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ANALYSIS OF SNOW SAMPLES
CONTAMINATED WITH CHEMICAL
WARFARE AGENTS - PART 4

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Electrochemical detection was developed for adamsite and found to be very
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and Lewisite C. Lewisite is too rapidly hydrolysed to be of any importance
in verification of an alleged use of chemical warfare agents. The two
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A method for analysis of thiodiglycol, the hydrolysis product of mustard,
has been developed. The method is based on the adsorption to porous poly-

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ABSTRACT (continued)

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CONTENTS

RESEARCH REPORT ON VERIFICATION OF A CHEMICAL WEAPONS CONVENTION
Sampling and analysis of chemical warfare agents under winter con-
ditions - Part IV

SUMMARY

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the nerve gas simulant DMMP. These results are further used
in a system analysis of sampling presented in this report.

1   INTRODUCTION

During the winters of 1981/82 (1), 1982/83 (2) and 1983/84 (3) the
possibility for verification of nerve agents, mustard and various
irritating agents under winter conditions were studied. The present
report is an extension of the previous work and is mainly concentrated
on the verification of arsenic compounds and the hydrolysis product of

mustard. Furthermore the report extends the previous work on sample handling which was performed during the winter 1983/84. This report also includes a system analysis of sampling. For the most unstable agents their hydrolysis products and impurities were analysed to extend the possibility for positive verification of these chemical warfare agents. Although our investigation is aimed at winter conditions, both the methods, procedures and results are of general interest for all winter conditions.

Lewisite is one of these very unstable chemical warfare agents which is almost immediately hydrolysed in contact with water. Verification of use of Lewisite itself is therefore of only limited value. However, during the production of Lewisite several byproducts (impurities) are formed which are more persistent to hydrolysis. These byproducts will be present in the Lewisite used as a chemical warfare agent and will increase the possibility for verification of its use. Therefore, these compounds are included in the study during the winter 1984/85. In addition, a new and more sensitive analytical method was tested for Adamsite. This method is based on separation by HPLC and electrochemical detection.

Mustard is another chemical warfare agent which hydrolyses relatively fast to thiodiglycol. This compound is highly soluble in water and is therefore impossible to remove from large quantities of water by liquid-liquid extractions. Therefore, the experiments were focused on the possibility of studying the efficiency of different adsorbents for concentration of thiodiglycol in water. This study was expanded to comprise the presence of mustard in urine samples.

In 1983/84 (3) different methods of sample handling were studied. The experiments were carried out to find the best methods for preparing snow samples under field conditions before they are transported and analysed in a laboratory. In 1983/84 a field laboratory was brought to the sampling area to test the work-up procedures immediately after sampling. During the winter of 1984/85 new methods of sample handling based on the adsorption to porous polymers were investigated. The

methods tested are compared with the work-up procedure previously developed in our laboratory.

2   EXPERIMENTAL

The field experiments during the winter of 1984/85 can be divided into three categories:

The first is a continuation of the field experiments on persistency determination of different chemical warfare agents. In 1984/85 the research was concentrated to the arsenic compound Lewisite and the hydrolysis product thiodiglycol of mustard. Simultaneously with these particular studies work was continued to improve the present analytical methods.

The second part of the work was a continuation of the sample handling experiments started during the winter 1983/84 (3). In 1984/85 the work was concentrated on finding porous polymers which are suitable to use in extraction of chemical warfare agents and their hydrolysis products from water.

The third part include a field experiment where the release of a teargas grenade (CS) and a shell filled with a nervegas simulant dimethylmethylphosphonate (DMMP) were used. The data from the analysis of snow samples from the area surrounding the release was used in the system analysis of sampling (Chapter 4).

2.1   Persistency determination

The experiments were performed as described previously (1, 2, 3) by applying a single droplet of the agents on a snow surface and let the samples be exposed to the prevailing weather conditions. Similar experiments were carried out with samples where the agents were

covered with a 5 cm snow layer to simulate the effect of a snowfall. The duration of the experiments varied between one and twenty-eight days before the samples were brought to the laboratory for analysis. Samples were usually collected for analysis after 14 and 28 days. Because of the low stability of Lewisite, samples were in some experiments also collected after 1 and 2 days. The experiments were carried out in different exposure periods over a total period of 10 weeks. The weather conditions (temperature and relative humidity) were recorded continuously and are given in Figures 2.1 to 2.2.

The experiments were grouped in four exposure periods. Table 2.1 shows the exposure periods for all experiments. All groups are exposed to the prevailing weather conditions. Since the weather conditions vary, it is important to take this into acount when the results are compared.

2.1.1 Lewisite (Chlorovinyldichloroarsine)

During the production of Lewisite (Lewisite A) it is very difficult to avoid the formation of dichlorovinylchloroarsine and trichlorovinylarsine which are often designated Lewisite B and Lewisite C respectively. Since these two impurities are more stable than Lewisite A they can be very useful in the verification of alleged use of this agent. The analytical method for detection of Lewisite A (L-A) was therefore developed also to include Lewisite B (L-B) and Lewisite C (L-C). The composition of Lewisite used in this experiment was 8:1:1 (L-A:L-B:L-C).

In addition to the standard procedure of analysing 1 mg samples also 3 mg samples were analysed to study the influence of droplet size on verification.

