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COMPARISON OF INK WRITING ON DOCUMENTS BY MEANS OF PAPER CHROMATOGRAPHY

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The examiner of questioned documents is frequently faced with a problem involving ink. Ink identification has many facets, and the problems which arise may have many forms which may require different approaches to a solution. Among document examiners it is generally understood that ink is usually a multicomponent mixture possibly containing a permanent factor such as iron gallotannate or carbon and one or more dyes to give desired color effects. In modern inks, the variety of colors or dyes which may appear in a particular ink is sometimes surprising especially with washable and permanent blacks.

In this paper the authors present a technique by means of which these components can be resolved into pure forms which immediately provide a basis for individual identification of an ink with a particular formula and separate the color components such that they may be further tested and identified. There are several ink problems concerning which much more work remains to be done, such as identifying exactly the particular dye or color substance from the R_f value of the chromatogram plus other tests, the effect of age on the removal and chromatography of the iron gallotannates, the development of other solvents and adsorbents, etc. The authors present the following technique in the hope that other workers will have an additional tool with which to work on some of these tasks.

In the examination of questioned documents it is often necessary to investigate the properties of the ink used in the writings on the document. One of the purposes of such investigations is to determine whether or not two writings were made with similar or different inks. Chemical methods (3, 4, 5, 6, 9) of analysis differentiate the inks into types depending upon the presence or absence of metallic salts, reaction with acids, bases, and oxidizing and reducing agents. These methods

seldom differentiate between two inks of the same type; therefore, unless the tested inks are of different types or differ in their metallic contents, the results are often inconclusive. Chemical methods have the disadvantage of being difficult to demonstrate in court and of exposing the document to the risk of accidental damage from chemical reagents. Physical methods of analysis which may be used include visual and microscopic examination and comparison using transmitted, reflected, or oblique lighting; fluorescence testing with ultraviolet light; photography with the aid of filters and appropriate films to accentuate color differences in inks; infrared or ultraviolet photography (3, 4, 5, 6, 8); long wave length X-rays (7); and reflection spectrophotometry (1). These methods may show differences in writings made with inks of the same type and of similar appearance. Physical methods have the advantage of being readily displayed in court in the form of photographs, demonstrations, reflection spectra, or photomicrographs; these methods have the added advantage of not altering the document or exposing it to the risk of damage or spillage. In the physical methods of comparison listed above, the process of photography using filters and appropriate film to accentuate color differences and reflection spectrophotometry, depend upon differences in light absorption properties of the questioned inks in the visible range. These direct comparisons are hampered by the fact that nearly all the incident light is absorbed; i.e., the color of most inks consists of variations of dark blue or black, and the amount of light reflected at any one wave length region is so low as to make the comparisons difficult.

It was, therefore, proposed to apply the methods of paper chromatography to resolve ink writing into separate colored components and to compare the colored components individually.

The first part of the investigation consisted of a study of the common fluid inks to determine whether or not sufficient differences existed to distinguish between them. The techniques used were those of macro-scale paper chromatography. Forty-six different kinds of locally available commercial writing inks of black, blue-black, blue, red, green, violet, and brown colors were employed. These inks are listed in Table I.

The second part of the investigation consisted of a study to find a means by which the pigmented lines remaining after drying of ink on a document could be transferred to a paper strip on a micro scale so as to change the document as little as possible; this to be followed by suitable development of the ink pigment on the paper which might resolve the colors of the writing into components for comparison. Writings

