Project Title:

# Fiberoptic Personal Exposure Monitor for Diisocyanates

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## Final Progress Report

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**Table of Contents**



# 1 List of Terms and Abbreviations

| | |
|---|---|
| HDI | 1,6-hexamethylene diisocyanate |
| TDI | toluene diisocyanate |
| LT | leuco triarylmethane dyes |
| LED | light emitting diode |
| A to D converter | analog to digital converter |
| USB | universal serial bus |
| nm | nanometer |
| μm | micrometer |
| ppb | parts per billion |
| HPLC | high performance liquid chromatography |
| MG-Ox | Malachite Green Oxalate |
| CV | Crystal Violet |
| MG-Deriv | Malachite Green N-butylamine derivative |
| CV-Deriv | Crystal Violet N-butylamine derivative |

# 2 Abstract

Spray-on polyurethane coatings applied during auto body repair expose workers to potentially harmful levels of diisocyanates. Workers also commonly risk exposure to harmful vapors during the manufacture of molded polyurethane foam products. Diisocyanates have been identified as the major cause of occupational asthma. Diisocyanates are highly toxic, used worldwide, and manufactured on a very large scale for the production of polyurethane and related chemical products. Since most human exposure occurs as the chemical vapors are transported by air, an air sampling based method having high sensitivity is required. Current measurement methods fail to provide adequate sensing of all diisocyanate species simultaneously.

This program aimed to develop a highly sensitive fiberoptic personal monitoring device, similar to a sampling badge, targeted for the simple and convenient measurement of diisocyanate airborne exposure. A chemically reactive coating applied to the fiber provides a direct integrated response to diisocyanate vapors during exposure. Real time electronic readout is provided by a compact, battery powered device that provides rapid, low cost, feedback to the user of unhealthy exposure levels that are recorded and reported via digital electronics. Humidity and temperature compensation is integrated into the device so as to make exposure measurement more accurate. An explicit program goal was to make the device size and cost suitable for consistent use during typical auto body repairs and factory operation.

The primary tasks of the program were:

1) Reagent selection, synthesis, and optical properties. Review literature to identify optimal chemical species for investigation. Obtain or synthesize necessary chemicals. Measure basic optical and chemical properties.
2) Electronic readout development. Develop fiber sensor circuit design. Develop and construct compact fiber cartridge design. Develop and construct compact final readout sensor unit for laboratory testing.
3) Exposure measurements. Develop fiber coating procedure. Prepare diisocyanate sample solutions. Make first stage exposure measurements of coated fibers to Diisocyanates.
4) Quantification of measurements. Refine performance measurement methods by comparison against calibrated sensing techniques.

The primary findings of the program are as follows.

A) An inexpensive, compact, optical fiber cartridge design was developed which can be quickly and reproducibly assembled from commercially available materials.
B) An inexpensive, compact, optical readout device based on common LEDs and photosensors was developed which provides a real time digital readout of the fiber cartridge with a precision of 1 part on 5000. The device is battery powered and readily interfaced to a common computer via a USB cable. Custom software with a graphic interface was developed for data acquisition, display and real time analysis.
C) The necessary chemical sensing agents were purchased or synthesized and a reproducible low cost dip coating process was developed for fiber sensor preparation. Spectral properties of these agents were characterized and matched with commercially available LED properties for optimal sensor performance.

D) The chemical sensing agents tested demonstrated the necessary sensitivity to airborne diisocyanates but only under elevated temperature conditions. Simultaneously, it was determined that the sensing agents are highly sensitive to temperature and humidity and these factors can be mistaken for diisocyanate exposure. This additional sensitivity to atmospheric conditions makes the reliable measurement of diisocyanate exposure difficult to the accuracy levels desired for assurance of worker health.

E) Further development of chemical sensing agents is required.

It was concluded that the selected chemical fiber coating did not have all of the properties necessary for reliable diisocyanate sensing in a workplace environment. The sensor cartridge developed and the readout electronics are low cost and potentially suitable for this and other chemical sensing applications. The optical performance achieved lays the groundwork for future low cost sensing devices. Further study is required to identify chemical coatings that provide the necessary response.

# 3 Highlights / Significant Findings

The overall program was only partially successful. Several of the major objectives were achieved, but the response of the sensor to diisocyanates was weak and room temperature and complicated by a high sensitivity to temperature and humidity.

The literature search indicated that a strong response by the candidate sensing materials based on malachite green and crystal violet could be expected. Synthesis of the necessary derivatives was made. Optical spectra confirmed the identities of these materials and indicated the best wavelengths for sensing measurements.

A simple, inexpensive, and reliable fiber cartridge design was developed that allowed for easy assembly and precision placement of the fiber for readout during testing. An electronic readout device was developed that exhibited low measurement noise and high sensitivity for the type of measurements desired. The design developed actually exceeded performance needs and future designs can be simplified with an associated cost savings. Operation at two wavelengths allowed for an accurate reference measurement for each sensing measurement. The composite measurement uncertainty was observed to be as low as 1 part in 5000.

The fiber stripping and dip coating procedure worked well and provided sensors of reproducible properties that would be sufficient for long term use. The sensors and the coatings were stable at room temperature. Tests of exposure to diisocyanates were performed using an apparatus design that had been used successfully in a previous program. The exposure tests led to several key observations.

1) The response of the sensor to diisocyanates at room temperature was quite weak. Exposure levels in excess of 100 ppb were needed to provide a reliable response.
2) Sensor response to diisocyanates increased significantly with a modest increase in temperature. A strong response was observed with a 20 ppb exposure at 40°C.
3) A sensor response was observed that was due to an increase in temperature alone. This was interpreted as being due to the thermal decomposition of the chemical derivative coating. This effect was seen to compete with the effects of diisocyanate exposure so as to make the observation of chemical exposure less certain.
4) Humidity was observed to play a significant role in sensor sensitivity. Sensor response was suppressed in the presence of modest humidity levels. Sensor response was good only in the presence of dry air.

These observations lead us to conclude that the response of the malachite green derivative to diisocyanate is not adequate as a basis for reliable chemical sensing. It is too sensitive to the effects of temperature and humidity to provide reliable readings. The response rate at room temperature is inadequate for practical real-time sensing.

The fundamental causes for these observatios are expected to be based on the underlying chemistry. Future efforts should focus on the selection of chemical sensing reagents for which the chemical mechanism is based on a direct reaction between the reagent and the diisocyanate.

# 4 Translation of Findings

The current findings cannot yet be used in the workplace. A low cost, high precision electronic readout device based on optical fibers has been developed. However, a fully useful exposure monitoring system requires that an improved chemically sensitive fiber coating be developed. Future work must focus on the identification of the correct chemical species for this application.

# 5 Outcomes / Relevance / Impact

The specific outcome of this program was aimed at demonstrating the basic capability to provide a chemical sensing device that would act as a personal real-time exposure dosimeter to airborne diisocyanates. The program involved the formulation of chemically reactive coatings specific to diisocyanates, optical fiber cartridge development, readout electronics and software development, and chemical exposure testing.

The positive findings of this program have shown that an inexpensive sensing device based on low cost optical fibers and LEDs can provide the basis for an atmospheric chemical exposure monitor. The optical performance achieved lays the groundwork for future low cost sensing devices.

The chemically sensitive fiber coating developed has not yet demonstrated the performance necessary to be the basis for a convenient and reliable diisocyanate sensing device. While the necessary chemical sensitivity was observed, a high sensitivity to temperature and humidity prevents a convenient route to a complete sensing system. Therefore, the targeted application of workplace monitoring airborne diisocyanates has not yet been successfully demonstrated. Further research on improved chemical formulations for the reactive coating are required.

# 6 Scientific Report

## *6.1 Project Background*

Diisocyanates are used worldwide and on a very large scale. Annual production estimates of all chemical forms of this class of chemicals exceed 2 million tons.[1] Production rates continue to increase primarily because of the usefulness of the chemical products obtained from diisocyanates. Chief among these chemical products is polyurethane. Polyurethane is a highly flexible chemical system that is used for coatings, lightweight plastic forms, paints, insulation, elastomers and glues. It is the most common material used in the refinishing of automobiles and is applied as a spray-on topcoat (and also a paint incorporating undercoat) that is highly resilient and provides excellent cosmetic benefits.

Unfortunately, diisocyanates can be highly toxic, and human exposure is intended to be very limited, typically in the several parts per billion range (ppb) or less. Many countries have established limits of exposure that are very stringent and handling techniques have been established to attempt to minimize human exposure. Since most exposure occurs when the chemical vapors are transported by air, an air sampling method of high sensitivity is required. Current measurement methods meet individual species sensitivity requirements but are generally inconvenient and expensive to carry out on a regular basis. Their use is feasible in some industrial environments but many applications exist, such as auto body repair shops, where diisocyanates are regularly used outside of such a controlled environment.

The occupational exposure to diisocyanates falls into two primary risk areas, 1) auto body repair and 2) the factory production of polyurethane foam products. While the primary goal of the proposed SBIR program is aimed at providing a personal exposure monitor for use during auto body repair, the same technology should be directly applicable to foam production. The exposure risk is somewhat insidious because the effects can be cumulative, vary between individuals, is often delayed in its effects, and a brief high dose exposure is more harmful than a low level long term exposure. Furthermore, the exposed individual can readily become hypersensitive to any further exposures, making continued occupational longevity a significant issue.

### 6.1.1 Present Sensing Technologies

Viewed from the process technology standpoint, there are presently two primary approaches to the airborne sensing of diisocyanates; 1) optical measurement of sensitized paper tape or 2) sample collection and then separation and evaluation by HPLC (high performance liquid chromatography) coupled with an appropriate detection method (such as UV absorption or fluorescence).

The paper tape approach is somewhat attractive from a practical standpoint, for it provides an optical change in paper color that is visible to the naked eye and can be somewhat quantified by comparison to a color coded card. Optical instruments can be used for further quantification, but this increases cost and reduces convenience. Concerns have been noted about the accuracy of this method, particularly with respect to changes in humidity and temperature. While still used,

[1] Mårten Spanne: [1998] *Derivatization and Analysis of Aromatic Isocyanates with Dibutylamine and Liquid Chromatography*, Licentiate Thesis, Lund University.

it has not been considered the standard method even though this approach was developed more than 20 years ago.

HPLC based methods rely on a derivatization reagent for selective reaction with diisocyanates. The HPLC instrument provides separation from the excess reagent in order to measure the diisocyanates quantitatively. Quantitative measurement of the HPLC column output is performed by UV absorption, fluorescence, electrochemical detection, mass spectroscopy, or some combination of these. Use of the HPLC process also has the important benefit of providing the collected samples in a form (uniform solution) that is readily measurable in a repeatable and quantifiable manner. Several chemical agents have been developed and provide good results.

The primary disadvantage of the HPLC procedures used is that sample measurement requires the use of expensive detection equipment operated by highly trained personnel. Sampling on sensitized filters is more convenient than the use of liquid filled impingers because they are more convenient to handle. The impinger process is a more efficient collection process but requires more care in the sampling system and then handling of a liquid sample. (An impinger is a small flask filled with solvent and reagent. Sampled air is passed through the solution and diisocyanates are selectively collected by the reagent chemical.) Because of the high equipment cost, and personnel training required, samples are often collected and sent out for analysis, a process that is slow, costly and delays feedback to the worker.

Both sensing methods are not really convenient for alerting the user when exposure limits are exceeded. The paper tape method requires a readout spectrometer that is not convenient to carry for personal monitoring, or the user must check the tape color visually himself to determine exposure, therefore readout is not automatic. The collection of samples via bubblers or filters is far from "real-time" because it requires laboratory processing by trained personnel.

Critical reviews are available of the comparative merits and deficiencies of various sensing methods.[2,3] This literature seems to generally indicate a perceived failure of existing methods to truly meet the needs of the industry. Efforts are underway to make sampling methods more reliable and also convenient. Convenience has been recognized as a serious shortcoming of most of the techniques based on the use of liquid impingers. There is also the need for faster results so that adjustments in work practices can be made more immediately.

Because of the high use of diisocyanates by industry and the pervasiveness of the resulting chemical products coupled with the serious nature of the toxic effects of these chemicals, diisocyanate sensor development and performance analysis has received extensive attention over the last three decades. Numerous publications and several books[4,5,6] are available concerning these issues. Particular attention to diisocyanates has been kindled by a collection of observations that the incidence of asthma in the general population is rapidly increasing. So

[2] "Isocyanate Interim Guidance": [22 April 2002] NAVENVIRHLTHCEN, www-nehc.med.navy.mil/downloads/ih/isocyanate_interim_guidance.pdf

[3] Steven P. Levine: [2002] "Critical Review of Methods for Sampling, Analysis and Monitoring of Vapor Phase Toluene Diisocyanate", *Applied Occupational and Environmental Hygiene* Vol. 17(12) 878-890.

[4] D. C. Allport (Editor), D. S. Gilbert (Editor), S. M. Outterside (Editor): [March 2003] *MDI and TDI: Safety, Health and the Environment: A Source Book and Practical Guide,*.

[5] Jacques Lesage (Editor), Irene DeGraff (Editor), Richard Danchik (Editor): [2001] *Isocyanates: Sampling, Analysis, and Health Effects,* American Society for Testing & Materials.

