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TNO Defence Research

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Preparation and analysis of samples for the third Round Robin verification exercise

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Summary

For the third international Round Robin verification exercise executed in the fall of 1991 the TNO-Prins Maurits Laboratory prepared the samples consisting of rubber, paint and concrete. These materials, which were selected to represent samples taken during an inspection at a military facility, were spiked with mustard gas and related vesicants as well as with decomposition products of mustard gas. Diesel fuel and an aromatic white spirit were added as a chemical background. In addition to a description of the spiked materials, details about the coding and transportation of the samples are presented.

A number of procedures was developed for the analysis of the samples. Rubber, which was spiked with mustard gas and its disulphide, could either be analysed by extraction with a nonpolar solvent or by thermodesorption. The latter procedure had advantages for the analysis by gas chromatography-mass spectrometry (GC-MS). Paint was spiked with sesquimustard (Q) and dimustard ether (T). Determination of these compounds was based on extraction with a nonpolar solvent, followed by spectrometric analysis (GC-MS, NMR). Concrete was spiked with two polar decomposition products of mustard gas viz. thiodiglycol and its sulphone. Extraction with water followed by analysis with thermospray-liquid chromatography-mass spectrometry (TSP-LC-MS) turned out to be the best method for the quantitative determination. All compounds added were rather stable in the materials. After a period of 7 weeks they could still be recovered with reasonable or even good efficiencies.

Samenvatting

Voor het derde internationale verificatie ringonderzoek dat in de herfst van 1991 werd uitgevoerd, heeft het Prins Maurits Laboratorium TNO de monsters aangemaakt die bestonden uit rubber, verf en beton. Deze materialen, die geselecteerd waren om als voorbeeld te dienen van monsters genomen tijdens een inspectie op een militaire basis, werden besmet met mosterdgas en verwante blaartrekkers als mede met ontledingsprodukten van mosterdgas. Dieselolie en een aromatische terpentine werden toegevoegd als chemische achtergrond. Behalve een beschrijving van de besmette materialen worden bijzonderheden over de codering en het transport van de monsters gepresenteerd.

Een aantal procedures werd ontwikkeld voor de analyse van de monsters. Rubber, dat besmet was met mosterdgas en zijn disulfide, kon zowel via extractie met een apolair oplosmiddel als via thermodesorptie geanalyseerd worden. De laatste procedure had voordelen voor de analyse met gaschromatografie-massaspectrometrie (GC-MS). Verf was besmet met sesquimosterd (Q) en

mosterdgasether (T). De bepaling van deze verbindingen was gebaseerd op extractie met een apolair oplosmiddel gevolgd door spectrometrische analyse (GC-MS, NMR). Beton was besmet met 2 polaire ontledingsprodukten van mosterdgas namelijk thiodiglycol en zijn sulfon. Extractie met water gevolgd door analyse met thermospray vloeistofchromatografie-massaspectrometrie (TSP-LC-MS) bleek de beste methode te zijn voor de kwantitatieve bepaling. Alle toegevoegde verbindingen bleken redelijk stabiel te zijn in de gebruikte materialen. Na een periode van 7 weken konden ze nog met redelijke of zelfs goede rendementen teruggevonden worden.

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1 INTRODUCTION

Since 1989 international Round Robin verification exercises are held annually, coordinated by the Finnish Research Project for Chemical Warfare Verification (1, 2).
The TNO Prins Maurits Laboratory (TNO-PML) participates for The Netherlands in these exercises (3, 4). The results of the second exercise were discussed at the expert meeting in Spiez (Switzerland) in March 1991. At that meeting TNO-PML volunteered to prepare the samples for the third exercise to be started at October 21, 1991. In this report the preparation and the transportation of the samples to the 16 participating laboratories from 14 countries (see Annex 1) will be described. Moreover, the analysis results obtained by TNO-PML during the development of the scenario of the exercise as well as those of the control samples will be presented here.

2 SCENARIO OF THE EXERCISE

Contaminated materials provide interesting samples for verification purposes. Three types of materials viz. rubber, paint and concrete were selected to represent samples taken during an inspection at a military facility. During recent trial inspections at military air bases in The Netherlands and Germany (5, 6) it was found that samples taken at these facilities contained relatively high levels of hydrocarbons (e.g. oil) and solvents. Therefore, the materials were not only spiked with compounds relevant to chemical warfare (CW) but also with a chemical background. The following points were considered:

- as the samples of Round Robin I and II were spiked with organophosphorus nerve agents the choice of non-phosphorus compounds such as vesicants seemed obvious;
- attention should be focussed on the problem of the finite GC-resolution leading to mass spectra of mixtures;
- the three materials should contain different but related compounds;
- some of the samples should be spiked with polar decomposition products in order to test procedures for these types of compounds as well;
- the same spiking level as used for the samples of Round Robin I, viz. 10-100 ppm (mg/kg) should be used;
- the degree of degradation of the spiked compounds should be small.

Finally, these starting points led to the following samples:

- rubber spiked with mustard gas, an aromatic solvent mixture of the same volatility as mustard gas, mustard gas disulphide (a well-known impurity of mustard gas) and Diesel fuel;
- paint spiked with the mustard gas related compounds sesquimustard (Q) and dimustard ether (T) as well as with Diesel fuel. These compounds were added to the paint in the above-mentioned aromatic solvent mixture;
- concrete spiked with two decomposition products of mustard gas e.g. thiodiglycol and thiodiglycol sulphone as well as an excess of Diesel fuel.

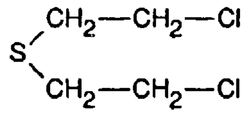
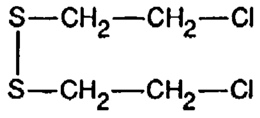
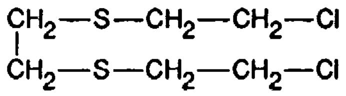
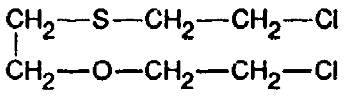
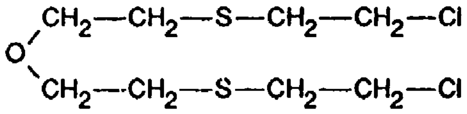
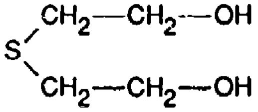
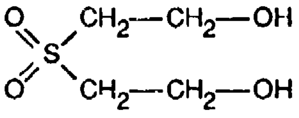
As the materials were spiked in duplicate and one blank was provided each participating laboratory received nine samples. To test for possible false positives the blank samples were not coded as such.

3 CHEMICALS

The CW relevant chemicals (see Table 1) were prepared at TNO-PML several years ago and are kept in stock as reference compounds. Their identity and purity were controlled by NMR and GC-MS before the preparation of the stock solutions. The purity of all compounds was over 95% except for sesquimustard, which contained about 7% of 2-chloroethyl-(2-chloroethoxyethyl)sulphide as well as smaller amounts of mustard gas and dimustard ether.

Shellsol AB, an aromatic white spirit with a boiling range of 165-220 °C, was obtained from Shell. The Diesel fuel was acquired from a petrol station. It consisted of aliphatic hydrocarbons with a boiling range of 150-350 °C. The other solvents used were of analytical grade.

Table 1 Names and formulas of the spiked compounds

Trivial name	Systematical name	CAS number	Structural formula
Mustard gas (HD)	bis(2-chloroethyl) sulphide	505-60-2	
Mustard disulphide	bis(2-chloroethyl) disulphide	1002-41-1	 $\begin{array}{l}\mathrm{S-CH_2-CH_2-Cl}\\ \vert\\ \mathrm{S-CH_2-CH_2-Cl}\end{array}$
Sesqui mustard (Q)	1,2-bis(2-chloroethylthio) ethane	3563-36-8	 $\begin{array}{l}\mathrm{CH_2-S-CH_2-CH_2-Cl}\\ \vert\\ \mathrm{CH_2-S-CH_2-CH_2-Cl}\end{array}$
	2-chloroethyl-(2-chloroethoxyethyl) sulphide [1]		 $\begin{array}{l}\mathrm{CH_2-S-CH_2-CH_2-Cl}\\ \vert\\ \mathrm{CH_2-O-CH_2-CH_2-Cl}\end{array}$
Dimustard ether (T)	bis(2-chloroethyl-thioethyl)ether	63918-89-8	
Thiodiglycol	bis(2-hydroxyethyl) sulphide	111-48-8	
Thiodiglycol sulphone	bis(2-hydroxyethyl) sulphone	2580-77-0	

1 Footnote: major impurity of sesquimustard

4 DESCRIPTION OF THE MATERIALS

4.1 Rubber

The rubber, which was used for sealing windows, was obtained from a car dump. It was a common type of black coloured rubber containing soot and relatively large quantities (about 30%) of high boiling hydrocarbons (plasticizers). Analysis of the rubber by pyrolysis-mass spectrometry pointed to an ethene-propylene copolymer.

The rubber was cut into pieces of about 8 g. Each piece was spiked with 165 µl of a methylene chloride solution resulting in the maximal addition of :

- 0.38 mg mustard gas [1];
- 0.21 mg mustard gas disulphide[1];
- 4.45 mg Shellsol;
- 7.32 mg Diesel fuel.

The solution was brought on the surface of the rubber by means of a syringe. The spiking was carried out as homogeneously as possible. After a period of approximately 15 min the rubber was visibly dry and was then wrapped in a piece of aluminium foil. Each piece of rubber was put into a 30 ml screw-capped glass bottle, which was provided with a unique number (see Annex 2). The glass bottle was in turn sealed in a polyethylene foil. The blank rubber sample was packed in the same way.

4.2 Paint

Metal plates (2 x 4 cm) covered with a layer of alkyd paint (film thickness of 60 µm) were used. This paint is used by the Dutch Army and possesses the characteristic military green colour. Metal plates of this type are used by TNO-PML for decontamination studies. The plates were prepared by the TNO Centre for Coatings Research and were stored at room temperature for approximately five months. The painted surface was spiked with 5 µl of a Shellsol solution, resulting in a maximal addition of:

- 0.067 mg sesquimustard gas (Q) [1];
- 0.098 mg dimustard ether (T) [1];
- 0.46 mg Diesel fuel.

The spiking and the packaging of the samples was performed in the same way as for the rubber samples.

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[1] Footnote : the purity of the spiked compounds was not taken into account

4.3 Concrete

The concrete was obtained from the construction of a new laboratory at the TNO location at Rijswijk, The Netherlands. A special mould was constructed with eighty holes, which were filled with concrete.

