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DEVELOPMENT OF HYDRAZINE/NITROGEN DIOXIDE FIBER OPTIC SENSOR

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ABSTRACT

Bromothymol Blue (BT)/Bromocresol Green (BG) mixture (1/1) in hydrogel (1/1), produces a blue-green indicator for HZ and/or NO_2. The stability over a two months period of this BT/BG (1/1) indicator solution was tested and no evidence of performance deterioration was detected. A dual HZ/NO_2 prototype sensor utilizing an acid-base indicator was previously constructed. A monitor and control circuit are also designed, built and tested during the course of this project. The circuit is controlled with Motorola MC68HC11 microcontroller evaluation board to monitor the voltage level out of the photodetector. Low-pass filter and amplifier are used to interface the sensor's small voltage with the microcontroller's A/D input. The sensor, interface circuit and the microcontroller board are then all placed in one unit and powered with a single power supply. The unit is then tested several times and the response was consistent and proved the feasibility of dual HZ/NO_2 leak detection. Other sensor types, suitable for silica glass fiber, smaller in size, more rugged and suitable for use on board of the Space Shuttle and missile canisters, are then proposed.

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1. INTRODUCTION

Gases formed by rocket propellants (hydrazine and nitrogen tetroxide), used in the Space Shuttle and other civilian and military applications, are very toxic to humans at low concentrations as well as flammable and explosive at high concentrations. The American conference of governmental industrial hygienists (ACGIH) has recommended that the exposure limits are 10 ppb for hydrazine (HZ) and 3 ppm for nitrogen dioxide (NO_2) [1]. The explosion limit for HZ in atmospheric pressure is 2.9% [2]. Accidental leak detection is of a great concern to protect personnel, wild life and the environment.
A fiber optic sensor is an ideal and inherently safe propellant leak detector due to the following advantages:

- Spark hazard free, which is an obvious requirement for propellant leak detection.
- Immunity to electromagnetic interference making it suitable for use in the closed environment of missile canister, spacecrafts and on board of the Space Shuttle.
- Distance to the measuring point can be great (several kilometers) due to small attenuation of optical fiber.
- Possibility of multiplexing several sensing elements to one remote data acquisition station.
- Low cost, lightweight, small size and low power component enables densely multiplexing sensor arrays for precise leak localization.
- Can withstand relatively extreme temperatures, which further justifies their suitability for aerospace and military applications.

Previous work was focused on the development of dual HZ/NO_2 prototype sensor utilizing an acid-base indicator that undergoes color changes depending on which gas is present [2]. The indicator is imbedded in a hydrogel matrix to aid long-term stability. This hydrogel is applied to a mirror that in turn is placed in front of two plastic fibers. One of the two plastic fibers is connected to a 630 μm LED while the other is connected to a photodetector. Light emitted from the first fiber is reflected and collected by the second fiber. The amount of the reflected light is a function of the hydrogel color i.e. dependent on detected gas. The purpose of this project is to further the development of the sensor to produce a unit with alarm to indicate either a fuel or an oxidizer leak is detected. Hence, the main objective of this project is to design and build an electronic interrogator board to monitor propellant gas leaks (utilizing existing prototype sensor) and to determine indicator solution stability over time. Another objective of the project is to propose a plan for the development of other fiber optic sensors more suitable for aerospace and military applications.
This report outlines an introduction of gas leak detection and two of the most common methods for detection, it then describes the hardware and the software of the electronic interrogator board designed during this summer, (the control code written in assembly language is attached as an Appendix). Finally, several other fiber optic sensor configurations are also recommended which may be lighter in weight, cheaper and more rugged than the present one in the laboratory.

2. WAVE PROPAGATION IN OPTICAL FIBERS

Optical fibers for communication systems are commodity items easily obtainable and competitively priced. The attenuation characteristics of these fibers, which are the important features in the context of remote chemical sensing, are well known and basically comprise a transparent window over the range 0.6

– 1.6 μm. Attenuation in this window varies from as high as 1 dB/km to as low as 0.2 dB/km. These fibers are obviously excellent transmission media and are supported by an infrastructure of optical components such as connectors, light sources, detectors, wavelength selective filters and numerous other components. An optical fiber is produced by forming concentric layers of low-refractive-index cladding material around a high-refractive-index core region. Light energy is contained within the higher-index core due to the reflection at the interface of the two materials [3]. Figure 1 illustrates the mechanism of the simplest class of fiber design, the step-index, where

η is the refractive index of air,
η_1 is the core refractive index,
η_2 is the cladding refractive index,
θ is the critical angle, and
θ_o is the acceptance angle, also called acceptance cone half angle [4].

