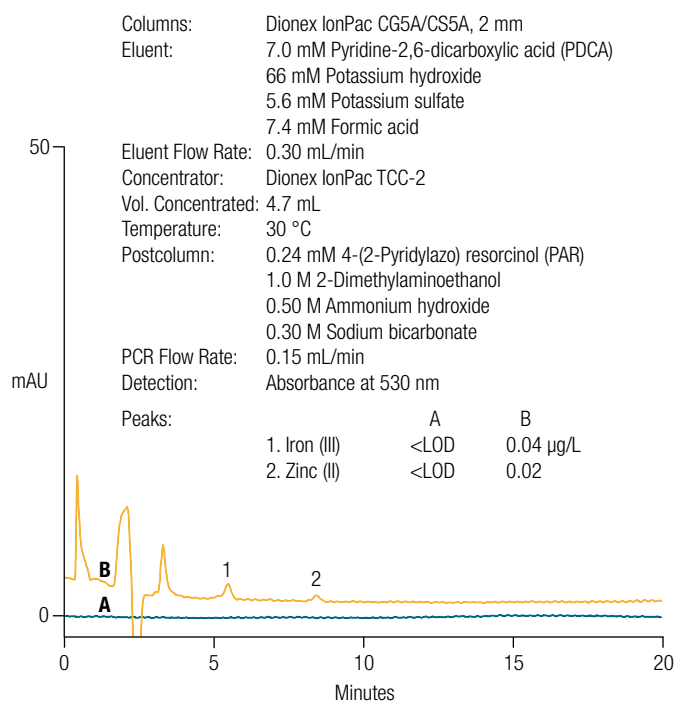| Peaks:	A	B
1. Iron (III)	<LOD	0.04 µg/L
2. Zinc (II)	<LOD	0.02

Figure 1. Comparison of representative blank chromatograms. Trace A: system (no inject.) blank. Trace B: DI water blank.

Calibration curves were prepared over two orders of magnitude for most of the target metals with the exception of nickel, which has a lower response relative to the other analytes. Excellent correlation coefficients using a linear least squares regression fit were obtained for all four target transition metals. The low RSD values in Table 2 show that the measured peak areas deviated <1.8% from the areas predicted by the calibration equations.

Method performance for BWR surrogate samples

DI water was the surrogate matrix used to simulate the liquid circulating in a BWR. Figure 2 compares the chromatograms from the matrix blank to a spiked matrix with 1 µg/L of each of the target transition metals. All four transition metals are well resolved from each other and from the early eluting system peaks.

Method performance was evaluated by spiking two concentrations of the four target transition metals in the DI water surrogate matrix (Table 3). Recoveries at 0.2 µg/L Fe, Cu, Zn, and 0.4 µg/L Ni ranged from 84 to 101% , whereas recoveries at 0.8 µg/L Fe, Cu, Zn, and 1.0 µg/L Ni ranged from 95 to 103%. These results demonstrated the ability of this method to accurately determine sub-µg/L concentrations of the target transition metals in BWR samples. The method precision was evaluated at two spiking concentrations by calculating retention time and peak area relative standard deviations (RSDs) from five replicate injections on each of three days (Table 4). Precision was also evaluated at two concentrations for each of the target transition metals: 0.2 µg/L Fe, Cu, Zn, and 0.4 µg/L Ni; and 1.0 µg/L Fe, Cu, Zn, and Ni. Retention time RSDs for all analytes at both concentrations were 0.15% or better. Peaks

Columns: Dionex IonPac CG5A/CS5A, 2 mm
Eluent: 7.0 mM Pyridine-2,6-dicarboxylic acid (PDCA)
66 mM Potassium hydroxide
5.6 mM Potassium sulfate
7.4 mM Formic acid
Eluent Flow Rate: 0.30 mL/min
Concentrator: Dionex IonPac TCC-2
Vol. Concentrated: 4.7 mL
Temperature: 30 °C
Postcolumn: 0.24 mM 4-(2-Pyridylazo) resorcinol (PAR)
1.0 M 2-Dimethylaminoethanol
0.50 M Ammonium hydroxide
0.30 M Sodium bicarbonate
PCR Flow Rate: 0.15 mL/min
PC Mixer: Knitted reaction coil, 2 mm
Detection: Absorbance at 530 nm

