Development of Sensing Techniques for Weaponry Health Monitoring

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ABSTRACT

Due to the costliness of destructive evaluation methods for assessing the aging and shelf-life of missile and rocket components, the identification of nondestructive evaluation methods has become increasingly important to the Army. Verifying that there is a sufficient concentration of stabilizer is a dependable indicator that the missile's double-based solid propellant is viable. The research outlined in this paper summarizes the Army Aviation and Missile Research, Development, & Engineering Center's (AMRDEC's) comparative use of nanoporous membranes, carbon nanotubes, and optical spectroscopic configured sensing techniques for detecting degradation in rocket motor propellant. The first sensing technique utilizes a gas collecting chamber consisting of nanoporous structures that trap the smaller solid propellant particles for measurement by a gas analysis device. In collaboration with NASA-Ames, sensing methods are developed that utilize functionalized single-walled carbon nanotubes as the key sensing element. The optical spectroscopic sensing method is based on a unique light collecting optical fiber system designed to detect the concentration of the propellant stabilizer. Experimental setups, laboratory results, and overall effectiveness of each technique are presented in this paper. Expectations are for the three sensing mechanisms to provide nondestructive evaluation methods that will offer cost-savings and improved weaponry health monitoring.

1. INTRODUCTION

It is common knowledge that (over a period of time) the chemical, electrical, and mechanical properties of missiles and rockets can change, degrade, and eventually result in the units becoming unusable. Throughout the life cycle of military armaments, weaponry health surveillances are implemented in order to evaluate the properties, characteristics, and performance capabilities of the hardware. The functionality of missiles and rockets are often evaluated by being fired or decomposed at routine time-frames after manufacturing and after prolonged storage. It is extremely costly to utilize destructive testing for determining long-term rocket motor aging and shelf-life

The main chemical compositions of solid propellant include nitrate (NO_2), carbon (C) and sulfur (S). During long-term (e.g., years of) storage of rockets/missiles, the compositions of the propellant can change due to the chemical reactions among the propellant ingredients, as well as the reaction with the ambient environment (e.g., O_2). Degradations associated with the propellant may include depletion of propellant stabilizer, materials cracking, and material/inert surface de-bonding. In order to ensure a successful firing of the rocket/missile, it is critical to be able to monitor the status (i.e., health) of the propellant and ensure proper propellant composition at the time of use by the warfighter. The optimal sensing system should be capable of nondestructively evaluating propellant degradation, rocket motor off-gassing, and measure (in real-time) the current percentage of propellant stabilizer.

Based on the fact that double-base propellants have minimum smoke signature and low manufacturing cost, these propellants [containing nitrocellulose (NC) and nitroglycerin (NG)] are widely used in many missile systems (such as Hydra 70 rocket systems aboard Apache helicopters). However, due to the slow chemical reaction between the stabilizers [e.g., 1,2,4-Butanetriol trinitrate (BTTN), 2-Methyl-4-nitroaniline (MNA)] and NOx released by NC and NG, the stabilizers are gradually depleted (the so called aging effect). Once the concentration of stabilizer is below a certain threshold level (e.g., 0.5%), the propellant is no longer safe to use. Thus, it is critical to monitor the aging effect of double base propellants.

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The US Army AMRDEC is continuously investigating methods to assess the degradation of the solid propellant that is used in rocket motors [1, 2]. Innovative methods to nondestructively evaluate the energetic materials that make up rocket motor propellant are of great interest to the Army and researchers at the AMRDEC. The researchers are working to subsequently develop a sensing system that can partially become a lab-on-a-chip component. The resulting systems can be deployed across a wide spectrum of hardware platforms for environmental monitoring and ensuing integration into weaponry health monitoring devices. The overall program can be cost-savings to the Army while providing a timely approach to enhance the Army's methodologies for measuring both propellant off-gassing and stabilizer depletion. Expectations are for the resulting sensor system to enhance the warfighters' ability to simultaneously detect a greater variety of analytes.

2. NANOPOROUS MEMBRANE SENSORS

The sensing technique described in this section utilizes a nanoporous alumina membrane as the filtering component of a sensing device that detects gases generated during the degradation of the solid rocket propellant. The nanoporous alumina membrane not only filters the gas molecules, but can accumulate them for estimating the life of propellant's stabilizer. During the propellant's degradation process, gases such as CO, CO_2, NO, NO_2, and N_2O are released, so the sensing method must be able to distinguish between the several molecules present; because, only some of the molecules are indicators of the propellant's health. The rate of evolution of N_2O, for example, is a direct indicator of the available amount of stabilizer that remains in the propellant. Figure **1** shows the production of gas before and after the stabilizer is depleted; the time scale is on the order of years [1, 2]. As N_2O is generated by the degrading rocket propellant, the stabilizer binds to the N_2O such that the N_2O is neutralized; however, once the stabilizer is depleted the amount of N_2O increases exponentially.

