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Analysis of mustard hydrolysis products by packed capillary liquid chromatography–electrospray mass spectrometry

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Abstract

Packed capillary column liquid chromatography (LC)–electrospray mass spectrometry (ESI-MS) was used to identify munitions grade mustard hydrolysis products, including five longer chain diols, two partial hydrolysis products and three ether/thioether macrocycles. All ESI-MS data were collected under collisionally activated dissociation (CAD) conditions optimized to facilitate acquisition of both molecular and product ion information that could be used for structural identification purposes. Interpretation of the ESI-MS data enabled characterization of the diols resulting from hydrolysis of all three principal sulfur vesicants, bis(2-chloroethyl)sulfide (mustard or H), bis(2-chloroethylthio)ethane (sesquimustard or Q) and bis[(2-chloroethylthio)ethyl] ether (T), as well as novel products not previously associated with sulfur vesicant hydrolysis. The developed packed capillary LC–ESI-MS method was successfully applied to the analysis of aqueous samples collected at a former mustard destruction site. Both thiodiglycol and the hydrolysis product of T, 6-oxa-3,9-dithia-1,11-undecanediol, were detected. © 1998 Published by Elsevier Science B.V.

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1. Introduction

The use of the chemical warfare agent mustard in the Iran/Iraq war [1,2], and threat of chemical weapons use in the Persian Gulf War emphasize the need for specific methods to detect and identify sulfur vesicants and their degradation products. Retrospective analysis of samples contaminated with chemical warfare agents will continue to be an important means for the verification of allegations of use claims and will be a critical component during future challenge inspections in support of the United Nations Chemical Weapons Convention.

Gas chromatography (GC) [3,4] and mass spectrometry (MS) [5–14] have been used extensively for the identification of mustard and mustard related compounds with capillary column GC–MS being the most commonly employed technique for the detection of these compounds in environmental [10,12,15], biological [16–20] and decontamination [21] samples. Mustard destruction by hydrolysis or natural weathering in the environment results in the formation of thiodiglycol [22,23], a non-toxic compound that may be easily handled. However, some munitions grade mustard formulations contain only 50 to 80% mustard with most of the remaining content being other sulfur vesicants [9] which would decompose to other products. GC–MS under both electron impact (EI) and ammonia chemical ionization (CI) conditions has been used for the mass

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spectrometric characterization of several hydrolysis products of longer chain sulfur vesicants commonly found in munitions-grade mustard [14]. Molecular ion information, critical for the confirmation of these hydrolysis products, was generally absent during EI analyses and ammonia (CI) was used to obtain complementary information on the intact molecule for the compounds or their trimethylsilyl (TMS) derivatives.

The hydrolysis products of sulfur vesicants would generally be associated with aqueous samples and development of capillary electrophoresis (CE) or liquid chromatography–mass spectrometry (LC–MS) methods for their detection and identification would reduce sample handling and derivatization requirements. Direct aqueous MS analysis methods for mustard hydrolysis products have made use of either loop injection MS or LC–MS. A notable exception involved the use of micellar electrokinetic chromatography with UV detection for the detection of thiodiglycol, 1,4-dithiane, 1,4-thioxane and 2,2′-sulfinyldiethanol [24]. Thermospray [25], atmospheric pressure chemical ionization (APCI) [26] and electrospray [27] mass spectrometric interfaces have all been used to facilitate the introduction and ionization of mustard hydrolysis products. In these cases, the investigations focused on the analysis of thiodiglycol, half-mustard, thiodiglycol sulfone and thiodiglycol sulfoxide, compounds commonly associated with the degradation of mustard.

