

Evaluation of Different Sample Preparation Methods for Detection of Degradation Products of Mustard Gas in Decontamination Solutions

Ullastiina Hakala,¹ Heikki Björk,¹ Harri Koskela,¹ Olli Kostainen,¹
Heikki Seulanto² and Paula Vanninen¹

¹Finnish Institute for Verification of the Chemical Weapons Convention (VERIFIN),
University of Helsinki

P.O. Box 55 (A.I. Virtasen aukio 1), FIN-00014 University of Helsinki, Finland
Ullastiina.hakala@helsinki.fi

² Finnish Defence Forces Technical Research Centre (PVTTC)
P.O. Box 5 (Paroistentie 20), FIN-34111 LAKIALA, Finland

Abstract

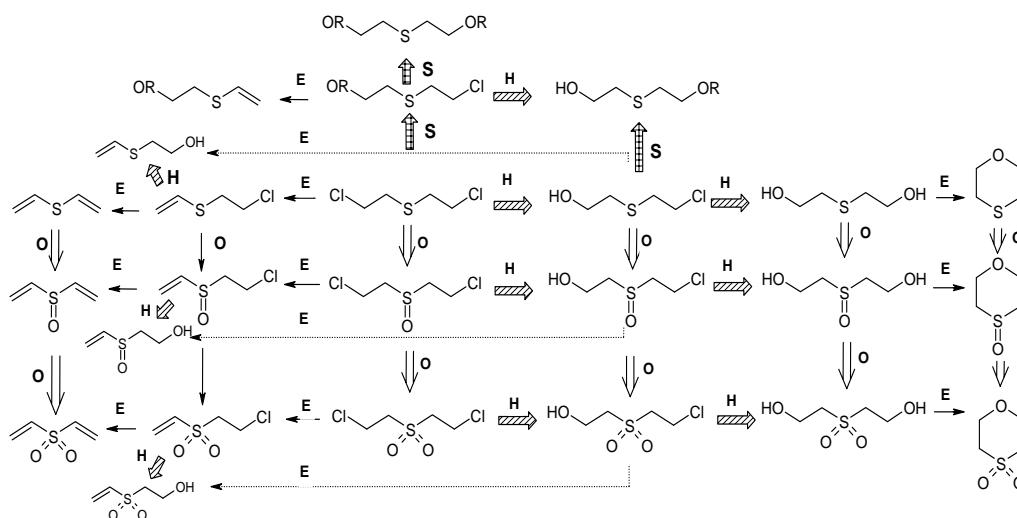
Several sample preparation methods were evaluated to find conditions for determination of the main reaction pathways and degradation products of mustard gas in four different decontamination solutions, i.e. Finnish emulsion E-2000, BX-24, GD-5 and GDS-2000.

Keywords: mustard gas, decontamination, sample preparation

1 Introduction

Decontamination solutions are detergents, salts and organic or aqueous solutions containing complex matrices, especially for analytical techniques.[1] To identify chemical warfare agents (CWAs) and their degradation products from these matrices enquires very effective sample preparation (SP) procedures.

The degradation of mustard gas consists of several reactions, namely oxidation, hydrolysis, elimination and substitution reactions and can produce numerous products (Scheme 1).[1-3] The produced degradation products have diverse physicochemical properties, such as vapour pressure and polarity, which determines the choice of sample preparation method and analytical technique.



Scheme 1. The reaction pathways and structures of mustard gas degradation products. O=oxidation, H= hydrolysis, E=elimination, S=substitution.[1-3]

In this collaboration project, the competence of three commercially available decontamination solutions, BX-24, GD-5 and GDS-2000, and Finnish emulsion E-2000 to destroy mustard gas was studied. The main aim was to identify the primary degradation products. The sample preparation methods were carried out using “Recommended operation procedures for sampling and analysis in the verification of chemical disarmament”[4] and methods developed recently at VERIFIN,[5] as a model. To detect various degradation products, several analytical methods were included, i.e. gas chromatography (GC), gas chromatography – mass spectrometry (GC-MS), liquid chromatography – mass spectrometry (LC-MS), liquid chromatography – tandem mass spectrometry (LC-MSMS) and nuclear magnetic resonance spectroscopy (NMR).

2 Experimental

The decontamination was investigated in two reaction times, 30 minutes and 24 hours, at room temperature. The mustard gas and decontamination solutions were provided from PVTT. The sample preparation methods were modified from Recommended Operation Procedures. [4] The GC and GC-MS experiments were carried out using GC/FPD(S) (Agilent 6890, USA) and GC-MS (Agilent 6890N and 5975B mass selective detector, USA) instruments. For LC-MS experiments, Quattro II triple stage quadrupole mass spectrometer (Micromass, Altrincham, UK) equipped with a Hewlett Packard Model 1100 LC binary pump and a HPLC autosampler (Waldbronn, Germany). NMR experiments were carried out using a DRX 500 NMR spectrometer (Bruker, Germany).

