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# Analytical Problem Solving

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## PREFACE

This collection of activities details many of the laboratories done in and developed by participants in the workshops offered at Miami University through the PACT project. This workshop was designed to introduce participants to analytical chemistry as a problem-solving tool.

## Organization of the Collection

Each of the six activities in this guide is divided into three parts, which are as follows:

- Introduction—This section describes the activity and the goals for the experiment.
- Activity—This section, written for the students, contains the series of handouts they will be given one at a time through the course of the activity.
- Teacher Notes—This section, written for the teacher, contains basic information such as time required; group size; materials needed; safety, handling, and disposal instructions; points to cover in the pre-lab; procedural tips and suggestions; sample results; plausible answers to questions; and references.

## An Inquiry-Based Analytical Chemistry Course

For years, Dr. Pacey has used the "just in time" principle of parceling information and supplies to students in his analytical chemistry course. Before the lab, he provides only a brief introduction to the activity without overwhelming students with background theory for which they as yet have no context. The overriding "theme" behind this approach is that students have time to think about and contemplate the questions posed, and if necessary, find information that is needed from other sources (texts, references, each other, etc.). This makes them active participants in the learning process.

Before the students begin the laboratory activity, Dr. Pacey gives them a brief introduction to the topic to be studied. This pre-lab talk is unlike traditional pre-lab lectures in that it does not provide a theoretical introduction to the topic. Instead, he raises questions to think about before entering the lab, discusses a real-world issue related to the chemistry topic, or reviews specific safety or procedural considerations. No theoretical introduction is necessary since the intent of the approach is to lead students to figure out the concepts for themselves.

During the lab, students are given only the necessary information when they need it and ask for it, and they discover for themselves what information and factors are extraneous, without Dr. Pacey's assistance. Equipment and supplies are sorted into modules, so only the necessary chemicals and instruments are in operation at the time of the lab. Students must decide what their needs are for that particular activity and then request specific chemicals or equipment. They learn to use available analytical instruments as needed for each activity. In some cases, they learn only how to operate laboratory instruments and get the data they need, learning the theory of operation at a later time. To check for understanding at each step of the activity, he often requires numerical answers to be expressed in different units or asks further questions about responses to ensure that students are not "parroting" other students' responses.

In some cases, students must make what they need themselves. For example, students are sometimes required to make their own stock solutions and calibration standards, just as they

would be required to do in industry. This skill is an important one for analytical chemists to learn. Often, this task forces them to think analytically about how much solution they really need, taking was disposal and handling into consideration. If time permits, students should make all solutions needed for an experiment. Using a "just in time" approach and requiring students to prepare some of their own materials helps students become familiar with the work needed in setup and cleanup, which is often overlooked in traditional lab activities.

Instrumental methods allow students to collect data, compile it, and use it in discussion during class time. Spreadsheets and other computer-based tools enable students to interpret data quickly. Activity 1, Choosing and Calibrating Glassware, can be used to introduce spreadsheets and data collection and to assess students' lab strengths and weaknesses. Students categorize and interpret data they collect, making hypotheses to explain the trends or lack of order. After they have collected and interpreted the data, they are encouraged to find information in their texts or other literature that supports their hypotheses.

In the post-laboratory discussion, students compile their data and discuss their results. In some laboratory experiments, students use their own data, while other experiments require that they pool data with other students or groups in order to find trends and categorize their observations. (Cooperative groups may be formed during the lab period, or the entire class can compile data later during class time.) Dr. Pacey sees his role in this step to be guiding the discussion in such a way that students are able to "discover" the concept for themselves. Closure on each topic occurs when a large group answers each question, as prompted by the instructor. This discussion process not only mirrors the process used by professional scientists but also emphasized the cooperative nature of the scientific method.

As a collective test of problem-solving ability, Dr. Pacey assigns a real-world project in the middle of the semester. Solving a real problem allows students to practice their skills, while the design of the activity keeps them within the boundaries of the classroom and academic laboratory.

In one such project, students test for different analytes in a nearby lake. An analyte is assigned to each pair of students, who must choose a "standard" analytical method by researching various standard methods in the library. After choosing a method, the pair must describe it to Dr. Pacey, who provides additional guidance, checks for safety concerns and other factors, and asks questions to make sure students are well versed in the details of the method and can use the needed instrumentation. Students are required to formulate an ideal sampling plan for the particular lake, given a map, unlimited funding, and no time constraints. The plan they actually follow may differ from the ideal due to practical considerations such as time and money. In this case, the actual sampling plan is outlined by the instructor to make the experiment fit within these constraints. Students are also required to provide proof of methods, similar in format to the requirements of the Environmental Protection Agency for the lake-sampling project. They then sample the lake, analyze the sample, and collect their results, using this data to write a report. Student submit reports about quality assurance and quality control and give a final oral presentation about the entire project.

## INTRODUCTION TO ACTIVITY 1
## Choosing and Calibrating Glassware

### Description

In this experiment, students calibrate volumetric glassware (pipets and volumetric flasks) with an analytical balance and statistical treatment of their data. They will also determine the total amount of error in a measurement based on the individual errors and calculation method.

### Goals for the Experiment (See Student Handout and below)

- Students will learn about propagation of error in calculations using experimental data.
- Students will develop their weighing and pipetting techniques.
- Students will learn the following terms: standard deviation and relative standard deviation.
- Students will learn that the larger the glassware, the lower the relative standard deviation and the lower the propagated error.
- Students will learn the correlation of mass to weight and weight to volume.

## ACTIVITY 1
## Choosing and Calibrating Glassware

### Part 1

#### Objective

The objective of this experiment is to illustrate the nature of experimental errors and their effects on results of chemical analyses. This investigation will also help you become familiar with the use of spreadsheets in data collection, organization, calculation, and analysis. An additional objective is to demonstrate that the choice of volumetric glassware can affect the precision of an analytical method.

#### Rationale

Normal volumetric glassware should always be tested for accuracy before use. Errors in the volume marks may exceed the permissible error of the determination. In addition, no matter how accurate a piece of glassware is, the user should test it personally and be assured beyond all doubt that the glassware is sufficiently accurate and that the user is sufficiently skilled to perform at the optimal level.

The concept of propagation of error is important to understand. This technique is used to evaluate the average expected error in an analytical method. This calculated error is then compared against the error which is permissible for the analyte of interest. If the calculated error exceeds the permissible error, then modifications in the procedure must be made to reduce the calculated error. However, it is important to remember that the calculated error estimates the overall precision with the assumption that the analyst performs his or her task reproducibly. It does not take into account sloppy work and does not replace the evaluation of precision of real data.

#### Theory

Volumetric glassware is calibrated by weighing the amount of pure water held (volumetric flask) or delivered (pipet) at a given temperature and calculating the volume. Before starting the experiment, it is important to note that the density of water and the volume of the glassware vary with temperature. In addition, the weight measurement is made in air.

Quality volumetric glassware is designed to hold and deliver a designated volume at a specified temperature, usually 20°C. Since the temperature of the laboratory may not be exactly 20°C, a formula must be used to calculate the volume of the glassware at the temperature of measurement. In order to perform this calculation, the density of water at that temperature must be known. By dividing the mass of the water by the density, the volume is directly obtained for any given temperature.

The mass of the water is obtained from its weight in air by reducing the weight in vacuo. For the later calculation, it is necessary to know the density of water, the density of the weights, and the density of air.

For this experiment it is assumed that the density of the weights is the density of brass, which is 8.4g/ml. The density of air can be calculated if the temperature (t), barometric pressure (p), and humidity (h) are known. The following density of air formula applies.

$$d_a = \frac{0.0012931p - 0.00049h}{760(1 + 0.00367t)}$$

where p is atmospheric pressure, mm Hg (reduced to 0°C), h is aqueous tension of the atmosphere, mm Hg, and t is temperature in degrees C. For this work it is assumed that the density of the air is 0.0012g/mL. Therefore, the calculation of weight in vacuo is

$$W_{vac} = W_{meas} + 0.0012\left(\frac{W_{meas}}{d_w} - \frac{W_{meas}}{8.4}\right)$$

where $W_{meas}$ is the weight measured, $d_W$ is the density of water at the measurement temperature, and $W_{vac}$ is the calculated weight in vacuo is:

Divide the weight in vacuo by the density of water at the measurement temperature; the resulting volume is the calculated volume of water in the glassware.

## Experimental Procedure

In this experiment, several pieces of glassware will be calibrated and a statistical treatment of the data will be performed to identify significant sources of error in an analytical measurement.

## Calibration of Pipets

Weigh a clean and dry weighing bottle at least three times to determine the empty weight and record the result. Then calibrate 1-mL, 2-mL, 5-mL, and 10-mL pipets as follows: Fill each pipet to the mark and deliver the volume to the weighing bottle. Reweigh the bottle and record the result. Perform the delivery and weighing step five times for each pipet.

Average the raw data for each pipet and determine the standard deviation and relative standard deviation using the computer. Which pipets are the most precise and why?

# Part 2

## Calibration of Volumetric Glassware

Weigh the clean and dry volumetric glassware: 10-, 25-, and 50-mL flasks. Fill each flask to the mark and reweigh. Perform this step five times for each flask. Average the data for each flask and determine the standard deviation and relative standard deviation using the computer. Which flask is the most precise and why?

It should be clear from your experimental results that the larger the volumetric glassware, the smaller the relative standard deviation. The reason for this is that in general the volume of imprecision is about the same for each piece of glassware, but the total volume increases.

Since the relative standard deviation is the standard deviation divided by the mean value and the standard deviations are similar, the calculated relative standard deviation is dependent on the magnitude of the mean value. In other words, the relative standard deviation decreases with increasing mean value. Therefore, the analyst should use the largest pieces of volumetric glassware possible; however, with flasks bigger than 1 L and pipets bigger than 50 mL, some of the advantages gained from precision are lost to practical handling considerations.

Another piece of volumetric equipment that is used routinely in titrations is a buret. Explain using calculations and words whether it is better to use 20, 49, or 56 mL of solution from a 50-mL buret. (Hint: What is the expected error in a pipet reading?)

