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Capillary column electron impact and ammonia chemical ionization gas chromatographic–mass spectrometric and gas chromatographic–tandem mass spectrometric analysis of mustard hydrolysis products

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ABSTRACT

Capillary column GC–MS and GC–MS–MS, under electron impact (EI) and ammonia chemical ionization (CI) conditions, were used to detect and identify longer-chain sulfur vesicant hydrolysis products. Interpretation of the MS data enabled the characterization of the partial and fully hydrolysed products of 2-chloroethyl (2-chloroethoxy)ethyl sulfide, bis(2-chloroethylthio)ethane (sesquimustard) and bis[(2-chloroethylthio)ethyl] ether before and after trimethylsilyl derivatization. EI data were generally lacking in significant molecular ion information while those obtained during ammonia CI contained valuable $(M+H)^+$ and/or $(M+NH_4)^+$ molecular ion information. The usefulness of this approach to degradation product analysis was demonstrated during the *3rd United Nations Conference on Disarmament Technical Group on Instrumentation Round Robin Analytical Exercise* held in 1991. Both thiodiglycol and thiodiglycol sulfone, the mustard degradation compounds spiked onto concrete samples circulated to fifteen international laboratories, were confirmed during capillary column GC–MS and GC–MS–MS analysis of the samples.

INTRODUCTION

The use of the chemical warfare agent bis(2-chloroethyl)sulfide (mustard) in the Iran/Iraq war [1,2], and threat of chemical weapons use in the recent 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 remains an important means for the verification of allegations of use claims and will be a critical component of the United Nations Chemical Weapons Convention. Analyses of this type have been performed on Iranian victims of an alleged attack with mustard gas [3] and considerable effort has been expended on the development of analytical methods for the detection of mustard and a hydrolysis product of mustard, thiodiglycol, in biological media [3–7].

Gas chromatography (GC) [8,9] and mass spectrometry (MS) [10–17] have been used 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 and biological samples. Destruction of mustard by hydrolysis or natural weathering in the environment results in the formation of thiodiglycol [18,19], a non-toxic compound that may be easily handled. However, munitions-grade mustard formulations typically contain only 50 to 80% mustard with most of the remaining content

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being other sulfur vesicants [14] which would decompose to other products. The characterization and identification of these degradation products would be valuable during chemical weapons destruction monitoring in support of the proposed Chemical Weapons Convention and for the verification of claims of allegations of chemical agent use.

Electron impact (EI) ionization has been used to characterize derivatives of mustard including thiodiglycol and the di-trimethylsilyl derivative of thiodiglycol [13]. The MS characterization of the hydrolysis products of longer-chain sulfur vesicants, commonly found in munitions-grade mustard [14], has not been previously investigated. During this study, two munitions-grade mustard samples, containing longer-chain sulfur vesicants were hydrolysed and analysed by capillary column GC–MS and GC–MS–MS in an attempt to obtain the MS data required for the verification of these compounds. Samples of the hydrolysed munitions-grade mustard were analysed by capillary column GC–MS under EI conditions before and after trimethylsilyl (TMS) derivatization. Molecular ion information, critical for the confirmation of the observed hydrolysis products, was generally absent during EI analyses. Chemical ionization (CI) [20] using ammonia [21] was evaluated as a complementary technique for the acquisition of molecular ion information, as this technique has proven its value during the analysis of organophosphorus nerve agents [22–26] and longer-chain sulfur vesicants [27].

Interpretation of the acquired MS data resulted in the characterization of both the partial and fully hydrolysed products of mustard and the longer-chain sulfur vesicants, 2-chloroethyl (2-chloroethoxy)ethyl sulfide, bis(2-chloroethylthio)ethane (sesquimustard) and bis[(2-chloroethylthio)ethyl] ether before and after TMS derivatization. In all cases complementary molecular ion information was obtained by the use of ammonia CI-MS. Tandem MS was particularly useful for the confirmation of the partial hydrolysis product of 2-chloroethyl (2-chloroethoxy)ethyl sulfide. This approach to mustard degradation product analysis was successfully applied during the analysis of spiked concrete samples during the *3rd United Nations Conference on Disarmament Technical Group on Instrumentation Round Robin Analytical Exercise* in 1991.

EXPERIMENTAL

Hydrolysis 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 removed leaving a pale yellow oil for each sample. The oils were then distilled in a Kugelrohr oven at 220°C at 0.1 Torr (1 Torr = 133.322 Pa). Hydrolysed HT and HQ samples were dissolved in dichloromethane and a standard containing both hydrolysed HT and HQ at 1 mg/ml was prepared in dichloromethane.

Trimethylsilyl derivatization of this sample was performed by combining 100 μl of the hydrolysis products of HT and HQ (1 mg/ml) with 50 μl pyridine and 50 μl bis(trimethylsilyl)trifluoroacetamide (BSTFA) (containing 1% trimethylchlorosilane) for 20 min at 60°C [28]. Analysis of derivatized samples was performed within 24 h to minimize degradation. All hydrolysed munitions-grade mustard samples and derivatives of these samples were stored in polytetrafluoroethylene (PTFE)-lined 1.8-ml glass vials at 4°C prior to analysis.

