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)

SAB-23/WP.2
25 May 2016

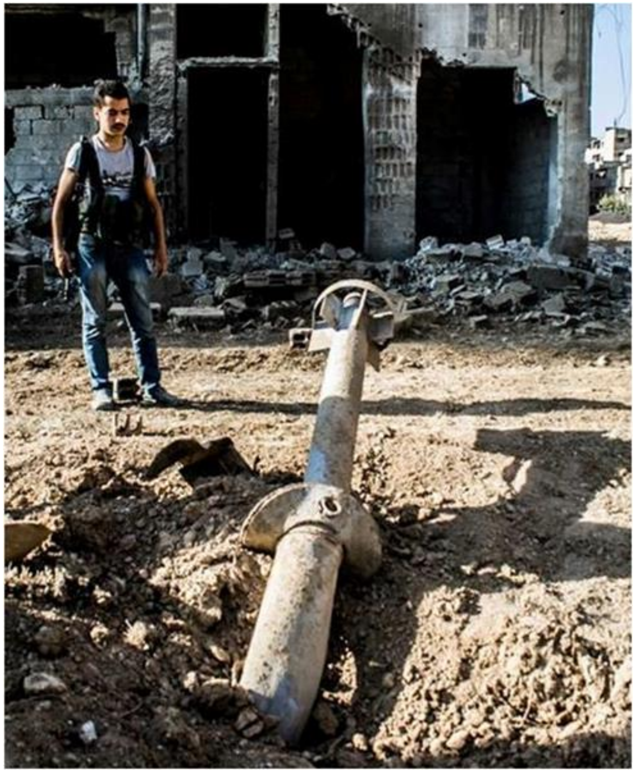
SAB Response
to the Director-General's request to the SAB to provide further advice on CW sample stability and storage

