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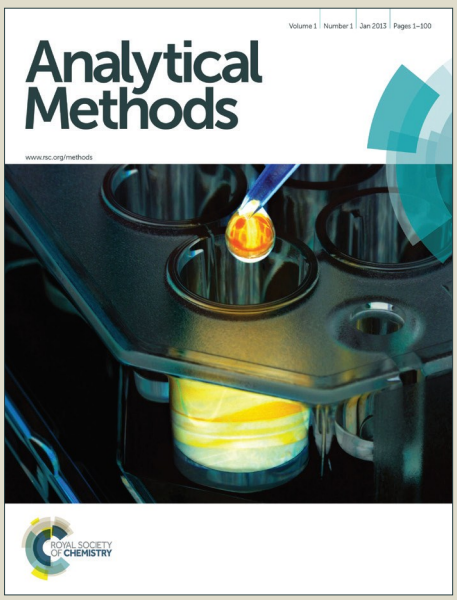

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DETERMINATION OF HYDRAZINE AT ONTARIO NUCLEAR POWER PLANTS

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ABSTRACT

In this study, we developed and validated a sensitive method for the determination of hydrazine in water samples using ion chromatography coupled with an amperometric detector (limit of detection (LOD) = 0.02 μg/L and limit of quantification (LOQ) = 0.1 μg/L). Given the instability of hydrazine in the environment, we further investigated the optimal conditions for sample preservation and shipping. We found that 10 mmol/L hydrochloric acid preserves hydrazine at concentrations from 0.1 to 100 μg/L. We then measured the concentration of hydrazine in water samples taken from Lake Huron near the Bruce Nuclear Power Plant (NPP) and from Lake Ontario near Pickering and Darlington NPPs. The concentrations of hydrazine in lake and condenser cooling water (CCW) samples (from <0.02 to 0.03 μg/L), were similar to the background and verified with both field and cooler blanks. Our results demonstrate that measured concentrations of hydrazine in the CCW and in surface waters influenced by the NPPs are well below the Canadian Federal Environmental Quality Guideline of 2.6 μg/L. The concentrations of hydrazine measured in service water samples from the three NPPs were in the range from 131 to167 μg/L, and represent the partial inventories of hydrazine in operating NPPs.

INTRODUCTION

Hydrazine (N_2H_4) is a colourless flammable liquid with an ammonia-like odour. It is used in nuclear power plants (NPPs) as a corrosion inhibitor in boilers by scavenging dissolved oxygen in the heat transport system.[1,2,3] Hydrazine is unstable and reacts rapidly with oxygen in environmental media to yield nitrogen and water.[4-9] The oxidation of hydrazine in fresh water is accelerated by the presence of copper.[4,7,9] At higher temperatures and pressures (>175 ^{o}C and 2.068 MPa), such as would be present in Pressurized Water Reactors (PWRs), hydrazine decomposes to ammonia.[10] Ammonia is known to be present in the secondary circuit of nuclear power plants, and may interfere with the determination of hydrazine.[1,2]

The Canadian Federal Environmental Quality Guideline (FEQGs) for hydrazine[11] in freshwater is 2.6 μg/L. This value represents the concentration below which one would expect a low likelihood of adverse effects on freshwater aquatic life. Given this water quality guideline, a sensitive and robust method for the determination of hydrazine at low μg/L levels in environmental water samples would be required for adequate environmental monitoring and hazard assessment.

There are several published analytical methods for the determination of hydrazine in environmental media such as air, water, soil, as well as in food, pharmaceuticals and biological fluids.[12-27] One of the most widely used method is the ASTM (American Society for Testing and Materials) spectrophotometric method for determination of hydrazine in water, which relies on the reaction of hydrazine with p-dimethylamino-benzaldehyde (Ehrlich's reagent) in acidic media to generate yellow p-dimethylaminobenzalazine.[12,13] This method is reasonably robust, but has a relatively high (5 μg/L) LOQ, which is not sensitive enough for monitoring hydrazine releases from power plants. Chromatographic methods[14-27] are generally more sensitive, e.g. gas

chromatography coupled with mass spectrometry (GC/MS) has a LOQ of ~0.01 μg/L. However, the use of GC/MS requires particular attention to cleanliness of the equipment to avoid cross-contamination, and may not be as readily available in the analytical laboratories for analyzing hydrazine in environmental samples, which makes it less suitable for routine environmental monitoring of hydrazine.[16]

In this study we initially attempted to improve on the Metrohm liquid chromatography method which utilizes 20 % acetone in 2 mmol/L nitric acid (HNO_3) as the mobile phase, and a cation exchange column (METROSEP C4-250) with a suppressed conductivity detector.[24] That method gives a well-resolved hydrazine peak and can measure hydrazine concentrations as low as 20 μg/L. By using similar ion chromatography with more sensitive amperometric detection we obtained a LOQ of 10 μg/L for hydrazine, which was too high for environmental monitoring purposes. Significant further improvements were achieved with a microbore silica based cation exchange column, Zorbax 300 SCX, and a pH 6 phosphate buffer as a mobile phase, which yields a LOQ of 0.1 μg/L. Such sensitivity is suitable for determination of hydrazine in environmental water samples for regulatory compliance and monitoring purposes.

Given the well-known instability of hydrazine in environmental water samples we have also studied a method to preserve field samples for accurate determination of hydrazine during normal operations and for estimating the initial concentration of hydrazine in a spill event.

At the Ontario NPPs, release of hydrazine-treated water to the aquatic environment is primarily via the Condenser Cooling Water (CCW) discharge. There are a number of authorized release points for hydrazine for routine and episodic boiler blow down, condensate make-up tank in the feedwater system, active liquid waste system (ALWS), and emergency cooling water

(ECW) system of the NPPs. Given that hydrazine is rapidly diluted and degraded in the CCW, measurable levels are not normally encountered in the aquatic environment. [28-32]

We used the newly developed method of sample preservation and analysis to measure concentration of hydrazine in surface water as a result of releases from operating NPPs. In the 2011 screening assessment document prepared by Health Canada and Environment Canada, the predicted environmental concentrations of hydrazine from the routine operation of the Ontario nuclear power plants were stated to range from 0.5 to 2.8 μg/L.[28] The goal of our study was to establish the levels of hydrazine in the environment during routine NPP operation.

MATERIALS AND METHODS

Reagents and Calibration Standards

All chemicals were of the highest purity available and were used without further purification. Hydrochloric acid (Optima grade) and potassium hydrogen phosphate were obtained from Fisher Scientific. Acetone, methane sulfonic acid, hydrazine mono-hydrochloride, ethanol amine and morpholine were obtained from Sigma-Aldrich. Ammonium hydroxide (25 %) was obtained from Fluka Analytical.

Millipore® water with resistivity greater than 18 MΩ/cm was used for preparing all standard solutions and also for the mobile phase for chromatography analysis.

Hydrazine standards were prepared by dissolving hydrazine mono-hydrochloride in Millipore® water and adding HCl to a concentration of 10 mmol/L as a preservative.

Hydrazine Stability

We used Rideau River water to study hydrazine stability under different conditions of sample preservation. The conditions were chosen to simulate realistic scenarios in environmental sampling campaigns (Table 1).

We collected water samples in July 2013 from the Rideau River in Ottawa, Canada, as typical for natural fresh water samples. The grab samples (4 L) were collected from the surface of the river.

Elemental analysis of Rideau River water sample was performed by the Inductive Coupled Plasma Mass Spectrometry (ICP-MS) using Agilent 7700x spectrometer to determine the concentration of metals which may catalyze oxidation of hydrazine. The concentrations of Cu (0.9 ± 0.5 μg/L) and Fe (24 ± 2 μg/L) were determined to be too low to affect hydrazine decomposition (for concentration dependence of Cu-catalyzed hydrazine decomposition consult [9]). The pH of the river water was measured to be 7.8. The river water was not filtered or otherwise treated before preparing the solutions for analysis.

