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ANALYSIS OF SNOW SAMPLES CONTAMINATED
WITH CHEMICAL WARFARE AGENTS

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| 8) ABSTRACT (continue on reverse side if necessary) <p>Snow samples contaminated with the chemical warfare agents sarin, soman, tabun, Vx and mustard gas have been analysed after outdoor exposure for 1, 4, 7, 15 and 30 days at normal Norwegian winter condition. After up to 15 days exposure, all agents were still present in concentrations sufficiently high for positive verification and quantitative analysis. After 30 days, the concentration of sarin, tabun and mustard gas was below detection limits, and analysis could only positively identify soman and Vx.</p> | | | | |
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ANALYSIS OF SNOW SAMPLES CONTAMINATED WITH CHEMICAL WARFARE AGENTS

SUMMARY

Snow samples contaminated with the chemical warfare agents sarin, soman, tabun, Vx and mustard gas have been analysed after outdoor exposure for 1, 4, 7, 15 and 30 days at normal Norwegian winter condition. After up to 15 days exposure, all agents were still present in concentrations sufficiently high for positive verification and quantitative analysis. After 30 days, the concentration of sarin, tabun and mustard gas was below detection limits, and analysis could only positively identify soman and Vx.

1 INTRODUCTION

The use of chemical weapons in warfare has been forbidden by international law since the ratification of the Geneva Protocol in 1925. Since then, however, several countries have been accused of violating the treaty. The difficulty of chemical agent identification is the critical problem in substantiation of these charges. Unless these weapons are used on a massive scale, solid analytical evidence was generally difficult to obtain due to the large number of different compounds that may be used as chemical weapons and their high toxicological potency. Chemical weapons are effectively used primarily against unprotected personnel, and all reports of their use after the ratification of the Geneva Protocol are against unprotected or poorly protected personnel. Military objectives may be achieved with relatively small amounts of agents, thus demanding sensitive analytical methods for positive identification. Further, many of the agents are highly volatile, and on a battlefield, the amount of residual agents to be found and sampled is often very small. The agents will be spread all over the ground, and will therefore be very diluted. In most cases further dilution occurs rapidly due to instability and

decomposition. To verify that such samples contain chemical warfare agents, to identify the agent, and to determine the quantity requires very selective and sensitive analytical methods, and the analysis itself must generally be performed in a well equipped laboratory by trained personnel. Analytical methods and procedures suited for this type of analysis have been reported previously in the open literature (1, 2, 3, 4a-d), for air, water, vegetation and soil.

2 EXPERIMENTAL

The experimental work was done partly outdoors, and partly in the laboratory. The work done outdoors was preparation and collection of samples and recording of meteorological data. All sample preparations and analysis was carried out in the laboratory.

2.1 Field experiments

The field experiments were planned to represent what might be expected to happen in a real chemical attack situation. Small samples of chemical warfare agents were placed on top of the snow surface, and samples were taken for analysis at intervals. During the whole period, the samples were left to the exposure of the prevailing weather conditions. To prevent snow from falling on top of the samples, a roof was erected about one meter above the samples. This also prevented the sun from shining directly on the samples.

Each individual sample consisted of a single 1 mg droplet of agent placed in the middle of the top surface of a snow filled 400 ml glass beaker. The snow in the beakers consisted of newly fallen snow taken in the near environment just prior to the start of the experiments. The diameter and height of the beakers were 70 and 105 mm respectively, giving a top surface of about 40 cm². This corresponds to a contamination density of 0.25 g/m², which is on the lower range of what might be expected in a real chemical attack situation.

A large number of chemical compounds are potential chemical warfare agents. For practical reasons the number of agents to be tested had to be restricted, and the agents chosen were the following five:

- 1: Ethyl NN-dimethylphosphoramidocyanidate (GA or tabun)
- 2: Isopropyl methylphosphonofluoridate (GB or sarin)
- 3: 1,2,2-Trimethylpropyl methylphosphonofluoridate (GD or soman)
- 4: Ethyl S-2-diisopropylaminoethyl methylphosphonothiolate (Vx)
- 5: Bis(2-chloroethyl) sulphide (HD or mustard gas)

A sufficiently large number of samples were prepared. After being exposed for the desired length of time, a number of the beakers were selected for analysis, and the snow in each beaker was divided into eight horizontal layers of about 1 cm using a plastic spoon. To avoid possible contamination, a new spoon was used for each layer. The snow in each layer was collected in a separate glass container, and were immediately brought into the laboratory for workup and analysis.

The experiments were performed during two different time periods. The 4, 15 and 30 days tests were carried out in the first period, and 1 and 4 days test in the other. Weather conditions during experiments were generally recorded three times a day; in the morning, at noon and in the evening. Samples were placed in a shielded location, and the wind was generally low (less than 1-2 m/s). The temperature and relative humidity for both exposure periods are given in Figure 1.

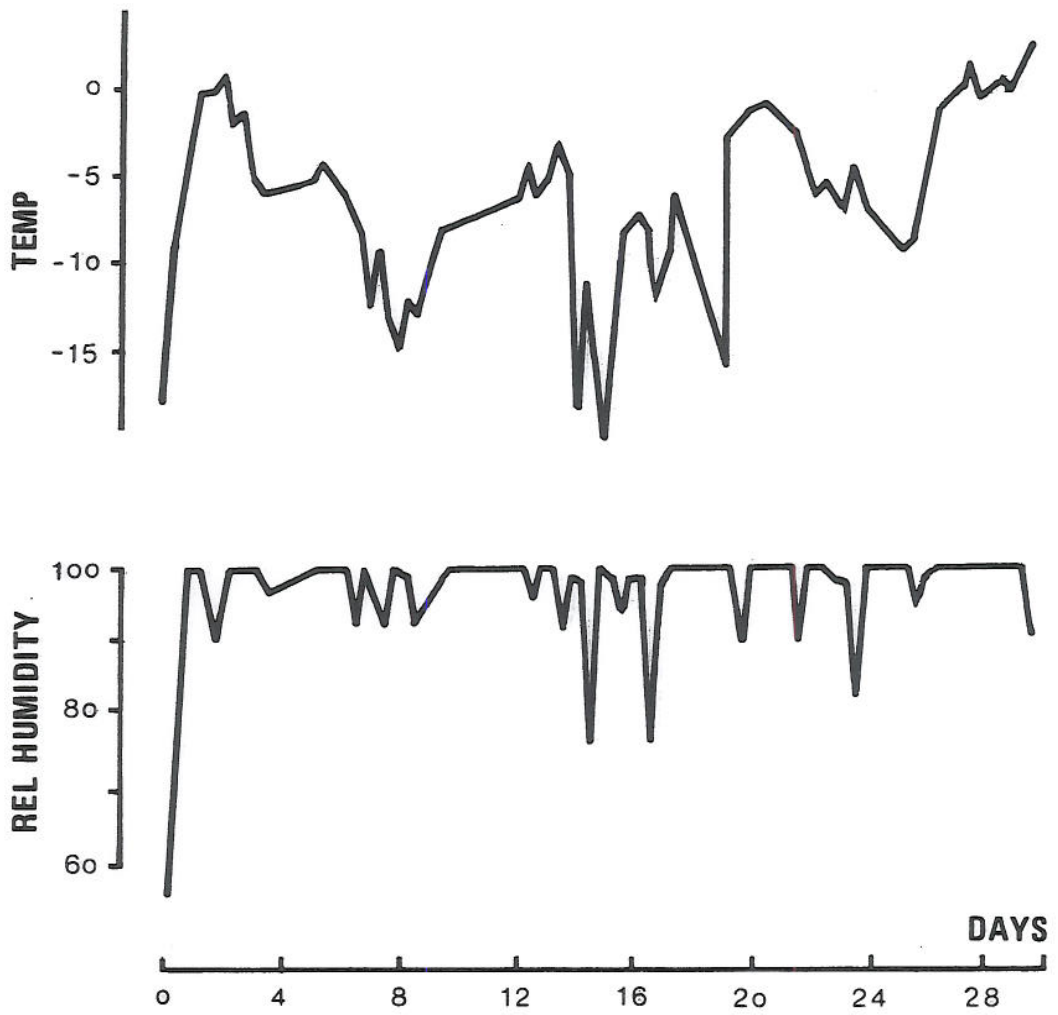


Figure 1a Plot of temperature ($^{\circ}\text{C}$) and relative humidity (per cent) in the time period for the 7, 15 and 30 days tests