After drying, round pieces of concrete (height 2.5 cm, OD 2.2 cm) of approximately 22 g were obtained. The concrete pieces were stored for about five months at room temperature before use. Each piece was spiked with 110 µl of a methylene chloride-methanol (15:1) solution resulting in the maximal addition of :

- 0.56 mg thiodiglycol [1];
- 0.57 mg thiodiglycol sulphone [1];
- 22.7 mg Diesel fuel.

The spiking and the packaging of the samples was performed in the same way as for the rubber samples.

5 TRANSPORTATION OF THE SAMPLES

The total of nine samples were packed in a wooden box (18 x 18 x 22 cm) approved for the transport of dangerous goods. Some simple packaging materials (plastic chips and foil with air bubbles) were used. The cover of the box was closed with four screws. The package was tested with positive results by dropping a box with nine test samples on a concrete floor from 1 m height a few times. Each box contained a letter with the content (see Annex 3).

The total of sixteen boxes were labelled with the addresses of the participating laboratories (see Annex 1) by the Finnish Embassy in The Hague (The Netherlands). The samples were then transported from the Ministry of Foreign Affairs (The Hague) to the Dutch embassies in the participating nations by diplomatic mail. The embassies were instructed to contact the responsible persons of the laboratories to arrange the local transport as quick as possible. These instructions were given in the middle of September. The embassies were informed about the start of the transport. Additionally, the laboratories were informed by a telefax sent in the beginning of October from TNO-PML (see Annex 3). Those responsible for the transport, were asked to keep the samples as cool as possible.

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[1] Footnote : the purity of the spiked compounds was not taken into account

6 TIME SCHEDULE

30 September	Setting of dates for the transport. Start of the preparation of the samples.
1 October	Preparation and control of solutions used for the spiking. Preparation of the blank samples (20 concrete, 20 rubber, 20 paint).
2 October	Preparation of 40 spiked concrete samples [1] Telefax message to most of the participants.
3 October	Preparation of 40 spiked rubber samples [1] Remaining telefax / telex messages to the participants.
4 October	Preparation of 40 spiked paint samples [1].
7 October	Packaging of samples in 16 wooden boxes. Transport to the Finnish Embassy in The Hague, where the boxes were labelled. Delivery of the boxes to Foreign Affairs in The Hague.
8 October	Transport to Australia, Finland, France, Germany, Canada and the UK.
9 October	Transport to Czechoslovakia, Norway, the USSR and the USA.
11 October	Transport to China, Switzerland.
14 October	Transport to India and Sweden.

7 RESULTS OF ANALYSES CARRIED OUT DURING THE DEVELOPMENT OF THE SCENARIO

7.1 Rubber

In the course of the investigation a work-up procedure for the rubber samples was developed (see Chapter 8). The piece of rubber was cut into smaller pieces and extracted by sonication using methylene chloride during 30 min. The relatively long extraction time proved to be necessary in order to obtain high recovery efficiencies (> 90 %). Using a shorter extraction time of 5 min could reduce the efficiency to below 30%.

The results of the stability test were positive both for mustard gas and its disulphide. The following recoveries were obtained after storing the spiked samples at room temperature (around 22 °C):

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[1] Footnote: after the preparation of the samples the sealed glass bottles were stored in a cold room (temperature around 4 °C) till 7 October.

time	mustard gas	disulphide
2 weeks	86 %	100 %
5 weeks	53 %	67 %

Two other compounds, which were not used for the spiking, were tested. Sesquimustard showed comparable stability to mustard gas and its disulphide, whereas mustard gas sulphone proved to be unstable. This last compound could not be recovered three days after spiking.

The large percentage of the high boiling hydrocarbons used as plasticizers caused problems during the GC-MS analyses of the extracts after on-column injection. Due to these hydrocarbons, peak broadening occurred, leading to a severe loss in GC-resolution and sensitivity. A characteristic gas chromatogram of a rubber extract is shown in Figure 1 (Annex 4). An alternative analytical procedure was developed based on dynamic headspace analysis. Heating a small piece of rubber (approx. 10 mg) at 120 °C in a flow of helium resulted in an almost quantitative release of compounds up to n-C18. As the plasticizer hydrocarbons were hardly desorbed no loss of GC-resolution was observed (see Annex 4, Figure 5).

7.2 Paint

The developed work-up procedure for the plates covered with paint consisted of scratching of the paint followed by extraction using sonication with methylene chloride. As the paint particles were slightly static, unexpected losses sometimes occurred. None of the tested compounds showed a recovery efficiency above 90%, even if the samples were worked-up immediately after the spiking. Decomposition by the paint components was ruled out as low recoveries were also found for unreactive hydrocarbons. It was found that compounds with the volatility of mustard gas and the aromatic hydrocarbons present in Shellsol AB gave rather low recoveries. After 15 min the recovery efficiency for mustard gas was less than 10%. Evaporation of the added compounds is the most probable explanation.

The stability test for the selected spiked compounds, sesquimustard (Q) and dimustard ether (T) turned out to be satisfactory. The following results were obtained after storage of the samples at room temperature:

time	sesquimustard	dimustard ether
3 weeks	55 %	33 %
6 weeks	43 %	25 %

7.3 Concrete

Two procedures were developed for the determination of the polar compounds on the concrete samples, both starting with crushing of the concrete pieces. The first one was based on the ultrasonic extraction with water, followed by centrifugation and analysis by TSP-LC-MS. The sequence of the second one was: ultrasonic extraction with acetonitrile, drying with sodium sulphate, filtration, derivatization with N-methyl-bis(trifluoroacetamide) (MBTFA) and GC-MS analysis. The procedure by TSP-LC-MS was more direct and was consequently selected for the stability test. The following recovery efficiencies were measured after storage of the samples at room temperature:

time	thiodiglycol	sulphone
2 weeks	65 %	90 %
5 weeks	51 %	62 %

The TSP-LC-MS analysis revealed that triethanolamine, a precursor of the nitrogen mustard tris(2-chloroethyl)amine (HN-3) was present in the samples. Triethanolamine is a known cement additive.

Some difficulties were encountered with the procedure based on extraction with acetonitrile, derivatization and GC-MS analysis. The extraction efficiencies of thiodiglycol and its sulphone with acetonitrile turned out to be lower compared to water. Despite the same extraction time values of around 30% for thiodiglycol and around 15% for its sulphone were obtained by means of a direct analysis of an extract with TSP-LC-MS. Thiodiglycol could be converted almost quantitatively into its trifluoroacaetyl (TFA) derivative, providing that the extract was dried before the derivatization which had to be carried out at elevated temperatures (60°C). However, the conversion of thiodiglycol sulphone proved to be rather small (ca. 30%).

8 ANALYSES OF CONTROL SAMPLES

In the period of October 21 till November 21, two sets of spiked samples (see Annex 2) prepared in the beginning of October were quantitatively analysed by extraction, followed by GC-MS or TSP-LC-MS in order to determine the remaining amounts of the scheduled compounds. Some control samples were additionally analysed in a qualitative way using other procedures based on GC-MS (e.g. thermodesorption, derivatization) as well as with proton NMR. Details of the experimental conditions used and the results obtained are described in this chapter.

8.1 Experimental

8.1.1 GC-MS analysis

An amount of 0.5 µl of an extract was injected on a fused silica capillary column (50 m x 0.3 mm ID, df = 0.25 µm) coated with CPSil5CB (Chrompack) by means of a Carlo-Erba on-column injector installed on an HP 5890A gas chromatograph. The column was directly connected to the ion source of a VG70-250S mass spectrometer. The temperature of the interface was 250 °C. The helium flow rate was 2 ml/min. The following temperature programme was used : 40 °C (1 min), 8 °C/min to 300 °C (25 min) for the rubber extracts. For the paint extracts the final temperature was 275 °C (5 min).

EI (70 eV) mass spectra were continuously scanned over the mass range m/z 25-500 every second. The temperature of the ion source block was around 200 °C.

CI measurements were carried out using isobutane at a source housing pressure of 10^{-4} mbar and a source temperature of 200 °C. Mass spectra were continuously scanned over the mass range 100-500 with a cycle time of 0.65 sec.

The performance of the analytical system was checked in advance by analysing a standard solution containing several compounds at a concentration level of 10 ng/µl.

Quantitative analyses were carried out by comparing peak areas of the analytes with those obtained from standards added to an extract of a blank material.

8.1.2 TSP-LC-MS analysis

LC-MS analyses were carried out using a Nermag R10-10C mass spectrometer combined with a Vestec thermospray interface. The interface was connected to an LC system consisting of the following parts: a Waters Model 501 solvent delivery system, a Valco injector with a 10 µl sample loop and a stainless steel column (250 mm x 5 mm ID) which was packed in the laboratory with

LiChrosorb C18 (7 µm particles). A second solvent delivery system, Waters Model 510, was connected through a pulse dampener to a low dead volume tee at the end of the column for post-column addition of ammonium acetate.

The eluent composition consisted of 0.1 M ammonium acetate : methanol (80 : 20). The flow through the column was 1 ml/min, whereas 0.2 ml/min 0.1 M ammonium acetate was post-column added. The tip temperature of the interface (ca. 200 °C) was optimized before the analysis using background ions. The ion block temperature was maintained at 200 °C. Mass spectra were scanned over the mass range m/z 100-200 at a scan rate of 1 sec.

Quantitative analyses were carried out by comparing peak areas of the analytes with those obtained from standards added to an extract of a blank material.

8.1.3 Pretreatment of the materials for GC-MS and TSP-LC-MS analysis

After spiking the control samples were stored in a cold room (temperature ca. 4 °C). Shortly before the extraction the samples were removed from the cold room.

The piece of rubber (ca 8 g) was cut into smaller pieces (approximately 20) and extracted by sonication using 20 ml of methylene chloride during 30 min. After extraction the solution was centrifuged for 5 min at 3000 rpm and directly analysed by GC-MS.

The paint (weight approximately 50 mg) was scratched from the plates with a scalpel and transferred to a small reaction tube (1 ml). Extraction was carried out by sonication with 0.5 ml of methylene chloride for 15 min, followed by centrifugation (5 min at 3000 ppm). Extracts were directly analysed by GC-MS.

