

WEST DESERT TEST CENTER
U.S. ARMY DUGWAY PROVING GROUND
Agent Fate

MEASUREMENT OF CHEMICAL WARFARE AGENT PERSISTENCE ON CONTAMINATED
SURFACES UNDER CONTROLLED ENVIRONMENTAL CONDITIONS

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An innovative 16 cell test fixture was constructed at the Kendall Combined Chemical Test Facility (CCTF) located at Dugway Proving Ground's West Desert Test Center to measure the vapor hazard of chemical warfare agents on contaminated surfaces under controlled environmental conditions. Vegetation, aged CARC coated steel, MHE coated steel and soil were tested at 35°C with 50% relative humidity (RH) and a wind speed of 1.65 miles per hour (mph). The test fixture accommodates 16 test items. At least two positive and two negative controls were included in each trial. Soman (GD) and VX were evaluated using two contamination levels: four 0.1 microliter (uL) drops of agent comprise the lower contamination level and one 40 microliter (uL) drop is used for the higher level. There is minimal GD vapor hazard 40 minutes after small drop deposition and 8 hours after large drop deposition on MHE coated steel. However there was a potential vapor hazard from GD evaporating from aged CARC or soil 24 hours after large drop agent deposition. VX vapor concentrations were still present above the minimum detection level 24 hours after agent deposition for both the small and large drop contamination levels.

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I. INTRODUCTION

Current U.S. military protection and operating procedures for chemical warfare agent (CWA)-contaminated environments depend upon an understanding of vapor and contact hazards that may threaten personnel and equipment over time and under certain environmental conditions. In practice, this knowledge has been collected over many years from numerous tests, experiments, reports, discussions, and various other sources.

Laboratory-scale experiments were conducted to measure evaporation profiles and persistency of CWAs. The two chemical agents selected were a persistent nerve agent (VX) and the volatile nerve agent soman (GD). The experiments were performed under controlled environmental conditions (35° C/50% RH with a 1.5-1.8 mph wind) and on five different surfaces. The five substrate materials are: carbon steel coated with material handling equipment MHE) paint, carbon steel coated with aged chemical agent-resistant coating (CARC), a compacted sandy-loam soil, and vegetation (wheat grass)

The test fixture allows reliable, standardized data collection relating to chemical agent off-gassing and qualitative persistency data. A variety of meteorological conditions can be replicated with consistency and accuracy over the test period. The fixture consists of sixteen cups which can accommodate the testing of different surface materials and controls while keeping test conditions (such as air flow over the substrate) constant.

II. FIXTURE DESIGN



Figure 1. West Desert Test Center, Dugway Proving Grounds Agent Fate Test Fixture.

A. Design Basis

The test fixture was engineered to address a number of concerns that were difficulties encountered during previous testing at Dugway Proving Grounds (See Figure 1). The first goal was to produce a test fixture that would allow for reliable data collection relating to chemical agent off-gassing and qualitative persistency data. It was critical for the test fixture to replicate a variety of meteorological conditions with consistency and accuracy over the test period. The fixture also needed to accommodate the testing of different surface materials while keeping test conditions (such as air flow over the substrate) constant.

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In addition to the general adaptability of the instrument, the design of the test fixture would address problems incurred during the previous WDTC agent fate and persistence testing. Of primary concern was minimizing or eliminating of plating effects caused by the re-condensation of agent on test cell walls. The design features that were modified to minimize plating effects are listed in the next paragraphs.

1. Sample lines were shortened. The distance between the test cell and sorbent tube was reduced so that effluent vapor could not condense on the sample tube walls. Also, the inner walls were coated with Sulfinert® to prevent agent adsorption. See Figure 2.

