DIONEX

Application Note 247

Determination of Morpholine, Ethanolamine, and Hydrazine in Simulated Nuclear Power Plant Wastewater

INTRODUCTION

Nuclear power plants (NPP) generate nearly 20% of the total electricity in the U.S. and nearly 30% in the E.U.[1] In NPPs, water in secondary and cooling systems controls the heat created from the fission of radioactive isotopes, to produce steam, which is used to generate electricity.[1] Stress-corrosion cracking and flow-assisted corrosion in the NPP boiler, secondary, and cooling systems can cause increased maintenance time and cost, and loss of power generation.[2–4] Therefore, it is important to minimize corrosion in NPPs to avoid or reduce these associated events.

In the secondary system, corrosion inhibitors and oxygen scavengers are added to control pH and create a reducing environment in both liquid and vapor phases.[2–4] Historically, ammonium, due to its widespread availability, was used as an alkaline reagent to control pH and prevent corrosion.[5] However, ammonium largely has been replaced by organic amines that are less volatile, which improves corrosion protection in the liquid phase.[2,4,5] Morpholine and ethanolamine (ETA), the most commonly used organic amines in E.U. and U.S. NPPs, respectively, minimize corrosion by maintaining the water and vapor phase pH of the cooling system between 9.5 and 9.8.[2,4] Field tests conducted by the Electric Power Research Institute (EPRI) showed that ETA was more effective than morpholine in maintaining pH and, therefore, was expected to result in the lowest steel corrosion rates.[5] A strong reducing compound, such as hydrazine, is also added as an oxygen scavenger to remove or displace oxygen and to passivate metal surfaces.[2,4]

Ammonium and organic acids from the degradation of morpholine, ethanolamine, and hydrazine accumulate in the secondary and condenser water systems, which require periodic flushing and blowout.[2,4] This wastewater effluent, regulated by national wastewater discharge permits, limits amine discharges at levels specified for the individual NPP that range from low µg/L to low mg/L concentrations.[6–8] Therefore, a sensitive method is needed to determine µg/L concentrations for compliance monitoring. However, the wastewater matrix can also contain high salt content from periodic flushes of the boiler (blowout) to remove salt buildup (i.e., scale). The determination of morpholine, ETA, and hydrazine in the presence of mg/L concentrations of ammonium is an analytical challenge due to their similar selectivity on cation-exchange phases and the presence of higher concentrations of ammonium and other common cations. These challenges were met by optimizing one method to determine both hydrazine and morpholine and a second method to determine ETA.

Ion-exchange chromatography with suppressed conductivity detection is a well established method to determine µg/L to mg/L concentrations of common cations and amines; therefore, it is the method of choice in the NPP industry.[9–11] Additionally, the introduction of

Reagent-Free™ Ion Chromatography (RFIC™) systems with eluent generation (RFIC-EG™) provides consistent separation of the analytes of interest by electrolytically generating precise and accurate eluents inline.[10,11]

The experimental study shown here describes the determination of µg/L concentrations of hydrazine, morpholine, and ETA in a simulated NPP wastewater sample containing mg/L concentrations of common cations. Morpholine and hydrazine are separated on a 3 mm IonPac® CS16 high-capacity (3 mEq) cation-exchange column set using electrolytically generated 15 mM methanesulfonic acid (MSA) to elute hydrazine within 16 min and a 15 to 40 mM MSA gradient to elute morpholine within 24 min. Morpholine and hydrazine are sequentially detected by suppressed conductivity and integrated pulsed amperometric detection (IPAD) with a disposable *AAA-Certified*™ Au working electrode and the waveform typically used for amino acid analysis.[12] Sodium hydroxide is added after the conductivity detector (CD) to produce an alkaline pH, which is optimum for the electrochemical detection of amines with a Au electrode. This method uses an electrolytically generated eluent, which provides the advantages of consistent eluent concentration, and saves time and labor by avoiding manual eluent preparation. The IonPac CS16 column was designed for disparate concentrations of ammonium relative to other cations; therefore, it is ideal for this application because it minimizes column overload from the samples' high salt content. Hydrazine is nearly baseline resolved from ammonium, and morpholine is well-resolved from hydrazine and detected by IPAD.

This study also describes the determination of µg/L concentrations of ETA in the same simulated NPP wastewater sample using a single pump and detector of the ICS-3000 system. The ETA is separated on a 2 mm IonPac CS15 column using electrolytically generated 5 mM MSA eluent at 50 °C and suppressed conductivity detection. The ETA is eluted within 10 min, followed by a column wash to remove the late-eluting common cations. This column has the unique advantage of eluting ETA before the disparately larger ammonium peak. This study also describes qualification results of both methods and ruggedness of the hydrazine and morpholine method.

EQUIPMENT

Dionex ICS-3000 system including:

- DP Dual Gradient Pump module with degas option
- EG Eluent Generator module with an EluGen EGC II MSA cartridge (P/N 058902) and a continuously regenerated cation trap column (CR-CTC II, P/N 066262) for each method
- DC Detector/Chromatography Module (dual-temperature configuration)
- AS Autosampler and 10 mL sample tray
- CD Conductivity Detectors (P/N 079829) with a Cation Self-Regenerating Suppressor (CSRS® 300), 2 mm (P/N 064557), one each per method

Chromeleon® Chromatography Data System (CDS) software

Vial Kit, 10 mL polystyrene with caps and septa (P/N 055058)

Filter unit for vacuum filtration, 0.20 µm nylon (Nalgene® Media-Plus with 90 mm filter, Nalge Nunc International, P/N 164-0020) or equivalent nylon filter

Vacuum pump

PEEK™ tubing:

- Red (0.127 mm or 0.005 in i.d., P/N 052310 for 5 ft) tubing used for liquid line connections from injection valve to guard, analytical columns, and CD cell
- Black (0.25 mm or 0.01 in i.d., P/N 052306 for 5 ft) tubing used for liquid line connections from pump to injection valve

