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Laser-induced fluorescence "tag" is key to rapid chemical detection

Sandia researchers Scott Bisson, Jeff Headrick, Tom Reichardt, Roger Farrow, and project leader Tom Kulp of the Remote Sensing and Energetic Materials department have demonstrated a non-contact method to rapidly detect chemicals adhered to surfaces. Chemical detection is achieved by applying a sequence of two laser pulses to the measurement zone—one to break apart the molecule to be detected and the other to sense a released molecular fragment by causing it to fluoresce. While the target molecule is not measured directly, the laser-induced fluorescence (LIF) of the fragment serves as a "tag" to indicate that the parent species is present. Currently, the targets of interest are organophosphonate chemicals such as nerve agents or pesticides. As shown in Figure 1 (page 5), the fragment that tags their location is phosphorous monoxide (PO).

This work is motivated by the need for an optical probe that can rapidly scan large areas for surface contamination. Many spectroscopic tools, such as infrared (IR) absorption, work well for detecting gases, but fail to measure solids or liquids on surfaces. In the case of IR detection, the surface measurement must be made in reflectance mode, which is subject to confusing artifacts caused both by scattering on porous surfaces and by mixing of the chemical spectrum with that of the background surface. Other spectroscopies, such

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Consequence analysis for unintended hydrogen releases within enclosed spaces

Commercialization of compressed hydrogen gas as an alternative transportation fuel is occurring within the material handling sector as hydrogen-powered fuel cells replace lead-acid batteries for indoor use applications (industrial forklifts). However, using compressed hydrogen within enclosed spaces introduces new hazards that must be addressed before this technology can be widely deployed. A CRF team consisting of Bill Houf, Greg Evans, and Isaac Ekoto has

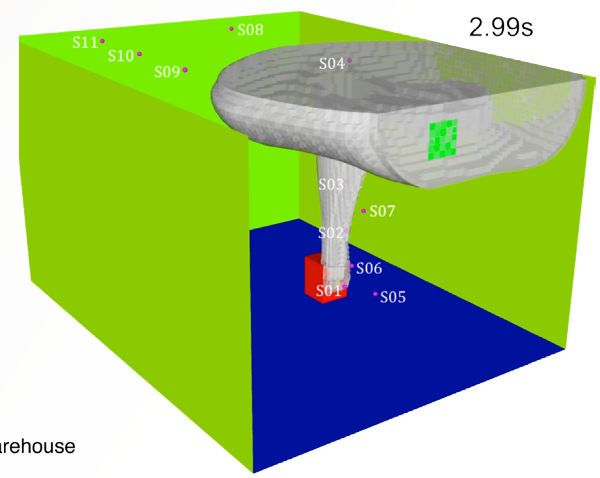

Figure 2. A hydrogen concentration snapshot 3 seconds after release in a scale-model warehouse.

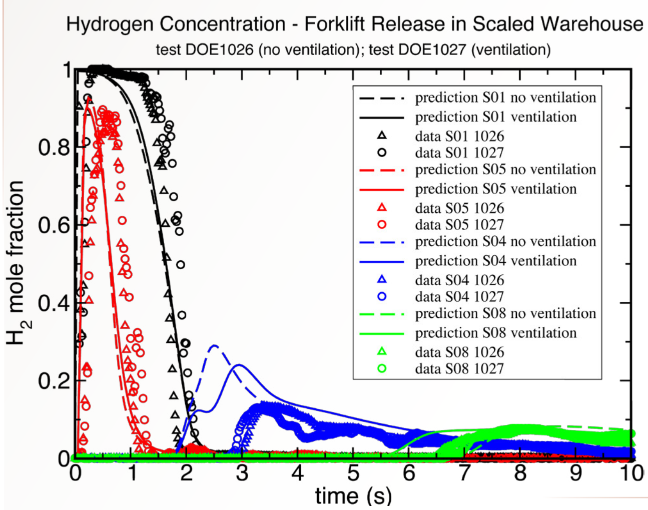

Figure 1. Graph of measured and FUEGO-predicted hydrogen concentrations with and without active ventilation.

