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Single fiber measurements for remote optical detection of TNT

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Single fiber optical measurements have been used to follow changes in the color of an initially clear poly(vinyl chloride) (PVC) membrane, which reacts with aqueous 2,4,6-trinitrotoluene (TNT) to form a colored product that absorbs strongly at 500 nm. Attempts to make this measurement via the effect of the colored product on the emission spectrum of a fluorophor incorporated into the PVC membrane were unsuccessful. However, single fiber absorption measurements were successful. Refractive index matching and a reflector behind the membrane to increase reflected intensity were essential to keeping the stray light levels small relative to the signal of interest. To compensate for drift, the reflected intensity at 500 nm is measured relative to the reflected intensity at 824 nm, a wavelength where intensity is not affected by color formation in the membrane. The rate at which the ratio of intensity at 500 nm to intensity at 824 nm increases is a function of TNT concentration. It is estimated that TNT levels below 0.10 ppm can be measured by this technique.

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PREFACE

This report was prepared by Yunke Zhang, W. Rudolf Seitz and Donald C. Sundberg, Departments of Chemistry and Chemical Engineering, University of New Hampshire. Funding for this research was provided by CRREL and the U.S. Army Toxic and Hazardous Materials Agency, Aberdeen Proving Ground, Maryland (R-90 Multi-Analytical Services), Thomas F. Jenkins and Martin H. Stutz, Project Monitors.

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Single Fiber Measurements for Remote Optical Detection of TNT

YUNKE ZHANG, W. RUDOLF SEITZ AND DONALD C. SUNDBERG

INTRODUCTION

We have developed an amine-containing plasticized poly(vinyl chloride) (PVC) membrane that reacts with trace amounts of aqueous 2,4,6-trinitrotoluene (TNT) to form a reddish-brown product (Zhang et al. 1988a,b, in press). This membrane can detect TNT in groundwater and munitions wastewater.

In previous work the colored product has been detected either visually or instrumentally. All instrumental measurements have been based on the absorbance of an exposed membrane relative to a reference membrane, which has been exposed to an aqueous blank. This procedure is suitable in the laboratory but is not readily implemented in the field.

The goal of the work reported here was to adapt the TNT-sensitive membranes to remote in-situ measurements through fiber optics. Rather than using a separate reference membrane, our goal was to design a system so that the intensity at the wavelength where the reddish-brown product absorbs would be compared to a reference intensity at another wavelength where the product does not absorb. The reference intensity should compensate for instrumental drift, variations in membrane optical properties, etc., such that the ratio of the two intensities depends only on the amount of reddish-brown product in the membrane. The reference intensity serves the same function as the reference membrane used in laboratory measurements.

Absorbance measurements through single optical fibers are subject to high levels of stray light from incident light reflected at interfaces where there is a change in refractive index (Coleman et al. 1984). Fluorescence measurements are less affected by this problem because the fluorescence is at a longer wavelength than the reflected intensity. Therefore, the first approach we tried was to incorporate a fluorophor into the PVC membrane. The idea was to measure fluorescence intensity at two sets of wavelengths. One set would be chosen so that either the excitation or the emission wavelength would be strongly absorbed by the reddish-brown product. The other set would be chosen so that it would be minimally affected by the reddish-brown product. The measured parameter would be the ratio of the intensities at the two wavelengths, which would change as the amount of reddish-brown product increased. However, all attempts to develop such a system encountered failure. The main problem is that PVC is a poor medium for fluorescence. We attribute this to the external heavy atom effect associated with the chlorine atoms on PVC.

Recently, Skogerboe and Yeung (1987) demonstrated the possibility of sensitive single fiber absorption measurements. The relative effect of stray light is minimized by two measures: refractive index matching minimizes the amount of light reflected at interfaces and a reflector behind the sample maximizes the intensity of the signal of interest, which is returned to the detector through the fiber. Skogerboe and Yeung's report inspired us to investigate the possibility of measuring the absorbance of the reddish-brown product directly through a single optical fiber. We have succeeded in demonstrating that such measurements are possible. The reference intensity is light at a wavelength that is not absorbed by the product.

