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# ANALYSIS OF SNOW SAMPLES CONTAMINATED WITH CHEMICAL WARFARE AGENTS - PART 3

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The probability of verification of use of the nerve agents sarin and soman (GB and GD) under winter conditions has been extensively studied. After 4 weeks of outdoor exposure the concentrations of the agents are close to the detection limits. By analyzing the hydrolysis products and known impurities of GB and GD the present verification procedure are greatly extended and improved. These compounds were present in high concentretions after 4 weeks outdoor exposure, and were easily detected. It is concluded that the use of breakdown products and impurities can extend the time limit for taking samples under winter conditions beyond 4 weeks after the attack. The effect of the droplet size of the G-agents on verification has been investigated. Both the recovery of the breakdown products and the hydrolysis products showed slight increase, but the presence of nerve agents were close to the detection limits even for large droplets. It is difficult to verify the presence of pure mustard gas in 1 mg droplets after 4 weeks of outdoor exposure. Larger droplets of pure mustard gas and mixtures of mustard gas

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CONTENTS

# ANALYSIS OF SNOW SAMPLES CONTAMINATED WITH CHEMICAL WARFARE AGENTS - PART 3


## SUMMARY

The probability of verification of use of the nerve agents sarin and soman (GB and GD) under winter conditions has been extensively studied. After 4 weeks of outdoor exposure the concentrations of the agents are close to the detection limits. By analyzing the hydrolysis products and known impurities of GB and GD the present verification procedures are greatly extended and improved. These compounds were present in high concentrations after 4 weeks outdoor exposure, and were easily detected. It is concluded that the use of breakdown products and impurities can extend the time limit for taking samples under winter conditions beyond 4 weeks after the attack.

The effect of the droplet size of the G-agents on verification has been investigated. Both the recovery of the breakdown products and the hydrolysis products showed slight increase, but the presence of nerve agents were close to the detection limits even for large droplets.

It is difficult to verify the presence of pure mustard gas in 1 mg droplets after 4 weeks of outdoor exposure. Larger droplets of pure mustard gas and mixtures of mustard gas and lewisite are generally more persistent and easier to verify. All 15 samples of pure mustard were detected after 4 weeks, and of 25 samples of mustard gas lewisite mixtures, 24 were detected.

Two exercises were carried out to study sample handling and transportation of samples from the field to a laboratory. Different methods for treating the samples during transport and storage were compared.

## 1 INTRODUCTION

This report covers an extention of previous research on verification of chemical warfare agents under winter conditions carried out during the winters 1981/82 (1) and 1982/83 (2). The aim of the investigations is to establish procedures for using snow samples for verification of the alleged use of chemical agents under winter condition. Previous studies have shown that most chemical warfare agents including VX, irritating agents, and G-agents could be detected after 4 weeks exposure to the prevailing weather conditions. Some of the least persistent agents, however, were only found in amounts near the detection limits. In order to improve the possibility of verifying the use of G-agents, the investigations were expanded to include breakdown products and byproducts from production. These compounds are not known to be present in high concentration in the natural environment.

Mustard gas of technical purity has a melting point between 5 and 10 °C, and is solid below these temperatures. Since frozen mustard gas is a less effective weapon, the melting point has often been lowered by mixing it with lewisite, another chemical warfare agent. Experiments have been carried out during the winter 1983/84 with mixtures of mustard gas and lewisite to evaluate the influence of lewisite on the stability of mustard gas. Previous investigations were limited to small droplets (1 mg), but during the winter 1983/84 also larger droplets (2 - 10 mg) were used.

The laboratory, where the analyses are to be carried out in a real event, may be situated far from the battlefield, and the samples may have to endure a long transport to the laboratory before being analyzed. To test complete verification procedures, snow samples containig four chosen agents (sarin (GB) and mustard gas (HD), the most unstable agents, and CN and CS, two stable irritants) were prepared at a place far from the laboratory, collected on the next day, and transported back for analysis. To establish satisfactory methods for handling and storage of samples, several sample treatments and transportation procedures were compared.

## 2 EXPERIMENTAL

After outdoor exposure the samples were brought to the laboratory for analysis. Meteorological conditions were recorded continuously during the exposure periods.

## 2.1 Field experiments

Two series of field experiments were carried out. The first was an extention of similar experiments carried out during the winters of 1981/82 and 1982/83. Samples were placed on snow outdoor, left to the prevailing weather conditions, and later collected and analyzed. Sample preparation, collection, and transportation to the laboratory for analysis were tested in two practical exercises. The purpose was to compare different methods in order to find a procedure giving minimal deterioration of the samples.

Figure 2.1 shows the open transport box and the equipment used in the exercises made ready for use at Hvalsmoen.

Figure 2.1 An improvised field laboratory set-up at Hvalsmoen

### 2.1.1 Persistency determinations

The experimental conditions for the persistency determinations were similar to those carried out during the winters 1982/83 and 1983/84. The agents investigated during the winter 1983/84 were the nerve agents GB and GD, both in pure form and mixed with 20 percent of a corresponding diester usually found as a production impurity. For sarin (GB) this is diisopropyl methylphoshonate (DIPMP) and for soman (GD) di(1,2,2-

trimethylpropyl) methylphosphonate (DTMP).

Similarily, the experiments with mustard gas included both pure mustard gas (HD) and mustard gas mixed with 20 percent lewisite (HD+L). In addition to the standard 1 mg droplets, samples were prepared using larger droplets (2, 4, 6, 8, and 10 mg). All agents were placed as a single droplet on the top of the snow. To simulate the effect of snowfall after the attack, similar samples were covered with 5 cm snow.

The samples were collected for analysis after 14 and 28 days. The experiments were carried out over a period of 13 weeks. The weather conditions (temperature and relative humidity) were recorded continuously and are given in Figures 2.2 - 2.4.

