

A SKETCH OF ANALYTICAL METHODS FOR DOCUMENT DATING PART II. THE DYNAMIC APPROACH: DETERMINING AGE DEPENDENT ANALYTICAL PROFILES^{1,2}

Further studies on the dating of documents and handwritten entries prepared in ink.

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ABSTRACT: This sketch of analytical methods for dating documents is broken into two parts. Part I, presented earlier [1], dealt with those methods that take the static approach; that is, the analytical profiles of the items they analyze (ink, paper, toner, etc.) do not change with age. Part II, presented here, deals with those methods that take the dynamic approach; that is, they determine analytical profiles that do change with age. The most studied methods are those applied to ink and paper.

KEYWORDS: Dating, relative age, documents, inks, paper, analytical methods

I. Preliminaries

A. Introduction and Background - Documents contain several items that can be chemically analysed for dating purposes. These items include paper, several types of inks, correcting fluids, and photocopy toners. The analytical profile of a given item consists of the results of one or more examinations. Part I of this sketch [1] dealt with analytical profiles that are stable (do not change with age). Consequently, these can be used to (1) distinguish among similar items (e.g., different formulas of inks of the same color and type) and (2) build a collection of reference standards (each with documented relevant manufacturing information such as date of first production). Such collections serve to determine the possible identity and the possible first production date of a questioned item.

This part deals with those properties that change with age. Consider, for example, the smell of a page freshly written with a ballpoint pen - the ink scent disappears with time. Or consider rubbing an alcohol-moistened swab on a series of ink entries written on the same paper with the same ballpoint ink at different times (such as a day, a week, a month, and a year before the testing) - the resulting smear pattern usually decreases in intensity with the age of the entry. These are just two simple aging properties of modern ballpoint ink.

Age determination of ink goes back to the first half of this century when iron gallotannate inks were shown to have aging properties. The aging of these inks was extensively studied between 1920 and 1940 mostly by in-situ analysis. In some cases, however, like the chloride or sulfate ion migration tests, pieces of paper with ink writing on them were removed, treated chemically to develop the ion's latent images, and placed back on the document⁴. Though all

examinations were done without the benefit of analytical instruments, these early pioneering studies laid the groundwork of subsequent, more analytical research. This began to happen as the practice of removing samples for analysis became more accepted; this gave scientists the opportunity to use analytical instruments to explore a variety of ink aging processes. Sections B through F that follow are taken from references [2] and [3].

B. The Aging Process and its Measurements - The composition of inks and paper contain several substances that could age or change with time. The effect of their aging is noticed in several aging properties (e.g., ink drying and paper yellowing). The actual aging process or processes responsible for an aging property may be simple (like the evaporation of ink solvents) or complex (like the hardening of ink resins on paper surfaces).

For paper, the aging process begins after it is manufactured. For inks, the aging process begins after it is exposed on paper. This is because after inks are manufactured, they are stored in containers (including pen cartridges and ink bottles) and their aging in these containers (closed systems) is negligible compared to the aging that begins after they are exposed on paper (opened system). This is by design in order to give the ink the necessary lifetime of use. The aging that does occur in a container begins on exposed regions, if any. For example, for ballpoint pen cartridges that have an opened end, a film is formed over time which eventually prevents the ink from flowing into the point. Breaking this film often restores the flow.

Inks are made up of colorants (dyes and pigments) and a carrier (vehicle). The carrier contains most of the substances that age or change with time. Two of the most prominent of these are the ballpoint ink solvents used to dissolve or disperse the colorants and the resins used to thicken the inks. The solvents evaporate with time and the resins harden or set (by oxidation) with time⁵. Each of these two aging processes cause measurable changes in several aging properties. More than one method is often used to measure the changes of a given property; each method is associated with an aging parameter.

The two more commonly studied ink aging properties are: how well an ink extracts into a weak solvent, and how much solvent remains in the ink. For fresh inks, both aging processes mentioned above (solvent evaporation and resin setting) contribute to each of these two properties. For older inks, the second aging process (setting of resins) predominates. Aging properties are often broken down into more specific properties and these are further divided into even more specific properties⁶.

¹The methods and techniques presented in this sketch are not necessarily employed by the U.S. Secret Service (USSS) unless specifically indicated.

²Material for this sketch was taken from presentations made to the combined meeting of the Association de Criminalistica de la Republica Argentina (sixth meeting) and the Asociacion Latinoamericana de Criminalistica (first meeting) held in Mar del Plata, Argentina, in November 1993; the Institut de Police Scientifique et de Criminologie, Universite de Lausanne in Lausanne, Switzerland, in January 1994; and the Department of Chemistry, George Washington University, Washington, D.C., in April 1994.

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⁴The technique of removing paper samples with ink on them, performing examination on these, placing them back on the document, and securing them with tape on the back is currently practiced in some laboratories (e.g. Germany).

⁵Some solvents like oleic acid do not easily evaporate but oxidize with age. Some fluid inks contain water soluble resins which harden upon drying forming

⁶For example; for extractability, one has (1) the rate of extraction and (2) the extent of extraction; for the rate, one has (1) the amount extracted at a given time relative to the amount at a later time and (2) the time to reach a certain level of extraction. Details are found in a later section (IIC1).

Paper contains a multitude of components that age with time. Their aging effect is noticed in measurable aging properties like folding endurance, fading, yellowing, etc. The actual aging process responsible for a given aging property is often rather complex.

In general, one can say that a measurement of a given aging property using a given method of measurement measures aspects of one or more aging processes. For a given property, the measured values⁷ of the changes plotted against time constitute an aging curve. Thus, for a given ink or paper, there are several aging curves - each dependent on the property being measured and the method used to measure it.

C. Some Basic Requirements - To be certain that the relative age of two inks being compared is not influenced by their composition, the paper they are on, and their storage history, these inks should (1) be of the same formula (removal of formula dependence; this means that they should have the same colorants and vehicle components⁸); (2) be on paper of the same composition (removal of paper dependence); and (3) have the same storage history (removal of storage condition dependence).

Requirements 2 and 3 are satisfied by having the inks being compared be on the same document⁹, all portions of which have the same storage history. Unless an ink aging parameter is shown to be insensitive to differences in the ink formula, the paper it is on, or its storage history, it is advisable to follow these requirements. Requirements 1 and 3 apply to the relative age comparison of papers.

D. Sampling and Mass Variance - In comparing the relative age of two inks, a portion is selected from each for sampling and testing. A sampling method is desired that gives the same measurement with repeated sampling. To achieve such reproducibility from repeated measurements, the following cautionary practices are suggested for the sampling.

To be certain that the aging measurements are not influenced by the amount of ink sampled, the line quality (thickness, pressure, width, etc.), and the ambient condition at the time of examination, the two portions of inks sampled and being compared should (1) be sampled equally in amount; (2) be of the same line quality, and (3) be sampled on the same day. Also, since paper is hygroscopic, inks on separate paper should have their paper achieve the same humidity before they are tested.

If two measurements depend linearly on the amount sampled, then their ratio is independent of the amount sampled. Taking such ratios relaxes the need to sample equal amounts. Such ratios are mass independent (invariant). Such ratios may also be independent of line pressure, line width, and line thickness, but until shown to be independent, sampling inks with similar line quality is recommended.

Time measurements such as the time taken to extract or dissolve a sample, are mass independent (provided the amount being extracted over time is linearly dependent on the amount sampled).

⁷To be useful for comparing ages (changes), these values should be independent of the amount being sampled. See next section.

⁸One could use the less strict requirement that the *inks being compared have the same vehicle components* since these appear to be responsible for the aging process. However, this is more difficult to ascertain since more information from the manufacturer is needed than is normally sought. Recall that to ensure that two inks are of the same formula often require identifying the ink using a reference collection in order to determine its uniqueness from the manufacturer.

⁹This is a stronger requirement than 2 and 3 taken separately. It is, however, recommended since assurance of having the same storage conditions is not always guaranteed.

In solution spectroscopy, the linear dependence of a measurement on the amount sampled is called Beer's Law¹⁰. Although taking ratios of measurements relaxes the need to sample equal amounts of ink, it is advisable to do so to reduce error. For paper comparisons, mass invariance can be achieved by taking measurements per unit amount (e.g., size or weight).

E. Ink Aging and Paper Aging - As a document ages, both the ink and paper age with the ink normally aging faster (see the Aging of Paper section). The effects of paper aging on ink aging may be small; however, they may not even be important as the following shows.

There are two ways to obtain an aging curve: (1) make a single large entry on paper at a given time and sample its age (through a given aging parameter using a given method) over a period of time (i.e. weeks, months, and years) and (2) make multiple entries on the same paper over a period of time (i.e. weeks, months, and years) and sample their age at a later time.

The difference between the two (if any) would reflect the effects of paper aging. The difference would be more pronounced at the beginning of the curves since the ends would have the points coinciding¹¹. Each curve would thus be affected by paper aging but in different ways. But this does not matter for comparison purposes unless one curve is compared with another. In case work, one encounters mostly the second situation¹².

F. The Shape of the Aging Curve - Aging properties of inks or paper have, in general, exponential-like aging curves - they decrease monotonically with age and eventually level off (aging ceases)¹³. Aging curves that increase monotonically can be mathematically inverted to give curves that decrease monotonically.

1. *Age Reliability* - If the error bars (measurement confidence limits) are equal throughout an exponential-like aging curve, then the reliability of age determination (the age error bars or age confidence limits) increase with age. Because of this, it is more likely that an age is determined to within a constant percent of that age rather than to within so many days, weeks, etc.

