Further Reading

- Bright FV and McNally MEP (eds) (1992) Supercritical Fluid Technology: Theoretical and Applied Approaches to Analytical Chemistry. Washington: American Chemical Society.
- Charpentier BA and Sevenants MR (eds) (1988) Supercritical Fluid Extraction and Chromatography: Techniques and Applications. Washington: American Chemical Society.
- Johnston KP and Penninger JML (eds) (1989) Supercritical Fluid Science and Technology. Washington: American Chemical Society.

- Lee ML and Markides KE (eds) (1990) Analytical Supercritical Fluid Chromatography and Extraction. Provo: Chromatography Conferences.
- McHugh MA and Krukonis VJ (1994) *Supercritical Fluid Extraction: Principles and Practice*, 2nd edn. Stoneham: Butterworth-Heinemann.
- Smith RM and Howthorne SB (eds) (1997) Supercritical Fluids in Chromatography and Extraction. Reprinted from *Journal of Chromatography A* 785. Amsterdam: Elsevier.
- Westwood SA (ed.) (1993) Supercritical Fluid Extraction and its Use in Chromatographic Sample Preparation. Boca Raton: CRC Press.

INKS: FORENSIC ANALYSIS BY THIN-LAYER (PLANAR) CHROMATOGRAPHY

L. W. Pagano, M. J. Surrency and A. A. Cantu, US Secret Service, Washington DC, USA

Copyright © 2000 Academic Press

Introduction

Because of the immense number of documents written, printed and copied each year, suspect documents generated by these methods have become common subjects for forensic examinations.

The forensic analysis of inks is performed to determine if inks are similar or different; to establish the authenticity of a document; to establish whether a document could have been produced on the purported date; or to determine the origin of a document. Although the chromatographic analysis of writing and stamp pad inks have been extensively documented, little has been written on the analysis of ink jet inks (jet inks) or photocopier/laser printer/LED printer toners, despite the volumes of such evidential documents under investigation.

All inks are composed of colorants in a vehicle. Today's inks include: writing, typewriting, stamp, printing, printer, jet and toner. The consistency of the vehicle ranges from liquids, such as those used in writing and jet inks; to paste, characteristic of some printing inks; to solids, such as those used in typewriting ribbons and toner.

This article only deals with inks whose colorants are separable by thin-layer chromatography (TLC). Such colorants include dyes and pigments that have some solubility in the extraction solvent. Since most printing inks use insoluble pigments as colorants, and therefore are not analysable by TLC, such inks are not considered here. Additionally, the jet inks and toner under consideration are those used in full colour systems (YMCK).

The TLC separation of soluble inks involves six steps: sampling, extraction, spotting, developing, vis-ualization/detection and interpretation.

A TLC method successfully used for the comparison of writing inks has translated well for the analysis of today's modern imaging media – jet ink and toner. Although colour toners are very different from classically defined 'ink', they are made up of separable dyes and TLC has proved useful in their analysis.

TLC is not an identification method unless used for comparison with a complete collection of standards. TLC is used in conjunction with a reference specimen library to match the manufacturer of an ink. These reference collections must contain samples of all inks manufactured throughout the world. Deficiencies in the library weaken the interpretation of a match and increase the number of nonmatches.

The most important criterion in the application of TLC to matching inks with library standard inks is that the inks under investigation and library inks be chromatographed under identical conditions using identical methods. A match becomes an identity only if the match is known to be unique and/or the library is complete.

Described in this article are procedures for analysing inks. The first step in an ink analysis is the identification of the ink type. This is best determined microscopically (**Figures 1–5**). This determination is critical because different chromatographic methods are used for different inks.

Once an ink is identified, the manufacturer may provide crucial information regarding the ink's formulation, earliest possible production date, and distribution.



Figure 1 (See Colour Plate 88). Offset lithography photographed at 25 \times .

