



Use of Synchrotron Reflectance Infrared Spectromicroscopy as a Rapid, Direct, Nondestructive Method for the Study of Inks on Paper

T. J. WILKINSON, D. L. PERRY,*
M. C. MARTIN, W. R. MCKINNEY,
and A. A. CANTU

Lawrence Berkeley National Laboratory, Berkeley, California 94720 (T.J.W., D.L.P., M.C.M., W.R.M.); and U.S. Secret Service, U.S. Department of the Treasury, Washington, D.C. 20373 (A.A.C.)

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INTRODUCTION

The analysis of inks and the paper to which they are applied is of great interest to a broad spectrum of science. From the historian and archaeologist to the forensic scientist, an understanding of ink–paper interactions is essential to the understanding of the ink and its subsequent changes upon application to paper.¹ Determining chemical and other details of ink in a signature, for example, can be an exceedingly difficult task. Modern ballpoint writing inks are frequently mixtures of ink vehicles (used to dissolve the dyes or disperse pigments), dyes and/or pigments, various resins and polymers (to control the viscosity of the ink and to serve as “fillers”), acidic materials (frequently fatty acids that function as lubricants), and surface-active agents. Additionally, other organics may be used to control corrosion or improve solubility of the dyes and pigments.^{2,3}

From the moment that a writing ink is applied to paper material, both the chemical composition of the ink and the ink/paper interface begin to undergo changes. Various physical and chemical processes occur, including the evaporation of solvents and other volatile compounds,

polymerization, oxidation, cross-linking, and, in some cases, paper corrosion. These processes can also include those that are caused by external factors such as heat and light, with possible chemical reactions being photolytically induced. Other interactions with the paper are also possible.^{3,4}

In the present work, the use of synchrotron radiation-based infrared spectromicroscopy (SR FT-IR) offers a powerful, nondestructive method for the study and identification of inks on paper and the comparison of them to one another without the need for chemical separations and related laboratory work that have previously been used. Also, this method allows for a detailed analysis without the inherent destruction of the ink samples on the paper by more commonly used techniques. No other cost-affordable experimental techniques that offer the analytical, spectral sensitivity of the present technique coupled with its nondestructive nature and ease of use of the technique exists for a criminal or forensics investigator at the present time.

When one examines an ink that has been applied to paper, several questions naturally arise. First, is the ink uniformly the same ink? Are several inks of the same color on one or several different documents the same ink? Can multiple writings on multiple documents in a similar ink be traced to the same pen? With regard to a given ink, another question is whether the ink is fresh or aged.

Current methods for the examination, identification, and comparison of inks on paper include a wide variety of techniques, ranging from a simple optical examination to more sophisticated experimental approaches. Optical examination approaches include the use of visible, ultraviolet, and infrared light combined with magnification to detect simple physical changes such as flaking. The more advanced techniques involve both microscopic and spectroscopic studies of the inks; however, to date all spectroscopic analyses are done only after extracting the ink from the paper using destructive methods involving dissolution, extraction, and other chemical separation methods such as chromatography. These approaches require damaging the sample by mechanically removing portions of ink with implements such as hypodermic syringe needles.

Work focusing on the use of infrared spectroscopy to analyze inks on paper has been published in the research literature. Varlashkin and Low⁵ reported the use of infrared spectroscopy to examine black drafting and writing inks on paper and the related black ink solids derived

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* Author to whom correspondence should be sent.

