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Forensic Examination of "Slightly Soluble" Ink Pigments Using Thin-Layer Chromatography

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ABSTRACT: A three-step thin-layer chromatographic procedure for examining colored components of printing and writing inks and other marking materials is described. The procedure uses the original stage of separating phthalocyanine pigments and other "slightly soluble" organic pigments.

Experimental conditions are given.

KEYWORDS: questioned documents, printing inks, artists' paints, toners, counterfeits, phthalocyanines, organic pigments, dyes, thin-layer chromatography, dimethylformamide (DMF), chloroform, concentrated sulfuric acid

There are many publications on the application of different analytical methods for the forensic examination of writing inks. Among these methods, thin-layer chromatography (TLC) remains the most widely used because it is very effective for determining the qualitative composition of colored components of these inks—synthetic dyes and their side-products [*1–3*]. At the same time, colored components of other writing, printing, and marking materials which are of forensic interest, such as printing inks, artists' paints, copy toners and color pencils,[2] could not be analyzed by TLC because these components (phthalocyanine pigments and some other organic pigments) were not soluble in the most of eluents applied [*4*].

In this work about 120 synthetic pigments and dyes used for commercial production of modern artists' paints, toners for copying machines, writing and printing inks in the former Soviet Union have been studied by TLC.

The general approach to the examination of these materials—using a three-step TLC procedure that is described in the paper—includes the original stage of chromatographic separation of "slightly soluble" organic pigments.

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[2]These materials were used often for making of counterfeit bank-notes and other documents in the former Soviet Union.

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Experimental Procedure

Ink Sampling

Approximately 2 to 3 mm^2 of printing ink, artists' paint, or copy toner area or approximately 2 to 3 mm length of ink line written by a pencil or other writing materials are removed by scratching (writing inks—by cutting) with help of a safety razor. The ink samples are placed into small vials such as, for example, Macherey-Nagel 1-mL glass vials N11-1.

Extraction Procedure

The samples are extracted for 1 min with 2 to 3 μL of dimethylformamide (DMF) using stirring with a needle. DMF dissolves most of the organic pigments present. Besides, it was noted that if a sample contained pigments insoluble in DMF (called "slightly soluble" in this paper) they, as tiny particles (after spotting the DMF-extracts onto a TLC plate these particles were easily observed under the microscope within the spots on the sorbent surface), had been partly (but in quantity quite detectable by TLC) transferred from the sample to the DMF-extract. When DMF leaves a colored residue on the sample after extraction, this residue can be reextracted for 1 min with 2 to 3 μL of concentrated sulfuric acid (conc. H_2SO_4).[3]

Thin-Layer Chromatography

The extracts are spotted onto a Merck 20 × 20 cm silica gel 60 TLC plates (without fluorescent indicator) using glass capillaries. The spotted samples are separated by the linear ascending mode using a multiple development procedure. The following eluents are successively used:

1) chloroform (a separation distance is about 10 cm): most of organic pigments are chromatographed, whereas practically all heteropolyacids of basic dyes (they are ingredients of many printing and writing materials), basic and acid dyes, oil-, ethanol-, and water-soluble dyes remain on the starting line;

2) ethyl acetate—isopropanol—water—acetic acid = 30:15:10:1, v/v[4] (a separation distance is about 7 cm): basic and acid dyes, heteropolyacids of basic dyes, oil-, ethanol-, and water-soluble dyes are developed separating on their colored components.

If after the two described steps of elution the starting line still contains colored zones, the third development of the plate is performed:

3) conc. H_2SO_4 (a development distance is near 2 cm): most of phthalocyanine and other "slightly soluble" organic pigments are separated forming well-shaped zones of colored components.

Several examples are represented in Table 1.

The described three-step TLC procedure allows one to get analytically valuable information about inks' colored organic components including the above mentioned "slightly soluble" ones, if they are present in inks analyzed. This procedure proved to be effective for forensic examination of fraudulent bank-notes and other documents and it is widely used in expert practice of criminalistics laboratories of Russia.

[3]Conc. H_2SO_4 dissolves practically all organic pigments [5]. So if the residue after the acid extraction is colored it is suggestive of the presence of inorganic pigments in the sample analyzed.

[4]For the last ten years in the criminalistics laboratories of Russia, this system of solvents has been the most applicable one for separating dye components of writing inks.

TABLE 1—*TLC separation of some "slightly soluble" organic pigments using conc. H_2SO_4 as an eluent.*

Dye	Color of zone[c]	R_f value
C.I. Pigment Green 7	Bright-green	0
C.I. Pigment Green 10	Yellow	0.85
C.I. Pigment Blue 15	Yellow-green	0.8
C.I. Pigment Blue 15:1	Yellow-green	0.7
Pigment greenish-blue phthalocyanine[a]	Green	0.8
Lacquer turquoise[a]	Blue-green	0.9
C.I. Pigment Blue 60	Brown	0.75
	Blue	0.8
C.I. Pigment Red 210	Red	0.8
C.I. Pigment Red 60:1	Yellow-red	0.85
C.I. Pigment Red 83	Orange	0.7
	Yellow	0.8
C.I. Direct violet 47[b]	Blue	0.65
	Violet	0.8
C.I. Pigment Yellow 17	Orange	0.4
C.I. Acid Brown 75[b]	Brown	0.9
C.I. Acid Black 2[b]	Grey	0.9
C.I. Pigment Black 1	Grey	0.95

[a]The pigments which do not have a Colour Index (C.I.) Number are given according to the Russian trade denomination of pigments.

[b]These pigments are soluble in DMF and so they are not "slightly soluble" ones. But in this work it proved to be impossible to move them off from the starting line of the TLC plate using most of widespread eluents, whereas by using conc. H_2SO_4 as a mobile phase they were easily chromatographed.

[c]After removing the plate from the eluent the colors of separated substances have been fading gradually (during more than 15–20 min). Therefore, to avoid the loss of analytical information after the third development of the plate, the resulting chromatogram should be observed as quickly as possible after the plate has been removed from the eluent.

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References

[1] Brunelle, R. L. and Pro, M. J., "A Systematic Approach to Ink Identification," *Journal of the Association of Official Analytical Chemists*, Vol. 55, No. 4, 1972, pp. 823–826.

[2] Kelly, J. D. and Cantu, A. A., "Proposed Standard Methods for Ink Identification," *Journal of the Association of Official Analytical Chemists*, Vol. 58, No. 1, 1975, pp. 122–125.

[3] Schweppe, H., "Thin-Layer Chromatography," *The Analytical Chemistry of Synthetic Dyes*, K. Venkataraman, Ed., Wiley, New York, 1977.

[4] Milovanovic, G. A., Ristic-Solajic, M., and Janjic, T. J., "Separation and Identification of Synthetic Organic Pigments in Artists' Paints by TLC," *Journal of Chromatography*, Vol. 249, 1982, pp. 149–154.

[5] Billmeyer, F. W., Salzman, M., and Kumar, R., "Identification of Organic Pigments by Solution Spectrophotometry," *COLOR Research and Application*, Vol. 7, No. 4, pp. 327–337.

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