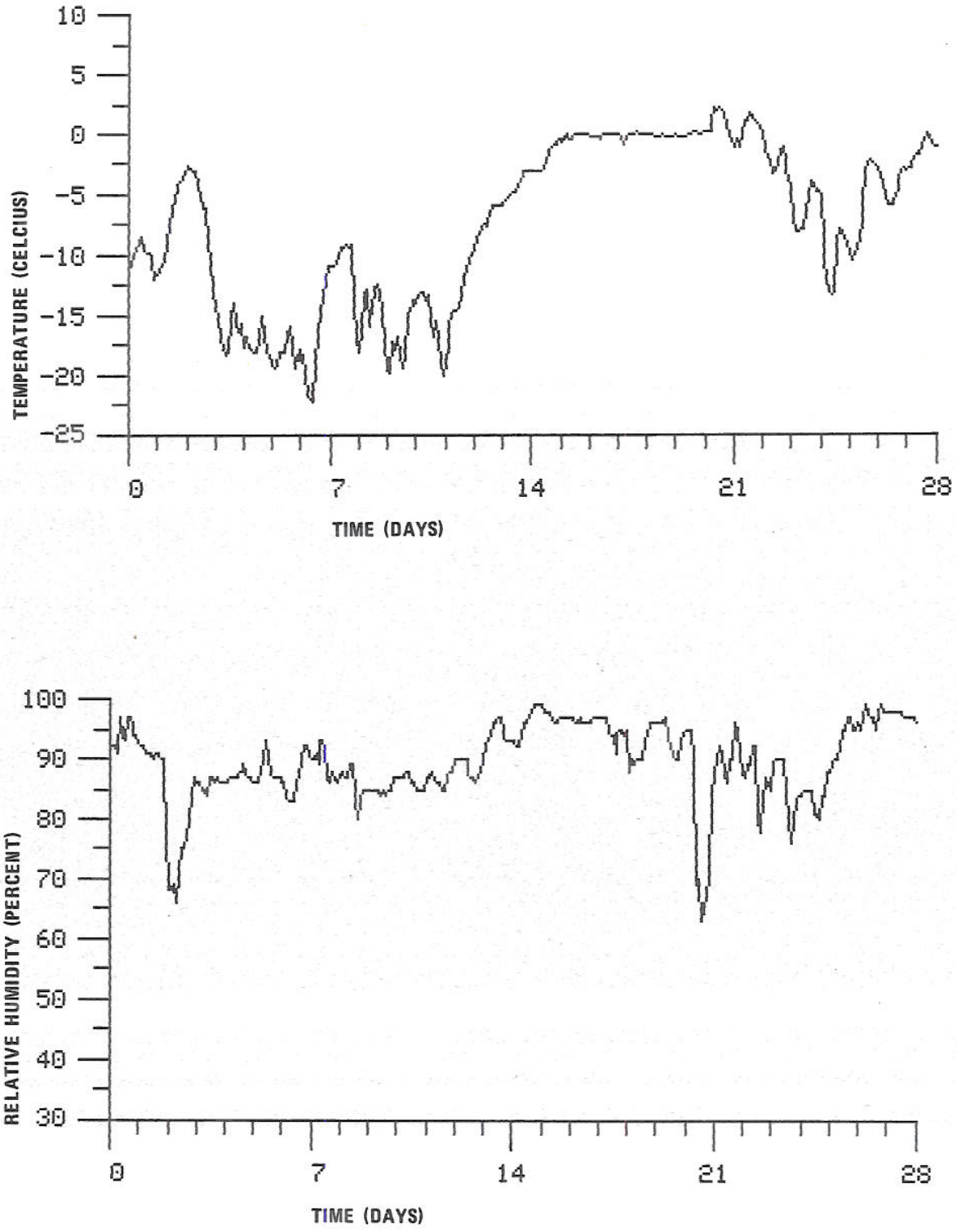



Figure 2.2 Plot of temperature ($^{o}$C) and relative humidity (percent) versus time during the period 16 January - 12 February 1984

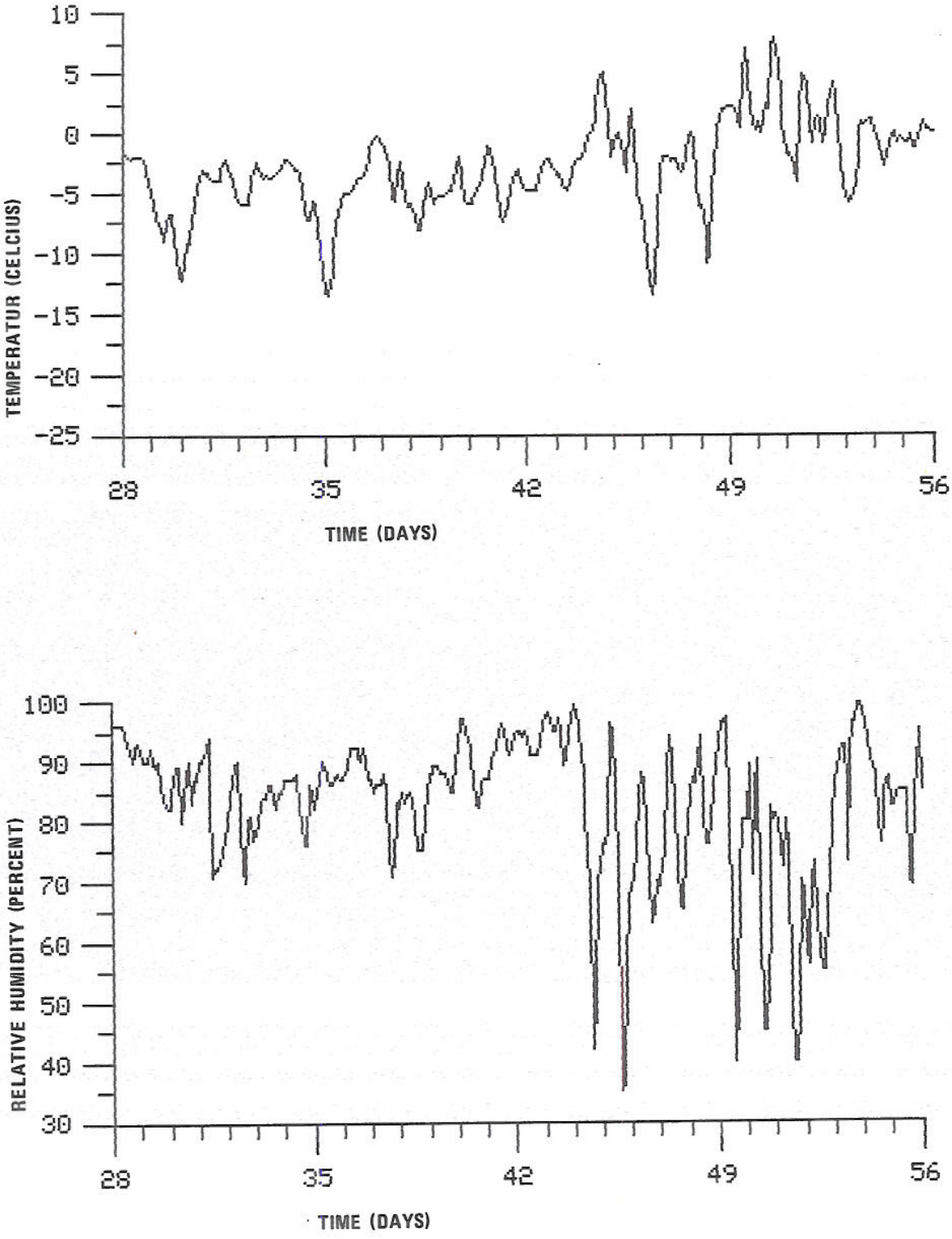
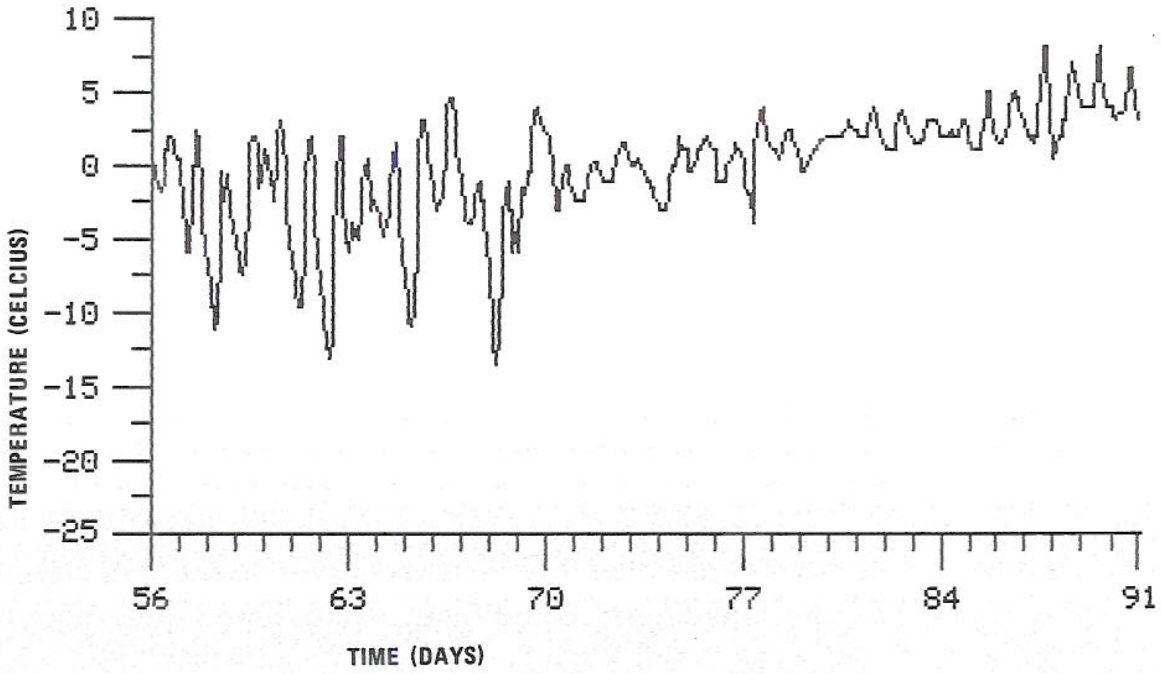



