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The determination of mustard gas and related vesicants in rubber and paint by gas chromatography-mass spectrometry

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Summary

The determination of mustard gas (2,2'-dichlorodiethyl sulfide) and some related vesicants in rubber and paint was investigated. The vesicants were isolated by extraction with methylene chloride or by dynamic headspace analysis at elevated temperatures. The latter procedure had the advantage that high boiling additives did not interfere during the analysis by capillary column gas chromatography-mass spectrometry. The stability of the vesicants in the materials used proved to be good. No great losses were found after storage for weeks at room temperature.

Samenvatting

De bepaling van mosterdgas (2,2'-dichloordiethylsulfide) en enige verwante blaartrekkers in rubber en verf werd onderzocht. De blaartrekkers werden geïsoleerd door extractie met methyleenchloride of door dynamische headspace analyse bij verhoogde temperatuur. De laatste procedure had het voordeel dat hoog kokende toevoegingen niet stoorden tijdens de analyse door middel van capillaire kolom gaschromatografie-massaspectrometrie. De stabiliteit van de blaartrekkers in de gebruikte materialen bleek goed te zijn. Er werden geen grote verliezen gevonden na opslag gedurende enkele weken bij kamertemperatuur.

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Voorwoord

Vaste materialen zoals kunststoffen behoren tot de mogelijke monsters die genomen kunnen worden op een slagveld na gebruik van chemische strijdmiddelen. Binnen het kader van de opdracht A84/K/159 "Identificatie van chemische strijdmiddelen" was er tot nu toe weinig aandacht besteed aan de analyse van dit soort monsters. Gezien de diversiteit van de vele materialen is het niet haalbaar alle combinaties van kunststoffen en chemische strijdmiddelen te onderzoeken. Daarom werd gekozen voor twee veel voorkomende kunststoffen, rubber en pvc, en enkele mosterdgassen. Het onderzoek heeft geleid tot twee mogelijke bepalingmethoden gebaseerd op gaschromatografie-massaspectrometrie. Beide methoden zijn universeel en kunnen tevens toegepast worden op andere met chemische strijdmiddelen besmette materialen. De resultaten van het onderzoek werden gepubliceerd in het tijdschrift Journal of Chromatography. Voor het nu volgende deel van het rapport werd de tekst van deze publicatie gebruikt.

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1 INTRODUCTION

Since the use of mustard gas (2,2'-dichlorodiethyl sulfide) in the Iran/Iraq conflict [1-3] several reports appeared describing the determination of this vesicant and its related compounds in various matrices. Attention was focussed on the environmental matrices air [4-8], water [9] and soil [10] as well as on biological samples. Analytical procedures for mustard gas and its degradation products were established for these last samples [11-18]. Up till now no procedures have been published for the determination of mustard gas and related vesicants in contaminated materials such as rubber and paint. It is to be expected that in comparison with aqueous samples degradation in these hydrophobic materials will be limited. Rubber and paint are possible samples to be taken on a battlefield or during an inspection of a facility under a future Chemical Weapons Convention. It is most likely that in both situations, a certain chemical background will also be present against which the possible presence of the sulfur vesicants has to be identified. Therefore, the fate of these vesicants in rubber and paint was not studied with the pure compounds themselves but in combination with Diesel fuel and an aromatic white spirit. Unambiguous identification of the presence of mustard gas and its related compounds in such complicated mixtures can only be achieved by a combination of chromatography and spectrometry. Due to its sensitivity and selectivity capillary column gas chromatography-mass spectrometry (GC-MS) is at present the most suitable technique for this purpose.

2 EXPERIMENTAL

2.1 Chemicals

The vesicants mustard gas (2,2'-dichlorodiethyl sulfide), mustard disulfide (2,2'-dichlorodiethyl disulfide), mustard sulfone (2,2'-dichlorodiethyl sulfone), sesquimustard {1,2-bis(2-chloroethylthio)ethane} and dimustard ether {bis(2-chloroethylthio)ether} were all prepared at TNO-PML. Their identity and purity were controlled by NMR and GC-MS before the preparation of stock solutions. The purity of all compounds was over 95% except for sesquimustard (Q), which contained about 7% of 2-chloroethyl-(2-chloroethoxyethyl)sulfide.