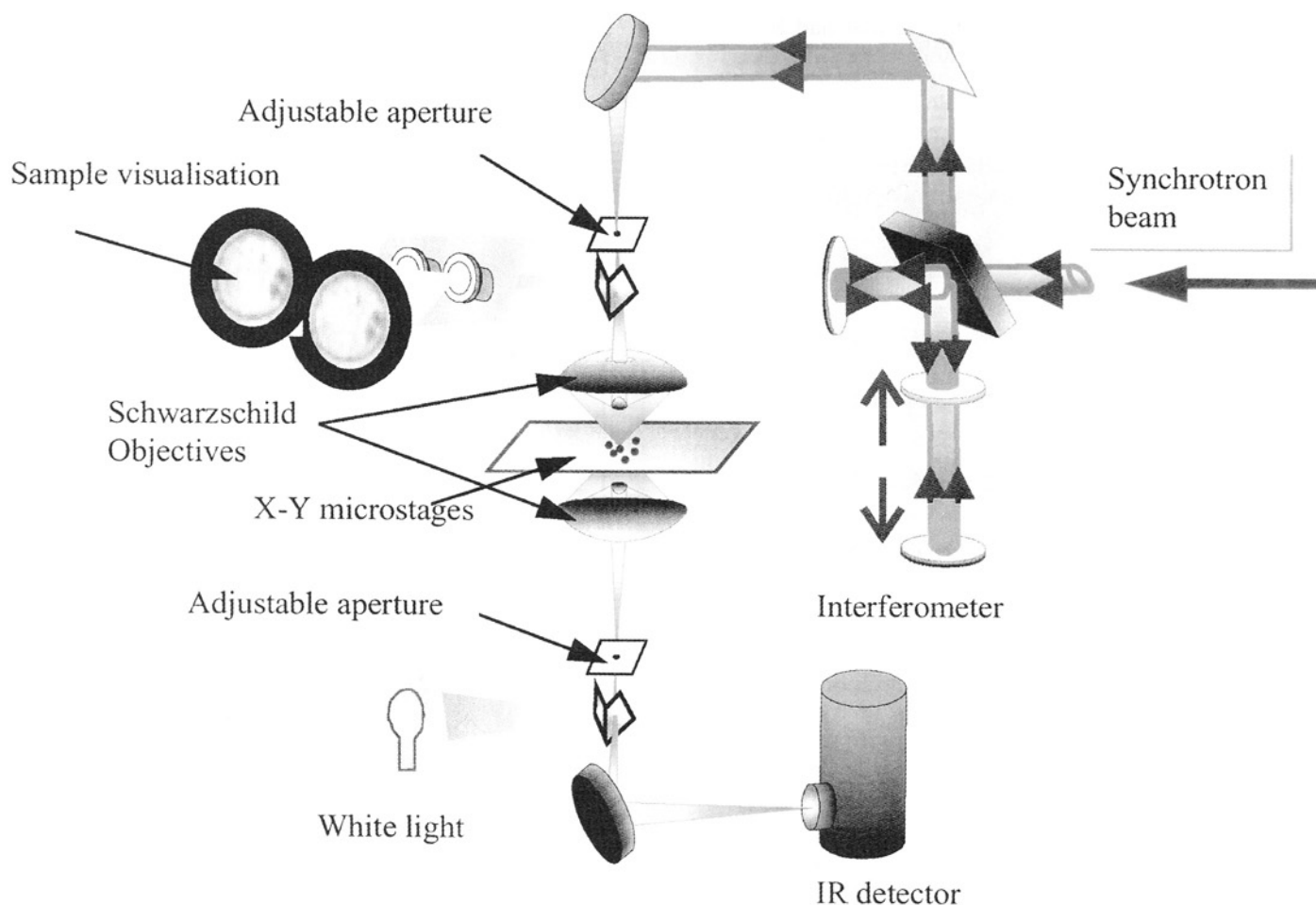


FIG. 1. Experimental arrangement for *in situ* synchrotron reflectance infrared microspectroscopy studies of ink on paper.

from the different inks. The study showed which inks contained carbon and, in some cases, was able to provide some differentiation among similar black inks. A portion of this investigation was dependent on the infrared spectroscopic examination of the ink solids that had been obtained by evaporation of the parent ink. Trzcinska⁶ applied infrared spectroscopy to the study of blue ballpoint inks, both the inks directly and ink samples that had been extracted from inscriptions on paper. This type of extraction has been one of the shortcomings of typical earlier attempts at using infrared to study inks on paper. It involves chemical manipulations of the ink such as separations that have the potential for introducing extremely small and subtle changes that either may not be truly representative of the differences in the inks or may indeed mask real changes that should be noted. Other extraction-based procedures used in conjunction with infrared have also been reported.^{7,8} Combined FT-infrared/microscopy has also been reported in the literature.^{9,10}