Figure 2.3 Plot of temperature ($^{o}$C) and relative humidity (percent) versus time during the period 13 February - 11 March 1984



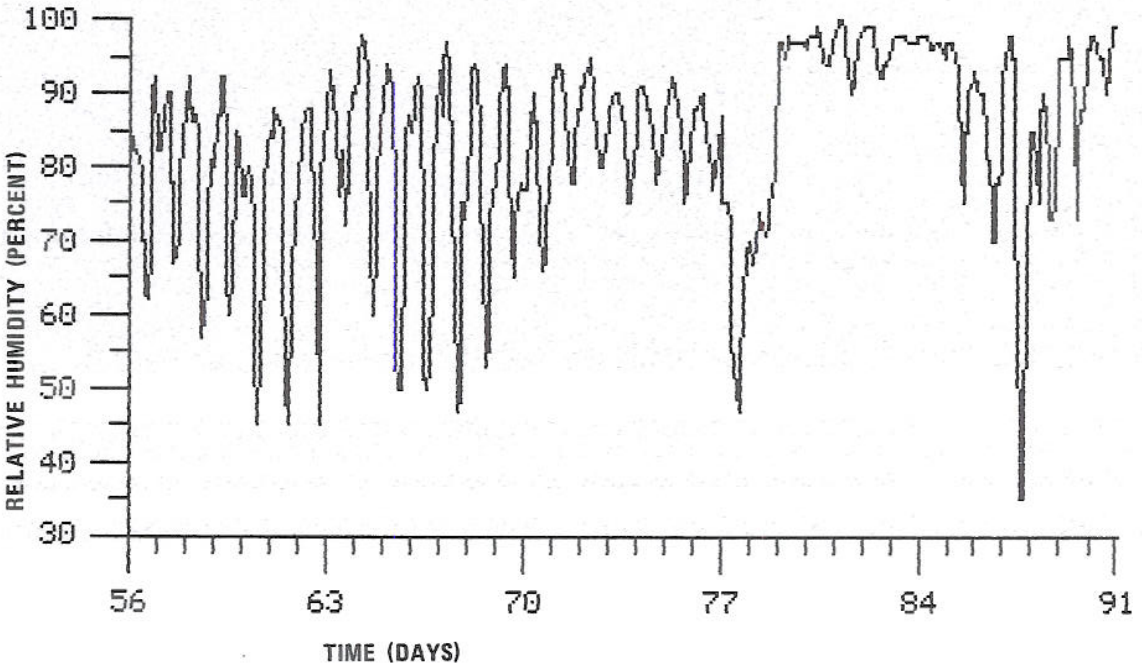




Figure 2.4 Plot of temperature ($^{o}$C) and relative humidity (percent) versus time during the period 12 March - 15 April 1984

The experiments were grouped in four exposure periods. Table 2.1 shows the exposure periods for all the experiments. Each group are exposed to the effects of the prevailing weather conditions.

| Group 1 Exposure period: (17.1-31.1) (17.1-14.2) | Group 2 Exposure period: (3.2-17.2) (3.2- 2.3) | Group 3 Exposure period: (17.2- 2.3) (17.2-16.3) | Group 4 Exposure period: (19.3- 2.4) (19.3-16.4) |
|---|---|---|---|
| GB (1 mg) | GB+ DIPMP (1 mg) | GB (2 mg) | HD (2 mg) |
| GD (1 mg) | GD+ DPMP (1 mg) | GB (4 mg) | HD (4 mg) |
| GB+DIPMP (1 mg) | HD+L (2 mg) | GB (6 mg) | HD (6 mg) |
| GD+DTMP (1 mg) | HD+L (4 mg) | HD (2 mg) | HD (8 mg) |
| HD (1 mg) | HD+L (6 mg) | HD (4 mg) | HD+L (2 mg) |
| HD+L (1 mg) | HD+L (8 mg) | HD (6 mg) | HD+L (4 mg) |
| HD+L (5 mg) | HD+L (10 mg) | HD (8 mg) | HD+L (6 mg) |
| | | HD+L (2 mg) | HD+L (8 mg) |
| | | HD+L (4 mg) | |
| | | HD+L (6 mg) | |
| | | HD+L (8 mg) | |

Table 2.1 Exposure periods and amount of agent in the experiments.

## 2.1.2 Collection, handling, and transportation of samples.

Two exercises were carried out in order to gain practical experience in the problems of sample collection, sample preparation, and transportation of samples.

The first exercise took place on the 10 and 11 April 1984 at Hvalsmoen about 100 km west of the main laboratory at Kjeller. On the first day four 1 mg samples of the following agents, sarin (GB), mustard gas (HD), and α-chloroacetophenone (CN) were prepared and left to outdoor exposure overnight. The temperature was not recorded continuously, but a few observations were taken. All the time the temperature was close to 0 °C. On the following day the samples were collected, and samples of each agent were treated in four different ways. Sampling bottles with snow samples containing each agent were stored, surrounded with dry ice (solid carbon dioxide), in a polystyrene box and thus kept at a temperature below -20 °C. Another set of samples was stored in a polystyrene box without any artificial cooling. The third set of samples was stored in the sampling bottle without any special precautions. The last set was melted in the sampling bottle by immersing it

in hot water heated on a simple commercial butane stove. When melted, the sample was extracted with 5 ml chloroform. The chloroform was separated from the water with a separation funnel and placed in a small bottle. About 100 mg dry sodium sulphate was added to dry the chloroform solutions. The samples were transported by car back to the laboratory at Kjeller, and were left as packed at room temperature in the laboratory until the analyses started on the next morning.

The second exercise took place on the 25 and 26 April 1984 at Banak in the far north of Norway about 1400 km from the laboratory at Kjeller. The procedures were the same as at Hvalsmoen except that 2-chlorobenzal malononitrile (CS) was chosen instead of α-chloroacetophenone (CN). The temperature was -1 °C when the samples were prepared and left to outdoor exposure. On the following day, when the samples were collected, the temperature was -3 °C. The sample were treated as described above. The samples were transported to Oslo by a army aircraft, and to Kjeller (20 km) by car. Onboard the aircraft, the samples were transported in the heated and pressurized luggage compartment. At arrival in Oslo, the outdoor temperature was +15 °C. In the laboratory the samples were left in their transportation containers overnight, and the analyses were started the next morning.

## 2.2 Analytical methods

All samples were first concentrated by chloroform extraction. Analyses were carried out after evaporation of the chloroform solution to near dryness.

