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HORIZONTAL PAPER CHROMATOGRAPHY IN THE IDENTIFICATION OF BALL POINT PEN INKS*

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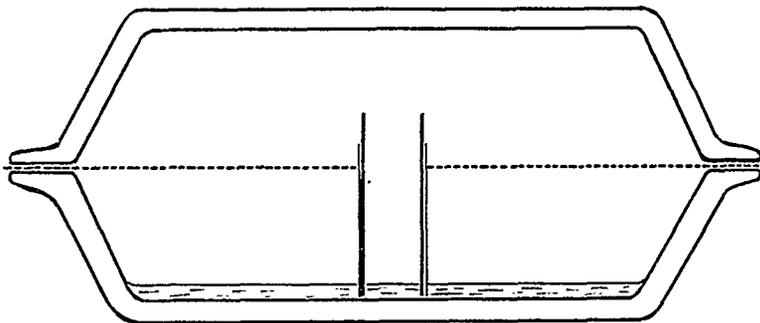
Paper chromatography is well known to virtually all chemists, biochemists, and biologists because of the tremendous achievements in those fields that it has made possible (1). Its bibliography is now so extensive (2, 3, 4, 5) that few people can hope to read even the more important papers in the field. Only within the last two or three years have publications appeared (6, 7, 8, 9) describing its application to the field of ink identification. The early work of Souder and Somerford (6, 7) utilizing an ascending strip method with water as the developing solvent for fluid ink was shown to be effective despite its somewhat crude technique. Later work (8) while more refined was still more difficult to apply to original ink lines from which minute quantities of ink must be removed than the technique described here.

No publication describing the application of paper chromatography to ball point pen inks has been noted, though this development is a very obvious one (8). The problem of identifying these inks is in several respects different from that of liquid writing inks, because of the completely different type of dye dispersing agents employed (10). In fact, treatment of ball point pen inks from the standpoint of the document examiner has been quite incomplete in all respects, though isolated papers have appeared (11, 12). Formulas of these inks have altered rapidly as the manufacturing information has increased. Early studies are virtually obsolete since now the oily vehicles so commonly used in the first ball point pens have been quite generally superseded, and a wider variety of dyes are now employed than at first. Another factor that has made the study difficult is the very large number of brands of pens that has appeared on the market and the almost bewildering rate of increase in them. It is nearly hopeless to attempt to obtain all of the pens of this type that are now sold. Positive identification of all of them does not now seem possible because various pens appear to contain the same or very similar inks possibly because a single manufacturer of ink may supply several manufacturers of pens. However, the technique described in this paper has been quite effective in identifying the group in which any such ink falls and in distinguishing between most of the inks that are used.

EXPERIMENTAL

Chromatographic Technique. The method adopted was similar to that of Giri and coworkers (13, 14). The chromatograms were made with whole circular Whatman # 1

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*Figure 1*

Small Horizontal Chromatography Outfit ($\frac{2}{3}$ rds actual size)

filter papers held between a pair of circular flat glass dishes with ground surfaces of contact as shown in Figure 1. Six inch diameter Pyrex pie dishes were found very satisfactory after the top surface of the flange was ground flat in the manner of a desiccator lid.¹ The papers were drilled in the center with a cork borer or punch of approximately $\frac{1}{2}$ inch diameter, and around the hole, but with the same center, were arranged the ink spots to be chromatographed equidistant from the center. A glass tube of very slightly less diameter than the center hole (a small vial is satisfactory) was wrapped with a strip of filter paper and placed at the center of the bottom vessel. This served as a wick up which the solvent in the bottom of the vessel was delivered to the circumference of the center hole. The solvent front, traveling as an expanding circle, encountered and acted upon all the spots approximately simultaneously moving each of them out in a narrow fan-shaped pattern. Ordinarily six or eight samples were placed on the same paper though more or less could be run simultaneously. An additional feature of this method was the fact that as the spot moved toward the periphery, it broadened in the circumferential dimension and narrowed in the radial so as to produce the chromatogram ultimately as a series of curved bands. In this study it was found advantageous to reduce the time so that band formation rarely occurred, but the dyes were completely separated and visible as individual colors. The rate of movement was such that a run consumed about 8 minutes under the conditions used here. This short time minimized diffusion effects which would tend to enlarge the colored areas and make them diffuse. The effect is very important with small samples such as may be readily obtained from single ink lines. With original ink, placed on the paper, the time factor is not very important because of the large amount of dye initially present.

