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Measurement of High Acidity Using a Renewable-Reagent Fiber Optic Sensor

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Introduction

The renewable-reagent sensor concept was initially developed to address shortcomings in fiber optic chemical sensors dependent on immobilized, reversible reagents to produce analyte specific responses(1). The renewable-reagent sensor incorporates semi-selective membranes, analyte specific reagents and remote spectroscopic detection to extract selective responses. While renewable-reagent fiber optic sensors have been demonstrated for a number of chemical sensing applications(2-6), the transfer of laboratory prototypes to real world applications require devices which oversample the measurement matrix to differentiate among environmental and analyte specific response components(7). For example, optical sensors which acquire broadband rather than single wavelength spectroscopic data provide diagnostics regarding the identity of and measurement error associated with matrix interferences. The following describes the fabrication and evaluation of two renewable-reagent fiber optic sensor designs for the measurement of HNO_3 in the 0.1 M to 10.0 M concentration range. Both sensor designs employ an internal pH indicator reagent and broadband visible spectroscopic detection to characterize HNO_3 concentration.

Experimental

Sensor Design

Two different renewable-reagent fiber optic sensor designs were fabricated for evaluation in HNO_3 sensing applications. The original design (Figure 1A) located the various tubular flow and optical components within the internal volume of a 1.0 mm i.d. tubular Nafion cation-exchange membrane. In this design, analyte extraction and optical detection takes place in a common reagent volume defined, in part, by internal membrane dimensions. A 250 μm i.d. reagent delivery capillary provided for reagent renewal within the internal probe volume via backflow from the membrane tip. A smaller 100 μm i.d. drain capillary located at the back end of the probe served as an outlet to waste. The relative capillary dimensions were chosen to maintain some backpressure across the exchange region to reduce the potential for air bubble formation. The endface of the source optical fiber (300 μm core/330 μm clad) was buried in optical epoxy to minimize variations in spatial illumination within the detection volume. A collection optical fiber (400 μm core/430 μm clad) was aligned on-axis with the source fiber and displaced 0.7 cm from the buried endface. The assembled high acid sensor body was inserted into standard 1/16" i.d., 1/8" o.d. Teflon tubing and the excess internal tubing volume filled with acid resistant epoxy. The original high acid sensor design had an estimated internal reagent volume of 4.3 μl and a measured absorbance pathlength of 0.5 cm.

The modified high acid sensor design (Figure 1B) produced a separation of analyte extraction and optical detection volumes. The modified design employed 100 μm i.d. capillary tubing for reagent delivery to the tip of a 0.9 cm length of 330 μm i.d. tubular Nafion membrane. Reagent backflow through the exchange region was collected in an optical detection volume. The optical detection cell was fabricated within the internal volume of a short length of 1/32" i.d., 1/16" o.d. Teflon tubing. The source optical fiber (300 μm core/330 μm clad) was buried in an optical epoxy plug centered in the internal diameter of the Teflon tubing. Reagent backflow from the exchange region to the optical detection region followed a path around the outside edges of the epoxy plug. The epoxy plug was coated with solution cast Teflon AF to prevent interaction with the reagent phase. The collection optical fiber (400 μm core/430 μm clad) was aligned on-axis

and offset 0.7 cm behind the source fiber endface. A short length of 250 μm i.d. capillary tubing served as a reagent drain. Backpressure for air bubble suppression was attained by connecting the drain capillary to an external length of 100 μm i.d. capillary tubing. The modified high acid sensor design had an estimated exchange region volume of 0.53 μl and an optical detection volume of 3.1 μl . The detection cell exhibited a measured absorbance pathlength of 0.4 cm

Instrumentation

High acid sensor reagent delivery capillaries were connected to a screw-driven syringe pump which produced average volumetric flow rates in the 20 $\mu\text{l}/\text{min}$ to 30 $\mu\text{l}/\text{min}$ range. The proximal endfaces of sensor source optical fibers were illuminated with the output of a 100 W tungsten-halogen light source. Both sensor designs provided sufficient intensity return from the respective optical detection cells to allow for broadband visible spectroscopic detection using a photodiode array system. Syringe pump flow rate and photodiode array data collection were controlled via computer and sensor data analysis was performed using MATLAB.