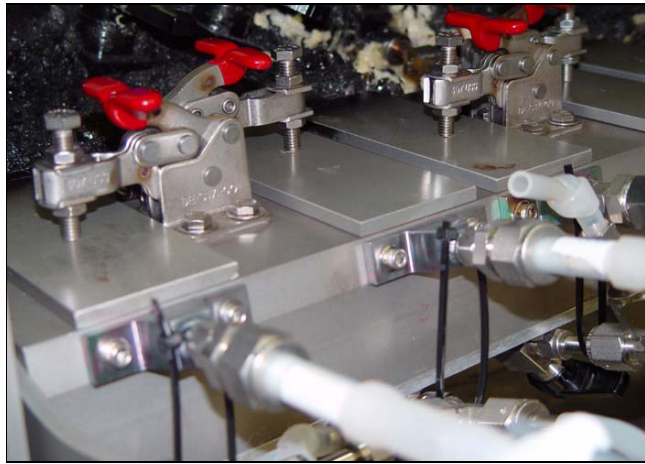


Figure 2. View of sample cell outlets and their connection to the solid sorbent tubes.

2. It was essential to normalize environmental conditions across all test cells, regardless of position in the block, and to maintain this thermal stability throughout the test period. The header (Figure 1) connects to the inflow tubes for each test cell and supplies environmentally conditioned air to the test fixture at near-laminar flow rates. The result is a reduction in turbid air entering the test fixture that can disturb isothermal conditions.

3. The test fixture was designed to operate under vacuum. The vacuum pulls the conditioned air across the test surface, through the cell outlet tubing and through the solid sorbent tubes where the agent is collected. See Figure 2.

4. The test fixture was fitted with gaskets to ensure proper sealing throughout the system. In the test cell, a clamp compressed the gasket between the top of the cell cavity and the lid, and between the test cup (housing the coupon) and the bottom of the cell cavity. This mechanically created seal served to reduce the possibility of agent vapor leakage. See Figures 3 and 4.



Figure 3. View from above the test cell showing the inlet port and sealing o-rings.



Figure 4. Fixture cell lid.

5. Each of the two sample shelves hold eight individual test cells. Heating and cooling was accomplished using fluid instead of air to improve the heat-up/cool-down response time and the thermal stability of the system. Reducing or eliminating thermal oscillations due to coil function was the imperative; however, design improvements yielding the shortest test duration (including ramp-up and conditioning periods) were favored, but not a requirement.

6. The test fixture instrumentation allowed for measurement of airflow across the sample coupon.

B. Fixture Details

The subsystems consist of the test fixture (the test cup, cell and block), chiller/heater units, the humidity generator, the vacuum pump system, system instrumentation, process control and data collection. One of the agents evaluated, VX, has been shown to react/adsorb with the chromium oxide that occurs on the 316 stainless steel surface. To prevent this adsorption, the 316 stainless steel surfaces have been treated with the Sulfinert[®] process.

The instrumentation consists of:

1. One temperature and humidity probe in each header feed pipe to the test fixture.

Process control and data collection is maintained by a laboratory computer equipped with the program, LabVIEW[®].

1. Test Cell Description

The test fixture consists of two aluminum blocks, each block holding eight test cells. The blocks contain coiled tubing for the circulating of fluids to heat/cool the test cells. The test cells contain a test cup (described below), influent tubing (bringing environmentally-conditioned air into the test cell), and effluent tubing (where air exits the test cell and is split between a bypass and sorbent tubes). Each test cell is equipped with a specially designed lid that is machined to be tight fitting and is equipped with grooves for rubber gaskets. The cell and lid are sealed by clamps which compress the rubber gasket surrounding the top of the test cell. All airflow from the test cell was collected with a solid sorbent tube. Critical orifices control the amount of airflow through the sorbent tubes. These constrictions act as a mass flow control device for the entire system. The total designed airflow rate is 1.5-1.8 miles per hour (mph) through the test cell.

The test cups are rectangular in shape to accommodate the test items, or coupons. Environmentally conditioned air enters and exits the cups through stainless steel tubing. Specially designed adapters transition airflow from the round tubing to the rectangular cup. These 316 stainless steel adapters direct air into the flow channel (4 x 10 mm) where the spiked substrates are presented. The flow channel has a Holland tunnel shape to improve sealing capabilities. The bottom of the test cup is spring-loaded such that differences in coupon height can be adjusted for in each test while air speed through the flow channel is kept constant.

