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WORKING PAPER

Verification of a Chemical Weapons Convention. Sampling and Analysis of Chemical Warfare Agents under Winter Conditions

Introduction

In connection with Norway's participation in the Ad hoc Committee on Chemical Weapons and as a Norwegian contribution to the work of the Conference on Disarmament, the Norwegian Ministry of Foreign Affairs initiated in 1981 a research programme on the sampling and identification of chemical warfare agents under winter conditions. The research programme is carried out by the Division for Environmental Toxicology of the Norwegian Defence Research Establishment at Kjeller.

A primary objective of the research programme is to focus on the verification issues which would have to be dealt with within the framework of a Chemical Weapons Convention. More specifically, the aim is to establish the possibility of positive verification some weeks after alleged use, and developing a system for selection, handling, transportation and analysis of samples.

The first part of the programme was carried out in 1981/82. The analytical methods and the results were included in a report, which was presented to CD in August 1982, together with Working Paper CD/311. The English version of the report was annexed to CD/311.

The report of the second part of the programme, which was carried out in 1982/83, was presented to CD in July 1983. The English version of the report was annexed to Working Paper CD/396. At the same time Norway submitted Working Paper CD/397 on verification of non-production of chemical weapons.

The present Working Paper is based on the results of the third part of the research programme, which was carried out during the winter 1983/84. The research report is circulated as a separate CD document.

