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ANALYSIS OF SNOW SAMPLES CONTAMINATED WITH CHEMICAL WARFARE AGENTS - PART 2

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8) ABSTRACT (continue on reverse side if necessary) <p>Snow samples contaminated with chemical warfare agents such as nerve agents (Vx, sarin, soman), mustard gas, irritating agents (CS, CN, DM), T-2 toxin and a mixture (1:1) of nerve gas precursors (methylphosphonyl dichloride and methylphosphonyl difluoride, didi precursor) have been analysed after outdoor exposure for 2 and 4 weeks under normal Norwegian winter condition. After 2 and 4 weeks all agents except mustard gas were still present in concentrations sufficiently high for positive verification. Mustard gas could be verified after 2 weeks, but after 4 weeks the concentration was below the detection limit of the method. It has further been demonstrated that snowfall covering the samples has a preserving effect, specially on the most unstable compounds, and in this case mustard gas was also verified after</p>														
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CONTENTS

		Page
1	INTRODUCTION	4
2	EXPERIMENTAL	5
2.1	Field experiments	5
2.2	Analytical methods	10
2.2.1	Sample preparation	11
2.2.2	Mass spectrometry	12
2.2.3	Analytical gas chromatography/mass spectrometry	20
2.2.4	Gas chromatographic analysis of dimethyl methylphosphonate	22
2.2.5	Analytical high performance liquid chromatography (HPLC) of DM	23
2.2.6	Recoveries	24
2.2.7	Detection limits	24
2.2.8	Influence of battlefield and environmental contaminants	25
3	RESULTS	26
4	CONCLUSIONS AND RECOMMENDATIONS	27
	References	29

## ANALYSIS OF SNOW SAMPLES CONTAMINATED WITH CHEMICAL WARFARE AGENTS

## PART 2

SUMMARY

Snow samples contaminated with chemical warfare agents such as nerve agents (Vx, sarin, soman), mustard gas, irritating agents (CS, CN, DM), T-2 toxin and a mixture (1:1) of nerve gas precursors (methylphosphonyl dichloride and methylphosphonyl difluoride, didi precursor) have been analysed after outdoor exposure for 2 and 4 weeks under normal Norwegian winter condition. After 2 and 4 weeks all agents except mustard gas were still present in concentrations sufficiently high for positive verification. Mustard gas could be verified after 2 weeks, but after 4 weeks the concentration was below the detection limit of the method. It has further been demonstrated that snowfall covering the samples has a preserving effect, specially on the most unstable compounds, and in this case mustard gas was also verified after 4 weeks. For added realism, a CS grenade was discharged, and snow samples were collected and analysed. CS was verified in all samples, as far as 70 m downwind and as long as 4 weeks after dissemination.

1 INTRODUCTION

This reports covers an extension of the work on verification of chemical warfare agents under winter conditions carried out during the winter 1981/82 (1). The aim of the investigation is to establish the possibility of using snow samples for verification of alledged use under winter conditions. In particular the possibility of getting a positive verification several weeks after alleged use, a realistic timeframe for establishing an international group of experts, have been investigated.

The investigations, during winter 1981/82 and winter 1982/83 were based on a scenario in which the chemical agents, nerve-, mustard- and irritating agents, mycotoxins and precursors, have been used at a low concentration ( $0.25 \text{ gm/m}^2$ ) against unprotected troops or civilians.

Particular attention has been paid to carrying out the experiments under field conditions, thus leaving the samples outdoor to deteriorate by exposure to the prevailing weather conditions such as wind, changing temperature, sunshine and snowfall.

The result of the previous investigation (1) showed that for all the agents examined, snow samples still contained sufficient amounts of agents for positive verification. Some of the agents were, however, too volatile or unstable to be positively identified after 4 weeks.

This year the investigations were extended to include other agents and precursors, and also to investigate the possible preserving effect of a snowfall after the attack. To make the approach as realistic as possible we also investigated the possibility of detecting CS in snow samples after the release of a grenade containing the training and riot control agent CS. Samples were taken as long as 4 weeks after the release and at a distance of up to 70 m from the release site. Control samples, not containing agents, were taken from several different environments. To simulate a battlefield, a large amount of TNT was exploded, and snow samples were taken in the immediate surroundings. Other snow samples were taken from both forest and urban areas.

## 2 EXPERIMENTAL

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

### 2.1 Field experiments

The field experiments were of two types. In the first type, samples (1 mg) were placed on top of a snow sample and left outdoor. The experimental conditions for these experiments were identical to those carried out last year (1). This year, the investigations included a number of new agents and precursors, and also the effect of snowfall

immediately after an attack. The latter was simulated by covering the samples with a snow layer of 5 cm immediately after application. The compounds included in the investigation were:

- 1) Isopropyl methylphosphonofluoridate (GB or sarin)
- 2) 1,2,2-Trimethylpropyl methylphosphonofluoridate (GD or soman)
- 3) Bis(2-chloroethyl) sulphide (HD or mustard gas)
- 4) 2-Chlorobenzalmalonitrile (CS)
- 5)  $\alpha$ -Chloroacetophenon (CN)
- 6) 10-chloro-5,10-dihydrophenarsazine (DM or adamsite)
- 7) Mixture (1:1) of methylphosphonyl dichloride and methylphosphonyl difluoride (didi, precursor)
- 8) 4 $\beta$ ,15-diacetoxy, 8 $\alpha$ -(3-methylbutyryloxy)-3 $\alpha$ -hydroxy-12,13-epoxytrichothec-9-ene (T-2 toxin)

The experiments carried out last year established that the agents did not particularly tend to migrate down into the snow, and the samples were therefore no longer divided into horizontal layers, but taken as a single large sample. The experiments were started on February the 2nd, and the samples were analysed after 14 and 28 days exposure. The weather conditions (temperature and relative humidity) was recorded continuously and is given in Figure 2.1.