Peaks:
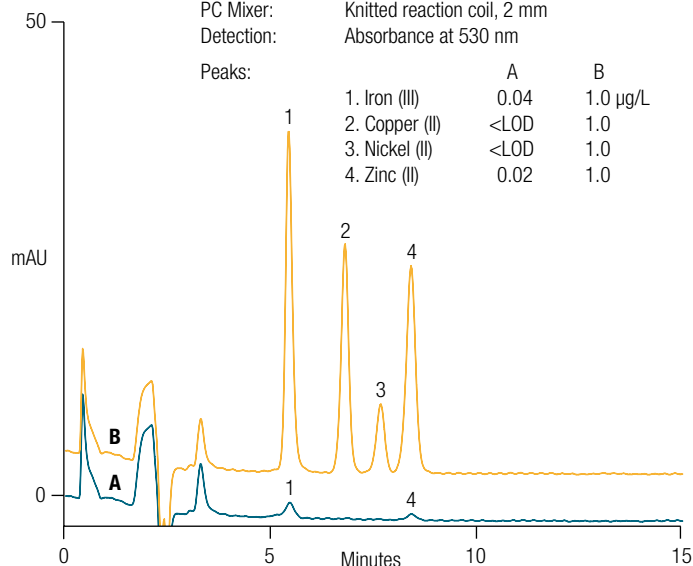|		A	B
1. Iron (III)		0.04	1.0 µg/L
2. Copper (II)		<LOD	1.0
3. Nickel (II)		<LOD	1.0
4. Zinc (II)		0.02	1.0

Figure 2. Chromatogram of transition metals in surrogate BWR sample. Trace A: BWR surrogate matrix. Trace B: BWR surrogate matrix spiked with 1 µg/L Fe^{3+}, Cu^{2+}, Ni^{2+}, and Zn^{2+}.

area RSDs ranged from 1.4 to 2.2% at the lower spiked concentrations and 0.6 to 1.9% at the 1.0 µg/L analyte concentrations. The results suggest that this method performed well for determining sub-µg/L concentrations of iron (III), copper (II), nickel (II), and zinc (II) in BWR nuclear power plant waters.

Table 2. Calibration data and estimated limits of detection and limits of quantification for selected transition metals in deionized water.[a]

Analyte	Range (µg/L)	Correlation Coefficient (r)	RSD	LOD[b] (µg/L)	LOQ[c] (µg/L)
Iron (III)	0.089–10.2	0.9999	1.1	0.012	0.038
Copper (II)	0.091–10.2	0.9999	0.9	0.018	0.060
Nickel (II)	0.21–10.3	0.9997	1.7	0.059	0.19
Zinc (II)	0.11–10.5	0.9997	1.8	0.020	0.066

[a]Noise calculated from system (no inject.) blank
[b]S/N = 3
[c]S/N = 10

Table 3. Average recoveries for selected transition metals spiked into deionized water.

Analyte	Amount in Matrix Blank (µg/L)	Amount Added (µg/L)	Average Recovery (%)
Iron (III)	0.04	0.20	97
		0.81	97
Copper (II)	<LOD	0.21	101
		0.81	103
Nickel (II)	<LOD	0.40	91
		1.02	95
Zinc (II)	0.02	0.21	84
		0.85	96

Five replicates at each spiking level

Table 4. Retention time and peak area precisions for selected transition metals spiked into deionized water.