A 500 mL river water sample at room temperature (22 ^{o}C) was spiked with the hydrazine standard. Subsamples were taken at desired time intervals and immediately acidified with HCl to a final concentration of 10 mmol/L to prevent further decomposition of hydrazine.

Table 1. Sample preservation conditions

Preservative	**Conditions**
No preservative	Under the fluorescent light at room temperature (22 ^{o}C).
Refrigeration	In the refrigerator (5 ± 1 ^{o}C) immediately after spiking with hydrazine.
Ice	In a plastic cooler filled with ice.
HCl	Acidified to a 10 mmol/L HCl, under the fluorescent light at room temperature (22 ^{o}C).

Liquid Chromatography

An Agilent 1260 Infinity® (Bio-inert) Liquid Chromatograph (LC) was used for ion chromatography. It was controlled by ChemStation software. We used a sample injection volume of 100 µL, column temperature of 20 °C, and isocratic elution for quantitative work. While developing the optimal composition of the mobile phase, we used the quaternary pump to mix aqueous and organic phases in desired proportions or to make desired dilutions. When the optimal composition of the mobile phase was determined, the LC was used in an isocratic mode drawing from a single mobile phase reservoir. The mobile phase was constantly purged with nitrogen to avoid oxidation of hydrazine by dissolved oxygen during chromatography.

In an attempt to increase sensitivity of the detection and reduce peak tailing, we added acetonitrile and methanol to the aqueous mobile phase. For concentrations of organic solvent ranging from 5 to 40 % we have not seen any improvement in either the sensitivity or the peak shape.

A Metrohm 896 Professional Detector was controlled by MagIC Net™ software. The working, reference, and auxiliary electrodes were glassy carbon, palladium, and steel, respectively. The amperometric cell volume was adjusted by using a 0.025 mm spacer.

In each run, the recovery of hydrazine from a quality control sample, which was a river water sample spiked with hydrazine to 10 µg/L and preserved with HCl, was checked after every 5 samples. To prevent deterioration of the sensitivity, the working electrode was cleaned by Al_2O_3 slurry after every 50 runs.

Sampling at NPPs in Ontario

Water samples were taken on Lake Huron in August 2014 and on Lake Ontario in October 2014 (for locations of the Ontario NPPs see Fig. 1). Sampling stations were selected along transects within the plume of the CCW discharge points at Bruce, Pickering and Darlington NPPs (Fig. 2A-C). The sampling stations were spaced approximately 100 m apart. Ambient (reference) stations were chosen in areas least likely to be affected by discharge plumes. Ambient (reference) stations for Pickering and Darlington NPPs were located approximately 2 km away from the CCW discharge. The ambient station for Bruce NPP was located further away (~18 km) at an Environment Canada routine monitoring station (Station 29).

Conductivity, pH, temperature and dissolved oxygen were measured at each sampling station (the complete data sets for each sampling location are given in the Supplementary material). Water samples were collected at each station approximately 0.5 m below the surface. Water samples were also taken 1 m below the surface, 1 m above the lake bottom and at the mid-point of the water column using a Niskin Bottle water sampler at two locations per NPP. True split duplicate field samples were also taken every third sampling station to verify laboratory precision. One field blank and cooler blank were prepared with Millipore® water for each NPP. All water samples were collected in Nalgene bottles and preserved with 10 mM HCl.

In addition to field sampling, water samples were collected within each NPP to determine the concentrations of hydrazine originating from the respective facility. Samples were taken from boiler feed water (BFW) and CCW from an appropriate sampling faucet, then transferred into a 1 L Nalgene bottle containing 10 mL of 1.0 mol/L HCl to preserve hydrazine.

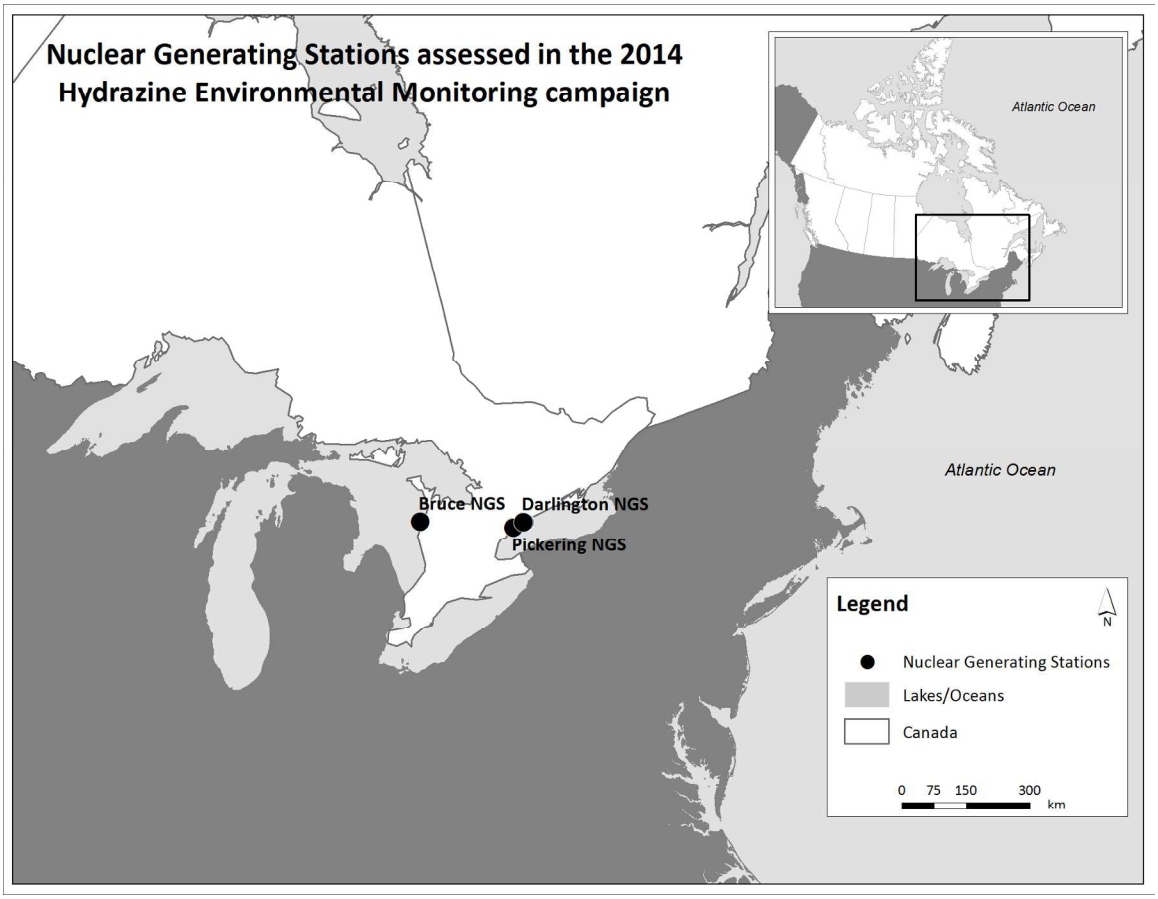

Figure 1. Map showing the locations of the three nuclear generating stations in Ontario, Canada where the sampling was conducted.