The concrete was crushed and extracted by sonication with 20 ml of water during 30 min. The solution was centrifuged for 5 min at 3000 rpm. Extracts were directly analysed by TSP-LC-MS. The same procedure was used for the extraction with 20 ml of acetonitrile. A part of the extract was dried with anhydrous sodium sulphate for 30 min and filtered. An amount of 200 µl of the extract was mixed with 200 µl of MBTFA (Pierce) in a reaction vial and heated at 60 °C during 30 min. The extract was analysed by GC-MS directly after the derivatization.

8.1.4 Thermodesorption-GC-MS of rubber

A piece of rubber (ca 10 mg) was transferred into a glass tube (16 cm, 0.6 cm OD) fitted with a quartz wool plug. The glass tube was placed in the flow system of a Chrompack Thermodesorption Cold Trap injector installed on an HP 5890A gas chromatograph as part of the above-described GC-MS combination. Volatile compounds were desorbed at a temperature of 120 °C in a helium flow (15 ml/min) during 10 min and trapped in a piece of deactivated fused silica at -120 °C. After completion of the thermodesorption step, the helium flow-rate was reduced to 2 ml/min. and the trap was flash heated to 220 °C. This temperature was maintained for 5 min. The same GC-MS conditions were used as described for the analysis of the extracts.

8.1.5 NMR analysis

400 MHz ^{1}H NMR spectra were measured at 30 °C using a Varian VXR 400S spectrometer. The following conditions were used : spectral width 5000 - 6500 Hz; digital resolution 0.2 - 0.3 Hz; pulse width 10.4 µs (flip angle approximately 60 °); pulse interval 3 - 7 s. The number of pulses applied varied between 3400 - 20000. TMS was used as a reference for the deuterated chloroform extracts, whereas for the deuterated water extract DSS was used.

During the recording of the spectra of the rubber samples the methylene signal at δ 1.25 was irradiated.

8.1.6 Pretreatment of the materials for NMR analysis

The rubber sample (ca. 8 g) was rinsed with 0.4 ml of deuterated chloroform and the resulting solution was transferred to a 5 mm NMR tube. This was repeated twice till the NMR tube contained about 0.7 ml solution.

The metal plate with the paint was placed in a vial and immersed with 0.6 ml of deuterated chloroform. The paint was extracted by sonication during 5 min, after which the paint became unstuck. The resulting solution was transferred to a 5 mm NMR tube. After repeating this procedure the final volume in the tube was about 0.7 ml.

The concrete sample was placed on a funnel and rinsed with deuterated water till 0.6 ml solution was collected in a 5 mm NMR tube. An amount of 50 µl of a DSS containing D_2O solution was added.

8.2 Results

8.2.1 Rubber

The rubber samples R49 and R50 were analysed by GC-MS on 22 October and the samples R52 and R53 on 20 November 1991, respectively. A characteristic gas chromatogram of sample R49 and EI mass spectra of the 2 spiked compounds are presented in Annex 4 (see Figures 1-4). The following amounts (mg/sample) were found :

Sample	mustard	mustard disulphide	time (days)
R49	0.27	0.20	19
R50	0.25	0.18	19
R52	0.26	0.17	48
R53	0.20	0.14	48

The average recoveries measured after 19 days, 69% for mustard gas and 90% for its disulphide, correspond with those found during the development of the scenario (see paragraph 7.1).

A piece of the sample R56 (ca. 10 mg) was also analysed qualitatively by means of thermodesorption-GC-MS (see Annex 4, Figure 5).

An extract of sample R55 was analysed qualitatively by NMR. Small changes in the NMR spectrum of the spiked sample were observed compared to that of a blank sample (see Annex 4, Figure 6 and 7, respectively), which could be attributed to the added compounds.

8.2.2 Paint

The paint samples P49 and P51 were analysed on 23 October and samples P52 and P54 on 21 November 1991, respectively. A characteristic gas chromatogram of sample P49 and EI mass spectra of the spiked compounds are presented in Annex 4 (see Figures 8-11). The following amounts (mg/sample) were found :

Sample	sesquimustard	dimustard ether	time (days)
P49	0.032	0.056	19
P51	0.039	0.065	19
P52	0.033	0.057	48
P54	0.042	0.057	48

Also the sesquimustard impurity 2-chloroethyl-(2-chloroethoxyethyl) sulphide could be recovered. The amount was estimated at around 0.001 mg/sample in sample P49.

The average recovery measured after 19 days for sesquimustard (53%) corresponds with that found during the development of the scenario (see paragraph 7.2). The average recovery for dimustard ether (62%) was roughly a factor 2 higher. As the added amount of dimustard ether was increased compared to the previous analyses it is possible that the recovery depends on the added amount.

As no molecular ion was found in the EI mass spectrum of dimustard ether, a paint extract was also analysed by isobutane chemical ionization (CI). The CI mass spectra of sesquimustard and dimustard ether are depicted in Annex 4 (see Figures 12-13).

An extract of sample P55 was qualitatively analysed by NMR. As indicated in the spectrum (see Annex 4, Figure 14) signals of methylene groups of both spiked compounds were found. No interferences from the paint were noticed.

8.2.3 Concrete

The concrete samples C50 and C51 were analysed on 31 October and the samples C53 and C54 on 18 November 1991, respectively. Quantitative analysis was based on extraction with water and TSP-LC-MS. A characteristic chromatogram of sample C51 and TSP mass spectra of the 2 spiked compounds are presented in Annex 4 (see Figures 15-17). The following amounts (mg/sample) were found :

Sample	thiodiglycol	thiodiglycol sulphone	time (days)
C50	0.34	0.38	29
C51	0.44	0.43	29
C53	0.42	0.38	47
C54	0.37	0.38	47

The average recoveries measured (around 70 %) for both thiodiglycol and its sulphone, correspond with those found during the development of the scenario (see paragraph 7.3).

The concrete sample C60 was also qualitatively analysed by extraction with acetonitrile and derivatization. The resulting gas chromatogram and mass spectra of the TFA derivatives of thiodiglycol and its sulphone are depicted in Annex 4 (see Figures 18-20).

A water extract of sample C56 was qualitatively analysed by NMR. As indicated in the spectrum (see Annex 4, Figure 21) characteristic triplets of the methylene groups of both spiked compounds were found.

9 AUTHENTICATION

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(Author)

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(Project manager)

10 REFERENCES

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5 Report on a Trial Challenge Inspection, CD/1018, 19 July 1990.

6 Report on a joint Chemical Weapons Trial Challenge Inspection,
CD/1052, 28 January 1991.

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Tel +1-301-671-3957
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ANNEX 2 CODING OF THE SAMPLES

The glass bottles were provided with labels containing a unique number. The indication of a blank (B) was not provided. The numbers 1 to 48 were sent to the participants. The numbers 49 to 54 were stored in a cold room (4 °C) and analysed quantitatively by TNO-PML. The numbers 55 to 60 were stored in a freezer (-12 °C). Some were used for additional analyses (R55, R56, P55, C56 and C60) by TNO-PML.

Rubber

R1
R2
R3 (B)
R4
R5
R6 (B)
R7
R8
R9 (B)
R10
R11
R12 (B)

R13
R14
R15 (B)
R16
R17
R18 (B)
R19
R20
R21 (B)
R22
R23
R24 (B)

R25
R26
R27 (B)
R28
R29
R30 (B)
R31
R32
R33 (B)
R34
R35
R36 (B)

R37
R38
R39 (B)
R40
R41
R42 (B)
R43
R44
R45 (B)
R46
R47
R48 (B)

Controls

R49
R50
R51 (B)
R52
R53
R54 (B)
R55
R56
R57 (B)
R58
R59
R60 (B)

Paint

P1
P2 (B)
P3
P4
P5 (B)
P6
P7
P8 (B)
P9
P10
P11 (B)
P12

P13
P14 (B)
P15
P16
P17 (B)
P18
P19
P20 (B)
P21
P22
P23 (B)
P24

P25
P26 (B)
P27
P28
P29 (B)
P30
P31
P32 (B)
P33
P34
P35 (B)
P36

P37
P38 (B)
P39
P40
P41 (B)
P42
P43
P44 (B)
P45
P46
P47 (B)
P48

Controls

P49
P50 (B)
P51
P52
P53 (B)
P54
P55
P56 (B)
P57
P58
P59 (B)
P60

Concrete

C1 (B)
C2
C3
C4 (B)
C5
C6
C7 (B)
C8
C9
C10 (B)
C11
C12

C13 (B)
C14
C15
C16 (B)
C17
C18
C19 (B)
C20
C21
C22 (B)
C23
C24

C25 (B)
C26
C27
C28 (B)
C29
C30
C31 (B)
C32
C33
C34 (B)
C35
C36

C37 (B)
C38
C39
C40 (B)
C41
C42
C43 (B)
C44
C45
C46 (B)
C47
C48

Controls

C49 (B)
C50
C51
C52 (B)
C53
C54
C55 (B)
C56
C57
C58 (B)
C59
C60

ANNEX 3 CORRESPONDENCE

1 LETTER IN THE BOX CONTAINING THE SAMPLES

Dear participant to the third Round Robin test,

Enclosed please find the 9 samples for the third Round Robin verification test. The samples are prepared as agreed upon the second expert meeting in Spiez. The following samples have to be analysed :
C-series : each containing a piece of concrete of about 22 g.
R-series : each containing a piece of rubber of about 8 g.
P-series : each containing a metal plate (2x4 cm) covered with a layer of paint (thickness 60 µm).
Each sample is wrapped in aluminium paper, packed in a screw-capped glass bottle, which in turn has been sealed in a polyethylene foil.

2 TELEFAX OR TELEX SENT TO PARTICIPANTS

Transport of the Round Robin III samples.

Dear participant to the third Round Robin test,

The samples for the Round Robin III exercise will be transported from the Ministry of Foreign Affairs (The Hague, The Netherlands) to the Dutch embassies in the participating nations by diplomatic post. The embassies are instructed to contact the responsible persons of the laboratories to arrange the local transport as quick as possible. The samples for your laboratory will leave The Netherlands on October .. , 1991.
The samples are prepared as agreed upon the second expert meeting in Spiez and consist of :

- 3 pieces of concrete of about 22 g each.
- 3 pieces of rubber of about 8 g each.
- 3 metal plates (2x4 cm), each covered with a layer of paint (thickness 60 µm).

Each sample is wrapped in aluminium paper, packed in a screw-capped glass bottle (30 ml), which in turn has been sealed in a polyethylene foil. The total of 9 samples are packed in a wooden box (18 x 18 x 22 cm) approved for the transport of dangerous goods.