been working with original equipment manufacturers (OEMs) to develop scientific understanding that forms the basis for risk-informed safety codes and standards. Per the 2010 edition of NFPA 52 (National Fire Protection Association Vehicular Gaseous Fuel Systems Code), indoor hydrogen dispensing rates within

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CRCV grand opening

On January 19th, the Combustion Research Facility celebrated the inauguration of its new building... (See page 4)

Newsletter

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unventilated warehouses are limited to 0.8 g per cubic meter of room volume provided a minimum 7.62-m ceiling height is met. Higher fueling rates are allowed if minimum forced ventilation rates are maintained. To provide a technical assessment of this requirement, Sandia used a combined numerical and experimental approach that illuminates the consequences and corresponding mitigation measures of indoor, unintended hydrogen release scenarios.

The release scenario was defined based on industry forklift specifications, NFPA 52 indoor refueling guidelines, and a failure mode and effects analysis (FMEA) that was developed with OEM consultation. Experimental data were recorded in a sub-scale warehouse test facility located at the

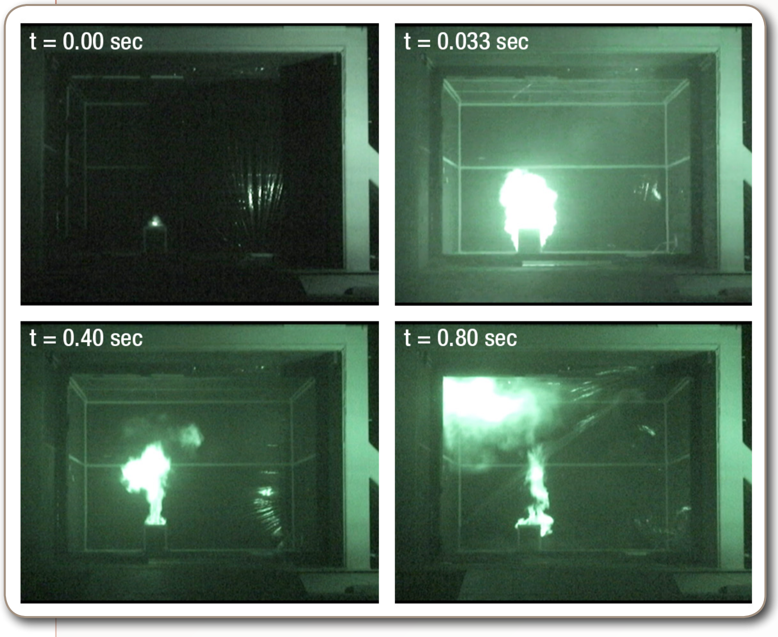

Figure 3. Infrared image sequence from the scaled warehouse at 0, 33, 400, and 800 msec after ignition. A highly luminous flame can be observed traveling upward along the released plume before propagating into the hydrogen/air mixture that collected along the ceiling.

SRI Corral Hollow Experiment Site. A 0.36-scale factor based on scaling relations developed by Hall and Walker (1997) was used to define the scaled warehouse geometry such that it matched a full-scale warehouse with a 1,000-m^3 internal volume and 7.62-m ceiling height. The scaling approach has been successfully applied in previous tests of hydrogen-powered vehicles within road tunnels (Houf et al., 2010). The hydrogen release rates and exit geometry were scaled to match the activation of a pressure relief device that vented along the vehicle side. Fast-response oxygen sensors were used to back out transient hydrogen concentrations from oxygen depletion measurements, and overpressures were measured with wall-mounted pressure transducers.

Measurements and simulation results agree well

Hydrogen dispersion from the scaled forklift release was modeled using FUEGO (Moen et al., 2002), a Sandia-developed computational fluid dynamics (CFD) code. From the graph of measured and predicted hydrogen concentrations from tests with and without forced-air ventilation in Figure 1, close agreement is observed between measured and simulation results. These results validate the modeling approach. Moreover, the effect of forced ventilation on concentration distributions is small, and thus its usefulness as a mitigation measure is likely negligible.