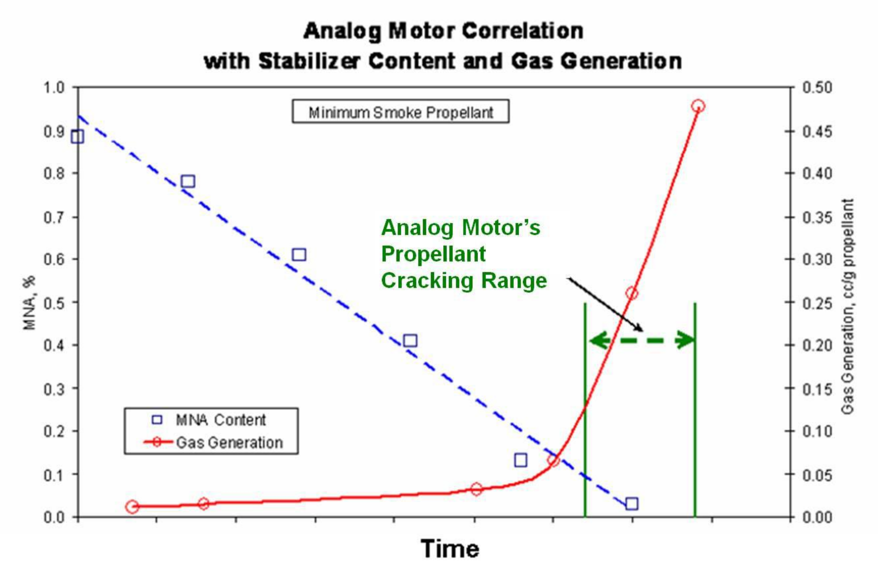


Figure 1. The production of gas from a degrading propellant is shown in relationship to the depletion of a stabilizer like MNA. The time frame is on the order of years. It can be seen that after the cross-over gas generation increases exponentially since the stabilizer is nearly depleted.

The gas sensor developed uses a nanoporous membrane to trap particles from rocket motor propellants. The average pore size in the nanoporous alumina is ~250 nm, which was verified by SEM (Figure 2) [3]. The nanoporous membrane is able to trap particles that are larger than the pores while smaller gas particles can pass through. The experimental setup shown in Figure 3(a) simulates the gases passing from the motor through the nanoporous membrane. The mechanism for filling the gas collecting chamber is the micro pump connected to the gas sensor such that the ambient air is pumped out of the gas collecting chamber, which forcibly brings gas through the nanoporous membrane

[Figure 3(b)]. The nanoporous membrane filters the gases travelling from the tubular chamber into the gas collecting chamber when the ambient air is pumped from the gas collecting chamber by means of a micro pump [Figure 3(a)]. Furthermore, the micro pump can blow inert gas (e.g., argon, helium, neon, krypton, xenon, radon, sulfur hexafluoride, nitrogen, and combinations thereof) into the gas collecting chamber and through the nanoporous membrane to flush the accumulated particles. As the ambient air is pumped out of the gas collecting chamber, gas from the solid propellant can be channeled to the gas analysis device with the help of a baffle by reducing the pressure of the chamber (via a micro pump) when the valves are open. In addition, there is a gas analysis device (e.g. Fourier Transform Infrared gas spectrometer) connected to the gas collecting chamber to measure the types and concentration levels of gases that travel through the nanoporous membrane and to collect in the gas chamber. Gas sensors are used to measure the concentrations of the gases within the chamber. Several different types of gas sensors can be employed (including the one based on IR absorption spectrum and/or chemical reductions).

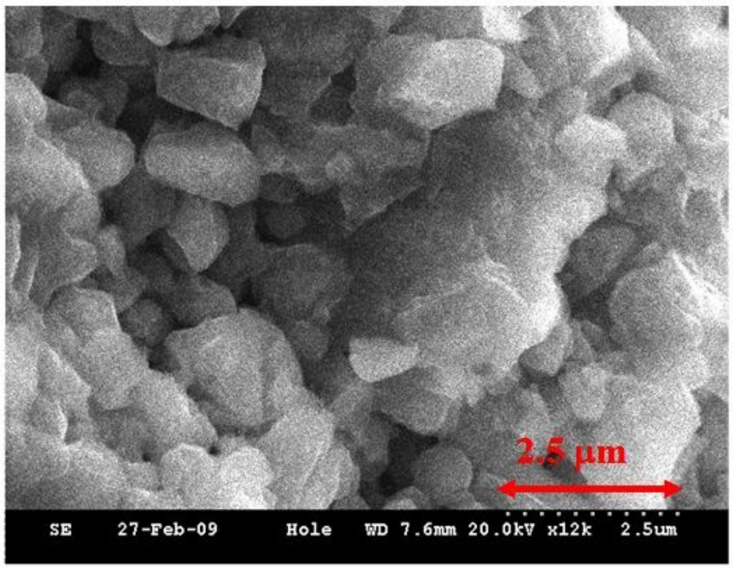
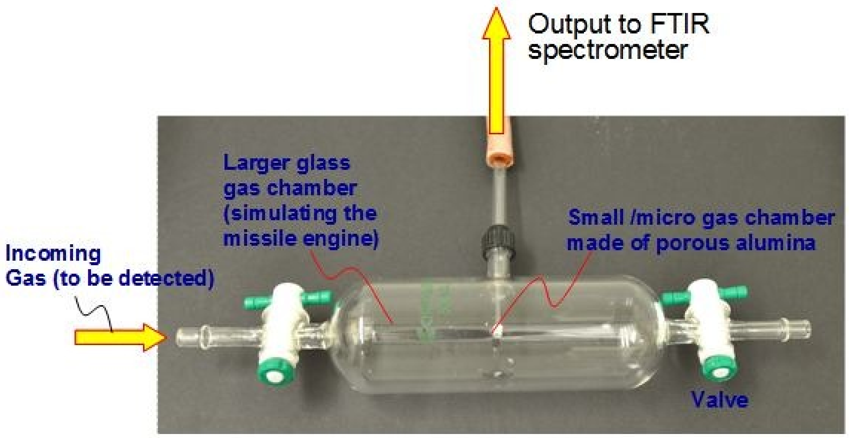


