Chapter III.
A review of spiking chemicals used in the first 40 OPCW Proficiency Tests

Authors Keith Norman, Stephen Johnson

Cranfield Forensic Institute
Cranfield University
Defence Academy of the United Kingdom
Shrivenham, Swindon SN6 8LA, UK
E-mail: kpaknnorman@iinet.net.au, s.johnson@cranfield.ac.uk

Reviewers Hugh Gregg

Organisation for the Prohibition of Chemical Weapons
Johan de Wittlaan 32, 2517 JR, The Hague, The Netherlands
E-mail: hugh.gregg@opcw.org

Harri Kiljunen

Finnish Institute for Verification of the Chemical Weapons Convention (VERIFIN)
P.O. Box 55, FI-00014 University of Helsinki, Finland
E-mail: harri.kiljunen@helsinki.fi

Chua Hoe Chee

DSO National Laboratories,
12 Science Park Drive, Singapore 118225
E-mail: choechee@dso.org.sg

Peter Siegenthaler

Spiez Laboratory,
Austrasse,CH-3700 Spiez, Switzerland
E-mail: peter.siegenthaler@babs.admin.ch

1. Scope

From 1997 until 2016, the Organisation for the Prohibition of Chemical Weapons (OPCW) has coordinated 40 proficiency tests for the analysis and identification of intact chemical warfare agents, precursor chemicals, degradation and reaction products. This chapter reviews the chemicals used to spike the proficiency test samples, identifying those that have been used multiple times and the distribution of chemicals based upon the schedules in the chemical warfare convention (CWC). The aim of this chapter is not to provide an easy route to pass the proficiency tests but rather to illustrate the range of chemicals that should be considered during method development and/or validation for laboratories participating in, or considering participating in the OPCW Proficiency Test regime.

2. Introduction

The production and use of chemical agents in warfare is not a new phenomenon but is one that appears to be on the resurgence. Johnson et al [1] commented on the use of sulfur containing smoke in the fourth century BC in the war between Sparta and Athens. Since then

the history of war has been littered with references of toxic smokes, vesicants and the application of chemistry to defeat enemies. In more recent times this was highlighted in the report on the use of chemical weapons in the Syrian Arab Republic. [2]

The Organisation for the Prohibition of Chemical Weapons (OPCW) entered into force in 1997 to provide a physical framework to enact the chemical weapons convention.[3] The aim of the OPCW is to promote destruction of the stockpiled chemical warfare agents and to ensure that such toxic materials are not used in conflicts. Chemical weapons are defined under the Chemical Weapons Convention[4] as:

"(a) Toxic chemicals and their precursors, except where intended for purposes not prohibited under this Convention, as long as the types and quantities are consistent with such purposes;

(b) Munitions and devices, specifically designed to cause death or other harm through the toxic properties of those toxic chemicals specified in subparagraph (a), which would be released as a result of the employment of such munitions and devices;

(c) Any equipment specifically designed for use directly in connection with the employment of munitions and devices specified in subparagraph (b)."

Also defined under the Chemical Weapons Convention[4] are three schedules used to categorize chemicals based upon their use as a chemical warfare agent or the ability to be used as a precursor to a chemical warfare agent. The schedules take into account the ability for chemicals to be used for multiple purposes and the requirements for large scale production of such compounds. Schedule 1 chemicals generally have no use other than as chemical weapons. Schedules 2 and 3 chemicals have some industrial uses. Each of the three lists of chemicals are further subdivided into A & B, where the A set are the agents and the B set are the precursor materials required for the production of chemical warfare agents or the degradation products formed from the schedule A materials. As the aim of this chapter is to illustrate the range of chemicals that should be considered during method development and evaluation the definitions and constraints of each of the three schedules have been included to provide guidance and focus to laboratory operations Laboratory needs to have a good knowledge in the schedule classification, definition, etc. for unambiguous identification. The definitions and constraints of each of the three schedules have been included to provide guidance to laboratory.

The CWC guidelines for the scheduled chemicals are as follows:

"Guidelines for Schedule 1

1. *The following criteria shall be taken into account in considering whether a toxic chemical or precursor should be included in Schedule 1:*

   (a) It has been developed, produced, stockpiled or used as a chemical weapon as defined in Article II;

   (b) It poses otherwise a high risk to the object and purpose of this Convention by virtue of its high potential for use in activities prohibited under this Convention because one or more of the following conditions are met:

      (i) It possesses a chemical structure closely related to that of other toxic chemicals listed in Schedule 1, and has, or can be expected to have, comparable properties;

(ii) It possesses such lethal or incapacitating toxicity as well as other properties that would enable it to be used as a chemical weapon;

(iii) It may be used as a precursor in the final single technological stage of production of a toxic chemical listed in Schedule 1, regardless of whether this stage takes place in facilities, in munitions or elsewhere;

(c) It has little or no use for purposes not prohibited under this Convention

Guidelines for Schedule 2

2. The following criteria shall be taken into account in considering whether a toxic chemical not listed in Schedule 1 or a precursor to a Schedule 1 chemical or to a chemical listed in Schedule 2, part A, should be included in Schedule 2:

(a) It poses a significant risk to the object and purpose of this Convention because it possesses such lethal or incapacitating toxicity as well as other properties that could enable it to be used as a chemical weapon;

(b) It may be used as a precursor in one of the chemical reactions at the final stage of formation of a chemical listed in Schedule 1 or Schedule 2, part A;

(c) It poses a significant risk to the object and purpose of this Convention by virtue of its importance in the production of a chemical listed in Schedule 1 or Schedule 2, part A;

(d) It is not produced in large commercial quantities for purposes not prohibited under this Convention.

Guidelines for Schedule 3

3. The following criteria shall be taken into account in considering whether a toxic chemical or precursor, not listed in other Schedules, should be included in Schedule 3:

(a) It has been produced, stockpiled or used as a chemical weapon;

(b) It poses otherwise a risk to the object and purpose of this Convention because it possesses such lethal or incapacitating toxicity as well as other properties that might enable it to be used as a chemical weapon;

(c) It poses a risk to the object and purpose of this Convention by virtue of its importance in the production of one or more chemicals listed in Schedule 1 or Schedule 2, part B;

(d) It may be produced in large commercial quantities for purposes not prohibited under this Convention." [4]

To prove the manufacture or use of chemical weapons requires a significant capability in analytical chemistry. The OPCW commenced a proficiency test regime in 1996 with the aim of identifying suitable laboratories able to detect and identify intact chemical warfare agents, precursor materials and degradation products in a wide variety of matrices. The laboratories that successfully meet the proficiency test requirements are certified as "OPCW designated laboratories". A designated laboratory can be engaged for off-site analysis of samples

collected from sites where there is a suspicion of the use, production or storage of scheduled chemicals.

Since 1996 the OPCW has issued two proficiency tests per year (except in 1997 & 1999 when only one test was conducted) to allow laboratories to either achieve or maintain designated laboratory status. The criteria for obtaining OPCW designated laboratory status is defined as follows:

> *"successful performance in the OPCW's Official Inter-Laboratory Proficiency Testing Programme. A combined rating of three maximum scores (three As), or two As and one B, shall be regarded as successful performance in proficiency tests".* [5]

The format of the OPCW Proficiency Test are detailed in the standard operating procedures prepared by the OPCW Technical Secretariat.[6-9] In addition to the technical competency requirement, laboratory trying to achieve or maintain designation status must also maintain a quality system in accordance with international standards[6]. The most common international standard designated laboratories are following is the ISO/IEC17025:2005. The laboratory accreditation must be for the purpose of the analysis of chemical warfare agents and related compounds in a range of matrices.

The importance for laboratories to maintain a quality assurance system for the analysis of chemical warfare agents was illustrated in the report by the United Nations Mission to Investigate Allegations of the Use of Chemical Weapons in the Syrian Arab Republic.[2] The report details the standard operating procedures that were used and formally stated:

> *"The OPCW-designated laboratories meet the following criteria:*
>
> *(a) Have established an internationally recognized quality assurance system in accordance with relevant standards (ISO/IEC 17025:2005 or equivalent);*
>
> *(b) Have obtained accreditation by an internationally recognized accreditation body for the analysis of chemical-warfare agents and related compounds in various types of samples; and*
>
> *(c) Regularly participate and perform successfully in inter-laboratory proficiency tests."* [2]

These stringent standards are consistent with those required for forensic science providers. Adherence to them allows the results to play a useful role in the political or legal proceedings that occur from positive results. This protects not only the reputation of the laboratories undertaking the analysis but also the OPCW as a whole.

In order to sustain designation, the laboratories must participate in at least one PT per year and have performed successfully in the last three consecutive tests with a minimum rating of three As, or two As and one B. This effectively means that only one spiking chemical can be missed in three consecutive tests.

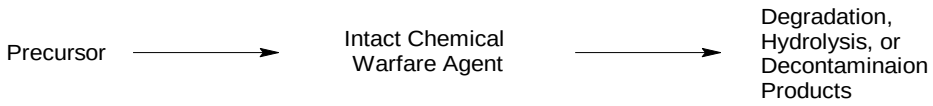
The regulation to maintain designated status is defined in the 1998 Note by the Director-General Designation of laboratories for the analysis of authentic samples: retention of designation status as:[5]

> *"(c) the designation of a designated laboratory will be withdrawn should there be either a substantial change in its accreditation status, or should its performance deteriorate, as follows:*
>
> *(i) a substantial change in accreditation status. Loss of accreditation or a change in its scope implying inadequate analytical capabilities in the analysis of chemical warfare agents and related compounds will be regarded as a substantial change;*
>
> *(ii) failure to participate once a year in a proficiency test organised by the Technical Secretariat (see paragraph 3 and subparagraph 5(b) above);*
>
> *(iii) an unsuccessful performance as a regular participant in the proficiency tests. A rating of C, D or Failure; or a second B in their last three consecutive tests (i.e. ABB or BAB) will be regarded as unsuccessful performance;*
>
> *(iv) an unsuccessful performance in the proficiency tests when preparing the test samples or evaluating the results; and*
>
> *(v) an unsatisfactory performance in the analysis of control samples distributed by the OPCW. When it comes to the off-site analysis of authentic samples (i.e. sample, control sample, and blank, when available) false positive identifications and failure to identify the chemicals present shall be regarded as unsatisfactory performance;"*

This chapter is based upon the list of spiked chemical used in the first 40 proficiency tests issued by the OPCW.[10-49] The collated information from these proficiency tests comprises of the number of times each compound has been used, the schedule it is classified under, name, structure and the CAS number (if available). This information has been compiled into a single table located in appendix 1. The table was compiled to include duplicate entries where the same compound has been used multiple times in the same proficiency test. From this table the compounds have been separated by how they relate to each schedule 1 chemical compound (appendix 2), it should be noted that neither ricin or saxitoxin are covered in this paper as they have not been used as spiking chemicals thus far in the proficiency test series.

The aim of the paper is to assist with method development for laboratories who intend to participate in the OPCW proficiency testing regime. This is achieved through detailing those chemicals that have been used as spiking chemicals, establishing the schedules they lie in, the relationship to the schedule 1 chemicals and the number of times they have been used during the testing regime. By establishing analytical methods capable of identifying the range of compounds that have been used thus far in the proficiency test program; the laboratory should be confident that they would be able to determine such compounds in samples collected during OPCW inspection operations. A crucial part of the method development is the ability to deal with the challenging matrices and unreportable compounds that may be present in the samples. The samples prepared for the proficiency tests are designed to mimic what may be collected during a response operation.

All of the spiked compounds fall within the following synthetic and degradation pathway:



Appendix 2 separates the spiked chemicals by schedule. The chemicals are listed as a precursor, intact agent or a degradation compound (chemicals formed production, degradation or decontamination).

3. Data review

Method

Details of the last 40 proficiency tests were obtained and a data table was created within Excel. This recorded the compounds used, their schedule and the date and trial. This allowed a frequency table to be produced showing duplication of compounds. It further allowed an analysis of the compounds by schedule. In addition to analysing the re-use of compounds; it also showed the level of testing across the possible schedules. These bins of analysis were performed at the sub-schedule level (i.e. 2.B.9, etc.) and they also categorised non-scheduled chemicals into 25 possible.

Results

Compound repetition. Over the past 40 proficiency tests, samples have been spiked with 288 chemicals. From this total of 288 spikes 157 different chemicals have been used, with 51 chemicals being used on more than one occasion. The duplication of the use of the spiked chemicals represents 32% of the total number of compounds used for this purpose. While the exact reason behind the choice of compounds has not been established, it could be assumed that these chemicals represent the commonly encountered precursor, reaction markers and degradation products which present the necessary analytical challenges for detection and identification required for this proficiency test regime. The list of duplicate spiking chemicals and the number of times they have been used is shown in Figure 1.

Note! *A laboratory considering participating in the proficiency test regime or in the process of developing their analytical capabilities would benefit by developing their analytical methodologies to identify the commonly spiked chemicals.*

Distribution of compounds across schedules. The distribution of chemicals based upon the overall schedules is shown in Figure 2. This figure illustrates that the majority of compounds are considered to be schedule 2. Figure 3 further classifies the spiking chemicals into the individual schedules under which they are considered.

The distribution of the chemicals within each proficiency test based upon their relevant schedules is detailed in Table 1. This table illustrates that the most common scheduled chemicals are from the class 2.B.4. The over representation of the schedule 2.B.4 chemicals as spiked compounds may be due to the limited stability of the schedule 1 compounds in the matrices used, the expectation that these are the more likely compounds to be detected following the use of a schedule 1 chemical and the reduced shipping burden for this class of chemicals. In addition, the inclusion of schedule 1 chemicals in the proficiency samples can cause difficulties for the import and export of these items due to national laws and regulations.

The other piece of information that can be drawn from table is that there is no pattern or required frequency for the inclusion of the specific schedules. As a general trend, it appears that over the course of the 40 proficiency tests there has been a move away from the inclusion of the schedule 1 compounds, intact agents, to the inclusion of more of the non-scheduled chemicals.

Note! *Currently the results seem to indicate a trend over time and also a bias towards the use of schedule 2.B.4 compounds.*

When reviewing the schedules under which chemicals are classified it became evident that 16% of the total number of spiking compounds, including all duplicates, were considered to be non-scheduled. The criteria for reporting of non-scheduled chemicals is detailed in the Work instruction for the for the reporting of the results of the OPCW Proficiency Tests QDOC/LAB/WI/PT04.[9] These chemicals are one reaction step from scheduled chemicals, such as precursor chemicals, reaction products or degradation products of scheduled chemicals. As there is a potential for a range of analogues for each of the scheduled compounds, it follows that there is a commensurate number of unscheduled compounds that would relate to these by way of their potential to be used to prepare the ultimate precursor or be formed during degradation, hydrolysis or decontamination of the scheduled compound. An example of the inclusion of non-scheduled compounds in a proficiency test is the inclusion of Bis(2-diisopropylaminoethyl)disulfide (280) and N,N-Diisopropylaminoethyl-2-methoxyethyl ether (281) in the 2016 proficiency test number 39. In accordance with Work instruction for the for the reporting of the results of the OPCW Proficiency Tests QDOC/LAB/WI/PT04,[9] these compounds can be considered to be associated with schedule 1.A.3 by virtue that they can be formed from the reaction of precursor materials to the V agents or during subsequent oxidation of these reaction products.