Lewisite was further tested in mixture with mustard (HD:L 4:1) since it decreased the freezing point of mustard and therefore make it more suitable for use under winter conditions.
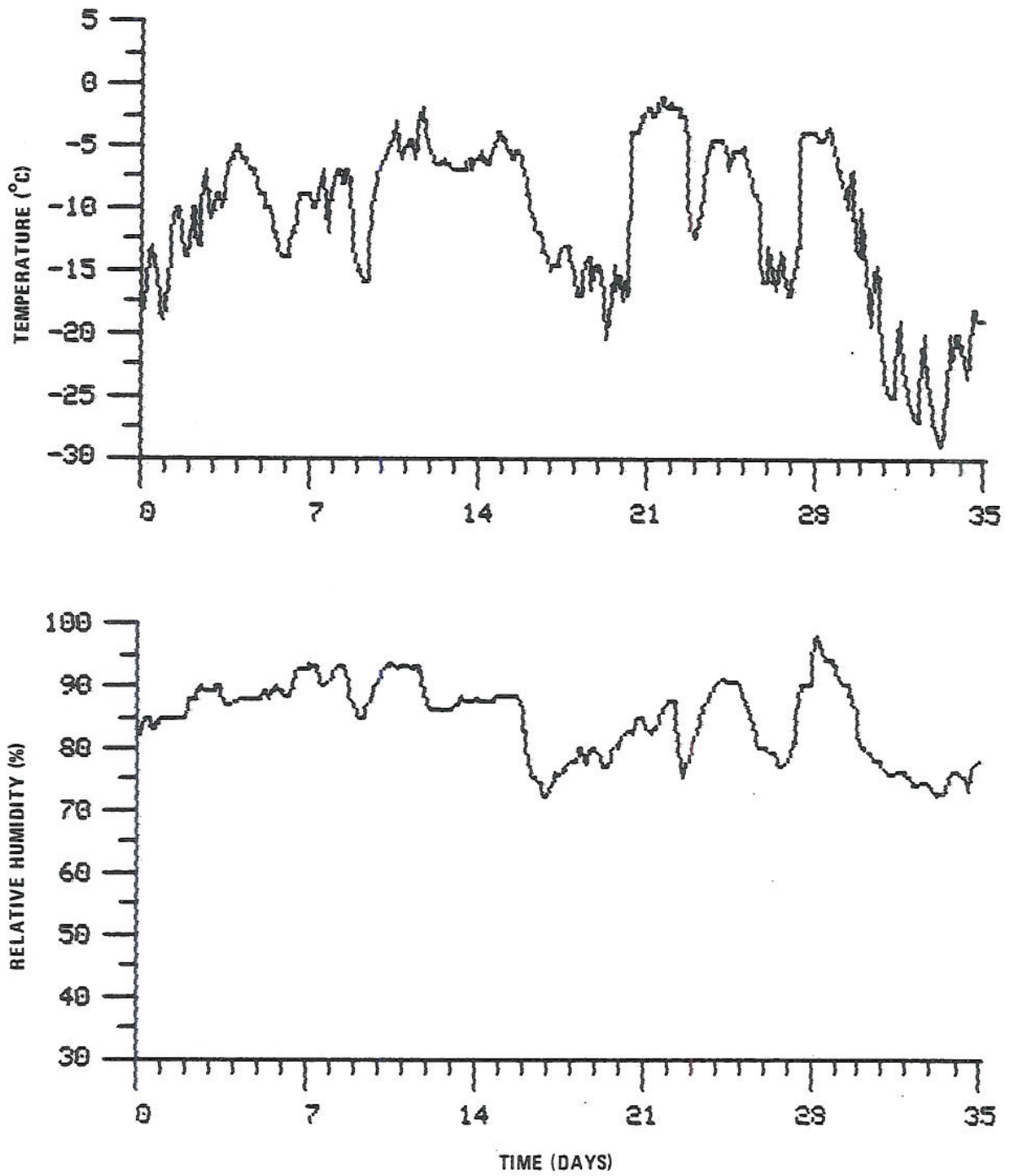
Figure 2.1   Plot of temperature (°C) and relative humidity (percent)
              versus time during the period 8 January - 11 February
              1985
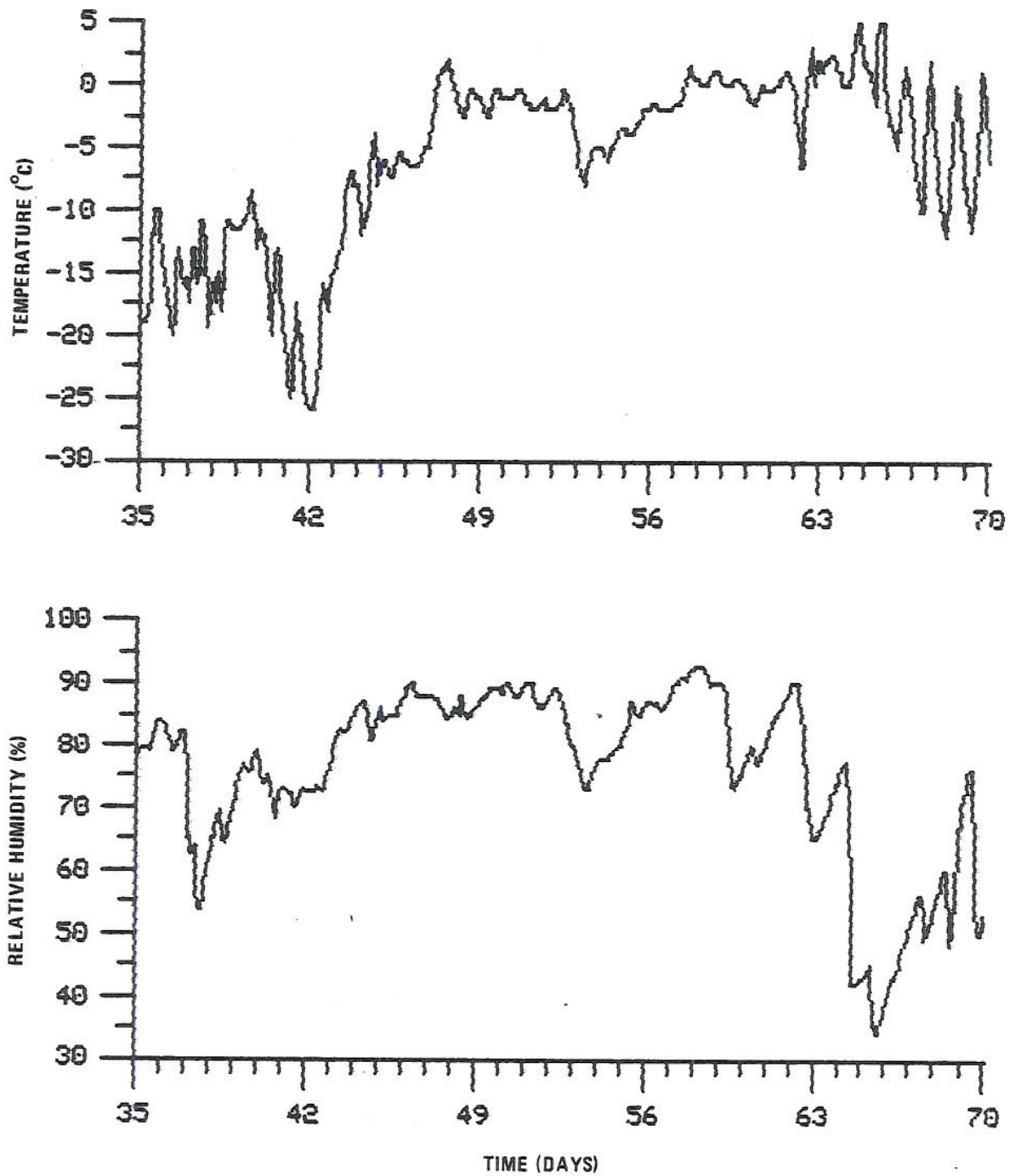
Figure 2.2   Plot of temperature (°C) and relative humidity (percent) versus time during the period 12 February - 18 March 1985

	Group 1	Group 2	Group 3	Group 4
Exposure period	9.1 – 10.1 9.1 – 11.1	30.1 – 31.1 30.1 – 13.2 30.1 – 27.2	31.1 – 1.2 31.1 – 14.2 31.1 – 28.2	14.2 – 28.2 14.2 – 14.3
Chemical warfare agent and amount of agent used	HD 4 mg L 1 mg HD 0.8 mg L 0.2 mg L 3 mg L 1 mg	L 3 mg L 1 mg	L 1 mg	L 1 mg

Table 2.1   Exposure periods and amount of agent used in the experiments
L = Lewisite and HD = Mustard

2.1.2 Mustard

According to the previous research (1, 2, 3) one of the agents that is most difficult to verify in snow samples after 4 weeks is mustard. This is due to the rapid hydrolysis of mustard to thiodiglycol. In 1984/85 the stability of thiodiglycol was tested by similar procedures as for the other agents. The main problem with thiodiglycol is, however, that it is highly watersoluble and therefore difficult to concentrate from diluted water samples. This is further discussed in Chapter 2.4.1.

2.2 Sampling

Two exercises were carried out to obtain information necessary for a system analysis of sampling. The first was a release of a CS-grenade and the second a release of a shell filled with the nervegas simulant dimethylmethylphosphonate (DMMP). Samples were collected to determine the extension of the area contaminated by both grenades. The two gre-

nades were chosen to represent a solid and a liquid agent respectively. The temperature was continually recorded during the experimental period and is given in Figure 2.3. The CS exercise was started 5 February 1985 and DMMP exercise 19 February 1985. Samples were collected for analysis 19 February, 5 March and 11 April 1985. During the period from 19 February to 5 March 1985 there were three large snowfalls which offered good opportunity to practice sampling under these winterconditions. The results showed that it was possible to verify the presence of agents even under these difficult weather conditions. Knowledge of the weather conditions during and after an alleged attack is therefore very important when deciding how and where to collect snow samples.
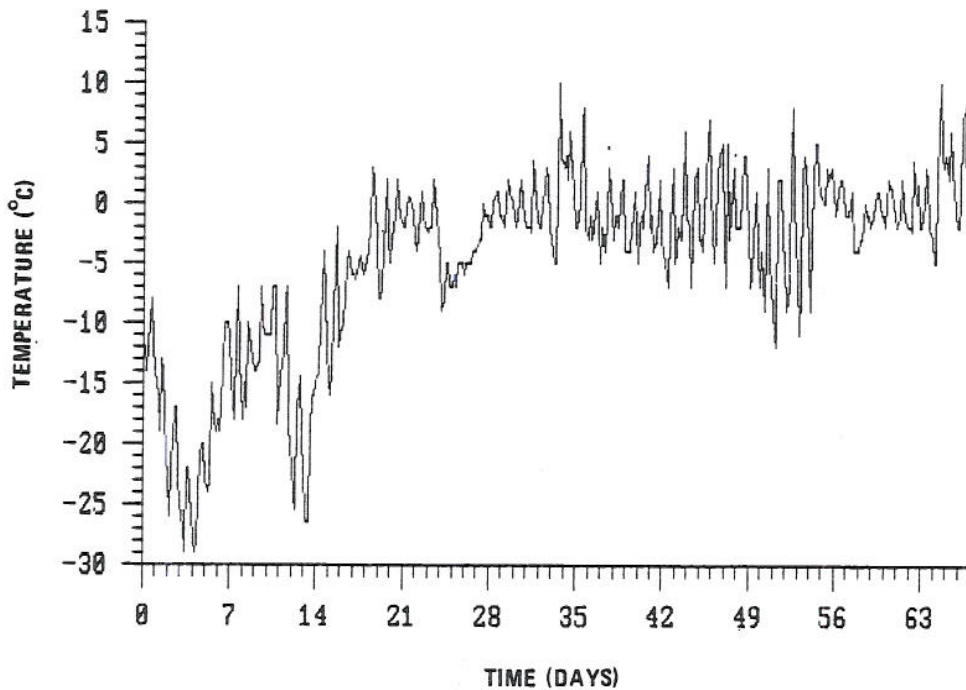
Figure 2.3 Plot of ambient temperature ($^{\circ}$C) versus time during the period 5 February - 11 April 1985
The CS exercise was started 5 February and DMMP exercise 19 February 1985

