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Polymer-Based Lanthanide Luminescent Sensor for Detection of the Hydrolysis Product of the Nerve Agent Soman in Water

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The techniques of molecular imprinting and sensitized lanthanide luminescence have been combined to create the basis for a sensor that can selectively measure the hydrolysis product of the nerve agent Soman in water. The sensor functions by selectively and reversibly binding the phosphonate hydrolysis product of this agent to a functionality-imprinted copolymer possessing a coordinatively bound luminescent lanthanide ion, Eu^{3+}. Instrumental support for this device is designed to monitor the appearance of a narrow luminescence band in the 610-nm region of the Eu^{3+} spectrum that results when the analyte is coordinated to the copolymer. The ligand field shifted luminescence was excited using 1 mW of the 465.8-nm line of an argon ion laser and monitored via an optical fiber using a miniature spectrometer. For this configuration, the limit of detection for the hydrolysis product is 7 parts per trillion (ppt) in solution with a linear range from 10 ppt to 10 ppm. Chemical and spectroscopic selectivities have been combined to reduce the likelihood of false positive analyses. Chemically analogous organophosphorus pesticides tested against the sensor have been shown to not interfere with determination.

The use of chemical and biological weapons as agents of war has been banned, and the production and stockpiling of such weapons have been prohibited. Nevertheless, several countries, including the United States and the former Soviet Union, are known to have manufactured and stockpiled such weapons and toxins. Two nerve gases of particular concern are the organofluorophosphorus compounds Sarin and Soman shown in Figure 1. These are the agents used on troops in the Iran/Iraq War and currently leaking from stockpiles of aging weapons in the United States.[2] Growing concerns over possible contamination of water supplies by nerve agents has prompted the desire for small portable devices that can quickly detect trace amounts of these substances in water.

Despite today's technology, few methods can be used to quickly detect these compounds at the required parts per trillion (ppt) levels. Much of the technology being used, such as gas chromatography/mass spectroscopy (GC/MS) and high-performance liquid chromatography (HPLC), are large (not portable), are expensive, or require sophisticated, often extensive analysis procedures.[3−5] These methods are only effective for postconflict analysis. The devices that do meet the needs of real time analysis, such as surface acoustic wave devices (SAW), typically lack selectivity, especially with respect to chemically similar pesticides and insecticides, making false positive readings a major concern.[6−8] The technology currently being used for field analysis is based on enzyme chemistry. These techniques, while very specific, can take 20−30 min to respond and are not reusable.[9,10]

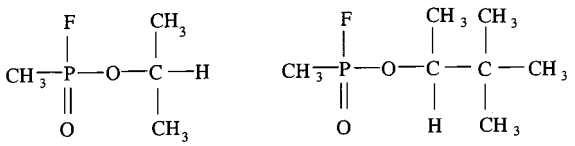

Figure 1. Chemical warfare nerve agents Sarin and Soman.

The sensor described here is a fiber optic probe utilizing a luminescent europium complex. The use of lanthanide ions as spectroscopic probes of structure and content is an established technique. The narrow excitation and emission peaks of lanthanide spectra (typically on the order of 0.01−1 nm full width at half-maximum) provide for highly sensitive and selective analyses.[11,12] Lanthanide complexes exhibit long luminescent lifetimes and are intensely luminescent when complexed by appropriate ligands. Proper ligand choice, used to both immobilize the lanthanide

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probe and provide the enhancements needed for trace analysis, has been shown to provide limits of detection in the parts per trillion, or lower.[13] This device has been constructed using europium as the probe ion since its luminescence spectrum is the least complex. Detection of the nerve agent is based upon the changes that occur in the spectrum when the hydrolysis product pinacolyl methylphosphonate is coordinated to Eu^{3+}. The combination of molecular imprinting and luminescence detection provides multiple criteria of selectivity to virtually eliminate the possibility for false positive readings.