Note! *Laboratories considering participating in the proficiency tests must be aware of the non-scheduled compounds and their link to the scheduled chemicals. This understanding is crucial to avoid reporting a false positive.*

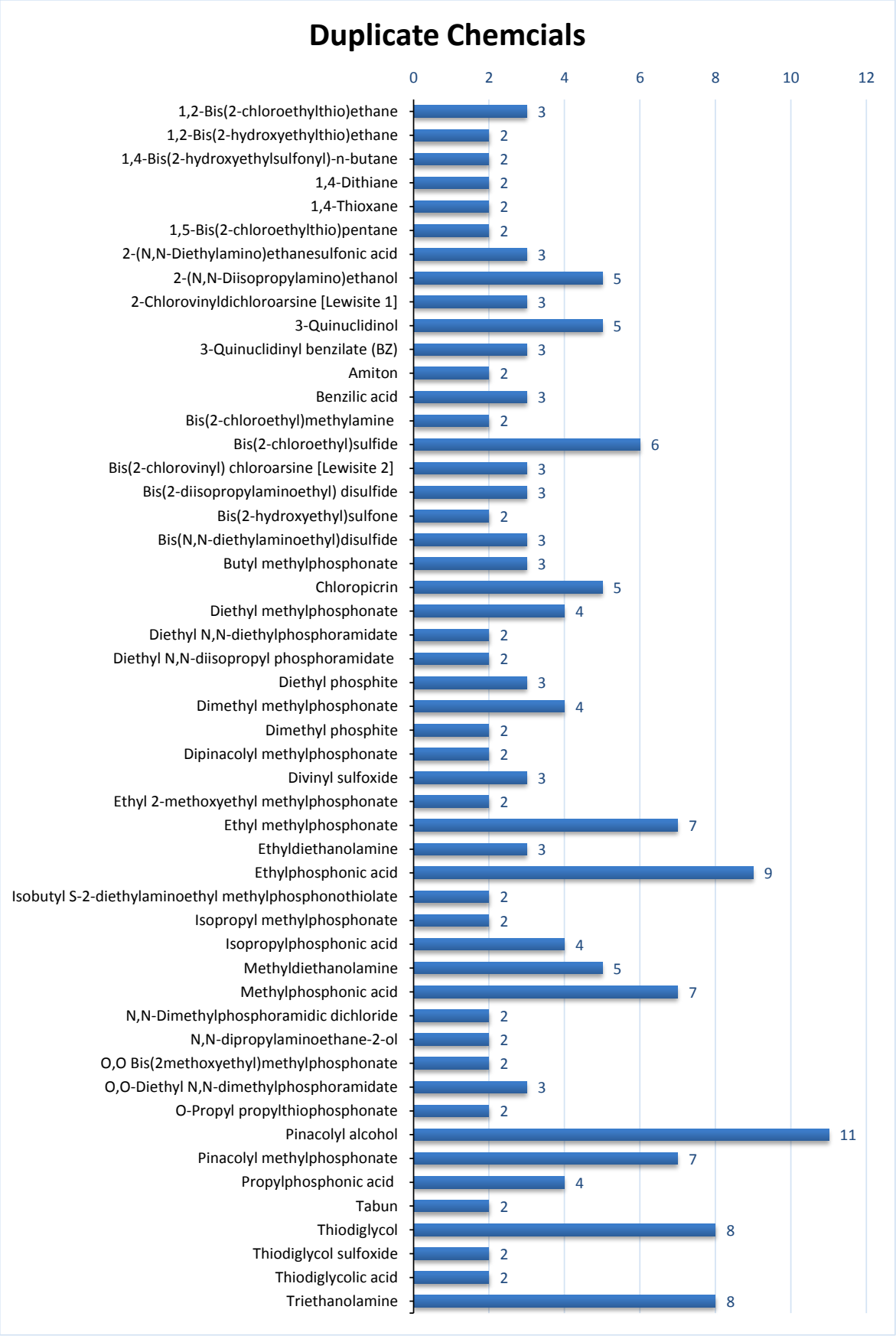


Figure 1. Duplicate chemicals from OPCW Proficiency Tests.

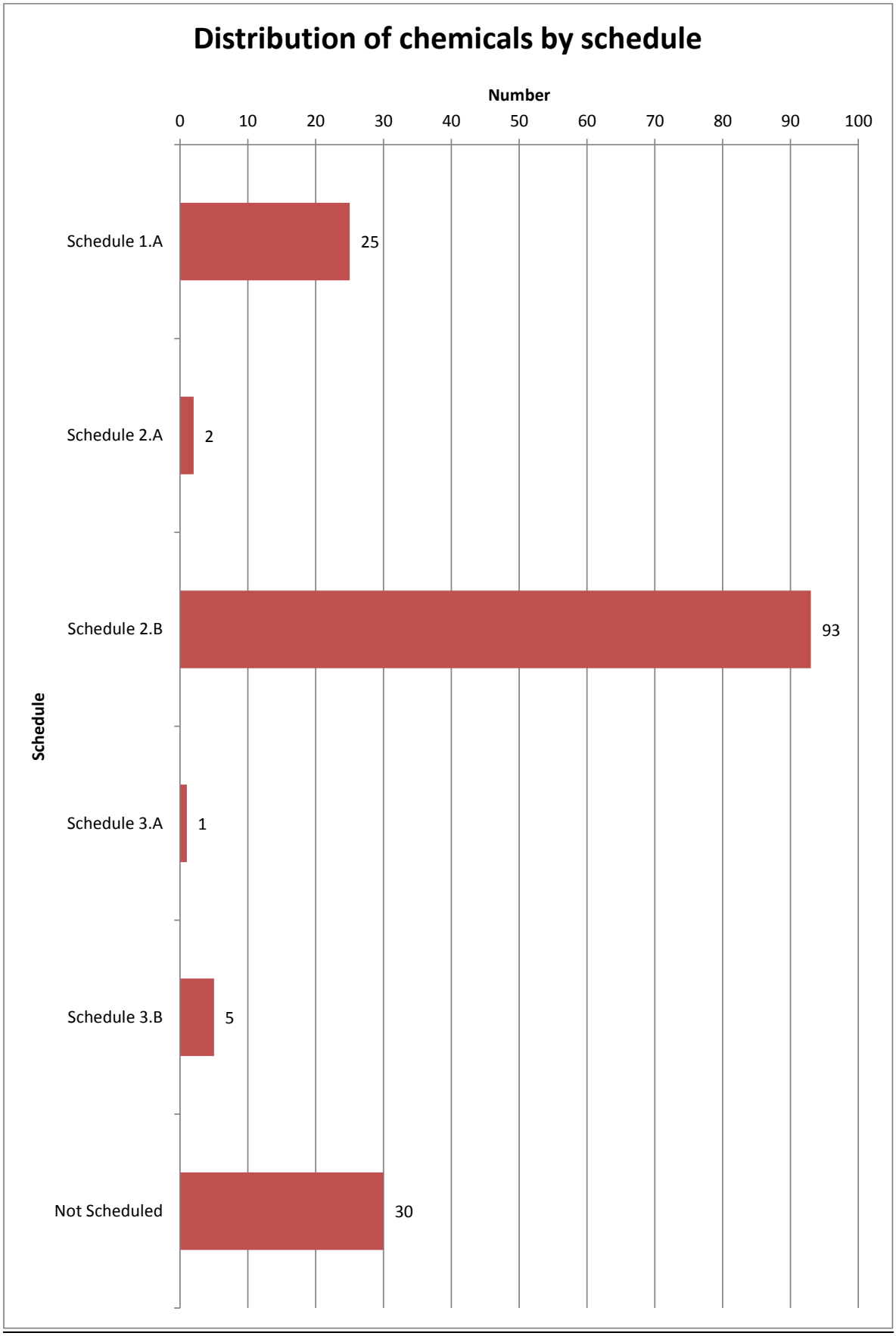


Figure 2. Distribution of spiked chemicals based upon schedules.

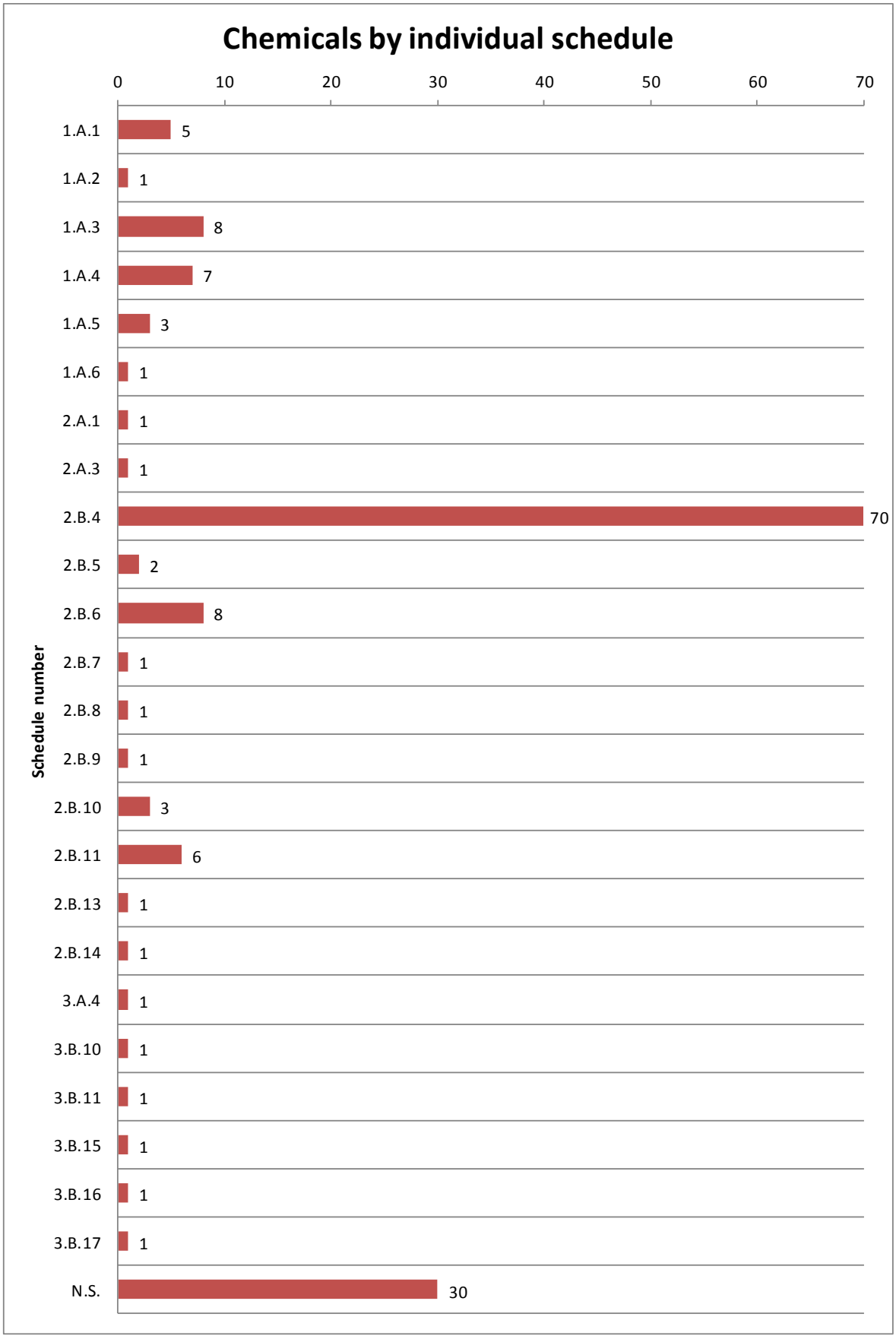


Figure 3. Distribution of spiked chemicals based upon individual schedules**.**

Table 1. Distribution of scheduled chemicals within each trial.

Schedule	Trial Number (bolded) and distribution of scheduled chemicals within each trial																			
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**	**17**	**18**	**19**	**20**
1.A.1			2											1	1				1	
1.A.2	1													1						
1.A.3		2	1							1				1	1					
1.A.4	3					1				1					1					
1.A.5						1			2											
1.A.6																				
2.A.1			1										1							
2.A.3				1													1			
2.B.4	1	5	3	4	7	2	5	6		2	5	2		2	2		1	6	7	8
2.B.5	1												1							
2.B.6	1							2				1	1	2						
2.B.7																				
2.B.8											1									
2.B.9																	1			
2.B.10																3				
2.B.11				1			1									1				1
2.B.13				1								1								
2.B.14	1								1		1						1		1	
3.A.4									1							1	1			
3.B.10										1										
3.B.11																		1		
3.B.15						1										1				
3.B.16						1										1				
3.B.17		1					1									2				
N.S.						1			2	2		2	3		2					

Schedule	Trial Number (bolded) and distribution of scheduled chemicals within each trial																			
	21	**22**	**23**	**24**	**25**	**26**	**27**	**28**	**29**	**30**	**31**	**32**	**33**	**34**	**35**	**36**	**37**	**38**	**39**	**40**
1.A.1																				
1.A.2																				
1.A.3						3														
1.A.4					2			2	4						1					
1.A.5	2				2															
1.A.6				1									1							
2.A.1																				
2.A.3																				1
2.B.4	2	6	5	4		1	3		2	3	1	2	3	3	2	1		3	5	2
2.B.5		1																		
2.B.6		1										2			1					
2.B.7					1															
2.B.8											1									1
2.B.9											1						2			1
2.B.10																				
2.B.11	1						1					2	1					1	1	
2.B.13					1		1	1		1	1						1			
2.B.14			1							1		1		1	1		1			
3.A.4							1											1		
3.B.10										1										
3.B.11			1									1								
3.B.15					1															
3.B.16											1		1					1		
3.B.17				1				2							1					
N.S.	2				2	1	2	2	2	1	2		1	4	3	6	3		2	

4. Discussion

The distribution of the chemicals used as spiking agents in the past 40 proficiency tests indicates the trend for the inclusion of a number of degradation products. The "focus" of the proficiency test regime on such degradation products indicates their potential to be useful evidence to support OPCW operational activities such as the investigation of alleged used or fact fining missions. The benefits of this approach are illustrated in the report of the United Nations Mission to Investigate Allegations of the Use of Chemical Weapons in the Syrian Arab Republic.[2] The ability to detect and identify a vast range of intact and degradation products in a variety of matrices is not only a credit to the laboratories analysing the samples but also to the proficiency test program that has emphasised these capabilities.

This chapter can only be used as guide to facilitate method development. It should be expected, in the event of an incident involving the dissemination of a chemical warfare agent, samples will be collected from a wide range of surfaces and matrices. The aim of the proficiency test is to challenge the laboratories to identify these compounds from real world complex matrices which can cause problems with respect to extraction, suppression of response, or the formation of insoluble/unreactive complexes. Sliwakowski, Dubey and Meseguer described the distribution of sample matrices used during the first 29 proficiency tests and identified that organic solvent, water and soil were the most frequent matrices employed.[50] These observations reflect the operational processes where the samples collected during a response are rapidly extracted with dichloromethane and water with the extracts forwarded to designated laboratories for analysis. This process maximizes the potential for the identification of intact agents as they are stabilised in the organic matrices once extracted. The practical application of the protocol of collecting samples from a range of matrices was demonstrated in the report on the analysis of samples collected in Syria.[2] Laboratories need to take into consideration other factors which are not covered in this chapter, for example background interferences in complex matrices. Laboratories interested in building verification capabilities for participation in OPCW proficient test could use the chemicals compiled in this chapter together with methodologies published in this blue book to establish their capabilities. This should be able to provide the laboratories with basic capability needed to participate in the OPCW proficient test.

More recently the OPCW has commenced a proficiency test regime based upon the identification of scheduled chemicals and biomarkers in biomedical samples. The results of the first official test was reported in 2016.[51] This move towards the analysis of biomedical samples shows a degree of maturity and development on the part of the OPCW. It would be expected that, as with classical forensic samples from mass casualty events involving chemicals, that there is a high probability that the agent or a diagnostic compound relating to the intact agent would be detected in samples collected from the victims of a chemical warfare agent attack. The benefit of development of the proficiency test for biomedical samples was demonstrated in the report on the use of chemical weapons in the Syrian Arab Republic.[2] This report details the results obtained from a range of both post mortem and ante mortem samples with sarin and sarin metabolites detected.