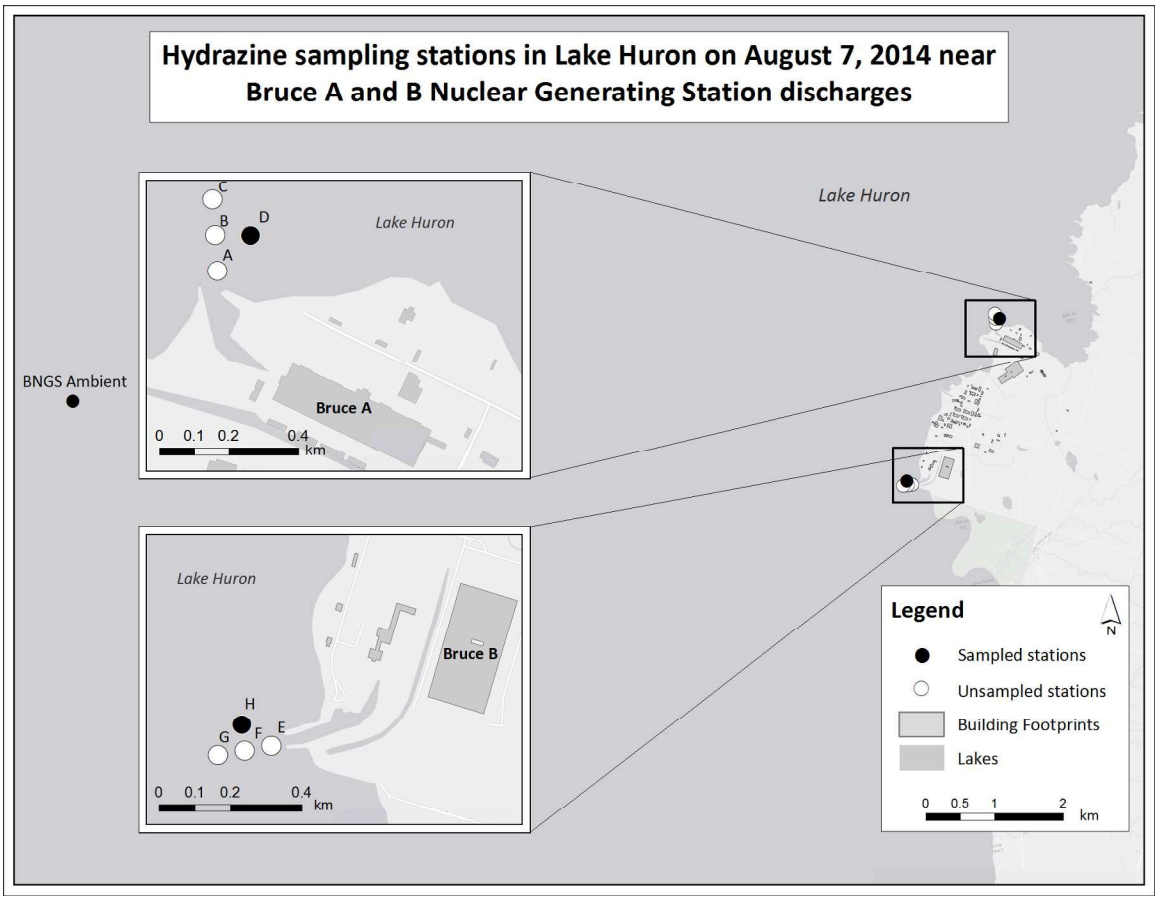

Figure 2A. Map of hydrazine sampling locations near Bruce NPP.

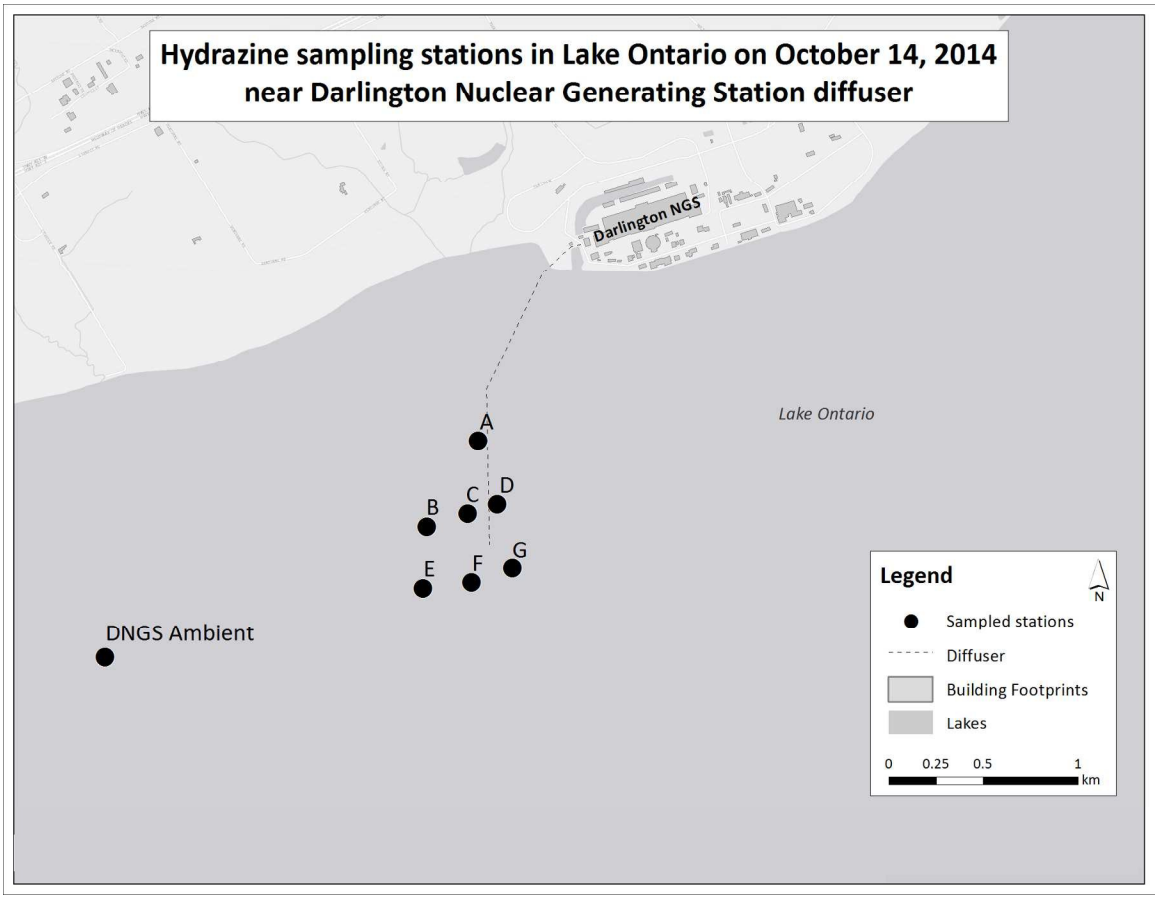

Figure 2B. Map of hydrazine sampling locations near Darlington NPP.

