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Abstract

An optical sensor system has been developed for the autonomous monitoring of NO_2 evolution in energetic material aging studies. The system is minimally invasive, requiring only the presence of a small sensor film within the aging chamber. The sensor material is a perylene/PMMA film that is excited by a blue LED light source and the fluorescence detected with a CCD spectrometer. Detection of NO_2 gas is done remotely through the glass window of the aging chamber. Irreversible reaction of NO_2 with perylene, producing the non-fluorescent nitroperylene, provides the optical sensing scheme. The rate of fluorescence intensity loss over time can be modeled using a numerical solution to the coupled diffusion and a nonlinear

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chemical reaction problem to evaluate NO_2 concentration levels. The light source, spectrometer, spectral acquision, and data processing were controlled through a Labview program run by a laptop PC. Due to the long times involved with materials aging studies the system was designed to turn on, warm up, acquire data, power itself off, then recycle at a specific time interval. This allowed the monitoring of aging HE material over the period of several weeks with minimal power consumption and stable LED light output. Despite inherent problems with gas leakage of the aging chamber we were able to test the sensor system in the field under an accelerated aging study of rocket propellant. We found that the propellant evolved NO_2 at a rate that yielded a concentration of between 10 and 100 ppm. The sensor system further revealed that the propellant, over an aging period of 25 days, evolves NO_2 with cyclic behavior between active and dormant periods.

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Introduction

Optical detection of nitrogen dioxide (NO_2) has emerged as a powerful alternative to sensors based on electrical resistance at elevated temperatures (*1*). An array of techniques have been developed that use a variety of reactive dyes and optical platforms (*2,3,4,5*). Several advantages are unique to the optical sensor systems, most important of which is the capability of remote detection. The ability to sense gaseous species without disturbing a specific environment and do so in the absence of electrical contacts and wiring is ideal for systems that concern aging of energetic materials. A current drawback of many current optical sensors, however, is the poor reversibility observed at room temperature (*2,4,6,7*). On the other hand, for specific applications where continuous NO_2 evolution is of interest these sensor films may be used in a dosimeter capacity and follow the outgassing and buildup of NO_2.

In particular applications involving the monitoring of aging HE materials (e.g., rocket fuel, explosives) optical sensor systems are well suited for in situ detection of NO_x evolution. HE materials are commonly composed of nitrated hydrocarbons that breakdown slowly over time to release NO_2, NO, N_2O, as well as other byproducts (*8*). Continuous monitoring of NO_2 evolution could provide a means to evaluate the level of HE material degradation. In such applications where the breakdown and release of NO_2 gases from stored material is on the order of months to years, a robust sensor with response times of hours to days would be suitable.

We recently described the development of a sensor material that is robust, inexpensive to prepare, and selectively detects NO_2 in the presence of common interferents (*9*). The material is a composite of perylene dye in a polymethylmethacrylate (PMMA) film. Films of the material can be prepared through spin casting of a chlorobenzene solution of perylene in PMMA on a glass surface. Excitation of the film with 417 nm light produces the expected perylene fluorescence emission with a maximum at 442 nm. Upon exposure to NO_2, the film's fluorescence is irreversibly quenched. Spectroscopic characterization identified that the NO_2 reacts directly with perylene to form the non-fluorescent nitroperylene. Response times of minutes to hours were observed for concentrations above 0.1% NO_2 in N_2 atmospheres. At mid-to-low ppm levels of NO_2, the response times were long, often running into days or weeks. The fluorescence response vs. time data could be described using a predictive model involving coupled diffusion and nonlinear chemical reaction kinetics. The model provides a means to identify unknown NO_2 gas concentrations under static conditions.

The research described herein follows up on previous work involving sensor material development with the development of a total sensor system for the detection of NO_2 in materials aging studies. We have prepared an autonomous sensor system that can monitor the evolution of NO_2 gas in an aging chamber at ppm level concentrations over a period of months to years. The

sensor was minimally invasive, requiring only the residence of a small sensor film within the aging chamber. All the optics were located outside the chamber where the film could be interrogated remotely through a glass window. A reference film was used to normalize the data for changes in source or detector intensity over time. An inexpensive blue LED coupled to a Hewlett-Packard E3632A power source provided a stable, consistent light source. The detector was a CCD spectrometer, which gave ample sensitivity and allowed signal averaging for enhanced signal-to-noise ratios. All the electronics, data collection, and data output were controlled and managed by a Labview program running off a laptop PC.

