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Final Report on the Detection of Green Monopropellants

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Executive Summary

In 2014, National Aeronautics and Space Administration (NASA) Kennedy Space Center (KSC) funded a project titled "Familiarization and Detection of Green Monopropellants" utilizing Independent Research and Technology Development (IR&TD) and Center Innovation Fund (CIF) funding. The purpose of the project was to evaluate methods of detection for ammonium dinitramide (ADN) and hydroxylammonium nitrate (HAN). An Engineering Services Contract (ESC) task order was created with the scope of evaluation of several methods of detecting ADN- and HAN-based propellants, as well as development of methods for detection. Detection methods include developed methods such as colorimetric indicating absorbent socks, and commercial-off-the-shelf (COTS) units for ammonia detection. An additional goal of the task order was for ESC to become familiar with ADN's and HAN's material properties and material compatibility.

Two approaches were initially investigated as possible methods for the detection of HAN (or AF-M315E) and ADN (or LMP-103S). These approaches were colorimetric analysis and instrumentation-based COTS vapor sensors utilization. Initial testing showed that the relatively non-existent vapor pressure of the AF-M315E (of which HAN is a major component) propellant would make the use of COTS sensors difficult for real-time area monitoring of HAN; a small response was detected through the use of active COTS sensors, including the RAE Systems MultiRAE Lite and Dräger X-act® 5000, but the levels detected were below the threshold limit value for the toxic gas ammonia. Therefore, a detection system based upon a colorimetric indicator impregnated into an absorbent material was developed. Preliminary analysis (ESC-245-FDG-001) identified a particularly outstanding candidate as a colorimetric indicator for the detection of the presence of AF-M315E in the form of a Methyl Red (Basic) indicator. Materials impregnated with this indicator exhibit significant color change and the materials are not susceptible to interference from exposure to water or carbon dioxide. The completed detection system for HAN/AF-M315E consists of absorbent socks packed with Fisher Universal Spill Absorbent capable of absorbing and containing any propellant spills that they come into contact with along with indicating wipes. The absorbent socks are also chemically treated with a Methyl Red (Basic) indicator solution to provide the end user with a visual indication that a leak has occurred and proper protective precautions must be undertaken. An added benefit of this detection system is that the absorbent socks should neutralize/absorb any commodity that it comes into contact with (until saturation is reached). Additional adsorbent socks can be deployed until a color change is not seen, indicating that the HAN/AF-M315E contamination has been contained. The indicating wipes provide the user the opportunity to wipe surfaces to determine if there is any HAN/AF-M315E or HAN/AF-M315E residue present. The wipes should allow the detection of fuel levels that may be too small to detect with the absorbent socks.

The development of a detection system for the ADN/LMP-103S focused on the use of various COTS sensors used as real-time area monitoring devices and personal dosimeters. These COTS-based sensor systems were of several different types, including both actively pumped and diffusion-based passive systems, as well as a "rope"-type chemical sensing cable. The results highlighted some of the major differences between the two monopropellants undergoing evaluation. Unlike HAN, ADN (which is the major constituent of LMP-103S) exhibits a much more volatile nature in comparison to AF-M315E. In fact, testing showed that a large percentage of the fuel was lost during the sampling measurement (greater than 10% by mass); although this

testing cannot tell if the volatile component is the ADN itself or another component of the monopropellant solution. Not surprisingly, all four of the procured vapor-based COTS sensors showed positive results when exposed to solutions of the LMP-103S (ESC-245-FDG-002). The completed detection system for ADN/LMP-103S consists of a combination of two of the tested COTS sensor systems, the RAE Systems MultiRAE Lite and the BW Technologies GasAlert Extreme. These systems are meant to be used in conjunction with one another, which allows for the end-user to have both real-time area monitoring (MultiRAE Lite) as well as a personal dosimeter device (GasAlert Extreme) which can be worn as additional personal protective equipment. An stainless steel extension wand was fabricated and included in the detection system for the MultiRAE Lite to allow for more remote sensing, and connects via the active pumping inlet of the sensor.

As stated, the final results of this testing resulted in the production of two "kits" which can be used for the detection of HAN/AF-M315E and ADN/LMP-103s (ESC-245-FDG-003).

Introduction

For decades, hydrazine monopropellant has been used in spacecraft propulsion and power systems for auxiliary power units, orbit raising and lowering, and attitude control. Two of the key advantages of hydrazine monopropellant over other monopropellants is that it is easy to use and reliable. The long history of use of hydrazine has given the aerospace community a thorough understanding of both its physical and chemical characteristics. However, hydrazine is highly toxic and is very corrosive. For these reasons, recent studies have focused on the development of replacement monopropellants that can be utilized that provide similar advantages as hydrazine (simple to use and reliable) but with the added benefits of lower toxicity and corrosivity.

Ammonium dinitramide (ADN) and hydroxylammonium nitrate (HAN) are major components of two "green" monopropellants (LMP-103S and AF-M315E, respectively) which will be appearing at KSC for processing in the next few years and will be used to test an F-16 Emergency Power Unit (EPU) through collaborations with Marshall Space Flight Center (MSFC). These are relatively safe replacements for hydrazine as a monopropellant; however, little is known about methods of leak detection, vapor scrubbing, air emissions, or cleanup that will be required for safe and environmentally benign operations at Kennedy Space Center (KSC). LMP-103S was developed by the Swedish Space Corporation (SSC), while AF-M315E was developed by the Air Force Research Laboratory (AFRL) to be a propellant. Orbital ATK is predominantly evaluating LMP-103S for future use, while Ball Aerospace was awarded a NASA Technology Demonstration Mission (TDM) to use AF-M315E as a monopropellant in a mission to be launched from KSC/Cape Canaveral Air Force Station (CCAFS) currently scheduled for 2016. KSC needs the technology in place prior to their arrival, and needs to make recommendations as to their adoption if significant issues are found.

In 2014, National Aeronautics and Space Administration (NASA) KSC funded a project titled "Familiarization and Detection of Green Monopropellants" utilizing Independent Research and Technology Development (IR&TD) and Center Innovation Fund (CIF) funding. The purpose of the project is to evaluate methods of detection for ADN and HAN. An Engineering Services Contract (ESC) task order was created with the scope of evaluation of several methods of detecting ADN and HAN propellants, as well as development of methods for detection. Proposed detection

techniques included methods such as colorimetric indicators and a variety of Commercial-Off-The-Shelf (COTS) vapor sensors. An additional goal of the task order was for ESC to become familiar with ADN's and HAN's material properties and material compatibility. As such, a safety analysis was conducted and can be found in Appendix A of this report.

Detection Methods

Colorimetric

Colorimetric detection involves the use of a color reagent to detect the presence and/or concentration of an analyte of interest. A wide variety of color reagents are available, including pH indicators. The use of pH indicator-based systems for the detection of hazardous gases such as ammonia is an area that has been of great interest for some time; however, it has been shown that these systems typically suffer from poor selectivity. Additionally, many of the pH indicators suffer from false-positive responses due to environmental changes (temperature, humidity, etc.).

Since one of the initial goals of this project was to simply detect the presence of HAN, a study was undertaken to evaluate the use of a variety of pH indicators to detect the presence of HAN. A wide range of pH indicators are available, many of which have noticeable color changes in the pH region associated with HAN (HAN is acidic in solution). An additional indicator, vanillin, was also evaluated since previous studies indicated that the presence of amines such as hydrazine produce changes in color of vanillin solutions. Table 1 provides a complete list of indicators evaluated, as well as their color-change properties.

Table 1. Color reagents evaluated for HAN detection.

Indicator	Properties
Acros Universal pH Indicator Solution	Initial color is green. Color changes: pH 4.0 (red), pH 4.5 (orange-red), pH 5.0 (orange), pH 5.5 (orange-yellow), pH 6.0 (yellow), pH 6.5 (yellow-green), pH 7.0 (green), pH 7.5 (green, slightly blue), pH 8.0 (green-blue), pH 8.5 (blue-green), pH 9.0 (blue)
Bromocresol Green (Basic)	Color change: pH 4.5 – 5.5
Bromocresol Purple (Basic)	Color change: pH 5.4 – 6.8
Bromothymol Blue (Basic)	Color change: pH 6.0 – 7.6
Methyl Red (Basic)	Color change: pH 4.8 – 6.0
Vanillin	Changes color when reacted with various reagents
VWR Universal Indicator	Initial color is green. Color changes: pH 4.0 (red), pH 5.0 (orange), pH 5.5 (orange-yellow), pH 6.0 (yellow-orange), pH 6.5 (yellow), pH 7.0 (green), pH 7.5 (green-blue), pH 8.5 (blue), pH 9.0 (blue-indigo), pH 9.5 (indigo), pH 10.0-11.0 (violet)
Yamada Universal Indicator (Acidic)	Initial color is red. Color changes: pH 4 (red), pH 5 (orange), pH 6 (yellow), pH 7 (green), pH 8 (blue), pH 9 (indigo), pH 10 violet
Yamada Universal Indicator (Neutral)	Initial color is green. Color changes: pH 4 (red), pH 5 (orange), pH 6 (yellow), pH 7 (green), pH 8 (blue), pH 9 (indigo), pH 10 violet

Four general types of colorimetric studies were undertaken to determine if the presence of HAN could be detected: 1) solution-based studies, 2) indicator wipe studies, 3) indicator material studies, and 4) indicating absorbent sock studies. The details of each developed method will be described below.

The methodology for the solution-based studies was as follows:

- Approximately 0.5 ml of the indicator solution was place in a sealed vial and initial color was recorded.
- Three drops of HAN (AF-M315E) was added to the vial and the mixture was shaken for 30 seconds.
- Color change (if visible) was recorded.

The methodology for the indicator wipe studies was a follows:

- 1" X 1" pieces of wipe material (Scotch-Brite Microfiber High Performance Cleaning Cloth) were cut.
- Approximately 2 ml of color reagent solution was added to the cut wipe to completely saturate the wipe.
- The saturated wipe was allowed to dry.
    - Two methods were employed for drying: air dry or vacuum dry.
- The initial color of the color-reagent impregnated wipe was recorded.
- Approximately three drops of HAN were added to the dry color reagent-impregnated wipe.
- Color change (if visible) was recorded.
- Control experiment conducted with 3 drops of water added to the dry color reagent-impregnated wipe.
- Color change (if visible) was recorded.

The general methodology for the indicator material studies was as follows:

- Different materials were selected as potential absorbent materials for further colorimetric detection testing using a Methyl Red (Basic) indicator solution.
- A small amount of each sample material was placed in a polyethylene weigh boat for testing.
- Enough Methyl Red (Basic) indicator solution was added to each material to ensure material was coated.
- Sample was allowed to dry (vacuum or low-temperature oven).
- Three drops of HAN (AF-M315E) was added to the sample.
- Color change (if visible) was recorded.

The general methodology for the indicating absorbent sock studies was as follows:

- Approximately 3" X 3" pieces of sock material (3M Chemical Absorbent Sock or Fisher Universal Spill Kit Liners) were cut.
- Absorbent material (3M Filler, Activated Alumina, or Pig Powder) was added to the sock material and sealed using zip ties.
- The sealed absorbent sock samples were dipped in Methyl Red (Basic) indicator solution for 30 seconds.
- Sample was allowed to dry (vacuum or low-temperature oven)

- An aliquot of HAN/AF-M315 (5 ml or 50 ml) was added to a polyethylene weigh boat.
- The indicating absorbent sock was placed directly into the HAN/AF-M315E.
- Color change (if visible) was recorded (some samples (5 ml tests) were dissected to determine relative uptake).

Commercial-Off-The-Shelf (COTS) Sensors

The use of sensors for the detection of HAN and ADN was evaluated using a wide variety of COTS sensors. The sensors evaluated included a multigas system and several single-gas sensor systems. The multigas sensor system was equipped with three different sensors, each for a specific class of analyte. The single-gas sensor systems were ammonia-specific systems; these sensors were chosen since one of the objectives of this project was to also detect the presence of ADN (which has the potential of off-gas ammonia vapor). The specifications for each of the COTS sensor systems evaluated are shown in the following paragraphs.

RAE Systems MultiRAE Lite

The RAE Systems MultiRAE Lite (Figure 1) is a versatile gas monitor with the capability to sense up to six different gases. The MultiRAE unit has active pumping and can be utilized for remote gas detection (leak detection). The MultiRAE is equipped with three sensors: 1) photoionization detector (PID) for volatile organic compound (VOC) detection, 2) catalytic bed for combustible gas detection, and 3) electrochemical sensor for ammonia detection. The PID sensor has 1 ppm resolution in the range from 0 – 1000 ppm. The catalytic bed sensor has 1% lower explosive limit (LEL) resolution in the range from 0 – 100% LEL. The ammonia sensor has 1 ppm resolution in the range from 0 – 100 ppm. The MultiRAE Lite has wireless connectivity and data logging capabilities.

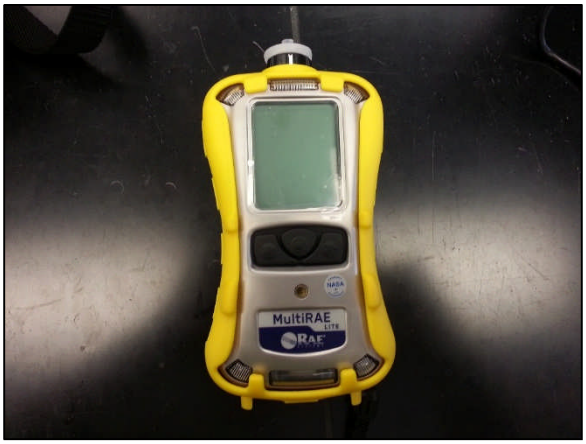


Figure 1. RAE Systems Multi-RAE Lite Instrument.

BW Technologies GasAlert Extreme

The BW Technologies GasAlert Extreme Portable Gas Monitor (Figure 2) is utilized for detection of ammonia in a wide variety of environments. The GasAlert Extreme is equipped with an ammonia sensor with capability to detect between 0 – 100 ppm ammonia in environments ranging from -20 – 40 °C and humidity ranging from 15 – 90%. The GasAlert Extreme is a diffusion-based sensor and does not have active pumping. The GasAlert Extreme is water resistant, has a

continuous liquid-crystal display (LCD) to show real-time gas concentrations, and has both visual and vibrating alarms.

Figure 2. BW Technologies GasAlert Extreme Portable Gas Monitor.

Dräger Pac® 7000 (with Dräger XXS Ammonia Sensor)

The Dräger Pac® 7000 personal gas monitor (Figure 3) is a diffusion-based sensor with the capability to measure ammonia concentrations ranging from 0 – 300 ppm with 1 ppm resolution. The Pac® 7000 can accurately detect ammonia concentrations down to 0.05 ppm and has a constant readout of ammonia concentration. The Pac® 7000 is fast responding, lightweight, and water and dirt resistant. The Dräger XXS ammonia sensor for the Dräger Pac® 7000 is a fast and accurate diffusion-based electrochemical sensor with the capability to measure ammonia concentrations ranging from 0 – 300 ppm with 1 ppm resolution. The XXS sensors have a high level of stability, exhibiting less drift than competing sensors. The XXS has a wide operating temperature range (-40 – 40 °C) and operating pressure range (700 – 1300 mbar). The XXS has the ability to withstand and recover from high concentration exposures.

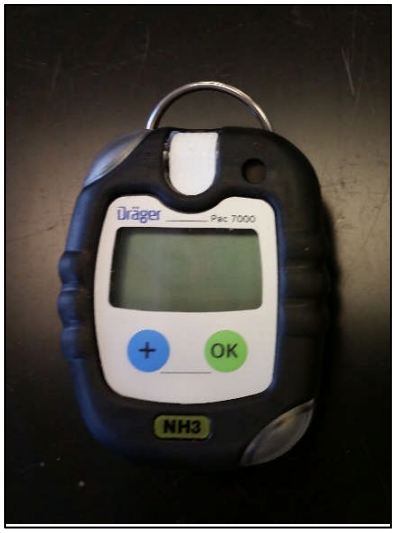


Figure 3. Dräger Pac® 7000 personal gas monitor.

Dräger X-act® 5000 (with Tubes)

The Dräger X-act® 5000 (Figure 4) is an automatic tube pump that utilizes the appropriate Dräger-Tube® for direct detection of analytes in air. The utilization of the X-act® 5000 reduces the average measurement time by 15 – 20% due to the unique capability to provide the required flow to the Dräger-Tube®. A variety of tubes are available for ammonia detection and were procured for evaluation. The tubes procured were: 1) 0.25 – 3 ppm, 2) 0.05 – 10% Volume, 3) 2 – 30 ppm, 4) 5 – 600 ppm, and 5) 5 – 100 ppm.

Figure 4. Dräger X-act® 5000.

RLE SeaHawk Chemical Sensing Cable

The SeaHawk Chemical Sensing Cable (Figure 5) is used to detect the presence of a variety of conductive chemical liquids (including corrosives such as acids and bases) very rapidly to allow for effective mitigation of damage. It is rated in accordance with ASTM D543, which means that it will function normally even after a full week's exposure to the following chemicals:

- Fresh deionized water
- Sulfuric acid (98%)
- Hydrochloric acid (37%)
- Sodium Hydroxide (10%)
- Aqua regia
- Ethylene glycol (60%)

Figure 5. RLE Technologies Chemical Sensing Cable.

The chemical sensing cable is constructed from a thermally bonded polymer-coated carrier which is formulated to resist bending and kinking. It is available in both standard and custom lengths to fit a wide variety of applications, and comes with pre-installed end connectors for quick installation. Embedded sensing wires are capable of detecting a conductive liquid on the surface of the cable and sending an alert to a connected SeaHawk Single Zone Monitor (Figure 6), which results in an audible alarm as well as a small visual alarm with a red blinking LED.

Figure 6. RLE Technologies SeaHawk LD310 Single Zone Monitor.

Testing Setups

The COTS sensors evaluated were either active (internal pumping) or passive (diffusion-based) devices. The details of the test methodologies for each type of sensor (active or passive) for each commodity are contained in the following paragraphs.

Active – AF-M315E

For active sensor testing using AF-M315E, a UNF 100 TTDC 24 V gas pump was connected to a variable voltage Lambda power supply (Model LLS8040, 0 – 40 V, 0 – 10 A). The voltage on the power supply was maintained between 8.5 V – 24 V. The inlet flow to the pump was exposed to room air. The outlet pump port was connected to stainless steel tubing that was inserted through a Teflon®-lined septa on a 20 ml borosilicate glass vial. The tubing was inserted through the septa as to impinge air on to the surface of the commodity, which enhances the likelihood of forced evaporation of the commodity into the headspace. Approximately 5 ml of AF-M315E was placed in the sample vial. An outlet tube from the sample vial (inserted through the septa) was connected to the inlet of the sensor under test with a vent in-line to ensure that a positive pressure or a vacuum scenario wouldn't occur (Figure 7). For the MultiRAE Lite testing, the pump was turned on (8.5 V – approximately 100 ml/min) and the MultiRAE was allowed to acquire measurements for 20 minutes. Then the voltage supplied to the pump was ramped incrementally from 8.5 V – 15 V – 24 V. This was done to ensure that the pump on the sensor wasn't overpowering the forced air (evaporation) pump, as well as to see if increased pump flow would affect the sensor readings. Once the test was complete, an identical setup was put in place with the AF-M315E removed (lab air used instead) as a control. The Dräger X-act® 5000 testing was conducted at a voltage of 15 V (approximately 330 ml/min) to prevent a vacuum from being created within the sample vial. One test was performed with a Dräger X-act® 5000 pump rate of 0.5 L/min for 15 minutes and the second was performed with a Dräger X-act® 5000 pump rate of 0.2 L/min for 15 minutes. The second test was performed due to the concern that the higher pump rate of the Dräger X-act® 5000 may have been diluting the Dräger tube reading.

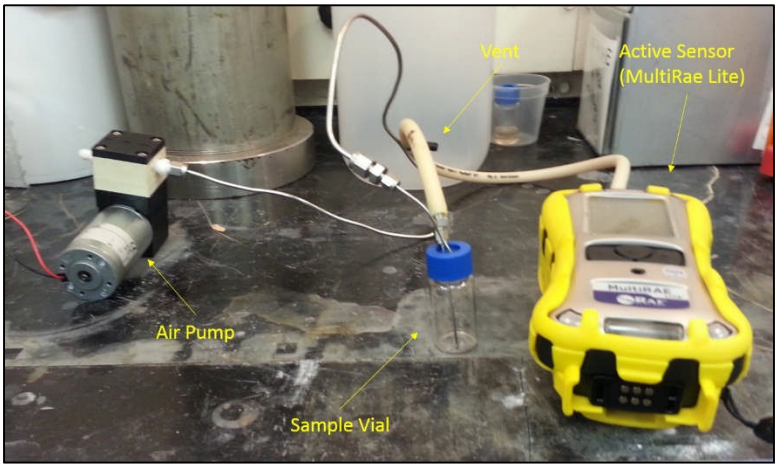


Figure 7. Setup for Evaluation of Active Sensors (AF-M315E).

Active – LMP-103S

For active sensor testing using LMP-103S, a UNF 100 TTDC 24 V gas pump was connected to a variable voltage Lambda power supply (Model LLS8040, 0 – 40 V, 0 – 10 A). This is the same setup as was previously used in the AF-M315E testing (Figure 7), although a few modifications

were made to the testing procedure. The voltage on the power supply was maintained at 13.0 V (corresponds to approximately 350 ml/min). The inlet flow to the pump was exposed to room air. The outlet pump port was connected to stainless steel tubing that was inserted through a Teflon®-lined septa on a 40 ml borosilicate glass vial. The tubing was inserted through the septa as to impinge air on to the surface of the commodity, which enhances the likelihood of forced evaporation of the commodity into the headspace. Approximately 1 ml of LMP-103S was placed in the sample vial, which was wrapped in opaque tape due to the light sensitivity of the propellant. An outlet tube from the sample vial (inserted through the septa) was connected to the inlet of the sensor under test with a vent in-line to ensure that a positive pressure or a vacuum scenario wouldn't occur (Figure 7). For the MultiRAE Lite testing, the pump was turned and the voltage was set to 13.0 V and the MultiRAE was allowed to acquire measurements for 30 minutes. Subsequent testing was done in shorter time periods (5 minutes) due to saturation of the sensors (particularly the NH_3 electrochemical sensor). Once the test was complete, an identical setup was put in place with the LMP-103S removed (lab air used instead) as a control. Active sensor testing with both 10% Dräger tubes and 600 ppm Dräger tubes were performed in conjunction with a Dräger X-act® 5000 pump. The Dräger testing was conducted at a voltage of 13.0 V (approximately 350 ml/min) to prevent a vacuum from being created within the sample vial. Approximately 1 ml sample vials of LMP-103S were used for the Dräger active sensor testing (as with the MultiRAE testing previously). The Dräger X-act® 5000 was initially set to a pump rate of 0.2 L/min for 15 minutes and was changed for additional testing to a pump rate of 0.1 L/min for 15 minutes. The second set of tests was done as the initial pump settings caused saturation of the tube extremely fast (in less than 4 minutes). Blanks (performed using laboratory air) were run prior to exposure to each sample of LMP-103S as a control measure. The mass of the LMP-103S was monitored before and after testing using both sets of active sensors in an effort to document the volatile nature of the commodity.

Passive – AF-M315E

For testing of the two passive sensors, a UNF 100 TTDC 24 V gas pump was connected to a variable voltage Lambda power supply (Model LLS8040, 0 – 40 V, 0 – 10 A). The voltage on the power supply was maintained at 8.5 V. The inlet flow to the pump was exposed to room air. The outlet pump port was connected to stainless steel tubing that was inserted through a Teflon®-lined septa on a 20 ml borosilicate glass vial. The tubing was inserted through the septa as to impinge air on to the surface of the commodity, which enhances the likelihood of forced evaporation of the commodity into the headspace. Approximately 5 ml of AF-M315E was placed in the sample vial. A second tube was run from sample vial (through the septa) to the inlet port on a 1-gallon Naglene® bottle (test chamber) equipped with inlet and outlet ports (Figure 8). Both passive ammonia sensors were activated and allowed to run though their self-diagnostic cycles prior to testing. Each sensor was placed in the test chamber (individually) face-up (readout visible from above), the pump activated (8.5 V, approximately 100 ml/min), and the system was allowed to equilibrate for 20 minutes. 20 minutes was chosen based on a determination this was more than enough time for several turnovers of the air volume (based on the flow rate). Once equilibrated, the lid was removed from the 1 gallon bottle and readings were taken from the unit under test to determine if any response was observed.

