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Comparison of Typewriter Ribbon Inks by Thin-Layer Chromatography

Examiners of questioned or disputed documents are frequently asked to ascertain whether or not the text of a typewritten document has been altered by the use of either a different typewriter or the same typewriter at a later date. Any technique that can distinguish among the various commercially available typewriter ribbon inks is a potentially valuable tool to the examiner of questioned documents.

Traditional methods for the detection of altered typewritten documents involve (1) identification of the type design; (2) identification of specific typewriters by detection of worn, broken, or misaligned type faces; (3) measurement of line spacing, margin spacings, and ribbon characteristics; and (4) measurement of vertical and horizontal alignment with ruled glass plates. These traditional methods are often sufficient to prove that typewritten entries were altered or added at a time subsequent to the original typewritten text.

When these methods fail to reveal this type of fraud, either the typewritten document is authentic or the methods used were not sufficiently discriminatory to detect the alleged fraud. Analysis of the typewriter ribbon ink can (1) provide additional corroborative evidence that the questioned document is authentic, (2) prove that a different typewriter ribbon ink was used for subsequent alterations or additions, or (3) provide inconclusive results if the original typewritten entries and the questioned entries were made with the same type of ribbon, either on the same or a different typewriter.

No extensive research studies have been reported on the chemical analysis of typewriter inks; however, a few feasibility studies have been reported. Somerford [*1*] reported that by using a paper chromatographic technique it was possible to analyze and compare the dyes in ribbon impressions. Brown and Kirk [*2*] described a reagent-type identification system used on fibers removed from the surface of the typewritten material. They also experimented with horizontal, circular paper chromatography as well as electrophoresis for the comparison of typewriter ribbon inks. In their study only ten typewriter ribbons were analyzed; however, all ten ribbons were found to be distinguishable by the reagent color reaction technique. The FBI Law Enforcement Bulletin [*3*] described a thin-layer chromatographic procedure for the comparison of typewriter ribbon inks; however, differentiation resulted in only 25% of the ribbons examined. Tholl [*4*] also experimented with the thin-layer

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chromatographic technique and applied this procedure to the analysis of all major types of writing inks as well as typewriter inks.

The limited success of previous studies warranted a more extensive investigation regarding the feasibility of distinguishing typewriter ribbon inks by thin-layer chromatography. This paper discribes the results obtained from the analysis of over 150 typewriter ribbons obtained from seven major manufacturers of typewriter ribbon inks: (1) Allied Carbon and Ribbon, (2) Phillips Processing, (3) Curtis Young, (4) Burroughs, (5) Olivetti, (6) Frye Copysystems, and (7) Carter.

Experimental Procedure

The procedure for the analysis of typewriter ribbon inks is similar to the procedure previously reported [5] for the comparison of ballpoint and other writing inks.

The typewriter ribbons were cut with scissors into 1-cm^2 pieces and placed into two-dram, screw-cap, disposable glass vials. Reagent-grade pyridine (3 ml) was added to each sample to extract the ink from the ribbons and allowed to remain for 30 min to insure sufficient extraction.

One microlitre of the dissolved ink was spotted on a Merck precoated silica gel glass plate by using a 1-μl disposable glass pipet. The ink spot was allowed to air-dry at room temperature for 15 min, and then each chromatographic plate was developed in covered glass tanks (8 by 8 by 3 in. or 20 by 20 by 8 cm) containing (A) ethyl acetate, ethanol, and water (70:35:30) and (B) n-butanol, ethanol, and water (50:10:15). The chromatographic plates were allowed to develop 30 min in Solvent system A and 60 min in Solvent B. After the plates were air-dried at room temperature they were compared visually with ordinary white light and ultraviolet light.

Results and Discussion

The thin-layer chromatography (TLC) procedure described is highly discriminatory for the various brands of typewriter ribbons. A wide variety of colors are available in typewriter ribbon inks, such as black, blue, red, green, purple, and brown. Figures 1 and 2 show the TLC results on several colored typewriter ribbon inks.

