SPECTROSCOPIC ANALYSIS

OF HAND-COLORED PHOTOGRAPHS

AND PHOTOGRAPHIC

HAND-COLORING MATERIALS

by

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ABSTRACT

Prior to the advent of color photographic processes, the only method of producing photographs in color was to apply coloring agents by hand. Though hand-colored photographs from every period of photography can be found in public and private collections throughout the world, little research has been done in developing methods for identifying the coloring agents on such photographs. The first aim of this research was to determine if spectroscopic methods—X-Ray Fluorescence Spectroscopy, Fourier Transform-Infrared Spectroscopy, Dispersive Raman Spectroscopy, Scanning Electron Microscopy-Energy Dispersive Spectroscopy, and Gas Chromatography-Mass Spectrometry—could be used to identify the components and pigments in period Marshall's Photo-Oils kits, which were immensely popular after their introduction in the 1920s and are still produced today. After successfully identifying the primary components of these paints, the next goal of the research was to determine which, if any, spectroscopic methods could be used to best identify these same paints when painted onto a photographic base. Finding that using XRF and Raman spectroscopy used in conjunction with one another was the best method for this task, photographs colored with unknown coloring media were examined to see if these same methods could then be used to identify the colorants. Early results are quite promising, though further research is needed.

Chapter 1

INTRODUCTION

1.1   Hand-Coloring – Definition, Materials, History

With the advent of inexpensive color photography in the 20th century, a
popular art form that began with the earliest photographs has gradually faded into the
realm of obscurity. While the hand-coloring of photographs is still practiced today by
amateurs and professionals alike, it has fallen mostly into the realm of hobbies and
specialized forms of art. The legacy of a long tradition of hand-coloring lives on in the
collections of institutions and individuals throughout the world.

The origins of hand-coloring lie well before the invention of photography.
Prior to photography, portraiture was the realm of both the academic and the folk artist,
who produced portraits in oil, watercolor, pastels, crayon, charcoal, and other media. In
America, the post-revolutionary period saw the development of the miniature portrait and
the silhouette, specialized forms of portraiture that served primarily the middle and lower
classes.[1] Miniature portraits, as their name implies, were small, averaging 2 × 3 inches,
were produced in a variety of materials, the most expensive of which was oil on ivory,
and were commonly enclosed in a small case or frame. Miniature portraits proved quite
popular even after the introduction of photography, employing artists such as the
Philadelphia-born John Carlin well into the 1850s. Ultimately, however, both miniature
portraits and silhouettes would prove to be unprofitable due to the rising popularity of the
photographic medium.

Louis-Jacques-Mandé Daguerre's discovery of the first practical method for "fixing the beautiful representations of objects obtained in the *Camera Obscura* upon a surface prepared in a certain manner, as to form a perfect picture" – the daguerreotype – was announced to the Paris *Académie des Sciences* in January 1839 by scientist François Arago, a supporter of Daguerre who facilitated negotiations between Daguerre and the French government for a stipend that would pay him to make the details of his photographic process available to the world. It was noted almost immediately that while "an exact representation of light and shade of whatever object may wish to be viewed is obtained with the precise accuracy of nature herself," his process did not "reproduce colour, but only outline the lights and shadows of the model."[2] The public soon learned of the daguerreotype and its hyper-realistic method of capturing images, and expected it to capture color as a matter of course. Because the process could not do so, photographers almost immediately sought remedies, ultimately resorting to filling in the "missing" color by painting it on by hand.[3] Despite oftentimes vociferous opposition to the practice in the "professional" photographic community, hand-coloring would almost immediately prove to be lucrative trade amongst the general public.[4]

Colorists began their work on daguerreotypes as early as 1839, and by the mid-1840s several methods were devised to color the silver plates. One of the earliest, and most difficult, was applying dry pigment powders mixed with a small amount of gum arabic binder to the image with fine brushes. Henry H. Snelling describes such a process in his 1849 work *The History and Practice of the Art of Photography*. "The rules we shall give for coloring daguerreotypes depends, and are founded, upon those observed in miniature painting," noted Snelling, and that "[i]n a majority of cases, the following [paints] will be found sufficient, viz. Carmine. Prussian Blue. White. Chrome Yellow, Gamboge, Yellow ochre; or all three. Light Red. Indigo. Burnt Sienna. Bistre, or Burnt

Umber."[5] Along with lamp black, Snelling asserted that these pigments could create most of the colors necessary for portraiture. However, as noted by Henisch and Henisch, the "dry" technique was somewhat of an oddity, as most colorists used liquid binding media such as fish glue or wine to render the surface of the silver plate smooth and sticky for the gradually application of the pigments.[6] But the age of colored daguerreotypes would be relatively brief; by the late 1850s, daguerreotypes would be on their way out.

The development of photographic print processes, such as albumen prints, in the 1850s signaled the demise of the daguerreotype and a new method of coloring photographs. To describe these methods as "new," however, is somewhat misleading, for the most common methods of painting photographic prints were those media found in drawings on paper, primarily watercolor, though oils and crayons were also used.[7] Marcus A. Root, in his 1864 work *The Camera and the Pencil*, noted that the colors required for watercoloring were "the same as are employed for miniature painting, with such difference in their combinations, as the tone of the photograph renders necessary." Listing and describing pigments such as carmine, cadmium yellow, raw sienna, Verona brown, Prussian blue, and Chinese white, among others. Root noted that these would best be applied to photographs by hatching, washing, and stippling using moderate-sized sable hair brushes.[8] Watercoloring of this nature was particularly popular in Japan, where colored prints were highly sought-after by Western collectors. However, the watercolor method was suitable almost exclusively for photographic prints on paper; for photographs on glass and other media, other methods were devised.[9]

For coloring photographic glass positives, such as ambrotypes, several methods met with success. One such method was to coat the glass with a varnish upon which dry powdered pigments would adhere smoothly; such a process is described by Root, noting that a Mr. Newman had recently developed such a varnish upon which "dry

colors will adhere like crayons."[10] Another method did not involve painting the glass

positive at all, but a card placed behind it. M. Carey Lea in 1865 described a method

whereby the contours of the photographic image were traced onto a paper, and the

coloring applied to it. After varnishing the back of the photographic plate, the paper and

plate were pressed closely together to appear as a single image.[11] Ambrotypes, however,

were quite delicate and prone to breaking. Thus, the more durable tintype would prove to

be more popular and long-lasting with professional photographers and the general public.

       The tintype, also called a ferrotype, differs in one crucial respect from the

ambrotype: namely, that its support is a black-lacquered (Japanned) flat sheet of metal,

often iron. Once coated with the lacquer and the light-sensitive collodion layer, the image

surface was rendered almost wholly unsuitable for coloring by watercolors.[12] This,

coupled with the relatively rigid support, made the use of heavier oil-based paints a

natural choice for hand-coloring and overpainting. The relative affordability and ubiquity

of tintypes from the 1860s through the last half of the 19th century meant that both

amateurs and professionals alike tried their hands at hand-coloring. Multiple techniques

of coloring were used, including crayons. Painted tintypes became popular enough in

America after the Civil War to allow many enterprising individuals to specialize in the

practice, and a number would go on to patent their techniques.[13] Sporting names such as

Electrograph, Ferro Chromo, Oilgraph, and Pennellograph, these professional

trademarked techniques marked the beginning of the commercialization of hand-coloring,

which by the end of the 19th century would come to dominate the trade.[14] Even so, by

the 1890s, the tintype would be displaced by other photographic media.

       The introduction in 1888 of the Kodak camera with flexible roll film would

allow anyone to become a photographer. Though methods of producing color

photographs were introduced around the turn of the century, most notably the

Autochrome in 1907, they remained technically and economically out of reach of most amateur photographers. Thus, hand-coloring remained the most widely-used option for producing color photographs until the advent of color film in the 1950s. Beginning around 1900, manufacturers began to introduce hand-coloring kits designed for both amateur and professional photographers alike. Kits such as Morton's Photo-Oil Paints, DeVoe Photo-Oil-Colors from the Devoe & Raynolds Co., Japanese Peerless Permanent Photo Oil-Colors, Brady Photo Colors, and Roehig's Transparent Oil Photo-Colors were first among the commercial oil-color kits; the kit that saw the most commercial success in the United States was Marshall's Photo-Oil Colors.

1.2   Marshall's Photo-Oil Colors

The history of Marshall's Photo-Oils begins with the firm of James A. Bostwick & Co. The firm was founded in Brooklyn, New York in 1895 by James Alba Bostwick (1846-1927), formerly a demonstrator (salesman) for the Eastman Dry Plate Company.[15] Bostwick had established himself as a photographer as early as 1865, and in 1891 was maintaining a large studio, where he made "a specialty of faithful and true-to life portraits in oil, water-colors, crayon, pastel, and India-ink from original pictures of life."[16] After partnering with Frederick J. Harrison early in 1897, the firm known as Bostwick, Harrison & Company, with a factory at 41 & 43 Marion Street in Brooklyn, manufactured photographic chemicals and preparations under the trade name "Meteor", and published the monthly magazine *The American Photogram*.[17] By 1903, the partnership had dissolved and Bostwick had moved to 1752 Atlantic Avenue in Brooklyn.[18]

In 1920, Bostwick's successor, John G. Marshall (1892-1953), a manufacturing chemist and former government engineer, took over the business and

continued producing developers, fixers, flash powders, and other products under the Meteor name. [19] With the development of flash bulbs, as noted in his 20 June 1953 obituary in the *New York Times*, Marshall turned to producing oil colors for hand-coloring photographs. The Marshall's Photo-Colors kit appears to have been introduced in 1922, when advertisements began appearing in popular photographic journals (**Figure 1.1**).[20]

Marshall's would produce a number of kits for both amateurs and professionals. Each kit included at least the basic tools and materials needed for hand-coloring, including paints, cotton, wooden skewers, and a cleaning solution, either Marshall's Prepared Medium, marlene, or turpentine. More expensive kits intended for professional colorists included additional colors and materials (see **Figures 1.2**, **1.3**, and **1.5**).

The kits proved to be immensely popular after their introduction. In 1944, Lucile Robertson Marshall, wife of John G. Marshall, and later owner of John G. Marshall, Inc., published *Photo-Oil Coloring for Fun or Profit*; within three years, the book saw six printings, and by 1964 the book was on the 13th printing of its 8th edition. Self-described as "America's Leading Authority" on hand-coloring, Marshall used her book to describe every aspect of hand-coloring using the Marshall's kits, from the proper lighting required to hand-color photographs, to the preparation of the photographs, and the application and mixing of the photo-oil colors.[21] Also included in the book is a chart of colors produced by the company in 1944. That chart is reproduced in **Figure 1.4**.

Though the Marshall Company has been bought and sold several times since the 1950s, Marshall's photo-oils are still produced today under the Marshall's name by the Brandess-Kalt-Aetna Group, Inc., of Vernon Hills, Illinois. The original product line of photographic oil sets has expanded substantially to include such things as inkjet paper

sheets for digital images, mixing trays, brushes, retouching colors, and oil color pencils, which were introduced in the late 1950s. Though the compositions of the photo paints likely have changed, they are still used by hobbyists and today.[22]

Figure 1.1: Earliest found Marshall's Photo-Oil advertisement, July 1922.
Reproduced from Juan C. Abel and Charles L. Able, eds., *Abel's*
Photographic Weekly **30, No. 758 (July 1, 1922): 14.**

MARSHALL COLOR PRODUCTS

All sets in regular strength except last two on list.

Separate Tubes (Regular or Ex. Strong)
½ x 2" Tube........$ .30   ¾ x 4"........$ .85

Students Complete Set $2.00
    Eight ½ x 2" Tubes (Group 1)
    Bottle of P. M. S.   Six Skewers
    Roll of Cotton   Direction Leaflet

Set of 15 Colors $2.75
    15—½ x 2" (Groups 1 and 2)

Set of 20 Colors $3.65
    In ½ x 2" Tubes (Groups 1, 2, 3)

No. 1 Complete Set $3.95
    15—½ x 2" (Groups 1 and 2)
    ½ x 2" Extender   Glass Palette
    ½ x 4" Drier   6 Skewers
    Bottle of Marlene   Roll of Cotton
    Bottle of Turpentine   Direction Sheet
    ¾ x 4" Medium

No. 2 Complete Set $4.90
    20—½ x 2" Tubes (Groups 1, 2 and 3)
    1 x 6" Extender   Glass Palette
    ¾ x 4" Drier   6 Skewers
    Bottle of Marlene   Roll of Cotton
    Bottle of Turpentine   Direction Sheet
    ¾ x 4" Medium

Set of 20 Colors $10.25
    In ¾ x 4" Tubes (Groups 1, 2, 3)

Set of 16 Extra Strong Colors $2.95
    In ½ x 2" Tubes (Marked *)

Set of 16 Extra Strong Colors $8.25
    In ¾ x 4" Tubes (Marked *)

MEDIUM

This preparation mixed with turpentine may be applied to matt paper before coloring. Facilitates coloring work but has nothing to do with the permanency of the colors. May be omitted entirely, at the discretion of the colorist.
    ¾" x 4" tube........$ .40   1" x 6" tube........$ .75

P. M. S.
(Prepared Medium Solution)
A solution of Marshall's Medium in Turpentine. Prepared as a convenience to the colorist.
    2 oz. bottle..........$ .35   8 oz. bottle..........$1.10

EXTENDER
Extender is a great time and labor saver. It is a colorless product of the same consistency and general properties as the colors themselves. Makes the colors paler without thinning them. It is also excellent for cleaning small areas.
    ¾" x 4" tube........$ .40   1" x 6" tube........$ .75

MARLENE
This liquid is perfect for removing undesired color. Colorless rapid evaporating, non-inflammable. Unlike turpentine, it will not spread, shine when dry, or leave a ring.
    4 oz. bottle..........$ .35   16 oz. bottle..........$1.10

MARSHALL'S DRIER
Marshall's Drier is a priceless aid to busy colorists who must rush their work to customers. A little of this salve-like product mixed with colors will dry even thick brush application of paint in three hours.
    Will not harm the colors nor cause peeling or cracking.
    ¾" x 4" tube........$ .40   1" x 6" tube........$ .75

TURPENTINE
Marshall's Turpentine is actually purified and redistilled at our factory. Ordinary turpentine is not suitable for use in photo coloring, because its gummy, sticky residue injures the paints. It is poor economy to ruin a day's work by using cheap, crude turpentine.
    2 oz. bottle..........$ .25   8 oz. bottle..........$ .75

DULL FINISHING VARNISH
Protects colored prints and permits their being cleaned. Applied with a cloth. Gives only slight sheen but depth and brilliancy to the colors.
    2 oz. bottle..........$ .50   8 oz. bottle..........$1.50

MARLAC
A waterproof quick-drying gloss varnish. Applied with a brush. Enhances colors greatly. Especially recommended for commercial subjects or portraits on linen or canvas finished papers.
    4 oz. bottle........$ .60   16 oz. bottle........$1.80
    1 gal. can........$10.75

Figure 1.2: Marshall's literature included with ca. 1939 kit, showing set types and other products available from the Marshall Corporation at the time. Note the paint smears. Image by the author.

NEW EXTRA STRONG COLORS

LIST OF COLORS

We make three shades of Flesh, ranging from ivory to pinkish tones. Each gives a living, warm flesh tone.

GROUP 1.

Flesh (very natural, slightly yellowish)
*Verona Brown (dark warm brown)
*Chinese Blue (sometimes known as Prussian Blue)
*Cadmium Yellow (lemon color)
*Raw Sienna (a yellowish brown)
*Carmine (dark red with violet cast)
*Viridian Green (blueish green)
*Oxide Green (bright yellowish green)

GROUP 2.

Cheek (a true red)
Lip (scarlet)
*Cobalt Violet (pure violet)
*Cadium Orange
*Sepia (cool dark brown)
*Tree Green (subdued green)
Neutral Tint (makes a true gray)

GROUP 3.

Flake White (opaque white)
*Ivory Black
*Ultramarine Blue
*Payne's Gray (slightly blue-violet)
Burnt Sienna (a reddish orange brown)

GROUP 4.

*Cad. Yel. Dp. (a pure golden yellow)
Cerise
Flesh No. 2 (slightly pinkish cast)
Flesh No. 3 (decidedly pinkish cast)
Serge Blue (a powerful navy blue)
Sky Blue
*Vermilion (bright warm red)

*ALSO MADE IN EXTRA STRONG.

Figure 1.3: Marshall's literature included with ca. 1939 kit, showing sets of colors included with various kits. Image by the author.
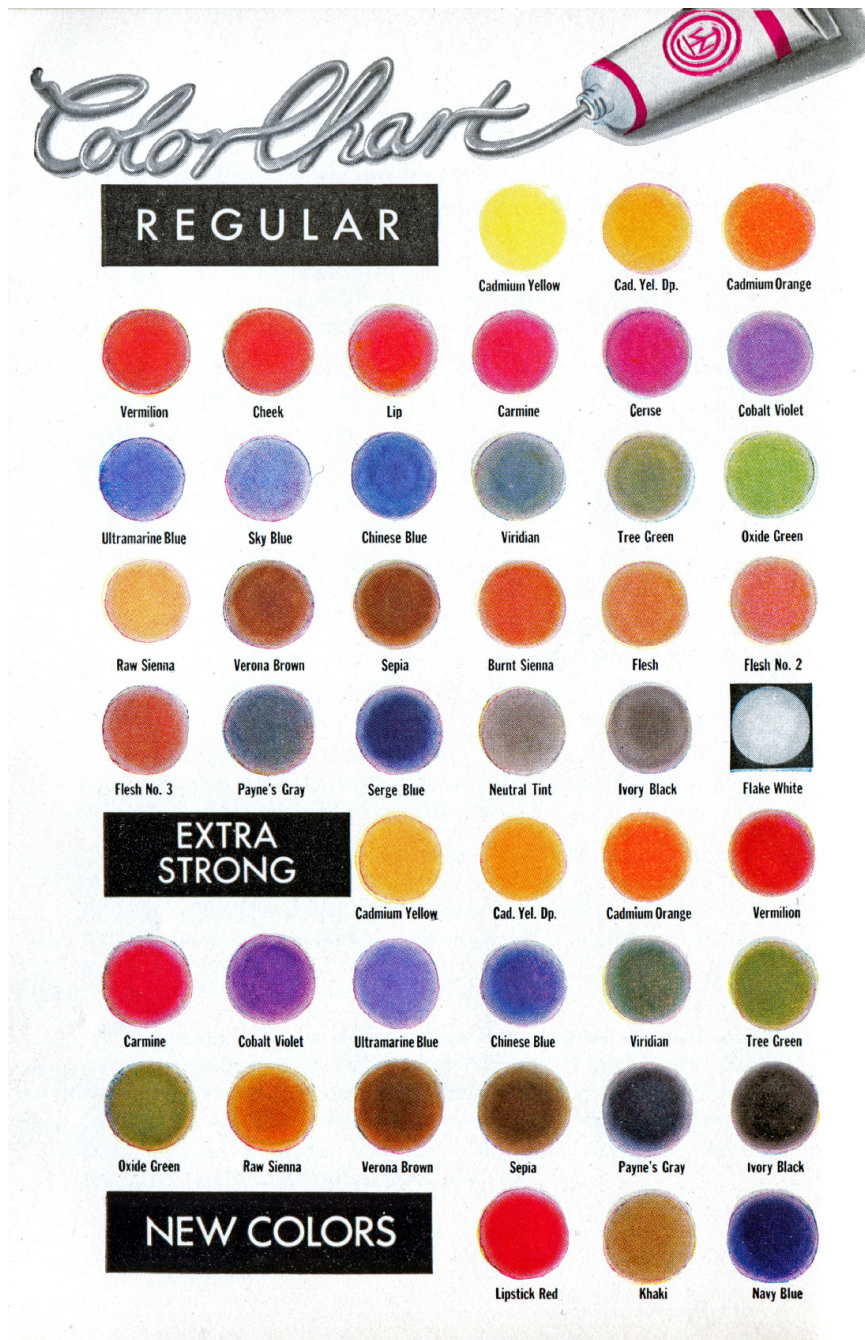
Figure 1.4: Chart showing photo-oil paints produced by the Marshall Company for use in its kits. Reproduced from Lucile Robertson Marshall's *Photo-Oil Coloring for Fun or Profit* (New York: Larum Publishing Company, 1947), 66. Color- and contrast-corrected using Adobe® Photoshop® CS2 9.0.2.

