TEAM PROJECT REPORT

Nanostructured Catalytic Membranes as Optical Sensors: A Research Experience and Classroom Implementation Plan

Submitted To

The RET Site
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"Sustainable Engineering for Urban Needs:
Research Experiences for Middle and High School Teachers"

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ABSTRACT

There is an increasing need to monitor and evaluate harmful volatile organic compounds (VOCs) in the environment. Finding a way to monitor these compounds as well as inhaled industrial hazards that workers are exposed to or chemicals in human breath in "real time" has been a challenge for researchers. Optical responses from a Nafion™ membrane (perfluorosulfonic acid membrane) can be obtained with exposure of the membrane to various concentrations of a given chemical. A UV-vis can be used to determine the absorption of ultra violet and visible light which can then be used to determine the chemical composition and/or the concentration of the given chemical. Drawing upon the concept of absorbance vs. concentration the high school teachers created a collaborative lesson utilizing the Beer Lambert Law to quantify the concentration of an unknown sample.

GOAL AND OBJECTIVES

The goal of this project is to determine if the UV-vis colorimeter can be used to produce optical responses from a Nafion™ membrane (perfluorosulfonic acid membrane) so that a calibration plot can be produced and a correlation between exposure levels for various chemicals can be determined. In order to achieve this goal, exposure procedures will be developed to monitor the flow of a particular VOC in the gas phase. Graphical analysis will be completed to determine if the optical response can be measured.

RESEARCH TASKS

The research tasks included investigating the usefulness of Nafion™ membranes as an optical sensor for a particular VOC. The following was accomplished:

- A UV-vis was used to obtain the absorbance vs. concentration of the given chemical (Sample A.)
- Exposure procedures were developed to monitor the flow of the particular VOC in the gas phase.
- Graphical analysis was completed to determine if the optical response could be quantified.

METHODOLOGIES USED

The following procedures were used to determine if a UV-vis spectrometer could be used to obtain optical responses from the reaction of an optically active organic dye imbibed in a Nafion™ membrane and a diffusing compound of interest, in this case acetone. The experimental set-up used is shown in **Figure 1** on next page. The Nafion™ membranes were initially exposed to the chemical dye by the Graduate Student Mentor at a controlled concentration. A quartz cuvette was then modified to allow for continuous controlled exposure of the VOC into the cuvette. The Nafion™ was then placed into the cuvette in line with the UV/Vis light beam. A protocol was developed to control the temperature of the membrane inside the cuvette to be maintained at the reaction temperature of 60°C. A nitrogen bubbling apparatus allowed for the control of the acetone exposure concentration within the experimental range of interest. This setup allows for in-situ analysis of the exposure of the material enabling the monitoring of the reaction occurring inside the membrane.

Figure 35. Set Up Showing UV-vis and Flow of VOC in the Gas Phase

Using the described methods, controlled concentrations of acetone were flowed into the cuvette cell and allowed to diffuse into the heated membrane. As the acetone comes into contact with the organic dye, a reaction occurs producing a UV/Vis response which can be measured using the spectrometer. Monitoring the peak formation at 400 nm over a period of 15 minutes allowed for observation of the effects of concentration on the reaction. Using the data at the 15 minute mark for several concentrations provided a calibration of acetone exposures for the range of interest for this work.

TRAINING RECEIVED

Following training was received during the summer RET program:

1. Generic safety training provided by the university staff.
2. Specific safety training provided by the PI and GA including this information:
3. Potential safety hazards:
    a. Chemical hazards: trimellitic anhydride, maleic anhydride, phthalic anhydride, bradykinin, acetone, ethanol, sulfuric acid (MSDS may be found in lab).
    b. Exposure route: chemicals are immobilized in polymeric matrix (membrane) and present only a contact hazard if samples are excessively handled.
    c. Exposure elimination: gloves will be worn at all times while handling samples. Also, participants have been shown location of eyewash fountain in case they inadvertently touch their eyes after handling samples.
    d. Mechanical hazards: Glassware is in constant use throughout lab and safety glasses must be worn at all times. Also, hot plates are in constant use to heat samples prior to analyses and present a contact hazards.

e. Participants have been shown location of safety shower in case of fire. In addition, there are a number of compressed gas cylinders present that have been secured in various locations. Participants must always be aware of the location of these hazards throughout the lab.