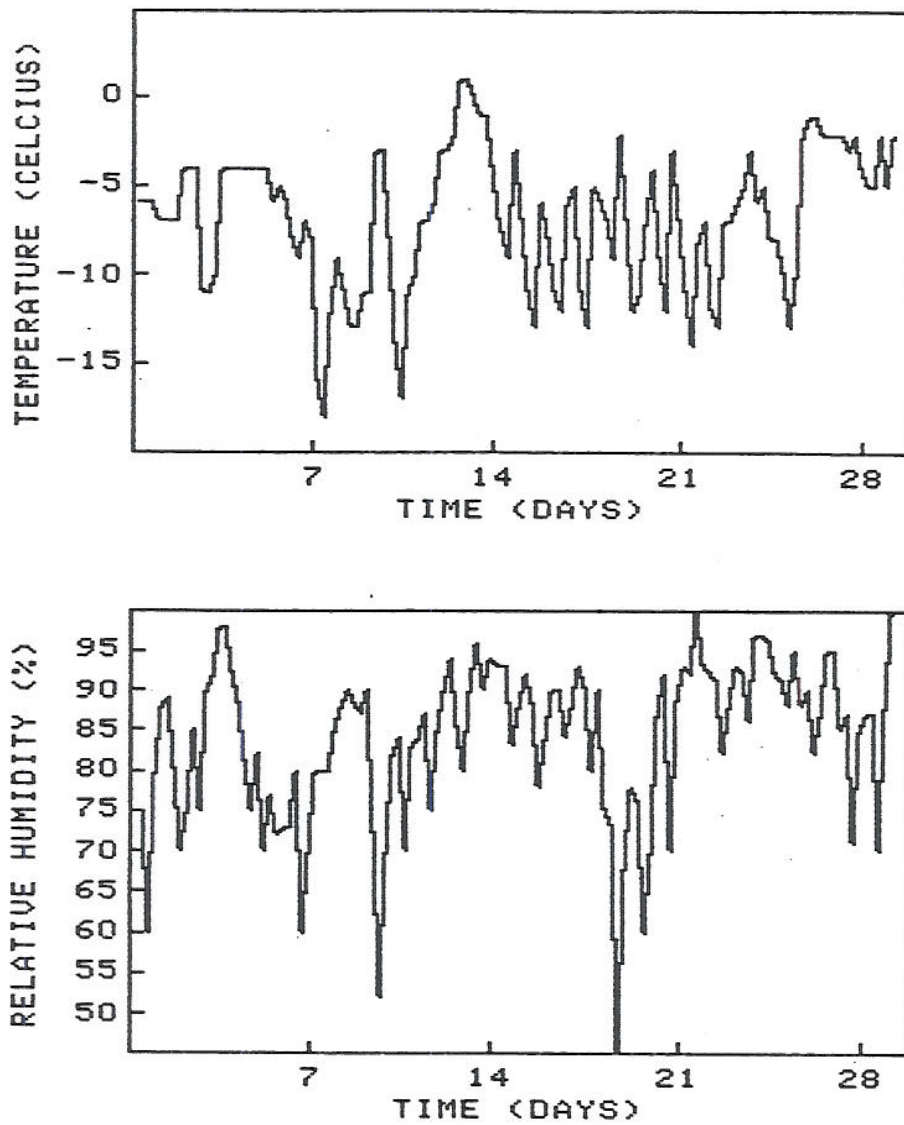


Figure 2.1 Plot of temperature ( $^{\circ}\text{C}$ ) and relative humidity (percent) against the time after the start of the experiment

To make the experiments as realistic as possible, experiments were also carried out with a pyrotechnic tear gas grenade, containing 250 g CS. A picture of the situation 30 seconds after ignition of the CS grenade is shown in Figure 2.2. The experiment was started on February the 17th, and was carried out in an enclosed military forest area. At the time of dissemination, the ground was covered with a snow layer having a thickness of about 10 cm. Snow samples were taken at increasing downwind distances (1,2,3,5,7 and 10 m) 30 minutes after setting off the grenade. The samples consisted of snow taken from the upper 2-3 cm of a 10 x 10 cm area using plastic spoons.

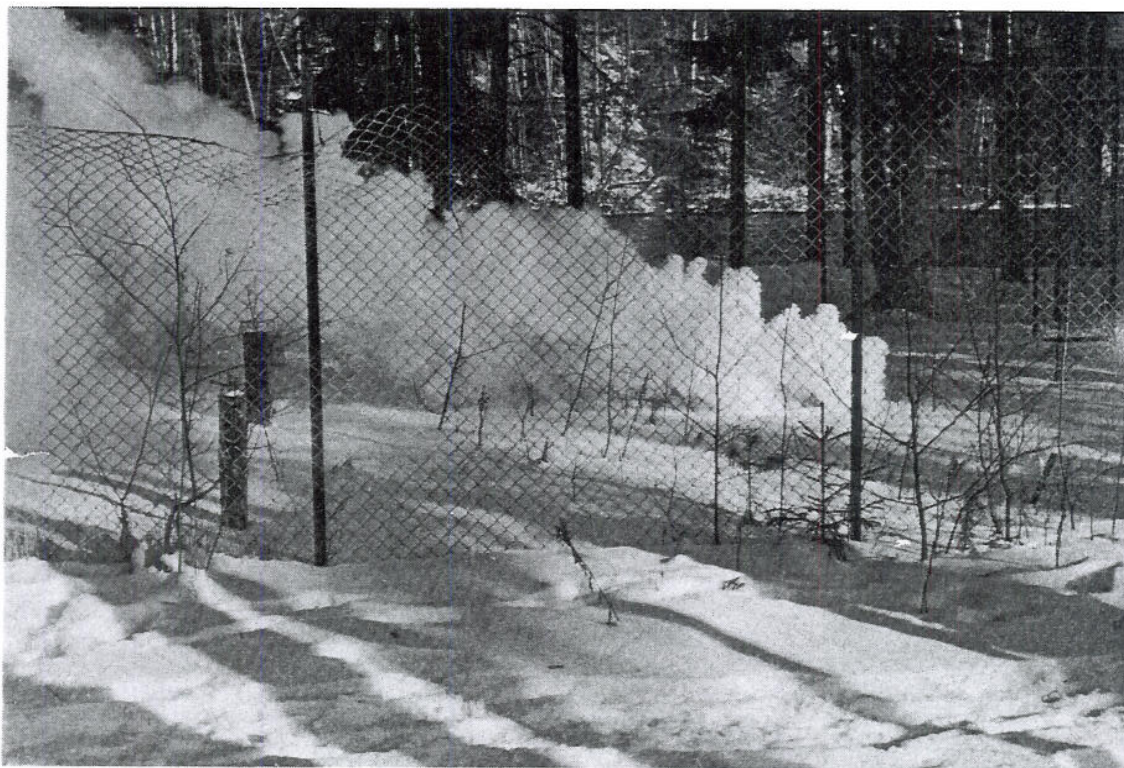


Figure 2.2 The cloud from a CS grenade 30 seconds after ignition





## 2.2 Analytical methods

The general method of analysis is outlined in the block diagram given in Figure 2.4.

