

A simple and economical chemical neutralization method for the destruction of sulfur mustard and its analogues

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Received 7 September 2005; received in revised form 29 April 2006; accepted 7 June 2006

Available online 10 June 2006

Abstract

A simple and economical chemical neutralization method is developed against highly toxic chemical warfare agent's viz. sulfur mustard (SM), sesquimustard, and their homologues/analogous. The method involves treatment of chemical warfare agents with sodium in inert solvents. This destruction method of sulfur mustards release innocuous products via desulfurization reactions. The products were characterized by GC–MS technique. The method is suitable in particular, for bulk destruction of heel of mustard stockpiles.

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Keywords: Sulfur mustard; Sesquimustard; Desulphurization; Chemical neutralization; GC–MS

1. Introduction

Sulfur mustard and its analogues (sulfur mustards) are highly toxic and alkylating chemical warfare agents (CWAs). This class of compounds encompasses total nine compounds namely 2-chloroethylchloromethylsulfide, bis(2-chloroethyl) sulfide, bis(2-chloroethylthio)methane, 1,2-bis(2-chloroethylthio)ethane, 1,3-bis(2-chloroethylthio)propane, 1,4-bis(2-chloroethylthio)butane, 1,5-bis(2-chloroethylthio)pentane, bis(2-chloroethylthiomethyl) ether and bis(2-chloroethylthioethyl) ether. These are included as schedule 1 chemicals in chemical weapons convention (CWC), which is an international treaty and has entered into force in April 1997. The treaty prohibits production, storage, and usage of chemical weapons; and so far more than 175 countries have endorsed it. An international organization, known as Organization for Prohibition of Chemical Weapons (OPCW) is responsible for implementation of the treaty by executing its strict verification program. As per CWC, all the member states are obliged to essentially destroy stockpiles of Chemical warfare agents in irreversible manner before the year 2007 [1–7]. The chemicals relevant to the convention (CRCs) not only include the popular chemical warfare agents but precursors and degradation products are also included.

It is well documented that thousands of tons of sulphur mustards have been declared as stockpiles by few nations. Huge quantities of the stockpiled sulfur mustards are being destroyed by these countries under the obligation of CWC and many more stockpiles will also be destroyed in the near future too. Hence destruction and demilitarization of sulfur mustards have evinced considerable interest to meet the requirement of OPCW. Various methods are known in the literature for neutralization of sulphur mustards, which make use of either chemical neutralization (oxidative/hydrolytic) or incineration [8–12]. Until 1980s sulphur mustards were mainly destroyed by incineration; however, this incurs the additional hazard of transportation to the incineration site and release of toxic gases during the process, which stimulate the negative reaction amongst the public health authorities.

Among the various chemical neutralization methods, oxidative and hydrolytic methods are considered as potential methods for deactivation of mustard gas and its analogues. The oxidizing procedures involving oxidizing agents, which results the formation of sulfone as one of the products, which is somewhat toxic and can even be reduced back to parent agent [13]. However, the hydrolytic neutralization method is extremely slow and has limited scope due to poor solubility of sulphur mustards and related compounds in water (solubility of mustard gas ~0.8 g/l) [8]. Recently desulphurization of alkyl and aryl organo-sulphur compounds with sodium was reported resulting in the formation of corresponding alkanes and small amount

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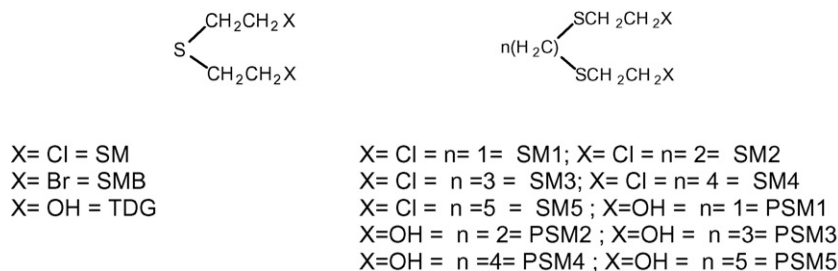


Fig. 1. Compounds selected for destruction with sodium metal.

