

5-2017

Advances in Chemistry, Part I: Noise, Calibration, and Educational Advances In Analytical Chemistry. Part II: Safety Oversight in Chemical Journals

Lauren E. Grabowski
University of South Carolina

Follow this and additional works at: <https://scholarcommons.sc.edu/etd>

 Part of the [Arts and Humanities Commons](#), and the [Chemistry Commons](#)

Recommended Citation

Grabowski, L. E. (2017). *Advances in Chemistry, Part I: Noise, Calibration, and Educational Advances In Analytical Chemistry. Part II: Safety Oversight in Chemical Journals*. (Doctoral dissertation). Retrieved from <https://scholarcommons.sc.edu/etd/4106>

This Open Access Dissertation is brought to you by Scholar Commons. It has been accepted for inclusion in Theses and Dissertations by an authorized administrator of Scholar Commons. For more information, please contact dillarda@mailbox.sc.edu.

ADVANCES IN CHEMISTRY. PART I: NOISE, CALIBRATION, AND EDUCATIONAL ADVANCES
IN ANALYTICAL CHEMISTRY. PART II: SAFETY OVERSIGHT IN CHEMICAL JOURNALS.

by

Lauren E. Grabowski

Bachelor of Science
Saint Francis University, 2012

Submitted in Partial Fulfillment of the Requirements

For the Degree of Doctor of Philosophy in

Chemistry

College of Arts and Sciences

University of South Carolina

2017

Accepted by:

Scott R. Goode, Major Professor

Stephen L. Morgan, Committee Member

Caryn E. Outten, Committee Member

Matthew Miller, Committee Member

Cheryl L. Addy, Vice Provost and Dean of the Graduate School

© Copyright by Lauren E. Grabowski, 2017
All Rights Reserved.

DEDICATION

To

My Parents

Joseph and Alaine Grabowski

ACKNOWLEDGEMENTS

Thank you to everyone I have ever met. Whether you know it or not, you helped shape my aspirations.

I would like to thank my committee members Dr. Morgan, Dr. Outten, and Dr. Miller. Thanks to my undergraduate advisor, Dr Balazs Hargittai, who encouraged me to attend graduate school. I also would like to thank Alice Flarend and Gene Yingling, my high school science teachers, whose enjoyable classes solidified my love of science.

The love and support of my family has allowed me to accomplish all that I have today. To Cassie for always believing in me, even though I didn't always believe in myself. I am forever grateful.

A special thank you to my advisor, Dr. Scott Goode. He was the best mentor I could ask for and he encouraged me to follow my passions. I only hope I took away a fraction of the teaching skills he possesses.

ABSTRACT

Part I

The accuracy and precision of the results of any chemical analysis depends on the calibration graph and its associated systematic and random errors. Least squares regression generally treats all data with equal weights. A weighted least-squares fit is an improvement but requires knowledge of the imprecision in each point of the calibration graph. The imprecision is not easy to estimate with high confidence because of the large number of replicates needed.

The imprecision depends on the types and magnitudes of the sources of noise. We characterized the noise sources in ICP-OES and UV/Vis and developed a model that effectively predicts the standard deviation of emission and absorption as a function of concentration.

Once a model is fit to the data, calibration designs were studied. These designs ranged from one to three decades of response and concentration in order to optimize precision over the entire calibration space for ultraviolet-visible spectrochemical analyses. Different calibration strategies, composed of different concentrations and numbers of replicates, have been evaluated determine the calibration design that minimizes imprecision as measured by the average relative concentration error integrated over the entire calibration graph.

A laboratory experiment utilizing potentiometric titrations was created to connect electrochemistry, stoichiometry, equilibria and reinforce acid-base

titrations. Students performed a potentiometric titration to determine the initial analyte concentration and reactant concentrations at varying points in the titration in order to determine the solubility product constant of a solid species.

Part II

Advances in chemistry are highly dependent on the procedures published in peer-reviewed journals. Some chemistry journals require authors to address safety considerations in their manuscripts but others do not. In this study, we examined 726 chemistry journals from 28 publishers to determine if they require the author to mention safety precautions. Journals supply information for authors that generally mention safety in two places. In the guidelines for authors, which are widely read by prospective contributors, 8% mention safety. Most journals have ethics guidelines of which 59% mention safety.

In order to determine the effectiveness of safety policies 100 articles from each of six journals that published research that involved extensive syntheses were selected. The results of the search indicated that the target compounds were mentioned 107 times but only one mention carried any safety precaution.

An outcome of the paper, *Review and Analysis of Safety Policies in Chemical Journals*, is the implementation of new safety policies in chemical journals by the American Chemical Society. The ACS now requires unexpected, new, and/or significant hazards or risks of the published work to be detailed.

TABLE OF CONTENTS

DEDICATION.....	iii
ACKNOWLEDGEMENTS	iv
ABSTRACT	v
LIST OF TABLES.....	viii
LIST OF FIGURES.....	ix
LIST OF ABBREVIATIONS.....	xi
CHAPTER 1: NOISE SOURCE CHARACTERIZATION OF INDUCTIVELY COUPLED PLASMA – OPTICAL EMISSION SPECTROSCOPY	1
CHAPTER 2: EXPERIMENTAL VALIDATION OF UNCERTAINTY RELATIONSHIPS IN CALIBRATIONS FOR ULTRAVIOLET/VISIBLE ABSORPTION SPECTROSCOPY.....	18
CHAPTER 3: DETERMINING A SOLUBILITY PRODUCT CONSTANT BY POTENTIOMETRIC TITRATION TO INCREASE STUDENTS’ CONCEPTUAL UNDERSTANDING OF POTENTIOMETRY AND TITRATIONS.....	40
CHAPTER 4: REVIEW AND ANALYSIS OF SAFETY POLICIES OF CHEMICAL JOURNALS.....	53
CHAPTER 5: RESPONSE TO <i>REVIEW AND ANALYSIS OF SAFETY POLICIES OF CHEMICAL JOURNALS</i>	77
APPENDIX A – CHAPTER 3 SUPPORTING INFORMATION.....	85
APPENDIX B – PERMISSION TO REPRODUCE PUBLISHED MATERIALS	100

LIST OF TABLES

Table 1.1 Calcium Wavelengths and Transitions.....	9
Table 1.2 Values of β at Ca Wavelengths.....	10
Table 2.1 Signal to Noise Ratio of Different Decades, 348.0 nm, NMC	30
Table 2.2 Calibration Designs, Relative Concentration of each of the ten standards	31
Table 2.3 Best 3 Calibration Designs for Each Decade, 348.0 nm, NMC	32
Table 3.1 Calculated K_{sp} Values Taken for Three Points After the Equivalence Point	50
Table 4.1 Appearance of Safety Keywords in Journal Guidelines for Authors	69
Table 4.2 Frequency of Reading Ethics Guidelines	70
Table 4.3 Perceptions of Contents of Ethics Guidelines	71
Table 4.4 Number of Journal Articles Containing a Safety Keyword.....	72
Table 4.5 The Number of Articles that Mentioned the Target Compounds	73
Table 4.6 Locations in Which Safety Should be Mentioned Specific by Guidelines for Authors	74
Table 4.7 The Use of Safety Keyword	75
Table A.1 Potentiometric Titration Data	98

LIST OF FIGURES

Figure 1.1 Experimental Measurements of Ca Emission at 393.4nm	11
Figure 1.2 Calcium Signal-to-Noise Ratio at 317.9 nm , 0.1-400 ppm	12
Figure 1.3 Calcium Signal-to-Noise Ratio at 318.1 nm, 3.13-1000 ppm	13
Figure 1.4 Calcium Signal-to-Noise Ratio at 370.6 nm, 5.00-1000 ppm	14
Figure 1.5 Calcium Signal-to-Noise Ratio at 393.4 nm, 0.05-6.25 ppm	15
Figure 1.6 Calcium Signal-to-Noise Ratio at 396.8 nm, 0.05-6.25 ppm	16
Figure 1.7 Calcium Signal-to-Noise Ratio at 422.7 nm, 0.1-400 ppm	17
Figure 2.1 Calibration Concentration Error of all designs, 3-decade concentration range, 348.0 nm, NMC	33
Figure 2.2 CCE Comparison of the UV region (348 nm) to the visible region (435 nm), 3-decade concentration range, MC, standard deviations not shown	34
Figure 2.3 Absorption Spectrum of Potassium Dichromate	35
Figure 2.4 Comparison of MC and NMC relative to the CCE of each design, 3-decade, 435.0 nm.....	36
Figure 2.5 Comparison of single-decade designs: 0.002-0.02 AU, 0.02-0.2 AU, and 0.2-2.0AU, without standard deviations, 348.0 nm, NMC.....	37
Figure 2.6 Two-Decade Concentration without standard deviations, 435.0 nm, MC..	38
Figure 2.6 Calibration Concentration Error Comparison for all designs, 348.0 nm, NMC.....	39
Figure 3.1 Schematic diagram of apparatus. Ground connection is pH reference and center connection is clean copper wire.	51

Figure 3.2 Experimental data. A) Titration curve B) Derivative (difference between successive points).	52
Figure 4.1 Distribution of safety keywords in journal ethics guidelines	76
Figure A.1 Titration set up with electrodes.....	87
Figure A.2 BNC-T connection to the LabQuest unit.....	87
Figure A.3 Potentiometric Titration Graph.....	99

LIST OF ABBREVIATIONS

ACS	American Chemical Society
AU	Absorbance Units
C&EN	Chemical and Engineering News
CAS	Chemical Abstract Service
CCE	Calibration Concentration Error
CCS	Committee on Chemical Safety
CHAS	Division of Chemical Health and Safety
CHED	Division of Chemical Education
GAANN	Graduate Assistance in Areas of National Need
ICP-OES	Inductively Coupled Plasma – Optical Emission Spectroscopy
JACS	Journal of the American Chemical Society
K_a	weak acid ionization constant
K_{sp}	solubility product constant
pK_{sp}	logarithmic value of the solubility product constant
PPE	personal protective equipment
RSC	Royal Society of Chemistry
rsd	relative standard deviation
SOP	Standard Operating Procedure
UV/vis	Ultraviolet/Visible absorbance

CHAPTER 1

NOISE SOURCE CHARACTERIZATION OF INDUCTIVELY COUPLED PLASMA - OPTICAL EMISSION SPECTROSCOPY

1.1 ABSTRACT

The accuracy and precision of the results of any chemical analysis depends on the calibration graph and its associated systematic and random errors.

Calibration graphs are, in theory, simple: results (emission intensities in the case of the ICP-OES instrument) are graphed as a function of concentration and an appropriate model is fit to the data by least squares regression. But this process generally treats all data with equal weights.

A weighted least-squares fit is an improvement but requires knowledge of the imprecision in each point of the calibration graph. The imprecision is not easy to estimate with high confidence because of the large number of replicates needed.

The imprecision depends on the types of magnitudes of the sources of noise. We present a characterization of the noise sources in ICP-OES and develop a model that effectively predicts the standard deviation of emission as a function of concentration.

1.2 INTRODUCTION

Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES) has risen to be a widely-used emission technique for determining the elemental composition of aqueous samples.¹ The principal advantages of ICP-OES is its wide linear dynamic range of 10^8 and relative freedom from inter-element interferences.²

A major advancement in ICP-OES was the introduction of a charge injection device (CID) detector. A CID detector allows for quick measurement of high intensity signals but longer measurement of low intensity signals for protection from saturation and optimal signal to noise.³ Blooming is also minimized compared to the more common charge coupled device (CCD) detector.

Multi-wavelength array detectors changed the course of measurements made with ICP-OES. ICP-OES is now a reliable, low cost, exceedingly efficient instrument for high-precision analysis.

This study was aimed at enhancing high-precision analysis by modeling the standard deviation. A detailed study of the heteroscedastic noise was analyzed to determine proper weights for the incorporation of weighted least-squares regression analysis.

1.3 NOISE SOURCES

Every analytical measurement is made up of two components, the first is the response that contains the information desired and the second is noise. Noise obscures and degrades our ability to interpret the response. For our purposes,

we will define “noise” as the imprecision as measured by the standard deviation of a measurement. If the noise in the experiment is constant and independent of the concentration (or response) then Gaussian statistics can be used. However, precision in measurements in a real laboratory setting depend upon the response, thus non-uniform precision (heteroscedasticity) is found.

Understanding heteroscedasticity requires a detailed study of noise sources.

There are a number of ways to classify noise sources but one of the most useful is based on the mathematical dependence of the noise to the response.^{4,5}

Independent of Response Noise sources independent of the response include thermal detector noise. This electronic noise occurs inside the electrical conductor as electrons are thermally agitated, which happens regardless of any applied voltage.⁶ Thermal noise is always present in a measurement and only disappears at absolute zero. The noise in components like resistor (Johnson noise) is similar.

Proportional to the Square Root of the Response Noise proportional to the square root of the response is dominated by the random arrival rate of electrons or charged particles across boundaries in semi-conductor circuits.⁴ The noise source is also called quantum noise. The random arrival rate of photons can be represented by a Poisson distribution and the variance is equal to the total number of photons or electrons collected. Thus, when the collected number of photons is small, quantum noise is a larger fraction of the signal. The primary way to reduce quantum noise is by reducing the bandwidth.⁶ In the ICP-OES instrument used in this study the bandwidth is reduced by increasing the

integration time, which allows for more photons and charge to accumulate on the charge injection device detector.

Directly Proportional to the Response Noise proportional to the response includes flicker noise that tracks fluctuations in source intensity and slight wavelength shifts along the detector axis.⁷ Noise proportional to the response is the limiting noise factor at high concentration.⁸

1.4 DEPENDENCE ON SIGNAL

Since the noise is heavily dependent on the response, a three parameter fit (the parameters are the magnitudes of the noise independent of the concentration, noise related to the square root of concentration, and noise related to the concentration) was fit to allow estimation of noise at intermediate concentrations.

The noise was modeled by the equation: $\sigma_I = \beta_1 + \beta_2\sqrt{I} + \beta_3I$ where β_1 , β_2 , and β_3 are constants for the instrument at a specific wavelength.⁴ At smaller intensities, β_1 is the dominant noise source, whereas at higher intensities, β_2 and β_3 dominate.⁹ Since ICP-OES is linear over a wide dynamic range, the limiting noise strongly depends on the analyte concentration.

1.5 EXPERIMENTAL MEASUREMENT OF SIGNAL TO NOISE RATIO

A Thermo Scientific iCAP 6300 inductively coupled plasma- optical emission spectrometer was employed. The detector was a RACID86 solid state CID. The CID delivers high contrast/low noise imaging and quantification from 166-847 nm which allows for low detection limits, such as that for calcium with a detection limit of 0.02 ppm at 393.4 nm.

All analyte solutions were prepared by diluting a calcium stock solution (1000 ppm Ca in 2% hydrochloric acid) with 2% HCl. Analyte concentrations were chosen to match the linear intensity range for each wavelength, discussed in the next section. Each aliquot was weighed such that the calculated concentrations of the standards were free from pipetting imprecision.

1.6 CHOICE OF WAVELENGTH

Calcium has a number of suggested analytical wavelengths with relative intensities of 40,000 to 70,000,000. These numbers indicate the signal magnitude per unit calcium concentration. Typically, low sensitivity wavelengths are chosen when the calcium concentrations in the sample are relatively high. The emission at the less-sensitive wavelengths will not saturate the detector so the sample can be analyzed without dilution. The more sensitive wavelengths afford the analysis of ultratrace (sub-mg/L, or sub-ppm) concentrations. These lines provide better limits of detection - the detection limit for calcium in the ICP is 0.05 ppm – and allow the experimenter to dilute the sample to minimize matrix effects.

The varying intensities or sensitivities arise from fundamental sources such as the ICP temperature and the excitation processes. The spectrum includes emission from neutral atoms as well as from ions and transitions that terminate in the ground state, others do not. And the population of the excited state is dependent on the plasma condition such as temperature and the energy level of the excited state.

Six calcium wavelengths (317.9, 318.1, 370.6, 393.4, 396.8, and 422.7 nm) were examined in this study. At each wavelength 100 readings of ten

different concentrations of Ca standard were obtained. Concentrations varied from 0.05-1,000 ppm depending on the intensity of calcium at each wavelength. The concentrations were all evenly spaced when converted to the log-log scale.

The fundamental characteristics of the lines are shown in Table 1.1. Ca I is traditional spectroscopic notation that indicates a neutral line and Ca II is the first ion line (emission from Ca^+). The relative intensities from the NIST database are included for completeness, but they are generated from a different emission system (a wall-stabilized arc) than the ICP.

1.7 RESULTS AND DISCUSSION

One hundred integrations of each solution were recorded and the signal and noise were calculated, as depicted in Figure 1.1. It can be noted that as the log of the signal increases, the log of the noise also increases. Though, the signal-to-noise ratio is fairly constant, thus flicker noise is the limiting noise source.

The values of β_1 , β_2 , and β_3 for calcium wavelengths are shown in Table 1.2. The constant, β , with the highest value identifies the limiting noise. At 393.4 nm, $\beta_1 = -7.0965$, $\beta_2 = -0.2922$, and $\beta_3 = 16.1294$. In this case, the larger value of β_3 is consistent with the limiting noise being flicker noise. At lower intensity wavelengths, such as 422.7nm, β_1 is the limiting noise source. These findings are consistent with previous research.⁹

Once the values of β are calculated, the noise at any intensity along the linear calibration range can be determined. Figures 1.2-1.7 depict the measured signal-to-noise ratios plotted as a function of concentration. The signal-to-noise ratio and the concentration axes are logarithmic.

The models are good representation of the predicted noise. In some cases, the experimental measurement such as the first point at 317.9nm skews the model since the concentration is relatively close to the detection limit. This issue could be eliminated by making measurements much greater than the limit of detection but the purpose of this study was to examine the largest possible linear dynamic range.

The two wavelengths with the highest relative intensities, 393.4 and 396.8 nm, are flicker noise limited at the three highest concentrations. The other four wavelengths show an initial increase in signal to noise ratio consistent with that of detector noise.

1.8 CONCLUSION

The model fits the data remarkably well, considering that we are modeling the uncertainty in the emission signal as a function of the concentration.

The application of this work is to improve the accuracy and precision of multi-decade calibration curves by using weighted least squares fits. Because the noise sources are heteroscedastic the magnitude of the noise depends on the emission signal; and this work provides informed estimates of the relationships that can be used to predict weights with some amount of confidence.

1.9 ACKNOWLEDGEMENTS

Thanks are given to High Purity Standards for their generous donation of standards. This project was supported in part by the U.S. Department of Education through the GAANN program, award number P200A120075.

