ANALYSIS OF N-NITROSODIMETHYLAMINE AND N-NITRODIMETHYLAMINE IN GROUNDWATER*

Ben Greene
Dion Mast
Honeywell Technology Solutions, Inc.
NASA Johnson Space Center White Sands Test Facility
Las Cruces, New Mexico

David L. Baker
NASA Johnson Space Center White Sands Test Facility
Las Cruces, New Mexico

ABSTRACT

A method for the analytical determination of N-nitrosodimethylamine (NDMA) and N-nitrodimethylamine (DMN) at parts-per-trillion (ppt) concentrations in groundwater is reported. The method uses a solid phase extraction (SPE) cartridge containing 2 g of activated coconut charcoal to extract a 500-mL water sample. NDMA and DMN are eluted from the SPE cartridge using acetone. The acetone is concentrated and brought to a final volume of 1.0 mL, which results in a theoretical 500-fold concentration of the analytes. The extracts are analyzed by gas chromatography (GC) with a nitrogen-phosphorous detector (NPD), which is a highly sensitive and relatively inexpensive technique. The measured extraction efficiencies averaged 61 percent for NDMA and 74 percent for DMN. Extraction efficiencies were independent of NDMA and DMN concentrations from 40 to 2000 ppt. Several samples could be extracted then analyzed in a single day with the use of an extraction manifold and GC autosampler. A reporting limit of 10 ppt for NDMA and DMN was achieved. The MDLs for NDMA and DMN were 6.4 and 5.8 ppt, respectively. A typical turn-around time from beginning of extraction to reporting was 4 h. The method avoids the use of halogenated solvents, such as dichloromethane, and subsequent solvent exchange procedures necessary for use of the NPD detector.

BACKGROUND

N-nitrosodimethylamine (NDMA) and N-nitrodimethylamine (DMN) are groundwater contaminants of concern at the NASA Johnson Space Center White Sands Test Facility. The occurrence of NDMA in groundwater is believed to be a result of treatment and release of 1,1-dimethylhydrazine (UDMH), a constituent of Aerozine 50 (A50) propellant tested in the Apollo era, with calcium hypochlorite:

$$(CH_3)_2NNH_2 + Ca(OCl)_2 \rightarrow (CH_3)_2NNO + H_2O + CaCl_2$$

DMN is an oxidation product of NDMA, although the reaction(s) that caused its formation at WSTF is not known [1]. A reaction showing the formation of DMN from NDMA with oxygen is:

$$(CH_3)_2NNO + ½\ O_2 \rightarrow (CH_3)_2NNO_2$$

The NASA White Sands Test Facility (WSTF) laboratory was tasked with providing rapid analytical results for NDMA and DMN in groundwater with a reporting limit of 10 parts-per-trillion (ppt). Because of the requirement for ppt reporting, a pre-concentration step was required. Additionally, the solvent system had to be compatible with our existing instrumentation, which consisted of a gas chromatograph (GC) with a nitrogen-phosphorous detector (NPD). An earlier report discussed our previous experience with the analysis of NDMA and other nitrosamines using a solid phase extraction (SPE) method coupled with GC-NPD [2]. This report describes the analytical method employed and its in-house validation.

---

* Approved for public release, distribution is unlimited.

NDMA is typically determined in contract laboratories for regulatory compliance reporting by the U.S. Environmental Protection Agency (EPA) Method 607 (40 CFR Part 136 reference). EPA Method 607 determines NDMA by the liquid-liquid extraction of a 1-L water sample using dichloromethane, followed by back-extraction with acid to remove basic amines, then drying and concentration by evaporation. A theoretical 500-fold concentration is achieved after the extract is exchanged to methanol and brought to a final volume of 2.0 mL. Analysis is typically performed by GC-NPD or GC-mass spectrometry (MS).

In the SPE method for NDMA and DMN reported here, a 500-mL water sample is passed through an SPE cartridge containing activated coconut charcoal. The column is then eluted with acetone and the acetone is evaporated and brought to a final volume of 1.0-mL. Analysis is performed by GC-NPD.

To our knowledge, DMN has not been identified as a groundwater contaminant elsewhere nor have the EPA regulatory-approved methods been applied to its analysis. In earlier experiences with the determination of NDMA, DMN was identified as a groundwater contaminant by GC-MS. A sample of purified DMN from Picatinny Arsenal, New Jersey, was obtained and its identity was confirmed by retention time by GC-NPD. As a result of this effort, DMN, in addition to NDMA, was quantified and reported by Method 607 in support of the WSTF groundwater monitoring program. During the initial investigation into an SPE method for the determination of NDMA and other nitrosamines [2], a chromatographic peak was observed from samples taken from NDMA-contaminated groundwater wells at WSTF. The peak eluted at the same retention time as DMN by Method 607, but did not assess DMN quantitation or recovery because that analyte was outside the scope of the project at that time. However, this knowledge was important to the success of the current effort because the expectations were that DMN would be a satisfactory analyte by this method.

OBJECTIVE

The objective of this paper is to describe a rapid method for the simultaneous determination of NDMA and DMN in groundwater at ppt concentrations.

APPROACH

WSTF's on-site capabilities for NDMA and DMN analyses had not been exercised since the mid 1990s. At that time, an SPE method adapted from Aerojet Corporation [3] (Sacramento, California) was evaluated in an attempt to use that method as an alternative to EPA Method 607 [4]. Given the turn-around time requirements for the effort described here, the only possibility of success was to use an SPE method in conjunction with a GC-NPD, which was the only available instrumentation in the laboratory.

The EPA Laboratory in Cincinnati, Ohio had contacted WSTF in December 2002 regarding the SPE method for N-nitrosamines reported earlier. WSTF provided them with background information and SPE cartridges. Before the latest work began, research was performed to find if EPA had made any improvements or promulgated a method based on this work. EPA had promulgated Method 521 for the determination of nitrosamines in water [5]. Although EPA Method 521 used instrumentation not available to WSTF, that method's water sample volumes and the charcoal masses were adapted. In addition, a modification of the EPA elution procedure used a familiar acetone solvent system. Additionally, EPA Method 521 listed a commercially available, pre-packed SPE cartridge, which was used to avoid the procurement of charcoal and packing of columns.

EXPERIMENTAL

REAGENTS AND APPARATUS

NDMA[†] was obtained from Aldrich (Sigma-Aldrich Biotechnology, Highland, Illinois). DMN was obtained from Los Alamos National Laboratory (New Mexico). Stock solutions of NDMA and DMN were

[†] Catalog Number N2,500-1

prepared using WSTF reagent water. Reagent water obtained at WSTF was first treated by reverse-osmosis water then deionized. J.T. Baker Ultra Resi-analyzed acetone®‡ was used for the preparation of GC calibration standards and for cartridge elution. SPE cartridges containing 2 g of activated coconut charcoal were obtained from Restek Corporation (Bellefonte, Pennsylvania). A 12-port extraction manifold≡ was obtained from Alltech Associates, Incorporated (Deerfield, Illinois) and was connected to a standard vacuum pump and protected by a liquid trap to collect process water and acetone. Sample transfer tubing√ was obtained from Supelco (Sigma-Aldrich Biotechnology, Highland, Illinois). Various solution reservoirs and connector fittings were obtained from Supelco, Alltech, and Restek. Graduated centrifuge tubes∂ were obtained from Fisher Scientific Company (Hampton, New Hampshire). A Zymark Turbovap II®∩ equipped with 200-mL concentrator tubes was used to concentrate acetone extracts. GC calibration standards were prepared by dilution of NDMA and DMN standards in acetone with a 47-percent by weight acetone/53-percent by weight water solution. All glassware and tubing were scrupulously cleaned with reagent water, Alconox,®ζ and acetone prior to use.

EXTRACTION PROCEDURE

Field samples were received on ice and stored in a refrigerator at 4 °C according to EPA Method 607 [6]. Samples were equilibrated to room temperature prior to extraction. Samples were extracted within 7 days after collection. SPE cartridges were connected to the extraction manifold and fitted with 70-mL reservoirs. The vacuum pump was started and the vacuum adjusted to 2-3 in. mercury (Hg). Each SPE cartridge was pre-conditioned by successively eluting three 5-mL aliquots of acetone, then three 5-mL aliquots of reagent water. The stopcock for each port was closed just before all the final aliquot of reagent water had eluted to maintain the SPE cartridge wet. The reservoir was then removed and the void volume of the SPE cartridges filled with water. Sample transfer tubing was then connected between the SPE cartridge and a bottle containing 500 mL of sample to be extracted. The vacuum was then initiated and the stopcock valves used to adjust the flow so the nominal time to extract a 500-mL sample was approximately 1 h.