EXPERIMENTAL SECTION

Reagents. Unless otherwise indicated, materials were obtained from commercial suppliers and used without further purification. Analytical reagent grade chemicals were used along with deionized water to prepare solutions. Pinacolyl methylphosphonate (PMP) and sodium phosphate were obtained from Aldrich (Aldrich, Milwaukee, WI). Neat liquid standards of Phosdrin and Dichlorvos as well as solid standards of Methyl Parathion and Dimethoate were obtained from Supelco (Supelco Chromatography Products, Bellefonte, PA). Malathion, Thionazin, and Dibutyl Chlorendate were obtained as neat liquid standards from Radian (Radian International, Austin, TX).

Instrumentation. Luminescence was excited using a model 60X argon ion laser (MWK Industries, Corona, CA). Spectra were collected using an *f*/4, 0.5-m monochromator (Chromex, Albuquerque, NM) equipped with a model ST-6 CCD (Santa Barbara Instruments Group, Santa Barbara, CA) using Kestrel Spec Software (K&M Co., Torrance, CA). Spectra were also obtained with an Ocean Optics S2000 miniature fiber optic spectrometer (Ocean Optics, Dunedin, FL) equipped with a 1200-line holographic grating, permanently installed 100-μm slits and a 440-nm cutoff filter.

Molecular absorbance spectra were obtained using a UV/visible spectrophotometer (Beckman Instruments Inc., Fullerton, CA). Radiative lifetimes and quantum efficiencies were measured using a Quanta Master spectrophosphorimeter (Photon Technologies Inc., Ontario, Canada). Electron micrographs were obtained using a Topcon DS-701 dual-stage scanning electron microscope (SEM) (Topcon, Paramus, NJ). Metal concentrations were determined using a Hewlett-Packard 4500 Series ICPMS model G1820A (Hewlett-Packard, Wilmington, DE). Graphs and spectra were plotted and calculations performed using Igor Pro Software (WaveMetrics Inc., Lake Oswego, OR).

Compound Preparation. Candidate compounds were synthesized using a stoichiometric ratio of 1 mol of europium to 1 mol of PMP and 3−7 mol of ligating molecules. (The number of ligating species depends on the number of ligands needed to acquire 9-coordinate Eu^{3+}.) The calculated amount of each ligand was added to the europium solutions. PMP was added to a 50:50 water/methanol mixture to enhance its solubility, and then added to the europium/ligand mixture. The resulting solutions were stirred ∼2 h and then left to evaporate the solvent. Analogous compounds without PMP were also synthesized. $Eu(DVMB)_3PMP(NO_3)_2$ and $Eu(DVMB)_3(NO_3)_3$ were synthesized in the manner detailed above. (Divinylmethyl benzoate (DVMB) was freshly prepared before use since it readily polymerizes.)[14] The stoichiometry of $Eu(DVMB)_3PMP(NO_3)_2$ was verified using ICPMS Eu 16.12% (calculated 16.36%). Low-temperature crystal spectra of both compounds were collected from 575 to 700 nm using 465.8-nm excitation. Spectra were interpreted to determine the symmetry changes associated with PMP inclusion. Lifetimes and time-resolved luminescence spectra of $Eu(DVMB)_3PMP(NO_3)_2$ and $Eu(DVMB)_3(NO_3)_3$ were obtained, and quantum efficiencies were evaluated with respect to a reference perchlorate solution.[15]

Polymer Preparation. Initially, polymers were prepared by dissolving 1−5 mol % complex compound in 94−98 mol % styrene. Approximately 1 mol % of azobisisobutylnitrile (AIBN) was added as an initiator. Cross-linked polymers were also prepared using 3 mol % compound with 1−5 mol % of a cross-linking agent divinylbenzene (DVB), styrene, and AIBN. The resulting solutions were placed in glass vials, purged with nitrogen, and sealed using Parafilm and screw-on tops. The polymers were sonicated for 2−4 h at 60 °C. (Sonication is believed to help maintain homogeneity in the polymer.)[16] After sonication, the partially polymerized material was placed in an oven at 60 °C and allowed to cure overnight. The resulting block copolymers were ground to expose a larger surface area of the polymer and facilitate the removal of the imprinting ion. Once ground, the template ion is removed in two steps:[16] (1) swelling in methanol and gradually increasing amounts of water[17] to remove unreacted monomer and expand the polymer pores (this produces accessible sites and facilitates the removal of the imprinting ion) and (2) removal of the imprinting ion by acid washing. Acid washing facilitates the removal of PMP and leaves in its place a weakly coordinated nitrate.

