



# Pressurised hot water extraction followed by headspace solid-phase microextraction and gas chromatography–tandem mass spectrometry for the determination of *N*-nitrosamines in sewage sludge

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## ABSTRACT

A method for the quantitative determination of the nine EPA *N*-nitrosamines in sewage sludge was developed by using pressurised hot water extraction (PHWE) followed by headspace solid-phase microextraction (HS-SPME) and gas chromatography coupled to chemical ionization ion trap tandem mass spectrometry (GC–CI–MS–MS).

The pressurised hot water extraction was optimized using a central composite design with regard to operational parameters such as temperature, extraction time and pH of water as extracting solvent. The optimum conditions were: water at pH 7.5 as extracting solvent, temperature of 125 °C and extraction time of 5 min. The sewage sludge extract was automatically analyzed by HS-SPME using a divinylbenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS) fiber and GC–CI–MS–MS.

The limits of detection of all compounds were lower than 0.15 µg/kg of dry weight (d.w.) of sewage sludge. The repeatability and reproducibility between days (10 µg/kg d.w.) expressed as relative standard deviation were lower than 16 and 19%, respectively. The method was applied to determine the *N*-nitrosamines in sewage sludge from urban and industrial sewage treatment plants (STPs) and from a potable water treatment plant. Some *N*-nitrosamines were determined in the samples and *N*-nitrosodiethylamine (NDEA) and *N*-nitrosodi-*n*-butylamine (NDBA) showed the highest values (371 and 305 µg/kg (d.w.), respectively) in sewage from industrial STPs.

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## 1. Introduction

Many *N*-nitrosamines, especially *N*-nitrosodimethylamine (NDMA), are considered probable human carcinogens. They have been found in many food products [1], beer [2], cosmetics [3,4], tobacco smoke [5], soils [6], water from chlorinated swimming pools [7], tap water, wastewater, treated wastewater, groundwater and drinking water [7–9]. Polymers, plasticisers, batteries, rocket fuel (incomplete oxidation of hydrazines), and other industrial products are the main anthropogenic sources of the *N*-nitrosamines [10]. They are usually formed by nitrosation or oxidation reactions of amine precursors [11,12]. However, research in recent years has shown that nitrosamines, particularly NDMA, can be generated in water and wastewater treatment systems by chlorine-based disinfection processes, making them an important group of potentially hazardous disinfection by-products (DBPs) [10,13–15].

Currently, *N*-nitrosodimethylamine (NDMA), *N*-nitrosomethylethylamine (NMEA), *N*-nitrosodiethylamine (NDEA), *N*-nitrosopyrrolidine (NPYR), *N*-nitrosodipropylamine (NDPA) and *N*-nitrosodibutylamine (NDBA), are included in the Unregulated Contaminant Monitoring Regulation (UCMR 2), listed in the recently proposed Contaminant Candidate List 3 (CCL 3) by the U.S. EPA. This organization has also established ng/L control levels in drinking water [7,8,16]. Several *N*-nitrosamines have been detected at concentrations between 1 and 2 orders of magnitude higher than their cancer risk levels in the effluents of water and wastewater treatment plants (WWTPs) [13,14,16–19]. The determination of these compounds in environmental samples is therefore of great interest due to the possible reuse of both water and sludge. However, to date, few studies have investigated the occurrence of *N*-nitrosamines in sewage sludge [13].

Several techniques have been used for the analytical determination of *N*-nitrosamines, the most common of which are liquid chromatography (LC) and gas chromatography (GC). LC has been used with UV, fluorescence, mass spectrometry (MS) and tandem mass spectrometry (MS–MS) detection [20–22]. Although LC–MS–MS may also be applied to determine *N*-nitrosamines, the sensitivity for most compounds was lower than that of GC–MS–MS

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[21,23]. GC is often the preferred choice as it provides good resolution and it is easy to couple with sensitive and selective detectors, such as thermal energy analysis (TEA), nitrogen–phosphorus, nitrogen chemiluminescence and MS [24–26]. When GC–MS detection is used, the low molecular weight of *N*-nitrosamines makes them susceptible to chemical interferences with electron ionization (EI) [1,18,26], which leads to poor sensitivity and selectivity, because EI is a hard ionization process and produces nondistinctive fragmentation patterns. This can be counteracted by using positive chemical ionization (CI) either with GC–MS or with GC–tandem mass spectrometry (GC–MS–MS), which is a softer ionization process that produces less molecular fragmentation [9,18,27].

Due to the low levels *N*-nitrosamines are present in environmental samples; an extraction/preconcentration technique is necessary in order to determine them. Pressurised hot water extraction (PHWE) is an environmentally friendly organic solvent free technique in which water is used as the extraction solvent at elevated temperature and under pressure to keep water in liquid state. PHWE has been recently used by our group to extract primary aliphatic amines from different sewage sludges [28]. However, PHWE extracts are relatively dilute aqueous solution and a subsequent preconcentration technique such as liquid–liquid extraction (LLE) [29], solid-phase extraction (SPE) [18,27,30,31] and solid-phase microextraction (SPME) [2,9,26] should be used. SPME is a solvent free technique that is simple to perform and easy to automate, among other advantages.