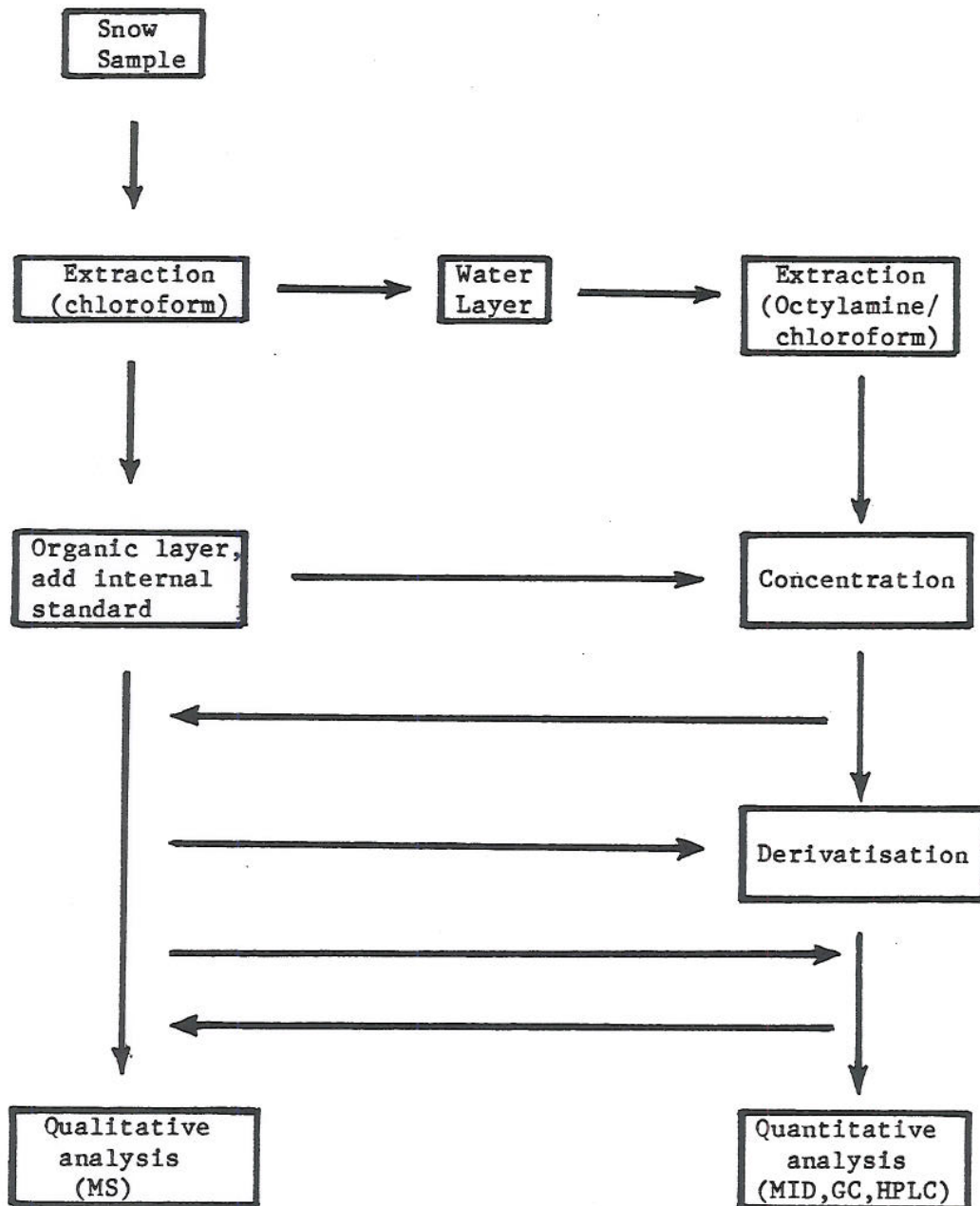


Figure 2.4 Block diagram of the procedure for sampling and analysis of chemical warfare agents

### 2.2.1 Sample preparation

The snow samples to be analysed were taken to the laboratory and immediately melted at room temperature. When melted, the volume of the solution varied from 100 to 150 ml. The total volume was transferred to a separation funnel and extracted with chloroform (Merck, Uvasol quality). It is important that the agents can be extracted as soon as possible when melted, since most of the agents are easily hydrolysed.

#### ADAMSITE (DM)

The samples containing adamsite were extracted twice with 5 ml chloroform. The organic phases were mixed, and the solvent evaporated under reduced pressure. The residue was resolved in 2 ml methanol and analysed by high performance liquid chromatography (HPLC) using UV-detection at 254 nm.

#### METHYLPHOSPHONIC ACID (MPA)

Methylphosphonic acid is poorly soluble in chloroform, but may be extracted with 5 ml 0.02 M trioctylamine in chloroform. The chloroform solution was dried with anhydrous sodium sulphate and treated with an excess of diazomethan in ether to form dimethyl methylphosphonate (DMMP). This ester is more volatile than the acid, and more suited for analysis by GC. n-Undecane was added as internal standard.

#### T-2 TOXIN

A sample to be analysed from T-2 toxin was extracted once with 5 ml chloroform. The solution was dried with sodium sulphate, and 3 $\alpha$ -hydroxy-4 $\beta$ ,15-diacetoxy-12,13-epoxytrichothec-9-ene (DAS) was added as an internal standard. Before analysis the trichothecenes were silylated with SYLON BTZ to make them more volatile. Analysis were carried out by GC-MS.

OTHER AGENTS

All other agents analysed were extracted once with 5 ml chloroform. The extract was dried with sodium sulphate, internal standard added (see Table 2.1), and analysed by GC-MS.

