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Extraction of acidic degradation products of organophosphorus chemical warfare agents Comparison between silica and mixed-mode strong anion-exchange cartridges

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Abstract

The analysis of alkyl alkylphosphonic acids (AAPAs) and alkylphosphonic acids (APAs), the hydrolyzed products of nerve agents, constitutes an important aspect for verifying the compliance to the Chemical weapons convention (CWC). This work devotes on the development of solid-phase extraction method using polymeric mixed-mode strong anion-exchange (Oasis MAX) cartridges for extraction of AAPAs and APAs from water. The extracted analytes were analyzed by GC–MS under full scan and selected ion monitoring mode. The extraction efficiencies of MAX and silica-based anion-exchange cartridges were compared, and results revealed that MAX sorbents yielded better recoveries. Extraction parameters, such as loading capacity, extraction solvent, its volume, and washing solvent were optimized. Best recoveries were obtained using 1 mL of acidic methanol (0.1 M), and limits of detection could be achieved up to 5×10^{-4} μg mL^{-1} (in SIM) and 0.05 μg mL^{-1} in full scan mode. The method was successfully employed for the detection and identification of alkylphosphonic acids present in soil sample sent by the Organization for Prohibition of Chemical Weapons (OPCW) in the official proficiency tests.

Keywords: Solid-phase extraction; Anion-exchange cartridges; Chemical warfare agents; Alkyl alkylphosphonic acids; Alkylphosphonic acids; Chemicals weapons convention; verification

1. Introduction

Extraction and analysis of chemical warfare agents (CWAs) and their degradation products from environmental matrices is of paramount importance from verification point of view of chemical weapons convention (CWC) [1–4]. The CWC restricts production, stockpiling and usage of CWAs strictly for non- prohibited purposes only [5,6]. Verification analysis of CWAs and their degradation products, aiming to prove compliance of CWC is performed by designated laboratories appointed by the Organization for Prohibition of Chemical Weapons (OPCW) seated at The Hague, The Netherlands [2–4]. Organophosphorus nerve agents such as sarin, soman and VX and their analogues (as depicted in Fig. 1) constitute most lethal class of CWAs hence included in schedule 1 category of CWC.

These toxic nerve agents are generally degraded by hydrolysis to first produce alkyl alkylphosphonic acids (AAPAs) and, secondly alkylphosphonic acids (APAs) as enumerated in Fig. 1 [7,8]. These hydrolytic degradation products of nerve agents are also included in schedule 2B4 category of CWC, hence are considered important markers of nerve agents for the verification of CWC. A number of analytical methods have been developed for their identification, involving capillary electrophoresis (CE) [9], an electrochemical sensor [10,11], liquid chromatography–electrospray ionization mass spectrometry (LC–ESI-MS) [12], CE microchip [13,14], matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF-MS) [15] and gas chromatography–mass spectrometry (GC–MS) [16]. Each of the above method has unique advantages and disadvantages

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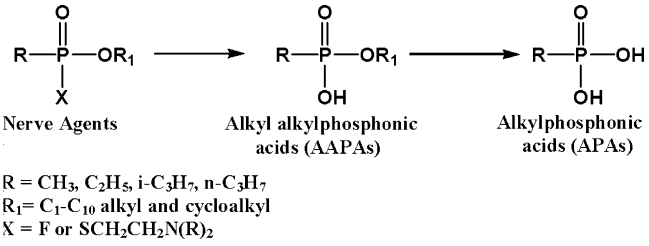

Fig. 1. Hydrolytic pathways of nerve agents.

with respect to sensitivity, precision, selectivity and simplicity. Owing to its sensitivity, selectivity and availability of wide spectral data base, GC–MS is one of the most preferred techniques for analysis of AAPAs and APAs [16,17]. Of course, the conversion of these involatile analytes to their volatile derivatives is essential before subjecting them to GC–MS analysis. For this purpose reactions involving methylation [18], trimethylsilylation [19], tert-butyl dimethylsilylation [20], pentafluorobenzylation [17,21] and alkylations [22] have been employed.

