

Determination of Trace Sodium and Transition Metals in Power Industry Samples by Ion Chromatography with Nonsuppressed Conductivity Detection

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Introduction

It is critical for power plants to continuously monitor corrosive ionic impurities in various plant water streams, such as cooling waters, boiler waters, feed waters, and steam condensates. The presence of impurities above a specified concentration can result in stress-corrosion cracking and other corrosion mechanisms, and therefore have a significant negative impact on power generation. Damage from corrosive ions can cause forced outages and component failures, costing millions of dollars in lost revenue.^{1,2} The continuous monitoring of ionic species provides valuable information regarding the source of contamination, assists power plants in understanding corrosion mechanisms, allows recommendations for appropriate treatment to prevent corrosion impacts, and produces concentration trends for individual ions over a length of time. This information can be used to minimize corrosive damage.

Corrosive contaminants—particularly sodium, chloride, and sulfate—have been implicated as a major source of corrosion and deposition-related plant shutdowns in nuclear and fossil-fueled plants.³ Ion chromatography (IC) can measure these contaminants and has been implemented in several U.S. power plant water chemistry monitoring programs. This methodology allows analysts to achieve parts per trillion (ppt) detection limits for individual anionic and cationic species and operate on-line to effectively measure and eliminate corrosive hideout, thereby reducing the plant's operating costs.

The measurement of ultratrace levels of sodium in boiler waters treated with amine additives, such as ethanolamine, is a particularly challenging analytical problem. The purpose of this all-volatile treatment (AVT) is to provide a high-pH and high-purity environment to minimize corrosion of metal surfaces. This environment is accomplished by adding the amine to the boiler water at concentrations typically in the range of 0.5–10 mg/L. In effect, the high amine concentration can preclude the separation and detection of sodium typically present in the low-ppt range. However, many of these challenges have been overcome by the development of efficient high-capacity cation-exchange columns capable of tolerating high-ionic-strength matrices.⁴

Other cationic species are also of interest to many power plants. For example, the determination of calcium and magnesium may be used to calculate water hardness and reveal the presence of condenser leaks and water polisher failures. These and other cationic species must be detected at the sub- $\mu\text{g/L}$ concentrations in power plant samples. The lowest detection limits are achieved by suppressed conductivity detection.

An alternative to suppressed conductivity detection is analysis without the suppressor (i.e., nonsuppressed conductivity). In this detection mode, the column effluent flows directly into the conductivity cell. Consequently, lower-capacity columns using dilute acidic eluents are required to achieve a reasonable background signal. Weakly acidic complexing agents, such as tartaric acid, pyridine-2,6-dicarboxylic acid (PDCA), and oxalic acid, are also commonly used with nonsuppressed IC columns.

Determination of cations by IC with suppressed conductivity detection has demonstrated detection limits that are at least an order of magnitude (i.e., 10 times) lower than nonsuppressed systems.⁵ This advantage has clearly made suppressed conductivity the preferred detection mode for the determination of cations, particularly low-ppt sodium determinations, in the power industry. Dionex (now part of Thermo Scientific) Application Note 157 provides a general discussion of suppressed versus nonsuppressed conductivity detection.

Nuclear and fossil-fueled power plants also require iron and copper monitoring at the sub- to low- $\mu\text{g/L}$ (ppb) concentrations at various locations in the steam cycle. These transition metals can accumulate or deposit in the steam generators as sludge. This accumulation can create areas where ultratrace ionic impurities present in the feed water can concentrate by several orders of magnitude, resulting in a highly corrosive environment. Additional metals, such as zinc, are also of interest to some power plants. Zinc is added to pressurized water reactors (PWRs) to control corrosion. Zinc additions to the PWRs can alleviate two key challenges for plant operators⁶: (1) reduce degradation of the coolant materials due to stress corrosion cracking, and (2) lower the shutdown radiation dose rates. The concentration of added zinc is typically in the range of 1–10 ppb.

IC provides a convenient and reliable methodology to separate and detect transition metals on-line at low- to sub-ppb concentrations. The separation of these metals requires the formation of a complex with a weak organic acid—such as citric acid, oxalic acid, tartaric acid, or PDCA—to reduce their effective positive charge. This complexation allows a change in selectivity of the metal ions that cannot be accomplished using only a monovalent eluent ion, such as hydronium.⁷ The most common mode of detection used for this analysis involves derivatization of the column effluent with 4-(2-pyridylazo)resorcinol (PAR) and subsequent photometric detection at 520–530 nm. PAR provides a very broad selectivity and sensitivity for transition metals.

Although suppressed and nonsuppressed conductivity can be used for the detection of alkali and alkaline earth metals, only nonsuppressed conductivity is suitable for the detection of transition metals. The formation of insoluble metal hydroxides from the suppressor reaction precludes the use of a suppressor for this analysis. However, in comparison to photometric detection, nonsuppressed conductivity does not provide the required specificity for many transition metals in high-ionic-strength matrices because all cations are detected.