Figure 2. SEM image of nanoporous alumina membrane. The average pore size is ~250 nm.

In order to test the gas sensor concept, a gas mixture is allowed to flow into the chamber and is collected by the nanoporous membrane for analysis. Two types of related, less toxic gases (CO_2 and N_2O) were tested. Figure 4 shows the experimentally measured IR absorption spectrum displayed by the Fourier Transform Infrared (FTIR) spectrometer, which clearly shows major IR absorption peaks for both gases. These experimental results demonstrated the feasibility of the nanoporous alumina membrane sensor approach. In order to verify that detection can be achieved at the required level of sensitivity, the concentration of N_2O gas of the larger chamber was gradually reduced to 1 ppm. A Bacharach's trace gas analyzer was used to monitor the concentration of N_2O in the larger gas chamber. Afterwards, the IR absorption level associated with the small gas chamber was measured, as shown in Figure 5. Absorption peaks for N_2O could still be clearly observed, which confirms the ppm level of sensitivity and selectivity.



(a)

(b)

Figure 3. (a) Experimental setup for testing the nanoporous membrane. (b) The nanoporous alumina membrane.

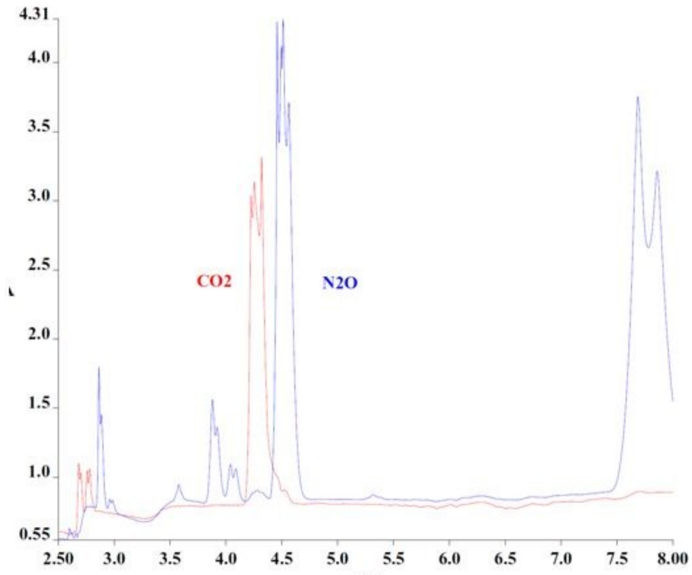


Figure 4. Experimentally measured absorption spectrum of CO_2 and N_2O.

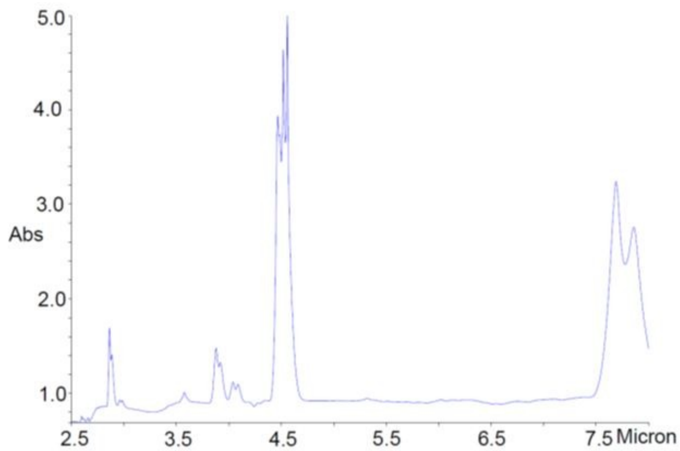


Figure 5. Experimentally measured absorption spectrum N_2O at 1 ppm.

