High-Sensitivity Gas Sensors Based on Gas-Permeable Liquid Core Waveguides and Long-Path Absorbance Detection

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A new fluoropolymer is proposed as the basis of a novel class of sensors. The devices are based on selective chromogenic reactions and in situ long-path optical absorbance measurement. The polymer is transparent from 200 to 2000 nm and has the lowest known refractive index (RI) of any synthetic polymer. The RI is less than that of water. A tube of this material, filled with an aqueous solution (or virtually any other liquid), behaves as a liquid core optical fiber. As a result, long-path length optical cells are possible without significant loss of light. The material is highly permeable to a number of trace gases of environmental interest. Relative to common poly(tetrafluoroethylene) (PTFE)-type Teflon, the new amorphous fluoropolymer (Teflon AF 2400) is more than 3 orders of magnitude more permeable to many gases. If a Teflon AF tube is filled with a reagent that responds to a gaseous analyte by undergoing a change that is spectroscopically detectable, an unusually versatile, sensitive, and inexpensive gas sensor can be made with conventional optical fibers at each end, connected respectively to an inexpensive light source such as a light-emitting diode and a photodiode detector. A capillary hollow fiber structure allows a high surface-to-volume ratio, allowing high sensitivity, and supports a thin wall, with response times down to subsecond periods. The potential for similar sensors for volatile organic compounds dissolved in water is also demonstrated.

According to the Lambert—Beer law, other factors remaining the same, the sensitivity of optical absorbance detection is directly related to the optical path length. Consequently, much effort has been spent over the years to design long-path cells, generally of capillary bore to reduce the measurement volume. Absorbance measurement cells with path lengths of several meters with lasers as a light source were described by Fuwa et al.1 Even earlier, when light-emitting diodes (LEDs) were first introduced as light sources, the first reported LED-based absorbance measurement cells utilized a 30-cm-long path.2 However, with divergent sources, so much source light is lost to the walls, the detector becomes light starved and noise increases at a rate faster than the sensitivity. For this reason, optimum detection limits in conventional cells are actually reached with fairly short path lengths;4,5 4–8-mm path lengths are most commonly used in current flow-through detectors such as those used in flow injection analysis (FIA) or high-pressure liquid chromatography (HPLC).

Light losses to the wall can be reduced with a reflective surface. Many liquid media of interest tarnish metallic or internally metallized tubes. Moreover, such tubes are far from totally reflective—high attenuation generally results within a short length. If a glass or quartz tube is externally metallized, sample compatibility problems are largely eliminated but attenuation losses are even higher. These problems could be solved if the sample cell behaved as a waveguide; i.e., within a given acceptance angle and except for the portion that is actually absorbed by the sample, the light launched into the cell is essentially totally transmitted to the other side. To behave as an optical fiber, the light must be trapped within an optically denser (higher refractive index, RI) medium. A clean glass capillary does behave in a fashion as a waveguide—light launched into the bore is reflected at the external glass–air interface. To keep light losses at a manageable level, the capillary must have a very thin wall and then be protected externally from soiling by incorporating it within a protective but noncontacting jacket. While this is indeed possible, it does make for a fragile and unwieldy arrangement. A decade ago, one of us described a liquid core waveguide based on a tube made of air, as it were, fabricated by pneumatically introducing air through the exposed sides of a vertically placed porous hydrophobic membrane tube.6 Again, the delicate balance of pressure necessary to maintain a gas shell but not introduce air bubbles into the liquid makes for an arrangement that is impractical for most purposes.

Of course, one can also achieve a liquid core waveguide by choosing a high RI liquid. Carbon disulfide has a RI higher than


that of glass (1.63 vs typically 1.52 for the sodium D-line) and was chosen early on for this purpose. Unfortunately, this odorous and toxic solvent is not particularly useful for most real analytical purposes. Some aqueous solutions of high concentrations, e.g., concentrated solutions of sucrose (saturated aqueous solution RI 1.50), etc., also show high transmission when used in a low-RI polymeric capillary, e.g., of poly(tetrafluoroethylene) (PTFE). However, it is debatable whether the transition from Cs to (highly viscous) sugar solutions represents any real step forward. Tsunoda et al. showed a more practical arrangement in working with ethanol (RI 1.36) in a fluorinated ethylene-propylene (FEP) copolymer (RI 1.34). Similarly, Hong and Burgess showed that, by incorporating large amounts of ethylene glycol (RI 1.43) in aqueous liquids, the overall RI can be raised sufficiently to attain good light transmission in PTFE conduits.

