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Short communication

Rapid method for monitoring *N*-nitrosodimethylamine in drinking water at the ng/L level without pre-concentration using high-performance liquid chromatography-chemiluminescence detection

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ABSTRACT

As a contaminant in drinking water, *N*-nitrosodimethylamine (NDMA) is of great concern because of its carcinogenicity; it has been limited to levels of ng/L by regulatory bodies worldwide. Consequently, a rapid and sensitive method for monitoring NDMA in drinking water is urgently required. In this study, we report an improvement of our previously proposed HPLC-based system for NDMA determination. The approach consists of the HPLC separation of NDMA, followed by NDMA photolysis to form peroxynitrite and detection with a luminol chemiluminescence reaction. The detection limit for the improved HPLC method was 0.2 ng/L, which is 10 times more sensitive than our previously reported system. For tap water measurements, only the addition of an ascorbic acid solution to eliminate residual chlorine and passage through an Oasis MAX solid-phase extraction cartridge are needed. The proposed NDMA determination method requires a sample volume of less than 2 mL and a complete analysis time of less than 15 min per sample. The method was utilized for the long-term monitoring of NDMA in tap water. The NDMA level measured in the municipal water survey was 4.9 ng/L, and a seasonal change of the NDMA concentration in tap water was confirmed. The proposed method should constitute a useful NDMA monitoring method for protecting drinking water quality.

1. Introduction

During the treatment of water with disinfectants such as chloramine [1] and ozone [2], *N*-nitrosamines such as *N*-nitrosodimethylamine (NDMA) can be formed [3]. NDMA is potentially carcinogenic to humans: the United States Environmental Protection Agency (U.S. EPA) has classified it as group B2 (probable carcinogenic effects on humans) [4], and the World Health Organization's (WHO) International Agency for Research on Cancer has classified it as group 2A (probably carcinogenic to humans) [5]. As a consequence, NDMA levels in drinking water are being increasingly regulated in many parts of the world. The Canadian province of Ontario has set a maximum allowable concentration for NDMA of 9 ng/L [6]. The State of Massachusetts (USA) has established a regulatory limit of 10 ng/L in drinking water [7], while the State of California (USA) has set notification levels of 10 ng/L for NDMA, *N*-nitrosodiethylamine, and *N*-nitrosodi-*n*-propylamine [8]. Australia has set a guideline level of 10 ng/L for NDMA concentrations in recycled water [9]. Health Canada proposed a maximum allowable concentration for NDMA in drinking water of 40 ng/L [10]. The WHO guidelines for drinking water quality have included a limit for NDMA of 100 ng/L [11]. Hebert et al. reported the potential public health impact of disinfection by-products in drinking water based on an original ranking method [12]. By their analysis, NDMA had a high score among various disinfection by-products. NDMA is one of the compounds of greatest concern in drinking water [13,14]. The monitoring and prevention of NDMA formation in drinking water are now a major focus in water treatment plants [15–17].

The regulatory limits on NDMA in drinking water require analytical methods that can detect nitrosamines at low ng/L levels. Currently, the analysis of NDMA in drinking water is primarily performed by gas chromatography [18,19] or liquid chromatogra-

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phy [20,21] equipped with mass- or tandem-mass spectrometric detectors. Concentration by ~1000-fold is needed for most of these methods for NDMA measurement in drinking water. Although solid-phase extraction (SPE) using an activated carbon sorbent can be employed, the recovery rate of NDMA alone often dictates the choice of sorbent and conditions used [22]. To correct for the recovery rate, an isotope dilution method is needed. These determination methods are powerful tools for the identification and quantification of NDMA in drinking water, however, these procedures require long analysis times and large sample volumes, and consequently reduce laboratory productivity. Hence, the daily measurement of NDMA in drinking water at water treatment plants is difficult. For this reason, a rapid and sensitive method for monitoring NDMA in drinking water is urgently required.

Chemiluminescence (CL) detection has been employed as a powerful tool in analytical chemistry [23,24]. Recently, we developed a novel, sensitive method for the determination of *N*-nitrosamines, nitrites, nitrates, and related compounds in water samples based on a system of HPLC separation, online UV irradiation, and subsequent luminol CL detection [25]. This chemiluminescent detection scheme was proposed to proceed as follows. NO is generated from the compound containing the nitrogen-oxide moiety (such as NDMA) by UV irradiation. At the same time, superoxide anion radicals are generated from the eluent by UV irradiation in the basic aqueous solution. NO reacts with the superoxide radical and generates peroxynitrite, $ONOO^-$, which then reacts with luminol through a peroxynitrite-bicarbonate intermediate and induces strong chemiluminescence. The detection limit for the method was 1.5 ng/L for NDMA, and the calibration curve was linear in the range of 5–1000 ng/L. As this system was ultra-sensitive without a preconcentration step, we suggested its use as a monitoring method for NDMA in drinking water. However, several problems were identified during its use as a routine NDMA analysis method.

In this study, we report an improved HPLC system for NDMA determination, the development of a simple sample preparation procedure, and application of the method in the long-term monitoring of NDMA in drinkable tap water in Japan.