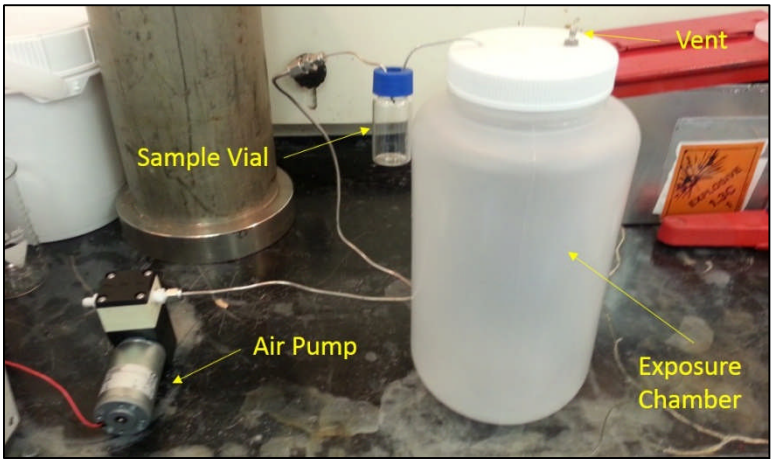


Figure 8. Setup for Evaluation of Passive Sensors.

Passive – LMP-103S

For testing of the two passive sensors, a UNF 100 TTDC 24 V gas pump was connected to a variable voltage Lambda power supply (Model LLS8040, 0 – 40 V, 0 – 10 A). The voltage on the power supply was maintained at 13.0 V (approximately 350 ml/min). The inlet flow to the pump was exposed to room air. The outlet pump port was connected to stainless steel tubing that was inserted through a Teflon®-lined septa on a 40 ml borosilicate glass vial. The tubing was inserted through the septa as to impinge air on to the surface of the commodity, which enhances the likelihood of forced evaporation of the commodity into the headspace. Approximately 1 ml of LMP-103S was placed in the sample vial. A second tube was run from sample vial (through the septa) to the inlet port on a 1-gallon Naglene® bottle (test chamber) equipped with inlet and outlet ports (Figure 9). Both passive ammonia sensors were activated and allowed to run though their self-diagnostic cycles prior to testing. Each sensor was placed in the test chamber (together) face-up (readout visible from above), the pump activated (13.0 V, approximately 350 ml/min), and the system was allowed to equilibrate for 7 minutes. This shorter equilibration time was used to try to minimize damage to the sensor systems. Once the time had elapsed, the lid was removed from the 1 gallon bottle and readings were taken from the unit under test to determine if any response was observed. As both units were saturated by this point, the time at which the alarms went off was recorded during the runs.

Figure 9. Setup for Evaluation of Active Sensors (LMP-103S).

Passive – Chemical Sensing Cable

The initial RLE Technologies Chemical Sensing Cable sensor tests were performed using the following aqueous solutions (for baseline purposes): 18 MΩ water, 0.5% sodium chloride solution, 0.1 M ammonium hydroxide solution, and 0.1 M sodium hydroxide solution. The RLE LD310 Single Zone Monitor was set to its highest sensitivity level with the JP1 jumper spanning the top two pins (Figure 10). According the manufacturer's specifications, in this configuration the system will alarm once exposed with 0.5-inch of wetted cable. In an attempt to accurately simulate a situation which might be experienced in the field, the chemical sensing cable was held vertically in a ring stand at both ends and the liquid under test was dripped down the rope using a peristaltic pump (Figure 11). This was done to simulate a drip/spray leak which may occur in a line or tank. Approximately 8-inches of sensing cable were exposed to the liquids for all tests. A stop watch was started concurrently with the pump turning on. The time was recorded when the alarm went off on the controller (RLE Technologies, LD310). The test time was 30 minutes or once an alarm sounded, which ever occurred first. Additional tests were performed as necessary to determine the necessary flow rate to trigger the alarms with all four of the test solutions.

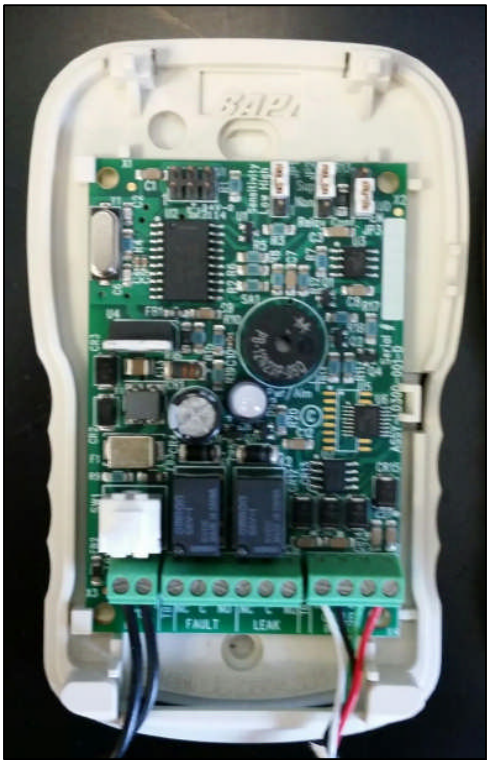


Figure 10. Jumper Settings for RLE LD310 Single Zone Monitor.

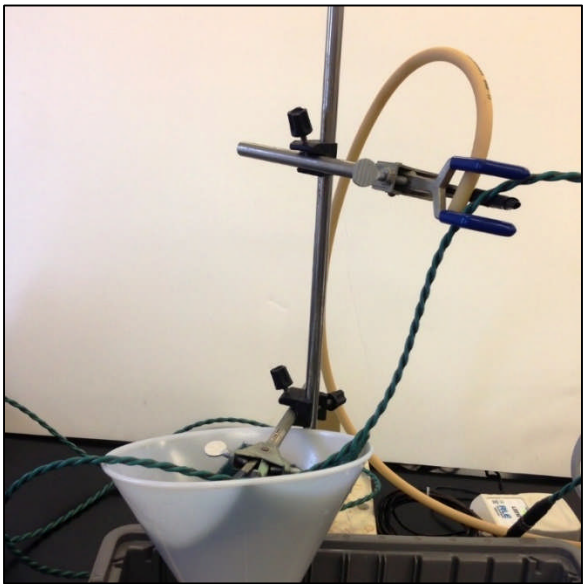


Figure 11. Setup for Drip/Spray Testing of Chemical Sensing Cable.

A second type of exposure test for the chemical sensing cable was run for the AF-M315E monopropellant which involved directly immersing varying lengths of cable in the propellant and measuring the amount of time it took for the sensor to respond. Again, the RLE LD310 Single Zone Monitor was set to its highest sensitivity level (as shown in Figure 10) and the cable was monitored with 6", 4", 2", and 1" of surface submerged within the monopropellant. To perform this test, a polypropylene bottle was cut in half length-wise and notched at both ends to allow for

positioning of the RLE Chemical Sensing Cable. Specific cable test lengths were marked on the test chamber. Approximately 50 ml of AF-M315E monopropellant was added to the chamber for the test to ensure complete submersion. The final setup for the submersion testing is shown in Figure 12.

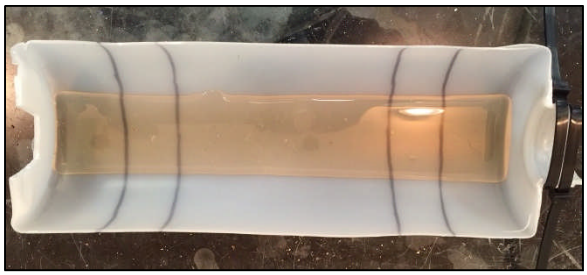


Figure 12. Setup for Submersion Testing (AF-M315E) of Chemical Sensing Cable.

Specific Details – Hydroxylammonium Nitrate (HAN)

Initial testing focused on the detection of the monopropellant AF-M315, which contains approximately 41.8% HAN. Initial research into this monopropellant determined that traditional vapor sensors would likely prove to be non-effective due to the relatively non-existent vapor pressure, although the COTS vapor sensors were tested with this commodity as well. The majority of development testing for this commodity was on the identification of an indicator suitable for identifying HAN/AF-M315E both quickly and reliably.

Results – Commercial-Off-The-Shelf (COTS) Sensors

RAE Systems MultiRAE Lite

A reproducible 1 ppm response was observed for the PID sensor of the MultiRAE when exposed to AF-M315E. The other sensors (catalytic bed and ammonia) did not show any response to exposure to AF-M315E. Testing was conducted to determine if the response observed for the PID sensor was real and reproducible. After a positive response was observed, the sample vial containing the AF-M315E was removed from the system and the PID response quickly dropped to zero. The sample vial containing the AF-M315E was then placed back in-line and the response rose to 1 ppm, indicating that the positive response was from the AF-M315E and that the response was reproducible. The exact commodity that caused the response is unknown at this time. The PID sensor is capable of detecting a wide range of volatile organic compounds, as well as ammonia. Preliminary headspace analysis of the AF-M315 propellant showed the possible presence of methanol when run at an elevated temperature (50°C), which could be responsible for the response on the PID sensor response. It should be noted that this headspace identification was made via retention time and standards (rather than Gas Chromatography-Mass Spectrometry (GC-MS) analysis). A GC-MS analysis could be performed in the future if necessary. The headspace analysis report for both AF-M315E and LMP-103S can be found in Appendix B of this report.

BW Technologies GasAlert Extreme

No response was observed when the GasAlert Extreme was exposed to AF-M315E.

Dräger Pac® 7000 (with Dräger XXS Ammonia Sensor)

No response was observed when the Dräger Pac® 7000 was exposed to AF-M315E.

Dräger X-act® 5000 (with Tubes)

A positive response was observed when the Dräger X-act® 5000 (with Dräger-Tube®) was exposed to AF-M315E. The Dräger-Tube® that was evaluated was the 0.25 – 3 ppm Ammonia Tube (Part # 8101711). Two replicates were performed to ensure reproducibility. For the first test, the Dräger X-act® 5000 was pulling at 0.5 L/min for 15 minutes (total of 7.5 L). The Lambda power supply set at 15.0 V (330 ml/min). The color change on the Dräger-Tube® was at the 2 ppm mark. For the second test, the Dräger X-act® 5000 was pulling at 0.2 L/min for 15 minutes (total of 3 L). The Lambda power supply set at 15.0 V (330 ml/min). The color change on the Dräger-Tube® was at the 1 ppm mark. The tubes showing the positive responses are shown in Figure 13. Additionally, a control experiment was conducted where the AF-M315E was removed from the sample stream. The results of the control experiment showed no color change, indicating that the color change observed in the initial testing was due to the presence of AF-M315E.

Figure 13. Results from 0 – 3 ppm Dräger-Tube® Evaluation (AF-M315E).

RLE Chemical Sensing Cable

As was discussed under the Testing Setup section, the initial evaluation using the RLE Chemical Sensing Cable was performed using a variety of aqueous solutions including 18 MΩ water, sodium chloride, sodium hydroxide, and ammonium hydroxide.

Results of this initial testing (Table 2) showed that a relatively large amount of surface area of the sensing cable was required to be "wetted" (Figure 14) to trigger the alarm setpoint as compared to the expected 0.5-inch stated by the manufacturer (in the jumper configuration chosen for this testing). However, some of this may have been due to the nature of the test in that it was done via a drip application rather than by fully submerging the sensing cable in the liquid. Regardless, this required a correspondingly large amount of liquid per test (approximately 25 ml) and it was therefore decided to initially forego testing using the LMP-103S and AF-M315E as the supply of these commodities was limited.

Table 2. Drip/Spray Test Results for RLE Technologies Chemical Sensing Cable.

	Sample Run	Rope Exposed (")	Flow Rate (ml/min)	Alarm Time (s)
18 MΩ Water	1	8	14.9	N/A
	2	8	14.9	N/A
	3	8	14.9	N/A
	4	8	107	N/A
	5	8	107	N/A
	6	8	107	N/A
	7	8	120	N/A
	8	8	120	N/A
	9	8	120	N/A
Sodium Chloride	1	8	14.9	N/A
	2	8	14.9	N/A
	3	8	14.9	N/A
	4	8	107	N/A
	5	8	107	N/A
	6	8	107	N/A
	7	8	120	12.2
	8	8	120	17.4
	9	8	120	15.6
Ammonium Hydroxide	1	8	14.9	N/A
	2	8	14.9	N/A
	3	8	14.9	N/A
	4	8	107	N/A
	5	8	107	N/A
	6	8	107	N/A
	7	8	120	15.4
	8	8	120	11.9
	9	8	120	15.2
Sodium Hydroxide	1	8	14.9	N/A
	2	8	14.9	N/A
	3	8	14.9	N/A
	4	8	107	N/A
	5	8	107	N/A
	6	8	107	N/A
	7	8	120	17.1
	8	8	120	17.3
	9	8	120	16.7

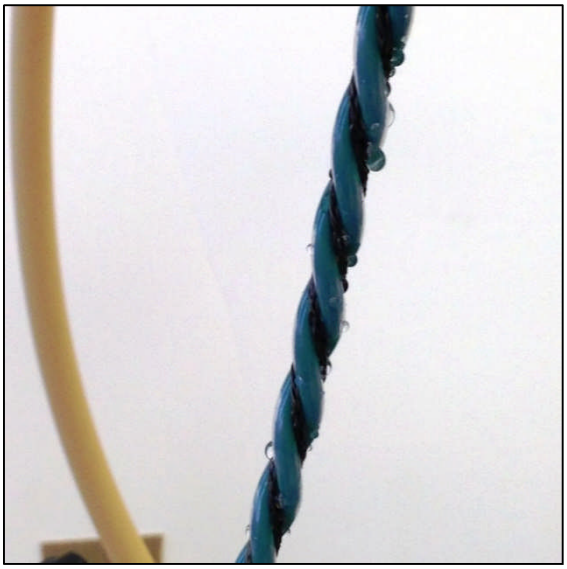


Figure 14. Close-up of RLE Chemical Sensing Cable Drip Test (18 MΩ Water).

Further Chemical Sensing Cable testing was decided upon using AF-M315E since there was a larger amount available for testing as compared to the LMP-103S. The cable was tested at under different submersion lengths (1", 2", 4", and 6") to determine if a specific length of the sensing cable needed to be submerged to set off the alarm. Additionally, the sensor was tested in different areas of the cable at the 4" test submersion length in an attempt to see if this would affect the sensor response in any way. Figure 15 shows the 4" submersion test using the middle section of the RLE Chemical Sensing Cable. A deionized H_2O test was run at the 4" submersion length as a control sample.

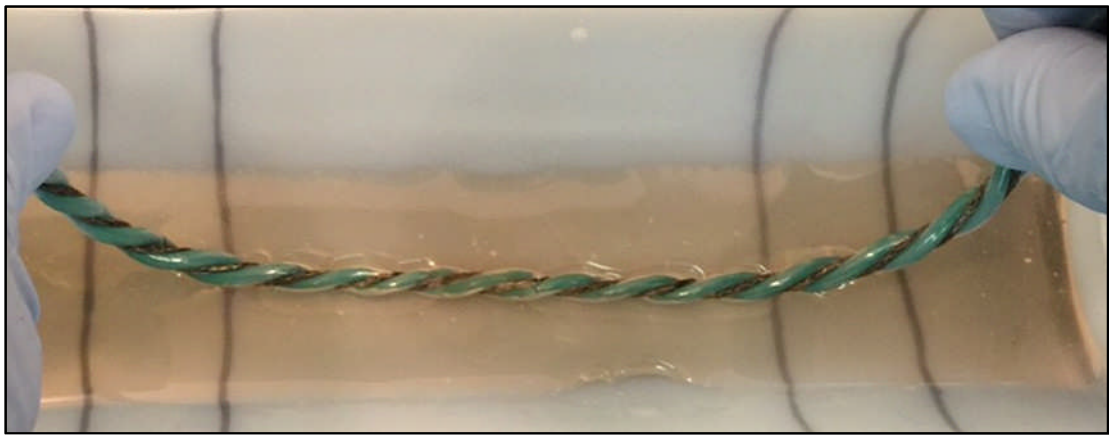


Figure 15. Close-up of RLE Chemical Sensing Cable Drip Test (18 MΩ Water).

Results of this testing (Table 3) indicate that the RLE Chemical Sensing Cable is capable of detecting AF-M315E within 10 seconds of submersion, regardless of affected area even at a surface coverage of 1". However, the deionized H_2O produced similar results, which suggests that the RLE Chemical Sensing Cable would not be useful in an environment in which moisture would be an issue, as this may lead to false positives.

Table 3. Submersion Test Results for RLE Technologies Chemical Sensing Cable (AF-M315E).

	Sample Run	Section of Rope	Rope Exposed (“)	Alarm Time (sec)
AF-M315E	1	Beginning	1	10.34
	2	Beginning	1	9.75
	3	Beginning	1	10.28
	1	Beginning	2	10.31
	2	Beginning	2	9.90
	3	Beginning	2	9.94
	1	Beginning	4	9.87
	2	Beginning	4	10.44
	3	Beginning	4	9.97
	1	Beginning	6	10.07
	2	Beginning	6	10.09
	3	Beginning	6	9.72
	1	Middle	4	9.47
	2	Middle	4	9.90
	3	Middle	4	10.44
	1	End	4	10.91
	2	End	4	9.78
	3	End	4	9.50
DI H_2O	1	Middle	4	9.31
	2	Middle	4	9.40
	3	Middle	4	9.19

Colorimetric - Solution

Acros Universal pH Indicator Solution

A noticeable color change was visible after the addition of 3 drops of AF-M315E to the Acros Universal pH Indicator Solution (Figure 16). The color change observed was from green to red.

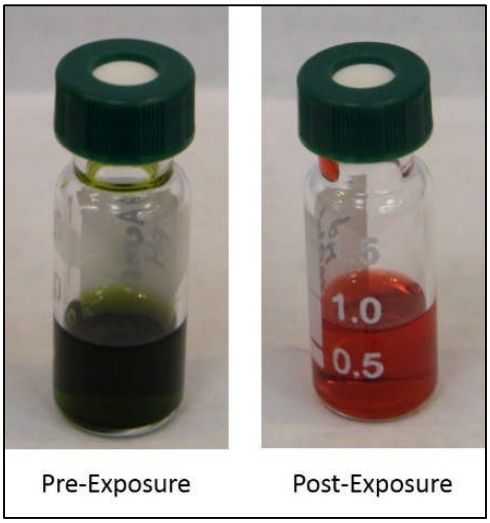


Figure 16. Pre- and Post-Exposure Results for Acros Universal Indicator.

Bromocresol Green (Basic)

A noticeable color change was visible after the addition of 3 drops of AF-M315E to the bromocresol green (basic) solution (Figure 17). The color change observed was from blue to green.

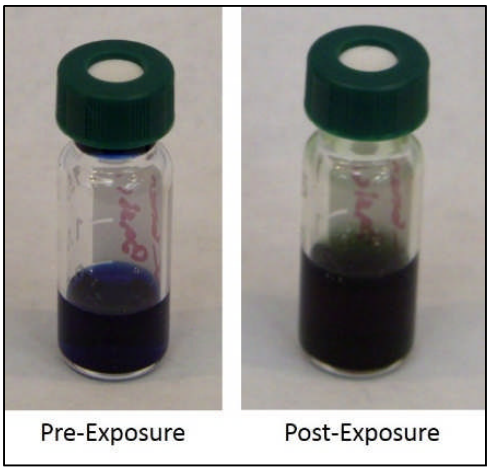


Figure 17. Pre- and Post-Exposure Results for Bromocresol Green.

Bromocresol Purple (Basic)

A noticeable color change was visible after the addition of 3 drops of AF-M315E to the bromocresol purple (basic) solution (Figure 18). The color change observed was from purple to yellow.

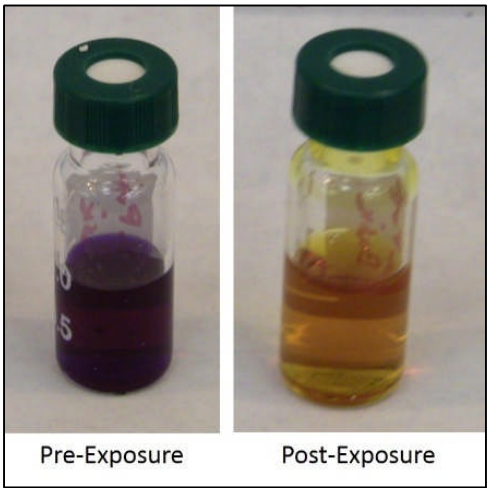


Figure 18. Pre- and Post-Exposure Results for Bromocresol Purple.

Bromothymol Blue (Basic)

A noticeable color change was visible after the addition of 3 drops of AF-M315E to the bromothymol blue (basic) solution (Figure 19). The color change observed was from blue to yellow-orange.

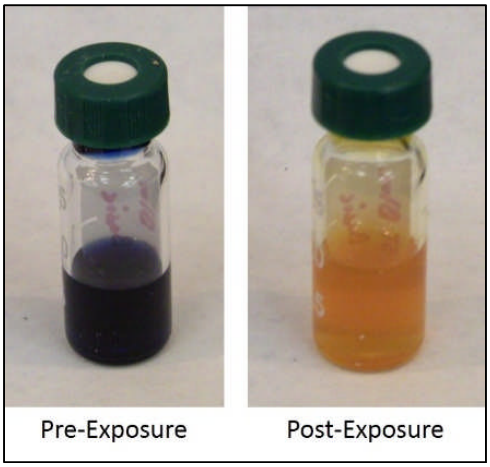


Figure 19. Pre- and Post-Exposure Results for Bromothymol Blue.

Methyl Red (Stock)

A noticeable color change was visible after the addition of 3 drops of AF-M315E to the methyl red (stock) solution (Figure 20). The color change observed was from orange to red.

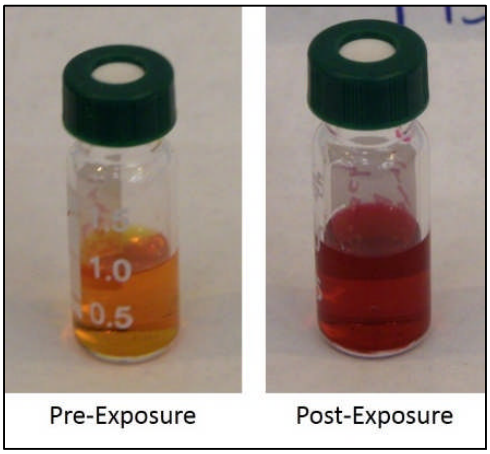


Figure 20. Pre- and Post-Exposure Results for Methyl Red.

Vanillin

No noticeable color change was visible after the addition of 3 drops of AF-M315E to the vanillin solution (Figure 21).

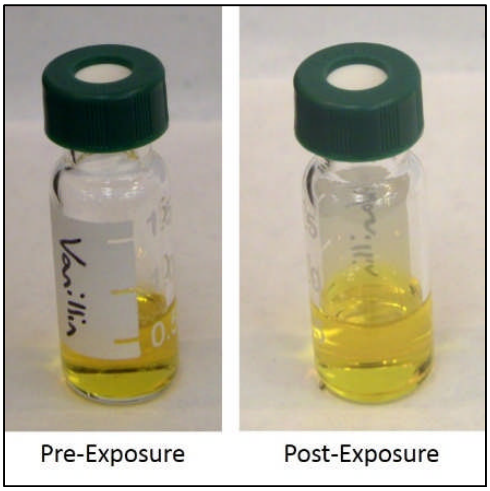


Figure 21. Pre- and Post-Exposure Results for Vanillin.

VWR Universal Indicator

A noticeable color change was visible after the addition of 3 drops of AF-M315E to the VWR Universal Indicator solution (Figure 22). The color change observed was from green to red.

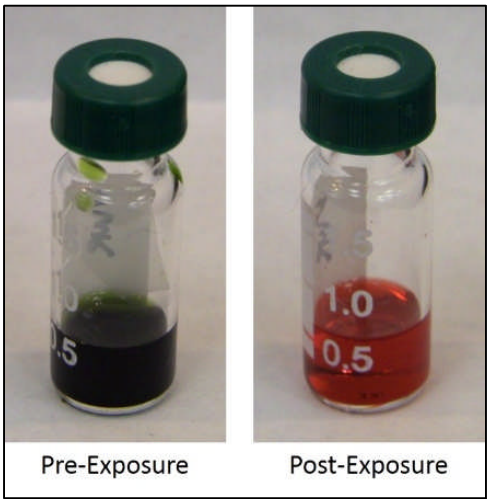


Figure 22. Pre- and Post-Exposure Results for VWR Universal Indicator.

Yamada Universal Indicator (Acidic)

No noticeable color change was visible after the addition of 3 drops of AF-M315E to the Yamada Universal Indicator (acidified) solution (Figure 23).