5. Future Expectations

During June 2016 the OPCW Scientific Advisory Board in cooperation with VERIFIN held a workshop in Helsinki titled "Chemical Forensics: Capabilities across the Field and the Potential Applications in Chemical Weapons Convention Implementation".[52] One of the presenters at the workshop, Dr Ralph Trapp, discussed the lessons learned from the OPCW missions in Syria highlighting the need to enhance the "*forensic capabilities of the OPCW and its network of Designated Laboratories, including the need to improvise and adapt procedures to the specific circumstances at the site of investigation whilst ensuring the required level of quality assurance, scientific rigour and chain of custody."*. The focus on the forensic aspects of the role of the designated laboratories may be emphasised in future proficiency tests.

The use of synthetic opioids for military applications was reported in 2002 with the fentanyl analogues such as carfentanil and remifentanil used to end a hostage incident.[53] Over recent years there has been an alarming increase in the illicit use of fentanyl and fentanyl derivatives as discussed in the 2017 publication by the U.S. Drug Enforcement Agency (DEA).[54] This publication details the hazards this class of compounds can pose to first responders and the actions to be taken to minimise exposure. With the potential for such chemicals to be used as warfare agents, it is not beyond imagination that future proficiency tests may include these compounds in the spiking regime.

In the United Nations Mission to Investigate Allegations of the Use of Chemical Weapons in the Syrian Arab Republic the presence of explosives and related compounds were included as part of the results of analysis.[2] Whilst the presence of such compounds is expected in the samples analysed in the context of the response, if such chemicals were reported during a proficiency test they may be considered as irrelevant chemicals and could lead to a failure under the rules of the program. Additionally, reporting the presence of explosives may actually fall outside the ISO 17025 accreditation for a laboratory dedicated to the identification of chemical warfare agent related compounds. Whilst this may be acceptable, based upon the laboratories quality system, these results cannot be considered to be covered under the international accreditation held by the organisation, with these exceptions noted on the final report.

If there is an expectation that reports from designated laboratories analysing samples from the suspected uses of chemical agents are to include identification of drug and explosive related materials this change in requirement should be replicated as part of the proficiency test program. In future proficiency tests it may be beneficial to include novel and emerging illicit drugs, explosives, explosive precursors or post blast residue to enable laboratories to establish a capability within these areas of expertise. However, if there is to be an inclusion of such materials the definitions of what is considered a non-scheduled, or irrelevant chemical and when they are to be reported would need to be reviewed. Details on when such compounds should be included and the range of compounds to be considered would have to be specified to maximize the capacities of the laboratories and minimize the potential for reporting non-reportable chemicals under the proficiency test format. Additionally, if drug and explosive related materials are to be reported by the designated laboratories consideration would have to be given on changes to the ISO accreditation for the facilities to allow them to report such compounds.

6. Conclusions

The continuation of the OPCW proficiency test regime is crucial to support aim of the complete destruction of chemical warfare agents. Through the ability to identify locations of production and use of such chemicals; the international community is able to reduce the risk posed by them. This can only be achieved with the open and impartial approach by an international organization such as the OPCW.

The challenges posed by the proficiency test samples forces laboratories to optimize all aspects of their analytical approaches. However, the matrices used and spiking chemicals included should bear resemblance to what is expected not what could be expected in the production and use of chemical warfare agents.

Finally, the proficiency tests must evolve to meet the changing demands placed on the OPCW. The proficiency test series should consider emerging threats and include explosive residue to mimic the samples expected following the functioning of a dissemination device.

7. Acknowledgements

The authors would like to thank Dr Hugh Gregg and Mrs Sanila Velikeloth from OPCW who supplied all of the background documents without which this review would have been incomplete.

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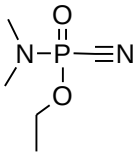
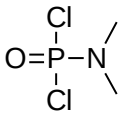
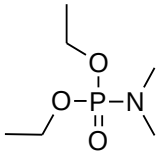
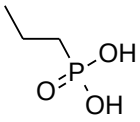
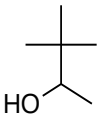
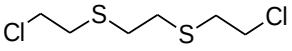
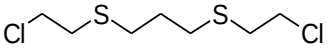
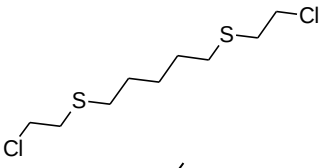
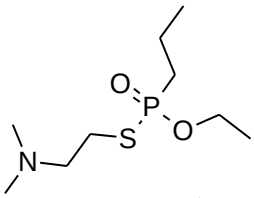
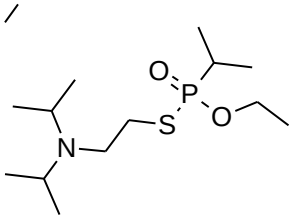
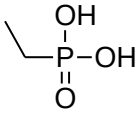
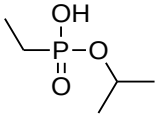
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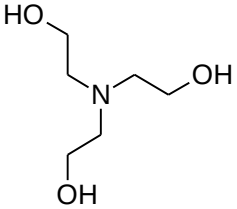
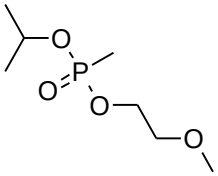
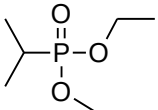
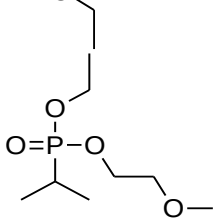
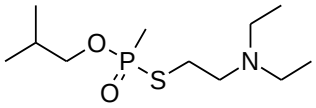
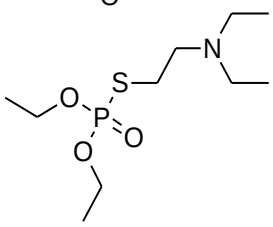
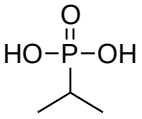
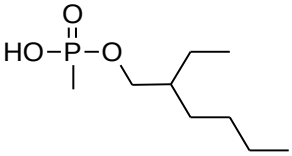
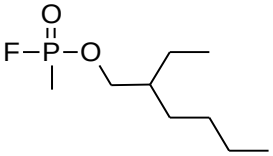
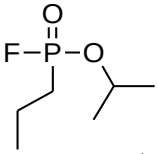
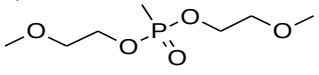
105. E. W. J. Hooijschuur, C. E. Kientz and A. G. Hulst, "Determination of Hydrolysis Products of Sulfur Mustards by Reversed-Phase Microcolumn Liquid Chromatography Coupled On-Line with Sulfur Flame Photometric Detection and Electrospray Ionization Mass Spectrometry Using Large-Volume Injections and Peak Compression", *Analytical Chemistry* **72** (2000) 1199-1206.

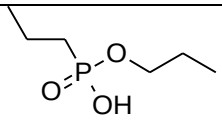
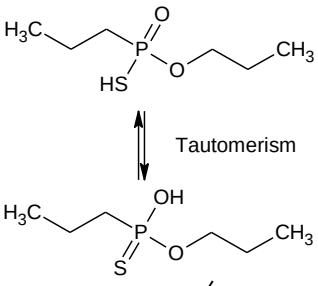
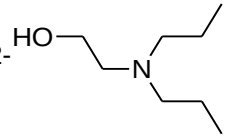
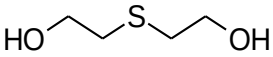
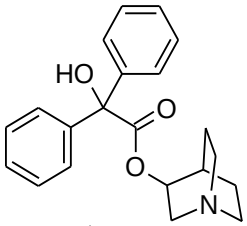
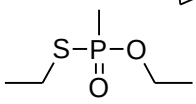
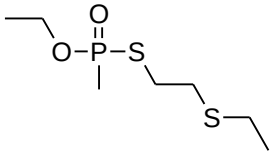
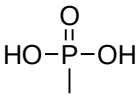
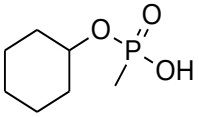
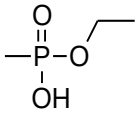
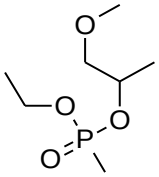
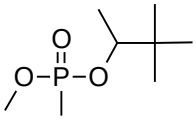
106. *USA Pat.*, US2465834A, 1949.

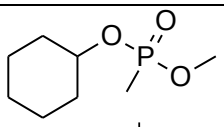
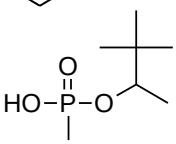
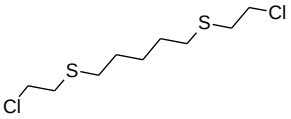
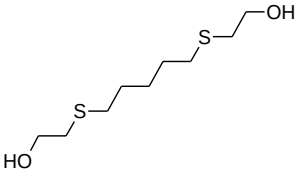
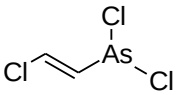
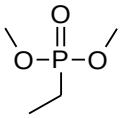
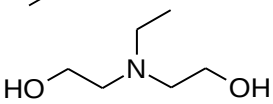
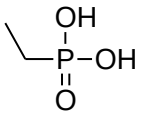
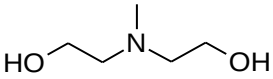
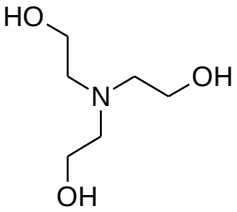
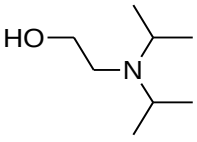
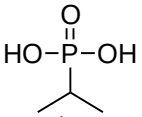
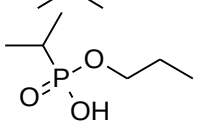
107. C. Golumbic, J. S. Fruton and M. Bergmann, "Chemical reactions of the nitrogen mustard gases. I. The transformations of methyl-bis(β-chloroethyl)amine in water", *The Journal of organic chemistry* **11** (1946) 581-585.

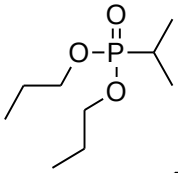
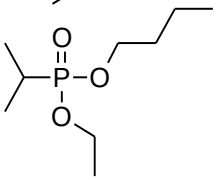
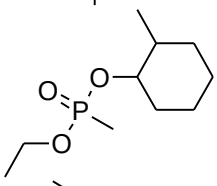
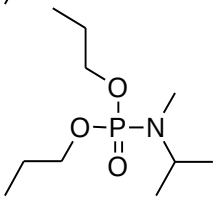
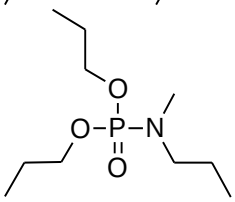
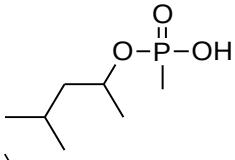
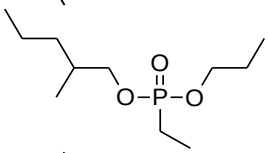
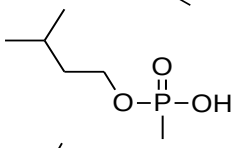
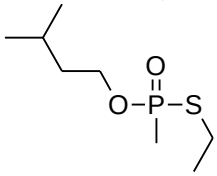
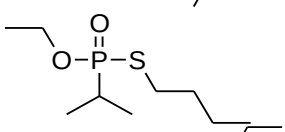
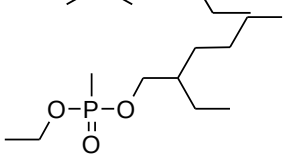
APPENDIX 1. List of spiked chemicals from OPCW Proficiency Tests [10-46]

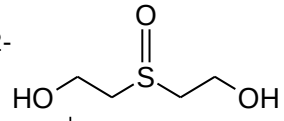
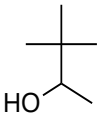
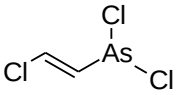
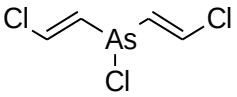
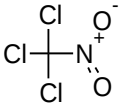
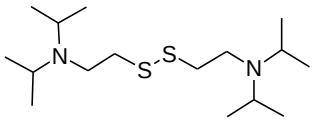
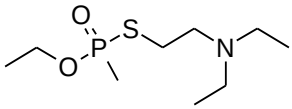
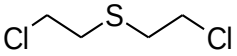
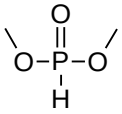
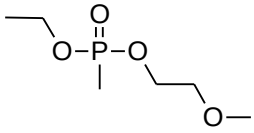
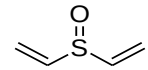
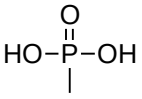
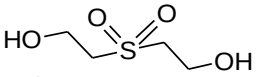
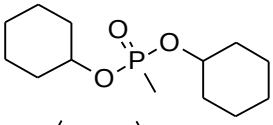
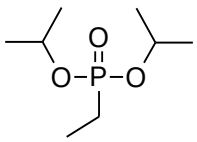
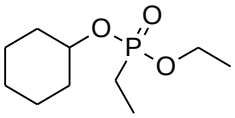
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	1	O,O-Diethyl N,N-dimethylphosphoramidate		2404-03-7	2.B.6	3
	1	Propylphosphonic acid		4672-38-2	2.B.4	4
	1	Pinacolyl alcohol (3,3-Dimethyl-2-butanol)		464-07-3	2.B.14	5
	1	1,2-Bis(2-chloroethylthio) ethane [Sesquimustard]		3563-36-8	1.A.4	6
	1	1,3-Bis(2-chloroethylthio) propane		63905-10-2	1.A.4	7
	1	1,5-Bis(2-chloroethylthio) pentane		142868-94-8	1.A.4	8
1996	2	O-Ethyl S-2-dimethylaminoethyl-n-propylphosphonothiolate			1.A.3	9
	2	O-Ethyl S-2-diisopropylaminoethyl-isopropylphosphonothiolate			1.A.3	10
	2	Ethylphosphonic acid		6779-09-5	2.B.4	11
	2	O-Isopropyl ethylphosphonate			2.B.4	12

