



Zirconia coated stir bar sorptive extraction combined with large volume sample stacking capillary electrophoresis-indirect ultraviolet detection for the determination of chemical warfare agent degradation products in water samples

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ABSTRACT

In this study, a sensitive, selective and reliable analytical method by combining zirconia (ZrO_2) coated stir bar sorptive extraction (SBSE) with large volume sample stacking capillary electrophoresis-indirect ultraviolet (LVSS-CE/indirect UV) was developed for the direct analysis of chemical warfare agent degradation products of alkyl alkylphosphonic acids (AAPAs) (including ethyl methylphosphonic acid (EMPA) and pinacolyl methylphosphonate (PMPA)) and methylphosphonic acid (MPA) in environmental waters. ZrO_2 coated stir bar was prepared by adhering nanometer-sized ZrO_2 particles onto the surface of stir bar with commercial PDMS sol as adhesion agent. Due to the high affinity of ZrO_2 to the electronegative phosphonate group, ZrO_2 coated stir bars could selectively extract the strongly polar AAPAs and MPA. After systematically optimizing the extraction conditions of ZrO_2 -SBSE, the analytical performance of ZrO_2 -SBSE-CE/indirect UV and ZrO_2 -SBSE-LVSS-CE/indirect UV was assessed. The limits of detection (LODs, at a signal-to-noise ratio of 3) obtained by ZrO_2 -SBSE-CE/indirect UV were 13.4–15.9 $\mu\text{g/L}$ for PMPA, EMPA and MPA. The relative standard deviations (RSDs, $n=7$, $c=200 \mu\text{g/L}$) of the corrected peak area for the target analytes were in the range of 6.4–8.8%. Enhancement factors (EFs) in terms of LODs were found to be from 112- to 145-fold. By combining ZrO_2 coating SBSE with LVSS as a dual preconcentration strategy, the EFs were magnified up to 1583-fold, and the LODs of ZrO_2 -SBSE-LVSS-CE/indirect UV were 1.4, 1.2 and 3.1 $\mu\text{g/L}$ for PMPA, EMPA, and MPA, respectively. The RSDs ($n=7$, $c=20 \mu\text{g/L}$) were found to be in the range of 9.0–11.8%. The developed ZrO_2 -SBSE-LVSS-CE/indirect UV method has been successfully applied to the analysis of PMPA, EMPA, and MPA in different environmental water samples, and the recoveries for the spiked water samples were found to be in the range of 93.8–105.3%.

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1. Introduction

Organophosphorus nerve agents, such as sarin, soman and VX, are some of the strongest chemical warfare agents (CWAs) [1]. Once absorbed through the skin or via respiration by human beings, they display rapid highly toxic effects. Now the use of these chemical warfare agents has been forbidden by international convention. However, they are still being produced and stockpiled by some countries and terrorist organization. With the rising concern of terrorist, trace detection of nerve agents has become increasingly significant. In general, organophosphorus nerve agents can readily hydrolyze to their corresponding alkyl alkylphosphonic acids (AAPAs), ultimately very slowly hydrolyze to methylphosphonic acid (MPA) [2], when they are exposed to the environment. Since AAPAs and MPA are much more stable comparing to their corresponding parent nerve agents, they are commonly considered as

important markers for the presence or use of CWAs in the environment [2]. Therefore, development of some sensitive and accurate methods for the analysis of AAPAs and MPA is very desirable.

