Analysis of N-Nitrosodimethylamine in Municipal Water Systems

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Abstract

N-Nitrosodimethylamine (NDMA) is a carcinogen formed during water treatment, especially with disinfection by chloramination. In this study we developed an extraction and analytical method that allows quantification of NDMA down to 0.6 ng/L. This method was used to detect NDMA in wastewater from treatment plants in western regions of the United States.

Introduction

NDMA is a chemical by-product of numerous industrial activities. It is also a disinfection by-product occurring mostly during disinfection of wastewater with chlorination or chloramination. Its formation can also occur when natural organic matter (NOM) or amine-based pharmaceuticals react with chloramine. NDMA's presence in municipal water systems is of concern because it is a known carcinogen, especially toxic to the liver, and therefore represents a threat for human health, particularly in drinking water.

While NDMA levels in municipal water systems are not currently regulated, this chemical is classified as a contaminant of emerging concern; it is in a group of chemicals that numerous states and even the Environmental Protection Agency (EPA) are interested in controlling in the near future. In order to develop a regulation for this compound there needs to be detection limits for NDMA that are robust enough to be implemented in samples from municipal water systems.

In this work, we developed an extraction procedure based on solid phase extraction to concentrate the nitrosamines in different types of water samples. For the analysis of these extracted samples, we created a sensitive analytical method for the measurement of NDMA using Gas Chromatography coupled with tandem mass spectrometry (GC-MS). This method allowed the successful measurement of NDMA in water samples with a quantification limit of 0.6 ppt (0.6 ng/L).

Material and Methods

- Sampling Campaign
  - Water samples from West Coast of the United States
  - Samples collected from October to December 2012
  - Samples shipped overnight on ice

- Sample Preparation
  - 500 mL water samples spiked with isotopically labeled NDMA