Thus, except for minor variations, essentially the same procedure is used for all agents.

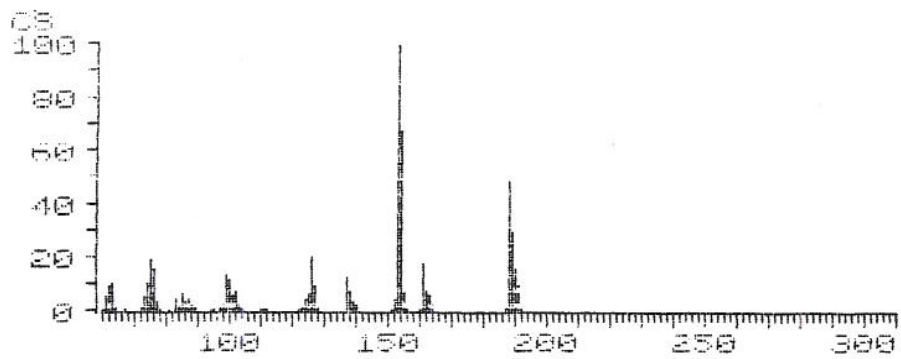
<u>Agent</u>	<u>Solvent</u>	<u>Int standard</u>	<u>Deriv agent</u>
GB	Chloroform	C9	
GD	"	C10	
HD	"	C12	
CS	"	C14	
CN	"	C14	
T-2	"	DAS	SYLON BTZ
DM	"	-	
MPA	Chloroform/ trioctylamine	C11	Diazomethan

Table 2.1 Extraction solvents, internal standards and derivatization agent used in sample preparation

## 2.2.2 Mass spectrometry

To establish the most suitable conditions for quantitative mass spectrometric analysis, mass spectra were recorded for all agents. The instrument, a LKB 2091 mass spectrometer equipped with a PYE UNICAM gas chromatograph, was the same as used for the analysis of nerve agents and mustard gas and for the recording of the mass spectra of sarin, soman and mustard gas (1). The experimental conditions were also the same.

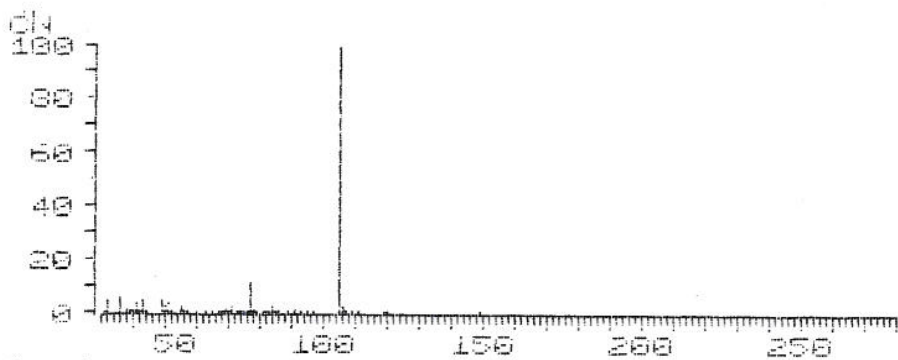
The mass spectra of CS, CN, DMMP and of the trimethylsilylethers of DAS and T-2 (DAS TMS and T-2 TMS) are given in Figures 2.5 to 2.9.



Mass :	153	154	188	189	126	75	161	190	76	99
Intensity :	100.0	68.1	48.6	30.5	21.5	19.6	17.9	16.2	15.7	13.7

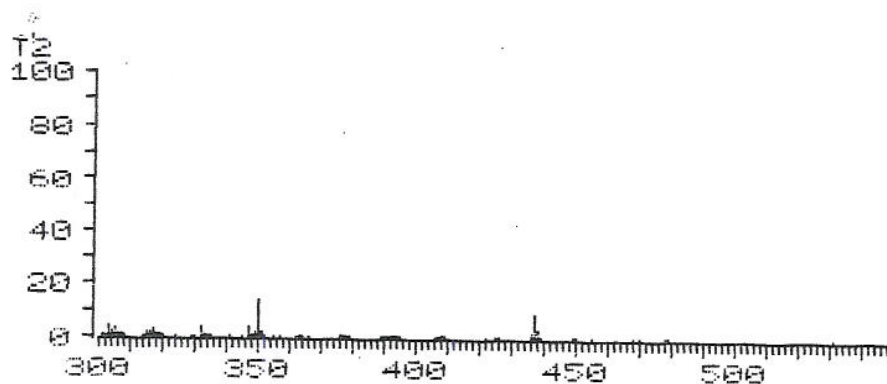
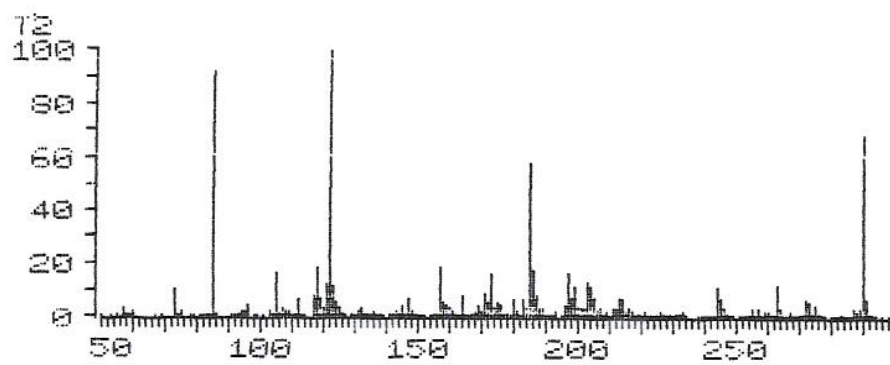
Mass	Int%	Mass	Int%	Mass	Int%	Mass	Int%	Mass	Int%	Mass	Int%
61:	5.8	62:	9.8	63:	10.7	73:	6.0	74:	11.1	75:	19.6
76:	15.7	83:	5.4	85:	6.7	99:	13.7	100:	12.3	101:	5.5
102:	8.1	125:	7.1	126:	21.5	127:	9.9	137:	12.6	138:	8.1
152:	5.1	153:	100.0	154:	68.1	155:	8.1	161:	17.9	162:	8.5
163:	5.9	188:	48.6	189:	30.5	190:	16.2	191:	9.9		