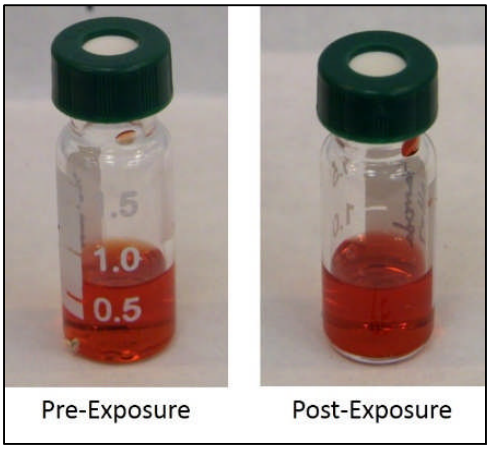


Figure 23. Pre- and Post-Exposure Results for Yamada Universal Indicator (Acidified).

Yamada Universal Indicator (Neutral)

A noticeable color change was visible after the addition of 3 drops of AF-M315E to the Yamada Universal Indicator (neutral) solution (Figure 24). The color change observed was from green to red.

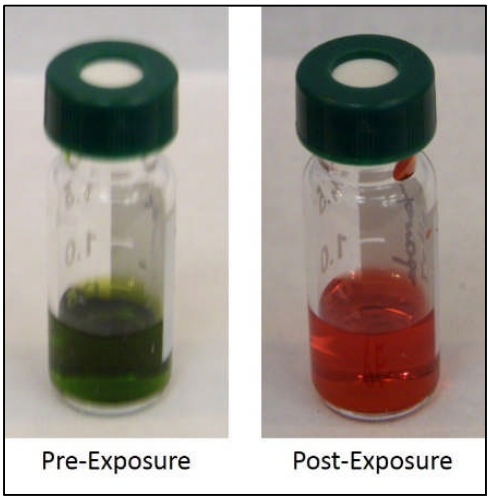


Figure 24. Pre- and Post-Exposure Results for Yamada Universal Indicator (Neutral).

Colorimetric - Wipes

Acros Universal pH Indicator Solution (Neutral)

The results of exposure of Acros Universal pH Indicator Solution (Neutral) indicator wipes (air dried) to 1 drop of AF-M315E and the control are shown in Figure 25. It can be seen that the color change due to exposure to AF-M315E is clearly visible for the test specimen. The results of exposure of Acros Universal pH Indicator Solution (Neutral) indicator wipes (vacuum dried) to 3 drops of AF-M315E and the control are shown in Figure 26. It can be seen that the color change due to exposure to AF-M315E is clearly visible for the test specimen. The control experiments for both wipes also showed a color change.

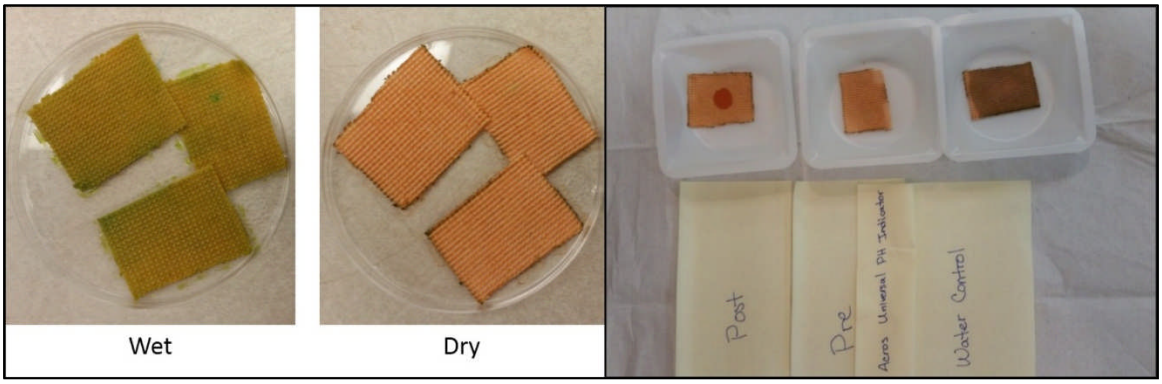


Figure 25. Acros Universal pH Indicator Solution (Neutral) Indicator Wipes. Left – Wet and Air Dried Wipes. Right – Exposure Results.

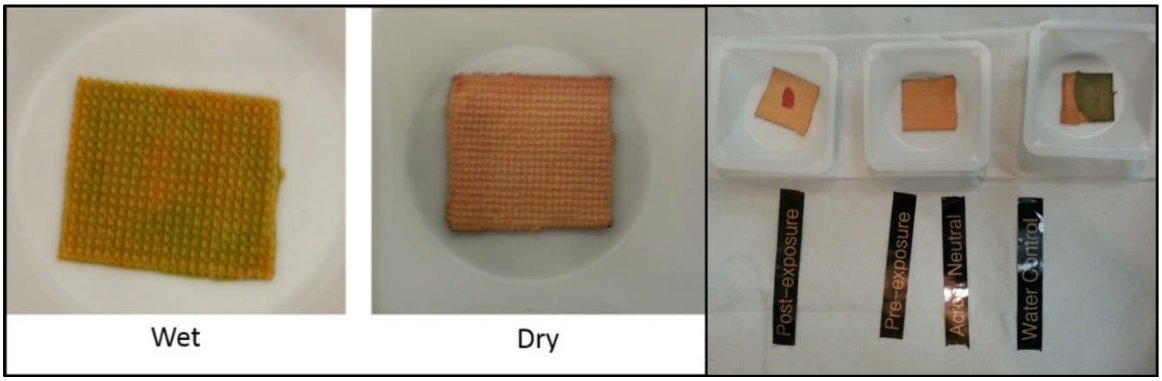


Figure 26. Acros Universal pH Indicator Solution (Neutral) Indicator Wipes. Left – Wet and Vacuum Dried Wipes. Right – Exposure Results.

Acros Universal pH Indicator Solution (Basic)

The results of exposure of Acros Universal pH Indicator Solution (Basic) indicator wipes (vacuum dried) to 3 drops of AF-M315E and the control are shown in Figure 27. It can be seen that the color change due to exposure to AF-M315E is clearly visible for the test specimen. The control experiment did show a significant color change (looks like the wet wipe).

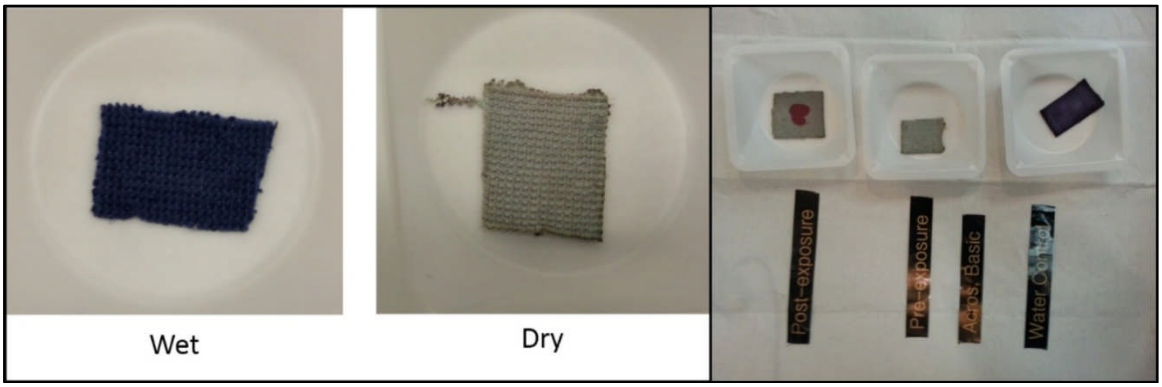


Figure 27. Acros Universal pH Indicator Solution (Basic) Indicator Wipes. Left – Wet and Vacuum Dried Wipes. Right – Exposure Results.

Bromocresol Green (Basic)

The results of exposure of Bromocresol Green (Basic) indicator wipes (air dried) to 3 drops of AF-M315E and the control are shown in Figure 22. It can be seen that the color change due to exposure to AF-M315E is not very visible for the test specimen (very similar to the wet wipe). The control experiment also did not show a color change.

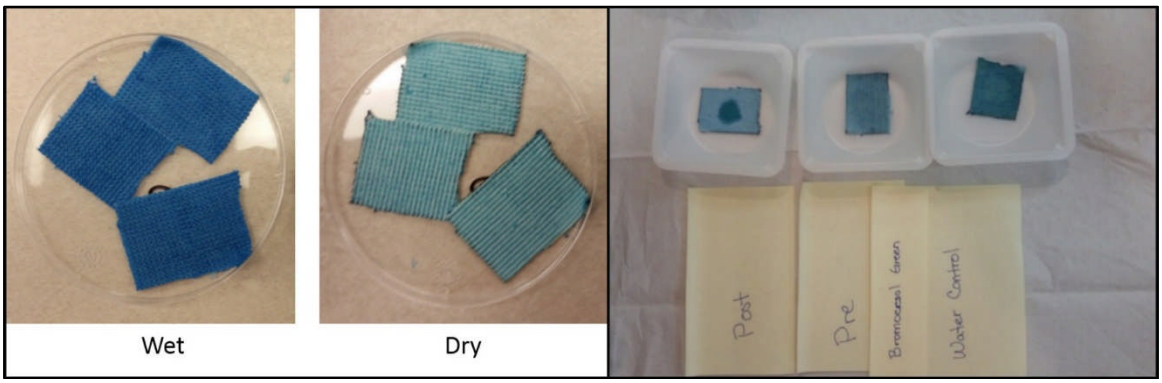


Figure 28. Bromocresol Green (Basic) Indicator Wipes. Left – Wet and Air Dried Wipes. Right – Exposure Results.

Bromocresol Purple (Basic)

The results of exposure of Bromocresol Purple (Basic) indicator wipes (air dried) to 3 drops of AF-M315E and the control are shown in Figure 29. It can be seen that the color change due to exposure to AF-M315E is not clearly visible for the test specimen. The results of exposure of Bromocresol Purple (Basic) indicator wipes (vacuum dried) to 1 drop of AF-M315E and the control are shown in Figure 30. It can be seen that the color change due to exposure to AF-M315E is not clearly visible for the test specimen. The control experiments for both wipes also showed minor color changes.

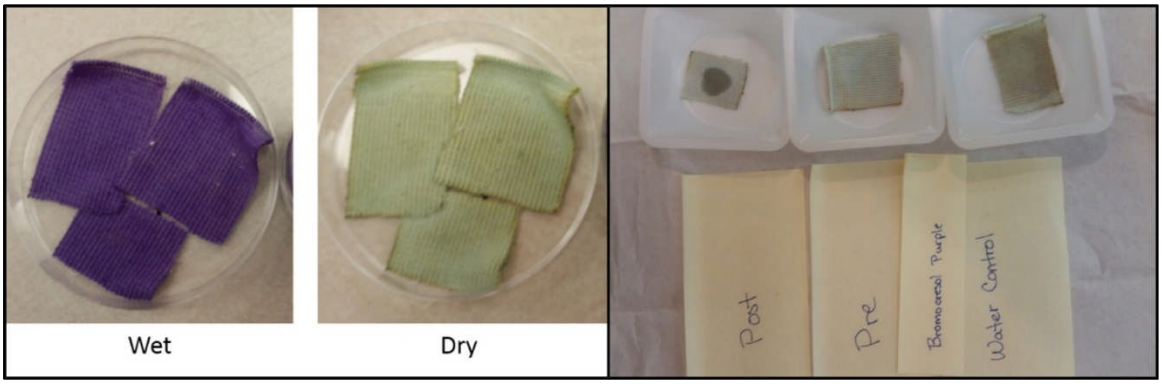


Figure 29. Bromocresol Purple (Basic) Indicator Wipes. Left – Wet and Air Dried Wipes. Right – Exposure Results.

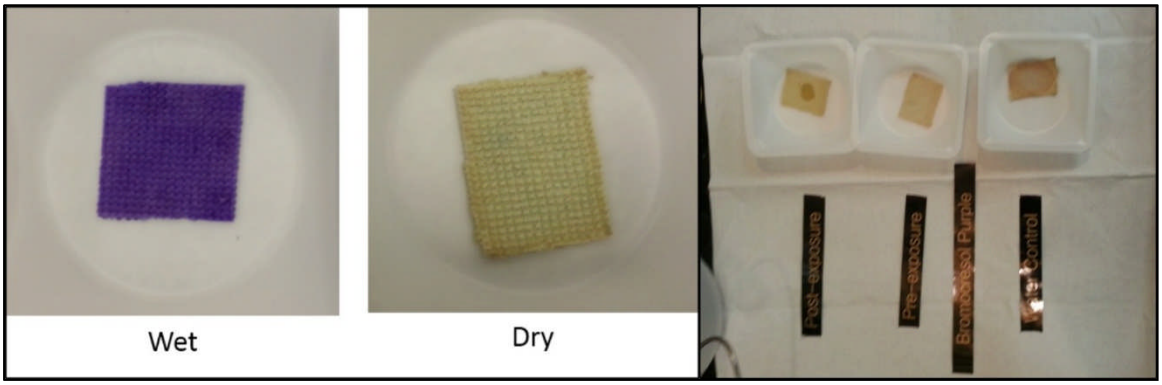


Figure 30. Bromocresol Purple (Basic) Indicator Wipes. Left – Wet and Vacuum Dried Wipes. Right – Exposure Results.

Bromothymol Blue (Basic)

The results of exposure of Bromothymol Blue (Basic) indicator wipes (air dried) to 3 drops of AF-M315E and the control are shown in Figure 31. It can be seen that the color change due to exposure to AF-M315E is not clearly visible for the test specimen. The results of exposure of Bromothymol Blue (Basic) indicator wipes (vacuum dried) to 3 drops of AF-M315E and the control are shown in Figure 32. It can be seen that the color change due to exposure to AF-M315E is not clearly visible for the test specimen. The control experiments for both wipes also showed color changes.

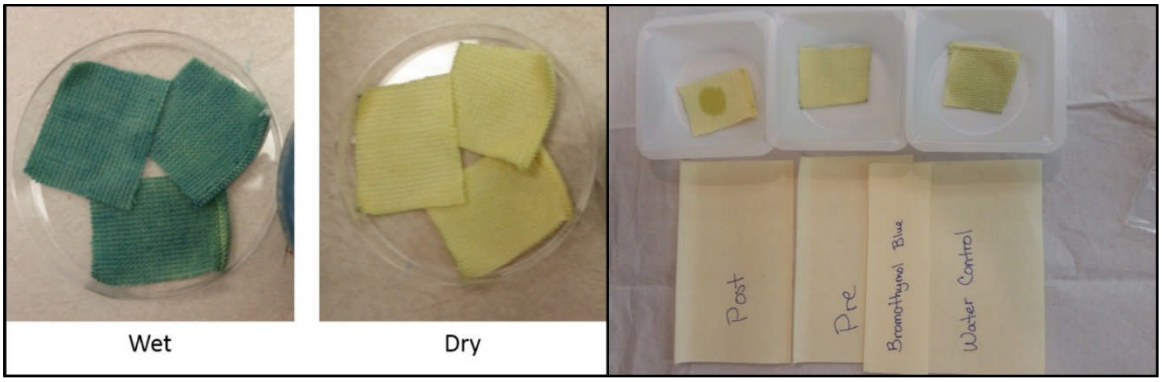


Figure 31. Bromothymol Blue (Basic) Indicator Wipes. Left – Wet and Air Dried Wipes. Right – Exposure Results.

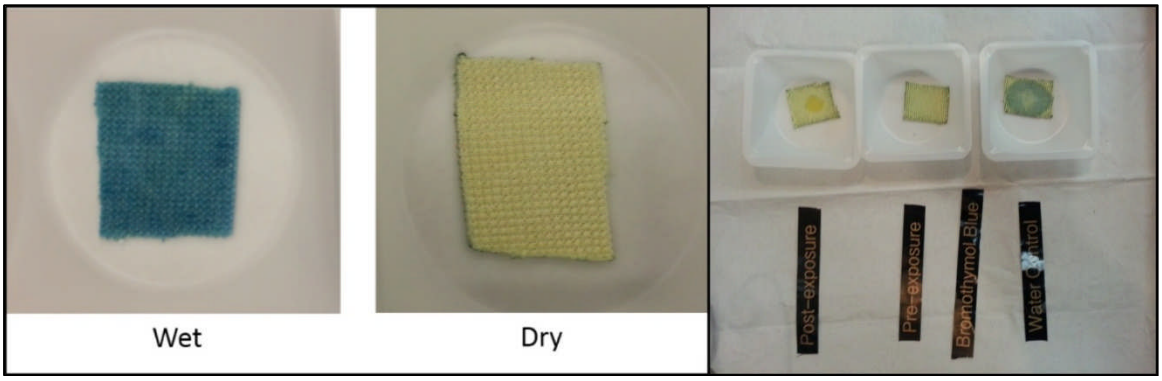


Figure 32. Bromothymol Blue (Basic) Indicator Wipes. Left – Wet and Vacuum Dried Wipes. Right – Exposure Results.

Methyl Red (Stock and Basic)

The results of exposure of Methyl Red (Stock) indicator wipes (air dried) to 3 drops of AF-M315E and the control are shown in Figure 33. It can be seen that the color change due to exposure to AF-M315E is not clearly visible for the test specimen (looks wet). The results of exposure of Methyl Red (Basic) indicator wipes (vacuum dried) to 3 drops of AF-M315E and the control are shown in Figure 34. It can be seen that the color change due to exposure to AF-M315E is clearly visible for the test specimen. The control experiments for both wipes also showed no color changes. An additional study was performed to determine the requirement for vacuum drying of the Methyl Red (Basic) indicator wipes. Data indicates that vacuum drying is not necessary for the Methyl Red (Basic) indicator wipes (no color change due to CO_2 absorption observed).

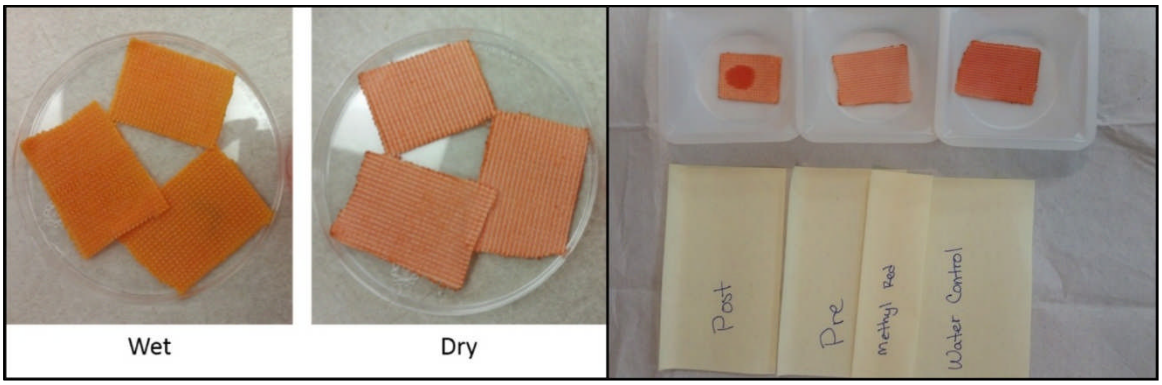


Figure 33. Methyl Red (Stock) Indicator Wipes. Left – Wet and Air Dried Wipes. Right – Exposure Results.

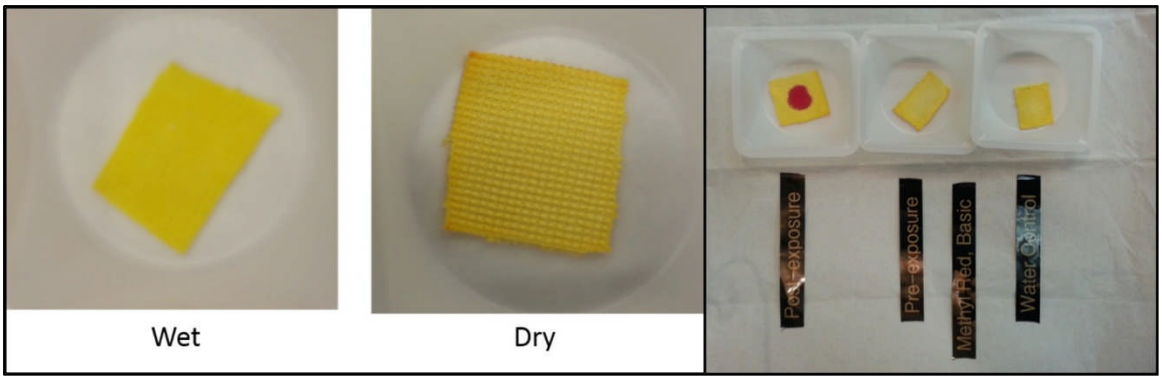


Figure 34. Methyl Red (Basic) Indicator Wipes. Left – Wet and Vacuum Dried Wipes. Right – Exposure Results.

Vanillin

The results of exposure of Vanillin indicator wipes (air dried) to 3 drops of AF-M315E and the control are shown in Figure 35. It can be seen that the color change due to exposure to AF-M315E is not very visible for the test specimen (very similar to the wet wipe). The control experiment also did not show a color change.

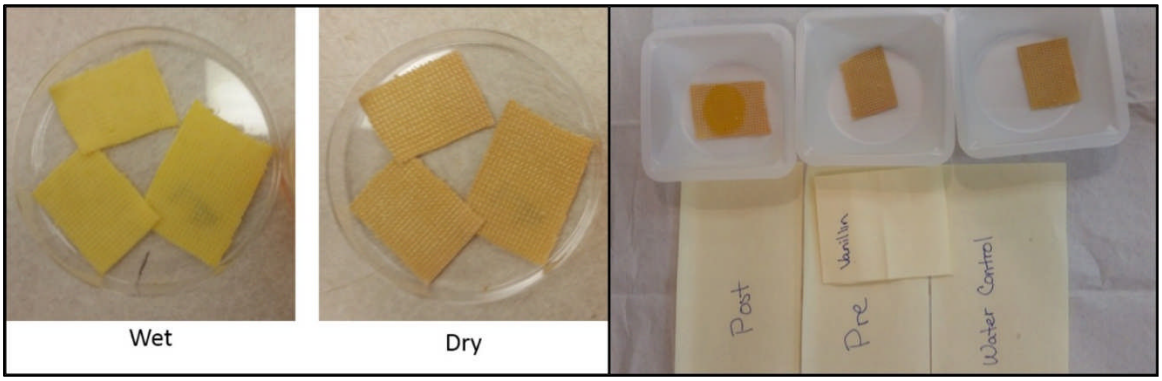


Figure 35. Vanillin Indicator Wipes. Left – Wet and Air Dried Wipes. Right – Exposure Results.

VWR Universal Indicator

The results of exposure of VWR Universal Indicator wipes (air dried) to 3 drops of AF-M315E and the control are shown in Figure 36. It can be seen that the color change due to exposure to AF-M315E is clearly visible for the test specimen. The control experiment did show a color change.

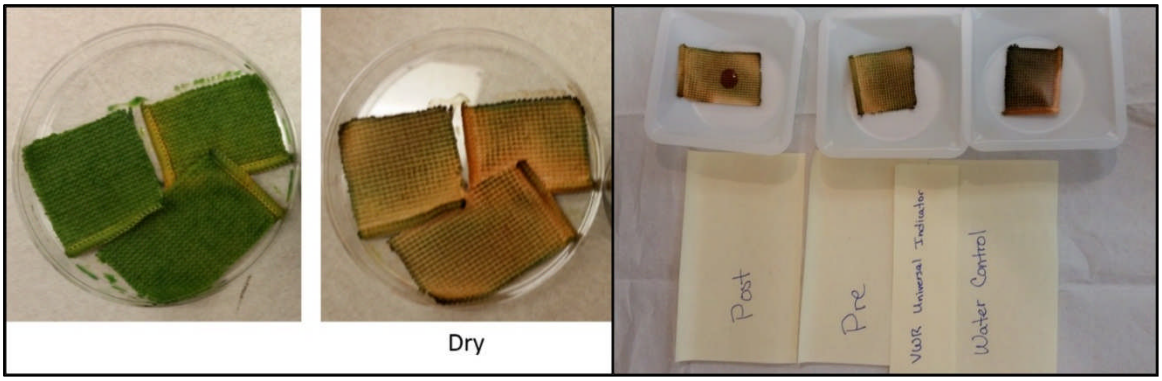


Figure 36. VWR Universal Indicator Wipes. Left – Wet and Air Dried Wipes. Right – Exposure Results.

Yamada Universal Indicator (Acidic)

The results of exposure of Yamada Universal Indicator (Acidic) indicator wipes (air dried) to 3 drops of AF-M315E and the control are shown in Figure 37. It can be seen that the color change due to exposure to AF-M315E is not clearly visible for the test specimen (looks wet). The control experiment did not show a significant color change.