2.3 Sample handling

During the winter 1983/84 it was clearly shown that the possibility
for positive verification of use of an agent was influenced by the
sample handling. The different methods of sample handling studied
differed greatly in recovery for the most unstable agents. In order
to minimize the amount of laboratory outfit needed in the field and
also to minimize the size of the sample to be brought to laboratory
for analysis, this point was further analysed. The method is based on
the adsorbing properties of some porous polymers for chemical com-
pounds. This extraction procedure has shown to be efficient when the
polymers have greater affinity for the chemical compounds than for
water. After adsorption to the polymeric material the compounds are
desorbed by a following eluation with ether. The polymers tested were
all of type XAD (see Table 2.3).

Trade name of adsorbent	Type and characterisation of adsorbent
XAD-2 XAD-4	Crossbonded copolymers of styrene and divinylbenzen, micro and macroporous, swelling in water and also adsorbing some water
XAD-7 XAD-8	Polymethacrylate structure with some hydrofilic character

Table 2.3 Adsorbents tested for trapping of chemical warfare
agents

2.3.1 Column adsorption

Snow samples were melted (100-150 ml) and applied onto glass columns
(1 cm x 15 cm) containing the porous polymer (1-1,5 g). The flow rate
of the column was normally 2-3 ml/min. The columns were drained and
the water finally forced out of the columns by a stream of nitrogen.

The polymers were then eluated with ether (10 ml) to desorb the agents. After addition of internal standard to the eluates the samples were analysed by gas chromatography. Factors which influence the adsorbtion of chemical warfare agents to the polymers, are sample size, time of contact, flowrate and amount of polymer used in the column.

The different polymers were investigated by using nerve agents (GA, GB and GD) and mustard.

2.4   Analytical methods

The analytical methods were based on an extraction to bring the chemical warfare agents from an aquous sample to an organic solvent. This is considered to be a necessary concentration step, but in this report it is also shown that analysis can be done directly from an aquous solution without prior concentration.

2.4.1   Sample preparation

The snow samples were melted on a water bath (70°C) and the chemical warfare agents were immediately extracted with chloroform. Identification was based on the use of combined gas chromatography/mass spectrometry (GC/MS) with multiple ion detection (MID).

Lewisite A (Chlorovinyldichloroarsine)
The samples containing Lewisite were extracted with 5 ml chloroform. A known amount of n-dodecane (C12) was added to each sample and used as an internal standard during analysis on GC/MS.

Lewisite B (Dichlorovinylchloroarsine)
In the production of Lewisite A there is also produced some Lewisite B, which is somewhat more stable than Lewisite A. Lewisite B can therefore be useful in the verification of Lewisite A. Lewisite B is extracted and analysed by the same method as for Lewisite A.

Lewisite C (Trichlorovinylarsine)

Also Lewisite C is a byproduct from the production of Lewisite A.
Lewisite C is very persistant to hydrolysis and may therefore be very
useful in verification of use of Lewisite A. Also Lewisite C are ana-
lysed by the same method as Lewisite A.

Thiodiglycol

Mustard is rather rapidly hydrolyzed in contact with water to produce
thiodiglycol. This compound is in contrast to mustard very stable and
can be used in the verification of use of mustard. Thiodiglycol,
however, are highly soluble in water and extremely difficult to
extract with an organic solvent. Therefore it is more convenient to
use an extraction column containing the porous polymer XAD-2 or XAD-4,
which adsorb thiodiglycol. The water sample was passed through the
column containing XAD-2 or XAD-4 in order to adsorb the thiodiglycol
to the polymer. The flow rate was 1 ml/min. Finally water was forced
out by a stream of N_2 before the column was eluated with ether. This
process released 1-2 ml water containing about 40% of the applied
amount of thiodiglycol. The concentrated water sample was added
diethyleneglycol as an internal standard and analysed by a gas chroma-
tographic method. If the concentration of thiodiglycol is low, analy-
sis on gas chromatography/mass spectrometry will be necessary. The
water sample has to be evaporated to dryness under reduced pressure,
the residue dissolved in methanol and added n-dodecane as an internal
standard before analysis.

Adamsite

Samples of Adamsite were analysed directly after melting the snow
without extraction and concentration by use of high performance liquid
chromatography with a electrochemical detector. This was shown to be
a very sensitive method that can detect Adamsite in ppb-amounts in
aquous solutions.

2.4.2 Analytical gas chromatography/mass spectrometry

The quantitative analysis of chemical warfare agents in snow samples were mainly carried out by using gas chromatography/mass spectrometry. In some cases when extreme sensitivity was not required only a gas chromatographic method was used. The gas chromatograph is a Hewlett-Packard 5880 A with flame ionization detector (FID). Further details about conditions are given i Table 2.3.

Agent	Column	Temp ($^{\circ}$C)	Int Std	Retention time (seconds)		Fragment	
				Int Std	Sample	Int Std	Sample
Lewisite A	3% SE-30	+	C12	100	67	57	145
Lewisite B	- " -	+	C12	100	134	57	87
Lewisite C	- " -	+	C12	100	231	57	136
Mustard	Chromosorb 101	230	C12	235	348	57	109
Thiodiglycol	- " -	230	C12	235	402	57	104

+, Programmed temperature: 100°C (1 min), 14°/min raising to 140°C

Table 2.3   Condition details for quantitative mass fragmentographic and gas chromatographic analysis of chemical warfare agents and derivatives

For the agents Lewisite A, Lewisite B and Lewisite C, mass fragmentograms are shown i Figures 2.4 - 2.6. A gas chromatogram of thiodiglycol is shown in Figure 2.7.

LEWISITE A

INTERNAL STANDARD
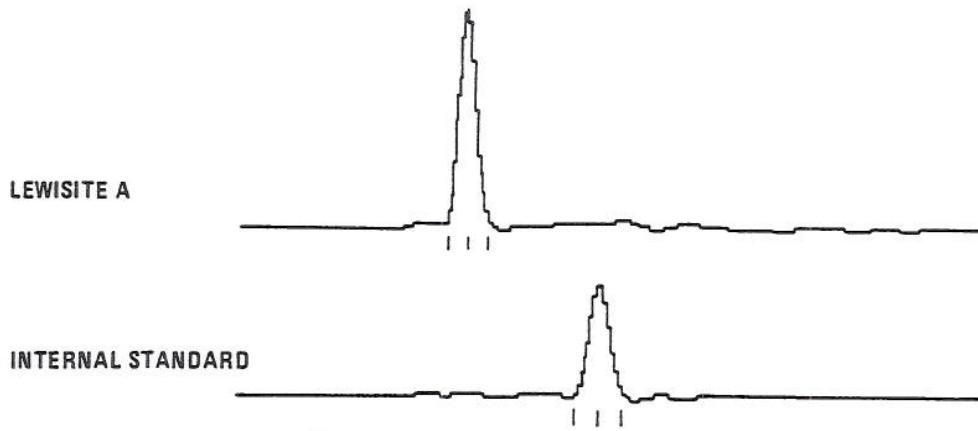
Figure 2.4   Mass fragmentogram of Lewisite A

LEWISITE B

INTERNAL STANDARD
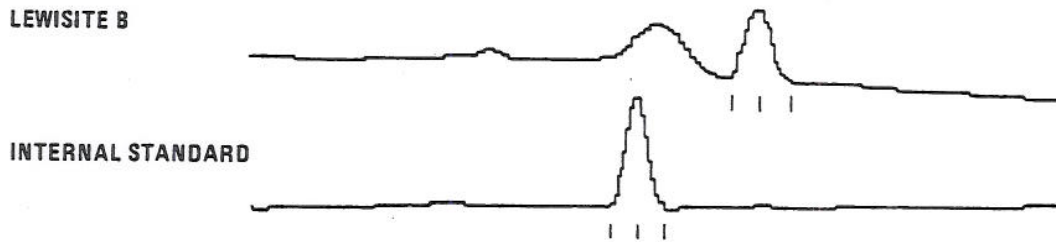
Figure 2.5   Mass fragmentogram of Lewisite B