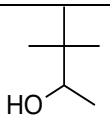
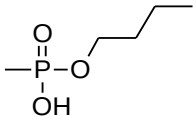
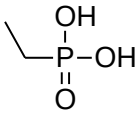
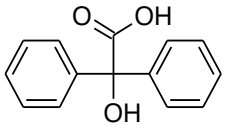
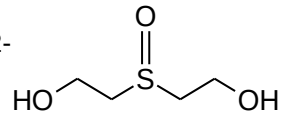
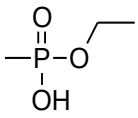
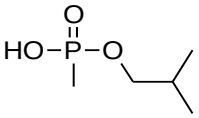
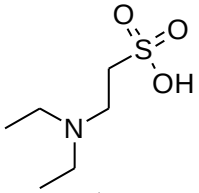
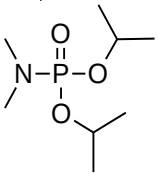
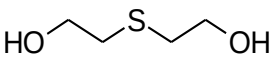
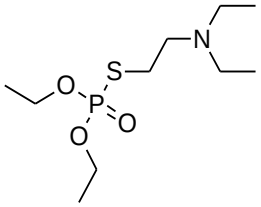
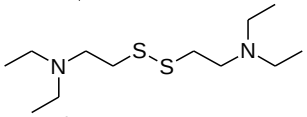
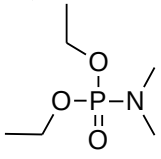
Year	Trial	Compounds	Structure	CAS No	Schedule	ID No
	2	Triethanolamine		102-71-6	3.B.17	13
	2	O-Isopropyl O-2-methoxyethyl methylphosphonate			2.B.4	14
	2	O,O-Diethyl isopropylphosphonate		1538-69-8	2.B.4	15
	2	O-Ethyl O-2-methoxyethyl isopropylphosphonate			2.B.4	16
1997	3	Isobutyl S-2-diethylaminoethyl methylphosphonothiolate		159939-87-4	1.A.3	17
	3	O,O-Diethyl S-2-diethylaminoethyl phosphorothiolate [Amiton]		78-53-5	2.A.1	18
	3	Isopropylphosphonic acid		4721-37-3	2.B.4	19
	3	O-2-Ethylhexyl methylphosphonic acid		13688-82-9	2.B.4	20
	3	O-2-Ethylhexyl methylphosphonofluoridate		458-71-9	1.A.1	21
	3	O-Isopropyl propylphosphonofluoridate		18358-37-7	1.A.1	22
	3	O,O-Bis(2-methoxyethyl) methylphosphonate		6069-09-6	2.B.4	23

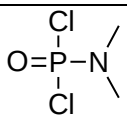
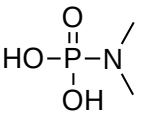
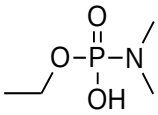
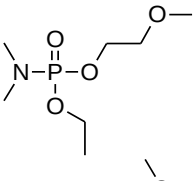
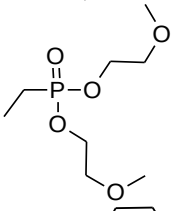
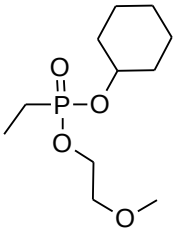
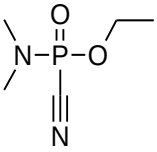
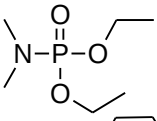
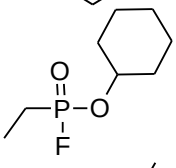
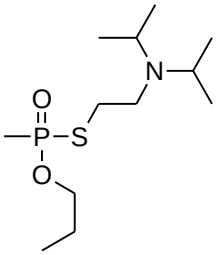
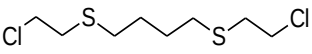
Year	Trial	Compounds	Structure	CAS No	Schedule	ID No
1998	4	Propyl propylphosphonate		21921-97-1	2.B.4	24
	4	O-Propyl propylthiophosphonate (sodium salt)		1280293-52-8	2.B.4	25
	4	N,N-Dipropylaminoethane-2-ol		3238-75-3	2.B.11	26
	4	Thiodiglycol (Bis(2-hydroxyethyl)sulfide)		111-48-8	2.B.13	27
	4	3-Quinuclidinyl benzilate [BZ]		6581-06-2	2.A.3	28
	4	O,S-Diethyl methylphosphonothiolate		2511-10-6	2.B.4	29
	4	O-Ethyl S-2-ethylthioethyl methylphosphonothiolate		556-75-2	2.B.4	30
1998	5	Methylphosphonic acid		993-13-5	2.B.4	31
	5	Cyclohexyl methylphosphonate		1932-60-1	2.B.4	32
	5	Ethyl methylphosphonate		1832-53-7	2.B.4	33
	5	Ethyl 2-(1-methoxypropyl) methylphosphonate			2.B.4	34
	5	Methyl pinacolyl methylphosphonate		7040-59-7	2.B.4	35

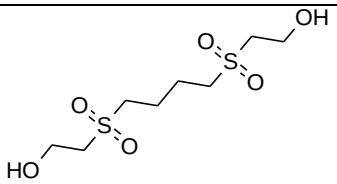
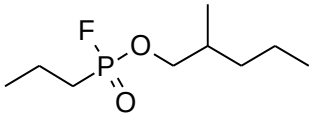
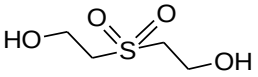
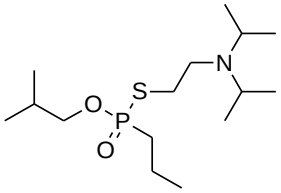
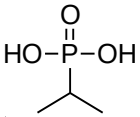
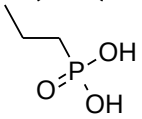
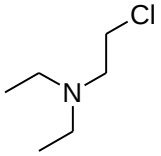
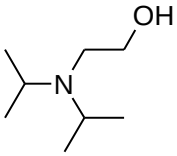
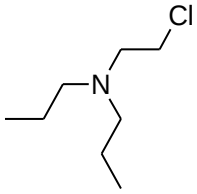
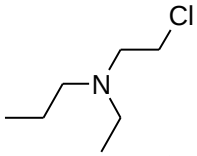
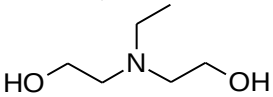
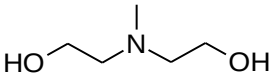
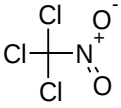
Year	Trial	Compounds	Structure	CAS No	Schedule	ID No
	5	Cyclohexyl methyl methylphosphonate		7040-52-0	2.B.4	36
	5	Pinacolyl methylphosphonate		616-52-4	2.B.4	37
1999	6	1,5-Bis(2-chloroethylthio) pentane		142868-94-8	1.A.4	38
	6	1,5-Bis(2-hydroxyethylthio) pentane			N.S.	39
	6	2-Chlorovinyldichloroarsine [Lewisite 1]		541-25-3	1.A.5	40
	6	Dimethyl ethylphosphonate		6163-75-3	2.B.4	41
	6	Ethyldiethanolamine		139-87-7	3.B.15	42
	6	Ethylphosphonic acid		6779-09-5	2.B.4	43
	6	Methyldiethanolamine		105-59-9	3.B.16	44
2000	7	Triethanolamine		102-71-6	3.B.17	45
	7	2-(N,N-Diisopropylamino) ethanol		96-80-0	2.B.11	46
	7	Isopropylphosphonic acid		4721-37-3	2.B.4	47
	7	Propyl isopropylphosphonate			2.B.4	48

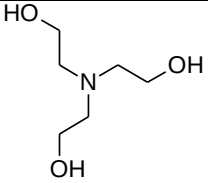
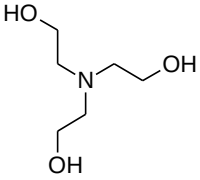
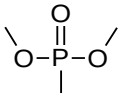
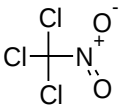
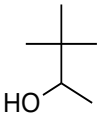
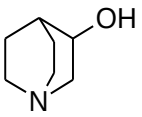
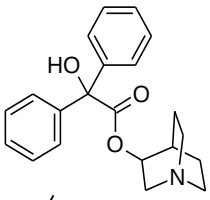
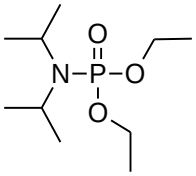
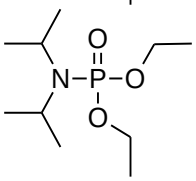
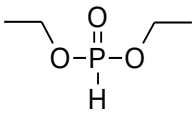
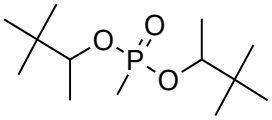
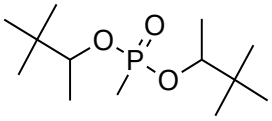
Year	Trial	Compounds	Structure	CAS No	Schedule	ID No
	7	Dipropyl isopropylphosphonate		192698-90-1	2.B.4	49
	7	Butyl ethyl isopropylphosphonate			2.B.4	50
	7	Ethyl 2-methylcyclohexyl methylphosphonate		161585-25-7	2.B.4	51
2000	8	O,O-Dipropyl N-methyl-N-isopropylphosphoramidate			2.B.6	52
	8	O,O-Dipropyl N-methyl-N-propylphosphoramidate			2.B.6	53
	8	O-1,3-Dimethylbutyl methylphosphonate		198885-55-1	2.B.4	54
	8	O-2-Methylpentyl O-propyl ethylphosphonate			2.B.4	55
	8	O-3-Methylbutyl methylphosphonate		3935-30-6	2.B.4	56
	8	O-3-Methylbutyl S-ethyl methylphosphonothiolate			2.B.4	57
	8	O-Ethyl S-butyl isopropylphosphonothiolate			2.B.4	58
	8	O-Ethyl-O-2-ethylhexyl methylphosphonate		88795-46-4	2.B.4	59

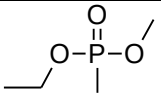
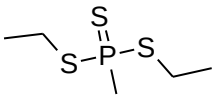
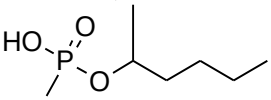
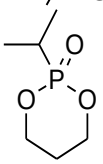
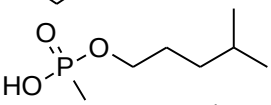
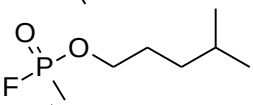
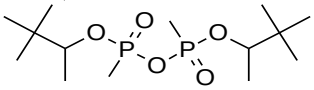
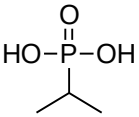
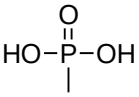
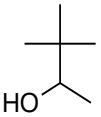
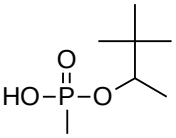
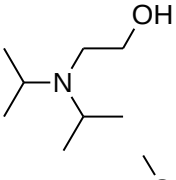
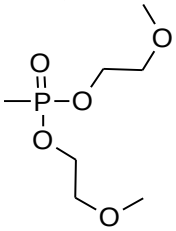
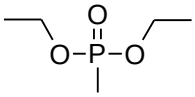
Year	Trial	Compounds	Structure	CAS No	Schedule	ID No
2001	9	Thiodiglycol sulfoxide (Bis(2-hydroxyethyl)sulfoxide)		3085-45-8	N.S.	60
	9	Pinacolyl alcohol (3,3-Dimethyl-2-butanol)		464-07-3	2.B.14	61
	9	2-Chlorovinyldichloroarsine [Lewisite 1]		541-25-3	1.A.5	62
	9	Bis(2-chlorovinyl) chloroarsine [Lewisite 2]		40334-69-8	1.A.5	63
	9	Chloropicrin		76-06-2	3.A.4	64
	9	Bis(2-diisopropylaminoethyl) disulfide		65332-44-7	N.S.	65
2001	10	O-Ethyl S-2-diethylaminoethyl methylphosphonothiolate		21770-86-5	1.A.3	66
	10	Bis(2-chloroethyl)sulfide [Mustard gas]		505-60-2	1.A.4	67
	10	Dimethyl phosphite		868-85-9	3.B.10	68
	10	Ethyl 2-methoxyethyl methylphosphonate		170082-62-9	2.B.4	69
	10	Divinyl sulfoxide		1115-15-7	N.S.	70
	10	Methylphosphonic acid		993-13-5	2.B.4	71
	10	Bis(2-hydroxyethyl)sulfone		2580-77-0	N.S.	72
2002	11	Dicyclohexyl methylphosphonate		7040-53-1	2.B.4	73
	11	Diisopropyl ethylphosphonate		1067-69-2	2.B.4	74
	11	Cyclohexyl ethyl ethylphosphonate			2.B.4	75

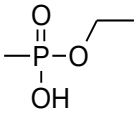
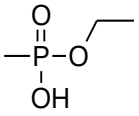
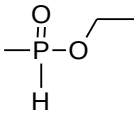
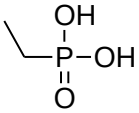
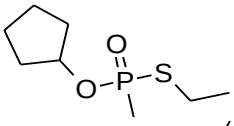
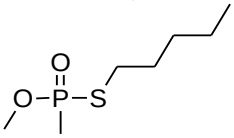
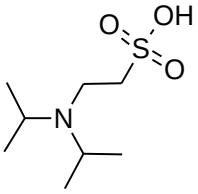
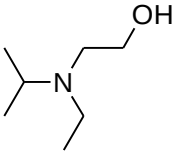
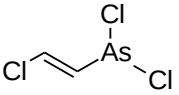
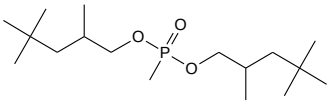
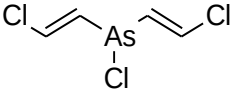
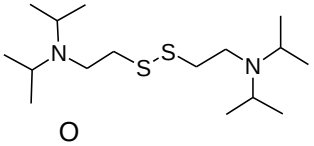
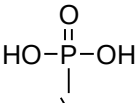
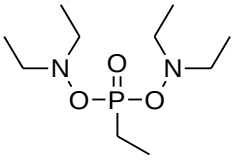
Year	Trial	Compounds	Structure	CAS No	Schedule	ID No
	11	Pinacolyl alcohol (3,3-Dimethyl-2-butanol)		464-07-3	2.B.14	76
	11	Butyl methylphosphonate		1832-55-9	2.B.4	77
	11	Ethylphosphonic acid		6779-09-5	2.B.4	78
	11	Benzilic acid (2,2-Diphenyl-2-hydroxyacetic acid)		76-93-7	2.B.8	79
2002	12	Thiodiglycol sulfoxide (Bis(2-hydroxyethyl)sulfoxide)		3085-45-8	N.S.	80
	12	Ethyl methylphosphonate		1832-53-7	2.B.4	81
	12	Isobutyl methylphosphonate		1604-38-2	2.B.4	82
	12	2-(N,N-Diethylamino) ethanesulfonic acid		15904-54-8	N.S.	83
	12	Diisopropyl N,N-dimethylphosphoramidate		2404-04-8	2.B.6	84
	12	Thiodiglycol (Bis(2-hydroxyethyl)sulfide)		111-48-8	2.B.13	85
2003	13	O,O-Diethyl S-2-diethylaminoethyl phosphorothiolate [Amiton]		78-53-5	2.A.1	86
	13	Bis(N,N-diethylaminoethyl) disulfide		589-32-2	N.S.	87
	13	O,O-Diethyl N,N-dimethylphosphoramidate		2404-03-7	2.B.6	88