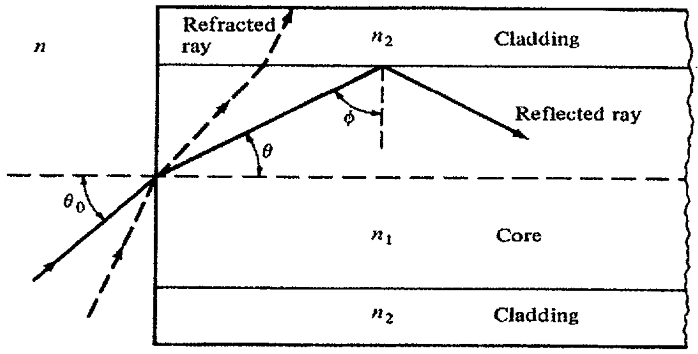


Figure 1. Structure of a step-index optical fiber.

As a light ray strikes the surface of the fiber, it is refracted slightly toward the center of the core with an angle that is a function of the glass/air interface refractive-index difference. Once the ray enters the core, it propagates and strikes the core/cladding interface. If the angle at which the ray strikes the core/clad interface is less than the critical angle defined by the core/cladding refractive-index difference, it reflects back into the core and continues to propagate in the same manner. Although the light energies are totally reflected, the electromagnetic fields still penetrate into the cladding as evanescent fields (Section 3.*b*). If the ray strikes the core/clad interface at an angle greater than the critical angle, it passes into the cladding and is eventually lost.

The critical angle within the fiber translates to an acceptance angle at the fiber surface. The sine of this angle defines the numerical aperture of the fiber. Numerical aperture is a parameter that defines the cone of optical-energy acceptance of the fiber and is critical to the coupling efficiency and propagation properties of the fiber.

3. SENSING TECHNIQUES

There are numerous gas sensing techniques, two of the most common methods are outlined in this Section.

a. Coupling Technique

Transducers in which the light exits from an optical waveguide and is coupled to the same or other waveguide/s are called coupling based transducers [5]. The light must be extracted from the waveguide in order to interact with the sensing material. This principle has led to a range of gas sensor designs: single or multiple fibers, either single-mode or multimode, in transmissive or reflective configurations. The existing HZ/NO_2 leak sensor utilizes the reflective configuration as shown in Figure 2, and the sensing material is a pH indicator solution. The coupled power collected by the receiver fiber changes according to color change in the sensing material upon exposure to acidic and basic gases.

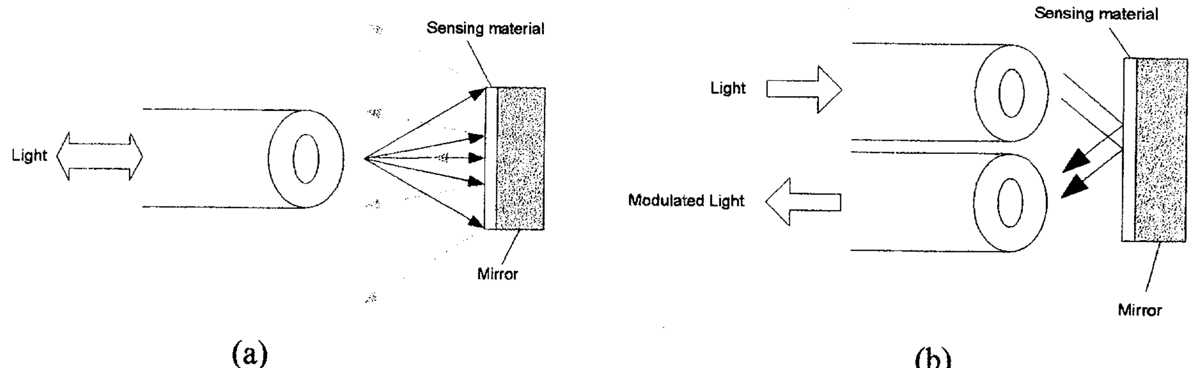


Figure 2. Reflective configuration of coupling-based HZ/NO_2 leak sensor using: (a) a single fiber acting as both emitter and receiver, (b) one fiber acting as emitter, another fiber acting as receiver.