LEWISITE C

INTERNAL STANDARD
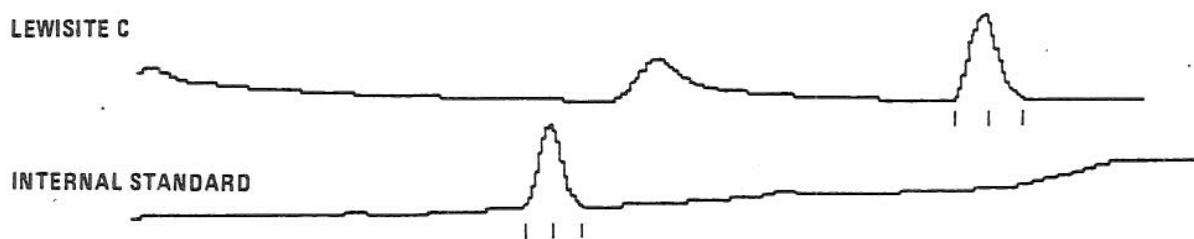
Figure 2.6   Mass fragmentogram of Lewisite C

INTERNAL STANDARD   3.92
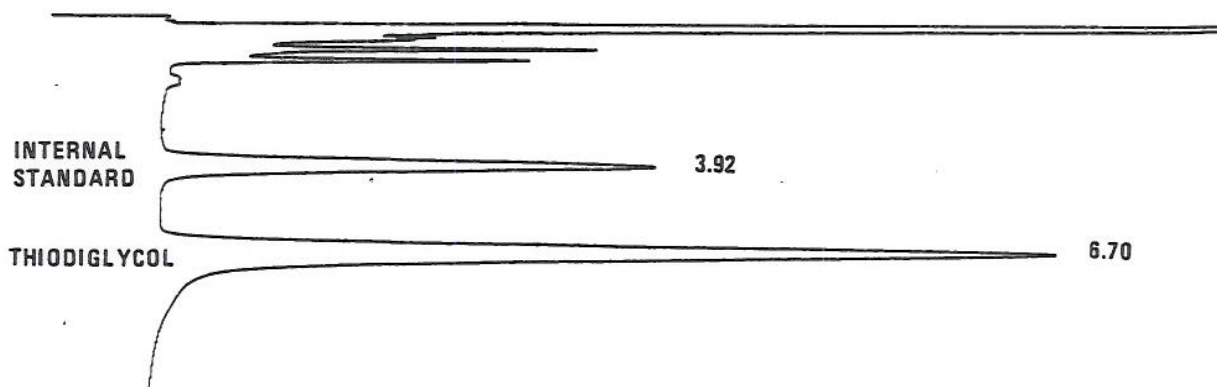
THIODIGLYCOL   6.70

Figure 2.7   Gas chromatogram of thiodiglycol

2.4.3   Mass spectrometry

To establish the most suitable conditions for quantitative mass
spectrometric analysis, mass spectra were recorded for Lewisite A,
Lewisite B, Lewisite C and thiodiglycol. The mass spectra are given
in Figures 2.8 - 2.11. The most important mass spectrometric peaks
are listed in Tables 2.4 - 2.7 also indicating the possible structure
of each fragment. The instrument is a LKB 2091 mass spectrometer
equipped with a Packard Becker 438 gas chromatograph. The most abun-
dant and specific fragments were selective for quantitative analysis
by multiple ion detection (MID).
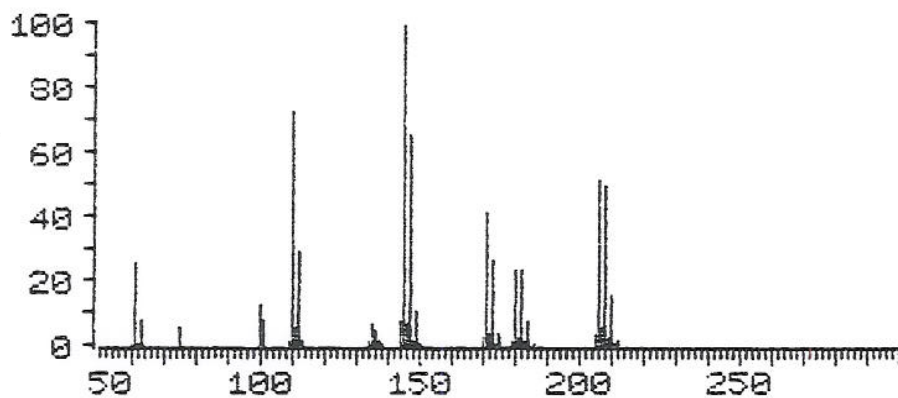
Mass:	145	110	147	206	208	171	112	173	61	180
Intensity:	100.0	72.6	66.3	51.6	49.8	42.4	30.3	27.0	25.9	24.3

Figure 2.8   Mass spectrum of Lewisite A
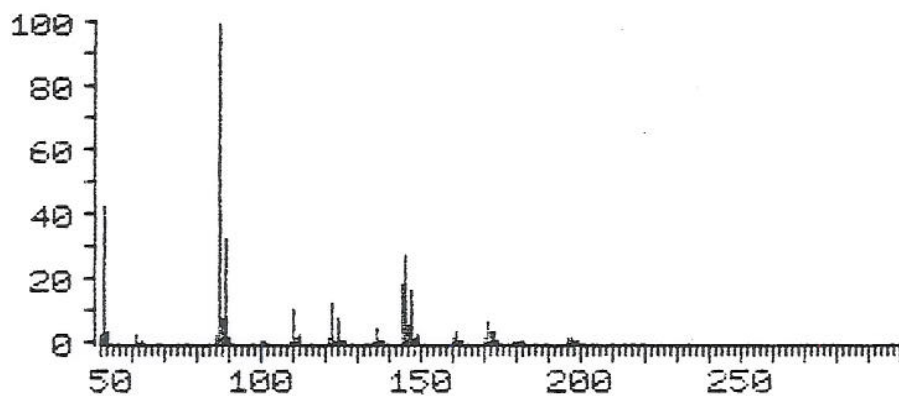
Mass:	87	51	89	145	144	147	122	110	88	124
Intensity:	100.0	43.1	32.5	28.4	18.9	17.2	12.8	11.4	8.5	8.0

Figure 2.9   Mass spectrum of Lewisite B
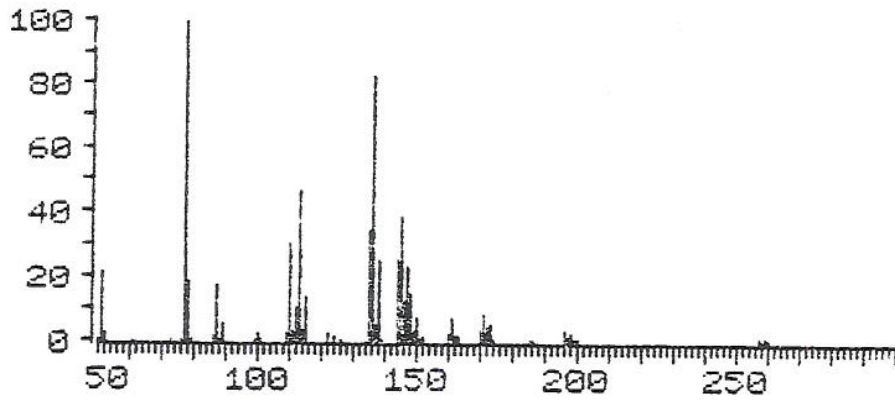
Mass:	77	136	113	145	135	110	138	144	147	51
Intensity:	100.0	82.5	46.7	38.8	35.1	30.8	25.7	25.7	24.3	22.0