2. *Conclusions about Measurements* - If two inks being compared satisfy the basic requirements, then their aging parameter measurements are values of an aging curve. Comparing these values involves comparing their error bars.

a. *Different* - If these values are different (their error bars do not overlap), then the inks are likely of different age. If one knows the direction of the aging curve (decrease or increase), then one can determine which of the two is older; otherwise, one has to test the inks before and after some natural (or accelerated) aging period to determine the direction.

¹⁰This law sometimes has other credited scientists associated with its title, namely, Lambert and Bouguer.

¹¹To see this, have both cases done on the same paper with the one (and only) ink entry in the first case being the first entry (of several) in the second case. The last entry of the first curve would then be from the same ink that gives the last entry of the second curve.

¹²Such comparison occurs if one needs to know if ink ages in the same way when placed on the same paper at two different times as in the case of a "planted" entry [2].

¹³The mathematical equation for an such an aging curve is $M(t) + [M(0) - M(\infty)]Y(t) + M(\infty)$ where $M(t)$ is the measurement at age t (using a given method of measurement) and $Y(t)$, the core function [3], monotonically decreases from 0 to 1.

b. *Not Different* - If these values show no differences (their error bar limits overlap), then their relative age depends on whether they are still aging. If both have ceased aging, then the two inks are older than the levelling-off age and may or may not be of different age; if they are still aging, then the two inks are younger than the levelling-off age and are of the same age. To determine if an ink is still aging requires testing the ink before and after some natural (or accelerated) aging period.

This qualitative description of error indicates the importance of statistics in age determinations.

G. Statistics [4] - Measurements come from instruments and these (along with the instruments that generated them) have an accuracy and a precision. Precision, which determines reproducibility, is associated with random error, while accuracy, which determines the deviation from the true value, is associated with systematic error. Accuracy and precision together are called reliability. Precision results from the statistical analysis on numerous measurements¹⁴ assuming no systematic error.

1. *A Scheme* - In normal analytical practice, one routinely takes several measurements (usually three) and from these obtains the mean, standard deviation, and confidence limits. Assuming no systematic error, the scheme is as follows:

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set of measurements $\{x_i\}$ \longrightarrow mean \bar{x} or $\langle x \rangle$ \longrightarrow std. dev. s_x

\longrightarrow coefficient of variation (RSD) $s_x/\langle x \rangle$ \longrightarrow std. dev. of the

for several test for significant

mean $s_{\langle x \rangle}$ \longrightarrow $\langle x \rangle \pm C.L.$ \longrightarrow difference

between

means pairs of means

Here the mean is also the average; std. dev. is the standard deviation; RSD is the relative standard deviation; and C.L. are the confidence limits (at a given level of confidence like 95%). The confidence interval (defined by the confidence limits) gets smaller (tighter) as the number of measurements increases. Significance tests determine if the difference between two means is significant (at some level of confidence) or may be the result of random error (chance).

2. *On Levels of Confidence* - If a mean has confidence limits at a 95% confidence level, for example, then there is a 5% chance (or 5 in 100 chance or 1 in 20 chance) that the true value (the universal mean) is outside of these limits. If the difference between two means is found to be significant at a 95% confidence level, for example, then there is a 5% chance

¹⁴To determine how precise a single measurement (and the instrument giving that measurement) is, one needs to take more measurements with that instrument. The only time one is safe with a single measurement from an instrument is when the instrument has a statistically established precision. This could also apply to instrumental methods that are preceded by laboratory preparatory procedures (the sampling step and the several sample preparation steps) *provided*, of course, they give reproducible results. Error can be introduced in each step and since they usually require an operator, there can be operator error. An analyst can develop skills and techniques, usually after much training and practice, that reduce the introduction of error in each step.

that the difference may be due to random error. If there is no evidence that the difference between two means is significant, then the difference may be due to random error. However, if one increases the number of measurements, the difference may become significant

3. *On Significance Tests* - For two inks being compared for age difference, significance tests determine if the difference between their aging parameters is significant or may be the result of random variations. If they are significantly different, and one knows how the aging parameter varies with age (increases or decreases), then one can determine which ink is older. In effect, with the knowledge of the direction of aging, a statistical difference is more than being not equal; it means an inequality (older than or younger than). Significance tests also determine where a questioned ink fits chronologically relative to inks of known age (See discussion under Shape of the Aging Curve).

4. *On Linearizations* - Returning to the shape of the aging curve and confidence limits, its curvilinear nature prevents the use of linear regression analysis techniques. To convert the aging curve into a straight line beginning at the origin, one first manipulates the measurements to make the graph begin at 1, decrease, and level off to zero. The resulting modified curve is then linearized. If the modified curve is truly exponential, then the negative \ln (natural log) linearizes it. The slope would then be the "rate constant." Straight line (linear) aging curves are useful for predicting age from measurements since all one needs is the slope. If the original aging curve had a constant confidence limit (error bar) envelope, its linearized form will have confidence limits that usually get larger with increasing age (see Shape of Aging Curve above).

II. Methods Involving The Dynamic Approach

Relative Age Of Ink Entries

A. Early Work - First Observations The question of when ink was placed on paper began to receive serious scientific scrutiny in the early 1920s. A good historical sketch of the early scientific work on ink aging is given by A. H. Witte [5]. At the time, the prevalent inks were iron gallotannate inks. Of interest in this historical development is the strong emphasis that was placed on estimating the age of ink. Less emphasis was placed on determining compositional profiles of inks and, consequently, in the static approach (matching profiles of questioned inks with those of standards). This is because there were only a few types of inks and variations within these (like different proportions of the same ingredients) could not be readily measured with the instruments available and the amount permitted for analysis. Most examinations were limited to optical examinations and chemical spot tests.

1. *Composition of Iron Gallotannate Inks* Composition of Iron Gallotannate Inks - A pre-1940 National Bureau of Standard formula given by Waters [6] for a "U. S. standard" iron gallotannate writing ink is:

tannic acid	11.7 g
gallic acid	3.8 g
ferrous sulphate (copperas or green vitriol)	15.0 g
10% hydrochloric acid	12.5 g
phenol (a preservative)	1.0 g
soluble blue (C.I. 707)	3.5 g
Water to make 1 L	

Tannic acid and gallic acid are related by hydrolysis: tannic acid + water = 2 gallic acid. Thus, if tannic acid is present, some will hydrolyze to gallic acid, but to what extent is not known. Tannic acid is also called digallic acid, galloylgallic acid, and gallotannic acid. These names indicate that tannic acid is from gallic acid, which name, in turn, suggests a gall nut source.

The reaction of ferrous sulfate with the tannic (gallotannic) acid to give the final water insoluble, black ink pigment is complex and not fully understood. A mechanism suggested by Mitchell [7] is that the reaction of ferrous sulfate with gallotannic acid first gives a water soluble, colorless, ferrous gallotannate complex. On exposure to air, this colorless complex is oxidized into two black pigments (ferric gallotannate complexes) at different rates and with different extents. One is formed quickly and the other is formed more slowly and eventually predominates. The quick-forming pigment is black, chalky, slightly water soluble, and soluble in dilute acid. The slow-forming pigment, which eventually predominates, is black, resinous, insoluble in water, and slightly soluble in acid. Oxalic acid readily dissolves and bleaches the fast-forming pigment but not the resinous one.

Hydrochloric acid is added to the ink to suppress the oxidation step. Oxidation is meant to occur only after the ink begins to dry and gets air-oxidized. Consequently, to give the ink initial or provisional color, a blue dye is added (in the past it was indigo made soluble by acidification). These blue dye-containing inks are sometimes called blue-black inks.

Iron gallate inks, which involve only gallic acid and no tannic acid, do not produce as dark an ink (upon oxidation) as iron gallotannate inks. Ferrous ions seem to also form a complex with gallic acid forming a water soluble colorless ferrous gallate complex which also oxidizes to a black, insoluble ferric gallate ink precipitate. This appears to be a reason why traditional iron gallotannate inks, as the one listed above, involve both tannic (gallotannic) and gallic acids. Needless-to-say, the chemistry is not simple compared to the art of making such inks.

Gum Arabic (10 g/L) is sometimes added to thicken the ink. Some believe it keeps any precipitated iron tannate (formed by the slow oxidation of the ink in solution) suspended in solution; others think it prevents the formation of the precipitate. Also, adding glycerol, glycol-ethers, or polyglycols improves the ink flow.

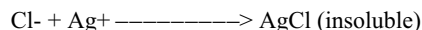
2. Aging Properties - When iron gallotannate inks are placed on a document, a series of aging processes begin to occur. Some measurable aging properties of these inks are:

- The inks change color with time.
- The iron in the ferrous state oxidizes to ferric state with time. (Ferrous iron decreases with time).
- The inks become insoluble with time.
- The blue dye oxidizes and becomes insoluble or discolored with time.
- The chloride (Cl⁻) ions migrate (diffuse) outwardly from the ink with time.
- The sulphate ions (SO₄⁻⁻) migrate (diffuse) outwardly from the ink with time.

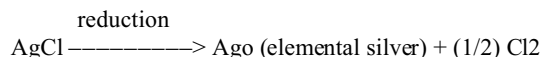
Witte [5] discusses different methods for measuring each of these. He devotes the most attention to the work of Mezger, Rall, & Heess [8] on the ion migration methods as these gained most popularity in those days [9,10] and were also used by his laboratory.