A complete history of the development of liquid core waveguide-based absorbance measurement is not necessary for our purposes; further, Altikorn et al. have recently reviewed this matter in admirable detail. Without a doubt, the most important development has been the introduction of a new fluorocarbon polymer, Teflon AF (amorphous fluoropolymer), a copolymer of perfluoro-2,2-dimethyl-1,3-dioxole (hereinafter called dioxole) and tetrafluoroethylene that has a RI that decreases with increasing dioxole content. Teflon AF 1600 and 2400 have dioxole contents of 65 and 85–90%, respectively, with RI values of 1.31 and 1.28. The polymers are optically transparent through 200–2000 nm. Teflon AF 1600 is also available as a solution in a fluorocarbon solvent. Capillaries made of Teflon AF are now semicommercially available. Conduits of other materials can also be coated internally with Teflon AF relatively easily because of its solution processability. Transparent capillaries, e.g., of quartz, can be coated on the exterior with Teflon AF as well and are commercially available.

We are aware of at least one publication that uses a Teflon AF-based long-path liquid core waveguide to attain nanomolar limits of detection (LODs) for the colorimetric detection of iron in seawater. However, the aspirin experimenter should note that a bewildering variety of patents, seemingly on the same subject, cover the use of Teflon AF in liquid core waveguides.

From a perspective of polymer morphology, Teflon AF has a very large free volume; this intrinsic property results in not only an exceptionally low RI but also a very high permeability to a variety of gases and vapors, often 3 orders of magnitude higher than PTFE. Further, the solution processability of the material and its greater rigidity compared to PTFE makes it facile to work with very thin walled tubes or thin-film devices of other geometry. This permits high transmembrane gas fluxes. Hong and Burgess made an asymmetric tubular membrane by coating a 1-μm-thick layer of Teflon AF 1600 inside a porous polypropylene tube. From the data presented, response times of this device to ammonia was ~1 min compared to ~15 and ~60 min for 84- and 150-μm-thick membranes of PTFE, respectively. Since the response time in such devices is proportional to the square of the thickness, these results are not especially encouraging (it can be easily computed from the above data that a 1-μm-thick PTFE film should result in a response time significantly less than 1 s) since diffusion through the physically porous outer membrane itself should occur in a subsecond time scale. In addition, adhesion of Teflon AF to a nonfluorocarbon material is usually not good and such an arrangement may not be stable unless a fluorinated interlayer is created.

In the present work, we show that, in conjunction with selective chromogenic reactions, Teflon AF 2400 capillaries make attractive gas sensors based on extended path absorbance measurements. We further show that very thin walled (below 20-μm wall thickness) tubular Teflon AF 1600 devices can be fabricated in the laboratory that respond in subsecond time scales. Different modes of the operation of such devices are discussed with illustrative test gases.

**EXPERIMENTAL SECTION**

**Materials and Equipment.** Teflon AF 2400 capillaries in different sizes were obtained from Bioengineer Inc. (San Diego, CA). Teflon AF 1600 capillaries were a gift of W. D. Van Hoeven, DuPont Fluoroproducts. Teflon AF 1600-coated fused-silica capillaries (100-μm id., 375-μm o.d., TSU 100375) were obtained from Polymicro Technologies (Phoenix, AZ). The light source in the photometric experiments with chlorine was a high-brilliance blue LED (Panasonic LNV992CFBW, manufacturer stated center emission wavelength 470 nm, band pass 481 nm, specified half-width 40 nm, band pass 32 nm, Digi-Key Corp., Thief River Falls, MN). A superluminous green LED (Nichia 5905S, manufacturer stated center emission wavelength 505 nm, band pass 495 nm, specified half-width 40 nm, band pass 47 nm) were used for experiments with H₂S and NO₂. Small silicon photodiodes (type 2S007, Electronic Goldmine, Phoenix, AZ) were used as photodetectors. Except as stated, reagents were obtained from Aldrich Chemical and used without further purification.