Fiber Optic Sensor. The fiber optic sensor consisted of a 400-μm optical fiber (Thor Labs, Newton, NJ) with the polymeric sensing element chemically bound on the distal end. The fibers were prepared by terminating one end with an SMA connector and removing the cladding from and polishing the distal end using the procedures outlined in the Thor Labs Guide to Connectorization and Polishing of Optical Fibers. The tips were dipped into the chemically initiated viscous copolymer leaving a uniform layer on the fiber. The polymer finished curing under a small UV lamp, overnight. Coated fibers were conditioned in a manner similar to the ground polymers as outlined above. Final versions of the sensor were prepared using a tapered fiber created by heating it in an air/acetylene flame and manually pulling the stripped end. The tapered fibers were much more efficient at coupling the evanescent field to the polymer and gave greatly improved results.

Analysis. Measurements for the calibration data, pH study, and interference testing were all performed using the same fiber. The analytical figures of merit were obtained using serial dilutions of a 100 ppm PMP standard in 0.01 M NaOH. The luminescence was excited using the argon laser, and the active end of the sensor was placed in a quartz cuvette containing one of the sample dilutions. Spectra were collected at each concentration after the sensor had equilibrated for 10 min. The sensor was rinsed with deionized water between exposure to each concentration. Standards were analyzed in order of both increasing and decreasing concentrations in order to demonstrate the reversibility of the

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sensor. Calibration curves were obtained, and linear regressions were performed.

The response of the sensor and the pH dependence of the temporal response were evaluated using a method similar to the one described above. A series of 100 ppm pinacolyl methylphosphonate standards with pH values ranging from 4.5 to 13.0 were prepared from the stock standard through the addition of 1.0 M nitric acid or 1.0 M sodium hydroxide. The sensor was placed in a cuvette with each solution, and spectra were collected at a variety of exposure times. Response was evaluated through a comparison of peak intensity at each time with pH.

A series of pesticide and insecticide standards along with a phosphate buffer solution were tested as possible interferences. Standard 1000 ppm solutions were prepared by the dissolution and/or dilution of the samples in deionized water when possible. The pesticides with limited solubility in water were prepared using a 50:50 water/methanol mixture. The pH of each of the solutions was adjusted to 12 using 1 M sodium hydroxide. Spectra from the fiber for each analyte were taken at regular intervals for 60 min. The resulting spectra were then compared with the response from the sensor in 100 ppm PMP. The sensor was cleaned using 1 M nitric acid and rinsed with deionized water between each analysis.

RESULTS AND DISCUSSION

Hydrolysis. Open air testing of actual chemical agents has been forbidden since the late 1960s when an agent was inadvertently sprayed on desert grazing land in Utah.[18] Therefore, a device designed for the detection of agents either cannot easily be tested or it must be designed to respond to a surrogate material, increasing the possibilities for false alarms. To circumvent this problem, this sensor was designed to measure the hydrolysis product of Soman, PMP. This approach allows for the indirect detection of the agents since the agents will rapidly hydrolyze in water. The inclusion of a hydrolyzing surface coating can be used if gas-phase sensing is required. This scheme minimizes the hazards and difficulties associated with working with these agents during the design and testing of the sensor. PMP, the hydrolysis product of Soman, is commercially available from Aldrich. The polymers used in the sensor were templated for PMP since the polymer-bound functional end of the molecule is the same for the hydrolysis product of either Soman or Sarin.