One of the major drawbacks of the use of coupling based transducers, especially with single-mode fibers, is the poor coupling efficiency between the fibers, which greatly affects the resolution of the sensor system. Intensity modulated optical sensors were developed to utilize volume or GRIN optics or fiber bundles to compensate for the limited displacement range of measurement with bare optical fibers. Other designs have been proposed: a single fiber acting as both emitter and receiver, or two or more receiver fibers as an alternate form of compensation.

b. Evanescent Field Technique

The evanescent field or wave is a well-known effect experienced by light at boundaries with a refractive index change: although the light can be totally reflected by the boundary, part of the electromagnetic field 'enters' the other side, occupying the two media [5]. This is the case for optical waveguides. As shown in Figure 3.a, light is guided by the core (inner medium of higher refractive index), but a small percentage of the field, called the evanescent field, travels in the cladding. If the cladding is removed, or its properties modified, the evanescent wave, and thus the guided light, is able to interact with the sensing material, providing the basis for many sensing schemes (see Figure 3.b).

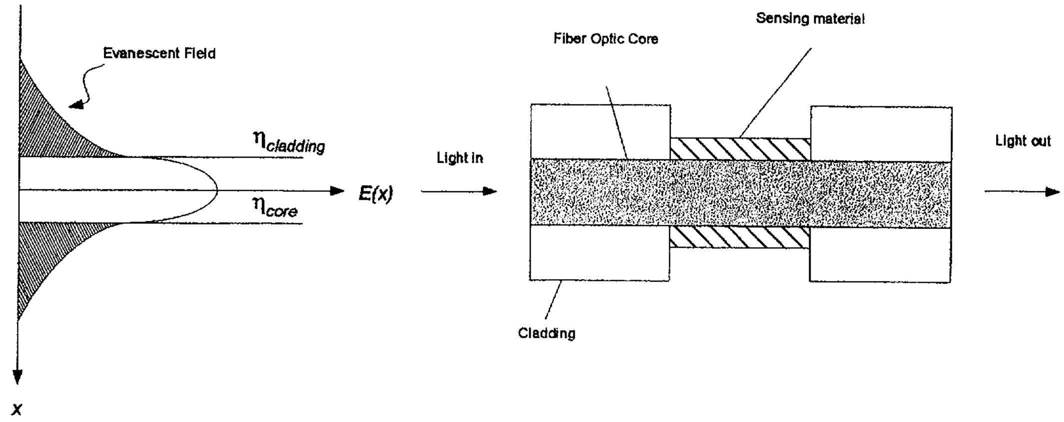
The simplest evanescent transducer is made of a segment of optical fiber with the cladding removed or side-polished. Many chemical species in gas form can be directly detected through the absorption of the evanescent wave. An indirect measurement can be performed by substituting the cladding with a material, layer or film whose optical properties can be changed by the substance to be detected, usually indicator dyes immobilized by a sol-gel film deposited on the core's surface. Sensitivity and the long-term reliability due to the surface contamination as well as the degradation of the indicator are major concerns in this design.

One of the drawbacks of evanescent field sensors based on conventional waveguides is the weak interaction with the sensing material due to the small excursion of the field into the cladding. In order to improve the weak interaction of the evanescent field with the sensing material, tapered segments of optical fibers have been proposed as shown in Figure 4. The field strength decreases exponentially outside the core regardless of the waveguide shape or modal distribution. The evanescent field penetration depth into the cladding is inversely proportional to the normalized frequency number, V, defined as:

$$V = \frac{2\pi a}{\lambda}\sqrt{\eta_1^2 - \eta_2^2}$$

where: a is the radius of the core, and
λ is the wavelength of the light ray.

The evanescent field penetration depth into the cladding is inversely proportional to the normalized frequency number V. The lower the value of V, the greater the evanescent field penetration into the cladding. The ratio of optical power through the cladding to the total optical power (P_{clad}/P) is controlled by several factors such as core diameter, operating wavelength and several other factors.



(a) (b)

Figure 3. (a) Evanescent field in a guided optical medium;
(b) Scheme of a transducer based on this principle (modified cladding).