Experimental

Sensor Films. All solvents and reagents were obtained from Aldrich as reagent grade and used as received. Tetrahydrofuran (Aldrich) used for UV-vis spectral analyses was of spectroscopic grade. For the preparation of the sensor films, perylene was dissolved in a solution of 20% PMMA (Mw = 75,000) in chlorobenzene at a concentration of 2 mM. The mixture was stirred on an orbit shaker for a few days to ensure complete solvation of the polymer and homogeneity of the solution. The solution was then spin cast onto circular aluminum mirrors (Edmund Scientific) at a rate of 3000 rpm for 30 seconds, then dried under vacuum (15"Hg) at room temperature for one day. Thin, homogeneous, transparent films were prepared with a thickness of 200 ± 10 nm, as determined using a Tencor P-10 Surface Profilometer (Phoenix, AZ). The films were stored in a dessicator in the absence of light at room temperature.

Aging Chamber. A Stainless-Steel Desiccator Cabinet (12 1/4" x 12 1/2" x 12 1/4") (Fisher Scientific) was outfitted with two gas valves positioned on the back of chamber with one on the top left and the other on the bottom right. One of the gas valves was the inlet and the other the outlet. The outlet was connected to a gas bubbler. The bottom of the chamber was bolted to a 15" x 20" x 3/8" aluminum plate that allowed for the optical mounts. All gaps around the chamber were sealed with clear, colorless RTV silicone (Duro) or a white epoxy (Epoxy-Patch, Dexter Co.) in an effort to achieve a hermetic seal about the chamber.

Optical Sensor System. A schematic of the sensor system is illustrated in Figure 4. An optical mount with a sample holder for the 1 cm diameter coated mirror was situated near the glass sidewall within the aging chamber. Four other optical mounts were located outside the box fixed to the aluminum base plate. Atop the mounts were placed optical tubes (Thor Labs) that contained the collimating lens and interference bandpass filters (440 nm, 10 nm FWHM) for the excitation light. Two optical tubes (excitation and emission) were dedicated to the coated mirror within the aging chamber while the other two were dedicated to the reference mirror. The reference mirror was coated with an identical perylene-PMMA spin cast film and held in a sealed scintillation vial place outside the chamber.

The optical tubes were aligned at ~ 90° from each other allowing excitation and collection of the fluorescence emission from the sensor films. Fiber optic cables (600 μm

diameter) were coupled to the optical tubes via SMA connectors. The light source was a flattened, polished blue-LED (Nichia Corp.) with an emission maximum at 480 nm. The light was split using a 600 μm diameter Y-type optical fiber with one end connected to the reference and the other to the sample. Both emission cables were connected directly to an Ocean Optics SD2000 (275 – 925 nm range) dual port spectrometer, with the reference connected to the Slave port and the sample to the Master port.

Both the power source (Hewlett-Packard E3632A), for the LED, and the spectrometer were configured to a laptop PC (IBM Thinkpad 365X) using PCMCIA-GPIB and DAQ cards for the respective instruments. A Labview program was developed to turn on the light source (at 20 mA, 3.3 V) and spectrometer, warm up the light source for one minute, collect a spectrum, then power down the source and spectrometer, and the cycle repeated at specific time intervals.

Data collection and processing. The spectral data was collected, stored, and plotted in graphical form in the laptop PC. Fluorescence emission was recorded as the area under the spectral curve between 470 - 480 nm. The data was normalized to the reference (Equation 1) to account for any drift in the instrumentation and power fluctuations that may affect the source. I_S and I_R are the fluorescence intensity from the sample and reference, respectively. The normalized data were then plotted against time and displayed in Figures 6 and 10.

$$\left((I_S/I_R) / (I_S/I_R)_O \right) \times 100 = normalized \qquad \text{(Equation 1)}$$

Control experiments with NO_2/N_2 gas. The two gas adapters, modified to the back of the aging box, were used to flush out and change gases in the chamber. The gases went in through the adapter located at the top left and out the adapter on the bottom right. Gas flow rates were measured using an Omega Model FMA-5607 flow meter. A typical experiment was performed as follows: First, the box was flushed with nitrogen gas at a rate of 300 mL/min for 2.5 hours. An NO_2/N_2 gas mixture was then purged into the system at the same rate for 2.5 hours, then the gas valves were closed and the sensor system activated. To determine the NO_2 concentration in the aging box over time the gas was sampled with a Draeger tube from the top left adapter. Each data point of the graph of NO_2 concentration vs. time (Figure 7) was a separate experiment. That is, the aging chamber was refilled with 100 ppm NO_2 after each sampling and the time reset to zero.