1.10 REFERENCES

1. Fassel, V. A.; Kniseley, R.N., *Anal. Chem.* **1974**, *46*, 1017-1021.
2. Watters, R. L.; Carroll, R. J.; Spiegelman, C. H., *Anal. Chem.* **1987**, *59*, 1639-1643.
3. Thermo Electron Corporation. *iCAP 6000 Series ICP Emission Spectrometer*, **2006**.
4. Ingle, J.D. Jr.; Crouch, S.R., *Spectrochemical Analysis*; Prentice Hall: Englewood Cliffs, 1988.
5. Ingle, J. D. Jr.; Crouch, S. R., *Anal. Chem.* **1972**, *44*, 1375-1386.
6. Skoog, D. A.; Holler, F. J.; Crouch, S. F., *Instrumental Analysis*; Brooks/Cole: Belmont, 2007.
7. Rothman, L. D.; Crouch, S. R.; Ingle, J. D. Jr., *Anal. Chem.* **1975**, *47*, 1226-1233.
8. Pennebaker, F.; Denton, M. B., *Appl. Spectrosc.* **2001**, *55*, 722-729.
9. Bubert, H.; Klockenkamper, R., *Anal. Chem.* **1983**, *316*, 186-193.
10. http://physics.nist.gov/PhysRefData/ASD/lines_form.html

Table 1.1: Calcium Wavelengths and Transitions.¹⁰

Wavelength, nm	Type	Relative Intensity	Transition probability, s ⁻¹	Ground state		Excited State	
				Energy, cm ⁻¹	Electron Configuration	Energy, cm ⁻¹	Electron Configuration
317.9	Ca II	180	3.6 x 10 ⁸	25,414	3p ⁶ 4p	56,858	3p ⁶ 4d
318.1	Ca II	150	5.8 x 10 ⁷	25,414	3p ⁶ 4p	56,839	3p ⁶ 4d
370.6	Ca II	170	8.8 x 10 ⁷	25,414	3p ⁶ 4p	52,166	3p ⁶ 5s
393.4	Ca II	230	1.5 x 10 ⁸	0	3p ⁶ 4s	25,414	3p ⁶ 4p
396.8	Ca II	220	1.4 x 10 ⁸	0	3p ⁶ 4s	25,192	3p ⁶ 4p
422.7	Ca I	50	2.2 x 10 ⁸	0	3p ⁶ 4s 4p	23,652	3p ⁶ 4s ²

6

Table 1.2: Values of β at Ca Wavelengths

Wavelength, nm	Minimum Concentration, ppm	Maximum Concentration, ppm	Relative Intensity	β_1	β_2	β_3
317.9	0.1	400	180	12.7577	4.6570	-14.9505
318.1	3.13	1000	150	7.4993	3.5037	-10.0264
370.6	5.00	1000	170	75.3647	18.3112	-73.7856
393.4	0.05	3.125	230	-7.0965	-0.2922	16.1294
396.8	0.05	6.25	220	-20.9867	-2.3300	15.8044
422.7	0.1	400	50	15.3221	4.9875	-16.7884