3. Ion Migration Tests - These tests essentially visualize the diffusion of chloride or sulfate ions by applying chemicals that react with these ions to give colored products. This is achieved by cutting out sections of paper containing the inks and submitting these to the chemical treatment; at the end of treatment, the section was placed back on the document.

a. *The Chemistry* - For the chloride ions, the test samples are placed in a silver nitrate solution which turns the chloride ion into silver chloride:



AgCl is then reduced to Ag with formaline or any other Reducing agent (even light in this case):



The finely elemental silver formed is black and provides the "chloride diffusion picture". The older the ink is, the more diffused is the chloride picture. According to Witte [5], the chloride migration ceases within 1 year. For the sulphate ions, a "sulphate diffusion picture" can be obtained using a different chemical treatment. The sulphate migration ceases within 1 or 2 years.

b. *Limitations* - The application of these tests was recognized early on to be very powerful, but rather limited for two reasons: (a) the ion migration tests do not work after the ion migration ceases (about one year for chloride ions and two years for sulfate ions), and (b) the ion migration tests depend on the ink composition, the paper it is on, and its storage history. The need to prove that inks being compared are of the same composition was quickly recognized as well as the need to have the inks on the same paper. In those days, formula-testing methods were limited to crude chemical spot tests and they seldom provided a full compositional profile. Most of the time the tests were to distinguish six major ink types [11]: iron gallotannate, logwood (with potassium chromate), logwood (with copper sulfate), nigrosin, vanadium, and resorcinol. The other major type, the India (carbon) ink, was easily distinguished from these. The equi-sampling condition (comparing samples of identical or nearly identical appearance) had to be strictly followed since mass invariant methods were not fully realized. These limitations are now well recognized and form the basis of the basic requirements discussed above for relative age determinations.

4. Color Change Tests - Mitchell's extensive work [7,12] on the measurement of color changes seemed very promising. It was based on the fact that as the ink on paper oxidizes, the color of the iron complexes goes from colorless (the ferrous complexes) to black (the ferric complexes) to yellow/brown (rust or ferric oxide). With the presence of the blue dye, the color goes from

blue, to blue-black, to yellow/brown (rust). The blue dye remains the same for some time but eventually degrades with time. According to Mitchell, inks attain their maximum intensity (black or blue-black) within 8 to 10 months after being placed on a document. Thus, if one saw that an ink was still getting darker (still aging), the ink writing could be declared to be relatively fresh (written within 8 to 10 months). Color measurements were done with an Osborn color comparison microscope (a modification of the Lovibond tintometer). It assigned three numerical values (the blue, red, yellow color coordinates) to a color. It was used to measure the aging of inks by measuring their color change. This was an attempt to assign an absolute date to an ink entry, but its reliability suffered.

a. *Determining "Freshness"* - If the color of an ink entry got progressively darker over time, then it was still aging and considered fresh (written within 8 to 10 months). Such tests that compare an ink property before and after some brief natural (or accelerated) aging period have their own limitations. These type of (non-relative) age estimates depend on the storage history of the document; and furthermore, the levelling-off age of the ink (the age after which the ink is not considered fresh), which is determined beforehand, depends on the ink composition, the paper it is on, and its storage¹⁵. These limitations are less restrictive than those for relative aging since they involve only one ink whose aging parameter (like color) is monitored over a brief period of time; but the age estimates are not as certain as the relative age estimates. Aware of these limitations, Mitchell favored those findings where an ink allegedly made much later than the levelling-off age was found to test fresh [12] (and was still aging).

b. *Accelerated Aging to Determine "Freshness"* - Other methods that determine if an ink is fresh (is still aging) include those that compares an ink with itself before and after some age-inducing treatment. These also have the same limitations mentioned above. Soderman and O'Connell [13] write about accelerating (inducing) the aging with an ultraviolet (UV) actinic¹⁶ source to see if a color change occurred; if it did, the ink was deemed fresh. They also use this induced aging concept in conjunction with solubility tests (next section). They attribute this discovery to Van Ledden-Hulsebosch in Amsterdam. Mitchell [7] also discusses subjecting an ink (shown to be blue-black iron gall ink by chemical tests) to light and air (oxidation) to induce color changes.

5. *Solubility Tests* - Mitchell's [12] pioneering work on the measurement of solubility provides the basis of work that followed later. His work is founded on the earlier observation that the "copying capacity" of inks decrease with age: as an ink ages, it becomes progressively more difficult to get a contact-transfer of the ink onto a moistened paper (the ink is

"hardening")¹⁷. Mitchell extended this idea by studying the solubility properties of iron gallotannate inks (with blue dye) into reagents. Of the several reagents tried, he settled on a 5% solution of oxalic acid. Using a capillary pipette, he placed a drop of this reagent on an ink line and followed the speed of the reaction (solubility and bleaching of the black pigment) and the amount of diffusion (solubility and diffusion of the blue dye). With this reagent, the black pigment of fresh inks immediately dissolves and bleaches and the blue dye readily extracts and diffuses onto the paper. After three or four years, the black pigment reacts more slowly with the reagent, and the blue dye hardly diffuses. After five years, the pigment reaction is extremely slow and the diffusion or the dye ceases.

To explain why this test worked, he relied on the mechanism suggested above for the formation of the iron gallotannate pigment precipitates. Mitchell's states (on p. 184 of reference 7), "the [ferric gallo] tannate first formed is sufficiently soluble to allow copies to be taken for a short time, and is readily soluble in dilute acids, but as the oxidation proceeds the resinous [ferric gallo] tannate is slowly formed, until eventually the ink becomes not only difficult to dissolve in weak acids, but also protects¹⁸ [emphasis added] the soluble aniline dyestuff from the action of the reagent. When oxidation has reached this stage the addition of acid will slowly cause the ink to turn blue if the blue dye has not yet faded, but there will be little, if any, sign of diffusion of smudging."

When this test is used to determine if an ink is fresh (is still aging), then it has its own limitations (see above). Recognizing these limitations, Mitchell and also Waters [6] suggested its use for comparing the relative age of inks and stressed the importance of having the inks be of the same composition, on the same paper, and be sampled equally. This determines the sequence of how ink entries were made relative to each other - so long as the inks are still aging.

B. Work of the 1950s and 1960s - Some Mass Invariant Approaches

1. Work of Kikuchi [14] - Extraction Methods - Dr. Kikuchi's work is based on Mitchell's finding that ink solubility decreases with age. She studied mostly blue-black iron gallotannate inks. Her work differs from Mitchell's in that she uses a much weaker oxalic acid reagent solution (between 0.01% to 0.025% compared to Mitchell's 5%). Her intent was to slow down the dissolution process in order to more accurately and numerically measure the time taken before the ink begins to dissolve (disperse).

Procedure: The procedure involves placing a drop of the (weak oxalic acid) reagent on an ink stroke, and under magnification,

¹⁵Color changes are strongly affected by the paper surface, storage conditions, and blotting (if any occurred). Also, iron gallotannate inks that differ in their composition (in the ratio of their components) differ in the way they change color with time.

¹⁶Actinic pertains to actinism - the property of radiation by which chemical effects are produced (the Random House College Dictionary (1982)).

¹⁷Rhodes [11] writes about the contact-transfer of inks onto surfaces such as reagent-soaked paper (Bischoff and Schneeberger) and later gelatinized films (Carrel, 1934) and performing examinations on the transferred ink. This, he writes, is a radical departure from *in situ* chemical spot testing approach founded by Robertson, Hoffman and others in the late 19th century. Transfer methods, however, showed degree of aging by the degree of transferability (Sittl, 1891; Habermann and Oesterreicher, 1901; Carré). (See Rhodes [11] and Mitchell [12] for references.)

¹⁸Rhodes [11] refers to this as *mechanically preventing the solvent to act on the provisional colouring matter* (the dye).

measuring with a stop watch the time it takes before the ink shows any dispersion into the drop. Due to the weakness of the reagent solution, this time is prolonged to several seconds (between 1 to 60 seconds). Based on her data, it appears (though not stated) that a weaker oxalic acid reagent is used for discerning fresh inks (probably 0.01%) than for discerning older inks (probably 0.025%). She does state, however, that the choice depends on the temperature, humidity, and material being tested.

With his procedure, Mitchell [12] was only able to describe his observations in words like: rapid diffusion, diffusion after a time, diffusion more rapid than or less rapid than, slight indication of diffusion, very slight diffusion, and no sign of diffusion. With Kikuchi's procedure, one gets an aging parameter (the time it takes to begin dispersion) that is numerical, gets longer as the ink ages, and equally important, does not depend on the amount of ink sampled (the time parameter is mass invariant)¹⁹ provided one samples inks of the same intensity (see weak-vs-strong test below).

Her procedure of using weak extracting solutions and measuring the time to reach the beginning of dissolution applies to other inks. In a private communication with this author [17], she expanded the application of her technique to ballpoint inks using dilute hydrochloric acid.

Experiments: After preparing standard dated material²⁰ and selecting actual dated material²¹, Kikuchi conducted five basic experimental tasks:

- Developing the extraction method for determining the aging parameter (time taken to reach point of dissolution).
- Developing an aging curve for the standard materials.
- Studying ten factors that can affect age determination.
- Developing an aging curve for the actual materials.
- Estimating the time of writing of a questioned ink entry.

In all extractions she repeated the test four times (giving five data points). For each set of quintuplet tests, an average result and average error was computed. The ten factors studied that affect age determination are treated separately below.

Findings:

- The shape of the aging curve (time before ink shows dispersion-vs-age) has four regions²²: These are where the time of writing is:

(a) between a few hours and a few days old - time parameter is very small (immediate dispersion).

(b) less than about 6 months - time parameter begins to increase (ink begins to show resistance).

(c) around 5 to 6 years - time parameter begins to level off (speed to dissolve quickly drops off).

(d) over 6 or 7 years - very slow increase in time parameter.

- Error for the first two regions is about 4 months and for the third is about 2 months (it is more difficult to get precise measurements for short times parameters).
- It is critical to sample all inks being compared under the same temperature and humidity conditions (also stressed by Cantu and Prough [2]).
- A method to estimate the age of a questioned ink and its margin of error is to bracket its time parameter with those from known standards and graphically use the margin of error of the measurements to determine the margin of error of the age.