Figure 2.10   Mass spectrum of Lewisite C
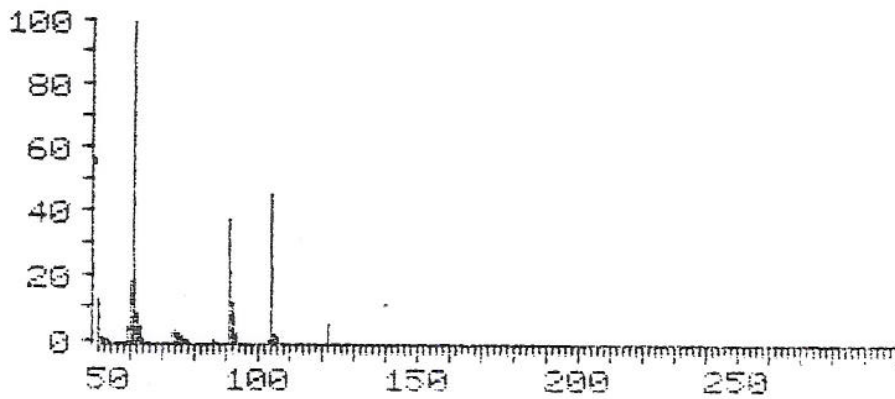
Mass:	61	104	91	60	50	92	62	122	63	59
Intensity:	100.0	46.2	38.3	18.8	13.0	11.8	9.5	6.5	5.3	5.1

Figure 2.11   Mass spectrum of thiodiglycol

Chlorovinyldichloroarsine (Lewisite A)

Formula: $C_2H_2AsCl_3$ MW = 207.42

$$Cl-CH = CH - As \underset{Cl}{\overset{Cl}{<}}$$
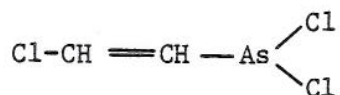
Fragments:

m/e	Possible structure:
61/63	$C_2H_2Cl^+$
110/112	$AsCl^+$
145/147/149	$AsCl_2^+$
171/173/175	$C_2H_2AsCl_2^+$
180/182/184	$AsCl_3^+$
206/208/210	M^+

Table 2.4   Mass spectrometric peaks for Lewisite A

Dichlorovinylchloroarsine (Lewisite B)

Formula: $C_4H_4AsCl_3$ MW = 233.46

$$Cl-CH = CH \underset{Cl-CH = CH}{\overset{}{>}} As-Cl$$
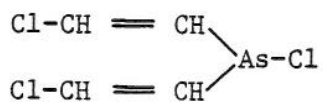
Fragments:

m/e	Possible structure:
87/89	$C_4H_4Cl^+$
110/112	$AsCl^+$
122/124	$C_4H_4Cl_2^+$
145/147	$AsCl_2^+$
171/173	$C_2H_2AsCl_2^+$
197/199	$C_4H_4AsCl_2^+$

Table 2.5   Mass spectrometric peaks for Lewisite B

Trichlorovinylarsine (Lewisite C)

Formula: $C_6H_6AsCl_3$ MW = 259.50

$$Cl-CH = CH$$
$$Cl-CH = CH$$
$$As-CH = CH-Cl$$
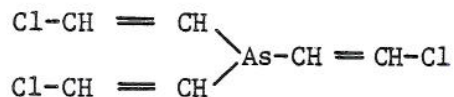
Fragments:

m/e	Possible structure:
77	$C_6H_5^+$
87/89	$C_4H_4Cl^+$
110/112	$AsCl^+$
113/115	$C_6H_6Cl^+$
136/138	$C_2H_2AsCl^+$
145/147	$AsCl_2^+$
148/156	$C_6H_6Cl_2^+$
171/173	$C_2H_2AsCl_2^+$
196/198	$C_4H_3AsCl_2^+$
258/260	M^+

Table 2.6   Mass spectrometric peaks of Lewisite C

Thiodiglycol

Formula: $C_4H_{10}O_2S$ MW = 122.19

$HOCH_2CH_2-S-CH_2CH_2OH$
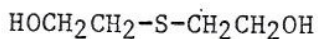
Fragments:

m/e	Possible structure:
61	$C_2H_5S^+$
91	$C_3H_7OS^+$
104	$C_4H_8OS^+$
122	M^+

Table 2.7   Mass spectrometric peaks of thiodiglycol

2.4.4   High performance liquid chromatography

Relatively little is known of analytical methods for arsen compounds.
In 1982/83 (2) a HPLC-method for analysis of adamsite (DM) was
established. That method was based on UV-detection. In order to

develop a method for arsen containing chemical warfare agents which
is based on the property of the arsin atom, the use of an electro-
chemical detector connected to a HPLC was investigated. The method
proved to be very sensitive. Adamsite could be detected directly from
melted snow samples without any concentration. A reversed phase
column (Supelcosil RP-18 25 cm x 4.6 mm) was employd. The mobil phase
was acetonitrile: 0.1 N sodiumacetate (7:3) with a flow rate of
1 ml/min. run at ambient temperature. The potensial of the detector
cell was 0.7 V. This value was chosen after establishing the oxidation
curve of adamsite (Figure 2.8). The injection volume was 20 µl. Since
the injection volume is constant the area of the adamsite peak is a
measure of the amount of adamsite in the sample. A calibration curve
was established by analysing samples containing known amounts of adam-
site, and detection of adamsite in ppb-amounts in snow samples was
easily performed by this method. The HPLC was a LDC/Milton Roy
constametric III with ESA Coulochem Electrochemical detector (Model
5100 A).
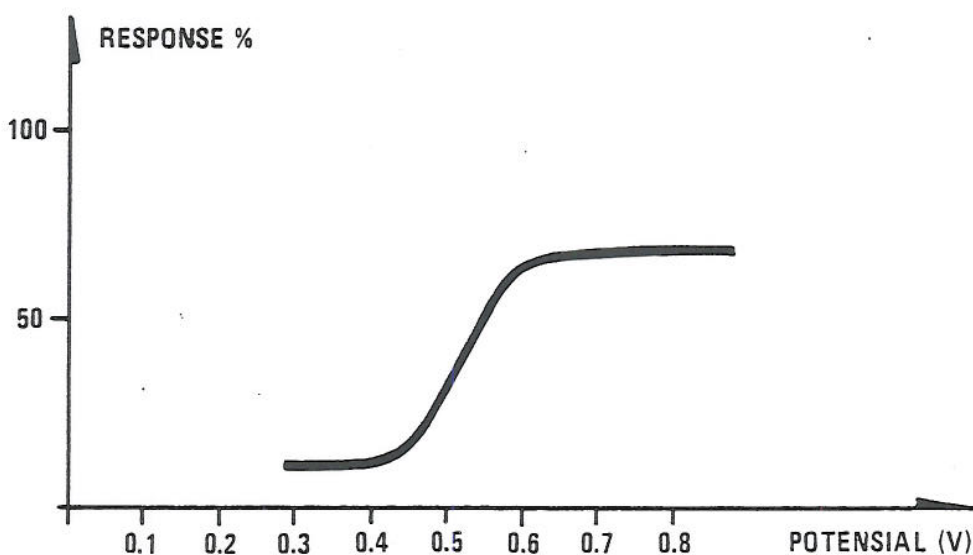
Figure 2.12   Oxidation curve of adamsite

2.4.5   Recoveries

The analysis of snow samples showed that Lewisite A hydrolyses too fast to be detected at all in such samples. Lewisite B was somewhat more persistant to hydrolysis and analysis of the snow samples showed 26% recovery for Lewisite B. Lewisite C was more stable and the recovery was 88%. Analysis showed further that thiodiglycol was detected in 42% of the amount applied.

2.4.6   Detection limits

The detection limits of Lewisite B and Lewisite C were found to be 500 pg when the practical detection limit were defined as signal/noise ratio equal to 5 for chemical warfare agents isolated from 100 g snow. This detection limit is a function of the sampling, chromatographic procedure and contaminants in the snow. The detection limits for pure agents will be several folds lower. Furthermore, it is also possible to improve the sensitivity by mass fragmentography of several ions. The detection limit of thiodiglycol was in the same order as for mustard (50 pg).

3   RESULTS

3.1   Analytical results

Four groups of snow samples contaminated with Lewisite were analysed after exposure for different periods to the prevailing weather conditions. As mentioned in a previous report (3) Lewisite may be mixed with 80% mustard in order to decrease the melting point of mustard to make it more efficient as a chemical warfare agent under winter conditions. The persistency determinations were therefore performed both with this mixture and also with pure Lewisite. Lewisite was in all experiments a mixture of Lewisite A (L-A), Lewisite B (L-B) and Lewisite C (L-C). Recovery experiments showed that Lewisite hydrolysed

almost immediately in water and was therefore more or less impossible to detect in snow samples. Also Lewisite B hydrolysed rather fast but could be detected after 14 days and will be a valuable parameter in a verification of an alleged use. The results showed however that Lewisite C will be the most important agent in verification of Lewisite. It was found to be relatively persistent and was detected even after 4 weeks. The effect of snow covering the samples to simulate the effect of a snowfall had a preserving effect on Lewisite B and Lewisite C was also found for all the other agents (2, 3). The experiments with larger droplet size of Lewisite showed that this had only minor effects on the amount detected. The results are shown in Table 3.1 and 3.2.