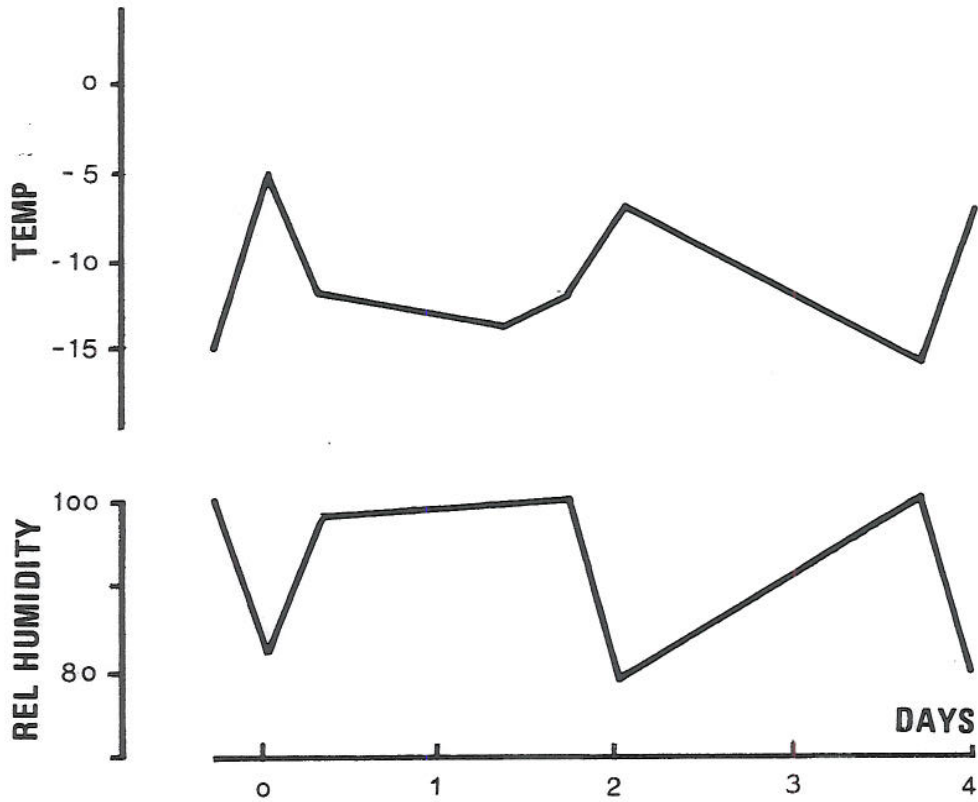


Figure 1b Plot of temperature ($^{\circ}\text{C}$) and relative humidity (per cent)
in the time period for the 1 and 4 day tests

Just before ending the 30 day experiment, a period of mild weather occurred, leading to a partial melting of the snow samples. This made it impossible to divide into the usual eight layers. Figure 2 illustrates the situation, and the content of the beakers were divided in three parts as indicated.

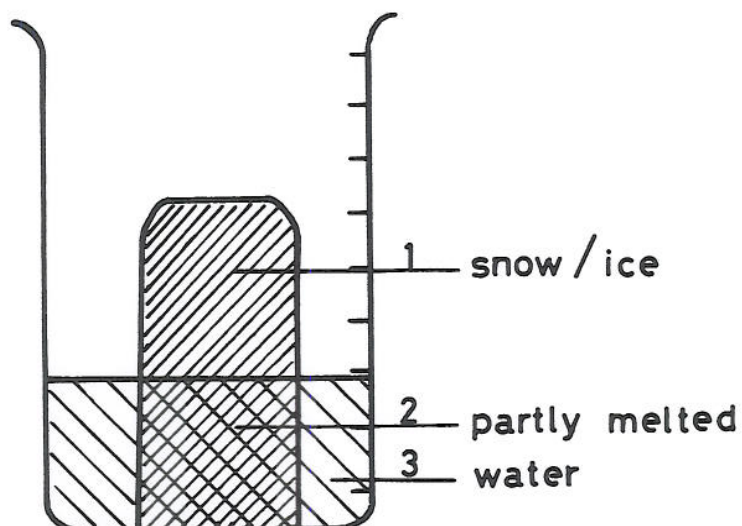


Figure 2 Partly melted snow sample after 30 days outdoor exposure

2.2 Analytical methods

The general method of analysis used is outlined in the block diagram given in Figure 3.

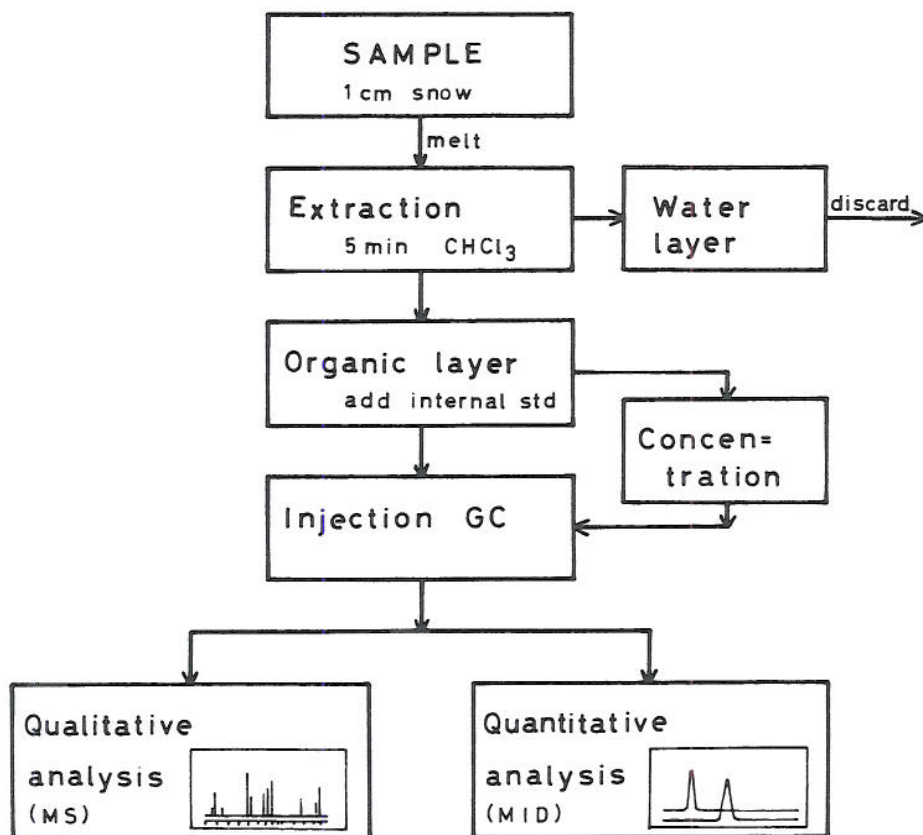


Figure 3 Block diagram of the procedure for sampling and analysis of chemical warfare agents

2.2.1 Sample preparation

After the samples were taken into the laboratory, they were immediately melted at room temperature. The total amount of liquid was measured, and 10 ml was transferred to a screw capped centrifuge tube containing 5 ml chloroform (spectr grade) and shaken for 5 minutes. The tubes were centrifuged at 1800 rpm for 5 minutes at room temperature. After removing the water phase, the organic phase containing the agent was transferred to another tube. An exactly known amount in the order of 500 ng of one of the n-alkanes was added as an internal standard. The specific alkane used for each of the different agents is given in Table 1. After workup the samples were found to be stable in the refrigerator for up to at least two weeks without any significant degradation.

| | Oven temp | Int std | Retention time(s) | | Fragment (m/e) |
|-------------|-----------|------------------------|-------------------|-------|----------------|
| | (C) | (n-alkane) | Std | Agent | |
| Sarin | 95 | C-9 (n-nonane) | 153 | 117 | 99 |
| Soman | 130 | C-10 (n-decane) | 104 | 167 | 126 |
| Tabun | 150 | C-13 (n-tridecane) | 286 | 173 | 70 |
| Vx | 180 | C-18 (n-octadecane) | 90 | 65 | 114 |
| Mustard gas | 90 | C-12 (n-dodecane) | 163 | 107 | 109 |

Table 1 Condition details of mass fragmentographic analysis of chemical warfare agents

2.2.2 Mass spectrometry

To establish the most suitable conditions for the quantitative mass spectrometric analysis, mass spectra were recorded for the five agents. The instrument used was a LKB 2091 mass spectrometer equipped with a PYE UNICAM Gas Chromatograph. In preliminary tests, the agents dissolved in isopropanol were injected into the gas chromatograph. The spectra for the agents are given in Figure 4. Figure 4a shows the background using column SP 1200/H3PO4 for sarin, soman and tabun, and Figures 4e and 4g demonstrates the background using column SE-30 for Vx and mustard gas respectively. Background interference was thus of little importance.