Several analytical methods, such as gas chromatography (GC) [3], high performance liquid chromatography (HPLC) [4], ion chromatography (IC) [5], and capillary electrophoresis (CE) [6–13], have been reported for the separation and quantification of AAPAs and MPA. Thereinto, CE has several advantages such as high resolution, low-sample/reagent consumption, no consumption of organic solvents, and intrinsic capability for the analysis of polar compounds, thus it is very complementary to other chromatographic techniques. However, insufficient detection sensitivity and intolerance to sample matrix limited the application of CE in real-world sample analysis. Such limitations can be overcome by incorporating both on-column concentration techniques or/and off-line sample pretreatment techniques with CE [5,6,14,15]. Regarding the on-column concentration techniques, field-amplified sample stacking (FASS) [14] and large volume sample stacking (LVSS) [6] have been employed to improve the detection sensitivity of CE for AAPAs analysis. Meanwhile, solid phase extraction (SPE) as one of

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sample pretreatment techniques has been utilized to both clean up the sample and enrich the target AAPAs. The used SPE materials include C₁₈ silica [16], C₁₈ cartridge [3], strong anion exchange cartridges [17–19], ZrO₂ cartridge [5] and ZrO₂ hollow fiber [15]. However, SPE is well known to suffer from some inherent drawbacks such as time-consuming and a large amount of solvent and sample required. Sometimes, a derivatization step is a prerequisite in SPE that makes the analytical procedure tedious and prone to errors [16].

In the last few years, efforts have been directed toward miniaturizing the conventional SPE, leading to the development of solid phase microextraction (SPME) and stir bar sorptive extraction (SBSE) methodologies. Because of the advantages of being fast, effective, inexpensive and virtually solvent-free or solvent-less, SPME and SBSE coupling with CE have shown the promising capabilities to determine biological and environmental sample and compounds [20], such as pesticides [21], alkaloids [22]. SBSE and SPME are both based on the partition of analytes between sample matrix and the selected extraction coatings. The main difference of these two techniques is that the much larger volume of sorbent was used in SBSE, resulting in a significant increase in recovery and extraction capacity. Due to the most developed coatings for SPME and SBSE are non-polar or weakly polar materials, both SPME and SBSE have been mainly applied to extract non-polar and weakly polar compounds [23,24]. For example, SPME with the copoly(dimethylsiloxane/divinylbenzene) fiber has been utilized to extract the non-polar CWAs such as sarin, soman and VX [25], and weakly polar dimethyl methyl phosphonate (DMMP) [26]. While to the best of our knowledge, there is no publication on the use of SBSE or SPME in direct analysis of highly hydrophilic and strong polar AAPAs and MPA till to present. Therefore, the exploration of highly polar coatings for SPME or SBSE direct extraction of strong polar AAPAs and MPA are extremely expected.

The purpose of this work was to explore the possibility of extraction of strongly polar AAPAs and MPA by using SBSE with nanometer-sized zirconia (ZrO₂) as the coating material, and establish a new method of ZrO₂-SBSE-LVSS-CE/indirect UV for the direct determination of AAPAs and MPA in environmental water samples. ZrO₂ coated stir bar was prepared by a simple PDMS-adhesion method [27]. Parameters affecting the ZrO₂-SBSE and LVSS procedures were investigated in details and the analytical performance of the method was evaluated. The developed method was validated by the analysis of strongly polar AAPAs and MPA in environmental waters.

2. Experimental

2.1. Reagents and materials

Methylphosphonic acid (MPA), AAPAs including ethyl methylphosphonic acid (EMPA) and pinacolyl methylphosphonate (PMPA) were all purchased from Aldrich (Milwaukee, WI, USA). The chemical structures and some of their chemical properties are given in [Supplementary material S1](#). Stock standard solutions of each target analyte were prepared in methanol at a concentration of 1000 mg/L, and stored at 4 °C in refrigerator. Analytical grade zirconyl chloride (ZrOCl₂·8H₂O) was obtained from China Medicine Group, Sinopharmic Chemical Reagent Company (Shanghai, China). Zirconium (IV) propoxide solution (70%, m/v in n-propanol) was purchased from Aladdin (Shanghai, China). Phenylphosphonic acid (PhPA) and cetyltrimethyl ammoniumbromide (CTAB) were of analytical grade and purchased from Acros Organics (NJ, USA). Polydimethylsiloxane (PDMS) (GE RTV 615) containing A- and B-sol components used as adhesion agent for preparation of ZrO₂ coated stir bar was obtained from Momentive

Performance Materials (NY, USA). Poly(methylhydrosiloxane) (PMHS) was obtained from the Chemical Plant of Wuhan University (Wuhan, China). Other reagents used were of analytical reagent grade. High purity water obtained by a Milli-Q water purification system (18.2 MΩ cm, Millipore, Bedford, MA, USA) was used throughout the whole experiment.