Figure 2.5 Mass spectrum of CS



Mass :	105	77	36	32	43	49	51	41	55	50
Intensity :	100.0	11.6	5.7	4.7	4.7	4.7	4.5	3.7	3.4	3.2

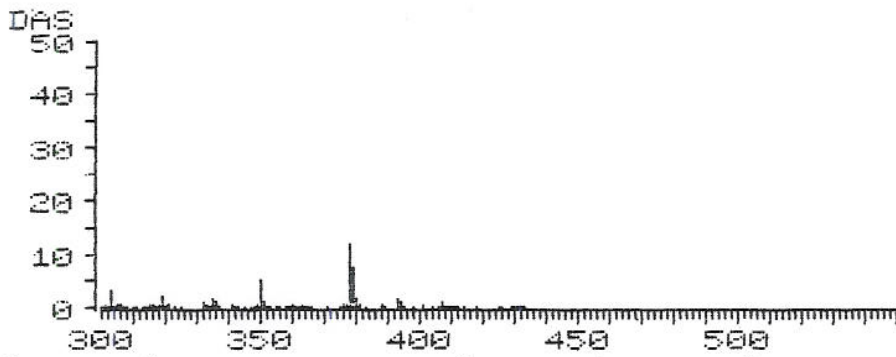
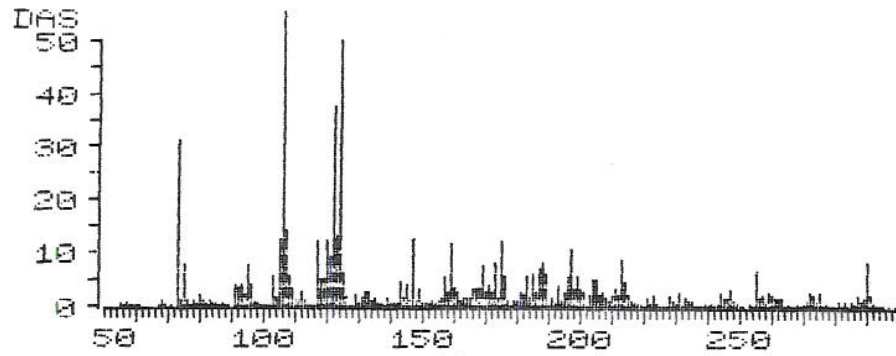
Figure 2.6 Mass spectrum of CN



Mass :	122	85	290	185	157	118	186	173	197	105
Intensity :	100.0	93.0	68.9	58.6	19.3	18.9	17.9	17.1	17.0	16.9

Topper over 10.00 %											
Masse	Int%	Masse	Int%	Masse	Int%	Masse	Int%	Masse	Int%	Masse	Int%
73:	10.8	85:	93.0	105:	16.9	118:	18.9	121:	13.2	122:	100.0
123:	11.9	157:	19.3	171:	10.2	173:	17.1	185:	58.6	186:	17.9
197:	17.0	199:	11.9	203:	13.7	204:	11.8	244:	11.9	263:	13.2
290:	68.9	350:	15.4	437:	10.2						

Figure 2.7 Mass spectrum of T-2 TMS

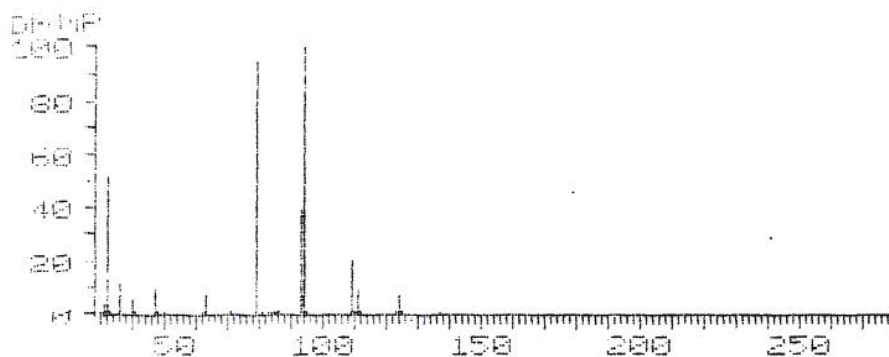


Mass : 106 124 122 73 107 123 147 105 378 117  
 Intensity : 100.0 50.7 38.0 31.4 14.5 13.3 13.2 12.9 12.6 12.5

Topper over 7.00 %

Mass	Int%	Mass	Int%	Mass	Int%	Mass	Int%	Mass	Int%	Mass	Int%
73:	31.4	75:	8.2	95:	7.8	105:	12.9	106:	100.0	107:	14.5
117:	12.5	120:	12.5	121:	9.4	122:	38.0	123:	13.3	124:	50.7
147:	13.2	159:	11.8	169:	8.2	173:	8.6	175:	12.5	187:	7.4
188:	8.4	197:	10.9	213:	9.0	255:	7.2	290:	8.6	378:	12.6
379:	7.9										

Figure 2.8 Mass spectrum of DAS TMS



Mass : 94 79 32 93 109 36 111 47 124 63  
 Intensity : 100.0 94.7 52.1 39.9 20.6 12.3 10.4 9.9 8.2 7.7

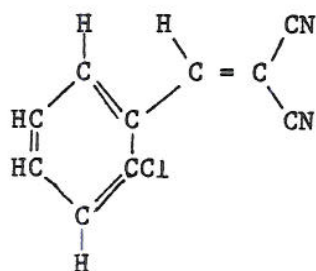
Mass	Int%	Mass	Int%	Mass	Int%	Mass	Int%	Mass	Int%	Mass	Int%
31	3.6	32	52.1	36	12.3	40	6.1	47	9.9	63	7.7
79	94.7	93	39.9	94	100.0	109	20.6	111	10.4	124	8.2

Figure 2.9 Mass spectrum of DMMP

The most important mass spectrometric peaks of the compounds are given in Tables 2.2 to 2.6.

o-Chlorobenzal malonitrile (CS)

Formula:  $C_{10}H_5ClN_2$ ; Mw = 188.01



Fragments:

