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AN INDEPENDENT ASSESSMENT OF INK AGE DETERMINATION BY A PRIVATE EXAMINER

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Abstract: This paper describes an independent assessment of the reliability of techniques currently in use in the United States for determining the relative age of writing inks. Techniques evaluated include the R-Ratio and Percent Extraction techniques, the Dye-Ratio method and the Accelerated Aging technique. Although considerable practice and experience was required to become proficient in the use of these procedures, it was found that all of the methods are useful for estimating the age of inks on questioned documents.

Key Words: forensic science, relative age of ink, R-Ratios, Dye-Ratios, percent extractions, thin-layer chromatography, densitometry, accelerated aging.

Opinions of ink dating chemists, both government and private, differ on the reliability of the above described ink aging methods. Therefore, before applying any of these methods to actual case work the author conducted an independent evaluation of the reliability of the R-Ratio, Percent Extraction, Dye-Ratio and Accelerated Aging techniques for estimating the age of writing ink on documents. Six experiments were conducted using the following procedures.

R-Ratio and Percent Extractions

1. Samples of the known and questioned ink are removed from the paper using a hollow needle punch with a plunger to push the sample out of the needle. Caution should be taken to not get any combination from such things as other inks, inks from the opposite side of the document, or printed stamps. Also, make sure to leave at least 1/2 of the ink so testing can be duplicated by another expert.
2. Place the plugs (10-18) in a vial. 3. Inject 20-30 microliters of a weak solvent like n-butanol, into the vial and make sure all the plugs are covered.
4. 4 microliter aliquots are then taken using a volumetric pipette after stirring by rotating the vial five times before such aliquots are taken and spotted on a Merck HPTLC plate.
5. After the desired aliquots have been taken at the desired times, usually 30 seconds, 90 seconds, 3 minutes and 10 minutes, 10 microliters of Benzyl Alcohol, or another strong solvent is then added and allowed to extract for 5 minutes.
6. Another 4 microliters aliquot is taken of this solution and spotted on the TCL plate as well.
7. The relative intensities of all 5 spots are calculated using a Densitometer and then using the following formulas:

R-Ratios

$$\frac{30 \text{ second extraction value}}{10 \text{ minute extraction value}}$$

$$\frac{90 \text{ second extraction value}}{10 \text{ minute extraction value}}$$

$$\frac{3 \text{ minute extraction value}}{10 \text{ minute extraction value}}$$

$$\frac{10 \text{ minute extraction value}}{10 \text{ minute extraction value}=1}$$

Percent Extraction

10 minute extraction value

Benzyl Alcohol value

Percent extraction can also be calculated at 30, 90, and 120 second times to obtain a percent extraction curve.

This will normalize all the values and make them mass independent. These will not be the exact values for rate or percent extractions, but all numbers are treated the same and can be compared without the correction factor for adding or removing volumes. It can, however, be done if desired, but has no bearing on the results.

Pvc Ratio Method

A dye ratio comparison is done using the following steps:

1. Remove samples from the paper, or if the spots for the Rratio are along the bottom of the plate, the dye ratio analysis can be done without taking more samples. If not, more samples can be taken and spotted at desired times for analysis.
2. Develop the plate in either solvent, system I or II, as outlined in ASIM standard 1422 E.30. as if the task was to identify the ink and separate it into individual bands.
3. The relative intensities of each dye band are calculated on a Densitometer, then normalized and made mass independent in the following manner:

Band 1 if only separated into 2 bands

Band 2

or:

Band 1 Band 1 and Band 2

Band 1 Band 3 Band 3

If three bands are present.

Note: Only like extraction times can be compared.

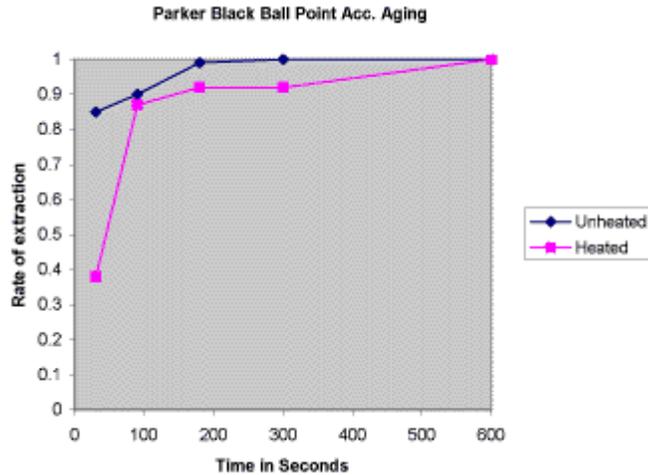
Accelerated Aging

Samples were heated for 30 minutes at 100 degrees Celsius and allowed to cool. Then the rate of extraction and percent of extraction comparisons were made as listed above.

Experiment 1 – R-Ratios After Accelerated Aging

Graph 1 below shows that the most discriminating extraction time for a Parker black ball point ink is 30 seconds, but as expected, there was a significant change in the rate of extraction caused by heating the ink. This finding demonstrates the ink is still drying and must be less than four years old, because changes in the dryness of ball point ink have not been detected beyond four years.