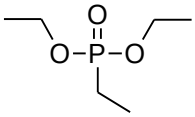
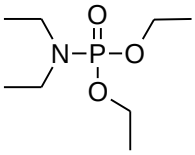
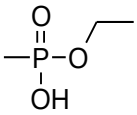
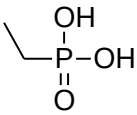
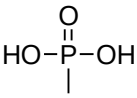
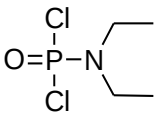
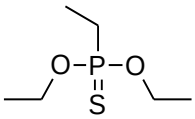
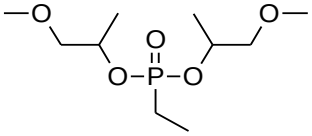
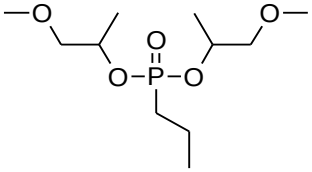
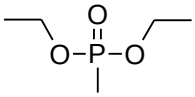
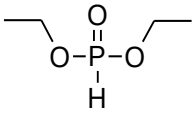
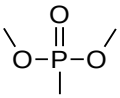
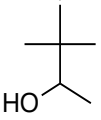
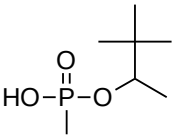
Year	Trial	Compounds	Structure	CAS No	Schedule	ID No
	13	N,N-Dimethylphosphoramidic dichloride		677-43-0	2.B.5	89
	13	N,N-Dimethylphosphoramidic acid		33876-51-6	N.S.	90
	13	O-Ethyl N,N-dimethylphosphoramidic acid		2632-86-2	N.S.	91
2003	14	O-Ethyl O-(2-methoxyethyl) N,N-dimethyl-phosporamidate			2.B.6	92
	14	Bis-(2-methoxyethyl) ethylphosphonate		170275-34-0	2.B.4	93
	14	O-Cyclohexyl O-(2-methoxyethyl) ethylphosphonate			2.B.4	94
	14	O-Ethyl N, N-dimethyl phosphoramidocyanidate [Tabun]		77-81-6	1.A.2	95
	14	O,O-Diethyl N,N-dimethylphosphoramidate		2404-03-7	2.B.6	96
	14	O-Cyclohexyl ethylphosphonoflouridate		7284-84-6	1.A.1	97
	14	O-Propyl S-2-diisopropyl-aminoethyl methyl-phosphonothiolate		52364-45-1	1.A.3	98
2004	15	1,4-Bis(2-chloroethylthio)-n-butane		142868-93-7	1.A.4	99

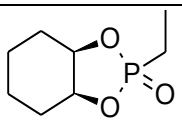
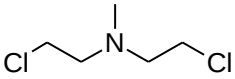
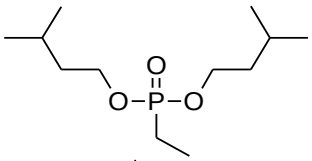
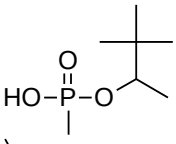
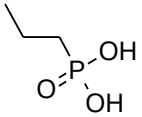
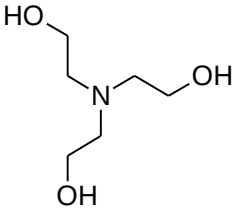
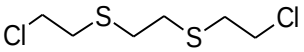
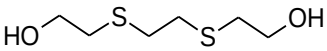
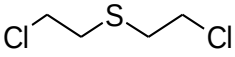
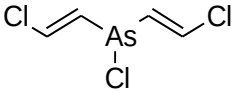
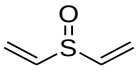
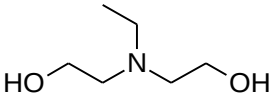
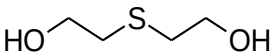
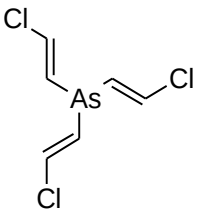
Year	Trial	Compounds	Structure	CAS No	Schedule	ID No
	15	1,4-Bis(2-hydroxyethylsulfonyl)-n-butane		7426-03-1	N.S.	100
	15	2-Methylpentyl propylphosphonofluoridate		333416-27-6	1.A.1	101
	15	Bis(2-hydroxyethyl)sulfone		2580-77-0	N.S.	102
	15	Isobutyl S-2-diisopropylaminoethyl propylphosphonothiolate			1.A.3	103
	15	Isopropylphosphonic acid		4721-37-3	2.B.4	104
	15	Propylphosphonic acid		4672-38-2	2.B.4	105
2004	16	2-(N,N-Diethylamino)ethylchloride		100-35-06	2.B.10	106
	16	2-(N,N-Diisopropylamino)ethanol		96-80-0	2.B.11	107
	16	2-(N,N-Diisopropylamino) ethylchloride		96-79-7	2.B.10	108
	16	2-(N-Ethyl-N-propylamino)ethylchloride			2.B.10	109
	16	Ethyldiethanolamine		139-87-7	3.B.15	110
	16	Methyldiethanolamine		105-59-9	3.B.16	111
	16	Chloropicrin		76-06-2	3.A.4	112

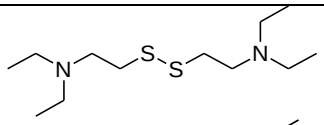
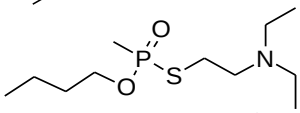
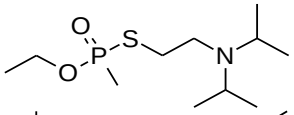
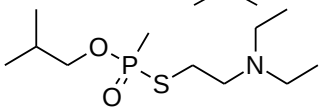
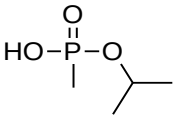
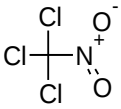
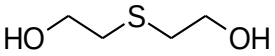
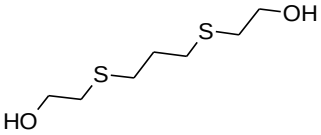
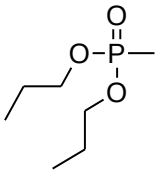
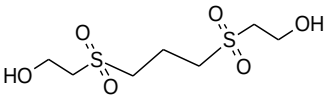
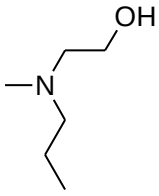
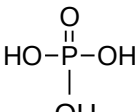
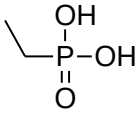
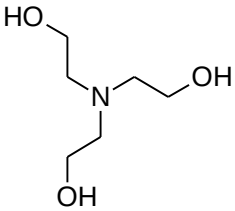
Year	Trial	Compounds	Structure	CAS No	Schedule	ID No
	16	Triethanolamine		102-71-6	3.B.17	113
	16	Triethanolamine		102-71-6	3.B.17	114
2005	17	Dimethyl methylphosphonate		756-79-6	2.B.4	115
	17	Chloropicrin		76-06-2	3.A.4	116
	17	Pinacolyl alcohol (3,3-Dimethyl-2-butanol)		464-07-3	2.B.14	117
	17	3-Quinuclidinol		1619-34-7	2.B.9	118
	17	3-Quinuclidinyl benzilate [BZ]		6581-06-2	2.A.3	119
2005	18	Diethyl N,N-diisopropyl phosphoramidate		76395-46-5	2.B.4	120
	18	Diethyl N,N-diisopropyl phosphoramidate		76395-46-5	2.B.4	121
	18	Diethyl phosphite		762-04-9	3.B.11	122
	18	Dipinacolyl methylphosphonate		7040-58-6	2.B.4	123
	18	Dipinacolyl methylphosphonate		7040-58-6	2.B.4	124

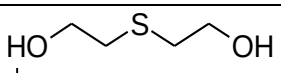
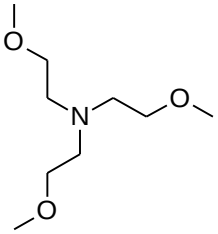
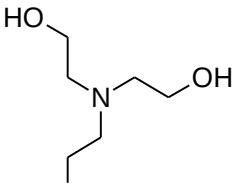
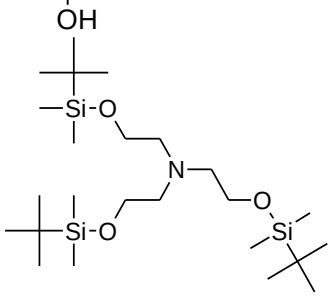
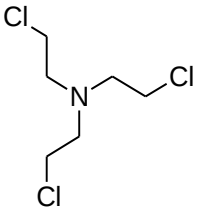
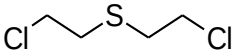
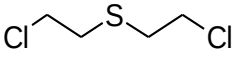
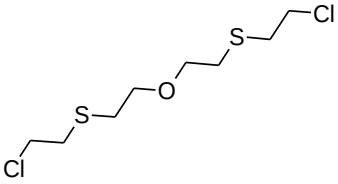
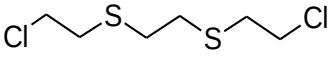
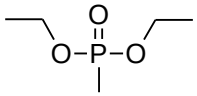
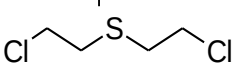
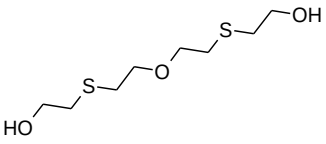
Year	Trial	Compounds	Structure	CAS No	Schedule	ID No
	18	Ethyl methyl methylphosphonate		18755-36-7	2.B.4	125
	18	S,S-Diethyl methylphosphonodithiolo-thionate		31650-57-4	2.B.4	126
2006	19	1-Methylpentyl methylphosphonate			2.B.4	127
	19	2-Isopropyl-1,3,2-dioxaphosphinane-2-oxide		118792-92-0	2.B.4	128
	19	4-Methylpentyl methylphosphonate			2.B.4	129
	19	4-Methylpentyl methylphosphonofluoridate			1.A.1	130
	19	Dipinacolyl dimethylpyrophosphonate		81397-56-0	2.B.4	131
	19	Isopropylphosphonic acid		4721-37-3	2.B.4	132
	19	Methylphosphonic acid		993-13-5	2.B.4	133
	19	Pinacolyl alcohol (3,3-Dimethyl-2-butanol)		464-07-3	2.B.14	134
	19	Pinacolyl methylphosphonate		616-52-4	2.B.4	135
2006	20	2-(N,N-Diisopropylamino)ethanol		96-80-0	2.B.11	136
	20	O,O Bis(2methoxyethyl) methylphosphonate		6069-09-6	2.B.4	137
	20	Diethyl methylphosphonate		683-08-9	2.B.4	138

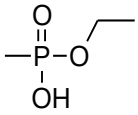
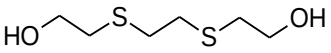
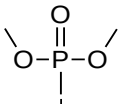
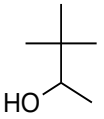
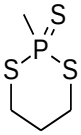
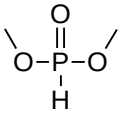
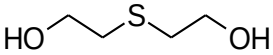
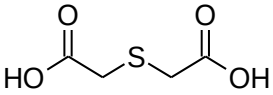
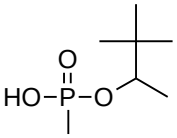
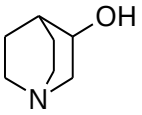
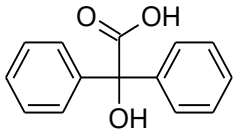
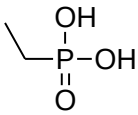
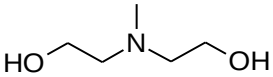
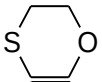
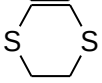
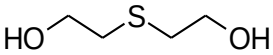
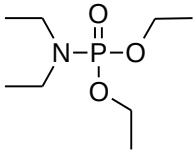
Year	Trial	Compounds	Structure	CAS No	Schedule	ID No
	20	Ethyl methylphosphonate		1832-53-7	2.B.4	139
	20	Ethyl methylphosphonate		1832-53-7	2.B.4	140
	20	Ethyl methylphosphinate		1832-53-7	2.B.4	141
	20	Ethylphosphonic acid		6779-09-5	2.B.4	142
	20	O-Cyclopentyl S-ethyl methylphosphonothiolate			2.B.4	143
	20	O-Methyl S-pentyl methylphosphonothiolate		871505-79-2	2.B.4	144
2007	21	2-(N,N-Diisopropylamino) ethanesulfonic acid		128869-82-9	N.S.	145
	21	2-(N-Ethyl-N-isopropylamino)ethanol		2893-61-0	2.B.11	146
	21	2-Chlorovinyldichloroarsine [Lewisite 1]		541-25-3	1.A.5	147
	21	Bis(2,4,4-trimethylpentyl) methylphosphonate			2.B.4	148
	21	Bis(2-chlorovinyl) chloroarsine [Lewisite 2]		40334-69-8	1.A.5	149
	21	Bis(2-diisopropylaminoethyl) disulfide		65332-44-7	N.S.	150
	21	Methylphosphonic acid		993-13-5	2.B.4	151
2007	22	Bis(N,N-diethylamino) ethylphosphonate		24842-44-2	2.B.4	152

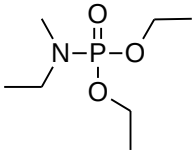
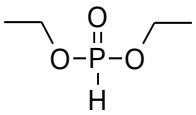
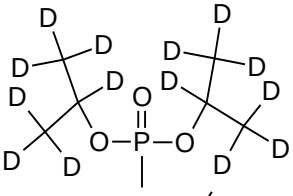
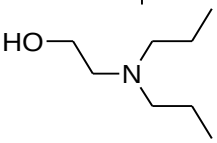
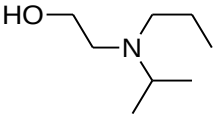
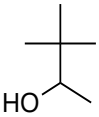
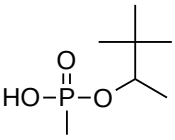
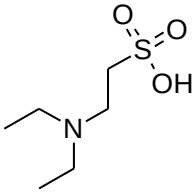
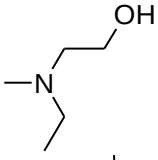
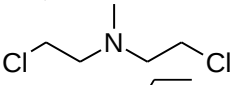
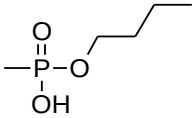
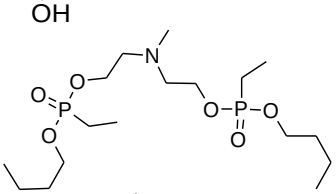
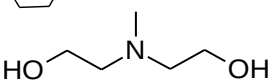
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	22	Diethyl ethylphosphonate		78-38-6	2.B.4	153
	22	Diethyl N,N-diethylphosphoramidate		3167-69-9	2.B.6	154
	22	Ethyl methylphosphonate		1832-53-7	2.B.4	155
	22	Ethylphosphonic acid		6779-09-5	2.B.4	156
	22	Methylphosphonic acid		993-13-5	2.B.4	157
	22	N,N-Diethylphosphoramidic dichloride		1498-54-0	2.B.5	158
	22	O,O-Diethyl ethylphosphonothionate		2455-45-0	2.B.4	159
2008	23	Bis(2-methoxy-1-methylethyl) ethylphosphonate			2.B.4	160
	23	Bis(2-methoxy-1-methylethyl) propylphosphonate			2.B.4	161
	23	Diethyl methylphosphonate		683-08-9	2.B.4	162
	23	Diethyl phosphite		762-04-9	3.B.11	163
	23	Dimethyl methylphosphonate		756-79-6	2.B.4	164
	23	Pinacolyl alcohol (3,3-Dimethyl-2-butanol)		464-07-3	2.B.14	165
	23	Pinacolyl methylphosphonate		616-52-4	2.B.4	166

