Chemical Warfare Agent (CWA) (VX, GB and HD) Vapor Characterization at the General Population Level (GPL) Using the Army's Optically Enhanced Flame Photometric Detector (ENFPD)

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Overview

This MINICAMS®, Miniature Continuous Air Monitoring System, incorporates a new optical light focusing concept enabling near-real-time sampling for the chemical warfare agents (CWAs) G, V and H at the general population level (GPL) for detection and analysis. The improved FPD system was developed at Dugway Proving Ground in 2005 and has met testing requirements for a Type 1 Safety Air Monitoring method as defined in the CASARM Quality Assurance Plan for Chemical Agent Monitoring, Rev. 6, May 2010, Aberdeen Proving Ground, MD 21010-5424. Present work has been accomplished using this detector to clear potentially contaminated TOCDF igloos for reuse to store conventional munitions. Table 1 shows the 8-hour GPL in (mg/m3) for the G, V and H agents and their corresponding mass on column as defined in the airborne exposure levels recommended by the Center for Disease Control and implemented by the Army in January 2005.

Background

Implementation of the new Army guidance on safety air monitoring created an expensive requirement for near-real-time monitoring of chemical warfare agents (CWAs) during chemical agent operations. Prior to January 2005, most Army facilities working with CWA were required to monitor for agent at the OSHA 8-hour time weighted average (TWA) level or today's short-term-exposure limit (STEL). This was done using the MINICAMS® or historical monitoring using solid-sorbent-tubes (SST). Dugway Proving Ground (DPG) initiated the strictest interpretation of the Department of Army Implementation Guidance adopting real-time monitoring at the Worker Population Limit (WPL). As of today all CWA agents at Dugway are monitored at the WPL. Monitoring for CWAs is an ongoing challenge being faced by the Army's Demilitarization, Research and Development and Test and Evaluation communities for characterization of non-contamination during test retrograde post chemical weapons exposure. This detector is currently used to detect and measure G, V and H series agents at levels that are safe to reuse previously contaminated articles post decontamination at the safest levels required today or the GPL.

Table 1: 8-Hour GPL DA Implementation Guidance

Agent	General Population Limit (mg/m^3)	Mass on Column (ng)
GA, GB	0.000001	0.005 to 0.007
VX	0.0000006	0.003 to 0.0036
HD, H	0.00002	0.1 to 0.2

Memorandum, OASA (I&E), 18 June 2004, Subject: Implementation Guidance Policy for New Airborne Exposures Limits for GB, GA, GD, GF, VX, H, HD, and HT.

Design

An investigation to enhance sensitivity for a typical FPD photo-multiplier tube (PMT) assembly was initiated to improve a commercially available MINICAMS® (Figure 1), as purchased from O.I. Analytical for G, V and H agent safety air monitoring at the WPL and GPL. Dugway Proving Ground (DPG) contracted ATK Mission Research, Santa Barbara, CA to assist in fabricating an optics design that would increase the amount of light delivered onto the FPD by a factor of 10. Figure 2 is a computer representation made using Raytrace Software showing the the Army's enhanced optics design of the FPD PMT assembly. This image gives you an idea of the improved capture efficiency of the light emitted during phosphorous and sulfur combustion using the modified detector. In the manufacturer's design the percent of light rays delivered to the PMT aperture is about 10%, whereas in the optically enhanced design the amount of light rays increases to about 98%.

Ultimately, the number of light rays reaching the photomultiplier tube is shown in Figure 2. The blue rays are for the mirror reflection and the green are straight to the PMT. This gain in efficiency is made by using a matched pair of culminating lenses, a Plano convex focusing lens, and inserting a spherical mirrored back plate on the back side of the detector combustion block. The Plano convex lens replaces the glass window on the front of the PMT coupling. The FPD coupling assembly supplied by O.I. Analytical was re-tooled to accommodate the lenses, spacers and locking clamp to hold the optical alignment stationary. The components inside the PMT coupling assembly for the optically enhanced FPD detector are displayed in Figure 3.