### 2.2.1 Sample preparation

The analyses were started by melting the snow samples. The volume of the melted samples varied from 100 to 150 ml. The samples were extracted with chloroform (Merck, Uvasol quality). The methods for the analyses of the chemical warfare agents were combined gas chromatography/mass spectrometry with multiple ion detection (MID) as described previously (1,2). The following is a description of the analytical methods used for analysis of the hydrolysis products of the GB and GD and for the diisopropyl and di(1,2,2-trimethylpropyl) esters of methylphosphonic acid.

#### Isopropyl methylphosphonic acid (IPMPA)

The samples containing sarin (GB) were first extracted once with 5 ml chloroform to remove unhydrolysed GB present in the samples. Isopropyl methylphosphonic acid, formed by the hydrolysis of GB, is poorly soluble in chloroform, but is readily extracted by chloroform containing 0.02 M trioctylamine (TOA). The extract

containing IPMPA was dried with anhydrous sodium sulphate and treated with an excess of diazomethan in diethylether to form isopropyl methyl methylphosphonate (IPMMP). The ester is more volatile than the acid, and is easier to analyse by gas chromatography. A known amount of n-decane (C10) was added and used as internal standard.

1,2,2-Trimethylpropyl methylphosphonic acid (TMPA)

The samples containing soman (GD) were treated in the same way as the samples containing sarin (GB). As the isopropyl homologe, the 1,2,2-trimethylpropyl methylphosphonic acid is poorly soluble in chloroform, but is readily extracted with chloroform containing 0.02 M trioctylamine (TOA). After drying with anhydrous sodium sulphate the chloroform solution was treated with an excess of diazomethane, and the methyl 1,2,2-trimethylpropyl methylphosphonate (MTMP) was analysed by gas chromatography using n-dodecane (C12) as internal standard.

Diisopropyl methylphosponate (DIPMP)

This is a usual impurity in technical grade GB. Snow samples of GB containing 20 percent of this compound were extracted with 5 ml chloroform. After drying with anhydrous sodium sulphate, n-decane (C10) was added as internal standard, and analyses were carried out by gas chromatography.

Di(1,2,2-trimethylpropyl) methylphosphonate (DTMP)

This is a corresponding impurity in GD, and snow samples were extracted with chloroform as above. After drying and addition of n-dodecane (C12) as internal standard the analyses were carried out by gas chromatography.

Other samples

The samples containing mustard gas or a 20 percent mixture of lewisite in mustard gas were analysed for mustard gas. Lewisite is rapidly hydrolysed, and both the hydrolysis products of lewisite and mustard gas are highly water soluble. The decomposition products are therefore not extractable with chloroform and will remain in the aqueous phase.

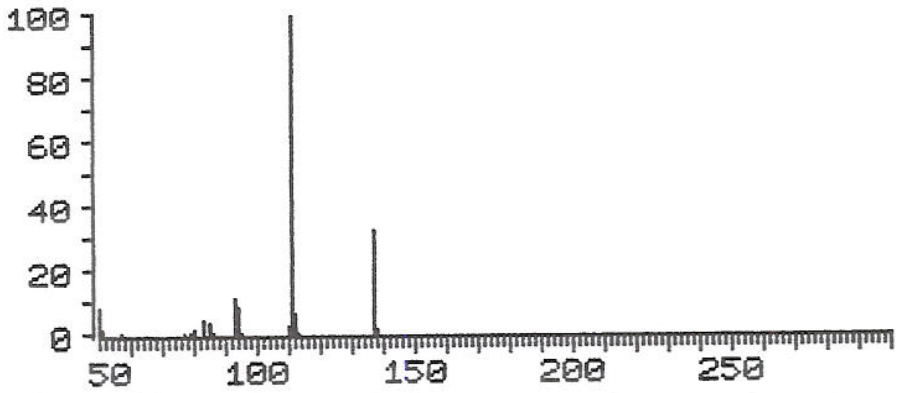
A summary of extraction solvents, internal standards, and the derivatization agents used for the different compounds are given in Table 2.2.

| Agent | Extract. solvent | Int. stand | Deriv. agent |
|---|---|---|---|
| GB | Chloroform | C9 | |
| HD | Chloroform | C12 | |
| IPMPA | Chloroform + TOA | C10 | Diazomethane |
| TMPA | Chloroform + TOA | C12 | Diazomethane |
| DIPMP | Chloroform | C10 | |
| DTMP | Chloroform | C12 | |
| CN | Chloroform | C14 | |
| CS | Chloroform | C14 | |

Table 2.2 Extraction solvents, internal standards and the derivatization agent used in the sample preparations

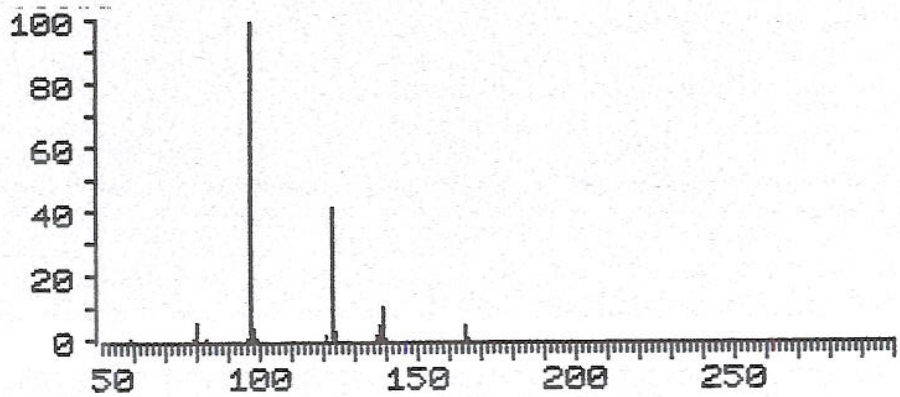
### 2.2.2 Mass spectrometry

Mass spectra were recorded for the methyl esters of the hydrolysis products of GB and GD as well as the diisopropyl and di(1,2,2-trimethylpropyl) esters of methylphosphonic acid. The mass spectrometer, a LKB 2091 was equipped with a PACKARD gas chromatograph MODEL 438. Recordings of the mass spectra at 14 eV are given in Figures 2.5 - 2.8.



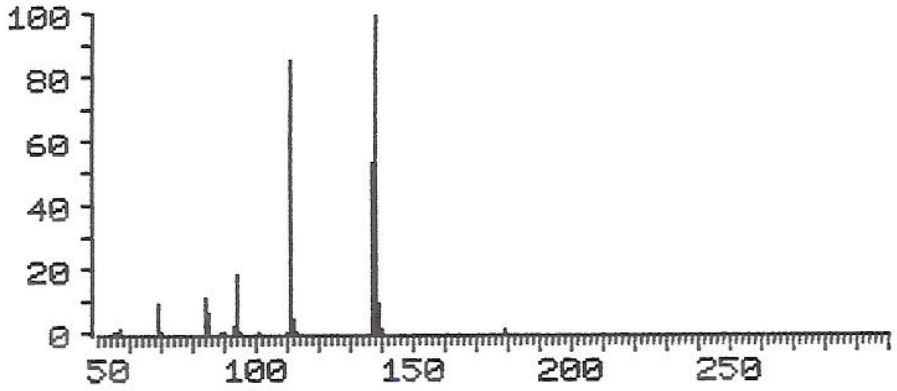

| Mass: | 111 | 137 | 93 | 94 | 50 | 112 | 83 | 85 | 110 | 80 |
|---|---|---|---|---|---|---|---|---|---|---|
| Intensity: | 100.0 | 32.7 | 12.1 | 8.9 | 8.9 | 7.0 | 4.6 | 4.5 | 3.4 | 2.2 |