For the studies undertaken in this thesis, two kits were found. The first kit found, named on its box as a "Learn to Color Photo Set" likely dates to after 1947, possibly to ca. 1950, given the typeface on the front cover (**Figure 1.6**) and its differing design from the kits shown in a 1947 advertisement (**Figure 1.5**). The kits featured in this advertisement are of an earlier design and are similar to the second kit analyzed (**Figures 1.9** and **1.10**). The ca. 1950 kit contained eight paints in what appeared to be lead tubes: Viridian, Raw Sienna, Verona Brown, Flesh, Chinese Blue, Cadmium Yellow, Cheek, and Extender, one box of long-fibre cotton for rolling cotton swabs; one bottle of Marshall's P.M. solution, and several skewers for rolling swabs. For the purposes of this study, this kit was given the Winterthur Scientific Research and Analysis Laboratory (SRAL) Object number of AL5249, which appears on some of the spectra

Figure 1.5: Marshall's Photo-Oil Colors featured in an advertisement for the Willoughby camera store, from the *New York Times*, 5 October 1947. Extraneous material cropped out using Adobe® Photoshop® CS2 Version 9.0.2.

Figure 1.6: Ca. 1950 Marshall's Photo-Oil kit, top cover design. Image by the author.

Figure 1.7: Ca. 1950 Marshall's Photo-Oil kit, with top cover open. At left is the bottle of P.M. Solution; at top, the box of long-fibre cotton for rolling swabs; at right, the wooden skewers. At the bottom, the paint tunes. Image by the author.

Figure 1.8: The paint tubes removed from the ca. 1950 kit. From left to right: Raw Sienna, Verona Brown, Cheek, Flesh, Extender, Cadmium Yellow, Viridian, and Chinese Blue. Image by the author.

The second kit analyzed (**Figures 1.9-1.11**) likely dates to ca. 1939. This determination is based on the literature contained with the kit, which features a probable printed date code "6·39" on its recto (**Figure 1.12**, left). The bottle of P.M. Solution in the kit also appears marked with the date code "2·39". Additionally, the literature and kit are both marked with the company's address of 1752 Atlantic Avenue, Brooklyn, New York, which was the company's address until about 1940. A 14 January 1940 classified advertisement in the *New York Times* lists the Atlantic Avenue property as for sale, with the new address of the company as 167 North 9th Street, Brooklyn. The literature accompanying this kit was accordingly stamped in red ink with the new address, indicating that the kit was likely produced before the move, but not sold until after (**Figure 1.12**, right).

Figure 1.9: Ca. 1939 Marshall's Photo-Oil Set, top cover. Image by the author.

Figure 1.10: Ca. 1939 Marshall's Photo-Oil set, with cover open. At left is the bottle of P.M. Solution; at top, the wads of cotton for rolling swabs; at right, the wooden skewers. At the bottom, the paint tunes. Image by the author.

Figure 1.11: The paint tubes removed from the ca. 1939 kit. From left to right: Cadmium Yellow, Raw Sienna, Verona Brown, Flesh, Flesh No. 2, Carmine, Oxide Green, Viridian, and Chinese Blue. Image by the author.

Figure 1.12: Marshall's pamphlets included with ca. 1939 set, showing corrected address (left) and the directions for the Students' Set (right). Note the possible date code at the upper left of these directions. Images by the author.

The label on the kit (**Figure 1.9**) and literature accompanying the kit (**Figure 1. 12**) identifies it as the "Student's Complete Set", comprising one bottle of Photo Medium Solution, one roll of cotton, six skewers, a direction leaflet, and eight tubes of paint: Flesh, Verona Brown, Chinese Blue, Cadmium Yellow, Raw Sienna, Carmine, Viridian, and Oxide Green. A ninth tube of paint, Flesh No. 2, is apparently not original to the set and is in a tube of differing design, indicating that it was likely purchased separately. See **Figure 1.11**. For the purpose of this study this kit was given the Winterthur SRAL object number AL5259.

1.3   Analysis of Marshall's Photo-Oils and Painted Photographs

Little definitive information regarding the composition of the photo-oils in the vintage kits can be found; what is known can be gleaned from Marshall's *Photo-Oil Coloring for Fun or Profit*. "The difference between artists' oil paints and photo-oils is that the former are opaque, while the latter are transparent," Marshall notes. "Photo-oil colors are much more finely ground than are artists' pigments and so balanced that when rubbed down they have good tinctorial strength." In this case, "rubbed down" refers to the method of application, whereby the paints are applied somewhat thickly with cotton-wrapped skewers and are then rubbed down with the cotton until the desired color is reached. Additionally, she notes, "photo-oils are designed to rub out smoothly and not stringy."[23] While these characteristics may give some insight into the properties of paints, they do not give any indication as to the identity of the pigments used to color the paints.

Making the identification of the pigments more difficult is the fact that the names used for the paints are trade names. "The actual pigments in the paints are often far superior to those whose names they bear," notes Marshall. "For example, Carmine is

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really alizarin crimson, and Verona Brown is burnt umber, both of which are standards of permanency."[24] To determine the composition of these paints and to verify the claims about the paints made in *Photo-Oil Coloring for Fun or Profit*, spectroscopic investigations of the photo-oils would be necessary. These investigations could also potentially answer related questions—if a positive identification of the paints could be made, could these same paints then be analyzed when applied thinly on a photographic surface? If indeed the Marshall's paints could be identified when applied as a thin coating, could those same techniques be used to identify paints of unknown composition on period hand-colored photographs?

1.4   Spectroscopic Study of Photographic and Hand-Coloring Materials

As of 2010, little investigative study has been made of hand-coloring materials for photographs. Thus far, no references to spectroscopic study of hand-painted photographs or the materials thereof have been found. A majority of what has been written on the subject of hand-coloring is related to methods of application of photographic paints, such as Marshall's *Photo-Oil Coloring for Fun or Profit* and Dorskind's *The Art of Handpainting Photographs*. Lucile Robertson Marshall can be considered the definitive source on hand-coloring using the Marshall's kits, being the wife of John G. Marshall and the vice-president of the Marshall Company. While her book may go into great detail as to methods of application of the paints, including mixing, cleaning, and application, little is mentioned directly as to the actual materials of the paints. As in Marshall's book, Cheryl Dorskin similarly discusses the application of Marshall's Photo-Oil Colors and Color Pencils to photographs to achieve the desired visual effects in her *The Art of Handpainting Photographs*.[25]

Attempts to understand the effects of hand-coloring media on photographs have been undertaken. Klaus Hendriks and Sebastian Dobrusskin undertook accelerated aging tests in a 1990 study to determine how various coloring media affect the photographic image and support of salted paper prints, gold-toned albumen prints, and silver gelatin developed-out prints. In regards to Marshall's Photo-Oils, they found that, in general, Marshall's Photo-Oils often caused the bleaching or yellowing of the medium and the discoloration of the filamentary and physically developed silver, while Marshall's Photo Pencils did not appear to affect the photographic base or the silver image material. Unfortunately, no explanations of the observed phenomena were offered.[26]

While spectroscopic analysis of hand-colored photographs and hand-coloring materials may be a relatively rare undertaking, conservators and conservation scientists have used spectroscopy to analyze other aspects of photographic materials. Clara von Waldthausen makes note of the use of attenuated total reflectance Fourier-transform infrared spectroscopy in a study of coatings on salted paper, albumen, and platinum prints.[27] Little information on these ATR-FT-IR studies was presented, but the two examples mentioned in photo captions demonstrated mixed results. Lee Ann Daffner had much greater success with that technique in studying the paper photographic negatives of Frédérich Flachéron. Using a combination of infrared spectroscopy augmented with Gas Chromatography-Mass Spectrometry, Daffner was able to positively identify the composition of transparentizing agents coating the papers such as beeswax mixed with a hydrocarbon wax on some and a mixture of oil, sandarac, and pine resin on others.[28] Daffner did note several limitations with this method of analysis of very thin layers, namely that sampling for Gas Chromatography-Mass Spectrometry (GC-Mass Spec) analysis had to be kept to a minimum, and thus the samples "remained at the low end of what is normally retrieved." Additionally, while the "mathematical subtraction of certain

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FT-IR spectra" may have revealed the presence of certain substances, "it may also have caused the loss of critical peaks for other components."[29]

Other researchers found greater success in studying photographic materials with other spectroscopic techniques. Sylvie Penichon found in a 1999 study that elemental analysis using Scanning Electron Microscopy-Energy Dispersive Spectroscopy (SEM-EDX) could be used to distinguish between and positively identify different toning protocols in matte collodion photographs, e.g. gold, platinum, etc.[30] Adam Gottlieb similarly used SEM-EDX to analyze platinum and palladium photographs by Alfred Stieglitz. Noting that the scanning electron microscope can analyze very small regions of photographs mostly without prior preparation, Gottlieb used this technique in conjunction with X-Ray Fluorescence Spectroscopy, noted for its low cost and nondestructive nature, to determine the elemental composition of the prints.[31] Using the acquired elemental compositions, Gottlieb was able to speculate with relative certainty about the chemicals used to create the prints, including sensitizers, intensifiers, and toners.[32]

This literature search showed that previous research could not be relied upon for these analyses, and that the experimental methods used to analyze the paints and the hand-colored photographs would have to be developed during the course of the experiments.

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Chapter 2

EXPERIMENTAL

2.1 Instrumental Method: X-Ray Fluorescence Spectroscopy

X-Ray Fluorescence (XRF) spectroscopy yields information about the elemental composition of a sample by bombarding a small area with X-rays and detecting the re-emitted fluorescent radiation. The atoms of the elements present in the sample absorb the energy carried by the incident X-rays, then re-emit lower energy X-rays in discrete bands of energy specific to each element. Known as X-ray fluorescence, the technique can be used not only for qualitative analysis of the elements present in a sample, but also quantitative analysis, as the intensity of the reading at an element's specific wavelengths depends upon the amount of an element present.

XRF Spectroscopy was carried out using a Röntec ArtTAX [now Bruker AXS] μ-XRF Spectrometer operated with a molybdenum X-Ray source at 50 keV. It was hoped that this nondestructive technique would yield elemental data that could provide tentative identifications to some materials, i.e. inorganic vs. organic pigments, iron-based pigments, etc. To prevent superfluous readings, the samples and photographic objects were positioned on top of a sheet of Ethafoam and the movable arm of the spectrometer positioned overtop the area to be sampled. Spectra were collected in air without the use of filters over a live time collection interval of 100 seconds. The spectra were analyzed and elemental identifications made using the dedicated Röntec GmbH Berlin software version 4.5.18.1 provided with the spectrometer.

2.2   Instrumental Method: Fourier Transform-Infrared Spectroscopy

Infrared spectroscopy yields information about the ways in which atoms in organic and inorganic compounds are bonded together. With considerably less energy than X-rays, infrared radiation can affect the ways molecules vibrate. The absorption of energy as the molecules are raised to higher states of energy produces broad vibrational absorption bands characteristic to each molecule. By collecting infrared spectra at multiple frequencies and applying the Fourier Transform mathematical operation, one can produce a unique spectrum for a material that can be used to identify the component compounds.

Fourier Transform-Infrared (FT-IR) Microscopy was performed using a Thermo Scientific Nicolet Continuum FT-IR Microscope attached to a Thermo Scientific Nicolet 6700 FT-IR Spectrometer with an auxiliary MCT detector. The attached microscope permits the analysis of microscopic samples. For absorbance mode, working samples were cut from the larger pigment samples on carbon studs using a scalpel and placed on a diamond sample cell, where they were rolled out using a small metal roller. For some photographs non-destructive methods of analysis were desired, so the spectrometer was set in the diffuse reflectance mode and the photographs were positioned on the microscope stage. In transmittance mode 128 scans were averaged at a spectral resolution of 4 cm^{-1}, while in absorbance mode 512 scans per sample and background were averaged at the same resolution. Both were viewed in the absorbance format between 4000 and 650 cm^{-1}.

OMNIC software version 8.0.342 was used to analyze the raw spectra; in the reflectance mode, some of the collected data were analyzed after applying the Kramers-Kronig transformation. The Infrared and Raman Users Group (IRUG) Spectral Library

Suite and approximately 30 other conservation-based libraries were used to identify the materials found in the samples.

2.3 Instrumental Method: Dispersive Raman Spectroscopy

Dispersive Raman spectroscopy is similar to IR spectroscopy in that it studies molecular vibrations, though unlike that technique, Raman spectroscopy relies on the scattering of radiation rather than absorption. As radiation passes through a sample, some is scattered by the molecules present in a sample. This Raman scattering results from a weak interaction between the radiation and the molecule. Though most of the wavelength of the scattering radiation is the same as that of the incident light, due to Rayleigh scattering photons are occasionally scattered with more energy, or less energy. This Raman scattering produces spectral lines that are distinct for each molecule. This phenomenon allows individual components of a substance to be identified from a single spectrum.

Raman spectroscopy was carried out using a Renishaw® inVia Raman Microscope with both a 785 nm Renishaw® red laser and a Spectrum Physics 514.5 nm green laser and a diffraction grating of 1200 lines/inch. Samples were placed on the microscope stage in the sample chamber and brought to a usable level with glass microscope slides as necessary. Spectra were collected in a range of 3200-120 cm^{-1} with a resolution of 3 cm^{-1}. The spectra were analyzed using the dedicated Renishaw® WiRE 2.0 service pack 9 software provided with the spectrometer. The OMNIC software provided with the FT-IR spectrometer was used to baseline correct the spectra by removing the effects of fluorescence as well as removing any peaks caused by cosmic rays striking the detector. Peaks in the spectra were identified using the University College London Chemistry Raman Spectroscopic Library [1] as well as Burgio and Clark's

2001 study.[2] Additionally, the Raman wave numbers republished in Cornell and

Schwertmann's *The Iron Oxides* were consulted when iron-based pigments were

encountered.[3]

2.4 Instrumental Method: Scanning Electron Microscopy-Energy Dispersive Spectroscopy

A scanning electron microscope operates on the two similar principles as

XRF spectroscopy. An electron beam that strikes a target will cause the emission of

characteristic X-rays, which, with the aid of high-magnification, high-resolution imaging

can show the distributions of the chemical elements within the sample. Backscattered

electrons can also provide information about the topography of the sample. It must be

noted that unlike XRF, which relies upon electromagnetic radiation, SEM-EDS relies

upon an electron beam to stimulate elements to fluoresce X-rays.

SEM-EDS was performed using a Topcon ABT-60 Scanning Electron

Microscope operated at 20 kV attached to a Bruker AXS 4010 XFlash Microanalysis

Detector, as well as a Robinson ETP SEM RA backscatter detector. Spectra were

collected at a tile angle of 20° and a working distance of either 26 or 23 mm, depending

on the sample. The spectra were analyzed and elemental compositions assigned using the

dedicated Bruker Quantax ESpirit 1.8.2 software provided with the XFlash detector.

2.5 Instrumental Method: Gas Chromatography-Mass Spectrometry

Gas Chromatography-Mass Spectrometry combines the two eponymous

techniques. Substances are first injected into a capillary column through which they

move at differential rates based on their affinity for the column substrate. They emerge

from the capillary tubes at differing times, allowing a mass spectrometer to analyze each

component separately. The gaseous components are ionized and accelerated through a

charged electric field then a quadripole mass analyzer, striking a detector at certain energies expressed as the ratio of the molecule's mass to its charge. Using this information, the investigator can determine the compositions of the ions, and from that, the structure of the original compounds.

Samples were analyzed using the Hewlett-Packard 6890 gas chromatograph equipped with a 5973 mass selective detector (MSD) and 7683 automatic liquid injector. The Winterthur RTLMPREP method was used with conditions as follows: inlet temperature was 300°C and transfer line temperature to the MSD (SCAN mode) was 300°C. A sample volume (splitless) of 1µL was injected onto a 30m×250µm×0.25µm film thickness HP-5MS column (5% phenyl methyl siloxane at a flow rate of 2.3mL/minute). The oven temperature was held at 55°C for two minutes, then programmed to increase at 10°C/minute to 325°C where it was held for 10.5 minutes for a total run time of 40 minutes.

2.6   Preparation of Marshall's Photo-Oil Samples

While several of the tubes, including Cadmium Yellow, Chinese Blue, and Viridian, were unopened at the time of examination, the metal caps of the other tubes were stuck fast. In her book Marshall recommends holding the cap of the tube "over the flame of a match for a second," as this will "melt the oil and loosen the cap."[4] Fearing that this approach could damage the tube or its contents, a gentler method was chosen. A water bath, heated to around 80° C, was used instead. The caps of the tubes only were submerged in the gently-stirred bath, causing them to expand and releasing them from their immobile state. All of the stuck caps were thusly freed, with the notable exception of Cheek, the tube having deteriorated to a state that made that effort impossible. Instead, the tube of Cheek was opened along the bottom seam using a scalpel.

After opening all of the tubes in the ca. 1950 set, 8 carbon studs were prepared to receive the paint samples. The SPI Supplies 15 mm pure carbon mount studs, manufactured by Structure Probe, Inc., were cleaned with methanol and engraved with the sample numbers 1-8 on the bottom using a pin vise. A sample of each paint was then placed on the corresponding stud (**Figure 2.1**). After opening Cheek, however, it was found that the contents had long since ceased to be fluid, and the paint deteriorated. A cross-section was cut out using a scalpel, and due to its brittle nature, a sticky carbon dot was used to adhere this sample to its stud. Based on the numbers on the studs, the paints were given the following designations, using "P" as in "Pigment" as a prefix:

Table 2.1: Paint Designations in ca. 1950 Marshall's Set

Designation	Paint Name
P1	Viridian
P2	Raw Sienna
P3	Verona Brown
P4	Flesh
P5	Chinese Blue
P6	Cadmium Yellow
P7	Cheek
P8	Extender

The paint Viridian was a homogenous blue-green color without any visible particulates. By contrast, Raw Sienna appeared to have some small brown particulates embedded in a light yellow-brown matrix. Verona Brown was a much redder brown than Raw Sienna, and appeared to be much more homogenous. Flesh, in concentrated form, was bright red in color, and was homogenous. Chinese Blue, as its name implies, was a dark blue color, and more glossy than most of the other paints. Cadmium Yellow was a bright lemon yellow color, and was mostly homogenous. Cheek was notably different

than any other paint; unlike the other paint tubes, which still maintained some whiteness to their paper labels, Cheek's label had turned noticeably brown. A tear in the tube near the neck had likely exposed the contents to air. The contents, unlike the other tube, felt hard and unpliable, and a semi-solid brown-black mass was observed sticking to the sides of the tube, coated with a thin oily layer, leaving a bright red mass of what appeared to be the red pigment in the center. Extender, unlike the other paints, was far more liquid and was a translucent white color.

Samples of the paints found in the ca. 1939 set were added to their own set of studs. These tubes were found to be used, and were opened using the heated water bath method described above. All but three of the paints found in this set were duplicates of those found in the ca. 1950 set, so those three, and the tube of Flesh for comparative analysis, were selected for sampling. These were given the designation Q, to differentiate them from the samples in the other set:

Table 2.2: Paint Designations in ca. 1939 Marshall's Set

Designation	Paint Name
Q1	Flesh No. 2
Q2	Oxide Green
Q3	Carmine
Q4	Flesh

The paint Flesh No. 2 was a homogenous earthy red-brown color, Oxide Green appeared yellow-green in color, and appeared heterogeneous; small particulates that were a darker green color were flecked throughout the mixture. Carmine was a deep hue of red, some of the outer portions that were likely in contact with the tube appearing

more brown that the other areas. Flesh appeared as a browner red than Flesh No. 2, looking like the other sample of Flesh from the ca. 1950 kit.

