SAMPLING AND ANALYSIS RELEVANT TO THE IMPLEMENTATION OF THE CHEMICAL WEAPONS CONVENTION

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I. INTRODUCTION

Sampling and analysis is widely used in many industries to assess workplace contaminants and health and safety protocol adherence. Chemical analysis, in many ways, is the focal point of the verification activities of the OPCW. The objective of the sampling and analysis activities of the OPCW is to prove the presence or absence of a particular scheduled chemical in a sample. Used in this manner, chemical analysis provides unambiguous evidence for the presence of scheduled chemicals.

S&A is invoked in three OPCW activities: inspections (for example, chemical weapons destruction facilities or chemical industries), challenge inspections (CI), and investigations of alleged use (IAU). In the case of an inspection at a chemical industry for example, S&A is used to prove that the activities in a particular location are consistent with the information provided in the declarations provided by the industry. In the case of a challenge inspection, S&A is used to validate the allegations proposed by one State Party toward another with regards to adherence to the CWC. No CI's have been required so far in the history of the OPCW but regular training in CI S&A techniques is provided in the form of ASSISTEX exercises. An investigation of alleged use (IAU) involves sampling of environmental and biomedical samples and their analysis in an area where chemical weapons were allegedly used; the main example of recent times being Syria.

S&A related to the implementation of the CWC is performed on-site, in the OPCW Laboratory, and in a network of designated labs around the globe. 8-10 inspection missions are carried out per year by the verification division and the inspectorate team of the OPCW.

Figure 2. An inspector collecting a liquid sample during and challenge inspection (CI) exercise

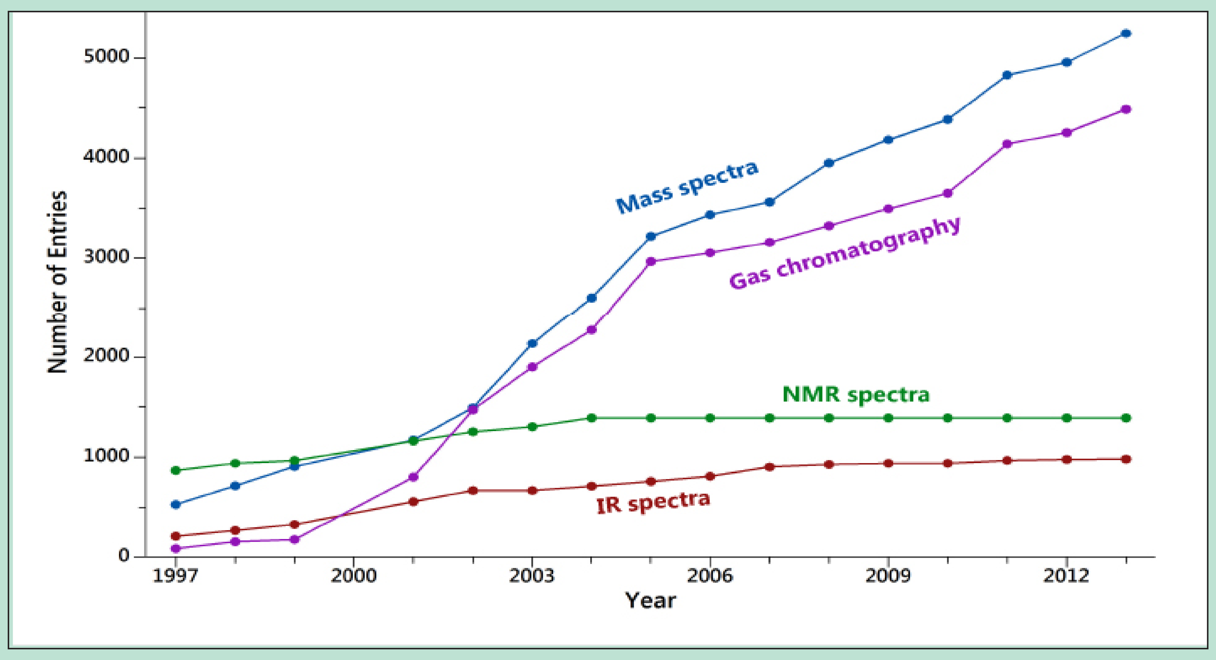


Figure 3. Additions to the OCAD from 1997-2014

II. TOOLS AND TECHNIQUES USED FOR S&A

Trained analytical chemists (ACs) perform the bulk of the S&A activities for the OPCW. Many of the AC inspectors hold chemical engineering or chemistry degrees, and are trained at the OPCW laboratory prior to departure on missions.