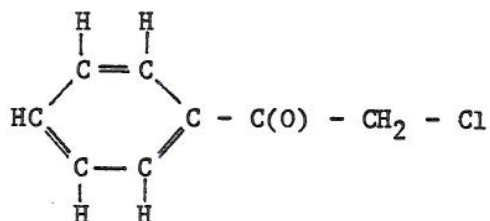
m/e	Possible structure:
126	$C_9H_4N^+$
137/139	$C_7H_4NCl^+$
153	$C_{10}H_5N_2^+$
161/163	$C_9H_5NCl^+$
188/190	$M^+$

Table 2.2 Mass spectrometric peaks for CS



$\alpha$ -Chloroacetophenon (CN)Formula:  $C_8H_7ClO$ ;

Mw = 154.02

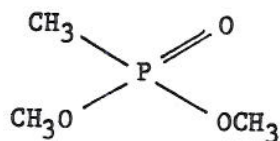


Fragments:

m/e	Possible structure:
51	$C_4H_3^+$
77	$C_6H_5^+$
105	$C_6H_5C=O^+$

Table 2.3 Mass spectrometric peaks for CNDimethyl methylphosphonate (DMMP)Formula:  $C_3H_9O_3P$ ;

Mw = 124.01



Fragments:

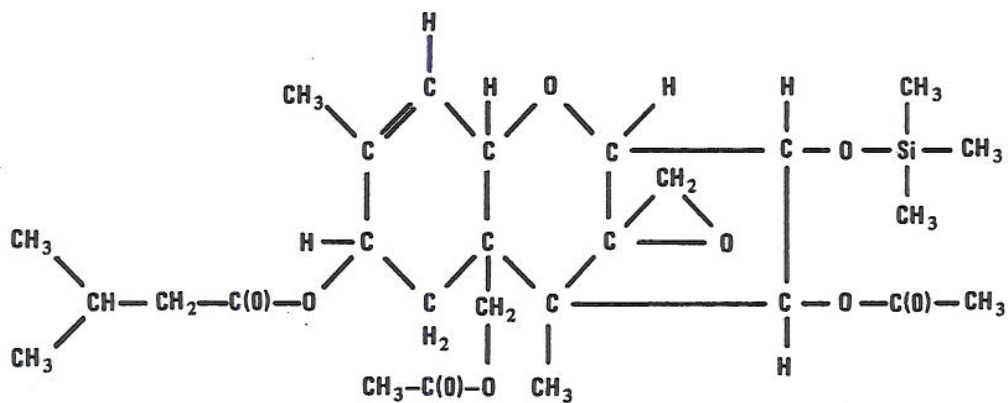
m/e	Possible structure:
63	$PO_2^+$
79	$PO_3^+$
93	$C_2H_6PO_2^+$
94	$CH_3PO_3^+$
109	$C_2H_6PO_3^+$
124	$M^+$

Table 2.4 Mass spectrometric peaks for DMMP

4 $\alpha$ ,15-Diacetoxy, 8 $\alpha$ -(3-methylbutyryloxy)-3 $\alpha$ -hydroxy-  
12,13-epoxytrichothec-9-ene trimethylsilylether (T-2 TMS)

Formula:  $C_{27}H_{42}O_9Si$ ;

Mw = 538.72



Fragments:

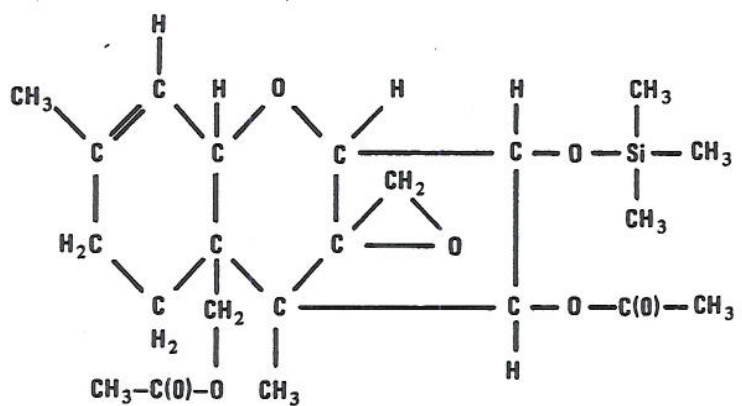
m/e	Possible structure:
85	$C_5H_9C^+$
122	$C_8H_{10}O^+$
185	$C_{13}H_{13}O^+$
290	$C_{16}H_{18}O_5^+$
350	$C_{18}H_{26}O_5Si^+$
436	$C_{22}H_{32}O_7Si^+$

Table 2.5 Mass spectrometric peaks for T-2 TMS

4 $\alpha$ ,15-Diacetoxy-3 $\alpha$ -hydroxy-12,13-epoxytrichothec-9-ene trimethylsily-  
lether (DAS TMS)

Formula: C<sub>22</sub>H<sub>34</sub>O<sub>7</sub>Si;

Mw = 438.60



Fragments:

m/e	Possible structure:
106	C <sub>8</sub> H <sub>8</sub> <sup>+</sup>
124	C <sub>8</sub> H <sub>12</sub> O <sup>+</sup>
175	C <sub>12</sub> H <sub>15</sub> O <sup>+</sup>
290	C <sub>16</sub> H <sub>18</sub> O <sub>5</sub> <sup>+</sup>
378	C <sub>20</sub> H <sub>30</sub> O <sub>5</sub> Si <sup>+</sup>

Table 2.6 Mass spectrometric peaks for T-2 TMS

## 2.2.3 Analytical gas chromatography/mass spectrometry

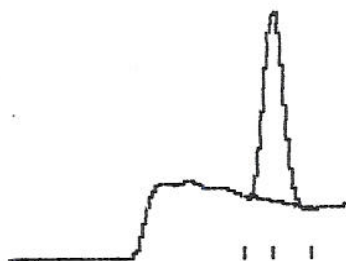
The quantitative analysis of the snow samples were carried out using the same method of gas chromatography/mass spectrometry as used for the experiments last year (1). Special condition details for the individual agents and internal standards are given in Table 2.7

Agent	Column	Temp (°C)	Int std	Retent time (seconds)			Fragment		
				Int	Std	Samp	Int	Std	Samp
GB	Sp-1200/ H <sub>3</sub> PO <sub>4</sub>	95	C9	128	163	57	99		
GD	"	130	C10	93	152	57	126		
HD	SE-30	90	C12	104	154	57	109		
CS	"	135	C14	82	126	57	153		
CN	"	115	C14	82	172	57	105		
T-2 TMS	OV-17	290	DAS	105	242	106	185		
DMMP	Sp-1200/ H <sub>3</sub> PO <sub>4</sub>	130	C11	177	80				

Table 2.7 Condition details for quantitative mass fragmentographic and gas chromatographic analysis of chemical warfare agents and derivatives

For the agents CS, CN and T-2 TMS, sample mass fragmentograms are shown in Figures 2.10, 2.11 and 2.12.