Soil and water are common environmental matrices that can get contaminated by deliberate or inadvertent spillage of CWAs and their degradation products. For detection and identification of AAPAs and APAs from such matrices, extensive sample preparation protocol is adopted to eliminate the background and extract the analyte [23]. Most common sample preparation protocol of AAPAs and APAs from water and water extract of soil, involve removal of interfering cations (by passing through cation-exchange cartridge) followed by evaporation of water with subsequent derivatization and analysis by GC–MS [23,24]. In addition, extraction of AAPAs and APAs from water and other matrices is also reported using solid-phase extraction (SPE) cartridges bearing molecularly imprinted polymers (MIPs) with which excellent recoveries of alkyl methylphosphonic acids were achieved [25–27]. But pre-requisite of extraction with MIPs is, the change of aqueous to organic solvent, as strong hydrogen bonding of water interferes with interaction of analytes on MIPs [27].

Anion-exchange is a selective isolation procedure for acidic compounds such as AAPAs and APAs. SPE using commercially available silica based strong anion-exchange (SAX) cartridges has been reported as extraction method for nerve agent hydrolysis products, but with insufficient recoveries [28,29]. Fredriksson et al. achieved good recoveries of alkyl methylphosphonic acids from SAX cartridges, which required additional pre-cleanup of water samples with strong cation-exchange (SCX) resin [30]. In all these anion-exchange isolations, only ionic interactions between analytes and cartridges were involved.

Kataoka et al. attributed good recoveries of alkyl methyl phosphonic acids on macro-porous strong anion-exchange resin (MSA), to its high ion exchange capacity (1.2 mequiv. mL^{-1} resin) [31]. Mixed mode polymeric strong anion-exchange (Oasis MAX) cartridges manufactured by Waters UK, are made of poly(divinylbenzene-co-vinylpyrrolidone) backbone, on which strong anion exchanging quaternary amine groups are covalently bonded. Extraction capability of these Oasis MAX cartridges has not been investigated so far against AAPAs and APAs. Owing to presence of carbonyl and tertiary amine groups in polymeric backbone, they are expected to exhibit the secondary interactions with acidic analytes that might help in their extraction and recovery. With this concept, we undertook this study to optimize the extraction parameters of AAPAs and APAs from water by mixed mode Oasis MAX cartridges and compare with conventionally used silica-based SAX cartridges. To the best of our information, no such elaborate and comparative extraction of AAPAs and APAs on MAX versus SAX is available in open literature. We wish to report here an investigation of optimization of extraction parameters of AAPAs and APAs from water on MAX cartridges followed by GC–MS analysis of their trimethylsilyl derivatives. Also, a comparison of extraction efficiencies of SAX versus MAX is reported with target analytes. The analytes selected for the study are shown in Fig. 2.

2. Experimental

2.1. Materials

The analytical grade solvents used for this investigation were purchased from E. Merck (Mumbai, India). The silica bonded strong anion-exchange AccuBond II (SAX) cartridges (200 mg, 3 ml and 0.6 mequiv. g^{-1}) were purchased from Agilent Technologies (Milwaukee, WI, USA). Oasis mixed mode anion-exchange (MAX) (30 mg, 1 ml and 0.25 mequiv. g^{-1}) cartridges were purchased from Waters (Milford, MA, USA). The Derivatizing agent *N*,*O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA) and internal standard tri-*n*-propyl phosphate were obtained from Lancaster, Morecambe, UK. The compounds *O*-isopropyl methylphosphonic acid (IMPA), *O*-*n*-hexyl methylphosphonic acid (HMPA), ethylphosphonic acid (EPA) and isopropylphosphonic acid (IPA) were prepared in house as per reported procedures [32]. All aqueous solutions were prepared in distilled deionized water.

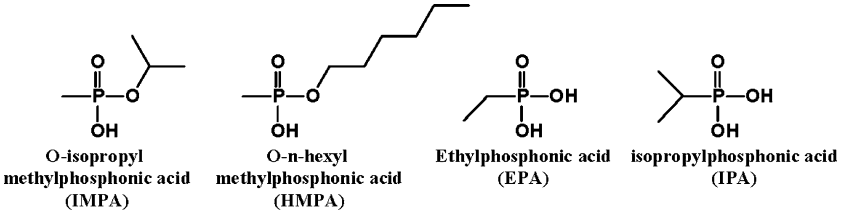

Fig. 2. Structures of analytes selected for the study.