2. Environmental Conditioning System

The Chiller/Heater Units are re-circulating bath type systems. These units provide temperatures with a control accuracy of $\pm 0.05^{\circ}\text{C}$ (0.09°F). Two systems are required, one to heat the the Nafion[®] tubes and the other unit is used to heat/cool the test fixture.

The humidity generation system is built around Nafion[®] tubes. Nafion[®] is a sulfonated Teflon polymer that allows selective diffusion of different compounds. With water on one side of the tubing and an air stream on the other, water will slowly diffuse into the dry air stream. Increasing or decreasing the water temperature can control the diffusion of water into the air. A mass flow controller controls the amount of air entering the tube. The rate of diffusion can thus be controlled by a set point input at the instrument-controlling computer.

3. Vacuum System

Airflow through all 16 test cups is maintained by a vacuum pump. The pump pulls the conditioned air across the substrate surface. The vacuum pump is self-lubricating with graphite vanes. This prevents the accumulation of large quantities of contaminated lubricating fluids. The discharge of the vacuum pump is equipped with an activated carbon filter, to remove organic compounds.

4. Sample Collection and Extraction System

All of the effluent from each test cell is directed through a ½" OD solid sorbent tube. The tubes are constructed of PFA and PTFE Teflon. The larger diameter tube allows for flow rates of up to 9 liters per minute (LPM). Chromosorb 106 was chosen as the sorbent material to use for both GD and VX. Each tube is packed with 250 mg of sorbent material.

After the tubes are finished sampling each tube is extracted using the MECADES 2000 automated tube extraction system. The extraction system pumps a predetermined quantity of solvent at a predetermined flow rate through the sorbent tube. During method development acetonitrile was selected as the best extraction solvent for GD. This was validated by performing a spiking study where 10 tubes were spiked with a known amount of agent. Each tube was then extracted using the procedure outlined in section III.C. and analyzed by GC/FPD-FID. The average recovery of the study was 95% with a relative standard deviation (RSD) of 5%.

VX is collected without derivatization. Since VX tightly adsorbs to many surfaces acetonitrile alone was not sufficient to extract the majority of VX present on the tube. Diisopropylaminoethanol was added to the acetonitrile to achieve a 20% concentration. An average recovery of 95% with a 5% RSD was obtained using the solution.

III. PROCEDURES

A. Agent Challenge

The test was set up and conducted in chemical fume hoods in the Kendall Combined Chemical Test Facility (CCTF). After the fixture reached an equilibrium condition, substrate materials were placed in the test fixture and allowed to condition at 35°C/50 percent RH for 30 minutes before the trial began. One droplet (40 µL) or four droplets (4x0.1µL) of agent was applied to the center of each substrate. Five replicates were used for each agent contamination level/substrate combination.

B. Sample Extraction and Analysis

After the samples are collected from the fixture using solid sorbent tubes they are extracted using the MECADES 2000 automated extraction system. The extract is then analyzed by a gas chromatograph configured with a split between a flame photometric detector (FPD) and a flame ionization detector (FID). This procedure allows the analyst to quantitate over a much wider range than either detector individually.

IV. RESULTS

A. GD Validation

During GD validation it was determined that due to the nature of the compound one hour sample times might be too long to gather adequate data to show a good evaporation profile. Three validation trials were performed. For the first trial sorbent tubes were collected after 1, 2, 3, 4, 6, 8, 12, 16, 20, and 24 hours. For the second trial, the small drop sample tubes were collected every 20 minutes for 6 hours and for the large drop sample tubes were changed every 40 minutes for 8 hours. This sample collection procedure was difficult to maintain as a result a third validation trial was conducted with sample tubes being collected every 40 minutes for 4 hours then at 8, 12, 16, 20 and 24 hours.