4. UV/Vis- Spectroscopy – Specific training was completed to learn how to test, collect and analyze exposed Nafion^{TM} samples using UV/Vis Spectroscopy. Training included using an OceanOptics Spectrometer and SpectraSuite software.
5. Training was completed for basic principles of matter and light, specific to how the Beer-Lambert Law will be used to determine the linear relationship between the absorbance and concentration for a test VOC sample.

RESEARCH FINDINGS

The goal of this project was to determine if the UV-vis colorimeter could be used to detect optical responses from a Nafion^{TM} membrane so that a calibration curve could be produced and a correlation between exposure levels for Sample A could be determined. In order to achieve this goal, exposure procedures were developed to monitor the flow of a particular VOC in the gas phase (Sample A).

Due to the nature of the research, specifics concerning the experimental design and test cannot be discussed in detail. However, an experimental design was developed and tested for data collection of Sample A in the gas phase. From this design a sample of data that was obtained is presented in this section and represents multiple time intervals with the exposure of the Nafion^{TM} to increasing concentrations of Sample A. **Figure 2** on next page includes time elapsed data for one of the test runs. The averages of the data for multiples runs over time at the wavelength of interest are presented in **Figure 3** on next page. The overall calibration plot using multiple concentrations of Sample A we were studying is presented in **Figure 4** on next page.

As a result of the collected data the calibration plot can be used in further studies to interpolate an unknown concentration of Sample A. From this information, there is the potential to develop non-invasive "real-time" medical monitoring, using Nafion^{TM} membranes and the unique color change that can be associated with a specific chemical, i.e., Sample A.

CLASSROOM IMPLEMENTATION PLAN

The purpose of this research project was to utilize nanostructured catalytic membranes as optical sensors to determine if a correlation could be found between exposure levels for a given chemical and the color it produced in the membrane.

To expose our students to this research, a modified absorbance experiment will be used to model data collection for various test sample concentrations. Students will measure and analyze the visible light absorbance for one dye using five known concentration samples. They will then measure the absorbance of an unknown sample and identify the concentration. In order to build a stronger understanding of this concept, students will run a second test using a different dye/absorbance. They will use graphing calculators to create a scatter plot of their findings for each dye and perform a linear