To sample the P.M. Solution found in the ca. 1950 kit, an aluminum stud was selected, as this would not interfere with the FT-IR or the Raman spectra of P.M. solution. The liquid was painted out on the stud using a glass pipette and allowed to evaporate. Using this method, multiple layers were laid down until a visible residue was left behind.

Smaller samples of the paints were prepared for analysis in the SEM and the Raman spectrometer. Smaller diameter carbon studs were prepared, and sticky carbon dots placed on each. Samples of each paint were cut from the dried samples on the larger studs with a scalpel and placed on the sticky dots of the smaller studs.

Several samples were selected for further analysis using GC-Mass Spectrometry: Viridian, Flesh, the red portion of Cheek, the black-brown portion of Cheek, and the P.M. Solution. Prior to running the samples through the chromatograph, they were treated with MethPrep II reagent to convert carboxylic acids and esters to their methyl ester derivatives. Each sample was placed in a tightly-capped, heavy walled vial (100-300μL) and approximately 100μL of 1:2 of Alltech MethPrep II reagent in benzene was added. The vials were warmed at 60°C for one hour in the heating block, removed from heat, and allowed to stand to cool. Analysis was carried out using the RTLMPREP method on the GC-MS described in **Chapter 2.5**. All GC-MS sample preparation and analysis was carried out by Chris Petersen of the Winterthur Scientific Research and Analysis Laboratory (SRAL).

Figure 2.1: Marshall's Photo-Oils, from top left: Viridian, Raw Sienna, Verona Brown, Flesh, Chinese Blue, Cadmium Yellow, Cheek, Extender, Flesh No. 2, Oxide Green, Carmine, Flesh. Photographs from XRF spectrometer camera.

2.7 Hand-Coloring Photographs with the Marshall's Kits

In order to gauge the effectiveness of the spectroscopic techniques to accurately identify hand-coloring materials applied to photographs, a control using the paints from the Marshall's kits was devised. By applying each usable paint onto period photographs in the manner prescribed by the literature accompanying the kits and in Lucile Robertson Marshall's *Photo-Oil Coloring for Fun or Profit*, the results of the spectroscopic examination of the paints *in situ* could be compared to the results of the analyses for the samples taken directly from the kits' paint tubes. The information learned from this could then be applied to examining hand-colored photographs hand-colored with unidentified pigments. For this purpose, two period photographs from the University of Delaware Department of Art Conservation's photographic study collection were selected. The photographs came from a collection of amateur family photographs sold at a garage sale on the East Coast, and unfortunately little identifying information accompanied them. However, information in the photographs themselves could be used for determining an approximate date for the images.

The first photograph selected was a small (2.75" × 3.75") half-length portrait of a young woman. On the lower right corner of the recto "Love, / Alice" was written in blue ink (**Figure 2.2 left**). The verso, fortunately, was dated in blue ink—"Taken March – 1944" (**Figure 2.2 right**). For the purposes of this study this photograph was given the Winterthur SRAL object number of AL5293.

Figure 2.2: "Alice," recto (left) and verso (right) before hand-coloring. Images by the author.

The second photograph selected depicts a half-length portrait of a soldier in dress uniform (**Figure 2.3**). Printed on 3" × 5" photographic paper for use as a postcard, the photograph only identifies the name of the soldier as "Ed" on the upper right corner of the verso (**Figure 2.3,** right). Fortunately, the photograph contains a vital visual clue. On the soldier's (henceforth referred to as "Ed") left arm, his unit patch is visible (**Figure 2.4**). This identifies him as a member of the United States Army's 14th Armored Division, which saw service in the Second World War (see **Figure 2.5**). Because the division was activated in October 1942 and deactivated in September 1945, the photograph presumable dates to this time period.[5] For the purposes of this study, this photograph was given the Winterthur SRAL object number of AL5292.

Figure 2.3: "Ed," recto (left) and verso (right), before hand-coloring. Images by the author.

Figure 2.4: Ed's unit patch (left) and the 14th Armored Division's patch (right). 14th armored division patch from
http://upload.wikimedia.org/wikipedia/en/f/f9/14th_Armored_Division.patch.jpg.

To hand-color the photographs, the instructions as laid out in Lucile Robertson Marshall's *Photo-Oil Coloring for Fun or Profit* were followed. "Alice" was colored by Jae Gutierrez using unmixed colors (**Figure 2.5**). Based on the recommendations in Marshall's book, a lamp with both fluorescent and incandescent bulbs positioned over the left should was used to light the work area to best approximate the color of daylight.[6] In lieu of an artist's adjustable drawing board, a piece of stiff blotter paper was used as a support. Filmoplast® P-90 tape was used in place of masking tape to secure the photo to the support and to keep the photograph's borders clean.[7] Next, a palette was laid out. Because the pre-made palettes supplied with the kits were missing, a separate palette was made on modern disposable palette paper. A pea-sized amount of each color, except Cheek, which had decayed to the point of being unusable, was squeezed onto the palette and labeled. A combination of pre-made cotton swabs and hand-rolled cotton swabs rolled on the skewers supplied with the kits were used to color

the print. After dipping the cotton swabs in the desired color(s), the colors were gently

rubbed onto the surface of the print. At first, the paints appeared far too thick and

concentrated to be in any way appropriate for hand-coloring photographs; but as indicated

in *Photo-Oil Coloring for Fun or Profit*, by "rubbing down" the paint with a dry cotton

swab, one could smooth out and reduce the concentration of the paint until the desired

tint was reached.[8] By varying the amount of "rubbing down", many different colors

could be produced. Errors in coloring were rectified using cotton swabs dipped in the

P.M. Solution to remove unwanted paint. For Alice, unmixed colors were used as

follows: for her skin, the color Flesh was used, while her hair was colored in Verona

Brown, the background colored in Viridian, her sweater, eyes, and hair band in Chinese

Blue, and her lips in Carmine (**Figure 2.6**).

Figure 2.5: Jae Gutierrez examining "Ed" (left), and "Alice" after painting (right). Note the bottle of P.M. Solution, palette, and unused swabs in the image on the right. Images by the author.

To maximize the differences that could be found in hand-coloring, the author

painted "Ed" using different techniques. The print was not taped down, and prior to

painting, the surface was gone over with the Marshall's P.M. and wiped off, as recommended in *Photo-Oil Coloring for Fun or Profit*.[9] Instead of applying fields of unmixed paints, combinations of paints were used to achieve the desired effects. For Ed's Army Uniform, lacking a green Khaki color and the Marshall's recommended Verona Brown, Tree Green, and Ivory Black combination, a combination of Oxide Green, Viridian, and Verona Brown was used. His tie was colored using a mixture of Cadmium Yellow, Flesh, Raw Sienna, and Verona Brown, and the brass uniform buttons with a mixture of Cadmium Yellow and Raw Sienna. The brim of his hat and his irises were colored with Verona Brown, and his unit patch colored with Carmine and Chinese blue. His face was colored with Flesh No. 2 with hints of Carmine (**Figure 2.7**).

When cleaning excess paint off the surface of the print with the P.M. Solution, it was found that the paint and the Solution would accumulate in any creased and cracked areas of the gelatin surface, allowing the oil to "soak into the paper and leave a dark streak," a possibility of painting and cleaning creases noted in *Photo-Oil Coloring for Fun or Profit*.[10] It was also noticed while coloring that some colors were easier to rub down to the desired level than others; Verona Brown was the easiest to spread out with the swabs, while Cadmium Yellow was stringy and hardly rubbed down at all. Of particular interest is the tinting strength of the Flesh colors and Carmine. Though all appear as bright red (or red-brown) hues when concentrated, they each required a great amount of rubbing down to appear "Caucasian" in color. This indicated that these pigments have a high tinting strength, and that only a small amount of paint was present in the "flesh" areas.

The differences between the painted and unpainted photographs were quite astounding, especially when juxtaposed side by side (**Figures 2.8** and **2.9**).

Figure 2.6: "Alice," after hand-coloring by Jae Gutierrez. Actual size. Scanned by the author using Epson V300 Photo Scanner.
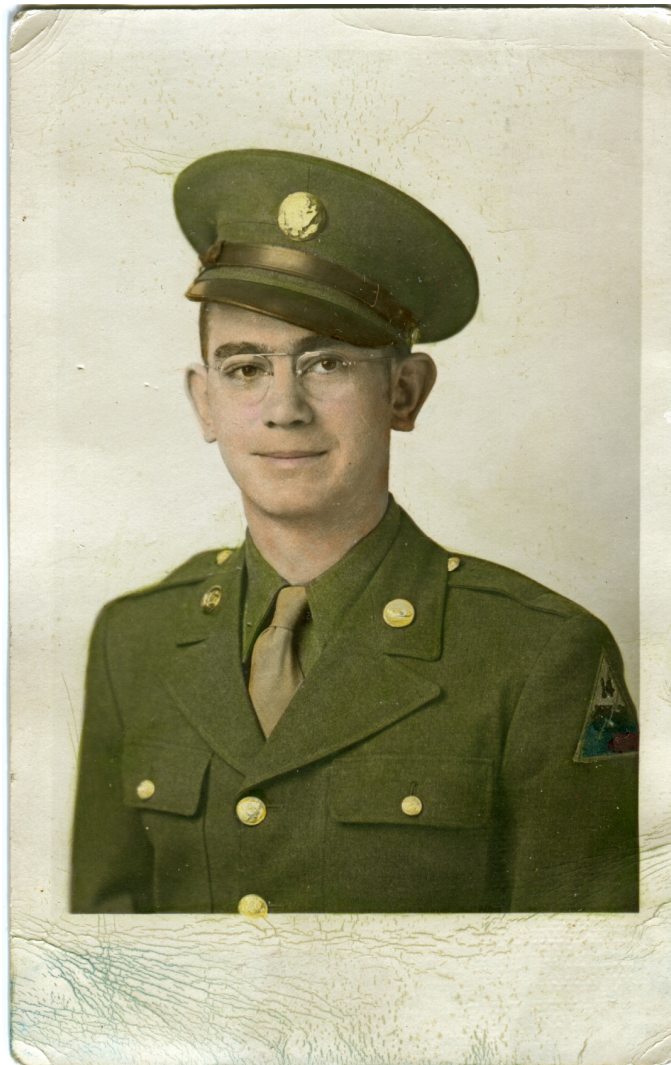
Figure 2.7: "Ed," after being hand-colored by the author. Actual size. Scanned by the author using Epson V300 Photo Scanner.
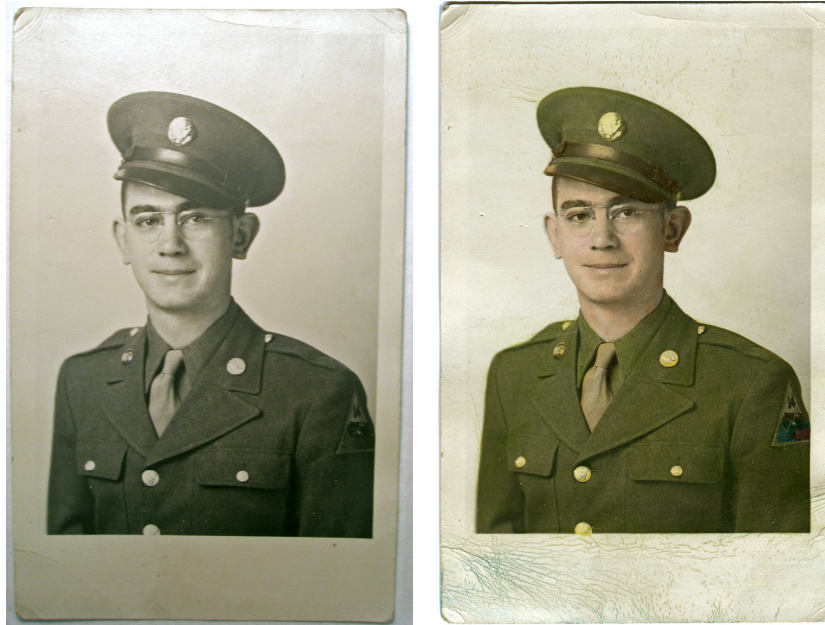
Figure 2.8: "Ed", before (left) and after (right) hand-coloring. Images by the author.

Figure 2.9: "Alice" before (left) and after (right) hand-coloring. Images by the author.

2.8   Hand-Colored Photographs with Unknown Coloring Media

Photographs from different eras were selected for study to give as wide a range as possible for methods of application and materials. One photograph came from the author's personal collection, while two were purchased from a West Chester, Pennsylvania dealer in rare books.

A stereograph was the first photograph purchased from the West Chester book dealer. The albumen prints on the stereograph depict an exhibition drill of the Apollo Commandery of the Knights Templar in Boston, taken in 1895 by B. W. Kilburn of Littleton, New Hampshire, a noted photographer of stereoviews that were distributed by the firm of James M. Davis. This stereoview was rather primitively colored at some point in its history with a bright hue of blue and a bright hue of red to accentuate the uniforms and the flag of the men in formation (**Figure 2.10**). For the purposes of this study, this photograph was given the Winterthur SRAL object number of Al5266.

The second purchased photograph is an albumen studio portrait depicting a child seated on a pillow reading a book (**Figure 2.11**). The pillow and floor areas were hand-colored in green, while the child's clothing was colored in magenta. The background curtains were colored in yellow, while the child's skin may have been painted in white or left unpainted. The date of the photograph is unknown, though it likely dates to the late 19$^{\text{th}}$ or early 20$^{\text{th}}$ century. For the purposes of this study, this photograph was given the Winterthur SRAL object number of Al5265.

The third photograph studied, a silver gelatin developed-out print (DOP) depicts the author's great-great grandparents, Christian Frederick. Bader (1874-1940) and his second wife Anna Elise Bader, *née* Schöpf (1886-1959), standing in a field of wildflowers on their farm at Ironsides, near Phoenixville, Pennsylvania, around 1930 (**Figure 2.12**). A variety of colors were used to finish both the figures and the landscape

of what appears to be a sepia-toned silver gelatin print, including blue, yellow, multiple variants of red, green, and brown. The similarity of some of the hand-coloring to the effects achieved with the Marshall's photo-oils on Alice and Ed suggests that this photograph may also be colored with them. Furthermore, the relative crudity of the coloring suggests that this photograph was colored by an amateur. Some ferrotyping of the image has occurred due to improper framing behind glass. Years of exposure to tobacco smoke have coated the photograph with a yellow film that has unfortunately distorted many of the color values. For the purposes of this study, this photograph was given the Winterthur SRAL object number of AL5294.

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Figure 2.10: Hand-colored albumen stereograph showing the Apollo Commandery of the Knights Templar on exhibition drill, 1895. Image by the author.

Figure 2.11: Hand-colored albumen print depicting a seated child reading a book. Date unknown. Image by the author.

Figure 2.12: Christian F. and Anna E. Bader on their farm at Ironsides, Pennsylvania. Hand-colored silver gelatin developed-out print. Note the yellowing due to exposure to tobacco smoke. Smaller than actual size. Scanned by the author using Epson V300 Photo Scanner.

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[3] R. M. Cornell and U. Schwertmann, *The Iron Oxides: Structure, Properties, Reactions, Occurrences and Uses* (Weinheim: WILEY-VCH Verlag GmbH & Co., 2003), 147.

[4] Ibid., 15.

[5] Joseph Carter, *The History of the 14th Armored Division* (Evansville: Unigraphic, Inc., 1977),

[6] Marshall, op. cit., 13

[7] Ibid., 10.

[8] Ibid., 26-27.

[9] Ibid., 34

[10] Ibid., 5.

Chapter 3

RESULTS AND DISCUSSION

The Marshall's paint and P.M. Solution samples discussed in **Chapter 2** were analyzed using some of all of the following instrumental methods: XRF, FT-IR, SEM-EDS, dispersive Raman, and GC-MS. The results of these analyses and a discussion of their interpretation follow in this chapter.

3.1   Compositions of Marshall's Photo-Oils Materials

3.1.1   Viridian

XRF analysis of the paint Viridian reveals the presence of a high amount of copper in the sample, in addition to chlorine, lead, and iron (**Figure 3.1**). The presence of molybdenum in the spectra seen in **Figure 3.1** is due to the molybdenum X-ray source, and is not part of the paint's composition. The copper content of paint is confirmed by FT-IR analysis, which indicates the presence of the blue-green pigment copper phthalocyanine green (PG 7). A mineral similar to sodium carbonate was also found, perhaps used as a filler, as well as a significant amount of linseed oil, which was likely the binder of the paint. Raman analysis confirmed the presence of copper phthalocyanine green in considerable quantity, with distinctive peaks at 684.5 cm^{-1}, 740.4 cm^{-1}, 776.0 cm^{-1}, 816.7 cm^{-1}, 979.0 cm^{-1}, 1082.3 cm^{-1}, 1212.2 cm^{-1}, 1281.5 cm^{-1}, 1338.2 cm^{-1}, 1389.0 cm^{-1}, 1445.5 cm^{-1}, 1506.1 cm^{-1}, and1537.3 cm^{-1} (**Figure 3.2**). The differences in peak intensity compared to the reference library used to identify the pigment (Burgio and Clark, 2001) can be attributed to these spectra being collected at 785 nm, whereas the

reference spectra were collected at 1064 nm. Slight differences in Raman shift were also noted (approximately 1-4 cm^{-1}), likely due to instrumentation or analytical error or wavelength calibration. It must also be noted that two peaks around 100 cm^{-1} are not actual peaks but are owed to a polarization filter which was changed out after most of the spectra were recorded.
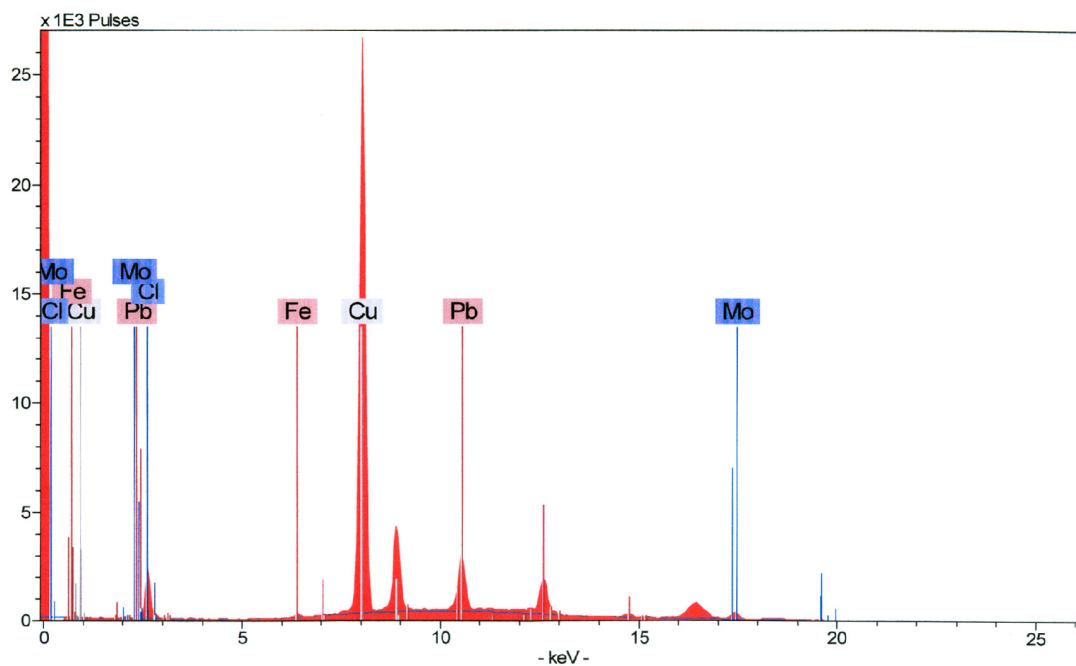
Figure 3.1: XRF spectrum of the paint Viridian. Note the relative abundance of copper compared to the other elements found in the sample.
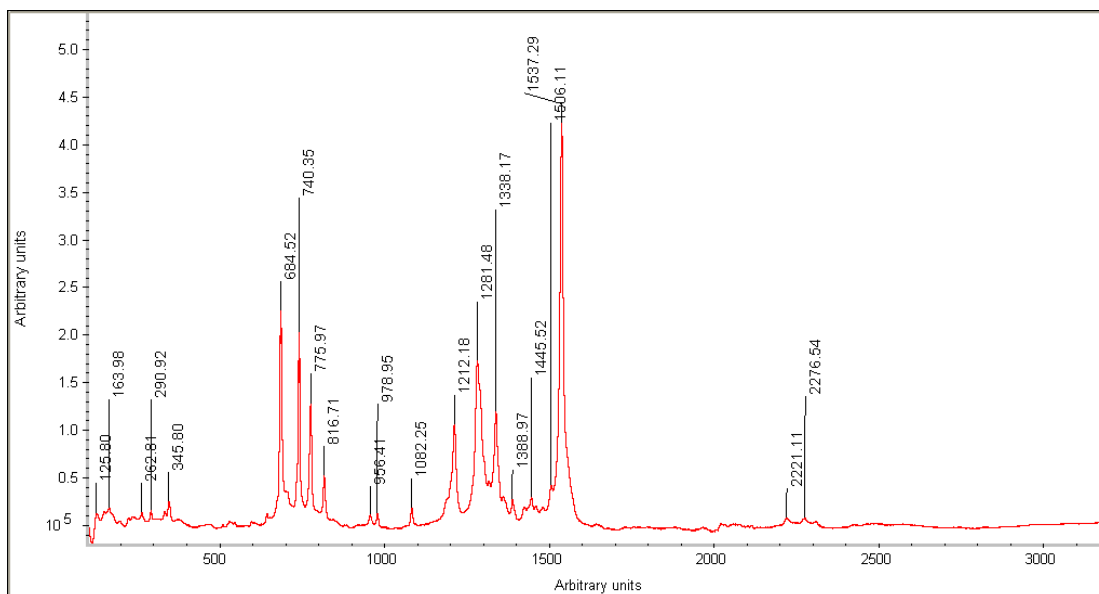
Figure 3.2: Raman spectrum of the paint Viridian.

