Chemistry 122 Lab Manual

University of Montevallo
Montevallo, AL 35115

Written by

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Chemicals & Instructions

Experiment # 1: Synthesis And Characterization Of Aspirin

Materials:	Salicylic Acid	[69-72-7]	Irritant
	Acetylsalicylic Acid	[50-78-2]	Irritant
	Ethanol	[64-17-5]	Flammable Liquid
	Hood use only		
	Acetic Anhydride	[108-24-7]	Corrosive/Lachrymator
	Phosphoric Acid 85%	[7664-38-2]	Very Corrosive: Caution

Experiment # 2: Determination of Aspirin Content Using Visible Spectroscopy

Materials:	Acetylsalicylic Acid	[50-78-2]	Irritant
	1 M NaOH	[1310-73-2]	Corrosive
	0.02 M $FeCl_3$	[10025-77-1]	Corrosive/Hygroscopic
	Commercial Aspirin		

Experiment # 3: Determination of Aspirin & Caffeine in Analgesics Using HPLC

Materials:	Acetylsalicylic Acid	[50-78-2]	Irritant
	Bayer		
	Excedrin		
	Anacin		
	Caffeine	[57-08-2]	Toxic
	HPLC Solvent 60/40 ratio MeOH/HOAc		
	Methanol	[67-56-1]	Flammable Liquid/Toxic
	Acetic Acid 1%	[64-19-7]	Corrosive
	C-18 reverse phase column		

Experiment # 4: Analysis of Aspirin Using Spectroscopy

Materials:	Salicylic Acid	[69-72-7]	Irritant
	Acetylsalicylic Acid	[50-78-2]	Irritant
	$CDCl_3$	[865-49-6]	Highly Toxic/Cancer Agent
			Use Gloves
	Ethyl Acetate	[141-78-6]	Flammable Liquid/Irritant

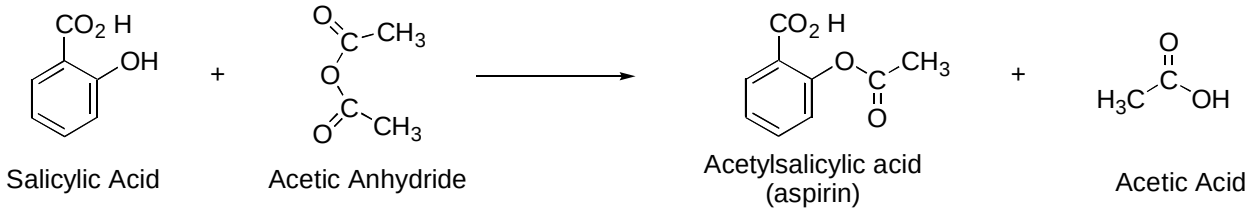
Experiment # 5: Determination of Ca in Buffered Aspirin by AA

Materials:	Buffered Aspirin		
	5% Lanthanum Oxide Solution	[1312-81-8]	Irritant
	$CaCO_3$	[471-34-1]	Irritant
	0.1 M HCl	[7647-01-0]	Corrosive

EXPERIMENT # 1
SYNTHESIS AND CHARACTERIZATION OF ASPIRIN

Aspirin, or acetylsalicylic acid (ASA), is a derivative of salicylic acid (SA) that is used as an analgesic (reduces and prevents pain) and antipyretic (reduces or prevents fever) medication. It is probably the most commonly used over-the-counter medication. Aspirin is broken back down in the intestines to reform salicylic acid, which is in fact the active ingredient. Salicylic acid is too acidic to be safely consumed by itself but its acidity is effectively neutralized in the intestinal tract.

Aspirin can easily be synthesized from salicylic acid by reacting the salicylic acid with acetic anhydride as shown in the following equation.



Salicylic Acid | Acetic Anhydride | Acetylsalicylic acid (aspirin) | Acetic Acid

Acetic anhydride is used because it is cheap and forms a by-product, acetic acid, which can easily be removed. In this experiment you will synthesize aspirin using the above reaction and then determine the purity of the initial product by melting point. You will then attempt to purify the crude by recrystallization and again use the melting point to determine purity of the final product.