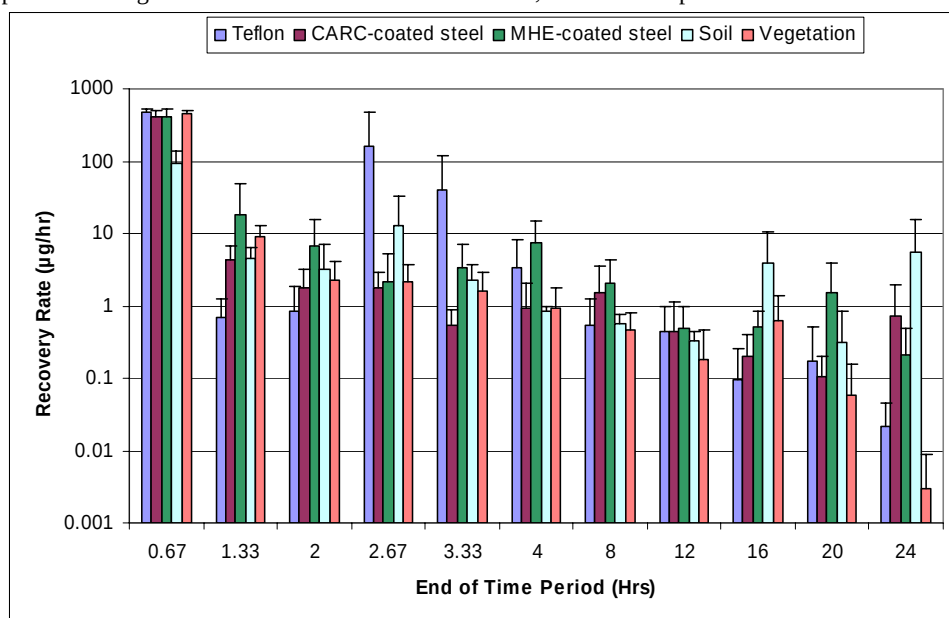
B. GD Persistence Results

At least five replicates of each substrate were spiked with both agent contamination levels. The fixture maintained a temperature of 35C and 50% RH. Two positive controls and two negative controls were run with each trial. The positive control surfaces were rectangular pieces of PTFE Teflon. The evaporation of the agent off of the Teflon provided a standard to measure each of the other test substrates and their corresponding evaporation rates.

For the small drop contamination (405.2 ug GD) there was a significant decrease in GD evaporation rates after 40 minutes on all test surfaces (Figure 5). Only minimal amounts of GD were collected between 40 minutes and 24 hours. There were no significant differences in the evaporation rates of GD for each of the substrates.

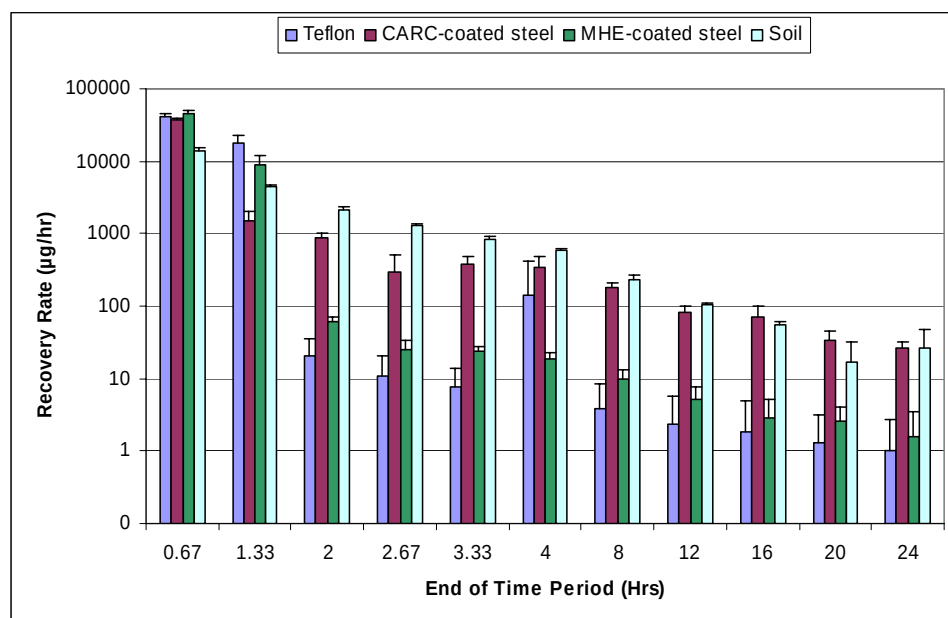
The large drop contamination (40,520 ug GD) showed slightly different results (Figure 6). The large decrease in GD evaporation rate occurs 80 minutes after agent deposition with the exception of the soil and the aged CARC. GD evaporated from the soil and aged CARC with a consistent decay through the 24 hour test. The MHE coated substrates had similarly shaped profiles to the Teflon controls.

