

Participation on official Proficiency Test of the OPCW: case study of Brazilian Army – IDQBRN

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Abstract: In recent years, Brazil has been the scene of international events, gaining worldwide repercussion. However, this increases the risk of terrorist attacks using chemical warfare agents. It brings the need to achieve proficiency to do a quick and unequivocal identification of these dangerous compounds. Thinking about it, the Laboratory of Chemical Analyzes (LAQ) of Brazilian Army, has participated since the end of 2010 in the interlaboratory tests promoted by the Organization for the Prohibition of Chemical Weapons (OPCW). In this article, we discuss about the participation of LAQ in the 40th OPCW Proficiency Test, one more step in the way to become a laboratory designated by OPCW and an international reference.

Keywords: Chemical weapons convention; Proficiency tests; OPCW

1. INTRODUCTION

Chemical agents have been used since earliest times, both in isolated acts and in large scale, as seen in terrorist attacks and in the case of the First World War. The devastating effect of these agents, even if such occurrences are not so frequent, has led to a legislative effort worldwide to ban the use of chemical warfare agents (CWA) under the Chemical Weapons Convention (CWC), which was opened for signature in January 1993 and came into force in 1997.¹

The threat of chemical weapons use emphasizes the need for specific methods to detect and identify CWAs and their degradation products. The Organization for the Prohibition of Chemical Weapons (OPCW), as the implementing body of the CWC, has been organizing and conducting Official Proficiency Tests (PT) since 1996 to certify laboratories for the analysis of authentic samples under the provision of the convention.

The manufacture of chemicals related to the convention cannot, however, be completely prohibited as some of them have potential industrial uses. Brazil has the largest industrial park in America Latina. In national territory, several companies work with precursor products of chemical warfare agents and, although the peaceful purposes of using such substances and the strict means of control imposed by the legislation and oversight bodies, there is always the risk of accidents or criminal use of these products. In addition, in recent years, the country has been scene of several events of international repercussion and it has become necessary to ensure the safety of the authorities and civilians involved.

With the objective of quickly and accurately detect agents and take necessary measures of containment, the Brazilian Army seeks to develop research in the CBRN Defense field. The Institute of Chemical, Biological, Radiological and Nuclear Defense, is the agency in Brazilian Army

with the mission to plan and execute the research and development of CBRN Defense, providing products, scientific advice and technical support. Among its laboratories is the Chemical Analysis Laboratory (LAQ), assembled with the objective of detecting chemical warfare agents through analytical techniques.

LAQ was the first laboratory on Latin American and Caribbean Group (GRULAC) region to be accredited in accordance with ISO 17025 (since 2015) to conduct assays involving chemical warfare agents. Besides that, LAQ is too the only one in GRULAC to regularly participate in official OPCW proficiency tests reaching the goal of identifying all chemical warfare agents present in submitted samples. These things are requirements for being an OPCW designated laboratory and demonstrate technical capacity, putting LAQ a few steps of becoming an international reference.

2. OPCW PROFICIENCY TESTS

These tests are part of a mechanism to ensure that there are around the world laboratories that have proven competence in the analysis of chemicals related to the CWC. To be designated the laboratory need to fulfill some requirements, like maintain a quality system, and successful completed three consecutives tests, what mean that only one spiking chemical can be missed in this period and no one false positive can be presented. The designation proves expertise in off-site analysis of CWC related compounds and makes the laboratory eligible to receive authentic samples. To maintain the designation status, a laboratory must achieve satisfactory results in at least one test offered per calendar year. The tests are organized with the assistance of two laboratories, one preparing the test samples, and other evaluating the test results.

OPCW PT is a qualitative proficiency test in which participating laboratories must determine the presence of any CWC scheduled chemicals, their precursors and/or degradation products spiked at 1–10 ppm level. The samples are received with unknown composition to be analysed for presence of many possible chemicals in various matrices (such as soil, water, organic waste, wipe, etc.).