This application note compares suppressed to nonsuppressed conductivity detection for the determination of sub-ppb concentrations of sodium in simulated power plant matrices. Linearity, limits of detection, and recovery of sub-ppb sodium spiked into simulated samples containing high concentrations of ethanolamine are reported. In addition, this application note describes the determination of transition metals by nonsuppressed conductivity detection.

Note: The equipment, analytical conditions, system preparation, and system setup for trace sodium determinations by suppressed conductivity detection and transition metals by postcolumn reaction with visible detection are available in Application Notes 152 and 131, respectively.

Equipment

Nonsuppressed Cation System

Thermo Scientific Dionex ICS-1000, Thermo Scientific Dionex ICS-1500, or Thermo Scientific Dionex ICS-2000 Ion Chromatography System* consisting of:

- Dual-piston pump
- Column heater
- Digital conductivity detector
- Pressurized Sample Vessel**
- Thermo Scientific Dionex DXP Single-Piston Pump**
- Thermo Scientific™ Dionex™ Chromatography™ Chromatography Data System (CDS) Software

*Equivalent or improved results can be achieved using the Thermo Scientific Dionex ICS-5000+, the Thermo Scientific Dionex ICS-2100, the Thermo Scientific Dionex ICS-1600, or the Thermo Scientific Dionex ICS-1100 system.

**This equipment was used for trace-level determinations

Reagents and Standards

- Deionized water, Type I reagent-grade, 18 M Ω -cm resistivity or better
- Lithium standard, 1000 mg/L
- Sodium standard, 1000 mg/L
- Ammonium standard, 1000 mg/L
- Potassium standard, 1000 mg/L
- Magnesium standard, 1000 mg/L
- Calcium standard, 1000 mg/L
- Lithium chloride (LiCl)
- Sodium chloride (NaCl)
- Ammonium chloride (NH₄Cl)
- Potassium chloride (KCl)
- Magnesium chloride hexahydrate (MgCl₂ • 6H₂O)
- Calcium chloride dihydrate (CaCl₂ • 2H₂O)
- Ethanolamine, 99%, reagent-grade
- Combined Six Cation Standard-II
- Tartaric acid
- Oxalic acid
- Copper, atomic absorption grade, 1000 mg/L
- Nickel, atomic absorption grade, 1000 mg/L
- Zinc, atomic absorption grade, 1000 mg/L
- Cobalt, atomic absorption grade, 1000 mg/L
- Manganese, atomic absorption grade, 1000 mg/L
- Cadmium, atomic absorption grade, 1000 mg/L

Conditions**Nonsuppressed Conductivity Detection of Trace Sodium**

Columns:	Thermo Scientific™ Dionex™ IonPac™ SCS 1 Analytical, 4 × 250 mm Dionex IonPac SCG 1 Guard, 4 × 50 mm
Eluent:	3 mM MSA
Flow Rate:	1 mL/min
Temperature:	30 °C
DXP Flow Rate:	2 mL/min
Sample Volume:	3 mL
Concentrator	
Column:	Thermo Scientific Dionex TCC-LP1 Trace Cation Concentrator Column, 4 × 35 mm
Detection:	Nonsuppressed conductivity
Background:	~1100 µS
Noise:	~5–10 nS peak-to-peak
Backpressure:	~2100 psi
Run Time:	15 min

Nonsuppressed Conductivity Detection for Transition Metals

Columns:	Dionex IonPac SCS 1 Analytical, 4 × 250 mm Dionex IonPac SCG 1 Guard, 4 × 50 mm
Eluent:	See Table 1
Flow Rate:	1 mL/min
Temperature:	30 °C
Injection:	25 µL
Detection:	Nonsuppressed conductivity
Noise:	~5–10 nS peak-to-peak
Backpressure:	~2100 psi

Preparation of Solutions and Reagents for Trace Sodium Analysis**Eluent Solution**

Prepare 1.0 N MSA stock solution by adding 96.10 g of methanesulfonic acid (MSA, >99% Dionex TCC-LP1 Trace Cation Concentrator Column, 4 × 35 mm) to a 1 L volumetric flask containing about 500 mL of deionized water. Dilute to the mark and mix thoroughly. Prepare 3 mM MSA by diluting 3 mL of the 1.0 N MSA stock solution to 1 L with deionized water. Degas the eluent by sonicating under vacuum for 10 min or by sparging with helium. Store the eluent in plastic labware. The eluent generator is not recommended for use with the nonsuppressed cation system because a significant increase in baseline noise is observed for this application.

Eluents containing complexing agents, such as tartaric acid, oxalic acid, or PDCA, can be prepared by weighing the appropriate amounts for the desired concentrations: (1) tartaric acid = 0.1501 g tartaric acid per mM for a 1 L solution, (2) oxalic acid = 0.0900 g oxalic acid per mM for a 1 L solution, (3) PDCA = 0.167 g PDCA per mM for a 1 L solution. PDCA does not dissolve readily in water; therefore, allow the solution to stir until the PDCA fully dissolves.

Table 1. Retention times (min) of common cations and transition metals on the Dionex IonPac SCG 1 and Dionex IonPac SCS 1 columns.

