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Analysis of Hydrazine in Drinking Water by Isotope Dilution Gas Chromatography/Tandem Mass Spectrometry with Derivatization and Liquid−Liquid Extraction

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A new isotope dilution gas chromatography/chemical ionization/tandem mass spectrometric method was developed for the analysis of carcinogenic hydrazine in drinking water. The sample preparation was performed by using the optimized derivatization and multiple liquid−liquid extraction techniques. Using the direct aqueous-phase derivatization with acetone, hydrazine and isotopically labeled hydrazine-$^{15}N_2$ used as the surrogate standard formed acetone azine and acetone azine-$^{15}N_2$, respectively. These derivatives were then extracted with dichloromethane. Prior to analysis using methanol as the chemical ionization reagent gas, the extract was dried with anhydrous sodium sulfate, concentrated through evaporation, and then fortified with isotopically labeled *N*-nitrosodimethylamine-d_6 used as the internal standard to quantify the extracted acetone azine-$^{15}N_2$. The extracted acetone azine was quantified against the extracted acetone azine-$^{15}N_2$. The isotope dilution standard calibration curve resulted in a linear regression correlation coefficient (*R*) of 0.999. The obtained method detection limit was 0.70 ng/L for hydrazine in reagent water samples, fortified at a concentration of 1.0 ng/L. For reagent water samples fortified at a concentration of 20.0 ng/L, the mean recoveries were 102% with a relative standard deviation of 13.7% for hydrazine and 106% with a relative standard deviation of 12.5% for hydrazine-$^{15}N_2$. Hydrazine at 0.5−2.6 ng/L was detected in 7 out of 13 chloraminated drinking water samples but was not detected in the rest of the chloraminated drinking water samples and the studied chlorinated drinking water sample.

Hydrazine is a highly reactive base and reducing agent, which has a wide range of industrial and military applications.[1,2] It is used in rocket and spacecraft fuels, for removal of halogens from wastewater, as an oxygen scavenger or corrosion inhibitor in water boilers, in the polymerization of urethane, and in the manufacture of textile dyes, agricultural chemicals, and pharmaceutical intermediates. Hydrazine is a hazardous substance.[3–7] Hydrazine inhalation for a long period of time has shown adverse effects to the lung, liver, spleen, and thyroid systems of animals.[5] Hydrazine is reported to be neurotoxic, hepatotoxic, and nephrotoxic in rodents.[6] In humans, exposure to hydrazine can damage the liver, kidney, and central nervous systems.[8,9] In the United States, hydrazine has not been regulated as a drinking water contaminant. However, it has been classified as a probable human carcinogen by the U.S. Environmental Protection Agency (EPA) and has a cancer risk level of 10^{-6} with an air concentration of 0.2 ng/m^3 and with a drinking water concentration of 10 ng/L.

Hydrazine drinking water contamination can originate from military and industrial wastes, wastewater treatment plant (WWTP) effluents, and possible formation in drinking water disinfection processes and distribution systems. Because hydrazine is often used for removal of halogens from wastewater treatment, it may enter drinking water sources that are impacted by wastewater or WWTP effluents. Particularly in recent years, reclaimed water has been increasingly used as part of drinking water sources through groundwater injection or surface water replenishment. Conventional chlorination techniques can result in the formation of various disinfectant byproduct (DBPs). Trihalomethanes (THMs) and haloacetic acids (HAAs) are two classes of drinking water DBPs currently regulated in the United States. The maximum contamination levels are 80 μg/L for total THMs and 60 μg/L for the HAAs.[10] Chloramination is an alternate disinfection technique that can be used to reduce the formation of THMs and HAAs. However, chloramination has been found to be increasingly associated with the formation of nitrogenous DBPs including

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N-nitrosodimethylamine (NDMA).[11] In addition, chloramination may also result in the formation of hydrazine that can be produced from the reaction of monochloramine with ammonia under certain conditions.[12–14] Because of its high health risks and potential formation as well as possible contamination in drinking water source supplies, it is very important to analyze hydrazine in drinking water, particularly in chloraminated drinking water.