**Gas Sensing Devices.** (a) Devices Made from Commercially Available Tubes. The basic construction of the annular tubular device is shown schematically in Figure 1. The Teflon AF 2400 tube constitutes the central element. Active lengths ranging between 15 and 30 cm were used in this work. A glass tube of 4-mm i.d. surrounds the Teflon tube and an inner pair of polypropylene tees that fit securely into the glass jacket provides the means of flowing gas around it. Spacers made from poly(vinyl chloride) (PVC) pump tubing (Elkay Products, Shrewsbury, MA) seal the exits of the Teflon tube from the tees. The Teflon tube then enters an outer tee at each end where an acrylic optical fiber (Edmund Scientific, Barrington, NJ) of appropriate

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Figure 1. Basic construction of an absorbometric liquid core waveguide-based gas sensor.

A diameter is inserted into it and is sealed in the exit arm of the tee by another PVC tubing spacer. One optical fiber leads to a photodiode and the second is cemented to an LED. A second photodiode cemented to the bottom of the LED acts as the reference detector. The two photodiode outputs are fed into a log-ratio amplifier (type 757N, Analog Devices, Norwood, MA), which thus constitutes a referenced absorbance detector.\(^{25}\)

(b) Devices Made from In Situ Fabricated Tubes. Two 1/16-in. barbed nylon tees (Ark-Plas, Flippin, AR) are inserted at the ends of a 20-cm × 3-mm-o.d. glass tube, and a 24-cm-long, 360-μm o.d., 100-μm i.d., 15-μm Teflon AF-coated silica capillary is inserted through both the tees. The tube is radially and longitudinally centered in the glass tube and affixed in place by applying epoxy adhesives at both ends. The epoxy covers the ends of the glass tube and the tees. A small area (0.1 mm × 0.05–0.1 mm) of Teflon AF coating is removed from both ends of the capillary, at a distance of ~1 mm from the ends, by scraping with a scalpel blade under a stereomicroscope. Larger diameter PVC tubes are connected at both ends to fit snug on the epoxy without touching the ends of the capillary. One of the PVC tubes is connected to waste while the other one is connected to a plastic disposable syringe installed in a syringe pump or any alternative arrangement (syringe affixed to a support and a weight put on the plunger) capable of pumping at a slow flow rate (~1 mL/h). An aqueous solution of 20% HF is pumped through the silica capillary until all the silica is etched out. (Caution: Handle HF with sufficient protection. HF is very corrosive and can easily diffuse through the skin. Work in a fume hood!) HF is then removed from the system by thoroughly flushing with deionized water.

From one end, the PVC tube is removed to expose the Teflon AF tubing and an acrylic optical fiber is axially inserted through the Teflon AF tube. A larger diameter fiber is preferred for greater light throughput. To achieve this, the end of a 0.5-mm-diameter acrylic optical fiber (E2542, Edmund Scientific) is tapered at one end by applying a longitudinal tension to the fiber while heating it with a hair dryer. The diameter of the tapered terminus is made such that is slightly less than the inner diameter of the Teflon AF tube. Next, the tapered fiber is inserted into the Teflon AF tube until there is a snug fit (the length of the fiber should be trimmed such that the fiber terminates within a short length (~1 mm) after the lateral aperture that was made by scraping with a scalpel). An outer tee is inserted over the joint and connected as described above. In this case, the optical fiber is already aligned in the tube and therefore no additional care is needed while the epoxy is applied. Since the fiber end is of conical shape, there will be sufficient gap between the fiber and the tube walls for liquid flow. Refer to Figure 2a for a detailed view of the terminus. The other end is prepared in the same fashion.

In another device of this type, the silica was etched out by pumping the solutions through apertures on the Teflon cladding made on the Teflon-coated capillary. This left a portion of the silica tube at each terminus. These were filled with high-RI, UV-cure optical adhesive by capillary action and then cured photochemically. These ends then themselves serve as the optical fibers (Figure 2b).

For the highest reproducibility and sensitivity, the sensor devices and connecting optical fibers (if not already jacketed) were protected from ambient light by wrapping with Al foil or electrical tape. However, the devices already have reasonable immunity to ambient light since an optical waveguide rejects transverse illumination. Many experiments were conducted without any shielding from ambient light because illumination in the laboratory is more or less constant.