Reagents and Procedures

Aqueous nitric acid (HNO_3) solutions in the 0.1 M to 10.0 M (0.6% to 63.4%) concentration range were chosen to evaluate the performance of high acid sensors. Aqueous sodium nitrate (NaNO_3) or deionized water was employed as an external reference solution. The internal reagent consisted of a 2.5×10^{-5} M cresol red solution(8) in 0.5 M $\text{NaNO}_3(\text{aq})$. Cresol red served as an internal pH indicator and Na^+ as a counter-ion for facilitating cation-exchange across the Nafion membrane.

To establish a stable baseline, internal reagent was continuously circulated through a given sensor device immersed in an external reference solution. The probe was then removed from the reference solution and exposed to a HNO_3 sample. The fiber optic sensor remained immersed in the acid sample matrix until a stable steady-state response level was obtained. Following measurement of the steady-state response, the sensor was removed from the acid sample, rinsed with deionized water and returned to the reference solution. Typically, 5 minutes were required to reach a steady-state response and 20 to 25 minutes were allowed for the sensor return to baseline. The high acid sensor response was monitored at one minute intervals throughout the experiment.

Results and Discussion

Optical Throughput

The epoxy used to assemble optical, flow and analyte extraction components into high acid sensors was chosen on the basis of its HNO_3 resistance and optical transmission. As the source fiber was isolated from the internal sensor environment by burial in epoxy, degradation of the transmissive properties of the epoxy represented a potential failure mode of the device. As it turns out, exposure of the epoxy to HNO_3 concentrations above about 0.1 M resulted in the formation of a dark green surface layer which severely reduced source throughput. Thus, the reagent flow rate and counter-ion concentration were adjusted to limit internal acid concentrations to less than 0.1 M.

Cresol Red Spectra

The absorbance behavior of the cresol red indicator in its transition region was characterized in a series of HNO_3 solutions. Figure 2 presents visible absorbance spectra for 2.5×10^{-5} M cresol red solutions collected with a spectrophotometer. In the absence of HNO_3 , a single cresol red absorbance peak at 434 nm was observed. Incremental increases in HNO_3 content produced a decrease in 434 nm absorbance while a new peak centered at 518 increased in absorbance. A sharp isobestic point at 474 nm indicated that the absorbances resulted from two different forms of the cresol red molecule, the neutral cresol red molecule and the cationic species.

Original High Acid Sensor Response

In the original sensor design, the collection fiber field-of-view includes a portion of the total internal probe volume and some length of the Nafion cation-exchange membrane. Inclusion of the Nafion membrane within the detection volume of the sensor leads to potential modulations in measured intensity related to the chemical and/or physical behavior of the membrane. For example, the overall membrane reflectivity is dependent on the refractive index contrast at the reagent/membrane and membrane/sample matrix interfaces. As sample characterization necessarily involves immersion of the sensor membrane in the sample matrix and extraction of analyte into the internal reagent, the sensor response was expected to include reflectivity modulations related to external and internal refractive index variations. The relatively large changes in external refractive index associated with HNO_3 solutions in the 0.1 M to 10.0 M concentration range were expected to be the primary source of perturbations in membrane reflectivity. The fabrication and testing of this probe design was pursued with the realization that modulations in sensor throughput would be an inherent component of the sensor response. The intention was to determine whether the cresol red absorbance response and sample matrix refractive index information could be combined to better characterize HNO_3 samples.

The original sensor absorbance responses to HNO_3 samples in the 0.1 M to 10.0 M concentration range for a reagent flow rate of 20 $\mu\text{L}/\text{min}$ are presented in Figure 3. Absorbance spectra obtained with the high acid sensor exhibited significant differences compared to spectrophotometer spectra. Common to all sensor spectra was significant noise in the spectral region below 450 nm due to limitations in short wavelength visible source output and sensor throughput. Referencing sensor spectra against the baseline cresol red absorbance produced 434 nm absorbance minima. The shape and position of the 434 nm cresol red absorbance changed significantly particularly for HNO_3 samples in the 0.1 M to 3.0 M concentration range. The change in shape of the 434 nm absorbance minima was accompanied by short-wavelength broadening of the 518 nm indicator absorbance peak. The 518 nm absorbance peak was further distorted by the appearance of a long-wavelength shoulder located at 543 nm. The notable persistence of the 543 nm absorbance feature 10 minutes after removal from an acid sample provided an important clue as to the identity of the absorbing species. The 474 nm isobestic point was notably absent from sensor absorbance spectra. Finally, at wavelengths longer than about 570 nm, sensor spectra exhibited baseline absorbance offsets in the 0.03 to 0.07 absorbance unit range.