Aging experiment with rocket propellant.[10] The aging box with all the mounted optics was placed in a Thermotron oven and all of the fiber optics were routed out through a hole located on the side of the oven. The computer, power source, LED, and spectrometer were positioned adjacent to the oven on a table. The instrumentation was kept at a room temperature of 22 ± 1 °C. A sample of rocket propellant (195 g), in two pieces shaped as oblong beams, were held in stainless steel beakers and placed in the aging chamber. Aging experiments were conducted at 40.0 ± 0.1 °C for varying lengths of time from weeks to months. The sampling time of the sensor system could be varied depending on the expected length of each experiment. A new experiment began by opening the chamber and removing the propellant, airing out the

aging chamber for several hours to the atmosphere, changing the sampling sensor film, then reintroducing the propellant. In all experiments, the gas valves on the back were closed and the same propellant sample was used.

Results and Discussion

NO$_2$ Sensor Materials

The optical response of the sensor materials is due to the fluorescence quenching of perylene as NO$_2$ reacts to form 1- and 3-nitroperylene (Figure 1) (*11*). The nitroperylenes are red colored solids that have very weak fluorescence. Immobilized at a 2 mM concentration in PMMA films, perylene yields a strong fluorescence emission upon excitation at 417 nm. Exposure to NO$_2$ diminishes the film's fluorescence and changes the initially light green-yellow colored film to a one that is reddish-orange. Fluorescence spectra of a representative film before and after a one hour exposure to 1000 ppm NO$_2$ in a nitrogen atmosphere is shown in Figure 2.

The material exhibits no optical response to high concentrations (1000 ppm) of other corrosive gases, such as SO$_2$, CO, Cl$_2$, and NH$_3$. The sensor films can be stored in air for several months without loss of its original spectral intensity or response to NO$_2$.
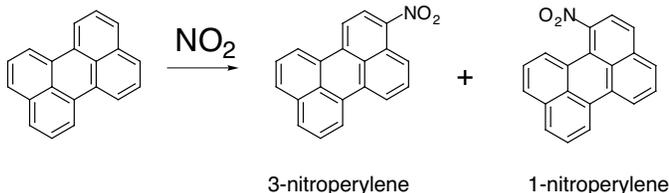
Figure 1. Nitrogen dioxide reaction with perylene.

The optical response of the perylene/PMMA sensor films to NO$_2$ was previously measured under controlled conditions using premixed gas concentrations of NO$_2$ in nitrogen gas (Matheson) (*9*). The sensor films were subjected to the gas in 500 mL glass vessels and the fluorescence intensity recorded at various intervals. Plots of the fluorescence intensity vs. time at 10, 100, and 1000 ppm NO$_2$ concentrations are shown in Figure 3. The optical response can be closely described by using a model by Barlett and Gardner that couples diffusion and nonlinear chemical reaction kinetics within a homogeneous thin film (*12*). Equation 2 describes the response as the concentration *a(x,t)* of the diffusing species reacts with a fraction of occupied sites represented by θ, and *N* is the concentration of binding sites, *D* the diffusivity, and k_f and k_b are the forward and backward binding or reaction constants.
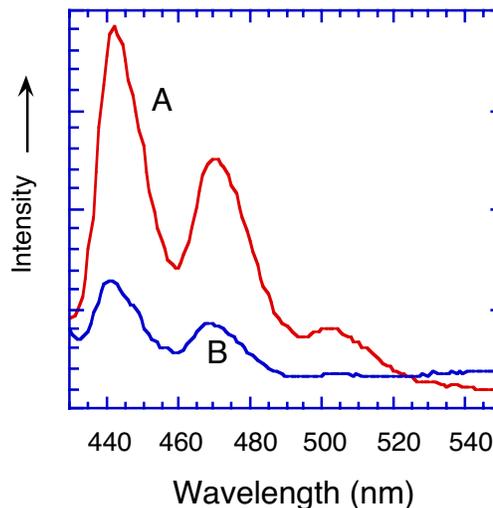
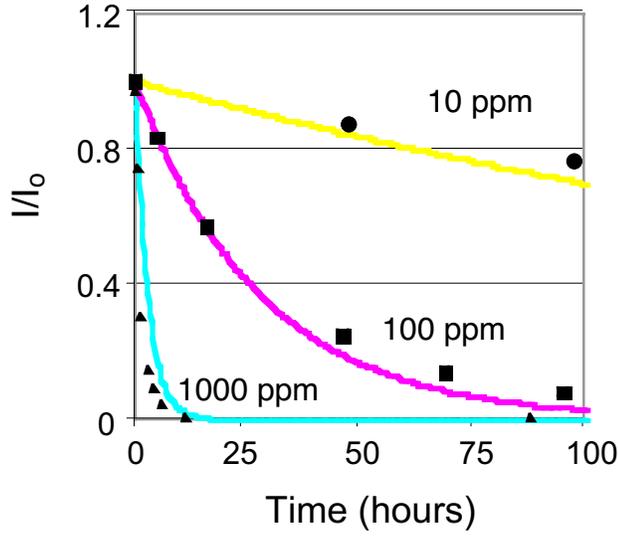Figure 2. Fluorescence spectra of perylene/PMMA sensor film (A) prior to and (B) after 1 hour exposure to 1000 ppm NO$_2$.

