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LOW-COST FIBER-OPTIC CHEMOCHROMIC HYDROGEN DETECTOR

D. K. Benson, C. E. Tracy, G. Hishmeh, P. Ciszek, and Se-Hee Lee
National Renewable Energy Laboratory
Golden, CO 80401

Abstract

The ability to detect hydrogen gas leaks economically and with inherent safety is an important technology that could facilitate commercial acceptance of hydrogen fuel in various applications. In particular, hydrogen fueled passenger vehicles will require hydrogen leak detectors to signal the activation of safety devices such as shutoff valves, ventilating fans, alarms, etc. Such detectors may be required in several locations within a vehicle - wherever a leak could pose a safety hazard. It is therefore important that the detectors be very economical. This paper reports progress on the development of low-cost fiber-optic hydrogen detectors intended to meet the needs of a hydrogen-fueled passenger vehicle. In our design, the presence of hydrogen in air is sensed by a thin-film coating at the end of a polymer optical fiber. When the coating reacts reversibly with the hydrogen, its optical properties are changed. Light from a central electro-optic control unit is projected down the optical fiber where it is reflected from the sensor coating back to central optical detectors. A change in the reflected intensity indicates the presence of hydrogen. The fiber-optic detector offers inherent safety by removing all electrical power from the leak sites and offers reduced signal processing problems by minimizing electromagnetic interference. Critical detector performance requirements include high selectivity, response speed and durability as well as potential for low-cost production.

A sensor based on the reversible, palladium-catalyzed reaction of amorphous tungsten oxide with hydrogen was studied extensively. While it was found to be adequately sensitive in a simple reflective sensor configuration, it was too slow. A new sensor configuration was invented and tested. The new design uses the coating in a surface plasmon resonance configuration so that very subtle changes in the refractive index of the coating can be detected at the resonance wavelength. This new design increased the response speed significantly, but introduced other

problems. We found that reversible desorption of water vapor from the amorphous tungsten oxide also changed its refractive index and gave rise to a false hydrogen signal. Increasing the thickness of the palladium catalyst layer to block the water vapor while still allowing the hydrogen to pass through proved to be effective at removing the false signals. However, this solution introduced an unexpected degradation in the sensor sensitivity over time. We eventually explained this degradation by a new interpretation of the reversible hydrogen reaction with the tungsten oxide. We believe that, contrary to conventional wisdom, oxygen is extracted from the tungsten oxide by hydrogen rather than hydrogen being inserted into the tungsten oxide. This reaction is only reversible if the film has access to oxygen. The thick palladium film that is needed to prevent false signals blocks the oxygen and allows mostly irreversible reactions and, hence degradation in sensitivity and response speed.

In view of the problems with the tungsten oxide sensor, we identified a new sensor coating, yttrium hydride and conducted preliminary tests. This material reacts reversibly with hydrogen in air to form a continuous range of compositions between the dihydride and the trihydride with dramatic changes in optical properties that are readily detected in a fiber-optic sensor configuration. Preliminary tests on an unoptimized sensor showed promising sensitivity to hydrogen and response speed much greater than in the tungsten oxide sensors. We plan to optimize the new sensor and evaluate its performance.

Background

The ability to detect hydrogen gas leaks economically and with inherent safety is an important technology that could facilitate commercial acceptance of hydrogen fuel in various applications. In particular, hydrogen fueled passenger vehicles will require hydrogen leak detectors to signal the activation of safety devices such as shutoff valves, ventilating fans, alarms, etc. Such detectors may be required in several locations within a vehicle - wherever a leak could pose a safety hazard. It is therefore important that the detectors be very economical. An optical fiber coated with a thin film chemochromic (a color change induced by a chemical reaction) coating offers the possibility of meeting the objectives of safety and low cost.

The reversible reaction between WO_3 and hydrogen has been well known since Schaefer showed that thin films of WO_3 with a superficial coating of platinum showed several orders of magnitude increases in electrical conductance when exposed to hydrogen in air. The reaction was thought to be the result of proton insertion into the tungsten oxide lattice in analogy to the electrochemical hydrogen insertion thought to occur during electrochromic coloration of tungsten oxide. Ito and coworkers (Ito 1984) showed that this hydrogen reaction also produced a broad optical absorption band just as its does in electrochromic coloration of tungsten oxide. They used the optical absorption as a means to detect hydrogen gas and suggested its possible use in a fiber-optic hydrogen detector. In their suggested detector design, light reflected from the thin film coating on the end of a fiber would be attenuated by the optical absorption band and indicate the presence of hydrogen at the sensor location.

Last year (Benson 1997) we tested the Ito suggestion by studying the reaction of tungsten oxide films in vacuum and in carefully controlled partial pressure mixtures of hydrogen with oxygen and hydrogen with air. Sensor response time constants were measured over a range of temperatures and hydrogen partial pressures. The reactions were shown to be reversible and samples tested over several months showed no evidence of degradation. The time constants, however, were too long - on the order of 30 seconds for response and nearly 30 minutes for recovery under typical room temperature testing conditions.

A new sensor design was invented (Benson 1998) which enhances the sensitivity to subtle changes in the coating. The chemochromic film is configured so that a surface plasmon resonance (SPR) occurs in it at a certain wavelength (Raether 1988). The hydrogen reaction produces a change in the optical index of the tungsten oxide which shifts the wavelength of the resonance absorption peak. The intensity of the reflected light at that wavelength is very sensitive to the shift in refractive index. Detecting the reflected light at or near the resonance wavelength enhances and speeds the hydrogen response signal. The new design also incorporated a means to produce a reference signal at a wavelength away from the resonance in the same optical fiber so that two outputs, a hydrogen-sensitive signal and a hydrogen-insensitive reference signal could be processed. The ratio of the hydrogen-sensitive signal to the reference signal should cancel much of the noise caused by changes in the optical transmittance of the optical fiber, a significant noise problem in a vibrating environment such as a vehicle.

This year's work has focused on testing the new SPR fiber-optic detector design.

Approach

Two parallel activities were pursued. In the first, we focused on the measurement of the hydrogen response characteristics of the sensor films in a configuration which produced a surface plasmon resonance absorption. For this purpose we deposited sensor films on large glass prisms for convenience of handling and measurement. The objective was to optimize the coating design and qualify it for the performance goals of speed, sensitivity, selectivity, and durability.

In the second activity, we designed and fabricated a complete prototype portable fiber-optic detector. This detector used a single, one millimeter diameter optical fiber that was either coated directly with the sensor film or had a small specially designed attachment to the fiber. The prototype instrument was designed to demonstrate the operation of a fiber-optic hydrogen detector and to determine the advantages of certain design features such as the ability to ratio a hydrogen signal to at reference signal for noise reduction.

Experimental Methods

Coatings

Thin film sensor coatings were deposited by thermal evaporation. Tungsten oxide powder (99.9%) was evaporated from a resistively heated tungsten effusion source. Palladium and silver metals were evaporated from tungsten boats. All depositions were monitored with a quartz crystal deposition rate monitor. Film thicknesses were measured with a stylus gauge.

Chemochromic Response Measurements

Thin films sensors were deposited on 20mm right angle prisms for easier characterization. The test apparatus was designed to seal the coated surface from the surrounding air and expose it to a flow of a predetermined gas mixture. Small percentages of hydrogen in air were simulated by mixing measured flows of oxygen and nitrogen with prepared sources of 10% and 1% hydrogen in nitrogen. A synthetic air source was used for flushing the sample between test runs.

A fiber-optic white light source illuminated the coating through one leg of the prism and a fiber-optic detector picked up reflected light through the other leg of the prism and directed it to a diode array spectrophotometer (Fig. 1). The locations of the ends of the fibers (functioning as entrance and exit apertures) were fixed so that only light internally reflected by the sensor coating at a 45° angle would reach the spectrometer.

Fast toggle valves on the gas mixing manifold and timed acquisition of spectra made it possible to measure the optical reflectance spectra as a function of time and to calculate the response time constant of the sensor.

Optical Modeling

The spectral transmittance, reflectance and other optical characteristics of the sensor films were modeled using software from the Thin Film Center (Macleod 1995). This software also solves the equations for the surface plasmon resonance condition and accurately predicts the reflectance spectra. Most of the optical constants for modeling the various materials used in the sensors were obtained from the American Optical Society (Palik 1995). The optical properties of tungsten oxide thin films with various amounts of hydrogen "inserted" (commonly referred to a H_xWO_3) were modeled using measured optical data from Rubin and von Rottkay for tungsten oxide films with lithium electrochemically "inserted" (Li_xWO_3). It is well known that the optical properties of these two materials are very similar and we found the model calculations using optical data from Li_xWO_3 to agree will enough with measurements on H_xWO_3 to be satisfactory for our design purposes.

Results

Evaluation of Sensor Coatings

Figure 2 shows a theoretical reflectance spectrum for a tungsten oxide sensor film in a surface plasmon resonance configuration. The sensor film consists of a stack of two layers: a 40 nm thick layer of gold and a 600 nm thick layer of WO_3. The shift in this spectrum from curve a to b is the predicted result of the "insertion" of hydrogen to a level of $H_{0.068}$ WO_3. In this model, as in the sensor test configuration, the incident light strikes the film from inside the glass prism at 45° , an angle which is greater than the angle for total internal reflection. Without the coating, all of the light would be reflected. However, at the resonance wavelength, the electric field of the incident light interacts resonantly with the free electrons in the gold to set up an electrical charge oscillation at the glass/gold interface. This is a so-called surface plasmon resonance (SPR). The wavelength at which the resonance occurs is strictly a function of the optical dielectric constants of the glass and gold. The light energy at this wavelength is dissipated by electrical losses in the gold and by re-radiation of the light by the electrons in all directions.

