Solutions and Dilutions

Learning Objectives

Students should be able to:

Content

- Design a procedure for making a particular solution and assess the advantages of different approaches.
- Choose the appropriate glassware to ensure the desired level of precision of a particular solution.
- Convert between different concentration units (e.g., ppm to M).

Process

- Develop alternative pathways for diluting solutions. (Information processing)
- Design approaches for preparing solutions. (Problem solving)
- Infer chemical processes based on reactions. (Critical thinking)

Prior knowledge

- Types of glassware for preparing solutions, including graduated cylinders, pipettes, burets, and volumetric flasks.
- Correct method for reading and dispensing from a graduated cylinder, pipette, buret, and volumetric flask.
- Definitions of primary standard, secondary standard, calibration standard, accuracy and precision, ppm, molarity.

Further Reading

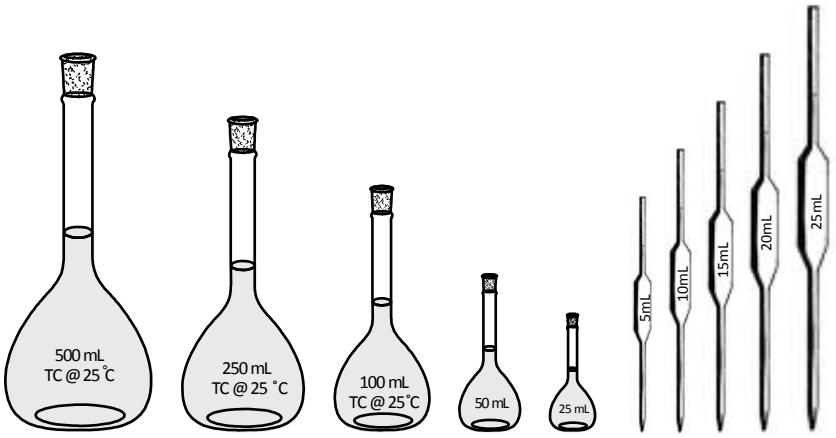
- Harris, D.C. 2010. Quantitative Chemical Analysis, 8th Edition, New York: W.H. Freeman. pp. 37-39.
- Skoog, D.A., D.M. West, F.J. Holler, and S.R. 2004. Crouch, Fundamentals of Analytical Chemistry, 8th Edition, Thompson Brooks/Cole: USA, Sections 13B and 13C, pp. 340-343.
- Louisiana Universities Marine Consortium (LUMCON) Bayouside Classroom, dissolved oxygen section, available at: http://www.lumcon.edu/education/studentdatabase/dissolvedoxygen.asp

Authors

Mary Walczak and Christine Dalton

Consider this…

Shelby needs to make a 3.00 M acetic acid solution from an acetic acid standardized solution that is 15.0 M. The analytical equipment available to Shelby in the lab includes the volumetric flasks and pipets shown below. Although several different size volumetric flasks are available, Shelby opts to use the 100-mL flask because it is both clean and dry.



Key Questions

1. What size pipet does Shelby need to use to make 100 mL of 3.00 M acetic acid solution? Devise a general mathematical expression for calculating the concentration of the resulting solution.

2. The dilution factor (initial volume of solution/final volume of solution) is a way of expressing the extent to which a solution is diluted. What dilution factor is used to prepare the solution described in Q1?

3. Shelby is not concerned about the dryness of the pipets. Explain, based on proper pipetting techniques and your laboratory experiences, exactly how Shelby should use the pipet. Why does proper lab technique eliminate the need for dry pipets?

4. Was it necessary for the volumetric flask to be dry? Discuss as a group and explain your answer and reasoning in a grammatically complete sentence.

5. Assign different volumetric flasks to group members. For each size flask, determine the volume necessary to prepare that volume of a 3.00 M acetic acid solution from the 15.0 M standard solution. Determine the dilution factor used to prepare any of these solutions. Check your group's answers by comparing with other groups. Resolve any differences.