Sensors for CO\(_2\) and Dissolved Organics in Water. A long Teflon AF 2400 tube (1.1-m × 450-μm i.d., 638-μm o.d., internal volume 175 μL) was provided with tee connections for liquid inlet/outlet and silica optical fibers at each end, coiled into a 50-mm-diameter coil and put inside a wide-mouth polypropylene bottle equipped with a gas inlet/outlet. The fiber optic ends were connected to a CCD-based spectrometer (Spectrimate, World Precision Instruments, Sarasota, FL) equipped with its own UV/visible light source. The same basic tube and end connections were used for the measurement of dissolved organics, except the total length of 30 cm was used of which a ~10 cm length was coiled and immersed into a 100-mL beaker containing the test analyte.

Test Arrangements. Compressed house air is fed through a pressure regulator and purified by a column containing, in sequence, silica gel, activated carbon, and soda lime. All air and gas flow rates were metered by mass flow controllers (model FC-280, Tylan General, Torrance, CA). The test gas was generated from permeation devices (VICI Metronics, Santa Clara, CA; gravimetrically calibrated respectively to be emitting 610 ng of C\(_2\)/min, 47 ng of NO\(_2\)/min, and 950 ng of H\(_2\)S/min). The permeation chamber was continuously flushed with dry air. The chamber and the thermal equilibration cell for the flush flow were housed in a thermostated enclosure maintained at 30 °C.

An aspiration pump sampled the test gas or clean air through the jacket of the sensing device at the desired flow rate (100 standard cubic centimeters per minute, scm, unless otherwise stated). A three-way PTFE solenoid valve (Biochem Valve Corp., Hanover, NJ) was used at the inlet of the gas-sensing device to rapidly switch between zero air and the test gas. Except as stated, chlorine exposures were conducted at a concentration of 1.4 ppm.

For response time testing, chlorine gas was generated in a stoppered 100-mL Erlenmeyer flask by mixing 5 drops of ~1% NaOCl with 5 drops of concentrated HCl. One milliliter or less of the headspace vapor in the flask was injected using a syringe into the outer jacket of the sensor as rapidly as manually possible. For very short response times, such as with the very thin walled device, the flow through the jacket was increased to 2000 scm.

When a constant liquid flow rate was desired, a Minipuls 2 peristaltic pump (Gilson Medical Electronics) was used to effect liquid flow through the device. Otherwise, the reagent was contained in a bottle, mildly pneumatically pressurized (~5 psi) and connected to the device. On the liquid exit side an on/off solenoid valve (Biochem Valve Corp.) was used to turn the flow on and off. A small length of a restriction tube was added to the valve exit to control the flow when the valve was on.

Reagents and Analytical Methods. Chlorine was measured by the reaction of the gas with acidic tetramethylbenzidine solution (TMB; this is a noncarcinogenic reagent for chlorine that results in an intensely yellow product via a very rapid reaction). NO₂ was measured by the relatively slow but sensitive Griess–Saltzman reaction; the preparation and the composition of the reagents were carried out as described in the literature respectively cited above. Hydrogen sulfide was measured by the formation of lead sulfide using a solution containing 1% lead acetate and 1% acetic acid.

The carbon dioxide-sensing arrangement was tested both with and without liquid flow. Phenol red (pK₈ 7.8) was used as the indicator: the stationary liquid arrangement used ~0.12 µM Phenol red (absorbance 0.9 at 556 nm for the 1.1-m cell) in a matrix of 10 mM NaHCO₃. The flowing liquid system used a ~0.26 µM solution of the dye adjusted to a pH of ~7.5 (absorbance ~1.45 at 556 nm) without any buffering agent. The dissolved organic-sensing arrangement contained HPLC-grade water as the internal filling solution.

PRINCIPLES

Consider a liquid core waveguide with gas-permeable walls with an active length of L cm (for both optical and analyte transport purposes) and inner and outer radii of r₁ and r₂ cm, respectively. If the device is exposed on its exterior with an analyte gas concentration of Cₐ µg/m² and the dimensionless partition constant for the gas-phase polymer-phase distribution of the analyte (solubility) is S, the concentration in the polymer phase in the outer wall, Cₐ is given (in units of mol/cm²) by

\[ C₀ = 10^{-12} SC₀/MW \]  

Equation 6 indicates that the rate of absorbance increase will linearly increase with Cₐ, while the sensitivity of the technique will increase with increasing DS (sometimes called the permeability constant, it is the hallmark of Teflon AF that it exhibits a high DS for a number of gases), increasing device length, and decreasing wall thickness and radius of the tube. Practical considerations on actually attainable limits of detection obviously also depend on total light throughput, and an increase in I or a decrease in r will obviously have practical limits depending on the nature and the brightness of the source light.