EXPERIMENTAL

Using an electronic pan balance, weigh out 2.0 g of salicylic acid and transfer it to a clean and dry 100 mL Erlenmeyer flask. Add 4.0 mL of acetic anhydride to the flask(**do in the hood**) and gently swirl the flask for a minute. CAREFULLY add 3-5 drops of concentrated phosphoric acid. (Caution: concentrated phosphoric acid is very corrosive and will attack both your skin and your clothes. If you spill any, quickly wash the affected area with water then with a solution of sodium bicarbonate, then with water again.) Place the Erlenmeyer flask in a hot water bath in the hood and let it heat for 5 minutes while swirling the flask occasionally. During this time period all of the salicylic acid should dissolve. Add 30 mL of distilled water to the flask, swirl it to mix all the reagents then let it sit in the water bath for 1 minute. The water you added will convert any unreacted acetic anhydride to acetic acid. Remove the flask from the hot water bath and let it cool to room temperature. The mixture should become gummy then a clump of solid should crystallize out. If an oily liquid forms instead of a solid, use the end of a glass rod to scratch the bottom of the flask underneath the oil. This is usually sufficient to initiate crystallization. Break any clumps up with a glass rod and stir the solution. When the mixture has cooled to room temperature, let it chill in ice water then collect as much of the solid as possible using vacuum filtration. Wash the flask and the collected aspirin in the funnel with two 10 mL portions of ice-

cold distilled water. Dry the solid by pulling air through the funnel for five more minutes. Weigh the crude aspirin and calculate the percent yield of the reaction (see below). Save a small portion of the crude product for a melting point determination and then recrystallize the rest.

Recrystallization is a procedure in which an impure substance is dissolved in a solvent then allowed to slowly crystallize out. Any small amount of impurity present that might have been trapped in the crude product will usually remain in solution. The most common way of controlling the rate of crystallization is to dissolve the solid in a warm solvent then let the solvent slowly cool, the solid usually being more soluble at the higher temperature than at the lower temperature. If the impurities are present only in small amounts, they should be equally soluble at both temperatures.

Record the weight of the remaining sample before starting the recrystallization. Dissolve the crude aspirin in 6-9 mL of ethanol (use as little as possible) in a 50 mL beaker. Then add 18-20 mL of hot distilled water to the beaker. If a solid precipitates out at this point, heat the solution, stirring with a glass rod, until the solid dissolves. Cover the beaker with a watch glass and let it cool slowly. After the mixture has cooled to room temperature, collect the solid aspirin using vacuum filtration and wash it with two 3-5 mL portions of ice cold distilled water then air-dry it. Compare the form and texture of the crude and recrystallized materials. Weigh the dry crystals and correcting for the fact that you didn't use the entire sample, calculate a percent yield for the entire reaction.

PERCENT YIELD CALCULATIONS

Based on the balanced equation for the reaction, you should obtain 1 mole of aspirin for every mole of salicylic acid. The percent yield (%-yield) is determined by

$$\%\text{-Yield} = \frac{100*(\text{actual mass of product})}{(\text{theoretical mass of product})}$$

$$\text{theoretical mass of product} = \frac{(\text{mass SA})\ (1\text{ mole ASA})\ (\text{MM ASA})}{(\text{MM SA})\ \ (1\text{ mole SA})}$$

(MM=Molar Mass)

References:

1. Olmsted, John A. III “Synthesis of Aspirin: A General Chemistry Experiment” *J. Chem. Educ.* **1998,** *75,* 1261.

2. Pandita, Sangeeta; Goyal, Samta “An Efficient Microscale Procedure for the Synthesis of Aspirin” *J. Chem. Educ.* **1998,** *75,* 770.

NAME_____ DATE_____
PARTNERS_____
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MASS OF SALICYLIC ACID (g)	MOLES OF SALICYLIC ACID	MOLES OF ASPIRIN (THEORETICAL)	MASS OF ASPIRIN (THEORETICAL)

CALCULATION OF THE PERCENT YIELD OF THE REACTION

SAMPLE	WEIGHT	%-YIELD
Initial Product		
Recrystallized Product		

Was there a difference in the melting points of the crude & pure aspirin? What can you conclude?

NAME_____ DATE_____
PARTNERS_____
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TITLE OF EXPERIMENT_____

Write, in your own words, a one-page summary of the experiment. State what you think the purpose of the experiment was and what you think you accomplished including a brief summary of the final results. Also include a brief synopsis of any important experimental procedures.

EXPERIMENT #2
DETERMINATION OF ASPIRIN CONTENT USING VISIBLE SPECTROSCOPY

Spectroscopy is the study of the interaction of electromagnetic radiation (EMR), 'light', with matter. EMR is a set of oscillating electric and magnetic fields which is characterized by a frequency (ν) and a wavelength (λ) which are related through the speed of light, c, as shown in the following equation:

