

# An Investigation Toward the Identification of Traditional Drawing Inks

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## ABSTRACT

Bistre, carbon, sepia and iron gall inks are all present in old master drawings. The manufacture and characteristics of these inks are discussed and visual clues which aid in the identification of the media are reviewed. Drawing inks of known composition were analyzed with x-ray fluorescence spectroscopy and Fourier-transform infrared spectrometry. Case studies of examinations of ink drawings are presented to illustrate how these methods can be used together to identify inks of unknown composition.

## INTRODUCTION

The identifying term "brown ink" is commonly used in the cataloging of master drawings. This broad descriptive term does little to indicate the richness or variety of tones of the inks which fall within this category. The goal of this study was to build on existing strategies for the identification of traditional drawing inks with the use of non-sampling analytical methods. This investigative project originated during an advanced internship at the Fogg Art Museum's Center for Conservation and has continued during my current Mellon Fellowship at the Art Institute of Chicago.

Traditional brown inks have differences in tonal range and handling qualities which artists have used with effect. This is most notable when inks of different composition are used in combination on a single drawing. A popular working mode is the application of a thin ink wash to establish composition, followed by darker lines, applied to define elements within the drawing.

Ink drawings which have been re-worked with a secondary ink invite technical investigation. The determination of whether the drawings were altered by the original artist, or later by a second hand, should be made cautiously and collaboratively with art historians. Regardless of the reason for the presence of more than a single ink on a drawing sheet, the occurrence is sufficient reason to question differences in ink types and regard variances in their aging qualities. If an ink which fades on exposure to light appears next to an inert pigment, the comparative aging will unquestionably alter a viewer's perception of the artist's intent.

## COMPOSITION, WORKING PROPERTIES AND CHARACTERISTICS

Inks can be either dyes or liquid suspensions of fine pigments; they are delivered to paper evenly by pen, or built up in washes by brush. The distinction between ink and watercolor can be somewhat tenuous and the drawing media are defined more clearly by historic characterization than by use or material composition.

The general types of brown ink addressed by this study are bistre, sepia and iron gall. The goal was to differentiate between these general ink categories while being mindful of the untold variations within each type. The foundation of a technical study of artist's materials is an understanding of the manufacture and the working properties of the materials in question. Throughout this study, consideration was made of other inks of historic use. Before contemplating the brown inks, it is worthwhile to reflect on the black ink which is so often found in their company.

## CARBON INK

Carbon ink is an aqueous suspension of flame carbon, or lampblack, obtained from soot. The pigment was ground with a binder, such as glue, gum or shellac to facilitate the storage of the ink in the form of a cake or powder. When manufactured in an artist's studio, the source of the pigment was commonly the soot which was collected from a dish held over the flame of a candle. Cennini (1960) also refers to the use of soot obtained from the burning of almond shells and peach stones. The greasier the soot component, the less binder is necessary for its manufacture. The ink has bluish undertones and indigo was sometimes added to make the washes appear more grey (Constable 1954). This ink is remarkably stable due to the inert nature of carbon. References exist to the use of carbon ink in China as early as 2500 B.C.

## BISTRE

Bistre, also known as brown lamp black or soot brown, is made from tarry soot collected from a wood chimney. Soot from the burning of beechwood was most popular for this use. It was dissolved in hot water and cold filtered. Cooling the mixture prior to filtering allowed the sedimentation of soot in the container, avoiding the expansion of the filtering paper's fibers, which would allow more particles to pass through, resulting in a less complete separation of the mixture

(Watrous 1957). This ink acts primarily as a dye, although particles of soot are invariably present to some degree. The color of this ink can be altered by concentrating the solution through boiling. The source of the soot also has an effect on the color of the resulting ink.

Bistre varies tremendously in appearance, from dark blackish-brown to brownish-saffron yellow to cool greenish-brown. It was valued for its strong, transparent effects in washes and the distinct variations which could be achieved in dark & light areas. The slightly resinous nature of the ink does not lend itself to easy mixture with other inks. However, red chalk was sometimes added to the ink to enhance its appearance (Meder 1978). Upon aging, bistre can have a greyish or warm brown appearance. It is historically noted as being impermanent (Mayer 1970).