Method 1: Hydrazine and Morpholine

ED Electrochemical Detector (P/N 079830)

Electrochemical cell (cell and reference electrode, P/N AAA-061756)

Combination pH–Ag/AgCl reference electrode (P/N 061879)

AAA-Certified disposable Au working electrode (P/N 055832, package of six)

EG/DP Vacuum Degas Conversion kit (P/N 063353)

Knitted reaction coil, 125 µL (P/N 053460)

PEEK mixing tee (P/N 048227)

4 L Plastic bottle assemblies, two each (P/N 063292) for external water delivery

Additional PEEK tubing:

Black (0.25 mm or 0.01 in i.d., P/N 052306 for 5 ft) tubing for liquid line connections from CD to mixer and ED cell

Yellow tubing, 20 ft (610 cm) (0.076 mm or 0.003 in i.d., P/N 052300 for 20 ft) to increase the system backpressure on the Pump 1 postcolumn reagent (PCR) pump

Green tubing 40 ft (1.2 m) (0.76 mm or 0.03 in i.d., P/N 052304 for 20 ft) to reduce noise on Pump 1 PCR delivery

25 µL PEEK sample loop (P/N 042857)

Method 2: Ethanolamine

Additional PEEK tubing:

Black tubing to create 5 µL PEEK sample loop

Yellow tubing, < 2 ft (< 61 cm) (0.076 mm or 0.003 in i.d., P/N 052301 for 5 ft) before injection valve to increase system backpressure to 2000–2500 psi

REAGENTS AND STANDARDS

Deionized water, Type 1 reagent-grade, 18.2 MΩ-cm resistivity

Use only ACS reagent-grade chemicals for all reagents and standards

Hydrazine monohydrate ($H_2N\text{-}NH_2 \bullet H_2O$, FW 50.06, 64–65% hydrazine, Sigma-Aldrich P/N 207942)

Morpholine (C_4H_9NO, FW 87.1, VWR International P/N AA31984-36)

Ethanolamine, re-distilled ($H_2NC_2H_3OH$, FW 61.08, Sigma-Aldrich P/N 411000)

Method 1: Morpholine and Hydrazine

pH 7 Buffer solution (yellow) (VWR International P/N BDH5046) to calibrate the reference electrode

pH 4 Buffer solution (red) (VWR International P/N BDH5018) to calibrate the reference electrode

Sodium hydroxide, 50% (w/w) certified (Fisher Chemicals P/N SS254-500)

Reagents for NPP Wastewater Matrix Sample

Certified Reference Standards, 1000 mg/L (ULTRA Scientific Analytical Solutions)

- Lithium (P/N ICC-104)
- Sodium (P/N ICC-107)
- Ammonium (P/N ICC-101)
- Potassium (P/N ICC-106)
- Magnesium (P/N ICC-105)
- Calcium (P/N ICC-103)

Ammonium chloride (VWR International P/N JT0660

Calcium chloride (VWR International P/N JT1311

Magnesium chloride, hexahydrate (VWR International P/N JT2444)

Lithium chloride (VWR International P/N JT2370)

Potassium chloride (VWR International P/N JT3040)

Sodium chloride (VWR International P/N JT3624)

CONDITIONS

Method 1: Hydrazine and Morpholine

Column:	IonPac CG16 Guard, 3 × 50 mm (P/N 079931) IonPac CS16 Analytical, 3 × 250 mm (P/N 059596)
Eluent (EG):	15 mM Methanesulfonic acid (MSA) from -10 to 15 min, 40 mM from 15 to 23 min, 40 to 65 mM from 23 to 25 min, 65 mM from 25 to 32 min
Flow Rate:	0.4 mL/min
Temperature:	40 °C (Lower compartment) 30 °C (Upper compartment)
Inj. Volume:	25 µL
Detection:	Suppressed conductivity, CSRS 300, 2 mm, external water mode, 77 mA
Background Conductance:	0.3–0.5 µS
Conductance Noise:	0.3–0.6 nS
Typical System Backpressure:	2200 psi

Postcolumn Reagent Addition

Detection:	IPAD, disposable *AAA-Certified* Au, Waveform in Table 1
Reagent Flow:	50 mM Sodium hydroxide at 0.14 mL/min
Data Collection Rate:	1.66 Hz
IPAD Background:	40–60 nC
IPAD Noise with Suppressor:	60–80 pC
IPAD System Backpressure:	2200 psi
Typical pH:	12.1–12.3
Run Time:	32 min

Method 2: Ethanolamine

Column:	IonPac CG15 Guard, 2 × 50 mm (P/N 052256) IonPac CS15 Analytical, 2 × 250 mm (P/N 052252)
Flow Rate:	0.3 mL/min
Source:	EGC II MSA with CR-CTC II
Eluent:	5 mM MSA from -10 to 11 min, 65 mM from 11 to 18 min
Temperature:	50 °C (Lower compartment) 30 °C (Upper compartment)
Inj. Volume:	5 µL
Detection:	Suppressed conductivity, CSRS 300, 2 mm, recycle mode, 68 mA
Typical Background:	<1 µS
Noise:	0.4–0.7 nS
Typical System Backpressure:	2200 psi
Run Time:	18 min

Table 1. Waveform[12]

Time (s)	Potential vs pH (V)	Gain Region[a]	Integration	Ramp[a]
0.00	+ 0.13	Off	Off	Ramp
0.04	+ 0.13	Off	Off	Ramp
0.05	+ 0.33	Off	Off	Ramp
0.21	+ 0.33	On	On (Start)	Ramp
0.22	+ 0.55	On	On	Ramp
0.46	+ 0.55	On	On	Ramp
0.47	+ 0.33	On	On	Ramp
0.56	+ 0.33	Off	Off (End)	Ramp
0.57	- 1.67	Off	Off	Ramp
0.58	- 1.67	Off	Off	Ramp
0.59	+ 0.93	Off	Off	Ramp
0.60	+ 0.13	Off	Off	Ramp

[a] The gain and ramp are instrument settings for the ICS-3000 and ICS-5000 electrochemical detectors.