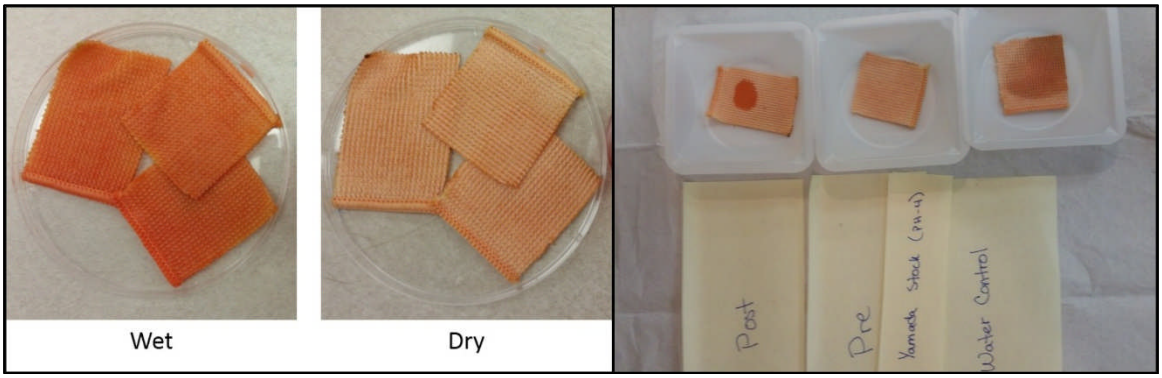


Figure 37. Yamada Universal Indicator (Acidic) Wipes. Left – Wet and Air Dried Wipes. Right – Exposure Results.

Yamada Universal Indicator (Basic)

The results of exposure of Yamada Universal Indicator (Basic) indicator wipes (vacuum dried) to 3 drops of AF-M315E and the control are shown in Figure 38. It can be seen that the color change due to exposure to AF-M315E is clearly visible for the test specimen. The control experiment also showed a significant color change.

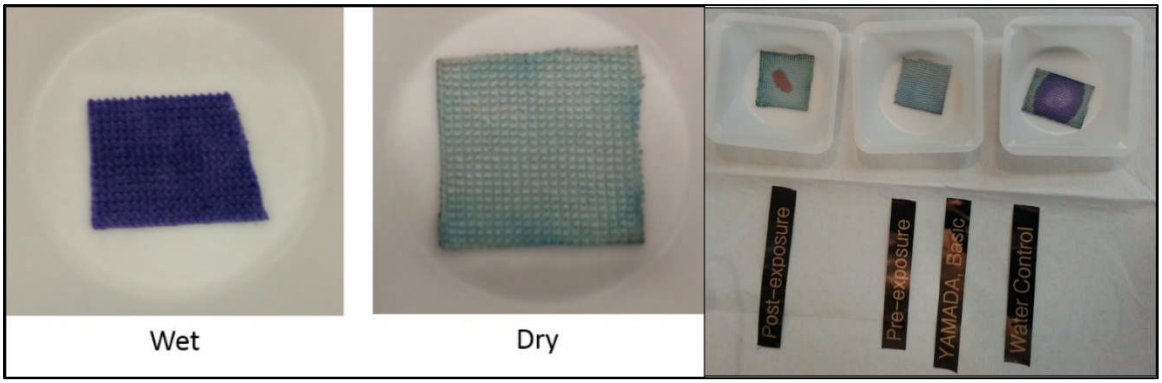


Figure 38. Yamada Universal Indicator (Basic) Wipes. Left – Wet and Vacuum Dried Wipes. Right – Exposure Results.

Yamada Universal Indicator (Neutral)

The results of exposure of Yamada Universal Indicator (Neutral) indicator wipes (air dried) to 3 drops of AF-M315E and the control are shown in Figure 39. It can be seen that the color change due to exposure to AF-M315E is not clearly visible for the test specimen (looks wet). The results of exposure of Yamada Universal Indicator (Neutral) indicator wipes (vacuum dried) to 3 drops of AF-M315E and the control are shown in Figure 40. It can be seen that the color change due to exposure to AF-M315E is not clearly visible for the test specimen (looks wet). The control experiments for both wipes also showed significant color changes.

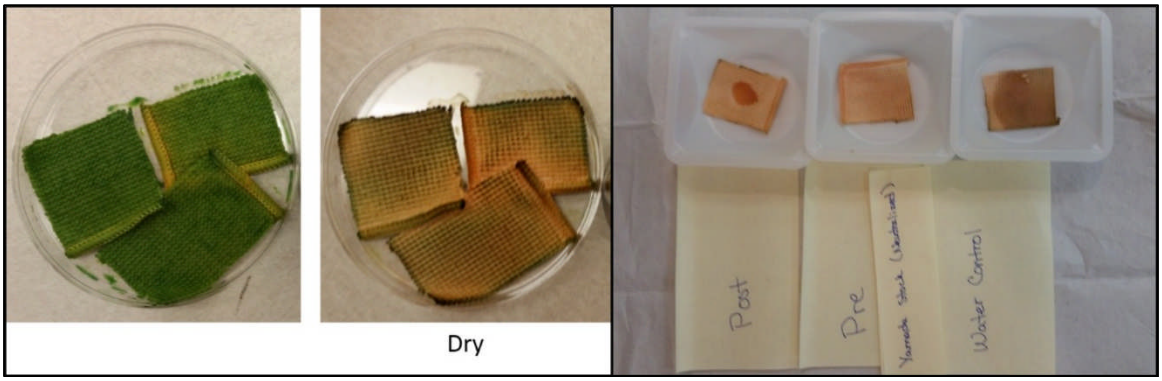


Figure 39. Yamada Universal Indicator (Neutral) Wipes. Left – Wet and Air Dried Wipes. Right – Exposure Results.

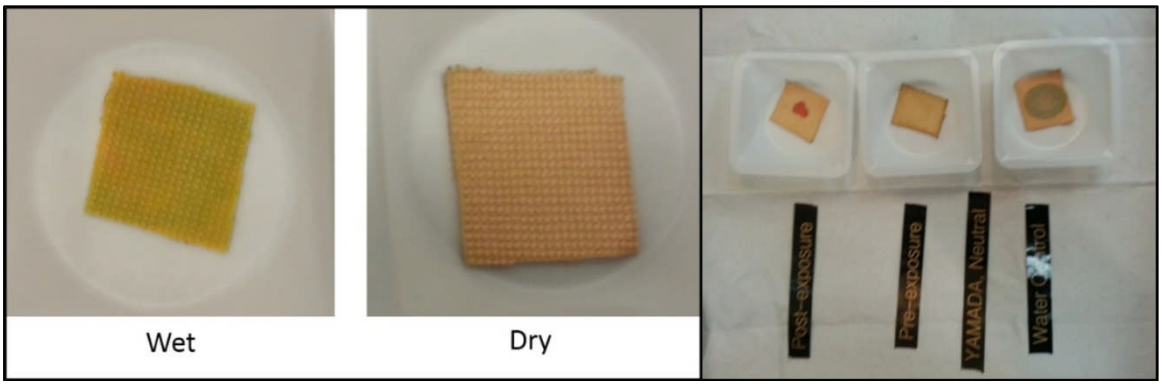


Figure 40. Yamada Universal Indicator (Neutral) Wipes. Left – Wet and Vacuum Dried Wipes. Right – Exposure Results.

Methyl Red (Basic) – Wipe Test

An additional test using the Methyl Red (Basic) indicating wipes was conducted to determine the wipes effectiveness in detecting a small amount of residual propellant liquid from a surface. An attempt was made to allow the AF-M315E to evaporate, however, the negligible vapor pressure prevented this from occurring. The surface of several 3" x 2" stainless steel test panels were wetted using a swatch of the material saturated with AF-M315E or deionized water and then wiped using the indicating wipes. The results from the testing are shown in Figure 41. As can be seen in the images, the wipes performed similarly to the drop test, showing a vivid color change upon direct exposure to the residual AF-M315E (Figure 39c). The deionized water control sample showed no change upon exposure, indicating that the indicating wipes are not susceptible to false positives from moisture.

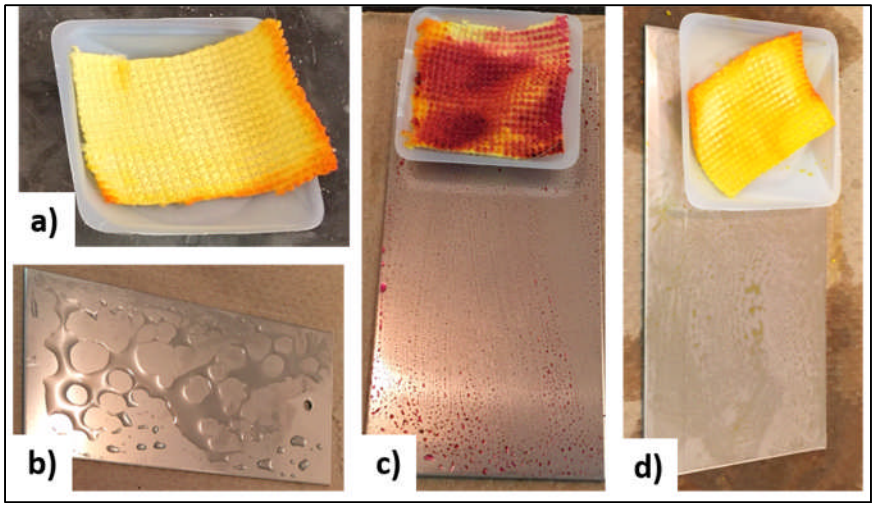


Figure 41. Methyl Red (Basic) Wipe Residue Test – a) pre-exposure, b) AF-M315E Test Panel, c) post-exposure (AF-M315E), d) post-exposure (DI H_2O).

Colorimetric – Vapor

Although previous testing indicated that a vapor-based detection system would not be an effective detection method, the successful results of the colorimetric indicator (Methyl Red, Basic) testing warranted an experiment to see if the indicator could detect small quantities of AF-M315E vapor. A test was setup to see if a Methyl Red (Basic) indicator could detect the presence of HAN vapor. A small piece of the Methyl Red (Basic) colorimetric indicating wipe (Figure 42a) was used as a replacement septum in a 20 ml borosilicate vial (Figure 42b/c). 1 ml of AF-M315E was added to the vial and the sample was allowed to sit for four days.

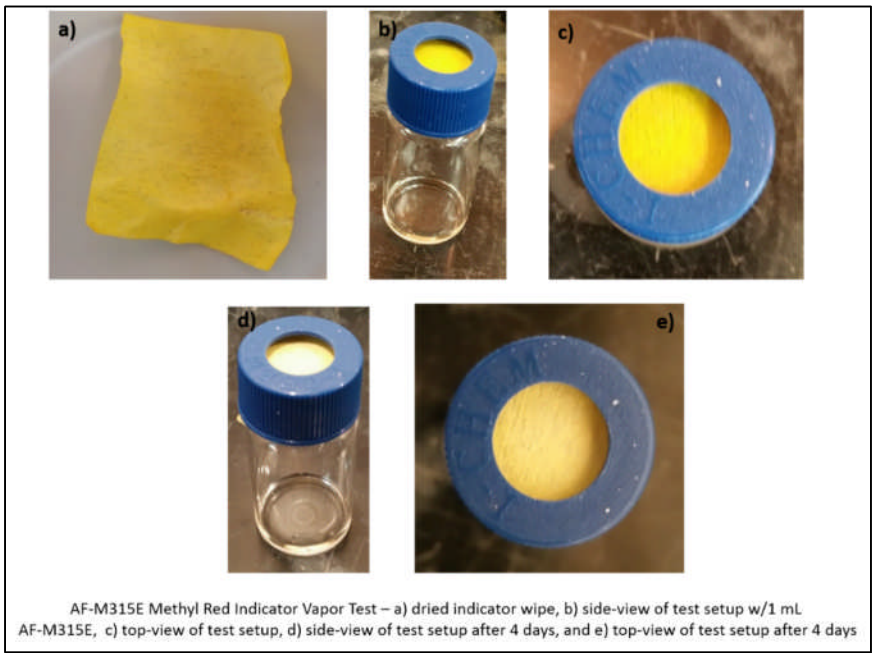


Figure 42. Yamada Universal Indicator (Neutral) Wipes. Left – Wet and Vacuum Dried Wipes. Right – Exposure Results.

Over the four day exposure period, there was no change in the color of the wipe material, indicating a negative response for AF-M315E vapor (Figure 42d/e).

Methyl Red Indicator Formulation Testing

Due to the acidic nature of the AF-M315E monopropellant (pH ~ 3.65) it is not surprising that an acid/base indicator would prove effective in its detection. Methyl Red undergoes a color change from red (acidic) to yellow (basic) in the pH range from 4.5 – 6.5. The initial formulation for the indicating solution was 60 ml of anhydrous ethanol, 40 ml of deionized water, and 40 mg of Methyl Red. This solution was acidic in nature and therefore had to be basified to be an effective indicator for the presence of AF-M315E. This was accomplished by adding a small aliquot (~7 ml) of 1.0 N sodium hydroxide to the prepared solution, which caused a visible color change to orange/yellow (as expected). Figure 43 and Figure 44 show previous testing using the Methyl Red (both Stock and Basic solutions) indicator on impregnated wipes and the color change upon exposure to AF-M315E.

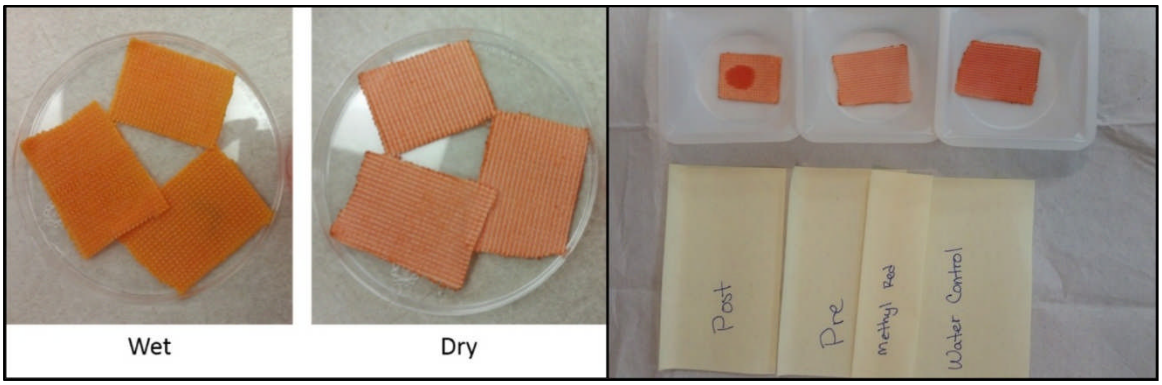


Figure 43. Methyl Red (Stock) Indicator Wipes. Left – Wet and Air Dried Wipes. Right – Exposure Results.

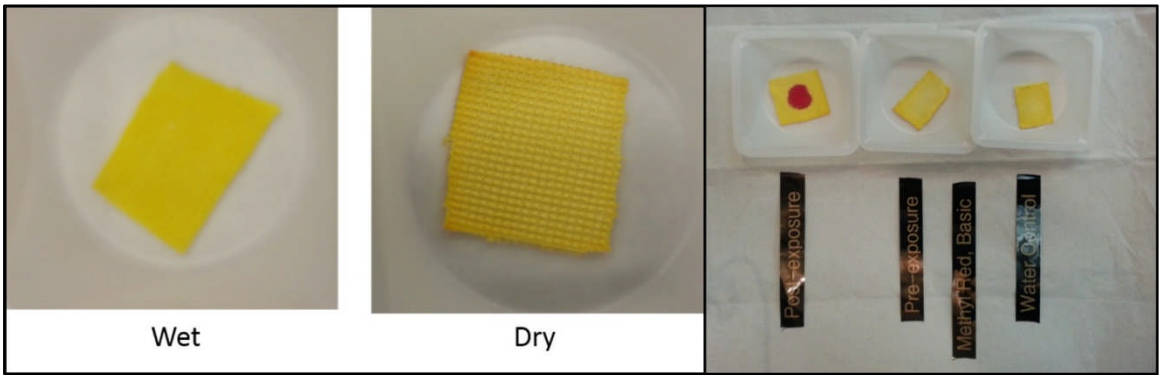


Figure 44. Methyl Red (Basic) Indicator Wipes. Left – Wet and Vacuum Dried Wipes. Right – Exposure Results.

As can easily be seen when comparing these tests visually, the color change is much more apparent when using the Methyl Red (Basic) indicator solution. Further testing was performed in an attempt to determine the optimum amount of base needed for indicating solution. Unfortunately, solutions will absorb carbon dioxide and produce carbonic acid, shifting toward a more acidic pH. In an aqueous sodium hydroxide solution, the absorbed carbon dioxide can react directly with the

sodium hydroxide, effectively neutralizing the effect of the added base. Several different formulations of the Methyl Red (Basic) were tested in an attempt to determine an optimum mixture. Testing was performed on different absorbent materials, including aerogel particles, specifically Cabot Nanogel TLD302, as these were initially identified as a promising substrate material. Figure 45 shows TLD302 particles impregnated with the original Methyl Red (Basic) indicator solution (both pre- and post-exposure, as well as an unaltered blank).

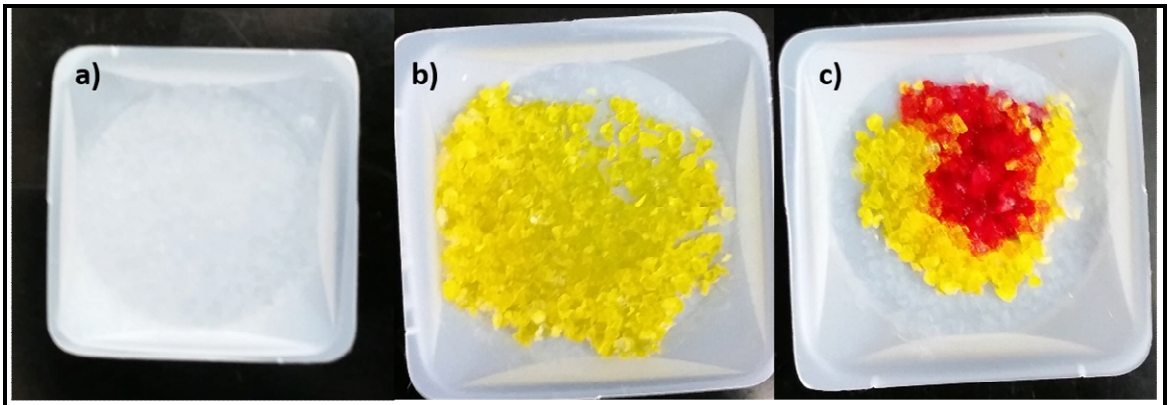


Figure 45. TLD302 Nanogel Indicator Testing.

As before, a striking color change is observed, and the aerogel can be seen to almost "grab" any fluid that it comes into contact with. TLD302 is a hydrophobic silica-based aerogel, which would be expected to repel aqueous-based solutions. However, the ethanol in the solution allows for penetration into the aerogel particles. While these results seem very promising, it should be noted that the samples in Figure 45 were tested without allowing the indicator to dry. Unfortunately, the behavior of the Methyl Red impregnated aerogel particles changes quite drastically once this occurs.

Figure 46 shows the full test panel for three different Methyl Red (Basic) indicating solution formulations.

- Formula 1 – 60 ml anhydrous ethanol, 40 ml deionized water, 40 mg Methyl Red, ~7 ml 1.0 N sodium hydroxide
- Formula 2 – 100 ml anhydrous ethanol, 40 mg Methyl Red, ~30 ml 1.0 N sodium hydroxide
- Formula 3 – 60 ml anhydrous ethanol, 40 ml 1.0 N sodium hydroxide, 40 mg Methyl Red

Attempts were made to increase the capacity of the particles to absorb carbon dioxide (thereby, improving HAN indicating capability) by increasing the amount of sodium hydroxide that was added to the formulation. Additionally, to try and prevent the hydrophobicity seen in the dried indicating particles (seen with Formula 1), the ethanol component of the mixture was increased as well. Formula 2 (increased ethanol:water ratio, increased base capacity) showed the most favorable results but there was still a distinct color shift upon drying (yellow to orange, Figure 46b) and, although the hydrophobic nature seemed to decrease, it was still apparent upon addition of the AF-M315E monopropellant to the dried impregnated aerogel particles. With all three formulations, the AF-M315E appeared to "bead-up" upon addition to dry aerogel particles (an

indication of greater intermolecular cohesive forces, Figure 46c), although this was decreased in the formulations with the increased ethanol content. A color change was still noticeable in all three formulations; however, it was much less apparent due to the starting color of the dried aerogel particles. Further absorbent material testing (Figure 47) shows that other materials do not suffer from the same carbon dioxide absorption issues evidenced by aerogel particles. Due to this, it was decided to continue using the original formulation ratio for the Methyl Red (Basic) indicating solution. One change, however, was to incorporate the base component into the aqueous component of the mixture. The final formulation (Formula 4) that was chosen for further testing was 60 ml anhydrous ethanol, 40 ml 0.2 N sodium hydroxide, and 40 mg of Methyl Red.

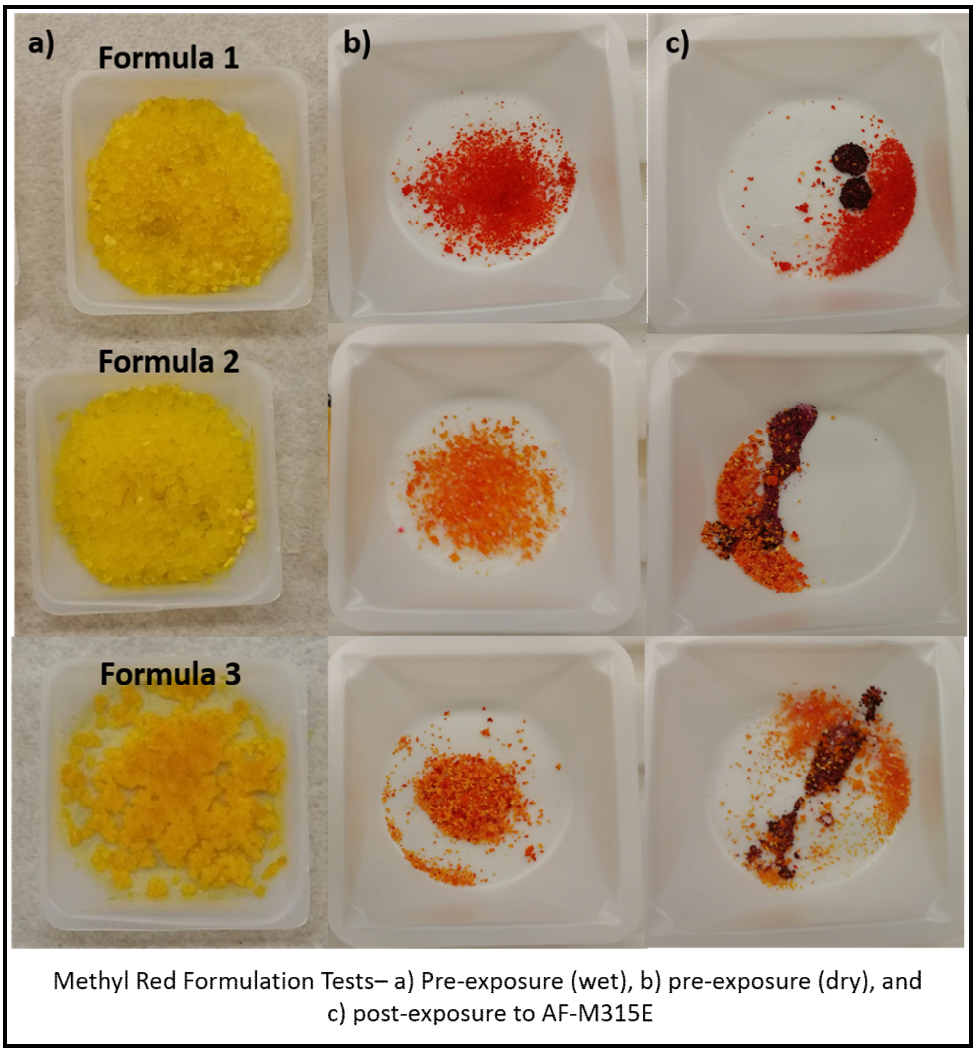


Figure 46. Methyl Red Formulation Tests Results.