[6] Henri Ulrich , *Chemistry and Technology of Isocyanates:* [March 17, 1997] John Wiley & Sons.

much so, that the US Secretary of HHS has identified it as a point of significant interest by that department.[7] Industry associations are also promoting research in this field.

### 6.1.2 Auto Body Repair

Auto body repair usually leads to a refinishing of the damaged area of the car that must be repainted and coated with a glossy protective polyurethane layer. This layer is generally applied at ambient or slightly elevated temperatures. Because of a desire for resistance to UV degradation, aliphatic diisocyanates, such as hexamethylene diisocyanate (HDI) are generally used as one of the major components of a two component mixture that is applied by spraying. To reduce exposure risks the form of HDI generally used is the larger molecular weight prepolymer which has the effect of greatly reducing the volatility of the reactive diisocyanate. However, these prepolymer mixtures generally contain as much as 1% of the highly volatile HDI monomer that is readily vaporized during spray applications.[8] Since most spray applications are only 30% efficient or less, we see that a typical spray operation has the opportunity to provide dangerous levels of HDI vapors in the near vicinity of the auto body worker.

The use of safety equipment involving full body coverings and respirators that provide an independent clean air supply are recommended but rarely adhered to by many smaller body shops. More common is the use of activated carbon filters that are specifically designed for removing both aerosols and diisocyanate vapors. A difficulty exists in knowing whether the capacity of these carbon filters has been exceeded so that "breakthrough" occurs. Furthermore, it is difficult to verify an adequate seal around the face for adequate protection with less expensive respirators. A particular issue is that sensor feedback to the user is slow. Therefore information as to whether the protective measures provided (clothing and respirators) are working properly is limited. This is partially because current sensors are not available that are small enough to be located in the mask and still work properly. Because current sensor response is not "real-time" enough, the exposure is only caught "after the fact". It would be most desirable to provide an active electronic alarm capability associated with a real-time measurement device that will fit inside the user mask.

Similar occupational exposure to diisocyanates also occurs for shipyard workers, particularly those involved in painting operations below deck and in enclosed spaces.

While exposure to aerosols containing diisocyanates is also hazardous, this particulate component of the airborne material is readily captured by particle filters in appropriate masks. Moreover, the diisocyanate aerosols are rarely present without the accompanying vapors. In this sense, the detection of the vapor can be readily utilized as a "flag" of hazardous exposure to all airborne diisocyanates.

### 6.1.3 Polyurethane Foam Production

Molded foam products are largely produced using aromatic diisocyanates that have very similar toxic effects but the exposure is generally limited to vapor exposure, without the accompanying aerosols. Full body protection and respirator use is recommended, but the same concerns exist for validation of adequate sealing around the face for air supply. Not all exposures occur during anticipated operations and plumbing leaks associated with valves can

[7] "Action Against Asthma A Strategic Plan for the Department of Health and Human Services": [May 2000] US Department of Health and Human Services. (Web site http://aspe.hhs.gov/sp/asthma/overview.htm)

[8] "Toxicological profile for Hexamethylene Diisocyanate" [August 1998] U.S. Dept. of Health and Human Services, p 107.

have serious consequences but are difficult to detect. Respirator use at all times is difficult because many facilities are in locations where weather conditions are hot and humid (i.e. the U.S. Gulf Coast region).

### 6.1.4 Fiberoptic Sensors

Optical fiber sensors have the potential to solve these problems because they precisely define an optical sensing situation that is supportive of precise optical measurements while allowing for high sensitivity and convenient handling. They are solid state devices that are compact, rugged, easy to handle, and should pose no chemical or physical hazard to the user. Given this superior "optical platform", chemical sensing reagents similar to those used for paper tapes can be implemented to provide the needed colorimetric response.

Optical fibers have their unique optical properties based on the phenomenon known as "total internal reflection". Light traveling through a high refractive index optical medium such as transparent glass can be totally reflected at a surface if there is a sudden decrease in refractive index at that surface and the angle of incidence (deviation from normal) is sufficiently high. For example, if light passing through glass having a refractive index of 1.5 reaches a surface with air (index = 1.0) and the angle of incidence exceeds 42 degrees (from normal), it will be totally reflected back into the glass.

This property is used in fiberoptic communications to transmit light signals. If the glass fiber is highly transparent and with few surface defects, the light can travel great distances (kilometers) with very little attenuation. Commercial fibers are now available that transmit in the spectral range from the UV into the near IR. Because modern fibers are inexpensive, rugged, lightweight, compact and easy to handle, they represent convenient means for the coupling of optical signals for many sensor applications. Typical optical fibers are constructed of a high purity silica glass or plastic core, surrounded by a lower index cladding whose optical properties are highly controlled. This structure is then usually covered by a rugged polymer jacket and cladding to protect it from the environment which can be easily stripped for signal coupling and sensing applications.

Fiberoptic sensors come in several types and work by a few different physical mechanisms. Signal loss from the optical fiber is clearly very sensitive to the optical properties of the fiber surface. Small changes in the surface properties, refractive index, or angle of incidence due to bending of the fiber, can have very measurable affects on the transmitted signal. This sensitivity is not just a surface effect relating to the properties of a few atomic layers of material at the glass surface. The electromagnetic wave properties of the light causes the sensing of optical properties from 50 to 1000 nm beyond the optical surface (into the cladding or fiber coating) through "evanescence".[9]

## *6.2 Investigated Approach*

The basic approach is to deposit selected reagents onto the surface of the optical fiber, expose the fiber surface to the sampled air, and then perform optical absorbance measurements on the fiber. Since no intermediate processing is required, readout is automatic and can be real-time if the chemical reagent's response time is fast enough. The characteristic chemical sensitivity and quantifiable optical change is provided by the choice of reagents (derivatizing agents).

[9] Gilbert Boisde and Alan Harmer [1996] *Chemical and Biochemical Sensing with Optical Fibers and Waveguides,* Artech House, Inc. p 219.

Diisocyanate sensing is typically based on the reaction with the reagent species containing primary or secondary amines. Amines are selected because their very rapid and selective reaction with diisocyanates is much faster than with water vapor or alcohols (two materials expected to also be present during polyurethane use). All of the derivatizing agents currently used for diisocyanate exposure monitoring are primary or secondary amines. The reaction with the amine must then result in a measurable optical change of the absorption (or fluorescence) of the reagent so that exposure can be quantified.

Our approach has chemical similarities to that used in paper tape sensing in that the coating applied to the paper tape undergoes a color change when exposed to the diisocyanate. Our primary advantage over paper tape is that the optical fiber provides a vastly superior format for making reliable optical measurements. The fundamental viability of the optical fiber approach was demonstrated in a prior Phase I SBIR program where it was shown that a coiled fiber sensor could readily provide one part per billion sensitivity to the measurement of common diisocyanate species.[10,11] The previous program did not provide real-time sensitivity because the chemical reagents selected required post processing in order to quantify readings. This program addressed the use of new reagents that are aimed at providing real-time readout capability.

### 6.2.1 Key Chemistry

The key to real-time readout is the correct choice of chemical reagent and appropriate compensation for environmental effects, such as temperature and relative humidity. Our selected reagent coating is based on leuco triarylmethane (LT) dyes (such as shown in Figure 1) that are selected to provide a strong optical absorption when exposed to diisocyanate vapor. LT dyes are characterized by the presence of a central carbon atom in a molecular structure dominated by surrounding aromatic groups. When the single hydrogen atom that is attached to the central carbon is removed by the appropriate chemical reaction, the molecular structure "snaps" into a planar arrangement so that the bonding orbitals of the aromatic structures couple. This provides extended molecular orbitals that allow for strong optical absorption bands in the visible and near infrared.

The specific chemical properties of the LT dye are largely controlled by the presence of the functional groups on the outer edges of the molecule, such as the amine group indicated in Figure 1. For our application, the secondary amine group is the target of the reaction for the diisocyanate molecule and provides the impetus to essentially "snap" into the colored form. This class of reactive dye molecule has been reported previously as a highly sensitive measure for microscopic quantities of diisocyanates.[12] The very high molecular absorption is well defined and occurs at visible wavelengths readily accessible by low cost LEDs and optical sensors.

[10] S.A. Lis [3/1/2005 - 8/31/2005] "*Fiberoptic Isocyanate Personal Monitoring Device*", Contract Number EP-D-05-018, Phase I SBIR Final Report.
[11] Steven A. Lis [2006] "Fiberoptic Diisocyanate Personal Monitoring Device", Proceedings of the SPIE, Vol 3677, paper 6377-11, from the conference on *Advanced Environmental, Chemical, and Biological Sensing Technologies IV*, Oct. 1-4, Boston, MA.
[12] K.A. Kubitz, *Analytical Chemistry,*Vol 29 (5) pp 814-816 (May 1957).

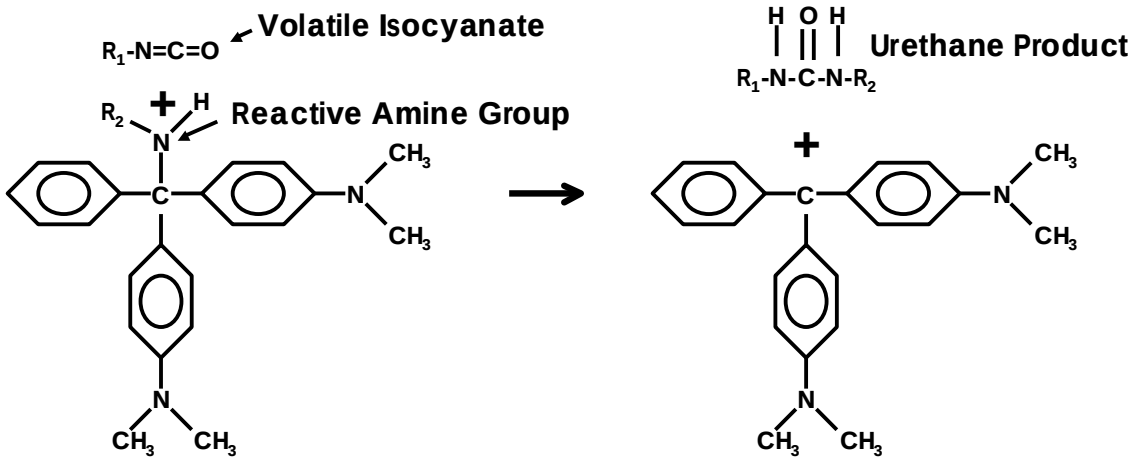


**Figure 1. Leuco triarylmethane dye reaction with isocyanate species that provides for the generation of highly colored products indicative of exposure.**

The most common interference to diisocyanate sensing is relative humidity. Water vapor also reacts with diisocyanates, although much more slowly, therefore it can readily reduce the species availability for sensing. Water also reacts with amines, potentially enabling the color-forming reaction shown above. These factors can be addressed in two ways, both of which can be independently implemented. The first is to provide a binding agent with the dye which is also serves to repel moisture. In the paper tape process such a binding agent can be a common plasticizing agent such as diethyl phthalate.[13] This does not provide a complete solution, because available paper tape sensors are still somewhat humidity sensitive.

**Figure 2. Photo of a typical low cost digital microchip humidity and temperature sensor that is now commercially available. Compare device size to match**

The second step towards solution is to provide a real-time humidity monitor so as to provide readout compensation. Modern microchip sensors are now available that inexpensively provide accurate digital readout of relative humidity and temperature while being compact and requiring very little power capacity. Such as device (as seen in Figure 2) can be readily integrated in to the electronic sensor package and provide the needed compensation. In this way, the amine based sensor chemistry can be made much more precise and properly compensate for atmospheric humidity and even temperature effects.

### 6.2.2 Device Design Approach

In order to translate the chemical and optical concepts outlined above into a working device, details as to the specific sensor operation and design need to be presented and discussed in

[13] D.A. Reilly: [March 1968] *Analyst*, Vol. 93, pp 178-185.

further detail. The conceptual optical measurement scheme is shown in Figure 3. The critical components are the two LED light sources, the reagent coated optical fiber, the two photodiodes, and the time synchronized readout and digitization electronics.