Munitions-grade mustard formulations contain bis(2-chloroethyl)sulfide (mustard or H), as well as additional sulfur vesicants, including bis(2-chloroethylthio)ethane (sesquimustard or Q), bis[(2-chloroethylthio)ethyl] ether (T) and longer chain sulfur vesicants. In some cases the munitions were purposely developed to contain multiple vesicants, with HT and HQ being two munitions containing relatively crude mixtures of H and T and, H and Q, respectively [9]. Mass spectrometric characterization of the additional degradation products that would arise following hydrolysis would be valuable during chemical weapons destruction monitoring by countries in compliance with the Chemical Weapons Convention, for the verification of these compounds in samples collected during challenge inspections of suspect production facilities or in support of allegations of chemical warfare agent use claims.

A packed capillary LC–ESI-MS method was developed to detect and identify thiodiglycol and the novel hydrolysis products of the longer chain sulfur vesicants contained in munitions grade HT and HQ samples. ESI-MS provided ample molecular ion information and structurally important product ion information were generated by promoting collisionally activated dissociation (CAD) in the ESI interface. The method was then applied to the analysis of aqueous samples collected from a former mustard destruction site.

2. Experimental

2.1. Samples

Samples of HT and HQ munitions-grade mustard formulations (2 ml) were hydrolysed in a 125-ml erlenmeyer flask with 50 ml water at 50°C overnight. Acetone was added to each sample to solubilize the remaining oil and each sample was stirred overnight at 50°C. Both hydrolysed samples cleared and the excess water was evaporated leaving a pale yellow oil for each sample. The oils were then distilled in a Kughlrohr oven at 220°C at 0.1 Torr. Hydrolysed HT and HQ samples were dissolved in water at the 1 mg/ml level prior to LC–ESI-MS analysis.

Aqueous samples were collected from a former mustard destruction site. Two of the samples were analysed directly, while the third sample was filtered through cotton gauze to remove the visible debris associated with this sample.

2.2. Instrumental

All electrospray mass spectra were acquired using a Micromass Autospec-Q tandem mass spectrometer (Manchester, UK) equipped with the Mark II electrospray interface. The electrospray needle was operated at 7.6 kV and ions were accelerated into the mass spectrometer at 4 kV. Sampling cone voltages of 20 to 90 V were utilized. Nitrogen (Very Dry, Liquid Carbonic, Scarborough, Canada) bath gas was introduced into the interface (80°C) at a flow-rate of

400 l/h. Nitrogen nebulizer gas was introduced at a flow-rate of 14 l/h. The electrospray interface was pumped with both a rotary and a turbomolecular pump, which enabled maintenance of a $4 \cdot 10^{-4}$ and $7 \cdot 10^{-6}$ Pa within the source and analyzer regions of the instrument, respectively. LC–ESI-MS data were acquired in the continuum mode by scanning the magnetic sector from 340 to 50 u (7 s/decade) or 600 to 100 u (7 s/decade) with a resolution of 1000 (10% valley definition). Three to five scans were typically averaged to enhance the signal-to-noise ratio.

The product spectra of m/z 167 for 8-chloro-6-oxa-3-thia-1-octanol and 14-chloro-6,12-dioxa-3,9-dithia-1-tetradecanol and the product spectrum of m/z 271 for 14-chloro-6,12-dioxa-3,9-dithia-1-tetradecanol were obtained during LC–ESI-MS–MS analysis under a variety of quadrupole collisional cell conditions in a effort to enhance product ion production. The quadrupole collisional cell energy was varied between 10 and 55 eV (laboratory scale) and the argon pressure was varied between $4.2 \cdot 10^{-5}$ and $1.4 \cdot 10^{-4}$ Pa (near the cell). In the end, increasing the cell pressure and/or energy was effective only in reducing the transmission efficiency. Product ion relative intensities remained low under all conditions investigated with relative intensities remaining being between 1 and 10% of the precursor ion intensity. The quadrupole was operated at unit resolution and scanned from 200 to 50 u at 4 s/scan or 300 to 50 u at 5 s/scan.

