"Science in Motion"

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Downhole Sensor for Long-Term Monitoring of Groundwater for Contamination by Explosives

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Downhole Sensor for Long-Term Monitoring of Groundwater for Contamination by Explosives

Introduction

This report concludes and details the efforts expended during 2004 and 2005 by Nomadics under the bridging effort for SERDP Project CU-1298. The scope of the work performed involved miniaturizing the SERDP Project CU-1298 Phase I explosives sensor in order to deploy the sensor in a two-inch groundwater monitoring well without compromising the performance of the sensor, as well as adding data logging capability to the sensor.

A prototype sensor capable of deployment in a two-inch groundwater monitoring well was constructed and tested extensively in the lab, and its performance is comparable to the previous laboratory prototype constructed under SERDP CU-1298 Phase I. Hence, the project objectives were successfully accomplished.

Technical Objective

The integration effort involved miniaturizing the flow cell, optics stack, PC board, and supporting hardware. A miniaturized prototype sensor was constructed, assembled, tested, and debugged. This prototype sensor was engineered using technology from two other Nomadics sensors, an underwater TNT sensor (SeaDog) and the Fido® TNT vapor sensor (Fido). Both sensors employ patented Amplifying Fluorescing Polymer (AFP) technology. The vapor sensor is capable of detecting TNT at the parts-per-quadrillion level, and the aqueous phase sensor can detect TNT in water at low parts-per-billion levels. Both sensors have been tested extensively in the field.

Several technologies have been borrowed from the Fido sensor and used in the prototype sensor including data logging capability. Data logging was implemented in order to record data while sampling, which will allow users to analyze the traces for TNT presence at a later time. The existing hardware from the previous SERDP effort was too large to meet the size requirements for deployment in a two-inch well. Therefore, the optics stack, flow cell, and circuit board were miniaturized in order to achieve this goal.

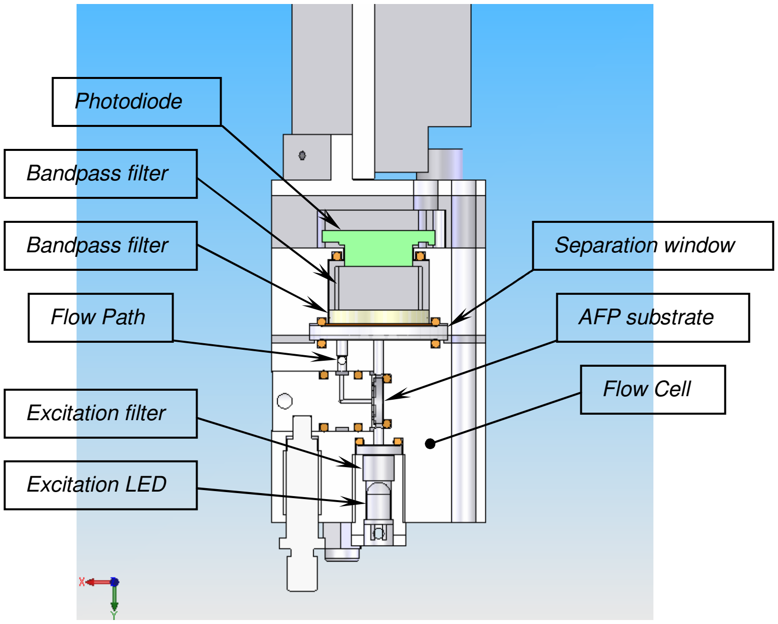

Figure 1 – Flow Cell Cross-section

The new prototype TNT sensor consists of a photodiode, two bandpass filters, a sapphire separation window, a sapphire substrate coated with AFP, and an excitation filter and LED (Figure 1).

Scope of Work

The project consisted of five distinct tasks:

1) **Prototype Design** - Design a prototype sensor that would meet the specified size requirements while retaining the capability of detecting low parts-per-billion levels of TNT in water.

2) **Optimize Prototype** - Optimize the operation of the prototype sensor by designing a miniaturized circuit board, which employs the standard Fido operational controls.

3) **Plumbing Control** - Design the prototype sensor software to control pump activity as well as control and actuate a 3-position valve.

4) **Data Logging** - Incorporate data logging into the board design.

5) **Test Results** - Test and debug the prototype sensor in the laboratory and report results.

Each of the above tasks and the accomplishments that accompany those tasks will be discussed in detail.