3. CARBON NANOTUBE SENSORS

The sensing technique described in this section utilizes carbon nanotubes' electrical characteristics to detect the presence of gas molecules. Carbon nanotubes have been studied for use in sensor applications [4-6]. The gas particles that interact with the CNT cause a charge transfer which changes the electrical resistance [4]. The viability of propellant can be detected based on changes in electrical resistance in the sensor. Multi-channel single-walled carbon nanotubes (SWCNT) sensor arrays, originally developed by researchers from the National Aeronautics and Space Administration (NASA) Ames Research Center (ARC), have been used as the baseline sensor for AMRDEC's propellant degradation research [7,8]. The SWCNT sensor array [Figure **6**. (a) Multi-channel sensor array (NASA-AMES)Figure 6(a)], has approximately 32 individually functionalized CNT sensor elements for simultaneously sensing up to 32 different analytes or targeted chemical agents, such as including propellant off-gassing.

(a) (b)

Figure 6. (a) Multi-channel sensor array (NASA-AMES) made with (b) interdigitated electrodes

The sensors developed detect gases based on changes in the electrical properties of CNTs. Four sensors were fabricated for testing (Table 1). The sensors were a polymer composite using CNTs as the filler material. The substrates used for the sensors were steel and foam; the baseline resistances were measured for each sensor. The differences in resistance are a combination of resistance at the interfaces of the CNTs and within the polymer, which is an electrically insulating material. The carbon nanotubes are depicted in Figure 7 as the randomly shaped particle dispersed across gold electrodes (the dark gray area). The carbon nanotube-based chemical sensor concept consists of the purified SWCNT on the interdigitated electrode, which was fabricated using photolithography.

Table 1. Characteristics of CNT Sensors

	Sensor 1	Sensor 2	Sensor 3	Sensor 4
Substrate	Steel	Steel	Steel	Foam
CNT mass	1.53 g	1.8 g	0.5 g	1.8 g
Epoxy mass	10.00 g	10.16 g	1.20 g	10.16 g
Hardener mass	9.975 g	10.010 g	1.200 g	10.010 g
Baseline resistance	1.55 kΩ	890 kΩ	2.60 kΩ	298 kΩ

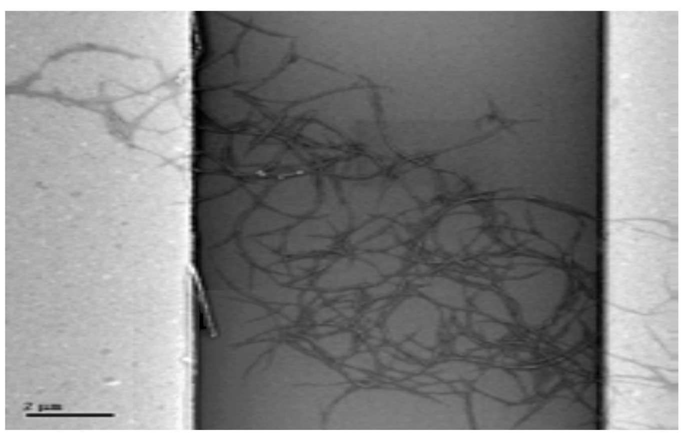


Figure 7. Single sensor element with carbon nanotubes across gold electrodes

Preliminary results of Sensor 3 indicate detection of off-gassing. Sensor 3 was exposed to 240, 320, 960, 3450, and 4440 ppm of propellant off-gassing. The result was a decrease in resistance from 2.60 kΩ to 2.2637 kΩ with exposure to 240 ppm of off-gas and another decrease to 2.1727 kΩ with exposure to 320 ppm; however, increased exposure of larger levels of off-gas did not exhibit any significant decrease in resistance. The sensor likely reached at saturation point around 2.17 kΩ where no additional resistance decrease is reached though exposure levels continue to rise.

4. OPTICAL SPECTROSCOPY

The sensing technique, described in this section, uses non-invasive fiber optic spectroscopy to monitor the status of double-base propellants. In order to noninvasively determine (in real time) the concentration level of stabilizer in the double-base propellant, a novel non-invasive inspection method (based on volume back scattering spectroscopy) was developed (Figure 8). The technique is based on the fact that the absorption property of propellant is directly related to its chemical composition. As the propellant ages, the chemical composition is constantly changing due to the chemical reaction between the stabilizer and outgas NO_x. By measuring the volume back scattering spectrum, the concentration level of the stabilizer can be detected; this in turn determines the status of the double-base propellant.

The sensor head includes two fibers: illuminating fiber and collecting fiber, which are close to each other with a separation around a couple of hundreds microns. Both fibers are in contact with the propellant surface. Thus, collecting fiber can be used to collect the back scattered light from the illuminating fiber, which is related to the absorption coefficient of the propellant material.