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

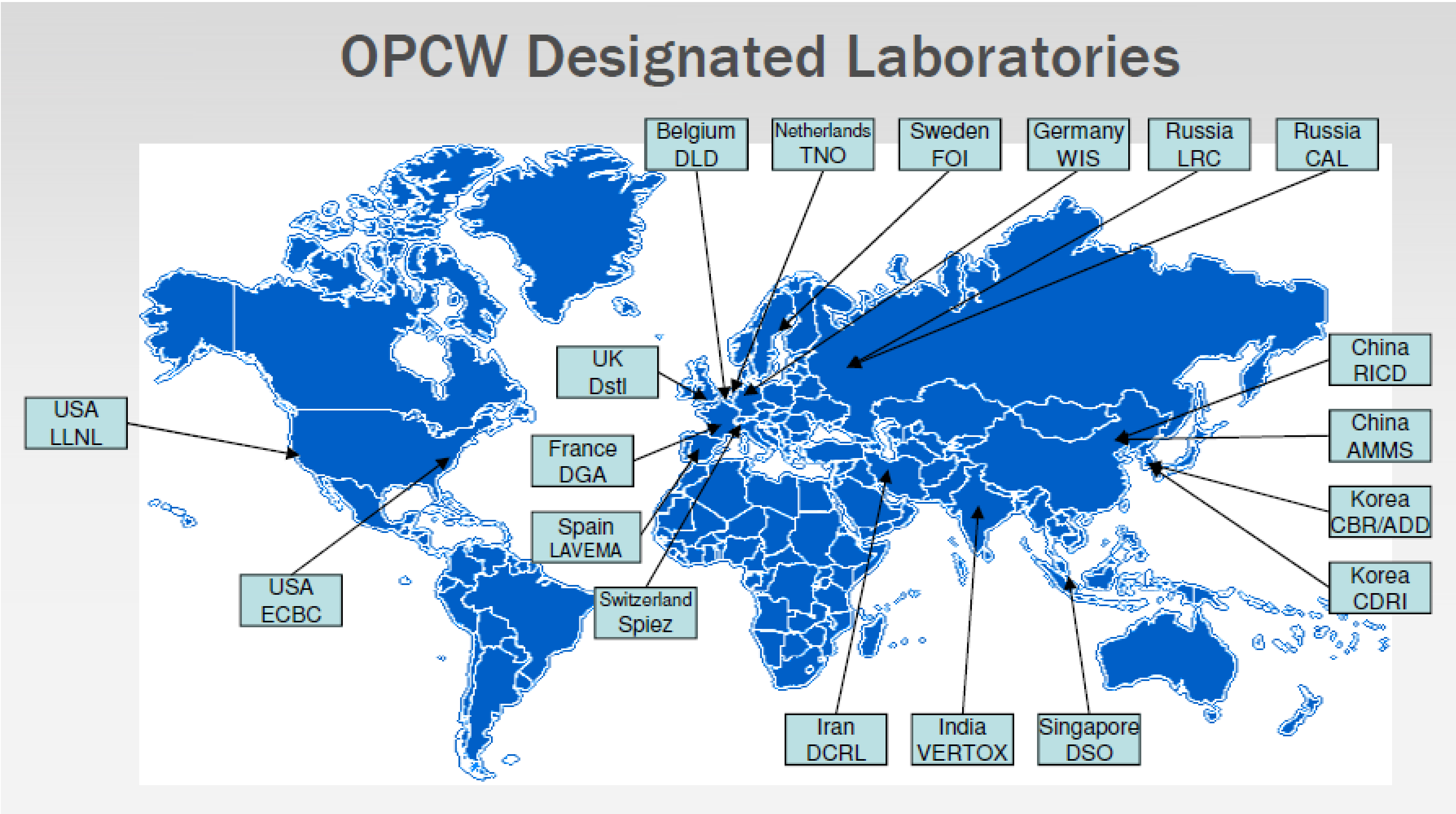
Background
Facts



Background
Investigation & Sampling

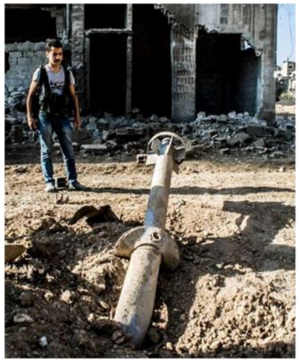
Background
Samples

Background
Analysis ⟹ Results



Background
Overview: from the facts to the analysis

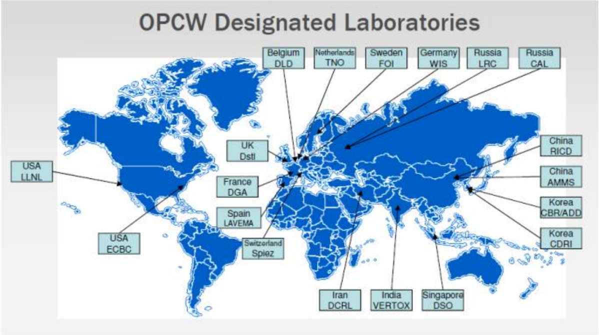
FACTS



MISSION

SAMPLES

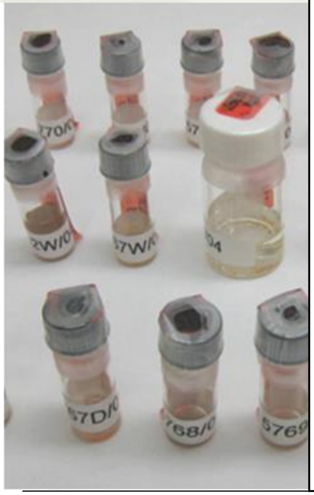
ANALYSIS



RESULTS

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.

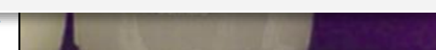
Sample types

- 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?

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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?

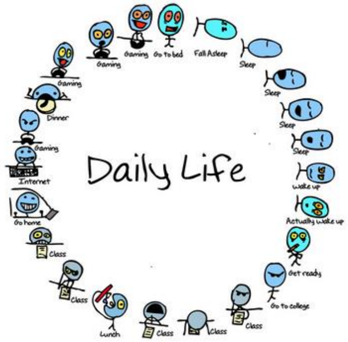
“Credible results”

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?



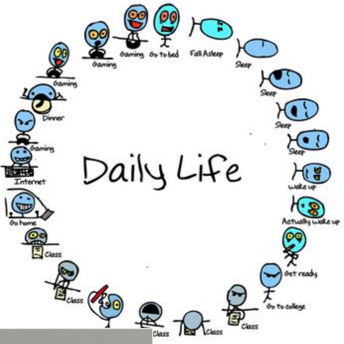
Degradation

Rotting

NATURAL PROCESS

Storage & Stability: what is known? Influenced by?

Storage & Stability: what is known? Influenced by?



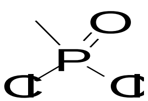
- Composition
- Temperature
- Packaging
- Atmosphere
- Duration
- Light
- Moisture
- …

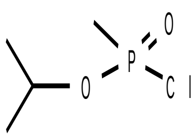
Storage & Stability : what is known? Chemistry

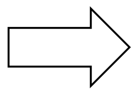
- Chemical
- Composition of sample
- Temperature
- Atmosphere
- Packaging
- Duration
- Light
- Moisture
- …

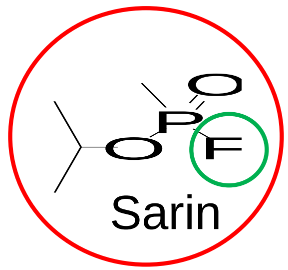
Storage & Stability: what is known?
Chemistry

