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Short communication

Single-step microwave assisted headspace liquid-phase microextraction of trihalomethanes and haloketones in biological samples

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ABSTRACT

A single-step microwave assisted headspace liquid-phase microextraction (MA-HS-LPME) method was developed for determination of trihalomethanes (THMs) and haloketones (HKs) in biological samples. In this method, a porous membrane envelope was filled with few microliters of extraction solvent and then placed inside the microwave extraction vial. A PTFE ring was designed to support the membrane envelope over a certain height inside the vial. An optimum amount of biological sample was placed in the vial equipped with magnetic stirrer. After that nitric acid was added to the vial for digestion of biological sample. The sample was digested and the volatile THMs and HKs were extracted at headspace in the solvent containing porous membrane. After simultaneous digestion and extraction, the extract was injected to gas chromatography/mass spectrometry for analysis. Factors affecting the extraction efficiency were optimized to achieve higher extraction performance. Quantification was carried out over a concentration range of 0.3–100 ng g^{-1} for brominated compounds while for the chlorinated ones linear range was between 0.5–100 ng g^{-1}. Limit of detections (LODs) were ranged from 0.051 to 0.110 ng g^{-1} while limit of quantification (LOQ) were in the range of 0.175–0.351 ng g^{-1}. The relative standard deviations (RSDs) of the calibrations were ranged between 1.1 and 6.8%. The MA-HS-LPME was applied for the determination of trace level THMs and HKs in fish tissue and green alga samples.

1. Introduction

Arabian Gulf area has undergone tremendous changes over the past few decades in relation to management of water resources. According to recent estimations, daily production of desalinated water in gulf countries reaches up to 23 million cubic meter and only Saudi Arabia produces a lion share of it which is 11 million cubic meter [1]. The contaminants which are produced during the desalination have been extensively reported in the literature. Desalination contaminants have impacted the marine ecological environment and their detectable concentrations were found in phytoplankton, invertebrate and fish [1,2]. Massive losses of coral, plankton and fish in the Hurghada region of the Red Sea have also been attributed to desalination discharges [3,4]. However, there exist only few reports on the impact assessment and bioaccumulation of disinfection by products (DBPs) in biota samples. Eastern province of Saudi Arabia where the world's largest water desalination plant is located has not been evaluated to assess the impact of DBPs on biota. In Saudi Arabia, drinking water supply is coming from desalination of seawater, after desalination, disinfection process has been used.

Disinfection is a process used in the water industry to destroy microorganisms and to produce safer drinking water. Chlorinated disinfection agents such as chlorine and chloramine are strong oxidizing agents introduced into water and these disinfectants may react with naturally present organic matter, as well as iodide and bromide ions, to produce a range of DBPs. In fact, most of these DBPs are unintentionally produced from the reactions of disinfectants with the natural organic matter in the water [5]. Many of the DBPs have been shown to cause cancer, reproductive and developmental disorders in laboratory animals [6]. They are also harmful to humans and are suspected carcinogens even at parts per billion (ppb) concentration levels. Trihalomethanes (THMs) and haloketones (HKs) are considered among the most prevalent DBPs [7,8]. USEPA clas-

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sified trichloromethane (TCM), bromodichloromethane (BDCM), and tribromomethane (TBM) as carcinogens, while chlorodibromomethane (CDBM) was listed as a possible carcinogen [9]. Some toxicological effects of HKs are also reported, more prominently, chromosomal aberrations are associated with trichloropropanone (TCP) [10], and 1,1-dichloropropanone (DCP) has been reported to reduce cellular glutathione levels prior to cytotoxic effects [11]. Therefore, exposure to such compounds can lead to serious health implications.

The determination of various DBPs requires an efficient sample preparation method prior to chromatographic analyses. During the last two decades, different approaches of sample preparation have been reported for DBPs. Liquid–liquid extraction and solid phase extraction are commonly used conventional approaches [12,13]. These methods have many shortcomings, including consumption of large volumes of hazardous solvents, time and labor extensive extractions which lead to low recoveries. Therefore, it is highly desirable to develop new extraction techniques for fast and accurate quantitation of trace level concentrations of DBPs in biological samples.

Microwave assisted extraction (MAE) has wide range of applications and it overcomes many of the above mentioned problems and is successfully applied to different biological samples such as plant and fish [14–18]. Minimizing the degradation of volatile and semi-volatile compounds, shortening the extraction time, lowering hazardous solvent consumption, and simplicity of operation are major advantages of MAE [19–22]. Combination of headspace extraction with MAE is not common approach because to perform headspace extraction, instrumental modifications are required [23], which is by itself a tedious job.