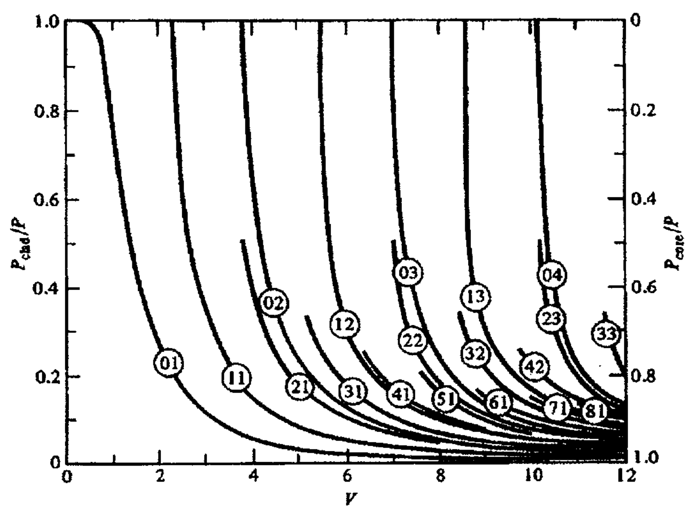


Figure 4. Fractional power flow of a step-index fiber as a function of V. [3].

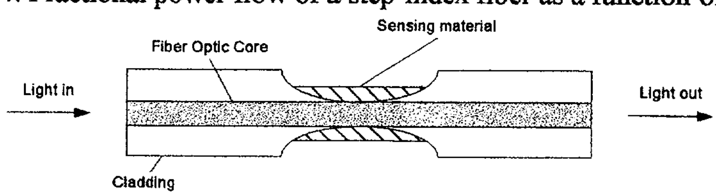


Figure 5. Optical fiber with a new proposed tapered segment.

As the sensing film changes its color P_{clad} will change accordingly. Manipulating the ratio P_{clad}/P could control sensor's sensitivity and insertion loss.

4. PROTOTYPE FIBER OPTIC SENSING SYSTEM

This section explains the hardware and the software designed to interrogate the prototype HZ/NO_2 leak sensor designed and built by Ms. Rebecca Young (KSC colleague). The sensor is a reflective configuration type with two plastic fibers: one fiber acting as emitter, and another acting as receiver as shown in Figure 2. Sensor's interrogator circuit is controlled with Motorola MC68HC11 microcontroller. The MC68HC11 microcontroller has built in 8-channels/8-bits analog-to-digital (A/D) converters. A/D channel #2 (pin # PE-1 connected to the amplifier output) is to monitor the voltage level out of the photodetector. The following two sections explain the hardware of the circuit needed to condition the output signal of the sensor to interface with the A/D input.

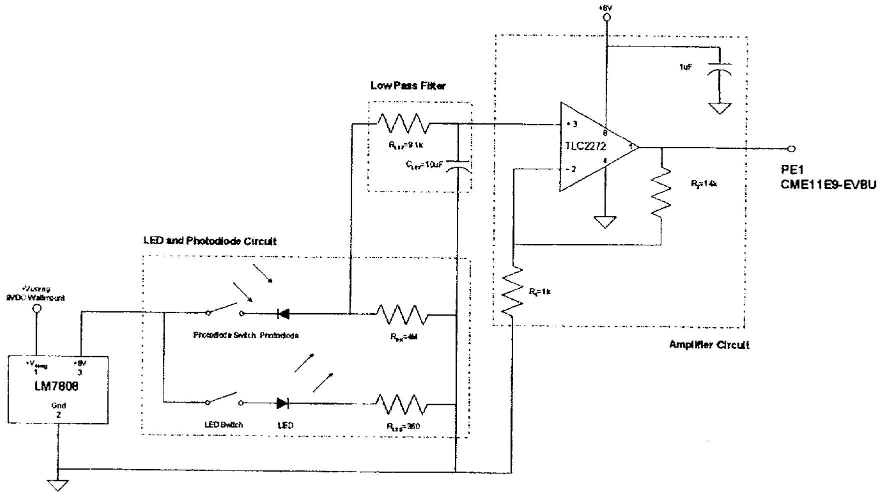


Figure 6. Leak sensor control circuit.