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Figure 1

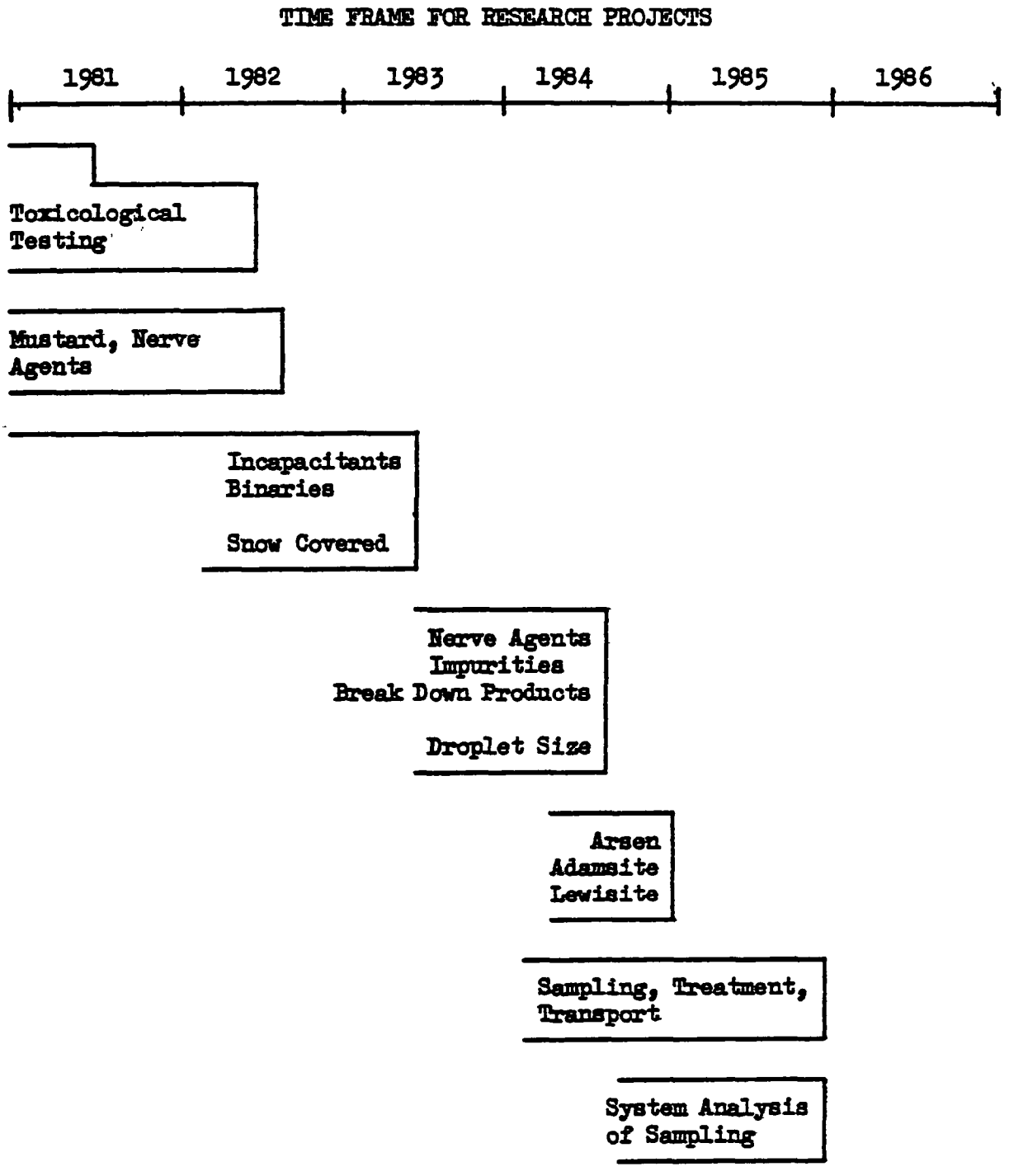


Figure 1 shows the progress of the Norwegian research programme. New factors and chemical warfare agents have been included in the investigation each year to establish complete verification procedures. The examination of sample treatment was started in 1983/84 and will be continued during the winter 1984/85. The main issue of future investigations is planned to be sampling procedures.

Description of the Research Programme

The research programme is based on experiments carried out under field conditions. This implies that the samples are kept outdoor to deteriorate by exposure to the prevailing weather conditions, such as wind, changing temperature and snowfall. The sample preparation, collection and transportation to the laboratory for analysis have been tested in two practical exercises. The purpose of this has been to compare different procedures in order to find a procedure giving minimal deterioration of the samples.

The first part of the research programme in 1981/82 covered an investigation of representatives of nerve agents and mustard gas, ref. CD/311.

The second part of the programme in 1982/83 comprised a similar investigation, including incapacitating agents and precursors, ref. CD/396.

The agents investigated during the winter 1983/84 were the nerve agents GB and GD, both pure and mixed with 20 per cent of a corresponding diester usually found as a production impurity. In addition to analysis of the two agents, their decomposition products were also analyzed. The experiments with mustard gas included both pure mustard gas (HD) and mustard gas mixed with 20 per cent 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, duplicate samples were covered with 5 cm snow. The samples were collected for analysis after 14 and 28 days.

In order to gain practical experience in the problems of sample collection, sample preparation and transportation of samples, two exercises were carried out in 1983/84. The first exercise took place 100 km west of the main laboratory, whereas the second exercise took place 1400 km north of the laboratory.

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. The methods used for the analyses of the chemical warfare agents were combined gas chromatography/mass spectrometry (GC/MS) with multiple ion detection (MID). 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 a gas chromatographic method was sufficient for the quantitative analysis.

Results of the Research Programme

Decomposition

The results of the analysis of the different groups of snow samples exposed to the prevailing winter conditions show that for the nerve agents GB and GD both the hydrolysis products and the impurities can be found in large amounts after two and four weeks. After four weeks most of the original agents have either evaporated or decomposed. For the diester impurities the recoveries were high, more than 50 per cent of the applied amount. For the decomposition products, the recoveries were slightly lower, generally between 10 and 50 per cent. This is in contrast to the recoveries for the agents themselves. After four weeks GB is present in concentrations about 100,000 times lower than the applied amount. The nerve agents were also applied in increasing droplet sizes to establish any effect on the agent recovery, but no significant 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 especially important, as mustard gas is very unstable towards hydrolysis when dissolved in water.

Other experiments on 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.

Sample preparation and transportation

In order to find the best method of transportation of samples the following methods were used in the two above-mentioned exercises of transporting the samples to the laboratory: on dry ice, in a polystyrene case, in chloroform solution, in water at room temperature and with no precaution.

For the most stable agents, the tear gas agents CN and CS, the results of the analysis of the samples show no significant difference between any of the transportation methods investigated. Recoveries are high and more than 50 per cent 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. During transportation of sarin (GB), deterioration is negligible if the samples are kept at a temperature below -20° on dry ice. If the samples are kept in water solution near zero, deterioration becomes slightly larger, but it is acceptable when the transportation time is one day or less. The rate of deterioration increases with temperature. In water at room temperature less than 10 per cent is left after one day of storage.

