Trace Detection of Ionic Species with Surface Enhanced Raman Spectroscopy

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This article describes the development of an optical fiber sensor for monitoring groundwater contamination using Raman spectroscopy. Also provided is a brief discussion of the fundamentals of resonance and surface enhancement of the Raman signals. The first stage of sensor development was the fabrication of stable, sensitive fiber-optic probes with surface enhanced Raman substrates attached. The next stage, a feasibility test, showed that Raman is sensitive enough to detect trace concentrations of metal ions in water. Next, anchoring the indicator compounds to the substrate was carried out using derivatization with disulfide linkages. The final stage was the development of surface-localized pH probes to help modify surface pH, and thereby, fine-tune the selectivity of the metal ion indicators.



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he ability to detect hazardous materials in situ and in real time is a challenging problem for spectroscopists. One approach to the problem involves using optical fibers to connect a remote sensor with a central analysis station. Optical fibers transmit visible radiation quite well over moderately long distances (up to several kilometers), and their use in transmitting spectroscopic information is well documented (1-3). A critical limitation of in situ optical-fiber spectroscopy is its inability to preconcentrate or purify the sample. When the sample comprises a mixture of similar compounds, the spectroscopic technique must be capable of distinguishing between mixture components. The method chosen here was Raman spectroscopy, a fingerprint technique that operates in the visible region of the spectrum where optical fibers transmit light efficiently. Because Raman scattering is an inherently weak process, surface enhanced Raman spectroscopy (SERS) is used to increase the sensitivity (4). The inability to preconcentrate the sample can be overcome by chemically modifying the optical fibers such that they concentrate the analyte at the fiber tip.

Our approach was to fabricate a SERS substrate on the end of an optical fiber and chemically modify the substrate with organic thiols. The thiol functionality bonds irreversibly to the silver, forming a compact layer and protecting the silver surface from oxidation (5,6). The organic functionalities tested to date are indicators that can chelate with metal ions or that change with pH. Many of the organic functionalities chosen have electronic absorptions in the frequency region of laser excitation. The result is a resonance enhancement that provides an additional improvement of signals beyond that provided by SERS. The spectra obtained contain Raman bands corresponding to both the complexed and uncomplexed indicator. The Raman bands associated with the uncomplexed indicator provide an internal standard, which is very important because it removes problems associated with variable laser power, varying SERS surfaces, and fiber attenuation. The result is a fiber system capable of preconcentrating the analyte through the use of indicator compounds that have a large $K_{formation}$ for the analyte, and a system that is ultrasensitive as a result of enhancements provided by SERS and resonance Raman.

RESONANCE RAMAN

The theoretical aspects of resonance Raman have been described previously (7,8). Resonance Raman occurs when the exciting light corresponds to an absorption band associated with the Raman scatterer. Figure 1 shows the energy level transitions that correspond to spontaneous spectroscopies (Raman scattering) and concerted electronic spectroscopies (relaxed fluorescence). In normal Raman scattering a molecule is excited to a virtual state, which corresponds to a quantum level relating to the electron cloud distortion created by the electric field of the incident light. A virtual state does not correspond to a real eigenstate (vibrational or electronic energy level) of the molecule, but rather is a sum over all eigenstates of the molecule. Resonance Raman occurs when the energy of the exciting beam is close to an electronic energy level of the molecule and one term in the sum of eigenstates dominates over all others. When this occurs, the electron cloud surrounding the molecule is more readily distorted by the electric field of the incident light. The transition has a higher probability, and there is an enhancement of the Raman process.

Often, resonance Raman is accompanied by relaxed fluorescence. The fluorescence signal is usually much stronger than the resonance Raman scattering and completely obscures the Raman signal. Fluorescence can be avoided with near-infrared (near-IR) excitation because few molecules have electronic absorptions in this spectral region. This is one of the motivations for Fourier transform (FT)-Raman and near-IR excitation (9). Fluorescence can also be avoided with SERS. The noble metal surfaces that provide SERS enhancements provide a path for rapid energy transfer from molecules adsorbed to the surface, and thereby, quench fluorescence (10,11).

THE SERS EFFECT

The enhancement of Raman scattering at noble metal surfaces can be attributed to two factors. One is an electromagnetic effect observed for molecules near roughened noble metal surfaces, and the second is a chemical interaction between the adsorbed molecule and the metal surface. The experimentally observed combined enhancement for pyridine on silver is on the order of 10⁶ (4). In many molecules a chemical enhancement does not exist and smaller total enhancements are observed.