Ignition of the hydrogen plume was modeled with FLACS software (GexCon, 2010), using FUEGO-predicted concentrations 3.0 seconds after the release as the input boundary

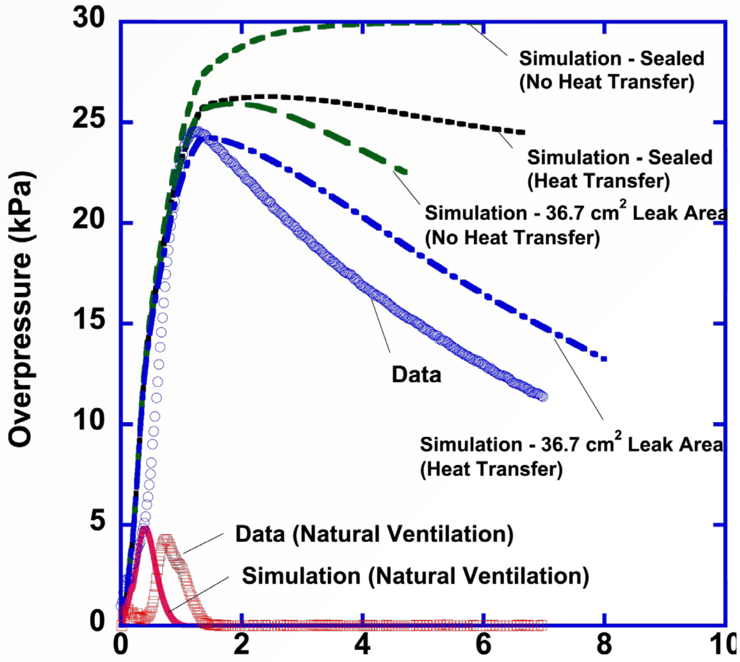

Figure 4. Measured overpressures within the well sealed and naturally ventilated warehouse, along with a comparison to simulation predictions. When effective leak area and wall heat transfer were incorporated into simulation results, peak overpressures were well matched.

condition (Figure 2). The spark was located 3.0 cm above the vehicle in a region where the mixture was expected to be relatively rich. A sequence of infrared video images of the transient flame structure is shown in Figure 3. A highly luminous flame can be observed traveling upward along

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Combustion Research Facility Visitor Program

Sage Kokjohn, visitor with Mark Musculus

Ph.D. student Sage Kokjohn completed an eight-month visit as part of his thesis work in a DOE collaborative project between the University of Wisconsin (Prof. Rolf Reitz) and Sandia. Sage's thesis topic is reactivity-controlled compression-ignition (RCCI), a new operating strategy for internal combustion engines that uses two fuels with differing autoignition characteristics (e.g., gasoline and diesel fuel). RCCI has the potential for very high thermodynamic efficiency (50% or more) with low pollutant emissions. The high-speed combustion luminosity and fuel-tracer measurements at Sandia serve as validation data for Sage's computational fluid dynamics simulations, and they also provide an improved understanding of the in-cylinder dynamics of RCCI.

Julia Wang, visitor with Carl Hayden

Julia Wang, from Cornell University in NY, served as a student intern from from June to December. Her work focused on inducing curvature in giant unilamellar vesicles with varying protein concentrations for the Combustion Chemistry and Biotechnology & Bioengineering departments.

Yao Zhang, visitor with Chris Shaddix

Postdoctoral researcher Yao Zhang, an expert on the application of laser diagnostics to turbulent flames, was recruited in 2008. He worked at the CRF measuring flame structure, soot properties, and radiation intensity in well-controlled, model-friendly turbulent jet diffusion flames. This unique database will aid in developing and refining soot models for application to aircraft engines. The funding for the work was provided by SERDP (Strategic Environmental R&D Program), which is a joint research program of DoD, DOE, and EPA that addresses environmental issues of concern to the U.S. military. For the last nine months, Yao has worked with Isaac Ekoto designing a new low-temperature hydrogen release system.