Screening Monomers. Synthesis and investigation of various europium compounds containing PMP with different ligands were performed. Ligands were selected for their ability to bind to and enhance the luminescence of the lanthanides as well as their ability to be incorporated into a polymer. Pyridine and dimethyldipyridyl were selected on the basis of the luminescence enhancement that pyridine rings have demonstrated with lanthanides and their commercial availability. The ligand methyl-3,5-dimethylbenzoate (DMMB) was selected since it can be converted into polymerizable methyl-3,5-divinylbenzoate, providing an avenue for self-cross linking. In addition, the conjugating oxygen atoms in the carbonyl groups are effective sensitizers for lanthanides and can act as an effective energy bridge.

Compounds were evaluated using both 488- and 465.8-nm excitation with ~1 mW of laser power. $Eu(DMMB)_3PMP(NO_3)_2$ demonstrated the most easily discernible spectral difference. (Figure 2) The luminescence intensity of this compound was not as large as some of the other candidates; however, the clarity of the spectral difference between the compound with and without the hydrolysis product made detection based on the spectrum a relatively simple process. To verify that the new peak was not simply a result of a mixture of $Eu(PMP)_3$ and the complex, $Eu(PMP)_3$ was prepared and its luminescence spectrum generated. The peak at 610 nm in the $^7F_2 \leftarrow {}^5D_0$ manifold of Eu^{3+} for the compound was clearly not in the spectrum of $Eu(PMP)_3$. The $Eu(PMP)_3$ displayed weak luminescence and poor resolution. The $Eu(PMP)_3$ spectra strongly suggest that the peak at 610 nm was due to the addition of the hydrolysis product to the compound and not an impurity.

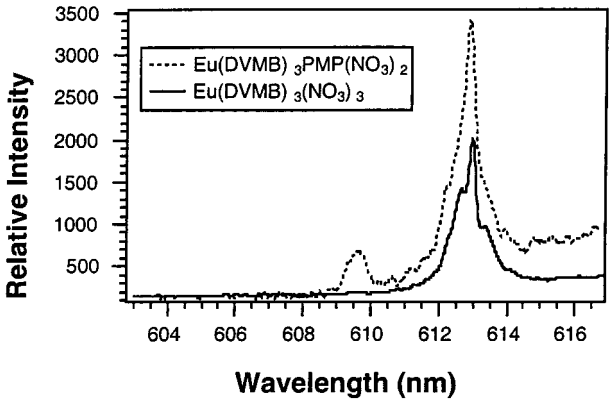

Figure 2. Laser-excited luminescence spectra of $Eu(DMMB)_3(NO_3)_3$ and $Eu(DMMB)_3(NO_3)_2(PMP)$ crystalline solids excited at 465.8 nm.

Low-temperature (77 K) luminescence spectra were analyzed using 465.8-nm excitation to determine the site symmetry of the europium in the compounds. Changes in the spectra were used to elucidate the effects of the substitution of PMP for nitrate. Structural inferences were based on the splitting patterns observed in the $^7F_n \leftarrow {}^5D_0$ (where $n = 0-5$) manifolds of the europium spectrum.[19] The spectra of both complexes displayed a single weak $^7F_0 \leftarrow {}^5D_0$ transition. The peaks in the $^7F_1 \leftarrow {}^5D_0$ manifold of the complex with the hydrolysis product had a singly and doubly degenerate transition and a singly and two doubly degenerate transitions in the $^7F_2 \leftarrow {}^5D_0$ manifold. An increase in the intensity of the peaks in the $^7F_3 \leftarrow {}^5D_0$ manifold of the complex without PMP also signaled a significant change in the symmetry of the two compounds. The transitions in the redder manifolds were unresolved and were not used for structural determination; however, they suggested a decrease in symmetry with PMP binding. The likely symmetry of this complex with PMP is either C_3 or a C_{3v} as compared to C_2 or a C_{2v} for $Eu(DMMB)_3(NO_3)_3$. The loss of symmetry for the nitrate compound may result from a unidentate nitrate as opposed to a bidentate PMP.