This SPR condition can be reinforced by the right choice of tungsten oxide thickness such that a constructive interference occurs at the resonance wavelength in the oxide layer. Under these conditions, the gold/WO_3 stack acts like a pair of coupled resonators and both the resonance wavelength and the resonance amplitude depend sensitively upon the optical dielectric constants of the glass, the gold and the WO_3. When the hydrogen reacts with the tungsten oxide, the oxide refractive index decreases and the resonance shifts as indicated in the figure.

The reaction of hydrogen and tungsten oxide is too slow without a catalyst. A thin layer of a catalyst such as palladium must be added. The palladium tends to absorb the resonance wavelength light and dampen the resonance. Figure 3 shows the theoretical reflectance spectrum from a sensor coating consisting of 40 nm gold/ 600 nm WO_3/ 3 nm Pd. For comparison, we show a measured reflectance spectrum from a sensor coating of this same configuration. The spectral characteristics of the light source and the light detector have not been removed, so the measured spectrum contains more structure than the theoretical one, but the SPR can be clearly seen. This resonance wavelength was very stable, with no significant shift detected over the temperature range tested from 24° to 69° C.

Figure 4 shows a set of spectra from a time series taken during exposure to 5% hydrogen in air at room temperature. The inset shows the change in reflected light intensity at the resonant wavelength over time. The change in signal amplitude is approximately exponential with a time constant of about 20 seconds. Similar measurements were made over a range of hydrogen concentrations and the time constant was found to decrease as the concentration increased. Over a range of concentrations up to 5%, the relationship between time constant and partial pressure appeared to be:

$$\tau \propto P_{H2}^{-2}$$

Unfortunately, the tungsten oxide readily exchanges water vapor with the atmosphere. Adsorbed water vapor increases its refractive index. Consequently, exposure of the sensor to dry air causes rapid loss of adsorbed water from the film and a shift in the SPR that mimics exposure to hydrogen! Of course, such a false alarm is unacceptable.

We applied a protective layer of poly-tetrafluoroethylene over the palladium by thermal evaporation. This retarded the exchange of water vapor without significantly affecting the SPR and the sensitivity to hydrogen. However, the sensor SPR was still susceptible to severe drift in changing humidity.

We next considered increasing the thickness of the palladium film to serve both catalytic and protective functions. Since the palladium adsorbs resonance light and tends to broaden the SPR, implementing this design option is tricky. However, if the film thicknesses are chosen correctly, a constructive interference resonance condition can be made to occur between the gold and palladium layers which coincides with the SPR. Figure 5 shows the theoretical and measured reflectance spectra from such a coating in the SPR configuration (45° incidence angle).

Measurements with this sensor film design confirmed that it was only very weakly sensitive to prolonged exposure to humidity while remaining sensitive to hydrogen. Figure 6 shows the response of the sensor during exposure to 0.9% hydrogen in air. The response time constant is a few seconds. Over time, however, this response time increased dramatically. Figure 7 shows the measured response time for such a sensor over a period of two days. The time constant is seen to increase from a few seconds to more than 200 seconds, approximately increasing in proportion to the square root of time the sensor was exposed to the test gases.

Considerable effort was spent in attempting to understand and correct this unexpected degradation. We now believe that the cause of the degradation is a natural result of the mechanism by which hydrogen reacts with the WO_3, a reaction which is commonly misrepresented in the technical literature. This issue is addressed in the Discussion section below.

In view of the inherent difficulties with the tungsten oxide sensor films, we searched for alternatives. Recent research, primarily at the Philips Laboratory (Huiberts 1996, Griessen 1997), has shown that the Lanthanide hydrides and related hydrides undergo reversible transitions between di-hydride and tri-hydride when exposed to hydrogen in air. Thin films of these materials exhibit dramatic changes in optical transmittance that may make them suitable for hydrogen sensing.

Figure 8 shows a very preliminary measurement of the reflectance from a yttrium hydride film during repeated exposure to 0.45% hydrogen in air. The sensor film was not optimized and yet its response time constant was fairly short, about 5.8 seconds. A YH_2 sensor coating incorporating the surface plasmon resonance design should show greater sensitivity and speed. The optical dielectric constants of the di-hydride will have to be determined before an optimized SPR sensor can be designed.

Prototype Sensor

A self-contained, hand-held portable fiber-optic hydrogen sensor was designed and built. The device makes use of off-the-shelf electronic components and analog circuitry (except for a digital voltage readout). It is powered by a 9 V battery. Stabilized voltages for the various components are supplied through DC-DC converters.

The light source is a high brightness, broad spectrum "white" (phosphor enhanced) LED. The light from the LED is projected into the proximal end of a 1 mm diameter polymer optical fiber and transmitted through a 1x2 coupler to an exit port on the instrument. The optical-fiber sensor is plugged into that port with a standard fiber-optic ST connector. Light reflected from the sensor coating on the distal end of the fiber is returned to the instrument and half of its power is directed through one of the coupler legs to a dichroic mirror. The dichroic mirror splits the return light beam into a long wavelength and a short wavelength portion which fall separately on two different photo-diode amplifiers. The voltage signals from the two photo-diodes are divided one by the other in an analog divide circuit. A three-way switch allows the user to monitor the output from either photo-diode separately or their ratio. Figure 9 shows a schematic illustration of the detector's design features.

When used with a WO_3/Pd sensor coating on the end of an optical fiber in a purely reflective mode (no SPR), the light reflected from the sensor is split into a short wavelength component ($\lambda < 500$nm) and a long wavelength component ($\lambda > 500$nm). When the tungsten oxide film reacts with hydrogen it develops an absorption band in the near infrared portion of the spectrum but remains unaffected in the blue end of the spectrum. Thus the long wavelength portion of the spectrum carries a hydrogen signal, whereas the short wavelength portion does not and can be considered as a "reference" signal.

Since both components of the spectrum follow the same path through the optical fiber, they are both affected similarly by changes in the transmittance through the fiber. Taking the ratio of the "signal" to the "reference" provides a means of canceling some of the changes in fiber transmittance, whatever its cause, and thereby reduces the noise level. Transmittance can be affected by bending in the fiber, by temperature gradients in the fiber and by changes in the light transmittance at the connections.

Figure 10 shows some measurements of the effect of fiber bending. The conditions at the instrument and at the sensor were kept constant and the signals returning to the instrument were recorded as the meter-long polymer optical fiber was intentionally bent through an increasingly sharp radius. The bend in the fiber caused reversible optical losses and attenuated the intensity of the reflected beam. In the figure, the percentage change in the signal voltage from each photo-diode due to fiber bending is shown separately along with the analog ratio of the two voltages. It is clear that the use of a reference signal, greatly decreases the effect of fiber bending.

In order to produce a sharp SPR in the sensor film, the light beam must strike the film at a single angle. In our design, where we want the reflected light to be returned along the same fiber path, the preferred angle is 45 ° and the best shape for the sensor "head" is a 90° prism acting as a retro-reflector. However, an optical fiber transmits a bundle of light rays which emerge from the end of the fiber in a cone of angles. If this cone of rays is used to illuminate the sensor coating on the retro-reflector, no SPR can be seen in the reflected signal. It is necessary to use a component that collimates the diverging bundle of rays before directing them to the sensor coating. The use of such optical components on the end of fiber-optic detectors is common enough that they have been given the name *optodes*, in analogy to the *electrodes* used in electrochemical sensors.

Remembering that our ultimate goal is a low-cost detector, we chose to design an optode that would be a small, single component that could be mass produced from polymer by low-cost means such as compression molding. A commercial, optical ray-tracing code was used for the design (anon. 1998).

The optode consists of a plano-convex lens integrally combined with a 90° prism. A simple spherical convex lens surface is not sufficient to collimate the emerging broad spectrum beam and focus the reflected light back onto the 1 mm diameter fiber tip. Therefore a conic surface was used in the optimization of the optode (radius of curvature 2.85 mm, conicity -2.055, 5.1 mm FL). Fig. 11 illustrates the optimized optode design assuming that it will be made from PMMA and will be coupled to a polymer optical fiber having a numerical aperture of 0.5.

Because of the expense of fabricating a single component of this design, we also designed a less than optimal optode that could be easily fabricated by cementing a commercially available stock BK7 glass plano-convex lens (10 mm diameter, 15 mm FL, radius of curvature 7.73 mm) to a glass 90° prism. Again, the optical ray-trace code, Zemax was used to design the optode.

Several glass optodes of this design were fabricated and coated with a sensor film (15 nm Ag / 440 nm WO_3 / 35 nm Pd). A holder was made to attach the optode to the optical fiber. [In a commercial polymer design, the attachment would be designed as an integral part of the optode.] Figure 12 shows the of the reflected light assuming an incidence angle of 45°: a, theoretical; and b, the measured spectrum. There is a close correlation between the theoretical reflectance spectrum and the measured spectrum.

Discussion

Sensor Films

The thin-film fiber-optic reflective sensor based on palladium catalyzed WO_3 first suggested by Ito (Ito 1984) appears to work well for detecting hydrogen. However, its response is too slow for critical safety applications. We showed that the sensitivity and the response speed of this sensor could be increased by use of a film configuration which produces a surface plasmon resonance. However this sensor configuration introduces additional problems.

