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Chemical Weapons and Problems of Verification

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ABSTRACT

This paper reviews the existing treaties for ban and verification of the production and use of chemical weapons. The proposed Chemical Weapons Convention, its thrust areas of verifications, the organisations for and process of verification are discribed briefly. Various technical verification measures including field techniques, such as detector papers, tubes, enzyme tickets, etc. and analytical methods such as gas chromatography, microsensors, different spectrometry methods including IR techniques and stationary systems are also discussed.

1. INTRODUCTION

Chemical Weapons do definitely grab the honour of being the most talked about weapons, about which every nation wants to do something, but seems incapable of any real action. The world comity of nations took it as a discussion point more than a century ago in 1874; further at the two Hague conferences at the turn of the century, these were clubbed with aircrafts and submarines for ban from warfare. The Geneva Protocol of 1925 prohibited the use, but not research, development, production and stockpile. Most of the nations accepted the Geneva Protocol reserving the right to retaliate in kind when used against them. There were no clauses for any verification in the Geneva Protocol. Since 1973, bilateral and multilateral parleys are going on in Geneva at the Chemical Disarmament Conference, while the nations, big and small are acquiring the skills to produce and use chemical weapons as shown by Iraq and alleged about Libya. This proliferation of chemical weapons to the Third World seems to prod the super powers to come to a negotiated bilateral settlement, at the same time lacking faith in the credibility of Third World, not openly expressed. This has made technical verification a very important aspect of chemical disarmament.

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The word, verification in terms of the proposed Chemical Weapons Convention, which is presently being discussed at Geneva, is the demonstration of compliance to the treaty by the state parties participating in the agreement. The US Arms Control and Disarmament Agency calls verification 'the critical element of arms control', while the USSR favours a 'reasonable balanced verification' without giving it an extraordinary pre-eminence and extension to absurd limits. It is apparent that the verification has a number of facets, which includes a political facet as well, because of the extent and nature of verification would depend on the faith amidst the parties; in multilateral treaties, as the proposed Chemical Weapons Treaty, this political element of verification has taken equal or more importance than others because of the proliferation of chemical weapons into the Third World.

2. WHAT IS TO BE VERIFIED?

Article VI (b) of the proposed Chemical Weapons Convention enjoins the signatories to ensure that toxic chemicals and their precursors are not developed, produced or otherwise acquired, retained, transferred or used within its territory or anywhere under its jurisdiction or control for purposes prohibited by the Convention. These toxic chemicals and their precursors have tentatively been categorised under three schedules; the first schedule includes the nerve gases, (soman, sarin, tabun and VX) sulphur and nitrogen mustards, lewisites, quiniclidinyl benzilate (BZ) and precursors for the binary weapon, codenamed DF and QL. The only use of these chemicals is for warfare and these are termed single purpose chemicals. The second schedule contains the key precursors for production of the above chemicals and the third schedule consists of toxic industrial chemicals like phosgene, cyanogen chloride, hydrogen cyanide and chloropicrin as also starting materials like phosphorous oxychloride, phosphorous trichloride, di and trimethyl esters of phosphorous, sulphur mono and dichlorides. Some of these have been used in World War I, but presently are more of industrial importance and as such are called dual purpose chemicals. Some important characteristics of Schedule I compounds which would be subjected to verification are given in Table 1.

Table 1. Characteristics of Scheduk I compounds of the proposed Chemical Weapons Convention

Substance	State at 25°C	Volatility at 25°C (mg per m^3)	Effect	Time taken for the appearance of symptoms
Tabun	Colourless (yellow-brown) liquid	5/6	Nerve agent	Inhalation : 1-5 minutes Skin : 30-60 minutes
Sarin	Colourless liquid	16,400	-do-	-do-
Soman	-do-	3,060	-do-	-do-
V-agents	Colourless (yellow) liquid	3-30	-do-	-do-
Hydrogen cyanide	Colourless liquid	16^6	General poison	Some minutes
Mustard gas	-do-	930	Injurious to skin	3 hours
BZ	Solid white substance		Affects nervous system	15-60 minutes

The proposed Convention demands declaration and destruction of all chemical weapons and production facilities in a specified period of time and also provides access to international teams for inspection and verification of compliance.