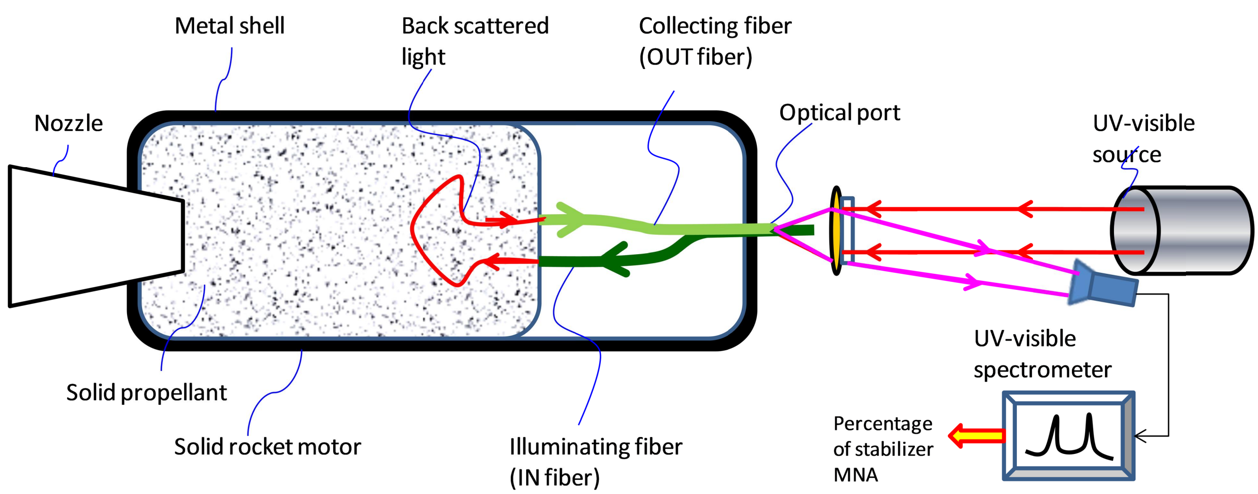


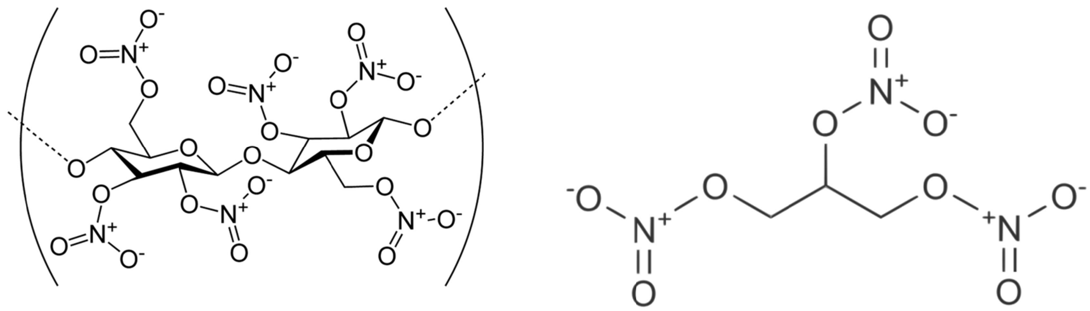
Figure 8. Conceptual sketch of fiber optic back scattering spectroscopic system used for measuring the concentration level of stabilizer MNA inside a rocket motor

Nitrate ester propellants are widely used as low emission signature solid state propellants and their stabilizers can be consumed during the storage process. A typical double-base solid state propellant is composed of nitrocellulose (NC) and nitroglycerin (NG); the propellant M9 is studied. The molecular structure of NC and NG are illustrated in Figure 9. Figure 10 shows a sample of M9 propellant that has a composition of 57.75% NC, 40% NG, 0.75%EC, and 1.50% KNO3. The stabilizer used was 2-methyl-4-nitroaniline (MNA), which is a typical stabilizer (Figure 11). The absorption coefficient of MNA has strong absorption in the UV/blue spectral range [12]. Determining the concentration of MNA by measuring the reflection, or back scatter, or transmission spectrum within the UV/visible/IR region of the propellant is possible [3]. The higher the concentration of MNA, the larger the absorption within this spectral range will be. On the other hand, the absorption spectrum at other wavelengths (e.g., green or red), the absorption of MNA will be compatible to other compositions, including NC, NG, and carbon. Thus, one can determine the concentration of MNA by measuring the spectrum at UV/visible/IR spectral range.

The following experiments were conducted to verify this sensing technique. Light sources with wavelengths of 473 nm and 532 nm were used. An Ocean Optics 2000 UV/visible spectrometer was used to measure the back scattered spectrum. The ratio between the detected light intensity was used to determine the concentration of MNA.

Initially, three samples with concentrations of 0%, 0.45%, and 0.7% of MNA in M9 propellant were used in the measurement. The red curves of Figure 12 (a), (b), and (c) show the experimentally measured back scattered spectra of M9 propellant with concentration levels of stabilizer MNA 0%, 0.45%, 0.7%, respectively [3]. For each sample the peaks are at the wavelengths 472.59 nm and 531.91 nm; the peak ratios are 5.11, 1.62, and 0.35 for the 0%, 0.45%, and

0.7% samples, respectively. It can be clearly seen that there is a dramatic change in the ratio between the signal intensity of blue light (473 nm) and green light (532 nm). The signal intensity of blue light is strongest at 473 nm when there are no MNA. The peak ratios are 3.45, 1.23, and 0.15 for the 0%, 0.45%, and 0.7% samples, respectively. The signal intensity of blue light decreases as the concentration level of MNA increases due to the heavy absorption of MNA at UV/blue spectral region.