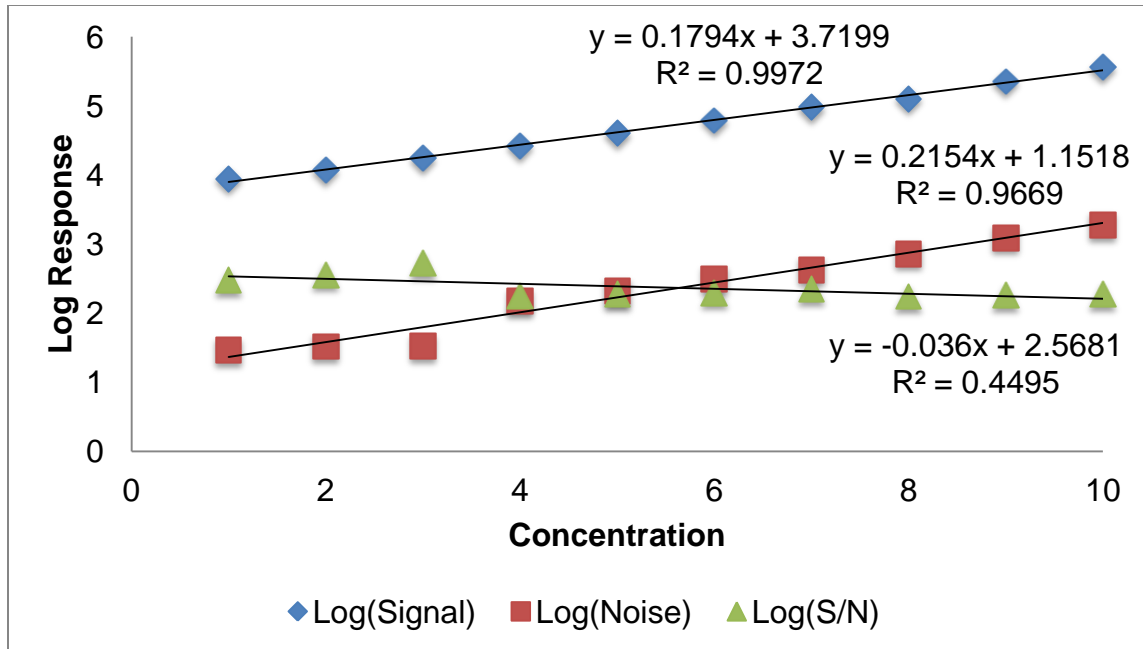


Figure 1.1: Experimental Measurements of Ca Emission at 393.4nm

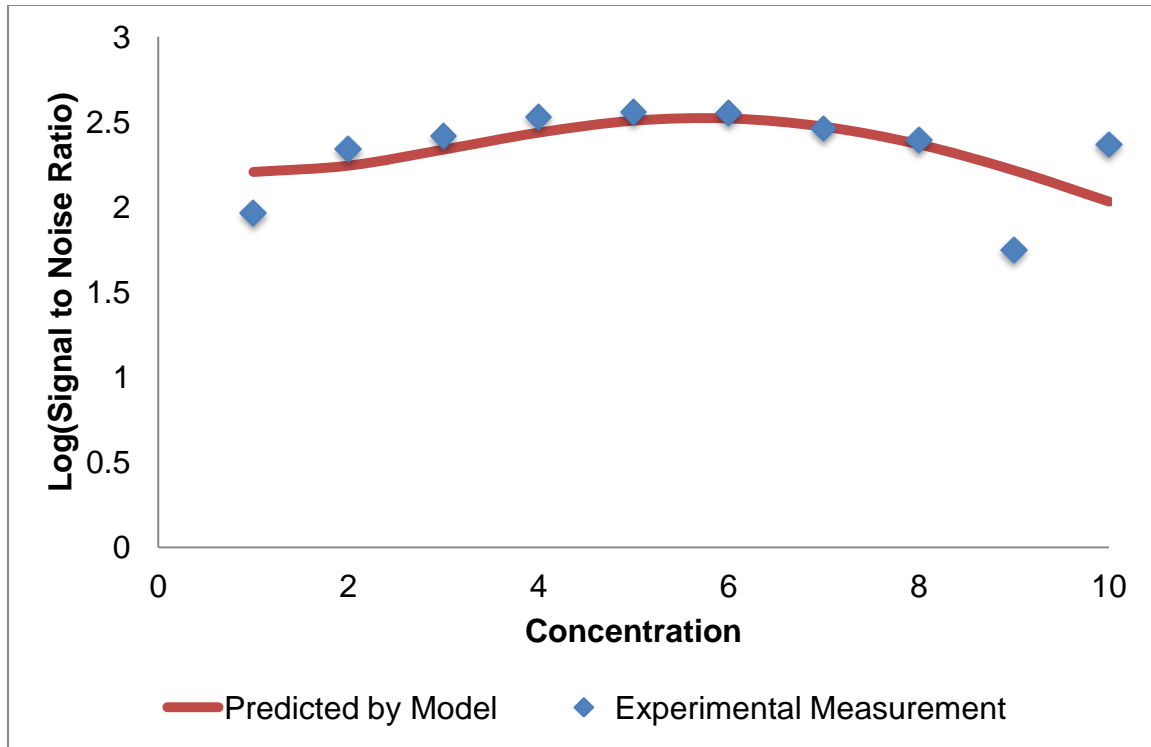


Figure 1.2: Calcium Signal-to-Noise Ratio at 317.9 nm, 0.1-400 ppm

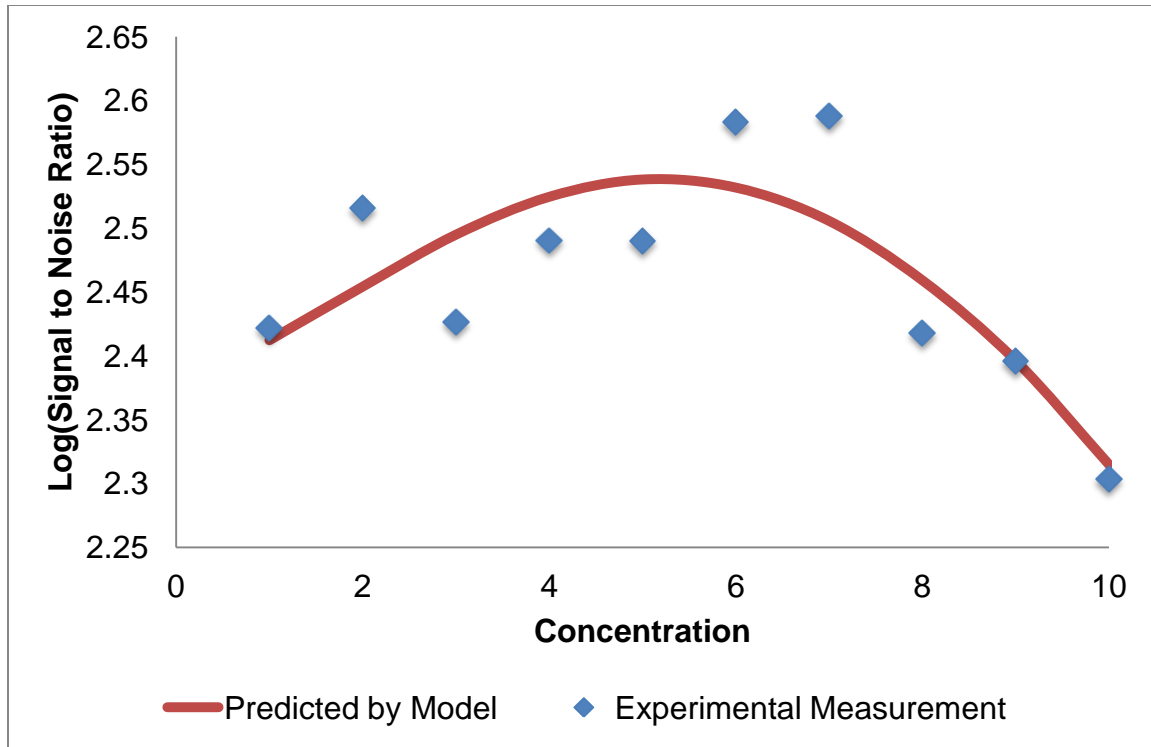


Figure 1.3: Calcium Signal-to-Noise Ratio at 318.1 nm, 3.13-1000 ppm

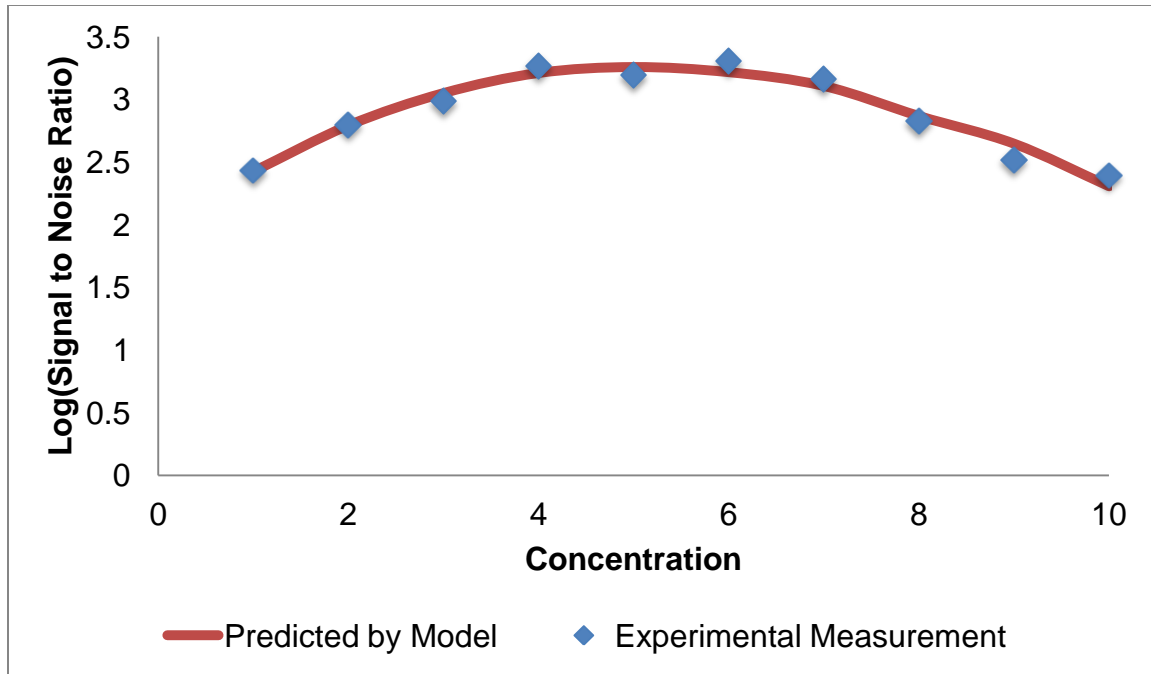


Figure 1.4: Calcium Signal-to-Noise Ratio at 370.6 nm, 5.00-1000 ppm

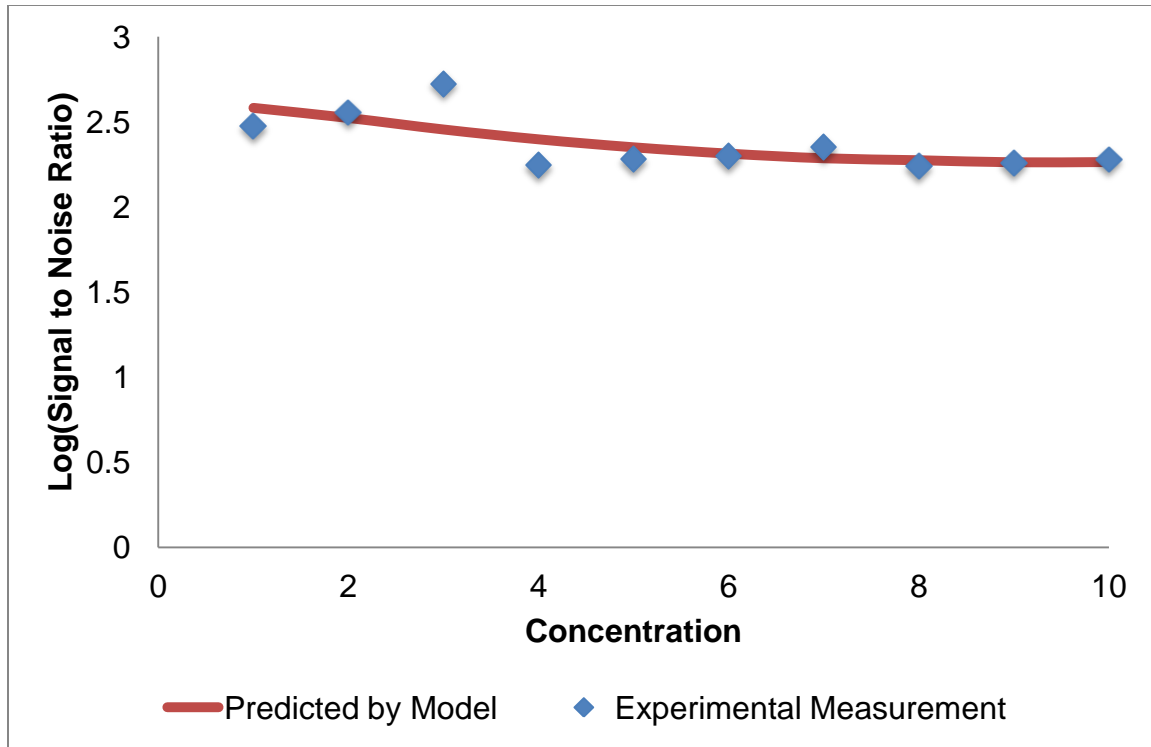


Figure 1.5: Calcium Signal-to-Noise Ratio at 393.4 nm, 0.05-3.125 ppm

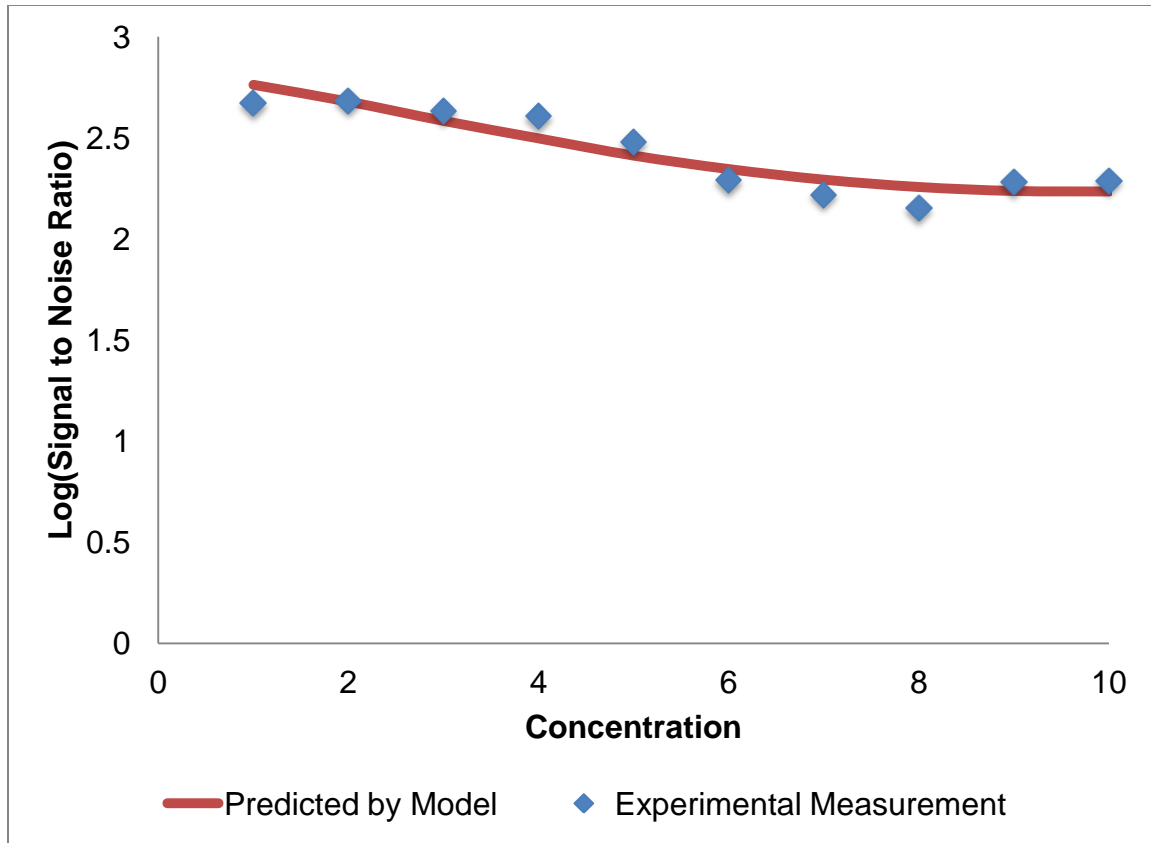


Figure 1.6: Calcium Signal-to-Noise Ratio at 396.8 nm, 0.05-6.25 ppm

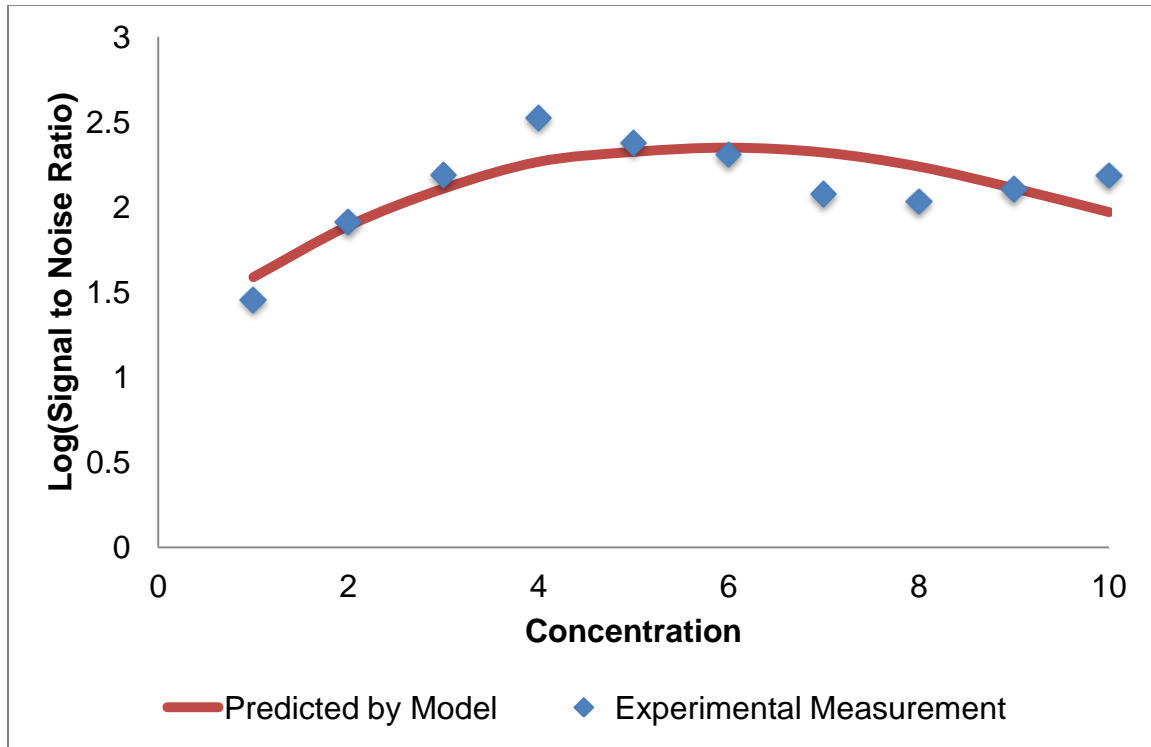


Figure 1.7: Calcium Signal-to-Noise Ratio at 422.7 nm, 0.1-400 ppm

CHAPTER 2

EXPERIMENTAL VALIDATION OF UNCERTAINTY RELATIONSHIP IN CALIBRATIONS FOR ULTRAVIOLET/VISIBLE ABSORPTION SPECTROSCOPY

2.1 ABSTRACT

Ultraviolet-visible absorption spectroscopy is a widely-used technique for quantitative analysis. Although there have been many studies examining the relative concentration error associated with ultraviolet-visible measurements, there is little that addresses the use of modern instruments capable of measuring absorbances that vary over three decades with high accuracy and precision. There is no information to help optimize calibration curves to minimize spectrophotometric imprecision.

The major source of this spectrophotometric imprecision is detector noise, which obscures and degrades the ability to interpret the response and is dominant at low concentrations. Random instrumental noise in spectrophotometric measurements can be divided into three classes: (1) sources that are completely independent of response; (2) sources with variance that is directly proportional to the response; and (3) sources of noise with variances that are related to the square of the response. The magnitudes of these noise

sources affect the signal-to-noise ratio of ultraviolet-visible absorbance measurements. The goal of this study was to design calibration strategies that optimize precision over the calibration graph for ultraviolet-visible spectrochemical analyses for one, two, or three decades of concentration. Different calibration strategies, composed of different concentrations and number of replicates, have been evaluated to try to determine the calibration design that will minimize imprecision as measured by the average relative concentration error integrated over the entire calibration graph.

2.2 INTRODUCTION

Calibration Graphs. Calibration graphs are utilized by chemists to determine the relationship between the analyte concentration and response. This research reports the influence of empirically-chosen calibration designs on the analysis precision.

Calibration Concentration Error. Most labs are comfortable with using the relative standard deviation (rsd) as a measure of precision, thus minimizing rsd (σ_c/C , which is equal to σ_A/A). Like many other researchers,¹⁻⁵ we propose to use the relative concentration error, σ_c/C , as the metric to be minimized. Early research⁶ showed that for absorbance measurements, the relative concentration error for an individual measurement depended on the absorbance or transmittance. Common advice for optimizing precision is to design the analysis so that the unknown concentration had a transmittance between 20 and 80 percent transmittance to maximize precision.

Ingle and Crouch⁷ noted that the precision was related to the noise sources that were often complex and had to be measured for an individual instrument. Previous work has examined the minimizing the rsd of individual measurements, though none have looked at the effects of noise on the overall calibration graph. If the relative standard deviation of the concentration can be predicted at each point along the calibration graph the relative concentration error can be integrated between the lowest standard and highest standard to determine the Calibration Concentration Error (CCE). Exploring how the CCE changes as a function of the choice of calibration concentrations was the objective of this research.

Transmittance Measurements. All spectrophometric instruments use detectors that response to intensity, so transmittance, rather than absorbance, is used. Since $A = \log(1/T)$, where T is the ratio of transmitted to radiant intensity ($T = I/I_0$), the variance in absorbance can be determined from the variance in transmittance. Propagation of uncertainty applied to Beer's Law states that $\sigma_c/c = \sigma_A/A$.⁸ The absorbance uncertainty is directly related to the standard deviation of the transmittance measurement; propagation of error treatment yields the

equation:
$$\frac{\sigma_A}{A} = \frac{0.434\sigma_T}{T \log(T)}$$

Noise. Every analytical measurement is made up of two components, the first is the response that contains the information desired and the second is noise.

Noise obscures and degrades the ability to interpret the response. For our purposes, we will define "noise" as the imprecision as measured by the standard deviation of a measurement. If the noise in the experiment is constant and

independent of the concentration (or response), then Gaussian statistics can be used to show the calibration graph with just two points at the extremes of concentration minimizes the imprecision.⁹

However, precision in measurements in a real laboratory setting is dependent upon the response. Thus, non-uniform precision (heteroscedasticity) is assumed for a given calibration graph.¹⁰ Heteroscedasticity requires a detailed study of noise sources and a numerical investigation of the average relative concentration error. This study focuses solely on the precision of measurements that are restricted by noise associated with the instrument.

There are a number of ways to classify noise sources but one of the most useful is based on the dependence of the noise source on the signal.⁶

Noise sources independent of the signal include detector noise, many electronic sources, and imprecision due to limited resolution of the readout or analog-to-digital convertor.⁷ Electronic noise occurs inside the electrical conductor as electrons are thermally agitated, which happens regardless of any applied voltage.¹¹ Thermal noise is always present in a measurement and only disappears at absolute zero. Readout noise is a form of electronic noise that interrupts the final signal upon readout of the device, whereas dark current noise is the constant response exhibited by a detector when it is not actively exposed to light. When readout and dark-current noise dominate, as is common in older instruments, the optimal precision in molecular absorption spectrophotometric measurements occur near 37% T.⁷

Noise proportional to the square root of the signal is dominated by quantum noise. One source of quantum noise is caused by the random movement of electrons or charged particles across boundaries in semi-conductor circuits.⁶ The magnitude of this variance increases with signal. A second source is the random arrival rate of photons, which follow a Poisson distribution. The variance is equal to the total number of photons collected. Thus, when the accumulated number of photons is small, quantum noise is more apparent.¹²

Instruments that use low noise amplification and high resolution readout devices have maximum precision in the range of 0-11% T and are quantum noise limited.⁷ The amplifier also has its own independent noise associated with it due to the use of resistors and op amps; which will amplify any noise already present in the system. To attenuate this noise, a difference amplifier can be employed.¹³

Noise proportional to signal includes source flicker noise and sample-cell positioning imprecision.¹⁴ Source flicker noise is due to fluctuation in source intensity. Unfortunately, flicker noise is not well understood, though it is known to be frequency dependent and larger at low frequencies.¹² Another source of noise proportional to the signal is cell positioning imprecision. Reflective losses and transparency differences because of cell imperfections result in position dependence.⁶ Systematic errors via reflective losses have been previously studied.¹⁵

2.3 DESIGN OF EXPERIMENT

A total of 100 measurements were obtained at each of the 10 concentrations for the three different decade options. The decade options were 1 decade: 0.002-

0.02 Absorbance Units (AU), 0.02-0.2 AU, 0.2-2.0 AU, 2 decade: 0.002-0.2 AU, 0.02-2.0 AU and 3 decade: 0.002-2.0 AU. The 2 and 3 decade concentrations were evenly spaced on the log scale. A three parameter fit (the parameters are the magnitudes of the noise independent of the concentration, noise related to the square root of concentration, and noise related to the concentration) was fit to the data to allow estimation of noise at intermediate concentrations, as depicted in Figure 2.1.

Thirty-six different calibration designs were employed to predict the standard deviation of the measurement at any particular concentration. Three-decimal place measurements were determined by generating random numbers with the appropriate standard deviations. A regression analysis of the calibration graph resulted in the slope, standard deviation of the slope, intercept and standard deviation of the intercept. Propagation of errors was used to determine the relative concentration errors: $\frac{\sigma_c}{C} = \sqrt{\frac{\sigma_M^2 + \sigma_{int}^2}{(M - int)^2} + \frac{\sigma_{slope}^2}{(slope)^2}}$ This process was equally spaced over the absorbance units range 199 times. The CCE were determined by summing the relative concentration errors over the calibration graph.

One hundred replicates for each concentration were acquired at 348.0 and 435.0 nm. One sample set required removing the cell between each replicate (MC); one sample set kept the cell stationary for each solution but was removed for refilling with a new solution (MCBS); the last set kept the cell stationary (NMC).

2.4 INSTRUMENTATION AND METHODS

Spectrophotometer. The instrument used in this study was a dual-beam molecular absorption spectrophotometer (Varian Cary 50) with a Czerny-Turner monochromator, dual Silicon diode detectors, and a full spectrum Xenon flash lamp with a limiting resolution and spectral bandwidth of 1.5 nm.

Reagents. All analyte solutions were prepared by diluting a potassium dichromate stock solution (1000 ppm $K_2Cr_2O_7$ in 0.01M sulfuric acid) with 0.01 M H_2SO_4 . Analyte solution concentrations were chosen to range from 0.002-2.0 AU. Each aliquot was weighed such that the calculated concentrations of the calibration standards were based on gravimetric data.

Measurements. One hundred replicates for each concentration were acquired at 348.0 and 435.0 nm. These measurements were made in the ultraviolet (348 nm) and visible (435 nm) regions because their noise sources are likely to differ. At each wavelength, measurements were made for MC, MCBS, and NMC.

Calibration Range. Calibrations over one decade change in absorbance were made for 0.002-0.02, 0.02-0.2, and 0.2-2.0 AU on the linear scale. Calibrations were performed on the log scale for 2, and 3-decade concentration ranges. Two decade comparisons were made between 0.02-2.0 and 0.002-0.2 AU, and the three decade concentration range was 0.002-2.0 AU.

2.5 RESULTS

Heteroscedastic Noise. The assumption that the data is heteroscedastic is confirmed by Table 2.1. Thus, there is a significant need for this work.

Designs. Thirty-six different designs were tested in which the number of replicates was changed along with calibration placement across one, two, or three decades of concentration. Table 2.2 lists the designs. When the design results are compared, as depicted in Figure 2.1, differences between the designs is small because the standard deviation of the calibration concentration error is high.

Wavelength Comparison. The samples were run in both the ultraviolet (348.0 nm) and visible (435.0 nm) regions, to enable comparison of noise sources in these regions. Upon overlapping the two wavelengths, as shown in Figure 2.2, it is apparent that the calibration graph designs are not wavelength dependent. Thus, these calibration designs are useful for different wavelengths of ultraviolet-visible absorption spectroscopy. It can also be seen that the CCE for 348 nm is much smaller than that of 435 nm, most likely because of the larger absorbance in the UV, as depicted by Figure 2.3.

Cell Positioning Error. Results indicate there is a correlation between higher imprecision and moving the cell between each sample, which agrees with that of others,³ shown in Figure 2.4. These results were expected, as reflective and transparency losses at the glass/air and glass/sample interface result in more noise.

One Decade Comparison. Comparison of the three different 1 decade combinations (0.002-0.02, 0.02-0.2, 0.2-2.0 AU) results in a significant difference. As shown in Figure 2.5, the CCE for 0.002-0.02 AU much larger than that of the other two. The average CCE for 0.002-0.02 AU was 8 ± 1 , whereas 0.02-0.2 AU

was 0.7 ± 0.1 and 0.2-2.0 AU was 0.4 ± 0.2 . This result is to be expected as the average signal to noise ratio of 0.002-0.02 was 112, with the other two being 1403 and 2962 respectively.

Two Decade Comparison. Two different two-decades were examined to determine whether the concentration of the standards (low 0.002-0.2 AU or high 0.02-2.0 AU) affected the calibration concentration error. Figure 2.6 depicts the differences between the two-decade concentrations.

The differences between the two-decades at different concentrations is apparent. At lower concentrations, 0.002-0.2 AU, the calibration concentration error is high. As noted before, at lower concentrations, k_1 is the dominant noise source. The value of k_1 at 0.002-0.2 AU is 0.004786, whereas 0.02-2.0 AU has a k_1 of 0.000105.

One, Two and Three Decade Comparison. When one, two, and three decades are compared, shown in Figure 2.7, decades composed of higher absorbances results in a lower CCE. For example, the lowest 1 decade (0.002-0.02 AU) and the lowest 2 decade (0.002-0.2 AU) result in the two highest average CCE. It should be noted that the decades with the lowest CCE are 0.02-0.2 AU and 0.2-2.0 AU. This is consistent with the assumption made by many chemists to minimize the calibration range and use absorbances well above the limit of detection.

Optimal Calibration Design. The three designs with the lowest CCE from each decade is depicted in Table 2.3. Design 20 was in the top three best designs for four of the six single-decade choices. This design (1, 6, 6, 7, 7, 8, 8, 9, 9, 10)

utilizes the variety of concentration with the majority at high concentrations. From Table 2.1, it is shown that higher concentrations result in a larger signal to noise ratio which correlates to the findings. Design 28 was best in half of the choices, and Designs 3, 19, and 25 appeared in two out of six decade choices. Once again, these designs utilize a higher concentration standards.

The top 3 calibration designs for one decade 0.2-2.0 resulted in the lowest average CCE of 0.2069. Thus, it can be inferred that higher concentration standards (which larger signal to noise ratios) do result in optimal calibration graphs.

1.5 CONCLUSION

Over one, two or three decade calibration ranges, precision is dependent upon the concentration of the standards in the calibration set. This study found that expanding a calibration graph to three decades made it difficult to get a calibration graph with high precision. A one-decade calibration with low standards (0.002-0.02 AU) resulted in the highest CCE with low signal to noise ratios. The preferential range for a calibration graphs would utilize concentrations within 0.02-2.0 AU.

Increased imprecision was seen when the cell was moved between samples, instead of keeping the cell stationary. Comparing UV to a visible line shows the same trends, so we infer that the calibration designs are independent of wavelength. Also, limiting the calibration range results in higher precision as indicated by the decade comparison. Overall, the location of standards, number of replicates, and cell positioning all affect the precision of the calibration graph.

Though some calibration designs may result in a lower CCE, the decade range choice has a larger impact. The results shown here suggest that the different calibration designs are wavelength independent, and that cell positioning does affect the precision of calibration graphs.

1.6 ACKNOWLEDGEMENTS

This project was supported in part by the U.S. Department of Education through the GAANN program, award number P200A120075.

1.7 REFERENCES

1. Watters, R. L.; Carroll, R. J.; Spiegelman, C. H., *Anal. Chem.* **1987**, *59*, 1639-1643.
2. Pimentel, M.F.; de Barros Neto, B.; Saldanha, T.C.B.; Arafijo, M.C.U., *J. Autom. Chem.* **1998**, *20*, 9-15.
3. Schwartz, L.M., *Anal. Chem.* **1977**, *49*, 2062-2068.
4. Shewell, C.T., *Anal. Chem.* **1960**, *32*, 1535.
5. Tellinghuisen, J., *Appl. Spectrosc.* **2000**, *54*, 431-437.
6. Ingle, J. D. Jr.; Crouch, S. R., *Spectrochemical Analysis*; Prentice Hall: Englewood Cliffs, 1988.
7. Ingle, J. D. Jr.; Crouch, S. R., *Anal. Chem.* **1972**, *44*, 1375-1386.
8. Laurier Research Instrumentation. *User Guidelines & Standard Operating Procedure for the Cary 50 UV-Vis Spectrophotometer*, **2007**.
9. Franke, J.P.; de Zeeuw, R.A.; Hakkert, R., *Anal. Chem.* **1978**, *50*, 1374-1380.
10. Schwartz, L.M., *Anal. Chem.* **1979**, *21*, 723-727.
11. Optical Technologies. *Noise in Photodetectors*;
<http://optical-technologies.info/tag/thermal-noise/> (accessed Aug 9, 2013).
12. Princeton University. *Shot Noise*;
http://www.princeton.edu/~achaney/tmve/wiki100k/docs/Shot_noise.html
(accessed Aug 9, 2013).
13. Skoog, D. A.; Holler, F. J.; Crouch, S. F., *Instrumental Analysis*; Brooks/Cole: Belmont, 2007.
14. Rothman, L. D.; Crouch, S. R.; Ingle, J. D. Jr., *Anal. Chem.* **1975**, *47*, 1226-1233.
15. Burnett, R. W., *Anal. Chem.* **1973**, *45*, 383-385.