Ten Factors Studied That Affect Age Determination:

- Ink brand differences.
- Paper differences.
- Ink age differences.
- Paper age differences.
- Document storage differences (light and humidity).
- Mixing of different ink brands.
- Others:
 - weak-vs-strong ink entries.
 - absorbent-vs-normal paper.
 - hand soiled-vs-clean document.
 - use of ink without sediments from top of bottle-vs-ink with sediments from bottom of bottle.

Effects: Difference in ink brand showed the strongest effect. Paper differences, interestingly enough, showed proportional differences. This indicates (though not stated by Kikuchi) that inks of the same formula on different paper can be compared if one has a common known dated reference on both. Differences in the age of ink (in bottle) has an effect only if the ink bottle was kept opened and constantly used. Differences in paper age had no effect. Light tended to make inks appear older while humidity made them appear younger. Mixing inks caused serious effects. Lastly, strong (-vs-weak) inks entries, writing on absorbent paper (-vs-normal paper), ink on clean paper (-vs-soiled paper), and ink from top of bottle (-vs-ink from bottom of bottle) tended to make the ink appear younger.

Kikuchi published two other works in the series concerning age determination. Part II [15] concerns studying brand and age differentiation through spectral measurements (C.I.E. chromaticity coordinates) and Part III [16] concerns analysis of samples from 1952 to 1962 to distinguish brands and age via

¹⁹This time is different from the time it takes for an ink entry to cease extracting. The latter also increases with the age of the ink entry is also mass invariant. The former (the Kikuchi measurement), however, is easier to measure.

²⁰The standard dated material consisted of ink entries prepared at different time intervals beginning in 1952 on stationary paper (and other papers) using each of 14 different brands of inks (stored in a dark place and opened only for use in preparing the standards using a fresh steel pen each time).

²¹The actual dated material consisted of 100 New Year's cards prepared between 1952 and 1958. Only those shown to be made with iron gallotannic ink were considered (that is, those confirmed by potassium ferrocyanide test). The color resulting from the sodium carbonate test was used to divide these into different brands. For each brand, seven cards from each year were then selected. Also, 25 checks, receipts, letters, used between 1952 and 1958 were considered.

²²Again, it appears (though not stated), that difference strength of oxalic acid were used for the different regions of the curve. Probably weak solutions were used for fresh inks and stronger solutions for older inks.

extraction methods (oxalic acid).

2. *Work of Sen and Ghosh* [18] - Extraction Methods - Sen and Ghosh tested the hypothesis that the dye content of iron gall inks becomes more resistant to extraction (in methanol) as the ink ages. They used a rather creative analytical procedure to assure that fragments of ink samples being compared contained the same amount of ink. The procedure is based on showing that the samples being compared have the same iron content (that is, iron is used as an internal standard). Here the amount of ink sampled is assumed to be proportional to the amount of iron present in it (that is, the manufacturing of iron gall ink consistently has the same iron content).

The Sample Set: Several iron gall ink entries of known ages ranging from January 1942 to December 1969 "written with the same type of ink on almost the same kind of paper and were stored under similar conditions."

Sampling and the Extraction of the Dyes: For each ink, a given number of samples were punched out and the dyes were multi extracted with methanol. The samples were moistened with methanol and stored in a refrigerator overnight and then extracted several times with fresh quantities of methanol. The dye solution was concentrated to a final volume of 0.5 mL. For each ink, the same number of samples were removed (the sample set) and the color intensities were approximately the same.

Dye Content per Sample Set (Quantitative TLC): For each ink, 25 microliters of the dye solution were spotted on a freshly prepared silica gel thin-layer chromatography (TLC) plate and the plate was developed using the solvent system n-butanol:acetic acid: water = (45:10:45). The resulting predominant band is deep blue and the total area of each band was measured with a photo-densitometer.

Iron Content per Sample Set (Spectrophotometry TLC Medium): The ink samples from which the dyes were removed were analysed for their iron content by ashing, digesting in 50% HCl, reacting with ammonium thiocyanate (with amyl alcohol), and spotting 10 microlitres of the colored amyl alcohol solution onto a TLC plate. The integrated spot area was determined photo-densitometrically.

Selection of Measurements: Only those integrated areas that came from sample sets containing the same amount of ink (same iron content) were chosen. They chose twelve that ranged in age between 1942 and 1969.

The Data: The plot of the log of the integrated area (of the deep blue dye extracted)-vs-time in years (0 to 27 years) shows an almost linear decrease in the dye extraction with age. If the integrated area (not its log) is plotted against time in years, one obtains the exponential-like behavior of measurement-vs-age. Remarkably, the aging curve does not appear to level off even after 27 years.

Mass Invariant Measurements: Sen and Ghosh were rather careful not to compare sample sets with different iron content. Yet they had all the tools necessary for considering them. That is, they could have used the principle of an internal standard and scaled the dye extraction measurements according to the amount of ink sampled. This is simply the ratio the dye extracted to the iron content. The ratio is called extent of extraction.

C. Recent Work - Increased Use of Analytical Method

1. *Work Initiated by Cantu and Prough* [2,3,19,20,21] - Extraction methods - The ink extraction work by Mitchell, Kikuchi, and Sen and Ghosh supported the hypothesis that as inks get older they are harder to extract into solvents (particularly weak solvents). This author sought to make this idea more quantitative by using analytical methods. He began by extracting bulk inks into several solvents, observing their color development using a visible spectrometer (Spectronic 20), and constructing their extraction curves - the plot of optical density-vs-extraction time. Some critical and useful observations he made follow along with some of Brunelle's observations [19,21]. This is followed by a brief outline of an analytical procedure built on these observations and a method to analyze the resulting data.

a. *Rate of Extraction* - Normalizing extraction curves (dividing each value by the last value) makes them mass invariant - they don't change with the amount of ink sampled. Each point on this normalized extraction curve is called an R-ratio because it involved a ratio of two values. The time taken to reach a certain fraction L of extraction ($0 < L < 1$) is also mass invariant. R-ratios and the time taken to extract a given fraction of ink reflect the rate of extraction.

b. *Weak Solvents-vs-Strong Solvents* - Weak Solvents discern age differences; usually very weak ones discern days to weeks of age, stronger solvents discern months and years, and strong all-extracting solvents do not discern at all regardless of age.

c. *Extent of Extraction* - Inks of different age often differ more in how much is extracted than in their rate of extraction²³. A way to determine this extent of extraction is by removing the sample already extracted in the weak solvent, drying it, and extracting it into a strong (all-extracting) solvent. The sum of the two optical densities²⁴ would then be proportional to the total amount of ink sampled. Thus, an optical density of an extraction divided by this sum represents a percent of extraction. A percent extraction curve²⁵ is obtained from an extraction curve by dividing each value by this sum (and multiplied by 100).

²³This has been observed by several examiners. The multiple approach discussed here and by Brunelle [19] test both rate and extent of extraction. Investigation a novel use of HPLC, Isaacs and Clayton [20] also noted that extents of extraction change more readily with age than rates. Their technique is presented later.

²⁴The sum may have to be weighted if the volumes of the two extraction volumes are different.

²⁵If the second solvent is not all-extracting, then monotonic behaviour may suffer. For example, if the extraction into the second strong solvent decreases with age (instead of being the same with age) and the extraction into the first weak solvent decreases with age (as expected) but levels off sooner than the extraction into the second strong solvent, then the percent extraction curve decreases up to the age where the extraction into the first weak solvent levels off and then begins to increase until it levels off at the age where the extraction into the second strong solvent levels off.

d. *Analytical Methodology* - Going from bulk samples to ink removed from a line of writing presented a challenge. Microspectrophotometric analytical methods still required too much sample and fluorescence methods worked well but not all inks contain fluorescent components. Capturing the ink color periodically (as the ink extracts) by spotting aliquots on a TLC plate and measuring their density (as reflectance or transmission) proved to be feasible. One trade-off is that the method is more technique dependent. For example, the uniformity and size of the (undeveloped) TLC spots and of the developed bands should always be the same to have good reproducibility. Furthermore, transforming a TLC density measurement into a parameter that is linear with concentration (Kubelka-Munk Theory) is not as simple as transforming a transmission measurement into absorbance in solution spectroscopy (Beer's Law). For weak spots, the -log transformation works well for both modes.

e. *Sampling* - The two sampling methods used were removing either about 10 micro discs (ca. 1 mm diameter) or a sliver (ca. 10 mm) of ink-on-paper from the document. Though the latter could consist of several slivers totalling 10 mm, it was found that an "edge effect", or surface area effect, could affect the extraction. This led to the requirement that all sampling be done in the same way. Furthermore, to avoid any effect relative humidity may have on the ink-paper bonding (recall, paper is hygroscopic), all sampling and measurements should be done on the same day.

f. *Induced Aging* - Heating inks normally makes their extraction harder. Heat, therefore, induces drying and aging (as measurement by extraction). In cases where a set of aged inks on paper is not available, one can create such a set by writing multiple entries on paper where after each entry, the paper is placed in an oven for a given amount of time. This method was used to determine certain observations about ink aging [2]. Since moisture sometimes plays a role in extractions, samples submitted to dry heat should let their paper substrate regain its moisture before analysis. Induced aging with ultraviolet radiation and its implications on ink age is discussed by Soderman and O'Connell [13].

As indicated above, induced aging can be used to establish if an ink is still aging. This assists in determining if two inks having the same value of an aging parameter are of the same age; they are only if they are shown to be still aging. If they have ceased aging, no conclusion about their relative age can be made.