Round robin concrete samples

Spiked concrete samples, typical of those expected during inspection of a military facility, were prepared by the Prins Maurits Laboratory TNO (Netherlands) and distributed to evaluate laboratory procedures as part of the *3rd United Nations Conference on Disarmament Technical Group on Instrumentation Round Robin Analytical Exercise*. The concrete round robin samples were extracted in their glass shipment bottles by ultrasonic vibration for 5 min with 15 ml of acetonitrile. The acetonitrile extract was removed and concentrated by nitrogen blowdown to 0.5 ml. Dichloromethane (4.5 ml) was added

to the acetonitrile extract (final volume of 5 ml) prior to analysis to improve chromatographic performance.

A 2-ml volume of the 5-ml volume (above) was concentrated by nitrogen blowdown to 300 μl and this concentrate was used for trimethylsilylation. Trimethylsilylation was performed by combining 100 μl BSTFA, 100 μl pyridine and the 300 μl extract in a 1.8-ml screw-capped (PTFE-lined) glass vial. This sample was heated for 20 min at 60°C prior to analysis [28]. Analysis was performed immediately after cooling to minimize degradation.

Instrumental

Capillary column GC–MS and GC–MS–MS analyses were performed with a VG AUTOSPEC-Q hybrid tandem mass spectrometer equipped with a Hewlett-Packard Model 5890 gas chromatograph. A 15 m × 0.32 mm I.D. DB-1701 J&W capillary column (0.25 μm film thickness) was used for all analyses with the following temperature program: 40°C (2 min) 10°C/min 280°C (5 min). All GC injections were cool on-column using an injector of our own design [29]. The EI operating conditions were as follows: source pressure, $3 \cdot 10^{-6}$ Torr; source temperature, 200°C; electron energy, 70 eV; and electron emission, 100 μA. Ammonia (99.99%, Anhydrous grade, Liquid Carbonic) CI operating conditions were as follows: source pressure, $8 \cdot 10^{-5}$ Torr ($NH_3^{+\cdot}$:NH_4^+ approximately 15:1); source temperature, 120–130°C, electron energy, 50 eV; and electron emission, 300 μA. Source pressure readings were taken near the source and CI source temperatures increased slightly during each GC–MS analysis due to filament heating. All EI and CI mass spectra were obtained using a VG EI/CI source at a resolution of 1000 to 2000 (10% valley definition) and an accelerating voltage of 8 kV. Mass spectral data were collected from 400 to 40 u at a scan rate of 0.5 s/decade. Deuterated ammonia (99%, MDS Isotopes) CI-MS analysis of the TMS derivatives of the hydrolysis products of HT and HQ was performed under conditions similar to the ammonia CI-MS conditions described above.

The daughter spectrum of m/z 167 for the TMS derivative of 2-chloroethyl (2-hydroxyethylthio)ethyl ether was obtained under ammonia CI conditions (above) with a collisional associated dissociation (CAD) cell energy of 13 eV and an argon pressure of 10^{-6} Torr (near CAD cell). Daughter spectra for thiodiglycol (m/z 122) and thiodiglycol sulfone (m/z 111) were obtained under EI conditions (above) with a CAD cell energy of 17 eV and an argon pressure of 10^{-6} Torr (near the CAD cell). The quadrupole was operated at unit resolution and scanned from 250 to 50 u at 0.5 s/scan during all capillary column GC–MS–MS analyses.

RESULTS AND DISCUSSION

HQ and HT, two munitions-grade mustard formulations, containing predominately mustard (H) and sesquimustard (Q), and mustard (H) and bis[(2-chloroethylthio)ethyl] ether (T), respectively [14], were hydrolysed in an attempt to characterize the principal hydrolysis products of these munitions samples. Fig. 1 illustrates the total-ion-current chromatogram for the principal hydrolysis products of mustard and the longer-chain sulfur vesicants, 2-chloroethyl (2-chloro-

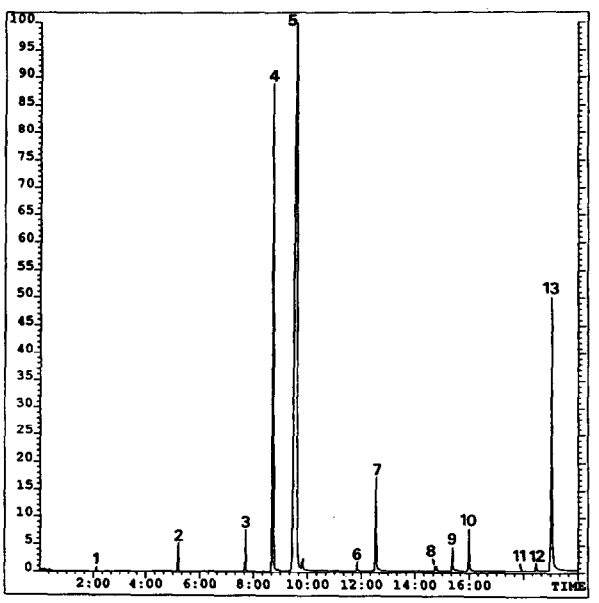

Fig. 1. Capillary column GC–EI-MS total-ion-current (400 to 40 u) chromatogram of the hydrolysis products of approximately 300 ng of HT and HQ. Compounds are identified in Table I. Time scale in min.