Even if the ink contained particulates, when it was stored in liquid form, its high tar content precluded the need for the addition of gum as an adherent. Because this ink tended to penetrate the structure of drawing paper, gum was sometimes added to retain the ink on the surface so it would appear richer in tone. The addition of too much gum caused cracking of the ink. The handling qualities of this ink required that it be brush applied if there was not a significant proportion of gum present. Bistre dates primarily from the 14th to the 19th centuries.

## SEPIA

Sepia is manufactured from the nitrogenous organic compounds obtained from the ink sacs of "sepia officinalis", a type of cuttlefish. The defense strategy of this sea creature involves the release of a black fluid into the water, which obscures its predator's view. For ink-making, the sacs of the cuttlefish are dried, ground and boiled with an alkaline solution such as lye, in which they are soluble. The pigment is then precipitated out of solution with acid. The precipitate is very fine and, although not soluble in water, it is easily suspended in it. It was also ground with gum arabic and used in cakes.

Sepia is known as an ink because artists used it to produce monochromatic drawings. Similar to watercolor in handling character, this ink is brush applied. Sepia makes a fluid wash, but due to its lack of solubility in water, it is characteristic to see particulate depositions at the edges of the washes. The tonal range varies from warm black at application to reddish brown-upon aging. It is more opaque than bistre and is noted historically as being semi-permanent.

There are references to the use of sepia in Classical times. The height of its popular use seems to date from the late 18th to the late 19th centuries (Meder 1978). It was mixed with a variety of pigments for effect; some of these combinations bore their own titles. Different sources identify Roman sepia as a mixture of sepia and

alizarin crimson or burnt sienna or any yellow pigment. Because of the popularity of the ink, it was not uncommon for substitutions of cheaper materials to be referred to by the same name; in fact true sepia may have been quite rare. At this time browns were often generically referred to as sepia. Watercolors are still marketed under the misnomer Sepia. The Wilcox guide (Wilcox 1991) lists twenty seven brands on the market today, none of which are made of cuttlefish.

## IRON-GALL INK

Iron gallotannate ink, also known as iron-gall ink, has an untold number of published recipes. The defining components of the ink are the iron and the tannic and gallic acids. Gallotannic acid is produced in trees as a response to the irritation caused by the presence of larvae of gall wasps, which puncture the tree bark to lay eggs. The resulting oak galls are soaked and boiled to procure the acids. Tannins alone can be used to produce a brown dye, but the addition of iron in the form of ferrous sulfate results in ferrous gallotannate which oxidizes upon application to produce ferric gallotannate, resulting in a darker colored ink. Because the atmospheric oxidation does not take place immediately, dyes such as indigo or logwood extract were often added to allow immediate visibility of drawing marks. Gum arabic is added to the ink to delay the saturation of the paper. The solution flows well, and due to the gum component it doesn't feather as bistre is prone to, therefore it is commonly applied with a pen (Baker 1985).

The inclusion of too much iron sulfate can cause the ink to turn brown, and due to the production of sulfuric acid, the paper may deteriorate and split along heavy ink lines. Copper sulfate was added to the ink in the belief that the resulting compounds would be less inclined to fade (Baker 1985). This ink does fade, however, on exposure to light. The bonding of iron-gall ink with paper and parchment made it superior to carbon ink for use in documents, as it could not be washed from the surface as gum bound carbon ink could. Iron-gall ink was widely used in Western manuscripts, as well as drawings, and it is better suited to the dark storage conditions which documents are more likely to enjoy. It should be noted that artists have been aware of the ink's tendency to fade, and they may have compensated for this expected change in their initial compositions. This ink was in use from the 12th to the early 20th centuries.

## THE EXAMINATION PROCESS

The technical examination process began by observing inks of known composition. Ink samples from the Forbes Collection of Painting Materials and the Gettens Collection of Aged Materials of the Artist<sup>1</sup> were examined as standards. Direct observation and

magnified examination of inks under normal light can provide preliminary clues toward identification. Particulates would be expected in washes of carbon or sepia but also in partially filtered bistre and, historically, red chalk and bistre have been added to iron-gall ink.

