# Development of a dynamic headspace gas chromatography–mass spectrometry method for on-site analysis of sulfur mustard degradation products in sediments

R. Magnusson [a,*], T. Nordlander [b], A. Östin [a]

[a] The Swedish Defence Research Agency, FOI CBRN Defence and Security, SE-90182 Umeå, Sweden
[b] The Swedish Armed Forces, National CBRN Defence Centre, CBRN-Analysis, SE-90176 Umeå, Sweden

## ABSTRACT

Sampling teams performing work at sea in areas where chemical munitions may have been dumped require rapid and reliable analytical methods for verifying sulfur mustard leakage from suspected objects. Here we present such an on-site analysis method based on dynamic headspace GC–MS for analysis of five cyclic sulfur mustard degradation products that have previously been detected in sediments from chemical weapon dumping sites: 1,4-oxathiane, 1,3-dithiolane, 1,4-dithiane, 1,4,5-oxadithiephane, and 1,2,5-trithiephane. An experimental design involving authentic Baltic Sea sediments spiked with the target analytes was used to develop an optimized protocol for sample preparation, headspace extraction and analysis that afforded recoveries of up to 60–90%. The optimized method needs no organic solvents, uses only two grams of sediment on a dry weight basis and involves a unique sample presentation whereby sediment is spread uniformly as a thin layer inside the walls of a glass headspace vial. The method showed good linearity for analyte concentrations of 5–200 ng/g dw, good repeatability, and acceptable carry-over. The method's limits of detection for spiked sediment samples ranged from 2.5 to 11 µg/kg dw, with matrix interference being the main limiting factor. The instrumental detection limits were one to two orders of magnitude lower. Full-scan GC–MS analysis enabled the use of automated mass spectral deconvolution for rapid identification of target analytes. Using this approach, analytes could be identified in spiked sediment samples at concentrations down to 13–65 µg/kg dw. On-site validation experiments conducted aboard the research vessel R/V Oceania demonstrated the method's practical applicability, enabling the successful identification of four cyclic sulfur mustard degradation products at concentrations of 15–308 µg/kg in sediments immediately after being collected near a wreck at the Bornholm Deep dumpsite in the Baltic Sea.

© 2015 Elsevier B.V. All rights reserved.

## 1. Introduction

Environmental concerns regarding sea-dumped chemical weapons (CW) have recently received appreciable attention at the international level after being neglected for some time [1–5]. Today, dumped chemical munitions in the Baltic Sea are in different stages of decomposition and their contents are leaking into the environment where they present significant risks to the surrounding ecosystems [2]. Furthermore, dumped CW are regularly retrieved in fishing nets during bottom trawling or washed ashore on beaches [3], and pose hazards during sea-bottom activities such as pipeline construction [5]. Sulfur mustard is the most abundant chemical

warfare agent (CWA) dumped in the Baltic Sea, accounting for 63% of all materials deposited in the region's largest dump site, which is located east of Bornholm [3]. Sulfur-mustard type materials are also the most abundant CW materials reported to have been trawled up by fishermen, accounting for about 88% of all reported incidents [6].

In the presence of water, sulfur mustard is degraded by hydrolysis to thiodiglycol [7]. However, its fate in the environment is complex and many other degradation products can be formed. Furthermore, munitions grade sulfur mustard often contains impurities that survive longer than the agent itself [8]. The rates of sulfur mustard hydrolysis and dissolution in sea water are lower than in fresh water [9], and low temperatures as well as the common formation of hard lumps coated with a shell of polymerized sulfur mustard further retard the processes of dissolution and hydrolysis [3]. Nevertheless, intact sulfur mustard is rarely detected in sediments collected from chemical weapon dumping sites, and

* Corresponding author. Fax: +46 90 106800.
*E-mail address:* roger.magnusson@foi.se (R. Magnusson).

surprisingly neither is thiodiglycol [3,8,10], whereas various cyclic degradation products of sulfur mustard have been found quite frequently [8,10]. The positive identification of several common cyclic degradation products or impurities in a sample may provide reliable proof of the original presence of sulfur mustard.

A common approach for verifying suspicions of the presence of sulfur mustard and other CWAs at chemical munition dumping sites at sea is to collect sediment or water samples and send them to shore-based laboratories for solvent extraction and subsequent GC–MS, GC–MS/MS or LC–MS/MS analysis of sulfur mustard and its degradation products [2,3,5]. However, this necessarily means that there is an extended time lapse between sampling and obtaining analytical data. It would be preferable if teams performing sampling work at sea had the ability to perform rapid on-site analyses to verify suspected CWA leakages.

One potential way of performing such on-board verification would be to use commercially available on-site mass spectrometric instruments [11–16] such as the Hazardous Air Pollution on Site (HAPSITE®) system. The HAPSITE® is a rugged GC–MS that is currently used by the military and emergency responders to detect and identify unknown chemicals [12]. The system is designed for the on-site detection and identification of volatile organic chemicals (VOCs) such as chemical warfare agents (CWA) and toxic industrial chemicals (TIC) and can hence provide on-scene commanders with valuable data, enabling them to rapidly make informed decisions.