The main workhorse of most of the chemical analysis relevant to the CWC is a hyphenated analytical method called gas chromatography-mass spectrometry (GC-MS). A GC-MS instrument separates individual components in a mixture and records their masses, making identification of target compounds facile. To assist with identification, the OPCW Central Analytical Database (OCAD), which contains data from over 5,000 compounds, is used. An advantage of using GC-MS as the main analytical tool is that it can detect compounds in extremely diluted samples, usually at the part per million (ppm) level. GC-MS instruments require continuous calibration with a calibration mix provided by the OPCW.

Other chemical analysis tools include infrared (IR) and Raman spectroscopy. These tools were used in Syria as qualitative methods that rapidly indicate the presence of a particular class of chemicals which contain similar structural features. Raman spectroscopy was also used at Marchwood Military Port in the United Kingdom to verify the identity of chemicals received from the hydrolysis of chemical weapons aboard the Cape Ray.

In addition to the analytical tools mentioned above, a range of other equipment is needed for S&A during inspections, such as sample collection kits, sample preparation kits, and portable fume hoods.

Figure 1. Inspectors performing S&A activities during an exercise

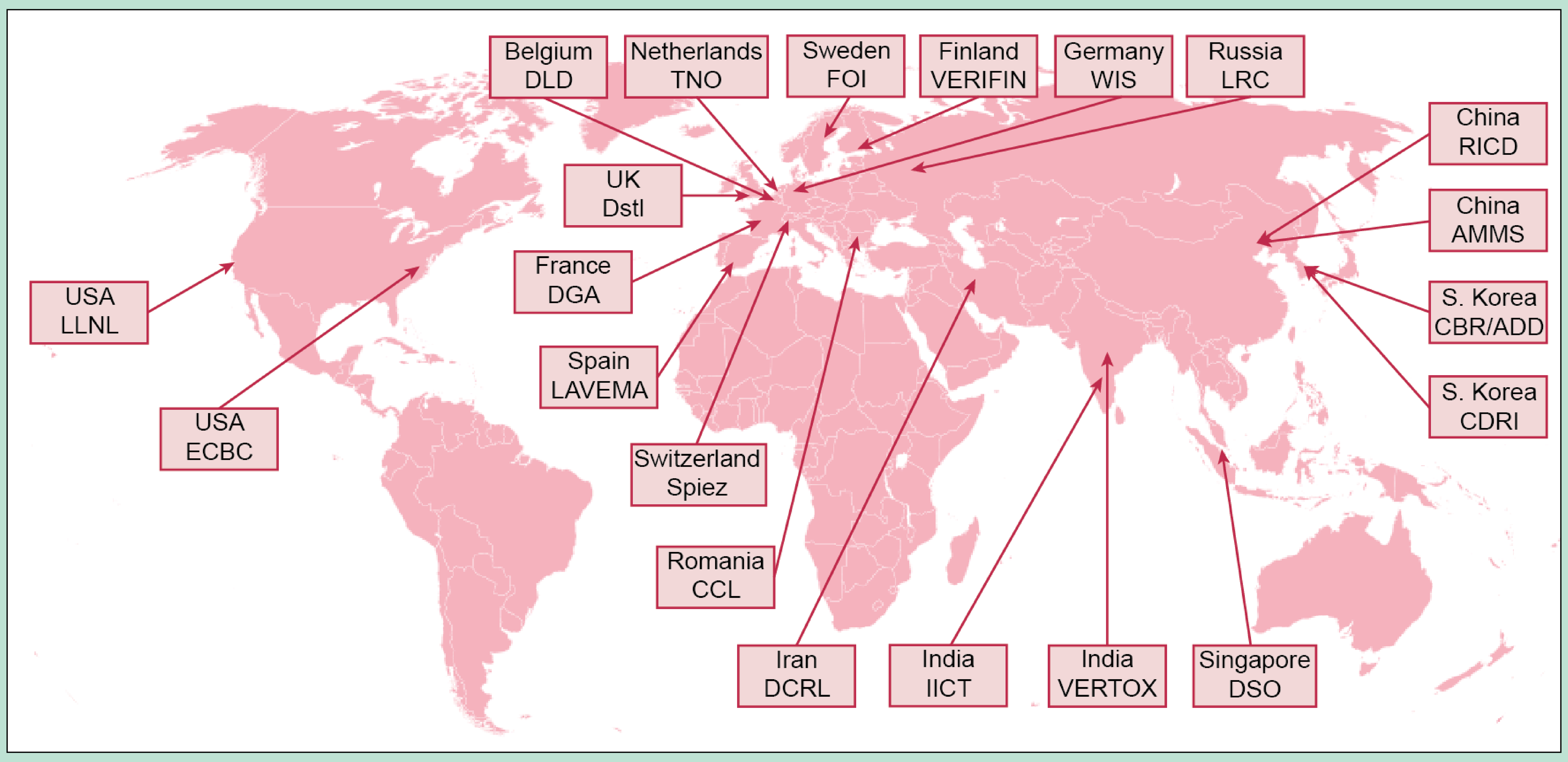
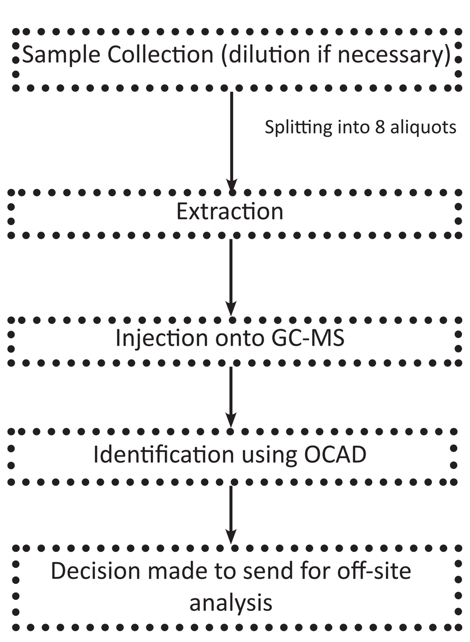