Shellsol AB, an aromatic white spirit with a boiling range of 165-220 °C, was obtained from Shell. Diesel fuel was obtained from a commercial petrol station. It consisted of aliphatic hydrocarbons with a boiling range of 150-350 °C. Methylene chloride (no. C14500) was purchased from Lamers & Pleuger (NL).

2.2 Materials and pretreatment

The rubber sample, which had been used for the sealing of a window of a car, was a common type of black coloured rubber containing soot and relatively large quantities (about 30%) of high boiling hydrocarbons used as plasticizers. An analysis by pyrolysis mass spectrometry pointed to an ethene-propylene copolymer. The rubber was cut into pieces of approximately 8 g, which were spiked as homogeneously as possible with mustard gas and other vesicants, an aromatic solvent mixture (Shellsol AB) with the same volatility as mustard gas and Diesel fuel. The spiked amounts of the vesicants were in the ppm (mg/kg) range, whereas the aromatic solvent mixture and the Diesel fuel were added at a higher level. A methylene chloride solution was brought on the surface of each piece by means of a syringe. After a period of approximately 15 min the rubber was visibly dry. For storage experiments the piece of rubber was wrapped in aluminium paper. Before the extraction the spiked 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.

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 possessed the characteristic military green colour. The plates were prepared by the TNO Centre for Coatings Research (Delft, NL) and were stored at room temperature for approximately 5 months. The painted surface was spiked with vesicants in a Shellsol solution (5 μl). The spiking and storage were performed in the same way as for the rubber samples. The paint (weight approximately 50 mg) was scratched off 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 rpm). Extracts were directly analysed by GC-MS.

2.3 Analysis of extracts

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 $^{\circ}\text{C}$; the helium flow rate was 2 ml/min. The oven temperature was 40 $^{\circ}\text{C}$ (1 min) and was raised at a rate of 8 $^{\circ}\text{C}/\text{min}$. The final temperature depended on the analysis viz. 300 $^{\circ}\text{C}$ (25 min) for the rubber extracts and 275 $^{\circ}\text{C}$ (5 min) for the paint extracts.

Electron impact (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 $^{\circ}\text{C}$.

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

2.4 Thermodesorption

A piece of rubber (ca. 10 mg) or paint (ca. 1 mg) was transferred to a glass tube (16 x 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 various temperatures (100-150 °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 trap was flash heated to 220 °C, which temperature was maintained for 5 min. The same GC-MS conditions were used as described for the analysis of the extracts.

3 RESULTS AND DISCUSSION

Two approaches for the determination of sulfur mustard gases were investigated. In addition to extraction followed by GC-MS analysis of the extracts dynamic headspace (thermal extraction or gas stripping) was carried out. Pieces of rubber were extracted by sonication using methylene chloride for 30 min. This relatively long extraction time proved to be necessary in order to obtain a high extraction efficiency of mustard gas (> 90%). Using an extraction time of 5 min could reduce the efficiency to below 30%. The large percentage of high boiling hydrocarbons used as plasticizers in the rubber caused problems during the GC-MS analysis of the extracts after on-column injection. As an example the gas chromatogram of an extract obtained from a piece of rubber (ca. 8 g) spiked with 0.38 mg of mustard gas, 0.21 mg of mustard disulfide, 4.45 mg of Shellsol and 7.32 mg of Diesel fuel is presented in Figures 1 and 2.