- Sample Extraction
  - Solid phase extraction conducted on Dionex AutoTrace 280
  - Extraction columns conditioned with dichloromethane, methanol, and HPLC grade water
  - Extracted NDMA eluted with 9mL DCM
  - Elute dehydrated with Sodium Sulfate Anhydrous
  - Samples concentrated to 1 mL under a gentle stream of nitrogen
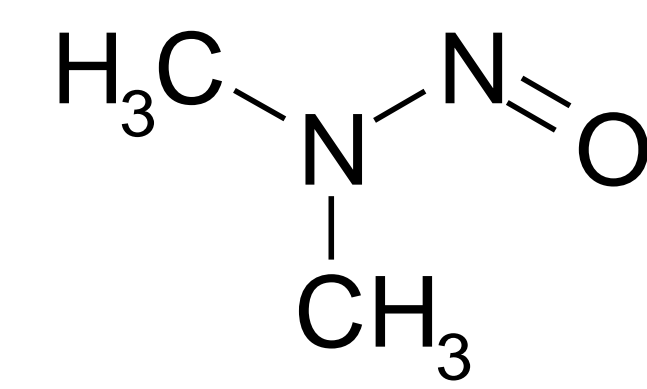
Molecular structure of NDMA
MW: 74.08 g/mol
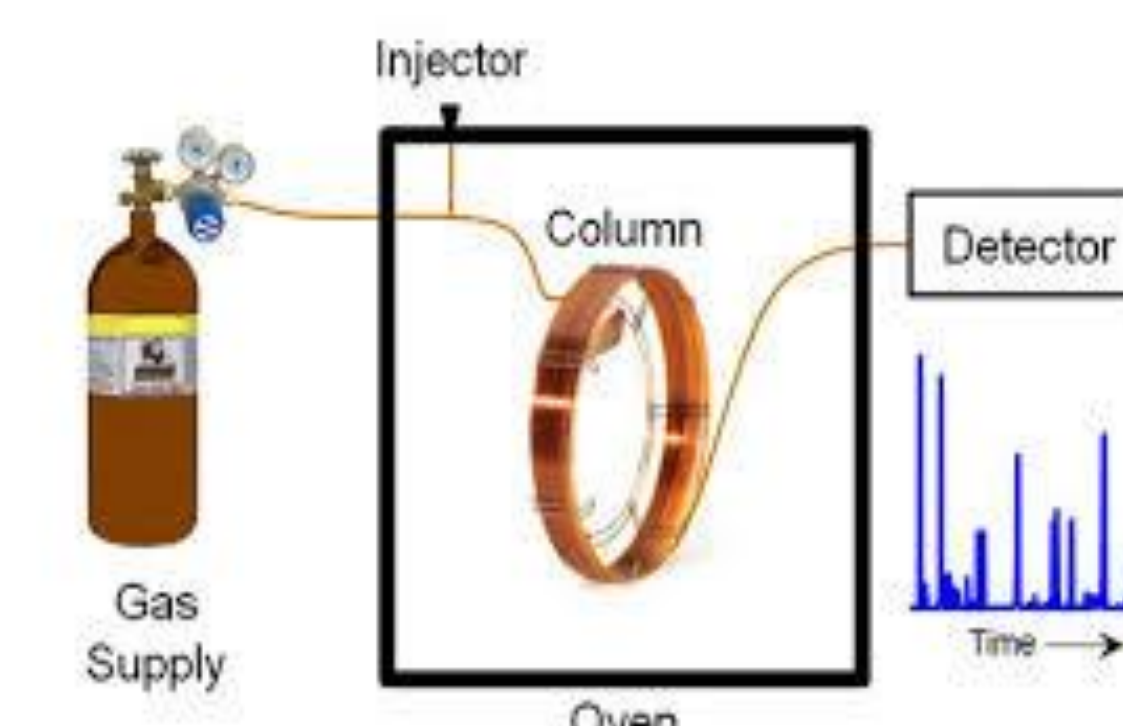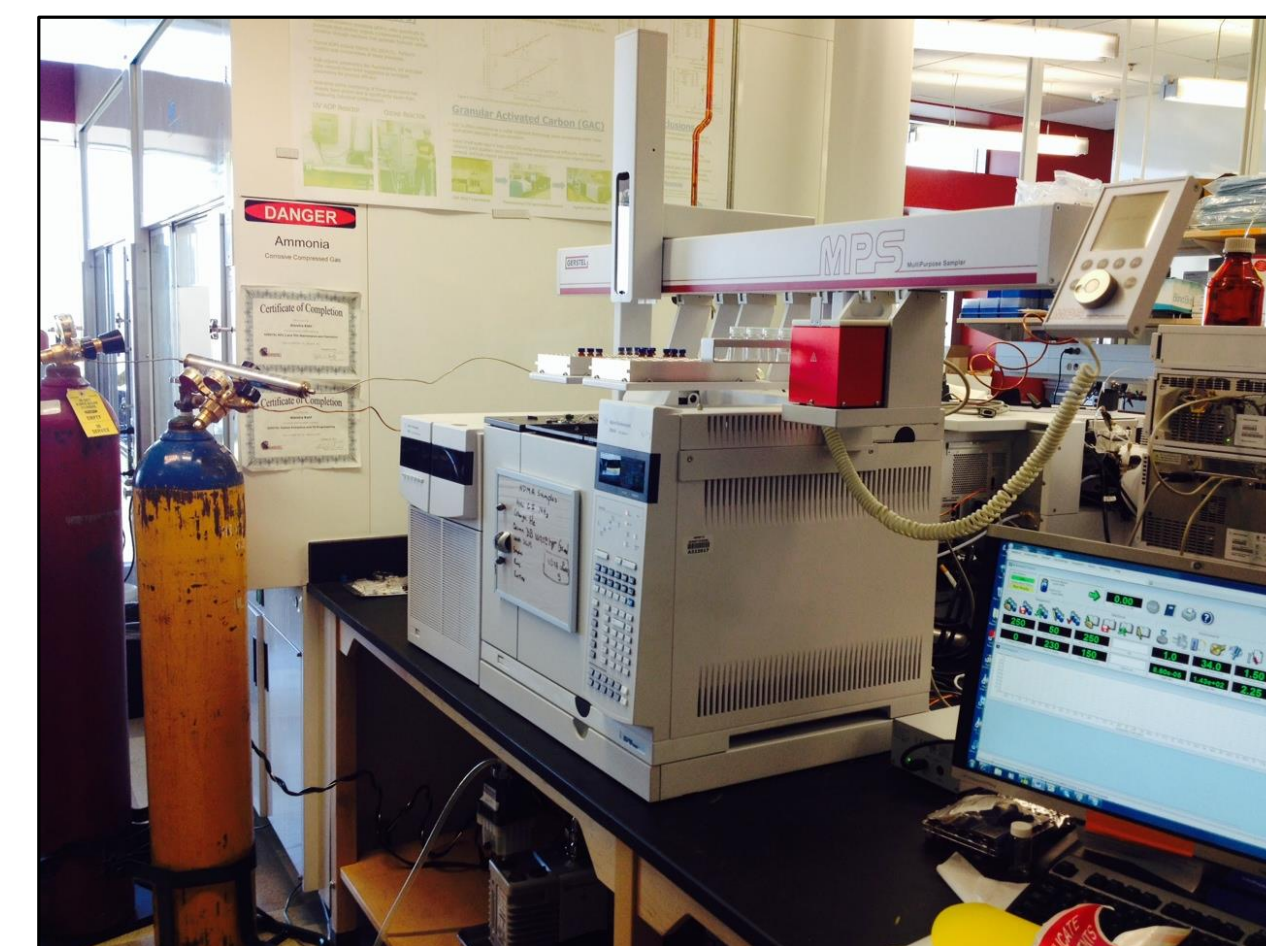
1 in 1,000,000 cancer risk from water at 0.7 ng/L