## Propagation of Errors

In most experiments the measured values are not the items of interest but are used to calculate the value of interest. Therefore, the individual errors associated with the values used to calculate the desired value contribute to the overall error in the calculation. For example, a titration of a weak acid by a strong base is used to determine the concentration of the weak acid. The values measured are the volume of the weak acid sample in the flask and the volume of strong base delivered from the buret. As you know, the formula used to calculate the concentration in this case is

$$V_{base} * M_{base} = V_{acid} * M_{acid}$$

where V is volume and M is molarity.

The volume of base has an error which is the standard calculated error for that volume of delivered base from the 50-mL buret. The molarity of the base would have a calculated error based on the method used to standardize the base. The volume of acid would have an error associated with the delivery of the pipet volume. All three contribute to the error of the calculated molarity of the weak acid.

Assuming that the volume of base used has a mean value of 43.56 mL with a standard deviation of 0.89 mL using five titrations, the molarity of base is 0.1012 with a standard deviation of 0.0025 and the volume of acid has a mean value of 50.00 mL with a standard deviation of 0.05 mL, what would be the calculated error associated with this measurement?

## Reference

Skoog, D.A.; West, D.M.; Holler, F.J. *Fundamentals of Analytical Chemistry*, 7th ed.; Saunders: Philadelphia, 1996.

## INSTRUCTOR NOTES FOR ACTIVITY 1
## Choosing and Calibrating Glassware

### Time Required

3 hours plus after lab activity.

### Group Size

At the instructor's discretion, students can work in groups of 2 or 3.

### Additional Instructor Objectives

The following skills are critical not only to this activity but also to future success in the course:

- pipetting technique
- volumetric flask dilutions
- weighing
- spreadsheet operation

### Materials Needed

- analytical balance
- pipets (1, 2, 5, and 10 mL)
- volumetric flasks (10, 25, and 50 mL)
- deionized water
- thermometer
- computer with spreadsheet program such as Lotus 1-2-3, or Excel or others

### Safety, Handling, and Disposal

This laboratory experiment involves no hazardous chemicals. Care should be taken when handling laboratory glassware. Do not allow students to pipet with their mouths. Make sure students wear safety goggles. Dispose of used reagents according to local ordinances.

### Points to Cover in the Pre-Lab

#### Part 1

To introduce the activity, create a scenario for students that involves a client who wants something analyzed. Have students ask questions of the "client," and guide their inquiry so their questioning will lead to discussion of topics such as the description of the problem, the matrix, number of samples, rarity of the analyte or sample, and precision the client needs. Students should be able to discuss how to find a method within the precision range of the clients' needs. Lead discussion into the choice of glassware and precision of each type of glassware, and begin the activity.

#### Part 2

Check analytical text for discussion of error and propagation of error.
Define the following terms for students:

- accuracy Closeness to the true or accepted value
- precision Repeatability of the experiment
- analysis The evaluation of the components of a sample
- determination The individual evaluate of quantity of a specific analyte
- ppm Parts per million

Define standard deviation, relative standard deviation, mean, and median.

## Experiment 1

Your client presents the analytical parameters for a particular determination. One of these parameters is that the precision be 3% or less. After several attempts at using the method, the best precision that you exhibit is 6%. What do you do?

Essentially, imprecision can be generated in three basic areas: 1) analyst techniques, 2) instrument fluctuations, and 3) the glassware used to make the required solutions. In the first case, practice will improve precision. In the second case, if the instrument is optimized and all components are within specifications, the chances are that you will not be able to improve the precision. Obviously one should make sure that the instrument is at peak performance.

The third case is less often considered but still very important. Careful choice of volumetric equipment can significantly improve the precision of the method. Expert laboratory analysts who are excellent at laboratory manipulation and have their instruments optimized can use only this area to improve the precision of a method.

Introduce the concept of cumulative errors in a method (i.e. propagation of errors) using the question at the end of the experiment handout. In this experiment students will discover the tricks that an analytical chemist uses to improve precision.

## Techniques

Introduce the weighing bottle, giving the following information: The purpose of this glassware is to hold a material that is to be weighed. Material is placed in the bottle and the filled bottle is weighed. The bottle is removed from the balance and a quantity of the material is removed. The bottle is returned to the balance and reweighed. The difference in weight is the weight of the material removed. This procedure can continue until the bottle is empty.

Ask the students, “How do we remove the bottle?” (Pick it up with a couple of fingers.) “Do we pick it up this way?” Students should answer “No,” because fingers are greasy, and that grease will add to the weight of the bottle and cause an inaccurate weight measurement. Then ask, “Do we pick it up with tongs?” (Demonstrate the tongs.) Students should answer that unless the tongs are brand new, probably not. Rust and other oxides that form on tongs can leave residues in the balance and fall into the weighing bottle material.

Now move on to the topic of filling the pipets. Emphasize that, for safety reasons, mouth pipetting is not permitted. Students must use pipet bulbs. Demonstrate the bulb, including wetting the hole to allow the pipet to slip more easily into the bulb. Point out that when attaching the bulb to the pipet, the pipet should be pointed away from the body (for safety

reasons) and that the tip of the pipet should never touch a surface, especially when the user is applying pressure to the top (for both safety and the accuracy of the pipet). Demonstrate that the pointer finger has more control than the thumb on top of the pipet. Remind the student that the meniscus bottom is read at the line and that the last bit of solution is not blown out. Show the students how to rinse the pipet. Tell the students not to take solutions from their original containers but to pour the solution into a secondary container to avoid contamination of the entire solution.

Now introduce the balance, giving the following information: A balance is used to measure weight. Analytical balances are highly accurate and precise tools that can weigh to 1/10,000th of a gram. The usual precision is also at 1/10,000th of a gram. Analytical balances usually cost at least $1,000 and can be as expensive as $5,000. Therefore, it is imperative that students treat these balances with respect. Any material left in the balance can destroy the delicate components. Emphasize the importance of removing the weighing bottle from the balance after weighing is finished, to ensure that no material is spilled in the balance. If something is spilled in the balance, students must clean it up immediately.

## Procedural Tips and Suggestions

Students will calculate the mass of the water in a vacuum using the given calculation and temperature reading and then calculate the volume of water in the glassware at room temperature. Have students create an organized system of measuring and recording data and record the data in a professional lab notebook. Have students put the water mass data in a spreadsheet for each pipet, then calculate the relative standard deviation for the five measurements. (See Table 1.)

Students should note trends in the data. Depending on their technique, students should find that the larger the volumetric glassware, the smaller the relative standard deviation. Larger-volume vessels are more precise up to a certain volume (50 mL for pipets, 1L for volumetric flasks), but at larger volumes the advantage based on precision and usability considerations are not worth the extra effort. Have students give reasons for this trend.
Lead them to conclude that as a volume gets smaller and smaller, the technician-controlled amount of substance is relatively larger in comparison. (For example, a drop of water is large compared to a 2-mL pipet but not as large compared to a 10-mL pipet.) The next question asks students to transfer the knowledge about the advantages of using the largest glassware practical for the job to using burets. The highest level you can fill a buret to is the best level to start with. For example, it is best to fill a 50-mL buret with 49 mL or more of titrating solution, but not so much more that the level goes above the 0.00 mL line.

Technique is an important component of this activity—students who are sloppy or have little experience with glassware will be discovered early because their results will not match those of a more experienced or careful student, nor will they display true trends.
Have students pool data with small groups or the entire class to see the trends with a larger sample size. Students should also realize that choice of glassware and method is important, and knowing the needed precision is important as well.

This activity could also be done as a "dry lab." Give students data collected from previous labs and have them use a spreadsheet to calculate the relative standard deviation and see the trend towards larger deviation with smaller pipets. Students will have "real" numbers to perform statistical operations on and can practice using the spreadsheet in a scientific context.

## Sample Results

Results are based on the assumption that the density of air is 0.0012 g/mL.

| Sample Results for 1 mL Pipet | | |
|---|---|---|
| Meas. Mass | Mass Vac. | Vol Calc. |
| 0.9993 | 1.000 | 1.002 |
| 1.0024 | 1.0035 | 1.0055 |
| 1.0020 | 1.0031 | 1.0051 |
| 1.0234 | 1.0245 | 1.0265 |
| 1.0118 | 1.0129 | 1.0149 |
| mean | | 1.0109 |
| standard deviation | | 0.0089 |
| rel. standard deviation (%) | | 0.88 |

| Sample Results for 5 mL Pipet | | |
|---|---|---|
| Meas. Mass | Mass Vac. | Vol Calc. |
| 4.9603 | 4.9656 | 4.9755 |
| 4.9648 | 4.9701 | 4.9801 |
| 4.9434 | 4.9486 | 4.9586 |
| 4.9646 | 4.9699 | 4.9799 |
| 4.9574 | 4.9627 | 4.9726 |
| mean | | 4.8733 |
| standard deviation | | 0.0079 |
| rel. standard deviation (%) | | 0.16 |

| Sample Results for 10 mL Pipet | | |
|---|---|---|
| Meas. Mass | Mass Vac. | Vol Calc. |
| 9.9731 | 9.9837 | 10.004 |
| 9.9639 | 9.9745 | 9.9945 |
| 9.9827 | 9.9933 | 10.013 |
| 9.9683 | 9.9789 | 9.9989 |
| 9.9701 | 9.9807 | 10.001 |
| mean | | 10.002 |
| standard deviation | | 0.006 |
| rel. standard deviation (%) | | 0.06 |

## Plausible Answers to Questions

### Part 1

1. Which pipets are the most precise and why?

   A. Although the error associated with pipetting is similar for all pipets, the larger the

volumetric glassware, the smaller the relative standard deviation.

$$RSD = \frac{SD}{\bar{x}} \times 100$$

The smaller the relative standard deviation, the greater the precision. Therefore, the larger pipets are the most precise.

2. Which flasks are the most precise and why?

   A. The larger flasks are the most precise, for the same reason given for Question 1.

3. Explain using calculations and words whether it is better to use 20, 49, or 56 mL of solution from a 50-mL buret.

   A. Use 49 mL. The larger the volume of the sample, the smaller its relative standard deviation, so 49 mL will give higher precision than 20 mL. If 56 mL were used, it would require four measurements which would increase the relative standard deviation. The error associated with each buret reading is one drop or 0.05 mL. To calculate the volume a buret delivers, two readings must be taken (both the start volume and end volume). Therefore, the total error associated with delivery of a solution via a pipet is 0.1 mL.