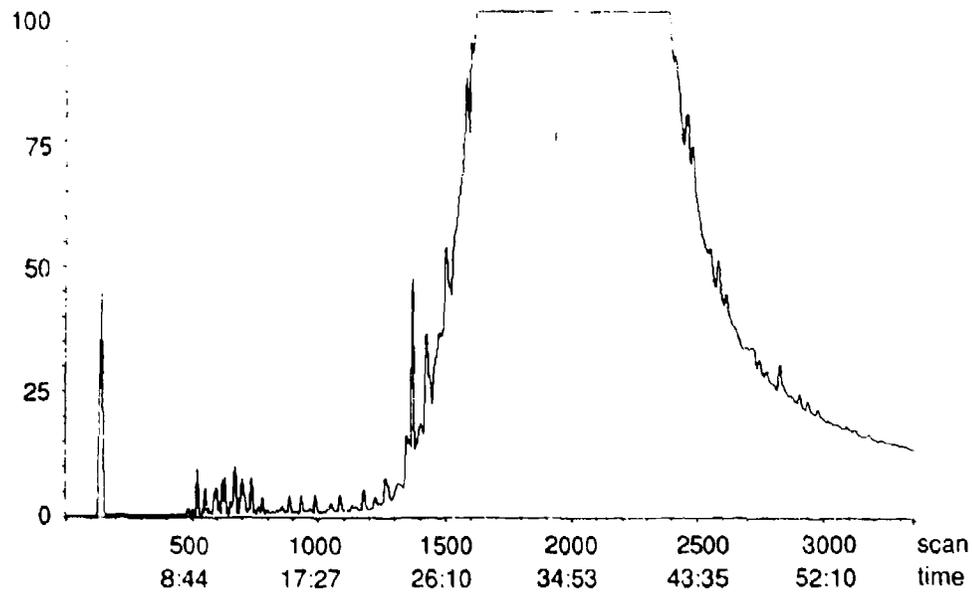


Figure 1 Gas chromatogram of a methylene chloride extract of a spiked rubber sample.
1: high boiling hydrocarbons used as plasticizers

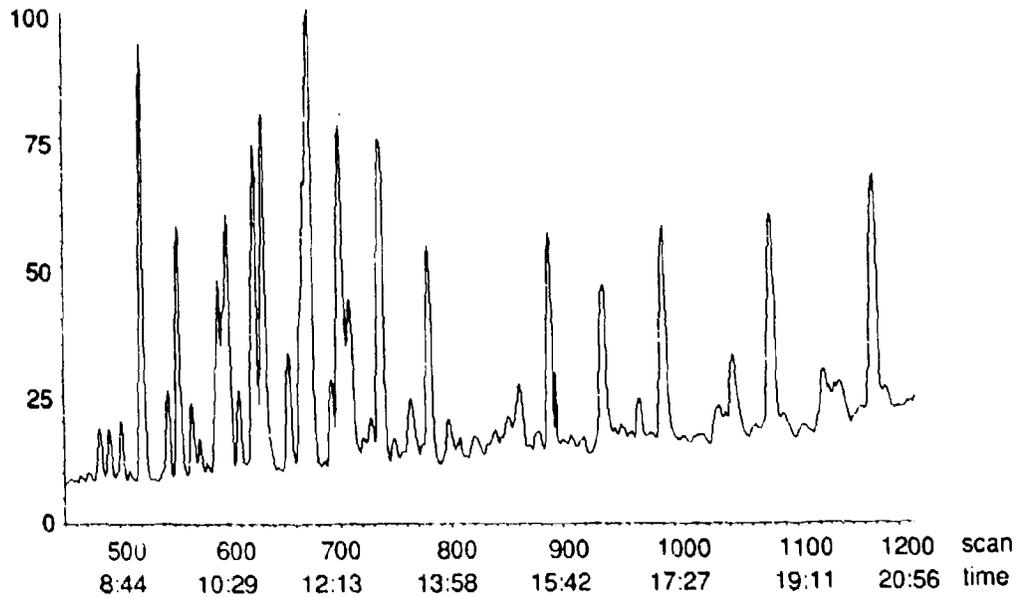


Figure 2 Gas chromatogram of a methylene chloride extract of the spiked rubber sample
shown in Figure 1 (expanded range).
1: mustard gas; 2: mustard disulfide

The recorded mass spectra of the vesicants were similar to those described in literature [10, 19, 20]. Due to the large amounts of high boiling hydrocarbons peak broadening occurred, leading to a severe loss in GC resolution. Optimal resolution will be a prerequisite for the determination of the studied vesicants in such complicated mixtures. Better results were obtained with the dynamic headspace procedure. In order to prevent unwanted thermal decomposition reactions and also to achieve maximal separation between the vesicants and the plasticizers the lowest possible temperature was evaluated. Heating a small piece of spiked rubber (ca 10 mg) at 120 °C in a flow of helium resulted in an almost quantitative release of mustard gas and its disulfide. As the major part of the plasticizer hydrocarbons were not released no loss of GC resolution was noticed (see Figure 3).