We can draw the conclusion that at 35C and 50% relative humidity GD poses no vapor hazard to an unprotected person after 40 minutes of small drop agent deposition on all test surfaces. However, with large drop contamination on either soil or aged CARC there is a potential vapor hazard to an unprotected person. For agent contaminated MHE coated surfaces, there is no vapor hazard after 8 hours.



NOTE: Error bars indicate upper bound of 95 percent confidence interval. CARC – chemical agent-resistant coating, MHE – material handling equipment.

Figure 5. Recovery Rate by Time of 0.4 μ L (405.2 μ g) of Soman (GD) by Substrate; Agent Fate.



NOTE: Error bars indicate upper bound of 95 percent confidence interval. CARC – chemical agent-resistant coating, MHE – material handling equipment.

Figure 6. Recovery Rate by Time of 40 μ L (40520 μ g) of Soman (GD) by Substrate; Agent Fate.

C. VX Validation

Due to VX having a low vapor pressure, 24 hour trials were suspected to be too short to allow for a well defined evaporation profile. 48 hours was chosen as an acceptable test length. A small drop comparison study was conducted to verify that agent spiking was consistent. Replicates of 3, 4 and 5 0.1uL drops of agent were tested. 4 drops of 0.1uL per drop was determined to be the lowest contamination level that demonstrated reliable consistency.

The large drop, 40 uL, was determined by the width of the airflow path in the cell. A drop larger than 40 uL would come too close to the walls of the cell lid. This could affect the flow of air through the cell and the evaporation of the agent off of the substrate.

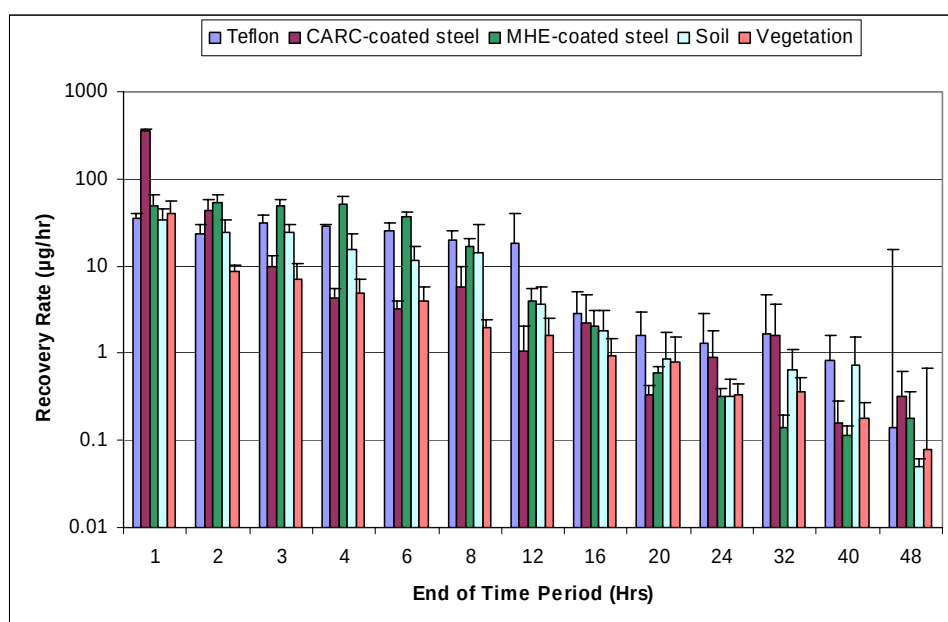
D. VX Persistence Results

At least five replicates of each substrate were spiked with both agent contamination levels. The fixture maintained a temperature of 35C and 50% RH. Two positive controls and two negative controls were run with each trial. The positive control surfaces were rectangular pieces of PTFE Teflon. The evaporation of the agent off of the Teflon provided a standard to measure each of the other test substrates and their corresponding evaporation rates.