ELUTION PROCEDURE

The SPE cartridge and its connector were then removed from the manifold and dried with a chemical wipe tissue to remove excess water, then returned to the manifold. The sample transfer tubing was then placed in a nitrogen accumulator bottle (a 1-L glass bottle purged with facility nitrogen) and nitrogen was aspirated through the SPE cartridge for 30 min to remove excess water. The vacuum was then relieved, the SPE cartridge was removed from the manifold, and the manifold cover was removed. Excess water was removed from the plastic eluant needles and associated fittings using a clean chemical wipe tissue. The manifold cover was replaced and vacuum was initiated. To remove residual water from the stopcock valves, each was opened and approximately 1-mL acetone was transferred into each valve and pulled by vacuum to waste. The valves were cycled using an additional approximate volume of 1-mL acetone. The vacuum was then shut off and the stopcock valves were closed. The SPE manifold elution rack was then assembled and the appropriate number of graduated, tapered, and labeled centrifuge tubes were inserted and the assembly was placed in the manifold. The manifold cover was then replaced ensuring the eluant needles were clearly inserted into the centrifuge tubes. The SPE cartridges were replaced on the manifold to correspond with their respective centrifuge tubes. The vacuum pump was turned on to establish a vacuum of 2-3 in. Hg; then a 70-mL reservoir was fitted to each SPE cartridge. 10 mL of acetone was transferred to each 70-mL reservoir. The stopcock was opened until the bed was just wetted and 1-2 drops of acetone was eluted from the cartridge; then the stopcock was closed. The acetone and the cartridges were allowed to equilibrate for 5 min; then the stopcock was opened and the

‡ Ultra Resi-analyzed acetone is a registered trademark of J.T. Baker, Phillipsburg, New Jersey.
≡ Catalog Number 210351
√ Catalog Number 57275
∂ Catalog Number 05 538 32B
∩ Zymark Turbovap II® is a registered trademark of Zymark Corporation, Hopkinton, Massachusetts.
ζ Alconox® is a registered trademark of Alconox, Incorporated, White Plains, New York.

acetone aspirated through the cartridge dropwise, slowly. When the acetone was fully eluted the stopcock was closed. The vacuum was then relieved using the manifold valve; then the vacuum pump was shut off. The manifold cover and the elution rack were removed. The acetone from each centrifuge tube was transferred to a labeled Turbovap vial by carefully pouring the solution directly to the nipple of the Turbovap vial. The walls of the centrifuge vial were then rinsed with approximately 1-mL acetone; then the acetone was transferred to the Turbovap vial. Finally, the walls of the Turbovap vial were rinsed with approximately 1-mL acetone yielding a total volume of acetone of about 12-mL. The Turbovap vial was placed into the instrument cell with set points: bath temp = 37 °C and end point detection set to "Sensor." The acetone extracts were evaporated to approximately 0.75 mL; then each vial was removed from the Turbovac II and the acetone extract was brought up to a final volume of 1.0 mL. The acetone extracts were then transferred with clean glass pipets to plastic syringes equipped with 0.20-µm syringe filters and filtered into labeled amber GC autosampler vials, then crimped shut. The autosampler vials were analyzed directly or stored refrigerated for up to 40 days before analysis.

ANALYSIS

Analyses were performed using an Agilent®[††] Model 6890 GC equipped with a split-splitless capillary injection port and an NPD. The analytical column was a 15-m long, 0.53-mm diameter, 1.0-µm thick Supelcowax 10®[‡‡] column[≡≡] obtained from Supelco. Sample injections (2.0 µL) were made using an Agilent Model 7683 Series Injector. The carrier gas was helium at a flow rate of 5.0 mL/min. The GC oven was temperature-programmed from 40 to 150 °C. The temperature was held at 40 °C for 2 min, ramped to 70 °C at 8 °C/min, and then ramped to 150 °C at 20 °C/min and held for 1 min. The injector and the detector temperatures were maintained at 220 and 300 °C, respectively. The hydrogen and the air flow rates to the NPDs were 3.0 mL/min and 60 mL/min, respectively. These were the optimized conditions required to detect and report 5.0 ppb concentrations NDMA and DMN in instrument standards. The GC-NPD data were collected using Agilent ChemStation software.

NDMA and DMN were quantified using the following equation:

[analyte in groundwater] = [instrument result in ppb]/500

Where 500 = concentration factor (500 mL groundwater reduced to 1 mL extract)

ELUTION PROFILE

An elution profile was generated in order to determine the appropriate amount of acetone to quantitatively extract NDMA and DMN from SPE cartridges. The experiment was performed by SPE extraction of 500 mL of unchlorinated WSTF groundwater spiked with 40 ppt each of NDMA and DMN. After drying, the SPE cartridge was eluted with three sequential 3-mL aliquots of acetone, collecting each aliquot separately. After the acetone extracts were concentrated and brought to a final volume of 1.0 mL, analysis by GC-NPD was performed.

DETERMINATION OF THE WATER CONTENT OF AN EXTRACT

A representative acetone extract was analyzed for water by Karl Fischer titration using an EM Science Aquastar®[√√] C3000 coulometric titrator.

[††] Agilent® is a registered trademark of Agilent Technologies, Incorporated, Palo Alto, California.
[‡‡] Supelcowax 10® is a registered trademark of Sigma-Aldrich Biotechnology, Highland, Illinois.
[≡≡] Catalog Number 25300-U
[√√] EM Science Aquastar® is a registered trademark of EM Industries, Hawthorne, New York.

EFFECT OF WATER ON ANALYTE CHROMATOGRAPHY

Solutions of 40, 60, 80, and 95 percent by weight of water in acetone were spiked to 50 ppb with NDMA and DMN and analyzed by GC-NPD.

EXTRACTION EFFICIENCY

Extraction efficiency was determined by the extraction and analysis of spiked samples. Unchlorinated WSTF drinking water obtained from an uncontaminated well was spiked with various concentrations of NDMA and DMN and analyzed as described above. Spike recoveries were calculated as follows:

$$Spike\,\mathrm{Re}\,\mathrm{cov}\,ery = 100\% \times ([concentrationofspikefound] - [unspikedconcentrationfound] \div [trueconcentrationofspike])$$

PRECISION

Precision was determined by the extraction and analysis of duplicate well samples. Samples were obtained from the WSTF Environmental Department and were prepared and analyzed blind to the analysts.

ACCURACY

Accuracy was determined by the extraction and analysis of matrix spikes and blind control samples. Matrix spikes were prepared by the laboratory analysts. Blind control samples disguised as field samples were supplied by a WSTF Quality Assurance Chemist.

SYSTEM CLEANLINESS

System cleanliness was determined by the periodic extraction and analysis of blank samples as well as blind control samples submitted by a WSTF Quality Assurance Chemist. Blanks were comprised of unchlorinated WSTF drinking water obtained from an uncontaminated well.

METHOD DETECTION LIMITS

Method detection limits (MDL) for NDMA and DMN were determined by the analysis of a 5-ppb NDMA and DMN calibration standards following the procedure described in SW-846.

RESULTS

EXTRACTION AND ELUTION

Four water samples can typically be extracted, eluted, and prepared for GC-NPD analysis in approximately 2 h. A blank is processed with each batch to ensure system cleanliness.

ELUTION PROFILE

Although all of the concentrations shown are below the 10-ppt reporting limit, the results were deemed reliable for the purpose of this experiment and were included in the plot shown in Figure 1. The results showed the 10 mL of acetone used for SPE column elution was a sufficient volume to obtain quantitative or near-quantitative elution of NDMA and DMN.

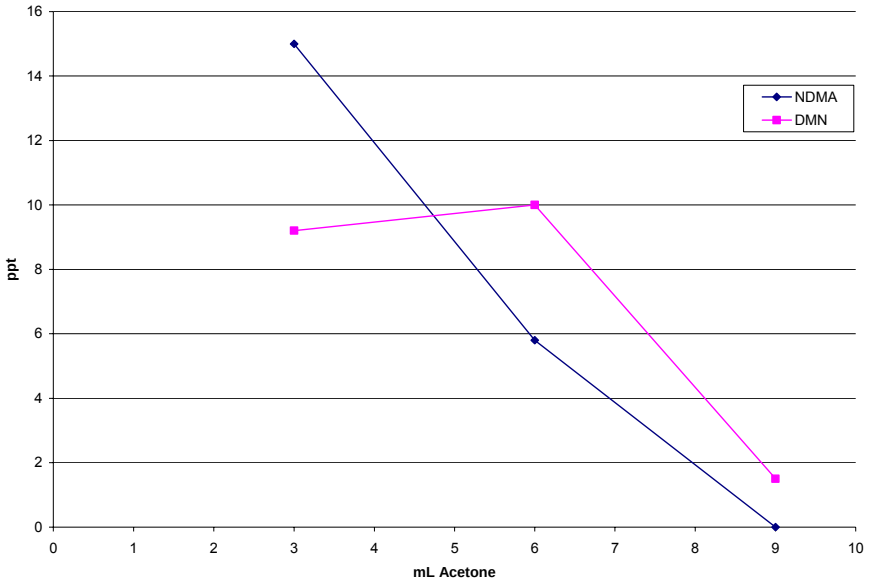


Figure 1. Elution of NDMA and DMN

DETERMINATION OF THE WATER CONTENT OF AN EXTRACT

The residual water content of an extract was 47 percent by weight. Residual water in the extracts was found to have an adverse effect on the chromatography of the analytes resulting in peak shapes and retention times that were different from those of the analytical standards. The retention times and accuracy of NDMA and DMN quantitation in the extracts were confirmed by spiking selected extracts; however, further improvement is necessary to produce more indisputable data. Several attempts to resolve this problem were made, including increased column drying times, filtration through desiccating media and solvent exchange. None of the results of these attempts were satisfactory. To compensate for the adverse effect of water on the chromatography, calibration standards were prepared and analyzed in the corresponding acetone/water matrix as the extract. This is referred to as “matrix-matching” and is a common analytical technique used to overcome interferences. The retention times for NDMA and DMN were about 8.3 and 9.9 min, respectively, on the chromatographic column used in this work. All results for the samples were reported using this calibration technique.