Figure 2.5 Mass spectrum of isopropyl methyl methylphosphonate (IPMMP)



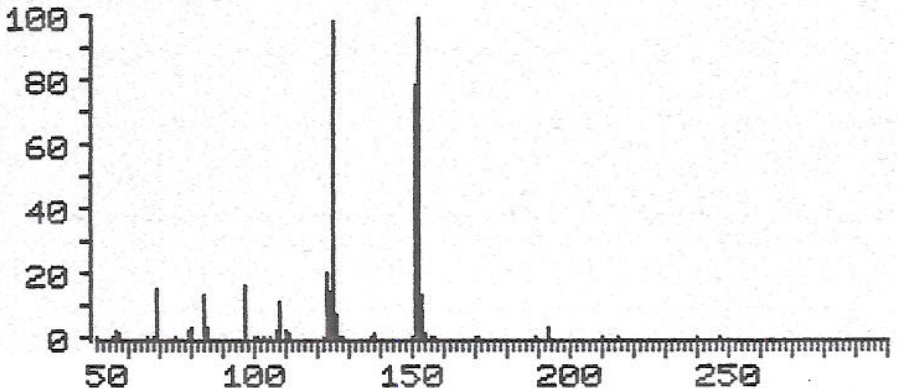

| Mass: | 97 | 123 | 139 | 80 | 165 | 138 | 98 | 124 | 137 | 121 |
|---|---|---|---|---|---|---|---|---|---|---|
| Intensity: | 100.0 | 42.4 | 10.9 | 6.2 | 5.4 | 4.8 | 4.4 | 2.5 | 2.2 | 1.9 |

Figure 2.6 Mass spectrum of diisopropyl methylphosphonate (DIPMP)




| Mass: | 138 | 111 | 137 | 94 | 84 | 69 | 139 | 85 | 112 | 93 |
|---|---|---|---|---|---|---|---|---|---|---|
| Intensity: | 100.0 | 85.9 | 54.2 | 19.4 | 11.8 | 10.4 | 10.2 | 6.8 | 5.2 | 3.4 |

Figure 2.7 Mass spectrum of methyl 1,2,2-trimethylpropyl methylphosphonate (MTMP)



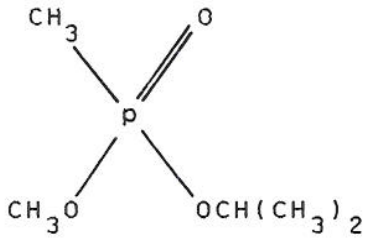

| Mass: | 152 | 125 | 151 | 123 | 97 | 69 | 124 | 84 | 153 | 108 |
|---|---|---|---|---|---|---|---|---|---|---|
| Intensity: | 100.0 | 99.1 | 78.7 | 20.7 | 16.6 | 16.4 | 15.1 | 14.5 | 14.4 | 12.4 |

Figure 2.8 Mass spectrum of di(1,2,2-trimethylpropyl) methylphosphonate (DTMP)

The most important mass spectrometric peaks are given in Tables 2.3 - 2.6.

Isopropyl methyl methylphosphonate (IPMMP)

Formula: $C_5H_{13}O_3P$ Mw = 152.13



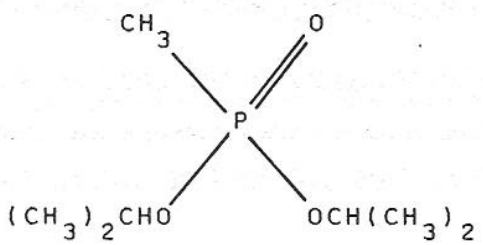

Fragments:

| m/e | Possible structure: |
|---|---|
| 93 | $C_2H_6PO_2^+$ |
| 94 | $C_2H_3PO_3^+$ |
| 111 | $C_2H_8PO_3^+$ |
| 137 | $C_4H_{10}PO_3^+$ |

Table 2.3 Mass spectrometric peak for isopropyl methyl methylphosphonate (IPMMP)

Diisopropyl methylphosphonate (DIPMP)

Formula: $C_7H_{17}O_3P$ Mw = 180.19



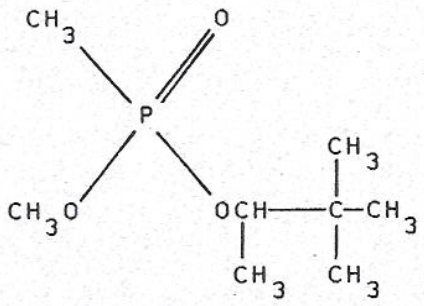
Fragments:

| m/e | Possible structure: |
|---|---|
| 80 | $H_3PO_3^+$ |
| 97 | $CH_3(OH)_3^+$ |
| 123 | $C_3H_8PO_3^+$ |
| 139 | $C_4H_{12}PO_3^+$ |
| 165 | $C_6H_{14}PO_3^+$ |

Table 2.4 Mass spectrometric peaks for diisopropyl methylphosphonate (DIPMP)

Methyl 1,2,2-trimethylpropyl methylphosphonate (MTMP)

Formula: $C_8H_{19}OP_3$ Mw = 194.22



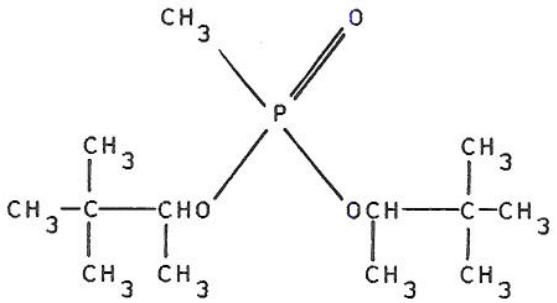
Fragments:

| m/e | Possible structure: |
|---|---|
| 69 | $C_5H_9^+$ |
| 84 | $C_6H_{12}^+$ |
| 94 | $CH_3PO_3^+$ |
| 111 | $C_2H_8PO_3^+$ |
| 138 | $C_4H_{11}PO_3^+$ |

Table 2.5 Mass spectrometric peaks for methyl 1,2,2-trimethylpropyl methylphosphonate (MTMP)

Di(1,2,2-trimethylpropyl) methylphosphonate (DTMP)

Formula: $C_{13}H_{29}OP_3$ Mw = 264.35



Fragments:

| m/e | Possible structure: |
|---|---|
| 69 | $C_5H_9^+$ |
| 84 | $C_6H_{12}^+$ |
| 97 | $CH_3P(OH)_3^+$ |
| 108 | $C_2H_5PO_3^+$ |
| 125 | $C_3H_{10}PO_3^+$ |
| 152 | $C_5H_{13}PO_3^+$ |

Table 2.6 Mass spectrometric peaks for di(1,2,2-trimethylpropyl) methylphosphonate (DTMP)

## 2.2.3 Gas chromatography

The quantitative analyses of the chemical warfare agents in the snow samples were carried out using the same method of gas chromatography/mass spectrometry as were used during the winter 1982/83 (2). The quantitative analysis of the methyl esters of the hydrolysis products of GB and GD, and the impurities of GB and GD, did not require the high sensitivity of GC-MS and therefore a gas chromatographic method was sufficient for quantitative analysis. The gas chromatograph was a Hewlett-Packard 5880A with FID detector. Further details about conditions are given in Table 2.7.

| Compound | Column | Temp ($^{o}$C) | Int std | Retention time (Seconds) Int std | Samp |
|---|---|---|---|---|---|
| IMPMP | SP-1200/ H3PO4 | 100 | C10 | 278 | 346 |
| DIPMP | " | 130 | C10 | 121 | 209 |
| MTMP | " | 150 | C12 | 238 | 302/316 |
| DTMP | " | 150 | C12 | 238 | 376/400 |

Table 2.7 Condition details for quantitative gas chromatographic analysis of derivatives of hydrolysis products and impurities of GB and GD

Gas chromatograms of IPMMP, DIPMP, MTMP, and DTMP are shown in Figures 2.9 - 2.12. As both MTMP and DTMP have two optically active centers, these compounds exist in two diastereomeric forms shown as partly resolved peaks in the gas chromatograms.