Preparation | **CWA** | **Degradation**

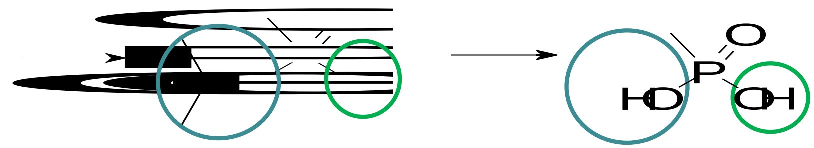




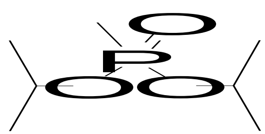




Sarin



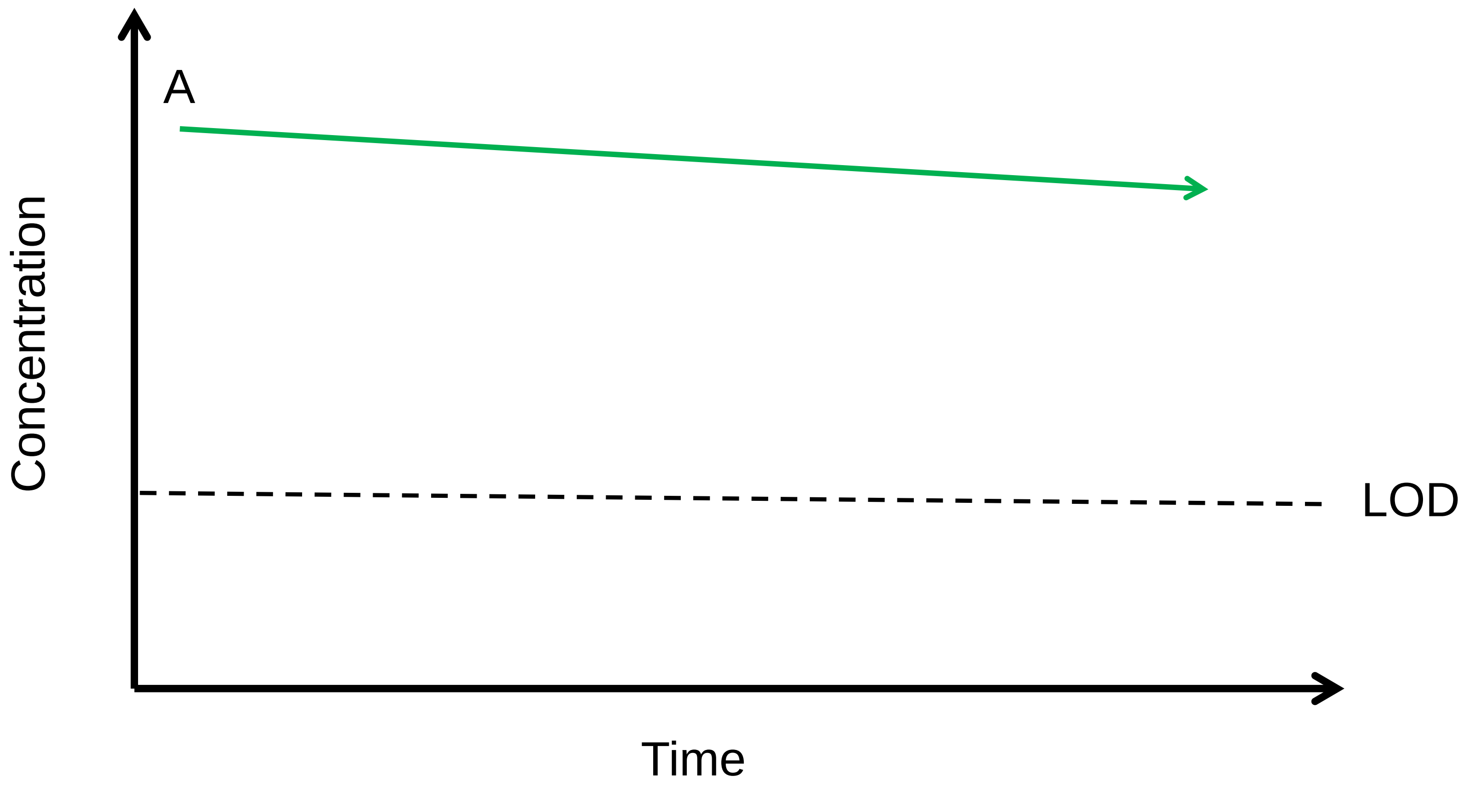
NATURAL PROCESS