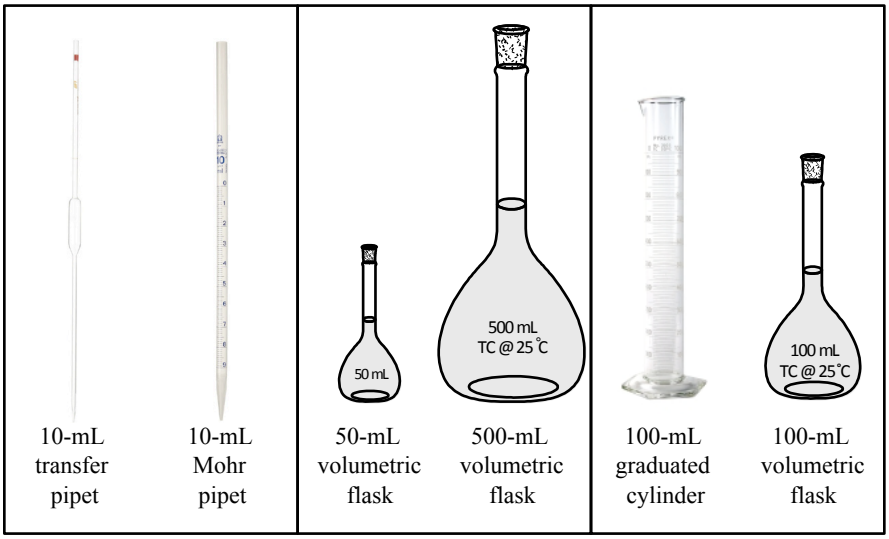
6. Suppose Shelby's supervisor said to make 250 mL of 3.00 M acetic acid solution. How would you suggest Shelby prepare this solution?

7. Shelby's supervisor asked for 100 mL of a 2.00 M acetic acid solution. Could Shelby prepare this from the 15.0 M standard solution using the available glassware in Model 1? If so, how? If not, what other glassware might Shelby want to use?

Consider this…

Making Solutions: *Rules of Thumb*

- Graduated cylinders are considerably less accurate and precise than glass transfer pipets.
- Dilution in one step is better than two.
- Larger glassware has less relative uncertainty.
- Measuring (Mohr) pipets are less precise than glass transfer pipettes.
- Waste handling is expensive.
- Glassware is designed to hold a specific volume only at a stated temperature.



Key Questions

8. Considering the "rules of thumb" listed above, circle the glassware in each pair above that will provide the lower uncertainty.

9. Under what conditions is it advantageous to use the smaller volumetric flask in the center panel above? When is the larger flask the optimum choice? Compare answers with group members and arrive at a consensus.

Consider this…

Reagan is doing an atomic absorption experiment that requires a set of zinc standards in the 0.4-1.6 ppm range. A 1000 ppm Zn solution was prepared by dissolving the necessary amount of solid $Zn(NO_3)_2$ in water. The standards can be prepared by diluting the 1000 ppm Zn solution. Table 1 shows one possible set of serial dilutions (stepwise dilution of a solution) that Reagan could perform to make the necessary standards. Solution A was prepared by diluting 5.00 mL of the 1000 ppm Zn standard to 50.00 mL. Solutions C-E are called "calibration standards" because they will be used to calibrate the atomic absorption spectrometer.

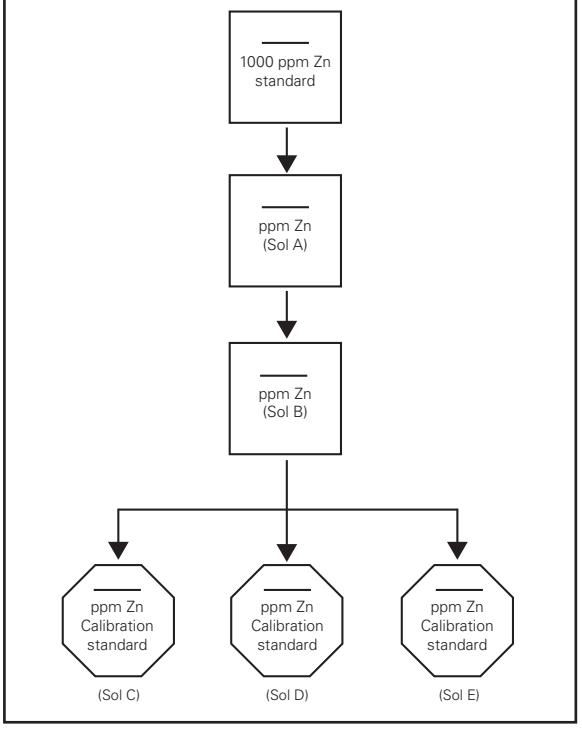
Table 1 ***Dilutions of Zinc Solutions***