Figure 3. Fluorescence response vs. time data of the sensor films exposed to 10 ppm (●), 100 ppm (■), and 1000 ppm (♦) NO_2/N_2 atmospheres. Theoretical curves derived from Equation 3 are plotted as solid lines.

$$D\frac{f^2 a}{fx^2} - k_f a(1-\theta)N + k_b \theta N = \frac{fa}{ft} \qquad \text{Equation 2}$$

While this equation does not have an exact analytical solution, the authors identified several limiting cases where approximate expressions for the concentration profiles are accurate. By using a dimensionless analysis the response data could be fit to curves generated from Equation 2. In the situation where the kinetics of the reaction/adsorption is slow relative to diffusion of the adsorbate, an analytical expression for the solution is,

$$\theta(\chi,\tau) \cup 1 - \exp(-\lambda\gamma\kappa\tau/\eta) \qquad \text{Equation 3}$$

where θ is still the fraction of occupied sites, χ and τ are the dimensionless distance (x/L) and time (Dt/L^2), $\lambda = Ka_\infty$ (a_∞ is the species concentration at infinite distance from the surface and K is the equilibrium reaction constant, k_f/k_b); $\gamma = a/a_\infty$; $\kappa = k_f NL^2/D$; and $\eta = KN$. This equation simplifies to $1-\exp(k_f a_\infty t)$, hence a plot of θ vs t as shown in Figure 3 fits nicely with the experimental data. The fraction of unoccupied sites was derived by computing the θ over the entire thickness of the film and then integrating the result, which then gives θ from Equation 3 as a function of time. Subtracting this value from 1 allows comparison with the experimental results shown in Figure 3.

In the current experiments, the same sensor films were prepared on round 1 cm diameter aluminum coated mirrors. The coated mirrors were used as both sample and reference

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materials. The fluorescence spectra from these films before and after exposure to NO_2 gas were identical with that shown in Figure 2. The mirrors were used to enhance the collection of the sensor material's fluorescence by the fiber optics.

Optical Sensor System

The optical sensor system was designed to readily configure with various aging containers, impose a minimum invasion upon the aging experiment, and provide an autonomous data collection routine for long term aging studies. A schematic of the sensor system built for a one cubic foot glass and stainless steel aging container is shown in Figure 4 and the actual system is shown in Figure 5. One sensor film sampled the gaseous environment within the aging box while another was hermetically sealed in a scintillation vial and served as a reference. The fluorescent films were excited by light produced by a blue LED. The LED light was split into two paths via a split 600 micron diameter fiber, filtered with a 440 ± 5 nm interference filter, then focused to a ~1 mm diameter spot on the sensor films. Emission light coming off the sensor materials was collected with collimating lenses and sent down 600 micron diameter fibers to a dual port CCD spectrometer.
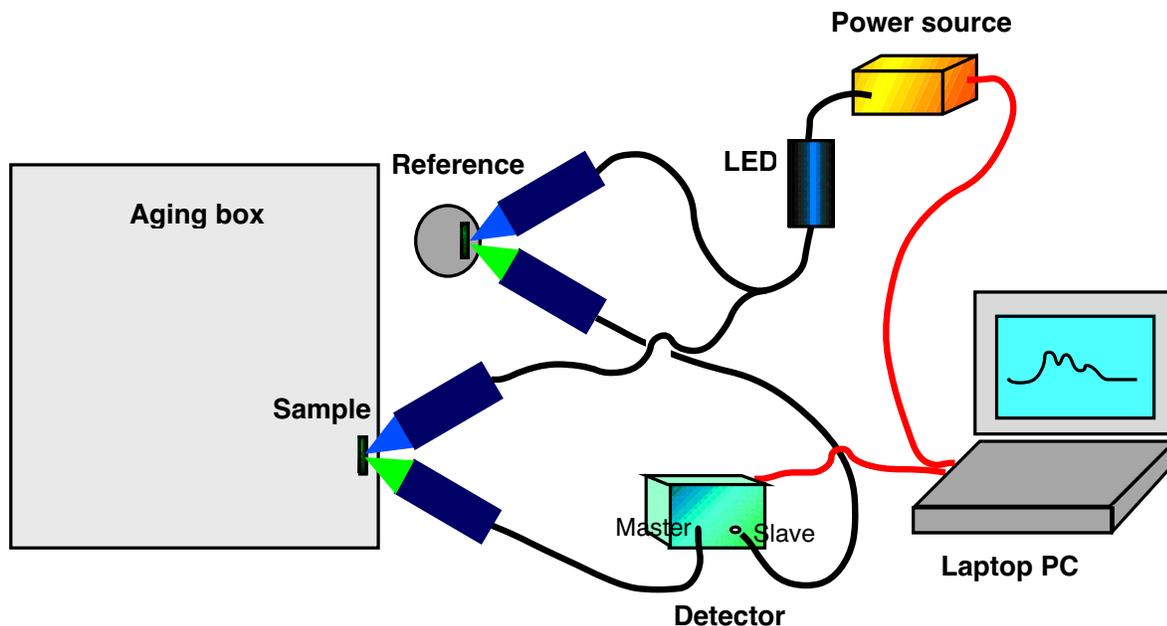

