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Abstract

Soil samples were taken for the first time at a number of locations and depths near a former mustard storage site as part of an environmental assessment. The contactor doing the sampling selected a number of soil samples from the site for mass spectrometric analysis. Mustard was not detected in the dichloromethane extracts of the soil samples during capillary column GC-MS. However, three of the soil sample extracts were found to contain thiodiglycol and/or related mustard hydrolysis products. A recently developed low resolution LC-ESI-MS method was applied to the identification of mustard hydrolysis products in aqueous extracts of soil. Thiodiglycol was detected by LC-ESI-MS in the aqueous extracts of two soil samples at the 200 μg/mL and 300 μg/mL levels, along with three longer chain diols associated with the hydrolysis of munitions grade mustard. Identification of a number of other related compounds was not possible by LC-ESI-MS. The recent acquisition of a high resolution LC-ESI-MS/MS at DRDC Suffield provided an opportunity to accurately determine elemental composition during analyses, a considerable advantage when confirming compound presence or when dealing with the identification of previously uncharacterized compounds in complex environmental samples. High resolution LC-ESI-MS/MS methods were developed for the determination of thiodiglycol and longer chain diols and applied to the analysis of these compounds in the aqueous extracts of the soil samples collected from the former mustard storage site. Detailed analysis of these aqueous extracts by high resolution LC-ESI-MS/MS resulted in the confirmation of thiodiglycol and three longer chain diols and the characterization of five new longer chain diols that could not be characterized during low resolution LC-ESI-MS analyses.

Résumé

Des échantillons de sols ont été retirés, pour la première fois, d'un certain nombre d'endroits et de profondeurs, près d'un ancien site d'entreposage d'ypérite, dans le cadre d'une évaluation d'un milieu. Le contacteur responsable de l'échantillonnage a sélectionné un certain nombre d'échantillons provenant du site pour l'analyse de spectrométrie de masse. L'ypérite n'a pas été détectée dans les extraits de dichlorométhane des échantillons de sol durant le couplage GC-SM de la colonne capillaire. On a cependant trouvé que trois des extraits d'échantillons de sol contenaient du thiodigycol et /ou des produits d'hydrolyse de l'ypérite. Une méthode CPL-IP-SM de faible résolution récemment mise au point a été appliquée pour identifier les produits d'hydrolyse d'ypérite dans des extraits aqueux de sol. Le thiodiglycol a été détecté par CPL-IP-SM dans les extraits aqueux de deux échantillons de sol à des niveaux de 200 µg/mL et 300 µg/mL, avec trois chaînes plus longues de diols associées à l'hydrolyse de l'ypérite de qualité d'usage militaire(?). L'acquisition récente de CPL-IP-SM / SM de haute résolution au RDDC Suffield a procuré une opportunité de déterminer avec précision une composition élémentaire durant les analyses, ce qui est un avantage considérable quand il s'agit de confirmer la présence de composés ou de traiter de l'identification de composants non caractérisés antérieurement dans des échantillons de milieu complexe. Les méthodes CPL-IP-SM / SM de haute résolution ont été mises au point pour déterminer le thiodiglycol et des chaînes plus longues de diols et elles ont été appliquées à l'analyse de trois composés dans les extraits aqueux d'échantillons de sols recueillis dans l'ancien site d'entreposage d'ypérite. Des analyses détaillées de ces extraits aqueux par CPL-IP-SM / SM de haute résolution ont résulté en la confirmation du thiodiglycol et de trois chaînes plus longues de diols ainsi qu'en la caractérisation de cinq nouvelles chaînes plus longues de diols qui n'avaient pas pu être caractérisées durant les analyses de faible résolution CPL-IP-SM.

Executive summary

Introduction: The Canadian Forces (CF) may be called on to perform peacekeeping or battlefield operations in regions of the world where there is a significant threat of chemical/biological (CB) warfare agent use. To operate effectively in these theatres the CF must be able to identify the CB agent used. Mass spectrometry (MS), is a powerful analytical technique for the identification of both known and unknown compounds and DRDC Suffield is currently investigating this instrumental technique in fulfillment of future CF detection and identification requirements.

Results: Soil samples were taken for the first time at a number of locations and depths near a former mustard storage site as part of an environmental assessment. The contactor doing the sampling selected a number of soil samples from the site for mass spectrometric analysis. Dichloromethane extracts of the collected soil samples were initially analysed by capillary column gas chromatography-mass spectrometry (GC-MS), the most commonly used analytical technique for the separation and analysis of mustard and other chemical warfare agents. Mustard was not detected but a number of related compounds including 1,4-thioxane, 1,4-dithiane and thiodiglycol were identified during this study. Low resolution LC-ESI-MS was also used in this investigation for the determination of thiodiglycol and three longer chain diols in aqueous extracts of the collected soil samples. The recent acquisition of a high resolution LC-ESI-MS/MS at DRDC Suffield provided the opportunity to accurately determine elemental composition during LC-ESI-MS and LC-ESI-MS/MS operation. a considerable advantage when confirming compound presence or when dealing with the identification of previously uncharacterized compounds in complex environmental samples. A high resolution LC-ESI-MS/MS method was developed for the determination of thiodiglycol and longer chain diols and applied to the analysis of these compounds in aqueous extracts of the collected soil samples.

Significance: GC-MS, low resolution LC-ESI-MS and high resolution LC-ESI-MS/MS methods were developed and applied to the analysis of soil samples collected from a former mustard storage site. GC-MS was used to show the absence of mustard in dichloromethane extracts of the soil samples. Analysis of aqueous extracts of the soil samples by high resolution LC-ESI-MS/MS resulted in the confirmation of thiodiglycol, three longer chain diols and the characterization of five new longer chain diols that could not be characterized during the prior low resolution LC-ESI-MS analyses.

Future Plans: The reported method will be a valuable addition to the present methods for the identification of chemical warfare agents and their hydrolysis products in samples collected by the Canadian Forces, RCMP or in support of Chemical Weapons Convention challenge inspections on Canadian soil. The application of tandem mass spectrometry to sample containing CB contamination is anticipated with the new instrument at DRDC Suffield.

D'Agostino, P.A., Hancock, J.R., Chenier, C.L., 2004. GC-MS, LC-MS and LC-MS/MS of Soil Samples from a Former Mustard Storage Site for the Presence of Mustard, Thiodiglycol and Related Compounds. DRDC Suffield TR 2004-021. Defence R&D Canada – Suffield.

Sommaire

Introduction: Les Forces canadiennes (FC) peuvent être appelées à entreprendre des opérations de maintien de la paix dans des régions du monde ou il existe une menace d'utilisation des agents de guerre chimiques et biologiques (CB). Pour être en mesure d'opérer efficacement dans ces théâtres, les FC doivent être capables d'identifier les agents CB qui ont été utilisés. La spectrométrie de masse (SM) est une technique analytique puissante pour l'identification des composés à la fois connus et inconnus et RDDC Suffield examine actuellement cette technique instrumentale visant à satisfaire de manière optimale les besoins futurs en détection et identification des FC.

Résultats : Des échantillons de sols ont été retirés, pour la première fois, d'un certain nombre d'endroits et de profondeurs, près d'un ancien site d'entreposage d'ypérite, dans le cadre d'une évaluation d'un milieu. Le contacteur responsable de l'échantillonnage a sélectionné un certain nombre d'échantillons provenant du site pour l'analyse de spectrométrie de masse. Des extraits de dichlorométhane provenant des échantillons de sol recueillis ont été d'abord analysés par la méthode de couplage entre la chromatographie en phase gazeuse et la spectrométrie de masse (CG-SM), la technique analytique utilisée le plus couramment pour la séparation et l'analyse de l'ypérite et autres agents de guerre chimiques. L'ypérite n'a pas été détectée mais un certain nombre de composés qui y sont liés comprenant notamment 1.4-thioxane. 1.4-dithiane et thiodiglycol ont été identifiés durant cette étude. CPL-IP-SM de faible résolution a aussi été utilisée dans cette étude pour déterminer le thiodiglycol et trois plus longues chaînes de diols dans les extraits aqueux des échantillons de sols recueillis. L'acquisition récente de CPL-IP-SM / SM de haute résolution au RDDC Suffield a procuré une opportunité de déterminer avec précision une composition élémentaire durant les opérations CPL-IP-SM et CPL-IP-SM / SM, ce qui est un avantage considérable quand il s'agit de confirmer la présence de composés ou de traiter de l'identification de composés non caractérisés antérieurement dans des échantillons de milieu complexe. Les méthodes CPL-IP-SM / SM de haute résolution ont été mises au point pour déterminer le thiodiglycol et des chaînes plus longues de diols et elles ont été appliquées à l'analyse de trois composants dans les extraits aqueux d'échantillons de sols recueillis dans l'ancien site d'entreposage d'ypérite.

La portée des résultats : Les méthodes de couplage CG-SM, de CPL-IP-SM de faible résolution et de CPL-IP-SM / SM de haute résolution ont été mises au point et appliquées à l'analyse des échantillons de sols recueillis dans les anciens sites d'entreposage d'ypérite. Le couplage CG-SM a été utilisé pour montrer l'absence d'ypérite dans les extraits de dichlorométhane des échantillons de sol. Des analyses de ces extraits aqueux de sol par CPL-IP-SM / SM de haute résolution ont résulté en la confirmation du thiodiglycol et de trois chaînes plus longues de diols ainsi qu'en la caractérisation de cinq nouvelles chaînes plus longues de diols qui n'avaient pas pu être caractérisées durant les analyses de faible résolution CPL-IP-SM.

Plans futurs : Cette méthode sera une précieuse addition aux méthodes actuelles pour identifier les agents de guerre chimiques et les produits de leur hydrolyse dans les échantillons recueillis par les Forces canadiennes, la GRC ou en soutien aux inspections sous mise en demeure sur sol canadien selon la Convention sur les armes chimiques. L'application de la spectrométrie de masse en tandem aux échantillons contenant une contamination CB est prévue avec le nouvel instrument à RDDC Suffield.

