



OPCW

## Science for Diplomats at EC-83

# Chemical Weapons Sample Stability and Storage

12 October 13:30 – 14:45

Ooms Room

(light lunch available at 13:00)



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SAB-23/WP.2  
25 May 2016

# SAB Response to the Director-General's request to the SAB to provide further advice on CW sample stability and storage

Dr Christophe Curty  
SAB Member  
SPIEZ LABORATORY  
12.10.2016





# Agenda

- Background
- DG's request
- What is known?
- SAB response to the DG's request
- Conclusion





# Background Facts





# Background Investigation & Sampling



Federal Office for Civil Protection FOCP  
SPIEZ LABORATORY

12.10.2016  
Science for Diplomats



# Background Samples

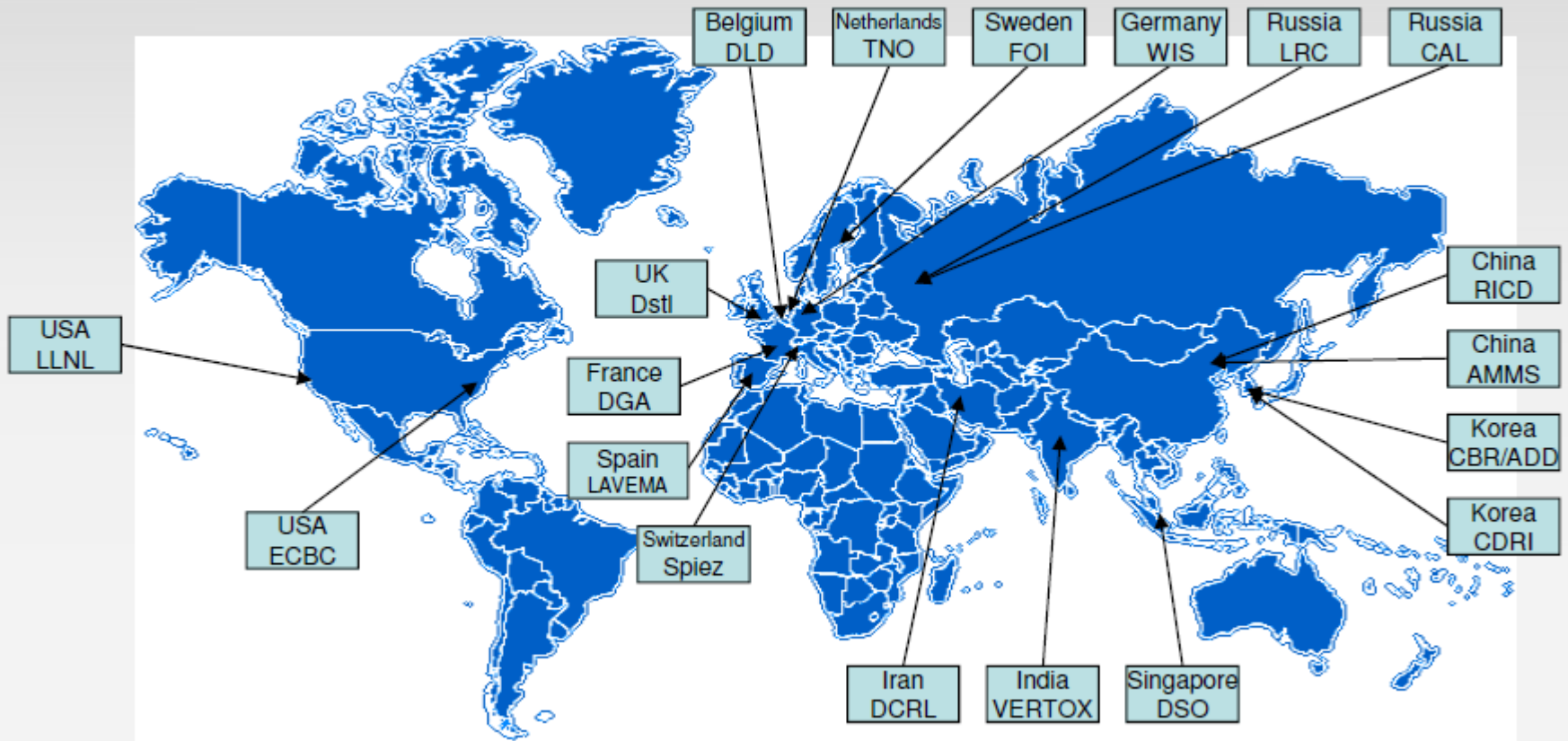




# Background

Analysis  $\Rightarrow$  Results

## OPCW Designated Laboratories





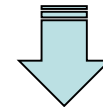
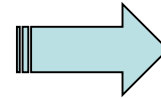
# Background

## Overview: from the facts to the analysis

### FACTS

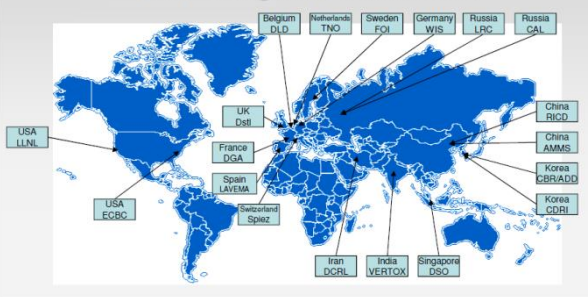


### MISSION

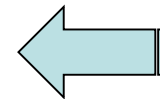
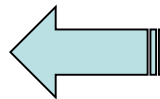


### ANALYSIS

#### OPCW Designated Laboratories



### RESULTS



### SAMPLES







# DG's request, 02.11.2015: Storage & Stability?



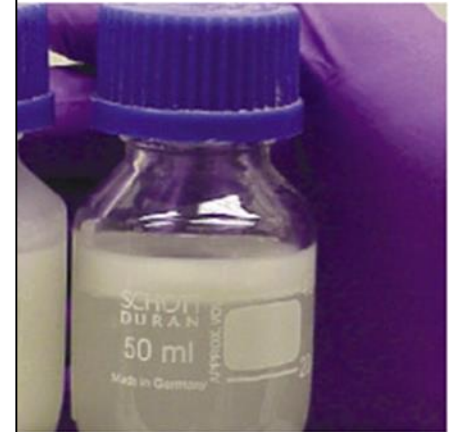


# DG's request, 02.11.2015: Storage & Stability?



## DIRECTOR-GENERAL'S REQUEST TO THE SCIENTIFIC ADVISORY BOARD TO PROVIDE ADVICE ON LONG-TERM STORAGE AND STABILITY OF SAMPLES COLLECTED IN RELATION TO POTENTIAL USE OF CHEMICAL WEAPONS

1. In order to be fully prepared to analyse any chemical potentially present in a wide range of types of samples in support of various operational missions, the OPCW must be able to store samples over several years and analyse those samples with high accuracy at any point in time.
2. In the context of the OPCW's investigations and fact-finding missions the Technical Secretariat has since 2013 received samples in relation to potential use of chemical weapons. These samples are stored at the OPCW Laboratory at room temperature or refrigerated at 4°C.
3. Sample types (whether current or future) – containing chemicals of interest, such as various nerve and blister agents as well as their immediate precursors and degradation products – may include in particular:
  - (a) Relatively pure samples;
  - (b) Liquid (including extracts) and solid samples containing either relatively high levels or trace levels of the chemicals of interest;
  - (c) Highly heterogeneous unprocessed samples – such as soil, metal fragments, paint chips, fragments of highly absorbent material, or wipes – containing either relatively high levels or trace levels of the chemicals of interest; and
  - (d) Biomedical samples: blood, plasma, urine, tissue.
4. The Director-General requests the Scientific Advisory Board (SAB) to address the following questions:
  - (a) Given the current storage conditions (set out in paragraph 2), how quickly and through what process could the types of samples mentioned in paragraph 3 degrade to a point where analysis of the samples would likely no longer return credible results?
  - (b) What are the best-practice conditions for long-term storage of the types of sample mentioned in paragraph 3?
  - (c) Given the best-practice storage conditions set out in the SAB's answer to question (b), how quickly and through what process could the types of sample mentioned in paragraph 3 degrade to a point where analysis of the samples would likely no longer return credible results?