Absorbent Material Selection

Based upon the previous results observed when attempting to use aerogel particles as the indicator substrate, it was decided to expand the test parameters to include additional absorbent materials. An initial experiment with six different absorbent materials was setup for testing using the original (Formula 1) Methyl Red (Basic) indicating solution. These materials included: a) alumina beads, b) Cabot Nanogel TLD302, c) pig powder (filler material from Fisher Spill Kit S47441), d)

activated alumina, e) Cabot Nanogel OBD301, and f) aerogel blanket. These materials are shown in Figures 47 – 49.

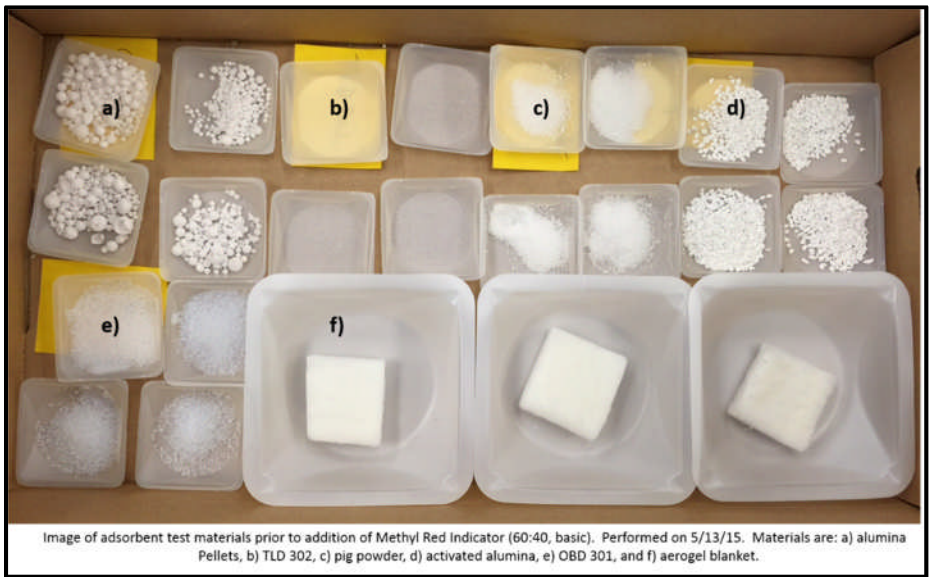


Figure 47. Different Absorbent Materials Evaluated.

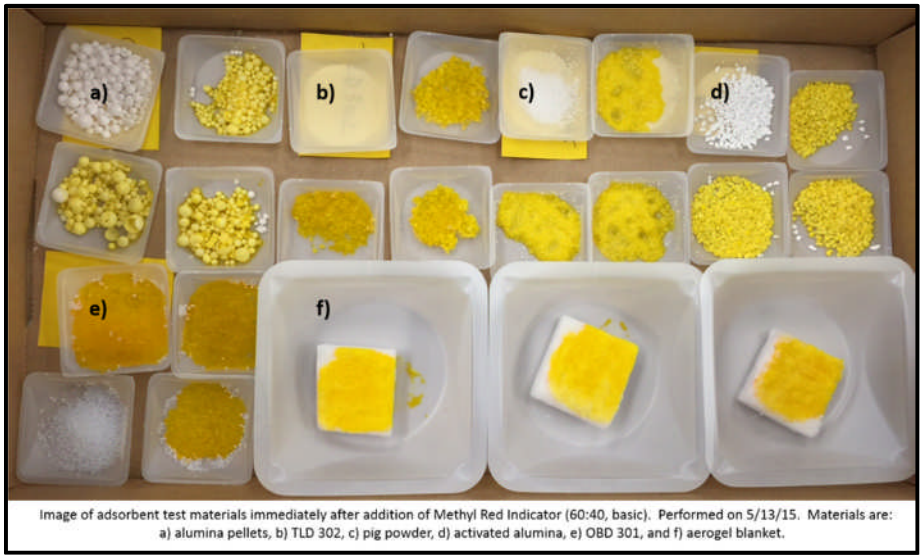


Figure 48. Different Absorbent Materials with Methyl Red (Basic) Indicator.

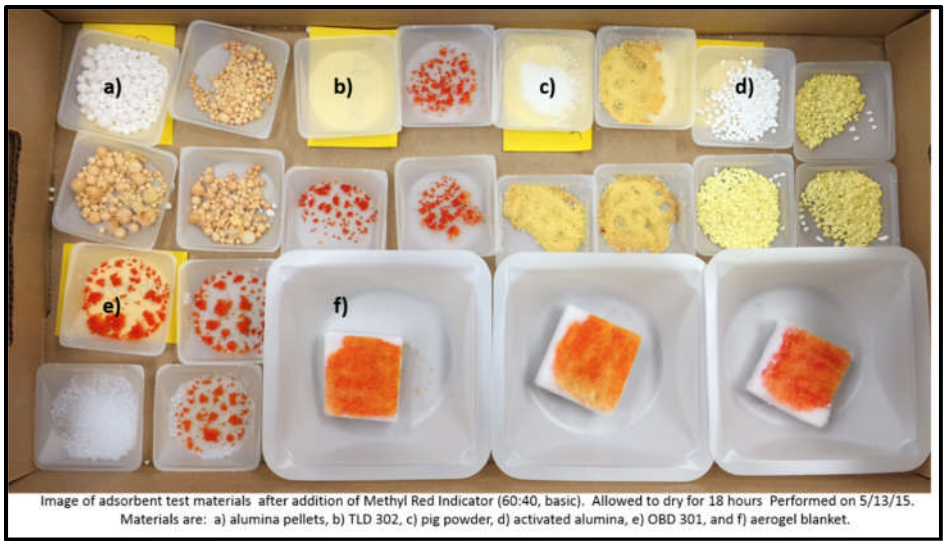


Figure 49. Different Absorbent Materials with Indicator Air Dried.

Based upon the previously obtained test data on the aerogel particles obtained during the Methyl Red (Basic) indicating formulation testing, it was decided to eliminate the Cabot Nanogel materials (both TLD302 and OBD301), as well as the aerogel blanket, from further testing. An additional sample material was included in this test, which was a polystyrene absorbent material from 3M Chemical Absorbent booms. Figures 50 – 53 show all four of these test materials during the various stages of the experiment, including: a) blank, b), pre-exposure, c) post-exposure (AF-M315E), and d) post-exposure (deionized water). The post-exposure (deionized water) is used as a control sample to ensure that the material is not susceptible to false positives.

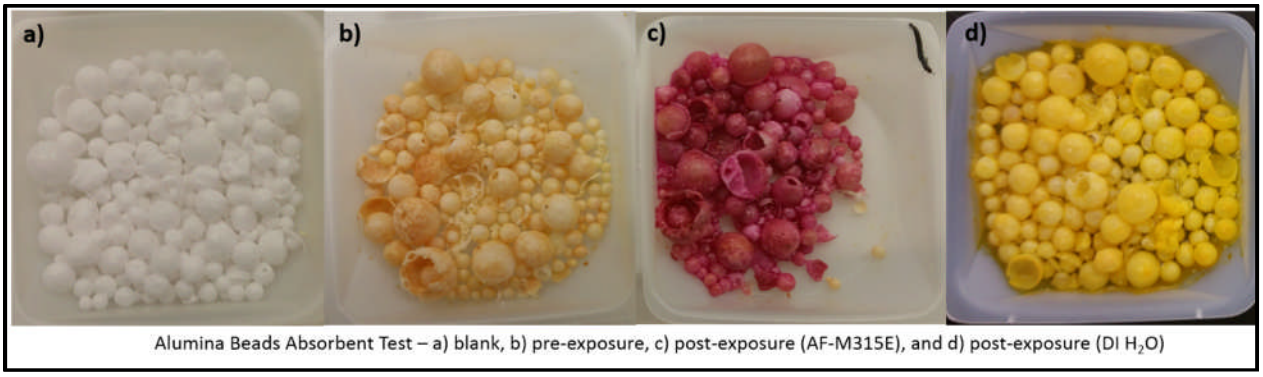


Figure 50. Alumina Bead Indicating/Absorption Test Results.

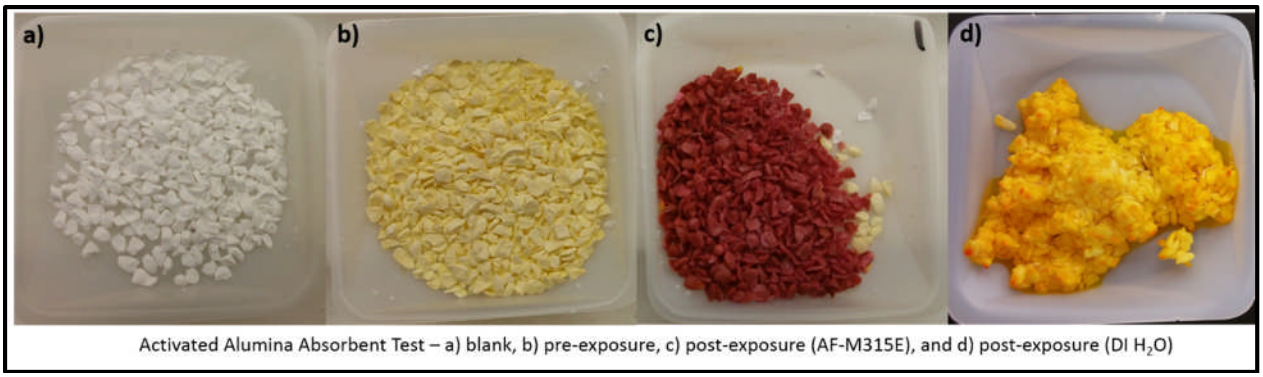


Figure 51. Activated Alumina Indicating/Absorption Test Results.

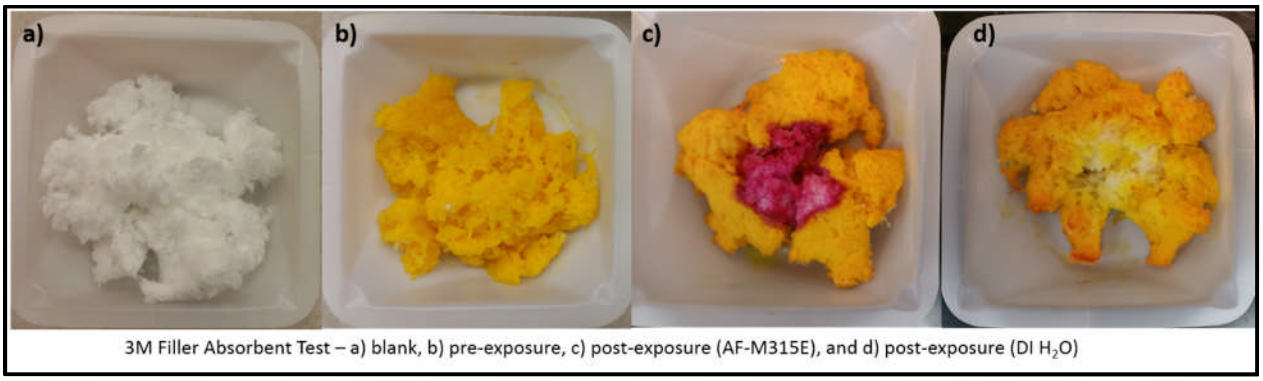


Figure 52. 3M Filler Absorbent Material Indicating/Absorption Test Results.

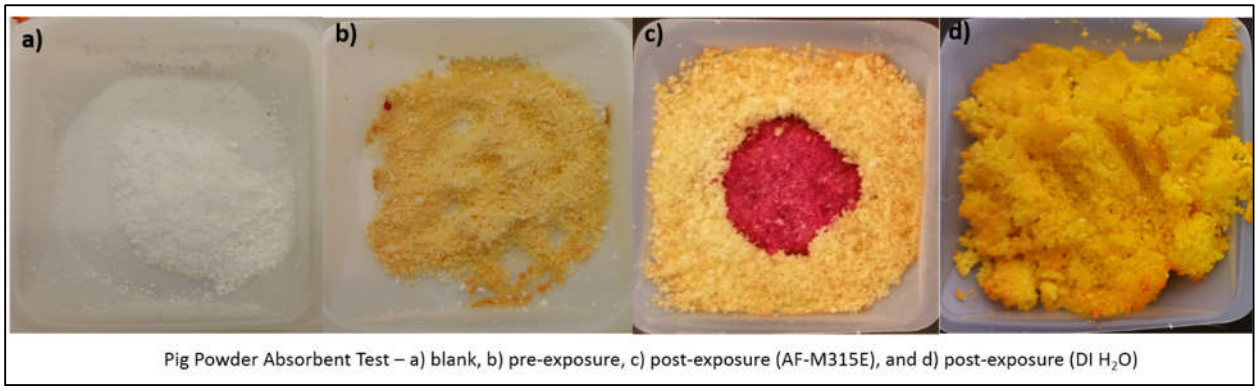


Figure 53. Pig Power Indicating/Absorption Test Results.

All four samples exhibited excellent color change upon exposure to the AF-M315E monopropellant. Additionally, of the samples tested, the 3M Filler and the Pig Powder showed better absorbance capability (at least qualitatively). However, at the time of testing, the 3M Filler had still not dried (after 3 days), which may be a concern moving forward.

Absorbent Sock Testing

The final phase of testing for the development of a detection system for HAN/AF-M315E was performed by preparing different test samples using the most promising candidates from the absorbent materials testing and encasing them within a compatible material. These "socks" were then immersed within the Methyl Red (Basic, Formula 4) indicating solution for a period of 30

seconds and allowed to dry over a period of three days prior to testing. The activated alumina, pig powder, and 3M Filler material were selected for this testing (the alumina beads were excluded due to limited availability as well as similar results to the activated alumina). Two different polymeric materials were used as "sock" materials. These were the liners from the Fisher Universal Spill Kit (PN #S47441) as well as the liners from the 3M Chemical Sorbent Booms (PN #M-MB304). To prepare the sample socks for testing, the original liners were cut open and completely emptied of all filler material. These empty liners were then cut into ~4" lengths and filled with the absorbent material that would be tested. The filled "sock" was then sealed using a zip-tie, treated with the Methyl Red (Basic) indicating solution, and allowed to dry. For the exposure test, 5 ml of AF-M315E monopropellant was placed in a weigh boat (Figure 54) and the "sock" to be tested was placed directly on the commodity (Figures 55 – 60). After approximately one hour, the samples were removed from the weigh boats to determine if any monopropellant remained unabsorbed.

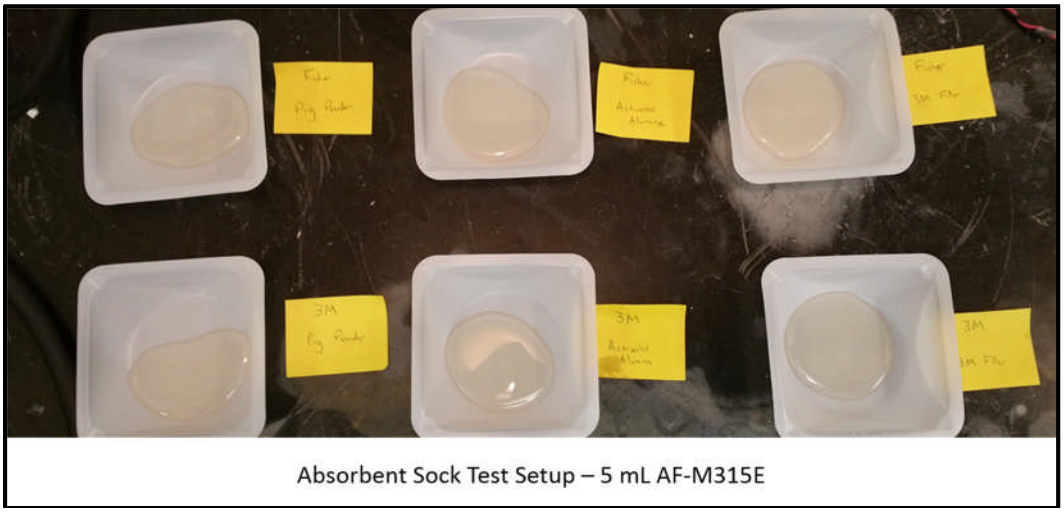


Figure 54. Absorbent Sock Test Setup.

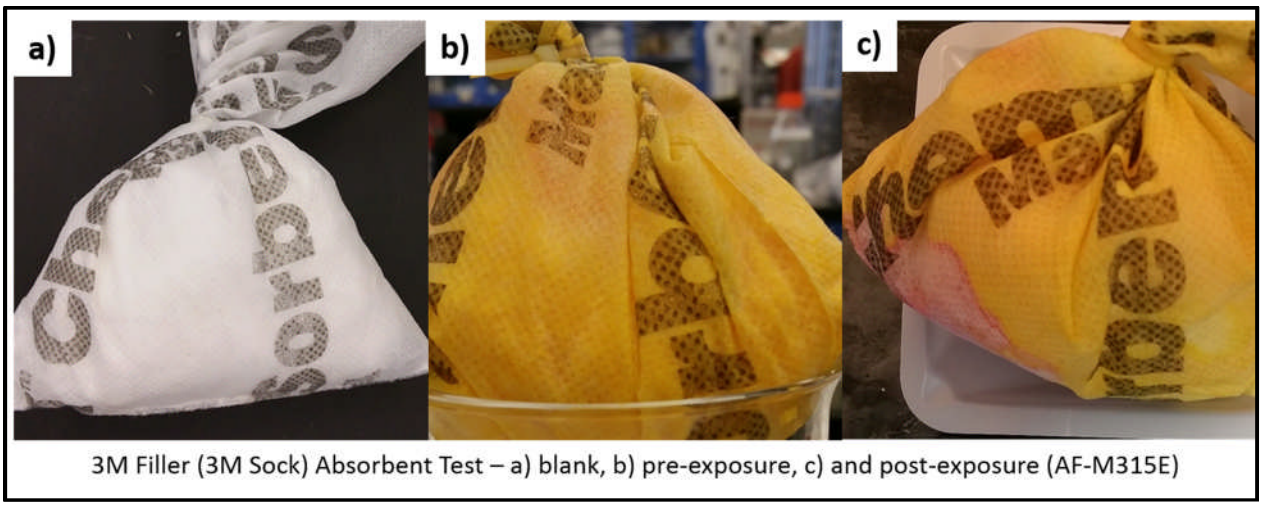


Figure 55. 3M Filler (3M Sock) Indicating/Absorption Sock Test Results.

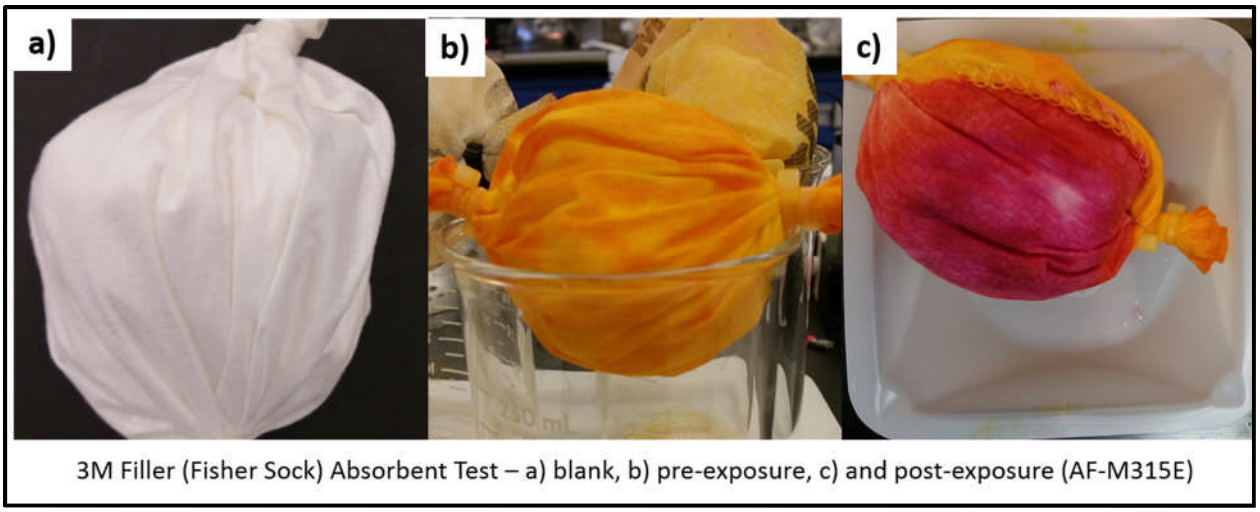


Figure 56. 3M Filler (Fisher Sock) Indicating/Absorption Sock Test Results.

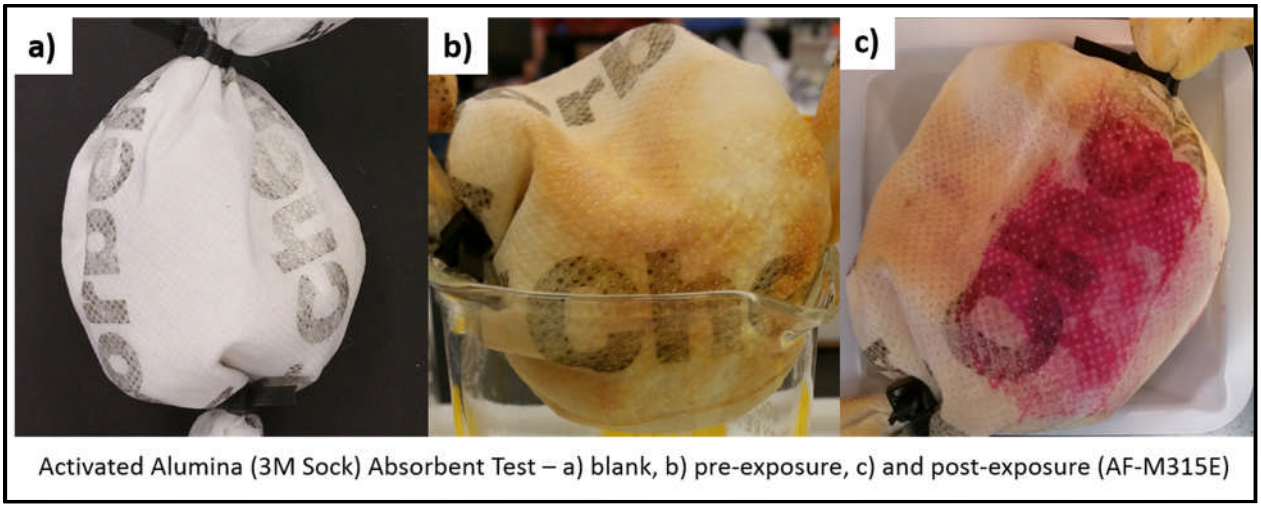


Figure 57. Activated Alumina (3M Sock) Indicating/Absorption Sock Test Results.

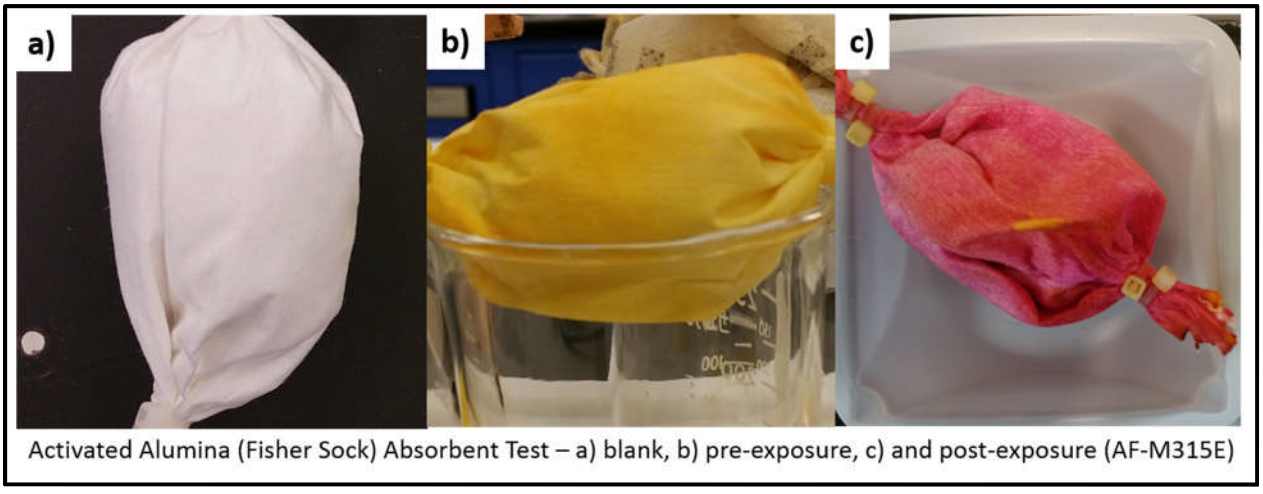


Figure 58. Activated Alumina (Fisher Sock) Indicating/Absorption Sock Test Results.