$$\lambda * \nu = c$$

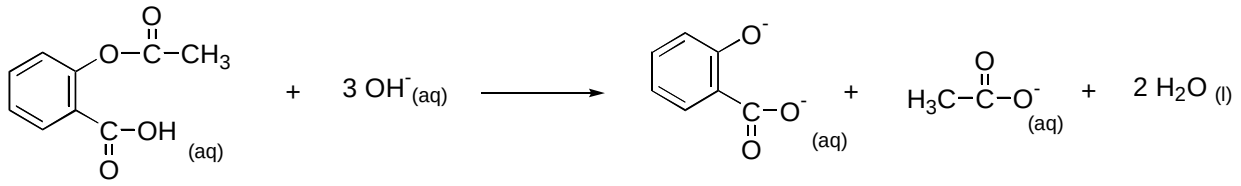
In the visible region of the spectrum the color of the sample indicates which regions of the electromagnetic spectrum are interacting with the sample, and which regions are passing through the sample with little or no interaction. The former are said to be 'absorbed' by the sample while the latter are said to be 'transmitted'. A sample that appears to be blue in color does so because only the blue region of the visible spectrum is passing through the sample; the red and green portions are interacting with the sample and are absorbed. The color and amount of light absorbed can be detected and measured using an instrument called a spectrophotometer. The major components of a spectrophotometer operating in the visible portion of the spectrum are a white-light source; a monochromator, a device that separates the white-light into its component colors; a detector which measures the amount of light passing through the sample; and various associated mirrors, lenses, and filters to change the light path within the instrument. The instrument is constructed in such a way that the output signal, called the absorbance, that it provides is directly proportional to the concentration of the light absorbing species. This relationship is known as the Beer-Lambert Law and is expressed mathematically as (1)

$$Absorbance = \varepsilon * [analyte] \qquad (1)$$

The constant of proportionality, ε, is called the molar absorptivity, and must be experimentally determined.

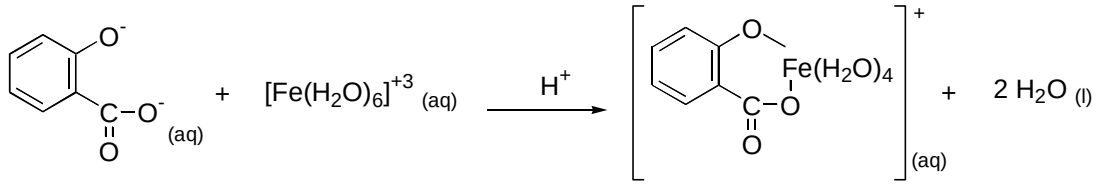
Aspirin, acetylsalicylic acid, is a white crystalline powder that forms a colorless solution when dissolved in water, i.e. it does not absorb visible light. It is also a weak acid, which can react with a strong base to form the salicylate ion as shown in equation (2):

(2)



The salicylate ion will react with Fe (III) in the presence of acid forming a reddish-purple complex (Fe (III)-SA) which absorbs light at a wavelength of 530 nm (equation 3).

(3)



The concentration of the complex can easily be determined by measuring the amount of light absorbed by the complex and rearranging equation (1).

(4)

$$[Fe(III) - SA] = \frac{Absorbance}{\varepsilon}$$

The concentration of the salicylate ion and hence the amount of acetylsalicylic acid are determined through the use of the appropriate stoichiometric factors (equations (2) and (3)).

EXPERIMENTAL

In order to use equation (4) we must first determine ε. This is done by reacting a known amount of aspirin (as the salicylate ion) with an excess of Fe (III) in order to drive reaction (3) to completion. Since the salicylate ion is the limiting-reagent, the amount of the complex formed can be readily calculated and the value of ε determined by measuring the absorbance and applying equation (4). A more common practice is to prepare several standards, solutions of different but known concentrations, and to plot the measured absorbance of each of the standards against the concentration of the Fe (III)-SA complex in each. The slope of the resulting line is equal to ε.

Accurately weigh out approximately 0.400 g (400 mg) of reagent grade acetylsalicylic acid and quantitatively transfer it to a 125 mL erlenmeyer flask. Record the weight of the aspirin used in Table I of your lab book. Go to the hood and using a graduated cylinder, very carefully add approximately 10 mL of 1 M NaOH. Warm the solution to near boiling on a hot plate taking care not to spatter the corrosive liquid outside the flask. Remove the flask from the hot plate and let it cool for several minutes then cool it to room temperature by very carefully swirling it under a stream of cold tap water. Quantitatively transfer the cooled solution to a 250 mL volumetric flask. Using a distilled water bottle, rinse the erlenmeyer flask several times, transferring the rinsings to the 250 mL volumetric flask. Now fill the volumetric flask to the mark with distilled water, cap it tightly with parafilm and mix thoroughly. This will be your 'stock' solution from which all of your standards will be prepared. Obtain five 100 mL volumetric flasks and label them STD 1 through STD 5. Using a calibrated glass pipette, transfer 1.00 mL of the 'stock' solution to the flask marked STD 1, 2.00 mL of the 'stock' solution to flask STD 2, 3.00 mL of 'stock to STD 3, 4.00 mL to flask STD 4, and 5.00 mL to flask STD 5. **Carefully fill each of the flasks to the mark** with the provided 0.02 M Fe (III)

solution. You should see the reddish-purple color of the Fe (III)-SA form immediately. Cap each flask tightly with parafilm then thoroughly mix each of them. Measure the absorbance of each of the solutions at 530 nm using water as a blank and record these values in Table I.

