

Introduction

The Environmental Monitoring Laboratory monitors air samples for CWA using Analytical Method MT-13 (AM MT-13) *Analysis of Chemical Warfare Agents and Degradation Products on DAAMS Tubes using Gas Chromatography/Mass Spectrometry*. This Internal Operating Procedure (IOP) falls under the scope of the Chemical Agent Standard Analytical Reference Material (CASARM) Quality Assurance Program. Air samples are collected onto DAAMS solid sorbent tubes (Fig. 1), undergo thermal desorption, and subsequently undergo analysis using a GC/MS. The QP is a quality control sample that has been spiked with a standard solution equivalent to the target level of the agents of interest and exposed to the sampling environment in the field to obtain a representative control to ensure the agents of interest can be detected in the sampling environment without matrix interferences. A minimum of two QPs must accompany every sample set, and there is, at minimum, one acceptable recovery QP per twenty samples. The current protocol stipulates that a QP must be aspirated within 72 hours of being spiked, and, samples must be analyzed within 72 hours.



Figure 1. A set of DAAMS Quality Process Samples

Materials and Methods

Test Matrix. A standard cocktail for spiking the DAAMS tubes was prepared using nine agents with masses that corresponded to one Worker Population Limit (WPL) at Calibration Level 2 (Table 1) in a volume of 24 Liters: 0.7 ng of Tabun (GA), Sarin (GB), Soman (GD), and Cyclosarin (GF); 9.6 ng of Sulfur mustard (HD); 20.0 ng of Nitrogen mustard (HN1) 2, 2'-Dichloroethylamine, Nitrogen mustard (HN3) 2, 2', 2'' Trichloroethylamine, and Lewisite (L) Dichloro (2-chlorovinyl) arsine. Prior to analysis, each DAAMS tube received 1 ng of the internal standard, 1-Bromo, 4-FluoroBenzene (BFB) and 10 ng of HexachloroBenzene (HCB) in 0.1% Bis Mercapto Ethanol (BME) in methanol (MeOH). BME in methanol was used to derivitize Lewisite for analysis by GC/MS.

Table 1. Calibration Levels and Concentrations (WPL)

CAL LEVEL	Spiking (μL)	GA/GB/GD/GF	HD	L/HN-1/HN-3	BFB
1	2	0.36	4.8	10	0.5
2	4	0.72	9.6	20	1.0
3	8	1.44	19.2	40	2.0

The test matrix consisted of thirty DAAMS tubes spiked with agent cocktail for each of five experimental conditions shown in Table 2. The refrigerated samples were allowed to warm to ambient room temperature (ART) before analyses.

Table 2. Test Matrix for Evaluating QP Performance for Chemical Agent Recovery Using DAAMS Tubes

Method	No. DAAMS Tubes Spiked	Aspiration Time (Min)	Flow Rate (mL/Min)	GC/MS Analyses	No. Samples Analyzed (Per Day)
1	30	0	--	Immediate	30
2	30	1	100	Post-aspiration	30
3	30	1	100	Day 1, 2, 3, 4, 7, 10	5
4	30	60	400	Day 1, 2, 3, 4, 7	5
5	30	480	50	Day 1, 2, 3, 4, 7, 10	5

Spiking and Handling of DAAMS Tubes. The DAAMS tube (SUPELCO Analytical, Bellefonte, PA.) dimensions were 0.6 cm x 11.5 cm and filled with Tenax™ material that trap large semi-volatile organic molecules released during thermal desorption. The DAAMS tube specifications cite a maximum temperature limit of 350°C, a conditioning temperature of 320°C and a desorption temperature of 300°C. For this study, the experimental parameters consisted of flow rates set at 50 - 400 mL/min to achieve a volume of 24 liters and aspiration times from 0 - 480 min. Thirty DAAMS tubes were spiked for each experimental condition at the WPL (Fig. 2).