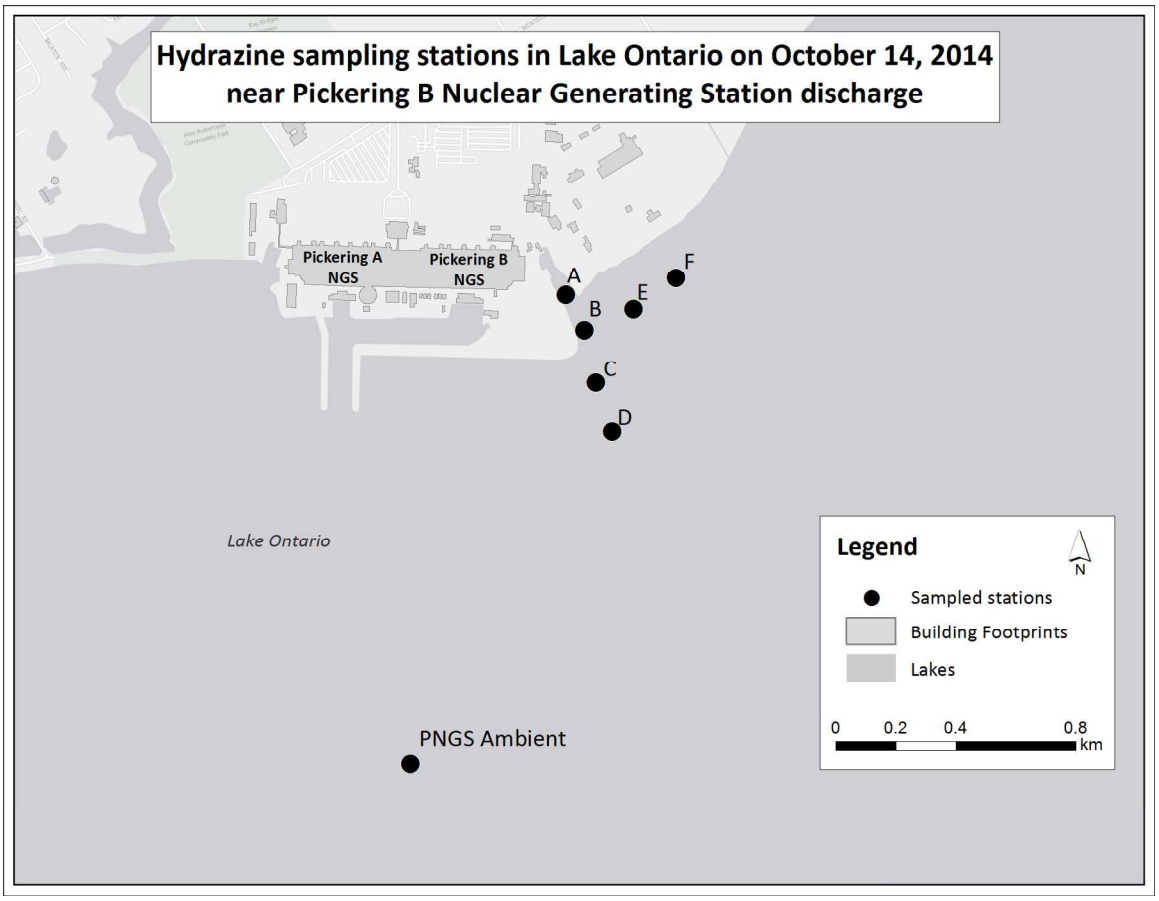

Figure 2C. Map of hydrazine sampling locations near Pickering NPP.

RESULTS AND DISCUSSION

Method Development and Validation

We initially attempted to improve upon the method published by Metrohm[24] to selectively and sensitively detect and measure hydrazine in environmental samples. It is known that hydrazine reacts with acetone to form acetone hydrazone, as follows:

$$2(CH_3)_2C{=}O + H_2N\text{-}NH_2 \longrightarrow (CH_3)_2C{=}N\text{-}N{=}C(CH_3)_2 + 2H_2O$$

Given that this reaction is likely quantitative under chromatographic conditions, it was acetone hydrazone which was separated and detected as hydrazine.

Figure 3 shows the hydrazone peak (3 mg/L) at 8.44 min. It is well separated from potential interferences, such as 400 mg/L ammonia (which appears at 4.64 min), 400 mg/L ethanolamine (6.73 min) and 400 mg/L morpholine (7.42 min). Notably, the selectivity of hydrazine detection (as acetone hydrazone) is several orders of magnitude higher than that of the interferences. However, the LOQ of approximately 10 μg/L, is inadequate for desired environmental monitoring, despite high working potential of 1.3 V (maximum allowable potential for the amperometric cell). It is noteworthy that the increase in the hydrazine signal with the working potential does not reach the plateau at 1.3 V in the acidic media. This is in agreement with the well-known redox properties of hydrazine, with high oxidation potential in acidic (well above 1.0 V) and much lower oxidation potentials in neutral and alkaline media.[9]

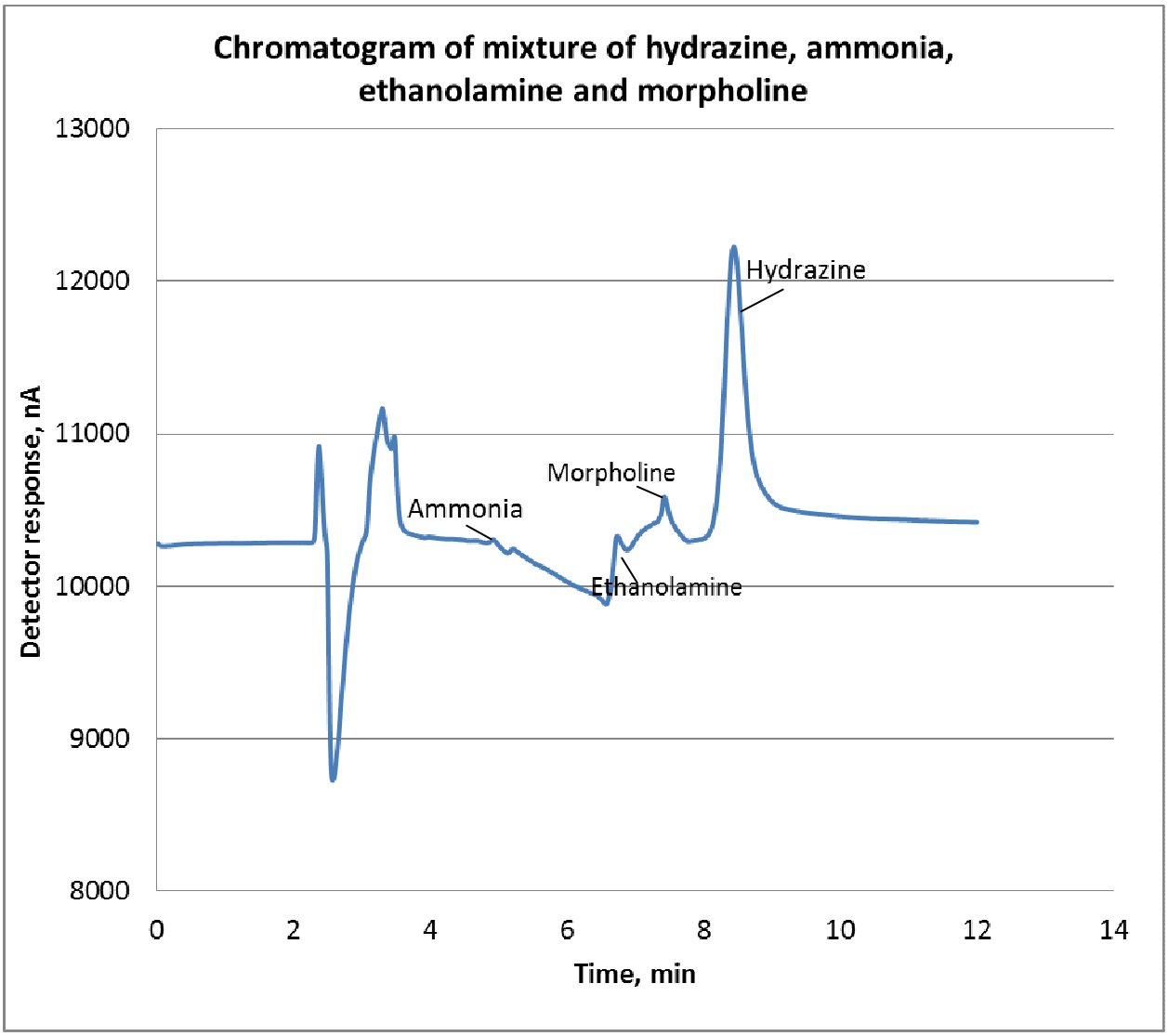

Figure 3. A chromatogram of 3 mg/L hydrazine, 400 mg/L ammonia, 400 mg/L ethanolamine and 400 mg/L morpholine. Column: Metrohm C4-250; Mobile phase: 20 % Acetone in 2 mmol/L methanesulfonic acid at a flow rate of 1 mL/min. Amperometric detector in DC mode, E = 1.3 V.