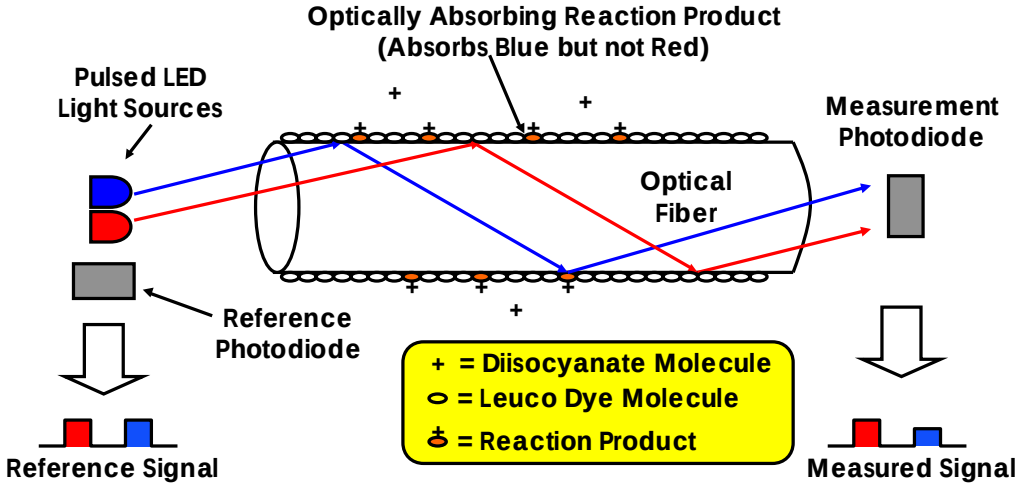


**Figure 3. Detailed schematic diagram of the optical fiber sensing approach. Two-color sensing is used so as to provide an internal reference measurement. The LEDs are sequentially pulsed and sensed at two locations, before and after transmission through the fiber. The measured and reference signals are compared so as to provide a direct "calibrated" absorption measurement at the "blue" wavelength.**

The basic measurement scheme operates as follows.

a) The leuco dye (LD) does not absorb in the visible but is selected so that upon reaction with the diisocyanate molecule it strongly absorbs in the blue (or any wavelength of choice).

b) The red LED is pulsed so as to measure the light transmission properties of the optical fiber. (The wavelength selected need only be defined as one for which no molecular absorption occurs.) The direct output is measured by the reference photodiode and the fiber transmission is determined by the signal from the measurement photodiode.

c) The blue LED is pulsed so as to measure the transmission at the wavelength where the dye reaction product strongly absorbs. The direct output is again measured by the reference photodiode and the fiber transmission is determined by the signal from the measurement photodiode.

d) The measurement electronics both operates the time synchronized LEDs and the signal amplification and digitization (A to D conversion) of the photodiode output.

The above process defines a single measurement cycle which can be accomplished in less than a millisecond. The measurement can be readily repeated for maximum accuracy and to average out external noise sources. The power requirement for each measurement is minimal due to the very low power consumption of the LEDs and supporting electronics. The time intervals between measurements can be selected to provide timely sensor response while consuming very little overall device power. A convenient time interval between measurements would probably be on the level of several minutes, but is primarily defined by the needs of the sensing application and can be user programmable.

### 6.2.3 A Coiled Fiber Cartridge

A key element of fiber optics is that the fiber can be of extended length with low transmission loss and is flexible, allowing for significant geometric freedom. This feature is often used to allow the sensing area to be remotely located from the light source, detectors, and electronics. Our innovation is to use the long surface region of the fiber to support an extended sensing region so that high sensitivity is obtained. Additionally, the flexibility of the fiber allows us to coil it into a compact cartridge that is easy to handle, despite the long fiber length contained.

Plastic fibers can endure a very tight bending radius, allowing for a very small cartridge design. Even glass fibers can sustain a bending radius compatible with such a cartridge design if the width of the cartridge is roughly 200 times the diameter of the fiber. This allows us to easily fabricate a cartridge that is 4 cm wide or less from glass fibers having a 200 μm core. The flexibility of the fiber allows it to be coiled into a convenient form-factor package that can be a low cost replaceable cartridge attached to a small readout electronics package.

Once the fiber is coiled and mounted in the cartridge, the fiber cladding can be chemically stripped from part of the fiber. The unclad region is then coated with the sensing chemicals. Because the fiber is coiled the unclad fiber length can easily be 30 cm, and allows for high optical sensitivity to be achieved in a low cost optical structure.

Even the remaining optical components can be low cost. Low cost LEDs used for conventional lighting can be combined with a plastic cylindrical lens to provide incoherent fiber illumination. A simple silicon photodiode provides high sensitivity light detection. A 200 μm core fiber readily captures sufficient light from the LEDs to allow for high sensitivity absorbance measurements to be carried out.

Optical fiber based sensors have also received much attention over the past three decades with hundreds of publications being printed each year.[14,15] This continues to be an area of active investigation for chemical and biochemical applications with national and international conferences being held that focus on this subject area. The coiled fiber design implemented in this device is a novel fiber sensor design that had not been extensively explored. Its ability to provide an extended fiber surface for sensing in a compact package format provides special advantages where low exposure levels of chemical substances must be monitored. The previous Phase I SBIR program at LightLine Technologies demonstrated the viability and sensitivity of this new device structure.

## *6.3 Program Plan*

All the key technical work was carried out at LightLine Technologies with Steven A. Lis, Ph.D. as the Principal Investigator. LightLine Technologies is fully equipped for the design, research, optical and electrical testing that must be performed. The preparing and handling of high purity chemicals for testing was carried out by using the chemical fume hood facilities at ElectroChem, Inc. of Woburn, MA. The technical effort had a duration of 6 months and addressed the key tasks defined below.

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[14] Gilbert Boisde, Alan Harmer: [August 1996] *Chemical and Biochemical Sensing With Optical Fibers and Waveguides*, Artech House.

[15] K. T. V. Gratten (Editor), B. T. Meggitt (Editor), K. T. V. Grattan (Editor): [June 15, 1999] *Optical Fiber Sensor Technology: Volume 4: Chemical and Environmental Sensing*, Kluwer Academic Publishers.

**Major Tasks**

1) Reagent selection, synthesis, and optical properties. Review literature to identify optimal chemical species for investigation. Obtain or synthesize necessary chemicals. Measure basic optical and chemical properties.
2) Electronic readout development. Develop fiber sensor circuit design. Develop and construct compact fiber cartridge design. Develop and construct compact final readout sensor unit for laboratory testing.
3) Exposure measurements. Develop fiber coating procedure. Prepare diisocyanate sample solutions. Make first stage exposure measurements of coated fibers to Diisocyanates.
4) Quantification of measurements. Refine performance measurement methods by comparison against calibrated sensing techniques.
5) Reporting of results. Prepare final report.

## *6.4 Results*

### 6.4.1 Reagent selection, synthesis, and optical properties.

**Reagent Selection:** An extensive literature search was performed with three primary objectives; a) search for additional chemical species that would be the basis of a chemical sensor for diisocyanates, b) refine our understanding of the chemical, physical and optical properties critical to sensor development, and c) refine our understanding of how to optimize chemical and sensor preparation.

A) Additional chemical species. The triarylmethane dyes remained our top choice as a sensing agent class. Previous work by Kubiz had shown a good response from an amine derivative based on Malachite Green. A general literature review showed no other class of chemicals predicted as good a general response to diisocyanates with a significant change in the visible absorbance spectrum. Within the triarylmethanes, an attempt was made to optimize chemical properties so as to be less sensitive to moisture. Towards this end, Crystal Violet was selected. Our interpretation of the literature suggested that an amine derivative based on this compound would be more stable against moisture. It also has an even higher native absorbance, potentially making it more sensitive to diisocyanates.
B) Critical Properties. Published optical spectra, chemical solubilities, and physical properties were collected for malachite green and crystal violet. The optical spectra were used to assist in the LED selection based on wavelength and output intensity. Chemical solubilities were used to select the appropriate solvents for sensor preparation and derivative preparation.
C) Sensor Preparation. Producing a uniform coating of consistent thickness on the fiber is important for quantitative reproducibility. Dip-coating is a process that has been used extensively for applying film coatings to metal and glass surfaces and is well studied. It works particularly well in the providing sol-gel coatings on glass that are quite reproducible and easy to control based on the selection of solvent and rate of withdrawal of the substrate from solution. Suitable properties were identified that allow us to control the thickness and absorbance properties of sub-micron thickness coatings on the optical fiber that provides the optical absorbance desired.

**Chemical Synthesis.** Amine derivatives based on malachite green and crystal violet are not commercially available, however a chemical synthesis method was outlined in the publication by Kubiz. This procedure was followed for both compounds. In the case of the malachite green N-butylamine derivative, the chemical product was identical to the published description in appearance and properties. Qualitative tests indicated that the white powdery derivative was reactive with diisocyanate and produced a deep green color on exposure.

The results with the crystal violet N-butylamine derivative were not as clear-cut. The procedure used by Kubitz specified use of the oxalate form, but the oxalate form of crystal violet was not available. Instead, the chloride form of crystal violet was used. The derivative product was dark colored rather that white, indicating that the derivative absorbed quite strongly in the visible. Indeed, during the separation process in the Soxhlet extractor, the derivative appeared to take on a dark brown color. This matched our expectations based on our literature review. However, attempts to form a crystalline product were more of a problem. The product did not readily form crystals, but instead tended to form a gooey mass. After several attempts at recrystallization, we let the product stand in a sealed glass container for several weeks. Upon reexamination, the product had crystallized, but now contained a strong violet color. From these observations, we expected that the obtained product was a mixture of crystal violet and the crystal violet derivative.

**Optical Properties.** Optical absorbance spectra can provide qualitative verification of the materials obtained as well as quantitative assurance of material purity. Absorbance spectra for the starting dyes (malachite green oxalate and crystal violet chloride) and the derivatives were measured over the range of 320 nm to 1000 nm. In all cases the solvent used was acetonitrile. Solutions of these materials were prepared by carefully weighing quantities (approximately 0.2 grams) of the dry materials and dissolution in acetonitrile, followed by stepwise dilution so as to obtain solutions having appropriate concentrations for convenient absorbance measurements. Because the absorption coefficients of these materials are so high, dilution of the starting solutions was required.

Solutions of the malachite green derivative had a faint green color that darkened somewhat on standing. This suggests that the derivative may tend to decompose slightly when mixed in solution. To verify reactivity of the malachite green derivative, the test solution was mixed with an excess of TDI and left to sit. A noticeable color darkening occurred within 10 to 20 minutes and the solution was left overnight before the absorbance measurements were made.

The absorbance spectra obtained are shown in Figure 4 and Figure 5. The spectra were normalized at about 620nm to allow for direct comparisons and the concentrations shown are those that would produce the indicated absorbance in a 1 cm cell. A number of observations are readily made and important conclusions can be drawn.

Malachite Green Results

1) The absorbance observed for malachite green oxalate (MG-Ox) is close to that reported in the literature and at the appropriate concentration.
2) The malachite green derivative (MG-Deriv) has an absorption coefficient at 620 nm that is roughly 400 times lower than MG-Ox. However, the absorbance in the ultraviolet (340 nm) is quite high for the MG-Deriv. This is as expected, since the leuco form of triarylmethanes always have a strong UV absorption. This suggests that the derivative contains only a small quantity of MG-Ox.
3) The absorbance associated with the MG-Deriv reaction with TDI is intermediate between these two cases, as would be expected. There is also a noticeable spectral

shift observed at approximately 650 nm. This is identified as a spectral point where the measurement will be most sensitive to diisocyanate exposure.

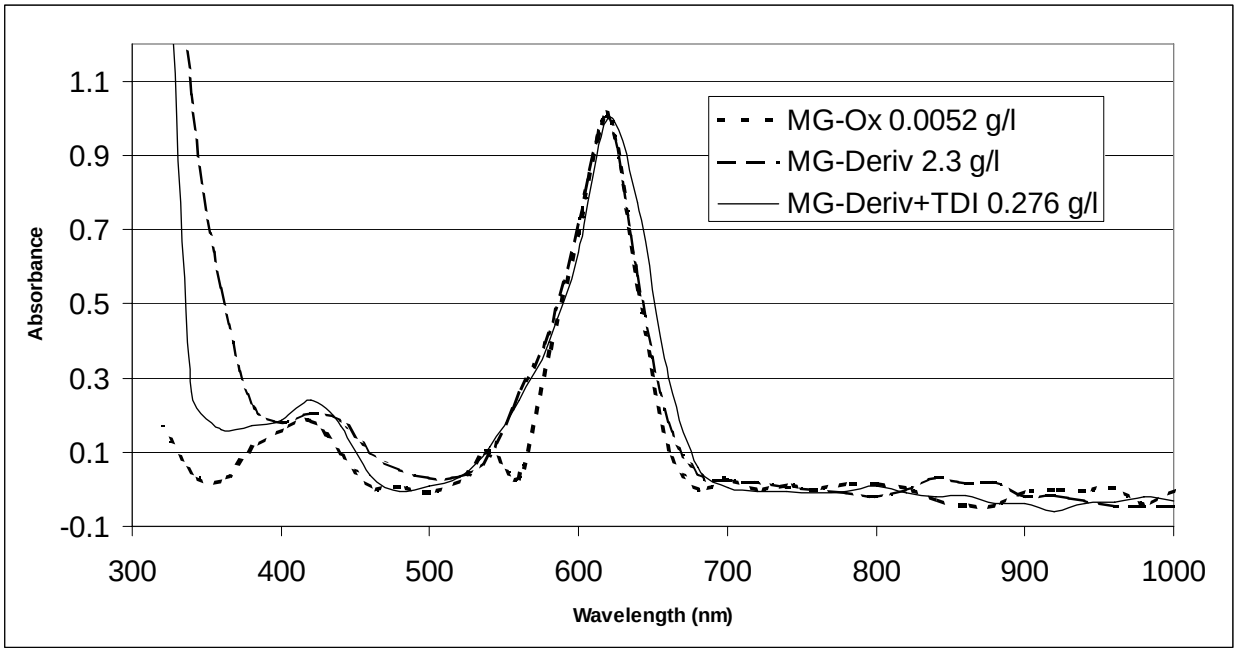


**Figure 4. Absorbance measurements of malachite green oxalate (MG-Ox), the malachite green derivative (MG-Deriv), and the reaction products of the malachite green derivative and toluene diisocyanate (TDI). In all cases, the solvent used is acetonitrile.**

Discussion: The response of the MG-Deriv to TDI is not as strong as might be expected. Had the reaction readily gone to completion, the absorbance should have been very high, nearly as high as that obtained for MG-Ox in solution. As it is, the observed absorbance is 50 times lower. This suggests that the response of the MG-Deriv to diisocyanates is not very strong in a dilute acetonitrile solution at room temperature. This does not necessarily indicate a problem when exposed to diisocyanates in room air, since the conditions are quite different chemically. Therefore further testing with an actual fiber sensor is required to confirm sensitivity of the lack thereof.

