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Dear Matt,

Hoping that all is well with you at Harvard, and that you are having a good summer.

I was talking to Julian PR recently about a broad spectrum of issues. During a conversation over a pint of an excellent English beer, he advised me that one of my Australian colleagues based in Geneva had promised an article for a recent CWC Bulletin, but had failed to deliver the goods. This led to the question of whether I would have anything to contribute to the next issue.

Last week I sent a fax to Julian telling him that I had a couple of articles which could be of interest. One possibility is a short paper which provides a comparison of the chemicals covered by the AG with those contained in the CWC Schedules. There is also a "non-paper" that I prepared for the recent PREPCOM Experts Group on Analytical Chemistry, dealing with on-site chemical analysis methods (perhaps could be used as a follow-up the the Pearson off-site analysis article in the current issue).

I was faxed by Julian last Friday before he left to spend a couple of weeks at your place, to say that I should send copies to you. You will find them enclosed. The AG List/Schedule comparison paper is being made available on the basis that, if accepted, no changes be made to the text without MRL/DFAT approval. With the "on-site analysis" paper, I would be quite happy to edit it to suit your audience/word limit.

I will be back in the Hague from 11 - 23 July. While there, I may be contacted through the Australian Embassy (Ph. +31-70-310-8225, Fax +31-70-310-7863, mark "Attn: Cate Steains"). I look forward to hearing from you soon (and hopefully seeing you again before too long). Would you please tell Julian that I will send him a copy of the revised Letts et al paper.

With best wishes,

Bob

8 July '93.

DSTO
AUSTRALIA

Australian "Non-paper"
1 June 1993

ON-SITE CHEMICAL DETECTION AND ANALYSIS METHODS FOR THE ROUTINE VERIFICATION OF CHEMICAL INDUSTRY

This paper is offered to the meeting of the Combined Group of Experts: Analytical Chemists (verification-related tasks involving chemical sampling and analysis) in the hope that it will contribute to their deliberations.

1. INTRODUCTION

A considerable amount of research and development has been undertaken, in a number of countries, related to the chemical analysis of chemical warfare agents and their related precursors, degradation products and by-products. To date, most of this work has been primarily focussed on methods employing laboratory installed analytical instruments. Most of these intruments are sophisticated and have been designed to be used as a fixed installation, and would not be suitable for operation as part of a mobile laboratory.

Most of the methods developed to date have been focussed on the analytical requirements for investigations of alleged use of chemical weapons or challenge inspections (1). These methods enable the complete identification of the sample, even the chemicals present as minor components, down to trace levels. Depending on the nature of the samples, the complete analysis of a single sample may take several days.

The objective of this paper is to outline some of the different technologies which have been utilized in the development of a number of portable (or transportable) chemical detection and analysis systems for a range of applications, which may also be applicable in the development of appropriate on-site analysis systems for the verification of the CWC.

2. CHEMICAL ANALYSIS REQUIREMENTS FOR ROUTINE INDUSTRY VERIFICATION

When the routine verification procedures for relevant parts of chemical industry were first being developed in the mid-1980s, there was an underlying assumption that the samples collected during these industry inspections would be analysed at accredited off-site laboratories.

However, more recently, the experiences gained from the conduct of a large number of National Trial Inspections have indicated that inspections can be conducted more efficiently if samples are analysed on-site. In addition, industry personnel have expressed concerns about the risk of loss of confidential business information and technical "know-how" that could result from detailed chemical analysis of industrial samples. This has resulted in an appreciation for the requirement of rapid screening methods suitable for on-site chemical analysis, to indicate the presence or absence of chemicals listed in the CWC Schedules, without providing information on other chemicals that may be present in the sample.

The requirement for on-site chemical analysis has been clearly stated in the CWC Text:

"Where possible, the analysis of samples shall be performed on-site. The inspection team shall have the right to perform on-site analysis of samples using appropriate equipment brought by it." (CD/1170, p 82, para 53).

In particular, in the Verification Annexes related to inspection procedures for Schedule 3 and "Other Chemical Production Facilities", it is stated:

"Sampling and on-site analysis may be undertaken to check for the absence of undeclared scheduled chemicals. In cases of unresolved ambiguities, samples may be analysed in a designated off-site laboratory, subject to the inspected State Party's agreement." (CD/1170, p 147 para 22, and p 152 para 19).