Figure 1. FM-3001 FPD MINICAMS

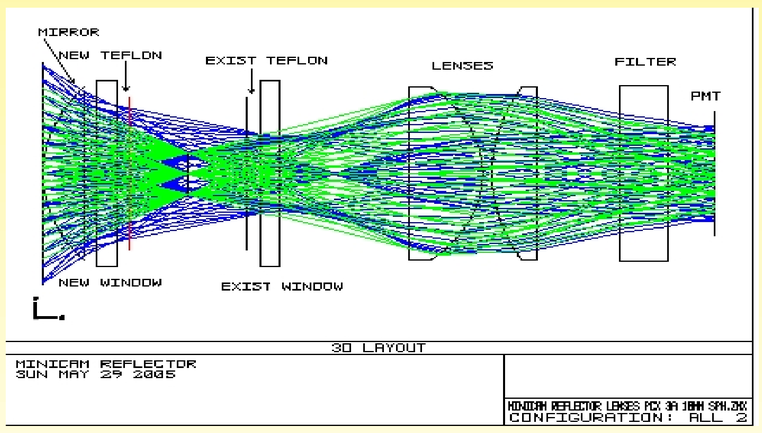

Figure 2. PMT redesign showing ray trace for Enhanced Optics detector

Detection System

The detection system is a standard PMT supplied with the MINICAMS® as manufactured by O.I. Analytical. The vapor sample is collected onto a Haysep D 60/80 mesh pre-concentrator tube (PCT). This PCT is essential to trap a consistent 5 pico-grams VX sample in air at 0.5 L/min flow rate for a 10 minute sampling period. The original Haysep D 40/60 mesh tube supplied by O.I. Analytical yielded inconsistent results with greater than 25% error in replicate calibration standard injections during parameter development to meet the WPL for VX. The optimum operating parameters are given in Table 2. The total single cycle time to collect sample and measure airborne concentration results was 13 minutes.

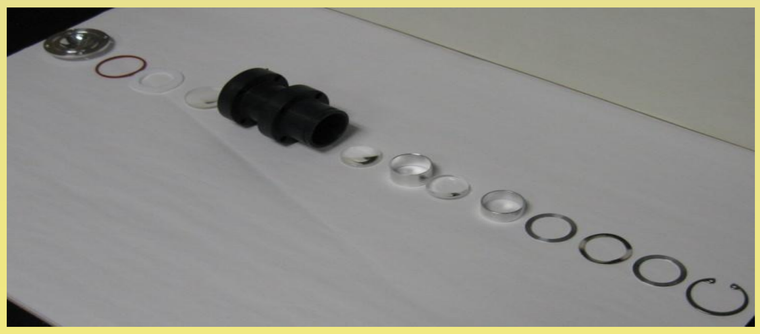

Figure 3. Individual components as assembled in the FM-3001 FPD MINICAMS coupling assembly

Table 2: MINICAMS® Operating Parameters

O·I·Analytical — CMS Field Products

Operating Conditions — MTF-11, ATC West — 23:54 09/11/2008

S/N 1820 — RUN NO ALARM

Method: ENVX	Parameter	Setpoint	Actual	Limit
TEMPERATURES, °C:	Ambient	40	38	± 15
	Inlet	50	51	± 15
	Detector Block	150	151	± 15
	Detector Flame	200	229	± 99
	Column		158	
	Column 1, Low	40	41	± 15
	Column 1, High	200	200	± 15
	Column 1, Rate, °C/min	150	151	± 30
	Column 2, High	200		
	Column 2, Rate, °C/min	0		
	PCT Heater		196	
	PCT Heater, Low	40	43	± 20
	PCT Heater, High	235	237	± 30
PRESSURES, psig:	Air	38	40	± 5
	Carrier (Nitrogen)	45	46	± 5
	Hydrogen	35	36	± 5
SAMPLE (2 L/min LMF):	Flow Rate, ccm	500	1328	± 99
	Avg. Flow Rate, ccm		544	
	Volume, L @ 21°C, 4350 feet		5.44	
VOLTAGE, VDC:	FPD Photomultiplier	1200	1200	± 50
ELECTROMETER:	FPD Signal, nA	401	FPD Zero, nA	1000
	FID Signal, nA	0	FID Zero, nA	0
TIMED EVENTS, sec:	Purge	0 - 180	Sample	180 - 780
	Desorb	5 - 65	Column 1	30 - 150
	Column 2	150 - 150		

CONCENTRATION REPORTS: — Alarm Setpoint, % ENVX 70

Cmpd	Status	Concn, mg/m3	Concn, ENVX	Height,* nA	Area, nA-sec	RT, sec	Width, sec	Gate On	Gate Off
VX	RUN	0	0.00	0	0	0.0	0.0	63	67

* Concentration readings are based on peak height

CALIBRATION INFORMATION:

Cmpd	Det	ENVX Level	Date	Time	Height,* nA	Area, nA-sec	RT, sec	Width, sec	Gate On	Gate Off
VX	FPD	1.0	09/09/2008	12:25	140	279	66.2	1.6	63	67