4. Assuming that the volume of base used has a mean value of 43.56 mL with a standard deviation of 0.89 mL using five titrations, the molarity of base is 0.1012 with a standard deviation of 0.0025 and the volume of acid has a mean value of 50.00 mL with a standard deviation of 0.05 mL, what would be the calculated error associated with this measurement?

$$M_A = \frac{M_B V_B}{V_A} = \frac{(0.1012 \pm 0.0025M)(43.56 \pm 0.89mL)}{(50.00 \pm 0.05mL)} = 0.08817M \pm S_a$$

   A. In multiplication and division (a=bcd), relative uncertainties are additive.

$$(S_a)_{rel} = \sqrt{(S_b)_{rel}^2 + (S_c)_{rel}^2 + (S_d)_{rel}^2}$$

$$(S_a)_{rel} = \sqrt{\left(\frac{0.0025}{0.1012}\right)^2 + \left(\frac{0.89}{43.56}\right)^2 + \left(\frac{0.05}{50.00}\right)^2} = 0.0321 = \text{relative error}$$

$$S_a = (0.08817M)(0.032) = 0.00283M = 0.00283 = \text{absolute error}$$

Therefore, the calculated molarity of the weak acid is 0.08817 ± 0.00283 M.

## Reference

Skoog, D.A.; West, D.M.; Holler, F.J. *Fundamentals of Analytical Chemistry*, 7th ed; Saunders: Philadelphia, 1996, Chapters 1-4.

## INTRODUCTION TO ACTIVITY 2
## Sampling, Sample Handling, and Calibration

### Description

In this activity, students measure the absorbance of a set of metal ion standards at various time intervals over a 3-hour lab period. Data is plotted in a spreadsheet so that students can observe trends. In another part of the activity, students monitor the change in concentration of a metal ion solution stored in different types of bottles.

### Goals for the Experiment

- Students learn to operate the atomic absorption spectrophotometer instrument.
- Students learn how to create and use a calibration curve.
- Students enhance their computer skills.
- Students learn how to use a check standard.
- Students learn that the type of storage container used in analysis and/or the solution matrix can affect their data.
- Students extrapolate that if storage of samples is important, so is storage of the standard.
- Students learn the terms “parts per million” (ppm) and “parts per billion” (ppb).

## ACTIVITY 2
## Sampling, Sample Handling, and Calibration

### Part 1

Experiment 1

For the first part of this experiment, make a 2.00 ppm concentration of either copper, iron, or nickel ion metal solution from a 20ppm stock solution and put it in some type of storage bottle. Once you put your diluted metal solution into the bottle, use atomic absorption and calibration standards provided to you to calculate the concentration of the metal in the solution. Store the bottle on the desktop. Remeasure the concentration at about 1, 2, and 3 hours after the initial readings. Plot the concentration versus the time. What is your conclusion? What would you do to stop any observed problems?

Experiment 2

After you make your first measurement (at 0 time), you will make a series of standards for your metal ion. Using the 20 ppm metal stock solution from Part 1, prepare 100 mL each of the following solutions: 10.00, 5.00, 4.00, 2.00, 1.00, 0.50 ppm. Also prepare a 1.5 ppm solution and label it "Check Standard." Use atomic absorption to measure the absorbance values of the standard solutions.

It may be helpful to think about what you want to do before you start to make the solutions. Consider that you have a stock solution that is approximately 20 ppm in your metal. Consider also that you will be preparing 100.00 mL of each solution.

Recall that $M_1V_1=M_2V_2$ where the M refers to Molarity and the V refers to Volume. Both molarity terms can be replaced by any other concentration units (such as ppm) as long as the units on both sides of the equation are the same.

The concentration of the stock solution ($C_1$) is 20 ppm. The concentrations of the final solutions ($C_2$) are listed above. The volume of the final solution ($V_2$) is fixed at 100.00 mL (the size of the volumetric flask you use). Calculate how many mL of the stock solution to pipet into a 100.00 mL volumetric flask to make the desired standard solution when the stock solution is diluted to the mark. The exact concentration of the stock solution is given on the bottle. Let the instructor check your calculated values.

Prepare these solutions including the "check standard" of 1.5 ppm.

When the time comes to measure your metal sample at time 1, 2, and 3 hours, take all of the standard solutions that you prepared and measure their absorbance.

Using the spreadsheet, prepare a plot of absorbance versus concentration. (Do not include the check standard.) Using the regression function, calculate the regression coefficients. Save the spreadsheet to a disk before exiting. What does the regression analysis tell us?

## Part 2

The regression analysis allows us to "fit" our data to a line equation

$$y = mx + b$$

where m=slope and b=y-intercept.

## Part 3

From the Lotus regression table you just prepared, the slope is listed as the "x coefficient" and the y-intercept is listed as "constant." Ask the instructor for assistance in creating your best fit line.

## Part 4

You have just prepared a **calibration plot**. How can this plot be used? What additional information can be obtained from this plot?

## Part 5

Compare your plots to the one the instructor has at the atomic absorption instrument. Are they the same or different? If they are different, why? Are your results different at time 1, 2, and 3 hours?

## Part 6

Calculate the % error of your check standard. Is the % error of your check standard large? It should be no more than 5% as a rule of thumb.

## Part 7

You should probably see a difference between the instructor's calibration plot and yours. Some of the differences can be attributed to random error, differences in techniques, etc. However, this difference exists for another reason, and one of the goals of this laboratory is for you to "figure out" the difference.

## Part 8

Every time you carry out an analysis, you should report all the calibration data as well as your Quality Assurance, check standard, data such as the % error on a check standard, and a standard not used in your regression analysis.

What is the lowest concentration you can measure? How did you determine this value?

## Part 9

The lowest possible concentration that can be reported with confidence is the limit of detection (LOD), or detection limit. Since there are several ways to determine this value, you should see your text or instructor for a plausible method to calculate the LOD.

## Question

We wish to sample local drinking water. Where would you sample the water? How long would you let the water run before you sampled? How much water would you take? How would you store that sample?

## Part 10

The way you answer the question about sampling methods may depend on what questions are to be answered by the analysis. If the question is how well is the treatment plant cleaning the water, the sample would be taken from the clearwells at the plant. If the question is how clean is the water at the household taps, then the water samples will be taken at the taps in the home.

The length of time to run the water depends on another set of questions. If the concern is about the purity of water after the water has sat in the pipes for a while, then the initial few mL of water would be important. If the concern is about the water under normal usage, then it would be important to let the water run for several minutes.

Storage is a tougher question! The type of tests to be run would determine whether you might store the samples in different ways for each test. The material of the storage bottle would be critical.

## Part 11

### After-Laboratory Assignment

Regression analysis or least squares is the statistical way to determine the line equation for a set of data points. The after-laboratory assignment is to program your spreadsheet program to perform linear least squares analysis. In other words, do not use the spreadsheet's canned regression analysis routine yet. Use the following data to demonstrate that your program works.

| Regression Analysis Data | |
|---|---|
| X | Y |
| 2.5 | 1567 |
| 5.0 | 3124 |
| 7.5 | 4702 |
| 10.0 | 6278 |
| 12.5 | 7809 |
| 15.0 | 9497 |

After you have completed calculations according to your own program, use the spreadsheet's canned regression analysis routine. Compare numbers from your program with the canned routine numbers. Are they different? If so, why?

## INSTRUCTOR NOTES FOR ACTIVITY 2
## Sampling, Sample Handling, and Calibration

### Time Required
3 hours

### Group Size
At the instructor's discretion, students can work in groups of 2 or 3.

### Additional Instructor Objectives
- calculations for dilution
- graphing

### Materials Needed
- atomic absorption instrument
- 2 new bottles made of different materials (e.g., one plastic, one glass)
- 20 ppm Cu, Fe, or Ni standard solution
- deionized water
- sample plot (see Part 5)
- 100-mL volumetric flasks
- pipets

### Safety, Handling, and Disposal
Dispose of used reagents according to local ordinances.

### Points to Cover in the Pre-Lab
How analytical chemists sample and how they treat the samples after acquisition is perhaps more important than the actual measurement. It is imperative that the samples be taken in a way representative of the sampling site.

Once students have the sample, they must maintain its integrity. This experiment will help them discover an important lesson about sample and standard preservation.

Set up a schedule for students' analysis and start the experiment.

### Procedural Tips and Suggestions
During the time students are making their standards, observe students to see if they are applying the principles they learned in Activity 1. Students should be using the largest volumetric glassware that is appropriate in order to minimize the error associated with making their standards. Questioning the students with regard to their glassware choice may help them to realize that the principles they learned in Activity 1 can help them to increase their accuracy in making their own solutions.

During the waiting periods, explain how students will use the data from the atomic absorption instrument. Avoid the use of the term "Beer's law," since students will discover

that later. Spend more time with students showing them how to get a calibration curve in the spreadsheet and how to use the regression analysis. The important point is that the real data points are shown but not the connect-the-dot line and that the regression line is shown but not the regression data points.

## Experiment 1

**In order for this experiment to work, it is imperative that students store their solutions in new bottles.** This will insure the greatest change in concentration that can be observed over a 3-hour lab period. Old bottles that have been through several acid washes tend to maintain sample integrity better than new bottles. The bottles should be filled completely to maximize the decrease in metal ion concentration.

Students should recognize that the concentration of a solution varies over time and that the variation depends on the material of the storage device. For example, storing a metal ion solution in a polymethacrylate bottle will cause significant lowering of concentration levels because the ions are attracted to negative spaces in the polymer and tend to become trapped in the matrix over time. Samples kept in glass bottles will degrade slowly over time, but for temporary storage glass is usually fine. Students should explore possible ways to prevent this "sample loss" from happening. Have students think of reasons for the loss and ways to treat the sample by asking questions such as, "What is glass made of?," "What chemical species would you expect to find on the surface?," and "Would you expect the surface species to change depending on the pH of the sample matrix?" Questions such as these, along with the information provided by the instructor, will help students to realize that one way to prevent "sample loss" is by adding acid to the sample to lower the pH. This will cause the ions to remain in solution longer because the $H^+$ will cap the $SiO^-$ groups on the glass surface. Ten mL of concentrated $HNO_3$ per liter of solution is sufficient. However, the purity of the acid is an issue. Contaminants in the acid may affect metal ion concentration and would need to be corrected for. Students should also be aware that their standard solutions may need to be made fresh daily.