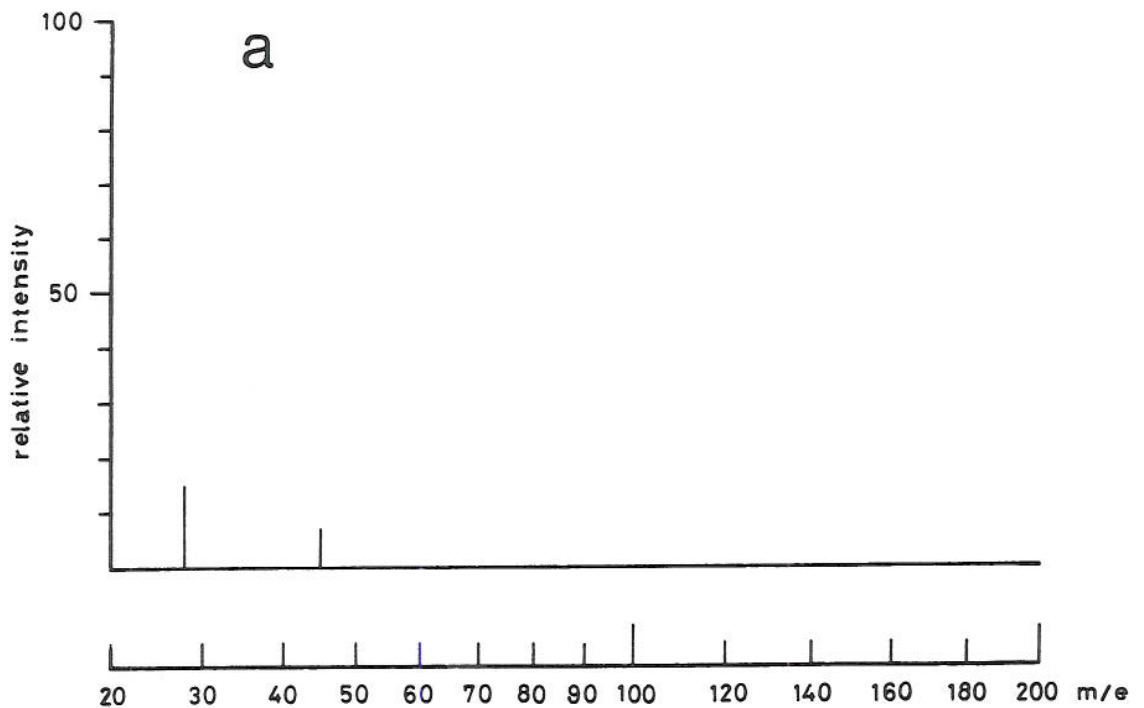


Figure 4a Background spectrum for column SP 1200/H3PO4 using same conditions as for sarin, soman and tabun

