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VERIFICATION OF ALLEGED USE OF CHEMICAL WEAPONS

SUMMARY OF RESEARCH RESULTS 1986/87

1 Introduction

The research programme on verification of alleged use of chemical weapons which was initiated in 1981 by the Norwegian Ministry of Foreign Affairs, is carried out by the Division for Environmental Toxicology of the Norwegian Defence Research Establishment at Kjeller. In 1986/87 the research was concentrated on identification of a contaminated area, but included as well testing of the procedures which have been developed for all phases of verification of alleged use. These procedures have been tested on an all year basis. The results of these tests, and the conclusions which can be drawn on that basis, are summarized in this Working Paper.

The development of the Norwegian research programme during the period 1981-1987 is illustrated in an Annex to this document. The research programme will be continued in 1988.

2 Survey of an alleged contaminated area

Identification of a contaminated area after an alleged use of chemical weapons starts with the International Inspectors collecting information from eyewitnesses and carrying out a visual inspection of the area. In addition, it is necessary to perform a field survey. This will not only be useful in identification of an alleged contaminated area, but also in order to give a preliminary identification of what agents may be present. For the purpose of performing such a survey, the International Inspectors have to bring with them suitable equipment.

Through field exercises different procedures for identification of a contaminated area have been tested. These methods include use of the British produced detector Chemical Agent Monitor (CAM) monitoring contamination in air samples, detection paper showing colour reaction after contact with liquid agents, and thin layer chromatography (TLC), based on separation of chemical agents extracted from solid or liquid samples. These field methods give useful indication of from where samples should be collected for subsequent laboratory analysis.

CAM detects nerve agents and mustard gas and differentiates between them. The instrument is simple to use, and simulants for nerve agents and for mustard gas were identified both on snow under winter conditions and on grass, soil and sand under summer conditions. CAM was also used to identify sarin and mustard gas on grass, soil and sand under summer conditions.

Detection paper identifies nerve agents and mustard gas. In addition to differentiating between the two classes of chemical agents, the detection paper differentiates between nerve agents of

G-type (sarin, soman, tabun) and V-type (VX). The paper contains different dyes which are selectively dissolved in the different types of agents to give different colour reaction. The detection paper was tested on samples of snow, sand, soil and grass in field exercises with satisfactory results. The detection paper may detect droplets containing as little as 50 micrograms of nerve agents or mustard gas.

The third method is thin layer chromatography (TLC). Use of TLC is more time consuming, but differentiates between the different agents and therefore gives a good first indication of which agents are present. The field exercises showed that TLC was possible to use both under summer and winter conditions, even though some special precautions were required. The detection limit for TLC varies from parts per million (ppm) to parts per billion (ppb) depending on which agents are to be detected.

The three methods were tested during two field exercises carried out during the winter 1986/87 and the summer of 1987 to get the best indication of the difficulties which the International Inspectors will have to face in a real situation.

3 Sampling

Under winter conditions snow samples have proved to be valuable for analytical purposes. Procedures for verification of alleged use of chemical weapons under winter conditions have been elaborated during the winters from 1981 to 1987. The procedures are applicable on an all year basis. During the summer of 1987 field experiments were carried out, and samples from sand, soil, grass and water were collected in the same way as snow samples.

The weather conditions will always play an important role in verification. The exercises and earlier studies have shown that temperature and windspeed influence considerably the persistence of a chemical agent. The experiments have further shown that snowfall will conserve the agents by decreasing the rate of evaporation. During summer conditions factors such as temperature and windspeed are even more important and it will be more difficult to verify an alleged use of chemical weapons. In most cases the chemical agents will evaporate within few days. Verification under summer conditions are therefore more dependent on collecting samples as soon as possible after an alleged attack.

The meteorological conditions should be taken into account in sampling in order to increase the possibility of positive verification. Wind direction, wind speed, temperature and precipitation are all important factors for these purposes. It should also be noted that during summer conditions, breakdown products and production impurities, which are persistent, may play a more important role in verification.

The experiments carried out during the year 1986/87 show that about 30% of the applied amount of sarin and mustard gas were recovered after 24 hours on snow at a temperature of -14 degrees C.

During the second field exercise under summer conditions, sarin was recovered after 24 hours in 49% from water, 18% from grass, 27% from sand and 9% from soil. For mustard gas the recoveries varied from 0.7% to 2.6% in water, grass and sand samples, and was 0.3% for soil samples. The recoveries are based on mean values from analysis by gas chromatography with flame ionization detector, gas chromatography with nitrogen phosphorus detector and gas chromatography with multiple ion detector.

Experiments with direct extraction with chloroform in the field showed a lower recovery for sarin, but higher for mustard gas. The recoveries of CS varied a lot, but this is due to low solubility in water. CS was, however, found in all samples.

4 Sample handling

The procedures for handling samples from snow are based on adsorption of chemical agents to a polymer. This adsorption takes place when the melted snow samples are passed through columns filled with a polymer. Aqueous extracts of sand, soil and grass were treated similarily. Both column adsorption and chloroform extraction were tested with good results in field exercises. The experiments showed that C-18 columns should be stored under cooled conditions. Both mustard gas and sarin were difficult to verify after one week when stored at room temperature, while 10% were recovered when stored at 5 degrees C and almost 100% at -20 degrees C.