of mercaptans [14]. Prompted by this property of sodium and non-availability of published data on desulphurization of mustard gas and related compounds, we undertook this study, and herein, we report the simple destruction method for sulphur mustard and its analogues. The method involves simple reaction of sodium with target compounds in inert solvents. In this study we selected bis(2-chloroethyl)sulphide or mustard gas (SM), sesqui-mustard [bis(2-chloroethylthio)ethane (SM 2)] and its lower and higher homologues, namely, bis(2-chloroethylthio)methane (SM 1), bis(2-chloroethylthio)propane (SM 3), bis(2-chloroethylthio)butane (SM 4) and bis(2-chloroethylthio)pentane (SM 5), bis(2-bromoethyl)sulphide (SMB) and “heel” of sulphur mustard. Heel is a viscous thickened material settled at the bottom of the SM flask which normally forms in the presence of water (5% w/w) and some of nitrogen containing heterocyclic stabilizers (1–2% w/w). In order to test the applicability of the method, precursors or hydrolysed products of sulphur mustards were also taken; which includes thiodiglycol (TDG), bis(2-hydroxyethylthio)methane (PSM 1), 1, 2-bis(2-hydroxyethylthio)ethane (PSM 2), 1, 3-bis(2-hydroxyethylthio)propane (PSM 3), 1,4-bis(2-hydroxyethylthio)butane (PSM 4) and 1,5-bis(2-hydroxyethylthio)pentane (PSM 5). The general structures of these compounds are given in Fig. 1. The complete irreversible destruction of compounds takes place via desulphurization reaction initiated by sodium in inert solvents.

2. Experimental section

2.1. Material and methods

Melting and boiling points were uncorrected. Proton NMR spectra were recorded on Bruker 400 MHz instrument with TMS as an internal standard. IR spectra were recorded on a Perkin-Elmer 577 Spectrophotometer. The HPLC instrumentation consists of a Waters 600 E pump, a Rheodyne injector with 5 μl loop, and Waters 486 tunable UV detector. Waters Symmetry C18 (4.6 mm \times 150 mm, 5 μm) column was used for analysis of dithioalkanediols (PSM-1–PSM-5). Detector was tuned at 200 nm. The chemicals and HPLC grade solvents were procured from E-Merck (India) Pvt. Ltd. The chemicals were dried prior to use. Sulphur mustard and its bromo derivative were prepared by known methods [8]. The mobile phases were prepared by filtering the solvents through 0.45 μm membrane filters. Dithiaalkanediols [bis(2-hydroxyethylthio)alkanes

and bis(2-chloroethylthio)alkanes] were prepared by the general method described below.

2.2. GC–MS analysis

The GC–MS analyses were performed by Varian 3400 GC coupled to a TSQ 7000 mass spectrometer (Finnigan Mat). GC operating conditions for gaseous products were as follows: injector temperature 250 $^{\circ}\text{C}$, transfer line temperature 280 $^{\circ}\text{C}$, column temperature programming 35 $^{\circ}\text{C}$ (2 min) at 8 $^{\circ}\text{C}/\text{min}$ –100 $^{\circ}\text{C}$ —at 20 $^{\circ}\text{C}/\text{min}$ –280 $^{\circ}\text{C}$ (2 min), carrier gas helium at pressure of 10 psi. GC operating conditions for other compounds were as follows: injector temperature 250 $^{\circ}\text{C}$, transfer line temperature 280 $^{\circ}\text{C}$, column temperature programming 50 $^{\circ}\text{C}$ (2 min) at 10 $^{\circ}\text{C}/\text{min}$ –280 $^{\circ}\text{C}$ (5 min), carrier gas helium at pressure of 10 psi. EI mass spectrometric operating conditions were as follows: ion source pressure 1.5×10^{-6} Torr, source temperature 150 $^{\circ}\text{C}$, electron energy 70 eV and emission current 400 μA . Chemical ionization (CI) mass spectrometric operating conditions were as follows: ion source pressure with methane as the reagent gas 1.5×10^{-3} Torr, source temperature 150 $^{\circ}\text{C}$, electron energy 100 eV and emission current 300 μA .