Analyte	Amount Added (µg/L)	N[a]	Retention Time RSD	Peak Area RSD
Iron (III)	0.2	15	0.14	1.4
	1.0	15	0.15	1.0
Copper (II)	0.2	15	0.11	1.8
	1.0	15	0.12	0.63
Nickel (II)	0.4	15	0.15	2.2
	2.0	15	0.10	1.9
Zinc (II)	0.2	15	0.12	2.1
	1.0	15	0.10	0.92

[a]Five replicates for each of three days

Method performance for PWR surrogate samples

Method performance was evaluated by determining the target analytes spiked into a total of six surrogate PWR matrices containing 1,000–2,500 mg/L boron (as boric acid) with corresponding lithium concentrations of 1.8–5.0 mg/L lithium (as lithium hydroxide). Zinc is another PWR matrix additive that has been used to minimize out-of-core radiation fields.[4]

Zinc concentrations of 0 or 15 µg/L were chosen to be part of the PWR surrogate matrix. Although surrogate samples spiked with 15 µg/L zinc were not analyzed for zinc, sample dilution, a smaller concentrate volume, or extended zinc calibration can be used to quantify zinc in those samples. Chromatograms from a 2,000 mg/L B + 1.8 mg/L Li surrogate sample without 15 µg/L zinc (Figure 3) and with 15 µg/L zinc added (Figure 4) show that all target transition metals were well resolved from each other and from system peaks. Adding zinc to the surrogate sample only decreased the calculated nickel to zinc resolution by 15%. Iron (III) and zinc (II) matrix blank peaks increased twofold to threefold when compared to these analytes in DI water due to the presence of trace levels of these analytes in the boric acid and lithium hydroxide used to prepare the samples. Even with 2,500 mg/L B + 5.0 mg/L Li matrix composition, iron (III) concentrations in the matrix blank were ≤0.1 µg/L.

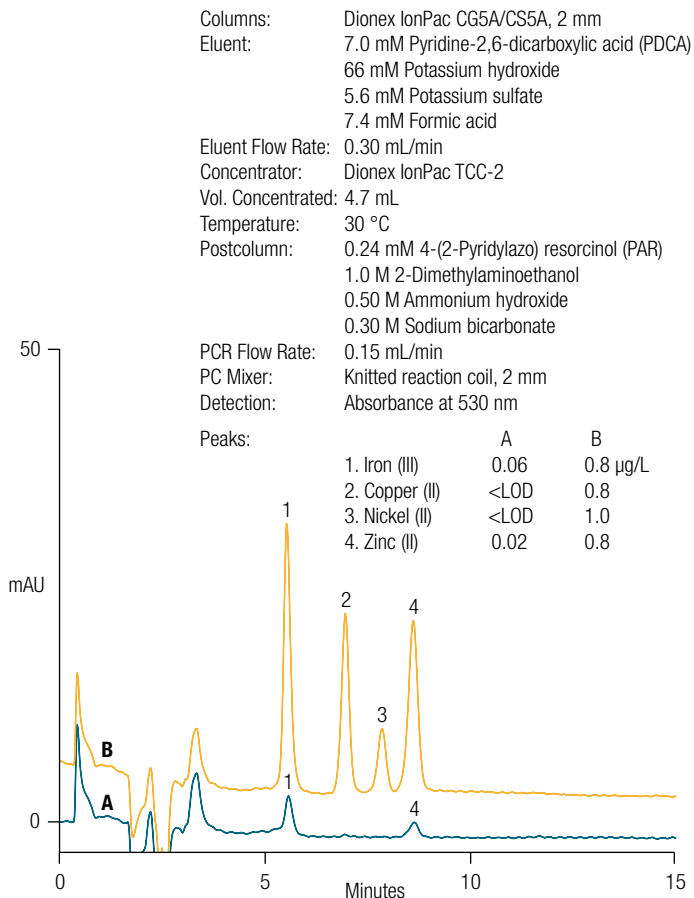|			
Columns:	Dionex IonPac CG5A/CS5A, 2 mm		
Eluent:	7.0 mM Pyridine-2,6-dicarboxylic acid (PDCA)		
	66 mM Potassium hydroxide		
	5.6 mM Potassium sulfate		
	7.4 mM Formic acid		
Eluent Flow Rate:	0.30 mL/min		
Concentrator:	Dionex IonPac TCC-2		
Vol. Concentrated:	4.7 mL		
Temperature:	30 °C		
Postcolumn:	0.24 mM 4-(2-Pyridylazo) resorcinol (PAR)		
	1.0 M 2-Dimethylaminoethanol		
	0.50 M Ammonium hydroxide		
	0.30 M Sodium bicarbonate		
PCR Flow Rate:	0.15 mL/min		
PC Mixer:	Knitted reaction coil, 2 mm		
Detection:	Absorbance at 530 nm		
Peaks:		A	B
	1. Iron (III)	0.06	0.8 µg/L
	2. Copper (II)	<LOD	0.8
	3. Nickel (II)	<LOD	1.0
	4. Zinc (II)	0.02	0.8