TABLE I

COMPOUNDS IDENTIFIED AFTER GC–MS AND GC–MS–MS ANALYSIS OF SAMPLES

Peak No.[a]	Molecular mass	Compound
1	104	1,4-Thioxane
2	120	1,4-Dithiane
3	158	Mustard
4	140	Hemisulfur mustard
5	122	Thiodiglycol
6	202	2-Chloroethyl (2-chloroethoxy)ethyl sulfide
7	184	2-Chloroethyl (2-hydroxyethylthio)ethyl ether
8	218	Sesquimustard
9	200	2-Chloroethyl (2-hydroxyethylthio)ethyl sulfide
10	182	Bis(2-hydroxyethylthio)ethane
11	262	Bis[(2-chloroethylthio)ethyl] ether
12	244	(2-Chloroethylthio)ethyl (2-hydroxyethylthio)ethyl ether
13	226	Bis[(2-hydroxyethylthio)ethyl] ether
14	212	TMS derivative of hemisulfur mustard
15	266	Di-TMS derivative of thiodiglycol
16	256	TMS derivative of 2-chloroethyl (2-hydroxyethylthio)ethyl ether
17	272	TMS derivative of 2-chloroethyl (2-hydroxyethylthio)ethyl sulfide
18	326	Di-TMS derivative of bis(2-hydroxyethylthio)ethane
19	316	TMS derivative of (2-chloroethylthio)ethyl (2-hydroxyethylthio)ethyl ether
20	370	Di-TMS derivative of bis[(2-hydroxyethylthio)ethyl] ether
21	298	Di-TMS derivative of thiodiglycol sulfone

[a] Refer to Figs. 1, 2 and 5.

ethoxy)ethyl sulfide, sesquimustard and bis[(2-chloroethylthio)ethyl] ether. The partial (*e.g.*, $HO-CH_2CH_2-S-CH_2CH_2-Cl$) and/or full (*e.g.*, $HO-CH_2CH_2-S-CH_2CH_2-OH$) hydrolysis products for mustard and the three other longer-chain sulfur vesicants were the predominate sample components, with a lesser contribution coming from intact sulfur vesicants and the commonly observed mustard impurities 1,4-thioxane and 1,4-dithiane [14].

Chromatography of partial hydrolysis products was excellent and equivalent to the gaussian peak shape routinely observed for the sulfur vesicants. However, the chromatographic quality deteriorates somewhat for the full hydrolysis products due to the polarity of two hydroxyl substituents. A small amount of tailing was typically observed (Fig. 1) during capillary column GC–MS of these compounds (peak numbers 5, 10 and 13). With more active or poorly conditioned capillary columns the quality of chromatography deteriorates significantly and low nanogram detection of full hydrolysis products, such as thiodiglycol, cannot be reliably made. Analysis of authentic reference standards (*e.g.*, thiodiglycol) prior to the analysis of unknown samples is recommended to ensure good quality control for this reason.

The activity of capillary columns becomes less critical during the analysis of the TMS derivatives of the hydrolysis products, as these compounds are much less polar than the underivatized compounds. Gaussian peak shape was observed (Fig. 2) during chromatography of the TMS derivatives of the full hydrolysis products (peak numbers 15, 18 and 20). Improved chromatographic performance and the fact that direct trimethylsilylation of samples, such as soil, enables extraction of chemical warfare agent hydrolysis products [17] makes derivatization an attractive complementary confirmation technique.

The EI mass spectra of the partial and full hydrolysis products of mustard and the longer-

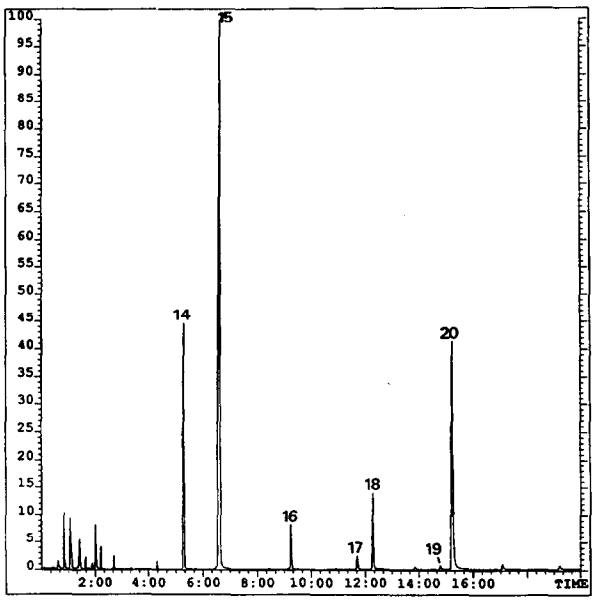

Fig. 2. Capillary column GC–EI-MS total-ion-current (400 to 40 u) chromatogram of the hydrolysis products of approximately 300 ng of HT and HQ after trimethylsilylation. Compounds are identified in Table I (minor sample components, with retention times near 2 min, were due to the TMS derivatizing reagent). Time scale in min.