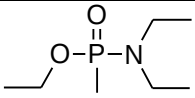
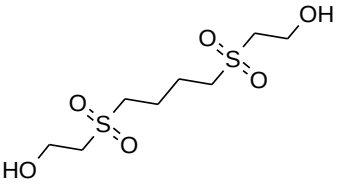
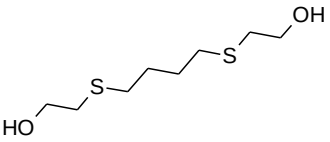
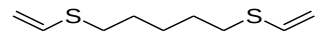
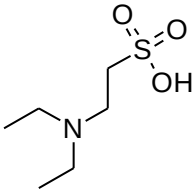
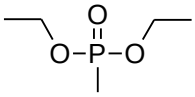
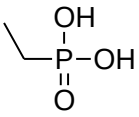
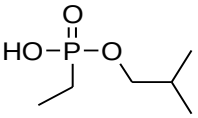
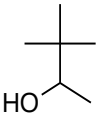
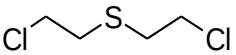
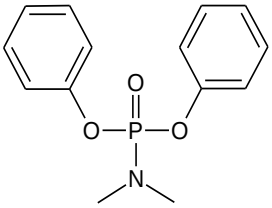
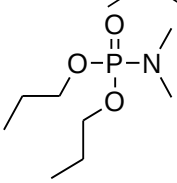
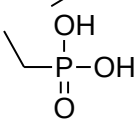
Year	Trial	Compounds	Structure	CAS No	Schedule	ID No
2008	24	(3aR, 7aS)-2-Ethylhexahydro-1,3,2-benzodioxaphosphole-2-oxide			2.B.4	167
	24	Bis(2-chloroethyl) methylamine		51-75-2	1.A.6	168
	24	Bis(3-methylbutyl) ethylphosphonate		97029-12-4	2.B.4	169
	24	Pinacolyl methylphosphonate		616-52-4	2.B.4	170
	24	Propylphosphonic acid		4672-38-2	2.B.4	171
	24	Triethanolamine		102-71-6	3.B.17	172
2009	25	1,2-Bis(2-chloroethylthio) ethane [Sesquimustard]		3563-36-8	1.A.4	173
	25	1,2-Bis(2-hydroxyethylthio) ethane [3,6-dithia-1,8-octanediol]		5244-34-8	N.S.	174
	25	Arsenic trichloride		7784-34-1	2.B.7	175
	25	Bis(2-chloroethyl)sulfide [Mustard gas]		505-60-2	1.A.4	176
	25	Bis(2-chlorovinyl) chloroarsine [Lewisite 2]		40334-69-8	1.A.5	177
	25	Divinyl sulfoxide		1115-15-7	N.S.	178
	25	Ethyldiethanolamine		139-87-7	3.B.15	179
	25	Thiodiglycol (Bis(2-hydroxyethyl)sulfide)		111-48-8	2.B.13	180
	25	Tris(2-chlorovinyl)arsine [Lewisite 3]		40334-70-1	1.A.5	181

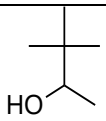
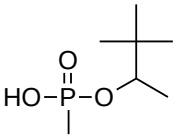
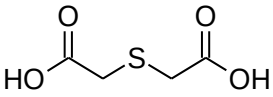
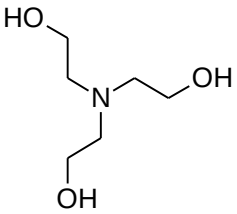
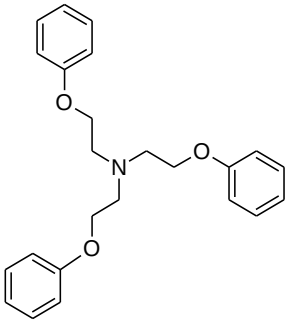
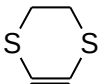
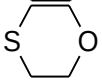
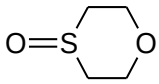
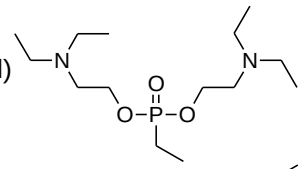
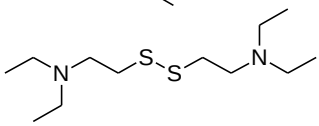
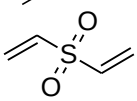
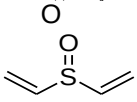
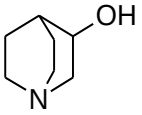
Year	Trial	Compounds	Structure	CAS No	Schedule	ID No
2009	26	Bis(2-N,N-diethylaminoethyl)disulfide		589-32-2	N.S.	182
	26	Butyl S-2-diethylaminoethyl methylphosphonothiolate		468712-10-9	1.A.3	183
	26	Ethyl S-2-diisopropylaminoethyl methylphosphonothiolate		50782-69-9	1.A.3	184
	26	Isobutyl S-2-diethylaminoethyl methylphosphonothiolate		159939-87-4	1.A.3	185
	26	Isopropyl methylphosphonate		1832-54-8	2.B.4	186
2010	27	Chloropicrin		76-06-2	3.A.4	187
	27	Thiodiglycol (Bis(2-hydroxyethyl)sulfide)		111-48-8	2.B.13	188
	27	1,3-Bis(2-hydroxyethylthio)propane		16260-48-3	N.S.	189
	27	Dipropyl methylphosphonate		6410-56-6	2.B.4	190
	27	1,3-Bis(2-hydroxyethylsulfonyl) propane		41123-71-1	N.S.	191
	27	2-(N-Methyl-N-propylamino)ethanol		2893-45-0	2.B.11	192
	27	Methylphosphonic acid		993-13-5	2.B.4	193
	27	Ethylphosphonic acid		6779-09-5	2.B.4	194
2010	28	Triethanolamine		102-71-6	3.B.17	195

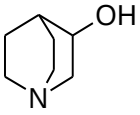
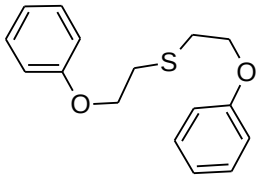
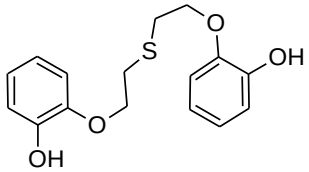
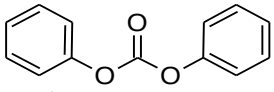
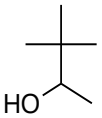
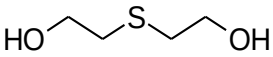
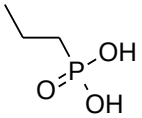
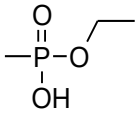
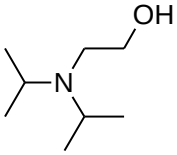
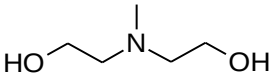
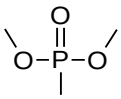
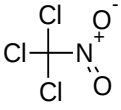
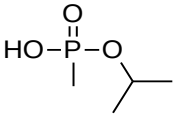
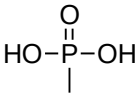
Year	Trial	Compounds	Structure	CAS No	Schedule	ID No
	28	Thiodiglycol (Bis(2-hydroxyethyl)sulfide)		111-48-8	2.B.13	196
	28	Tris(2-methoxyethyl)amine		3235-51-6	N.S.	197
	28	Triethanolamine		102-71-6	3.B.17	198
	28	Tris(2-tert-butyldimethylsilyloxyethyl) amine			N.S.	199
	28	Tris(2-chloroethyl)amine		555-77-1	1.A.4	200
	28	Bis(2-chloroethyl)sulfide [Mustard gas]		505-60-2	1.A.4	201
2011	29	Bis(2-chloroethyl)sulfide [Mustard gas]		505-60-2	1.A.4	202
	29	Bis(2-chloroethylthioethyl) ether		63918-89-8	1.A.4	203
	29	1,2-Bis(2-chloroethylthio) ethane [Sesquimustard]		3563-36-8	1.A.4	204
	29	Diethyl methylphosphonate		683-08-9	2.B.4	205
	29	Bis(2-chloroethyl)sulfide [Mustard gas]		505-60-2	1.A.4	206
	29	Bis(2-hydroxyethylthioethyl) ether		7429-02-0	N.S.	207

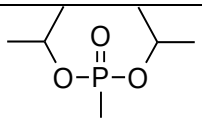
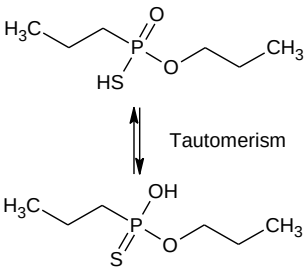
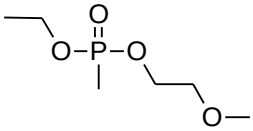
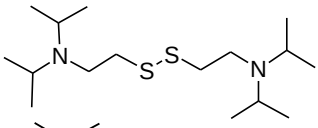
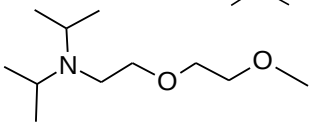
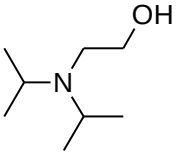
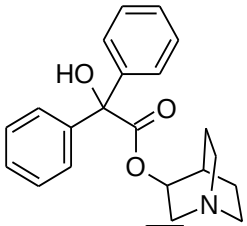
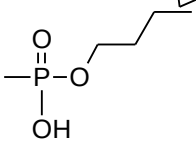
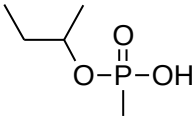
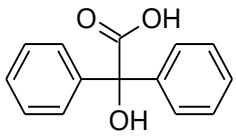
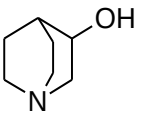
Year	Trial	Compounds	Structure	CAS No	Schedule	ID No
	29	Ethyl methylphosphonate		1832-53-7	2.B.4	208
	29	1,2-Bis(2-hydroxyethylthio) ethane [3,6-dithia-1,8-octanediol]		5244-34-8	N.S.	209
2011	30	Dimethyl methylphosphonate		756-79-6	2.B.4	210
	30	Pinacolyl alcohol (3,3-Dimethyl-2-butanol)		464-07-3	2.B.14	211
	30	2-Methyl-1,3,2-dithiaphosphinane-2-sulfide		18882-24-1	2.B.4	212
	30	Dimethyl phosphite		868-85-9	3.B.10	213
	30	Thiodiglycol (Bis(2-hydroxyethyl)sulfide)		111-48-8	2.B.13	214
	30	Thiodiglycolic acid		123-93-3	N.S.	215
	30	Pinacolyl methylphosphonate		616-52-4	2.B.4	216
2012	31	3-Quinuclidinol		1619-34-7	2.B.9	217
	31	Benzilic acid (2,2-Diphenyl-2-hydroxyacetic acid)		76-93-7	2.B.8	218
	31	Ethylphosphonic acid		6779-09-5	2.B.4	219
	31	Methyldiethanolamine		105-59-9	3.B.16	220
	31	1,4-Thioxane		15980-15-1	N.S.	221
	31	1,4-Dithiane		505-29-3	N.S.	222
	31	Thiodiglycol (Bis(2-hydroxyethyl)sulfide)		111-48-8	2.B.13	223
2012	32	Diethyl N,N-diethylphosphoramidate		3167-69-9	2.B.6	224

Year	Trial	Compounds	Structure	CAS No	Schedule	ID No
	32	Diethyl N-ethyl-N-methylphosphoramidate		53279-98-4	2.B.6	225
	32	Diethyl phosphite		762-04-9	3.B.11	226
	32	Diisopropyl-(d14) methylphosphonate		1205608-66-7	2.B.4	227
	32	N,N-Dipropylaminoethane-2-ol		3238-75-3	2.B.11	228
	32	N-Isopropyl-N-propylaminoethane-2-ol		4535-77-7	2.B.11	229
	32	Pinacolyl alcohol (3,3-Dimethyl-2-butanol)		464-07-3	2.B.14	230
	32	Pinacolyl methylphosphonate		616-52-4	2.B.4	231
2013	33	2-(N,N-Diethylamino) ethanesulfonic acid		15904-54-8	N.S.	232
	33	2-(N-Ethyl-N-methylamino)ethanol		2893-43-8	2.B.11	233
	33	Bis(2-chloroethyl) methylamine		51-75-2	1.A.6	234
	33	Butyl methylphosphonate		1832-55-9	2.B.4	235
	33	Methyl-bis[2-butoxy(methyl)-phosphoryloxyethyl]amine			2.B.4	236
	33	Methyldiethanolamine		105-59-9	3.B.16	237

Year	Trial	Compounds	Structure	CAS No	Schedule	ID No
	33	O-Ethyl N,N-diethyl methylphosphonoamidate		2404-81-1	2.B.4	238
2013	34	1,4-Bis(2-hydroxyethylsulfonyl)-n-butane		7426-03-1	N.S.	239
	34	1,4-Bis(2-hydroxyethylthio)-n-butane		7425-93-6	N.S.	240
	34	1,5-Bis(vinylthio)-n-pentane		86089-62-5	N.S.	241
	34	2-(N,N-Diethylamino) ethanesulfonic acid		15904-54-8	N.S.	242
	34	Diethyl methylphosphonate		683-08-9	2.B.4	243
	34	Ethylphosphonic acid		6779-09-5	2.B.4	244
	34	Isobutyl ethylphosphonate		170082-56-1	2.B.4	245
	34	Pinacolyl alcohol (3,3-Dimethyl-2-butanol)		464-07-3	2.B.14	246
2014	35	Bis(2-chloroethyl)sulfide [Mustard gas]		505-60-2	1.A.4	247
	35	Diphenyl N,N-dimethylphosphoramide		6415-21-0	N.S.	248
	35	Dipropyl N,N-dimethylphosphoramidate		98543-28-3	2.B.6	249
	35	Ethylphosphonic acid		6779-09-5	2.B.4	250

Year	Trial	Compounds	Structure	CAS No	Schedule	ID No
	35	Pinacolyl alcohol (3,3-Dimethyl-2-butanol)		464-07-3	2.B.14	251
	35	Pinacolyl methylphosphonate		616-52-4	2.B.4	252
	35	Thiodiglycolic acid		123-93-3	N.S.	253
	35	Triethanolamine		102-71-6	3.B.17	254
	35	Tris(2-phenoxyethyl)amine		26253-40-7	N.S.	255
2014	36	1,4-Dithiane		505-29-3	N.S.	256
	36	1,4-Thioxane		15980-15-1	N.S.	257
	36	1,4-Thioxane oxide		109-03-5	N.S.	258
	36	Bis(2-N,N-diethylaminoethyl) ethylphosphonate		101098-30-0	2.B.4	259
	36	Bis(N,N-diethylaminoethyl) disulfide		589-32-2	N.S.	260
	36	Divinyl sulfone		77-77-0	N.S.	261
	36	Divinyl sulfoxide		1115-15-7	N.S.	262
2015	37	3-Quinuclidinol		1619-34-7	2.B.9	263

Year	Trial	Compounds	Structure	CAS No	Schedule	ID No
	37	3-Quinuclidinol		1619-34-7	2.B.9	264
	37	Bis(2-phenoxyethyl)sulfide		13755-14-1	N.S.	265
	37	Bis-[2-(2-hydroxyphenoxy)ethyl] sulfide		27627-83-4	N.S.	266
	37	Diphenylcarbonate		102-09-0	N.S.	267
	37	Pinacolyl alcohol (3,3-Dimethyl-2-butanol)		464-07-3	2.B.14	268
	37	Thiodiglycol (Bis(2-hydroxyethyl)sulfide)		111-48-8	2.B.13	269
2015	38	Propylphosphonic acid		4672-38-2	2.B.4	270
	38	Ethyl methylphosphonate		1832-53-7	2.B.4	271
	38	2-(N,N-Diisopropylamino) ethanol		96-80-0	2.B.11	272
	38	Methyldiethanolamine		105-59-9	3.B.16	273
	38	Dimethyl methylphosphonate		756-79-6	2.B.4	274
	38	Chloropicrin		76-06-2	3.A.4	275
2016	39	Isopropyl methylphosphonate		1832-54-8	2.B.4	276
	39	Methylphosphonic acid		993-13-5	2.B.4	277

Year	Trial	Compounds	Structure	CAS No	Schedule	ID No
	39	Diisopropyl methylphosphonate		1445-75-6	2.B.4	278
	39	O-Propyl propylthiophosphonate		1280293-52-8	2.B.4	279
	39	Ethyl 2-methoxyethyl methylphosphonate		170082-62-9	2.B.4	280
	39	Bis(2-diisopropylaminoethyl) disulfide		65332-44-7	N.S.	281
	39	N,N-Diisopropylaminoethyl-2- methoxyethyl ether		936619-91-9	N.S.	282
	39	2-(N,N-Diisopropylamino) ethanol		96-80-0	2.B.11	283
2016	40	3-Quinuclidinyl benzilate [BZ]		6581-06-2	2.A.3	284
	40	Butyl methylphosphonate		1832-55-9	2.B.4	285
	40	sec-Butyl methylphosphonic acid		143663-81-4	2.B.4	286
	40	Benzilic acid (2,2-Diphenyl-2-hydroxyacetic acid)		76-93-7	2.B.8	287
	40	3-Quinuclidinol		1619-34-7	2.B.9	288

APPENDIX 2. Distribution of chemicals based upon schedules

Within each of the following tables the chemicals relating the specific schedule are presented in the following manner:

Precursor

Final product

Hydrolysis/decontamination products

Chemicals are listed under the designated headings depending upon their position within the synthetic procedure detailed prior to the table:

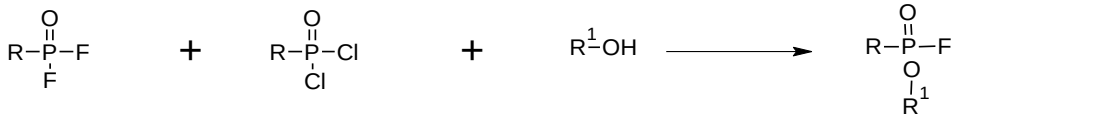
E.g. N,N-Diethylphosphoramidic dichloride (158) as a precursor to schedule 1.A.2 chemicals.