PREPARATION OF SOLUTIONS AND REAGENTS

Eluent Solutions

When preparing eluents, it is essential to use high-quality, Type 1, 18.2 MΩ-cm resistivity deionized water that contains as little dissolved gas as possible, which can cause increased noise in electrochemical detection. To prepare 2 L of water for eluent generation, degas 2 L deionized water by using vacuum filtration and ultrasonic agitation with applied vacuum for 10 to 20 min. Connect the eluent bottle to the corresponding eluent line, place the eluent bottle under ~ 4 to 5 psi nitrogen or another inert gas, and prime the pump with the new eluent. Prepare 1 L degassed Type 1 water weekly for the AS Autosampler flush solution.

Method 1: 50 mM Sodium Hydroxide Postcolumn Reagent

Use high-purity 50% sodium hydroxide for PCR preparation. Sodium hydroxide pellets are coated with sodium carbonate and are very hygroscopic, which may cause inaccurate preparations of sodium hydroxide solutions.

To prepare 1 L of 50 mM sodium hydroxide PCR, add 997.4 g degassed Type 1, deionized water into a 1 L pre-cleaned high-density polyethylene (HDPE) eluent bottle. This is measured on a top-loader balance accurate to ± 0.01 g. Using a 25 mL transfer pipette, position the pipette in the center of the sodium hydroxide bottle and transfer 50% sodium hydroxide solution to the PCR bottle until 4 g (2.6 mL) has been added. Immediately close and cap the hydroxide and PCR bottles, connect the PCR bottle to Eluent A line from Pump 1, and place the same bottle under ~ 4 to 5 psi of nitrogen or another inert gas. Swirl the bottle to thoroughly mix the PCR and prime the pump with the new PCR. Prepare the PCR on a weekly basis for consistent analytical results.

Standard Stock Solutions

To prepare the 1000 mg/L individual hydrazine stock solution, transfer 155 mg of hydrazine monohydrate reagent solution (64–65% hydrazine) into a 100 mL volumetric flask on an analytical balance. Remove the flask from the balance, add deionized water to 100 mL, and mix the standard solution thoroughly. Prepare separate 1000 mg/L morpholine and ethanolamine stock solutions in the same manner using 100 mg each of morpholine and ethanolamine reagents.

Intermediate Standards

To prepare separate individual 10 mg/L hydrazine, morpholine, and ethanolamine intermediate standard solutions, pipet 200 µL from their respective 1000 mg/L stock standard solutions into separate 20 mL scintillation vials on an analytical balance. Add deionized water to 20.000 g total weight and mix thoroughly.

Method 1: Hydrazine and Morpholine Working Standard Solutions

To prepare the combined hydrazine and morpholine working standards, pipet 20, 40, 80, and 100 µL of 10 mg/L hydrazine and 200, 400, 800, and 1000 µL of 10 mg/L morpholine, respectively, into individual 20 mL scintillation vials placed on an analytical balance. Add deionized water to 20.000 g total weight and mix thoroughly. To prepare the limit of detection (LOD) and limit of quantification (LOQ) standards, dilute the 10 µg/L hydrazine and 100 µg/L morpholine working standards to 1:4 and 1:2 dilutions, respectively, with deionized water. Prepare working standards daily, intermediate standard weekly, and stock standard monthly. Store at 5 °C.

Method 2: Ethanolamine Working Standard Solutions

Prepare ethanolamine standards similarly by pipetting 100, 200, 400, 800, and 1600 µL, respectively, of 10 mg/L ethanolamine intermediate standard solution into individual 20 mL scintillation vials placed on an analytical balance. Add deionized water to 20.000 g total weight and mix thoroughly. To prepare the LOD and LOQ standards, dilute the 50 µg/L ethanolamine working standard sequentially to 4-fold and 2-fold dilutions with deionized water. Prepare working standards daily, intermediate standard weekly, and stock standard monthly. Store at 5 °C.

Table 2. Amount of Reagent Needed to Prepare 100 mL of 1000 mg/L Simulated NPP Wastewater Matrix Stock Solutions

Reagent	Cation	FW	Amount (mg)
Ammonium chloride (NH_4Cl)	Ammonium	53.49	297
Calcium chloride ($CaCl_2$)	Calcium	110.98	277
Lithium chloride (LiCl)	Lithium	42.39	611
Magnesium chloride, hexahydrate ($MgCl_2 \cdot 6H_2O$)	Magnesium	203.30	846
Potassium chloride (KCl)	Potassium	74.55	191
Sodium chloride (NaCl)	Sodium	58.44	254

Sample Preparation

To prepare the samples in the simulated NPP wastewater matrix, add ethanolamine, morpholine, and hydrazine to a high salt solution containing 1 mg/L lithium, 10 mg/L potassium, and 50 mg/L ammonium, sodium, calcium, and magnesium. Prepare this simulated NPP wastewater matrix from purchased 1000 mg/L certified reference standards by pipetting 100 and 1000 µL of lithium and potassium standards, respectively, and 5000 µL each of ammonium, sodium, calcium, and magnesium standards into a 100 mL HDPE bottle. Add deionized water to a total weight of 100.00 g and mix thoroughly. Alternatively, prepare the same matrix from individual reagents by first preparing stock solutions using weights listed in Table 2. Measure into separate 100 mL HDPE bottles containing 100.00 g deionized water and gently shake to dissolve reagents and thoroughly mix solutions. The remainder of the preparation is the same as described with the purchased reference standards.

