Experiment 12

Analysis of Aspirin

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PURPOSE

Colorless acetylsalicylic acid in an aspirin tablet will be converted to the reddish-purple salicylatoiron(III) complex to determine the percent acetylsalicylic acid in the tablet spectrophotometrically.

ANALYSIS OF ASPIRIN

Acetylsalicylic acid is the component of aspirin that relieves pain and suppresses inflammation. It is a colorless compound, so it must be converted to a colored compound in order for it to be analyzed spectrophotometrically.

In this experiment, acetylsalicylic acid, $C_9H_8O_4$, is converted to sodium salicylate, $NaC_7H_5O_3$ (see figure 1).

$$C_9H_8O_4 + 2\,NaOH \rightarrow NaC_7H_5O_3 + NaC_2H_3O_2 + H_2O \quad (1)$$

The sodium salicylate is then reacted with a large excess of iron (III) ions to form salicylatoiron(III), $[FeSal]^+$, a reddish-purple complex ion (see figure 1).

$$NaC_7H_5O_3 + Fe(III) \rightarrow [FeSal]^+ + H^+ + Na^+ \quad (2)$$

The amount of $[FeSal]^+$ formed is then determined by spectrophotometric analysis at the wavelength of maximum absorbance, λ_{max}. (Note: here the square brackets indicate that the species inside them is a complex ion, not the concentration of the species, as is usually the case. If it meant concentration the charge would be inside the brackets.)

It is essential that all of the acetylsalicylic acid be converted to $[FeSal]^+$. Reaction 1 goes to completion by simply boiling acetylsalicylic acid with a slight excess of NaOH for a few seconds. However, reaction 2 is somewhat more sensitive to conditions:

(a) If the reaction mixture is too basic, iron(III) hydroxide, $Fe(OH)_3$, will precipitate out.

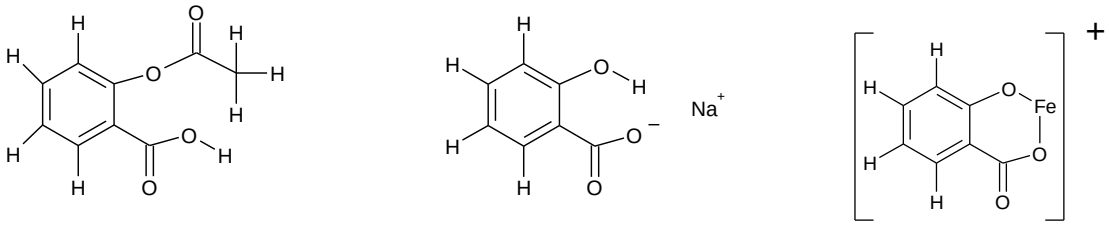
(b) If the reaction mixture is too acidic, the sodium salicylate will not be completely converted to $[FeSal]^+$.

(c) If the Fe(III) is not present in large excess, more than one mole of sodium salicylate may react with each mole of Fe(III).

The procedure and the composition of the reagent solutions are designed to minimize chances of these three undesirable conditions from interfering with the analysis.

IN THIS EXPERIMENT

Five standard solutions of $[FeSal]^+$ will be prepared. The absorbance of these solutions will be measured at λ_{max}, and a standard curve (Beer's law plot) will be constructed. An aspirin tablet will be analyzed for total salicylate content. The concentration of an unknown solution will also be determined from its absorbance using the standard curve.



Acetylsalicylic acid | Sodium salicylate | [FeSal]$^+$

Figure 1. Structures of the reaction species.

PRE-LABORATORY PREPARATION

1. Read the procedure and data analysis sections of the experiment.

2. Complete the PRELAB assignment in Canvas. Refer to the procedure and data analysis sections of the experiment as needed. The prelab questions for this experiment replicate some of the questions in the data analysis section.

3. Construct a complete, organized data sheet. You will want to record the concentration of the stock sodium salicylate provided, the volumes used to prepare the five standard solutions, the wavelength of maximum absorbance, all absorbance readings, and the mass of your aspirin sample.

EXPERIMENTAL SECTION

REAGENTS PROVIDED

0.20 M Fe(III), dissolved in 0.050 M HCl-KCl.
Sodium hydroxide, 1*M*.
Sodium salicylate, 0.004*M*. This will be dispensed by an auto-fill buret.
Unknown solution of sodium salicylate.

