



Selective enrichment of the degradation products of organophosphorus nerve agents by zirconia based solid-phase extraction

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ABSTRACT

Selective extraction and enrichment of nerve agent degradation products has been achieved using zirconia based commercial solid-phase extraction cartridges. Target analytes were *O*-alkyl alkylphosphonic acids and alkylphosphonic acids, the environmental markers of nerve agents such as sarin, soman and VX. Critical extraction parameters such as modifier concentration, nature and volume of washing and eluting solvents were investigated. Amongst other anionic compounds, selectivity in extraction was observed for organophosphorus compounds. Recoveries of analytes were determined by GC–MS which ranged from 80% to 115%. Comparison of zirconia based solid-phase extraction method with anion-exchange solid-phase extraction revealed its selectivity towards phosphonic acids. The limits of detection (LOD) and limit of quantification (LOQ) with selected analytes were achieved down to 4.3 and 8.5 ng mL⁻¹, respectively, in selected ion monitoring mode.

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1. Introduction

Retrospective identification of chemical warfare agents (CWAs) and related chemicals in environmental matrices requires efficient sample preparation. It has extensively attracted attention of researchers because of high degree of toxicity associated with CWAs and need of ensuring compliance to Chemical Weapons Convention (CWC) [1–5]. CWC is an international treaty, administered by the Organization for Prohibition of Chemical Weapons (OPCW) and prohibits production, storage and use of CWAs other than the purposes not prohibited in convention [2,5,6]. Compliance of CWC is ensured by the OPCW through on-site inspection of declared and suspected sites; and off-site analysis of collected samples in designated laboratories [2,3].

Organophosphorus nerve agents belong to the most lethal class of CWAs; they comprise G-agents such as (tabun, sarin, soman and cyclosarin) and V-agents (VX) [7]. In the environment, water hydrolyzes these nerve agents initially to alkyl alkylphosphonic acids and eventually to alkylphosphonic acids as shown in Fig. 1 [8]. As a result, these phosphonic acids (PAs) are considered as environmental markers (signatures) of their corresponding nerve agent

because their identification indicate prior presence of nerve agents. Identification of PAs in environmental samples can be achieved by mass spectrometry coupled to gas chromatography (GC–MS) or liquid chromatography (LC–MS). However, extraction and enrichment of PAs from environmental samples is prerequisite before subjecting to GC–MS or LC–MS analysis. Hence, development of extraction methods of degradation products of nerve agents from environmental matrices has evinced attraction of several workers [9–13]. PAs are acidic degradation products of nerve agents with their pK_{a1} and pK_{a2} values of ~2.5 to ~7.0, respectively; hence they tend to remain in their anionic state in neutral water (pH ~7). Anion-exchange solid-phase extraction (SPE) is highly suitable for extraction and enrichment of such chemicals from water [14,15], but undesired organic anions (as carboxylic acids) are also likely to be co-extracted with PAs. Other sample preparation protocols for extraction of these PAs from water and aqueous extracts of soil involve removal of interfering cations (by passing through cation-exchange SPE cartridges) followed by evaporation of water with subsequent derivatization and analysis by gas chromatography mass spectrometry (GC–MS) [9,16]. With this method, removal of neutral interferents such as polyethylene glycols is not possible. In addition, molecularly imprinted polymers have been used for their extraction from water with good recoveries; the prerequisite of this method is change of sample matrix from aqueous to organic phase, as strong hydrogen bonding of water molecules interferes with interaction of analytes [17,18].

Recently, metal oxides such as TiO₂ and ZrO₂ and others have been investigated as selective extraction materials for several

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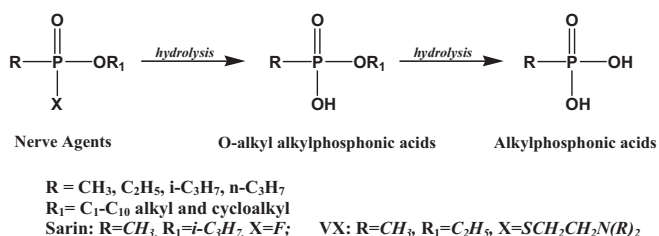


Fig. 1. Hydrolytic pathways of nerve agents.

classes of organic compounds [19–23]. In particular, zirconia's surface chemistry, chemical and thermal stability have drawn attention of researchers to explore it as a potential chromatographic phase [24]. Zirconia has been studied as a material for selective extraction/removal of phospholipids and other phosphorus containing endogenous components in biological matrices [19–23]. Zirconia strongly exhibits Lewis acid properties and interacts with Lewis bases present in the sample. Phospholipids (phosphates) being strong Lewis base interact with zirconium by donating electrons in its empty d-orbitals and therefore can be effectively removed from biological fluids by this mechanism. Besides, there are a number of investigations in which this property of zirconia has been exploited for the extraction of small organic species. Li et al. extracted melamine residues in dairy products employing zirconia hollow fibre sorptive micro extraction exploring hydrogen bonding between Zr–OH and H₂N– of melamine [25]. Du et al. reported SPE of organophosphate pesticides at zirconia nanoparticles modified electrode followed by stripping voltammetric detection [26]. In a similar study, zirconia nanoparticles based electrochemical immunosensor was developed for the detection of phosphorylated acetyl cholinesterase [27]. Preparation and characterization of zirconia hollow fibre was reported by Xu and co-workers with its successful application in the micro extraction of pinacolyl methylphosphonic acid (degradation marker of soman) [28]. However, it required the cumbersome preparation of hollow fibre, and lack of commercial availability restricted its application.