Color can be deceiving, as there is a considerable range within each ink type. The darkest iron-gall ink can appear relatively black, and be confused with carbon ink. Pale brown iron-gall ink can be confused with bistre. In fact, due to changes in ink, which occur naturally over time, it is not prudent to rely too heavily on interpretation of color when identifying inks. Stylistic considerations may be of service, as Meder (1978) points out in his drawing tome; in Rembrandt's school, "when [associated] with a black carbon ink a brown [ink] must be bistre because if it were acid ink, it would have been black when it was applied and non-sensical."

The degree of saturation may provide clues; bistre's saturated brushstrokes tend to soak through paper, especially if the gum content is low. These marks will not exhibit the same damage to paper fibers which iron-gall might in the same concentration.

In some instances the presence of gum will result in a gloss to the ink surface. Although gum may appear in any of the traditional inks, it is most likely to be abundant in iron-gall ink. The total deterioration of paper which sometimes occurs at heavily inked lines is a certain indication of iron-gall ink.

## INTRODUCTION TO THE ANALYTICAL EXAMINATION

At the outset of analysis, it is important to acknowledge the variables in ink composition likely to be encountered in actual drawings. One must also incorporate a recognition of the limitations of the analytical techniques employed. Results obtained by any given method should be weighed against others for reliability. Remember the 18th century advice to artists that a mixture of bistre and sepia is good for depicting "gloomy scenes from nature".

Examination of ink drawings using infrared reflectography may offer a limited amount of information. Carbon is highly absorbent in IR and has an appearance not characteristic of the other inks. Sepia, bistre and iron-gall are all absorbent to a degree, although according to one study (Baker 1985), iron-gall becomes less absorbent with age, while the absorbence of bistre has been noted to increase.

Ultraviolet examination may also offer clues but does not yield conclusive information. Bistre has been noted to fluoresce in UV, but this is not a consistent observation, particularly when the ink is heavily applied.

A limitation of these techniques is the familiarity one must have with the materials to distinguish the subtle

variances of appearance of the inks under these circumstances, particularly in the absence of naturally aged standards for comparison. In addition, the appearance of the paper beneath the ink may make interpretation more problematic.

There is obvious difficulty in obtaining samples for technical study from works of art on paper. I have been working toward a methodology for ink identification which would not require sampling. The two methods of point analysis with which I have been working, XRF and FT-IR microscopy with a reflectance objective, were chosen for that reason.

## X-RAY FLUORESCENCE SPECTROMETRY

An X-Ray Fluorescence Spectrometer<sup>2</sup> was employed for elemental analysis. A limitation of using this instrument in air, is that it is only capable of identifying trace elements with an atomic weight greater than that of potassium. Of the elements within the detection range, iron and copper are indicators of an iron-gall ink. Magnesium and potassium may be present in sepia, bistre or the nearly ubiquitous suspension agent, gum arabic. Consequently, the iron content deserves the most scrutiny.