2. Materials and methods

2.1. Reagents

A certified 100 mg/L NDMA methanol solution was purchased from Ultra Scientific (Kingstown, RI, USA). It was diluted to 10 ng/mL by the addition of methanol and stored at −15 °C in the dark. Working standard solutions of NDMA were prepared by diluting the 10 ng/mL NDMA solution with ultrapure water.

A luminol stock solution (20.0 mM) was prepared by dissolving luminol (70.9 mg, 5-amino-2,3-dihydro-1,4-phthalazinedione, Wako Pure Chemical Industries Ltd., Japan) in a sodium carbonate buffer (0.5 M, pH 10.0), after which it was stored at 4 °C in the dark. Water for all the solutions was purified using an Elix 5 UV (Millipore, Tokyo, Japan) and a Milli-Q Advantage system (Millipore). All other chemicals were analytical reagent grade or higher, and were used without further purification.

2.2. Apparatus

NDMA measurements were conducted using the HPLC separation, online UV irradiation, and chemiluminescence detection (HPLC-*hv*-CL) system shown in Fig. 1. The components comprised three LC-10ADvp HPLC pumps (Shimadzu, Kyoto, Japan), a DGU-$20A_3$ degasser (Shimadzu), a SIL-20AC autosampler (Shimadzu), a CTO-20AC column oven (40 °C, Shimadzu), a coupled Capcell Pak C_{18} MGII column (5 μm, 100 mm + 250 mm length; 4.6 mm i.d., Shiseido, Tokyo, Japan), a CL-2027 chemiluminescence detector (JASCO, Tokyo, Japan), and a Chromato-PRO data processor (Runtime Instruments, Kanagawa, Japan). The homemade photochemical reactor consisted of a low-pressure mercury lamp (15 W, CL-15, National, Tokyo, Japan) and a reaction coil in a plastic box covered with an aluminum tape. The reaction coil was a knitted PTFE tube (1/16″ o.d. × 0.5 mm i.d.). The ion chromatography (IC)–conductivity detection system for measurement of the principal anions (such as Cl^-, NO_3^-, and SO_4^{2-}) consisted of a Dionex DX-120 ion chromatograph (Dionex, USA), an Ion-Pac AS23 anion exchange column (250 mm length; 4.6 mm i.d.) equipped with an Ion-Pac AG guard column, and a Waters 717plus autosampler (Waters, USA). Total organic carbon (TOC) was measured using a TOC-V analyzer (Shimadzu).

2.3. Analytical conditions for NDMA analysis

The eluent consisted of 10 mM phosphate buffer–methanol (99:1, v/v, pH 6.9) that was delivered at a flow rate of 1.5 mL/min. The pH conditioning solution consisted of 40 mM sodium phosphate that was delivered at a flow rate of 0.50 mL/min. The sample solution injection volume was 200 μL, unless otherwise noted. The duration of the online UV irradiation was 20 s. Further, a 0.05 mM luminol solution was prepared by diluting the luminol stock solution (2.5 mL) to 1 L with carbonate buffer (0.5 M, pH 10); this was delivered at a flow rate of 0.50 mL/min.

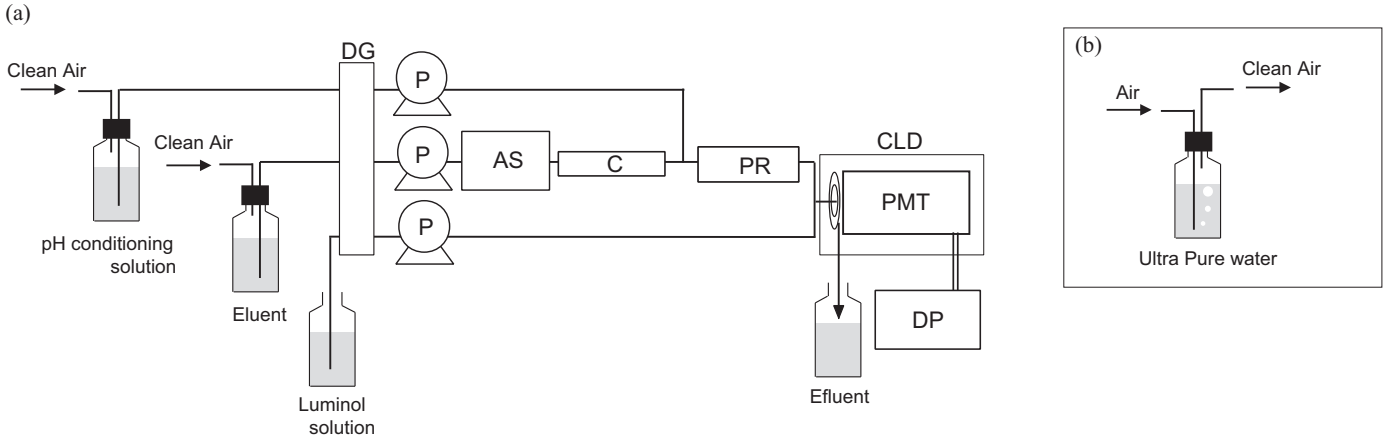

Fig. 1. Schematic diagrams of (a) the HPLC-*hv*-CL system and (b) the air-washing system. DG: degasser; P: pump; AS: autosampler; C: separation column; PR: photochemical reactor; CLD: chemiluminescence detector; PMT: photomultiplier; DP: data processor.