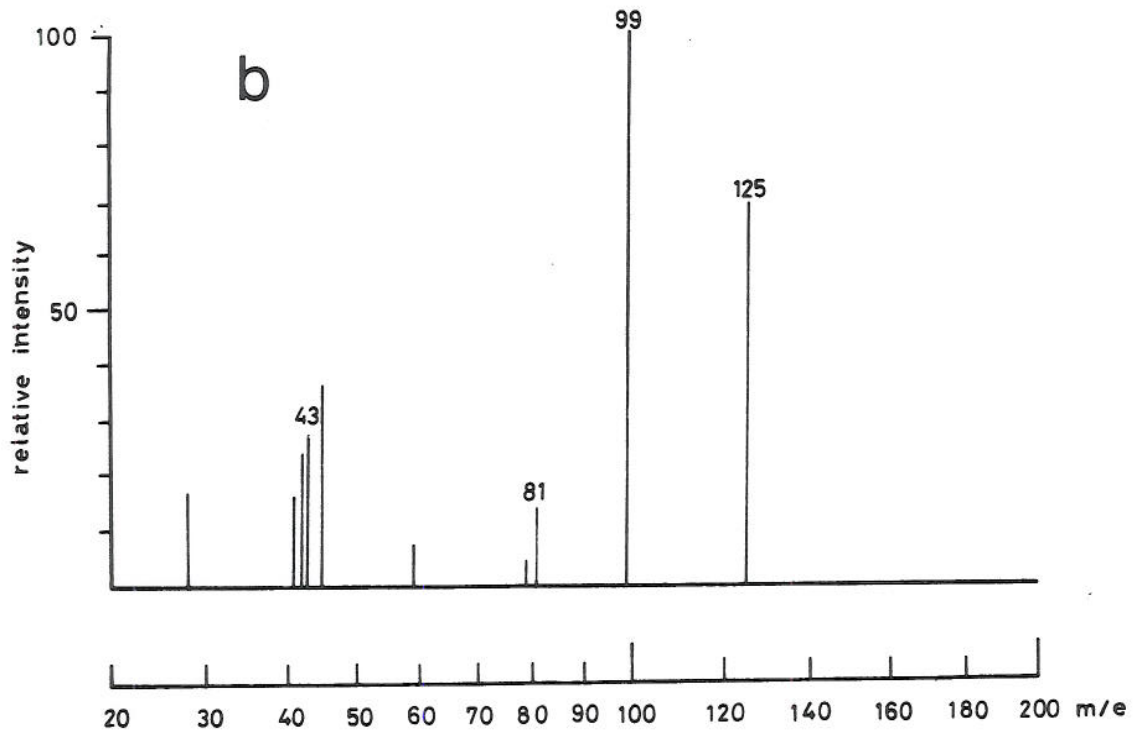


Figure 4b Mass spectrum of sarin

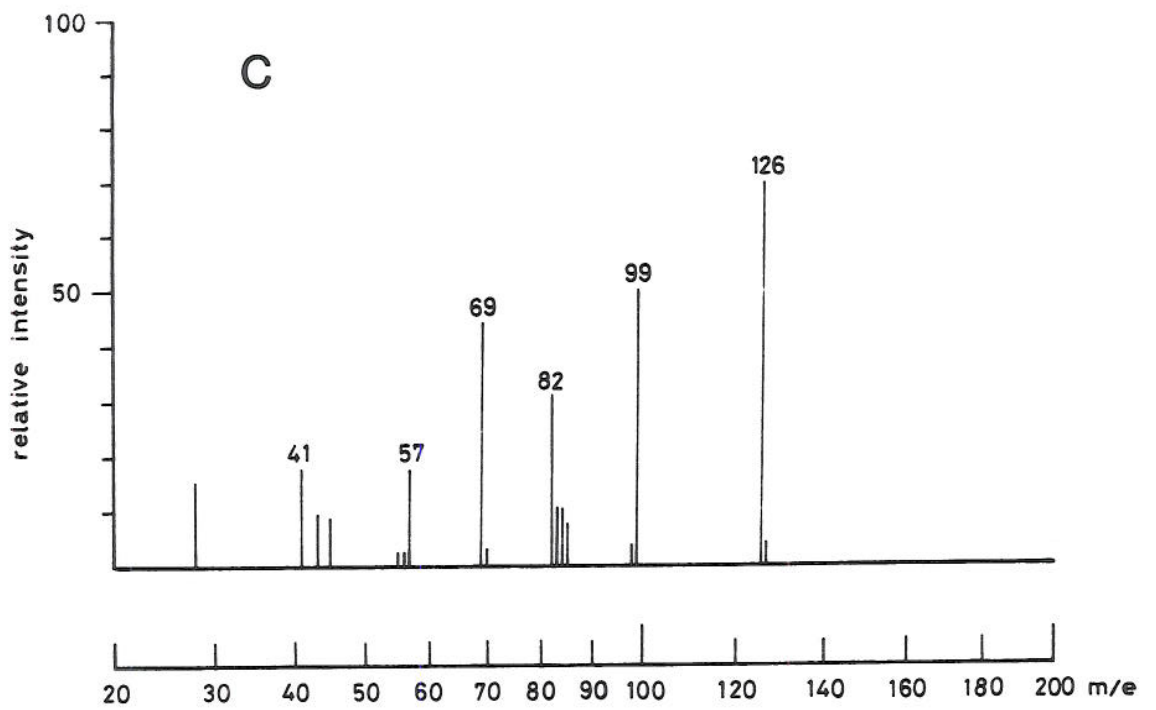


Figure 4c Mass spectrum of soman

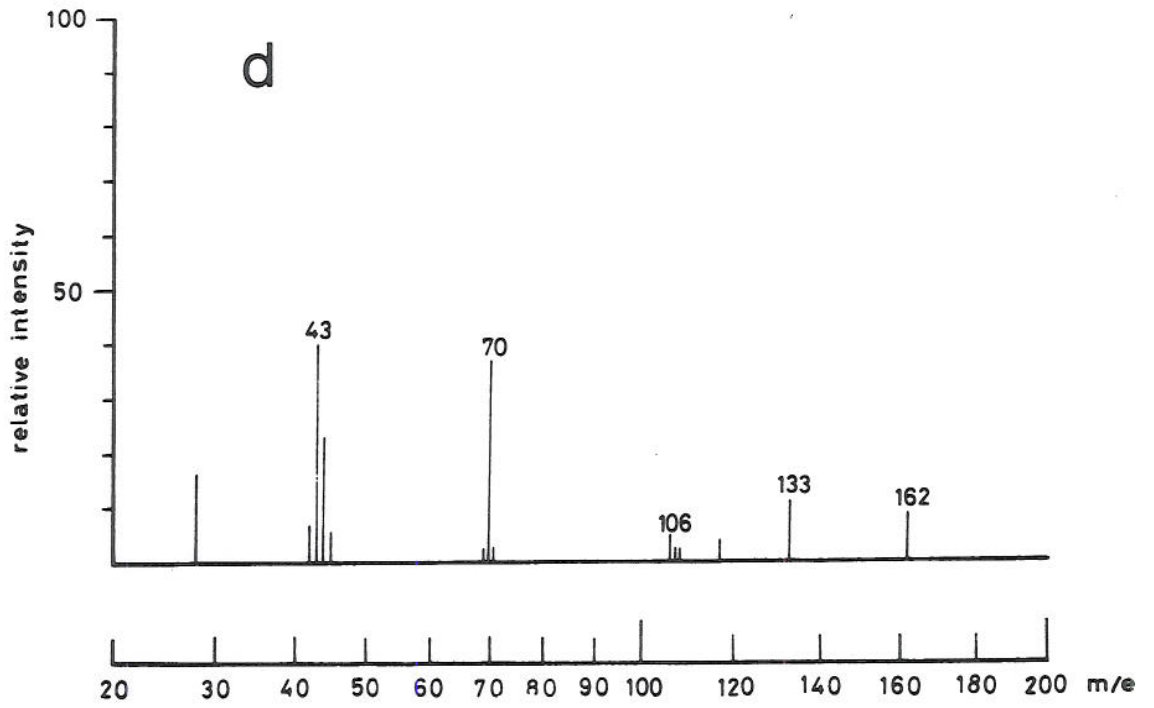


Figure 4d Mass spectrum of tabun

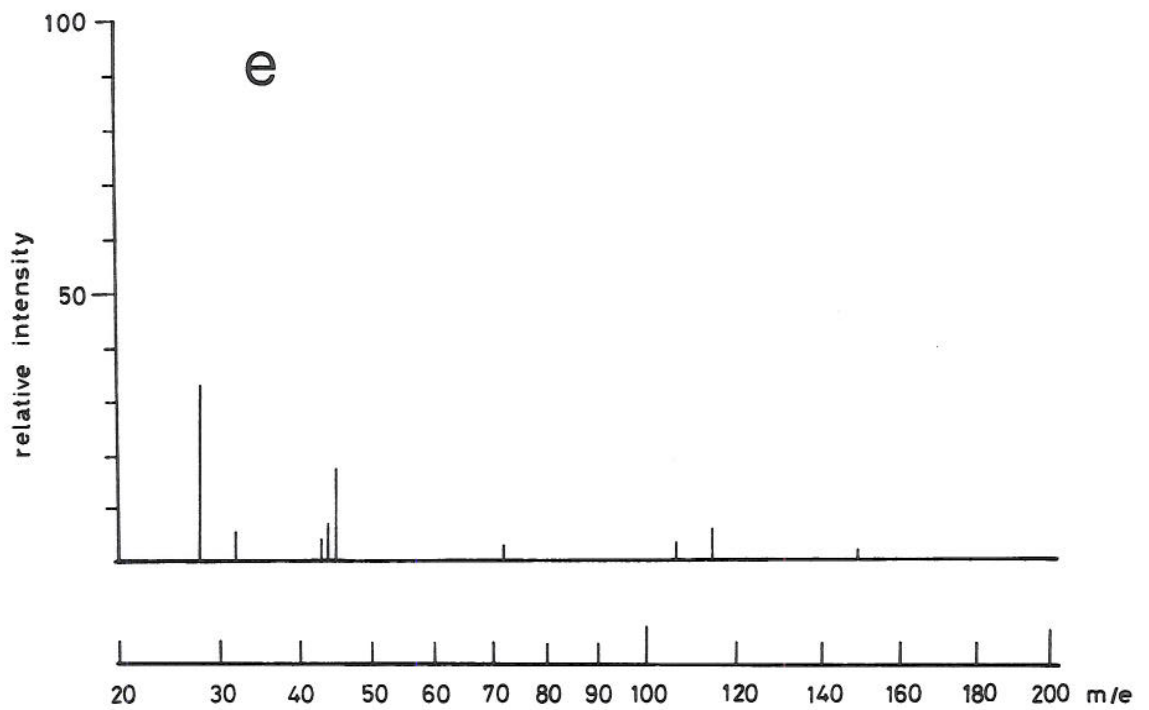


Figure 4e Background spectrum from column SE 30 under same conditions as for Vx

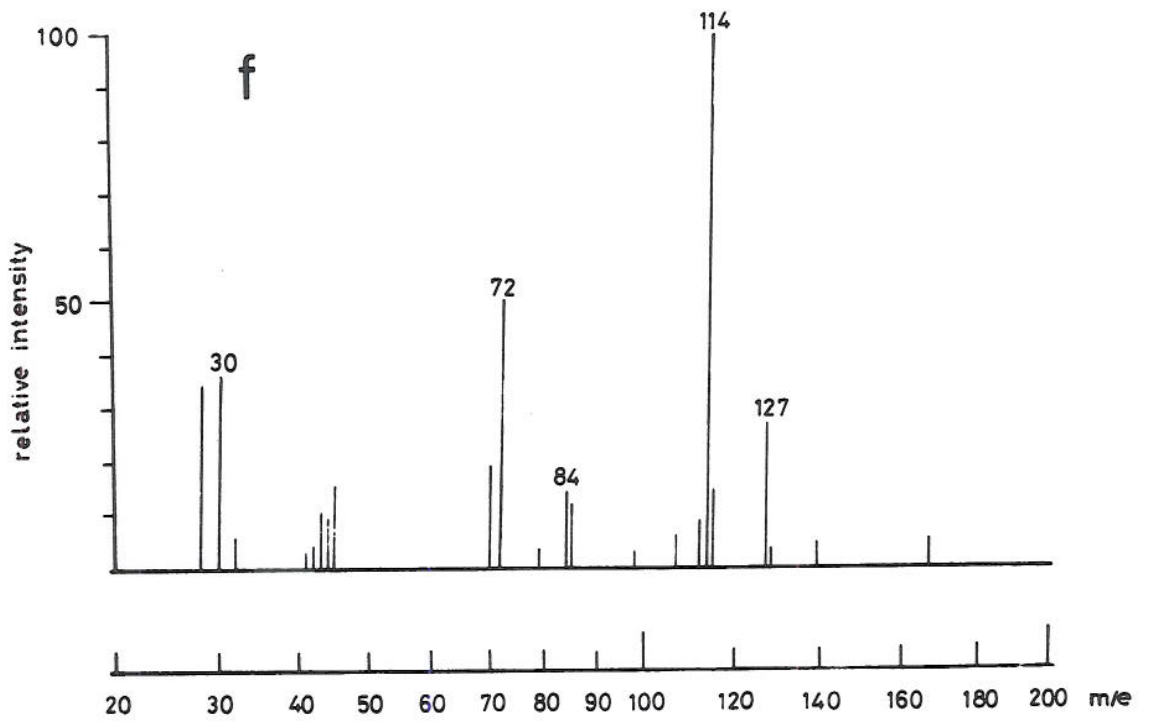


Figure 4f Mass spectrum of Vx

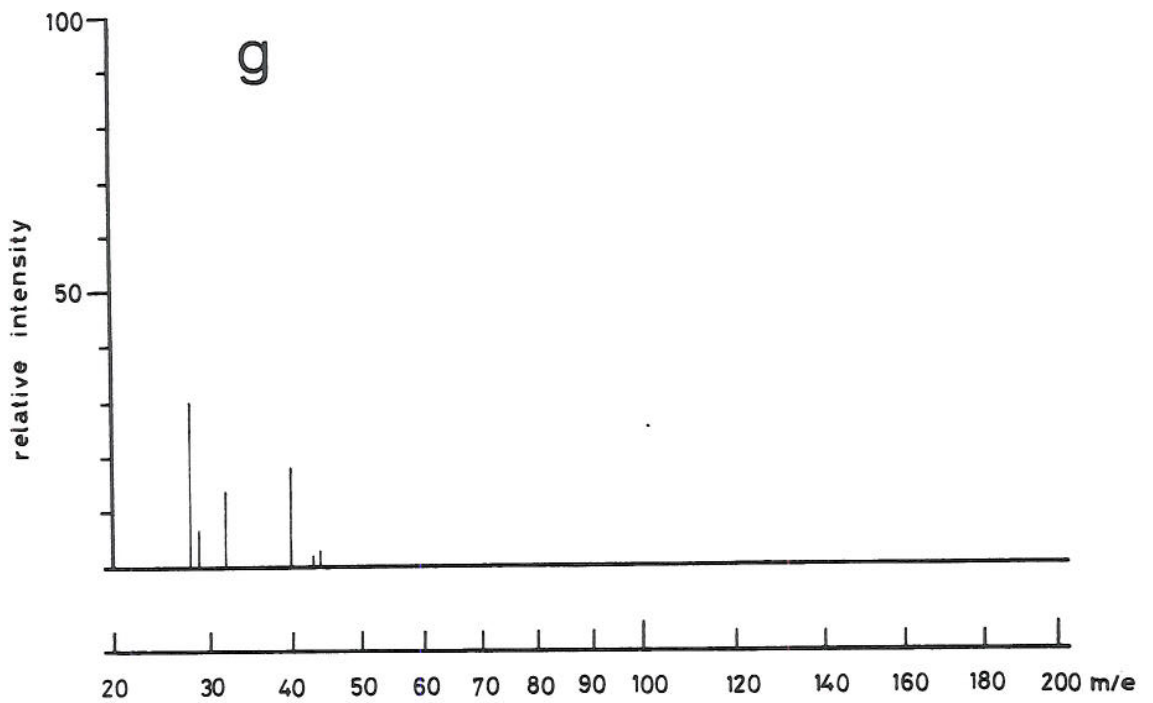


Figure 4g Background spectrum from column SE 30 under same conditions as for mustard gas

