Preparation and application of sol–gel acrylate and methacrylate solid-phase microextraction fibres for gas chromatographic analysis of organoarsenic compounds

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HIGHLIGHTS

- Sol–gel SPME fibres coated by methacrylates and acrylates have been prepared.
- Sol–gel coatings were chemical bonded to the fibre.
- SPME fibres designed for analysis of organoarsenic CWA's have been investigated.
- Extraction efficiency of obtained fibres has been compared with commercial fibres.
- K_{fs} value for obtained fibres were determined and compared with commercial fibres.

GRAPHICAL ABSTRACT
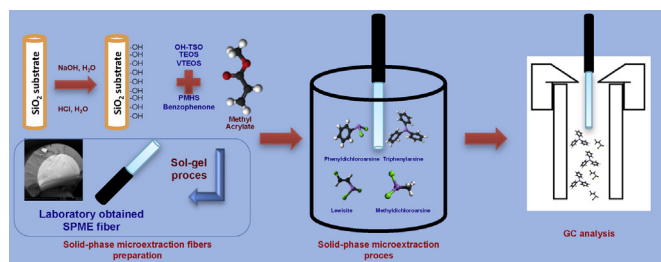
ABSTRACT

Novel solid-phase microextraction (SPME) fibres containing methyl, ethyl, butyl acrylate and methacrylate were first prepared by a sol–gel technique and investigated for determination of selected organoarsenic compounds (lewisite, methyldichloroarsine, phenyldichloroarsine, diphenylchloroarsine and triphenylarsine) from water samples. The influence of sorption and desorption temperature and time for extraction efficiency were examined. The best new fibre coatings (methyl acrylate (MA), methyl methacrylate (MMA) and combination of methyl acrylate and methacrylate (MA/MMA)) for analysis of organoarsenic compounds were selected and compared with commercial fibres. The distribution coefficients K_{fs} were determined for the best novel fibres and for absorption commercial fibres. The highest K_{fs} value were obtained for MA/MMA and MMA fibres and were respectively 9458 and 6561 for lewisite and 6458 and 5884 for triphenylarsine. The limit of detection and quantification were determined for the three laboratory obtained fibres (MA, MMA and MA/MMA). LODs for tested fibres, at a signal-to-noise of 3, were 0.03–0.3 ng mL^{-1}. LOQs for selected coatings, at signal-to-noise of 10, were 0.1–0.8 ng mL^{-1}. The relative standard deviations (RSD) for all measurements were 4.3–6.5% ($n = 9$) and relative errors were 2.5–5%. The laboratory obtained fibres were used for environmental analysis of pore water samples from the Baltic Sea.

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1. Introduction

The Chemical Weapon Convention (CWC) of the 29th April 1997 prohibits the development, production, acquisition, stockpiling and use of chemical weapons (CW) and requires that all CW possessed by its signatories have to be destroyed [1]. Despite the Convention, chemical warfare agents (CWA) still pose a threat to both civilians and the military. In warfare, CWAs were used in the 1980s during the Iraq–Iran conflict [2], and have also been used recently against the civil population in Syria [3]. CWAs may also potentially be used in terrorist attacks. In 1995 sarin was used in the attack on the Tokyo subway, killing 12 and injuring over 5000 [4]. Chemical ammunition dump in the Baltic Sea is another serious problem [5]. Chemical agents released from rusting projectiles pose a great threat to marine ecosystems. Hence, constant monitoring of dumped ammunition and of CWA degradation products is necessary.

Detection and identification of CWAs and their degradation products are of the utmost importance for the CWA compliance verification program [6,7] and for monitoring chemical ammunition dump in the Baltic Sea. The CWA verification system and the process of environmental monitoring (including the marine environment) are based on inspections, field analyses, sampling and lab analyses carried out by laboratories designated by the Organisation for the Prohibition of Chemical Weapons (OPCW) [8–10]. For that reason there is still considerable interest in the development of improved analytical methods for the detection and identification of CWAs and their degradation products.

Gas chromatography–mass spectrometry (GC–MS) has been widely used for separation and identification of CWAs and their degradation products [11–13]. GC–MS is a suitable technique for direct analysis of CWAs in organic solvents, but it cannot be directly applied to the analysis of aqueous samples. Those samples are most commonly analysed with liquid chromatography–mass spectrometry (LC–MS) [14,15].

Considering the fact that samples containing CWAs or their degradation products may exist in various matrices, including artillery shells or their fragments, water, soil, air, bottom sediment, blood, urine and various plastics [16], the stage of sampling and sample preparation for the analysis is very important.

