Spectrophotometric Determination of pH

Author's Name: Bradley Davey **Coach Name:** Debra Dimas
Host Organization: Stanford **ETP Type:** **Report** **Subject/Grade:** Chemistry/11

Abstract (~150 words)

Water chemistry measures minute changes in concentrations (often at the milli/micromolar scale) and pH. Traditional methods (electrochemical probes) to determine pH have uncertainty ranges on the scale of tenths or hundredths, and are therefore not reliable methods to determine changes in microscale processes. This project deals with the use of a spectrophotometer to determine pH, which research has shown to have uncertainty in the thousandths or ten-thousandths. In addition, the data from spectrophotometers is generated from an input (wavelength) and an output (absorbance), which allows for more rigorous analytical techniques. When using pH probes, uncertainty is only observed and measured, but by using spectrophotometry to determine pH, we use calculations that must incorporate uncertainty. These calculations confront students with more authentic and challenging methods to analyze their results and build on analytical techniques used in the Mitch lab at Stanford University.

Focal Content & Supporting Practices

NGSS (SEP 2: Interpreting Data)

- Apply concepts of statistics and probability (including determining function fits to data, slope, intercept, and correlation coefficient for linear fits) to scientific and engineering questions and problems, using digital tools when feasible.
- Consider limitations of data analysis (e.g., measurement error, sample selection) when analyzing and interpreting data.

NGSS (DCI: HS-PS4)

- Multiple technologies based on the understanding of waves and their interactions with matter are part of everyday experiences in the modern world (e.g., medical imaging, communications, scanners) and in scientific research. They are essential tools for producing, transmitting, and capturing signals and for storing and interpreting the information contained in them.

21st Century Skills and Applications (1 - 2)

Problem solving
Addresses problem in greater context, including contributing factors and long-range effects. Students will show evidence of this skill by learning about statistical error and using this error to determine the reliability and validity of their data. This demonstrates problem solving because students need to develop methods to reduce the error in their experiments and confront contributing factors.

Measurable Objective(s)

Students will be able to construct a calibration curve based on pH and absorbance values.

Students will be able to interpret a pH/absorbance calibration curve to determine the pH of an unknown sample.

Formative Assessment(s)

Students will interpret a calibration curve to determine the pH of a solution based on its absorbance in a spectrophotometer.

Summative Assessment(s)

Students will complete a performance task to show evidence of their learning: Students will use their constructed calibration curves to determine the pH of unknown samples collected after an ocean acidification experiment. This experiment will determine how varying levels of pH are correlated to changes in mass of a pure $CaCO_3$ shell. Students will use a spectrophotometer to determine absorbances of their acidic solutions. They will then use these absorbances against their calibration curves to determine the starting and ending pH of their samples. In addition, students must account for error in their measured absorbances and correlated pH values by using a propagation of error method.

Fellowship Description (300-500 words)

The goal of our research is to use electrochemical processes to remove trace disinfectant byproducts (DBPs) from treated wastewater. Many cities in the arid west are interested in reclaiming municipal wastewater as a drinking water supply. It is a secure and local source of water, while traditional water supplies imported from northern California are insecure due to prolonged periods of drought and increasing competition for water reserves. Disinfection of this municipal wastewater is critical, but chemical disinfectants react with organic matter in the water to generate unwanted byproducts. San Jose is operating a pilot disinfection system at their recycling plant that will permit us to systematically vary the disinfection conditions and monitor tradeoffs between pathogen kill and byproduct formation. We hope to identify an optimal balance.

Our aim is to show that small amounts of current can bring about the degradation of known water contaminants and byproducts of the disinfection process. These molecules are typically characterized by low molecular mass and avoid treatment by most traditional means (e.g., reverse osmosis and advanced oxidation processes). Our target compound for the summer of 2019 is trichloroethylene (TCE) and tetrachloroethylene (PCE), both known by the state of California and the USEPA as toxic compounds. TCE and PCE are introduced into groundwater systems through agricultural runoff, and thus this project hopes to show a proof-of-concept water decontamination process that can be scaled to treat realistic quantities of water. By using granular activated carbon (GAC), TCE and PCE will be sequestered from the water stream and subjected to small amounts of current over varying time periods and in different electrochemical conditions such as pH, ionic concentration, and voltage/current.

Fellowship Connection to School/Classroom (300-500 words)

This summer's work is focused on water chemistry, in which spectrophotometric analysis is a common tool to determine unknown concentrations (Beer's Law) and kinetics. In the broader scope of water chemistry, in particular seawater chemistry and climate change research, spectrophotometric analyses are increasingly important due to the instrument's high accuracy and low uncertainty (+/- 0.002 mmolar) in determining pH versus more traditional pH probes (electrode/reference electrode systems). This context will be given to students in the form of discussions and examinations of experimental uncertainty.

I teach a five-week project focused on ocean acidification and use the project to introduce ideas such as pH, acids, bases, and acid-base chemistry. This ocean acidification project is the second of a five project sequence and introducing students to experimental error and validity is important. An area of growth for this project and my teaching in general is the use of more rigorous analytical techniques and data analysis. To fill this gap, I plan to teach students how to use a spectrophotometer, which is a common analytical tool used in the Mitch lab. Students will use the spectrophotometer to determine absorbances of samples and determine the pH of a sample based on constructed calibration curves. Calibration curves, or standard curves, are used in almost every experiment that we've conducted in the lab, and represent a common way to standardize experimental findings. The error analysis method that we will use is known as propagation of error. This method is different from other error methods such as standard deviation and standard error because propagation of error shows how error in a measurement (in this case absorbance) causes error in a related variable (in this case pH). Standard deviation and standard error are techniques to measure error in collected data, but these calculations are not used to determine values in other variables.

