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Development of a membrane for in-situ optical detection of TNT

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19. ABSTRACT (Continue on reverse if necessary and identify by block number) A membrane has been developed for in-situ determination of polynitroaromatic hydrocarbons in ground-water at levels as low as 10 ng/mL. A typical membrane is prepared by dissolving the following in tetrahydrofuran: 0.5 g poly(vinyl chloride) (PVC), 0.2 mL dioctyl phthalate to serve as a plasticizer and 0.12 mL Jeffamine T403, a polyoxyethyleneamine that also acts as a plasticizer, as well as reacting with polynitroaromatic hydrocarbons to produce a colored product. The membrane is formed by casting the solution into a glass Petri dish with a diameter of 8 cm and allowing the solvent to slowly evaporate. Trace amounts of 2,4,6-trinitrotoluene (TNT), 1,3,5-trinitrobenzene (TNB), 2,4,5-trinitrotoluene (2,4,5-TNT), and methyl-2,4,6-trinitrophenyl nitramine (tetryl) react with the membrane to produce a visually observable reddish brown color. No pretreatment of water samples is required. Recoveries of 0.1 to 4.0 ppm TNT from spiked groundwater ranged from 95% to 105%. Direct analysis of water samples agreed with HPLC results.					
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PREFACE

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

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Development of a Membrane for In-Situ Optical Detection of TNT

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

INTRODUCTION

One of the Army's most serious water pollution problems is how to dispose of wash waters used to clean equipment and interior surfaces at munition manufacturing and demilitarization facilities. Walsh et al. (1983) have estimated that up to two million liters of this type of wastewater is generated daily from a single production line. Although this water is pumped through a carbon adsorption column prior to discharge, small amounts of compounds such as TNT remain in solution and larger amounts can escape if the carbon adsorption column is not replaced in time. Because of the possibility that these munitions can reach groundwater, it is necessary for the Army to periodically determine whether groundwater has been contaminated. Currently, this requires that a well be drilled so that groundwater samples can be brought to the surface for analysis in the laboratory.

The goal of this project is to develop a system for in-situ optical detection and estimation of 2,4,6-trinitrotoluene (TNT) in groundwater, which would reduce the need to collect groundwater samples for laboratory analysis. Earlier we reported that plasticized poly(vinyl chloride) (PVC) membranes containing primary and secondary amines react with aqueous TNT to form a brown product that can be detected either visually or instrumentally through fiber optics (Zhang et al. 1988). While these membranes showed promise for an in-situ optical device for estimating TNT, they were unstable. In contact with water, amine was leached from the membrane, causing it to lose sensitivity. Also, membranes in contact with water became cloudy after a few hours, interfering with the optical measurement of TNT concentration.

In the past year we have formulated new membranes that are more stable in both air and water. We have shown that plasticized PVC membranes extract TNT from aqueous solution even when amine is not added to the membrane. We have evaluated the effects of pH, membrane thickness

and time on response to TNT and have shown that the membrane reacts with several different polynitro aromatic hydrocarbons to form a colored product. Using the new formulation, we have established that the membranes respond as expected to field samples provided by the Army.

RESULTS AND DISCUSSION

Choice of poly(vinyl chloride)

The original PVC used for making the membrane was prepared by emulsion polymerization. It contains residual surfactant with ionic functional groups that act as sites for water accumulation in the membrane (Van der Berg et al. 1987). The small pockets of water that develop within the PVC are responsible for membrane cloudiness.

Four other types of PVC were evaluated this year: Geons 142 and 143 from B.F. Goodrich, reagent grade PVC from Aldrich, and 1.8% carboxylated PVC from Aldrich. The 1.8% carboxylated PVC was the least suitable for this application. Membranes prepared from this material rapidly became cloudy in contact with water because the carboxyl groups act as hydrophilic sites that attract water. The best PVC is Geon 143. Unlike the earlier PVC we used, Geon 143 is prepared by a bulk polymerization process, which does not require added surfactant. Membranes prepared from this material remain clear for months in contact with water. They can be exposed to aqueous TNT for longer periods, allowing more of the brown product to form, which results in lower reporting limits.

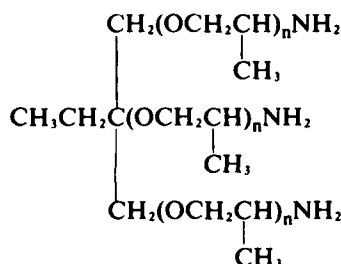
Because membranes prepared from Geon 143 remain clear in water, their spectral properties in the visible and ultraviolet regions of the spectrum, down to 300 nm, can be examined directly by transmission spectroscopy. This was done using a Shimadzu double beam recording spectrophotometer. An unexposed membrane was used as a reference. Before recording a spectrum, we adjusted

the absorbance at 800 nm to zero to compensate for any differences in optical properties between the reference and sample membranes.