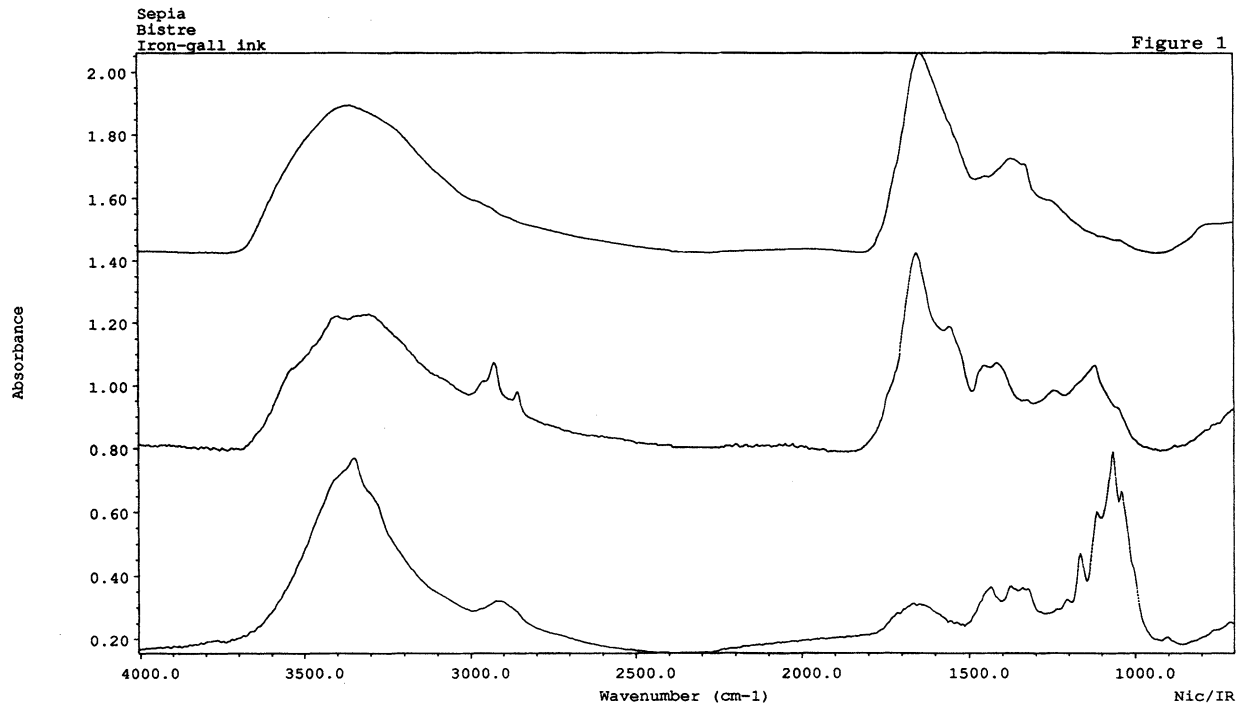
Iron is a primary component of some inks, but it tends to show up in most ink samples, to varying degrees. This complicates the evaluation of XRF spectra. Iron containers have historically been used in the preparation of inks. It is difficult to determine the amount of iron expected to appear in a bistre sample which was adulterated during manufacture in an iron container. Bistre samples which I prepared in a cast iron pot were drawn out as samples and examined by XRF. These samples displayed a significant iron content and visually could have been mistaken for a dilute iron gall ink.

Iron is also present in many papers. If the iron peaks in an ink spectrum are negligible, by comparing spectra of ink and paper, it may be possible to infer that the paper substrate is the primary source of iron.

## FOURIER-TRANSFORM INFRARED SPECTROMETRY

Fourier-transform infrared spectrometry<sup>3</sup> was used to complement the elemental information provided by XRF. Wavelengths in the infrared correspond to the various functional groups present in compounds. With the use of FT-IR it is possible to differentiate among different classes of inks. Spectra collected from standards of sepia, bistre and iron-gall inks are illustrated (fig. 1).

FT-IR is a powerful tool for the identification of pure samples. The identification of mixtures, however, can be difficult with this technique. Peaks overlap and tend to shift in mixtures. Components which comprise less than

