J20 Differentiation of Black Permanent Marker Inks by Thin-Layer Chromatography and Gas Chromatography-Mass Spectrometry

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After attending this presentation, attendees will understand how brands of permanent marker ink can be differentiated by thin-layer chromatography and gas chromatography-mass spectrometry.

This presentation will impact the forensic science community by demonstrating how thin-layer chromatography and gas chromatography- mass spectrometry can aid document examiners in the differentiation of brands of permanent markers.

Identifying the formulation of ink can be important for questioned document examination. Knowledge of ink formulations can help determine the authenticity of a document, including its age and the presence of any alterations of the document. Permanent markers are commonly available and widely used writing instruments; they are used particularly for labeling items made from non-porous materials, such as glass and plastic. Thin layer chromatography and gas chromatography- mass spectrometry are well established methods for determining the composition of ball pen and gel pen inks. It is believed that thin layer chromatography and gas chromatography-mass spectrometry would also have significant value in the analysis of permanent marker inks.

Fifteen brands of black permanent marker were purchases in Virginia, Ohio, and the District of Columbia. For brands that had more than one marker per pack, all markers in the pack were tested separately to ensure consistency within the brand. This gave a total of forty-eight markers. Scribble sheets were created with each marker using 1-inch squares of filter paper. The ink was then extracted from a 7mm circle of the scribble sheet using 40µL methanol in a small glass vial. This extract was used for both thin-layer chromatography and gas chromatography- mass spectrometry. The inks were examined by thin-layer chromatography by spotting approximately 4µL extract on silica gel plates without fluorescent indicator. A mobile phase consisting of ethyl acetate, ethanol, and water (75:35:30) was used. The solvent front was allowed to migrate 4 cm before the plate was removed from the mobile phase. For gas chromatography-mass spectrometry a non-polar 30-meter capillary column was used. The oven temperature program had an initial hold at 50°C for one-minute, followed by a ramp to 200°C at a rate of 10°C per minute with a two-minute hold. Finally the oven temperature was increased to 300°C at a rate of 25°C per minute with a final hold for two-minutes. The mass analyzer was an ion trap operating in electron impact mode with a scan range from 40 m/z to 650 m/z. The samples analyzed by thin-layer chromatography were run in duplicate, and those analyzed by gas chromatography-mass spectrometry were run in triplicate to ensure reproducibility. Splitless injection was used for the samples analyzed by gas chromatography-mass spectrometry to make sure that all volatile organic ink components were detected.

Thin-layer chromatography separates the dyes used in the ink, while gas chromatography-mass spectrometry appears to identify mainly other ink components. These two analytical methods are therefore complementary. It was determined that one group of three brands and one group of two brands could not be differentiated by thin-layer chromatography. The Discriminating Power (DP) for thin-layer chromatography was determined to be 0.962 with 105 total possible pairs of permanent marker brands. All brands of permanent marker tested could be differentiated by gas chromatography-mass spectrometry based on the presence or absence of specific peaks in the chromatograms. Gas chromatography without mass spectrometry would therefore also appear to be a highly discriminating method for the analysis of permanent markers. Further work is underway to identify as many of the volatile organic components detected by gas chromatography-mass spectrometry as possible. The effects of aging of permanent marker inks are also being examined. These methods can aid document examiners in the differentiation of brands of permanent markers.

Questioned Documents, Thin-Layer Chromatography, Gas Chromatography-Mass Spectrometry

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