Kind regards,

E.R.J. Wils

Research Group Analytical Chemistry.

ANNEX 4 CHROMATOGRAMS AND SPECTRA OBTAINED DURING THE ANALYSES OF THE CONTROL SAMPLES

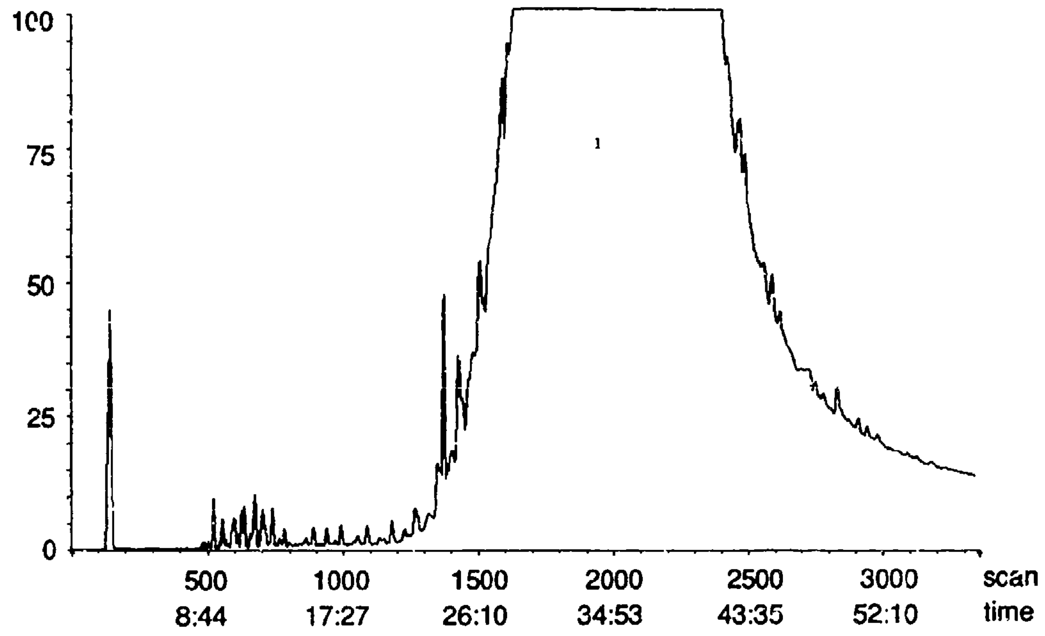


Figure 1 Gas chromatogram of the methylene chloride extract of the rubber sample R49

1. high boiling hydrocarbons used as plasticizers

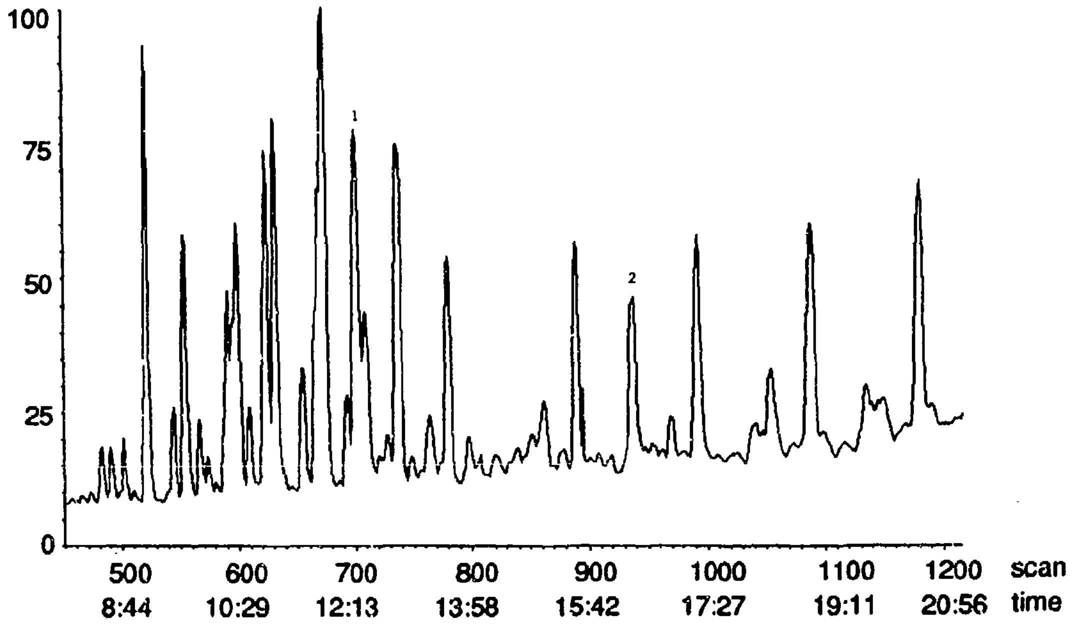


Figure 2 Gas chromatogram of the methylene chloride extract of the rubber sample R49 (expanded range)

1. mustard gas
2. mustard disulphide

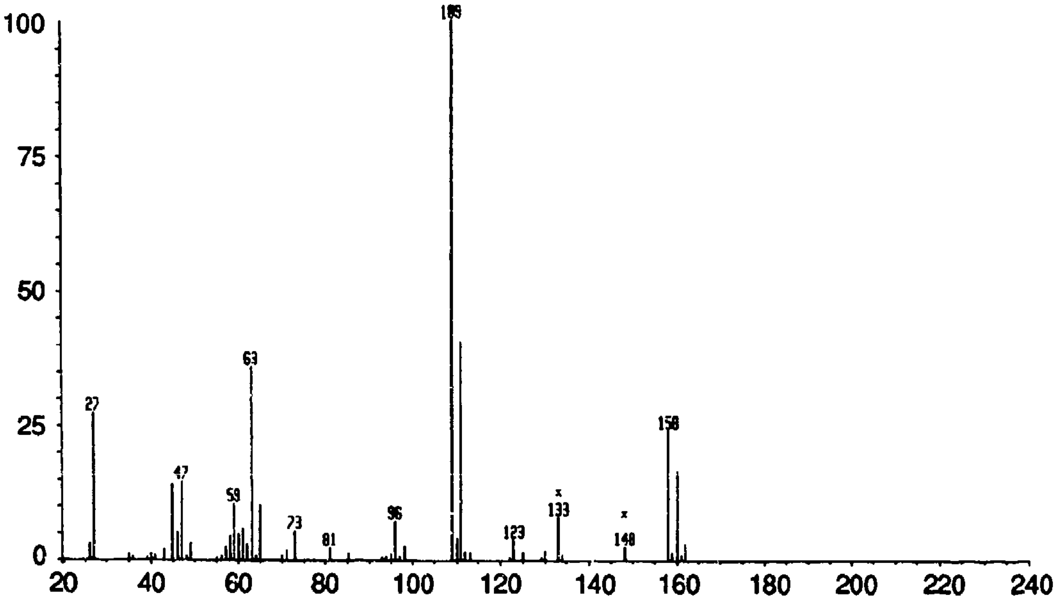
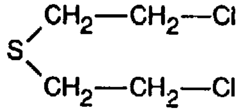


Figure 3 EI mass spectrum (impure) of mustard gas, taken from the analysis of sample R49



MW 158

x : impurity

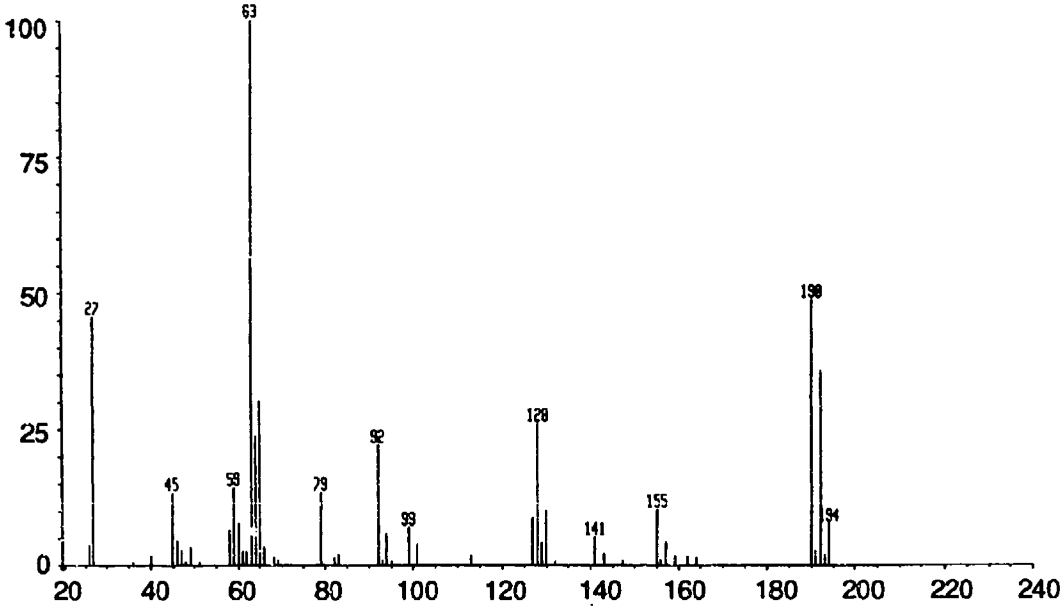
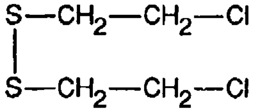