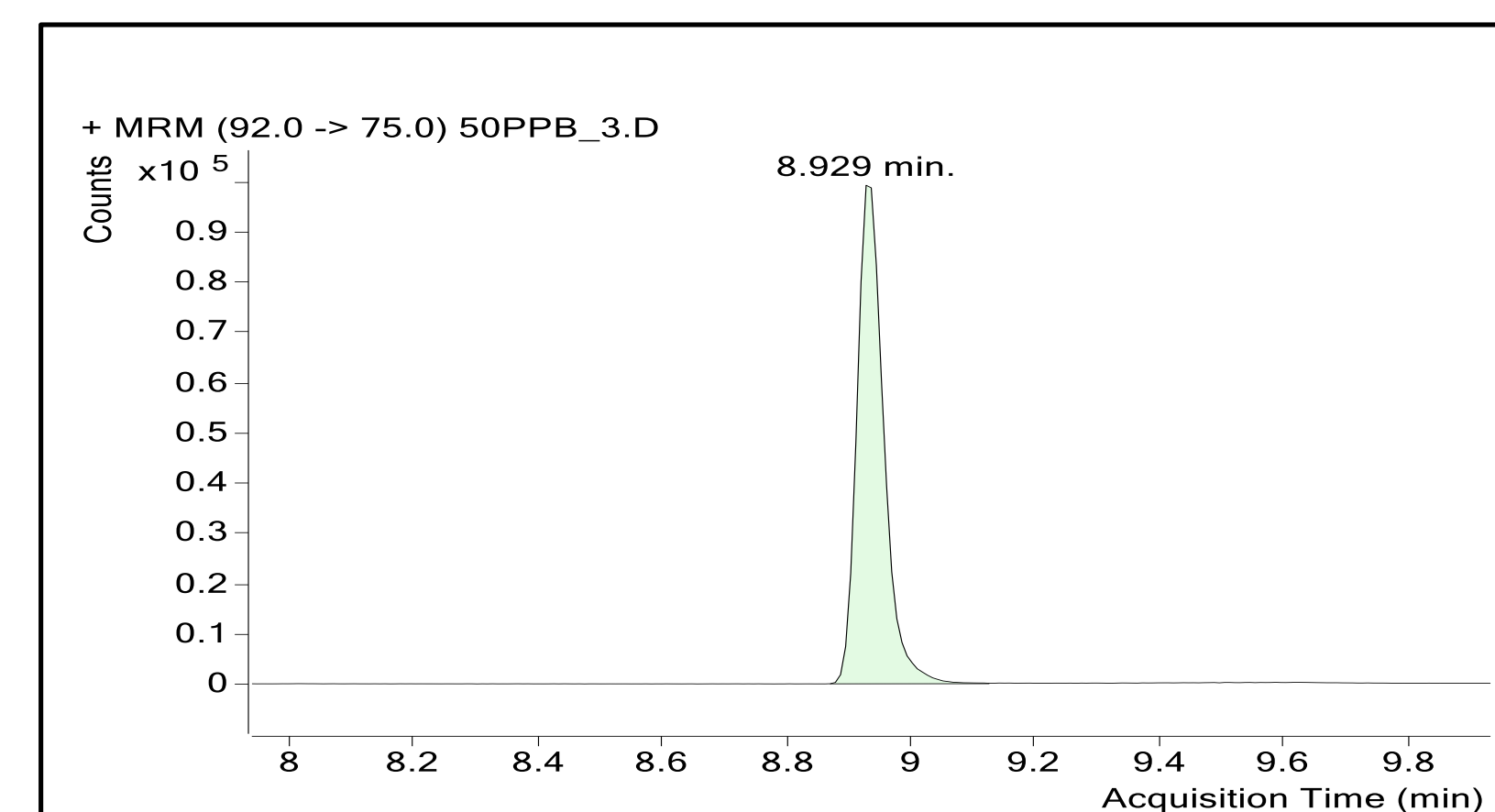Figure 1: Basic setup of the GC/MS. (Image taken from Agilent.com)