Figure 3. Chromatogram of transition metals in surrogate PWR matrix (2,000 mg/L B + 3.8 mg/L Li). Trace A: PWR surrogate matrix. Trace B: PWR surrogate matrix spiked with 0.8 µg/L Fe^{3+}, Cu^{2+}, Zn^{2+}, and 1.0 µg/L Ni^{2+}.

Columns:	Dionex IonPac CG5A/CS5A, 2 mm
Eluent:	7.0 mM Pyridine-2,6-dicarboxylic acid (PDCA)
	66 mM Potassium hydroxide
	5.6 mM Potassium sulfate
	7.4 mM Formic acid
Eluent Flow Rate:	0.30 mL/min
Concentrator:	Dionex IonPac TCC-2
Vol. Concentrated:	4.7 mL
Temperature:	30 °C
Postcolumn:	0.24 mM 4-(2-Pyridylazo) resorcinol (PAR)
	1.0 M 2-Dimethylaminoethanol
	0.50 M Ammonium hydroxide
	0.30 M Sodium bicarbonate
PCR Flow Rate:	0.15 mL/min
PC Mixer:	Knitted reaction coil, 2 mm
Detection:	Absorbance at 530 nm

Peaks: A B
1. Iron (III) 0.05 0.8 µg/L
2. Copper (II) <LOD 0.8
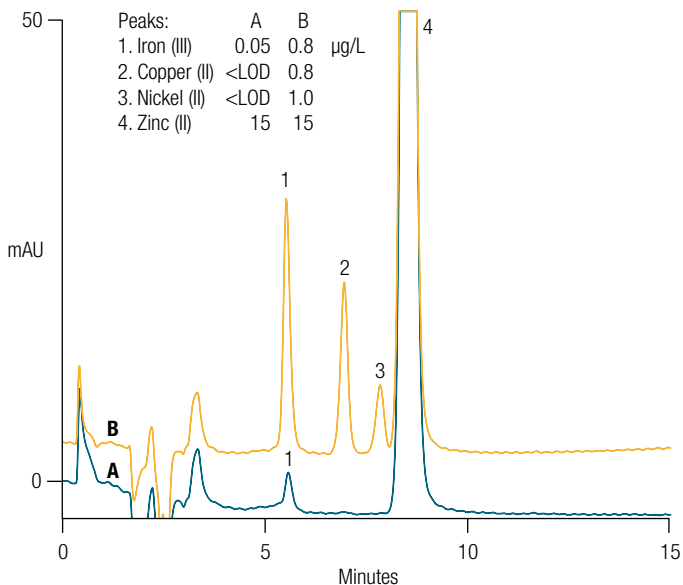3. Nickel (II) <LOD 1.0
4. Zinc (II) 15 15

Figure 4. Chromatogram of transition metals in surrogate PWR matrix (2,000 mg/L B + 3.8 mg/L Li + 15 µg/L Zn^{2+}). Trace A: PWR surrogate matrix. Trace B: PWR surrogate matrix spiked with 0.8 µg/L Fe^{3+}, Cu^{2+}, and 1.0 µg/L Ni^{2+}.