Chuck Mueller receives the 2011 Forest R. McFarland Award from the Society of Automotive Engineers

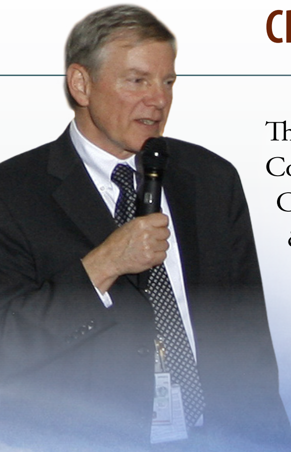
CRF engines and fuels researcher Chuck Mueller will be presented with a 2011 Forest R. McFarland award at the 2011 Society of Automotive Engineers (SAE) World Congress awards ceremony on April 12 in Detroit. This award recognizes individuals for their outstanding contributions toward the work of the SAE Engineering Meetings Board (EMB) in the planning, development, and dissemination of technical information through technical meetings, conferences, and professional development programs or outstanding contributions to the EMB operations in facilitating or enhancing the interchanges of technical information.

Chuck is being recognized for organizing technical sessions and other meetings at both the international and U.S. Powertrains, Fuels and Lubricants meetings over the course of several years. He has also acted as Chair for many of these and other sessions. Chuck is a regular reviewer of technical papers, having reviewed an average of almost eight per year over the last seven years.

Established in 1979, this award is administered by the EMB and honors the late Forest R. McFarland, who was himself an outstanding session organizer, a chairman of the Passenger Car Activity, and a member of the EMB. Funding for this award is through a bequest by Mr. McFarland to SAE and consists of a framed certificate presented at the SAE World Congress.

Chuck received a Ph.D. in aerospace engineering from the University of Michigan in 1996 and also holds a M.Sc.E. in aerospace engineering from the University of Michigan and B.Sc. degrees in aeronautics and engineering physics from Miami University. He has authored or co-authored more than 40 technical papers in the field of engine combustion and fuels and is the recipient of a number of awards.

CRCV grand opening celebration



The long-anticipated dedication of the CRF's 8,400-square-foot Combustion Research Computation and Visualization (CRCV) laboratory was celebrated on January 19, 2011. Co-funded by two Department of Energy (DOE) Offices—Science, and Energy Efficiency & Renewable Energy (EERE)—the CRCV provides interactive data visualization and collaborative workspaces as well as a 2,000-square-foot machine room for dedicated computational capability. The CRCV is in the process of achieving LEED certification for the use of "green" technologies in its construction.

The event featured presentations by Rick Stulen and Bob Carling (Sandia), Eric Rohlfing (Office of Science) and Stephen Goguen (EERE); several representatives from local and state government; and special guest speakers Jeffrey Nichols (Oak Ridge National Laboratory) and Daniel Haworth (Penn State University).

> *"Today we celebrate yet another milestone in terms of increasing our collaboration space from the point of view of providing the kinds of resources we need to develop those new sophisticated models we need—predictive capabilities that are so important for future efficient engines and reduced pollutants.*
>
> *– Bob Carling, director of the Transportation Energy Center"*

Stephen Goguen noted that the CRCV will provide the resources to greatly expand and more fully explore the potential of high-fidelity simulation tools. "This new venue," he said, "will be comparable to the experimental research labs that will enable our modeling and simulation program to provide a much higher level of impact, especially when closely coupled with experimental research. The addition will provide a collaborative focal point to methodology to perform and analyze high-fidelity simulation flows of chemical systems, provide wider access to these massive data sets, and expand collaboration at the CRF and beyond."

A ceremonial ribbon cutting (or rather, ribbon burning—this is the Combustion Research Facility, after all) and reception in the new building followed the presentations.

> *"The CRCV is a natural part of the evolution of this combustion science and technology and we are delighted to help co-sponsor it.*
>
> *– Eric Rohlfing, Office of Science"*

> *"We've got all these crazy engineers thinking about all new things we can work on to make things better. And that is what it's all about.*
>
> *– Stephen Goguen, EERE"*

Photos by Randy Wong

Laser-induced fluorescence "tag" is key to rapid chemical detection *(Continued from page 1)*