chain sulfur vesicants generally provide little or no molecular ion information (Figs. 3 and 4). This fact, coupled with the lack of higher-mass structurally significant EI ions for several compounds, prompted the evaluation of ammonia CI as a complementary confirmation technique. Ammonia CI-MS, a technique recently reported for longer-chain sulfur vesicants [27], provided $(M+H)^+$ and/or $(M+NH_4)^+$ pseudo-molecular ions for all the hydrolysis products along with structurally significant CI fragmentation ions.

Mustard hydrolysis

Mustard hydrolysis results in the production of the partial hydrolysis product, hemisulfur mustard, and the full hydrolysis product, thiodiglycol. The EI mass spectra of hemisulfur mustard (Fig. 3a), thiodiglycol (Fig. 3e) and the di-TMS derivative of thiodiglycol (Fig. 3g), included for completeness, were similar to those reported by Wils and Hulst [13]. The EI mass spectrum of the TMS derivative of hemisulfur mustard (Fig. 3c) exhibited higher-mass ions at m/z 197 and m/z 176 due to $(M-CH_3)^+$ and $(M-HCl)^+$ but did not exhibit a molecular ion.

$(M+H)^+$ and/or $(M+NH_4)^+$ pseudo-molecular ions were observed for hemisulfur mustard (Fig. 3b), the TMS derivative of hemisulfur mustard (Fig. 3d), thiodiglycol (Fig. 3f) and the di-TMS derivative of thiodiglycol (Fig. 3h). Hemisulfur mustard exhibited an intense CI fragmentation ion at m/z 105 due to protonated 1,4-thioxane and the TMS derivative was characterized by ions at m/z 177 and m/z 123 due to $(M+H-HCl)^+$ and $(C_2H_4–S–C_2H_4Cl)^+$. Thiodiglycol exhibited a weak CI fragmentation ion at m/z 105 due to protonated 1,4-thioxane and the di-TMS derivative of thiodiglycol was characterized by an intense CI ion at m/z 177 due to $[M+H-(CH_3)_3Si(OH)]^+$. CI ions characteristic of TMS derivatization at m/z 73, $(CH_3)_3Si^+$, and m/z 90, $[(CH_3)_3SiNH_3]^+$ were observed for the TMS derivatives of hemisulfur mustard, thiodiglycol and the other longer-chain sulfur vesicant hydrolysis products. The structure of the ammonia CI ion at m/z 90, observed for all TMS derivatives, was confirmed by the observation of an ion at m/z 93, due to $[(CH_3)_3N^2H_3]^+$, during deuterated ammonia CI-MS analysis.

2-Chloroethyl (2-chloroethoxy)ethyl sulfide hydrolysis

Only the partial hydrolysis product of 2-chloroethyl (2-chloroethoxy)ethyl sulfide was detected during EI and CI analysis of the hydrolysed sample. Under EI conditions 2-chloroethyl (2-hydroxyethylthio)ethyl ether exhibited an intense protonated 1,4-thioxane ion (Fig. 3i) and the TMS derivative of this hydrolysis product contained a weak ion at m/z 241 due to $(M-CH_3)^+$ (Fig. 3k). Under ammonia CI conditions molecular ion information was obtained for both 2-chloroethyl (2-hydroxyethylthio)ethyl ether (Fig. 3j) and its TMS derivative (Fig. 3l). An ion at m/z 167 due to $(C_2H_4–S–C_2H_4–O–C_2H_4–Cl)^+$ was observed during both ammonia CI analyses.

It was not obvious after interpretation of the EI and CI data as to whether the hydroxyl substituent was nearer the sulfur or oxygen position and only the following general structure was initially assumed: $ClC_2H_4–X–C_2H_4–X–C_2H_4OH$ (where one X was an oxygen and the