The portion of the SERS effect attributed to electromagnetic amplification occurs for noble metal surfaces with roughness features smaller than the wavelength of light (12,13). To maximize SERS enhancement, the size and shape of the surface roughness features are "tuned" to couple the electromagnetic energy of the exciting light into the metal substrate.

The electromagnetic enhancement observed for SERS arises from the unique optical properties of noble metals. The zero oxidation

Excited state

Virtual state

Virtual

state

Ground state

Resonance

Raman

(a)

Normal

Raman

electronic configuration of these metals is d¹⁰s¹. The single s electron is well shielded by the inner shell electrons and behaves as a free electron. In the visible region of the spectrum this free electron behavior causes the dielectric constant of the metal to have a large negative real component and a small imaginary component. The large negative component of the real part means that the electrons react very strongly to incident radiation and their displacement is such that the field due to the polarization of the particles assists further polarization. The result is a resonance condition that absorbs energy from the incident light and creates a locally intense electric field within the metal particle. This is illustrated in Figure 2.

The theory describing the optimal particle size and shape was developed at the turn of the century by Lorentz (14). He derived an equation to describe the scattering efficiencies of small spherical particles:

$$E_{local} = \frac{1}{\varepsilon(\omega) + 2} E_o \qquad [1]$$

Excited state

Vibrational

relaxation

Relaxed

fluorescence

Ground state

where $\epsilon(\omega)$ is the real part of the dielectric constant of the metal, ω is the frequency of the

j

(b)

Absorption

incident light, E_{local} is the electric field due to the polarization of the metal particle, and E_{α} is the electric field of the incident light. For silver excited in the near-UV, $\varepsilon(\omega) = -2$. Under this condition, the denominator approaches zero and a resonance condition is observed. The electric field in the particle (E_{local}) does not reach infinity because of the small imaginary part of the dielectric constant omitted from the above equation for simplicity. Of more importance to SERS is the equation for an elliptical particle:

$$E_{local} = \frac{1}{1 + A[\varepsilon(\omega) - 1]} E_o \qquad [2]$$

where A is a geometric factor that is a function of the eccentricity of the noble metal particle (15). As the particle becomes more elliptical,



dent light, E_{o} . The lower diagram illustrates

the enhancement of the induced dipole in

pyridine adsorbed on a SERS particle.



troscopy and (b) relaxed fluorescence.

A becomes smaller. The condition for resonance occurs at more negative dielectric constants that are found at longer wavelengths. In this case, for an elliptical particle, the resonance splits. One component still lies in the near-UV, and the second component, along the long axis of the ellipsoid, occurs in the visible. It is the resonance along the long axis of the ellipsoid that best describes the SERS effect.

When the incident radiation interacts with

the surface it causes the free electrons to oscillate with the incident electric field and polarizes the noble metal particles. This creates a strong local electric field at the particle surface known as a surface plasmon, which is illustrated in Figure 2. When a molecule is in close proximity to a noble metal particle the molecule can be polarized by E_{local} of the noble metal particle. This leads to an enhancement of the Raman signal because Raman scattering is proportional to E_{local}^2 . Further en-



hancement arises as a result of reciprocity of optical phenomena. Just as the incident field can polarize the particle and induce a dipole, the induced dipole can polarize the particle and create a large radiative field. The total enhancement can then be represented by two terms. One is the enhancement of the incident field associated with ω_{laser} , and the other is the enhancement of the radiated field at ω_{Raman} .

The imaginary part of the dielectric constant and the particle size limit the SERS enhancement. The imaginary part of the dielectric constant is related to the lifetime of the excited free electron state. If the electron is truly free, then it can oscillate forever and the imaginary component is zero. However, interband transitions (transitions between valence and conduction bands) can absorb the energy of the free electron and decrease its lifetime. In copper and gold, strong interband transitions in the blue-green restrict the SERS effect to the red portion of the spectrum. In silver, the interband transitions are farther in the blue and SERS is possible at shorter wavelengths. Small particles will also have large imaginary components to the dielectric constant because the free electron can inelastically collide with the particle surface (16). When the particles become large, the free electron loses energy through radiative losses as it accelerates across the particle (17). The enhancement is also diminished by dynamic electric field effects as the size of the particles approaches the wavelength of light (18).