3.1.2 Raw Sienna

XRF analysis of the Raw Sienna revealed the presence of a large amount of iron, with trace amounts of copper, vanadium, and zinc, which likely came with the iron pigment. Trace amounts of calcium and lead were also found in the sample. The presence of iron was confirmed with FT-IR analysis, which revealed the presence of both the iron pigment burnt sienna and trans-yellow oxide, another iron-based pigment (**Figure 3.3**). Because the library match for burnt sienna already exhibited a possible absorption due to clay, a separate library match for a clay substance, as found in the paint Viridian, was not found in this sample.
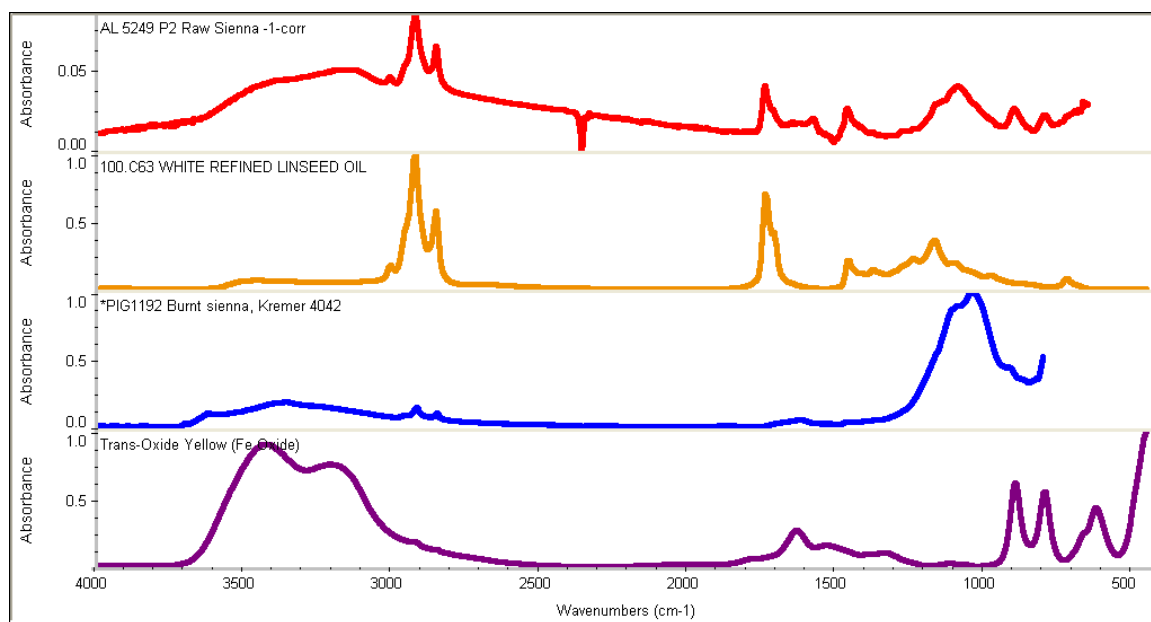
Figure 3.3: FT-IR spectrum of Raw Sienna (top) with library matches of linseed oil (yellow), burnt sienna (blue), and trans-oxide yellow (purple).

SEM-EDS analysis revealed a strong correlation between the elements phosphorous, aluminum, and sodium, which likely composed the filler used in the paint (**Figures 3.4**). Additionally, this analysis revealed the presence of larger particles of silicon and iron (**Figures 3.5** and **3.6**), which may indicate the iron comes from a natural ferrous clay and not artificial sources, though that is strictly speculation. Raman analysis showed that the form of iron found in the pigment was Goethite, α-FeOOH (ferric hydrate), also known as raw sienna, with identifying peaks at 246.8 cm^{-1}, 300.3 cm^{-1}, 387.1 cm^{-1}, 484.1 cm^{-1}, and 553.9 cm^{-1}.
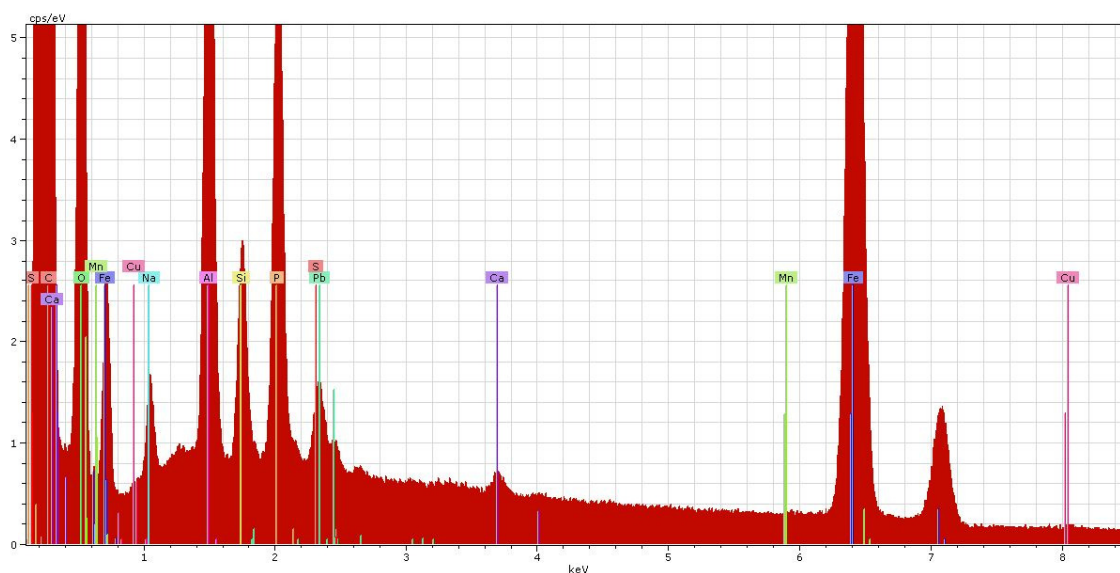
Figure 3.4: SEM-EDS spectrum of Raw Sienna, showing elemental identifications overlaid. Calcium is indicated in purple, manganese in yellow-green, iron in blue, copper in red, aluminum in magenta, oxygen in green, sulfur in red, phosphorous in orange, silicon in yellow, and sodium in cyan.
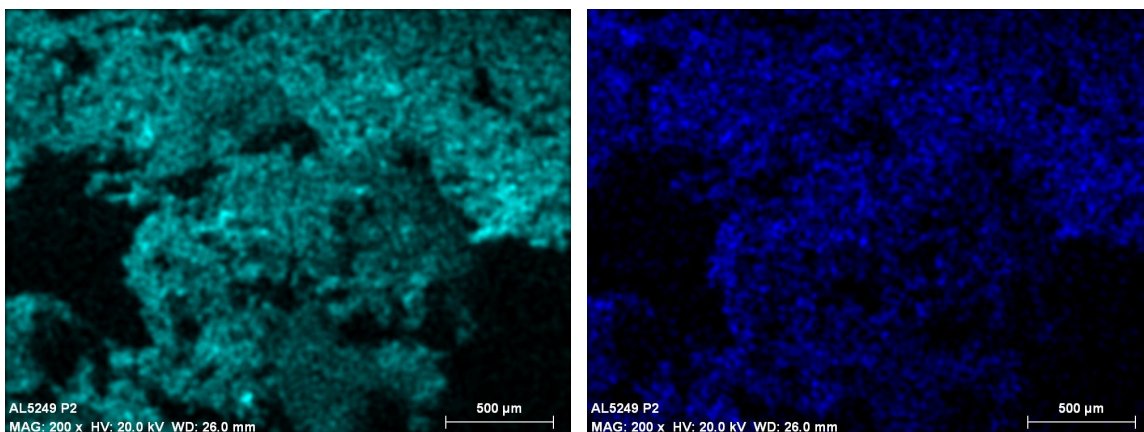
Figure 3.5: SEM-EDS elemental map showing distribution of aluminum (left) and sodium (right) in sample.
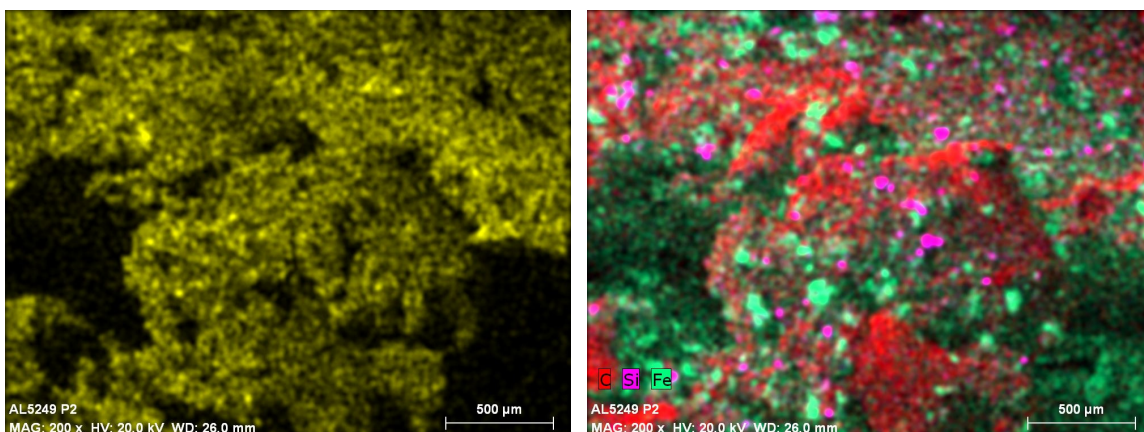
Figure 3.6: SEM-EDS elemental map showing distribution of phosphorous in sample (left) and carbon, in red, silicon, in purple, and iron, in green (right).

3.1.3   Verona Brown

As in Raw Sienna, XRF found an abundance of iron in the Verona Brown. Manganese, lead, and calcium were also found in trace amounts. FT-IR analysis found

the presence of an iron oxide pigment similar to German light brown ochre, mixed with kaolin—likely the combined result of the pigment and the clay filler. SEM-EDS analysis elucidated the nature of that filler and the iron oxide pigment. Like Raw Sienna, the Verona Brown showed the presence of iron and silicon particles. Unlike that paint, however, Verona Brown also contained manganese, as well as distinct particles of calcium (**Figure 3.7**). Because of the presence of manganese, this pigment may be described as burnt umber and not burnt sienna, umbers are similar to sienna pigments, but contain manganese dioxide as well as iron oxides. Burnt umber, as the name implies, is made by calcining the Goethite-containing raw umber to convert the ferric hydrate to ferric oxide, hematite, to produce a warmer, redder color.[1] Raman analysis showed the presence of hematite with identifying peaks at 228.2 cm^{-1}, 295.5 cm^{-1}, 410.2 cm^{-1}; the presence of manganese dioxide may be indicated by a peak at 655 cm^{-1} (**Figure 3.8**). Four significant peaks at 1166 cm^{-1}, 1307 cm^{-1}, 1439 cm^{-1}, and 1609 cm^{-1} could not be correlated with any material in the spectral databases, and thus some components remain unidentified.
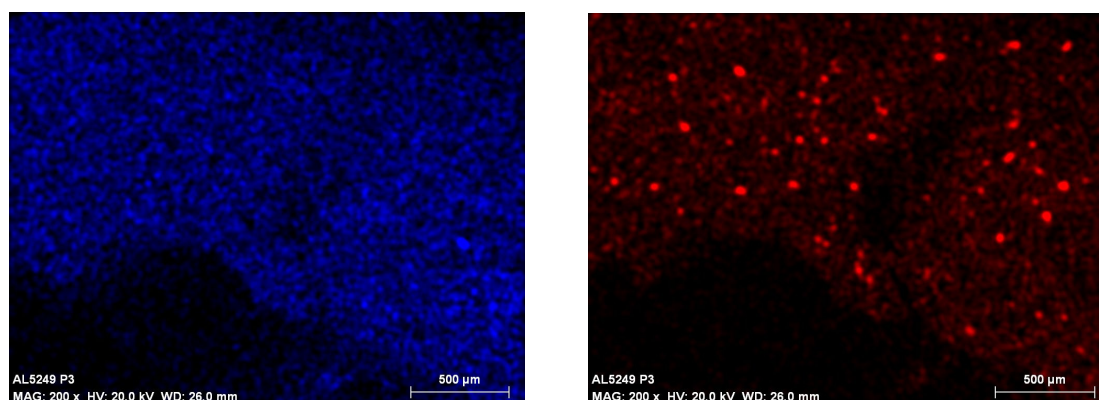
Figure 3.7: SEM map of Verona Brown, showing manganese (left) and particulate calcium in the sample (right).
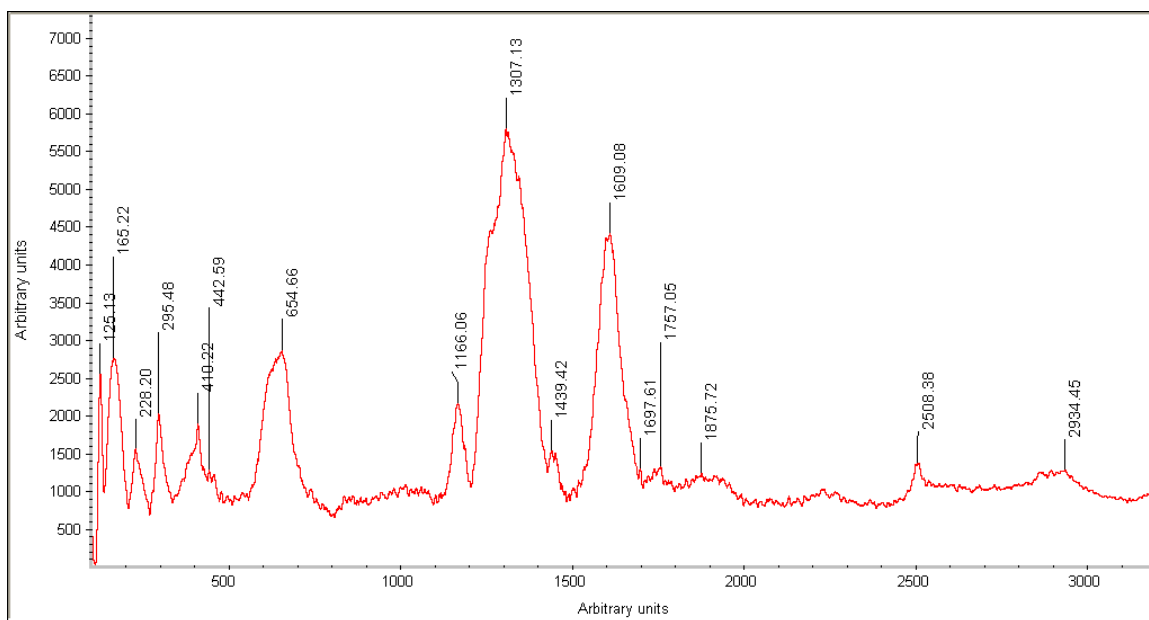
Figure 3.8: Raman spectrum of Verona Brown. Note the size of the peaks at 1166 cm^{-1}, 1307 cm^{-1}, and 1609 cm^{-1} compared to the hematite peaks in the 228-410 cm^{-1} range.

3.1.4 Flesh

XRF analysis of Flesh revealed the presence of a large amount of iron. FT-IR analysis showed the presence of burnt green earth, an iron oxide pigment, the linseed oil binder and a clay filler similar to halloysite, an aluminum silicate clay. SEM-EDS showed the presence of particulate iron and silicon as in the other iron-based pigments, which suggests that it may come from a natural rather than synthetic source. Raman confirmed the presence of hematite, which accounts for the intense red hue of the paint.

3.1.5 Chinese Blue

XRF analysis of Chinese Blue showed that a large amount of iron and lead were present in the sample. FT-IR analysis revealed the presence of Prussian blue

pigment (PB 27), ferric ferrocyanide, accounting for both the blue hue of the paint, as well as the iron found in the XRF spectrum.[2] Linseed oil and a clay similar to calcined kaolin clay were also matched to the FT-IR spectrum. The identification of Prussian blue was confirmed with Raman spectroscopy, which showed the characteristic peaks of the material at 2093 cm^{-1} and 2055 cm^{-1}. The large amount of lead found by XRF suggests that the source of the element is likely not the lead-alloy tube in which the paint was packaged, but a component of the paint, perhaps as flake white to dilute the intense pigment strength of the Prussian blue pigment. SEM-EDS showed a fairly homogenous mixture, with silicon present not in particles, but interspersed evenly throughout—which may indicate that the filler was very finely ground.

3.1.6 Cadmium Yellow

XRF spectroscopy of Cadmium Yellow showed a preponderance of lead present in the sample, as well as a large amount of chromium. FT-IR analysis revealed the presence of the pigment chrome yellow (lead chromate) (PY 34), confirming the presence of lead and chromium found in the XRF spectrum. FT-IR also found linseed oil, as well as some lead sulfate and a clay similar to montmorillonite. The latter identification is likely due to the clay filler used in the paint. Raman analysis confirmed the presence of lead chromate with peaks at 337.7 cm^{-1}, 359.8 cm^{-1}, 376.8 cm^{-1}, 403.3 cm^{-1}, and 843.0 cm^{-1}. SEM-EDS revealed a homogenous mixture with lead and chromium among the most prominent elements, as well as a large amount of aluminum, sodium, phosphorous, and oxygen—the latter likely being the clay filler.