Spectrophotometric or colorimetric determination was often used for the analysis of hydrazine. Colorimetric methods could provide a detection limit of submicrogram per liter to milligram per liter for treated wastewater and boiler feed waters as well as natural well waters.[15,16] However, sample matrices such as colors, turbidities, and coexisting aromatic amines could interfere with colorimetric determination. High-performance liquid chromatography (HPLC) with UV detection was also used to analyze hydrazine in sludge samples after it was derivatized to hydrazones with benzaldehyde, which provided a detection limit of 20 μg/L for hydrazine.[17] The derivatization HPLC/UV technique was used in the Occupational Safety and Health Administration (OSHA) methods for the analysis of hydrazine in air samples, which provided a detection limit of 0.058 parts per billion (0.076 $\mu g/m^3$).[18,19] Ion chromatography was also used for hydrazine analysis, which could separate hydrazine from monomethylhydrazine and 1,1-dimethylhydrazine and provided a detection limit of 2.2 mg/L for hydrazine.[20]

Gas chromatography (GC) was another technique used for hydrazine analysis.[21,22] Hydrazine was derivatized with acetone in an aqueous phase. The formed acetone azine had much lower solubility in water than hydrazine and could be extracted into a low-polarity organic solvent. A detection limit of 0.1 μg/L was obtained for the analysis of hydrazine in steam condensate, tap water, and distilled water. Combined with acetone derivatization and liquid−liquid extraction (LLE) techniques, GC coupled with chemical ionization (CI)/tandem mass spectrometry (MS/MS) was recently used for the analysis of hydrazine in drinking water and provided a method detection limit of 3.7 ng/L.[14]

The objective of this work was to develop a more sensitive and reliable isotope dilution GC/CI/MS/MS method combined with the optimized direct aqueous acetone derivatization and multiple LLE techniques. The method sensitivity, accuracy, and precision were investigated. Positive results were obtained for the chloraminated drinking water samples included in this work. The reported method could be used to analyze hydrazine at concentration levels of sub to low nanogram per liter, which was sufficiently sensitive for analyses and formation studies of hydrazine in drinking water.

EXPERIMENTAL SECTION

Standards and Reagents. Pure acetone azine (98%), hydrazine dihydrochloride (>99.99%), and isotopically labeled hydrazine-$^{15}N_2$ dihydrochloride (98%) standards were purchased from Sigma-Aldrich (St. Louis, MO). Isotopically labeled *N*-nitrosodimethylamine-d_6 (NDMA-d_6) and *N*-nitroso-di-*n*-propylamine-d_{14} (NDPA-d_{14}) were purchased from Restek (Bellefonte, PA). Ultra-Resi-analyzed grade dichloromethane was purchased from Mallinckrodt Baker (Phillipsburg, NJ). Optima grade acetone and methanol were purchased from Fisher Scientific (St. Louis, MO). Certified ACS grade sodium sulfite, anhydrous sodium sulfate, sodium hydroxide, and potassium phosphate monobasic were also obtained from Fisher Scientific.

NDMA-d_6 and NDPA-d_{14} were purchased as standard stock solutions at 1.0 mg/mL in dichloromethane. The standard stock solutions of hydrazine, hydrazine-$^{15}N_2$, and acetone azine were prepared at 1.0 mg/mL in methanol. The 4 N NaOH was prepared in reagent water and was extracted with dichloromethane to remove any impurities prior to use. NDMA-d_6 and NDPA-d_{14} were used as the internal standards (IS), which were fortified into the extracts after sample extraction. Hydrazine-$^{15}N_2$ was used as the surrogate standard (SS), which was fortified into the samples before derivatization.

Sample Collection and Storage. Drinking water samples were collected in 250-mL precleaned amber glass bottles containing 25 mg of Na_2SO_3. Na_2SO_3 was used to remove free chlorine or chloramines. The preserved samples were stored at 1−5 °C until derivatization and extraction.

GC/CI/MS/MS. GC/MS/MS analysis was performed on Varian 4000 GC/MS and Saturn 2200 GC/MS systems, which included a Varian 3800GC equipped with a Varian CP8400 autosampler (Walnut Creek, CA). The separation was performed on a Restek Rtx-5Sil MS capillary column (60 m × 0.25 mm i.d. × 1 μm film thickness). The GC temperature program was initially held at 35 °C, ramped to 100 °C at a rate of 15 °C/min and held for 5 min, ramped to 110 °C at a rate of 3 °C/min, ramped to 180 °C at a rate of 5 °C/min and held for 2 min, and then ramped to 220 °C at a rate of 50 °C/min and held for 1 min. Helium was used as the carrier gas at a constant flow of 1.1 mL/min. The GC injector was set to 150 °C. The 2-μL extracts or calibration standard solutions were injected onto the GC column in a splitless mode.

