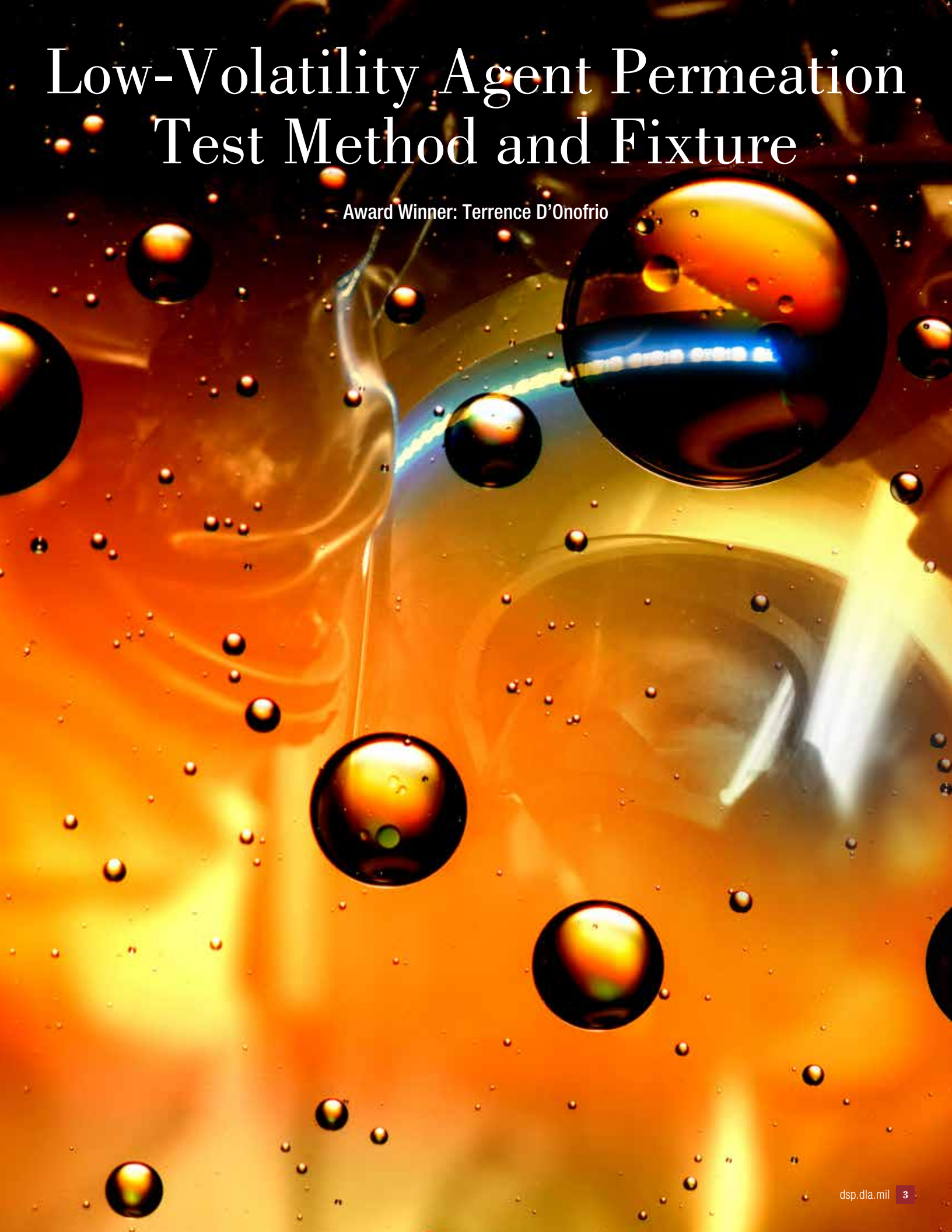
Low-Volatility Agent Permeation Test Method and Fixture

Award Winner: Terrence D'Onofrio



Terrence G. D'Onofrio, of the U.S. Army Edgewood Chemical Biological Center (ECBC) at Aberdeen Proving Ground, MD, invented a contact-based permeation research fixture and method that invoked standardization to close a critical gap in protection testing. The low-volatility agent permeation (LVAP) system is the first contact-based method capable of accurately quantifying the permeation hazard of low-volatility contaminants, such as the chemical warfare nerve agent VX, through clothing and protective equipment. Applying traditional, vapor-based permeation test methods to low-volatility compounds can yield unreliable and dangerously misleading results. The LVAP method enables low-volatility agent testing that is nearly 10-fold more precise than vapor-based testing at one-tenth the cost. The LVAP system is an open architecture design; components are easily sourced, modified, and replaced. Key LVAP components are reusable commercial off-the-shelf (COTS) items, and required consumables are commercially sourced.

