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CANADIAN CONTRIBUTOR TO THE 1991 UNITED NATIONS ROUND ROBIN ANALYTICAL VERIFICATION EXERCISE

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by

P.A. D'Agostino, J.R. Hancock, C.A. Boulet, L.R. Provost,
C.E. Lough, R.P. Hicken and A.S. Hansen

65 pgs

March 1993

DEFENCE RESEARCH ESTABLISHMENT SUFFIELD, RALSTON, ALBERTA

Canada

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ABSTRACT

Nine samples, typical of those taken during inspection of a military facility, were received by Defence Research Establishment Suffield as part of a United Nations sponsored international round robin analytical exercise designed to evaluate laboratory capabilities. This report summarizes Canada's contribution to the round robin analytical verification exercise. Canada confirmed the presence of all the spiked CW relevant compounds, including mustard and mustard related compounds following analysis of the provided samples by capillary column GC-MS, GC-MS/MS, GC-FTIR, GC-FID and GC-FPD.

RÉSUMÉ

Dans le cadre d'un exercice d'analyse, parrainé par les Nations-Unies et destiné à évaluer la capacité des laboratoires par analyses inter-laboratoires à l'échelle internationale, le Centre de recherche pour la défense de Suffield a reçu neuf échantillons caractéristiques de ceux prélevés au cours de l'inspection d'installations militaires. On résume, dans ce rapport, la contribution du Canada à cet exercice de vérification analytique. Le Canada a confirmé la présence de tous les composés utilisables comme agents chimiques qui avaient été additionnés aux échantillons, dont l'ypérite et les composés apparentés, après l'analyse des échantillons fournis par CG sur colonne capillaire - SM, par CG-SM/SM, par CG - IRTF et par CG - DPF.

INTRODUCTION

Nine samples, typical of those taken during inspection of a military facility, were received by Defence Research Establishment Suffield (DRES) as part of a United Nations sponsored round robin analytical exercise. The participating laboratories in Canada, Australia, China, USSR (2 laboratories), Finland, France, Germany, The Netherlands, Norway, Sweden, 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.

All participating laboratories received their samples about one week prior to the exercise and were asked to refrigerate the samples until the official start of the exercise, October 21, 1991. DRES began analysis of the round robin samples on October 21, 1991 and finished all analyses on October 30, 1991. Solvent extracts of the painted panels (P46, P47, P48), rubber (R46, R47, R48) and concrete (C46, C47, C48) samples were analysed by capillary column GC-MS (EI and ammonia CI), GC-MS/MS, GC-FTIR, GC-FPD (simultaneous S/P) and GC-FID. All CW relevant compounds found in the set of nine samples were confirmed by comparing acquired chromatographic/spectrometric data with that obtained for authentic standards. Trimethylsilylation was performed on all sample extracts in order to identify nonvolatile components. All chromatographic analyses were completed by the five analysts in seven working days (175 man hours). Report writing and figure preparation was undertaken by two persons on October 31, 1991 and was completed by November 4, 1991 (3 working days or 50 man hours).

This report summarizes Canada's contribution to the 3rd United Nations round robin analytical exercise. Table I lists the CW relevant compounds found during analysis of the painted panels, rubber and concrete samples provided for analysis. The Experimental portion of this report summarizes the instrumental methods used, the semi-quantitation methods employed and the detection limits of the methods. The sample handling details, chromatographic/spectrometric results and compounds identified during analysis of each sample are provided in the Results section. A summary of the data acquired and the general analytical philosophy followed is presented in the Discussion.

EXPERIMENTAL

A semi-quantitative estimate of the amount (μg) of CW relevant components in each sample was calculated using the FID and FPD (S) responses for mustard.

a) Instrumental Conditions

GC-MS Conditions	
Country	Canada
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	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	
Country	Canada
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)	1000
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-FTIR CONDITIONS	
Country	Canada
IR Spectrometer	Nicolet 730
Resolution	8 cm^{-1}
Light Pipe Dimensions	15 cm x 1 mm
Detector Type	MCT
Scan Rate	approx. 2 scans/s
Accumulated Scans/Spectrum	nominally 10 scans
Wavenumber Range	4000 to 600
Make-up Gas Flow Rate in Light Pipe	0.3 mL/min
Light Pipe Temperature	260°C
Detection Limit	1 ng/component (based on a 50 µL injection)
GC Parameters	
Instrument:	Hewlett Packard 5890
Column:	J&W 15 m x 0.25 mm ID DB-1701 (0.25 µm)
Carrier Gas:	Helium approx. 20 cm/s
Temperature Program:	40°C then 10°C/min to 250°C (20 min)
Injection Mode:	On-column at 40°C

Comments:

Large injections (50 µL) using an 8 m retention gap were employed to improve FTIR sensitivity.

Temperature programming was started following complete elution of the solvent (typically 20 minutes following large volume injection).

GC-FPD CONDITIONS	
Country:	Canada
Instrument:	Varian 3700
Column:	J&W 15m x 0.53mm ID DB-1701 (1.0 μm)
Detector:	FPD (simultaneous S/P)
Carrier Gas:	Helium 40 cm/s
Temperature Program:	50°C (2 min) then 10°C/min to 280°C (5 to 20 min)
Injection Mode	Flash vaporization at 150°C
Detection Limit	FPD (S) 1 ng/component FPD (P) 20 pg/component

GC-FID Conditions	
Country:	Canada
Instrument:	Hewlett Packard 5890
Column:	J&W 15m x 0.32mm ID DB-1701 (0.25 μm)
Detector:	FID
Carrier Gas:	Helium approx. 40 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	0.5 ng/component

RESULTS

a) Painted Panels (P46, P47, P48)

Sample Handling

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 bis(trimethylsilyl)-trifluoroacetamide (BSTFA), 100 μL pyridine and 300 μL of hexane extract (P46) in a 1.8 mL screw-capped (Teflon 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. Trimethylsilylation (TMS) was performed by combining 100 μL BSTFA, 100 μL pyridine and 300 μL of this second extract in a 1.8 mL screw-capped (Teflon 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.

Results

Figures 1 and 2 illustrate capillary column GC-FID and GC-MS (EI) chromatograms obtained during analysis of 1 μL aliquots of the hexane extract of P46, P47 and P48. Figures 3 and 4 illustrate EI-MS for the three CW relevant compounds, sesquimustard, bis[(2-

chloroethylthio)ethyl]ether and 2-chloroethyl (2-chloroethoxy)ethyl sulfide found in the hexane extracts of P46 and P48. P47 did not contain compounds of CW relevance and appears to be a control. The molecular weight of each of these sulfur vesicants were confirmed by the presence of $(M+NH_4)^+$ ions during ammonia CI-MS analysis (Figures 5 and 6). Additional 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 7 and 8). The presence of sulfur in each of these vesicants was confirmed during GC-FPD (S) (Figure 9) and FTIR spectra were obtained for all three compounds (Figure 10).

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

b) Rubber (R46, R47, R48)

Sample Handling

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) were 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 (R46) in a 1.8 mL screw-capped (Teflon 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.

Results

Figures 11 and 12 illustrate capillary column GC-FID and GC-MS (EI) chromatograms obtained during analysis of 1 μL aliquots of the hexane extract of R46, R47 and R48. Figure 13 illustrates EI-MS for the two CW relevant compounds, mustard and bis(2-chloroethyl)disulfide found in the acetonitrile extracts of R46 and R47. R48 did not contain compounds of CW relevance and appears to be a control. The exact mass of the molecular ion for both compounds was determined 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

Additional MS/MS data were obtained by acquiring the daughter spectrum of m/z 123 (an ion common to sulfur vesicants) for mustard (Figures 14 and 15). The presence of sulfur in each of these compounds was confirmed during GC-FPD (S) (Figure 16) and FTIR data were obtained for mustard (Figure 17).

No CW relevant compounds were detected during analysis of the trimethylsilyl extract. The 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 difficult 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.

c) Concrete (C46, C47, C48)

Sample handling

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) were 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 (Teflon 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.

Results

Figures 18 and 19 illustrate capillary column GC-FID and GC-MS (EI) chromatograms obtained during analysis of 1 μL aliquots of the acetonitrile extracts of C46, C47 and C48. Figure 20 illustrates EI-MS 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. 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 21). Additional MS/MS data were obtained by acquiring the daughter spectrum of m/z 122 (molecular ion) for thiodiglycol (Figures 22 and 23) and the daughter spectrum of m/z 111 for thiodiglycol sulfone (Figures 24 and 25).

Figures 26 and 27 illustrate capillary column GC-FID and GC-MS (EI) chromatograms obtained during analysis of 1 μL aliquots of the derivatized acetonitrile extract of C46, C47 and C48. Figure 28 illustrates EI-MS for the di-TMS derivatives of thiodiglycol and thiodiglycol sulfone found in the acetonitrile extracts of C47 and C48. C46 did not contain compounds of CW relevance and appears to be a control. 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 29 and 30).

The presence of sulfur in each of these compounds and their di-TMS derivatives was confirmed during GC-FPD (S) (Figures 31 and 32) and FTIR data were obtained for thiodiglycol, thiodiglycol sulfone and their di-TMS derivatives (Figures 33 and 34).

Thiodiglycol, thiodiglycol sulfone and their di-TMS derivatives chromatographic/spectrometric data were confirmed with available authentic standards.

DISCUSSION

DRES adopted the following general philosophy for the analysis of the nine samples received for analysis. The following steps indicate the order of analysis at DRES:

a) Capillary column GC-FID was used to screen solvents (e.g., hexane, dichloromethane and acetonitrile) used for extraction of samples. Capillary column GC-FID and GC-FPD (and when required GC-MS) was employed to screen solvent blank extracts to ascertain the levels of potential interference and the presence of any CW relevant or unusual compounds.

b) Standard mixtures of CW relevant compounds were analysed daily by all the techniques to assure both chromatographic and spectrometric quality prior to sample extract analyses.

c) One sample (or group of samples) at a time was extracted and analysed by capillary column GC with MS, MS/MS, FTIR, FID and FPD (simultaneous S/P) detection. The order was painted panels (October 21, 1991) followed by concrete (October 22, 1991) and rubber (October 23, 1991) samples.

d) CW relevant compounds 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 published data (E. R. J. Wils, Fresenius Z. Anal. Chem. 321, 471-474 (1985)). CI-MS and EI-MS data for the sulfur containing vesicants found in the samples have also been previously published (P. A. D'Agostino and L. R. Provost, Biomed. Environ. Mass Spectrom., 15, 553-564 (1988)). Annex A contains the

Synthesis and Reference Spectroscopic Data for Tniodiglycol Sulfone.

e) Trimethylsilylation of sample extracts was performed to aid in the identification of nonvolatile degradation products.

f) All sample extract components were screened for the presence of sulfur and phosphorus atoms by GC-FPD. No phosphorus containing compounds were detected.

g) Capillary column GC-MS (EI) chromatograms of all extracts of the samples were screened for the presence of the common CW agents GB, GD, GA, GF, VX, H, Q and T using reconstructed ion current chromatograms. Minor or trace sample component EI mass spectra were checked to be sure that they did represent, in the best opinion of the laboratory, scheduled compounds. Only mustard related compounds were found in the samples. Table II lists the compounds identified in the samples and the techniques used to confirm the presence of each component.

h) A semi-quantitative estimate of major sample components was obtained using capillary column GC-FID and/or GC-FPD data. Table III lists the semi-quantitative results of the sample analyses.

i) The sample detection limit of GC-FTIR was greatly enhanced over previous round robin exercises by the use of an 8 m retention gap. This allowed larger volume (50 μL) injections.

j) The high specificity of GC-MS/MS and GC-MS (ammonia CI) is clearly demonstrated by comparison of sample extract chromatograms with either GC-FID or GC-MS (EI) chromatograms.

CONCLUSIONS

Solvent extracts of the painted panels, concrete and rubber samples circulated for analysis were analysed by capillary column GC-MS (EI and ammonia CI), GC-MS/MS, GC-FTIR, GC-FPD (simultaneous S/P) and GC-FID. Trimethylsilylation was performed on all sample extracts in order to identify non-volatile degradation components.

Canada identified and confirmed the presence of the chemical warfare relevant compounds, sesquimustard, bis[(2-chloroethylthio)ethyl]ether and 2-chloroethyl (2-chloroethoxy)ethyl sulfide in the hexane extracts of two of the painted panel extracts. The molecular weight of each of these sulfur vesicants were confirmed by the presence of $(M+NH_4)^+$ ions during ammonia CI-MS analysis. Additional 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.

Two chemical warfare relevant compounds, mustard and bis(2-chloroethyl)disulfide were found in the acetonitrile extracts of two rubber samples. The exact mass of the molecular ion for both compounds was determined at 10,000 resolution during GC-MS (EI) analysis. Additional MS/MS data were obtained by acquiring the daughter spectrum of m/z 123 (an ion common to sulfur vesicants) for mustard. FTIR data were not obtained for bis(2-chloroethyl)disulfide.

Two chemical warfare relevant compounds associated with mustard degradation, thiodiglycol and thiodiglycol sulfone, were found in the acetonitrile extracts of two concrete samples. 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. Additional MS/MS data were obtained by acquiring the daughter spectrum of m/z 122 (molecular ion) for thiodiglycol and the daughter spectrum of m/z 111 for thiodiglycol sulfone. The trimethylsilyl (TMS) derivatives of thiodiglycol and thiodiglycol sulfone were confirmed by capillary column GC-MS analysis of the concrete acetonitrile extracts. The presence of sulfur in each of these compounds and their di-TMS derivatives was confirmed during GC-FPD, and FTIR data were obtained for thiodiglycol, thiodiglycol sulfone and their di-TMS derivatives.

Thiodiglycol sulfone was synthesized to provide an authentic reference standard. The EI-MS data obtained for this synthesized standard and the di-TMS derivative of thiodiglycol sulfone agreed with published data. CI-MS and EI-MS data for mustard and other sulfur containing vesicants found in the samples also agreed with published data.

Table II summarizes the mustard related compounds confirmed by DRES in the painted panels, concrete and rubber samples. Only five of the participating laboratories including Canada, identified all the spiked compounds. In addition to the spiked compounds reported, some laboratories also reported false positives, or the presence of compounds which were not deliberately spiked in the samples.

