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ABSTRACT

Sample handling and analysis procedures have been developed for the verification of soman, sarin, triethyl phosphate and mustard in contaminated paint, concrete and rubber. Triethyl phosphate and mustard were generally recovered from the sample media with efficiencies greater than 65%. Soman was usually recovered with slightly less efficiency (20% to 60%) and sarin was recovered in the lowest yield (5% to 40%). Each extra was quantitatively analysed by capillary column GC-FID and confirmation of all spiked chemical agents was performed by capillary column GC-MS. The developed methods were successfully applied during the 1991 round robin analytical exercise organized by the United Nation Conference on Disarmament Technical Group on Instrumentation. Defence Research Establishment Suffield, the only participating Canadian laboratory, positively confirmed all the spiked mustard related compounds in the samples provided for round robin analysis and did not detect any artifacts or false positives in the samples.

RÉSUMÉ

On a mis au point des méthodes de manutention et d'analyse des échantillons pour vérifier la présence de soman, de sarin, de phosphate de tri-éthyle et de gaz moutarde dans de la peinture, du béton et du caoutchouc contaminés. Le phosphate de tri-éthyle et le gaz moutarde ont généralement été récupérés du milieu échantillon avec un rendement supérieur à 65%. Le soman était habituellement récupéré avec un rendement légèrement plus faible (20% à 60%) et le sarin, avec le rendement le plus faible (5% à 40%). Chaque extrait a été analysé quantitativement par CG-DIF sur colonne capillaire et la présence de tous les agents chimiques utilisés pour le dopage a été confirmée par CG-SM sur colonne capillaire. Les méthodes mises au point ont été appliquées avec succès en 1991, au cours de l'exercice comparatif inter-laboratoires organisé par le groupe technique sur l'appareillage de la Conférence des Nations Unies sur le désarmement. Le Centre de recherche pour la défense à Suffield, le seul laboratoire canadien participant, a décelé tous les composés apparentés au gaz moutarde présents dans les échantillons dopés soumis dans le cadre des tests inter-laboratoires et n'a décelé aucun artéfact ni de faux-positifs parmi les échantillons.

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INTRODUCTION

Chemical weapons use, although prohibited by the 1925 Geneva Protocol, has been reported in several armed conflicts including the Iran/Iraq War (1-4). The use of these weapons during this conflict and the concern over possible use of chemical weapons during the Persian Gulf War has heightened international awareness and prompted many nations to pursue with increased vigour the signature of a new Chemical Weapons Convention. The rolling text of the most recent draft of the Chemical Weapons Convention contains a number of provisions aimed at developing a treaty that will enable nations to ensure compliance by all signatory nations. It follows from this draft treaty that compliance monitoring, with a high level of analytical support, will be required under the following scenarios to ensure the establishment of an enforceable treaty:

a) Chemical weapons storage declaration.
b) Chemical weapons movement to a destruction facility.
c) Destruction of chemical weapons.
d) Closure of a chemical weapons facility.
e) Elimination of chemical weapons production facilities.
f) Monitoring of permitted production of scheduled chemicals.
g) Monitoring of permitted production of precursors.
h) Monitoring of industrial production of chemical warfare agents.
i) Monitoring of other permitted production of toxic chemicals.
j) Verification of allegations of use of chemical weapons.

The United Nations Conference on Disarmament, through the Technical Group on Instrumentation, has placed an emphasis on the development and evaluation of analytical techniques for the determination of chemical warfare (CW) agents, their degradation products and other scheduled compounds under scenarios that might be encountered to ensure treaty compliance. Two prior international round robin analytical exercises in 1989 and 1990 focused on the application of appropriate methods for the determination of these compounds in an allegation of use scenario (5,6) and during inspection of an industrial plant suspected to be producing chemical warfare agents (7,8). In 1991 concrete, rubber and painted panel samples contaminated with scheduled (controlled) compounds were distributed in a round robin manner to simulate samples that may be encountered during inspection of a military facility. As in the previous international exercises the emphasis was on the unequivocal identification and confirmation of scheduled compounds in these samples.

Capillary column gas chromatography with flame ionization (FID) or flame photometric detection may be used for the routine screening of sample extracts for the presence of chemical warfare agents. However, it is generally agreed by the Technical Group on Instrumentation that confirmation of the chemical warfare agents and their decomposition products involve identification by capillary column gas chromatography-mass spectrometry (GC-MS). Electron impact (EI), the traditional MS method of ionization, has gained wide acceptance for the verification of chemical warfare agents, as the EI mass spectra of numerous chemical warfare agents, their decomposition products and related compounds have been published. Comparison of acquired mass spectra with published data, along with supporting chromatographic and/or other spectroscopic data meets suggested confirmation criteria (9).

Both the NATO defence sciences community, through NATO AC/225(Panel VII/SICA), and the Finnish Research Project for Chemical Warfare Verification have published numerous methods for the detection of chemical warfare agents, their degradation products and related compounds in environmental matrices typical of those expected during an allegations of use scenario. However, the development and application of analytical methods for samples such as concrete, rubber and painted surfaces by these groups appears to be quite limited. The U.K. through NATO AC/225(Panel VII/SICA) reported the successful extraction of mustard from mustard contaminated concrete samples with chlorinated solvents (10). Norway, in a paper highlighting the applicability of C_{18} sorbent cartridges (11), demonstrated the detection of sarin and soman in aqueous extracts of contaminated butyl rubber. Aqueous extracts of the rubber were passed through the C_{18} sorbent cartridge and the chemical warfare agents were eluted from the sorbent with chloroform. This approach, while useful for organophosphorus chemical warfare agents, was not particularly successful for the sulfur vesicant, mustard. No method was found in these sources for the extraction and analysis of chemical warfare agents from painted panels. An analytical study was initiated for these reasons and the perceived Chemical Weapons Convention requirement for the clean-up and analysis of chemical warfare agents, their decomposition products and other scheduled compounds in concrete, rubber and paint. This study focused on the development and validation of sample handling procedures that would allow capillary column GC-MS and GC-MS/MS verification of several representative compounds, sarin, soman, triethyl phosphate and mustard in contaminated concrete, rubber and painted panel samples.

Concrete, rubber and painted panels were spiked at the 50 $\mu g/g$ and 5 $\mu g/g$ level with three chemical warfare agents, sarin, soman and mustard, as well as the soman simulant, triethyl phosphate, and extracted with a number of candidate solvents in a manner similar to that employed for the concentration of chemical warfare agents from soils (12-13). Ultrasonic extraction with hexane of contaminated paint panels was the most promising approach for the concentration of these compounds from alkyd paint, while ultrasonic extraction with acetonitrile was effective for the concentration of sarin, soman, triethyl phosphate and mustard from concrete and rubber. In all cases, extract sample components were quantitated by capillary column GC-FID and confirmed by one or more capillary column GC-MS technique.

The methods developed were successfully utilized during the 3rd round robin verification exercise (1991) involving the analysis of contaminated samples from a military facility. All the spiked compounds including mustard, other scheduled sulfur vesicants and related degradation products were confirmed in the round robin samples by Defence Research Establishment Suffield, the participating Canadian laboratory, using GC-MS and GC-MS/MS under both electron impact and ammonia chemical ionization.

EXPERIMENTAL

a) Spiking Studies

Sarin, soman, mustard and triethyl phosphate used in the spiking studies were provided by the DRES Organic Chemistry Laboratory. Distilled in glass solvents were purchased from BDH Chemicals Ltd. (Edmonton, Alberta).

Concrete samples were obtained from a damaged precast parking barrier and the painted metal panels were finished with NATO alkyd paint. The following rubber samples were used in this study:

i) Bromobutyl rubber from a Canadian C4 mask
ii) Weathered rubber from a vehicle tire tread
iii) Nitrile rubber from an O-ring
iv) Viton rubber from a gasket

One gram samples of concrete, painted panel and rubber were spiked with either 50 μL of a 1 mg/mL (spike level: 50 μg/g) or 50 μL of a 0.1 mg/mL (spike level: 5 μg/g) standard containing sarin, soman, triethyl phosphate and mustard in dichloromethane. Spiked samples and blanks were placed in PTFE-lined screw-capped 16 x 125 mm glass culture tubes and allowed to stand at 4°C for 60 minutes prior to extraction.

Two extraction methods were investigated for the extraction of sarin, soman, mustard and triethyl phosphate from concrete. In the first method spiked concrete samples and blanks were extracted with 2 x 2 mL of hexane by ultrasonic vibration (10 min) and then centrifuged (10 min at 700 g). The concrete was re-extracted with the above procedure using dichloromethane. Each of the extracts was then concentrated to 1 mL by nitrogen blowdown prior to chromatographic analysis. In the second method spiked concrete samples and blanks were extracted with 2 x 2 mL of acetonitrile by ultrasonic vibration (10 min) and then centrifuged (10 min at 700 g). Acetonitrile extracts were then concentrated by nitrogen blowdown to 0.1 mL and diluted to 1 mL with dichloromethane to enhance chromatographic performance.

Alkyd painted panels were spiked and air dried for approximately 5 min and stored at 4°C for 60 min in the glass culture tubes. Spiked paint panels and blanks were extracted by ultrasonic vibration (10 min) with 2 x 3 mL of hexane and then centrifuged (10 min at 700 g). Hexane extracts were concentrated by nitrogen blowdown to 1 mL prior to chromatographic analysis.

Rubber samples were handled by several different approaches. Initial investigations utilized sequential extraction with hexane and dichloromethane in a manner similar to that used for the concrete samples. A more successful approach involved the extraction of spiked rubber samples and blanks by ultrasonic vibration (10 min) with 2 x 3 mL of acetonitrile. Acetonitrile extracts were centrifuged (10 min at 700 g), concentrated by nitrogen blowdown to 0.1 mL and diluted to 1 mL with dichloromethane to enhance chromatographic performance. An alternative approach to the acetonitrile method involved the extraction of spiked rubber samples and blanks with 2 x 3 mL of distilled water. Aqueous extracts were centrifuged (10 min at 700 g), extracted with 2 x 1 mL of dichloromethane, and concentrated to 1 mL prior to chromatographic analysis.

b) 1991 Round Robin Analyses

i) Painted Panels (sample numbers P46, P47 and P48)

The plastic pouches containing the glass bottles were cut with scissors and the glass bottle removed. The first panel extracted, P47, was removed and the foil removed with disposable tweezers. Paint panel P47 was then placed in the bottom of a 100 mL glass beaker containing 7 mL of hexane. The panel was extracted by ultrasonic vibration for 5 minutes and the hexane removed and concentrated by nitrogen blowdown to 1 mL prior to analysis. Paint panels P46 and P48 were treated identically with the exception that 10 mL of hexane was used for extraction.

Trimethylsilylation (TMS) was performed by combining 100 μL BSTFA, 100 μL pyridine and 300 μL of hexane extract (P46) in a 1.8 mL screw-capped (PTFE lined) glass vial. Paint panel P46 was re-extracted by ultrasonic vibration (5 min) with 7 mL of acetonitrile and the extract was concentrated to 300 μL by nitrogen blowdown. A second trimethylsilylation (TMS) was performed by combining 100 μL BSTFA, 100 μL pyridine and 300 μL of the acetonitrile extract in a 1.8 mL screw-capped (PTFE lined) glass vial. Samples were heated for 20 minutes at 60°C prior to analysis. Analysis of both samples was performed immediately after cooling to minimize degradation.

ii) Rubber (sample numbers R46, R47 and R48)

The plastic pouches containing the glass bottles were cut with scissors and the glass bottle removed. Each rubber sample was removed and the foil removed with disposable tweezers. Rubber samples were then placed back into the shipment bottle and extracted by ultrasonic vibration for 5 minutes with 12 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.

Two mL of the 5 mL volume (above) was concentrated 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 (R46) in a 1.8 mL screw-capped (PTFE lined) glass vial. This sample was heated for 20 minutes at 60°C prior to analysis. Analysis was performed immediately after cooling to minimize degradation.

iii) Concrete (sample numbers C46, C47 and C48)

The plastic pouches containing the glass bottles were cut with scissors and the glass bottle removed. Each concrete sample was removed and the foil removed with disposable tweezers. Concrete samples were then placed back into the shipment bottle and extracted by ultrasonic vibration for 5 minutes 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.

Two mL of the 5 mL volume (above) was concentrated to 300μL and this concentrate was used for trimethylsilylation. Trimethylsilylation was performed by combining 100 μL BSTFA, 100 μL pyridine and the 300 μL extract (C48) in a 1.8 mL screw-capped (PTFE lined) glass vial. This sample was heated for 20 minutes at 60°C prior to analysis. Analysis was performed immediately after cooling to minimize degradation.

c) Instrumental Conditions

GC-MS Conditions	
Mass Spectrometer	VG AUTOSPEC-Q
Accelerating Voltage	8 kV
Mass Range/Scan Function	400 - 40 u (0.5 sec/decade)
EI (source conditions)	70eV / 200μA / 2 x 10^{-6} Torr / 200°C
CI (source conditions)	50eV / 300μA / 8 x 10^{-5} Torr / 120°C
Detection Limit	EI: full scanning 0.1-0.5 ng/component
	CI: full scanning 0.2-0.5 ng/component
Resolution (10% valley)	1800
GC Parameters	
Instrument:	Hewlett Packard 5890
Column:	J&W 15 m x 0.32 mm ID DB-1701 (0.25 μm)
Carrier Gas:	Helium approx. 100 cm/s
Temperature Program:	40°C (2 min) then 10°C/min to 280°C (5 to 20 min)
Injection Mode:	On-column at 40°C

Comments:

10,000 resolution (250 - 100 u, 1 sec/decade) used to the confirm molecular weight of mustard and bis(2-chloroethyl)disulfide.

GC-MS/MS Conditions	
Mass Spectrometer	VG AUTOSPEC-Q
Accelerating Voltage	8 kV
Quadrupole Mass Range (daughter experiments)	250 - 50 u (0.5 sec/decade)
EI (source conditions)	70eV / 200μA / 2 x 10^{-6} Torr / 200°C
CAD Cell	10^{-6} Torr Argon / 17 eV
Detection Limit	Daughter spectrum: 0.5 ng/component
Resolution (sector)	1800
Resolution (quadrupole)	unit
GC Parameters	
Instrument:	Hewlett Packard 5890
Column:	J&W 15 m x 0.32 mm ID DB-1701 (0.25 μm)
Carrier Gas:	Helium approx. 100 cm/s
Temperature Program:	40°C (2 min) then 10°C/min to 280°C (5 to 20 min)
Injection Mode:	On-column at 40°C
Comments:	

GC-FID Conditions	
Instrument:	Hewlett Packard 5890
Column:	J&W 15m x 0.32mm ID DB-1701 (0.25 μm)
Detector:	FID
Carrier Gas:	Helium approx. 35 cm/s
Temperature Program:	40°C (2 min) then 10°C/min to 280°C (5 to 20 min)
Injection Mode	On-column at 40°C
Detection Limit	approx. 0.5 ng/component

RESULTS AND DISCUSSION

a) Spiking Studies

Sample handling and analysis procedures that allow the verification of chemical warfare agents on contaminated paint, cement, and four types of rubber samples have been developed. The above mentioned samples were spiked at the 50 μg/g and 5 μg/g levels with sarin, soman, mustard and triethyl phosphate and extracted with a number of candidate solvents including hexane, dichloromethane, acetonitrile and water. Recovery efficiencies for these spiked compounds from the media were determined using external standards by capillary column GC-FID and confirmation was performed by capillary column GC-MS.

i) Alkyd Paint

Preliminary studies using a previously developed method suitable for soil analysis (12,13) involving sequential extractions with hexane followed by dichloromethane were performed on the alkyd paint panels. Dichloromethane dissolved the alkyd paint and the resulting extract was not suitable for chromatographic analysis. Hexane extraction provided good recoveries ranging from 60% to 80% for soman, triethyl phosphate, and mustard at both the 50 μg/g and 5 μg/g spike levels (Table 1). As was the case for soil (12,13), sarin was recovered with lower efficiency from the alkyd paint (20%). Figure 1 illustrates chromatograms obtained for a typical extract of the alkyd painted panels by capillary column GC-FID. Spiked sample components were confirmed by both high and low resolution capillary column GC-MS. Figure 2 illustrates total ion current GC-MS chromatograms obtained for typical hexane extracts. The electron impact mass spectra for each sample component obtained during this analysis are illustrated in Figure 3. High resolution mass spectrometric data (10,000) were acquired to confirm the exact mass of the molecular ions and key electron impact fragment ions. Errors between the expected and experimental data were low with most errors being less than 1.5 mmu (Table 2).

ii) Concrete

The same extraction methods used with soil (hexane followed by dichloromethane) (12,13) were performed on contaminated concrete samples. The hexane extract provided good recovery of mustard and dichloromethane extracted triethyl phosphate with high efficiency. However, the recovery of sarin and soman was very poor (Table 3). Acetonitrile was evaluated as an alternative extraction solvent. This solvent provided good recovery of triethyl phosphate and mustard (55% to 75%) at the 50 μg/g and 5 μg/g spike levels. Recoveries were lower for both soman (20%) and sarin (5%). Figure 4 illustrates typical chromatograms obtained during capillary column GC-FID of the acetonitrile extracts of contaminated concrete.

iii) Rubber

Preliminary extractions of bromobutyl rubber from a Canadian C4 mask with dichloromethane and hexane resulted in extract chromatograms with a high chemical background in the region of interest for chemical warfare agents. A water extraction followed by extraction of the water with dichloromethane, gave a recovery of approximately 10% for all chemical warfare agents, except mustard, which was not detected. This was consistent with the Norwegian aqueous extraction method (11), where the recovery of mustard was very low. Extraction of spiked bromobutyl rubber with acetonitrile proved to be the most successful method with the recovery of all agents being between 10% and 30% (Table 4). Figures 5c and 6c illustrate typical chromatograms obtained during capillary column GC-FID analysis of contaminated bromobutyl rubber extracts.

Acetonitrile extraction was performed on spiked nitrile o-rings composed of a random polymerization of acetonitrile with butadiene. Recoveries were excellent for all chemical warfare agents with recoveries in the 60% to 100% range (Table 5). However, the chromatographic performance was the poorest of all contaminated rubber samples tested with peak broadening and poor resolution being observed (Figure 5b & 6b). The poor chromatography was likely due to either contamination or activation of the column by compounds extracted from the nitrile rubber with acetonitrile. Extraction of the nitrile rubber with water, followed by extraction of the water with dichloromethane, was attempted to improve the chromatography. The chromatography improved, but this method was unacceptable as recovery of the chemical warfare agents was considerably lower (5%-25%) (Table 5).