Jet Ink

Ink Jet Technology

Surprisingly, ink jet technology has been around for over 35 years, but only recently has it gained widespread use, most notably in desktop computer printers. This digital printing technology directs small droplets of ink to the substrate surface. Although there are several methods for accomplishing this, the two most common methods are continuous jets and drop-on-demand. Continuous jets create a stream of uniformly sized and spaced drops, which are deflected to produce an image. Drop-on-demand generates only the drops needed for image creation.

Fluid Jet Ink Chemistry

Most copiers/printers, which use ink jet technology, utilize a fluid, water-based ink. During the developmental stages of ink jet technology, researchers initially used fountain pen inks. These fountain pen inks caused corrosion on the print head surfaces, clogged

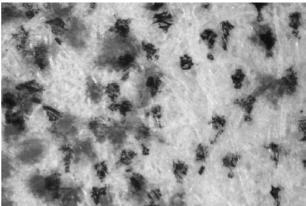


Figure 3 (See Colour Plate 90). Full colour ink jet photographed at $25 \times .$

jet orifices, and had long drying times and excessive ink bleeding. Although these inks provided a starting point, it became apparent that this new technology would require specially formulated inks.

The early dyes were borrowed from the textile industry, then reworked and purified. Most of the organic dye counterions were replaced with larger ions, decreasing the activity and pH to a more suitable level and improving solubility, thus minimizing corrosion and crusting of the jet orifices. Along with the direct dyes, acid dyes and basic dyes used in textiles and food dyes were also adapted for ink jet systems. Organic dyes generally consist of threedimensional compounds with ring structures having electron configurations that interact with incident radiation in the visible light range. Although these dyes must be soluble in water, they must be waterfast enough on the printed substrate to be used in an office environment. Amines and carboxylic functional groups were added to improve the binding of the dyes to the paper, and thus increase waterfastness.

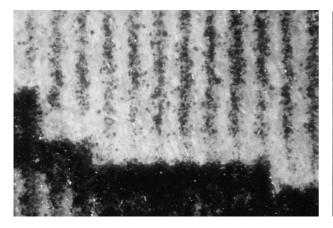


Figure 2 (See Colour Plate 89). Full colour toner photographed at $25 \times$.



Figure 4 (See Colour Plate 91). Letterpress ink photographed at $25 \times$.

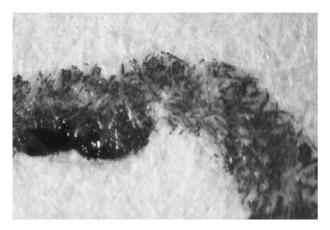


Figure 5 (See Colour Plate 92). Writing ink photographed at 25 ×.

Today, the majority of commercially available jet inks are specifically formulated by the manufacturers of the print-head and delivery systems, to several performance and aesthetic requirements. In addition, the ink must be chemically compatible with the components used to construct the ink reservoir and deliverv and head assemblies; it must have sufficient relative density and surface tension to remain in the nozzle without leaking out of the orifice; and when ejected it must produce the desired drop shape and radius. The ink also needs to have good wetting properties, while maintaining rapid drying times, and must have chroma, hue and optical density suitable for producing colours pleasing to the end user. In addition, the ink must be nontoxic and environmentally safe.

Dyes are the most useful colorants for jet inks; however, pigments also have properties valuable to these systems. Pigments, which are insoluble and must be suspended in the ink, have many advantages over dyes, including optical density, light- and waterfastness and stability. The main disadvantage is the lack of commercially available pigments with particle sizes less than 1 μ m; most pigments are simply too large for use in ink jet systems. Advances in micropigments are producing more suitable pigments for use in ink jet systems.

To enhance ink performance, additives are incorporated. Often a low vapour pressure solvent, such as polyethylene glycol, is added to inhibit crusting. Other additives aid in buffering the solution, stabilizing the dyes (i.e. pyrollidone), and wetting the paper (i.e. glycols, butyl ethers). To inhibit organic growth, biocides and fungicides are carefully selected and added to the formula. Like other water-based ink systems, bacteria and fungus thrive in jet inks.