The part of the SERS effect attributed to chemical enhancement does not require highly roughened noble metal surfaces. The chemical effect is a result of the formation of chargetransfer complexes between a molecule adsorbed to the metal surface and the metal. If the adsorbate possesses groups or atoms capable of acting as ligands toward the metal surface, a chemical enhancement can occur. An example would be pyridine, which is known to coordinate with silver. The resulting complex contains charge-transfer bands with transition energies in the visible region. This leads to a resonance enhancement of the adsorbate. Because the lifetime of excited states is drastically shortened on noble metal surfaces, the charge-transfer absorption bands will be broadened to cover a very large frequency range. The distinction between chemical enhancement and electromagnetic enhancement has been very elegantly shown by Seki (19).

SERS on optical fibers. SERS is an excellent technique for obtaining strong Raman scattering from molecules at surfaces. However, the gains offered by SERS come at the cost of difficult and delicate surface preparation techniques. Silver substrates provide the largest enhancements of the Raman signal.

Unfortunately, silver surfaces rapidly degrade in air or water. Another difficulty encountered when combining SERS with optical fibers is the extraneous signal generated in the fiber that carries the laser light. The intense laser light excites Raman scattering in the fiber that is observed as broad bands between 200 and 1000 cm^{-1} . This scattering is so intense that it can completely obscure the Raman signal. The solution is to use separate excitation and collection fibers and prevent the laser light from coupling into the collection fiber.

Several techniques for combining SERS with optical fibers have been developed. Schwab and McCreery (20) used an opticalfiber bundle to excite and collect Raman scattering at an electrode surface roughened by oxidation-reduction cycles. A large background signal generated in the excitation fiber interfered with the analyte signal, so they modified the system by shining the laser beam directly on the electrode at a glancing incidence. They collected the Raman scattering with an array of 27 fibers suspended above the electrode.

Vo-Dinh and Bello (13) successfully used fibers to carry both the exciting beam and the Raman-scattered light. They found that the background scattering in the excitation fiber varied depending on the fiber used. A soft plastic-clad fiber from General Fiber Optics, Inc. (Cedar Grove, NJ), was found to give minimal scattering interference. Their approach was to convey the exciting light to a SERS surface with one fiber and collect the Raman-scattered light with a second fiber. They used a SERS substrate fabricated on a glass microscope slide. They coated the slide with 0.1 μ m of alumina to provide the necessary roughness features, then deposited 75 nm of silver.

Myrick and Angel (21) investigated another arrangement for collecting SERS spectra at an electrode. A narrow band-pass filter placed at the end of an excitation fiber removed the background scattering from the fiber. The laser line was prevented from entering the collection fiber with a long pass filter between the SERS surface and the collection fiber. This arrangement minimized the background scattering to a level that allowed them to obtain Raman spectra over 250 m of fiber.

The methods described above involve a SERS substrate detached from the fiber. It was our desire to fabricate the SERS surface directly on the end of the fiber. In our initial attempt we deposited island films on the fiber tip. Island films are formed by vacuum depositing a very thin layer of silver, about 5 nm, onto a surface. The silver aggregates into particles of appropriate size and shape for large SERS enhancements. We found that island films on fibers produced very weak Raman signals and, perhaps more importantly, could not block the excitation laser beam from entering the collection fiber. This resulted in a large background signal.

The technique that seems to produce the best substrates involves roughening the fiber tip with a coarse grade of alumina and vacuum depositing 20-40 nm of silver on the roughened fiber tip (22). We tested several sizes of alumina particles for roughening and found the optimum alumina particle size to be between 15 and 32 µm. This size of alumina polishing paper produces scratches on the fiber tips visible under 50× magnification. According to elementary SERS theory, these surface features should be too large to produce enhancements. An explanation is that we have produced sharp edges and grating-like structures on the surface that are capable of coupling the incident photons into surface plasmons (23).



A major advantage these surfaces offer is efficient blocking of the laser beam from the collection fiber, thus minimizing or eliminating background signals from the fibers. We tested various combinations of alumina particle size and silver thickness by dipping the prepared fiber tip into a solution of cobalt phthalocyanine and comparing the intensities of the Raman peak at 685 cm⁻¹. We tested silver thicknesses from 15 nm to 60 nm. The SERS signal decreased from a high of 3986 counts per second (cps) with 20 nm of silver to 1155 cps with 60 nm of silver. We observed a large decrease in the background scattering associated with the optical fiber between 15 and 30 nm of silver because this thickness effectively reflected the incident beam. We found that our best roughened optical fiber gave a signal enhancement 87% as large as for a spectra collected from an island film deposited on a glass slide.

