FY97 Report on Moisture Sensors for Enhanced Surveillance Program Project LL-ESP96-13

by

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ABSTRACT

Several compounds were evaluated in a number of optical configurations in order to test the optical response of these compounds to changes in humidity. Reichardt's betaine (Reichardt's dye, ET-30 dye, 2,6-diphenyl-4-(2,4,6-triphenyl-N-pyridinio)phenolate), a solvatochromic molecule, and several vapochromic compounds were tested, and each responded to a wide range of humidity by exhibiting shifts in visible absorption. All compounds in the study suffered from some degree of hysteresis upon humidity cycling. It is unclear as to the mechanism for this hysteresis, but future work will attempt to either model or remove the hysteresis effects. In the case of the vapochromic compounds, the hysteresis may be due to structural changes in the crystal lattice of the solid state compound. A prototype sensor configuration was also developed involving an attenuated total reflectance probe. The future of the project will deal with elucidating the hysteresis mechanisms for each compound, evaluating several other vapochromic compounds, and testing different immobilization schemes for the compounds under study. In addition, several other optical technologies will be investigated for application in optical humidity sensing.

INTRODUCTION

This report is a deliverable for ESP task LL-ESP96-13, Chemically Amplified Optical Sensors. The goal of this task is to develop sensors for compounds such as water and hydrogen whose presence is indicative of aging (HE decomposition, material degradation, or outgasing) in the weapons stockpile. Optical technology, and specifically fiber optics, provides a means to interrogate head spaces and other inaccessible locations safely and remotely without the use of electrical energy in the fiber or sensor element. A previous report identified suitable indicators, matrices, and technologies for the use in a fiber-optic sensor for moisture in the vapor phase¹. This report details investigations of the response of three moisture indicators and progress in the development of a sensor prototype

EXPERIMENTAL

Apparatus

The humidity sensor testing system consists of a fiber-optic spectrophotometer, light source, optical multiplexer, humidity chamber, and a humidity controller and sensor. An experimental schematic is given in figure 1.

Humidity Sensor, Chamber, and Controller

The humidity chamber is approximately a cube with sides of length one foot. The "front side" of the chamber opens completely to allow introduction of samples, adjustments of equipment, etc. An electrical humidity sensor is fed through the top of the chamber and positioned as closely as possible to the location of the optical humidity sensors being developed as part of this project. A circulation fan is mounted inside the chamber to insure good mixing of the chamber atmosphere. The humidity sensor covers the range 0-100% RH with an accuracy of $\pm 2\%$ and a precision of $\pm .2\%$. The sensor provides feedback to the controller, which alternately turns on a humidifier or a circulating pump and drying tube depending on the humidity adjustment needed. The system has a dead band of about 1.5% RH around the setpoint. The calibration of the sensor was checked using standard humidity salt solutions and found to be within specifications prior to data collection. The humidifier feed-through is at the center top of the back panel of the chamber. This inlet tube is equipped with a manual valve to allow isolation of the chamber from the water source in the humidifier for easier attainment of humidities below 20% RH. The drying tube inlet/outlet hookups come through one side of the chamber cube. Dry nitrogen may also be swept through the chamber, to aid in reaching humidity levels below 5% RH. The humidity reading from the sensor is output through the controller to an amplifier (gain = 19) and then to a PC card A/D converter for automatic computer recording of the chamber humidities during an experiment. The chamber is not temperature controlled, and all experiments were conducted at room temperature, generally 26-30°C.

Optical System

During the course of this year's work, two different spectrometers were used with the system. An Oriel miniature spectrophotometer was used for the earliest work, and the most recent. A Control Development miniature spectrophotometer was used in between. The Control Development unit covered a larger wavelength region than the Oriel unit, but proved to have some flaws in its grating which placed artifacts in the sensor spectra and made evaluation difficult. The Control Development unit is a 512-element diode array with a software corrected pixel spacing of 1 nm. The Oriel unit is more sensitive and provides a better overall signal without artifacts and, in addition, provides better data depth by incorporating a 1024-element diode array with a coverage of 0.42 nm per diode and a maximum range of 376-801.8 nm. The light source is an Ocean Optics tungsten-halogen bulb equipped with a shutter. Light is carried from the source via optical fiber to

an optical multiplexer, which allows selection of one of up to 10 different probes for measurement. Optical fibers for the probes leave the multiplexer and are fed into the chamber either through the top of the cube, or through one of the sides. The return fiber from the probe comes back to the multiplexer and matches up with the fiber leading to the spectrometer.