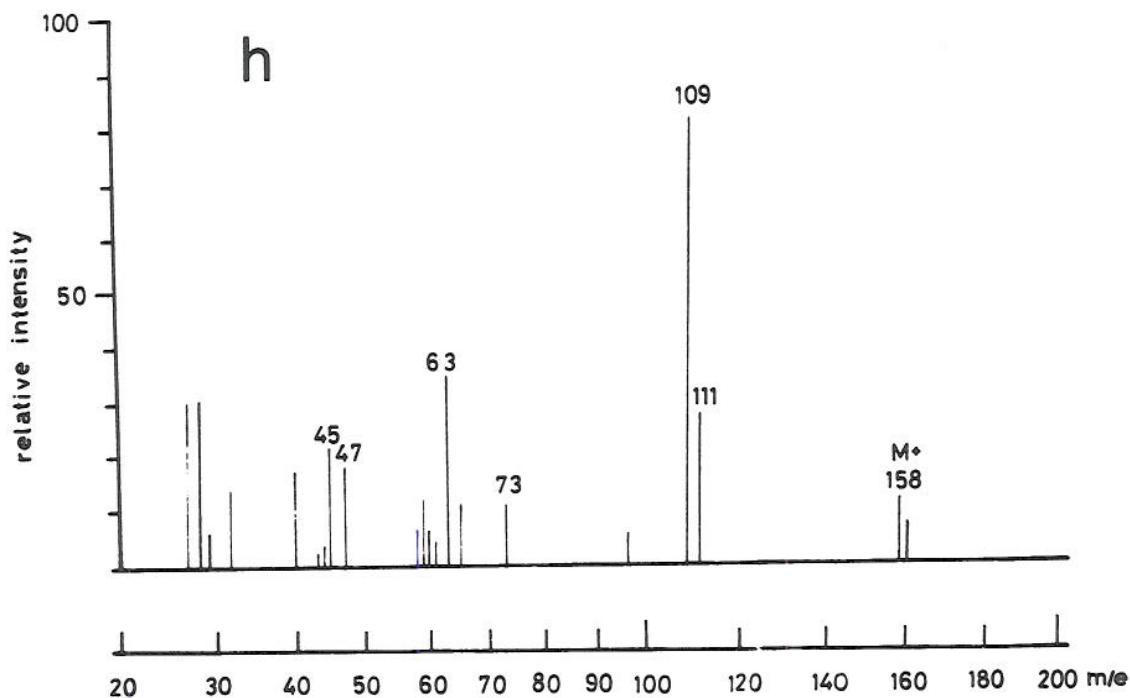
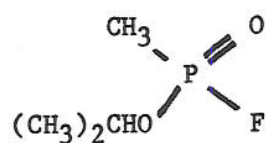


Figure 4h Mass spectrum of mustard gas

The most important mass spectrometric peaks for the different agents are listed in Table 2 together with their structures.

Isopropyl methylphosphonofluoridate (GB or sarin)

Formula:



Molecular weight: 140.10

Fragments:

m/e Possible structure (2):

43 C_3H_7^+

81 $\text{CH}_3\text{P}(\text{O})\text{F}^+$ or $\text{CH}_2\text{P}(\text{OH})\text{F}^+$

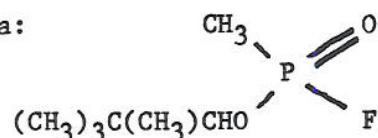
99 $\text{CH}_3\text{PF}(\text{OH})_2^+$

125 $\text{C}_2\text{H}_5\text{O}-(\text{CH}_3)\text{P}(\text{OH})\text{F}^+$

Table 2a Mass spectrometric peaks for sarin.

1,2,2-Trimethylpropyl methylphosphonofluoridate (GD or soman)

Formula:



Molecular weight: 182.18

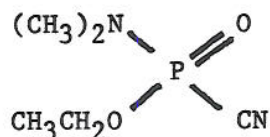
Fragments:

m/e Possible structure:

| | |
|-----|---|
| 41 | C_3H_5^+ |
| 57 | C_4H_9^+ |
| 69 | C_5H_9^+ |
| 82 | $\text{C}_6\text{H}_{10}^+$ or $\text{CH}_3\text{P}(\text{OH})\text{F}^+$ |
| 99 | $\text{CH}_3\text{P}(\text{OH})_2^+$ |
| 125 | $\text{C}_2\text{H}_5\text{O}(\text{CH}_3)\text{P}(\text{O})\text{F}^+$ |

Table 2b Mass spectrometric peaks for somanNN-dimethylphosphoramidocyanidate (GA or tabun)

Formula:



Molecular weight: 162.13

Fragments:

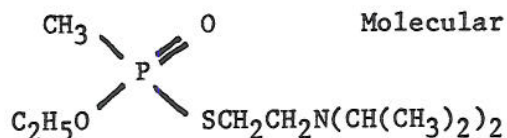
m/e Possible structure:

| | |
|-----|--------------------------------------|
| 43 | $\text{CH}_2 = \text{N-CH}_3^+$ |
| 70 | |
| 106 | $\text{C}_2\text{H}_5\text{NPO}_2^+$ |
| 133 | |
| 162 | The molecule (M^+) |

Table 2c Mass spectrometric peaks for tabun

Ethyl S-2-diisopropylaminoethyl methylphosphonothiolate (Vx)

Formula:



Molecular weight: 267.37

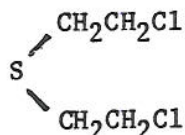
Fragments:

m/e

| | |
|-----|---|
| 30 | $\text{CH}_2 = \text{NH}_2^+$ |
| 70 | $\text{C}_4\text{H}_8\text{N}^+$ |
| 72 | $\text{CH}_2 = \text{NH}-\text{CH}(\text{CH}_3)_2^+$ |
| 84 | $\text{C}_5\text{H}_{10}\text{N}^+$ |
| 114 | $\text{CH}_2 = \text{N} = (\text{CH}(\text{CH}_3)_2)_2^+$ |
| 127 | |

Table 2d Mass spectrometric peaks for VxBis(2-chloroethyl) sulphide (HD or mustard gas)

Formula:



Molecular weight: 159.078

Fragments:

m/e Possible structure:

| | |
|-----|--|
| 47 | CH_3S^+ |
| 63 | $\text{CH}_2\text{CH}_2\text{Cl}^+$ |
| 73 | $\text{S} = \text{CHCH}_2\text{CH}_2^+$ |
| 109 | $\text{ClCH}_2\text{CH}_2\text{SCH}_2^+$ |
| 158 | The molecule (M^+) |

Table 2e Mass spectrometric peaks for mustard gas

2.2.3 Analytical gas chromatography/mass spectrometry

The quantitative analysis of the snow samples were carried out using a method of gas chromatography/mass spectrometry combined with the use of mass fragmentography. The gas chromatograph was equipped with a 1.5 m packed glass column. Helium was used as carrier gas, and the flow rate was 20 ml per minute. The column materials were the same as used for the recording of the mass spectra. Figure 5 shows the gas chromatogram of a mixture of sarin, soman and tabun in isopropanol. The detection signal used was the total ion current.