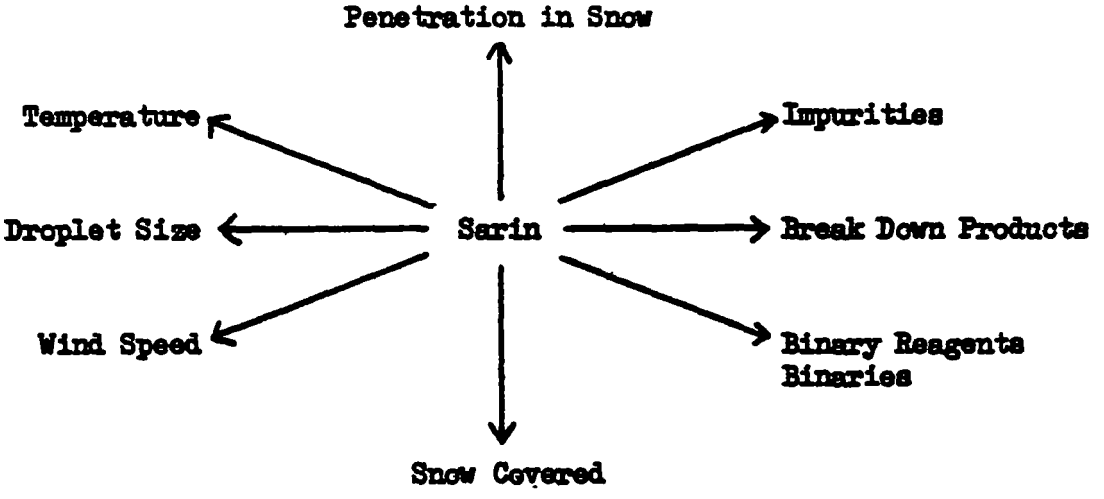
For mustard gas the difference in the results of the various transportation methods are even more pronounced. Samples transported at temperatures below -20° show a slight, but significant deterioration. When the samples were transported at temperatures near zero, about 10 to 20 per cent were present after one day. Without any precaution regarding temperature, only 2 and 9 per cent were still present. After one day at room temperature most of the agent had hydrolyzed, and the concentration had decreased to less than 1/10,000 of its original value.

Conclusions

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 four weeks after alleged use.

There are many factors that influence the possibility to verify chemical warfare agents. During this research programme an in-depth investigation of the most important factors has been carried out. Figure 2 illustrates the factors investigated, using sarin as an example.

Figure 2



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 four weeks. For these hydrolytically unstable agents, the temperature will have strong influence on the amount of agent to be found. In fact, both high temperature and strong wind is unfavourable to positive verification. On the other hand, a snowfall covering the samples reduce evaporation and has a preserving effect on the agents.

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 this extension is very useful in the verification of the unstable 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 of the use of the corresponding nerve agents.

Mustard gas has proved to be difficult to verify after four weeks. Increased droplet size of the agent, however, improves the possibility for verification of mustard gas. The reasons for this is that mustard gas dissolves slowly from the droplet surface, and hydrolyses rapidly when dissolved in water. Larger droplets have relatively less surface, and decomposition is retarded. The nerve agent GB is so rapidly dissolved in water that this is not the main factor determining the rate of breakdown of the agent. Increased droplet size is therefore of less importance.

This means that use of selective and sensitive analytical methods, including analysis of decomposition products and production impurities make it possible to verify use of at least the following agents even after four weeks: the physical incapacitating agents CS, CN and DM, the immediate decomposition product of the "didi" precursor, the nerve agents VX, GA, GB, GD and the blister agent HD.

The collection of samples is of particular importance. The penetration of agents down through the snow layers differs from one agent to another, but as they migrate only a few centimeters this difference is of insignificant practical importance. This means that when collecting snow samples it is usually only necessary to take the upper three centimeters of the snow. Additional snowfall will have to be removed before taking the samples.

Sample handling is an important factor 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 unstable samples. When the samples are brought to the laboratory, they are extracted with chloroform, and experience has shown that the stability increases when the samples are transferred to this solvent. A good method would therefore be to extract the samples in an improvised field laboratory. The exercises in 1983/84 showed that this was a practical method. The stability of the samples may also be increased by lowering the temperature. The results show that transportation on dry ice induces a minimum of further decomposition, and this method may be as useful as extraction in the field. Both methods have, however, the disadvantage that prior preparation is needed as well as trained personnel. Transportation in a thermically insulated polystyrene box gives high recoveries of sarin (GB) and the tear gas agents CN and CS and satisfactory recovery for mustard gas. When no precautions are taken, the unstable compounds will undergo significant decomposition. Samples of unstable agents should therefore be transported at as low temperature as possible, or extracted into a chloroform solution.