

## Pen Ink Analysis by Visible Spectrophotometry and Reverse Phase Liquid Chromatography

### References

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### Goal

To determine the color and composition of pen inks.

### Suggested Methods of Analysis

Visible absorbance spectrophotometry of the mixture of ink components and separation of the components by normal phase liquid chromatography.

### Preparing the Ink Samples

Most inks from black ball-point type pens and black felt-tip type pens should be soluble in an extraction solvent with the composition 55% acetonitrile : 45% aqueous heptanesulfonic acid (0.005 M, pH 4.7). The same solvent will be used as the mobile phase in reversed-phase liquid chromatography.

Take some time to develop a workable technique for removing paper chads (microplugs) from a plain piece of paper. Do so before tackling the questioned documents or known inks. Score and then break off the tip of a 20-gauge syringe needle to prepare a blunt-end needle. Lay a piece of paper flat on some cardboard and press down firmly with the needle tip. Some rocking or twisting of the tip may be necessary to produce chads. Use a piece of copper wire to remove the microplug from the needle, if necessary.

Take 10 microplugs from the questioned and known documents and add the sets of chads to separate, 2-mL chromatography vials. Add 500  $\mu$ L of extraction solvent to each tube, cap the tubes, and place the tubes in the ultrasonic bath for 15 minutes to extract the ink. Let the mixture settle for a few minutes and take the top portion for analysis to avoid interference from the microplugs or fibers from the paper.

### Visible Absorbance Spectrophotometry

Follow the operating instructions for the spectrophotometer and small-volume cuvettes. Handle the expensive small-volume, blackened cuvettes with great care; fill and empty the cuvettes with a Pasteur pipet. Scan the entire visible region (350 nm – 750 nm) at a spectral bandwidth of 1 nm. Record a baseline first (both cuvettes filled with extraction solvent) and then record the spectrum of each ink solution against this baseline. Make dilutions of an aliquot of

the sample solution with the extraction solvent if the maximum absorbance is too large. Save and print each spectrum.

Compare the spectra with regard to the number, wavelength position, and relative heights of the component peaks.

### **Liquid Chromatographic Analysis**

The chromatograph should be set up with a C18 reversed-phase column and a mobile phase composition of 55% acetonitrile : 45% aqueous heptanesulfonic acid (0.005 M, pH 4.7). Pump the mobile phase at 0.300 mL/min. Choose 3 or 4 sample wavelengths based on the spectra you collected earlier at which to monitor the separation. Save and print each chromatogram.

Compare the chromatograms with regard to the number, retention times, and relative heights of the component peaks.