The ink solution is a dynamic environment. Upon entering the delivery system or cartridge, the ink reacts with the polymers, foams and metals of the container. Therefore, the ink in the printer or cartridge is no longer in its original state. The ink also changes composition, depending on its location in the cartridge and what materials are used. In systems that use low vapour pressure solvent(s) for crusting prevention, the actual chemical composition of the ink changes near the orifice as the solvent(s) evaporate.

Ink–Paper Interaction

In addition to the critical compatibility of the ink and print system, ink and substrate compatibility also plays a crucial role in print quality. The print quality is partially determined by the surface tension, viscosity, delivery angle and velocity of the ink and the sizing, surface energy and topography of the substrate. When paper is used as the substrate, print problems such as spread (dot-gain), absorption (bleed through the paper) and paper curl are quite apparent. Initially these problems were addressed by developing special paper coatings to control these factors, as well as to enhance contrast and to improve the colour gamut, optical density and water-fastness. Many of these coatings contain silica and starch and have a large surface pore volume to absorb large quantities of ink quickly. Other ink jet papers include multilayer configurations and polymerized coatings, designed to interact with the dyes, to adjust and render them insoluble in water and adjusting for the pH of the ink.

Analysing Jet Ink

Extraction solvent The solubility of the jet inks in their sampled state determines the solvent used for their extraction. Since the ink to be forensically examined is almost always on a document, the primary focus is the solubility of the ink in its dried state on a particular substrate. The most useful method is classical solubility testing by sampling and determining solubility in pure solvents, then binary combinations, in dimple plates. Once the best extraction solution has been determined, the solvents used should be chromatographic grade to avoid contamination. For jet inks an extraction solution of ethanol/water (1:1) has been found to be the most successful.

Solvent (mobile phase)/stationary phase Because of the complexity of the jet inks, the colorants generally cannot be separated using a single solvent. Therefore, solvent mixtures must be used. Chromatographically these solvents are chosen for their selectivity and strength. Additionally, the solvent should be made just before chromatographing. If the mobile phase is not made fresh, the concentrations will change as the higher vapour pressure solvents escape into the gas-

Table 1	Ink solve	ent system I
---------	-----------	--------------

Solvent	Eluotropic value (ε°) solvent strength on silica gel	Snyder group (selectivity)	Parts
Ethyl acetate	4.4	VI	70
Absolute ethanol	4.3	II	35
Water	10.2	VIII	30

eous portion of the container. One solvent system, widely used for examining writing inks, has been found useful in the analysis of jet inks; this is solvent system I (Table 1). Additionally, solvent system V (Table 2) has been found to be another successful system.

The stationary phase, which is as important as the mobile phase, dictates the interactions between itself and the sample and solvent. Although there are several different stationary phases available (e.g. diol, reversed-phase, etc.) silica gel has proved to be most useful. Since some dyes have fluorescent characteristics, fluorescent indicators should be absent from the plate. It is highly advisable to clean the plates to remove any contaminants. This is performed by running the plate in the chosen solvent for the length of the plate and drying prior to spotting.

Sample preparation The substrate from which the inks are sampled is critical. Inks sampled from coated papers, which chemically and/or physically bind the ink, will chromatograph differently from the same ink printed on noncoated paper. Further, samples of ink taken directly from the cartridge versus drying the ink on a neutral substrate may also affect the chromatograms. Therefore, it may not be possible to analyse reliably documents produced on certain substrates by TLC.

