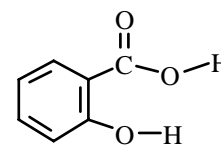


Spectrophotometric Analysis of Iron(III)-Salicylic Acid Complexes

Salicylic acid does not absorb in the visible region of the spectrum, but it does form an intensely colored 1:1 complex with Fe^{3+} . In this series of experiments you will:

- ◆ determine the absorption spectrum and λ_{max} of the iron(III)-salicylate complex; and
- ◆ prepare a calibration curve to determine the amount of salicylic acid in an unknown and/or an over-the-counter medicine.



Salicylic acid

Reagents

Iron(III) solution: Prepared for you. Calculate concentration from these instructions.

Dissolve 2.020 ± 0.005 g $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in ~ 200 mL distilled water in a 500-mL volumetric flask, add 6 mL concentrated hydrochloric acid (measured with a graduated cylinder), and dilute to volume with distilled water. Mix well and store in a labeled plastic bottle.

Sodium Salicylate solution: Prepared for you. Calculate concentration from these instructions.

Salicylic acid itself is not very soluble in water, so it is converted to its sodium salt with the minimum volume of aqueous NaOH. Place 0.300 ± 0.005 g salicylic acid in a 500-mL volumetric flask, and add ~ 25 mL distilled water. Pour in 2 mL 10% NaOH and swirl the flask until all the solid dissolves. Bring to volume with distilled water, mix well, and store the sodium salicylate solution in a labeled glass bottle. Note: in the instructions below this solution will be called both "salicylic acid" and "salicylate."

Experiment 1: Determination of the Iron-Salicylate Absorption Spectrum

Allow the spectrophotometer to warm up while you prepare the sample.

Place 5.00 mL iron(III) solution and 2.00 mL sodium salicylate solution (use separate volumetric pipettes for each) in a 25.00-mL volumetric flask. Bring the mixture to volume with distilled water and mix well. This is the iron-salicylate complex solution.

Place 5.00 mL iron(III) solution alone in another 25.00-mL volumetric flask and dilute to volume with distilled water. This is the "blank" – used as a colorless reference for the complex solution.

Obtain two matched spectrophotometry cells; fill one with some of the dilute iron(III) solution ("blank"), and the other, with the just-prepared iron-salicylate complex solution. Clean the outside of each cell with tissue paper.

Set the wavelength knob to 360 nm and adjust the 0% Transmittance with no sample tube in the cell compartment. Be sure to view the scale with the mirror image of the needle directly behind the needle. Place the sample tube containing the "blank" iron(III) solution in the cell compartment and set the 100% Transmittance knob. Remove this tube; insert the tube of complex solution and position it in the matching position. Record the %T observed and the uncertainty in the reading.

Determine the % Transmittance of the colored complex at wavelengths between 360 and 600 nm in 40-nm increments. Each time the wavelength is changed reset the 100% T knob with the blank solution. Do *not* adjust the 0% T knob.

When you have approximately located the λ_{max} for the complex (= the λ of minimum transmittance), determine the %T of the complex at wavelengths differing by about 10 nm until the exact λ_{max} has been found. All subsequent experiments are performed at this wavelength.

Place the leftover sample solutions in the container marked "Reclaimed Iron-Salicylate Solutions."

Experiment 2: Preparation of a Calibration Curve to Find the Quantity of Salicylic Acid or Salicylate Ion in an Unknown

Salicylic acid can not be determined directly by visible spectrophotometry because it is colorless. However, addition of a large excess of iron(III) converts all the salicylate in the sample to the colored complex. Hence, the Absorbance of the complex is directly related to the concentration of the salicylate ion.

Procedure

Allow the spectrophotometer to warm up at λ_{\max} for at least 15 minutes.

Prepare the following mixtures in 50.00-mL volumetric flasks:

sample:	A	B	C	D	E	F	
mL stock iron(III):	10.00	10.00	10.00	10.00	10.00	10.00	} use volumetric pipette
mL stock salicylate:	1.00	2.00	3.00	4.00	5.00	6.00	} use 10.00-mL grad pipette

Dilute each mixture to volume with distilled water and mix well.

Set the 0% T knob on the spectrophotometer. Use a sample cell filled with diluted Fe(III) from Experiment 1 to set the 100% T.

Empty the cell, rinse it with some of solution A, wipe the tube clean with tissue, and record the %T and the uncertainty. Between samples, rinse the cuvet with distilled water and then some of the next solution. Take care to position the tube the same way in the cell compartment each time.

Place the waste in the container marked "Reclaimed Iron-Salicylate Solutions."