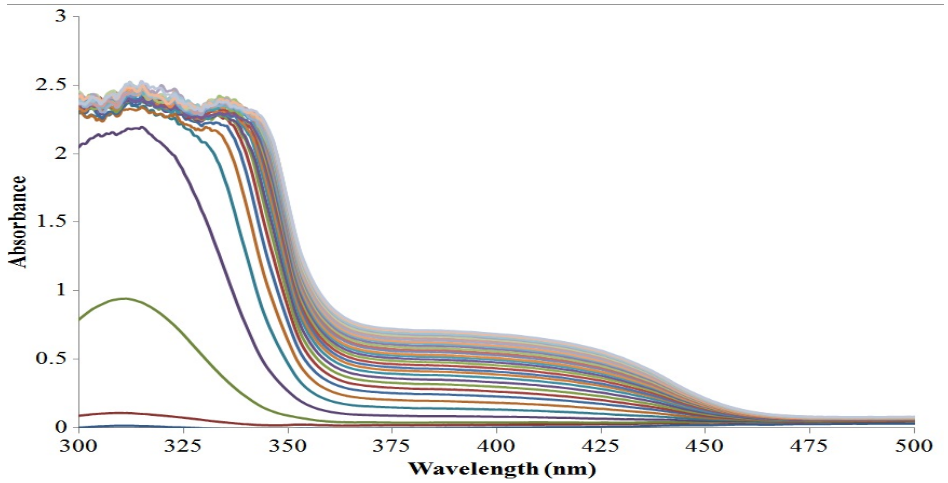

Figure 36. Time Elapsed Raw Data for 0.6 ppm for Test Sample A

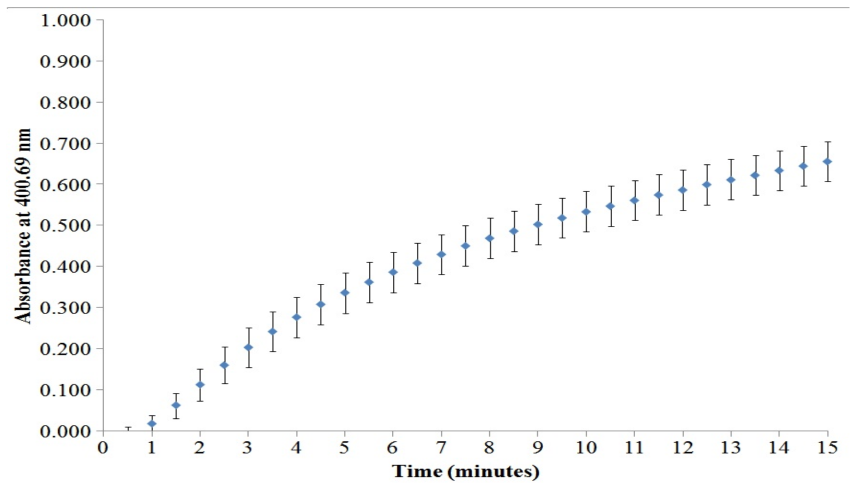

Figure 37. Average Absorbance Data For 0.60 ppm Run for Sample A

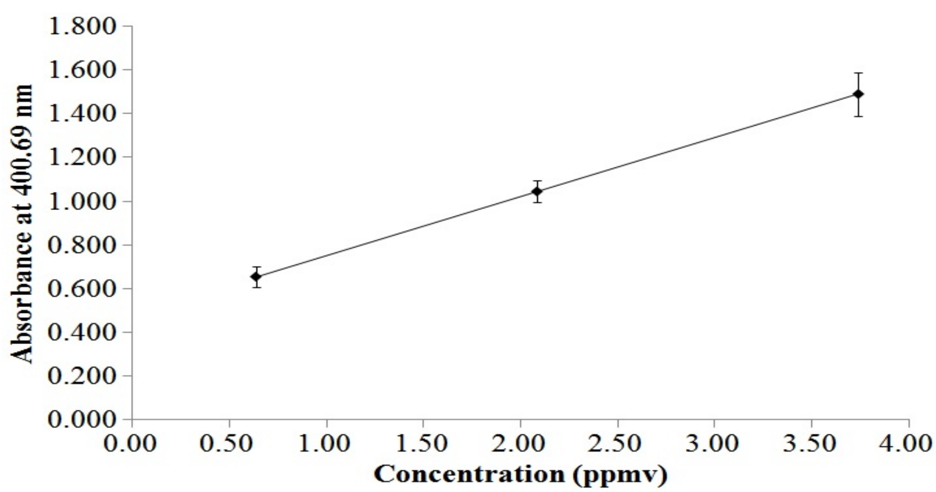

Figure 38. Flow Cell Absorbance Calibration Plot for Sample A

regression if it is appropriate. A plot of residuals will be analyzed and finally a hypothesis test for slope performed. Students will then determine if their unknown sample lies within a certain interval. The entire class data will then be analyzed and confidence interval constructed for 3 different confidence levels.