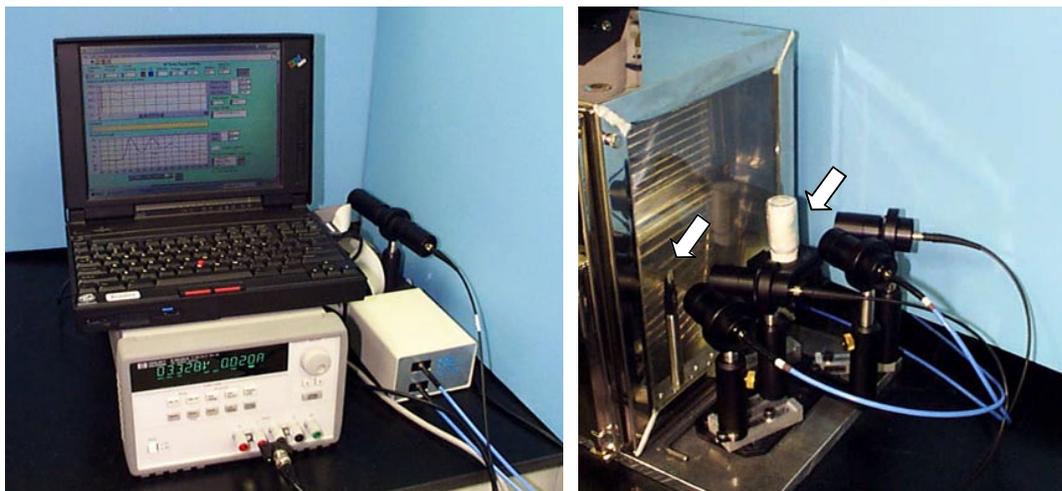Figure 4. Schematic of the autonomous gas optical-sensor system.

Figure 5. Autonomous gas sensor system. The computer, power source (below computer), spectrometer, and LED are shown on the left side. Right side picture shows the optics as they are configured with the aging box. The sample and reference sensor films are indicated by the white arrows.

Both the power source for the LED (Figure 5, beneath the laptop PC) and the CCD spectrometer (Figure 5, next to the power source) had on-off cycles that were controlled by a laptop computer. A Labview program was used to turn on the power source and spectrometer, allow the system to stabilize for one minute, acquire a spectrum, turn off the power and spectrometer, then restart the cycle over at a designated time interval. This routine was developed to minimize fluctuations in the LED's light output over time and to minimize overall power consumption of the system during the course of an experiment. The concern with a continuously lit LED was that the intensity would diminish, or the LED would burn out, over a period of months to years, a typical time frame for an aging experiment.

The atmosphere in the aging box was interrogated remotely by sampling the sensor film, located within the aging box, with the excitation and fluorescence collection optics located outside the box. Both the excitation and emission lights were transmitted through the aging box's glass window. Another sensor film, sealed in a glass vial located outside adjacent to the aging box, was used as a reference to monitor and normalize fluctuations that might occur with heating, power surge, intensity of the LED, or degradation of the sensor film. The orientation of the films and the source and collection optics were optimized to obtain maximum fluorescence output.

The optical response of the system was tested against 10, 100 and 1000 ppm NO_2 gas mixtures in nitrogen. As a control, the system was run in an atmosphere of air at room temperature for several days at a sampling interval of once every hour. The output was constant with no detectable optical degradation of the film (data not shown). Gas mixtures of NO_2 were added to the box through the gas valves modified onto the back of the aging box. The box was

first flushed with nitrogen to replace the air, then flushed with the NO_2 gas mixture. The amount of gas used was in 70% excess of the total volume of the chamber to ensure complete gas exchange. A Draeger tube sampling of the gas confirmed that the NO_2 mixture within the box was initially at the same concentration as that of the gas mixture from the manufacturer (Matheson).