Brunelle [19] uses heat to induce aging on ballpoint inks (as Van Ledden-Hulsebosch [13] used ultraviolet actinic radiation on iron gall inks) to establish if an ink is still aging. In Brunelle's technique, two samples of an ink entry are removed and one is subjected to induced aging (100°C for 20 minutes). The two are then compared using a number of methods. Brunelle finds that for the inks he has tested, the ink parameters he measures level off on the average after 3 to 4 years (no confidence limits provided). Of interest there is no need to identify the ink since the comparison is between two ink samples taken from the same ink entry - one sample is artificially aged and the

other is not. The main hypothesis is that induced aging takes an ink aging parameter to where it would be had it ceased aging naturally. Aginsky applied this induced aging idea to the measurements of volatile components (see below).

g. *Dye Ratios* - Brunelle and Lee [21] followed up on a suggestion made by this author regarding ratios of dyes separated by TLC without reference to the second (strong solvent) extraction [2]. They found that these vary sufficiently with age and are useful for age determination. In rare occasions, however, aging curves using dye ratios "turn direction"; that is they are not monotonic²⁶. This happens, for example, when the aging curves of the dyes being ratioed cross at two or more points - the ratio is 1 at the crossing points.

h. *Rudimentary Outline of a Procedure*²⁷ - A procedure²⁸ that covers some of these observations was prepared for the Lausanne presentation². It has two parts. The first part involves spotting a TLC plate. It has six basic steps:

- Sample the ink (removing micro discs, for example).
- Extract the ink in a weak extracting solvent (like n-butanol).
- Record the optical density several times during the extraction by removing aliquots and spotting these on a TLC plate. The aliquot removal could be at four extracting times: $t_{wk} = t_1, t_2, t_3,$ and t_4 spread out over a 20 minute period.
- Remove the weak solvent²⁹ and dry the sample.
- Extract in an all-extracting strong solvent (like pyridine or benzyl alcohol for ballpoint inks).
- Record its optical density after a given period of extraction (t_{str}) by removing an aliquot and spotting it next to the other spots on the same TLC plate.

The second part involves developing the TLC plate. It has two basic steps:

- Develop the TLC plate.
- Record the optical density of the developed spots.

²⁶A version of this procedure is provided in the article by Brunelle [19].

²⁷All computations that involve a ratio of two values, each of which change with age, have the potential of "turning direction" with age (i.e. of not being monotonic).

²⁸Details of this procedure appear in a memorandum to Dr. Chris Lennard (University of Lausanne) from this author dated January 18, 1994 and titled, "On the Relative Aging of Writing Inks - a Systematic Approach."

²⁹One could also remove the solvent by evaporation (drying); this has the advantage of reducing error. Since such removal affects the optical density of the second extraction, it can be accounted for with a proper weighted sum of the two optical densities (of the first and second extraction). This idea was provided by Dr. Pat Grant, Lawrence Livermore National Laboratory.

Every detail of the techniques used in the procedure (techniques used to sample, extract, spot, etc.) must be followed exactly for other ink entries being compared including the amount and line quality sampled. The reproducibility of the procedure, like most procedures, depends very much on the techniques used and the experience and skills of the examiner.

i. *Data Analysis* - Consider first the four undeveloped spots (from the weak solvent extractions). The "stick" plot points (connected with a line) of their optical densities

[D(1), D(2), D(3), and D(4)] against their corresponding four extracting times [t₁, t₂, t₃, and t₄] is monotonically increasing. This plot is the extraction curve. The corresponding "stick" plot made by dividing each optical density by the last one, D(4), (forming R-Ratios) is normalized to one, is mass invariant, and is the normalized extraction curve. The time where this R-Ratio plot crosses a horizontal line drawn at 0.9 units above the time-axis is a mass invariant time. It is the time taken to reach 90% of the extraction and is denoted by t_{0.9}. The three R-Ratios (the fourth always has a value of 1) and the time t_{0.9} are associated with the rate of extraction.

Consider now the optical density D(str) of the fifth undeveloped spot (from the strong solvent extraction). For each of the four optical densities, four percentages [P(1), P(2), P(3), and P(4)] are formed according to the formula

$$P(i) = \{D(i)/[D(4) + D(\text{str})]\} \times 100$$

for i = 1, 2, 3, and 4. This is called the percent of extraction (into a weak solvent) at time t_i and the plot of these against their corresponding four extraction times gives a percent extraction curve. The idea here is that the denominator D(4) + D(str) represents the total amount of ink sampled making. Each P(i) value is associated with the extent of extraction.

After developing the plate, each original spot on the plate gets separated into several bands along the plate. Each band can then be treated as was done above; that is, for each band one can obtain a normalized extraction curve, a 90% extraction time t_{0.9}, and a percent extraction curve.

This data analysis method was applied to data used by Brunelle in his recent publication [19]. The ink analyzed was a Formulab 587 black ballpoint ink. Two samples were taken; one was heated for 20 minutes at 100°C and the other was left untreated. To determine their extent of extraction both samples were first extracted in n-butanol for 12 minutes and then for 15 minutes in pyridine. Only the four central methyl violet bands of the developed TLC plate were considered. In terms of these four individual components, the overall decrease in extent of extraction from 31% (unheated) to 27% (heated) reported by Brunelle is given by 31% = 3% + 11% + 11% + 6% and 27% = 3% + 10% + 9% + 5% where the position in the sum refers to the same component.

Since it often happens that extents of extraction in a weak solvent are more sensitive to aging than rates of extractions, one can simplify the procedure by removing

the steps that provide the rate information³⁰. For this, one only needs to remove one aliquot (during the first extraction into a weak solvent) at a time when the extraction is nearly complete, e.g., at t_{wk} = 20 minutes.

Whatever time is chosen, it must be used throughout, however. The percent extraction value is then given by the above formula with P(i) replaced with P(wk), D(i) replaced with D(wk), and D(t_i) replaced with D(t_{wk}).

2. *Work Of Stewart* [22] - GC Analysis of Volatile Solvents in Inks - In 1985 Stewart published the first paper relating volatile components with age of ballpoint ink writing. He confirmed the hypothesis that as ballpoint ink ages on paper the volatile components decrease. He developed a gas chromatographic (GC) method based on that used by the ink industry to do quality control of their ink vehicles. The major challenge was to develop a technique for detecting volatile components from very small fragments of ink writing on paper as opposed to bulk ink samples tested by industry.

Procedure: The procedure involved removing about 15 micro discs (removed using a 20 gauge blunted hypodermic needle), placing these in a tapered bottom 0.5 dram micro vial, carefully adding 10 to 15 microliters of methanol, capping and placing it in an ice bath undisturbed for 5 minutes. After extraction, 5 to 10 microliters were removed and injected into a GC with a flame ionization detector and a 6 foot stainless steel column packed with 3% Tenax GC on 60-80 Supelcoport.

Mass Invariance: To achieve mass invariance, two or more well resolved GC peaks are required in order to obtain mass invariant ratios. One ink sample tested showed two GC components and their ratio decreased from a value of 8.0 (fresh ink on paper) to a levelling-off value of 1.0 (135 days on paper). This particular aging curve (for the ink tested) is exponential-like in that it levels off to an asymptote. Consequently, the margin of error increases as the ink ages.

Appliances: The technique can be used for comparing the relative age of two inks of the same formula on the same document provided; (a) the inks have at least two well resolved GC peaks so that peak heights or ratios can be obtained; and, (b) the ratios change monotonically with age - rather than "turn direction" with age²⁶. The absolute age of a questioned ink writing can also be obtained using the aging curve provided the questioned ink is of the same formula, on the same type of paper, and similarly stored as the ink writing that provided the aging curve.

3. *Work of Humecki* [23] - Micro IR Analysis of Ink Extracts - Martin and Pearl Tytell, document examiners from New York City, had a case that needed ink dating. The ink was identified by one ink examiner as a Formulab blue ballpoint ink formula (no. 353) and its first production date did not assist in the

³⁰Details of this procedure is in an internal USSS manuscript entitled, "Determination of the Percent of Extraction of Writing Ink on Paper Into a Weak Solvent."

dating problem. Knowing of the work on relative aging and the need to work with dated standard samples of the same formula, the Tytells then obtained from the ink manufacturer dated test writing samples, prepared under controlled conditions on a write out machine, of the desired formula of ink. The dates ranged over a 22 year period.

The Examination: For the examination, they went to W. C. McCrone Associates, Inc. in Chicago, IL who was familiar with the relative aging methods. Mr. Howard Humecki worked on this case and decided to try an entirely different approach than the existing extraction methods. Being one of the leading experts in the microanalysis of materials using infrared spectroscopy, he developed a method for obtaining an aging curve from the dated standard samples provided by the Tytells. (The parties were aware that the standard inks were not on the same paper as the questioned ink and were to deal with this after obtaining an aging curve).

Method: For the aging curve, 0.25 inch ink samples were removed, extracted in pyridine, and the extract was transferred to a salt window. A 1x4 mm masking window was used with a 6x beam condenser on a Digilab (FRS-20C) infrared spectrometer with a triglycine sulfate (TGS) detector. Spectra were run for each test sample. A salt control and paper control showed little interference from the paper extract. A method was also developed for the micro analysis of 1 mm micro discs of ink sample.

Results: Changes in the OH band (at 3 microns), the CH band (at 3.4 microns), and the CO band (at 5.8 microns) with age suggest that both evaporation of volatile solvents and oxidation process are occurring as the ink ages. The mass invariant ratio of the OH band and the CH band decreases monotonically (it does not "turn direction")²⁶ with age and levels off after 10 years.

Despite this outstanding work, it did not help date the questioned ink. The technique does show great promise and deserves further research.

4. *Work of Aginsky [24,25,26] - Multiple Techniques* - No ink researcher has done as much investigation into so many diverse methods to determine the age of inks as Dr. Valery N. Aginsky of Moscow, Russia. The following exemplifies his ideas.