2.2. Instruments

All capillary electropherograms were recorded from G1600AX CE system (Agilent, Waldbronn, Germany), equipped with a diode-array UV detector (190–600 nm). The detection wavelength used was 200 nm, and the capillary temperature was maintained at 25 °C. Fused-silica capillary dimensions of 48.5 cm (40 cm to the detector) × 50 μm i.d. × 360 μm o.d. (Yongnian Optical Fiber, Hebei, China) was used for CE separation. Prior to its first use, the capillary was sequentially flushed with 1 mol/L NaOH for 30 min, high purity water for 30 min, and running electrolyte for 10 min. Between runs, the capillary was rinsed with running buffer for 3 min. At the end of each day, the capillaries were flushed with high purity water for 20 min, and kept in high purity water overnight. A modified CE automatic sample vial was used for sample injection in CE analysis [28]. Transmission electron microscope (TEM, JEM-100CX, Japan) and X-650 scanning electron microscope (SEM, Hitachi, Tokyo, Japan) were employed to characterize the prepared nanometer-sized ZrO₂ particles and ZrO₂ coated stir bars.

2.3. Preparation of ZrO₂ coated stir bars and operation procedure of ZrO₂-SBSE

2.3.1. Syntheses of nanometer-sized ZrO₂ particles

The nanometer-sized ZrO₂ particles were synthesized according to the method described by Blin et al. [29]. In brief, 1.82 g CTAB and 3.2 g zirconyl chloride were dissolved in 90 mL water, respectively, and stirred at 40 °C to obtain a clear solution. Then the zirconyl chloride solution was slowly added into the CTAB solution under stirring, and the pH value was adjusted to 11.6 with 2 mol/L NaOH. After reaction for 1 h by stirring, the homogeneous gel obtained was sealed in Teflon autoclaves, and placed into a constant temperature drier at 90 °C for 24 h. The resulting solid product was calcined at 500 °C for 5 h in X2-6-13 muffle furnace (Yingshan Yahua Instrument Factory, Hubei, China).

2.3.2. Preparation of stir bars

In order to reduce the friction loss of coatings resulting from high stirring rate, “dumbbell-shaped” stir bars as described in Ref. [30] were used in this work. Twenty millimeter length and 1 mm inter-diameter of bare glass “dumbbell-shaped” stir bars were prepared and activated referring to Ref. [30].

The nanometer-sized ZrO₂ particles coated stir bar was prepared using an adhesion method as described by Yu and Hu [27]. To assure a good reproducibility, the commercially available PDMS-sol (GE RTV 615) was employed as adhesion agent instead of the home-made PDMS-sol used by Yu and Hu [27]. Firstly, the mixture of component A:B (10:1, v/v) of commercially available PDMS-sol was stirred to form a homogenous sol. The degassed PDMS-sol was stored at –20 °C in refrigerator until use. At this temperature, the PDMS-sol was found to be stable for at least 30 days. Then the activated bare glass “dumbbell-shaped” stir bar was coated with a thin film of PDMS-sol. After heat treatment at 70 °C for 2 min, the PDMS coated stir bar was covered with synthesized ZrO₂ particles by rolling the stir bar in ZrO₂ nanometer-sized particles bed. After the surface of the PDMS-stir bar was completely coated with ZrO₂ particles, the prepared stir bars were placed into a constant temperature drier at 80 °C for 1 day. Prior to use, the ZrO₂-stir bars were activated in 0.1 mol/L HNO₃ by ultrasonication for 30 min.

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