Instructional Plan (This is the bulk of your ETP and may take several pages.)

Background
This ETP is a lesson for an 11th-grade chemistry course, and uses spectrophotometry as a technique to measure pH. This is a non-traditional method that is used widely in oceanography and water chemistry (my fellowship) because the pH measurements are more precise (on the order of 10^{-3}).

Summative assessment
This summative assessment (teacher-facing version here) drives weekly instruction. Students will use the pH/absorbance calibration curves that they made during the prior week of instruction to complete the summative assessment.

Formative assessment
This formative assessment drives daily instruction. Students use known pH values and determined absorbances to create a calibration curve. Teachers review and give feedback on the calibration curves, in particular on the error of the absorbance values that are calculated from the class database and how the values show up in student analysis of unknown pHs. For example, if the pH 5 samples have an absorbance error of +/- 0.05, then students should use this error in the back-determination of their pHs, which should be a range of pH values rather than a single value.

Lesson timings
1 - 10 minutes: introduction to spectrophotometry
- Students will have 10 minutes to “mess around” with spectrophotometers, make observations and ask questions

10 - 20 minutes: debrief of observations and wonderings and introduce connection to fellowship
- Students will share their observations and questions with each other and the class and teacher will introduce connections and applications of spectrophotometers from summer research (Beer’s law) [connection to lab work presentation and brief overview here]
- Introduce my research from the summer by showing my poster and discussing project goals; project chromatograms from GCMS and IC data; show how a chromatogram is made by discussing how known concentration samples are loaded into an instrument and then the data is graphed versus the known concentrations; discuss that a line of best fit is developed from these data and then the x value in the line of best fit is used to find the y value, which is the unknown concentration; have students practice using x values from my datasets to find unknown concentrations

15 - 20 minutes: partner pairs formative assessment and familiarize themselves with the work
- Students ask clarifying questions and internalize activity objective

20 - 40 minutes: partner pairs collect data using known pH samples and spectrophotometers
- Students will use pH 4, 5, 6, 7, 8, 9 and 10 samples pre-loaded into cuvettes to collect absorbance data at two wavelengths (443nm and 558nm), which are the absorbance maxima for the yellow and red forms of phenol red, respectively. Students will input this data into the class database, which will autocalculate averages and standard errors.

40 - 60 minutes: partner pairs make their calibration curves using the class database
- Students will use the class database to make scatterplots of both absorbances vs. pH (as per the activity procedure) and fit an equation to the values.

60 - 80 minutes: partner pairs use calibration curves to determine the pH of unknown matrices on the summative assessment and teacher circulates to assess how error is used in the determination of pH. Teacher provides formative feedback to students who do not use the standard error calculation in their calibration curve (i.e., students do not argue that a range of pH values exists for an unknown sample).

80 - 90 minutes: students individually complete the summative assessment and turn in as an exit ticket

Supply List

1. Vernier Spectrophotometer (ideally 1 spec for every 4 students)
2. Phenol red
3. 0.1M NaOH
4. 0.1M HCl

References

Bellerby, Richard G.J., David R. Turner, Geoffrey E. Millward, and Paul J. Worsfold. "Shipboard Flow Injection Determination of Sea Water PH with Spectrophotometric Detection." *Analytica Chimica Acta* 309, no. 1–3 (June 1995): 259–70. https://doi.org/10.1016/0003-2670(95)00054-4.

Easley, Regina A., Mark C. Patsavas, Robert H. Byrne, Xuewu Liu, Richard A. Feely, and Jeremy T. Mathis. "Spectrophotometric Measurement of Calcium Carbonate Saturation States in Seawater." *Environmental Science & Technology*, January 10, 2013, 130110104920006. https://doi.org/10.1021/es303631g.

Friis, Karsten, Arne Körtzinger, and Douglas W.R. Wallace. "Spectrophotometric PH Measurement in the Ocean: Requirements, Design, and Testing of an Autonomous Charge-Coupled Device Detector System: Spectrophotometric PH Measurement." *Limnology and Oceanography: Methods* 2, no. 5 (May 2004): 126–36. https://doi.org/10.4319/lom.2004.2.126.

Lamp, Brian. "Spectrophotometric Determination Of The Pka Of Bromothymol Blue," n.d., 7.

Robert-Baldo, Gillian L., Michael J. Morris, and Robert H. Byrne. "Spectrophotometric Determination of Seawater PH Using Phenol Red." *Analytical Chemistry* 57, no. 13 (November 1985): 2564–67. https://doi.org/10.1021/ac00290a030.

Sharp, Jonathan D., Robert H. Byrne, Xuewu Liu, Richard A. Feely, Erin E. Cuyler, Rik Wanninkhof, and Simone R. Alin. "Spectrophotometric Determination of Carbonate Ion Concentrations: Elimination of Instrument-Dependent Offsets and Calculation of In Situ Saturation States." *Environmental Science & Technology* 51, no. 16 (August 15, 2017): 9127–36. https://doi.org/10.1021/acs.est.7b02266.

Yao, Wensheng, and Robert H. Byrne. "Spectrophotometric Determination of Freshwater PH Using Bromocresol Purple and Phenol Red." *Environmental Science & Technology* 35, no. 6 (March 2001): 1197–1201. https://doi.org/10.1021/es001573e.

Keywords

pH, acid, base, spectrophotometry, ocean acidification, ocean chemistry, water chemistry

Links to Files in this ETP

1. Fellowship Connection Presentation
2. Formative assessment (student-facing)
3. pH/absorbance database(student-facing)
4. Summative assessment (student-facing)
5. Formative assessment (teacher-facing)
6. pH/absorbance database (teacher-facing)
7. Summative assessment (teacher-facing)