ASPIRIN ANALYSIS

Accurately weigh out approximately 325 mg of your synthesized aspirin into a 125 mL Erlenmeyer flask and treat with 10 mL of 1 M NaOH as before. Quantitatively transfer the solution to a 250 mL volumetric flask and dilute to the mark with distilled water. Cap with parafilm and mix thoroughly. Using a pipette, transfer 5.0 mL of this solution to a 100 mL volumetric flask and fill to the mark with the 0.02 M Fe (III) solution. Cap tightly with parafilm and mix thoroughly.

Repeat the above procedure using a commercial aspirin product. Accurately weigh one tablet and transfer it to a 125 mL Erlenmeyer flask. Add the 1 M NaOH as before and heat and swirl until the table completely disintegrates (it probably will not completely dissolve). Quantitatively transfer the mixture to a 250 mL volumetric flask and fill to the mark with water. Cap tightly with parafilm then mix thoroughly. Let any solids settle to the bottom, then using a pipette, transfer 5.0 mL of the solution to a 100 mL volumetric flask and fill to the mark with the 0.02 M Fe (III) solution.

Measure the absorbance of each of the two solutions at 530 nm and record these values in Table 2.

ANALYSIS

The concentrations of the solutions in Table 1 can be calculated using dilution factors

$$[Fe(III)\text{-}SA]\left(\frac{mg}{mL}\right) = \frac{mass \cdot aspirin \cdot reagent(mg)}{250.0mL} * \frac{volume \cdot of \cdot stock(mL)}{100.0mL}$$

Plot the measured absorbance (y-axis) versus the calculated concentration of Fe (III)-SA (X-axis). Draw the best straight line through these points and determine the slope, which is ε (If time permits, have your instructor show you how to do this using a spreadsheet).
The mass of aspirin in each of the two samples can be calculated using the equation below.

$$\frac{mg \cdot aspirin}{sample} = \left(\frac{Absorbance(530nm)}{\varepsilon(530nm)}\right) * \left(\frac{100.0mL}{5.0mL}\right) * (250.0mL)$$

Compare your calculated amounts of aspirin with the expected or known amounts using the following equations:

% difference (synthetic) = |exp value - mass sample| x 100

mass of sample

$$\% \text{ difference (commercial)} = \frac{|\text{exp value - stated value}|}{\text{stated value}} \times 100$$

In the above equations, 'exp values' are the values that you obtained in this experiment and the 'stated value' is the value on the aspirin bottle.

Reference:

Pinnell, Robert P.; Motz, Leonard P. "A Colorimetric Determination of Aspirin in Commercial Preparations", *Modular Laboratory Program in Chemistry Anal-126,* Neidig, H. A., Ed. Willard Grant Press, Boston, MA, 1973, 1.

Name_____
Section_____ Date_____

TABLE 1. DETERMINATION OF ε

		weight of aspirin = _____ g		
Flask	Volume of Salicylate Stock (mL)	Total Volume (mL)	Calculated Concentration Fe (III)-SA mg/mL	Measured Absorbance λ =
STD 1				
STD 2				
STD 3				
STD 4				
STD 5				
			CALCULATED VALUE FOR ε	

TABLE 2. ASPIRIN SAMPLE

SAMPLE	MASS	ABSORBANCE	CALCULATED MASS	PERCENT DIFFERENCE

NAME_____ DATE_____
PARTNERS_____
_____

TITLE OF EXPERIMENT_____

Write, in your own words, a one-page summary of the experiment. State what you think the purpose of the experiment was and what you think you accomplished including a brief summary of the final results. Also include a brief synopsis of any important experimental procedures.

EXPERIMENT #3
DETERMINATION OF ASPIRIN & CAFFEINE IN ANALGESICS USING HPLC

HPLC(High Performance Liquid Chromatography) is just column chromatography done at high pressures. It has the advantage that the separation can be carried out in a much shorter time than would be necessary for normal open column chromatography, but it requires much more elaborate equipment and thus is a more expensive operation. In this experiment you will analyze various analgesics to determine the amount of aspirin and if caffeine, salicylic acid, or any other additive are present.