2.3. General procedure for the preparation of dithiaalkanediols (PS1–PSM 5)

The 2-hydroxyethyl thiol 7.8 g (0.1 mol) was added slowly in the suspended solution of freshly prepared sodium methoxide in a 250 ml round bottom flask. Sodium methoxide was prepared by addition of 2.3 g sodium pieces (0.1 mol) in methanol (100 ml). The reaction mixture was refluxed for 15 min for complete conversion of 2-hydroxyethyl thiol in to corresponding sodium thiolate. The flask was cooled at room temperature, and ω , ω' -dibromoalkane (0.05 mol) was added drop wise from a dropping funnel at such a rate so that the temperature of the reaction mixture does not exceed to 60 $^{\circ}\text{C}$. The reaction mixture was refluxed for 1–2 h. The progress of reaction was monitored by thin layer chromatography (TLC) (silica plates, 10% chloroform in methanol). The resulting solution was filtered and solvent was removed by distillation and finally under vacuum. The residue was crystallized with 2-propanol followed by addition of petroleum ether till turbidity and cooled. The dithiaalkanediols were obtained nearly in quantitative yields. The purity of compounds was verified by TLC (silica plates, 10% chloro-

form in methanol) and high performance liquid chromatography (HPLC) [18]. All the dithiaalkanedioles were characterized by spectroscopic techniques and the details are given below.

2.3.1. Bis(2-hydroxyethylthio)methane (PSM1)

Viscous liquid, b.p. 115 (0.5 mm), yield 84%; IR (KBr) 3365, 2918, 2875, 1465, 1063, 647 cm^{-1} ; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 3.7 (t, 4H), 3.6 (s, 2H), 2.8 (t, 4H), 2.2 (bs, 2H); MS (EI) m/z 168 (M^+), 151, 124, 105, 91, 61.

2.3.2. 1,2-Bis(2-hydroxyethylthio)ethane (PSM2)

Solid, m.p. 64 °C, yield 88%; IR (KBr) 3284, 2958, 2931, 1477, 1050, 632 cm^{-1} ; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 3.7 (t, 4H), 2.7 (m, 8H), 2.2 (bs, 2H); MS (EI) m/z 182 (M^+), 164, 138, 105, 91, 61.

2.3.3. 1,3-Bis(2-hydroxyethylthio)propane (PSM3)

Viscous liquid, b.p. 200 (4 mm), yield 86%; IR (KBr) 3367, 2921, 2872, 1418, 1046, 654 cm^{-1} ; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 3.7 (t, 4H), 2.7 (t, 4H), 2.6 (t, 4H), 2.1 (bs, 2H), 1.7 (m, 2H); MS (EI) m/z 196 (M^+), 178, 151, 119, 107, 61.

2.3.4. 1,4-Bis(2-hydroxyethylthio)butane (PSM4)

Viscous liquid, b.p. 207 (3 mm), yield 89%; IR (KBr) 3368, 2923, 2869, 1422, 1045, 722, 655 cm^{-1} ; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 3.6 (t, 4H), 2.6 (t, 4H), 2.4 (m, 4H), 1.9 (bs, 2H), 1.6 (m, 4H); MS (EI) m/z 210 (M^+), 192, 165, 133, 115, 87, 61.

2.3.5. 1,5-Bis(2-hydroxyethylthio)pentane (PSM5)

Viscous liquid, b.p. 210 (3 mm), yield 93%; IR (KBr) 3361, 2926, 2856, 1458, 1045, 725, 655 cm^{-1} ; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 3.6 (t, 4H), 2.6 (t, 4H), 2.447 (t, 4H), 2.2 (bs, 2H), 1.5 (m, 4H), 1.4 (m, 2H); MS (EI) m/z 224 (M^+), 207, 179, 165, 147, 129, 101, 61.

2.4. General procedure for the preparation of bis(2-chloroethyl thio)alkanes (SM1–SM5)

Bis(2-hydroxyethylthio) alkanes (0.1 mol) and HCl 36% (50 ml) were mixed in a 100 ml round-bottomed flask equipped with a condenser. The flask was warmed at 90 °C on water bath for 1–2 h. An oily layer was separated, which was extracted with CH_2Cl_2 , and dried over anhydrous Na_2SO_4 and desired products were obtained nearly in quantitative yield by vacuum distillation after removal of solvent. The purity of these compounds was checked by GLC. Except SM2, all other compounds became solid on storing in deep freeze. The compounds were characterized by spectroscopic techniques and the details are given below.