Table I: Chemical Warfare and Related Compounds Identified in the Third UN Round Robin

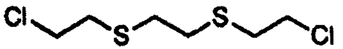
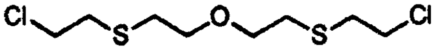
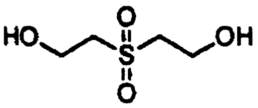
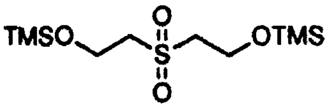
Chrom. Peak No.	STRUCTURE	Mol. Wt.	CAS No.
1.	 2-chloro(2-chloroethoxy)ethyl sulfide	202	114811-38-0
2.	 sesquimustard	218	3563-36-8
3.	 bis[(2-chloroethylthio)ethyl]ether	262	63918-89-8
4.	 mustard	158	505-60-2
5.	 bis(2-chloroethyl)disulfide	190	1002-41-1
6.	 thiodiglycol	122	111-48-8
7.	 thiodiglycol sulfone	154	2580-77-0
8.	 di-TMS der. of thiodiglycol	266	
9.	 di-TMS der. of thiodiglycol sulfone	298	

TABLE II. Techniques Used to Identify Compounds in Samples from the Third Round Robin Exercise

Compound Name	Peak No.	CAS Registry Number	TECHNIQUE						
			GC-FID	GC-MS (EI)	GC-MS (EI) (10,000)	GC-MS/MS (EI)	GC-MS (NH_3-CI)	GC-FPD(S)	GC-FTIR
2-Chloro(2-chloroethoxy)ethyl sulfide	1	114811-38-0		x[a]		x	x	x	x
Sesquimustard	2	3563-36-8	x	x		x	x	x	x
Bis[(2-chloroethylthio)ethyl]ether	3	63918-89-8	x	x		x	x	x	x
Mustard	4	505-60-2	x	x	x	x		x	x
Bis(2-chloroethyl)disulfide	5	1002-41-1	x	x	x			x	
Thiodiglycol	6	111-48-8	x	x		x	x	x	x
Thiodiglycol sulfone	7	2580-77-0				x	x	x	x
di-TMS derivative of thiodiglycol	8		x	x			x	x	x
di-TMS derivative of thiodiglycol sulfone	9		x	x			x	x	x

[a] - interference ions detected with component

TABLE III. Semi-Quantitative Estimates of Compounds Identified

Compound Name	SEMI-QUANTITATIVE ESTIMATES (μg)*																	
	P46		P47		P48		R46		R47		R48		C46		C47		C48	
	FID	FPD	FID	FPD	FID	FPD	FID	FPD	FID	FPD	FID	FPD	FID	FPD	FID	FPD	FID	FPD
2-Chloro(2-chloroethoxy) ethyl sulfide																		
Sesquimustard	31	23	-	-	25	25												
Bis[(2-chloroethylthio)ethyl] ether	47	32	-	-	42	33												
Mustard							12	12	15	16	-	-						
Bis(2-chloroethyl)disulfide							9.5	13	11	16	-	-						
Thiodiglycol													-	-	125[a]	70	155[a]	70
Thiodiglycol sulfone													-	-		20		35
di-TMS derivative of thiodiglycol													-	-	246		278	
di-TMS derivative of thiodiglycol sulfone													-	-	171		196	

[a] - coeluting interferences

\- Blank

* - all semi-quantitative estimates were based on mustard response

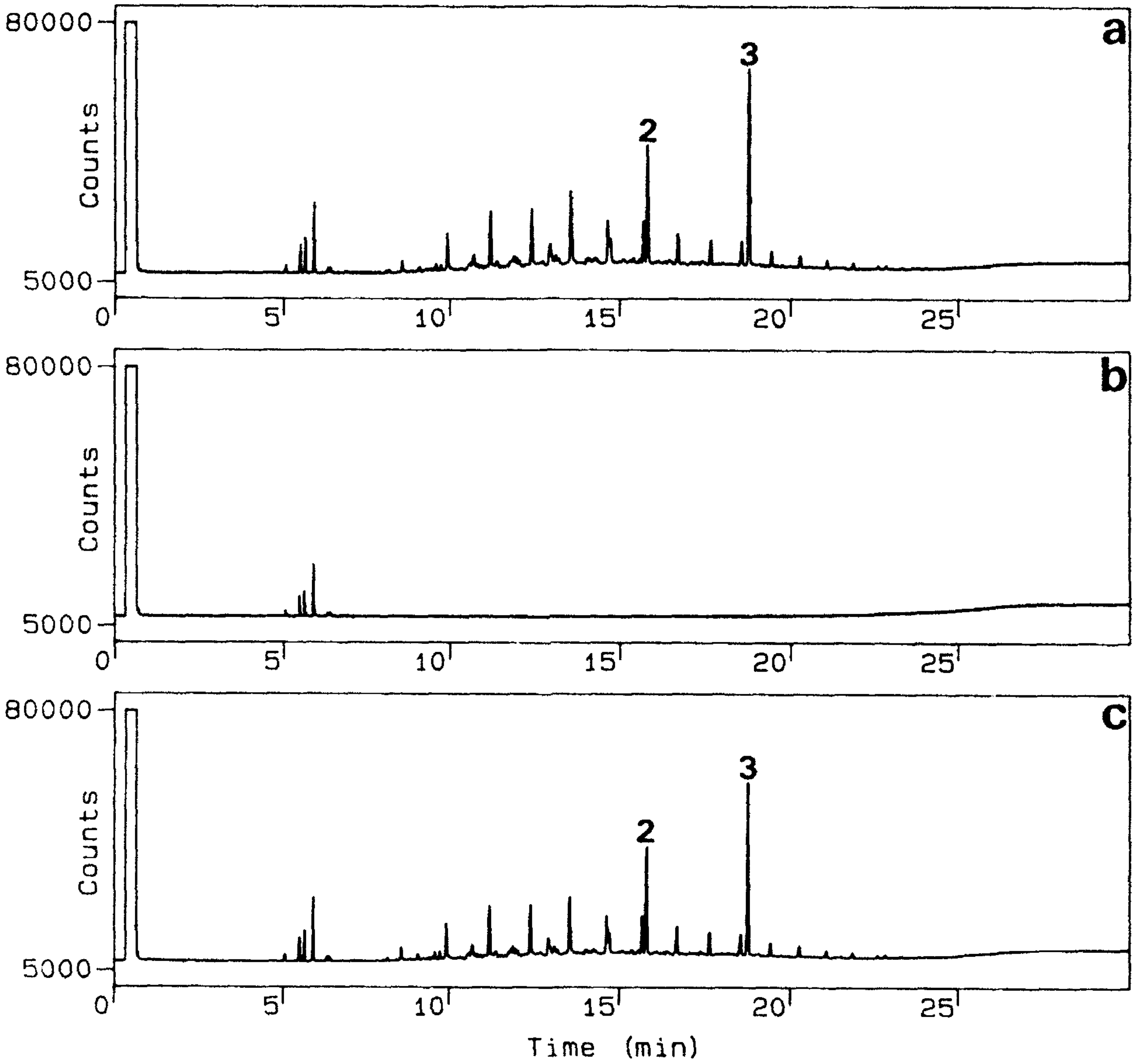


Figure 1: Capillary column GC-FID chromatogram of the hexane extract of a) P46, b) P47 and c) P48 painted panels. Numbered components are listed in Table I.

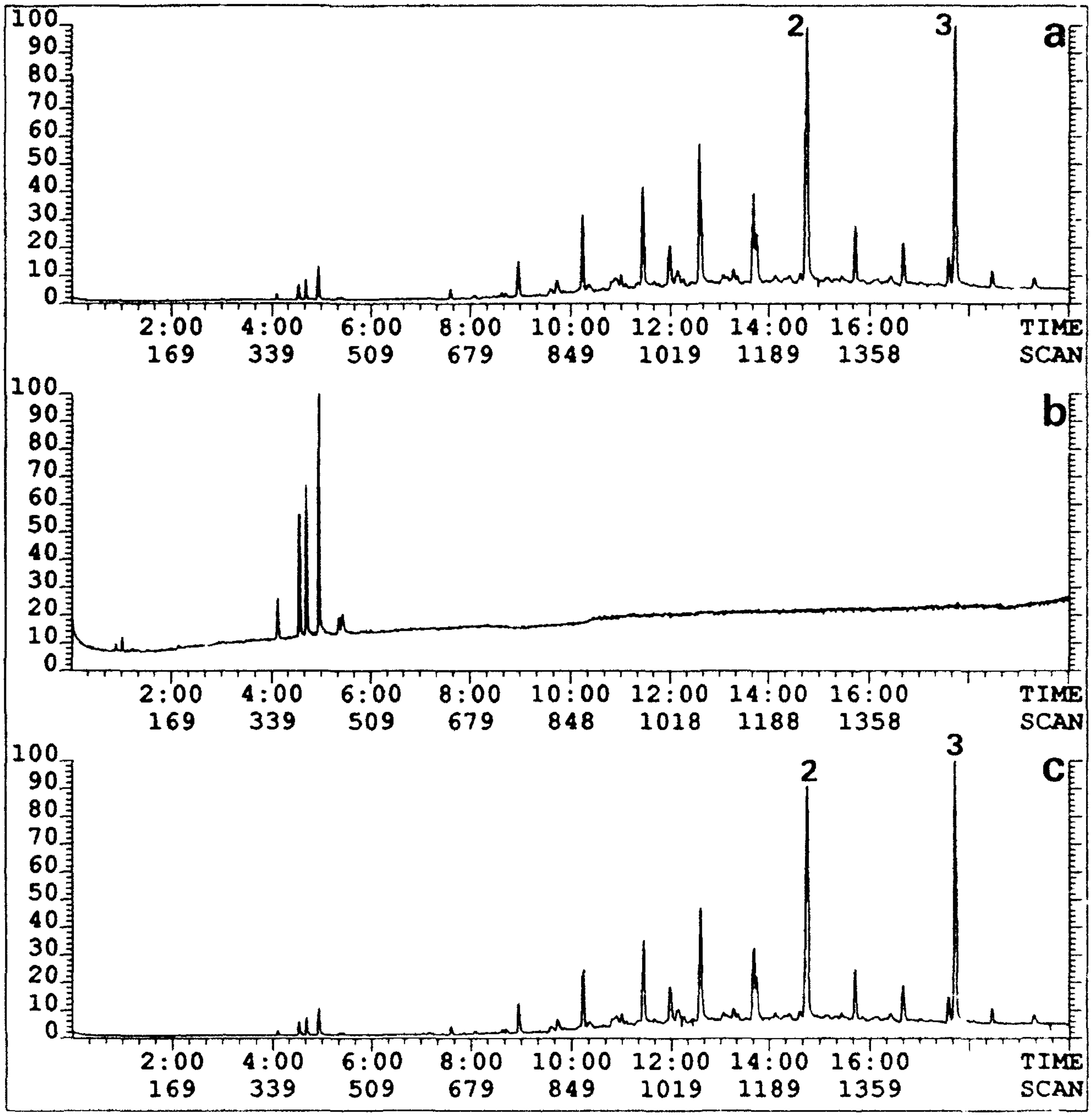


Figure 2: Capillary column GC-MS (EI) total-ion-current (400 to 40 u) chromatogram of the hexane extract of a) P46, b) P47 and c) P48 painted panels. Numbered components are listed in Table I.

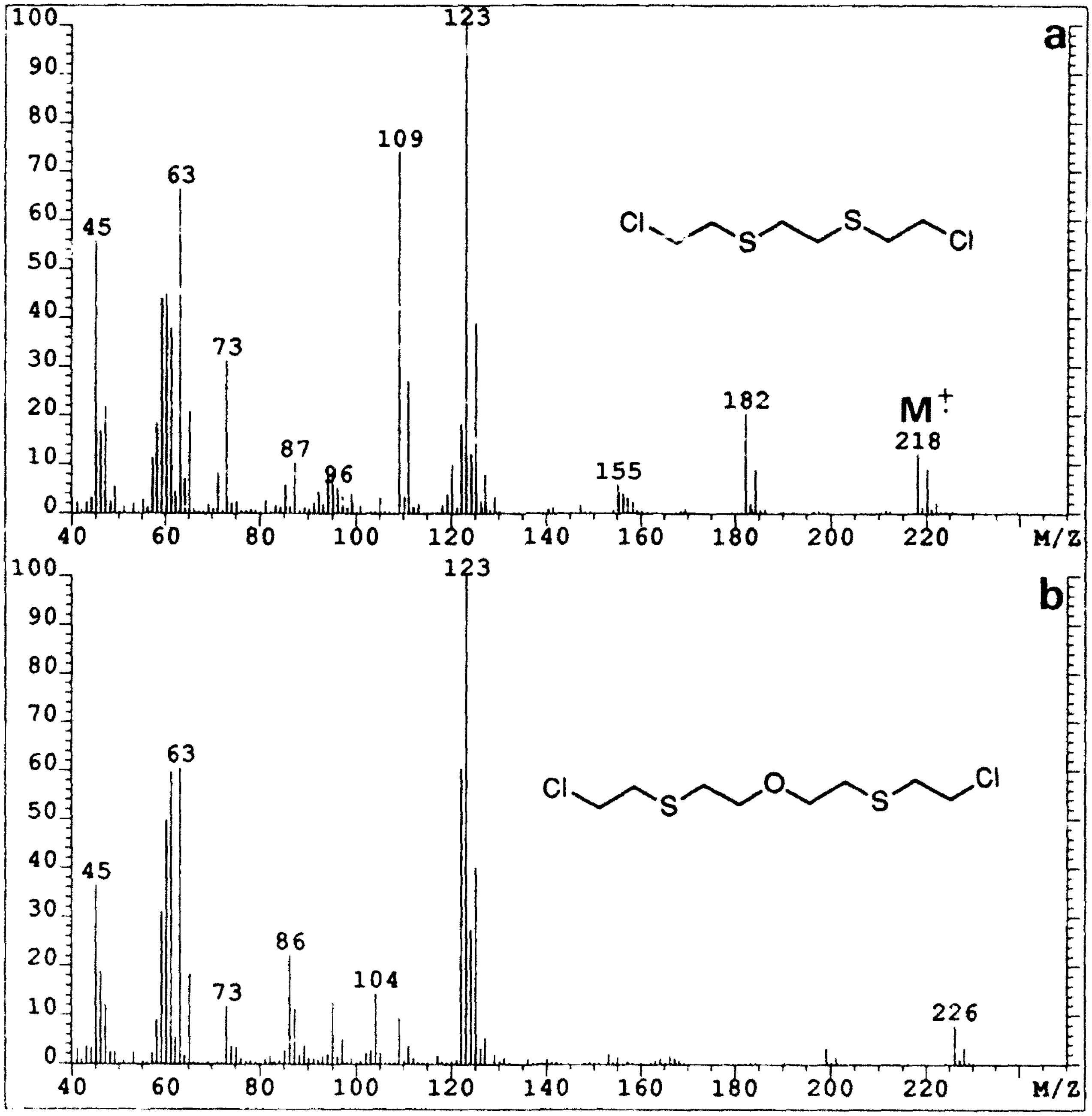


Figure 3: Electron impact mass spectra of a) sesquimustard and b) bis[(2-chloroethylthio)ethyl]ether (found in P46 and P48).

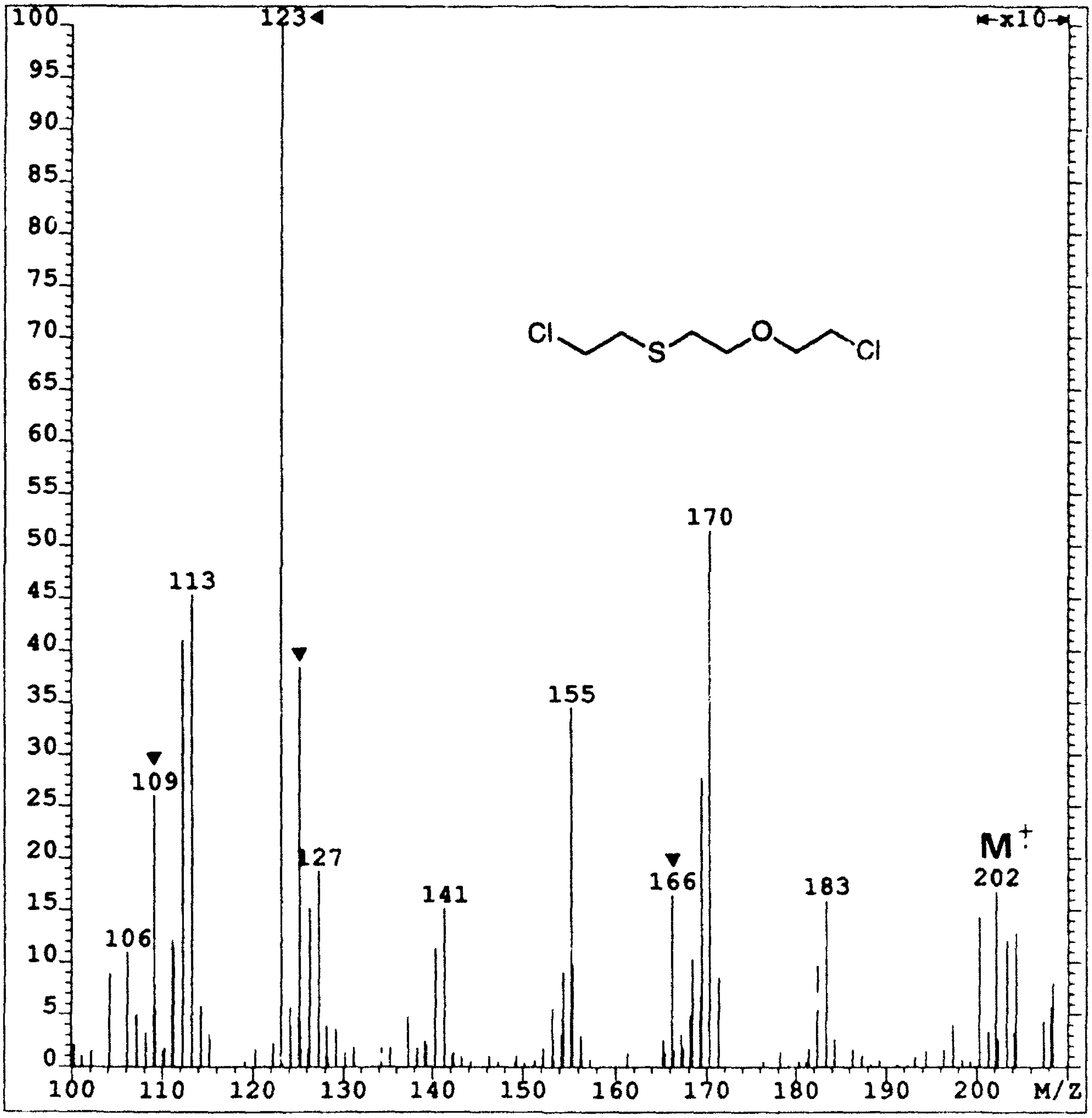


Figure 4: Electron impact mass spectrum of 2-chloroethyl (2-chloroethoxy)ethyl sulfide (found in P46 and P48). This minor component co-eluted with another compound and only the ions marked with a triangle and the molecular ion at m/z 202 were due to 2-chloroethyl (2-chloroethoxy)ethyl sulfide.