D'Agostino, P.A., Hancock, J.R., Chenier, C.L., 2004. GC-MS, LC-MS and LC-MS/MS of Soil Samples from a Former Mustard Storage Site for the Presence of Mustard, Thiodiglycol and Related Compounds. DRDC Suffield TR 2004-021. R & D pour la défense Canada – Suffield.

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Introduction

During World War II over 700 tons of the chemical warfare agent mustard were shipped to Defence Research Establishment Suffield (DRES) and stored in lead-lined concrete vaults at the old Building 12 site [1]. In the early 1970's it was decided that this stockpile of mustard would be destroyed by hydrolysis. Batch hydrolysis using 1000 gallons of mustard, 5000 pounds of lime ($Ca(OH)_2$) and 2500 gallons of water was carried out according to a method developed at DRES [2,3].

The principal reactions involved in the hydrolysis of mustard are shown in the equations below. Conversion of mustard, through hemisulfur mustard to thiodiglycol, was essentially complete provided the ratio of water to mustard was large, the temperature was elevated to 100°C and the pH was maintained above 7 [2].

$$Cl\text{-}CH_2CH_2\text{-}S\text{-}CH_2CH_2\text{-}Cl + H_2O \rightarrow Cl\text{-}CH_2CH_2\text{-}S\text{-}CH_2CH_2\text{-}OH + HCl$$

$$Cl\text{-}CH_2CH_2\text{-}S\text{-}CH_2CH_2\text{-}OH + H_2O \rightarrow HO\text{-}CH_2CH_2\text{-}S\text{-}CH_2CH_2\text{-}OH + HCl$$

$$Ca(OH)_2 + 2\,HCl \rightarrow Ca(Cl)_2 + 2\,H_2O$$

Following batch hydrolysis the mustard hydrolysate was transferred from the reaction vessel into one of five empty storage vaults. After a cooling and settling period the hydrolysate separated into two layers. The upper or liquid layer was very fluid and ranged in colour from clear to a pale yellow in colour. The lower or sludge layer was paste-like and yellow-brown in colour. Samples of the liquid and sludge layers from the vaults containing the mustard hydrolysate were analysed for thiodiglycol, mustard and other organic content. Thiodiglycol was found in the 2 to 10 mg/mL range in the liquid hydrolysate and 6 to 14 mg/g range in the sludge hydrolysate [4]. Mustard was found at trace levels in two sludge samples [4] and a number of other sulfur containing compounds were identified in extracts of the sludge and liquid samples [5].

Although the majority of the mustard hydrolysate was removed from the vaults, a residual amount remained. The remaining hydrolysate was contained and buried with the remains of the vault after mustard destruction. Monitoring wells were established near the old Building 12 site to enable future water sampling. Sampling was performed in 1984, 1986 and 1987 and thiodiglycol was found at 3.9 mg/mL, 0.6 mg/mL and 2.2 mg/mL, respectively [6,7, at one of the locations near the buried vaults. Hexane extracts of these aqueous samples were analysed by capillary column gas chromatography-mass spectrometry (GC-MS) under electron impact (EI) and isobutane chemical ionization (CI) conditions. Mustard was not detected, but the hexane extracts did contain a number of sulfur containing compounds including 1,4-thioxane and 1,4-dithiane [6,7].

Munitions grade mustard formulations typically contain additional sulfur vesicants, including bis(2-chloroethylthio)ethane (sesquimustard or Q), bis[(2-chloroethylthio)ethyl] ether (T) and longer chain sulfur vesicants [8-10]. 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 [5]. These munitions grade mustard formulations often contain only 50% to 80% mustard with most of the remaining content being other sulfur vesicants which would hydrolyse to longer chain diols. Munitions mustard samples were therefore deliberately hydrolysed at DRDC Suffield to enable characterization of these compounds by EI-MS, ammonia CI-MS [11,12] and electrospray (ESI)-MS [13,14].

Sampling of the monitoring wells was not performed again until 1997 when TTCP E-AG-42 (Chemical Weapons Convention Analytical Technologies), as part of its mandate, analysed aqueous samples from three of the monitoring wells, including the one that contained thiodiglycol in the past. Only that location contained compounds indicative of the prior presence of mustard. Thiodiglycol was estimated to be in the 0.06 to 0.2 mg/mL range based on liquid chromatographic-electrospray mass spectrometric (LC-ESI-MS) analysis by Canada and GC-MS (as the trimethylsilyl derivative) by the United States [15]. 1,4-thioxane and 1,4-dithiane, two compounds commonly associated with the degradation of mustard, were also detected by GC-MS in the organic extracts by both countries. Canada also detected 6-oxa-3,9-dithia-1,11-undecanediol, the hydrolysis product of the longer chain sulfur vesicant, bis[(2-chloroethylthio)ethyl] ether (T) during LC-ESI-MS analysis of the aqueous sample.

Soil samples were taken for the first time at a number of locations and depths near a former mustard storage site as part of an ongoing environmental assessment. The contactor doing the sampling selected a number of soil samples from the site for mass spectrometric analysis. The headspace above the collected soil samples was sampled for safety reasons using a Chemical Agent Monitor (CAM). Mustard was not detected with the CAM but on several occasions an odour was noted. Six of these soil samples were selected by the consultant for mustard and thiodiglycol analysis by mass spectrometry at DRDC Suffield as part of this ongoing environmental assessment.

Dichloromethane extracts of the collected soil samples were initially analysed by capillary column gas chromatography-mass spectrometry (GC-MS), the most commonly used analytical technique for the separation and analysis of mustard and other chemical warfare agents [16-18]. Mustard was not detected but a number of related compounds including 1,4-thioxane, 1,4-dithiane and thiodiglycol were identified during this study. Thiodiglycol [19-24] and several related longer chain diols [21,22,24] have been successfully analysed without the need for derivatization by liquid chromatography-mass spectrometry (LC-MS) using either electrospray or atmospheric pressure chemical ionization. Low resolution LC-ESI-MS was initially utilized in this investigation for the determination of thiodiglycol and three longer chain diols in aqueous extracts of the collected soil samples using a sample handling and analysis method initially developed for the determination of soman, sarin and their hydrolysis products in soils [25,26]. The recent acquisition of a high resolution LC-ESI-MS/MS at DRDC Suffield provided the opportunity to accurately determine elemental composition during LC-ESI-MS and LC-ESI-MS/MS operation, a considerable advantage when confirming compound presence or when dealing with the identification of previously uncharacterized compounds in complex environmental samples. A high resolution LC-ESI-MS/MS method was developed for the determination of thiodiglycol and longer chain diols and applied to the analysis of these compounds in aqueous extracts of the collected soil samples. Detailed analysis of these aqueous extracts by high resolution LC-ESI-MS/MS resulted in the confirmation of thiodiglycol, three longer chain diols and the characterization of five new longer chain diols that could not be characterized during the preliminary low resolution LC-ESI-MS analyses.

Experimental

Former Mustard Storage Site Soil Samples

In 2002, a consultant was contracted to take soil samples at a number of locations and depths near a former mustard storage site on the Suffield Experimental Range as part of an environmental assessment. The soil samples (a to f) were extracted and analysed by GC-MS and LC-ESI-MS for the presence of mustard and mustard degradation products.

A portion of each soil sample was weighed (1.5 – 2.0 g) and ultrasonically extracted with 4 mL dichloromethane in a 15 x 125 mm screw-capped Teflon-lined glass culture tube for 10 minutes. The contents were then centrifuged and an aliquot of the dichloromethane layer (1 mL) was removed and stored in a screw-capped Teflon-lined 1.8 mL sample vial prior to GC-MS analysis.

A second portion of each soil sample was weighed (1.5 – 2.0 g) and ultrasonically extracted with 2 mL water in a 15 x 125 mm screw-capped Teflon-lined glass culture tube for 10 minutes. The contents were then centrifuged and an aliquot of the aqueous layer (1 mL) was removed and stored in a screw-capped Teflon-lined 1.8 mL sample vial prior to LC-ESI-MS or LC-ESI-MS/MS analysis.

GC-MS Analysis

Dichloromethane samples and extracts were analysed by GC-MS (Agilent 5973N under EI conditions: 70 eV, 0.035 mA, 230°C) using a 15m x 0.25mm ID J&W DB-35MS capillary column and the following temperature program: 40°C (2 min) 10°C/min 280°C (5 min). All injections (1 µL) were cool on-column at 43°C. The mass spectrometer was operated in full scanning mode and scanned from 40 to 400 Da at 2.08 scans/sec (unit resolution).

LC-ESI-MS Analysis

LC-ESI-MS data were acquired using a Micromass LCT time-of-flight mass spectrometer equipped with the Z-spray electrospray interface. The electrospray capillary was operated at 3.2 kV with sampling cone voltages in the 20 to 50 volts range. Nitrogen desolvation gas was introduced into the interface (80 °C) at a flow rate of 480 L/h. Nitrogen nebulizer gas was introduced at a flow rate of 66 L/h. ESI-MS data were acquired from 70 to 700 Da (1 sec) in the continuum mode with a resolution of 5000 (50% valley definition).

LC separations were performed with a MicroTech 150 mm x 0.32 mm i.d fused-silica capillary column packed with Zorbax C_{18} SB (5 µm particle size). The following solvent compositions were prepared for the mobile phase: Solvent A (0.1% trifluoroacetic acid (TFA) in water) and Solvent B (0.1% TFA in acetonitrile/water, 95:5). Chromatographic separations were performed with an Applied Biosystems model 140B dual syringe pump. A 5 to 75% B (30 min) gradient was used for the analysis of the aqueous soil extracts (1 µL injection volume). During these analyses the mobile phase was delivered at 150 µL/min and split prior to the injector such that the flow through the column was 10 µL/min.