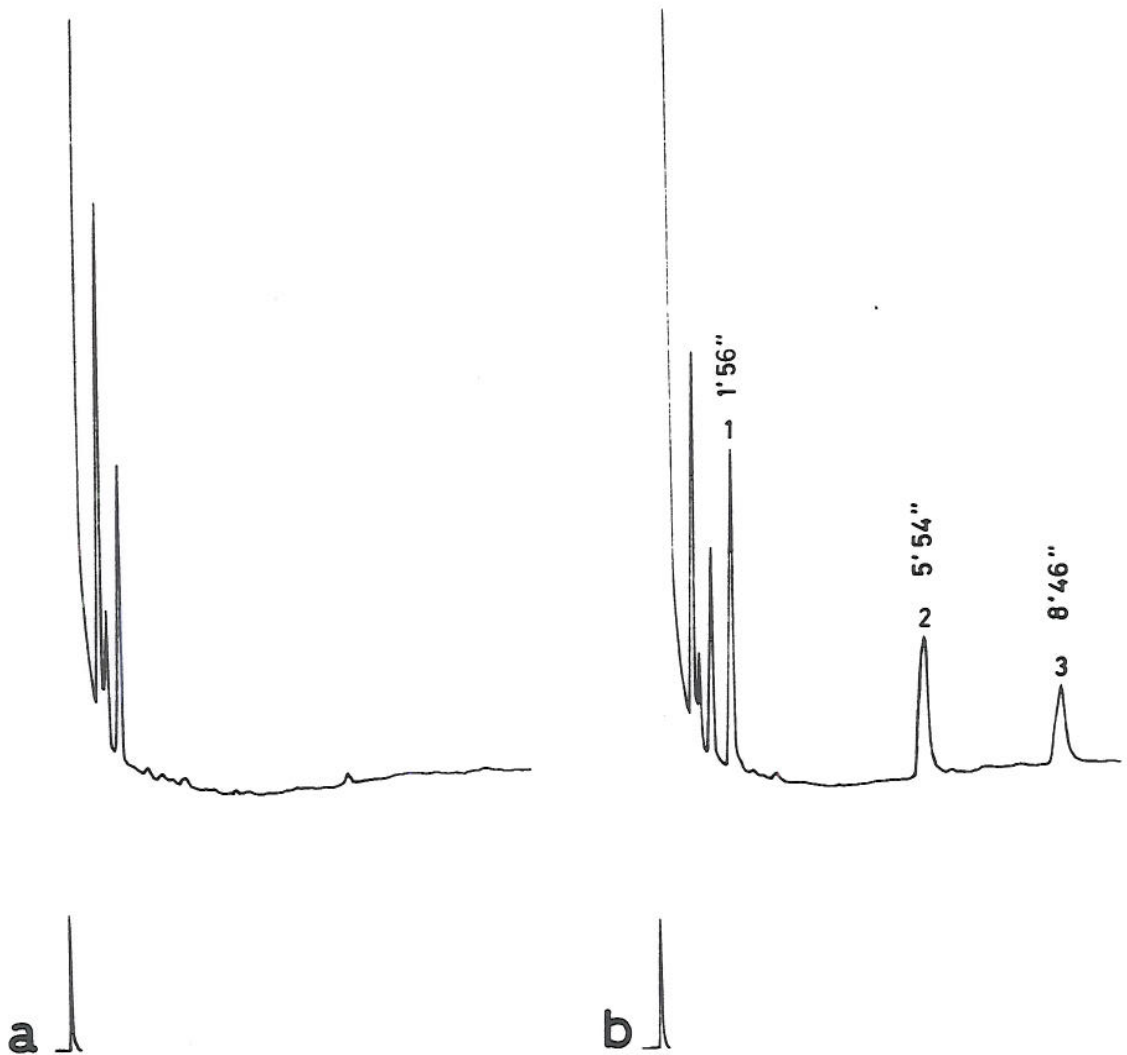


Figure 5 Gas chromatogram of a) isopropanol and b) a mixture of sarin (1), soman (2) and tabun (3) in isopropanol. Column temperature: 95°C isothermally for 30 s, programmed 95-130°C, 8°C per minute

Figure 6 shows a mass fragmentogram of the same mixture, using a MID-unit (multiple ion detector) for the fragmentation. The mass fragments used for detection were 70, 99 and 126 for tabun, sarin and soman respectively.

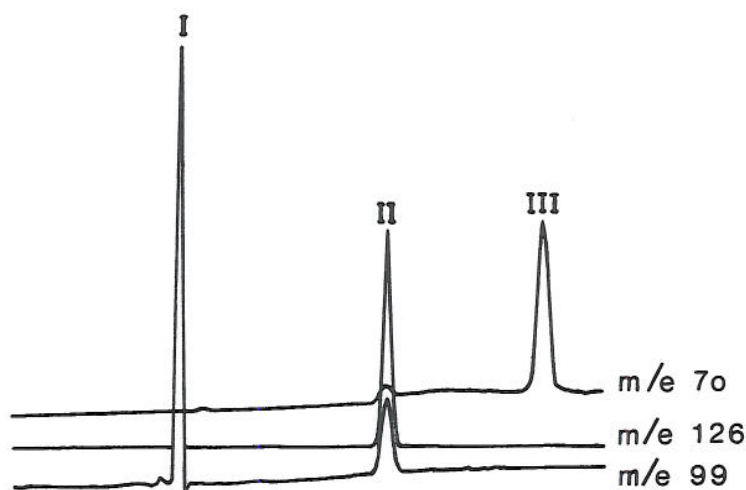


Figure 6 Mass fragmentographic analysis of sarin (I), soman (II) and tabun in a mixture. The conditions were the same as in Figure 5.

The agents Vx and mustard gas were analysed on another column, 5% SE-30 on 80-100 mesh Supelcoport, which is a general purpose methylsilicone column. As can be seen from Figure 7, good separation, acceptable curve shapes and negligible background disturbances were obtained for both agents.

Two examples of typical analysis are given in Figure 7. The figure shows the mass fragmentographic analysis of sarin and mustard gas. Oven temperatures and other details are given in Table 1.

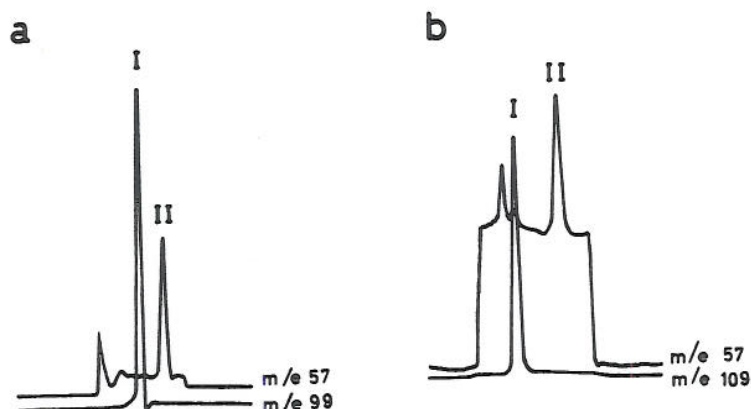


Figure 7 Mass fragmentographic analysis of a sarin (a, peak I) and mustard gas (B, peak I). Peak II are internal standards

In preliminary tests of all the n-alkanes used as internal standards, the fragment 57 (m/e) was the highest and best suited for detection. Using this fragment for all internal standards made it unnecessary to refocus the instrument each time a new agent was to be analysed. Complete analysis could therefore be carried out in a minimum of time, which is of great importance in an actual situation, where results are needed as fast as possible.

When utmost sensitivity was needed, the samples were concentrated by blowing dry air into the sample tubes to remove most of the solvent. The detection limits for a single injection is given in Table 3.

| Compound | Amount (pg) |
|-------------|-------------|
| Sarin | 100 |
| Soman | 10 |
| Tabun | 500 |
| Vx | 500 |
| Mustard gas | 50 |

Table 3 Detection limits for chemical warfare agents

2.2.4 Recoveries

As the agents are known to be instable in water, and because of possible loss of agent due to evaporation and possible less than 100 per cent efficient extraction, recoveries were determined for all agents. This was carried out by analysing the upper layer of snow by the same procedure as described above. The only difference was that the analysis followed immediately after application of the agent. Analysis were carried out in parallel, and mean results are given in Table 4.

| Compound | Per cent recovery |
|-------------|-------------------|
| Sarin | 66 |
| Soman | 73 |
| Tabun | 95 |
| Vx | 66 |
| Mustard gas | 55 |

Table 4 Mean recoveries after extraction of different chemical warfare agents from snow samples

3 RESULTS

The analytical results of all the snow samples contaminated with chemical warfare agents are given in Table 5 a-e and also in Figure 8. The results indicate as expected in general that the amount of chemical warfare agent remaining in the snow samples decreases with time. After 1 day, analysis of the top layer showed that 15 per cent of the original sarin still remained, for the other agents from 25 to 90 per cent. For longer time periods, the amount was decreased by factors of several decades. Up to 15 days, however, all agents were still present in amounts high enough to be positively identified and quantitatively determined. After 30 days, this was still the case for soman and Vx, but the amount of sarin, tabun and mustard gas was below the detection limit. (At this time the experiments were discontinued).

The tendency to penetrate down through the snow layers differed from one agent to another. The ability to do this seems to be connected both to agent volatility and solubility. Hydrolytic stability is also an important factor. In Table 5d more than 7 per cent of Vx was recovered as long as 30 days after application. This agent penetrated only a short distance down into the snow. For mustard gas, it was observed that the agent froze on contact with snow. This is probably the reason why the agent was found mainly in the top layer.