Prototype Design

The miniaturization of the sensor was accomplished by constructing a flow cell in which samples are introduced at normal incidence to the AFP-coated substrate. The AFP film is excited by light from an LED. Light from the LED is injected into the edge of the substrate which functions as a planar waveguide. The intensity of fluorescence exiting the edge of the substrate is measured with a photodiode.

Flow Cell

The flow cell is the analysis chamber for TNT-contaminated groundwater. Three-dimensional models of the prototype assembly were completed using SolidWorks (an engineering design software package) to aid in visualization of the prototype (Figure 2). 3D models were created and design reviews held before any parts were machined.

The first and second revisions of the flow cell included several large-volume voids within the flow path, which caused air bubbles to collect. The flow path was optimized in the third design revision by removing the voids from the flow path. By breaking the surface tension in each bubble using the high face velocity of the water, bubbles can effectively be cleared from the sensor. It was observed that bubbles could be injected into the flow path and would exit the flow cell (See Lessons Learned and Discussion).

Optics Stack

The optics stack design was borrowed from Fido. This design was modified so it could be housed in a round container (Figure 2), which meets the size requirements. The optics stack has been tested in the lab and functions as designed.

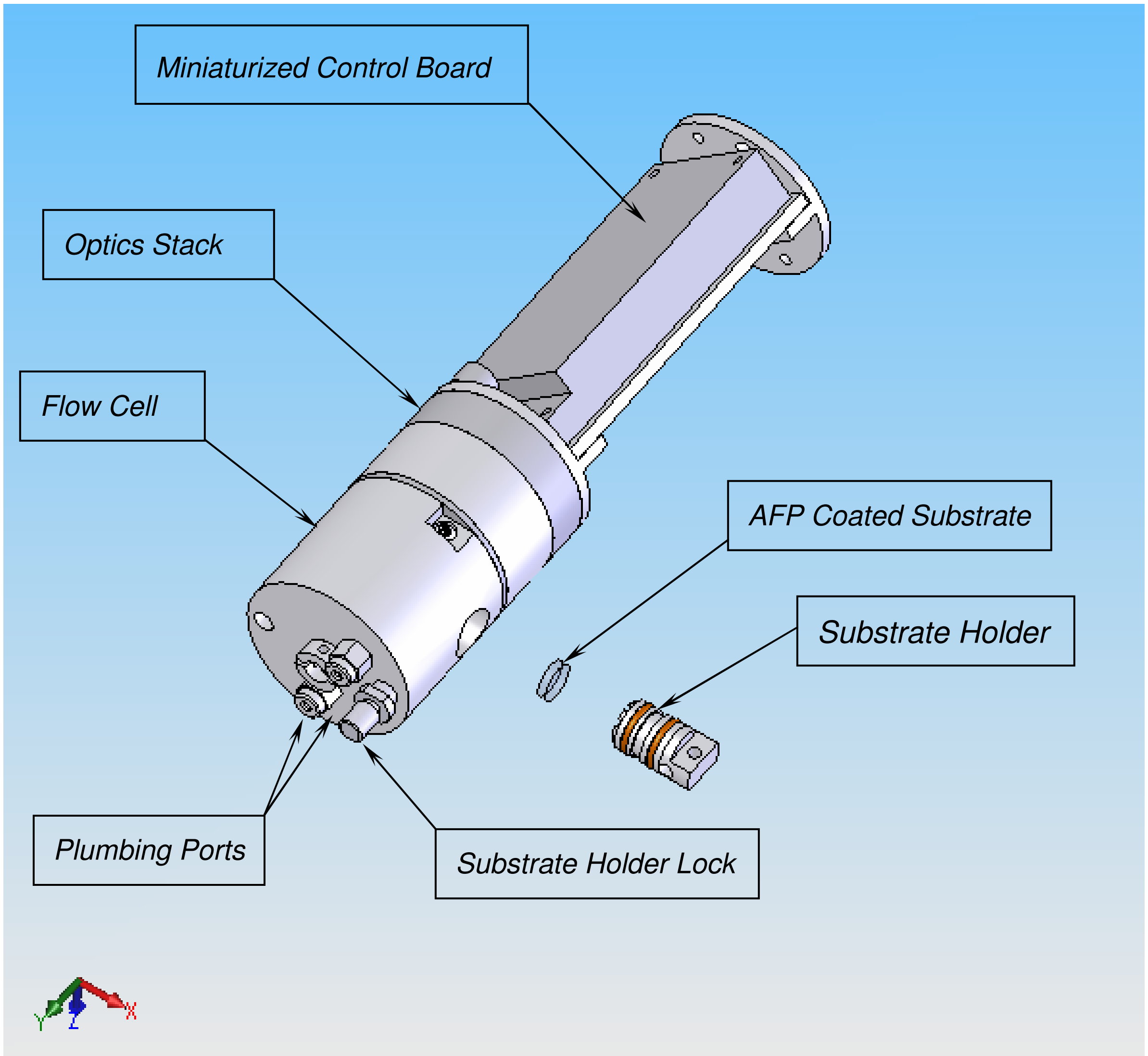

Figure 2 – 3D SolidWorks Model of Prototype

Prototype Construction

All wetted parts were made from 304 stainless since the design is still in the prototype stage. 304 stainless has a better free machining index than 316 stainless, but is not as corrosion resistant as 316 stainless. When a field-deployable sensor is built, 316 stainless will be the material of choice as it has molybdenum added for corrosion resistance.