EFFECT OF WATER ON ANALYTE CHROMATOGRAPHY

Figures 2 and 3 depict chromatographic overlays from an experiment in which the water content of 50-ppb NDMA/DMN standards was varied from 20 weight percent to 95 weight percent.

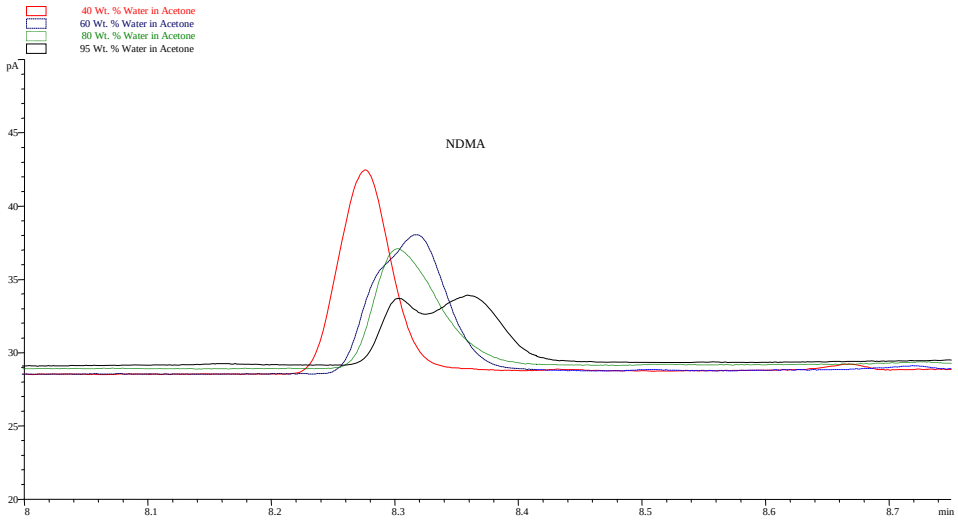


Figure 2. Effect of Water on NDMA

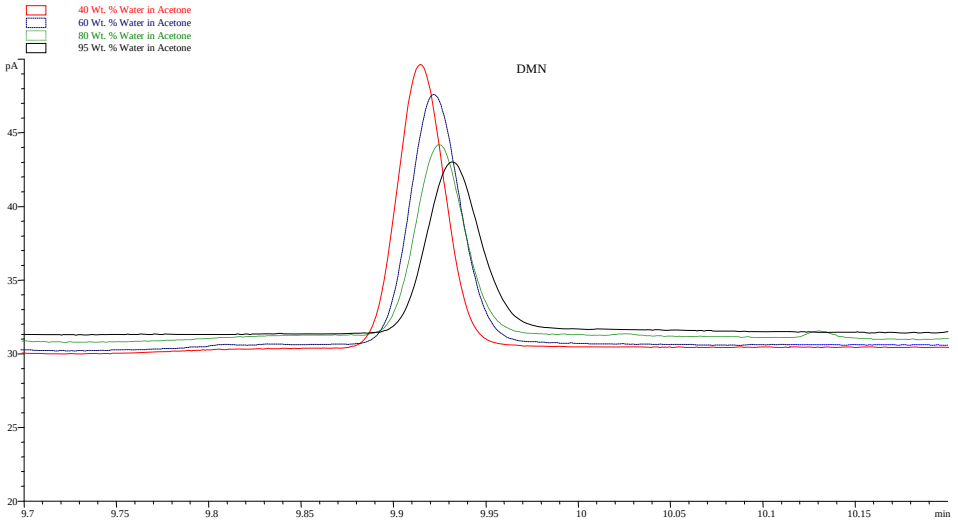


Figure 3. Effect of Water on DMN

EXTRACTION EFFICIENCY

Table 1 summarizes the extraction efficiencies for NDMA and DMN obtained from spiked water samples over a two-month period.

The average extraction efficiencies for NDMA and DMN were 61 ± 7 percent and 74 ± 7 percent, respectively, for spike concentrations ranging from 40 to 2000 ppt.

Table 1. Extraction Efficiencies for NDMA and DMN at Various Spike Concentrations Over a 2-Month Period

ANALYSIS DATE	SPIKE CONCENTRATION (ppt)	NDMA EXTRACTION EFFICIENCY (%)	DMN EXTRACTION EFFICIENCY (%)
11/24/04	40	60	75
	40	73	83
	40	60	75
12/6/04	20	65	70
	40	78	98
	400	58	78
12/10/04	40	56	65
	40	58	70
	40	63	76
1/19/05	40	53	71
	100	48	72
	200	47	69
	500	64	69
	1000	67	71
1/21/05	100	53	69
	500	60	80
	1000	61	72
	1500	58	71
	2000	59	69
1/26/05	100	66	71
	500	68	75
	1000	67	73
	1500	64	74
	2000	63	71

PRECISION

The data for NDMA and DMN show precision was within 10-percent RPD for the samples analyzed (Tables 2, 3, and 4).

Table 2. Precision of WSTF Duplicate Extraction and Analysis – Analyst's Duplicate

ANALYTE	E0412071507 RESULT (ppt)	E0412071507 RESULT (ppt)	RELATIVE PERCENT DIFFERENCE (% RPD)*
NDMA	41	45	9.3
DMN	15	16	6.5

Comment [e1]: What does this go to?

Table 3. Precision of WSTF Blind Duplicate Extraction and Analysis – Blind Duplicate

ANALYTE	E0412071301 RESULT (ppt)	E0412071302 RESULT (ppt)	RELATIVE PERCENT DIFFERENCE (% RPD)
NDMA	39	39	0.0
DMN	15	16	6.5

Table 4. Precision of WSTF Blind Duplicate Extraction and Analysis – Blind Duplicate

ANALYTE	E0501041320 RESULT	E0501041320 RESULT	RELATIVE PERCENT DIFFERENCE (% RPD)
NDMA	ND[a]	ND	NC[b]
DMN	ND	ND	NC

[a] ND indicates not detected (< 10 ppt)
[b] NC indicates not calculated

ACCURACY

The data show the matrix spikes and the blind control recoveries for NDMA and DMN were between 70 and 110 percent for the samples analyzed (Tables 5 and 6).

Table 5. Matrix Spike Results – 40 ppt Spikes

SAMPLE ID	ANALYTE	CONCENTRATION BEFORE SPIKE	CONCENTRATION AFTER SPIKE	% RECOVERY
E0412071303	NDMA	39	78	98
	DMN	16	58	110
E0501041221	NDMA	ND	32	80
	DMN	ND	31	78

Table 6. Blind Control Results

SAMPLE ID	ANALYTE	SPIKE CONCENTRATION (ppt)	RESULT (ppt)	% RECOVERY
E0412071437	NDMA	30	21	70
	DMN	Not added	ND	NC
I0501041051	NDMA	20	18	90
	DMN	20	20	100

SYSTEM CLEANLINESS

No NDMA or DMN was detected at or above the reporting limit of 10 ppt in any of the method blanks or field blanks analyzed by this method.

METHOD DETECTION LIMIT

The MDL is the minimum concentration of a substance that can be measured and reported with 99-percent confidence that the analyte concentration is greater than zero. An instrument MDL was determined using NDMA and DMN standards in acetone at a concentration of 5.0 ppb (corresponding to 10 ppt in groundwater). The instrument MDL data was determined using 6 replicate injections and the corresponding t-statistic of 3.36 in accordance with the procedure described in SW-846 (EPA 1992). The instrument MDL for NDMA is 1.3 ppb, which corresponds to 2.6 ppt in groundwater. The instrument MDL for DMN is 2.0 ppb, which corresponds to 4.0 ppt in groundwater.

