

Determination of Ten Nitrosamines in Drinking Water by Gas Chromatography/Electron Ionization Tandem Mass Spectrometry

ASMS 2013 WP-027

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1. Introduction

N-nitrosamine compounds exhibit mutagenic, carcinogenic, and teratogenic activities. It is demonstrated that *N*-nitrosamines developed a carcinogenic effect in a wide range of animal species like fishes, reptiles, birds, and mammals, including five species of primates. In 1989, *N*-nitrosodimethylamine (NDMA) was found in tap water in Ontario, Canada, and was identified as disinfection byproduct. Since then, researchers have discovered many *N*-nitrosamine compounds in drinking water. U.S. Environmental Protection Agency established risk significant levels from 1 to 15 ng/L for seven nitrosamines in drinking water, and for this reason, a sensitive and selective method for trace analysis for these compounds is required.

The most commonly method for trace analysis of *N*-nitrosamines is US EPA method 521, determination of *N*-nitrosamines in drinking water by solid phase extraction and gas chromatography with large-volume injection and chemical ionization mass spectrometry. In this paper, a gas chromatography/electron ionization-tandem mass spectrometry method for quantification and validation of *N*-nitrosamines in drinking water is described.



2. Method and Materials

Sample Preparation

N-nitrosamine standards were purchased from Sigma-Aldrich (Shanghai, China). Stock solution of mixed *N*-nitrosamines were prepared to concentration of 10 mg/L in dichloromethane. A series of standard solutions were prepared in dichloromethane, each standard solution contained 20 µg/L of NDPA-d14 as internal standards.

Ultrapure water was produced by using Milli-Q integral system. Target compounds were enriched in carbon GCB coupled with coconut charcoal cartridge. After the extraction was completed, the cartridge was dried by applying vacuum. The extract was eluted by dichloromethane, and then evaporated to 1 mL with a gentle stream of nitrogen.

