Case File 9

Killer Cup of Coffee:
Using colorimetry to determine concentration of a poison

Determine the concentration of cyanide in the solution.

A Killer Cup of Coffee? GlobalTech Manager Dies

SOUTH PAINTER, Tuesday: It was a normal Monday morning at GlobalTech Industries until the mail boy discovered project manager Patrick Marchand dead in his cubicle, head on his desk. Mr. Marchand had died while writing an email, in a room full of people hard at work. An early examination of the crime scene yielded no clues.

Mr. Marchand was known to have a serious heart condition, and many signs pointed to cardiac arrest as the cause of his death. However, as police canvassed the office space, the distinct odor of bitter almonds was detected, and a vial containing a small amount of an unknown chemical was found discarded in a communal trash can.

Based on the bitter almond odor, police have tentatively identified the substance as cyanide. The existence of this possible poison has lead police to suspect foul play in Mr. Marchand's death. The police have no leads.

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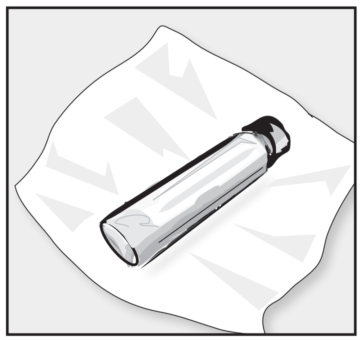


This vial, wrapped in a piece of tissue, was discovered in the bottom of a communal trash can near the GlobalTech office bathroom. It once contained an unspecified amount of cyanide.

LAB NOTES

Technician: Beverly Chin

- received vial containing 20 mL cyanide solution—concentration unknown
- reacted cyanide (CN^-) solution with potassium polysulfide (K_2S_x) to produce potassium thiocyanate (KSCN)
- reacted KSCN solution with iron(III)chloride ($FeCl_3$) to produce iron(III)thiocyanate ion ($FeSCN^{2+}$)
- determination of amount of $FeSCN^{2+}$ in reacted solution will allow estimation of concentration of CN^- in original solution
- included in package: $FeSCN^{2+}$ solution of unknown concentration

Forensics Objective

- use Beer's law to determine the concentration of iron(III)thiocyanate ($FeSCN^{2+}$) in an unknown solution

Science and Mathematics Objectives

- use colorimetry to determine the concentration of a colored species in a solution
- use a linear relationship to model Beer's law
- learn the importance of carefully prepared standards

Materials (for each group)

- TI-83/TI-84 Plus™ Family
- Vernier EasyData™ application
- Vernier EasyLink™
- Colorimeter
- 7 cuvettes
- colored wax pencil
- distilled or deionized water
- 50 mL of 0.15 M stock FeSCN2^{+} solution
- 5 mL of FeSCN2^{+} solution with unknown concentration
- two 10 mL pipettes or graduated cylinders
- two 50 mL beakers
- 5 stirring rods
- 2 droppers
- 5 test tubes
- test-tube rack
- lint-free tissues
- waste beaker
- goggles (1 pair per student)

Procedure

Part I: Preparing the Solutions

Goggles must be worn at all times during this lab activity! CAUTION: Be careful not to ingest any solutions or spill any on your skin. Inform your teacher immediately in the event of an accident.

1. Obtain all the solutions and label them with a wax pencil.
   a) Pour 50 mL of stock 0.15 M $FeSCN^{2+}$ solution into a 50 mL beaker. Label the beaker "0.15 M $FeSCN^{2+}$."
   b) Pour 30 mL of deionized or distilled water into a 50 mL beaker. Label the beaker "H_2O."

2. Prepare the standard solutions.
   a) Label five clean, dry test tubes with numbers 1 through 5.
   b) The table below shows how much water and stock $FeSCN^{2+}$ solution to add to each test tube. Use a pipette or a dropper and graduated cylinder to measure the correct amount of $FeSCN^{2+}$ solution into each test tube. (Note: Use a separate pipette or graduated cylinder and dropper for the water and the $FeSCN^{2+}$.)