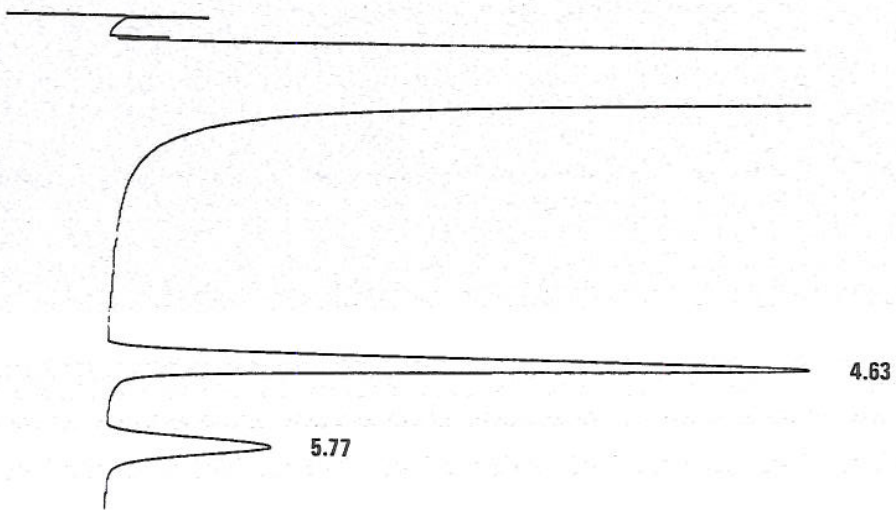



Figure 2.9 Gas chromatogram of isopropyl methyl methylphosphonate (IPMMP)

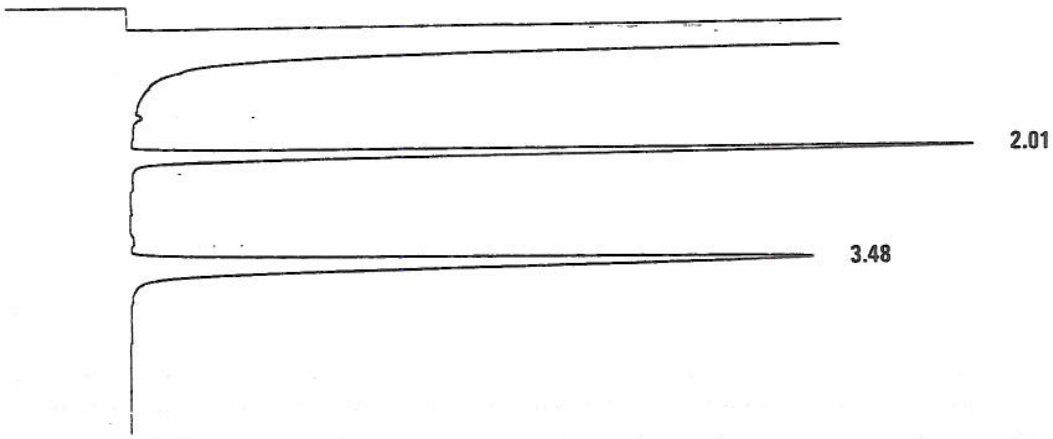



Figure 2.10 Gas chromatogram of diisopropyl methylphosphonate (DIPMP)

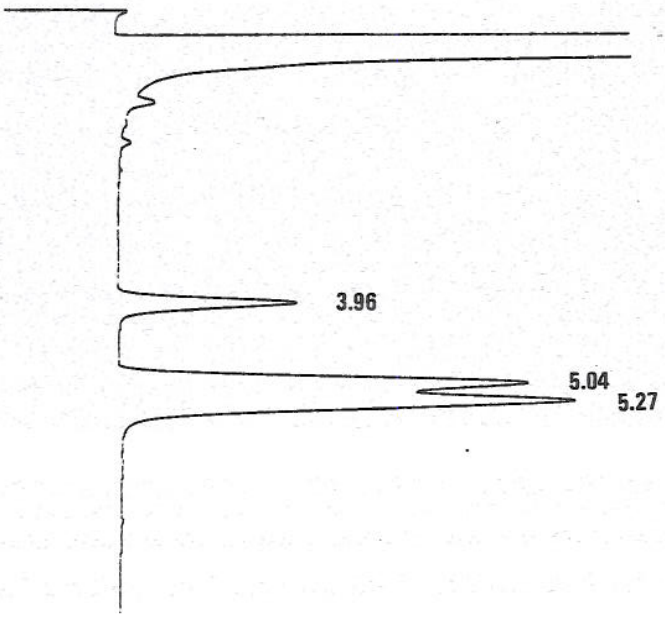



Figure 2.11 Gas chromatogram of methyl 1,2,2-trimethylpropyl methylphosphonate (MTMP)

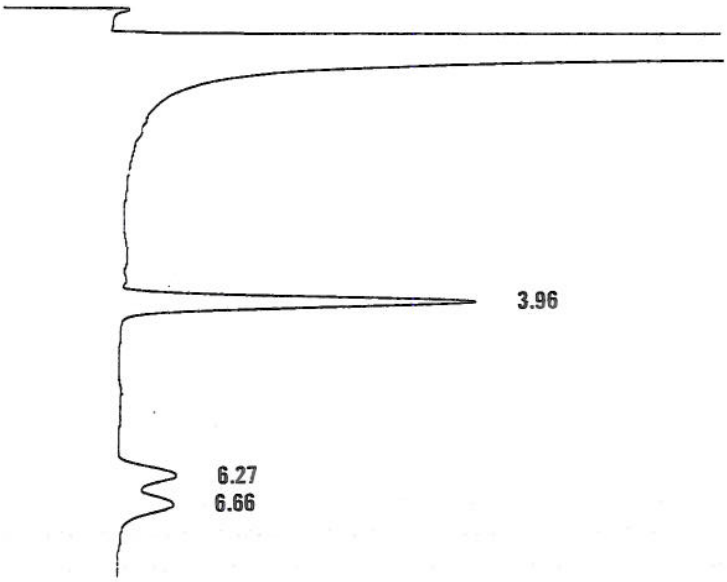



Figure 2.12 Gas chromatogram of di(1,2,2-trimethylpropyl) methylphosphonate (DTMP)

## 2.2.4 Recoveries

The hydrolysis products and impurities of GB and GD are all relatively stable compounds, and the recoveries are high. In the concentration range used in the experiments during the winter 1983/84, the recoveries were found to be 82, 77, 79, and 85 percent for IPMPA, PMPA, DIPMP, and DPMP respectively.