Sample Treatment. Ink samples were treated in two ways. Original ink was placed with the pens as a single spot of ink on the paper. All spots were placed in a circle around the center wick. Ink removed from pen lines was taken up by means of acetone-water mixtures. A fine capillary pipet was used to deposit a droplet of solvent, either an equal mixture of acetone-water, or for more rapid solution, 2:1 acetone-water. Immediately, before the droplet could soak extensively into the paper and spread, it was taken up with a fine capillary with a small enough diameter to allow capillary action to draw up the solvent rapidly. The paper on which the ink

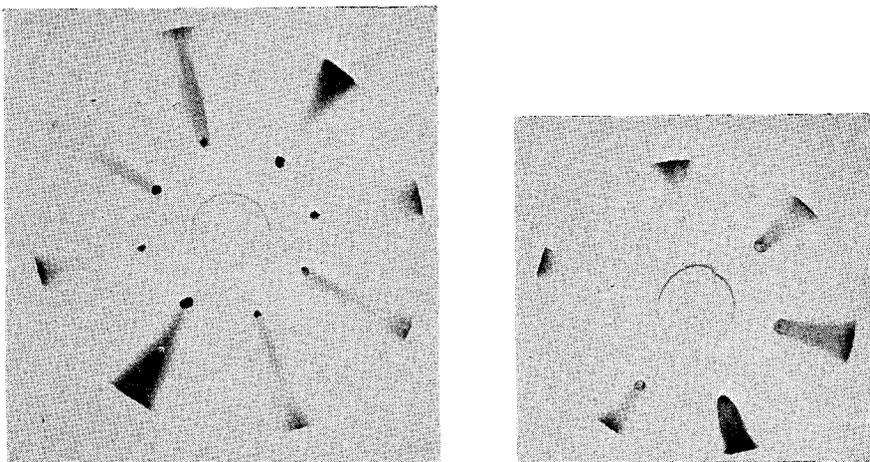


Figure 2

Horizontal Chromatograms of Typical Ball Point Inks

Left: Standard inks; right: Removed from ink lines. Dyes separated but run stopped before zones move apart.

was to be deposited was placed between two aluminum rings¹ to hold it over the vertical delivery tube of a hot air blower such as is used for hand hair dryers. On touching the capillary to the paper, the liquid was drawn out by capillary action, and rapidly dried so that a very small spot could be formed. This was critical to obtaining sharp separation and minimizing diffusion of the dyes during their movement on the paper.

As soon as the samples were placed on the paper and dried, the paper was forced over the wick in the center of the bottom vessel, solvent was added to the vessel, and the top chamber placed so as to hold the edge of the paper between the ground surfaces. After the solvent had run a satisfactory distance to produce good separation of dyes, the top chamber was removed, the paper taken off the wick and dried for inspection. Movement was limited here to a total of about $\frac{1}{2}$ to $\frac{3}{4}$ inch since complete separation was achieved in this distance without serious spreading and loss of color intensity. Chromatograms similar to those shown in Figure 2 were obtained.

Solvent. Various solvents were tested for this system. Since the solubilities of ball point inks were completely different from those of liquid writing inks, such simple solvents as water were not satisfactory, even for preliminary results. Organic solvents of various types showed such large differences in the observed R_f values that it was difficult to locate a solvent that did not carry some dyes with the solvent front while leaving others very close to the origin. The most generally satisfactory solvent tested was a mixture of 15 ml. of Shellacol² with 8 ml. water. This mixture was chosen because the separations were slightly cleaner than with other solvents, and the

¹ Horizontal paper chromatography equipment is supplied by Microchemical Specialties Co., 1834 University Avenue, Berkeley, Calif.

² A mixed solvent manufactured by Commercial Solvents Corporation and obtainable in paint and hardware stores.

cost and difficulty of making the solvent were negligible. Other solvents that produced essentially the same degree of differentiation were:

- a. t-butanol:water:acetone:Hydrochloric acid (conc). (10:20:10:1)
- b. n-butanol:acetone:water (4:2:1)
- c. n-butanol:acetone:water (2:1:2)
- d. n-butanol:acetone:Shellacol:water (50:25:7:15)

Solvent mixture a. was essentially as good as the mixture recommended but involved more difficulty in obtaining and mixing the constituents. The others had similar drawbacks and produced slightly less clean-cut results including: n-butanol:acetone (1:1); acetone: Shellacol (1:1); several acetic acid-containing solvents and others. Even acetone water mixtures produced separations that were definite but with very high R_f values that showed small differences only.

