Analysis of Nitrosamines in Drinking Water Using the Agilent 5977A Series GC/MSD System

Application Note

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Abstract

A method has been developed on the Agilent 5977A Series GC/MSD System that can provide detection of N-nitrosamines in water at sub-part per trillion (ppt) levels and with limits of detection (LOD) that are well below those cited in EPA Method 521.

Introduction

Chloramination is used in wastewater treatment facilities to reduce trihalomethanes which have been associated with an increased risk of bladder cancer. However, nitrosamines such as N-nitrosodimethylamine (NDMA) are inadvertent by-products of wastewater treatment through chloramination. NDMA itself has been classified by national and international regulatory authorities as a probable human carcinogen, and numerous laboratory animal studies have linked NDMA exposure to various cancers.

NDMA is considered a priority pollutant, but few regulatory limits exist for the concentration of NDMA in the environment and drinking water in particular. However, a number of international, national, and subnational authorities have set regulatory guidelines or assessment levels for nitrosamines in drinking water. California has established a notification level of 10 ng/L (ppt). Internationally, the World Health Organization in 2008 added NDMA to its guidelines for drinking water quality. In March 2010, Health Canada proposed a maximum acceptable concentration for NDMA in drinking water of 0.04 µg/L.

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As of October 2009, the US Environmental Protection Agency (EPA) listed five nitrosamines, including NDMA, on its contaminant candidate list, a list of priority drinking water contaminants for which EPA will research whether regulations are needed. The EPA has established Method 521 for the determination of nitrosamines in drinking water by solid phase extraction and capillary column gas chromatography with large volume injection and chemical ionization tandem mass spectrometry (MS/MS). This application note demonstrates the ability of the 5977A Series GC/MSD System to exceed the LOD stated in Method 521 by almost an order of magnitude, without the need for large volume injection or the use of MS/MS.

Experimental

Standards and Reagents

Standards and solvents were commercially obtained, and calibration curves and working standards were prepared in methylene chloride using the Agilent 7696A Sample Prep WorkBench.

Instruments

This method was developed on an Agilent 7890B gas chromatograph equipped with a multimode inlet (MMI) and coupled to a 5977A Series GC/MSD System in positive chemical ionization (PCI) mode. Table 1 lists the instrument conditions.

Sample Preparation

One-half liter water samples were extracted using solid phase extraction (SPE) procedures similar to those described in EPA Method 521. NDMA-d6 was added to samples as a surrogate before sample preparation to monitor extraction efficiency. The analytes were eluted from the SPE column in methylene chloride, and the volume was reduced to 1 mL using a gentle stream of nitrogen at room temperature. The final concentration factor was 500 fold. NDPA-d14 was then added as an internal standard.

Acquisition Parameters

Table 2 shows the acquisition parameters used.

Table 1. Agilent 7890/5977A Gas Chromatograph and Mass Spectrometer Conditions

GC run conditions

Analytical column	VF-624ms 20 m × 0.15 mm, 0.84 µm (p/n CP9100)
Inlet temperature	250 °C
Injection mode	Splitless
Injection volume	2 µL
Liner	Low pressure drop, ultra inert liner with glass wool (p/n 5190-2295)
Flow	Constant flow, 1 mL/min
Oven program	35 °C for 4 minutes 10 °C/min to 195 °C 15 °C/min to 240 °C Hold at 240 °C for 2 minutes
Carrier gas	He
Transfer line temperature	280 °C

PCI MS conditions

Solvent delay	8.5 minutes
Acquisition mode	Full scan mode, m/z 40 to 200; single ion monitoring (SIM)
Gain factor	1
CI gas flow	Methane 20%
Extractor source temperature	300 °C
Quadrupole temperature	150 °C