LC-ESI-MS/MS analysis

Additional LC-ESI-MS and LC-ESI-MS/MS data were acquired using a Waters/Micromass QTOF Ultima tandem mass spectrometer equipped with a Z-spray electrospray interface. The electrospray capillary was operated at 1 kV with a sampling cone voltage of 35 volts. The collision energy was maintained at 5 volts for LC-ESI-MS operation and was varied from 2 to 12 volts (depending on the precusor ion selected) for LC-ESI-MS/MS operation. Argon was continually flowing into the collision cell at 11 psi during both LC-ESI-MS and LC-ESI-MS/MS operation. Nitrogen desolvation gas was introduced into the interface (80°C) at a flow rate of 500 L/h and nitrogen cone gas was introduced at a flow rate of 50 L/h. ESI-MS data were acquired from 40 to 700 Da (1 sec with a 0.1 sec interscan delay) and ESI-MS/MS (product mass spectra) data were acquired from 40 to 350 Da (1 sec with a 0.1 sec interscan delay). All data were acquired in the continuum mode with a resolution of 9000 (V-mode, 50% valley definition) using a lock mass.

Chromatographic separations were performed with a Waters CapLC using a 5% to 75%B gradient over 30 minutes and a flow rate of 10 µL/min. The following solvent compositions were prepared for the mobile phase: Solvent A (0.1% trifluoroacetic acid (TFA) in water) and Solvent B (0.1% TFA in acetonitrile/water, 95:5). All LC separations were performed with a MicroTech 150 mm x 0.32 mm i.d fused-silica capillary column packed with Zorbax C_{18} SB (5 µm particle size). The CapLC autosampler was used to introduce 1 to 3 µL samples of the aqueous soil extracts.

Results and discussion

GC-MS and LC-ESI-MS analysis

Soil samples were taken for the first time at a number of locations and depths near a former mustard storage site as part of an environmental assessment. The contactor doing the sampling selected a number of soil samples from the site for mass spectrometric analysis. Headspace above the six soil samples selected for mass spectrometric analysis was sampled for safety reasons using a Chemical Agent Monitor. Mustard was not detected.

Each of the six soil samples was extracted with dichloromethane and these extracts were screened for the presence of mustard by GC-MS. Mustard was not detected (sample detection limit: 0.2 µg/g; based on the acquisition of an interpretable full EI mass spectrum) in any of the soil sample extracts. However three of the soil sample extracts were found to contain thiodiglycol and/or related mustard hydrolysis products. Figure 1 illustrates the GC-MS total-ion-current chromatograms obtained for the three soil sample extracts containing thiodiglycol, and/or related mustard hydrolysis products (compounds identified in Table 1).

A recently developed sample handling and LC-ESI-MS analysis method for soils contaminated with sarin, soman and their initial hydrolysis products was evaluated for thiodiglycol determination. Aqueous extraction and LC-ESI-MS analysis offered significantly improved recoveries over dichloromethane extraction, derivatization and GC-MS analysis for the determination of organophosphorus chemical warfare agent hydrolysis products in soil [25,26]. A similar advantage was expected for the hydrolysis product of mustard, thiodiglycol. A sandy clay loam, a loamy sand and two control soil samples from near the former mustard storage site, were spiked in triplicate at the 20 µg/g level with thiodiglycol to estimate recovery efficiency. Thiodiglycol recovery, while variable due to differences in soil composition, was sufficient to confirm the presence of this chemical warfare agent hydrolysis product in contaminated soils. It was recovered from all the soils, with 52±4% and 51±3% efficiency for the two control soils, 85±7% efficiency for the sandy clay loam and 54±6% efficiency for the loamy sand.

Each of the aqueous extracts of the soil samples was screened for the presence of thiodiglycol by LC-ESI-MS. Figure 2 illustrates the LC-ESI-MS total-ion-current chromatograms obtained for the two soil sample extracts containing thiodiglycol and related mustard hydrolysis products (compounds identified in Table 1). A major sample component(s) with a retention time in the 2 to 3 minute range was detected in the water extract of all the soil samples. It did not appear to contain any compounds associated with mustard degradation. Thiodiglycol was detected in the water extracts of soil samples b and c at 200 µg/g and 300 µg/g (semi-quantitative estimate), respectively. Thiodiglycol was not detected (sample detection limit: 1 µg/g; based on the acquisition of an interpretable full ESI mass spectrum) in the other four soil sample extracts.

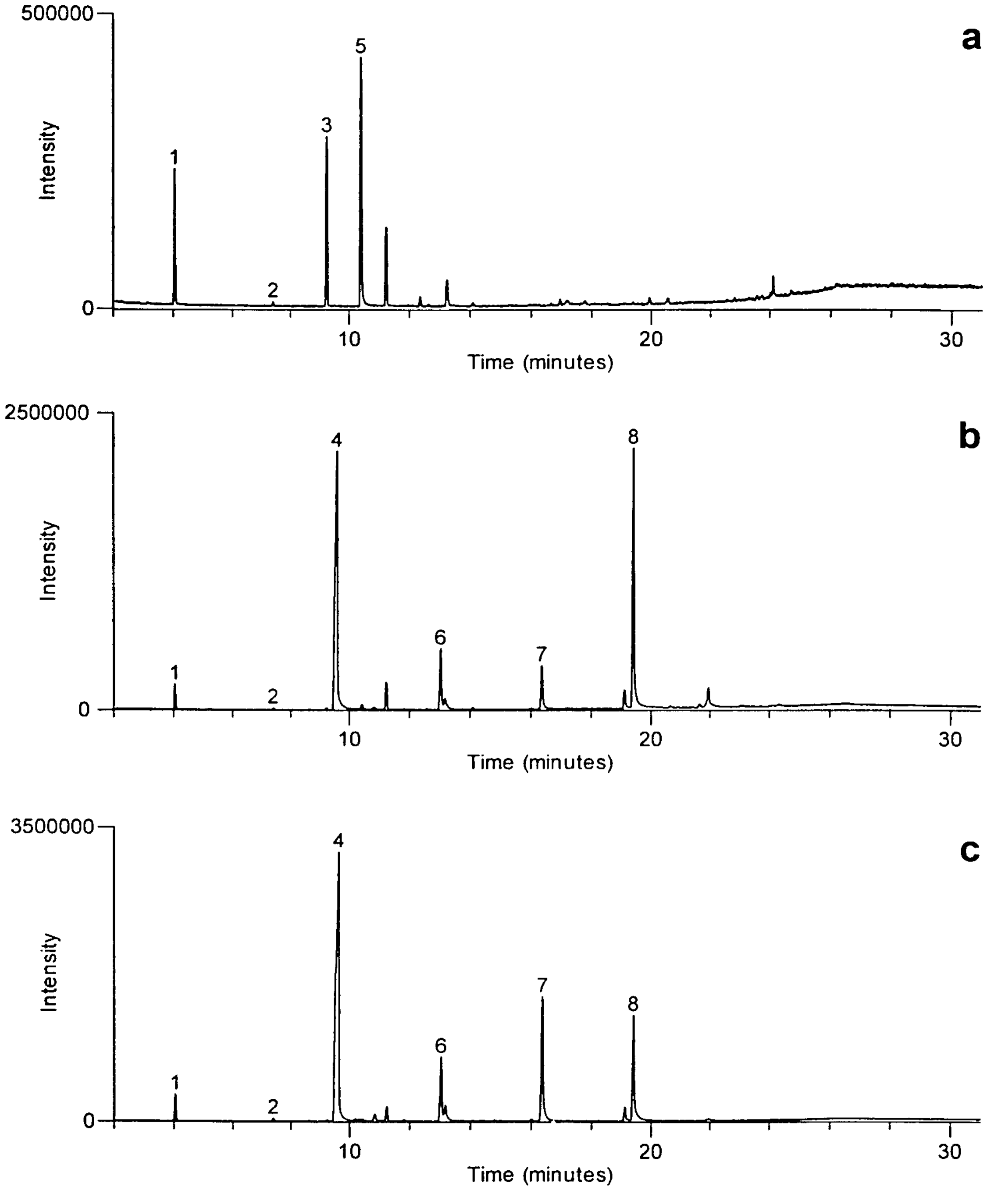


Figure 1. *GC-MS total-ion-current chromatograms obtained for dichloromethane extracts of a) soil sample a, b) soil sample b and c) soil sample c. Compounds are identified in Table 1.*

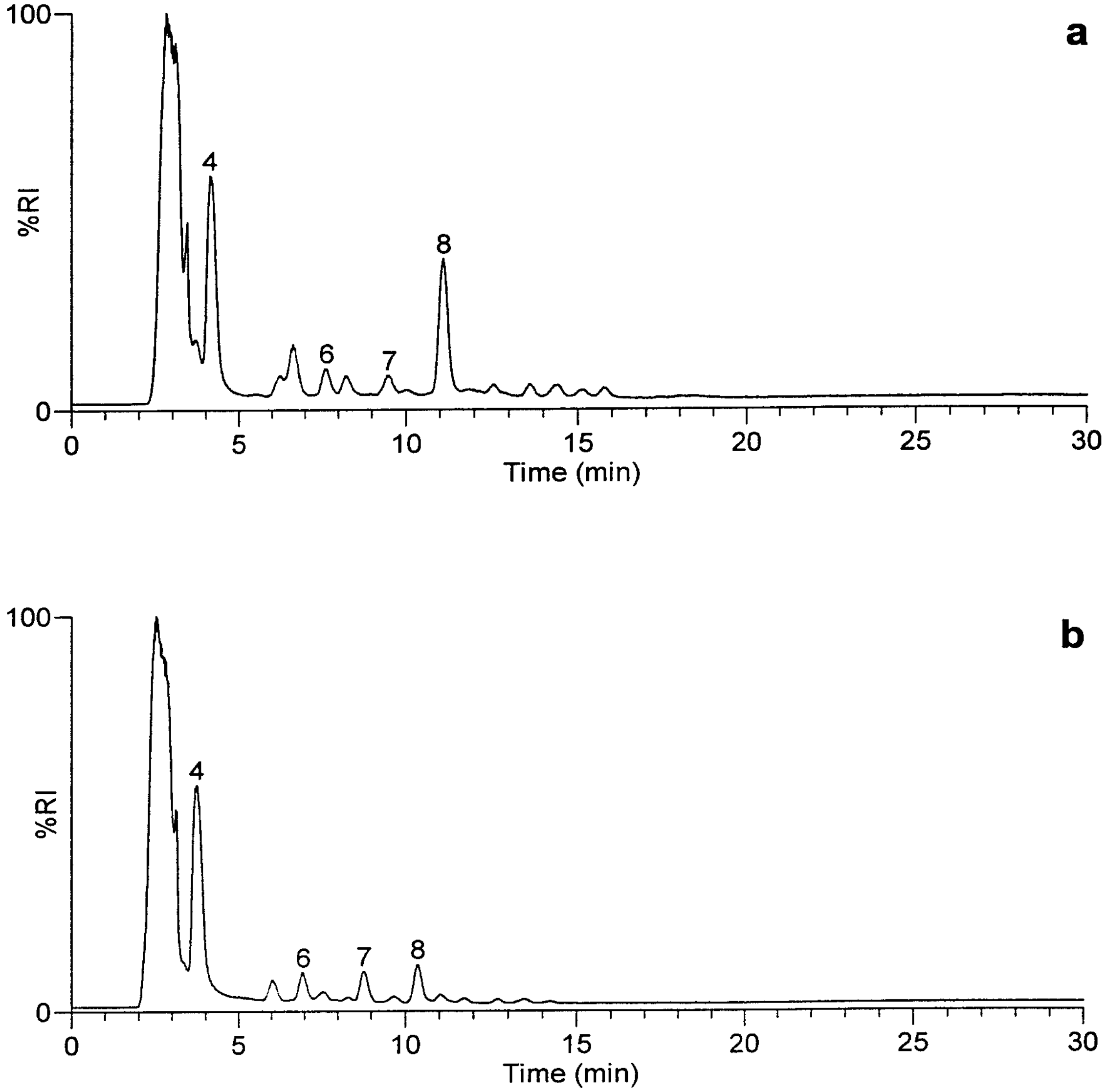
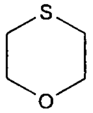
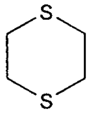
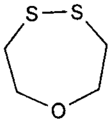
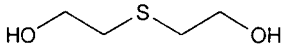
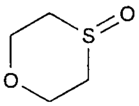
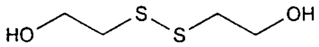
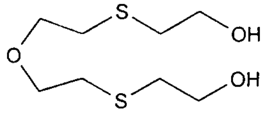