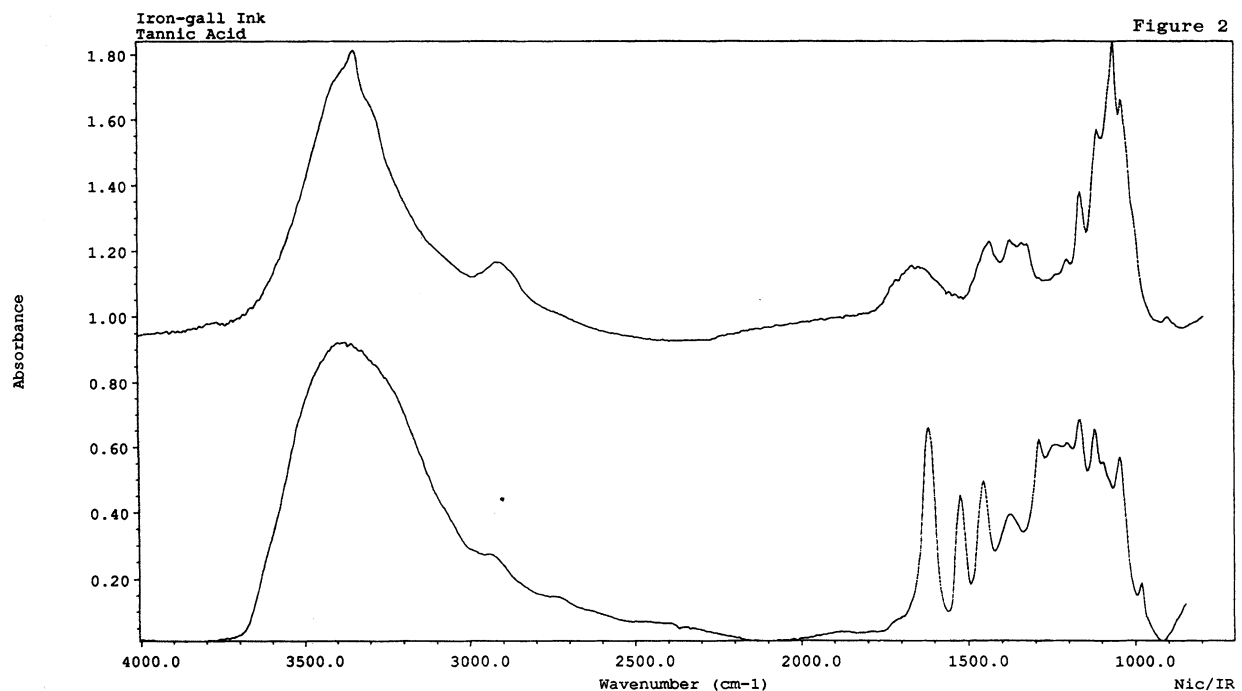


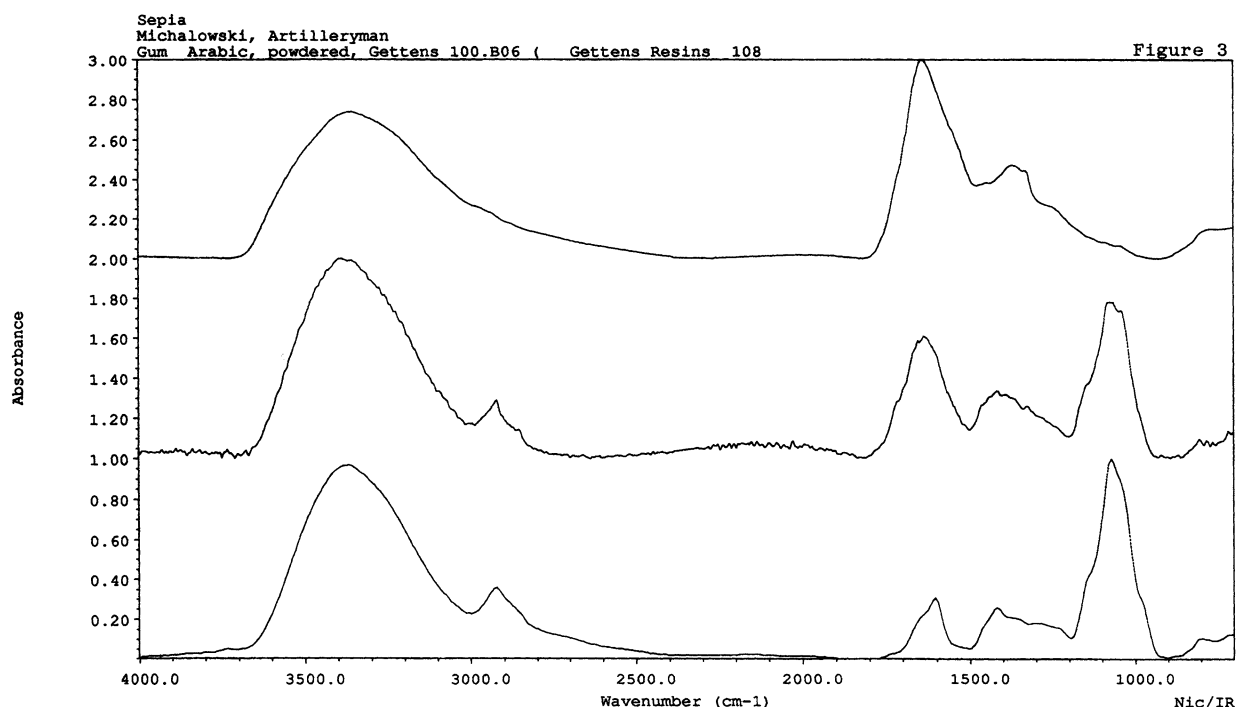
five percent of a mixture are unlikely to show peaks. FT-IR is used commonly as a survey tool to match unknowns to spectra of library standards.