3.1.7 Cheek

XRF analysis of Cheek showed a great deal of lead, as well as trace amounts of other transition metals—cobalt, iron, and zirconium. FT-IR analysis of the red portion

of the paint revealed the presence of the organic red pigment Hansa Red, a.k.a. toluidine

red (PR 3) (**Figure 3.9**), as well as a fatty alcohol—likely the result of the reduction of

the linseed oil by a chemical reaction. In the black portion of the decomposed paint, basic

lead carbonate was found, as well as linseed oil and some fatty alcohol. This seems to

indicate that a reaction occurred with the Hansa dye, possibly with the lead of the tube,

which caused the paint to break down in some manner. GC-MS of the degraded paint

showed the presence of bathocuproine and 2-(2-naphthyl)imidazo[1,2-a]pyridine (**Figure

3.10**), compounds that were not observed in other paints analyzed using GC-MS. It is

speculated that these compounds are degradation products of the toluidine dye. SEM-

EDS analysis of this paint showed that in the red portion of the paint the areas of carbon

were fairly segregated from areas of the clay filler material, marked by the presence of

aluminum, calcium, phosphorous, and sodium (**Figure 3.11**). This was also the case in

the black portion of the paint. Raman analysis of both portions of the paint confirmed the

presence of the toluidine red pigment (**Figure 3.12**).
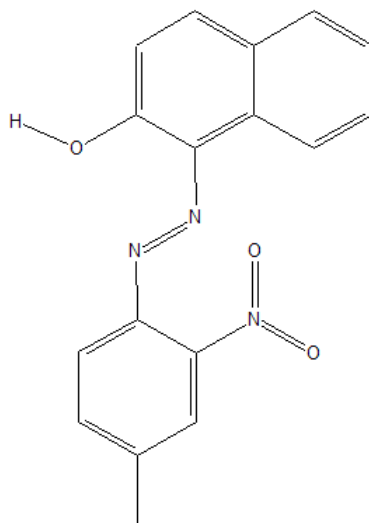
Figure 3.9: Structure of toluidine red (PR 3).
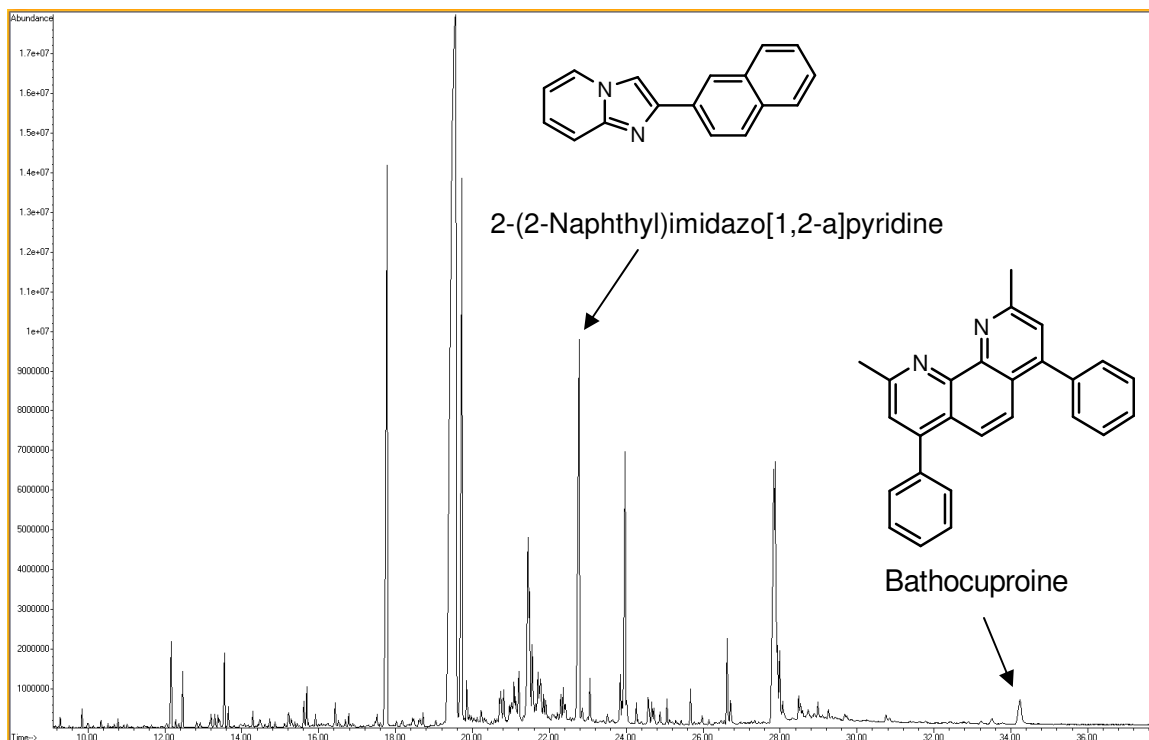
Figure 3.10: GC-MS spectrum of Cheek, showing presence of bathocuproine and 2-(2-naphthyl)imidazo[1,2-a]pyridine.
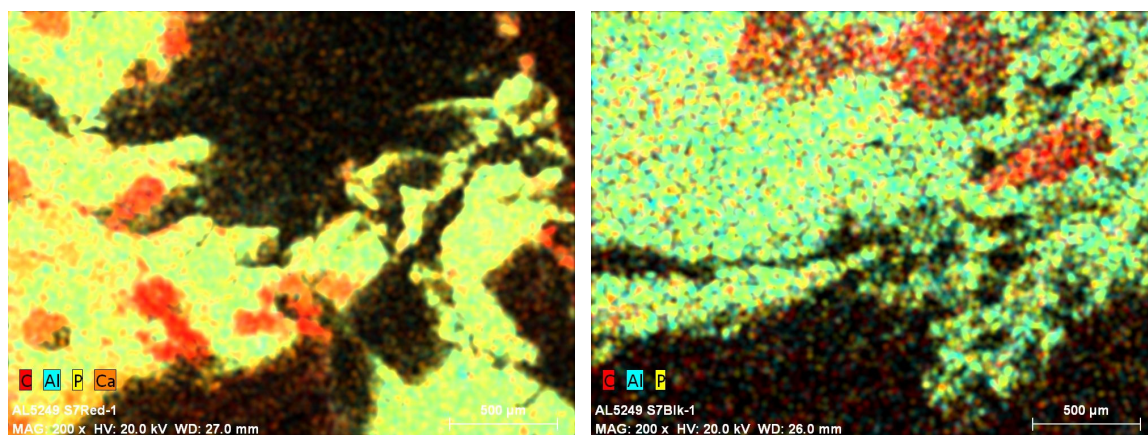
Figure 3.11: SEM-EDS maps of Cheek showing distribution of carbon (red), aluminum (blue), phosphorous (yellow), and calcium (orange), in the red portion (left) and black portion (right) of the paint.
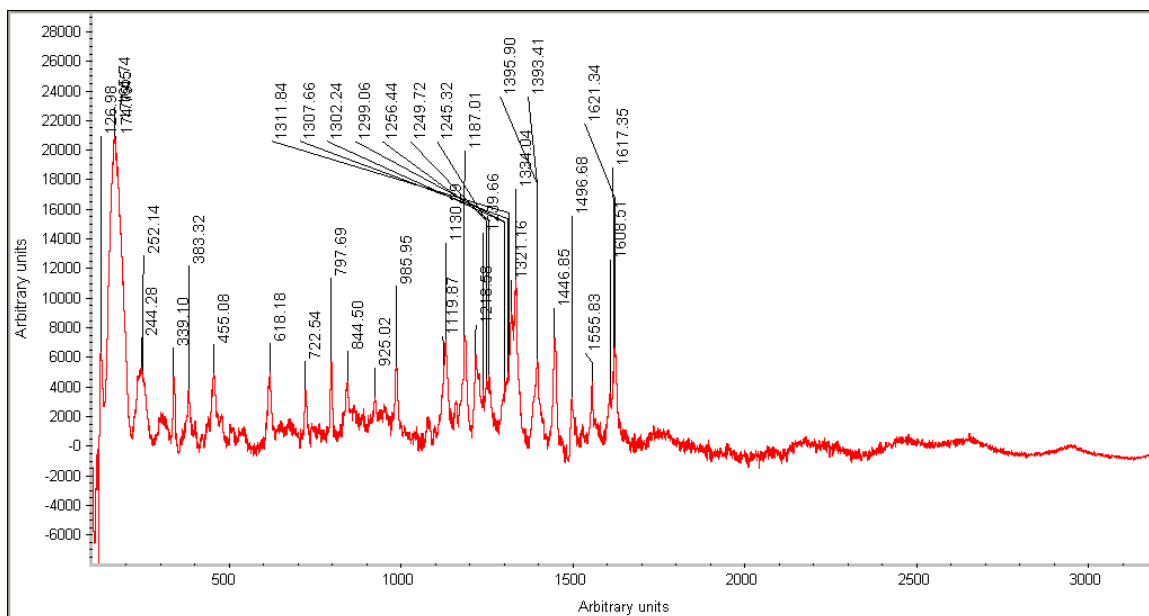
Figure 3.12: Raman spectrum of the red portion of Cheek, showing the numerous peaks associate with toluidine red.

3.1.8 Extender

XRF analysis of the Extender revealed the presence of a large amount of organic material, indicated by the almost complete lack of heavy inorganic elements in the XRF spectrum (**Figure 3.13**) as well as in the SEM-EDS. FT-IR analysis showed a large amount of linseed oil present, as well as a claylike material similar to alumina hydrate. SEM-EDS analysis showed the presence of a great deal of aluminum, carbon, phosphorous, and sodium, all of which were nearly homogenously dispersed in the mixture. The Raman spectrum of the Extender showed primarily the presence of linseed oil, with several unidentified peaks at 1024 cm^{-1}, 974 cm^{-1}, and 1268 cm^{-1}. These peaks (**Figure 3.14**) may be indicative of the clay filler material, though this assignment is speculative.

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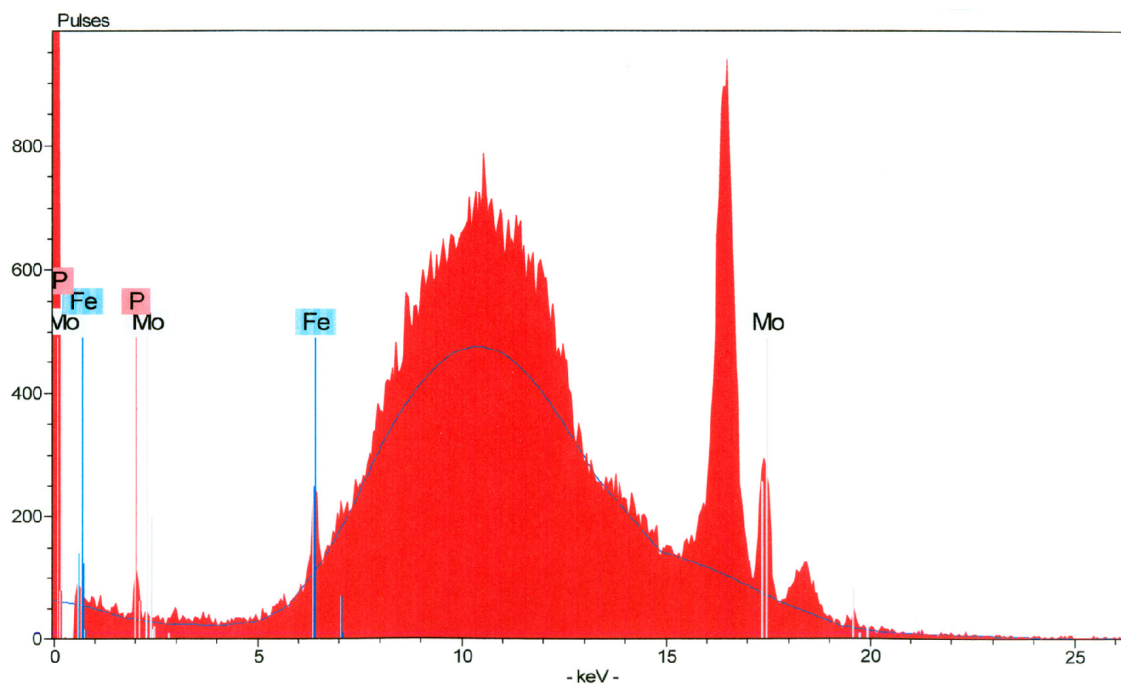
Figure 3.13: XRF spectrum of the paint Extender.
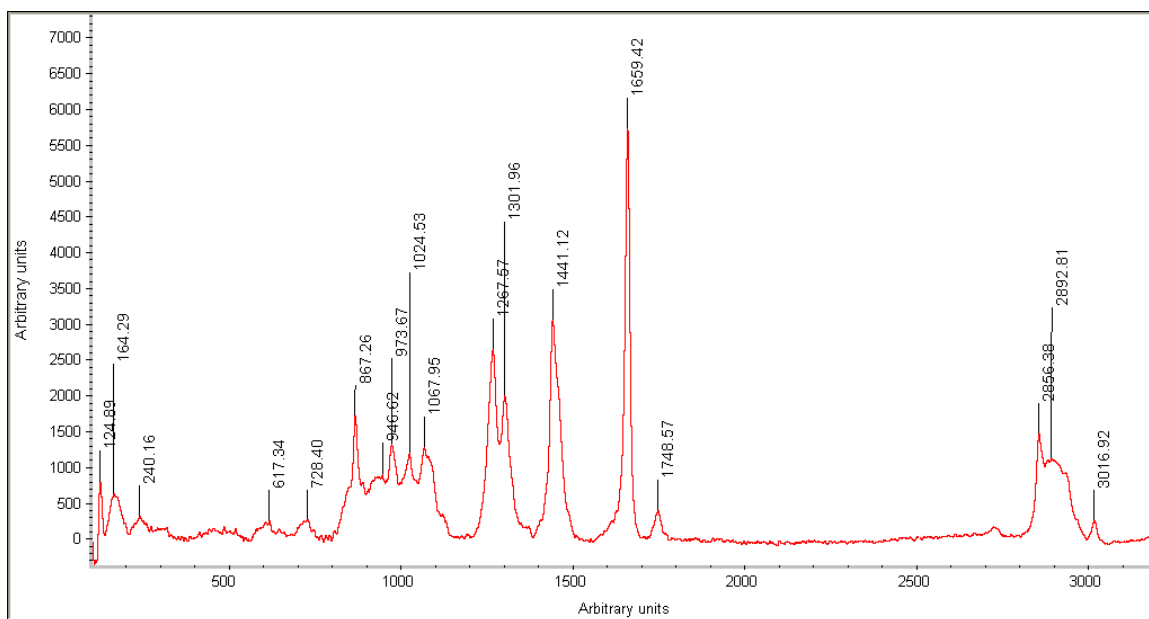
Figure 3.14: Raman spectrum of Extender, showing linseed oil and unidentified peaks.

3.1.9 Flesh No. 2

XRF analysis of Flesh No. 2 showed a large amount of iron present in the sample, as well as smaller amounts of manganese, calcium, and lead. FT-IR analysis showed the presence of red iron oxide as well as linseed oil. Raman analysis showed this red iron oxide to be hematite. SEM-EDS analysis of the paint showed a distinct separation of the areas of carbon, likely representing the linseed oil binder, from the iron particles. Unlike the other iron-based pigments, Flesh No. 2 showed distinct conglomerations of sodium, phosphorous, calcium, and sulfur, in addition to silicon. The sodium and sulfur conglomerations (**Figure 3.15**) seemed to be correlated with one another, possibly indicating the presence of sodium sulfate or a similar material.
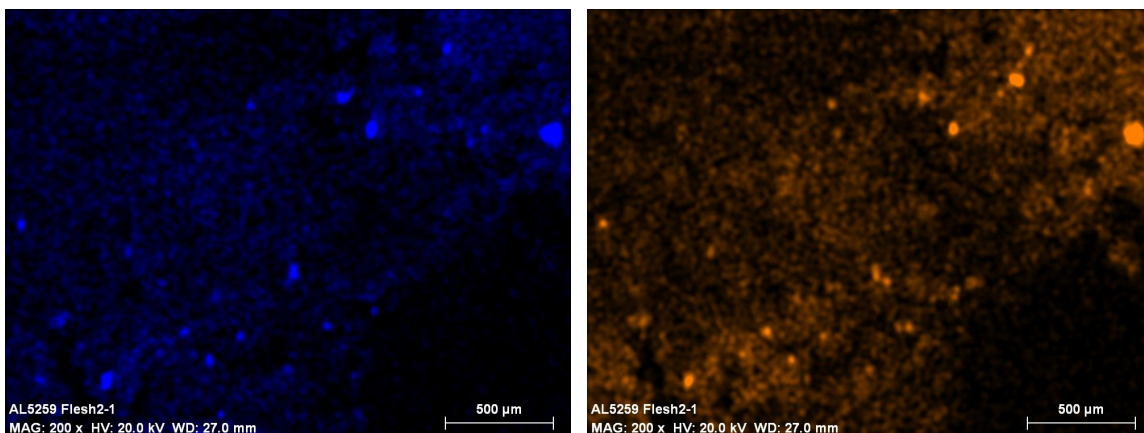
Figure 3.15: SEM map of sodium (left) and sulfur (right) in the paint Flesh No. 2.

3.1.10 Oxide Green

XRF analysis of this paint showed an abundance of lead and chromium in the sample, as well as iron. The source of these elements was revealed by the FT-IR spectrum, which showed the presence of both chrome yellow and Prussian blue in the mixture. This mixture, commonly known as Chrome Green or Cinnabar Green (PG 15),

was once one of the most widely-used green pigments until lead was banned from use in most paints and pigments.[3] The presence of both pigments was confirmed with Raman spectroscopy. SEM-EDS showed a homogenous mixture of these elements with the elements found in the clay filler. This latter result is not altogether surprising, given that the pigment was usually mixed wet with a slurry of the Prussian blue added to a mixture of the chrome yellow and China clay, producing a very homogenous mixture.[4]

3.1.11 Carmine

XRF spectroscopy showed a preponderance of iron in the Carmine sample, as well as barium, calcium, and lead. FT-IR analysis revealed the presence of alizarin crimson (PR 83), confirming what was stated in Marshall's *Photo-Oil Coloring for Fun or Profit* about the paint, as well as linseed oil. This lake pigment, 1,2-dihydroxyanthraquinone, can be deposited on a variety of bases, which may explain the presence of calcium and barium in the XRF spectrum if these were used in mineral form as the base for the alizarin. Raman spectroscopy confirmed the presence of alizarin crimson in the paint. SEM-EDS analysis showed a relatively homogenous mixture of aluminum, iron, barium sodium, phosphorous, silicon, and calcium. Areas of calcium and sulfur appear to correlate more than other areas, which may indicate the presence of calcium sulfate (gypsum) filler or a related material for the pigment (**Figure 3.16**).
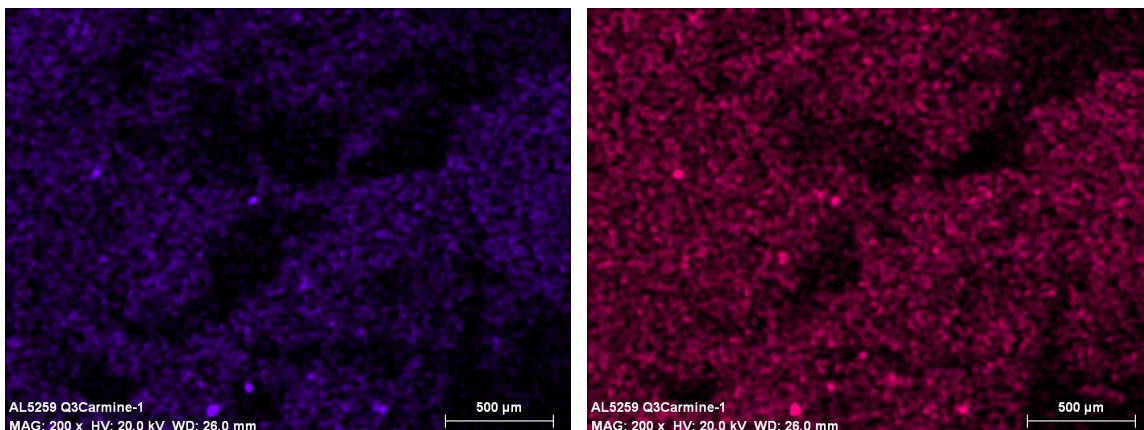
Figure 3.16: SEM map of sulfur (left) and calcium (right) in Carmine sample.