Using a scalpel, ink should be removed from the uppermost layer of paper containing the ink. This method not only increases the ink-to-paper ratio, but also reduces potential contamination from ink on the reverse of the document. Samples must contain all of the imaging colours on the document, preferably in

Table 2 Ink solvent system V

Solvent	Eluotropic value (ε°) solvent strength on silica gel	Snyder group (selectivity)	Parts
Water	10.2	VIII	32
Acetic acid	6.0	IV	17
N-Butanol	3.9	11	41
Butyl acetate	_	-	10

equal amounts. If the document does not contain all four of the process colours, changes to the library comparison and confirmation test methods are performed with only those colours found in the sample in question. Additionally, samples of plain areas of the paper must also be taken to identify any components contributed by the paper. Depending upon the subject of the document, little if no plain areas may exist for a proper substrate blank. This is often the case when the background of the original is not white. The scalpel method should help to minimize paper influence.

Extraction/spotting/development The amount of ethanol/water is dependent on the size of the sample. The concentration of the samples should be within the relative range of the library specimens. The extract is spotted using a Camag Nanomat with $1.0 \,\mu\text{L}$ micropipettes at 1 cm from the bottom of a Whatman polyester silica gel plate. Once spotted, the plate is placed in a 95°C oven for 3 min to remove the extraction solvent. The plate is cooled to room temperature, then placed in a saturated vertical chamber containing solvent system I. The plate is allowed to develop to 4 cm from the origin, removed and dried.

Comparison/interpretation The developed plate is then compared with the chromatograms within the jet ink library and a list of possible matches is recorded. The possible library specimens are then sampled using the above mentioned method. The questioned ink and library specimens are spotted on a precleaned Whatman HPKF silica gel 60 plate. The plate is developed in a Camag saturated horizontal chamber containing solvent system I. After developing, the plate is dried. Once dry, the plate is interpreted under both UV and visible light (**Figure 6**).

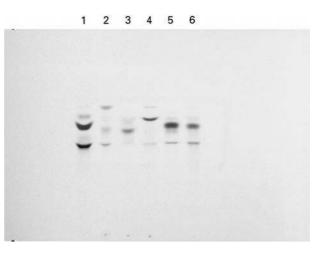


Figure 6 (See Colour Plate 96). Thin-layer chromatogram of full colour jet inks, solvent system I.

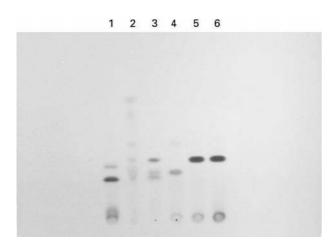


Figure 7 (See Colour Plate 97). Thin-layer chromatogram of full colour jet inks, solvent system V.

It should be noted that the interpretation of jet ink chromatograms is very different from interpretation of standard writing inks such as ball-point ink. Writing ink is eliminated if the relative dye concentrations are different between the questioned ink and a library specimen. This elimination is based on the fixed dye ratios within a writing ink, which is as characteristic as the dye composition itself. In ink jet systems, the concentrations of each of the four process colours varies according to the colour being reproduced; the relative concentrations of the dyes within the chromatograms will therefore also vary. As a result, relative concentration differences are not grounds for eliminating a jet ink specimen for consideration, as in the case of writing inks.

To confirm any matches to the library, a second plate with both the questioned sample and the matching library specimen is chromatographed using a Whatman HPKF silica gel 60 plate in solvent system V (Table 2). The match is then confirmed by interpreting the plate under both UV and visible light (Figure 7; see also Table 3).

If no matches are found, there may be deficiencies within the library or this may be caused by the use of post-market inks, i.e. inks made to refill original cartridges. In the case of such inks, a new range of reactions take place. Even though post-market inks may be well represented in the library, when they are added to existing cartridges the interaction with the original ink and container components may alter their chromatograms to the extent that they do not resemble either the original ink or the post-market ink. For example, the post-market ink will initially force the original ink to the print-head. Farther back in the cartridge the old and new inks mix, forming gradients. The changes that occur are often greater than the sum of the components.

