



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.

To US Government
Give us
\$50 million
or you will never
get your program!

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The Ink is Still Wet

OBJECTIVES

- Identify an unknown ink by its light absorbance characteristics.
- Measure a solution's absorbance of different colors (wavelengths) of light.

MATERIALS

computer
Vernier computer interface
Logger *Pro*
Vernier Colorimeter
6 cuvettes
colored wax pencil

distilled water
5 dropper bottles, with 10 mL samples
of different diluted black inks
1 dropper bottle, with 10 mL of diluted
unknown black ink
lint-free tissues

PROCEDURE

CAUTION: *Obtain and wear goggles during this experiment. 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 water.
 - b. Use the colored wax pencil to write a zero on the lid of the cuvette.
 - c. Fill the cuvette 3/4 full with distilled 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 distilled 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 the Colorimeter to the computer interface. Prepare the computer for data collection by opening the file “05 Ink Still Wet” from the *Forensics with Vernier* folder of Logger *Pro*.
 3. Calibrate the Colorimeter.
 - a. Open the Colorimeter lid. Place the blank (cuvette 0, containing distilled 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. Press the < or > button on the Colorimeter to select a wavelength of 635 nm (Red).
 - c. Press the CAL button until the red LED begins to flash. Then release the CAL button. When the LED stops flashing, the calibration is complete.

Case 5

4. You are now ready to collect absorbance-concentration data at 635 nm for the solutions.
 - a. Click to begin data collection.
 - b. Place cuvette 1 in the Colorimeter, with the cuvette clean, dry, and with a transparent face pointing toward the reference mark.
 - c. After closing the lid, wait for the absorbance value displayed on the monitor to stabilize, then click .
 - d. Enter the sample number (from the lid) and press the ENTER key. The data pair you just collected should now be plotted on the graph.
 - e. Remove the cuvette from the Colorimeter.
 - f. Repeat Steps 4b–4e for the remaining samples in cuvettes 2 through 6.
5. Click when you have collected data for all the samples.
6. In your Evidence Record, write down the absorbance values displayed in the data table.
7. Measure the absorbance of each solution at the three other wavelengths (or colors) that the Colorimeter can measure.
 - a. Repeat Steps 3–6 for the 565 nm (green) wavelength setting on the Colorimeter.
 - b. Repeat Steps 3–6 for the 470 nm (blue) wavelength setting on the Colorimeter.
 - c. Repeat Steps 3–6 for the 430 nm (violet) wavelength setting on the Colorimeter.
8. Discard the solutions as directed by your teacher.

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 the samples had been blue ink instead of black? Why or why not?

TEACHER INFORMATION**The Ink Is Still Wet****TEACHER NOTES**

- Teaching time: one class period
- This lab utilizes colorimetry to identify inks as unique mixtures of pigments.

TIPS

1. The student pages with complete instructions for data collection using LabQuest App, Logger *Pro* (computers), and EasyData (calculators) can be found on the CD that accompanies this book. See *Appendix A* for more information.
2. Make sure that all solution preparation and cuvette filling is done before beginning the experiment.
3. 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).
4. The cuvette must be from 55% to 100% full in order to get a valid absorbance reading. If students fill the cuvette 3/4 full, as described in the procedure, they should easily be in this range. To avoid spilling solution in the cuvette slot, remind students not to fill the cuvette to the brim.

LAB PREPARATION

1. Use rubber gloves to prepare all the ink solutions.
2. 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 the same five for the unknown solution.
3. To prepare each ink solution, disassemble the pen (or purchase a refill ink cartridge), cut the ink cylinder, and put the cylinder parts into 300 mL of Isopropyl alcohol (rubbing alcohol) and allow the ink to dissolve in it. Each ink will dissolve at a different rate, so the soak times will vary.
4. To prepare each of your final ink solutions, add 100 mL of the ink/alcohol solution to 400 mL of distilled water. Mix the solution thoroughly before adding to each of the dropper bottles. Repeat for each of the ink solutions that will be tested. 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

The following Web site contains information about the properties of different inks.

<http://chemistry.about.com/library/weekly/aa121602a.htm>

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

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. Find the set of absorbances that most closely matched those of the unknown.
2. 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. 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.