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## COMPARISON OF WRITING INKS BY PAPER CHROMATOGRAPHY

Albert W. Somerford

Albert W. Somerford is an examiner of questioned documents and Director of the Handwriting Evidence Laboratory, Bureau of the Chief Post Office Inspector, Washington, D. C. During the last few years he has been associated with Dr. Wilmer Souder of the Bureau of Standards in a research project involving the application of chromatographic analysis of writing inks. The method was first described by Dr. Souder at the meeting of the International Association for Identification during the summer of 1951, and Mr. Somerford in this present paper describes briefly the procedure and its value.—EDITOR.

Questioned document analysts have often been confronted with the problem of determining whether all of the writing on a particular document or on different documents was done with the same ink.

Solutions to these problems have heretofore been undertaken by various methods such as the use of chemical reagents, infrared photography, and spectrography. These methods and their limitations are well known to the profession and need not be discussed here. Recently, a new approach known as "paper chromatography" was introduced in the field of ink examination. This method has already been found a valuable aid in many cases and offers the advantage, among others, of permitting results of laboratory tests to be graphically illustrated before courts of justice.

Weil<sup>1</sup> traces the origin of the method of filter paper capillary analysis to the German scientist F. F. Runge who, in 1850, described the use of blotting paper for the analysis of mixtures of dyes. In 1885 J. U. Lloyd submitted a report on filter paper partition to the American Pharmaceutical Association. Pliny (23-79 A. D.) is reported to have used a test paper for detecting ferrous sulphate. It was not until 1951, however, after extensive research, that the merits of the technique in relation to the examination of writing inks was publicly revealed.<sup>2</sup>

During the 17th, 18th, and the greater part of the 19th centuries, iron-gall inks were used almost exclusively in the United States. The 20th century brought about the use of increased amounts of aniline dyes (unavailable before 1860) and less iron and tannin. The chromatographic method of analysis is especially applicable to dye-base inks. Comparisons are further facilitated by the frequent occurrence of several dyes in a single ink.

*Ink in Liquid Form.* Two inks in liquid form can be readily compared by chromatography using only distilled water and filter paper.

1. Herbert Weil, Scientific American, June 1951.

2. Wilmer Souder, and Albert W. Somerford, (Conference of International Association for Identification at Philadelphia).

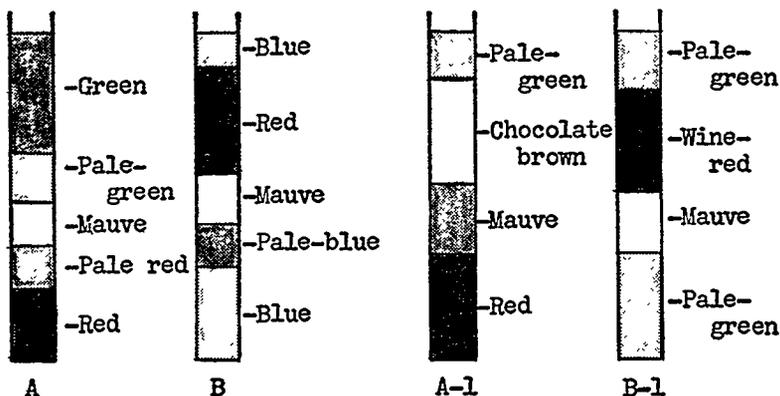


Figure 1

Filter paper chromatograms of two inks in liquid form, showing different compositions. (A & B) Appearance in daylight. (A-1 & B-1) Appearance in filtered ultraviolet radiation.

This may be accomplished as follows: A droplet of a known sample A and a droplet of an unknown sample B are diluted with distilled water in a ratio of 1 to 20, using separate crystallizing dishes. One end of a strip of Whatman #1 filter paper about 10 cm long and 6 mm wide is dipped in each of the dilutions. After the dilutions rise approximately one-fourth the length of the paper, the strips are withdrawn.

The same tips of the paper strips are then suspended for several minutes in a crystallizing dish containing plain distilled water. As the water is absorbed, the soluble ingredients continue their vertical expansion on the paper. In the case of inks containing more than a single dye, the colors will phenomenally arrange themselves in individual zones. It is highly important that, at the commencement of this second phase of treatment, small beakers containing hot water be placed alongside the crystallizing dish, and the whole covered with a glass bell or similar unit to achieve the desired saturating atmosphere so essential for optimum elution. The transparent cover also allows the analyst to observe and control the degree of vertical expansion of the soluble substances on the filter paper by enabling treatment to be arrested at the proper time. When this occurs, the chromatograms of inks A and B are withdrawn, for visual comparisons after drying.