Sample no	Agents in sample	Amount (mg)	Percent of applied amount detected in sample			
			1 day		2 days	
			Uncov	Snow cov	Uncov	Snow cov
1	HD	4	–	–	–	–
	L-A	0.8	0	0	0	0
	L-B	0.1	13	21	15	10
	L-C	0.1	29	23	33	42
2	HD	0.8	–	–	–	–
	L-A	0.16	0	0	0	0
	L-B	0.02	2.7	26	4.8	3.5
	L-C	0.02	37	31	30	29
3	L-A	2.4	0	0	0	0
	L-B	0.3	9	9	2.5	8
	L-C	0.3	29	25	46	28
4	L-A	0.8	0	0	0	0
	L-B	0.1	7	26	3.5	11
	L-C	0.1	35	34	25	46

Table 3.1   Analytical results for Group 1
The group includes samples of the size of 1, 3 and 5 mg of agents. Mixtures of Lewisite and mustard were also studied to see if this affect the stability of Lewisite in snow samples. Uncov means that the agent was applied on the snow surface, and snow cov means that the agent was covered with snow to simulate a snowfall. The variation in data is due to analyses of snow samples from different areas. Analysis not performed are marked (–)

As mentioned earlier mustard is readily hydrolysed to thioglycol. To determine whether this hydrolysis product can be useful in verification of mustard the stability of thidiglycol in snow sample was studied. The analysis showed that thiodiglycol was very persistant under winter condition and there was no difficulties to detect it after 4 weeks. The results are given in Table 3.2.

Sample no	Agents in sample	Amount (mg)	Percent of applied amount detected in sample					
			1 day		14 days		28 days	
			Uncov	Snow cov	Uncov	Snow cov	Uncov	Snow cov
1	L-A	2.4	0	0	0	0	0	0
	L-B	0.3	3	18	0	0	0	0
	L-C	0.3	59	65	0.6	3.2	0.3	1.1
2	L-A	0.8	0	0	0.	0	0	0
	L-B	0.1	0.8	3.5	0	0	0	0
	L-C	0.1	23	88	0.2	2.4	0.1	0.4
3	L-A	0.8	0	0.5	0	0	0	0
	L-B	0.1	1.4	1.9	0.2	0.7	0	0.5
	L-C	0.1	35	24	1.2	3.6	0.1	0.8
4	L-A	0.8	-	-	0	0	0	0
	L-B	0.1	-	-	0.1	0.3	0.1	0.3
	L-C	0.1	-	-	2.0	2.6	0.4	0.9
5	TDG	1	-	-	91	90	88	93

Table 3.2   Analytical results for Group 2 (sample 1 and 2), Group 3 (sample 3) and Group 4 (sample 4 and 5)
These analysis are a continuation of analysis of snow samples contaminated with Lewisite. In addition snow samples with thiodiglycol (TDG) are tested for stability. Analysis not performed are marked (-)

To test the new analytical HPLC-method for Adamsite snow samples were analysed after 4 weeks. As seen from the results in Table 3.3 the stability of Adamsite was high.

Applied amount (µg)	Total amount detected in sample	
	(µg)	%
20	18.6	93
500	441.0	88

Table 3.3   Total amount of Adamsite found in snow samples after 4 weeks exposure to the prevailing weather conditions

3.2   Sample handling results

The experiments performed during the winter 1983/84 (3) clearly showed that sample handling was of great importance for the preservation of agent found in the samples. The most important factors of a sample handling procedure to be considered are good recovery, a procedure easy to perform in the field, reduction of the sample size and little need of equipment. To continue this work porous polymers of XAD type were tested with respect to chemical warfare agents.

The great advantage of this method is that the sample size is reduced from a snow or water sample of 100 g to a small column containing about 1 g of porous polymer. This makes it more convenient to transport the samples. Furthermore, as stated in the report from the experiments in the winter 1983/84 (3) it reduced the need of precautions to prevent the snow sample from melting. The capacity of the polymers are usually in the range of 10 wt% of its weight, which means that a column of 1 g can adsorb 100 mg of a chemical compound.

For comparison with the different methods, an extraction with chloroform of a melted snow sample was performed at the same time as adsorption to the porous polymer and defined as 100% recovery. The hydrolysis before extraction with either chloroform or XAD would be the same in all samples, and the higher the recovery by the different adsor-

bents the better is the method. As seen from Table 3.4 the different adsorbents gave variable results for the different chemical warfare agents. XAD-7 and XAD-8 gave poor results for GB while XAD-4 was inefficient for extraction of HD. In general it seems that XAD-2 is the best adsorbent of the XAD types tested.

Method	Percent recovered			
	GD	GB	GA	HD
XAD-2	89	74	52	95
XAD-4	67	60	60	36
XAD-7	85	35	71	91
XAD-8	80	37	61	95
In chloroform solution	$\dfrac{100}{(156 \ \mu g)}$	$\dfrac{100}{(201 \ \mu g)}$	$\dfrac{100}{(296 \ \mu g)}$	$\dfrac{100}{(526 \ \mu g)}$

Table 3.4   Results of experiments based on adsorbtion of CW-agents to porous polymers from melted snow samples
The result of a chloroform extraction immediately after melting is used as comparison for the efficiency of the methods.

Several factors may influence the efficiency of porous polymers to adsorb chemical warfare agents. First of all the amount of polymer used in the column will influence the amount of agent to be adsorbed. The experiments this winter have however showed similar results with columns of 1 g and 5 g of porous polymers.
Another important factor is the flow rate of the sample solution through the column after application. This may be critical because the time of contact between polymer and chemical agent are of importance for the adsorbing efficiency of the polymer. The flow rate should therefor be low, 2-3 ml/min. The washing effect with larger

samples of melted snow (more than 100 g) can also decrease the amount bound to the polymer. Experiments have however showed that for samples up to 200 g this was not a problem.

3.3 Sampling results from field experiments

During the winter 1982/83 (2) a CS grenade (250 g) was released and the analysis of snow samples from the surrounding area showed that CS could be verified 70 m downwind 4 weeks after the release.

The experiments in 1984/85 were carried out to determine the size of contaminated areas after explosions of a CS grenade (250 g) and a shell filled with the nervegas simulant DMMP (250 g). The agents represent examples of an aerosol and a liquid agent respectively. From the midline in the downwind direction samples were collected to both sides to define the size of the contaminated area. The results from the analysis of snow samples in these experiments are shown in Table 3.5 and 3.6.

	Total amount of CS (μg) found in sample					
Distance downwind (m)	15			40		100
Days after discharge	14	28	65	14	28	65
−8		0	0	−	−	−
−7	0.05	0	−	−	−	−
−6	0.07	0	−	−	0	−
−5	0.07	0.03	−	+	+	−
−4	0.2	0.04	+	0.03	+	−
−3	0.1	0.1	−	0.08	−	−
−2	0.9	0.2	−	0.36	0.17	−
−1	1.74	0.9	0.1	0.78	−	0.10
0	1.13	0.6	0.1	0.67	0.26	−
+1	0.3	0.1	0.1	0.17	−	0.06
+2	0.03	0.03	0.1	0.33	+	−
+3	0.1	0.04	0.03	0.09	−	−
+4	0.03	0.01	−	0.04	0	−
+5	0.07	+	−	0.04	−	−
+6	0.07	+	−	0.04	0	−
+7	0.03	−	0.05	0.04	0	−
+8	−	0	−	−	0	−

(Left column label: Distance from the downwind midline (m))

Table 3.5   Total amount of CS found in snow samples taken at 15, 40 and 100 m downwind and at different distances from a midline in the contaminated area after the discharge of a CS grenade (250 g)
Entries marked (−) signifies that no samples were taken and (+) signifies that traces of CS was found

In connection with the CS grenade experiment it should be mentioned that branches of a pinetree standing 10 meters from the release site were brought to the laboratory and analysed. Samples taken 7 and 14 days after the release contained 0.37 μg and 0.43 μg. The branch size was approximately 5 g.