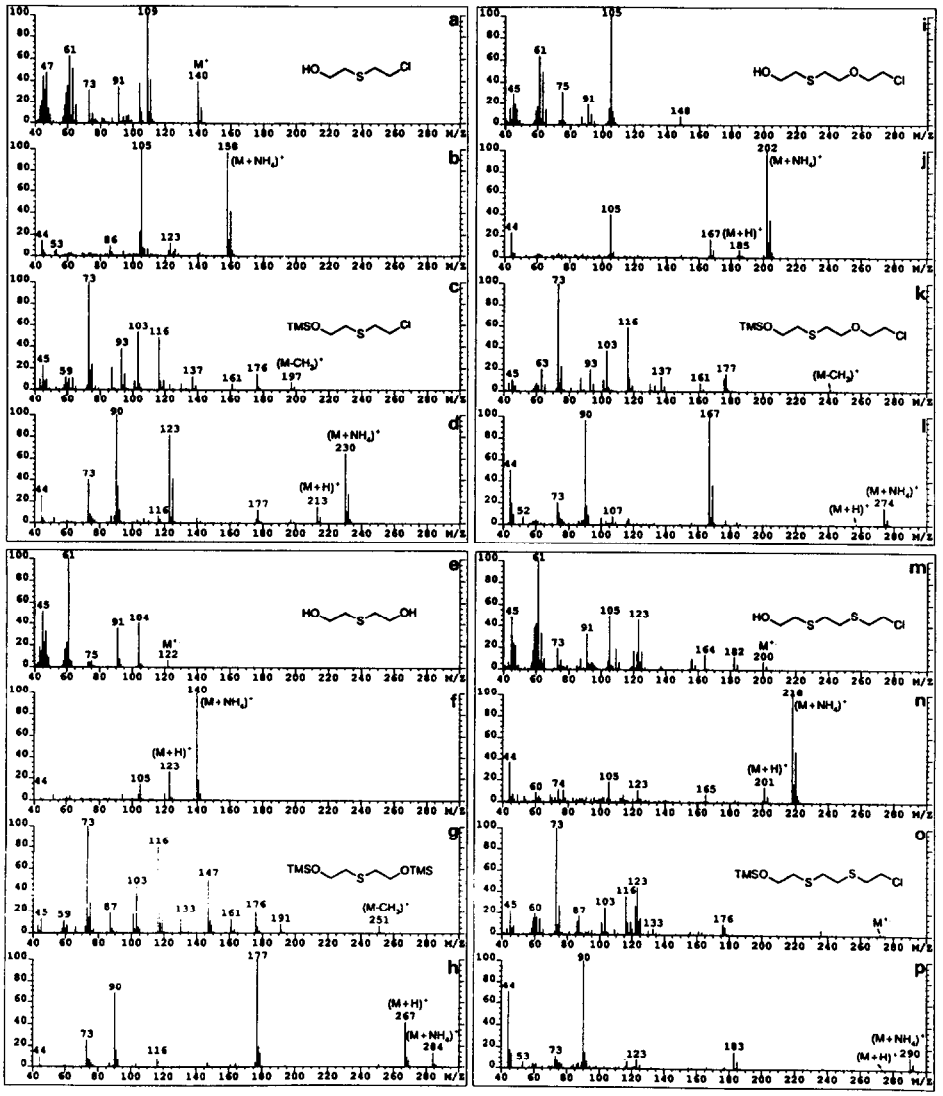

Fig. 3. (a) EI and (b) ammonia CI mass spectra of hemisulfur mustard and (c) EI and (d) ammonia CI mass spectra of TMS derivative of hemisulfur mustard. (e) EI and (f) ammonia CI mass spectra of thiodiglycol and (g) EI and (h) ammonia CI mass spectra of the di-TMS derivative of thiodiglycol. (i) EI and (j) ammonia CI mass spectra of 2-chloroethyl (2-hydroxyethylthio)ethyl ether and (k) EI and (l) ammonia CI mass spectra of TMS derivative of 2-chloroethyl (2-hydroxyethylthio)ethyl ether. (m) EI and (n) ammonia CI mass spectra of 2-chloroethyl (2-hydroxyethylthio)ethyl sulfide and (o) EI and (p) ammonia CI mass spectra of TMS derivative of 2-chloroethyl (2-hydroxyethylthio)ethyl sulfide.

second X was a sulfur). However under ammonia CI the TMS derivative of this compound exhibits an intense *m/z* 167 ion and GC–MS–MS analysis of this ion was performed as the daughters might provide the required structural data. The daughters of *m/z* 167 (Fig. 4m) for this compound at *m/z* 63, *m/z* 87 and *m/z* 107 were due to $(ClC_2H_4)^+$, $(C_2H_3–S–C_2H_4)^+$ and $(ClC_2H_4–O–C_2H_4)^+$, respectively, which strongly suggested the presence of the partial hydrolysis product, 2-chloroethyl (2-hydroxyethylthio)ethyl ether or $ClC_2H_4–O–C_2H_4–S–C_2H_4OH$.

Sesquimustard hydrolysis

Both the partial hydrolysis product, 2-chloroethyl (2-hydroxyethylthio)ethyl sulfide, and the full hydrolysis product, bis(2-hydroxyethyl-