Table 2.1: Signal to Noise Ratio of Different Decades, 348.0 nm, NMC

	1 Decade			2 Decade		3 Decade
	0.002- 0.02 AU	0.02-0.2 AU	0.2-2.0 AU	0.002- 0.2 AU	0.02-2.0 AU	0.002-2.0 AU
Standard 1	5	128	3462	16	137	13
Standard 2	27	682	5237	18	247	23
Standard 3	23	777	5597	56	346	43
Standard 4	86	1245	3704	154	620	102
Standard 5	103	1341	4178	104	875	48
Standard 6	149	1370	2561	374	1426	345
Standard 7	168	1621	1721	564	1519	639
Standard 8	137	1496	1541	772	1352	1751
Standard 9	301	1907	997	1743	1282	2862
Standard 10	128	3462	622	1451	2162	2154
Average	112	1403	2962	525	996	798

Table 2.2: Calibration Designs, Relative Concentration of each of the ten standards

Design Number	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Standard 1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
Standard 2	2	1	1	2	4	2	3	4	3	1	4	1	2	1	1	5	2	3
Standard 3	3	1	3	2	4	2	5	4	3	1	4	1	3	1	1	5	2	3
Standard 4	4	5	3	2	5	3	5	4	3	4	4	3	4	1	1	5	2	3
Standard 5	5	5	5	2	5	3	5	4	7	5	5	3	5	1	1	5	5	3
Standard 6	6	5	5	9	6	8	5	6	7	6	5	3	10	6	5	10	5	8
Standard 7	7	5	7	9	7	8	5	6	7	7	6	7	10	7	5	10	9	8
Standard 8	8	10	7	9	7	9	5	6	9	10	6	7	10	8	5	10	9	8
Standard 9	9	10	9	9	10	9	7	6	9	10	6	7	10	9	5	10	9	8
Standard 10	10	10	9	10	10	10	9	10	9	10	10	9	10	10	10	10	10	10

31

Design Number	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36
Standard 1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
Standard 2	1	6	2	1	1	1	5	1	1	1	1	1	1	1	1	1	1	1
Standard 3	1	6	2	1	1	5	10	1	1	1	1	1	5	5	5	5	5	1
Standard 4	4	7	3	1	5	10	10	1	1	1	1	5	5	5	5	5	5	1
Standard 5	4	7	3	5	10	10	10	1	5	1	1	5	5	5	5	5	10	5
Standard 6	7	8	4	10	10	10	10	5	5	10	1	5	5	5	5	10	10	5
Standard 7	7	8	4	10	10	10	10	5	5	10	5	5	5	5	10	10	10	10
Standard 8	10	9	5	10	10	10	10	5	5	10	5	5	5	10	10	10	10	10
Standard 9	10	9	5	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10
Standard 10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10

Table 2.3: Best 3 Calibration Designs for Each Decade, 348.0 nm, NMC

	Best 3 Designs	Average CCE
One decade		
0.002 – 0.02	19, 20, 28	7.6876
0.02 – 0.2	14, 19, 28	0.7349
0.2 – 2.0	12, 15, 21	0.3766
Two decade		
0.002 – 0.2	3, 20, 28	0.9894
0.02 – 2.0	16, 20, 25	0.6245
Three decade		
0.002 – 2.0	16, 20, 25	0.5762

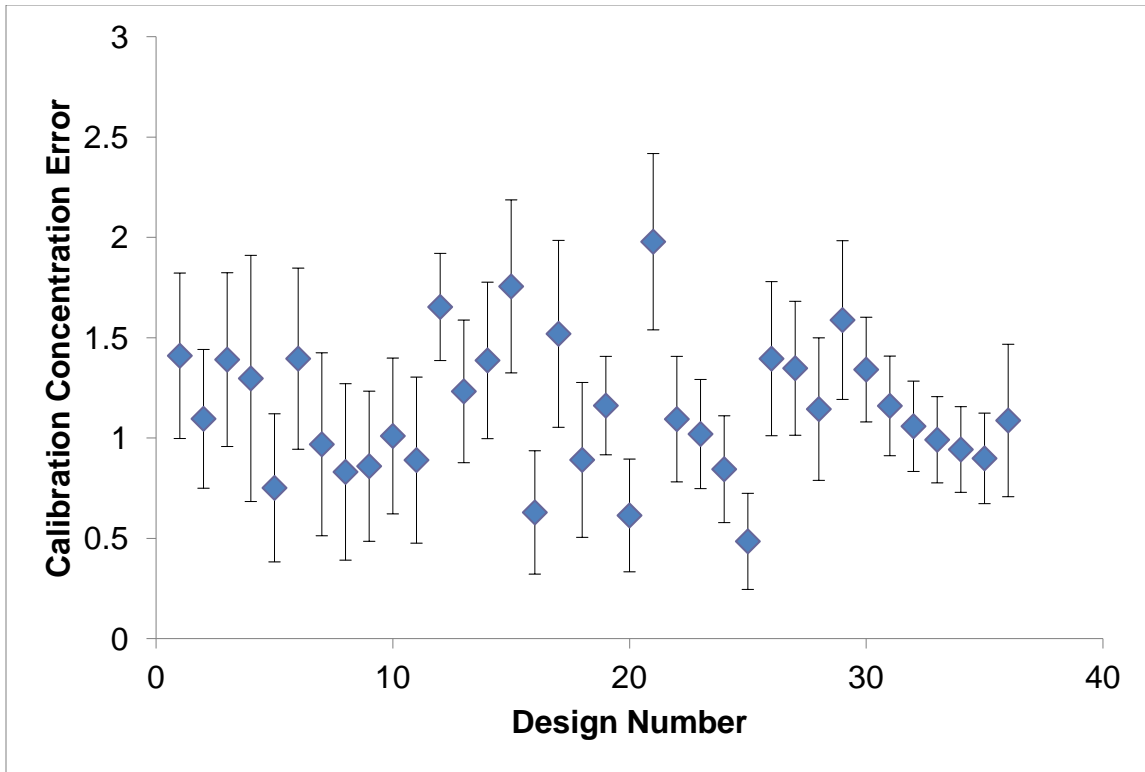


Figure 2.1: Calibration Concentration Error of all designs, 3-decade concentration range, 348.0 nm, NMC

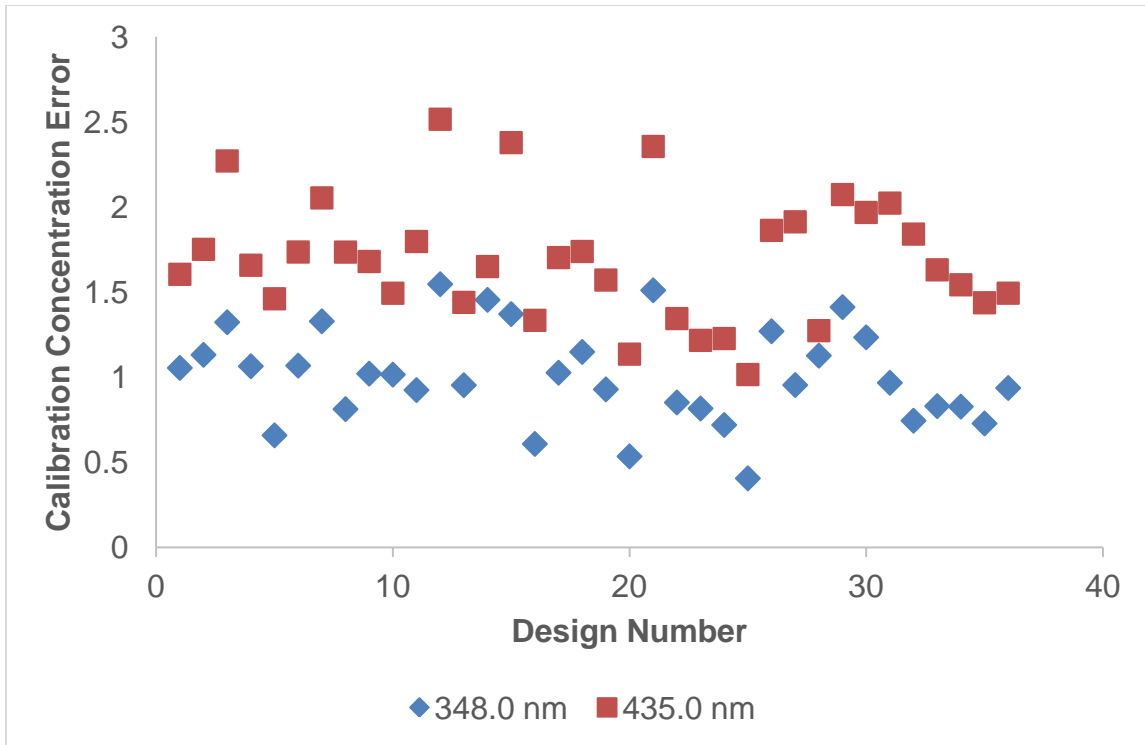


Figure 2.2: CCE Comparison of the UV region (348.0 nm) to the visible region (435.0 nm), 3-decade concentration range, MC, standard deviations not shown.

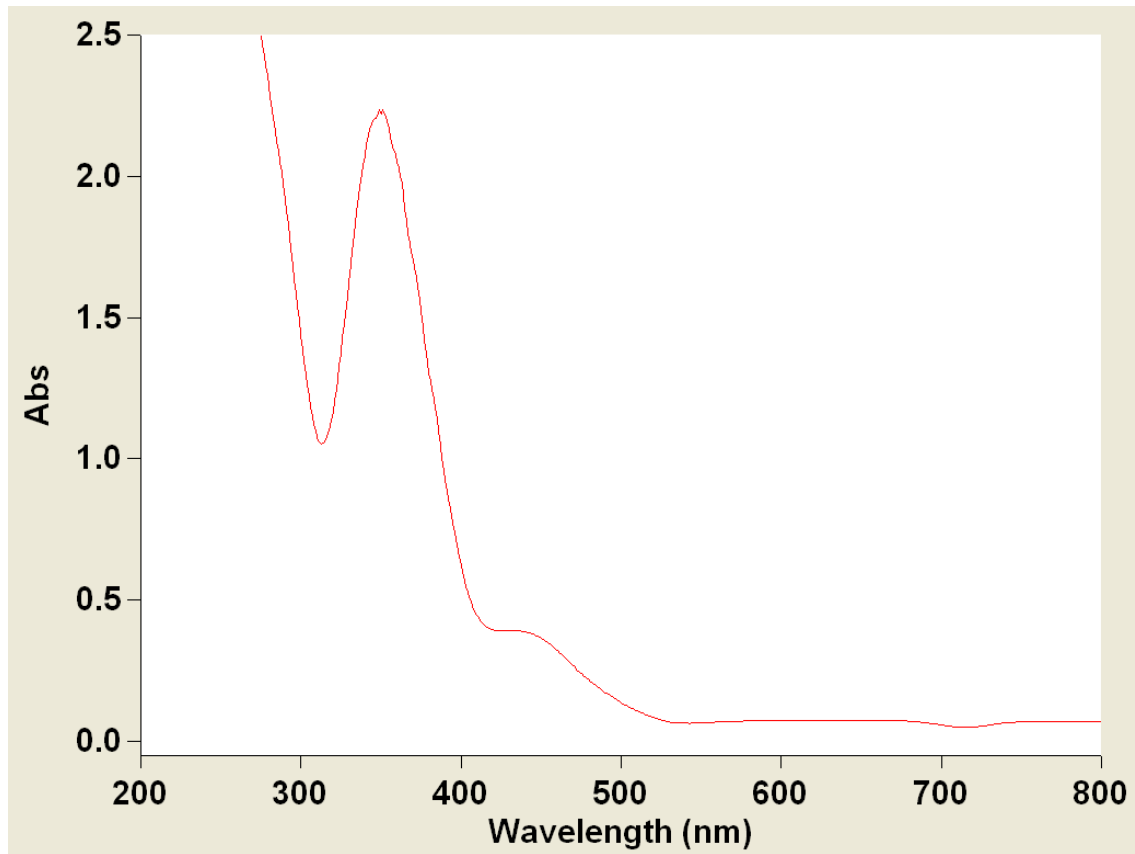


Figure 2.3: Absorption Spectrum of Potassium Dichromate

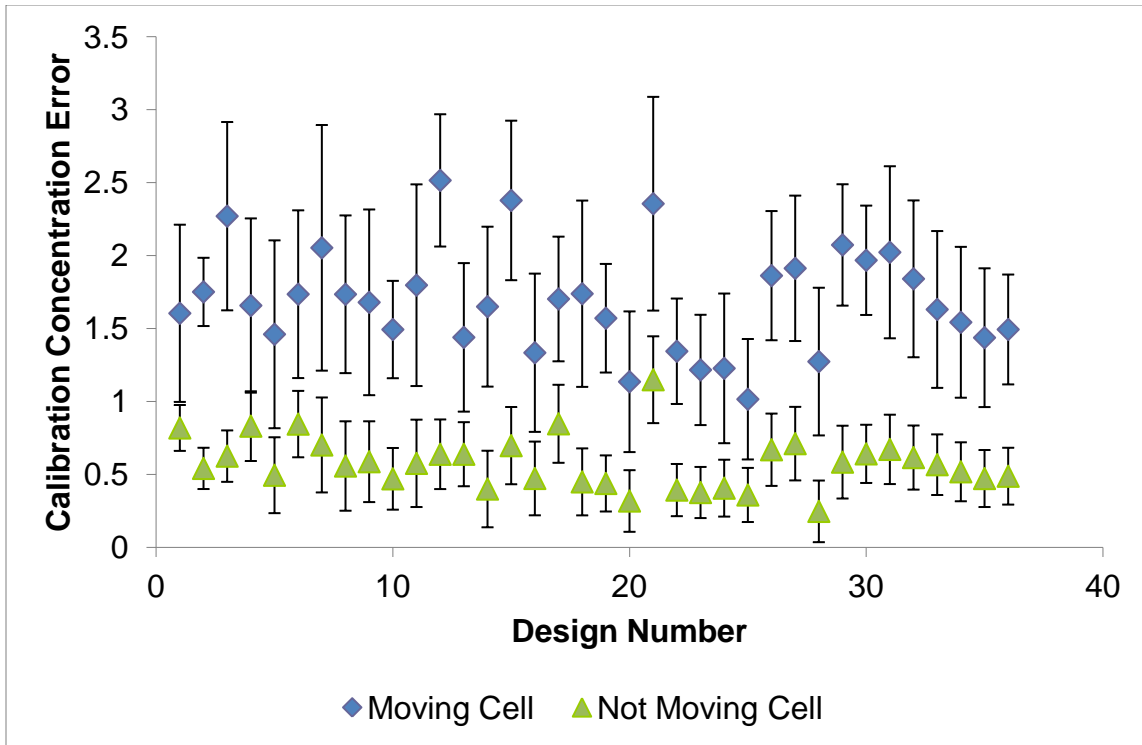


Figure 2.4: Comparison of MC and NMC relative to the CCE of each design, 3-decade, 435.0 nm

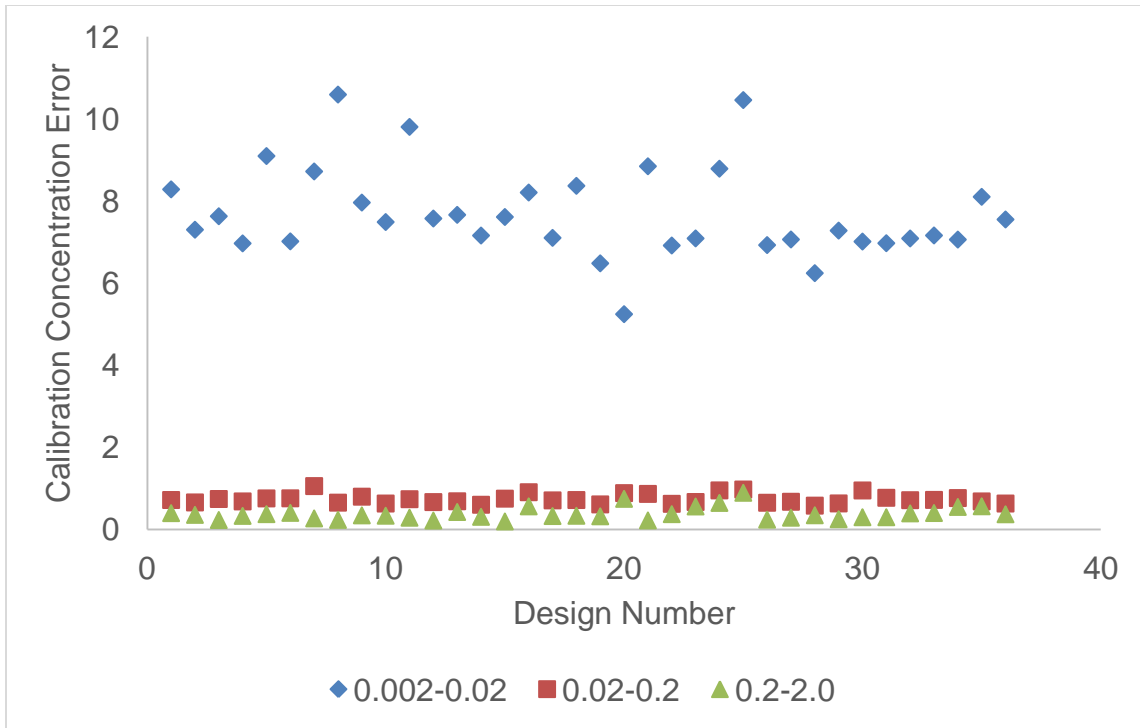


Figure 2.5: Comparison of single-decade designs: 0.002-0.02 AU, 0.02-0.2 AU, and 0.2-2.0 AU, without standard deviations, 348.0 nm, NMC

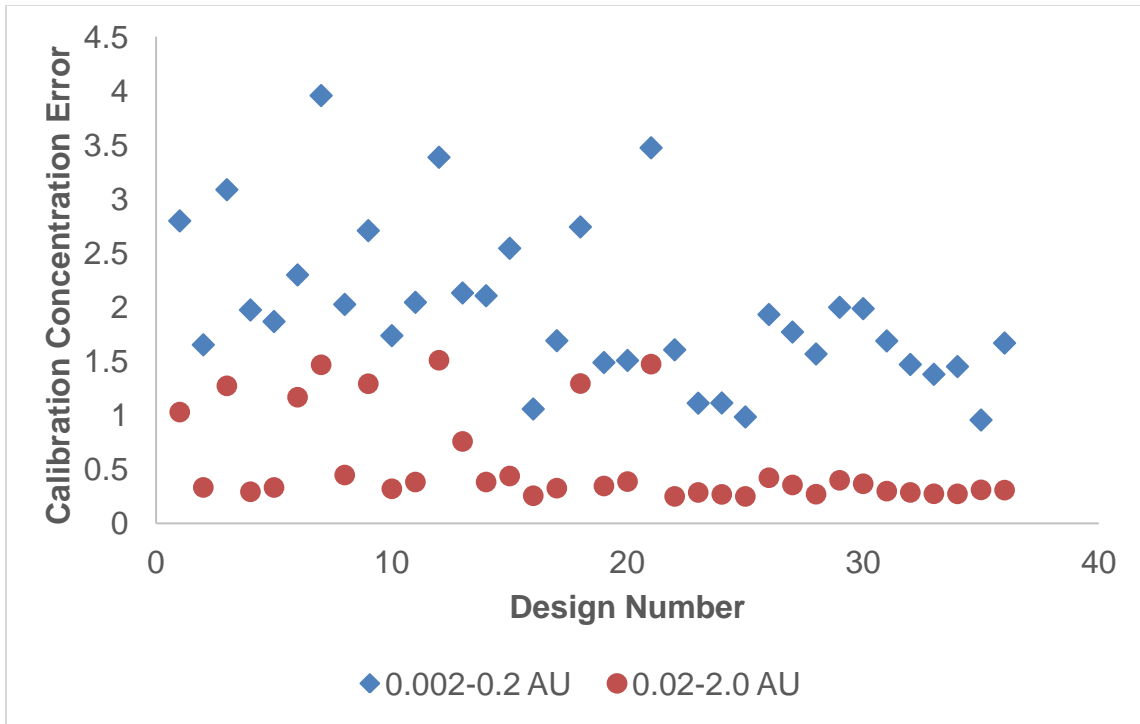


Figure 2.6: Two-Decade Concentration without standard deviations, 435.0 nm, MC.

