Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Ziderman, Irving I.(1982) 'Inverse Paper Chromatography', Separation Science and Technology, 17: 10, 1253 — 1260
To link to this Article: DOI: 10.1080/01496398208060648
URL: http://dx.doi.org/10.1080/01496398208060648

SEPARATION SCIENCE AND TECHNOLOGY, 17(10), pp. 1253–1260, 1982

Inverse Paper Chromatography*

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Abstract

Available methods of examination do not provide absolute certainty that two samples of paper have the same origin. A new technique for testing paper, known as inverse paper chromatography (IPC), is based on using a strip of paper as the chromatographic sorbent medium on which a mixture of known probes is separated under standardized conditions. The resulting chromatogram will uniquely designate the paper grade and composition. This principle has been validated with 36 types of paper in a standard test, using cresol red, chlorophenol red, bromothymol blue, fuchsine, and methylene blue as the probe mixture and *n*-butanol as the eluant. The machine direction in the paper is distinguishable by this method. The experimental technique is simple, inexpensive, and essentially nondestructive. Exposure of paper sheets to physical influences such as printing, wetting, humidity, and filtered sunlight does not alter their characteristic chromatographic behavior. However, baking (artificial aging) and exposure to direct sunlight change the chromatographic performance of the paper, evidently by inducing chemical changes. Incorporating colored pigments in the paper also alters the chromatographic separations obtained. The application of IPC to forensic science, product testing, and paper chemistry is discussed. A facile stiffness test for unequivocally determining the machine direction in a paper sheet is described that provides a technique for revealing fraudulent page insertion in a multipage document.

*A preliminary communication has appeared in the *Journal of Forensic Sciences* (*1*).
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INTRODUCTION

In inverse chromatography the properties of a stationary phase sorbent are characterized by studying the chromatographic behavior of known probes carried in the mobile phase eluant. This principle has been applied in inverse gas chromatography (IGC) to determine polymer properties such as glass transitions, solution activity coefficients, and surface adsorption isotherms (*2*), and in inverse gel permeation chromatography (IGPC) to study porous materials and resolution in packed columns (*3*). If paper too were not to act purely as a passive stationary phase, it should be possible to characterize papers by an inverse paper chromatography (IPC).

This work was initiated in order to provide a novel technique for comparing and identifying documents and other forms of forensic paper evidence.

EXPERIMENTAL

The technique used is described in detail elsewhere (*1*). Colored probe compounds, permitting continuous visualization of the chromatogram, were applied in methanol (0.5% solution) to a small paper strip attached to the underside of a cork and then separated by ascending development with *n*-butanol in a graduated cylinder (50 mL) for 3 h.

TABLE 1

Compounds Used as IPC Probes

No.	Name	Hue	Source	R_f[a] DM	R_f[a] CM
		A. pH Indicators[b]			
1.	Cresol red	Yellow	Merck	0.30	0.43
2.	Chlorophenol red	Yellow	Merck	0.28	0.42
3.	Bromothymol blue	Yellow	Riedel-deHaen	0.67	0.75
		B. Basic Dyes			
4.	Fuchsine (rosaniline, CI 42510[c])	Purplish pink	Riedel-deHaen	0.48	0.68
5.	Methylene blue (CI 52015[c])	Blue	Merck	0.12	0.16
6.	Malachite green (CI 42000[c])	Green	BDH	0.21	0.44
7.	Rhodamine B (CI 45170[c])	Pink	Merck	0.34	0.61
8.	Gentian violet (CI 42555[c])	Violet	Allied Chemical	0.51	0.71

[a]On paper number 1.

[b]γ-Sultones of the sulfonephthalein series.

[c]Number in *Colour Index*, compiled and published jointly by the Society of Dyers and Colourists of Great Britain and the American Association of Textile Chemists and Colorists.

Both acidic and basic probes (Compounds 1–3 and 4–8, respectively, in Table 1) were assayed so as to study possible ion-exchange effects resulting from inorganic fillers in the papers and from carboxylic acid functional groups in the cellulosic fibers. By adopting a fixed development time (3 h), differences in paper capillarity were revealed as an additional identifying characteristic and the experimental procedure was simplified.