Sensor data from the gas experiments, however, revealed a problem with the system concerning the containment of NO_2 within the aging chamber. The expectation was to achieve response vs. time curves identical to that of Figure 3. Figure 6 shows data from 100 and 1000 ppm NO_2 gas concentration studies. At the highest NO_2 concentration level of 1000 ppm the response was similar to that of the data shown in Figure 3. At the 100 ppm level, the response was reproducible but very different from that of Figure 3. Numerous trials were conducted all producing curves that leveled off at ~ 70% fluorescence intensity from the initial level. Moreover, experiments performed with 10 ppm NO_2 produced virtually no response, even over the course of five days.
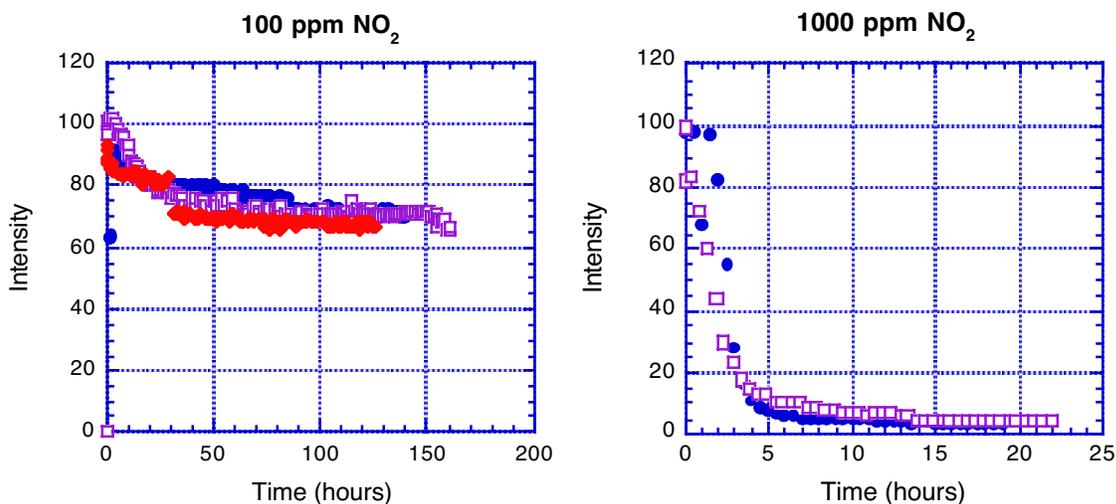

Figure 6. Optical response of sensor system to 100 ppm and 1000 ppm NO_2 in aging box. Different symbols represent separate trials run at different times.

Close inspection of the data revealed that the chamber appeared to lose NO_2 concentration over time. A study was performed to specifically measure the loss of NO_2 concentration within the chamber. Using the 100 ppm NO_2 gas mixture, the chamber was first charged with the gas, then the chamber gas sampled at various times using a Draeger tube. After each gas sampling a new experiment was started with fresh 100 ppm NO_2 gas. The data for the NO_2 concentration in the box over several days is shown in Figure 7, along with the sensor material's response under controlled conditions in sealed glass vessels, and from the aging box. Over a period of less than 10 hours the NO_2 concentration dropped to 50 ppm. Over 3 – 4 days

the concentration dropped to near zero. The sensor material's fluorescence intensity responds in accord with the NO_2 concentration. Initially, over the first several hours, when the NO_2 concentration was still high, the sensor response was relatively rapid. However, after about one day, when the NO_2 concentration had fallen to less than 30 ppm, the sensor's response flattened.
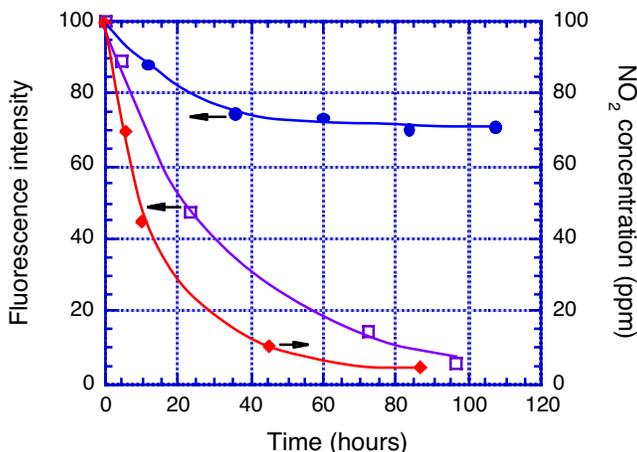

Figure 7. Loss of NO_2 from closed aging box as measured by Draeger tube analysis (♦). The optical response of the sensor materials during the loss of 100 ppm NO_2 gas is also shown (●) along with data from Figure 3 representing a controlled experiment (□) using sealed glass vessels (Page 9). Lines are drawn to aid the reader.