In most instances, typewriter ribbon inks of the same color produced by different manufacturers could be easily distinguished after running just one TLC with Solvent A. All inks

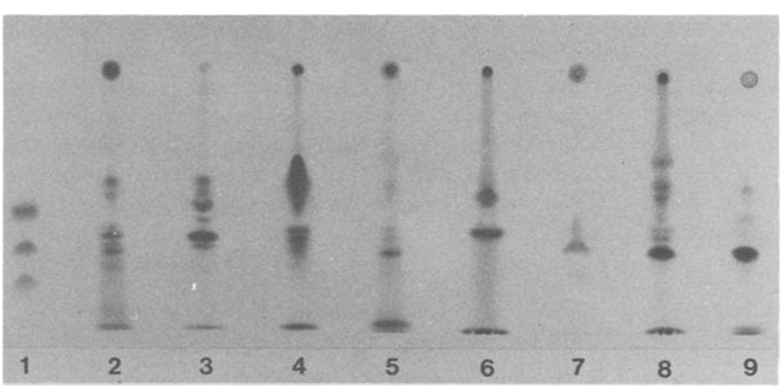

FIG. 1—*Comparison of different colored typewriter ribbon inks manufactured by Allied Carbon and Ribbon;* (1) *red;* (2) *black;* (3) *blue;* (4) *purple;* (5) *brown;* (6) *green;* (7) *red;* (8) *blue; and* (9) *black.*

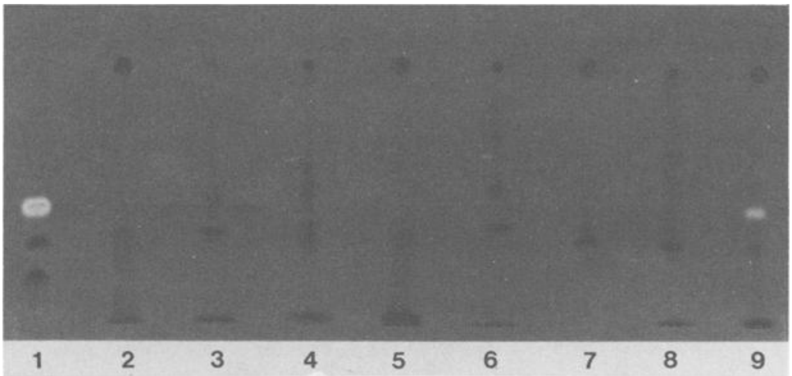

FIG. 2—*Comparison under ultraviolet light of different colored typewriter ribbon inks manufactured by Allied Carbon and Ribbon;* (1) *red;* (2) *black;* (3) *blue;* (4) *purple;* (5) *brown;* (6) *green;* (7) *red;* (8) *blue; and* (9) *black.*

of the same color from different manufacturers could be distinguished when two solvent systems were used. Typical manufacturer differences are shown in Figs. 3 to 6 (black and red ink ribbons). Either the inks have different dye and fluorescent components or the components are present in different concentrations.

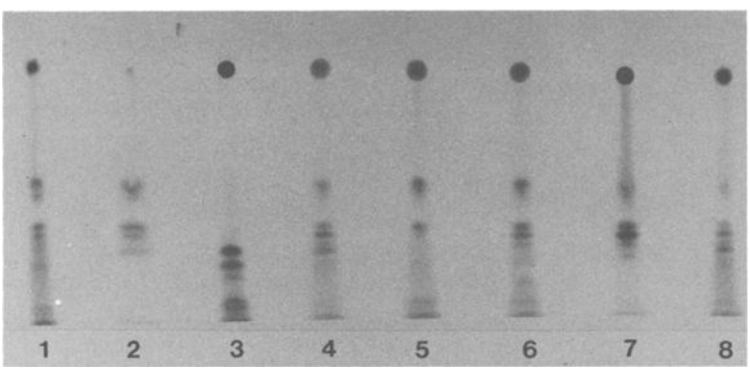

FIG. 3—*Variations in black ribbon inks made by different manufacturers;* (1) *and* (2) *Olivetti;* (3) *Carter;* (4) *Allied Carbon and Ribbon;* (5) *Burroughs;* (6) *Curtis Young;* (7) *Phillips Processing; and* (8) *Frye Copysystems.*

Figure 7 shows a typical comparison of chromatograms run on different batches of the same formula ink produced by the same manufacturer. The results were inconsistent; some inks showed insignificant batch variations while others showed dramatic differences from batch to batch. Figures 8 to 11 illustrate that some manufacturers of typewriter ribbon inks produce several different formulations of the same color ink.