If comparisons of the two chromatograms reveal bands of different color and elementary ingredients, the two inks are obviously dissimilar in composition. In the event the color zones are of the same shade and distributed in analogous fashion on the chromatograms, one should not at this stage conclude that A and B are of the same composition. To more definitely establish this identity, it is necessary only to mix

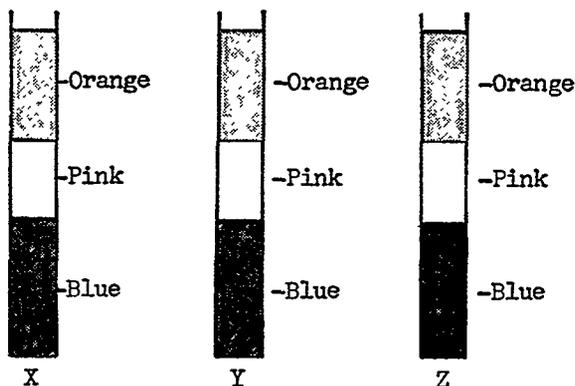


Figure 2

The identity of two ink writings are shown by the location and presence of the same color zones in the separate (X & Y) and combined (Z) filter paper chromatograms, as viewed in daylight.

samples of inks A and B and prepare a separate or third chromatogram thereof in the manner heretofore described. If the resultant chromatogram of the combined inks exactly matches the two preceding ones, it can be said that chromatograms A and B are identical. Should, however, the chromatogram containing the combined inks differ by the presence of more numerous color bands than in chromatograms A and B, or if the same colors in chromatograms A and B and on the combined strip appear displaced with reference to one another, the two inks are of different composition. Further distinctions may be observed by examination of the strips in filtered ultraviolet radiation (Figure 1), as in the case of colorless chromatograms discussed later in this paper.

*Inks in Dried Form.* To establish the identity or diversity of two inks in dried form, simply place a minute droplet of water with a pipette or a platinum wire micro-loop of .4 mg capacity, directly on a written stroke of each document, preferably where there is a generous deposit of ink. As soon as dissolution takes place, generally within two minutes, take up this residue with a narrow strip of Whatman #1 filter paper about 1 mm wide and 6 mm long, holding it obliquely on the area being treated for the time necessary to absorb the entire droplet. Then proceed with the second phase of the treatment mentioned under *liquid* inks, except that the time allowed must be restricted, due to the use of the smaller strips. Where the chromatograms of the two inks match, their identity can be further established by preparing a third chromatogram (Figure 2). This is achieved by applying distilled water with a pipette to each writing in proper sequence, successively combining the residues of both on the same paper strip, and according it the prescribed final treatment.

Conclusions concerning the identity or non-identity of two inks should, of course, not be reached until a control test has also been made of the surface coating of the paper, which may be tinted or contain impurities.

The subsequent use of reagent indicators on the chromatograms may further serve to distinguish between dyes by their specific color reactions. This phase, however, requires additional research.

The chromatographic method can be adapted to work on greatly varying scales. No definite rules can be advanced for the most suitable size of filter paper to use or for the time required for treatment under the glass bell (generally one to fifteen minutes for ink in both dried and liquid form), since this is largely determined by the variety, quantity, tinctorial power, and solubility of the dyes present. It should be mentioned that if the chromatograms, when inserted in the distilled water, are allowed to remain beyond the period when the dyes are observed to be properly dispersed, the colors will eventually group at the opposite end of the paper strip.

By the new method of analysis some inks (like Sanford's, Shaeffer's, and Carter's black) were found to produce distinctive color bands readily distinguishable from all other brands tested. It follows that, in the absence of previous or subsequent formula duplication, one may establish with a reasonable degree of accuracy the identity of a particular brand of ink.

The majority of the so-called "permanent" inks contain mineral salts as a base. These are in the blue-black category to which dyes have been added to render the writing more pleasing in color. Since the dyes in writings of this group are more resistant to the application of water due to oxidation, the resultant chromatogram may appear colorless. This, however, raises some question concerning the propriety of the term "chromatogram." Williams<sup>3</sup> believes "adsorption analysis" is more fitting than "chromatographic analysis," because the former applies equally to colored and colorless substances. The merit of this appears obvious. Where the chromatograms are colorless, they may be exposed to the rays of filtered ultraviolet, which in some instances produces characteristic color fluorescences, as in the case of chromatograms of similar color but visually indistinguishable. Examination by this radiation as a routine procedure is, therefore, strongly recommended.

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3. Trevor I. Williams, *An Introduction to Chromatography*, Chemical Publishing Company, 1947, Brooklyn, N. Y.