The participants receive two sets of three samples each (test sample + control + blank) without indication; each sample must be analysed in the same way to be identified. Laboratories are not restricted as to sample preparation or analytical methods. Sample preparation procedures often require clean-up, extraction, derivatization and concentration steps. Identifications must be confirmed by at least two different analytical techniques giving consistent results, of which one technique must be spectrometric.

In addition, a laboratory creates its own solvent blank to prove the absence of reported chemicals prior to introduction of sample. Reports must contain names, structures, CAS numbers (if available) of identified chemicals; description of sample preparation methods employed; description of analytical methods employed; analytical data (chromatographic and/or spectrometric) with analytical conditions. There should be an unbroken chain of evidence linking each test sample to each reported chemical in the entire report.

For means of performance scoring, as shown in Table 1, each correct identification is positively scored (+1 point). If the original spiking chemical is no longer present, identification of a degradation product(s) instead of the spiking chemical is positively scored (+1 point). False negative results arising from not finding a spiking chemical or its degradation product is scored negatively (-1 point). Identification of minor constituents of the spiking chemical(s) is considered correct, but does not add to the score. Reporting any false positive result will constitute failure of the proficiency test, even if the identification is not supported by sufficient data.

Besides that, all work need to be done in a short period: participants have only 15 calendar days upon receipt of samples to perform analysis and dispatch the report.

Table 1. Method of evaluating laboratory performance

Criteria fulfilled	Identification	Scoring	Rating
Yes	Lab identifies all chemicals	Maximum score	A
Yes	Lab identifies all chemicals except one	Maximum score minus two	B
Yes	Lab identifies more than half of the chemicals	Score between zero and maximum minus two	C
Yes	Lab misses more chemicals than it identifies	Negative score	D
No	Lab reports a false positive	No score, failure	F

3. LAQ WORKING SYSTEM

The Brazilian Army Chemical Analysis Laboratory participates in OPCW Proficiency Tests since 2010 using gas chromatography as the main technique used, in the various configurations allowed (different columns, sources and parameters).

The current laboratory staff works as follows: a team for preparation of each sample group, a team to carry out chromatographic tests, a team to analyze the experimental results and a team to prepare the report. All members carry out the report review.

4. RESULTS AND DISCUSSION

4.1 Test scenario and Sample preparation

In the 40th PT the test scenario presented was that the samples were collected one month after an explosion in a residential area on a territory under conflict. It was informed that victims close to the blast area presented symptoms of nerve agent poisoning. During the investigation, the team collected a metal fragment, believed to be a part of an exploded munition with evidence of a residue on its surface; and water present in a crater believed to be associated with the site or explosion.

Upon arrival at the laboratory, the samples were recorded and verified for their integrity; then

were divided into aliquots and prepared according to the recommended procedures³. Each aliquot received a code for its unambiguous identification, and each compound found was identified with the CAS, the name and structure so as not to break the chain of evidence. All preparation steps are described briefly in the following flowchart (Figure 1).