Figure 2. *LC-ESI-MS total-ion-current chromatograms obtained for aqueous extracts of a) soil sample b and b) soil sample c. Compounds are identified in Table 1.*

Table 1. *Compounds identified in soil sample extracts by GC-MS and LC-ESI-MS.*

Peak No[1]	Compound Name	Structure	Dichloromethane Extract (GC-MS analysis)	Aqueous Extract (LC-MS analysis)
1	1,4-Oxathiane		Soil sample a Soil sample b Soil sample c	
2	1,4-Dithiane		Soil sample a Soil sample b Soil sample c	
3	1-Oxa-4,5-dithiapane		Soil sample a	
4	Thiodiglycol		Soil sample b Soil sample c	Soil sample b Soil sample c
5	1,4-Oxathiane sulfoxide		Soil sample a	
6	Bis(2-hydroxyethyl)disulfide		Soil sample a Soil sample b Soil sample c	Soil sample b Soil sample c
7	3,6-Dithia-1,8-octanediol		Soil sample b Soil sample c	Soil sample b Soil sample c
8	6-Oxa-3,9-dithia-1,11-undecanediol		Soil sample b Soil sample c	Soil sample b Soil sample c

[1] Refer to Figure 1 and 2.

Figures 3 and 4 illustrate typical ESI-MS data for thiodiglycol, the hydrolysis product of mustard, and the hydrolysis products of three longer chain sulfur vesicants, bis(2-hydroxyethyl)disulfide, 3,6-dithia-1,8-octanediol, and 6-oxa-3,9-dithia-1,11-undecanediol (sampling cone voltage: 30 volts). The diol ESI-MS data contained both molecular ion and product ion content, enabling structural identification of these hydrolysis products. The ESI-MS data obtained for 6-oxa-3.9-dithia-1,11-undecanediol (Figure 4b), the hydrolysis product of bis[(2-chloroethylthio)ethyl]ether (T), was typical. The mass spectrum contained a significant MH^+ ion at m/z 227 and a MNa^+ ion at m/z 249. 6-Oxa-3,9-dithia-1,11-undecanediol exhibited a product ion due to loss of H_2O at m/z 209 along with product ions at m/z 181, m/z 149 and m/z 105 due to $[MH{-}H_2O{-}C_2H_4]^+$, $[MH{-}H_2O{-}SC_2H_4]^+$ and $[MH{-}H_2O{-}SC_2H_4{-}OC_2H_4]^+$, respectively, that could be used to establish relative S and O positioning.

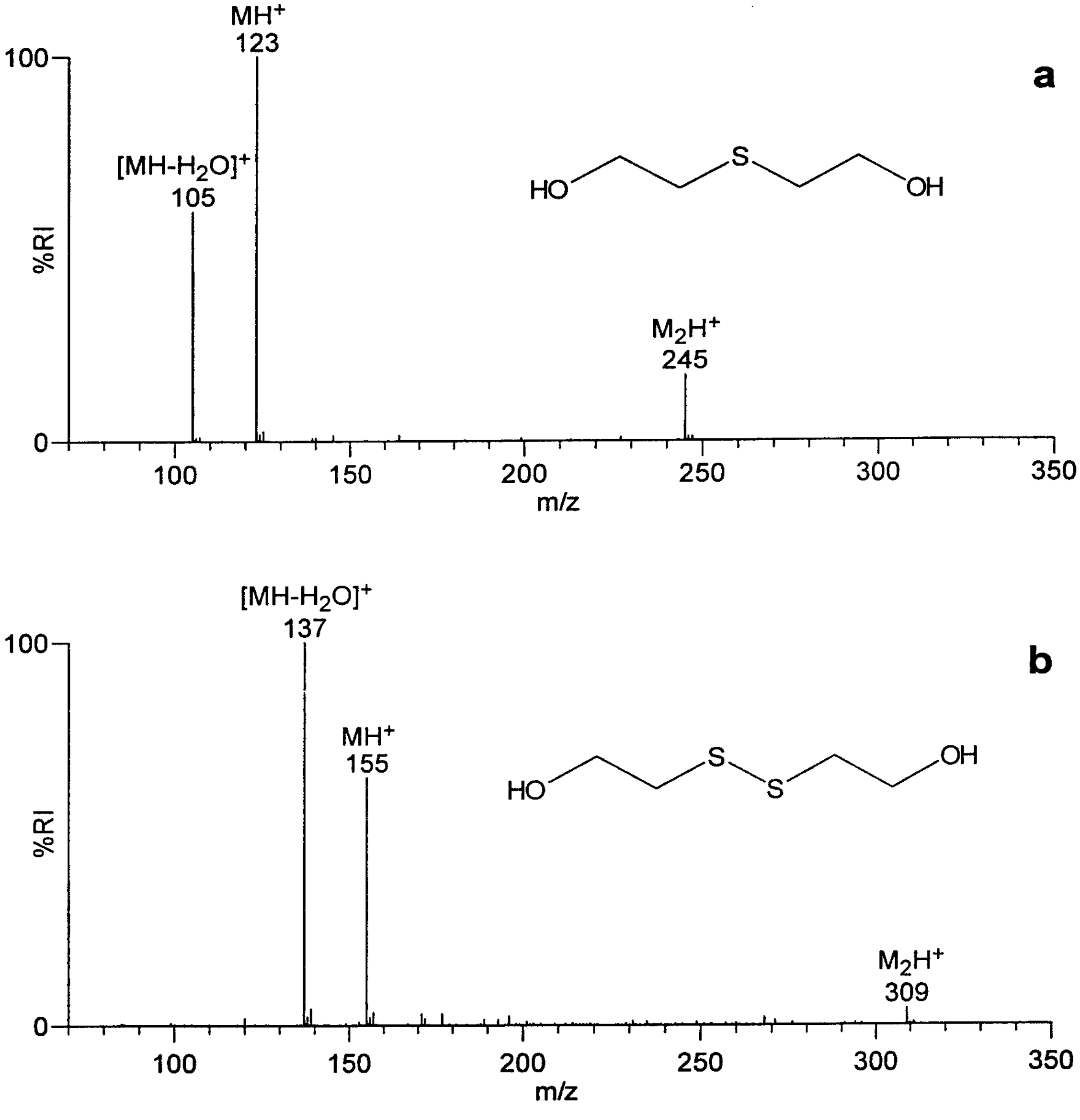


Figure 3. *ESI-MS data obtained for a) thiodiglycol (sampling cone voltage of 20 volts) and b) bis(2-hydroxyethyl)disulfide (sampling cone voltage of 20 volts) during LC-ESI-MS analysis.*