A full MDL was determined by spiking 3 unchlorinated, uncontaminated groundwater samples with 10 ppt NDMA and DMN. These were processed through the entire method. The instrument results were back calculated to concentration in the water samples, then treated using the corresponding t-statistic of 6.96 in accordance with the procedure described in SW-846 (EPA 1992). The MDL for NDMA is 6.4 ppt. The MDL for DMN is 5.8 ppt.

Figure 4 shows the chromatogram of a 10 ppt spike overlaid on its respective method blank.

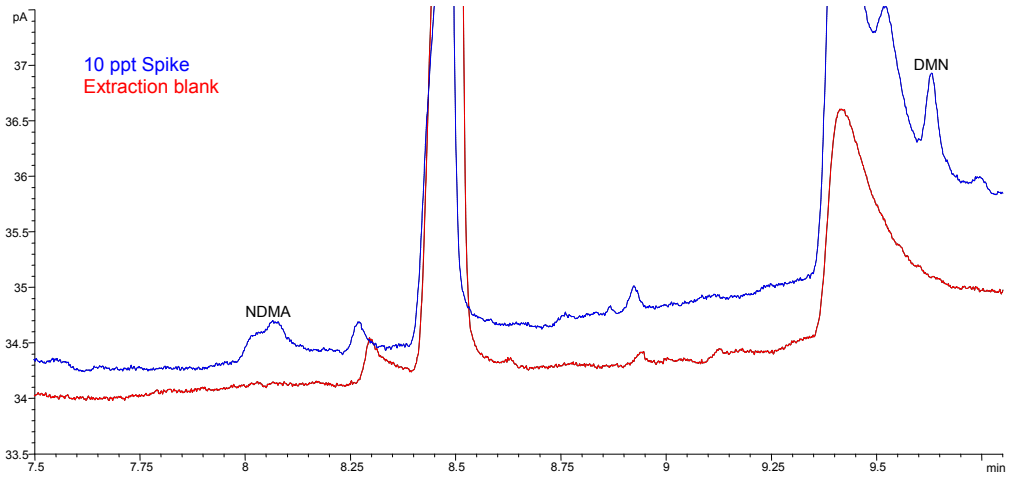


Figure 4. A 10 ppt Spike and Its Method Blank

The NDMA peak at about 8.1 min and the DMN peak at about 9.7 min are clearly seen at concentrations above the extraction blank. Their estimated concentrations for NDMA and DMN, back-calculated to the water sample, are 6.9 and 6.8 ppt respectively. These values, however, would be reported as "ND" at the reporting limit of 10 ppt.

DISCUSSION

This method differed from the method reported in 1995 [2] in a number of ways.

First, DMN was extracted and analyzed. In the previous method, DMN was not characterized although it was observed in the chromatograms.

Second, the time to extract and elute samples was approximately 2 h for four samples. In the previous method, this time was approximately 1 h for 12 samples. The additional time required for this method was due to additional time required for the SPE extraction. Although the flow rates were similar, the volume extracted using the current method was double, the additional time was required for water removal, and solvent evaporation was not required by the previous method. Although water was not quantified in extracts obtained in the previous method, a higher water content in the current method is expected as a result of the increased sample volume, increased charcoal mass, and decreased final extract volume. The current method uses 2-g charcoal and yields a final extract volume of 1 mL, while the previous method used 0.5-g charcoal and yielded a final extract volume of 2 mL. This resulted in a theoretical 8-fold increase in the water concentration of the final extracts assuming water was proportionately extracted by charcoal and eluted by acetone.

It was observed that water in the extracts had the effect of increasing the analyte retention times and altering their peak shapes. This caused difficulties in the identification and quantitation of NDMA and DMN. Figures 2 and 3 show the effects on chromatography became more pronounced as water concentration increased. These difficulties were reduced by attempting to match the water concentration in the extracts to the standards. However, the variability of water content from extract to extract was not studied so precise matrix matching was not achieved. Alternate eluting solvents that are immiscible with water might also be adapted to the current SPE method but would require additional experiments and validation. However, one of the problems with alternate solvents is that chlorinated solvents, such as dichloromethane, are not suitable for use with the NPD detector and if employed a solvent exchange would be required and would increase the time and number of manipulations required for an extraction.

The reporting limit achieved using the current method (10 ppt) was an order of magnitude lower than that obtained in the previous SPE method (0.1 ppm, 100 ppt) because of combined increased instrument sensitivity and increased analyte concentration factors (500- versus 250-fold).

CONCLUSIONS

A method for the simultaneous determination of NDMA and DMN in groundwater is reported. This is also the first account of the trace analysis of DMN in groundwater. The method uses SPE to concentrate a 500-mL water sample to 1.0 mL using acetone eluant. The acetone extract is analyzed by GC-NPD. A reporting limit of 10 ppt for NDMA and DMN was achieved. A ten-fold improvement in reporting limit over a previous method used at WSTF was obtained. The MDLs for NDMA and DMN were 6.4 and 5.8 ppt, respectively. The method is rapid and samples can be extracted and analyzed the same day. A typical turn-around time from beginning of extraction to reporting is 4 h. The extraction efficiencies averaged 61 percent for NDMA and 74 percent for DMN. The method avoids the use of halogenated solvents typically used in other liquid-liquid and SPE extraction methods.

REFERENCES

1. Tuazon, E.C., Carter, W.P.L., Atkinson, R., Winer, A.M., and Pitts Jr., J.N. "Atmospheric Reactions of N-nitrosodimethylamine and Dimethylnitramine." Environmental Science and Technology 18:49-54 (1984).

2. Greene, B., Moffett, G., and Baker, D. "Solid Phase Extraction of N-Nitrosodimethylamine from Groundwater," JANNAF Propulsion and Subcommittee Meeting, Tampa, Florida (1995).

3. Snarr J.T. "Determination of Low Level NDMA." Aerojet Corporation Environmental Laboratory; Method No. EDL-EA-012:1-7 (Aug 1991).

4. EPA. "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods," SW-846 Chapter 1, Revision 1 (Jul 1992). http://www.epa.gov/epaoswer/hazwaste/test/main.htm

5. Munch, J.W., and Bassett, M.V. "Method 521 Determination of Nitrosamines in Drinking Water by Solid Phase Extraction and Capillary Gas Chromatography with Large Volume Injection and Chemical Ionization Tandem Mass Spectrometry (MS/MS)." National Exposure Research Laboratory Office of Research and Development. U.S. Environmental Protection Agency, Cincinnati, Ohio (2004).

6. Office of the Federal Register National Archives and Records Administration Title 40, Part 136, App. A, Method 607-Nitrosamines, p. 405 (Jul 1993).

Honeywell

Analysis of N-Nitrosodimethylamine and N-Nitrodimethylamine in Groundwater

Ben Greene

Dion Mast

Honeywell Technology Solutions, Inc.

NASA White Sands Test Facility

David L. Baker

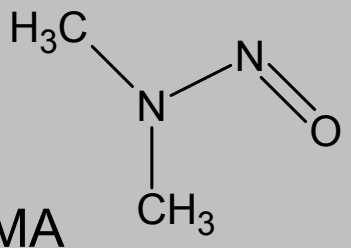
NASA Johnson Space Center

White Sands Test Facility

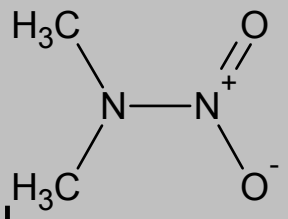
Honeywell

Background

N-nitrosodimethylamine (NDMA) and N-nitrodimethylamine (DMN) are groundwater contaminants of concern at the NASA Johnson Space Center White Sands Test Facility (WSTF).