In the SPR configuration, the resonance wavelength depends very sensitively upon the refractive index of the WO_3 film, whereas, in the Ito, purely reflective sensor configuration, only a change in the optical absorption of the film mattered. The amorphous WO_3 is micro-porous and readily exchanges water vapor with the air. Consequently, exposure of the SPR sensor to dry gas causes a decrease in the amount of adsorbed water and a decrease in the WO_3 refractive index. This change shifts the surface plasmon resonance and mimics exposure to hydrogen. Of course, such a false alarm is unacceptable in a safety device.

The conventional interpretation of the reaction between catalyzed WO_3 and hydrogen suggests that it should be possible to block the water vapor while still allowing the hydrogen to pass through simply by increasing the thickness of the palladium film. However, we discovered that such a sensor coating is subject to severe degradation due to irreversible reactions. This observation casts doubt upon the conventional interpretation of the chemochromic reaction between hydrogen and WO_3 thin films.

Most of the understanding of reactions between WO_3 thin films and hydrogen come from the extensive literature on electrochromism in this material and is based on electrochemical "insertion" of hydrogen into the amorphous WO_3 (Granqvist 1995). The hydrogen is thought to be inserted as an ion-electron pair with the proton residing in a WO_3 lattice interstice adjacent to a W^{+5} ion. This is the "double-charge injection model." The characteristic optical absorption is thought to be due to either electron exchange between adjacent W^{+5} and W^{+6} ions or by self-trapped, nearly free electrons called polarons. Most recent evidence favors the polaron absorption model.

Some published results challenge the conventional interpretation. We have recently summarized this evidence and suggested some modification to the electrochromic model including the importance of electron exchange between the W^{+4} and W^{+5} ions rather than W^{+5}-W^{+6} exchange (Zhang 1996). Among other puzzling observations reported in the literature is the inability to find evidence of the added hydrogen after an a-WO_3 film has been colored by hydrogen electrochemical "insertion" (Wagner 1990). Our SPR results are also puzzling in this regard because we observed a shift in resonance with hydrogen reaction that is characteristic of lowered refractive index. A decrease in refractive index suggests a lowering of the molar polarizability which is inconsistent with the *addition* of hydrogen ions within the WO_3 lattice. It is more consistent with the removal of something.

When a-WO_3 films are irradiated with short wavelength light, they become blue just as they do when colored by electrochemical insertion of hydrogen or by chemochromic coloration in hydrogen gas. It has been shown (Bechinger 1993) that this is probably due to photo-dissociation of chemically bound water with resulting "insertion" of the hydrogen as the oxygen radical is either trapped by an oxygen vacancy in the partially reduced WO_3 or escapes as O_2. In the Bechinger photochromic study, the authors found that the coloration was irreversible unless the film was exposed to oxygen.

Our results are consistent with the Bechinger observations and the following model (Zhang 1996). Hydrogen in air reacts with oxygen at the surface of palladium. Part of the hydrogen is oxidized to water and part is dissolved in the palladium where it readily diffuses to the Pd/WO_3 interface. Atomic hydrogen spontaneously reduces the tungsten oxide to form WO_{3-y} plus H_2O that is adsorbed by the WO_3. The reaction is:

$$H + WO_{3-y}.nH_2O = WO_{3-y-x/2}\,[nH_2O\,(x/2)H_2O]$$

If the palladium catalytic layer is thin enough to be incoherent, the excess water readily escapes until equilibrium is reached with the humidity of the surrounding atmosphere and the sensitivity is unaffected. However, if the palladium is thick, the water cannot escape and its build-up over time suppresses the forward reaction and slows the response of the sensor to hydrogen gas. Paradoxically, the thicker palladium film which protects against false hydrogen signals from desorbing water vapor also introduces a reduces hydrogen sensitivity by the same mechanism.

The inherent interference in the SPR detection of hydrogen by pervasive water vapor makes the WO_3 chemochromic sensor a poor choice for this application. A simpler chemical reaction is needed for the reversible chemochromic sensor.

Detector

The use of a fiber-optic hydrogen gas leak detector has advantages of inherent safety (no electrical power in the vicinity of the sensor), reduced EMI, light weight, and (potentially) low cost. The prototype portable fiber-optic hydrogen detector provided a convenient means of demonstrating some of the features of a chemochromic sensor and the advantages of incorporating a reference beam in the design. The prototype incorporates many components such as operational amplifiers, DC-DC converters, an analog divide component as well as photo-diode amplifiers. Most, if not all of these separate components could be integrated into a single application-specific integrated circuit (ASIC) for economical mass-production. If that is done, then it may be more appropriate to use digital rather than analog circuitry for better compatibility with other digital electronics commonly used in vehicles. An analysis (Spath 1997) of the probable manufacturing costs has shown that it should be possible to mass-produce similar detectors for about $5 each (not including the cost of the optical fiber which is proportional to the length required in each application).

Conclusions

The evaluation of a fiber-optic chemochromic hydrogen gas detector has been partially successful, but more work is required to develop a suitable sensor coating. The chemochromic reaction between tungsten oxide and hydrogen in air is too slow to be used in a safety device without some kind of enhancement. The sensitivity and speed of hydrogen detection can be enhanced by using the sensor film in a surface plasmon resonance configuration. However, in such a configuration, the rapid desorption of adsorbed water vapor from the tungsten oxide can cause a false indication of hydrogen whenever the sensor is exposed to a dry gas. Blocking the migration of water vapor by increasing the thickness of a palladium catalytic layer also blocks the migration of oxygen to and from the tungsten oxide. Without access to oxygen, the chemochromic reaction is at least partially irreversible and the sensitivity to hydrogen and response speed degrade over time. For these reasons, the tungsten oxide sensor is now believed to be unsatisfactory for the intended application.

Preliminary experiments with yttrium hydride showed promising speed and sensitivity in a simple sensor configuration. Optimization of the YH_2 sensor design, including the use of surface plasmon resonance, should provide the needed sensitivity and speed. The YH_2 sensor (and related hydrides films) should be evaluated for performance and durability.

A prototype portable fiber-optic hydrogen detector was designed and built to demonstrate the operation of the sensor. The novel design proved to be successful and limited only by the chemochromic sensor used on the optical fiber. The incorporation of a reference beam in the detector's design was shown to reduce signal noise significantly. A potentially low-cost polymer optode was designed to operate with the fiber-optic hydrogen detector in the surface plasmon resonance configuration. Tests of a glass approximation to the optimized optode design showed that the polymer optode should operate well in the surface plasmon sensor configuration.

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Figure Captions

1. Schematic cross-section through the SPR sensor sample holder.

2. Theoretical reflectance spectrum showing the surface plasmon resonance (SPR) absorption at nm: a, before exposure to hydrogen; b, after reaction with hydrogen to form (nominally) $H_{0.068}WO_3$. Coating consists of 40 nm Au / 600 nm WO_3 and is illuminated at 45°.

3. Reflectance SPR spectrum from a coating : 40 nm Au / 600 nm WO_3 / 3 nm Pd: a, theoretical; b, measured.

4. Selected reflectance spectra from a time series during exposure to 5% H_2 in air. Inset shows reflected intensity at 627 nm versus time. Coating is 40 nm Au / 600 nm WO_3 / 3 nm Pd.

5. Reflectance SPR spectra from a coating with a thicker palladium layer: 17 nm Ag / 330 nm WO_3 / 100 nm Pd: a, theoretical; b, measured.

6. Initial response of sensor coating [17 nm Ag / 330 nm WO_3 / 100 nm Pd] to 0.9% H_2 in air.

7. Sensor response time constant for film [17 nm Ag / 330 nm WO_3 / 100 nm Pd] over a period of two days. Sample exposed to 5% H_2 in air for periods of about 2 minutes, then to dry air. Response time constant measured away from SPR, at 800 nm. The fitted curve varies as the square-root of time.

8. Initial response measurements for a yttrium hydride film [17 nm Ag / 100 nm Y / 20 nm Pd] to 0.45% H_2 in air. The first reduction in the signal corresponds to conversion of Y metal to YH_2 and subsequent cycles to increases in hydrogen content toward the tri-hydride, YH_3. The response was measured in reflection (no SPR) at 700 nm. The time constant of the hydrogen response is about 5.7 seconds.

9. Schematic diagram of the prototype portable fiber-optic hydrogen gas leak detector showing selected design features.

10. Detector signal attenuation due to controlled bending of the optical fiber. Note that the attenuation is nearly the same for the hydrogen signal (long wavelength) and the hydrogen-insensitive, reference signal (short wavelength) and consequently the analog ratio of the two signals is only weakly affected by fiber bending.

11. Design for a PMMA SPR optode. The lens portion is a conic section optimized to minimize chromatic aberration and maximize signal return to the optical fiber.