The MS/MS was operated in the CI mode using methanol as the CI reagent gas. The manifold temperature, trap temperature, and transfer line temperature were set to 40, 170, and 220 °C, respectively. The filament emission current was set to 40 μA. The optimized excitation amplitude was 0.4 V for hydrazine derivative (acetone azine), hydrazine-$^{15}N_2$ derivative (acetone azine-$^{15}N_2$), and NDMA-d_6 and 0.5 V for NDPA-d_{14}. The mass scan ranges were 41−83 Da for NDMA-d_6, 90−150 Da for NDPA-d_{14}, and 52−117 Da for acetone azine and acetone azine-$^{15}N_2$ with an isolation window of 2.0 Da for NDMA-d_6 and NDPA-d_{14}, and 3.0 Da for acetone azine and acetone azine-$^{15}N_2$. The precursor ion > product ion transitions used for quantitation were m/z 113 > 56 for acetone

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azine, m/z 115 > 57 for acetone azine-$^{15}N_2$, m/z 81 > 46 for NDMA-d_6, and m/z 145 > 97 for NDPA-d_{14}, respectively.

Acetone Derivatization. For the study on the effects of the amount of acetone on the derivatization efficiency of hydrazine, 0.3, 0.4, 0.5, and 0.6 mL of acetone were added into a series of 50-mL reagent water samples that contained 0.5 g of KH_2PO_4, and hydrazine at a concentration of 20 ng/L, which corresponded to 0.6, 0.8, 1.0, and 1.2% of the sample volume, respectively. KH_2PO_4 was used to maintain a sample pH value of ~5. The samples were shaken at room temperature for 30 min and then extracted with 2 mL of dichloromethane. After drying with anhydrous Na_2SO_4, the extracts were analyzed and the peak areas of m/z 56 ions resulting from the produced acetone azine were measured.

For the final optimized derivatization procedures, 25 mg of Na_2SO_3 and 2.5 g of KH_2PO_4 were also added into the 250-mL water sample. Na_2SO_3 was used for sample dechlorination. After Na_2SO_3 and KH_2PO_4 were dissolved, 10 μL of 0.5 μg/mL hydrazine-$^{15}N_2$ SS solution was fortified into the sample and mixed well. The 2.5 mL of acetone was then added and mixed into the sample for derivatization. The sample was held at room temperature for 30 min to complete the derivatization.

Liquid−Liquid Extraction. For the study on the effects of the sample pH value on the extraction efficiency of acetone azine, 250 mL of reagent water samples containing 2.5 g of KH_2PO_4, 20 g of Na_2SO_4, and 2.5 mL of acetone were fortified with pure acetone azine standard at 20 ng/L, which in turn corresponded to 5.7 ng/L hydrazine. Na_2SO_4 was used to adjust the ionic strength. For one set of extractions, the samples were extracted directly without adjusting the pH value of the samples. For the other set of extractions, the samples were extracted after adjusting the pH value to ~10 with 5.5−6 mL of 4 N NaOH. The samples were then extracted with one, two, and three times 20 mL of dichloromethane, respectively. After drying the extracts with anhydrous Na_2SO_4 and concentrating through evaporation, the extracts were then fortified with 10 μL of 50 μg/mL NDPA-d_{14} IS solution and diluted to 1.0 mL with dichloromethane prior to analysis. The extraction recoveries were measured by using an internal standard calibration curve resulting from a series of calibration standard solutions that were prepared directly from acetone azine without going through the extraction procedures and NDPA-d_{14} IS.

