



Comparison of gas chromatography-mass spectrometry and gas chromatography-tandem mass spectrometry with electron ionization for determination of *N*-nitrosamines in environmental water



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HIGHLIGHTS

- Systemic comparison on *N*-nitrosamine analysis in water using GC-MS and GC-MS/MS-EI.
- Environmental water samples were analyzed to characterize the influence of the water matrix.
- Miscellaneous adverse effects were found using GC-MS.
- GC-MS/MS allowed the quantification of nine *N*-nitrosamines at the low-nanogram-per-liter level.

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ABSTRACT

N-nitrosamines are trace organic contaminants of environmental concern when present in groundwater and river water due to their potent carcinogenicity. Therefore, *N*-nitrosamine analysis is increasingly in demand. Gas chromatography-mass spectrometry (GC-MS) and GC-tandem mass spectrometry (GC-MS/MS), both with electron ionization (EI), were compared for analysis of nine *N*-nitrosamines extracted from environmental water matrices. A total of 20 fishpond water, river water, and groundwater samples from Sihui and Shunde, China were collected for a survey of *N*-nitrosamine concentrations in real water samples. Various solid-phase extraction (SPE) conditions and GC conditions were first examined for the pre-concentration and separation steps. The analysis of *N*-nitrosamines in environmental waters demonstrated that their quantification with GC-MS poses a challenge due to the occurrence of co-eluting interferences. Conversely, the use of GC-MS/MS increased selectivity because of the fragmentation generated from precursor ions in the 'multiple reaction monitoring' (MRM) mode, which is expected to extract target analytes from the environmental water matrix. Thus, the high performance of GC-MS/MS with EI was used to quantify nine *N*-nitrosamines in environmental waters with detection limits of 1.1–3.1 ng L⁻¹. *N*-nitrosodimethylamine (NDMA) concentrations were in the range of N.D. to 258 ng L⁻¹. Furthermore, other *N*-nitrosamines, except *N*-nitrosomethylethylamine (NMEA), *N*-nitroso-di-*n*-propylamine (NDPA) and *N*-nitrosopiperidine (NPIP), were also detected. Our findings suggest that GC-MS/MS with EI would be widely applicable in identifying *N*-nitrosamines in environmental waters and can be used for routine monitoring of these chemicals.

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1. Introduction

N-nitrosamines are exceptionally toxic to animals, potent human carcinogens, and mutagens (IARC, 2014). The occurrence of *N*-nitrosamines has been widely investigated in drinking water and wastewater, as these compounds have been recognized as an

emerging group of disinfection by-products, with the level reaching 700 ng L^{-1} (Liao et al., 2015; Zhou et al., 2009). River water and shallow groundwater are the main sources of drinking water. Therefore, the occurrence of *N*-nitrosamines in such environmental waters is of great concern.

N-nitrosamines have been detected in river water in China (Ma et al., 2012; Wang et al., 2016, 2011), the United States (Zhou et al., 2009), New Haven (Schreiber and Mitch, 2006), and Japan (Asami et al., 2009; Kosaka et al., 2010; Van Huy et al., 2011). The concentrations of *N*-nitrosamines in groundwater have been reported in China (Ma et al., 2012; Wang et al., 2016), the United States (Zhou et al., 2009), and Japan (Van Huy et al., 2011). The occurrence of *N*-nitrosamines in river water is commonly attributed to the release of recycled water from wastewater treatment plants, industrial by-products, and domestic discharge (Ma et al., 2012; Wang et al., 2016). The appearance of *N*-nitrosamines in groundwater is commonly attributed to the infiltration of surface water polluted by *N*-nitrosamines, due to their high potential for leaching from surface water to groundwater (Van Huy et al., 2011; Zhou et al., 2009). However, due to the lack of detailed environmental water surveys, information regarding the occurrence and concentrations of multiple *N*-nitrosamines in environmental water is still notably limited (Krasner et al., 2013). Sihui City and Shunde District in Guangdong Province, China, which are important agricultural and industrial areas, respectively, in the Pearl River Delta, have an increasing incidence of liver cancer and nasopharyngeal cancer among local residents. It is suspected to be related to the consumption of surface water and untreated shallow groundwater, which is the main source of drinking water (Lin and Lai, 2004; Zeng et al., 2015). The excess nitrogen-loading in these areas is a major concern because *N*-nitrosamines tend to be detected more frequently in water that contains high concentrations of ammonia, nitrite, and nitrate (Wang et al., 2016). However, the concentration of *N*-nitrosamines in these areas has not been investigated.