All LC separations were performed with an Applied Biosystems Model 140B dual syringe pump (Foster City, CA, USA) equipped with a Zorbax 150 mm×0.32 mm I.D. C_{18} SB (5 μm) packed fused-silica capillary column and a Rheodyne 8125 (Cotati, CA, USA) injector with a 5-μl sample loop. The following solvent compositions were prepared for sample introduction: solvent A [0.1% trifluoracetic acid (TFA) in water] and solvent B (0.1% TFA in acetonitrile–water, 95:5). Chromatographic separations were performed using a 1 to 75% B gradient over 30 min. In order to minimize dead volume effects and ensure reproducible mixing, the mobile phase was delivered at 200 μl/min and split prior to the injector such that the flow through the column was 5 μl/min.

3. Results and discussion

HQ and HT munitions-grade mustard formulations, containing predominately mustard (H), and sesquimustard (Q) and mustard and bis[(2-chloroethylthio)ethyl] ether (T), respectively [9], were hydrolysed in an attempt to characterize the principal hydrolysis products associated with these samples. Mustard hydrolysis results in the production of the partial hydrolysis product, hemisulfur mustard, which converts to the full hydrolysis product, thiodiglycol. Detection of thiodiglycol in suspect samples could provide evidence for the prior presence of mustard, but the presence of only thiodiglycol may not provide the conclusive evidence required to prove prior mustard presence. Detection of longer chain diols, partial hydrolysis products or ether/thioether macrocycles formed following hydrolysis of longer chain sulfur vesicants could provide much needed additional evidence to verify prior mustard presence.

Fig. 1 illustrates typical total ion current chromatograms obtained following LC–ESI-MS analysis of the two hydrolysis samples. Thiodiglycol was the principal diol detected in both samples. Five addi-

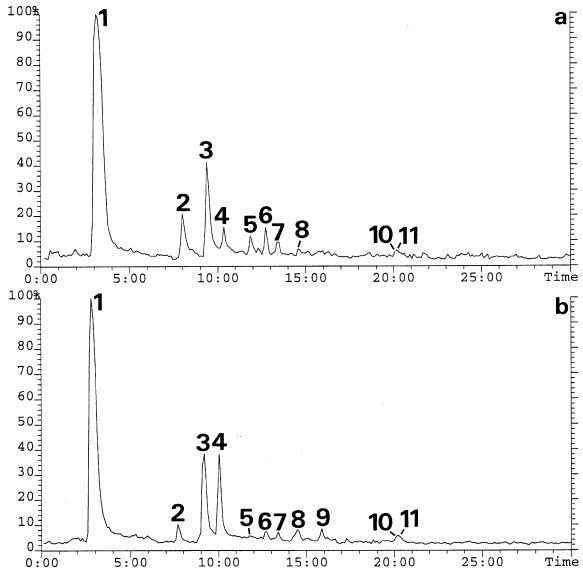


Fig. 1. LC–ESI-MS total ion current (600 to 100 u) chromatograms obtained for (a) HQ and (b) HT hydrolysis samples (compounds identified in Table 1).

tional diols related to Q, T and longer chain sulfur vesicants were also detected along with two partial hydrolysis products and three ether/thioether macrocycles (refer to Table 1). The higher mass diols were separated by LC but could prove difficult to analyse by GC. They were not observed during a prior GC–MS study [14]. In general, some peak tailing occurs during GC separation of diols. With more active or poorly conditioned capillary columns the quality of chromatography deteriorates significantly and detection of these hydrolysis products, including thiodiglycol, would be unreliable. The activity of GC columns becomes less critical during the analysis of the TMS derivatives of the hydrolysis products, as these compounds are less polar than the underivatized compounds [14]. Use of LC for the separation of sulfur vesicant hydrolysis products prior to MS characterization offers a number of potential advantages over GC. Most samples containing sulfur vesicant hydrolysis products would be aqueous in nature and these samples could then be analysed directly without the need for additional sample handling and/or derivatization. In addition, thermal degradation, a distinct possibility with increasing diol mass, would be minimized during LC–ESI-MS analysis.