Viton rubber, a copolymer of vinyldiene fluoride and hexafluoropropylene, was also spiked at the 50 μg/g and 5 μg/g levels and extracted with acetonitrile. The chromatography of the extract of the contaminated viton samples (Figure 5d & 6d) was much improved over the contaminated nitrile rubber extracts. Recoveries of sarin, soman, triethyl phosphate and mustard were in the 30% to 100% range (Table 6).

The final rubber sample evaluated was a weathered vehicle tire. Extraction of contaminated vehicle tire with acetonitrile gave the best chromatography of the four rubber samples (Figure 5a & 6a). Acetonitrile extraction of contaminated vehicle tire rubber resulted in recoveries in the 40% to 90% range for all spiked chemical agents (Table 7).

iv) Detection Limits

The detection limit for the scanning mode of capillary column GC-MS operation is difficult to specify, since manufacturers use a variety of criteria to express the sensitivity of their instruments. Since the user is usually interested in an arbitrary level that results in an interpretable mass spectrum, this definition was used. This arbitrary definition defies standardization because the instrument's sensitivity will vary with the compound analysed, the level of interfering substances in the sample and the instrumental background levels. Full scanning GC-MS detection limits of approximately 100 pg for the four spiked chemical agents were obtained under electron impact conditions. This standard detection limit corresponds to a sample detection limit of about 0.1 μg/g.

The standard detection limit for capillary column GC-FID was 300 pg of analyte (S/N=12:1) which corresponds to a sample detection limit of 0.3 μg/g. Sample volumes during the spiking study were high and both the capillary column GC-FID and GC-MS sample detection limits could be lowered by concentrating the extracts to lower volumes.

b) 1991 Round Robin Analyses

Nine samples, typical of those taken during inspection of a military facility, were received by Defence Research Establishment Suffield (DRES) as part of a multinational round robin analytical exercise. The participating laboratories in Canada, Australia, USSR (2 laboratories), Finland, France, Germany, The Netherlands, Norway, Sweden, China, Switzerland, Czech and Slovak Federal Republic, United Kingdom and United States of America (2 laboratories) were given the samples with no prior knowledge of their content and were asked to report in a semi-quantitative manner the presence of any CW relevant compounds.

i) Painted Panels (sample numbers P46, P47 and P48)

Figure 7 illustrates capillary column GC-MS (EI) chromatograms obtained during analysis of 1 μL aliquots of the hexane extract of P46, P47 and P48. Figures 8 illustrates the acquired EI mass spectra for two of the three CW relevant compounds (sesquimustard and bis[(2-chloroethylthio)ethyl]ether) detected during analysis of the hexane extracts of P46 and

P48. The EI mass spectrum of the third compound, 2-chloroethyl (2-chloroethoxy)ethyl sulfide, was poor as this component co-eluted with a hydrocarbon component(s) (Figure 9). The final sample, P47, which did not contain compounds of CW relevance, was subsequently confirmed to be a blank.

Ammonia, a highly specific CI reagent gas, was used to provide molecular ion data for the CW relevant compounds as this reagent gas does not ionize hydrocarbons. This specificity resulted in a considerably simplified total ion current chromatogram (Figure 10) and excellent quality full scanning MS data. All three sulfur vesicants exhibited base ions due to $(M+NH_4)^+$ and characteristic CI fragmentation ions (Figure 11) (14).

Capillary column GC-MS/MS data were obtained by acquiring the daughter spectra of m/z 123 (an ion common to sulfur vesicants) for sesquimustard, 2-chloroethyl (2-chloroethoxy)ethyl sulfide and bis[(2-chloroethylthio)ethyl]ether (Figures 12 and 13). The GC-MS/MS chromatogram obtained was considerably less complex than was obtained by EI-MS, as m/z 123 (with a sector resolution of 1800) was not observed in the hydrocarbon background. All three compounds exhibited similar daughter spectra with daughters at m/z 63 and m/z 61 due to loss of C_2H_4S and C_2H_3Cl respectively from $(C_2H_4\text{-}S\text{-}C_2H_4Cl)^+$ (m/z 123).

Sesquimustard, 2-chloroethyl (2-chloroethoxy)ethyl sulfide and bis[(2-chloroethylthio)ethyl]ether chromatographic/spectrometric data were confirmed with available authentic standards and no CW relevant compounds were detected during analysis of trimethylsilyl extracts.

ii) Rubber (sample numbers R46, R47 and R48)

Figure 14 illustrates capillary column GC-MS (EI) chromatograms obtained during analysis of 1 µL aliquots of the acetonitrile extracts of R46, R47 and R48. EI mass spectra were obtained for two CW relevant compounds, mustard and bis(2-chloroethyl)disulfide, found in the acetonitrile extracts of R46 and R47 (Figure 15). R48 did not contain compounds of CW relevance and appears to be the blank. Further confirmations were obtained by acquiring the exact mass of the molecular ion for both compounds at 10,000 resolution during GC-MS (EI) analysis.

Compound	Calc. Mass	Measured	Difference
Mustard	157.9724	157.9720	0.4 mmu
Bis(2-chloroethyl)disulfide	189.9444	189.9462	1.8 mmu

Capillary column GC-MS/MS data were obtained by acquiring the daughter spectrum of m/z 123 (an ion common to sulfur vesicants) for mustard (Figures 16 and 17). The daughter spectrum for mustard contained the same ions in approximately the same ratio as was observed during GC-MS/MS analysis of the sulfur vesicants in the painted panel extracts.

A second acetonitrile extract of R46 (used for TMS study) contained about 80% as much mustard and bis(2-chloroethyl)disulfide as the first which suggests relatively poor recovery of these compounds from this type of rubber with acetonitrile. Multiple extractions would be required for complete recovery.

Mustard and bis(2-chloroethyl)disulfide chromatographic/spectrometric data were confirmed with available authentic standards and no CW relevant compounds were detected during analysis of trimethylsilyl extracts.

iii) Concrete (sample numbers C46, C47 and C48)

Figure 18 illustrates capillary column GC-MS (EI) chromatograms obtained during analysis of 1 μL aliquots of the acetonitrile extracts of C46, C47 and C48. Figure 19 illustrates the EI mass spectrum obtained for one of the two CW relevant compounds, thiodiglycol, found in the acetonitrile extracts of C47 and C48. The second compound, thiodiglycol sulfone, was not discernable above the chemical background during EI-MS analysis.

The molecular weight 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 (Figure 20). The high hydrocarbon content, observed during EI-MS, was not ionized and highly specific detection of these two CW relevant compounds was possible during CI-MS.

Capillary column GC-MS/MS data were obtained by acquiring the daughter spectrum of m/z 122 (molecular ion) for thiodiglycol (Figures 21 and 22) and the daughter spectrum of m/z 111, $[(HO)_2SC_2H_4OH]^+$, for thiodiglycol sulfone (Figures 23 and 24). In both cases the principal daughter was due to loss of H_2O. The use of moderate resolution (1800) in the sector significantly reduced the chemical background and resulted in chromatograms that were considerably less complex than under EI-MS.

Figure 25 illustrates capillary column GC-MS (EI) chromatograms obtained during analysis of 1 μL aliquots of the TMS derivatives of the acetonitrile extract of C46, C47 and C48. The EI mass spectra for the di-TMS derivatives of thiodiglycol and thiodiglycol sulfone, found in the acetonitrile extracts of C47 and C48 (Figure 26), were similar to previously published data (15). C46 did not contain compounds of CW relevance and appears to be the blank.

The molecular weight of each of the derivatives was confirmed by the presence of $(M+H)^+$ and $(M+NH_4)^+$ ions during GC-MS (ammonia CI) analysis (Figures 27 and 28).

No sulfur vesicants were detected and thiodiglycol, thiodiglycol sulfone and their di-TMS derivatives chromatographic/spectrometric data were confirmed with available authentic standards.

iv) Round Robin Summary

Defence Research Establishment Suffield, the only participating Canadian laboratory, positively confirmed all the spiked CW relevant compounds in the round robin samples and did not detect any artifacts or false positives in the samples. A summary of the Canadian results and comparison to other laboratories will be reported in a forthcoming report (16). All CW relevant compounds (and their di-TMS derivatives), listed in Table 8, were confirmed by comparison of chromatographic/spectrometric data with authentic standard data. Thiodiglycol sulfone (the only compound not available at DRES) was synthesized to meet this goal and the EI-MS data obtained for this synthesized standard and the di-TMS derivative of thiodiglycol sulfone agreed with previously published data (15). EI-MS data for the sulfur containing vesicants found in the samples also agreed with previously published data (17).

CONCLUSIONS

Sample handling and analysis procedures have been developed for the verification of soman, sarin, triethyl phosphate and mustard in contaminated paint, concrete and rubber samples at 50 $\mu g/g$ and 5$\mu g/g$ levels. Acetonitrile proved to be the best solvent for the extraction of contaminated concrete and rubber samples and hexane was the best extraction solvent for contaminated painted panel samples. Triethyl phosphate and mustard were generally recovered from the sample media with efficiencies greater than 65%. Soman was usually recovered with slightly less efficiency (20% to 60%) and sarin, a compound that was difficult to extract from soil and other media, was recovered in the lowest yield (5% to 40%).

The developed methods were successfully applied during the 3rd United Nations Conference on Disarmament Technical Group on Instrumentation round robin analytical exercise held in 1991. Defence Research Establishment Suffield, the only participating Canadian laboratory, positively confirmed all the spiked CW relevant compounds in the round robin samples and did not detect any artifacts or false positives in the samples. The samples provided were found to contain compounds related to mustard and the presence of these compounds would warrant explanation had the samples been taken in support of the proposed Chemical Weapons Convention.

REFERENCES

1. "Report of the Specialists Appointed by the Secretary-General to Investigate Allegations by the Islamic Republic of Iran Concerning the Use of Chemical Weapons", United Nations Security Council S/16433, 26 March 1984.

2. "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", United Nations Security Council S/17911, 12 March 1986.

3. Andersson, G. NBC Defence and Technology International April 1986, 62-65.

4. "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", United Nations Security Council S/20070, 20 July 1988.

5. "International Interlaboratory Comparison (Round Robin) Test for the Verification of Chemical Disarmament. F.1.Testing of Existing Procedures", Ministry of Foreign Affairs of Finland, Helsinki, 1990.

6. D'Agostino, P.A., Provost, L.R., Sawyer, T.W. and Weiss, M.T., "Canadian Analysis of Soil Samples for Chemical Warfare Agents: A Multinational Round Robin Analytical Exercise", Suffield Memorandum No. 1331, April 1990, UNCLASSIFIED.

7. D'Agostino, P.A., Hancock, J.R., Provost, L.R., Lough, C.E., Boulet, C.A. and Hansen, A.S., "Canadian Contribution to the 1990 United Nations Round Robin Analytical Verification Exercise", Suffield Memorandum No. 1370, November 1991, UNCLASSIFIED.

8. "International Interlaboratory Comparison (Round-Robin) Test for the Verification of Chemical Disarmament. F.2. Testing of Procedures on Simulated Industry Samples", Ministry of Foreign Affairs of Finland, Helsinki, 1991.

9. "Criteria for Confirmation of CW Agents Identification". NATO AC/225(Panel VII/SICA) WP/25(Revised), 1990, NATO UNCLASSIFIED.

10. "Some Recent UK Identification Experiences", NATO AC/225(Panel VII/SICA) N/121, 1988, NATO UNCLASSIFIED.

11. "Use of Sorbent Extraction in Verification of Alleged Use of Chemical Warfare Agents - Part 9 ", NATO AC/225(Panel VII/SICA) N/201, 1990, NATO UNCLASSIFIED.

12. D'Agostino, P.A., Provost, L.R., and Ouellette, S.D.,"Confirmation of Chemical Warfare Agents and their Hydrolysis Products in Soil", Suffield Report No. 541, January, 1991, UNCLASSIFIED.

13. D'Agostino, P.A. and Provost, L.R., J. Chromatogr., **589**, 1992, 287-294.

14. D'Agostino, P.A. and Provost, L. R., J. Chromatogr., (in press).

15. Wils, E. R. J., Fresenius Z. Anal. Chem. **321**, 1985, 471-474.

16. "International Interlaboratory Comparison (Round-Robin) Test for the Verification of Chemical Disarmament", Ministry of Foreign Affairs of Finland, Helsinki, (in press).

17. D'Agostino P.A. and Provost L. R., Biomed. Environ. Mass Spectrom., **15**, 1988, 553-564.

Table 1: Recovery of sarin (GB), soman (GD), triethyl phosphate (TEP), and mustard (H) from alkyd painted panels at the 50 μg/g and 5 μg/g level.

METHOD	% RECOVERED[a]			
	GB	GD	TEP	H
a) 50 μg/g Spike				
Hexane (2 x 3 mL)	21±3	59±7	73±8	76±7
b) 5 μg/g Spike				
Hexane (2 x 3 mL)	19±3	75±3	78±4	77±10

[a] Mean ± SD (n=4 for 50 μg/g spike and n=3 for 5 μg/g spike)

Table 2: High resolution (10,000) EI-MS data obtained for sarin, soman, mustard and triethyl phosphate.

COMPOUND	NOMINAL MASS	CALCULATED MASS	OBSERVED MASS	ERROR (mmu)
SARIN	125	125.0168	125.0182	1.4
	99	99.0011	99.0014	0.3
SOMAN[a]	126	126.0246	126.0257	1.1
	99	99.0011	99.0012	0.1
	82	81.9984	82.0025	4.1
	69	69.0704	69.0707	0.3
SOMAN[b]	126	126.0246	126.0254	0.8
	99	99.0011	99.0006	-0.5
	82	81.9984	82.0012	2.8
	69	69.0704	69.0707	0.3
MUSTARD	158	157.9724	157.9738	1.4
	109	108.9879	108.9895	1.6
	63	63.0002	63.0006	0.4
TRIETHYL PHOSPHATE	182	182.0708	182.0685	-2.3
	155	155.0473	155.0478	0.5
	127	127.0160	127.0162	0.2
	99	98.9847	98.9842	-0.5

[a] First chromatographic component

[b] Second chromatographic component

Table 3: Recovery of sarin (GB), soman (GD), triethyl phosphate (TEP), and mustard (H) from concrete at the 50 μg/g and 5 μg/g level.

METHOD	% RECOVERED[a]			
	GB	GD	TEP	H
a) 50 μg/g Spike				
Hexane (2 x 2 mL)	ND	ND	1.4±0.6	64±7
Dichloromethane (2 x 2 mL)	0.9±0.8	1.3±1.1	52±9	2±1
TOTAL	0.9±0.8	1.3±1.1	53±9	66±8
b) 50 μg/g Spike				
Acetonitrile (1 x 2 mL)	5±4	13±9	48±8	41±7
c) 50 μg/g Spike				
Acetonitrile (2 x 2 mL)	7±3	30±10	75±8	67±2
d) 5 μg/g Spike				
Acetonitrile (2 x 2 mL)	2.4±0.6	19±6	69±12	56±11

[a] Mean ± SD (n=3)

ND: Not Detected

Table 4: Recovery of sarin (GB), soman (GD), triethyl phosphate (TEP), and mustard (H) from Canadian C4 mask bromobutyl rubber samples at the 50 μg/g and 5 μg/g level.

METHOD	% RECOVERED[a]			
	GB	GD	TEP	H
a) 50 μg/g Spike				
acetonitrile (2 x 3 mL)	11±3	9±3	11±4	20±7
b) 50 μg/g Spike				
water (2 x 3 mL) followed by dichloromethane extraction of water (2 x 1 mL)	8.2±0.6	10.0±0.3	12.6±0.6	ND
c) 5 μg/g Spike				
acetonitrile (2 x 3 mL)	8.6±0.6	15.4±0.5	20±1	26±1

[a] Mean ± SD (n=3)

ND: Not Detected

Table 5: Recovery of sarin (GB), soman (GD), triethyl phosphate (TEP), and mustard (H) from nitrile rubber samples at the 50 μg/g and 5 μg/g level.

METHOD	% RECOVERED[a]			
	GB	GD	TEP	H
a) 50 μg/g Spike				
acetonitrile (2 x 3 mL)	65±9	76±5	88±5	89±8
b) 50 μg/g				
water (2 x 3 mL) followed by extraction with methylene chloride of the water (2 x 1 mL)	12.0±0.1	17±2	24±2	1.1±0.1
c) 5 μg/g Spike				
acetonitrile (2 x 3 mL)	58±4	77±3	89±4	103±11

[a] Mean ± SD (n=3)

Table 6: Recovery of sarin (GB), soman (GD), triethyl phosphate (TEP), and mustard (H) from viton rubber samples at the 50 μg/g and 5 μg/g level.

METHOD	% RECOVERED[a]			
	GB	GD	TEP	H
a) 50 μg/g Spike				
acetonitrile (2 x 3 mL)	26±5	53±12	75±12	43±16
b) 5 μg/g Spike				
acetonitrile (2 x 3 mL)	37±1	58±2	104±11	69±7

[a]Mean ± SD (n=3)

Table 7: Recovery of sarin (GB), soman (GD), triethyl phosphate (TEP), and mustard (H) from weathered vehicle tire rubber samples at the 50 μg/g and 5 μg/g level.

METHOD	% RECOVERED[a]			
	GB	GD	TEP	H
a) 50 μg/g Spike				
acetonitrile (2 x 3 mL)	36±10	59±14	72±17	69±15
b) 5 μg/g Spike				
acetonitrile (2 x 3 mL)	42±7	65±8	90±8	89±1

[a]Mean ± SD (n=3)

Table 8: Compounds identified during United Nations sponsored round robin analysis.