Thus there will be a requirement for chemical analysis equipment which is portable (or at least, readily transportable) to enable on-site analysis at the inspection site.

3. RECENT DEVELOPMENTS IN CHEMICAL ANALYSIS INSTRUMENTATION

3.1 General Trends

In recent years, a number of chemical analysis methods which had previously been limited to fixed installation in a laboratory, have been successfully developed into either portable or transportable detection and analysis systems. The methods include infrared spectroscopy (IR), gas chromatography (GC), mass spectrometry (MS), photoionization detection (PID), ion mobility spectrometry (IMS), electron capture detection (ECD), flame ionization detection (FID) and flame photometric detection (FPD). On-site intruments based on these methods are available for a number of applications, including:

(a) industrial monitoring (eg., IR, GC, MS, PID, IMS, FID);

(b) chemical warfare agent detection (eg., IR, MS, IMS, FPD);

(c) detection of concealed explosives (eg., GC, ECD, IMS, MS);

and

(d) illicit drug detection (eg., MS, IMS).

Because of the range of techniques involved, it is difficult to generalize about the sensitivity, selectivity, portability and cost of the different systems. Instruments employing IMS, IR, GC and FPD will respond to levels from ppm (parts per million) to parts per billion (ppb). They are man-portable (some are held in one hand, others require an attache case or backpack) and may cost between $10,000 and $30,000. Instruments employing MS will respond to chemicals at the ppb level (sometimes better), cost more than $100,000, and are relatively bulky and heavy (usually vehicle-installed rather than man-portable, although a "large suitcase" sized MS has recently become available for industrial monitoring).

This present trend in instrument development towards increased portability and miniaturisation has been greatly facilitated by the "computer revolution", in particular the development of portable personal computers (PCs). This has enabled the above instruments to be interfaced to a PC, which can be programmed to respond only to chemicals relevant to the CWC, and not identify other chemicals (the "negative proof" approach).

3.2 Nomenclature

Over the years, a number of terms have been given to the portable "black boxes" (or in some cases green/kakhi boxes) that have been designed to indicate the presence or absence of certain chemicals in particular environments. Such terms include:

- Detectors;

- Monitors;

- Portable gas analyzers; and

- Transportable chemical analysis systems.

However, with the recent trends in miniaturisation and sophistication of portable chemical analysis systems, the use of these terms has become a source of confusion, even among some so-called "English speakers".

For example, consider a well known commercial portable IR system:

- it can be installed "in the field" and give an audio warning when the concentration of a particular chemical is exceeded (detector);

- it can be carried by an operator, for example, to determine the source of a vapour leak (monitor);

- it can be operated in a room using a sample introduction port, with IR spectra obtained and stored on a PC (on-site analysis).

Therefore, we suggest that a term such as "chemical detection and analysis system" be used rather than "detector" or "monitor" to describe a particular piece of hardware. The terms "Detection", Monitoring" and "On-site analysis" could be more appropriately used to describe how a particular piece of hardware is being used.

3.3 Portable Detection and Analysis Systems for CWC Verification

During the National Trial Inspections (NTIs) that were undertaken by some member and observer nations of the Conference on Disarmament (CD), some inspection teams made use of portable detection and analysis systems, including military equipment designed for chemical warfare agent detection and monitoring. For example, in one of the Australian NTIs, a portable ion mobility spectrometer system (Chemical Agent Monitor, CAM) was used to monitor the absence of vapours of certain Schedule 1 chemicals. Another CAM was adapted so that it would respond to low vapour concentrations of the declared Schedule 2 chemical, and was used to check that the drums containing the declared chemical were correctly labelled, and that drums with different labels did not contain the declared chemical (there was enough vapour near the top of the closed storage drums to give a response) (2).

We have also used portable IMS-based systems in other NTIs (for example, to check for the absence of a Schedule 1 chemical corresponding the the declared Schedule 3 precursor chemical (3)), and in a Practice Challenge Inspection (PCI).

We have concluded that there are several applications for portable detection and analysis systems during inspection involving the verification of non-production of chemical warfare agents, including:

1. Detection of the presence of chemical warfare agents. In addition to the obvious verification objective of detecting present or recent production or storage of chemical warfare agents, the system response would also provide a warning to the inspectors that they should consider their personal safety.