Substrate Holder

The substrate holder was redesigned to fit into the side of the flow cell (Figure 3). The flow path was redirected through the center of the substrate holder so the flow is introduced against the round face of the substrate at normal incidence. The substrate holder has been tested in the lab and functions as designed. A change in the substrate excitation method was discussed, which meant changing the flow chamber design to include wetting only one side of the substrate and sealing off the substrate in a chamber of its own, removed from the water-filled flow chamber.

However, this design was not implemented due to time constraints.

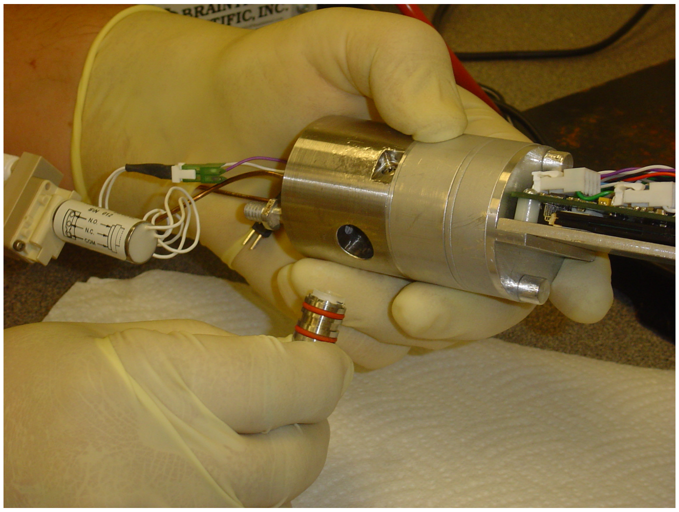

Figure 3 – Substrate Insertion Water Filtration

In order to create a stable baseline for comparison, the sensor is designed to first draw a sample of TNT-free water into the sensor and then take a reading to establish the baseline fluorescence intensity. Next, a sample of potentially contaminated water is drawn into the sensor and another reading is taken. Finally, the two readings are compared to determine if the fluorescence was reduced by target analytes in the sample. TNT-free water is supplied by extracting nitroaromatics and other organics by passing the water through an activated charcoal filter. The pump will draw water at low flow through this filter for two reasons. The first reason is to sorb explosives from the water, providing an explosive-free baseline. Second, flows are low to prevent work-heating the water that can result in fluctuations in baseline emission intensity.

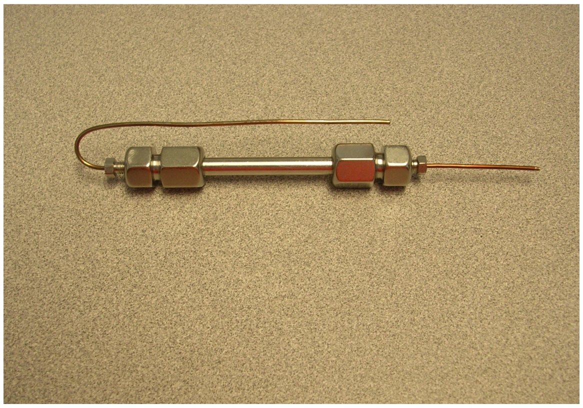

Figure 4 – Carbon Filter

As testing began, a carbon filter was purchased and installed (Figure 4). The filter is constructed from 316 Stainless Steel. Glass Wool was packed in the ends of the filter to trap any carbon particles from lodging in the pump.