12. SPR reflectance spectrum using a glass optode made by cementing a plano-convex spherical lens to a 90° prism.

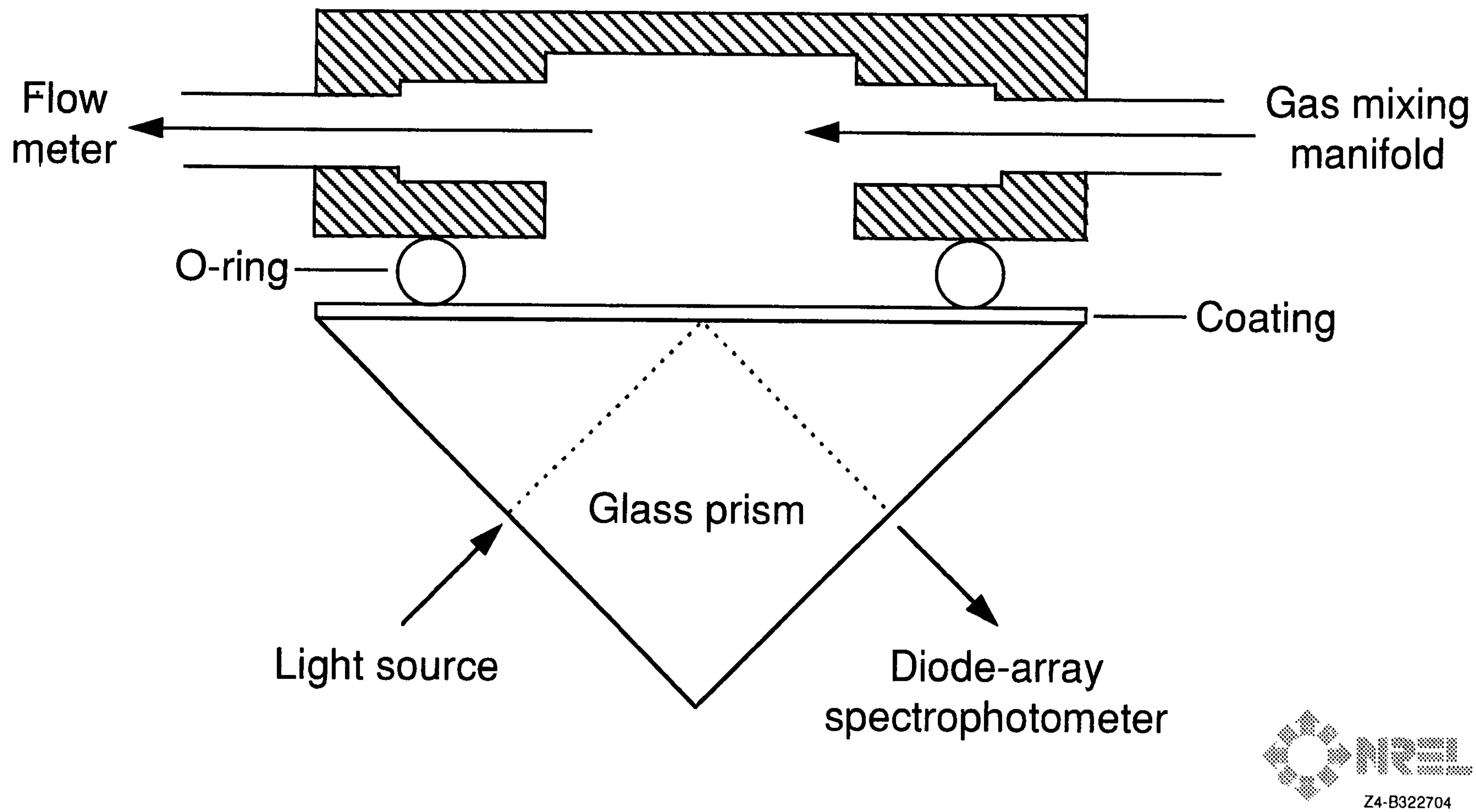

Flow
meter
Gas mixing
manifold
O-ring
Coating
Glass prism
Light source
Diode-array
spectrophotometer
NREL
Z4-B322704

Figure 1

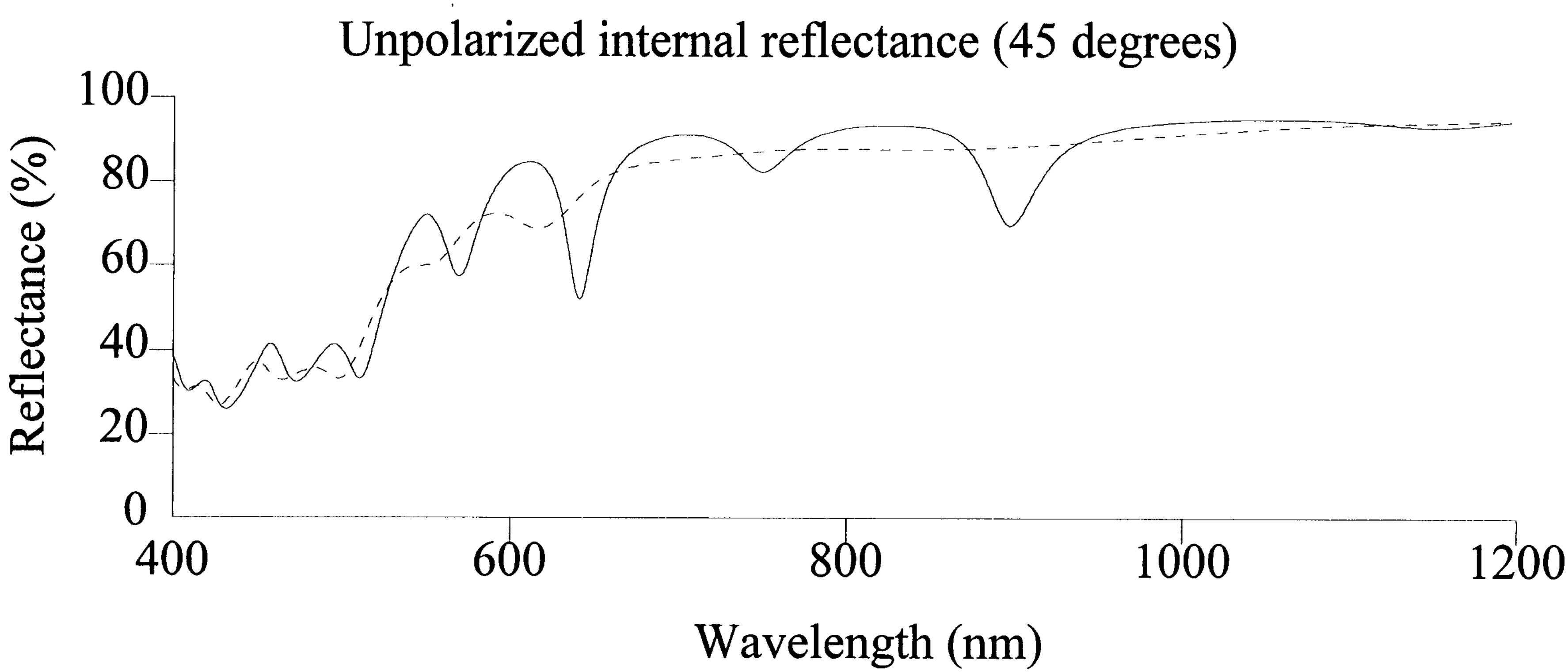

Unpolarized internal reflectance (45 degrees)
Reflectance (%)
100
80
60
40
20
0
400
600
800
1000
1200
Wavelength (nm)