Lifetime determinations were performed on the DMMB compounds. Using weighted regression, the lifetimes for $Eu(DMMB)_3PMP(NO_3)_2$ and $Eu(DMMB)_3(NO_3)_3$ were calculated to be 337.6 and 312.5 μs, respectively. Quantum efficiencies for the compounds were determined using a europium perchlorate compound of known quantum efficiency, 1.9%. The determination

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was based on the ratios of the peak areas in the 500−800-nm region of the spectra of three compounds. The quantum efficiencies with and without PMP were 8.54 and 7.76%, respectively. The molar absorptivities were the same for all the compounds (0.0083 L cm^{-1} mol^{-1}). The spectra of the analogous divinyl compounds were examined and found to produce the same spectra as the dimethyl complex. The position of the 610-nm band of interest remained unaffected by the vinyl substitution.

Preparation of the Polymers. Styrenic block copolymers were prepared, and the optimal mole percent complex for the preparation of the polymer coating was determined. The resulting translucent polymers displayed a slight yellow tint and, upon excitation with a UV lamp, displayed the characteristic red-orange luminescence of europium. The best results were obtained from the 3 mol % complex. The 610-nm peak was intense and easily discernible from other Eu(III) peaks. Lower percent complex polymers displayed weak luminescence characteristics, and higher percent polymers, although more intense overall, had a diminished analyte peak. Polymers with greater than 5 mol % complex are not used since they tend to become opaque, reducing optical transduction. Polymers cross-linked using DVB were found to inhibit the performance of the sensor.

The conditions for the removal of the template molecule, the PMP hydrolysis product, were also investigated. The optimal conditions for swelling the polymer were determined to be a series methanol/water washes, followed by washing with a weak nitric acid solution. The spectrum of the washed polymer shows the 610-nm peak was no longer visible, demonstrating that PMP was effectively removed. A small residual peak at 610 nm was viewed in some of the polymers resulting from some hydrolysis product trapped in the deeper levels of the polymer. The overall intensity of the polymer's luminescence also decreases upon washing since the nitrate is only weakly coordinated, possibly allowing water to enter the coordination sphere of the lanthanide. The washed polymer was tested for its ability to rebind PMP by exposing it to a 150 ppm PMP solution in aqueous 1 M NaOH and obtaining its luminescence spectra. The 610-nm peak was again observable in the spectra.

Preparation of the Sensors. The sensors were prepared using 400-μm multimode optical fibers. (Larger fibers, although able to pass more light, did not provide the resolution necessary to isolate the analyte band.) Differing thicknesses of the polymeric coating were used in order to evaluate the effects of polymer thickness on response time, background signal, and signal intensity. Thickness was controlled by the number of times the fiber was dipped into the viscous polymer. Digital images of the coated and uncoated fibers were taken using a SEM. The fibers were analyzed at low acceleration voltages with no prior sample preparation. (Low acceleration voltage was used to minimize charging artifacts on the fibers.) The images were acquired using SM701_AP software available from the vendor. During the imaging, measurements of the polymer thickness were performed (Figure 3), and the average thickness resulting from each dip was estimated to be between 15 and 20 μm.

It was observed that increasing the thickness of the coating increased the time required for response and the intensity of a residual 610-nm peak in the background. This is consistent with the fact that thicker coatings have cavities that are deeper in the polymer and are relatively inaccessible. Thus, a larger amount of PMP could remain trapped in the polymer, increasing the residual peak. A thickness of four coats, 60−80 μm, was determined to be optimal for the design of the sensors since it gives an 80% response within a reasonable time (less than 8 min).