2. Monitoring of the declared precursor chemical. A system which can be programmed to respond to a declared precursor chemical can be used to check that the quantity of the chemical being stored at the inspected site is consistent with the declaration.

3. Detection and Monitoring of undeclared scheduled chemicals. If a scheduled chemical was detected at an undeclared facility, the use of the system would enable the monitorinng/rapid screening of storage areas to determine whether the quantity of chemical at the site is below the reporting threshold.

4. Assist in the selection of samples for chemical analysis. The use of an appropriately programmed system would assist in the selection (and reduce the number - perhaps in some cases to zero) of samples for required for on-site or off-site chemical analysis.

Based on our experience, an IMS detection and analysis system based on CAM, but housed in an attache case and controlled by a portable PC, would enable very selective detection and monitoring of a number of chemicals relevant to the CWC. The system could contain a key-pad, which would enable the operator to specify the target chemical(s) to be detected or monitored, and could include a screen display of the spectrum.

There may be situations in which a field programmable IMS system outlined above may give an unacceptable rate of interfering responses or "false alarms". In this case a hybrid system could be used. Thus, if a system was constructed containing both an IMS cell and a FPD cell, and a positive indication for each system was required to trigger a response, the number of false alarms would be greatly reduced. Such a system could be installed in an attache case containing a PC, drying cartridge (for the IMS) and a small hydrogen cylinder (for the FPD).

In some situations, there could still be an unacceptable rate of interfering responses/false alarms, for example, if complex mixtures of chemically similar vapours were present. These problems could be overcome by using a sample preconcentration inlet and a short GC column, which would separate the vapours being sampled prior to their introduction to the IMS/FPD cells. There are several explosives vapour detection and analysis systems that already employ such a preconcentration/GC column inlet.

Some of these considerations have been discussed in greater detail in Reference 4.

3.4. Rapid Screening Method For Families of Scheduled Chemicals

One of the problems in defining the chemicals to be monitored under the CWC is that certain classes of chemical warfare agents and precursors cannot be represented as short lists of chemicals. For example, there are several families of CW agents in Schedule 1 which contain several thousand members. For the majority of these chemicals, analytical data are not available.

Two of the methods which have been suggested as suitable for on-site chemical analysis for CWC verification are GC-MS (with either electron impact or chemical ionization) and GC with selective detectors, including the FPD for phosphorus or sulphur containing chemicals (5). We have chosen these two methods as the basis of a rapid screening procedure for the "Sarin family" of alkyl methylphosphonofluoridates, which are included in item 1 of Schedule 1 (6).

We are also developing a similar classification system for the dialkyl methylphosphonates, which are covered under Item 4 of Schedule 2. Based on our results to date, we are confident that it will be possible to develop similar classification schemes for the other families of chemicals in Schedule 1 and related chemicals in Schedule 2.

4. CONCLUDING COMMENTS

The objective of this short paper has been to outline some of the different technologies which may be applicable in the development of appropriate systems for the verification of the CWC.

The discussion of the technologies has not been intended to be exhaustive. Other technologies may also have potential applications. However, the methods discussed have already been developed for other applications and are in commercially available systems.

There will be considerable efforts required in the selection, development, production and validation of the appropriate detection and analysis systems to enable reliable and efficient detection, monitoring and on-site analysis of samples. One could argue that there will be the need for early planning if appropriate detection and analysis systems are to be available by entry into force of the CWC.

5. REFERENCES

1. "International Inter-laboratory Comparison (Round-Robin) Test for the Verificationof Chemical Disarmament" F3. Testing of Procedures on Simulated Military Facility Samples, Ministry of Foreign Affairs of Finland (Helsinki, 1992).

2. Australia, "Report of an Australian National Trial Inspection based on the Provisions of the Annex to Article VI[2], CD/CW/WP.234, 5 April 1989.

3. Australia, "Trial Inspection of a Schedule 3/ "Other Relevant" Facility, CD/CW/WP.385, 20 February, 1992.

4. R J Mathews, "The application of portable vapour detectors in verification of non-production of chemical warfare agents", Chapter 6 in "Verification of Dual-use Chemicals under the Future Chemicals Weapons Convention: The case of Thiodiglycol", SIPRI C&BW Studies 13, (ed. S J Lundin, OUP: 1991)

5. "Report of the Technical Group on Instrumentation", CD/CW/WP.272, 22 January, 1990.