Hydrazine, Morpholine, and Ethanolamine in a Simulated NPP Wastewater Matrix

To prepare hydrazine, morpholine, and ethanolamine samples in the simulated NPP wastewater matrix, pipet 40, 400, and 400 µL of 10 mg/L hydrazine, morpholine, and ethanolamine intermediate standards, respectively, into a 20 mL scintillation vial. Add the simulated NPP wastewater matrix to 20.000 g total on an analytical balance. Gently shake to mix the solution. To prepare the same concentration of analytes in 80% of the simulated

NPP wastewater matrix solution, add the same amount of 10 mg/L intermediate standards as previously described and 4.000 g deionized water to a 20 mL scintillation vial on an analytical balance. Add the simulated NPP wastewater matrix solution to 20.000 g total.

SYSTEM PREPARATION AND SETUP

Method 1: Determination of Hydrazine and Morpholine

Configuring the Systems

In Method 1, the ICS-3000 system is configured for sequential detection: suppressed conductivity detection in external water mode, and electrochemical detection by IPAD facilitated by a postcolumn addition of sodium hydroxide after the CD into a mixing tee, and a reaction coil to mix postcolumn reagent into the eluent stream (Figure 1). Pump 1 is used to deliver 50 mM sodium hydroxide PCR and Pump 2 is used to deliver eluent. For electrochemical detection with eluent generation, it is necessary to install the ICS-3000 EG vacuum degas conversion kit.[13] This conversion kit reconfigures the vacuum degasser pump to degas the electrolytically generated eluent through the CR-CTC II *Regen Out* line, thus reducing baseline noise. The *Regen In* port of the CR-CTC II is capped for the vacuum degasser pump.

To configure System 2 for hydrazine and morpholine determinations, hydrate the CSRS 300 suppressor, the CR-CTC II, and the EluGen EGC II MSA cartridge according to their respective QuickStart instructions. Install the tubing, suppressor, CR-CTC II, columns, and CD detector according to the configuration shown in Figure 1. Install a temporary waste line on the suppressor of the CD *Eluent Out* port to a waste container. Do not add backpressure loops on the suppressor because the electrochemical cell adds sufficient backpressure. Insert a section of yellow PEEK tubing before the injection valve to increase system backpressure to 2000–2400 psi at 0.4 mL/min. Do not allow system backpressure to exceed 3000 psi because this may damage the degas module. Configure the suppressor in external water mode by using deionized water as the regenerant flowing at 3 to 5 mL/min from the *Regen In* port and exiting the *Regen Out* port to waste. Allow the column to equilibrate overnight. Configure Pump 1 to deliver 50 mM NaOH PCR as described in the Assembling the PCR Delivery System section.

Assembling the PCR Delivery System

Pump 1 is used to consistently deliver the PCR at the low flow rates needed for this application note. To configure the PCR delivery on Pump 1, install black PEEK tubing from Pump 1 to ~ 610 cm of coiled yellow tubing to increase the system backpressure to ~ 2000 psi at 0.14 mL/min, and 152 cm of green PEEK tubing as a pump pulse dampener to reduce the system noise. Connect the free end of the green PEEK tubing to a 30 cm section of black PEEK inserted into the PEEK mixing tee. Install a 125 µL knitted reaction coil in the outlet of the mixing tee (Figure 1). Remove the temporary waste line on the CD Eluent Out port and install a small section (5–15 cm) of black PEEK tubing to the mixing tee.

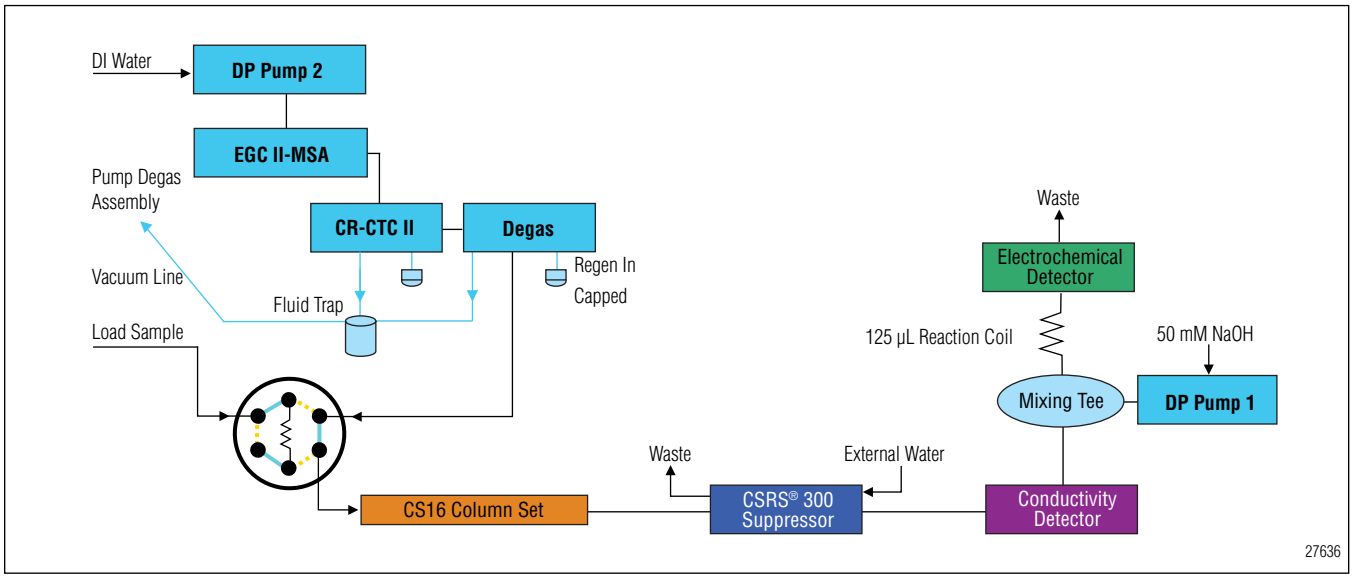

Figure 1. System configuration for Method 1 to determine hydrazine and morpholine using suppressed conductivity and integrated pulsed amperometric detections.