# DG's request, 02.11.2015: Storage & Stability?

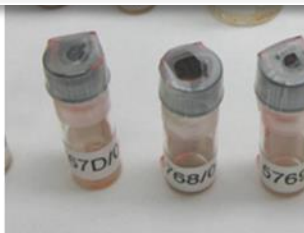


DIRECTOR-GENERAL'S REQUEST TO THE SCIENTIFIC ADVISORY BOARD TO PROVIDE ADVICE ON LONG-TERM STORAGE AND STABILITY OF SAMPLES COLLECTED IN RELATION TO POTENTIAL USE OF CHEMICAL WEAPONS

1. In order to be fully prepared to analyse any chemical potentially present in a wide range of types of samples in support of various operational missions, the OPCW must be able to store samples over several years and analyse those samples with high accuracy at any point in time.

Sample types

- Relatively pure samples
- Liquid (including extracts) and solid samples containing either relatively high levels or trace levels of the chemicals of interest
- Highly heterogeneous unprocessed samples – such as soil, metal fragments, paint chips, fragments of highly absorbent material, or wipes – containing either relatively high levels or trace levels of the chemicals of interest
- Biomedical samples: blood, plasma, urine, tissue



degrade to a point where analysis of the samples would likely no longer return credible results?

- (b) What are the best-practice conditions for long-term storage of the types of sample mentioned in paragraph 3?
- (c) Given the best-practice storage conditions set out in the SAB's answer to question (b), how quickly and through what process could the types of sample mentioned in paragraph 3 degrade to a point where analysis of the samples would likely no longer return credible results?



# DG's request, 02.11.2015: Storage & Stability?



DIRECTOR-GENERAL'S REQUEST TO THE SCIENTIFIC ADVISORY BOARD TO PROVIDE ADVICE ON LONG-TERM STORAGE AND STABILITY OF SAMPLES COLLECTED IN RELATION TO POTENTIAL USE OF CHEMICAL WEAPONS

1. In order to be fully prepared to analyse any chemical potentially present in a wide range of types of samples in support of various operational missions, the OPCW must be able to store samples over several years and analyse those samples with high accuracy at any point in time.

Questions?

- Given the current storage conditions (set out in paragraph 2), how quickly and through what process could the types of sample mentioned in paragraph 3 degrade to a point where analysis of the samples would likely no longer return **credible results**?
- What are the **best-practice** conditions for long-term storage of the types of sample mentioned in paragraph 3?
- Given the best-practice storage conditions set out in the SAB's answer to question (b), **how quickly** and through what process could the types of sample mentioned in paragraph 3 degrade to a point where analysis of the samples would likely no longer return **credible results**?



- (c) Given the best-practice storage conditions set out in the SAB's answer to question (b), how quickly and through what process could the types of sample mentioned in paragraph 3 degrade to a point where analysis of the samples would likely no longer return credible results?



# “Credible results”

Comment



- OPCW Proficiency Tests
- ISO 17025
- National Accreditation

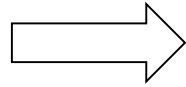
«The SAB notes that the analytical findings of the Designated Laboratories (...) will always be scientifically accurate (...), the findings will always return ‘credible results’.»



# Storage & Stability: what is known?



Degradation



Rotting

**NATURAL PROCESS**



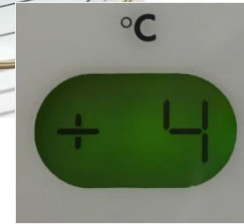
# Storage & Stability: what is known? Influenced by?





# Storage & Stability: what is known? Influenced by?

- Composition
- Temperature
- Packaging
- Atmosphere
- Duration
- Light
- Moisture
- ...







# Storage & Stability : what is known? Chemistry

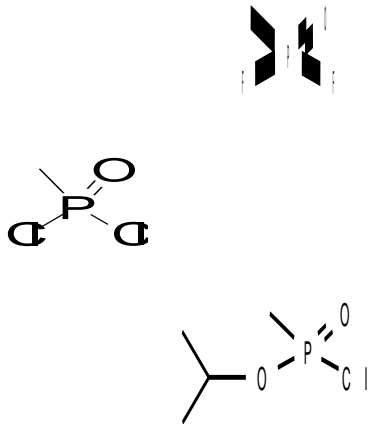
- Chemical
- Composition of sample
- Temperature
- Atmosphere
- Packaging
- Duration
- Light
- Moisture
- ...