RESULTS AND DISCUSSION

Irreversible Reactions. Most chromogenic reactions that are discussed in the following are irreversible; the chromogenic product once formed is stable irrespective of the analyte gas concentration. In a second type of system, the optical status of the sensor changes with the status of the analyte gas, for example, when the sensor contains a lightly buffered solution of a pH
where the sensor is repeatedly exposed to pulses of the analyte gas. In the stationary reagent mode, the proposed device is truly an integrating sensor that responds to the cumulative exposure (the $C_{st}$ product). This is unlike most real-time monitors that just respond to the concentration $C_t$. In many cases that relate to health concerns, either from occupational or otherwise chronic exposures, it is often the cumulative exposure that is of interest; instantaneous concentration vs time profiles merely overburden the task of interpreting the data. Indeed, regulatory limit values of all criteria pollutants for ambient air applications are specified with significant integrating/averaging periods.

Nevertheless, it is of interest to examine what limitations exist when the $A$ vs $t$ data are differentiated to determine the underlying $C_t$ vs $t$ profile. Aside from limitations of the reaction rate to form the chromogen, the attainable temporal resolution is limited by the overall absorbance resolution, the absorbance range over which this resolution can be attained, and over which a linear absorbance/concentration relationship prevails. Fortunately, optical absorbance is an analytical parameter where a large linear dynamic range and a high degree of absorbance resolution are easily and inexpensively attainable. In our experience, in the absence of chemical complications, absorbance linearity spans $\geq 4$ orders of magnitude ($<0.1$ mAU to $\sim$ AU) with a resolution of at least 0.1 mAU, when the monitoring wavelength, source bandwidth, and chromogen absorbance spectra are well matched and the integration time is 1 s or longer. Of course, all measurement systems have an upper absorbance limit above which concentration linearity is poor, noise levels are too high, or both. For measurement schemes that are based on selective bleaching (for example, a practically important measurement for ambient gaseous $O_3$, may be based on the selective decolorization of Indigosulphonate, this forms the basis of standard measurement methods for aqueous ozone), it is the starting absorbance that has to be within the acceptable range of the measurement system; the device will no longer function when all the dye is bleached and the lower absorbance limit is reached.

An automatically functioning device is very simply configured: when the device reaches its preselected absorbance limit (high or low, measured with a comparator circuit), the liquid valve is

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**Figure 3.** Linear increase in absorbance as an AF 2400 sensor (12 cm long, 787-µm i.d. × 1041-µm o.d.) is exposed continuously to 5.7 ppm H$_2$S. The gas exposure was started 3 min into the run. The induction period for the observed increase in absorbance is $\sim 2$ min, which includes the induction period for precipitation.

**Figure 4.** Output from a AF 2400 sensor (15-cm × 279-µm i.d., 533-µm o.d.) periodically exposed to pulses of chlorine (1.4 ppm, 1-min duration).

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tuned on for a brief preset period of time (in our arrangement, well below 1 min) to refill the device and begin a measurement cycle anew. A device can be deliberately made insensitive and a measurement cycle can be run for as long as 24 hr. Note that, even in such a case, a dynamic range of $10^4$ then means that if a device reaches its absorbance limit in 24 hr, the attainable temporal resolution is $10^{-4}$ day (<10 s), assuming exposure at constant concentration. In real applications, the measurement/reagent refill cycles are likely to be much shorter than a day. The temporal resolution attainable with such a long measurement cycle will still be more than adequate for ambient measurements and in fact will rival the capability of many continuous monitors for ambient pollutant gases now commercially available. In a situation where the most common complaint is that of being overburdened with data, the possibility that the intrinsic averaging period can be chosen at will and thus only as much data as necessary can be collected, can be very attractive.