Caffeine is a common constituent of most soft drinks and many over the counter medications. It is a white crystalline solid that acts physiologically as a stimulant. At higher doses it can be toxic. In the past caffeine was a common additive to a number of different products. In recent years manufacturers, due to customer demand, have started removing caffeine from those products in which it is naturally occurring, coffee for example. They also have stopped adding it to others, caffeine-free Coke and Pepsi being examples, but it is still added to many medications. Salicylic acid forms in the slow hydrolysis of aspirin and is thus is an indicator of a breakdown of the active ingredient of the analgesic. In order to analyze the analgesics for aspirin, caffeine, and salicylic acid, you must separate them from other possible components, which might interfere with the analysis. This will be done using HPLC. This has the added advantage in that the separation and quantitative analysis are performed simultaneously.

EXPERIMENTAL

Obtain 3 analgesic samples and 3 clean 50 mL volumetric flasks from your instructor. Weigh each of the tablets then carefully crush each tablet in a mortar & pestle. For each sample, accurately weigh out about 150 mg of the powdered tablet and transfer it to a separate volumetric flask. Record the weight in the data table. Fill the flask about half full with the solvent labeled ‘mobile phase’, cap it with parafilm and shake vigorously for several minutes. Not all of the solid will dissolve. Fill the flask to the mark with solvent then cover and mix thoroughly. Set this flask aside to let undissolved solids settle to the bottom. Be sure to include one analgesic that is labeled 'caffeine-free' as well as one whose label indicates that it does contain caffeine.

To determine the amount of aspirin in each tablet, standards must be prepared. Again obtain 5 clean 50 mL volumetric flasks from your instructor and label four of them 1-4. Weigh out, as close as possible 100 mg of pure commercially synthesized acetylsalicylic acid and place it in flask labeled #1, recording the weight in Table 1. Then weigh out 125 mg, 150 mg and 175 mg of pure aspirin and place it in flask 2, 3, & 4, respectively. In addition, place about 15 mg of caffeine in flask #1 and about 15 mg of salicylic acid in flask #4. Fill each volumetric flask about half-full with the solvent, cap and shake vigorously until all the solid has dissolved. Fill each flask to the mark with solvent and mix thoroughly. Obtain a fifth 50 mL volumetric flask and label it #5. Accurately weigh out about 150 mg of the aspirin you prepared in experiment 1 and treat as with the standards. Record the exact weight in Table 1.

To determine the amount of aspirin in various over the counter analgesics a calibration curve

must first be prepared. Set the pump flow rate for 2.0 mL/min. Make sure that the detector is on the 0.050 range, that the baseline has been zeroed, and that the Injection Valve is in the LOAD position. The Peaksimple software should already be up and running. Rinse the 100 μL microliter syringe by filling it with the first standard(flask#1) then emptying it. Repeat this fill/empty cycle twice more. Now fill the syringe and carefully push it all the way into the Injection Port, then push the plunger all the way in. Fill the syringe again with the same sample and inject it. Repeat this process twice more. Rotate the Injection Valve to the INJECT position to start the analysis. The computer will start to record the sample absorbance as soon as you turn the valve and the results will be displayed on the screen. As soon as the run is over, click on the 'View' button then on 'Results'. Record the retention time and the area of the acetylsalicylic peak in Table 1. Record the retention times for the caffeine or salicylic acid if they are also present. Repeat this procedure for each of the four standards. Following the same procedure inject and analyze the sample containing your synthesized aspirin then each sample of the commercial tablets. For the commercial tablet, pour some of the sample into two centrifuge tubes and spin the solids to the bottom of the tubes. **DO NOT INJECT SOLID MATERIALS.** Record the retention times and areas as before.

ANALYSIS

A calibration curve is a plot of instrument response versus concentration of a sample. To determine the amount of aspirin in each tablet, the slope of the calibration curve is necessary because it indicates how the HPLC responds to a given amount of aspirin. To make a calibration curve, plot of the area (y-axis) of the standard aspirin versus the amount of aspirin (x-axis) initially weighed into the flasks. Draw the best straight line through these points and calculate the slope. The aspirin in each tablet can then be calculated using the following equation:

$$\text{Slope of Calibration curve} = \frac{\text{Peak area}}{\text{Amount of Aspirin}}$$

Compare your calculated amounts of aspirin with the expected or known amounts using the following equations:

$$\%\ \text{difference (commercial)} = \frac{|\text{exp value - stated value}|}{\text{stated value}} \times 100$$

References:
Beaver, Rodney W.; Bunch, John E.; Jones Louis A. "Qualitative Analysis of Analgesic Tablets: An Experiment Employing High Pressure Liquid Chromatography" *J. Chem. Educ.* **1983,** *60,* 1000.
Kagel, R. A.; Farwell, S. O. "Analysis of Currently Available Analgesic Tablets by Modern Liquid Chromatography" *J. Chem. Educ.* **1983,** *60,* 163.
Haddad, Paul; Hutchins, Stephen; Tuffy, Michael "High Performance Liquid Chromatography of Some Analgesic Compounds" *J. Chem. Educ.* **1983,** *60,* 166.
NAME_____ DATE_____
PARTNERS_____