Solution	Zinc Solution Concentration (ppm Zn)	Volume used (mL)	Diluted Volume (mL)	Solution Concentration (ppm Zn)	Solution Concentration (ppm $Zn(NO_3)_2$)	Solution Concentration (M $Zn(NO_3)_2$)	Solution Concentration (M Zn)
A	1000	5.00	50.00	1.00×10^{2}	2.90×10^{2}	1.53×10^{-3}	1.53×10^{-3}
B	Solution A	5.00	100.00				
C	Solution B	5.00	50.00			7.65×10^{-6}	
D	Solution B	10.00	50.00	1.000			
E	Solution B	25.00	100.00				1.911×10^{-5}

Key Questions

10. Using your general scheme for calculating the concentration of diluted solutions devised in Q1, calculate the resulting concentration (ppm Zn) for each solution A-E above. Enter your answers into the diagram in Figure 1 and into the boxes in Table 1. Verify answers provided in Table 1.

Figure 1 ***Preparation of calibration standards by serial dilutions.***



11. The atomic mass of Zn is 65.4094 amu and the molar mass of $Zn(NO_3)_2$ is 189.4194 amu. Devise a scheme to calculate the solution concentrations in units of ppm $Zn(NO_3)_2$. Calculate the resulting solution concentrations in ppm $Zn(NO_3)_2$ for Solutions A-E. Enter your results in Table 1.

12. Devise a scheme to calculate the solution concentrations in units of molarity (M $Zn(NO_3)_2$) and (M Zn). Calculate the resulting solution concentrations in M $Zn(NO_3)_2$ and M Zn for Solutions A-E. Enter your results in Table 1.

13. Compare the solution concentrations expressed as ppm Zn and ppm $Zn(NO_3)_2$. Compare the concentrations expressed as M Zn and M $Zn(NO_3)_2$.

Which units allow easy conversion between chemical species (e.g., Zn and $Zn(NO_3)_2$)?

Which units express concentrations in numbers with easily expressed magnitudes?

Suppose you have an analyte for which you don't know the molar mass. Which concentration units would you use?

14. For the concentrations involved in this particular experiment, which set of units is most convenient? Explain your reasoning.

15. Write a laboratory procedure for the preparation of Solution B from Solution A for Reagan to carry out.

16. Although only 50 mL of each calibration standard (Solutions C-E) are needed for the experiment, Reagan made 100 mL of Solution E. Give a rationale for this decision.

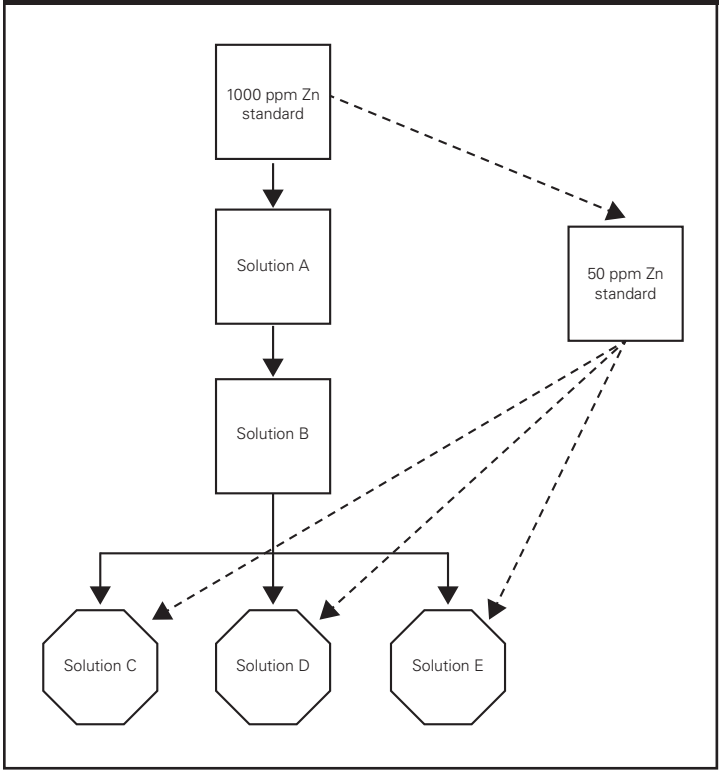
17. Suppose Reagan made an error in preparing Solution A and ended up with a 100.5 ppm Zn solution. What is the impact of this error on Solutions B-E?