Chrom. Peak No.	Mol. Wt.	Compound
1	202	2-Chloroethyl (2-chloroethoxy)ethyl sulfide
2	218	Sesquimustard
3	262	Bis[(2-chloroethylthio)ethyl]ether
4	158	Mustard
5	190	Bis(2-chloroethyl)disulfide
6	122	Thiodiglycol
7	154	Thiodiglycol sulfone
8	266	di-TMS derivative of thiodiglycol
9	298	di-TMS derivative of thiodiglycol sulfone

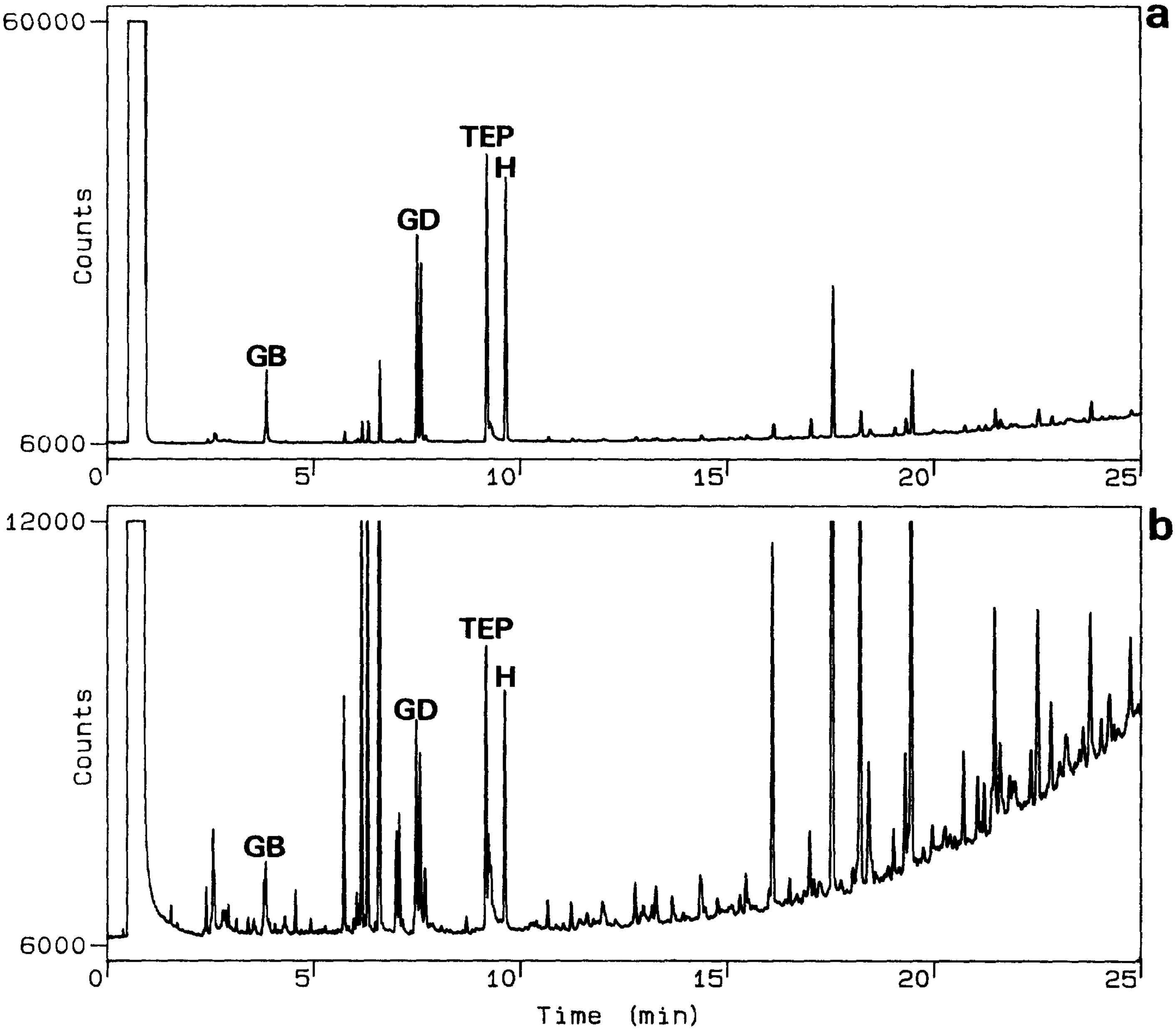

Figure 1

Capillary column GC-FID chromatograms of hexane extract of alkyd painted panels spiked at the a) 50 μg/g and b) 5 μg/g levels with sarin (GB), soman (GD), triethyl phosphate (TEP) and mustard (H) (15 m x 0.32 mm I.D. J&W DB-1701; 40°C (2 min) 10°C/min 280°C (2 min)).

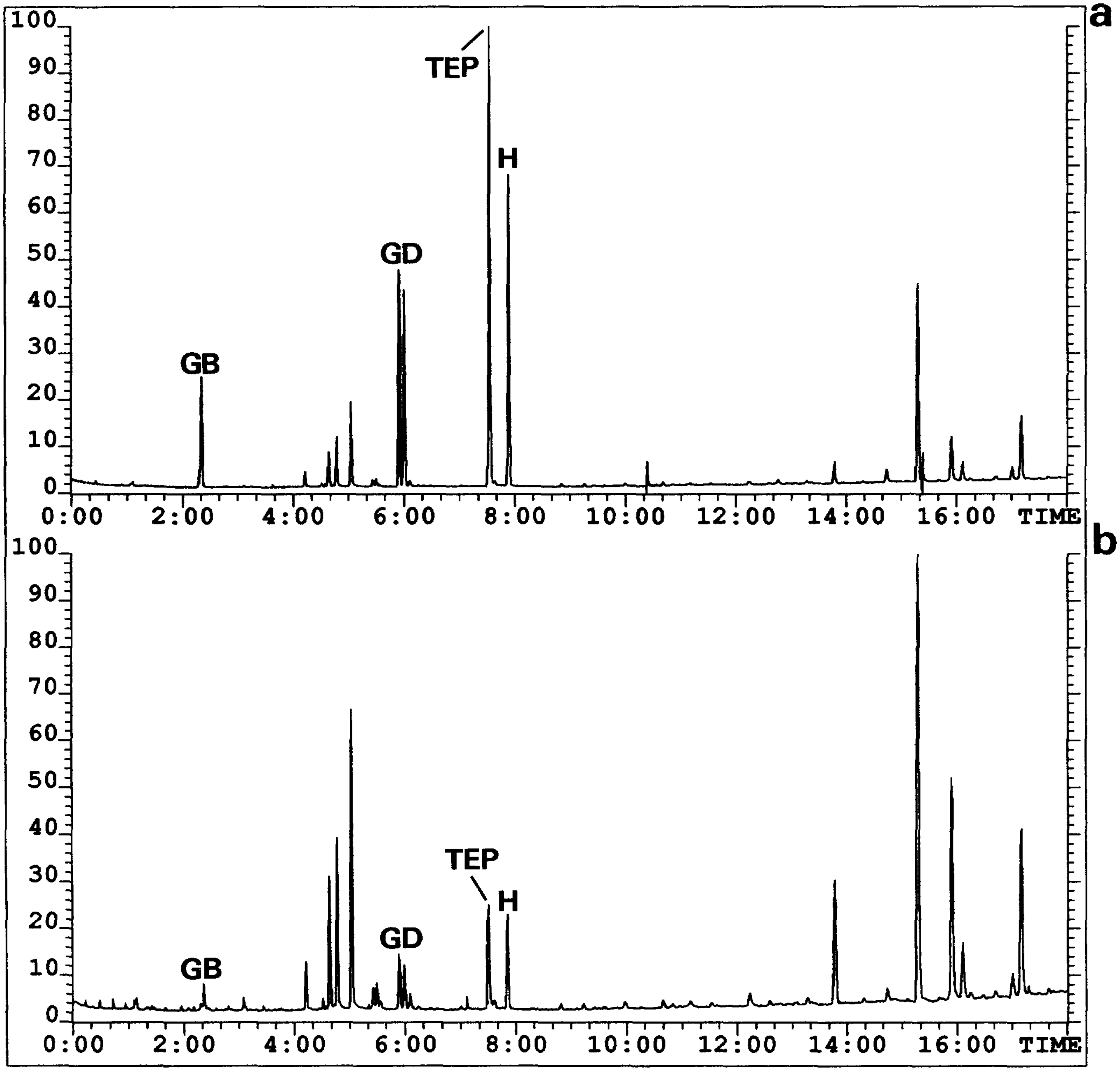

Figure 2

Capillary column GC-MS total-ion-current (400 to 40 u) chromatograms of hexane extract of alkyd painted panels spiked at the a) 50 μg/g and b) 5 μg/g levels with sarin (GB), soman (GD), triethyl phosphate (TEP) and mustard (H). (15 m x 0.32 mm I.D. J&W DB-1701; 40°C (2 min) 10°C/min 280°C).

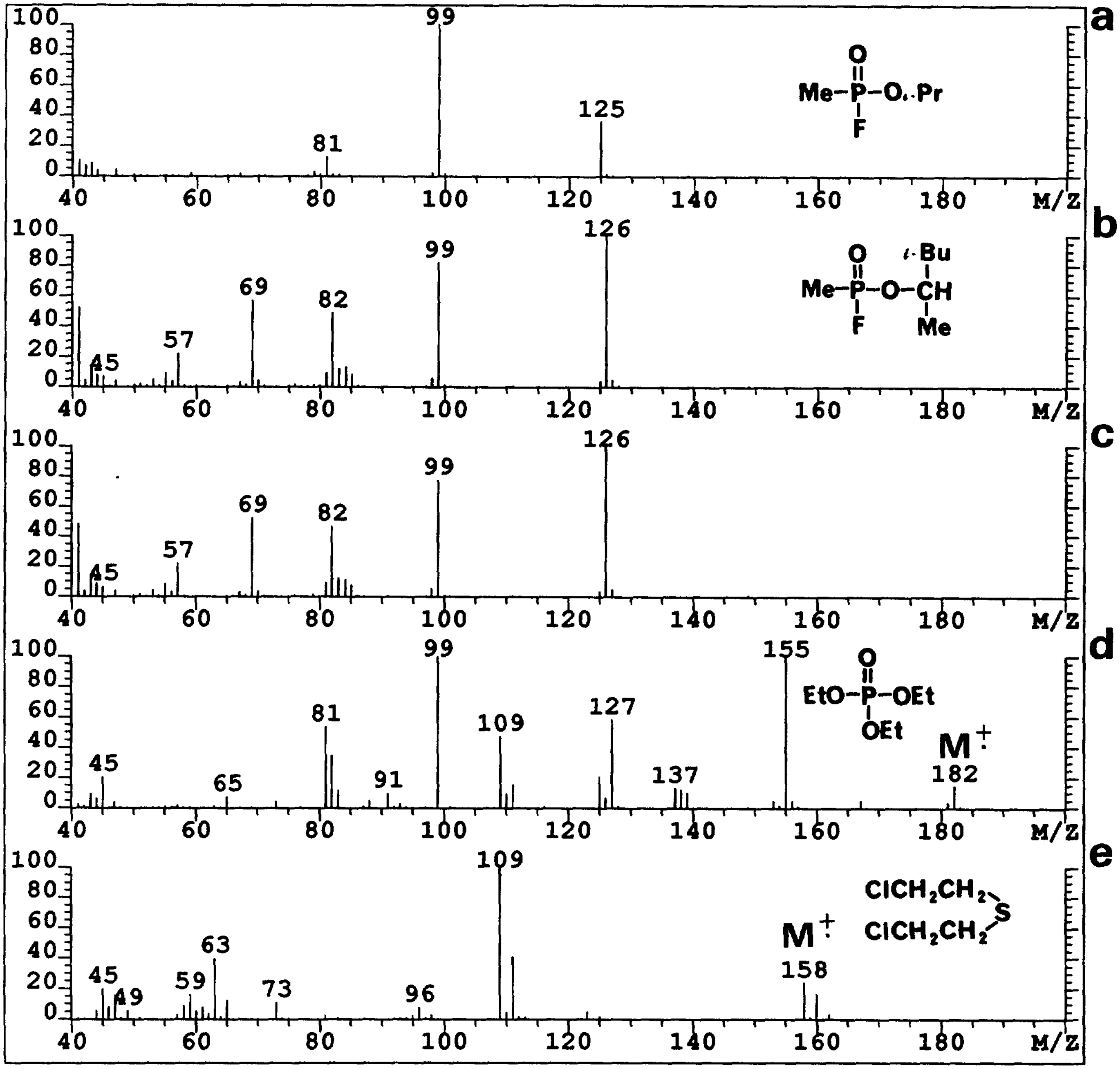

Figure 3

Electron impact mass spectra of a) sarin (GB), b) and c) soman (GD), d) triethyl phosphate (TEP) and e) mustard (H) at 1000 resolution. Data were obtained from the hexane extract of alkyd painted panels spiked at the 50 μg/g level. (15 m x 0.32 mm I.D. J&W DB-1701; 40°C (2 min) 10°C/min 280°C)

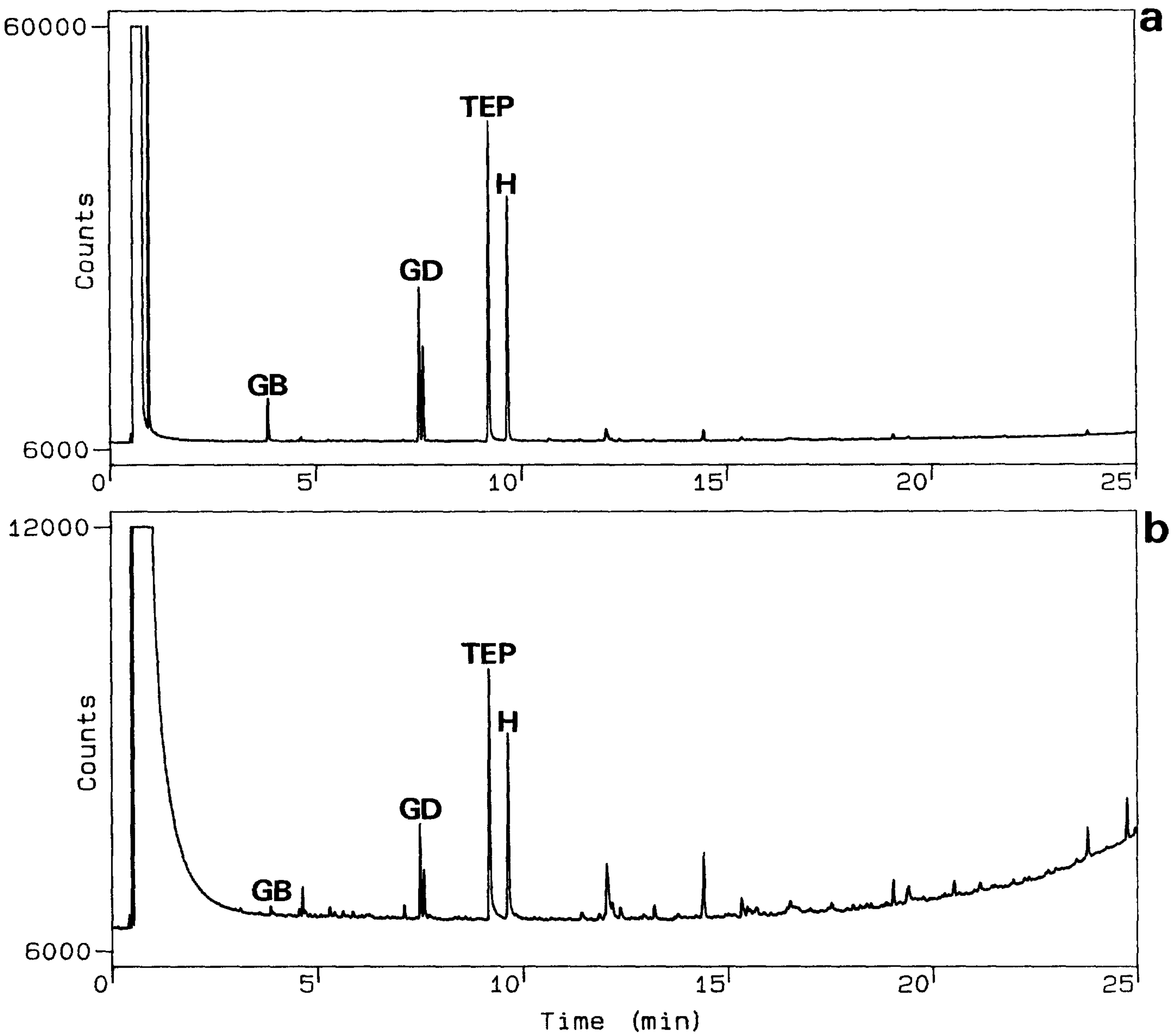

Figure 4

Capillary column GC-FID chromatograms of acetonitrile extract of concrete samples spiked at the a) 50 μg/g and b) 5 μg/g levels with sarin (GB), soman (GD), triethyl phosphate (TEP) and mustard (H). (15 m x 0.32 mm I.D. J&W DB-1701; 40°C (2 min) 10°C/min 280°C (2 min)).

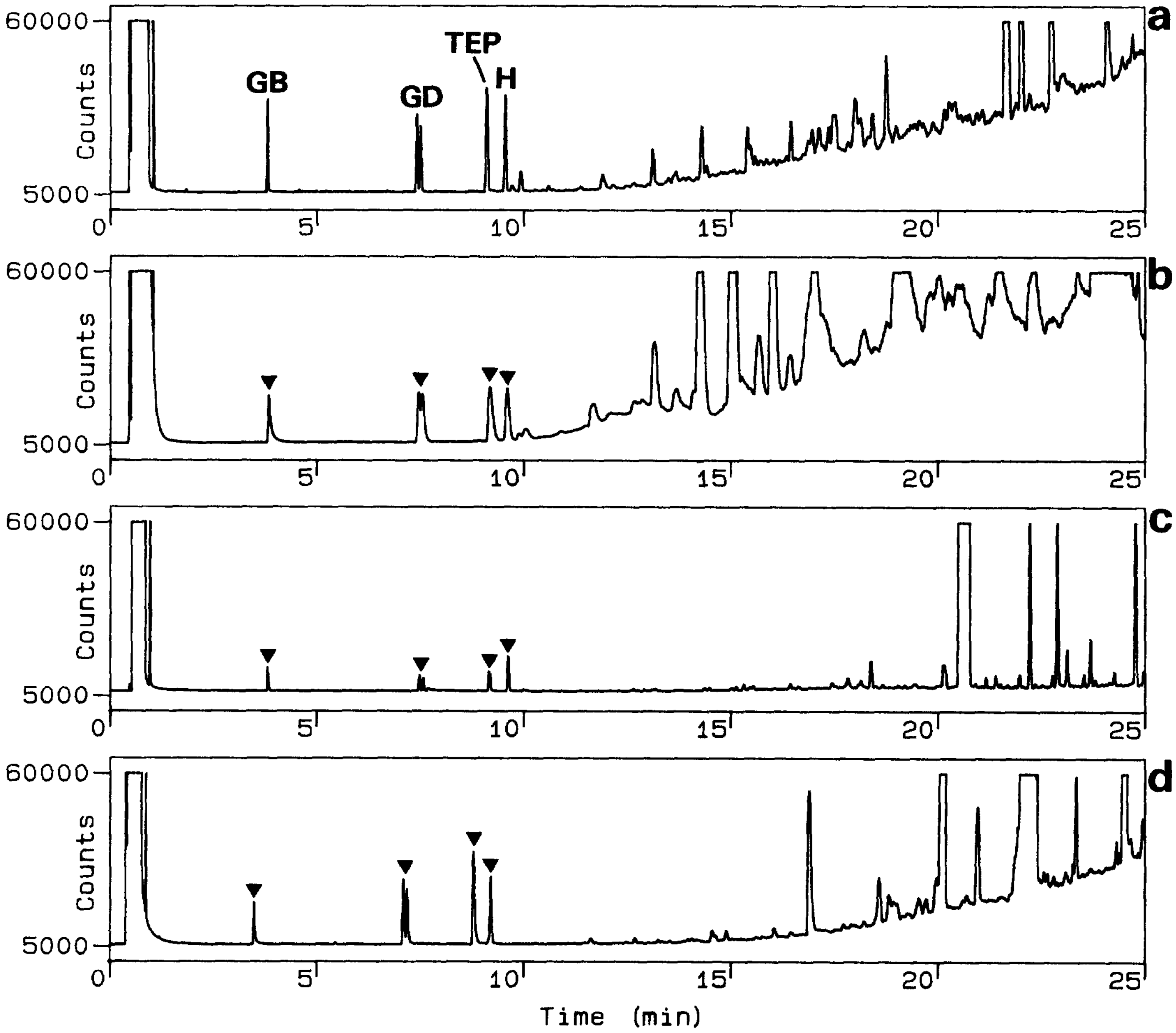

Figure 5

Capillary column GC-FID chromatogram of acetonitrile extract of a) weathered vehicle tire, b) nitrile, c) bromobutyl and d) viton rubber samples spiked at the 50 µg/g level with sarin (GB), soman (GD), triethyl phosphate (TEP) and mustard (H). (15 m x 0.32 mm I.D. J&W DB-1701; 40°C (2 min) 10°C/min 280°C (2 min)).