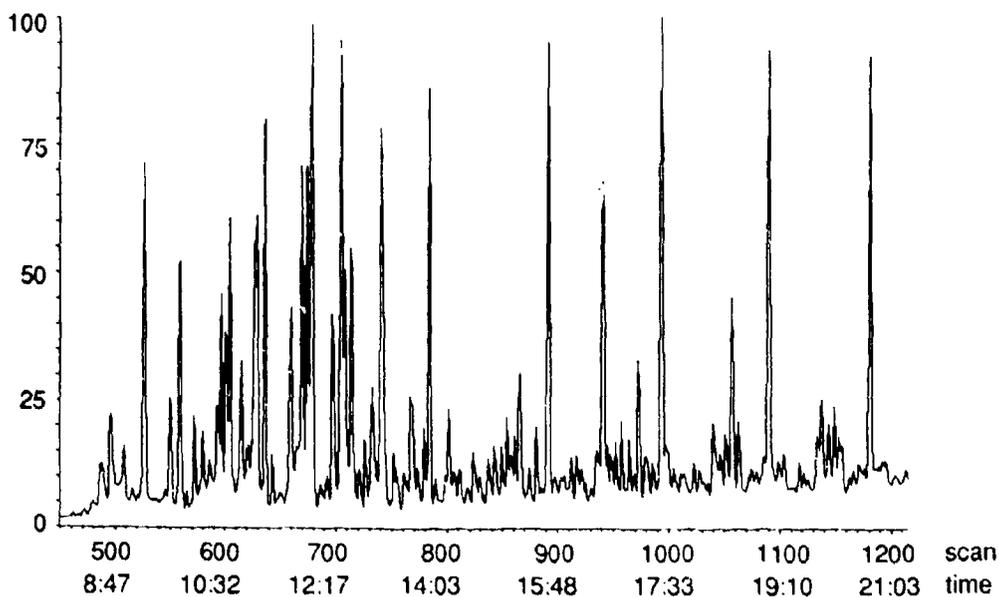


Figure 3 Gas chromatogram obtained after the thermodesorption of a spiked rubber sample at 120 °C (expanded range).
1: mustard gas; 2: mustard disulfide

The temperature of 120 °C was too low for a complete release of the higher boiling vesicant sesquimustard (Q) from the rubber. For this compound the lowest temperature needed, proved to be 150 °C.

The developed work-up procedure for the plates covered with paint consisted of scratching off the paint followed by extraction using sonication with methylene chloride. As the paint particles were somewhat static unexpected losses sometimes occurred. None of the tested compounds showed a

recovery 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 measured for unreactive hydrocarbons. It was found that compounds with the volatility of mustard gas and the aromatic hydrocarbons present in Shellsol gave very low recoveries. After 15 min the recovery for mustard gas was less than 10%. Evaporation of the added compounds before they were adsorbed by the paint is the most probable explanation. Therefore, experiments were mainly carried out with the higher boiling vesicants sesquimustard (Q) and dimustard ether (T). A characteristic gas chromatogram of an extract obtained from a paint sample spiked with 67 µg of sesquimustard (Q), 98 µg of dimustard ether (T) and 460 µg of Diesel fuel is presented in Figure 4.