Choice of amine

The primary amines used in formulating TNT-sensitive PVC membranes are subject to leaching. They can dissolve in water or can volatilize in air. Furthermore, if they are not chemically compatible with PVC, they will tend to segregate into a separate phase during membrane preparation.

Our efforts were directed toward finding a primary amine similar in structure to PVC plasticizers. After attempts to synthesize some amino esters to serve as plasticizers, we learned that a commercial polyoxyalkyleneamine is available from Texaco Chemical Company under the trade name Jeffamine T403. This material is formed by causing trimethylolpropane to react with propylene oxide followed by amination of the terminal hydroxyl groups. The structure of Jeffamine T403 is shown below:



The average molecular weight is 403. The sum of the three "n" values is between 5 and 6 per molecule and the primary amine content is 6.1 mmol/g.

Unlike the aminoester of sebacic acid that we prepared last year (Zhang et al. 1988), Jeffamine T403 is highly soluble in tetrahydrofuran (THF), the solvent used for preparing membranes. Furthermore, it is sufficiently chemically compatible with PVC that it can serve as a plasticizer. Membranes formed from PVC and Jeffamine T403 without the addition of any other plasticizer are clear and respond sensitively to TNT. However, because high concentrations of Jeffamine T403 are subject to leaching in water, we found that it was better to incorporate dioctyl phthalate (DOP) into membrane formulations to serve as the primary plasticizer.

Membrane preparation

Membranes are prepared by solvent casting from THF. Exposure to the atmosphere is minimized to avoid absorption of water vapor.

We consider the best procedure to be the following. PVC (0.5 g) is placed in a 25-mL glass beaker, which has been dried at 130°C. After 11.0 mL of anhydrous THF is added, the beaker is covered with a piece of Parafilm to prevent contact with the atmosphere. The PVC gels in about two hours. After it has gelled, the beaker is gently heated and the contents are stirred to make a homogeneous solution. DOP (0.20 mL) and Jeffamine T403 (0.12 mL) are added. Gentle warming and stirring is continued until all components are well mixed and the solution appears clear and completely uniform. The solution is then added to a dried and warmed Petri dish (8.8 cm diam) and covered with a layer of dry Kimwipes or ordinary filter paper. After three days or more, a clear membrane will form that is ready for use.

Effect of dioctyl phthalate

DOP serves as a plasticizer, keeping the membrane soft even after significant loss of amine. This makes the membrane easier to handle. The presence of DOP in the membrane increases the rate of diffusion for both TNT and amine, leading to a faster response. DOP may also help to keep the amine in the membrane while excluding water.

If too much DOP is added, membranes tend to become cloudy in water. A 2:5 DOP-PVC ratio was found to be optimum and was used to obtain all the results reported here.

Response mechanism

To confirm the roles of DOP and amine, we conducted the following experiment. Three membranes with similar weights and surface areas were prepared with the following:

1. 0.80 g pure PVC
2. 0.50 g PVC and 0.30 mL DOP
3. 0.50 g PVC, 0.20 mL DOP and 0.10 mL amine.

We put 15-cm² sections of each membrane into 30-mL portions of a solution containing 2 ppm TNT and into 30-mL portions of TNT-free solvent. For each of these solutions, the absorbance of TNT at 230 nm was monitored as a function of time and compared to the absorbance of a control 2-ppm TNT solution prepared at the same time. No change in TNT absorbance was observed for the solution containing the pure PVC membrane; TNT did not partition into pure PVC to a significant extent.

Figure 1 shows the change in TNT concentration versus time for the plasticized membranes with and without amine. The absorbance of the so-

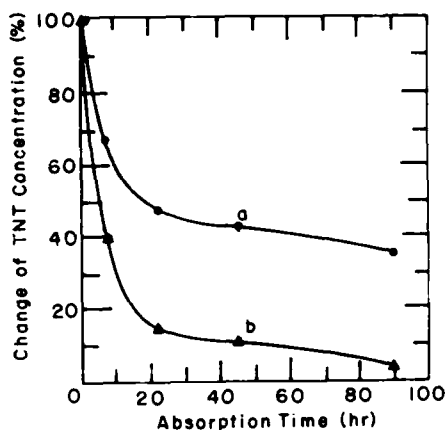


Figure 1. Absorption of TNT by a) membrane without amine; b) membrane with amine.

lution containing the plasticized membrane without amine decreased rapidly at first, then more gradually, approaching a steady state after 90 hours. If it is assumed that the decrease in TNT concentration in solution is due only to partitioning into the membrane, the partition coefficient can be calculated to be 272, where the partition coefficient = [TNT] in membrane / [TNT] in water.