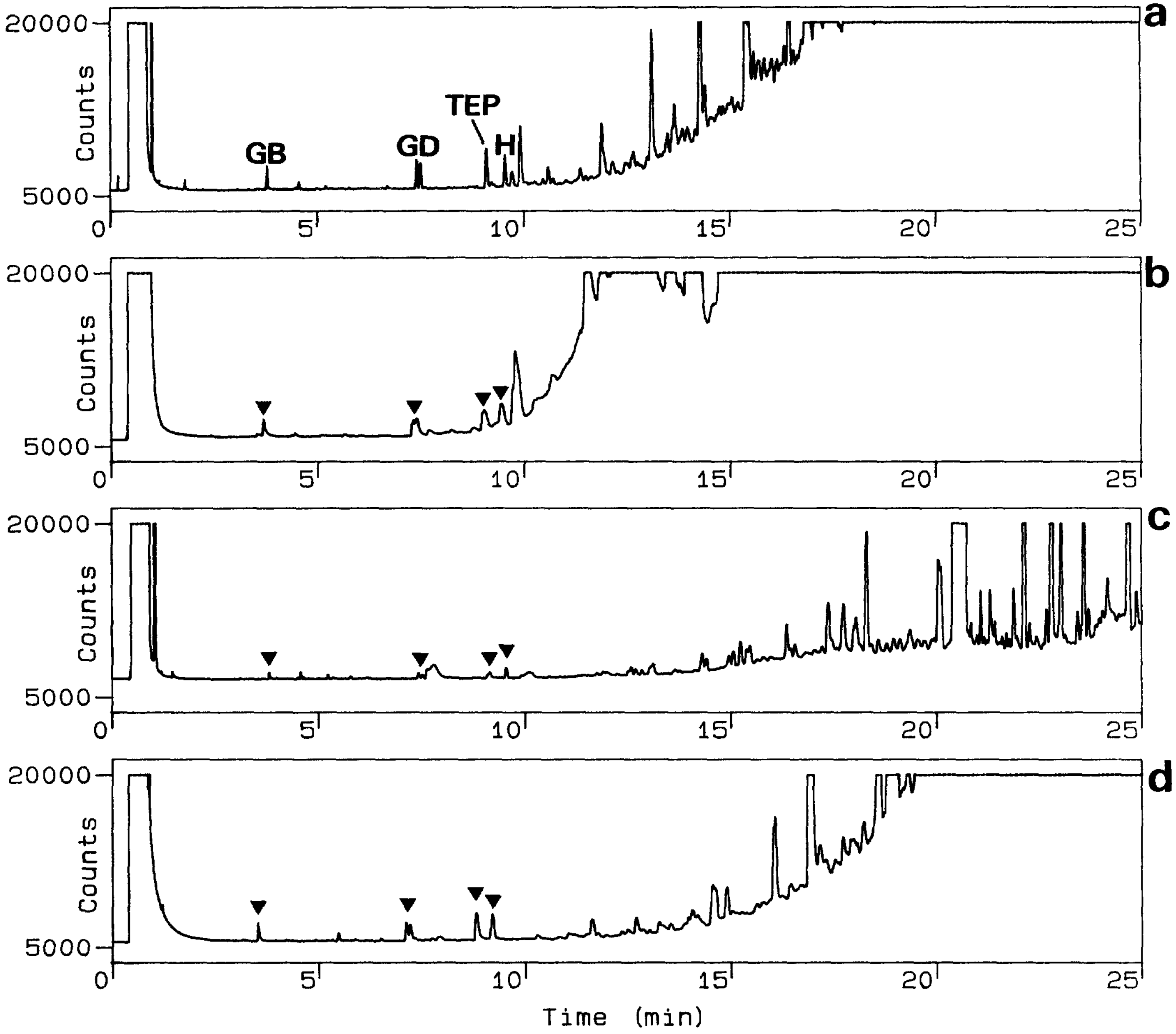

Figure 6

Capillary column GC-FID chromatogram of acetonitrile extract of a) weathered vehicle tire, b) nitrile, c) bromobutyl and d) viton rubber samples spiked at the 5 μg/g level with sarin (GB), soman (GD), triethyl phosphate (TEP) and mustard (H). (15 m x 0.32 mm I.D. J&W DB-1701; 40°C (2 min) 10°C/min 280°C (2 min)).

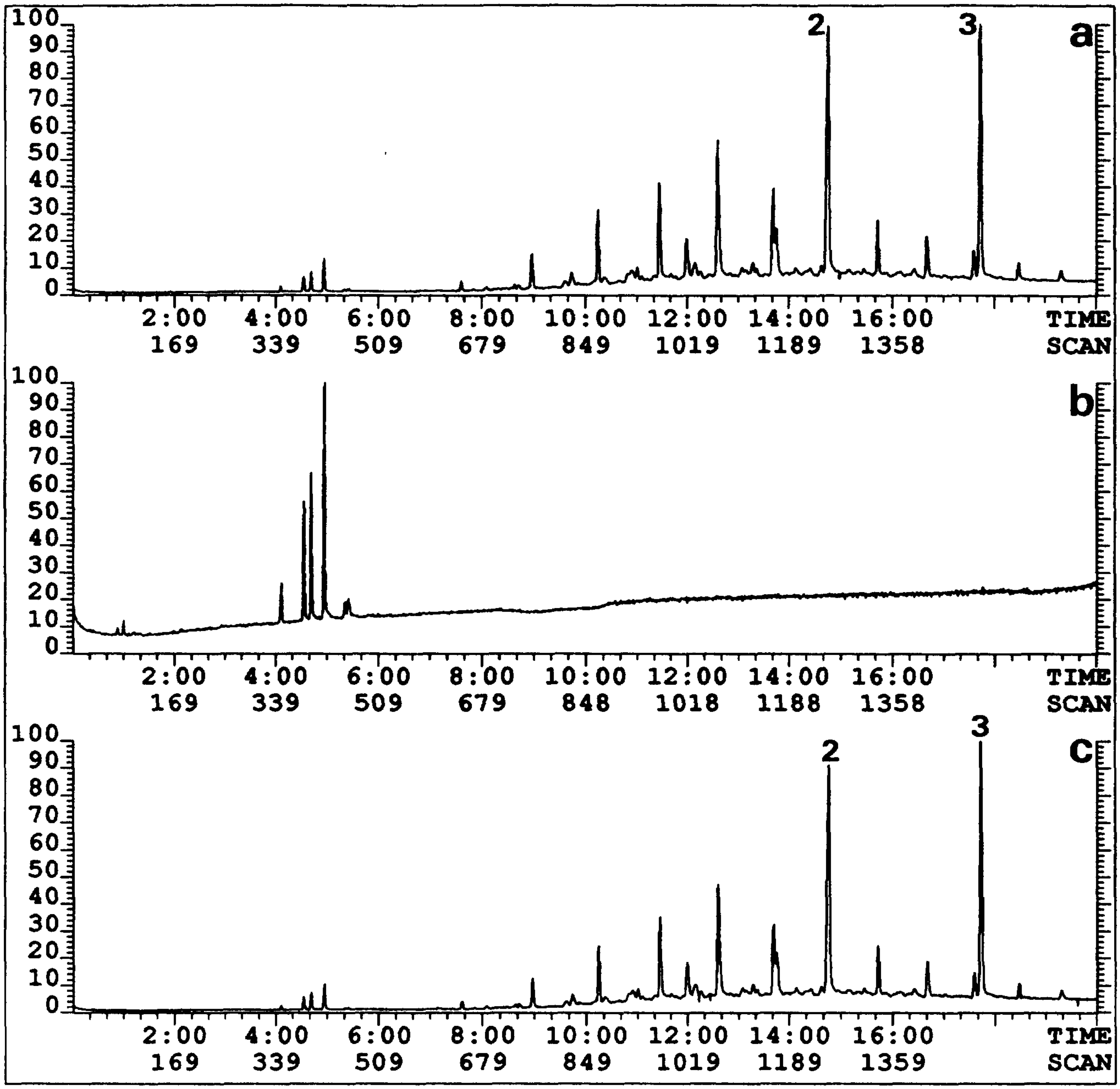

Figure 7

Capillary column GC-MS (EI) total-ion-current (400 to 40 u) chromatogram of the hexane extract of a) P46, b) P47 and c) P48 painted panels. Numbered components are listed in Table 8.

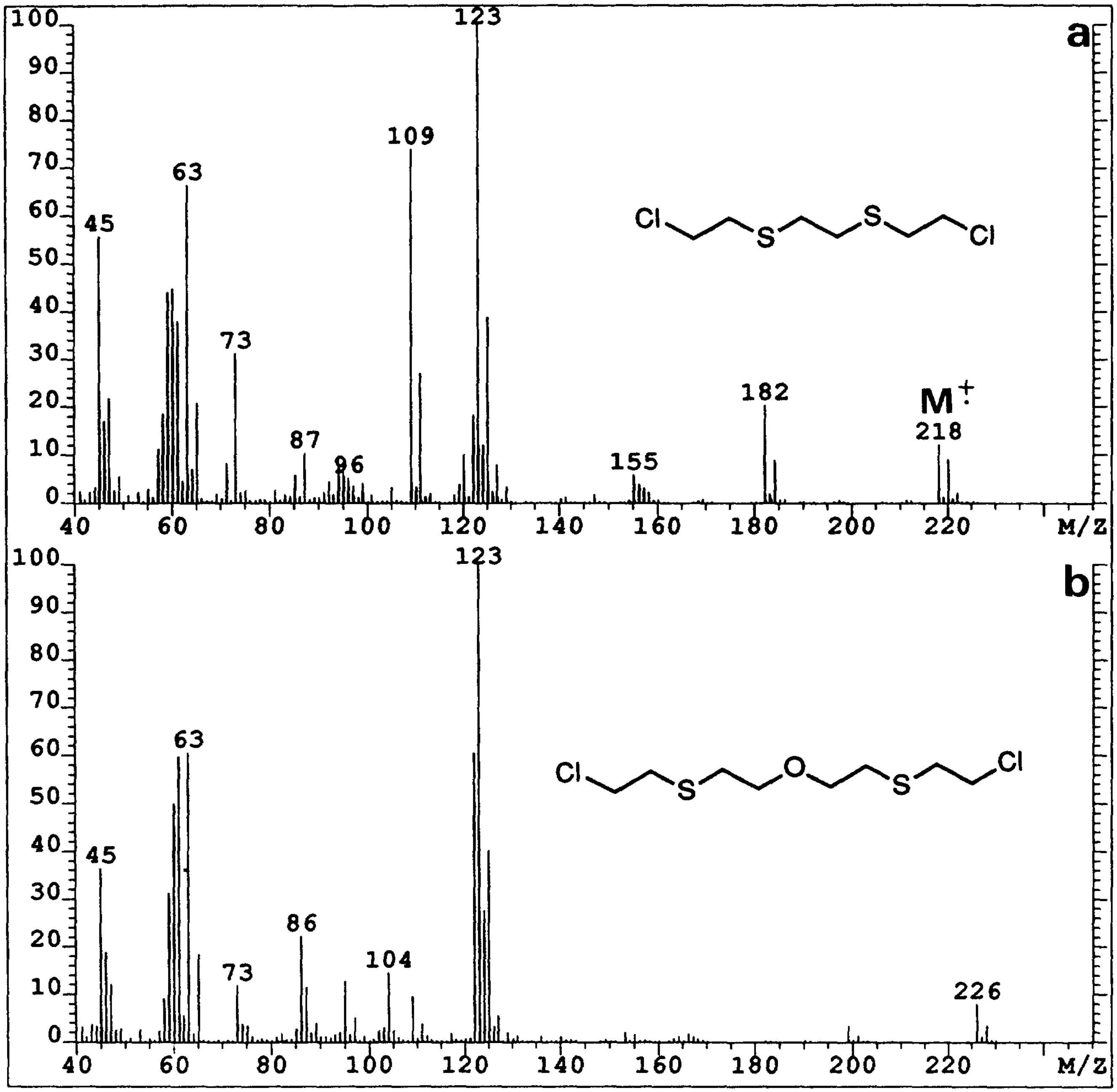

Figure 8

Electron impact mass spectra of a) sesquimustard and b) bis[(2-chloroethylthio)ethyl]ether (found in P46 and P48).

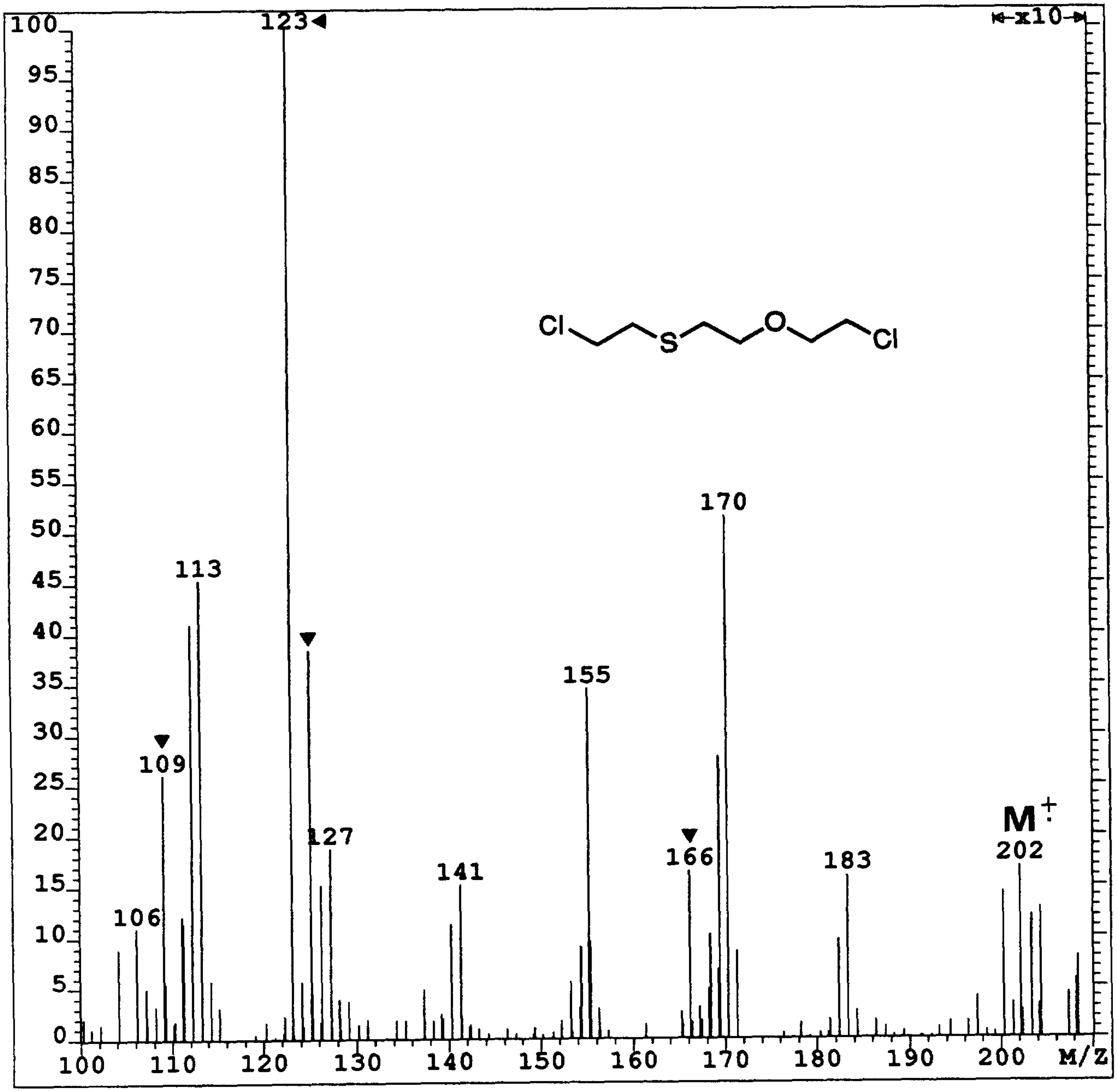

Figure 9

Electron impact mass spectrum of 2-chloroethyl (2-chloroethoxy)ethyl sulfide (found in P46 and P48). This minor component co-eluted with another compound and only the ions marked with a triangle and the molecular ion at m/z 202 were due to 2-chloroethyl (2-chloroethoxy)ethyl sulfide.