An experiment was conducted to determine the effects, if any, of paper and ribbons on typewriter ink. Samples of the same pure liquid ink, ink dissolved from sufficient typewriting on paper, and ink dissolved from ribbons were analyzed by TLC and compared. Figure 12 shows that, except for concentration differences, the results are the same. This finding indicates that paper and ribbons have no deterioration effect on the pure ink.

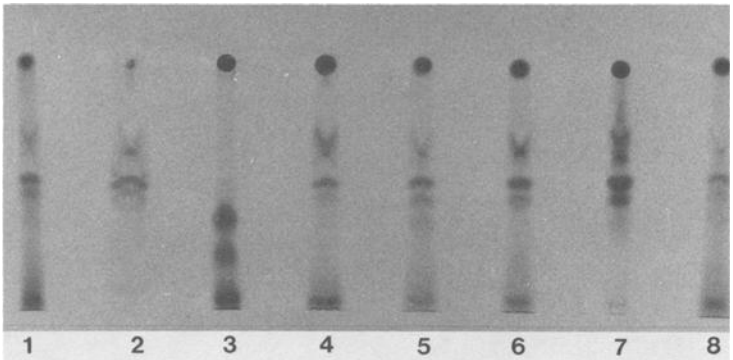

FIG. 4—*Variations as determined by Solvent B in black ribbon inks made by different manufacturers;* (1) *and* (2) *Olivetti;* (3) *Carter;* (4) *Allied Carbon and Ribbon;* (5) *Burroughs;* (6) *Curtis Young;* (7) *Phillips Processing; and* (8) *Frye Copysystems.*

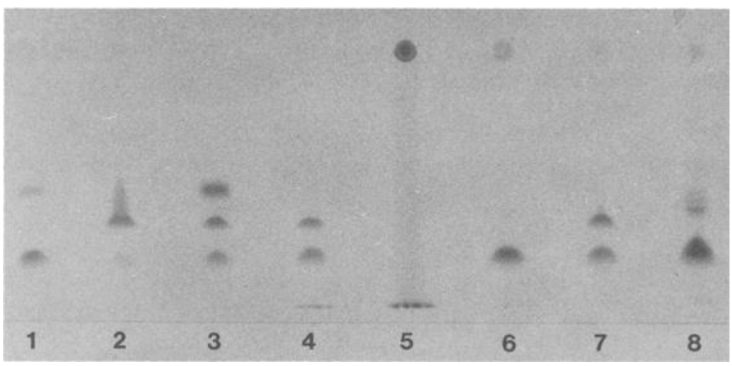

FIG. 5—*Variations in red ribbon inks made by different manufacturers;* (1) *Olivetti;* (2) *Carter;* (3) *and* (4) *Allied Carbon and Ribbon;* (5) *Burroughs;* (6) *Curtis Young;* (7) *Frye Copysystems; and* (8) *Phillips Processing.*

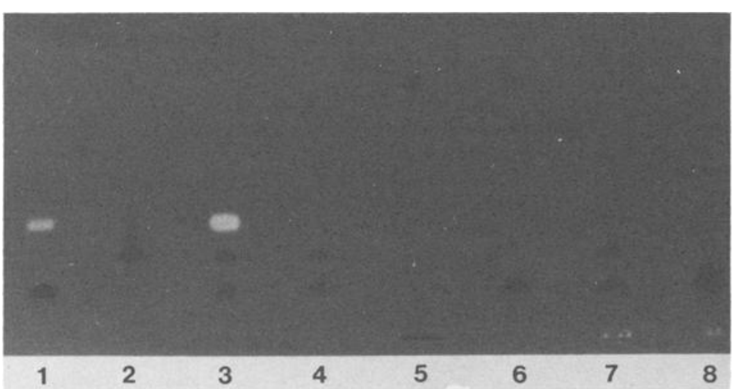

FIG. 6—*Variations under ultraviolet light in red ribbon inks made by different manufacturers;* (1) *Olivetti;* (2) *Carter;* (3) *and* (4) *Allied Carbon and Ribbon;* (5) *Burroughs;* (6) *Curtis Young;* (7) *Frye Copysystems; and* (8) *Phillips Processing.*