3.1.12 Flesh

XRF of the Flesh found in the ca. 1939 kit revealed several similarities with that found in the ca. 1950 set; iron was the predominant element, while some lead was present as well as traces of other transition elements. FT-IR spectroscopy also found red iron oxide, which was confirmed as hematite by Raman spectroscopy.

3.1.13 P. M. Solution

A sample of P.M. solution was pipetted onto a thin card of polytetrafluoroethylene (PTFE) and a spectrum collected before the solvent had a chance to fully evaporate. In the resultant spectrum both turpentine as well as linseed oil were identified. That the turpentine was the likely solvent for the solution was further supported when the FT-IR spectrum of a sample of the dried solution showed only linseed oil to be present (**Figure 3.18**). GC-Mass Spectrometry showed the presence of α-pinene, a turpene commonly found in turpentine (**Figure 3.17**).
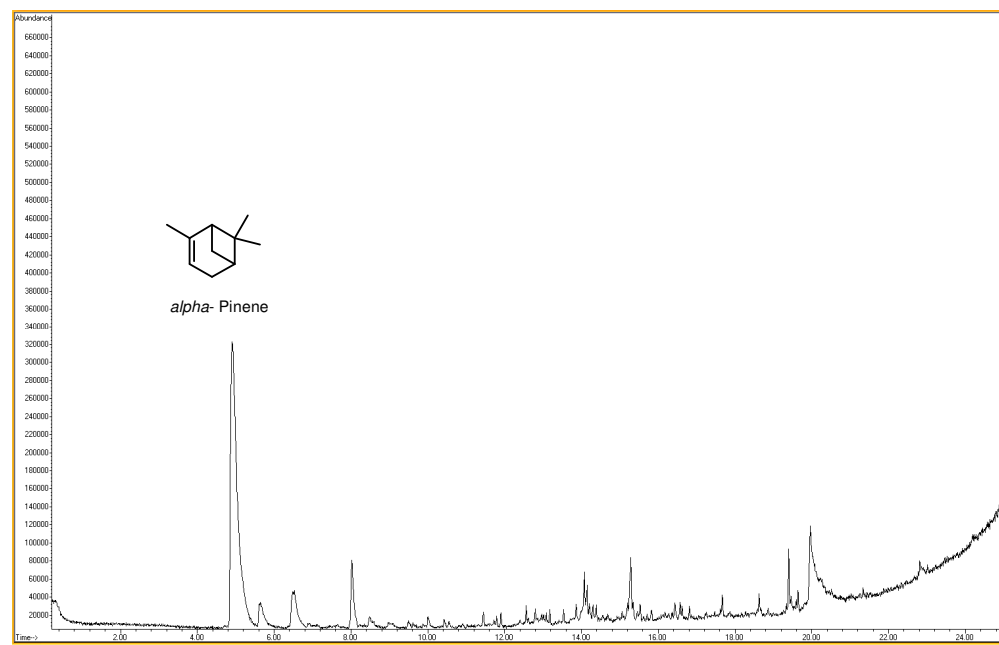
Figure 3.17: GC-MS spectrum of the P.M. Solution showing high percentage of α-Pinene from the turpentine solvent.
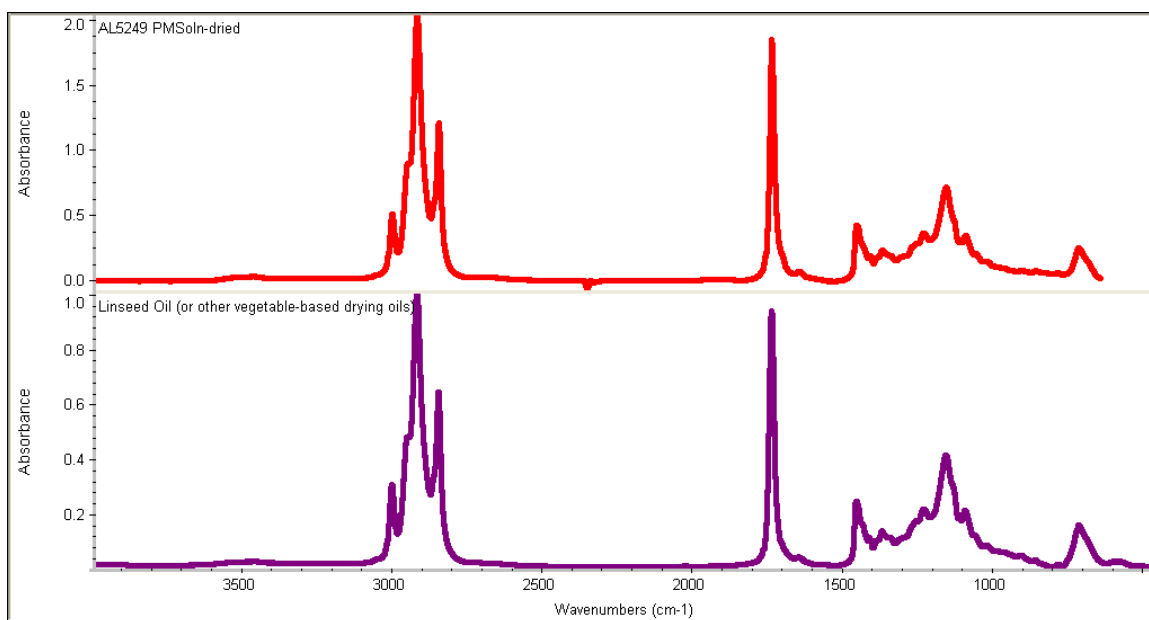
Figure 3.18: FT-IR spectrum of dried P.M. Solution (top) and the FT-IR spectrum of linseed oil (bottom).

3.1.14 Paint Binder

FT-IR spectroscopy of each of the paints showed the presence of linseed oil. This identification is supported by the collected Raman spectra, which found evidence of linseed oil in the paints Raw Sienna, both samples of Flesh, Cadmium Yellow, Flesh No. 2, and Oxide Green. The Raman spectra of the paint Extender (**Figure 3.19**) and the P.M. Solution (**Figure 3.20**) showed a large amount of the substance in both cases, with peaks around the reference library peaks for linseed oil at 865 cm^{-1}, 1076 cm^{-1}, 1302 cm^{-1}, 1443 cm^{-1}, 1658 cm^{-1}, 1744 cm^{-1}, and 2855 cm^{-1}.

GC-mass spectrometry revealed a number of plant sterols present in each of the samples tested as well as in the P.M. Solution, including 3,5-tigmastadiene, campesterol, sitosterol, cycloartenol, and 24-methylenecylcoartenol (**Figure 3.21**). Such sterols are found in linseed oil and their presence confirms the use of the oil medium as a binder.
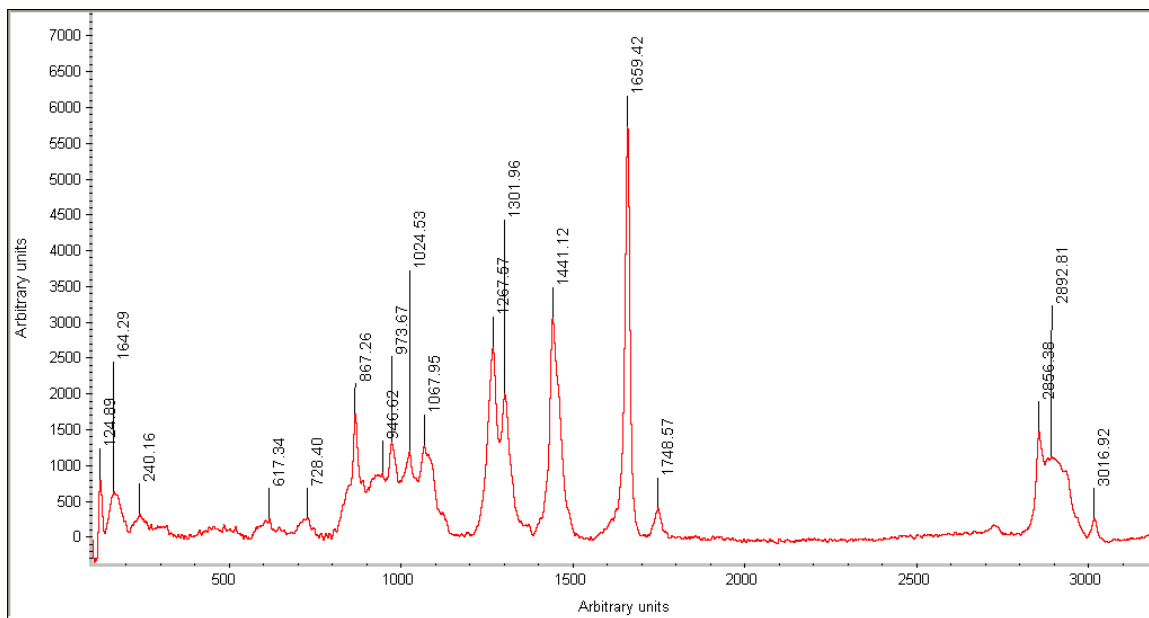
Figure 3.19: Raman spectrum of the paint Extender.
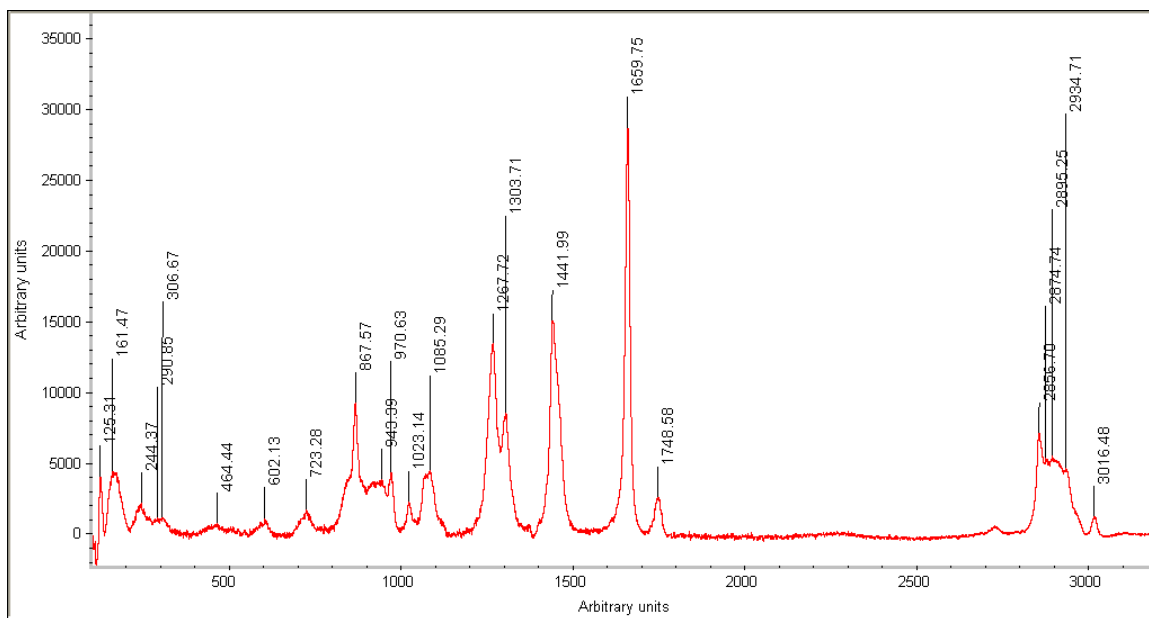
Figure 3.20: Raman spectrum of the P.M. Solution.
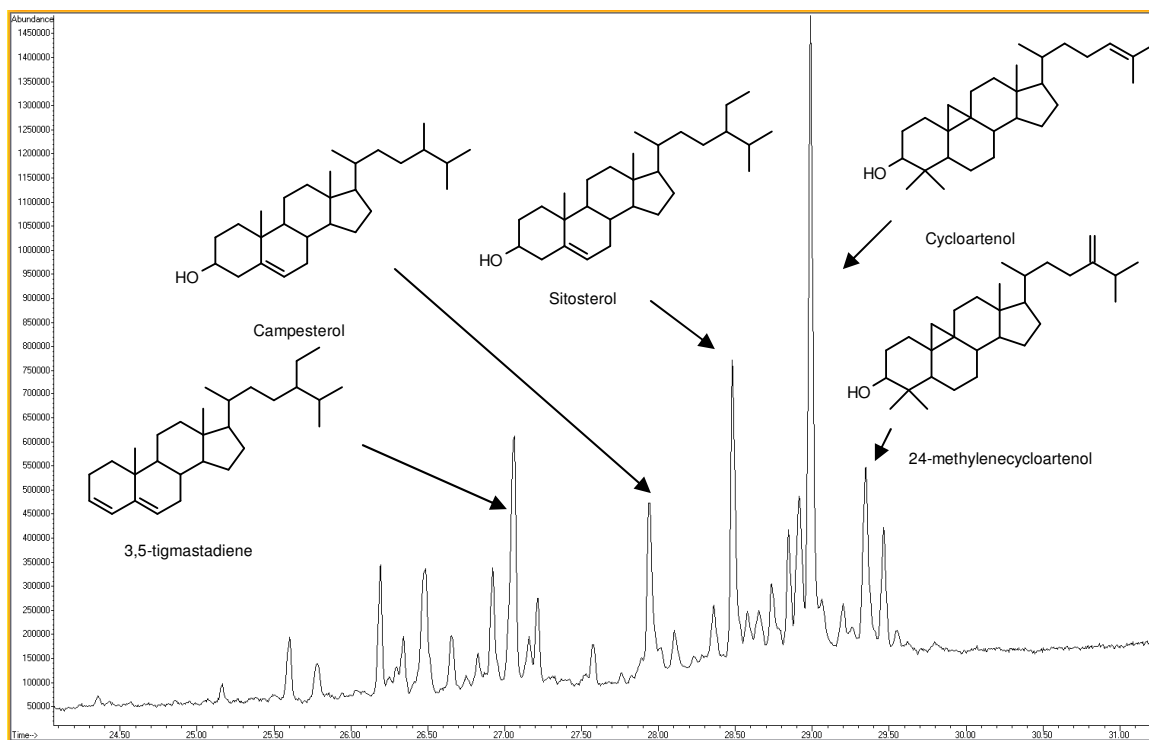
Figure 3.21: Mass spectrum of the oil medium, showing sterol content.

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3.1.15 Paint Filler used in Marshall's Photo-Oils

Paints consist not only of a pigment in a medium such as linseed oil, but also of a filling material that bulks up the paint and gives it a greater volume. As stated in the introduction (**Chapter 1.4**), what is known about the filler is that it is much more finely ground than in other artists' paints, and little else. Noting that, several conclusions can be drawn from the spectra collected of the paints in the kits.

In each of the paints examined, the elements sodium, phosphorous, aluminum, oxygen and carbon were found via SEM-EDS. In each case, aluminum, sodium, and phosphorous showed a strong correlation with one another. The carbon and oxygen similarly showed a correlation, though whether this is due to the presence of the linseed oil binder or another material such as a carbonate cannot be determine through these techniques. In the case of eight paints—Raw Sienna, Verona Brown, Chinese Blue, Cadmium Yellow, Cheek, Flesh No. 2, Carmine, and Flesh—calcium was found, with conglomerations of the element found in Verona Brown (**Figure 3.7**). Silicon was also found in all paints except Viridian, Cadmium Yellow, Cheek, and Oxide Green, with particulate silicon found in the paints with iron oxide-based pigments. The distribution of the elements within the paints suggests their use as a filling material.

FT-IR spectroscopy elucidated this relationship further, providing a library match for sodium carbonate in Viridian, Halloysite ($Al_2Si_2O_5(OH)_4$) in Flesh, calcined kaolin clay, another aluminum silicate clay, in Chinese Blue, montmorillonite in Cadmium yellow, and alumina hydrate ($Al(OH)_3$) in Extender. It should be noted that each of these claylike materials (with the exception of sodium carbonate) has a large, broad peak around 1100 cm^{-1}, and that a similar peak was observed in every paint not listed previously. Despite the similarities, the identity of the filler could not be determined from these spectroscopic techniques. It is speculated that it is a sodium and/or

aluminum phosphate and/or carbonate mineral, with some instances of silicon or silicates in some paints. It must be noted that the same filler material may not be used in all of the paints analyzed.

3.2 Spectroscopic Analysis of Marshall's Photo-Oils Painted on Photographic Bases

After reviewing the data obtained with each spectroscopic technique for the samples of paint, it was decided to focus upon non-destructive methods for analysis of hand-colored photographs. XRF and Raman were the primary methods utilized, while diffuse reflectance FT-IR was also attempted. SEM-EDS, GC-Mass Spectrometry, and absorbance FT-IR were decided against due to their need for sampling. Areas of concentrated paint were selected for analysis, as it was thought they would yield the best results as they would have more sample present.

3.2.1 "Alice"

3.2.1.1 Unpainted Background

In order to gauge the effectiveness of the various spectroscopic techniques, a spectrum of the white, unpainted background was first collected. In "Alice", a spot was chosen on the recto of the photograph outside the photographic image area. XRF analysis showed the predominance of barium in the sample as well as some sulfur, likely owed to the presence of a baryrta ($BaSO_4$) layer of whitening. Strontium was also found, which is a common minor component in baryta. Trace amounts of iron were also found, which may be owed to the water used in the production of the paper or in the developing process. Raman spectroscopy showed the predominance of the white pigment barium sulfate, from the baryta layer.

3.2.1.2 Chinese Blue

For XRF analysis of the blue paint used on "Alice", a concentrated area of the paint near the edge of the image border was selected. As in the white background, a predominance of barium and sulfur was detected, as well as strontium. A much greater amount of iron than was present in the background was also detected.