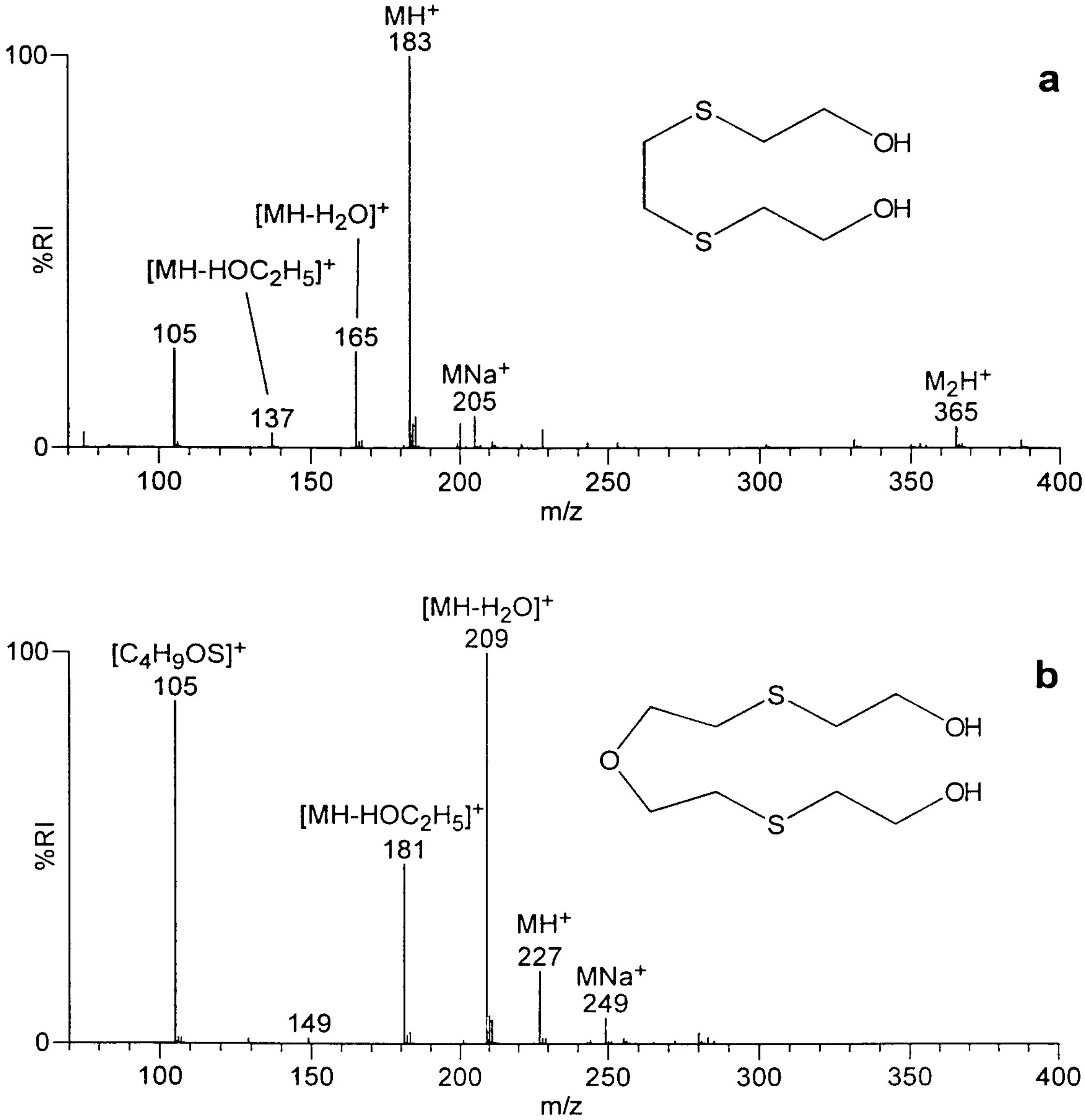


Figure 4. *ESI-MS data obtained for a) 3,6-dithia-1,8-octanediol (sampling cone voltage of 20 volts) and b) 6-oxa-3,9-dithia-1,11-undecanediol (sampling cone voltage of 30 volts) during LC-ESI-MS analysis.*

Mustard cannot be detected by LC-ESI-MS. The relatively non-polar compounds related to mustard (chromatographic peak numbers 1, 2, 3 and 5 in Table 1), identified in the dichloromethane extract of the soil samples during GC-MS analysis, were not detected during LC-ESI-MS analysis of the aqueous extracts. These compounds are soluble in water and have been detected in aqueous samples taken from bore holes at the former mustard storage site in the past [6,7]. The inability to ionize these relatively non-polar compounds by ESI-MS was confirmed by gently drying (under nitrogen) a dichloromethane extract and taking it up in water for subsequent LC-ESI-MS analysis. Only thiodiglycol and the longer chain diols were detected by LC-ESI-MS.

The molecular mass of several uncharacterized chromatographic components (Figure 2) was determined but these compounds could not be identified during LC-ESI-MS analysis of the aqueous extracts, as this method was not selective enough to enable characterization of these components.

LC-ESI-MS/MS analysis

The recent acquisition of a high resolution LC-ESI-MS/MS at DRDC Suffield provided the opportunity to accurately determine elemental composition during LC-ESI-MS/MS operation, a considerable advantage for the selective identification of previously uncharacterized compounds in a complex environmental sample. A high resolution LC-ESI-MS/MS method was developed for the determination of thiodiglycol and longer chain diols and applied to the analysis of these previously uncharacterized compounds in the aqueous extracts of the soil samples b and c (Figure 5).

High resolution LC-ESI-MS/MS data were acquired with collision energies between 2 and 12 volts in order to determine an appropriate setting for each diol that resulted in the acquisition of product mass spectra containing both precursor and structurally significant product ion data. Figures 6 to 8 illustrate representative ESI-MS/MS data acquired for each of the diols at the selected collision energy setting and Table 2 summarizes the acquired high resolution data that was used for identification purposes. MH^+ data were acquired during high resolution LC-ESI-MS analyses and MH^+ product ion data were acquired during high resolution LC-ESI-MS/MS. The average error and standard deviation associated with the 10 MH^+ measurements was 0.0004 ± 0.0004 (equivalent to 2 ppm at m/z 200). Slightly larger average errors, due in part to weaker signals for some of the product ions, were observed for the 38 product ions measured. An average error and standard deviation of 0.0010 ± 0.0009 (equivalent to 5 ppm at m/z 200) was associated with these mass measurements.

Figure 6 illustrates typical ESI-MS/MS data for thiodiglycol, the hydrolysis product of mustard, and the hydrolysis products of three longer chain sulfur vesicants, bis(2-chloroethyl)disulfide, bis(2-chloroethylthio)ethane (sesquimustard or Q), and bis[(2-chloroethylthio)ethyl] ether (T) initially identified by LC-ESI-MS in the soil extracts (27). A significant product ion due to the loss of water for the precusor ion (MH^+) was observed for these and the other diols, along with structurally significant product ions that could be used to establish chain length. The ESI-MS/MS data obtained for the hydrolysis product of sesquimustard, 3,6-dithia-1,8-octanediol, was typical of a longer chain diol. Product ions due to $(MH{-}H_2O{-}C_2H_4)^+$ and $[MH{-}H_2O{-}SC_2H_4]^+$ were observed at m/z 137 and 105, respectively. The product ion at m/z 105, due to protonated 1,4-thioxane, proved to be a common product ion for all the diols analysed and could be considered for extract screening purposes.

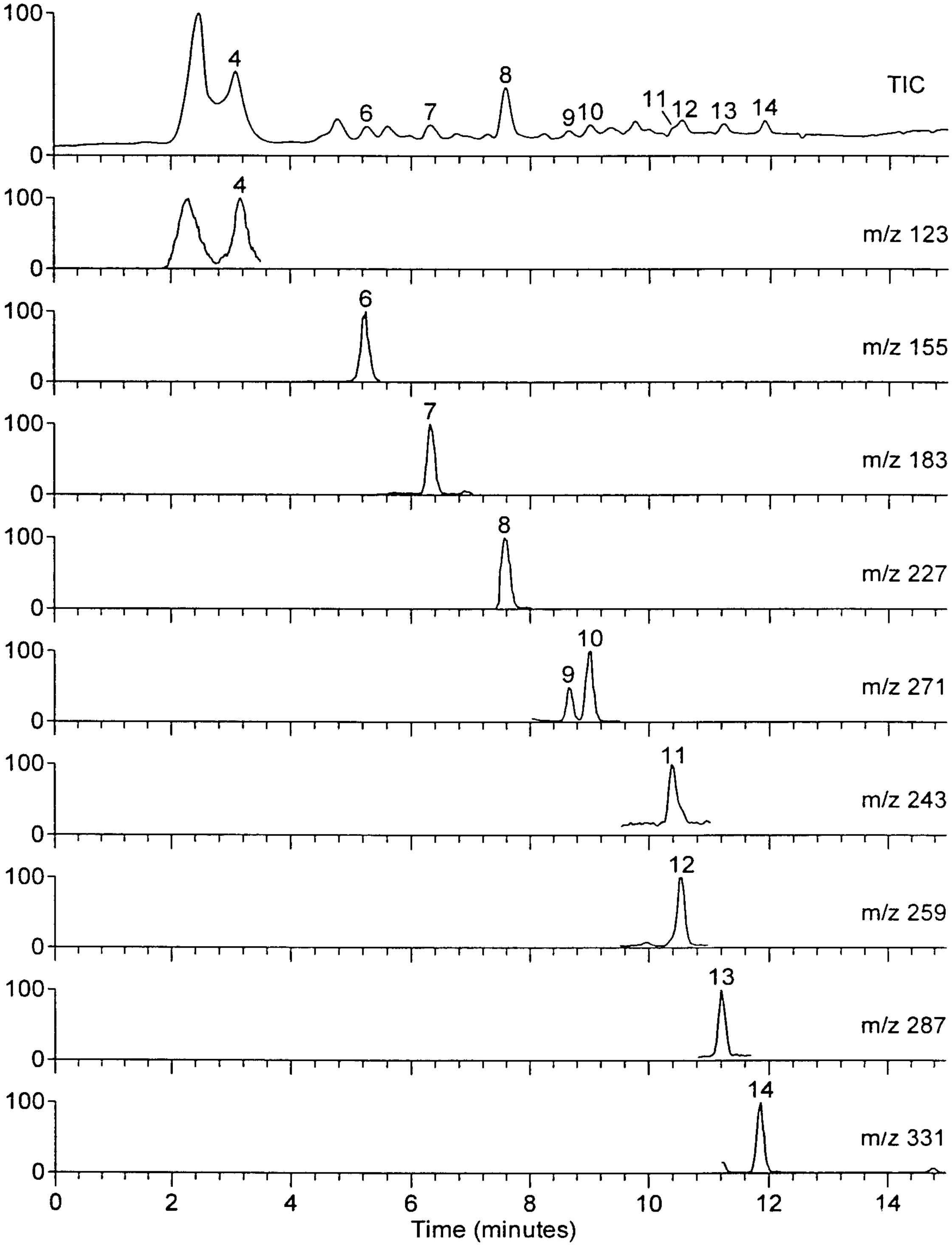
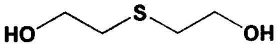
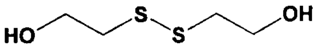
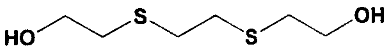
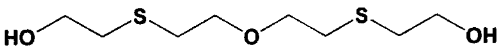
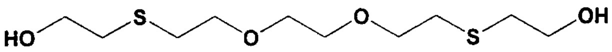
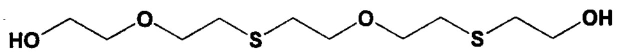
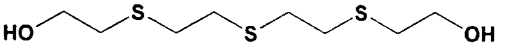
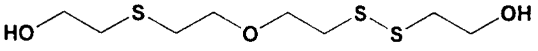
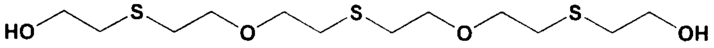