Figure 4 EI mass spectrum of mustard disulphide, taken from the analysis of sample R49



$$\begin{array}{l} S-CH_2-CH_2-Cl \\ | \\ S-CH_2-CH_2-Cl \end{array}$$

MW 190

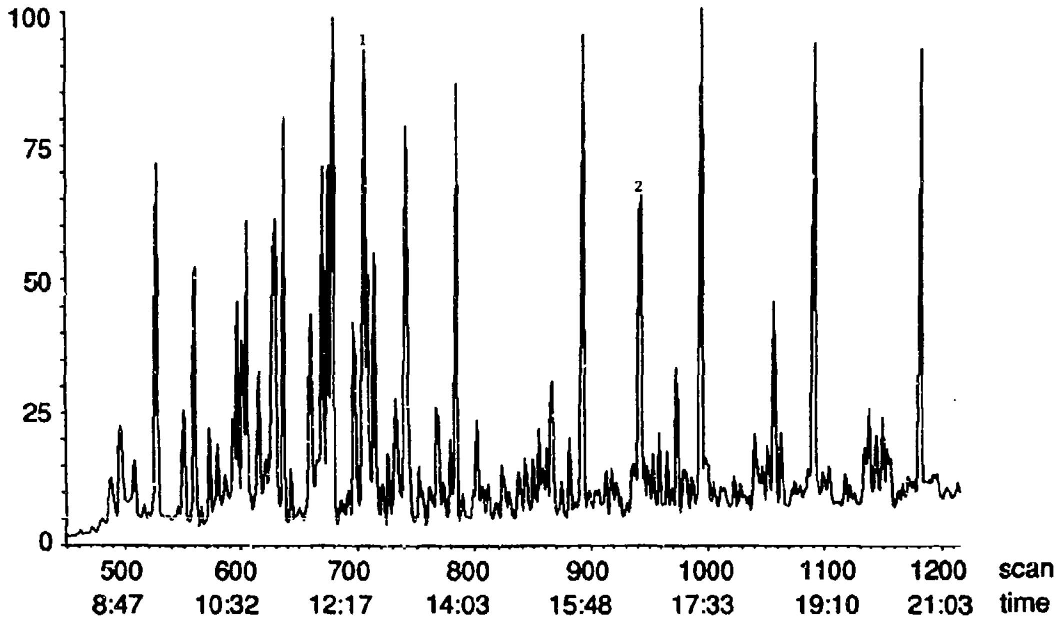


Figure 5 Gas chromatogram obtained after the thermodesorption of the rubber sample R56

1. mustard gas
2. mustard disulphide

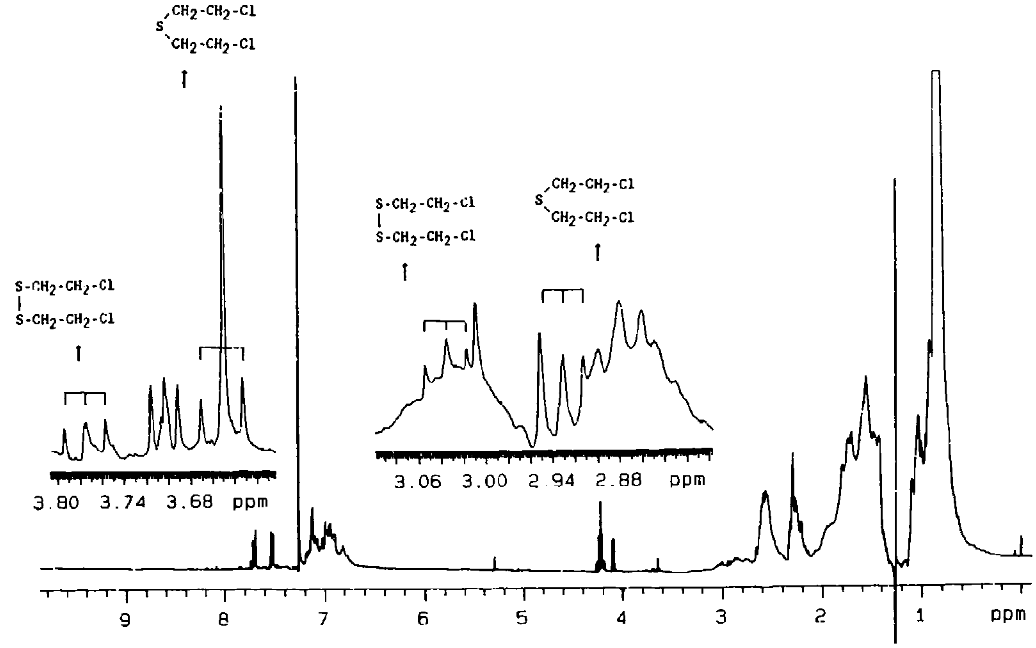


Figure 6 400 MHz ^1H NMR spectrum of the $CDCl_3$ extract of the rubber sample R55

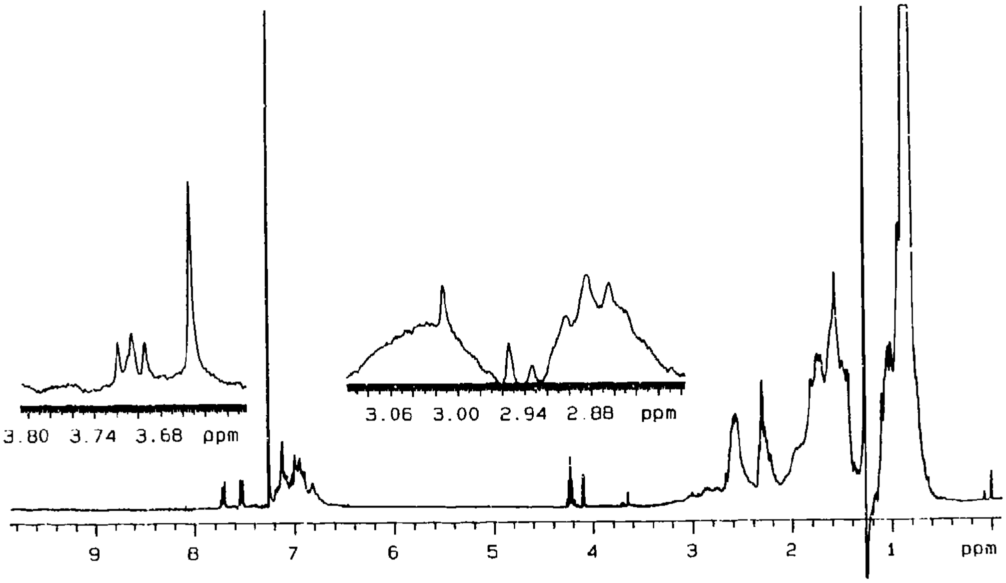


Figure 7 400 MHz ^1H NMR spectrum of the $CDCl_3$ extract of a blank rubber sample

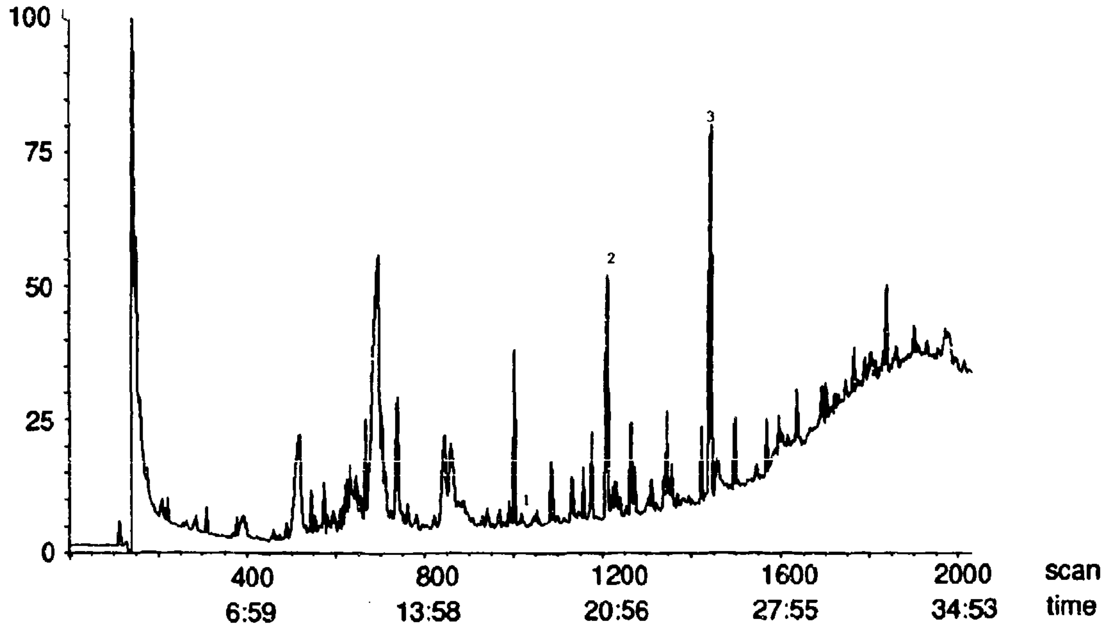


Figure 8 Gas chromatogram of the methylene chloride extract of the paint sample P49

1. 2-chloroethyl-(2-chloroethoxyethyl)sulphide
2. sesquimustard (Q)
3. dimustard ether (T)

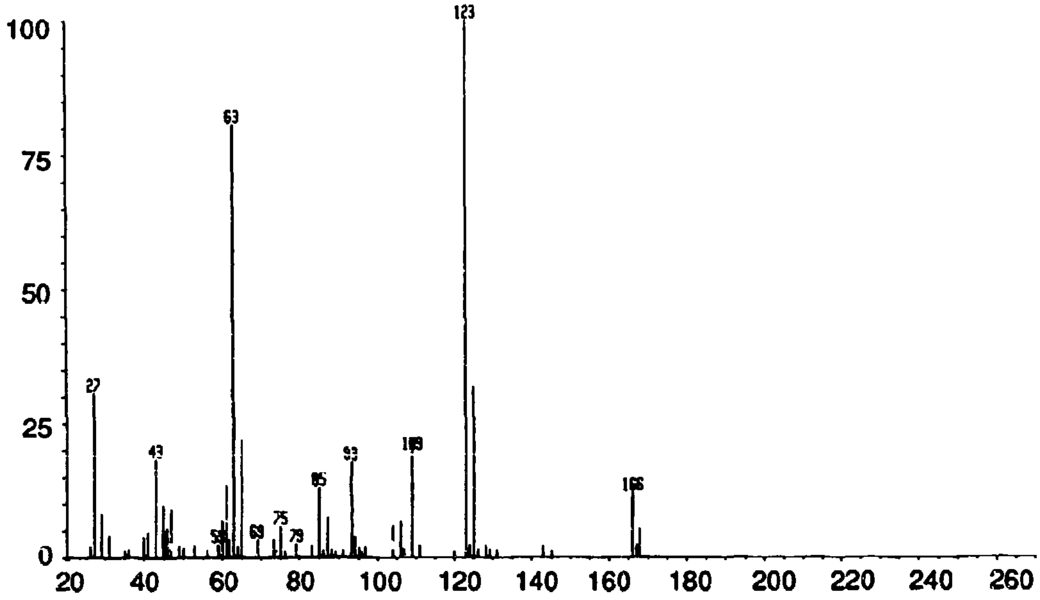
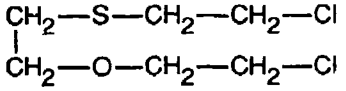