Test Tube	$FeSCN^{2+}$ Solution (mL)	Distilled Water (mL)	Final Concentration of $FeSCN^{2+}$ (mol/L)
1	10	0	0.15
2	8	2	0.12
3	6	4	0.09
4	4	6	0.06
5	2	8	0.03

c) Carefully stir the contents of each test tube with a clean stirring rod. (Note: Use a separate rod for each test tube *or* carefully clean the stirring rod with deionized water and dry it with a tissue before using it in the next test tube.)

3. Prepare the blank, the five standard solutions, and the unknown for colorimetry. Use deionized water as the blank; use solutions from the five test tubes as standards.
   a) For each standard solution, rinse an empty cuvette twice with about 1 mL of the sample; do the same with deionized water for the blank.
   b) Fill the cuvette three-fourths full with the sample, and seal it with a lid.
   c) Label the lid with the sample number, "B" for the blank, or "?" for the unknown.
   d) Wipe the outside of the cuvette with a tissue.

   Remember the following:
   - All cuvettes should be clean and dry on the outside.
   - Handle a cuvette only by the top edge or the ribbed sides.
   - All solutions should be free of bubbles.
   - Label the *lid* of the cuvette so the label does not interfere with the beam of light.

Part II: Collecting the Data

4. Connect the Colorimeter to EasyLink. Connect EasyLink to the USB port on the calculator. The EasyData application should start automatically.

5. Set up the EasyData App to collect absorbance readings.
   a) Select **File** from the Main screen, and then select option **1: New** to reset the application.
   b) Select **Setup** from the Main screen, and then select option **3: Events with Entry**.

6. Calibrate the Colorimeter.
   a) Place the blank in the cuvette slot of the Colorimeter. Make sure that one of the transparent faces of the cuvette is pointing toward the white reference mark. Close the lid of the Colorimeter.
   b) Set the wavelength on the Colorimeter to 470 nm. This will set the Colorimeter's light emitter and receiver to emit and record blue light.
   c) Calibrate by pressing the CAL button on the Colorimeter.
   d) When the red light on the Colorimeter stops flashing, remove the cuvette from the Colorimeter.

7. You are now ready to collect absorbance data for the five standard solutions.
   a) Place cuvette 1 into the Colorimeter and close the lid.
   b) Select **Start** to begin data collection.
   c) When the value displayed on the calculator screen has stabilized, select **Keep** to record the absorbance of the first standard.
   d) The calculator will ask you to enter a value. Enter the concentration of $FeSCN^{2+}$ in the solution (from the table in step 2). Select **OK** to store this absorbance-concentration data pair.

e) Repeat steps 7a-7d for each of the remaining standards. Be sure to enter the correct concentration for each standard in step 7d.

8. Select **Stop** when you have finished collecting data for all the standards.

9. EasyData should display a graph showing concentration of $FeSCN^{2+}$ on the *x*-axis and absorbance of blue light on the *y*-axis. Examine the data points on the displayed graph. As you move the cursor right or left with the arrow keys, the values for concentration, **X**, and absorbance, **Y**, for each data point are displayed above the graph. Write the absorbance value, rounded to the nearest 0.001, for each standard solution in your Evidence Record.

