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DETERMINATIONS OF N-NITROSODIMETHYLAMINE (NDMA) AT PART-PER-TRILLION (ng/L) CONCENTRATIONS IN CONTAMINATED GROUNDWATERS AND DRINKING WATERS FEATURING CARBON-BASED MEMBRANE EXTRACTION DISKS

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DETERMINATIONS OF N-NITROSODIMETHYLAMINE (NDMA) AT PART-PER-TRILLION (ng/L) CONCENTRATIONS IN CONTAMINATED GROUNDWATERS AND DRINKING WATERS FEATURING CARBON-BASED MEMBRANE EXTRACTION DISKS

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ABSTRACT

A new solid phase extraction procedure extracts *N*-Nitrosodimethylamine (NDMA) at part-per-trillion (ng/L) concentrations from aqueous samples using a C_{18} (reversed-phase) membrane extraction disk layered over a carbon-based extraction disk. The reversed-phase disk removes nonpolar water-insoluble neutrals and is set aside; the carbon-based disk is extracted with a small volume of dichloromethane. NDMA is quantitated in the organic extract using a gas chromatograph equipped with both a short-path thermal desorber and a chemiluminescent nitrogen detector (CLND). The Method Detection Limit for the procedure is 2 ng of NDMA/L; the analyte recovery is approximately 57%. A related procedure substitutes a standard automatic sampler for the short-path thermal desorber, and is suitable for determining NDMA in heavily-contaminated aqueous samples. The Method Detection Limit for the "high-level" procedure, which employs an automatic sampler, is 180 ng of NDMA/L, with an analyte recovery of approximately 64%.

The detection limits and measured recovery values are comparable to those observed in earlier work in which a conventional continuous overnight extraction with dichloromethane was used to remove NDMA from the aqueous samples. The newer procedures described herein offer a fiftyfold savings in extraction time and a one-hundredfold reduction in dichloromethane consumed per sample, while maintaining the wide range (three to four orders of magnitude concentrations of NDMA) observed for the original procedures used in a tandem.

The proposed procedure was challenged during a sampling campaign in which 100-200 groundwater samples were analyzed. In most cases, concentrations ranging between <5 to 200 ng NDMA/L were measured without difficulty, and were confirmed by GC/MS operated in the single-ion monitoring mode. Some samples required an extra C_{18} membrane extraction disk to reduce the concentrations of neutral contaminants. High concentrations of sulfur-bearing species present in groundwater samples may suppress NDMA recovery.

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INTRODUCTION

In previous work[1], we demonstrated that *N*-nitrosodimethylamine (NDMA, CAS Registry No. 62-75-9) can be quantitated readily at the part-per-trillion (ng/L) level in groundwaters after they are extracted continuously overnight with dichloromethane[2]. Briefly, a substantial portion of the resulting dichloromethane concentrate is then spiked onto a dual-sorbent carbon trap and dried before the residues (including NDMA) are desorbed onto a fused-silica gas chromatographic column. These residues are then separated in the usual manner; NDMA is detected selectively using a chemiluminescent nitrogen detector (CLND) optimized in its nitrosamine-selective mode. This procedure, while effective, exhibits a lengthy sample turnaround time (approximately three days per batch of eight samples, including a blank and appropriate QA/QC sample) and generates a substantial volume (approximately 300 mL per 1-L aqueous sample) of dichloromethane waste. For these reasons, it was most desirable to develop alternate procedures which would be effective, rapid, and generate smaller volumes of dichloromethane waste[3].

Both Taguchi *et al* [4,5] and Jenkins *et al* [6] have described extraction procedures for NDMA in which a small mass (200 mg) of Ambersorb 572, a carbonaceous sorbent, was used to extract NDMA effectively from 500 mL drinking water. We have extended this procedure by employing a carbon-based membrane extraction disk for removing NDMA from aqueous samples[7]. The procedure described herein employs a preconditioned C_{18} membrane extraction disk, laid over the carbon-based disk, to remove the unwanted neutral water-insoluble species. The former disk is set aside; the latter is dried and extracted with a small volume of dichloromethane. NDMA may then be quantitated using the various procedures described in Reference 1. Both the extraction time for a 1-L aqueous sample and the volume of waste dichloromethane are reduced approximately one hundredfold when the membrane disks are used instead of the continuous overnight extraction procedure. The calculated Method Detection Limit (MDL)[8] concentrations are 2 and 180 ng NDMA/L for the "low-level" (manual injection) and "high-level" (automatic injection) procedures, respectively. The use of the two procedures in a tandem permits the quantitation of NDMA concentrations ranging over approximately three orders of magnitude, from ng/L to the μg/L levels.