Crystal Violet Results

1) The absorbance observed for crystal violet (CV) is close to that reported in the literature and at the appropriate concentration.
2) The crystal violet derivative (CV-Deriv) has an absorption coefficient at 620 nm that is roughly 2.3 times lower than CV. This suggests that the derivative is not very pure and contains a high fraction of CV (roughly 40%).

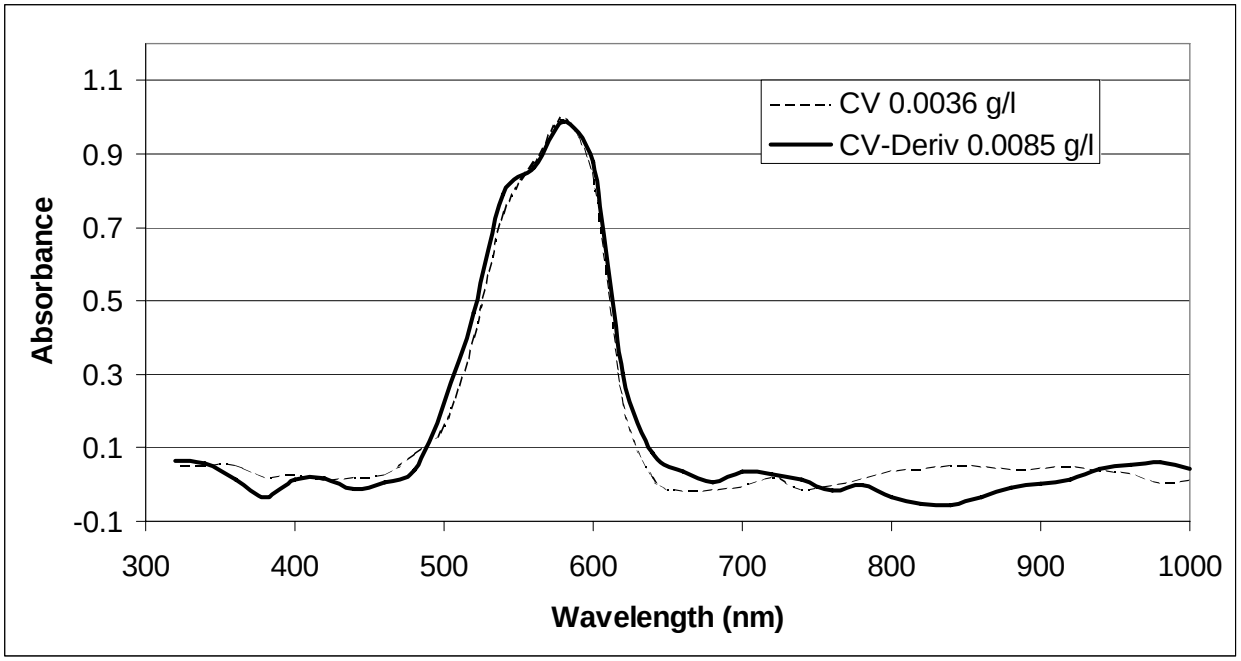


**Figure 5. Absorbance measurements of crystal violet (CV) and the crystal violet derivative (CV-Deriv). In both cases, the solvent used is acetonitrile.**

Discussion: These results suggest that the crystal violet derivative product obtained is not very pure. This may be related to the difficulties observed in the synthesis process. In order to concentrate the product and induce crystallization, excessive heat may have been applied to the solution. As will be seen, we have observed that the malachite green derivative is quite sensitive to heat. (It readily decomposes on heating.) A similar sensitivity to heat can be expected for the crystal violet derivative, leading to its partial (40%) decomposition to crystal violet on heating.

### 6.4.1.1 Conclusion:

The literature search provided no clear-cut candidates for investigation beyond the triarylmethane compounds. Crystal violet and malachite green were selected for experimentation, with the hope that crystal violet would be less sensitive to air humidity. Both amine derivatives were synthesized and the optical properties of the products were measured. A preliminary test of exposure to diisocyanate in solution was carried out which showed the expected response, but at a level that was lower than expected. The higher purity of the malachite green derivative suggested that this material should be used for fiber sensor testing first.

## 6.4.2 Electronic Readout Development.

This task couples the optical, mechanical, electronic and software aspects of the readout device. The goal was to develop a well-packaged unit that is small enough to allow both laboratory testing and field testing. It needs to be battery powered and operate with convenient to control software. The device size need not be small enough to be worn by the user, but further development should allow for such miniaturization. The specific requirements for this program can be summarized as follows.

### 6.4.2.1 Objectives

1) Optical: Two inexpensive LED's with the desired spectral output must illuminate the input end of a 200 μm thick multimode optical fiber. Sufficient light must be launched down the fiber to permit excellent signal to noise when detected by a photodiode at the opposite end of the fiber. A reference photodiode must be used to verify that constancy of the LED output over time and from pulse to pulse. Low cost can be maintained if the use of beamsplitters or complex focusing optics are avoided. The optical fiber under test needs to be conveniently and rigidly mounted in a low cost cartridge that is easy to handle and reproducibly mates with the readout hardware.
2) Mechanical: The optical and electronic components need to be contained in a convenient package that is portable for testing purposes. The mountings of the optical components needs to be rigid and the cartridge needs to be reproducibly located in alignment with the illuminating LEDs and the readout photodiodes. The readout electronics must be contained in a case that is readily shielded from electrical and optical interference, and allows for power to be supplied by a small battery.
3) Electronic: The spectrally selected LEDs need to be independently pulsed during measurements at power levels sufficient to provide maximum light output. During the light pulse, two photodiodes (the sensing diode and the reference diode) need to be read simultaneously and the signals precisely digitized. Low detection noise is required and a comparison must be made with the light levels present prior to LED pulsing. Digital readout of an on-board temperature and humidity sensor also needs to be supported by the readout electronics. Readout via a convenient computer interface cable needs to be supported. A small battery must provide the required power for operation.
4) Software: A flexible graphic interface needs to be implemented that can allow for laboratory diagnostics and testing using a laptop computer without special additional hardware. Data needs to be conveniently acquired and saved to data files that are readily redisplayed through standard packages such as Excel™.

### 6.4.2.2 Findings

1) Optical: Inexpensive LEDs and photodiodes (costing only a few dollars each) were found to provide the required performance over the spectral range from 450 nm to 1000 nm. The standard plastic encapsulated "High Brightness" LEDs can be used if those having an 8° or smaller viewing angle are selected. This allows the light to be sufficiently collimated so that it can be concentrated on the input end of the sensing fiber. The LEDs can be mounted on a printed circuit board at an angle with respect to the end of the fiber of +/- 15°. A small plastic cylindrical lens allows for some concentration of the light intensity at the input end of the fiber, thereby increasing the illumination efficiency by about a factor of 10. No additional optical elements are required. An optical cartridge was developed that mounted the optical fiber on a printed circuit board with adhesive tape. (See Figure 6.) A simple fixture allows us to produce a neatly coiled fiber structure within a few minutes. Once mounted, the fiber cartridge is easily handled and can be reproducibly mounted in front of the readout optics by alignment pins and mechanical guides in a few seconds.
2) Mechanical: An inexpensive extruded aluminum case provides a good mechanical structure for the readout of the sensor. (See Figure 7.) The electronics are all

contained on a single rigid PC board that is mounted inside the case using standoffs and screws. Typical machining tolerances (+/- 0.005 in) are sufficient to provide the positioning accuracy needed. Small L-brackets on the front plate provide vertical positioning accuracy for the cartridge relative to the electronic sensor and LEDs. Lateral positioning accuracy is assured through the use of electrical connectors mounted on the cartridge and the electronics board. When these connectors are interlocked, the cartridge is properly aligned. Fine alignment of the LEDs and one of the photodiodes was enabled by simple set screws located on the walls of the case. Once these are set, the device is properly aligned for all cartridges.

3) Electronics: Conventional, commercially available, electronic components were used throughout. (See Figure 8 and Figure 9.) Noise was minimized through use of a 4 layer PC board with ground and power planes. An A to D converter chip was selected that provided 16 bit resolution and allowed for switchable data acquisition from two pairs of inputs than can be acquired simultaneously. USB communication to and from the board was provided by a commercially available interface device complete with driver software that was readily mounted as a standard component. LEDs were flashed ON for a period of 100 microseconds and had very reproducible light output. It was found that LED output was very reproducible. The reference photodiodes were of value only in verifying basic operation of the LEDs. Use of the reference photodiode readings for calibration was not necessary. It was also found that one did not need two separate reference photodiodes (one for each LED). A single reference photodiode would have sufficed if properly placed. Noise and LED reproducibility were tested and the composite output signal had a consistent reproducibility of 1 part in 5000. Based on this, the A to D resolution of 12 bits would have been adequate. These observations indicate that future designs can be simplified and use a lower cost A to D chip. The sensor chip used for humidity and temperature measurement worked well and also had a digital readout. The electronics was designed to operate either under external power or on-board battery power. As expected, battery power provided significantly lower noise and better data quality. Device operation for many hours was possible using a single 9 volt battery.

4) Software: Using a combination of C++ and FORTRAN a Windows® based graphic interface was developed which provided a complete real-time display of all of the data as it was acquired. It operated well on a standard laptop computer connected by a single USB cable to the readout device. Data was automatically retained in active memory and was easily saved as an ASCII file suitable for reading and further analysis by conventional software packages such as Excel™. In practice, data acquisition was typically performed at a rate of 1 set of readings each second up to a rate of 1 reading every 10 seconds. Because the USB interface component actually contains an on-board microprocessor chip, future software development can include on-board programs for data acquisition, control and data display eventually avoiding the need for the laptop computer

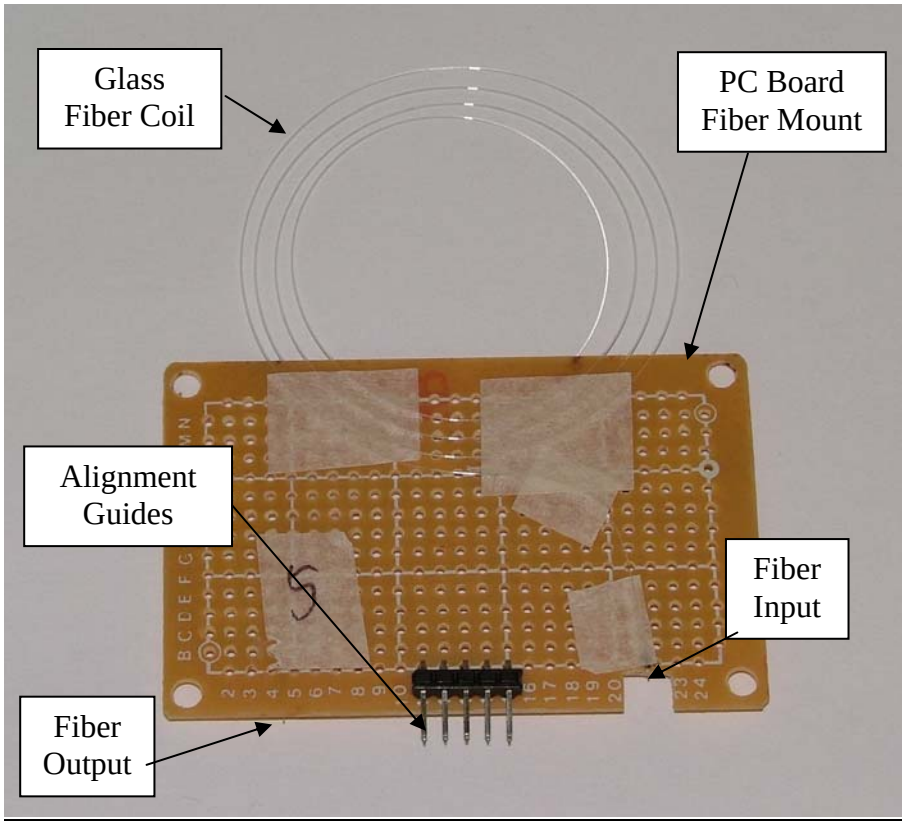


**Figure 6. Close-up view of the glass core fiber cartridge. The glass fiber is wound on a simple fixture (not shown) and mounted on a low cost PC board with adhesive tape. The exposed fiber ends are readily illuminated by LEDs. The coil segment that is exposed to air can be stripped of its cladding and dip coated to complete the cartridge preparation. The final cartridge would be shielded by a cover to protect it from damage and reduce the effect of scattered room light on the photodiode sensors.**