It was observed that the MicroPump did not have the dynamics to defeat the pressure impedance offered by the carbon bead bed (see the Plumbing Control section below). Therefore, the carbon filter was removed from the flow system for lab testing purposes. Since the filter was removed from the plumbing and the system still needed to switch from clean water to contaminated water, one valve inlet was submersed in a beaker containing de-ionized water while the other valve inlet was submersed in a beaker containing aqueous TNT or a solution of the interferent being tested. As part of future development, a pump capable of handling the pressure impedance of the carbon bed will be substituted for the MicroPump.

Optimize Prototype

Miniaturized Circuit Board

The circuit board technology was borrowed from Fido. The Fido circuit board contains the circuitry necessary to operate the Fido sensor. However, in order to make the circuit board smaller in size, some sensor functionality was eliminated. All standard Fido functionality was retained except for the following:

- Dual channel output
- Audio channel output
- LCD display output
- Battery operation

The miniaturized circuit board was designed to be 1.5" W x 3.5" L (Figure 5). Once the new boards were available, the new design was tested and shown to retain full functionality with the exception of the removed features listed above. Within experimental error, the sensor performs at essentially the same level as the earlier lab prototype.

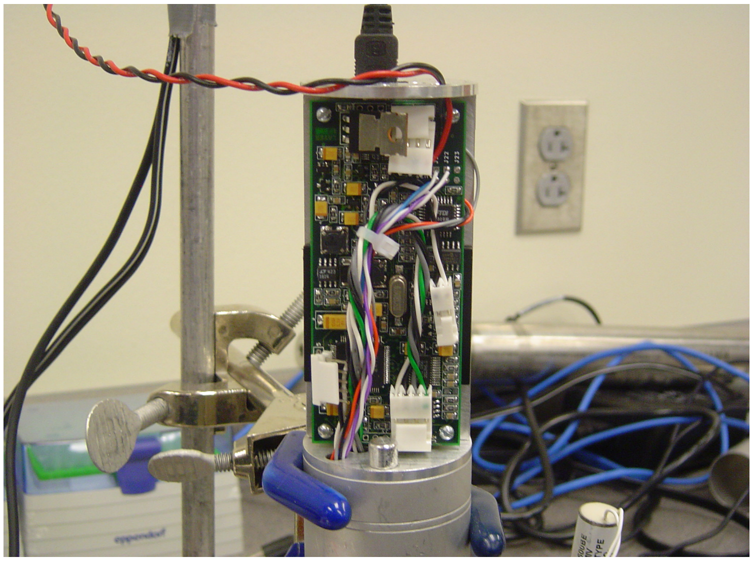

Figure 5 – Miniaturized Circuit Board

Plumbing Control

Pump System

The flow cell, optics, and smaller board were assembled and tested as a unit using a MicroPump MZR-2921 as the pump (Figure 6). The MicroPump is a micro-annular gear pump, a reliable pump type for handling high differential pressure in downhole applications such as this. As this sensor will be deployed up to approximately 100 feet below the earth's surface, static pressure is estimated to be 3 Bar or 45 PSI. Several pumps were considered but most of the low flow high/pressure pumps on the market are diaphragm pumps, which rely upon the diaphragm being able to oscillate back and forth to create differential pressure. The MicroPump is a micro-annular gear pump, which relies upon rotary motion of the internal gears to create differential pressure.