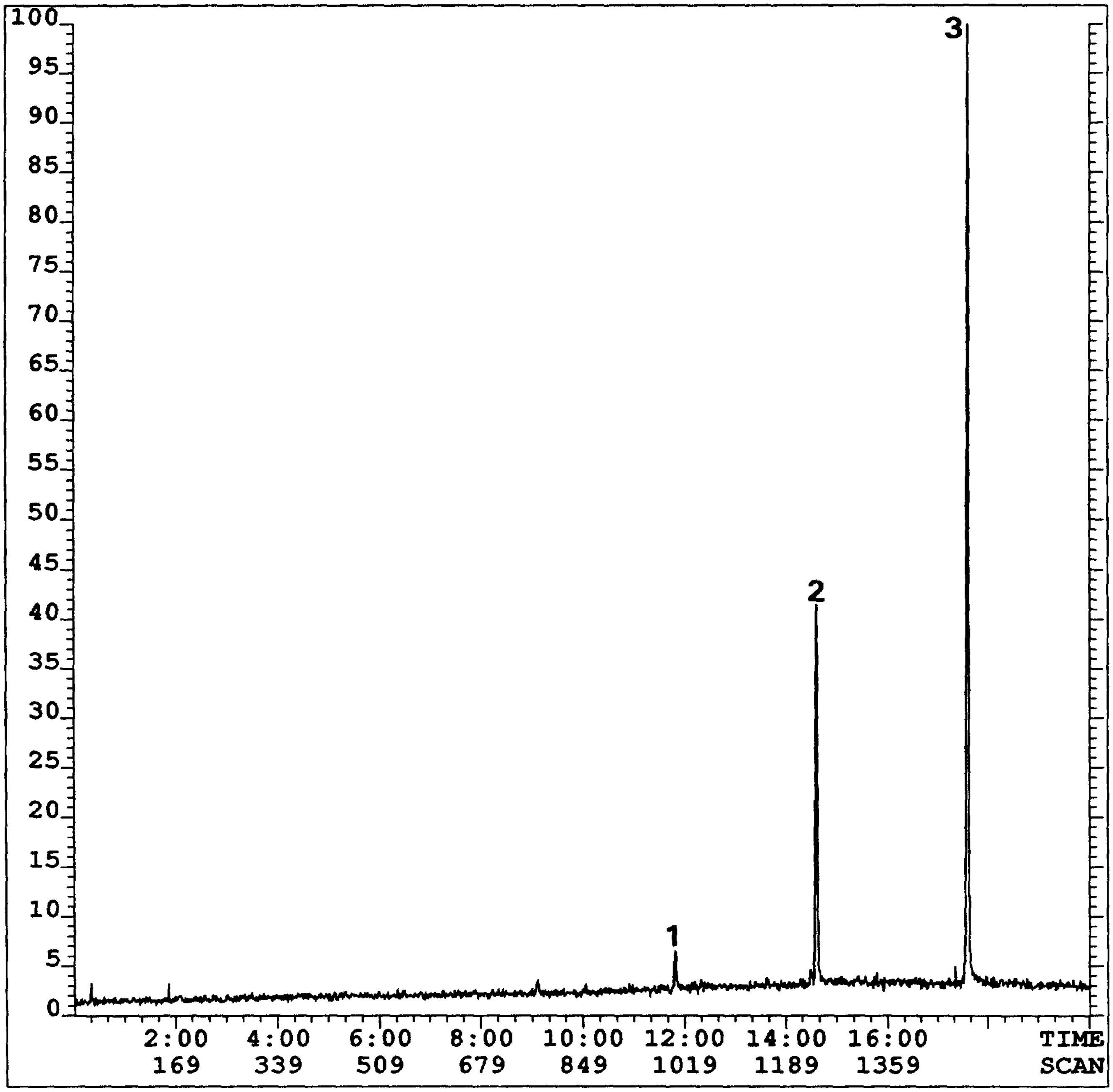

Figure 10

Capillary column GC-MS (ammonia CI) total-ion-current (300 to 200 u) chromatogram of the hexane extract of P46 painted panel. Numbered components are listed in Table 8.

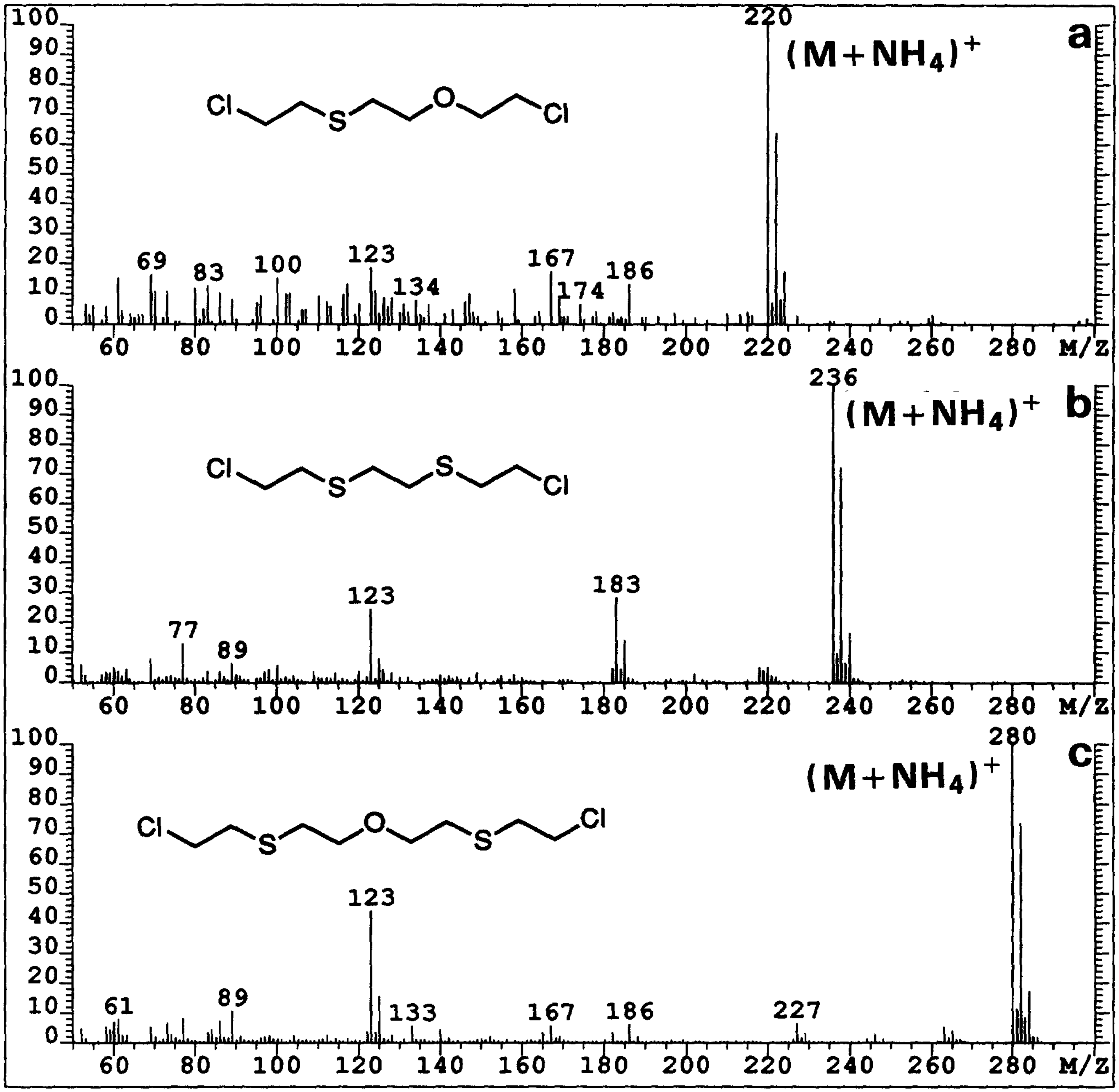

Figure 11

Ammonia chemical ionization mass spectra of a) 2-chloroethyl (2-chloroethoxy)ethyl sulfide, b) sesquimustard and c) bis[(2-chloroethylthio)-ethyl]ether (found in P46 and P48).

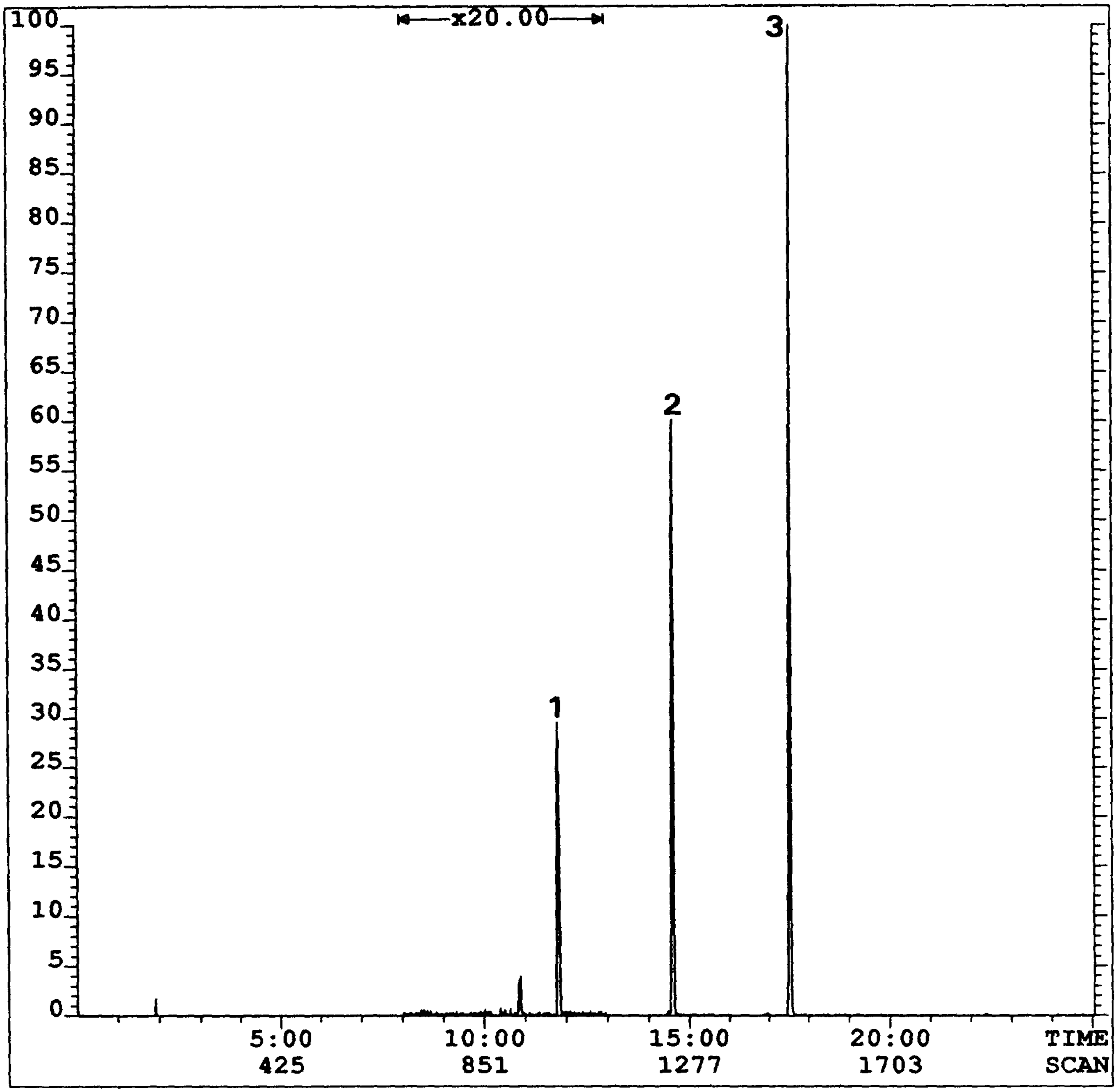

Figure 12

Collisional activated dissociation capillary column GC-MS/MS chromatogram for the daughters of m/z 123 of the hexane extract of P46 painted panel. Numbered components are listed in Table 8.

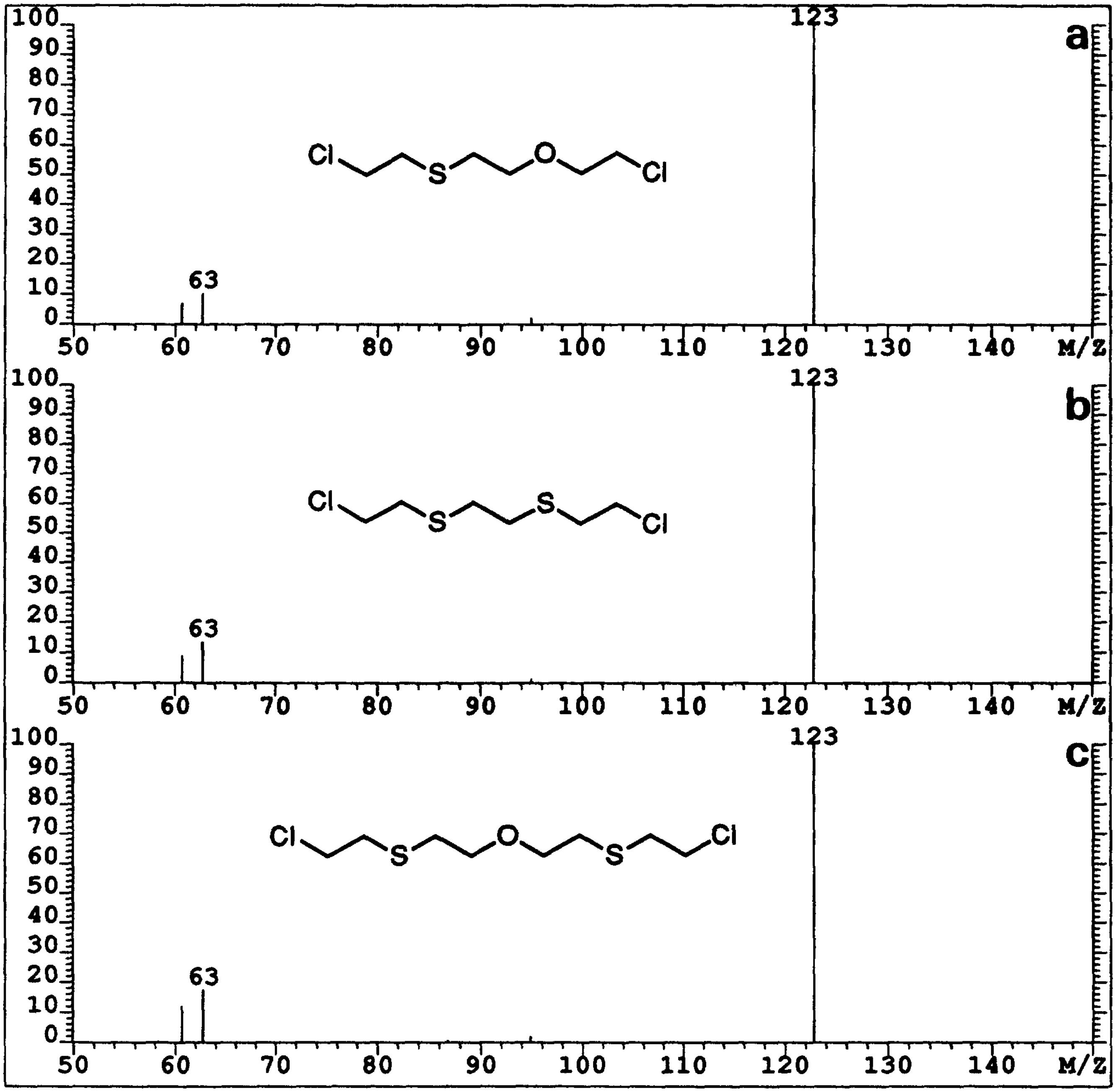

Figure 13

Daughter spectra (m/z 123) of a) 2-chloroethyl (2-chloroethoxy)ethyl sulfide, b) sesquimustard and c) bis[(2-chloroethylthio)ethyl]ether (found in P46 and P48).

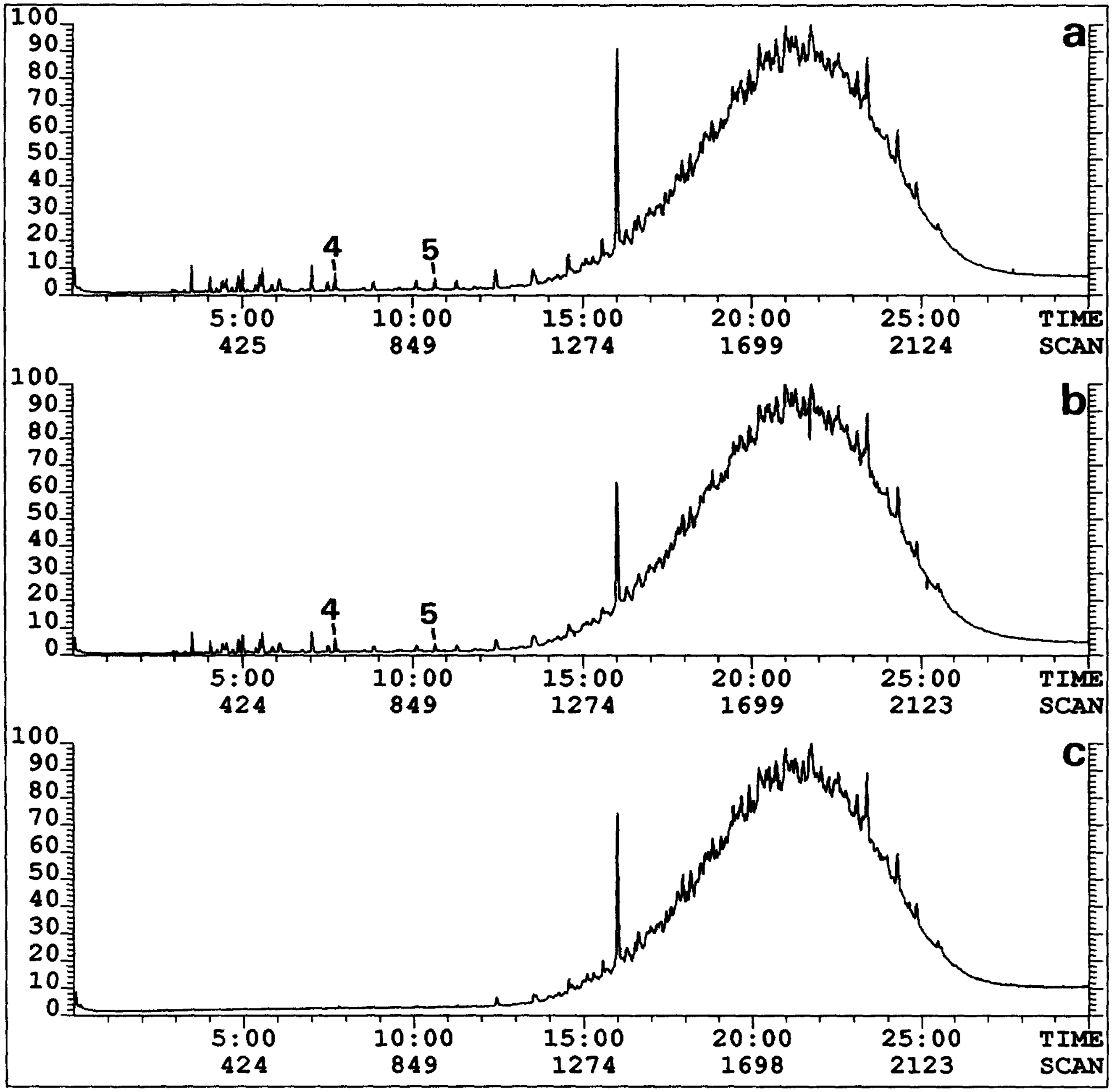

Figure 14

Capillary column GC-MS (EI) total-ion-current (400 to 40 u) chromatogram of the acetonitrile extract of a) R46, b) R47 and c) R48 rubber samples. Numbered components are listed in Table 8.