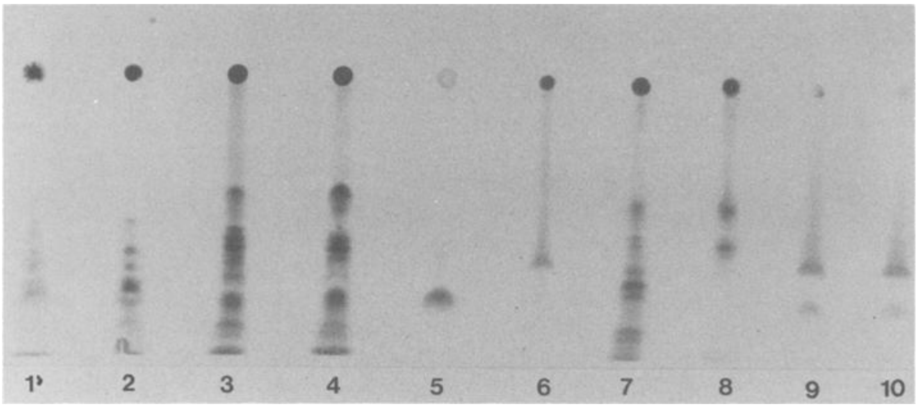

FIG. 7—*Batch variations;* (1) *through* (6) *Curtis Young;* (1) *A1 black;* (2) *A2 black;* (3) *B1 black;* (4) *B2 black;* (5) *C1 red;* (6) *C2 red;* (7) *through* (10) *Carter;* (7) *A1 black;* (8) *A2 black;* (9) *B1 red; and* (10) *B2 red.*

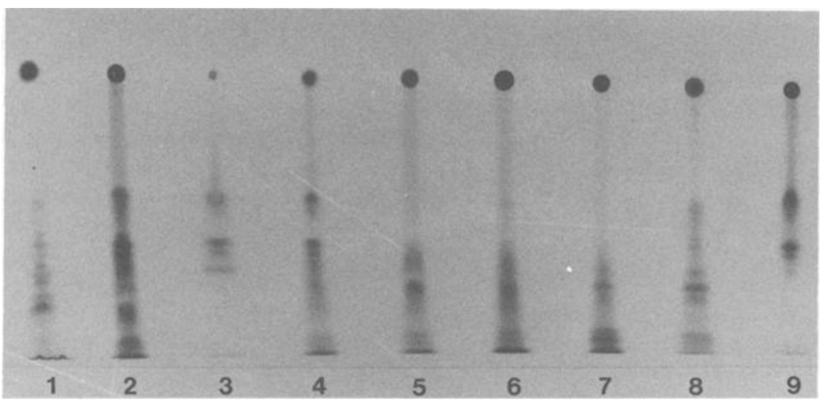

FIG. 8—*Variations within manufacturers in formulas for black inks;* (1) *and* (2) *Curtis Young;* (3) *through* (7) *Olivetti; and* (8) *and* (9) *Carter.*