Writing Ink

Writing Ink Chemistry

All writing inks consists of colorants and a vehicle containing solvents and resin binders (ballpoint). Writing inks can generally be placed into two categories: ballpoint (**Figure 8**) and non-ballpoint inks (**Figures 9** and 10). Non-ballpoint inks can be further subdivided into inks that are water-based (i.e. fountain pens, felt-tip markers, roller-ball) and those that are solvent-based ('permanent' markers). For ballpoint inks, the vehicle is commonly a mixture of glycol(s) (i.e. 2,3-butanediol, 1,2-propanediol), alcohols with low relative molecular mass (i.e. 2-phenoxy-ethanol, benzyl alcohol) and resin binders, which result in a paste-like consistency.

Most writing inks contain complex mixtures of mostly soluble dyes and occasionally suspended pigments (carbon or inorganic pigment), which result in unique formulations. Some of the more popular dyes and pigments are pthalocyanine blue, rhodamine, nigrosine and methyl violet.

Analysing Writing Ink

Extraction solvent The method for choosing an extraction solvent for writing ink is the same as that used for jet inks. For writing inks, extraction solvents

Table 3 Thin-layer chromatography of full colour jet inks as shown in Figures 6 and 7

Spot	Post-market Co.	Manufacturer	Model	Colours
1		Canon	BJC 620	YMCK
2		Epson	Stylus Colour 400	YMCK
3		Hewlett Packard	DeskJet 600	YMCK
4		Lexmark	2050	YMCK
5	American Ink Jet	Used in Hewlett Packard	DeskJet Series	YMCK
6	High Resolution	Used in Hewlett Packard	DeskJet Series	YMCK

Extraction solvent: ethanol/water. Whatman HPKF Silica Gel 60.

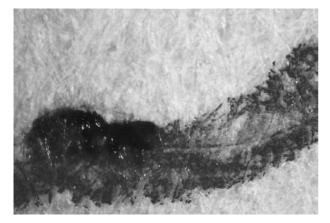


Figure 8 (See Colour Plate 93). Ballpoint writing ink photographed at $25 \times$.

include ethanol/water for water-based and some solvent-based inks and pyridine for ballpoint and most solvent-based inks.

Solvent (mobile phase)/stationary phase Writing inks are complex mixtures and generally cannot be separated using a single solvent. Therefore, solvent mixtures are used to enhance separation of the colorants. Several different systems have been developed and tried. Solvent systems I and II (Table 1 and Table 4) are the most successful. Other solvent systems such as III and IV (Tables 5 and 6) can be more effective when inks are highly polar or contain Nigrosine.

Silica gel is the most useful stationary phase. The dyes and pigments used in writing inks may have fluorescent characteristics that are very helpful in their examination; fluorescent indicators should therefore be absent from the plate. Once again, the plates should be cleaned to remove any contaminants.



Figure 9 (See Colour Plate 94). Non-ballpoint writing ink (solvent-based) photographed at $25 \times$.



Figure 10 (See Colour Plate 95). Non-ballpoint writing ink (fountain pen) photographed at $25 \times$.

Sample preparation Sampling is often accomplished by removal of the ink by use of a scalpel, a blunted 16–20 gauge hypodermic needle, or a commercially available forensic document sampling punch. If a scalpel is used, approximately 1 cm of an ink line is removed and placed into a vial. If the hypodermic needle or sampling device is used approximately ten plugs of ink ($\sim 0.1 \,\mu g$ of ink) are removed from the document and transferred to a vial. As with ink jet analysis, samples of paper/substrate should be taken and examined to identify its contribution to the ink sample extract.

Extraction/spotting/development The ink is extracted by adding a minimum of appropriate extraction solvent and spotted onto the plate with 1.0 μ L micropipettes at 1 cm from the bottom of a Whatman polyester silica gel plate. Once spotted, the plate is placed in a 95°C oven for 3 min to remove the extraction solvent. The plate is cooled to room temperature, then placed in a saturated vertical chamber containing solvent system I. The plate is allowed to develop to 4 cm from the origin. The plate is removed and allowed to dry by evaporation.