Data Analysis

- 1) Prepare a properly labeled table that gives for each sample: the mL salicylic acid solution used, the concentration of salicylic acid, the % Transmittance, and the Absorbance.
- 2) A Beer's Law calibration curve plots absorbance on the y-axis versus concentration or mass units on the x-axis. If the analysis is oriented toward finding concentrations of analyte, the abscissa is generally in units of Molarity, g/mL, ppm, or the like. If the analysis is focused on finding the mass of analyte, the x-axis can be plotted in units of g or mg contained sample. **Here**, make the x-axis in units of Molarity of salicylic acid.

Making use of the Excel "Scatter graph" tool, plot your concentration and Absorbance data as a smooth curve with the data points shown. Also have the spreadsheet compute the linear regression line with the slope, intercept, and correlation coefficient printed on the graph. When Absorbance is plotted versus Molarity, Beer's Law is written as $A = \epsilon bc$, where ϵ = molar absorptivity. Determine ϵ for the iron-salicylate complex with the correct units and significant figures.

Experiment 3: Analysis of an Unknown Liquid Salicylate Sample

The instructor will give you a solution of sodium salicylate of unknown concentration that is too high to be used directly for analysis. Take a 5.00-mL aliquot by pipette, dilute it to 50.00 mL with distilled water in a volumetric flask, and mix thoroughly.

Place 10.00 mL of the stock iron(III) solution in a 50.00-mL volumetric flask, and add a measured volume of the diluted unknown by pipette – in the range of 2.00 to 5.00 mL. Dilute to volume with distilled water, mix well.

Determine the %T of the diluted unknown and its uncertainty at λ_{\max} . If the reading is not on scale, prepare another sample with less of the diluted unknown. (Note: Use a sample cell filled with diluted Fe(III) from Experiment 1 to set the 100% T.

Data Analysis

Using the %Transmittance of the diluted unknown, calculate the molarity of the salicylate ion in the original, undiluted sample given to you. Obtain the "true" value from the instructor and calculate the percentage relative error in your answer.

Experiment 4: Analysis of a Over-the-Counter Pain Killer for Backaches

Long ago, "primitive" peoples learned to make tea from willow bark to treat fever and aches; in the 19th century chemists discovered that the active pain-killer in willow bark is salicylic acid. However, the acid is quite irritating to the stomach and promotes gastric bleeding. Clever German chemists found that converting salicylic acid to acetylsalicylic acid preserved the useful pain-killing properties of salicylic acid, but greatly reduced stomach irritation; thus was born the wonder drug aspirin.

Patent medicine (over-the-counter stuff sold without prescription) for lower back pain often contains magnesium salicylate, $\text{Mg}(\text{C}_7\text{H}_5\text{O}_3)_2$, as the active ingredient. The rest of the tablet is made up of starch, anti-caking agents, whiteners, ant-acids, and sometimes flavorings.

In this experiment you will determine the actual salicylate content of a back-ache pain-killer and check the value claimed by the manufacturer.

Procedure

Obtain a pain-killer tablet from the instructor and record the mass of magnesium salicylate in each pill claimed by the manufacturer.

Weigh the pill on the analytical balance and record its mass.

Place the tablet in a 400-mL beaker along with ~100-150 mL distilled water. Crush the pill gently with a glass stirring rod and stir the mixture magnetically for about 5 minutes.

Line a short-stemmed funnel with a cone of coarse paper (an ordinary white paper table napkin works well). Suspend the tip of the funnel in the mouth of a 500-mL volumetric flask. Filter the entire solution of the back-ache pill through the paper, collecting all the filtrate in the flask. Rinse out the beaker several times with distilled water to transfer all the insoluble solids to the funnel.

Bring the magnesium salicylate solution in the volumetric flask to the mark with distilled water. Mix the solution well.

[NOTE: the instructor will prepare the pill solution in advance and make the data available.]

Place 10.00 mL of the stock iron(III) solution in a 25.00-mL volumetric flask. Add to it a 2.00 to 5.00-mL aliquot of the magnesium salicylate solution by pipette (record the exact volume used). Bring the mixture to volume with distilled water and mix well.

Determine the % Transmittance of the iron-salicylate solution at λ_{max} , having first set the 100%T with the dilute iron (III) solution from Experiment 1. If the reading is off-scale for the unknown, prepare a new sample with less magnesium salicylate solution in it.

Data Analysis

- Convert the %T reading of the solution in the 25.00-mL flask to Absorbance and work backwards to determine the mass of magnesium salicylate in one entire pill.
- Also calculate the percent by mass of $\text{Mg}(\text{salicylate})_2$ in the pill. The instructor will provide the manufacturer's stated composition of the pill, which is used as the "true" value.
- Calculate the percentage relative error in your result for the mass of the $\text{Mg}(\text{salicylate})_2$ found in one pill.