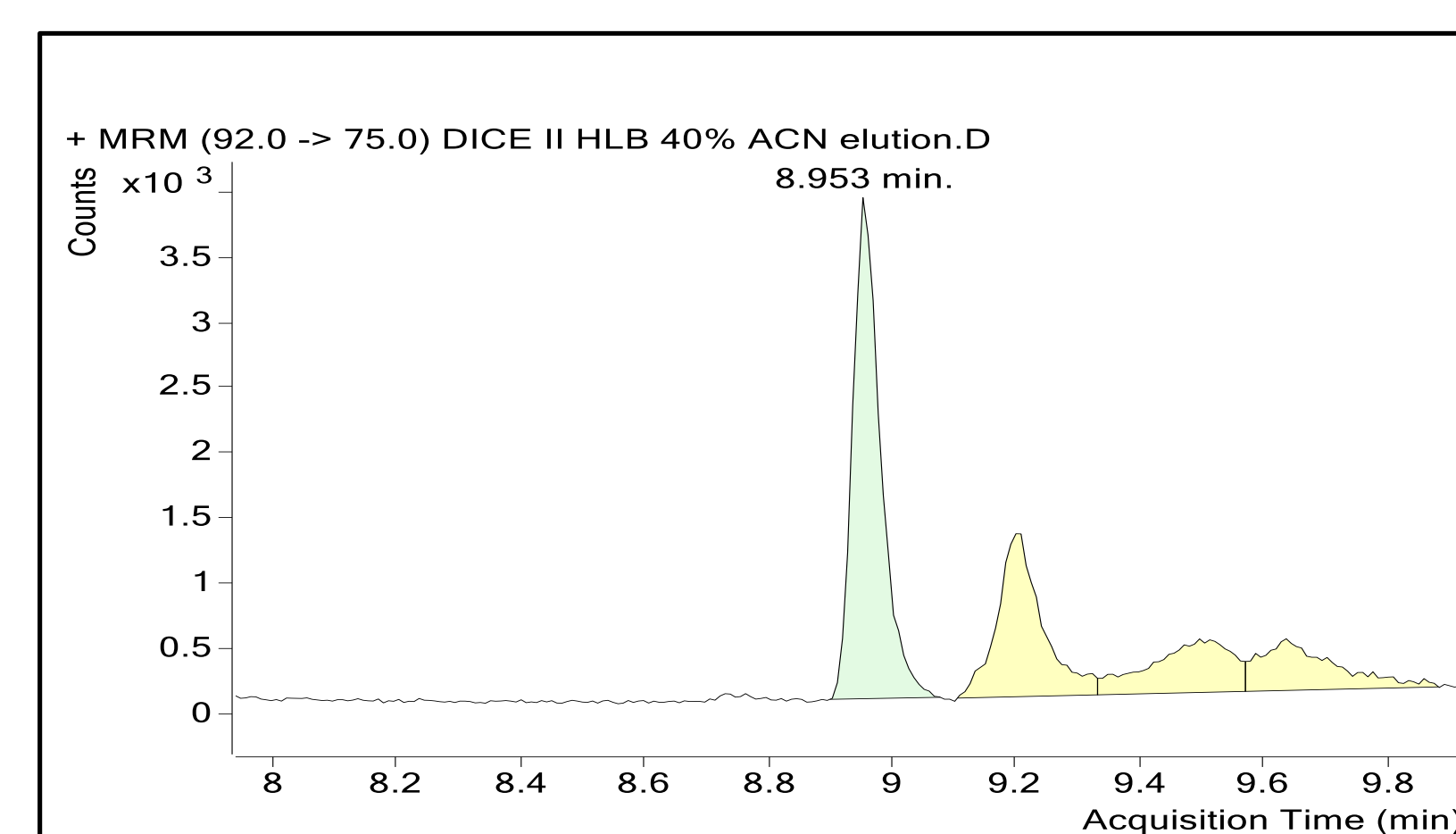Figure 2: The chromatogram of the 50 ppb (50 ug/L) calibration standard of NDMA.