The high acid sensor absorbance spectra had three directly observable response components. The first and primary response component was due to cresol red absorbance as identified by the absorbance features at 434 nm and 518 nm. The pH transition of cresol red produced an increase in 518 nm absorbance and a corresponding decrease in 434 nm absorbance with increasing HNO_3 sample concentration.

The second response component was a broadband absorbance offset related to the external refractive index effect on membrane reflectivity. The variation in interfacial refractive index contrast produced by membrane contact with HNO_3 samples in the 0.1 to 10.0 M concentration range exhibited a minimum. In theory, the minimum in interfacial contrast occurred when the HNO_3 sample and the Nafion membrane refractive indices were equal. As membrane reflectivity was modulated in an identical manner, the reflected intensity within the optical detection cell approached, matched and then exceeded a minimum over the range of HNO_3 samples tested. The resultant reflectivity variations were observed as offsets in absorbance at wavelengths longer than about 580 nm. Broadband absorbance offsets approached a maximum for 0.1 M to 3.0 M HNO_3 samples and then decrease for HNO_3 concentrations above 5.0 M.

The remaining high acid sensor response component was created by entrapment of cresol red within the Nafion membrane phase. In the reference state, cresol red existed as a neutral molecule

dissolved in the reagent solution. However, exposure to HNO_3 converted a significant fraction of neutral cresol red molecules to the cationic species. The existence of anionic charge sites and an extensive non-polar polymer backbone within the Nafion membrane phase provided an environment suitable for cresol red cation solvation. The resulting entrapment of cresol red within the membrane phase produced a shift in the primary indicator absorbance from 518 nm to 543 nm. Following removal of the sensor from contact with HNO_3 , conversion of membrane phase cresol red cations to the neutral species required baseline return times greater than 1 hour. Entrapped cresol red was retained in the Nafion membrane phase following conversion back to the neutral species. The membrane phase cresol red concentration was stable against deionized water, aqueous NaNO_3 and HNO_3 reference solutions. However, exposure of the sensor to a 10^{-3} M NaOH solution resulted in conversion to the cresol red anion and eventual removal from the membrane phase. The 543 nm absorbance peak was observed to shift towards the 518 nm reagent phase peak during cresol red removal from the membrane. In addition to producing the observable 543 nm shoulder on the 518 nm reagent absorbance peak, the overlapping reagent and membrane phase absorbances produced broadened cresol red spectral features.

The similarity in 518 nm sensor absorbance magnitudes for the 0.1 M thru 3.0 M HNO_3 samples suggests the existence of an additional response component. The 518 nm absorbance differences among HNO_3 samples should be greater due to the additive effects of indicator absorbance and a baseline absorbance offset. A possible cause for the noted reduction in apparent absorbance sensitivity could be a decrease in internal reagent refractive index associated with the H^+/Na^+ exchange pair. The increase in collection fiber numerical aperture accompanying a decrease in internal refractive index would produce a decrease in broadband sensor absorbance.

The original high acid sensor design generated absorbance spectra which were complicated combinations of membrane reflectivity, reagent phase indicator absorbance, and membrane phase indicator absorbance. As such, the extraction of response components for HNO_3 prediction over the targeted 0.10 M to 10.0 M concentration range was not possible for this particular sensor design.

Despite the complexity of the high acid sensor absorbance spectra, the overall response reproducibility was quite good. The average relative standard deviation in 518 nm absorbance taken for replicate HNO_3 sample determinations produced a value of 0.96% for this sensor design.