Abstract

Chemical Warfare Agent (CWA) sampling events require baselining the sampling environment to establish a reference point for historical, perimeter and matrix conditions. For this evaluation, the Chemical Biological Applications and Risk Reduction's (CBARR) Environmental Monitoring Laboratory (EML) conducted air-monitoring activities co-locating Depot Area Air Monitoring System (DAAMS) sampling tubes in close proximity with positive control DAAMS tubes challenged with nine agents of interest to evaluate the effects on chemical agent recovery resulting from variable aspiration times, flow rates and extended holding periods. Ambient air samples were collected onto DAAMS tubes and examined using Gas Chromatography/Mass Spectrometry (GC/MS) analysis. The test matrix consisted of five experimental laboratory conditions with parameters to evaluate percent agent recoveries resulting from immediate and delayed GC/MS analyses after spiking DAAMS tubes with the cocktail and aspirating at 1, 60 and 480 min over a period of 1 - 10 days sample storage. For each experiment, thirty DAAMS tubes were challenged at the Worker Population Limit (WPL) with the agent cocktail plus an internal standard. The results of this study were used to verify optimal control conditions for Quality Process (QP) samples to ensure that the analytes of interest could be detected after extended holding periods.

Materials and Methods (Cont'd)

Thermal Desorption. A Dynatherm® (Dynatherm Analytical Company, Inc., Kelton, PA) was used to thermally desorb agent trapped on the DAAMS tube using a helium carrier gas (Fig. 3). A 1-min tube dry, a 3-min tube heat at 300°C, followed by a 2 min heat trap at 300°C allowing for the transfer of the collected sample from the tube to a focusing trap in the desorber. During the trap heat step, the focusing trap was heated and the sample was injected onto the GC column.



Figure 2. Spiking the DAAMS tubes.



Figure 3. (Left) A model 900-GG/EPC Dynatherm; (Right) The Agilent 6890 N GC with a 5975 MS used for analyzing the DAAMS QP samples.

GC/MS Analysis. Liquid extracts from the DAAMS tubes were prepared for analysis and examined using GC/MS. The sample was introduced by thermal desorption or extraction of the sample followed by liquid injection onto the analytical column. The mass selective detector breaks each compound down into ion fragments specific to that compound for both qualitative and quantitative analyses. Peak identification was based upon retention time comparison with internal or external standard calibration and by evaluation of the unique spectrum. MS ChemStation software was used for data acquisition, data analyses, and reporting. All samples were analyzed using an Agilent (Santa Clara, CA) 6890 N gas chromatograph (Fig. 3) with an Agilent 5975 mass selective detector mass spectrometer system. The GC was equipped with a 30 m x 0.25 mm, 1 μm film thickness (Agilent DB-1701) silicone-coated fused-silica capillary column. Identification of target analytes was achieved by comparing their Extracted Ion Current Profile mass spectra with the electron impact reference standards. Quantitation occurred via comparison of the major quantitation ions to known responses using a 3-point calibration curve. Following the calibration of the instrument, an Initial Calibration Verification Quality Laboratory (QL) sample was analyzed by spiking 4 μL onto QL DAAMS tubes. The calibration curve was verified before analyzing the QP samples requiring acceptance criteria

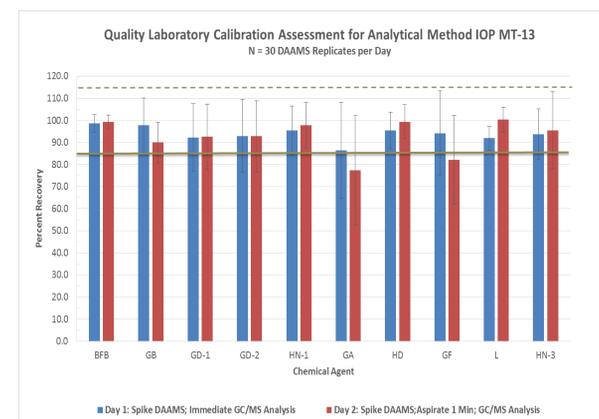


Figure 4. Percent recovery for chemical agent calibration verification of Quality Laboratory samples analysis in accordance with criteria found in AM-MT-13 procedure.

equivalent to ±15% of the initial source value. The calibration verification QL experiments were conducted over a 2-day period to meet AM MT-13 quality control criteria requiring a ±15% chemical warfare agent recovery from DAAMS tubes analyzed by GC/MS. On Day 1, thirty DAAMS tubes were spiked with 4 μL of standards and analyzed immediately. All QL samples from Day 1 met acceptance criteria values of falling within the ±15% agent recovery requirement. On Day 2, thirty DAAMS tubes were spiked with 4 μL of standards, aspirated for 1 min, followed by GC/MS analysis. All Day 2 QL samples met acceptance criteria values by falling within the ±15% agent recovery requirement with the exception of GA (77.4%) and GF (82.1%) shown in Figure 4.