Figure 5. *Packed capillary LC-ESI-MS and LC-ESI-MS/MS chromatograms obtained for an aqueous extract of soil sample b taken from a former mustard storage site. The top chromatogram illustrates the total-ion-current (40 to 700 Da) obtained during LC-ESI-MS analysis. The lower nine chromatograms illustrate the LC-ESI-MS/MS data that were obtained during a single analysis, with the mass of the selected precursor ion (MH^+) changing with time. Numbered sample components are identified Table 2.*

Table 2. *LC-ESI-MS/MS identification of compounds in aqueous extract of soil sample b. MH^+ data were obtained during LC-ESI-MS analysis. MH^+ product ion data for each compound were obtained during LC-ESI-MS/MS analysis.*

Peak #[1]	Compound Name	Ion Identity	Observed Mass (Da)[2]	Theoretical Mass (Da)	Error (Da)
4	Thiodiglycol 	MH^+ $(MH-H_2O)^+$	123.0480 105.0377	123.0480 105.0374	0.0000 0.0003
6	Bis(hydroxyethyl)disulfide 	MH^+ $(MH-H_2O)^+$	155.0197 137.0098	155.0200 137.0095	0.0003 0.0003
7	3,6-Dithia-1,8-octanediol 	MH^+ $(MH-H_2O)^+$ $(MH-H_2O-C_2H_4)^+$ $(MH-H_2O-SC_2H_4)^+$	183.0518 165.0412 137.0101 105.0373	183.0513 165.0408 137.0095 150.0374	0.0005 0.0004 0.0006 0.0001
8	6-Oxa-3,9-dithia-1,11-undecanediol 	MH^+ $(MH-H_2O)^+$ $(MH-H_2O-C_2H_4)^+$ $(MH-H_2O-SC_2H_4-OC_2H_4)^+$	227.0777 209.0668 181.0360 105.0373	227.0775 209.0670 181.0357 105.0374	0.0002 0.0002 0.0003 0.0001
9	6,9-Dioxa-3,12-dithia-1,14-tetradecanediol 	MH^+ $(MH-H_2O)^+$ $(MH-H_2O-C_2H_4)^+$ $(MH-H_2O-SC_2H_4-OC_2H_4)^+$ $(MH-H_2O-SC_2H_4-OC_2H_4-OC_2H_4)^+$	271.1044 253.0934 225.0631 149.0617 105.0382	271.1038 253.0932 225.0619 149.0636 105.0374	0.0006 0.0002 0.0012 0.0019 0.0008
10	6,12-Dioxa-3,9-dithia-1,14-tetradecanediol 	MH^+ $(MH-H_2O)^+$ $(MH-H_2O-C_2H_4)^+$ $(MH-H_2O-OC_2H_4)^+$ $(MH-H_2O-OC_2H_4-C_2H_4)^+$ $(MH-H_2O-OC_2H_4-SC_2H_4)^+$ $(MH-H_2O-OC_2H_4-SC_2H_4-OC_2H_4)^+$	271.1040 253.0937 225.0628 209.0688 181.0382 149.0648 105.0384	271.1038 253.0932 225.0619 209.0670 181.0357 149.0636 105.0374	0.0002 0.0005 0.0009 0.0018 0.0025 0.0012 0.0010

11	3,6,9-Trithia-1,11-undecanediol	MH^+	243.0560	243.0547	0.0013
		$(MH\text{-}H_2O)^+$	225.0465	225.0441	0.0024
		$(MH\text{-}H_2O\text{-}C_2H_4)^+$	197.0163	197.0128	0.0035
		$(MH\text{-}H_2O\text{-}SC_2H_4)^+$	165.0432	165.0408	0.0024
		$(MH\text{-}H_2O\text{-}SC_2H_4\text{-}C_2H_4)^+$	137.0109	137.0095	0.0014
		$(MH\text{-}H_2O\text{-}SC_2H_4\text{-}SC_2H_4)^+$	105.0377	105.0374	0.0003
					
12	6-Oxa-3,9,10-trithia-1,12-dodecanediol	MH^+	259.0489	259.0496	0.0007
		$(MH\text{-}H_2O)^+$	241.0397	241.0390	0.0007
		$(MH\text{-}H_2O\text{-}C_2H_4)^+$	213.0109	213.0077	0.0032
		$(MH\text{-}SC_2H_4)^+$	199.0478	199.0462	0.0016
		$(MH\text{-}H_2O\text{-}SC_2H_4)^+$	181.0370	181.0357	0.0013
		$(MH\text{-}H_2O\text{-}SC_2H_4\text{-}OC_2H_4)^+$	137.0104	137.0095	0.0009
		$(C_4H_9S_1O_1)^+$	105.0373	105.0374	0.0001
					
13	6-Oxa-3,9,12-trithia-1,14-tetradecanediol	MH^+	287.0813	287.0809	0.0004
		$(MH\text{-}H_2O)^+$	269.0699	269.0703	0.0004
		$(MH\text{-}H_2O\text{-}SC_2H_4\text{-}OC_2H_4)^+$	165.0416	165.0408	0.0008
		$(MH\text{-}H_2O\text{-}SC_2H_4\text{-}OC_2H_4\text{-}C_2H_4)^+$	137.0084	137.0095	0.0011
		$(MH\text{-}H_2O\text{-}SC_2H_4\text{-}OC_2H_4\text{-}SC_2H_4)^+$	105.0389	105.0374	0.0015
					
14	6,12-Dioxa-3,9,15-trithia-1,17-heptadecanediol	MH^+	331.1072	331.1071	0.0001
		$(MH\text{-}H_2O)^+$	313.0967	313.0966	0.0001
		$(MH\text{-}H_2O\text{-}SC_2H_4\text{-}OC_2H_4)^+$	209.0680	209.0670	0.0010
		$(MH\text{-}H_2O\text{-}SC_2H_4\text{-}OC_2H_4\text{-}C_2H_4)^+$	181.0376	181.0357	0.0019
		$(MH\text{-}H_2O\text{-}SC_2H_4\text{-}OC_2H_4\text{-}SC_2H_4)^+$	149.0632	149.0636	0.0004
		$(MH\text{-}H_2O\text{-}SC_2H_4\text{-}OC_2H_4\text{-}SC_2H_4\text{-}OC_2H_4)^+$	105.0378	105.0374	0.0004
					

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[1] Refer to Figure 5.

[2] Average of (typically) 4 to 7 full scans (40 to 350 Da) across the chromatographic peak.

Figure 7 illustrates the different ESI-MS/MS data obtained for two isomers with identical elemental composition that have not been previously characterized. 6,9-Dioxa-3,12-dithia-1,14-tetradecanediol (Figure 7a) and 6,12-dioxa-3,9-dithia-1,14-tetradecanediol (Figure 7b), two compounds which differ in their relative O and S positioning, were identified based on the acquired ESI-MS/MS data. Both compounds exhibited common ions due to $(MH\text{-}H_2O)^+$ and $(MH\text{-}H_2O\text{-}C_2H_4)^+$ at m/z 253 and m/z 225 and a protonated 1,4-thioxane ion at m/z 105 that could be formed by loss of OC_2H_4 from the ion at m/z 149. 6,12-Dioxa-3,9-dithia-1,14-tetradecanediol was differentiated from 6,9-dioxa-3,12-dithia-1,14-tetradecanediol by the presence of ions at m/z 209 and m/z 181 due to $MH\text{-}H_2O\text{-}OC_2H_4)^+$ and $(MH\text{-}H_2O\text{-}OC_2H_4\text{-}C_2H_4)^+$. The remaining ions at m/z 149 and 105 due to $(MH\text{-}H_2O\text{-}OC_2H_4\text{-}SC_2H_4)^+$ and $(MH\text{-}H_2O\text{-}OC_2H_4\text{-}SC_2H_4\text{-}OC_2H_4)^+$ suggested a structure consistent with alternating O and S positioning within the diol. The ion at m/z 149 for 6,9-dioxa-3,12-dithia-1,14-tetradecanediol results from the loss of 1,4-thioxane (and water) from one end of the protonated molecule, with a subsequent loss of OC_2H_4 giving rise to the m/z 105 ion. The only possible relative positioning of the S and O atoms, other than the alternating pattern proposed for the other isomer, would be a structure with both oxygens occupying the central positions in the diol.

