National Defence Défense nationale

DRES

UNCLASSIFIED

SUFFIELD REPORT

NO. 586

# MASS SPECTROMETRIC CHARACTERIZATION OF SULFUR VESICANT HYDROLYSIS PRODUCTS

by

Paul. A. D'Agostino and Lionel R. Provost

PCN 351 SQ

February 1993

DEFENCE RESEARCH ESTABLISHMENT SUFFIELD : RALSTON : ALBERTA

DEFENSIO PER SCIENTIAM

Canada

WARNING
"The use of this information is permitted subject to recognition of proprietary and patent rights".

Suffield Report 586

# Mass Spectrometric Characterization of Sulfur Vesicant Hydrolysis Products

by

Paul A. D'Agostino and Lionel R. Provost

WARNING
"The use of this information is permitted subject to recognition of proprietary and patent rights".

**SUMMARY**

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, sesquimustard and bis[2-chloroethylthio)ethyl] ether before and after trimethylsilyl derivatization. EI data were generally lacking in significant molecular ion information while data obtained during ammonia CI contained valuable $(M+H)^+$ and/or $(M+NH_4)^+$ molecular ion information.

**RÉSUMÉ**

On a utilisé la CG sur colonne capillaire-SM et la CG-SM/SM, dans des conditions d'ionisation par impact d'électrons (IE) et d'ionisation chimique (IC) dans l'ammoniac, pour détecter et déterminer la nature des produits d'hydrolyse de vésicants soufrés à chaînes longues. L'interprétation des données obtenues par SM a permis de caractériser les produits partiellement et complètement hydrolysés du sulfure de 2-chloroéthyle et de (2-chloroéthox)éthyle, du gaz sesquiypérite et de l'éther bis[(2-chloroéthylthio)éthylique], avant et après formation du dérivé triméthylsilylique. En général, les données obtenues par IE ne renseignaient guère sur les ions moléculaires, tandis que celles obtenues par IC dans l'ammoniac renfermaient des informations importantes sur les ions moléculaires $(M + H)^+$ et/ou $(M + NH_4)^+$.

## 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 emphasizes 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 and will be a critical component of the proposed 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 being other sulfur vesicants (14) which would decompose to other products. The characterization and identification of decomposition products, obtained by hydrolysis of characterized munitions formulations (14), would be valuable during chemical weapons destruction monitoring in support of a Chemical Weapons Convention and for the verification of allegations of use.

Electron impact (EI) ionization has been used to characterize derivatives of mustard including, thiodiglycol and the di-trimethylsilyl derivative of thiodiglycol (13). The mass spectrometric 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 partially 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 mass spectrometry 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 held in 1991 (28,29).

## 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. The acetone and excess water were removed under vacuum leaving a pale yellow oil for each sample. The oils were then distilled in a Kughlrohr oven at 220°C at 0.1 mm. 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 $\mu$L of the hydrolysis products of HT and HQ (1 mg/mL) with 50 $\mu$L pyridine and 50 $\mu$L bis(trimethylsilyl)trifluoroacetamide (BSTFA) (containing 1% trimethylchlorosilane) for 20 min at 60°C (30). Analysis of derivatized samples was performed within 24 hours 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.

### 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 x 0.32 mm ID DB-1701 J&W capillary column (0.25 $\mu$m film thickness) was used for all analyses with the following temperature program: 40°C (2 min) 10°C/min to 280°C (5 min). All GC injections were cool on-column using an injector of our own design (31). The EI operating conditions were as follows: source pressure, 3 x

$10^{-6}$ Torr; source temperature, 200°C; electron energy, 70 eV; and electron emission, 100 $\mu$A. Ammonia (99.99%, Anhydrous grade, Liquid Carbonic) CI operating conditions were as follows: source pressure, 8 x $10^{-5}$ Torr ($NH_3^{+\cdot}$ : $NH_4^+$ approximately 15 : 1); source temperature, 120-130°C, electron energy, 50 eV; and electron emission, 300 $\mu$A. 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 sec/decade.

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). The quadrupole was operated at unit resolution and scanned from 250 to 50 u at 0.5 sec/scan during capillary column GC-MS/MS analysis.

## 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. Figure 1 illustrates the total-ion-current chromatogram for the principal hydrolysis products of mustard and the longer chain sulfur vesicants, 2-chloroethyl (2-chloroethoxy)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 predominant 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 (Figure 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. For this reason, analysis of authentic reference standards (e.g., thiodiglycol) prior to the analysis of unknown samples is recommended to ensure good chromatographic performance.

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 (Figure 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 chain sulfur vesicants generally provide little or no molecular ion information. 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 (Figure 3a), thiodiglycol (Figure 4a) and the di-TMS derivative of thiodiglycol (Figure 4c), included for completeness, were similar to those reported by Wils (13). The EI mass spectrum of the TMS derivative of hemisulfur mustard (Figure 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 (Figure 3b), the TMS derivative of hemisulfur mustard (Figure 3d), thiodiglycol (Figure 4b) and the di-TMS derivative of thiodiglycol (Figure 4d) during ammonia CI analysis. 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 $(C_2H_4\text{-}S\text{-}C_2H_4Cl)^+$. 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 only TMS derivatization at m/z 73, $(CH_3)_3Si^+$, and m/z 90, $(CH_3)_3Si(OH)^{+\cdot}$ were frequently observed for the TMS derivatives of hemisulfur mustard, thiodiglycol and the other longer chain sulfur vesicant hydrolysis products.

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 (Figure 5a) and the TMS derivative of this hydrolysis product contained a weak ion at m/z 241 due to $(M\text{-}CH_3)^+$ (Figure 5c). Under ammonia CI conditions molecular ion information was obtained for both 2-chloroethyl (2-hydroxyethylthio)ethyl ether (Figure 5b) and its TMS derivative (Figure 5d). An ion at m/z 167 due to $(C_2H_4\text{-}S\text{-}C_2H_4\text{-}O\text{-}C_2H_4\text{-}Cl)^+$ was observed during both ammonia CI analyses.

It was not obvious after interpretation of the EI and CI whether the hydroxyl substituent was nearer the sulfur or oxygen position and only the following general structure was initially assumed.

$$ClC_2H_4\text{-}X\text{-}C_2H_4\text{-}X\text{-}C_2H_4OH$$

(where one X was an oxygen and the second X was a sulfur)

Under ammonia CI the TMS derivative of this compound exhibits an intense m/z 167 ion. GC-MS/MS analysis of this ion was performed as the daughters might provide structural data required for the identification of this compound. The daughters of m/z 167 (Figure 6) for this compound at m/z 63, m/z 87 and m/z 107 were due to $(ClC_2H_4)^+$, $(C_2H_3\text{-}S\text{-}C_2H_4)^+$ and $(ClC_2H_4\text{-}O\text{-}C_2H_4)^+$, respectively, which strongly suggested the presence of the partial hydrolysis product, 2-chloroethyl (2-hydroxyethylthio)ethyl ether or $ClC_2H_4\text{-}O\text{-}C_2H_4\text{-}S\text{-}C_2H_4OH$.