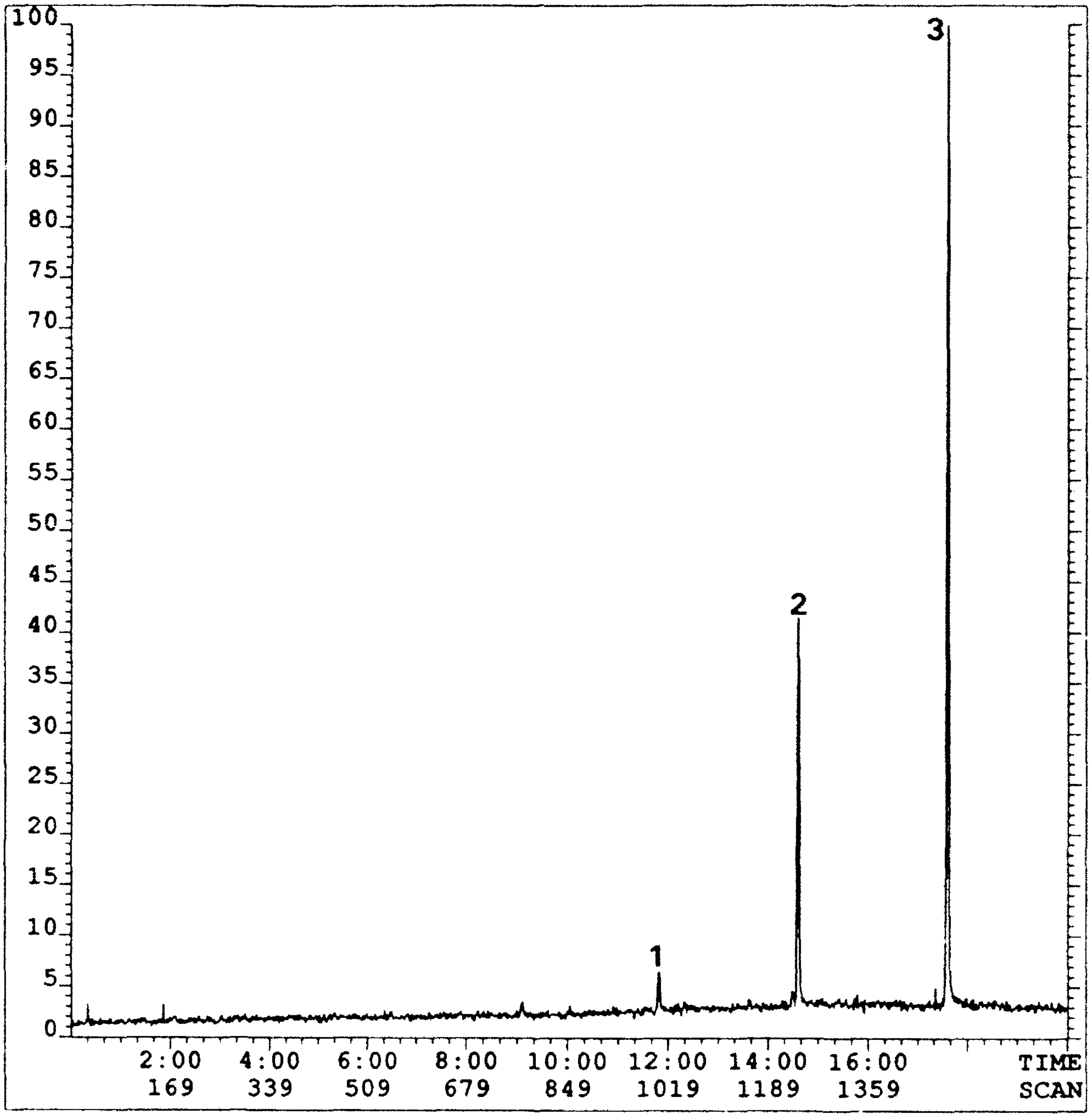


Figure 5: Capillary column GC-MS (ammonia CI) total-ion-current (300 to 200 u) chromatogram of the hexane extract of P46 painted panel. Numbered components are listed in Table I.

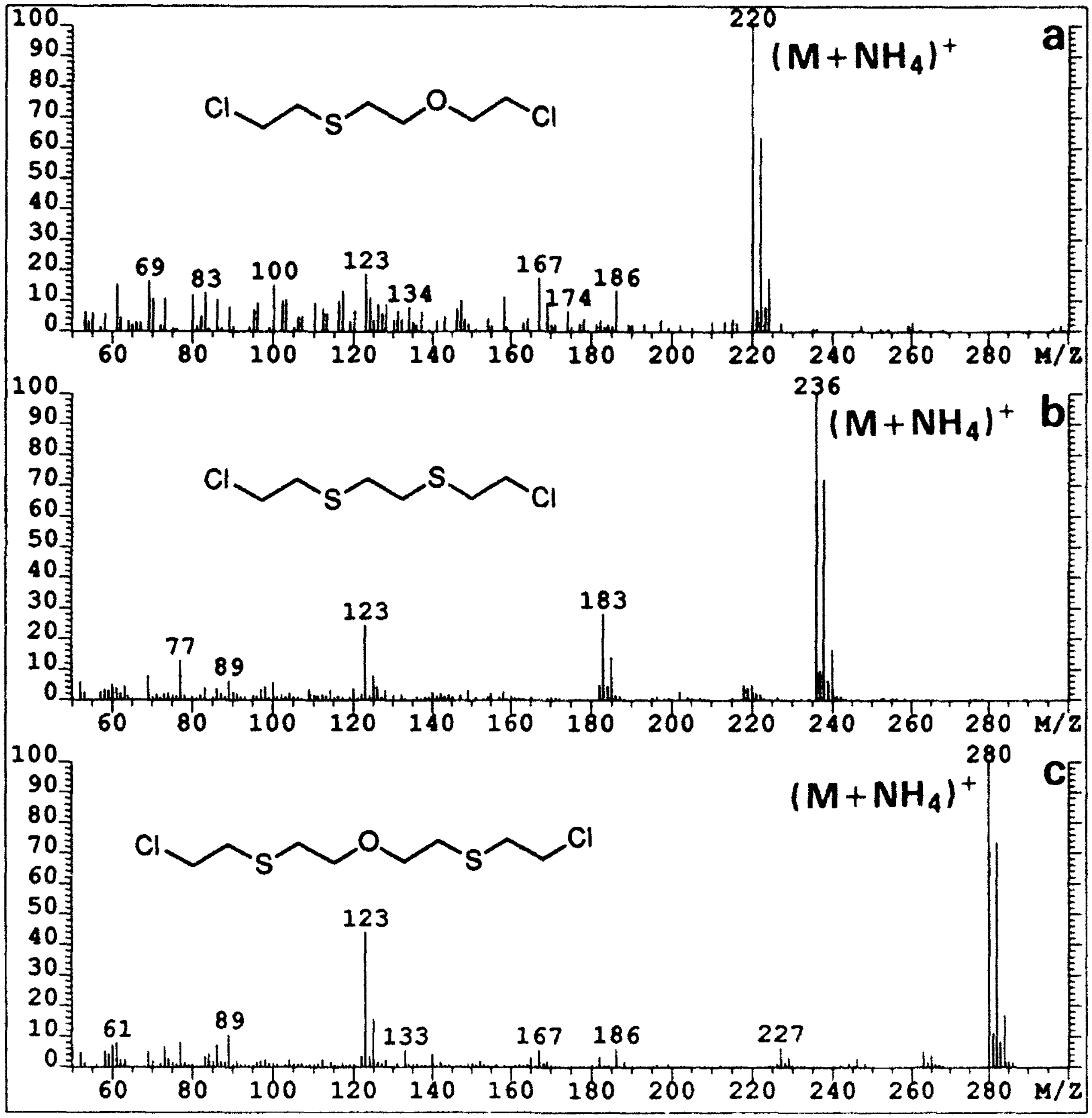


Figure 6: Ammonia chemical ionization mass spectra of a) 2-chloroethyl (2-chloroethoxy)ethyl sulfide, b) sesquimustard and c) bis[(2-chloroethylthio)-ethyl]ether (found in P46 and P48).

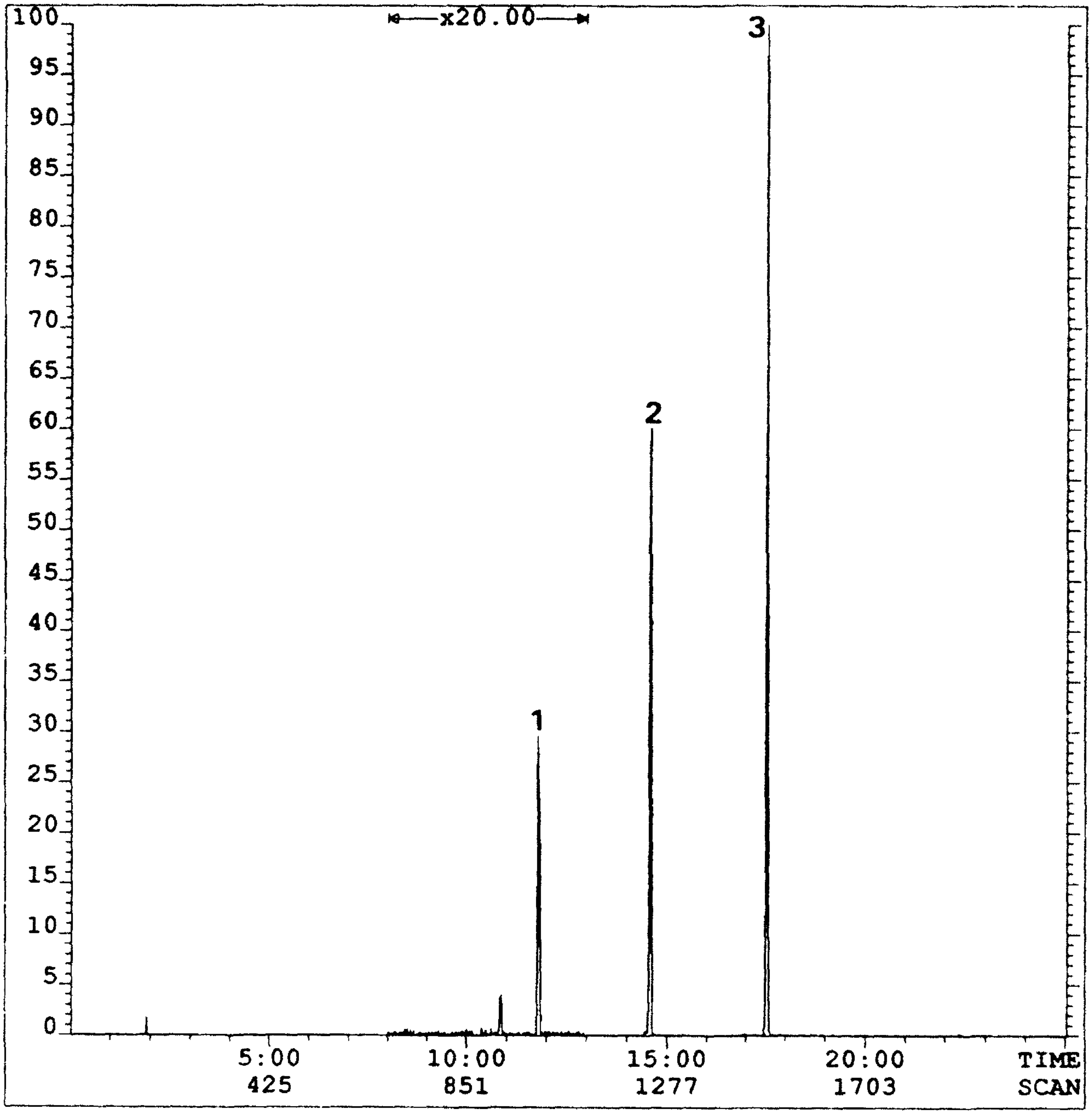


Figure 7: Collisional activated dissociation capillary column GC-MS/MS chromatogram for the daughters of m/z 123 of the hexane extract of P46 painted panel. Numbered components are listed in Table I.

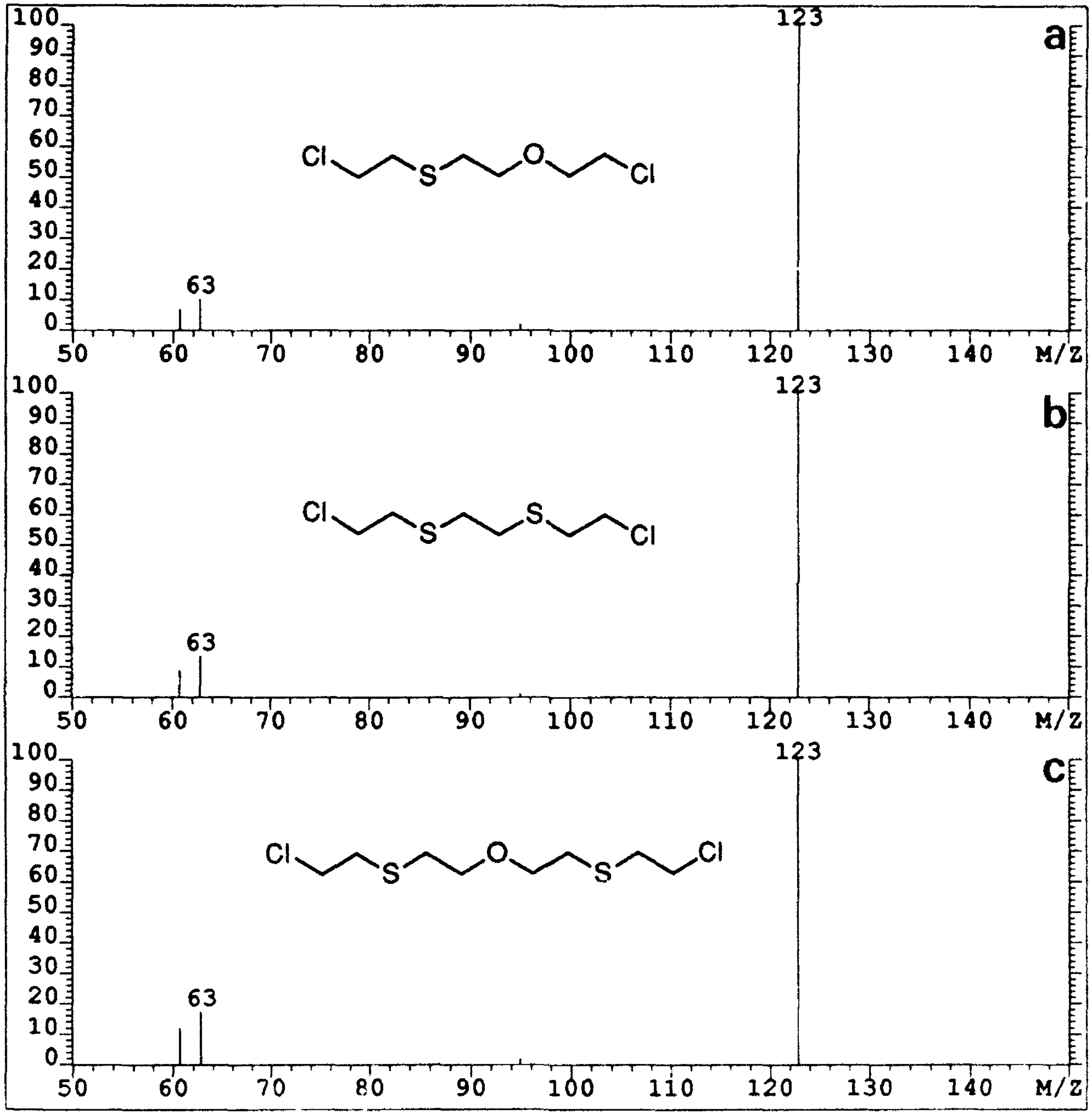


Figure 8: Daughter spectra (m/z 123) of a) 2-chloroethyl (2-chloroethoxy)ethyl sulfide, b) sesquimustard and c) bis[(2-chloroethylthio)ethyl]ether (found in P46 and P48).