In order to accomplish these classroom implementations students will complete the following:

- Obtain the above materials from the equipment table.
- Prepare testing samples of 100%, 80%, 60%, 40%, and 20% from one of the original stock solutions and distilled water. The sock solution is the original 100% solution of 500ml of distilled water and one drop of the specified food dye.
- Fill a cuvette ¾ full of the given concentration and determine the absorbance of the sample.
- Collect absorbance measurements at two minutes for each sample.
- Organize data into tables.
- Create a scatter plot, once the absorbency for the 5 samples has been determined.
- Communicate via a written format, any unusual findings and note any outliers.
- Perform a least squares regression, and write down the equation.
- Write down their coefficient of determination and correlation coefficient.
- Write a few sentences explaining what the slope (Extinction coefficient), coefficient of determination, and the correlation coefficient mean in the context of this problem. As accurately as possible, students will sketch their line of best fit through their scatter plot.
- Check the residual plot, sketch a copy to turn in and note/discuss any findings. Is your model representative of direct variation? Why or why not?
- Perform a hypothesis test for slope. Use α=.05
- Check assumptions and show all necessary steps.
- Compose a well written concluding statement.
- Pick up your unknown sample and using your model, determine the concentration.
- As a class, combine and reanalyze the data.

This activity is being introduced at different ability levels. Some of the students will have had advanced physics, but the majority will have had very little exposure to the concept of light, absorbance, wavelength and transmittance. It is anticipated that there will be frustrations on the part of the students from simple things like how to make their own dilutions, what absorbency should be used to test the sample. Students may also struggle determining which variable should be the independent and dependent variable. Students typically have a difficult time deciding on a reasonable scale and tend to not label their work accurately. Generally students aren't the best written communicators, so this may also pose difficulty.

BIBLIOGRAPHY

Andria, S. (2010). "Simultaneous Detection of Two Analytes Using a Spectroelectrochemical Sensor." *Anal.Chem.(Wash.),* 82(5), 1720-1726.

Ayyadurai, S. (2010). "Perfluorosulfonic Acid Membrane Catalysts for Optical Sensing of Anhydrides in the Gas Phase." *Anal.Chem.(Wash.),* 82(14), 6265-6272.

Kolev, S. D., Cardwell, T. J., Cattrall, R. W., and Coo, L. D. (2010). "Mathematical modeling of a Nafion membrane based optode incorporating 1-(2-pyridylazo)-2-naphthol under flow injection conditions." *Talanta,* 82(4), 1156-1163.

Ram, M. K., and Bhethanabotla, V. R. (2010). *Sensors for chemical and biological applications.* CRC Press/Taylor & Francis, Boca Raton, FL.

Rivin, D., Kendrick, C. E., Gibson, P. W., and Schneider, N. S. (2001). "Solubility and transport behavior of water and alcohols in Nafion™" *Polymer,* 42(2), 623-635.

APPENDIX: LESSON PLAN

1A. Lesson Name: The Use of Color to Identify Materials and Quantify their Concentration

Fellow or Teacher Name: Jean Becker and Peggy Dunn

Subject: AP Biology and AP Statistics

Grade Level: 11 and 12

Duration: 3 Days (52 min. bells)

1B. Analyze Learners:

Overview & Purpose (Engineering theme)

- What will be learned and why it is useful.
- **A** – Engineering application
- **C** – Engineering career connections
- **S** – Societal impact

The purpose of this research project was to utilize nanostructured catalytic membranes as optical sensors to determine if a correlation could be found between exposure levels for a given chemical and the colors it produced in the membrane. To expose our students to this research, a modified absorbance experiment will be used to model data collection for various test sample concentrations. Students will measure and analyze the visible light absorbance for one color food dye using five known concentration samples. In order to build a stronger understanding absorbance, students will run a second test using a different color food dye. They will use graphing calculators to create a scatter-plot of their findings for each dye and perform a linear regression if it is appropriate. A plot of residuals will be analyzed and finally a hypothesis test for slope performed. Applying the Beer-Lambert law, the students will determine the concentration of an unknown sample. Students will then determine if their unknown sample lies within a certain interval simulating a diagnostic lab test. This lesson is especially useful to students because it is a collaborative lesson that shows students that math explains science.

