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Ordered mesoporous carbon as sorbent for the extraction of *N*-nitrosamines in wastewater and swimming pool water

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ABSTRACT

The analysis and determination of *N*-nitrosamines (NAs) in water samples are challenging and demanding. In this study, a simple, reliable, and practical methodology is reported for the quantitative determination by gas chromatography-tandem mass spectrometry with electron impact ionization (EI) and triple quadrupole analyzer (GC-EI-MS/MS) of eight NAs after micro-solid-phase extraction (μ-SPE) from wastewater and swimming pool water. Thirty milligram of an ordered mesoporous carbonaceous material, oxidative surface-modified CMK-3, enclosed within a porous polypropylene membrane bag, were used as sorbent for μ-SPE. A central composite design approach was applied to optimize the μ-SPE parameters. An isotopically-labeled NA was used as internal standard. Under the optimized conditions, μ-SPE-GC-EI-MS/MS was validated for an NA concentration range of between 0.1–100 ng/mL. The precision of the method was evaluated and an average relative standard deviation of 4.8% (n = 8) for a standard solution spiked at 50 ng/mL of each NA was obtained. The limits of detection were measured to be in the range of 0.005–0.283 ng/mL. Domestic wastewater and swimming pool water samples were used to evaluate the applicability of the method. NAs were detected in swimming pool water and wastewater at concentrations of <2 ng/mL and 11 ng/mL, respectively.

1. Introduction

N-nitrosamines (NAs) are an important group of disinfection by products (DBPs) that has received widespread attention. In 2010, the US EPA administrator announced that NAs were among a set of drinking water contaminants considered for regulation as a group [1]. However, there are still several basic limitations and drawbacks for routine monitoring and determination of NAs. For example, some of the NAs exhibit high water solubility and relatively low partition coefficients in octanol/water (K_{OW}). Due to this property, currently their extraction and pre-concentration has relied only on sorbent-based extraction [2–6]. Additionally, these compounds possess a wide range of polarities [7]. This acts as an obstacle for successful extraction to achieve acceptable recoveries for all of the NAs in a mixture [8]. Moreover, NAs are found at trace (and ultra trace) concentration levels which necessitate a powerful sample preparation methodology along with sensitive and accurate instrumental analysis. All these issues make the extraction, analysis and determination of NAs a challenging topic. Nevertheless, for the same reasons, the subject of NA extraction continues to attract strong interest from the analytical chemistry community.

In wastewater, NAs can originate from some industrial sources such as food and cosmetics processing, dye and rubber manufacturing, as well as leather tanning and metal casting [9]. Many pharmaceuticals (for both humans and livestock) and pesticides are secondary or tertiary amines. These compounds may act as precursors for nitrosamine formation in wastewater treatment processes [10]. In addition, amine-based herbicides—often employed along with nitrogen fertilizers—may be particularly susceptible to nitrosation [10], and can also be present as impurities in nitrogenous pesticides [11,12]. Consequently, NAs can appear in sewage treatment plant effluents, and wastewater is a potential source matrix of NAs with high concentrations [13,14]. With respect to swimming pool water, DBPs in swimming pool water have become a topic of interest, as epidemiological research has shown increased incidence of asthma and bladder cancer with an exposure to DBPs in indoor pools. Swimming pools may contain additional precursors (including components of human sweat, urine, sunscreen products, etc.) for the formation of NAs [15]. Moreover, aware-

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ness of the need for the analysis of NAs in swimming pool water has increased when it was revealed that swimming can actively increase dermal adsorption or inhalation of these compounds [16]. Studies show that swimming contributes to equivalent, or even greater, exposure to NAs than ingestion of disinfected drinking water. For instance, *N*-nitrosodimethylamine (NDMA) has the same skin permeability as hydrocortisone (10^{-4} cm/h), an active ingredient of topical ointments used for treatment of skin illness [15,17]. Hence, the analysis and determination of NAs in swimming pool waters has significant importance from the view point of public health safety.High-performance liquid chromatography with tandem mass spectrometry (LC–MS/MS) has been reported for the analysis of NAs [9,18–23]. Gas chromatography-high resolution MS has been also applied for the monitoring and analysis of NAs from different matrices [24,25]. Besides, the US Environmental Protection Agency (EPA) Method 521 for determination and analysis of NAs, is based on GC–MS/MS, that uses large volume injection in an ion trap MS with chemical ionization (CI) [26]. The Method 521 with some modifications, is the most commonly applied for the trace analysis of NAs [16,27–29]. As mentioned, increasing concerns about NAs has provided the impetus for routine monitoring of these chemicals. Since ion trap MS systems are becoming rare, as a simplified alternative, gas chromatography-electron impact ionization-MS/MS equipped with a triple quadrupole MS analyzer (GC-EI-MS/MS) was developed recently [30] for NA determination.