Table 5a

Amount Sarin added: 1 mg, mean recovery 66 percent

| Layer | Measured value (mg) | Corr for volume (mg) | Corr for vol and rec (mg) |
|----------------------|------------------------|-------------------------|------------------------------|
| Exposure time: 1 day | | | |
| 1 | 5.08×10^{-2} | 9.24×10^{-2} | 0.14 |
| 2 | 5.95×10^{-3} | 1.14×10^{-2} | 1.7×10^{-2} |
| 3 | 5.40×10^{-3} | 7.36×10^{-3} | 1.1×10^{-2} |
| 4 | 8.11×10^{-4} | 1.25×10^{-3} | 1.9×10^{-3} |
| 5 | 1.77×10^{-4} | 2.41×10^{-4} | 3.7×10^{-4} |

| Layer | Measured value (mg) | Corr for volume (mg) | Corr for vol and rec (mg) |
|-----------------------|------------------------|-------------------------|------------------------------|
| Exposure time: 4 days | | | |
| 1 | 6.53×10^{-4} | 8.31×10^{-4} | 1.3×10^{-3} |
| 2 | 1.26×10^{-3} | 1.49×10^{-3} | 2.3×10^{-3} |
| 3 | 2.35×10^{-3} | 2.78×10^{-3} | 4.2×10^{-3} |
| 4 | 2.71×10^{-3} | 3.20×10^{-3} | 4.9×10^{-3} |
| 5 | 1.48×10^{-3} | 1.75×10^{-3} | 2.7×10^{-3} |

| Layer | Measured value (mg) | Corr for volume (mg) | Corr for vol and rec (mg) |
|-----------------------|------------------------|-------------------------|------------------------------|
| Exposure time: 7 days | | | |
| 1 | 2.45×10^{-5} | 3.98×10^{-5} | 6.0×10^{-5} |
| 2 | 3.59×10^{-5} | 5.83×10^{-5} | 8.8×10^{-5} |

| Layer | Measured value (mg) | Corr for volume (mg) | Corr for vol and rec (mg) |
|------------------------|------------------------|-------------------------|------------------------------|
| Exposure time: 15 days | | | |
| 1 | 1.79×10^{-5} | 2.91×10^{-5} | 4.4×10^{-5} |
| 2 | 2.30×10^{-5} | 3.74×10^{-5} | 5.7×10^{-5} |
| 3 | 4.36×10^{-5} | 7.09×10^{-5} | 1.1×10^{-4} |
| 5 | 6.80×10^{-5} | 1.11×10^{-4} | 1.7×10^{-4} |
| 8 | 2.60×10^{-5} | 4.23×10^{-5} | 6.4×10^{-5} |

| Layer | Measured value (mg) | Corr for volume (mg) | Corr for vol and rec (mg) |
|------------------------|--------------------------------|-------------------------|------------------------------|
| Exposure time: 30 days | | | |
| 1 | * $<1.0 \times 10^{-7}$ (30)** | | |
| 2 | $<1.0 \times 10^{-7}$ (53) | | |
| 3 | $<1.0 \times 10^{-7}$ (40) | | |

* Less than estimated detection limit.

** Weight (in grams) of layers, ref text s 8.

Table 5b

Amount Soman added: 1 mg, mean recovery 73 percent.

| Layer | Measured value (mg) | Corr for volume (mg) | Corr for vol and rec (mg) |
|----------------------|------------------------|-------------------------|------------------------------|
| Exposure time: 1 day | | | |
| 1 | 0.25 | 0.34 | 0.47 |
| 2 | 6.34×10^{-3} | 1.10×10^{-2} | 1.5×10^{-2} |
| 3 | 2.74×10^{-4} | 5.73×10^{-4} | 7.8×10^{-4} |
| 4 | 1.13×10^{-4} | 1.85×10^{-4} | 2.5×10^{-4} |
| 5 | 5.28×10^{-5} | 9.12×10^{-5} | 1.2×10^{-4} |

| Layer | Measured value (mg) | Corr for volume (mg) | Corr for vol and rec (mg) |
|-----------------------|------------------------|-------------------------|------------------------------|
| Exposure time: 4 days | | | |
| 1 | 4.31×10^{-2} | 6.27×10^{-2} | 8.6×10^{-2} |
| 2 | 1.22×10^{-2} | 2.11×10^{-2} | 2.9×10^{-2} |
| 3 | 7.13×10^{-3} | 9.72×10^{-3} | 1.3×10^{-2} |
| 4 | 1.35×10^{-3} | 1.96×10^{-3} | 2.7×10^{-3} |
| 5 | 4.17×10^{-4} | 6.82×10^{-4} | 9.3×10^{-4} |

| Layer | Measured value (mg) | Corr for volume (mg) | Corr for vol and rec (mg) |
|-----------------------|------------------------|-------------------------|------------------------------|
| Exposure time: 7 days | | | |
| 1 | 1.91×10^{-4} | 3.10×10^{-4} | 4.2×10^{-4} |
| 2 | 7.33×10^{-4} | 1.19×10^{-3} | 1.6×10^{-3} |

| Layer | Measured value (mg) | Corr for volume (mg) | Corr for vol and rec (mg) |
|------------------------|------------------------|-------------------------|------------------------------|
| Exposure time: 15 days | | | |
| 1 | 1.28×10^{-4} | 2.08×10^{-4} | 2.8×10^{-4} |
| 2 | 3.13×10^{-4} | 5.09×10^{-4} | 7.0×10^{-4} |
| 3 | 4.25×10^{-4} | 6.91×10^{-4} | 9.5×10^{-4} |
| 5 | 4.32×10^{-4} | 7.02×10^{-4} | 9.6×10^{-4} |
| 8 | 2.12×10^{-4} | 3.45×10^{-4} | 4.7×10^{-4} |

| Layer | Measured value (mg) | | Corr for volume (mg) | Corr for vol and rec (mg) |
|------------------------|------------------------|-------|-------------------------|------------------------------|
| Exposure time: 30 days | | | | |
| 1 | 1.19×10^{-5} | (26)* | 3.09×10^{-5} | 4.2×10^{-5} |
| 2 | 4.72×10^{-5} | (66) | 3.12×10^{-4} | 4.3×10^{-4} |
| 3 | 9.20×10^{-5} | (25) | 2.30×10^{-4} | 3.2×10^{-4} |

* Weight (in grams) of layers, ref text s 8.

Table 5c

Amount Tabun added: 1 mg, mean recovery 95 percent.

| Layer | Measured value (mg) | Corr for volume (mg) | Corr for vol and rec (mg) |
|------------------------|---------------------------|-------------------------|------------------------------|
| Exposure time: 1 day | | | |
| 1 | 0.14 | 0.24 | 0.25 |
| 2 | 8.53×10^{-4} | 1.16×10^{-3} | 1.2×10^{-3} |
| 3 | 2.63×10^{-4} | 3.59×10^{-4} | 3.8×10^{-4} |
| 4 | 2.53×10^{-4} | 3.91×10^{-4} | 4.1×10^{-4} |
| 5 | 2.08×10^{-4} | 3.03×10^{-4} | 3.2×10^{-4} |
| | | | |
| Layer | Measured value (mg) | Corr for volume (mg) | Corr for vol and rec (mg) |
| Exposure time: 4 days | | | |
| 1 | 2.01×10^{-3} | 2.01×10^{-3} | 2.1×10^{-3} |
| 2 | 1.58×10^{-3} | 1.58×10^{-3} | 1.7×10^{-3} |
| 3 | 5.61×10^{-4} | 5.61×10^{-4} | 5.9×10^{-4} |
| 4 | 3.13×10^{-4} | 3.13×10^{-4} | 3.3×10^{-4} |
| | 2.16×10^{-4} | 2.16×10^{-4} | 2.3×10^{-4} |
| | | | |
| Layer | Measured value (mg) | Corr for volume (mg) | Corr for vol and rec (mg) |
| Exposure time: 7 days | | | |
| 1 | 1.28×10^{-5} | 2.08×10^{-5} | 2.2×10^{-5} |
| 2 | 1.30×10^{-5} | 2.11×10^{-5} | 2.2×10^{-5} |
| | | | |
| Layer | Measured value (mg) | Corr for volume (mg) | Corr for vol and rec (mg) |
| Exposure time: 15 days | | | |
| 1 | 1.30×10^{-5} | 2.11×10^{-5} | 2.2×10^{-5} |
| 2 | 3.05×10^{-5} | 4.96×10^{-5} | 5.2×10^{-5} |
| 3 | 1.05×10^{-5} | 1.71×10^{-5} | 1.8×10^{-5} |
| 5 | $< 5.00 \times 10^{-7} *$ | | |
| 8 | $< 5.00 \times 10^{-7}$ | | |

* Less than estimated detection limit.

Table 5d

Amount Vx added: 1 mg, mean recovery 66 percent.

| Layer | Measured value (mg) | Corr for volume (mg) | Corr for vol and rec (mg) |
|----------------------|--------------------------|-------------------------|------------------------------|
| Exposure time: 1 day | | | |
| 1 | 0.20 | 0.39 | 0.59 |
| 2 | $<5.00 \times 10^{-7}$ * | | |
| 3 | $<5.00 \times 10^{-7}$ | | |
| 4 | $<5.00 \times 10^{-7}$ | | |
| 5 | $<5.00 \times 10^{-7}$ | | |

| Layer | Measured values (mg) | Corr for volume (mg) | Corr for vol and rec (mg) |
|-----------------------|-------------------------|-------------------------|------------------------------|
| Exposure time: 4 days | | | |
| 1 | 0.16 | 0.23 | 0.35 |
| 2 | $<5.00 \times 10^{-7}$ | | |
| 3 | $<5.00 \times 10^{-7}$ | | |
| 4 | $<5.00 \times 10^{-7}$ | | |
| 5 | $<5.00 \times 10^{-7}$ | | |

| Layer | Measured value (mg) | Corr for volume (mg) | Corr for vol and rec (mg) |
|------------------------|------------------------|-------------------------|------------------------------|
| Exposure time: 15 days | | | |
| 1 | 3.37×10^{-3} | 4.48×10^{-3} | 8.3×10^{-3} |
| 2 | $<1.00 \times 10^{-3}$ | | |
| 3 | $<1.00 \times 10^{-3}$ | | |

| Layer | Measured value (mg) | | Corr for volume (mg) | Corr for vol and rec (mg) |
|------------------------|------------------------|--------|-------------------------|------------------------------|
| Exposure time: 30 days | | | | |
| 1 | 2.41×10^{-2} | (21)** | 5.06×10^{-2} | 7.7×10^{-2} |
| 2 | 2.77×10^{-3} | (57) | 1.58×10^{-2} | 2.4×10^{-2} |
| 3 | 2.02×10^{-3} | (36) | 7.27×10^{-3} | 1.1×10^{-2} |

* Less than estimated detection limit.