	Total amount of DMMP (µg) found in sample				
Distance downwind (m)	5		10	30	
Days	1	14	1	1	14
Distance from the downwind midline (m) −5	–	0.3	–	–	0.1
−4	–	0.3	9.4	–	0.4
−2	0.9	22	4	2.9	–
0	3.6	411	305	30	1.6
+2	3203	–	1700	3.8	–
+4	1632	–	59	1.4	0.1
+6	200	1.2	–	–	0.1
+7	–	0.4	–	–	–
+8	–	0.2	–	–	0.05
+9	–	0.3	–	–	–

Table 3.6   Total amount of DMPP found in snow samples taken at 5, 10 and 30 m downwind and at different distances from a midline in the contaminated area after the discharge of a DMMP (250 g) CW-shell simulant
Entries marked (–) signifies that no samples were taken

The samples taken after 14 days for DMMP and after 28 days for CS were taken after three snowfalls of totally 0.5 meter. The sampling were therefore difficult and it was a great opportunity to test how to take samples after snowfall and evaluate where to collect them. As shown in Table 3.5 and 3.6 the sampling procedure was successful even after a snowfall.

3.4   Concentration of thiodiglycol

As indicated in the experimental part mustard hydrolyses quite rapidly to thiodiglycol. Mustard is therefore difficult to detect from aquous solution and it would be of great value to have analytical methods for detection of thiodiglycol in verification of the use of mustard. Since snow samples often contain more than 100 ml water when melted,

thiodiglycol must be concentrated before analysis. Experiments have shown that thiodiglycol could not be extracted from water by organic solvents. Porous polymers, tested as adsorbents for other chemical warfare agents in connection with sample handling, yielded good results. It was therefore of interest to test such polymers as adsorbents for thiodiglycol. The first experiments gave rather poor recovery. The amount of polymer used was 1-1.5 g. Later the amount of polymer was increased to 5 g and the results were greatly improved. The amount of water was reduced from 100 ml to 5 ml by this procedure, i.e. a concentration of about 20 times. The results from the experiments are shown in Table 3.7.

Method	Amount of polymer (g)	Amount TDG (mg)	Amount of TDG (μg) detected in snow samples after concentration
XAD-2	1.5	1	37
XAD-4	1.5	1	209
XAD-7	1.5	1	25
XAD-8	1.5	1	42
XAD-2	5	1	417
XAD-4	5	1	387

Table 3.7   Results of concentration experiments of TDG from water with different types and amounts of XAD

4   SYSTEM ANALYSIS OF SAMPLING

The crucial step in any verification procedure will always be the sampling procedure. It is therefore of critical importance to know exactly the location of the alleged attack since samples collected too far outside the attacked area may not contain any agent. If a sample

is collected at the border of the contaminated area it may contain only traces of the agent, but due to the sensitive analytical methods available it may still be positively verified. The credibility of the analysis will, however, always in some way be linked with the detected amount of agent, and shows the importance of taking adequate samples.

It is difficult to define chemical attacks in general terms, but the problems involved may be illustrated by an example. If the nerve agent GB (Sarin) is chosen, a small attack might be carried out using about 40 individual shells or rockets each containing about 3 kg pure agent (totally 120 kg). If the shells fall randomly within an area of 60 000 m^2 (200 x 300 m) this will give an average contamination density of 2 g/m^2. From a verification point of view, the most difficult case would be when the agent is designed to act as vapor through the respiratory system. In this case the munition will be designed to vaporize the agent as fast and completely as possible. Therefore a large proportion of the agent will disappear with the wind immediately after the attack. A proportion of the agent will, however, fall to the ground as liquid droplets. The weight fraction deposited on the ground will very much depend on the weather conditions and type of agent. Under winter condition, the field experiment with the GB simulant dimethyl methylphosphonate may be taken as an example of expected GB behaviour. The recoveries from this field experiment is given in Table 3.6, and we find more than 3 mg in a sample collected from an area of 100 cm^2 near the release site. In terms of gram and meter units this is 0.3 g/m^2. Table 3.6 show that other samples contain smaller amount of agent, but the simulant droplets were spread over a large area. The results showed also that all samples taken inside this area contained the simulant, in concentrations high enough to allow verification.

An accurate determination of how much of the agent simulant reached the ground as liquid droplets would have required a very large number of individual samples over a very large area and was not considered practical nor necessary. Judging from the data in Table 3.6 we estimate that roughly an area of about 150 m^2 was covered with about

0.1 g/m^2. The total amount in this area is estimated to add up to about 25 g, or 10 percent of the total amount in the simulated bomb. Outside this area there was a larger area where the agent was in a much lower concentration, but still in amounts high enough to be positively verified. It is estimated that this area was at least 1000 m^2. Even if the area is large, the concentration is estimated to be so low that the total amount of agent deposited is less than 10%.

Bearing in mind that the simulant shell was less than 10% of the 3 kg shell assumed in our example, we would estimate that in the actual case about 250 m^2 would be covered with more than 0.1 g/m^2, and more than 2000 m^2 would be covered with enough liquid droplets to give a definite positive analytical result.

The results from the experiments with the CS grenade shown in Table 3.5 shows that for aerosols, less agent is deposited on the ground than in the case of liquid agents. The contaminated area from which samples were collected and positively verified was, however at least as large as for the liquid simulant.

4.1 Who should take samples and how samples should be transported

It should always be borne in mind that samples collected on the battlefield for chemical analysis of possible CW agent content in this respect are, and should be treated as judicial legal evidence. This makes it specially important to have a sampling team of the highest standard possible, not only with reference to professional quality, but also political integrity. The team would at least have to include a chemist and a military expert with knowledge in chemical defence. In addition a toxicologist with knowledge of the medical effects of chemical warfare agents would be strongly recommended.

The samples should preferably be collected by the team itself, and samples should as soon as possible be processed and carefully packed and sealed so they may be transported to the selected analytical

laboratories in a tamperproof condition. Each sample should be marked with a uniqe coded identification (non revieling), and separate written records should be made to link the codes to when, where, how, and by whom the samples were collected as well as other relevant information. These records should not be sent together with the samples if they are transported by others than members of the team. Detailed written records should also be made of all relevant information concerning the transport of the samples.

To send all samples to a specially chosen reference laboratoy for division into subsamples and distribution to other laboratories should generally be avoided. This procedure has few advantages, but represents handling by more people than necessary and increases the possibilities for cross contamination and mismanagement.

4.2   Where should samples be collected

It is necessary for the team to have a fairly close knowledge of where the alleged attack has taken place. This means that the area should be determined to be within not more than 1 km^2, preferably for a small attack not more than 100 000 m^2. If the area is as large as 1 km^2, the area should be inspected for signs of battle activity to reduce the area.

Samples should be collected within this area where the highest concentrations of chemical agents are believed to be found. Time and knowledge of the contaminated area are crucial factors. If possible the samples should be collected in the target area or in the downwind direction. Sampling upwind from the target area should be avoided. Liquid or solid samples from unexploded weapons are especially important.

4.3   How should samples be collected

The team should always take care not to dilute the samples more than neccesary. Our experiments have shown that the agents generally do not migrate far into snow even after several days, and this would probably also be the case for samples in soil. The samples should therefore be collected close to the surface. Samples collected from deeper layers are less likely to contain high concentrations of agents. However, after a snowfall it is often necessary to distinguish between different snow layers to collect the sample most likely to contain the agent. The size of a snow sample will typically be in the order of 100 g.

4.4   How many samples should be collected

The higher the number of samples the higher will the probability be to verify a chemical attack. In practice, however, the number of samples will always depend on the available resources (both for the sampling team and the laboratories doing the analyses). If the exact location is unknown, the samples should be collected over a wide area, rather than collecting all samples from a small area. For an alleged incident like the one described above, 10 to 20 samples is considered practical and adequate.