Reflectance FT-IR spectroscopy of the blue paint immediately made it apparent that some peaks were in the range that must be corrected by the Kramers-Kronig transform. These areas were noted and the transformation applied. Matching library spectra to this spectrum showed that the presence of the gelatin layer could be detected, as could the baryta layer (**Figure 3.22**). Most importantly, however, the distinct peak of Prussian blue was readily observed (**Figure 3.23**). Raman spectroscopy confirmed this result, detecting the distinctive peaks of Prussian blue as well as the baryta layer.
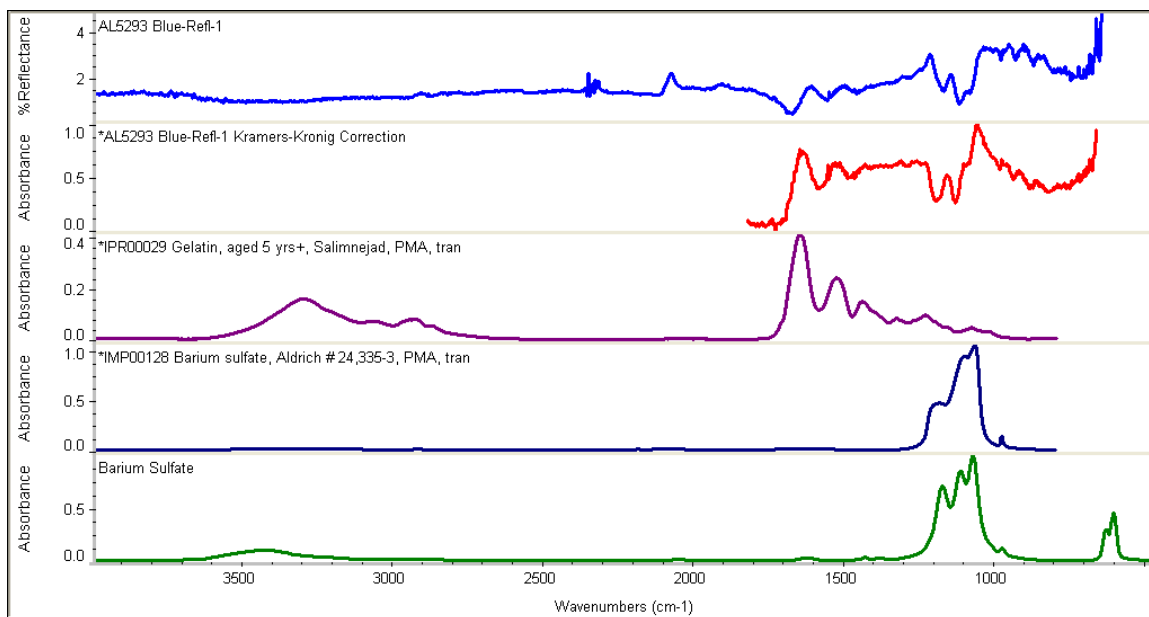
Figure 3.22: The reflectance FT-IR spectrum of the blue paint on "Alice," showing the Kramers-Kronig corrected area (red) and the matched materials.
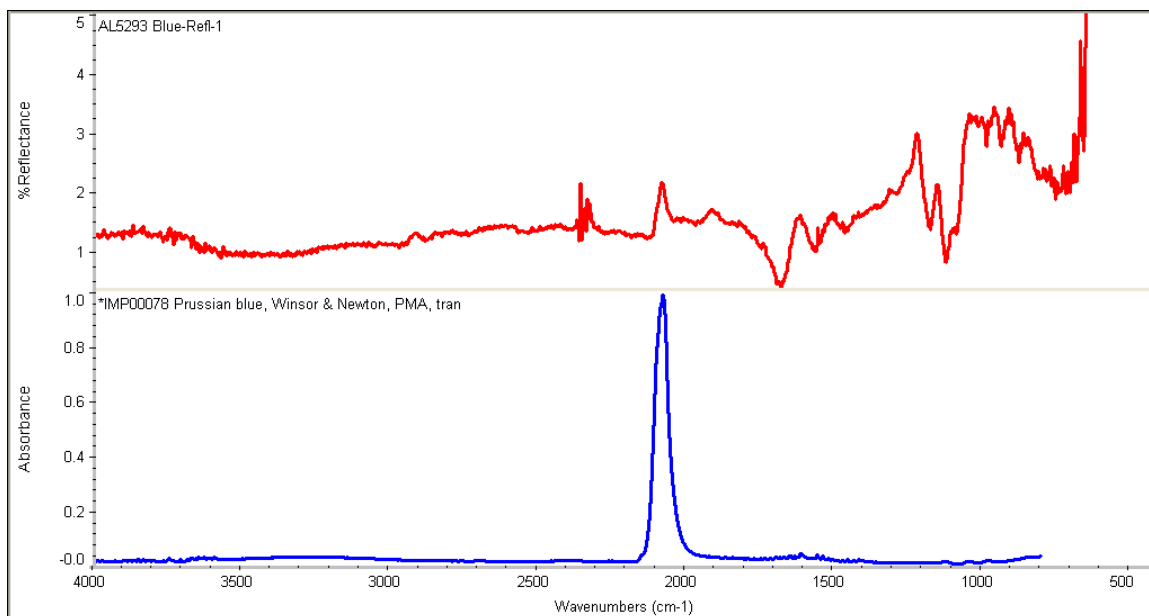
Figure 3.23: FT-IR spectrum of the blue paint on "Alice" (top) showing the spectrum of Prussian blue (bottom).

3.2.1.3 Viridian

For XRF analysis of the painted green background, an area of paint concentrated in a crack in the gelatin of the image area was analyzed. As in the Case of the Chinese Blue, barium, sulfur, and strontium were the elements found in the greatest quantity. Copper was also detected, albeit a trace amount. FT-IR spectroscopy showed evidence of the presence of copper phthalocyanine green (**Figure 3.24**), though whether this would be detected without prior knowledge of its presence seems doubtful, owing to the almost undetectable amounts of the materials observed with this technique. Applying the Kramers-Kronig correction to the curve revealed that the presence of the gelatin layer, represented in **Figure 3.24** by cow hide glue drops, was also found, as was the baryrta layer.

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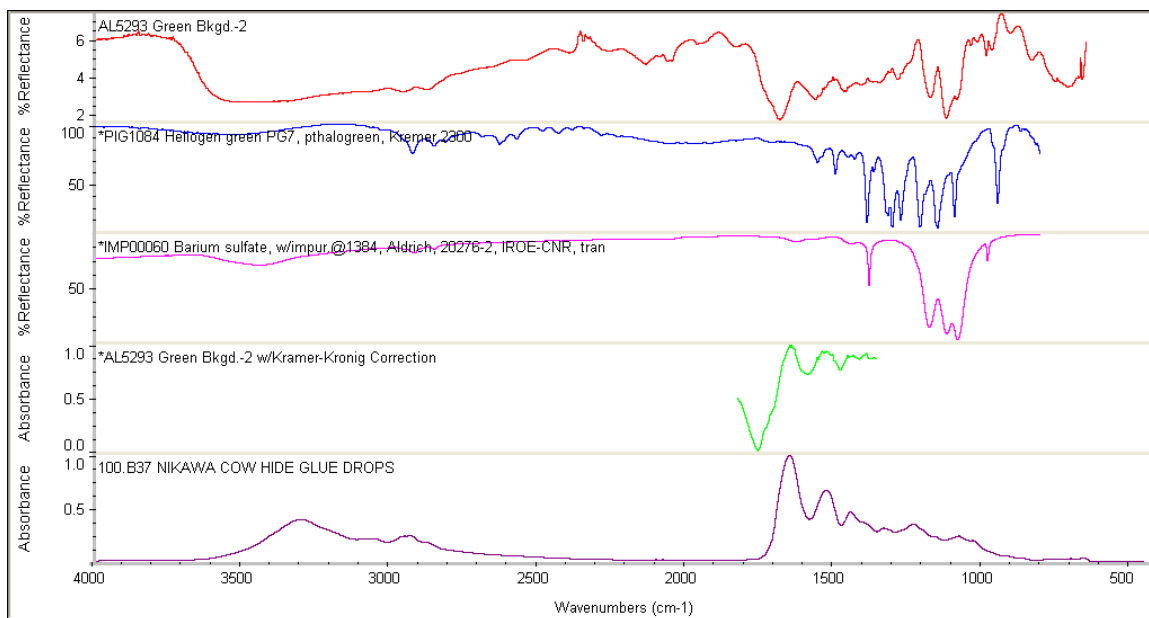
Figure 3.24: Reflectance FT-IR spectrum of the paint Viridian on the "Alice".

While reflectance FT-IR did not show much evidence of the presence of the copper phthalocyanine green pigment, Raman spectroscopy showed its presence quite clearly, with peaks at 164.8 cm^{-1}, 233.7 cm^{-1}, 685.3 cm^{-1}, 740.8 cm^{-1}, 777.0 cm^{-1}, 817.9 cm^{-1}, 1214.9 cm^{-1}, 1283.8 cm^{-1}, 1339.8 cm^{-1}, 1392.5 cm^{-1}, 1508.1 cm^{-1}, and 1539.6 cm^{-1}. Barium sulfate peaks were also identified at 461.3 cm^{-1}, 616.8 cm^{-1}, 644.3 cm^{-1}, and 989.0 cm^{-1} (**Figure 3.25**).
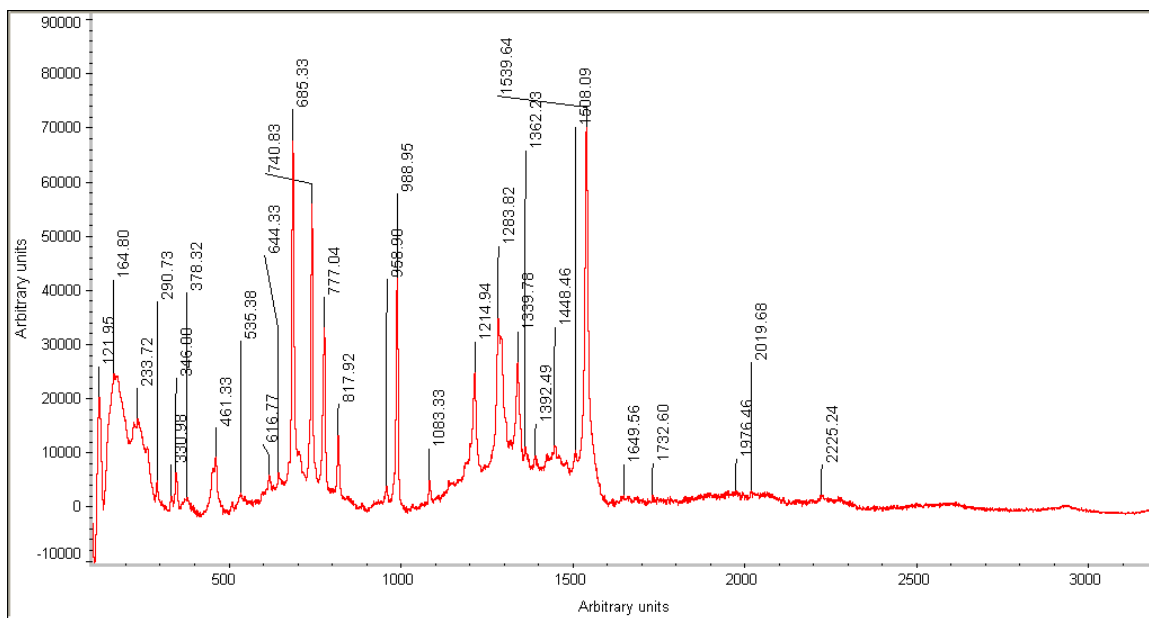
Figure 3.25: Raman spectrum of the green background area on "Alice".

3.2.1.4 Verona Brown

XRF spectroscopy of an area of the brown hair painted Verona Brown revealed an abundance of iron, in addition to the expected barium, sulfur, and strontium. Trace amounts of silver were also found. Reflectance FT-IR, however, proved difficult, as it was determined that the peaks for the iron pigment overlapped with the peaks for the gelatin layer (**Figure 3.26**) and because of the low amount of IR radiation that was refelected from the dark surface. As a result, not much could be gained from this spectrum; neither was the Raman spectrum any more enlightening, as only the largest peak for barium sulfate could be detected; no peaks for hematite could be found (**Figure 3.27**). While XRF spectroscopy did show the presence of an iron-based pigment in this case, little about that pigment could be discerned from the spectroscopic techniques performed.

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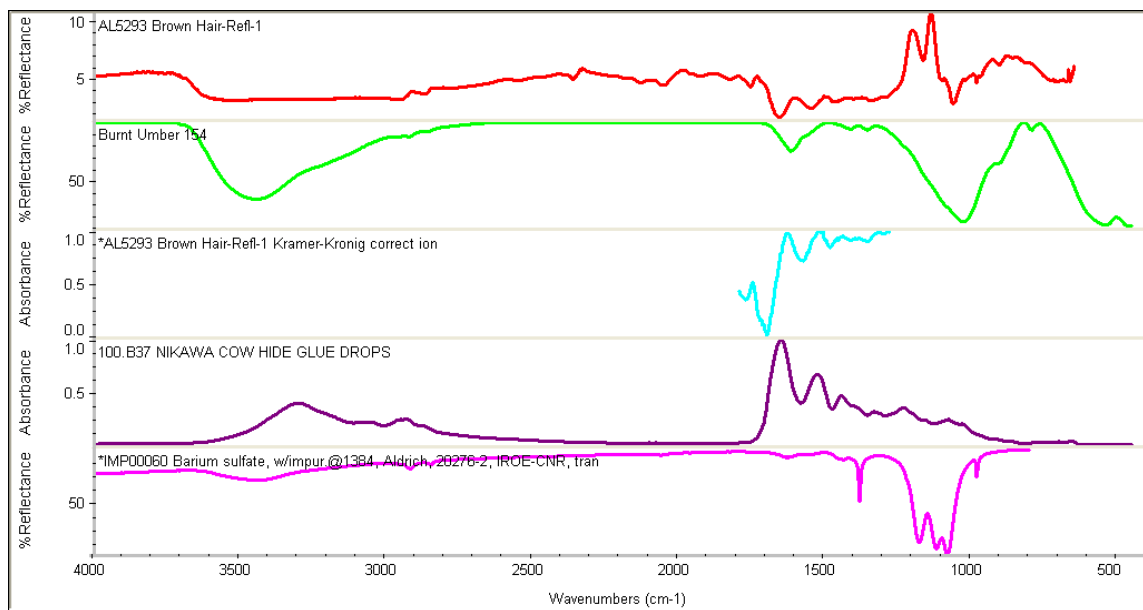
Figure 3.26: Reflectance FT-IR spectrum of "Alice's" painted with Verona Brown (top), showing matches, burnt umber in green, the brown-hair with the Kramers-Kronig transformation in cyan, cow hide glue drops (gelatin) in purple, and barium sulfate in magenta.
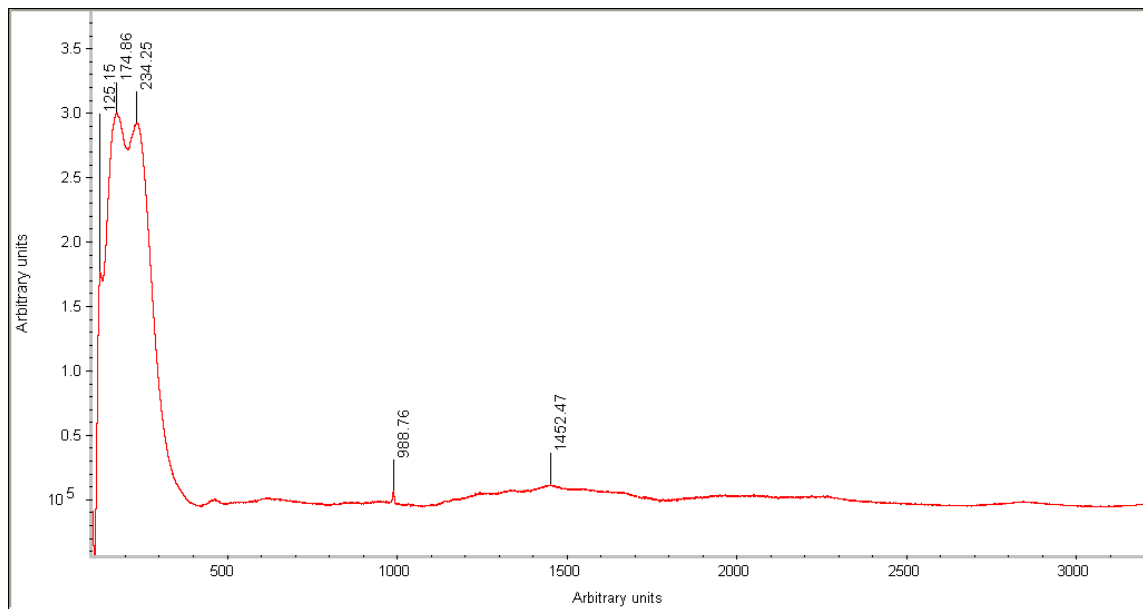
Figure 3.27: Raman spectrum of "Alice's" brown hair. Note the $BaSO_4$ peak at 988.8 cm^{-1}.

3.2.1.5 Flesh

XRF spectroscopy of a small patch of the red Flesh paint used on "Alice's" face below and to the right of her mouth revealed a very high concentration of iron, as well as the expected barium, sulfur, and strontium. Reflectance FT-IR spectroscopy was of little aid in this case, as interfering peaks made identifications of most materials virtually impossible. As in the case of Verona Brown, Raman spectroscopy revealed only the presence of barium sulfate, without a trace of iron to be found.

3.2.1.6 Carmine

XRF spectroscopy of an area of Carmine on "Alice's" lips showed the presence of a small amount of iron, as well as the expected barium, sulfur, and strontium. The reflectance FT-IR spectrum of this area showed only a hint of the presence of alizarin crimson; it is unlikely that its presence would have been detected if its presence was not already known. Raman spectroscopy did not indicate the presence of the lake pigment, only barium sulfate.

3.2.2 "Ed"

3.2.2.1 Unpainted Background

XRF spectroscopy of an area of the recto of "Ed" outside of the image area showed a preponderance of barium, sulfur and strontium in the sample, as well as a small amount of iron. Raman spectroscopy revealed the source of the barium and sulfur in the sample: barium sulfate, from the baryta layer. As in "Alice", Ed likely has a baryta whitening layer coating the paper below the gelatin binder and image material. In the unpainted gray background in the image area, a large, broad peak was observed at 228.7 cm^{-1}; because this peak was also found in other areas of the image where concentrations

of metallic silver were high, and not in the background or other white areas, it is surmised that it relates to the presence of silver.

3.2.2.2 Green Uniform

An XRF spectrum of "Ed's" green uniform, painted with a mixture of Oxide Green, Viridian, and Verona Brown, showed the presence of a quantity of iron, lead, and trace amounts of copper and chlorine, as well as large amounts of barium, sulfur, and strontium. FT-IR spectroscopy was not performed on this sample. Raman spectroscopy (**Figure 3.28**) showed the presence of barium sulfate as well as calcium sulfate (gypsum), with peaks at 1010.9 cm^{-1} and 1132.2 cm^{-1}. The gypsum was likely used as a white filling material in the photographic paper. Three peaks at 684.4 cm^{-1}, 1535.9 cm^{-1}, and 1562.1 cm^{-1} may be several peaks of copper phthalocyanine, but these were too weak to make a positive identification. Several distinct peaks at 711.1 cm^{-1}, 1275.7 cm^{-1}, 1396.29 cm^{-1}, 1455.0 cm^{-1}, and 1585.6 cm^{-1} could not be correlated with any material in the Raman reference libraries. However, no traces of any other pigment could be found.
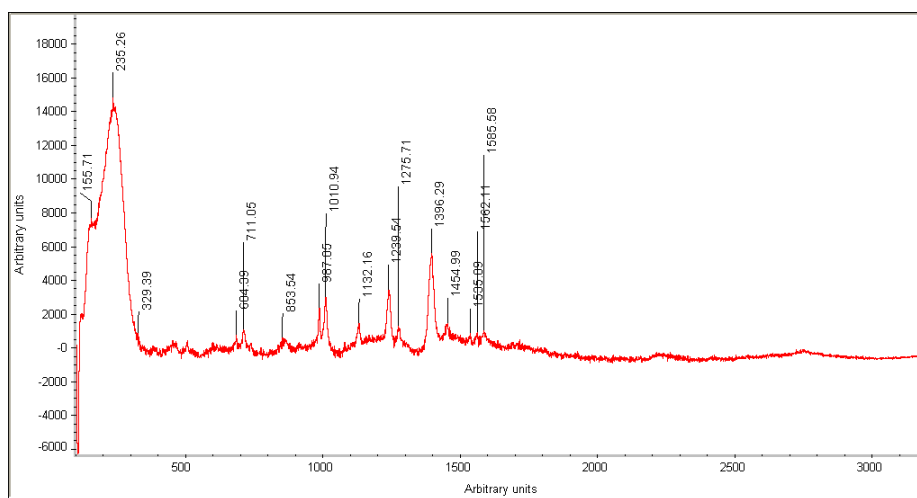
Figure 3.28: Raman spectrum of the green painted uniform on "Ed".