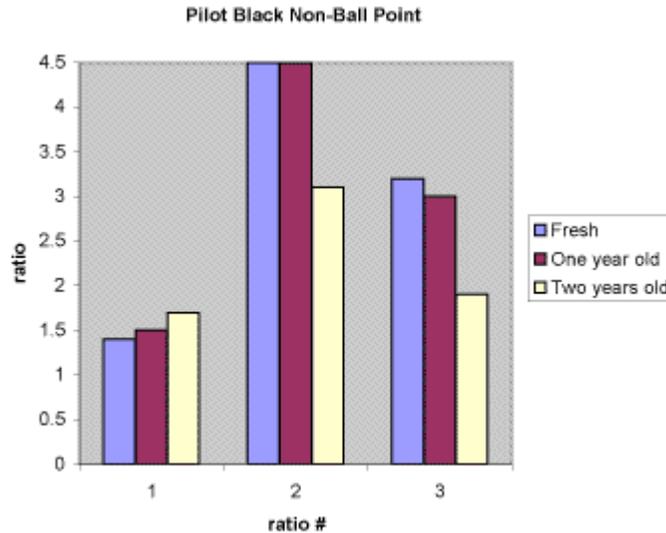
GRAPH 1



Experiment 2- Dye Ratios on Known Dated Inks

For this test a Pilot black non-ball point ink was used. The inks were written on copy paper during 1993, 1994 and 1995. **Graph 2 below** shows that the 1994 and 1995 inks were not distinguishable using the dye-ratio method; however, the 1993 ink is clearly different than the other two. While in this case, 2 of the 3 dye-ratios calculated reflect a difference, only a difference in one dye-ratio is necessary to establish that the age of the ink is different

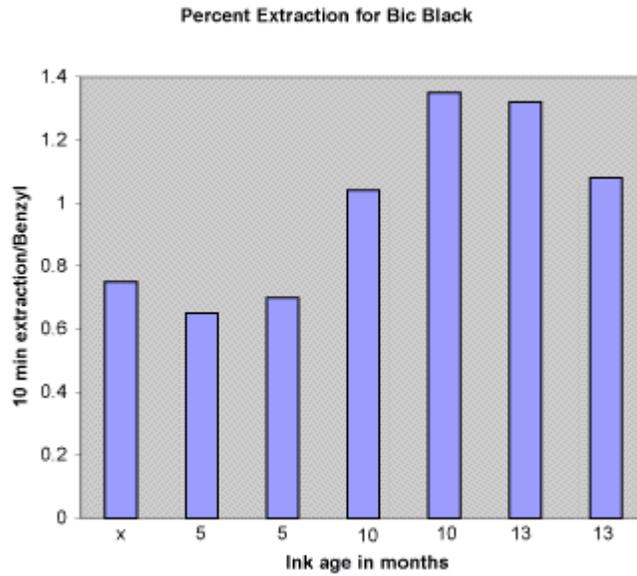
GRAPH 2



Experiment 3- Percent Extraction

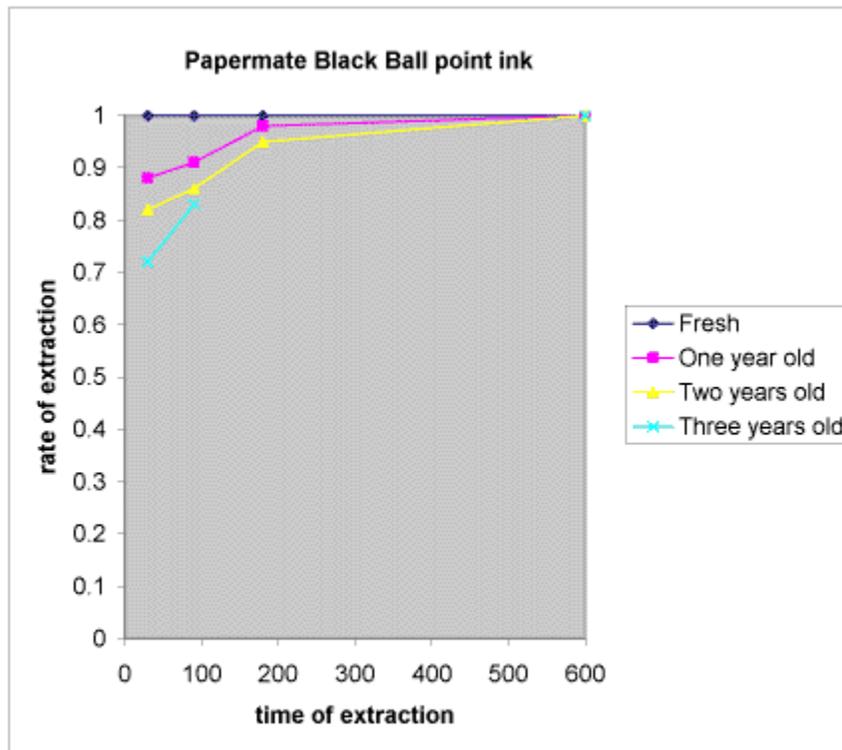
For this experiment a Bic black ball point ink was used. Seven samples of ink written on copy paper and ranging in age from fresh to 13 months were analyzed. **Graph 3 below** shows the results. Experimental variation for the 10 and 13 month old samples makes these two ink samples indistinguishable. However, the 0 to 5 month old samples are clearly different from the 10 and 13 month old samples. It is interesting to note that this Bic black ball point ink written on copy paper extracted faster with age. This is the opposite of most inks which usually extract slower as the ink ages.

GRAPH 3



Experiment 4- R-Ratios on a Papermate Black Ball Point Ink
Known dated inks written in 1992, 1993, 1994 and 1995 on bond paper were analyzed using the R-Ratio method. **Graph 4 below** shows the results that all of these inks were distinguishable as to age. Note the 3 minute extraction time is missing for the 1992 sample, because the pipette was dropped.

GRAPH 4



Experiment 5- R-Ratio on Bic Black Ball Point Ink

For this test inks written in 1992, 1994 and 1995 were used. **Graph 5 below** again demonstrates that Bic black ball point ink written on copy paper extracts faster with age. The R-Ratios technique easily distinguished the age of these inks.

GRAPH 5