Research on *N*-nitrosamine surveys in waters is impossible unless sensitive analytical methods are developed. There are many methods to analyze trace levels of *N*-nitrosamines. The most commonly used analytical method is based on gas chromatography (GC) with chemical ionization (CI) mass spectrometry (MS) (Charrois et al., 2004; Munch and Bassett, 2004). With the rapid development of analytical methods, some high-performance instruments, such as tandem MS (MS/MS) (Munch and Bassett, 2004; Yoon et al., 2012) and high-resolution (HR) MS (Gerrity et al., 2015; Planas et al., 2008), have been applied. Because very few water utilities currently have affordable access to GC-MS/MS instruments enabled for CI, GC-MS/MS with EI is rapidly gaining prominence in many environmental and water quality control laboratories, McDonald et al. (2012) utilized GC-MS/MS with EI to detect *N*-nitrosamines in drinking water and wastewater samples. In recent years, several sensitive methods based on liquid chromatography (LC) coupled to a triple-quadrupole MS/MS have been developed to detect *N*-nitrosamines, especially thermally unstable species, such as *N*-nitrosodiphenylamine (NDPhA) (Qian et al., 2015; Zhao et al., 2006). The use of the linear ion trap-orbitrap hybrid instrument at high mass resolution (LTQ Orbitrap MS) technique further increases the selectivity (Krauss and Hollender, 2008). Recently an HPLC-chemiluminescence method has been developed, while this method had not been proven on complex environmental matrix samples (Fujioka et al., 2016; Kodamatani et al., 2009). In practice, these methods are typically expensive and their execution requires a high level of expertise. Thus, GC-low-resolution (LR) MS with EI has been used in the determination of *N*-nitrosamines in drinking water and river water (Kawata et al., 2001; Kim et al., 2013; Raksit and Johri, 2001), due to its cost-effectiveness and availability in most laboratories worldwide. However, the sensitivity and

selectivity of LRMS techniques for the determination of *N*-nitrosamines in part-per-trillion concentrations from genuine waters are doubtful.

Though the occurrence of *N*-nitrosamines in environmental water is believed to be important, literatures mainly reported analytical methods concerning tap water (McDonald et al., 2012) and effluent matrix (Krauss and Hollender, 2008; McDonald et al., 2012), and limited studies have investigated the method performance with other environmental matrix. Development and refinement of methods for environmental waters with complex matrices may benefit the water supply and public health. The primary goal of this study was to determine the GC-MS and GC-MS/MS performance in detecting *N*-nitrosamines in fishpond water, river water, and groundwater samples collected from Sihui and Shunde, China. Nine *N*-nitrosamines were studied, including *N*-nitrosodimethylamine (NDMA), *N*-nitrosomethylethylamine (NMEA), *N*-nitrosodiethylamine (NDEA), *N*-nitroso-di-*n*-propylamine (NDPA), *N*-nitrosomorpholine (NMOR), *N*-nitrosopyrrolidine (NPYR), *N*-nitrosopiperidine (NPIP), *N*-nitrosodibutylamine (NDBA), and NDPhA. Initially, different SPE conditions and GC conditions were tested for the pre-concentration and separation steps. GC-MS and GC-MS/MS, both with EI, were then compared for the determination of *N*-nitrosamines in environmental water samples. Finally, the high performance of GC-MS/MS with EI was used to investigate the concentrations of nine *N*-nitrosamines in fishpond water, river water and groundwater samples from China. This manuscript is expected to assist researchers and laboratories approaching improved *N*-nitrosamine analysis for more complex environmental samples. The occurrence levels of *N*-nitrosamine in Sihui and Shunde will be of interest to those laboratories studying the source and fate of *N*-nitrosamines in the environment.

2. Experimental

2.1. Chemical and materials

Dichloromethane (J.T. Baker, Phillipsburg, NJ, USA) and methanol (Tedia, Fairfield, OH, USA) were of GC grade. Sodium thiosulfate (analytical grade), sodium bicarbonate (analytical grade) and anhydrous sodium sulfate (ACS reagent grade) were obtained from Sigma-Aldrich (Oakville, ON, Canada). *N*-nitrosamine-free reagent water was produced with a Heal Force water purification system (Cannex Analytic Instrument, Shanghai, China). The SPE materials, CNWBOND and Supelco coconut charcoal SPE tube (2 g/6 mL, 80–120 mesh), were obtained from CNW Technologies GmbH (Germany) and Supelco (Oakville, ON, Canada), respectively. The glass reaction tubes with PTFE frits (6 mL) were obtained from Supelco.

An *N*-nitrosamine standard containing $2000 \text{ ng } \mu\text{L}^{-1}$ of the nine *N*-nitrosamines in methanol (NDMA, NMEA, NDEA, NDPA, NPYR, NMOR, NPIP, NDBA, and NDPhA), was purchased from Supelco. Two deuterated standard solutions, containing $1000 \text{ ng } \mu\text{L}^{-1}$ of NDMA- d_6 and NDPA- d_{14} in deuterated dichloromethane, were obtained from AccuStandard, Inc. (New Haven, CT, USA).

2.2. Standard solutions

A primary stock solution ($10 \text{ ng } \mu\text{L}^{-1}$) containing the nine *N*-nitrosamines was prepared in dichloromethane. Aliquots were diluted in dichloromethane sequentially to final concentrations in the range of $100\text{--}5000 \text{ pg } \mu\text{L}^{-1}$ of mixed *N*-nitrosamine, spiked with NDMA- d_6 (surrogate standard (SS)), and NDPA- d_{14} ($500 \text{ pg } \mu\text{L}^{-1}$, internal standard (IS)) to prepare for calibration standards for the 'GC-MS' method. Calibration standards in the range of $5\text{--}400 \text{ pg } \mu\text{L}^{-1}$, containing *N*-nitrosamine, NDMA- d_6 (SS)

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