Headspace sampling is the preferred injection technique for volatile compounds present in difficult sample matrices [17–21]. It requires minimal sample preparation and is based on the effective extraction of the components of interest from the sample matrix in a way that enhances the sensitivity of the analysis while preventing the contamination of the GC system and column with matrix components. There are a number of related headspace sampling techniques available, based on either static headspace analysis or dynamic headspace approaches including the so-called purge-and-trap technique, used in a wide range of applications [18,22]. In static headspace approaches, a solid or liquid sample is placed in a vial that is sealed and heated, causing the volatile components to migrate out of the sample matrix and into the vial's headspace. When equilibrium is reached, a portion of the headspace is sampled and transferred to a GC for analysis. Dynamic headspace techniques, which in general are more sensitive than traditional static headspace methods [18,19], remove volatiles from a solid or liquid sample by heating it while passing a continuous flow of an inert gas over its surface or through it. The volatiles are trapped and concentrated onto a solid adsorbent, from which they are released by thermal desorption and transferred to a GC for analysis.

Recently, Røen et al. [8,23] presented a method for trace determination of sulfur mustard and some related cyclic sulfur compounds in soil and water samples using headspace-trap GC–MS, and demonstrated its usefulness in the analysis of a sediment sample collected from an old chemical munitions dumping site. The transfer of such a method to rugged field equipment appropriate for on-board sediment analysis would enable on-site verification of the presence of sulfur mustard and thus expand the capabilities of sampling teams by allowing them to obtain rapid information on the samples they collect. To our knowledge, no GC–MS applications for the on-board verification of sulfur mustard leakages have yet been reported. To be useful, such a method would have to enable confident detection of target analytes even at the low concentrations expected in sediment samples and under the challenging conditions encountered in a sampling vessel at sea.

The objective of this study was to develop a dynamic headspace sampling method for the HAPSITE® GC–MS for rapid and confident determination of cyclic sulfur mustard degradation products present at low ppb levels in sediments. Five target analytes suitable for headspace analysis were selected on the basis of previous analysis results from CW dumping sites [8,10]. Other more complex sulfur mustard degradation products and additives would require alternative analysis techniques. The intention was to develop an optimized method by means of experimental design and then validate it in order to establish a reliable measurement technique that can be used in the field (i.e. under shipboard conditions) to obtain instant information on the status of CW dumping sites and assist sampling teams in their work.

## 2. Experimental

### 2.1. Chemicals

1,4-Oxathiane (98% purity), 1,3-dithiolane (97%) and 1,4-dithiane (98%) were obtained from Sigma–Aldrich. 1,4,5-Oxadithiephane and 1,2,5-trithiephane were synthesized in house (>98%). 2-Methyl-1,3-dithiolane (98%) and 2-methyl-1,3-dithiane (99%) were obtained from Sigma–Aldrich. Dichloromethane (Analytical reagent grade, ≥99.99%), acetonitrile (HPLC grade, ≥99.99%), and methanol (HPLC grade, ≥99.99%), were supplied by Fisher Scientific. Purified water was supplied from a Milli Q system (Merck Millipore, MA, USA). Silicon dioxide (quartz, purum p.a., acid purified) was obtained from Sigma–Aldrich.

### 2.2. Chemical properties of analytes

Five cyclic sulfur mustard degradation products that were previously detected in sediments at CW dumping sites [8,10] were selected as target analytes: 1,4-oxathiane, 1,3-dithiolane, 1,4-dithiane, 1,4,5-oxadithiephane, and 1,2,5-trithiephane. Some chemical properties of the analytes and internal standards are listed in Table 1.

### 2.3. Sediment samples

Two batches of non-contaminated sediment from the Baltic Sea collected during the CHEMSEA project [2,10] were used in the method development. Authentic sediments were used to ensure that the method was optimized for the primary matrix of interest. The batch used for the initial development and optimization consisted of freeze-dried sediment, enabling the use of dry weight as a variable parameter in designed experiments, whereas a batch of wet sediment was used primarily for validation of the final method. The freeze dried sediment was stored in double reclosable soil sampling bags and the wet sediment in a plastic jar at −20 °C, which was defrosted at +8 °C shortly before use. Furthermore, a number of sediment samples were collected from the Bornholm Basin for shipboard analysis as described in Section 2.10.3.

### 2.4. Standard solutions

Mixed standard solutions in two different solvents were prepared from individual stock solutions (1000 ng/μL in acetonitrile) of each target analyte by dilution with dichloromethane (DCM) and water to concentrations of 7.5 and 20 ng/μL. Standard spiking solutions were prepared by further dilution of the standard solutions with each respective solvent to concentrations of 0.025–2.0 ng/μL. Mixed internal standard spiking solutions in DCM and water were prepared in similar way from individual stock solutions (1000 ng/μL in acetonitrile) of 2-methyl-1,3-dithiolane and 2-methyl-1,3-dithiane to a concentration of 8.0 ng/μL. All solutions were stored at 4 °C.