Figure 2

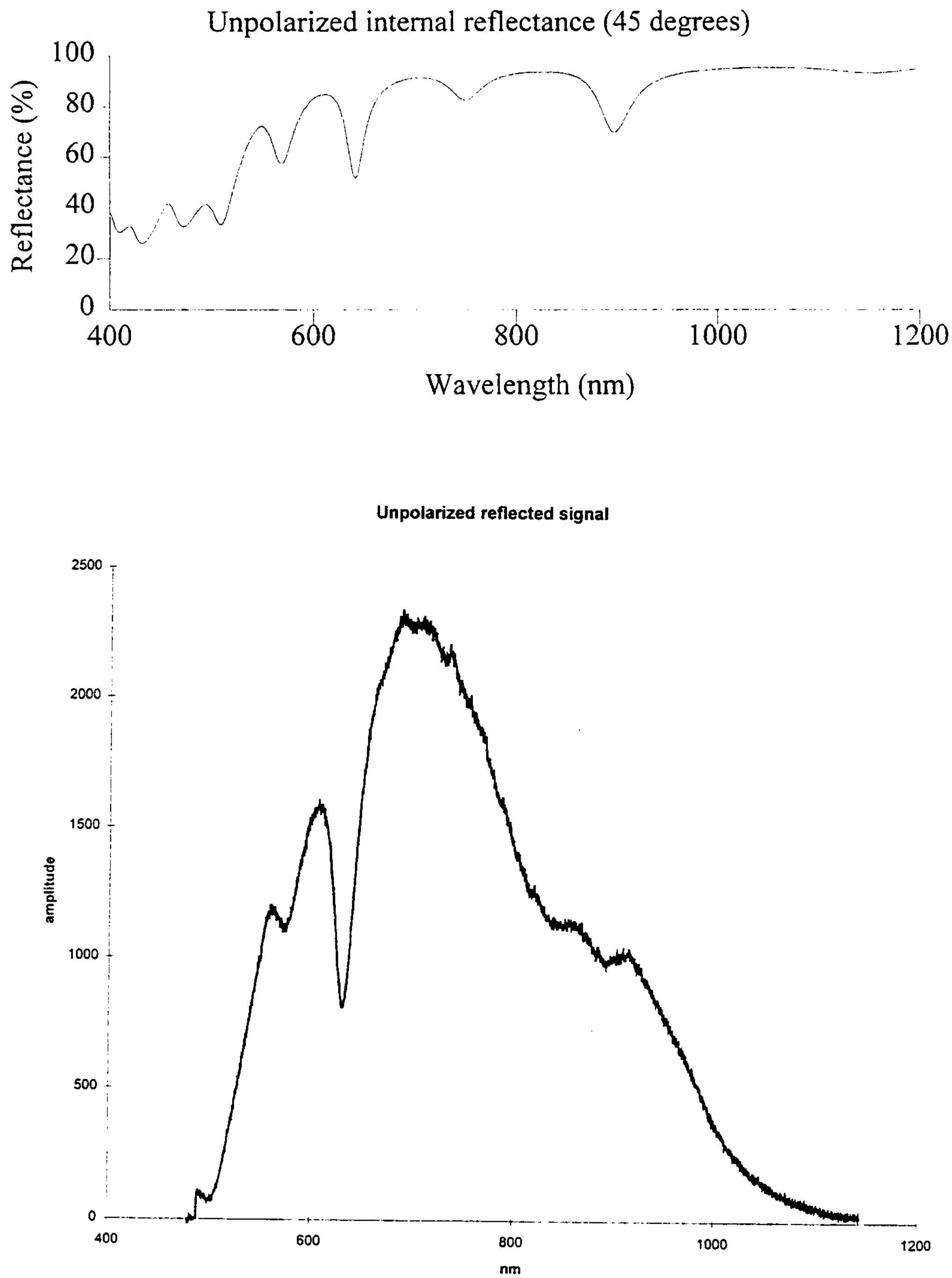

Unpolarized internal reflectance (45 degrees)
Reflectance (%)
100
80
60
40
20
0
400
600
800
1000
1200
Wavelength (nm)
Unpolarized reflected signal
amplitude
2500
2000
1500
1000
500
0
400
600
800
1000
1200
nm

Figure 3

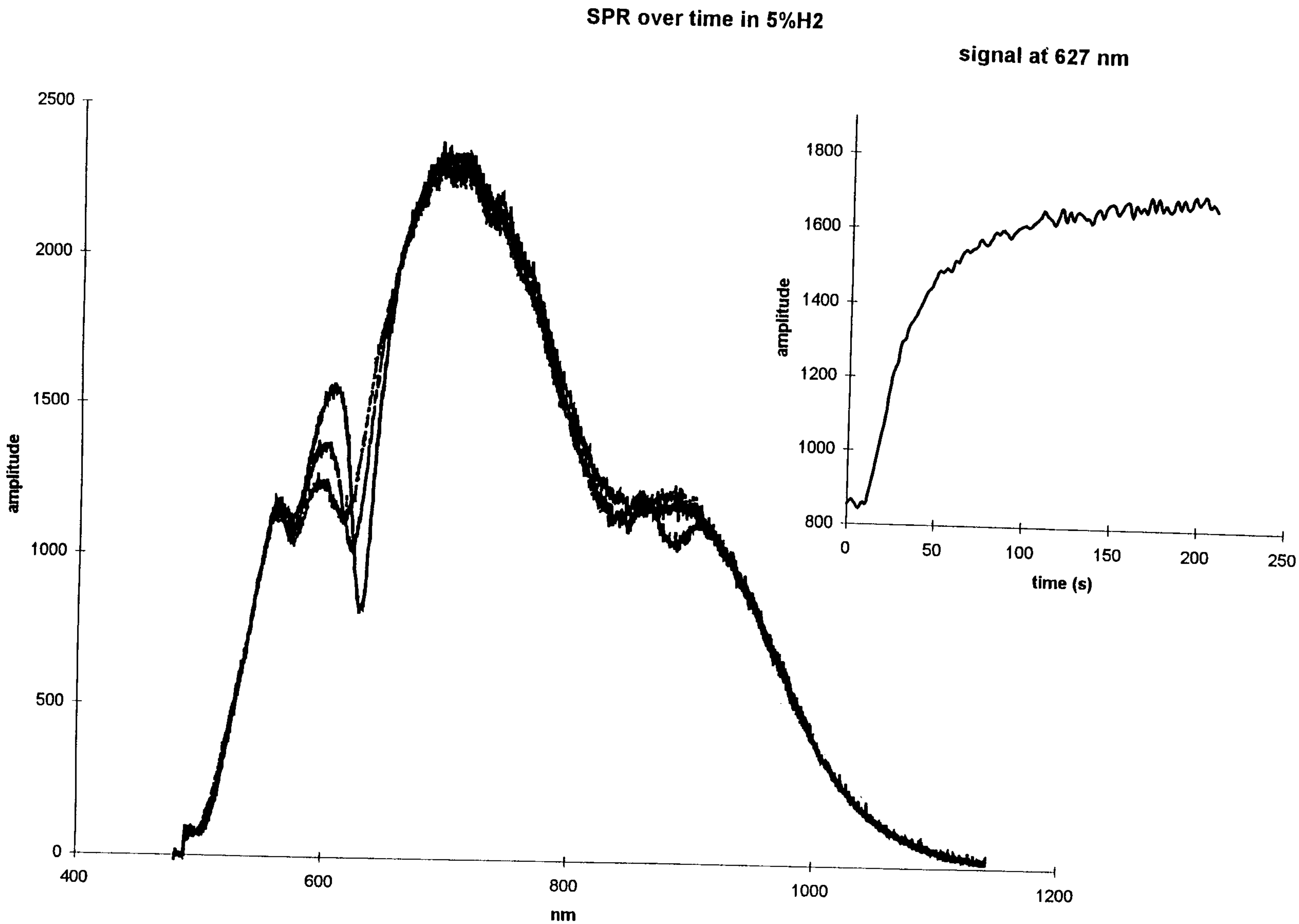

SPR over time in 5%H2
signal at 627 nm
amplitude
2500
2000
1500
1000
500
0
400
600
800
1000
1200
nm
1800
1600
1400
1200
1000
800
0
50
100
150
200
250
time (s)

Figure 4

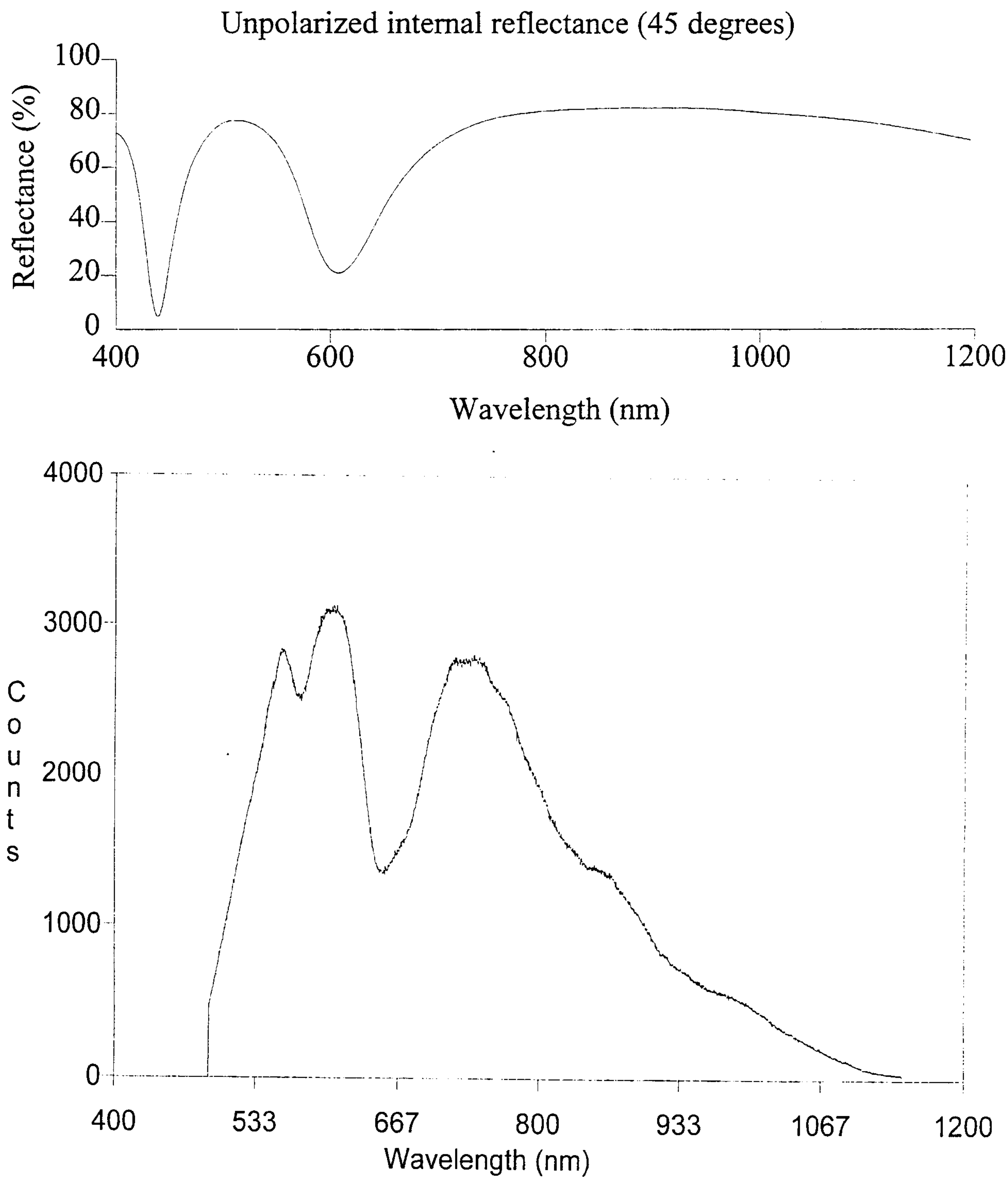

Unpolarized internal reflectance (45 degrees)
Reflectance (%)
100
80
60
40
20
0
400
600
800
1000
1200
Wavelength (nm)
Counts
4000
3000
2000
1000
0
400
533
667
800
933
1067
1200
Wavelength (nm)