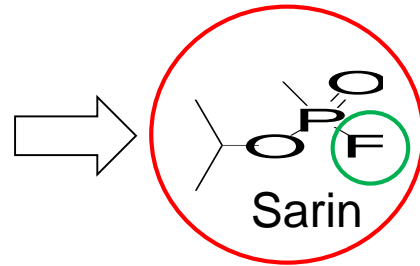


# Storage & Stability: what is known? Chemistry

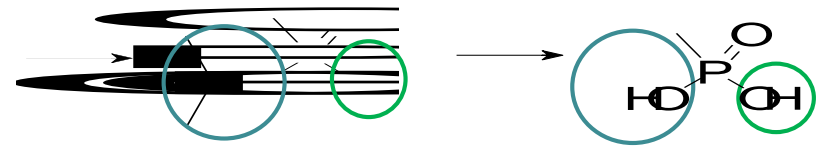
## Preparation



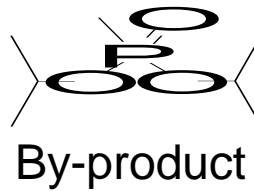
## CWA



## Degradation



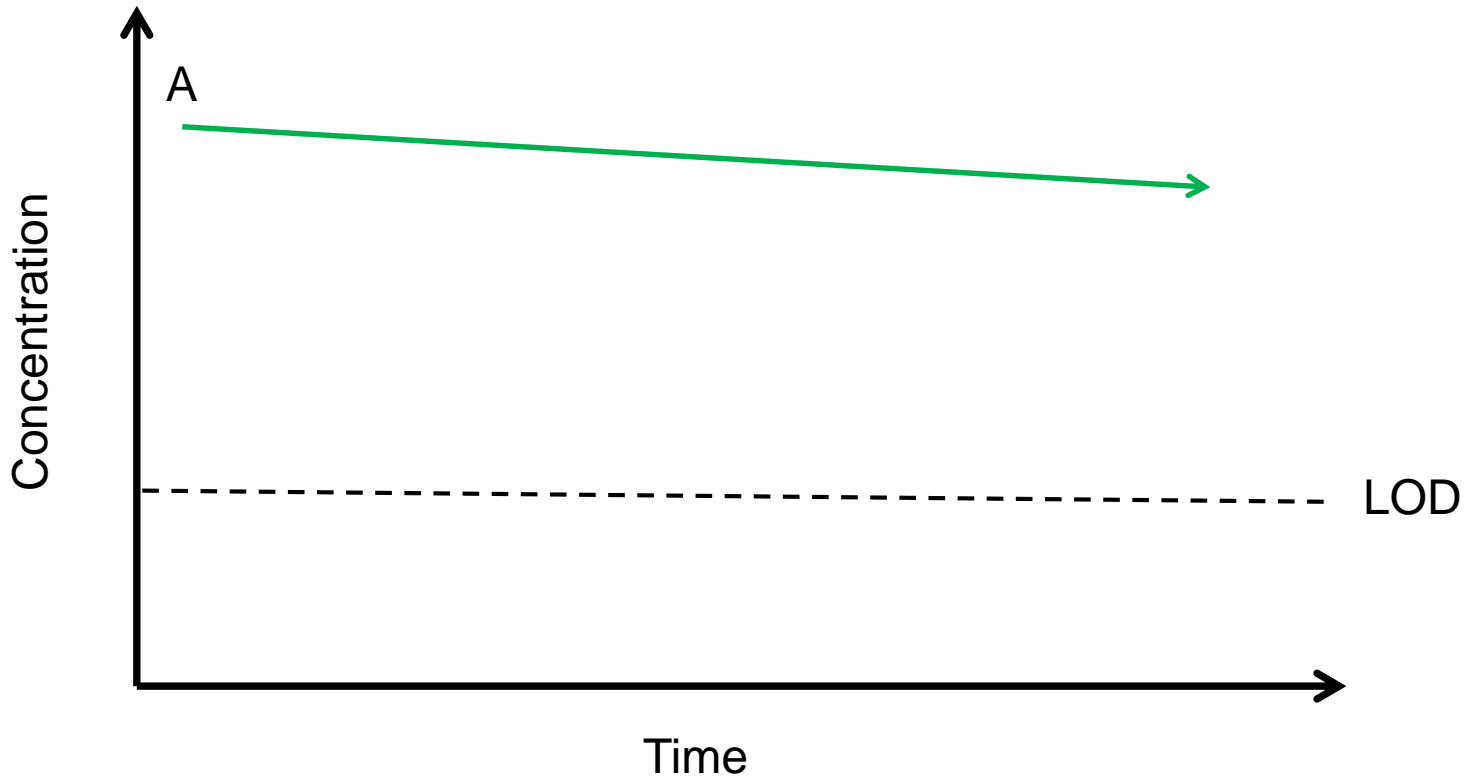
NATURAL PROCESS





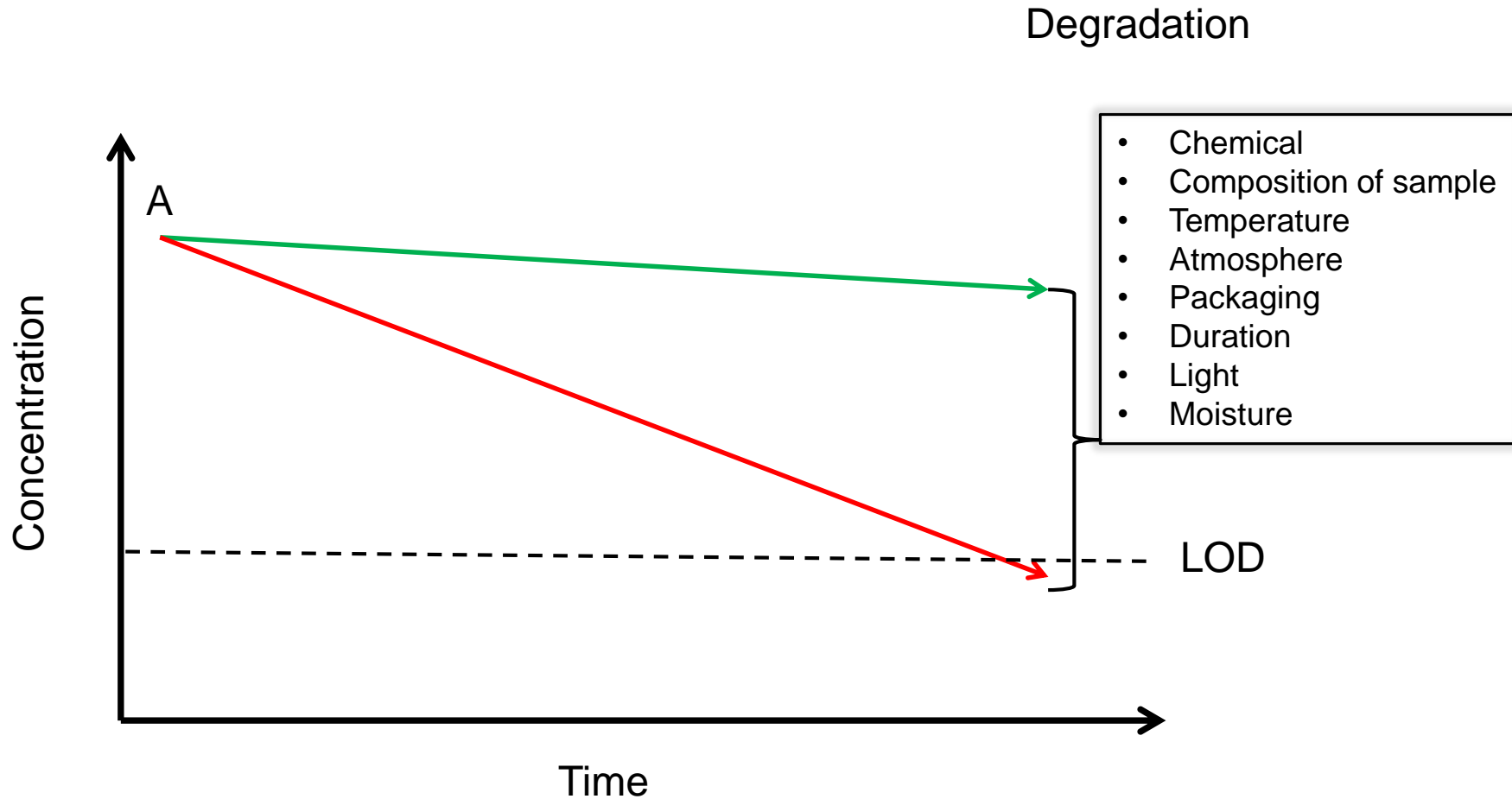
# Storage & Stability: what is known? Chemistry