Sesquimustard Hydrolysis

Both the partial hydrolysis product, 2-chloroethyl (2-hydroxyethylthio)ethyl sulfide, and the full hydrolysis product, bis(2-hydroxyethylthio) 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 $(M\text{-}H_2O)^{+\cdot}$ and $(M\text{-}HCl)^+$ at m/z 182 and m/z 164 under EI conditions (Figure 7a). 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 (Figure 7c). However, under ammonia CI conditions 2-chloroethyl (2-hydroxyethylthio)ethyl sulfide provided both $(M+H)^+$ and $(M+NH_4)^+$ pseudo-molecular ions (Figure 7b). Following TMS derivatization of 2-chloroethyl (2-hydroxyethylthio)ethyl sulfide the ammonia CI mass spectrum exhibited a reasonable $(M+NH_4)^+$ pseudo-molecular ion and ions due to $[M+H - (CH_3)_3Si(OH)]^+$ and $(CH_3)_3Si(OH)^{+\cdot}$ at m/z 183 and m/z 90 respectively (Figure 7d).

Bis(2-hydroxyethylthio) ethane was characterized by a weak EI molecular ion and ions at m/z 164 and m/z 138, due to $(M\text{-}H_2O)^{+\cdot}$ and $(M\text{-}OC_2H_4)^{+\cdot}$ respectively (Figure 8a). The EI mass spectrum of the TMS derivative (Figure 8c) 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 (Figure 8b) and after TMS derivatization (Figure 8d). 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 (Figures 9a and 10a) and after trimethylsilylation (Figures 9c and 10c) were void of molecular ion information and were characterized by higher mass ions due to $(M-H_2O)^+$ or $(M-HCl)^+$. Ammonia CI was used to obtain molecular ion information for both hydrolysis products. Prior to derivatization both (2-chloroethylthio)ethyl (2-hydroxyethylthio)ethyl ether (Figure 9b) and bis[(2-hydroxyethylthio)ethyl] ether (Figure 10b) 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 $(CH_3)_3Si(OH)^{+\cdot}$ at m/z 334, m/z 227 and 90 (Figure 9d) and, m/z 388, m/z 281 and m/z 90 (Figure 10d) were detected for the partial and full hydrolysis products of bis[(2-chloroethylthio)ethyl] ether respectively.

## 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 partially and fully hydrolysed products of 2-chloroethyl (2-chloroethoxy)ethyl sulfide, sesquimustard and bis[(2-chloroethylthio)ethyl] ether before and after TMS derivatization. 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 the MS data 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.

**REFERENCES**

1. G. Andersson, NBC Defence and Technology International p. 62 April 1986.

2. United Nations Report S/20060, "Report of the Mission Dispatched by the Secretary-General to Investigate Allegations of the Use of Chemical Weapons in the Conflict Between the Islamic Republic of Iran and Iraq", 20 July 1988.

3. E. R. G. Wils, A. G. Hulst, A. L. de Jong, A. Verweij and H. L. Boter, J. Anal. Toxicol. 9, 254 (1985).

4. W. Vycudilik, Forensic Science International 35, 67 (1987).

5. E. R. J. Wils, A. G. Hulst and J. van Laar, J. Anal Toxicol. 12, 15 (1988).

6. R. M. Black and R. W. Read, J. Chromatogr. 449, 261 (1988).

7. E. M. Jakubowski, C. L. Woodard, M. M. Mershon and T. W. Dolzine, J. Chromatogr. 528, 184 (1990).

8. P. A. D'Agostino and L. R. Provost, J. Chromatogr. 436, 399 (1988).

9. Z. Witkiewicz, M. Mazurek and J. Szulc, J. Chromatogr. 503, 293 (1990).

10. Systematic Identification of Chemical Warfare Agents B.3. Identification of Non-Phosphorus Warfare Agents, The Ministry of Foreign Affairs of Finland, Helsinki, 1982.

11. E. Ali-Mattila, K. Siivinen, H. Kenttamaa and P. Savolahti, Int. J. Mass Spectrom. Ion Phys. 47, 371 (1983).

12. D. N. Tripathi, A. Bhattacharya and R. Vaidyanathaswamy, Can. Soc. Forens. Sci. J. 17, 55 (1984).

13. E. R. J. Wils and A. G. Hulst, Fresenius Z. Anal. Chem. 321, 471 (1985).

14. P. A. D'Agostino and L. R. Provost, Biomed. Environ. Mass Spectrom. 15, 553 (1988).

15. P. A. D'Agostino and L. R. Provost, Biomed. Environ. Mass Spectrom. 18, 484 (1989).

16. E. R. J. Wils, Fresenius J. Anal. Chem. 338, 22 (1990).

17. P. A. D'Agostino and L. R. Provost, J. Chromatogr. 589, 287 (1992).

18. W. H. Stein, S. Moore and M. Bergmann, J. Org. Chem. XI, 664 (1946).

19. R. Trapp, "The Detoxification and Natural Degradation of Chemical Warfare Agents", Stockholm International Peace Research Institute, Taylor and Francis, London and Philadelphia, 1985.

20. L. Field and C. H. Foster, J. Org. Chem. 35, 749 (1970).

21. J. B. Westmore and M. M. Alauddin, Mass Spectrom. Rev. 5, 381 (1986).

22. P. A. D'Agostino, A. S. Hansen, P. A. Lockwood and L. R. Provost, J.Chromatogr. 347, 257 (1985).

23. P. A. D'Agostino and L. R. Provost, Biomed. Environ. Mass Spectrom. 13, 231 (1986).

24. A. Hesso and R. Kostiainen, Proc. 2nd. Int. Symp. Protection Against Chemical Warfare, Stockholm, Sweden, 15-19 June 1986, pp. 257-260.

25. P. A. D'Agostino, L. R. Provost and J. Visentini, J. Chromatogr. 402, 221 (1987).

26. P. A. D'Agostino, L. R. Provost and K. M. Looye, J. Chromatogr. 465, 271 (1989).

27. P. A. D'Agostino and L. R. Provost, J. Chromatogr. 600, 267 (1992).

28. International Interlaboratory Comparison (Round Robin) Test for the Verification of Chemical Disarmament, F.3. Testing of Procedures on Simulated Military Facility Samples, Ministry of Foreign Affairs of Finland, Helsinki, 1992.

29. P. A. D'Agostino and L. R. Provost, Verification of Chemical Warfare Agents in Contaminated Concrete, Rubber and Paint Samples, Suffield Report No. 571, July 1992, UNCLASSIFIED.

30. W. C. Butts, Anal. Biochem. 46, 187 (1972).

31. P. A. D'Agostino and L. R. Provost, J. Chromatogr. 331, 47 (1985).

Table I: Compounds Identified after GC-MS and GC-MS/MS Analysis of Samples

| Peak No.[1] | Mol. Wt. | 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 |

[1]Refer to Figures 1 and 2.