SAMPLING SEQUENCE: — SOFTWARE: 07022007 — ELAPSED TIME: 77 sec

Printed : 11/19/2008 4:42 PM — Facility: MTF (Host 1) — Station: Station 11 — Analysis : 300388

Discussion of Results

The Enhanced Optics FPD system meets testing requirements for a Type 1 Safety Air Monitoring method using the Precision and Accuracy procedures as defined by CASARM in the Quality Assurance Plan and the provided DEPOT P&A, Revision 5, April 2001 analytical software to certify analytical methods. The P&A data for this method was performed on GC columns DB-1and DB-210. Each column met criteria for detection limit (LOQ), certified reporting limit (CRL), target action level (TAL), found action level (FAL) and uncertainty in found mass (UIFM). Typical enhanced optics chromatogram at the GPL for G, V and H agents are shown in Figures 4,5 and 6, respectively. The typical signal height, greater than 115 nA, yields a signal to noise ratio greater than 5, indicating excellent resolution of true peak detection from the detector noise at the GPL action level. The performance of the enhanced optics FPD detector was compared to a commercial pulsed flame photometric detector (PFPD) purchased from O.I. Analytical. This was done to determine if migration to this detector was required to accurately measure CWA vapor at these trace levels. As you can see in Figure 7, the enhanced optics demonstrated greater sensitivity to mass of VX over the range from 5 to 40 pico-grams. Typically, a factor of 3 to 5 enhanced sensitivity was observed from lower to higher mass challenges. In Figure 8, the linearity of the detector over the same mass is seen.

Conclusions

The Enhanced Optics FPD system significantly advances air monitoring capabilities. Since solid sorbent tube sampling and analysis are no longer required, using the enhanced detector has lowered the cost and increased the expedition of decontamination verification test results. An additional cost savings can be considered when comparing the cost of a PFPD versus the cost of installing the enhanced optics on a standard FPD MINICAMS®. The detector, a modified FPD MINICAMS® (which occupies minimal laboratory space), provides selective and sensitive detection for a wide range of test chemicals, even in the presence of contaminants. Future work is required to determine detector saturation in the presence of gross contamination. The Department of Defense CWA Demilitarization efforts have a specific need for this Type 1 monitoring capability during closure operations. The Chemical Materials Agency (CMA) has installed thirty ENFPD detectors to date in support of demilitarization facility closure activities currently ongoing at TOCDF, UMATILLA and ANNISTON.

Acknowledgements

The Dugway Proving Ground Safety Air Monitoring staff, Dr. Matt Thomas, ATK Mission research, John R. Schaub, Dugway Test Technology, Eric Garff, GEOMET LLC, and Chuck Evans, Jacobs Dugway Team electrical engineering support.

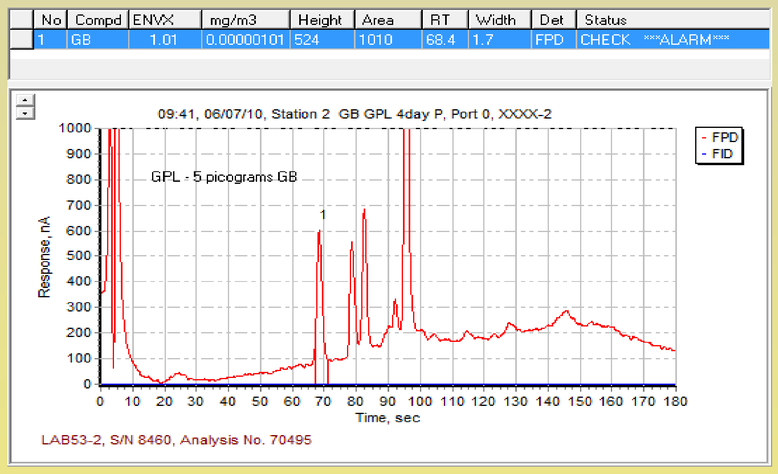

Figure 4. GB at 0.000001 (mg/m3) or 5 pg on column for Enhanced Optics detector.

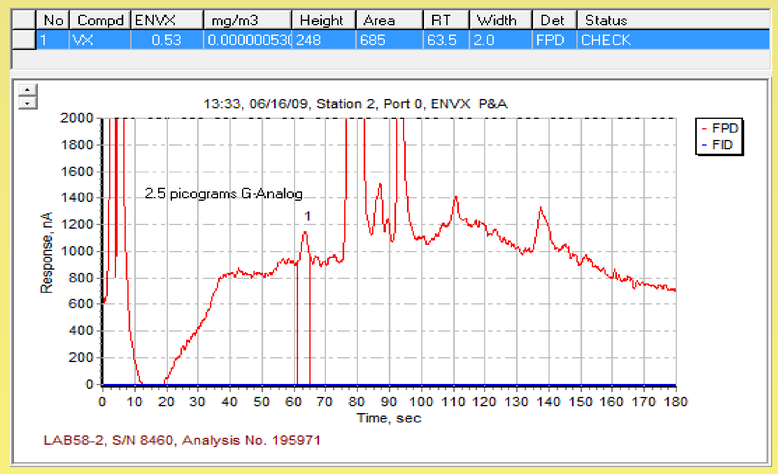

Figure 5. VX at 0.0000006 (mg/m3) or 2.5 pg on column for Enhanced Optics detector.