EXPERIMENTAL

The ink/paper combinations were analyzed using infrared Beamline 1.4.3 at the Advanced Light Source (ALS) at Lawrence Berkeley National Laboratory.^{11–13} All spectra were obtained using collimated synchrotron light directed into a Nicolet Magna 760 FT-IR bench (Fig. 1). The light is modulated by a moving mirror in a

N₂ purged environment Michelson FT-IR interferometer and passed into a Nicolet/Spectra-Tech Nic-Plan IR microscope equipped with a mid-IR mercury cadmium telluride (MCT-A) detector. For the purpose of these experiments, the spectra were taken at either 4 or 8 cm⁻¹ resolution. The FT-IR bench was equipped with Nicolet's Omnic ESP Version 5.2A for spectral acquisition. The deconvolution work of several of the parent ink infrared spectra was performed using the Nicolet software in conjunction with search libraries from Sigma-Aldrich that are copyright-assigned to Nicolet.

All samples were analyzed by collecting a minimum of 256 scans in the mid-IR range (4000–400 cm⁻¹). Residual water and carbon dioxide were subtracted where appropriate, and baselines were normalized using the correction routines present in the software.

To prepare samples for infrared study, ink was applied to paper strips (~2.5 × 5 cm). The paper strips were placed on the infrared microscope sample holder and were measured in reflectance mode. The paper used was measured to have a transmittance of <1% throughout the mid-IR, so reflection-absorption (IR passing through the paper, reflecting off the microscope stage, and then passing back through the paper) can be ruled out. The measurements obtained were therefore dominated by specular reflectance, with some diffuse reflected light collected as well. Also, some ink component compounds were iden-

tified by taking the spectra of the ink that had been directly applied to a silver coated microscope slide (Kevley Technologies, Chesterland, OH).

Several different commercial ink pens were used in the study, with all pens being manufactured in either the United States or Japan. A standard multipurpose business paper (Xerox 4200DP) and an extremely pure chromatographic paper (Whatman 3MM Chr) were used for the studies described here.

RESULTS AND DISCUSSION

As mentioned above, the chemistry of inks in commercial pens is highly complex, each ink consisting of a mixture of chemical compounds that serve a variety of purposes. Many of these compounds are in turn very complex on a molecular basis, with many of them being large organic molecules. As a result, the infrared spectra of the inks tend to be quite complicated because of the overlap of many of the vibrational bands from the different constituents.[†] Figure 2 shows the infrared spectra of three typical commercial inks from several pens used in the present study, the inks being on a high-purity chromatographic paper. All of the spectra exhibit bands in some areas that are common to many compounds that are typically used in ink formulations. One area of the infrared spectrum that is readily assignable with respect to the vibrational modes of the ink spectra is the 2900–3000 cm^{-1} region associated with the $\nu(\text{C-H})$ stretch for aliphatic hydrocarbons. The $\sim 3500 \text{ cm}^{-1}$ region is associated with the $\nu(\text{OH})$ stretch (Fig. 2) of water and alcohol solvents that are typical for many ink systems.^{3,17} More complicated, however, is the $\sim 800\text{--}1700 \text{ cm}^{-1}$ “fingerprint region” in which many of the ink constituents’ infrared spectra overlap with one another. In yet another region ($1700\text{--}3500 \text{ cm}^{-1}$) for blue, black, and red inks, such as shown in Fig. 2, the spectra are seen to be equally complex. All of these regions contain multiple vibrational bands such as $\text{C}=\text{C}$, $\text{C}=\text{N}$, $\text{C}-\text{O}$, $\text{C}=\text{O}$, $\text{C}-\text{N}$, $\text{C}-\text{S}$, $\text{S}-\text{O}$, ring modes (both aromatic and aliphatic), and combination bands from the dozens of compounds that constitute each ink.^{2,10}

The use of synchrotron-based FT-infrared microspectroscopy described herein for the study of inks and their interactions with paper affords several advantages over other experimental and spectroscopic approaches that have been previously used. First, it is a direct method with no necessity for any pre-chemical separations such as chromatography; the ink on the paper may be observed