In his first paper [24], he treated ballpoint inks. As they age, he basically measured three basic mass invariant parameters.

a. *Sensitivity of Ink to Changes in Color upon Exposure to Certain Gases* - On exposure to gases of organic bases such as benzylamine or piperidine, many relatively fresh inks undergo a visual, reversible color change. To measure the change, Aginsky built a system containing a chamber for gassing the document and a reflectance photometric microscopy attached to a chart recorder for measuring the reflectance of the exposed ink. The wavelength chosen is that which gives the largest difference in color and is obtained by comparing the reflectance curves of the ink before and after exposure to the gas. For those inks which undergo reversible discoloration on exposure, the reflectance first decreases (ink luster decreases) then increases (discoloration occurring) at a rate that depends on age. This slope (rate) is the measured parameter. It

decreases with age and levels off after a few months (ca. 4 months for a Soviet Soyuz blue-violet ballpoint ink). Provided one measures inks of similar thickness, homogeneity, and surface characteristics [24] these parameters are mass invariant.

It is of interest to mention that during the author's presentation of Aginsky's work in Argentina², several Brazilian document examiners mentioned hearing in their country of a similar gassing technique for determining sequence of strokes.

b. *Amount of Volatile Vehicle Ink Components* - Aginsky amplified Stewart's work on the decrease of volatile components with age. Like Stewart, the thrust of his work is to measure the volatile components. The difference, however, is that he uses two rather clever techniques to obtain aging parameters that (a) do not depend on having more than one volatile component; (b) always decrease with age (as opposed to a ratio of volatile component peaks which could reverse itself with age)²⁶, and (c) are more directly associated with the content of volatile components than ratios of volatile component peaks. These two mass invariant aging parameters are:

The Vehicle-to-Dye Ratio - In an example given, Aginsky first extracted a 2 cm sample with carbon tetrachloride for 60 minutes and then ran a GC on the extract. He got two well separated peaks (called x and y) and, using an internal standard in his carbon tetrachloride, he obtained their amount, m_x and m_y . Like Stewart, he computed the ratio of volatile components. But he went further. He took the extracted residue, dried it, re-extracted it with 1.2 mL dimethylformamide to remove the dyes, ran a UV-vis spectra on the extract, and obtained the wavelength of maximum absorption, A. He then computed the ratio of the vehicle content m_x or m_y to the absorbance value A at the absorbance maximum. He plotted all three computable ratios: m_x/m_y , m_x/A , and m_y/A . All three leveled off after about 70 days for this ink (an Italian violet ballpoint ink).

The Ratio of a Sequential Solvent Extractions - Aginsky applied an idea developed by Cantu and Prough [2] to the volatile components. He extracted an ink into two solvents sequentially, running a GC after each extraction. First he extracted the sample in a slow extraction weak solvent (carbon tetrachloride) for an hour, after which he ran a GC; he next removed the first solvent and dried the sample; then he extracted this in fast extracting strong solvent (chloroform)²⁵ for 2 minutes after which he took a GC. For the sample tested (Soyuz blue-violet ballpoint ink), there was only one reliable volatile component. The percent extraction computed from the sequential solvent extraction is:

$$\%M = [M_1/(M_1 + M_2)] \times 100$$

where M_1 is the amount of volatile component after the first extraction and M_2 is the amount of volatile component after the second extraction. This percent (which represents the amount extracted into a weak

solvent relative to the total amount present) decreased with age and levelled off after about 3 months.

c. *Relative Content of Non-volatile and Colorless Vehicle Ink Components* - This procedure studies changes in the non-volatile and colorless ink components (such as resins) with age. Such components may have different stability with age. The procedure calls for extracting these components in a suitable solvent; spotting the extract on a TLC plate; running a paper control; developing the plate in a selected solvent system; viewing the developed plate under 254 nm UV light; and measuring the relative content using densitometry. Aginsky studied two sets of ballpoint ink entires prepared over a 6 year period. One involved a blue Parker ink and other, a blue-violet Soyuz ink. They were extracted in chloroform for 2 minutes or carbon tetrachloride for 60 minutes. These solvents, fortunately, do not extract ink dyes very well; but they extract paper components. The extracts were spotted on a silica gel TLC with fluorescent indicator plate and developed in acetone:hexane = 1:4 (v/v) for the Soyuz set and in acetone:hexane:ethanol = 5:20:1(v/v) for the Parker set. Each set showed two non-volatile, colorless components. For the Parker set, one component increased with age and the other decreased; their mass invariant ratio levelled off at about 3 years. For the Soyuz set, one component disappeared after one and a half years while the other remained constant.

There are two other works of Aginsky worth mentioning.

d. *Use of Polarizing Microspectrophotometry to Determine Optical Surface Changes in Inks with Age* [25] - In this work Aginsky [25] investigated the appearance of ink under normal and polarized light as the ink ages. He considered a Parker blue ballpoint ink which has a blue copper phthalocyanine dye and a methyl violet dye. The blue dye is relatively stable with age while the violet dye is less stable (it fades with age due to oxidation and photodegradation). Since this makes it difficult to show that two inks being compared are of the same formula³¹, Aginsky assumed that one has information that the inks are of the same formula. His procedure was built on a hypothesis regarding the ink's surface - as ink ages, the color (ratio of dye content) of the surface layer changes more due to aging (through oxidation) than the color of the interior layer. Using non-polarized light, he measured the specular reflectance from the surface layer and using crossed polarized light (to block surface specular reflectance), he measured the diffused reflectance from the interior layer. He did this using a microspectrophotometer with polarized light and analyzer capabilities. For each, he took measurements at two

different wavelengths (associated with the absorbance of the dyes) and then essentially took the ratio of the measurements (giving a mass invariant measurement). He did not study how these two ratios change with age, but how their ratio does. This aging parameter (reflectance ratio/diffused ratio) decreased with age (levelling off at about 6 years) but had a rather large error envelope. Of interest, is that the hypothesis of the ink aging of the surface layer resulted from earlier work he did involving the transfer of an ink entry written on one substrate onto another substrate. Such work resembles the early work involving the "copying capacity" of inks (see Mitchell's solubility test above) - or "copying power" as Witte [5] sometimes calls it. Yablokov also considered this in Russia back in 1961 as well as other relative aging ideas [27].

e. *An Accelerated Aging Technique for Determining Solvent Components of Inks Using GC/MS* [26] - In his latest work, Aginsky uses GC/MS to characterize the ink, to identify the ink solvent components, and to assure inks being compared have the same solvent components. He maintains that the aging of many classes of inks (besides all ballpoint inks, many stamp pad, jet printer, roller pen, porous tip, India, and cash machine inks) can be studied this way so long as there is sufficient "binder" to retard the evaporation of the solvents. The aging approach he takes involves an accelerated aging method to determine if an ink is still aging. He takes two portions of a single ink entry, induces aging using heat on one and not the other, and determines the difference in their levels of solvent components. His method is different from Brunelle's [19] in that Brunelle determines the difference in their solvent extractability parameters. Aginsky proposes two procedures for measuring the levels of solvent components using GC/MS:

The Extraction Efficiency of Ink Volatile Components into Weak Solvents - This is the same "ratio of sequential solvent extractions" procedure considered before by Aginsky [24] (see above) but now considers weak solvents that are a blend of carbon tetrachloride and chloroform (at most 25% chloroform) and uses GC/MS. He extracts into one of these for 30 minutes (using an internal standard) and then extracts into chloroform (the strong solvent)²⁵ for 2 minutes. The inks examined were a Senator black, Bic blue, and several Soyuz blue ballpoint inks. GC/MS showed the presence of phenoxyethanol and benzyl alcohol in these, and the extraction efficiencies for each were measured. A second set of samples were submitted to induced aging for 1 hour at 70°C and the extraction efficiencies were calculated. The difference between the percent extraction efficiencies before and after inducing heat decreases with age and leveled off between 6 to 12 months of aging, depending on the ink and the volatile solvent extracted.

The (Relative) Amount of Ink Volatile Components - This is built on the work of Stewart but uses GC/MS to identify volatile components and an internal standard to quantify them. The inks examined were Senator black ballpoint, MonAmi black Roller pen ink, Trotto porous tip pen, Moshbitchim violet stamp

³¹The instability of violet dye may also cause a change (fading) in the overall ink color over time (besides the change in dye composition). Consequently, for such inks that change in color and dye composition with age, inks of the same formula that differ in age could be considered different (false non-match) - unless one has other information (tags, unique dyes, etc.) that indicates they are the same.

pad ink, and HP DeskJet-500 printer black ink. He extracted their volatile components for 2 minutes with acetonitrile containing m-cresol as an internal standard. GC/MS found benzyl alcohol, phenoxyethanol, and phthalic anhydride (a solid volatile component) in the Senator ink; 2-pyrrolidone in the jet printer ink; and diethylene glycol in the stamp-pad, roller ball, and porous tip pen ink. For each ink, the amount of volatile components were calculated³². A second set of samples were submitted to induced aging for 1 hour at 70°C and the amount of volatile components were calculated. The induced aging was for 1 hour at 70°C. The relative difference between the measured amount P of a volatile component before heating and the amount PT after heating is

$$R(\%) = \{(P - P_T)/P\} \times 100$$

In all cases R(%) levelled off after about 3 to 5 months of aging.

As to why acetonitrile, which appears to be a good all extracting strong solvent, was not used as in the first procedure as the second solvent is not clear.