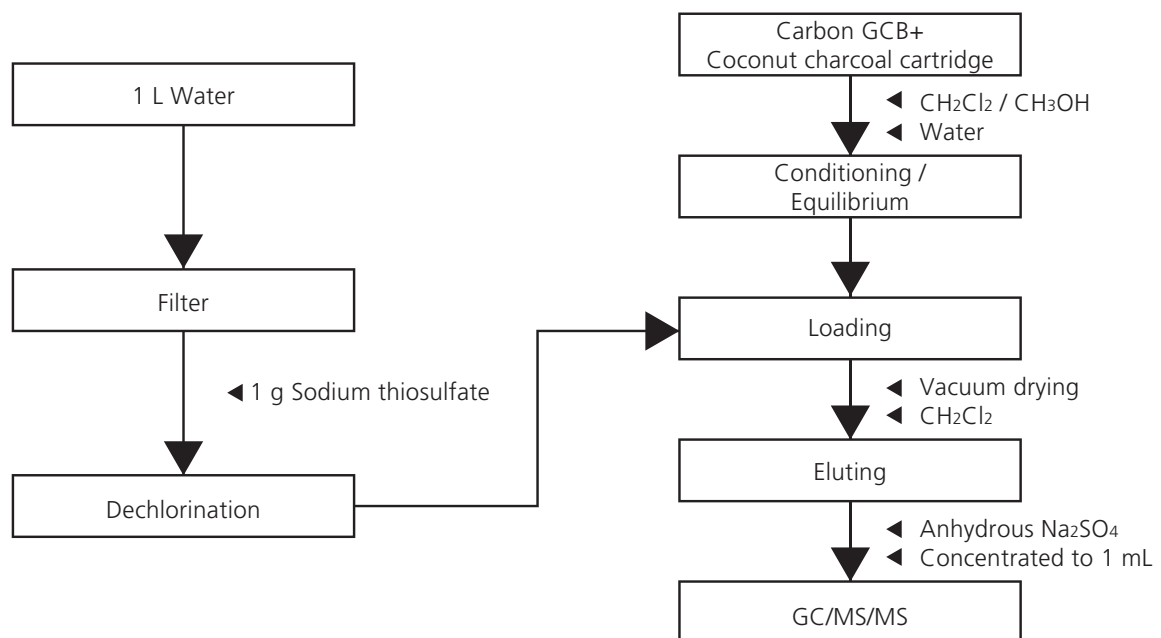


Fig. 1 Scheme of solid phase extraction procedure

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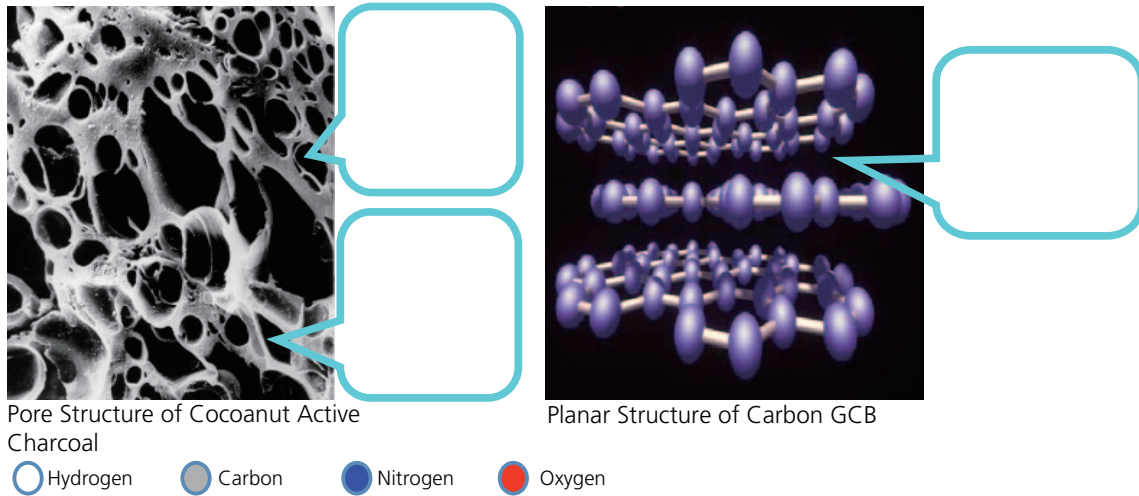


Fig. 2 Enrichment of *N*-nitrosamines in SPE cartridges

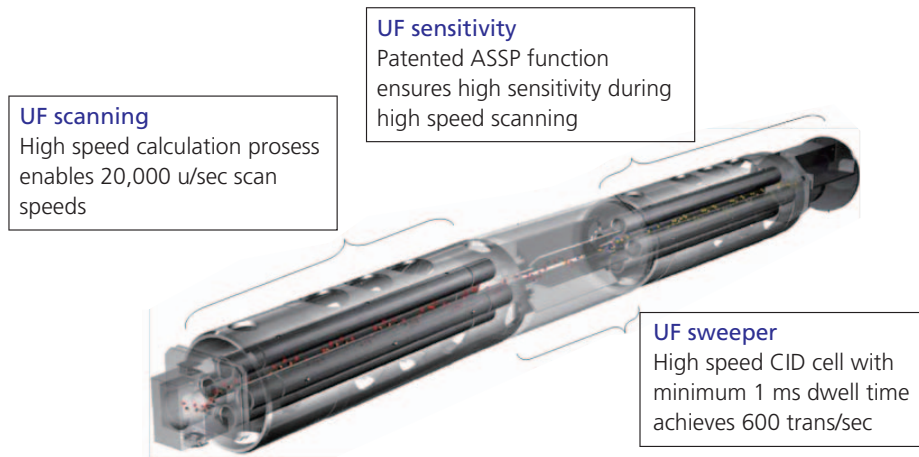


Fig. 3 High-performance supported by "UF technologies"

Instrument conditions

Final solution were analyzed with MRM mode using a gas chromatograph-triple quadrupole mass spectrometer (GCMS-TQ8030, Shimadzu Corporation, Japan.).