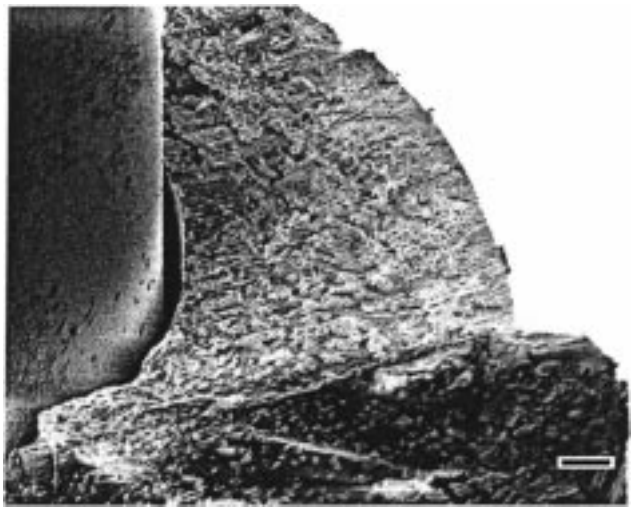

Figure 3. SEM of the polymer-coated vinylized fiber used to measure the thickness of the coating. The separation between the fiber and the coating demonstrates the ineffectiveness of silanization.

Excitation. Two argon ion excitation wavelengths, 465.8 and 488 nm, were used with the polymer. The spectrum of the sensor excited with the 465.8-nm laser line displayed better spectral resolution of the 610-nm analyte peak from the 615-nm luminescence peak of the parent europium. The luminescence of the compound excited at 465.8-nm was also more intense. This increase indicates that excitation using the 465.8 nm line results in a near-resonant excitation transition from the ground $^7F_0$ level to the $^5D_2$ level. As a result, 465.8 nm was chosen as the excitation wavelength for the sensor.

Analytical Figures of Merit. The performance of the fiber optic sensor with the $^1/_2$-m monochromator was evaluated to obtain figures of merit. The sensor used to determine the limit of detection consisted of a 400-μm optical fiber with a tapered end. A 50−75-μm layer of the 3 mol % polymer was directly deposited onto the end. The fiber was cleaned using the method previously described. Using 1 mW of 465.8 nm for excitation, 200-μm slits with the monochromator, and an exposure time of 5 s, the luminescence spectrum of the sensor in a series of PMP solutions at pH 13, was obtained. The response of the sensor to increasing concentrations of PMP exhibits an increase in the luminescence intensity of the primary europium band as well as an increase in the intensity of the analyte peak. This increase in luminescence is indicative of the rebinding of the PMP product into the primary coordination sphere of the lanthanide and the exclusion of water.

The structural determination performed for the characterization of the compound also supports this conclusion. The resulting peak areas in the 609−611-nm spectral region of the analyte were calculated using Igor Pro Software, and plotted as a function of concentration. Peak areas have been shown to provide a longer, more linear calibration curve than direct peak height, since the bandwidths as well as the peak heights of the lanthanides increase as a function of concentration. Linear regression analysis was performed on the data and a limit of detection of 750 ppq

Table 1. Comparison of the Analytical Figures of Merit for the Two Systems

	lab bench system	portable system
limit of detection	660 ppq	7 ppt
linear dynamic range	750 ppq to 10 ppm	10 ppt to 10 ppm
correlation coefficient (r^2)	0.9984	0.9973
slope	1.949 counts ppt^{-1}	1.484 μV ppt^{-1}
80% response time	8 min	8 min

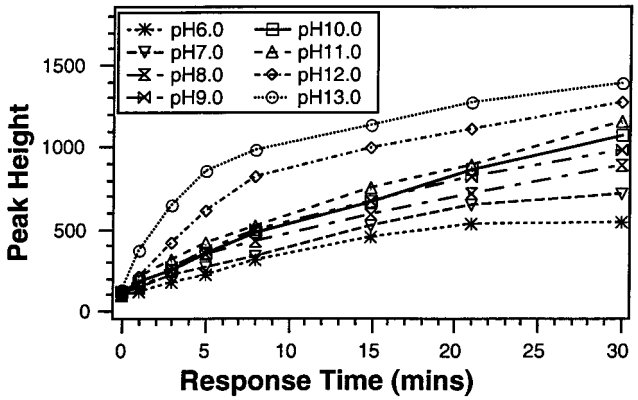

Figure 4. Effect of pH on the temporal response of the sensor.

calculated. The analytical figures of merit for the sensor with the benchtop apparatus are given in Table 1. Concentrations below 750 ppq show no change in the intensity of either band. The residual 610-nm band remains visible even when the sensor is cleaned and should be subtracted out with the background for application purposes. Variations in the residual peak, the background, or other slight differences between sensors appear to have little effect on the overall calibration curve, linear dynamic range, and limit of detection. The typical 80% response time for the sensor was less than 8 min.