Degradation



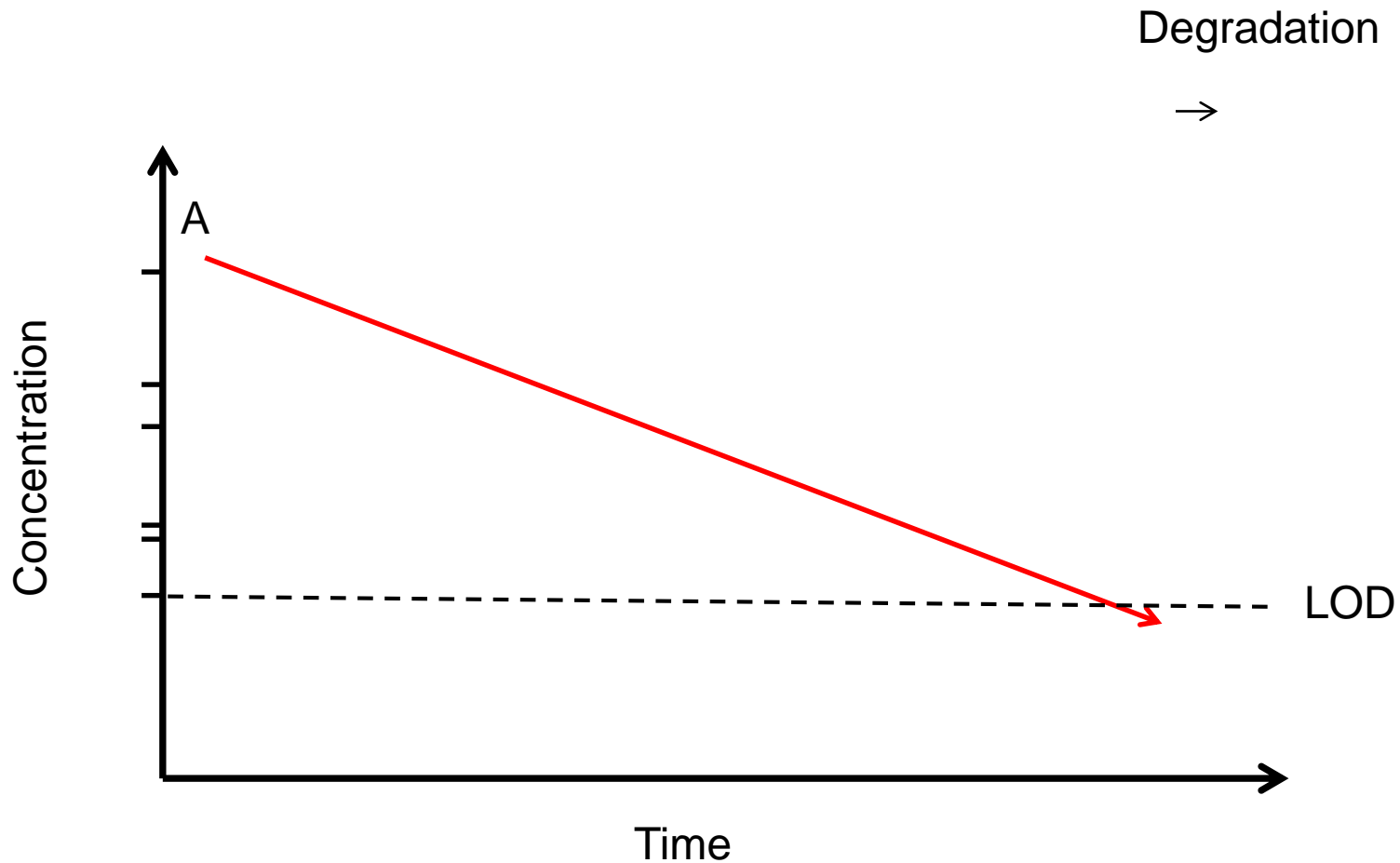


# Storage & Stability: what is known? Chemistry



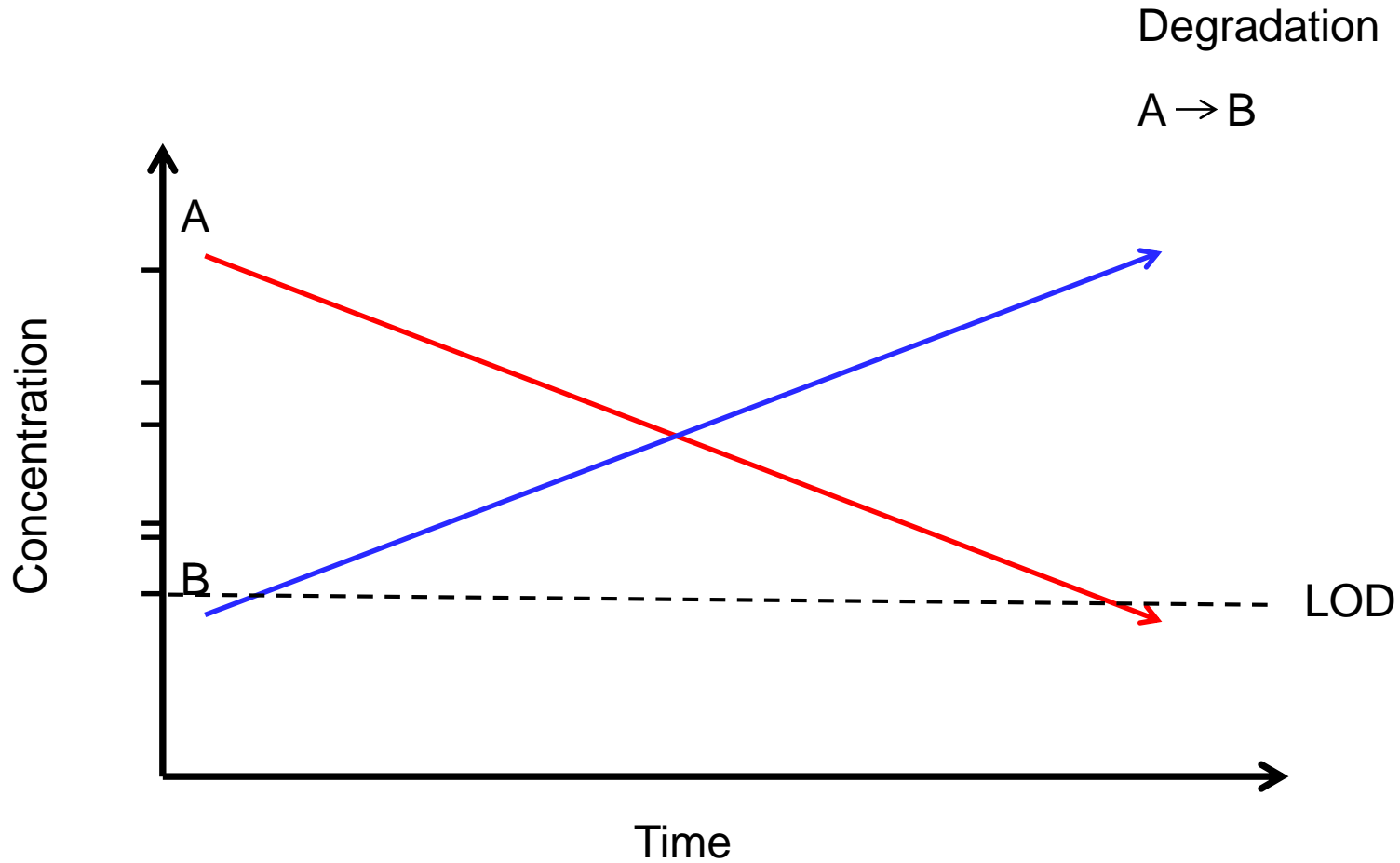


# Storage & Stability: what is known? Chemistry



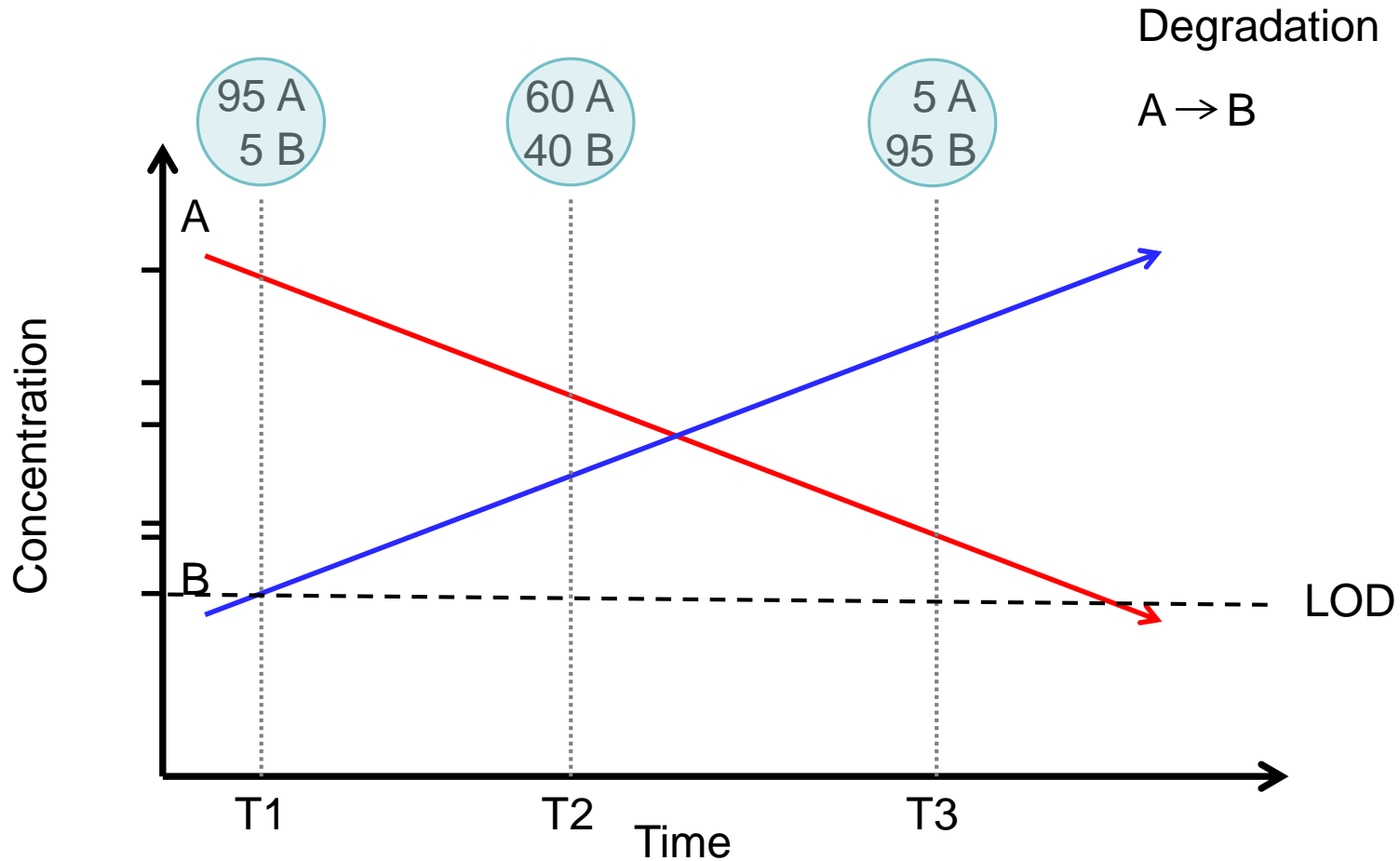


# Storage & Stability: what is known? Chemistry



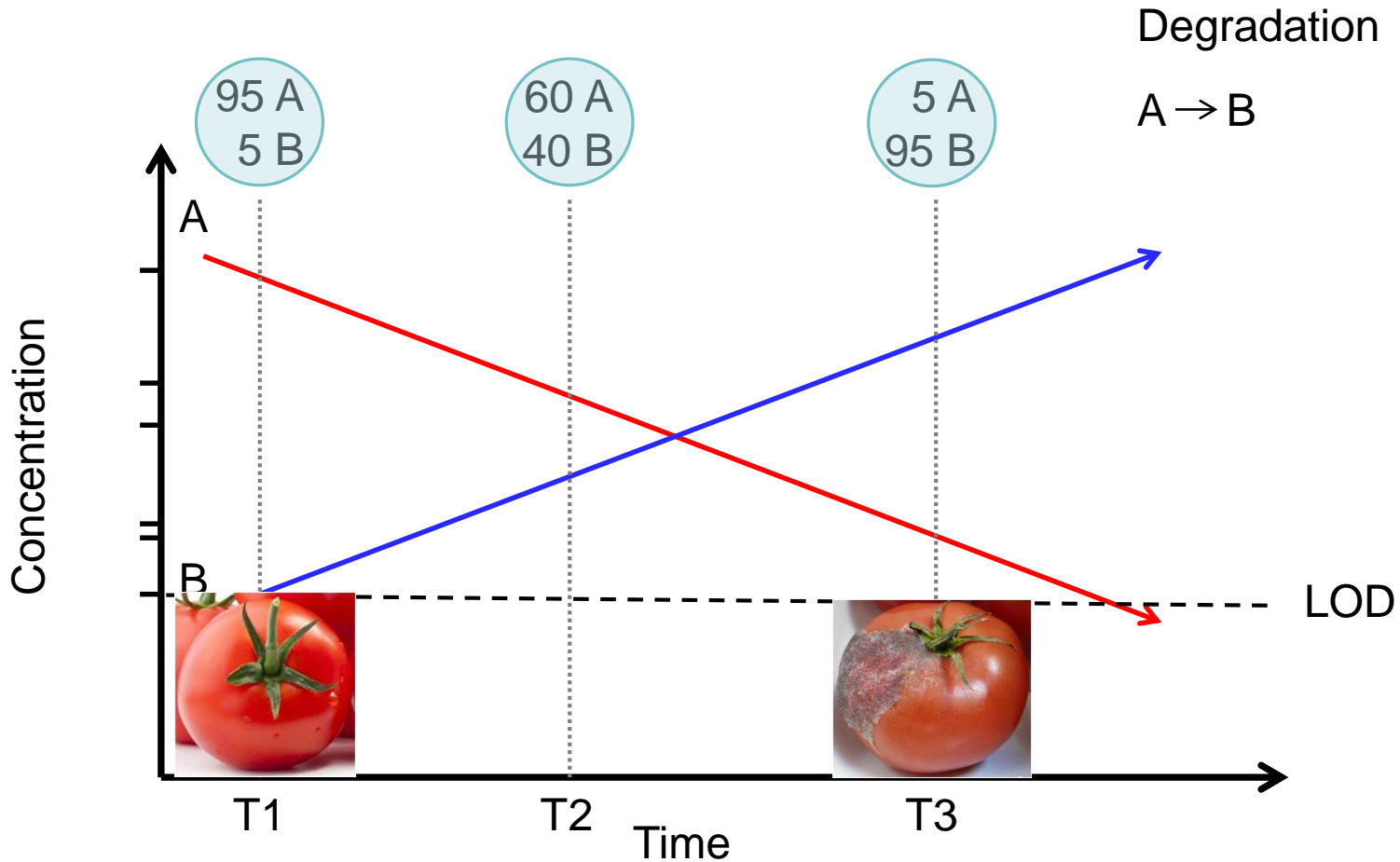


# Storage & Stability: what is known? Chemistry





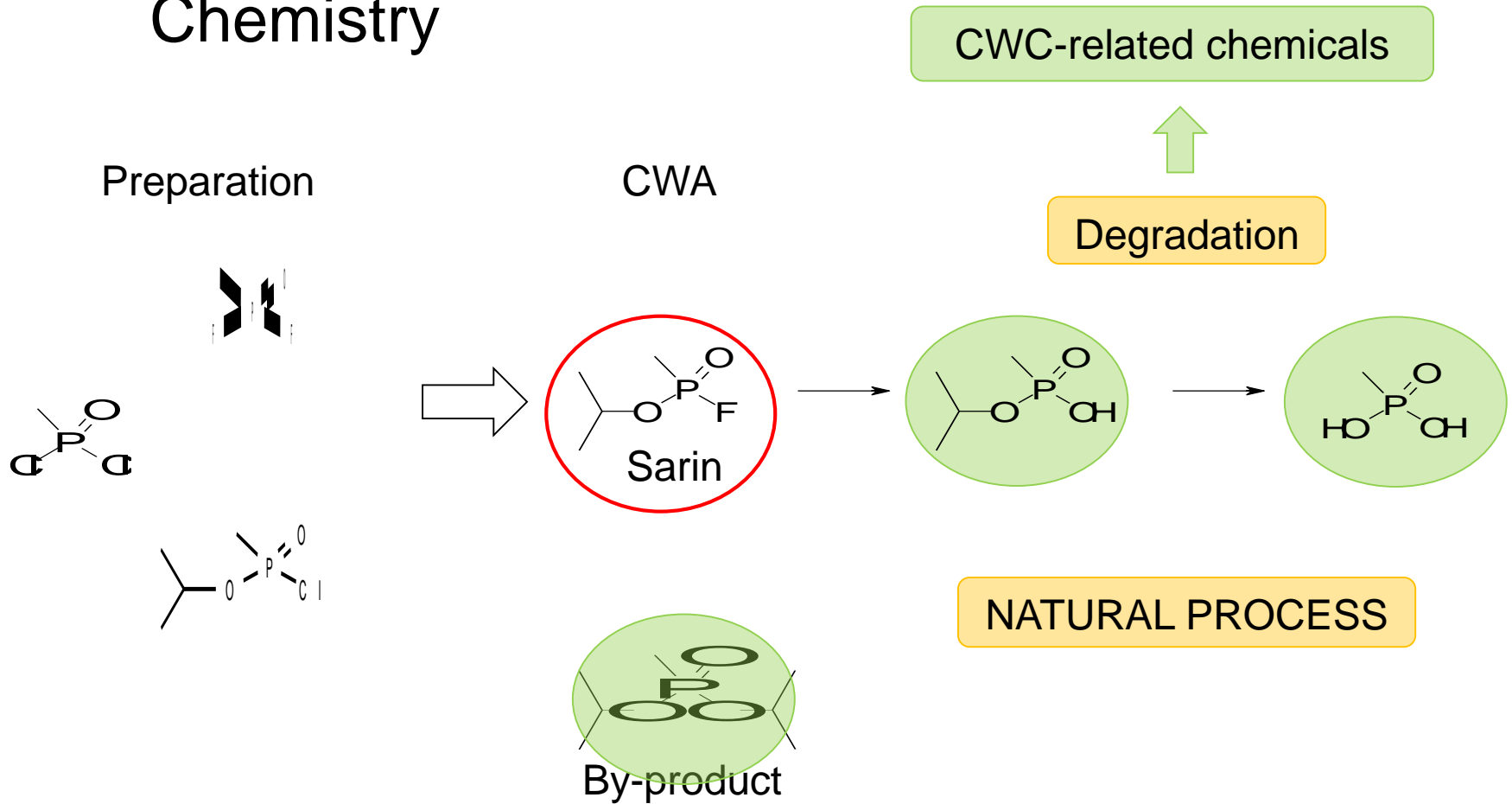
# Storage & Stability: what is known? Chemistry







# Storage & Stability: what is known? Chemistry





# Storage & Stability: what is known? Chemistry

Table 