Results

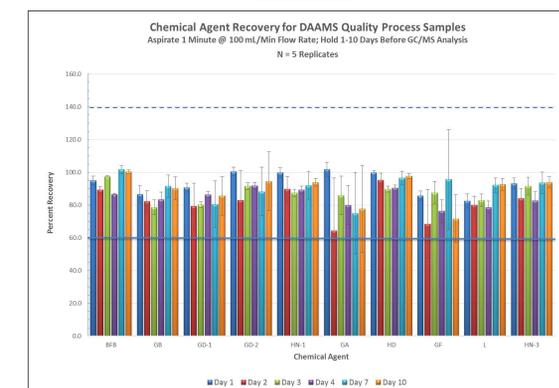


Figure 5. Percent chemical agent recovery for QP samples held from 1-10 days. Samples were aspirated 1 min at 100 mL/min flow rate, followed by GC/MS analysis. All agent recovery values met the acceptance criteria ±40% for Class I agents. The method excludes values for obtained for L, HN-1, HN-3 since they typically do not meet Class 1. The error bars represent the standard deviation within the data sets.

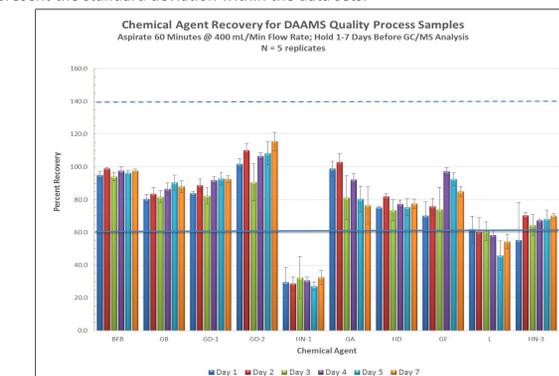


Figure 6. Percent chemical agent recovery for QP samples held from 1-7 days. Samples were aspirated 60 min at 400 mL/min flow rate, followed by GC/MS analysis. All agent recovery values met the acceptance criteria ±40% for Class I agents. The method excludes values obtained for HN-1 (30.1%), L (56.9%) and HN-3 (Day 1, 55.3%) since they typically do not meet Class 1. The error bars represent the standard deviation within the data sets.

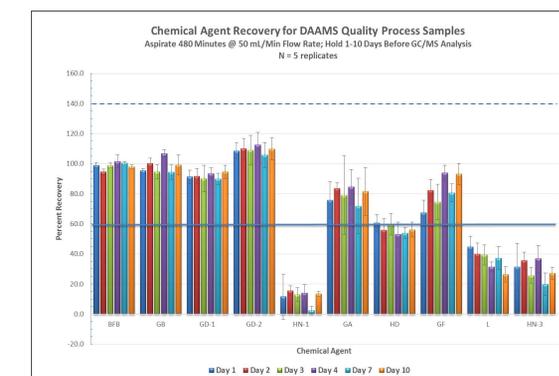


Figure 7. Percent chemical agent recovery for QP samples held from 1-10 days. Samples were aspirated 480 min at 50 mL/min flow rate, followed by GC/MS analysis. All agent recovery values met the acceptance criteria ±40% for Class I agents for the exception of HD (56.5%). The method excludes values obtained for HN-1 (11.7%), L (36.5%) and HN-3 (29.3%) since they typically do not meet Class 1. The error bars represent the standard deviation within the data sets.

Discussion

This study confirmed that acceptable QP recovery results for each of the 9 agents were achieved over a 10-day period when aspiration time and flow rate conditions were set at 1 min and 100 mL/min, respectively. However, when conditions were modified to increase aspiration time (60, 480 min) and fluctuate flow rate (400 and 50 mL/min), the H agents and L agent were not stable over a 10-day period.