EXPERIMENTAL

Sample Collection and Storage. Groundwater samples should be collected in commercially available precleaned 1-L narrow-neck amber glass bottles, stored at 4°C, and extracted within 7 days of sampling.

NDMA Standard Solutions. Stock solutions with certified concentrations of NDMA in methanol may be purchased from several vendors. These include NSI Environmental Solutions, Inc. (Research Triangle Park, NC; 5000 μg NDMA/mL); AccuStandard (New Haven, CT; 1000 μg NDMA/mL); Polysciences (Niles, IL; 1000 μg NDMA/mL); and Ultra Scientific (North Kingstown, RI; 100 μg NDMA/mL). Aliquots are diluted sequentially to final concentrations ranging between 2 and 240 ng of NDMA/mL in highest purity dichloromethane (GC^2 grade, Burdick & Jackson, Muskegon, MI, or equivalent) to form calibration standards for the "low-level" method, which employs the short-path thermal desorber, or between 50-4000 ng of NDMA/mL dichloromethane, prepared similarly, for the "high-level" method, which employs the automatic sampler. Fresh standards should be prepared every 60 days.

Preparation of Blanks and Spiked Samples for Method Certification and Quality Assurance. Aliquots (1-L) of synthetic groundwater are prepared from HPLC-grade water (Burdick & Jackson, J. T. Baker (Phillipsburg, NJ), or equivalent) which is fortified to 100 mg/L each in sulfate and chloride, as described elsewhere[9]. These are spiked to concentrations ranging between 2 and 40 ng of NDMA/L using a master spiking solution containing 0.1 µg of NDMA/mL of water for the "low-level" procedure. Spiked samples for the "high-level" procedure are prepared from a master spiking solution containing 10 µg of NDMA/mL water; the final concentrations range between 100-4000 ng of NDMA/L. Water produced from typical "on-demand" systems may not be used, as described in Reference (1).

Sample Preparation and Extraction. Aqueous samples are filtered through Empore C_{18} filter disks (47 mm diameter, J. T. Baker or Varian Sample Products Division, Harbor City, CA) layered over a carbon-based Empore disk[10,11]. An all-glass funnel/support assembly (DELTAWARE, with a 1-L filtering flask and a 300-mL reservoir, handles 47 mm diameter disks, VWR, part no. KT 93825-47 or equivalent) is used to support the disk and hold the filtrate. The two disks are preconditioned simultaneously with two 10-mL portions each of methanol and water. Each aliquot remains on the disk for 1 min prior to removal. *Do not permit the disk to become dry during the conditioning sequence.* A separate all-glass funnel/support assembly should be arranged for drying the carbon-based disks. Here, the 1-L flask is replaced with a custom-prepared "cap" fashioned from an "inner" Ŧ (standard taper) 40/35 glass joint; dimensions are 37 mm o.d., 60 mm high. These "caps" are large enough to accommodate pre-cleaned tared 20-mL screwcap vials.

Desorption Equipment. The sorbent trap contains 125 mg each of Carbotrap and Carbotrap C (Supelco, Inc., Bellefonte, PA), which are packed and conditioned as described in Reference 1. The short-path thermal desorber (SPTD), Model TD-1 (Scientific Instrument Services, Ringoes, NJ), is installed and arranged as described in Reference 1. Sample residues are first dried at room temperature using ultrapure (99.9999%) helium for 2 min at 25-30 mL/min, then desorbed for 5 min at 150°C using ultrapure helium (3 mL/min).