When iron gall ink spectra were searched against a biological library, tannic acid was found as a near match (fig. 2). Samples of unknown composition which contain iron, can be examined with FT-IR with attention to the tannic peaks. If they are not found, it may be that the iron

is present as a contaminant rather than as a deliberate component of the ink.

Elemental carbon does not appear in FT-IR, the spectrum of carbon ink will indicate the binding medium. Proteinaceous structures in sepia tend to be overridden by the binding media. Bistre displays peaks indicative of its resinous nature. This is true even when iron is detected with XRF.





For the initial portion of this study, I built FT-IR spectral libraries from ink standards in transmission in order to have a basis for comparison with unknown inks. Small samples were then taken from standards and a few original artworks, and analyzed in transmission. Since the preliminary FT-IR study provided valuable information, an Attenuated Total Reflectance objective was borrowed from Spectra-Tech for the continuation of the study. With an ATR microscope objective, it is possible to obtain spectra by direct surface contact of a drawing, without the need for sampling.

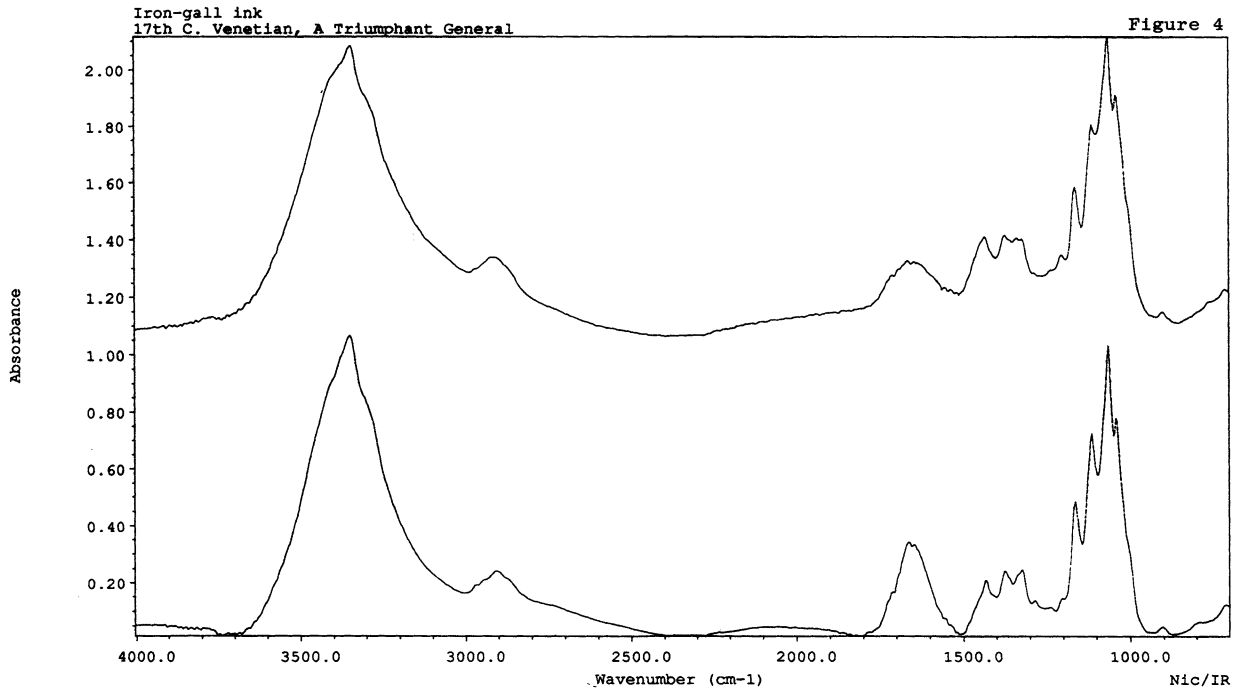
Using the ATR objective is a relatively straightforward, but delicate matter. The microscope at the Fogg was not equipped with a strong lighting source intended for use with the ATR objective. Viewing paper through the Zinc-Selenide crystal of the objective is difficult under these conditions. The working method begins with the viewing of the sample through the normal microscope objective. Beginning with the focus above the sample, the stage is raised. The first areas to come into focus are the high points, which are most suitable for contact analysis. The high point is centered and the ATR objective is rotated into position. With eye level parallel to the microscope stage, the sample is raised within a few millimeters from the objective. While viewing through the eyepiece, the stage is carefully raised. Initially, the surface of the specimen is visible as an illuminated blur, when a dark area appears in the range of view, the sample has been contacted. It takes some practice to become proficient with this technique. Once accomplished, there is a significant savings of time compared to preparing samples for transmission, with