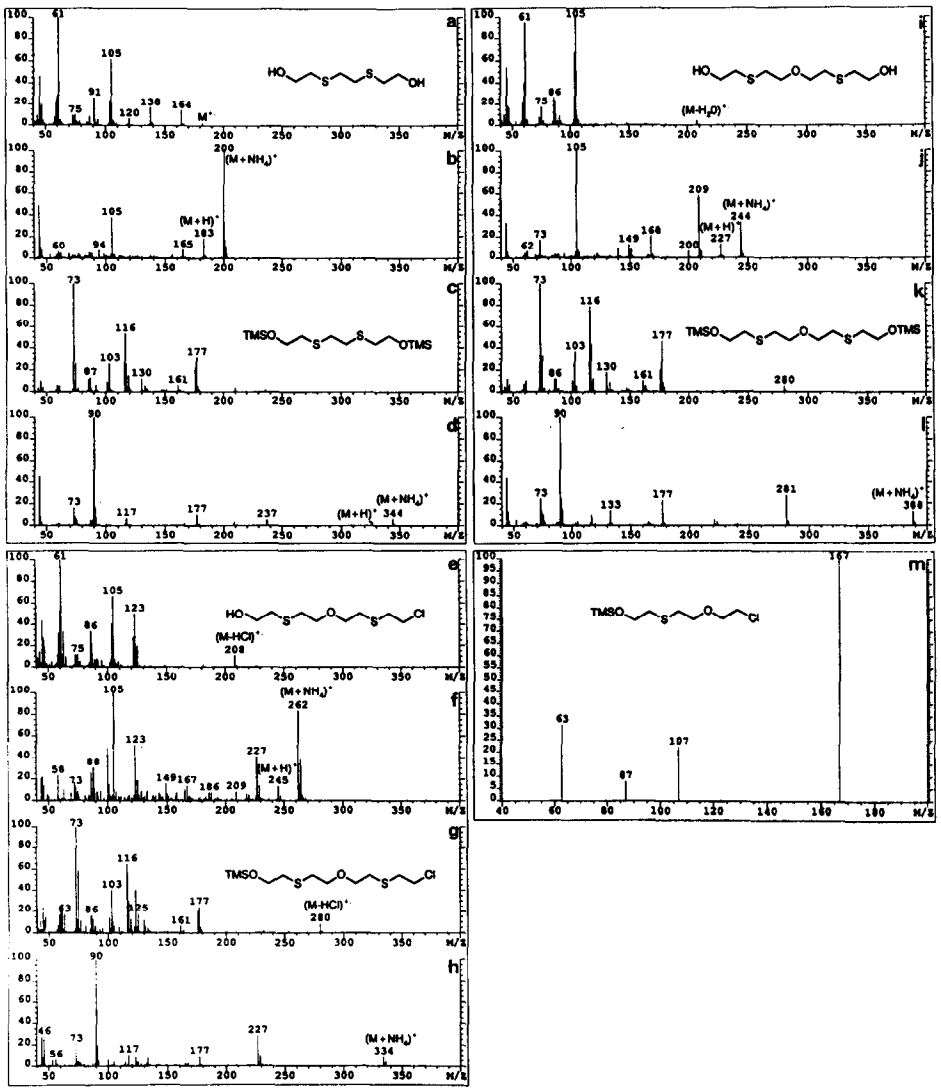

Fig. 4. (a) EI and (b) ammonia CI mass spectra of bis(2-hydroxyethylthio)ethane and (c) EI and (d) ammonia CI mass spectra of the di-TMS derivative of bis(2-hydroxyethylthio)ethane. (e) EI and (f) ammonia CI mass spectra of (2-chloroethylthio)ethyl (2-hydroxyethylthio)ethyl ether and (g) EI and (h) ammonia CI mass spectra of TMS derivative of (2-chloroethylthio)ethyl (2-hydroxyethylthio)ethyl ether. (i) EI and (j) ammonia CI mass spectra of bis[(2-hydroxyethylthio)ethyl] ether and (k) EI and (l) ammonia CI mass spectra of the di-TMS derivative of bis[(2-hydroxyethylthio)ethyl] ether. (m) Daughter spectrum (m/z 167) for TMS derivative of 2-chloroethyl (2-hydroxyethylthio)ethyl ether acquired during ammonia CI.

thio)ethane, of sesquimustard were detected during analysis. 2-Chloroethyl (2-hydroxyethylthio)ethyl sulfide exhibited a molecular ion at m/z 200 and higher mass ions due to $(M-H_2O)^{+\cdot}$ and $(M-HCl)^{+\cdot}$ at m/z 182 and m/z 164 under EI conditions (Fig. 3m). Lower-mass ions at m/z 61, $(C_2H_5S)^+$, m/z 105, protonated 1,4-thioxane, and m/z 123, $(C_2H_4\text{–}S\text{–}C_2H_4Cl)^+$, were typical of those observed for other partial or full hydrolysis products. The EI mass spectrum after TMS derivatization yielded a very weak molecular ion (Fig. 3o). However, under ammonia CI conditions 2-chloroethyl (2-hydroxyethylthio)ethyl sulfide provided both $(M+H)^+$ and $(M+NH_4)^+$ pseudo-molecular ions (Fig. 3n). Following TMS derivatization of 2-chloroethyl (2-hydroxyethylthio)ethyl sulfide the ammonia CI mass spectrum exhibited a reason-

able $(M + NH_4)^+$ pseudo-molecular ion and ions due to $[M + H - (CH_3)_3Si(OH)]^+$ and $[(CH_3)_3SiNH_3]^+$ at *m/z* 183 and *m/z* 90, respectively (Fig. 3p).