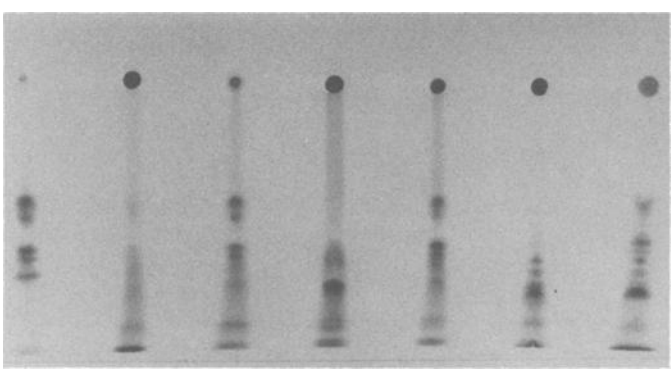

FIG. 9—*Variations in black inks made by Olivetti.*

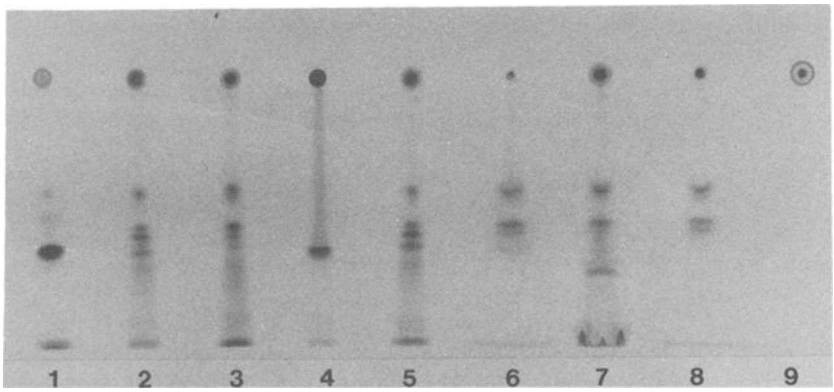

FIG. 10—*Variations in black inks;* (1) *through* (5) *Allied Carbon and Ribbon; and* (6) *through* (9) *Burroughs.*

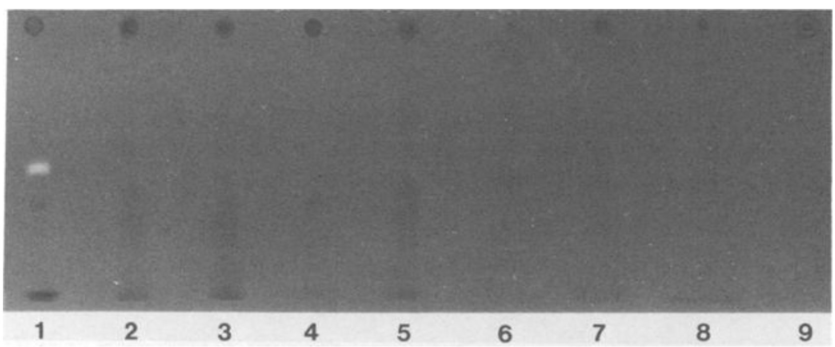

FIG. 11—*Variations under ultraviolet light in black inks;* (1) *through* (5) *Allied Carbon and Ribbon; and* (6) *through* (9) *Burroughs.*

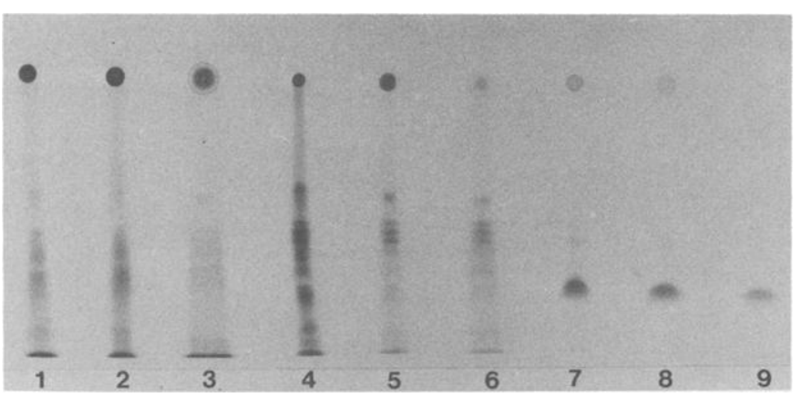

FIG. 12—*Comparison of liquid, ribbon, and dry inks;* (1) *through* (3) *Olivetti;* (1) *black liquid;* (2) *black ribbon;* (3) *black dry;* (4) *through* (9) *Curtis Young;* (4) *black liquid;* (5) *black ribbon;* (6) *black dry;* (7) *red liquid;* (8) *red ribbon; and* (9) *red dry.*