Internal standard



Sample



Figure 2.10 Mass fragmentogram of CS  
Sample: CS grenade, 1 week, 1 m

Internal standard



Sample



Figure 2.11 Mass fragmentogram of CN  
Sample: 4 weeks, not snow covered

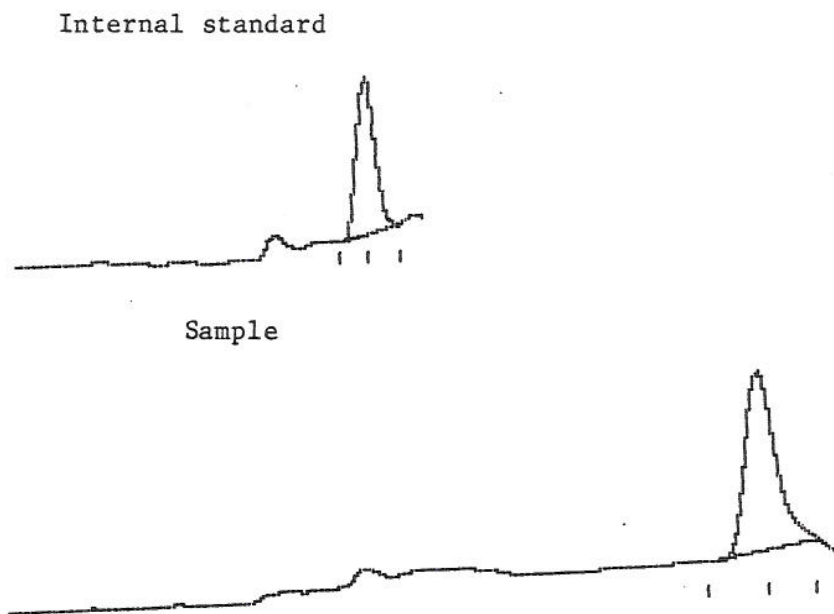


Figure 2.12 Mass fragmentogram of T-2 TMS  
Sample: 4 weeks, not snow covered

#### 2.2.4 Gas chromatographic analysis of dimethyl methylphosphonate

The didi precursor hydrolysed immediately after application on snow to the methylphosphonic, hydrochloric and hydrofluoric acid. Hydrochloric and hydrofluoric acid or their salts are abundant in nature, and are therefore not suited for use as a marker for this compound. The methylphosphonic acid, however, is very rare in the natural environment, and is therefore a good marker. It is very stable on snow, both to chemical decomposition and evaporation. It might have been analysed by combined GC/MS, but in this case, the extreme selectivity and sensitivity of this method was not necessary, and the analyses were carried out using a GC method. Because of low volatility and low solubility in chloroform, the methylphosphonic acid (MPA) was converted to the methyl ester (DMMP) by methylation with diazomethan and extracted and analysed as such. The gas chromatograph used was Hewlett-Packard model 5880A with FID detector. Further details about conditions are given in Table 2.7.

## 2.2.5 Analytical high performance liquid chromatography (HPLC) of DM

The analysis of adamsite (DM) is difficult to perform by the use of GC-MS because of its very low volatility (vapor pressure at 20°C is 0.002 Torr). The analyses were therefore carried out using a high performance liquid chromatograph (HPLC, Varian Model 5000, with UV detection at 254 nm). A reversed phase column (BioRad RO-18, ODS-5  $\mu\text{m}$ ) was employed. The mobile phase was methanol:water (9:1) with a flow rate of 1 ml/min and at ambient temperature. 10  $\mu\text{l}$  DM, dissolved in methanol, were injected on the column. Since the injection volume is constant, the area of the adamsite peak is a measure for amount of adamsite in the sample. A calibration curve was established by analysing samples containing known amounts of adamsite. Sample chromatograms of a standard and a sample is given in Figure 2.13.

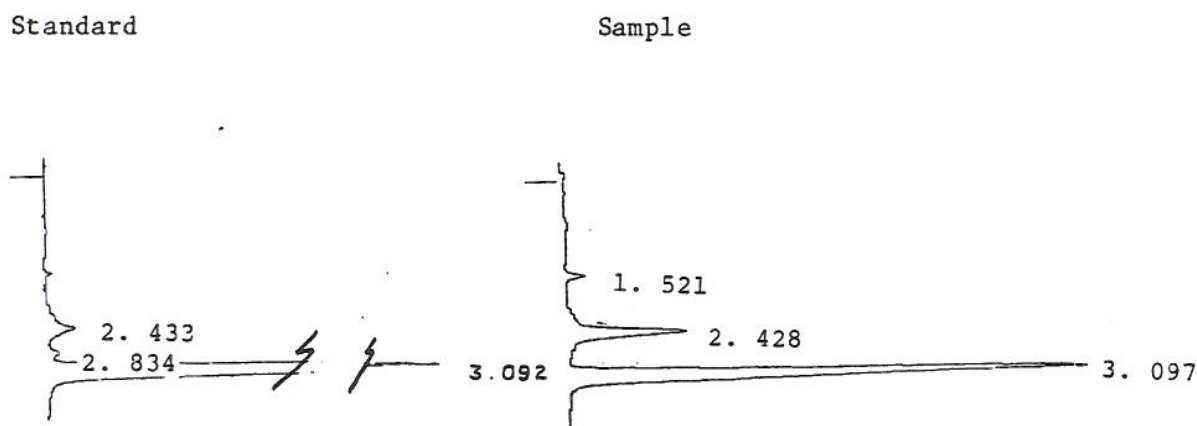


Figure 2.13 High performance liquid chromatography of adamsite (DM) (standard and sample, 4 weeks). The retention times (min) are shown in the figure

### 2.2.6 Recoveries

Since some of the agents are unstable in water, and because of possible loss of agent due to evaporation and incomplete extraction, recoveries were determined for all agents. This was done by analysing snow samples by the same procedure as described above. The analysis followed, however, immediately after application of the agent. The analyses were carried out in duplicate, and the mean results are given in Table 2.8.