This activity increases students' comfort level with instrumentation early in the semester, helping them become familiar with the available instruments for later projects.

From the concentration vs. time data collected in Experiment 1, students should organize a table for data and format a plot using a spreadsheet.

## Experiment 2

Allow students time to decide the best way to conserve stock solution and still make the series of dilutions. Dilution series are important everyday tasks for lab technicians, so practicing these techniques whenever possible is helpful to the students. This also serves as a checkpoint for instructors. If students cannot calculate volumes or manipulate glassware to make a good calibration curve, then they need to work on their skills.

Have students perform a regression analysis on the data they obtained for absorbance vs. concentration from atomic absorption techniques. Next, students should plot both the experimental results and the calculated results using the regression formula. The calibration

plot is used to find unknowns from their measured absorbance and to allow students to compare their curves to the instructor's curve and realize their own curves need improvement.

The check standard serves as a quality control check. A students' calibration curve can be precise but not accurate. The check standard is a way to determine the accuracy of the calibration curve. Discuss detection limits in class or lab, referring to government agencies' requirements. For example, the U.S. Environmental Protection Agency has helped define many of the detection limits in use today and has its own requirements for reporting. Your textbook should have more information, or for further reference, see current materials from governmental agencies such as the EPA.

Students should draw from their previous experience with the sample handling of metal ion solution and realize that storage container material is important. Other answers require thinking critically about what to look for in the water sample. Students should know to ask more questions until they narrow down the analyte, what type of problems occur during water analysis, and other such focal issues. Lead them through the inquiry by asking, "What environmental issues are usually brought up involving drinking water? What things influence the quality of drinking water?" Question students so that they think about the source of the water, where the water travels, whether the water is moving or stationary, and other such variables. You may wish to follow up this activity with the Comparison of Analytical Methods lab.

## Plausible Answers to Questions

See the student handouts.

## INTRODUCTION TO ACTIVITY 3
## Absorption/Emission

### Description

This experiment is designed to engage students in the interaction of matter and light. Students will first do simple flame tests and form hypotheses explaining what they see. They will then record absorbances of a dye solution on a UV/VIS spectrophotometer at various cell pathlengths and concentrations. By using a spreadsheet to plot data, students will discover for themselves factors that combine to give the Beer-Lambert law, often called Beer's Law.

### Goals for the Experiment

- Students "discover" Beer's law.
- Students learn factors influencing absorption or emission of light by matter.
- Students learn how to operate a UV/Vis spectrophotometer.
- Students enhance their computer skills.

## ACTIVITY 3
## Absorption/Emission

### Part 1

Hold a spatula containing LiCl in a flame. Do the same thing for NaCl. What do you see?

### Part 2

The lithium produced a red color in the flame, and the sodium produced a yellow-colored flame. Why do these compounds produce different-colored flames?

### Part 3

LiCl and NaCl produce different-colored flames because the light that is observed is the emission of energy from the excited-state atomic orbitals of the metals. What is the difference between lithium and sodium that causes them to produce different colors?

### After Laboratory

Look up the most intense line in the visible spectra for lithium and sodium atoms in the CRC Handbook's Line Spectra of the Elements Table. Using the energy relationship E=hc/l, calculate the energies associated with the predominant lithium and sodium atom lines.

### Part 4

Would you expect similar types of processes to exist with molecules? Why or why not?

### Part 5

Just like atomic electrons, the electrons of a molecule occupy low-level molecular orbitals. When the appropriate amount of energy is introduced to the sample, some of the electrons are excited to higher-energy molecular orbitals. This process is called absorption. Since a molecule will not stay in the excited state indefinitely, the absorbed energy must be released. In many cases this energy is released in the form of light. This process is called emission.

In analytical chemistry the amount of light absorbed or emitted can be measured and eventually equated to the concentration of the analyte of interest. In absorption-based measurements, the measurement is usually taken at the maximum peak signal or l (max).

Let's do another experiment. Obtain the entire UV/visible spectrum for Dye 1. Do the same thing for Dye 2.

### Part 6

What was the difference in the spectra?

### Part 7

Clearly, the maximum peaks are at different wavelengths and the general shape of the two spectra are different with varying intensities. The spectra are not the same because the amount of energy needed to create the electron transitions between molecular orbitals are different.

Can the differences in molecular absorption or emission be used as an analytical tool?

## Part 8

Absorption and emission are very important analytical tools. The general name for these techniques is spectrophotometry. When atomic orbitals are involved as in atomic absorption spectrophotometry, they are considered atomic spectrophotometric techniques. When molecular orbitals are involved, they are molecular spectrophotometric techniques.

In spectrophotometry the amount of light absorbed or emitted from a sample is measured. Therefore, a relationship between concentration and absorption or emission must be established in order for these processes to be used in analytical methods. Let's start with absorption.

The hypothesis is that for absorption spectrophotometry a simple relationship must exist between the measured signal (absorbance) and the concentration of the absorbing material (moles/L) in the sample. A typical inexpensive spectrophotometer consists of a source light, a wavelength selector, a sample cell, and a detector.

Let's make a few ideal behavior assumptions about the instrument: Assume that the intensity of the source light, the conversion of photons to electrical signal in the detector, the number of photons lost in the system, and the sample cell path are all constant.

To establish the relationship between absorbance and concentration, we must make a few assumptions about the chemistry of the system. The absorbing compound must absorb light at a constant rate at constant cell paths and compound concentrations. Temperature, pressure, and solvent used to dissolve the sample are the same at all times.

Our hypothesis can be expressed as an equation:

*Absorbance = a mixture of variables and constants?*

where one variable must be concentration. We can perform a simple experiment to test our hypothesis. First, the absorbance of a 1 x $10^{-5}$ M solution of Dye 1 will be measured using 1-, 2-, 3-, and 10-mm path length cells. Observe and record the absorbance. Plot the recorded absorbance versus cell path length.

What relationship appears to exist between absorbance and cell path length? Turn in your spreadsheet and plot of the data.

## Part 9

Next, using a standard 10-mm path length cell, observe and record the absorbance of 5.0 x $10^{-6}$M, 7.5 x $10^{-6}$ M, 1.0 x $10^{-5}$M, 2.5 x $10^{-5}$ M, 7.5 x $10^{-5}$ M and 1.0 x $10^{-4}$ M Dye 1 solutions. Plot the recorded absorbance versus Dye 1 concentration.
What relationship appears to exist between absorbance and concentration? Use a spreadsheet and plot the data.

## Part 10

You should get two straight line plots with $R^2$ values of 0.9997 or better. What do these plots tell us?

## Part 11

In the first experiment it is clear that a proportional relationship exists between absorbance and cell path length (b). Therefore, our basic hypothesis can be written to read:

$$Abs = b + \text{other constants and variables?}$$

The second experiment demonstrates that another proportional relationship exists between absorbance and absorbing material concentration (c). The basic hypothesis can be written to read:

$$Abs = c + \text{other constants and variables?}$$

Combining these two experiments the hypothesis is now:

$$Abs = bc + \text{other constants and variables?}$$

Now we must address a new question: do any other variables or constants exist? Given the stated conditions of the experiment, no additional variables would appear to exist in this experiment. But what about constants? We assumed that the same compound consistently gives the same absorbance at a set concentration and cell path length, but is this assumption true? Do all compounds give the same absorbance at set concentrations and cell path lengths? (Look at the data for Dye 1 and Dye 2.)

## Part 12

It appears that the same concentrations of both dyes with the same cell path length give different absorbance. But the equation generated at this point states absorbance is equal to the cell path length and the analyte concentrations. The current equation is inconsistent with the observation. Whenever a difference appears to exist between current theory and observation, some compensation must be made. Let's add a constant, e, to the hypothesis equation to represent absorption efficiency.

$$Abs = ebc$$

Calculate, using the newly hypothesized equation, what the factor would be for Dye 1 and for Dye 2.

Each dye has a different e value at different wavelengths. The e factor is in fact a constant value for a given wavelength of a particular compound. It is called the molar extinction coefficient. The equation:

$$Abs = ebc$$

is known as the Beer-Lambert Law (Beer's Law for short). Any absorbance or emission-based measurement is initially governed by Beer's Law.

Another experiment should be performed. You have already measured Dye 1 and Dye 2; measure a solution that is $1 \times 10^{-4}$ M Dye 1 with $1 \times 10^{-4}$ M Dye 2. What can be said about Beer's Law when multiple compounds are measured together? Do the compound spectra interfere or add to each other?

## Part 13

The answer is that Beer's Law is additive. The absorbance at all wavelengths of Dye 1 added to the absorbance at all wavelengths of Dye 2 should be equal to the absorbance measured from the mixed solution. In a practical application this means that if the molar extinction coefficients for both dyes are known at two wavelengths, a simultaneous equation can be established to solve for unknown concentration.

## INSTRUCTOR NOTES FOR ACTIVITY 3
## Absorption/Emission

### Time Required

3 hours

### Group Size

At the instructor's discretion, students can work in groups of 2 or 3.

### Materials Needed

- UV/Vis spectrophotometer (variable wavelength)
- analytical balance
- 1, 2, 5, 10 mm spectrometer cells
- 1 x $10^{-4}$ methyl orange
- 1 x $10^{-4}$ bromothymol blue
- spatula tip LiCl
- spatula tip NaCl
- computer with a spreadsheet program such as Lotus 1-2-3, Excel or others

### Safety, Handling, and Disposal

Consult the instrument manual for proper operation of the UV/Vis spectrophotometer. Dispose of used reagents according to local ordinances.

### Pre-Lab Discussion

Activities 3 and 4 are used to introduce the two most important, basic analytical equations for measurement; Beer's Law for absorbance and the Nernst equation for electrochemical potential. After weighing, these two equations account for more than 70% of the measurements made on a routine base. These two experiments are designed to be totally discovery-based in their approach. Students must perform the tasks on the individual sheets and give the correct answer to you before they receive the next sheet. Do not give out all the handouts at one time.

