

## Colorimetric Determination of Aspirin

prepared by R. C. Kerber and M. J. Akhtar, SUNY at Stony Brook (Rev 10/08, RFS)

**Purpose of this Exercise:** To analyze your synthesized aspirin samples spectrophotometrically. To compare the results of titrimetric and spectrophotometric analyses of your synthesized aspirin samples.

### Concepts & Techniques:

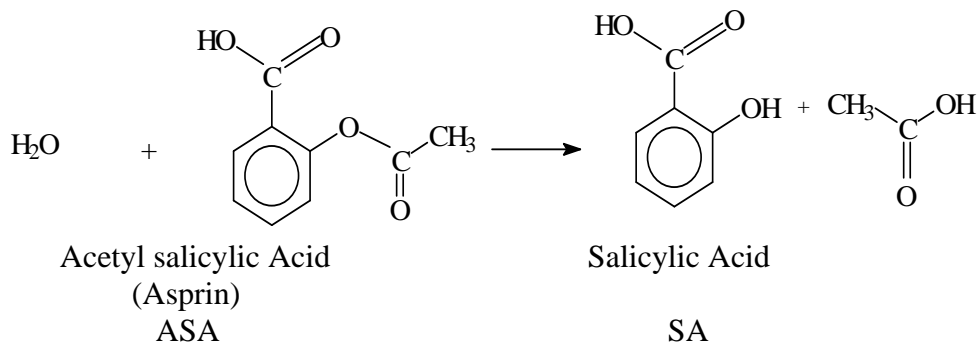
Color and light absorption: Absorbance/Percent Transmission; Analytical Wavelength; Blank; Beer's Law; relationship between concentration and absorbance; absorptivity, path length, Beer's Law Plot; slope of linear graph; complexation of SA vs ASA; hydrolysis; preparing precise dilutions; using Spectrophotometer

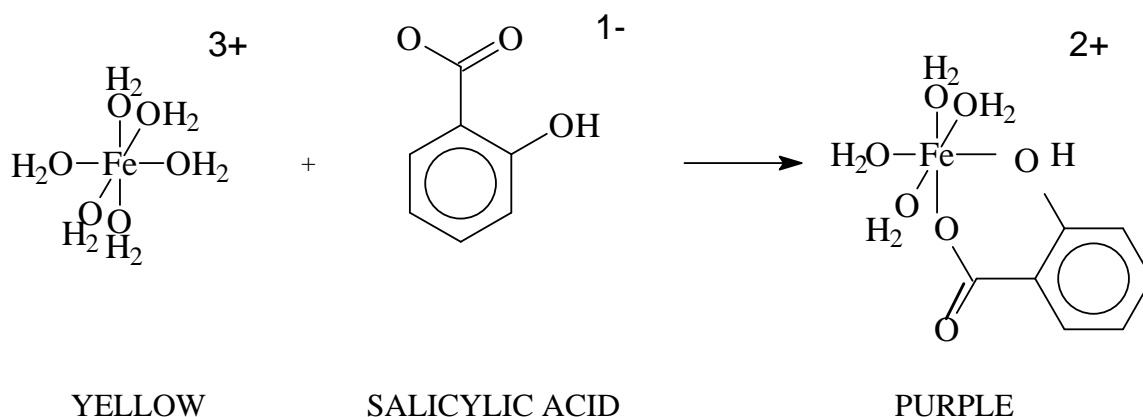
### Background Information

You should have already read substantial background information on aspirin in earlier modules and that information will not be repeated here. The module **SUPL-005**, which reviews the principles of spectrophotometric analysis should be read, or re-read before reading further in this one.

Review: The relationship between absorbance and concentration is expressed in the Beer-Lambert Law which states that **absorbance** at a given wavelength is directly related to **concentration** of the colored species which absorbs at that wavelength. We can readily measure absorbance using Spectronic 20 or 21 spectrophotometers. If we first make up a series of solutions of accurately known concentrations and measure their absorbances, then we can relate concentration to absorbance by preparing a calibration plot, as shown in **SUPL-005**. We can then use that calibration plot to determine the concentration of unknown samples.