The areas for verification would be: (a) non-production of chemical weapons, (b) destruction of stock-piles, (c) non-diversion of dual purpose chemicals from industrial use to weapon production, and (d) alleged use of any toxic chemicals in war in violation of the convention.

The Convention also desires implementation of all these functions in a very non-intrusive manner without hampering the economic or technological development of the parties. This verification is to some extent different from espionage activities for intelligence collection as it will be with the consent of the parties.

3. THE ORGANISATIONS FOR VERIFICATION

It is interesting to note here that the Geneva Convention of 1925 on Chemical and Biological Weapons, as also the Biological Weapons Convention of 1972 have not mentioned the aspects of verification, or suggested any institutional structure for the purpose. The nuclear weapon treaties like the Partial Test Ban Treaty of 1963, Non-proliferation Treaty of 1968, Strategic Arms Limitation Talks I and II, etc. have all incorporated a variety of monitoring techniques by national technical means, black boxes or automated recording instruments, selective as also unrestricted on-site inspection and an international organisation, the International Atomic Energy Agency, for ensuring safeguards and checking violations.

The proposed Convention envisages setting up a National Implementation Authority with a technical secretariat for data collection, verification and reporting. Article VIII of the Convention structures an international organisation with a technical secretariat to whom the national organisations would report. It is obvious that nations having chemical weapons would need a strong and large national organisation, while nations like India, which have opted not to go in for chemical weapons, need only a rudimentary set-up for the purpose. Essentially, a national organisation would depend on the importance and gravity of the threat chemical weapons as also the avowed policy and attitudes of the national governments.

4. THE PROCESS OF VERIFICATION

A number of activities are called for involving different agencies in the process of verification of non-production/alleged use of chemical weapons as shown in Fig. 1. Confidence building measures like exchange of information, on-site inspection, etc. are built into the system. But unlike the development of nuclear weapons and test explosions, which need fairly large facilities for production which are difficult to conceal, the chemical weapons production facilities can be comparatively small and concealed easily. The ensuing sections concisely describe the methodsof verification.

4.1 Economic Monitoring

It is possible to find out diversion of raw materials, products, etc. from normal production to clandestine purposes, provided that all the commercial data is kept

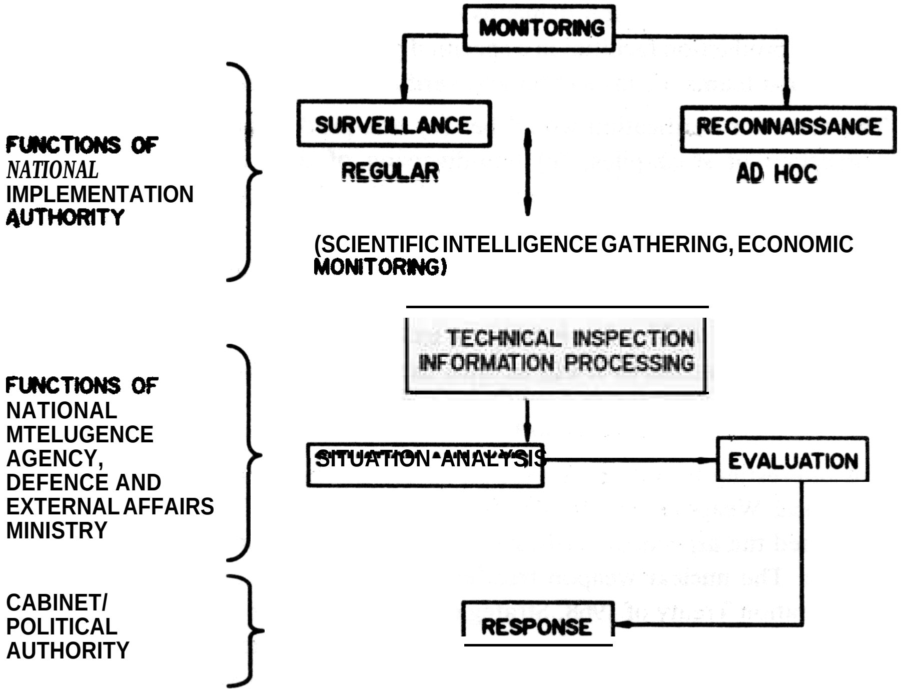

Figure 1. Activities of various agencies involved in the verification of production and usage of chemical weapons.

truthfully. But it is too much to expect from any nation/chemical industry clandestinely producing chemical weapons to present the correct data on a platter. It would need a deep scrutiny to make out the fudging of data. It is very difficult to put much faith on economic monitoring, but a proper surveillance can deter to a small extent any illegal activity.