The number listed in parenthesis after the compound name, in this case (158), is the unique identifying number from Appendix 1. Reference to this entry in Appendix 1 will show the year of the proficiency test, the proficiency test number, the name, structure, CAS number (if available) and schedule for the compound.

The references used to identify the preparative method and those chemicals expected due to hydrolysis or decontamination processes are listed in the square brackets:

E.g. Hydrolysis/decontamination products [44-83].

Schedule 1.A.1



Alkylphosphonic difluoride | Alkylphosphonic dichloride | Alkyl alcohol | O-Alkyl alkyl phosphonfluoridate

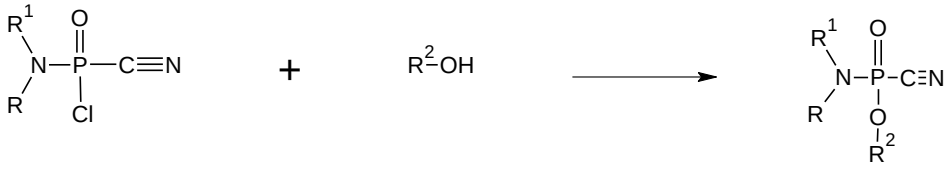
Figure 4. Synthetic pathway for Schedule 1.A.1 chemicals. [55] R = Methyl, Ethyl, Propyl or Isopropyl and $R^1 = \leq$ C10, including cycloalkyl.

Table 2. Schedule 1.A.1 compounds and related chemicals.

Precursor: Alkylphosphonic dichloride and difluoride
Precursor: Alkyl alcohol
Pinacolyl Alcohol (5, 61, 76, 117, 134, 165, 211, 230, 246, 251, 268)
Final Product: O-Alkyl alkylphosphonofluoridate
2-Methylpentyl propylphosphonofluoridate (101)
4-Methylpentyl methylphosphonofluoridate (130)
O-2-Ethylhexyl methylphosphonofluoridate (21)
O-Cyclohexyl ethylphosphonoflouridate (97)
O-Cyclohexyl ethylphosphonoflouridate (98)
O-Isopropyl propylphosphonofluoridate (22)
Hydrolysis/decontamination products:[56-95]
1-Methylpentyl methylphosphonate (127)
2-Isopropyl-1,3,2-dioxaphosphinane-2-oxide (128)
4-Methylpentyl methylphosphonate (129)
(3aR, 7aS)-2-Ethylhexahydro-1,3,2-benzodioxaphosphole-2-oxide (167)
Bis(2-methoxy-1-methylethyl) ethylphosphonate (160)
Bis(2,4,4-trimethylpentyl) methylphosphonate (148)
Bis(2-methoxy-1-methylethyl) propylphosphonate (161)
Bis-(2-methoxyethyl) ethylphosphonate (93)
Bis(3-methylbutyl) ethylphosphonate (169)
Butyl ethyl isopropylphosphonate (50)
Butyl methylphosphonate (77, 235, 285)
sec-Butyl methylphosphonic acid (286)
Cyclohexyl ethyl ethylphosphonate (75)
Cyclohexyl methyl methylphosphonate (36)
Cyclohexyl methylphosphonate (32)
Dicyclohexyl methylphosphonate (73)
Diethyl ethylphosphonate (153)
Diethyl methylphosphonate (138, 162, 205, 243)
Diethyl phosphite (122, 163, 226)
Diisopropyl ethylphosphonate (74)
Diisopropyl-(d14) methylphosphonate (227)
Dimethyl ethylphosphonate (41)
Dimethyl methylphosphonate (115, 164, 210, 274)
Dimethyl phosphite (68, 213)
Dipinacolyl dimethylpyrophosphonate (131)
Dipinacolyl methylphosphonate (123, 124)
Dipropyl isopropylphosphonate (49)
Hydrolysis/decontamination products:[56-95]
Dipropyl methylphosphonate (190)

Diisopropyl methylphosphonate (278)
Ethyl 2-(1-methoxypropyl) methylphosphonate (34)
Ethyl 2-methoxyethyl methylphosphonate (69, 280)
Ethyl 2-methylcyclohexyl methylphosphonate (51)
Ethyl methyl methylphosphonate (125)
Ethyl methylphosphinate (141)
Ethyl methylphosphonate (33, 81, 139, 140, 155, 208, 271)
Ethylphosphonic acid (11, 43, 78, 142, 156, 194, 219, 244, 250)
Isobutyl ethylphosphonate (245)
Isobutyl methylphosphonate (82)
Isopropyl methylphosphonate (186, 276)
Isopropylphosphonic acid (19, 47, 104, 132)
Methyl pinacolyl methylphosphonate (35)
Methylphosphonic acid (31, 71, 133, 151, 157, 193, 277)
O,O Bis(2methoxyethyl)methylphosphonate (23, 137)
O,O-Diethyl isopropylphosphonate (15)
O-1,3-Dimethylbutyl methylphosphonate (54)
O-2-Ethylhexyl methylphosphonic acid (20)
O-2-Methylpentyl O-propyl ethylphosphonate (55)
O-3-Methylbutyl methylphosphonate (56)
O-Cyclohexyl, O-(2-methoxyethyl) ethylphosphonate (94)
O-Ethyl O-2-methoxyethyl isopropylphosphonate (16)
O-Ethyl-O-2-ethylhexyl methylphosphonate (59)
O-Isopropyl ethylphosphonate (12)
O-Isopropyl O-2-methoxyethyl methylphosphonate (14)
Pinacolyl methylphosphonate (37, 135, 166, 170, 216, 231, 252)
Propyl isopropylphosphonate (48)
Propyl propylphosphonate (24)
Propylphosphonic acid (4, 105, 171, 270)

Schedule 1.A.2



dialkylphosphoramidocyanidic chloride Alkyl alcohol O-Alkyl N,N-dialkyl phosphoramidocyanidate

Figure 5. Synthetic pathway for Schedule 1.A.2 chemicals.[96,97] R and R^1 = Methyl, Ethyl, Propyl or Isopropyl, and $R^2 = \leq C_{10}$, including cycloalkyl.

Table 3. Schedule 1.A.2 compounds and related chemicals.

Precursor: Dialkylphosphoramido cyanidic chloride
N,N-Diethylphosphoramidic dichloride (158)
N,N-Dimethylphosphoramidic dichloride (2, 89)
Precursor: Alkyl alcohol
Final Product: O-Alkyl N, N dialkyl phosphoramidocyanidate
O-Ethyl N, N-dimethyl phosphoramidocyanidate (Tabun) (1, 95)
O-Ethyl N,N-diethyl methylphosphonoamidate (238)
Hydrolysis/decontamination products:[56-94]
Diethyl N,N-diethylphosphoramidate (154, 224)
Diethyl N,N-diisopropyl phosphoramidate (120, 121)
Diethyl N-ethyl-N-methylphosphoramidate (225)
Diisopropyl N,N-dimethylphosphoramidate (84)
Diphenyl N,N-dimethylphosphoramide (248)
Dipropyl N,N-dimethylphosphoramidate (249)
N,N-Dimethylphosphoramidic acid (90)
O,O-Diethyl N,N-dimethylphosphoramidate (3, 88, 96)
O,O-Diisopropyl N-methyl-N-propylphosphoramidate (52)
O,O-Dipropyl N-methyl-N-propylphosphoramidate (53)
O-Ethyl N,N-dimethylphosphoramidic acid (91)
O-Ethyl, O-(2-methoxyethyl) N,N-dimethyl-phosporamidate (92)

Schedule 1.A.3

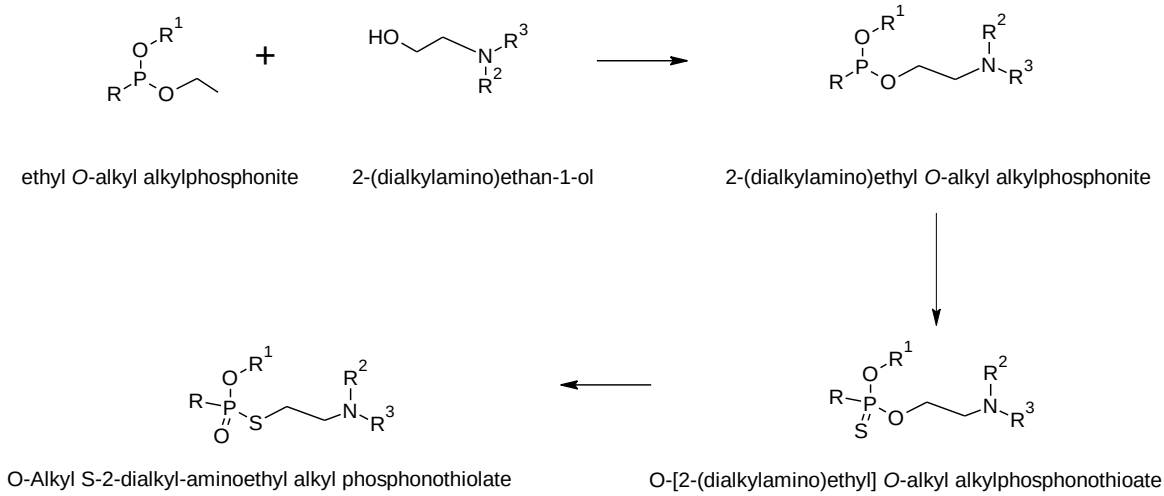


Figure 6. Synthetic pathway for Schedule 1.A.3 chemicals.[98] **R, R2 and R3= Methyl, Ethyl, Propyl or Isopropyl, and** R1 = ≤ C10, including cycloalkyl.

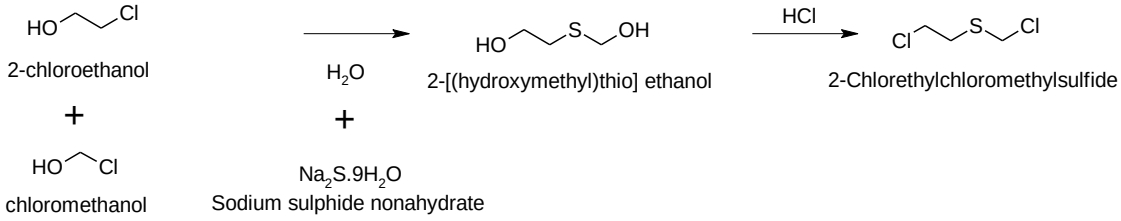
Table 4. Schedule 1.A.3 compounds and related chemicals.

Precursor: ethyl *O*-alkyl alkylphosphonite
Precursor: 2-(dialkylamino)ethanane alcohol, halide, thiol
2-(N,N-Diethylamino)ethylchloride (106)
2-(N,N-Diisopropylamino)ethanol (46, 107, 136, 272, 283)
2-(N,N-Diisopropylamino)ethylchloride (108)
2-(N-Ethyl-N-isopropylamino)ethanol (146)
2-(N-Ethyl-N-methylamino)ethanol (233)
2-(N-Ethyl-N-propylamino)ethylchloride (109)
2-(N-Methyl-N-propylamino)ethanol (192)
N,N-Dipropylaminoethane-2-ol (26, 228)
N-Isopropyl-N-propylaminoethane-2-ol (229)
Precursor: 2-(dialkylamino)ethyl *O*-alkyl alkylphosphonite
Precursor: O-[2-(dialkylamino)ethyl] *O*-alkyl alkylphosphonothioate
O,O-Diethyl S-2-diethylaminoethyl phosphorothiolate (Amiton) (18, 86)
Final Product: O-Alkyl S-2-dialkyl-aminoethyl alkyl phosphonothiolate
Butyl S-2-diethylaminoethyl methylphosphonothiolate (183)
Ethyl S-2-diisopropylaminoethyl methylphosphonothiolate (184)
Isobutyl S-2-diethylaminoethyl methylphosphonothiolate (17, 185)
Isobutyl S-2-diisopropylaminoethyl propylphosphonothiolate (103)
O-Ethyl S-2-diethylaminoethyl methylphosphonothiolate (66)
O-Ethyl S-2-diisopropylaminoethyl isopropylphosphonothiolate (10)
O-Ethyl S-2-dimethylaminoethyl-n-propylphosphonothiolate (9)
Hydrolysis/decontamination products:[56-95, 99]
2-(N,N-Diethylamino)ethanesulfonic acid (83, 232, 242)
2-(N,N-Diisopropylamino)ethanesulfonic acid (145)
2-Isopropyl-1,3,2-dioxaphosphinane-2-oxide (128)

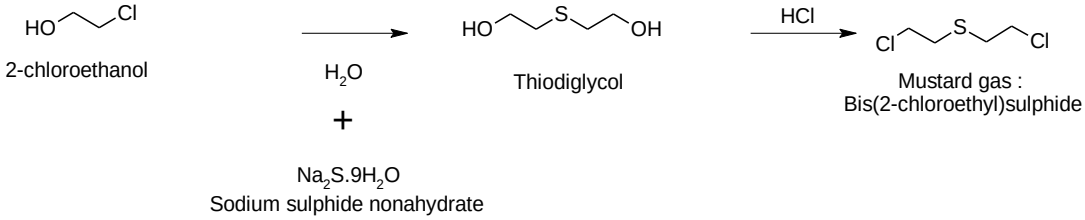
Hydrolysis/decontamination products:[56-95, 99]
2-Methyl-1,3,2-dithiaphosphinane-2-sulfide (212)
Bis(2-diisopropylaminoethyl)disulfide (65, 150, 281)
Bis(2-N,N-diethylaminoethyl) ethylphosphonate (259)
Bis(2-N,N-diethylaminoethyl)disulfide (182)
Bis(N,N-diethylamino) ethylphosphonate (152)
Bis(N,N-diethylaminoethyl)disulfide (87, 260)
Butyl methylphosphonate (77, 235, 285)
sec-Butyl methylphosphonic acid (286)
Diethyl ethylphosphonate (153)
Diethyl methylphosphonate (138, 162, 205, 243)
Diethyl phosphite (122, 163, 226)
Diisopropyl ethylphosphonate (74)
Dimethyl ethylphosphonate (41)
Dimethyl methylphosphonate (115, 164, 210, 274)
Dimethyl phosphite (68, 213)
Ethyl methyl methylphosphonate (125)
Ethyl methylphosphinate (141)
Ethyl methylphosphonate (33, 81, 139, 140, 155, 208, 271)
Ethylphosphonic acid (11, 43, 78, 142, 156, 194, 219, 244, 250)
Methyl-bis[2-butoxy(methyl)-phosphoryloxyethyl]amine (236)
N,N-Diisopropylaminoethyl-2- methoxyethyl ether (282)
O,O-Diethyl N,N-dimethylphosphoramidate (3, 88, 96)
O,O-Diethylethylphosphonothionate (159)
O,S-Diethyl methylphosphonothiolate (29)
O-3-Methylbutyl S-ethyl methylphosphonothiolate (57)
O-Cyclopentyl S-ethyl methylphosphonothiolate (143)
O-Ethyl S-2-ethylthioethyl methylphosphonothiolate (30)
O-Ethyl S-butyl isopropylphosphonothiolate (58)
O-Methyl S-pentyl methylphosphonothiolate (144)
O-Propyl propylthiophosphonate (sodium salt) (25, 279)
Propylphosphonic acid (4, 105, 171, 270)
S,S-Diethyl methylphosphonodithiolothionate (126)