MATERIALS AND METHODS

Materials

Membranes were prepared by the solvent casting procedure described previously (Zhang et al. 1988a,b, in press). A typical procedure involves a solution of 0.50 g PVC, 0.20 mL of dioctyl phthalate (DOP) and 0.20 mL of Jeffamine T403 in 10 mL of tetrahydrofuran (THF). This solution is poured into a Petri dish and solvent is allowed to evaporate away, leaving a clear elastic membrane. To prepare fluorescent membranes, the fluorophor was also dissolved in THF prior to membrane casting.

Sources for fluorophors were Eastman Kodak for coumarin 314, Aldrich for 9,10-diphenylanthracene, perylene and 3,4,9,10-perylenetetracarboxylic acid, and Molecular Probes, Inc., for the others.

Methods

Fluorescence spectra were measured on an SLM 8000 spectrofluorometer with a double excitation monochromator and a single emission monochromator. The bandpass for all measurements was 2 nm.

Single fiber absorption measurements were made with components of the SLM 8000 spectrofluorometer. The arrangement is shown in Figure 1. Light from the excitation monochromator of the SLM spectrofluorometer is focused into one arm of a four-port fiber optic coupler with glass-on-glass fiber having a 200-μm core diameter (ADC Corporation, Westborough, Massachusetts). This is accomplished with a specially machined hollow aluminum cylinder. One end of the cylinder fits over the end of the lens housing in the SLM sample compartment. The other end accommodates an SMA 905 style fiber optic connector on the coupler. In practice the aluminum cylinder is adjusted to the position that gives the greatest intensity on the detector and is then secured in place with a set screw.

Light is transmitted through the coupler and a splice to HCS plastic-clad silica fiber with a 200-μm-core diameter (Ensign-Bickford, Avon, Connecticut), which leads to the TNT-sensitive membrane. The end of the unused arm of the coupler

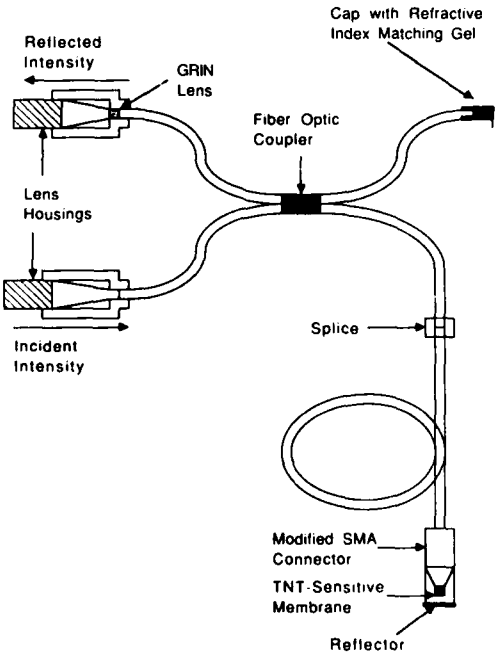

Figure 1. Experimental arrangement of coupling fiber optics to SLM 8000 spectrofluorometer. The lens housings extend into the sample chamber and provide the support for mounting the fiber optics to the spectrofluorometer.

is immersed in refractive index matching gel and covered with a black connector cap to minimize the amount of reflected light. Refractive index matching gel is also put in the splice to minimize reflection. Light from the TNT-sensitive membrane returns through the coupler directly to one of the photomultipliers of the SLM 8000, bypassing the emission monochromator. A Graded Refractive Index (GRIN) lens is used to focus light on the detector.

For many measurements the plastic-clad silica fiber was omitted, and the TNT-sensitive membrane was mounted directly on one arm of the coupler. Fiber ends were polished until a shiny surface could be observed under a microscope.