The testing shows steady VX evaporation rates for the small drop contamination (403.2 ug VX) through 8 hours and a steady decay in the rate from 8 to 48 hours for MHE coated steel, soil and the Teflon control. (Figure 7). The CARC coated steel and vegetation substrates showed a decreasing evaporation rate for VX through 4 hours then tapering to a steadier rate from 4 hours to 48 hours. There were significant differences in the evaporation rates of VX for each of the substrates.

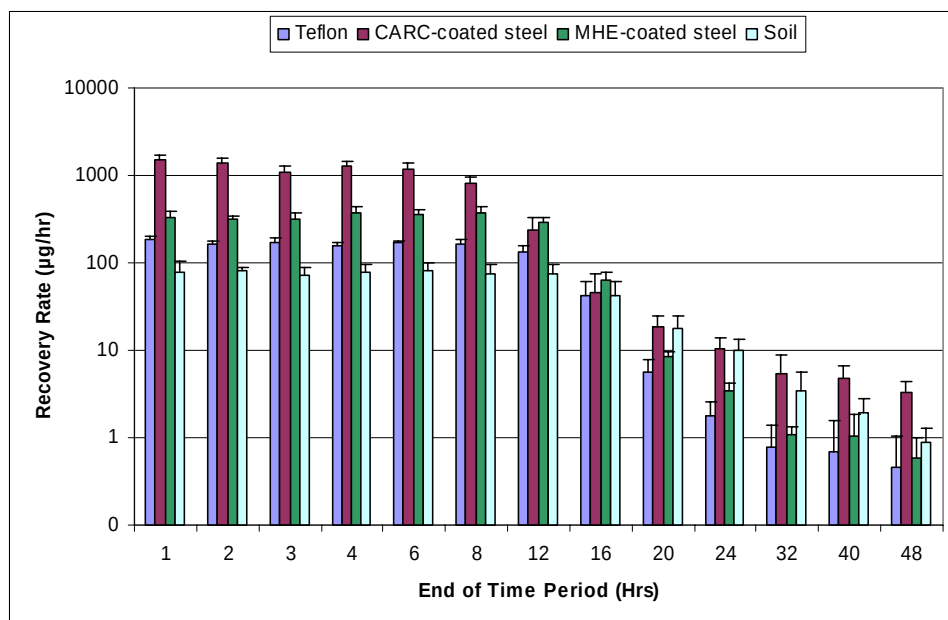
The large drop contamination (40,320 ug VX) showed slightly different results. Aged CARC coated steel had the highest evaporation rate that was consistent through 8 hours then slowly decayed from 8 to 48 hours (Figure 8). The remaining substrates had similarly shaped profiles.

We can draw the conclusion that at 35C and 50% relative humidity VX poses a vapor hazard for an unprotected person from either contamination level (small drops or large drop) on each of the tested substrates for 24 hours after agent deposition.



NOTE: Error bars indicate upper bound of 95 percent confidence interval. CARC – chemical agent-resistant coating, MHE – material handling equipment.

Figure 7. Recovery Rate by Time of 0.4 µL (403.2 µg) of Persistent Nerve Agent (VX) by Substrate; Agent Fate.



NOTE: Error bars indicate upper bound of 95 percent confidence interval. CARC – chemical agent-resistant coating, MHE – material handling equipment.

Figure 8. Recovery Rate by Time of 40 µL (40320 µg) of Persistent Nerve Agent (VX) by Substrate; Agent Fate.

V. CONCLUSIONS

This fixture has shown some promising data on understanding the evaporation rates of chemical warfare agents from various substrates under consistent environmental conditions. The testing has indicated that contamination density is an important factor to consider. Also, some minimal amount of personal protection would be required for the quickest response after a chemical event. With additional testing the fixture will provide a more accurate look at the behavior of chemical evaporation. Procedure and policy makers will have additional information to assist them in their efforts.

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