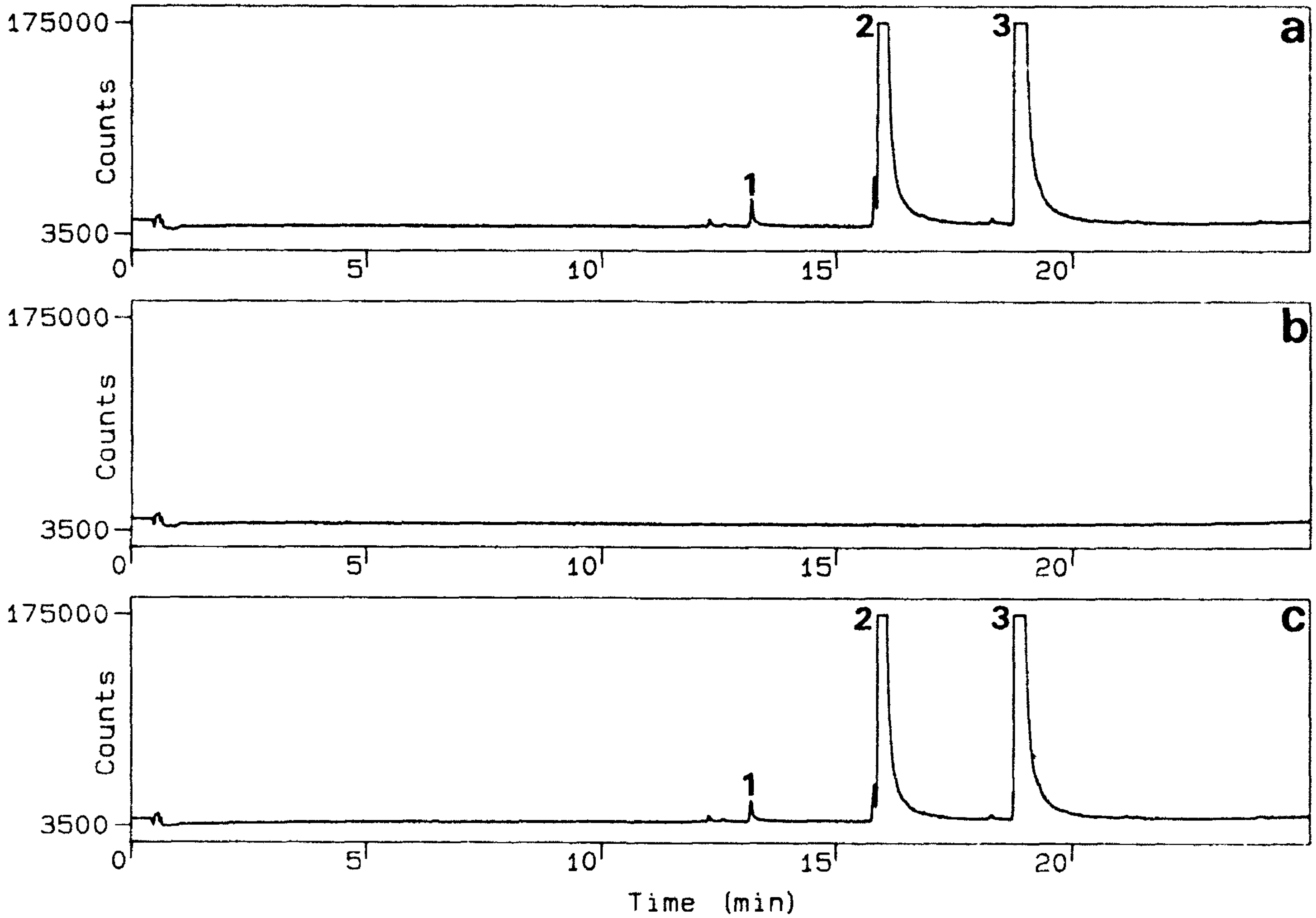


Figure 9: Capillary column GC-FPD (sulfur mode) chromatogram of the hexane extract of a) P46, b) P47 and c) P48 painted panels. Numbered components are listed in Table I.

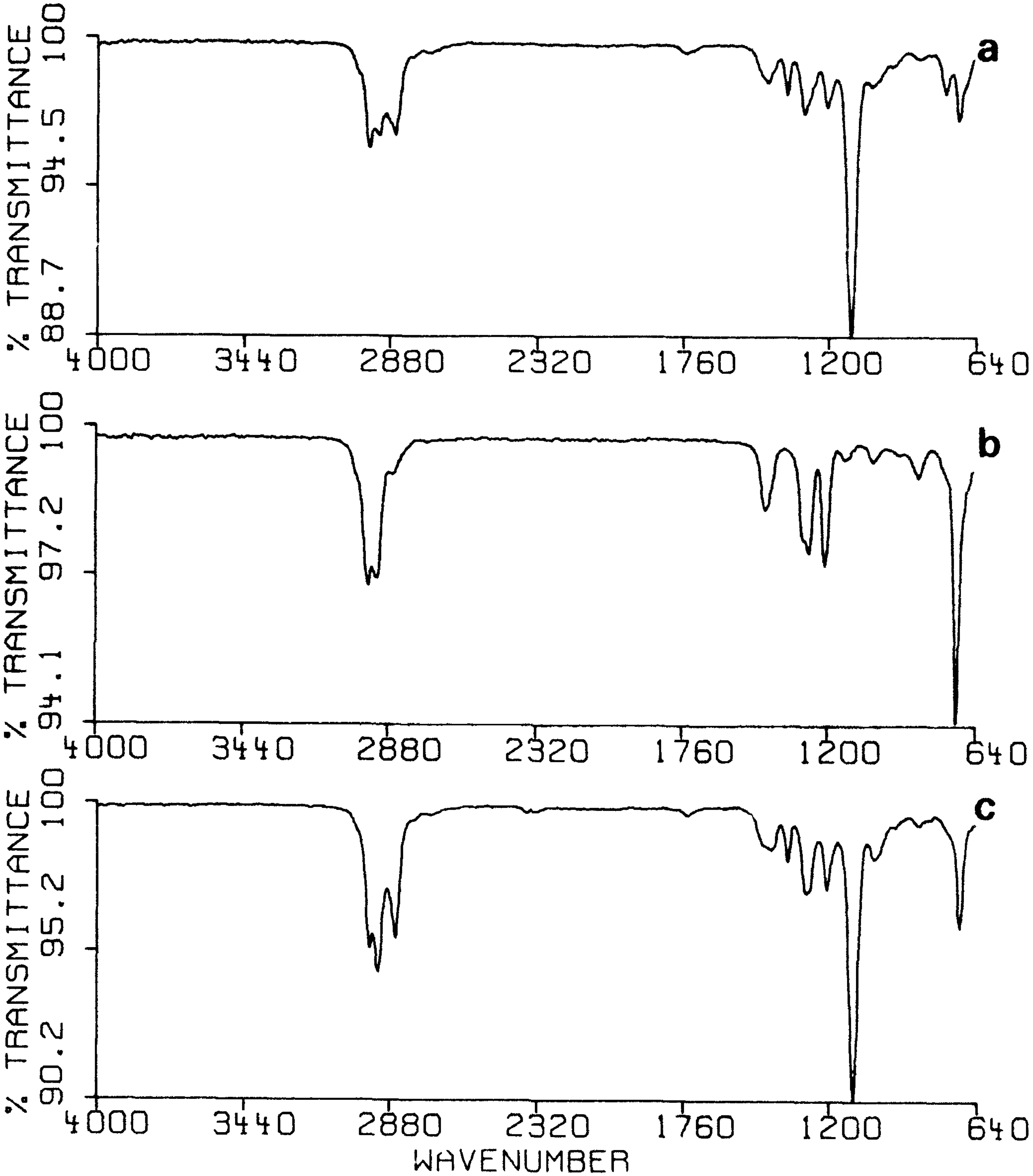


Figure 10: FTIR spectra of a) 2-chloroethyl (2-chloroethoxy)ethyl sulfide, b) sesquimustard and c) bis[(2-chloroethylthio)ethyl]ether (found in P46 and P48).

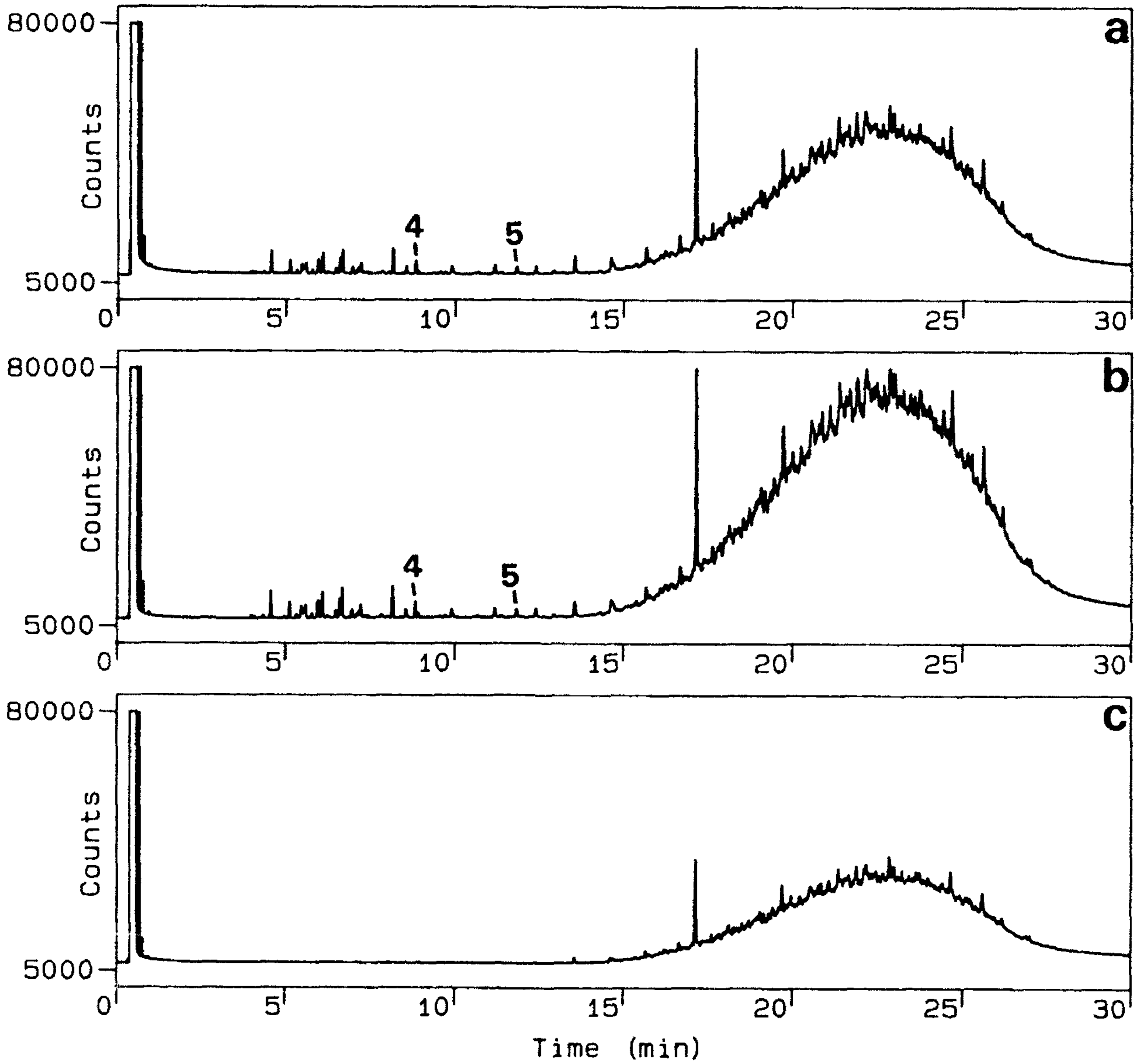


Figure 11: Capillary column GC-FID chromatogram of the acetonitrile extract of a) R46, b) R47 and c) R48 rubber samples. Numbered components are listed in Table I.

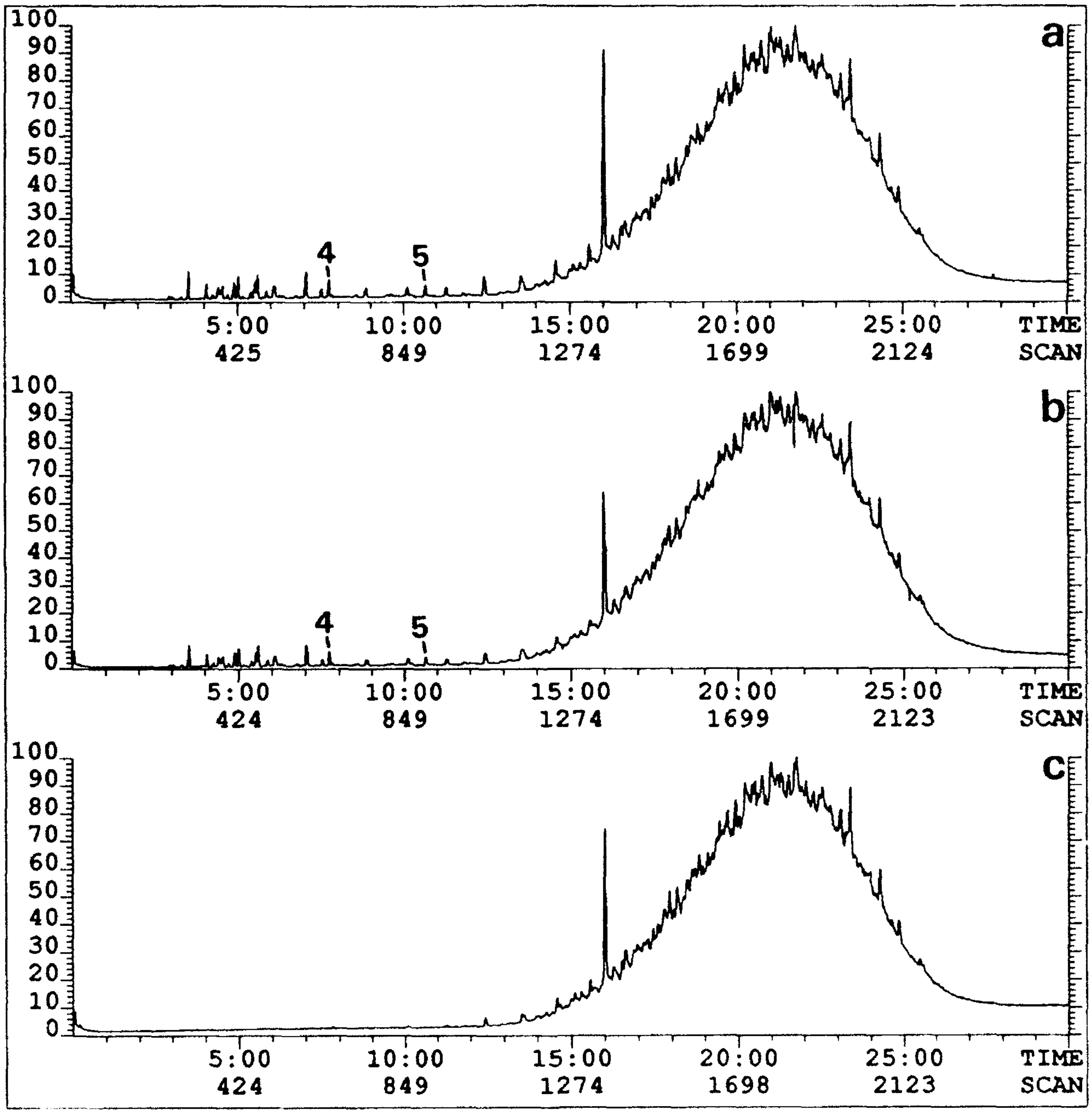


Figure 12: Capillary column GC-MS (EI) total-ion-current (400 to 40 u) chromatogram of the acetonitrile extract of a) R46, b) R47 and c) R48 rubber samples. Numbered components are listed in Table I.