The membrane was attached to the end of the fiber as shown in Figure 2. An SMA style connector was put on the end of the fiber. The end of the connector was tapered with a file until it was only slightly larger than the fiber diameter. This makes the end of the fiber more accessible to the sample solution, increasing sensitivity. Epoxy resin, Norland optical adhesives, THF and a series of greases were evaluated as media for coupling the membrane to the fiber. Epoxy resins, THF and optical adhesives need to be cured for more than one day to get the membrane to adhere to the end of the optical fiber. THF may also cause the membrane to become cloudy when it is used as an adhesive. Because it best combined satisfactory adhesion with convenience, Thomas Lubriseal was used for most measurements. For best results a thin layer of the grease is applied to the end of the optical fiber. It is then put into water for a couple minutes to saturate the grease with water. A small disk of TNT-sensitive membrane is cut from a larger piece with a no. 18 syringe needle and pressed against the end of the fiber. The resulting sensor is placed in distilled water for several minutes and reflected intensity is monitored. A stable signal confirms satisfactory attachment between the membrane and the fiber.

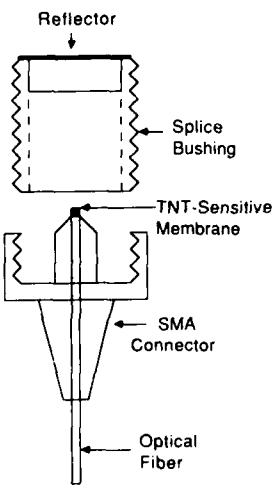

Figure 2. Schematic of sensor tip. The top part of the splice bushing under the reflector is filed away so that the sample solution has access to the TNT-sensitive membrane.

Although light reflected at the interface between the PVC membrane and aqueous sample provides a signal, it is weak because of the relatively small refractive difference between the two media. To minimize the effect of stray light on the signal, it is important to use a reflector. Two approaches were evaluated. One approach was to use metal grids of the type used to support samples for electron microscopy. Gold grids (200 mesh) and nickel grids (1000 mesh) were obtained from Polysciences, Inc. Epoxy resin was used to attach the grids to a splice bushing that fits into the SMA connector. As shown in Figure 2, most of the bushing near the grid was filed away to allow maximum contact between the sample and the membrane. The threaded bushing is inserted in the SMA connector so that the grid presses against the membrane, helping to hold it in place. Gold grids increased relected intensities by a factor of five while still allowing contact between the sample and the membrane.

Although the gold grid was used successfully, it is subject to several disadvantages: 1) gold has reduced reflectivity at 500 nm and below, 2) the grid blocks part of the surface, reducing the rate of membrane response, and 3) the epoxy resin used to glue the grid to the threaded tube can slowly spread over the grid, blocking contact with the sample after a week or so.

The nickel grid was found to be unsatisfactory because of poor reflectivity and lack of mechanical strength.

Because of the inconvenience of using the gold grid, an alternative approach using a stainless steel mirror was devised. A strip of stainless steel is glued into the end of the bushing in place of the grid. The bushing is threaded into the SMA connector until the mirror is about 1 mm away from the membrane. Advantages of this arrangement are that it does not block solution access to the membrane and reflects more light back into the fiber. Reflected intensities in-

creased by factors as large as 19 when the metal mirror was placed behind a clear membrane. However, this arrangement is subject to error if the sample absorbs at the wavelengths used to probe the membrane. Unlike the grid arrangement, the mirror does not help to hold the membrane in place.

Because the SLM 8000 spectrofluorometer was required for other projects, experiments evaluating the long-term response of membranes were conducted with a fiber optic photometer described previously (Zhang et al. 1988a). The membrane is placed on the common end of a bifurcated fiber optic bundle with a diameter of 3 mm. An incandescent source is used with filters for wavelength selection. For these measurements 660 nm was used as the reference intensity. Because this arrangement uses separate fibers to conduct light to and from the membrane, it is less subject to stray light. However, it is not as practical for remote in-situ field measurements, particularly if they have to be made over distances greater than a few meters.