Figure 5

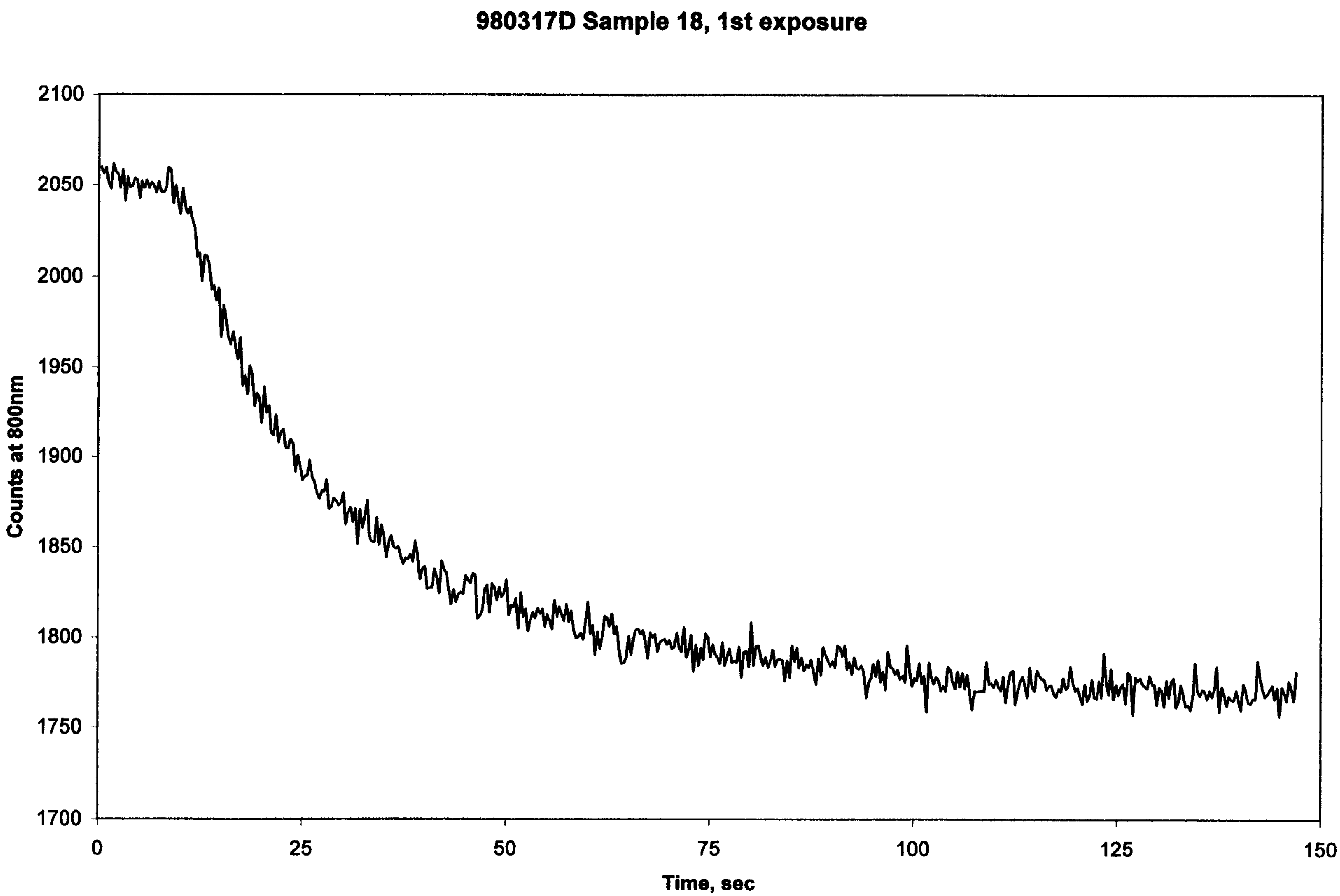
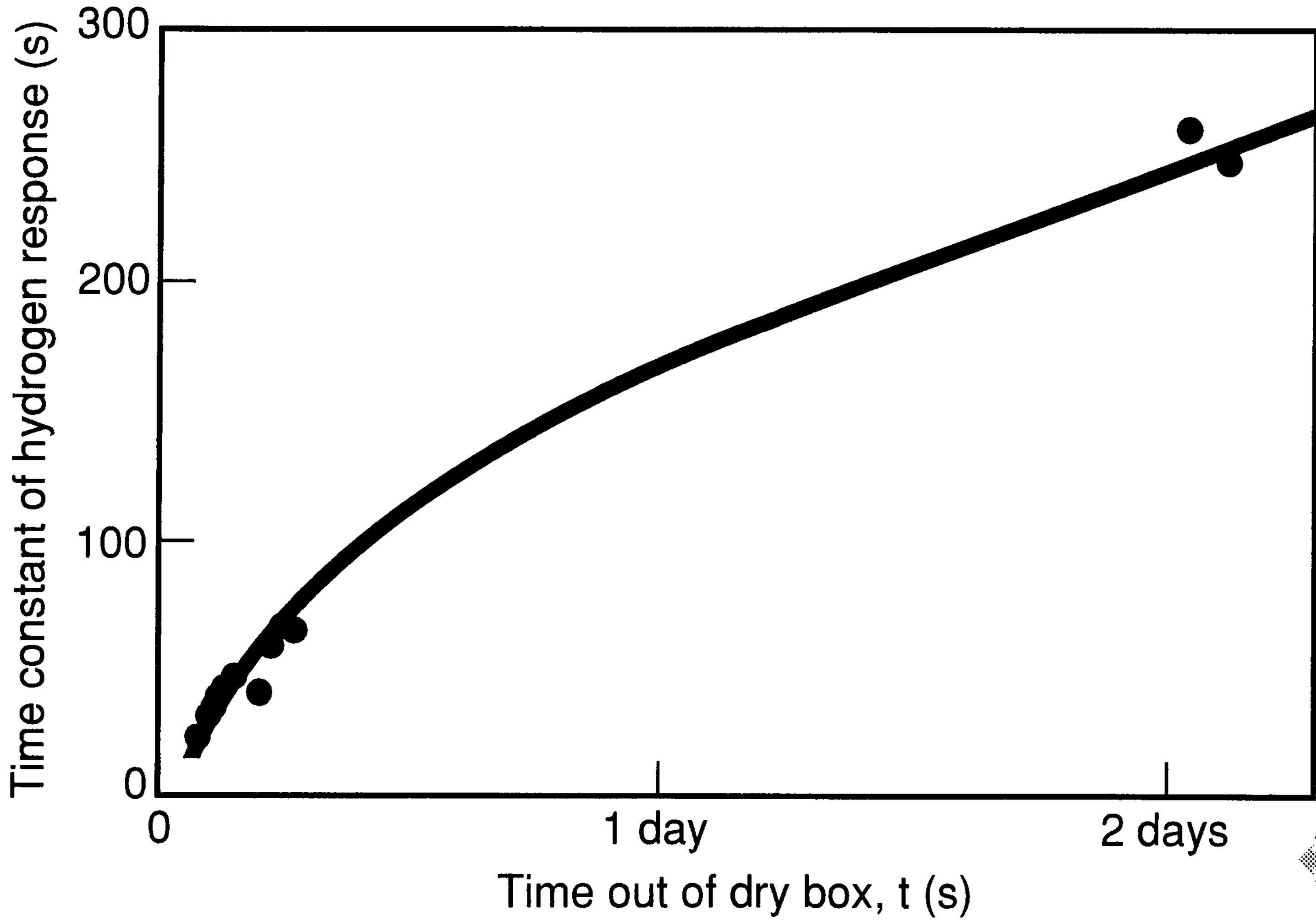

980317D Sample 18, 1st exposure
2100
2050
2000
1950
1900
1850
1800
1750
1700
Counts at 800nm
0
25
50
75
100
125
150
Time, sec