4.2 Technical Verification

Technical verification is essential for (a) field detection necessary for warning the troops to wear protective equipment as also for notifying international agencies for violation of the Convention, and (b) for verification of clandestine production through ambient air and effluent monitoring. We shall deal with these aspects at length as quite some progress in applied instrumentation has resulted in the developments of equipment needed for the purpose.

The developments in this field could be categorised into (a) field techniques, which are equipped with portable or vehicle mounted equipment, and (b) more elaborate stationary systems which can be used in analytical laboratories for analysis of air and effluent samples.

4.2.1 Field Techniques

There are a variety of inexpensive but reliable detectors, which can be used by the soldiers in the field for the detection. of war gases.

Detector papers : Chemical impregnated filter papers are the simplest of the devices for the purpose. The change in colour of these papers denotes the presence of toxic gases in the atmosphere. Dimethylaminobenzaldehyde, dinitrobenzyl pyridine and dichloroindophenol are commonly used. 'These are specific for individual toxic agents and a number of these papers have to be used for detection of all the agents.

Detector tubes : These are hermetically sealed glass tubes with a small quantity of silica gel impregnated with specific chemicals. The tubes are broken at both the ends and aerated with a pump. Change of colour denotes the presence of toxic gases, for which the tube is specific. The shelf life of these tubes are longer than of the paper detectors and these are highly economical to produce.

The ***button :*** It is a refined form of detector exclusively for nerve gas with cholinesterase enzyme immobilised on a filter paper. The substrate is on another paper disc and these are brought together, after moistening with a bubble of water kept in between, by pressure. The button is kept near the nose or (at the inlet of the gas mask in case it is worn) and the inhaled air passes through the button. If the enzyme is inhibited by toxic nerve gases in the atmosphere, there will be no change in colour, otherwise it turns blue. These are commercially produced by Duphar of Netherlands and provided to the NATO troops.

Enzyme tickets : This is again a simple device based on enzyme inhibition ability of nerve gases. The enzyme used is plaice (a variety of fish) cholinesterase and the substrate is 2, 6, dichloroindophenylacetate on Whatman filtef paper discs. The two are brought together with moisture and when there is no colour change, the air is contaminated with toxic nerve gases. This has been developed by the Swedes and the shelf life is claimed to be 5 years.

Automatic detectors : Many of the automatic detectors for nerve gas detection make use of the same basic principle of inhibition of cholinesterase enzyme. Vapour pressure of the mustards are low to employ a vapour sampling technique at lower temperatures.

Nerve agent immobilised enzyme alarm and detector (NAIAD) : Developed in UK, NAIAD is designed to suck in ambient air through pads of immobilised cholinesterase enzyme kept moist with a solution of the substrate, normally thiocholinyl butyrate. Detection is by an electro-chemical detector sensing the changes in p^H as butyric acid is formed on hydrolysis of the substrate by the enzyme, when nerve gases are present in the atmosphere, cholinesterase enzyme is inhibited and there would be no change in p^H due to the absence of butyric acid formation. The detector is latched on to a remote audio alarm unit. These can be mounted on a vehicle as well. Cholinesterase pads have to be changed every 12 hours and the equipment needs constant attention.

Alarm system, chemical agent, local (ACAL) : Developed in Netherlands, ACAL is based on the same enzyme inhibition principle but with a slight variation. The reactions take place on a moving tape .wetted with enzyme solution and subtrate, through which ambient air is sucked in and is kept in continuous motion. The change in colour is recorded by a photometer connected to an audio-alarm. This again has the drawback of using liquid solutions, the stability of which are important.

4.2.2 Gas Chromatographic Systems

The major problem in using gas chromatographic (GC) systems for field detection has been the size of the equipment and the need to carry cylinders of the carrier gas, nitrogen or argon. The systems developed initially, attempted to miniaturise the equipment, and an automated continuous air monitoring system (ACAMS) was developed in the US around 1980. The toxic gas (mustards or nerve gas) is adsorbed on a resin column (poropak Q or tenax GC) by air sampling and then thermally desorbed on to the GC column flushing with nitrogen. Detection is by a flame photometric detector.

