Case File 5

The Ink Is Still Wet: Using colorimetry to identify an unknown ink

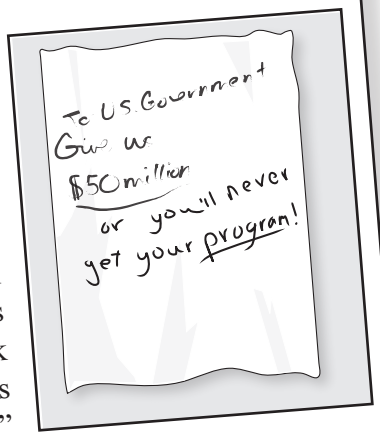
Identify the ink on the ransom note to narrow down the suspects.

4 **Springfie**

TrueMind AI Kidnapping Case Solved! Mystery ink proves key to case

SPRINGFIELD, September 10: Science has proven indispensable in solving yet another kidnapping case. This time, a special kind of fingerprint—a chemical fingerprint—proved to be the crucial clue in recovering the victim, 22-year-old Shawn Morgan, unharmed.

It was only in the last month that Morgan sold his design for the TrueMind artificial intelligence system to the United States government for $100 million. As fate would have it, a day later, Morgan vanished. When investigators forcibly entered Mr. Morgan's apartment, they found it empty except for a ransom note written on a piece of computer paper. The note was written in black ink, and the handwriting varied in style, so police handwriting experts were at a loss to come up with a profile.



Using advanced chemical analysis, investigators determined that the ink used to write the infamous "To US Government" ransom note came from a specialized marker used in photo retouching. These pens are unusual and unusually expensive, and investigators found one at the apartment of one of the prime suspects, Tamyra Elliot, 32. Ms. Elliot is currently being held without bail.

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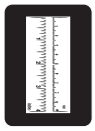
Forensics Objective

- identify an unknown ink by its light absorbance characteristics

Science and Mathematics Objective

- measure a solution's absorbance of different colors (wavelengths) of light



Materials (for each group)

- TI-83/TI-84 Plus™ Family
- Vernier EasyLink™
- Vernier EasyData™ application
- Colorimeter
- 6 cuvettes
- colored wax pencil
- 5 dropper bottles, with 10 mL samples of 5 different diluted black inks
- 1 dropper bottle with 10 mL of diluted unknown black ink
- deionized or distilled water
- lint-free tissues
- goggles (1 pair per student)

Procedure

Wear goggles at all times! CAUTION: Be careful not to ingest any solution or spill any on your skin. Inform your teacher immediately in the event of an accident.

1. Prepare the blank, each of the five standards, and the unknown for analysis.
   a) Rinse an empty cuvette twice with about 1 mL of distilled or deionized water.
   b) Use the colored wax pencil to write a zero on the lid of the cuvette.
   c) Fill the cuvette three-fourths full with deionized water. Seal the cuvette with the lid. Dry the outside of the cuvette with a tissue.
   d) Repeat steps 1a–1c, using the five standard solutions and the unknown, rather than deionized water, and labeling the lids of the cuvettes appropriately (1 through 5 for the standard solutions and 6 for the unknown).

   Remember the following:
   - All cuvettes should be clean and dry on the outside.
   - Handle a cuvette only by the top edge or ribbed sides, not the transparent 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.

2. Connect EasyLink to the USB port of your calculator, and connect the Colorimeter to EasyLink. The EasyData App should open automatically.

3. Set up EasyData 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**.

4. Calibrate the Colorimeter.
   a) Place the blank (cuvette 0, containing deionized water) 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 635 nm (red).

c) Calibrate the Colorimeter by pressing the CAL button.
d) Remove the blank cuvette from the Colorimeter.

5. You are now ready to collect absorbance-concentration data at 635 nm for the solutions.
   a) Place cuvette 1 in the Colorimeter, with the cuvette clean, dry, and with a transparent face pointing toward the reference mark.
   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, or known sample.
   d) The screen will ask you for a value. Enter the sample number (from the lid) and select OK to store this absorbance–sample-number data pair.
   e) Remove the cuvette from the Colorimeter.
   f) Repeat steps 5a–5e for the remaining samples in cuvettes 2 through 6.

6. Select Stop when you have collected data for all the samples. EasyData should display a graph of the data.

7. Examine the data points along the curve on the displayed graph. As you move the cursor right or left, the sample number, **X**, and absorbance value, **Y**, of each data point are displayed above the graph. Write the absorbance values in your Evidence Record (round to the nearest 0.001).