Gas Chromatograph, Automatic Sampler, Chemiluminescent Nitrogen Detector (CLND), and Data System. An Antek Model 705D pyro-chemiluminescent nitrogen detector was retrofitted to a gas chromatograph (described below), with details given in Reference 1.

A Hewlett-Packard Model 5890 Series II gas chromatograph equipped with a split/splitless injector both supported and was physically interfaced to the SPTD ("low-level" procedure), CLND, data system, and automatic sampler ("high-level" procedure). One of the existing data interface boards was replaced with a Hewlett-Packard analog input board so that the output from the CLND could become part of the overall system network. The gas chromatographic parameters and conditions were optimized and are reported in Reference

(1). All gas chromatography was performed with a fused-silica capillary column, Rtx®-200 (Crossbond trifluoropropylmethyl), 3.00 µm film thickness, 0.53 mm i.d. x 30 m (Restek Corp., Bellefonte, PA) connected to a deactivated and uncoated fused silica guard column, 0.53 mm i.d. x 5 m using a Universal Press-Tight connector (Restek).

When the "high-level" procedure was used, a Hewlett-Packard Model 7673 Automatic Sampler replaced the short-path thermal desorber and injected 2 µL sample on column. The gas chromatographic operating parameters are the same as those described above with the exception of the purge valve settings, which are "OFF" at 0.00 min and "ON" at 0.25 min.

The presence of NDMA in contaminated groundwaters was verified using a Hewlett-Packard Model 5972 GC/MS equipped with a DB-5 analytical column (30 mm x 0.25 mm i.d., 1 µm film thickness). The column oven temperature was programmed from 40°C (hold for 4 min) to 310°C (hold for 14 min) at 10°C/min. Dwell time was maintained at 1000 msec. The presence of NDMA was established by its retention time (8.3 min) and two major m/e ratios (74 and 42). The presence of the surrogate d_4-dichloromethane was verified using its retention time (14.7 min) and major m/e ratios (150 and 152).

Procedure: Aqueous samples are filtered simultaneously through C_{18} and carbon-based Empore disks under vacuum at approximately 40-50 mL/min (a 1-L sample such as drinking water or filtered groundwater, which contains little or no particulate matter, is typically finished in approximately 20 min). The extraction apparatus is then dismantled; the C_{18} disk is set aside or may be used for related independent analyses. The carbon-based Empore disk is transferred to the second all-glass filter support where the "cap" has replaced the normal 1-L filtration flask, then dried for 10 min under vacuum. When the disk is thoroughly dry, a precleaned tared 20-mL screwcap vial is placed in the "cap," which is then reattached to the all-glass filter support. A 3-mL aliquot of highest-purity dichloromethane is added to the reservoir. After the solvent remains over the carbon-based disk for 1 min, it is drawn through the disk under vacuum (*slowly*, if at all possible); approximately 2 mL is collected in the screwcap vial. The vial is then reweighed to determine the mass (and later, the accurate volume) of the dichloromethane extract.

The determination of NDMA at ultratrace concentrations (between 2 and 40 ng of NDMA/L water) proceeds in the manner described in Reference 1. A 100 µL aliquot of the dichloromethane concentrate is added slowly to the Carbotrap C end of the dual sorbent trap, allowing sufficient time for the liquid to soak into the trap bed. The trap is then mounted into the short-path thermal desorber (Carbotrap C end is connected to the "top tube" without the needle attached) and dried with ultrahigh purity helium for 2 min at 25-30 mL/min. This procedure is repeated, leaving the residues from 200 µL of concentrate on the trap. The trap is then disconnected from the "top tube" and inverted. The needle is connected to the Carbotrap C end of the trap, and the remaining Carbotrap end is screwed into the "top tube." The residues present on the trap are then desorbed directly from the sorbent trap onto the guard and analytical gas chromatographic columns, both maintained at 35°C, using a 150°C desorption temperature maintained for 5 min and a helium desorption flow rate of 3 mL/min. The column oven temperature program commences immediately after completion of desorption.

