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Determination of nitrosamines in water by liquid chromatography tandem mass spectrometry

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Introduction

Nitrosamines

Nitrosamines, particularly nitrosodimethylamine (NDMA), are contaminants found in drinking water and of interest to the environmental community due to potential health concerns. NDMA is found in high concentrations and produced by industrial sources such as direct contamination from the manufacture of rocket fuel. In addition, NDMA is a disinfection by-product from the chlorination, chloramination, and ozonation of drinking water and wastewater [1].

The World Health Organization (WHO) issued a health advisory level for NDMA in drinking water at 100 ng/L[2]. The Canadian Health Association regulates the maximum allowable level of NDMA in drinking water at 40 ng/L[3]; However, in China, no maximum allowable levels for nitrosamines are regulated in either drinking water or environmental water.

The USEPA method 521 analyzes nitrosamines with an Ion-Trap and can be modified to use a GC-MS/MS in EI mode to achieve sub ng/L detection levels in drinking water as described elsewhere[4]. Here we demonstrate a sensitive and precise method for the determination of eight common nitrosamines in water using liquid chromatography-tandem mass spectrometry.

Agilent 1290 Infinity II UHPLC Parameters		
Column	Agilent Poroshell 120 EC-C18 （100mm×2.1mm， 2.7μm）	
Column temp	40 ℃	
Injection volume	10 μL	
Mobile phase	A: 0.1% formic acid in water B: Methanol	
Flow rate	0.4 mL/min	
Gradient	Time (min)	B (%)
	0	5
	1	20
	4	95
	6	95
Post time	3 min	

Table 1: LC Parameters

Experimental

Sample preparation

Water samples were filtered using 0.22 μm membrane and then internal standard D_{14}-NDPA was added. 500 mL of the filtrate was prepared in accordance with the procedure outlined in the USEPA method 521[5]. After SPE steps, extracts were ultimately concentrated to dryness and re-constituted to a 1 mL volume with 5% methanol in water for analysis using LC-MS/MS.

Instrument parameters

The LC-MS analysis was performed using Agilent 1290 Infinity II UHPLC system coupled to Agilent 6470 triple quadrupole mass spectrometer. Poroshell EC-C18 column was chosen to separate eight compounds efficiently. The mobile phase A, 0.1% formic acid in water, and B, methanol, were used and the linear gradient eluted from 5 % to 95 % B in 4 minutes. The flow rate was 0.4 mL/min. 2 MRM transitions were monitored in APCI positive mode for each compound. The detailed LC and MS parameters were shown in table 1 and table 2.

Agilent 6470 Triple Quad MS Parameters	
Ionization source	APCI (positive mode)
Gas temperature	325 ℃
Gas flow	4 L/min
Nebulizer	35 psi
Vaporizer	250 ℃
Capillary	3000 V
Corona current	4 μA

Compound	Precursor ion(m/z)	Product ion(m/z)	Fragmentor (V)	Collision energy (V)
NDBA	159.2	41.1/57.1	80	25/14
NDEA	103.1	47.1/75.1	90	17/9
NDMA	75.1	43.1/58	90	18/12
NDPA	131.2	43.1/89.1	80	14/9
NMEA	89.1	43.1/61.1	80	11/12
NMor	117.1	45.1/87.1	80	21/11
NPip	115.1	41.1/69.1	100	25/15
NPyr	101.1	41/55.1	90	30/19
NDPA-d14	145.1	50.1/97	100	16/11