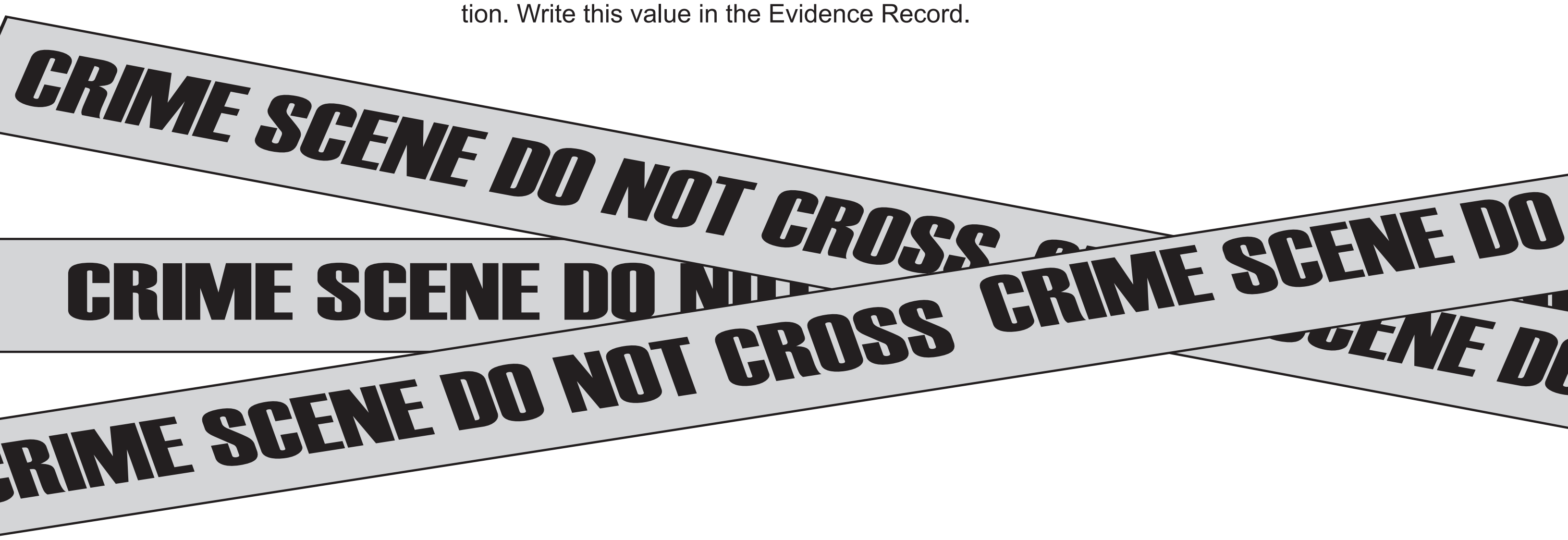
10. Select **Main** to return to the Main screen.

11. Place the cuvette with the unknown solution in the Colorimeter. Monitor the absorbance value displayed on the calculator. When this value has stabilized, round it to the nearest 0.001 and write it in your Evidence Record.

12. Discard the remaining solutions as directed by your teacher.

Part III: Analyzing the Data

13. To determine the concentration of $FeSCN^{2+}$ in the unknown solution, plot a graph of absorbance vs. concentration for your *standard* solutions and fit a straight line to the points. Then use the absorbance value of the unknown to estimate its concentration of $FeSCN^{2+}$.
   a) Select **Graph** from the Main screen.
   b) Select **Anlyz** from the graph screen, and then select **Linear Fit**. The equation for a straight line is $y = ax + b$, where y is absorbance, x is concentration, a is the slope, and b is the *y*-intercept. The screen will display the values of **a** and **b** that give the best fitting line to your data points. The correlation coefficient, **R**, indicates how well the data points match the regression line. A value of 1.00 indicates a perfect fit. Record the values of a, b, and *r* in the Evidence Record.
   c) To display the straight line on the graph of absorbance vs. concentration, select **OK**. The line should closely fit the five data points and pass through, or near, the origin of the graph. The linear relationship between absorbance and concentration is known as Beer's law.
   d) The cursor is initially on the first data point. Press ⏶ to move from the data points to the line. The **X** and **Y** coordinates of the cursor will be shown on the screen above the graph. Use the arrow keys to move the cursor left and right along the line to the absorbance value, **Y**, that is closest to the absorbance reading you obtained for the unknown. The corresponding **X** value is the estimated concentration of $FeSCN^{2+}$ in the unknown solution. Write this value in the Evidence Record.



Name: ____________________________________
Date: ____________________________________

Evidence Record

Solution Number	Concentration of $FeSCN^{2+}$ in Solution (mol/L)	Absorbance
1	0.15	
2	0.12	
3	0.09	
4	0.06	
5	0.03	
?	Unknown	

