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THE USE OF THIN-LAYER CHROMATOGRAPHY IN THE IDENTIFICATION OF HISTORIC ARTIFICIALLY COLORED VARNISHES AND GLAZES

Judith J. Bischoff, Scott W. Nolley and Jonathan Thornton

Abstract

Historically, natural dyes and resins have been used in the polychromed decoration of wood, as well as in clear colored coatings and glazes employed in the finishing of other types of artifacts. Largely impermanent as colorants, the presence of these materials in their aged and faded states can often go unrecognized when encountered in a darkened and yellowed varnish. Thus, it is important that the conservator be able to easily determine when an object has been intentionally colored. The goal of this study was to find a simple, low-cost method for the detection of colorants used in the historic production of such artifacts.

Thin-layer chromatography (TLC) was the principal method chosen for this investigation, based on its simplicity and low-cost. Some resinous materials used in the formulation of traditional varnishes, along with colored resins and natural and synthetic dye materials, were studied, alone and in combination. The method was assessed for its feasibility in the chromatographic separation of the various colored components and for its ability to aid in identification of these components.

Introduction

Capable of evoking sensation and emotion, color has always been an important element in human culture throughout its history. Colored materials such as pigments and dyes have historically been employed not only to embellish and enhance appearance, but to also indicate hierarchy and status. As the colored component in film forming materials, pigments and dyes have historically been employed to impart brilliant and transparent color to a wide variety of objects. Though a great deal of research has focused on the analysis of pigmented films, the research addressing the analysis of dyes and colored resins in colored varnishes appears limited.

For the conservator, identification of these materials in colored varnishes is problematic. Very often a pigmented surface coating, colored with a dyestuff and seemingly devoid of any colorant with discernible particle size, can be mistaken for a discolored varnish. The detection of such a colorant can be complicated by the altering effects of age. These determinations become even more of a problem to the conservator without access to the expensive analytical instrumentation that is required for these analyses. Often, the resulting data can only be accurately evaluated by someone having a great deal of experience with these materials.

What will be presented here is a brief overview of the colorants traditionally employed in these coatings, followed by methods for their identification including thin-layer chromatography (TLC). TLC was chosen for use in this investigation because it can be carried out on fairly small samples, requires only simple and inexpensive equipment, and has remarkable resolution in the separation of complex mixtures.

History

The procurement and use of dyes and pigments is as old as mankind. Tyrian purple, an early dye extracted from mollusks of the genus *Murex*, was used to dye the robes of senators in Rome. The extensive use of the blue dye indigo has been documented in India as long ago as 3000 BC. Important because of its exceptional lightfastness, this product of various species of the genus *Indigofera* was subsequently grown and exported around the world.

Of the red colorants, one of the most important was madder. This dye is a mixture of components, all anthraquinone derivatives, whose proportions are largely dependent on the source plant and the extractive process by which these materials are isolated.

The red dyes of insect origin are also anthraquinone derivatives. A by-product of the same infestation that produces shellac, Lac dye comprises up to 10% of the produced encrustation and is extracted with an aqueous base. Lac dye from India was so important in Europe that it gave its name to all other dye-based pigments as the term "lake." It was well known in Egypt and has been identified in Persian textiles from the 13th century. Kermes is the dye extracted from the bodies of the kermes insect . It was the principal insect dye in Europe before cochineal, also a scale insect, was discovered by Europeans in the Americas, where it had been used as a dye for centuries.

Red dyes extracted from the wood of several species of *Caesalpinia* were known as *brasil wood.* Having been imported from South East Asia, these materials were known in Europe long before the discovery of South America.

Natural yellow dyes are largely flavinoids, compounds quite common in the vegetable kingdom. Quercitrin, for example, was widely used in the 19th century. The most colorfast of the natural yellow dyes is obtained from weld, or dyers weed, and can be found in European textiles as well as Anatolian carpets. Saffron, the dried stamen of the bloom of the *Crocus sativus* yields a rather expensive yellow dye containing as its main colorant the glucoside crocin. A compound from buckthorn berries was used to produce the yellow lake called *Dutch pink.*

Most dyes can be made into insoluble pigments by precipitating the organic coloring material or dye onto an insoluble, transparent inorganic inert material. These materials possess particle sizes in the range of other pigments and are called lakes. Known for their bright colors and transparency in organic binding media, these pigments lend themselves for use in the colored pellicular or binder-rich films known as glazes.