## 2.2.5 Detection limits

The detection limits for the chemical warfare agents have been reported previously (1,2). The detection limits of the hydrolysis products and impurities of GB and GD analysed by gas chromatography are given in Table 2.8 together with estimated detection limits for the MID method.

| Compound | Detection limit | |
|---|---|---|
| | GC/FID | MID |
| IPMPA (as IPMMP) | 10 ng | 10 pg |
| MTPA (as MTMP) | 10 ng | 10 pg |
| DIPMP | 1 ng | 10 pg |
| DTMP | 1 ng | 10 pg |

Table 2.8 Detection limits in the analysis of hydrolysis products and impurities of GB and GD

Gas chromatography is less sensitive than analytical gas chromatography/mass spectrometry with multiple ion detection (MID). The sensitivity of MID was not necessary for the quantitative analyses of IPMMP, DIPMP, MTMP and DTMP, and the MID method has therefore not yet been tested. It is estimated, however, that detection limits of the MID method will be about 10 pg. The MID method is sufficiently sensitive for the detection and analysis of the breakdown products and impurities of nerve agents in snow samples, and probably also for samples of body fluids of victims poisoned by GB and GD where high sensitivity is needed.

# 3 RESULTS

## 3.1 Analytical results

The results of the analyses of the different groups of snow samples exposed to the prevailing winter conditions for 2 and 4 weeks are shown in Tables 3.1 - 3.4. For the nerve agents GB and GD the results show that for these agents both the hydrolysis products and the impurities can be found in large amounts after 2 and 4 weeks. After 4 weeks most of the original agents have either evaporated or decomposed. For the diester impurities the recoveries were high, more than 50 percent of the applied amount. For the decomposition products, the recoveries were slightly lower, generally 10 to 50 percent. This is in contrast to the recoveries for the agents themselves where after 4 weeks, GB is present in concentrations about 100000 times lower than the applied amount. The nerve agents were also applied in increasing droplet size to establish any

influence on the agent recovery, but no significantly effects were found.

For mustard gas, increasing droplet size was postulated to increase both stability and recovery. The results showed a marked increase in recovery with increased droplet size. Larger droplets both evaporate and dissolve in water more slowly. The latter is specially important, as mustard gas is very unstable towards hydrolysis when dissolved in water.

Other experiments with mustard gas were carried out to study the effects of mixing mustard gas with lewisite. These experiments showed an increase in recovery with increased droplet size. The effects were, however, smaller than for pure mustard gas. This may be due to lewisite and its hydrolysis products making mustard gas more soluble in water.

Table 3.1 and 3.3 show remarkable high recoveries of mustard gas in both the samples containing pure mustard gas and mustard gas/lewisite mixtures. During these periods the temperature were relatively low and almost continuously below the freezing point. The samples were thus only exposed to water (melted snow) for a short time. Decomposition by hydrolysis was therefore much less pronounced than in the other, relatively warmer periods.

| Agent | Amount (mg) | | Anal-lysed as | Total amount found in sample (µg) | | | |
|---|---|---|---|---|---|---|---|
| | | | | 2 weeks 17 - 31 Jan 84 | | 4 weeks 17 Jan-4 Feb 84 | |
| | Agent | Added | | Uncov | Snow cov | Uncov | Snow cov |
| GB | 1 | | IPMMP | 185 | 341 | 208 | 311 |
| GD | 1 | | MTMP | 290 | 650 | 398 | 798 |
| GB+ | 0.8 | | IPMMP | 215 | 293 | 259 | 346 |
| DIPMP | | 0.2 | DIPMP | 106 | 134 | 112 | 151 |
| GD+ | 0.8 | | MTMP | 389 | 590 | 415 | 409 |
| DTMP | | 0.2 | DTMP | 127 | 169 | 110 | 155 |
| HD | 1 | | HD | 0.01 | 3 | 0 | 0.04 |
| HD+L | 0.8 | 0.2 | HD | - | 0.06 | 0 | 0 |
| HD+L | 4.0 | 1.0 | HD | 358 | 393 | 0.05 | 0.68 |

Table 3.1 Analytical results for Group 1 (winter 1983/84) (Sample not analysed is marked with -)

| Agent | Amount (mg) | | Anal-lysed as | Total amount found in sample (µg) | | | |
|---|---|---|---|---|---|---|---|
| | | | | 2 weeks 3 - 17 Feb 84 | | 4 weeks 3 Feb - 2 Mar 84 | |
| | Agent | Added | | Uncov | Snow cov | Uncov | Snow cov |
| GB+ | 0.8 | | IPMMP | 197 | 271 | - | - |
| DIPMP | | 0.2 | DIPMP | 65 | 109 | 66 | 105 |
| GD+ | 0.8 | | MTMP | 475 | 593 | 351 | 626 |
| DPMP | | 0.2 | DTMP | 132 | 168 | 129 | 134 |
| HD+L | 1.6 | 0.4 | HD | 0 | 0.1 | 0.002 | 0.007 |
| HD+L | 3.2 | 0.8 | HD | 0.03 | 0.03 | 0.004 | 0.04 |
| HD+L | 4.8 | 1.2 | HD | 0.05 | 0.09 | 0.011 | 0.005 |
| HD+L | 6.4 | 1.6 | HD | 0.01 | 0.09 | 0.004 | 0.015 |
| HD+L | 8.0 | 2.0 | HD | 0.03 | 0.24 | - | 0.074 |

Table 3.2 Analytical results for Group 2 (winter 1983/84) (Samples not analysed are marked with -)

| Agent | Amount (mg) | | Anal-lysed as | Total amount found in sample (µg) | | | |
|---|---|---|---|---|---|---|---|
| | | | | 2 weeks 17 Feb-3 Mar 84 | | 4 weeks 17 Feb-16 Mar 84 | |
| | Agent | Added | | Uncov | Snow cov | Uncov | Snow cov |
| GB | 2 | | GB | 0.001 | 0.006 | 0 | 0 |
| | | | IPMMP | 138 | 168 | 111 | 93 |
| GB | 4 | | GB | 0.013 | 0.165 | 0 | 0 |
| | | | IPMMP | 683 | 1064 | 767 | 880 |
| GB | 6 | | GB | 0.008 | 0.014 | 0 | 0 |
| | | | IPMMP | 1231 | 1445 | 1202 | 1377 |
| HD | 2 | | HD | 3 | 34 | 0.006 | 0.01 |
| HD | 4 | | HD | 80 | 672 | 0.018 | 0.064 |
| HD | 6 | | HD | 1587 | 3151 | 0.013 | 0.027 |
| HD | 8 | | HD | 960 | 2688 | 0.035 | 0.031 |
| HD+L | 1.6 | 0.4 | HD | 0.01 | 0.24 | 0.009 | 0 |
| HD+L | 3.2 | 0.8 | HD | 0.78 | 672 | 0.008 | 0.025 |
| HD+L | 4.8 | 1.2 | HD | 26 | 105 | 0.008 | 0.036 |
| HD+L | 6.4 | 1.6 | HD | 1234 | 2459 | 0.022 | 0.023 |

Table 3.3 Analytical results for Group 3 (winter 1983/84)

| Agent | Amount (mg) | | Anal-lysed as | Total amount found in sample (µg) | | | |
|---|---|---|---|---|---|---|---|
| | | | | 2 weeks 19 Mar-2 Apr 84 | | 4 weeks 19 Mar-16 Apr 84 | |
| | Agent | Added | | Uncov | Snow cov | Uncov | Snow cov |
| HD | 2 | | HD | 0.007 | 0.013 | 0.019 | 0.012 |
| HD | 4 | | HD | 0.016 | 0.013 | 0.004 | 0.046 |
| HD | 6 | | HD | 0.005 | 0.049 | 0.012 | 0.023 |
| HD | 8 | | HD | 0.014 | 0.131 | - | 0.021 |
| HD+L | 1.6 | 0.4 | HD | 0.006 | 0.029 | 0.006 | 0.011 |
| HD+L | 3.2 | 0.8 | HD | 0.010 | 0.075 | 0.003 | 0.008 |
| HD+L | 4.8 | 1.2 | HD | 0.011 | 0.017 | 0.012 | 0.01 |
| HD+L | 6.4 | 1.6 | HD | 0.02 | 0.072 | 0.009 | 0.046 |

Table 3.4 Analytical results for Group 4 (winter 1983/84) (sample not analysed is marked with -)

## 3.2 Exercises

Previous experiments have shown that the chloroform solutions from extraction of snow samples may be kept for several days without any significant decomposition or loss of agent. The results of the analyses of the samples transported in chloroform solution have therefore been regarded as a measure of the content of agent at the time of sampling. In Tables 3.1 and 3.2 these values are shown in parenthesis. These values were arbitrarily set to 100 percent, and all other results within each group are given in percent of these values. The figures therefore mainly reflect the differences in the treatment of the samples after the time of sampling.

