Forensic Chemistry of Inks

Name _____

Reference: Michael Quigley and Hongyan Qi, *J. Chem. Educ.* **1991** *68*(7) 597 and JCE Editorial Staff, *JCE* **2000** *77*(2) 176A&B

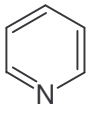
Background:
Professional forensic chemists can take advantage of a collection of more than 9500 different pen inks that have been collected since the 1920's by the International Ink Library, maintained by the US Secret Service and the US Internal Revenue Service. [By the way, the Forensic Laboratory of the Secret Service is headed by an UMSL graduate, Joe Bono.] By comparison with known specimens, it is often possible to identify the type and brand of writing instrument used, and also to determine the early possible date that a document could have been written. Unfortunately, you will not have access to that resource for this experiment!

Purpose:
The owner of a the Last Will and Testament provided by your Teaching Assistant has claimed that he recently found it among the belongings of his late uncle. If proved to be genuine, the man may be entitled to a share of the estate, since it supersedes all previous wills. While graphological investigations and physical dating of the paper show that the document appears to be authentic, the circumstances behind its discovery suggest fraud. Since the estate is a large one, it is important to establish the truth behind these mysterious circumstances. Your challenge is to determine whether the document is authentic, by comparing the ink in the signature on the paper with inks from several sample pens. The date at which each pen went on the market will be provided and may prove useful.

Nearly every ink sample consists of several different pigments. Separation of ink pigments can be done quite simply, using a technique known as chromatography. "Chromatography" comes from two Greek roots, meaning "color" and "write". In chromatography, a mixture is separated into its components on the basis of the differences in the attraction of the components for an immobile (stationary) phase and a moving (mobile) phase. There are a number of varieties of this technique; their names generally are based on the phases used for the stationary and mobile phases.. For example, there is liquid/solid chromatography, gas/liquid chromatography, and numerous variations. Some of these are very simple, yet also very powerful. You will be using "paper chromatography" to solve the mystery today. In paper chromatography, a liquid phase slowly wets a piece of suitable paper. The paper must not dissolve in the liquid, it must not include soluble contaminants, and it must also allow the liquid to slowly wet the paper. The characteristics needed are those of the papers chemists use to filter liquids, so they are called "filter paper". (Writing paper is generally not suitable for chromatography.) The liquid used for paper chromatography can be pure water, but better separations of mixtures often results if

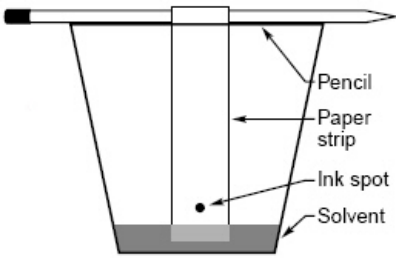
solvents such as alcohol, vinegar, ammonia, are mixed with each other and/or water. You will be provided with several of these solvents, which you may wish to mix in order to produce effective separations.

Procedure:

The first problem you will face is to get the ink off of the paper on which it is written, and into a form that will allow you to chromatograph it. This can be done with a solvent with the name "pyridine", which will dissolve completely the inks with which you will be working. Pyridine has the structure 

. It is somewhat toxic, it can be absorbed through the skin, and it has an unpleasant odor. As a consequence of these properties, it should be handled with care, and used only in the hood. Cut out all or a part of the signature on the document you wish to test. Dissolve the ink with a very small amount of pyridine (a drop or a few) with a Berel pipet or a medicine dropper, and save the liquid. Try to keep it as concentrated in ink as you can.

Cut a rectangular piece of filter or chromatography paper (coffee filters also work for this) about 3-4 cm wide and long enough to reach to the bottom of the beaker or plastic cup that will be your chromatography chamber. See the figure below, which shows an arrangement in a plastic cup.



Near the bottom of the chromatography paper (about 1.5 cm from the end), make a very small dot of the dissolved ink sample, and a dot from each comparison sample. A clean, inert, sharply-pointed object such as a pencil will probably work for this purpose. The dots should be placed far enough apart so that their chromatographs will not overlap as the solvent rises up the paper. A cm or so is usually sufficient. The experiment does not work well if the solvent is evaporating too quickly as it spreads, so it will probably be best if the container is closed with a watch glass or similar cover.

For the solvent, first try
1. water
2. alcohol
3. vinegar
4. household ammonia solution.

Place the chromatographs that result from these trials on a piece of clean paper and save them for comparison. Try the experiment again with other solvents, such as
1. 50% ammonia/50% alcohol
2. 50% vinegar/50% alcohol
3. other mixtures of the solvents.
You may be able to discern the separated pigments in the chromatogram more easily if you illuminate the chromatograms with a ultraviolet light because many pigments fluoresce under such conditions.

Laboratory Report:

Your laboratory report should clearly state your conclusion about which pen wrote the contested Will, but it should also indicate your degree of confidence in your conclusion as an Expert Witness in this matter. Which solvent combination did you find to be most effective in differentiating between the ink samples? How did you decide which mixtures might be best?

In your opinion, did your laboratory partners contribute fairly to the completion of this experiment? _____. If not, describe any discrepancy. Turn in this sheet along with relevant pages from your laboratory notebook.

Your name _____

Laboratory partner(s) _____ _____