### Procedural Tips and Suggestions

Feel free to substitute other dyes for the methyl orange and bromothymol blue. Try to pick dyes that absorb in different regions of the spectrum and be sure to have a copy of the spectra for your students.

For Beer's Law demonstrate the correct way to handle spectrophotometer cells (edges only) and no wiping of liquids from the surfaces, only tamping. Tell the students to rinse the cell with the solution, dump that portion out, and fill the cell with fresh solution.

### Parts 1-7

This time should be used to give students an understanding of how light interacts with matter. Be sure to include a description of ROYGBIV and how light observed relates to light absorbed.

Students probably have learned about atomic orbitals previously, so ask questions that challenge their conceptual base and allow them to hypothesize and reason through it themselves. You may discuss the differences between absorption, reflection, and emission, reasons for the different colors, atomic orbital levels, the organization of the periodic table, and molecular orbitals depending on the direction of questioning.

## Parts 8 and 9

Students can make their own solutions or use those already provided. Students should organize data in a spreadsheet table and graph their results as shown in Figures 1 and 2.

**Table 1**

| pathlength | trial 1 | trial 2 | trial 3 | mean | blank |
|---|---|---|---|---|---|
| 1 mm | 0.029 | 0.028 | 0.028 | 0.029 | -0.005 |
| 2 mm | 0.058 | 0.058 | 0.058 | 0.058 | -0.009 |
| 5 mm | 0.164 | 0.164 | 0.164 | 0.164 | -0.006 |
| 10 mm | 0.334 | 0.334 | 0.334 | 0.334 | -0.006 |

| **Regression Analysis** | |
|---|---|
| regression equation | y = a + bx |
| y-intercept (a) | -0.008 |
| slope (b) | 0.034 |
| correlation coefficient | 0.9999 |
| number of observations | 4 |

## Figure 1: Pathlength vs. Absorbance

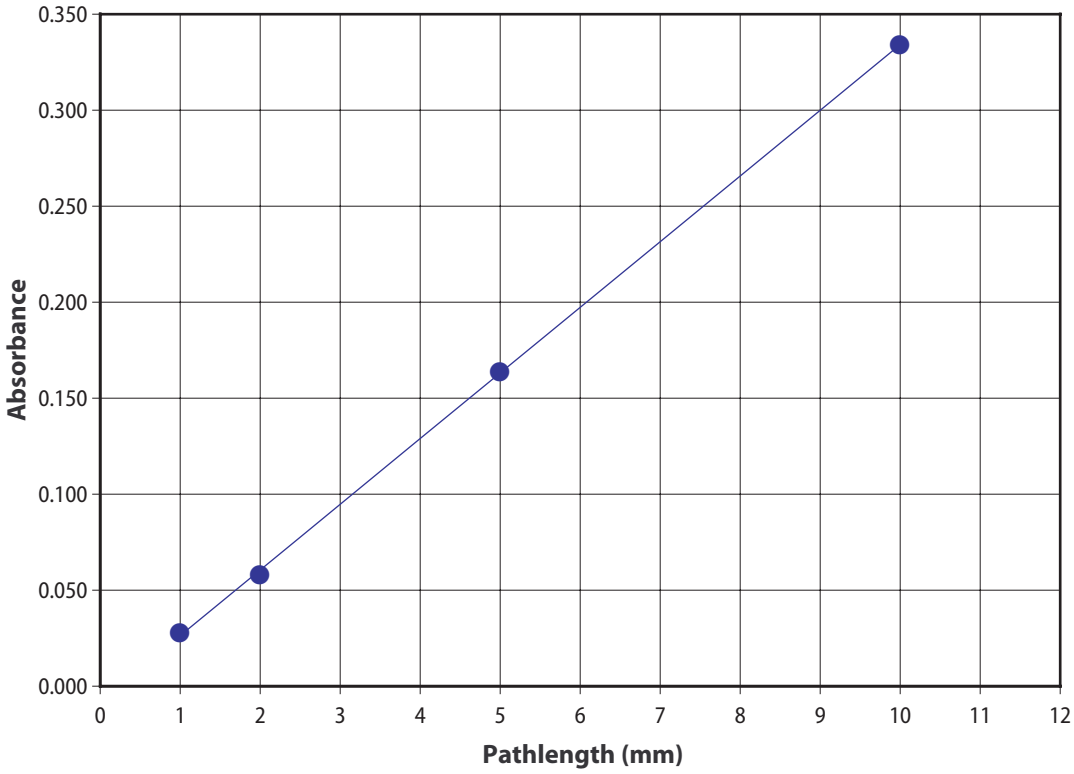
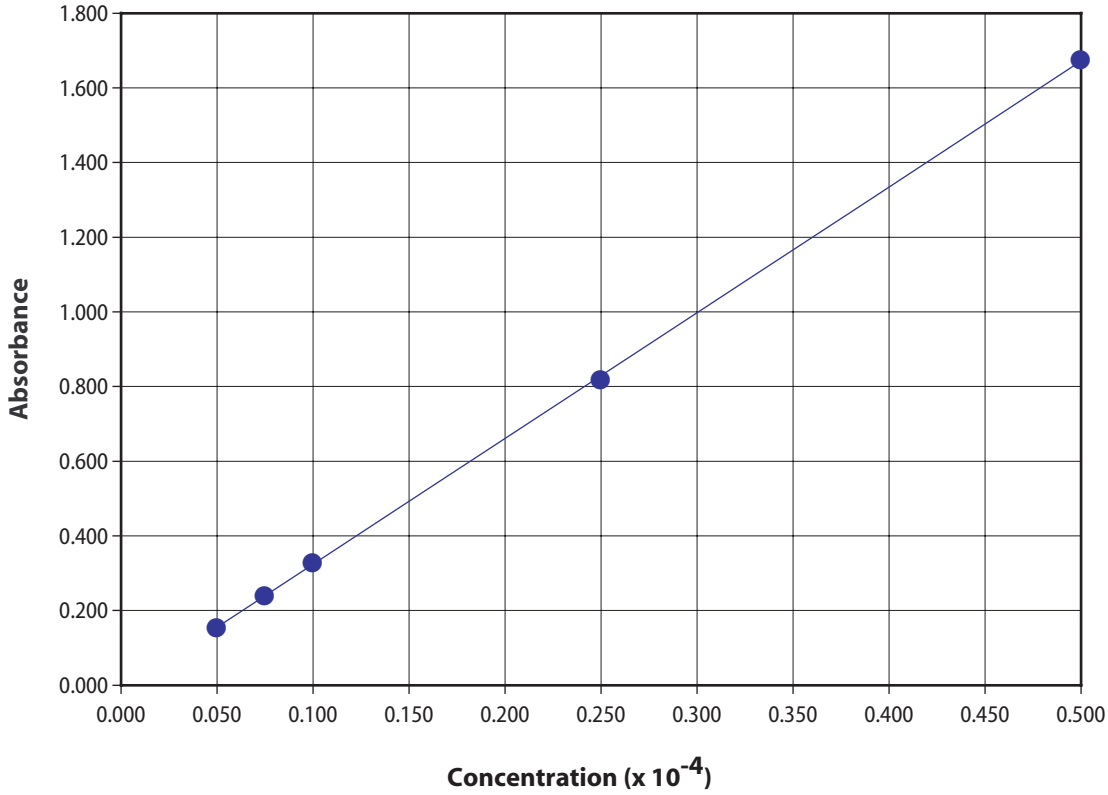



**Table 2**

| Concentration [x $10^{-4}$] | Absorption 1 | Absorption 2 | Absorption 3 | Mean |
|---|---|---|---|---|
| 0.050 | 0.155 | 0.154 | 0.155 | 0.155 |
| 0.075 | 0.241 | 0.241 | 0.241 | 0.241 |
| 0.100 | 0.329 | 0.329 | 0.329 | 0.329 |
| 0.250 | 0.820 | 0.820 | 0.820 | 0.819 |
| 0.500 | 1.675 | 1.677 | 1.675 | 1.675 |
| 0.800 | 2.545 | 2.536 | 2.531 | 2.538 |
| 1.000 | 3.018 | 3.110 | 3.007 | 3.045 |

**Figure 2: Absorbance vs. Dye Concentration**




| Regression Analysis* | |
|---|---|
| regression equation | y = a + bx |
| y-intercept (a) | -0.013 |
| slope (b) | 3.369 |
| correlation coefficient | 0.9999 |
| number of observations | 5 |

* Regression analysis was performed using only the first five data points in Table 2. [The line should go through (0.0).] This would be a good time to discuss deviation from the straight line at high absorbances.

## Parts 10-13

From the previous experiments, students should be able to "discover" Beer's Law. Help the students relate their experimental data to Beer's Law equation and finally to a physical meaning of Beer's Law. For example, one can talk about the fact that molecules absorb light and the more "absorbers" that are in the light's path, the greater overall absorption. An increase in absorption can be caused by having a longer pathlength or a more concentrated solution—either way there are more "absorbers" in the path of the light. Talk about deviations from Beer's Law and the condition under which it occurs.

Students should also "discover" that Beer's law is additive. A mixture of Dye 1 and Dye 2 contains two types of molecules. As long as these two molecules absorb light at the chosen wavelength and do not interfere with each other, their individual absorbances will add up to the total amount of light absorbed by the solution.

## Sample Results

See Figures 1 and 2.

## Plausible Answers to Questions

The answers to the student questions are given in the handouts.

## Reference

Skoog, D.A.; West, D.M.; Holler, F.J. *Fundamentals of Analytical Chemistry*, 7th ed.; Saunders: Philadelphia, 1996.

## INTRODUCTION TO ACTIVITY 4
## Discovering the Nernst Equation

### Description

This experiment engages students in potentiometric measurements applied in oxidation-reduction reactions. The results from these measurements are plotted and compared with theoretically calculated values to determine the factors affecting electrochemical measurements. By manipulating equations and data, students eventually "discover" the Nernst equation and find that it is based on the activities of the species and not merely concentrations.