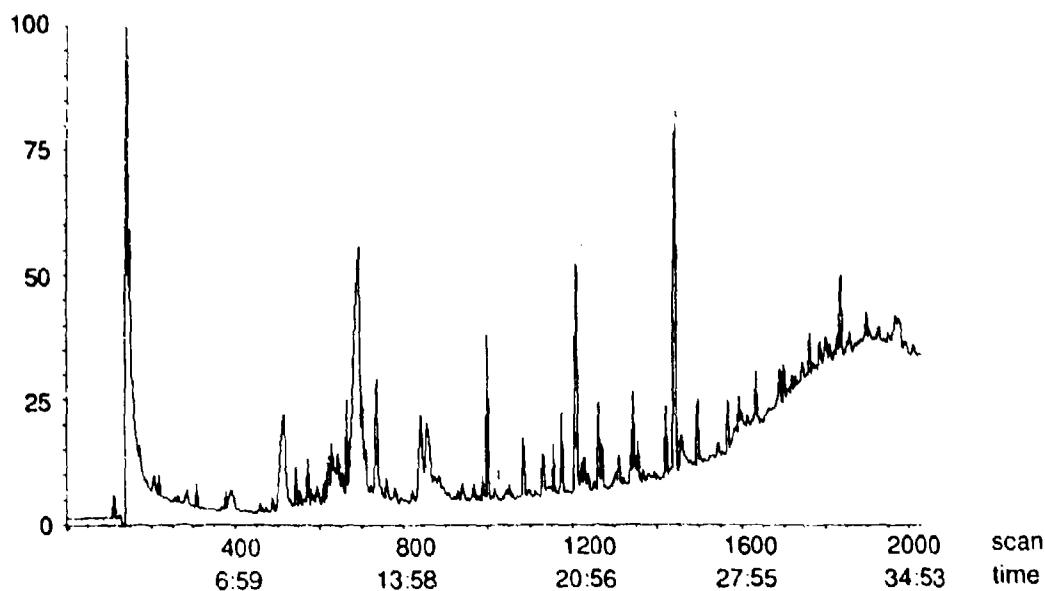


Figure 4 Gas chromatogram of a methylene chloride extract of a spiked paint sample.
1: 2-chloroethyl-(2-chloroethoxyethyl)sulfide;
2: sesquimustard (Q); 3: dimustard ether (T).

Despite the fact that a Shellsol solution was used for the spiking of the paint hardly any aromatic compounds could be detected. The relatively large broad peak in the beginning of the chromatogram corresponded with 2-ethylhexanoic acid. In addition to the two vesicants the impurity in the used sesquimustard (Q), viz. 2-chloroethyl-(2-chloroethoxyethyl)sulfide, could also be detected. Paint could also be thermally desorbed. For an almost quantitative release of the highest boiling vesicant tested, dimustard ether (T), a temperature of 150 °C was necessary. For sesquimustard (Q) 120 °C turned out to be sufficient. As the paint did not contain large amounts

of additives hardly any differences between the extraction and the thermodesorption results were found. However, care should be taken that during the removal of the paint from the plates by scratching the paint does not become contaminated with metal particles. These may catalyse unwanted thermal decomposition reactions at elevated temperatures.

The stabilities of the vesicants in the investigated materials were determined. The recoveries obtained after storage of the samples at room temperature (around 22 °C) are presented in Table 1. Due to the relatively large spread (upto 20% between duplicate experiments) the values have to be considered more as an indication. Although there was a decrease, after 6 weeks of storage more than 50% of the added mustard gas and its disulfide could still be recovered in the rubber sample. However, the rubber material used was not completely inert as was experienced with mustard sulfone. Although this compound could initially be retrieved with a recovery of around 85%, it could not longer be detected (recovery < 1%) 3 days after the spiking. The recoveries found with the paint samples were lower than those obtained with the rubber. This was mainly due to initial losses during the spiking of the samples as explained above.

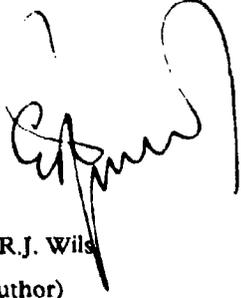
The relatively good stabilities of the sulfur vesicants in hydrophobic materials such as rubber and paint are in marked contrast with their instabilities in environmental and biological samples. The hydrolysis of mustard gas in water is very fast ($t^{1/2}$ 10 min at 20 °C) [21]. The degradation on soil will depend on the type of soil and its wetness. In a number of soil samples (humic sand, humic loam and clayey peat) mustard gas could not be retrieved with a recovery greater than 1% one day after applying the agent to the soil [22]. Therefore, materials such as rubber and paint may be considered as good samples for the retrospective identification of mustard gas and related vesicants.

Table 1 Recoveries (%) of sulfur mustard gases in rubber and paint

Compound	material	30 min	3 weeks	6 weeks
mustard gas	rubber	86	60	57
mustard disulfide	rubber	100	92	84
sesquimustard (Q)	paint	68	55	43
dimustard ether (I)	paint	59	33	25

4

AUTHENTICATION



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