RESULTS AND DISCUSSION

Preparation of fluorescent membranes

We incorporated several fluorophors into PVC membranes in attempts to develop a system in which exposure to TNT would change the relative intensities at two sets of wavelengths. The first fluorophor we tried was fluorescein. The isothiocyanate derivative of fluorescein was covalently coupled to Jeffamine T403 and incorporated into the membrane. However, the fluorescence efficiency was much lower in the membrane than in aqueous solution. Membranes containing large amounts of fluorescein (25 mg fluorescein isothiocyanate per 0.5 g PVC) fluoresced strongly. However, the absorption characteristics were dominated by the fluorescein rather than the product of the reaction between TNT and amine.

Next, 4-(N,N-dioctylamino-7-nitrobenz-2-oxa-1,3-diazole) was directly incorporated into membranes. However, as with fluorescein, very high amounts were required to get measurable fluorescence.

Pyrene isothiocyanate fluorescence was almost completely quenched when it was incorporated into the PVC membrane. Benzofluoranthene also failed to fluoresce strongly when incorporated into PVC. Diphenyl anthracene was incorporated into PVC, yielding moderately fluorescent membranes. However, the accumulation of brown product did not lead to measurable changes in spectral distribution.

Coumarin 314 did give a highly fluorescent membrane. However, it has only one emission band at 490 m. We observed no significant change in spectral distribution upon reacting the membrane with TNT.

The only fluorophor that showed promise was perylene. Intensities were greater than for the other fluorophors and the formation of the brown product did lead to observable changes in the shape of the perylene emission spectrum that could be related to TNT concentration. However, perylene is not stable in PVC. Instead the fluorescence signal decreases during membrane storage. We attribute this to aggregation of the perylene. Furthermore, absolute fluorescence intensities at all wavelengths decreased when membranes were exposed to TNT. We attribute this to fluorescence quenching by TNT, since nitro compounds are known to be efficient quenchers.

To avoid the aggregation problem associated with perylene we tried to covalently bond perylenetetraacetic dianhydride to Jeffamine T403. However, the reagent did not dissolve in the amine–THF solution and a fluorescent product could not be prepared.

Single fiber absorption spectra

Figure 3 shows single fiber absorption spectra for a membrane before and after exposure to 5 ppm TNT for 24 hours. Because this is a single beam measurement, the initial spectrum is simply the power spectrum of the lamp modified by the various optical elements that the beam traverses en route to the detector. After the exposure to TNT, reflected intensity decreases at the wavelengths where the reddish-brown product of the reaction between TNT and membrane absorbs.

Because it provides a strong signal at a wavelength far from the absorption band of the reddish-brown product, the band at 824 nm was chosen as the reference intensity. The TNT signal was measured at 500 nm, close to the absorption maximum for the reddish-brown product. The measured parameter was the ratio of the intensity at 824 nm to the intensity at 500 nm. Experimentally, we found that the initial values of the intensity ratio varied by as much as 7% from day to day. Therefore, response to TNT was meas-

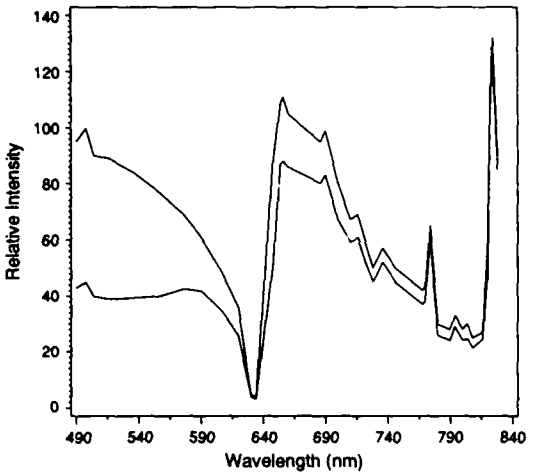

Figure 3. Single fiber reflectance spectra for TNT-sensitive membrane. The top spectrum is prior to exposing the membrane to TNT. The botton spectrum shows the decrease in reflected intensity after the membrane is exposed to a solution containing 5 ppm of aqueous TNT for 24 hours.

ured in terms of the percent increase in intensity ratio. This provides a common initial point for all measurements and can be implemented in the field.