### Goals for the Experiment

- Students will "discover" the Nernst equation.
- Students will learn factors affecting potentiometric measurements.
- Students will enhance computer skills.

## ACTIVITY 4
## Discovering the Nernst Equation

### Student Handout

Objective

The objective of this experiment is to allow the student to discover the Nernst Equation. This is the equation that governs the majority of electrochemical techniques.

Introduction

The two most often-used techniques for analytical measurements are spectroscopy and electrochemistry. Electrochemical techniques involve the oxidation-reduction chemical reaction. They require that the system have both a reduction and oxidation reaction occurring in some part of the electrochemical cell. Electrochemical techniques are based on Ohm's Law, which states that current, I, is equal to the potential, E, divided by the resistance, R (I = E/R). The potential is also related to free energy, ΔG. Free energy, ΔG, is equal to the negative of the number of moles, n, times Faraday's constant, F, times the potential (ΔG = -nFE).

In practice, oxidation-reduction reactions change the relative amounts of the electroactive species, which in turn produces a change in potential. For example, when making a pH measurement, the signal measured is a potential change created by a change in hydrogen ion concentration. This potential range is then calibrated to represent pH. Other electrochemical techniques hold the potential constant and measure the change in current. For the purpose of this experiment the potential measurement technique, potentiometry, will be the focus of the work.

### Part 1: Free Energy Calculation

Given that ΔG = -nFE, calculate the voltage that would be measured in a simple cell given that the anode is a cadmium bar and the cathode is a silver bar and both are in contact with a solution of 0.0167M $CdCl_2$. The Faraday's constant is 9.649 x $10^4$ Coulomb/mol and free energy for Cd is-150 KJ/mol. First write the balanced half cell reactions. Identify which half cell is the anode and which is the cathode. (1 volt=1 J/C.)

### Part 2

The answer is 0.777 J/C=0.777V. The balanced half cell reactions are:

$$Cd_{(s)} \leftrightarrow Cd^{2+}_{(aq)} + 2e^-$$

$$2AgCl_{(s)} + 2e^- \leftrightarrow 2Ag_{(s)} + 2Cl^-_{(aq)}$$

From the half cell reaction we see that 2 moles of electrons are required. The calculation of potential is:

$$E^0 = \frac{-\Delta G}{nF} = \frac{-(-150 \times 10^3\, J)}{2\ mol * 9.649 \times 10^4\, C / mol} = 0.777\, \frac{J}{C}$$

Every half cell reaction has a standard potential, E0. This standard potential has been

measured against the standard hydrogen electrode, which by convention has a potential of zero. In addition, the activities of all reactants and products in the cell is unity. Unfortunately, the majority of electrochemical measurements are not made at unity. Therefore some type of equation which adjusts the standard potential for the actual conditions of the cell is needed. Once the equation is established, it should allow us to calculate the expected potential under conditions other than reactants and products at unity. This equation is called the Nernst Equation.

A rough form of this equation would be:

$$E' = E^0 + (K * \textit{species activities})$$

where E′ is the measured potential, K is a constant or combination of constants.

Let's perform the following experiment. Using a pH meter set to measure millivolts, measure the following solutions with a copper wire and a Ag/AgCl electrode: 0.5, 0.1, 0.05, 0.01M $CuSO_4$. Plot this data.

## Part 3

Depending on how you plotted the data, a variety of curves could be realized. However, here is a clue:

$$aA + bB \leftrightarrow cC + dD$$

According to chemical thermodynamics, the free energy change when a reaction proceeds to the right is:

$$\Delta G = \Delta G^0 + RT \ln\left(\frac{a_C^c a_D^d}{a_A^a a_B^b}\right)$$

where R is the gas constant, T is absolute temperature, and $a_C$ is the activity of the species C. At equilibrium, ΔG=0 and therefore

$$\Delta G^0 = -RT \ln\left(\frac{a_C^c a_D^d}{a_A^a a_B^b}\right)$$

or

$$\Delta G^0 = -RT \ln K_{eq}$$

Plot the log concentration on the x-axis and millivolts on the y-axis. What do you get and what is the slope?

## Part 4

You should get a straight line with a slope of 29.5 mV/decade of concentration changed. How can we predict this?

Now combine the free energy expression in Part 3 with the one in Part 1.

## Part 5

Combining from Part 1 ΔG=-nFE and Part 3

$$\Delta G = \Delta G^0 + RT \ln\left(\frac{a_C^c a_D^d}{a_A^a a_B^b}\right)$$

gives

$$-nFE = \Delta G^0 + RT \ln\left(\frac{a_C^c a_D^d}{a_A^a a_B^b}\right)$$

Using the fact that $\Delta G^0 = -nFE^0$ and converting ln to log (ln = 2.303 log), using the Faraday constant number, temperature at 25°C (298 K) and a gas constant value of 8.314 (V*C)/(K*mol), what is the new equation?

## Part 6

The new equation is

$$E_{measured} = E^0 - \frac{0.0591}{n} \log\left(\frac{a_C^c a_D^d}{a_A^a a_B^b}\right)$$

This is the Nernst equation. Now using the concentration of $CuSO_4$ in the solutions, the E value from your text for the $Cu^{2+}/Cu$ couple, and the fact that $E_{cell} = E_{cathode} - E_{anode}$ and the Ag/AgCl electrode is 0.222 V, calculate what potential should have been measured and compare these values against the experimental values. Why do they differ?

## Part 7

The calculated value differs from the experimental value because you have calculated and plotted the data as concentration, not activities; however, the calculation of activity is beyond the scope of this course.

## INSTRUCTOR NOTES FOR ACTIVITY 4
## Discovering the Nernst Equation

### Time Required

3 hours

### Group Size

At the instructor's discretion, students can work in groups of 2 or 3.

### Materials Needed

Per group

- pH meter
- copper electrode
- emery cloth
- Ag/AgCl electrode
- balance
- 0.02 g $CuSO_4 \cdot 5H_2O$
- computer with spreadsheet program such as Lotus 1-2-3, Excel or others

### Safety, Handling, and Disposal

Consult the manual for proper operation of the pH meter. Dispose of used reagents according to local ordinances.

### Pre-Lab Discussion

Activities 3 and 4 are used to introduce the two most important, basic analytical equations for measurement: Beer's Law for absorbance and the Nernst equation for electrochemical potential. After weighing, these two equations account for more than 70% of the measurements made on a routine basis. These two experiments are designed to be totally discovery-based in their approach. Students must perform the tasks on the individual sheets and give the correct answer to you before receiving the next sheet. Do not give out all the handouts at one time.

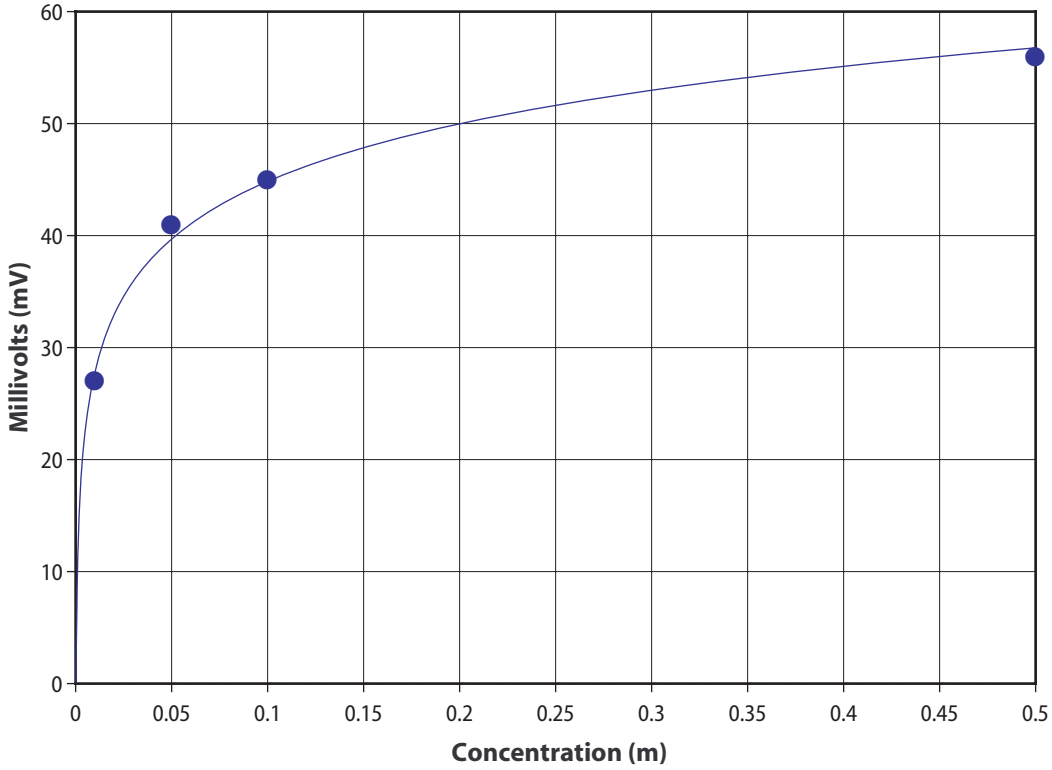
### Procedural Tips and Suggestions

The copper electrode must be sanded clean of oxide with emery cloth for best results. Also, condition the wire by soaking it in $CuSO_4$ for 1 hour.

For calculations, students may have to look up different constants in the CRC or a similar handbook. If label of the constant differs from the units they need to work with, students will use dimensional analysis skills.