For the final optimized LLE procedures, after adjusting the ionic strength and pH value, the derivatized sample was extracted with 16 mL of dichloromethane for 6 min followed with 15-min phase separation. The same extraction procedures were repeated for two more times. The three extracts were then combined into a 60-mL vial. The combined extract was then dried by mixing with 12 g of anhydrous Na_2SO_4 for 30 min. After the combined extract was concentrated to ~5 mL using a Zymark TurboVap evaporator (Caliper Life Sciences, Hopkinton, MA), it was then transferred into a 15-mL conical tube and was continuously concentrated down to ~0.9 mL. The extract was transferred into a 1-mL volumetric flask, fortified with 10 μL of 5 μg/mL NDMA-d_6 IS solution, diluted to the 1.0-mL mark with dichloromethane, and then transferred into an amber autosampler vial. In to order to achieve the maximum removal of water from the extract, 0.4 g of anhydrous Na_2SO_4 was added into the autosampler vial and the resultant mixture placed in a freezer for a minimum of 6 hours. Finally, the extract was transferred into another amber glass autosampler vial before analysis.

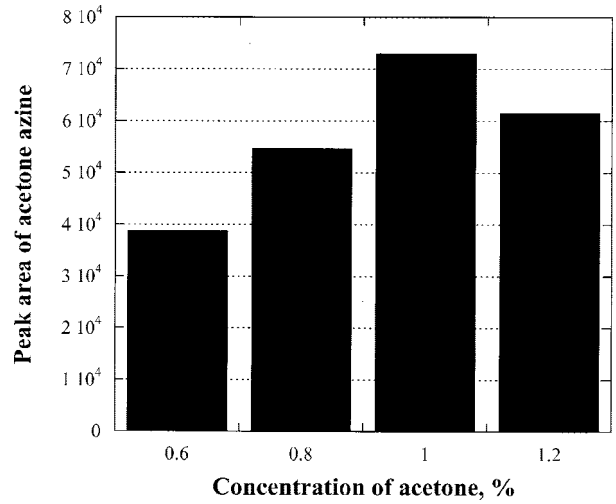

Figure 1. Effects of the amount of acetone on derivatization efficiency.

Calibration and Quantitation. The procedural calibration standard solutions were prepared by following the same optimized derivatization and LLE procedures as described above. Hydrazine and 10 μL of 0.5 μg/mL hydrazine-$^{15}N_2$ SS solution were added into a series of 250-mL reagent water samples containing 25 mg of Na_2SO_3, 2.5 g of KH_2PO_4, 20 g of Na_2SO_4, and 2.5 mL of acetone to give concentration levels of 0.5, 2, 5, 10, 20, and 40 ng/L for hydrazine and a constant concentration of 20 ng/L for hydrazine-$^{15}N_2$ SS. 10 μL of 5 μg/mL NDMA-d_6 IS solution was added into each extract after extraction to give a constant concentration of 200 ng/L.

The three types of calibrations investigated in this study included procedural external standard, internal standard, and isotope dilution standard calibrations. Peak areas were used for the measurement of the linear regression calibration curves measured with a $1/X$ weight for all calibrations. For hydrazine, the procedural isotope dilution standard calibration curve was used to quantitate the resulted acetone azine against the resulted acetone azine-$^{15}N_2$ SS, the procedural internal standard calibration curve was used to quantitate the resulted acetone azine against the NDMA-d_6 IS, and the procedural external standard calibration curve was used to quantitate the resulted acetone azine by using its peak area versus the concentration of hydrazine. In addition, the injection was evaluated by measuring the recoveries of NDMA-d_6 IS using an external standard calibration curve. Moreover, the resulted acetone azine-$^{15}N_2$ could be quantitated against the NDMA-d_6 IS. The recoveries of acetone azine-$^{15}N_2$ could be used to evaluate the derivatization and extraction efficiency of hydrazine, which subsequently reflected the method sensitivity.