Consider this…

Alternatively, Reagan could prepare the same calibration standards by first preparing a 50 ppm standard and then diluting this standard to make the three calibration standards, as shown in Figure 2. The advantage to this approach is that only one dilution of the 1000 ppm Zn standard is needed before preparing the calibration standards.

18. Brainstorm ideas about how the 50 ppm standard can be prepared. As a group, come to a consensus on a dilution scheme to prepare this standard and explain the rationale behind choosing this particular method.

Figure 2 ***Preparation of calibration standards by an alternative serial dilution strategy.***



19. Divide the calibration standards, Solutions C, D, and E, among group members. For each calibration standard, determine how the 50 ppm standard could be diluted using the volumetric flasks and pipets available (see Q1) to prepare the solution. The calibration standard concentrations are the same as in Figure 1 and 2 Solutions C, D and E.

20. Compare the dilution schemes of Figures 1 and 2. Which is the better method in terms of the following parameters?

a. Time
b. Error
c. Waste generation
d. Amount of glassware requiring cleaning

Based on your answers, which model is better and why?

21. Reagan decides another calibration standard is needed between 0.5 and 1.0 ppm. Using Figure 1 or 2 (whichever you decided was better in Q20), how would you make a 0.75 ppm Zn calibration standard (Solution F)?

22. List important considerations when developing a procedure to make a solution.

23. Explain the process of designing an experiment in which calibration standards (solutions used to calibrate an instrument) must be made from a standard solution.

Applications

24. List the advantages and disadvantages of preparing a 1:1000 dilution in a single step. Consider time, resources and error.

25. A bottle is labeled 56.2 ppm $FeCl_3$. Express this concentration in ppm Fe^{3+} and in molarity.

26. If the lab equipment in Q1 is available for use, explain how you would prepare a 0.02000 M potassium permanganate ($KMnO_4$) solution from a standardized $KMnO_4$ solution with a concentration of 0.1000 M. Write a lab procedure for preparing the 0.02000 M solution.

27. Potassium dichromate, $K_2Cr_2O_7$, is a carcinogen, however it still plays a useful chemistry role in some procedures. Suppose you need to make a 0.1000 M $K_2Cr_2O_7$ solution from a 1.000 M stock solution. Using glassware in Q1, how would you prepare the smallest quantity of this 0.2000 M solution?

28. Shelby and Reagan have been hired by a forensic science lab to analyze trace metal content in crime scene evidence. Their current project involves determining zinc content in human hair. Shelby and Reagan prepare a nitric acid solution to dissolve the hair using a process called digestion. The nitric acid oxidizes the keratin protein. Shelby and Reagan need 100 mL of an aqueous 0.3 M HNO_3 solution for this procedure. They remember their chemistry training and plan to "add acid to water," and add the necessary volume of concentrated (16.0 M) HNO_3 to a sufficient quantity of water.