To improve the sensitivity of detection, we investigated the use of a microbore strong cation ion exchange column, Agilent Zorbax 300-SCX®, with an aqueous phosphate buffer at pH 6.0. While further increase in the pH could have yielded even better sensitivity, it is detrimental to the column stability (manufacturer recommendation is ≤ pH 6.0). Optimal buffer concentration for determination of hydrazine was found to be 5 mmol/L. At higher concentrations hydrazine elutes earlier, e.g. at 10 mmol/L phosphate buffer, and is not adequately separated from the injection peak (retention time of hydrazine was ~ 4 min).

Optimal oxidation potential for sensitive determination of hydrazine was studied by injecting a 100 μg/L hydrazine standard, while increasing working electrode potential by 0.1 V stepwise from 0.5 to 1.0 V and measuring the peak area. The peak area increased up to 0.8 V and then remained unchanged at higher potentials. Consequently, the working electrode potential of 0.8 V was chosen for the highest sensitivity of hydrazine determination.

Figure 4 shows the chromatograms of hydrazine, ethanolamine, ammonia and morpholine. The separation of hydrazine (7.6 min) from ammonia (7.9 min) is not as efficient as under the more acidic conditions using the Metrohm Metrosep C-4 column (Fig. 3). Clearly, there is a significant overlap between the peaks corresponding to hydrazine and ammonia. However, the selectivity for detection of hydrazine remains high. The detection of ammonia, ethanolamine and morpholine are respectively ~40000, ~7200 and ~230 times less

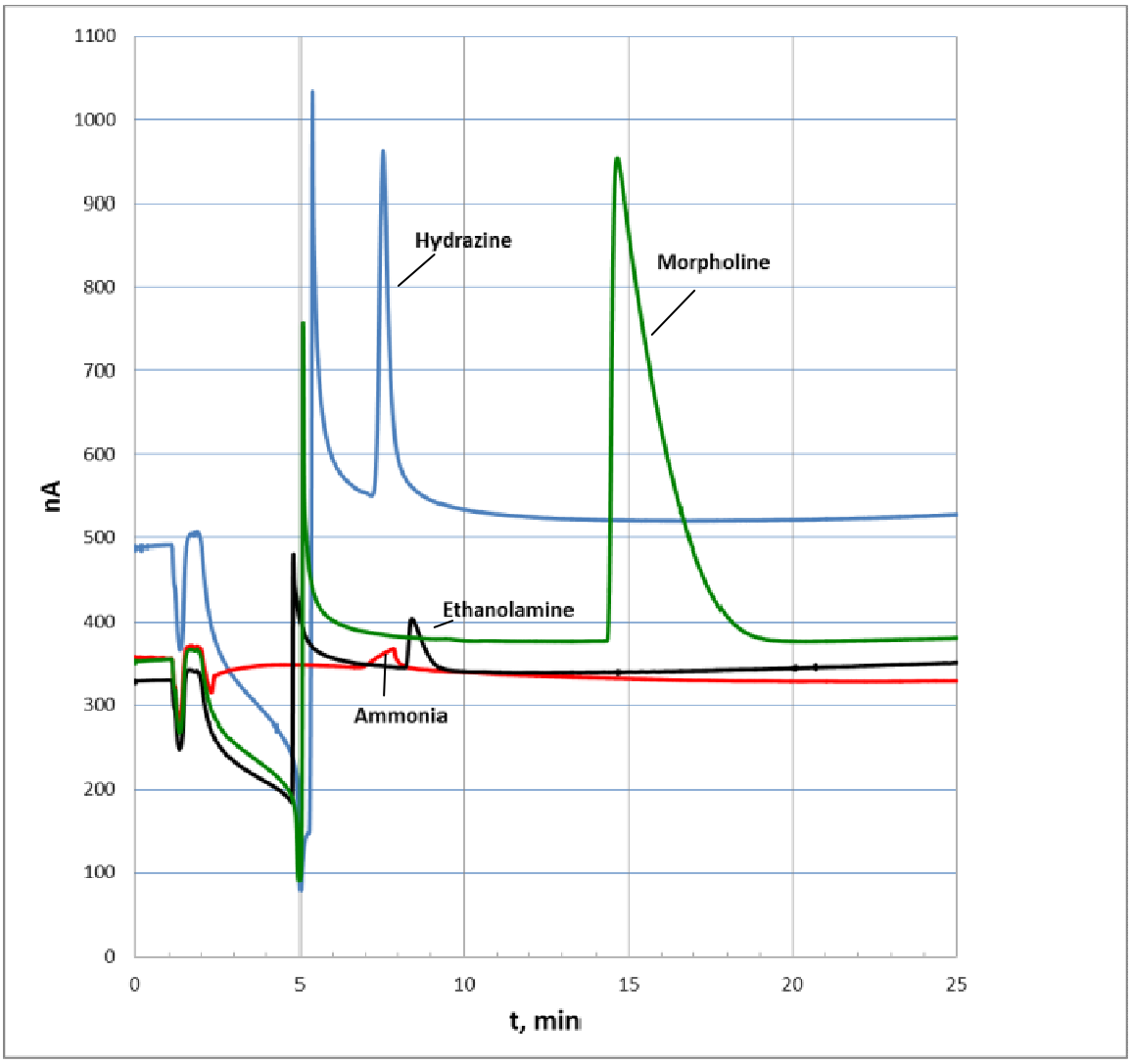

Figure 4. Chromatograms of 67 µg/L hydrazine (blue), 300 mg/L ammonia (red), 300 mg/L ethanolamine (black) and 300 mg/L morpholine (green). Column: Zorbax 300-SCX (150x2.1 mm) with a 300-SCX Guard Column (12.5x4.6 mm). Mobile phase: 5 mmol/L Phosphate buffer (pH 6.0); Flow rate: 0.5 mL/min; Amperometric detector in DC mode, E= 0.8 V.

sensitive than that of hydrazine. In order for ammonia to contribute to an error equivalent to 0.2 µg/L of hydrazine, the required concentration would be ~8000 µg/L (8 mg/L). In most cases, the average concentration of ammonia in environmental waters is less than 1 mg/L,[10] thus making its interference with hydrazine quantification negligible.

The calibration curve was found to be linear in the range from 0.1 to 200 μg/L of hydrazine in Millipore water. The regression analysis of the 82 data points from 12 calibration runs performed over a period of 6 months is presented in Figure 5. The regression line has 0 intercept. The slope of the regression line is 0.475 ± 0.008 (μg/L)/(nAxmin), where 0.008 is the standard deviation (SD) of the slope. The LOD was calculated as 3x SD of the slope, (i.e. 3 x 0.008) = 0.024 μg/L, and the LOQ as 10x SD of the slope (i.e. 10 x 0.008) = 0.08 μg/L, or ≤ 0.1 μg/L.

The method was validated by quantification of hydrazine in spiked river water samples preserved by HCl based on the calibration curve using hydrazine standards. The typical pH of the spiked river water samples was 2.35 ± 0.02 vs. 2.00 ± 0.02 measured in Millipore water. The recovery of hydrazine from river water samples measured over the period of 6 months (54 samples) was found to be 100 ± 10 %.