The decrease in solution concentration of TNT with time is greater for the membrane containing amine because reaction with amine depletes free TNT in the membrane, causing more to diffuse in.

Membrane response to other explosives

Besides 2,4,6-TNT, the membrane also reacted with 2,4,5-TNT, methyl-2,4,6-trinitrophenylnitramine (tetryl) and 1,3,5-trinitrobenzene (TNB),

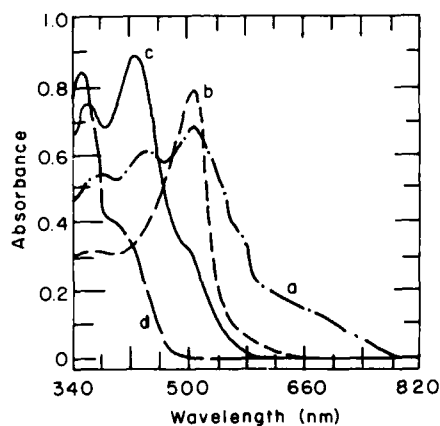


Figure 2. Absorption spectra of membrane to a) TNT, b) TNB, c) tetryl, d) 2,4,5-TNT.

forming colored products. However, the absorption spectra of the products differ for different explosives. Figure 2 shows absorption spectra for 2-cm² pieces of membrane exposed to 200 mL of each explosive in water for 24 hours. The analyte concentrations were 5 ppm, except for 2,4,5-TNT, which was 2 ppm. Differences in the absorption spectra mean that the membrane can be used to discriminate among different polynitroaromatic hydrocarbons.

Experiments indicated that the membrane does not react with hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) or octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) to form a colored product. With 2-amino-4,6-dinitrotoluene (amino-DNT), we saw a light yellow color. The spectrum corresponded to the solution absorption spectrum of amino-DNT. Thus, amino-DNT is preconcentrated by the membrane, but it does not react with the amine. We believe that RDX and HMX also enter the membrane. However, their absorption is at a shorter wavelength, where it is obscured by the intrinsic absorption of the membrane.

Membrane stability

Membranes prepared from Geon 143 with the optimum amount of DOP remain clear in water indefinitely. However, the Jeffamine T403 still tends to leach from the membrane, although at a much slower rate than amines used previously. Therefore, experiments were undertaken to characterize the leaching process. Loss of Jeffamine T403 from membranes stored in air was determined by elemental analysis for nitrogen. Figure 3 shows the decrease in relative amine content of the membranes as a function of storage time. While there is

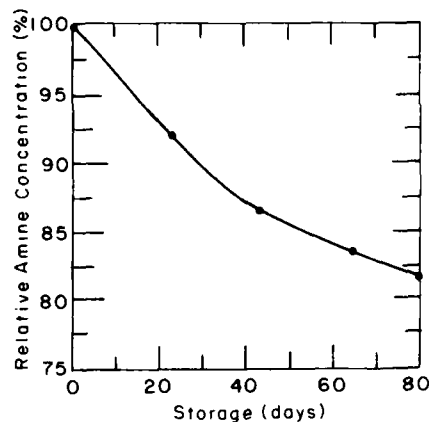


Figure 3. Amine loss during storage.

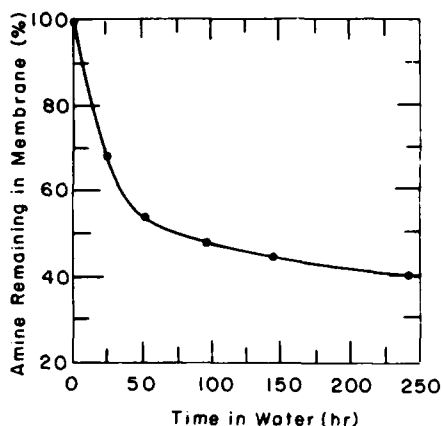


Figure 4. Amine loss in water.

a measurable loss of amine, over 80% of it remains in the membrane after storage for 80 days. Furthermore, the rate of amine loss appears to be decreasing with time.