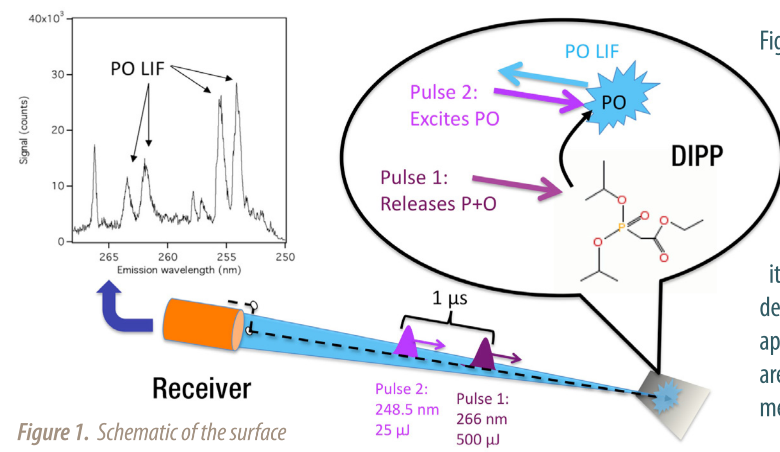


Figure 1. Schematic of the surface contamination detection method. PO LIF signal is produced by measurement of DIPP on aluminum.

as Raman scattering or direct LIF, can provide simpler signals; however, the former is weak and the latter cannot be used for the many materials that do not fluoresce. The current method overcomes these limitations by converting a non-fluorescent molecule into a highly fluorescent fragment.

The new method was tested in the laboratory using available hardware. A pulse produced by a frequency-quadrupled Nd:YAG laser (266 nm) was used to photolyze the sample, and a pulse from a frequency-converted dye laser (248 nm) stimulated the LIF. The sample to be measured (the chemical agent surrogate DIPP, whose structure is shown in Figure 1) was sprayed onto various common materials such as concrete or metal. The PO LIF signal was measured by a spectrograph equipped with an intensified gated-array detector.

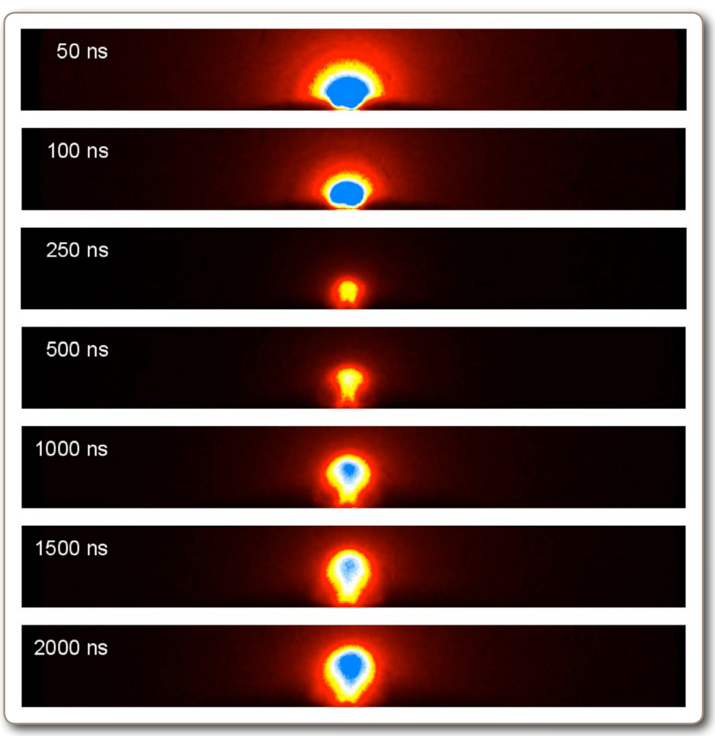


Figure 2. Planar laser-induced fluorescence images of the PO emission from the plume induced by the 266-nm laser. The time between photolysis and LIF laser pulses is shown. At early times (50–100 ns), the signal is dominated by plasma emission from the surface. At later times, it is dominated by PO LIF. The late onset of the signal suggests a possible recombination of P and O atoms to form PO.