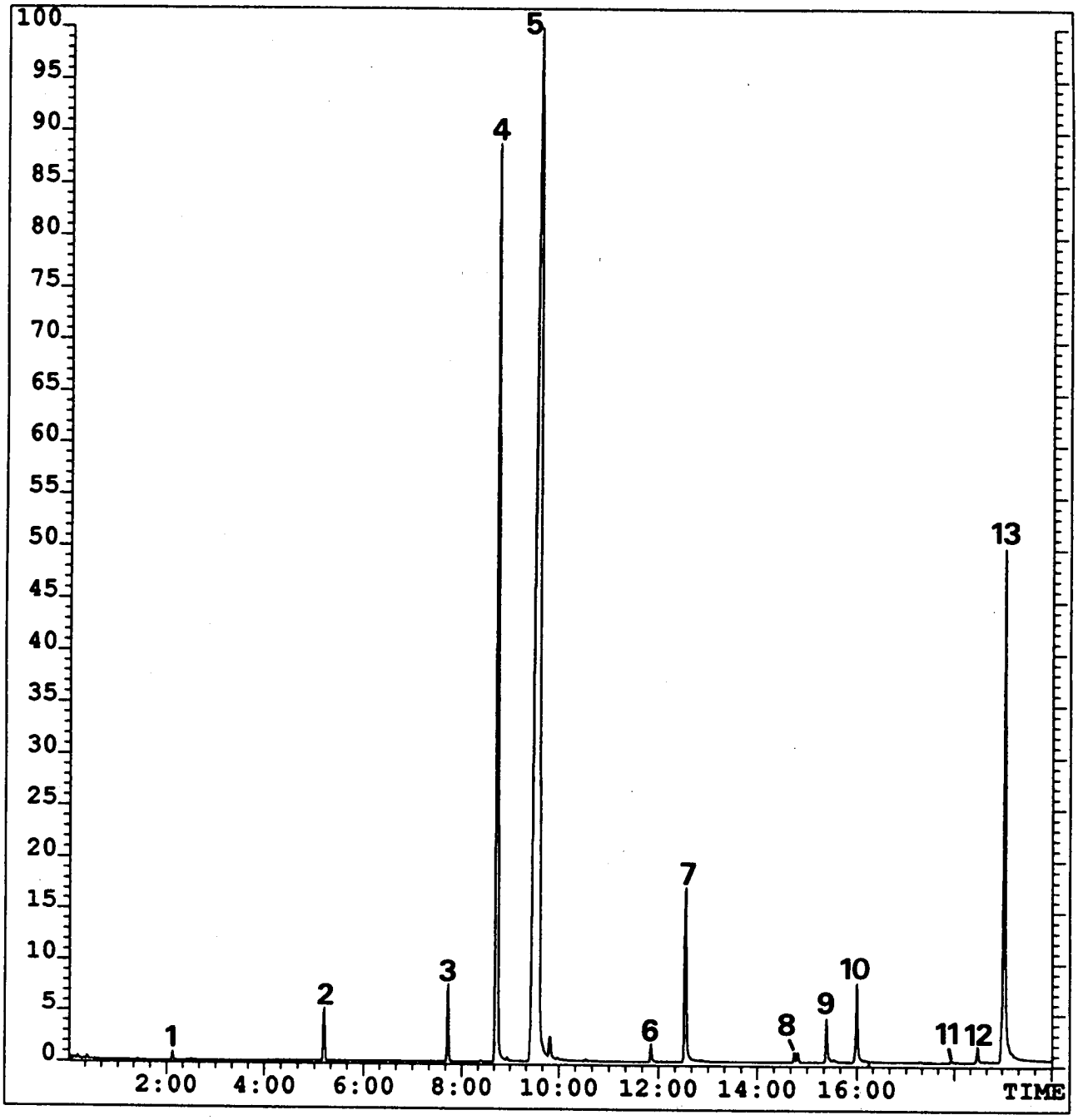


Figure 1: Capillary column GC-MS(EI) total-ion-current (400 to 40 u) chromatogram of the hydrolysis products of approximately 300 ng of HT and HQ. Compounds are identified in Table I.

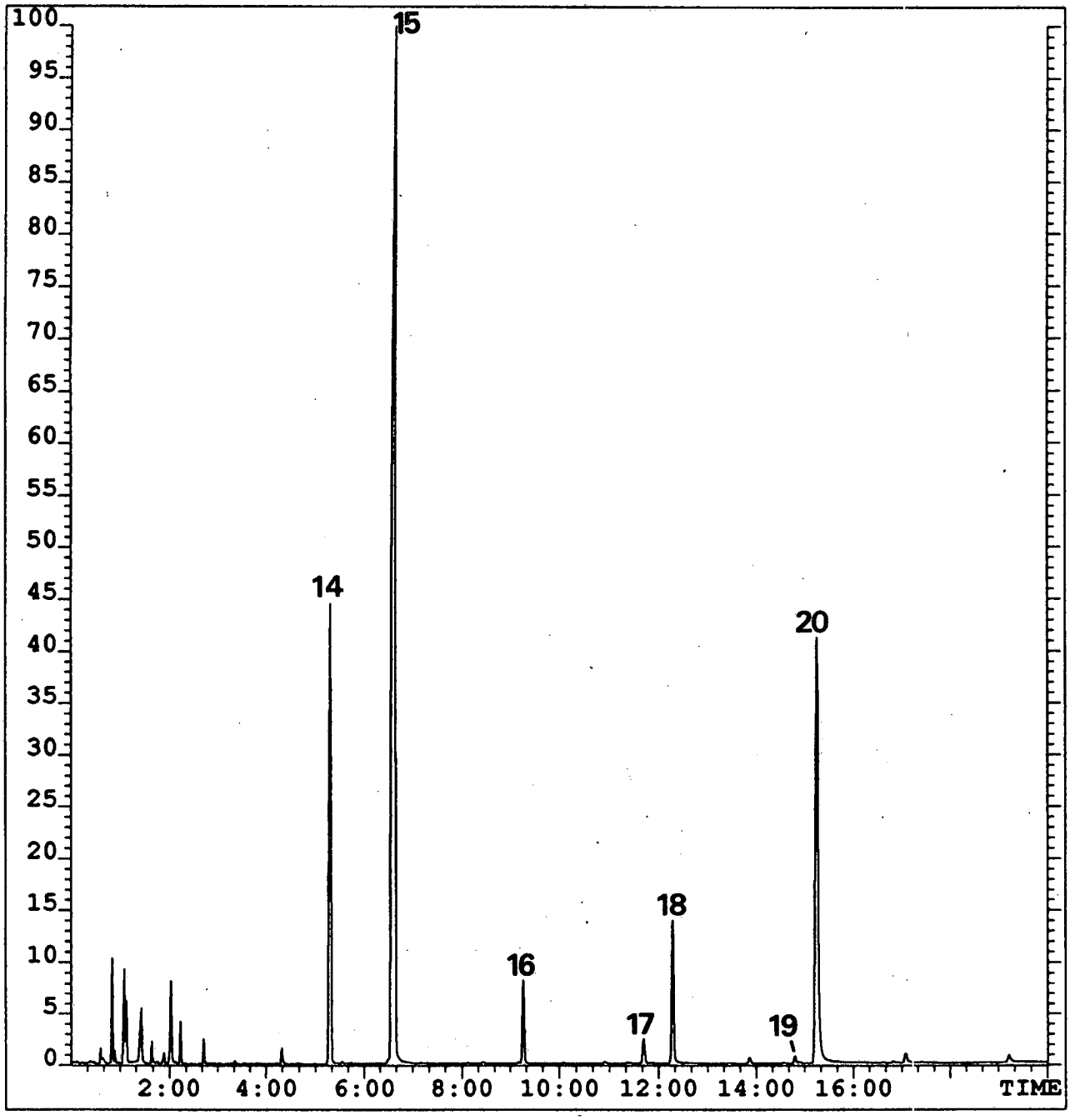


Figure 2: Capillary column GC-MS(EI) total-ion-current (400 to 40 u) chromatogram of the hydrolysis products of approximately 300 ng of HT and HQ after trimethylsilylation. Compounds are identified in Table I.