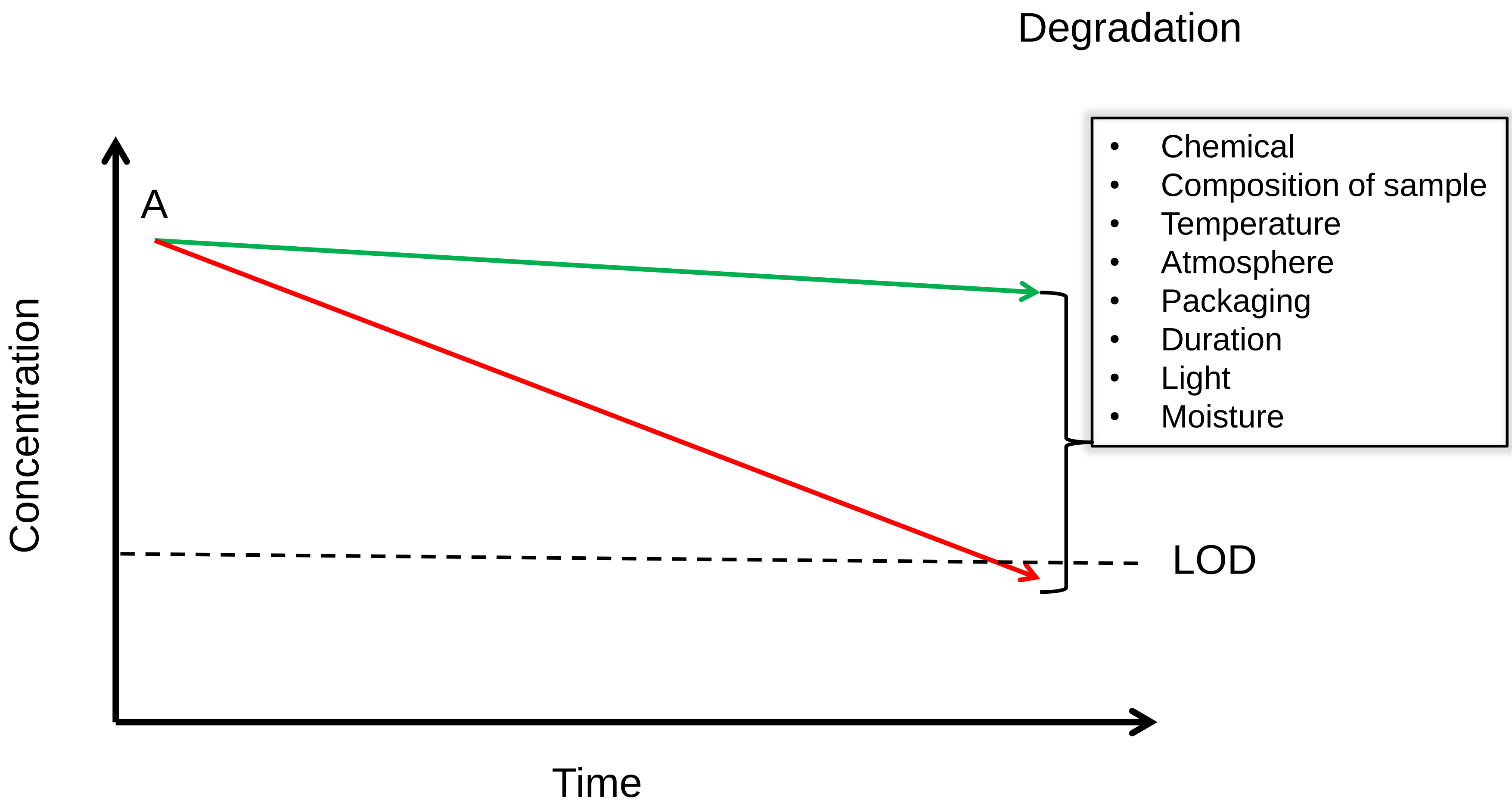
By-product

Storage & Stability: what is known? Chemistry

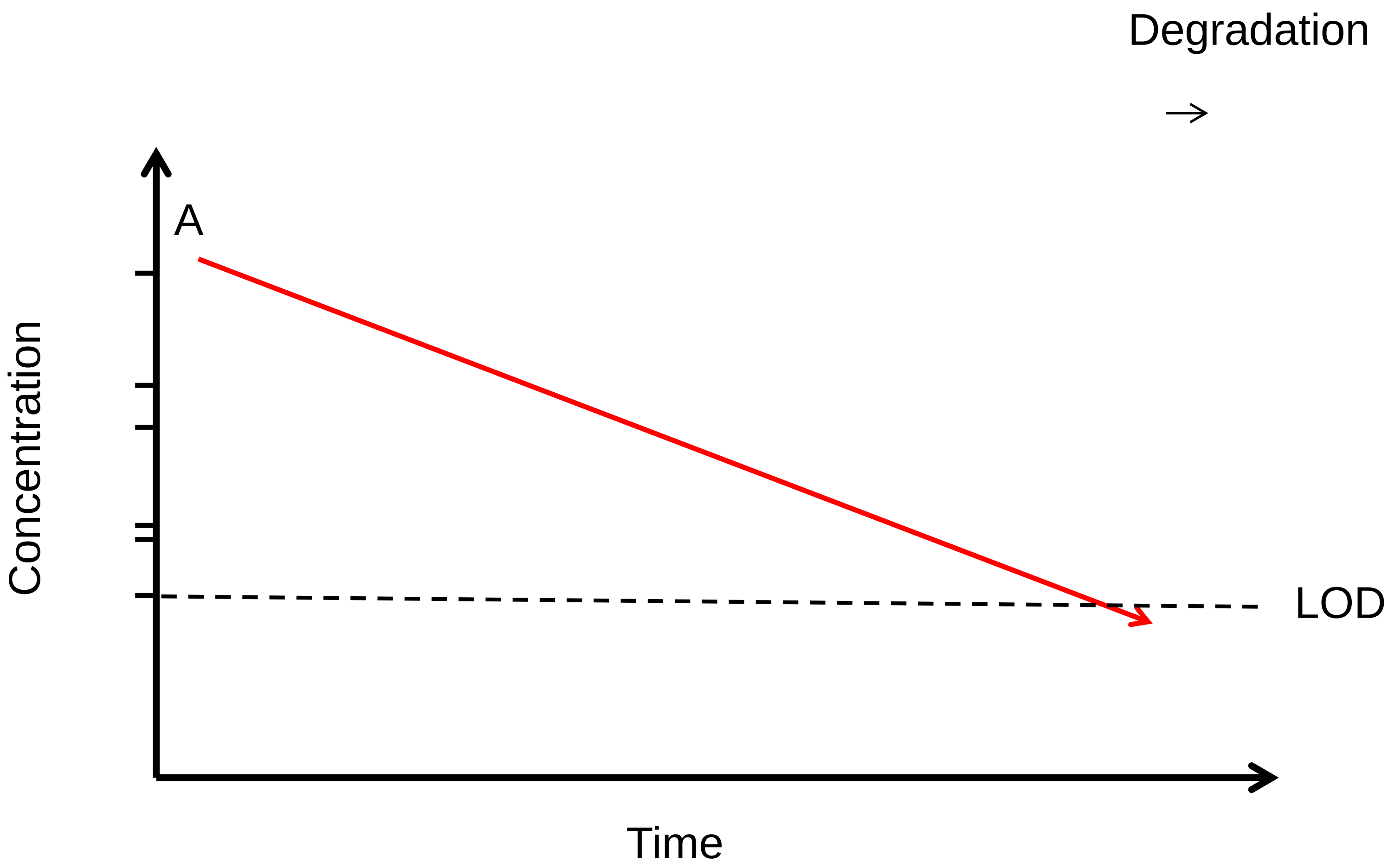
Degradation



Storage & Stability: what is known? Chemistry



