



Extraction and derivatization of chemical weapons convention relevant aminoalcohols on magnetic cation-exchange resins



Varoon Singh, Prabhat Garg, Sridhar Chinthakindi, Vijay Tak, Devendra Kumar Dubey*

Vertex Laboratory, Defence Research and Development Establishment, Gwalior, India

ARTICLE INFO

Article history:

Received 1 October 2013

Received in revised form

25 December 2013

Accepted 28 December 2013

Available online 2 January 2014

Keywords:

Aminoalcohols

Chemical weapons convention

Magnetic cation-exchange resins

Derivatization

GC-MS

ABSTRACT

Analysis and identification of nitrogen containing aminoalcohols is an integral part of the verification analysis of chemical weapons convention (CWC). This study was aimed to develop extraction and derivatization of aminoalcohols of CWC relevance by using magnetic dispersive solid-phase extraction (MDSPE) in combination with on-resin derivatization (ORD). For this purpose, sulfonated magnetic cation-exchange resins (SMRs) were prepared using magnetite nanoparticles as core, styrene and divinylbenzene as polymer coat and sulfonic acid as acidic cation exchanger. SMRs were successfully employed as extractant for targeted basic analytes. Adsorbed analytes were derivatized with hexamethyldisilazane (HMDS) on the surface of extractant. Derivatized (silylated) compounds were analyzed by GC-MS in SIM and full scan mode. The linearity of the method ranged from 5 to 200 ng mL⁻¹. The LOD and LOQ ranged from 2 to 6 ng mL⁻¹ and 5 to 19 ng mL⁻¹ respectively. The relative standard deviation for intra-day repeatability and inter-day intermediate precision ranged from 5.1% to 6.6% and 0.2% to 7.6% respectively. Recoveries of analytes from spiked water samples from different sources varied from 28.4% to 89.3%.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

The international treaty chemical weapon convention (CWC) entered into force in 1997 with the objective of prohibition of chemical weapons. The CWC is implemented through its strict verification regime by the Organization for Prohibition of Chemical Weapons (OPCW) [1]. Although the CWC has reduced the threat of chemical weapons to a great extent, their use in conflicts and in act of terrorism is still reported [2,3]. Thus, mitigation and augmentation of analytical capabilities of chemical weapons still remain an area of current research [4]. Especially, the stringent verification requirement of CWC for on- and off-site analysis of CWC related chemicals (CRCs) prompted researchers to develop analytical methods that match with the advances in science and technology [5–9]. Analytical methods of CRCs comprised of appropriate combination of sample preparation and analytical techniques. Sample preparation is the summation of extraction, enrichment and derivatization of analytes from environmental and biological samples. Derivatization facilitates the identification of analytes by enhancing its chromatographic and/or detector response.

In case of CRCs, gas-chromatography coupled with mass spectrometry (GC-MS) is the widely used analytical technique, thanks to rich spectral database, available commercially and developed by the OPCW [10]. Consequently, several sample preparation protocols have been developed to suit the GC-MS analysis of CRCs [11,12]. These sample preparation protocols are applicable to various matrices, e.g. soil, water, organic liquid, etc. Amongst these, water is most common matrix for which various sample preparation methods such as liquid-liquid extraction (LLE), solid-phase extraction (SPE), solid-phase microextraction (SPME) and liquid-phase microextraction (LPME) have been developed [11]. But all these methods suffer from one or other kinds of limitations. For example, LLE requires organic solvents in large quantity and complicate extraction from emulsified samples. SPE is limited by loading, washing and elution kinetics. Slow mass transfer and carryover of analytes limit the use of SPME. To overcome these limitations there is a dire need to develop new sample preparation protocols for extraction, enrichment and derivatization of CRCs.