NDMA



DMN

$(CH_3)_2NNH_2 + Ca(OCl)_2 \rightarrow (CH_3)_2NNO + H_2O + CaCl_2$

$(CH_3)_2NNO + ½\ O_2 \rightarrow (CH_3)_2NNO_2$

Honeywell

Background

The WSTF Lab was tasked with providing rapid analytical results for NDMA and DMN in groundwater with a reporting limit of 10 parts-per-trillion (ppt)

Previous (>10 years prior) applicable experience was with:

- EPA Method 607 for NDMA and DMN
- An SPE method derived from an Aerojet Corporation (Sacramento, CA) procedure for the extractive pre-concentration of NDMA
- Observations at the WSTF Lab confirmed that the SPE method extracted DMN from groundwater and that it chromatographed under Method 607 conditions

Honeywell

Background

- The U.S. Environmental Protection Agency (EPA) Laboratory in Cincinnati, Ohio contacted WSTF in December 2002 regarding the SPE method for N-nitrosamines
- WSTF provided EPA with some SPE cartridges, procedures, and Aerojet Corporation contact information to support their efforts to establish an SPE-based method for extractive pre-concentration of NDMA and other nitrosamines
- For this project, WSTF inquired in 2004 whether EPA had made any improvements and found that EPA Method 521 “Determination of Nitrosamines in Drinking Water by Solid Phase Extraction and Capillary Gas Chromatography with Large Volume Injection and Chemical Ionization Tandem Mass Spectrometry (MS/MS)” had been issued the month before and that a copy was in the mail

Honeywell

Background

- The Method 521 MS-MS technique was not available to WSTF, but GC-NPD was available
- Method 521 used dichloromethane as an eluant, which is not compatible with the nitrogen-phosphorous (NPD) detector
- The risk was accepted to adapt the Method 521 water volume/charcoal mass ratio (500 mL/2.0g vs. 250 mL/0.5g) to the acetone eluant WSTF and Aerojet Corporation used earlier
- SPE cartridges were COTS from Restek as an alternative to purchasing activated charcoal, cartridges, frits, and to manually pack columns in the laboratory

Honeywell

Experimental

- Description of Method
  - Sample equilibration to room temperature
  - Sample volume adjustment (500 mL)
  - SPE cartridge conditioning (acetone, water)
  - SPE extraction (aspiration using SPE manifold)
  - SPE cartridge and system drying
    (physical removal of water, aspiration of dry nitrogen)
  - Elution of SPE cartridge into graduated centrifuge tubes
  - (10 mL acetone)
  - Evaporative concentration of acetone
    (use of Turbovac instrument to 1 mL acetone)
  - Transfer to GC auto-sampler vial
  - Analysis by GC-NPD
  - Calculation of GC-NPD results back to original water sample (÷500)

Honeywell

Extraction Apparatus

Honeywell

Extraction Apparatus

Honeywell

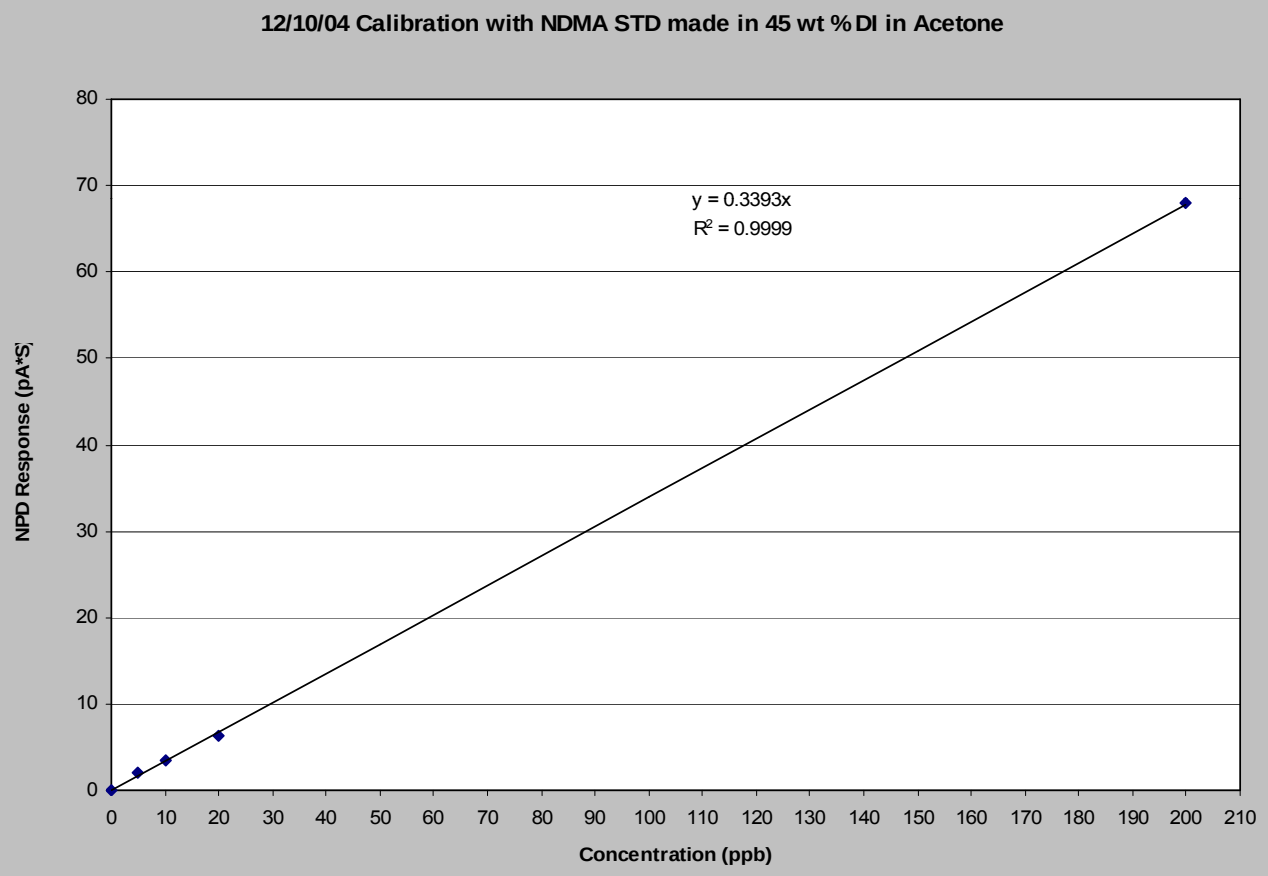
Analysis

Description of Analysis

- GC and column parameters
  - Agilent Model 6890 GC
  - Split-splitless capillary injection port
  - NPD detector.
  - 15-m long, 0.53-mm diameter, 1.0-µm thick Supelcowax 10® column
  - 2.0 µL autosampler injections
- Standards
  - NDMA prepared from neat material (Aldrich) in DI/acetone solution
  - DMN prepared from neat material (Picatinny Arsenal or LANL) in DI/acetone solution
  - Standards were nominally matrix-matched to samples (based on a Karl Fischer determination) to account for shifting retention times and peak-broadening that occurred as a result of water
- GC results divided by 500 to account for concentration factor (500:1); results reported in ppt along with extraction efficiency of spiked samples