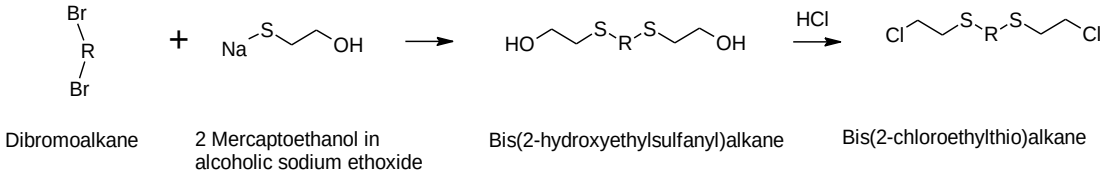
Schedule 1.A.4 Sulfur Mustards

2-Chloroethylchloromethylsulfide (CAS 2625-76-5)

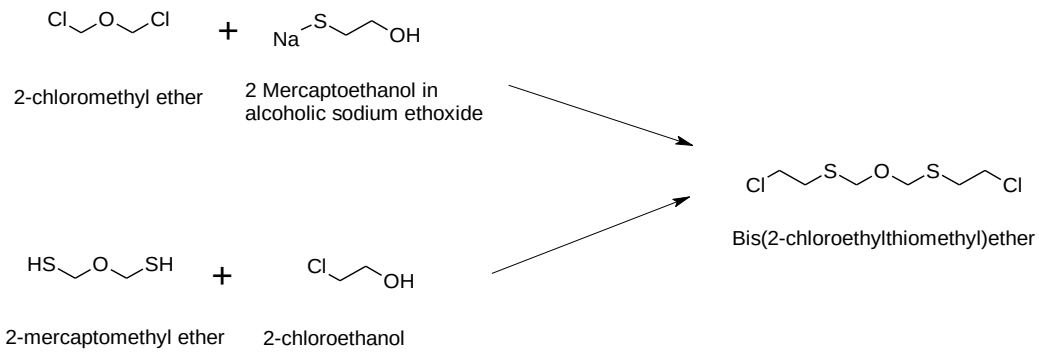


Mustard gas: Bis(2-chloroethyl)sulfide (CAS 505-60-2)





Bis(2-chloroethylthiomethyl)ether (CAS 63918-90-1)



O-Mustard: Bis(2-chloroethylthioethyl)ether (CAS 63918-89-8)

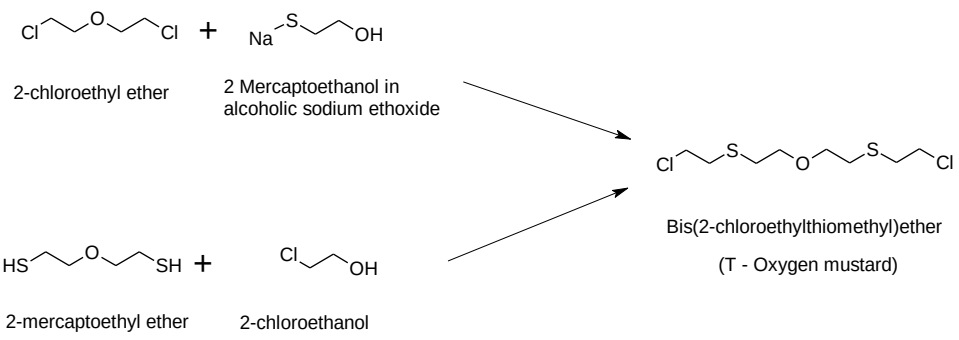


Figure 7. Synthetic pathways for Schedule 1.A.4 chemicals.[100,101]

In Figure 7: R = C1 – C5

1. Bis(2-chloroethylthio)methane (CAS 63869-13-6)
2. Sesquimustard: 1,2-Bis(2-chloroethylthio)ethane (CAS 3563-36-8)
3. 1,3-Bis(2-chloroethylthio)-n-propane (CAS 63905-10-2)
4. 1,4-Bis(2-chloroethylthio)-n-butane (CAS 142868-93-7)
5. 1,5-Bis(2-chloroethylthio)-n-pentane (CAS 142868-94-8)

Table 5. Schedule 1.A.4 compounds and related chemicals.

Precursors
1,2-Bis(2-hydroxyethylthio)ethane [3,6-dithia-1,8-octanediol] (174, 209)
1,3-Bis(2-hydroxyethylthio)propane (189)
1,4-Bis(2-hydroxyethylthio)-n-butane (240)
Bis(2-hydroxyethylthioethyl)ether (207)
Thiodiglycol (Bis(2-hydroxyethyl)sulfide) (27, 85, 180, 188, 196, 214, 223, 269)
Final Product
1,2-Bis(2-chloroethylthio)ethane [Sesquimustard] (6, 173, 204)
1,3-Bis(2-chloroethylthio)propane (7)
1,4-Bis(2-chloroethylthio)-n-butane (99)
1,5-Bis(2-chloroethylthio)pentane(8, 38)
Bis(2-chloroethyl)sulfide [Mustard gas] (67, 176, 201, 202, 206, 247)
Bis(2-chloroethylthioethyl)ether (203)
Hydrolysis/decontamination products [56-95, 101-105] :
1,2-Bis(2-hydroxyethylthio)ethane [3,6-dithia-1,8-octanediol] (174, 209)
1,3-Bis(2-hydroxyethylsulfonyl)propane (191)
1,3-Bis(2-hydroxyethylthio)propane (189)
1,4-Bis(2-hydroxyethylsulfonyl)-n-butane (100, 239)
1,4-Bis(2-hydroxyethylthio)-n-butane (240)
1,4-Dithiane (222, 256)
1,4-Thioxane (221, 257)
1,4-Thioxane oxide (258)
1,5-Bis(2-hydroxyethylsulfinyl)pentane (39)
1,5-Bis(vinylthio)-n-pentane (241)
Bis(2-hydroxyethyl)sulfone (72, 102)
Bis(2-hydroxyethylthioethyl)ether (207)
Bis(2-phenoxyethyl)sulfide (265)
Bis-[2-(2-hydroxyphenoxy)ethyl] sulfide (266)
Divinyl sulfone (261)
Divinyl sulfoxide (70, 178, 262)
Thiodiglycol (Bis(2-hydroxyethyl)sulfide) (27, 86, 180, 188, 196, 214, 223, 269)
Thiodiglycol sulfoxide (Bis(2-hydroxyethyl)sulfoxide) (60, 80)
Thiodiglycolic acid (215, 253)

Schedule 1.A.5 Lewisites

Lewisite 1: 2-Chlorovinyldichloroarsine (CAS 541-25-3)

Lewisite 2: Bis(2-chlorovinyl)chloroarsine (CAS 40334-69-8)

Lewisite 3: Tris(2-chlorovinyl)arsine (CAS 40334-70-1)

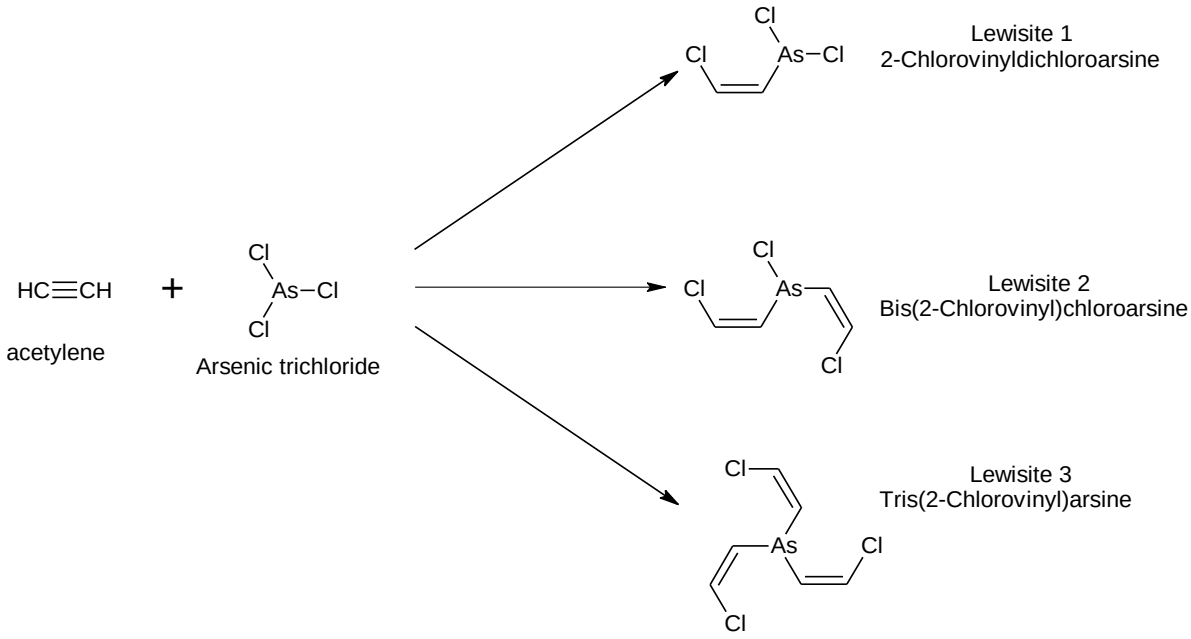


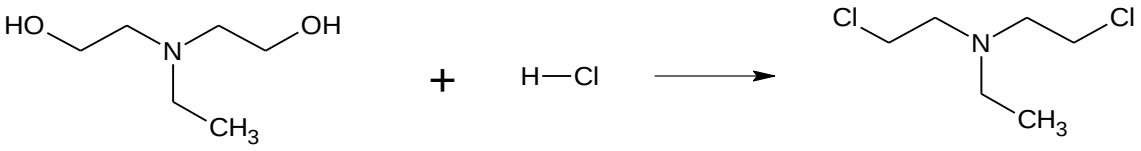
Figure 8. Synthetic pathways for Schedule 1.A.5 chemicals.[106]

Table 6. Schedule 1.A.5 compounds and related chemicals.

Precursors
Arsenic trichloride (175)
Final Products
2-Chlorovinyldichloroarsine (40, 62, 147) Bis(2-chlorovinyl)chloroarsine (63, 149, 177) Tris(2-chlorovinyl)arsine [Lewisite 3] (181)
Hydrolysis/decontamination products:[56-94]

Schedule 1.A.6 Nitrogen Mustards

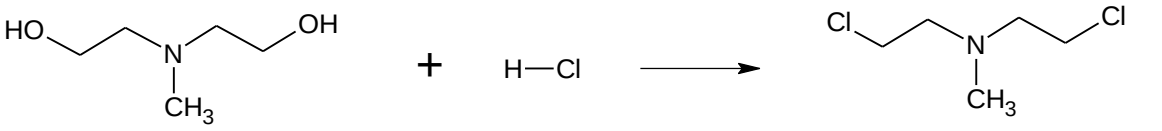
HN1: Bis(2-chloroethyl)ethylamine (CAS 538-07-8)



N-ethyldiethanolamine

Mustard, HN1
Bis(2-chloroethyl)ethylamine

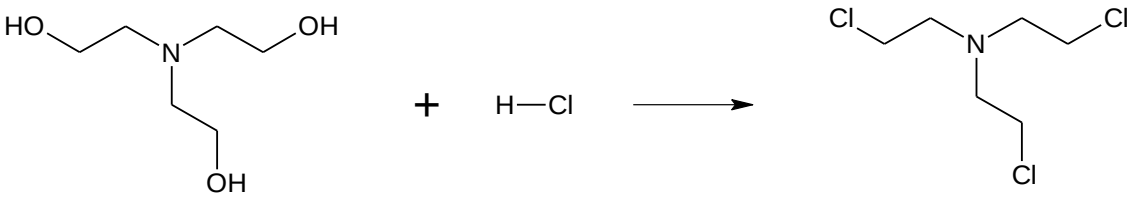
HN2: Bis(2-chloroethyl)methylamine (CAS 51-75-2)



N-methyldiethanolamine

Mustard, HN2
Bis(2-chloroethyl)methylamine

HN3: Tris(2-chloroethyl)amine (CAS 555-77-1)



Triethanolamine

Mustard, HN3
Tris(2-chloroethyl)amine

Figure 9. Synthetic pathways for Schedule 1.A.6 chemicals.[107]

Table 7. Schedule 1.A.6 compounds and related chemicals.

Precursors
Methyldiethanolamine (44, 111, 220, 237, 273)
Ethyldiethanolamine (42, 110, 179)
Triethanolamine (13, 45, 113, 114, 172, 195, 198, 254)
Final Products
Bis(2-chloroethyl)methylamine (168, 234)
Tris(2-chloroethyl)amine (200)
Hydrolysis/decontamination products:[56-91, 95, 102]
Methyldiethanolamine (44, 111, 220, 237, 273)
Ethyldiethanolamine (42, 110, 179)
Triethanolamine (13, 45, 113, 114, 172, 195, 198, 254)
Tris(2-tert-butyldimethylsilyloxyethyl)amine (199)
Tris(2-methoxyethyl)amine (197)
Tris(2-phenoxyethyl)amine (255)

Other scheduled chemicals

Table 8. Other scheduled compounds and related chemicals.

Precursor	**Schedule**
3-Quinuclidinol (118, 217, 263, 264, 288)	2.B.9
Benzilic acid (2,2-Diphenyl-2-hydroxyacetic acid (79, 218, 287)	2.B.8
Final Product	**Schedule**
Chloropicrin (64, 112, 116, 187, 275)	3.A.4
3-Quinuclidinyl benzilate (BZ) (28, 119, 284)	2.A.3
Hydrolysis/decontamination products [56-94] **:**	**Schedule**
Diphenylcarbonate (267)	N.S.

Change History of the ROP

1.0	11 Dec 2017	First Edition

List of Authors

Keith Norman (1.0)

Stephen Johnson (1.0)

List of Reviewers

Hugh Gregg (1.0)

Harri Kiljunen (1.0)

Chua Hoe Chee (1.0)



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A review of spiking chemicals used in the first 40 OPCW Proficiency Tests

Johnson, Stephen; Norman, Keith

2017-12-11
University of Helsinki
http://www.helsinki.fi/verifin/bluebook/Blue Book 2017_1st-ed.pdf
Norman K, Johnson S. (2017) A review of spiking chemicals used in the first 40 OPCW Proficiency Tests. In: Recommended operating procedures for CWC-related analysis, Finland: University of Helsinki, pp. 753-807

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