Assembling the Electrochemical Cell

To assemble the electrochemical cell, follow instructions in Dionex AN 188: install a *AAA-Certified* disposable Au working electrode, calibrate from pH 7 to pH 10, and install the reference electrode.[14] Install the free end of the knitted reaction coil to the ED cell inlet tube. Install a small section of black PEEK tubing on the ECD outlet, which may be connected to the waste line. In this configuration, the CD cell does not need additional backpressure tubing because the backpressure is provided by the ED cell. The *AAA-Certified* disposable Au working electrode was designed to determine amines and amino acids using the waveform under alkaline conditions.[15,16] Typically, the background of a system using a new *AAA-Certified* disposable working electrode will stabilize within 10 min. After the pumps are delivering PCR and eluent to the ED cell and the pH > 9, turn on the ED cell and load the waveform.

Configuring Virtual Channel to Monitor pH

The continuous monitoring of pH during sample analyses provides details on reference electrode drift and noise, and also serves as a check to confirm that the PCR has been properly prepared. To continuously monitor and record the pH, follow the instructions in Dionex AN 188 to create a virtual channel using the Server Configuration program.[14] Once configured, the pH virtual channel becomes one of the available signal channels.

Method 2: Determination of Ethanolamine

To determine ethanolamine using Method 2, configure one ICS-3000 system as a typical RFIC-EG system by hydrating the CSRS 300 suppressor, the CR-CTC II, and the EluGen EGC II MSA cartridge according to their respective QuickStart instructions and installing the tubing, the suppressor in recycle mode, CR-CTC II, columns, and CD detector. Install black PEEK tubing from the pump to the injection valve, and red PEEK tubing from the injection valve to the columns, CD, and suppressor in recycle mode. Add a sufficient length of yellow PEEK tubing (~ 30 cm) before injection valve to increase total system backpressure at 0.3 mL/min to 2000–2200 psi. Allow the column to equilibrate overnight.

To prepare a 5 µL sample loop, cut a 10 to 12 cm length of black PEEK tubing. Weigh the tubing on an analytical balance before and after filling the tubing with deionized water. Adjust the length until the net weight is 5 ± 1 mg (equivalent 5 ± 1 µL). Record the calibrated weight into the AS autosampler module and install the sample loop in the injection valve.

RESULTS AND DISCUSSION

The high-capacity IonPac CS16 (3 mEq, 3 × 250 mm) cation-exchange column provides the best resolution of low concentrations of hydrazine and morpholine from high concentrations of ammonium and other common cations. However, the column cannot resolve low concentrations of ethanolamine from high ammonium concentrations. Therefore, the IonPac CS15 column, which has different selectivity than the IonPac CS16 column, was used for this separation.

The IonPac CS15 column was developed by grafting carboxylate, phosphonic, and crown ether functional groups onto the resin substrate, resulting in a mildly hydrophilic column with less retention of ethanolamine. The IonPac CS16 column has grafted carboxylate functional groups that retain hydrazine slightly more than ammonium. Both high-capacity columns were designed to prevent overloading and resolve small concentrations of analytes in mg/L concentrations of common cations. Although each column has different selectivity for the analytes of interest, neither column can simultaneously resolve hydrazine, ethanolamine, and morpholine from ammonium.

The IonPac CS15 column was optimized to elute ethanolamine before ammonium at elevated temperatures, which is ideal for determining µg/L concentrations of ethanolamine in mg/L concentrations of ammonium. The IonPac CS16 column was optimized for maximum separation of small amounts of ammonium from higher concentrations of sodium, but it also works with the reverse relationship. In addition, morpholine is strongly retained with this column chemistry, so it is well-resolved from ammonium, hydrazine, and ethanolamine. Therefore, to accurately determine 20 µg/L hydrazine, 200 µg/L morpholine, and 200 µg/L ethanolamine in a simulated NPP wastewater matrix, the IC methods were optimized to determine hydrazine and morpholine separately from ethanolamine. In Method 1, hydrazine is resolved from ammonium and elutes within 16 min, and morpholine elutes within 24 min using a gradient separation on the IonPac CS16 column. In Method 2, ethanolamine is resolved from ammonium on the IonPac CS15 column using 5 mM MSA at 50 °C.

Method 1: Determination of Hydrazine and Morpholine

To optimize the method for hydrazine, multiple detection methods were evaluated: pulsed amperometric detection (PAD) with a Pt working electrode, IPAD using an *AAA-Certified* Au working electrode, and suppressed conductivity detection. The results demonstrated an increase in sensitivity of more than an order of magnitude and two orders of magnitude for hydrazine and morpholine, respectively, when using the Au working electrode compared to the Pt working electrode. The increased sensitivity allows determinations of hydrazine to critical µg/L concentrations needed for regulatory effluent permits. However, the Au working electrode with IPAD waveform requires an alkaline pH, unlike detection with the Pt working electrode. Therefore, a postcolumn addition of 50 mM sodium hydroxide at 0.14 mL/min is used to produce an alkaline effluent pH needed for detection with the Au working electrode. Figure 2 shows the separation of 20 µg/L hydrazine and 200 µg/L morpholine on the 3 mm IonPac CS16 column using a multi-step MSA gradient to elute morpholine followed by IPAD. The hydrazine and morpholine peaks have good peak symmetry and the peak responses are well above the baseline.