3 Results and Discussion

The representative sample preparation methods for different analytical techniques and detected degradation products are illustrated in Figure 1. Since oxidative aqueous solution, i.e. E-2000 and BX-24, mainly produces degradation products by oxidation and/or hydrolysis reactions with different polarity, it was necessary to carry out several SP methods, including organic extraction and derivatization, for GC-MS, and direct analysis of aqueous phase using LC-MS. Three new chemicals (1-3) were detected in the LC-MS studies. The chemical 3 was produced in the BX-24 solution as mustard gas reacts with the active component of the solution, sodium *N,N*-dichloroisocyanurate. Basic organic solutions, GD-5 and GDS-2000, are immiscible only into hexane of the most commonly used organic solvents. Hexane is highly non-polar solvent and suffers from weak liquid-liquid extraction capacity for slightly polar degradation products. However, dichloromethane (DCM) extraction was carried out after the solution was diluted with water. Divinylsulfide was the main degradation product in both GD-5 and GDS-2000, as elimination reaction is the most expected reaction in basic non-aqueous reaction media. Several substitution products were also detected in the LC-MS studies. Structures of these proposed degradation products will be verified after synthesis of reference chemicals.

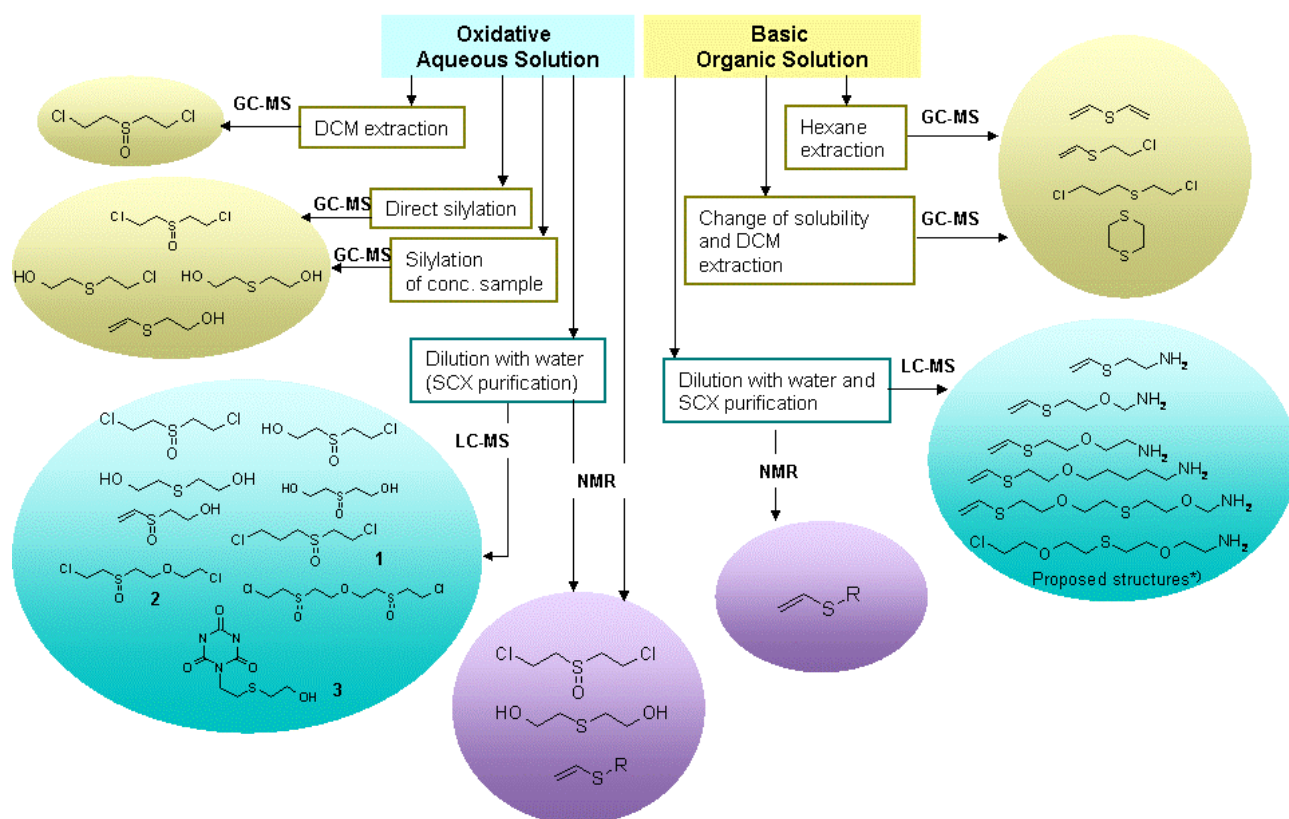


Figure 1. Sample preparation methods for oxidative aqueous and basic organic decontamination solutions and formed degradation products detected by GC-MS, LC-MS and ^1H NMR (*Proposed structures found by AMDIS software).

References

- [1] Talmage, S.S., Watson, A.P., Hauschild, V. Munro, N.B. and King, J. Chemical warfare agent degradation and decontamination. *Current Organic Chemistry*, 2007, 11, 285-298.
- [2] Popiel, S., Witkiewicz, Z. and Nalepa, T. The reaction of sulphur mustard with the active components of organic decontaminants. *Journal of Hazardous Materials B*, 2005, 123, 269-280.
- [3] *Chemical Weapons: Destruction and Conversion*. Stockholm International Peace Research Institute. Taylor & Francis Ltd, London, 1980.
- [4] Rautio, M (Ed.) *Recommended Operation Procedures for Sampling and Analysis in the Verification of Chemical Disarmament*, 1994 Edition, Ministry of Foreign Affairs of Finland, Helsinki, 1994.
- [5] Kuitunen, M-L. Sample preparation for analysis of chemicals related to the chemical weapons convention in an off-site laboratory. *Chemical Weapons Convention Chemicals Analysis*, (Ed. Mesilaakso, M.), p. 163-183, John Wiley & Sons Ltd, West Sussex, 2005.