After the LVAP completed verification and validation (V&V) under the auspices of the Deputy Under Secretary of the Army for Test and Evaluation (DUSA TE), the V&V report earned concurrence from representatives of the four services and joint offices. The LVAP method is now endorsed as a DoD Test and Evaluation standard. Use of the LVAP method will yield improved operational readiness and safety among all service branches with a concomitant benefit to emergency responders, federal agencies, and international partners.

Background

Accurate permeation testing[1] is an essential component of comprehensive safety assessment for clothing and personal protective equipment (PPE) used by soldiers and many civilians, including law enforcement personnel, first responders, and agricultural and industrial workers. It is impossible to fully evaluate the suitability and safety of any clothing or PPE without reliable data to describe how well the item excludes chemical contaminants.

Traditional, vapor-based permeation test methods (i.e., Test Operations Procedure 8-2-501) are appropriate for measuring the permeation of volatile contaminants, such as the nerve agent sarin. However, these vapor-based methods are insufficient for identifying and quantifying the permeation of low-volatility contact hazards, such as the nerve agent VX. Attempts to use traditional methods to quantify a contact hazard can result in a 20-fold under-prediction of the potential hazard.[2]

[1] All testing for the V&V was performed with materials that are known to be permeable to VX. At no time was military PPE found deficient outside the given specifications. No inference of vulnerability is intended or implied.

[2] D'Onofrio, T.G., *Development of a Contact Permeation Text Fixture and Method*, Technical Report ECBC-TR-1141, U.S. Army Edgewood Chemical Biological Center, Aberdeen Proving Ground, MD, 2013.

The lack of a contact-based method raised questions regarding laboratory safety and test readiness. To resolve this problem, Dr. D'Onofrio designed and developed a contact-based method for permeation testing of low-volatility contaminants. The LVAP test fixture and method is the result of years of research at ECBC that has been supported by the Joint Science and Technology Office (Ft. Belvoir, VA), the U.S. Army Natick Soldier Research, Development and Engineering Center (Natick, MA), and the Joint Program Executive Office for Chemical and Biological Defense including the Joint Project Manager for Nuclear, Biological, and Chemical Contamination Avoidance (both at Aberdeen Proving Ground, MD). After a lengthy process of equipment and method design and redesign, implementation, and capability testing, Dr. D'Onofrio's LVAP system has been accepted and approved as a Test and Evaluation standard. Implementation of the LVAP standard enables PPE testing that is both scientifically rigorous and appropriate for contact hazards. The LVAP system also offers advantages over current ASTM standards (such as ASTM F-739); for example, no solvents are required during the contamination period. This allows the LVAP method to be used to test air-breathable materials and also allows for testing within operationally relevant contact scenarios, such as when an individual grasps a contaminated object.

Problem/Opportunity

Without a consistent standard for measuring the potential contact hazard of low-volatility contaminants, questions were raised about the efficacy of the test for evaluating PPE in such a scenario. Consequently, associated decisions affecting capabilities, risk management, and operational readiness were subject to the variability in the traditional test methods. The initial purpose of this research was the protection of laboratory personnel handling these types of contaminants. However, it was quickly realized that the LVAP method is also appropriate for first responders; industrial and agricultural workers; and Environmental Protection Agency (EPA), National Institute for Occupational Safety and Health, and law enforcement personnel. In addition to increasing the safety of personnel handling low-volatility contaminants, Dr. D'Onofrio's work has been motivated by the opportunity to develop and apply a new standard to close this gap in protection research and testing.

Approach

The LVAP test fixture consists of a preconditioning chamber built from COTS polycarbonate sheets and wire shelves, where material swatches are acclimated to controlled temperature and humidity levels; a test chamber, which is a COTS incubator that maintains appropriate environmental conditions during testing; and test cells, where potentially contaminated material swatches are contact tested. Each test cell is a stacked assembly of a PTFE-lined polycarbonate petri dish, a solid sorbent pad, a material swatch, a PTFE disk, an O-ring gasket, and a stainless

steel weight, all contained within an inverted glass jar. The weight placed on top of the material swatch ensures that contact occurs between the swatch and sorbent pad layers. This contact is a crucial element of the system; it provides the necessary conditions for accurate measurement of agent permeation through the material.