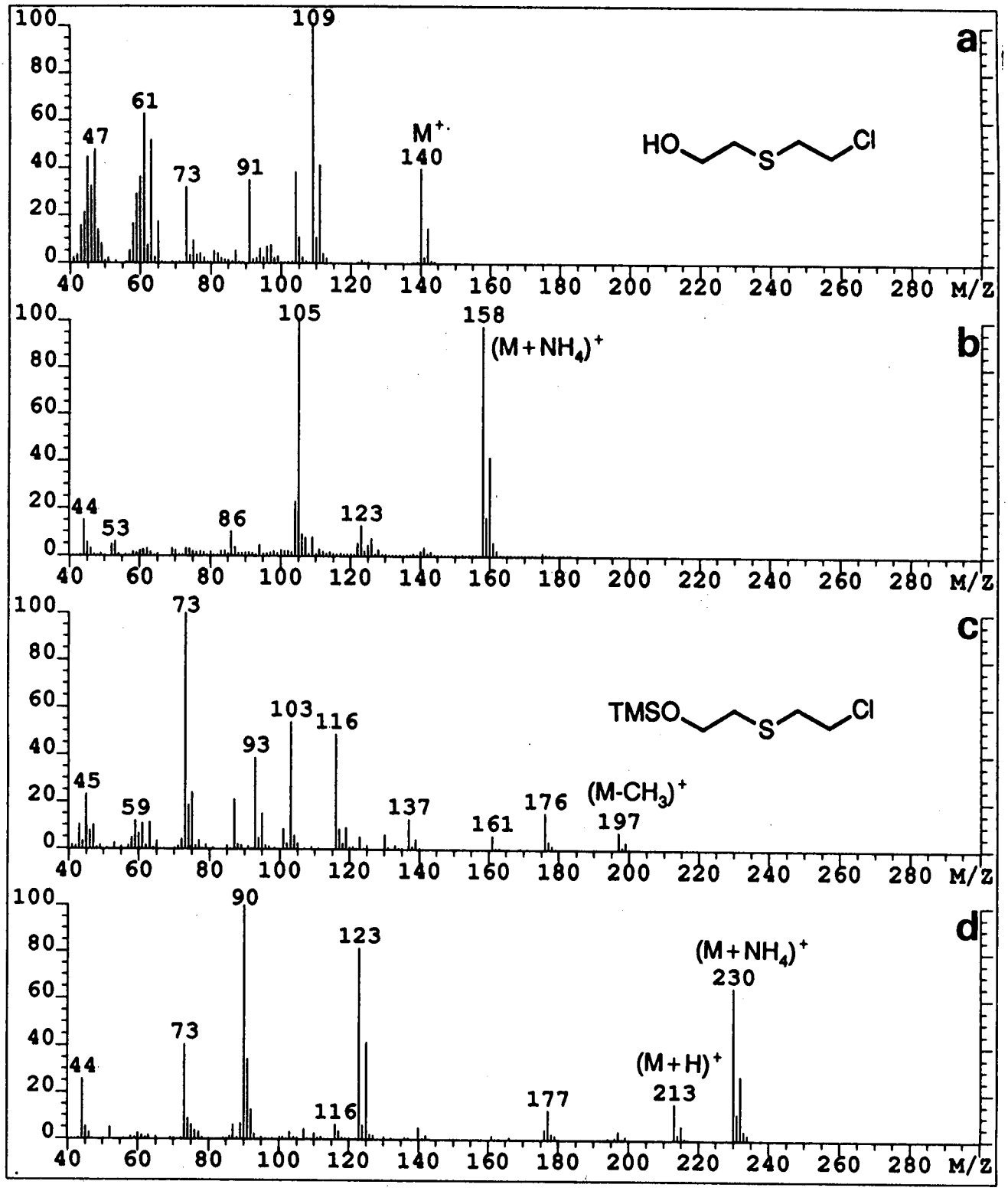


Figure 3: a) EI and b) ammonia CI mass spectra of hemisulfur mustard and c) EI and d) ammonia CI mass spectra of TMS derivative of hemisulfur mustard.

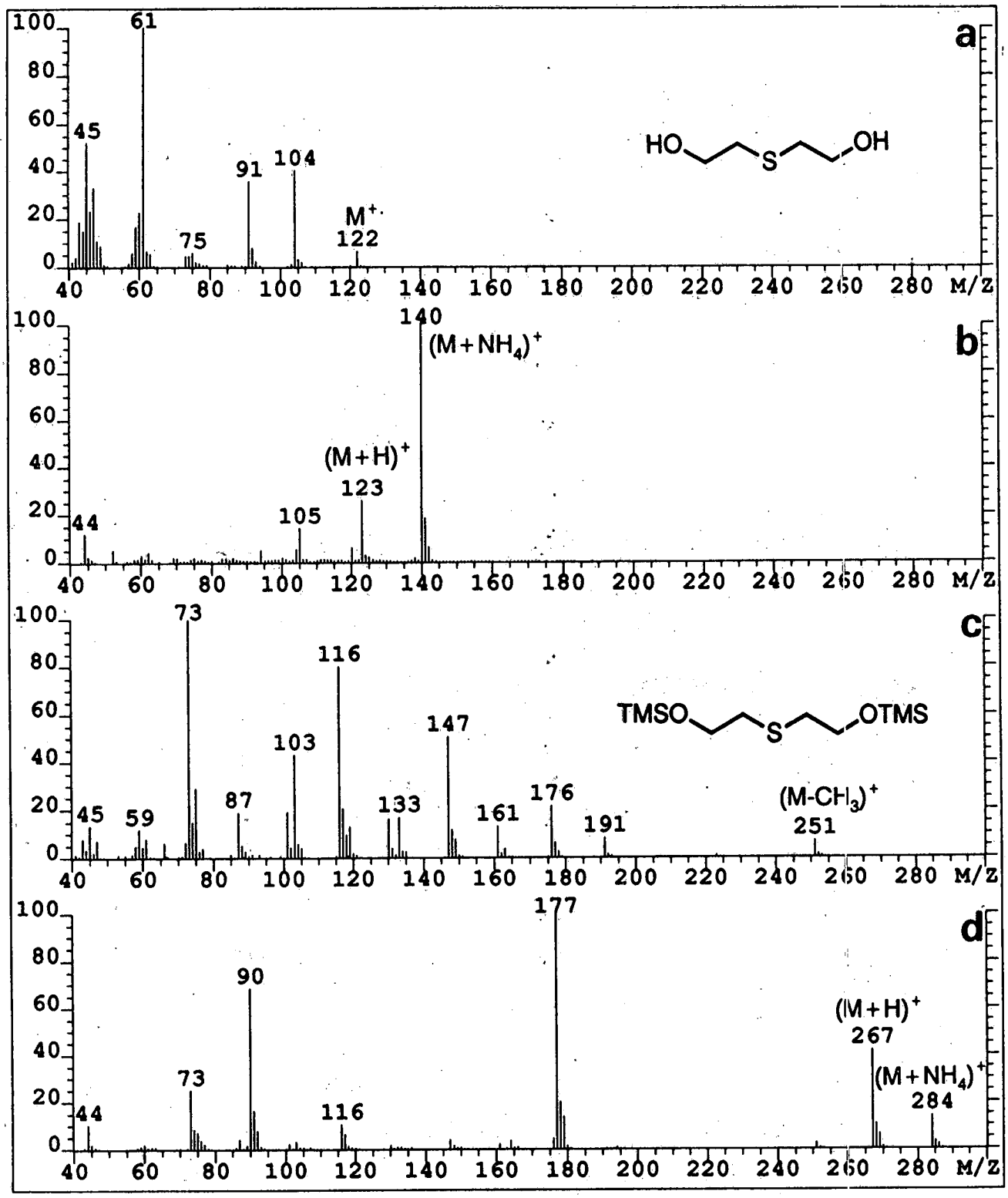


Figure 4: a) EI and b) ammonia CI mass spectra of thiodiglycol and c) EI and d) ammonia CI mass spectra of the di-TMS derivative of thiodiglycol.