Response Time and pH Dependence. The response time of the sensor is the most crucial characteristic of detectors and sensors for real time monitoring.[18] The sensor must be fast enough to provide a warning with enough time for an appropriate response such as evacuation of the area. A study was performed using a sensor with a 200 μm coat to determine the effect of pH on the response time. The study was performed on solutions of PMP prepared with pH values ranging from 4.5 to 13 over a period of 24 h. Figure 4 demonstrates the response of the sensor over the initial 30-min time period. Additional readings were obtained for each pH value at 1 h and at 24 h. (Since these points remained at the same value, they were excluded for reasons of clarity.) The sensors show a positive response to the presence of PMP after 3 min for all pH values from 6 to 12 and a positive response after 1 min for the solution with a pH of 13. At low values of pH (below 6), the response of the sensor is indicative of the removal of PMP from the sensor. This demonstrates the washing process that occurs under acidic conditions. Neutral and basic values (pH from 6 to 11) provide a response that is consistent over the entire pH range. The full response time for this sensor is 30 min. (Response times are typically reported as the time it takes the sensor to reach 80% of maximum.)[9] The response at pH 12 was faster than the response at lower pH levels and had a steeper, more linear response over the initial range of concentration. At lower pH, the response time of the sensor was 15 min.

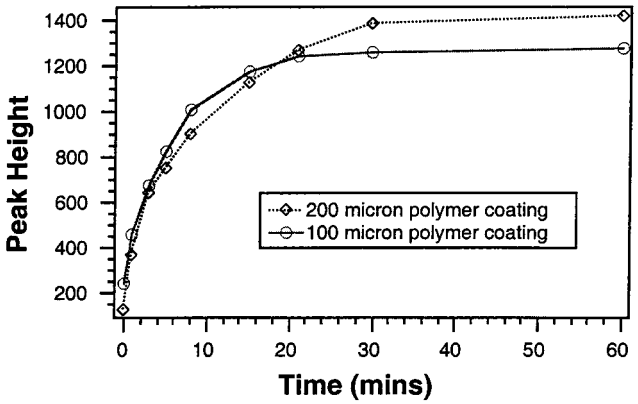

Figure 5. Effect of the thickness of the polymer coating on the temporal response.

The fastest response for the sensor with the 200 -μm coat was obtained using a PMP solution adjusted to pH 13 with NaOH. Using this pH, a response time of 14 min was obtained. These results indicate that the more basic the solution, the faster the response time of the sensor. Since the response of the sensor will be based on the hydrolysis of the agents, the strongly alkaline solution used for the hydrolysis of the nerve agents will also enhance the response time of the sensor. (All solutions above pH 6 were prepared using deionized water, 1 M sodium hydroxide, and PMP.)

The effect of coating thickness on the response time of the sensor was also evaluated. Figure 5 shows the response of a sensor coated with a 100-μm layer and that of a sensor coated with a 200-μm layer to a 10 ppm PMP solution at pH 13. As previously stated, the fiber with a 200-μm coat reaches a maximum response within 14 min. The response time of the 100-μm coated fiber is decreased to 8 min. For an on-line monitor, the time for initial response is the most important factor. Using a pH of 13, a distinct response occurred within 1 min.

Interferences. The compounds that are most chemically analogous to nerve agents are organophosphorus pesticides and herbicides. Many of these compounds exist as liquids, oils, or solids at ambient temperatures. Several common pesticides, along with those most chemically similar to the agents Sarin and Soman, were tested using the sensor in order to determine the degree of interference from each pesticide. The concentration used for screening, 1000 ppm, is much higher than typically found in water systems even with runoff from nearby agriculture. The pesticide dichlorvos, commonly found in flea collars, was screened as a possible interference due to its chemical similarity.