This system was further improved by the Swedes. The inlet consists of an adsorbent tube which can be desorbed thermally. The tube acts as sample concentrator during the sampling period, as injector at desorption and for purification of sampled air so that'it can be used as carrier gas, which eliminates the need for cylinders. Capillary column with photo-ionisation detectors are used. The heart of the instrument is the microprocessor which regulates inlet, oven, detector and pump; as also it processes the signal from the detector for the desired presentation of data. The instrument can be programmed exclusively for mustards and nerve gases.

The Finnish work : Since 1973, the Finns have taken up work on improving the gas chromatograph for detection purposes. From 1977 onwards, their results are published through books by their Ministry of Foreign Affairs, presently well-accepted as Finnish Blue Books'. A microprocessor-controlled precision gas chromatograph, Micromat, was developed by the Finnish industry in the early 1980s for this purpose. Reliability of the gas chromatography has been increased by using two parallel columns with different stationary phases, one polar and another non-polar phase, together with index of standard compounds and both universal and selective detectors. Retention index values, i.e., the time spent by each compound on the column, are stored in the computer memory and when a particular sample contains any of, the agents tallying with the stored retention indices, identification can be done by matching.

This has been further modified using six short capillary columns instead of two with different stationary phases. When a single compound elutes through the bunch of columns, in an ideal case, the retention spectrum will have as many peaks as columns and will be very characteristic of a particular chemical. In this case, the chemical is not really identified, but a 'finger print' comparison with recorded spectra is effected. But one drawback here is the overlap of signals, which has also been eliminated by more refinement of the technique.

Furhter separation is effected by connecting two capillary columns in series and only the set of peaks in which the analyst has interest is carried on to the second column. The Finns have named this 'heart cutting' technique. Selected peaks from six parallel columns can be flushed on to the analytical column and with the heart cutting technique, retention spectra of the pure compound can be obtained. This is also called as high resolution gas chromatography. These are not really field techniques and need highly skilled scientists and excellent laboratory facilities.

4.2.3 Chemical Microsensors

A number of sensitive detectors for chemical vapours using piezo electric devices, surface acoustic wave (SAW) devices, optical waveguide spectrometers and semiconductor devices have also been developed.

Piezo electric devices : A gold plasted crystal of quartz (as used in oscillator circuits) is coated with a layer of chemical which can selectively absorb or interact with the agent of interest. If the crystal is made a part of the oscillator circuit, the resonant frequency of the crystal shifts due to additional mass of the contaminant. This frequency shift is measured in terms of the concentration of agent.

Another variant of piezo electric method is the SAW device. Here the time of propagation of mechanical Rayleigh surface waves from one end of the crystal surface to another end is measured. If the surface coating on the crystal absorbs or interacts with a particular vapour or gas, a shift in propagation velocity is observed. High sensitivities are possible. There are some problems related, to irreversibility and long term stability of coatings.

Organic semiconductors : Conductivity cells coated with monolayer of organic semiconductors or materials which exhibit selective interaction with organophosphorous compounds (like materials containing complexed copper ions) are used. Measurements using two identical cells (one isolated from ambient air as a reference cell), are made and the change in conductivity measured. Similar coating on active devices like junction field effect transistors has also been tried.

Optical waveguides : Chemically coated optical waveguides when challenged with a chemical agent produce colour changes which can be measured as a shift in transmittance. Devices using a coating of oxazine dye film on a capillary tubing, optically coupled to 560 nm pulsed light emitting diode have been developed for detection of ammonia at ppm levels. However, like other semiconductor devices, selectivity is poor and the system is quite complex.

4.2.4 Ion Mobility Spectrometry

A chemical agent monitor (CAM) has been developed in UK to monitor the chemical warfare agents based on ion mobility spectrometry. Here the sampled air is ionised by a radioactive source. The ions of the agent thus produced form ionic clusters. These clusters then enter a drift tube which has a voltage gradient and an ion collector at the other end. The rate (mobility) at which the ion clusters travel to the collector is used to characterise the agent. A voltage controlled grid of wires at the entrance of drift tube controls the entry of ion clusters of interest.