Modified High Acid Sensor Response

The separation of cation exchange and optical detection volumes removed the membrane from the field-of-view of the collection optical fiber. Thus, the modified high acid sensor design was insensitive to membrane reflectivity variations and membrane phase indicator absorbance contributions.

High acid sensor absorbance responses to HNO_3 samples in the 0.1 M to 10.0 M concentration range for an internal reagent flow rate of 20 $\mu\text{l}/\text{min}$ are presented in Figure 4. Cresol red absorbance produced an increase in 518 nm absorbance and a corresponding decrease in 434 nm absorbance as external HNO_3 sample concentration increased. An isobestic point was observed at 474 nm which indicated that absorbance features arose exclusively from the interconversion of the cresol red molecule. Similarly, the minimal long-wavelength (>580 nm) absorbance offset confirmed that indicator dilution was insignificant and suggested stable performance of the overall sensor evaluation system. Internal refractive index perturbations due to cation exchange were not a noticeable component of the modified sensor absorbance response.

Following sensor characterization of a given HNO_3 sample, the membrane was exposed to deionized water for 25 minutes prior to testing of the next sample. Typically, the baseline return was complete 15 minutes after removal of the sample and immersion water. The reasonably fast return time were facilitated by the fast reagent flow rate, the small internal sensor volumes, and the short Nafion membrane equilibration time.

Figure 5 describes a series of calibration curves for the modified high acid sensor generated by varying internal reagent flow rates. The same experimental procedure was followed as in the determination of HNO_3 sample responses at a 20 $\mu\text{l}/\text{min}$ reagent flow rate. The 518 nm absorbance responses were baseline corrected for slight variations in broadband throughput prior to presentation. Actual measurement points taken at each flow rate were fitted with a second order polynomial curve. The calibration curves exhibited similar slopes and shapes for measurements made at volumetric flow rates of 20, 23, 26 and 29 $\mu\text{l}/\text{min}$. As would be expected, the sensor calibration curves showed an increase in 518 nm absorbance for a given HNO_3 sample with decreasing reagent flow rate. At lower HNO_3 sample concentrations, fast proton transport and minimal internal sensor dilution produced only slight differences in internal acid concentrations. The loss of sensor calibration curve linearity above 3.0 M HNO_3 was consistent with the spectrophotometer calibration curve for 0.02 M to 0.10 M HNO_3 concentrations. Incomplete dissociation of HNO_3 for sample concentrations greater than 4.0 M possibly contributed to the reduction in sensor sensitivity.

The high acidity sensor measurement precision was estimated as the average relative standard deviation taken over all replicate HNO_3 sample determinations included in Figure 5. The resulting estimate of sensor reproducibility produced a value of 0.97% for the modified high acid sensor design.

Conclusions

The two renewable-reagent fiber optic sensor designs evaluated for the detection of HNO_3 samples exhibited steady-state response times of about 5 minutes. The complexity of the absorbance spectra for the original high acid sensor design precluded HNO_3 prediction under controlled laboratory conditions. In contrast, the modified sensor design reproduced cresol red absorbance spectra without notable interferences. In both sensor designs, resetting of the reagent phase absorbance baseline was achieved within 15 minutes. However, the inclusion of membrane phase cresol red in the original sensor design produced slow returns to the initial baseline state. The measurement precision was similar for both sensor designs despite comparative differences in absorbance spectra complexity.

Acknowledgments

References

- (1) Berman, R. J.; Burgess, L. W. *Proceedings of SPIE-Chemical, Biochemical and Environmental Fiber Sensors* 1990, 1172, 206-214.
- (2) Lin, Z.; Burgess, L. W. *Anal. Chem.* 1994, 66(15), 2544-2551.
- (3) DeGrandpre, M. D. *Anal. Chem.* 1993, 65(4), 331-337.
- (4) Varineau, P. T.; Duesing, R.; Wangen, L. E. *Appl. Spectrosc.* 1991, 45(10), 1652-1655.
- (5) Berman, R. J.; Christian, G. D.; Burgess, L. W. *Anal. Chem.* 1990, 62(19), 2066-2071.
- (6) Berman, R. J.; Burgess, L. W. *Proceedings of SPIE-Chemical, Biochemical and Environmental Fiber Sensors II* 1990, 1368, 25-35.
- (7) Lin, Z.; Booksh, K. S.; Burgess, L. W.; Kowalski, B. R. *Anal. Chem.* 1994, 66(15), 2552-2560.
- (8) Jorgensen, B.; Nekimken, H.; Sellon, D. Internal document, "Report on Indicators for Optical High Acidity Sensor."