ATTACHING INDICATORS

Most indicators are designed to have high water solubilities for aqueous titrations. This property is achieved by the addition of a functionality that has a very low pK_a and ionizes readily in water. Typically the modifications are a carboxylic or sulfonic acid group. We have taken advantage of these modifications by forming either an amide or sulfonamide linkage with cystamine. This produces a disulfide-modified indicator. Disulfides are well known for their ability to bind to noble metals and form compact monolayers (5,6). The monolayers protect the silver surface from deterioration. The sites that chelate or change in the presence of the analyte are still exposed to the solution. This technique also assures that the indicators are held in close proximity to the SERS surface to produce strong enhancements.

RAMAN INDICATORS

Eriochrome Black T (EBT). Our intention is to monitor analytes by observing changes in the vibrational spectrum of indicators as illustrated in Figure 3. To test the feasibility of our idea we monitored the change in the spectrum of EBT when complexed with metal ions. Figure 4 shows spectra of EBT uncomplexed and complexed with Cu²⁺. The peak at 1403 cm⁻¹ is present in the complexed form of EBT, whereas the peak at 1274 cm⁻¹ is present in the uncomplexed form and disappears when EBT complexes with a metal ion. The intensity of the 1403-cm⁻¹ peak corresponds to the concentration of Cu²⁺ in solution.

Our initial tests with EBT were performed with SERS substrates on glass microscope slides cut into 1-in. squares. The SERS surfaces were produced by vacuum depositing a layer of CaF₂ followed by 50 nm of silver. The CaF₂ deposits as microcrystallites on the surface of the glass. The silver-coated microcrystallites are of a size and shape that result in large SERS enhancements (22). In this case we did not form the disulfide derivative of the indicator. The EBT spectra were collected by spin coating a buffered aqueous solution directly on these SERS surfaces. The spectra were obtained with a custom-built scanning Raman system described elsewhere (24).

The enhancement obtained from a SERS surface is dependent on several features. For example, the microscopic roughness is difficult to accurately reproduce, laser power can create both reversible and irreversible loss of signal, and surface morphology changes are possible. This means we cannot directly correlate the intensity of the 1403-cm⁻¹ peak with Cu²⁺ concentration. However, if we compare the intensity of the 1403-cm⁻¹ peak with the 1274-cm⁻¹ peak we have an internal standard that compensates for lack of control over surface conditions. The calibration curve developed by spin coating 10⁻⁴ M EBT in a solution buffered to pH 9 with NH₄Cl is displayed in Figure 5. The accepted definition for detection limit is when the signal-to-noise ratio (S/N) = 3 (25). Based on this definition, our detection limit for Cu²⁺ is 85 ppb. This detection limit was obtained with a 3-s integration time. In real applications, integration times of 100 s would be very reasonable. This would lower the detection limit for Cu2+ to less than 20 ppb.

We performed a similar analysis for Pb²⁺. In this case we extracted the EBT complex with pentanol, evaporated the pentanol, and redissolved the residue in methanol. Spectra were obtained on a CaF₂ SERS surface spin coated with the methanol solution. The Pb²⁺ spectra and calibration curve were presented



tion of EBT. (Reprinted with permission





[24].}

in reference 24. At a S/N of 3 we were able to detect Pb^{2+} at 270 ppb with 3-s integration times. Integrating for 100 s would lower the detection limit to about 50 ppb for Pb^{2+} .

We further examined the selectivity of the technique by attempting to resolve the chemically similar alkaline earth metals (24). From spectra included in reference (24), we found the peaks for the complexed metals were as follows:

Metal	Peak position
Magnesium	1364 cm ⁻¹
Calcium	1358 cm ⁻¹
Strontium	1316 cm ⁻¹
Barium	1310 cm ⁻¹

It is evident that the complexed peak shifts in conjunction with ion size. We defined the resolving power (R) of our technique as

R = peak separation/FWHM [3]

If R > 1, then we can distinguish the peaks in a mixture. Using this definition we were able to distinguish magnesium from strontium and barium (but not from calcium), whereas visible absorption measurements could not distinguish between any of these species.

We discovered that it was important to use sufficient EBT to coat the surface with more than a monolayer. As shown in Figure 6a, the spectra obtained with 10^{-5} M EBT were independent of the concentration of Cu²⁺. The spectra were identical and lacked the characteristic Cu²⁺ peak at 1403 cm⁻¹. As seen in Figure 6b, the spectrum for 10^{-5} M EBT alone was identical to those with Cu²⁺. The absence of the peak at 1274 cm⁻¹ suggested that EBT was in a complexed state, perhaps with the silver SERS surface. This was confirmed, as shown in Figure 6c, by using a larger concentration of EBT and adding AgNO₃ to the solu-



tion to form the Ag–EBT complex. Earlier experiments with these higher concentrations of EBT showed the peak at 1274 cm⁻¹, suggesting that at these higher concentrations there was an excess of EBT that remained uncomplexed on the surface.