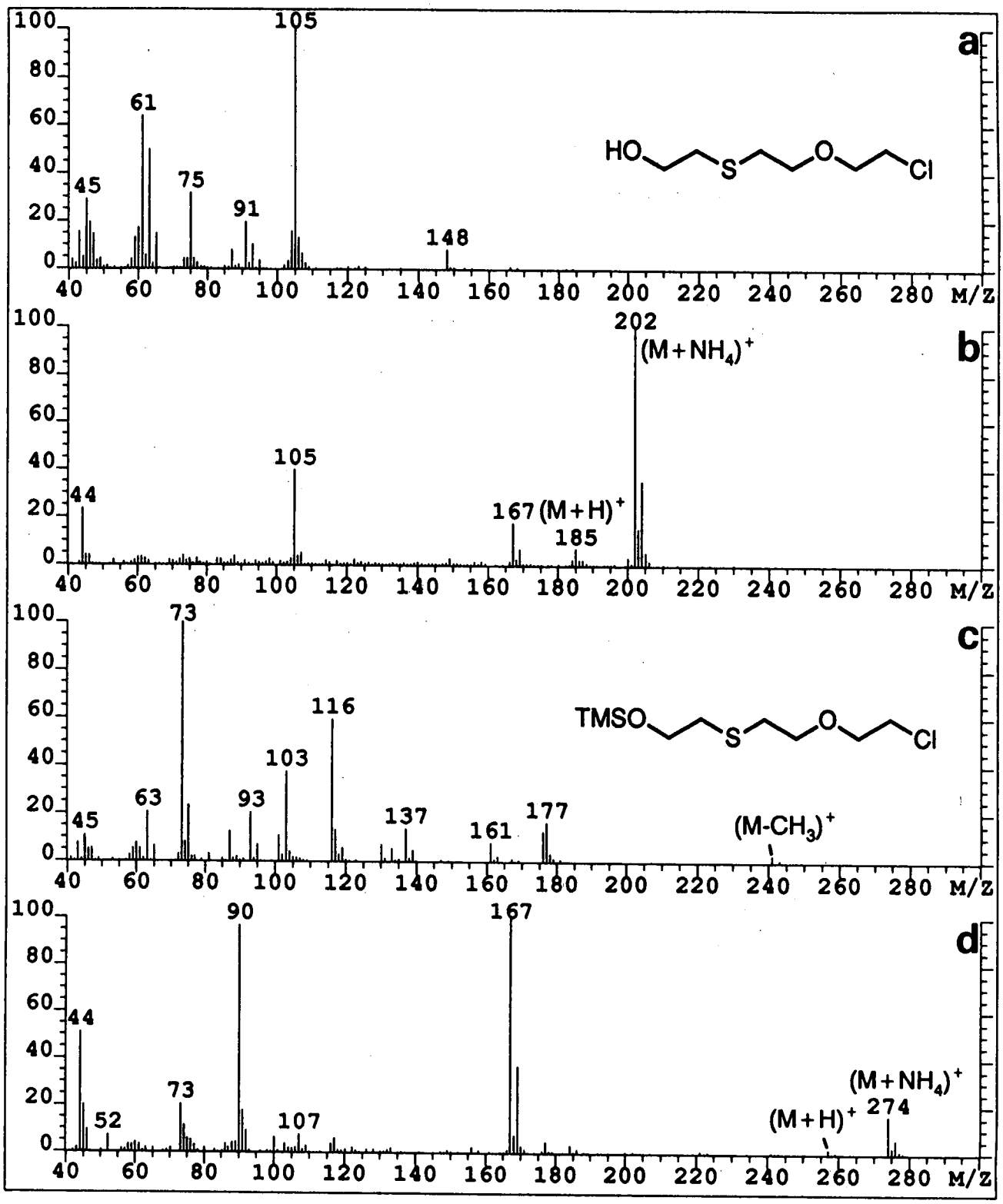


Figure 5: a) EI and b) ammonia CI mass spectra of 2-chloroethyl (2-hydroxyethylthio)ethyl ether and c) EI and d) ammonia CI mass spectra of TMS derivative of 2-chloroethyl (2-hydroxyethylthio)ethyl ether.

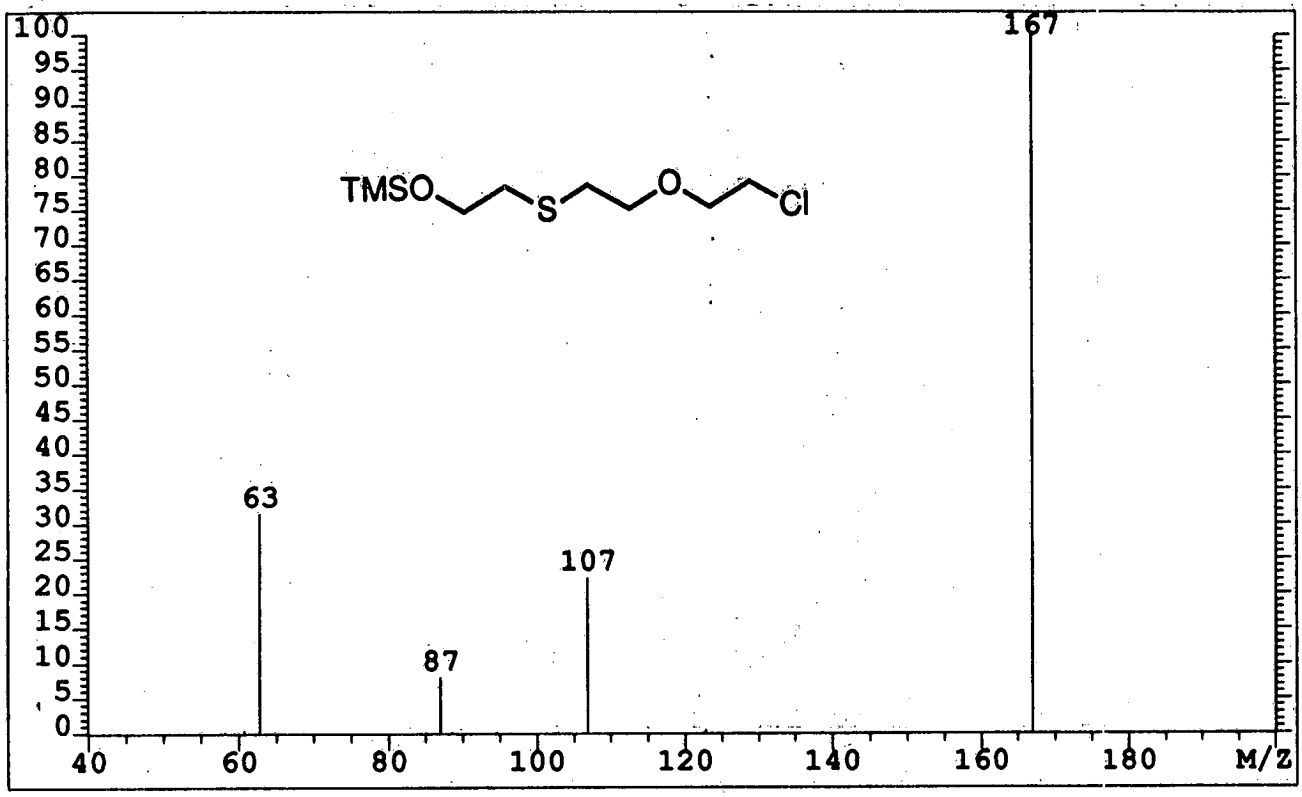


Figure 6: Daughter spectrum (m/z 167) for TMS derivative of 2-chloroethyl (2-hydroxyethylthio)ethyl ether acquired during ammonia CI.