Eluent Concent. / Analyte	3 mM MSA	2 mM MSA / 0.5 mM Oxalic Acid	4 mM Oxalic Acid	3 mM Oxalic Acid	3 mM Oxalic Acid / 0.5 mM MSA	5 mM Tartaric Acid / 0.16 mM PDCA	4 mM Tartaric Acid / 2 mM Oxalic ^b
Lithium	6.70	6.80	7.10	8.60	7.40	9.10	7.40
Sodium	8.70	8.80	9.20	11.3	9.60	11.9	9.60
Ammonium	10.0	10.1	10.5	13.1	11.0	13.7	10.9
Potassium	13.9	13.8	14.4	18.1	15.0	18.7	15.0
Magnesium	25.6	27.5	27.4	45.5	31.7	58.8	32.2
Calcium	33.7	35.8	36.8	61.9	42.3	64.1	41.8
Copper	>60.0	7.50	2.98	—	3.40	—	3.90
Zinc	29.6	24.1	10.8	16.8	13.8	4.80	16.6
Cobalt	29.3	25.6	12.7	20.2	16.2	9.90	19.4
Manganese	— ^a	—	24.3	41.0	29.4	46.9	30.7
Cadmium	—	—	32.1	—	38.6	—	39.8

^a Not determined

^b See Figure 7

Standard Solutions

Certified stock solutions can be purchased or 1000 mg/L standards can be prepared for the cations of interest. Dissolve the appropriate amounts of the required analytes in deionized water in a 100 mL plastic volumetric container according to the amounts in Table 2. Dilute to volume with deionized water. Store in a plastic container at 4 °C. Working standards were prepared by serial dilutions from the 1000 mg/L (ppm) concentrate. For trace sodium analysis, working standards containing less than 1 ppm sodium were prepared every 2–3 days, standards containing less than 1 µg/L (ppb) were prepared daily and analyzed almost immediately after preparation.

1000 mg/L Ethanolamine Standard Solution

Dissolve 0.100 mL of ethanolamine in 100 mL of deionized water.

Matrix Preparation

In this study, two different matrices were prepared containing 3 and 5 ppm ethanolamine from the stock standard solution. Each matrix was spiked with ~0.250 ppb sodium.

System Preparation and Setup

The Dionex ICS-1000, Dionex ICS-1500, or Dionex ICS-2000 integrated IC systems can be used for nonsuppressed cations analysis. This application note describes the proper setup and system preparation of the Dionex ICS-2000 system for nonsuppressed cations. Configure the IC system for trace sodium analysis as shown in Figure 1. Install the 4 × 50 mm Dionex IonPac SCG 1 and 4 × 250 mm Dionex IonPac SCS 1 columns in the column oven. Set the signal polarity by navigating to the dropdown menu on the LCD screen and press "Detector". In the conductivity polarity option, change the polarity to "Inverted". The conductivity polarity of the Dionex ICS-1000 system must be changed using Chromeleon software because there is no LCD screen.

The eluent generator on the Dionex ICS-2000 system should be bypassed by placing a 10–32 in union in place of the inlet and outlet fittings of the Thermo Scientific Dionex EluGen Cartridge because the eluent generator is not used. A separate union should be placed between the inlet and outlet fittings for the continuously regenerated trap column. Connect the conductivity detector cell outlet to the tubing labeled "Regen Out"; because a suppressor is not used in this work, the column effluent will be directed to waste. The Chromeleon CDS software (*.pgm file) should have an MSA concentration of 0 mM and the suppressor should be set to "None".

Equilibrate the columns with 3 mM MSA at 1 mL/min for at least 60 min. Assess the stability of the baseline and peak-to-peak noise by measuring a representative section of the baseline where no peaks are eluting. An equilibrated system should have a background signal of <1100 µS and peak-to-peak noise of <10 nS. We strongly recommend equilibrating the system overnight for trace-level analysis with the analytical conditions described in this application note. For optimal system performance for trace analysis, we recommend continuously running the system.

Table 2. Mass of compound required to prepare 100 mL of a 1000 mg/L standard solution.

Cation	Compound	Mass (g)
Li ⁺	Lithium (LiCl)	0.6108
Na ⁺	Sodium (NaCl)	0.2542
NH ₄ ⁺	Ammonium (NH ₄ Cl)	0.2965
K ⁺	Potassium (KCl)	0.1907
Mg ²⁺	Magnesium (MgCl ₂ •6H ₂ O)	0.8365
Ca ²⁺	Calcium (CaCl ₂ •2H ₂ O)	0.3668

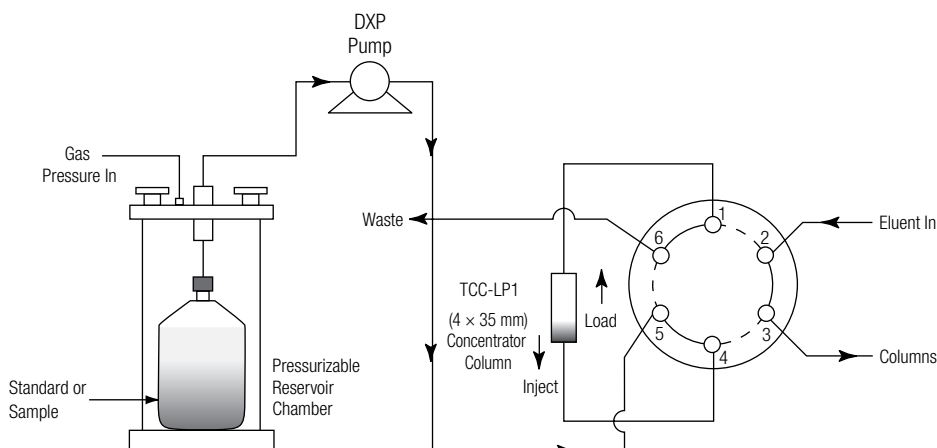


Figure 1. Ion chromatography preconcentration system (sample loading position shown).