Software and Computers

The entire system is controlled by software developed at SRTC over the past decade. This software allows collection of spectral data with the capability for on-line prediction by chemometric models. One PC controls the spectrometer, shutter, multiplexer, and signals a second computer to collect humidity readings at the appropriate times. The second PC, a notebook, collects the humidity readings via its A/D PC card and stores them in a time-stamped file. A third program, working off-line, is used to combine the spectral data files and the humidity data files and produce a single data file with humidity readings assigned to each spectrum. An SRTC-developed program analyzes the data and creates the chemometric models. Alternatively, some data analysis for this project was performed with MATLAB™ (Mathworks) and the PLS_Toolbox (Eigenvector Research, Inc.)

Candidate Sensors

The mid-year report¹ on candidate sensors listed the indicators Reichardt's betaine and three cobalt compounds, as well as near-infrared spectroscopy and grating light reflection spectroscopy. Shortly after this report was issued, we became aware of some new compounds that showed good promise of responding to moisture; these compounds are known as vapochromic compounds and were developed at the University of Minnesota by Kent Mann^{2,3}. Work during the summer of 1997 has focussed on developing sensors using Reichardt's betaine and the two vapochromic compounds.

Reichardt's Betaine

Reichardt's betaine (Reichardt's dye, ET-30 dye, 2,6-diphenyl-4-(2,4,6-triphenyl-N-pyridinio)phenolate) is a solvatochromic molecule. Solvatochromism is a phenomenon by which the UV-visible spectrum of a molecule (position, intensity, or shape) changes with the polarity of the medium in which it is contained. Reichardt's dye has one of the largest known shifts in its spectrum due to changes in the polarity of its environment⁴.

Incorporation of this molecule into a thin film would create a sensor for water vapor. Possible host films include (polymethyl) methacrylate (PMMA), silica gel, Si or Ti sol gels, or (polyethylene) oxide⁵. The sensing film could then be combined into a fiber-optic system by several different means: deposit the film on a fiber-optic lens or optical fiber tip for a transmission or reflectance measurement, deposit the film on a substrate or on the optical fiber itself for an evanescent wave configuration, or deposit the film on an attenuated total reflectance (ATR) probe. The sensor will be used with a miniature diode

array spectrophotometer and tungsten-halogen light source to form a compact, portable moisture sensing instrument.

For a first test of Reichardt's betaine (RB), solutions of RB, PMMA, and 1,4-dioxane were prepared. 1,4-Dioxane is a relatively non-polar solvent, thus it was hoped that a good response to the polar water molecule would result as it diffused into the polymer matrix. The solution was spin cast onto microscope slides and allowed to dry. The resulting films were transparent and pale yellow in color. The slides were evaluated in the humidity chamber and spectra recorded in transmission mode; unfortunately, no significant response to moisture was seen in these slides. In addition, the optical density of the films was very low, resulting in a poor signal-to-noise ratio.

The solvent was switched to the more polar acetone and solutions of RB and PMMA were prepared once again. Slides spin cast from this solution were milky blue in appearance. Again, however, the optical density of the films was too low to give good spectra in transmission mode. Slides were prepared using a drop coat method. This puts much more material in a smaller region of the slide, and resulted in a dark blue, opaque spot suitable for reflectance spectroscopy. The spectra of slide PMMA-61 at 10 and 90% RH is shown in Figure 2 and approximately a 50 nm shift in the peak maximum is seen. Figure 3 is a plot of the peak maximum for slide PMMA-64 as determined by the zero crossing of the first derivative of the spectra versus the %RH measured by the humidity sensor. The peak maximum moves from 662 nm at 10% RH to 608 nm at 90% RH, a shift of 54 nm. This plot also reveals some hysteresis in the sensor response. A cycle test was conducted on slide PMMA-61 between 20 and 70% RH. This data was analyzed using principal components analysis (PCA). Figure 4 is a plot of the measured relative humidity and the first PCA score (which represents the humidity response of the slide) versus time. Hysteresis can be seen here too, in the changing score of the 20% RH data from cycle to cycle.

Reichardt's betaine shows good promise as a broad-range humidity sensor if hysteresis problems can be overcome. The next step for evaluation of this indicator is to coat it onto the ATR probe and collect additional response data.