Comparison/interpretation The developed plate is then compared with the chromatograms within the writing ink library and a list of possible matches is

Table 4 Ink solvent system II

Solvent	Eluotropic value (ε°) solvent strength on silica gel	Snyder group (selectivity)	Parts
<i>N</i> -Butanol Absolute ethanol	3.9 4.3	 	41 35
Water	10.2	VIII	32

Table 5	Ink	solvent	system	Ш
---------	-----	---------	--------	---

Solvent	Eluotropic value (ε°) solvent strength on silica gel	Snyder group (selectivity)	Parts
Cyclohexane Chlorobenzene Absolute ethanol	0.04 0.3 4.3	VII - II	10 2 1

recorded. The possible matches are sampled using the above mentioned method. The questioned ink and possible matching standards are then spotted on a precleaned Whatman HPKF silica gel 60 plate. The plate is developed in a horizontal chamber containing solvent system I. After developing, the plate is dried by evaporation and interpreted under both UV and visible light (Figure 11).

Unlike ink jet ink interpretation, the concentrations of the dye components from nonrefillable cartridge pens will not vary between the questioned document and the library samples. Therefore, relative concentration differences are grounds for eliminating an ink specimen.

To confirm any matches to the library, a second plate with both the questioned sample and the matching library specimen is chromatographed on a precleaned HPKF plate in solvent system II (Table 4). The match is then confirmed by interpreting the plate under both UV and visible light (**Figure 12**; see also **Table 7**).

Toner

Toner Technology

Electrophotography dates back to 1938 and has become the most widely used plateless printing technology. Electrophotography is a process that consists of a photoreceptive drum that is charged in darkness with a corona discharge and exposed to an original document through an optics system. The light reflected from the original image discharges the photoconductor where the light strikes it, creating a latent image on the drum corresponding to the dark areas on the original. This latent charged image is de-

Table 6 Ink solvent system IV (modified)

Solvent	Eluotropic value (ε°) solvent strength on silica gel	Snyder group (selectivity)	Parts
Ethyl acetate Absolute ethanol Chlorobenzene	4.4 4.3 0.3	VI II	2 2 10

Two-phase liquid; the top phase is used as the solvent system.

1 2 3 4 5 6

Figure 11 (See Colour Plate 98). Thin-layer chromatogram of ballpoint inks, solvent system I.

veloped with oppositely charged toner. The toner is transferred to a substrate and fixed. Today's digital electrophotographic machines use lasers or light emitting diodes (LED) driven by digital data to create the latent image on the photoreceptive drum.

Dry Toner Chemistry

Toners are electrostatically transferred to the paper or print substrate and are fused by heat, pressure or a combination of both. As with other inks, toners must meet certain print parameters, such as waterand light-fastness, but because of their unique way of imaging they must also meet a unique set of chemical and physical parameters, such as triboelectric properties.

Dry toners are very fine powders consisting primarily of a polymer resin binder and colorants. These colorants, pigments and dyes, are chosen primarily for their chroma, hue and colour purity. The most common pigments and dyes are carbon black,

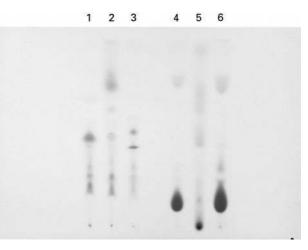


Figure 12 (See Colour Plate 99). Thin-layer chromatogram of ballpoint inks, solvent system II.

Spot	Manufacturer	Model	Colours
1	Papermate	Flexgrip	Blue
2	Skilcraft	Stick	Blue
3	Bic	Round Stic	Blue
4	Papermate	Flex Grip	Black
5	Skilcraft	Stick	Black
6	Bic	Round Stic	Black

Table 7 Thin-layer chromatography of ballpoint inks as shownin Figures 11 and 12

Extraction solvent: pyridine.