Limit of Detection, Limit of Quantification, Linear Range, and Precision

To qualify the method, the estimated LOD, LOQ, linear range, and precision were determined. The LODs and LOQs were determined by measuring peak-to-peak noise in 1 min increments from 20 to 60 min in four replicate runs without a sample injection. The results showed low noise, with averages of 64 ± 0.94 pC. The estimated LOD and LOQ of hydrazine (Table 3) were calculated as 2.3 and 8.6 µg/L, respectively, based on the peak response of the standard at 3× and 10× the signal-to-noise (S/N). The estimated LOD and LOQ of morpholine were calculated as 24.8 and 147 µg/L, respectively. These determinations demonstrate the sensitivity needed to meet the regulatory effluent requirements. To determine method linearity, four calibration standards from 10 to 50 µg/L hydrazine and 150 to 500 µg/L morpholine, respectively, in deionized water were injected in duplicate. The results were linear with correlation coefficients (r^2) of 0.9997 each. The retention time and peak area precisions, based on seven replicate injections of a 20 µg/L hydrazine and 200 µg/L morpholine standard were similar for hydrazine and morpholine with RSDs of < 0.1 and < 3, respectively.

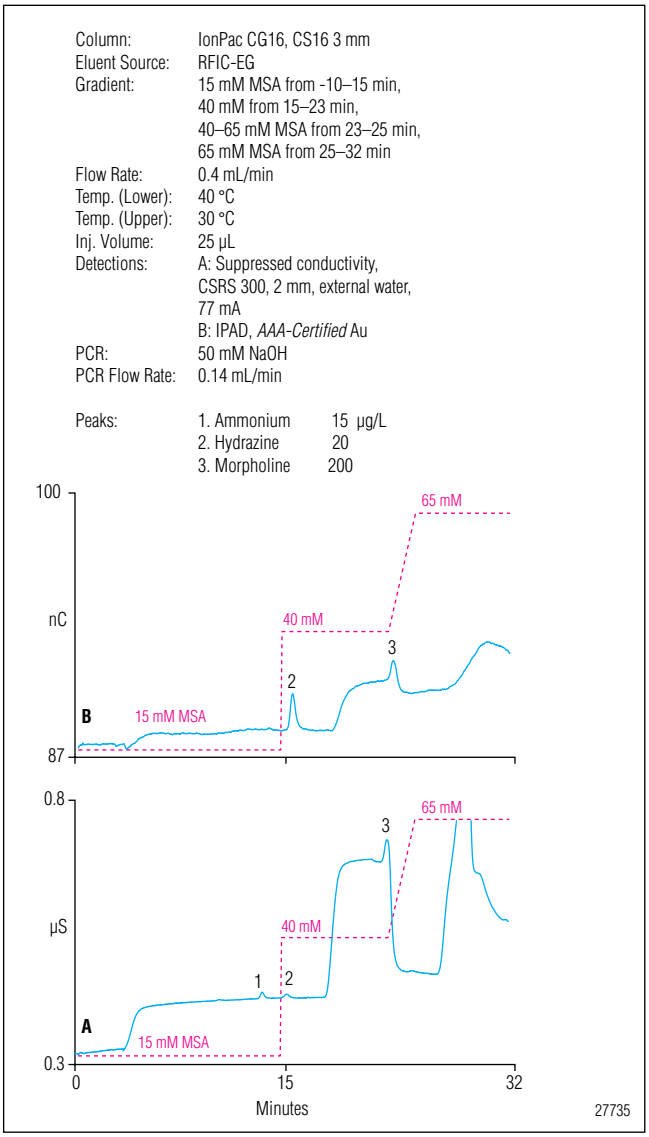

Figure 2. Separation of hydrazine and morpholine standard solution by IC with A) suppressed conductivity and B) IPAD detection.

Table 3. LOD, LOQ, and Linearity

	Linear Range (µg/L)	Correlation Coefficient (r^2)	LOD (µg/L)	LOQ (µg/L)
Hydrazine	10–50	0.9997	2.3	8.6
Morpholine	150–500	0.9997	24.8	147
Ethanolamine	50–800	0.9997	13	54

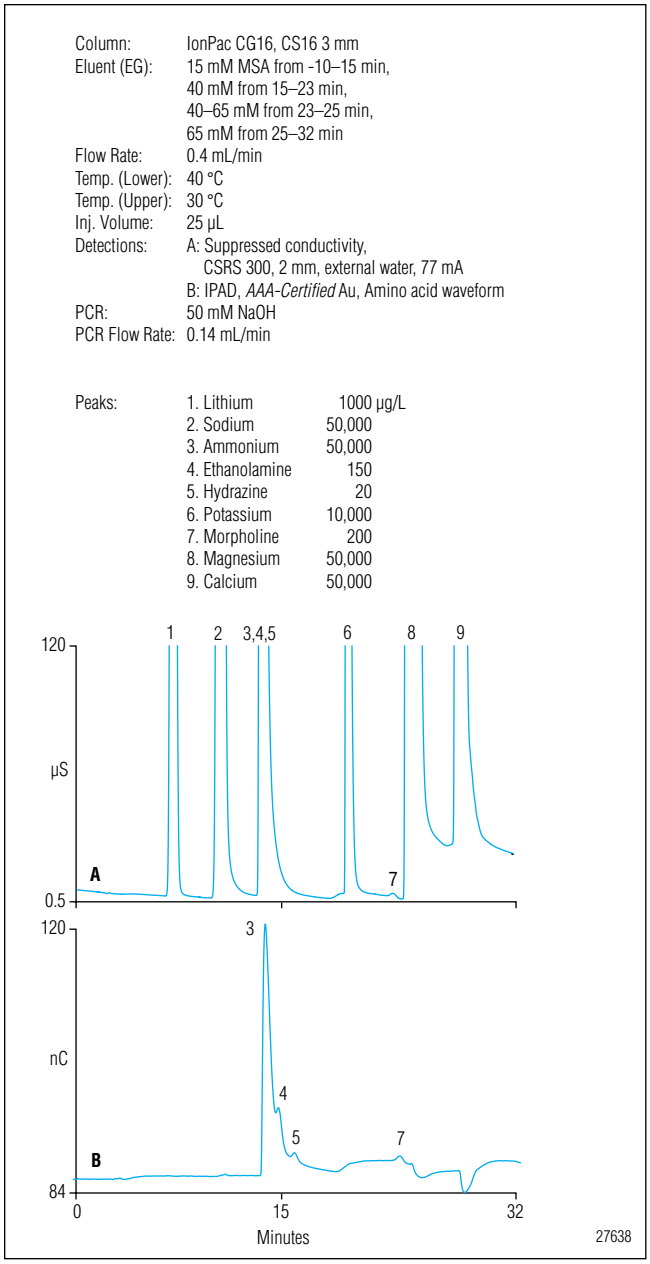

Figure 3. Comparison of hydrazine and morpholine in a simulated NPP wastewater matrix by A) suppressed conductivity detection and B) IPAD.