(a) (b)

Figure 9. Molecular structures for (a) nitrocellulose and (b) nitroglycerin [9,10]

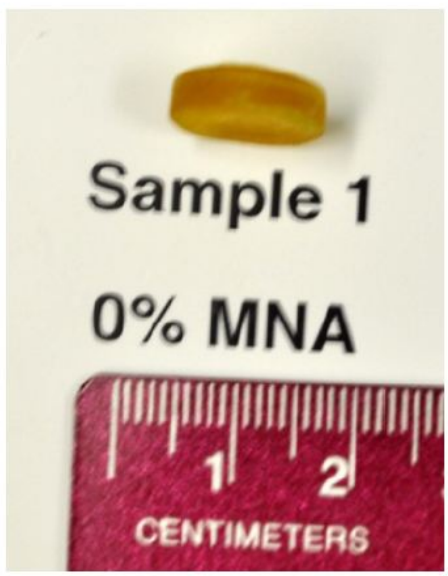


Figure 10. M9 propellant sample

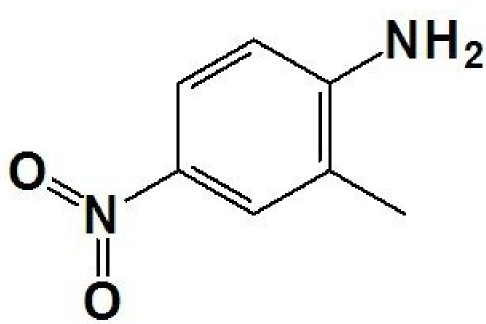


Figure 11. Molecular structure for 2-methyl-4-nitroaniline (MNA) [11]

S A T R I
60000
40000
20000
0
Intensity (counts)
380
400
420
440
460
480
500
520
540
560
580
600
Wavelength (nm)
Source:
USB2+F05604
Wavelength (nm):
549.34
373.79

(a)

S A T R I
60000
40000
20000
0
Intensity (counts)
380
400
420
440
460
480
500
520
540
560
580
600
Wavelength (nm)
Source:
USB2+F05604
Wavelength (nm):
549.34
410.20

(b)

(c)

Figure 12. Back scattered spectra of M9 propellant samples with (a) 0%, (b) 0.45%, and (c) 0.7% MNA.

For the next experiment, 1% carbon black is used in samples with the same percentages of MNA to simulate the real propellant used in the missile system. Figure 13 shows the pictures of three samples used in the experiment. Figure 14 (a), (b), and (c) show the experimentally measured back scattered spectra of M9 propellant with concentration levels of stabilizer MNA 0% + 1% carbon black, 0.45% + 1% carbon black, 0.7% MNA + 1% carbon black, respectively [3]. For each sample the peaks are at the wavelengths 472.59 nm and 531.91 nm; the peak ratios are 5.11, 1.62, and 0.35 for the 0%, 0.45%, and 0.7% MNA samples, respectively. Again, it can be clearly seen that there is a dramatic change in the ratio between the signal intensity of blue light (473 nm) and green light (532 nm). The signal intensity of blue light is strongest at 473 nm when there are no MNA. The signal intensity of blue light decreases as the concentration level of MNA increases due to the heavy absorption of MNA at UV/blue spectral region. Thus, the concentration level of MNA can be measured even in the case with carbon black.