Whatman HPKF Silica Gel 60.

nigrosines, copper phthalocyanines, azo-pigments and quinacridone.

The polymer or copolymer resin binder is chosen for its thermal characteristics such as glass transition temperature and flow viscosity. Polystyrene acrylates and epoxy polymers are used for hot roll and flash fusing. Small chain homologue polymers, e.g. polyethylene and polypropylene, and vinyl acetates are used for cold pressure and roll fusing. Polyester is used primarily for radiant fusing. Often additives are incorporated into the toners to alter physical properties: pigments and dyes are added for colour; magnetite salts are added to enhance control of the toner; ammonium salts are used for positive charge control; acidified carbon black and metal complexes are added for negative charge control; silica and zinc sterate are added as a lubricant and flow enhancement; and silicone oils and low weight polyethyl and polypropyl waxes are used as release agents to prevent the toner from adhering to the fusing roller.

Analysing Toner

Extraction solvent The method for choosing an extraction solvent for toner is the same as that used for jet and writing inks. It must first be determined in which solvent(s) the toner is soluble, then whether mixtures of solvents are needed to enhance solubility. Pure chloroform was found to be the most successful.

Solvent (mobile phase)/stationary phase Like jet and writing ink, toners generally cannot be separated using a single solvent. Therefore, solvent mixtures must be used to accomplish separation of the colorants. The most successful solvent system for toners are solvent systems I (Table 1) and modified IV (Table 6).

Silica gel is the most useful stationary phase. The dyes and pigments used in toners often have fluorescent characteristics that are very helpful in their examination, hence fluorescent indicators should be absent from the plate. Once again, the plates should be cleaned to remove any contaminants. Sample preparation Sampling toner documents has advantages over jet ink documents. Although, as with ink jet documents, toner documents may have little or no clean paper areas, this is of little concern with toner sampling because the toner is removed from the document thermally. To remove the sample, a clean scanning electron microscope (SEM) aluminium stub placed over the sampling area is heated with a soldering iron. The heat causes some of the toner to be transferred to the stub. Since this method removes only the toner, paper interactions are avoided. Again, as with jet inks, all of the process colours should be sampled from the document in equal proportions. If the document does not contain all four of the process colours, changes to the library comparison and conformation test methods are performed with only those colours found in the sample.

Extraction/spotting/development The toner is washed from the stub with chloroform into a sampling vial. The toner wash is spotted onto the plate using 2.0 μ L micropipettes at 1 cm from the bottom of a Whatman polyester silica gel plate. Once spotted, the plate is placed in a 95°C oven for 3 min to remove the extraction solvent. The plate is cooled to room temperature, then placed in a saturated vertical chamber containing solvent system I. The plate is allowed to develop to 4 cm from the origin, removed and allowed to dry by evaporation (Figure 13).

Comparison/interpretation The developed plate is then compared with the chromatograms within the toner library and a list of possible matches is recorded. The possible library specimens are sampled using the abovementioned method. The questioned toner and library specimens are then spotted on a precleaned Merck silica gel 60 plate. The plate is

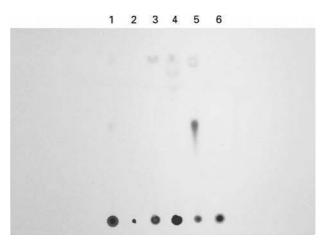


Figure 13 (See Colour Plate 100). Thin-layer chromatogram of full colour toner, solvent system I.

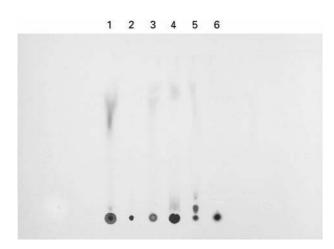


Figure 14 (See Colour Plate 101). Thin-layer chromatogram of full colour toner, solvent system IV.

developed in a Camag saturated horizontal chamber containing solvent system I. After developing, the plate is dried by evaporation. Once dry, the plate is interpreted under both UV and visible light.