+ MRM (92.0 -> 75.0) 50PPB_3.D
8.929 min.

Figure 3: Chromatogram of NDMA transition in a water sample.

+ MRM (92.0 -> 75.0) DICE II HLB 40% ACN elution.D
8.953 min.
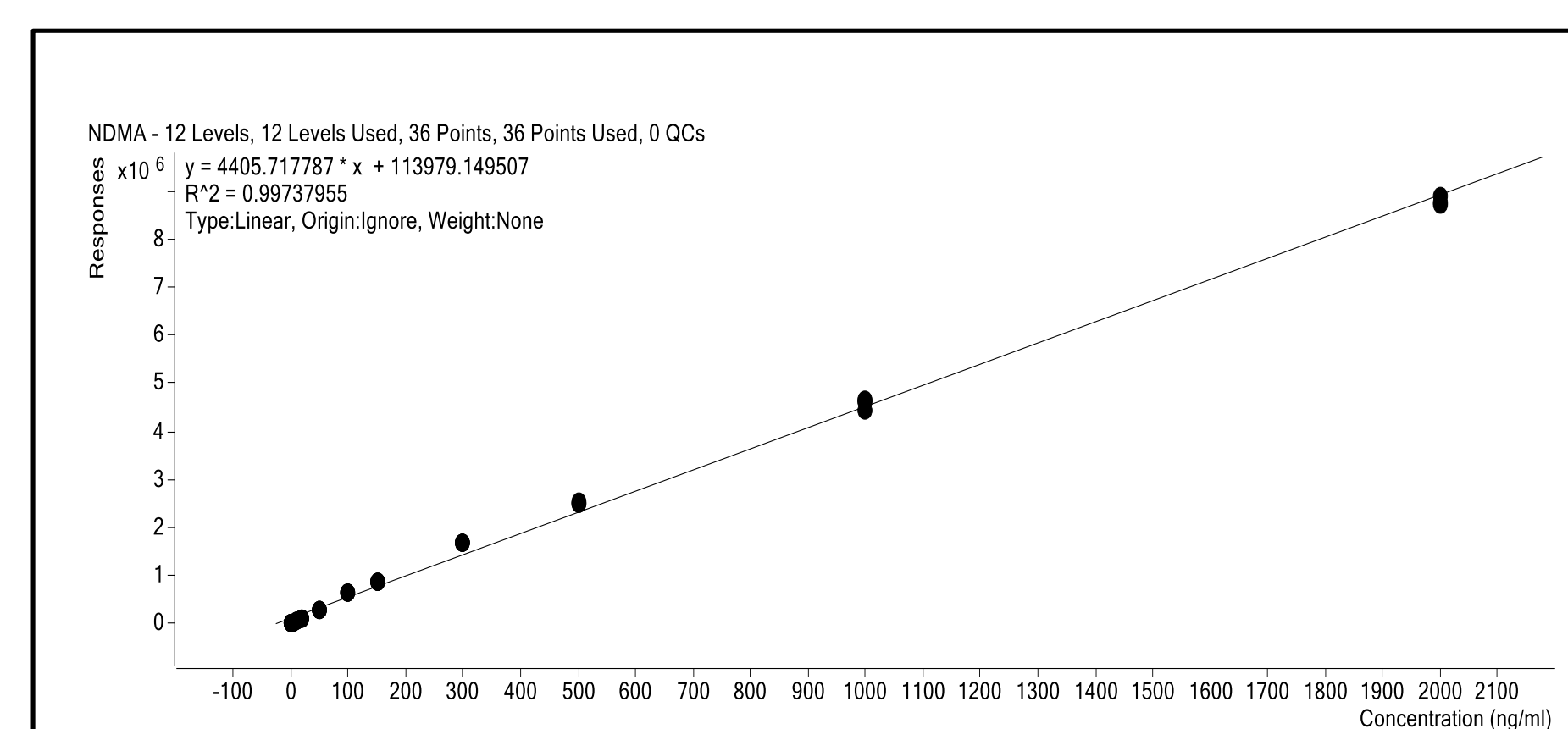
Figure 4: Calibration curve using NDMA standard in the range of 1 ppb to 2000 ppb (1ug/L – 2000ug/L).

NDMA - 12 Levels, 12 Levels Used, 36 Points, 36 Points Used, 0 QCs
y = 4405.717787 * x + 113979.149507
R^2 = 0.99737955
Type: Linear, Origin: Ignore, Weight: None

Analysis of samples done on Agilent 7000 GC/MS triple quad

- 5 uL injected from samples
- Run in PCI mode (positive chemical ionization) with ammonia gas
- Less molecular fragmentation and greater sensitivity than other modes such as EI mode (electron ionization)
- MRM mode (Multiple Reaction Monitoring) used to look for transitions
- Compounds are identified by elution time and transitions
- Two transitions were used for identification: NDMA 92 →75 and isotopically labeled NDMA 98→ 81
- Serial dilution of standards run in triplicate to create 12 point calibration curve using values from 1 ppb to 2000 ppb (1ug/L to 2000 ug/L).

Results

Method Performance
- Limit of Detection of 0.2 ppt (0.2 ng/L)
- Limit of Quantification of 0.6 ppt (0.6 ng/L) (Kahl, 2013)
- A high degree of confidence in the data obtained by the GC analysis was reinforced by R^2 = 0.9974 (fig. 4)