Thiodiglycol has been recently analysed by ESI-MS following loop injection [27] and by LC–APCI-MS [26] with both authors reporting similar spectra. The mass spectra contained the protonated adduct at m/z 123 and a base ion at m/z 105 due to loss of H_2O from the $(M+H)^+$ ion. Additional molecular ion evidence was provided by the presence of a $(M+Na)^+$ adduct ion during ESI-MS analysis. ESI-MS conditions, in particular the sampling cone voltage, can have a considerable impact on mass spectrometric content. For this reason, thiodiglycol standards were analysed under a variety of conditions during LC–ESI-MS method development. Sampling cone voltage was varied between 20 and 90 V with the effects tabulated in Table 2 for a 0.1 mg/ml standard. In general, the relative intensity of the product ion due to loss of H_2O increased with increasing sampling cone voltage, with 40 V being selected as a reasonable compromise between molecular ion and product ion content for this study. A readily interpretable full scanning ESI mass spectrum could be obtained with as little as 10 ng of thiodiglycol with a sampling cone voltage of 40 V. Selected ion monitoring, which typically results in a 10–100-fold increase in sensitivity, was not evaluated.

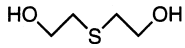
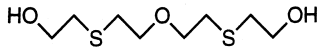
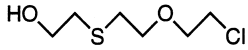
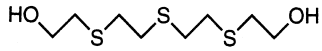
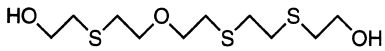
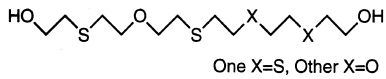
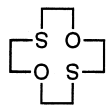
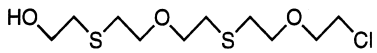
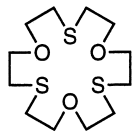
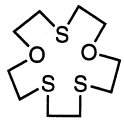
Concentration also has an effect on the nature of the ESI-MS data acquired. At higher concentrations (approximately 0.5 to 0.8 mg/ml), such as those encountered during the analysis of the HT and HQ hydrolysis samples, the thiodiglycol mass spectra contained slightly higher $(M+H)^+$ relative intensity and a significant $(2M+H)^+$ dimer at m/z 245. Minor adduct ions due to $(M+NH_4)^+$, $(M+Na)^+$, $(M+CH_3CN+H)^+$ and $(2M+Na)^+$ were also observed at m/z 140, m/z 145, m/z 164 and m/z 267, respectively. Table 1 contains typical ESI-MS data obtained for thiodiglycol at higher concentrations with a sampling cone voltage of 40 V.

EI and ammonia CI-MS data have been reported for the two longer chain diols, 3,6-dithia-1,8-octanediol and 6-oxa-3,9-dithia-1,11-undecanediol, that result from the hydrolysis of Q and T, respectively [14]. ESI-MS has not been previously used for the identification of these important hydrolysis products (peaks 2 and 3) and was used to characterize these and three novel higher mass diols (peaks 5, 6 and 7). Fig. 2a–c illustrates typical ESI-MS data obtained for three longer chain diols, 3,6-dithia-1,8-octanediol, 6-oxa-3,9-dithia-1,11-undecanediol and 6,12-dioxa-3,9,15-trithia-1,17-heptadecanediol (or 6,15-dioxa-3,9,12-trithia-1,17-heptadecanediol), respectively. The ESI-MS data for others have been summarized in Table 1.

Diol ESI-MS data were rich in both molecular ion and product ion content, enabling structural identification of these hydrolysis products. The ESI-MS information obtained for 6-oxa-3,9-dithia-1,11-undecanediol, the hydrolysis product of T, was typical of that acquired. The mass spectrum contained a significant $(M+H)^+$ ion at m/z 227, a $(2M+H)^+$ ion at m/z 453, and a sodium adduct at m/z 249. A significant product ion due to loss of H_2O was observed at m/z 209 along with product ions at m/z 181, m/z 149 and m/z 105 due to $(M+H-H_2O-C_2H_4)^+$, $(M+H-H_2O-SC_2H_4)^+$ and $(M+H-H_2O-SC_2H_4-OC_2H_4)^+$, respectively (Fig. 2b). The ion at m/z 105, thought to be a protonated 1,4-thioxane ring was significant for all the diols and represented the lowest mass product ion recorded above m/z 50.