Results and Discussion

Trace Sodium Analysis

Special precautions must be taken when performing trace analysis. Use only the highest-quality deionized water to prepare eluents, standards, and dilutions. To achieve the low sodium concentrations specified in this application note, an autosampler should not be used. Application Note 152 provides a more detailed discussion of the necessary precautions required for the determination of trace sodium.

In the power industry, it is critical to determine trace amounts of sodium at sub-ppb concentrations in boiler water treated with amine additives, such as ethanolamine. However, the amine is often present at significantly higher concentrations than the target analyte. The preconcentration of a high-ionic-strength sample can cause the sample to act as an eluent and therefore prevent the retention of the analytes of interest on the concentrator column.⁸ Because the resin in a concentrator column has a finite capacity (i.e., the column can only retain a given amount of ions from a sample matrix), the target analytes are no longer retained if the capacity of the column is exceeded. The volume of sample that just exceeds the capacity of the concentrator column is defined as the breakthrough volume. In this application note, trace levels of sodium were measured in the presence of high concentrations of ethanolamine. The high amine concentration in these samples limits the sample volume that can be concentrated. For a sample containing 0.500 ppb sodium in the presence of 5000 ppb ethanolamine, the breakthrough volume of the Dionex TCC-LP1 (4 × 35 mm) column was determined to be ~4.5 mL. This volume is significantly less than the breakthrough volume of ~30 mL for 0.250 ppb sodium in a matrix of 5000 ppb ethanolamine using the higher-capacity Dionex IonPac CG16 (5 × 50 mm) column as the concentrator column with suppressed conductivity detection.⁴ Therefore, the suppressed conductivity system can detect significantly lower analyte concentrations in higher-ionic-strength matrices than the nonsuppressed system.

In this application note, sub-ppb concentrations of sodium were determined in the presence of high concentrations of ethanolamine—a common additive found in boiler water—using nonsuppressed conductivity detection. This determination was accomplished by concentrating 3 mL (70% of the breakthrough volume) on a Dionex TCC-LP1 column. The Dionex TCC-LP1 column is packed with a 20 µm carboxylate-functionalized resin, has high pH stability, and a cation-exchange capacity of 260 µeq/column. The Dionex TCC-LP1 column is preferred for concentrating amine-treated samples because of the resin's higher pH stability and higher capacity compared to the 4 × 50 mm Dionex IonPac SCG 1 column (63 µeq/column). However, eluents containing PDCA should not be used with this concentrator.

It is important to initially establish a blank and ensure the stability of the blank analyses over a period of several days. The quality of the blank depends on several factors, such as the cleanliness of the laboratory, purity of the water source, presence of contaminants in the IC system, and other factors that can contribute to high blank levels. In this study, no sodium was detected in the blank. Previous studies of our in-house deionized water system revealed sodium concentrations of ~5 ng/L (ppt),^{4,9} significantly below the detection limit for the nonsuppressed system using a 3 mL sample volume. Figure 2 shows a representative blank chromatogram of deionized water with only a trace amount of ammonium detected. Because ammonia is ubiquitous, its concentration can vary from day to day.

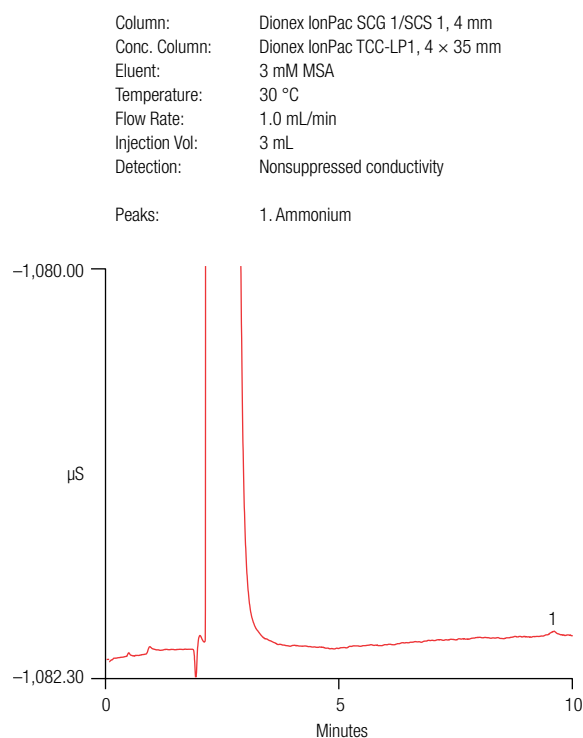


Figure 2. Trace anion standard in deionized water.