Supplementary Tests. A number of inks that could not be distinguished on the basis of chromatographic separation alone could be further differentiated by spraying with dilute HCl (1:5) solution. Most of the chromatograms were essentially unaltered by this treatment except for dulling or bleaching of the colors. Other reagents were tried but none aided in the differentiation except the hydrochloric acid. Ultraviolet light also did not greatly aid in further differentiation because the only constituent with marked fluorescence was a red dye found in several inks and which was already very apparent on the chromatogram.

RESULTS

A total of 58 ball point pens or refills were tested. Of these 41 were essentially blue inks, 3 were black, 8 red, and 6 green. The blue inks, of special interest, were readily and distinctly divided into seven main groups as follows.

- I. Turquoise and red dyes. Rol-rite (green cap); Rol-rite (maroon cap); Flo-ball; Skripto; King retractable; Waterman; Arnold; Lord Baltimore; Flo-ball (new Coronation ink); Cascade; One for All refill; Lindy Pen blue.
- II. Blue green dye only. E. Faber (old pen).
- III. Single blue dye. Spraying with HCl separated Windsor from remainder. Windsor Jet-O-matic; Rite King; Eversharp "CA"; Wahl refill.
- IV. Deep blue dye only. Howard (old pen); No designation (Made in U.S.A.).
- V. Purple dye only. King (old pen); Presdon (old pen); Dura (old pen).
- VI. Lavendar dye only. All Rite; Sheaffer; Long Writer; Top Riter; Venus Pen-cil; Presdon Vu-Riter; Val-U-Riter; Wearever; Perma Matic.
- VII. Turquoise dye and blue dye. Spraying with HCl divided this group into three subgroups as follows:
 - A. Two bands of blue green. Bankers Approved.
 - B. Blue-green and green bands. Esterbrook desk set; Venus American approved; Wear-ever; Best Rite.
 - C. Blue-green and blue bands. Eversharp Star Reporter; Papermate regular; Papermate deluxe; Eversharp "Kec-54"; Folgers.

The broad classes into which the inks studied fell leave much to be desired as regards individual identification. Some of this may be accomplished with a considerable degree of certainty by direct comparison of chromatograms with each other in the

same class. The amounts of dye present vary considerably in some instances, and this may be determined directly from duplicate chromatograms of the inks compared, especially when two or more dyes are present. When only one dye may be distinguished, differences in quantity of dye are more likely to arise from a different amount of ink than from a different proportion in the ink though small color differences become much more apparent on the chromatogram than in the ink line. Another useful comparison may be made by carefully comparing the original ink lines. In several cases differences were noted that allowed distinctions to be made between inks with almost identical chromatograms. This may be due to differences in composition of vehicle which could impart a different appearance to the ink line. Such comparisons also must be made with great care to avoid effects from different types of paper, soiling of the paper, and other similar effects not related to the ink composition.

Inks of other colors than blue were compared similarly and found to be distinguishable in most cases. They divided into the following groups.

Black Ink

- A. Papermate black
- B. Eversharp black "Kec-54"
- C. Lindy Pen black

Red Ink

- A. All rite; Wearever Tri-color; Velvet Pen-cil; Three Way reload.
- B. One for All refill; Eversharp red "Kec-54"; Papermate red; Lindy Pen red.

Green Ink

- A. Wearever Tri-color green
- B. Three-Way reload
- C. Eversharp "Kec-54"
- D. Papermate Green; One for All refill; Ready (Lindy Pen) green.

Despite the fact that dyes of some of the above inks were apparently identical, there were in most instances marked differences, presumably in the composition of the vehicle, to allow differentiation of the inks on the basis of the way they appeared in the ink line. It is unfortunate that the technique of paper chromatography has not yet been sufficiently refined to study in detail the vehicle of ball point inks, for it is here that some of the most marked differences in such inks apparently occur. It is also this factor that is most significant in the behavior of the pen, and the reliability of its operation as well as the physical character of the line.

SUMMARY

An improved technique for the chromatography of ink is described, and its application to the identification of ball point pen ink discussed. Blue inks (including purple) could be divided rapidly into 7 groups, and distinctions made between many of the members of the multi-component groups. Identification of every ink individually was not found possible from the dye components separated by chromatography. Identification of nearly all of the inks was possible from the chromatogram combined with study of the ink line to reveal major differences in vehicle.

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