2.4.1. Bis(2-chloro ethyl thio)methane (SM1)

Viscous liquid, b.p. 128 °C/0.5 mmHg, yield 95%; IR (KBr) 2958, 2825, 1435, 1133, 757, 690 cm^{-1} ; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 3.70 (t, 4H), 3.06 (s, 2H), 2.68 (t, 4H); MS (EI) m/z (Int.%): 204 (3), 168 (12), 111 (35), 109 (100), 79 (15), 73 (65), 63 (61), 47 (42).

2.4.2. 1,2-Bis(2-hydroxyethylthio)ethane (SM2)

b.p. 140 °C/2 mm, solid, m.p. 56 °C, yield 90%; IR (KBr) 2960, 2922, 1437, 1294, 1272, 1217, 1135, 752, 692 cm^{-1} ; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 3.67 (t, 4H), 2.87 (m, 4H), 2.81 (m, 4H); MS (EI) m/z (Int.%): 218 (3), 182 (22), 123 (73), 109 (50), 73 (64), 61 (69), 46 (34).

2.4.3. 1,3-Bis(2-hydroxyethylthio)propane (SM3)

Viscous liquid, b.p. 132 °C/0.4 mm, yield 96%; IR (KBr) 2958, 2924, 1438, 1342, 1294, 1260, 1126, 930, 836, 755, 694 cm^{-1} ; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 3.64 (t, 4H), 2.87 (t, 4H), 2.68 (t, 4H), 1.89 (m, 4H); MS (EI) m/z (Int.%): 232 (4), 196(8⁺), 171 (35), 169 (81) 107 (73), 74 (40), 63 (62), 45 (100).

2.4.4. 1,4-Bis(2-hydroxyethylthio)butane (SM4)

Viscous liquid, b.p. 142 °C/0.5 mm, yield 92%; IR (KBr) 2953, 2927, 1439, 1361, 1293, 1213, 1196, 851, 752, 695 cm^{-1} ; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 3.66 (t, 4H), 2.86 (t, 4H), 2.59 (m, 4H), 1.62 (m, 4H); MS (EI) m/z (Int.%): 248 (3), 218 (12), 183 (48), 115 (55) 109 (74), 87 (89), 63 (73), 60 (54), 47 (52).

2.4.5. 1,5-Bis(2-hydroxyethylthio)pentane (SM5)

Viscous liquid, b.p. 145 °C/0.01 mm, yield 93%; IR (KBr) 2950, 2933, 1442, 1347, 1290, 1212, 1190, 945, 832, 755, 693 cm^{-1} ; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 3.65 (t, 4H), 2.85 (t, 4H), 2.57 (t, 4H), 1.64 (m, 4H), 1.58 (m, 2H); MS (EI) m/z (Int.%): 260 (3), 224 (32), 197 (22), 165 (49), 129 (69), 109 (63), 101 (82), 87 (25) 69 (100).

2.5. Typical procedure for the chemical destruction of sulfur mustards

Sodium pieces 13.8 g (0.6 mol) were taken in a solvent (50 ml decane) in a 250 ml two-necked round bottom flask fitted with a condenser having a joint on top to connect it with Tedlar bag. The sulfur mustard (0.1 mol, 1.59 g) was added slowly. The Tedlar bag had been used for the collection of evolved gaseous products. The gaseous products and the sample drawn from the reaction mixture were analyzed for the identification of volatile and non-volatile products monitored by GC–MS in EI mode. The reaction mixture was vigorously stirred and refluxed till the SM was totally consumed (Table 1). After cooling the reaction mixture at room temperature, un-reacted sodium was destroyed by addition of ethanol at 0 °C, followed by saturated aqueous NH_4Cl (50 ml) at room temperature. The aqueous and organic layers were separated after extractive workup with diethyl ether. The organic layer was analyzed by GC–MS in both EI and CI modes as such, and after derivatization with *N,O*-bis(trimethylsilyl) trifluoroacetamide (BSTFA) at 80 °C for 2 h. One portion of the aqueous layer was directly evaporated to dryness on rotary evaporator followed by reconstitution in methanol. It was further evaporated to dryness and silylated with BSTFA for GC–MS analysis. Another portion of the aqueous layer was evaporated to dryness and reconstituted with acidic methanol (HCl/methanol 0.5N). It was further evaporated to dryness and silylated with BSTFA before GC–MS analysis. The results were compared with authentic samples. The gaseous contents in the Tedlar bags