Figure 9 EI mass spectrum of 2-chloroethyl-(2-chloroethoxyethyl) sulphide, taken from the analysis of sample P49



$$\begin{array}{l} CH_2—S—CH_2—CH_2—Cl \\ | \\ CH_2—O—CH_2—CH_2—Cl \end{array}$$

MW 202

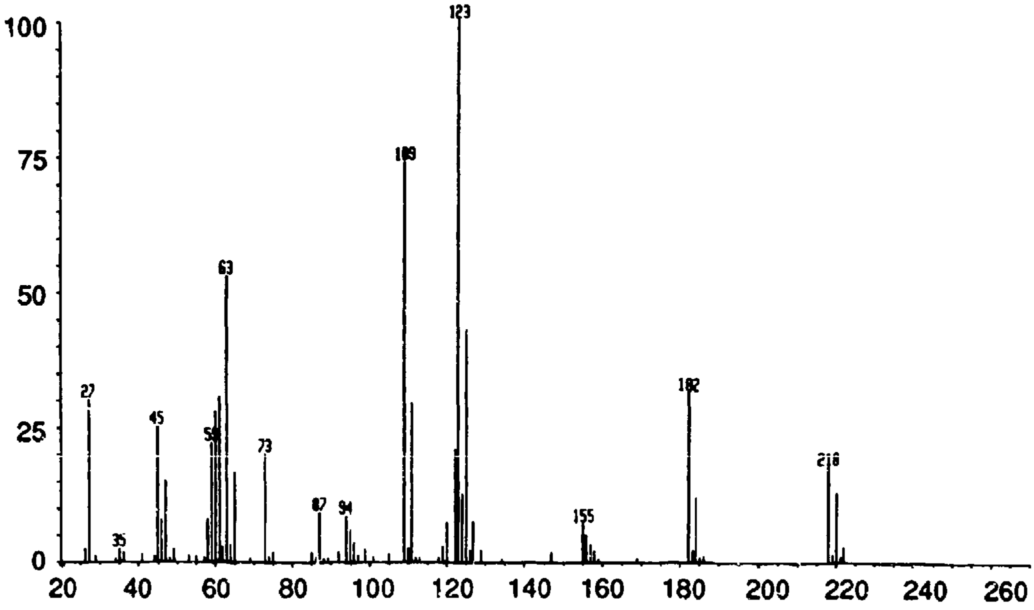
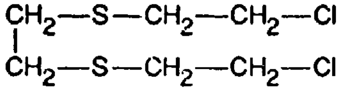


Figure 10 EI mass spectrum of sesquimustard, taken from the analysis of sample P49



$$\begin{array}{l} CH_2-S-CH_2-CH_2-Cl \\ | \\ CH_2-S-CH_2-CH_2-Cl \end{array}$$

MW 218

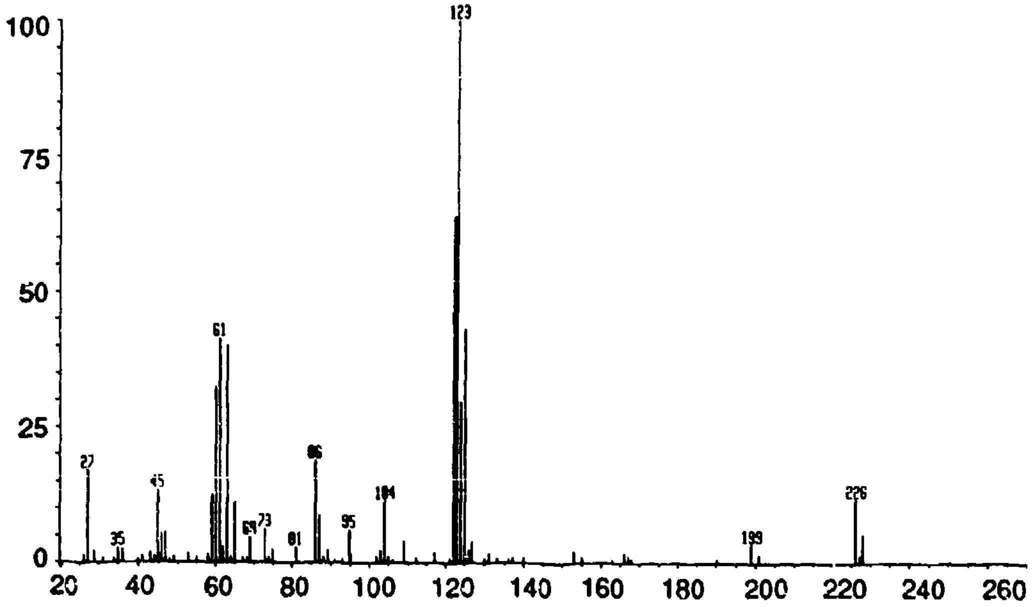
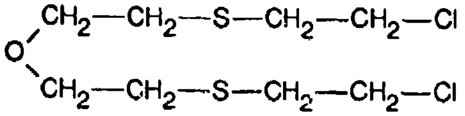


Figure 11 EI mass spectrum of dimustard ether, taken from the analysis of sample P49



MW 262

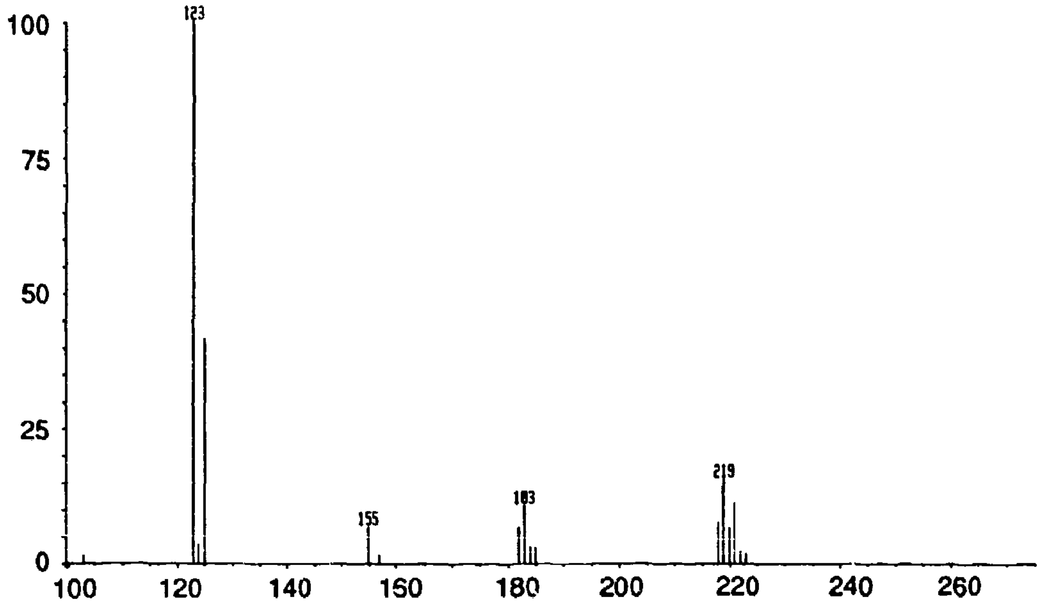
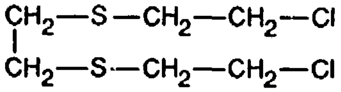


Figure 12 Isobutane CI mass spectrum of sesquimustard



$$\begin{array}{l} CH_2-S-CH_2-CH_2-Cl \\ | \\ CH_2-S-CH_2-CH_2-Cl \end{array}$$

MW 218

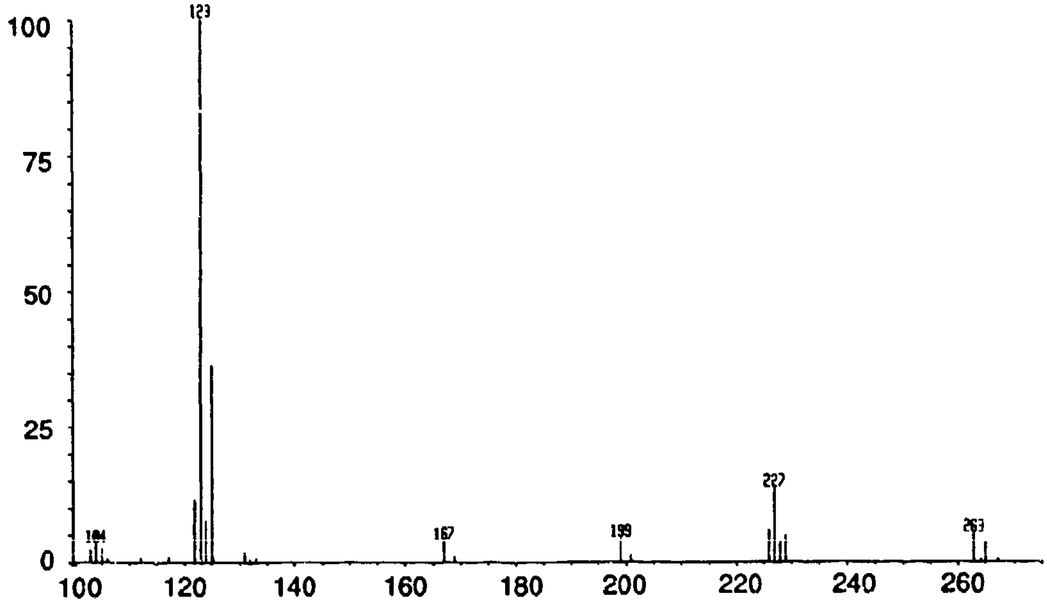
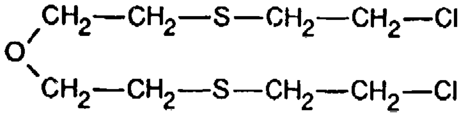


