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Identification of chemicals relevant to the Chemical Weapons Convention using the novel sample-preparation methods and strategies of the Mobile Laboratory of the Organization for the Prohibition of Chemical Weapons

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ABSTRACT

The standard approach to on-site sample preparation for gas chromatography-mass spectrometry analysis of chemicals relevant to the Chemical Weapons Convention provides relatively good coverage of the target analytes, but it suffers from a number of drawbacks, such as low sample throughput, use of bulky equipment, extensive manual work, extensive use of organic solvents, problems in preparing multiphase-sample systems and relatively large amounts of hazardous waste generated. We present the analytical strategies and the novel sample-preparation methods developed for the Mobile Laboratory of the Organization for the Prohibition of Chemical Weapons (OPCW) that deal efficiently with these issues. We illustrate the effectiveness of the approach with several practical examples.

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1. Introduction

The Organization for the Prohibition of Chemical Weapons (OPCW; www.opcw.org) was established in 1997 as the administering body of the Chemical Weapons Convention (CWC), an international treaty that prohibits production, stockpiling, transfer and use of chemical weapons (CWs), and requires the destruction

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of existing stockpiles. Ever since, the OPCW has been maintaining a strict verification regime covering both military and commercial industry activities of CWC member states. This verification regime relies essentially upon on-site inspection activities conducted by OPCW inspectors. Amongst the verification tools available to OPCW inspectors, on-site sampling and analysis are certainly of the utmost importance.

Toxic chemicals and their precursors that are subject to the OPCW verification measures are classified on the basis of their degree of toxicity, history of use in chemical warfare and commercial utility into three Schedules attached to the CWC [1]:

- Schedule 1 chemicals include those that have been or can be easily used as CWs and that have very limited, if any, uses for peaceful purposes. These chemicals are therefore subject to very stringent restrictions. Classical CW agents (CWAs) [e.g., bis(2-chloroethyl)sulfide (sulfur mustard, HD), 2-chlorovinyldichloroarsine (Lewisite 1, L1), O-isopropyl methylphosphonofluoridate (sarin, GB), O-pinacolyl methylphosphonofluoridate (soman, GD), O-ethyl N,N-dimethylphosphoramidocyanidate (tabun, GA) and O-ethyl S-2-diisopropylaminoethylmethyl phosphonothiolate (VX)] are listed amongst the other chemicals.
- Schedule 2 lists toxic chemicals and precursors used for peaceful purposes in industry, although they are not produced in large quantities.
- Schedule 3 chemicals are usually produced by industries in large quantities for purposes not prohibited by the CWC, but still posing a risk to the CWC.

Any State Party (SP) to the CWC producing, processing, consuming, importing or exporting any of the scheduled chemicals above the threshold quantity defined by the CWC must meet certain legal requirements. During inspections of industries dealing with the Schedule 2 and 3 chemicals, the OPCW team verifies the correctness of declarations submitted by the inspected SP and checks for the absence of undeclared scheduled chemicals, in particular, Schedule 1 chemicals. The samples can be collected from storage containers containing raw materials, intermediaries and products, from process equipment, or even waste effluents, then prepared and analyzed using the OPCW Mobile Laboratory. Annually, 8–10 Schedule 2 industrial inspections with sampling and analysis are conducted worldwide. So far, no Schedule 3 industrial inspection with sampling and analysis has been conducted; however, the Technical Secretariat of the OPCW has been preparing for such an event.

The SPs that have declared CWs are obliged to destroy them. On the CW-destruction sites, samples are collected from the CW-munitions/storage containers and process lines by the site representatives under close observation of the OPCW inspectors and analyzed following an agreed procedure. The aim is to confirm the identity of the CWA(s) being destroyed and to verify the end product of destruction.