Hazardous Chemicals

Hot 1 M sodium hydroxide can cause serious damage to eyes. If NaOH gets on your skin, wash it off with copious amounts of tap water.

WASTE DISPOSAL

All of the chemicals used in this experiment may be safely disposed of by washing down the sink.

PROCEDURE

Work with a partner, unless told otherwise. However, each student must analyze his/her own unknown sodium salicylate solution.

PREPARATION OF 0.02 *M* Fe(III)

1. Measure 100 mL of 0.20 M Fe(III) solution and pour it into a clean 1 L plastic bottle. Add distilled water until the bottle is filled up to where it starts to narrow. Cap the bottle and mix thoroughly.

The 1 L plastic bottle should be designated cabinets in the front and back of each room.

It is not necessary to be precise in these measurements. This solution will be used to prepare the $[FeSal]^+$ solutions.

If you run out of this solution, and have to prepare more, you will be substantially increasing the amount of error in your results.

2. Fill a cuvet with the solution you prepared in step 1. This will be the *blank cuvet* used to calibrate the spectrometer.

PREPARATION OF $[FeSal]^+$ SOLUTIONS

3. Transfer 5.00 mL of the stock sodium salicylate solution from the auto-fill buret directly into a 50 mL volumetric flask.

On your data sheet, be sure to *record the exact concentration of the stock sodium salicylate solution* written on the bottle label. Also, *record the exact volume of sodium salicylate used (to the nearest 0.01 mL)*.

4. Return to your bench and add 0.02 M Fe(III), made in step 1, until the meniscus rests on the flask's calibration mark. Cap the flask and mix thoroughly by inverting it several times.

This converts the sodium salicylate into salicylatoiron(III), see reaction (2).

To avoid adding too much Fe(III) solution, use a medicine dropper or carefully pour from a beaker (or graduated cylinder) to bring the bottom of the meniscus to the 50 mL mark.

5. Fill a clean cuvet with this solution.

Rinse the cuvet before filling it. Empty the 50 mL volumetric flask and rinse it thoroughly before reusing it.

6. Prepare cuvets containing four other standard solutions of $[FeSal]^+$ by taking 4.00, 3.00, 2.00, and 1.00 mL, respectively, of the stock sodium salicylate solution and diluting each aliquot (to 50.00 mL) with the 0.02 M Fe(III) you prepared.

Proceed in the same manner as described in steps 3-5, above. *Record the exact volume used (to the nearest 0.01 mL) for each solution*.

7. Calculate the concentrations of the standard solutions you have prepared and record them in the Data Analysis section. (This is Data Analysis question 1.)

Each concentration can be obtained by performing a dilution calculation using the volume and concentration of sodium salicylate used and the final volume of solution (50 mL). In your calculation, be sure to use the actual *stock sodium salicylate* concentration, as recorded on your data sheet.

PREPARATION OF THE BEER'S LAW PLOT

8. Turn on the LabQuest2 and connect the spectrometer to the USB port.

9. Using the blank cuvet prepared in step 2, calibrate the spectrometer as follows:

a. Tap on **Sensors** from the menu line at the top of the screen. Next choose **Calibrate** and then **USB: Spectrometer**.
b. Allow the spectrometer to go through the 90 second warm up if you have just connected it. (Otherwise, you may skip the warm up.)
c. Insert the blank cuvet into the spectrometer. The clear sides of the cuvet should be facing in the direction of the ► on the spectrometer.
d. Tap **Finish Calibration**. The calibration will finish in a couple of seconds. Then tap **OK**.

10. Place the cuvet containing solution #1 (5.00 mL) in the spectrometer and tap the Start button to measure the spectrum.

Wait a few seconds for it to stabilize and then tap on the **Stop button**.

11. Tap on your A vs. λ curve at its highest point to change the wavelength to λ_{max}. Record the wavelength of maximum absorbance, λ_{max}, on your data sheet.

The selected wavelength (and corresponding absorbance) is displayed in a box on the right side of the graph. (You will re-measure and record the absorbance later.) *This is very important since the subsequent readings you take will be at this wavelength*. λ_{max}, should be somewhere around 540 nm.

12. Change mode to collect absorbance vs. concentration data as follows:

a. Tap on the Meter icon (in the screen's upper left corner) to return to the initial screen.
b. Tap on the Mode box (on the screen's right side).
c. Select ***Events with Entry*** from the top scroll box.
d. Enter c*onc* as the name and *M* for the units. Tap **OK**.
e. Choose to ***Discard*** your spectral data.