5. *Other Techniques* - Though not as developed, other ideas have been proposed for investigating relative aging. Some are:

a. Using an HPLC Flow Cell to Measure Extraction - Issacs and Clayton [20] noted that the existing extraction methods "relied heavily upon the manipulative skill of the examiner." Their attempt was to reduce such demands by continuously extracting (using a polar solvent) a single ink/paper microdot directly into an HPLC micro flow cell in a diode array spectrophotometer. The plot of absorbance (at a chosen wavelength) -vs-time (of extraction) begins with a sharp rise from zero as extraction begins and then levels back to zero as the extraction ends. Typical heights for the initial rise of these "extraction" curves are 100 and 200 micro absorbance units. Seven ballpoint inks were studied and twelve polar solvents were considered. The only mass invariant measurement available with this method is a measure of the rate of extraction (how rapid a given solvent extracted). This was shown not to be reliable. However, the extent of extraction (the rise in the extraction curve) is more reliable - but it requires equal sampling. Clearly, this approach merits further research.

b. *Observing the Residue Rather than the Extract in Extraction Methods* - When this author was researching the extraction techniques, Ms. Ellen Pinchney (a bright college summer intern at the FBI academy working with

him) proposed comparing the color of an ink before and after extraction as a guide to how much was extracted (the extent of extraction). The problem was obtaining a reliable measure of the color that would be linear with amount of ink deposited. The Kubelka-Munk theory of reflectance offered a solution but at the microscopic level its reliability was questioned. If such measurements could be done, then a mass invariant parameter can be obtained by taking the ratio of the extracted ink color to the unextracted ink color. The whole procedure would be much simpler than the sequential solvent extraction method used to get extent of extraction. Under controlled conditions, the method works well just by using visual observation. This approach also deserves further research.

c. *Reinvestigating the Copying Capacity Methods* - Mitchell built his solubility test on the observation made by several of his predecessors that the "copying capacity" of inks decreases with age¹⁷. Witte [5] used it in a ballpoint ink dating case. Using Kromekote as the transfer media, Caponi [28] used it for differentiating ballpoint inks but also noticed the effect of age. Yablokov [27] discusses several methods to create the transfer media and recently, Aginsky used it as an aid for his hypothesis on ink surface aging-vs- ink interior aging (see above). This author used it in conjunction with accelerated aging (using heat) as a quick guide for seeing if the ink was still aging and for selecting the solvent for an extraction measurement. He observed that what transfers from an ink onto a substrate impregnated with a solvent is not only ink and solvent dependent, but can be quite different from what extracts into a solvent. One ink, for example, was found not to transfer onto a pyridine-soaked substrate (but it extracted well into pyridine); yet it transferred well into an n-butanol-soaked substrate. This and other observations reflect Aginsky's hypothesis on ink surface aging. Direct contact transfer methods appear to offer clues of the aging process.

Absolute Age of Ink Entries

A. **Background** - In his chapter on dating problems, Harrison [29] presents several methods for static³³, absolute, and relative age determinations. Absolute age, according to him, is "the maximum age a document is likely to be" and its determination is "demanded when the whole document is suspected to be a fabrication". We shall restrict our definition of the absolute age of an item on a document to mean the establishment of the preparation date of that item by following its aging process.

The following discussion is based on published results by Roderick

³²Due to the presence of only one volatile component in all inks except the Senator, no mass invariant measurements could be made (an internal standard in the extraction solvent does not help), so one had to very carefully sample equal amounts (see above under mass invariance). For the Senator ink, Aginsky did use mass invariant ratios of the volatile solvent components and the volatile solid component.

³³Of interest is Harrison's method to distinguish oil-based and glycol-based ballpoint inks (introduced around 1951). At the time he wrote his book (first published in 1958), these inks could be distinguished using a drop of petroleum ether on an ink stroke (Harrison [29], p. 217); the petroleum ether disperses the oil-based ink more readily than the glycol-based ink. In the 1970s this author tested ballpoint inks known to have been written in the 1940s (therefore oil based). The test did not work. This is probably due to the age-setting (oxidation) of the oil-based inks with age. Thus what was thought to be an age independent test turned out to be age dependent.

McNeil and reports about his findings on several cases [30-36]. His claim that (a) certain metal ions migrate outwardly from an ink line as the ink ages (as determined using scanning Auger microscopy) and (b) this migration is independent of temperature and humidity, has not been independently verified. Hopefully, this discussion will encourage interested investigators to evaluate McNeil's technique and assess its merits and limitations.

B. Work of McNeil [30-33] - Roderick McNeil made the empirical observation that once iron gallotannate inks dry and the capillary migration ceases (such migration sometimes cause feathering), a secondary, age dependent, migration occurs within the paper fibrils

This secondary migration is of iron ions (ferrous ions, Fe⁺⁺) and is measured using scanning Auger microscopy. This iron migration is not to be confused with the chloride or sulfate observed by Mezger, Rall, and Heess [8] and discussed earlier. Iron migration is much slower, more microscopic, and seems to continue for over 700 years. For example, the iron ions migrate about one micron every 29 years. These facts are based on the analysis of inks from a large collection of old manuscripts.

The spacial resolution and elemental specificity of Scanning Auger microscopy allows one to measure the iron ion migration changes to within 700 Angstroms (0.07 microns). As indicated above, after 700 years, the migration of iron ions is about 24 microns. If the migration is linear with age, the instrument's high resolution should provide an accuracy in dating to be within $(700/24) \times 0.07 = 2$ years. Due to the non-linearity of migration-vs-age, the error bar is not constant but increases with age. Furthermore, multiple measurements show statistical inter- and intra-sample variations. These factors and the non-linearity, give an average accuracy for dating of 44 years (± 22 years) at the 90% confidence limits [30].

The aging curve for the iron ion migration is dependent on whether the ink is on paper, vellum, or parchment³⁴. All, however, show an increase in migration with age over a 700 year period. Most inks studied were iron gallotannate inks, but some contained mercury (such as cinnabar-based vermilion inks) or lead (such as some impure ink ingredients, ink additives, chrome yellow or red lead inks). The ions of these elements also undergo secondary migration and McNeil has aging data for these.

1. *Sampling*: McNeil's instrument can sample a page up to 36 square inches. Preferred, however, are hole punches (obtained using an eight-gauge hollow hypodermic needle) since the examinations are done under high vacuum and the de-gassing time for the chamber is highly reduced with smaller samples. For each ink, McNeil samples at five different sites (different fibrils) and makes triplicate measurements at each site (same fibril).

2. *The Auger Electron Phenomena*: The sample is bombarded with electron (not x-rays) and these eject (Auger) electrons from each atom (above atomic number 15) in the sample. The energy of each of these ejected electrons is dependent on the atomic number of the atom. The escape depth of these electrons is 10 Angstroms making the technique a highly specific surface analysis technique.

³⁴McNeil does not provide a mechanism as to why ions migrate in vellum or parchment, as he does for paper. Paper, he contends, contains paper fibrils which act as cellulosic paths for the migration.

3. *Iron Counts-vs-Migration Distance*: If one takes measurements perpendicular to an ink line, the shape of the iron count grows sharply as the sample probe enters the inked area and decreases sharply after it leaves the inked area. To obtain mass independence, McNeil normalized his curves to 100% and a most interesting phenomena emerged at the edges at the "capillary shoulder." All iron count-vs-distance curves begin at 100% (where the probe is at the ink edge) and drop down to an inflection at about 4.7 microns from the ink edge (this portion McNeil calls the lead tail, its the same for all inks). After this, the curves descend in an exponential-like manner to zero at a distance that is characteristic of the ink age.

This portion of the curve McNeil calls the skewed tail and its shape is characteristic of the ink age. As the age of the ink gets older, the shape of the "skewed tail" grows less steep and it levels off to zero at a progressively longer distance.

4. *Linearization*: McNeil does not measure this migration distance directly; he takes instead the integrated area of the skewed tail since this is a more precise measurement than the distance travelled. Because of the exponential-like behaviour, the natural log (ln) of this area can be shown to be directly related to the migration distance. Furthermore, this $\ln[\text{area}]$ gives a nearly-linear increasing curve with age. (The curve has a gentle downward curvature as the ink gets older). This is the closest he got to a "linearized" working curve for computing ink age from an aging parameter.

C. Effects of Accelerated Aging - McNeil evaluated the effects of temperature and relative humidity on the aging process over a six month period. He made his own ink using a prescribed formula and applied it to standard paper and unknown vellum and parchment. Temperatures ranged from 100°C to 200°C and all were at their saturated dew points. He found no detectable change in the integrated area. He concludes that so far, "no environmental conditions have been found that could produce the tailing effect described" [30]. Thus, once the ink dries on the paper, the migration process begins - apparently unaffected by environmental factors - for over 700 years. The extent of migration seems to provide the absolute age of ink (to within some confidence limits).

D. Exceptions - McNeil found that acid neutralization stops the migration process [32]. Before doing an Auger analysis of ink, one should establish if the document has been acid neutralized. If it is not known, a non-inked area is scanned using EDAX (Energy Dispersive Analysis by X-Rays) for the presence of high concentrations of iron, zinc, and calcium (elements whose cations are used in acid neutralization). Such cations saturate the carboxyl groups in the fibril cellulose and inhibit the ink's ferrous ion migration process. Though acid neutralization treatments halt the migration, it does not affect the migration that has already taken place.