Response Time. The response time of the sensor (defined to be the time period for the sensor output to change from 10 to 90% of its ultimate value as a result of an analyte pulse at the input) is a combined function of several parameters. These include the transmembrane transport rate of the analyte, the rate of production of the chromogen from the analyte, and the optoelectronic arrangement. About the latter, signal-processing electronics can easily be configured so as not to be a contributing factor. However, the optical arrangement can potentially contribute to the apparent response time. Consider that the colored product is formed at the inner wall of the waveguide and the only motive force that exists for homogenization of the colored product is liquid-phase diffusion, a slow process. In the extreme case of a short, large-bore tube and a coherent source, light rays will go through the device largely as a parallel beam and the final absorbance will not be attained until the internal liquid is homogenized. In contrast, for a narrow-bore waveguide and a divergent source beam, light will propagate by multiple internal reflections and the nature of the light propagation will result in averaged probing of the liquid, regardless of its radial inhomogeneity.

Fortunately, we have found that, with virtually all of our devices, the optical arrangement is not a factor in contributing to the response time. Experiments to determine response time were conducted with chlorine because the formation of the colored product between TMB and chlorine proceeds extremely fast. Under these circumstances, the response times obtained are listed in Table 1. The response of the thin-walled (17.5-µm wall thickness) device to chlorine is shown in Figure 5. To our knowledge, this is the first time subsecond response speed of a membrane-based optochemical reaction-based sensor has been demonstrated. In reality, because of the ability to form thin films of this polymer by solution spin coating, a variety of alternative device configurations with a highly permeable thin film may lead to a new generation of ultrafast devices that may or may not take advantage of the optical properties of this film. It is interesting to note that for a short, larger bore thick-walled (152-µm) Teflon AF 1600 device, we did note a response time of ~8 min in the same experiments. This was so far out of line with the other devices that we believe optical inhomogeneity played a role in this particular case.

When the transmembrane transport is the limiting factor, the characteristic time is given by $\delta/D$ where $\delta$ is the wall thickness of the membrane and $D$ is the diffusion coefficient of the analyte in the polymer. Considering that five characteristic time periods are needed for attaining a plateau response, the value of $D$ can be calculated from the observed response time and is also reported in Table 1. Within the limits of precision of wall thickness measurement, the $D$ values are remarkably consistent for the same polymer type and are also remarkably large. A diffusion coefficient of the order of $10^{-5}$ cm$^2$/s is typical of a low-molecular-weight solute dissolved in a low-viscosity solvent, rather than the typical diffusion coefficient of a solute in a solid polymer phase. The difference between Teflon AF 2400 and 1600 is also of interest. Although the latter is known to be less permeable than the former for He, H$_2$, O$_2$, N$_2$, CO, and some hydrocarbon gases, whether the lower permeability originates from a lower solubility (partition constant $S$) or a lower diffusivity has never been determined. The diffusion coefficients of chlorine calculated for two very different Teflon AF 1600 tubes (of very different origin and method of production) are remarkably consistent. Overmore, the diffusion coefficients are nearly twice that observed with that in Teflon AF.
Figure 6. System response to NO\textsubscript{2}, 14-cm x 787-\textmu m i.d., 1041-\textmu m o.d. device. All flow rates were 200 sccm except one blank run, as indicated. The linear \textit{R} values of each temporal response are indicated, and the inset shows that these slopes exhibit excellent linearity vs concentration.

2400, leaving little doubt that the lower permeability of the 1600 polymer originates from a lower partition constant.

Response Magnitude. According to eq 5, the response from a given exposure should be proportional to \( \frac{1}{r/r} \Delta r \). The response to 1.4 ppm chlorine from a 6-min exposure was measured, and these data also appear in Table 1. When the response is plotted against the \( \frac{1}{r/r} \Delta r \) value for a device (all data retrievable from Table 1), the linear correlation coefficient is greater than 0.95, indicating the soundness of the model. The response of the Teflon AF 1600 thin-film tube is 2-fold less relative to the linear relationship observed for the Teflon AF 2400 devices. This result is comparable to the 5-fold lower permeability of Teflon AF 1600 relative to the 2400 polymer reported for CO\textsubscript{2}.\textsuperscript{12} Bearing in mind that the diffusion coefficient of chlorine is actually 2-fold higher in Teflon AF 1600, the solubility of chlorine in 1600 is then lower by a factor of ~4 relative to the 2400 polymer.