Table I.
FLUID INKS USED TO PREPARE CHROMATOGRAMS

<u>Name of Ink</u>	<u>Reference Number</u>	<u>Name of Ink</u>	<u>Reference Number</u>
Carters American Blue.....	1	Sanfords Penit Blue-Black.....	39
Beaver Brown	83	Penit Cardinal Red.....	53
Permanent Midnight Black.....	71	Penit Dubonnet	49
Permanent Midnight Blue.....	69	Penit Green	57
Tulip Purple	85	Penit Jet Black.....	59
Higgins Carbon Eternal Black.....	73	Penit Royal Blue.....	51
Morriset Black	77	Penit Violet	55
Blue Black	79	Permanent Blue-Black	63
Royal Blue	91	Permanent Royal Black.....	67
Green	89	Royal Violet	65
Red	87	Skrip Emerald Green.....	11
Parker 51 China Red.....	81	Permanent Blue-Black.....	5
Quink Permanent Black.....	19	Permanent Jet Black.....	7
Permanent Blue-Black	21	Permanent Red	3
Permanent Brown	61	Permanent Royal Blue.....	9
Permanent Red	15	Persian Rose	47
Permanent Royal Blue.....	17	Washable Black	13
Washable Blue	25	Washable Blue	41
Washable Brown	23	Washable Brown	43
Washable Green	27	Washable Purple	45
Washable Violet	29	Superchrome Blue-Black	75
		Jade Green	37
		Jet Black	33
		Red	31
		Turquoise Blue	35

two months old of thirty different inks of black, blue-black, blue, red, green, violet, and brown colors were used in this phase of the investigation.

DEFINITION OF TERMS

1. Paper refers to chromatographic paper, ED #613.
2. Document refers to material which bears questioned inked writing.
3. The R_f value of a substance in a particular system is the proportional travel of a solute in respect to the total travel of a solvent through an absorbing column (For example; if the solvent travels 25 centimeters through adsorbent after passing through the sample, a dye moving only 5 centimeters would have an R_f value of 0.2). For a particular R_f value, the solute must be a single pure substance, the solvent and absorbing materials must be defined, and the R_f then becomes a reproducible constant. Because of small variations in materials, R_f values should be determined experimentally.
4. Transfer solvent means solvent used to transfer pigments from document to paper.
5. Developing solvent or developer means solvent system used to resolve ink spot on chromatographic paper into components.
6. All reference to water means chemically pure, distilled water.

EXPERIMENTAL

The ascending chromatographic technique of Tennent, Whitla, and

Florey (10) was adopted without modification for the resolution of the fluid inks. An amount of fluid ink varying from .003-.005 ml. was applied as a line approximately 5 centimeters above the end of a chromatographic paper 1.25 centimeters wide and 65 centimeters long. The ink was allowed to dry on the paper for 20 minutes. The end of the paper containing the ink spot was cut off to a point about 4 centimeters below the line. The paper was then placed in a glass tube 18 mm o.d. and 60 cm. long, until the point of the paper was even with the end of the glass tube. Then the other end of the tube was sealed with a cork, which also supported the upper end of the paper. The open end of the tube was immersed in the solvent to a depth sufficient to wet the point for a distance of 0.5 cm., and the tube was suspended vertically. Development was allowed to continue until the desired separation occurred. The time of development varied from 6-24 hours. After development the paper was removed from the tube and air-dried.

Questioned documents were tested as follows:

1. An ink line selected for comparison was observed under 20X magnification of a stereoscopic binocular microscope, and a droplet of transfer solvent was touched to it with a fine pointed glass rod.
2. This droplet was made to dissolve or disperse some of the ink line by teasing and rubbing.
3. Portions of the dissolved material in the droplet were then successively transferred to 1.0-1.6 mm. wide x 12 cm. long chromatograph paper to a point 8 mm. from the tip by means of the glass rod tip. Between successive additions the paper was dried by warming over a lamp. When sufficient ink pigment was transferred to the paper strip the strip was air-dried for twenty minutes and then weighted at the pigmented end to facilitate handling.
4. The solvent container which was used was a 15 x 125 mm. test tube held upright by placement on a block of plasticene clay and sealed at the top by a stopper.
5. The paper containing the unresolved spot was allowed to stand in the solvent container out of contact with the solvent for fifteen minutes to equilibrate with the solvent vapor. Then development was started by lowering the paper until the bottom end made contact with the liquid solvent. Time of development varied from 20 minutes to one hour. On completion of development the paper was removed and air-dried. After drying, the chromatograms were examined in visible and ultraviolet light, and in visible light in atmospheres of hydrochloric acid gas, ammonia, and thiocyanic acid. Satisfactory separations were obtained with Eaton-Dikeman Company #613 filter paper which was used in all experiments. Solvent systems tried included water, ethyl alcohol, isopropyl alcohol, butyl alcohol, isobutyl alcohol, and acetic acid in various combinations with each other and ammonium hydroxide. All chemicals used were of analytical reagent quality. All chromatograms were made at room temperature—20-26° C.