A supplementary evaluation may often be achieved by exposing the developed chromatogram to acidic or alkaline vapors (e.g., formic acid and ammonia, respectively), in which the pH indicator probes change color.

Unless otherwise stated, paper number 1 (Table 2) with probe mixture 1–5 (Table 1) were used in the experiments.

RESULTS

The 15 paper grades from the catalog of Israel's main paper mill listed in Table 3 gave clearly distinguishable chromatograms (Fig. 1), using a five-component probe mixture. Papers number 30 and 31 of the same quality but differing slightly only in weight (90 and 118 g) gave similar chromatograms.

TABLE 2

Commercial Papers Tested

No.	Description
1	Wood-free writing paper 60 g
2	Copy paper
3	Plantograph paper
4	Duplicating paper
5	Lined writing paper
6	Cardboard
7	Letter paper (M 1053)
8	Memorandum (1010)
9	Computer printout
10	Fingerprint form
11	Multilith
12	Gestetner Durotype 6
13	Back leaf to paper no. 12
14	Schneider & Schull Number 0.859 × .25214 filter paper
15	Large brown envelope (30)
16	Medium-size brown envelope (Sakyot Niar)
17	Calculating machine printout A
18	Calculating machine printout B
19	Paper for forged dinars
20	Blue airmail envelope
21	Long brown envelope (Mashaz)

TABLE 3

Hadera Mills New Paper Grades Tested

No.	Manufacturer's designation	Weight (g)	Description
22	WO D/C	100	Bleached, double calendar, woodfree offset
23	WOHB	90	Bleached, woodfree offset
24	WO CR	80	Cream-shade, woodfree offset
25	Zohar	70	Woodfree offset, colored yellow
26	Zohar	70	Woodfree offset, colored blue
27	Zohar	70	Woodfree offset, white
28	Zohar	70	Woodfree offset, colored peach
29	Label	90	Polished, one-side coated, woodfree
30	Barak	90	Polished, coated both sides, woodfree
31	Barak	118	Polished, coated both sides, woodfree
32	Matt Barak	n.d.[a]	Unpolished, coated both sides, woodfree
33	WFB	80	Swollen woodfree offset, high opacity and caliper
34	WON	80	Woodfree offset
35	WOW	70	Woodfree offset
36	FBB WB	300	White-backed cardboard

[a]n.d. = no data

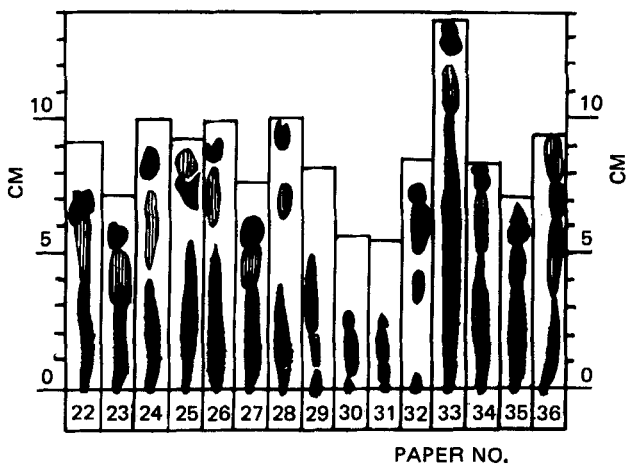

FIG. 1. Paper strip chromatograms of papers listed in Table 3 using mixture of dyes numbered 1–5 in Table 1. Colors: violet (black spots), green (horizontal grid), blue (crossed grid), and yellow (vertical grid).

The incorporation of pigments in paper number 27 to produce colored papers numbers 25, 26, and 28 altered the chromatographic behavior and increased the paper capillarity.

The 21 commercial papers listed in Table 2 were assayed in both the machine direction (DM) and the perpendicular cross-machine dimension (CM), DM in the sheets having been unequivocally determined by the stiffness test illustrated in Fig. 2. The chromatograms on DM strips (Fig. 3) are clearly distinguishable from each other with respect to both the distance advanced by the eluant front and the chromatographic separation of the probe mixture: a similar result was obtained with CM strips (Fig. 4). The contrast was especially dramatic between papers numbers 17 and 18 (Fig. 3), taken from two otherwise indistinguishable printout rolls supplied with different calculating machines: front mobility and methylene blue R_f were, respectively, 3 cm and 0.83 for one and 12.7 cm and 0.08 for the other. With strips cut in DM (Fig. 3) more probe tailing, increased eluant mobility, and lower R_f values were obtained compared with the CM direction (Fig. 4).