Figure 13 Isobutane CI mass spectrum of dimustard ether



MW 262

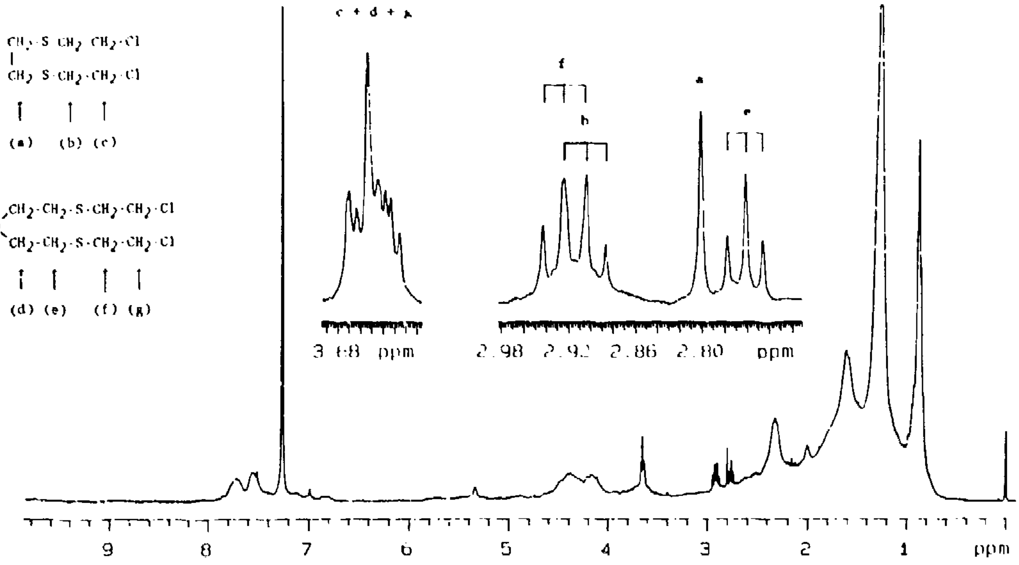


Figure 14 400 MHz ^1H NMR spectrum of the $CDCl_3$ extract of the paint sample P55

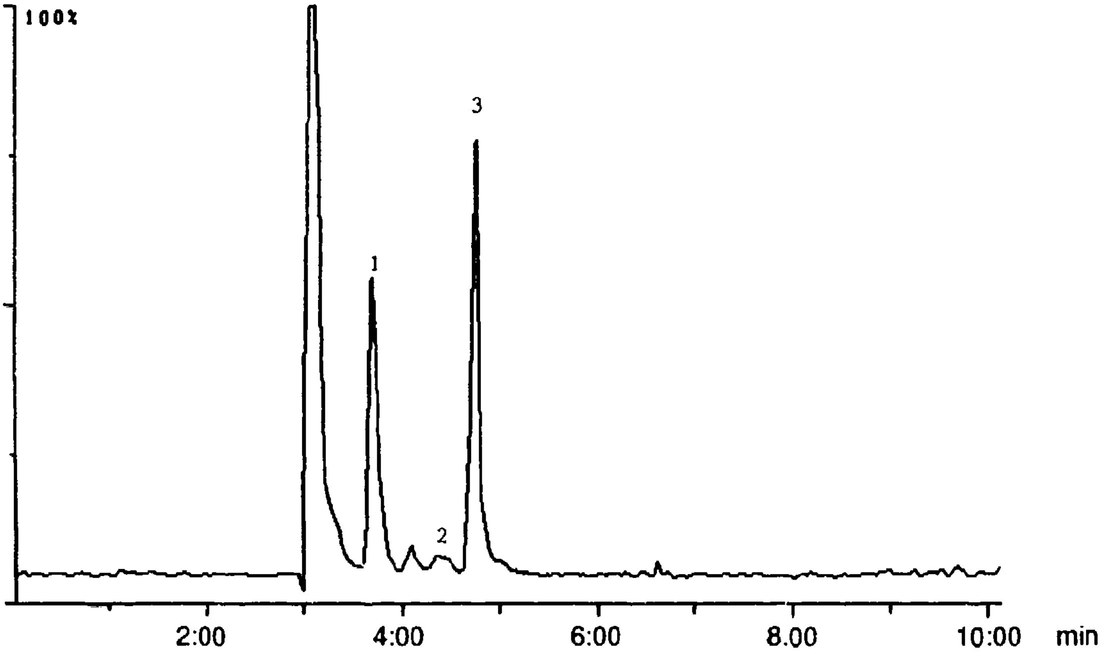


Figure 15 Chromatogram of the water extract of the concrete sample C51

1. thiodiglycol sulphone
2. triethanolamine
3. thiodiglycol

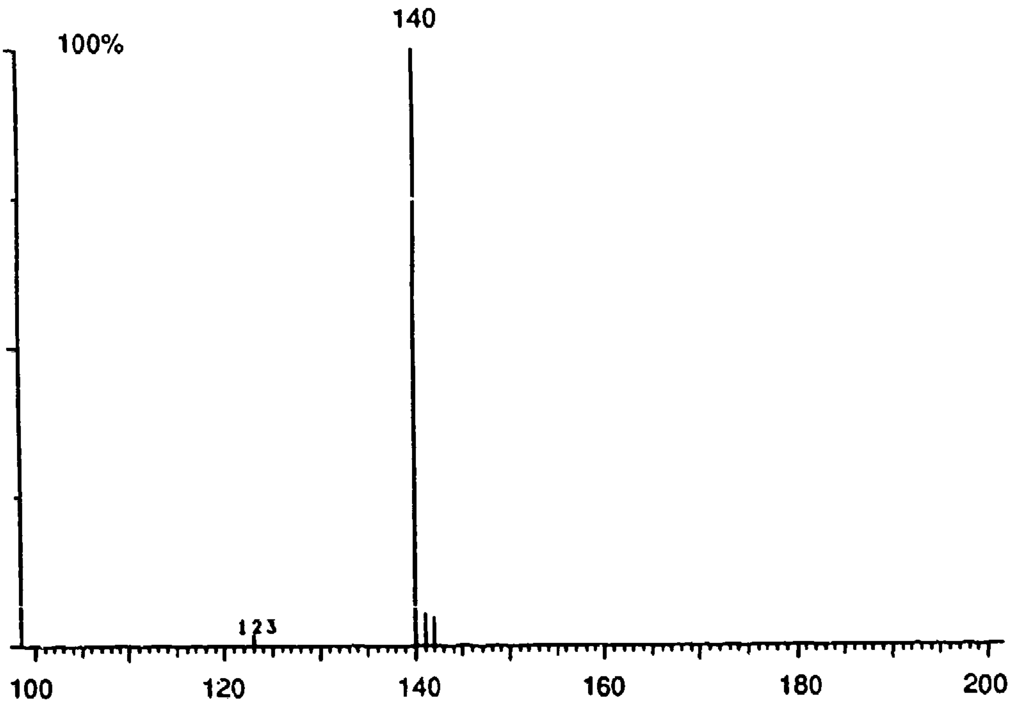
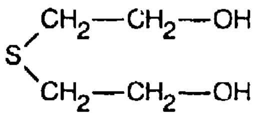


Figure 16 TSP mass spectrum of thioglycol, taken from the analysis of sample C51



MW 122

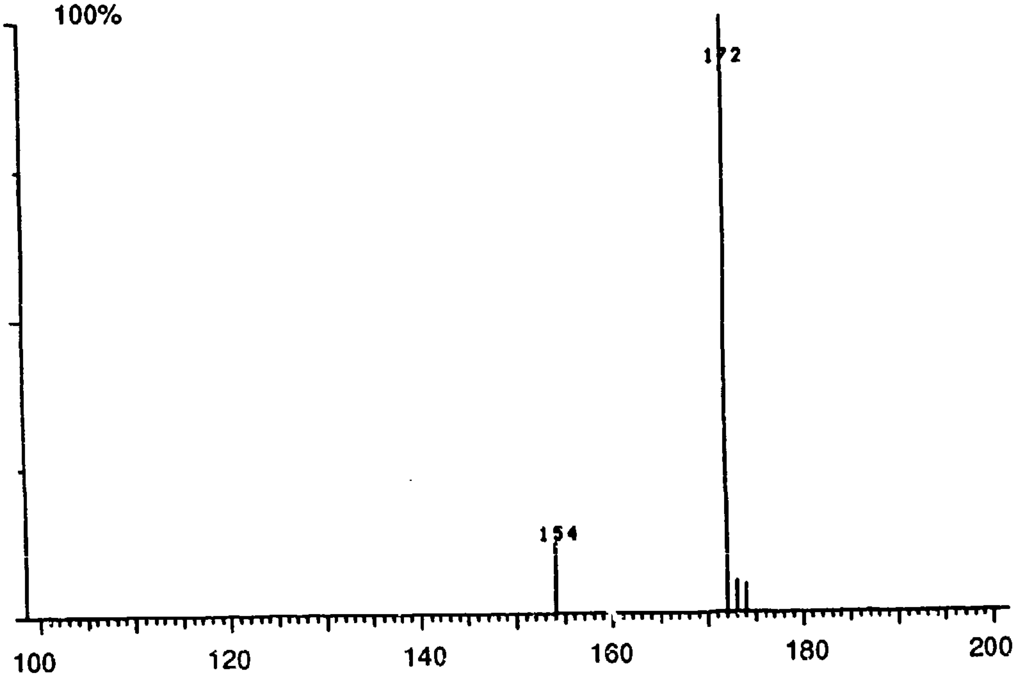
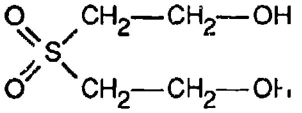


Figure 17 TSP mass spectrum of thioglycol sulphone, taken from the analysis of sample C51



MW 154

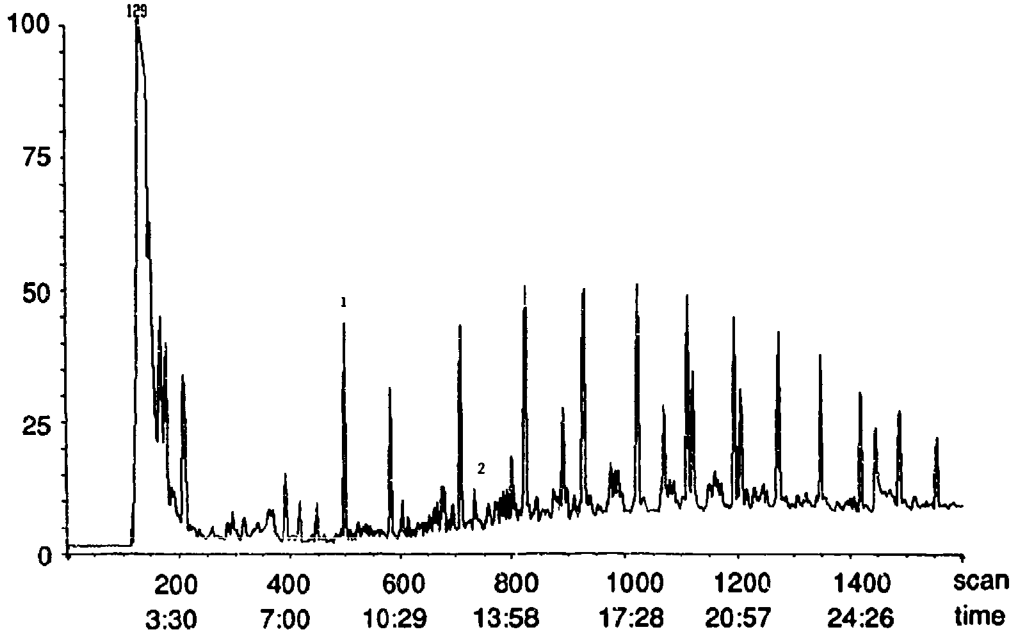


Figure 18 Gas chromatogram of the derivatized acetonitrile extract of the concrete sample C60