2. Estimated number of possible chemicals that can be derived from the definitions for scheduled chemicals contained in the Annex on Chemicals of the CWC not counting corresponding protonated or alkylated salts, where this is applicable

Schedule number	(Estimated) number of chemicals	Schedule number	(Estimated) number of chemicals	Schedule number	Number of chemicals
1.A.1	>20 000 <sup>a</sup>	2.A.1	1	3.A.1	1
1.A.2	>50 000 <sup>a</sup>	2.A.2	1	3.A.2	1
1.A.3	>200 000 <sup>a</sup>	2.A.3	1	3.A.3	1
1.A.4	9	2.B.4	Millions	3.A.4	1
1.A.5	3	2.B.5	20 <sup>b</sup>	3.B.5	1
1.A.6	3	2.B.6	100	3.B.6	1
1.A.7	1	2.B.7	1	3.B.7	1
1.A.8	1	2.B.8	1	3.B.8	1
1.B.9	4	2.B.9	1	3.B.9	1
1.B.10	>200 000 <sup>a</sup>	2.B.10	10	3.B.10	1
1.B.11	1	2.B.11	8	3.B.11	1
1.B.12	1	2.B.12	10	3.B.12	1
-	-	2.B.13	1	3.B.13	1
-	-	2.B.14	1	3.B.14	1
-	-	-	-	3.B.15	1
-	-	-	-	3.B.16	1
-	-	-	-	3.B.17	1

<sup>a</sup>Including branched chains and cyclo alkane chains, not including bicyclo alkane chains and stereoisomers and not including corresponding protonated and alkylated salts

<sup>b</sup>Chemical Weapons Convention Chemicals Analysis: Sample Collection, Preparation and Analytical Methods, Ed. M. Mesilaakso, John Wiley & Sons, 2005.