The calibration curve for sodium was obtained by preparing standards in deionized water. Table 3 shows the calibration and method detection limits (MDLs) for sodium using nonsuppressed conductivity detection. The calculated MDL, based on seven replicate injections of a 200 ppt sodium standard in a 3 mL sample volume, was 68 ppt. The precision of the retention times, based on the same replicate injections, yielded an RSD of 0.02%. Figure 3 shows a representative chromatogram of 200 ppt sodium prepared in deionized water. In contrast, the MDL for suppressed conductivity detection using a 10 mL sample volume was ~3 ppt.^{4,9} However, extrapolating the MDL from a 10 mL to 3 mL volume on the suppressed system results in a detection limit of ~10 ppt, a difference of nearly an order in magnitude compared to the nonsuppressed system.

The method performance for trace sodium analysis using nonsuppressed conductivity detection was evaluated by analyzing 3 mL of synthetic samples containing ethanolamine concentrations of 3 and 5 ppm that simulate samples encountered in the power industry. The detection of sub-ppb sodium in a matrix of 10 ppm ethanolamine cannot be performed by this method. This matrix is equivalent to concentrating 6 mL of 5 ppm ethanolamine, approximately 45% above the breakthrough volume of the Dionex TCC-LP1 column. Furthermore, concentrating less than 3 mL for this matrix would not allow the sodium concentration examined (i.e., 250 ppt) to be detected. As expected, only ammonium was detected in the 3 ppm ethanolamine matrix (Figure 4A). The most likely source of the ammonium is as a breakdown product of ethanolamine. Figure 4B shows the same matrix spiked with ~250 ppt sodium. The average spiked recoveries for 250 ppt sodium, based on triplicate injections, was 97.3%.

Table 3. Calibration and MDL for sodium using nonsuppressed conductivity detection with a 3 mL sample volume.

Analyte	Range ^a (ng/L)	Linearity (r ²)	Calculated MDL ^b (ng/L)	MDL Standard (ng/L)
Sodium	100–500	0.9998	68	200

^a Calibration levels were 100, 250, and 500 ng/L (each standard injected in duplicate)

^b MDL = $t \times S$ where t = Student's t value for a 99% confidence level and a standard deviation estimate with $n - 1$ degrees of freedom ($t = 3.14$ for seven replicates of the MDL standard), and S = standard deviation of the replicate analysis

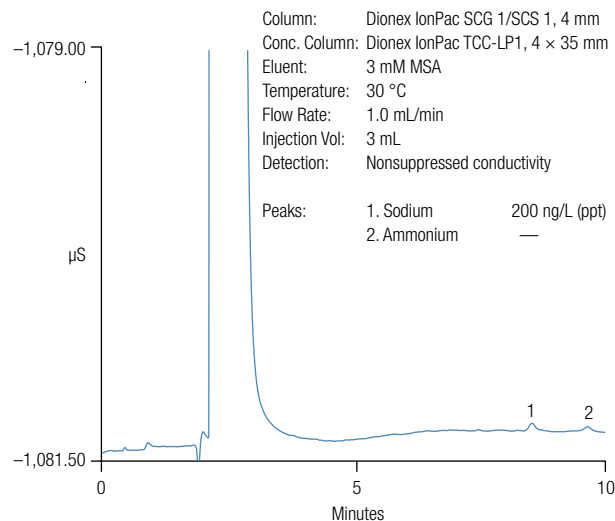


Figure 3. Determination of 200 ng/L sodium spiked into deionized water using a 3 mL sample volume.