Figure 6

Degradation of Hydrogen Response



Z4-B322703

Figure 7

Yttrium Sample 38, alternating exposure to 0.45% H_2

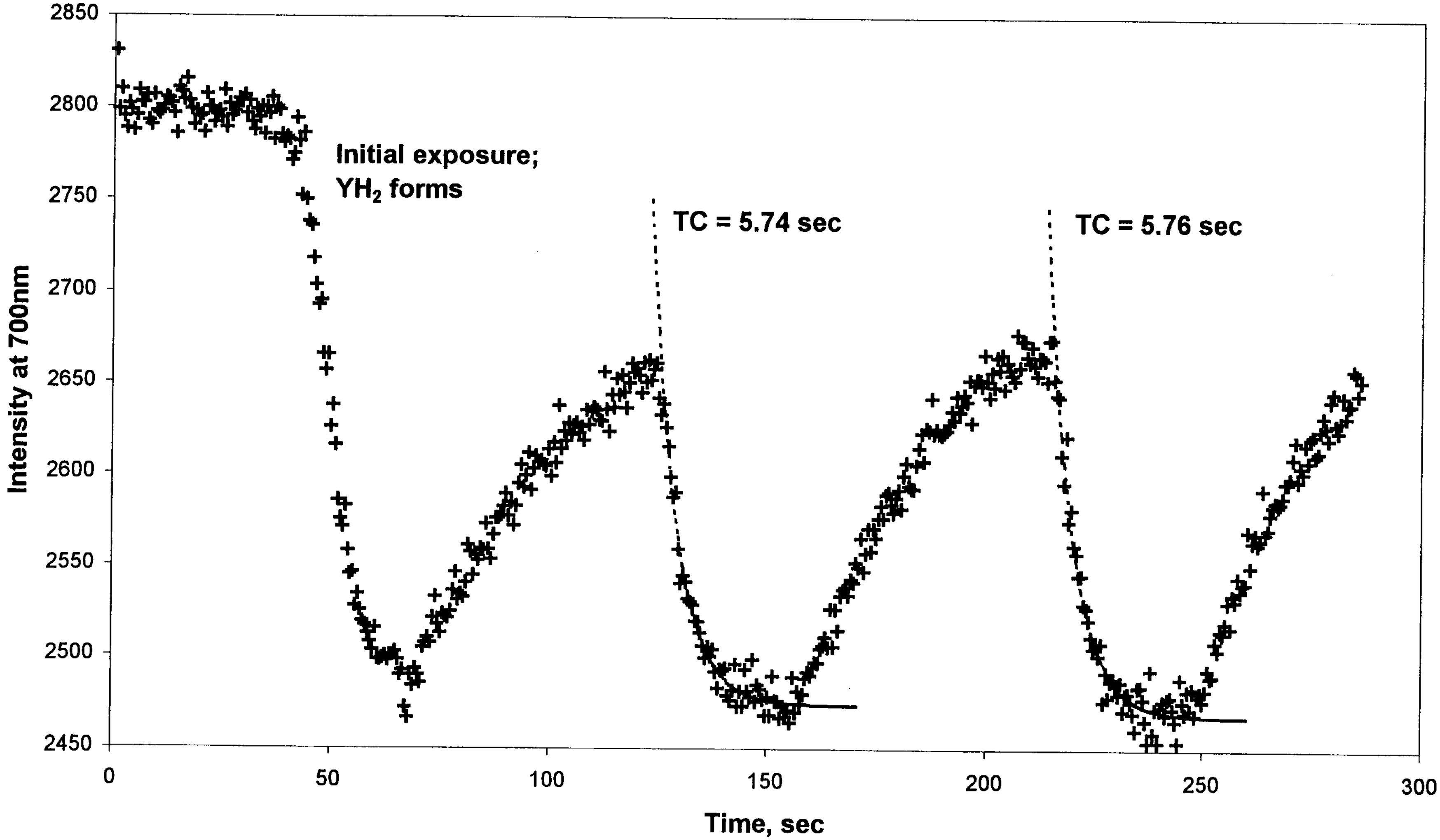
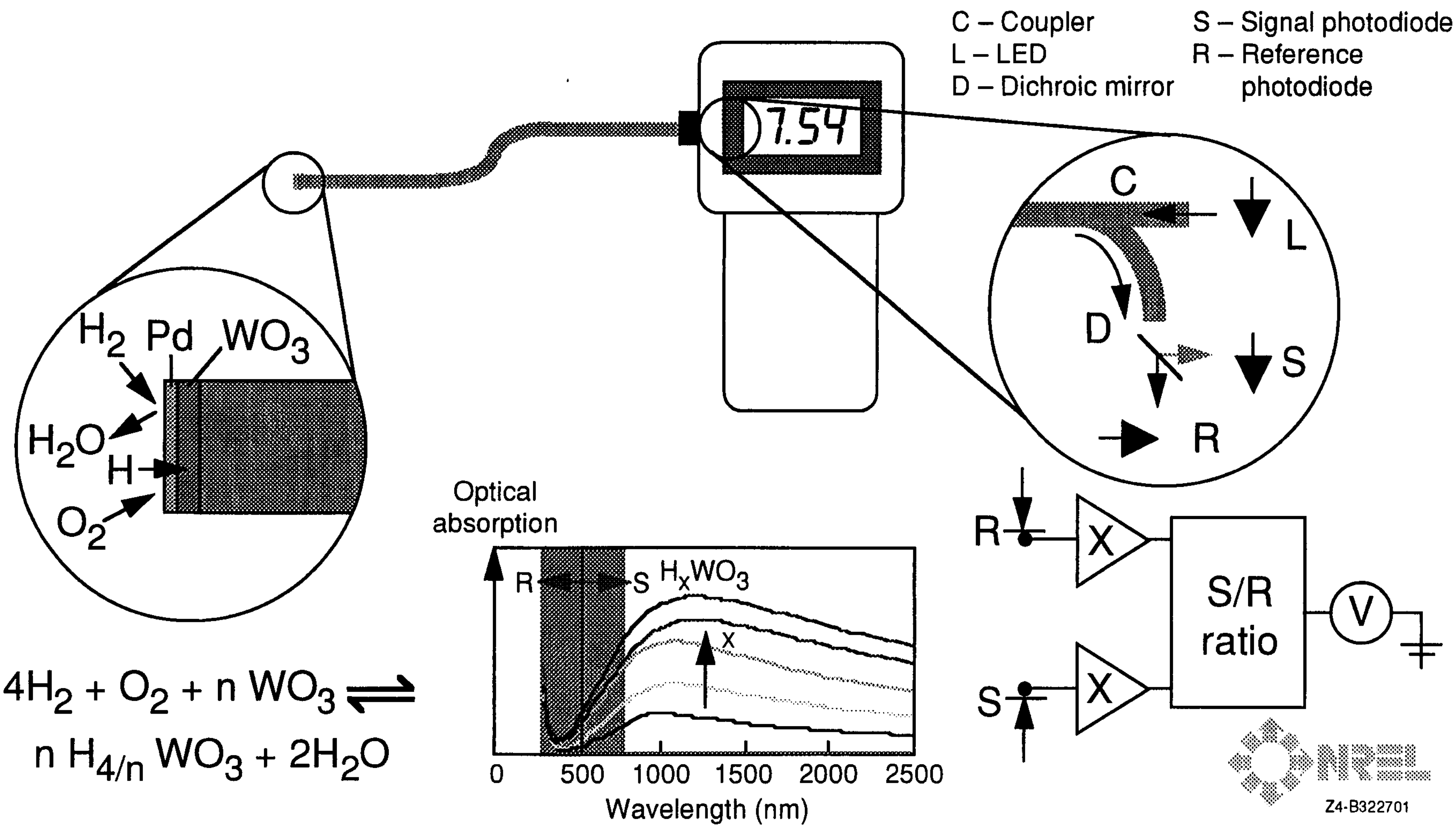