Table 4. Precisions and Accuracies of Amine Determinations in a Simulated NPP Wastewater Matrix[a]

Analyte	Retention Time RSD	Peak Area RSD	Amount Added (µg/L)	Average Recovery (%)
Hydrazine[b]	0.05	1.9	20	109.0
Morpholine[b]	0.08	2.9	200	97.2
Ethanolamine[c]	0.43	1.8	200	101.7

[a] The simulated NPP wastewater matrix contains 1 mg/L lithium, 10 mg/L potassium, and 50 mg/L each of sodium, ammonium, calcium, and magnesium.

[b] The precision and recoveries of hydrazine and morpholine are determined in 100% of the simulated NPP wastewater matrix.

[c] The precision and recovery of ethanolamine are determined in 80% of the simulated NPP wastewater matrix.

Hydrazine and Morpholine in a Simulated NPP Wastewater

Figure 3 compares the separation of 20 µg/L hydrazine and 200 µg/L morpholine fortified in a simulated NPP wastewater matrix sample solution using suppressed conductivity detection and IPAD. Replicate injections of the spiked sample produced an average recovery of 109% for hydrazine (n = 7) with retention time and peak area RSDs of < 0.1 and 1.9, respectively (Table 4). Morpholine had average recoveries of 97.2% (n = 7) and retention time and peak area RSDs of < 0.1 and 2.9, respectively.

To evaluate method robustness, the effects of minor variations in paramenters such as PCR concentration, PCR stability, and column temperature, and a change in working electrode lot and column, on hydrazine and morpholine peak responses were determined.

Table 5. Results of Robustness Experiments for Method 1									
Parameter		**Hydrazine Average Retention Time[a] (min)**	**Difference (%)**	**Hydrazine Peak Area[a] (nC-min)**	**Difference (%)**	**Morpholine Average Retention Time[a] (min)**	**Difference (%)**	**Morpholine Peak Area[a]**	**Difference (%)**
PCR Concentration (mM NaOH)	47	15.83 ± 0.01	-0.1	0.690± 0.011	-1.2	23.27 ± 0.01	-0.1	0.548 ± 0.001	+2.1
	50	15.84 ± 0.01	—	0.698 ± 0.015	—	23.30 ± 0.02	—	0.537 ± 0.015	—
	53	15.83 ± 0.01	-0.1	0.717 ± 0.004	+2.7	23.26 ± 0.01	-0.2	0.539 ± 0.005	+0.4
PCR Preparation	Fresh	15.96 ± 0.02	—	0.377± 0.005	—	23.30 ± 0.02	—	0.537 ± 0.015	—
	1 week old	15.87 ± 0.01	+0.2	0.693 ± 0.010	-0.7	23.31 ± 0.03	—	0.435 ± 0.010	-18.9
Column Temperature (°C)	38	16.14 ± 0.01	+1.9	0.676 ± 0.017	+1.3	23.51 ± 0.01	+0.9	0.392 ± 0.022	-27.0
	40	15.84 ± 0.01	—	0.698 ± 0.015	—	23.30 ± 0.02	—	0.537 ± 0.015	—
	42	15.56 ± 0.01	-1.8	0.667 ± 0.004	-4.5	23.05 ± 0.02	-1.0	0.516 ± 0.015	-4.0
Working Electrode (Lot)	090916a	15.84 ± 0.01	—	0.698 ± 0.01	—	23.30 ± 0.02	—	0.537 ± 0.015	—
	090723a	15.80 ± 0.01	-0.3	0.704 ± 0.002	+0.8	23.22 ± 0.00	-0.3	0.567 ± 0.005	+5.8
Column (Lot 009-11-013)	1	15.84 ± 0.01	—	0.698 ± 0.01	—	23.30 ± 0.02	—	0.537 ± 0.015	—
	2	15.91 ± 0.01	+0.4	0.711 ± 0.00	+1.8	23.15 ± 0.02	-0.6	0.543 ± 0.018	+5.8

[a]n = 3

Table 5 summarizes the results, showing that column temperature had a small effect on hydrazine retention time and peak area response, relative to other method conditions. Change in column temperature had a similar small effect on morpholine retention time but a significant impact on peak area, with a 27% decrease in peak area from the 2 °C temperature decrease. Small variations in PCR preparation from 48 to 52 mM NaOH had minimal effect on retention time and peak area for both analytes. However, the PCR prepared a week earlier produced a significant decrease in morpholine peak area response (18.9%). The robustness experiments with the 50 mM NaOH PCR preparation showed the need to prepare fresh PCR every week. Hydrazine had similar peak area responses and retention times with disposable *AAA-Certified* working electrodes within the same lot, from different lots, and on columns within the same lot. Using different working electrodes and columns had a slightly higher effect on morpholine peak areas.

Method 2: Determination of Ethanolamine by an RFIC-EG System

To optimize the method for ethanolamine, the separation of ethanolamine from ammonium on the IonPac CS15 column using an RFIC-EG system with an electrolytically generated MSA eluent at concentrations from 5 to 25 mM MSA at 50 °C was evaluated. Figure 4 shows a standard chromatogram of 200 µg/L ethanolamine separated on the IonPac CS15 column. The 200 ug/L ethanolamine peak has a good response and is well above the baseline.