Advances in analytical sciences have led to development of novel sample preparation techniques; magnetic dispersive solid phase extraction (MDSPE) is one of them [13]. In MDSPE, a sorbent is custom synthesized to enhance the extraction and enrichment requirement of a given analyte from aqueous samples. In this technique, an iron oxide composite is prepared with an adsorbent (e.g. carbon nanotubes) or iron oxide particles are coated with silica or organic polymer. Surface of this coat is suitably functionalized to trap the analyte from aqueous samples. These beads are dispersed in the aqueous sample and eluted with appropriate solvent

* Corresponding author at: Vertex Laboratory, Defence Research and Development Establishment, Jhansi Road, Gwalior 474002, India. Tel.: +91 751 2233488; fax: +91 751 2341148.

E-mail addresses: dkdubey@rediffmail.com, vertoxdrde@gmail.com (D.K. Dubey).

after collecting by an external magnet. MDSPE has been reported for variety of analytes such as polycyclic aromatic hydrocarbons, chlorophenols and esters [14]. However, this technique is scarcely reported for CWAs and their related compounds [15].

We contemplated that combination of MDSPE with on-sorbent derivatization might enhance the overall efficiency of sample preparation where derivatization and extraction of analytes take place on the surface of extractant [16].

Solid-phase derivatization of alkylphosphonic acids, the degradation products of nerve agents, is reported using anion-exchange membrane [17]. However, MDSPE in conjunction with on-resin derivatization (ORD) is not reported for degradation products of CWAs. Thus prompted by the virtues of MDSPE and ORD, we hereby report the extraction, enrichment and derivatization of aminoalcohols, the basic degradation products and/or precursors of CWAs from water.

For MDSPE the magnetic sorbents were prepared in our laboratory. Most common reagent employed for derivatization of degradation products of CWAs is *N,O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA). BSTFA, an efficient reagent, nevertheless generates artifacts in total ion chromatogram (TIC) of GC–MS analysis. These artifacts can mask the peaks of other CRCs present in the sample [18,19]. Therefore, for this study hexamethyldisilazane (HMDS) was selected as the derivatization reagent as it is reported to silylate the alcohols at room temperature [20]. HMDS was used to silylate the aminoalcohols to produce volatile and chromatographically non-interfering ammonia as the by-product.

2. Experimental

2.1. Materials

Iron (III) oxide nanoparticles <50 nm (Fe_3O_4), oleic acid, styrene (St), divinylbenzene (DVB), azobisisobutyronitrile (AIBN), polyvinyl alcohol (PVA), acetic anhydride, 1,2-dichloroethane, ammonium chloride (NH_4Cl), 2-(diethylamino)ethanol (DEA), 2-(diisopropylamino)ethanol (DIPA), *N*-ethyl-diethanolamine (EDEA), triethanolamine (TEA), 3-quinuclidinol, pentadecane, HMDS, polyethylene glycol-200 (PEG) were purchased from Sigma–Aldrich Chemical Pvt. Ltd. (Bangalore, India) and were used as received except styrene and DVB, which were passed through inhibitor removing column and then vacuum distilled before use. The abbreviations and structures of the analytes and chromatographic standard are presented in Figure SF 1 of supporting information. H_2SO_4 and all HPLC grade solvents used in sample preparation were purchased from E.Merck (Mumbai, India). All the solutions were made in Milli-Q water (Millipore, Billerica, MA, USA). Acetyl sulphate, for the sulfonation of magnetic polystyrene divinylbenzene (PSDVB) resin, was synthesized as per the reported procedure [21].

2.2. Synthesis and functionalization of magnetic PSDVB resin

Magnetic PSDVB resins were synthesized as per the reported procedure by following steps [21].

2.2.1. Grafting of oleic acid on Fe_3O_4 nanoparticles

Fe_3O_4 nanoparticles (0.5 g) and oleic acid (0.5 mL) were mixed in 10 mL beaker for 10 min. After mixing, they were washed with 2×10 mL ethanol to remove excess non-chemisorbed oleic acid.

2.2.2. Synthesis of magnetic PSDVB resin

In a three necked (100 mL) flask PVA (0.25 g) was dissolved in 50 mL Milli-Q water and purged with nitrogen for 10 min. Fe_3O_4 particles (0.5 g) grafted with oleic acid were added to this solution.