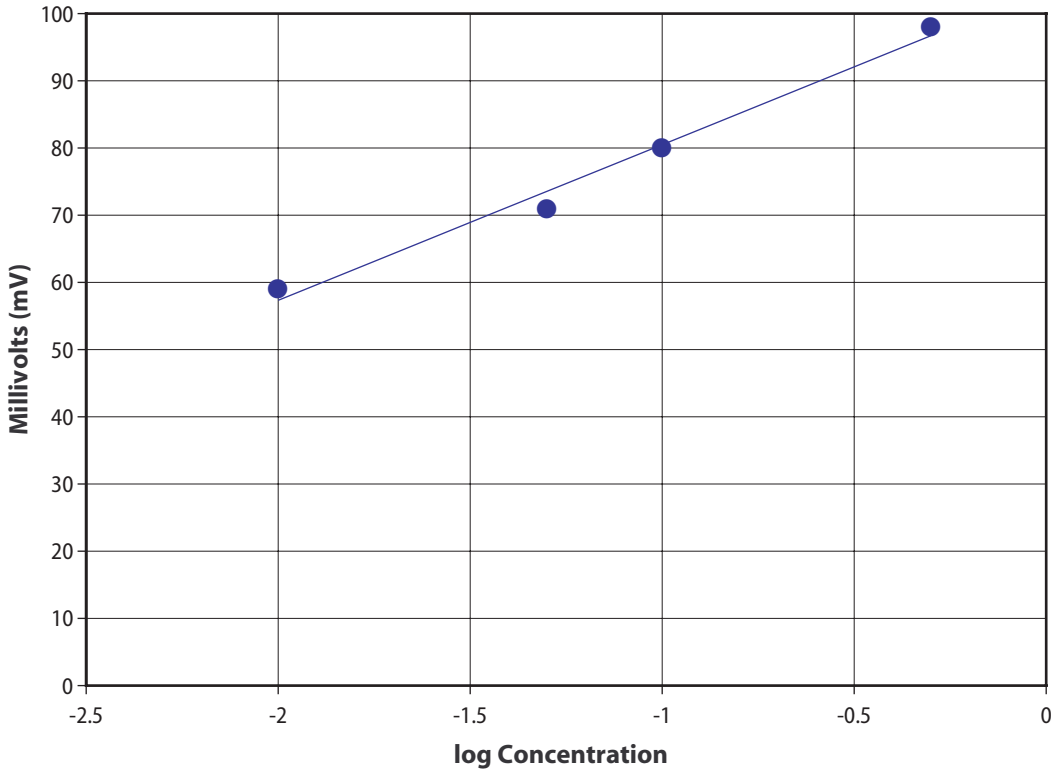
Students' data from Part 2 should look similar to Figure 3, which appears to have no correlation.

**Figure 3: Concentration $CuSO_4$ vs. Millivolts**




However, when students plot the log concentration versus millivolt change, they should get a straight line plot with a slope of 29.5 mV/decade of concentration change. (See Figure 4.)

**Figure 4: log Concentration vs. Millivolts**




| Regression Analysis | |
|---|---|
| regression equation | y = a + bx |
| y-intercept (a) | 103.65 |
| slope (b) | 23.17 |
| correlation coefficient | 0.9931 |
| number of observations | 4 |

Students can then determine the Nernst equation by using the handouts to walk through the derivation and substituting variables.

## Sample Results

See Figures 3 and 4.

## Plausible Answers to Questions

See student handouts.

## References

*CRC Handbook of Chemistry and Physics: A Ready-Reference Book of Chemical and Physical Data*, 78th ed.; Lide, D.R., Ed.; CRC: Boca Raton, 1997.

Skoog, D.A.; West, D.M.; Holler, F.J. *Fundamentals of Analytical Chemistry*, 7th ed.; Saunders: Philadelphia, 1996, Chapters 1-4.

## INTRODUCTION TO ACTIVITY 5
## Separation of Cation

### Description

In this activity students will determine the concentration of several cations in solution using titrations, masking, and ion exchange resin conversion. Given the methods for analysis of the various cations, students are to determine an analysis plan.

### Goals for the Experiment

- Students will learn how to use two types of selectivity techniques—masking and ion exchange chromatography.
- Students will learn how to plan an experiment.
- Students will practice titration skills.
- Students will develop problem-solving skills.

## ACTIVITY 5
## Separation of Cation

### Objective

The objective of this experiment is to demonstrate two types of selectivity techniques, masking and ion exchange resin conversion (chromatography), that are commonly used in analytical chemistry. In the vast majority of cases, the analyte of interest is in a sample that contains other materials that may interfere with the analytical determination. Therefore, some type of selectivity step has to be employed. The tools available to an analytical chemist are masking, trapping, conversion, extraction, gas diffusion, dialysis and chromatographic separation.

### Introduction

In this experiment $[H^+]$, $[Na^+]$, and the sum of $[Zn^{2+}]$ and $[Mg^{2+}]$ will be determined through a variety of techniques. [H+] will be determined first by direct titration using standardized base. Then an aliquot of sample will be passed through a cation exchange resin to convert, replace all metal ion into $[H^+]$. This sample is titrated with standardized base. Another aliquot of sample is adjusted to pH 10, and the sum of $[Mg^{2+}]$ and $[Zn^{2+}]$ is determined by titration with EDTA. If you wish to investigate the amount of $Mg^{2+}$ in the system, this can be done by application of a $Zn^{2+}$ masking reagent. Potassium cyanide is typically used for this purpose. However, due to the extreme toxicity of this reagent, it is paramount that all established procedures and correct handling of this reagent be followed explicity. Details can be found in *Fundamentals of Analytical Chemistry* (Skoog, 1996).

## Part 1

Explain how each ion concentration is calculated. What titration steps are used in the calculation of the ion concentration determinations? For example, titration 1 determines the $[H^+]$.

## Part 2

Titration 1: determines total moles $H^+$ using ($V_{base}$ * $M_{base)}$ * (total sample volume/$V_{sample\ used}$).

Titration 2: determines total moles of cation using ($V_{base}$ * $M_{base)}$ * (total sample volume/$V_{sample\ used}$).

Titration 3: determines moles of $Zn^{2+}$ and $Mg^{2+}$ using ($V_{EDTA}$ * $M_{EDTA)}$ * (total sample volume/$V_{sample\ used}$).

Therefore, moles hydrogen ion originally present is the moles calculated from titration 1.

Moles of sodium ion originally present is the moles calculated from titration 2 minus moles from titration 1 minus 2 time the moles calculated from titration 3.

Why in the calculation for sodium ion is it two times the moles calculated in titration three?

## Part 3

The cation exchange process must be electroneutral. In other words, the number of cation charges in must equal the number of cation charges out. Therefore, $Zn^{2+}$ and $Mg^{2+}$ each release two $H^+$. Since the titration is acid titrated by base, the result is in terms of total $H^+$. Total $H^+ = H^+ + Na^+ + 2(Zn^{2+}) + 2(Mg^{2+})$.

### Procedures

Prepare your ion exchange column by using one of your burets and filling it about half full of resin. The best way to pack a column is to place the resin into distilled water to make a slurry. The slurry is poured into the column which has a glass-wool plug and the water allowed to drip out to the point just above the resin. Do not let your resin go dry. To ensure that the resin is in the hydrogen form, pour 25 mL of 6 molar HCl through the column, then pour 25 mL of distilled water through the column six times (fresh water each time) to remove the excess acid.

!! Use extreme caution when working with 6 M HCl. It is damaging to the skin, eyes, and mucous membranes and will damage clothing items. Disposal of the solution must be done in the hoods.

To save time you should start the ion exchange process and as it proceeds perform your other titrations. Place a 10-mL aliquot of your sample into the column. Collect the effluent into a titration flask. You will use at least three aliquots, each one individually titrated.

### Titrations 1 and 2

Titrate three 10-mL aliquots using standardized NaOH and phenolphthalein indicator.

### Titration 3

Use a standardized EDTA solution to titrate three 10-mL aliquots after adding enough NaOH to neutralize the acid, 50 mL of ammonia buffer, and three drops of calmagite indicator.

## INSTRUCTOR NOTES FOR ACTIVITY 5
## Separation of Cation

### Time Required

3 hours

### Group Size

At the instructor's discretion, students can work in groups of 2 or 3.

### Materials Needed

Per group

- Dowex 50W-X4
- 4 g EDTA standard
- 20 drops calmagite
- 250 mL 0.1 M NaOH standard
- concentrated $HNO_3$
- litmus paper
- 150 mL of unknown which contains HCl, NaCl, $ZnCl_2$, and $MgCl_2$. Make sure the concentrations of the ions are low enough so that each titration requires no more than 50 mL of titrant.

### Safety, Handling, and Disposal

Sodium hydroxide (NaOH) is very caustic and can cause severe chemical burns and destroy cell membranes. Concentrated $HNO_3$ is very corrosive. It can cause severe chemical burns. The vapor is extremely irritating to the skin, eyes, and respiratory system. Work involving concentrated nitric acid should be performed in a fume hood. With both sodium hydroxide and nitric acid, contact with the skin and eyes must be prevented. Should contact occur, rinse the affected area with water for 15 minutes. If the contact involves the eyes, medical attention should be sought while the rinsing is occurring. Dispose of used reagents according to local ordinances.

### Pre-Lab Discussion

As part of the pre-lab discussion, the instructor can remind students that prior to most analytical measurements, some type of selectivity step is performed. Most measurement steps/techniques are not that specific for the analyte of interest. The steps contain some type of analyte transplantation or conversion. The classical separations methods include crystallization, distillation, and extraction. All these methods are time-consuming and labor intensive. In some cases a chemical masking of the interfering species or matrix components could be used. As our interest in measuring lower and lower concentrations of chemicals in samples increased, it became clear that a new type of separation technique was needed; that technique was chromatography. The instructor can share the history of chromatography with students, starting with the Russian botanist Mikhail Tswett, on the separation of plant pigments in the late 1890s. (A translation of Tswett's first publication can be found in *Chem. Rev.*, **1989**, 89, 279-285.) A discussion of the various types of chromatography, the mode of separation, and their different uses should follow.

In this experiment you will use the techniques of conversion and ion exchange column chromatography to determine the concentrations of four cationic species: hydrogen, sodium, magnesium, and zinc ions.

## Procedural Tips and Suggestions

Students should use 0.1 M NaOH and 0.025 M EDTA in their titrations. $H^+$ should be present in all unknowns. $Zn^{2+}$, $Mg^{2+}$, and $Na^+$ can be added in the concentrations desired. The total concentration of the unknowns should be no more than 5 moles.

## Sample Results

The calculations of the amount of each component from the titration data is straight forward. The values will differ depending on the amount of the prepared unknowns as well as the concentration of the NaOH.

## Plausible Answers to Questions

See student handouts.