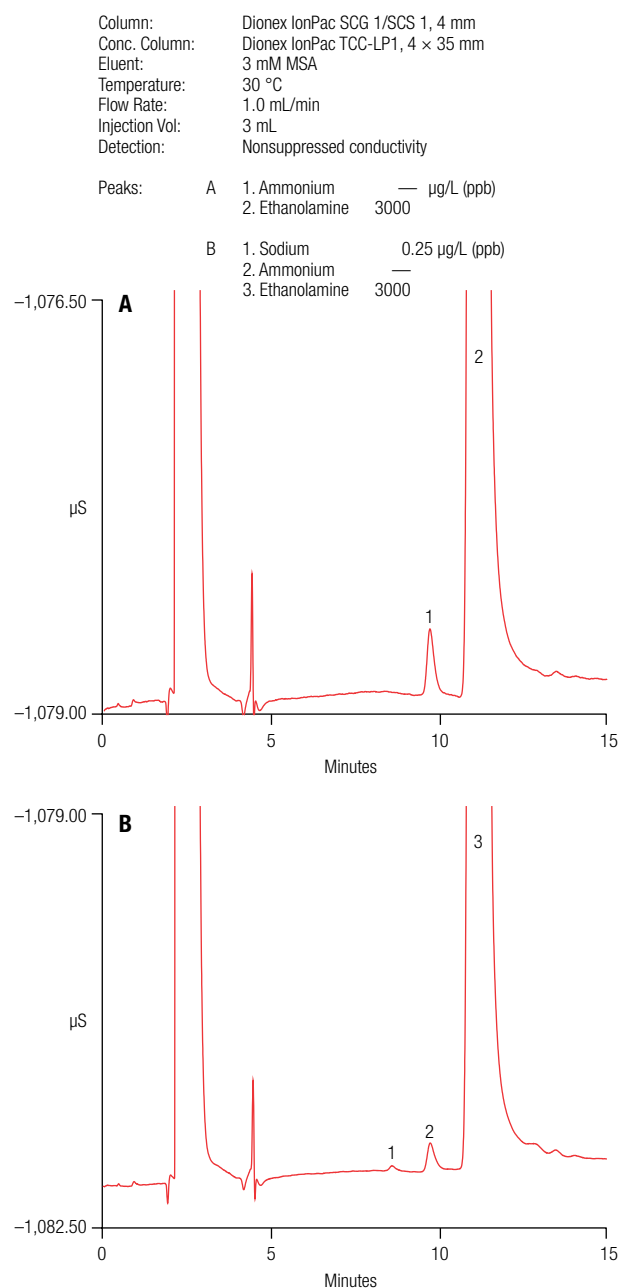


Figure 4. A representative chromatogram of 3000 µg/L ethanolamine spiked with (A) no sodium, and (B) 0.25 µg/L sodium.

Table 4 summarizes the spiked recovery data for sodium in simulated ethanolamine-treated matrices. As shown, the method performed well for samples spiked with sub-ppb sodium in the presence of up to 5 ppm ethanolamine. In general, it is not recommended to spike these sample with <250 ppt sodium because of low signal-to-noise (S/N) ratio with the nonsuppressed system. Table 5 compares suppressed to nonsuppressed conductivity detection for trace sodium in ethanolamine-treated samples. As shown in Table 5, considerably more sample volume is required with nonsuppressed conductivity detection to achieve single-digit ppt sodium detection limits, because of the lower S/N obtained with this detection mode. Consequently, nonsuppressed detection cannot achieve the required sensitivity for sodium in these matrices.

Table 4. Spiked recovery data for sodium in the presence of 3000 and 5000 µg/L ethanolamine using nonsuppressed conductivity detection.

Spiked Sodium Concentration (µg/L)	Ethanolamine Concentration (µg/L)	Average ^a Sodium Recovery (%)	RSD ^a (%)
0.242	3000	97.3	3.2
0.257	5000	92.7	9.7

^aThe average recovery and relative standard deviations were calculated from triplicate injections (n = 3)

In some power plants, the determination of trace concentrations of sodium in high concentrations of ammonium may be required. Unlike ethanolamine-treated samples, samples containing high concentrations of ammonium cause column overloading at much lower concentrations. For example, concentrating a 3 mL sample containing 1 ppm ammonium spiked with 250 ppt sodium causes severe broadening of the sodium peak and a recovery of ~60%. The lower capacity of the Dionex IonPac SCS 1 column compared to the Dionex IonPac CS16 column is a significant contributor to this result. Therefore, the concentration volume was decreased from 3 mL to 1.5 mL and the amount of sodium spiked was increased from 250 ppt to 1000 ppt. Figure 5 illustrates this separation and shows an excellent resolution between sodium and ammonium, as well as good sodium peak shape. The average spiked recoveries of sodium in this matrix was 99.9%, based on duplicate injections.

Separation of Transition Metals Using the Dionex IonPac SCS 1 Column

Nuclear and fossil-fueled power plants also require the monitoring of certain transition metals, particularly iron and copper, down to the low ppb concentrations. To achieve the best selectivity and sensitivity, the samples should be preconcentrated and optical detection after postcolumn reaction should be used.¹⁰ However, an alternative detection mode is to use nonsuppressed conductivity detection. As with trace sodium analysis, the determination of trace transition metals is limited by the purity of the water source and the reagents. In addition, the use of PEEK metal-free flow paths is essential to maintain the integrity of the analytical system. In contrast to common cations, the separation of transition metals requires a complexing agent in the eluent to achieve the necessary selectivity.

Table 5. Comparison of suppressed to nonsuppressed conductivity determinations in ethanolamine-treated matrices.

Feature	Nonsuppressed Conductivity Detection	Suppressed Conductivity Detection ^a
Columns Compared	SCG 1, SCS 1, 4 mm TCC-LP1 as conc.	CG16, CS16, 3 mm CG16 (5 mm) as conc.
Max. Sample Volume ^b (based on sample containing 5000 ppb ethanolamine)	4.5 mL	30 mL
Sample Volume Used	3 mL ^c	10 mL ^d
Sodium Calibration Range	100–500 ppt	25–250 ppt
Sodium MDL	68 ppt	3.2 ppt
Estimated Volume Required to Achieve Single-Digit ppt MDLs for Sodium	~70 mL ^e	10 mL
ppb Sodium in High Ethanolamine Matrices	Yes	Yes
Low ppt Sodium in High Ethanolamine Matrices	No (capacity limited)	Yes