In addition to dyestuffs, another group of colored organic materials have also been employed in the fabrication of works of art. These brightly colored, water-insoluble plant exudates, known as resins, have always been attractive materials, historically incorporated into sealing waxes, adhesives and finish formulations based on other film-forming resins.

The foremost of these, the red resin dragon's blood, exists as two distinct types. One, the exudate of large trees that grow on Socotra and the Atlantic islands, the second, most commonly found today, is the product of the family *Palmae* originating in South East Asia. Other examples of red resins used as colorants are the accroides resins from the grass-tree, native to Australia. Dissolved in the coating, the presence of these materials is characterized by no distinguishable particles suspended in the film.

Natural dyes such as cochineal, turmeric, madder, and henna remained primary sources of dye colors until the commercial production of the first synthetic dye in 1856. This began the replacement of natural dyes with synthetics such as crystal violet and the triphenylmethyl dyes. In 1862 the discovery of the azo dyes, dyes manufactured from aromatic amines, revolutionized the dye industry.

Documentary evidence for the use of dyes in paints and coatings goes back to the 9th century *Mappae Clavicula*, a compilation of often fragmentary formulas from earlier sources that included recipes containing woad, indigo and lac.

When used as completely dissolved colorants in a drying oil, spirit varnish or oil-resin varnish these glaze formulations have served to expand the palette of wood polychromy. They have been used as a gold tone for white metal leafs and light woods and as translucent glazes for fine and decorative painting. In the 19th century colored varnishes and glazes were employed in the manufacture of japanned tin coated iron ware, papier maché and often over metal leafs and mother-of-pearl inlay. Toned varnishes and glazes were often applied to a paint in order to impart luminance and depth, for example a cochineal lake glaze over a red lead paint.

Preliminary Identification of Materials

When using any sophisticated analytical technique for the identification of colored materials, an historical understanding of the object as well as its visual examination can help to narrow the field of possibilities. For example, preliminary examination (prior to analysis by thin layer chromatography) of a varnish believed to be colored can not only reveal the presence of a colorant but can help to characterize the material. One such method is the examination of the film in question with ultraviolet illumination. This can be clearly seen when reference samples of lake pigments in various binders are partially faded and compared to their respective controls under normal illumination and ultraviolet illumination .

Microscopic examination of a glaze or varnish sample is another simple diagnostic method. The presence of lake pigments is often clearly indicated by the characteristic appearance of the dye material bound to the insoluble inorganic substrate. In samples where the coloring material has faded, examination of the sample between crossed-polars can show the characteristic birefringence of the inorganic substrate when it is an anisotropic material. Conversely, colored resins and synthetic dyes do not typically exhibit particulate character under microscopic examination.

By integrating methods usually employed in the isolation of dyes from textiles, and the analytical technique of solvent extraction in sample preparation of colored varnishes for thin-layer chromatography, general assumptions regarding the identity of the colorant can be made. This information can then be used to fine tune the optimum conditions for accurate and clearly resolved chromatographic analysis.

Samples colored with lake pigments are treated with a few drops of sulfuric acid, which releases the dye from the inorganic substrate. Reference standards to be analyzed alongside the prepared unknown sample are treat ^G^Aimilarly. Certain polygenetic dyes, dyes that display different hues under acidic and basic conditions, can be identified by their color changes at different pH values. For example, the synthetic dye brilliant yellow turns red when extracted under basic conditions.

Further characterization of a dye material can be made by examination of the organic phase in a solvent extraction of the dissolved film. For example, when samples of red dyes are extracted with acid, diluted with 1 milliliter of deionized water and shaken with an equal amount of low boiling point petroleum ether, madder and kermes go into the petroleum ether phase, coloring it orange. Cochineal and lac dye remain in the aqueous phase and can be extracted with pentanol. Ultraviolet illumination can be used to differentiate between madder and kermes, as madder exhibits a characteristic orange fluorescence. The petroleum ether and pentanol extracts can be washed with water to remove residual acid and used for identification of the dyes using thin-layer chromatography.

