



Evaluation of carbon aerogel-based solid-phase extraction sorbent for the analysis of sulfur mustard degradation products in environmental water samples

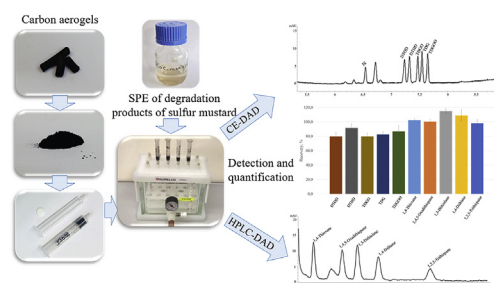
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HIGHLIGHTS

- A method was developed for extraction of 10 degradation products of sulfur mustard.
- Carbon aerogel-based sorbent was evaluated for extraction of target compounds.
- The obtained recoveries were at least 80%.
- Applied for analysis of target compound in environmental water samples.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, SPE method using a carbon aerogel(CA)-based sorbent was developed and evaluated for the simultaneous extraction of sulfur mustard (HD) degradation products from environmental water samples. Applied CAs proved to be very promising materials for use as SPE sorbents, due to their high porosity, very low density and a large specific surface area. 10 degradation products of HD, both aliphatic and cyclic (thiodiglycol (TDG), TDG sulfoxide, TDG sulfone, 3,5-dithia-1,7-heptanediol, 3,6-dithia-1,8-octanediol, 1,4-thioxane, 1,3-dithiolane, 1,4-dithiane, 1,2,5-trithiepane, and 1,4,5-oxadithiepane) were extracted on a CA-based SPE cartridge. The concentrations of target analytes in the eluate were determined by HPLC-DAD and CE-DAD. Several parameters affecting the extraction efficiency, including the kind and volume of the eluting solvent, sample loading flow rate, volume and ionic strength as well as the reusability of the cartridge, were investigated and optimized to achieve the best performance for the analytes. A series of quantitative parameters such as linear range, coefficient of determination, LOD, LOQ and precision were examined under the optimized conditions. High sensitivity (LODs 0.17–0.50 μM) and high precision (intraday RSD = 2.0–7.7% and interday RSD = 2.7–9.9%) for all the analytes were achieved. The performance of the CA-based sorbent was compared with that of commonly used SPE sorbents. Applied for the analysis of spiked pore water samples collected from the Bornholm Basin, one of the largest chemical warfare dumping sites in the Baltic Sea, the proposed method allowed high SPE recoveries of all the analytes ranging from 83.5 to 99.7% to be obtained.

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1. Introduction

Sulfur mustard (HD) (bis-(2-chloroethyl)sulfide) is a blister

Abbreviations

HD	sulfur mustard
CWA	chemical warfare agent
TDG	thiodiglycol
TDGO	thiodiglycol sulfoxide
TDGOO	thiodiglycol sulfone
CWC	Chemical Weapons Convention
CA	carbon aerogel
MR/C	5-methylresorcinol to catalyst molar ratio
DTHD	3,5-dithia-1,7-heptanediol
DTOD	3,6-dithia-1,8-octanediol
ACN	acetonitrile
MeOH	methanol
R ²	coefficient of determination

agent (vesicant), and, as an alkylating agent, readily reacts with a wide variety of different biological molecules and thereby affects many processes in the living tissue (Ghazanfari and Hassan, 2013). HD was used during World War I and the Iran-Iraq War and stockpiled by countries as a chemical warfare agent (CWA). The Chemical Weapons Convention (CWC) prohibits the development, production, stockpiling and use of CWAs (“Organisation for the Prohibition of Chemical Weapons”; Szinicz, 2005). In addition to HD itself, there are eight more analogs which have been included in the CWC Schedule 1 of chemicals (“Organisation for the Prohibition of Chemical Weapons: Annex on Chemicals”). Longer-chain analogs are more vesicant and persistent than the parent compound, however, due to their lower volatility, the analogs do not produce casualties by the action of the vapor (Lemire et al., 2007; Timperley et al., 2003).

In dilute aqueous solutions, degradation of HD occurs primarily through hydrolysis. HD is converted first to a sulfonium ion and then to the hemimustard and thiodiglycol (TDG). Then TDG may slowly oxidize to thiodiglycol sulfoxide (TDGO) and thiodiglycol sulfone (TDGOO). There are known many more open-chain and cyclic degradation products of HD and its analogues (Munro et al., 1999). TDG as a precursor of HD production is also included in the CWC Schedule 2 of chemicals (“Organisation for the Prohibition of Chemical Weapons: Annex on Chemicals”).