^aData from Dionex Application Note 152

^bBreakthrough volume

^cVolume represents ~70% of the breakthrough volume

^dVolume represents ~30% of the breakthrough volume

^eEstimated volume by extrapolating data using suppressed conductivity detection from 10 mL to 3 mL, where suppressed conductivity detection was calculated with a 7× lower MDL

Column: Dionex IonPac SCG 1/SCS 1, 4 mm
 Conc. Column: Dionex IonPac TCC-LP1, 4 × 35 mm
 Eluent: 3 mM MSA
 Temperature: 30 °C
 Flow Rate: 1.0 mL/min
 Injection Vol: 1.5 mL
 Detection: Nonsuppressed conductivity

Peaks: 1. Sodium 1 µg/L (ppb)
 2. Ammonium 1000

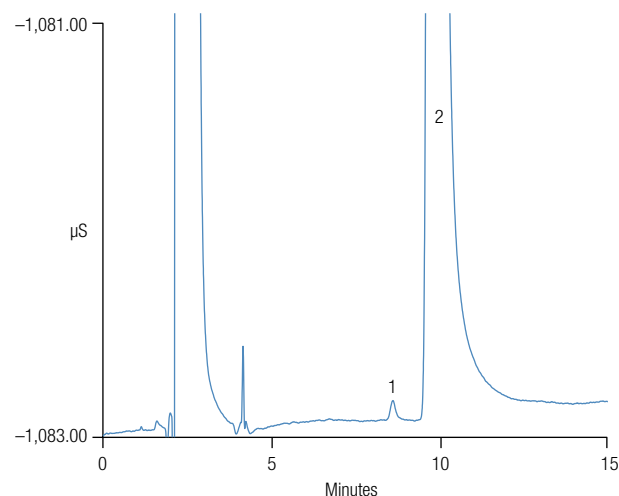


Figure 5. Separation of trace sodium in a high concentration of ammonium.

Table 1 lists the retention times of common cations and transition metals using various eluent components and concentrations, including MSA, oxalic acid, tartaric acid, and PDCA. Because PDCA forms very strong complexes with the metal ions, very low PDCA concentrations are required to elute the metals from the column. However, at low-PDCA concentrations, calcium and magnesium are more retained, resulting in longer run times. In addition, PDCA generally does not provide an optimum selectivity for resolving many transition metals from the common cations often present at much higher concentrations. Therefore, for most transition metal applications, PDCA is not recommended for use with a weak cation exchanger, such as the Dionex IonPac SCS 1 column. Eluents containing MSA and oxalic acid are best for separating common cations and most transition metals. The oxalic acid is primarily used to control the selectivity of the transition metals and alkaline earth metals, whereas the MSA contributes to the separation of alkaline earth metal ions and alkali metal ions.

Figure 6 shows a chromatogram of a 3 mL simulated feed water sample containing 7 ppm ethanolamine spiked with sub-ppm levels of common cations, diethanolamine, zinc, cobalt, and manganese. As this figure illustrates, most cations, including the transition metals, were well separated with the exception of magnesium and manganese.

Cation-exchange with nonsuppressed conductivity detection can separate many transition metals at nominal concentrations, including copper, nickel, zinc, cobalt, manganese, and cadmium. Note that the separation of iron was not included in this study. However, high concentrations of other common cations can interfere with the separation of some transition metals. Figure 7 shows a separation of the six transition metals and common cations in a single analysis at ppm concentrations using a 25 μ L injection.

Sensitivity of Copper and Zinc with a Standard-Loop Injection Using Nonsuppressed Conductivity Detection

Copper and zinc often require continuous monitoring in the power industry. For trace-level analysis of these transition metals, samples should be preconcentrated rather than injected directly. However, in this application note, it was only of interest to determine the linearity and MDLs of these metals using a standard-sized 25 μ L loop injection. Table 6 shows the calibration linearity and MDLs for copper and zinc. The MDLs were determined by performing seven replicate injections of 125 ppb copper and 25 ppb zinc. These injections resulted in calculated MDLs of 33 and 6.7 ppb for copper and zinc, respectively. The retention time precisions, based on the replicate injections, were 0.85% and 0.13%, respectively. Figure 8 shows a separation of copper and zinc at sub-ppm concentrations.

Column: Dionex IonPac SCS 1/SCS 1, 4 mm
 Conc. Column: Dionex IonPac TCC-LP1, 4 \times 35 mm
 Eluent: 2.5 mM MSA/0.8 mM oxalic acid
 Temperature: 30 $^{\circ}$ C
 Flow Rate: 1.0 mL/min
 Injection Vol: 3 mL
 Detection: Nonsuppressed conductivity

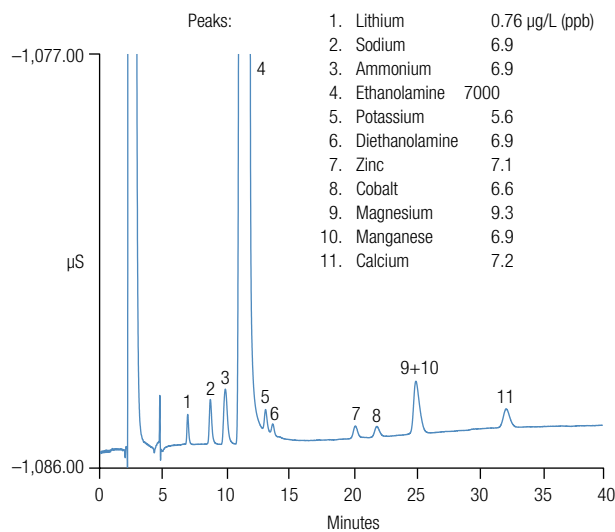


Figure 6. Chromatogram of a simulated feed water sample.