** Weight (in grams) of layers, ref text s 8.

Table 5e

Amount Mustard added: 1 mg, mean recovery 55 percent.

| Layer | Measured value (mg) | Corr for volume (mg) | Corr for vol and rec (mg) |
|----------------------|------------------------|-------------------------|------------------------------|
| Exposure time: 1 day | | | |
| 1 | 0.27 | 0.49 | 0.89 |
| 2 | 1.29×10^{-5} | 1.99×10^{-5} | 3.6×10^{-5} |
| 3 | 8.90×10^{-6} | 1.29×10^{-5} | 2.4×10^{-5} |
| 4 | 1.39×10^{-5} | 2.27×10^{-5} | 4.1×10^{-5} |
| 5 | 1.30×10^{-5} | 1.89×10^{-5} | 3.4×10^{-5} |

| Layer | Measured value (mg) | Corr for volume (mg) | Corr for vol and rec (mg) |
|-----------------------|---------------------------|-------------------------|------------------------------|
| Exposure time: 4 days | | | |
| 1 | 3.36×10^{-2} | 5.19×10^{-2} | 9.4×10^{-2} |
| 2 | 2.17×10^{-6} | 2.56×10^{-6} | 4.7×10^{-6} |
| 3 | $< 5.00 \times 10^{-8}^*$ | | |
| 4 | $< 5.00 \times 10^{-8}$ | | |
| 5 | $< 5.00 \times 10^{-8}$ | | |

| Layer | Measured value (mg) | Corr for volume (mg) | Corr for vol and rec (mg) |
|------------------------|-------------------------|-------------------------|------------------------------|
| Exposure time: 15 days | | | |
| 1 | 1.46×10^{-6} | 2.37×10^{-6} | 4.3×10^{-6} |
| 2 | 4.12×10^{-7} | 6.70×10^{-7} | 1.2×10^{-6} |
| 3 | 1.86×10^{-7} | 3.02×10^{-7} | 5.5×10^{-7} |
| 5 | 1.84×10^{-7} | 2.99×10^{-7} | 5.4×10^{-7} |
| 8 | $< 5.00 \times 10^{-8}$ | | |

| Layer | Measured value (mg) | Corr for volume (mg) | Corr for vol and rec (mg) |
|------------------------|--------------------------------|-------------------------|------------------------------|
| Exposure time: 30 days | | | |
| 1 | $< 5.00 \times 10^{-8}$ (25)** | | |
| 2 | $< 5.00 \times 10^{-8}$ (45) | | |
| 3 | $< 5.00 \times 10^{-8}$ (63) | | |

* Less than estimated detection limit.

** Weight (in grams) of layers, ref text s 8.

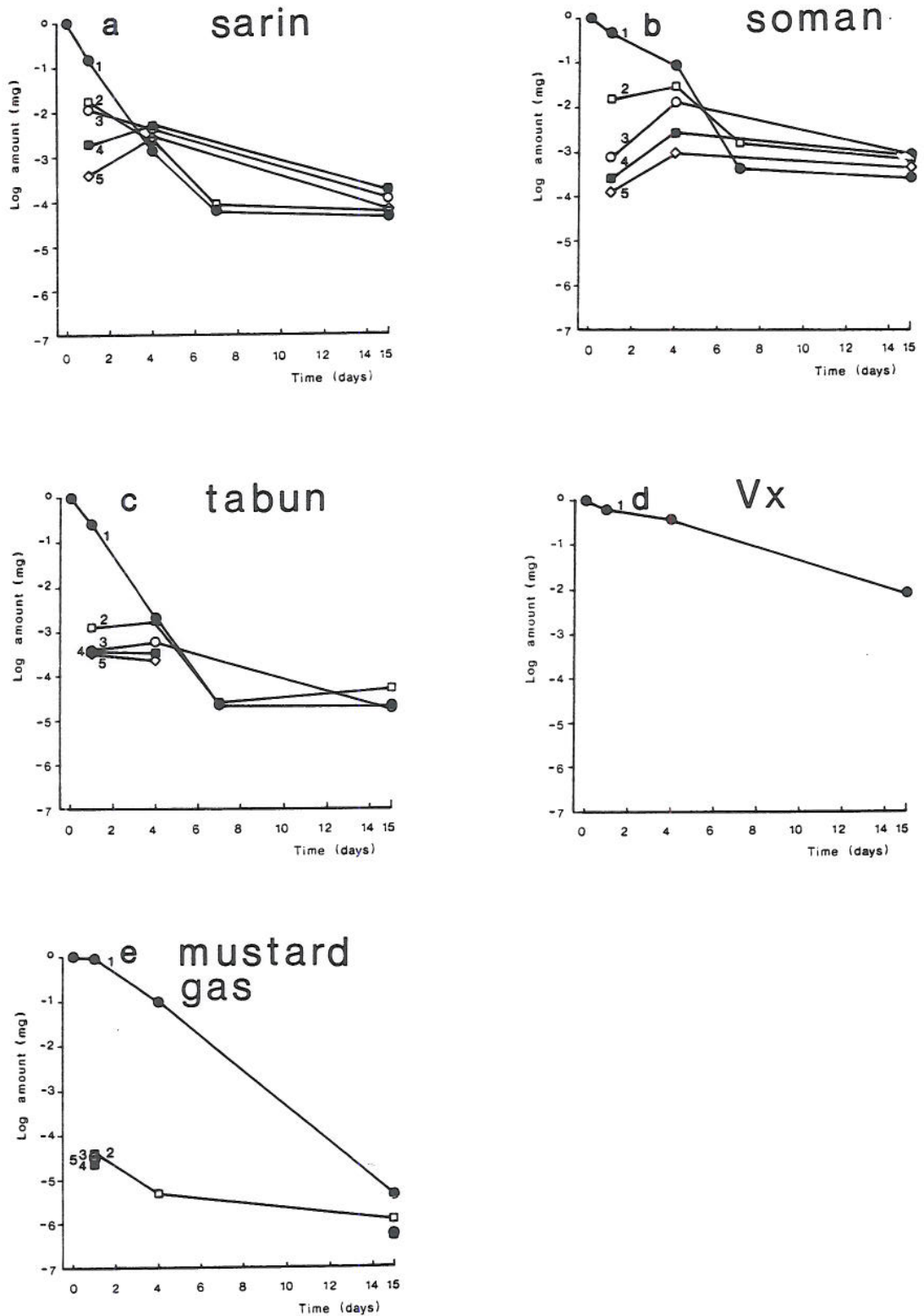


Figure 8 Analytical results from snow samples contaminated with different chemical warfare agents. ● = layer 1, □ = layer 2, ○ = layer 3, ■ = layer 4 and ◇ = layer 5.

4 CONCLUSIONS AND RECOMMENDATIONS

If one of the agents sarin, soman, tabun, Vx or mustard gas are used in a chemical attack under winter conditions, one may reasonably expect that verification can be effected by analysis of snow samples taken as long as 15 days after the event. For samples taken even as late as 30 days after the event, Vx and soman are probably still present in sufficient quantities, but verification of sarin, tabun and mustard gas is more doubtful.

Analysis of the samples were performed immediately after collection, and therefore decomposition of the agents in the time between sampling and analysis was unimportant. In a real situation this may, however, be an important complicating factor, and should therefore be evaluated. A possible method to stabilize the samples is by extraction at the time of collection, using a suitable inert organic solvent. Further work in this direction is needed and recommended.

This report has been concerned only with the analysis of the agents themselves, as this was judged to give the best verification. Verification of agent decomposition products might, however, be very useful in situations when intact agents no longer are present (4b).

REFERENCES

- (1) Odden E and Malthe-Sørensen D (1981): Detection of organophosphates by Gas chromatography/Mass spectrometry: Extraction from earth, vegetation and biologic material (in Norwegian), FFI/RAPPORT-81/6002.
- (2) Fagerlind L et al (1971): Nerve gases and related phosphorus compounds. Synthesis, chromatography, IR-, Mass- and NMR-Spectrometric analysis (in Swedish), FOA 1 Rapport A 1541-C2(C4).
- (3) Prepared for The Ministry for foreign affairs of Finland by The advisory board of disarmament (1977): Chemical and instrumental verification of organophosphorus warfare agents.
- (4) The Ministry for foreign affairs of Finland (1979):
 - a) Identification of potential organophosphorus warfare agents (1979).
 - b) Identification of degradation products of potential organophosphorus warfare agents (1980).
 - c) Trace analysis of chemical warfare agents (1981).
 - d) Identification of non-phosphorus warfare agents (1982).