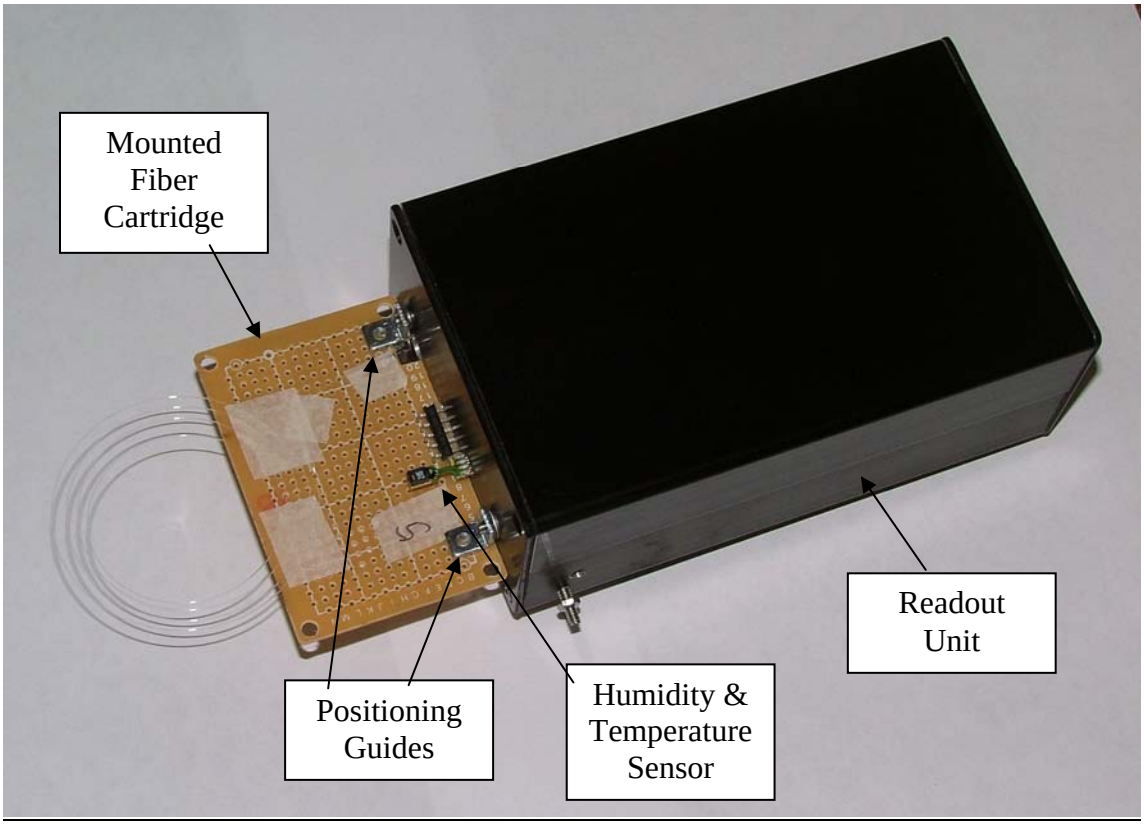


**Figure 7. Fiber cartridge mounted on the readout unit. Positioning guides provide a simple means for reliable positioning of the cartridge so as to assure stable optical performance. A humidity and temperature sensor also protrudes from the housing so as to measure these atmospheric factors.**

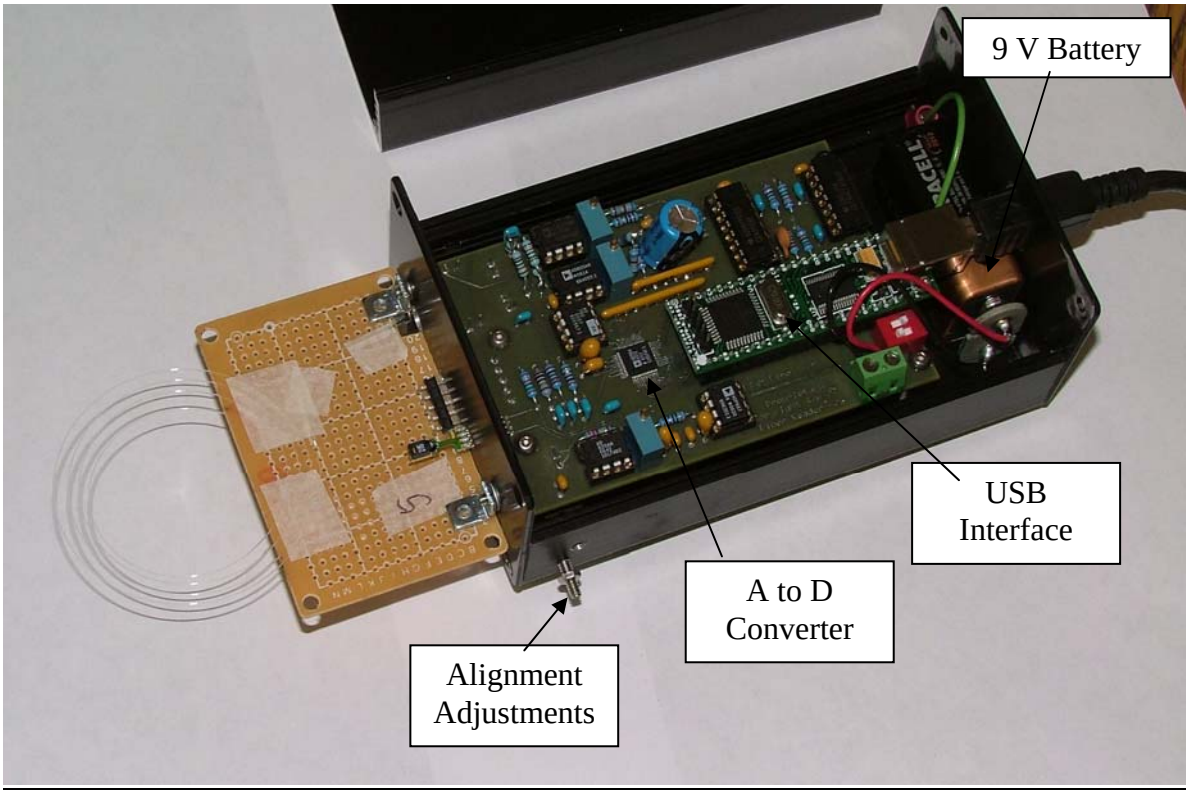


**Figure 8. An inside view of the readout unit showing the core electronics package. The A to D converter digitizes the optical sensor response while the USB interface allows for computer control of the LED flashing and digital readout. Small alignment screws allow the 2 LEDs and sensing photodiode to be adjusted for optimal performance. Such adjustment only needs to be performed once when the readout unit is first assembled. The readout unit can be powered either through the USB cable or via an on-board 9 volt battery.**

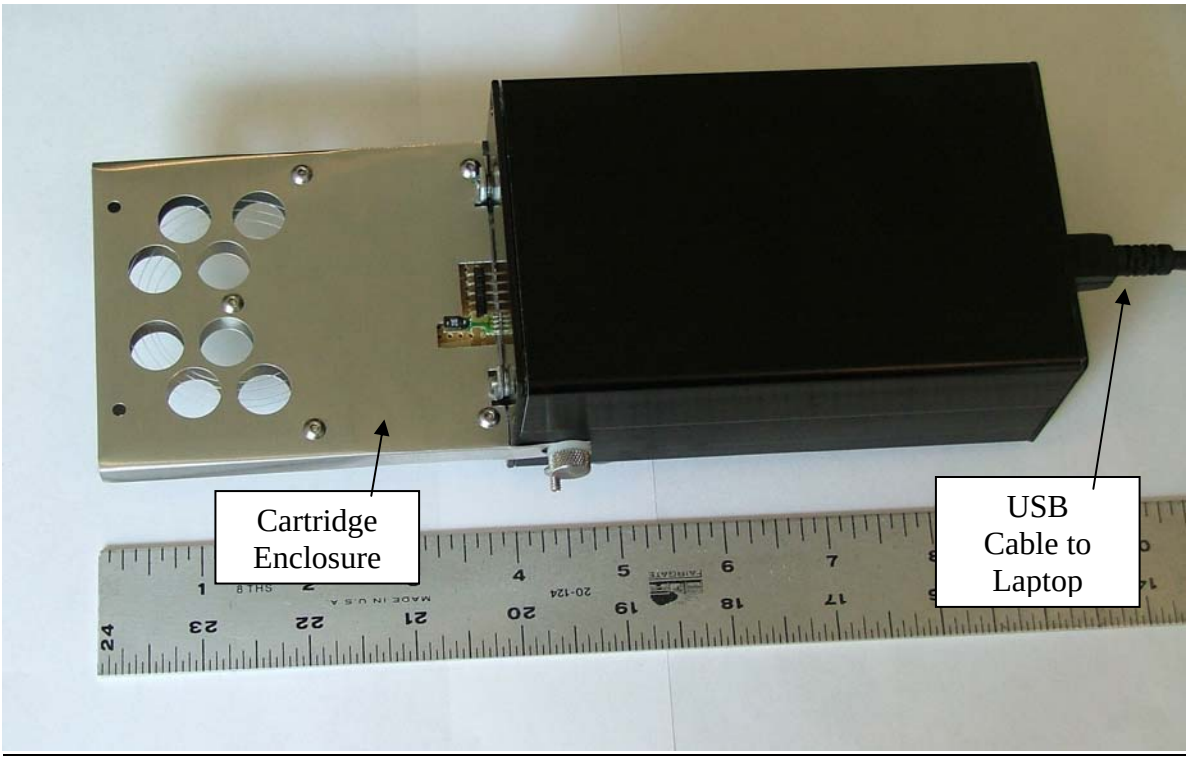


**Figure 9. An external view of the compete Fiber Cartridge and Readout Unit. The outer shield of the cartridge is an integral part of the cartridge and can be made very inexpensively. The cartridge can be quickly replaced and is rigidly attached to the readout unit. The complete package is readily handled and can be used for laboratory and field testing when coupled to a laptop computer for data acquisition.**

### 6.4.3 Exposure Measurements

The exposure testing was comprised of sensor preparation and optical measurements in a controlled atmosphere containing known quantities of diisocyanates.

#### 6.4.3.1 Fiber Stripping

The glass fiber selected for use has a 200 μm core with a hard polymer cladding and buffer. The cladding and buffer are readily stripped by partially dipping the coiled cartridge into hot concentrated sulfuric acid. After gentile washing in distilled water and drying, the resulting fiber is ready for coating. In this unclad state the fiber is relatively fragile and will slowly deteriorate on long term exposure to air. The dip coating process actually prevents deterioration by reducing exposure of the glass surface to air and moisture. Therefore the dip-coating should be accomplished soon after the fiber stripping process is completed.

#### 6.4.3.2 Dip Coating

The primary purpose of dip coating is to apply the sensing reagents to the surface of the fiber in a thin uniform coating over a substantial length of the fiber. Prior research[10,11] had shown that a reagent coating applied over a moderate length of fiber (6 to 8 inches) provided a good response to diisocyanate exposure. This was readily accomplished in a consistent and

reproducible manner. The secondary purpose is to assure that the glass fiber surface is coated to protect the fiber from deterioration by air and moisture.

Dip coating can be as simple as it sounds. A clean surface is dipped into a solution containing the materials of interest and then withdrawn at a controlled rate. Upon drying the excess solvent evaporates away, leaving a uniform coating of the solute on the fiber. The key is determination of the proper solution composition. Our goal was to obtain a coating that is less than 1 μm thick in a consistent manner. Some guidance on this matter is provided by published models of the dip coating process based on work of Landau and Levich[16]. In their model the thickness of the liquid film that forms on the surface is simply related to the viscosity of the liquid, its density, its surface tension and the rate of withdrawal.

The optical properties of the coating are determined by two factors, its refractive index and the absorptive properties of the film. The refractive index plays a role because light can interact with the surface film in two possible approaches. If the refractive index of the film is lower than that of the glass core, the light undergoes total internal reflection and the light interaction with the film is limited to evanescence. In evanescence, the interaction is limited by the refractive index difference and is weaker at the film outer surface. If the refractive index of the film is higher than that of the glass core, then light readily enters the film and experiences its full absorptive properties. In our case, the refractive index of the film is expected to be higher than that of the glass core. This allows us to then estimate the absorbance of the fiber coating based on known models of fiber transmission and the properties of the dye molecule.[17]

It was quickly determined that solution would be quite dilute, therefore the viscosity of the solution could be readily approximated as the viscosity of the pure solvent. In our case, acetonitrile was selected as the solvent. A fiber withdrawal rate of 1 cm/sec was estimated. It was also estimated that enough dye derivative should be placed in the coating so that the final absorbance of the fiber (if all of the dye reacted with the diisocyanate) would be about 3.0 (only 0.1% of the light would be transmitted by the fiber). Using these criteria, a calculation can be made relating solution components to film thickness as shown in Figure 10. Using this calculation, we targeted a coating thickness of 0.1 to 0.2 μm, because this would maximize exposure of the malachite green derivative to airborne diisocyanate.