5 Analysis

A great variety of analytical methods have been developed for qualitative and quantitative measurements of organic compounds. The analytical methods may be based on different principles for identification and at the same time vary in sensitivity and specificity. The selection of analytical methods depends on the samples which should be analysed. Analysis of pure compounds or a mixture of a few compounds may be performed by methods like mass spectrometry (MS), infrared spectrometry (IR) and nuclear magnetic resonance spectroscopy (NMR). Among these methods MS is the most sensitive and specific. In analysis of a more complex mixture, chromatographic methods should be employed to separate the different compounds before detection.

In connection with the testing of the complete procedures for verification, the following analytical methods were used for analysis of the chemical agent sarin (GB), mustard gas (H) and the riot control agent CS.

- Mass spectrometry (MS)
- Gas chromatography with flame ionization detector (GC-FID).
- Gas chromatography with nitrogen phosphorus detector (GC-NPD).
- Gas chromatography with multiple ion detector (GC-MID).
- Thin layer chromatography (TLC).
- Infrared spectrometry (IR).
- Nuclear magnetic resonance spectroscopy (NMR).

The gas chromatographic methods give excellent separation of organic compounds in complex mixtures. GC-FID is the most universal method and FID responds to almost all organic compounds. The NPD is a selective detector responding to nitrogen and phosphorus containing compounds and is especially useful in analysis of nerve agents. The NPD was about ten times more sensitive than FID in the analysis of sarin. The analytical work

carried out in 1986/87, has shown that MID besides being a specific method was also the most sensitive method. MID was about 100 times more sensitive than FID for sarin and about 1000 times more sensitive for mustard gas and CS. The specificity of MS combined with the separating power of GC makes GC-MS the most useful tool in analysis of complex mixtures. IR and NMR are both methods that require larger amounts of sample and are less sensitive than the various GC methods. In particular, NMR can be useful in analysis of more concentrated samples such as residues from munitions and war heads. This method can be more selective and specific when used in fluorine, carbon or phosphorus mode instead of that from protons. NMR can therefore be effective in analysis of nerve agents. NMR may also be suitable for analysis in samples from production and destruction plants. IR is less useful in analysis of chemical agents, but can give information about specific chemical groups rather than the whole compound.

TLC can be used in a preliminary screening to obtain information of what agents, if any, are present in the samples both by application in the laboratory and in the field. The specificity and sensitivity are rather low.

6 Complete procedures for verification

In the two field experiments carried out in 1986/87, complete procedures for verification of alleged use of chemical weapons on an all year basis were tested. The exercises were performed by releasing shells filled with simulants for nerve agents and for mustard gas and with the riot control agent CS. At the same time some samples were spiked with sarin, mustard gas and CS. After the release the contaminated area was identified by use of CAM, detection paper and TLC. All methods indicated the presence of a nerve agent and mustard gas and TLC indicated also the presence of CS. After identification samples were collected from a grid put up in the area. During the winter 1986/87 this grid contained 12 areas for sampling and during summer only 4 areas (4 types of samples were tested). After extraction of the different samples with water, the solutions were passed through commercially available Sep-Pak C-18 columns. In analysis of sand and soil samples a pre-filtration was necessary in order to prevent blocking of the columns. The samples were coded and the history of the samples were recorded.

After coding the columns, they were placed in a container with dry ice to be transported to the laboratory. In the laboratory the columns were eluted and prepared for analysis by gas chromatography with both flame-ionization detector, nitrogen-phosphorus detector and multiple ion detector. All these methods are sensitive and used in qualitative and quantitative analysis of chemical warfare agents.

7 Conclusions

The experiments carried out during 1986/87, have shown that methods such as detection paper, Chemical Agent Monitor (CAM) and thin layer chromatography (TLC) may be useful in identification of an alleged contaminated area and in giving a first indication of which agents may be present.

Samples of soil, sand, water and vegetation, as well as

snow samples can be used in verification of an alleged use. The system of using columns containing porous polymers showed some practical difficulties with sand and soil owing to blocking of the columns, but no problem with analysis. The problem with the columns was solved by a pre-filtration of the aqueous extracts. The recoveries of agents from soil were lower than recoveries from grass, sand and water. The samples should be stored and transported under appropriate cooled conditions if it takes more than 24 hours to reach the laboratory.

Analysis of samples may be carried out by gas chromatographic methods, where flame ionization is the most universal detector. Increased selectivity and sensitivity are obtained by nitrogen phosphorus and multiple ion detectors. Mass spectrometry is a highly specific analytical method and should be included in a verification procedure. In addition to these methods, nuclear magnetic resonance may be used in analysis of more concentrated and less complex samples.

The complete procedures for verification of alleged use of chemical weapons were tested in two field exercises. These exercises confirmed that the procedures can be used on an all year basis.

Annex

THE NORWEGIAN RESEARCH PROGRAMME ON VERIFICATION OF ALLEGED USE OF CHEMICAL WEAPONS

1981/82	ANALYTICAL METHODS PERSISTENCE OF AGENTS ON SNOW NERVE AGENTS, MUSTARD
1982/83	ANALYTICAL METHODS PERSISTENCE OF AGENTS ON SNOW IRRITATING AGENTS, NERVE GAS PRECURSORS
1983/84	FIELD LABORATORY DECOMPOSITION PRODUCTS PRODUCTION IMPURITIES
1984/85	SAMPLING SAMPLE HANDLING LEWISITE
1985/86	SAMPLE HANDLING ALL YEAR PROCEDURES
1986/87	SURVEY OF AN ALLEGED CONTAMINATED AREA FIELD ANALYSIS TESTING OF ALL YEAR PROCEDURES
1987/88	PROCEDURES FOR VERIFICATION OF ALLEGED USE OF CHEMICAL WEAPONS