Ions representing sequential loss of either SC_2H_4

Table 1
Compounds identified following packed capillary LC–ESI-MS analysis of samples

Peak No.[a]	M_r	Compound name	Partial ESI-MS data: m/z (% relative intensity)	Structure
1	122	Thiodiglycol	245(47) 164(4) 145(3) 123(60) 105(100)	
2	182	3,6-Dithia-1,8-octanediol	365(4) 183(43) 165(15) 137(11) 105(100)	
3	226	6-Oxa-3,9-dithia-1,11-undecanediol	453(12) 227(89) 209(100) 181(35) 149(6) 105(89)	
4	184	8-Chloro-6-oxa-3-thia-1-octanol	369(3) 185(9) 167(65) 105(100)	
5	242	3,6,9-Trithia-1,11-undecanediol	485(11) 243(76) 225(100) 197(60) 165(36) 137(34) 105(79)	
6	286	6-Oxa-3,9,12-trithia-	573(10) 309(14) 287(73) 269(100) 209(11) 165(16) 137(14) 105(72)	
7	330	6,12-Dioxa-3,9,15-trithia-1,17-heptadecanediol or 6,15-Dioxa-3,9,12-trithia-iol 1,17-heptadecaned	353(15) 331(47) 313(100) 285(3) 209(39) 181(7) 149(3) 105(15)	 One X=S, Other X=O
8	208	1,7-Dioxa-4,10-dithiacyclododecane[b]	231(63) 226(12) 209(100) 181(53)	
9	288	14-Chloro-6,12-dioxa-3,9-dithia-1-tetradecanol	311(36) 306(60) 289(44) 271(100) 243(28) 209(31) 181(23) 167(83) 105(41)	
10	312	1,7,13-Trioxa-4,10,16-trithiacyclooctadecane or another isomer	335(25) 330(40) 313(100)	
11	268	1,7-Dioxa-4,10,13-trithiacyclopentadecane[b]	291(44) 286(61) 269(100)	

[a] Refer to Figs. 1 and 3.
[b] Probable isomer based on MS data obtained in a prior study (Ref. [14]).

or OC_2H_4 from higher mass ions enabled assignment of S and O positioning for all the diols except chromatographic peak 7. In this case (Fig. 2c) molecular mass was determined to be 330 u based on the presence of $(M+H)^+$, $(M+NH_4)^+$ and $(M+Na)^+$ ions at m/z 331, m/z 348 and m/z 353, respectively. The ESI mass spectrum contained significant product ions at m/z 313, m/z 285, m/z

Table 2
Typical m/z 123 and m/z 105 relative intensities obtained with different sampling cone voltages

Sampling cone voltage (V)	Relative intensity	
	m/z 123	m/z 105
20	83	100
40	40	100
60	31	100
90	7	100

209, m/z 181, m/z 149 and m/z 105 that could be attributed to $(M+H-H_2O)^+$, $(M+H-H_2O-C_2H_4)^+$, $(M+H-H_2O-SC_2H_4OC_2H_4)^+$, $(M+H-H_2O-SC_2H_4OC_2H_4-C_2H_4)^+$, $(M+H-H_2O-SC_2H_4OC_2H_4-SC_2H_4)^+$ and $(M+H-H_2O-SC_2H_4OC_2H_4-SC_2H_4-OC_2H_4)^+$, respectively. The order of S and O at positions 12 and 15 could not be determined since a product ion due to neutral loss of OC_2H_4 or SC_2H_4 in the ESI interface from the $(M+H-H_2O)^+$ was not recorded. In this case one of two possible hydrolysis products, 6,12-dioxa-3,9,15-trithia-1,17-heptadecanediol or 6,15-dioxa-3,9,12-trithia-1,17-heptadecanediol, was postulated. This ambiguity was not resolved through the use of LC–ESI-MS–MS.