There is still concern about that HD could be used by terrorists in a chemical attack against civilians or it could be involved in industrial accidents, as a consequence of which emergency physicians must treat persons having been exposed to HD (Davis and Aspera, 2001). Therefore, the physicians must recognize HD and its degradation products and know how to manage HD-exposed patients, while in such cases timely information about the accident is of critical importance (Weibrecht et al., 2012).

In recent years, chemical weapons (CWs) have received much attention because of the problem of dumped chemical munitions. After World War II at least 50 000 tons of CWs was dumped in the Baltic Sea because their use had been prohibited. These weapons, most of which contained HD, have been lying at the bottom of the sea for more than 70 years. The munition shells have corroded and toxic HD has already been leaked into the seawater and decomposed (Beidowski et al., 2016; CHEMSEA FINDINGS: Results from the CHEMSEA project). Therefore, interest in determination of HD degradation products in environmental water samples has been increasing in recent times.

In real environmental samples from the dumpsite area there have been detected both aliphatic hydrolysis and oxidation

products, and cyclic decomposition products of HD (Christensen et al., 2016; Mazurek et al., 2001). It has been assumed that the concentration of hydrolysis products in the samples should be higher and the products should be more easily detectable because hydrolysis is expected to be the main breakdown pathway for sea-dumped CWAs (Greenberg et al., 2016). Despite that cyclic degradation products of HD have been detected much more frequently in the Baltic Sea water samples than aliphatic hydrolysis products (Christensen et al., 2016; Söderström et al., 2018). Unlike other CWAs, HD and its degradation products have been detected only in a limited number of samples from the known dumpsites, and in small quantities (Greenberg et al., 2016). The undetectability might be related to the slow dissolution and formation of the polymeric crust (Munro et al., 1999). Aliphatic HD degradation products have been detected in sediment samples, not in pore water samples (Missiaen et al., 2010; Popiel et al., 2014; Söderström, 2014). Cyclic degradation products of HD have been found in both, sediment samples and pore water samples (Magnusson et al., 2016; Røen et al., 2010a; Söderström, 2014). The maximum levels of HD degradation products established in pore water samples during implementing the Baltic Sea-related research projects in the past decade have been quite low, 19 µg L⁻¹ for 1,4,5-oxadithiepane and 3.4 µg L⁻¹ for 1,2,5-trithiepane. However, much higher concentrations of five target analytes, 35–610 µg kg⁻¹, have been detected in sediment samples (Christensen et al., 2016). In the next decades, more and more chemical weapons will corrode, target compounds may leak into the sediments and even more into the seawater.

At present days, various analytical methods are being employed to analyze different degradation products of HD including mainly LC and GC using MS detection (Beidowski et al., 2016; D'Agostino et al., 2004; Magnusson et al., 2016; Ohsawa et al., 2004; Pardasani et al., 2004; Røen et al., 2010a, 2010b; Östin, 2012). In addition to the above mentioned analytical techniques, also CE-DAD methods are being used for determination of some of HD degradation products (Cheicante et al., 1995a, 1995b; Jöul et al., 2015; Lees et al., 2017).

To analyze real environmental water samples, pretreatment for the concentration and purification of HD degradation products in water samples is an important part of the whole procedure. The techniques recommended by the Organisation for the Prohibition of Chemical Weapons for the preparation of CWA degradation products-containing samples are liquid-liquid, liquid-solid and solid-phase extractions (Vanninen, 2011). The degradation products of HD are non-ionic compounds and thus the widely-spread ion-exchange SPE phase for the determination of ionic nitrogen mustards degradation products, cannot be used (Kanaujia et al., 2008). Both cyclic and aliphatic compounds have been determined using solvent extraction and subsequent GC–MS, GC–MS/MS or LC–MS/MS analysis (Beidowski et al., 2016). Cyclic degradation products have been determined using headspace extraction, the recoveries were up to 60–90% (Magnusson et al., 2016). Nawała et al. (2016) applied SPME fibers for the extraction of cyclic degradation products from environmental samples. D'Agostino et al. (2004) applied solvent extraction for the determination of hydrolysis products of HD in aqueous extracts of soil. Tomkins and Segal (2001) used two SPE columns in tandem to extract TDG from groundwater samples: the reversed-phase C18 removed extraneous interferences from the groundwater sample and a synthetic carbonaceous sorbent Amborsorb 572 column enabled extraction of TDG with the recovery not more than 40%. Boyer et al. (2004) extracted TDG from urine samples by using a reversed-phase Oasis HLB SPE cartridge and achieved a recovery of 28%. Leong et al. (1998) evaluated the adsorptive capacity of four carbonaceous sorbents towards four organosulfur compounds, including

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