To determine the minimum amount of typewriting sample required to conduct a meaningful comparison, an additional experiment was conducted by TLC. The lowercase *l* was used as the sample for this test. Thin-layer chromatograms were prepared using one *l*, two *l*'s, three *l*'s, and so on to nine *l*'s. The results of this experiment are shown in Figs. 13 and 14. Inspection of Figs. 13 and 14 reveals that comparison of typewriter ribbon inks can

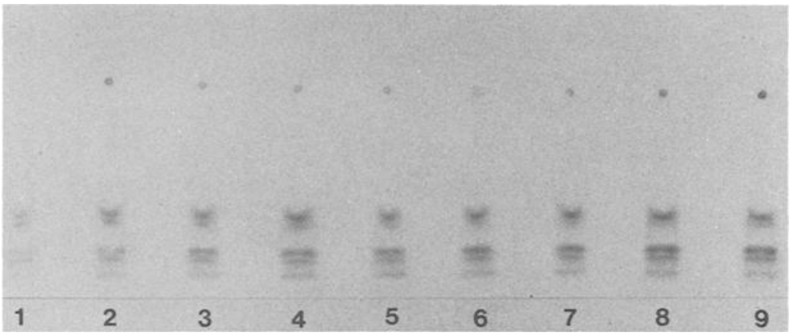

FIG. 13—*Effect of quantity of ink on chromatogram; numbers* 1 *through* 9 *refer to the number of lowercase letter l's used for samples.*

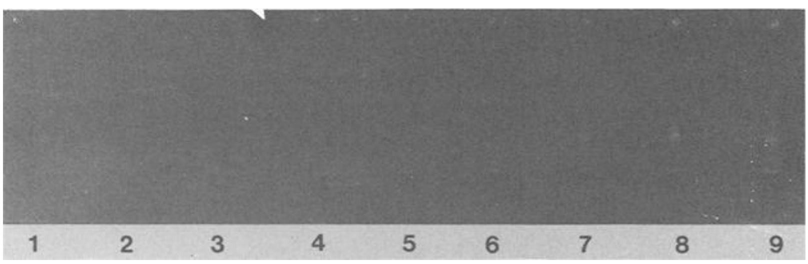

FIG. 14—*Effect of quantity of ink on chromatogram with ultraviolet light; numbers* 1 *through* 9 *refer to the number of lowercase l's used for samples.*

be readily made with just one typewritten letter. In certain instances only a fragment of a letter is required to distinguish between two or more typewriter ribbon inks. A minimal amount of pyridine was used to extract the inks.

The results of this study indicate that a large number of comparable components are visible by TLC with either white or ultraviolet light. This large number of comparable characteristics makes it relatively easy to compare questioned samples of typewriting. The findings can be easily demonstrated in court by referring to the original chromatograms, or the chromatograms can be photographed and 35-mm colored slides prepared for court demonstration.

Typewriter ribbon inks were found to be similar to ballpoint and other writing inks in that combinations of dye components are commonly used to produce specific colors. These combinations produce a large number of points of comparison that can be used to distinguish among many different typewriter ribbon inks. Up to now we have not found any two different manufacturers who produce matching typewriter ink formulations.

Summary

The results of this study reveal that TLC is a rapid, highly discriminatory technique for

distinguishing typewriting inks. A meaningful comparison can be conducted with only one typewritten character and, in many instances, even less of a sample is required.

Excellent separation and resolution of dye components were achieved. More than 150 typewriter ribbon inks from seven major manufacturers were analyzed and compared. Typewriter inks manufactured by different companies could be readily distinguished by comparison of the dye components present or by examination of the TLC plates under ultraviolet light. Also distinguishable were typewriter ribbon inks of different dye mixtures from the same manufacturer. It was not possible to identify the manufacturer of a typewriter ribbon ink. However, it was possible to prove that two or more typewritten entries contained different ink formulations.

If the inks are indistinguishable by TLC, then the typewriting was done with either the same ribbon or another ribbon that has the same ink formulation. This study confirms that TLC analysis of typewriter ribbon inks provides an excellent investigative tool to the examiner of questioned documents.

References

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