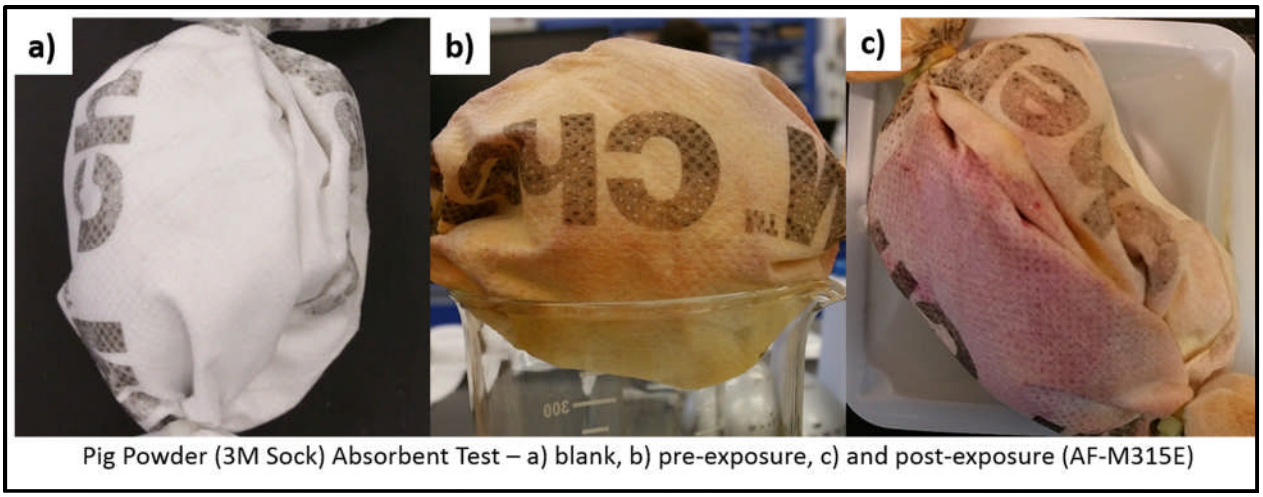


Figure 59. Pig Powder (3M Sock) Indicating/Absorption Sock Test Results.

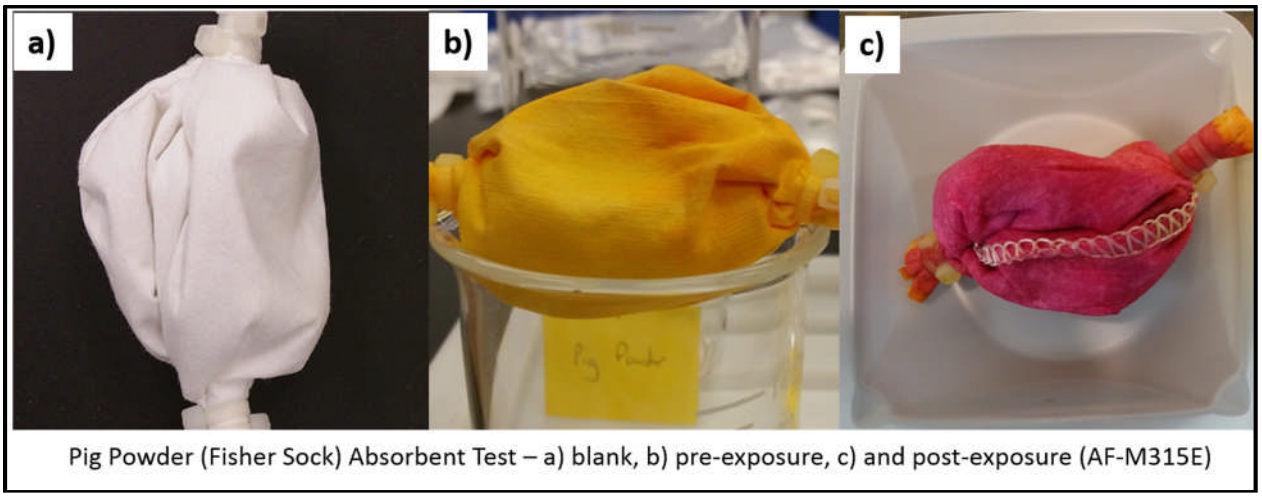
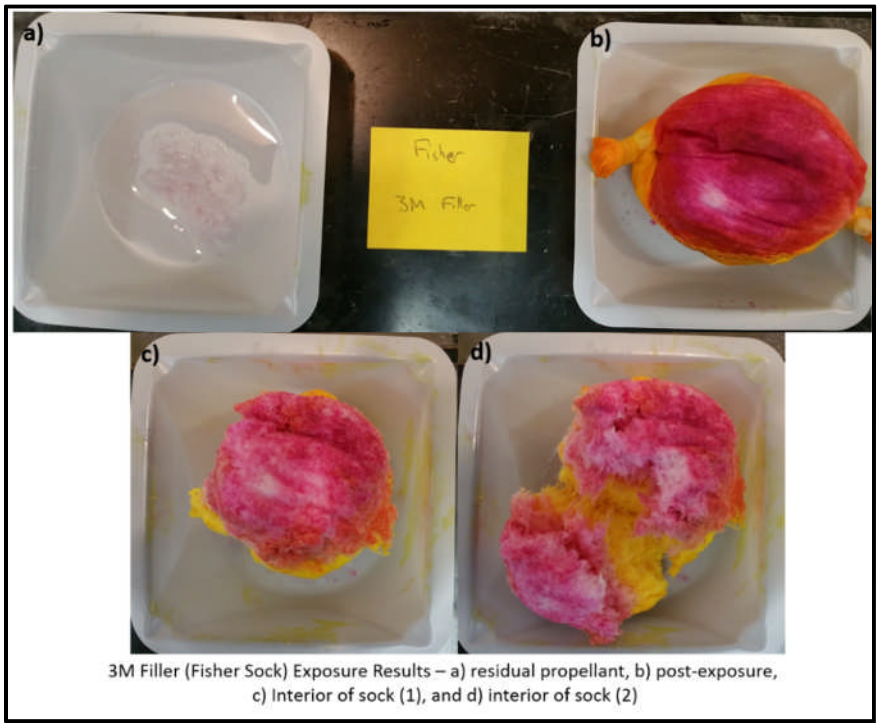


Figure 60. Pig Powder (Fisher Sock) Indicating/Absorption Sock Test Results.

In all of the cases, it was readily apparent that the "socks" were absorbing the AF-M315E (as evidenced by the color change). As was seen previously in the absorbent material testing, the samples containing the 3M Filler material were still very wet even after several days of drying time. However, all six samples tested showed a strong color change upon exposure to AF-M315E. It was noticed that the 3M Chemical Sorbent liner material appeared to have a less uniform color (Figure 57 and Figure 59) as compared to the samples prepared in the Fisher Universal Spill Kit liners. In addition, the exposed "socks" were dissected in an attempt to determine the level of saturation that had occurred within the filler material and to verify that the color change had extended beyond the surface layer of the liner material (Figures 61 – 66).

3M Filler (3M Sock) Exposure Results – a) residual propellant, b) post-exposure, c) Interior of sock (1), and d) interior of sock (2)

Figure 61. 3M Filler (3M Sock) Exposure Results Showing Interior.

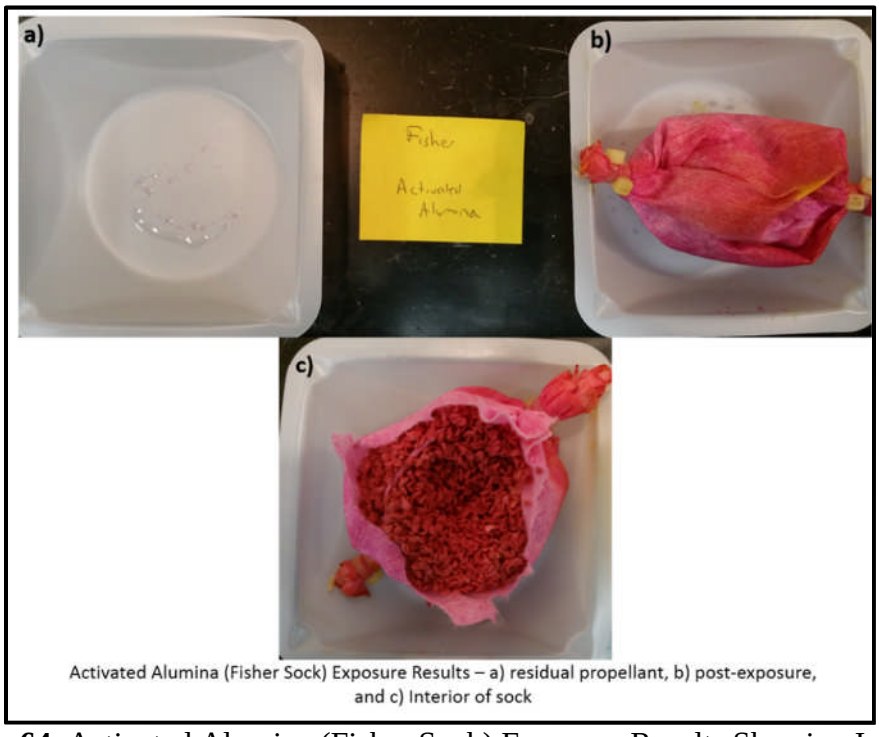


3M Filler (Fisher Sock) Exposure Results – a) residual propellant, b) post-exposure, c) Interior of sock (1), and d) interior of sock (2)

Figure 62. 3M Filler (Fisher Sock) Exposure Results Showing Interior.

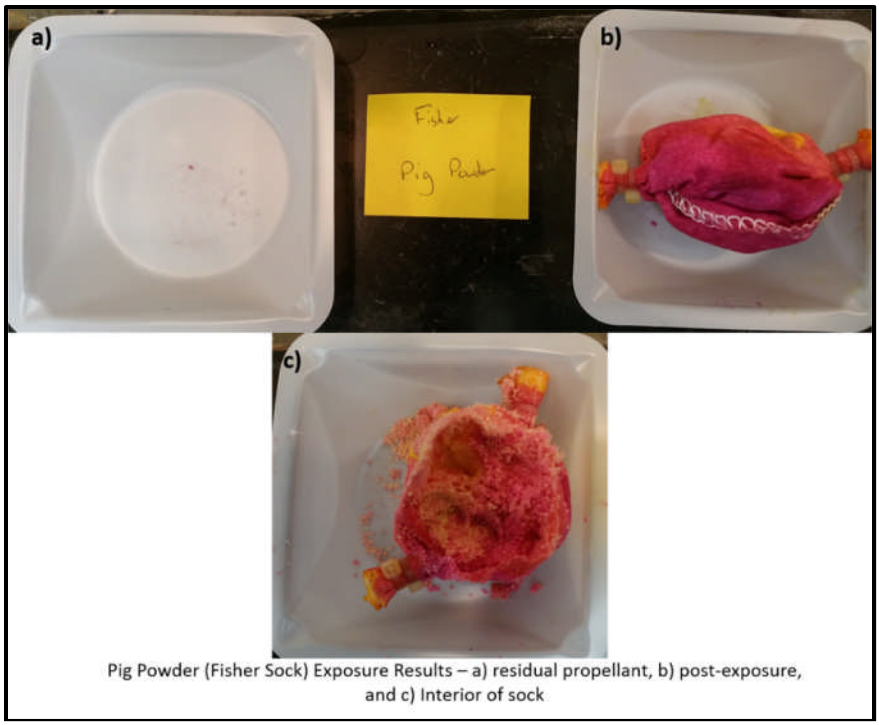
Activated Alumina (3M Sock) Exposure Results – a) residual propellant, b) post-exposure, and c) Interior of sock

Figure 63. Activated Alumina (3M Sock) Exposure Results Showing Interior.



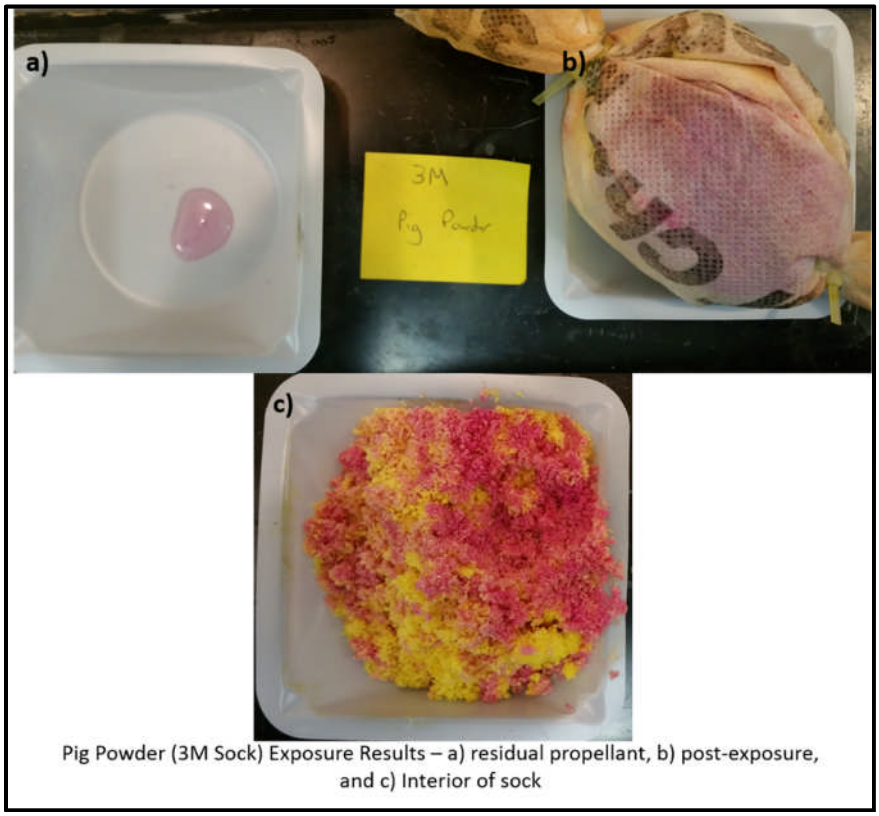
Activated Alumina (Fisher Sock) Exposure Results – a) residual propellant, b) post-exposure, and c) Interior of sock

Figure 64. Activated Alumina (Fisher Sock) Exposure Results Showing Interior.



Pig Powder (Fisher Sock) Exposure Results – a) residual propellant, b) post-exposure, and c) Interior of sock

Figure 65. Pig Power (Fisher Sock) Exposure Results Showing Interior.



Pig Powder (3M Sock) Exposure Results – a) residual propellant, b) post-exposure, and c) Interior of sock

Figure 66. Pig Powder (3M Sock) Exposure Results Showing Interior.

All samples appear to have removed the vast majority of the commodity upon physical exposure. Further sorption would likely be observed if the "sock" had been physically manipulated into contact with the propellant. The activated alumina samples (Figure 63 and Figure 64) show that the substrate appears to be fully saturated, indicating less capacity for absorbing AF-M315E. Based upon these results, additional test specimens were prepared using the Fisher Universal Spill Kit liners with the three leading absorbent candidates: 3M Filler, activated alumina, and pig powder. These samples were prepared as before, with the only major change being that the 3M Filler samples were allowed to dry in an oven (55 °C, nitrogen purge). This allowed for testing all sample in a dry state (unlike previously). For this exposure test, each sample was exposed to approximately 40 ml of AF-M315 (or deionized water) (Figures 67 – 69).

Figure 67. 3M Filler (Fisher Sock) Exposure Test Results.

Figure 68. Activated Alumina (Fisher Sock) Exposure Test Results.

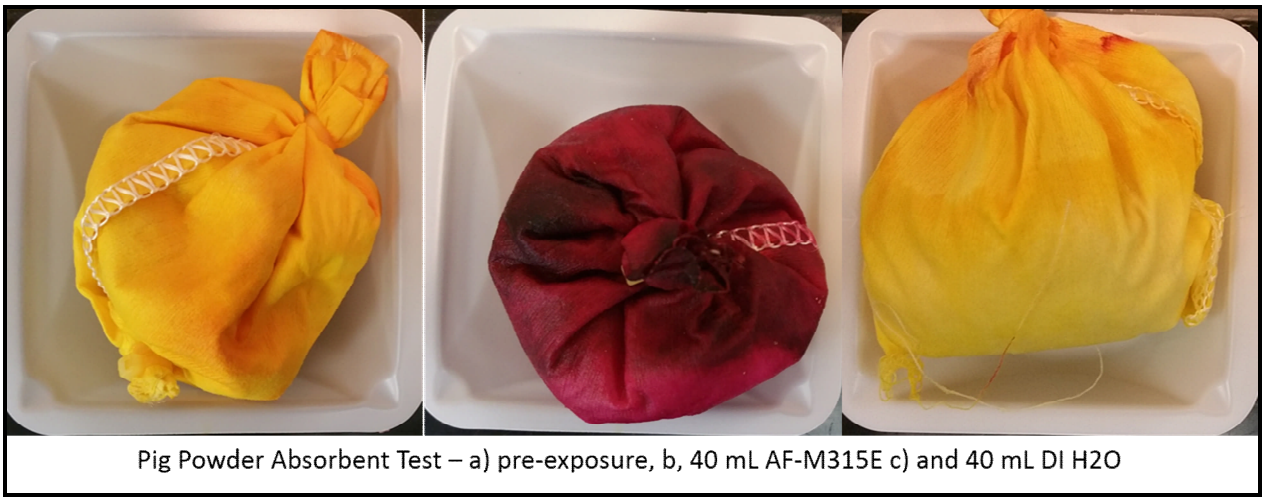


Figure 69. Pig Power (Fisher Sock) Exposure Test Results.

All samples appear to have removed the vast majority of the commodity upon physical exposure. However, even though the relative absorptive capability of the materials is equal (qualitatively) on a volume basis, the activated alumina is much denser, and so, is less effective on a mass basis. This factor, coupled with the higher cost of the activated alumina substrate material, allows for its elimination as a possible candidate for the final AF-M315E detection system. Of the final two remaining candidates, the 3M Filler material is less desirable due to fact that it retains so much moisture after the addition of the Methyl Red (Basic) indicator, which allows for the possibility of carbon dioxide absorption and continued color change. Finally, as the Fisher Universal Spill Kit liners have already been chosen as the material for the AF-M315E detection system, the use of the pig powder allows for a streamlined, efficient preparation process. The Fisher Universal Spill Kit Liners (PN #S47441) can be ordered and directly immersed in the Methyl Red (Basic) indicating solution, allowed to dry, and set-aside until needed.

HAN/AF-M315E Detection System

The development of a detection system for HAN was approached in a different manner than that of ADN. Although a variety of COTS sensors were tested as possible methods of detection for HAN and AF-M315E, the non-volatile nature of the monopropellant made this a non-viable route for sensing the commodity. Rather, a variety of chemical indicators were evaluated as possible means of identifying the presence of AF-M315E. Initial results pointed to the use of Methyl Red (Basic) indicating solution as the best candidate for further testing (ESC-245-FDG-001). Further testing determined that the Methyl Red (Basic) indicator could be used in conjunction with an absorbent boom to allow both detection and containment within a single package (ESC-245-FDG-003). As such, the detection system package consists of several pre-made indicating absorbent booms which have been vacuumed sealed (to prevent CO_2 absorption over time), along with several unaltered booms to aid in further containment once a leak has been identified. Additionally, several indicating wipes containing Methyl Red (Basic) indicator have been included (these have also been vacuum sealed to minimize CO_2 absorption over time) to provide detection of leaks that may be too small to detect using the absorbent boom. Figure 70 shows the detection kit.

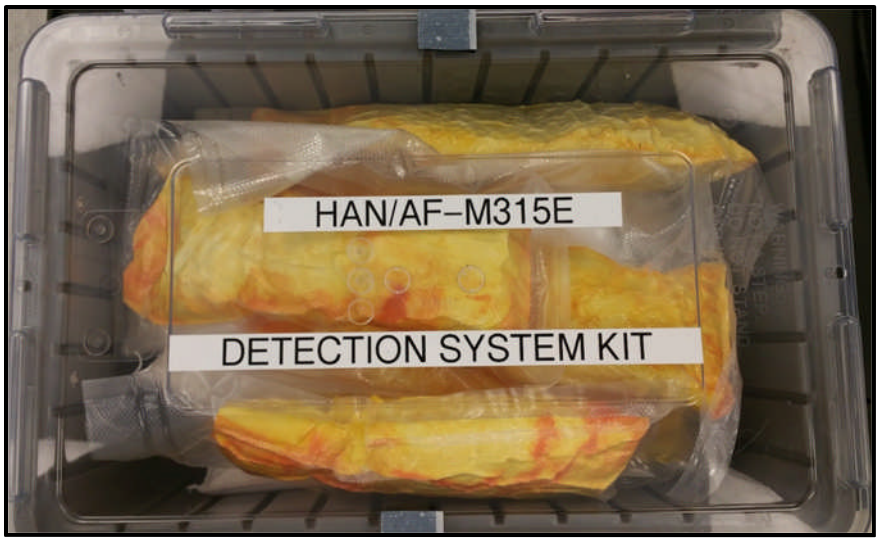


Figure 70. HAN Detection Kit.

Specific Details – Ammonium Dinitramide (ADN)

Testing for the development of a detection method for ADN/LMP-103S focused on the use of COTS vapor sensors which were equipped with sensor heads capable of detecting ammonia, due to both the higher vapor pressure of the monopropellant and the presence of ammonia in the commodity itself. All of the procured COTS sensors proved capable of detecting the LMP-103S commodity, although it is currently unclear if the ADN or the ammonia solvent was being identified by the sensor (a preliminary headspace analysis is attached in Appendix B).

Results – Commercial-Off-The-Shelf (COTS) Sensors

RAE Systems MultiRAE Lite

All three sensors (catalytic bed, ammonia, and PID) of the MultiRAE unit showed extremely high and rapid response when exposed to LMP-103S. Three individual tests were run (although the last was shortened due to sensor saturation and the suspected possibility of damaging the electrochemical ammonia sensor) and the results are given in Tables 4 – 6.

Table 4. Sample 1 LMP-103S MultiRAE Lite Testing.

Time (min)	LEL (%)	NH_3 (ppm)	VOC (ppm)
1	32	99	257
2	28	99	268
3	26	99	268
4	24	99	262
5	23	99	248
10	16	99	169
15	12	99	124
20	9	99	97
25	7	99	81
30	4	99	64

Table 5. Sample 2 LMP-103S MultiRAE Lite Testing.

Time (min)	LEL (%)	NH_3 (ppm)	VOC (ppm)
1	33	99	257
2	28	99	268
3	25	99	268
4	24	99	262
5	22	99	248
10	16	99	169
15	13	99	124
20	10	99	97
25	7	99	81

Table 6. Sample 3 LMP-103S MultiRAE Lite Testing.

Time (min)	LEL (%)	NH_3 (ppm)	VOC (ppm)
1	34	99	167
2	30	75	154
3	27	46	112
4	26	35	110
5	24	27	106

In addition to the individual sensor readings taken during the propellant exposures, the MultiRAE Lite was monitored post-exposure to determine how long it would take for each individual sensor to begin to decrease in signal and ultimately return to baseline line. These results are given in Tables 7 – 9.

Table 7. Sample 1 LMP-103S Post-Exposure Evaluation – MultiRAE Lite.

	Initial Signal Decrease	Return to Baseline
LEL (Catalytic Bed)	00:00	00:00
NH3 (Electrolytic Cell)	34:13	43:15
VOC (PID)	00:00	1:00:00*

Table 8. Sample 2 LMP-103S Post-Exposure Evaluation – MultiRAE Lite.

	Initial Signal Decrease	Return to Baseline
LEL (Catalytic Bed)	00:00	00:00
NH3 (Electrolytic Cell)	**	**
VOC (PID)	00:00	1:00:00*

Table 9. Sample 3 LMP-103S Post-Exposure Evaluation – MultiRAE Lite.

	Initial Signal Decrease	Return to Baseline
LEL (Catalytic Bed)	00:00	00:00
NH3 (Electrolytic Cell)	00:00	9:37
VOC (PID)	00:00	35:00

A fresh air zero calibration was performed between testing of Sample 2 and Sample 3 due to the fact that sensor failed to return to zero at the end of testing. It was dropping below zero, likely due to exposure to high levels of ammonia present within the LMP-103S monopropellant (ammonia makes 3% - 6% of the composition) as is noted by ** in Table 8. It was also decided to lower the exposure time for the third test in an attempt to limit this; however, as can be seen in a comparison of the data in all three tables, while the NH_3 concentration is constant in Samples 1 and Sample 2, it immediately begins to decrease in Sample 3. This lower exposure time most likely also explains why that during testing of Sample 3 the PID (VOC) sensor was able to return to baseline within the 60 minute period, when during the previous two tests it only was able to return to 1 ppm within that same period of time (as noted by * in Table 7 and Table 8). In fact, of all three sensors in the MultiRAE Lite gas-sensing instrument, only the response seen from the catalytic bed (LEL) sensor remained consistent over all three exposures to LMP-103S. The decrease in response observed in both the catalytic bed (LEL) and PID (VOC) sensors during each individual test is attributed to the loss of the volatile components of the propellant.