RESULTS AND DISCUSSION

Derivatization and Liquid−Liquid Extraction. The effects of the amount of acetone on the derivatization efficiency of hydrazine were studied by measuring the peak areas of acetone azine resulting from the reagent water samples with varied sample-to-acetone volume ratios. As shown in Figure 1, the highest peak area of acetone azine was obtained from the reagent water sample

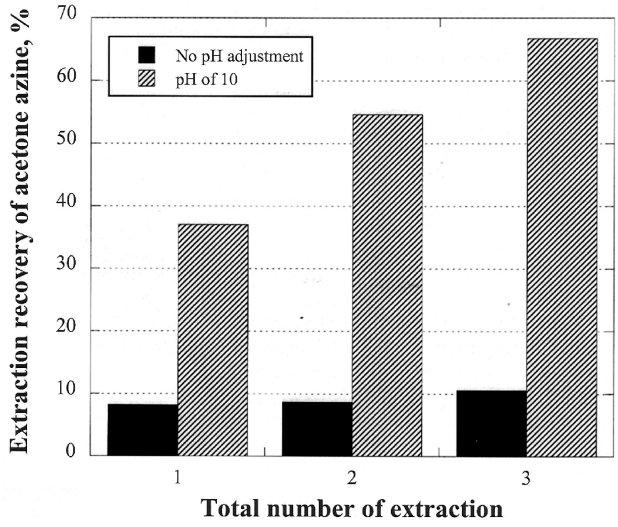

Figure 2. Effects of extraction times on the recoveries of acetone azine.

containing 0.5 mL or 1.0% acetone. Therefore, 2.5 mL of acetone was used for 250-mL samples in the following studies.

In the early development of LLE procedures, a series of 250-mL reagent water samples containing 2.5 g of KH_2PO_4, 2.5 mL of acetone, and varied amounts of Na_2SO_4 were fortified with acetone azine at 12 ng/L. The samples were extracted with 20 mL of dichloromethane for 2, 4, 6, 8, 10, 12, 14, and 16 min, respectively. The obtained recovery differences of acetone azine were not significant for the extractions using 20, 40, and 60 g of Na_2SO_4 with an extraction time of 2−16 min. Therefore, 20 g or 8% Na_2SO_4 and an extraction time of 6 min were used for the later development of LLE procedures, considering the potential difference in the ionic strength of sample matrixes.

Figure 2 shows the effects of sample pH values and multiple extractions on the recoveries of acetone azine. As shown in Figure 2, the multiple extractions without adjusting the sample pH value before extraction did not significantly increase the recoveries of acetone azine. The obtained absolute recoveries were 8.2, 8.7, and 10.6% for one, two, and three dichloromethane extractions, respectively. However, the recoveries of acetone azine were significantly increased after the sample pH was adjusted to ~10. The obtained absolute recoveries were 37.0, 54.6, and 66.7% for one, two, and three dichloromethane extractions, respectively. Therefore, the multiple LLE with a pH adjustment was included in the final optimized LLE procedures.

Calibrations. Hydrazine-$^{15}N_2$ was selected as the SS because the isotopically labeled nitrogen ($^{15}N_2$) would be retained in the final acetone azine structure, which would distinguish the precursor and product ion masses from those resulting from the hydrazine acetone derivative. In theory, the procedural isotope dilution using hydrazine-$^{15}N_2$, an isotopically labeled hydrazine analogue, could effectively compensate for the effects of matrix interferences, procedural performance variations on the derivatization, extraction efficiency, and precision of hydrazine, and instrument performance variations resulting from the injection, separation, and detection processes. However, hydrazine-$^{15}N_2$ was very expensive. Therefore, procedural external standard and internal standard calibrations were also evaluated in a concentration range of 0.5−40 ng/L for the measurement of hydrazine. As

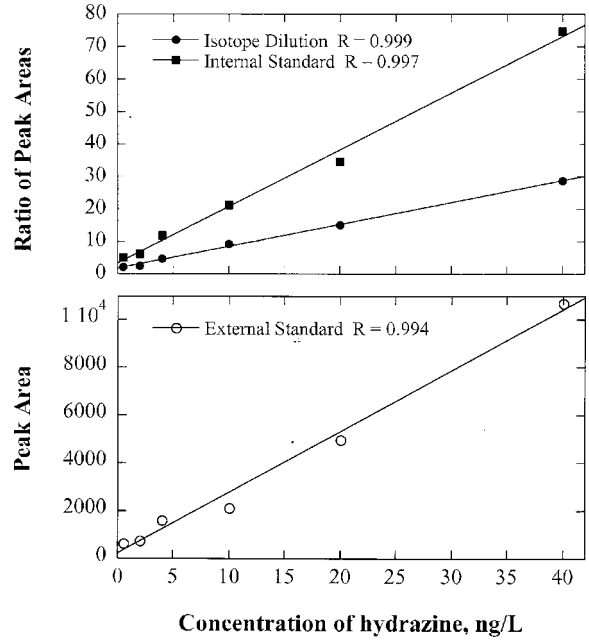

Figure 3. Procedural calibration curves of hydrazine with 250-mL sample extracted. Isotope dilution calibration, hydrazine-$^{15}N_2$ used as the SS; internal standard calibration, NDMA-d_6 used as the IS.