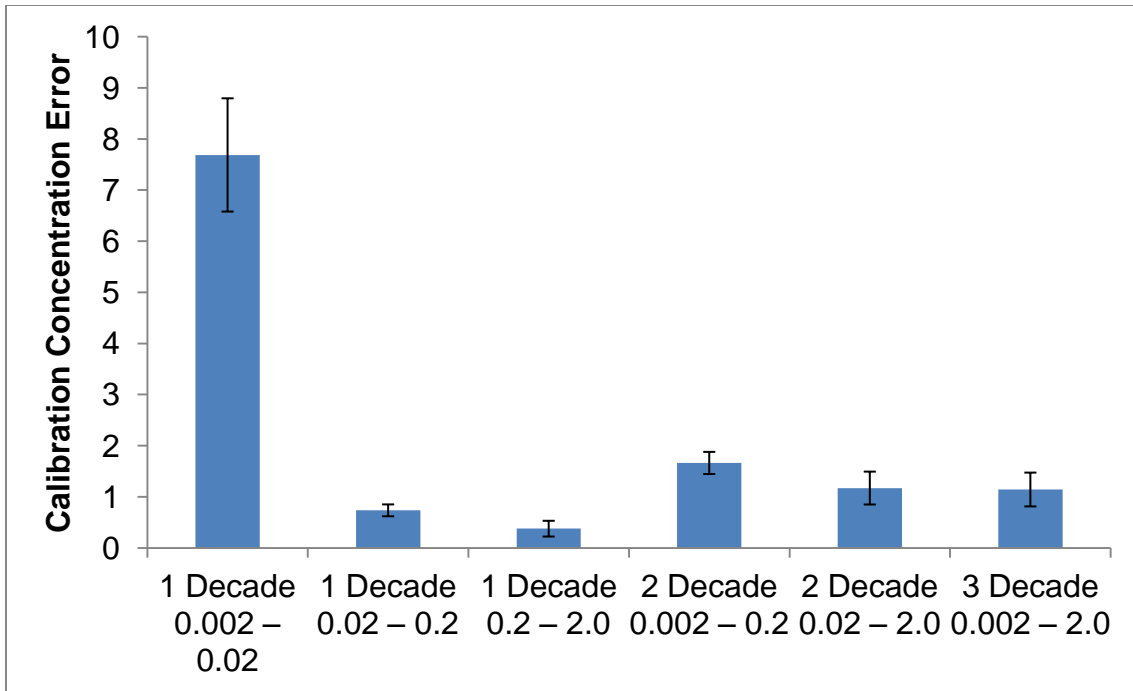


Figure 2.7: Calibration Concentration Error Comparison for all designs, 348.0 nm, NMC.

CHAPTER 3

DETERMINING A SOLUBILITY PRODUCT CONSTANT BY POTENTIOMETRIC TITRATION TO INCREASE STUDENTS' CONCEPTUAL UNDERSTANDING OF POTENTIOMETRY AND TITRATIONS¹

3.1 ABSTRACT

Potentiometric titrations are widely taught in first-year undergraduate courses to connect electrochemistry, stoichiometry, equilibria and reinforce acid-base titrations. Students perform a potentiometric titration that is then analyzed to determine analyte concentrations and the solubility product constant of the solid species.

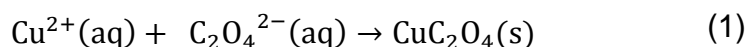
3.2 INTRODUCTION

Incorporating a direct potentiometric titration into the general chemistry laboratory adds a hands-on learning experience to electrochemistry. Potentiometric titrations have numerous and varied applications including determining protein binding of bacterial exudates,² characterizing functional groups,³ and characterization of surface chemistry.⁴ These diverse applications

¹ Adapted with permission from Grabowski, Lauren E.; Goode, Scott R. "Determining a Solubility Product Constant by Potentiometric Titration To Increase Students' Conceptual Understanding of Potentiometry and Titrations." *J. Chem. Educ.* **2017**, *94*, DOI: 10.1021/acs.jchemed.6b00460. Copyright 2017 American Chemical Society and the Division of Chemical Education.

underline the importance of potentiometric titrations being introduced in the undergraduate laboratory.

There are a number of publications in the *Journal of Chemical Education* that describe potentiometry with inexpensive yet functional electrodes.⁵⁻⁷ This experiment utilizes a copper wire indicator electrode. The potential of the cell is measured as a standard sodium oxalate solution is added to a copper solution.



The students obtain a titration curve and analyze it to determine the solubility product constant of copper oxalate. This experiment is designed to enhance the students' problem solving and analytical reasoning skills and increase their conceptual understanding of both potentiometry and titrations.

3.3 EXPERIMENTAL OVERVIEW

This experiment was performed by honors general chemistry students working in pairs in the second semester of their laboratory during each of the last four years. Students learned the foundations of potentiometry prior to the laboratory. The experiment requires an analysis of the experimental titration curve to determine fundamental parameters, an experience that is quite different from calculating a titration curve using provided constants, most often the weak acid ionization constant, K_a . Students make an approximate copper solution then titrate with standardized sodium oxalate; from the equivalence point they calculate the initial amount and initial concentration of $\text{Cu}^{2+}(\text{aq})$. The measured potential is described by Eqn 2:

$$E = E^{\circ} + E_{\text{error}} - \left(\frac{0.05916}{2} \right) \log_{10} \left(\frac{1}{[\text{Cu}^{2+}]} \right) - E_{\text{Ref}} \quad (2)$$

Combining the terms for standard potential (the reduction of Cu^{2+} to Cu), error (junction potential) and reference electrode potential (AgCl to Ag, when the Ag/AgCl reference electrode is used) into a single term, E , results in Eqn 3:

$$E = E' - \left(\frac{0.05916}{2} \right) \log_{10} \left(\frac{1}{[\text{Cu}^{2+}]} \right) \quad (3)$$

Students measure the initial potential E , in volts and calculate the initial molar concentration (from the equivalence point of the titration curve) allowing them to evaluate E' .

Beyond the equivalence point the concentration of the excess sodium oxalate can be calculated from the volumes and concentrations of the reagents and the $[\text{Cu}^{2+}]$ calculated from the potential and Eqn 3. The solubility product constant can be calculated at several points beyond the equivalence point as well as from replicate titrations.

Students were provided with the laboratory handout (see Appendix A) containing a pre-lab assignment, some background on potentiometric titrations including equations, a list of materials, procedure, data analysis to be performed, a list of questions for the post-lab report, two forms of a post-lab quiz, and the rubric used to determine grades. The pre-lab exercise consisted of an example problem and safety question. The example problem required that the students demonstrate their ability to determine K_{sp} of a similar chemical system when they knew initial and final potentials along with the equivalence point volume of standard. The safety question ensured they knew the hazards of the lab and how

to minimize risks associated with the hazards. Reading a safety data sheet (SDS) is a skill emphasized in all lab experiments in the course.

Prior to lab the students turned in their pre-lab exercise and the teaching assistant reviewed the calculations. Safety information and titration setup were also discussed. In the lab, groups prepared their own electrode, set up their titration apparatus, and tabulated their potentials using a LabQuest system (Vernier Scientific, Beaverton, OR). Sample potentiometric titration data can be found in Appendix A.

3.4 EXPERIMENTAL APPARATUS

The reference electrode is the Ag/AgCl electrode used in a pH combination electrode. Even a pH electrode in which the pH sensing glass is broken can be used. The indicator electrode is the copper wire. We attached a BNC-T to the pH meter or LabQuest voltage amplifier but we drilled the central connector on one half of the T so only the ground from the pH electrode, which is the Ag/AgCl reference, made electrical contact. The copper electrode was connected to a BNC-alligator clip cable and the ground (shield) black alligator clip was removed. Thus the copper electrode was connected to the central contact and the reference electrode to the shield/ground of the pH meter, as shown in Fig. 3.1. A photograph appears in Appendix A.

In general, metal electrodes do not equilibrate rapidly and the potential takes a time to stabilize. Using a mercury/copper amalgam electrode was investigated, and we found improved electrode response, but the clean copper electrode provided about the same results without generating mercury-containing

waste. The data presented all come from a copper electrode that was cleaned in 6 M nitric acid.

A reviewer points out that if we are not interested in determining the standard potential, we could set up a concentration cell with two copper electrodes connected by a salt bridge. As the titration proceeds, the titration curve will be identical in shape to that shown in Fig 3.2 but the potential will begin at zero and decrease.

3.5 HAZARDS

This experiment utilizes 6 M nitric acid which is made in advance and kept in the hood. Students wear lab coats over protective clothing, gloves and eyewear whenever in laboratory.

3.6 RESULTS AND DISCUSSION

The pedagogical aims for this laboratory are focused on teaching the fundamentals of potentiometry. The first goal of this experiment was to understand that many electrodes need not be purchased but can be made by chemists. Second, students develop lab skills by obtaining a titration curve by measuring potential and plotting against the volume of standard titrant. Last, students learn how fundamental constants like K_{sp} can be determined by experiment.

The degree of difficulty for this experiment was set for a first-year honors general chemistry laboratory course but can easily be modified for different levels ranging from freshman chemistry to instrumental analysis. Students should be familiar with electrochemistry, the Nernst equation, and calculations involving

sparingly soluble substances along with previous lab experience performing titrations.

The initial solution is made by dissolving copper(II) sulfate hydrate, which is not a pure substance, to make a known volume of solution. Measuring the mass is not as accurate as determining the concentration by titration due to the uncertainty of the number of waters of hydration, which depend on the age and storage of the copper sulfate. While it is true that copper sulfate kept in a desiccator can be expected to assume a stable, known stoichiometry, many other hydrates do not.

From the titration data the equivalence point can be determined via the derivative, as shown in Fig 3.2, and K_{sp} can be calculated as described previously. The average pK_{sp} at three points after the equivalence point, along with a measure of the standard deviation, can be calculated and is shown in Table 3.1. This value can then be compared to the literature K_{sp} value of 1.4×10^{-8} or $pK_{sp} = 7.85$.

Internet research shows values for K_{sp} ranging from 3×10^{-8} to 2.2×10^{-10} but none of the web pages provided references to the primary literature. The two references we found both reported 1.4×10^{-8} , which is the value we provide to students.^{8,9}

Student grades were assessed by evaluating their lab technique along with grading a post-lab report. The post-lab questions and discussion asked students to compare their experimental result to the literature value and recognize the magnitudes and sources of errors along with suggestions for

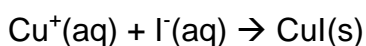
minimizing errors. The class mean K_{sp} was 7.8 ± 0.5 (\pm one sample standard deviation, $n = 31$) and was within experimental error of the literature value of 7.85.

As a reviewer mentioned, the complex formation is more complicated than presented here and affected by factors such as pH and ionic strength. In addition, a second complex with 1:2 stoichiometry is known to form with potassium and calcium ions ($[K_2 \text{ or } Ca]Cu(C_2O_4)_2$).¹⁰ Such a complex might be inferred from the systematic reduction in K_{sp} as the titration proceeded (Points 1, 2, and 3 in Table 1) past the equivalence point, but a second inflection point could not be seen when the titration was extended. This lab could easily be adapted to an upper-level course in analytical chemistry in which these topics are discussed.

We assessed problem solving skills with quizzes two weeks after the lab. The quiz problem used K_{sp} to calculate potentials as opposed to the experiment that used potentials to calculate K_{sp} . Neither potentiometric titrations nor precipitation titrations are covered in the lecture portion, so the problem presented could not be solved by a formulaic approach. The quiz problem follows.

Potentiometric titration quiz problem. Consider the potentiometric titration of 50.0 mL 0.100 M $Cu^+(aq)$ with 0.500 M iodide ion, $I^-(aq)$.

The chemical equation for the reaction is:



Before any iodide was added the initial potential of the Cu^+ electrode against a reference electrode is 0.200 V. Calculate the potential after 10.0 mL ($n= 12$) or 12.0 mL ($n = 15$) of iodide is added. The solubility product constant of copper(I) iodide is 1.0×10^{-12} .

Step 1. Analyze a precipitation titration to compute the concentration of Cu^+ after 10 mL (equimolar) or 12 mL (excess iodide) was added.

Results: 95% of the students coupled the titration and K_{sp} to try to calculate $[\text{Cu}^+]$ at the equivalence point. About 50% of the class made an error-free calculation when the sample and titrant were present in equimolar amounts and about 60% when the titrant was in excess.

Step 2. Students had to express the Nernst equation in the form that fit the problem and correctly compute E .

Results: 75% used $E = E^\circ - 0.059 \log (1/[\text{Cu}^+])$ and used 0.200 V (the initial potential) for E° .

Although disappointing, we realized the quiz question should have been reworded to emphasize the difference between calculating the potential of a cell in which the reference electrode potential is not known. Nearly all class examples and homework problems that required the Nernst equation had two cells in which E° values were known.

15% used $E = E' - 0.059 \log (1/[\text{Cu}^+])$ and correctly calculated E' from the initial data.

10% used $E^\circ = - 0.059 \log (1/K_{\text{sp}})$

3.7 CONCLUSIONS

General chemistry is a prerequisite for upper-level chemistry and the critical thinking, analytical reasoning, and laboratory skills in this experiment prepare the student for these advanced courses. This experiment integrates and adds a concrete application to the student's background knowledge of electrochemistry, cell potentials, solubility, and titrations. The electrode can be fabricated and the titration duplicated with three calculations of K_{sp} from each titration within two hours. The students in each group collaborate to determine the equivalence point and prepare graphs that can be cut and pasted in to their reports, but each individual calculates the solubility product constant and writes a lab report. Particular attention has been made to making this experiment cost effective, with chemicals and equipment readily available. Overall, the experiments described were successful and the goals were achieved.

3.8 ACKNOWLEDGEMENTS

We would like to acknowledge the contribution of the undergraduate students and teaching assistants of CHEM 142 honors general chemistry course for sharing their data and observations on this experiment.

3.9 REFERENCES

1. Grabowski, L.E.; Goode, S.R. Determining a Solubility Product Constant by Potentiometric Titration To Increase Students' Conceptual Understanding of Potentiometry and Titrations . *J. Chem. Educ.* **2017**, *94*, DOI: 10.1021/acs.jchemed.6b00460.
2. Seders, L. A.; Fein, J. B. Proton binding of bacterial exudates determined through potentiometric titrations. *Chem. Geol.* **2011**, *285*, 116-123.
3. Calero, M.; Hernáinz, F.; Blázquez, G.; Martín-Lara, M. A. Potentiometric Titrations for the Characterization of Functional Groups on Solid Wastes of the Olive Oil Production. *Environ. Prog. Sustain. Energy* **2010**, *29* (2), 249-258.
4. Gorgulho, H. F.; Mesquita, J. P.; Gonçalves, F.; Pereira, M. F. R.; Figueiredo, J. L. Characterization of the surface chemistry of carbon materials by potentiometric titrations and temperature-programmed desorption. *Carbon* **2008**, *46*, 1544-1555.
5. Berger, M. Potentiometric Determination of Chloride in Natural Waters: An Extended Analysis *J. Chem. Educ.* **2012**, *89*, 812-813.
6. Bendikov, T. A.; Harmon, T. C. A Sensitive Nitration Ion-Selective Electrode from a Pencil Lead *J. Chem. Educ.* **2005**, *82* (3), 439-441.
7. Thomas, J. M. Student Constructions of a Gel-Filled Ag/AgCl Reference Electrode for Use in a Potentiometric Titration. *J. Chem. Educ.* **1999**, *76* (1), 97-98.
8. Zhuk, N. P. Thermodynamic constants of sulfates, carbonates, chromates, bromates, iodates, oxalates, and other salts slightly soluble in water. *Zhurnal Fizicheskoi Khimii* **1954**, *29*(9) 1690-1697.
9. Shchigol, M.B. Copper borates, oxalates and salicylates. *Zhurnal Neorganicheskoi Khimii* **1965**, *10*(9) 2097-2107.
10. Cui, A-L.; Wei, J-Z.; Yang, J.; Kou, H-Z. Controlled Synthesis of Two Copper Oxalate Hydrate Complexes: Kinetic versus Thermodynamic Factors. *J. Chem. Educ.* **2009**, *86* (5), 598-599.

Table 3.1 Calculated K_{sp} Values Taken for Three Points After the Equivalence Point

Data point	Vol oxalate added, mL	Measured Potential (mV)	$[Cu^{2+}]$, M	$[C_2O_4^{2-}]$, M	K_{sp}	pK_{sp}
Initial	0	95.0	5.01×10^{-3}	0	0	-
1	6.15	37.2	1.31×10^{-5}	1.07×10^{-3}	1.41×10^{-8}	7.85
2	6.52	32.4	1.46×10^{-5}	1.42×10^{-3}	2.07×10^{-8}	7.68
3	7.10	25.5	1.71×10^{-5}	1.95×10^{-3}	3.35×10^{-8}	7.48
Average						7.67
Standard deviation						0.19

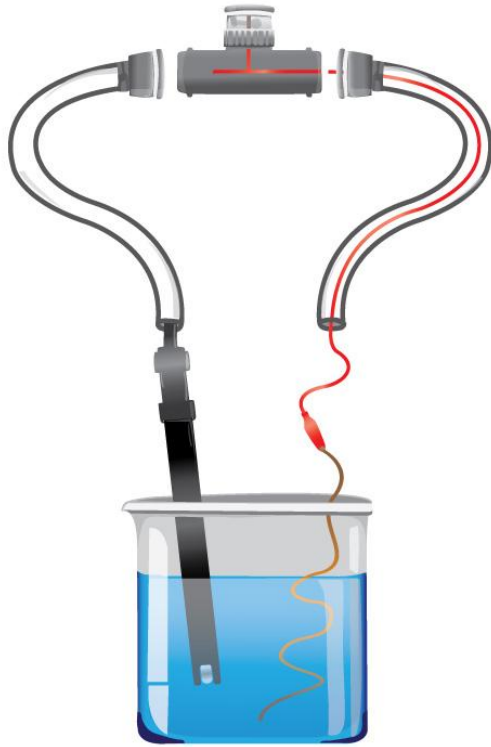


Figure 3.1: Schematic diagram of apparatus. Ground connection is pH reference and center connection is clean copper wire.

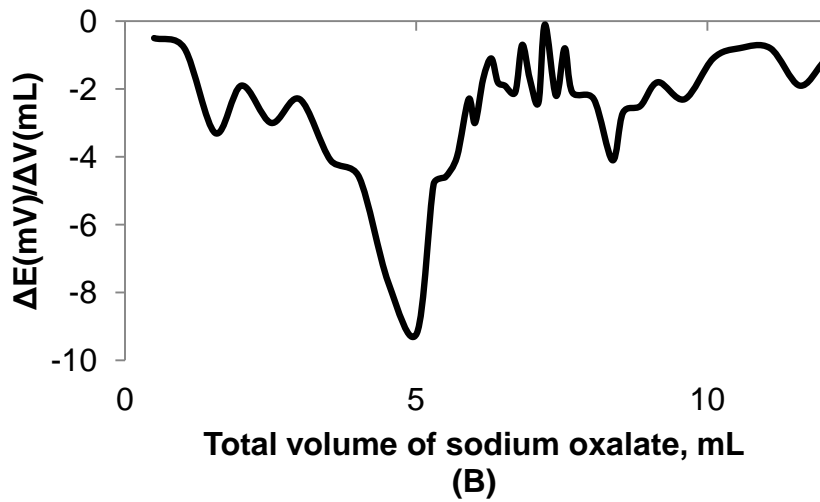
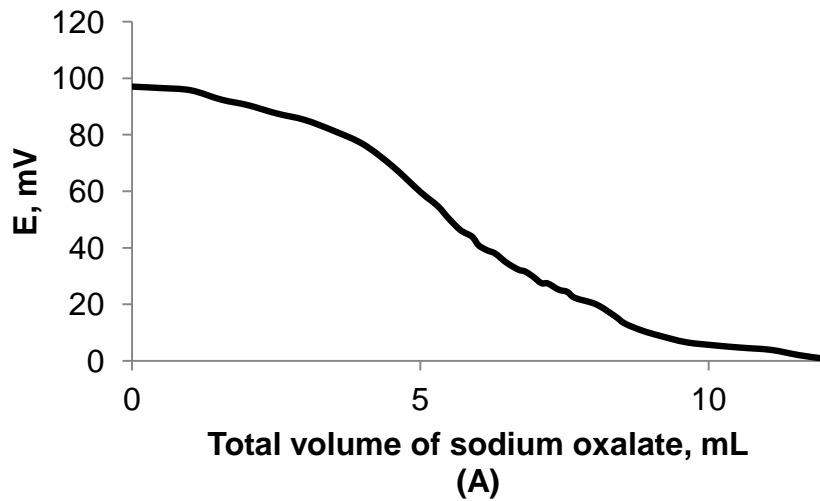


Figure 3.2: Experimental data. A) Titration curve B) Derivative (difference between successive points)

CHAPTER 4

REVIEW AND ANALYSIS OF SAFETY POLICIES OF CHEMICAL JOURNALS¹

4.1 ABSTRACT

Advances in chemistry are highly dependent on the procedures published in peer-reviewed journals. Some chemistry journals require authors to address safety considerations in their manuscripts but others do not. In this study, we examined 726 chemistry journals from 28 publishers to determine if they require the author to mention safety precautions. Journals supply information for authors that generally mention safety in two places. In the guidelines for authors, which are widely read by prospective contributors, 8% mention safety. Most journals have ethics guidelines of which 59% mention safety.