Figure 4. Current designated laboratories that the OPCW uses for off-site analysis (as of July 2014). All the designated laboratories have to maintain strict analytical practices and take part in annual profiency tests run by the OPCW Laboratory in Rijswijk

III. OVERVIEW OF THE S&A PROCESS



Beforehand:

- The number and category of samples to be collected and the equipment necessary is determined beforehand. Sample collection forms are initiated. OPCW-approved PPE appropriate to the mission is prepared.

Sample collection:

- In the case of a suspected neat agent (highly toxic), the sample would be diluted at the collection point before collection and storage. The sample would also be split into aliquots at the site of collection.

Sample types and usual quantities collected:

1. Aqueous (250 ml)
2. Organic liquid, non CW (5 ml)
3. Organic liquid, CW or super toxic (2.5 ml)
4. Soil (250 g)
5. Bulk solid chemical (10 g)
6. Wipe (1 wipe per solvent)
7. Paint, rubber, wood (surface scrape)

Sample extraction:

- The complexities of the sample matrix and possibility of contaminants oftentimes means that extraction has to be carried out. Extractions are usually performed in dichloromethane (DCM), water, or triethylamine (TEA)/methanol mixture. Lewisites require a different extraction procedure. Analysis using GC-MS and identification of compounds using the OCAD database.

- Samples are injected and analysed using the GC-MS instrument and the chromatograms and mass spectra of each compound are recorded. Unless run on "restricted" mode, mass spectral libraries can be used to compare data with the sample (common libraries include the NIST, and the Wiley). The laptop connected to the GC-MS has AMDIS (automated mass spectral deconvolution and identification system) software installed, which is a software used to deconvolute co-eluting peaks (different compounds eluting at similar retention times) on chromatograms.

Decision to send samples off-site:

- The inspection team leader (ITL) recommends to the Director-General if off-site analysis is required. Of the 8 aliquots prepared from the authentic sample, one is handed over to the Inspected State Party as a reference sample, 2 are used in on-site S&A activities, and the remaining 5 are set aside for off-site analysis if the occasion arises.

- If off-site analysis is required, the samples are sent to at least two off-site independent accredited laboratories to increase confidence in OPCW S&A testing results. Therefore, the need to properly develop a strong network of designated laboratories is realized (Figure 4).