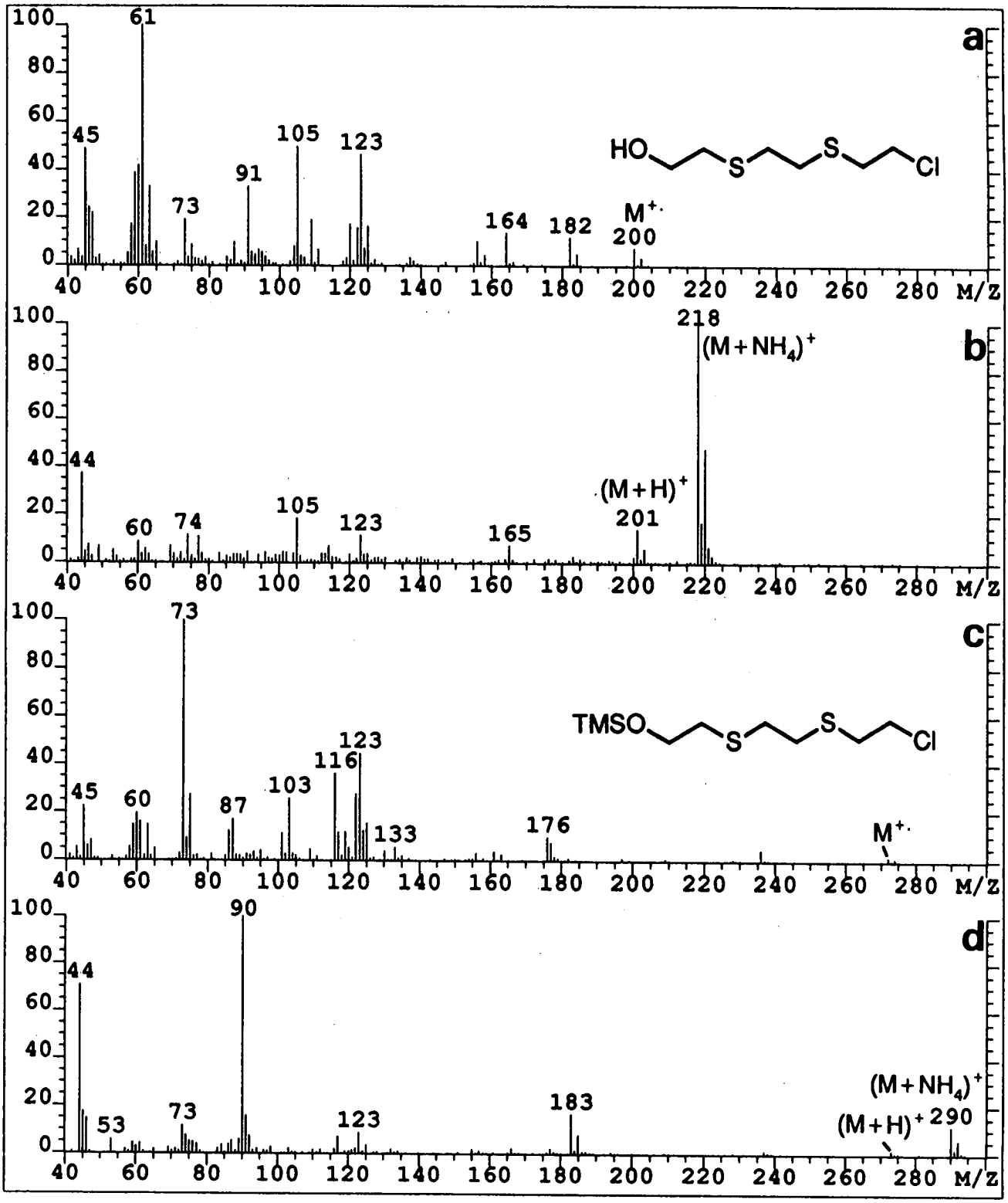


Figure 7: a) EI and b) ammonia CI mass spectra of 2-chloroethyl (2-hydroxyethylthio)ethyl sulfide and c) EI and d) ammonia CI mass spectra of TMS derivative of 2-chloroethyl (2-hydroxyethylthio)ethyl sulfide.