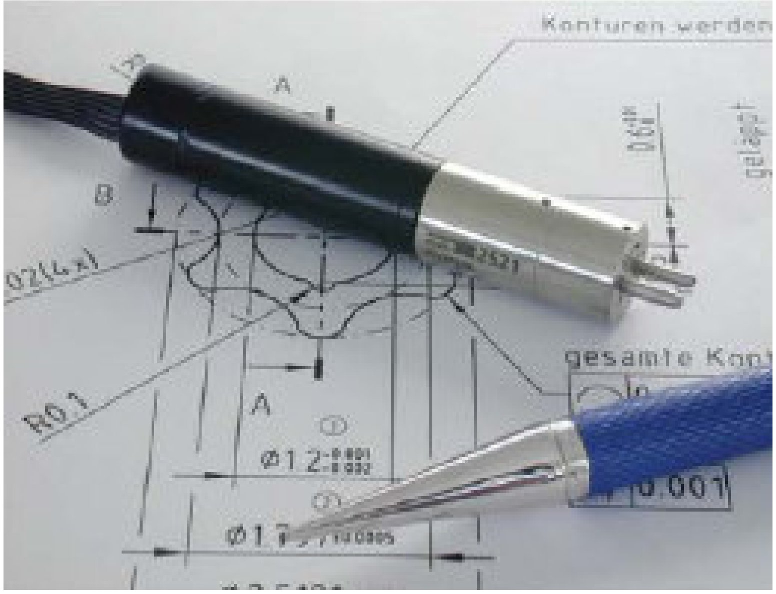

Figure 6 – MicroPump

In order to reach steady state, a control system was needed to control the pump flow rate. A software algorithm was programmed and added to the sensor firmware to control the flow rate. However, an optimal flow rate was not achievable using the MicroPump. Erratic flow was observed, which resulted in a very choppy and unstable baseline. This greatly increased system noise. The pump control algorithm was disabled to determine if the control was the reason for the erratic flow but the baseline remained erratic, thereby implicating the pump as the source of the flow instability.

The MicroPump was removed and replaced with a Braintree Scientific BS-8000 syringe pump (Figure 7). The baseline was markedly smoother after installing the BS-8000 syringe pump. Hence, the MicroPump was not used during laboratory testing (see Lessons Learned and Discussion).

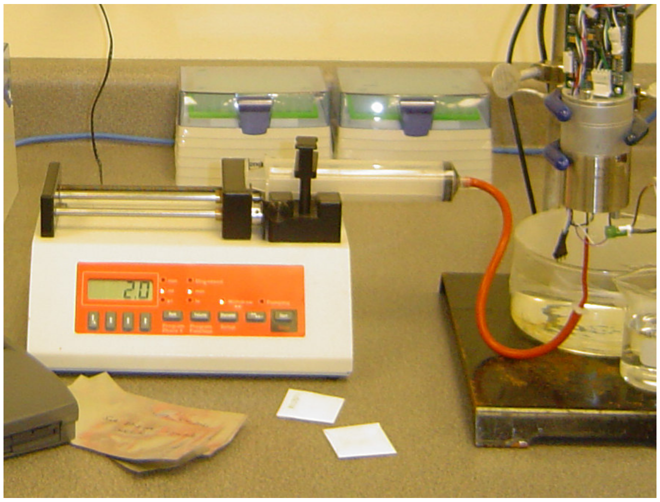

Figure 7 – BS-8000 Syringe Pump

Addition of the Syringe Pump

For the purpose of system testing, an optimal flow rate was established by replacing the MicroPump with a syringe pump. With the syringe pump, a stable baseline was achieved. It was observed that as the flow rate increased from 1.0 mL/min to 5.0 mL/min, the baseline would degrade or experience a downward slope. The most stable baseline was observed at a flow rate of 2.0 mL/min. Thus this was the flow rate used for all testing. The inlet to the syringe pump was connected to the suction side of the sensor (Figure 7), the flow rate was set to 2.0 mL/min and testing commenced.

Valve Switching

A Clippard two-position/three-way valve was used to switch the flow from the TNT-contaminated water supply to the clean water supply. An electronic switching circuit was added to the circuit board to handle switching the valve through the software interface. The switching has been tested in the lab and functions as designed.

Data Logging

Data logging was added to the prototype as a “tag-along” feature that comes standard with the Fido sensor. Data is captured on a Compact Flash (CF) memory card that is inserted in the CF card slot on the main circuit board (Figure 8).

The Fido software uses this CF card to log the data that is generated by the sensor. With data logging, the traces can be downloaded and analyzed at a future date. The data stored on the CF card can be offloaded to a PC via a standard USB cable connected directly into the sensor (Figure 9). The data-logging feature has been tested in the lab and functions as designed.

Test Results

Substrate Coating Procedure

An AFP solution of 0.25mg/ml in toluene was used to spin-cast AFP films onto each substrate. It was discovered that AFP was dripping down the edges of the substrate during spin coating, which resulted in large areas of unquenchable polymer and reduced sensitivity. The AFP on the edges of the substrate was unquenchable because it was isolated from the water flow path, and hence would not come into contact with the sample. This problem was solved by removing the AFP with a cotton swab soaked in toluene to leave only one face of the substrate coated with AFP.