In the present case, it is important to remember that the purple color to be used for analysis comes from salicylic acid (SA), **not** from acetylsalicylic acid (ASA). The existence of salicylic acid in your synthesized samples may be the result of an incomplete reaction in the synthesis of aspirin or subsequent hydrolysis of the product. The equations for the hydrolysis reaction and the formation of the colored species are given below.





### Procedures

**CAUTION:** This exercise involves working with hydrochloric acid solutions. This is a highly corrosive material, capable of causing severe and painful burns upon contact with the skin or eyes. It will also damage clothing with which it comes into contact. Avoid all contact. If contact occurs, immediately flush any skin or clothing with copious amounts of cold water.

Before coming to class, it will be helpful if you prepare a table in your laboratory notebook in the same format as that in Datasheet 1 for the Beer's law data.

**Part 1. Preparation of calibration curve.** You may work in assigned groups of three for this part of the procedure. Each member of the group should include all of the group's data in his or her laboratory notebook, and report the data on **Data Sheet 1**. *If you have doubts about a colleague's data, you should perform the measurement in question yourself.*

[Note that you should begin the preparation of the solution of your synthesized aspirin for Part 2 while you are collecting the data in Part 1. See Part 2.]

Weigh out about 0.2 g of **authentic** salicylic acid (SA) accurately, by difference, and quantitatively transfer the sample to a 250-mL Beaker. Record the exact mass of the SA in your notebook. Add 10 mL of ethanol and **after the sample is completely dissolved**, add approximately 150 mL of distilled water. Transfer the solution *quantitatively* into a 250-mL **volumetric flask** using a funnel. Thoroughly rinse the beaker with several portions of distilled water, pouring the rinsings into the volumetric flask. Fill the volumetric flask to the base of the neck with distilled water, stopper it, invert it, and mix the contents thoroughly. Put it down on the bench, allow any air bubbles to rise to the surface, then add distilled water very carefully until the meniscus just rests on the calibration mark on the neck of the volumetric flask. It is suggested that you use a dropper to bring the liquid level to the mark. Mix again.

This solution should be labeled **Solution 1**. Calculate the concentration of salicylic acid in Solution 1.  $[\text{SA}]_1 = \text{mmoles SA} / \text{mL of Solution 1} (= \text{moles SA} / \text{L of Solution 1})$   
 $= (\text{mass in mg. of SA} / \text{molar mass of SA}) / 250.0 \text{ mL}$

Drain the water from a buret, and rinse the buret, including the tip, with two to three small portions of Solution 1. Set the buret up on a stand, and fill it with Solution 1. Make sure that the buret tip contains the solution, and no air bubbles. Each member of the group should now prepare two different dilutions of Solution 1 by taking an initial buret reading, running an arbitrary volume of Solution 1 (between 1 and 10 mL) into a 100-mL volumetric flask, taking a final buret reading, and subtracting the readings to determine the net volume delivered. *Be sure the buret is read to the appropriate precision!* In each case, the solution in the 100-mL volumetric flask is diluted by adding 0.02 M FeCl<sub>3</sub>-KCl-HCl solution (pH 1.6) so as to make the total volume exactly 100.0 mL. Thoroughly mix each resulting solution, and label it with a letter (A, B, C,...). After you bring each of the dilutions up to the mark in the volumetric flask, you can transfer the solution to a *clean, dry* beaker so that the volumetric flask can be reused. Keep careful records in your notebook of the amount of Solution 1 diluted to make each lettered solution. Use a well-dispersed set of volumes of Solution 1 in preparing these lettered solutions, so that the points on your calibration curve will be well spread out over a substantial range of final concentrations. Calculate the concentration of salicylic acid (SA) in each lettered solution:

For example, if the concentration of Solution 1 is 0.006143 M and Solution A is made by diluting 7.38 mL of Solution 1 to 100 mL, the concentration of Solution A will be

$$[\text{SA}]_{\text{A}} = 7.38 \times 0.006143 / 100.0 = 4.53 \times 10^{-4} \text{ M}$$