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DATA TABLE 1

Sample	Mass (mg)	Time	Peak area
Flask 1			
Flask 2			
Flask 3			
Flask 4			
Flask 5			

DATA TABLE 2

Sample	Time	Peak Area	Calculated Mass (mg)	Stated Mass (mg)	% Difference	Caffeine or other peaks (Y/N)

NAME_____ DATE_____
PARTNERS_____
_____

TITLE OF EXPERIMENT_____

Write, in your own words, a one-page summary of the experiment. State what you think the purpose of the experiment was and what you think you accomplished including a brief summary of the final results. Also include a brief synopsis of any important experimental procedures.

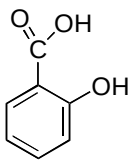
EXPERIMENT #4
ANALYSIS OF ASPIRIN USING SPECTROSCOPY

Spectroscopy is the study of the interaction of electromagnetic radiation (EMR), 'light', with matter. EMR is a set of oscillating electric and magnetic fields which are characterized by a frequency (ν) and a wavelength (λ) which are related through the speed of light, c, as shown in the following equation:

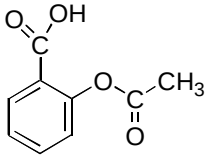
$$\lambda * \nu = c$$

Most are familiar with the visible region of the spectrum, since this is the region that our eyes can detect. For example, color indicates which regions of the electromagnetic spectrum are interacting with the sample, and which regions are passing through the sample with little or no interaction. The former are said to be 'absorbed' by the sample while the latter are said to be 'transmitted'. This experiment is designed to introduce you to two different regions of the EMR spectrum, ones that cannot be observed by the human eye. Since energy is related to the frequency of EM-radiation, $E = h\nu$, each region of the EM-spectrum interacts with molecules very differently. For example, microwaves cause polar molecules to rotate, whereas, infrared radiation (IR) causes molecules to vibrate. We will use IR and radio frequencies to determine the purity of your aspirin.

Infrared radiation is of lower energy than visible radiation but of higher energy than radio waves. A molecule can absorb radiation when some parts (group of atoms) of the molecules vibrate at the same frequency of the IR light. After absorbing the IR light the molecules vibration increases. Over the years it has been determined that certain groups of atoms, called functional groups, absorb about the same frequency of radiation even if these functional groups are found in different molecules. This allows one to detect the functional groups that are present in different molecules. It has also been shown that each molecule has a unique IR pattern; therefore, molecules can be identified from their IR spectra. For example, look at the structures of salicylic acid & acetylsalicylic acid shown below.

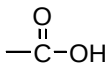


Salicylic Acid

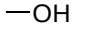


Acetylsalicylic Acid
(Aspirin)

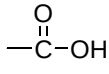
Functional Groups



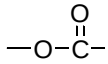
(Carboxyl)



(Hydroxyl)



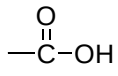
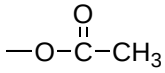
(Carboxyl)



(Ester)

Both contain the same functional group, carboxyl, but both also contain a different functional group.

From the vibrations of these groups, the compounds can be distinguished. A list of the vibrations is provided in the table below.

Functional Group	Vibration	Frequency (cm^{-1})
 (Carboxyl)		1700-1650
—OH (Hydroxyl)	—OH	3500-2700
 (Ester)		1750-1700

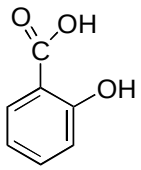
EXPERIMENTAL

Infrared Analysis

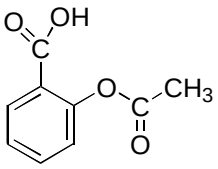
Obtain from your instructor, two salt plates, IR holder, ethyl acetate and pure salicylic acid and pure acetylsalicylic acid. The instrument is designed to look for differences between spectra; therefore, you must take a blank spectrum of the pure salt plates. Once that is done, dissolve about 100 mg of salicylic acid in ~ 1 mL of the ethyl acetate. Add 2-3 drops of this solution to one of the salt plates and let the ethyl acetate evaporate leaving a film of the salicylic acid. Take an IR spectrum of this, by placing the other salt plate on top then clamp it down with the IR holder. The displayed spectrum is the IR pattern for salicylic acid. Save the spectrum clean the salt plates and repeat the process for the pure acetylsalicylic acid and your synthesized aspirin. **Note, to clean the salt plates, rinse with ethyl alcohol then dry thoroughly with a Kimwipe.** Compare the spectrum of your aspirin with that of the salicylic acid and the acetylsalicylic acid.