RESULTS

With Fluid Inks. The solvent that separated an ink cleanly and sharply into the largest number of components was isobutyl alcohol saturated with 1.25N aqueous ammonium hydroxide. Satisfactory separations were also achieved with n-butyl alcohol saturated with 1.25N aqueous ammonium hydroxide. Solvents which gave less satisfactory resolution of the inks tested but with much greater Rf value were n-butyl alcohol saturated with water, and isobutyl alcohol saturated with water. Unsatisfactory separations were obtained with water alone because the separations were not clear cut. The majority of the solvents tested were discarded because they did not satisfactorily separate the inks into components or produced no movement of the ink components or resolved the ink into very diffuse overlapping bands which weakened the colors.

The chromatograms produced depended strikingly upon the solvent used. In general, solvents with ammonia produced more bands, sharper separations, lowered Rf values, and a much different sequence of colors than the same solvent systems without ammonia. Noticeably different and unreproducible chromatograms were obtained from the same solvent system on the same ink if the ammonia in the solvent reservoir was permitted to evaporate during development. Characteristic and reproducible chromatograms were obtained from each ink tested, provided that the solvent system was protected from change due to evaporation. Rf values obtained for an ink with a given solvent system were reproducible to approximately 5%.

Choice of the solvent system depends upon the object of the test. If a large amount of sample is available for test, a highly resolving combination like isobutyl alcohol-ammonia is preferable which produces large Rf values; but when the test sample is limited, a solvent of less spreading ability and producing low Rf values is advisable because sharp bands of high concentration of pigment are thus obtained and are separated sufficiently to identify. The system n-butyl alcohol saturated with 1.25N aqueous ammonium hydroxide was adopted as the solvent most suitable for work with micro size samples of color removable from the dried lines of inked writing. Of the twenty-four black, blue-black, and blue inks are shown in Figure 1. (n-butyl alcohol-ammonia solvent travel alone except one group of two inks and one group of three inks. Nos. 9, 69 and 17, 51, 91 in illustration)

Chromatograms produced with this solvent system on twenty-seven

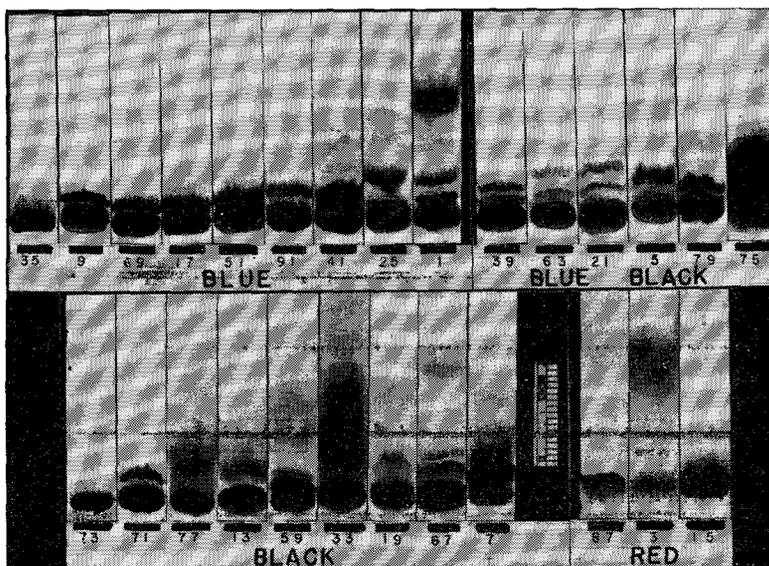


Figure 1.