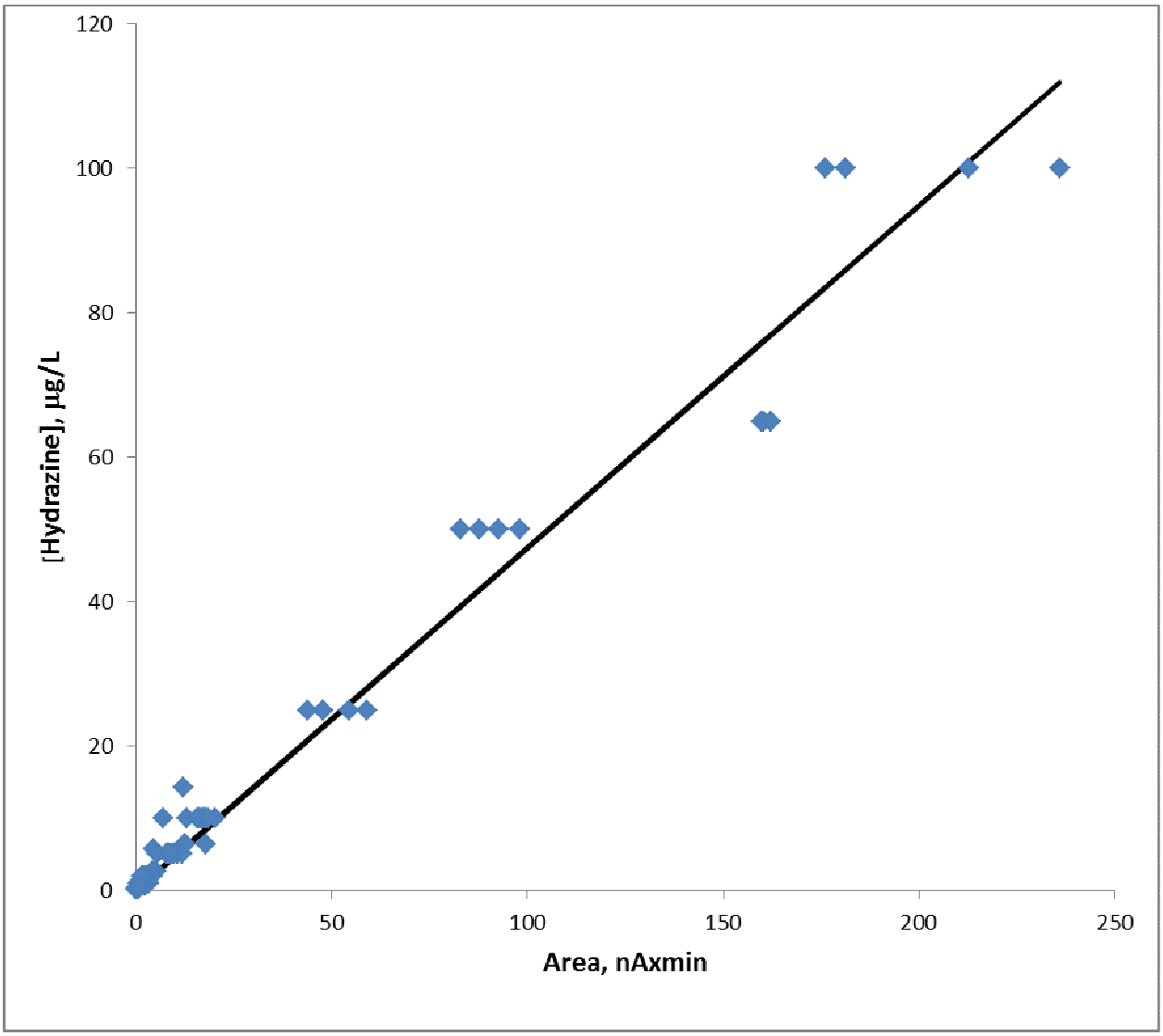

Figure 5. Regression analysis of the hydrazine calibration including 82 data points over the period of 6 months by using MS Excel. Multiple R= 0.989; R^2= 0.978; observations 82; slope= 0.475; standard deviation= 0.008**.**

Preservation of Environmental Water Samples

Hydrazine decomposes by redox processes under both aerobic and anaerobic conditions, yielding nitrogen, water, ammonia and hydrogen peroxide.[4,9,28] The rate of decomposition is increased by the presence of copper,[9] and is slowed down in acidic media.[9,17] In fact, the rate of decomposition in river water was slowed down to only 5-6 % of the initial concentration of hydrazine over a time period of two days by acidifying the sample with sulphuric acid to pH 1.[17]

To avoid the use of highly reactive and toxic sulphuric acid, we opted for hydrochloric acid. We first investigated the effects of varying concentrations of HCl on hydrazine stability. Rideau River samples spiked with 90 μg/L of hydrazine and acidified by HCl to final concentrations ranging from 2 to 10 mmol/L were monitored over 24 h (Fig. 6).

Hydrazine is almost completely depleted (>90 %) in an unpreserved water sample over 24 h (See Fig. 6; 0 mmol/L HCl). Addition of HCl to a final concentration of 2 mmol/L results in a marked decrease of the rate of hydrazine degradation. It appears that 5 mmol/L HCl is sufficient to preserve hydrazine in Rideau River water. However, for preservation of environmental samples containing higher concentrations of carbonates and/or having a high initial pH, we selected 10 mmol/L HCl.

To investigate stability of hydrazine in realistic sampling scenarios, we compared the concentration of hydrazine in Rideau River water samples left at room temperature with those preserved with HCl, refrigeration (5 ± 1 ^{o}C), and ice. The changes in the hydrazine concentration are presented in Figure 7.

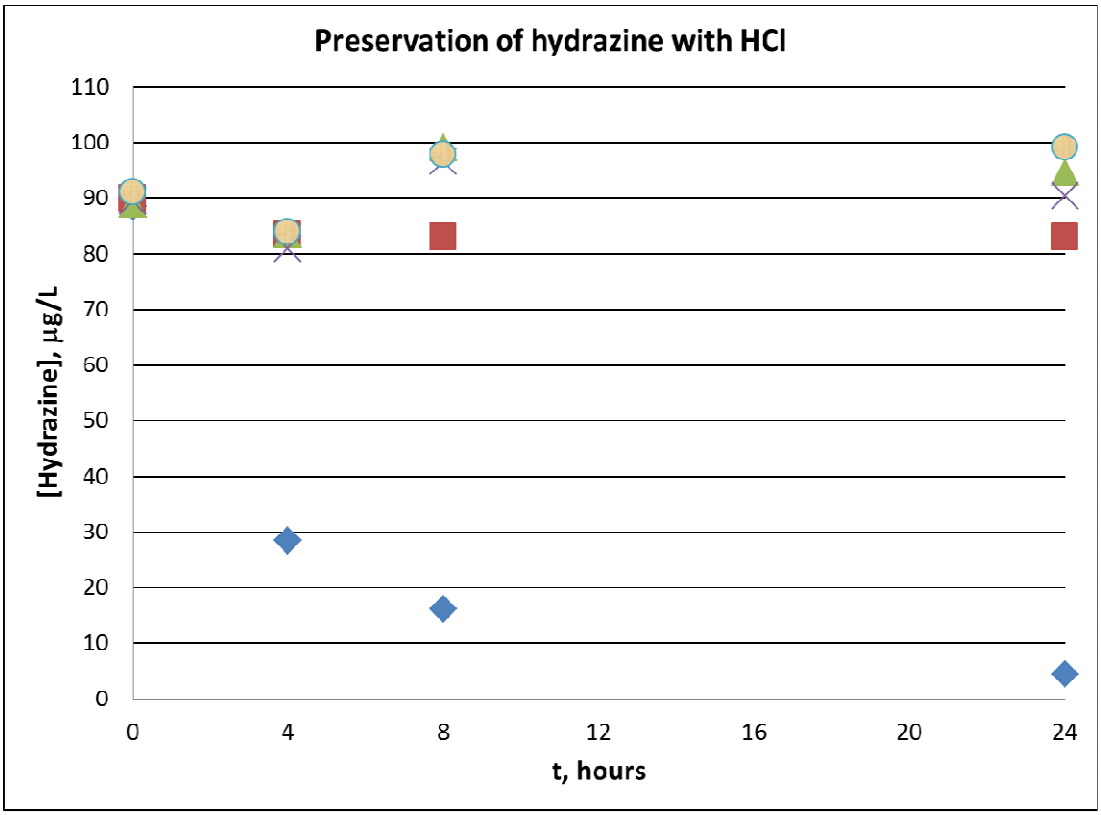

Figure 6. The effect of varying concentrations of HCl on hydrazine concentration in Rideau River water sample spiked with 90 µg/L hydrazine. ◆ – 0 mmol/L HCl; ■ - 2 mmol/L HCl; ▲ - 5 mmol/L HCl; **X** – 10 mmol/L HCl; ● - 20 mmol/L HCl.