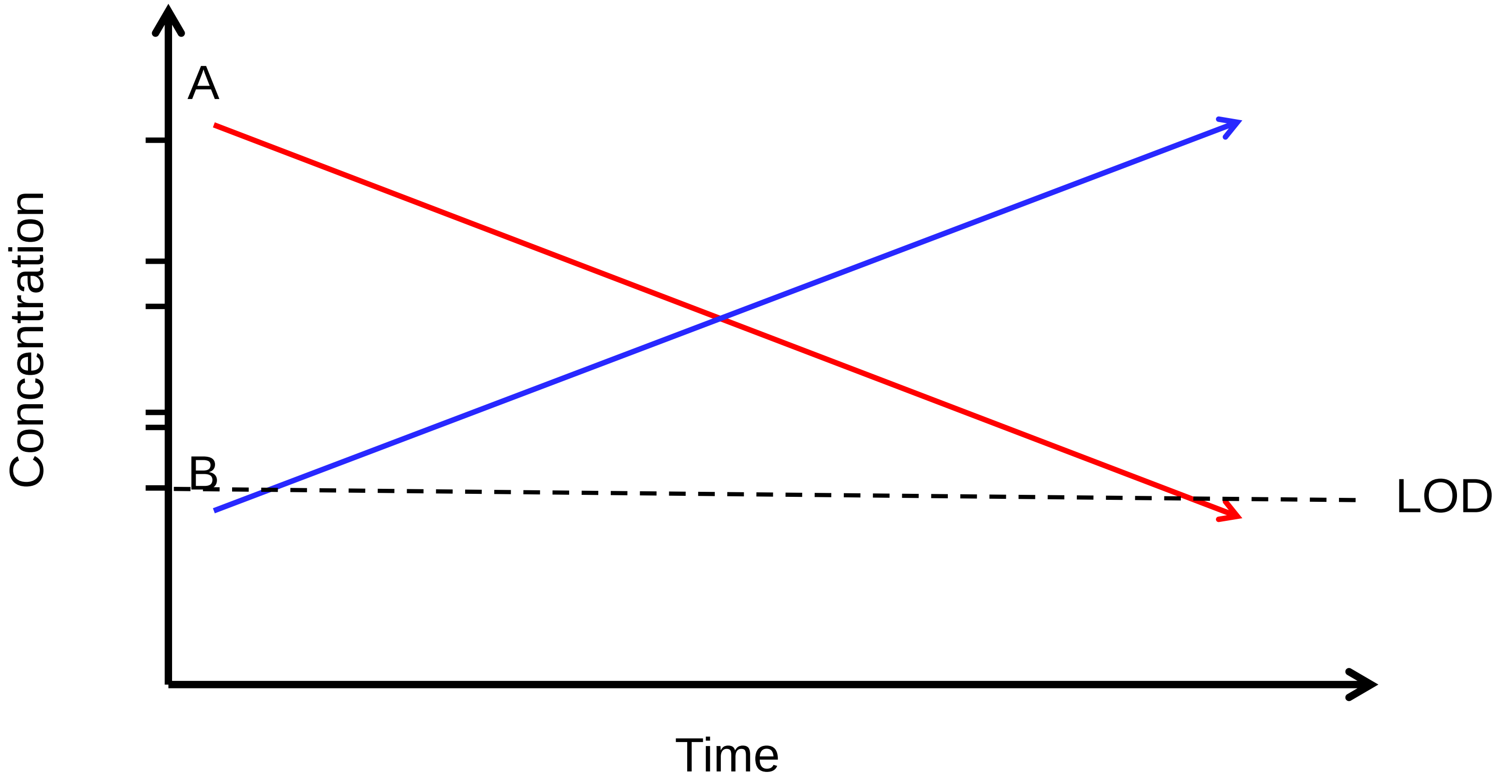
Storage & Stability: what is known? Chemistry



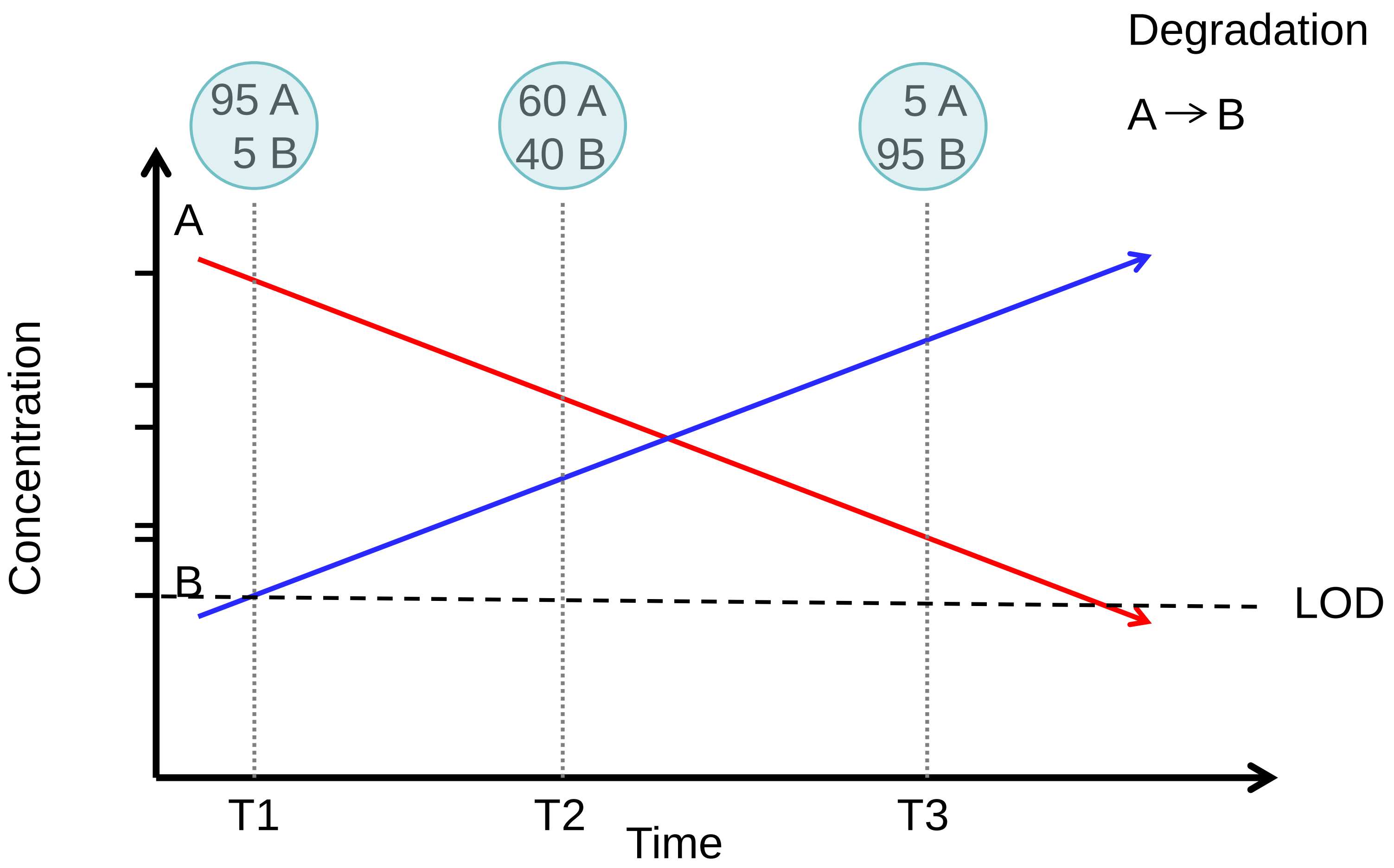
Storage & Stability: what is known? Chemistry