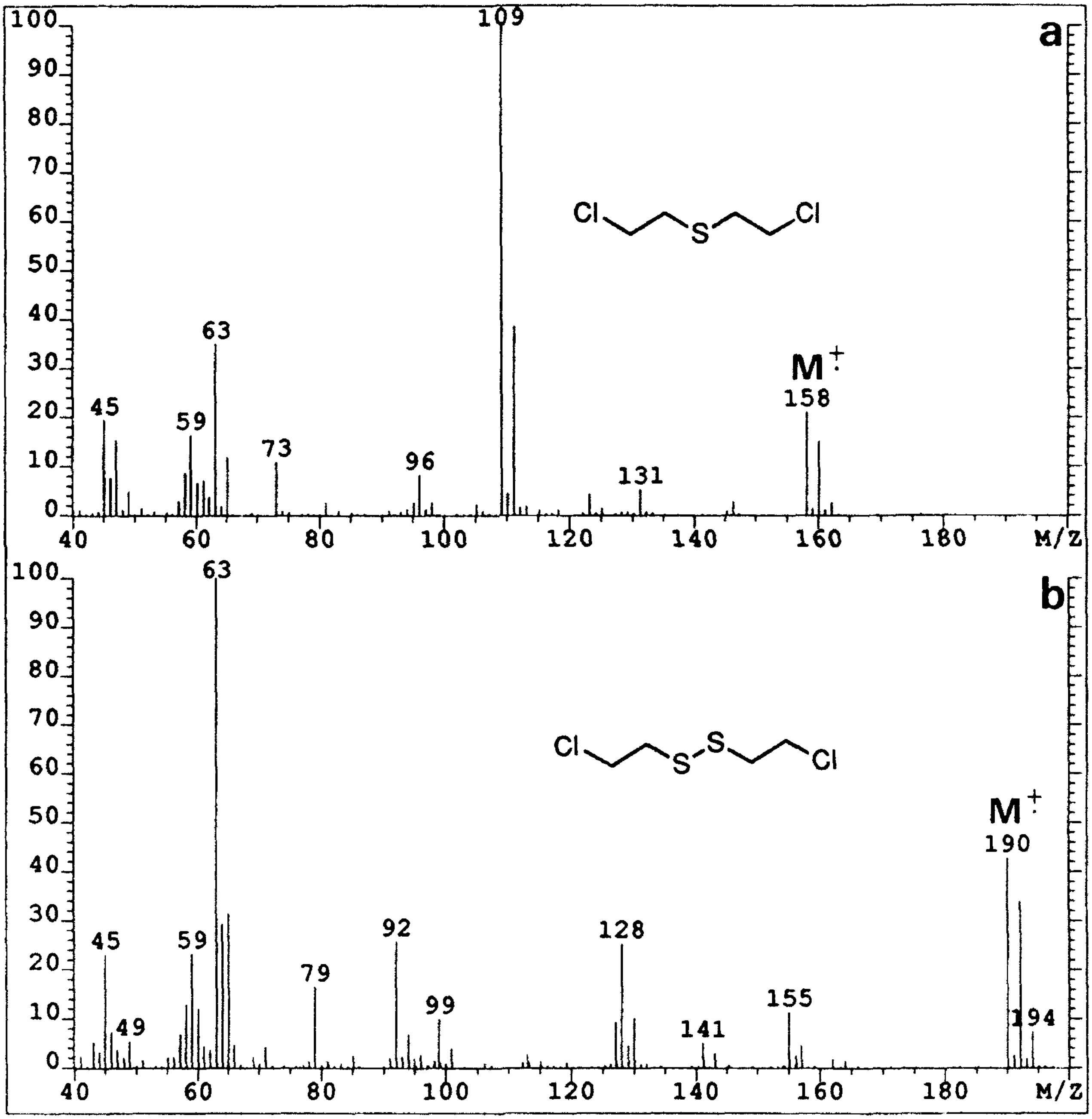


Figure 13: Electron impact mass spectrum of a) mustard and b) bis(2-chloroethyl)-disulfide (found in R46 and R47).

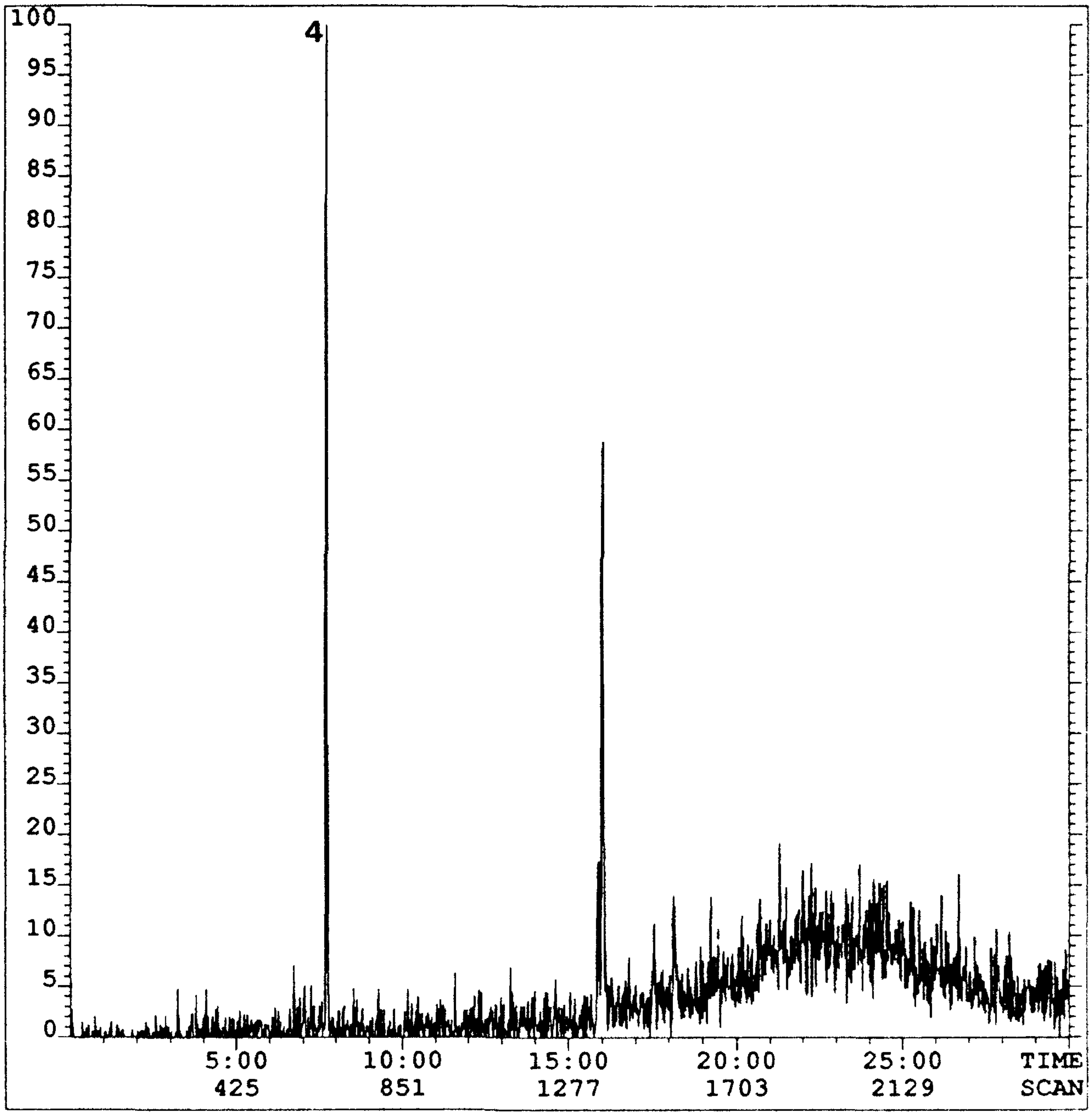


Figure 14: Collisional activated dissociation capillary column GC-MS/MS chromatogram for the daughters of m/z 123 of the acetonitrile extract of R46 rubber sample. Numbered components are listed in Table I.

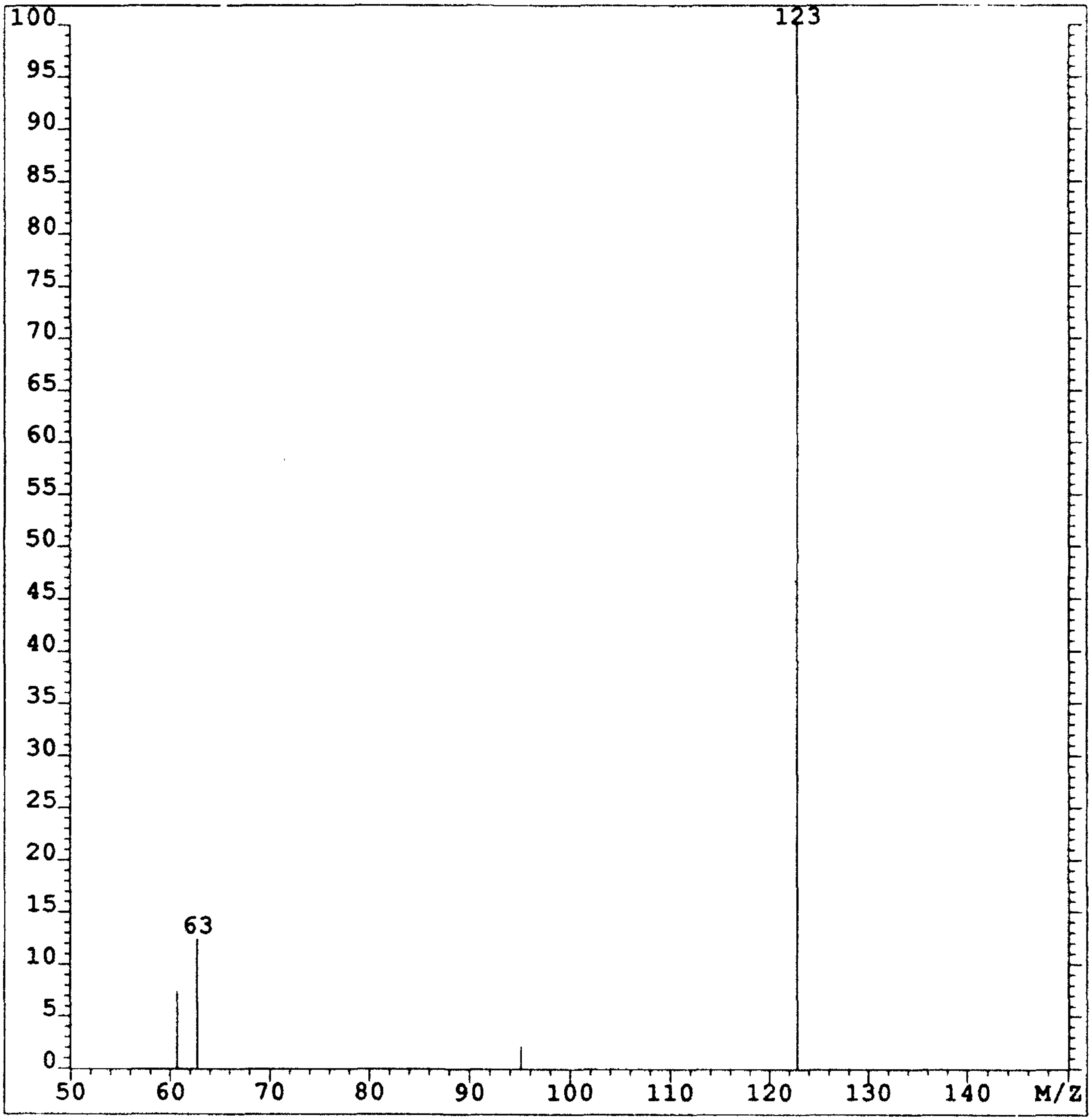


Figure 15: Daughter spectrum (m/z 123) of mustard (found in R46 and R47).

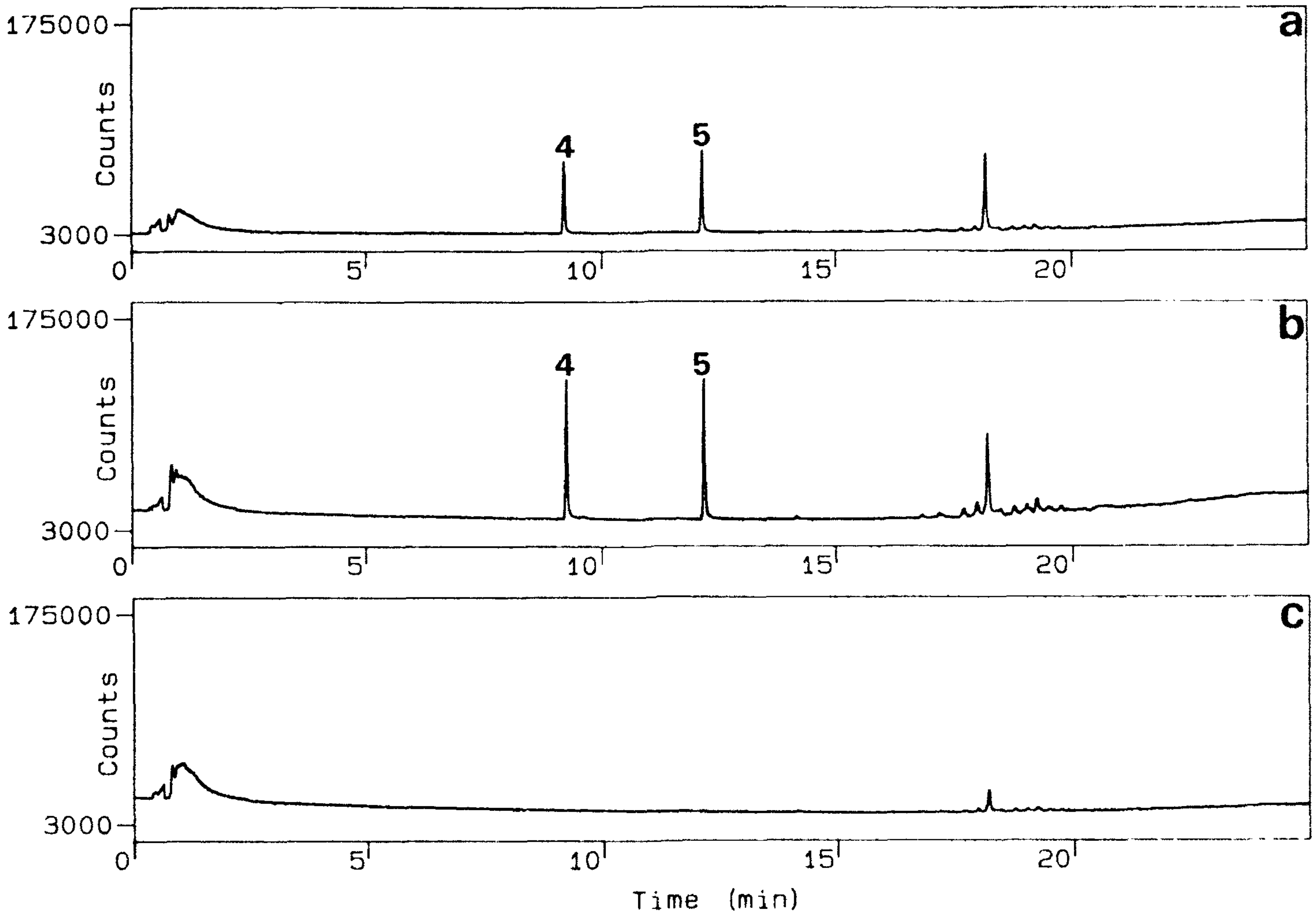


Figure 16: Capillary column GC-FPD (sulfur mode) chromatogram of the acetonitrile extract of a) R46, b) R47 and c) R48 rubber samples. Numbered components are listed in Table I.

