J16 The Examination of Permanent Markers Using UV-VIS-NIR Spectrophotometry, Thin-Layer Chromatography and Gas Chromatography-Mass Sepctrometry

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After attending this presentation, attendees will learn about the value of UV-visible-near infrared spectrophotometry, thin-layer chromatography and gas chromatography-mass spectrometry to the analysis of questioned documents, specifically to the examination of permanent markers.

This presentation will impact the forensic community and/or humanity by familiarizing the forensic community with the value of UV- visible-near infrared spectrophotometry and with the potential of high-performance thin layer chromatography for forensic analyses.

Permanent markers have been available for decades. They are widely used in homes, offices, and laboratories. Despite the ubiquity of these writing instruments there has been little forensic analysis of their inks. Permanent markers are available in with a variety of tip sizes, ranging from ultra-fine to wide. They are also available with a variety of tip shapes: chisel, bullet, and bristle. The inks in permanent markers consist of dyes and resins dispersed in volatile solvents. The solvent in a permanent marker may be a low-molecular weight alcohol such as n- propanol or a mixture of alcohols (e.g. ethanol and 2-propanol or n- propanol, n-butanol and diacetone alcohol). A series of permanent markers were purchased in the Washington, DC, metropolitan area for analysis. The permanent markers analyzed in this study are listed in the table below.

Brand	Type	Color			
		Black	Blue	Green	Red
Bic	Fine point	X	X	X	X
Fisherbrand	Fine point		X		
Foray Manstays	Chisel point	X	X	X	X
Office	Fine point				
Marks-A-Lot	Chisel point	X	X	X	X
Papermate	Fine point	X	X	X	X
RoseArt	Fine point	X	X	X	X
RoseArt	Retractable, Chisel point	X			
Sharpie	Chisel point	X	X		X
Sharpie	Fine point	X	X	X	X
Sharpie	Twin, fine point		X		
Staples	Chisel point	X	X		X

"Scribble" sheets were prepared with black, blue, green, and red permanent markers on Whatman quantitative hardened low ash grade 54 filter paper (Whatman, Florham Park, NJ). The "scribble" sheets were photographed with a Sony Cyber-shot 5.0 megapixel digital camera equipped with a Carl Zeiss 10X precision digital zoom lens. This camera has infrared capability. The sheets were photographed under normal room light, long wavelength (375 nm) ultraviolet light, green light (570 nm) and infrared light. The green (570 nm) light was provided by a FLS 5000 Forensic Light Source (Evident Crime Scene Products, Union Hall, VA). The "scribble" sheets illuminated with green light were photographed through the red viewing plate provided with the FLS 5000 and through an infrared filter.

Ultraviolet-visible-near infrared reflectance spectra were recorded using a Jasco V-570 Spectrophotometer (Jasco Inc., Easton, MD), equipped with a specular reflectance accessory. Permanent marker ink samples were placed on the dull side of a sheet of aluminum foil. Their spectra were recorded from 200 nm to 2000 nm at a resolution of 0.1 nm. Spectra were recorded in %R mode. The reflectance data were then subjected to a log(1/R) transformation. This transformation has been frequently applied to near infrared spectra because it accentuates subtle differences between spectra.

Samples of the permanent marker inks were also analyzed by thin- layer chromatography (TLC). Six-millimeter diameter disks were punched out of the scribble sheets with a single-hole punch. The disks were divided in half and one half was extracted with 20 µL of methanol. The 20-µL extracts were spotted on Silica Gel 60 TLC plates without fluorescent indicator (EMD Chemicals, Gibbstown, NJ). Extracts were similarly spotted on high-performance thin-layer chromatography (HPTLC) plates (EMD Chemicals, Inc., Gibbstown, NJ). The TLC and HPTLC plates were developed in an ethyl acetate:ethanol:water (75:35:30) mobile phase. The TLC plates were allowed to develop over a 10-cm distance, while the HPTLC plates were allowed to develop over a 5-cm distance. The developed TLC

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and HPTLC plates were photographed under normal room light, long wavelength (375 nm) ultraviolet light and infrared light.

The permanent markers were also analyzed by gas chromatography-mass spectrometry (GC-MS). Six millimeter disks were punched from the scribble sheets and extracted with 40 µL of methanol. A 1-µL aliquot of the extract was injected into a Varian Saturn 2000 gas chromatograph-mass spectrometer. A 30-m Restek Rtx-1MS capillary column with a 0.25 mm internal diameter and 0.5 µm film thickness was used. The injector and transfer line temperatures were 250ºC and 270ºC, respectively. The following column oven temperature program was used: 50ºC for 1 min, 10ºC/min ramp to 200ºC and a 2-min hold at the final temperature. A 2 ¾ min solvent delay was also incorporated into the GC-MS method of analysis. Mass spectra were scanned from 10 m/z to 650 m/z.

Examination of the permanent markers under the different illuminants had limited value for the discrimination of black permanent markers. Under visible light the black permanent markers could not be differentiated from one another. Two black permanent markers were effectively transparent to infrared light. The different illuminants did provide somewhat better discrimination of the colored permanent markers; nevertheless, a number of the colored permanent markers could not be distinguished from one another.

The ultraviolet-visible-near infrared reflectance spectra allowed a high degree of discrimination of the colored permanent markers. The reflectance spectra of the black permanent markers fell into three groups. In Group 1, the visible-near infrared reflectance changed abruptly from low reflectance to high reflectance between 600 and 800 nm; in Group 2, the reflectance increased slowly between 600 nm and 1000 nm; and in Group 3, the reflectance remained low between 600 nm and 1000 nm. The visible-near infrared reflectance spectra of black gel pen inks have been observed to behave in a similar fashion.

TLC was able to differentiate all of the permanent markers except for the Foray and Staples black, blue, and red markers and the Bic and Sharpie red markers. The HPTLC plates developed in approximately one third the time required for the regular TLC plates but showed the same resolution of the permanent marker dyes.

In general, GC-MS was not highly discriminating of the permanent markers. Their total ion chromatograms typically showed only one or two major components. The Foray and Staples black, blue, and red
+permanent markers, which could not be discriminated by TLC, could also not be differentiated by GC-MS. These markers are “house brand” markers produced in China. It is possible that the Foray and Staples markers were actually produced by the same Chinese company from the same ingredients. The Bic and Sanford Sharpie red permanent markers could be differentiated by GC-MS: their chromatograms contained different components. The identification of the permanent marker components appearing in the GC-MS chromatograms is on-going.

This research shows that TLC has the greatest power to discriminate between permanent markers. When TLC fails to differentiate permanent markers, GC-MS may provide additional useful information.

GC-MS, TLC, HPTLC

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