the added advantage of there being no physical loss to the artwork. The quality of spectra obtained in this experiment was good considering they were obtained under a compromised situation. Even better results would be expected when the microscope was optimized for use with the ATR objective.

#### CASE STUDIES

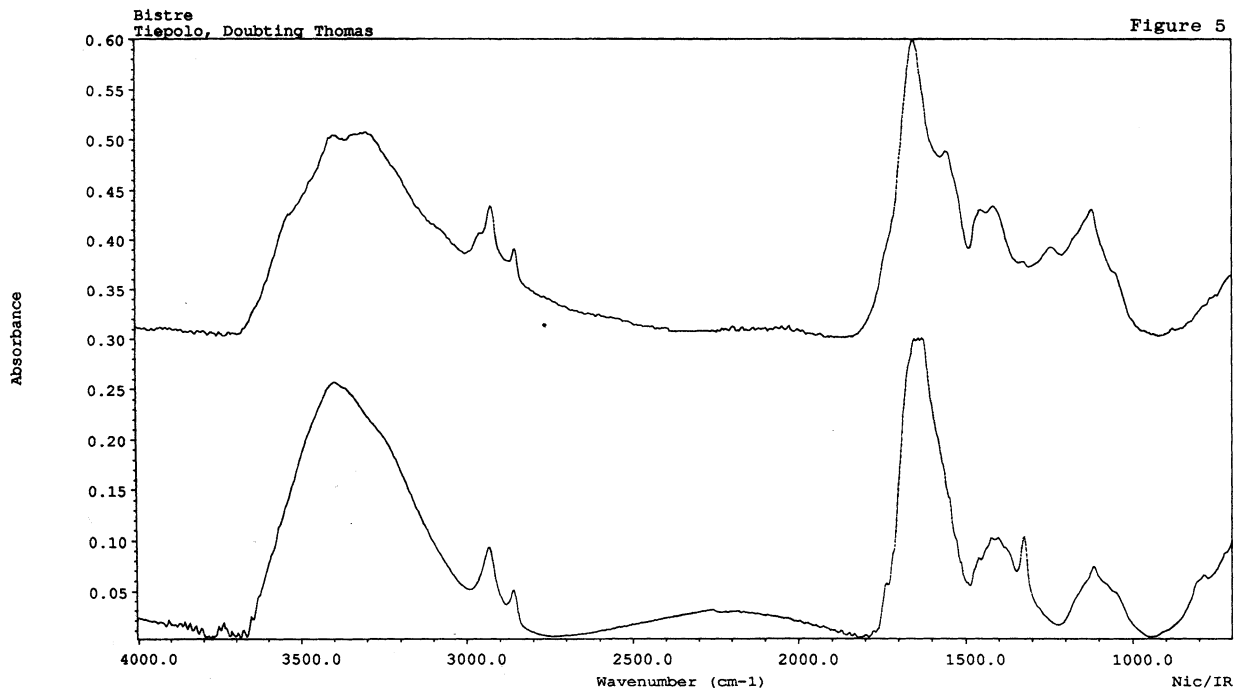
In *The Craft of Old Master Drawing*, James Watrous offers a Géricault drawing, *An Artilleryman Leading His Horses Into the Field*,<sup>4</sup> as an example of the use of sepia. Pigment particles are visible and there is a red cast to the brown wash. The XRF spectrum for this drawing indicates the presence of a substantial amount of iron. Another spectrum was run on the paper substrate and it also contains iron. The FT-IR spectrum was a close match to the sepia standards which contained gum (fig. 3). Watrous's observation that the media of this drawing is sepia appears to be correct. However, the drawing is no longer considered a Géricault. Based on stylistic considerations, the curatorial department has re-attributed the sketch to Piotr Michalowski.