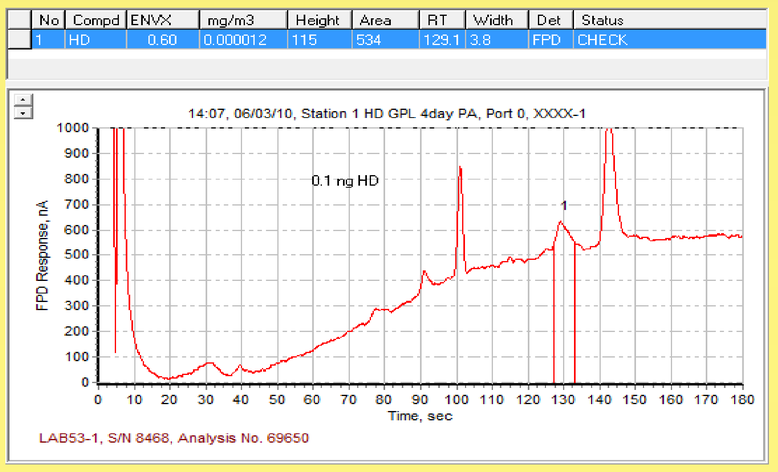

Figure 6. HD at 0.00002 (mg/m3) or 100 pg on column for Enhanced Optics detector.

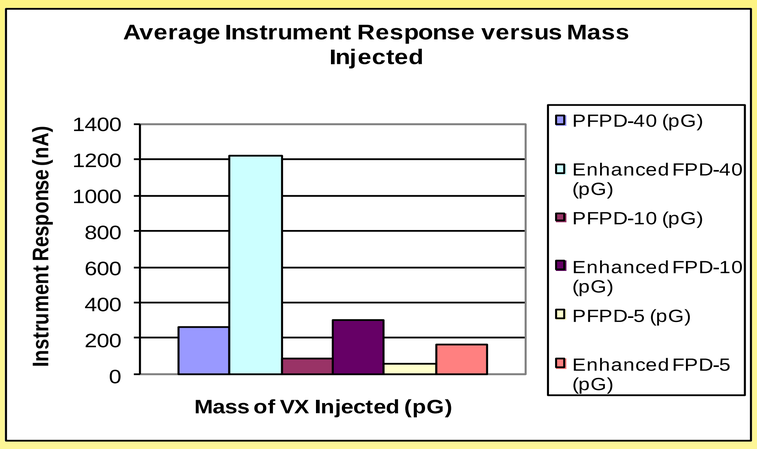

Figure 7. VX at 0.000001 (mg/m3) or 5 pg on column for Enhanced Optics detector.

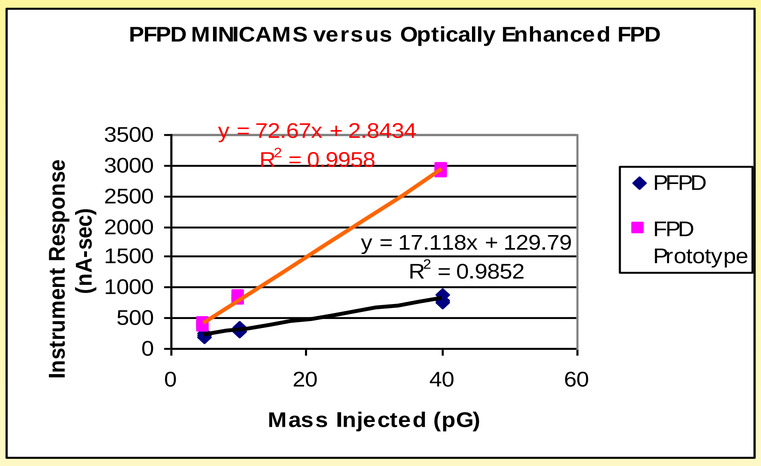

Figure 8. Linear response for VX at 0.000001 (mg/m3) to 0.00001 (mg/m3) for Enhanced Optics detector.