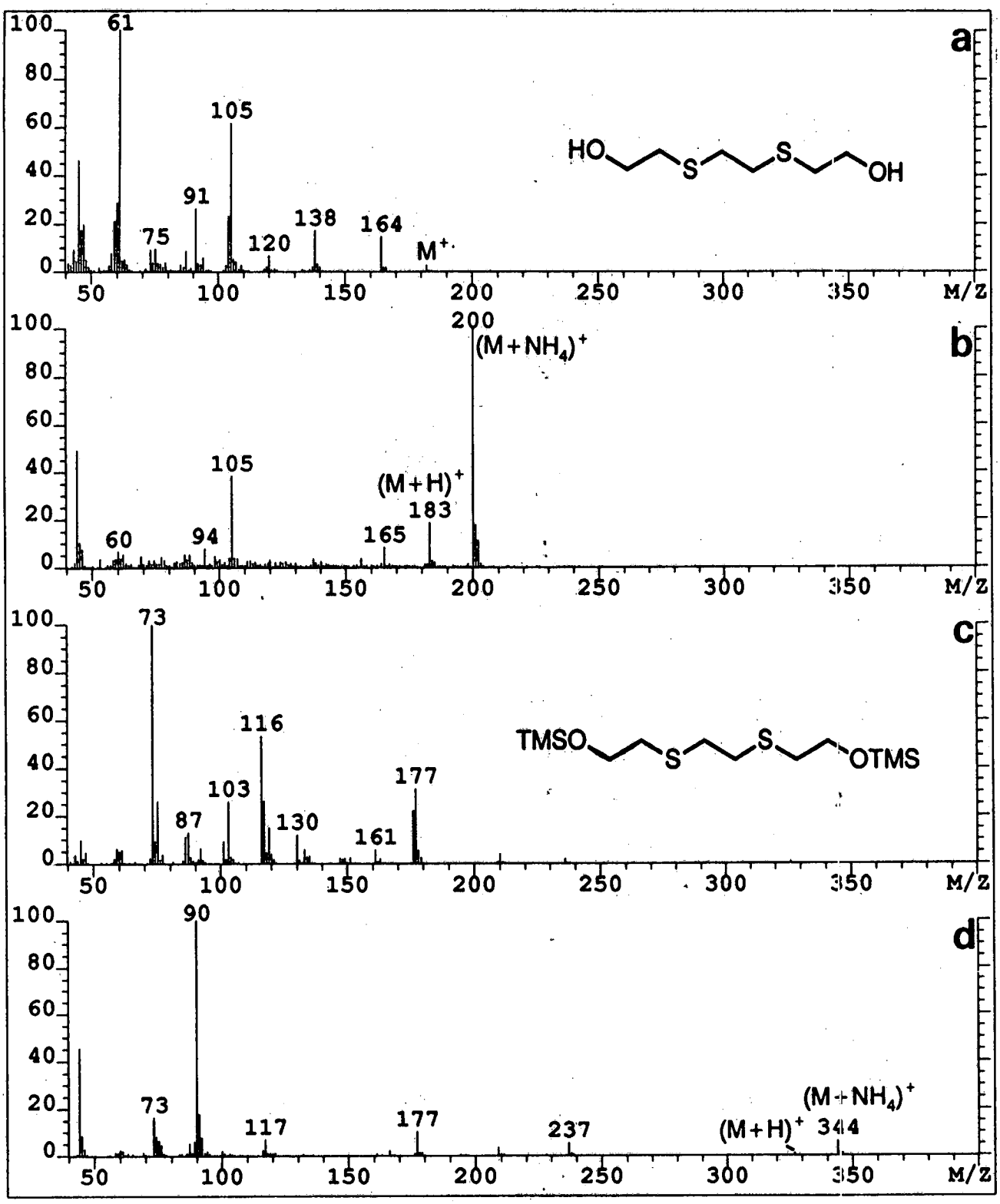


Figure 8: a) EI and b) ammonia CI mass spectra of bis(2-hydroxyethylthio) ethane and c) EI and d) ammonia CI mass spectra of the di-TMS derivative of bis(2-hydroxyethylthio) ethane.

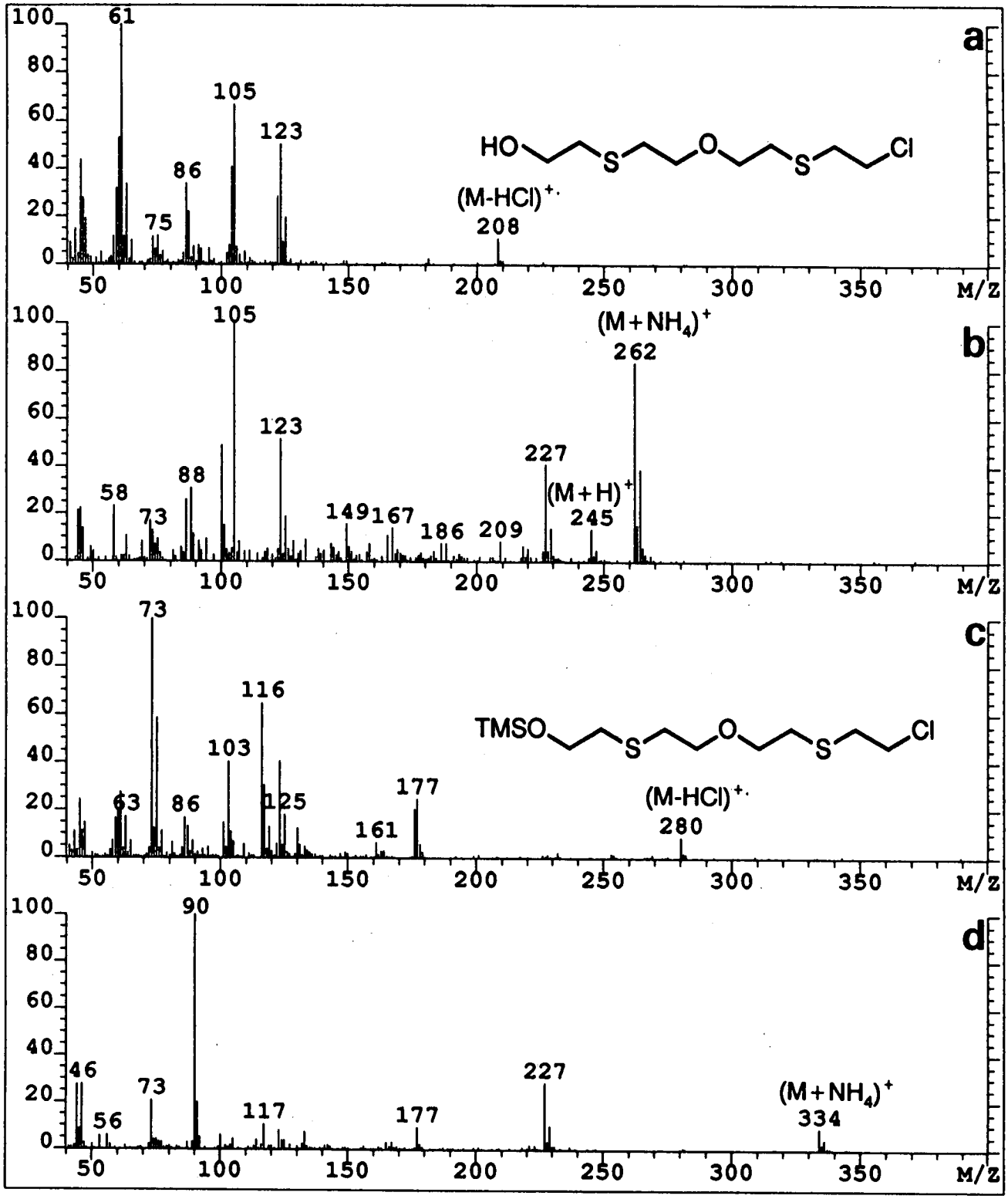


Figure 9: a) EI and b) ammonia CI mass spectra of (2-chloroethylthio)ethyl (2-hydroxyethylthio)ethyl ether and c) EI and d) ammonia CI mass spectra of TMS derivative of (2-chloroethylthio)ethyl (2-hydroxyethylthio)ethyl ether.