The media of *A Triumphant General*, by a 17th century Venetian artist, was identified by Watrous as bistre. The saturated appearance of the ink could support that conclusion. The spectrum obtained through XRF indicated an unusually high iron content. The FT-IR spectrum was a much closer match to the iron-gall standards in the spectral library (fig. 4). It appears that this drawing may in fact be iron-gall with a low percentage of gum, which would account for the dullness of color and extensive penetration of the paper.



A final case study is *Doubting Thomas*, a drawing by Giovanni Battista Tiepolo, historically thought to be bistre, due to its clear, golden tones. Scanning electron microscopy carried out by a previous Fogg intern revealed a significant proportion of iron in the ink, and the media had been tentatively re-identified as iron-gall ink (Mickelson 1981). XRF spectra of the ink and the paper both indicate the presence of iron, with a much

larger iron content in the ink than the paper. Although initial analysis supports an identification of the ink as iron-gall, in searching the FT-IR spectral library, the closest matches were with bistres. In this case, it seems the iron may be present as a contaminant rather than a characteristic component.



## CONCLUSION

As FT-IR internal reflectance spectroscopy becomes more accessible to conservators, it will be an increasingly valuable technique for media analysis on paper. When used in conjunction with x-ray fluorescence and the connoisseurship of master drawings, it is a valuable tool for distinguishing among some of the commonly confused general ink classes.

## ACKNOWLEDGMENTS

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This has been a rewarding investigation. The topic of inks poses endless questions for study. I plan to continue looking at inks, and to build on the standards in the FT-IR spectral library. In the near future I intend to expand this project to include aging comparison and treatment studies of inks. Through this project, it has been my pleasure to have met a number of people who share an interest in inks; I welcome the chance for further dialog.

## NOTES

1. The Forbes Collection of Painting Materials and the Gettens Collection of Aged Materials of the Artist are housed in the Center for Conservation and Technical Studies in the Fogg Art Museum, Cambridge, Massachusetts.
2. A Noran Instruments Voyager, Z max 30 Series Light X-Ray Dispersive X-Ray Spectrometer was used to collect spectra at 40 kV for 1.5 minutes. An NEC personal computer with 40 meg HD was used to operate Kevex XRF toolbox on a DOS 3 operating system.
3. A Spectra-Tech IR-Plan microscope attached to a Nicolet 510M Spectrometer with an auxiliary MCT detector was used to collect data at a spectral resolution of 8cm<sup>-1</sup> with 200 scans.
4. The case studies described are all from the collection of the Fogg Art Museum: Piotr Michalowski *An Artilleryman Leading His Horses Into the Field*, accession # 1965.286. 17th Century Venetian Artist *A Triumphant General*,

accession # 1965.429. Giovanni Battista Tiepolo *Doubting Thomas*, accession # 1961.173.

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