The problem with NO_2 concentration loss in the aging chamber may be one of gas leaks about the chamber as well as the reaction of NO_2 with the sealants and adhesives that hold the box together. All obvious gaps and joints were initially sealed with silicone and epoxy in our best effort to achieve a gas tight chamber. However, in a gas flow experiment, where a flow rate of 1 L/min was passed through the chamber, we found that approximately 65 mL/min was lost through leaks about the box. Concerning the reaction of NO_2 with the materials of the box we could qualitatively evaluate the reactivity by observing the discoloration of materials after each experiment. The reactive materials are the two-way foam core tape, used to hold the glass panes to the stainless steel frame, and the RTV silicone and white epoxy used to seal windows and gaps in the steel frame and glass-steel joints. After experimental runs with 100 and 1000 ppm NO_2, the tape discolored to a brownish color. The initially white epoxy also discolored to a light tan color over the course of several experiments. The clear and colorless silicone, on the other hand, did not incur any noticeable physical changes. Due to these problems we have begun the development of an all glass/stainless steel chamber that uses only one joint to form the chamber.

For the following experiment, however, we used the current aging chamber, as was tested, to allow us to gauge the capability of the autonomous sensor system as well as to obtain a qualitative understanding of NO_2 evolution from aging HE material.

Propellant Aging Experiment

The optical sensor system was relocated to an explosion proof vault and the aging box, with all the attached optics, placed in a Thermotron oven. The computer, power source, LED,

and spectrometer were located outside and adjacent to the oven with the fiber optics routed through a hole in the oven's sidewall. All windows and open holes about the oven were covered to shield the optics to any external light. Pictures of the sensor system and aging box in the oven are shown in Figure 8.

Figure 8. Sensor system in the explosion proof vault with the aging box and associated optical components located in an oven. The computer, power supply, LED, and spectrometer are located outside the oven. Fiber optics were run through a port on the left side of the oven (hole can be seen in top picture through the aging box's side window).

To establish the stability of the system several tests were run in the absence of propellant at an oven temperature of 40.0 ± 0.2 °C. The fluorescence intensity of the sample and reference were stable over 15 days at a sampling rate of once per three hours. No significant change in fluorescence intensity of the films occurred upon change in temperature (data not shown).

Rocket propellant was then introduced into the aging chamber. The propellant, in the form of oblong blocks, was placed in stainless steel beakers (Figure 9) and introduced into the chamber. The aging box was then closed and the sensor system started. Numerous runs were conducted over various periods of times. Data from some of the experimental runs are shown in Figure 10. The left side graph of Figure 10 shows two experiments conducted over 15 days. The 10 and 100 ppm NO_2 data from the controlled experiments of Figure 3 are also included for comparison. The first several response curves produced during these experiments were fairly reproducible, a couple of which are shown with the data from 6-14 and 6-30. From these data we find that there is an initial delay period of about three days before NO_2 evolution begins. Such behavior may correspond with the action of the NO_2 scavengers used in the propellant

Figure 9. Propellant in steel beakers.

[13]. Over the first few days the scavengers may be able to accommodate the rate of NO_2 being produced by the propellant. Beyond those first few days the NO_2 evolution rate may increase or the scavenger consumption rate may decrease, either cases resulting in the NO_2 production overwhelming the scavengers and the increase of NO_2 concentration within the chamber. Through a qualitative analysis with the controlled experiment data, we determine that the NO_2 concentration in the chamber builds to somewhere between 10 to 100 ppm. The precise NO_2 amount produced by the propellant was difficult to assess due to the inherent gas loss from the chamber.

Further propellant aging studies find two important observations (Figure 10, right side graph). The first is that with successive experiments the NO_2 evolution rate increases and the initial delay period becomes increasingly shorter. This is consistent with the depletion of NO_2 scavenger with each successive experiment. Secondly, for the experiments run over the course of 25 days we observe an unusual cyclic NO_2 production activity of the propellant. After the first several days of NO_2 outgassing the material reaches a state of dormancy that lasts about ten days. Through the inherent loss of NO_2 from the chamber the NO_2 concentration rapidly reaches undetectable levels after those initial days of material aging. The sensor thus maintains a stable output during this dormancy period. Following this period the propellant suddenly begins to evolve NO_2 again, completely quenching the sensor material within a few days. The two runs started on 7-16 and 9-13 gave consistent results regarding this active-dormant-active behavior.