Figure Captions

1) Renewable-reagent fiber optic high acid sensors: A) original design and B) modified design. a-delivery capillary tubing, b-source optical fiber, c-collection optical fiber, d-drain capillary tubing, e-1/16" i.d., 1/8" o.d. Teflon tubing, f-HNO₃ resistant optical epoxy, g-1/32" i.d., 1/16" o.d. Teflon tubing, h-silver-filled epoxy, and i-tubular Nafion cation-exchange membrane

2) Visible spectrophotometer absorbance spectra for 2.5×10^{-5} M cresol red pH indicator in a series of HNO₃ solutions taken using 1.0 cm pathlength cell. a-0.00 M HNO₃, b-0.02 M HNO₃, c-0.03 M HNO₃, d-0.05 M HNO₃, e-0.07 M HNO₃, f-0.09 M HNO₃ and g-0.10 M HNO₃

3) Original high acid sensor absorbance response to HNO₃ samples. a-0.1 M HNO₃, b-0.5 M HNO₃, c-1.0 M HNO₃, d-3.0 M HNO₃, e-5.0 M HNO₃, f-8.0 M HNO₃ and g-10.0 M HNO₃

4) Modified high acid sensor absorbance response to HNO₃ samples. a-0.1 M HNO₃, b-0.5 M HNO₃, c-1.0 M HNO₃, d-3.0 M HNO₃, e-5.0 M HNO₃, f-8.0 M HNO₃ and g-10.0 M HNO₃

5) Modified high acid sensor 518 nm absorbance response to HNO₃ samples in the 0.10 M to 10.0 M range at various reagent flow rates. a-29 μ l/min, b-26 μ l/min, c-23 μ l/min, and d-20 μ l/min

A)

B)

FIGURE 1

Figure 2

Figure 3

Figure 4

Figure 5

Measurement of High Acidity Using a Renewable- Reagent Fiber Optic Sensor

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INTRODUCTION

Renewable-Reagent Fiber Optic Sensor

Berman, R. J.; Burgess, L. W. *Proceedings of SPIE-Chemical, Biochemical and Environmental Fiber Sensors* 1990, 1172, 206-214. "Renewable Reagent Fiber Optic Based Ammonia Sensor"

APPLICATION

High Acid Sensor

Membrane

Nafion cation-exchange membrane

External Reference

0.08 M $\text{NaNO}_{3(\text{aq})}$ or deionized H_2O

Samples

$\text{HNO}_{3(\text{aq})}$ in the 0.10 M to 10.0 M conc. range

Internal Reagent

2.5×10^{-5} M Cresol Red in 0.05 M $\text{NaNO}_{3(\text{aq})}$

Colorimetric Interaction

Cresol Red Indicator

HIGH ACID SENSOR

High Acid Sensor Instrument

HIGH ACID SENSOR

Initial High Acid Sensor Design

HIGH ACID SENSOR

Initial Design - High Acid Sensor HNO_3 Response

HIGH ACID SENSOR

Initial Design - Sensor HNO_3 Response Summary

HIGH ACID SENSOR

Modified High Acid Sensor Design

Modified Design - High Acid Sensor HNO_3 Response

HIGH ACID SENSOR

High Acid Sensor Absorbance with Varying Reagent Flow Rate

HIGH ACID SENSOR

Summary

HNO₃ (0.1M to 10.0 M) sensor characteristics

failure mode - epoxy optical degradation

optimizational constraints

reagent usage - 1.7 ml/hr

response time - 5 minutes

recovery time - 15 minutes

sensor measurement precision - $\pm 1.0\%$

future emphasis

cationic interferences - Na⁺, K⁺, Fe²⁺

recovery times

response reproducibility