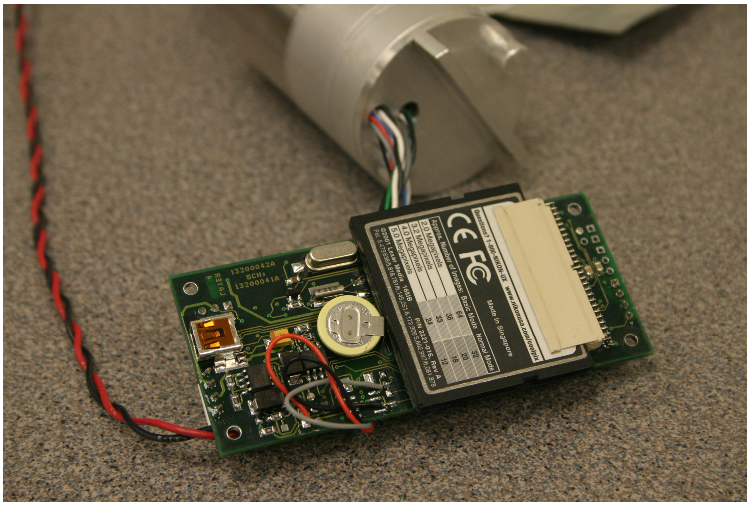

Figure 8 – CF Card On Board

Test Plan

The tests performed with the sensor include:

- TNT detection limit tests
- Interferent screening
- pH and ionic sensitivity tests
- AFP longevity test

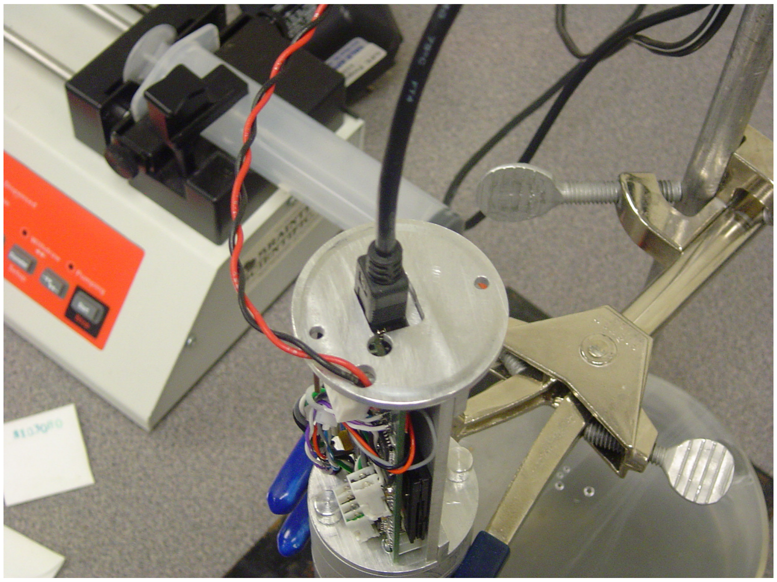

Figure 9 - USB Connection

TNT Detection Limit Test

The purpose of this test was to establish the sensor's minimum detection limit (MDL) for TNT. Solutions of each analyte in water were prepared over a range of concentrations spanning the dynamic range of the sensor. These solutions were then introduced into the sensor and the magnitude of response to each solution was recorded.

Figure 10 illustrates the quenching response of the groundwater probe to aqueous TNT solutions. The solutions ranged in concentration from 10 to 500 ppb by mass. As can be seen from Figure 10, the response of the sensor increases as the concentration of TNT in the sample increases. Figure 11 is the TNT response curve for the sensor. The least-squares fit to the data is also plotted, along with the equation of the line. The RMS noise of the sensor was calculated at

0.0093%. Using this value for the noise and the least-squares fit to the data, the minimum detection limit of the sensor based on this data set is 2.7 ppb at a signal-to-noise ratio of 3:1.