The data presented in Figure 4 for exposure steps of 1.4 ppm-min make it clear that even though this particular device is neither particularly long nor are its walls especially thin, it is readily capable of quantitating exposures of the order of 0.25 ppm-min. This simple inexpensive device will thus be able to quantitate, without modification, single-digit ppb concentrations of the analyte gas. An illustration, perhaps more relevant to routine pollutant measurements, is shown in Figure 6 for different concentrations of the criteria pollutant nitrogen dioxide. Presently the regulatory limit for this pollutant is based on an annual arithmetic mean concentration of 100 \( \mu g/m^3 \) (53 ppb).\textsuperscript{21} The Griess–Saltzman reaction is not nearly as fast as the TMB reaction for chlorine, and an initial induction period for response is discernible at the lower concentrations. All the flow rates in this experiment were 200 sccm, except for one of the two clean air runs, which was conducted at 2000 sccm. The difference between these two response lines can be regarded as the maximum artifact response that can be caused due to evaporation. For each of the concentration runs, the linear \textit{R} values for the time vs absorbance data are reported for the period shown. Further, in the inset, the slopes of these lines are plotted against the concentration sampled and indicate excellent linear response. The slope values for the blank sampled at 200 sccm, the blank sampled at 2000 sccm, and 9.0 ppb NO\textsubscript{2} sampled at 200 sccm are respectively 0.1923 ± 0.0023, 0.2442 ± 0.0015, and 0.6314 ± 0.0026 mAU/min. If the uncertainty of the slope of the 200 sccm blank is regarded as the limiting factor, one calculates a detection limit of 0.15 ppb as the LOD based on 3 times this uncertainty. If the difference between the 200 and 2000 sccm is regarded as the maximum uncertainty due to evaporation loss, one still calculates a detection limit of 3 ppb. It is clear that the method is easily capable of providing hourly measurements at levels down to ±10% of that of the regulatory limit. Current commercial instrumentation that can accomplish this approach uses U.S. $10,000 in cost.

Dependence on Gas Flow Rate. Experiments with H\textsubscript{2}S show that, for a 20-cm long device fabricated from a 787 × 1092-\textmu m AF 2400 tube, the sensitivity to a given gas concentration is independent of flow rate at flow rates of ≥100 sccm. Below flow rates of 50 sccm, the response decreases continuously with flow rate. Similar behavior is expected with other gases. As long as the flow is sufficient to prevent a significant depletion zone around the sensor membrane, no flow dependence is expected and none is observed. At flow rates lower than this, the analyte depletion around the sensor membrane due to transmembrane transport causes the sensor actually to experience lower concentrations. Obviously, the exact flow rate above which no flow effect is observed will depend on the rate of transmembrane transport, dependent in turn on the nature of the gas and the device dimensions.

Reversible Reactions. For the CO\textsubscript{2} sensor tested here, gain or loss of CO\textsubscript{2} causes a decrease or increase of the pH of the filling medium that is reflected in turn by the optical behavior of the indicator. The color change of the indicator, a proton-transfer reaction, is extremely rapid, so the speed of response is controlled by other factors. The results of the experiments conducted in this mode are shown in Figure 7. We were primarily interested in the capability of the sensor to monitor breath CO\textsubscript{2} levels and the speed with which the sensor responded. Device response was tested by exhaling lightly, exhaling deeply, or purging the enclosure with nitrogen. Three separate panels are shown. In (a), with a buffering agent present, the response is lower and slower than that observed with a flowing unbuffered reagent. Response time in this system is controlled not only by transmembrane transport (note that the tube used in this experiment has a relatively thick wall among the tubing used in this work) but also by hydration and dehydration of CO\textsubscript{2}, which are not especially fast processes.\textsuperscript{33} In panel b, the response time of the device is faster than in (a) but the residence time of the liquid in the lumen is still of the order of 1 min. The recovery rate can be improved by simply flushing the solution faster, as in (c); note that the device begins to recover even before the nitrogen purging begins.

The overall response behavior is thus dependent on the individual time constants related to transmembrane transport, chromogenic reaction/bleaching (which includes the underlying phenomena, in this case, the hydration/dehydration of CO₂), and the hydrodynamic clearance. The contribution of each can be assessed through experiments that alter the membrane thickness, the pulse width of the analyte gas impulse, and the liquid flow rate.