Column: Dionex IonPac SCS 1/SCS 1, 4 mm
 Eluent: 4 mM tartaric acid/2 mM oxalic acid
 Temperature: 30 $^{\circ}$ C
 Flow Rate: 1.0 mL/min
 Injection Vol: 25 μ L
 Detection: Nonsuppressed conductivity

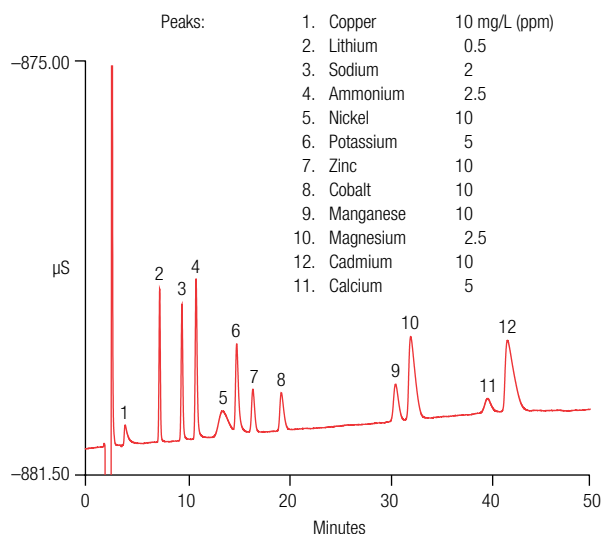


Figure 7. Separation of common inorganic cations and transition metals.

Table 6. Calibration and MDL for copper and zinc using nonsuppressed conductivity detection.

Analyte	Range ^a (ng/L)	Linearity (r^2)	Calculated MDL ^b (ng/L)	MDL Standard (ng/L)
Copper	0.125–1.00	0.9998	33	125
Zinc	0.025–0.50	0.9999	6.7	25

^a 25 μ L injection volume

^b MDL = $t \times S$ where t = Student's t value for a 99% confidence level and a standard deviation estimate with $n - 1$ degrees of freedom ($t = 3.14$ for seven replicates of the MDL standard), and S = standard deviation of the replicate analysis

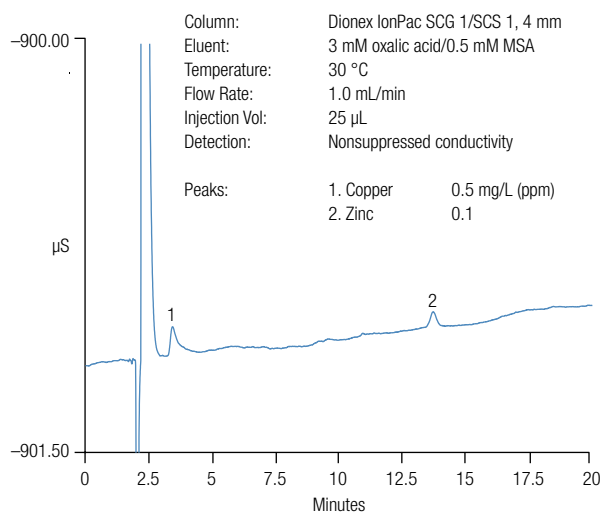


Figure 8. Determination of low concentrations of copper and zinc on the Dionex IonPac SCS 1 column.

Conclusion

This application note demonstrates the capability of nonsuppressed conductivity detection for the determination of trace sodium in ethanolamine-treated samples and the determination of some transition metals. This method yielded good recoveries for sodium spiked at the sub-ppb concentrations in ethanolamine samples containing up to 5 ppm. However, higher ethanolamine concentrations will overload the concentrator and analytical columns, causing decreased peak response and increased peak broadening for sodium. In effect, the low breakthrough volume of the Dionex TCC-LP1 column in combination with the Dionex IonPac SCS 1 column with nonsuppressed conductivity detection reduces the sensitivity that can be achieved by this method. This characteristic makes cation exchange with suppressed conductivity detection a more favorable approach because it does not suffer from these limitations. Suppressed conductivity allows the use of higher-capacity columns, such as the Dionex IonPac CS16 column, which tolerates high-ionic-strength matrices and higher samples volumes such as those required in the power industry. In addition, the improved sensitivity achieved by suppressed conductivity detection requires significantly lower samples volumes to obtain single-digit ppt detection limits of sodium compared to nonsuppressed conductivity detection. However, the Dionex IonPac SCS 1 column nonsuppressed column offers good selectivity for many transition metals of interest that cannot be accomplished by columns used with suppressed conductivity.

References

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