13. Tap the *Start* button.

14. Measure the absorbance of each of the five standard solutions.

a. Insert a sample cuvet (start with the most concentrated, which is already in the spectrometer).
b. Wait for the absorbance reading to stabilize and tap ***Keep***. Absorbance readings should typically be between 0 and 1. If your absorbance is outside of this range, you may have a problem. Get help, if necessary. (Furthermore, the absorbances should decrease as the concentration decreases.)
c. Enter the concentration of the solution (calculated in Data Analysis question 1) into the box. *If you use exponential notation to enter concentrations, use e (or E) before the exponent, not ^. For example, 2.0e-3.*
d. Record the absorbance, to the nearest 0.001, on your Data Sheet (next to the volume of the sample). Remember that A is unitless.
e. Repeat steps a-d for the remaining standard solutions. Do them in order from most to least concentrated. *Do NOT tap on the Stop button until you have collected all five points*.

If you enter the wrong concentration, you can edit it after you have stopped data collection. Just tap on the data table icon (in the upper right), double-tap on the cell, and enter the new concentration.

By default, the LabQuest2 will display entered data to 2 places after the decimal in the Data Table. To change this, tap on the data column name and then choose the desired precision.

15. Inspect your data for bad points.

Your data points should be linear. If not, re-measure any suspect readings or remake the solutions. It is always good to get an instructor's opinion if you are not sure.

Note that there is always an extra point on the screen showing the current absorbance reading. This extra point will disappear once you tap the Stop button.

16. Tap the *Stop Button* after five good points have been collected.

Bad points can be removed by going to the Data Table screen, tapping on the row in the data table and then selecting ***Table*** from the top menu, followed by ***Strike Through Data***. (A data point can be restored by following the same procedure, but tapping on ***Restore Data***, instead.)

You can collect additional data by tapping the **Start button** and then choosing ***Append***. Be sure to tap the Stop button when finished.

17. Perform linear regression on your data.

If you are not on the Graph screen, tap the Graph icon to return to it. By default, all of the points will be used. A smaller range of points can be selected by dragging your finger/stylus across the graph. Choose ***Analyze***, then ***Curve Fit***, and tap on the name of your data set that appears. Then select ***Linear*** for the Fit Equation. *Record the slope and y-intercept (with units) on your data page.* Finally, tap ***OK***.

18. Print out your Beer's law plot.

Print out your standard curve by tapping on ***File***, from the top menu, then ***Print*****,** then ***Graph***. Enter a graph title and then tap ***Print***.

ANALYSIS OF ASPIRIN SAMPLE

This part can be done individually or in groups to save time. Assume you will work with your same group unless your instructor specifies otherwise.

19. Weigh out about 0.1 g of an aspirin tablet.

Place a tablet on a watch glass or piece of weighing paper and use your metal spatula (or any other sharp object to which you have access)

to cut off a piece of your aspirin tablet which weighs about 0.1 ± 0.02 g. Most aspirin tablets weigh about 0.4 g, so you need about ¼ of a tablet.

Record the mass of the sample on your data sheet (to the nearest 0.001 g).

20. Transfer your sample to a 125 mL Erlenmeyer flask, and add about 5 mL of 1 M NaOH. Heat the mixture over a Bunsen burner flame until it begins to boil.

This converts the acetylsalicylic acid into sodium salicylate, see reaction (1).

A simple way to do this is to hold the flask over the flame with a pair of crucible tongs, gently swirling the contents. As soon as the mixture starts to boil, remove the flask from the flame and rinse the inside walls of the flask with a small volume of distilled water. Repeat the boiling-rinsing process. Most brands of aspirin create a white precipitate at this point. If you have a precipitate, repeat the boiling-rinsing process. If there is still a precipitate after three boiling-rinsing cycles go on with the experiment.

21. Allow the flask to cool, and transfer the contents into a 50-mL volumetric flask. Rinse the Erlenmeyer flask with distilled water, and pour the rinse solution into the volumetric flask.

Repeat the rinsing process a couple of times so that all of the original mixture is transferred to the flask.

22. Fill the volumetric flask with distilled water until the meniscus rests on the 50 mL mark and mix thoroughly.

We will call this solution A.

23. Use a 1-mL volumetric pipet to transfer 1.00 mL of solution A from the volumetric flask into a clean 50 mL volumetric flask. Fill the new flask to the mark by adding the 0.02 M Fe(III) solution you prepared.