Extraction and pre-concentration of NAs before their determination has been mainly achieved by carbonaceous sorbents [4,22,31]. However, the non-polar or relatively less polar NAs are strongly absorbed on the carbonaceous surface of such sorbents, leading to low extraction recoveries [9,11,20,23,24]. We recently introduced a carbonaceous sorbent by surface modification of CMK-3 (O-CMK-3) for extraction of eight NAs [32]. Different carboxylic groups were attached to the CMK-3 surface to create a hydrophilic/hydrophobic balance on the inert surface of the carbonaceous sorbent. This new sorbent was compared with 10 different kinds of commercial carbonaceous sorbents, and was shown to have the best extraction results for both polar and non-polar NAs [32]. We were interested to use O-CMK-3 to develop an analytical methodology for the aforementioned GC-EI-MS/MS determination of NAs from complex matrices such as swimming pool water and domestic wastewater. These two matrices have been considered as important in terms of the presence of NAs [33,34].

In the present study we developed a sensitive, practical, and reliable extraction method using O-CMK-3 as a sorbent for the μ-SPE of eight NAs from environmental water samples with subsequent analysis by GC-EI-MS/MS.

2. Experimental

NAs are toxic and hazardous compounds. All safety and handling considerations that have been mentioned in the literature [32], must be rigorously followed.

2.1. Chemicals and solutions

NAs containing NDMA, *N*-nitrosodiethylamine (NDEA), *N*-nitroso-di-*n*-propylamine (NDPA), *N*-nitroso-di-*n*-butylamine (NDBA), *N*-nitrosopyrrolidine (NPYR), *N*-nitrosopiperidine (NPIP), *N*-nitrosomorpholine (NMOR) (all with 99.9% purity), and *N*-nitrosodiphenylamine (NDPhA) (96.58% purity) were purchased from Supelco (Bellefonte, PA, USA). In addition, isotopically-labeled [6-2H] *N*-nitrosodimethylamine (NDMA-d6), (98%, 1 mg/L in dichloromethane (DCM)-d_2) was purchased from Cambridge Isotope Laboratories (Tewksbury, MA, USA) and used as internal standard (IS). Sodium thiosulfate ($Na_2S_2O_3$, ≥98.0%)was purchased from Sigma–Aldrich (St. Louis, MO, USA). Accurel polypropylene flat sheet membrane (200 μm wall thickness, 0.2 μm pore size) was bought from Membrana (Wuppertal, Germany). Sulfuric acid (H_2SO_4, 95%) and potassium chloride (KCl) were obtained from BDH (Poole, Dorset, UK). All organic solvents including methanol, acetonitrile, acetone, DCM, chloroform, and carbon tetrachloride, were of HPLC grade and bought from Fisher Scientific (Fair Lawn, NJ, USA). Ultrapure water was used for all experiments.

Stock standard solutions of individual NAs (10 mg/L concentrations of each) were prepared, with extreme care during weighing (solid or liquid) and dissolving in methanol (LC–MS-grade). The secondary stock standard solutions were prepared by diluting each stock solution in methanol to obtain a mixture of standards in the concentration range of between 100 and 1000 μg/L. All stock solutions were stored at −23 °C and prepared freshly every month. Working standard mixture solutions were prepared daily in the desirable concentration range by spiking the secondary standard solutions into ultrapure water. Some NAs degrade when exposed to UV light; hence their prolonged exposure to fluorescent light was avoided. The standards and extracts were stored in the freezer in amber-colored bottles or foiled-covered containers. O-CMK-3 was synthesized and characterized as explained previously [32]. Filter paper (grade 1, 11 μm, cellulose filters) (Whatman, Maidstone, England) was used to filter genuine water samples before μ-SPE.

2.2. Sample collection

Water samples were collected in disposable 500 mL polypropylene bottles (which were then covered with aluminum foil to avoid exposure to light). Bottles were pre-cleaned with ultrapure water and methanol and baked at 110 °C for 3 h prior to use. Domestic wastewater samples (from the primary clarifier of the Ulu Pandan water reclamation plant, Singapore), and swimming pool water samples (from three different outdoor pools in the campus of the National University of Singapore) were collected between August and September 2014. Bottles were filled completely up to the rim to eliminate the headspace. In order to quench any residual chlorine (that might be used for disinfection), $Na_2S_2O_3$ as a preservative was added to bottles (50 mg per bottle) before sample collection. Samples were filtered and stored at 4 °C prior to processing. Analyses were carried out within two weeks of sample collection. Blank samples containing ultrapure water and preservative reagent were maintained at same conditions for blank control analysis. Samples were used in their original condition without any pH and temperature adjustment, or dilution.

2.3. Extraction procedure

The μ-SPE device consisted of a polypropylene membrane envelope or bag (2 × 2.5 cm) holding the O-CMK-3 sorbent. The synthesis and characterization of O-CMK-3 was previously reported [32]. The preparation of the membrane bag has also been described [35]. Briefly, one piece of a membrane sheet was folded over and two of its open sides were heat-sealed. After the appropriate amount of O-CMK-3 was placed inside the bag, the final open side was heat-sealed to secure the contents. To condition it, the bag was sonicated in methanol for 10 min followed by drying with lint-free tissue. For extraction, the bag was placed in the sample solution and maintained under shaker conditions of 300 revolutions per minute (KS 4000i control orbital shaker incubator, IKA, Koenigswinter, Germany) at 30 °C for a specified extraction time. After extraction, the bag was taken out of the sample solution using a pair of tweezers, dried thoroughly with lint-free tissue, and placed in a vial for desorption with 200 μL of solvent under ultrasonication. One microliter of the extract was injected into the GC–MS/MS for anal-