The CWC grants each SP the right to request an on-site "challenge" inspection of any facility or location of another SP in order to resolve questions concerning possible non-compliance with the CWC. Such inspections might be conducted anywhere and without delay by an OPCW inspection team, after being triggered and approved through the special mechanism. Each SP also has the right to request assistance and protection, if it considers that a CW has been used against it. In that case, the OPCW team could be mandated to conduct investigations to provide a foundation for further actions. During these events, sampling and analysis can be used in collecting the evidence, securing the site or for safety reasons. Although no inspection of these types has taken place, mock inspections and international exercises are held regularly. In cases of the alleged use of a CW involving a State not party to the CWC or in a territory not controlled by an SP to the CWC, the Secretary-General of the United Nations (UN) can request the OPCW to put its resources at his disposal, including providing a team of experts and specialized equipment to conduct fact-finding activities. In 2013, a team of the OPCW inspectors participated in investigating allegations of use of a CW conducted under the UN lead in the Syrian Arab Republic [2].

The OPCW Mobile Laboratory was designed to meet the inspection requirements [3]. It is modular, so that it can be customized to the specific inspection type. The Laboratory uses only the items previously approved by the SPs to the CWC [4]. Fourier-transform infrared (FTIR) spectrometry and gas chromatography-mass spectrometry (GC-MS) are the principal analytical techniques. FTIR has found very limited application, primarily due to the limitations of the technique and the fact that GC-MS can cover the field of applications of FTIR for OPCW purposes.

The OPCW Technical Secretariat and Laboratory have opted for a bench-top version of GC-MS instead of portable GC-MS, choosing a strategy where sampling and analysis are separated. The instrument is usually set up at a fixed location considered free of contamination, but near the area of sampling. This approach has allowed a computer to be attached to the instrument, utilizing more elaborate sample-preparation procedures to deal with a broader range of sample matrices and analytes, and using more sample-introduction options compared to the portable systems currently available.

The analytical strategies of the mobile OPCW Laboratory have to tackle the very demanding task of checking for the absence (qualitative analysis) of all undeclared scheduled chemicals and their degradation products in different sample matrices. The number of scheduled chemicals that it is theoretically possible to synthesize is vast. The chemicals may also differ widely in polarity, volatility and reactivity. Consequently, the sample-preparation procedures are generic. The standard approach adopted by the OPCW Mobile Laboratory is based on the work of technical experts from the member states, brought together by working groups before entry into force with the CWC. It includes laborious sample processing using solid-liquid extraction (SLE) and liquid-liquid extraction (LLE) [5]. Fig. 1 shows the general flowchart of the standard OPCW approach to sample preparation of environmental samples.

The main objective is to extract as many analytes as possible from the sample matrix, making them suitable for GC-MS analysis, using derivatization when necessary. While the approach provides a relatively good coverage of the target analytes, it suffers from a number of weaknesses, such as low sample throughput, use of bulky equipment, extensive manual work, extensive use of hazardous solvents, problems with preparing multiphase sample systems and generating relatively large amounts of hazardous wastes.

The low sample throughput limits the number of samples that can be processed in a restricted inspection time, and may have an impact on the outcome of any type of sampling and analysis inspection, but especially Schedule 3 inspections. The CWC allows only 24 h for inspection activities on Schedule 3 facilities. Within this timeframe, the inspection team has to set up and to validate the equipment, plan and perform sample collection, preparations, and analysis, and, finally, produce a full report on analytical activities.

Longer inspection timeframes of 96 h and 84 h are available for Schedule 2 inspections, and investigations of alleged use and challenge inspections, respectively. However, on these kinds of inspection, a larger number of samples could also be expected. Often, the inspection dynamics, which include negotiations, logistic problems and on-site situations, further restrict the time available for the sampling and analysis activities. Preparations of aqueous samples, water solutions and water extracts of solids have long been recognized as a rate-limiting step for the entire sample-preparation process. Less volatile and more polar compounds soluble in water require derivatization prior to GC-MS analysis. The OPCW Laboratory