a. *Interrogator Circuit Hardware*

The minuscule voltage from the photodiode circuit needed to pass through a low pass filter to remove unwanted higher frequency components, and a non-inverting amplifier with a gain of 15 for the voltage to fall within the 2-5V input range of the microcontroller (input pin PE1). The voltage resolution is calculated using the equation $\frac{(V_{rH} - V_{rL})}{G \times 2^n}$, where $V_{rH} = 5V$ (reference voltage high), $V_{rL} = 2V$ (reference voltage low), G is the amplifier's voltage gain, and n is the number of bits per sample of the A/D (8 bits/sample for the HC11). The calculated resolution is found to be 0.78 mV/division. Circuit schematic diagram is shown in Figure 6.

b. *Interrogator Circuit Software*

Due to the fact that the output voltage drifts slowly, the output voltage per minute is allowed to drift within certain tolerance. Therefore, three tolerances are imbedded in the code: one is when no gas leak is suspected (TOL) and the other two are when gas leak is suspected (HZTOL for hydrazine and NO2TOL for NO_2). A flow chart of code flow is shown in Figure 7. The microcontroller software would be able to effectively detect the presence of Hydrazine (52 ppm) in one minute and Nitrogen Dioxide (400 ppm) in two minutes. However, for convenience detection time is set to be two minutes for both gasses. More detailed flowcharts for the code are included in Appendix A. The control code, written in assembly language, is included in Appendix B.

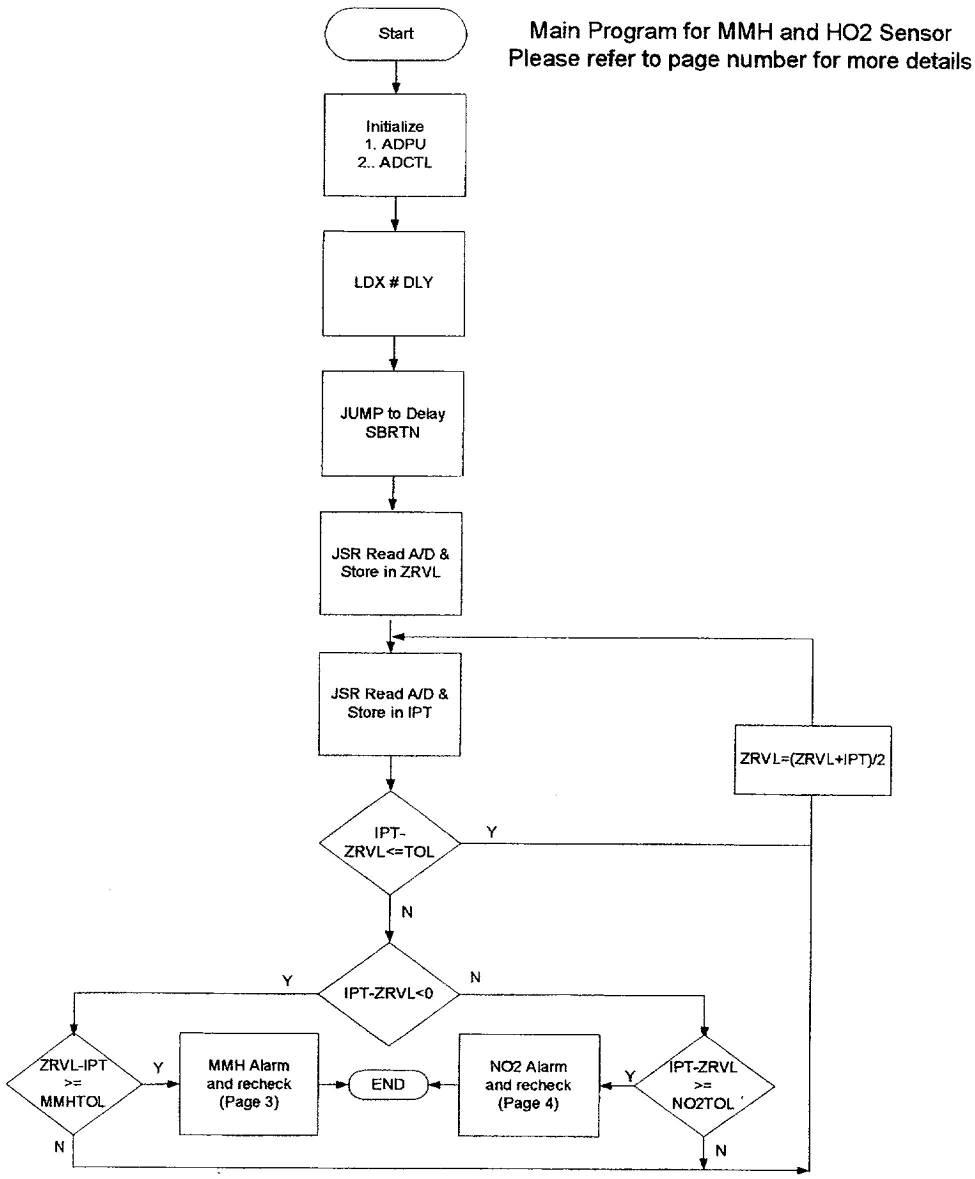
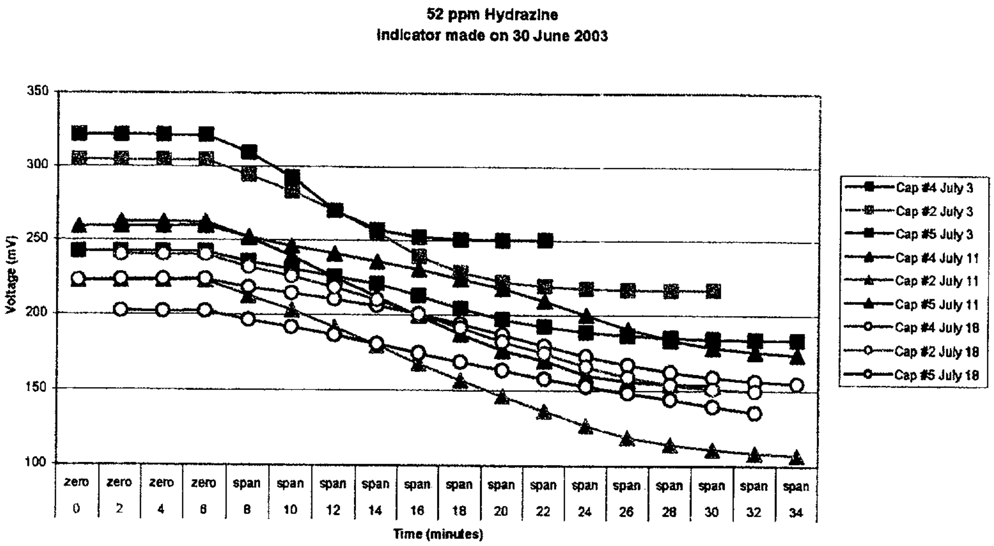