In general, the concentration of dilution X is given by:

$$[\text{SA}]_{\text{X}} = [\text{SA}]_{\text{1}} \times V_{\text{X}} (\text{mL}) / 100.0 \text{ mL, where}$$

$V_{\text{X}}$  = Vol. of Soln. 1 used in preparing solution "X" and  
 $[\text{SA}]_{\text{1}}$  = Concentration of Solution 1

Check that the wavelength setting for your spectrophotometer is at 530 nm, the wavelength of maximum absorbance for the iron-SA complex. Note that the blank in this exercise is the FeCl<sub>3</sub>-KCl-HCl solution, **not water**). Place some reference solution (**blank** - the same 0.02 M FeCl<sub>3</sub>-KCl-HCl stock solution used to prepare the lettered solutions) in a cuvette and set the 100%T point on your spectrophotometer, using the appropriate knob. With no cuvette in the machine, set the 0%T point, using the appropriate knob. Save the cuvette containing the blank solution so you can check the spectrometer settings periodically during the exercise.

Use the same cuvette for all measurements of the stock solution dilutions in order to avoid discrepancies between different cuvettes. Orient the cuvette so that its mark always points towards the front of the spectrometer. Measure the absorbance of each lettered solution by using some to rinse the cuvette (three times), then filling the cuvette, carefully wiping the outside of the cuvette to remove fingerprints or droplets of solution, and placing it in the spectrophotometer. You should measure the most dilute solutions first. Read the absorbance directly or calculate it from the transmittance using the relationship

$$A = 2.00 - \log (\%T).$$

Record the absorbance reading of each lettered solution. It will be necessary to reuse the 100-mL volumetric flasks. After making the solution and recording the spectrophotometer reading,

you should save the solution in a clean dry container until you have confirmed that you have an appropriate Beer's Law plot in case you wish to repeat an absorbance measurement. Rinse the volumetric flask several times with distilled water to remove all traces of SA, then reuse the wet flask.

When each partner has prepared and measured the absorbance of two solutions, you will have six sets of data points, each being a concentration of SA in a lettered solution, and an absorbance for that solution. Plot these data using the laboratory computers. The computer program requires 6 data points (in addition to the blank). It produces the slope of the best straight line through the data and  $R^2$ , a measure of the "goodness of fit" of the line to the data. The value of  $R^2$  should be 0.98 or larger.

**Part 2. Analysis of your synthesized aspirin sample.** This analysis assumes that your synthesized sample of aspirin contains at least a trace of the starting material, salicylic acid (SA). The sample may be difficult to dissolve so you should begin the dissolution procedure as early in the exercise as possible – presumably while you are engaged in collecting the Beer's law data.

Accurately (on the analytical balance) weigh out about 0.2 g of your synthesized aspirin sample into a clean 250 mL beaker. Add 10 mL of ethanol and **after the sample is completely dissolved**, add approximately 150 mL of distilled water. Transfer the solution into a (clean) 250-mL volumetric flask, using a funnel to assure you do not lose any of the solution.. Rinse the beaker with several small amounts of distilled water delivered from your wash bottle. Mix well. Adjust the volume in the volumetric flask to the mark with distilled water, using a dropper for the last few additions. Mix again. Call this solution X

Pipet 5.00 mL of solution X into a 100-mL volumetric flask, and dilute to the mark with 0.02 M  $\text{FeCl}_3\text{-KCl-HCl}$  solution. Call this solution Y. Measure the absorbance of solution Y. **If the measured absorbance of solution Y is less than 0.1**, prepare another (more concentrated) dilution of solution X by pipetting 25.00 mL (a 25 mL pipet will be provided) into a clean 100 mL flask and diluting to the mark with the  $\text{FeCl}_3\text{-KCl-HCl}$  solution. Call this latter solution, solution Z, and measure its absorbance. Do not prepare solution Z if solution Y showed an absorbance of 0.1 or larger.

From the measured concentration in either solution Y or solution Z, calculate the concentration of iron-SA complex in solution X. From this, you can calculate the mmoles and mass of SA in the weighed sample, and thus the percent purity. Turn in your results on Data Sheet 2. If you have previously analyzed your synthesized aspirin sample by pH titration, compare the two sets of results.