shown in Figure 3, all three procedural calibration curves were linear in the studied concentration range but the procedural isotope dilution standard calibration resulted in a slightly better linearity. The obtained linear regression correlation coefficients (R) were 0.999 for the procedural isotope dilution standard calibration, 0.997 for the internal standard calibration curve, and 0.994 for the external standard calibration curve, respectively. Therefore, the procedural isotope dilution standard calibration was used in the following studies on the demonstration of method sensitivity, accuracy, and precision and drinking water samples and as well as matrix effects.

Chromatograms. Figure 4 shows the GC/CI/MS/MS chromatograms resulting from the lowest calibration standard solution with at a concentration of 0.5 ng/L for hydrazine under the optimized sample preparation and instrumental conditions. As shown in Figure 4, sharp and symmetric peaks were obtained for the IS (NDMA-d_6), derivatized hydrazine, and derivatized hydrazine-$^{15}N_2$ SS. Their retention times were approximately 9.08, 12.37, and 12.37 min, respectively. The measured peak-to-peak signal-to-noise ratio (ptp S/N) was 320 for the acetone azine resulting from hydrazine at 0.5 ng/L.

Sensitivity, Precision, and Accuracy. Method sensitivity, accuracy, and precision were studied through the measurement of seven replicate fortified reagent water samples. The method detection limit (MDL) was measured from 3.14 times the standard deviation of the seven analyses (3.14 is the Student t value for the 99% confidence level with −1 degrees of freedom).[23] The accuracy was measured as the mean percent relative recovery. The precision was measured as the percent relative standard deviation (RSD).

As shown in Table 1, the obtained MDL of hydrazine was 0.70 ng/L for seven reagent water samples fortified at 1.0 ng/L. The

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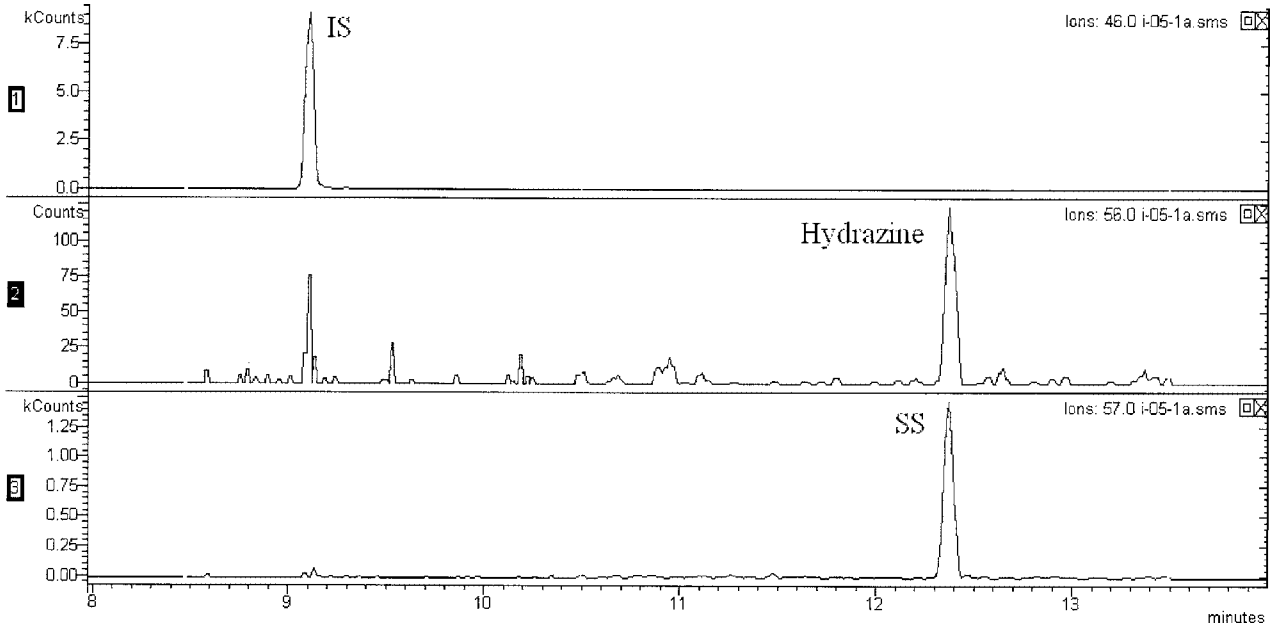