8. Select Main to return to the Main screen.

9. Measure the absorbance of each solution at the three other wavelengths (or colors) that the Colorimeter can measure.
   a) Repeat steps 4–8 for the 565 nm (green) wavelength setting on the Colorimeter.
   b) Repeat steps 4–8 for the 470 nm (blue) wavelength setting on the Colorimeter.
   c) Repeat steps 4–8 for the 430 nm (violet) wavelength setting on the Colorimeter.

10. Discard the solutions as directed by your teacher.

NAME: _____

DATE: _____

Evidence Record

Sample	Type of Ink; Appearance in Alcohol	Absorbance at 635 nm	Absorbance at 565 nm	Absorbance at 470 nm	Absorbance at 430 nm
1					
2					
3					
4					
5					
6	**Unknown**				

Unknown is most likely _____

Case Analysis

1. How did you identify the unknown?
2. Why did the inks show different absorbance patterns if they all appeared to be the same color?
3. Do you think you would have seen the same large variations in absorbance if all the samples had been red ink or all had been blue ink instead of black? Why or why not?

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Teacher Notes

Teaching time: one class period

This lab utilizes colorimetry to identify inks as unique mixtures of pigments.

Tips

- Use of the Colorimeter with the calculator is extremely battery intensive. Keep extra batteries on hand. You should 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.
- Before assigning the lab, you may want to review the spectrum of visible light and the concept of absorbance of light. Remind students that different colors are actually different wavelengths in the spectrum and that an object appears to be a specific color because it absorbs all wavelengths of light *except* that specific color. It may also be helpful to review the difference between colors of light (white light is a combination of all wavelengths, and darkness is the absence of all wavelengths) and colors of pigment (white pigment *reflects* all wavelengths, and black pigment *absorbs* all wavelengths).

Lab Preparation

- Use rubber gloves to prepare all the ink solutions.
- Use five different brands of pens (e.g., Pilot, Bic, Zebra) and/or different types of pens (e.g., erasable ink, archival ink) for the known solutions. Use one of those five for the unknown.
- To prepare each ink solution, disassemble the pen (or purchase a refill ink cartridge), cut the ink cylinder, and put the cylinder parts into alcohol to allow the ink to dissolve in it. Each ink will dissolve at a different rate, so the soak times will vary.
- Prepare each dropper bottle sample by diluting an ink-and-alcohol sample with deionized water. The six different diluted samples should look similar. Of the black inks used to obtain the sample data, the Bic, Pentel, and Zebra had a purplish hue and were indistinguishable from one another when diluted; the Pilot ink was black in dilution; ink from the erasable Paper Mate was blue in dilution.

Background Information

The Colorimeter works by passing a beam of a single wavelength of light through the sample and then measuring how much of that light is transmitted. The Colorimeter can then calculate how much of that wavelength was absorbed by the sample. This technique can help identify materials because different materials absorb different amounts of light at different wavelengths.

Most inks are mixtures of different-colored pigments. When we separate those mixtures, we can define their parts, and the percentages of the parts allow us to identify the original ink. Many companies have their own formulas for the inks that they use. Each pigment has distinctive spectral properties. We can see those properties when we examine the solutions in light of different wavelengths.

Resources

http://chemistry.about.com/library/weekly/aa121602a.htm
This Web site contains information about the properties of different inks.

Modifications

More-advanced students may want to explore the absorbance of different-colored inks (red, blue, green) to see if the variations in absorbance pattern are as great as they are for black inks.

Sample Data (using pens that write in black)

Sample	Type of Ink; Appearance in Alcohol	Absorbance at 635 nm	Absorbance at 565 nm	Absorbance at 470 nm	Absorbance at 430 nm
1	Pilot gel ink; black	0.408	0.498	0.539	0.492
2	Paper Mate erasable; blue	0.951	0.986	0.958	0.926
3	Bic; purple	0.278	0.681	0.433	0.402
4	Pentel; purple	0.111	0.355	0.217	0.182
5	Zebra; purple	0.181	0.379	0.262	0.241
6	**Unknown;** purple	0.288	0.673	0.437	0.395

Unknown is most likely 3 Bic

Case Analysis Answers

1. How did you identify the unknown?
   I found the set of absorbances that most closely matched those of the unknown.
2. Why did the inks show different absorbance patterns if they all appeared to be the same color?
   Even though the inks are the same color, the amount of colorant(s) and the kind of colorant(s) present may vary, causing the absorbance readings to vary.
3. Do you think you would have seen the same large variations in absorbance if all the samples had been red ink or all had been blue ink instead of black? Why or why not?
   The variations in absorbance patterns would probably have been smaller if we had used red or blue ink because those inks tend to be mixtures of fewer pigments.