Applications:

- Real-time analysis of air quality where harmful VOCs are used
- Real-time analysis for reactant chemicals in breath samples

Careers:

- Industry
- Medical fields

Societal Impact:

- Improve health and long term welfare of factory workers
- Improved method for detecting unhealthy levels of adverse organic compounds

2. Education Standards Addressed

KY or OH Standards:

Address 2 to 4 off the STEM Components *

National Science Standards:

E.B.3: Light, heat, electricity, and magnetism

a. Light travels in a straight line until it strikes an object. Light can be reflected by a mirror, refracted by a lens, or absorbed by the object.

Kentucky Science Academic Expectations:

2.1 Students understand scientific ways of thinking and working and use those methods to solve real-life problems.
2.2 Students identify, analyze, and use patterns such as cycles and trends to understand past and present events and predict possible future events.
2.4 Students use the concept of scale and scientific models to explain the organization and functioning of living and nonliving things and predict other characteristics that might be observed.
2.5 Students understand that under certain conditions nature tends to remain the same or move toward a balance.

AP Statistics Standards:

Exploring bivariate data

1. Analyzing patterns in scatter-plots
2. Correlation and linearity
3. Least-squares regression line
4. Residual plots, outliers, and influential points

Tests of significance:

Test for the slope of a least-squares regression line

STEM Components:

- Students will experience what it would be like to perform a diagnostic test in medical lab.
- Students will use math to describe observations in the physical world. Particularly they will use the Beer Lambert Law to explain absorbance and to determine the concentration of an unknown sample.

- Students will use technology such as the Vernier LabQuest with the colorimeter probe and the Texas Instrument TI-84 graphing calculator to collect and then to analyze the data gathered.

3. **Goals** (learn/understand) **And Objectives** (measurable)

(Specify skills/information that will be learned.)

Goal: Drawing upon their understanding of the math and science intrinsic to color, students will collect and analyze absorbance data to create a mathematical model from which further inferences can be made.

Objectives: Students will:

- define color
- collect and analyze absorbance data to determine an unknown concentration.
- compare and contrast absorbance and transmittance
- construct a linear model relating absorbance and concentration

4. **Misconceptions** about this topic:

When you see a color, you are actually observing the color that is being transmitted. All of the other colors are being absorbed.

So, is grass green?

When viewing absorbance vs. wavelength, the peaks are representative of the color that is absorbed and the troughs are the color that is observed/transmitted.

5. **Materials Needed:**

Materials needed per lab group

- Distilled H_2O – 1 L per group
- Five 100ml beakers
- One 500 ml beaker
- Red food coloring (500 ml stock solution with 1 drop of coloring)
- Blue food coloring (500 ml stock solution with 1 drop of coloring)
- Vernier LabQuest
- Vernier Colorimeter
- Cuvette
- TI-84
- Graph paper
- Pencil
- Ruler
- Computer/PowerPoint for presentations

6. Select Instructional Strategies

- Direct instruction
- Inquiry Lesson
- Hands on activity
- Student presentation

7. Utilize Technology

- Vernier LabQuest
- Vernier Colorimeter
- TI-84

8. Require Learner Participation

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9. **Evaluate (Assessment)**

(Steps to check for student understanding; Evaluate goals and Assess objectives)

- Teacher check for understanding through Socratic dialog, class observation, analysis of student data collected and increase in learning as demonstrated through percentage change in pretest/posttest.

10. **Essential/Review questions** are outlined (at least 5 from different levels of Bloom's taxonomy)

Questions pre/post

1. Define color
2. Compare and contrast absorbance and transmittance
3. Construct a linear model using x to explain y (regression equation)

x	**y**
1	5
2	7
5	12
8	14

4. Using your linear model from the previous question, predict the x value that would be associated with a y value of 10.