After dip-coating with this solution we generally observed that the optical transmission of the fiber was reduced by about 50% and would achieve a stable optical performance after being allowed to dry in room air for 30 minutes. It was estimated that this absorbance was optimal for achieving maximum sensor readout precision. The coating could be easily removed by dissolution in a mixture of isopropyl alcohol and acetone and the fiber re-used multiple times with equivalent results.

[16] L. D. Landau, B. G. Levich: [1942] Acta Physiochim, U.R.S.S., 17, 42-54.

[17] Thomas Lee S, Nibu A. George, P. Sureshkumar, P. Radhakrishnan, C.P.G. Vallabhan, and V.P.N. Nampoori: [2001]"Chemical sensing with microbent optical fiber" *Optics Letters* Vol. 26 (20) 1541-1543.

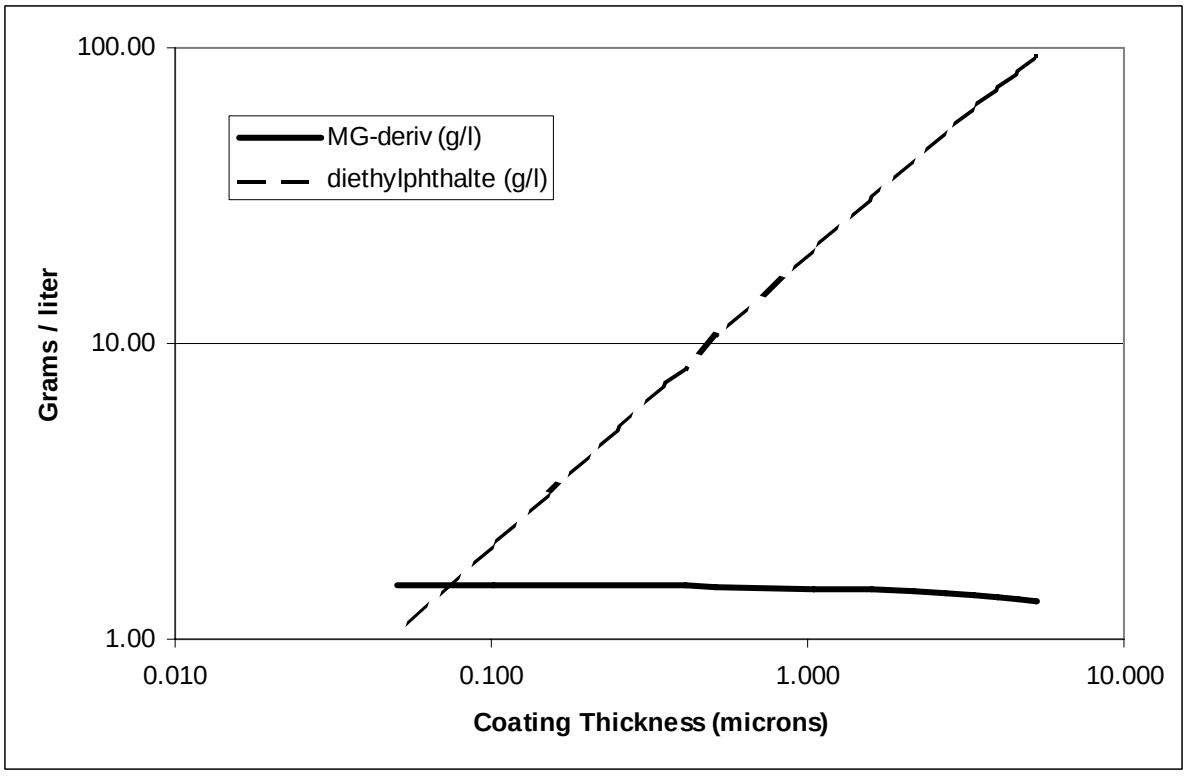


**Figure 10. Calculated relationship between fiber coating thickness and solution concentrations. It is readily seen that the film thickness is primarily a function of the diethyl phthalate concentration and a coating of 0.1 μm can be achieved quite readily. It is also seen that the concentration of malachite green derivative in solution was fairly constant.**

### 6.4.3.3 Fiber Sensor Exposure Experiments

The apparatus used for the exposure experiments was nearly identical to that used in our previous program and is shown below in Figure 11. Its simple structure allows for a controlled air flow rate (1 liter/minute) to be passed through a filtered drying tube to assure air cleanliness and humidity level. The air then passes through a heated glass sampling bulb (heated so as to readily vaporize the injected samples). The sampling bulb has an injection port through which the diisocyanate containing solution can be injected. The air then passes on to a sealed plastic bag that contains the sensor after which the output gas is safely vented.

Prior experience had shown that this procedure provided very reproducible results when microgram quantities of TDI and HDI were dissolved in acetonitrile. Typical injection volumes were a 1 ml of acetonitrile solution.

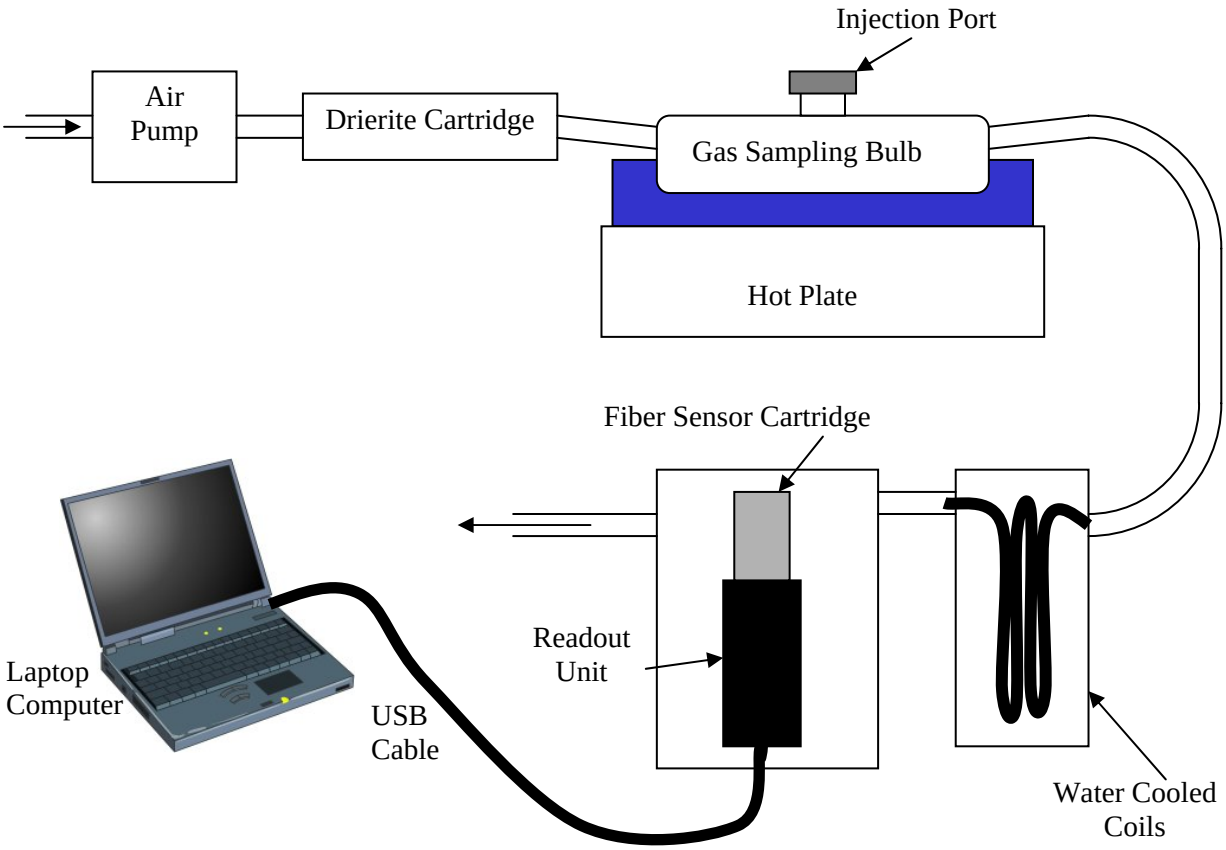


**Figure 11. Schematic diagram of the exposure apparatus used in these tests. A controlled air volume is dried and passed through a heated reservoir (hot water bath) into which the diisocyanate solution is injected. This air flow then passes to the readout unit and fiber cartridge which are sealed inside a disposable polyethylene bag. The entire exposure system is contained inside a chemical fume hood.**

### 6.4.3.4 The Measure of Success

The technical goal was to determine whether the chemical species selected could be made to provide a convenient and reliable measure of airborne diisocyanate exposure. The ideal case would be for the measured sensor response to have a quantitative linear relationship to the level of exposure and that response would be sufficiently rapid so as to be useful to the user. The simplest relationship expected would be;

Fiber Absorbance = constant x [diisocyanate concentration] x (time) + (starting absorbance).

The simplicity of this relationship assumes that other factors such as temperature (T) and humidity (H) have little influence. However, such complete independence of T and H could not be expected, and was indeed planned for as is evidenced by the fact that the readout unit included a temperature and humidity sensor. If the sensitivity to T and H were weak, the sensor response could be reliably adjusted by simultaneous measurement of these factors so that the sensing of the diisocyanates could be reliably determined.

A practical sensor should be capable of providing a significant optical absorbance change when exposed to a diisocyanate concentration of about 20 ppb for 20 minutes. Such a response

should be readily achieved at room temperature. Variations in T or H should not alter the observed signal by more than 20%. Such performance would be the basis of a reliable sensing approach that could be reliably compensated when atmospheric conditions are taken into consideration. What was actually found was that the sensing materials chosen were far more sensitive to T and H than acceptable.

### 6.4.3.5 Sensitivity to Diisocyanates

Two important tests define the sensor response to diisocyanates and are described below.

1) Exposure to high concentration TDI. A few drops of TDI were placed on a watch glass very close to the fiber sensor. Previous experience had shown that significant vaporization of the TDI will occur at room temperature. The sensor should then respond quickly and strongly. Relatively little sensor response was observed, even after 20 minutes.
2) Exposure to controlled atmospheres of HDI and TDI at room temperature. The temperature of the air flow was assured by passing the air through a copper coil immersed in a water bath at room temperature. Sample injections corresponding to atmospheric concentration of approximately 400 ppb were made with HDI and TDI. The test results seen in Figure 12 and Figure 13 show that the sensor response is quite weak. In an attempt explore the potential for maximum sensitivity, the dip coating process was modified, to eliminate the use of diethyl phthalate entirely. This left a coating of pure malachite green derivative on the fiber surface. The tests showed increased sensitivity, but the response was still considered quite weak (see Figure 14).

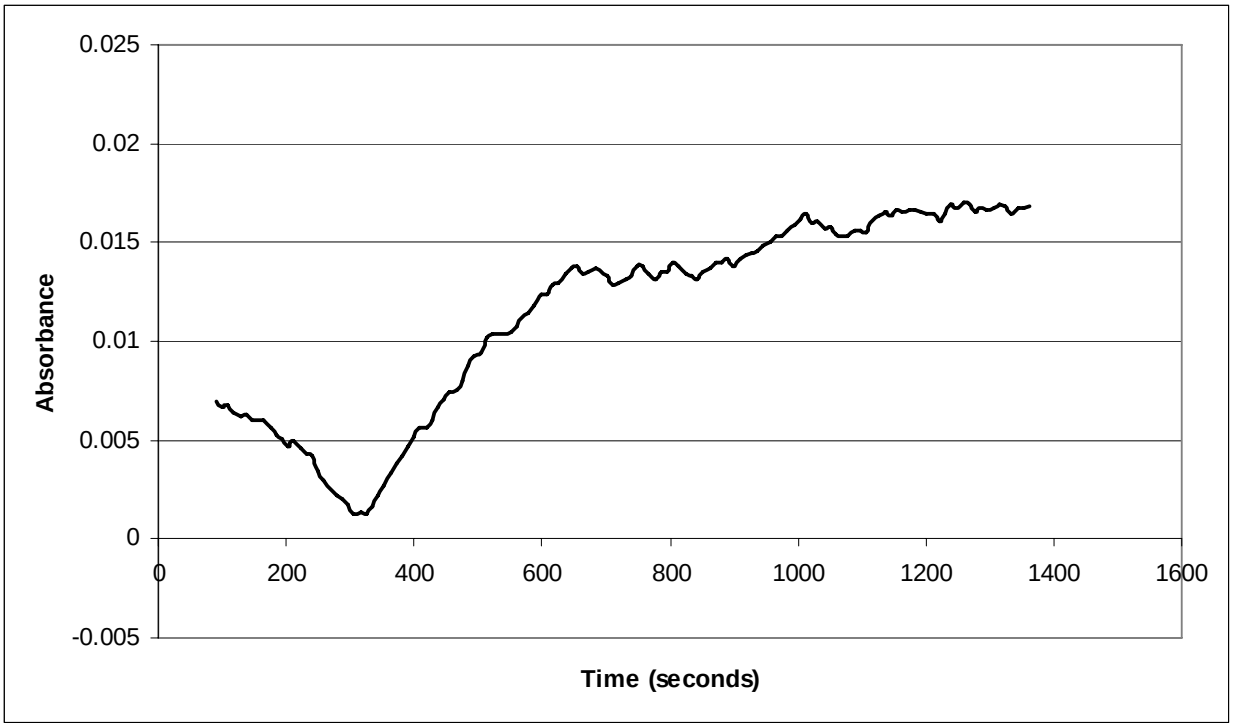


**Figure 12. Sensor response with exposure to approximately 400 ppb HDI at room temperature. The sample injection occurred at 190 seconds. A temporary decline in absorbance is observed due to the effect of the acetonitrile. A small net absorbance change of 0.02 is observed, corresponding to a transmission change of less that 2%.**