It is difficult to satisfactorily dry membranes exposed to water. As a result, leaching of amine from membranes stored in water was evaluated by a titration technique. Pieces of membrane with an area of 60 cm² (corresponding to 0.80 g) were placed in 30.0 mL of distilled water. After exposure for a known period of time, the leached amine was titrated with 0.012 N HCl, which was standardized against Jeffamine T403 using methyl orange as the indicator. Results are shown in Figure 4. The initial leaching rate is quite high, but it decreases with time. At the point where 50% of the amine has left the membrane, the leach rate is less than 1% of the remaining amine per day.

The initial high leaching rate may be influenced by two factors. One is that there may be an excess of amine at the membrane surface prior to exposure to water. The second is that the fresh membrane may be oversaturated with amine. By decreasing the amount of amine used when preparing the membrane it may be possible to make membranes that are more resistant to leaching. However, they will not be as sensitive to TNT.

We also conducted experiments in which membranes were soaked in water prior to being exposed to a sample containing TNT. A membrane was soaked in distilled water for 10 days and then exposed to a well water sample spiked to contain 0.10 ppm TNT. The absorbance after 10 days was 0.15. A fresh membrane exposed to the same sample for the same period of time gave an absorbance of 0.24.

In another experiment, membrane stored in a pH 7 blank solution for over a month was shown to respond to 1 ppm TNT, giving an absorbance of 0.13 after 24 hours.

In actual practice, membranes will not be exposed to water prior to use. Thus, present membrane formulations are sufficiently stable for practical use, although it would be advisable to evaluate the effect of long-term storage in air (i.e., 1 or 2 years), on the sensitivity of response.

Effect of pH on response

The influence of pH on the membrane's response to TNT was evaluated by exposing 2-cm² pieces of membrane to 200 mL of 2-ppm-TNT solutions adjusted to the following pH's: 4.96, 6.10, 7.00, 7.90 and 8.80. Acetate buffer was used for the pH 4.96 solution, trishydroxyamino-methane for pH 8.8, and phosphate for the middle three pH's. Figure 5 shows absorbances measured after 12 and 24 hours. For the pH range from 6.0 to 8.8, the 12-hour response was not significantly influenced by pH. However, at pH 5, initial color formation is weaker and gradually disappears with time. At the lower pH, there is a stronger tendency for the Jeffamine T403 to be protonated. Furthermore, the acetic acid used in the buffer system is a neutral molecule, which may be able to enter the membrane and interact with the Jeffamine, interfering with its ability to react with TNT. In any event the membrane may not be suitable for analysis of acidic environmental samples.

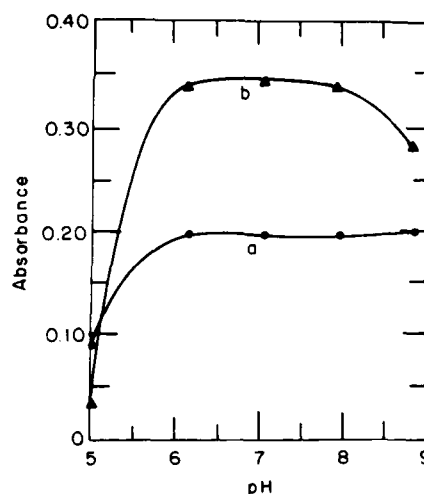


Figure 5. Response to TNT at different pH solutions. a) Absorbance at 12 hours; b) absorbance at 24 hours.

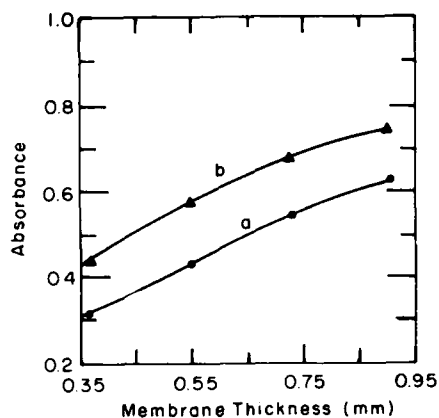


Figure 6. Response to TNT of different membranes a) at 20 hours; b) at 38 hours.

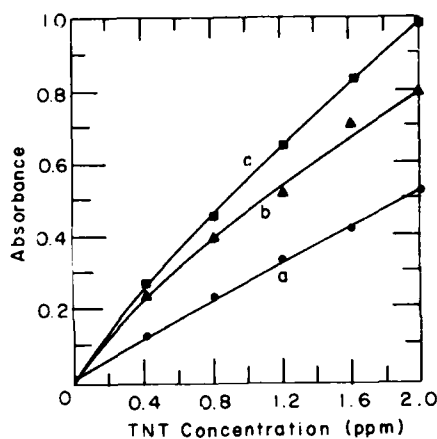


Figure 7. Response of membrane to TNT standard solutions for three different membranes (a-c).