PVA, a non-ionic surfactant, helps in maintaining the suspension of oleic acid coated Fe_3O_4 particles in water. St (2.5 mL), DVB (0.5 mL) and AIBN (0.03 g) were mixed in a beaker and added to the suspension. The mixture was stirred at 800 rpm at 60°C for 1 h on a magnetic stirrer. After 1 h, St (2.5 mL), DVB (0.5 mL) and AIBN (0.03 g) were added again to the suspension. The stirring rate and temperature were increased to 1100 rpm and 90°C respectively. The mixture was allowed to react for 5 h. Polystyrene coated magnetic resins were collected with the external magnet and washed with water and ethanol. Resins were dried in a vacuum oven at 60°C for 5 h.

2.2.3. Sulfonation of magnetic PSDVB resin

The dried magnetic PSDVB resins were swollen in 10 mL of 1,2-dichloroethane for 2 h at room temperature. Then the sulfonation of these resins was carried out by reacting with acetyl sulfate. Acetyl sulfate was synthesized by reacting sulfuric acid (3 mL) with acetic anhydride (10 mL) in 10 mL of 1,2-dichloroethane at 20°C . The mixture was stirred until the formation of pale yellow liquid.

The swollen polystyrene coated magnetic resins were added to this liquid and sulfonation was carried out for 2.5 h at room temperature. Sulfonated magnetic cation-exchange resins (SMRs) were then separated and washed with Milli-Q water until the pH of effluent became neutral. SMRs were dried in vacuum oven for 5 h at 60°C .

2.3. Characterization

The cation-exchange capacity of the synthesized resin was calculated as per the reported procedure and found to be 2.15 mmol g^{-1} [22]. Infrared spectroscopy data were collected on Thermo FT-IR Nicolet 6700 spectroscope equipped with deuterated triglycine sulfate (DTGS) detector. The shape and size of magnetic polystyrene resin were determined by Scanning Electron Microscopy (SEM) (FEI-Quanta 400 Model). The amount of sulfonic acid groups on the surface of SMRs, i.e. extent of sulfonation or ion exchange capacity, was also determined by elemental analysis (Vario Micro elemental analyzer 15081009).

2.4. GC–MS analysis

The GC–MS analysis was performed in the electron ionization (EI) mode with an Agilent 6890N gas chromatograph equipped with 5973N mass-selective detector (Agilent Technologies, USA). A DB-5MS (Agilent technologies) capillary column ($30 \text{ m} \times 0.25 \text{ mm I.D.}$, $0.25 \mu\text{m}$ film thickness) was used. The temperature for GC oven was programmed from 50°C (2 min) to $30^\circ\text{C min}^{-1}$ to 300°C (3 min). Helium was used as carrier gas at a flow rate of 1.0 mL min^{-1} in the constant flow mode. The samples were analyzed in the splitless mode at an injection temperature of 250°C . A $10 \mu\text{L}$ microsyringe was used to inject the samples and the injection volume was kept at $1 \mu\text{L}$. The EI source was kept at 230°C , ionization energy was 70 eV and quadrupole temperature was 150°C . In SIM mode the dwell time was 100 ms and in full scan mode scan range was from m/z 35 to 450 (3.47 scans per second). Quantitation studies were performed in the selected ion monitoring (SIM) mode. The retention times of the analytes with the ions selected for monitoring are given in ST 1 of supporting information.

2.5. Standard spiking solutions

For MDSPE, individual stock solutions of analytes were prepared in acetonitrile. For this approximately 100 mg analyte was weighed in 10 mL volumetric flask and diluted to the required volume with acetonitrile. From stock solutions, a working standard solution of each analyte was prepared at a concentration of $100 \mu\text{g mL}^{-1}$. The

Download English Version:

<https://daneshyari.com/en/article/7613722>

Download Persian Version:

<https://daneshyari.com/article/7613722>

[Daneshyari.com](https://daneshyari.com)