Response to Dissolved Organics. Permeation occurs due to a difference in activity between two sides of a membrane; it is not necessarily uniquely applicable to only gas-phase analytes. While permeation-based passive monitors were first described for gaseous analytes, it has been demonstrated that essentially identical devices can be used for the measurement of un-ionized organic compounds in water. The nonpolar cladding of a fiber optic can take up organics from water, and such a device can thus be useful for monitoring dissolved organics. Using mode-filtered light detection, an LOD of 1 mg/L for trichloroethylene has been reported. However, in general, evanescent wave probing offers relatively poor sensitivity. Figure 8 shows the spectral response of a very limited length of the sensor dipped in aqueous acetone samples; as indicated, not only is the permeation of the acetone readily detectable but the dependence of the response on the Ct product is readily apparent. Permeation of any prospective analyte is dependent on its polarity, which greatly influences the value of the partition constant. The sensor is readily able to measure halogenated organics at levels meaningful to polluted water; under conditions identical to those in Figure 8, the absorbance at 230 nm rises linearly with time at a rate of 1.21 mA/min upon exposure to 10 ppm aqueous trichloroethylene (a compound that exhibits a much greater level of partition constant in Teflon AF) with a linear r² value of 0.9998. Of course, UV-visible absorption spectrometry is unable to make any meaningful speciation of different compounds that can permeate into the optical path. It has already been shown that Raman

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Figure 7. Response of sensor to CO₂ in breath: (a) static liquid, 10 mM NaHCO₃ containing phenol red; (b) liquid containing Phenol red, pH 8.5, flowing at 0.2 mL/min; (c) same liquid as in (b) flowing at 0.8 mL/min. Note abscissa scaling in (a) spans twice as long a period and ordinate scaling is also different in the three panels.

Figure 8. Spectrum obtained with 10-cm length of a 30-cm water-filled sensor tube upon immersion in (a) 5% acetone for 1 min and (b) 0.5% acetone for 10 min.
spectroscopy can be carried out with much greater sensitivity in liquid core waveguides and is applicable to aqueous solutions.\textsuperscript{39,40} In other cases, selective reactions such as the Fujwara reaction for halogenated organics may be directly applicable.\textsuperscript{41}

Implications to Passive Monitoring. In passive dosimetry, used for both area and personnel monitoring, the analyte is collected on a sorbent by exposing it to the analyte through some transport/diffusion barrier, e.g., a membrane or an orifice.\textsuperscript{42} The transport barrier limits mass transport and makes the device reasonably independent of the face velocity of the air sample to which it is exposed. It is obvious that much like the sensor dipped in water to sense organic compounds, an unjacketed reagent-filled tube, with integral optical fibers, possibly mildly pressurized through a miniature elastomeric reservoir at one end, can be easily deployed as a passive monitor, either for area monitoring or for personnel monitoring applications. Such devices can be interrogated at desired intervals by a light source/detector that does not need to be integral to the collector. After reading, the reagent can be refilled from the integral reservoir (depending on reagent life and the capacity of the reservoir). Similar devices can be deployed in water for monitoring organic compounds. To provide a suitable sink for organic compounds of interest as well as to have minimum permeation loss to the outside, a low-vapor-pressure optically transparent filling fluid such as a glycol or a polyol can be used as the internal liquid.

In summary, a new class of inexpensive and versatile sensors are described that can potentially be used for continuous area monitoring and cumulative exposure monitoring for either workplace or ambient air use. In the active gas sampling mode, strict flow control is not necessary as long the flow rate is kept above some minimum value. Selective chromogenic reactions are available for a large number of analyte gases of interest, including NO\textsubscript{2}, SO\textsubscript{2}, CO, and O\textsubscript{3}, criteria pollutant gases so designated by the EPA. The same device can be readily reconfigured to measure different gases by changing the reagent and the light source. Fluorometric measurements are also possible because the liquid core waveguides also make possible uniquely simple fluorometry; this will be discussed in a separate article. An active participation in environmental monitoring is a key to ensure proper stewardship of this planet; the affordability of the present concept can extend such efforts routinely to high school levels and thus attract our future citizens to this effort.

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