4.5   The probability of collecting representative snow samples

When collecting samples from an area after an alleged attack the sampling team should be reasonably certain (more than 90% probability) that at least some of the samples will contain the agent in sufficiently high concentrations. Judging from the experimental evidence obtained during the Norwegian research project, the most important factor for correctly verifying a chemical attack is the time factor, i e the time between attack and sampling. A short time also allows better location of the alledged contaminated area. This can be .

illustrated by the example above where 40 shells randomly covered
60 000 m^2. If each shell contaminates about 2000 m^2, the probability
of missing the agent if 10 to 20 samples are taken randomly spaced
over the area, is small. Even if the area to be searched is increased
to 100 000 m^2 we believe that the chance of verifying the agent would
be above 90%. The contamination area after an attack of 40 grenades
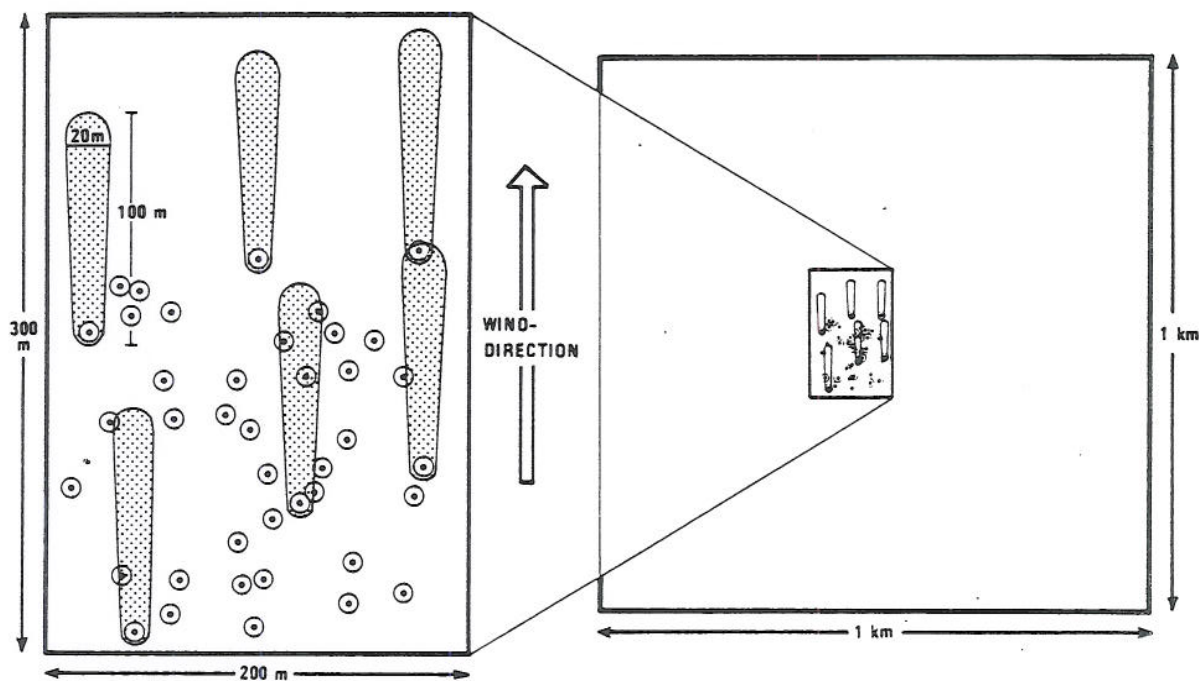is illustrated in Figure 4.1.

Figure 4.1   An example illustrating the random distribution of 40
shells containing chemical warfare agent in an area of
60 000 m^2

In six examples we have also shown the area which may be used for
verification of use downwind for the site of release.

5   MUSTARD IN URIN SAMPLES

In connection with verification of alleged use of chemical warfare agents, it is also possible to analyse biological samples from humans which have been in the actual area during the attack.

Our success with the isolation of thiodiglycol pointed us to investigate urine samples spiked with mustard and thiodiglycol. The experiments showed that specially mustard but also thiodiglycol was easily adsorbed from the urine by use of porous polymers. The method was further improved by addition of 10 ml HCl (conc) to a 100 ml urine sample spiked with thiodiglycol, since under these conditions mustard was formed.

It is no doubt that mustard was more effectively adsorbed to XAD-2 and XAD-4 than thiodiglycol and a method based on this transformation with HCl will be better than analysing thiodiglycol directly.

Sample	Method	Agent	Applied amount (mg)	Amount (µg) detected in samples	
				HD	TDG
Urine (100 ml)	XAD-2	HD	1	534	0
Urine (100 ml)	XAD-4	TDG	1	0	263
Urine (100 ml) + HCl (10 ml)	XAD-2	TDG	1	525	173

Table 5.1   Analytical results from analysis of mustard and thiodiglycol in spiked urine samples

6   CONCLUSIONS AND RECOMMENDATIONS

The objects of the experiments carried out during the four winters
from 1981/82 to 1984/85 have been to focus on the complete verifica-
tion procedure of non use. This includes procedures for sampling,
sample handling, analyses and on the probably of obtaining correct
results. The results of these studies have been presented in three
previous reports (1, 2, 3) in addition to the present report.
Verification is only possible if the agents to be verified are per-
sistent under the climatic conditions. Therefore, persistency deter-
minations of chemical warfare agents in snow samples under winter con-
ditions have been an important part of this work. The research has
clearly proved that chemical warfare agents (all nervegases, mustard
and lewisite) and several riot control agents can be verified in snow
samples even 4 weeks after an attack. In some cases the use of pro-
duction impurities and decomposition products increased dramatically
the chances for verification. However, the probability of positive
verification will certainly increase if this period is shorter.

6.1   Verification of Lewisite and mustard

In the present investigation attention was focused on the very
unstable agents Lewisite and mustard. Lewisite A was found to be so
unstable that only traces were recovered after a few days. Lewisite B
and Lewisite C which are impurities from the production of Lewisite A
are however much more persistent and may therefore be used in the
verification of use of Lewisite A. Lewisite B was detected in snow
samples after 2 weeks but only in some samples after 4 weeks of expo-
sure. Lewisite C was detected in all samples even after 4 weeks. Snow
coverage improved the chances of detection for Lewisite B and
Lewisite C.

The verification of mustard in snow has proved to be difficult due to
its rapid hydrolysis to thiodiglycol. Methods have now been developed
for both the isolation and analysis of thiodiglycol, and thiodiglycol

was found to be very persistent under winter conditions. Thiodiglycol constitute therefore an important tool in verification of use of mustard.

The methods were expanded to allow the detection of mustard and thiodiglycol in urine.

Experiments last year showed that with the use of a field laboratory, samples could be treated before being transported to a laboratory either by extraction with chloroform or by storage of snow samples in dry ice. The first method gave excellent results under field conditions. The other method also gave good results but are less practical in use. In the present investigation we have examined the use of porous polymers XAD-2, 4, 7 and 8 to adsorb the chemical warfare agents. The results were very promising and nerve agents and mustard were adsorbed with a high recovery. Interestingly this allowed also the adsorption of thiodiglycol from aquous solutions.

This method is a valuable alternative and supplement to the chloroform extraction, and the work will continue with test in a field laboratory to develope practical procedures.

6.2 System analysis of sampling

An important part of the verification procedure is a system analysis of sampling which was evaluated this year. This part focus on the problems involved in collection of samples and describes where, when, and how to take samples, how many samples should be collected and who should be involved in these matters. Finally an estimation of the probability of collecting a representative sample is given.

Several field experiments including both aerosol and liquid agents have been carried out to determine the extention of both contaminated areas from single shell explosion. It was found that both 250 g of a tear agent and a simulant for nerve agent contaminated an area of at least 1000 m^2. A real attack will normally be carried out with several shells of a much larger size, spread over a large area.

Depending upon the information available from the attack one can make an estimate of the size of the contaminated area. In the example given in this paper it is obvious that the target area will be largely covered. This means that several samples taken inside the attacked area should have a high probability for positive identification. Outside the target area, samples should be taken as close near as possible downwind. The probability for detection of agents are then less. Knowledge and experience in sampling and adequate knowledge about the chemical warfare agents is imperative and require a group of experts. In all cases there should be an evaluation by the experts of the probability of finding samples containing chemical warfare agents.

Experiments have shown that the chemical warfare agents do not migrate very fast nor far into the snow, even after several days. This means that the samples should normally be taken from the surface layer of the snow if no snowfall has occured since the alleged attack. However, if snowfall has occured, it will be neccesary to take samples from the deeper layers. In this case, it is very important that samples are taken from the correct layer, and this illustrates the need for an experienced team. Sample sizes of 100 g snow will generally be practical and adequate.

If the target area (40 bombs of 3 kg) is 100 000 m^2 the probability for successful verification with 20 randomly collected samples of snow is very high, better than 98%. On the other hand if the target area is 1 km^2 the probability is 80%. Therefore, the probability for positive verification after an alledged attack is highly dependent on the localization of target area.

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