Table 1
Chemical neutralization of SM, sesqui-mustard and their analogues with sodium metal^a

Entry	Substrate	Ratio (subs.:Na)	Solvent	Time (min)
1.		1:10	Decane	15
2.		1:6	Decane	25
3.		1:5	Decane	45
4.		–	Decane	240 ^b
5.	HEEL	1:8	Decane	45
6.		1:10	Decane	40
7.		1:10	Decane	40
8.		1:10	Decane	40
9.		1:10	Decane	40
10.		1:10	Decane	40
11.		1:6	Octane	45
12.		1:6	Mesitylene	45
13.		1:6	Octane	35
14.		1:6	Octane	50
15.		1:10	Decane	120
16.		1:10	Decane	120
17.		1:10	Decane	120
18.		1:10	Decane	120
19.		1:10	Decane	120

^a Products obtained by desulphurization reaction are mixture of alkanes, alkenes. Vinyl alcohol and ethyl alcohol were also identified when hydroxyl derivatives were subjected for desulphurization reaction. Heel gave mainly ethane and ethane as major products and approximately 10% unidentified minor products.

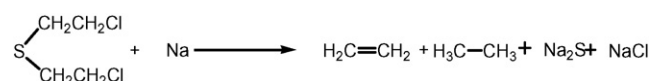
^b Entry 4 is a control experiment in which reaction was performed without use of sodium metal, reaction was monitored up-to 240 min, sulfur mustard was found to be intact.

were analyzed as such by GC–MS using gas tight syringe, the analysis results showed the formation of ethane and ethene, which were matched with spectral library.

Caution: These compounds are extremely toxic therefore trained and authorized persons should be allowed for this type of work. All the reactions must be performed in an efficient fuming hood and full body protection along with respiratory protection is required during the synthesis and handling of these chemicals. To avoid any accident sufficient amount of decontamination solution should be available at working place.

3. Results and discussion

The chemical reaction for the desulphurization of sulfur mustard is depicted in Scheme 1. In order to examine the desulphurization ability of sodium metal various experiments of sulfur



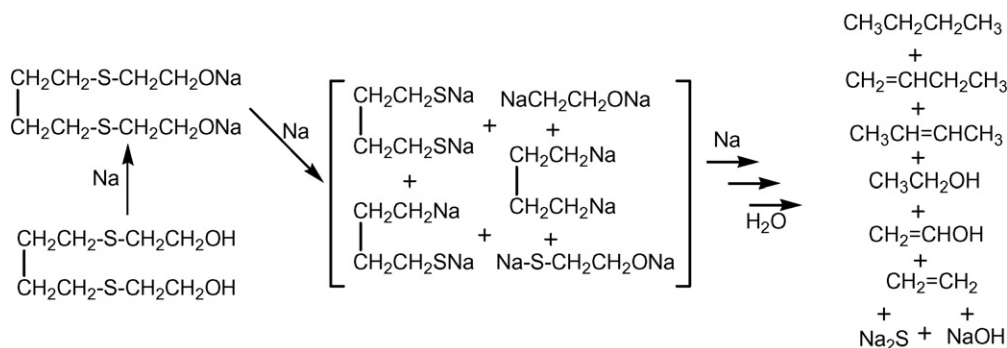
Scheme 1. The desulphurization reaction of bis(2-chloroethyl) sulfide by sodium metal.

mustard and sodium metal were performed by changing the mole ratios of sulfur mustard and sodium metal. The optimum molar ratio of substrate to sodium metal was found to be 1:6 in compounds having one sulphur atom such as sulfur mustard, SMB and TDG. However, compounds having two sulphur atoms per molecule, the ideal molar ratios for desulphurization of SM1–SM5 and PSM1–PSM5 were found to be 1:10. Furthermore, to examine the effect of solvents and temperature, variations experiments of desulphurization reaction were performed in different solvents at different temperatures. We found that solvents like mesitylene, octane and decane gave similar reaction products, with marginal difference in neutralization reaction time of SM and boiling temperature of solvents is essentially required for complete desulphurization reaction (Table 1).