Vapochromic compounds

A class of vapochromic compounds have been developed in recent years by researchers at the University of Minnesota,^{2,3} and elsewhere. Two compounds were received from Kent Mann (University of Minnesota) for evaluation as indicator systems for relative humidity. Vapochromic compounds are similar to solvatochromics in that they exhibit spectral changes in solid state absorption and emission based on the interaction between the compound and a given analyte. However, vapochromics respond based on the intercalation of specific solvent molecules into the crystal lattice. This is in contrast to solvatochromic compounds, which respond to the polarity of the solvent matrix. These compounds are promising sensor material candidates for a number of reasons: fast, reversible response to specific vapors, selective response for different vapors (i.e. each

analyte produces a different vapochromic shift), and insolubility in organic and aqueous solvent systems. These factors, coupled with coarse preliminary experiments showing the response of several compounds to vapor phase water, were key in selecting two compounds for evaluation in the ESP humidity sensor program.

The two compounds received were $[\text{Pt}(\text{phen})_2(\text{CNBenzyl})_2\text{Pt}(\text{CN})_4]$ and $[\text{Pt}(\text{phen})_2\text{Pt}(\text{C}_2\text{O}_4)_2]$, which are insoluble stacked complexes exhibiting vapochromic shifts in the visible portion of the spectrum. Compounds were received as dry powers and upon receipt were suspended in isopropanol in order to coat the optical elements to be used in the study. Initial suspensions were achieved via grinding in a mortar and pestle, and subsequent samples prepared by mild sonication, which afforded more uniform suspensions. No appreciable dissolution of the compounds was evident, and initial tests were performed by drop coating and slowly spinning out thin, scattering films of each compound on microscope slides for transmission measurements in the optical system described above. The chamber humidity was set at an initial high value and then ramped downward as the nitrogen purge was activated. Spectra were acquired at regular intervals while the humidity data were recorded by hand. Later experiments made use of the automated humidity data collection routines. For these transmission measurements, each compound exhibited an overall decrease in absorbance with decreasing humidity, as shown in figure 5 (a and b). The sloped baseline is due to the scattering nature of the films, where shorter wavelengths of incident light are more highly scattered due to Rayleigh scattering, resulting in larger absorbance values. At compound specific ranges of relative humidity, sharp changes were seen in the absorbance peak positions and absorbance baseline magnitude. In order to deconvolute effects and gain a better understanding of the relationship between the experimental variance and humidity, principal components analysis was performed. As can be seen from the eigenvectors (scores) in figure 6 (a and b), two effects are present which account for a majority of the variance associated with the response to decreased humidity. Absorbance magnitude effects and peak position shifts appear to be orthogonal in that high humidity sensitivity is achieved via absorbance magnitude shifts, and lower humidity ranges (below crossover) are sampled via a peak position shift. From these data, the phenyl oxalate compound was chosen for further study as it exhibited the largest vapochromic shift and also the widest range of apparent linear response to decreasing humidity.

After the initial spectroscopic characterization, studies were undertaken to define the lower particle size limit achievable for the suspensions. This will affect the optical configuration of the prototype and also allow for a better understanding of the optical signals generated. Therefore, SEM studies were performed on samples that were sonicated for differing times and drop coated from water suspensions on 5 mm by 5 mm square glass coupons suitable for introduction into the high resolution portion of the SEM. The dried coupons were imaged at varying magnifications to determine, qualitatively, average particle size and shape. It appears that the average particle size increased slightly with sonication time, indicating that the compounds may be slightly soluble. A reasonable explanation would be that at higher sonication times, more material was driven into solution, and after relaxation, the normal solubility would return, with material recrystallizing on existing crystals, forming on average larger crystals. From this it was

determined that 1 minute was the optical sonication time, yielding rod-shaped particles ranging in length from .3 μm to .9 μm , as seen in the SEM image given in figure 7.

Based on the low signal and high scattering of the thin transmission films used initially, a sapphire attenuated total reflection probe was obtained and utilized in the subsequent characterization. An optical schematic of the probe is given in figure 8. The phenyl oxalate compound was dispersed in isopropanol and drop coated onto the curved ATR crystal. The effective penetration (1/e) depth⁶ of the interrogating optical field, calculated for an air/sapphire interface (neglecting the refractive index of the oxalate compound) at an average wavelength of 575 nm is 142 nm, and for a three bounce ATR probe, results in an effective absorbance pathlength of 427 nm. This is an estimate based on the materials and known constants associated with the probe. Assuming that the vapochromic compound has a real refractive index larger than that of air, the effective pathlength would be increased accordingly.