Chromatography of various combinations of the probe compounds listed in Table 1 indicated that a mixture of fuchsine, malachite green, cresol red, and

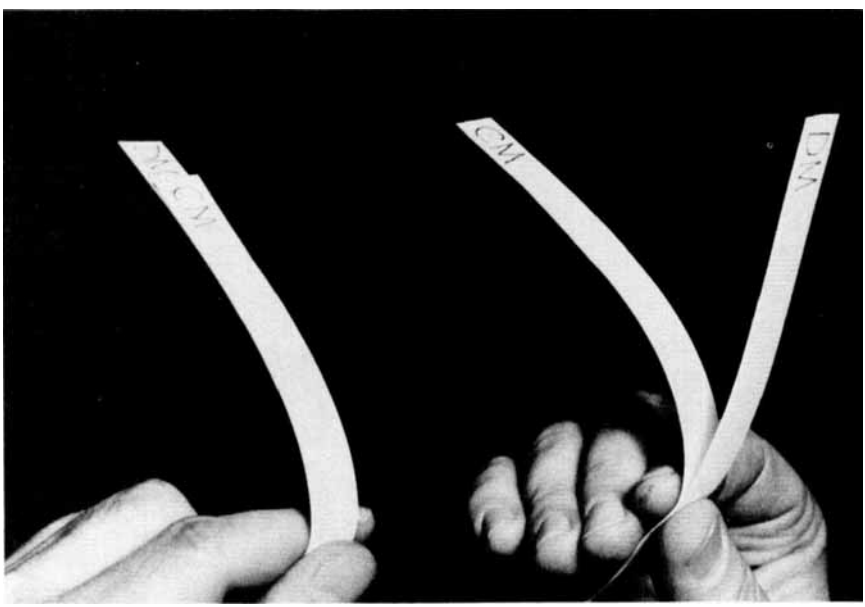

FIG. 2. Test to reveal machine direction (DM) in paper sheet. Strips cut from each of two perpendicular directions are held together horizontally. The stiffer strip is designated DM and the other CM (cross-machine).

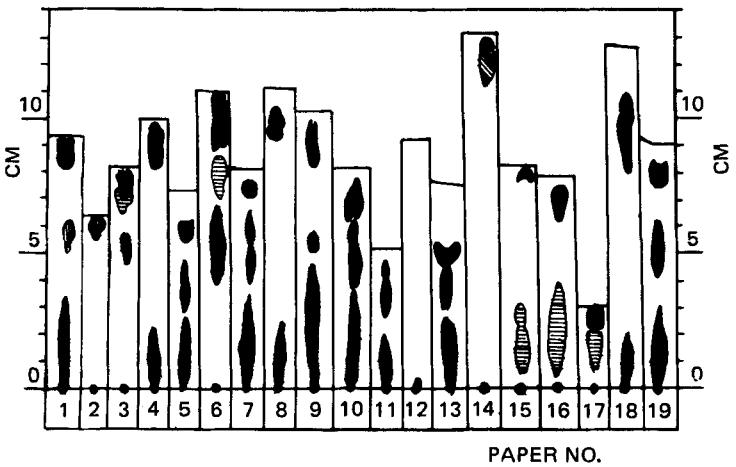

FIG. 3. As Fig. 1, using DM strips listed in Table 2.