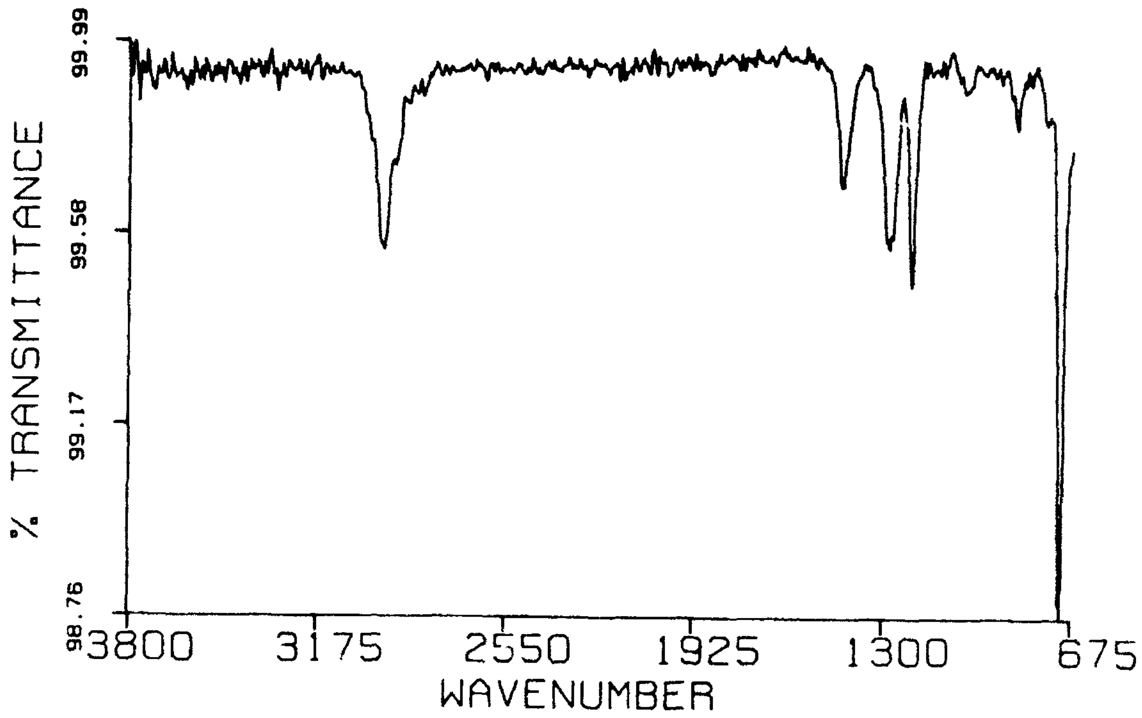


Figure 17: FTIR spectrum of mustard (found in R46 and R47).

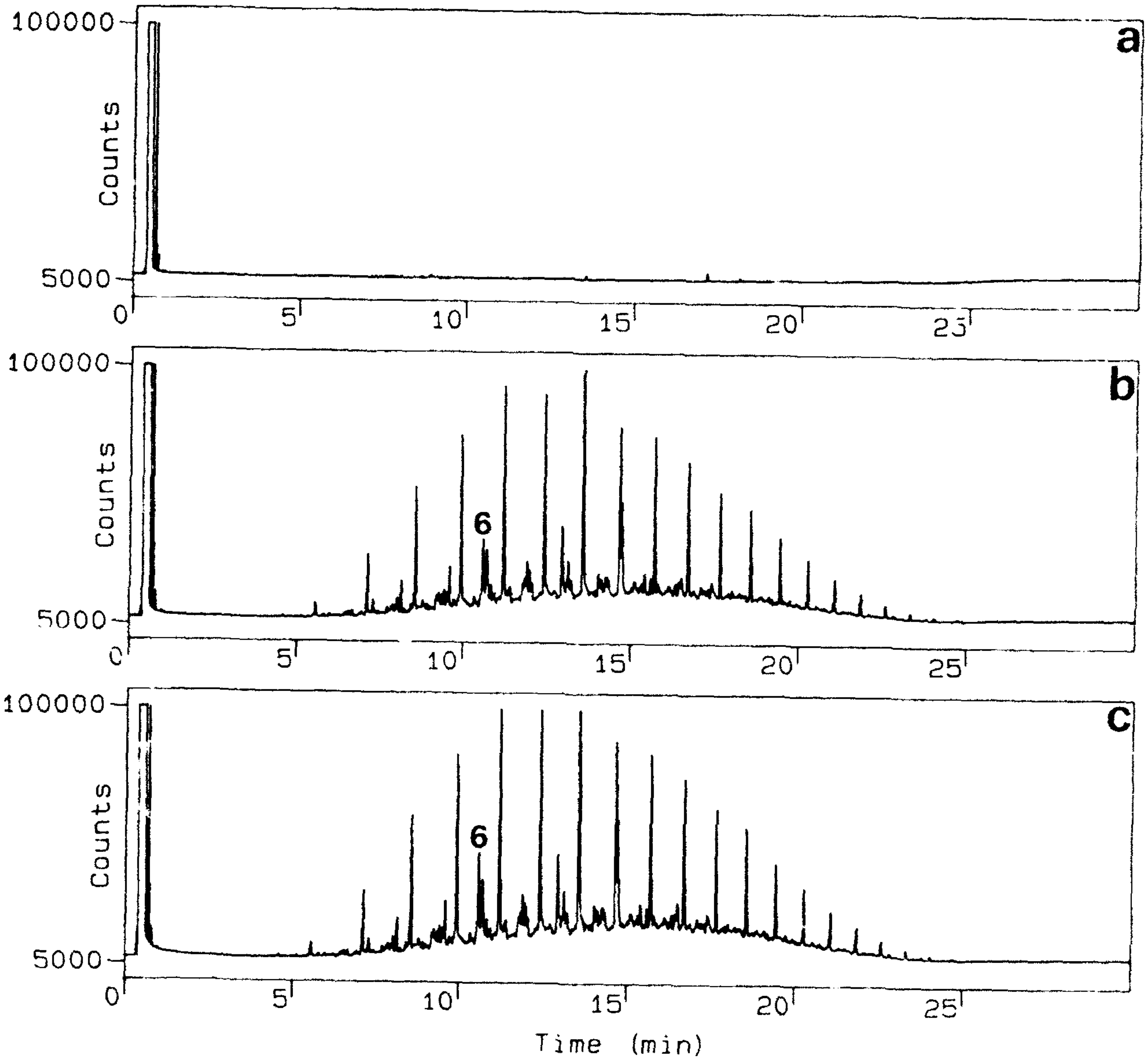


Figure 18: Capillary column GC-FID chromatogram of the acetonitrile extract of a) C46, b) C47 and c) C48 concrete samples. Numbered components are listed in Table I.

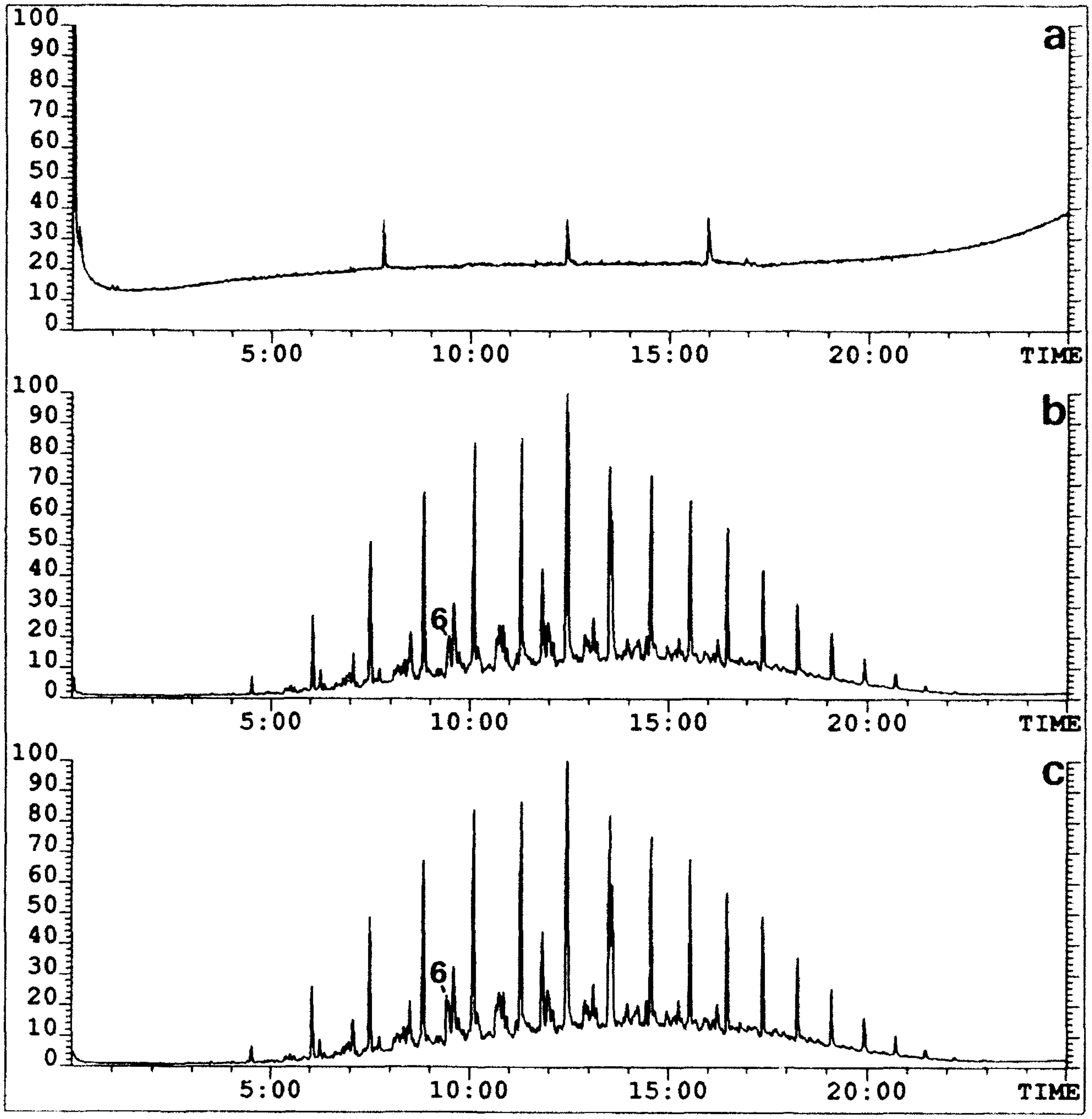


Figure 19: Capillary column GC-MS (EI) total-ion-current (400 to 40 u) chromatogram of the acetonitrile extract of a) C46, b) C47 and c) C48 concrete samples. Numbered components are listed in Table I.

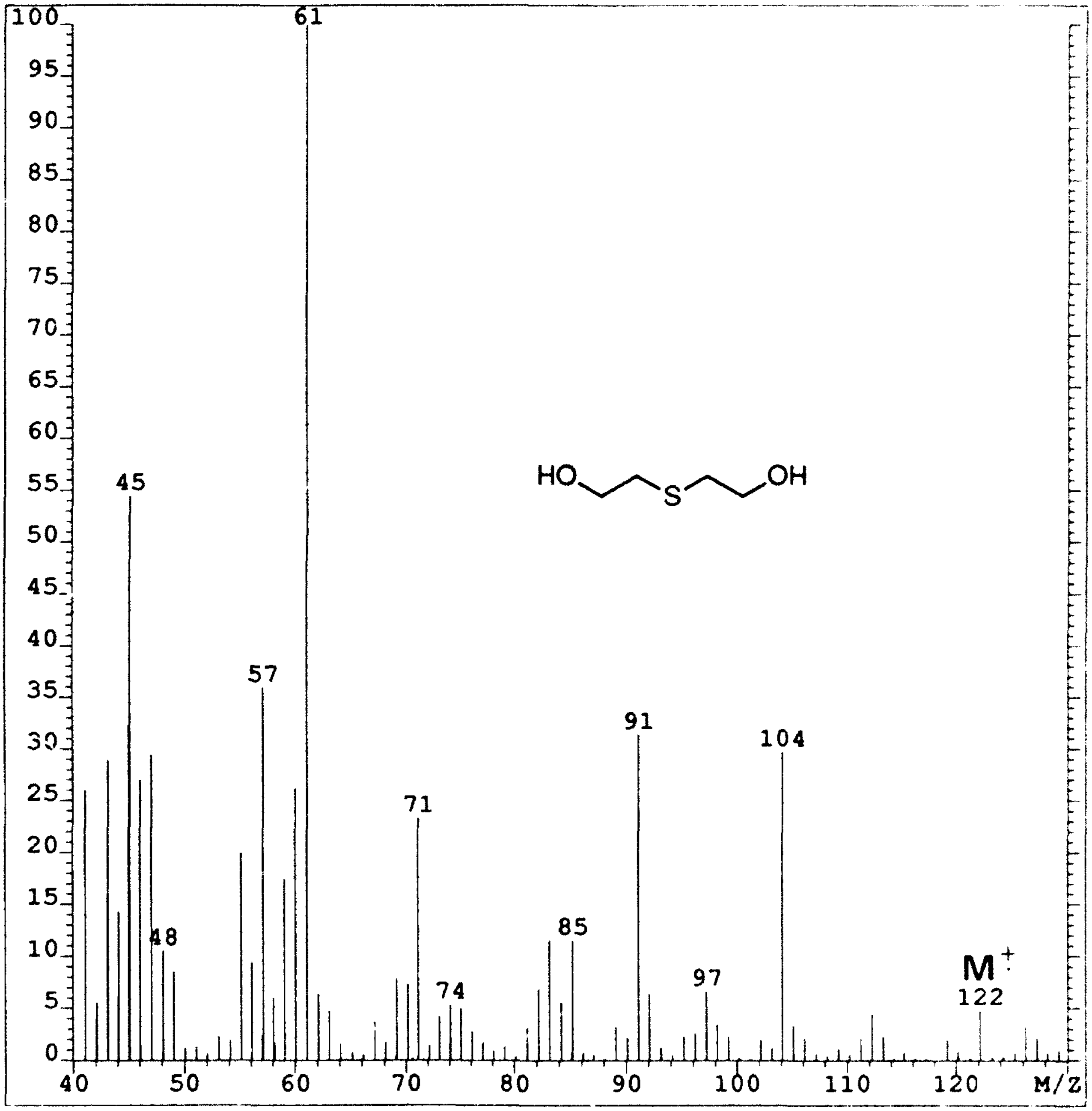


Figure 20: Electron impact mass spectrum of thiodiglycol (found in C47 and C48).