The aim of this study is to develop a novel and environmentally friendly method to determine the nine EPA *N*-nitrosamines in sewage sludge from various urban and industrial wastewater treatment plants and from a potable water treatment plant. This method is based on pressurised hot water extraction of sewage sludge followed by headspace solid–phase microextraction (HS–SPME) and gas chromatography–tandem mass spectrometry detection system using chemical ionization (HS–SPME–GC–CI–MS–MS).

## 2. Experimental

### 2.1. Safety considerations

*N*-nitrosamines are potential or actual carcinogens and must be handled with extreme care inside a fume hood with ventilation. They must not be inhaled or come into contact with the skin, and appropriate personal protective equipment must be used (latex gloves, lab coat, and safety glasses).

### 2.2. Reagents and solutions

A standard solution containing 2000 mg/L of the 9 *N*-nitrosamines in methanol was purchased by Sigma–Aldrich (Buchs SG, Switzerland) in the highest purity available (EPA 8270/Appendix IX Nitrosamine Mix Catalog No. 502138): *N*-nitrosodimethylamine (NDMA), -methylethylamine (NMEA), -diethylamine (NDEA), -*di-n*-propylamine (NDPA), -morpholine (NMOR), -pyrrolidine (NPYR), -piperidine (NPIP), *di-n*-butylamine (NDBA), and *di-n*-phenylamine (NDPhA). Working standard solutions of 10 mg/L were prepared in methanol weekly. All solutions were stored in darkness in the freezer.

Methanol and acetone were purchased from SDS (Peypin, France) and were of gas chromatography (GC) grade. Sodium chloride was supplied by Sigma–Aldrich. Sodium hydroxide and hydrochloric acid were obtained from Scharlau Chemie (Barcelona, Spain). Ultrapure water was obtained using a Milli-Q purification system (18.2 M $\Omega$  cm) (Millipore, Bedford, MA, USA). Helium and nitrogen of 99.995% purity were obtained from Carbueros Metálicos (Tarragona, Spain). Cellulose filters of 20 mm obtained from

Tecknokroma (Barcelona, Spain) and diatomaceous earth (95%) from Sigma–Aldrich were used for PHWE.

### 2.3. Sampling and sample pre-treatment

Several types of sewage sludge samples were collected from an urban wastewater treatment plant (A), three industrial wastewater treatment plants (B, C and D) and a potable water treatment plant (E). All these plants are located on the outskirts of Tarragona (Spain). These sludge samples had different origins and matrix complexities and had also undergone different treatment processes, such as conventional activated sludge (CAS) treatment or membrane bioreactor (MBR) treatment.

The urban WWTP A is a CAS treatment plant that uses reverse osmosis after secondary treatment. It treats water from a population of approximately 140,000 inhabitants. The industrial WWTP B is a CAS treatment plant that treats a mixture of wastewater from three different chemical plants that make products of various types, such as surfactants, vinyl acetate and plastics (isocyanides, polyurethanes and ABS). The industrial WWTP C is an MBR treatment plant that uses ultrafiltration membranes to treat wastewater from any industrial plants. The industrial WWTP D is an MBR treatment plant that uses ultrafiltration membranes to treat wastewater from the distillation of used oil. The potable water plant E is a CAS treatment plant that uses carbon filters in the last process to obtain a high-quality effluent.

We had two types of sludge depending on the WWTPs: digested and activated sludge. The digested sludge samples were taken in WWTP A, B and E, and it is the total sludge collected in the WWTP dehydrated and digested. The activated sludge samples were taken in WWTP C and D, and this sludge come from the biological reactors of the secondary treatment in the WWTPs. All samples were frozen after collection.

Each frozen sludge sample was lyophilized using the freeze-dry system (Labconco, Kansas City, MO, USA) and sieved through a 125  $\mu$ m screen.

The spiked sewage sludge was prepared by adding a dilution of the working standard solution in acetone. To optimize the PHWE, 20  $\mu$ L of the working standard solution were diluted in 100 mL of acetone and adding 25 mL of this solution to 5 g of dry sewage sludge. Subsequently, the solvent was slowly evaporated at room temperature under frequent homogenization.

### 2.4. Pressurised hot water extraction

PHWE extraction was performed on a Dionex (Sunnyvale, CA, USA) ASE 200 instrument. One cellulose filter followed by 1 g of diatomaceous earth was placed at the bottom of each 33 mL stainless steel extraction cells. After loading 5 g of the pretreated sludge previously mixed with diatomaceous earth, the remaining volume in the cell was filled with diatomaceous earth.

Each sample was extracted using Milli-Q water at pH 7.5. The operating conditions were as follows: extraction temperature, 125 °C; extraction pressure, 1500 psi; preheating period, 6 min; static extraction, 5 min; number of cycles, 2; flush volume, 60% of extraction cell volume; final extraction volume, ~44 mL; and nitrogen purge, 60 s. The extraction temperature, extraction time and pH of water as extracting solvent were the parameters optimized by a central composite design. For this optimization the experimental design matrix and data analysis were performed using the Statgraphics statistical computer package “Statgraphics Plus 5.1” (Manugistics Inc., Rockville, MD, USA).

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