Bis(2-hydroxyethylthio)ethane was characterized by a weak EI molecular ion and ions at *m/z* 164 and *m/z* 138, due to $(M - H_2O)^{+\cdot}$ and $(M - OC_2H_4)^{+\cdot}$, respectively (Fig. 4a). The EI mass spectrum of the TMS derivative was void of molecular ion information and exhibited ions characteristic of TMS substitution (*e.g.*, *m/z* 73). Ammonia CI was particularly useful as molecular ion information in the form of $(M + H)^+$ and $(M + NH_4)^+$ pseudo-molecular ions were observed before (Fig. 4b) and after TMS derivatization (Fig. 4d). As in the case of the partial hydrolysis product, 2-chloroethyl (2-hydroxyethylthio)ethyl sulfide, the most intense pseudo-molecular ions were obtained prior to TMS derivatization.

Bis[(2-chloroethylthio)ethyl] ether hydrolysis

Both the partial hydrolysis product, (2-chloroethylthio)ethyl (2-hydroxyethylthio)ethyl ether, and the full hydrolysis product, bis[(2-hydroxyethylthio)ethyl] ether, of bis[(2-chloroethylthio)ethyl] ether were detected in the hydrolysis sample. The EI mass spectra of the hydrolysis products prior to derivatization (Fig. 4e and i) and after trimethylsilylation (Fig. 4g and k) were void of molecular ion information and were characterized by higher-mass ions due to $(M - H_2O)^{+\cdot}$ or $(M - HCl)^{+\cdot}$. Ammonia CI was used to obtain molecular ion information for both hydrolysis products. Prior to derivatization both (2-chloroethylthio)ethyl (2-hydroxyethylthio)ethyl ether (Fig. 4f) and bis[(2-hydroxyethylthio)ethyl] ether (Fig. 4j) exhibited ions due to $(M + NH_4)^+$, $(M + H)^+$ and $(M + H - H_2O)^+$. After TMS derivatization ammonia CI ions due to $(M + NH_4)^+$, $[M + H - (CH_3)_3Si(OH)]^+$ and $[(CH_3)_3SiNH_3]^+$ at *m/z* 334, *m/z* 227 and *m/z* 90 (Fig. 4h) and *m/z* 388, *m/z* 281 and *m/z* 90 (Fig. 4l) were detected for the partial and full hydrolysis products of bis[(2-chloroethylthio)ethyl] ether, respectively.

Round robin concrete samples

Concrete samples, typical of those taken during inspection of a military facility, were received by Defence Research Establishment Suffield as part of a multinational Round Robin Analytical Exercise organized by the *United Nations Conference on Disarmament Technical Group on Instrumentation*. The participating national laboratories in Canada, Australia, the Russian Federation (two laboratories), Finland, France, Germany, Netherlands, Norway, Sweden, China, Switzerland, Czech and Slovak Federal Republic, UK and the USA (two laboratories) were given the concrete samples with no prior knowledge of their content and were asked to report in a semi-quantitative manner the presence of any chemical warfare-relevant compounds.

Prior to TMS derivatization, only thiodiglycol could be detected during capillary column GC–MS under EI conditions. The second compound spiked onto the concrete, thiodiglycol sulfone, was not discernable above the hydrocarbon chemical background during EI-MS analysis. The molecular mass and presence of each of the compounds was confirmed by the presence of $(M + H)^+$ and/or $(M + NH_4)^+$ ions during GC–MS (ammonia CI) analysis. The high hydrocarbon content on the concrete samples, visible as an envelope of compounds in Fig. 5, was not ionized during ammonia CI-MS and highly specific detection of these two chemical warfare relevant compounds was possible. Fig. 6a illustrates the ammonia CI mass spectra for thiodiglycol sulfone obtained during analysis of the concrete extract.

Both thiodiglycol sulfone and thiodiglycol were characterized by tandem MS prior to derivatization of the concrete extract. Capillary column GC–MS–MS data were obtained by acquiring the daughter spectrum of *m/z* 122 (molecular ion) for thiodiglycol and the daughter spectrum of *m/z* 111, $[(HO)_2SC_2H_4OH]^+$, for thiodiglycol sulfone (Fig. 6b). The thiodiglycol sulfone EI fragmentation ion at *m/z* 111 was used for the MS–MS study as this was the highest mass ion (above 5% relative abundance) observed during MS analysis of a standard (refer to reference 30 for EI mass spectrum). For both compounds the principal daughter was due to loss of H_2O. The use of moderate resolution (1800 with 10% valley) in the sector significantly reduced the chemical background due to hydro-