Table 2. Agilent 5977A Series GC/MSD System Acquisition Parameters

Nitrosamine	RT (min)	Target ion	Qualifier ion
N-Nitrosodimethylamine (NDMA)	9.97	75	115
Deuterated N-Nitrosodimethylamine (NDMA-d6)	9.95	81	121
N-Nitrosomethylethylamine (NMEA)	11.68	89	129
N-Nitrosodiethylamine (NDEA)	13.02	103	131
N-Nitrosopyrollidine (NPYR)	16.06	131	159
N-Nitrosodi-n-propylamine (NDPA)	16.43	101	141
Deuterated N-Nitrosodi-n-propylamine (NDPA-d14)	15.94	145	173
N-Nitrosopiperidine (NPIP)	16.97	115	143
N-Nitrosodi-n-butylamine (NDBA)	19.03	159	187

Results and Discussion

Method Performance

Calibration curves performed using standards in methylene chloride from 0.5 to 50 parts per billion (ppb) exhibited high linearity, with correlation coefficients (R^2) no lower than 0.9985, and an average R^2 value across all six nitrosamines of 0.9992 (Figure 1). The use of automation such as the Agilent 7696A Sample Prep WorkBench to prepare standards assures reproducible R^2 values.

The LOD, defined as 3.3 times the standard deviation at 0.5 ppb, were determined for the standards in methylene chloride, using seven replicates. These varied from as low as 0.018 ppb to as high as 0.166 ppb. The limits of quantitation (LOQ) defined by the EPA as 10 times the LOD, ranged from 0.187 ppb to 1.662 ppb (Table 3).

These LOD values were compared to the values listed in Method 521, both for the determined concentration after 500 fold concentration, and the equivalent concentration in the original sample. In spite of the fact that a 2-µL injection
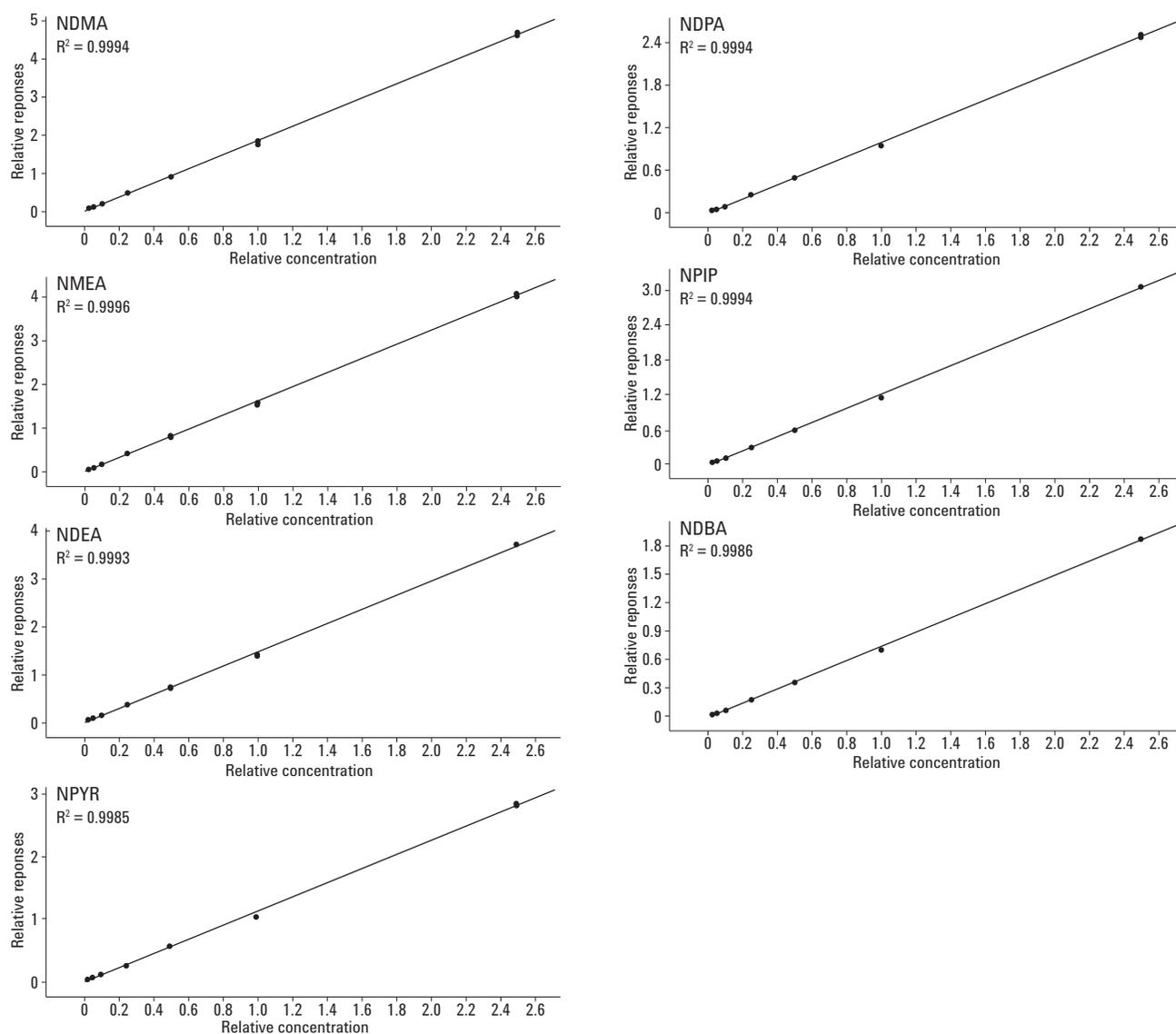