Stray light

Stray light levels were measured as the residual reflected intensity at 550 nm for membranes exposed to high concentrations of TNT for extended periods of time, such that membrane transmittance was less than 1%. The lowest stray light levels were observed when the membrane was attached directly to one arm of the fiber optic coupler and the stainless steel reflector was used. Under these conditions stray light could be as little as 7.7% of the initial intensity observed before the membrane was exposed to TNT. When the gold grid was used as the reflector, stray light levels were typically on the order of 15% of the incident intensity for unexposed membranes. Stray light levels did not change when the room lights were switched off, indicating that ambient room light is not significantly contributing to the observed stray light levels.

When the membrane was placed on the end of the plastic-clad, fused silica fiber, which was spliced to the fiber optic coupler, the stray light level increased significantly. Typical stray light levels were 18% of the initial intensity with the stainless steel mirror as the reflector and 28% with the gold grid membrane. Two factors contribute to this increase. One is reflection at the interfaces in the splice. The other is the intensity loss at the splice. Both factors can be improved if the same type of optical fiber is used throughout instead of coupling glass-on-glass fiber with a low numerical aperture (0.20) to plastic-clad fused silica with a higher numerical aperture (0.37).

Intensity levels

Reflected intensity levels are typically 500 times greater than the dark current of the photomultiplier. This is a significant advantage of single fiber absorption measurements relative to single fiber fluorescence measurements. Single fiber fluorescence measurements are reduced in intensity for several reasons, including: 1) indicator levels are usually too low to absorb all incident radiation, 2) because fluorescence goes off randomly in all directions, only a small fraction of the total emitted intensity is collected by the fiber, and 3) fluorescence quantum yields are often significantly less than unity. As a consequence, single fiber fluorescence measurements often require high incident intensity, which can lead to problems caused by photodegradation. In contrast, single fiber absorption measurements are possible with much weaker incident intensities. TNT detectability will be limited by drift in the background rather than variability in measured intensity values.

Response to TNT

Figure 4 shows the percent increase in intensity ratio as a function of exposure time for separate pieces of membrane exposed to solutions with 0, 1, 2, 4, 8 and 16 ppm of aqueous TNT. These data are measured with the membrane attached directly to one arm of the fiber optic coupler. The data curve upward slightly, an effect most evident at the higher concentrations. This is expected given the logarithmic relationship between absorbance and concentration. For solutions with 16 ppm of TNT, response becomes level at long exposure time as the membrane absorbance becomes large, and stray light becomes the main contributor to the intensity at 500 nm.

Figure 5 shows the intensity ratio at 3, 9 and 23 hours as a function TNT concentration. Response approaches linearity, falling off at high concentrations, which correspond to high membrane absorbances.

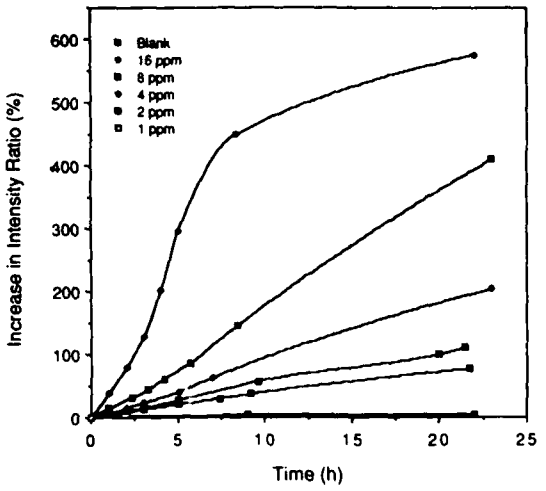

Figure 4. Percent increase in the ratio of intensity reflected at 824 nm to the intensity reflected at 500 nm as a function of time for various TNT concentrations.