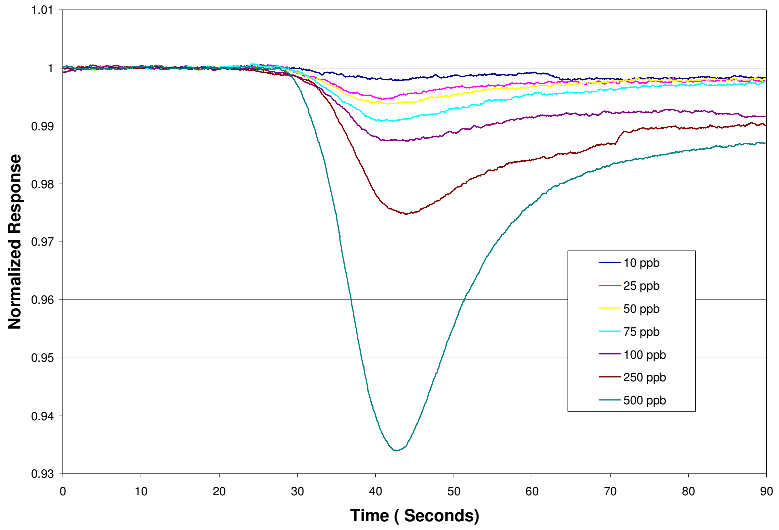

Figure 10 – Groundwater Probe Responses to TNT Solutions

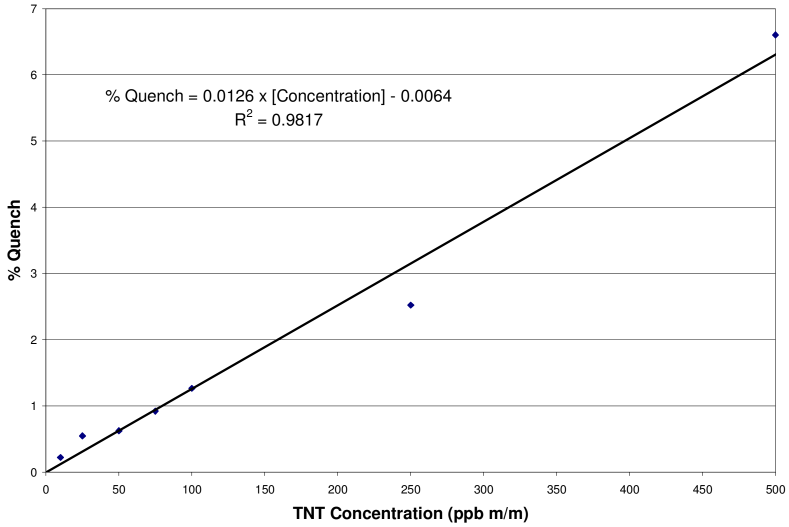

Figure 11 - TNT Response Curve

Interferent Screening

The purpose of this test was to determine the effects of common groundwater contaminants on the operation of the sensor. Potassium perchlorate and trichloroethylene (TCE) were chosen as test compounds. Saturated aqueous solutions of these compounds were presented to the sensor for analysis. The results are illustrated in Figure 12.

Both compounds did cause a sensor response, but the response was not a typical of a response to nitroaromatics. In this case the response was actually an increase in fluorescence intensity. Increases in fluorescence intensity have also been observed with the Fido vapor sensor when exposed to high concentrations of certain volatile organic compounds. The reason for the increase in intensity is unknown, but may be due to swelling of the AFP films that occurs when high concentrations of certain compounds partition into the AFP films. Although a response to TCE and perchlorate were registered, the response can be easily differentiated from that to a nitroaromatic such as TNT. Since these responses were to saturated solutions of these compounds, they represent worse-case scenarios for these contaminants as interferents. Large concentrations of these contaminants could conceivably mask responses to low levels of nitroaromatics. More testing against potential interferents is necessary.