Concentration of $FeSCN^{2+}$ in the unknown solution __________________

y	**a*x* + b**
a	
b	
r	

Case Analysis

1. Write the equation for the line in the form $y = ax + b$, using the values for a and b that you recorded in the Evidence Record. For example, if a = 3 and b = 6, then the equation for the line is $y = 3x + 6$.
2. Use the equation to calculate the concentration of $FeSCN^{2+}$ in the unknown solution. How does the value you calculate compare with the value you read from the graph?
3. The volume of the cyanide solution that was found at the scene was 20 mL. Based on the calculated concentration of $FeSCN^{2+}$ in the unknown solution, determine the concentration of potassium cyanide, KCN, in the original poison. Show all your work. Give your answer in milligrams of KCN per milliliter of solution.
   (Hint: One mole of KCN will produce one mole of $FeSCN^{2+}$. Assume that all of the KCN in the poisoned solution reacted to form $FeSCN^{2+}$. Assume that the 20 mL of original solution was not diluted during the reaction to form $FeSCN^{2+}$ and that the sample you received was also undiluted. The molecular weight of $FeSCN^{2+}$ is 114 g/mol. The molecular weight of KCN is 65 g/mol.)
4. For most people, swallowing 300 mg of KCN is fatal. Based on the concentration of KCN in the poison that you calculated in question 3, determine the approximate volume of poison that the victim would have to have swallowed for it to have killed him. Show all your work.
5. Is it likely that the poison was the direct cause of death? Explain your answer. (Hint: Remember that the vial was mostly empty and may, at one time, have held more than 20 mL.)
6. Suppose you found out that the concentration of $FeSCN^{2+}$ in the unknown was actually very different from the value you calculated in question 2 and the value you read off the graph. What factors could have caused that to happen?

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Using colorimetry to determine concentration of a poison

Teacher Notes

Teaching time: one class period

This lab introduces students to colorimetry. Students will calculate the concentration of an unknown by measuring how it absorbs a specific wavelength of light. The activity also demonstrates the importance of accurately made standard solutions.

Tips

- Use of the Colorimeter with the calculator is extremely battery intensive. Keep extra batteries on hand. Make sure that all solution preparation and cuvette filling is done *before* turning on the Colorimeter, in order to minimize the battery drain on the calculator.
- If class time is limited, prepare the solutions (Part I) for the students before class.
- Before assigning the activity, you may want to review the visible spectrum of light and the concept of light absorbance. In addition, you may want to discuss the chemistry involved in the reactions. (See Background Information below.)
- The concentration and type of dye, as well as the size of the drops, can vary in different brands of food coloring. You may need to test several brands of food coloring in order to get consistent results. The stock solution directions and sample data below were obtained when Durkee® red food coloring was used.

Lab Preparation

- You will be preparing a solution of red food coloring dissolved in water to simulate the cyanide-laced poison found at a crime scene. Food coloring is used so that preparation and disposal are easier, and safety issues with students handling the solutions are minimized.
- Prepare the simulated 0.50 M $FeSCN^{2+}$ stock solution by adding 2 drops of red food coloring to 100 mL of deionized water.
- To prepare the unknown so that the test will determine that it is lethal, mix 7 mL of the stock solution with 3 mL of deionized water. This will give an unknown concentration of about 0.105 M, which corresponds to a fatal dose of about 1.5 oz (equivalent to about three or four coffee creamers).
- To prepare the unknown so that the test will determine that it is not lethal, mix 1 mL of the stock solution with 9 mL of deionized water. This will give an unknown concentration of about 0.015 M, which corresponds to a fatal dose of about 10.4 oz. Although this is not a huge amount, it seems unlikely that anyone could have added that much solution to Mr. Marchand's coffee without his noticing.

Background Information

The primary objective of this experiment is to use a Colorimeter to determine the concentration of an unknown solution. In this device, blue light (470 nm) from the LED light source will pass through the solution and strike a photocell. A complementary color is used when a solution is tested in this way. We see the solution as a red color because the substances in the liquid are reflecting specific wavelengths of visible light and absorbing other wavelengths. Blue light is used in the test because the solution is absorbing those wavelengths, and the amount of blue light absorbed is proportional to the concentration of the substance in solution. A colored solution of higher concentration absorbs more light, and transmits less light, than a solution of lower concentration.

The reaction of the ferric ion (Fe3+) and thiocyanate ion (SCN–) produces the red brown solution simulated in this experiment. The table below shows the relationship between ion species and color.