GC

Column : Stabilwax, 30 m × 0.25 mm, 0.25 μm
 Carrier gas : He
 Constant linear velocity : 40 cm/sec
 Injector temperature : 230°C
 Injection mode : Splitless, 1min
 High pressure injection : 250 kPa, 1min
 Oven temperature : 60°C (2 min)-8°C/min-140°C (8 min)-30°C/min-240°C (10 min)
 Injection volume : 2 μL

MS/MS

Ionization : Electron ionization
 Ion source temperature : 200°C
 Interface temperature : 240°C
 Solvent cut time : 5.5 min
 Monitoring mode : MRM

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3. Results and discussion

MRM chromatograms

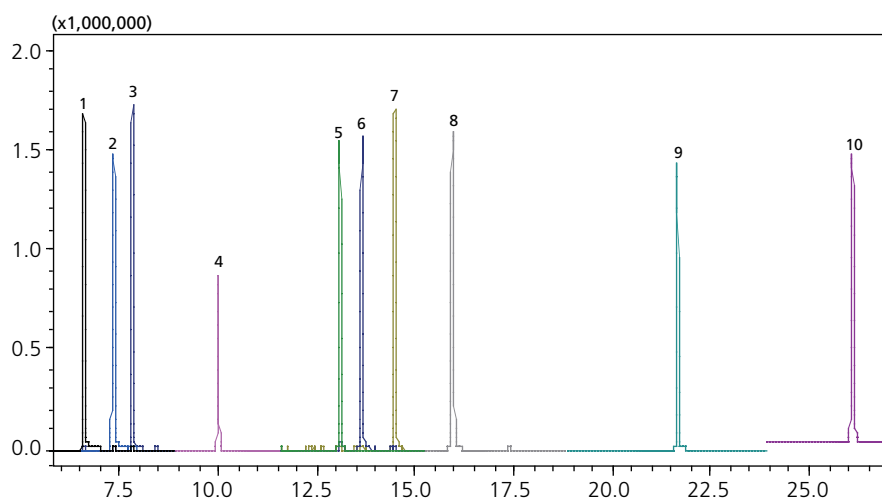


Fig. 4 Chromatograms obtained from 100 µg/L *N*-nitrosamines standard solution in MRM mode

Table 1 Name, retention times, structure and MRM parameters of investigated *N*-nitrosamines

ID	Compound Name	Abbreviation	Retention Time (min)	Molecular Structure	Precursor ion>Product ion (m/z)	CE (V)
1	<i>N</i> -nitroso dimethylamine	NDMA	7.350	<chem>CN(C)N=O</chem>	74.00>42.00 74.00>44.00	21 7
2	<i>N</i> -nitroso methyl-ethylamine	NMEA	8.158	<chem>CCN(C)N=O</chem>	88.00>71.00 88.00>57.00	5 10
3	<i>N</i> -nitroso diethylamine	NDEA	8.658	<chem>CCN(CC)N=O</chem>	102.00>85.00 102.00>57.00	5 13
4	<i>N</i> -nitroso dipropylamine	NDPA	10	<chem>CCCN(C)N=O</chem>	130.00>113.00 130.00>102.00	5 5
5	<i>N</i> -nitroso dibutylamine	NDBA	14.075	<chem>CCCCN(C)N=O</chem>	158.00>141.00 158.00>99.00	5 9
6	<i>N</i> -nitroso piperidine	NPIP	14.258	<chem>C1CCN(C1)N=O</chem>	114.00>84.00 114.00>55.00	9 20
7	<i>N</i> -nitroso pyrrolidine	NPYR	14.350	<chem>C1CCN(C1)N=O</chem>	100.00>70.00 100.00>68.00	7 9
8	<i>N</i> -nitroso morpholine	NMOR	14.625	<chem>C1CCN(C1)N=O</chem>	116.00>86.00 116.00>56.00	5 12
9	<i>N</i> -nitroso diphenylamine	NDPhA	15.467	<chem>C1=CC=C(C=C1)N(C2=CC=CC=C2)N=O</chem>	169.00>141.00 169.00>115.00	26 30
10	<i>N</i> -nitroso dibenzylamine	NDBzA	16.942	<chem>C1=CC=C(C=C1)CN(C2=CC=CC=C2)N=O</chem>	226.00>181.00 226.00>166.00	20 5

Linearity range, detection limits, repeatability and recoveries

To test linearity of the calibration curve, various concentration of the ten *N*-nitrosamines ranging from 1 to 100 µg/L were analyzed. Calibration curves were constructed by calculating the ratio of peak area of the reference standard to that of the internal standard

(NDPA-d14). A good linearity was obtained for each compound in this range (six-point calibration). The correlation coefficients ranged from 0.9995 to 0.9999.