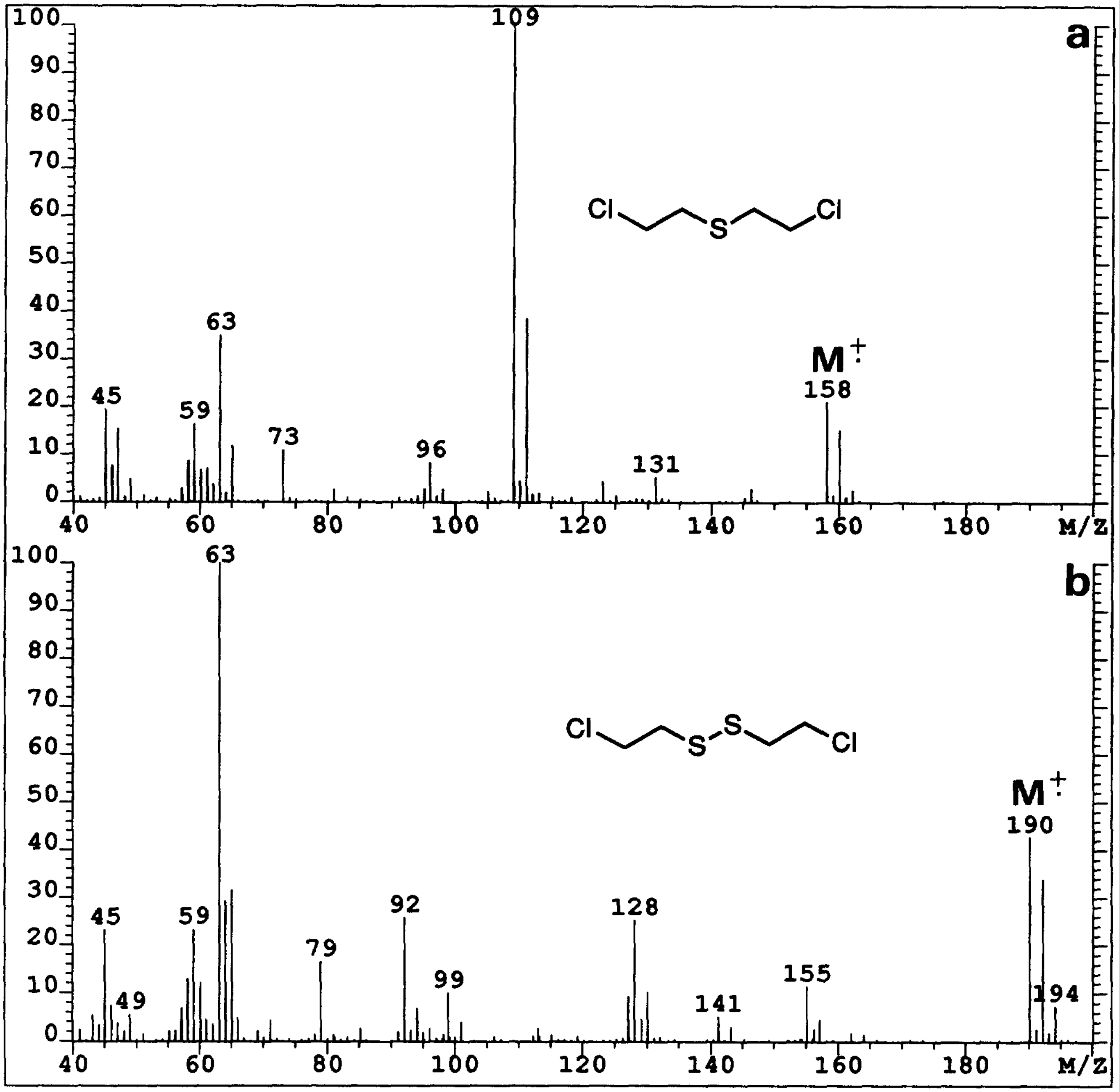

Figure 15

Electron impact mass spectrum of a) mustard and b) bis(2-chloroethyl)-disulfide (found in R46 and R47).

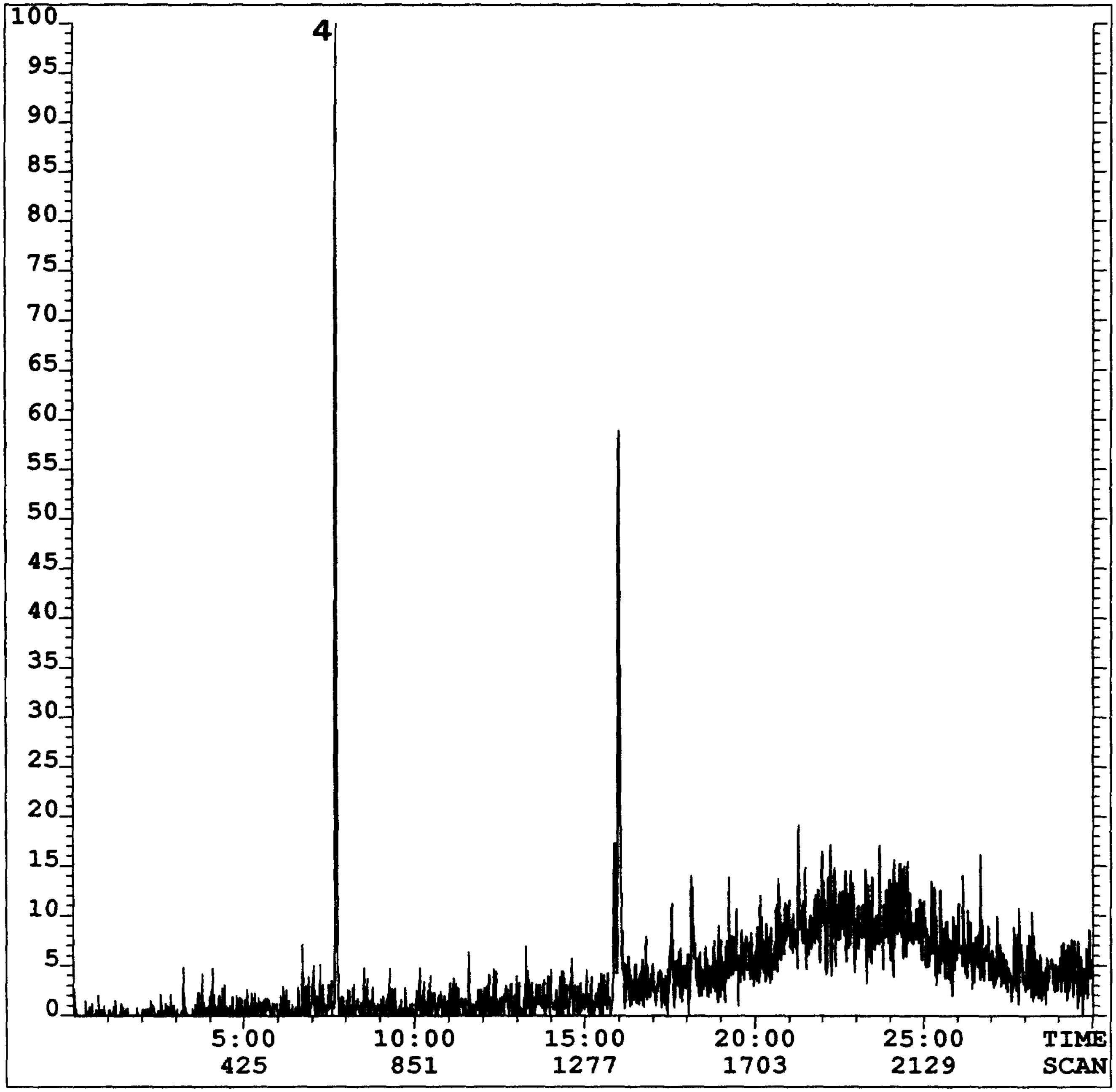

Figure 16

Collisional activated dissociation capillary column GC-MS/MS chromatogram for the daughters of m/z 123 of the acetonitrile extract of R46 rubber sample. Numbered components are listed in Table 8.

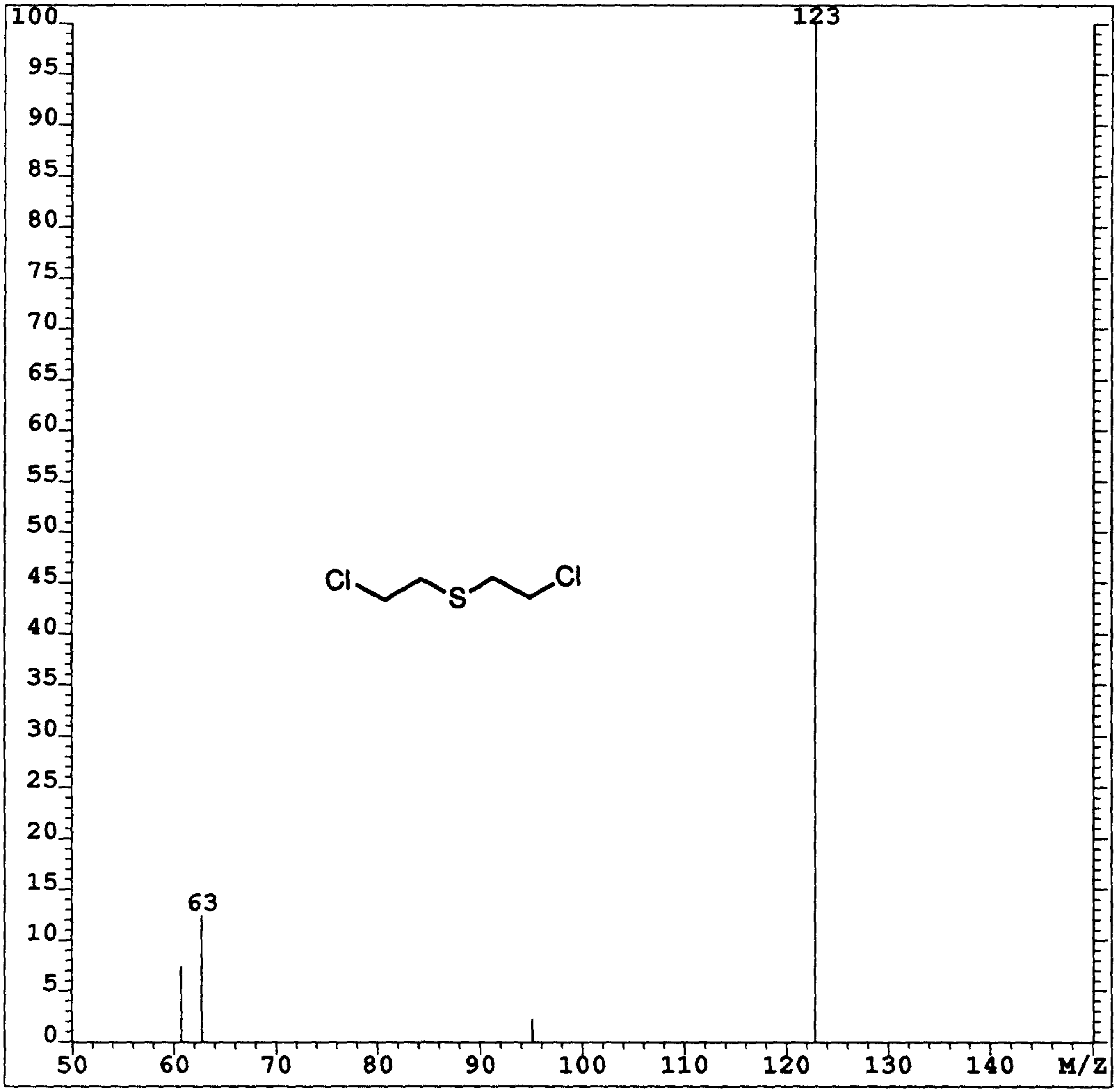

Figure 17

Daughter spectrum (m/z 123) of mustard (found in R46 and R47).

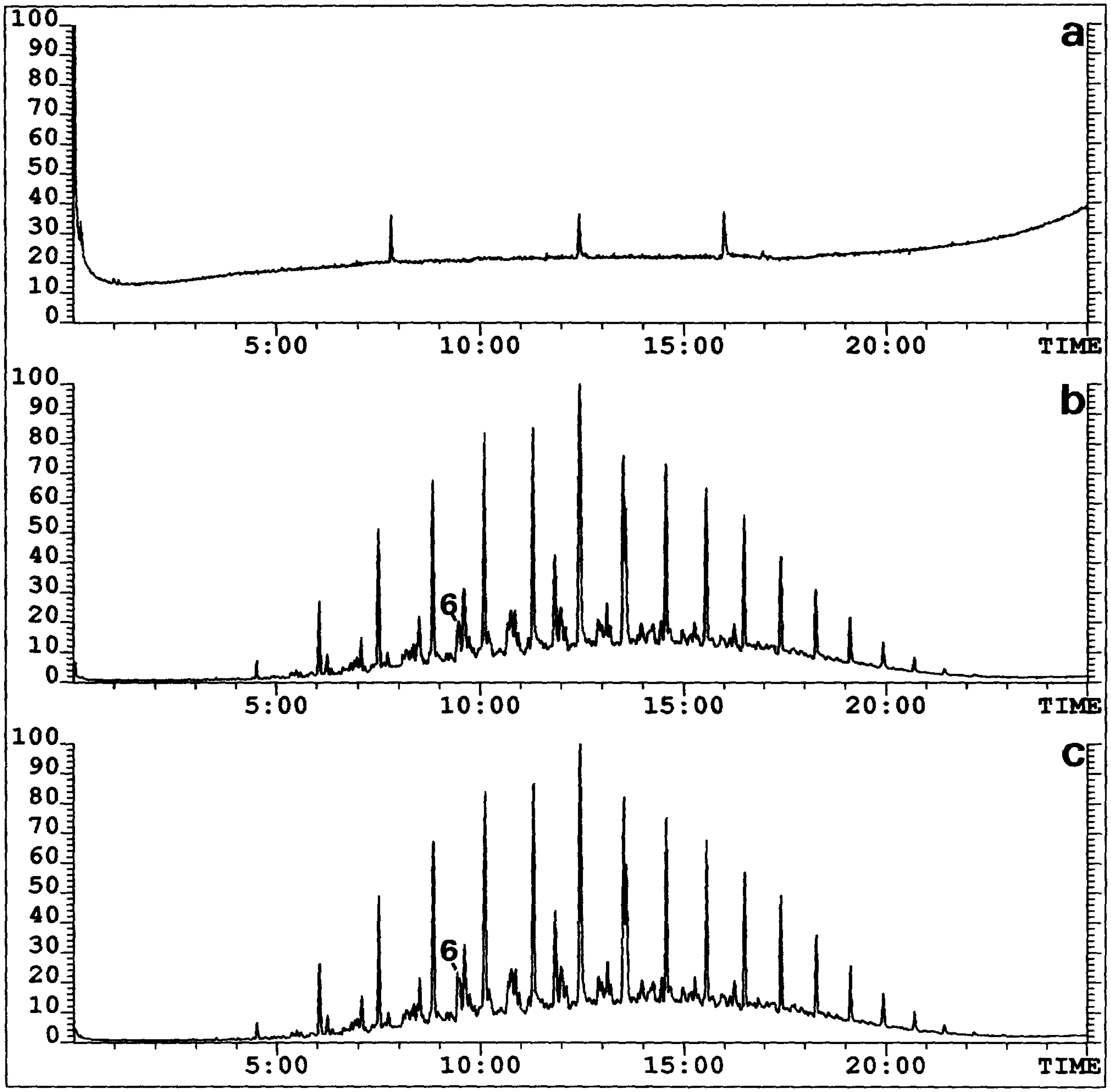

Figure 18

Capillary column GC-MS (EI) total-ion-current (400 to 40 u) chromatogram of the acetonitrile extract of a) C46, b) C47 and c) C48 concrete samples. Numbered components are listed in Table 8.

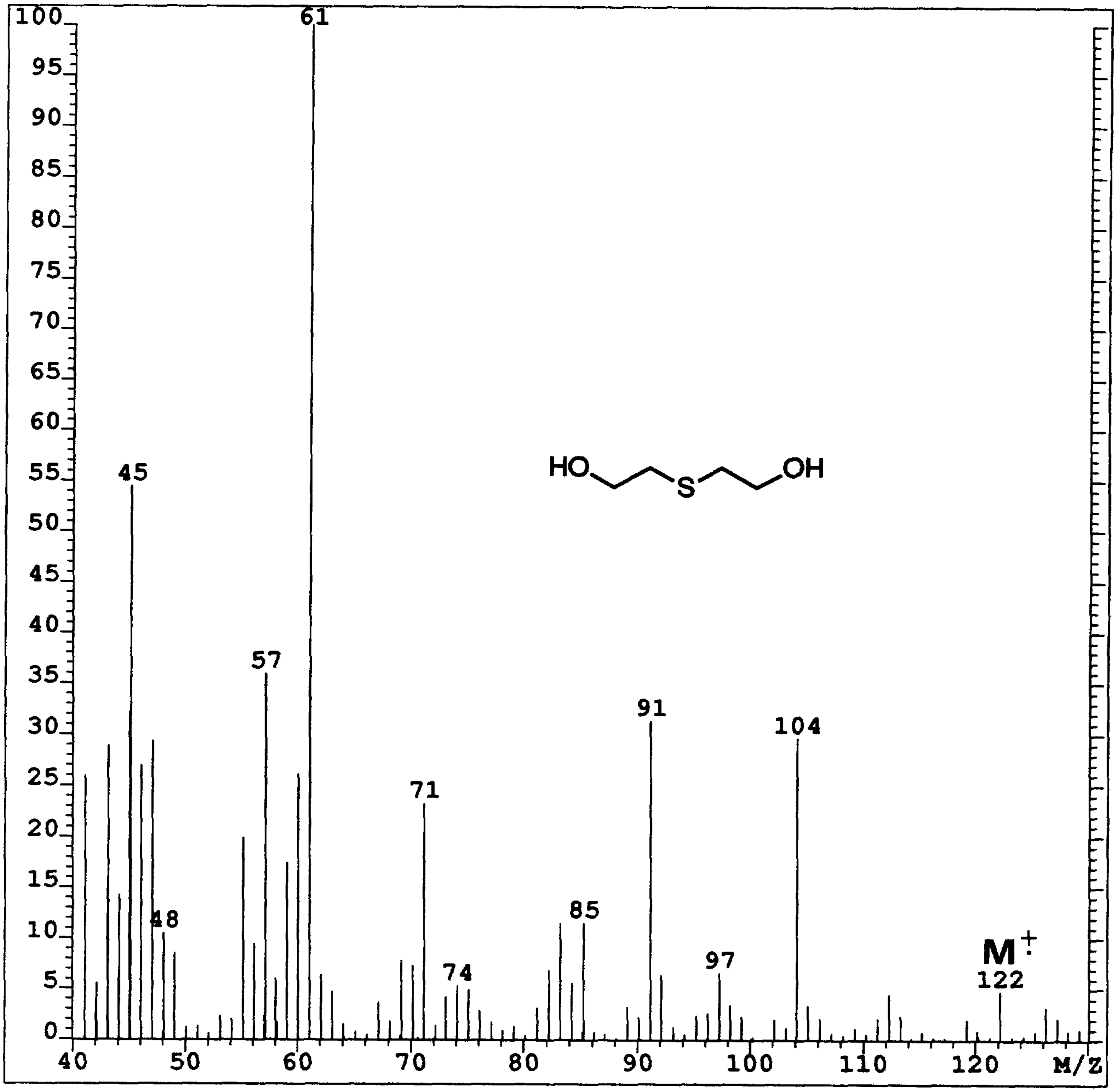

Figure 19

Electron impact mass spectrum of thiodiglycol (found in C47 and C48).