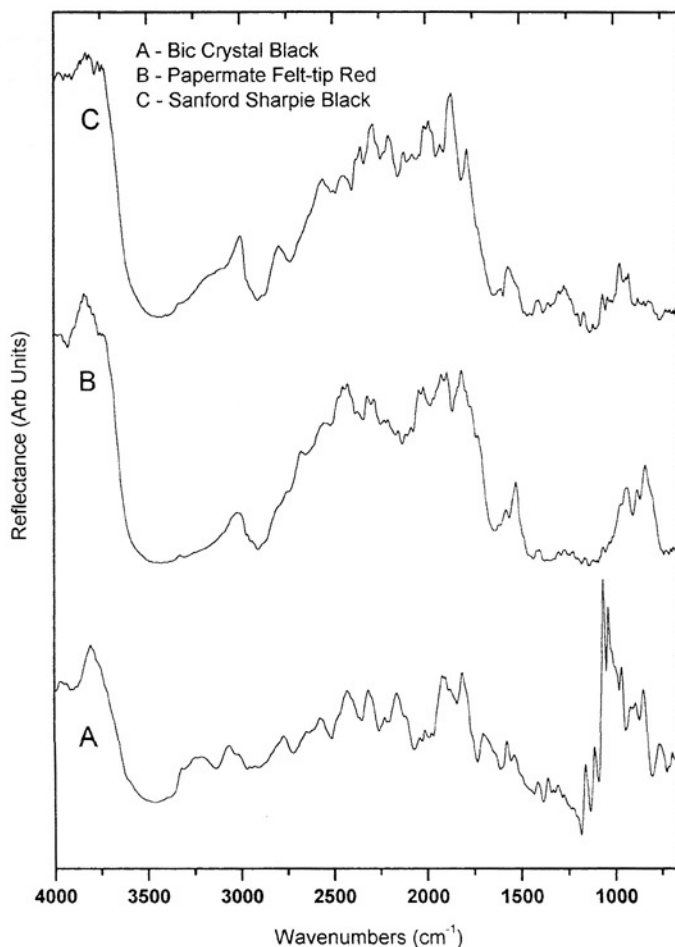


FIG. 2. Infrared spectra of (A) a commercial black ink on Whatman 3MM Chr chromatography paper, (B) a commercial red ink on a commercial paper, Whatman 3MM Chr chromatography paper, and (C) a commercial black ink on the same Whatman 3MM Chr chromatography paper.

with no preparation whatsoever. Second, the technique represents a method for obtaining a molecular fingerprint of different inks that make them easily and readily distinguishable. Third, it offers an extremely high lateral spatial resolution of as little as $10 \mu\text{m}$, much smaller than any line made on paper by normal ball point or fountain pens and much smaller than the “worst case” situation for examining ink samples on paper (“... probably the true worst case is the examination of a single dot ...”¹⁴). Fourth, the sensitivity of the synchrotron-based infrared technique is 200 times greater than a regular FT-infrared instrument for a $10 \mu\text{m}$ spot size,¹⁷ thus making it possible to see spectroscopic detail in some instances that would be missed by traditional spectrometers. Fifth, because of the mapping capability relative to the spatial resolution of the synchrotron spectromicroscopic technique, it is possible to study infrared spectroscopic profiles of the actual line interfaces of the different inks in a line or signature on paper (actually, spectroscopically seeing where one ink ends and another begins in the same signature, for example).

The issue of sensitivity and resolution as advantages to using synchrotron-based FT-IR microspectroscopy over traditional stand-alone infrared instrumentation for the study of ink on paper is dramatically illustrated in

[†] In preliminary studies of separating and identifying the components of various inks in the present work, several compounds known to be extensively used in the ink/pen industry have been identified in conjunction with using commercially published infrared databases to assess possible chemical components in the inks. One compound, for example, methyl violet BB^{3,14,15} (also called methyl violet 2B, Gentian violet, basonyl violet 600, etc.; (*Chemical Abstracts Service* [CAS] Number [8004-87-3]) exhibits an infrared spectrum that is inherently quite complex due to multiple aromatic rings and amine and ammonium salt functional groups. Another compound tentatively identified as a component of one of the inks was lissamine green (also called acid green 50, lissamine green BN (6Cl), hexacol green S, etc.; CAS [3087-16-9]). This dye, in addition to the aromatic ring and ammonium salt-related functional groups it has in common with methyl violet BB, also contains additional vibrational bands related to sulfonic acid groups.