1. bis(trifluoroacetyl) derivative of thiodiglycol
2. bis(trifluoroacetyl) derivative of thiodiglycol sulphone

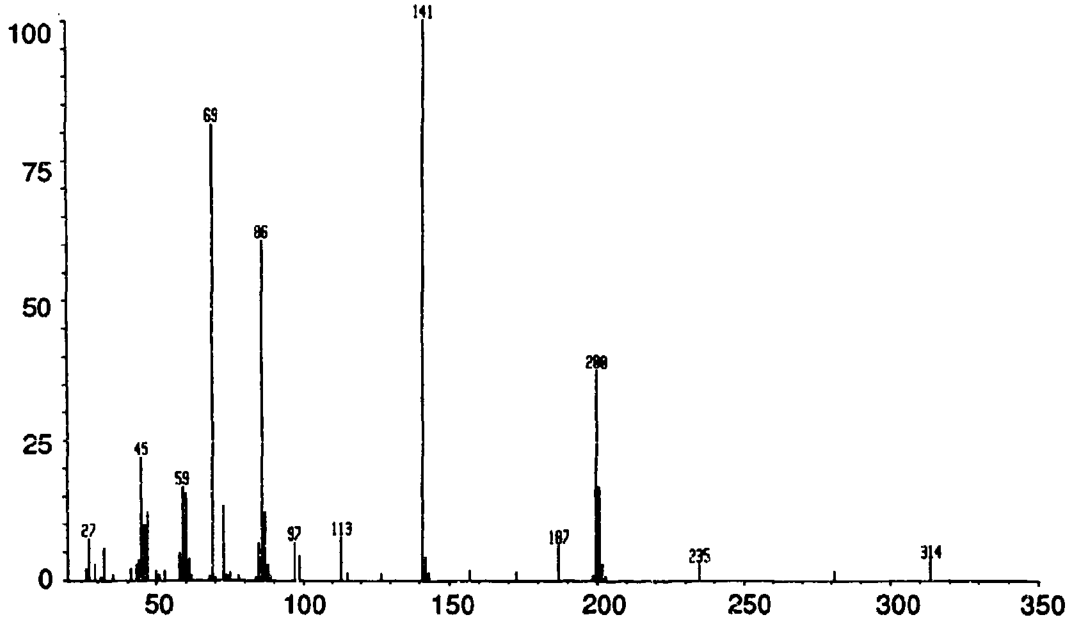
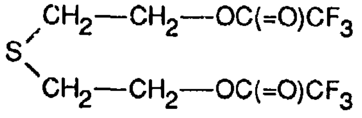


Figure 19 EI mass spectrum of the bis(trifluoroacetyl) derivative of thiodiglycol



MW 314

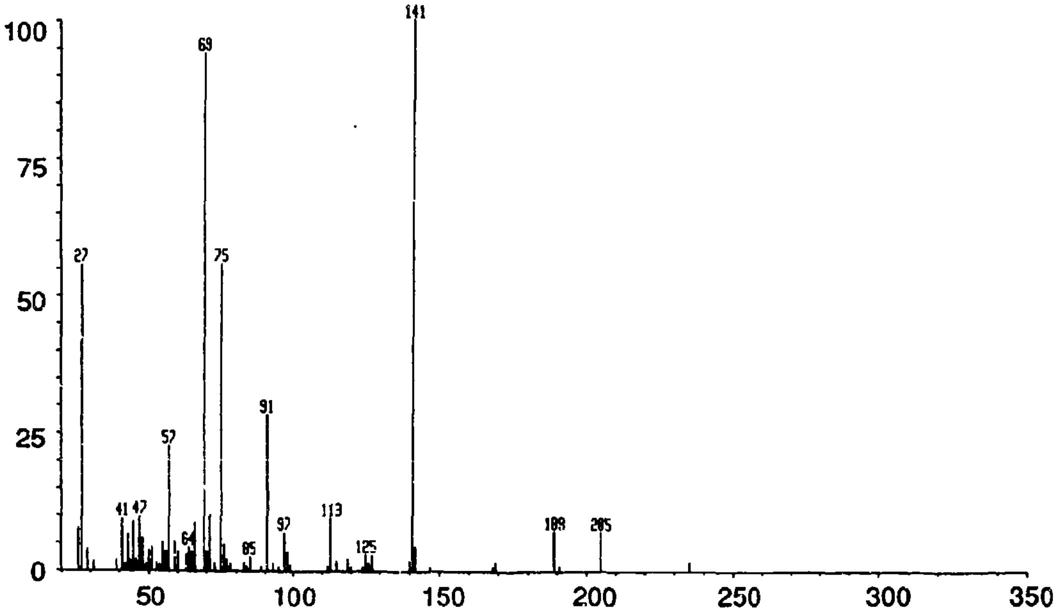
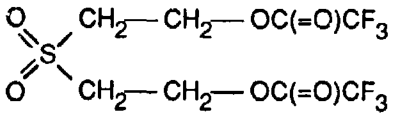


Figure 20 EI mass spectrum of the bis(trifluoroacetyl) derivative of thiodiglycol sulphone



MW 346

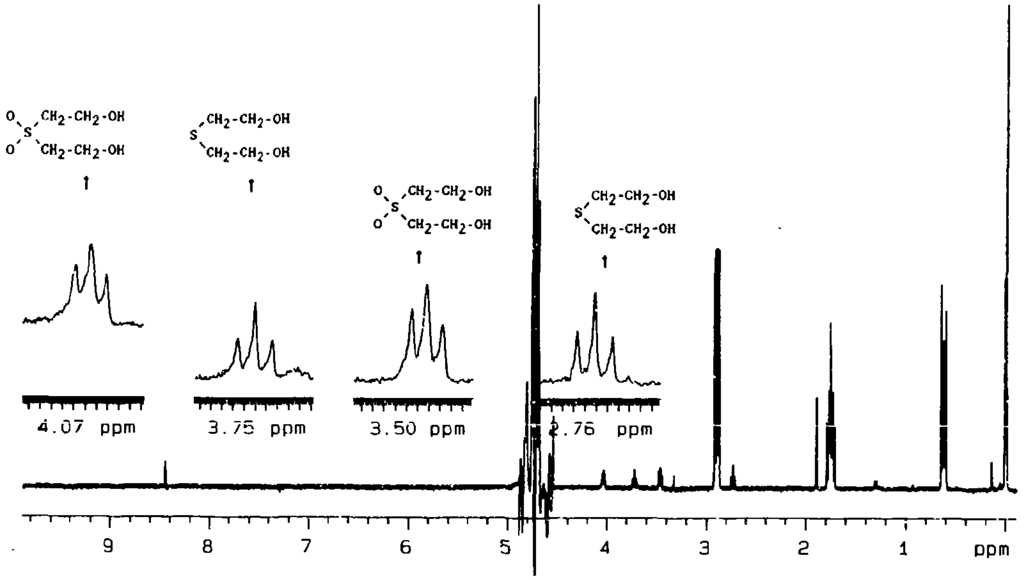


Figure 21 400 MHz ^1H NMR spectrum of the D_2O extract of the concrete sample C56

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10. TITLE AND SUBTITLE

Preparation and analysis of samples for the third Round Robin verification exercise

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14. SUPPLEMENTARY NOTES

15. ABSTRACT (MAXIMUM 200 WORDS (1044 BYTE))

For the third international Round Robin verification exercise executed in the fall of 1991 the TNO-Prins Maurits Laboratory prepared the samples consisting of rubber, paint and concrete. These materials, which were selected to represent samples taken during an inspection at a military facility, were spiked with mustard gas and related vesicants as well as with decomposition products of mustard gas. Diesel fuel and an aromatic white spirit were added as a chemical background. In addition to a description of the spiked materials, details about the coding and transportation of the samples are presented.
A number of procedures was developed for the analysis of the samples. Rubber, which was spiked with mustard gas and its disulphide, could either be analysed by extraction with a nonpolar solvent or by thermodesorption. The latter procedure had advantages for the analysis by gas chromatography-mass spectrometry (GC-MS). Paint was spiked with sesquimustard (Q) and dimustard ether (T). Determination of these compounds was based on extraction with a nonpolar solvent, followed by spectrometric analysis (GC-MS, NMR). Concrete was spiked with two polar decomposition products of mustard gas viz. thiodiglycol and its sulphone. Extraction with water followed by analysis with thermospray-liquid chromatography-mass spectrometry (TSP-LC-MS) turned out to be the best method for the quantitative determination. All compounds added were rather stable in the materials. After a period of 7 weeks they could still be recovered with reasonable or even good efficiencies.

16. DESCRIPTORS	IDENTIFIERS
Mustard Gas	Verifying
Samples	Vesicants
Rubber	Decomposition Products
Paint	Chemical Analysis
Concrete	

17A. SECURITY CLASSIFICATION (OF REPORT)	17B. SECURITY CLASSIFICATION (OF PAGE)	17C. SECURITY CLASSIFICATION (OF ABSTRACT)
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED

18. DISTRIBUTION AVAILABILITY STATEMENT	17D. SECURITY CLASSIFICATION (OF TITLES)
Unlimited distribution	UNCLASSIFIED

Distributielijst

1 DWOO

2 HWO-KL

3/4 HWO-KLu

5 HWO-KM

6 Hoofd Afdeling Militair Geneeskundig Beleid
Directoraat Generaal Personeel
Ministerie van Defensie

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26 Inspecteur Geneeskundige Dienst (KL)

27 Inspecteur Geneeskundige Dienst (KLu)

28 Inspecteur Geneeskundige Dienst (Zeemacht)

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38/40	PML-TNO, Secretariaat Divisie 1, Groep 4
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