This converts the sodium salicylate into salicylatoiron(III), see reaction (2).

We will call this solution B.

24. Tap the *Meter icon* to return to the meter screen. Measure and record solution B's absorbance.

Insert a cuvet containing solution B into the spectrometer and record the absorbance reading on your data sheet. It is not necessary to use the Collect or Keep buttons since this data is not part of your Beer's law plot.

ANALYSIS OF UNKNOWN

Assume you will do this part individually, unless your instructor specifies otherwise.

25. Obtain your unknown solution.

Each student should obtain an unknown. Bring the instructor or laboratory assistant a clean, dry 50 or 100 mL beaker. You will receive about 25 mL of unknown solution. *Record the unknown number on your data sheet.*

26. Use a rinsed pipet to transfer 10.00 mL of unknown into a clean volumetric flask. Fill to the 50 mL mark by adding the 0.02 M Fe(III) solution you prepared.

The 10 mL pipet should be rinsed with a portion of the solution to be transferred (discarding the rinse solution) before using it to transfer the 10 mL to the flask.

27. Measure the absorbance of the solution.

Record the absorbance on your data sheet.

29. Once you and your partner have both measured your unknown absorbances, shut down the LabQuest2.

Tap ***File*** – ***Quit*** – ***Discard***. Then ***System*** – ***Shut Down*** – ***OK***.

Use a brush and tap water to clean your glassware. Then rinse it with distilled water, dry it, and return it to your drawer.

RETURN EVERYTHING TO WHERE IT WAS AT THE START OF LAB. HAVE AN INSTRUCTOR CHECK YOUR STATION BEFORE LEAVING.

Wash your hands before leaving lab.

Name | Station Used | Instructor/Day/Time

Partner | Station Checked & Approved

DATA SHEET

You must construct a complete, organized data sheet to be used for recording all data during the experiment. It is most efficient to set up a table for your absorbance data (see your previous experiment for an example). Be sure to record all data with the proper number of significant figures and the correct units.

DATA ANALYSIS

All calculations should be clearly organized, make proper use of significant figures and include the units.

1. Calculate the concentration of $[FeSal]^+$ in each standard solution. Show a sample calculation for standard solution 1 below:

standard solution #1_____

standard solution #2_____

standard solution #3_____

standard solution #4_____

standard solution #5_____

2. Copy the linear regression results for your Beer's law plot below. You should enter the proper units (if any) for each. *Turn in your Beer's law plot with your report.*

slope _____ y-intercept _____

3. Perform the following steps to calculate the percent acetylsalicylic acid in the aspirin sample:

a. Use the standard curve's slope and intercept to calculate the $[FeSal]^+$ in solution B.

Concentration of $[FeSal]^+$ _____

b. How many moles of $[FeSal]^+$ were in the 50.0 mL of solution B?

Moles of $[FeSal]^+$ _____

c. How many moles of sodium salicylate were in the 1.00 mL aliquot of solution A used to prepare solution B? [Hint: look at the stoichiometry of reaction (2).]

Moles of Sodium Salicylate_____

d. How many moles of sodium salicylate were in the 50.0 mL of solution A?

Moles of Sodium Salicylate_____

e. How many moles of acetylsalicylic acid were in the aspirin sample? [Hint: look at the stoichiometry of reaction (1).]

Moles of Acetylsalicylic Acid_____

f. Use the mass of the aspirin sample and the answer to part (e) to calculate the mass percent acetylsalicylic acid, $C_9H_8O_4$, in the aspirin sample.

Percent Acetylsalicylic Acid_____

EACH PERSON SHOULD ATTACH A SEPARATE PAGE WITH THE CALCULATIONS AND RESULTS FOR HIS/HER OWN UNKNOWN.

4. Calculate the molar concentration of sodium salicylate in the unknown as follows:

a. Use the standard curve's slope and intercept to calculate the $[FeSal]^+$ in the 50.0 mL solution prepared from 10.0 mL of your unknown.

Concentration of $[FeSal]^+$_____

b. Calculate the concentration of sodium salicylate in the original unknown sample that you received. [Hint, they are two ways to do this: (1) determine the moles of $[FeSal]^+$ in the 50.0 mL solution; use this to get the moles of sodium salicylate in the 10.0 mL aliquot of unknown; and then use the moles and volume to get the concentration OR (2) do it as a dilution problem.]

Concentration of Unknown Sodium Salicylate _____

Unknown Number _____

Name _____