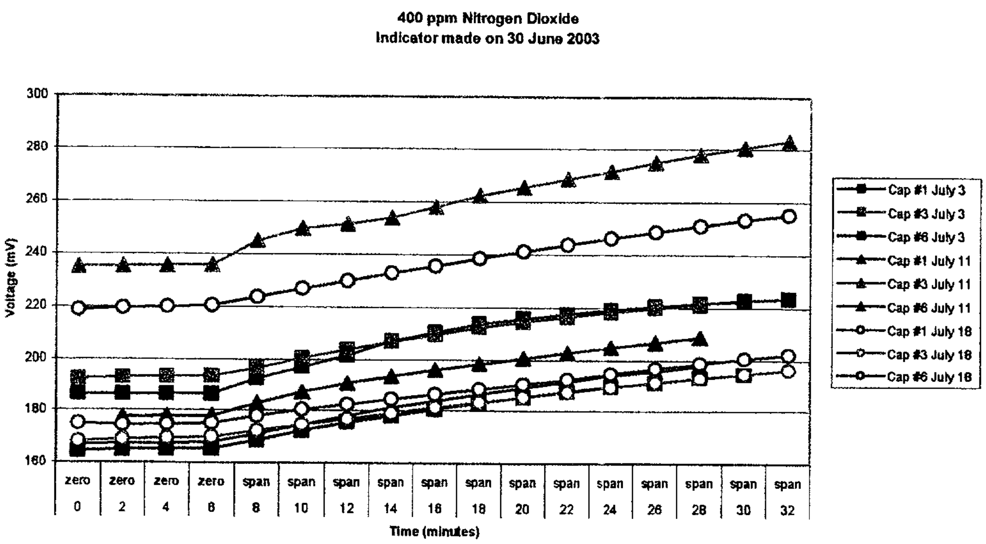
Figure 7. Control code flow chart.