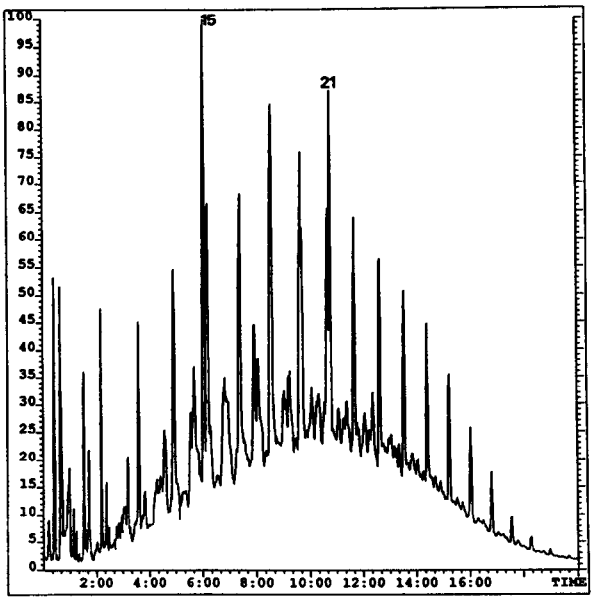

Fig. 5. Capillary column GC–EI-MS total-ion-current (400 to 40 u) chromatogram of the acetonitrile extract of an United Nations round robin concrete sample after trimethylsilylation. Compounds are identified in Table I. Time scale in min.

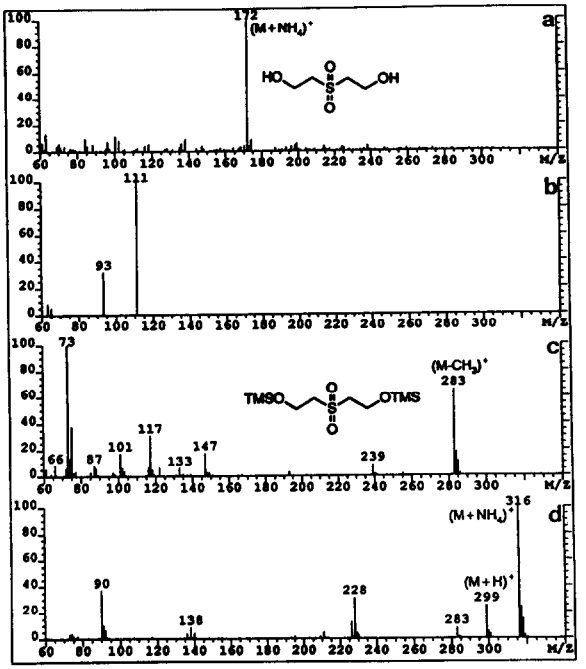

Fig. 6. (a) Ammonia CI and (b) daughter (m/z 111) spectra of thiodiglycol sulfone acquired during EI-MS and (c) EI and (d) ammonia CI mass spectra of di-TMS derivative of thiodiglycol sulfone.

carbons and resulted in chromatograms that did not contain the envelope of hydrocarbons observed during EI-MS.

Fig. 5 illustrates the capillary column GC–MS (EI) chromatogram obtained during analysis of the TMS derivative of the acetonitrile extract of the concrete sample. The EI mass spectra for the di-TMS derivatives of thiodiglycol and thiodiglycol sulfone (Fig. 6c), found in the acetonitrile extracts, were similar to previously published data [13]. The molecular mass of each of the derivatives was confirmed by the presence of $(M+H)^+$ and $(M+NH_4)^+$ ions during ammonia CI-MS analysis. Fig. 6d illustrates the ammonia CI mass spectrum for the di-TMS derivative of thiodiglycol sulfone.

Defence Research Establishment Suffield, the only participating Canadian laboratory, positively confirmed the two spiked chemical warfare-relevant compounds in the round robin concrete samples and did not detect any artifacts or false positives in the samples. During each analysis of thiodiglycol, thiodiglycol sulfone and their di-TMS derivatives the chromatographic/spectrometric data were confirmed with available authentic standards. A full summary of the round robin results and a comparison of laboratory results has been recently published in a Finnish report [30].

CONCLUSIONS

Capillary column GC–MS and GC–MS–MS, under EI and ammonia CI conditions, were used to detect and identify longer-chain sulfur vesicant hydrolysis products. Interpretation of the MS data enabled the characterization of the partial and fully hydrolysed products of 2-chloroethyl (2-chloroethoxy)ethyl sulfide, bis(2-chloroethylthio)ethane (sesquimustard) and bis[(2-chloroethylthio)ethyl] ether before and after TMS derivatization. The usefulness of this approach to degradation product analysis was demonstrated during the *3rd United Nations Conference on Disarmament Technical Group on Instrumentation Round Robin Analytical Exercise* held in 1991. Both thiodiglycol and thiodiglycol sulfone, the mustard degradation compounds spiked onto concrete samples circulated to fifteen international laboratories, were confirmed

by capillary column GC–MS and GC–MS–MS analysis of the samples. The EI and CI data acquired for the hydrolysis products of munitions-grade mustard and their trimethylsilyl derivatives should prove valuable to researchers confronted with the analysis of samples containing mustard or other sulfur vesicants. Application of this approach, and the MS data presented, is anticipated during GC–MS analysis of these or similar hydrolysis compounds in weathered environmental samples, where the original sulfur vesicants have undergone extensive degradation, or for reaction progress monitoring during the destruction of chemical weapons stockpiles.

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