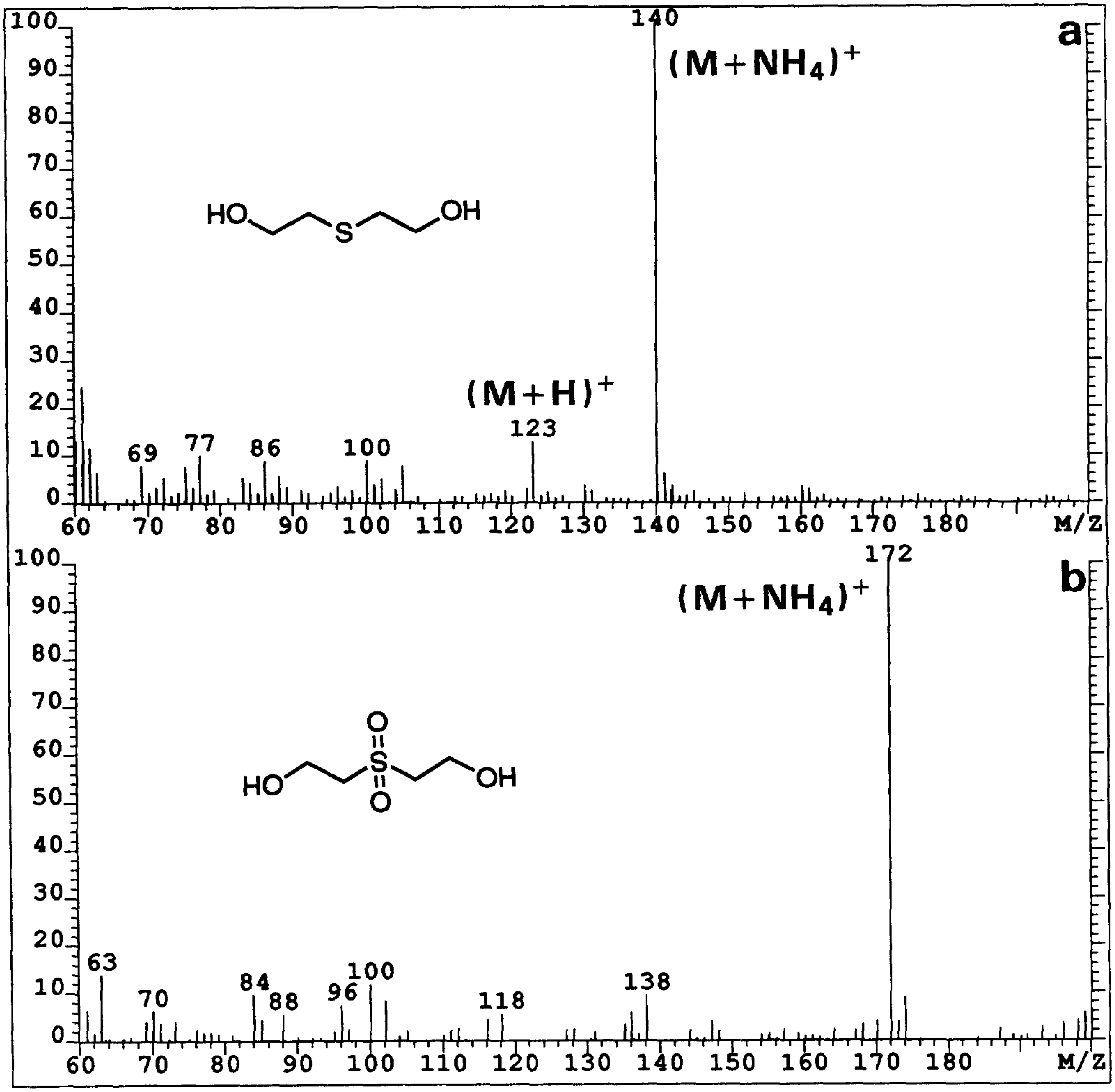

Figure 20

Ammonia chemical ionization mass spectra of a) thiodiglycol and b) thiodiglycol sulfone (found in C47 and C48).

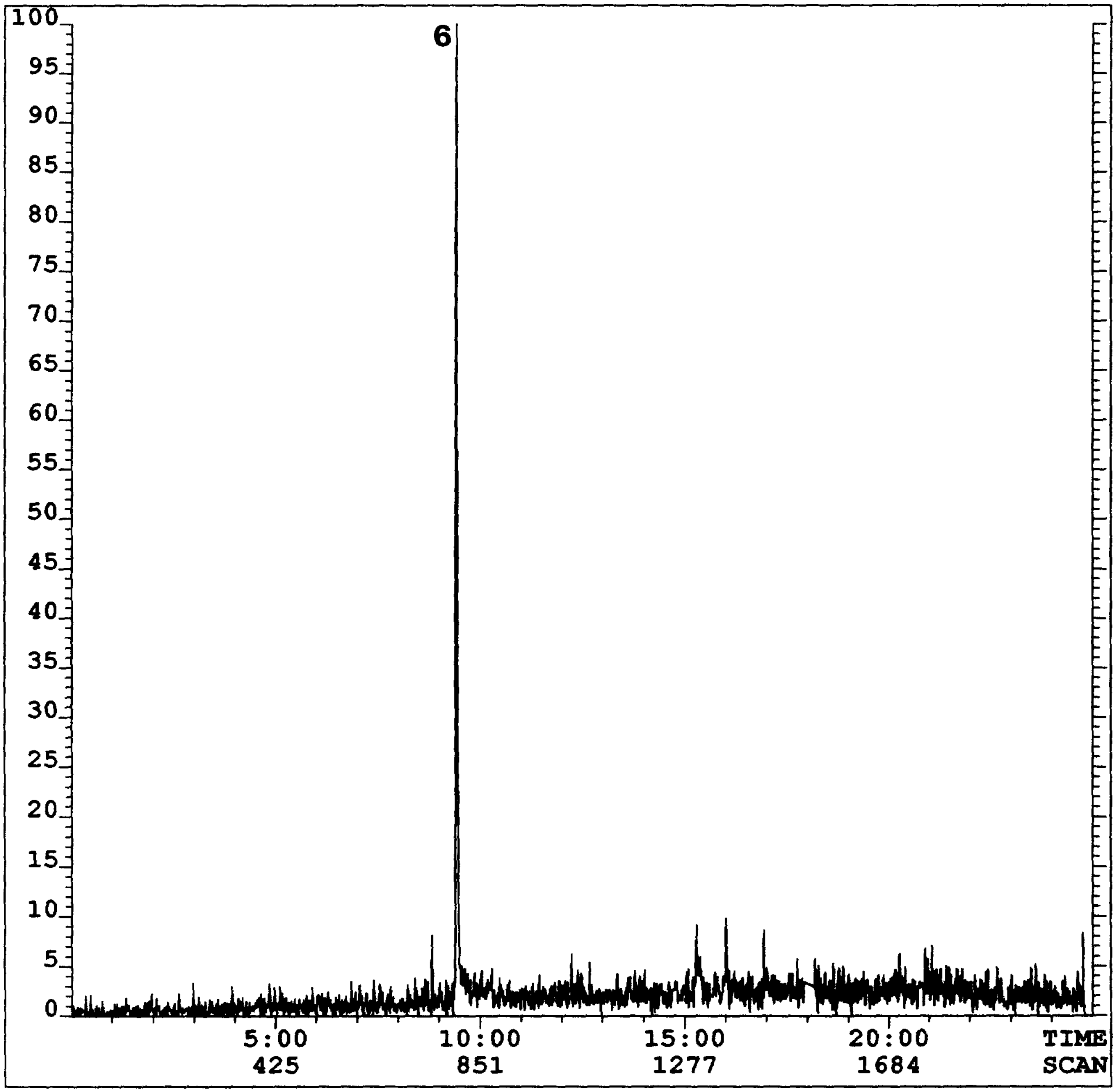

Figure 21

Collisional activated dissociation capillary column GC-MS/MS chromatogram for the daughters of m/z 122 of the acetonitrile extract of C48 concrete sample. Numbered components are listed in Table 8.

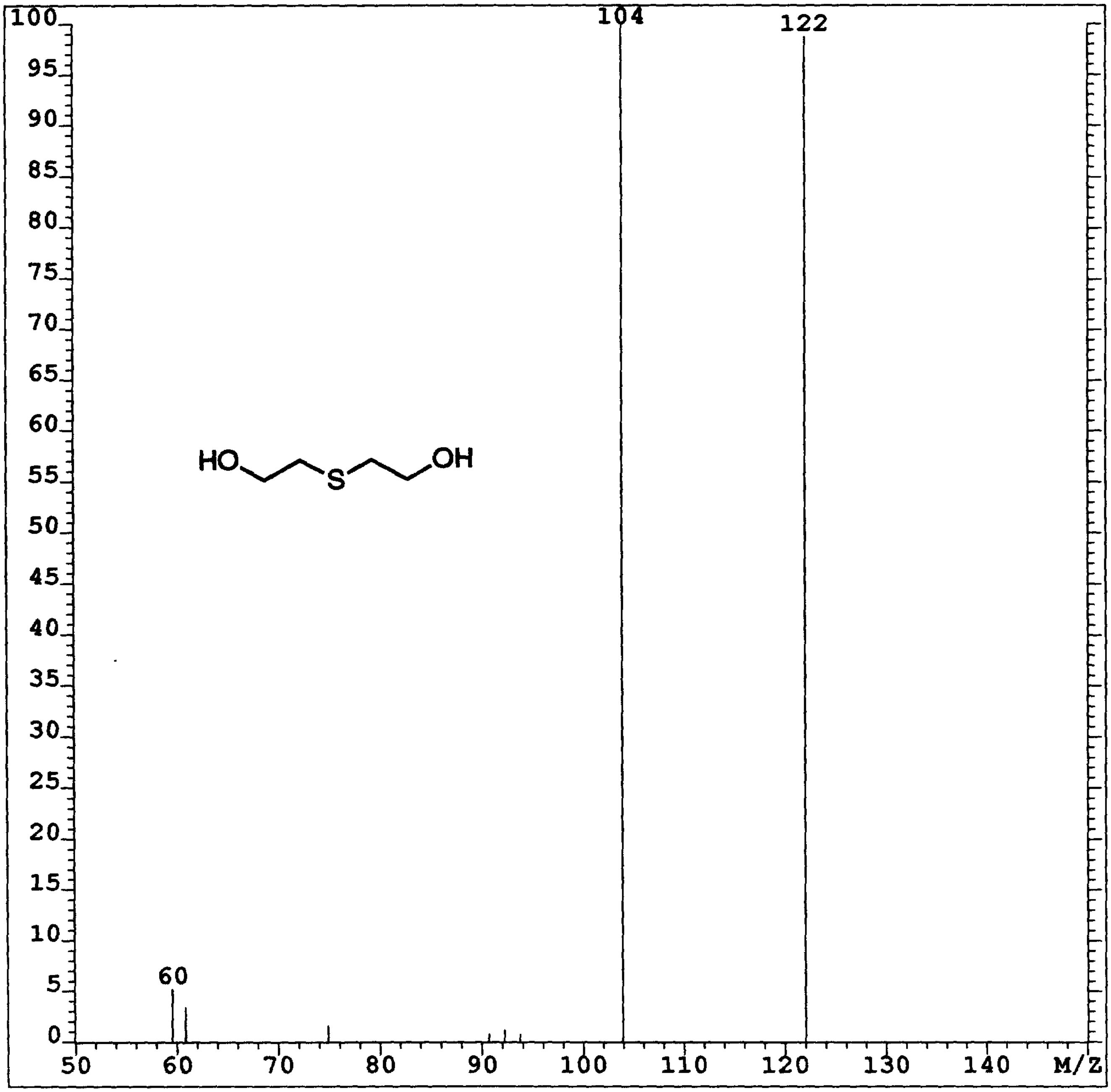

Figure 22

Daughter spectrum (m/z 122) of thiodiglycol (found in C47 and C48).

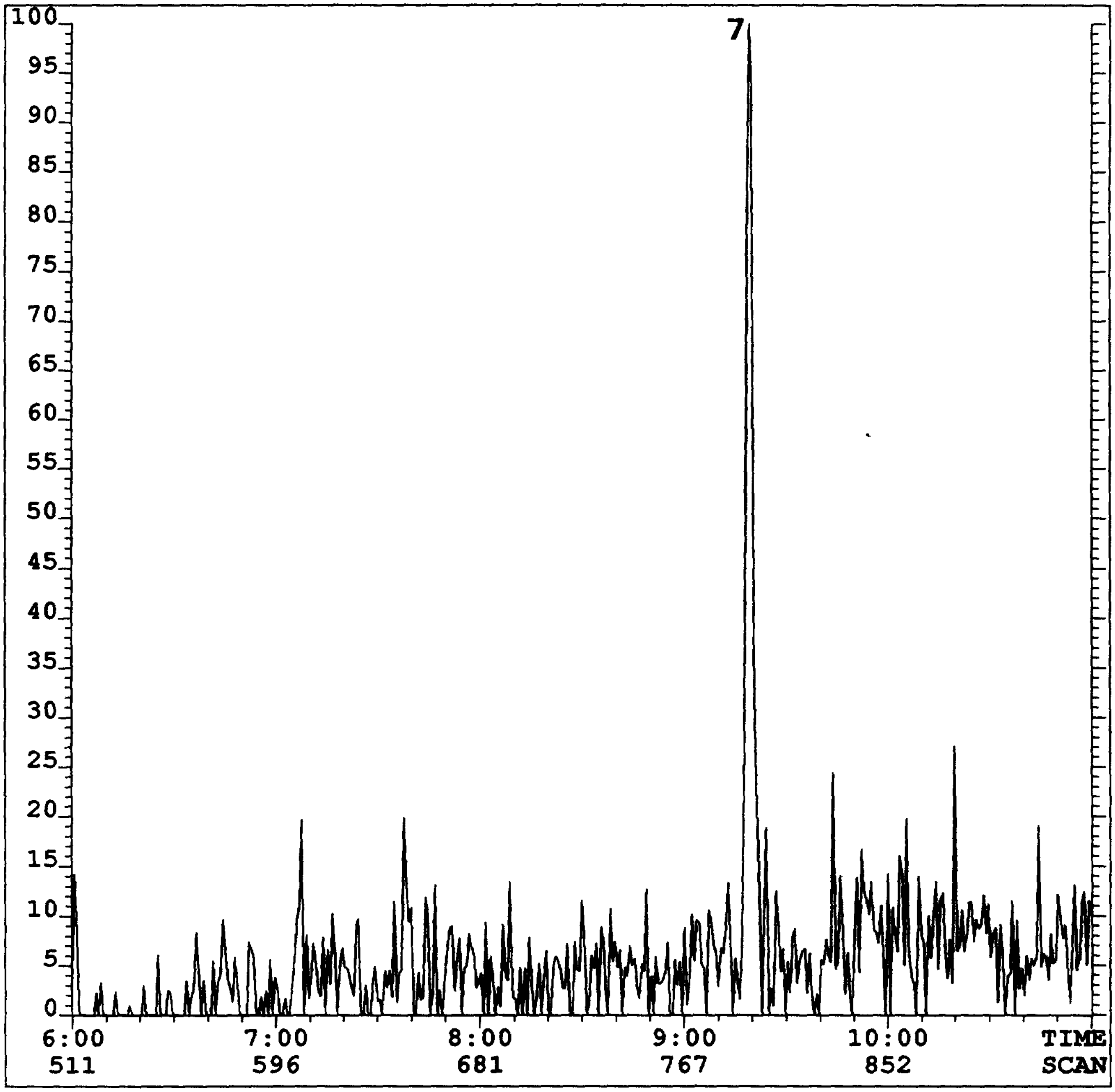

Figure 23

Collisional activated dissociation capillary column GC-MS/MS chromatogram for the daughters of m/z 111 of the acetonitrile extract of C48 concrete sample. Numbered components are listed in Table 8.