All the reactions were monitored by gas chromatography coupled with mass spectrometry (GC–MS) in both EI and CI modes, as it is most favored analytical technique for on- and off-site analysis [15–17]. To analyze the gaseous products formed during the course of the reaction, a Tedler Bag (purchased from Aldrich USA, capacity 1.6 lit. material-Tedler PVF Fluoro polymer) was connected at the top of the condenser to collect the gaseous products. The gaseous products evolved by desulphurization reaction were also analyzed by GC–MS using gas tight syringe. It was observed that, chemical neutralization reaction of SM with sodium metal (1:6 mol) in decane, completely consumed SM within 25 min and gave non-toxic products (Scheme 1, Table 1 and entry 3).

We also studied the reproducibility and scale-up feasibility of optimized chemical neutralization method. The feasibility of above procedure was successfully tested on sulfur mustard at 0.1–0.5 mol levels. Table 1 summarizes the mole ratios of reactants, time and solvent for the desulphurization reactions. To extend the generality and scope of the method, for chemical destruction of precursors of SM2 and its homologues (PSM1–PSM5) reactions of sodium with these compounds were also studied. It was found that all these compounds gave the mixture of corresponding bridging alkanes and alkenes. The hydroxyl derivatives of SM2 and its analogues showed the formations of ethanol and vinyl alcohol in decane (see Section 2). These hydrocarbons along with ethanol and vinyl alcohol were confirmed on the basis of their GC–MS data which were compared with authentic compounds. Ethanol and vinyl alcohol formed in hydroxy analogues (TDG and PSM1–PSM5) were also analyzed and identified as their silyl derivatives after extraction of the reaction mixture with dichloromethane followed by their silylation with *N,O*-bis(trimethylsilyl) trifluoroacetamide (BSTFA). The probable mechanism for the formation of various non-toxic products is depicted in Scheme 2 by a typical representative example of 1,4-bis(2-hydroxyethylthio)butane (PSM4).

The main advantage of this method is applicability for destruction of SM, SM-2–SM-5 and their hydroxyl derivatives.



Scheme 2. Probable mechanism for the formation of various non-toxic products in 1,4-bis(2-hydroxyethylthio)butane (PSM4).

The interesting features of these reactions were observed that solvents could be recycled after washing as they are insoluble in water. Furthermore, it has been found that this method has additional advantage for destruction of thickened heel of sulfur mustard; which is difficult to destroy by conventionally used incineration. The another positive aspect of this method is that the commercial grade sodium with out cleaning and even peelings of sodium can also be used for the deactivation of these agents which resolves problem to dispose off sodium bark and also minimized the hazards. Interestingly, the products of reaction are solid and gaseous in nature; however the gaseous products are only lower hydrocarbons, which can be used as fuels after trapping. The solid products are completely non-toxic; therefore disposal of effluents becomes easier. Furthermore, the edge of the method lies in its fast reaction time as complete reaction time for sulfur mustard was observed within 25–120 min at appropriate mole ratios.

4. Conclusion

In conclusion, we have presented a simple and economical chemical destruction method for sulfur mustard and its analogues, which could also be useful to destroy the thickened heel and thus meets the requirement of CWC.

Acknowledgement

We thank Ms. Mamta Sharma and Dr. R.P. Semwal for recording the NMR spectra and FT-IR spectra, respectively.

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Glossary

- BSTFA*: *N,O*-bis(trimethylsilyl) trifluoroacetamide.
CRCs: Convention related chemicals.
CWAs: Chemical warfare agents are the chemicals which are used by army.
CWC: Chemical weapons convention.
GC–MS: Gas chromatography coupled with mass spectrometry.
Heel: Heel is a viscous thickened material settled at the bottom of the SM flask which normally forms in the presence of water (5%, w/w) and it contains some of nitrogen containing hetero cyclic stabilizers (1–2%, w/w).
Of-site analysis: Collected samples are sent to designated laboratories and these laboratories have expertise in the field of trace analysis and their capabilities are regularly checked by OPCW by conducting inter laboratory official proficiency tests twice in a year.
Onsite analysis: Samples collected at the site of production, storage, or from the field and are analyzed there it self.
OPCW: Organization for the prohibition of chemical weapons.