Fe^{3+}(aq)	+	SCN^{-} (aq) →	$FeSCN^{2+}$(aq)
yellow		colorless	red brown

Modifications

- For less-advanced students, prepare the standard solutions (Part **I**) in advance.
- For more-advanced students, use several different unknowns. More-advanced students may also benefit from using qualitative chemical components. You can create stock solutions of KSCN and $FeCl_3$ or $Fe(NO_3)_3$ and have the students carry out the reaction in the Background Information section. Please note that even low concentrations of these chemicals give intensely colored solutions that may not give linear results when blue light is used. You may have to use very dilute solutions in order to get usable data.

Sample Data

Solution Number	Concentration of $FeSCN^{2+}$ in Solution (mol/L)	Absorbance
1	0.15	0.623
2	0.12	0.486
3	0.09	0.365
4	0.06	0.243
5	0.03	0.128
?	Unknown	0.436

Concentration of $FeSCN^{2+}$ in the unknown solution 0.105 mol/L

y	**ax + b**
a	4.11
b	-9×10^{-4}
r	0.9995

Case Analysis Answers

1. Write the equation for the line in the form *y* = *ax* + b, using the values for a and b that you recorded in the Evidence Record. For example, if a = 3 and b = 6, then the equation for the line is *y* = 3*x* + 6.

   Answers will vary. For the sample data, $y = 4.11x - 9\times10^{-4}$.
2. Use the equation to calculate the concentration of $FeSCN^{2+}$ in the unknown solution. How does the value you calculate compare with the value you read from the graph?

   Answers will vary. For the sample data, $y = 4.11x - 9\times10^{-4}$.

$$x = \frac{y + 9\times10^{-4}}{4.11} = \frac{0.436 + 9\times10^{-4}}{4.11} = 0.106 \text{ mol/L}$$

   The equation and the graph yield almost the same value for the $FeSCN^{2+}$ concentration.

3. The volume of the cyanide solution that was found at the scene was 20 mL. Based on the calculated concentration of $FeSCN^{2+}$ in the unknown solution, determine the concentration of potassium cyanide, KCN, in the original poison. Show all your work. Give your answer in milligrams of KCN per milliliter of solution.
(Hint: One mole of KCN will produce one mole of $FeSCN^{2+}$. Assume that all of the KCN in the poisoned solution reacted to form $FeSCN^{2+}$. Assume that the 20 mL of original solution was not diluted during the reaction to form $FeSCN^{2+}$ and that the sample you received was also undiluted. The molecular weight of $FeSCN^{2+}$ is 114 g/mol. The molecular weight of KCN is 65 g/mol.)
Answers will vary, depending on the concentration of $FeSCN^{2+}$ that you use in the unknown. A sample calculation for an unknown concentration of 0.105 mol/L is given below:

$$\frac{0.105\text{ mmol }FeSCN^{2+}}{1\text{ mL solution}} \times 20\text{ mL solution} = 2.1\text{ mmol }FeSCN^{2+} = 2.1\text{ mmol KCN in original solution}$$

$$2.1\text{ mmol KCN} \times 65\text{ mg/mmol} = 137\text{ mg KCN in original solution}$$

$$\frac{137\text{ mg KCN}}{20\text{ mL solution}} = 6.83\text{ mg KCN/mL solution}$$

4. For most people, swallowing 300 mg of KCN is fatal. Based on the concentration of KCN in the poison that you calculated in question 3, determine the approximate volume of poison that the victim would have to have swallowed for it to have killed him. Show all your work.
Answers will vary depending on the concentration of KCN in the original solution. A sample calculation for a 6.83 mg/mL KCN solution is given below:

$$\frac{1\text{ mL solution}}{6.83\text{ mg KCN}} \times 300\text{ mg KCN} = 44\text{ mL solution, or about 1.49 oz}$$

5. Is it likely that the poison was the direct cause of death? Explain your answer. (Hint: Remember that the vial was mostly empty and may, at one time, have held more than 20 mL.)
In this case, it seems likely that the victim swallowed enough cyanide to kill him, given the size of the vial.
6. Suppose you found out that the concentration of $FeSCN^{2+}$ in the unknown was actually very different from the value you calculated in question 2 and the value you read off the graph. What factors could have caused that to happen?
Factors that can cause error include inaccurately prepared standards, an uncalibrated or improperly calibrated Colorimeter, equipment error, impurities in the standard or unknown solutions, and mistakes in following the procedures.