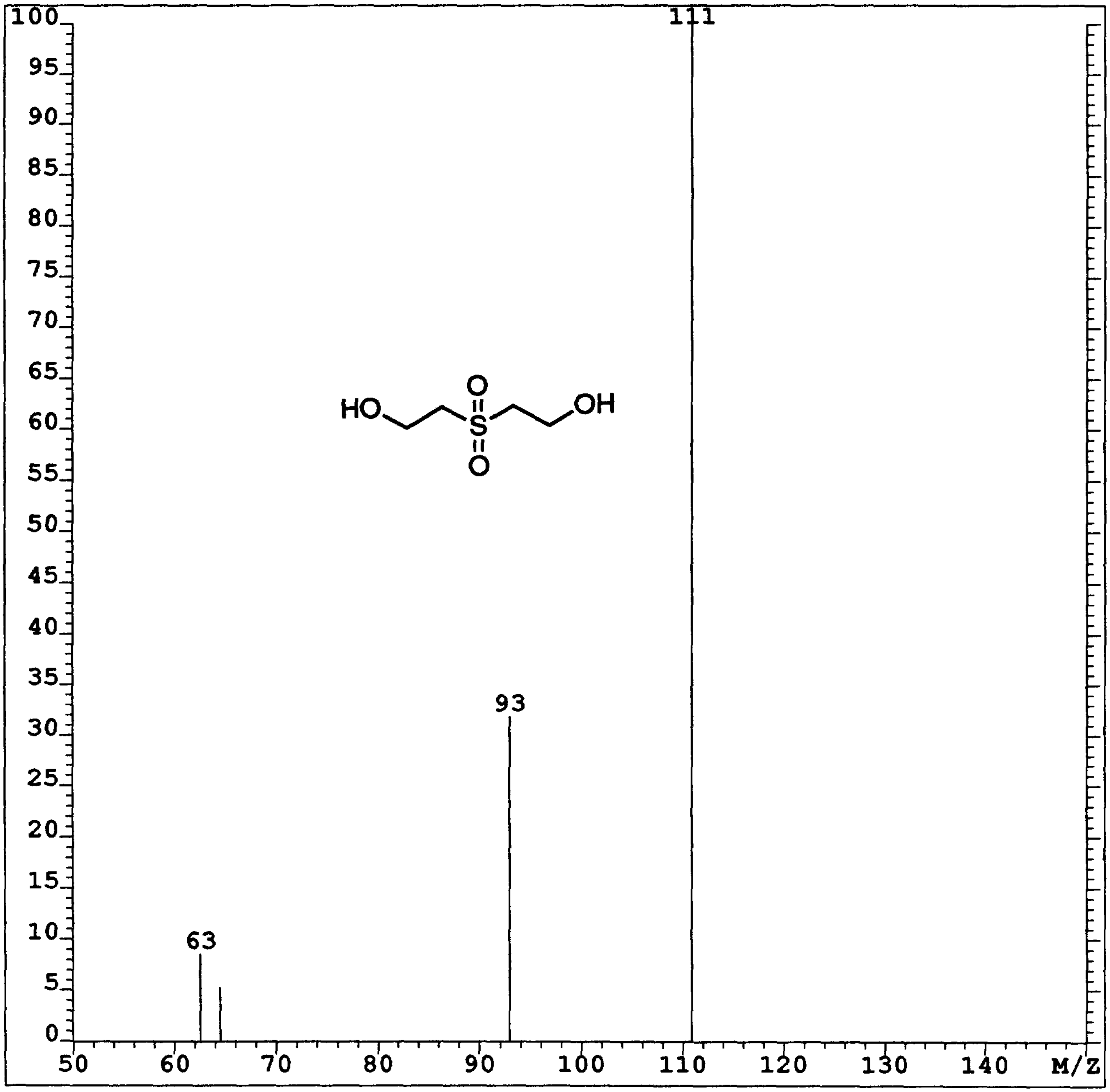

Figure 24

Daughter spectrum (m/z 111) of thiodiglycol sulfone (found in C47 and C48).

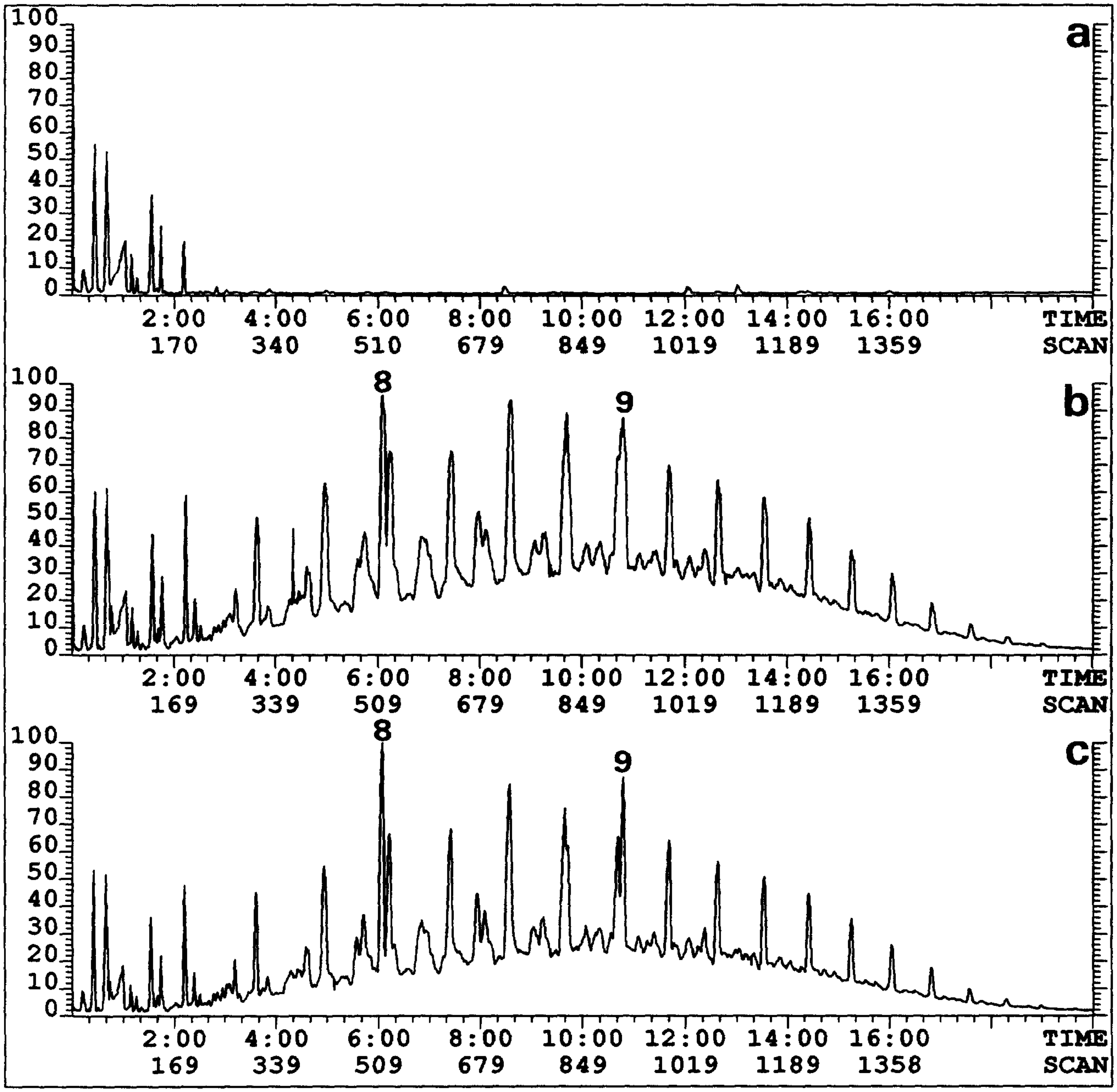

Figure 25

Capillary column GC-MS (EI) total-ion-current (400 to 40 u) chromatogram of trimethylsilylated acetonitrile extract of a) C46, b) C47 and c) C48 concrete samples. Numbered components are listed in Table 8.

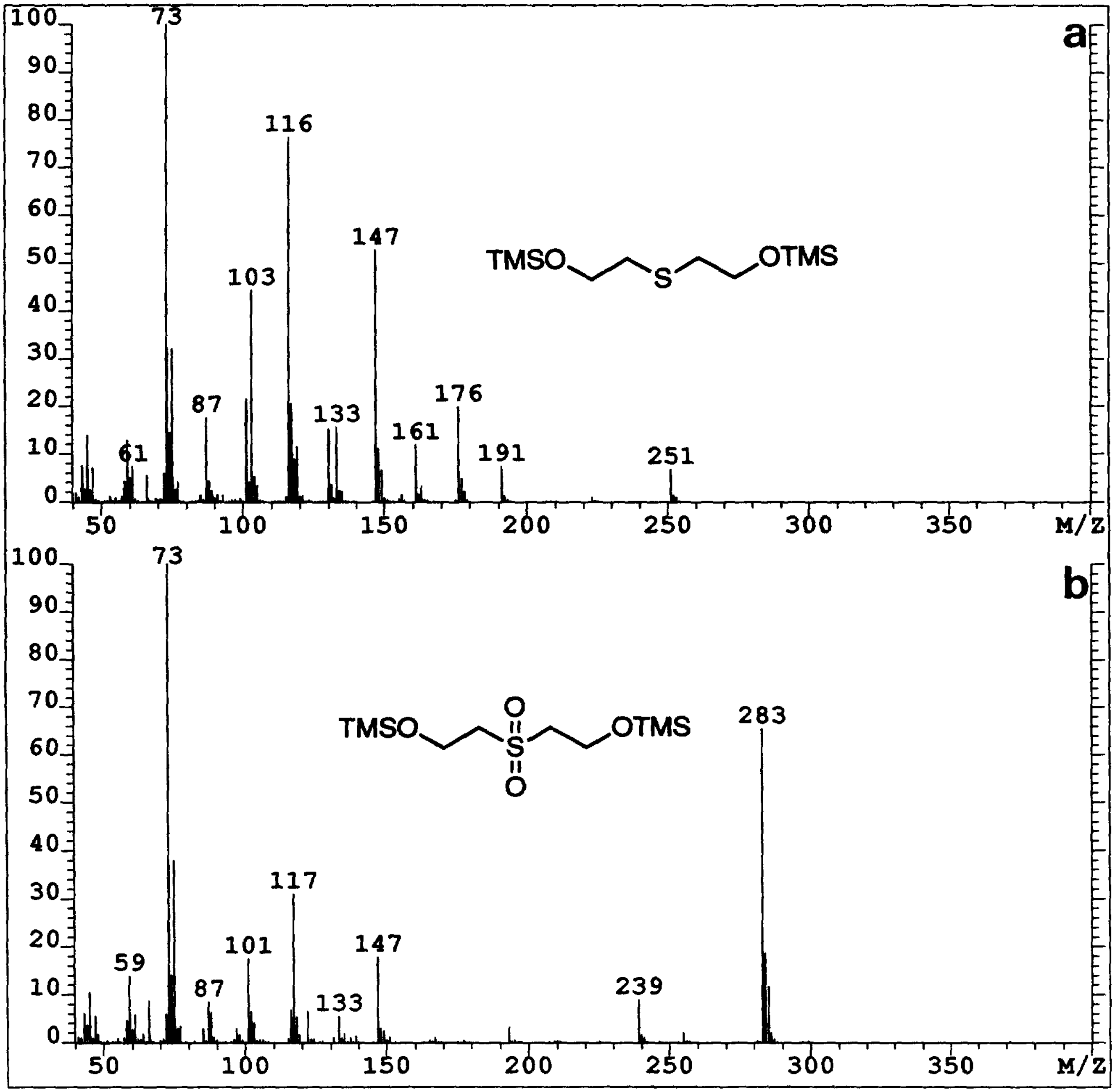

Figure 26

Electron impact mass spectra of a) di-TMS derivative of thiodiglycol and b) di-TMS derivative of thiodiglycol sulfone (found in C47 and C48).

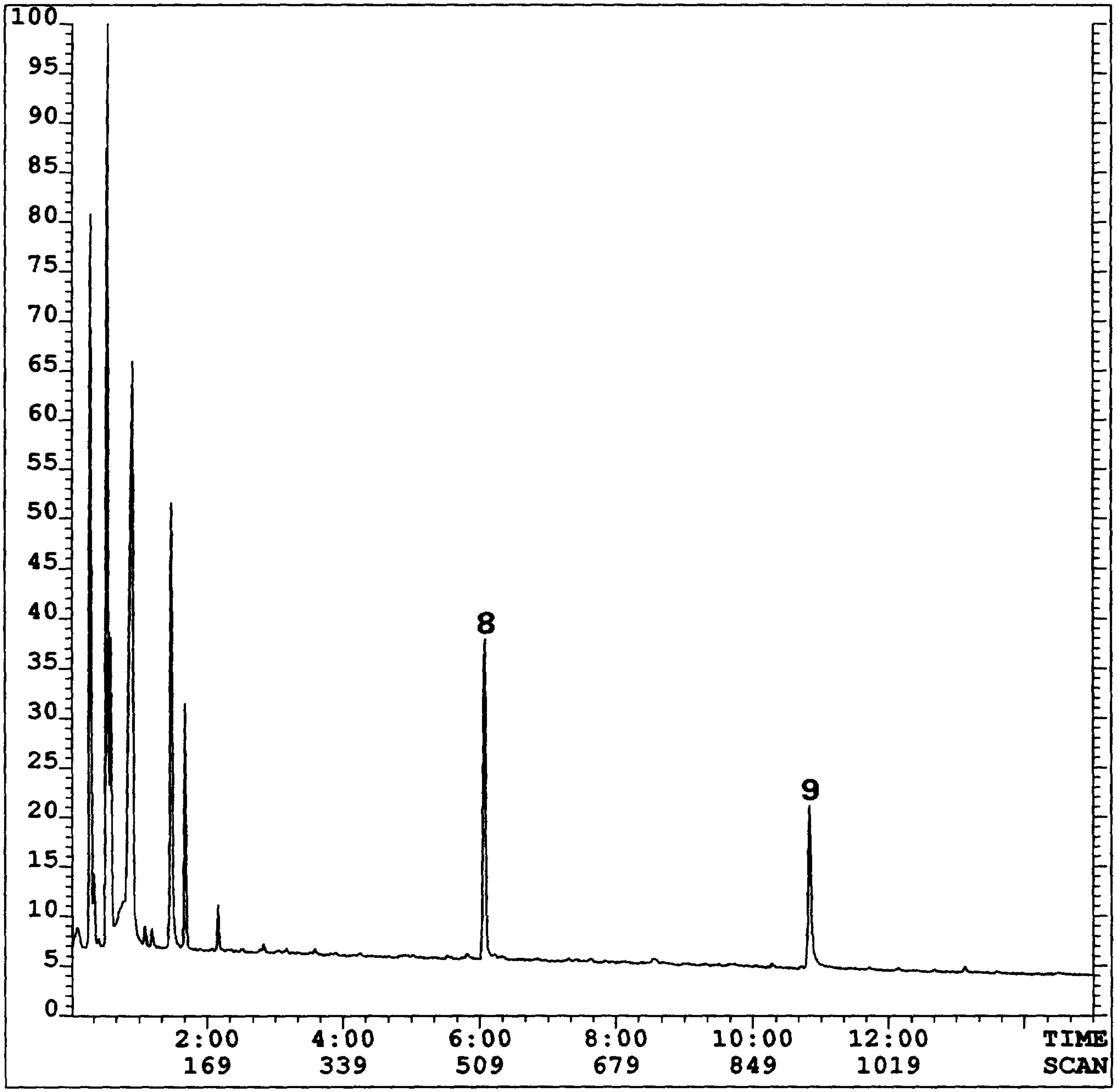

Figure 27

Capillary column GC-MS (ammonia CI) total-ion-current (400 to 60 u) chromatogram of trimethylsilylated acetonitrile extract of C48 concrete sample. Numbered components are listed in Table I.

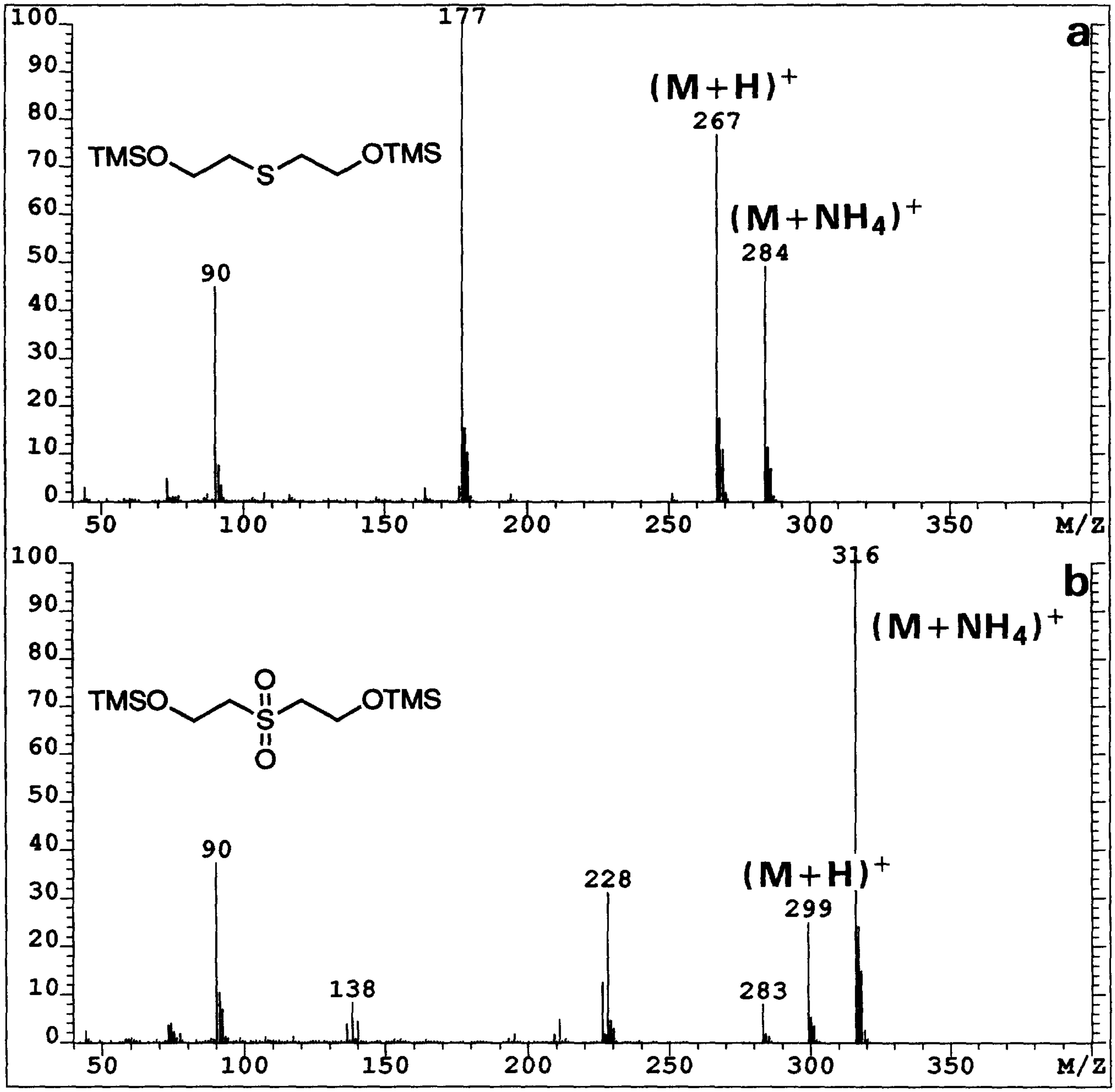

Figure 28

Ammonia chemical ionization mass spectra of a) di-TMS derivative of thiodiglycol and b) di-TMS derivative of thiodiglycol sulfone (found in C47 and C48).

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591 Sample handling and analysis procedures have been developed for the verification of soman, sarin, triethyl phosphate and mustard in contaminated paint, concrete, and rubber. Triethyl phosphate and mustard were generally recovered from the sample media with efficiencies greater that 65%. Soman was usually recovered with slightly less efficiency (20% to 60%) and sarin was recovered in the lowest yield (5% to 40%). Each extract was quantitatively analysed by capillary column GC-FID and confirmation of all spiked chemical agents was performed by capillary column GC-MS. The developed methods were successfully applied during the 1991 United Nations sponsored round robin analytical exercise. Defence Research Establishment Suffield, the designated Canadian laboratory, positively confirmed all the spiked mustard related compounds in the samples provided for round robin analysis and did not detect any artifacts or false positives in the samples.))

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