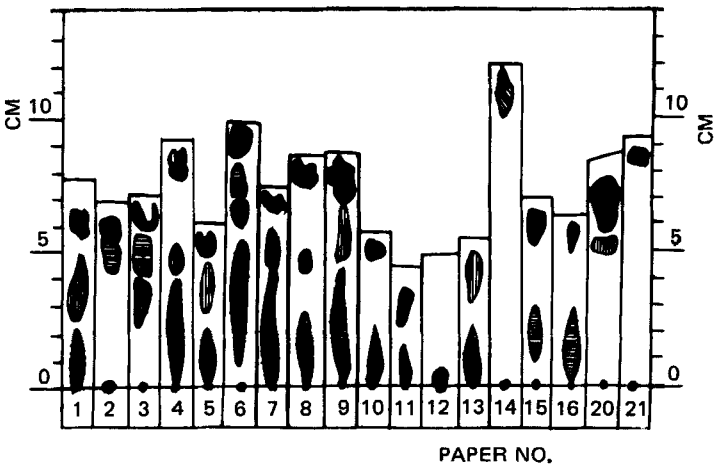

FIG. 4. As Fig. 3, using CM strips.

methylene blue gives the best color separation ($R_f = 0.76$, 0.63, 0.40, and 0.11, respectively, in DM).

Having established the validity of the IPC principle, it was necessary to determine whether chromatographic performance is affected by exposing the paper to physical and chemical agents, particularly those relevant to forensic applications. Exposure overnight to an atmosphere of high humidity followed by air-drying did not affect the paper's chromatographic performance, even though the damp paper had shrunken in the DM and regained its dimensions on drying. Similarly, exposure to filtered sunlight (through plain glass) for 56 h was without effect. Paper that had been wetted with water, in order to simulate removal of water-soluble impressions, and then air-dried retained its chromatographic characteristics too. Printing a counterfeit bank note did not alter the chromatogram obtained with the plain paper.

However, 14 h exposure to direct sunlight increased the mobility of the probes, cresol red and chlorophenol red, from $R_f = 0.50$ to 0.78. Furthermore, after artificial aging by baking in an oven at 200°C for 30 min, the paper exhibited enhanced mobility of both the eluant and the fast-moving fuchsine but retarded the migration of slow-moving methylene blue.

DISCUSSION

Besides their importance for forensic science, these results indicate that exposure of paper to physical influences does not cause any permanent change in chromatographic performance, while those agents that do cause such changes probably act by inflicting chemical damage to the paper. This conclusion is indicative of the potential use of IPC in studying the chemical reactions of paper.

In addition to the demonstrated effects of colorants, it is considered that the nature of the other constituents—cellulose, fillers, and sizing—also influence paper's characteristic chromatographic performance. IPC may therefore contribute to paper testing and quality control in industrial laboratories.

For purposes of document identification in forensic and other applications, a systematic examination of the paper in five stages is required (*4*):

(1) Measurement of physical characteristics: color, dimensions, weight, opacity and fluorescence
(2) Watermark examination, including embossings, aided with UV illumination
(3) Microscopic fiber analysis after staining

(4) Chemical analysis of ingredients such as sizing and loading materials, fillers, whiteners, plasticizers, and waxes
(5) Trace elemental analysis by neutron activation analysis and x-ray fluorescence, scanning electron microscopy, or emission spectrography

While these procedures provide numerous points of comparison that may reveal conclusive evidence that paper samples are different, they do not permit one to determine with absolute certainty whether or not the specimens have the same origin. Furthermore, implementation of this complete systematic analysis is prohibitively expensive, time-consuming, and multifariously highly-specialized. Being inexpensive, available, and facile, IPC should become an important new technique for paper identification. The method is essentially nondestructive, providing a permanent exhibit for presentation as evidence, or alternatively, the original sample may be regenerated, when necessary, by a suitable elution of the colored probes from the chromatogram.

The stiffness test (*1*) for determining the direction in which the cellulosic fibers are orientated in a paper sheet (termed "machine direction") has now inspired a novel forensic application as an advantageous method for revealing the fraudulent replacement or addition of a page in a multipaged document (*5*).

Acknowledgments

Dr J. Almog, deputy head of the Research and Development Division, and Dr S. Kraus, director of the Analytical Laboratory, Criminal Identification Branch, and their staffs are sincerely thanked for their kind hospitality and cooperation in providing the facilities for carrying out this project at the Israel Police Headquarters. Capt A. Betsaleli of the Documents Laboratory is also thanked for helpful discussions of the forensic science aspects. The excellent work of the Photography Laboratory is greatly appreciated.

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Received by editor January 29, 1982