In order to determine the effectiveness of safety policies 100 articles from each of six journals that published research that involved extensive syntheses were selected. The results of the search indicated that the target compounds were mentioned 107 times but only one mention carried any safety precaution.

¹ Adapted with permission from Grabowski, Lauren E.; Goode, Scott R., *J. Chem. Health Saf.*, **2016**, 23 (3), 30-35. © 2016 Elsevier.

4.2 INTRODUCTION

Advances in chemical sciences build on the results of others which are peer-reviewed and published in reputable journals. Unfortunately, too many peer-reviewed papers make no mention of the hazards and risk-minimization activities that were often developed in concert with the research. Langerman mentions this problem in a recent commentary²: “A researcher today, going back in JACS or JOC to the early 1900s will find a detailed explanation of how the work was done, but they will not find any description of the hazards involved. Even if the synthesis of an organometal poly azido detonated the first six times the chemist did it, the published paper will very likely not mention it.”

As knowledge progresses one might hope that safety notifications are more common. In this study, we searched the publication guidelines for 726 chemical journals to see if safety information is required and how this requirement is communicated to authors. We then searched 600 manuscripts published in early 2015 from journals that describe synthetic chemistry to determine if the authors communicated that a particular chemical mentioned in the paper was designated as a Particularly Hazardous Substance.

4.3 PUBLICATION SAFETY REQUIREMENTS COMMUNICATED TO AUTHORS

Every journal has a web site that provides information to potential authors often with hyperlinks to other pages. In general, the journal's safety information requirements are found in one of two different environments, described below.

Journal Guidelines for Authors Journal guidelines are set by the specific journal and usually appear under a name such as “guidelines for authors.” The guidelines inform the author of the scope of the journal and the content that should be contained in the author’s manuscript. These guidelines frequently describe different types of manuscripts that are accepted by the journal and the format for the prepared manuscript.

Ethics Guidelines Most journals have ethics guidelines that present the values and standards each publisher expects of its journal authors. Ethics guidelines can include but are not limited to, plagiarism, data manipulation, simultaneous submission, and authorship criteria. Ethics guidelines are often common to all journals of a particular publisher but some are found within the journal guidelines for authors. Other journals do not have readily apparent ethics guidelines that do not appear on the journal home page or on links from the home page or on the publisher’s home page. It is possible that ethical requirements are located elsewhere within the web of information.

A small poll asked researchers about their familiarity with ethics guidelines and their perceptions of the important issues mentioned in these guidelines.

4.4 EVALUATING JOURNAL SAFETY REQUIREMENTS

Selecting Journals A total of 726 chemistry journals were examined. All chemistry journals with an impact factor placing them in the top 40, all American Chemical Society (ACS) journals, all Royal Society of Chemistry (RSC) journals as well as nearly all the chemical offerings from Springer, Elsevier, Wiley, and

Taylor & Francis were included. In all, 28 publishers were represented in the group.

The list of 726 does not include every chemistry journal. To be included on the list the journal must be currently publishing and accepting manuscripts, contain peer-reviewed chemistry manuscripts that are written in English, and have available guidelines for authors. Journals that specialize in review articles and databases were omitted because safety warnings might have been present in the primary publications but deleted from the reviews.

Locating Safety Information The journal and ethics guidelines were searched for the following four safety keywords: “caution,” “hazard,” “danger,” and “safety.” Guidelines that contained any of those words were further examined to evaluate the safety information required in the manuscript.

Evaluating the Effectiveness of Safety Guidelines To determine the effectiveness of the guidelines a subset of the 726 journals was chosen for closer examination. Because most people feel that many chemical reactions have inherent risks that can be mitigated by proper safety procedures, journals that described the synthesis of new compounds were selected. One hundred journal articles were examined for each of the following journals: The Journal of Organic Chemistry (published by the ACS), Organic and Biomolecular Chemistry (RSC), Catalysis Letters (Springer), Tetrahedron (Elsevier), The European Journal of Organic Chemistry (Wiley), and Organic Preparations and Procedures International: The New Journal for Organic Synthesis (Taylor & Francis). The articles were all published between January and May 2015 other than for the

Taylor & Francis publication which required a longer time period to accumulate 100 articles. Only original papers were examined; review articles would be unlikely to include safety warnings. Each of the 600 articles was searched for the presence of the four safety keywords as well as for mention of the following 11 compounds: butyl lithium, lithium aluminum hydride, silane, germane, hydrogen peroxide, hydrofluoric acid, trifluoroacetic acid, phosphine, diazomethane, white phosphorous, and arsine. These reagents were chosen because they are useful chemical reagents and all can be found on published lists of Particularly Hazardous Substances.³⁻⁵ The OSHA Laboratory Standard (29 CFR 1910.1450(e)(viii)) does not include a list of Particularly Hazardous Substances but requires that employers protect and train workers who handle “select carcinogens,” reproductive toxins and substances which have a high degree of acute toxicity.⁶ These terms are interpreted by safety professionals at individual organizations who publish lists of Particularly Hazardous Substances and the methods by which the organization safeguards the health of its workers.

4.5 RESULTS

Location of Safety Information

Journal Guidelines for Authors Only 62 of the 726 journals included a safety keyword in their journal guidelines for authors but three of the 62 equivocated by stating it was optional, or needed under special circumstances. Thus, only 59 journals (8% of the Chemistry journals surveyed) included a safety keyword in the journal guidelines for authors. It is logical to infer that journals that do not mention safety in their guidelines do not require mention of safety in their

manuscripts. Table 4.1 depicts the number of journals by each publisher along with the number of journal guidelines for authors that contained a safety keyword and the percentage of journals by the publisher that mentioned a safety keyword in the author guidelines.

Ethics Guidelines The ethics guidelines of journals from 28 different publishers were examined. Three publishers – ACS (48 journals), RSC (38), and Taylor & Francis (82) have ethics guidelines that include a safety keyword as do 217 of 221 Elsevier journals. These publishers largely have one ethics statement, which includes a safety keyword, referenced by their journals. The other three publishers in Table 4.1, DeGruyter, Springer and Wiley, did not have a consistent ethics policy for their journals. The ethics statements differed among journals from the same publisher; some lacked an ethics statement, some had a separate ethics statement and some had the ethics statement in the author guidelines. Of those journals that had ethics statements, some included a safety keyword and others did not.

Of the six publishers that had ethics guidelines that included a safety keyword (ACS, RSC, Elsevier, Wiley, DeGruyter and Taylor & Francis), four publishers stated that any “unusual hazards” inherent in the chemicals, procedures, or equipment should be clearly stated in the manuscript. None defined “unusual hazard.”

Of the 21 “Other” publishers 10 lacked ethics guidelines and none of the other 11 included a safety keyword.

The percentage of journals that have ethics guidelines that contain a safety keyword are shown in Figure 4.1.

Faculty Perceptions of Ethics Guidelines Faculty at several institutions were asked if they read ethics guidelines and what information they recalled from these guidelines. The results are summarized in Tables 4.2 and 4.3.

Effectiveness of Guidelines One hundred articles from each of the six publishers were searched for the safety keywords. Table 4.4 depicts the number of articles that contained a safety keyword for each grouped by publisher.

The 600 articles were searched for mention of the 11 target compounds. Of the compounds examined, white phosphorous and arsine were not mentioned in any articles. The other nine compounds and the number of articles in which they were mentioned are shown in Table 4.5. Of 107 mentions of these compounds only one mentioned safety (in the use of hydrogen peroxide).

4.6 DISCUSSION

Journal Guidelines for Authors The journal guidelines for authors contain the majority of information needed for an author to publish an article and widely read by most manuscript authors. RSC, Springer, DeGruyter, and Taylor & Francis make no mention of safety in any of their journal guidelines. The ACS is the only major publisher in which the majority (83%) of its guidelines require the author mention safety in the manuscript.

The 59 journals that had a safety keyword in the author guidelines generally indicated the section of the manuscript in which safety would be addressed, as outlined in Table 4.6. Most journals (56%) suggest safety

keywords belong in the experimental/methods section but one journal asked that safety be addressed in the cover letter.

The majority of the journals utilize phrases such as “Precautions for handling dangerous materials or for performing hazardous procedures must be explicitly stated.” Other journals say that any unusual or new hazards (never defined) should be clearly identified; some require the addition of the word ‘Caution’ followed by a brief description which draws the reader’s attention when a hazardous material or procedure occurs.

Ethics Guidelines Most ethics guidelines are set by the publisher, though some publishers have different ethics guidelines for some of their journals. Nearly all (98%) of the journals published by the ACS, RSC, Elsevier, and Taylor & Francis include a link to separate ethics guidelines that contain a safety keyword. Readily found ethics statements were found in some of the journals published by Wiley (76%), Springer (58%) and Other (43%).

Effectiveness of Guidelines By examining the published articles it is possible to determine whether the safety precautions are actually mentioned. Safety keywords were found in less than 10% of the published articles in the six synthetic journals surveyed.

ACS The journal’s guidelines for authors states that “special attention should be called to hazardous compounds or operations, and appropriate precautions should be described.⁷” Most chemists would define “hazardous compounds” as those that appear on one of the widely used Particularly Hazardous Substances list. Unfortunately, the usage of butyl lithium, lithium

aluminum hydride, hydrogen peroxide, hydrofluoric acid, and trifluoroacetic acid was described in 19 of the articles and none provided a caution. The ACS also publishes safety requirements in their ethics guidelines: “any unusual hazards inherent in the chemicals, equipment, or procedures used in an investigation should be clearly identified in a manuscript reporting the work.⁸”

The Journal of Organic Chemistry by the American Chemistry Society was found to contain a safety keyword in 11 of the 100 articles examined. Six of the cautions were related to hazardous operations such as the need for PPE.

RSC The Royal Society of Chemistry’s journal Organic and Biomolecular Chemistry has no safety requirements in the author guidelines. Ethics guidelines are found in Author responsibilities that include Authenticity & professionalism guidelines that state “Identify clearly in the manuscript any unusual hazards inherent in the use of chemicals, procedures, or equipment in the investigation.⁹” Although there were 22 mentions of target compounds (Table 4.5) only two RSC articles mention using PPE or other precautions.

Springer Springer’s journal Catalysis Letters was the only journal that lacked a safety keyword in either the journal guidelines for authors or the ethics guidelines of the publisher. Springer does not have a global ethics guideline for its journals. Of the 132 Springer journals examined, 11 of them had separate ethics guidelines, all lacking a safety keyword. The ethics guidelines were found in the journal guidelines for authors in 65 of the journals but none included a safety keyword. No ethics guidelines were found in the other 56 journals. Thus, Springer was found to have no mention of a safety keyword in any of their

guidelines for authors. Searching of the 100 journal articles found the word “caution” mentioned one time, and the mention was in the context of urging the reader take caution when using the results or methods described in the article. None of the nine target compounds found in the articles were cautioned.

Elsevier Tetrahedron by Elsevier has clearly stated safety guidelines: “Authors are requested to draw attention to hazardous materials or procedures by adding the word CAUTION followed by a brief descriptive phrase and literature references if appropriate.¹⁰” Only two of the articles used caution to represent an exothermic reaction or that a specific chemical was hazardous. Both of those journals did state the word caution followed by a description of the caution. Target compounds appeared 29 times in these articles but none received a caution.

Wiley None of the Wiley journals contained a safety keyword in their guidelines for authors. Some Wiley journals had different external ethics guidelines, others included ethics guidelines within the author guidelines (without safety mentions) and yet others lacked ethics guidelines. The European Journal of Organic Chemistry uses the ethics guidelines of the European Association of Chemical and Molecular sciences that asks authors “to identify clearly in the manuscript any unusual hazards inherent in the use of chemicals, procedures or equipment in the investigation.¹¹” This ethics statement is identical to that of the RSC.

Of the mentions of safety in Wiley articles, only two mentions referred to precautions for substances or procedures; the other mentions were in contexts

such as using the data with “caution.” There were, however, two articles whose authors chose to mention that none of the compounds or procedures required extra precautions.

Taylor & Francis Taylor & Francis’ journal guidelines for authors lacked a safety keyword but all journals have a separate ethics guidelines that stated “authors must include all appropriate warnings concerning any specific and particular hazards that may be involved in carrying out experiments or procedures described in the article or involved in instructions, materials, or formulae in the article; include explicitly relevant safety precautions, and cite, if an accepted standard or code of practice is relevant, a reference to the relevant standard or code.¹²” This ethics guidelines was the most easily accessible of any publisher’s ethics guidelines.

Even though the journal guidelines for authors of Organic Preparations and Procedures International: The New Journal for Organic Synthesis did not explicitly state the need for safety to be in their articles, Taylor & Francis had the highest number of articles that used one of the safety keywords with regard to identifying hazards; six of the articles had the word “CAUTION” in all upper case, which made the information stand out. Org Prep Proced Int is the only journal that mentioned problems related to scaling up an experiment. In addition, Org Prep Proced Int is the only journal with an article that mentioned safety in relation to one of the target compounds listed in Table 4.5 specifically that hydrogen peroxide is easy to handle but handling must always be done with caution. Eight other mentions of target compounds did not contain any caution.

The context and usage of each safety keyword found in the 600 articles is shown in Table 4.7. Many of the articles only mentioned safety in terms of the fact that the operation described was safer than the previously published method. Seven authors cautioned against using their results or methods mostly because they were considered to be preliminary. Articles in which the authors specified PPE or indicated an experiment was done under a hood are very helpful to the reader. Only seven articles made direct note of a specific chemical that was being used and that is indeed hazardous.

4.7 ANALYSIS

A number of holes are present in the safety net that underlies the communication of chemical information. Only 8% of the 726 journals had author guidelines that required safety to be mentioned in the manuscript although the majority (59%) had links to a separate ethics statement that contained a safety keyword.

Even when journals ask the authors to call attention to hazards, clear instructions for identifying hazards are absent as is the method that should be used to communicate the hazard. The most common request is to ask the authors to warn readers about unusual hazards, but the word “unusual” is not defined. The hazards associated with hydrofluoric acid are “usual” to the experienced user but the inexperienced user should be warned of its dangers.

Although the 9 target compounds were mentioned 107 times, only one article provided any cautionary information.¹³

Overall, publishers clearly want their journals to promote safety, most asking the author to note an “unexpected” hazard. But even then, how the

hazard is communicated is not consistent in most journals. Tetrahedron requires the use of the word “caution” followed by a descriptive phrase or literature reference. Six of the articles in Organic Preparations and Procedures International: The New Journal for Organic Synthesis had the word “CAUTION” in all capital letters.

4.8 RECOMMENDATIONS

Journal editors and editorial boards can take a few proactive steps that will greatly increase safety associated with the published information. The increase in safety consciousness in preparing a manuscript for publication will likely initiate a safety dialog among authors and act to improve the safety culture of chemical research laboratories.

Because most authors do not look for safety information in ethics guidelines the journal’s guidelines for authors should have a separate section that outlines the journal’s safety notification requirements. A reasonable expectation is that authors designate hazards that might not be recognized by a first-year graduate student who has been asked to replicate the published procedure. Substances or processes that are potential (as opposed to “unusual”) hazards should be flagged.

All compounds that require a Standard Operating Procedure should be noted by the manuscript author. Some journals might require a special symbol, for example: “. . . and t-butyl lithium† was added.” (†Hazardous, requiring a Standard Operating Procedure.)

Other journals might require the word CAUTION: “. . . and t-butyl lithium was added (CAUTION – requires SOP).”

Some journals may choose to ask authors to address safety in a separate section of the manuscript. Laboratory experiments published by the *Journal of Chemical Education* have a subsection entitled Hazards, in the Experimental section; if there are no hazards, that information is presented: “There are no physical hazards involved with this experiment.¹⁴” Other journals may ask authors to provide safety information with supplementary materials that will be archived electronically.

Reviewer forms should include a separate area in which the reviewer is asked if all Particularly Hazardous Substances are noted and all potentially hazardous procedures and processes flagged.

Proper training, procedures, engineering controls and personal protective equipment afford safe handling of nearly all substances. We note that it is not “unexpected” for flammable solvents to burn in the presence of an open flame but each year we read of injuries as the result of a solvent like methanol transferred from one container to another while a flame is nearby. These injuries could be avoided by adding a few cautionary words to the procedure.

4.9 ACKNOWLEDGEMENTS

The authors would like to acknowledge Neal Langerman for his help in identifying target compounds. This project was supported in part by the U.S. Department of Education through the GAANN program, award number P200A120075.

4.10 SUPPLEMENTARY DATA

<http://www.sciencedirect.com/science/MiamiMultiMediaURL/1-s2.0-S1871553215001048/1-s2.0-S1871553215001048-mmc1.xlsx/273458/html/S1871553215001048/99ebfaa98cd98c14b3ad37c498fe5d95/mmc1.xlsx>

4.11 REFERENCES

1. Grabowski, Lauren E.; Goode, Scott R., *J. Chem. Health Saf.*, **2016**, 23 (3), 30-35.
2. Langerman, N. *J. Chem. Health Saf.* **2015**, 22(3), 44.
3. http://web.ornl.gov/sci/psd/mst/rsg/pdf/OSHA_Haz_List_.pdf (verified 10.07.15).
4. https://www.safety.duke.edu/OHS/Documents/PHS_by_CAS.pdf (verified 10.07.15).
5. <http://www.safety.vanderbilt.edu/chem/managing-particularly-hazardous-substances.php> (verified 10.07.15).
6. <http://www.gpo.gov/fdsys/pkg/CFR-2010-title29-vol6/pdf/CFR-2010-title29-vol6-sec1910-1450.pdf> (verified 11.09.15).
7. http://pubs.acs.org/paragonplus/submission/jocean/jocean_authguide.pdf (verified 10.07.15).
8. <http://pubs.acs.org/userimages/ContentEditor/1218054468605/ethics.pdf> (verified 10.07.15).
9. <http://www.rsc.org/journals-books-databases/journal-authors-reviewers/author-responsibilities/#authenticity-professionalism> (verified 10.07.15).
10. http://www.elsevier.com/wps/find/journaldescription.cws_home/942?generate_pdf=true (verified 10.07.15).
11. http://www.euchems.eu/fileadmin/user_upload/Publications/Ethicalguidelines_tcm23-54057.pdf(verified 10.07.15).
12. <http://journalauthors.tandf.co.uk/preparation/ethics.asp> (verified10.07.15).
13. Shi, X. J.; Tan, F. F.; Chen, Q. Q.; Su, W. K. *Org. Prep. Proced. Int.* **2015**, 47(1), 80.
14. Pritchard, B. P.; Simpson, S.; Zurek, E.; Autschbach, J. *J. Chem. Educ.* **2014**, 91,1058.

Table 4.1 Appearance of Safety Keywords in Journal Guidelines for Authors. Organized by Publisher.