5. SUMMARY OF RESULTS

The six sensor caps had different baseline values for each trial. This could be due to inconsistencies in the fiber distance to the mirror, inconsistencies of the thickness of the indicator solution on the mirror, and/or instability of the power supply (first set of trials were done on 9V batteries while the rest were done using a wall pack power supply). Overall, the performance curves of the sensor caps were consistent over the two months period, as shown in Figure 8.



(a)



(b)

Figure 8. Sensor response using indicator solution made on 30 June 2003.
Test conducted on 3, 11 and 18 of July 2003 for the detection of
(a) 52 ppm Hydrazine and (b) 400 ppm Nitrogen Dioxide.

6. RECOMMENDED DEVELOPMENT PLAN

The objective of this plan is to design, fabricate and test a more advanced, dual HZ/NO_2, leak detector. The ultimate goal is to detect concentrations as low as ACGIH recommended exposure limits. The research will be conducted in phases, vapor's concentration will be decreased in later phases.
Rather than fabricating just a fiber optic sensor, the final outcome of this proposed project includes a fiber

optic sensor, signal conditioning circuit, microcontroller system and alarm system.

a. Sensor

As indicated in Section 3, two types of sensors could be used for this application; coupling type and modified cladding (evanescent field) type. The coupling type is the one experimented with in the previous section. In this section, suggestions are given to, fabricate the coupling-type sensor using silica fiber and to fabricate cladding type sensor using the same sensing chemical as the one used in this experiment.

Coupling Type: To facilitate using silica fiber in a coupling type sensor, collimators could be attached to the emitting and the collecting fibers as shown in Figure 9. However, in this configuration the two collimators have to be placed at equal angles with respect to the reflecting mirror. While this configuration could be hard to align, the success of the preliminary work guarantees its validity.

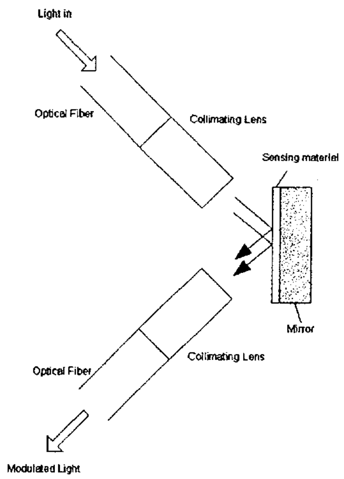


Figure 9. Silica fiber coupling type sensor using collimators.

Modified Cladding Type: Based upon the success of this preliminary work, the following conclusion could be drawn; the red light (λ= 633 nm) reflected off a mirror covered with a sensor film is a function of the gas applied to the film. The same concept is applicable for the second type of sensors: evanescent wave type. The basic modified cladding type sensor configuration as the one shown in Figure 2b should be fabricated and the following parameters should then be evaluated with HZ as well as NO_2:

- Percentage change of received optical power per unit time vs. chemical exposure run.
- Percentage change of received optical power per unit time vs. wavelength.
- Percentage change of received optical power per unit time vs. gas concentration.

b. Electronic Interrogator

An amplifier is a suitable electronic circuit to interface the photodetector to the A/D input. Amplifier gain could be determined to adjust sensor's output voltage to match A/D input allowable range.
To increase the resolution of the detector system, 16 bits - 10-bit A/D microcontroller is suggested to monitor the sensor (Motorola MC68HC12 is suggested).

7. CONCLUSIONS

The stability of the BT/BG mixture in hydrogel was tested over a period of two months and no evidence of performance deterioration was detected. However, there was no permanent baseline value for the start of each trial. The six sensor caps had different baseline values that fell in the range from 150 mV to

350 mV. The differences could be due to inconsistencies in the fiber distance to the mirror, the thickness of the indicator solution on the mirror, and/or impurities (in the form of bubbles or dust particles) in the indicator solution or on the surface of the mirror. The experiment was repeatable with consistent response.

An alarm unit, to monitor sensor's output voltage based on the MC68HC11 microcontroller, was successfully built and tested. This alarm unit successfully detected the presence of HZ (52 ppm) and the presence of NO_2 (400 ppm) in two minutes time. Detection time could be smaller, however the system may be more prone to false alarms.

Recommended development plan includes the development of other sensor types, such as the modified cladding sensor. Several parameters to be tested are suggested such as response vs. chemical exposure run, response vs. wavelength, and response vs. gas concentration. Future development plans also include a 16 bits - 10-bit A/D microcontroller to monitor the sensor.