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Spiked mixed standard solution into blank samples. The final concentration of spiked samples was 5 ng/L. The average recoveries ranged from 73.2% to 97.6%, with

%RSD less than 10% (n=5). The limit of detection of 10 N-nitrosamines examined were below 0.05 ng/L.

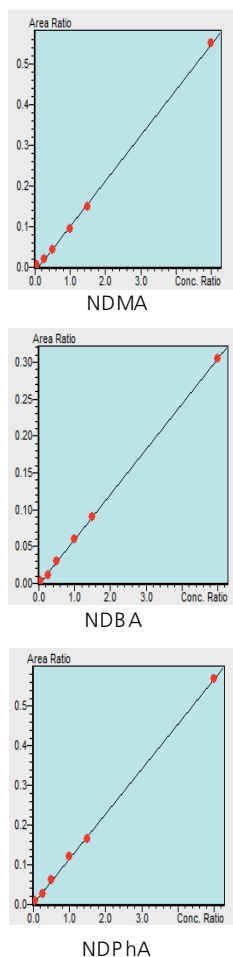


Fig. 5 Calibration curves of 3 N-nitrosamines

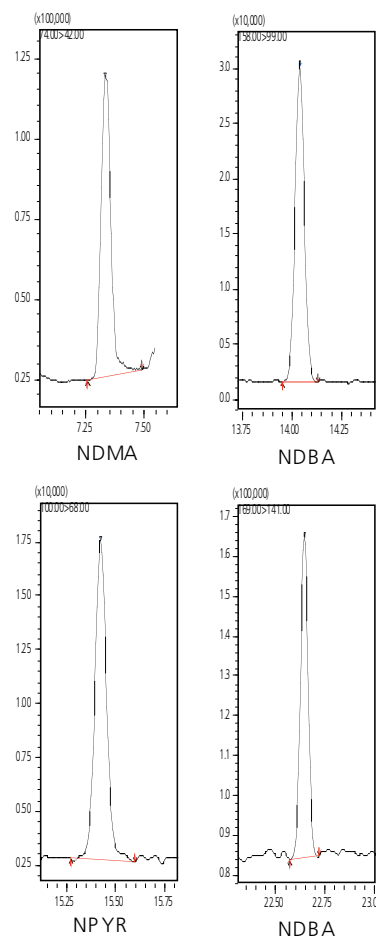


Fig. 6 Chromatograms obtained from 0.1 µg/L N-nitrosamines standard solution

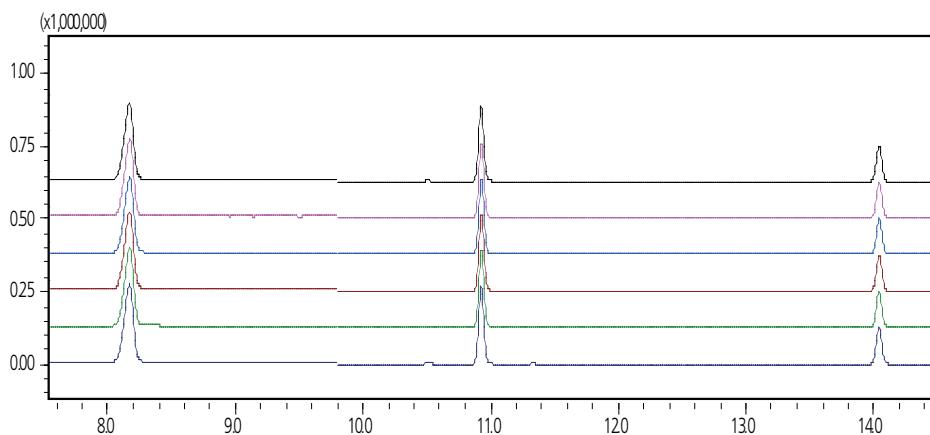


Fig. 6 Repeatability of NMEA, NDPA, NDBA in concentration of 0.5 µg/L

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4. Conclusions

A simple and rapid procedure is described for the determination of 10 *N*-nitrosamines in drinking water, using solid-phase extraction and GC/MS/MS. With high sensitivity, good linearities, and low MDL, this method is a

very useful tool for monitoring and determination of *N*-nitrosamines in drinking water.