Chromatography

Chromatography, from the Greek for "color writing", is a method used in analytical chemistry to separate and identify the components of mixtures. The name derives from the earliest application of the technique, which was the separation of colored substances extracted from plants. Thin-layer chromatography was chosen for use in these investigations as it can be carried out on extremely minute samples, requires only simple apparatus and has remarkable resolution in the separation of complex mixtures.

Thin-layer chromatography employs a stationary phase on an inert solid support, typically glass, aluminum or plastic. The thin layer, or adsorbent, is usually silica gel, alumina or polyamide powder deposited as a homogeneous layer on the inert support. The mixture to be separated is first dissolved in a volatile solvent, and a small sample of this solution is placed on one end of the plate with a small capillary tube. The solvent evaporates, and only the mixture to be separated remains on the plate in the form of a small spot. A glass tank is filled to a depth of approximately one centimeter with a carefully chosen developing solvent and the tank is covered to allow saturation of the tank atmosphere with the solvent vapor. The plate is placed in an upright position and the liquid rises along the plate by capillarity.

As the solvent comes in contact with the sample mixture, each molecule is transported in the flowing liquid, becoming attached, or adsorbed, to the stationary solid. The rate at which they do so depends on the mobility of the molecules, the temperature, and the binding forces involved. The length of time that each type of molecule spends in the mobile phase leads to a difference in the separation of substances. When the mobile phase has risen to within a few centimeters of the top of the plate, the development is stopped and the plate is dried. The plate is then examined under the appropriate visualization conditions for the material analyzed.

Plates spotted with resinous materials are developed twice with 5% methanol in xylenes, rotating the plate 90° for the second development. Plates spotted with extracted lake and synthetic dyes are developed once, with a solvent system consisting of chloroform, methanol, butanone and formic acid in the proportions of 6:2:1:1 respectively.

Visualization of Developed Chromatograms

Visualization of the developed chromatograms can be achieved by several methods, each giving different appearances. For example, iodine complexes with many organic materials and forms brown spots that are easily detected.

The most successful method of visualization for these materials, however, is ultraviolet illumination. In chromatograms visualized using UV illumination each of the natural colorants has a fluorescence fingerprint specific to that material, a pattern of spots of intensity and color that clearly identify the substance even in small concentrations. Ultraviolet illumination is also suitable in visualizing developed plates of synthetic dyes.

Analysis of Mixtures

These patterns seen for natural colorants are often identifiable even when present in complex mixtures. For example, TLC analysis of a colored shellac recipe from Robert Dossie's *Handmaid to the Arts*[1] clearly exhibited the three spots characteristic of turmeric standard. Traveling the same distances on the plate as the reference materials, and distinguishable by their different colors under ultraviolet illumination, were the characteristic pale-orange spots indicating annatto, saffron and shellac.

Another example, even more complex, is Vernis d'Or, a gold varnish from a late 19th C. formulary[2]. Characteristic bands can found in the TLC analysis; most notable are the spots indicating the presence of gamboge, sander's wood, dragon's blood and shellac.

Case History: A 19th Century Box

An example of the practical application of these techniques is presented in the analysis of a 19th century tinned-iron tobacco box coated with a varnish film colored with a yellow material. The exterior of the box displayed marked fading of the yellow colorant most notable in the exterior surfaces of the box protected by the lid. A sample of the coating was removed from the inside of the lid. Microscopic examination of the sample revealed a homogeneous film that did not appear to contain any pigment characterized by visible particles. The colorant appeared to be dissolved in the film, suggesting a colored resin or a synthetic dye.

For this analysis, a small amount of sample was dissolved in a 1:1 methanol:toluene solvent mixture and spotted on a polyamide plate against standards for a number of early synthetic yellow dyes historically used in paints and coatings. The standards for this analysis came from a reference collection generated by a workshop on early synthetic dye analysis given at the Smithsonian Institution's Conservation Analytical Laboratory.