Degradation

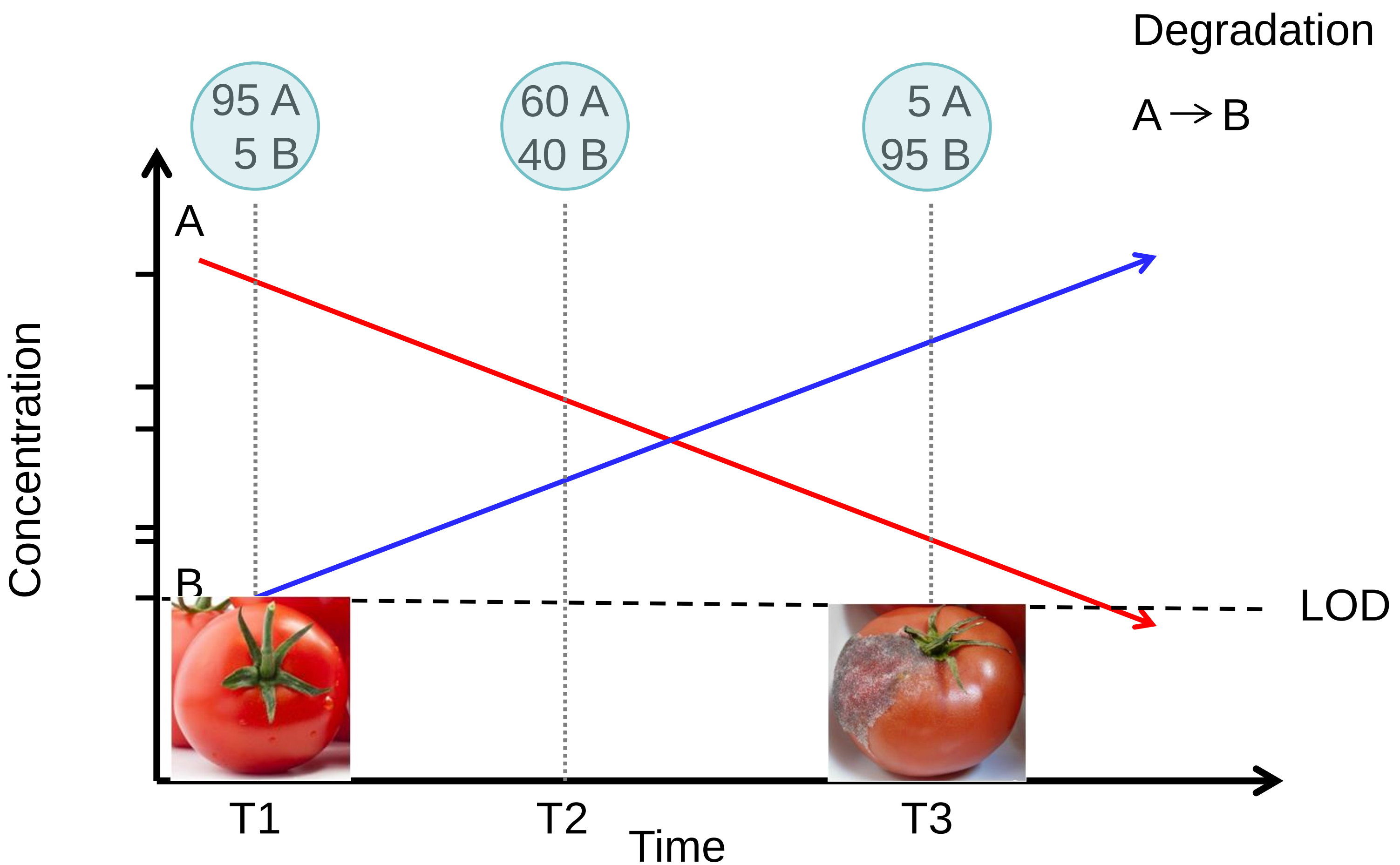
$A \rightarrow B$



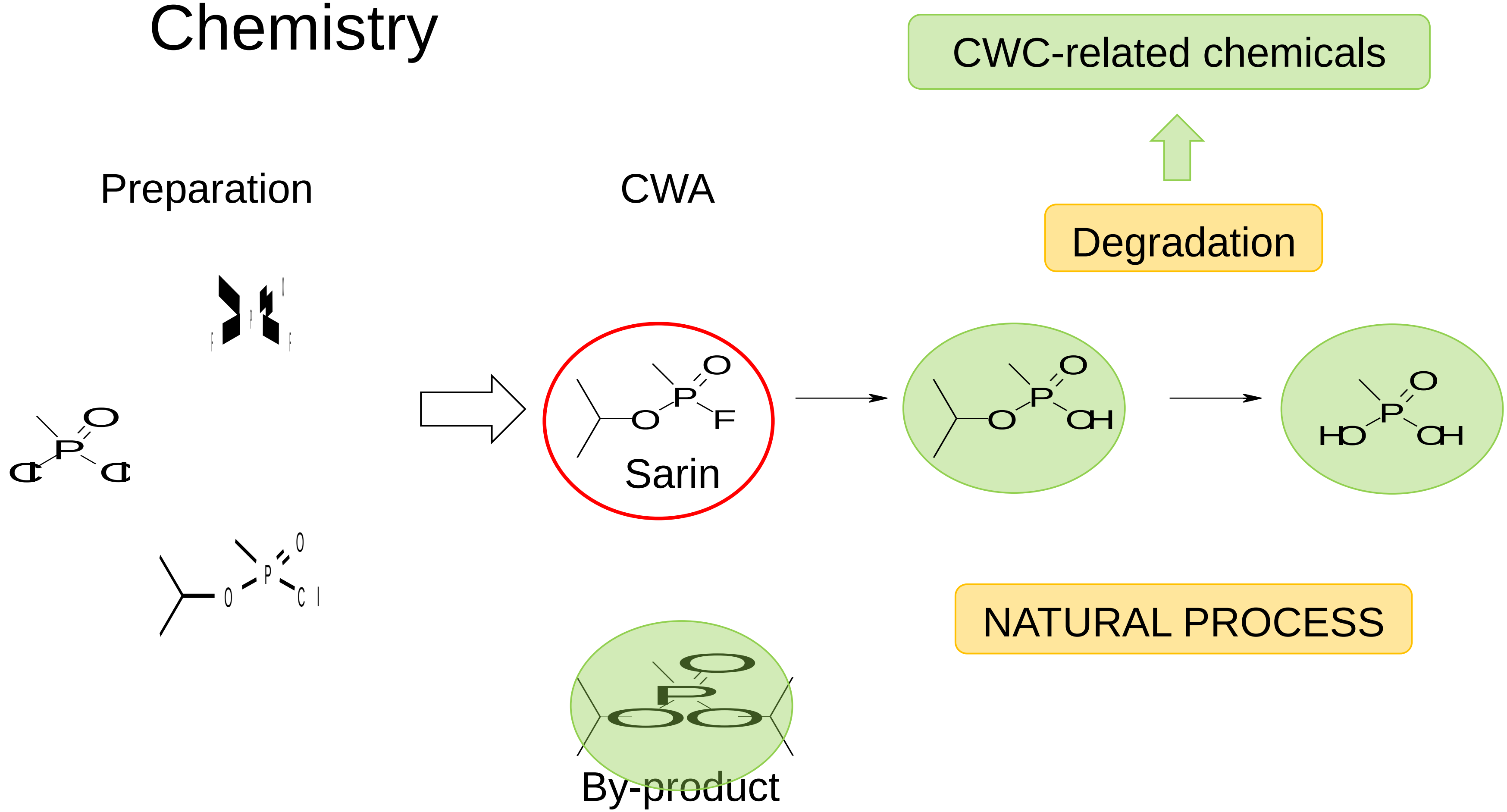
Storage & Stability: what is known? Chemistry