BW Technologies GasAlert Extreme

A positive response was observed when the GasAlert Extreme was exposed to LMP-103S. This testing was done in concert with that of the Dräger Pac® 7000. The tests were performed in triplicate and the results are given in Table 10.

Table 10. Results of GasAlert Extreme Testing with LMP-103S.

	LMP-103S (ml)	Alarm Time (sec)	Max (ppm)	Baseline Return (Hours)
Sample 1	1	14	100	1.5***
Sample 2	1	8	100	3.5
Sample 3	1	8	100	3.5

As compared to the other passive gas sensor, the GasAlert Extreme seemed to be more consistent in the response upon exposure to the LMP-103S. The response was very rapid in all three exposure tests (less than 15 seconds). The time for the system to return to baseline was quite long, taking over three hours (Sample 1*** was performed at the end of the day, and had only returned to 0 – 3 ppm at the 1.5 hour mark).

In addition to the results described above, the masses of each sample tested were monitored pre- and post-exposure in an attempt to determine the mass loss of propellant during each sample run. The results of these studies are shown in Table 11.

Table 11. Mass Loss Results of Passive Sensor Testing with LMP-103S.

	Sample 1	Sample 2	Sample 3
Mass, Pre-Exposure (g)	1.201	1.21	1.201
Mass, Post-Exposure (g)	1.111	1.114	1.109
Mass Lost (g)	0.09	0.096	0.092
Mass Lost (%)	7%	8%	8%
Exposure Time (min)	7	7	7
Flow Rate (ml/min)	350	350	350

Dräger Pac® 7000 (with Dräger XXS Ammonia Sensor)
A positive response was observed when the Dräger Pac® 7000 was exposed to LMP-103S. This testing was done in concert with the testing of the GasAlert Extreme. The tests were performed in triplicate and the results are given in Table 12.

Table 12. Results of Dräger Pac® 7000 Testing with LMP-103S.

	LMP-103S (ml)	Alarm Time (sec)	Max (ppm)	Baseline Return (Hours)
Sample 1	1	58	302	1.5****
Sample 2	1	17	302	3.5
Sample 3	1	27	302	3.5

As compared to the other passive gas sensor (GasAlert Extreme) the reproducibility of the Dräger Pac® 7000 seemed less consistent as that the time for the system to alarm varied considerably. That said, the Dräger Pac® 7000 still responded very quickly (all tests within 1 minute). The time for the system to return to baseline was also quite long, taking over three hours (Sample 1**** was performed at the end of the day, and had only returned to 15 ppm at the 1.5 hour mark).

In addition to the results described above, the masses of each sample tested were monitored pre- and post-exposure in an attempt to determine the mass loss of propellant during each sample run. The results of these studies are shown in Table 11.

Dräger X-act® 5000 (with Tubes)
A positive response was observed when the Dräger X-act® 5000 (with Dräger-Tube®) was exposed to LMP-103S. The Dräger-Tubes® that were evaluated were the 5 – 600 ppm Ammonia Tube (Part # CH20501) and the 0.05 – 10% Ammonia Tube (Part # CH31901). The 0.05 – 10% was the primary Dräger-Tube® that was evaluated due to the volatile nature of the propellant and the very high readings of ammonia previously observed using the MultiRAE Lite multigas sensor evaluation. The results from these exposure tests are provided in Table 13.

Table 13. Results of Dräger X-act® 5000 (with Dräger-Tube®) Testing with LMP-103S.

	Dräger Tube	LMP-103S (ml)	Flow Rate (LPM)	Total Flow Time (min)	Final Reading	Total Volume Pulled (L)
Sample 1	10%	1	0.2	3:30	10%	0.7
Sample 2	10%	1	0.1	6:45	10%	0.645
Sample 3	10%	0.1	0.1	15:00	0.75%	1.5
Sample 4	600ppm	0.1	0.1	0:32	600	0.032

Initially the testing was performed with the Dräger X-act® 5000 pulling at 0.2 L/min for 15 minutes total; however, the tube became fully saturated within the first five minutes of the test. It was decided for the following two replicates to have the Dräger X-act® 5000 pulling at 0.1 L/min (lowest possible setting). As can be seen from Sample 2 in Table 13, even this did not prevent the 0.05 – 10% tube from becoming fully saturated within the 15 minute pull time (Figure 71). For the last sample using this Dräger-Tube®, the volume of propellant used was reduced from 1 ml to 0.1 ml. An additional experiment was conducted using the second highest capacity Dräger-Tube® available (5 – 600 ppm) under the same conditions as Sample 3 (0.1 L/min, 0.1 ml LMP-103S) in

an effort to validate the previous results; however, the comparatively low-maximum level for this Dräger-Tube® caused saturation to occur within the first minute of exposure.

Figure 71. Results from 0 – 10% Dräger-Tube® Evaluation (LMP-103S).

Prior to each test, controls were run where laboratory air was run through each tube for a period of 15 minutes using the same parameters as were to be used with the test. All controls showed no color change in the Dräger-Tubes®, indicating that the color change observed in the initial testing was due to the presence of LMP-103S.

In addition to the results described above, the masses of each sample tested were monitored pre- and post-exposure in an attempt to determine the mass loss of propellant during each sample run. The results of these studies are shown in Table 14.

Table 14. Monitoring of Mass Loss of Volatile Components from LMP-103S (Dräger Test).

	Sample 1	**Sample 2**
Mass, Empty Vial (g)	31.454	30.607
Mass, Pre-Exposure Vial (g)	32.649	31.796
Mass, Post-Exposure Vial (g)	32.539	31.689
Mass, Propellant (g)	1.195	1.189
Mass Lost (g)	0.11	0.107
Mass Lost (%)	9%	9%
Exposure Time (min)	9.5	9
Flow Rate (LPM)	0.2	0.1

The mass loss data shows that a significant portion of the sample (approximately 10%) is lost within 10 minutes of exposure to a gas flow. As a follow-up to this, a test was performed using the same aliquot of LMP-103S propellant consecutively on two separate Dräger-Tubes® to determine if the volatiles lost were significantly impacting the detection capabilities of the Dräger-Tubes® (and possibly the other ammonia-based sensors as well). Table 15 shows that there is a definite correlation between the loss of volatile components of the LMP-103S propellant and loss of sensitively in the ammonia Dräger-Tubes®. It required more than twice as long to duplicate the same concentration level.

Table 15. Comparison of LMP-103S after Consecutive Exposures.

	Dräger Tube	**LMP-103S (ml)**	**Flow Rate (LPM)**	**Total Flow Time (min)**	**Final Reading**	**Total Volume Pulled (L)**
New LMP-103S	10%	1	0.1	6:45	10%	0.645
Old LMP-103S	10%	1	0.1	14:00	10%	1.4

ADN/LMP-103S – Detection System

Due to the volatility of the LMP-103S, and the fact that ammonia is in fact a constituent of the propellant (3%-6%), it was decided to focus on the use of the COTS sensor systems for the detection system for ADN/LMP-103S. The detection system package consists of a combination of both an active and a passive COTS sensor. Figure 72 and Figure 73 show the detection kit and identifies the contents inside. The kit contains both the RAE Systems MultiRAE Lite and GasAlert Extreme Sensor. Attached to the outside of the kit is a 6-foot stainless steel collapsible wand, which is used with the MultiRAE Lite sensor to allow for remote sensing or when entering an unknown environment. Laboratory tests have shown that LMP-103S samples are detected by the wand within 15 seconds of exposure.

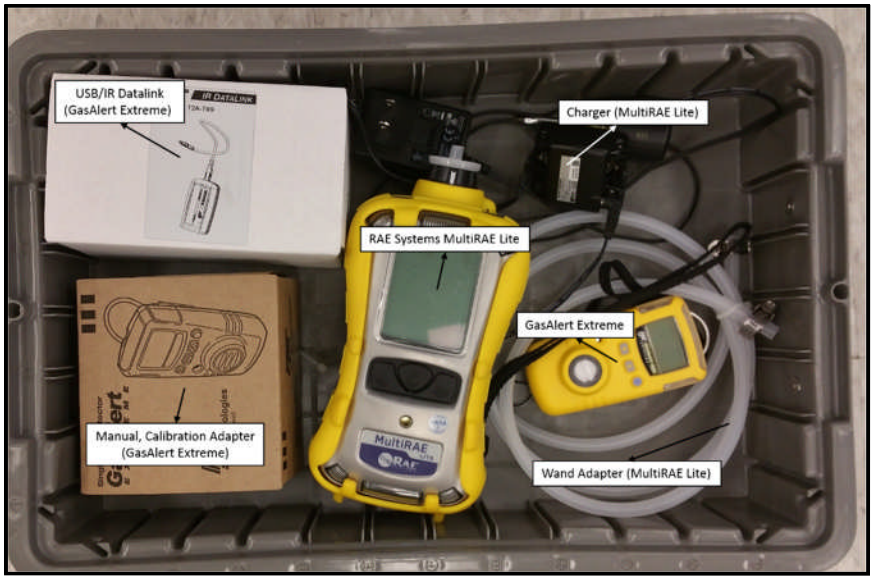


Figure 72. Interior of ADN/LMP-103S Kit.

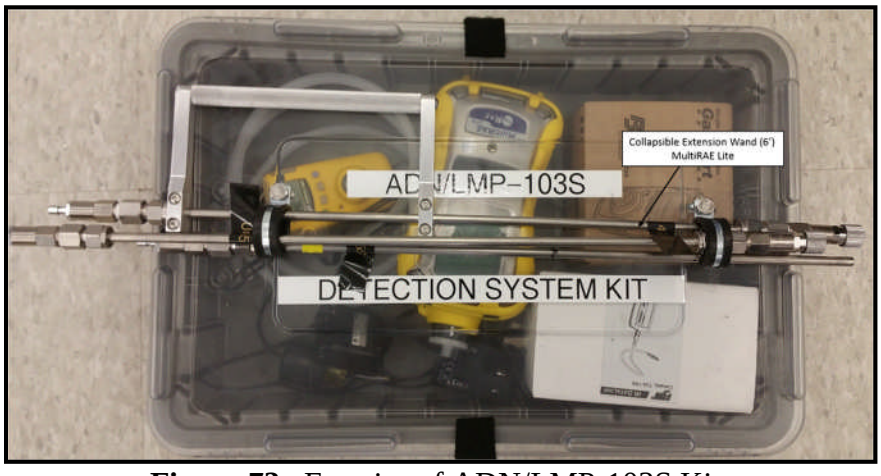


Figure 73. Exterior of ADN/LMP-103S Kit.

Summary and Recommendations

Several different techniques were evaluated as possible detection methods for the both hydroxylammonium nitrate (HAN) and ammonium dinitramide (ADN), which are two of the primary components of the "green" propellants AF-M315E and LMP-103S, respectively. The two techniques selected for the detection of these commodities were colorimetric analysis (AF-M315E) and gaseous-based COTS sensors (LMP-103S). The differences in the chosen analysis methods stems from the nearly non-existent vapor-pressure of the AF-M315E, which made the use of the COTS sensors not feasible.

An indicating absorbent detection system (Figure 70) for HAN/AF-M315E has been developed which is capable of both detecting (via a distinct color change) the presence of AF-M315E and helping to contain any spill/leak which has occurred. The detection system utilizes an indicator solution containing Methyl Red, which exhibits a distinct color change from red – yellow at a pH range of 4.5 – 6.5. The indicator solution is basified prior to use since AF-M315E has a pH of ~3.65. Testing shows that this system is not susceptible to false positives in the presence of water. The absorbent socks are prepared from commercially available, polystyrene-based chemical absorbent booms (Fisher Universal Spill Kit, PN # S47411) which are compatible with a wide range of chemicals (with the exception of hydrofluoric acid). These booms/socks are immersed within the prepared indicator solution, removed, allowed to dry, vacuum sealed (to prevent carbon dioxide absorption), and stored until needed. Additional unaltered booms are included for containment of a leak/spill once detection has occurred. Additionally, indicating chemical wipes are included in the detection system for detection of spills too small for detection using the sorbent socks. An instruction manual for the use of the HAN/AF-M315E detection system can be found in Appendix C.

Based on the results of this study, a detection system (Figure 72 and Figure 73) for ADN/LMP-103S has been developed which consists of a combination of two COTS sensors: the RAE Systems MultiRAE Lite and the GasAlert Extreme. The MultiRae Lite is an actively-pumped sensor equipped with three different sensors: 1) photoionization detector (PID) for volatile organic compound (VOC) detection, 2) catalytic bed for combustible gas detection, and 3) electrochemical sensor for ammonia detection. All three sensors detect the presence of the LMP-103S (due to extremely volatile nature of several of the components); however, it is recommended that the ammonia sensor be utilized as the primary sensor for this instrument (as this commodity is likely to have highest associated health hazards). This COTS unit has been modified by the addition of a 6-foot stainless steel sensor wand which allows the user real-time area monitoring of a remote area. The GasAlert Extreme, which is a passive, diffusion-based sensor system which is used for ammonia detection, is meant to be used in conjunction with the MultiRAE Lite. The GasAlert Extreme functions as a personal dosimeter badge for the user as it is designed to clip onto the outer clothing and functions as alert if the immediate environment has become hazardous. An instruction manual for the use of the AND/LMP-103S detection system can be found in Appendix D.

Appendix A – Safety Analysis

June 30, 2015

Safety Assessment for Personal Protective Equipment During the Handling of High Performance Green Propellants (LMP-103S and AF-M315E)

Charles Hughes, ESC HSO

Table of Contents

Section 1 - Executive Summary

1. Purpose:

The goal of this safety assessment is to review previous documents and air monitoring data to determine if the current Personal Protective Equipment (PPE) for handling High Performance Green Propellants (HPGP) in the laboratories is adequate.

2. Background

This analysis was performed as part of recent research activities: TO260 – "Green Propellant Infusion Mission (GPIM) Assay Analysis" and T0245 – "Familiarization and Detection of Green Monopropellants" in NASA/ESC Laboratories at the Kennedy Space Center involving the handling of LMP-103S and AF-M315E.

Ammonium dinitramide (ADN) and hydroxylammonium nitrate (HAN) are major components of two HPGP which will be used at KSC for processing in the next few years and will be used to test an F-16 Emergency Power Unit (EPU) through collaborations with Marshall Space Flight Center (MSFC). These are relatively safe replacements for hydrazine as a monopropellant; however, there are still precautions necessary when handling them. LMP-103S was developed by the Swedish Space Corporation (SSC), while AF-M315E was developed by the Air Force Research Laboratory (AFRL) to be a propellant. Orbital ATK is predominantly evaluating LMP-103S for future use, while Ball Aerospace was awarded a NASA Technology Demonstration Mission (TDM) to use AF-M315E as a monopropellant in a mission to be launched from KSC/Cape Canaveral Air Force Station (CCAFS) currently scheduled for 2016.

Section 2 – Analysis

Methodological Approach

In March 2012, the American Chemical Society (ACS) published a report: Creating Safety Cultures in Academic Institutions in response to a number of accidents involving chemicals in Academic Institutions. As part of the report, the ACS recommended a risk assessment process to identify, evaluate and mitigate hazards.

The figure below, drawn from the ACS report, illustrates the relationship between the most basic elements of the scientific process (represented by the circle) and the basic elements of the risk assessment process (in the corresponding boxes).

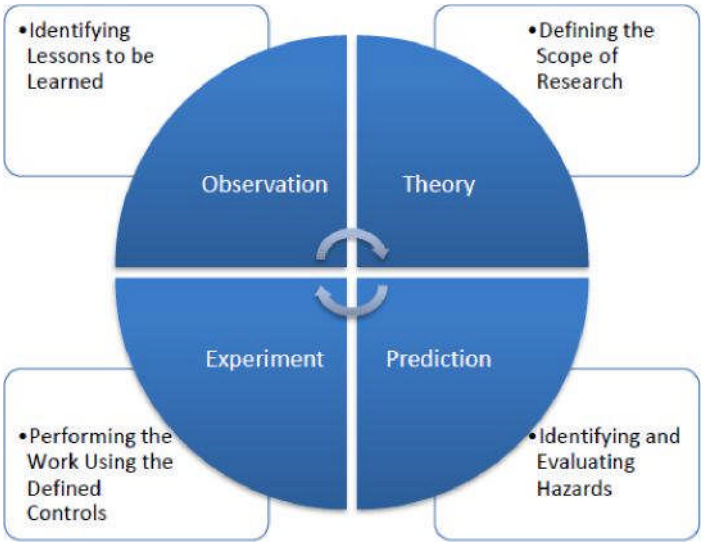


Figure 1: ACS Integration of Scientific Hazards Analysis with the Scientific Method

The risk assessment process requires consideration of the inherent physical and health hazard of the constituent or chemical, as well as the hazard posed by the processes/procedures/manipulations.

Portions of the ACS process were used as part of this Hazard Analysis and Risk Assessment for handling of HPGP.

Hazard Discussion:

The ACS process was used as part of this Safety Assessment for determining the appropriate PPE when handling HPGP (LMP-103S and AF-M315E) using the following criteria;

Defining the Scope of Research

- Ascertain published information on the reactivity and toxicity of the chemicals used or generated in the proposed experiment. For novel preparations or those having unstable reactants/products, determine appropriate safe approaches to carry out operations, such as running reactions on a small scale. Identify emergency procedures and equipment needed for this proposed work.

Identifying and Evaluating Hazards

- Hazards to the investigator and risks to the environment and the success of the experiment are identified and evaluated. Safety Data Sheets (SDS's) should be utilized for reagents, especially for new reagents.
- Routes of potential exposure are identified; these routes may include exposure to hazards through skin or inhalation but they may be other hazards that result from handling or processing chemicals, such as being hit by flying objects (from explosions), receiving cuts (preparation steps with sharp objects), or adverse contact with equipment (contact with moving parts, pinching, burns, pressure, or electrical shocks). Eliminating or minimizing potential routes of exposure is a critical component of hazards assessment and management.
- A questioning or challenging attitude is welcomed to ensure the best analysis possible.
- Potential, credible accident or event scenarios are hypothesized and discussed.
- Controls are identified that will eliminate the hazard, control it, or protect the investigator in the event the thinkable or unthinkable happens.
- Regulatory requirements, which are often hazards-based, are identified.
- Tools are used to facilitate a thorough review and to lend a reasonable consistency across the organization. These tools may take a number of forms (for example, checklists, what-if analyses, barrier analyses, failure modes analyses, control banding, and so forth).
- While the experiment may be completed by an individual, this investigator should call upon others to help or advise with the process, deferring to those who may have more experience. This could be a senior investigator, a health and safety professional, or another student. The expertise of others is valued.

Performing the Work with the Identified Controls and Protective Measures in Place

- Confirm that the agreed-upon controls and protective measures are in place and functioning before the work begins. This includes a conscious evaluation of the skills and capabilities of the individuals who will complete the work.

- Conduct the experiment with the identified controls in place. If unexpected conditions are found, the investigator pauses and ensures the scope of the work or the necessary controls have not changed significantly enough to warrant additional analysis.
- Question or remind investigators about their controls, especially if they suspect a necessary control is not in place or is not being used.
- Seek to avoid at-risk behavior in your work and help others recognize risky behavior in their work, as needed. At-risk behavior, a leading cause of incidents, results when personnel bypass safe practices to reduce the time or level of effort. Examples of at-risk behavior include: not wearing personal protective equipment; not using hoods; skipping safety plans or steps; poor housekeeping; and scaling up a reaction without adequate planning. Prevention of at-risk behavior is a key component of safety.

Identifying Lessons to be Learned

- The investigator approaches the end of an experiment the same way he or she began and asks even more questions. For example, "Did a hazard manifest itself that was not previously identified? Did a control perform the way it was expected to or do I need another option if I repeat this experiment? Did something go really well that others can learn from? Did I recognize any close calls that can serve as a warning for identifying areas of needed improvement?
- Hazards analysis documents are continually improving and not something that are created once and never looked at again.
- If an incident occurs, students and investigators could learn how to conduct investigations and root cause analyses, and then communicate the lessons learned to others.

The laboratory is a unique environment. Hazard identification, hazard assessment, and hazard management collectively known as hazards analysis in laboratory operations (including research) are critical skills that need to be part of all personnel working in a laboratory. Learning how to prepare for emergencies is also a critical skill. It is important to remember that some hazards may not have been identified, assessed, or managed correctly when the laboratory operation was designed. Safety is an integral part of all laboratory operations but it requires that the laboratory worker consider this every time they start work. In this way, the process of hazards analysis becomes an integral part of the laboratory process, just like the scientific method.

Section 3.0 Assessment

The results of the four elements from the ACS risk assessment process are as follows;

Theory

In support of NASA's research into research involving HPGP LMP-103S and AF-M315E, ESC personnel provide support during TO260 – "Green Propellant Infusion

Mission (GPIM) Assay Analysis" and T0245- "Familiarization and Detection of Green Monopropellants" activities.

Prediction

The hazards identified and evaluated as part of this assessment include;

- Toxicity

Characteristic	**Hydrazine**	**HAN 82%**	**AF-M315E[1]**	**ADN[2]**	**Methanol[2]**	**NH3 gas[2]**
LD50 (rat), mg/kg	60	882	550	832	5628	350
Dermal (rabbit), irritant	Corrosive	Slight	Slight	Slight	Yes	Yes
Dermal (rabbit), sensitizing	Yes	No[3]	No[3]	No[4]	No	No
Genotoxicity (Ames)	Positive	Negative	Positive	4 Neg 1 Pos	Negative	-

Notes
[1] AF-M315E is composed of HAN, hydroxyethylhydrazinium nitrate (HEHN) and water
[2] LMP-103S is composed of ADN, methanol, ammonia (dissolved) and water
[3] Sensitization was reported in one worker (human subject) exposed to HAN in 1991
[4] Lymph node assay (mouse)

Table Excerpted From LMP-103S (ECAPS Green Monopropellant) Properties, Hazards and Handling Presentation by Stephen F. Palopoli, Ph.D.

- Personal Protective Equipment:
  - Eye / Face Protection
  - Protective Clothing (Flame Retardant)
  - Protective Gloves
  - Respiratory Protection (When no local ventilation is available)

Experiment

Current HPGP activities are performed in accordance with ALC-ACL-003, the Applied Chemistry Authorized Laboratory Capability for Analytical Instrumentation. All planned activities are performed in accordance with the Applied Chemistry Lab Management Plan.

Observation

The HPGP research activities performed in the Applied Chemistry Lab per ALC-ACL-001, "Vapor Generation (Includes Hypergolic and/or Organic Vapors)" and ALC-ACL-004 – "General Laboratory Chemistry" have been adequate in mitigating the exposure to HPGP during laboratory operations.

Section 4 - Conclusion

Findings of this Hazard Analysis and Risk Assessment indicate that current mitigations used by laboratory personnel is adequate for hazards associated with the handling of HPGP in a laboratory setting, which includes;

- Flame retardant lab coat or coveralls
- Nitrile rubber gloves
- Safety glasses with side shields covered by a face shield
- Work performed in a fume hood

These findings are consistent with the PPE requirements required by Alliant Techsystems Proprietary (ATK).

The handling of HPGP outside the controlled laboratory environment are not included in this assessment due to the potential variability in the handling techniques, work environment, proposed research and available mitigations. This type of research or testing should be assessed independently to ensure mitigations are adequate for the work being performed.