Commercial SPE cartridges named HybridSPE™ available with Supelco, Sigma–Aldrich have found large number of applications in the method development and recovery optimization for biomolecules. Its packed bed of proprietary adsorbent comprise zirconia coated silica particles and is primarily applicable to reduce phospholipids that cause ionization suppression in mass spec-

trometric analysis of biological samples containing phospholipids as endogenous interferents. A number of reports are available in the literature involving use of HybridSPE in removal of phospholipids background from urine, plasma and other biomatrices [19,20,23,29,30].

Thus considering the selective adsorption of phosphorus compounds on zirconia, inadequacy of anion- and cation-exchange based solid-phase extraction to remove anionic, cationic and neutral interferents and commercial availability of zirconia based SPE cartridges, we envisaged their use as selective extractants for enrichment of PAs from water samples; for which the mechanistic outline is presented in Fig. 2. In this study, we report the selective extraction of various PAs from water containing various saturated carboxylic acids (CAs) as background. For this purpose, commercially available SPE cartridges (HybridSPE) were used which exhibited selectivity towards organophosphorus nerve agent's markers. It remained non-selective towards a range of basic, neutral and acidic background compounds. Various extraction parameters were optimized during the course of study and validity of the method for aqueous samples was demonstrated.

2. Experimental

2.1. Materials

The analytical grade solvents were obtained from Merck Specialties Pvt. Ltd. (Mumbai, India). The names, structures and abbreviations of acidic degradation products of nerve agents (PAs) used in optimizing various extraction parameters are *O*-isopropyl methylphosphonic acid (IMPA), *O*-propyl ethylphosphonic acid (PrEPA), *O*-sec-butyl ethylphosphonic acid (BEPA), *O*-pentyl methylphosphonic acid (PMPA), *O*-pentyl isopropylphosphonic acid (PIPA) and ethylphosphonic acid (EPA). Three additional PAs namely *O*-cyclohexyl methylphosphonic acid (CHMPA), methylphosphonic acid (MPA) and isopropylphosphonic acid (IPA) were used during internal validation. All the PAs were synthesized in house as per the reported procedure [31]. Carboxylic acids (CAs) which were used as background chemicals throughout the study included hexanoic acid (HA), 5-phenyl valeric acid (PVA), octanedioic acid (ODA) and decanedioic acid (DDA). Heptanoic acid (HPA) and octanoic acid (OA) were used during internal validation. All the carboxylic acids were obtained commercially from Sigma Aldrich Chemicals Pvt. Ltd. (Banga-

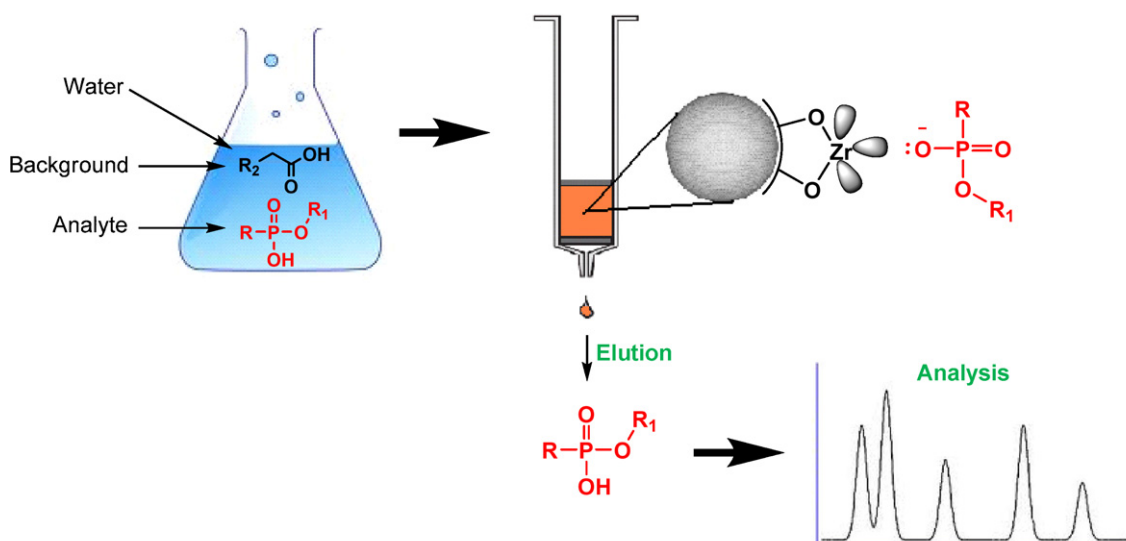


Fig. 2. Zirconia mediated selective extraction of organophosphorus degradation products of nerve agents.

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