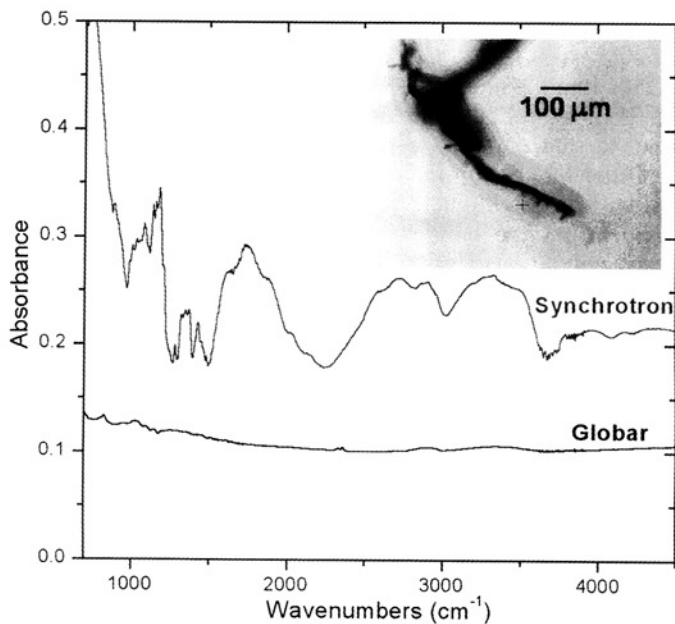


FIG. 3. Infrared spectra of ink on a paper fiber using both synchrotron and GlobalTM infrared sources. The difference in the two spectra is due to the much greater brightness of the synchrotron impinging on the fiber.

Fig. 3. The inset photograph shows ink on a paper fiber studied using both a synchrotron infrared source on Beamline 1.4.3 at the ALS and a GlobalTM infrared source in conjunction with the Nicolet Magna 760 FT-IR spectrometer. The synchrotron is a diffraction-limited source in the mid-infrared. This means that all of the light is focused to a diffraction-limited spot size (3–10 μm) at the sample in the infrared microscope. By contrast, a GlobalTM is physically large (several millimeters square) and can only be focused to $\sim 100\text{-}\mu\text{m}$ -diameter spot size without a significant loss of intensity. The total flux for the two sources is comparable. Therefore, the brightness (flux/area) for the synchrotron is ~ 100 times higher than that of the GlobalTM for samples on the order of 10 μm .¹⁷

The two spectra shown were taken using the two different infrared sources representing an ink spot on the paper fiber of $\sim 10\text{-}\mu\text{m}$, and they were taken using the same number of scans. The superior sensitivity and resolution of the synchrotron-based approach shown in Fig. 3 emphasizes the nearly unlimited possibilities for the use of the techniques for looking at very small fragmentary samples of ink on paper and for other ink/paper systems such as printed material. Investigators can use the technique to look at printed samples such as those printed by dot matrix printers, both in black and white and in color.

Two comments on the use of background subtraction in this study should be made. First, paper, even the same brand and type, is never pure or totally reproducible at the micrometer level. Different paper batches are processed from different pulp sources, several of which may be from trees in different geographical regions but blended together for the final product. Thus, there is a very high probability that multiple point analyses on the same sheet of paper may differ slightly. Second, when one ex-

amines microscopically ink on paper from a pen that has been used to apply it under normal writing conditions, he sees both paper and ink, not just an area of paper covered totally by the ink. The ratio of the ink-to-paper area being studied in a several micrometer squared area may vary slightly. In any rigorous study of ink/paper combinations, an investigator should take a sampling of locations on the ink/paper line so as to get a more complete and truer spectromicroscopic picture of the sample of interest.

CONCLUSION

High resolution synchrotron infrared spectromicroscopy has potential for the direct facile and rapid comparative identification of writing inks. The technique can be used for the direct analyses of inks on paper without mechanically damaging the ink and paper or having to chemically extract or separate the ink. This method should be useful in other areas of studying ink, such as both qualitative and quantitative analysis of the ink components, verification of the identical nature of several inks, and the relative determination of the age of the ink.

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