Figure 1 also shows the PO LIF signal produced by measurement of DIPP on aluminum. The signal appears as two pairs of lines that represent emission between two spin-split vibrational states. A similar signal was produced when three other nerve-agent surrogates were tested, indicating the general applicability of the method. In addition to aluminum, tests were also successful in detecting DIPP on other common surfaces such as concrete, paint, wood, and steel. Background fluorescence from the surface was found to be negligible because it tends to be shifted further from the probe laser wavelength than the PO LIF. The detection limit was measured at 30 µg/cm² when a single pair of laser pulses was applied. Because the pulse energies required (500 µJ for dissociation; 25 µJ for LIF) are low, high-repetition-rate lasers can be used to make thousands of measurements per second at this sensitivity.

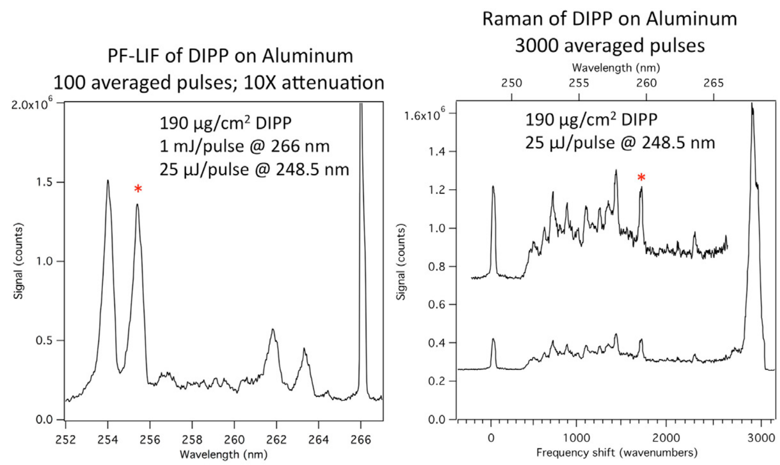


Figure 3. Comparison of photofragment-LIF (PF-LIF, left) and Raman (right) measurements of the same 190-µg/cm² DIPP-on-aluminum sample. After normalization for number of averaged pulses and attenuation, the PF-LIF signal is 3,300 times stronger in amplitude than the Raman signal (for the marked peaks).

The optimum time separation between the laser pulses was found to be 1 µs, which was unexpectedly long. This finding raised the question as to whether the PO is either (1) formed in an excited state that must relax before it can be detected, or (2) formed from recombination of phosphorus and oxygen atoms that are initially produced when the molecule breaks up. This question motivated some optical diagnostic studies to understand the measurement dynamics. One was planar laser-induced fluorescence (PLIF) imaging, in which the plume was illuminated with a planar laser pulse and a filtered camera was used to image the PO LIF. Images produced by that measurement are shown in Figure 2. Another study measured the presence of phosphorus atoms at early times after dissociation. At this time, the results of these diagnostics appear to be consistent with the recombination mechanism.

Because Raman scattering is a competing method, the performance of PO-LIF was compared against it. The results, shown in Figure 3, demonstrate that, when 7-ns-duration laser pulses are used for both measurements, the PO-LIF is 3,300 times stronger than the Raman signal. Under these conditions, the Raman measurement was limited to excitation intensities below the surface breakdown threshold. The use of a longer pulse length could avoid this problem; however, powerful long-pulse or continuous-wave lasers that emit in the deep UV are currently lacking.

This work was funded by a Laboratory-Directed Research and Development (LDRD) project.

Consequence analysis for unintended hydrogen releases (Continued from page 2)

the released plume before propagating into the hydrogen/air mixture that collected along the ceiling. Figure 4 compares predicted and measured overpressures for cases with and without natural ventilation (open area approximately 0.124% of the total surface area). Although sealed, a small leakage area nonetheless existed in the scaled warehouse (approximately 0.005% of the total surface area). If this effective leak area and the impact of radiative heat transfer are included in the simulations, peak overpressure predictions agree well with the measurements.

With open-area natural ventilation, peak overpressures decreased by nearly a factor of five. These results demonstrate that passive natural ventilation is an effective overpressure mitigation measure and future indoor refueling hydrogen safety requirements can be informed by these results.

FLACS Version 9.1 User's Manual, GexCon, Bergen, Norway, 2010.

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