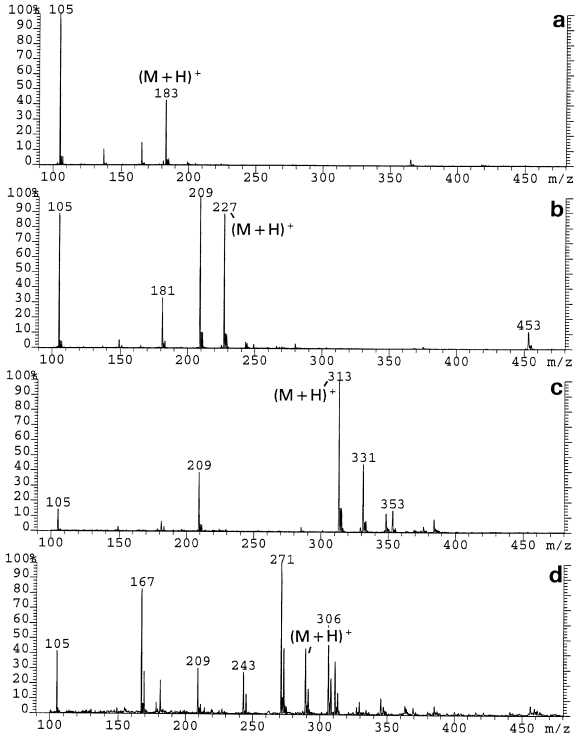


Fig. 2. Typical ESI-MS data for compounds identified as (a) 3,6-dithia-1,8-octanediol, (b) 6-oxa-3,9-dithia-1,11-undecanediol, (c) 6,12-dioxa-3,9,15-trithia-1,17-heptadecanediol (or 6,15-dioxa-3,9,12-trithia-1,17-heptadecanediol) and (d) 14-chloro-6,12-dioxa-3,9-dithia-1-tetradecanol. Data were obtained during LC–ESI-MS analysis of HT and HQ hydrolysis samples.

Three ether/thioether macrocycles, two of which had been previously detected during GC–MS analysis of aqueous samples containing mustard hydrolysis products [10], were also identified during LC–ESI-MS analysis (Table 1). The molecular mass for all three ether/thioether macrocycles could be determined by the presence of an intense $(M+H)^+$ ion and adduct ions due to $(M+NH_4)^+$ and $(M+Na)^+$. The ring structures resisted fragmentation and few product ions were observed. Loss of H_2O from the $(M+H)^+$ ion, a significant fragmentation pathway for diols, was absent and consistent with the ether/thioether macrocyclic structures postulated. All three ether/thioether macrocycles, 1,7-dioxa-4,10-dithiacyclododecane, 1,7,13-trioxa-4,10,16-trithiacyclooctadecane (or another isomer) and 1,7-dioxa-4,10,13-trithiacyclopentadecane could be expected to form by ring closure (with loss of H_2O) of the detected diols, 6-oxa-3,9-dithia-1,11-undecanediol, 6-oxa-3,9,12-trithia-1,14-tetradecanediol and 6,12-dioxa-3,9,15-trithia-1,17-heptadecanediol (or 6,15-dioxa-3,9,12-trithia-1,17-heptadecanediol), respectively.

Two partial hydrolysis products, 8-chloro-6-oxa-3-thia-1-octanol and 14-chloro-6,12-dioxa-3,9-dithia-1-tetradecanol, the former having been previously characterized during GC–MS analysis [14], were identified following interpretation of acquired LC–ESI-MS and LC–ESI-MS–MS data. The ESI mass spectrum for 8-chloro-6-oxa-3-thia-1-octanol (Table 1) contained characteristic chlorine isotopic clusters and $(M+H)^+$ and $(2M+H)^+$ ions at m/z 185 and 369, respectively. Product ions, due to loss of H_2O from the hydroxyl terminal of the $(M+H)^+$ ion, at m/z 167 and the protonated 1,4-thioxane ion (m/z 105) were also observed. The 1,4-thioxane ion could arise from either loss of HOC_2H_4Cl from the $(M+H)^+$ ion or loss of H_2O followed by loss of C_2H_3Cl. The latter possibility was discounted following LC–ESI-MS–MS analysis since the m/z 105 ion was not