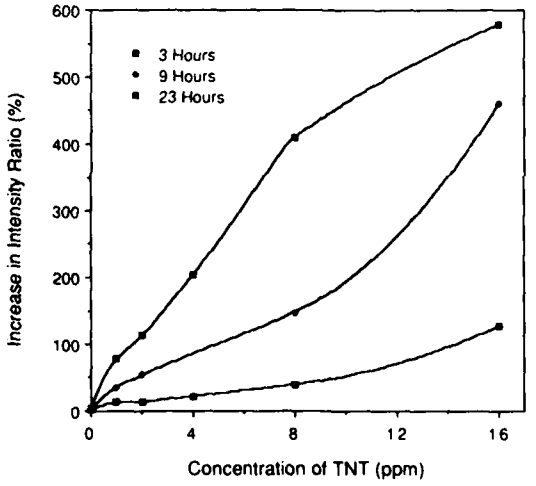

Figure 5. Percent increase in intensity ratio as a function of TNT concentration for membranes exposed to TNT for 3, 9 and 23 hours.

In field applications, membranes are likely to be exposed to the sample for several days. Therefore, an experiment was undertaken to determine the long-term stability of the intensity ratio. The results of this experiment are shown in Figure 6. Over 9 days the intensity ratio slowly drifts upward by an average of about 2% per day. This compares to an increase in intensity ratio of 76% per day measured for solutions containing 1 ppm of TNT. This indicates that it

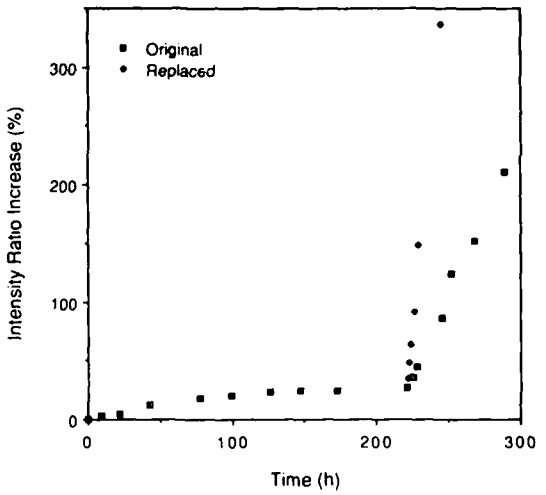

Figure 6. Percent increase in intensity ratio for a membrane exposed to aqueous blank for nine days, then exposed to a solution containing 10 ppm of aqueous TNT. This experiment was performed with a filter photometer using reflected intensity at 660 nm as a reference.

should be possible to detect TNT concentrations at levels slightly below 0.10 ppm.

Figure 6 includes data showing response to solutions containing 10 ppm of TNT after 9 days exposure to an aqueous blank. When the sensor was removed from the blank and immersed in 10 ppm TNT, the intensity ratio increased relatively slowly because some of the aqueous blank solution remained in the immediate vicinity of the membrane. When the membrane was replaced by another piece that had also been exposed to aqueous blank for 9 days, the intensity ratio increased much more rapidly because there was no blank contamination of the sensor. Both sets of data are shown.

CONCLUSIONS

We have demonstrated that trace levels of aqueous TNT can be measured remotely by coupling a TNT-sensitive PVC membrane to single fiber absorption measurements. The procedures are amenable to convenient field implementation.

TNT detectability is limited by instrument drift. Consequently, any further work on response to TNT should be done on an instrument designed for field measurements. Such an instru-

ment is available at Lawrence Livermore National Laboratory. Although designed for fluorescence, it is readily adapted to single fiber absorption measurements.

We have developed a membrane and reflector arrangement that has performed well in laboratory measurements. However, problems may be encountered in the field. The stainless steel mirror may be subject to fouling or corrosion. Furthermore, any obstruction to light in the zone between the mirror and membrane will interfere with the measured intensity values. In the field, it may prove to be more practical to make measurements with the gold grid pressed against the membrane. Field applications may also require a more robust means of attaching the membrane to the single fiber so that it can't be dislodged mechanically.

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