Acknowledgements

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APPENDIX A

Hydrazine Detection and Recheck
Page 3

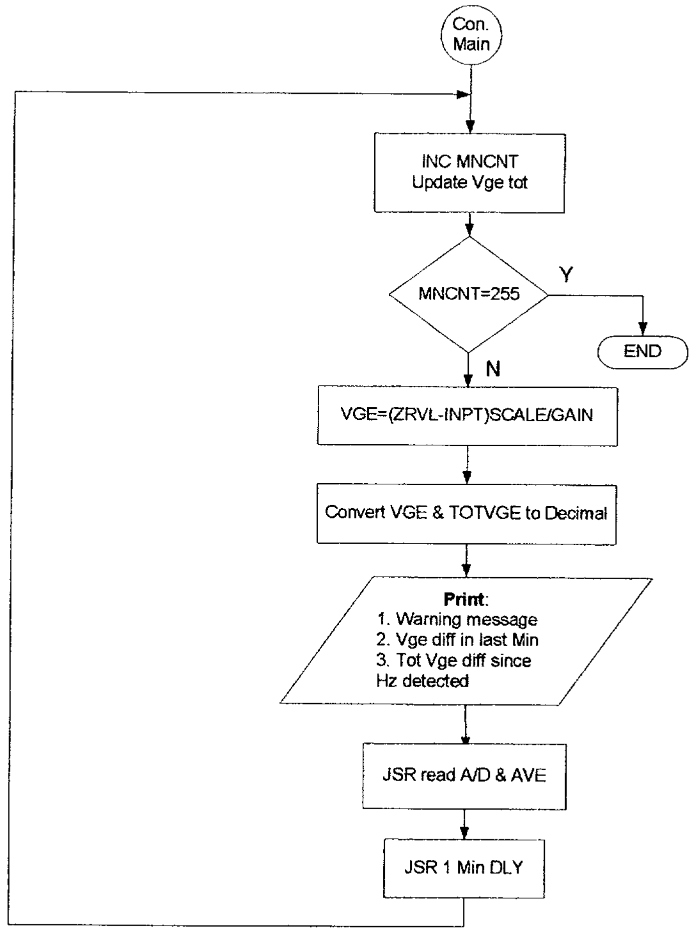

Figure a. Code segment for HZ detection routine (NO_2 routine i.e. Page 4 is very similar)

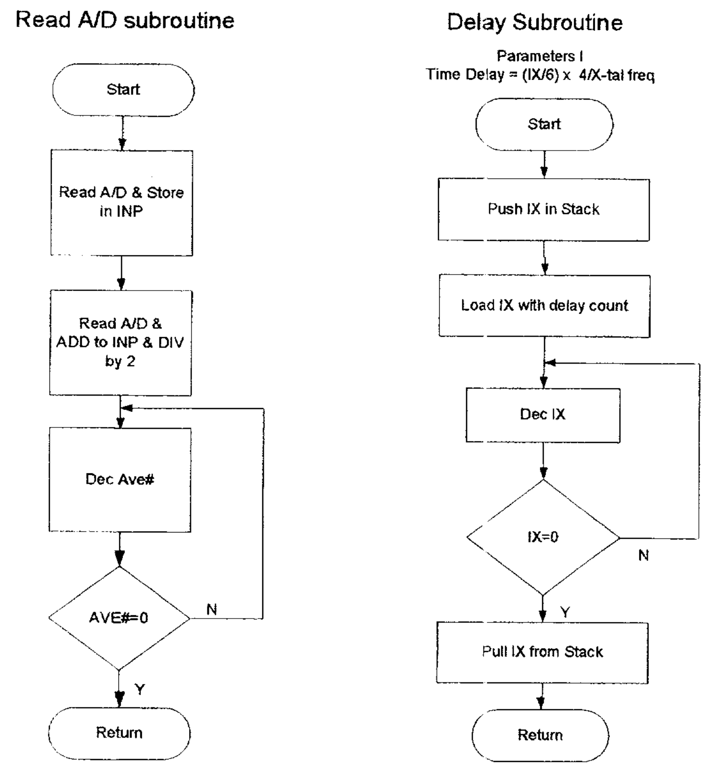

Figure b. A/D Read and Average and Delay subroutines