6. Australia, "On-site Chemical Analysis for Verification of Non-Production of Families of Scheduled Chemicals", CD/CW/WP.353, 15 July 1991.

ANNEX 1

CHEMICAL WEAPONS PRECURSORS

		CAS No.	CWC Schedule
1.	Thiodiglycol	[111-48-8]	2B
2.	Phosphorus Oxychloride	[10025-87-3]	3B
3.	Dimethyl Methylphosphonate	[765-79-6]	2B
4.	Methyl Phosphonyl Difluoride (DF)	[676-99-3]	1B
5.	Methyl Phosphonyl Dichloride (DC)	[676-97-1]	2B
6.	Dimethyl Phosphite (DMP)	[868-85-9]	3B
7.	Phosphorus Trichloride	[7719-12-2]	3B
8.	Trimethyl Phosphite (TMP)	[121-45-9]	3B
9.	Thionyl Chloride	[7719-09-7]	3B
10.	3-Hydroxy-1-methylpiperidine	[3554-74-3]	---
11.	N,N-Diisopropyl-(beta)-Aminoethyl Chloride	[96-79-7]	2B
12.	N,N-Diisopropyl-(beta)-Aminoethane Thiol	[5842-07-9]	2B
13.	3-Quinuclidinol	[1619-34-7]	2B
14.	Potassium Fluoride	[7789-23-3]	---
15.	2-Chloroethanol	[107-07-3]	---
16.	Dimethylamine	[124-40-3]	---
17.	Diethyl Ethylphosphonate	[78-38-6]	2B
18.	Diethyl N,N-Dimethylphosphoramidate	[2404-03-7]	2B
19.	Diethyl Phosphite	[762-04-9]	3B
20.	Dimethylamine Hydrochloride	[506-59-2]	---
21.	Ethyl Phosphinyl Dichloride	[1498-40-4]	2B
22.	Ethyl Phosphonyl Dichloride	[1066-50-8]	2B
23.	Ethyl Phosphonyl Difluoride	[753-98-0]	1B
24.	Hydrogen Fluoride	[7664-39-3]	---
25.	Methyl Benzilate	[76-89-1]	---
26.	Methyl Phosphinyl Dichloride	[676-83-5]	2B
27.	N,N-Diisopropyl-(beta)-Aminoethanol	[96-80-0]	2B
28.	Pinacolyl Alcohol	[464-07-3]	2B
29.	O-Ethyl 2-Diisopropylaminoethyl Methylphosphonite (QL)	[57856-11-8]	1B
30.	Triethyl Phosphite	[122-52-1]	3B
31.	Arsenic Trichloride	[7784-34-1]	2B
32.	Benzilic Acid	[76-93-7]	2B
33.	Diethyl Methylphosphonite	[15715-41-0]	2B
34.	Dimethyl Ethylphosphonate	[6163-75-3]	2B
35.	Ethyl Phosphinyl Difluoride	[430-78-4]	2B
36.	Methyl Phosphinyl Difluoride	[753-59-3]	2B
37.	3-Quinuclidone	[3731-38-2]	---
38.	Phosphorus Pentachloride	[10026-13-8]	3B

39.	Pinacolone	[75-97-8]	---
40.	Potassium Cyanide	[151-50-8]	---
41.	Potassium Bifluoride	[7789-29-9]	---
42.	Ammonium Bifluoride	[1341-49-7]	---
43.	Sodium Bifluoride	[1333-83-1]	---
44.	Sodium Fluoride	[7681-49-4]	---
45.	Sodium Cyanide	[143-33-9]	---
46.	Tri-ethanolamine	[102-71-6]	3B
47.	Phosphorus Pentasulphide	[1314-80-3]	---
48.	Di-isopropylamine	[108-18-9]	---
49.	Diethylaminoethanol	[100-37-8]	---
50.	Sodium Sulphide	[1313-82-2]	---
51.	Sulphur Monochloride	[10025-67-9]	3B
52.	Sulphur Dichloride	[10545-99-0]	3B
53.	Triethanolamine Hydrochloride	[637-39-8]	---
54.	N,N-Diisopropyl-2-Aminoethyl Chloride Hydrochloride	[4261-68-1]	2B