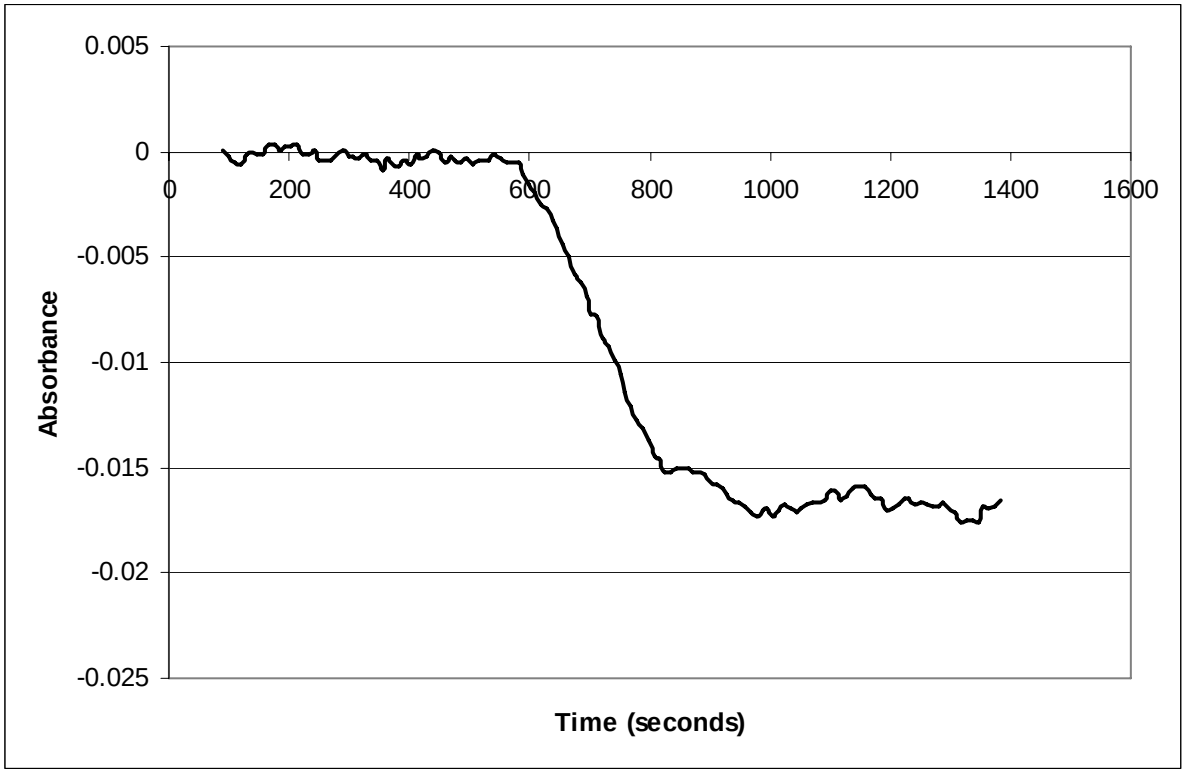


**Figure 13. Sensor response to exposure to approximately 400 ppb TDI at room temperature. The sample injection occurred at 600 seconds. Only a decrease in absorbance is observed due to solvent effects.**

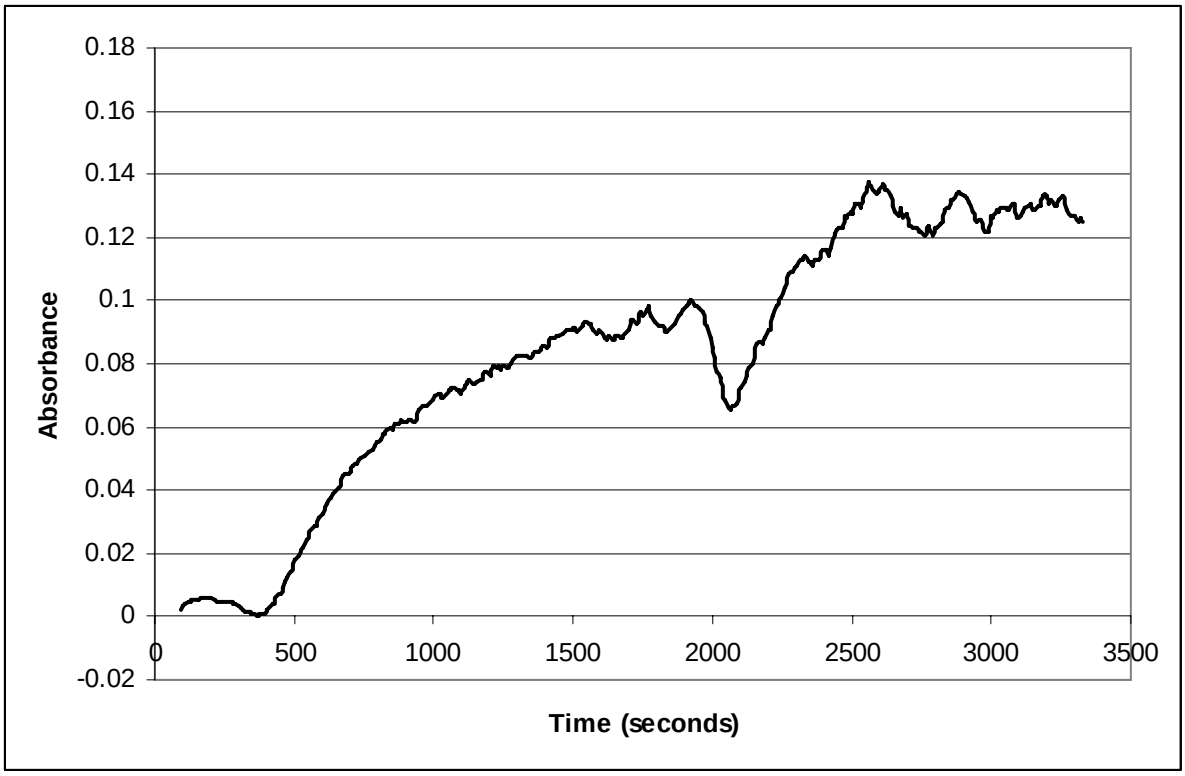


**Figure 14. Sensor response to exposure when the fiber is coated with pure malachite green derivative. Sequential exposures are performed with 400 ppb of HDI injected at 250 seconds and 400 ppb of TDI injected at 1900 seconds. The response is stronger but not as strong as expected or needed.**

Observations: These results indicate that a significant sensitivity problem exists. The response is quite weak and relatively slow. The response to HDI is somewhat stronger, than TDI. Elimination of the diethyl phthalate improves sensitivity, but not by much.

### 6.4.3.6 Sensitivity to Temperature

To explore temperature effects, the cooling coils were removed from the test apparatus shown in Figure 11. A fiber sensor was prepared with a coating that contained malachite green derivative and diethyl phthalate. Warm airflow without any diisocyanate was initiated at 150 seconds. The injection bulb was also heated so that the air temperature around the sensor increased to about 60° C. After 700 seconds the sensor was removed to room temperature and continued to be observed. These results are shown in Figure 15. This experiment indicates a significant sensitivity to temperature that is only partially reversible. The recovery is exponential, and suggestive of a zero order process. This strongly indicates that we are observing the thermal decomposition of the malachite green derivative.

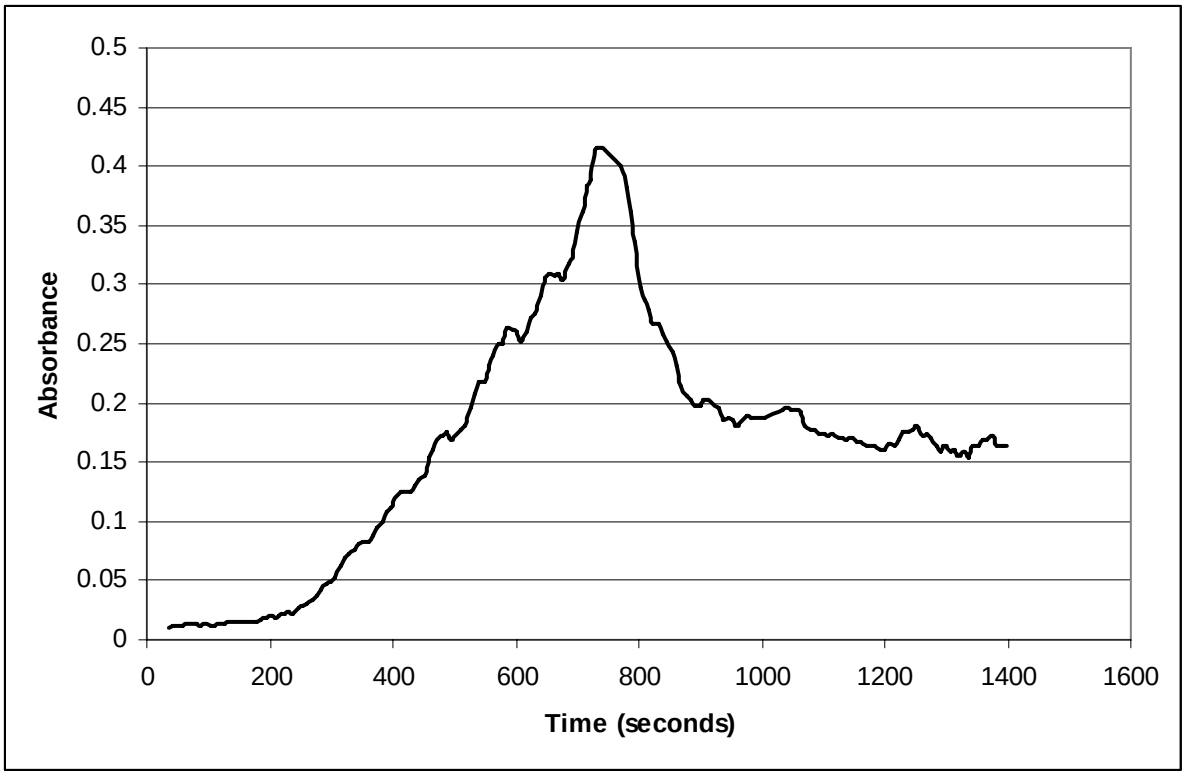


**Figure 15. Test of temperature change on fiber sensor response. The sensor was initially in still room temperature air. At 150 seconds a warm air flow of 60°C was initiated and ended at 700 seconds. The sensor was then returned to room temperature.**

In the test shown in Figure 16 the temperature was reduced to about 40°C and a constant air flow was passed over the fiber sensor. The response of the fiber is much lower at lower temperature, but is still significant. This suggests that elevated temperature significantly shortens the available life of the sensor for exposure measurements.

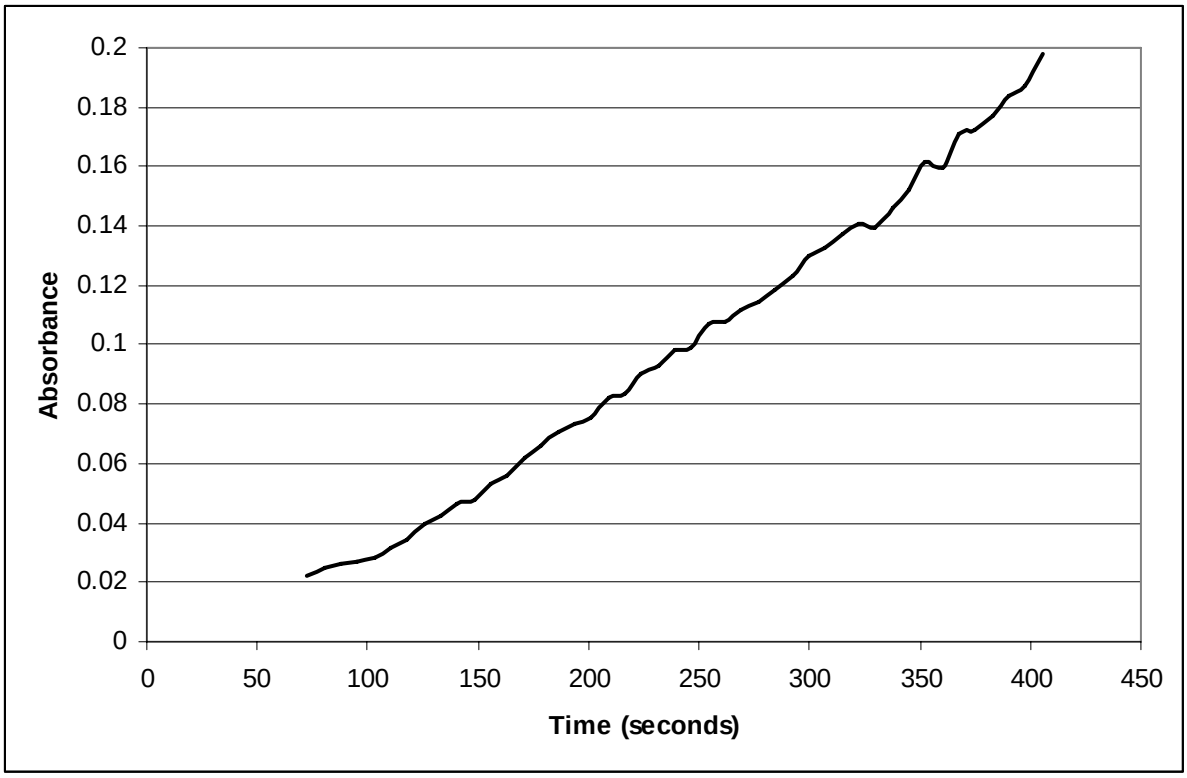


**Figure 16. Reduced temperature test (40°C) on the fiber sensor. This result indicates that reduced temperature has a reduced impact on measured absorbance, but is stilled marked.**

The combination of elevated temperature and diisocyanate exposure was investigated next. It is seen in Figure 17 that the fiber sensor shows the same slow rise when exposed to elevated temperature. At 850 seconds, an exposure to HDI atmosphere is initiated equivalent to 20 ppb. A strong response is observed that is the result of the coupled effects of temperature and diisocyanate exposure.