# Storage & Stability: what is known? Chemistry

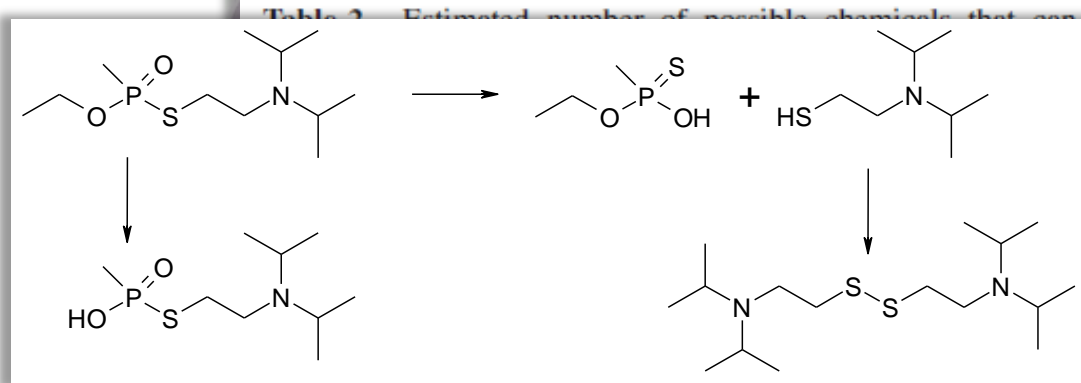
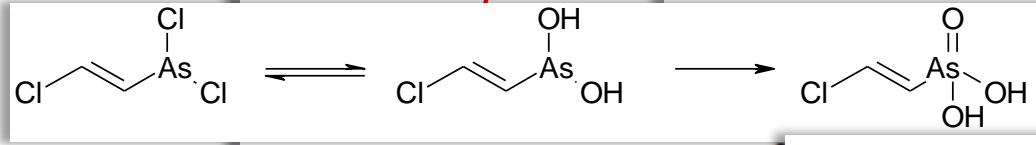
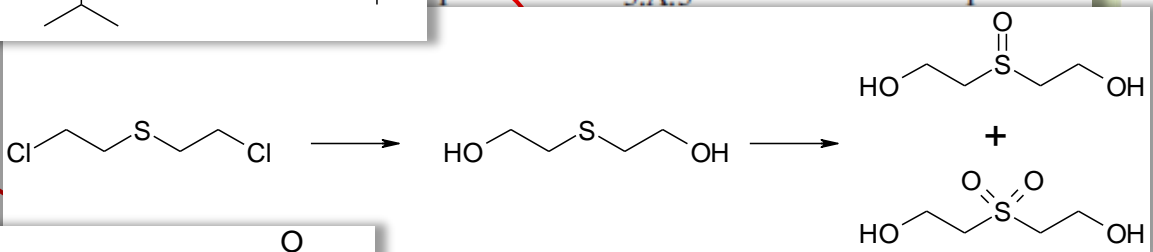


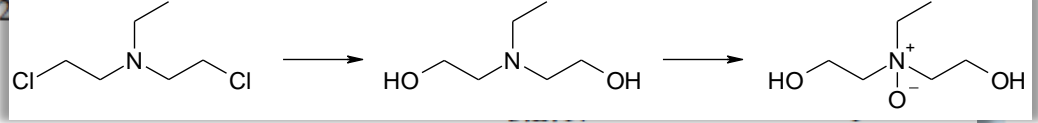
Table 2. Estimated number of possible chemicals that can be derived from the definitions for scheduled chemicals (not counting corresponding protonated or alkylated

Schedule number	Number of chemicals
3.A.1	1
3.A.2	1
3.A.3	1

1.A.5	3
1.A.6	3
1.A.7	1
1.A.8	1
1.B.9	4



8	3.B.11	1
10	3.B.12	1
1	3.B.13	1



<sup>a</sup>Including branched chains and cyclo alkane chains, not including bicyclo alkane chains and stereoisomers and not including corresponding protonated and alkylated salts

Chemical Weapons Convention Chemicals Analysis: Sample Collection, Preparation and Analytical Methods, Ed. M. Mesilaakso, John Wiley & Sons, 2005.



# Response to the DG's request



**OPCW**

**Scientific Advisory Board**

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Twenty-Third Session  
18 – 22 April 2016

SAB-23/WP.2  
25 May 2016  
ENGLISH only

**RESPONSE TO THE DIRECTOR-GENERAL'S REQUEST TO  
THE SCIENTIFIC ADVISORY BOARD TO PROVIDE FURTHER ADVICE ON  
CHEMICAL WEAPONS SAMPLE STABILITY AND STORAGE**



# Response to the DG's request


**OPCW** Scientific Advisory Board  
 Twenty-Third Session  
 18 – 22 April 2016  
 SAB-23/WP.2  
 25 May 2016  
 ENGLISH only  
**RESPONSE TO THE DIRECTOR-GENERAL'S REQUEST TO THE SCIENTIFIC ADVISORY BOARD TO PROVIDE FURTHER ADVICE ON CHEMICAL WEAPONS SAMPLE STABILITY AND STORAGE**

- Review of > 180 scientific papers

**RCM** RCM  
**AOC** Applied Organometallic Chemistry  
**Journal of the Society of Chemical Engineers**  
**INDUSTRIAL WASTE RESOURCE GUIDELINES**  
**SAMPLING AND ANALYSIS OF WATERS, WASTEWATERS AND WASTES**

- Questionnaire to Designated Laboratories

**Questionnaire on the storage of samples in relation to the potential use of chemical weapons**

1. Please provide details of storage conditions used at your organisation for pure reference chemicals (chemical warfare agents, precursors, synthesis by-products, and degradation products) including container type, temperature, use of any stabilising materials or other special conditions associated with storage and/or packaging. Please provide an estimate of maximum storage times after which the reference materials degrade and are no longer fit for purpose. In the comment section, please provide details of any evidence for these estimates.

Sample type	Best practice storage conditions (incl. container type, temperature, use of stabilisers or any special conditions associated with storage and/or packaging)	Estimate of maximum storage times after which analysis of the samples is unlikely to show the intact original chemical(s) of interest	Comment (including details of evidence base for the estimate of maximum storage times)
Commercially available pure chemical			
Synthesised over-made pure chemicals, including Schedule and non-Schedule chemicals			
Solutions of commercially available and synthesised over-made pure chemicals			

2. Please provide details of storage conditions that you regard as best practice for the following sample types, in relation to potential use of chemical weapons. Please provide an estimate of maximum storage times after which analysis is unlikely to show the intact original chemical(s).

Sample type	Best practice storage conditions (incl. container type, temperature, use of stabilisers or any special conditions associated with storage and/or packaging)	Estimate of maximum storage times after which analysis of the samples is unlikely to show the intact original chemical(s) of interest	Comment (including details of evidence base for the estimate of maximum storage times)
Organic liquid samples containing chemical warfare agents			
Aqueous liquid samples containing chemical warfare agents			
Solid and/or highly heterogeneous impregnated samples containing chemical warfare agents, including: wood, soil, vegetation, wood, plaster/plasterboard, brickwork, wall, fragment, clothing, rope, cord, aluminium (e.g. Chita, Tapes), Air samples			

3. In the management of the storage of the samples part of the accreditation/quality assurance at your organisation? If yes, which accreditation system is in use and what are the recommendations regarding sample management?