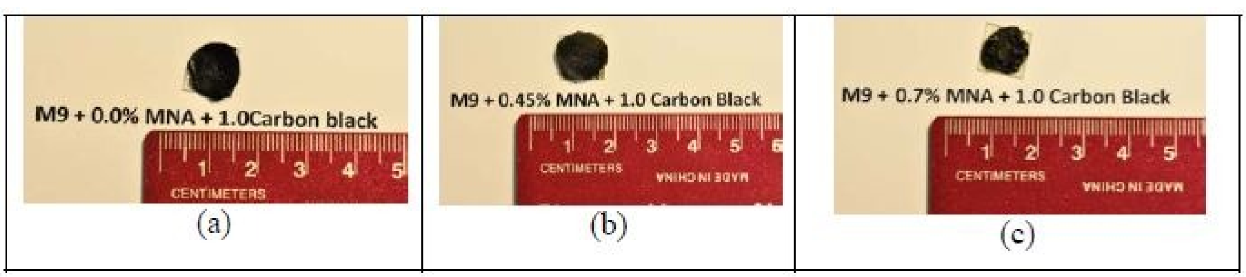
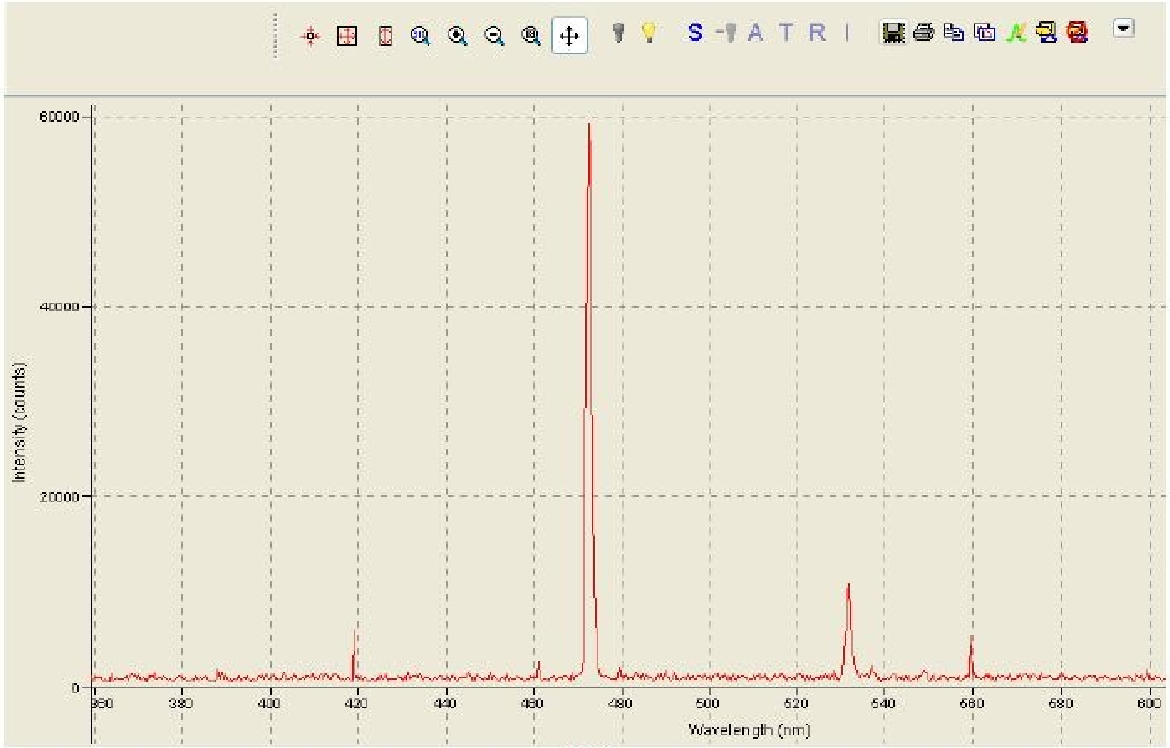
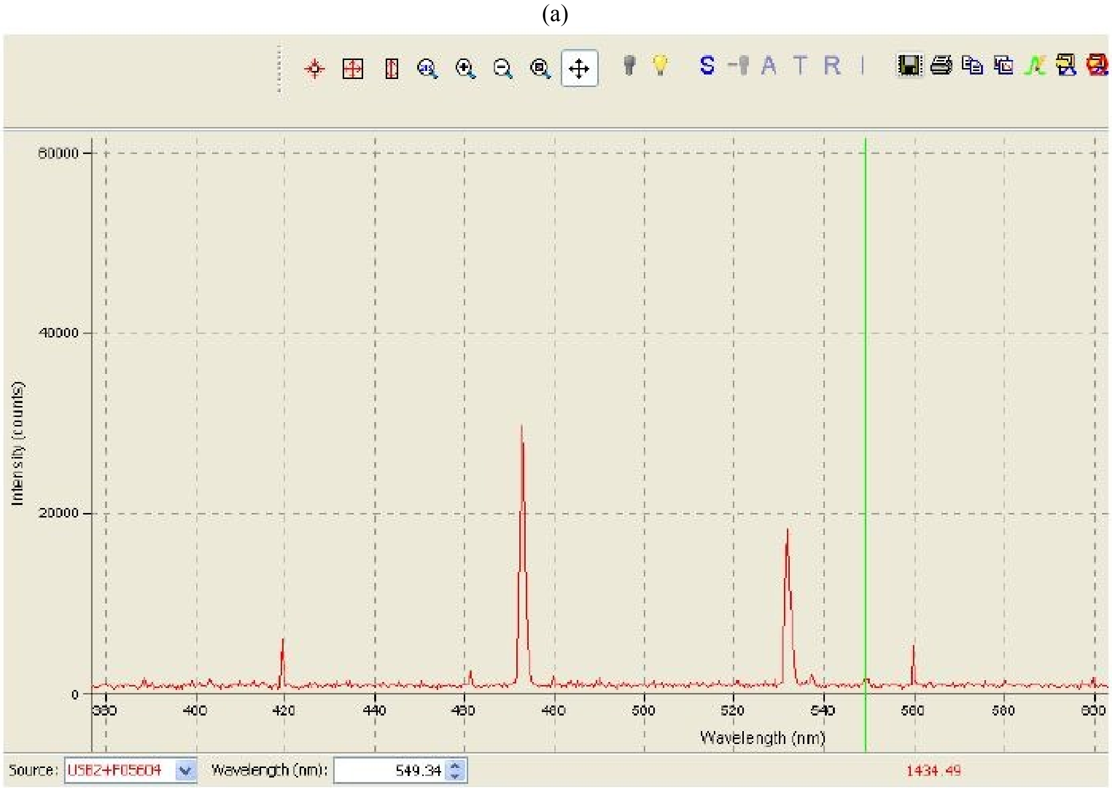


Figure 13. M9 propellant samples with carbon black added.