NMR analysis

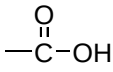
Nuclear magnetic resonance (NMR) spectroscopy is based on the measurement of radio frequency absorption. In contrast to other absorptions, the nuclei of atoms absorb the energy, hence the name nuclear. However in order for the nuclei to absorb the radio waves, the sample must be placed in a strong magnetic filed. The advantage of this technique is that structures of compounds can be determined. The most common use of this technique is proton (H^1) NMR. Proton NMR allows one to determine to which atoms the H atom is bonded and therefore, the structure of the molecules can be determined. Again, look (next page) at salicylic acid and aspirin and notice the different number of hydrogens. There are some similarities in the



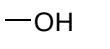
Salicylic Acid



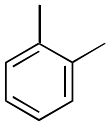
Acetylsalicylic Acid
(Aspirin)



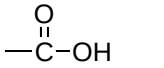
1-Hydrogen



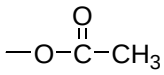
1-Hydrogen



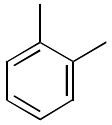
4-Hydrogens



1-Hydrogen

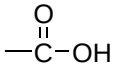
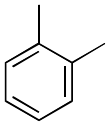
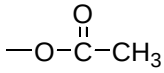


3-Hydrogens



4-Hydrogens

compounds, but the differences can be seen in the NMR spectra. Each hydrogen will absorb a different radio frequency depending on what type of atom it is bonded to. As a standard, the hydrogens are compared to a reference (TMS) that is set at 0 ppm. The table below gives an approximate range in which the hydrogen will absorb.

Hydrogens	Reference to TMS
 1-Hydrogen	9.5-10 ppm
 1-Hydrogen	11-12 ppm
 4-Hydrogen	6.5-8 ppm
 3-Hydrogen	2.5-2.8 ppm

Obtain three NMR tubes, pure salicylic acid and acetylsalicylic acid & $CDCl_3$ (chloroform in which the hydrogens have been replaced with deuterium) from your instructor. Place a small amount of SA on the end of a spatula and transfer it to the NMR tube. Add $CDCl_3$ drop wise into the NMR tube until the height is approximately 1 inch. Cap the NMR tube and invert a few times until the SA is dissolved. Place the tube in the NMR and obtain a spectrum. Repeat for your aspirin that you synthesized. Compare both spectra with an NMR of pure aspirin.

NAME_____ DATE_____
PARTNERS_____
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TITLE OF EXPERIMENT_____

IR Analysis
Attach the IR spectra to this laboratory sheet and answer the following questions.

1. Are there any major differences between the IR of salicylic acid and your aspirin?

2. Which peak(s) did you use to determine if you had converted the SA to aspirin?

3. How does your aspirin spectrum compare to that of the pure aspirin?

NMR Analysis
Attach the IR spectra to this laboratory sheet and answer the following questions.

1. Are there any major differences between the NMR of salicylic acid and your aspirin?

2. Which peak(s) did you use to determine if you had converted the SA to aspirin?

3. How does your aspirin spectrum compare to that of the pure aspirin?

NAME_____ DATE_____
PARTNERS_____
_____

TITLE OF EXPERIMENT_____

Write, in your own words, a one-page summary of the experiment. State what you think the purpose of the experiment was and what you think you accomplished including a brief summary of the final results. Also include a brief synopsis of any important experimental procedures.

EXPERIMENT #5
DETERMINATION OF Ca IN BUFFERED ASPIRINS USING ATOMIC ABSORPTION SPECTROSCOPY

In this lab, you will determine the amount of Ca in a variety of buffered aspirins. Aspirin is an acid and has been known to irritate the stomach lining. Buffered aspirins are tablets that have been coated with a base, usually $CaCO_3$, which is the same ingredient found in TUMS. Calcium can easily be determined using a technique known as Atomic Absorption spectroscopy(AAS). AAS is an optical technique used to determine the presence of metal atoms or ions in a sample. In this technique a sample is dissolved, and the resulting solution is aspirated into a very hot flame. In this flame, the metal ions are converted into neutral atoms in the gaseous state. UV or visible light with a wavelength unique to the element of interest is passed through the flame. If atoms of the element are present in the flame, they will absorb some of that light. The higher the concentration of the species, the more light is absorbed. The relationship between the amount of analyte present and the amount of light absorbed is given by the Beer-Lambert law.