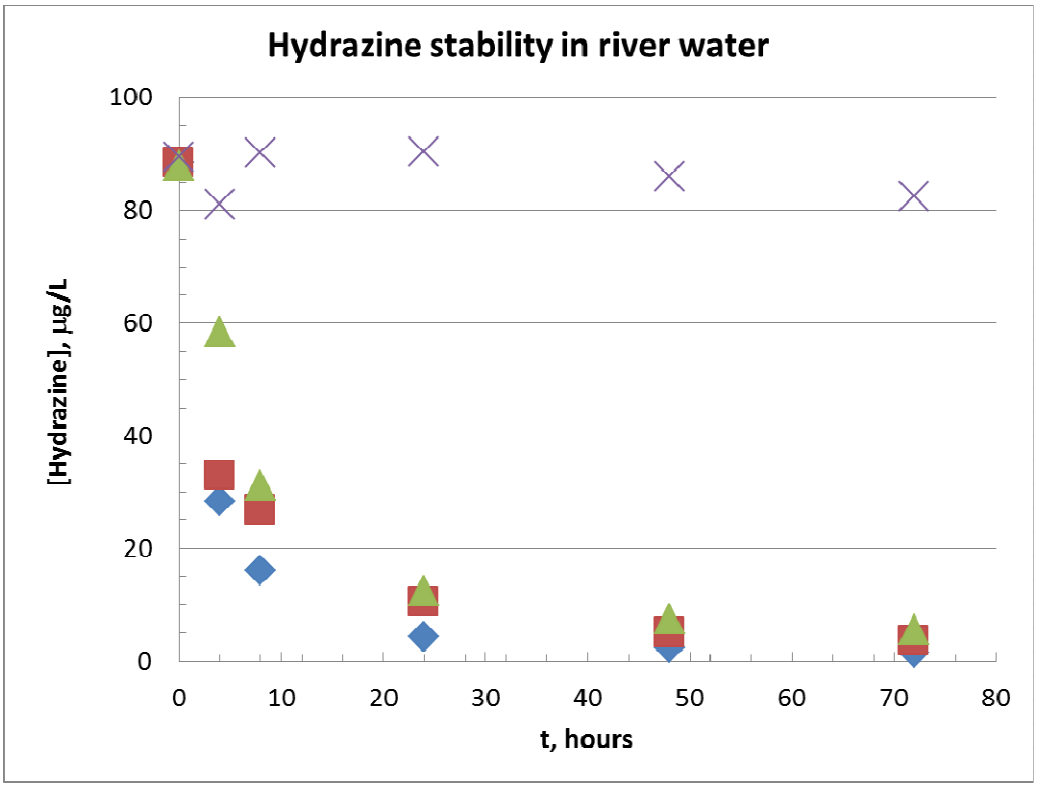

Figure 7. The effect of preservation by 10 mmol/L HCl, refrigeration, and ice on hydrazine stability in Rideau River water spiked with 90 µg/L hydrazine over a 3-day period. ◆ - non-preserved; ■ - refrigerated; ▲ - ice; X – 10 mmol/L HCl.

In unpreserved samples stored at room temperature of 22 ^{o}C, hydrazine was almost completely depleted within 24 h. For refrigerated samples, it takes several hours to cool from 22 ^{o}C to 5 ^{o}C (for a 0.5 L sample, the temperature at 4 h and 8 h after storage in the refrigerator was 8.7 ± 0.1 ^{o}C, and 7.0 ± 0.1 ^{o}C, respectively). With the ice preservation, the cooling of water sample is somewhat faster (temperature at 4 h and 8 h after storage was 6.1 ± 0.1 ^{o}C and 1.4 ± 0.1 ^{o}C, respectively), which results in better preservation of hydrazine over the first 24 h. While cooling the sample in refrigerator and in ice slows the degradation of hydrazine, almost complete depletion occurs within 72 h. These results unequivocally demonstrate that the use of 10 mmol/L HCl is superior to any other form of preservation (Fig. 7).

Hydrazine at NPPs in Ontario

The results of the analyses of the service water (BFW and CCW) samples from Bruce, Darlington and Pickering NPPs are summarized in Table 2. These results demonstrate that hydrazine concentration in the secondary loop of the heat transport system is within the expected operational range from 100 to 200 µg/kg.[33] Water samples taken concurrently at the CCW sampling points for each of the NPP units indicate levels of hydrazine at less than the limit of detection (<0.02 µg/L).

Table 2. Results of the measurements of hydrazine in NPP service water.

Bruce NPP	
Sample	[Hydrazine], µg/L, ± 10 %
BFW (Unit 7)	145
BFW (Unit 4)	147
CCW	<0.02
Darlington NPP	
BFW (Unit 1)	144
BFW (Unit 2)	134
BFW (Unit 3)	148
BFW (Unit 4)	158
CCW discharge duct (all units)	<0.02
Pickering NPP	
BFW (Unit 1)	167
BFW (Unit 4)	146
BFW (Unit 5)	164
BFW (Unit 6)	152
BFW (Unit 8)	131
Unit 1 CCW, Unit 4 CCW, Unit 058 CCW (common to units 5 to 8)	<0.02

To validate our analytical method, we used a standard addition for determination of hydrazine in the service water of the Bruce NPP. In short, the service water sample was first analysed to determine the hydrazine content using the calibration done with Millipore water standards. Based on that result, the sample was sub-sampled and the subsamples were spiked with appropriate concentrations of hydrazine to yield approximately 1.5, 2, and 3 times hydrazine in the non-spiked sample.

We measured <0.1 and 145 ± 5 μg/L by standard addition method in the CCW and BFW samples, respectively. These results are in agreement with the expected concentrations (~100 μg/L [1,2,33]), and were found to be reproducible over several months. The use of standard addition method in the CCW sample is illustrated in Figure 8.