Chromatographs of Twenty-Seven Inks

Reproductions in black and white only partially portray the effective and distinctive color separations achieved by this technique. Colors range among the blue inks from light blue-green through blue to violet. (Photographed with A-filter.) Among the blue-black inks was a red-purple area in specimen 5 in addition to the range noted for the blue inks. (Photographed with B-filter.)

The black inks proved to be mixtures of various shades of blue, yellows, greens, oranges, and reds with several inks containing four or more different color bands. (Photographed with B-filter.)

Red inks separated into distinguishable shades of red. (Photographed with C-5 filter.)

inks are shown in Figure 1. (n-butyl alcohol-ammonia solvent travel was 10 inches in each case shown in Figure 1)

With Dried Inked Lines Two Months Old. The solvent used to transfer the pigment from the ink line to the paper was either water or .83N (5%) acetic acid. Other solvents tried had tendencies to evaporate too rapidly or soak into the document. If the ink line did not dissolve or disperse in the transfer solvent, another was tried. In the case of water resistant inks such as those used in ballpoint pens and stamp pad inks, isopropyl alcohol was used successfully. If no color was removable from the inked line, no chromatogram was possible with this technique. The chromatograph paper had to be wetted thoroughly with the ink pigments through its entire thickness to the walls of the paper or unsatisfactory resolution occurred. The spot of transferred ink on the chromatograph paper was found to give cleanest separation of components when the transferred spot was held to less than 3 mm. height. The method of transfer described above gave the best results.

Micro scale chromatograms from the same kind of inked lines were reproducible with respect to R_f and number of color bands provided the ink samples for transfer to the chromatographic paper were taken from portions of the ink lines not previously extracted.

The micro scale chromatograms in almost all of the tested cases were easily identified by reference to the large scale chromatogram made using fluid ink. In some cases color bands were present in the large chromatograms that were lacking in the corresponding micro scale chromatograms, but the remaining color bands were of the proper sequence and of similar R_f value, although not necessarily of the same relative intensity. By means of visible and ultraviolet light comparison, the micro chromatograms could be distinguished from one another in all cases except two groups of three each.

It was shown that two inked lines of the same composition and age, differing only in the respect that one was blotted and one was not, are identifiable by this technique; however, some of the colors may be differentially removed to a certain extent by blotting. Color bands observed in both cases were, under the same conditions, of the same R_f values and properties. In no case tested did the blotted ink produce a color band not present in the chromatogram produced from the same ink line unblotted. Considerable difficulty was experienced in transferring sufficient colored material from the blotted ink line to the paper, as 6 to 15 times the inked area was needed as compared with the inked area used with unblotted ink samples.

DISCUSSION

From the facts presented in the above paragraphs it is concluded that paper chromatography of fluid inks may be of value in comparing two fluid inks, a fluid ink with a writing on a document, or two writings. A given ink or ink writing may thus be identified with a particular formula, and if any one manufacturer is the exclusive user of this formula, the manufacturer is then identified.

Preliminary tests should be made with the transfer solvent on the margin of the document to determine whether or not the transfer solvent would alter the face of the document or diffuse into the document material too rapidly to be of use.

The technique using the micro chromatograms is adaptable to the comparison of inked writings on a document or similar documents which have been prepared and stored under the same conditions. The following

observations are suggested as a basis for an opinion after examination by the chromatographic technique presented:

1. Note reaction of inked line on document to application of transfer solvent. Is solvent repelled? Does ink go readily into solution, or is color a suspension?
2. Note appearance of inked line on document after sufficient color has been transferred to paper. Is the color of the ink, by reflected and oblique lighting changed from its original color due to removal of solvent soluble ink components?
3. Note area of inked line needed to transfer sufficient color for chromatography.
4. Note appearance of transferred ink spots on paper strips while wet and after drying.
5. Note reaction of transferred ink spot to vapors of developing solvent. Does color change or fade?
6. Note appearance of separated colors on development. Are colors visible when dissolved in developer? Do colors change or new colors appear on evaporation of developer? Do colors disappear on evaporation of developer?
7. Note appearance of transferred ink spot on paper after development but before and after evaporation of developer.
8. Compare chromatograms after developer has evaporated.
9. Note appearance of chromatograms under ultraviolet light. Compare chromatograms.
10. Note reaction of colors to HCl gas.
Note reaction of colors to NH₃ gas.
Note reaction of colors to HCNS gas.
Do any colors change? Disappear? Do any new colors appear?