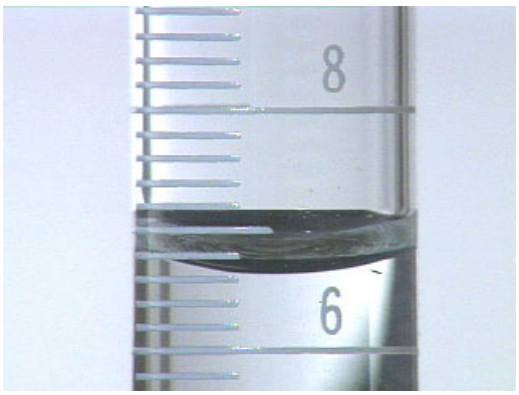
Reagan decides to use a 100-mL volumetric flask to prepare the solution. The flask is filled about three-quarters full of deionized water and the acid is measured using a 10-mL graduated cylinder. After mixing the solution well, Reagan fills the flask with enough deionized water to bring the level to the mark on the neck and mixes the solution well again. Shelby, on the other hand, uses a 100-mL graduated cylinder to measure 100 mL of deionized water, pours it into a beaker, adds the HNO_3 from a 10-mL graduated cylinder and stirs well.

a. How many milliliters of the concentrated HNO_3 are needed to make 100 mL of 0.3 M solution?

b. What advantages are there to using a volumetric flask to prepare the HNO_3 solution? Explain.

c. What advantages are there to using the graduated cylinder to prepare the HNO_3 solution? Explain.

d. Consider the photograph of a 10-mL graduated cylinder at the right. Estimate the uncertainty in the volume of concentrated HNO_3 that Shelby and Reagan measure using this glassware.



http://homepages.ius.edu/DSPURLOC/c121/week3A.htm

e. As they are working in the lab, Shelby and Reagan notice the different approaches they have taken to making this solution. What are the advantages and disadvantages of each approach? Which student made the better choice? Why?

f. Considering the role of the nitric acid solution in the hair analysis, how important is the accuracy of the concentration?

g. If another student asked you for advice on what glassware to use in preparing the HNO_3 solution, what would you tell him or her?

29. In order to measure the amount of Zn in hair using an atomic absorption instrument Shelby needs to prepare a calibration curve of atomic absorbance for five solutions of known Zn concentration. For each concentration 100 mL of solution is needed and the standards need to be in the 0.4 – 1.6 ppm Zn range. The available glassware is listed in Q1 and a 1000 ppm Zn primary standard solution is available.

Table 2 ***Capacity and Tolerance of Available Graduated Cylinders, Volumetric Flasks and Pipettes***

Graduated Cylinders		Volumetric Flasks		Volumetric Pipets	
Capacity, mL	**Tolerance, ±mL**	**Capacity, mL**	**Tolerance, ±mL**	**Capacity, mL**	**Tolerance, ±mL**
10	0.05	50	0.05	10	0.03
100	0.5	100	0.08	15	0.03
250	1	200	0.10	20	0.03

a. Which glassware would be the best to use to prepare the calibration standards?

b. Describe how you would make five calibration standards in the 0.4–1.6 ppm range starting with the 1000 ppm Zn primary standard solution.

c. Explain, using complete sentences, why the glassware chosen for this problem is the best of those listed in Table 2.

30. What type of glassware should be used for making up solutions when you need to know concentrations accurately? Under what circumstances can graduated cylinders be used to prepare solutions?

31. State in your own words why the precision of the zinc solution in Q29 is important, but the nitric acid solution precision in Q28 is not.

32. Shelby needs to perform dilutions of a 52.08 ppm $CaCl_2$ solution to prepare a set of calibration standards for atomic absorption spectroscopy. The Ca working range for AA is 1-4 ppm Ca. The pipettes and volumetric flasks in Q1 are available for use.

a. Convert the concentration of the 52.08 ppm $CaCl_2$ solution to units of ppm Ca and in molarity.

b. Explore combinations of available pipets and volumetric flasks to determine how to dilute the 52.08 ppm $CaCl_2$ solution to make five calibration standards that fall into the 1-4 ppm Ca range. Make a table showing how to prepare the five calibration standards and the resulting concentrations (ppm Ca).

c. Write a set of instructions for a technician to follow when preparing these calibration standards. Be specific about which glassware should be used.

d. Under what circumstances would you opt for the next smaller size volumetric flask than you chose in question Q32b and Q32c? When would you choose the next larger size volumetric flask?