As with jet ink interpretation, the concentrations of the dye components will vary owing to the varying concentrations of the four process colours between the questioned document and the library samples. Therefore, relative concentration differences are not grounds for eliminating a toner specimen, as in the case of writing inks.

To confirm any matches to the library, a second plate with both the sample and the matching library specimen is chromatographed using a Merck silica gel 60 plate, without fluorescent indicator, in modified solvent system IV (Table 6). The match is then confirmed by interpreting the plate under both UV and visible light (Figure 14; see also Table 8).

Conclusions

Through the use of colorant separation by TLC in conjunction with comparison libraries, the various original manufactures' inks can generally be distinguished from each other. At the time of this article,

Table 8Thin-layer chromatography of full colour toner asshown in Figures 13 and 14

Spot	Manufacturer	Model	Colours
1	Canon	CLC 1000	YMCK
2	Konica	7728	YMCK
3	Minolta	CF 900	YMCK
4	Ricoh	8015	YMCK
5	Sharp	CX 7500	YMCK
6	Xerox	5775	YMCK

Extraction solvent: chloroform. Merck Silica Gel 60. total distinguishability is obtained for full colour jet inks and toners. The comparison of the colour components has proved to be more discriminating than the comparison of other components, such as resins within ballpoint inks and toner. The ability to discriminate inks, coupled with the low cost, ease and multiple samples per run, make TLC a powerful forensic tool for the analysis of modern documents produced by traditional and new inks.

See Colour Plates 88, 89, 90, 91, 92, 93, 94, 95, 96, 97, 98, 99, 100, 101.

See also: **II/Chromatography: Thin-Layer (Planar):** Instrumentation; Layers.

Further Reading

- American Society for Testing and Materials (ASTM) (1991) Standard Guide for Test Methods for Forensic Writing Ink Comparison. ASTM STANDARD E1422-91.
- Aginsky VN (1993) Comparative examination of inks by using instrumental thin-layer chromatography and microspectrophotometry. *Journal of Forensic Sciences* 38(5): 1111–1130.
- Andrasko J (1994) A simple method for sampling photocopy toners for examination by microreflectance Fourier transform infrared spectroscopy. *Journal of Forensic Sciences* 39(1): 226–230.
- Brunelle RL and Reed WR (1991) Forensic Examination of Ink and Paper, pp. 165–170. Springfield, IL: Charles C Thomas.
- Cantu AA (1995) A sketch of analytical methods for document dating. Part I. The static approach: determining age independent analytical profiles; and Part II. The dynamic approach: determining age dependent profiles. *International Journal of Forensic Document Examiners* 1(1): 40–51; and 2(3): 192–208.
- Diamond AS (1991) Handbook of Imaging Materials, pp. 548–562. New York: Marcel Dekker.
- Fishman DH (1997) Ink jet technology. American Ink Maker June: 36-39.
- Hackleman D (1985) Where the ink hits the paper Hewlett-Packard Journal May: 32.
- Maze C, Loren EJ, Kearl DA and Shields JP (1992) Ink and print cartridge development for the HP DeskJet 500 C/DeskWriter C Printer Family. *Hewlett-Packard Journal* August: 69–76.
- Pagano B (1985) Identification of Photocopies by their Physical and Chemical Properties. Canadian Society of Forensic Science.
- Pagano L (1991) Colour Photocopy Analysis by Thin Layer Chromatography. Mid-Atlantic Association of Forensic Science, Bethesda, Maryland, May 1991.
- Snyder LR (1968) *Principles of Adsorption Chromatography*, pp. 193–221. New York: Marcel Dekker.
- Solodar W (1998) Designing dyes for ink jets. *International Journal of Forensic Document Examiners* 4(1): 22–24.
- Tsujita J (1998) Copier/printer market research. J & F Associates, Inc., Great Neck, New York.