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[a]	2.A.1	1	3.A.1	1
1.A.2	>50 000[a]	2.A.2	1	3.A.2	1
1.A.3	>200 000[a]	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[b]	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[a]	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

[a]Including branched chains and cyclo alkane chains, not including bicyclo alkane chains and stereoisomers and not including corresponding protonated and alkylated salts

[b]

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

Storage & Stability: what is known? Chemistry

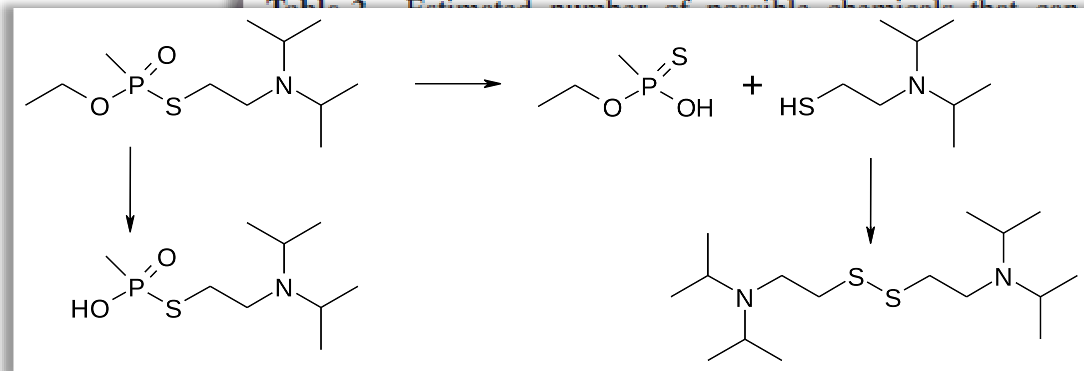
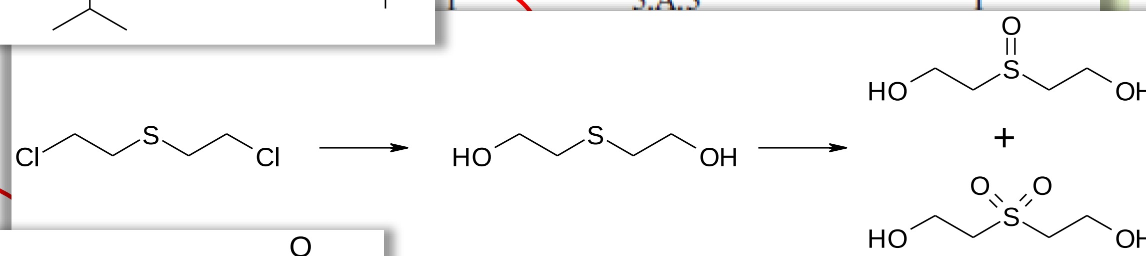
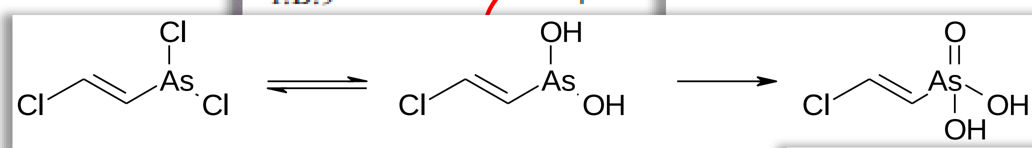


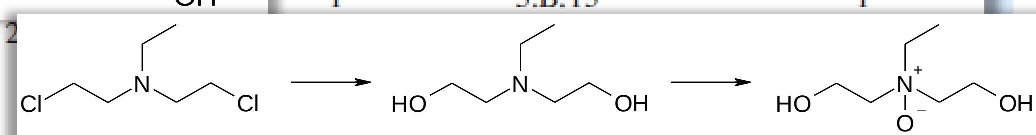
Table 2 Estimated number of possible chemicals that can be derived from the definitions for scheduled ... t counting corresponding protonated or alkylated