4. Are you aware of any emerging technologies that could be used to store/package samples more effectively (e.g. blood spot papers, vacuum packing, or flame-sealed samples for liquid samples)?

5. Which further approaches/strategies would help reduce the effect of sample storage on the stability of the chemicals of interest? Please consider aspects of the storage of the samples before and after the analytical work.

Chemical	Type	Storage Condition	until assignment completed	manufacturer's recommendation	up to 2 weeks	up to 1 month	several months	up to 3 months	up to 6 months	at least 6 months	up to 1 year	several years	up to 3 years	up to 5 years	more than 10 years
Sample, organic solutions	General	refrigerator													
		freezer (-18°C)													
Sample, aqueous solutions	General	glass container													
		original container													
Sample, solid/heterogeneous	General	sealed													
		refrigerator													
Sample, air	General	glass container													
		HDPE container													
		original container													
		sealed													
		refrigerator													
		freezer (-18°C)													



# Executive Summary

**1. Given the current storage conditions in the OPCW Laboratory, how quickly and through what process could the aforementioned types of sample degrade to a point where analysis of the samples would no longer return credible results?**



## Storage conditions at the OPCW Laboratory

→ RT and 4°C

- Always credible analytical results
- Depends on many factors!
- Hydrolysis, oxidation and polymerisation
- Inevitable and natural (weeks to months!)
- Reduce time between collection and analysis



# Executive Summary

1. Given the current storage conditions in the OPCW Laboratory, how quickly and through what process could the aforementioned types of sample degrade to a point where analysis of the samples would no longer return credible results?

Process

**Recommendation 1.** Samples should be analysed as soon after collection as possible and the need for storage eliminated or, less favourably, the storage time minimised. **Prompt analysis** should be viewed as urgent, as the intact original chemicals will provide the strongest basis for confirming the use of chemicals prohibited by the Chemical Weapons Convention. (This is because the sample stability, and potential impacts of any matrix or environmental factors on the stability of any CWC-relevant chemicals in the sample, will not be known prior to analysis.)

**Recommendation 2.** **Further work** on the storage of samples just after sampling and during transport to the OPCW Laboratory, sample handling during splitting, handling and storage of samples at the OPCW Laboratory, should be pursued.



# Executive Summary

## 2. What are the best-practice conditions for long term-storage of the different types of sample?

**Recommendation 3.** Commercial chemical samples should be stored in glass containers with Teflon-lined caps in the dark: those in

- (i) Schedules 1A01, 1A02, 1A03, 1A06, 1B09, 1B10, 1B11 and 1B12 at  $-18\text{ }^{\circ}\text{C}$  under argon (to enable stability for 5-10 years).
- (ii) Schedules 1A04 and 1A05 at room temperature (for stability  $> 10$  years).
- (iii) Schedule 1A08 (ricin) as a precipitate in 6 M ammonium sulfate at  $4\text{ }^{\circ}\text{C}$  (for stability  $> 10$  years).

Types of sample





# Executive Summary

## 2. What are the best-practice conditions for long term-storage of the different types of sample?

**Recommendation 3.** Commercial chemical samples should be stored in glass containers with Teflon-lined caps in the dark: those in

**Recommendation 4.** Extracts of chemicals should be made in dichloromethane and stored in glass containers at 4 °C with Teflon-lined caps in the dark, to ensure stability of the intact original chemical for up to one year. (Swabs or wipes should be analysed within one month of collection or otherwise disposed of due to likely storage instability; wherever possible they should be extracted as soon as possible into dichloromethane and the extracts stored instead).

(iii) Schedule 1A08 (HCN) as a precipitate in 0.1 M ammonium sulfate at 4 °C (for stability > 10 years).

Types of sample



# Executive Summary

## 2. What are the best-practice conditions for long term-storage of the different types of sample?

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**Recommendation 4.** Extracts of chemicals should be made in dichloromethane and stored in glass containers at 4 °C with Teflon-lined caps

**Recommendation 5.** Highly heterogeneous unprocessed samples – such as soil, metal fragments, paint chips, or fragments of highly absorbent material – containing relatively high levels or trace levels of the chemicals of interest, should be stored in sealed glass or high-density polyethylene containers at -18 °C, to guarantee the stability of the samples for up to 6 months.

Types of sample



# Executive Summary

## 2. What are the best-practice conditions for long term-storage of the different types of sample?

Types of sample

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**Recommendation 5.** Highly heterogeneous unprocessed samples – such as soil, metal fragments, paint chips, or fragments of highly absorbent

**Recommendation 6.** Biomedical samples – for example, urine or plasma – should be stored in polypropylene or polyethylene terephthalate containers in a freezer at -80 °C (except for whole blood which should be refrigerated at 4 °C) to ensure the integrity of the samples for as long as possible (up to several years).



# Executive Summary

## 2. What are the best-practice conditions for long term-storage of the different types of sample?

Types of sample

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**Recommendation 5.** Highly heterogeneous unprocessed samples – such as soil, metal fragments, paint chips, or fragments of highly absorbent

**Recommendation 6.** Biomedical samples – for example, urine or plasma – should be stored in polypropylene or polyethylene terephthalate

**Recommendation 7.** Larger volumes of chemicals/samples should be split into subsamples and the subsamples used for repeated analytical manipulations. This will reduce the number of warming-cooling cycles the samples have to encounter. This is important especially for materials stored in a freezer or deep freeze (-80 °C). It will also help to minimise degradation of the chemical(s) in the unused portions of samples.



# Executive Summary

## 2. What are the best-practice conditions for long term-storage of the different types of sample?

Types of sample

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**Recommendation 7.** Larger volumes of chemicals/samples should be split into subsamples and the subsamples used for repeated analytical

**Recommendation 8.** Samples of neat Scheduled chemicals required for long-term banking within the OPCW Laboratory should be flame-sealed in glass ampoules; the use of the flame-sealed ampoule technique appears to offer some storage and shipping advantages for which there is an evidence base.



# Executive Summary

3. Given these best-practice storage conditions, how quickly and through what type of process could the different types of samples degrade to a point where analysis of the samples would no longer return credible results?

- Always credible analytical results
- Inevitable and natural (weeks to months!)
- Extend “life” of original chemical
- Chemical forensics

**Recommendation 9.** The Technical Secretariat should monitor advances in sampling and analysis, and with the SAB, any new innovations relevant to chemical forensics.

**Recommendation 10.** A reference sample collection at the OPCW Laboratory should be kept to provide a range of chemical forensic options for current and future samples suspected of containing CWC-relevant chemicals.<sup>7</sup>

Future work



# Conclusion

Based on this review of processes by which CWC-relevant chemicals degrade, it is assessed that it is difficult, given the incomplete knowledge worldwide of the fate of CWAs in different matrices, to specify precisely when analysis of a sample ‘would likely no longer identify the intact original chemicals’. Analytical results, produced under stringent quality control in OPCW Designated Laboratories, are always ‘credible’. The main conundrum is how long after sample collection and storage will key markers of CWA use, or other CWC-prohibited activity, remain detectable? The passage of time will certainly lower the probability of identifying the original intact chemical(s), but the degradation products will remain detectable, proving CWA use.