IV. THE OCAD

During routine S&A inspections, the OCAD database is used to identify the presence or absence of scheduled chemicals in a given sample. However, in the case of an IAU, the analysis of the sample is not limited to scheduled chemicals alone and encompasses any chemicals that may not be found in OCAD up to that point.

The OCAD currently contains recorded data on 5,000 scheduled chemicals. Most of the data is in the form of mass spectra and retention indices recorded from GC-MS analyses of chemicals, however, data from infrared (IR) and nuclear magnetic resonance (NMR) analyses of chemicals are also present, albeit fewer entries are included for those techniques.

The OCAD is updated every year based on a stringent screening procedure for new entries. Data for the OCAD is generated by the OPCW laboratory and the designated laboratories. The data is then validated by external experts and submitted for review to the Executive Council (EC), which approves the material for inclusion onto the OCAD.

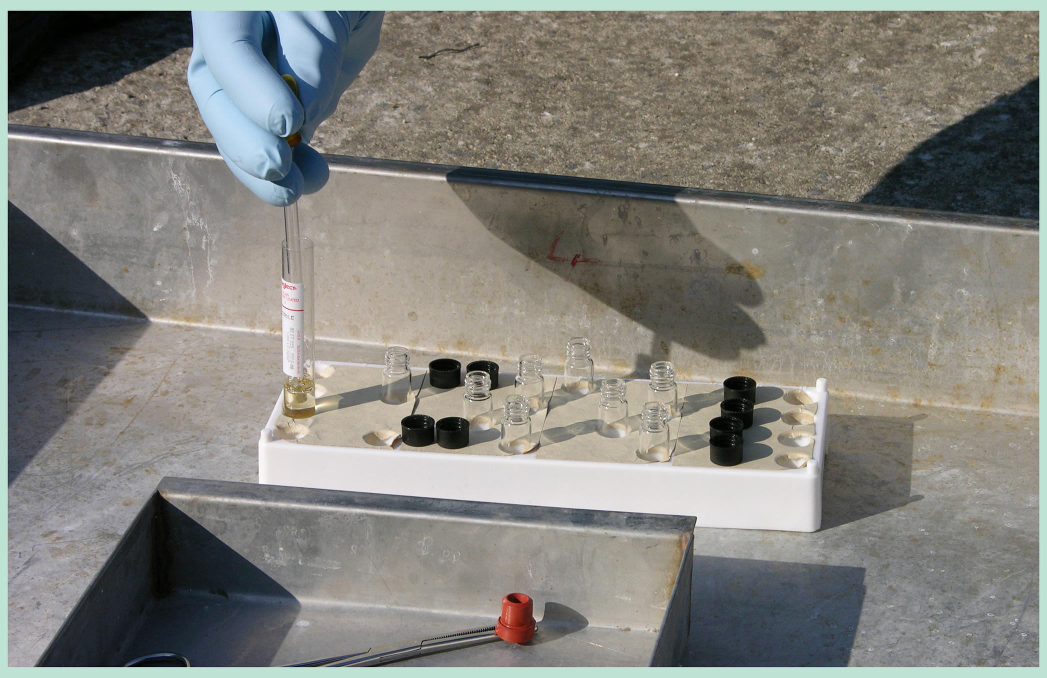


Figure 5. Sample splitting into 8 aliquots during a 2005 ASSISTEX field exercise

Figure 6. Sample preparation by an analytical chemist (AC) during and on-site inspection

V. LIMITATIONS AND CHALLENGES POSED BY S&A

- The biggest challenge posed by S&A are process related impurities and "false positives", which undermine the credibility of the results. For example, a false positive may indicate that a scheduled chemical is present when in fact it is not in the mixture. This of course has far-reaching implications in terms of politics and international relations.

- Another issue is the possibility that the OCAD may not contain the scheduled chemical being manufactured in a particular inspected location. Therefore, it is important to constantly keep updating the database.

- The restricted mode of analysis required by some businesses or companies (imposed to protect trade secrets and keep confidentiality) may limit analytical chemists' ability to fully characterize the constituents of the sample.

- Finally, if an IAU occurs, S&A may not be appropriate due to a range of factors including a dangerous military environment, limited time, and the lack of certain infrastructures in the location.