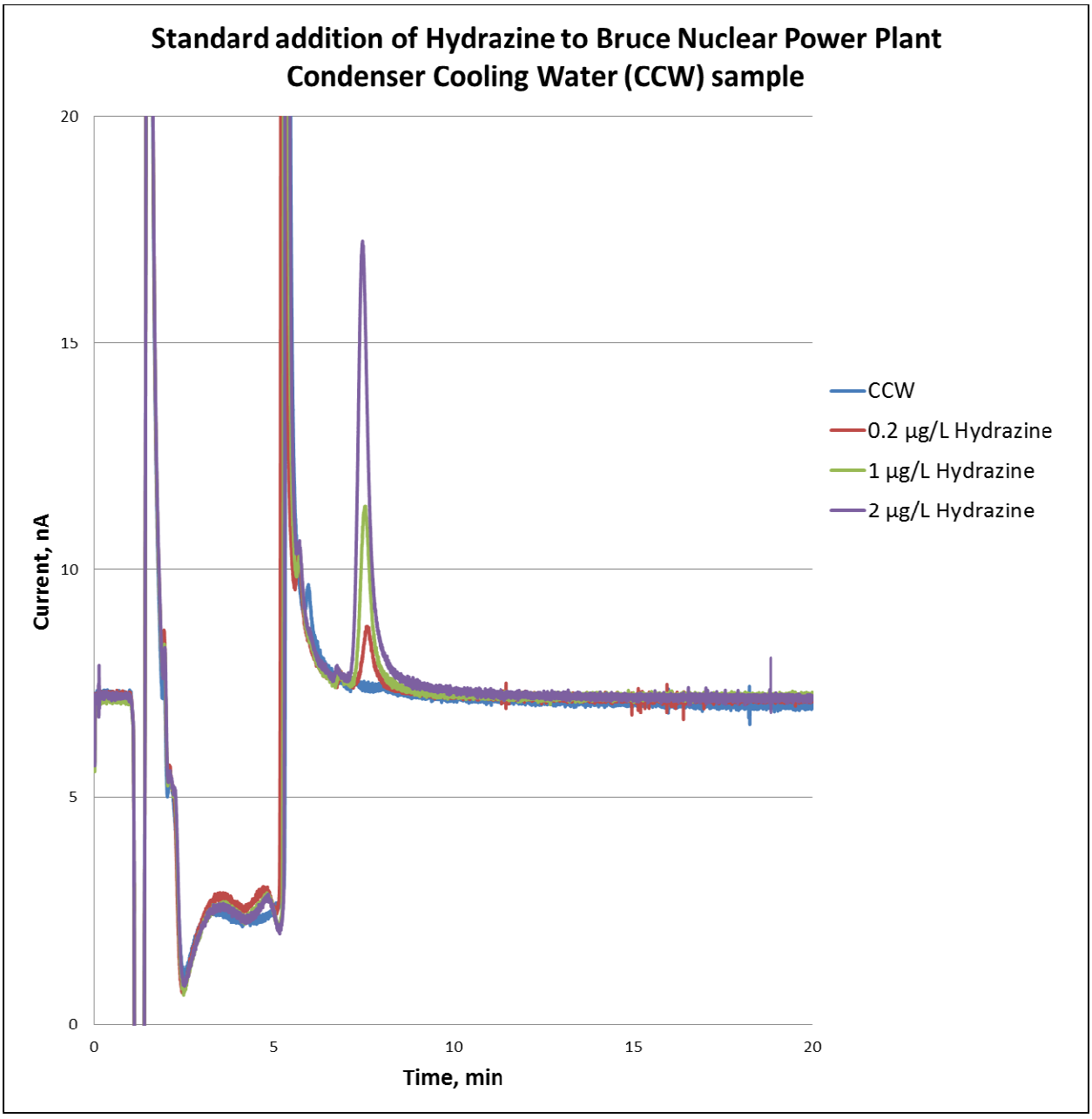

Figure 8. Standard addition method showing the chromatograms of CCW sample, with no hydrazine, and then spiked with 0.2, 1.0 and 2.0 µg/L hydrazine.

The value obtained by the standard addition method for the boiler feed water, 145 ± 5 µg/L, is similar to the 144 ± 14 µg/L from the direct measurement (Table 2). The slope of the linear fit of the standard addition method, 0.93, is very close to the expected value of 1.0, which

means negligible matrix effect. It should be noted that our method showed negligible matrix effects in vastly different matrices such as Millipore water, Rideau River water, BFW and CCW (lake water).

The measured concentrations of hydrazine in BFW represent partial inventory of hydrazine in operating NPPs. To assess the release of hydrazine from routine operation of NPPs, we measured the concentrations of hydrazine along the discharge channels of Bruce, Darlington and Pickering NPPs (Table 3). Only two of the eight proposed sampling stations at Bruce Power were actually sampled. The transects in line with each of the outfall channels at Bruce Power were not sampled due to safety concerns (Figure 2A).

Table 3. Measured concentrations of hydrazine near discharge channels of Ontario NPPs

Bruce NPP		
Sample	Depth	**$[Hydrazine]_m$, µg/L**
Site D	Surface, 1 m, 1 m duplicate, 2 m (bottom- 1m)	<0.02
Site H	Surface, 1m, 2 m (mid depth), 4 m (bottom -1 m)	<0.02
Ambient (reference) site	Surface	<0.02
Darlington NPP		
Site A	Surface	<0.02
Site B	Surface	<0.02
Site C	Surface, surface duplicate	<0.02
Site E	Surface	<0.02
Site F	Surface, 1 m, 6 m, 12 m	<0.02

Site G	Surface, 1 m, 6 m, 12 m	<0.02
Ambient (reference site)	Surface	<0.02
Pickering NPP		
Site A	Surface, 1 m, 3 m	<0.02
Site B	Surface	<0.02
Site C	Surface, surface duplicate	0.02
Site D	Surface	0.03
Site E	Surface	<0.02
Site F	Surface, 1 m	<0.02
Ambient (reference) site	Surface	<0.02

At the Ontario NPPs, hydrazine-treated water is released to the environment in variable amounts, either routinely or intermittently, for the maintenance of water quality in the heat transport system. However, there may be unintended releases (e.g. spills) during upset or abnormal conditions within the NPP which may result in a pulse release of hydrazine-treated water in the CCW. Such releases may be detectable for a short period of time in the vicinity of the facility.

For all NPPs, except Pickering NPP, the levels of hydrazine detected in lake water samples taken from the vicinity of the facilities were below limits of detection for hydrazine (see Table 3). Three lake water samples at two stations near Pickering NPP contained detectable, albeit extremely low concentrations of hydrazine. As noted above, concentrations of hydrazine in CCW water samples taken at Pickering NPP were below the limits of detection. This

inconsistency could be related to the different dates of sampling at the CCW effluent and lake water, and the timing of boiler blowdown releases. Our results demonstrate that measured concentrations of hydrazine in the CCW and in surface waters influenced by the NPPs are well below FEQG of 2.6 μg/L. We acknowledge that these results represent concentrations of hydrazine in lake water and service water at the time of sampling. However, given the known environmental fate of hydrazine, our results are likely to be representative of conditions in the vicinity of Ontario NPPs under routine operating conditions.

Conclusions

We have developed and validated a sensitive and selective method for hydrazine determination in environmental water samples using ion chromatography coupled with amperometric detection. The hydrazine LOQ is 0.1 μg/L. The uncertainty of hydrazine concentrations determined by our method is ±10 % in the concentration range from 0.1 to 200 μg/L.

Selectivity of the method is sufficient to compensate for possible interference of ammonia on hydrazine determination. The detection of ammonia, ethanolamine and morpholine is respectively ~40000, ~ 7200 and ~230 times less sensitive than hydrazine. Typical concentrations of ammonia in environmental waters are sufficiently low to preclude potential interference with quantification of hydrazine in environmental samples using this method.

For sample preservation, acidifying environmental water samples with HCl to a concentration of 10 mmol/L results in long term stability of hydrazine at μg/L concentrations.

The method was validated by taking samples and measuring the concentrations of hydrazine in Lake Huron and Lake Ontario as well as in BFW and CCW samples from Ontario NPPs. The measured concentrations of hydrazine in the CCW and in surface waters influenced by the NPPs, from <0.02 to

0.03 μg/L, are well below the Canadian Federal Environmental Quality Guideline of 2.6 μg/L. The concentrations of hydrazine measured in BFW samples from the three NPPs were in the range from 131 to167 μg/L, and represent the partial inventories of hydrazine in operating NPPs.

ACKNOWLEDGEMENTS

We acknowledge the contribution of Mr. Dan Roumbanis, senior engineer with the Energy and Transportation Directorate of Environment Canada, who provided invaluable information and advice regarding the FEQG for hydrazine and the proposed pollution prevention plan notice development under CEPA 1999 for our work.

We are deeply indebted to the Lake Ontario Management Unit of the Ontario Ministry of Natural Resources and Forestry (OMNRF) and the crew of the CCGS LIMNOS who enthusiastically offered vessel transportation and sampling support in Lake Ontario and Lake Huron, respectively.

We would like to thank Joyce Au and Susan Hollan-Hibbert of Environment Canada for the GIS mapping support.

Finally, we would like to thank the NPP operators, Bruce Power and Ontario Power Generation, for their assistance in enabling the sampling within the NPPs.

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In this study, we developed and validated a sensitive method for the determination of hydrazine in water samples using ion chromatography coupled with an amperometric detector (limit of detection (LOD) = 0.02 µg/L and limit of quantification (LOQ) = 0.1 µg/L).