The extraction procedure for "high" levels of NDMA, typically exceeding 300 ng of NDMA/L water, is the same as that described above. Upon completion of the carbon disk extraction, the dichloromethane extract is transferred to a 2-mL amber autosampler screwcap vial equipped with a Teflon®/Silicone/Teflon® septum (National Scientific Co., Lawrenceville, GA). A 2 µL aliquot is injected onto the column using the automatic sampler, and analyzed using the gas chromatographic conditions described above.

RESULTS AND DISCUSSION

The MDL values for both the "low-" and "high-" level procedures were calculated as described in Reference (8). In the "low-level" procedure, eight (minimum seven required) 1-L synthetic groundwater samples were fortified to 10 ng NDMA/L and analyzed as described above. The standard deviation, which was calculated for both seven and eight replicates, was then multiplied by the appropriate one-tailed Student's-t statistic for 99% confidence. The resulting value is the MDL, approximately 2 ng of NDMA/L when all eight experimental data points. When the "best seven" values were employed (that is, those with the smallest spread), were employed, the MDL was reduced to 1 ng of NDMA/L groundwater. A similar approach was taken for the "high-level" procedure, where the eight groundwater samples were fortified to 1000 ng NDMA/L. The MDL calculated using all eight data was 180 ng of NDMA/L; that using the "best seven" data (that is, those with the smallest spread) was 100 ng of NDMA/L. All raw and calculated data are presented in Table 1.

The performance of the disk-based procedure was evaluated initially by quantitating NDMA in two small batches of drinking and contaminated groundwater samples. In both cases, additional QA/QC samples were analyzed to ensure the quality of the results. The latter included dichloromethane solvent blanks (no detectable NDMA), synthetic groundwater blanks (NDMA detected at levels at or below the MDL), and synthetic groundwater samples which had been fortified to 10 ng of NDMA/L (NDMA detected at a minimum recovery of 55%). These results were deemed sufficient to consider the resulting NDMA concentration data valid.

This procedure was challenged rigorously during a sampling campaign at a military defense site during the fall of 1995. Approximately 100-200 individual groundwater samples, with accompanying blanks and matrix spikes, were withdrawn from monitoring wells and analyzed. While most of these samples were processed without difficulty, a modest number required additional modifications to the procedure described above. Heavily-contaminated samples frequently required an additional C_{18} Empore disk to reduce the number of extraneous peaks. Furthermore, the presence of mustard gas by-products and degradation products, such as dithiane and thioxane (oxathiane), in substantial concentrations in the groundwater samples suppressed the chemiluminescent signal for NDMA. The reasons for this effect are not well understood at this time.

The concentration of NDMA in most of the samples examined was below the MDL calculated above. A number of the monitoring wells were resampled in February 1996. The resulting groundwaters were not only re-analyzed, but the presence or absence of NDMA was confirmed by GC/MS in the single-ion monitoring (SIM) mode. The resulting data are presented in Table 2. In general, there is good agreement between the chemiluminescence and GC/MS-SIM data, particularly for the resampled data set. Furthermore, the agreement between all data for a given site (Fall 1995 and February 1996) is generally acceptable if NDMA was detected above approximately 20 ng/L.

SUMMARY

The above discussion demonstrates that analytical procedures based on carbon-based extraction membrane disks are capable of quantitating NDMA in aqueous samples with recoveries equal to or greater than existing procedures which employ conventional overnight dichloromethane extractions. The detection limits using the disks were calculated using a procedure given in the *Code of Federal Regulations*; the values were virtually interchangeable with those obtained previously[1]. When the "low-level" (2-40 ng of NDMA/L) and the "high-level" (100-4000 ng of NDMA/L) procedures are used in a tandem, it is possible to quantitate NDMA over approximately three to four orders of magnitude. In cases where the aqueous NDMA sample concentration falls between the upper bound of the "low-level" procedure and the lower bound of the "high-level" procedure, an accurate quantitation may be performed by simply spiking dichloromethane concentrate volumes smaller than the usual 200 µL on the dual-sorbent trap. It has been demonstrated[1] that the trap performance is independent of the volume of dichloromethane applied to it, up to at least 200 µL. Procedures which employ the membrane extraction offer considerable savings in both labor and the volume of hazardous waste organic solvent produced compared to conventional methodology. In this case, the volume of dichloromethane employed was reduced ***one-hundredfold*** compared to that required by conventional continuous extractions. Furthermore, the overall turnaround time for a lot of eight samples was improved from three days to a single day. It was also feasible to process a single "emergency" sample within three hours.