...ated) ...ber of ...icals	Schedule number	Number of chemicals
1	3.A.1	1
1	3.A.2	1
1	3.A.3	1
8	3.B.11	1
10	3.B.12	1
1	3.B.13	1

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







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Response to the DG's request

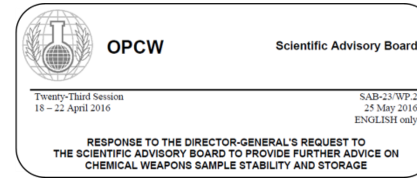
OPCW **Scientific Advisory Board**

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

Response to the DG's request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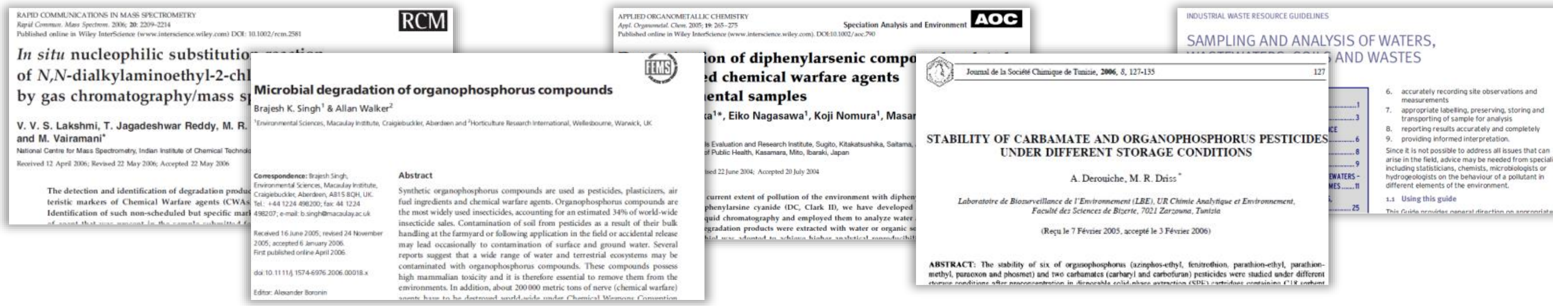
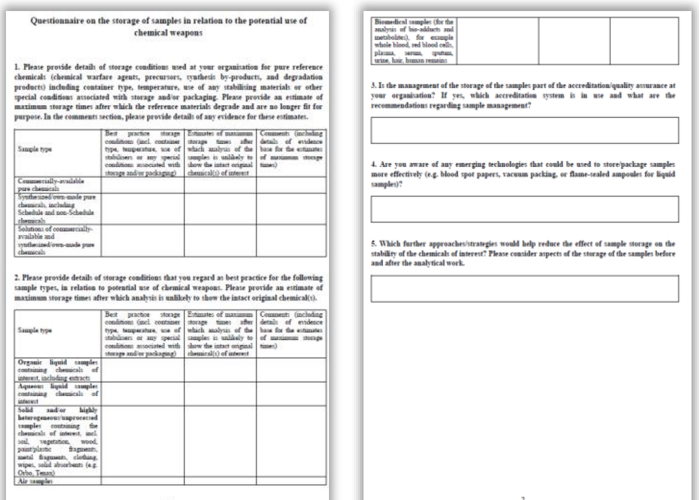
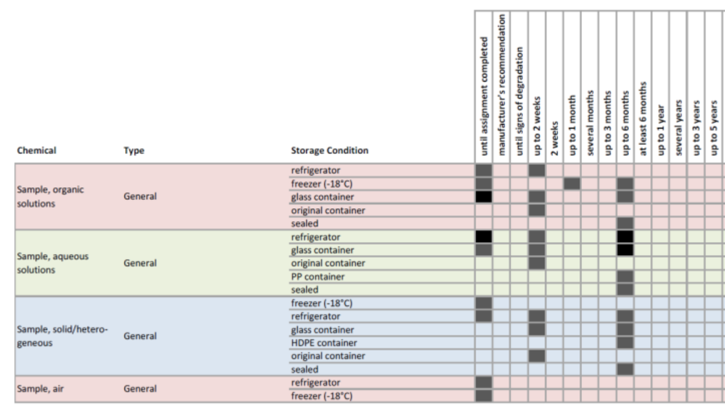
- Review of > 180 scientific papers



- Questionnaire to Designated Laboratories


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



Executive Summary

OPCW Scientific Advisory Board

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

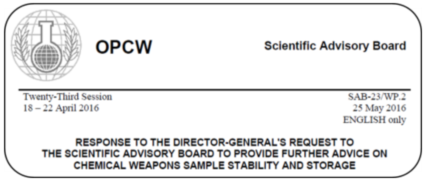
1. Given the current storage conditions in the OPCW Laboratory, how quickly and through what process could the aforementioned types of sample degrade to a point where analysis of the samples would no longer return credible results?

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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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 resu ?

Process

Recommendation 1. Samples should be analysed as soon after collectio 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.

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

Types of sample

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

(i) Schedules 1A01, 1A02, 1A03, 1A06, 1B09, 1B10, 1B11 and 1B12 at -18 °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 °C (for stability > 10 years).

Recommendations 3 to 8 Type of containers, extracts, biomedical samples, splitting

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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 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 (HEM) as a precipitate in 6 M ammonium sulfate at 4 °C (for stability > 10 years).

Recommendations 3 to 8 Type of containers, extracts, biomedical samples, splitting

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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.

Recommendations 3 to 8 Type of containers, extracts, biomedical samples, splitting

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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).

Recommendations 3 to 8 Type of containers, extracts, biomedical samples, splitting

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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.

Recommendations 3 to 8 Type of containers, extracts, biomedical samples, splitting

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Recommendation 3. Commercial chemical samples should be stored in gl 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

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

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.

Recommendations 3 to 8 Type of containers, extracts, biomedical samples, splitting

Executive Summary

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Twenty-Third Session
18 – 22 April 2016

SAB-23/WP.2
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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

Future work

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.[7]

Conclusion

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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.