Figure 4. GC/CI/MS/MS chromatograms of selected quantitation ions. IS, *m*/*z* 46 ion resulting from NDMA-d_6 at 200 ng/L; hydrazine, *m*/*z* 56 ion of acetone azine resulting from hydrazine at 0.5 ng/L (*m*/*z* 56); and SS, *m*/*z* 57 ion of acetone azine-$^{15}N_2$ resulting from hydrazine-$^{15}N_2$ at 20 ng/L.

Table 1. Method Sensitivity, Precision, and Accuracy Based on Seven Replicate Fortified Reagent Water Samples

	fortified concentration (ng/L)	mean recovery (%)	RSD (%)	MDL (ng/L)
hydrazine	1.0	82	27.4	0.70
	20.0	102	13.7	na[a]
hydrazine-$^{15}N_2$	20.0	106	12.5	na

[a] na, not applicable.

mean relative recoveries were 102% with a RSD of 13.7% for hydrazine at a concentration of 20.0 ng/L and 106% with a RSD of 12.5% for hydrazine-$^{15}N_2$ at a concentration of 20.0 ng/L.

Drinking Water Analysis and Matrix Study. Fourteen drinking water samples from 6 different utilities were studied, which included one chlorinated drinking water sample and thirteen chloraminated drinking water samples. Three samples were selected and fortified with hydrazine at 20.0 ng/L in triplicate to study the matrix effects on recoveries and precision. As shown in Table 2, hydrazine was not detected above the lowest calibration point of 0.5 ng/L in the chlorinated drinking water and six chloraminated drinking water samples, but was detected in seven chloraminated drinking water samples at concentrations ranging from 0.5 to 2.6 ng/L. For the matrix spikes, the obtained mean recoveries varied from 118 to 132% with a RSD of 2.9 to 9.3%.

Table 2. Results of Drinking Water (DW) Samples and Matrix Studies[a]

DW sample	sample concentration (ng/L)	fortified concentration (ng/L)	mean recovery (%)	RSD (%)
chlorinated S1	<0.5	20.0	122	6.6
chloraminated S1	0.50	20.0	132	9.3
chloraminated S2	<0.5	na[b]	na	na
chloraminated S3	2.6	20.0	118	2.9
chloraminated S4	1.8	na	na	na
chloraminated S5	1.6	na	na	na
chloraminated S6	<0.5	na	na	na
chloraminated S7	0.86	na	na	na
chloraminated S8	0.90	na	na	na
chloraminated S9	<0.5	na	na	na
chloraminated S10	<0.5	na	na	na
chloraminated S11	0.73	na	na	na
chloraminated S12	<0.5	na	na	na
chloraminated S13	<0.5	na	na	na

[a] The mean recovery and RSD results were based on triplicate fortified DW samples. Chloraminated samples S1 and S2 were from the same utility. Chloraminated samples S3−S6 were from the same utility. Chloraminated samples S7−S10 were from the same utility. [b] na, not available.

CONCLUSIONS

This paper clearly demonstrated that the isotope dilution GC/CI/MS/MS method, combined with the optimized direct aqueous-phase acetone derivatization and multiple LLE techniques, provided good sensitivity, recoveries, and precision for the analysis of hydrazine in drinking water. The procedural isotope dilution calibration with good linearity could effectively compensate for matrix interferences and procedural performance variations. The reported method was successfully applied to drinking water samples. Hydrazine at sub to low nanogram per liter levels was detected in some chloraminated drinking water samples, which indicates that it is very important to further study the occurrence concentration levels and formation potential of hydrazine in chloraminated drinking water.

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