Water Analysis
- NDMA was observed to occur in the raw water samples collected from October through December 2012 at levels ranging from 0 to 100 ng/L
- NDMA was observed to form in the ozonated water samples collected from October 2012 through December 2012 from 100 to 550 ng/L (fig. 5).
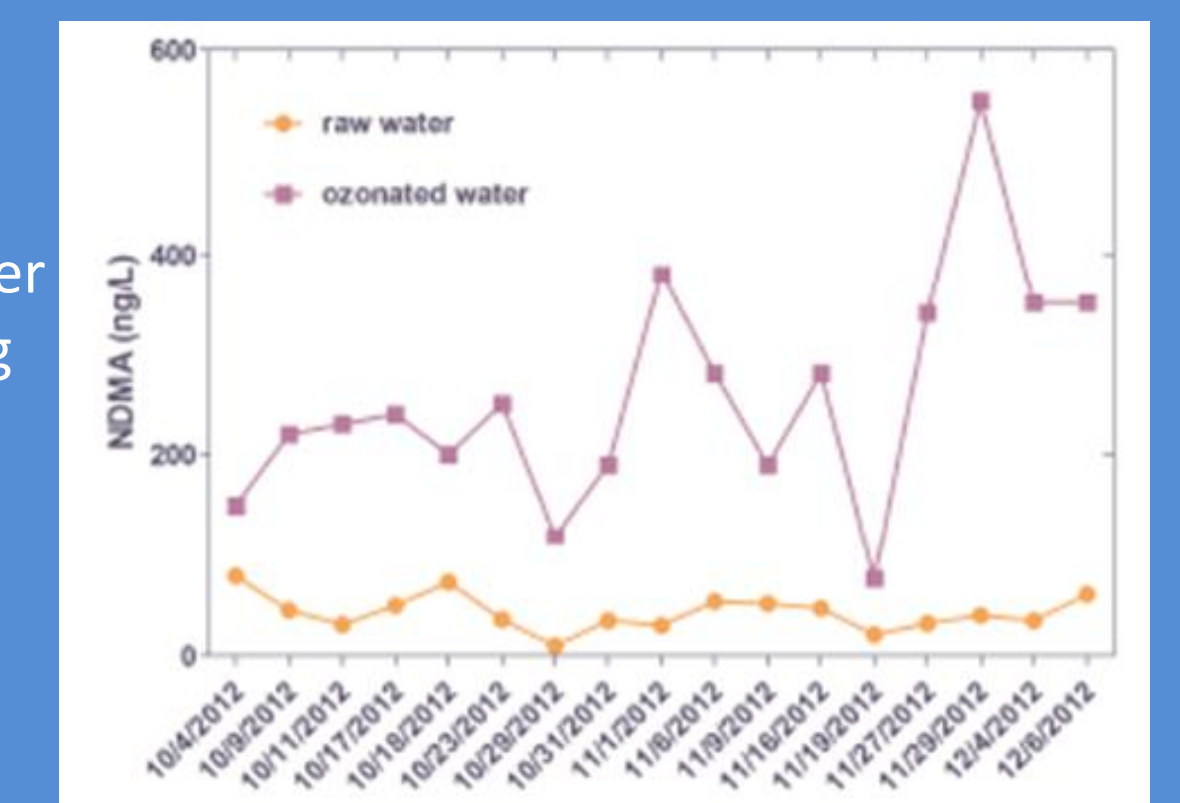- Ozonation was found to be the cause of NDMA formation.

Figure 5: NDMA formation observed October through December 2012 in western states water source. (Sgroi, 2013)

Conclusions

- The method developed to extract NDMA from water samples on the autotrace was successful in concentrating the target analyte 500 times.
- There is confidence that the method developed is robust because recovery has been in the range of 70% - 130% according to the Environmental Protection Agency method 521 recommendations.
- Future work needs to be done to determine the precursors for NDMA formation.

References

Sgroi, Massimiliano. Formation and Control of N-Nitrosodimethylamine (NDMA) in Wastewater Reclaimed for Indirect Potable Reuse. Ph.D. dissertation. Department of Civil and Environmental Engineering, University of Catania, Italy. 2013 .

Kahl, A., et. al. (2013) Analysis of N-nitrosodimethylamine (NDMA) in water using GC triple quadrupole mass spectrometry. Application note. Agilent Technologies Inc. Wilmington, DE USA.

Acknowledgements