4-(2-Pyridylazo)-resorcinol (PAR). Our success with EBT proved that it is indeed possible to use the vibrational changes of an indicator to monitor an analyte. The next step toward developing a sensor was to attach the indicator to the SERS surface. This was done for PAR by coupling it with a disulfide bridge. The synthesis was accomplished by reacting PAR with the acid chloride derivative of 3-mercaptopropionic acid. The product has been characterized as an asymmetric disulfide with the single PAR segment reacting through the phenolic hydroxide para to the azo bridge.

As with EBT, we conducted the initial investigations on SERS surfaces that are easier

to fabricate and work with than fibers. For our work with PAR we used an alternate method for making SERS surfaces that does not require vacuum deposition (26). A thin piece of 99.9% pure silver foil (Aldrich Chemical Company, Milwaukee, WI) is dipped into a rapidly stirred solution of 30% nitric acid for 60-90 s. The silver foil turns white as it is etched by the nitric acid. It is then removed and rinsed well with Millipore (Bedford, MA) water. To form the monolayer of PARDS (the PAR disulfide), a piece of nitric acid-roughened silver foil was soaked in a dilute methanol solution of PARDS for 24 h and rinsed with methanol, leaving only the PARDS that has reacted with the surface. Figure 7 shows the spectra observed when this silver foil is exposed to a blank solution, a solution containing Pb2+, and a solution containing Fe³⁺. The peaks at 1329 cm⁻¹, 1023 cm⁻¹, and 969 cm⁻¹ shift when PAR com-



Figure 6. SERS spectra demonstrating EBT complexation with Ag surface: (a) same spectrum obtained for concentrations of Cu²⁺ from 10^{-4} M to 10^{-8} M with 10^{-5} M EBT; (b) 10^{-5} M EBT only; and (c) 10^{-3} M EBT with an excess of AgNO₃. Spectra were obtained with 3-s integration times and 20 mW of 531-nm light.



Figure 7. SERS spectra of etched silver foil coated with the anchored thiolate of the indicator PARDS immersed in: (a) blank solution showing PARDS only; (b) in presence of Pb²⁺; and (c) in presence of Fe³⁺. Spectra were obtained with 5-s integration times and 5 mW of 514.5-nm light for resonant excitation of PARDS.

plexes with Pb²⁺. A calibration curve was developed by plotting the log of the ratio of peak intensities, 1023 cm⁻¹/1005 cm⁻¹, versus pPb²⁺ ($-\log Pb^{2+}$) concentration. The calibration was linear for Pb²⁺ concentrations from 10⁻³ to 10⁻⁵ M with an R^2 value of 0.99. Similar results were obtained for Fe³⁺ with the cali-



Figure 8. Spectra of disulfide form of cresol red anchored to SERS surface formed at tip of optical fiber showing peaks at 1600 and 1390 cm⁻¹ used to create a calibration curve: (a) in pH 6 buffer; and (b) in pH 3 buffer. Spectra were obtained with 30-s integration times and 5 mW of 514.5-nm light. (Reprinted with permission [28].)

bration curve being developed using the log of the ratio of peak intensities, $1329 \text{ cm}^{-1}/1362 \text{ cm}^{-1}$, versus pFe³⁺. The lowest concentration observed for either metal was in the $10^{-6}-10^{-7}$ M range (27).

pH determination. We tested three pH indicators: methyl red, cresol red, and 4-pyridinethiol (28). Our goal was twofold in this case. First, pH can be used as a marker to determine the quality of groundwater. Second, the selectivity of most metal indicators is a function of pH, and we are interested in developing a spectroscopic tool for the determination of the local pH at a surface. Once we have developed a method for pH determination at the surface we plan to bind charged species to the surface. In this way we will be able to finetune the selectivity of our metal ion indicators.