For material testing, specific quantities of VX are applied to material swatches within a defined contamination area. Test cells are assembled and placed in the test chamber for a specific contact-time period. The sorbent pad from each test cell is then removed, and liquid chromatography–tandem mass spectrometry is used to quantify how much contaminant has permeated the swatch and absorbed into the pad.

During the V&V testing of the new method, extensive precision and accuracy calculations were conducted and documented in accordance with ISO 5725:3, Accuracy (Trueness and Precision) of Measurement Methods and Results. These statistics provided the necessary metrics for evaluating the LVAP system as a reliable test method.

The LVAP system design is based on open-architecture concepts. Given that the main LVAP components and consumables are commonly available commercial products, the LVAP system is resistant to many of the cost and technical risks associated with product obsolescence. Users can take advantage of supplier competition to minimize costs and simplify life-cycle management.

Outcome

Standardization permitted the creation of a capability where previously none existed. Previous permeation test methods were based on vapor-collection methods, which have been proven inappropriate for contact-hazard scenarios. This is illustrated by the nearly 10-fold increase in precision that was documented during V&V testing of the LVAP system: variability was improved from ±80% using vapor-collection methods to ±8% using the LVAP contact-based method. Statistical comparisons consistently indicate that contact-based testing enabled by use of the LVAP method is more representative of the threat scenario for contact-based hazards.

LVAP method users gain the capability to accurately measure the mass of low-volatility agent that has permeated material swatches. This translates to the ability to reliably test PPE and other materials for vulnerability to permeation by toxic agents or other contaminants. Ultimately, this capability will benefit protection programs that rely on Test and Evaluation data to make programmatic and milestone decisions. From the perspectives of safety, risk management, and operational readiness, this capability will ultimately benefit the warfighter.

The modular LVAP system has a relatively small logistical footprint. Vapor-based permeation test fixtures are custom-built and cost on the order of $400,000 each. The LVAP system uses a COTS incubator for temperature control with modified shelving (to facilitate sample handling),

multiple smaller COTS components, and customized stainless steel weights (to apply contact pressure). The LVAP fixture costs approximately $30,000 to implement, a savings of more than 10-fold over vapor-based test systems. The simplified, open-architecture design of the LVAP also enables a significant cost savings for system setup and maintenance. The modularity of the fixture design is well illustrated by the use of a different incubator in each of the four LVAP systems that are currently being established, including one each at ECBC, the West Desert Test Center (Dugway Proving Ground, UT), the Battelle Hazardous Materials Research Center (Jefferson, OH), and the Defence Science and Technology Laboratory (Porton Down, UK). The incubator, weight, and much of the supportive equipment are not only reusable, they are COTS items that are available from many vendors. On a cost basis, approximately 93 percent of the system fixture is reusable, and all of the consumables associated with the LVAP (except the chemical agent) are easily sourced COTS items.

By focusing on contact permeation and removing the vapor-collection components, the physical footprint of the fixture decreased from an 8 × 3 ft (24 ft^2) area for vapor-collection racks to a 2 × 2 ft (4 ft^2) region for the LVAP. The simplified design also allows for more samples to be incorporated into the smaller region; while using the same number of operators, throughput increased from 27 samples per experiment for a vapor-collection system to 40 samples per experiment for the LVAP system. For the same operating costs, 27 samples could be processed through the traditional method with a variability of ±80 percent and no true contact capability; alternatively, 40 samples could be processed through the LVAP method with a variability of only ±8 percent, using a proven contact-based capability that also has a smaller footprint and a lower initial setup investment.

Current Status

The LVAP V&V report earned O-6 level concurrence signatures from the following: the Joint Science and Technology Office, the Joint Requirements Office for Chemical, Biological, Radiological, and Nuclear Defense, the Joint Program Executive Office for Chemical and Biological Defense, and the operational test authorities for the Army, Air Force, Navy, and Marine Corps. The V&V report was endorsed by Test and Evaluation Executive James C. Cooke, with the DoD Chemical and Biological Defense Program, as a Test and Evaluation standard. With this endorsement, the LVAP transitioned from Science and Technology research to the Test and Evaluation community, and it is now available to DoD Programs of Record for all services.