So far it can be concluded that temperature both causes a thermal decomposition of the malachite green derivative and also enhances its response to the presence of diisocyanates.

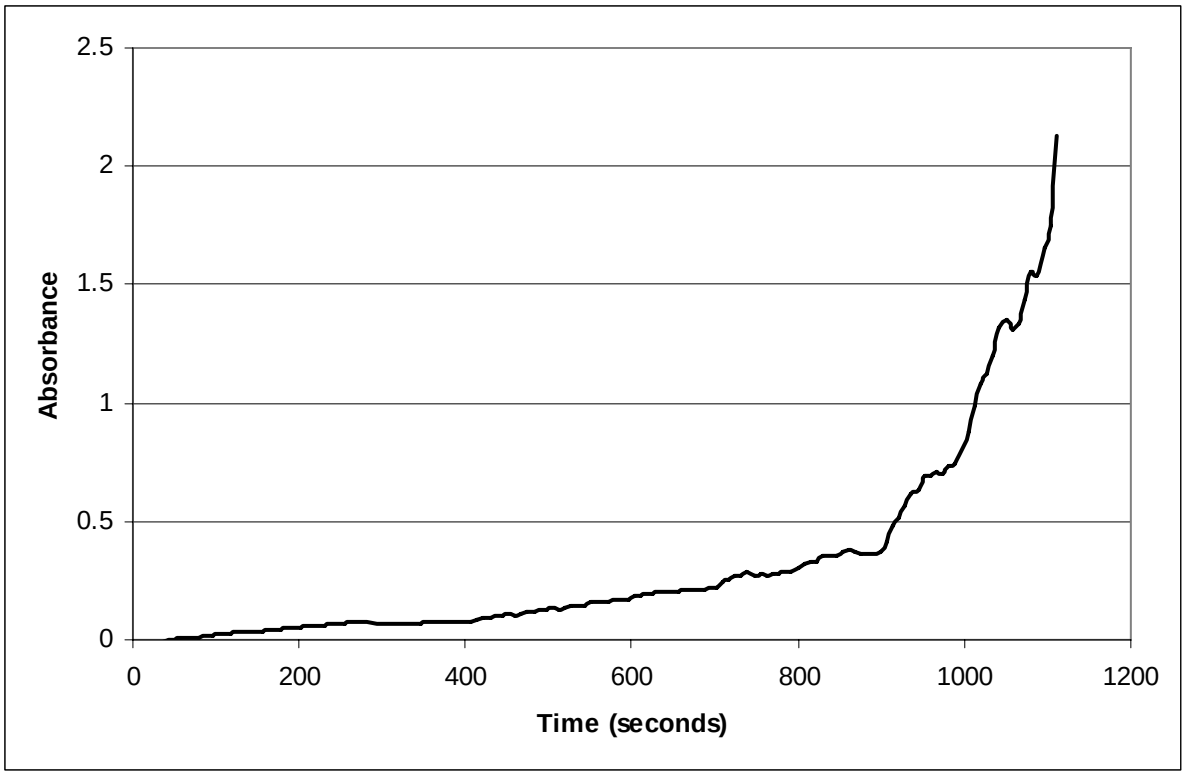


**Figure 17. Combination of temperature and exposure to HDI. The sensor is initially exposed to clean warm air (40°C). After 850 seconds an injection of HDI solution equivalent to 20 ppb exposure in air occurs. The observed sensor response is strong.**

### 6.4.3.7 Sensitivity to Humidity

The tests described above were carried out in dry air. To test the effects of modest humidity levels, the following test was carried out and the results are shown in Figure 18. A fiber sensor was prepared and placed in the apparatus without a Drierite cartridge. The temperature was somewhat elevated at 40°C. At 250 seconds an injection of 20 ppb HDI was made, followed by an injection of 20 ppb TDI at 1500 seconds. The observed response was modest at best. At 2200 seconds a fresh Drierite cartridge was inserted. At 2230 seconds an injection of 20 ppb TDI was made, followed at 3400 seconds by an injection of 20 ppb HDI. Temporary sensor responses due to the solvent effects are clearly visible after each injection.

The observed results indicated that the sensor response was significantly suppressed when air moisture was present. The removal of air moisture by the drying cartridge coupled with the warm temperature provided a strong response. Both HDI and TDI gave similarly strong responses.

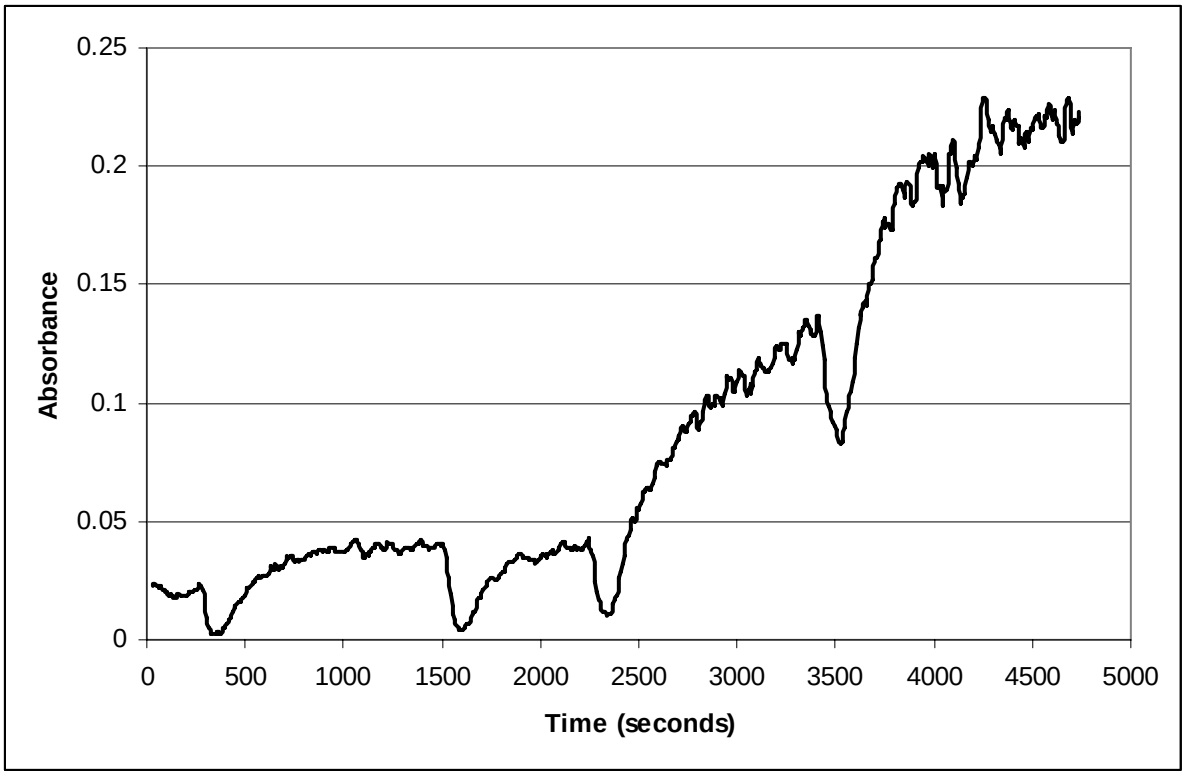


**Figure 18. Test of the combined effects of elevated temperature and changes in humidity during diisocyanate exposure.**

### 6.4.3.8 Conclusions

A fiber sensor preparation method involving fiber stripping in sulfuric acid followed by a dip coating process was developed. The method was controllable and reproducible. The coating developed had the optical properties desired and supported good quality optical measurements.

The exposure measurements indicated that the sensor response to diisocyanates can be quite strong, but is complicated by a high sensitivity to the atmospheric effects of temperature and humidity. Also, the sensor responds only weakly at room temperature even though the response at slightly elevated temperatures is very strong. Finally, keeping the sensor at elevated temperatures for prolonged periods resulted in a constant increase in absorbance which we attribute to the thermal decomposition of the malachite green derivative.

The weak response of the malachite green derivative to diisocyanates at room temperature was particularly disappointing. Our expectation of a similar response for the crystal violet derivative discouraged us from performing any tests using this compound.

## 6.4.4 Quantification of Measurements.

The tests described in the previous section showed that the formulation chosen was excessively sensitive to the effects of temperature and humidity. These coupled effects would be expected to provide unreliable readings under field test conditions. Based on these results, further refinement of performance was not deemed to be of value.

### 6.4.5 Reporting of Results.

This final report was prepared. No publications or patent applications are planned at this time.

## *6.5 Overall Conclusions*

The overall program was only partially successful. Several of the major objectives were achieved, but the response of the sensor to diisocyanates was weak at room temperature and complicated by a high sensitivity to temperature and humidity.

The literature search indicated that a strong response by the candidate sensing materials based on malachite green and crystal violet could be expected. Indeed, this response was confirmed, but only when the atmospheric temperature was increased to 40°C. Synthesis of the necessary derivatives was made and was quite successful for malachite green. The crystal violet derivative was perceived to be of lower purity. Optical spectra confirmed the identities of these materials and indicated the best wavelengths for sensing measurements.

A simple, inexpensive, and reliable fiber cartridge design was developed that allowed for easy assembly and precision placement of the fiber for readout during testing. An electronic readout device was developed that exhibited low measurement noise and high sensitivity for the type of measurements desired. The design developed actually exceeded performance needs and future designs can be simplified with an associated cost savings. Operation at two wavelengths allowed for an accurate determination of a reference measurement for each sensing measurement. The composite measurement uncertainty was observed to be as low as 1 part in 5000.

The fiber stripping and dip coating procedure worked well and provided sensors of reproducible properties that would be sufficient for long term use. The sensors and the coatings were stable at room temperature. Tests of exposure to diisocyanates were performed using an apparatus design that had been emplyed successfully in a previous program. The exposure tests led to several key observations.

1) The response of the sensor to diisocyanates at room temperature was quite weak. Exposure levels in excess of 100 ppb were needed to provide a reliable response.
2) Sensor response to diisocyanates increased significantly with a modest increase in temperature. A strong response was observed with a 20 ppb exposure at 40°C.
3) A sensor response was observed that was due to an increase in temperature alone. This was interpreted as being due to the thermal decomposition of the chemical derivative coating. This effect was seen to compete with the effects of diisocyanate exposure so as to make the observation of chemical exposure less certain.
4) Humidity was observed to play a significant role in sensor sensitivity. Sensor response was suppressed in the presence of modest humidity levels. Sensor response was good only in the presence of dry air.

These observations lead us to conclude that the response of the malachite green derivative to diisocyanate is not adequate as a basis for reliable chemical sensing. It is too sensitive to the effects of temperature and humidity to provide reliable readings. The response rate at room temperature is inadequate for practical real-time sensing.

The fundamental causes for these observations are expected to be based on the underlying chemistry. Our initial model of the chemical mechanism expected that the interaction of the diisocyanate with the derivative was a simple and direct one to one interaction where the

diisocyanate caused the chemical breakdown of the derivative, leading to an observed increase in absorbance. It would appear that this chemical mechanism is not correct. A more likely mechanism is that the diisocyanate will only react with the derivative after it has partially decomposed, releasing the amine component. The amine component can then react with the diisocyanate, allowing the absorbance change to remain permanent. This alternate mechanism would explain the high sensitivity to temperature and the increased response to diisocyanates when the temperature is increased.

Future efforts should focus on the selection of chemical sensing reagents for which the chemical mechanism is based on a direct reaction between the reagent and the diisocyanate. The sensing chemicals should not need to undergo thermal decomposition in order to be sensitive to reaction.

# 7 Publications

None.

# 8 Materials Available for Other Investigators

None.