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Table 1. Calculation of MDL Values for the "Low-Level" and "High-Level" Procedures for NDMA in Groundwater

Replicate No.	"Low-Level" Procedure[a] Calculated NDMA (ng/L)[b]	"High-Level" Procedure[c] Calculated NDMA (ng/L)[b]
1	7.4	710
2	7.0	680
3	6.8	660
4	6.6	710
5	8.6	680
6	7.0	740
7	7.0	560
8	7.6	750
Standard deviation, all samples	0.6	60
MDL, all samples[d], ng/L	2	180
Standard deviation, "best seven" samples	0.3	30
MDL, "best seven" samples[e], ng/L	1	100

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[a] Spiked water concentration is 10 ng NDMA/L.

[b] Values not corrected for recovery

[c] Spiked water concentration is 1000 ng NDMA/L

[d] Student's t-value (one-tailed) at 99% confidence, eight samples = 2.988.

[e] Student's t-value (one-tailed) at 99% confidence, seven samples = 3.143.

Table 2. Summary of NDMA Results on U. S. Geological Survey Resampling by Chemiluminescence (CLND) and by GC/MS in the SIM Mode

	Original Sampling	Resampling		
Sample ID	CLND ng NDMA/L[a]	CLND ng NDMA/L	GC/MS SIM, ng NDMA/L, by area	GC/MS SIM, ng NDMA/L, by height
Method blank	<5	1	<5[b], *1*[c]	<5, *1*
50 pptr spike/H_2O	40	29, 32	52, *74*	81, *120*
A	20	2	<5, *2*	<5, *3*
B	20	2	<5, *3*	<5, *3*
C	<5	4	5, *9*	5, *10*
D	<5	5	5, *8*	5, *10*
E	<5	1	<5, *2*	<5, *2*
F	<5	1	<5, *1*	<5, *1*
G	29	24	33, *54*	38, *85*
H	34	27	27, *39*	33, *65*
I	26	19	24, *41*	25, *54*
J	<5	2	<5, *2*	<5, *2*
Matrix spike	42	26	41, *61*	49, *100*
K	21	11	12, *18*	11, *17*
Method Blank	<5	1	<5, *1*	<5, *1*
50 pptr spike/H_2O	39	35	50, *68*	50, *61*
L	21	12	14, *17*	14, *19*
M	43	68	104, *178*	134, *225*
N	<5	2	<5, <5	<5, *2*
O	<5	1	<5, *1*	<5, *1*
Matrix spike	36	26	31, *40*	30, *34*
40 ng/mL standard	Not performed	Not performed	53, *86*	47, *75*

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[a] Chemiluminescence method employs method of external standards exclusively for calculation of NDMA concentrations

[b] First number given uses the method of external standards to calculate NDMA concentration by GC/MS SIM.

[c] Italicized number uses the method of internal standards to calculate NDMA concentration by GC/MS SIM.

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8. Appendix B to Part 136—Definition and Procedure for the Determination of the Method Detection Limit—Revision 1.11. *Code of Federal Regulations: Protection of the Environment,* Parts 100-149; Title 40; U. S. GPO: Washington, DC, Revised Jul 1, 1990.

9. *Program Manager for Rocky Mountain Arsenal: Chemical Quality Assurance Plan.* Version 1, Sep 1993.

10. The carbon-based Empore disks are currently not available through normal vendors. They should be ordered directly through: Mr. Chuck Haskins, National Sales Manager; 3M; Building 220-9E-10; St. Paul, MN 55144-1000.

11. Physical parameters of the disks: Carbon type, acid-washed coconut charcoal. Surface area > 1000 m^2/g. Nominal particle diameter, 15-20 μm. Weight of carbon in the disk, ca. 90% w/w of the disk (about 400-450 mg). Pore size distribution is proprietary.

DISCLAIMER