$$\text{Absorbance} = \varepsilon * [\text{analyte}] \qquad (1)$$

To determine how much Ca is in the buffered aspirin you must first determine ε by measuring the absorbencies of a set of solutions of known $[Ca^{2+}]$. A plot of the measured absorbance versus $[Ca^{2+}]$ should yield a straight line with a slope equal to ε. Once ε is known the concentration of a given analyte in a solution of an unknown can easily be calculated by measuring the absorbance of that solution and applying equation (1) in a rearranged form:

$$[\text{analyte}] = \text{Absorbance}/\varepsilon \qquad (2)$$

To construct the calibration curve, obtain five 50 mL volumetric flasks, a 5% lanthanum solution, calcium carbonate and one 10 mL glass volumetric pipet from your instructor. Carefully measure out about 100 mg of Calcium carbonate and add it to a 1-L volumetric flask. **Record the exact mass in Table 1.** Add approximately 10 mL of 1 M HCl solution and swirl gently until all the $CaCO_3$ has dissolved. This solution is a 100 mg Ca^{2+}/L **stock** solution from which all the standards will be prepared. Label the five 50 mL volumetric flasks 2, 4, 6, 8, 10 and add 1 mL of the 5% lanthanum solution to each of these flasks. Then using the dilution equation given below calculate how much of the 100 mg Ca^{2+}/L stock solution must be added to the 50 mL volumetric flasks to prepare solutions which are 2 mg/L, 4 mg/L, 6 mg/L, 8 mg/L, and 10 mg/L in Ca^{2+}.

$$M_c V_c = M_d V_d \qquad (2)$$

Once the stock solution has been added to the each of the 50 mL volumetric flasks, fill each to the mark with distilled water. Cap each flask with parafilm and mix well.

Make sure the instrument is set to a wavelength of 422.7 nm and that the slit width is 0.7 nm. Have your instructor ignite the air/acetylene burner. The small plastic tube in the front of

the burner is used to draw the sample into the flame. Place it in a beaker of distilled water and let the burner flush for about a minute. Zero the instrument by pressing the A/Z key then when the display reads 0.000 press the READ key. Wait until a value shows on the display then remove the beaker of water and place the plastic tubing into the flask containing your most dilute standard. Press the READ key and wait till an absorbance values shows on the display. Record this value and press the READ key again. Take a total of three readings for each standard and record the average absorbance in Table 1. Repeat this procedure for all of your standards.

ANALYSIS OF COMMERCIAL BUFFERED ASPIRIN TABLETS

Obtain two different buffered aspirins from your instructor and grind each into a fine powder using a mortar and pestle. For each sample, accurately weigh out 200 mg of the powder into a 100 mL beaker and record the weight in Table 2. Then, **in the hood**, carefully add 20 mL of concentrated HCl to the beaker and stir for a minute. Not all of the sample will dissolve. Carefully and quantitatively transfer this solution to a 100 mL volumetric flask, rinsing the beaker out several times with distilled water and transferring the rinsing to the volumetric flask. Dilute to the mark with distilled water. Filter 30-40 mL of this solution using a glass funnel and some coarse filter paper. Using a glass pipet transfer 5.00 mL of the filtered solution to a second 100 mL volumetric flask and dilute to the mark with distilled water. Cap this flask with parafilm and mix thoroughly. Using another glass pipet, transfer 5.00 mL of this second solution to a 50 mL volumetric flask. Add 1 mL of the 5 % lanthanum solution and dilute to the mark with distilled water. Cap the flask tightly with parafilm and mix thoroughly. Use distilled water to zero the instrument then measure the absorbance using the same procedure that was used with the standards. Record the absorbance of each of the samples in Table 2.

The %Ca in each tablet can be calculated from the following equation:

(3)

$$\%\ \text{Ca in tablet} = \frac{(10)(20)(X\ \text{mg Ca/L})(0.100\ \text{L})}{\text{mg of tablet powder}} \times 100$$

In this equation 10 & 20 are factors of dilution, X mg Ca/L is the amount of calcium as found by the AAS and mg of tablet is the amount of the crushed tablet you weighed to make the first solution.

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Reference:
Quigley, Michael N. "Determination of Calcium in Analgesic Tablets Using Atomic Absorption Spectroscopy" *J. Chem. Educ.* **1994,** *71,* 800.

NAME_____ DATE_____
PARTNERS_____
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TITLE OF EXPERIMENT_____

Data Table 1

Amount of $CaCO_3$ _____ mg

Concentration of $CaCO_3$ Solution _____ mg/L

Slope of Calibration Curve _____ L/mg

Stock Solution	Concentrations mg/L	Absorbance
2		
4		
6		
8		
10		

Data Table 2

Sample	Amount of Tablet (mg)	Absorbance	Concentration of Ca (mg/L)	%Ca in tablet

NAME_____ DATE_____
PARTNERS_____
_____

TITLE OF EXPERIMENT_____

Write, in your own words, a one-page summary of the experiment. State what you think the purpose of the experiment was and what you think you accomplished including a brief summary of the final results. Also include a brief synopsis of any important experimental procedures.