These monitors are portable and rugged and are used as standard equipment by the western armies. There are models which are available for civilian use for monitoring different toxic gases in industries.

4.2.5 Mass Spectrometry

Though a laboratory based technique, it has now been modified for performing chemical agent reconnaissance by Bruker Franzen for mobile use by mounting on a vehicle. This is a conventional quadrupole mass spectrometer with a difference. The air inlet system is a flexible 3.5 m capillary column with silicone membrane filters at both ends. The inlet membrane is heated and preferentially absorbs the agent. The GC column coupled to the mass spectrometer helps in the separation of interferents from the agent. The second silicone membrane couples the GC column to the spectrometer. The capillary assembly is flexible and can be directed to the point of interest. Measurement of concentration of the agent in air can be made in a few minutes. The resolution can be further increased by using a 15 m column and preconcentration of dilute sample on a tenax adsorbent tube.

4.2.6 Infrared Techniques

Infrared spectrometers are ideal for characterising warfare agents. However, the sensitivity is very low. The sensitivity can be increased either by concentrating the sample before introduction or by increasing the path length of the IR beam through the sampled air. The latter method has been used by Foxboro Inc. in their MIRAN gas analyser. By an ingenious arrangement of mirrors, the path length can be increased upto 20 m and sensitivity of the order of ppm can be achieved.

Another approach has been to use an extremely sensitive microphone to detect photoacoustic signal from the cell. The cell is actually a chamber with a selectable IR filter window and a sensitive microphone. Absorption of IR energy by the sample increases the temperature and this causes an increase in the pressure. If IR beam is chopped, then an acoustic signal is produced at the chopping frequency. This technique has been used by Ms. Bruel and Kjaar of Denmark and they have produced very sensitive monitors for industrial/environmental applications.

Laser beams in the IR range have been used for monitoring a gas cloud from a distance of few kilometers. A system known as LIDAR, an acronym for light detection and ranging, makes use of a tunable carbon dioxide laser which scans the suurounding atmosphere. In the presence of an agent cloud, the beam is absorbed and the reflected beam is compared with another beam tuned to non-absorbing region, the difference being indicative of the presence of a chemical agent. The reflectance time difference helps in ranging, for example, finding distance to the cloud. Rain, dust, ordinary clouds, etc. are interferents. However, with the data processing techniques available at present, this clutter can be reduced: This system is very expensive and only the US and France are working on it at present.

4.2.7 *Stationary Systems*

A pre-requisite for all the stationary analyses is a sample from the field which necessitates field sampling techniques. Sampling in liquids by bubblers is the earlier method, which had the drawbacks of (a) carrying the bubblers and sampled solutions, and (b) vapourisation of the sampled toxicant alongwith sampling liquid, if vapourisation is high as in the case of cyanides. The more recent method is the sampling on synthetic resins like tenax or XAD with an efficient constant flow rate battery-operated portable pump. The resins are packed into small tubes of uniform diameter and air sucked through the same. A constant flow rate would permit calculation of the total air sampled. Surface characteristics of the resins and their polarity judge their suitability for adsorption of specific chemicals and it is essential to know the breakthrough volume or the maximum amount of chemical which can be adsorbed on the given quantity of resin. The desorption from the resins has to be ideally total without any amount being retained. Solvent elution is used in many cases for desorption but thermal desorption is a more elegant technique. Carbon is hardly ever used for the purpose solely because of the difficulty in desorption.

All the analytical instruments like IR spectrophotometer, nuclear magnetic resonance spectrometer, mass spectrometer, gas-liquid chromatograph and liquid chromatograph as mentioned earlier can be used for analysis of the samples. It is essential for all nations to have their own computerised databases even though such data is available from the Finnish work. When these analyses are internationalised, it would be very essential to lay down standard equipment and operating procedures, to avoid furore over faulty experimental techniques.

5. CONCLUSION

We have to remember that chemical production cannot be identified by a remote analysis and on-site surprise inspections would be very necessary for verifications. As for us in the Third World, who are avowed by policy not to produce chemical weapons, simple inexpensive equipment should be the basis for developing all tests.

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FURTHER READING

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