	ACS	RSC	Springer	Elsevier	Wiley	Taylor & Francis	DeGruyter	Other Publishers
Total Number of Journals	48	38	132	221	148	82	29	28
Journals with Safety Keywords	39	0	0	10	5	0	0	5
Journals without Safety Keywords	6	38	132	211	143	82	29	23
Other	3	0	0	0	0	0	0	0
Percentage of Journals mentioning a safety keyword	83%	0%	0%	5%	3%	0%	0%	18%

Table 4.2 Frequency of Reading Ethics Guidelines (n=28)

Frequency of use	Percentage
Always	11%
Sometimes	19%
Occasionally	19%
Rarely	26%
Never	26%

Table 4.3 Perceptions of Contents of Ethics Guidelines (n=28)

Topic	Number of mentions
Integrity	13
Data (trimming, omission, archiving)	10
Authorship	10
Simultaneous submission	4
Conflicts of interest	4
Permissions	4
Prior publication	3
Citations	3
Safety	0

Table 4.4 Number of Journal Articles Containing a Safety Keyword

Keyword	ACS	RSC	Springer	Elsevier	Wiley	Taylor & Francis
Safety	2	0	0	0	3	3
Caution	8	3	1	3	4	9
Danger	0	0	0	0	0	1
Hazard	1	1	0	3	4	1

Table 4.5 The Number of Articles that Mentioned the Target Compounds

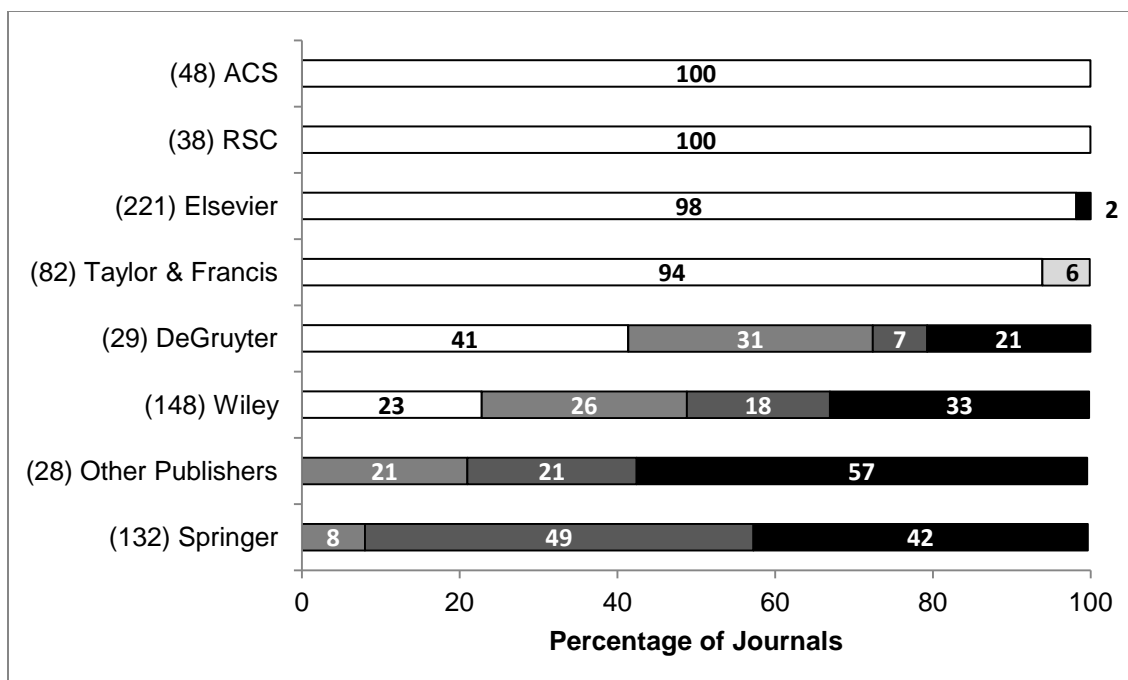
	ACS	RSC	Springer	Elsevier	Wiley	Taylor & Francis
butyl lithium	1	0	0	0	0	0
lithium aluminum hydride	2	4	1	8	1	3
silane	0	1	0	2	0	0
germane	0	0	0	1	0	0
hydrogen peroxide	4	0	3	2	2	4
hydrofluoric acid	1	2	3	1	0	0
trifluoroacetic acid	11	14	1	10	15	2
phosphine	0	0	1	5	0	0
diazomethane	0	1	0	0	1	0
Total	19	22	9	29	19	9
Safety warning related to target compound	0	0	0	0	0	1

Table 4.6 Locations in Which Safety Should be Mentioned Specific by Guidelines for Authors

Safety Location	Number of Journals
Abstract	1
Both Experimental & Discussion	1
Unspecified Location	24
Experimental / Methods	33

Table 4.7 The Use of Safety Keywords

	ACS	RSC	Springer	Elsevier	Wiley	Taylor & Francis
No precautions necessary	0	0	0	0	2	0
Use PPE / fume hood	2	1	0	0	2	2
Exothermic / corrosive vapors from reaction	2	1	0	1	0	0
Caution adding chemical or heating	2	0	0	0	0	4
Caution scaling up reaction	0	0	0	0	0	1
Specific chemical is hazardous	0	0	0	1	0	6
Take "caution" when using these results / methods	2	1	1	1	2	0
Chose this method because it is "safer"	3	1	0	3	7	1



- Separate ethics statement that contains a safety keyword
- Separate ethics statement that contains a safety keyword but also an ethics statement in the guidelines for authors that does not contain a safety keyword
- Separate ethics statement that lacks a safety keyword
- Ethics statement in the guidelines for authors that lacks a safety keyword
- Ethics statement not found

Figure 4.1 Distribution of safety keywords in journal ethics guidelines with numbers of journals in parentheses

CHAPTER 5

RESPONSE TO REVIEW AND ANALYSIS OF SAFETY POLICIES OF CHEMICAL JOURNALS

5.1 INTRODUCTION

Recently, many tragic events, such as a hydrogen tank explosion at Tsinghua University in China and a massive fire at Jubail United Petrochemical in Saudi Arabia, have called the question the importance of safety in the chemical industry. A number of tragedies have also occurred in academia including an explosion at Texas Tech University and a fatal chemical fire at the University of California, Los Angeles. The publication of our article, *Review and Analysis of Safety Policies of Chemical Journals*, helped open up a conversation about the safety policies of chemical journals.¹

The American Chemical Society (ACS) is the “world’s largest scientific society and one of the world’s leading sources of authoritative scientific information.”¹ The ACS provides a leadership role within the realm of chemical education to “identify new solutions, improve public health, protect the environment and contribute to the economy.”²

5.2 ACS’S ROLE IN SAFETY

Thomas Connelly, ACS Executive Director and Chief Executive Officer, wrote a comment in *C&EN* discussing the ACS’s role in safety.³ A number of preventable

accidents have occurred in academic chemistry laboratories. “The safety gap is not due to a lack of available knowledge.” The ACS has a long-standing commitment to chemical safety though Connelly poses “what more should ACS be doing to promote safety?”

Connelly invited comments, ideas, and suggestions to his proposed questions, including:

“Should ACS publications and CAS increase safety content and considerations in our publications and online information?”

“Should ACS include safety explicitly within its core values?”

5.3 RESPONSE TO THE ACS’S ROLE IN SAFETY

A number of statements from ACS divisions and committees were received in response to Connelly’s request for comments.

Division of Chemical Health and Safety (CHAS)⁴ The CHAS recommends that authors should be required to address safety in publications and presentations. Explicit instructions should be included where highly toxic, reactive, or energetic materials, and dangerous processes are concerned.

“The recently published work of Grabowski and Goode¹ demonstrates the lack of safety information in chemical science publications. The recommendations of Grabowski and Goode should be adopted by ACS publications and modified to be applicable for media other than journals. These recommendations are summarized below, with brief explanations as appropriate.

- All compounds, procedures, or processes which require a Standard Operating Procedure should be noted by the manuscript author. This

connects safety information directly to the OSHA Laboratory Standard (29 CFR 1910.1450).

- “Instructions to Authors” for every journal should have a separate section that outlines the journal’s safety notification requirements. A reasonable expectation is authors identify hazards that might not be recognized by a first-year graduate student who has been asked to replicate the published procedure. Substances or processes that have potential high risks should be flagged.
- All Materials and Methods sections should have a mandatory safety subsection. Peer review must be designed to critically comment on this section. Reviewer forms should include a separate area in which the reviewer is asked if all high-hazard substances (e.g. pyrophors, carcinogens, reproductive toxins, etc.) and hazardous procedures/processes are flagged with sufficient detail to alert a first year graduate student.
- Media other than journals, including ACS webinars, should contain a safety moment, when applicable. CHAS recommends that safety is part of the fabric of everything the Society is doing. “⁴

“YES, without a doubt” was the response of the CHAS when answering if the ACS should include safety explicitly within its core values.

Division of Chemical Education, Inc. (CHED)⁵ “The CHED recognizes the importance and central role of safety knowledge, skills, attitudes, and values” A

mission of the CHED is to embed accurate chemical safety instruction at all educational levels.⁶

CHED's response to increasing safety content was a resounding "Yes! All publications should summarize the results of hazard and risk analysis for experimental procedures, as described in the new *Guidelines for Chemical Laboratory Safety* published by CCS. We believe the best approach is to require a clear statement of hazards and risks that includes direct explanations of how procedures and safety precautions have been designed to eliminate or mitigate risks.

In a recent analysis of required safety statements in a wide range of chemistry journals (both ACS and non-ACS) the authors concluded that the descriptions of hazards and risks and the inclusion of steps to minimize risk are dramatically lacking.¹ The ACS can take a leadership position by requiring all ACS journals to review their policies on safety statements for authors and reviewers.

Raising the standards for writers, reviewers, and editors of ACS journals will have an added benefit of raising awareness of safety among a broader population of chemists than those who consider themselves safety professionals. In this fashion, all publications can do a better job of teaching the knowledge and skills inherent in safe chemistry laboratory work."

"Yes!" the ACS should include safety explicitly within its core values. "Safety and ethics are so closely tied to the overall value of the chemistry enterprise that they must be part of the Society's core values. Chemical safety is

the foundation of the ACS vision and its mission, and it should be explicitly acknowledged as such.”

Committee on Chemical Safety David Finster, Safety Education Subcommittee Chair, of the ACS Committee on Chemical Safety (CCS) endorsed the CHAS reply to the Connelly comment.

5.4 NEW POLICY FOR ACS JOURNALS

The ACS has taken action and beginning in 2017, “all ACS publications will require experimental details to address and emphasize any unexpected, new, and/or significant hazards or risks associated with the reported work.”⁷ The aims for this new requirement are to 1) use the literature to educate researchers about the risks inherent in the published experiments and 2) integrate safety as an important role for scientists. Authors should highlight in the results, discussion, or even the abstract when unanticipated hazards or risks are apparent.

Sarah Tegen, vice president for global editorial and author services at ACS, says that ACS Publications editors and staff looked closely at how journals addressed safety after a “confluence of events” that included high-profile accidents and a survey¹ of safety policies of chemical journals.⁸ Journals are to include the language in guidelines for authors and reviewers. Though journal editors are left to decide how this new requirement is implemented.

The overall reaction from journal editors has been positive. *Inorganic Chemistry* editor-in-chief William B. Tolman said, “there is a strong sense that this is the right thing to do.” Tolman added a check box to the form that *Inorganic*

Chemistry reviewers fill out that asks whether authors have appropriately addressed safety.

Previously, *Chemistry of Materials* had no safety precautions in the guidelines for authors.¹ As of January 2017, safety has its own section in the guidelines for authors that states: “Authors must emphasize any unexpected, new, and/or significant hazards or risks associated with the reported work. This information should be in the experimental details section of the full article or communication.”⁹

The *Journal of Chemical Education* previously only required hazards to be mentioned in laboratory experiments.¹ Since the new requirement “Authors must emphasize any unexpected, new, and/or significant hazards or risks associated with the reported work. This information should be in a separate Hazards section.”¹⁰ Though, on the page of reviewers, there are no specific regulations that reviewers must ensure a hazards section is present.¹¹

5.5 EFFECTIVENESS OF NEW ACS SAFETY POLICY

As of the end of February 2017, the *Journal of Natural Products* is the only one of 48 ACS peer-reviewed journal containing new research that does not have a hazard warning in the guidelines for authors (author guidelines last revised Dec 2015).¹²

One scientist pointed out that the first JACS issue of 2017 contained procedures for two known explosives without any hazard warning.¹³ Though the paper was reviewed and published before the new safety policies went into effect, the JACS editor Peter Stang noted when there are known safety issues

“we will require authors to provide a warning, even if they don’t know the full details of extent of toxicity, explosiveness, or other properties.” JACS has issued a correction to the paper that adds the following statement to the materials and experimental sections: “Warning: 2,4,6-Trinitroaniline (TNA) and 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) are very sensitive and highly explosive. They should be handled with extreme caution.”¹⁴

5.6 REFERENCES

1. Grabowski, L.E.; Goode, S.R., *J. Chem. Health Saf.*, **2016**, 23 (3), 30-35.
2. <https://www.acs.org/content/acs/en/about/aboutacs.html>, (verified 3.12.17).
3. Connelly, T., *Chem. Eng. News*, **2016**, 94 (26), 35.
4. <https://dchas.org/wp-content/uploads/2016/10/DCHAS-Comments-on-ACS-Role-in-Safety.pdf>, (verified 3.12.17).
5. http://www.divched.org/sites/default/files/documents/ACSSocietyRoleinPromotingChemicalSafety_101416.pdf, (verified 3.12.17).
6. <http://www.divched.org/committee/safety>, (verified 3.12.17).
7. Bertozzi, C., *ACS Cent. Sci.* **2016**, 2, 764–766.
8. Kemsley, J., *Chem. Eng. News*, **2016**, 94 (48), 7.
9. http://pubs.acs.org/paragonplus/submission/cmatex/cmatex_authguide.pdf, (verified 3.12.17).
10. http://pubs.acs.org/paragonplus/submission/jceda8/jceda8_authguide.pdf, (verified 3.12.17).
11. <http://pubs.acs.org/page/jceda8/submission/reviewers.html>, (verified 3.12.17).
12. http://pubs.acs.org/paragonplus/submission/jnprdf/jnprdf_authguide.pdf, (verified 3.12.17).
13. <http://cenblog.org/the-safety-zone/2017/02/safety-correction-in-jacs/>, (verified 3.12.17).
14. Lahiri, N.; Lotfizadeh, N.; Tsuchikawa, R.; Deshpande, V.V.; Louie, J., *J. Am. Chem. Soc.*, **2017**, 139 (1), 19–22.

APPENDIX A – CHAPTER 3 SUPPORTING INFORMATION

Determining a Solubility Product Constant by Potentiometric Titration to Increase Students' Conceptual Understanding of Potentiometry and Titrations

Supporting Information

Lauren E. Grabowski, Scott R. Goode*

Department of Chemistry and Biochemistry, University of South Carolina,
Columbia, South Carolina 29208, United States

Laboratory Instructor Preparation Notes

Chemicals Required

VWR Catalog Number

Concentrated Nitric Acid.....	470301-539
16-Gauge Copper Wire.....	66249-021
Copper Sulfate Pentahydrate.....	AAAA11262-0B
0.100M standard sodium oxalate.....	RC750016

Making Dilute Nitric Acid:

6M HNO₃: 190 mL conc HNO₃ in 500mL volumetric flask with de-ionized water

0.1M HNO₃: 33mL of 6M HNO₃ in 2L volumetric flask with de-ionized water

Equipment Needed:

2 L volumetric flask

500 mL volumetric flask

100 mL volumetric flasks

150 mL beakers

LabQuest Units (Vernier Scientific)

pH meters w/special electrodes (see Figures S1 and S2)

25 mL burets

Buret holders & clamps

USB drives

All waste needs to go in a hazardous waste container

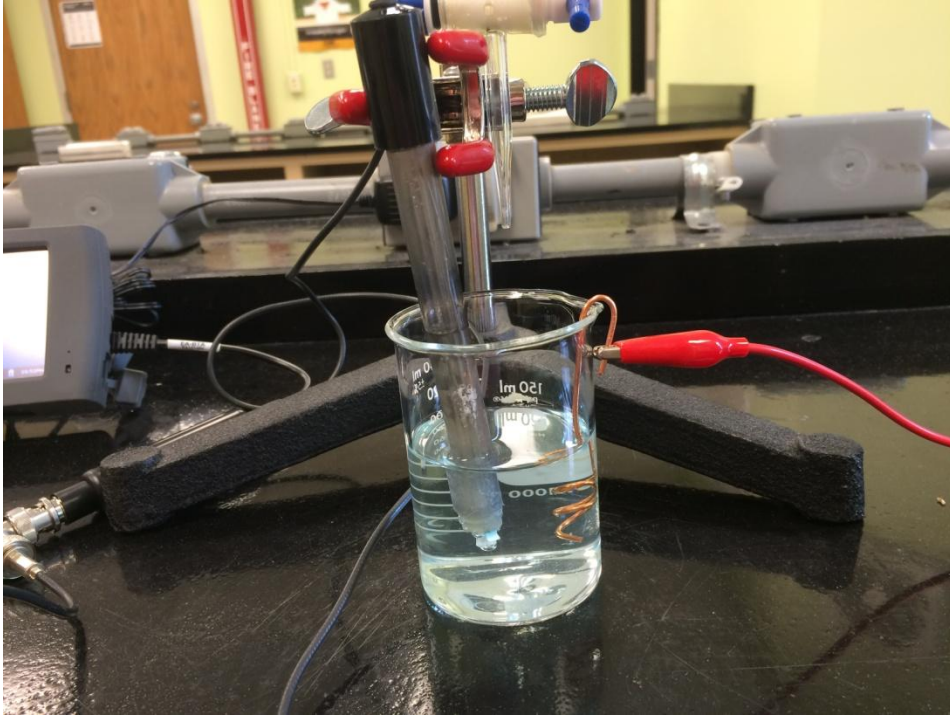


Figure A.1 Titration set up with electrodes

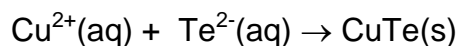


Figure A.2 BNC-T connection to the LabQuest unit

Pre-Lab Exercise

1. Sample Calculation.

A copper solution is made by adding about 1 mmol of copper sulfate into a volumetric flask and diluting to exactly 100 mL. In the titration of Cu^{2+} with standardized sodium telluride, the initial potential (copper electrode vs reference electrode) is 0.122 V (122 mV) and the equivalence point is reached after 9.52 mL of 0.100 M telluride ion is added.



After exactly 10.00 mL of 0.100 M sodium telluride was added, the potential is -0.213 V (-213 mV). Calculate pK_{sp} of copper telluride.

2. Safety.

Identify the most dangerous hazard in the lab experiment and download the (M)SDS. Make sure that the (M)SDS is appropriate and the exposure conditions and amounts used in the lab are consistent with the (M)SDS.

Explain how you minimize the risk of handling this material.

Experiment Handout

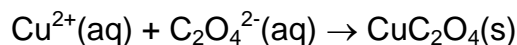
Introduction

Titration is not strictly limited to the reaction of acids and bases. Potentiometric titrations, in which the potential of a cell is measured as a standard reagent is added, are also quite common. Measuring the pH during an acid-base titration is a common example of a potentiometric titration. Other potentiometric titrations utilize the potential of other types of electrodes.

This experiment will demonstrate the use of the potentiometric titration curve data to determine the solubility product constant for copper (II) oxalate.