Figure 8

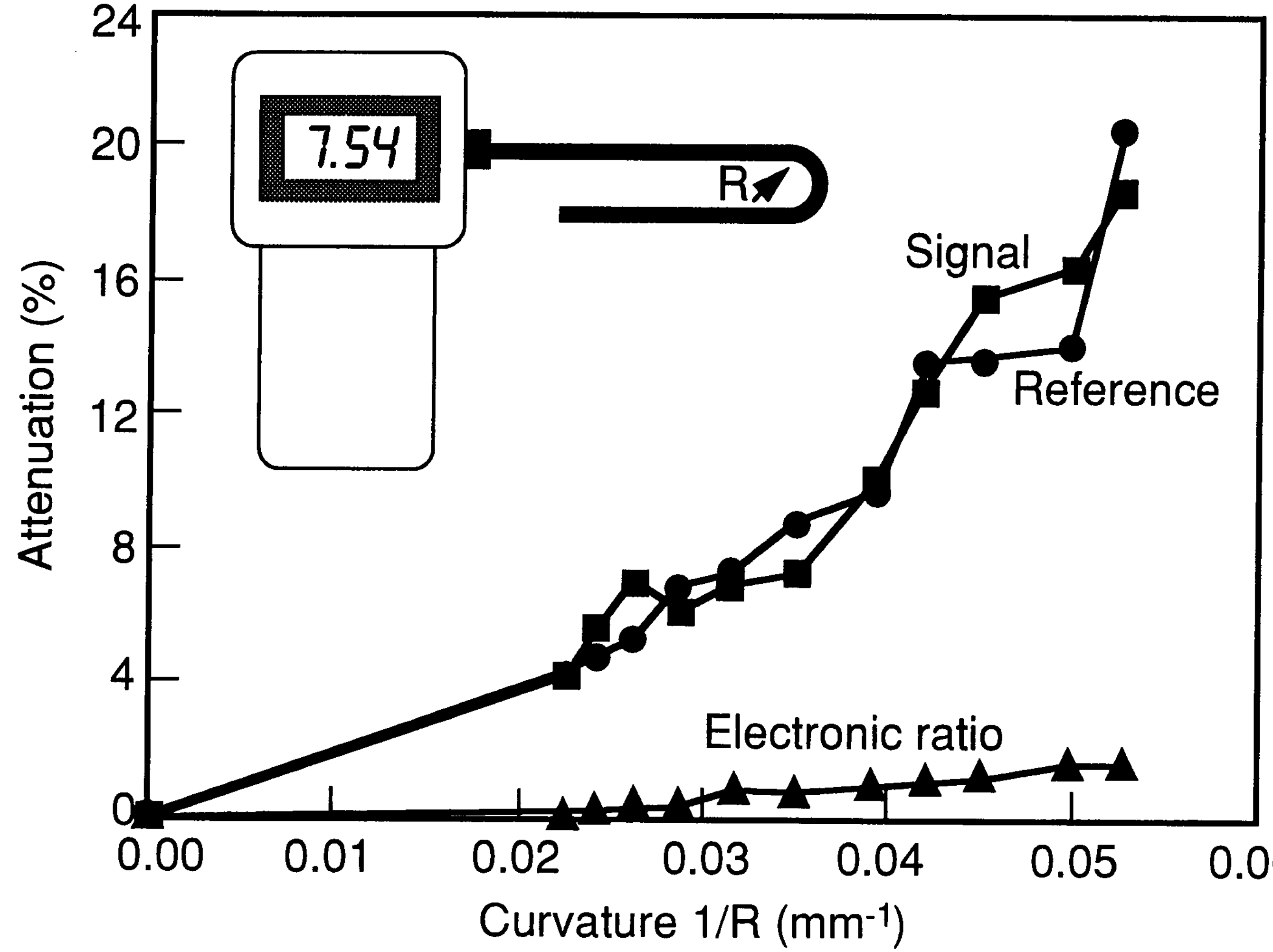
Portable Fiber-Optic Hydrogen Detector



$$4H_2 + O_2 + n\,WO_3 \rightleftharpoons n\,H_{4/n}WO_3 + 2H_2O$$

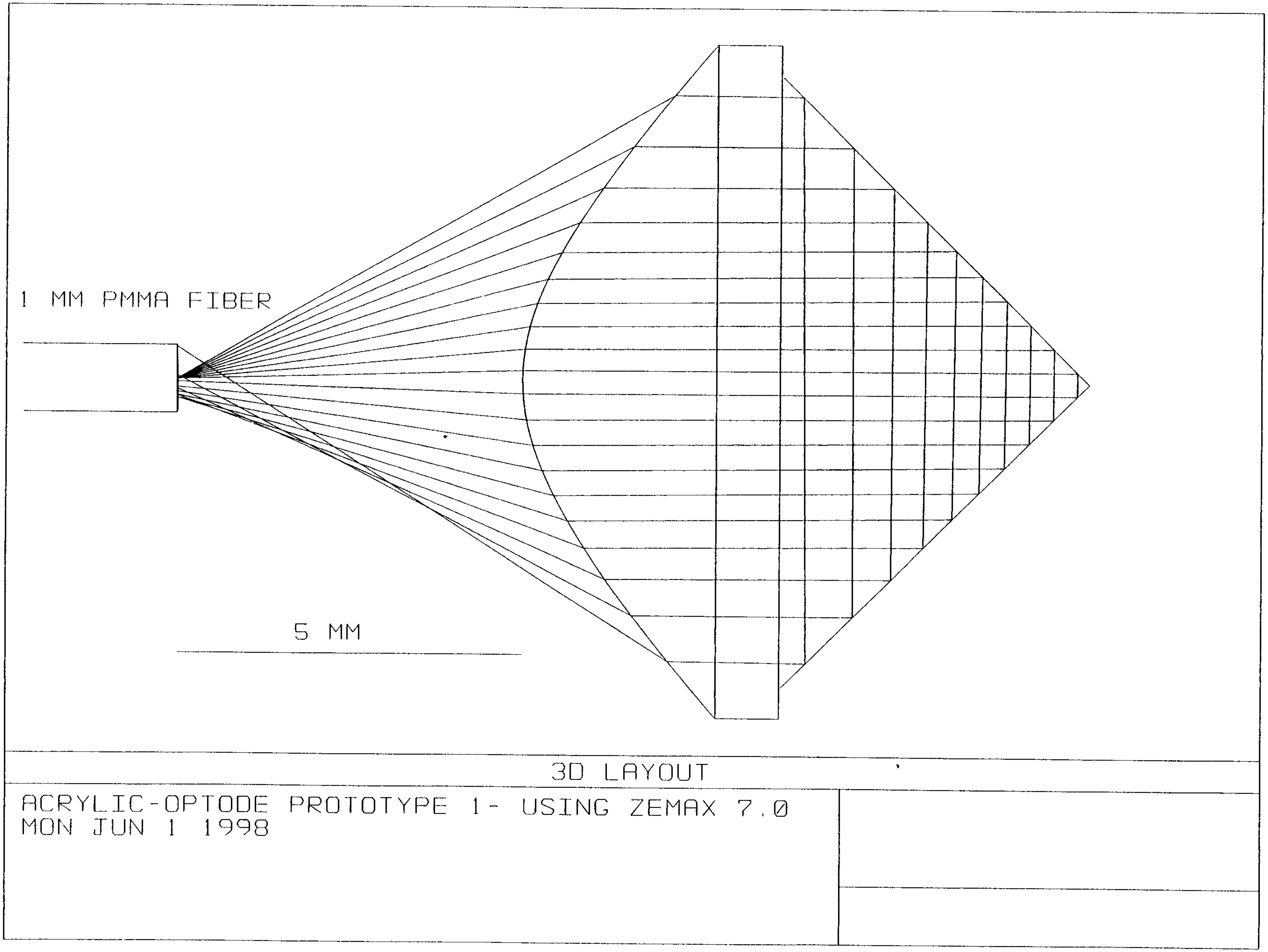
Figure 9

Attenuation Due to F-O Bending



NREL Z4-B322702

Figure 10



1 MM PMMA FIBER
5 MM
3D LAYOUT
ACRYLIC-OPTODE PROTOTYPE 1- USING ZEMAX 7.0
MON JUN 1 1998

Figure 11

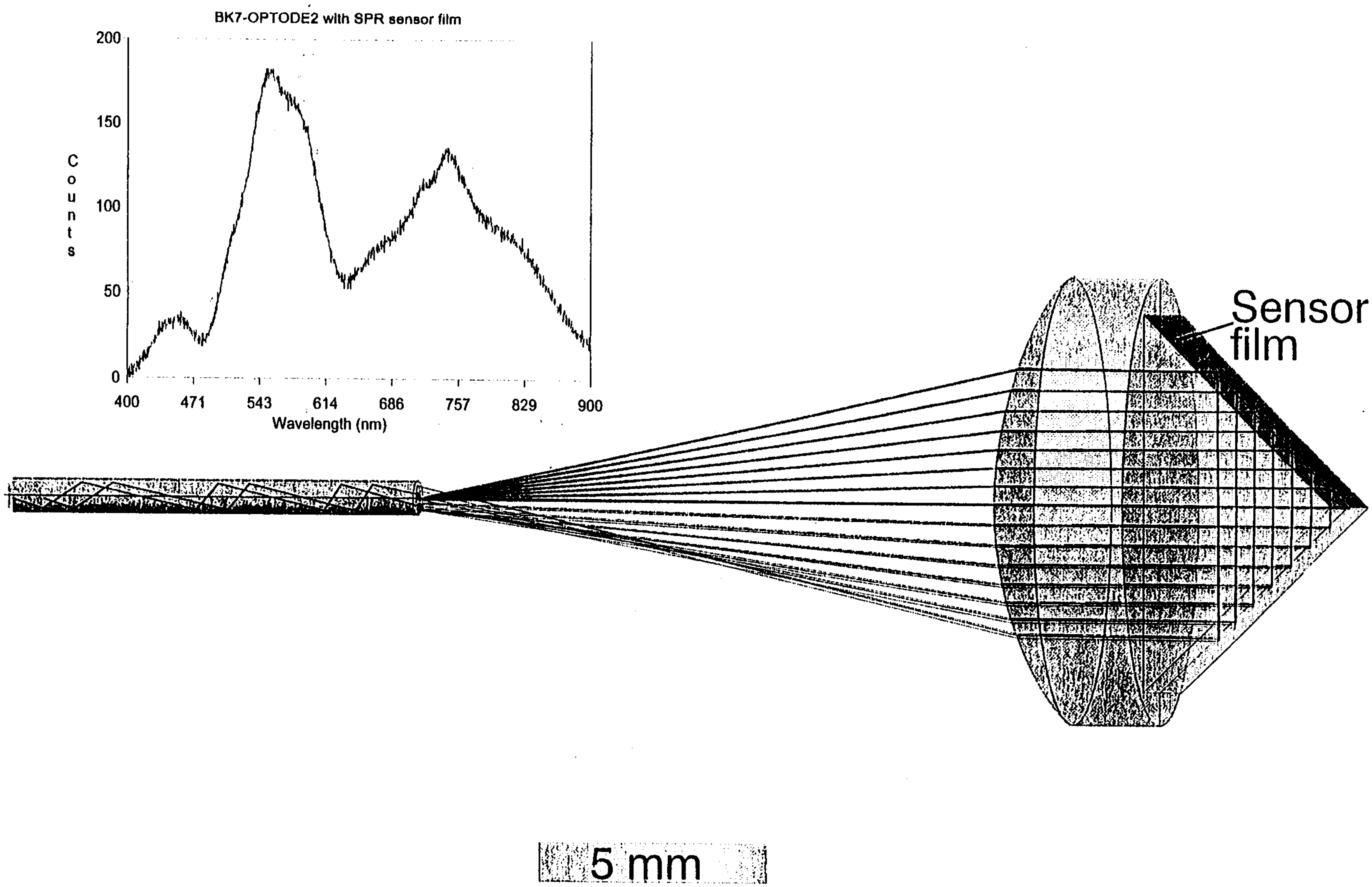

BK7-OPTODE2 with SPR sensor film
Counts
200
150
100
50
0
400
471
543
614
686
757
829
900
Wavelength (nm)
Sensor film
5 mm

Figure 12