The absorbance data are presented for the ATR/vapochromic probe in figure 9 for stepwise decreases and increases in %RH over time. It is clear from the spectra that three individual peaks at 541.3 nm, 562.9 nm, 582.8 nm, are present which are not present in either the transmission (given in figure 5) or diffuse reflectance data (not shown). As the humidity is decreased, the peak at 541.3 nm decreases in magnitude and begins to shift while the peaks at the longer wavelengths begin to increase in magnitude. Note that the absorbance magnitude tracks in the opposite direction with respect to the transmission data, indicating that the spectral response is sampled differently via ATR. In discussions with Kent Mann, it was determined that several as yet unknown crystal structures are responsible for the different crossover points evident in the data, where a dramatic shift is seen at 15-20% RH for a negative going %RH trend, and an opposite shift is seen at 35-40% RH for a positive going %RH ramp. Therefore, differences in response at similar humidity values may be due to differing energy barriers, or structural preferences based on the direction and history of the humidity ramp. A combination of all three structures is most likely present, as all three peaks appear in the entire ramp sequence, except for dry conditions, where only the two longer wavelength peaks are present. The hysteresis demonstrated by the score plot in figure 10 is reproducible and the crossover points are fixed, i.e. they do not drift as a function of time or age of the compound immobilized on the probe. The mechanism that results in this hysteresis remains to be understood, and future work should yield insight into the response mechanisms of these and other candidate compounds.

CONCLUSIONS AND FUTURE DIRECTIONS

It is clear from the data presented here that hysteresis is a factor in each of the compounds discussed. The spectral responses are more reproducible for the vapochromic compounds, partly due to the absence of a binding hygroscopic polymer. In contrast, the Reichardt's dye compound exhibited a much more linear response over a wider spectral bandpass, which is more easily modeled by current calibration routines. Therefore, it is possible that each compound may have application in different sensing regimes, depending upon the nature of the sensing needs. The hysteresis in each configuration will need to be characterized and the mechanisms for its presence understood in order for a deployable

sensor to be realized. Therefore, future directions will include continued experimentation and modeling with the current compounds. The ATR probe is the preferred configuration at this time due to the insolubility of the vapochromics and the high extinction coefficients of the solid phase sensor materials. Specifically, the $[\text{Pt}(\text{phen})_2(\text{CNBenzyl})_2\text{Pt}(\text{CN})_4]$ compound will be immobilized onto the probe and studied after studies are complete with the phenyl oxalate compound. An important point to be made here is that the UV-Vis spectral response of the vapochromic compounds to dynamic humidity conditions has not been reported in the literature, and therefore these data are presented here for the first time. Also, several other candidates in the vapochromic family exist that have not been characterized with respect to water response, and these will be investigated as well. In addition, the Reichardt's dye will be immobilized onto the ATR probe in order to test differences in response time, peak shape, and other factors as the concentration of dye and polymer is varied. Finally, other technologies, such as grating light reflection spectroscopy^{7,8,9} or surface plasmon resonance¹⁰, may be explored in response to different sensor needs not addressed by the current indicator dye methodology. These techniques would utilize specific optical phenomena that are related to physical material factors, rather than spectroscopic changes in an indicator dye, to measure vapor phase water concentration. However, the main thrust of research will be in the continued characterization and development of a probe based on the work presented in this report.

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Figure 1. Humidity Sensor Test Apparatus

Figure 2. Spectra of Slide PMMA-61

Figure 3. Response of Slide PMMA-64

Figure 4. Cycle Test of Slide PMMA-61

Figure 5a. Transmission Response Spectra of $[\text{Pt}(\text{phen})_2(\text{CNBenzyl})_2\text{Pt}(\text{CN})_4]$ to Decreasing Humidity.

Figure 5b. Transmission Response Spectra of $[\text{Pt}(\text{phen})_2\text{Pt}(\text{C}_2\text{O}_4)_2]$ to Decreasing Humidity.

Figure 6a PCA Score Plots, $[\text{Pt}(\text{phen})_2(\text{CNBenzyl})_2\text{Pt}(\text{CN})_4]$ Response.

Figure 6b. PCA Score Plots, [Pt(phen)₂Pt(C₂O₄)₂] Response.

Figure 7. SEM Image of $[\text{Pt}(\text{phen})_2\text{Pt}(\text{C}_2\text{O}_4)_2]$ sample, One Minute Sonication Time.

Figure 8. Prototype ATR Probe Configuration.

Figure 9. ATR Response Spectra of $[\text{Pt}(\text{phen})_2\text{Pt}(\text{C}_2\text{O}_4)_2]$ to increase humidity.

Figure 10. PCA Score Two Plot, Cycle Response of ATR Probe.