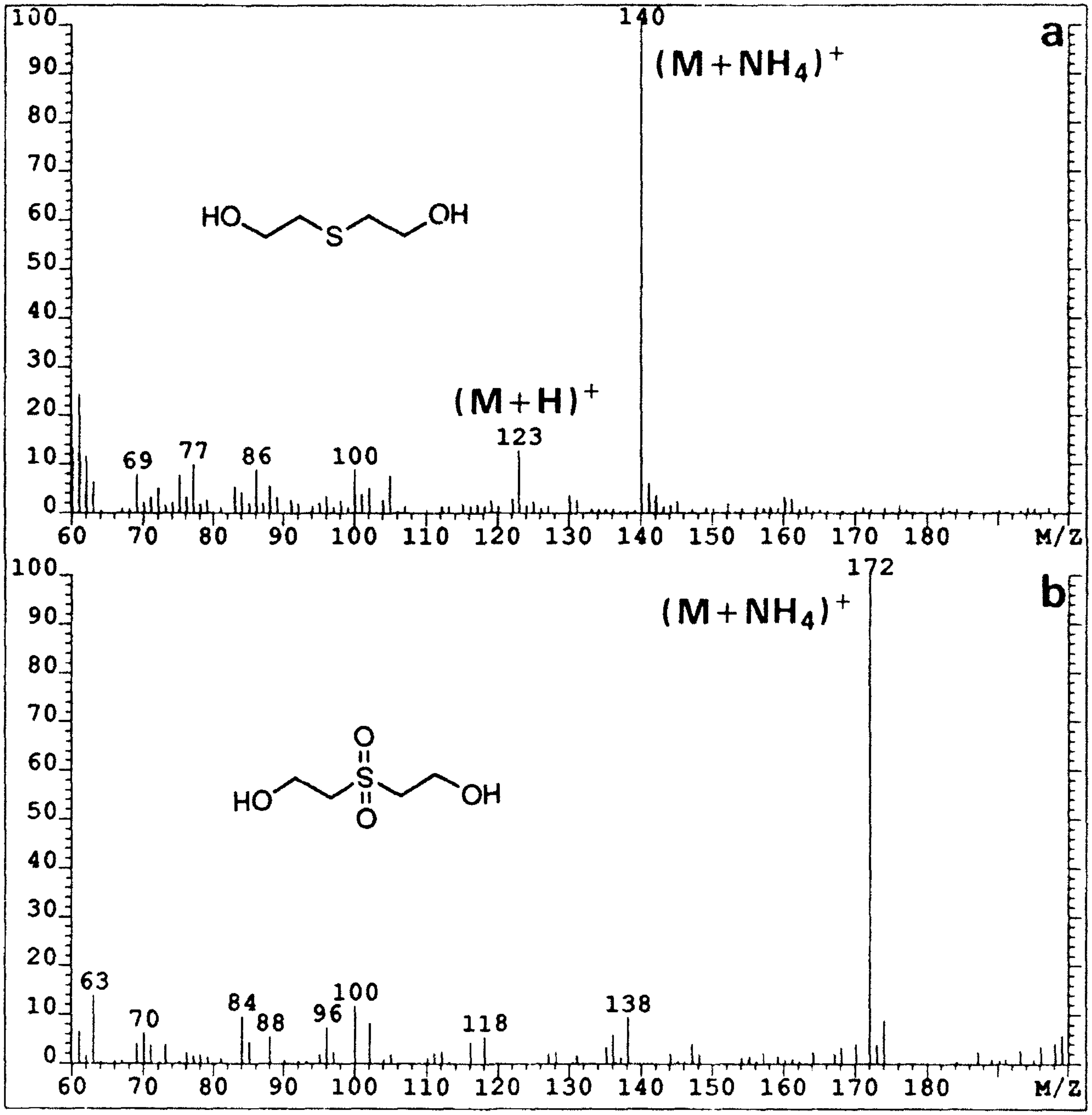


Figure 21: Ammonia chemical ionization mass spectra of a) thiodiglycol and b) thiodiglycol sulfone (found in C47 and C48).

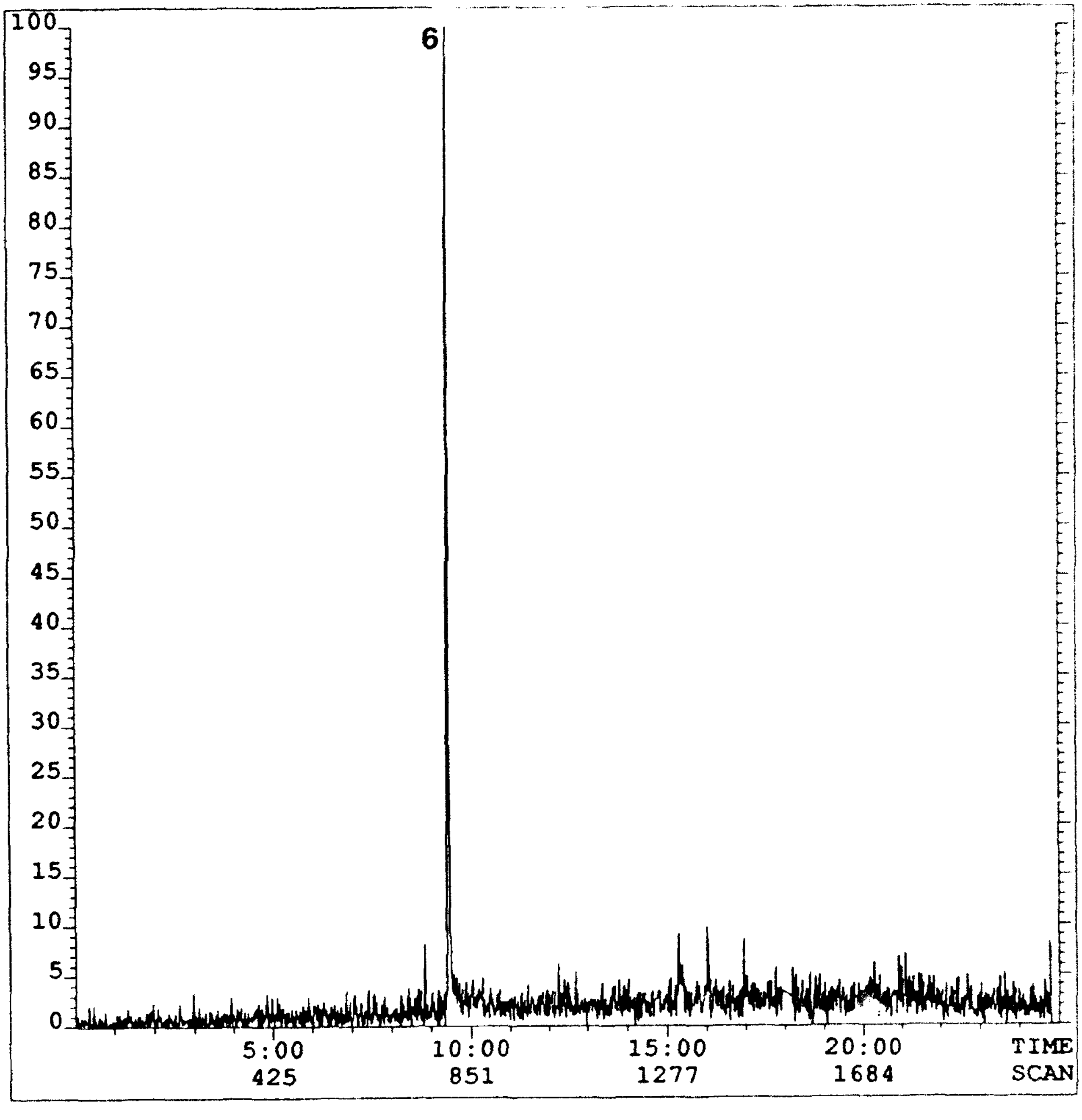


Figure 22: Collisional activated dissociation capillary column GC-MS/MS chromatogram for the daughters of m/z 122 of the acetonitrile extract of C48 concrete sample. Numbered components are listed in Table I.

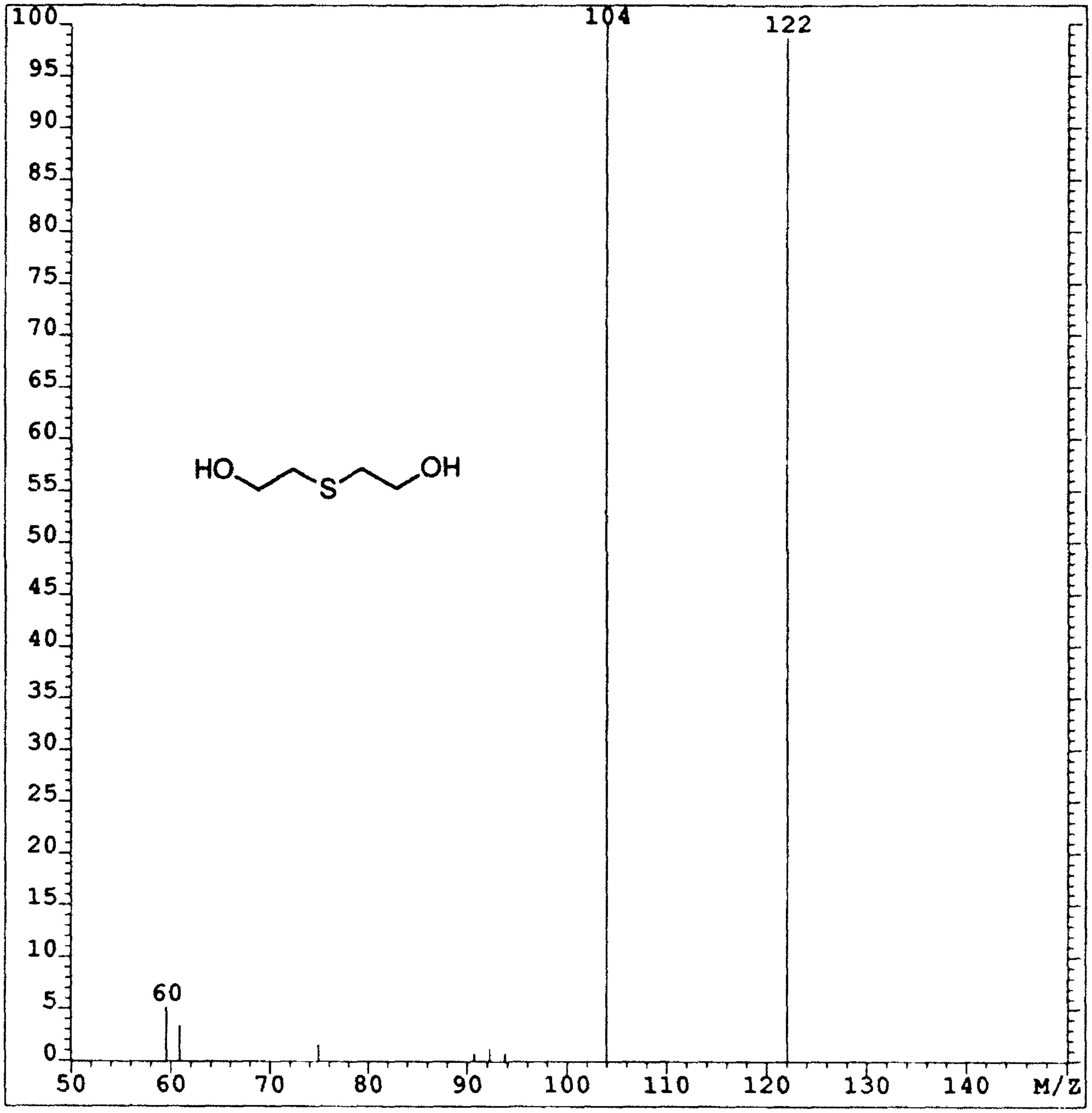


Figure 23: Daughter spectrum (m/z 122) of thiodiglycol (found in C47 and C48).

UNCLASSIFIED

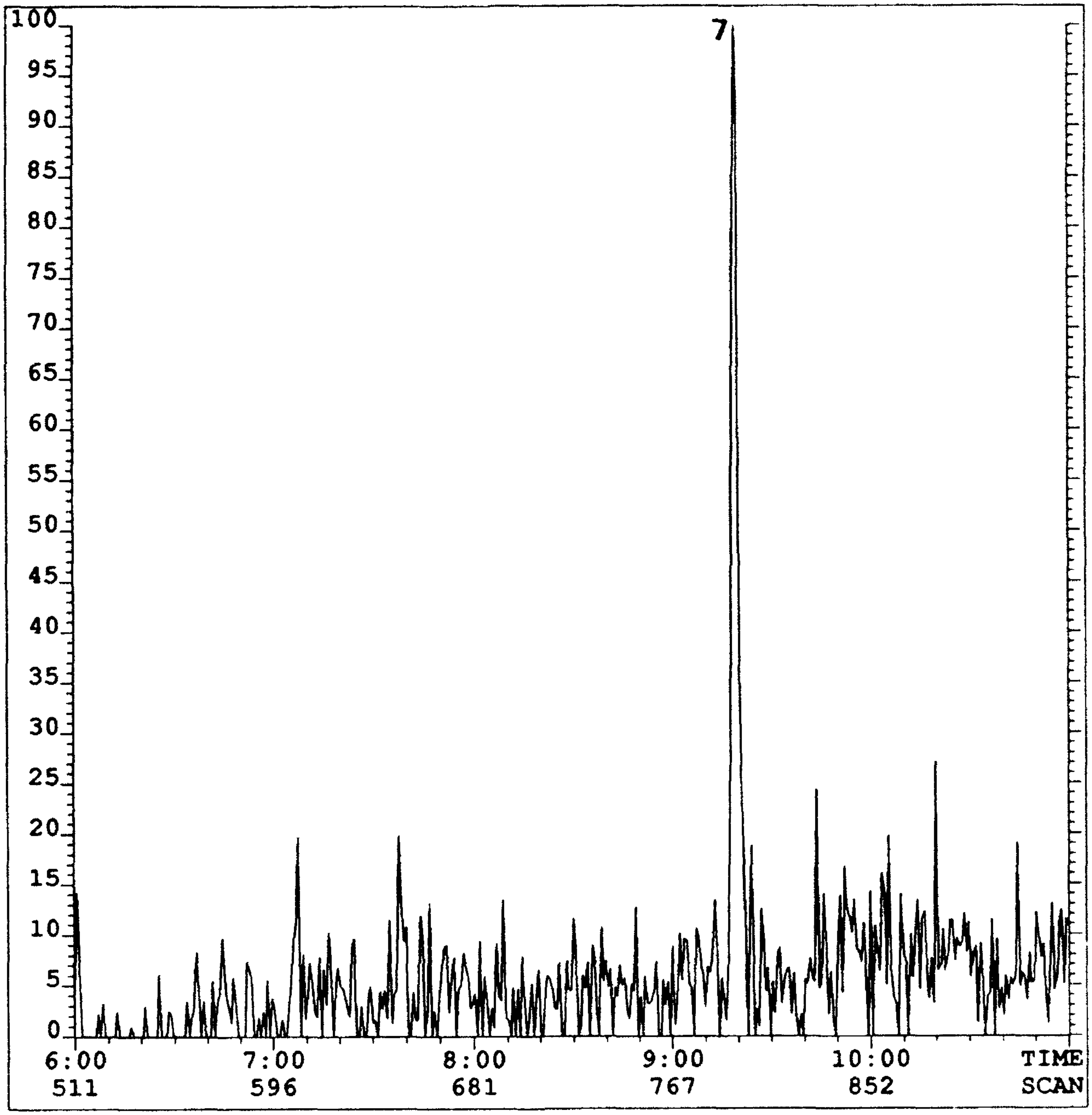


Figure 24: Collisional activated dissociation capillary column GC-MS/MS chromatogram for the daughters of m/z 111 of the acetonitrile extract of C48 concrete sample. Numbered components are listed in Table I.