## Reference

Skoog, D.A.; West, D.M.; Holler, F.J. *Fundamentals of Analytical Chemistry*, 7th ed.; Saunders: Philadelphia, 1996.

## INTRODUCTION TO ACTIVITY 6
## Comparison of Analytical Methods

### Description

In this experiment students determine the amount of $Ca^{2+}$ in tap water using an EDTA titration and also atomic absorption. The results of these two methods are compared with statistics to determine if the two methods are equivalent.

### Goals for the Experiment

- Students will determine the hardness of tap water by a complexometric EDTA titration.
- Students will determine the $Ca^{2+}$ concentration by atomic absorption.
- Students will demonstrate the statistical techniques used to evaluate the equivalency between methods.
- Students will learn to use a calibration curve to determine $Ca^{2+}$ concentration by atomic absorption.
- Students will improve computer analysis of data skills.

## ACTIVITY 6
## Comparison of Analytical Methods

### Objective

The objective of this experiment is to demonstrate the techniques used to evaluate the equivalency between methods. When a new method is developed, it is critical to evaluate its performance against known approved analytical methods. In fact, when dealing with extremely low detection limits, it is now the recommended policy to use at least three methods initially and to evaluate the differences between the results from the three methods.

### Introduction

You will use two experimental techniques will measure the amount of calcium in drinking water. The first method is the titration of calcium using EDTA. The second method is atomic absorption. After obtaining the results, you will perform statistical analysis to evaluate the equivalency between methods.

### Experiment

1. Put 4.0 g disodium EDTA in a 500-mL Erlenmeyer flask and dissolve in about 100 mL distilled water plus 10 mL concentrated ammonium hydroxide. Warm the solution slightly if necessary. When the EDTA has completely dissolved, add 0.1 g $MgCl_2 \bullet 5H_20$, swirl to dissolve, and transfer to a polyethylene bottle. Add distilled water to bring the total volume to about 1L and mix thoroughly.
2. Accurately weigh to four significant figures a 0.5 g sample of primary standard $CaCO_3$ that has been previously dried at 110°C. Transfer the solid to a 250-mL beaker and cover with a watch glass. Then cautiously add 6 M HCl by means of a pipet until the $CaCO_3$ dissolves. Swirl to be sure the calcium carbonate has dissolved completely, then rinse the watch glass into the beaker. Add 50 mL distilled water and transfer the solution quantitatively to a 500-mL volumetric flask. Dilute to the mark and mix thoroughly.
3. Pipet a 50-mL aliquot of the standard calcium chloride solution into a 250-mL flask. Add successively with mixing 10 mg ascorbic acid, 10 mL of the $NH_3/NH_4OH$ buffer (pH 10) and 3-4 drops calmagite indicator. Titrate with your EDTA solution. Continue the titration to a point where the last tinge of red just disappears. Repeat at least two more times.
4. The unknown in this case is tap water. Titrate this sample at least three times using the same procedure as in Part 3.
5. Using AA, create a calibration curve based on calcium standards from 0.5 ppm to 15 ppm.
6. Using the same unknown measure the calcium concentration by atomic absorption.

### Data Analysis

The question to be answered is whether the two methods give equivalent results. Use what you have previously learned about statistical analysis of data to answer this question.

### Reference

Laitinen, H.A., Harris, W.E. *Chemical Analysis: An Advanced Text and Reference,* 2nd ed.; McGraw-Hill: New York, 1975.

## INSTRUCTOR NOTES FOR ACTIVITY 6
## Comparison of Analytical Methods

### Time Required

3 hours

### Group Size

At the instructor's discretion, students can work in groups of 2 or 3.

### Materials Needed

- computer with spreadsheet program such as Lotus 1-2-3, Excel or others
- atomic absorption instrument
- analytical balance

### Per group

- 4 g EDTA
- 0.5 g primary standard $CaCO_3$
- 30 mg ascorbic acid
- 80 mL $NH_3/NH_4^+$ buffer (pH 10)
- 10 mL 6 M HCl
- 20 drops calmagite indicator
- 10 mL concentrated NH4OH
- 1-L polyethylene bottle
- 250-mL beaker
- watch glass
- 500-mL volumetric flask
- 250-mL Erlenmeyer flask
- 50-mL pipet
- distilled water
- $MgCl_2 \cdot 5H_20$
- tap water (or standard $Ca^{+2}$ unknown if the $[Ca^+]$ in tap water is less than 15 ppm)

### Safety, Handling, and Disposal

$NH_3$(aq) is a base and can burn the skin. 6 M HCl is a strong acid that can cause burns. Use caution! Dispose of used reagents according to local ordinances.

### Pre-Lab Discussion

For most analytical chemists, the method used is chosen for you by some standard methods group. As the instrumental and automation techniques have proliferated, it has become increasingly difficult for these committees to evaluate all the methods. Therefore, the concept of equivalency has been introduced. It is possible to perform the standard method in tandem with your chosen method and perform the statistical analysis to prove that the two methods give equivalent results. Once this is proven, then your method can be used instead of the standard method.

Recently, one additional approach has been chosen; performance-based standards. In this situation known standards are sent to the laboratory as blind samples. The results from these blind samples are reported to the accrediting agency, and the laboratory is certified as being competent for that analyte in that sample matrix.

In this experiment, students will use two methods to determine calcium in drinking water. They should perform the determinations using both methods and use statistical analysis to establish whether the methods are comparable. If the methods are not statistically comparable, then students must explain why they do not give similar results.

The color change in this titration can be difficult to see. It goes from reddish purple to purplish blue. Titrate until you see the first tinge of blue.

Statistical methods are used to give a yes or no answer to a data question. The answer is qualified by a confidence limit that indicates the degree of certainty of the answer. This approach is called hypothesis testing.

The usual approach is to set up a null hypothesis stating that there is no significant difference between two sets of data or that a specific variable exerts no significant effect. Usually a confidence limit of 95-99% is chosen for null hypotheses.

## Procedural Tips and Suggestions

Using two different methods for analyzing calcium in drinking water allows students to compare methods and test them for equivalency using standard statistics.

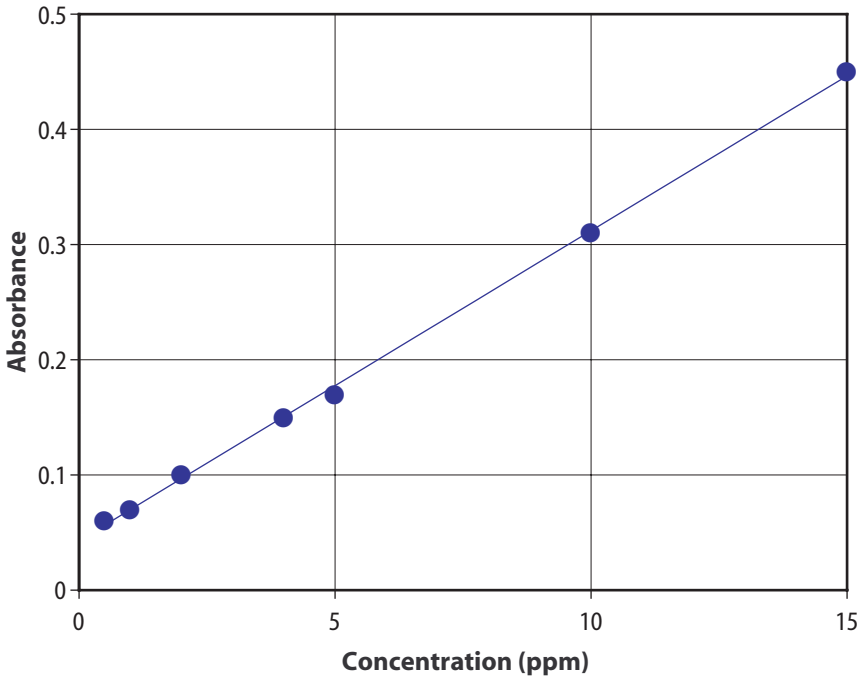
For the EDTA titration, students can calculate the total hardness of water using the spreadsheet.

For the second part of the experiment, use atomic absorption methods to create a calibration curve based on standards from 0.5 ppm to 15 ppm. Allow students to aspirate the sample directly into the flame. The sample should be more than 15 ppm, so the students will have to decide on a way to treat the sample so that it fits in the standard calibration curve. Let them decide for themselves the best way to make the unknown fall within the range. Students must determine a dilution factor that will dilute the unknown sample down to a concentration range within the calibration curve concentration range. This is a tough concept for them to grasp—the fact that they are diluting water with water. Then they will use a spreadsheet to create a data table and graph of the calibration curve and the data from the drinking water samples. Initially, most students will compare the calcium molarity obtained from the EDTA titration to the calcium ppm obtained from atomic absorption. Students must make the concentration units equivalent if they want to make an accurate comparison.

If using tap water, your students should get a higher number using titration than atomic absorption. It is not readily apparent to them why this might be the case. Let them think up some reasons for the discrepancies. They may come up with the idea that there may be something else complexing the EDTA besides $Ca^{2+}$. After they've had time to think, then tell them that this method also measures the amount of $Mg^{2+}$ as well as $Ca^{2+}$. Here is where the discrepancy lies.

## Sample Results

**Figure 5: Absorbance vs. Concentration Ca**




| Regression Analysis | |
|---|---|
| regression equation | y = a + bx |
| y-intercept (a) | 0.0419 |
| slope (b) | 0.0272 |
| correlation coefficient | 0.9997 |
| number of observations | 7 |

## Plausible Answers to Questions

The two methods are not equivalent. At pH 10 EDTA titrates magnesium as well as calcium. AA measures only $Ca^{2+}$. AA is more accurate for determining $Ca^{2+}$, and EDTA is more accurate for hardness determination. The relative standard deviation could be similar in the two methods depending on student skills. An additional question to ask is the following: If a new method gives a higher or lower result than the old "standard method," what does that mean? Three possibilities exist, assuming good analytical technique: (1) the standard method is not so good, (2) the new method is not so good, or (3) matrices have effects on one of the methods.

## Reference

Skoog, D.A.; West, D.M.; Holler, F.J. *Fundamentals of Analytical Chemistry*, 7th ed.; Saunders: Philadelphia, 1996.