Liquid–liquid, liquid–solid and solid-phase extraction are the most commonly used techniques of sample preparation. These techniques are recommended for preparation of CWA and/or CWA degradation products-containing samples [17]. However, the methods are burdened with some disadvantages, including: lengthy sample preparation time, the use of organic solvents (often in large amounts) and the necessity for large numbers and volumes of environmental samples. Therefore, studies are continuing to develop new techniques for sample preparation that will be devoid of most of these disadvantages.

One such sample preparation technique that may be devoid of the above-mentioned drawbacks is solid-phase microextraction (SPME). The method was developed by Arthur and Pawliszyn [18] in 1990. This technique is based on separation of an analyte between the sample matrix and a stationary phase deposited on fused silica fibre. Currently available commercial fibres are divided into two groups: adsorption [19] (e.g. carboxen-polydimethylsiloxane CAR-PDMS), and absorption (e.g. polyacrylate PA) [18]. SPME allows the elimination of large volumes of organic solvents, simultaneous preparation and condensation of a sample, as well as selective sorption of analytes.

Despite numerous advantages, the technique also has some flaws, including: the relatively low operating temperature of commercial fibres (up to 280 °C), fibre instability in organic solvents (largely limiting the use of SPME in combination with liquid chromatography), the fragility of the fibres, a high susceptibility of sorption coatings to mechanical damage, and the relatively high cost and short useful lifetime of sorption coatings [19]. The low thermal stability and short lifetime of the fibres may be due to the absence of strong chemical bonding between the polymer coating and the fibre surface made of fused silica [20,21]. That is why new stationary phases that could be used for highly efficient and selective solid-phase microextraction are still sought after and developed.

Many new types of SPME fibres have been developed to date. Their stationary phases contain: graphene, carbon nanotubes, ionic liquids, polymeric ionic liquids, molecularly-imprinted polymers, metal-organic framework, polypyrrole and polythiophene and their derivatives, metals and metal oxides [22].

Some problems associated with the production and embedding of new stationary phases have been solved by use of the sol–gel technique [23]. Sol–gel chemistry offers a rapid and convenient method to synthesize advanced materials, due to its combination of organic polymeric structures and inorganic structures under mild temperature conditions [24,25]. Sorption coatings formed in the sol–gel process are chemically bound to the physical substrate. Therefore they become thermally stable and resistant to solvents. This technique has been used for the production of SPME stationary phases containing: polydimethylsiloxane, polyvinyl alcohol, β-cyclodextrin, crown ethers, calixarenes, hydroxyfluorene, polyethylene glycol, ionic liquids, polytetrahydrofuran and dendrimer [26].

One group of compounds that may be used for the production of new stationary phases for analysis of CWAs and their degradation products are acrylates possessing a vinyl substituent in their structure. These compounds are standard hydrophobic monomers used in organic and inorganic coatings [27] and polymeric membranes [28], and may also be used for the production of stationary phases for SPME [29]. Butyl acrylate has been successfully used to produce new fibres for the analysis of 2-chloroethyl ethyl sulfide (CEES)—a functional analogue of sulfur mustard [29]. Acrylates have also been used in sulfur mustard- and CEES-absorbing membranes [30].

One group of CWAs known to be sunken in the Baltic Sea is the group of organoarsenic compounds. Monitoring of these compounds is obligatory as a consequence of the fact that in addition to their toxic properties they contain arsenic in their structure, and arsenic is harmful in virtually any form. Therefore, all degradation products of these compounds are also toxic. Butyl methacrylate has proven to be an appropriate SPME fibre coating used for the analysis of sulfur mustard and its analogues. Organoarsenic compounds belonging to the CWA group have similar physico-chemical properties as sulfur mustard (water solubility, polarity). Therefore a decision was made to produce SPME stationary phases containing acrylates and methyl-, ethyl- and butyl- methacrylates, and to examine their usefulness during the microextraction that precedes the chromatographic analysis of selected organoarsenic compounds (methyldichloroarsine, phenyldichloroarsine, diphenylchloroarsine, triphenylchloroarsine and lewisite).

2. Experimental

2.1. Chemicals and materials

Methyl acrylate (MA), methyl methacrylate (MMA), ethyl acrylate (EA), ethyl methacrylate (EMA), butyl acrylate (BA), butyl methacrylate (BMA), methyltrimethoxysilane (MTMOS), and methylhydrosiloxane [(50–55% methylhydrosiloxane)-dimethylsiloxane-copolymer] (MHS-DMS) were purchased from ABCR GmbH & Co. KG (Germany). Trifluoroacetic acid (TFA, 99%), diphenylamine (DPA), 1,4-tioxane, dichlorvos (DDVP), trimethyl