UNCLASSIFIED

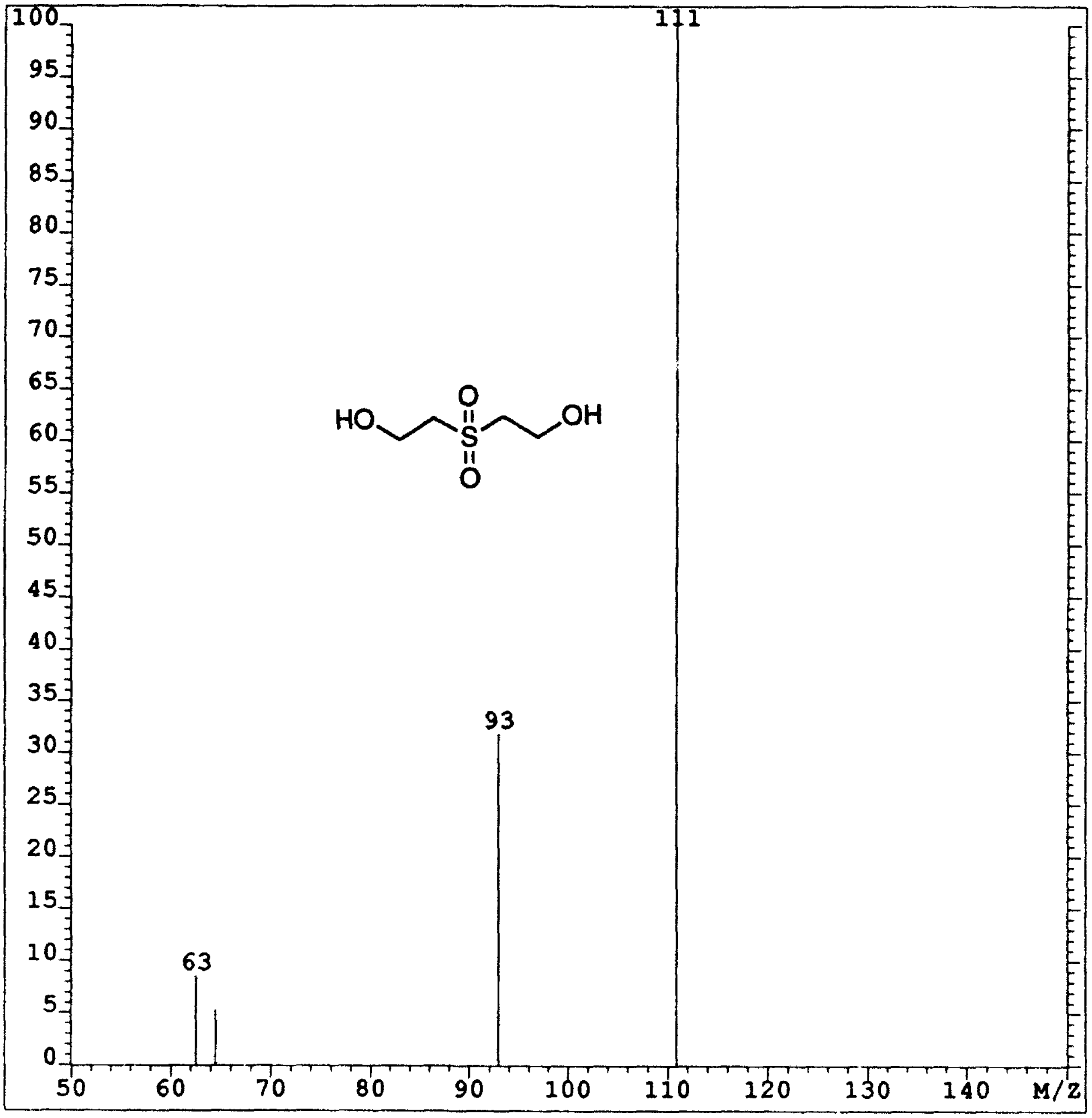


Figure 25: Daughter spectrum (m/z 111) of thiodiglycol sulfone (found in C47 and C48).

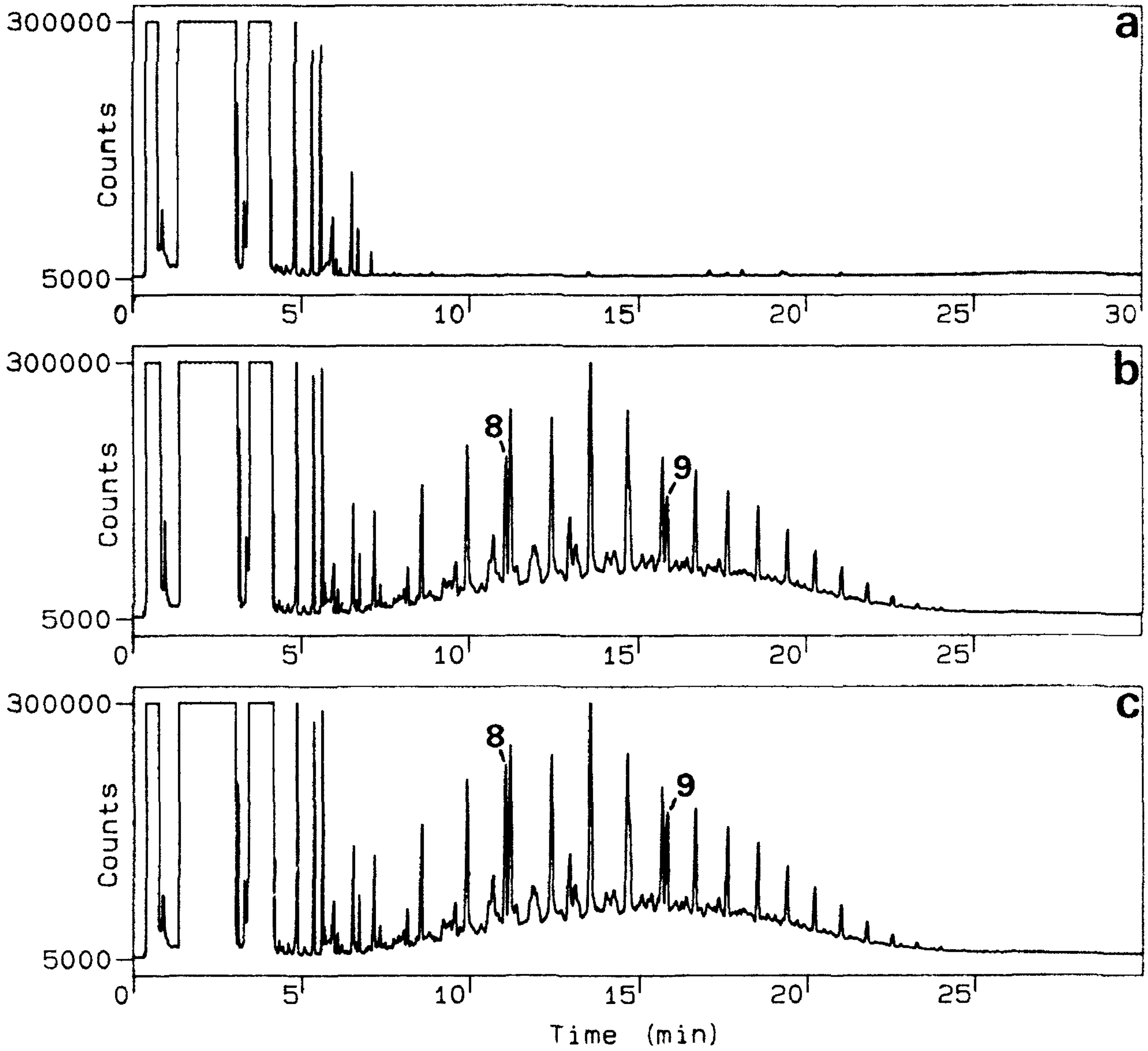


Figure 26: Capillary column GC-FID chromatogram of trimethylsilylated acetonitrile extract of a) C46, b) C47 and c) C48 concrete samples. Numbered components are listed in Table I.

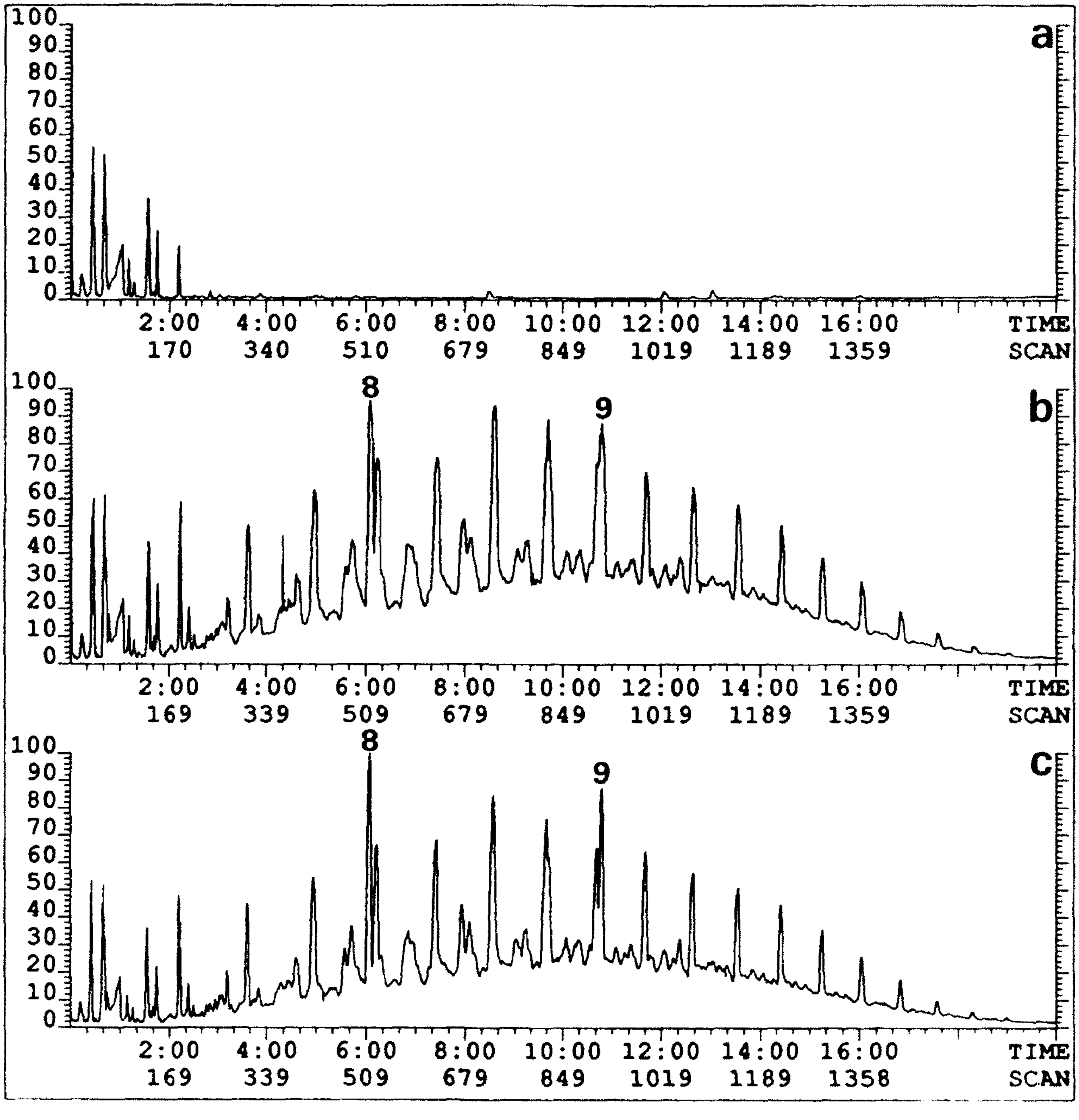


Figure 27: Capillary column GC-MS (EI) total-ion-current (400 to 40 u) chromatogram of trimethylsilylated acetonitrile extract of a) C46, b) C47 and c) C48 concrete samples. Numbered components are listed in Table I.

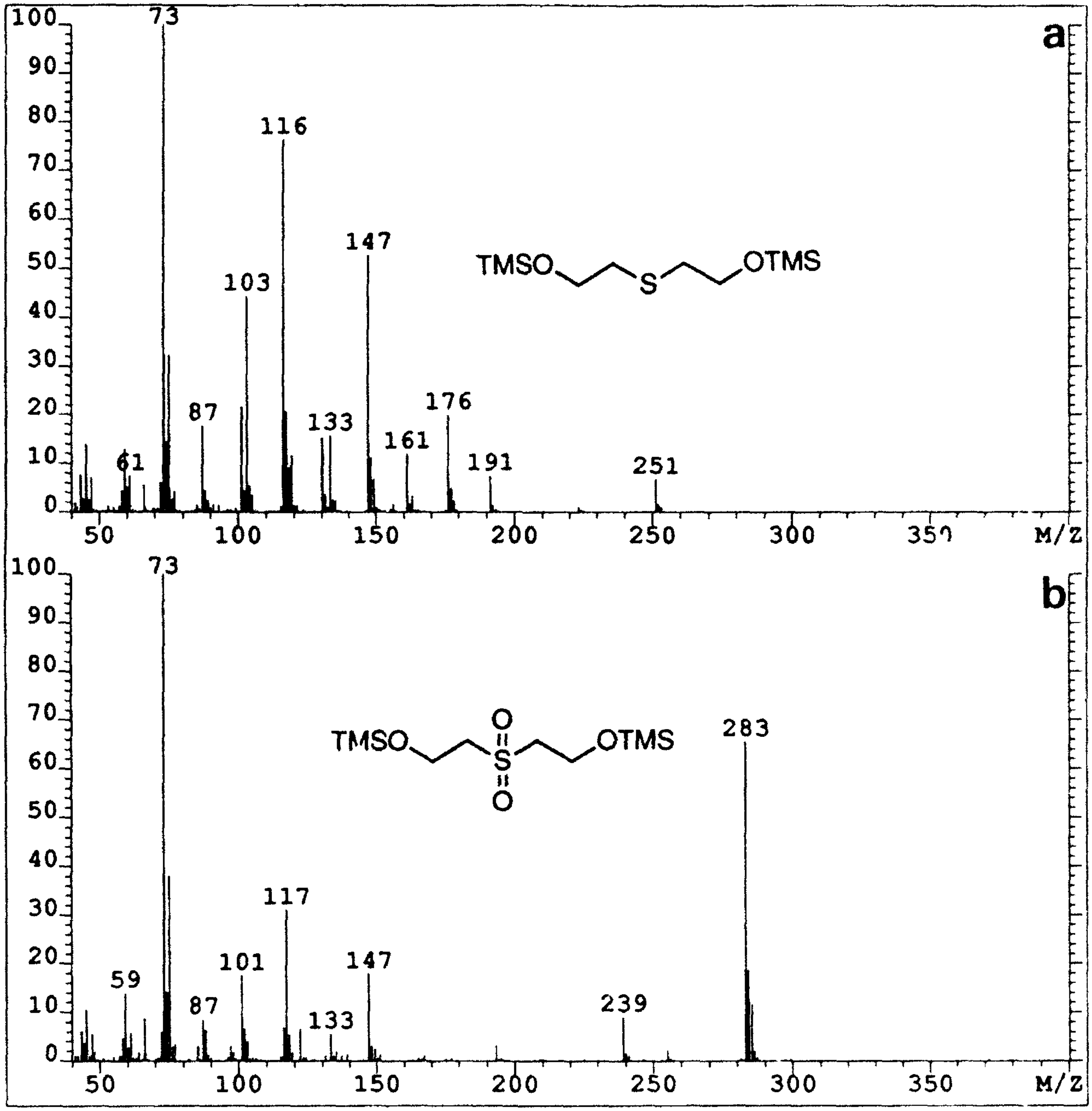


Figure 28: Electron impact mass spectra of a) di-TMS derivative of thiodiglycol and b) di-TMS derivative of thiodiglycol sulfone (found in C47 and C48).