33. Shelby is going to analyze drinking water samples for sodium and calcium using inductively coupled plasma – atomic emission spectroscopy. Calibration standards containing both NaCl and $CaCO_3$ within the 1–10 ppm range are needed. Shelby wants to prepare 100 mL of each calibration standard in order to ensure there is enough solution. Explain how Shelby should prepare a primary standard solution containing 100 ppm of each element from primary standard grade solid NaCl and $CaCO_3$. How should Shelby prepare eight 100 mL calibration standards within the range given? Do the calculations using a spreadsheet program. In your narrative response comment on the types of glassware used to prepare the solution.

34. Shelby is measuring chloride concentration in environmental samples using a chloride ion selective electrode. In order to calibrate the electrode a set of five chloride standards in the 10^{-1} to 10^{-5} M range is needed. Shelby has a standard solution of 1.000 M NaCl to use in preparing the standards. The glassware available in the lab includes an ample supply of all the volumetric flasks and pipettes displayed in Q1.

a. Shelby pipets 10 mL of the 1.000 M NaCl solution into the 100-mL volumetric flask, dilutes to volume and mixes the solution by inverting the flask 30 times. What is the concentration of the resulting solution?

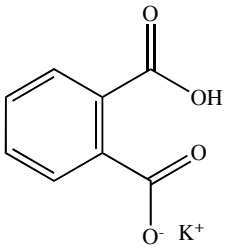
b. What volume of the 1.000 M NaCl solution is required to make 100 mL of the 10^{-5} M chloride solution? How do you suggest Shelby measure this volume?

c. Calculate the volume required for the three remaining concentrations. What practical difficulties might be encountered when preparing these solutions?

d. List ideas about how Shelby might prepare these other three solutions using the available equipment.

e. Develop a strategy for Shelby to prepare the five chloride standards. Write instructions for a lab technician to use in preparing the standards necessary for this analysis.

35. Sodium hydroxide is a hygroscopic solid, meaning that it absorbs moisture from the atmosphere. Consequently, if the concentration of a NaOH solution must be known precisely, it must be standardized against an acid. Furthermore, the acid must be a primary standard, a substance that can be weighed precisely resulting in a well-known amount of acid. This process, called standardization, is a titration of the known quantity of acid with the NaOH solution. A commonly used primary standard weak acid for standardizing NaOH solutions is potassium acid phthalate, often abbreviated "KHP."



a. If 2.61 g NaOH was dissolved in 1 L of deionized water, estimate the resulting NaOH solution concentration.

b. What type of laboratory glassware would you use to prepare this NaOH solution? Explain your rationale.

c. Titrations of KHP with the NaOH solution were performed to determine the actual NaOH concentration. Data for titration of KHP with NaOH are provided below. Use the data to determine the actual concentration of the NaOH solution. Comment on the quality of the data provided.

Mass KHP (g)	Volume NaOH solution (mL)
0.2432	19.10
0.2358	18.66
0.2327	18.63

d. Given the concentration determined by titration and the expected concentration calculated in part a, comment on the purity of the weighed NaOH sample.

36. The wet chemical method for measuring dissolved oxygen in water was developed by Winkler in 1888 and is still in use today. This method involves oxidation of iodide ion to iodine by the oxygen in the sample. The amount of iodine produced is determined by titration with a sodium thiosulfate solution. Since the titration is often not conducted at the time of sampling, the dissolved oxygen in a collected sample is "fixed" by precipitation as manganese (III) hydroxide ($Mn(OH)_3$). This stabilizes the oxygen from the water sample until a later time when the titration in performed. Overall, the stoichiometric reactions involved are:

Reaction	Purpose
1. $Mn^{2+} + 2\ OH^- \rightarrow Mn(OH)_2$	Mn^{2+} is loosely bound to hydroxide in basic solution
2. $2Mn(OH)_2 + ½\ O_2 + H_2O \rightarrow 2Mn(OH)_3$	Mn^{2+} is oxidized to Mn^{3+} in the presence of strong base and fixes oxygen from the water sample
3. $2Mn(OH)_3 + 2I^- + 6H^+ \rightarrow 2Mn^{2+} + I_2 + 6H_2O$	Iodine (I_2) is produced upon acidification of the sample with stoichiometry of one I_2 molecule for every oxygen atom
4. $I^- + I_2 \rightarrow I_3^-$	Iodine complexes with excess I^- to form triiodide (I_3^-)
5. $I_3^- + 2S_2O_3^{2-} \rightarrow 3I^- + S_4O_6^{2-}$	Triiodide is reduced to iodide with thiosulfate via titration using starch indicator