observed in the product spectrum of *m/z* 167. The only products of *m/z* 167 (relative intensity 100%) were at *m/z* 107 (relative intensity 5%), *m/z* 87 (relative intensity 2%) and *m/z* 63 (relative intensity 1%), indicating loss of SC_2H_4, HOC_2H_4Cl and 1,4-thioxane, respectively, from the $(M+H-H_2O)^+$ precursor ion. For these product ions to be detected the *m/z* 167 must contain $-OC_2H_4Cl$ at the chloro terminal in the partial hydrolysis product. Positions 3 and 6 must therefore contain S and O, respectively.

The ESI-MS data acquired for 14-chloro-6,12-dioxa-3,9-dithia-1-tetradecanol (Fig. 2d) contained $(M+H)^+$, $(M+NH_4)^+$ and $(M+Na)^+$ ions at *m/z* 289, *m/z* 306 and *m/z* 311, respectively, that indicated a molecular mass of 288 u. The molecular ion adduct isotopic clusters were consistent with the presence of chlorine. Product ions at *m/z* 271, *m/z* 243, *m/z* 209, *m/z* 181, *m/z* 167 and *m/z* 105 were likely due to $(M+H-H_2O)^+$, $(M+H-H_2O-C_2H_4)^+$, $(M+H-HOC_2H_4Cl)^+$, $(M+H-HOC_2H_4Cl-C_2H_4)^+$, $(M+H-H_2O-SC_2H_4OC_2H_4)^+$, $(M+H-HOC_2H_4Cl-SC_2H_4OC_2H_4)^+$, respectively. Interpretation of the ESI-MS data indicated a compound with the following structure: $HOC_2H_4-X_3-C_2H_4-X_6-C_2H_4-X_9-C_2H_4-O-C_2H_4Cl$, [where if X_3 is S then X_6 is O (or vice versa) based on loss of 1,4-thioxane from *m/z* 271, and if X_6 is O then X_9 is S (or vice versa) based on loss of 1,4-thioxane from *m/z* 209].

If the 1,4-thioxane ring at *m/z* 105 ion includes the O from the hydroxyl portion of the compound then X_3 must be a S. This would require X_6 to be O, which in turn means that X_9 would be S.

Evidence to support this assumption was provided during LC-ESI-MS–MS acquisition of the product ions of *m/z* 167 and *m/z* 271. The product spectrum for *m/z* 167 was virtually indistinguishable from that obtained during analysis of 8-chloro-6-oxa-3-thia-1-octanol, which was consistent with a $-C_2H_4-S-C_2H_4-O-C_2H_4Cl$ structure at the chloro terminal. Position 9 (X_9) would be occupied with an S atom. The product spectrum of *m/z* 271 (relative intensity 100%), contained a product ion at *m/z* 243 (relative intensity 8%) due to loss of C_2H_4 and three additional product ions at *m/z* 211, *m/z* 167 and *m/z* 107 (all with 1% to 2% relative intensity), due to sequential losses of SC_2H_4, OC_2H_4 and SC_2H_4 from the $(M+H-H_2O)^+$ precursor ion, respectively. This would suggest the following structure, $HO-C_2H_4-S-C_2H_4-O-C_2H_4-SC_2H_4-$, at the hydroxyl terminal, where S occupies positions 3 (X_3) and 9 (X_9) and O occupies position 6 (X_6). The structure of this partial hydrolysis product was determined to be 14-chloro-6,12-dioxa-3,9-dithia-1-tetradecanol based on this evidence.