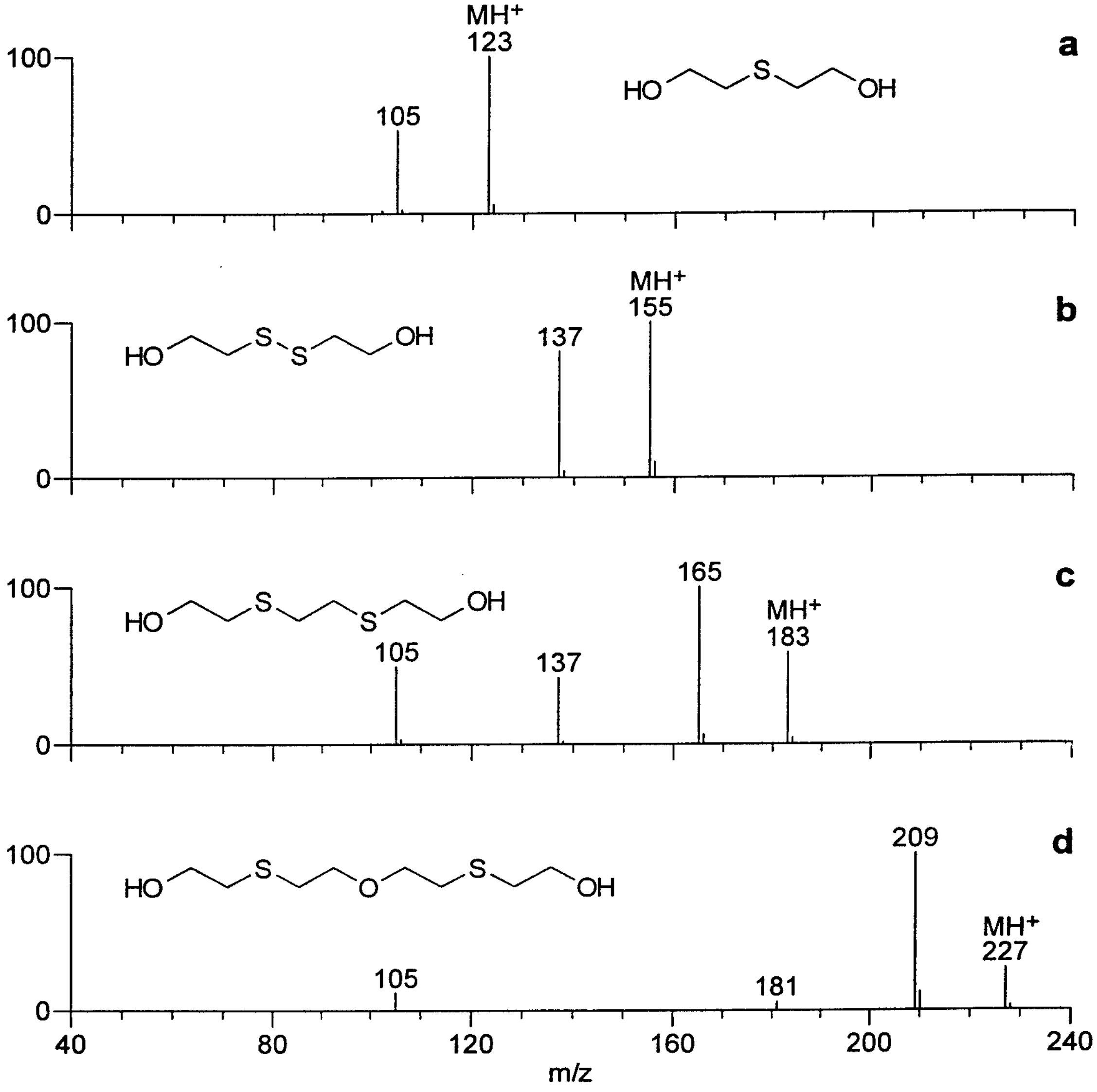


Figure 6. *ESI-MS/MS product mass spectra obtained for the MH^+ ion of a) thiodiglycol (collision energy: 2 volts), b) bis(hydroxyethyl)disulfide (collision energy: 2 volts), c) 3,6-dithia-1,8-octanediol (collision energy: 4 volts) and d) 6,9-dioxa-3,12-dithia-1,14-tetradecanediol (collision energy: 5 volts) during LC-ESI-MS/MS analysis of an aqueous extract of soil sample b taken from a former mustard storage site.*

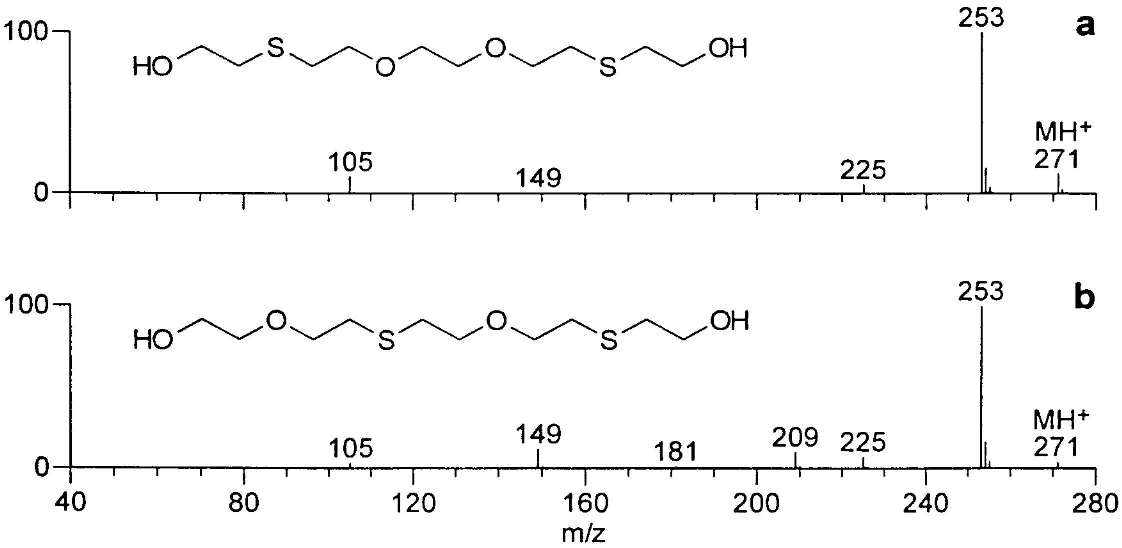


Figure 7. *ESI-MS/MS product mass spectra obtained for the MH$^+$ ion of a) 6,9-dioxa-3,12-dithia-1,14-tetradecanediol (collision energy: 7 volts) and b) 6,12-dioxa-3,9-dithia-1,14-tetradecanediol (collision energy: 7 volts) during LC-ESI-MS/MS analysis of an aqueous extract of soil sample b taken from a former mustard storage site.*

Figure 8 illustrates the ESI-MS/MS data for the remaining longer chain diols that could not be identified during LC-ESI-MS study. Table 2 indicates the identity of the product ions that were observed, leading to identification of 3,6,9-trithia-1,11-undecanediol (Figure 8a), 6-oxa-3,9,10-trithia-1,12-dodecanediol (Figure 8b), 6-oxa-3,9,12-trithia-1,14-tetradecanediol (Figure 8c) and 6,12 -dioxa-3,9,15-trithia-1,17-heptadecanediol (Figure 8d) in an aqueous extract of the soil sample.

The relative positioning of the S and O atoms was augmented by the acquisition of complementary ESI-MS/MS data for the $(MH-H_2O)^+$ precursor ions for each of the diols as well. In all cases the best product mass spectra were obtained with slightly higher collision energies (7 to 12 volts) than were used to acquire MH$^+$ product mass spectra. Figure 9 illustrates this ESI-MS/MS data for two of the diols, 3,6,9-trithia-1,11-undecanediol (Figure 9a) and 6-oxa-3,9,12-trithia-1,14-tetradecanediol (Figure 9b) and Table 3 summarizes product ion identities and associated mass measurements. In both cases it was possible to assign the relative O and S positioning based on the observed product ions. The mass differences in the product mass spectrum of 3,6,9-trithia-1,11-undecanediol alternated between losses of 28 Da (loss of C_2H_4) and 32 Da (loss of S), consistent with the assigned structure where sulfur atoms were present at positions 3,6 and 9. The same initial alternating pattern, loss of 28 Da (m/z 241), followed by loss of 32 Da (m/z 209), 28 Da (m/z 181) and finally 32 Da (m/z149) was also observed for 6-oxa-3,9,12-trithia-1,14-tetradecanediol, indicating the presence of a sulfur atom at positions 9 and 12. In addition, there was a mass difference of 44 Da (due to loss of OC_2H_4) between the ions at m/z 149 and m/z 105 (protonated 1,4-thioxane), indicating an oxygen atom at the 6 position. The remaining sulfur was assigned to the 3 position.