At present, the LVAP system is being used at several DoD-associated facilities in support of the Uniform Integrated Protection Ensemble Increment 2 (UIPE2) Program, to ensure the performance of candidate protective equipment for fielding. The LVAP system is also currently being used in partnership with the U.S. Army Natick Soldier Research, Development and Engineering Center; the Battelle Hazardous Materials Research Center; and ECBC to research and develop

novel materials for future protective ensembles. At the University of Maryland Eastern Shore (Princess Anne, MD), the LVAP system has been incorporated into academic research to ultimately identify protective clothing standards for agricultural workers.

Partners from the Department of Homeland Security, EPA, the Federal Bureau of Investigation, and the intelligence community are considering incorporating LVAP systems into their programs to protect operators, law enforcement personnel, and first responders from low-volatility threats. Dr. D'Onofrio has shared the V&V report with academic and industrial partners to broaden the implementation of the LVAP method. He has an active and ongoing relationship with ASTM to implement LVAP as a new ASTM method.

The transition of this method to an official Test and Evaluation standard closed a significant and longstanding gap in protection research: it established the first contact-based research and test method capable of quantifying the permeation hazard of the chemical warfare agent VX (and other low-volatility hazards) through protective equipment.

Dr. D'Onofrio is cross-training personnel at other organizations in the use and implementation of the LVAP method standard. At present, LVAP systems are being set up in several DoD-affiliated laboratories. He is currently helping to establish an LVAP system at the Defence Science and Technology Laboratory (UK).

Challenges

Many hurdles were crossed during the LVAP standardization process. Some were technical, such as the need to characterize the proportion of background signal from vapor cross-contamination, which caused a potential bias in the results in the previous designs. This problem was solved by incorporating a COTS O-ring gasket into each test cell, which effectively removed the vapor cross-contamination without interfering with permeation testing. Several other "lessons learned" for avoiding potential cross-contamination and improving reproducibility were also documented. As part of the LVAP implementation, bench chemists, technicians, and operators from other organizations were invited to observe testing at ECBC. Encouraging dialogue between personnel who perform the experiments facilitates understanding beyond that provided by printed documentation, and it enables effective leveraging of lessons learned.

Some challenges were political and derived from the assembly of a large group of diverse stakeholders and the need for concurrence within a short suspense. The LVAP test plan and V&V report both required O-6 level concurrences from the operational test authority from each service branch, the Joint Requirements Office, the Joint Program Executive Office for Chemical and Biological Defense, the Joint Science and Technology Office, and the DUSA TE. The planning and testing was completed within 9 months of V&V initiation, with final concurrence and transition occurring 7 months later. This accelerated timeline was required to enable LVAP to be used for upcoming Programs of Record.

The political challenges were overcome by open communication with all stakeholders for improved management of expectations, rigorous documentation of results, and leveraging of lessons learned. All data, including those incorporating mistakes and efforts that did not meet requirements, were clearly presented during update briefings. Stakeholders and potential LVAP users were invited to the laboratory to witness testing and offer input. The personal interactions between the laboratory staff and the stakeholders helped to build a relationship of trust that ultimately enabled the success of this effort.

About the Award Winner

Terrence G. D'Onofrio has been researching permeation methods for improved safety performance since 2007. To address the critical need for contact-based permeation testing, he invented the LVAP fixture and method (U.S. Patent 9,021,865, May 2015). The LVAP system is the basis for the new Test and Evaluation standard.

Dr. D'Onofrio was directly involved in the laboratory research. In fact, he often wore the same PPE being tested in the LVAP experiments. During the standardization process, he initiated discussions with stakeholders from all four service branches, joint offices, and the DUSA TE to ensure that all of the stakeholders' needs were incorporated into the final standard. Dr. D'Onofrio led the research effort, wrote the test plan, conducted the research, wrote many technical reports, coordinated discussions with stakeholders, and authored the final V&V report to document the precision and accuracy of the new LVAP test method standard. The successful transition of the method to a Test and Evaluation standard was recognized by the DUSA TE, which presented Dr. D'Onofrio with a Department of the Army Achievement Medal for Civilian Service.

Dr. D'Onofrio is now cross-training personnel at other organizations in the implementation and use of the LVAP method standard. At present, he is participating in a 1-year exchange program at the Defence Science and Technology Laboratory (the UK equivalent of ECBC), where he is helping to institute the LVAP method as an international standard.