The plate was developed, dried and examined under ultraviolet illumination. The solvent front, clouded by the fluorescence of the sample binder, indicated a single dark spot common to both the sample from the box and the reference for Martius yellow, an early azo dye used in paints, varnishes and lacquers as well as in the textile industry.

In an attempt to free the colorant from the binder material, the sample was extracted with a sulfuric acid and petroleum ether mixture. The two layers were separated and the yellow colored aqueous phase was extracted with pentanol. The pentanol extract was run against the martius yellow standard using the developing solvent best suited for dyes. After drying, the plate was visualized with ultraviolet light. A single spot, similar in color and position on the plate was found for both materials. This suggested that the yellow colorant used in the box coating is Martius yellow.

Two-dimensional Chromatography

Two-dimensional thin layer chromatography, also known as bi-directional thin layer chromatography, is a technique which is used for the separation of extremely complex mixtures. In such cases it is often necessary to use more than one solvent system in order to completely separate and resolve all components in the mixture. In this method, a square TLC plate is spotted at one corner with the sample to be analyzed and developed with the first solvent system. The plate is dried, rotated 90° and then developed with the second solvent system. Single spots arising from development in the first solvent system may be further separated into two or more spots upon development in the second solvent. This technique generally gives better overall separation and resolution than development in a single direction with a single solvent system.

Since a different solvent system is required for the separation of resinous mixtures than is used for dye mixtures, it was thought that two-dimensional (bi-directional) thin layer chromatography would be uniquely suited for the analysis of complex mixtures containing both classes of materials, such as the coating material on the tin tobacco box. This method has been used successfully for the separation of resin mixtures and for complex mixtures of dyes.

This method was applied to the analysis of a sample from the tobacco box. Two separate square plates were spotted at their lower right corners, one with the sample from the box and the other with the reference standard for Martius yellow. The two plates were developed first with the solvent system for resins. The plate was dried, rotated 90°, and developed with the solvent system for dyes. In this case, the similarities in color and position of the spots developed in both directions on the two plates clearly identified the dye in the yellow varnish to be Martius yellow.

This above example suggests that this technique shows promise for the analysis of complex resin-dye mixtures that have been used historically in the polychromed decoration of wood, as well as in the clear colored coatings and glazes employed in the finishing of other types of artifacts. Work is under way to further demonstrate the general use of this method for the analysis of metal alloys and mineral based pigments.

Conclusions

In a comparison of several natural dyes colored resins and synthetic dyes, thin-layer chromatography demonstrated remarkable resolving power and an ease of identification of materials when compared against reference standards. Coatings that appear largely faded to the eye were easily characterized using these techniques. As with any analytical method, a certain fine-tuning of the procedure was often required to achieve optimum results and clearly resolved chromatograms. The resultant patterns clearly identify these materials when compared to their corresponding references. It should be noted that numerous factors can confuse the results however. Examples of these complication factors include extracting the colorants from extremely polymerized films, the knowledge that one might be visualizing the degradation products of these materials and the possibility that, over time, the applied film has incorporated extractives or other resinous compounds from the substrate. Nonetheless, dye identification techniques usually employed on textile materials and microscopic examination, in combination with thin-layer chromatographic analysis have demonstrated their value as valuable low-tech methods with which to approach the characterization of these materials.

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Endnotes

1. "1 oz. turmeric, ground; 2 drams annatto; 2 drams saffron; 12 pts. spirits of wine (ethanol); 3 oz. seed lac." from Dossie, R. 1758. *Handmade to the Arts*. London.:J. Nourse bookseller.

2. “5 parts dragon’s blood, 5 parts elemi, 25 parts gamboge, 20 parts mastic, 12 parts sandarac, 20 parts shellac, 15 sanders wood, 10 parts venetian turpentine, 600 spirits of wine.” *Vernis d’or* from Andres, 1882. *Varnishes, lacquers, Siccatives and Sealing-Waxes.*

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