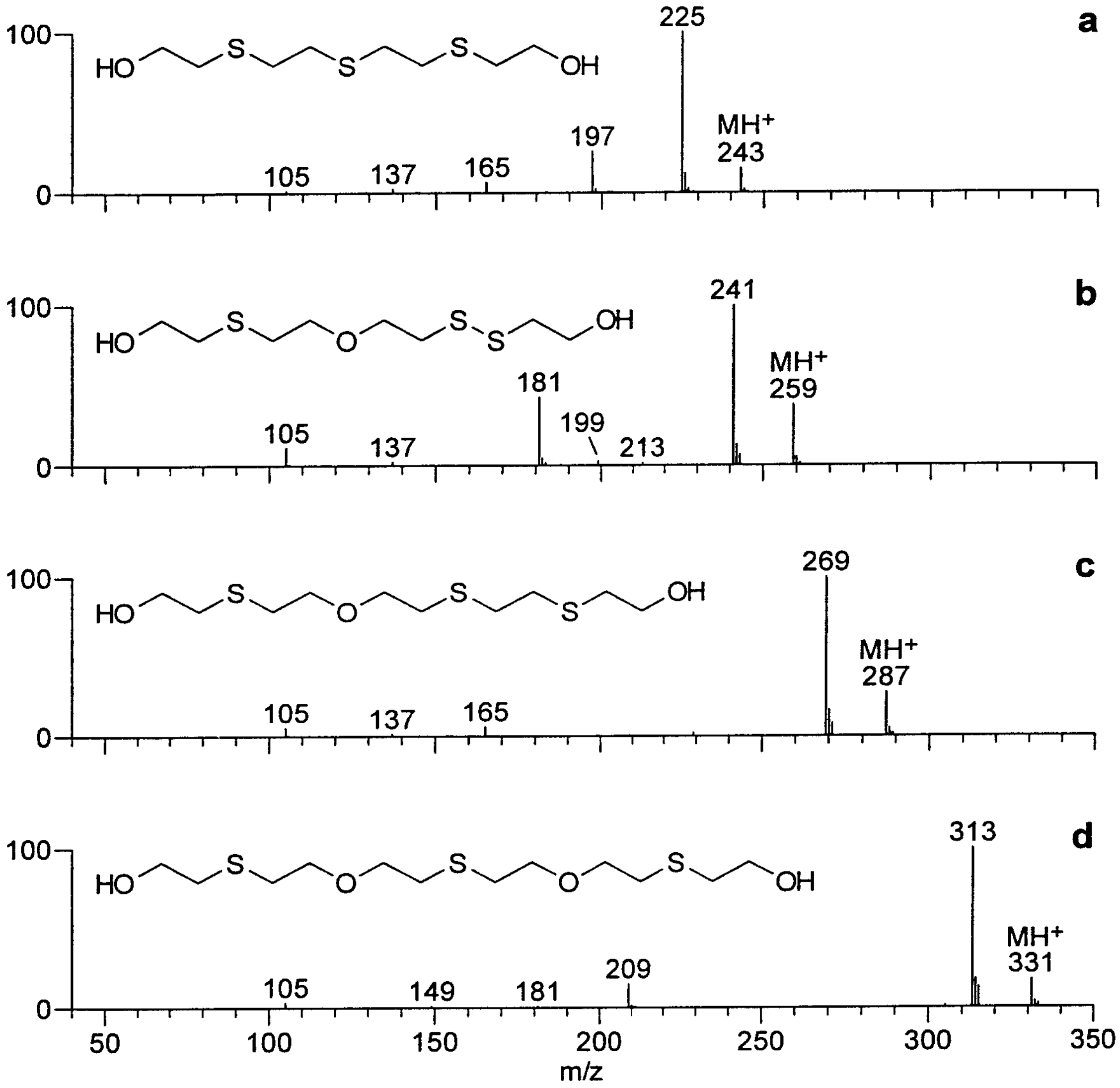


Figure 8. *ESI-MS/MS product mass spectra obtained for the MH$^+$ ion of a) 3,6,9-trithia-1,11-undecanediol (collision energy: 5 volts), b) 6-oxa-3,9,10-trithia-1,12-dodecanediol (collision energy: 5 volts), c) 6-oxa-3,9,12-trithia-1,14-tetradecanediol (collision energy: 5 volts) and d) 6,12-dioxa-3,9,15-trithia-1,17-heptadecanediol (collision energy: 7 volts) during LC-ESI-MS/MS analysis of an aqueous extract of soil sample b taken from a former mustard storage site.*

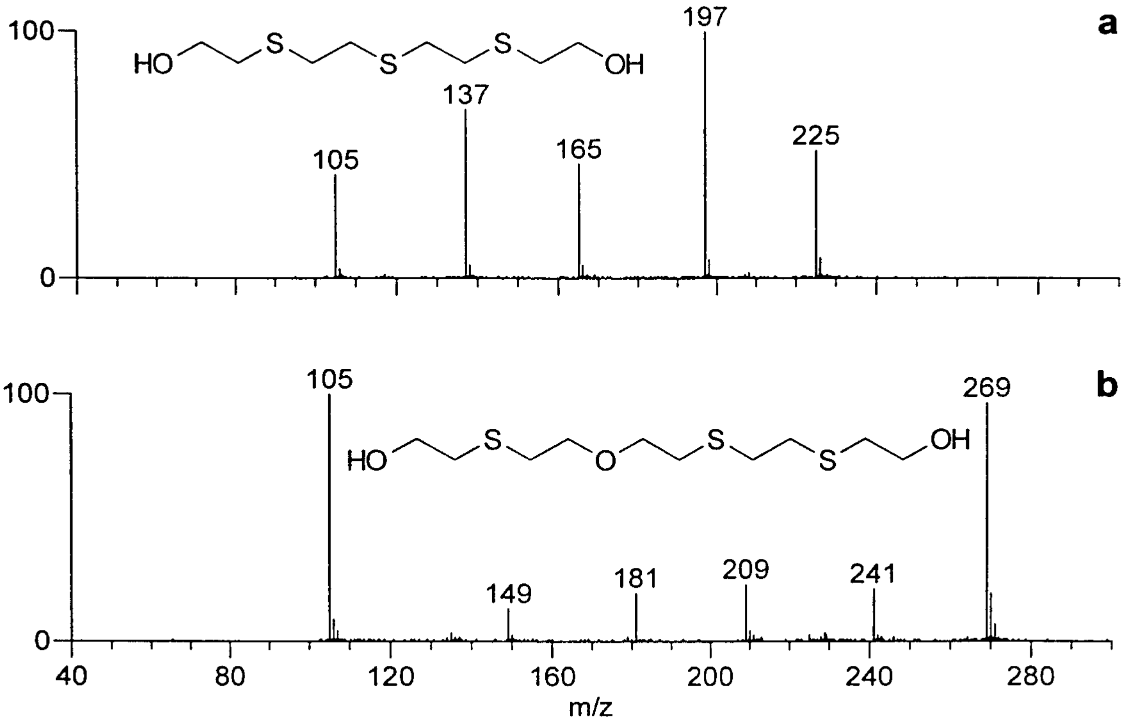
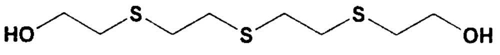
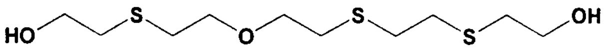


Figure 9. *ESI-MS/MS product mass spectra obtained for the* $(MH-H_2O)^+$ *ion of a) 3,6,9-trithia-1,11-undecanediol (collision energy: 10 volts) and 6-oxa-3,9,12-trithia-1,14-tetradecanediol (collision energy: 10 volts) during LC-ESI-MS/MS analysis of an aqueous extract of soil sample b taken from a former mustard storage site.*

Table 3. *Production data obtained for* $(MH-H_2O)^+$ *precusor ions of 3,6,9-trithia-1,11-undecanediol and 6-oxa-3,9,12-trithia-1,14-tetradecanediol (found in soil sample b).*

Peak #[1]	Compound Name	Ion Identity	Observed Mass (Da)[2]	Theoretical Mass (Da)	Error (Da)
11	3,6,9-Trithia-1,11-undecanediol	$(MH-H_2O-C_2H_4)^+$ $(MH-H_2O-SC_2H_4)^+$ $(MH-H_2O-SC_2H_4-C_2H_4)^+$ $(MH-H_2O-SC_2H_4-SC_2H_4)^+$	197.0125 165.0399 137.0103 105.0373	197.0128 165.0408 137.0095 105.0374	0.0003 0.0009 0.0007 0.0001
					
13	6-Oxa-3,9,12-trithia-1,14-tetradecanediol	$(MH-H_2O-C_2H_4)^+$ $(MH-H_2O-SC_2H_4)^+$ $(MH-H_2O-SC_2H_4-C_2H_4)^+$ $(MH-H_2O-SC_2H_4-SC_2H_4)^+$ $(MH-H_2O-SC_2H_4-SC_2H_4-OC_2H_4)^+$	241.0386 209.0667 181.0383 149.0630 105.0381	241.0390 209.0670 181.0357 149.0636 105.0374	0.0004 0.0003 0.0026 0.0006 0.0007
					

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[1] Refer to Figure 5.

[2] Average of (typically) 4 to 7 full scans (40 to 350 Da) across the chromatographic peak.

Additional product ions, all of which could be assigned based on their accurate mass data, were also observed in the $(MH-H_2O)^+$ product mass spectra of several other diols. A single product ion at m/z 87 (relative intensity ~3%) due to loss of H_2O was observed for thiodiglycol. Three mass deficient, product ions at m/z 119 (relative intensity ~6%), 109 (relative intensity ~60%) and 91 (relative intensity ~4%), due to loss of H_2O, $H_2O + C_2H_4$ and $(H_2O)_2 + C_2H_4$, respectively, from the $(MH-H_2O)^+$ precursor ion were observed for bis(hydroxyethyl)disulfide. Both 6,9-dioxa-3,12-dithia-1,14-tetradecanediol and 6,12-dioxa-3,9-dithia-1,14-tetradecanediol exhibited a weak product ion at m/z 89 (relative intensity ~1-2%) due to protonated 1,4-dioxane, $(C_4H_9O_2)^+$, consistent with the fact that these were the only two diols containing $HO-C_2H_4O-C_2H_4-$ or $-O-C_2H_4-OC_2H_4-$ substructures that could give rise to this ion. It should be noted that an alternative ion structure with the same nominal mass, $(C_4H_9S)^+$, was not considered as its theoretical mass was at least an order of magnitude higher than the errors typically associated with the observed mass measurements.

Conclusions

Soil samples were taken for the first time at a number of locations and depths near a former mustard storage site as part of an environmental assessment. The contactor doing the sampling selected a number of soil samples from the site for mass spectrometric analysis. Headspace above the collected soil samples was sampled for safety reasons using a Chemical Agent Monitor (CAM). Mustard was not detected. Mustard was also not detected in the dichloromethane extracts of the soil samples during capillary column GC-MS. However, three of the soil sample extracts were found to contain thiodiglycol and/or related mustard hydrolysis products.

A low resolution LC-ESI-MS method was applied to the identification of mustard hydrolysis products in aqueous extracts of soil. Thiodiglycol was detected by LC-ESI-MS in the aqueous extracts of two soil samples at the 200 μg/mL and 300 μg/mL levels, along with bis(hydroxyethyl)disulfide, 3,6-dithia-1,8-octanediol and 6,9-dioxa-3,12-dithia-1,14-tetradecanediol, three longer chain diols associated with the hydrolysis of munitions grade mustard. Identification of a number of other related compounds was not possible.

The recent acquisition of a high resolution LC-ESI-MS/MS at DRDC Suffield provided an opportunity to accurately determine elemental composition during analyses. High resolution LC-ESI-MS/MS methods were developed for the determination of thiodiglycol and longer chain diols and applied to the analysis of these compounds in the aqueous extracts of the soil samples collected from the former mustard storage site. Detailed analysis of these aqueous extracts by high resolution LC-ESI-MS/MS resulted in the confirmation of thiodiglycol and three longer chain diols and the characterization of five new longer chain diols that could not be characterized during low resolution LC-ESI-MS analyses. The average error and standard deviation associated with the MH^+ measurements for the diols was 0.0004 ± 0.0004 Da. Slightly larger average errors, due in part to weaker signals for some of the product ions, were observed. An average error and standard deviation of 0.0010 ± 0.0009 Da was associated with these mass measurements.

Application of the developed mass spectrometric methods is anticipated during future analyses of aqueous samples or extracts containing mustard hydrolysis products. The mass spectra acquired during LC-ESI-MS/MS exhibited protonated molecular ions and structurally significant product ions that could be used for the identification of these compounds in suspect samples.

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