In this work, for the first time, a single step microwave assisted headspace liquid-phase microextraction (MA-HS-LPME) was developed for determination of THMs and HKs in biota samples. In this method, a PTFE ring was placed inside the extraction vial to support the solvent containing porous membrane envelope, thus, no changes in the microwave instrument were required.

2. Material and methods

2.1. Chemicals and standards

A mixture of DBPs standard (Suppl. Fig. 1) was obtained from Sigma–Aldrich (Bellefonte, PA, USA). This standard mixture contained THMs and HKs at 2000 ppm, which was prepared in methanol. Suppl. Table 1 shows the physical properties of target compounds.

A 10 ppm stock solution was prepared in methanol. By appropriate dilution of the stock solution of DBPs in the same solvent, the working standard solutions were prepared on daily basis. Method optimization was carried out at concentration of 50 ng g^{-1}. Required solvents were obtained from Supelco (Bellefonte, PA, USA). Double deionized water was obtained from a Milli-Q system (Millipore, Bedford, MA, USA). HNO_3 was obtained from Merck (Darmstadt, Germany). All glassware were washed with concentrated nitric acid and then rinsed with deionized water and acetone and then dried at 100 °C for 1 h in oven before use. A porous polypropylene membrane (2.5 cm × 2.5 cm with 0.03 mm wall thickness) was obtained from Membrena (Wuppertal, Germany).

2.2. GC–MS analysis

Analyses were carried out using GC–MS (Shimadzu technologies, QP 2010 ultra system). HP-1 methyl siloxane column (Shimadzu Rxi-5Sil MS; 30.0 m × 0.25 mm × 0.25 μm thickness) was used. Carrier gas was helium with high purity (>99.999%) and a constant flow of 1.0 mL min^{-1} was used for analyzing samples. The following temperature program was used for the analyses: initial temperature of column was 40 °C and it was held for 5 min and then increased to 150 °C at 10 °C min^{-1} and held for 5 min. The total run time was 21 min. The injection port, ion source and interface temperatures were 200 °C, 220 °C, and 200 °C, respectively. For qualitative determinations, scan mode was operated from m/z 50 to 550 and for quantitative analysis selective ion monitoring mode was used.

2.3. Fish and green alga samples

Fresh fish samples (Striped Red Mullet) were obtained from fish markets in Dammam, Eastern province, Saudi Arabia. Fish samples were directly transferred to icebox (−4 °C) for temporary storage before reaching the laboratory where stored at −18 °C prior to analysis.

Green alga samples were collected from nearest desalination plant in Jabil, Eastern province, Saudi Arabia, and then used in the experiments after being air dried.

2.4. MA-HS-LPME procedure

MA-HS-LPME experiments were carried out using laboratory microwave extraction system with programmable temperature and pressure (Anton Paar, Graz, Austria). The microwave has enhanced safety features and suitable for the simultaneous extraction of 16 samples. The vessels volume is 100 mL and it can maintain high temperature and pressure (240 °C and 40 bars).

Aqueous solutions are highly suitable for microwave digestion of biological samples, additionally; tissues are easily digested by acidic or basic solutions [24]. 3 g of biological samples were transferred to the cleaned microwave vessels equipped with magnetic stirrer bars. 15 mL of 100 mM HNO_3 solution was added to each vessel. A porous polypropylene membrane bag was filled with 500 μL of an organic solvent and heat sealed. This bag was suspended to certain depth in the microwave vessel via a PTFE ring. The extraction solvent toluene is compatible with the porous membrane and it dilates the pores of the membrane which allows the permeation of analytes in gaseous form. Fig. 1 shows a schematic for the setup used.

This extraction system can be described as combination of two partitioning equilibria, digested sample versus headspace, and headspace versus organic phase (OP). Therefore,

$$C_0Vds = Ca,eqVds + Chs,eqVhs + Cop,eqVop$$

where C_0 is the original concentration of analytes in the digested sample. Ca,eq, Chs,eq, and Cop,eq are analytes concentrations in the digested sample, headspace, and OP, respectively. Vds, Vhs, and Vop are their corresponding volumes.

3. Results and discussion

MA-HS-LPME utilizes microwave energy for fast heating of the solutions by rotation of the molecules through migration of ions and dipoles [24]. The efficiency of the extraction method is controlled by different experimental parameters, such as type of extraction solvent, depth of the membrane envelope inside microwave vessel, extraction temperature, sample weight and extraction time.

3.1. Optimization of extraction parameters

Selection of solvent plays major role in MA-HS-LPME. Dielectric constant and the polarity of the solvent are important parameters to