Appendix B – Headspace Analysis Report

February 4, 2015

TO 245: Green Propellant Headspace Analysis

Reporting Authors: Jan Surma & Janelle Coutts, Ph.D.
Engineering Services Contract
Chemical & Biological Sciences
Kennedy Space Center, FL

Analysis System & Conditions:

GC System:	Thermo Scientific Trace GC (ECN 2295564)
Column:	Restek RTX-1, 30 m x 0.53 mm x 5 µm df (S/N: 1256095)
Oven Program:	Initial temperature of 30°C, ramped to 80°C at a rate of 5°C/min then to 200°C at a rate of 10°C/min, and held at the final temperature for 5 minutes.
Inlet:	LMP-103S Analysis: Split injection at 150°C; split time of 1 minute followed by a split flow of 10 mL/min with constant septum purge. AF-M315E Analysis: Splitless injection at 150°C with constant septum purge.
Carrier:	Helium, Constant Flow Setting, 5.0 mL/min
Detectors:	Photoionization Detector (PID): 10.6 eV lamp, Base temperature of 300°C, makeup nitrogen flow of 5 mL/min, sheath gas helium flow of 30 mL/min. Flame Ionization Detector (FID): Base temperature of 250°C, air flow of 350 mL/min, hydrogen flow of 35 mL/min, makeup nitrogen flow of 30 mL/min.
Injection Vol.	10 µL for LMP-103S samples, 100 µL for AF-M315E (100-µL Hamilton 1710 SL syringe, #100-4)

Samples Analyzed:

Six 2-mL, amber autosampler vials were filled with 0.25 mL of a designated propellant and sealed. Equilibriation was allowed to occur for 24 hours for all samples at room temperature. After 24 hours, headspace samples for room temperature were analyzed in triplicate via GC-PID-FID (method above). The three remaining samples were equilibriated at 50°C in a Pierce Reacti-Therm unit and analyzed via GC-PID-FID.

Results & Discussion:

LMP-103S Headspace Analysis Results

The only major constituents found in both the room temperature and 50°C headspace samples for the LMP-103S propellant were ammonia and methanol. Ammonia was detected via PID and methanol via FID. Table 1 shows the approximate concentrations for these two constituents found in all samples. All three replicates for the room temperature headspace samples showed equivalent, reproducible amounts of both constituents (Figure 1 and Figure 2).

Table 1: Approximate Concentrations for Methanol and Ammonia in LMP-103S

Sample	Methanol (ppm)	Ammonia (ppm)
Room Temperature Samples		
LMP-103S Vial #4	30,000	42,000
LMP-103S Vial #5	42,000	46,000
LMP-103S Vial #6	40,000	45,000
50°C Samples		
LMP-103S Vial #1	Saturated	40,000
LMP-103S Vial #2	Saturated	10,500
LMP-103S Vial #3	Saturated	N/A

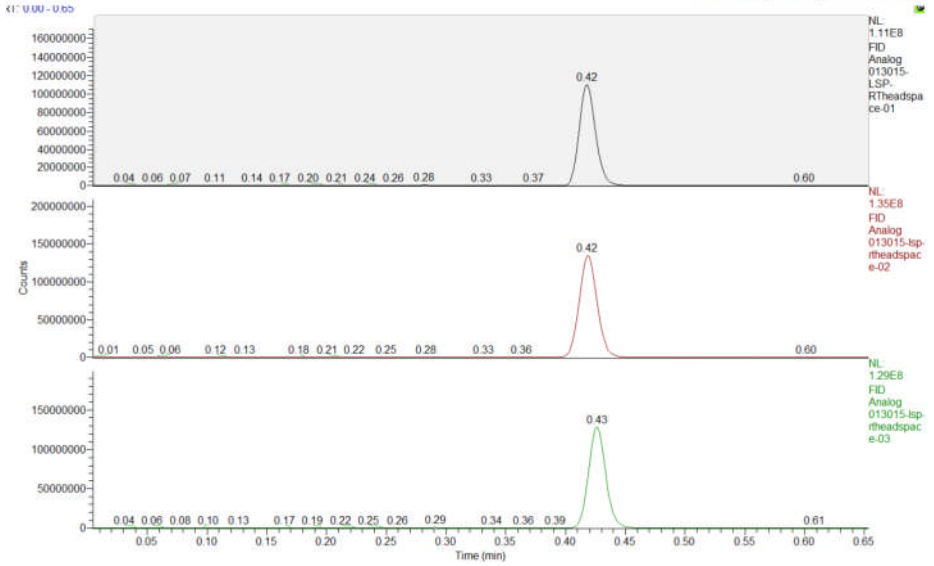


Figure 1: Chromatogram (FID) for Room Temperature LMP-103S Headspace. Chromatograms are for Vials 4, 5, and 6 (Top to Bottom), respectively.

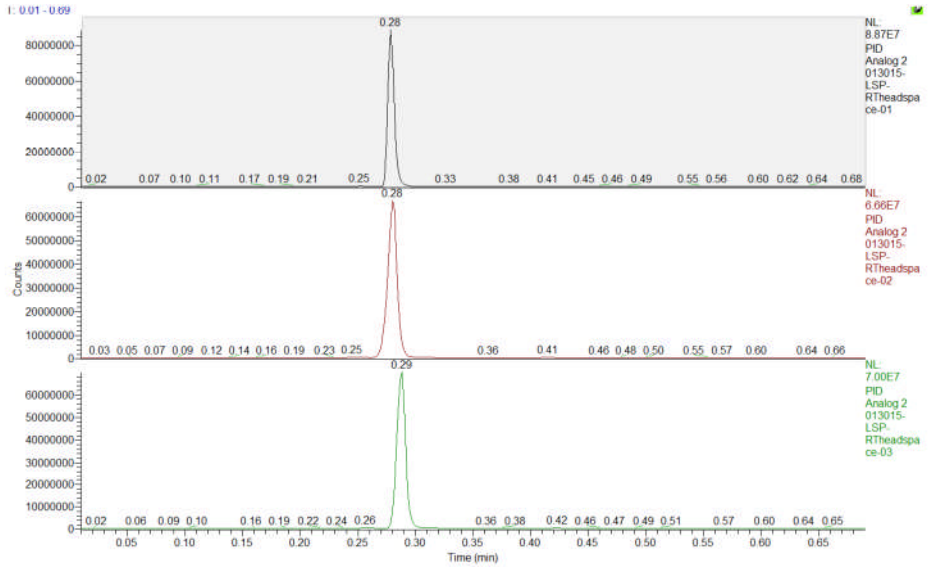


Figure 2: Chromatogram (PID) for Room Temperature LMP-103S Headspace. Chromatograms are for Vials 4, 5, and 6 (Top to Bottom), respectively.

The 50°C headspace samples were taken after 4.5 hours (Vial 1) or 6 hours (Vials 2 and 3) of equilibration. Time differences in the sample analysis time arose due to the Vial 1 sample saturating both detectors and alterations to the method to correct with varied split ratios and injection volumes. At the maximum split ratio and lowest injection volume (100:1, 10-µL), the amount of methanol still saturated the FID (Figure 3), but the ammonia peak was resolved for the PID (Figure 4). For Vial 2 FID chromatogram (Figure 3), the appearance of two peaks is a result of over-loading the column/saturating the detector, and is likely not a second compound eluting. It should also be noted for the Figure 3 chromatograms that a peak at ~0.60 min was present in all samples that was not detected in any of the room temperature samples; the identity of this compound is not known at this time. For Vial 3 PID chromatogram (Figure 4), it appears to possibly be another compound eluting, as you can see smaller peaks at 0.25 min in Vial 1 and 2 chromatograms as well. At this time, there is no information on what compound the peak at 0.25 min might be. All concentrations presented in Table 1 are based on calibrations using currently available standards; in some cases, the maximum available concentration of available standards was below that needed for a calibration capturing the range of peak areas detected. Thus, the best estimate, assuming a full linear dynamic range was used to gain approximate amounts.

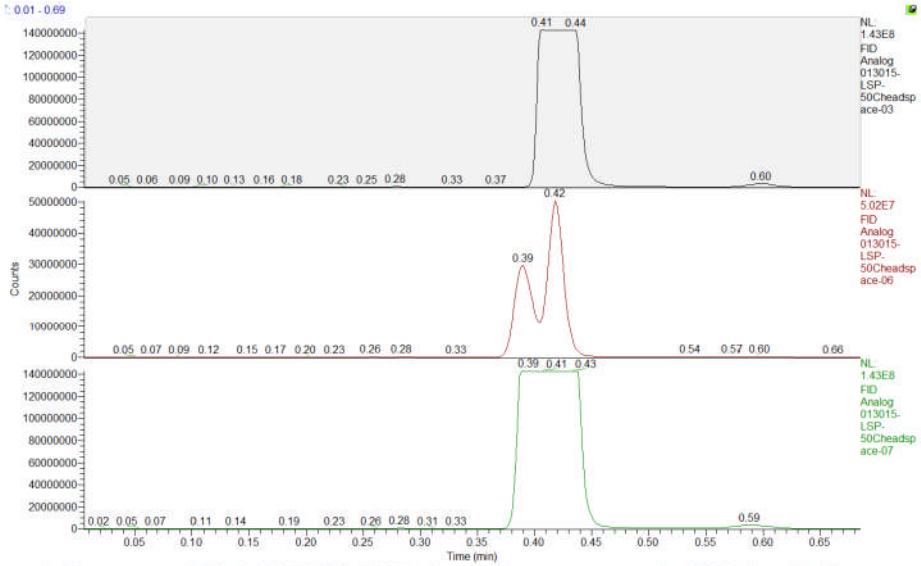


Figure 3: Chromatogram (FID) for 50°C LMP-103S Headspace. Chromatograms are for Vials 1, 2, and 3 (Top to Bottom), respectively.

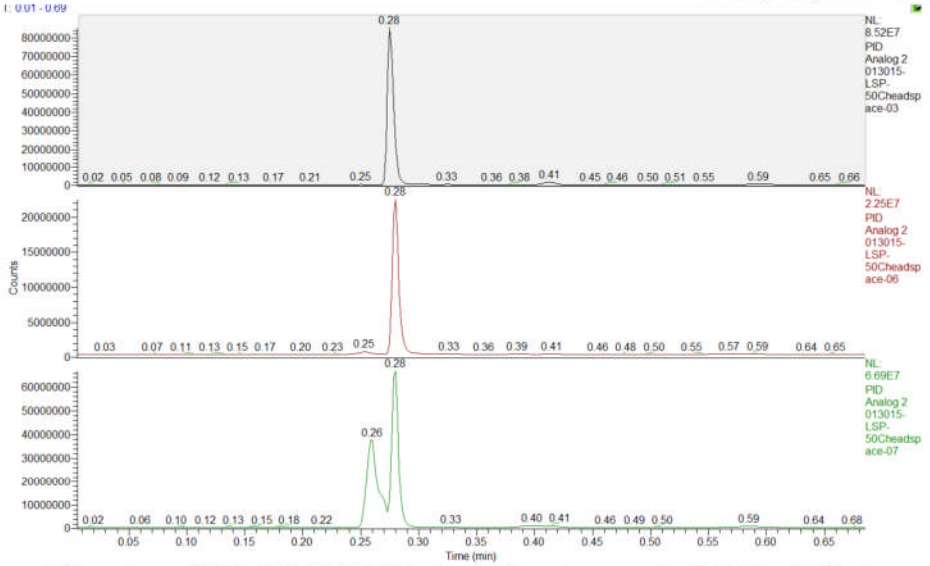


Figure 4: Chromatogram (PID) for 50°C LMP-103S Headspace. Chromatograms are for Vials 1, 2, and 3 (Top to Bottom), respectively.

AF-M315E Headspace Analysis Results

The 24-hour equilibrated room temperature headspace samples did not show any major off-gassing from the AF0M315E propellant (Figure 5 and Figure 6). Vial 1 and 2 samples was run at a high split ratio as previously used for the LMP-103S analysis. Since both chromatograms showed no compounds present, the injection type was changed to splitless to allow more sample introduction to the column for Vial 3 and for the 50°C samples. A small peak at ~16.05 minutes was present in the FID chromatogram after changing to the splitless injection, but the identity of this compound is unknown.

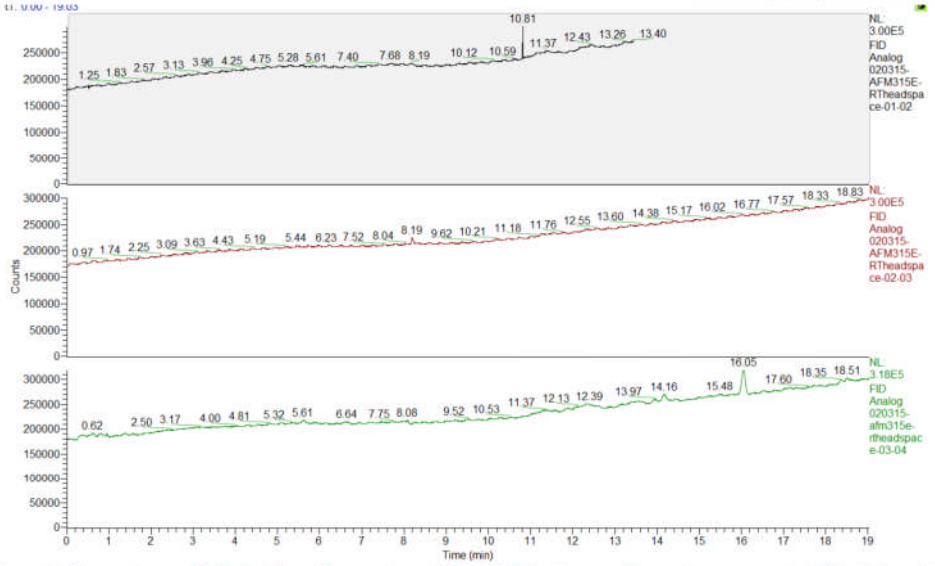


Figure 5: Chromatogram (FID) for Room Temperature AF-M315E Headspace. Chromatograms are for Vials 1, 2, and 3 (Top to Bottom), respectively.

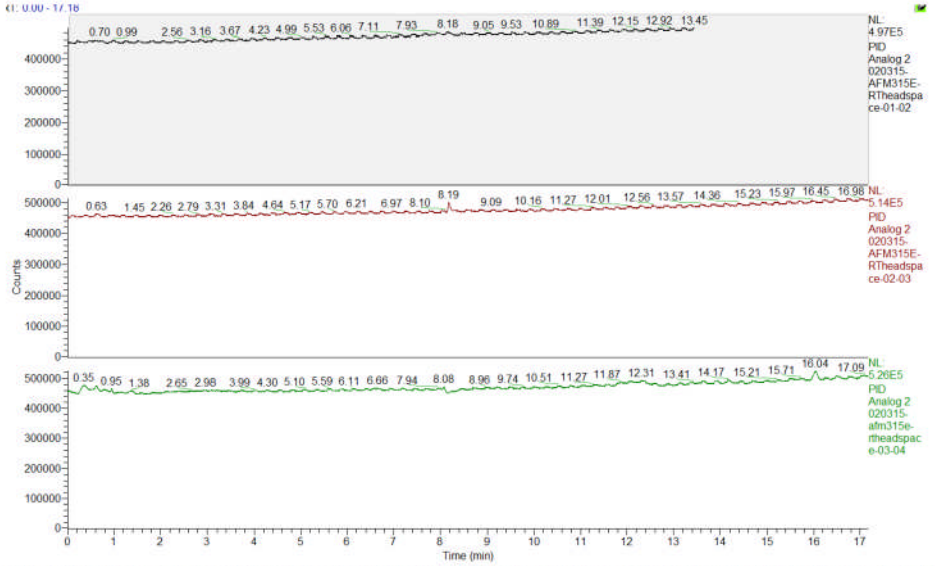


Figure 6: Chromatogram (PID) for Room Temperature AF-M315E Headspace. Chromatograms are for Vials 1, 2, and 3 (Top to Bottom), respectively.

The 50°C headspace samples were taken after ~8 hours of equilibration. Upon heating for this period of time, several peaks were detected by both the FID and PID (Figure 7 and Figure 8) for the AF-M315E. The FID chromatograms (Figure 7) show approximately seven resolved peaks, mostly within the first 1.5 minutes of the GC run, and one also present at ~19.65 minutes. The retention time (RT) of 0.45 minutes could be methanol as it corresponds to the RT seen in the LMP-103S samples for methanol. Most of the sample peaks were also detected via PID, with a more sensitive response. The identification of these constituents remains unknown; if desired, this experiment can be repeated and analyzed via GC-MS in an attempt to gain information on these compounds.

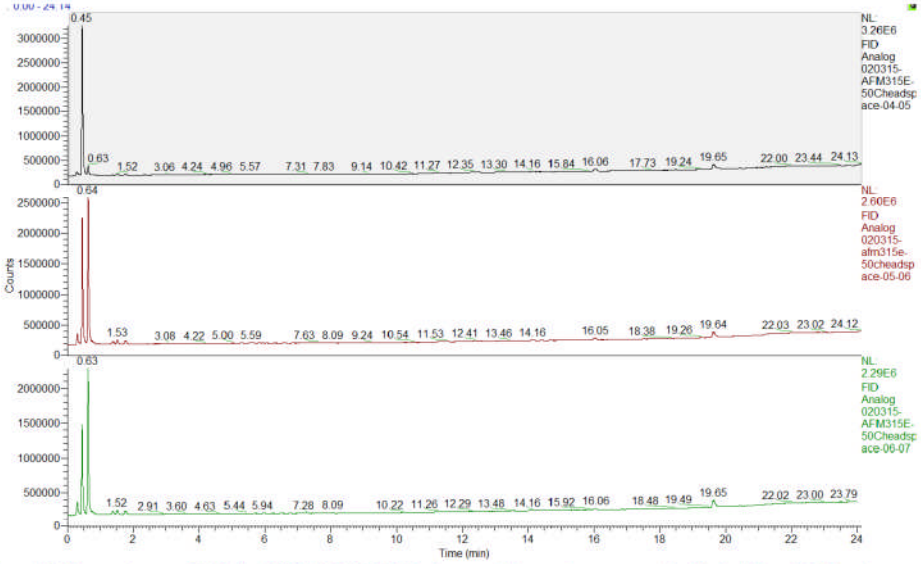


Figure 7: Chromatogram (FID) for 50°C AF-M315E Headspace. Chromatograms are for Vials 4, 5, and 6 (Top to Bottom), respectively.

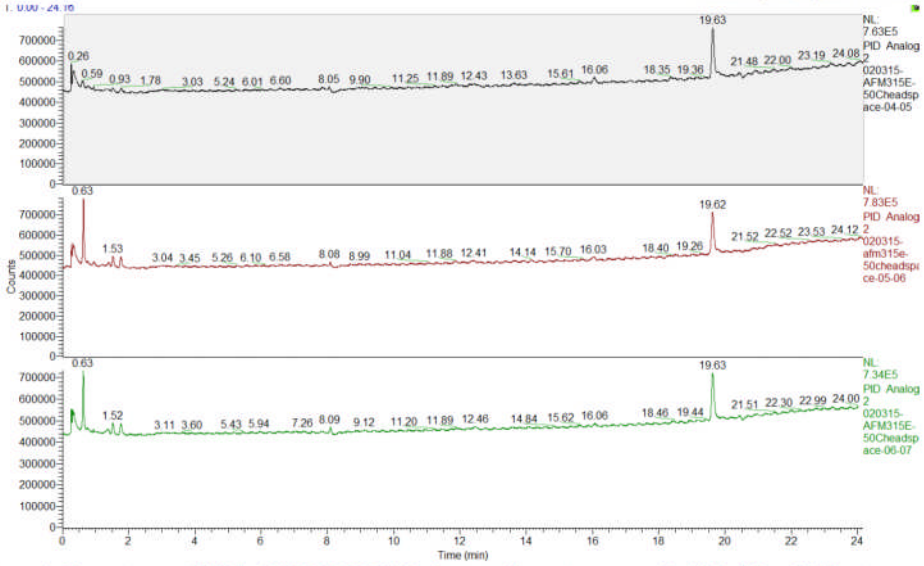


Figure 8: Chromatogram (PID) for 50°C AF-M315E Headspace. Chromatograms are for Vials 4, 5, and 6 (Top to Bottom), respectively.

Appendix C – HAN/AF-M315E Detection System Instruction Manual

Indicating Wipes

Don appropriate personal protective equipment (PPE).

- Safety glasses with side shields covered by a face shield
- Nitrile rubber gloves
- Flame retardant lab coat or coveralls

Wipe the surface of interest with the indicating wipe. If no color change is observed, the surface is to be considered "clean". The definition of clean in this case is that there is no observable trace of HAN/AF-M315E present on the surface. If a color is observed, then the surface is to be considered contaminated. Contaminated wipes are to be disposed of by placing them in a sealable plastic bag and treated as hazardous waste.

Indicating Absorbent Socks

Don appropriate personal protective equipment (PPE).

- Safety glasses with side shields covered by a face shield
- Nitrile rubber gloves
- Flame retardant lab coat or coveralls

Place the indicating absorbent socks in an area of interest (where a suspected leak has occurred or could occur). If no color change is observed, the area is to be considered "clean". The definition of clean in this case is that there is no observable liquid HAN/AF-M315E present in the area of interest. If a color is observed, then the area of interest is to be considered contaminated. Depending on the degree of color change (or the volume of the spill), additional absorbent socks (either indicating or non-indicating) can be deployed. After cleanup, an indicating absorbent sock can be deployed to verify that liquid HAN/AF-M315E is no longer present (indicating absorbent sock does not change color). Contaminated absorbent socks are to be disposed of by placing them in a sealable plastic bag and treated as hazardous waste.

Appendix D – ADN/LMP-103S Detection System Instruction Manual

Before entering the area of interest:

- Attach the MultiRAE Lite sensor sample line to the MultiRAE Lite sensor unit using the provide hose clamp
- Assemble the stainless steel sampling wand (Figure 1)

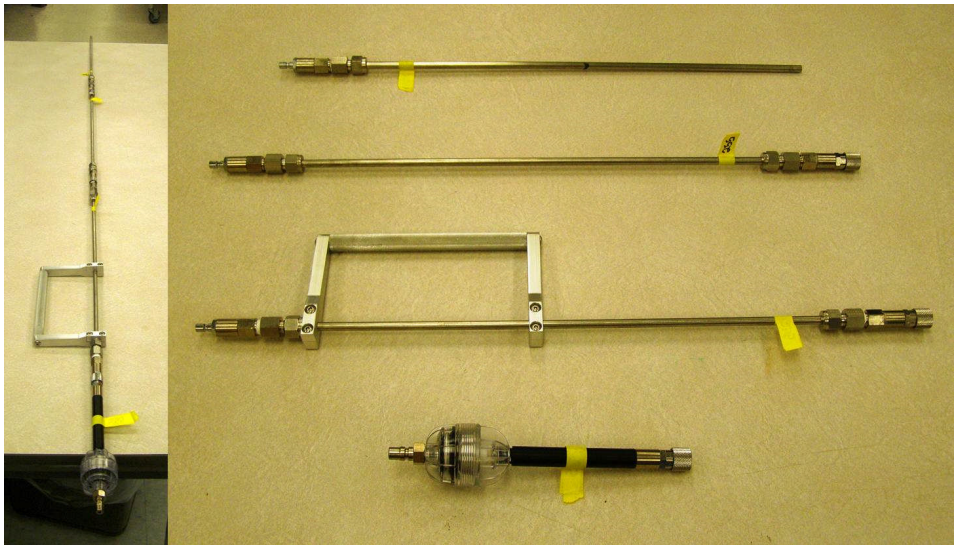


Figure 1. Stainless steel sampling wand.

  - The stainless steel sampling wand is comprised of 3 individual sections of stainless steel tubing that are connected together using quick disconnects
    - Section 1 has a connection for the sample line connected to the active sensor and a handle, as well as one quick disconnect
    - Section 2 has two quick disconnects (one on each end)
    - Section three is the sampling section and has one quick disconnect
- Attach the stainless steel sampling wand to the MultiRAE Lite sensor sample line using the provided hose clamp
- Power on the MultiRAE Lite sensor unit and allow it to equilibrate for at least 10 minutes
- Don a flame retardant lab coat or coveralls
- Don the GasAlert Extreme portable ammonia gas detector by hanging it around the neck or attaching it to the outer area of the lab coat or coveralls
- Power on the GasAlert Extreme unit and allow it to equilibrate for at least 10 minutes

Don the remaining personal protective equipment (PPE).

- Safety glasses with side shields with half-face respirator equipped with an organic cartridge (alternative – full-face respirator equipped with an organic cartridge)
- Nitrile rubber gloves

Enter the area of interest and monitor the response of the MultiRAE Lite and GasAlert Extreme sensor units. If ADN/LMP-103S is present, all three sensors (catalytic bed, ammonia, and PID)

of the MultiRAE Lite sensor unit will respond. Additionally, the GasAlert Extreme will respond if ADN/LMP-103S is present.

In testing performed in the Applied Chemistry Laboratory at KSC, it was shown that the ammonia sensor of the MultiRAE Lite sensor unit saturated within one minute in the presence of ADN/LMP-103S. The GasAlert Extreme responded within 15 seconds in the presence of ADN/LMP-103S. It should be noted that the MultiRAE Lite and GasAlert Extreme sensor units only show that ADN/LMP-103S is present and do not provide the concentration of ADN/LMP-103S present. After sampling, it is recommended that the units be allowed to return to baseline (0 values for all sensors) before using the units for additional sampling.