The developed LC–ESI-MS methodology was applied to the analysis of aqueous samples taken from a former mustard destruction site. Mustard related hydrolysis products were only found in one of the aqueous samples, a brackish sample containing decomposing animal matter that required filtration through cotton gauze prior to analysis. Indole and a methylated indole were detected during GC–MS analysis of a hexane extract of the aqueous sample but no other specific attempts were made to identify the additional sample contaminants. Fig. 3a illustrates the total ion current chromatogram obtained for the aqueous sample. Thiodiglycol was detected at approximately 0.2 mg/ml along with the hydrolysis product of T, 6-oxa-3,9-dithia-1,11-unde-

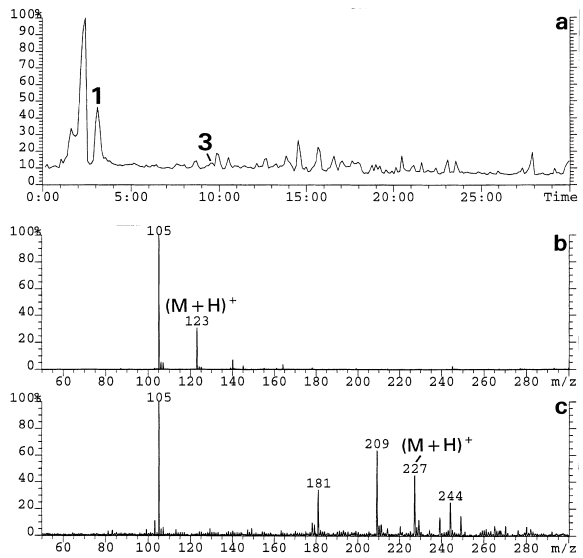


Fig. 3. (a) LC–ESI-MS total ion current (340 to 50 u) chromatogram obtained for aqueous sample from a former mustard destruction site (compounds identified in Table 1). ESI-MS data obtained for (b) peak number 1, thiodiglycol (approximately 0.2 mg/ml) and (c) peak number 3, 6-oxa-3,9-dithia-1,11-undecanediol.

canediol[1]. Fig. 3b and Fig. 3c illustrate the ESI-MS data acquired for both hydrolysis products. Molecular masses were confirmed by the presence of $(M+H)^+$, $(M+NH_4)^+$ and $(M+Na)^+$ ions and both spectra contained product ions observed during analysis of these compounds in the HT and HQ hydrolysis samples.

4. Conclusions

Packed capillary column LC–ESI-MS was used to characterize thiodiglycol and ten related longer chain diol, partial hydrolysis and ether/thioether macrocyclic compounds formed following hydrolysis of munitions grade mustard samples. ESI-MS data were collected with a sampling cone voltage that promoted collisionally activated dissociation, with the resultant mass spectra being rich in both molecular and product ion information. The developed packed capillary LC–ESI-MS method was successfully applied to the analysis of aqueous samples collected from a former mustard destruction site. Both thiodiglycol and the hydrolysis product of T, 6-oxa-3,9-dithia-1,11-undecanediol were identified.

LC–ESI-MS has been demonstrated for higher mass sulfur vesicant hydrolysis product analysis, extending the range of analytical options available to the researcher confronted with the identification of chemical warfare agents or their decomposition products. This technique appears to be an attractive alternative to GC–MS for the analysis of aqueous samples containing the hydrolysis products of sulfur vesicants since the aqueous samples may be analysed directly with little risk of thermal decomposition and without the need for additional sample handling or derivatization. The reported ESI-MS data could prove valuable for the verification of thiodiglycol and other sulfur vesicant hydrolysis products in samples collected during Chemical Weapons Convention inspections. Presence of longer chain diols, partial hydrolysis products or ether/thioether macrocycles formed following hydrolysis of longer chain sulfur vesicants would augment thiodiglycol detection, and greatly strengthen the argument for prior mustard presence.

[1]Thiodiglycol was also detected and externally quantitated at 0.2 mg/ml in this sample by capillary column GC–flame ionization detection and GC–MS using a J&W Scientific DBWAX column.

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