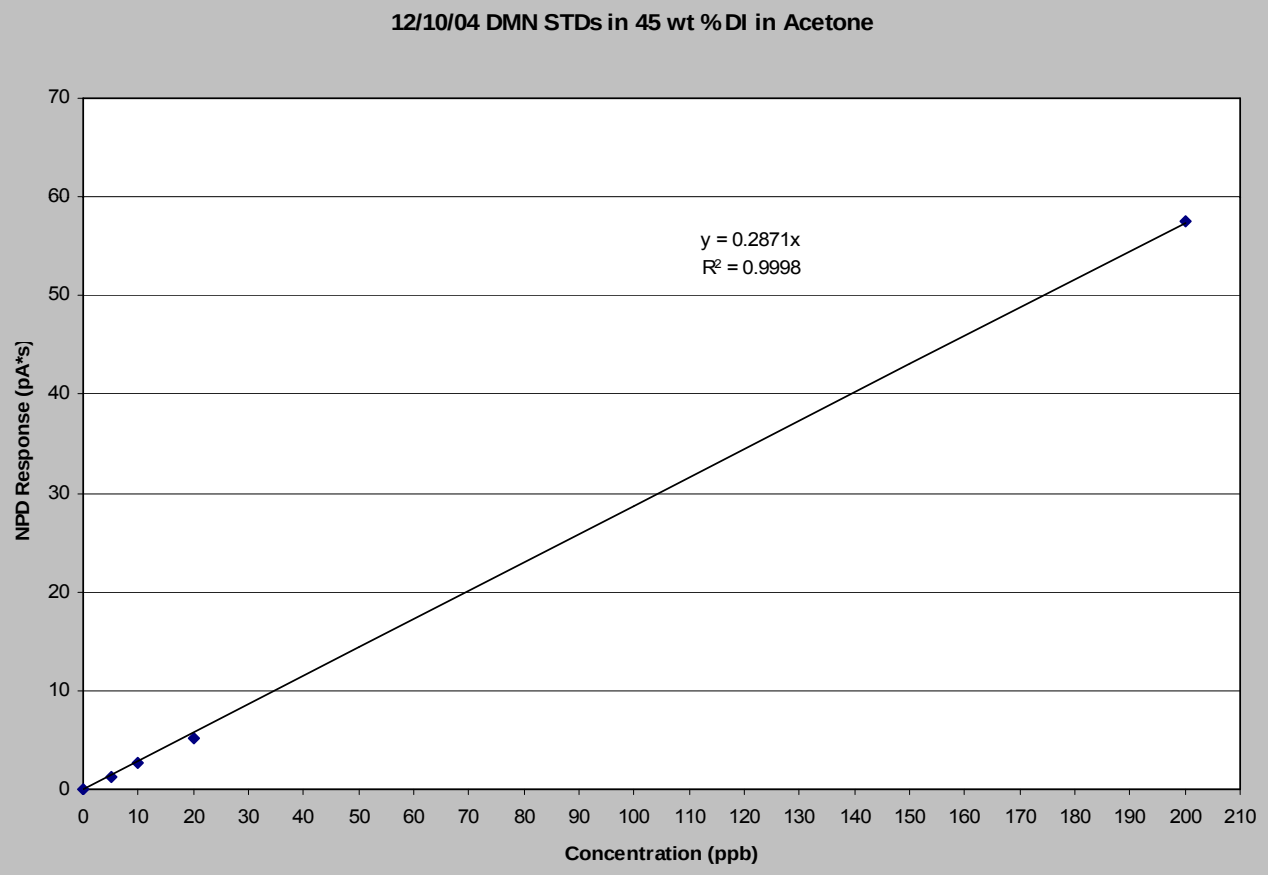
Honeywell

NDMA Calibration Curve



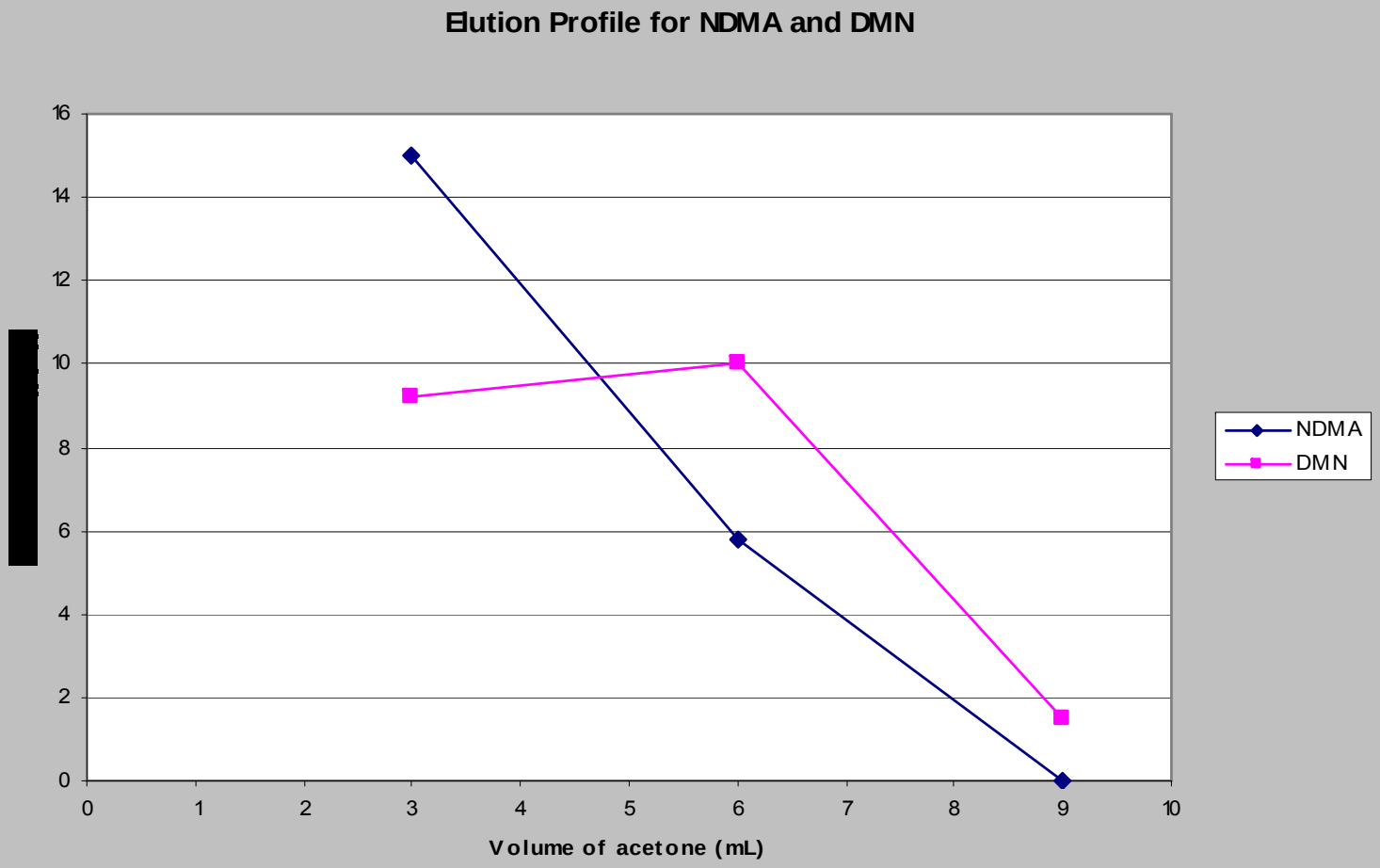
Honeywell

DMN Calibration Curve



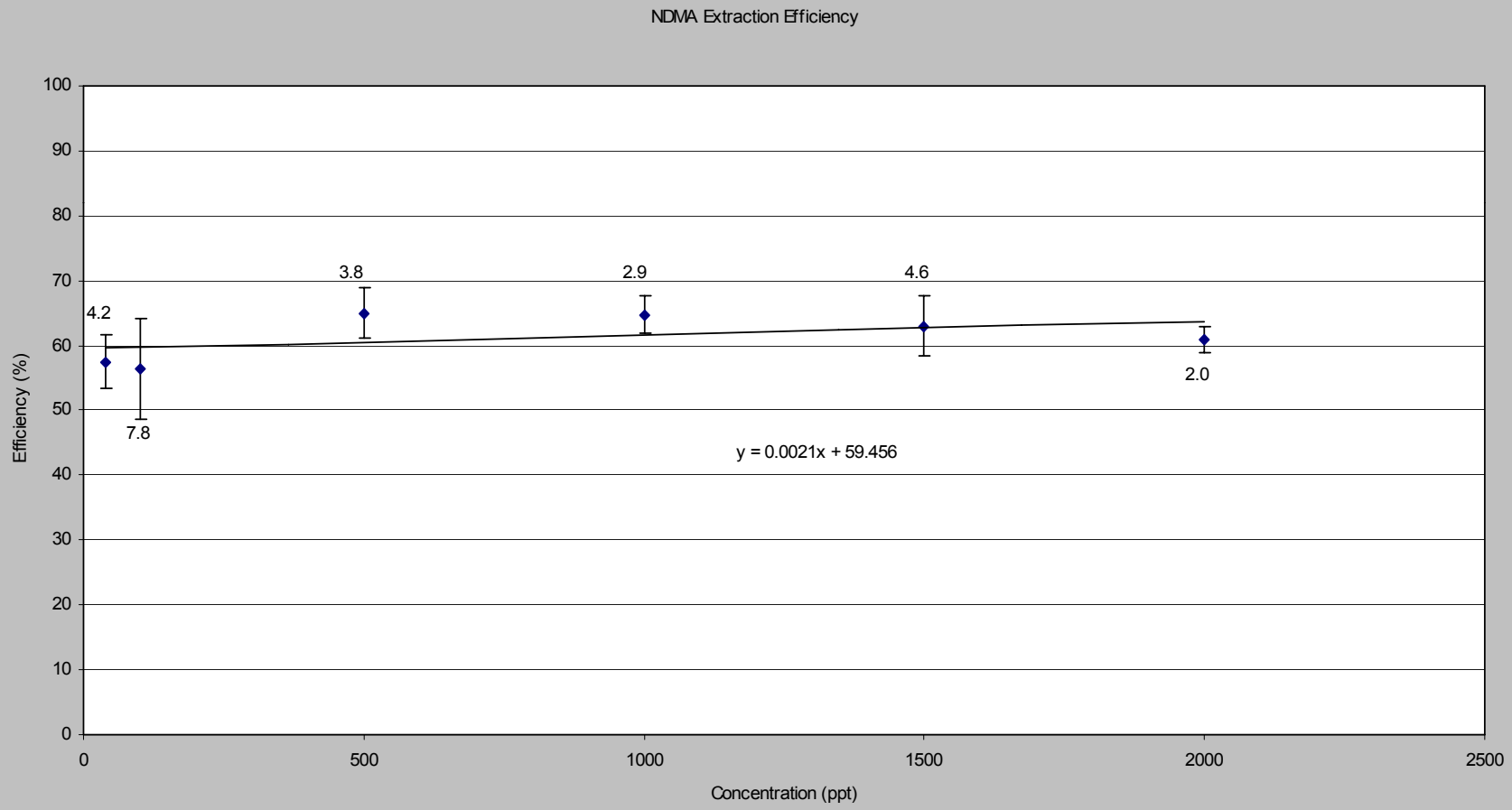
Honeywell

Elution Profile



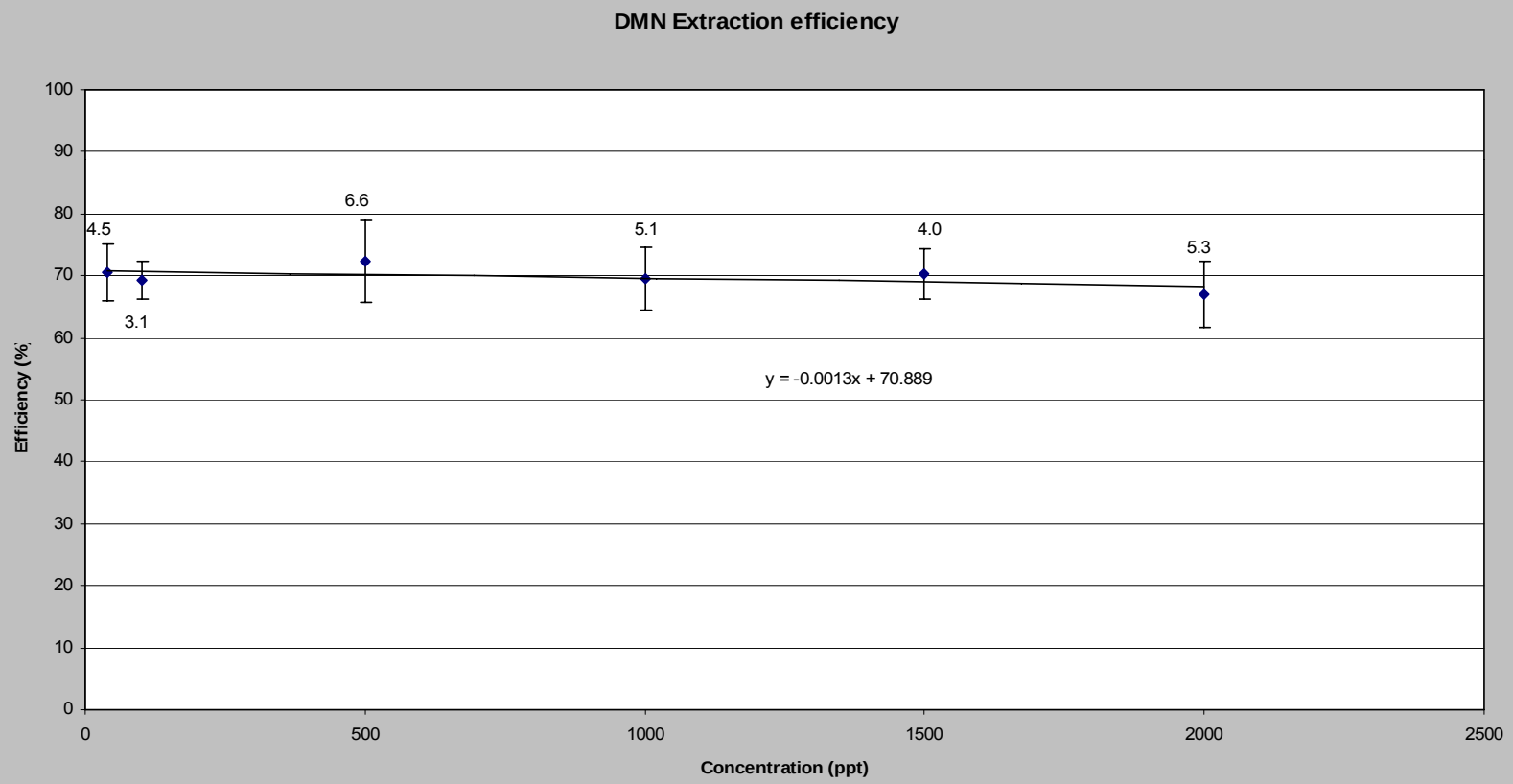
Honeywell

NDMA Extraction Efficiencies



Honeywell

DMN Extraction Efficiencies



Honeywell

Reporting and Detection Limits

Method Detection Limit (MDL) was determined by the extraction and analysis of 3 unchlorinated, uncontaminated groundwater samples spiked with 10 ppt NDMA and DMN, and then treating the results according to EPA SW-846.

Results were:

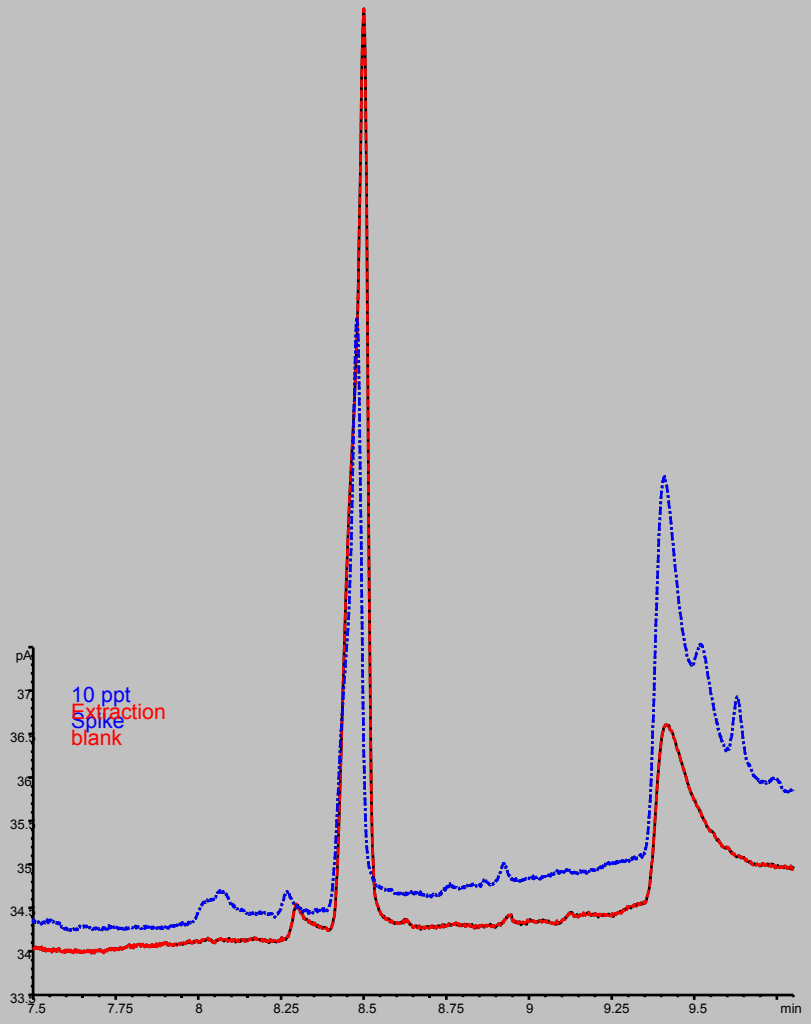
- NDMA: 6.4 ppt
- DMN: 5.8 ppt

Trace contamination (<10 ppt) was typically not a problem

- Glassware was scrupulously cleaned with water, detergent, and acetone
- Consumables were treated as such
- Tubing was rinsed with DI water after use

Honeywell

Chromatogram of a 10 ppt Spike



Honeywell

Effect of Water

- Residual water in the extracts was found to have an adverse effect on the chromatography of the analytes, especially for NDMA, resulting in peak shapes and retention times that were different from those of the analytical standards
- This problem was not encountered in the previous work but is attributed to a theoretical 8-fold increase in the water content of the extracts achieved by using 2g charcoal and 1 mL final volume vs. 0.5 g charcoal and 2 mL final volume (assuming the charcoal is fully saturated with water and the water sample volume is irrelevant).
- The residual water content of an extract was found to be 47 percent by weight by Karl Fischer titration.