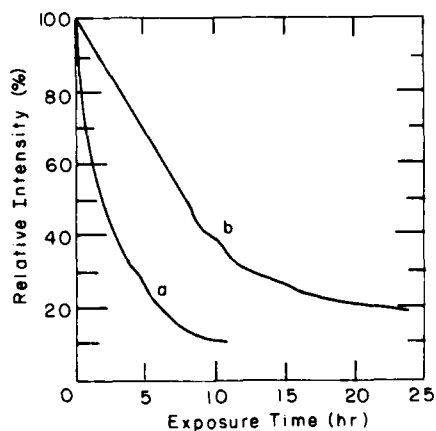


Figure 8. Intensity changes with time monitored by fiber optic photometer in 2-ppm solutions (a) and in 10-ppm solutions (b).

The 24-hr response to TNT was slightly smaller at pH 9 than at pH 6 to 8. However, this effect is not very large and should not interfere with the projected use of the membrane.

Effect of membrane thickness

Increasing the thickness of the membrane leads to an increase in sensitivity, as shown in Figure 6. However, the membranes that were 0.72 and 0.90 mm thick tended to be slightly cloudy. Most measurements were made with 0.36-mm-thick membranes.

Response to TNT

Absorbance is proportional to TNT concentration for a constant exposure time, provided the total absorbance remains low. Figure 7 shows response curves for pieces of the same lot of membrane exposed to a series of TNT standard solutions at pH 7 for different period of time. The membrane area was about 2 cm², the sample volume was 200 mL and the exposure time was 24 hours. Measurements were made using a spectrophotometer with an unexposed membrane as a reference as described in the *Choice of Poly(vinyl Chloride)* section.

Figure 8 shows reflected intensity versus time monitored continually with the fiber optic photometer using the method described in Zhang et al. (1988). While there is a rapid decrease in intensity initially, the intensity tends to approach a constant value at high exposure. We found that the shape of the absorption spectrum changes for highly exposed membranes. The shorter wavelength bands get stronger at the expense of the main band at 510 nm.

Application to real samples

We received five uncontaminated groundwater samples from CRREL that we used for recovery studies. The pH of the well water was 7.6. Portions of the well water were spiked to contain 0.10, 1.0 and 4.0 ppm TNT. The absorbances of membranes exposed for 24 hours to the spiked well water were compared to the absorbances for a series of standard solutions. The calculated percent recoveries were 105, 103 and 95% for 0.10, 1.0 and 4.0 ppm TNT, respectively.

The other four samples all had pH's close to 7.0. They were analyzed for TNT at the University of New Hampshire using the TNT-sensitive membrane and at CRREL by RP-HPLC (Jenkins et al. 1985). Results are summarized in Table 1.

Table 1. Comparison of results obtained with the membrane and results obtained with RP-HPLC.

Sample no.	Measured by membrane (ppm TNT)	Measured by HPLC (ppm TNT)
1	87	103
2	< d*	< d
3	< d	< d
4	18	17.7

* Below detection limits.

Because the concentrations of samples 1 and 4 were so high, they were diluted prior to analysis by factors of 10 and 2 respectively. Membranes were exposed to a sample for 24 hours to get a strong signal. Absorption spectra run on membranes exposed to samples 1 and 4 were identical to spectra for samples exposed to aqueous TNT standards, confirming that the observed membrane color was caused only by TNT. The RP-HPLC results also showed that no other polynitroaromatic hydrocarbons were present. The samples as received were colored and turbid; however, this did not interfere with the TNT measurement.

CONCLUSIONS AND FUTURE DIRECTIONS

We have prepared membranes that respond sensitively and selectively to TNT and other polynitroaromatics. While questions remain concerning extended shelf life, stability of the membranes is otherwise adequate to screen groundwater samples for TNT. The membranes have responded accurately in field samples tested to date. The membranes can be used for either visual or instrumental detection. At this point, we believe our membranes are ready for more extensive field testing.

Further work needs to be done if these membranes are to be adapted to remote in-situ measurements through fiber optics. We plan to pursue the possibility of single fiber absorption measurements at the University of New Hampshire. We also hope to collaborate with Lawrence Livermore National Laboratory to develop a fluorescence-based approach if funding is available.

The membranes responded to polynitroaromatics and can even distinguish different polynitroaromatics if the visible absorption spectrum is recorded. However, they do not respond to HMX or RDX. According to Wyant (1977), RDX can be determined by reducing it in the presence of naphthylamine. We would like to try to incorporate this reaction into the PVC membrane to get a membrane that would be sensitive to RDX.

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