Ionic Strength and pH Tests

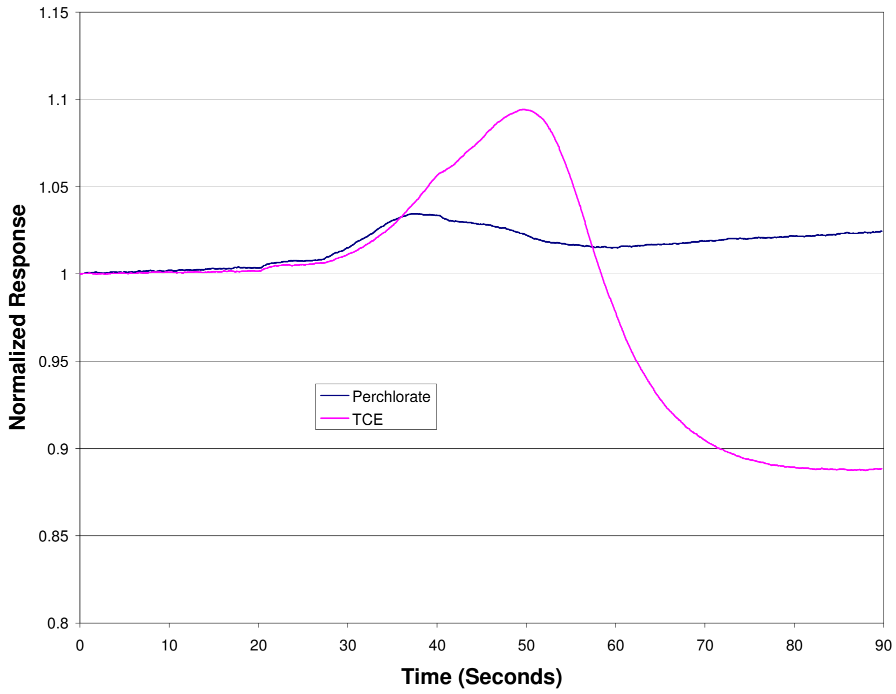

Figure 12 - Response of the Probe to Common Groundwater Contaminants

The purpose of this test was to determine the sensitivity of the sensor to possible differences in ionic strength and pH levels. Since the earlier tests conducted during the initial sensor development used low ionic strength solutions, much higher concentrations of sodium chloride along with a broad range of pH were tested. The range of ionic strength was tested from 1.0 mM up to 1.0M NaCl solutions. The solutions tested had a pH range of 2.35 to12.33.

The results of the pH tests (summarized in Table 1) show the baseline only being seriously affected by very low or very high pH.

Table 1 - pH Test Results

pH	Average Response - %Q
2.35	0.54
4.28	0.17
6.47	-0.06
8.87	0.23
10.64	0.52

The effect of ionic strength on sensor response is summarized in Table 2. Increasing ionic strength resulted in an increase in emission intensity as the concentration of NaCl in the test solutions increased.

Table 2 - Ionic Strength Test Results

NaCl Concentration (Molar)	Average Response - %Q
0.001	0.00
0.010	-0.28
0.100	-1.68
1.000	-9.13

AFP Substrate Lifetime Test

The purpose of this test was to determine the longevity of the AFP-coated substrate while submersed in water. The longevity of the AFP was determined by creating a new AFP coated substrate at the beginning of each test, recording the beginning photon counts, then leaving the film immersed in water until the counts for each specific substrate fell below 100,000 (Table 3).

Table 3 - AFP Longevity in Water

Substrate #	Date	Starting Counts	Ending counts
2	4-5-05	233,000	163,000
2	4-6-05	203,000	163,000
2	4-7-05	157,000	180,000
2	4-8-05	166,000	163,000
2	4-11-05	115,000	131,000
2	4-12-05	96,000	

After exposing Substrate #2 to seven days of extreme testing, the counts dropped below the usable threshold. AFPs have been developed that can be covalently attached to the substrate, but these were not tested with the groundwater probe. The covalently-attached films tested to date are less responsive to TNT for reasons that have not been determined, but are not prone to delamination (as are standard AFP films) and are less susceptible to attack by solvents.

Lessons Learned and Discussion

For future reference, in order to construct a real-time field deployable sensor, a plumbing control system accompanied with a water filtration system will need to be designed taking into consideration the pump dynamics. An engineering analysis should be performed to record the pressure drop across the carbon filter bed with pressure readings taken at multiple flow rates. The resulting pressure vs. flow curve should then be overlaid onto the pump curve of the pump being sought for this application. In order to determine the maximum net flow a pump can achieve pumping against the impedance, a vertical line could be traced from the intersection of the two curves downward to the horizontal flow axis. Static downhole pressure should also be taken into consideration while making this analysis in order to properly size the pump.

During the testing procedures, repeated occurrences of bubbles trapped in the system were observed while removing the suction inlet from the water source. One major optimization of the flow cell was implemented to cause the cell to automatically clear itself of any air bubbles in the system, which can cause sensor fluctuations due to optical aberrations during steady state operation. However, bubbles were still getting trapped in the flow cell in spite of the optimization of the flow path. The bubble-trapping dilemma was remedied by tapping the side of the sensor with a wrench or by pinching the waste tube and quickly releasing to suction out the bubbles before each test procedure began. Further optimization is needed.

Summary

The objectives for this project as laid out in the statement of work were successfully achieved. These objectives included miniaturizing the SERDP Project CU-1298 Phase I explosives sensor in order to deploy the sensor in a two-inch groundwater monitoring well, as well as adding data logging capability to the sensor. A prototype sensor has been constructed and tested in the lab, and its performance is comparable to the previous laboratory prototype constructed under SERDP CU-1298 Phase I. The project objectives were accomplished, demonstrating that an AFP-based groundwater probe could be developed. Additional AFP materials are being developed with funding from other sources. Successful development of these materials could expand the capability of the probe to detect other explosives such as RDX and HMX, further increasing the utility of the technology for environmental monitoring applications.