Honeywell

Effect of Water

- Several attempts were made to further minimize or eliminate the effect of water:

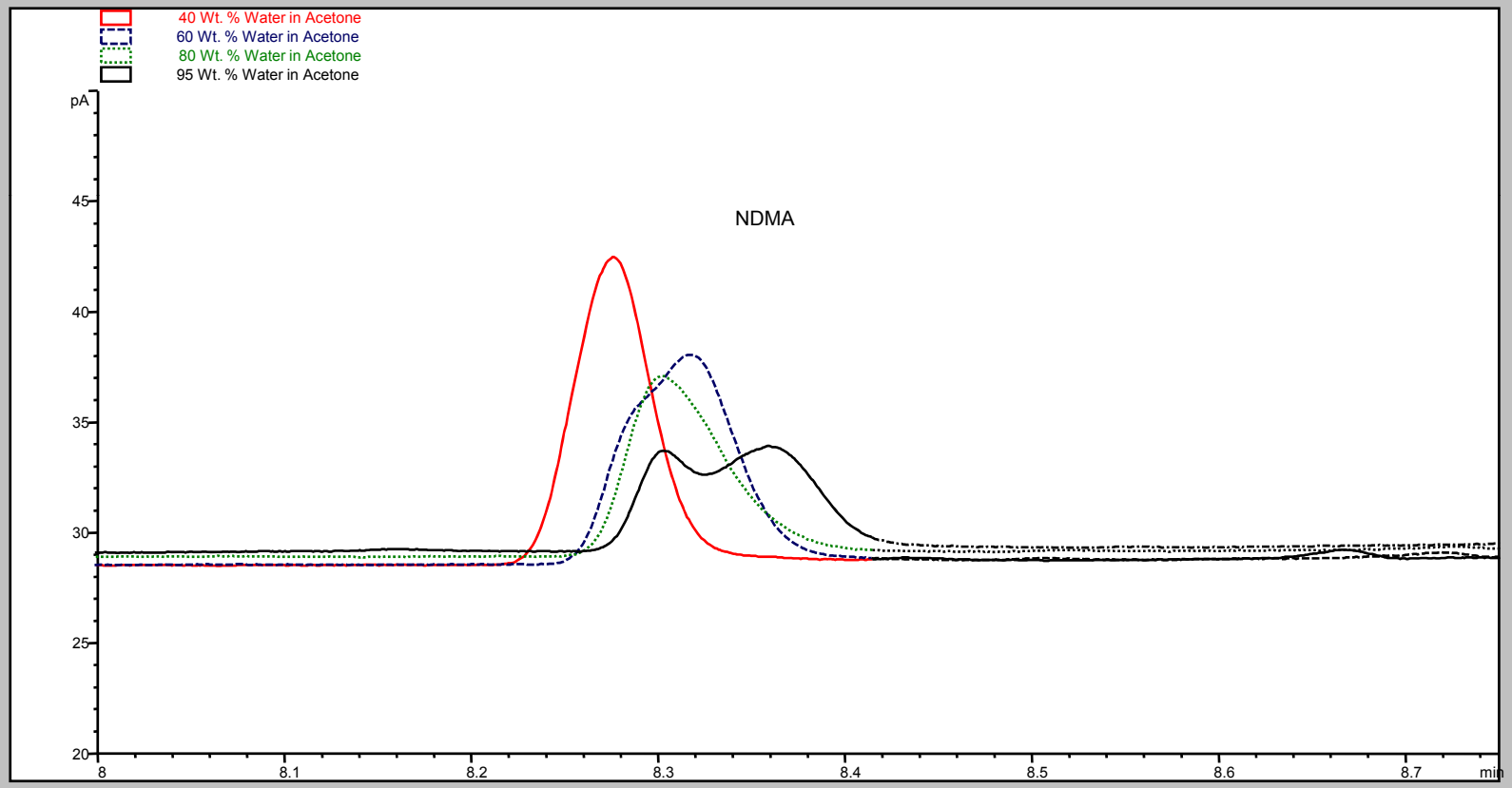
  Increased SPE cartridge drying times

  – Filtration through desiccating media

  – Solvent exchange
- None of these proved satisfactory
- Standards were prepared in an acetone/water matrix match helped considerably
  – Variations in retention times amongst samples still occurred, but the problem was understood and could be managed.

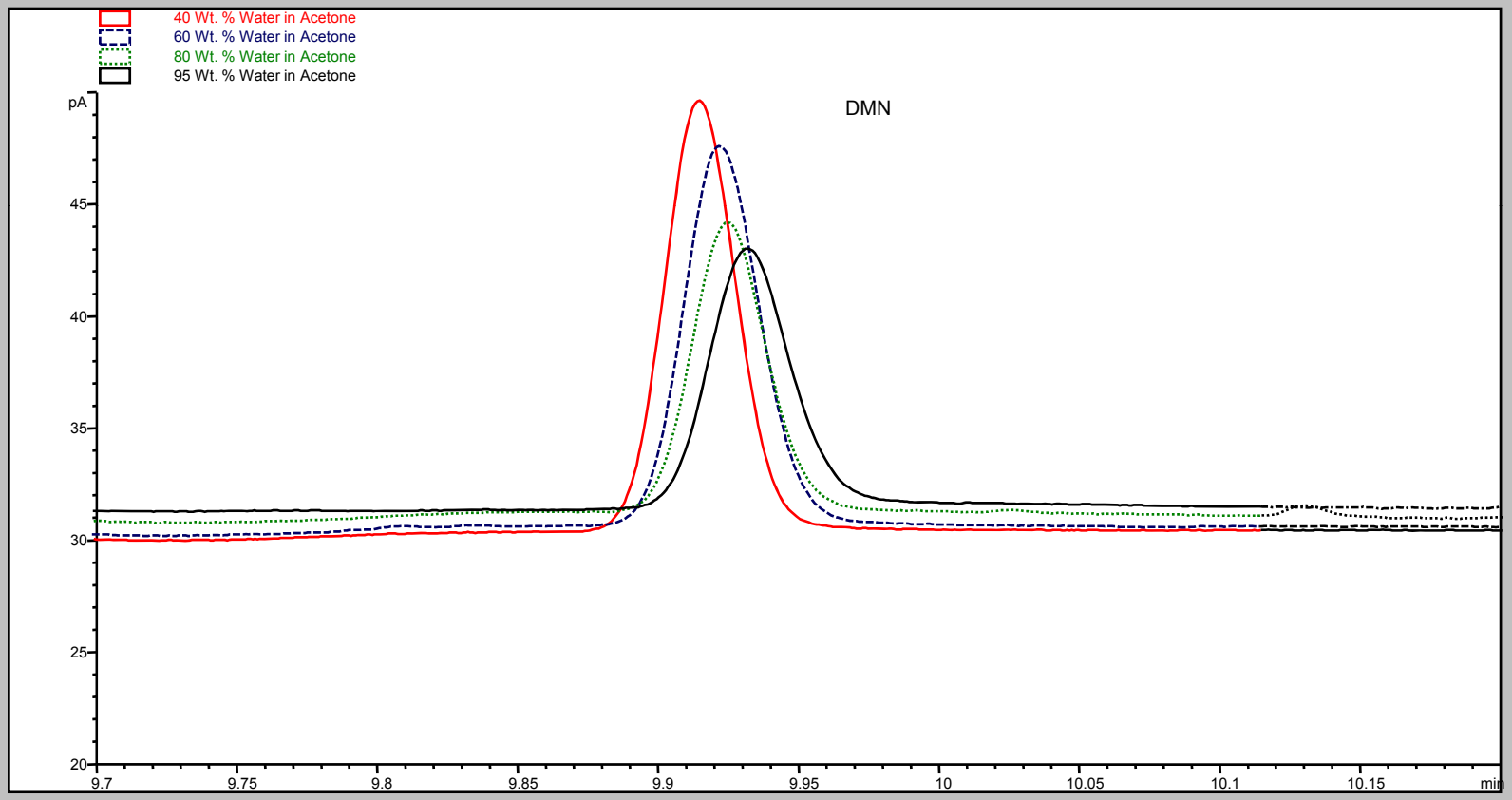
Honeywell

Effect of Water on NDMA Peak Shape and Retention Time



Honeywell

Effect of Water on DMN Peak Shape and Retention Time



Honeywell

NPD Detector Limitations

- Instability
  - Calibration drift
  - Sensitivity changes
- Limited and variable life span
- Sensitivity to water
  - Water “dip” in chromatogram
  - “Dip” correlates with water concentration
- Variable warm up time
  - Can result in delay to analysis
- Dependence on retention time not mass spectral identification
  - Could result in interferences or false positive results

Honeywell

Conclusions

- A method for the simultaneous determination of NDMA and DMN in groundwater is reported.
- This is the first reported method for the trace determination of DMN in groundwater.
- The method uses SPE to concentrate a 500-mL water sample to 1.0 mL using acetone eluant. The acetone extract is analyzed by GC-NPD.
- A reporting limit of 10 ppt for NDMA and DMN was achieved. The MDL for NDMA was 6.4 ppt and for DMN was 5.8 ppt in groundwater.
- The extraction efficiencies averaged 61% for NDMA and 74% for DMN over a concentration range of 40-2000 ppt.
- Matrix matching of standards to samples helps to minimize the effect of water and avoids a drying step (e.g. sodium sulfate) and associated time and disposal considerations.
- The method is rapid and samples can be extracted and analyzed the same day. A typical turn-around time from beginning of extraction to reporting is 4 hours.
- The method avoids the use of halogenated solvents typically used in other liquid-liquid extraction or SPE methods.