Target analyte recoveries were evaluated at two spiking concentrations in all six surrogate samples (Table 5). At the lower spiked concentrations (0.2 µg/L Fe, Cu, Zn, and 0.4 µg/L Ni), recoveries ranged from 83 to 110%. At the higher spiked concentrations (0.8 µg/L Fe, Cu, Zn, and 1.0 µg/L Ni), similar results were observed with recoveries ranging from 83 to 106%. Retention time and peak area RSDs (Table 6) were evaluated by spiking low concentrations of target transition metals (0.2 µg/L Fe, Cu, Zn, and 0.4 µg/L Ni) into 2,500 mg/L B + 5.0 mg/L Li matrix (with or without 15 µg/L zinc). All retention time RSDs were ≤0.21% and were independent of the presence of higher concentrations of zinc in the sample. Peak area RSDs ranged from 0.9 to 2.9% and appeared to be slightly higher for nickel in the absence of 15 µg/L zinc. When compared to the results in Table 4, method precision appears to be independent of the presence of PWR surrogate matrix components, suggesting that the method performed well for determining sub- and low-µg/L concentrations of the targeted transition metals in borated nuclear power plant waters.

Table 5. Average recoveries for selected transition metals spiked into surrogate PWR samples.

Analyte	Amount Added (µg/L)	1,000 mg/L Boron + 1.8 mg/L Lithium		2,000 mg/L Boron + 3.8 mg/L Lithium		2,500 mg/L Boron + 5.0 mg/L Lithium	
		No Zinc	15 µg/L Zinc	No Zinc	15 µg/L Zinc	No Zinc	15 µg/L Zinc
Iron (III)	0.20	96	104	93	87	101	83
	0.80	90	105	89	85	88	83
Copper (II)	0.20	104	106	109	106	106	106
	0.80	101	100	101	100	102	102
Nickel (II)	0.41	88	85	95	91	89	92
	1.00	93	97	96	106	93	103
Zinc (II)	0.20	99	—[a]	110	—[a]	99	—[a]
	0.80	100		104		104	

Five replicates
[a]Not measured

Table 6. Retention time and peak area precisions for selected transition metals spiked into surrogate PWR samples.

Analyte	Amount Added (µg/L)	N[a]	2,500 mg/L Boron + 5.0 mg/L Lithium		2,500 mg/L Boron + 5.0 mg/L Lithium + 15 µg/L Zinc	
			Retention Time RSD	Peak Area RSD	Retention Time RSD	Peak Area RSD
Iron (III)	0.2	21	0.17	1.4	0.19	1.1
Copper (II)	0.2	21	0.21	1.1	0.19	0.9
Nickel (II)	0.4	21	0.17	2.9	0.18	1.9
Zinc (II)	0.2	21	0.19	1.5	—[b]	—[b]

[a]Five replicates for each of three days
[b]Not measured

Conclusion

An IC method with 530 nm absorbance detection was evaluated for the determination of iron (III), copper (II), nickel (II), and zinc (II) at sub- and low-µg/L concentrations in boiling water and the primary cooling circuit of pressurized water nuclear power plant reactors. The Dionex IonPac CS5A column with a PDCA eluent allowed the separation of the four target transition metals in less than 10 min., even in the presence of high concentrations of boric acid and lithium that constitute the PWR primary coolant surrogate matrix. Excellent recoveries were achieved for the target analytes in DI water and boric acid/lithium hydroxide matrices, with and without additional zinc added. Method performance was further demonstrated by the fact that no significant differences were observed in the retention time and peak area RSDs for the target analytes in both surrogate samples. The method was not subject to interference from common cations that is typically observed using nonsuppressed conductivity detection. Additionally, the method produced sub-µg/L LODs and LOQs and good linearity applicable for the determination of the four target transition metals in nuclear power industry waters.

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