Potentiometric titration

A solution of copper sulfate can be titrated by the addition of sodium oxalate to form the insoluble copper oxalate:



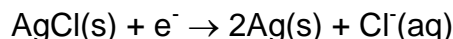
If a copper electrode (the indicator electrode) is immersed into the solution, its potential, E_{ind} , will change as the copper is consumed in the course of the titration:

$$E_{\text{ind}} = E^\circ - \left(\frac{0.05916}{2} \right) \log_{10} \left(\frac{1}{[\text{Cu}^{2+}]} \right)$$

The cell potential is determined by a voltage measurement of the difference between the indicator electrode and a reference electrode:

$$E_{\text{cell}} = E^\circ - \left(\frac{0.05916}{2} \right) \log_{10} \left(\frac{1}{[\text{Cu}^{2+}]} \right) - E_{\text{ref}}$$

The reference electrode you will be using is the silver/silver chloride electrode that is built into the pH sensitive glass electrode.



The potential of the reference electrode is constant throughout the titration and has the value $E_{\text{ref}} = +0.197 \text{ V}$.

The titration curve

If we record E as a function of the volume of oxalate added, we obtain a titration curve, in this case a graph of E as a function of the volume of sodium oxalate added.

When you record the potential as a function of volume during the titration, you have sufficient data to calculate E° for the reduction of Cu^{2+} to $\text{Cu}(\text{s})$ as well as

the concentration of the copper solution and the solubility product constant for CuC_2O_4 .

It is not possible to use the mass of a copper sulfate for making a solution of known concentration because the purity varies. But the inflection point in a titration with standardized oxalate signals the point at which the number of mmol of oxalate is equal to the number of mmol of Cu^{2+} . Because you know the starting volume of the solution, you can combine the number of mmol of Cu^{2+} from the titration with the initial volume to determine the initial molarity, $[\text{Cu}^{2+}]_0$.

If you were asked to calculate the concentration of 25 mL of a HCl solution that required 22.0 mL of 0.100 M NaOH, you could do it, and the calculation of the concentration of a copper solution from the titration with oxalate ion is conceptually identical.

The shorthand electrochemical cell is



Before you add any oxalate, the initial concentration of copper is $[\text{Cu}^{2+}]_0$ and the initial cell potential is E_{init} .

$$E_{\text{init}} = E^\circ - \left(\frac{0.05916}{2} \right) \log_{10} \left(\frac{1}{[\text{Cu}^{2+}]_0} \right) - E_{\text{Ag/AgCl}}$$

If you record a titration curve, your first potential is E_{init} . After you finish the titration, you will know the volume of sodium oxalate needed to precipitate the copper and can calculate $[\text{Cu}^{2+}]_0$ then can calculate E° .

Your experimental value of E° probably will not agree exactly with the textbook value for E° . There are errors inherent in potential measurements of this type. Fortunately, an error in E° will not influence your measurement of K_{sp} .

It is convenient to lump E° , E_{ref} , and the error potentials into one term, which we shall designate E' :

$$E = E' - \left(\frac{0.05916}{2} \right) \log_{10} \left(\frac{1}{[\text{Cu}^{2+}]} \right)$$

Again, you measure E and determine the initial concentration of $[\text{Cu}^{2+}]$ from the equivalence point, so you can calculate E' .

Once you know E' , you will use this value and the potential at different points in the titration to calculate K_{sp} and $\text{p}K_{\text{sp}}$. The determination of K_{sp} will require knowing $[\text{Cu}^{2+}]$ and $[\text{C}_2\text{O}_4^{2-}]$:

$$K_{sp} = [\text{Cu}^{2+}] [\text{C}_2\text{O}_4^{2-}]$$

$$\text{p}K_{sp} = -\log(K_{sp})$$

It is simplest to choose a point after the equivalence point. From the measured E you can calculate $[\text{Cu}^{2+}]$ and from the amount of oxalate you added (oxalate is in excess beyond the equivalence point) you can calculate the oxalate concentration in the same manner as you calculate excess hydroxide ion concentration beyond the equivalence point in an acid-base titration.

Materials

Heavy copper wire

0.1 M HNO_3

6 M HNO_3

Copper sulfate pentahydrate solid, formula weight 250 g/mol

Two 100 mL volumetric flasks

Two 150 mL beakers

pH meters and special adapters for homemade electrodes

LabQuest unit

0.100 M standard sodium oxalate solution

25 mL buret

Procedure

Preparing the electrode

1. First, you will make your own copper electrode. Obtain about 10 inches of pure, heavy copper wire. Twist about half of it into a spiral. It's better to have too long a piece than too short a piece.
2. Obtain 150 mL of 0.1 M HNO_3 from the hood and move it to your work station.
3. You will find a 450-mL beaker of 6 M HNO_3 in the hood. Clean the bottom (helix) part of your copper electrode by placing it into the 6 M HNO_3 for about 15 seconds. It should become bright and shiny.
4. Place the electrode in the 0.1 M HNO_3 solution to "age" for at least 15 minutes. Keep the electrode in this solution when it is not in use.

Titration

1. Clean, rinse, and fill a 25 mL buret with 0.100 M sodium oxalate standard solution.
2. Weigh about 0.5 mmol of copper sulfate into a weighing boat. Transfer quantitatively to a 100-mL volumetric flask and wash any remaining CuSO_4 from the weighing boat with a stream of water from your wash bottle. Dilute to the mark with deionized water. The concentration of this solution is about 0.5

mmol/100 mL = 0.005 M. This concentration is probably known to one decimal place because the copper sulfate is not high purity and there may be excess water from room humidity in the copper sulfate. These issues do not affect your results because you will titrate with standardized oxalate with a concentration of 0.100 ± 0.001 M and the titration will determine the exact concentration of the copper solution.

3. Set up the titration apparatus: Connect the adapter into channel 1 on the LabQuest unit. Turn the LabQuest unit on by pressing the Power button on top left of the LabQuest unit.

4. Make sure the pH electrode (you are using the built-in Ag/AgCl reference) is attached to the adapter and the alligator clip is attached to the copper coil. Transfer the copper sulfate solution from the 100 mL volumetric flask to the 150 mL beaker and immerse your electrodes in the solution.

Before you connect the electrodes to the Electrode Amplifier you need to check the zero.

- Click on the LabQuest App
 - On the top toolbar, click on Sensors → Change Units
 - Electrode Amplifier
 - Select mV
 - Click on Sensors → Calibrate
 - Electrode Amplifier
 - Check 1-point calibration
 - Ensure the units are mV
 - Connect a small wire between the terminals on the connector. Your TA will demonstrate this operation.
 - Click calibrate now
 - For value 1, enter 0 mV
 - Click keep
 - Click ok
 - Click on Sensors → Data Collection
 - Mode: Events with Entry
 - Columns: 1
 - Name: Volume (mL)
 - Units: mL
 - Press Ok
 - Connect the electrodes to the electrode amplifier
5. Click on the graph icon on the top right of the menu bar (first icon on left)
- Press Green Play button in the bottom left corner
 - Allow to reach equilibrium and press Keep (next to the red stop button on the bottom menu bar). Record the volume of titrant added. The first

data point will be 0 mL. Press ok

6. Start your titration

- Add approximately 0.5mL of titrant, stir, and allow to stabilize, press keep, and enter EXACT mL of titrant added (to 2 decimal places).
- Continue adding 0.5mL of titrant at a time, stir, allow to stabilize, press keep, and enter the EXACT mL of TOTAL titrant added thus far (to 2 decimal places).
- Continue until you get close to the equivalence point
- Upon almost reaching the equivalence point, slow down and add 1-3 drops at a time.
- Try to get several readings in the vicinity of the equivalence point and at least 4 readings just beyond the equivalence point (these points should be when the graph levels out).
- Ensure your graph is shaped like a titration curve

7. When you are finished with the titration, press the red stop button on the bottom left hand corner.

- Click File on the top menu bar
- Click Export and plug in your USB device
- Click the USB icon on the top left corner
- Enter your Initials & Run Number as your title
- Click Ok
- Optional: Unplug your USB and check on the computer that your data is on there is you have any doubts

8. Repeat the measurement on the second sample of copper sulfate.

- Click File → New
- This will delete unsaved data and you will have to start again from Step #5.

9. Bring your USB to the computer

- Open excel and LabQuest Logger Lite from the desktop
- In Logger Lite, open your data files and copy and paste the raw data table to excel.
- Save excel files to your USB
- Safety eject your USB device from the computer

Data Analysis

Tabulate your titration data in three columns (data point number, titrant volume (mL), measured potential (mV)). Leave room for other columns. Prepare a graph of the titration curve to include with your lab report. You may find it easiest to use Excel because several of the other calculations can be automated.

Your titration curve probably will not be textbook sharp, with an easy-to-determine equivalence point. The copper electrode does not respond instantaneously – it has a little memory effect – and your curve will be drawn out. You will find that you can, however, estimate the equivalence point volume reasonably well by eye. You are, of course, welcome to use other methods such as calculating the derivative.

Calculate the equivalence point volume and the number of mmol of oxalate at the equivalence point. Determine the initial concentration of Cu^{2+} and calculate E° and E' from that concentration.

For at least 3 points beyond the equivalence point calculate the concentration of $[\text{C}_2\text{O}_4^{2-}]$ (from the concentration of the oxalate solution you determine from the sRf table) and $[\text{Cu}^{2+}]$ (from E' and the Nernst equation). Show all calculations and record the other results in the extra columns of your table.

Calculate pK_{sp} for each of the data points, recording the results in a final column in your results table. Calculate an average pK_{sp} and report the standard deviation and percent relative standard deviation of your results.

Questions

1. Compare your experimental E° to the E° value found in the text for the course. If different, provide reasons why they might be different. For each error source state if it is random, systematic, and how you can minimize this source of error.
2. Some pH electrodes use a reference other than the Ag/AgCl electrode. How would your results be affected if, unknown to you, E_{ref} was 0.244 V instead of 0.197 V?
3. Compare your value of pK_{sp} to the literature value ($K_{\text{sp}} = 1.4 \times 10^{-8}$). Calculate mean standard deviation, and the % relative error:

$$\% \text{ relative error} = (\text{Experimental} - \text{True})/\text{True} \times 100\%$$

4. Identify at least two important sources of error in the experiment, at least one systematic and one random, and explain how to minimize the error. For the systematic error discuss how you know if the error always gives you a high or low value for pK_{sp} and compare to your experimental results.

Post-Lab Grading Rubric

(20) Pre-lab Exercise

(2) Title

(3) Name of investigators and date

(15) Abstract

(15) **Experimental** (procedures and apparatus used in the experiment)

(15) **Results** (Show sample calculations. Average measurements and calculate standard deviations.)

(30) **Discussion and Conclusions.** Discuss the main points and results of the lab. Include the answers to the questions enumerated individually so they are easier to grade.

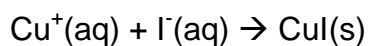
Reference

Silver/silver chloride reference electrode

http://www.google.com/url?sa=t&rct=j&q=&esrc=s&source=web&cd=5&ved=0CDwQFjAE&url=http%3A%2F%2Fcommunity.asdlib.org%2Factivelearningmaterials%2Ffiles%2F2014%2F01%2FPotentiometry_Reference_Electrodes.pdf&ei=uH21VN_bDlingwTWmIPICA&usg=AFQjCNEKRecP16gCWT02HB0IDfNFzc41Cg&sig2=VfoTvMGqgYb1fccIT6laXq&bvm=bv.83339334,d.eXY

Post-Lab Assessment Quiz: Form A

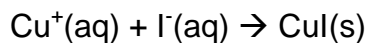
Potentiometric titration. Consider the potentiometric titration of 50.0 mL 0.100 M $\text{Cu}^+(\text{aq})$ with 0.500 M iodide ion, $\text{I}^-(\text{aq})$. The chemical equation for the reaction is:



Before any iodide was added the initial potential of the Cu^+ electrode against a reference electrode is 0.200 V. Calculate the potential after 10.0 mL of iodide is added. The solubility product constant of copper(I) iodide is 1.0×10^{-12} .

Post-Lab Assessment Quiz: Form B

Potentiometric titration. Consider the potentiometric titration of 50.0 mL 0.100 M $\text{Cu}^+(\text{aq})$ with 0.500 M iodide ion, $\text{I}^-(\text{aq})$. The chemical equation for the reaction is:



Before any iodide was added the initial potential of the Cu^+ electrode against a reference electrode is 0.200 V. Calculate the potential after 12.0 mL of iodide is added. The solubility product constant of copper(I) iodide is 1.0×10^{-12} .

Potentiometric Titration Data

Table A.1 Potentiometric Titration Data

Data Point	Titrant Volume (mL)	Measured Potential (mV)
1	0.00	95.0
2	0.50	94.5
3	1.02	93.7
4	1.55	90.4
5	2.00	88.5
6	2.51	85.5
7	3.00	83.2
8	3.53	79.1
9	4.02	74.5
10	4.52	66.8
11	5.01	57.6
12	5.30	52.8
13	5.50	48.2
14	5.70	44.2
15	5.90	41.9
16	6.01	38.9
17	6.15	37.2
18	6.29	36.1
19	6.40	34.3
20	6.52	32.4
21	6.70	30.3
22	6.82	29.6
23	6.95	27.9
24	7.10	25.5
25	7.21	25.4
26	7.40	23.2
27	7.55	22.4
28	7.68	20.3
29	8.05	18
30	8.37	13.9
31	8.55	11.2
32	8.85	8.7
33	9.15	6.9
34	9.61	4.6

Data Point	Titrant Volume (mL)	Measured Potential (mV)
35	10.10	3.5
36	10.55	2.0
37	11.08	1.4
38	11.58	0.8
39	12.00	0.5

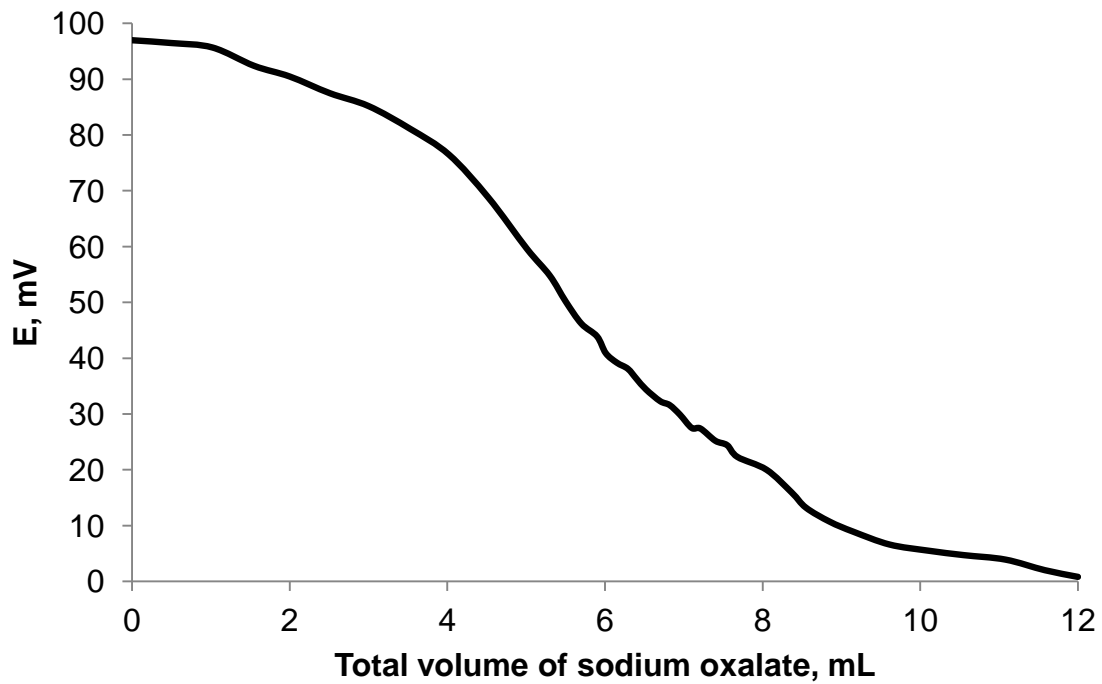


Figure A.3 Potentiometric Titration Graph

APPENDIX B – PERMISSION TO REPRODUCE PUBLISHED
MATERIALS

Chapter 3

ACS Journal Publishing Agreement User's Guide SECTION II: Permitted Uses by Author(s)

1. Reuse/Republication of the Entire Work in Theses or Collections:

Authors may reuse all or part of the Submitted, Accepted or Published Work in a thesis or dissertation that the Author writes and is required to submit to satisfy the criteria of degree-granting institutions. Such reuse is permitted subject to the ACS' "Ethical Guidelines to Publication of Chemical Research" (<http://pubs.acs.org/ethics>); the Author should secure written confirmation (via letter or email) from the respective ACS journal editor(s) to avoid potential conflicts with journal prior publication**/embargo policies. Appropriate citation of the Published Work must be made. If the thesis or dissertation to be published is in electronic format, a direct link to the Published Work must also be included using the ACS Articles on Request author-directed link (see <http://pubs.acs.org/page/policy/articlesonrequest/index.html>).

Here is the official permission for the reuse of the article
DOI: 10.1021/acs.jchemed.6b00460 in a thesis/dissertation:

The Journal of Chemical Education grants permission for the request to reuse DOI: 10.1021/acs.jchemed.6b00460 in a thesis or dissertation for print and electronic formats, and translations, at no charge. Figures and tables may be modified. Appropriate credit should be given and should read: "Reprinted with permission from Grabowski, Lauren E.; Goode, Scott R. "Determining a Solubility Product Constant by Potentiometric Titration To Increase Students' Conceptual Understanding of Potentiometry and Titrations." J. Chem. Educ. 2017, 94, DOI: 10.1021/acs.jchemed.6b00460. Copyright 2017 American Chemical Society and the Division of Chemical Education."

As noted below, if the thesis or dissertation is to be published in electronic format, a direct link to the Published Work must also be included using the ACS Articles on Request author-directed link (see <http://pubs.acs.org/page/policy/articlesonrequest/index.html>).

Mary Saecker
Managing Editor
Journal of Chemical Education
University of Wisconsin–Madison
209 N. Brooks Street
Madison, WI 53715-1116
phone: 608.262.2072
<mailto:msaecker@jce.acs.org>

Chapter 4

ELSEVIER LICENSE TERMS AND CONDITIONS

Feb 28, 2017

This Agreement between Lauren Grabowski ("You") and Elsevier ("Elsevier") consists of your license details and the terms and conditions provided by Elsevier and Copyright Clearance Center.

License Number	4057671188674
License date	Feb 28, 2017
Licensed Content Publisher	Elsevier
Licensed Content Publication	Journal of Chemical Health and Safety
Licensed Content Title	Review and analysis of safety policies of chemical journals
Licensed Content Author	Lauren E. Grabowski, Scott R. Goode
Licensed Content Date	May-June 2016
Licensed Content Volume	23
Licensed Content Issue	3
Licensed Content Pages	6
Start Page	30
End Page	35
Type of Use	reuse in a thesis/dissertation
Portion	full article
Format	both print and electronic
Are you the author of this Elsevier article?	Yes
Will you be translating?	No
Order reference number	
Title of your thesis/dissertation	ADVANCES IN CHEMISTRY. PART I: NOISE, CALIBRATION, AND EDUCATIONAL ADVANCES IN ANALYTICAL CHEMISTRY. PART II: SAFETY OVERSIGHT IN CHEMICAL JOURNALS.
Expected completion date	Apr 2017
Estimated size (number of pages)	150
Elsevier VAT number	GB 494 6272 12
Requestor Location	Lauren Grabowski 631 Sumter St COLUMBIA, SC 29208 United States Attn: Lauren Grabowski
Publisher Tax ID	98-0397604
Total	0.00 USD