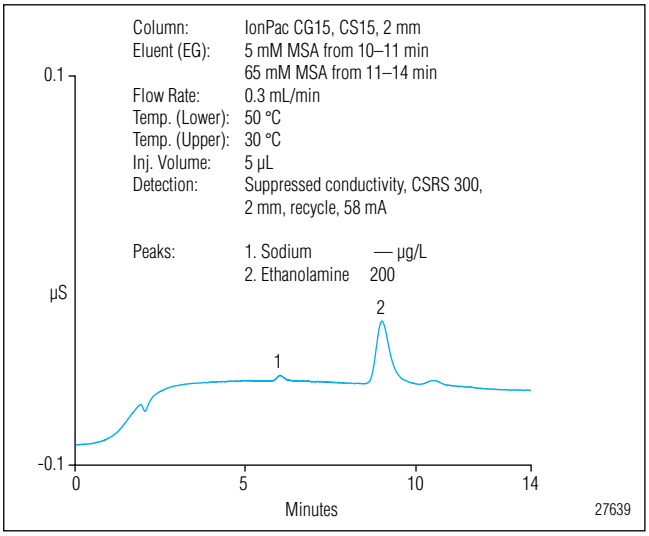

Figure 4. Separation of 200 µg/L ethanolamine standard solution on an IonPac CS15 column.

LOD, LOQ, Linear Range, and Precision

To qualify the ethanolamine method, the same parameters evaluated for Method 1 were evaluated. The estimated LOD and LOQ, based on average peak-to-peak noise of 0.6 ± 0.2 nS, were 13 and 54 µg/L ethanolamine, respectively (Table 3). A calibration from 50 to 800 µg/L ethanolamine demonstrated linearity by producing a correlation coefficient (r^2) of 0.9997. Retention time and peak area precision studies of a 200 µg/L ethanolamine (n = 7) standard produced RSDs of < 0.1 and 1.6, respectively, which demonstrates the column and methods stability that will result in reliable ETA determinations.

Ethanolamine in Simulated NPP Wastewater

To determine method accuracy and precision, 200 µg/L ethanolamine was added to the simulated NPP wastewater matrix, which produced a recovery of 86.4%. This recovery indicated that the sample matrix might be overloading the column. Therefore, the matrix was diluted by 20% with the same amount of ethanolamine added (200 µg/L) (Figure 5). The results showed an improved average recovery of 101.7% with retention time and peak area RSDs of 0.43 and 1.8, respectively (Table 4). This demonstrated the need to account for the ionic strength of the sample matrix when determining ethanolamine.

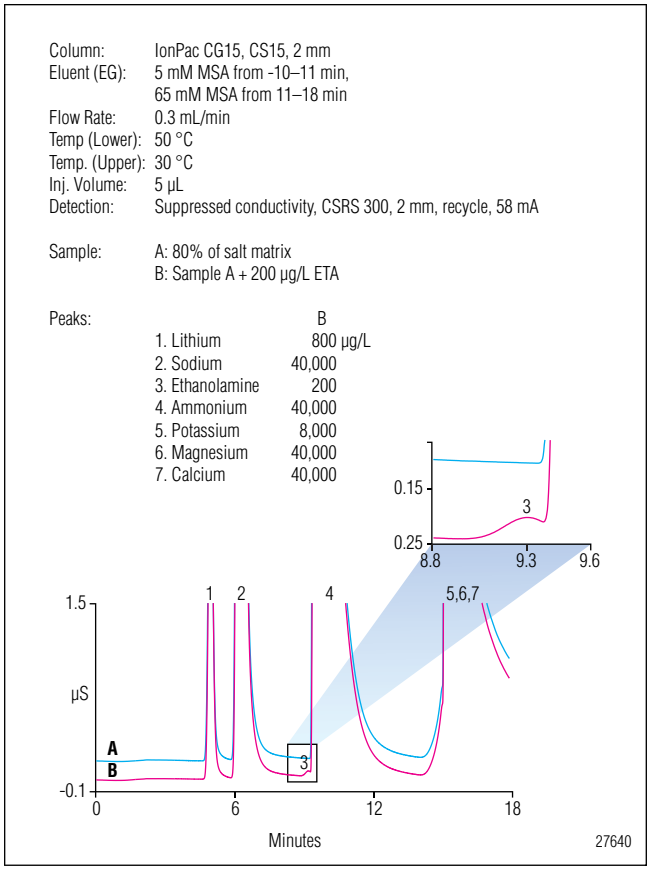

Figure 5. Comparison of 80% simulated NPP matrix A) without and B) with 200 µg/L ethanolamine (ETA) added.

CONCLUSION

This application note describes two methods to determine µg/L concentrations of hydrazine, morpholine, and ethanolamine in disparately larger concentrations of ammonium and other cations in a simulated NPP wastewater sample. Hydrazine and morpholine were determined in the simulated NPP wastewater matrix on the IonPac CS16 column by suppressed conductivity detection and IPAD. This hydrazine and morpholine method takes advantage of the dual pump and detector capabilities of the ICS-3000 system to accurately and precisely deliver the sodium hydroxide PCR required to selectively detect hydrazine and morpholine in the presence of ammonium by IPAD. Ethanolamine is separated by cation-exchange chromatography on the IonPac CS15 column with suppressed conductivity detection using the column's selectivity to elute ethanolamine before ammonium, along with the precise eluent preparation capabilities of the RFIC-EG system.

SUPPLIERS

Fisher Chemicals, part of Thermo Fisher Scientific, 2000 Park Lane Drive, Pittsburgh, PA 15275 U.S.A. Tel: 1-800-766-7000. www.fishersci.com

Sigma-Aldrich, Inc., P.O. Box 951524, Dallas, TX 75395-1524 U.S.A. Tel: 1-800-325-3010. www.sigmaaldrich.com

ULTRA Scientific Analytical Solutions, 250 Smith Street, N. Kingstown, RI 02852 U.S.A. Tel: 1-800-338-1754. www.ultrasci.com

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

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