Figure 1.   Calibration curves for nitrosamine standards in methylene chloride: 0.5, 1, 2, 5, 10, 20, and 50 ppb.

Table 3. *LOD and LOQ for Nitrosamine Standards in Methylene Chloride (ppb)*

| | Replicate number | | | | | | | | | |
	1	2	3	4	5	6	7	SD	LOD (SD*3.3)	LOQ (LOD*10)
NDMA*	0.789	0.788	0.794	0.800	0.784	0.786	0.784	0.006	0.019	0.187
NMEA	0.736	0.733	0.717	0.727	0.719	0.739	0.726	0.008	0.028	0.275
NDEA	0.793	0.804	0.793	0.798	0.805	0.791	0.798	0.006	0.018	0.182
NPYR	0.774	0.802	0.780	0.729	0.798	0.856	0.805	0.038	0.133	1.330
NDPA	0.890	0.826	0.833	0.800	0.953	0.868	0.861	0.050	0.166	1.662
NPIP	0.846	0.814	0.857	0.846	0.860	0.824	0.846	0.017	0.057	0.572
NDBA	0.998	1.026	0.969	1.002	1.023	0.978	1.084	0.038	0.126	1.263

*Analyte concentration 0.5 ppb
SD: Standard deviation
LOD: Limit of Detection
LOQ: Limit of Quantitation

was used as opposed to the 20-µL injection called for in Method 521, the LODs determined on the 5977A Series GC/MSD System ranged from 1.9 to 11 fold lower (Table 4). This increased sensitivity was achieved with a single quadrupole and single ion monitoring, versus the tandem mass spectrometer (MS/MS) used in Method 521.

Conclusion

Using only a 2-µL injection and PCI with methane, the Agilent 5977A Series GC/MSD System can provide the sensitivity, reproducibility, and reliability required to detect sub-part ppt of nitrosamines in water, at LOD below those cited in EPA Method 521.

Table 4. *Comparison of LODs with Method 521*

	EPA 521 METHOD		Agilent 5977A Series GC/MSD System	
	After 500x concentration (ppb)	Equivalent sample concentration (ppt)	After 500x concentration (ppb)	Equivalent sample concentration (ppt)
NDMA	0.14	0.28	0.019	0.038
NMEA	0.14	0.28	0.028	0.050
NDPA	0.16	0.32	0.166	0.332
NDEA	0.13	0.26	0.018	0.036
NPYR	0.175	0.35	0.133	0.260
NPIP	0.33	0.66	0.057	0.114
NDBA	0.18	0.36	0.126	0.252

For More Information

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