If the comparison chromatograms are both prepared with approximately equal amounts of ink transferred from the inked writings to the paper, the above observations made on the process should be the same for both chromatograms if the two ink lines compared are of the same or very similar composition and have received the same treatment since their deposition on the document. If the two chromatograms differ from each other with respect to the above observations, particularly in appearance to visible and ultraviolet light after solvent has evaporated, the conclusion may be drawn that the inked lines are of different composition. The observations may also give rise to an opinion as to whether or not one line was blotted with respect to the other, if the lines are otherwise of the same composition as revealed by chromatography and if microscopic examination suggests blotting.

On documents twelve years old, using this technique, it has been shown that writings from the same ink source produced identical chromatograms and that writings of different inks having the same appearance produced different chromatograms.

For purposes of comparison of chromatographic technique vs. infra-

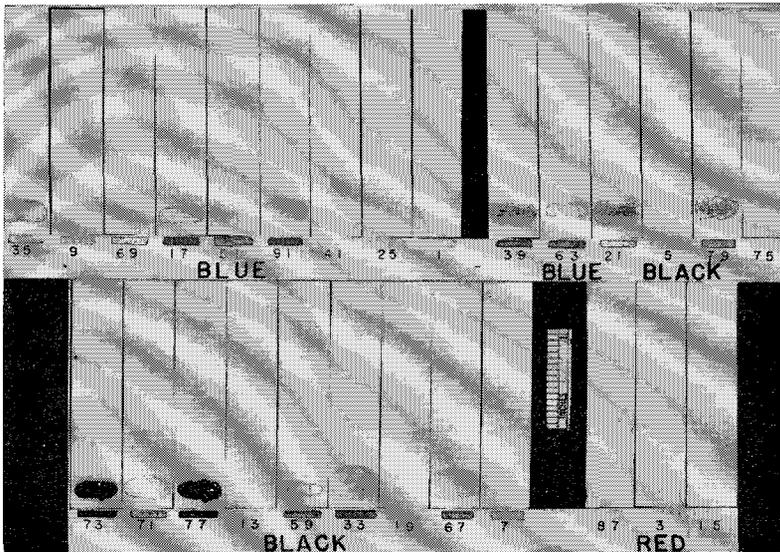


Figure 2.

The same chromatographs as Figure 1 photographed with infrared film and Wratten 87 filter.

red photography an infrared photo of the original chromatograms, reproduced in Figure 1, is shown as Figure 2. (Eastman infrared film, #87 filter) The untreated ink is shown in the block directly below the chromatogram and above the number. The ink in this figure is unblotted and had dried 24 hours before being photographed. From this photo it is apparent that the infrared technique divides the ink into about four categories which differ from each other by varying density in the photograph. The differences in density which are demonstrated by infrared photography may not be entirely the result of differences in composition. In addition to composition, density differences may be the result of blotting and the rate of flow of ink from the pen. Examples of flow differences are found in variations of pen nibs, writing pressure, and amount of ink on the point, which latter factor may show differences between writing which is made with a freshly dipped point as against the same point running dry. It is apparent that paper chromatographic investigation of inked lines would be a valuable addition to the infrared examination and to chemical spot tests.

After separation of the inked lines into components, the individual components may be cut off the chromatogram, and the color dissolved and subjected to whatever chemical or physical test may be applicable. It is believed that the spectral absorption characteristics of individual

components might lead to further comparisons and the micro cells described by Kirk (2) would be of value in this type of analysis.

The chromatographic technique is tedious and requires painstaking care. It exposes the document to the risk of being damaged or smudged. On the other hand it may reveal information not available by any other means, and if properly carried out, provides a striking demonstration in support of the conclusion rendered.

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