<u>Compound</u>	<u>Percent recovery</u>
Sarin	66
Soman	73
Mustard gas	55
CS	91
CN	88
DM	96
T-2	92
Didi (as DMMP)	96

Table 2.8 Mean recoveries for the analyses of the different chemical warfare agents

### 2.2.7 Detection limits

The agents CN, DM, T-2 and the hydrolysis products of the precursors (didi) were remarkably stable. The amounts found were far higher than even the practical detection limits for these agents. The detection limit of CS was found to be 150 ng when isolated from a sample containing 150 g snow.

For the other agents when utmost sensitivity was needed, the samples were concentrated by evaporating most of the organic solvent with dry



nitrogen. The practical detection limits defined as signal/noise ratio equal to 5 for chemical warfare agents isolated from 40 cc snow are given in Table 2.9. The practical detection limit is a function of the sampling, chromatographic procedures and contaminants in the snow. The detection limits for pure agents were several folds lower. The sensitivity could be considerably improved by the mass fragmentography of several ions.

<u>Compound</u>	<u>Amount (picogram = <math>10^{-12}</math> gram)</u>
Sarin	100
Soman	10
Tabun	500
Vx	500
Mustard	50

Table 2.9 Detection limits for chemical warfare agents from 40 cc snow

#### 2.2.8 Influence of battlefield and environmental contaminants

Chemical detection may be influenced by the presence of known or unknown natural occurring contaminants. To investigate the contribution of such contaminants to the analytical procedure used in these experiments, snow samples were taken from different natural environments (forest and urban areas) and also in a simulated battlefield environment. Snow samples were taken in densely populated areas, near roads, and in a wood. To simulate a battlefield area, a block of 3 kg of TNT was exploded and samples were taken at and around the explosion site. All the samples were analysed by the same methods and under the same conditions as described above, but none of them showed any false positive responses to any of the agents.

3 RESULTS

The analytical results of the snow sample analyses are given in Tables 3.1 and 3.2. Table 3.1 shows the experiments where controlled amounts of agent were applied to the surface of snow samples contained in glass beakers. When evaluating the results it must be considered that the experiments have not been designed for high quantitative analytical precision as this is essentially unnecessary. Application of the small solid samples of CS, CN, DM and T-2 toxin is difficult to do quantitatively, and this may be the reason for the variation in the results of these compounds.

	Time (Days)	Total amount of agent found in sample ( $\mu\text{g}$ )			
		Uncovered	Snowcovered	Uncovered	Snowcovered
Agent:		GB		GD	
	14	0.005	7	7	26
	28	0.032	0.47	0.58	16
Agent:		HD		T-2 TMS	
	14	0.005	0.04	830	870
	28	0	0.002	960	790
Agent:		CS		CN	
	14	500	400	890	540
	28	940	787	380	470
Agent:		DM		DMMP	
	14	660	480	850	970
	28	570	750	760	940

Table 3.1 Total amount of agent found 14 and 28 days after application of 1 mg agent to different snow samples. Half of the samples were covered with snow immediately after application

Table 3.1 shows the analytical results of the experiment using a CS grenade. Analyses verified the presence of CS in all samples taken, the sensitivity limit of the method is, however, estimated to be close to the amounts found in the most diluted samples.

Distance (m)	Total amount of CS found in sample ( $\mu\text{g}$ )				
	1	7	14	20	29 (days)
1	230	470	300	44	-
2	100	110	160	19	-
3	30	13	33	4	4
5	6	9	7	3	-
7	4	2	3	2	-
10	18	2	2	1	-
13	-	0.7	1	0.15	0.4
20	-	0.8	0.6	3	0.15
35	-	2	2	0.4	0.2
50	-	-	0.3	-	-
70	-	-	-	-	0.3

Table 3.2 Total amount of CS found in snow samples taken at increasing distances downwind and at different time intervals after the discharge of a CS grenade. Entries marked (-) signifies that no sample was taken.

#### 4 CONCLUSIONS AND RECOMMENDATIONS

The experiments carried out during the last two winters have shown that under winter conditions the stability of different chemical warfare agents vary. This will markedly influence the possibility of verification of use of chemical warfare agents by means of chemical analysis of snow samples taken some time after the alleged attacks. Of the agents investigated the following are relatively stable:

- The physical incapacitating agents CS, CN and DM
- The immediate decomposition product of the didi precursor
- The mycotoxin T-2
- The nerve agent VX

For these compounds, except for VX, it is expected that at least 25 per cent of the original agent is still available for analysis in samples taken as long as 1 month after the attack. VX is slightly less stable, the values are here between 1 and 10 per cent. Very selective and sensitive analytical methods are available for all compounds and there would be no difficulties in verifying the presence of these agents long after a chemical attack during winter conditions.

The nerve agents GA, GB, GD and the blister agent HD were found to be markedly more unstable. After 2 weeks, generally less than 0.1 per cent of the original agents were still present in the samples. The analytical methods used are, however, very selective and sensitive, and verification of use by chemical analysis of snow samples would be most likely. After 1 month, it was still possible to analyse the nerve agents, but the content of mustard gas was below the sensitivity limit of the method. The amount of nerve agents still left in the samples were in the order of 1/100000 of the original amount. The verification of use of sarin and to an even larger extent mustard gas is uncertain and highly dependent upon the weather condition. This was demonstrated by the experiments last year, where sarin was not detected after 4 weeks (1). High temperature and strong wind is unfavourable to positive verification. As expected, a snowfall covering the samples reduce evaporation, and increase the possibility for verification. This was confirmed by the experiments and was specially important for the agents GB, GD and HD. Under such condition it was also possible to detect and analyse HD after 4 weeks.

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.