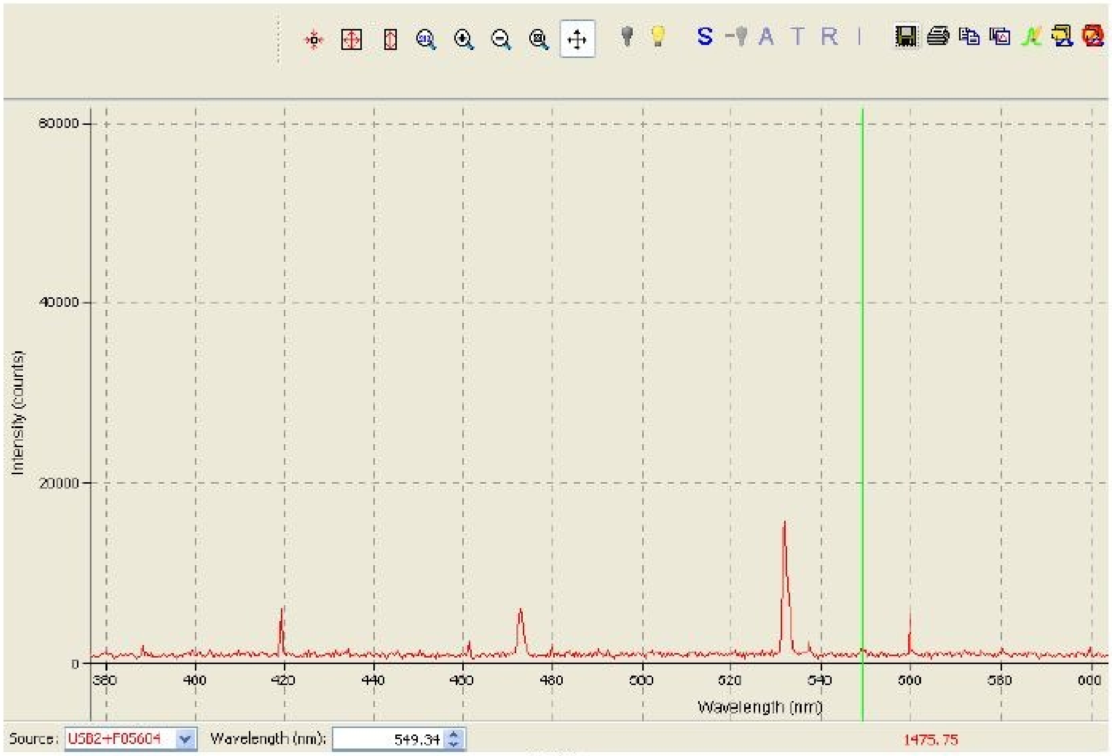
Intensity (counts)
Wavelength (nm)

(a)



Intensity (counts)
Wavelength (nm)
Source: USB2+F05604
Wavelength (nm): 549.34
1434.49

(b)



(c)

Figure 14. Back scattered spectra of M9 propellant with 1% carbon black added to the (a) 0%, (b) 0.45%, and (c) 0.7% MNA samples.

5. SUMMARY

Ongoing AMRDEC research and development of weaponry health monitoring techniques and devices for use in missile applications have been presented. Three different design approaches for assessing the aging and shelf-life of missile and rocket components have yielded promising results. Sensing techniques for the detection of rocket motor off-gassing, as well as for toxic industrial chemicals, have been successfully demonstrated via laboratory experiments. Preliminary results are summarized below for each sensing method.

Nanoporous Alumina Membrane Sensors

- Utilized nanoporous membrane to filter and compile varying propellant off-gassing analyte
- Successfully detected cumulative amounts of various rocket motor propellant ingredients
- Successfully obtained critical experimentally measured absorption spectrum of CO_2 and N_2O
- Effectively demonstrated the feasibility of using nanoporous membrane sensors for determining propellant degradation

Carbon Nanotube (CNT) Sensors

- Successfully demonstrated the usefulness of the CNTs for sensing propellant off-gassing
- Significant designs for CNT sensors that detects gases based on changes in the electrical properties of CNTs
- Successfully functionalized CNTs in order to ignore any analyte except the targeted analyte

Fiber Optic Spectroscopy (FOS) Sensors

- Successfully developed non-invasive fiber optic spectroscopy sensing system to monitor the shelf-life status of double-base propellants
- Successfully tested the FOS missile health monitoring system performance and detected critical analyte

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