We are uncertain as to the cause of this behavior but are considering further investigations into this phenomenon.

       With regard to the sensor itself, we find a peculiar behavior of the sensor material's optical performance on the 9-13 experiment. The fluorescence intensity of the sensor film increases after the 8th day of the aging experiment to a high of around 30% on the 13th day from its low of 25% on the 7th day. All previous experiments had not observed such behavior of the sensor film. The sensor material performs as a dosimeter and cannot undergo reversible conversion from nitroperylene to perylene. Another pathway that reversibly quenches perylene must play a role. This may be a consequence of successive aging experiments performed with the same propellant sample. After months of these aging experiments the propellant may begin to outgas presently unknown compounds that can reversibly bind to perylene quenching its fluorescence.
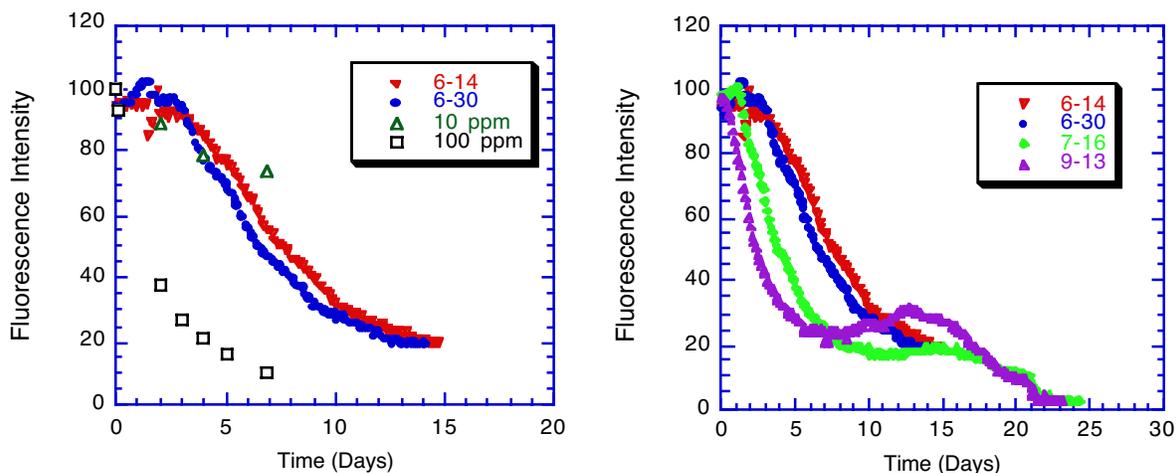

Figure 10. Propellant aging experiments monitored with the autonomous optical sensor system. Left – Aging experiments performed over 15 days plot with controlled experimental data from 10 and 100 ppm NO_2 experiments shown for comparison. Right – Longer aging times shows the NO_2 active-dormant-active behavior of the propellant. Different symbols represent separate trials run at different times.

Conclusion

       A complete optical sensor system with autonomous control has been developed and tested for long-term monitoring of NO_2 gas evolution from HE materials. The sensor has a sensitivity limit at the low ppm level and an upper limit of ca. 0.1% NO_2. The system is minimally invasive requiring only the placement of a 1 cm^2 sensor film within the chamber of interest. Optical interrogation of the sensor material was performed remotely via optical fibers. All electronic components of the system were located away and isolated from the aging chamber

that contained the HE material, thereby minimizing ignition sources. The aging chamber with the associated optical package neatly fit into a Thermotron oven and the sensor system was stable over long periods of time at the elevated temperatures (40 °C) of the accelerated aging experiments. Through a series of calibration experiments with known mixtures of NO_2 gas we found that the aging chamber was not a hermetically sealed containment and lost NO_2 rapidly over a period of days. A portion of the gas was lost through leaks in the chamber while some was absorbed by the sealants used in the construction of the chamber. Although we were unsuccessful in the mitigation of the NO_2 loss the system was tested in a propellant aging experiment to assess the autonomous sensor system in the field and gain some insight into the evolution of NO_2 from aging HE material. The results demonstrated that the sensor system could readily acquire data over a period of several weeks with excellent stability and reproducibility of the data. The data also found that aging rocket propellant produces significant amounts of NO_2 within the first two weeks yielding a build up of between 10 to 100 ppm in a 1 cubic foot box. The HE material then appears to reach a chemically dormant state for a period of ten days, then suddenly evolves with NO_2 evolution again. From this data it appears that the aging of HE materials is a non-linear process that could complicate predictive models concerning component degradation.

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