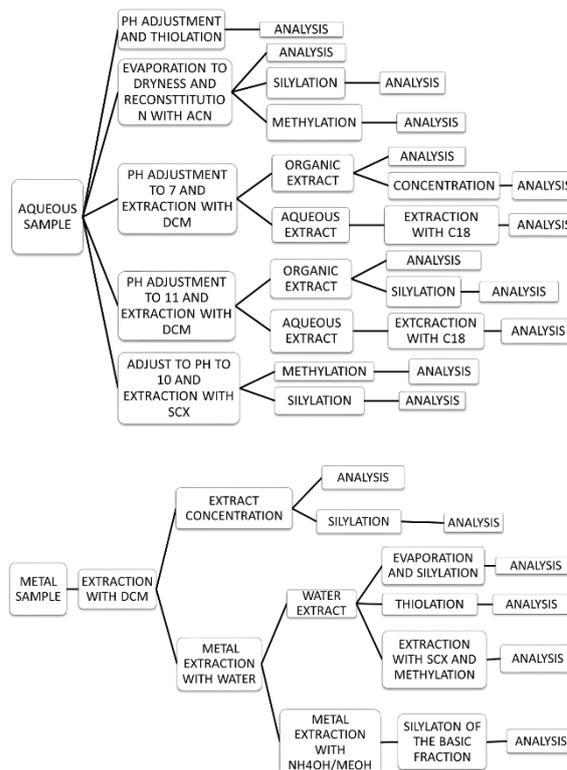


Figure 1. Scheme of Sample preparation.

4.2 Analysis Evaluation

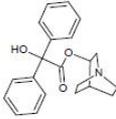
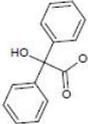
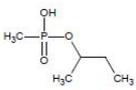
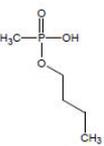
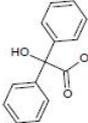
AMDIS tool and Gas Chromatography (GC) with flame photometric detector (FPD) and GC with nitrogen-phosphorous detector (NPD) techniques were used for screening purposes.

Analyzing the aliquot resulting from Dichloromethane (DCM) extraction of metal sample identified with the numeric code 739 was verified the presence of two relevant chemical compounds identified by LAQ as A1 and A2. In addition, screening of the aliquot resulting from silylation of DCM extract of the same metal sample using N,O-Bis(trimethylsilyl) trifluoroacetamide (BSTFA) could reveal the presence of silylated derivative of the same

compound A2 and a new one identified as A3. The screening of all aliquots originated from other two metal samples, 740 and 741, such as other aliquots prepared with sample 739 not indicated the presence of any spiking chemicals.

As the next step, the unambiguous identification was achieved by at least two different spectrometric techniques. A2 was identified by the mass spectrum of its trimethylsilyl (TMS) derivative using GC and mass spectrometry (MS) with electron impact ionization (EI). This spectrum showed the base peak at m/z 255 and corresponded with the reference spectra from the OPCW Central Analytical Database (OCAD).

Table 2. Spiking Chemicals and relevant analytical data.

Sample code	Chemical reported	Compound structure	GC-MS		
			EI (m/z)	CI (m/z)	RI (m/z)
739 (metal)	3-Quinuclidinyl benzilate A1		183	183	-
	2,2-Diphenyl-2-hydroxyacetic acid A2		255	-	255
	3-Quinuclidinol A3		73, 199	200	-
742 (aqueous)	sec-Butyl methylphosphonate D1		153	-	153
	Butyl methylphosphonate D2		153	-	153
743 (aqueous)	2,2-Diphenyl-2-hydroxyacetic acid E1		255	-	255
	3-Quinuclidinol E2		73, 199	200	-

The identification of A2 was confirmed by a chromatographic parameter with comparison between retention index (RI) obtained experimentally and the RIs value in the OCAD. The unambiguous identification of A1 e A3 was achieved in a similar way. Both compounds were initially identified by GC-MS-EI, A1 as original compound and A3 as its TMS derivative. The confirmation technique was confirmed by GC-MS with chemical ionization (CI).

The screening of the aliquots resulting from evaporation to dryness and reconstitution with acetonitrile (ACN) and DCM of water samples identified with the numeric code 742 and 743, followed by silylation using BSTFA could indicate the presence of four relevant chemical compounds identified by LAQ as D1, D2, E1 and E2. The screening of all aliquots originated from the other aqueous sample, 744, such as other aliquots prepared with samples 742 and 743 not indicated the presence of any spiking chemicals.