For the most stable agents, the tear gas agents α-chloroacetophenone (CN) and 2-chlorobenzal malononitrile (CS), the results of the analyses of the samples show no significant difference between any of the transportation methods investigated (Tables 3.5 and 3.6). Recoveries are high and more than 50 percent of the amount of agent originally applied were found.

For the nerve agent GB and mustard gas there are significant differences between the different methods of transportation (Tables 3.5 and 3.6). During transportation of sarin (GB), deterioriation is neglible if the samples are kept at a temperature below - 20 °C on dry ice. If the samples are kept in water solution close to 0 °C, deterioriation becomes slightly larger. It is,however,

acceptable as long as the transportation time does not exceed 1 day. The rate of deterioriation increases with temperature. In water at room temperature less than 10 percent is left after one day of storage.

For mustard gas the difference in the results of the various transportation methods are even more pronounced. Samples transported at temperatures below -20 °C show a slight, but significant deterioriation. When the samples were transported at temperatures close to 0 °C, about 10 to 20 percent were present after one day. Without any precaution regarding temperature, only 2 and 9 percent were still present. After one day at room temperature most of the agent had hydrolysed, and the concentration has decreased to less than 1/10000 of its original value.

| Method | Percent remaining after 1 day | | |
|---|---|---|---|
| | GB | HD | CN |
| On dry ice. | 97 | 60 | 94 |
| In polystyrene box. | 76 | 21 | 94 |
| In chloroform solution. | 100 (697 µg) | 100 (171 µg) | 100 (888 µg) |
| No precaution. | 55 | 2 | 85 |
| In water at room temp. | 7 | 0.006 | 82 |

Table 3.5 Results from the exercise at Hvalsmoen (winter 1983/84)

| Method | Percent remaining after 1 day | | |
|---|---|---|---|
| | GB | HD | CS |
| On dry ice. | 100 | 35 | 100 |
| In polystyrene box. | 86 | 13 | 99 |
| In chloroform solution. | 100 (330 µg) | 100 (413 µg) | 100 (826 µg) |
| No precaution. | 52 | 9 | 98 |
| In water at room temp. | 7 | 0.006 | 79 |

Table 3.6 Results from the exercise at Banak (winter 1983/84)

## 4 CONCLUSIONS AND RECOMMENDATIONS

Experiments carried out during the winters 1981/82 to 1983/84 have shown that it is possible to verify use of chemical warfare agents under winter conditions. This can be accomplished by chemical analysis of snow samples at least 4 weeks after an attack. Most agents are sufficiently persistent and stable to be verified as the original agent, but there are also some that are relatively unstable and difficult to verify as the original agent after 4 weeks. For these hydrolytically unstable agents, the temperature will have strong influence on the amount of agent to be found. To increase the reliability of the verification procedure, methods for analysis of decomposition products and production impurities of some agents have been developed. The experiments carried out during the winter 1983/84 have shown that the incorporation of analyses of possible impurities and decomposition products is very useful in the verification of the nerve agents sarin (GB) and soman (GD). The decomposition products and impurities of both agents are very persistent. They are not known to occur naturally in the environment in significant concentrations, and their presence is therefore a strong indication for the use of the corresponding nerve agents.

Mustard gas is difficult to verify after 4 weeks. Increased droplet size of the agent, however, improves the possibility for verification of mustard gas. The reasons for this are that mustard gas dissolves slowly from the droplet surface, and hydrolyses rapidly when dissolved in water. Larger droplets have relatively less surface area, and decomposition is retarded. Increasing droplet size does not increase the persistency of the nerve agent GB, probably because it is rapidly dissolved in water.

Sample handling is an important step in all analyses when samples are to be moved from one place to another, or are to be stored before analysis can be carried out. This is specially important for samples containing unstable compounds. The exercises carried out during the winter 1983/84 show the importance of correct sample handling. When the samples were brought to the laboratory, they were extracted with chloroform, because the stability of the agents increases when they are transferred to this solvent. It would therefore be recommended to extract the samples in an improvised field laboratory. The exercises showed that this can be carried out without any practical difficulties. The stability of the agents in the samples may also be increased by lowering the temperature. The results show that transportation on dry ice gives a minimum of further decomposition, and that this may be as useful as immediate extraction with chloroform in the field. Both methods have, however, the disadvantage that prior preparation is needed as well as trained personnel. It was also interesting to observe that transportation in a termically insulated polystyrene box gave high recoveries of sarin (GB) and the tear gas agents CN and CS and satisfactory recovery for mustard gas. This method may therefore be acceptable if the other methods cannot be carried out. When no precautions are taken, the unstable compounds will undergo significant decomposition. After one day, recovery of sarin (GB) is only about 7 percent when transported in water at +20 $^{o}$C. For mustard gas, the recovery is much lower. For this agent the recovery is 2 percent when transported with no precautions, and 0.006 percent when transported in water at 20 $^{o}$C. This clearly shows that samples of unstable agents should be transported at the lowest possible temperature, or immediately extracted into a chloroform solution.

## References

(1) Blanch, J H, Odden, E, Karlsen, P J (1982): Analysis of snow samples contaminated with chemical warfare agents, FFI/RAPPORT-82/6003, Norwegian Defence Research Establishment.

(2) Blanch, J H, Johnsen, B A, Odden, E (1982): Analysis of snow samples contaminated with chemical warfare agents - Part 2, FFI/RAPPORT-83/6003, Norwegian Defence Research Establishment.

## APPENDIX

The dimensions of the wooden box, shown on page 6, containing the field laboratory equipment are 50 cm x 50 cm x 70 cm.

The box contained the following items:

### Laboratory equipment.

| | |
|---|---|
| 4 | Separation funnels (250 ml) |
| 2 | Pipettes (10 ml) |
| 2 | Pipette peleus balloons |
| 1 | Casserole (1.5 l) |
| 20 | Sample tubes (10 ml) |
| 20 | Sampling bottles (250 ml) |
| 1 | Polystyrene box |
| 1 | Polystyrene box (containing solid carbon dioxide) |
| 4 | Funnels |
| 1 | Butane stove |
| 2 | Spatulas |
| 20 | Gloves |
| 1 | Pack of matches |
| 1 | Pack of kleenex tissues |
| 1 | Pack of aluminum foil |
| 3 | Marking pens |
| 3 | Pencils |
| 1 | Notebook |

### Laboratory chemicals.

| | |
|---|---|
| 50 g | Sodium sulfate |
| 1 l | Chloroform |
| 1 l | Water |

### Antidotes and decontamination chemicals.

| | |
|---|---|
| 2 | Atropine/toxogonine autoinjectors |
| 0.5 l | Concentrated sodium hydroxide solution |
| 200 g | Calcium hypochlorite (bleaching powder) |

The field laboratory was constructed to accomplish these specific exercises of sample handling, and may be regarded as an example of a field sampling laboratory.