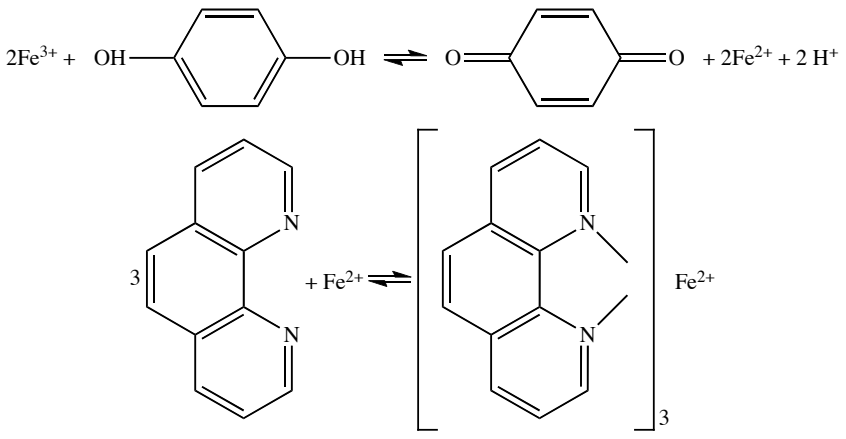
The reagents necessary for the procedure include:

3 M Manganese (II) chloride
4 M sodium iodide *and* 8 M sodium hydroxide
50% v/v sulfuric acid
1.0 g/1000 mL starch indicator solution
0.018 M sodium thiosulfate solution.

a. For each reaction 2-5 above, identify the stoichiometric relationship between the analyte of interest (oxygen) and the species in each reaction.

b. Considering the relationships explored in Q31 above, which of the five solutions listed above must be know to a precise concentration (e.g., 3 or 4 significant digits)? Which solutions need only approximate concentrations? Explain how you arrived at your answers.

37. Iron can be determined spectrophotometrically after reaction with a ligand that results in a highly colored complex. In one determination, iron is reduced with hydroquinone to ensure it is all in the Fe^{2+} oxidation state. Then, o-phenanthroline is added to complex with the Fe^{2+}. The reactions are:



The reagents necessary to perform this experiment include a solution of hydroquinone, citric acid buffer, a solution of o-phenanthroline, and an $Fe(NH_4)_2(SO_4)_2 \bullet 6H_2O$ solution. The concentrations of which of these solutions must be known precisely in order to make an accurate determination of iron in an unknown sample? Explain your rationale.

38. Shelby is measuring the concentration of lead (as Pb^{2+}) in paint samples using an atomic absorption instrument. A primary standard solution of aqueous $Pb(NO_3)_2$ is used to prepare standards for calibrating the instrument. Shelby weighs out 0.2500 g of primary standard grade $Pb(NO_3)_2$, quantitatively transfers it to a container and dissolves it in DI water for a total solution volume of 250 mL. Various pieces of glassware are available including a 250 ± 0.8 mL graduated cylinder and 250 ± 0.12 mL volumetric flask.

a. Calculate the solution concentration if the 0.2500g of $Pb(NO_3)_2$ is dissolved to a total of 250 mL of solution. Determine the concentration in units of ppm Pb and ppm $Pb(NO_3)_2$.

b. Estimate the uncertainty associated with preparing the solution using (1) the volumetric flask and (2) the graduated cylinder. Report the uncertainty as a range of concentrations (ppm Pb). Compare results.

c. What do these ranges of concentrations reveal about the difference in accuracy between the graduated cylinder and the volumetric flask? Explain, using results from part b above, why volumetric flasks should always be chosen over graduated cylinders for analytical methods.