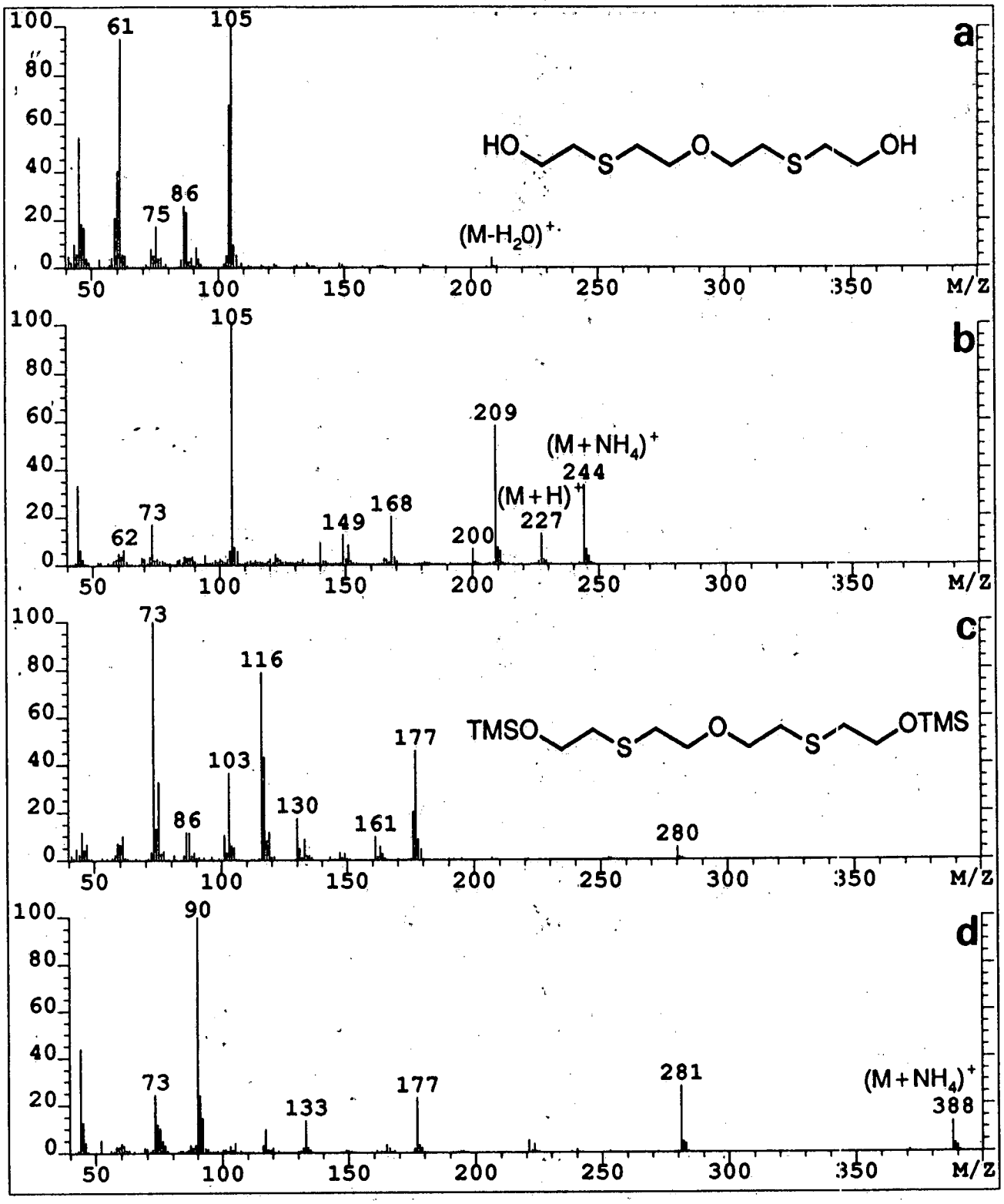


Figure 10: a) EI and b) ammonia CI mass spectra of bis[(2-hydroxyethylthio)ethyl] ether and c) EI and d) ammonia CI mass spectra of the di-TMS derivative of bis[(2-hydroxyethylthio)ethyl] ether.

**********

5

Accessn #: 93-01493
Security: UNCLASSIFIED
Sensitivity: UNLIMITED
Title: MASS SPECTROMETRIC CHARACTERIZATION OF SULFUR VESICANT HYDROLYSIS PRODUCTS
Report Date: 01 Feb 93
CA Name: Defence Research Establishment Suffield, Ralston ALTA (CAN)
Report Num: DRES-586
Author: D'Agostino, P.A.
Provost, L.R.
Num Pages: 30
Num Refs: 31
Country: CAN

# DOCUMENT CONTROL DATA

(Security classification of title, body of abstract and indexing annotation must be entered when the overall document is classified)

1. ORIGINATOR (the name and address of the organization preparing the document. Organizations for whom the document was prepared, e.g. Establishment sponsoring a contractor's report, or tasking agency, are entered in section 8.)

Defence Research Establishment Suffield
Box 4000
Medicine Hat, AB T1A 8K6

2. SECURITY CLASSIFICATION (overall security classification of the document. including special warning terms if applicable)

Unclassified

3. TITLE (the complete document title as indicated on the title page. Its classification should be indicated by the appropriate abbreviation (S,C,R or U) in parentheses after the title.)

Mass Spectrometric Characterization of Sulfur Vesicant Hydrolysis Products

4. AUTHORS (Last name, first name, middle initial. If military, show rank, e.g. Doe, Maj. John E.)

D'Agostino, P.A.; Provost, L.R.

5. DATE OF PUBLICATION (month and year of publication of document)

January 1993

6a. NO. OF PAGES (total containing information. Include Annexes, Appendices, etc.)

27

6b. NO. OF REFS (total cited in document)

31

6. DESCRIPTIVE NOTES (the category of the document, e.g. technical report, technical note or memorandum. If appropriate, enter the type of report, e.g. interim, progress, summary, annual or final. Give the inclusive dates when a specific reporting period is covered.)

Suffield Report #586

8. SPONSORING ACTIVITY (the name of the department project office or laboratory sponsoring the research and development. Include the address.) Defence Research Establishment Suffield
Box 4000
Medicine Hat, AB
T1A 8K6

9a. PROJECT OR GRANT NO. (if appropriate, the applicable research and development project or grant number under which the document was written. Please specify whether project or grant)

9b. CONTRACT NO. (if appropriate, the applicable number under which the document was written)

351SQ

10a. ORIGINATOR'S DOCUMENT NUMBER (the official document number by which the document is identified by the originating activity. This number must be unique to this document.)

Suffield Report #586

10b. OTHER DOCUMENT NOS. (Any other numbers which may be assigned this document either by the originator or by the sponsor)

11. DOCUMENT AVAILABILITY (any limitations on further dissemination of the document, other than those imposed by security classification)

(X) Unlimited distribution
( ) Distribution limited to defence departments and defence contractors; further distribution only as approved
( ) Distribution limited to defence departments and Canadian defence contractors; further distribution only as approved
( ) Distribution limited to government departments and agencies; further distribution only as approved
( ) Distribution limited to defence departments; further distribution only as approved
( ) Other (please specify):

12. DOCUMENT ANNOUNCEMENT (any limitation to the bibliographic announcement of this document. This will normally correspond to the Document Availabilty (11). However, where further distribution (beyond the audience specified in 11) is possible, a wider announcement audience may be selected.)

13. ABSTRACT ( a brief and factual summary of the document. It may also appear elsewhere in the body of the document itself. It is highly desirable that the abstract of classified documents be unclassified. Each paragraph of the abstract shall begin with an indication of the security classification of the information in the paragraph (unless the document itself is unclassified) represented as (S), (C), (R), or (U). It is not necessary to include here abstracts in both offical languages unless the text is bilingual).

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, sesquimustard and bis[(2-chloroethylthio)ethyl] ether before and after trimethylsilyl derivatization. EI data was generally lacking in significant molecular ion information while that obtained during ammonia CI contained valuable $(M+H)^+$ and/or $(M+NH_4)^+$ molecular ion information.

14. KEYWORDS, DESCRIPTORS or IDENTIFIERS (technically meaningful terms or short phrases that characterize a document and could be helpful in cataloguing the document. They should be selected so that no security classification is required. Identifiers, such as equipment model designation, trade name, military project code name, geographic location may also be included. If possible keywords should be selected from a published thesaurus. e.g. Thesaurus of Engineering and Scientific Terms (TEST) and that thesaurus-identified. If it is not possible to select indexing terms which are Unclassified, the classification of each should be indicated as with the title.)

Military Chemical Agents
Chemical Agent Detection
Mustard
Gas Chromatography
Mass Spectrometry
Tandem Mass Spectrometry