Detection and Identification of Chemical Warfare Agents in Environmental Samples

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Introduction

In 1997 the Chemical Weapons Convention (CWC) entered into force. Its aim is to eliminate chemical weapons by prohibiting their development, production, acquisition, stockpiling, retention, transfer or use by States Parties. The Organization for the Prohibition of Chemical Weapons (OPCW) is the implementing body of the CWC (1). The Nobel Prize for Peace was awarded to the OPCW in 2013.

The OPCW relies on a global network of highly qualified, designated laboratories for analytical tasks resulting from inspections and other needs for the implementation of the CWC. In order to obtain and maintain the designation status, a laboratory must have a national accreditation by an internationally recognized accreditation body and must participate annually and perform successfully in inter-laboratory OPCW Proficiency Tests (PT). The Director-General of the OPCW designates the laboratories that fulfill the OPCW criteria.

The Analytical Chemistry group of SPIEZ LABORATORY has been operating an OPCW designated laboratory since 1998 to support the OPCW in the verification of the CWC. In September 2013 SPIEZ LABORATORY was one of four laboratories which analyzed samples taken by UN weapons-inspectors in Syria.

A good overview about chemical weapons and the CWC can be found at the *Center for Security Studies* (CSS) at ETH Zurich.

The Analysis of CWC-related Chemicals (see Lit. 1)

Chemicals. The analytical task is challenging because the number of chemicals covered by the CWC is huge (see List of Chemicals under Schedule 1, 2 and 3 or in the Appendix of this document): the actual warfare agents and Scheduled chemicals but also their respective precursors as well as degradation products. Included and thus relevant are further those chemicals that are one reaction step away from Scheduled chemicals!

Analysis. The chemicals have to be detected in environmental samples with different matrices, e. g. liquids (water, sea water, organic solvents, mixtures, emulsions,…), soil (sand, clay, grass,…), surfaces (metal, concrete, wood, textile…), gases, etc. The concentrations are most often not known, they can range from trace level to the undiluted chemical. Thus, a variety of analytical methods is required for the analysis of CWC-related chemicals in environmental samples.

The OPCW has defined criteria for the unambiguous identification of CWC-relevant chemicals. Amongst others:

- A sample has to be analyzed by at least two different analytical techniques. At least one of these techniques has to be a spectrometric technique.
- Identification must be confirmed by the comparison with reference data.

Literature

1. Mesilaakso, Markku. *Chemical Weapons Convention Chemicals Analysis*. John Wiley & Sons, 2005. ISBN: 0-470-84756-5.

Problems

1. *Off-site* analysis plays a key role in the verification program of the Chemical Weapons Convention (CWC). The analytical task is to detect and identify all chemicals relevant to the CWC. A crucial step is screening for relevant substances. Due to the broad chemical variety and large number of Scheduled chemicals in the CWC this task is exceptionally challenging.

Questions: **a)** Estimate the number of possible chemicals which are covered by the different Schedules of the CWC. To do this, examine the Schedules (see Appendix) and identify particular Schedule numbers which cover larger classes of chemicals.

- See Table 2 below (literature 1).

b) Try to develop suitable screening strategies to cope with the numbers you have found under **a)**.

- Elemental analysis: CWC-relevant elements P, S, Cl, As, F contained in the samples? Use GC-AED, ICP-MS, ICP-OES, …
- NMR for detection of ^{31}P- or ^{19}F-containing chemicals
- Use different analytical techniques in combination with comprehensive data libraries (OCAD, NIST/Wiley,…)
- Screen for substructures which are common to all compounds in a class. Use in-source CID for screening with LC-MSMS and screen using full scan mode and MRM (followed by a precursor ion scan to determine the molecular mass).
- Consider all background information given about the scenario (can some chemicals or classes of chemicals be excluded?). I.e. nerve agents vs. blister agents,….)

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

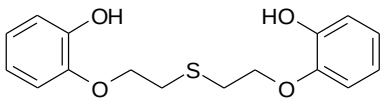
[a]Including branched chains and cyclo alkane chains, not including bicyclo alkane chains and stereoisomers and not including corresponding protonated and alkylated salts
[b]Only including dichlorides and difluorides

2. You are head of an analytical laboratory which is specialized in the *off-site* analysis of environmental samples for CWC-relevant chemicals. You get a phone call that announces the delivery of samples requiring urgent analysis.

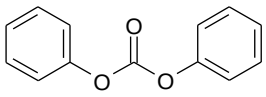
Question: Which questions do you ask to get all the necessary information to be able to start the analysis of the samples at once? Explain in each case why the respective question is important.

- What is the task?
- Is there any information about victims, impact on environment -> scenario
- Any information about possible compounds involved?
- How many samples?
- Which type of samples (gas, liquid, solid)
- Amount of each sample?
- Which matrices?
- Any blank samples?
- Are the samples dangerous, are there any measurements already made?
- How are they labelled?
- How are they delivered?
- Deadline(s)?
- Can I accept the order (manpower, lab situation, technical agreement, Q-System)?
- Confidentiality requirements
- Any forms which describe the individual samples?
- What to report?
- ….

3. In the last international OPCW proficiency test *PT-37* the two chemicals A and B were spiked in a test sample together with other chemicals. The only information available about the sample was that it origins from a decontamination tank of a facility that has been accused of performing chemical weapon research. The task was to analyze the sample for any Scheduled chemicals and/or their degradation or reaction products.



A



B

During the analysis several chemicals were identified in the sample: sulfolane, several alcohols, diesel oil, lubricating oil, toluene, phenol and 1,2-dihydroxy phenol.
However, the detection and identification of relevant chemicals A and B (although at concentrations of 5 - 10 ppm) posed a major challenge for all participating laboratories. Chemical B was only reported by 3 out of 17 laboratories!

Questions: **a)** Try to classify chemicals A and B on the basis of the chemicals listed in the Schedules in the Appendix. Keep in mind that the sample origins from a decontamination tank and consider the "one reaction step away" rule (see page 1).

- A: 1 reaction step away from 1.A.04. Reaction product of sulfur mustard with 1,2-dihydroxybenzene -> Relevant.
- B: 1 reaction step away from 3.A.01. Reaction product of phosgene with phenol -> Relevant.

b) Would you have been able to detect chemical B in an unknown sample based on the strategies you propose for Problem **1b)**? Explain how.

- Detection/identification with GC-EIMS, data library search.
  Big question: do you realize that it's relevant to the CWC?

c) What made chemical B especially challenging for the participating laboratories?

- No heteroatom(s) -> elemental analyses yield no result (see 1b))
- "1 reaction step away"-chemical -> do you recognize phosgene (a 3.A.01 Scheduled chemical) in the structure as an educt?
- Need to investigate all chemicals found in the sample: Could they be produced using Scheduled Chemicals as educts by a 1-step reaction?
- All alcohols present in the sample could react with phosgene. Also asymmetric products possible (two different alcohols react with one phosgene molecule). Leads to a large number of possible compounds, which might not all be in data libraries -> screening with *ad hoc* high resolution MS data libraries.
- Heavy background: ^{1}H-NMR difficult or impractical

d) Which additional information about the sample (see Problem 2) would have helped enormously to detect and identify B?

- Hints of phosgene used in the facility under investigation (production, stockpiling, production of organic carbonates involves phosgene as a building block)
- Description of the injuries of victims (if available) or other information about the presence of phosgene.
  Phosgene disrupts the blood-air barrier, causing suffocation
- Any information about the decontamination reagent such as composition, type, brand name, etc.