Table 2: MS Source and MRM Parameters

Nitrosamines MRM chromatogram

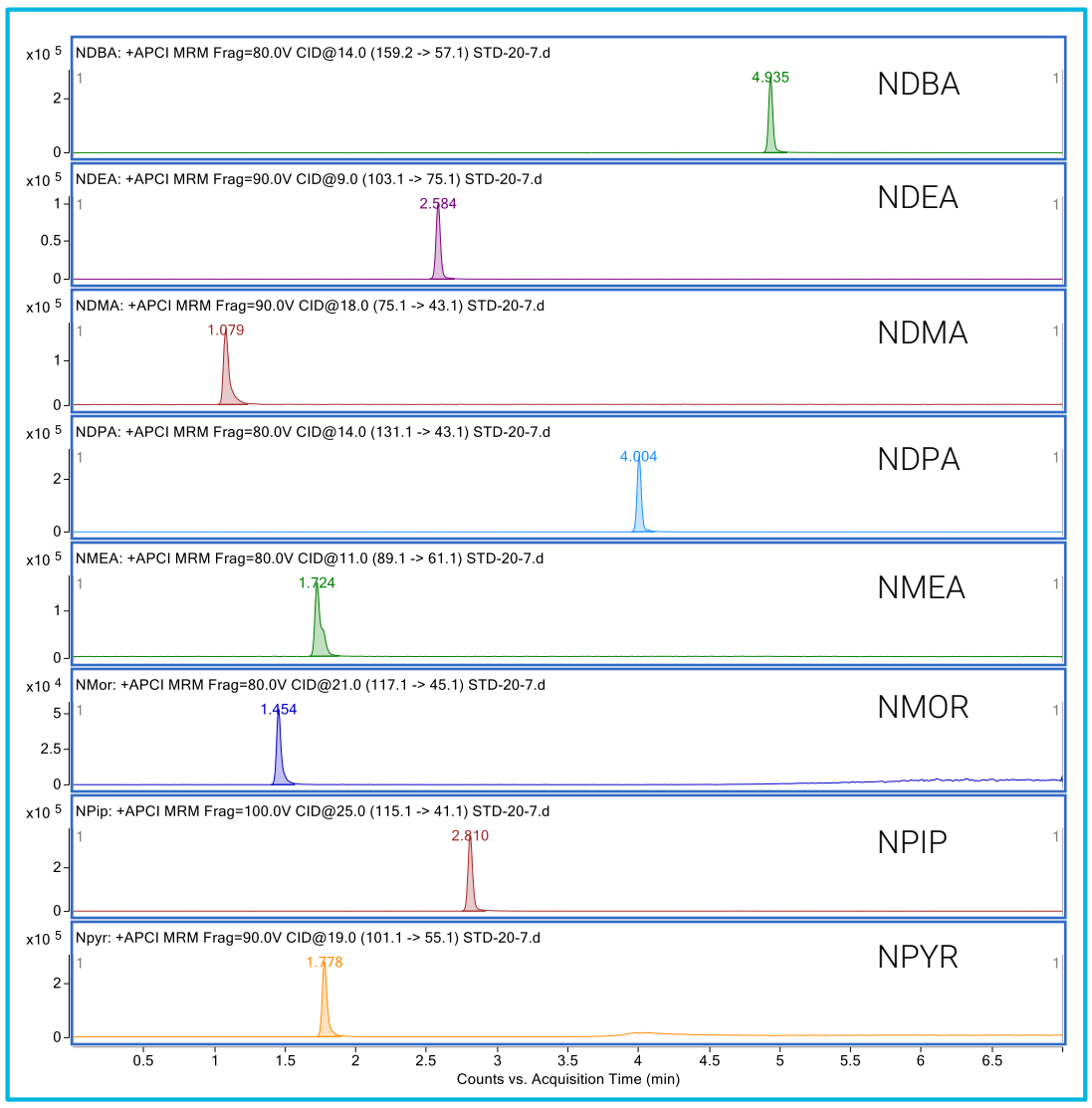

Figure 1 Nitrosamines MRM chromatogram at 20 µg/L

Method linearity

The calibration solution was prepared from the standard mixture solution, with concentrations ranging from 1 to 200 µg/L, and internal standard at a concentration of 10 µg/L. These concentrations in the extract would correspond to 2~400 ng/L in the actual water sample with the 500 fold concentration factor obtained through SPE. The ratios of the peak area of the target compound over the peak area of its internal standard were plotted against the ratios of the concentrations for the target and internal standard in the solution. Figure 2 shows the calibration curves of 8 nitrosamines. All compounds show excellent linear relationship in the range of 1~200 µg/L, with the linear regression coefficients reaching 0.996.

Sensitivity

The sensitivity of the method was demonstrated at a 1 ng/L spiking level of nitrosamines in pure water and the limits of detection (LOD) is calculated as 3 times of signal-to-noise ratio (S/N). As shown in table 3, the LOD for all compounds are less than 0.5 ng/L. The developed method has the capacity to detect extremely low, trace amounts of nitrosamines in water.