All indicators were obtained from Aldrich and purification was performed after derivatization. A similar approach to that used for PAR was exploited to form the disulfide of these indicators, except that we used cystamine and DCC as a coupling agent. The product for cresol red was an asymmetric disulfide formed with a sulfonamide linkage. With methyl red, a symmetric disulfide was formed. We initially tested the indicators on roughened silver foil and island films. All three indicators provided linear log relationships with pH. The correlated changes in peak intensity ratios to pH have R² values of 0.95 or better. Methyl red is an azo compound and was found to be particularly sensitive to laserinduced degradation and chemical deterioration at low pH, probably by protonation of the azo bond. Methyl red changed from red to yellow in the window of useful pH range. In order to minimize laser damage we excited it off resonance at 647 nm. 4-Pyridinethiol represents purely nonresonant excitation because it does not possess an absorption in the visible. Cresol red possesses optical absorptions in the green. It was quite durable and we were able to excite it in resonance with 514.5-nm light. We compared the S/N for resonant and nonresonant excitation and found that resonant excitation improved the S/N by ninefold after correcting for differences in laser power and the fourth power frequency dependence associated with Raman scattering.

Cresol red proved to be our best pH indicator. As well as testing it with a large substrate, we tested it on an optical fiber. A monolayer was formed on the abrasively roughened SERS surface by immersing the fiber tip in a 10⁻⁴ M methanol solution of the derivatized indicator for 24 h. Figure 8 shows spectra collected from a fiber immersed in pH 6 and pH 3 buffer solutions (28). As the pH increases, the ratio of the peak intensities at 1600 cm⁻¹/1390 cm⁻¹ increased. The calibration curves developed in pHydrion (Aldrich) buffer solutions for cresol red on island films and on optical fibers are shown in Figure 9. The reversibility of the indicator was investigated by obtaining the spectra in a random order using the same substrate over a period of several days. We found the surface to be durable and the indicator to be completely and rapidly reversible.

The sigmoidal shape of the curve between pH 4 and pH 5 is a result of charge buildup at the surface for this diprotic indicator. At low pH the indicator is mostly in the conjugate acid form and the surface is positively charged. The positively charged surface repels protons and this causes the local surface pH to



Figure 9. Calibration curve for disulfide form of cresol red anchored to SERS surfaces: (a) on island films; and (b) on an optical fiber tip. The plot shows ratio of peak intensities for peaks at 1600 and 1390 cm⁻¹ versus pH. (Reprinted with permission [28].)



Figure 10. The ratio of the intensities for the peaks at 1600 and 1390 cm⁻¹ versus the volume of acetic acid added to 500 mL of distilled water. The pH of the distilled water was initially adjusted to 7.9 with NaHCO₃ to cover the entire active range of cresol red. The pH values shown on the right axis are from calibration curve (b) in Figure 9. (Reprinted with permission [28].)

be higher than the bulk pH. At the inflection point the pH of the solution is increased to the point where the indicator is in the neutral form and the surface charge becomes zero. As the pH is increased further the conjugate base of the indicator is formed at the surface, resulting in a negative potential at the surface. The surface attracts protons and the surface pH falls below the bulk pH (28).

The probe was tested under flowing conditions to determine its dynamic response. We monitored the pH of distilled water as we added glacial acetic acid. The result is shown in Figure 10. We used a peristaltic pump to circulate water from a beaker containing 500 mL of water through a flow cell that held the fiber. The flow cell has a glass window that allowed us to direct the laser beam onto the fiber end. We used a second peristaltic pump to meter glacial acetic acid into the beaker containing distilled water at a rate of 0.22 mL/min. The ratio of the intensities of the 1600-cm⁻¹ and the 1390-cm⁻¹ peaks was collected in real time by a programmed data collection routine that slewed between the two points and reported the ratio of the peak intensities versus time. In Figure 10 the time axis was plotted with respect to the volume of acetic acid added. The distilled water was initially adjusted to pH 7.9 with NaHCO3. This allowed us to scan over the entire active range of cresol red. After scanning the initial solution for 10 min the second peristaltic pump was turned on to begin the flow of acetic acid into the test beaker. The ratio of peak intensities began to fall immediately. As would be expected for the addition of a weak acid to water, the pH fell rapidly at first, followed by an asymptotic approach toward a minimum value.

CONCLUSIONS

We have demonstrated a technique for monitoring analytes in aqueous systems by observing changes in the Raman spectra of an indicator. This technique has proved particularly amenable for use with optical fibers. We suggest here an effective method for forming a durable, strongly enhancing SERS surface on an optical fiber by abrasively roughening the fiber end with polishing paper followed by vacuum depositing a layer of silver. We have anchored indicators to the SERS surface by synthesizing the disulfide of the indicator. The indicator is anchored to the SERS surface by forming the silver thiolate of the indicator. In addition to holding the indicator in close proximity to the SERS surface the thiol protects the silver surface from degradation.

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