To report E2 was identified by the mass spectrum of its TMS derivative by GC-MS-EI. This spectrum showed the base peak at m/z 73 and the molecular peak at m/z 199, according with the reference spectra from the OCAD. Its identification was confirmed by GC-MS-CI technique, which spectrum showed the main characteristic signals for the compound with a strong signal at m/z 200 $[M+H]^+$. Chemicals D1, D2 and E1 were identified in a similar way by the mass spectrum of its TMS derivatives using GC-MS-EI technique. For their unambiguous identification, once again, the chromatographic parameter was used with comparison between RIs obtained experimentally and the RIs values in OCAD. Relevant analytical data are summarized in Table 2.

4.3 Report and Results evaluation

At the end of the analysis it was generated a report with all the relevant information of the identified compounds, their structural formula, details of the sample preparation and used analytical procedures, as well a compilation of all pertinent chromatograms and spectral data.

The Proficiency Test reports of all participating laboratories were sent for evaluating

laboratory that checks the data presented, verifying if they meet the criteria established. The evaluation was based on the criteria for acceptable performance, defined in specific PT quality system documentation and in agreement with the procedure for the evaluation of the results of an OPCW PT.

In the 40th Proficiency Test, all participants submitted their analytical report within the test period. There were sixteen A's, four B's, one C, one D and one F in the test score for the 23 regular participants, including the two A's of the assisting laboratories. No score was assigned to one trial participant. In this test, LAQ could detect five spiking chemicals and two non-scoring chemicals,

but lost one spiking chemical in the report evaluation, getting score B. In order to have an overview of the results of the participating laboratories OPCW elaborates Table 3. The laboratories that reached performance index A and B have considered results for the designation, requiring in three consecutive proficiency tests at least two results A and one B.

Preliminary results were discussed in a meeting with all participating laboratories at OPCW headquarters. After this, the result was issued and the laboratories had 30 days to present the follow up report, containing the corrective actions to eliminate the presented errors.

Table 3. Summary of Final Results for the 40th Proficiency Test. Blank space indicates that the chemical was not reported; 'X' indicates that the chemical was identified and its identification was supported by sufficient analytical data; 'O' indicates that insufficient data were presented to support identification; "F" (not for Chem. ID) indicates failure of the test; and "#" indicates trial participation.

	Sample code	Chemical reported	Participant code																											
			1	2	3	5	6	7	8	9	10	11	12	13	14	15	16	17	18	20	21	22	23	28						
Scoring chemicals	739	3-Quinuclidinyl benzilate	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	O	O	X	X	X						
	742	n-Butyl methylphosphonate	X	X	X	O	X	X	X	X	X	X	X	O	X	X		X		X	O	X	X							
	742	sec-Butyl methylphosphonate	X	X	X	X	X	X	X	X	X	X	X	X	X	X		O		X	X	X	X							
	743	2,2-Diphenyl-2-hydroxyacetic acid	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X		X	O	X	X	X	X						
	743	Quinuclidin-3-ol	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X		X		O	X	X	X						
Non-scoring chemicals	739	2,2-Diphenyl-2-hydroxyacetic acid	X	X	X	X	X	X		X		X	X		X	X	X	X			X	X	X							
	739	Quinuclidin-3-ol			O			X										O	X			X	X							
	739	Methyl benzilate													X								X							
	739	Benzophenone																					X							
	742	Methylphosphonic acid						X		X						X							X							
Score			A	A	A	B	A	A	A	A	A	A	A	B	A	A	#	B	D	C	B	F	A							

5. CONCLUSIONS

GRULAC, as strategic region, needs a laboratory infrastructure that provide chemical analysis relevant to the CWC with a high degree of confidence. Brazilian Army Chemical Analysis Laboratory demonstrated in 40th Proficiency Test its ability to unambiguous identify chemical agents. LAQ will continue to seek knowledge and improvements in its infrastructure, methodologies

and equipment to achieve the goal of becoming accredited by OPCW.

6. ACKNOWLEDGEMENTS

The authors wish to thank OPCW for the continuous support for qualification and training of LAQ team.

7. REFERENCES

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