**SUSB-013 Data Sheet 1**  
**Standard Solutions and Beer's Law Calibration Plot**

Notebook Grade: \_\_\_\_\_

Safety Grade: \_\_\_\_\_

\_\_\_\_\_  
 Name Section Date

Partners' Names \_\_\_\_\_

Initial Mass of SA and vial \_\_\_\_\_ g

Mass of SA and Vial after transferring \_\_\_\_\_ g

Mass of SA \_\_\_\_\_ g

Mass of SA \_\_\_\_\_ mg

mmoles of SA \_\_\_\_\_ mmol

Volume of Solution 1 \_\_\_\_\_ mL

Conc. of SA in Soln. 1,  $[SA]_1$  \_\_\_\_\_ M.

<b>Solution</b>	<b>Vol. of Sol'n. 1 Used</b>	<b>Conc. of Fe(SA)</b>	<b>Absorbance, A</b>
F	_____ mL	_____ M.	_____
E	_____ mL	_____ M.	_____
D	_____ mL	_____ M.	_____
C	_____ mL	_____ M.	_____
B	_____ mL	_____ M.	_____
A	_____ mL	_____ M.	_____

Slope of Beer's Law plot,  $dAbs/dConc$  (Indicate units) \_\_\_\_\_

**SUSB-013 Data Sheet 2**  
**Analysis of Synthesized Sample**

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Name	Section	Date
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Synthesized. Sample

Mass of sample	_____ g	
Mass of sample	_____ mg	
Absorbance of solution Y (or Z)	(Y)_____	(Z)_____
Percent transmittance (if measured)	(Y)_____ %	(Z)_____ %
Concentration of Fe(SA) complex (from Graph)	(Y)_____ M	(Z)_____ M
Volume of Solution X used to prepare Y (or Z)	_____	
mmoles of SA in solution Y (or Z)	(Y)_____ mmol	(Z)_____
mmoles of SA in 250 mL Solution X	_____ mmol	
mmoles of SA in original sample	_____ mmol	
Mass of SA in original sample	_____ mg	
Mass of ASA in original sample	_____ mg	
% ASA in original sample	_____ %	

If you used the same synthesized sample in this exercise as you did in the pH titration, compare the percents obtained by this method and by pH titration. Discuss any differences. If not, explain why you did not use the same sample.

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## SUSB-013 Pre-Laboratory Assignment

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Name

Section

Date

1. After completing all of her absorbance measurements in Parts I-III of this exercise, Shana Chemikerin realizes that her spectrophotometer has been set to make measurements at a wavelength of 520 nm instead of 530 nm. How will this affect her results? Should Shana repeat the entire exercise?

2. Another student, Ninotchka Otchki, discovers that her spectrophotometer is set for the wrong wavelength after completing Part I. She corrects it to 530 nm before doing Parts II and III, but does not repeat Part I. How will this affect her results? Should she repeat the entire exercise?

3. In the standardization, we add the  $\text{FeCl}_3 - \text{KCl} - \text{HCl}$  solution to the samples that are used to prepare the several dilutions. Why don't we add it only to the SA stock solution we prepare and then dilute the samples with pure water?

4. 200 mg of salicylic acid is weighed for the preparation of the Beer's Law stock solution (solution 1). If 10.00 mL of solution 1 were used in preparing solution H, how many mmoles of salicylic acid are in 100 mL of solution H? How many mL of 0.02 M  $\text{FeCl}_3$  would be necessary to completely react with the salicylic acid in solution H?

**(OVER)**

### SUSB-013 Pre-Laboratory Assignment

5. Solution X is made by dissolving **Q** mg of synthesized aspirin in 250.0 mL of water. Calculate the weight **Q** by adding the last two digits of your student ID in mg to 150 mg. Solution Y is made by diluting 5.00 mL of Solution X to 100.0 mL with 0.02 *M*. FeCl<sub>3</sub>-KCl-HCl solution. The Beer's law constant for the Fe-salicylate complex is 1350 L/mol. Solution X shows an absorbance of 0.135. What is the percent of ASA in the synthesized aspirin?