E. Examples - Out of the numerous documents of historical importance that McNeil has analyzed, four may be known to forensic scientists. Two of these pertain to forgeries made by Mark Hoffman (Utah). One is the Mormon salamander letter [32] and the other is the less-known "Oath of a Freeman" [33]. The third is the Jack the Ripper diary that surfaced in 1992 [34,35]. The fourth is a "sixth final draft" of the Gettysburg Address [36]. The following summarizes the results of these analyses:

	Alleged Date	Determined Date \pm C.L. at 90% (95% for 6th copy of Gettysburg Address)	Element Measured
Salamander Letter [32]	1834	1965 \pm 35 yrs	Fe
Oath of a Freeman [33]	1792 (1 st copy)	1956 \pm 75 yrs	Pb
	1638/39 (2 nd copy)	1940 \pm 50 yrs	Fe
Jack the Ripper Diary [34,35]	1889	1921 \pm 12 yrs	Fe
"6th" Gettysburg Address [36]	1863	1869 \pm 10 yrs (body)	Fe
		1875 \pm 15 yrs (obverse)	Fe

Some of these results have caused controversy in the historical and scientific community particularly with the accuracy and precision (reliability) of the determined date. McNeil, however, states the statistical fact that the percent confidence (90% or 95%) taken for the confidence limits (C.L.) allows for the true date to be outside these limits but at a considerably lower probability the further out it goes. Also note that date authenticity does not necessarily imply authorship authenticity.

At present, McNeil is the only person using scanning Auger microscopy to study the outward, age-dependent migration of (iron, lead, or mercury) ions from inks on a surface. Though his overall analysis covers determining the elemental profiles of inks (using EDAX, for example), the use of such profiles for dating inks via the static approach is rather limited since, as far as this author knows, the only library of elemental profiles of inks is rather small, limited to printing inks, and obtained using the PIXE technique [1].

Aging of Paper

A. Introduction - Suppose all the pages of a multi-page document have the same watermark, chemical/elemental profile, and, except for one, the same folding endurance. This indicates that the odd sheet may be a substitute, and the question of its age relative to the age of the others may be important. This may be answerable since folding endurance happens to be an aging parameter that has been extensively studied and its aging curves exist for many papers. Other aging parameters include tensile strength (similar to folding endurance), optical reflectance, yellowing, and fluorescence.

B. Folding Endurance Aging Curves [37-41] - The change in folding endurance with age (at a given ambient temperature and relative humidity) is extremely slow; therefore, scientists study the changes under several accelerated aging conditions (like several elevated temperatures) and extrapolate to ambient conditions. The relative humidity for each elevated temperature is kept the same as that at the given ambient conditions.

At a given elevated temperature, the \ln [folding endurance] is found empirically to decrease linearly with age. The slope is a parameter called the rate constant. Thus, the folding endurance aging curve decreases non-linearly (exponentially) with age. The rate constant governs the shape of the curve. The equation for the folding endurance aging parameter $P(t,T)$ as a function of age t and temperature T (in $^{\circ}\text{C}$) is:

$$P(t,T) = P(t=0,T) \times \exp[-k(T)t]$$

where $k(T)$ is the rate constant as a function of temperature T . Its units are in "per age unit" (such as days^{-1} to years^{-1}). $P(t,T)$ begins with the value for fresh paper and levels off to zero as the paper ages. Its linearized form is:

$$\ln[P(t,T)] = -k(T)t + \ln[P(t=0,T)]$$

Folding endurance aging curves determined at several elevated temperatures have different shapes and, consequently, different rate constants. The \ln [rate constant] is found empirically to decrease linearly with the inverse of the temperature (in degrees Kelvin, $^{\circ}\text{K} = ^{\circ}\text{C} + 273.16$). The slope provided the parameters called the activation energy of the aging process. Thus, the rate constant increases non-linearly³⁵ with temperature. The activation energy governs the rate of this increase (the sensitivity to temperature). The equation for $k(T)$ as a function of temperature T (in $^{\circ}\text{C}$) is:

$$k(T) = \text{constant} \times \exp[-E^*/R(T + 273.16)]$$

where $R = 1.987 \text{ cal/mol}\cdot\text{degree}(\text{K})$ is the gas constant and E^* is the activation energy in cal/mol . Its linearized form is:

$$\ln[k(T)] = -[E^*/R] \times [1/(T + 273.16)] + \ln[\text{constant}]$$

By computing rate constants for several elevated temperatures, one can deduce the rate constant at ambient temperature (and thus the natural aging curve) by extrapolation. This is called the Arrhenius method since the above equation for $k(T)$ was empirically found by Arrhenius to hold for the kinetics of many first order chemical reactions. Consequently, there is a strong tie between folding endurance and the "chemical" kinetics of paper aging.

C. Equivalence of Natural and Accelerated Aging [38] - Another way to deduce the rate constant at ambient temperature is by computing the activation energy E^* and using the Arrhenius equation as follows. By taking the ratio of the rate constant at an elevated temperature to the rate constant at an ambient temperature (to be determined), one obtains an equation that is solely dependent on the activation energy E^* . From this, the rate constant at an ambient temperature can be obtained. This ratio also provides the number of days at an ambient temperature that are equivalent to the number of days at an elevated temperature. This equivalence is only with respect to the particular aging parameter under consideration. The dependence on E^* is exponential as seen in the following reported values [38]³⁶ for the folding endurance tested on ten different permanent/durable book papers (Roberson) and on other paper:

³⁵Since the rate constant decreases *exponentially* with $1/\text{temperature}$ and $1/\text{temperature}$ increases *hyperbolically* with decreasing temperature, then the rate constant decreases non-linearly with decreasing temperature.

³⁶The (3 days at 100°C) equivalence values were cited by Roberson [38]; the 19 year (Wilson/Rasch) value is the average of 18.5 and 20.5 years; the (4 min. at 100°C) equivalence values follow by substitution; the rate constant ratios also follow by substitution; and the activation energies were computed using the Arrhenius equation.

Activation Energy E* in Kcal/mol	Ratio of k(100°C) to k(22°C)	Number of Years @ 22°C Equivalent to 3 Days @ 100°C	Number of Days @ 22°C Equivalent to 4 Min @ 100°C
21.7	2,311.7	19 (Wilson/Rasch)	6
22.5	3,041.7	25 (Barrow)	8
22.8	3,406.7	28 (van Royen)	9
25.3	8,273.4	68 (Roberson)	23
30	37,230.1	306 (Browning/Wink)	103

This reporting says nothing about the actual rate constants. Some typical values as a function of temperature are graphically reported by Roberson [38] for the paper he studied. Computing from these the value $t_{1/2} = \ln 2/k = 0.693/k$ which is the time taken to get half way down the folding endurance aging curve, we have:

Rate Constant k	$t_{1/2} = \ln 2/k$	Temperature
0.1/day	6.93 days	87°C
0.01/day	69.3 days	65°C
0.001/day	693 days (1.9 yrs)	44°C
0.0001/day	6930 days (19 yrs)	24°C

The thing to notice is that at room temperature, for example, it takes 19 years for the folding endurance to get 1/2 way down on the aging curve, another 19 years to get 3/4 the way down, another 19 years to come 7/8 the way down, and so on. To level off to the point where after this no differences are detected, it may take an excess of 100 years - depending on the margin of error.

D. A Relationship to Ink Aging [3] - An important thing to notice is that paper ages (in folding endurance) more slowly than ink (in extractability, solvent evaporation, etc.) since the studies presented here on ink aging indicate the *levelling Off* age is somewhere within 10 years (or perhaps longer for the Sen and Ghosh [18] analysis). An ink aging equivalence has been determined for the extent of extraction (into a MeOH:H₂O = 1:3 solution) of a Rhodamine-type dye from a Fisher black ballpoint ink on Nashua (photocopy) paper [3]. For this particular ink, paper, and aging parameter, 4 minutes of induced ink aging at 100°C is equivalent to 72 days of natural ink aging at 22°C. This equivalence (which corresponds to an activation energy of 29.2 Kcal/mol) shows that the sensitivity of the ink aging rate constant to changes in temperature is within those sensitivities of paper.

E. Some Recent Studies - At least fifteen presentations were made on the effects of aging on printing and wiring paper at a recent workshop held in July, 1994 at the ASTM headquarters in Philadelphia, PA. Two of these were on artificial and accelerated aging. Priest [39] addressed the extrapolation of artificial aging to natural aging. He emphasized the empirical nature of the Arrhenius method and pointed out the limitations, criticisms, and misunderstandings which have resulted from its use. He offered suggestions for improving the methodology. Shahani [40] questioned if accelerated age testing can predict the permanence of paper. He studied the accelerated aging of paper as a group in a stack; as individual sheets; and as sealed within polyester film. These yielded aging curves that are not easily linearized by a logarithm function (and thus do not follow the Arrhenius method to relate to natural aging). At a different gathering, Erhardt and Mecklenburg [41] reported how temperature and relative humidity (RH) affect several individual reactions involved in the aging process of paper cellulose. They pointed out that to properly relate accelerated aging to natural aging, the induced aging must accelerate the complex aging process

(involving many individual aging processes) without fundamentally altering it. By studying the individual reaction products in cellulose (at conditions between 60-90°C and 30-80% RH), they showed that the cellulose aging process is highly dependent on RH and relatively independent of temperature. Thus, raising the temperature at constant RH accelerates the cellulose aging process without essentially altering it; however, if the RH changes, an equivalent aging state cannot be reached. This supports the importance of retaining the same relative humidity in accelerated aging determinations as that of the natural aging sought. This assists in retaining the same moisture content.

III. Conclusion

This final part of the sketch on dating documents outlines currently known methods for determining and following changes in ink or paper as they age and how these methods are used to establish their approximate age. For inks, the aging process usually begins when they are placed on paper. For paper, it begins after it is manufactured. Aging measurements are vast and different. Some measure slow processes that cease after a long time, others measure fast processes that cease quickly, while some measure a combination of both. For inks, some processes continue for several years, while for paper some continue for many more years. Most of the methods presented attempt to determine when inks of the same formula were placed on a sheet relative to one another. These determine relative aging. The aim of the methods has not only been to determine if an ink entry was prepared at a later date than purported (detection of backdating fraud), but to answer the more difficult question of determining if an ink was actually placed on a document on the alleged date (detection of date authenticity).

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