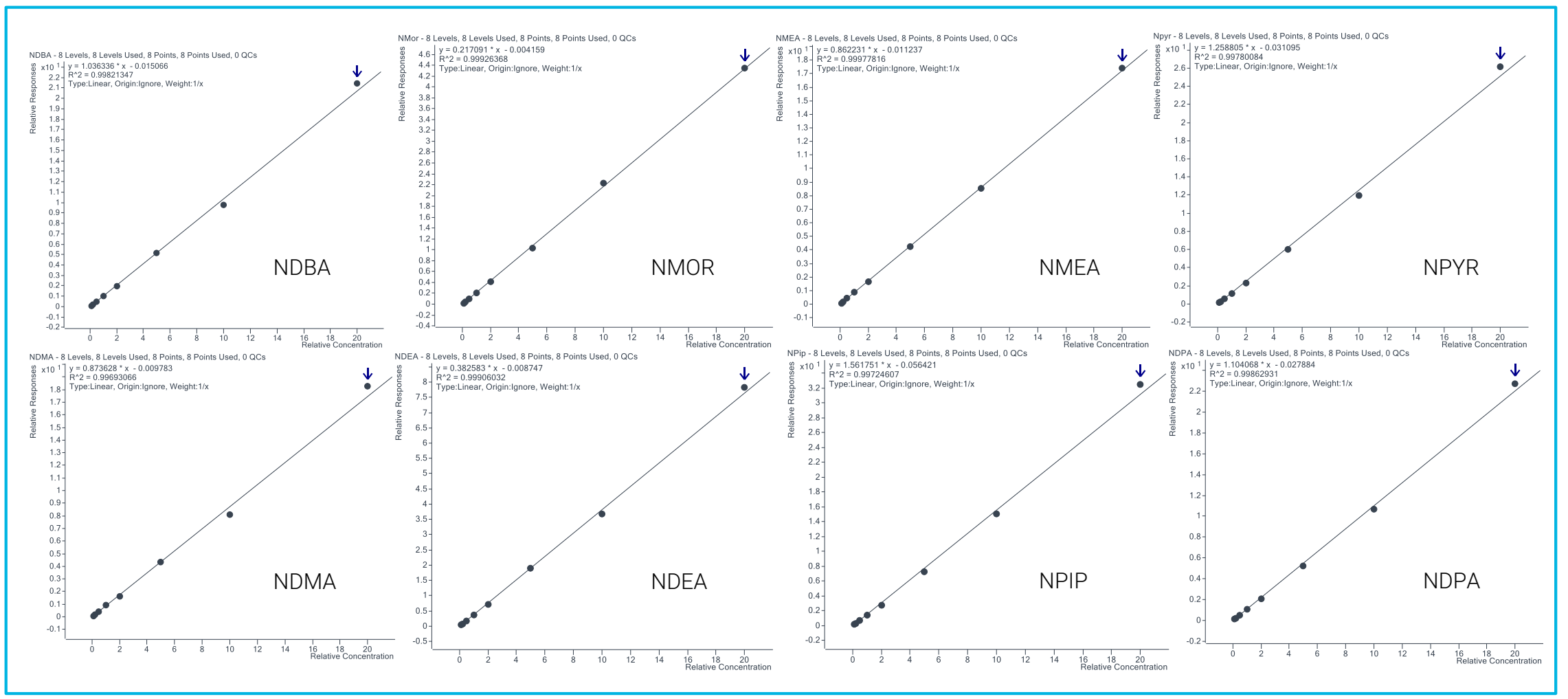

Figure 2 Calibration curves of 8 nitrosamines

Results and Discussion

Cmpd	LOD (ng/L)	5.0 ng/L		20.0 ng/L	
		Recovery(%)	RSD(%)	Recovery(%)	RSD(%)
NDMA	0.11	68.1	3.8	74.2	4.8
NMOR	0.27	67.3	4.5	81.8	4.5
NMEA	0.23	74.1	2.5	83.2	3.0
NPYR	0.34	74.5	4.8	85.5	3.6
NDEA	0.18	77.5	5.3	80.2	3.2
NPIP	0.19	79.7	3.9	89.4	2.7
NDPA	0.16	73.3	3.2	76.8	2.7
NDBA	0.16	74.5	2.9	83.3	1.9

Table 3 LOD and recovery of nitrosamines in river water (n=6)

Precision and Accuracy

Spiking experiments were used to evaluate the accuracy and precision of the method and river water was selected as test matrix. The average spiking recoveries at 5.0 ng/L and 20 ng/L levels range 67~89%, with relative standard deviations (n=6) within 1.9 %~5.3 %. (shown in table 3)

Real sample analysis

The method was used to monitor the level of 8 nitrosamines in surface water collected locally. The results suggested that local surface water contains a very low level of nitrosamines, and most compounds weren't detected in these samples.

Conclusions

The 1290 Infinity II LC, coupled with the 6470 quadrupole mass spectrometer, was applied to detect 8 common nitrosamines in environmental water. With SPE cleanup and enrichment, the LOD for nitrosamines in blank water can be as low as sub-ng/L. The isotopic dilution calibration demonstrates a good linear relationship within the test range of 1 to 200 µg/L, with regression coefficients as high as 0.996. The method is also accurate and precise, with spiking recoveries in tested matrices ranging from 67 to 89%, with RSDs within 1.9–5.3%. It demonstrates that the developed method is very sensitive, selective and accurate, and can meet the criteria for routine monitoring of trace nitrosamines in environmental water.

References

[1] Jeffrey W. A.; et al. Detecting N-Nitrosamines in Drinking Water at Nanogram per Liter Levels Using Ammonia Positive Chemical Ionization, Environ. Sci. Technol. 2004, 38, 18, 4835-4841

[2] Guidelines for Drinking-Water Quality, 3rd edition including 1st and 2nd addenda, 2008, World Health Organization

[3] Health Canada (2011). Guidelines for Canadian Drinking Water Quality: Guideline Technical Document — N-Nitrosodimethylamine. Water, Air and Climate Change Bureau, Healthy Environments and Consumer Safety Branch, Health Canada, Ottawa, Ontario. (Catalogue No H128-1/11-662E).

[4] Nitrosamines Analysis in Drinking Water Using GC/MS/MS—Meeting Equivalence to EPA Method 521, Agilent application note, 5991-9224EN

[5] 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), U.S. Environmental protection agency, EPA Document #: EPA/600/R-05/054

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