Each of the pesticides and a sodium phosphate solution were exposed to the sensor for 1 h with measurements taken during scheduled intervals. None of the pesticides produced a luminescence peak in the region of the PMP peak. The spectra resulting from the exposure of selected pesticides (concentration 1000 ppm) with the sensor are shown in Figure 6. The spectrum of the sensor with 100 ppm of the hydrolysis product is shown for comparison purposes. The influence of these chemicals is apparent as indicated by the changing intensity of the major 617-nm europium luminescence band. Dichlorvos, the pesticide most structurally similar to the nerve agents, exhibited a response to the sensor with a weak band centered at 621.5 nm. This resulting band does not inhibit the acquisition or detection of the agents by the sensor.

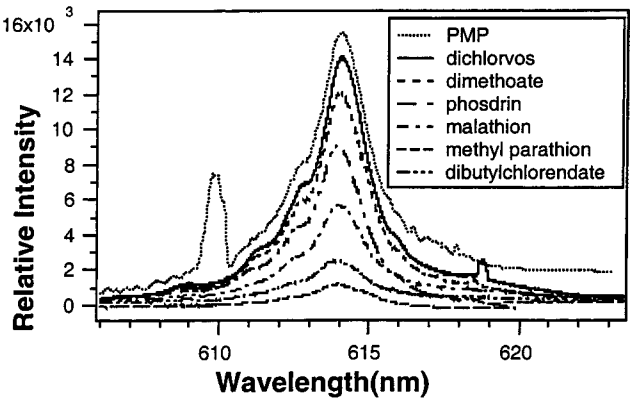

Figure 6. Response of the sensor to selected interferences excited at 465.8 nm.

Since the chemicals that are the most likely interferences do not cause false positive readings, other less similar compounds should be unlikely to interfere. None of the pesticides screened bound irreversibly to the sensor, so poisoning is not a concern.

Miniaturization. The device based on the Ocean Optics spectrometer showed promise for both sensitivity and selectivity in detecting the agents on a smaller scale. Using the miniature spectrometer, the entire instrument fits on a board 3.5 ft × 2.5 ft. The limit of detection for this device was determined using the same procedure used to determine the limit of detection for the larger system. This system provides a limit of detection of 7 ppt using ~1 mW of 465.8-nm laser power and an integration time of 500 μs. The linear dynamic range of the device is from 7 ppt to 1 ppm using a 75-μm coating of polymer. Although the thinner coating limits the number of sites available for rebinding, thereby limiting the upper end of the dynamic range, it provides a faster response time for the sensor, on the order of 1 min at a pH of 12. Three averages were used for the determination of detection limit. Signal averaging and smoothing using the Savitzsky−Golay method was kept to a minimal 3 point average to get the required resolution. Figures of merit for this device are presented in Table 1.

CONCLUSIONS

Sensors for hazardous materials are characterized in terms of sensitivity, selectivity, response time, adaptability, and portability. The device described here shows benefits in all of these areas. The benchtop version provides a detection limit of 660 ppq, and the portable version a limit of 7 ppt. A high degree of selectivity is obtained by combining both chemical and spectroscopic selectivities, giving freedom from false positives. The 80% response time of the sensor is less than 8 min. The main size-limiting factor for the device is the argon laser and its power supply. However, recent advances in the field of blue LEDs may eliminate the need for the "large" laser, and further miniaturization is underway.

The technology developed here is also very adaptable. The sensor presented in this paper could be modified to detect new agents or species as they become available. Adaptation would include the design of a new molecularly imprinted polymer. A variety of sensors for both military and civilian use can be designed using this approach. Ideally, several of these devices could be coupled together to allow simultaneous detection for a wide array of chemical species. Devices such as the one described here could be used to detect the presence of chemical agents or pollutants near battlefields, in hospitals or military installations, or in community water supplies.

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