3.2.2.3 Brass Button

XRF analysis of one of the brass buttons of "Ed's" uniform, colored with Cadmium Yellow and Raw Sienna, showed a greater amount of iron than in the background, as well as a significant amount of lead, in addition to the expected barium, sulfur, and strontium. The presence of lead, but not chromium, was surprising, as the pigment lead chromate formed the basis of the yellow color; it may be that the area focused on had too little of the pigment present to get a suitable reading. Some evidence of silver was also found. Raman spectroscopy showed the presence of a barium sulfate from the baryta as well as two peaks at 357.8 cm^{-1} and at 840.0 cm^{-1} (**Figure 3.29**). The latter peaks are near the Raman shift values, the two strongest peaks found by Raman spectroscopy of the lead chromate pigment (**Figure 3.30**), and their presence in the spectrum of the painted button is indicative of that pigment's presence in the paint mixture. Taken together with the XRF spectrum, it is possible that the iron-lead chromate mixture could be identified without prior knowledge of its presence. However, additional study with other techniques would be warranted to confirm that conclusion.
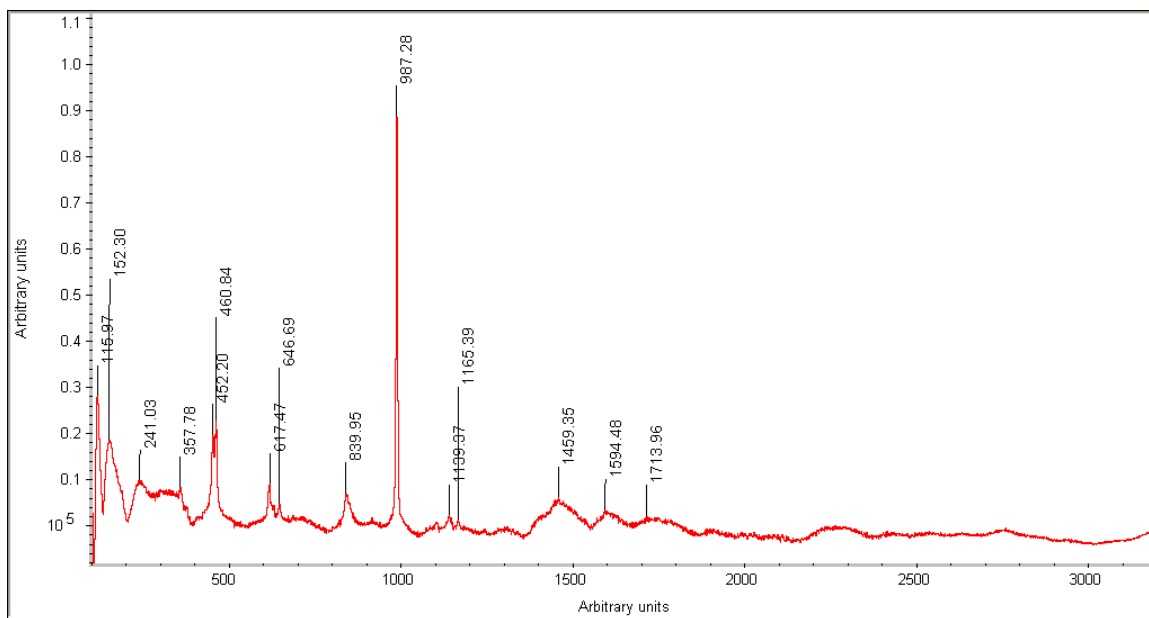
Figure 3.29: Raman spectrum of the gold-colored buttons on "Ed's" uniform, showing barium sulfate and lead chromate peaks.
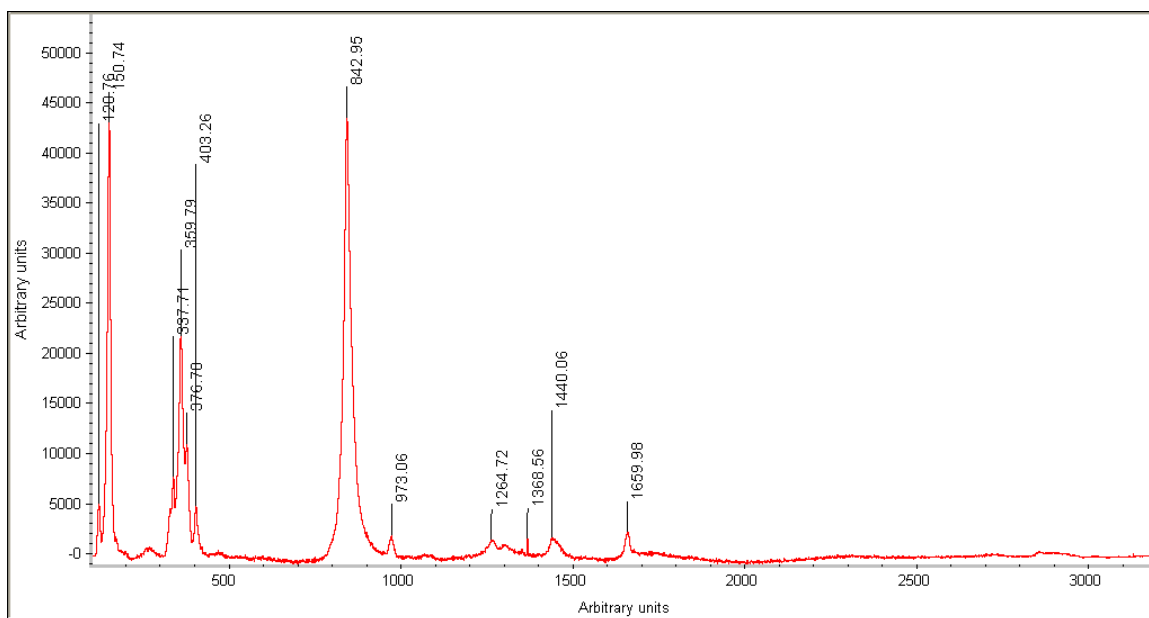
Figure 3.30: Raman spectrum of the paint Cadmium Yellow, showing strong peaks for the pigment lead chromate.

3.2.2.4 Red Patch

The red portion of "Ed's" 14th Armored Division unit patch, colored with Carmine, was examined first with reflectance FT-IR spectroscopy. The collected spectrum showed little relevant information, as the area was largely opaque and provided little reflectance. The spectrum showed hints of the presence of alizarin crimson, the pigment in the paint, though it is the opinion of the author that it would not be noticed if one was not looking specifically for it. Raman spectroscopy, however, proved more fruitful, showing the presence of alizarin as well as gypsum (from the paper support) as well as Prussian blue; the presence of the latter pigment is likely owed to the method in which the patch was painted, and it is likely that some mixing of the Carmine with the paint Chinese Blue occurred during painting. A number of other peaks that could not be correlated to any material, similar to those found in the analysis of the green uniform, were also found.

3.2.2.5 Blue Patch

Raman spectroscopy of the area of "Ed's" unit patch that was painted with Chinese Blue showed the presence of Prussian blue, as well as barium sulfate and gypsum. As in the last analysis, distinct peaks of unknown cause were also noted in the spectrum.

3.2.2.6 Brown Hat Brim

XRF spectroscopy of the brown brim of "Ed's" cap, colored with Verona Brown showed an abundance of iron, as well as some lead, silver, and a large amount of barium, sulfur, and strontium. The presence of lead is likely owed to the lead chromate-containing Oxide Green paint which may have gotten mixed in this area. Raman

spectroscopy showed the presence of both barium sulfate and calcium sulfate as well as a number of unidentifiable peaks. No traces of iron pigments could be found.

3.2.2.7 Tan Tie

"Ed's" tan colored tie, painted with a mixture of Cadmium Yellow, Flesh, Raw Sienna, and Verona Brown, showed an abundance of iron as well as trace amounts of lead and other materials with XRF spectroscopy. As expected, a great amount of barium, sulfur, and strontium was also found. Raman spectroscopy showed the presence of barium sulfate only as well as a large grouping of unidentified peaks (**Figure 3.31**); no traces of either the iron pigments or the lead chromate pigment were observed.
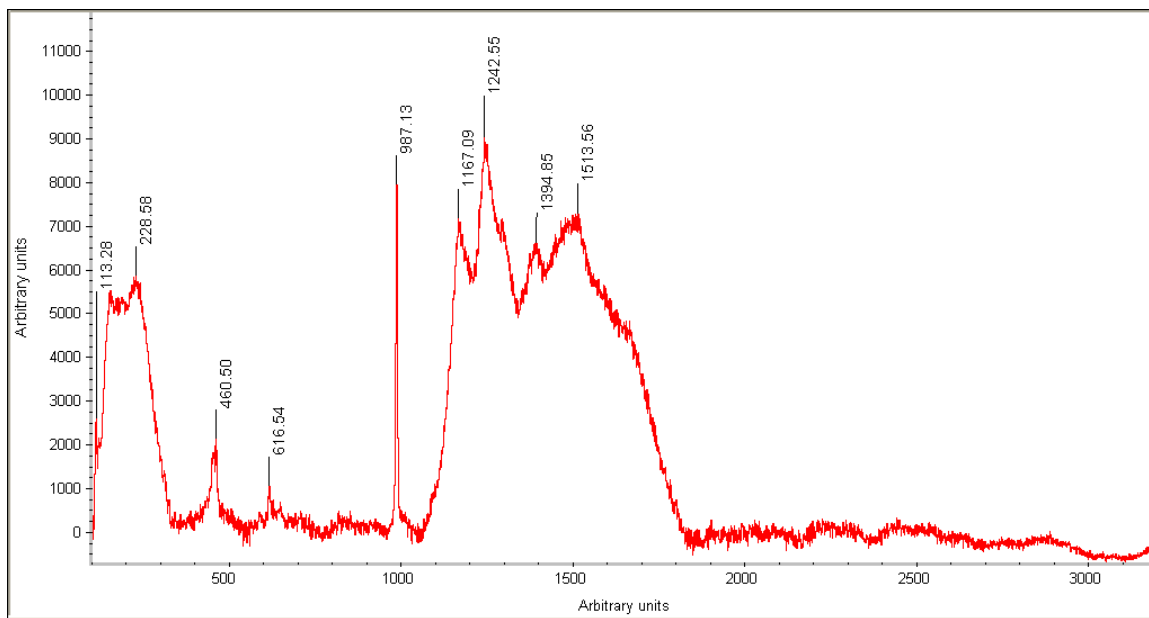
Figure 3.31: Raman spectrum of the tan-colored tie on "Ed".

3.2.2.8 Flesh and Lips

XRF spectroscopy of Ed's flesh, painted with Flesh No. 2, and his lips, painted with Carmine, showed the presence of iron, as well as the expected barium, sulfur, and strontium. Raman analysis showed only the presence of barium sulfate; no traces of alizarin crimson or any iron oxide pigment were observed.

3.3   Spectroscopic Analysis of Hand-Painted Photographs with Unknown Coloring Media

3.3.1 Stereoview of the Apollo Commandery

3.3.1.1 Red

XRF spectroscopy of the red painted areas showed an abundance of iron, though this was thought to be due to its presence in the paper support and not indicative of an iron-based pigment. Trace amounts of lead, zinc, gold, silver, chromium, barium, calcium, and zirconium were also found. A small area of the photographic surface was sampled using a scalpel for reflectance FT-IR spectroscopy, which showed the presence of cellulosic fibers (from the paper photographic base), albumen (from the photographic binder), and kaolin—likely used as a whitening layer in the photographic paper. No trace of pigment was found. Raman spectroscopy produced a spectrum with a number of broad and not well-defined peaks. Several peaks at 379.5 cm^{-1}, 440.7 cm^{-1}, 458.2 cm^{-1}, 1097.6 cm^{-1}, 1127.1 cm^{-1}, 1153.8 cm^{-1}, 1341.6 cm^{-1}, and 1383.4 cm^{-1} were distinctly sharp, but they nevertheless could not be matched to any material—pigment or otherwise—in the reference libraries.

3.3.1.2 Blue

XRF spectroscopy of the blue painted area showed an almost identical elemental distribution as in the red colored area. An area of this blue colored area was similarly sampled and subjected to diffuse reflectance FT-IR spectroscopy, which, as was the case with the red pigment, only the presence of albumen, cellulose, and kaolin was detected. Raman spectroscopy showed a number of non-distinct and broad peaks, though peaks at 242.7 cm^{-1}, 3305.1 cm^{-1}, and 376.4 cm^{-1} were comparatively sharp. However, no material or pigment from the reference libraries could be correlated to any of these peaks.

3.3.2 Portrait of Seated Child Reading a Book

3.3.2.1 White

The presumably unpainted area of the child's skin was used as a gauge for comparison against areas with colorants. XRF spectroscopy showed a high amount of iron, present in the area, likely from the water used in the developing or manufacturing process of the photographic paper. Trace amounts of lead, zinc, and titanium were also found. Gold was also detected, and was likely used as a toning agent in the processing of the photographic image. Trace amounts of potassium, calcium, and copper were also found. Raman spectroscopy did not reveal any identifiable pigment materials.

3.3.2.2 Green

XRF spectroscopy of an area of concentrated green pigment on the pillow showed no major differences from the area of white, with the same elements found in almost the same proportions. A small area of the green was sampled by removing a tiny area of the gelatin binder containing green pigment with a scalpel. FT-IR spectroscopy of this sample showed the presence of cellulosic fibers, from the paper, as well as a protein

similar to cow hide glue drops—the gelatin binder. A mineral similar to albite
($NaAlSi_3O_8$) may also have been found; the latter identification may be due to a mineral
whitening layer in the photographic paper, such as kaolin or another sodium aluminum
silicate mineral. Raman spectroscopy produced a number of broad, nondistinct peaks that
could not be correlated to pigments in the reference libraries (**Figure 3.32**). It seems
probable that the green pigment used to color this photograph is a modern organic
dyestuff or other material that was not listed in the reference libraries.
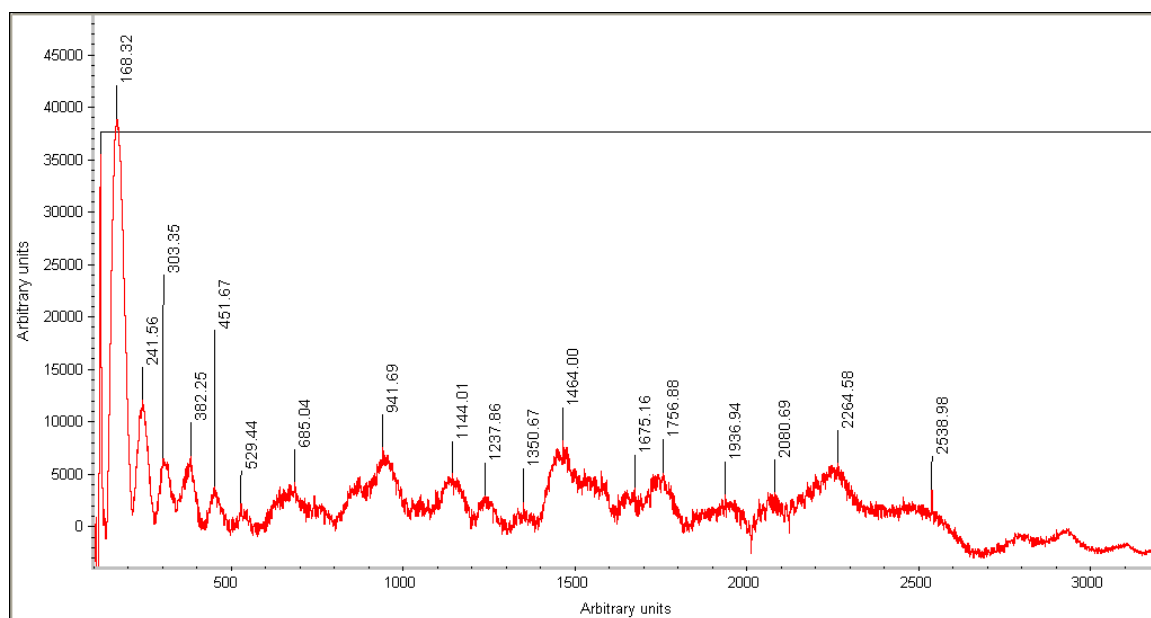
Figure 3.32: Raman spectrum of the green pigment on the seated child photograph.

3.3.2.3 Magenta

XRF spectroscopy showed a similar elemental distribution in this pigmented
area as in the two previous areas—indicating that an organic pigment was likely present.
Reflectance FT-IR spectroscopy did not reveal the identification of the pigment, only the

presence of cellulose and gelatin. Raman spectroscopy showed the presence of a number of broad peaks which could not be correlated to reference materials.

3.3.2.4 Yellow

XRF spectroscopy showed a nearly identical elemental distribution as in the other areas of the photograph, indicating the presence of an organic pigment. Raman spectroscopy did not show the presence of any identifiable material.

3.3.3 Ca. 1930 Silver Gelatin Print

3.3.3.1 Unpainted Background

XRF spectroscopy of unpainted background around the edge of the photograph showed an abundance of barium in the sample, as well as calcium, strontium, and sulfur. These elements in all likelihood formed the baryta layer with strontium present as a minor component in the layer.

3.3.3.2 Yellow

XRF spectroscopy of a yellow-painted flower showed a significant amount of barium, calcium, sulfur, and strontium. A significant amount of iron was also found, but this is likely due to a red iron-based pigment that was mixed in around the sample area (**Figure 3.33**). Because no trace of lead, chromium, or other components of inorganic yellow pigments were found, it was assumed that an organic pigment was present. Raman spectroscopy confirmed this hypothesis, finding on another area painted with the same yellow color a mixture of the pigments Hansa red, the same pigment used in Marshall's Cheek, and Hansa yellow (PY 3). It is speculated that this paint may be Marshall's Cadmium Yellow Deep paint (refer to **Figure 3.34**), although this conclusion would have to necessarily be confirmed by analyzing a period sample of that paint.
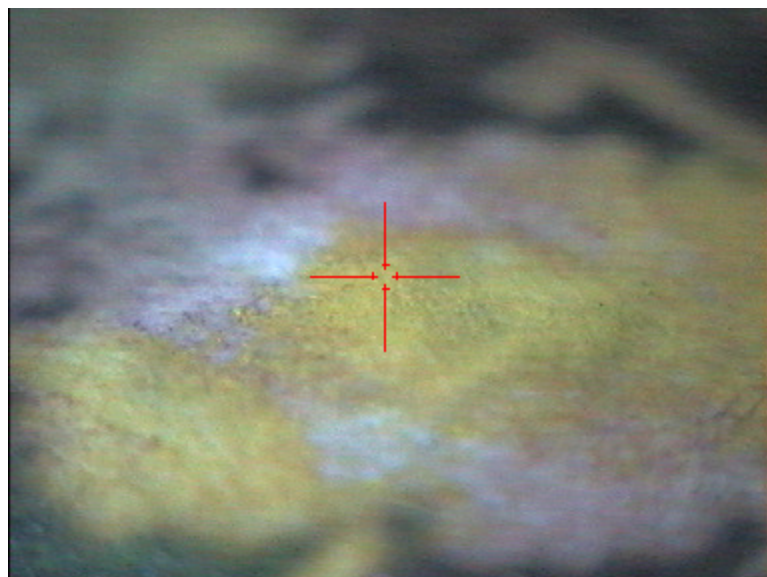
Figure 3.33: Yellow flower analyzed with XRF. Note the presence of the red pigment around the sample area.
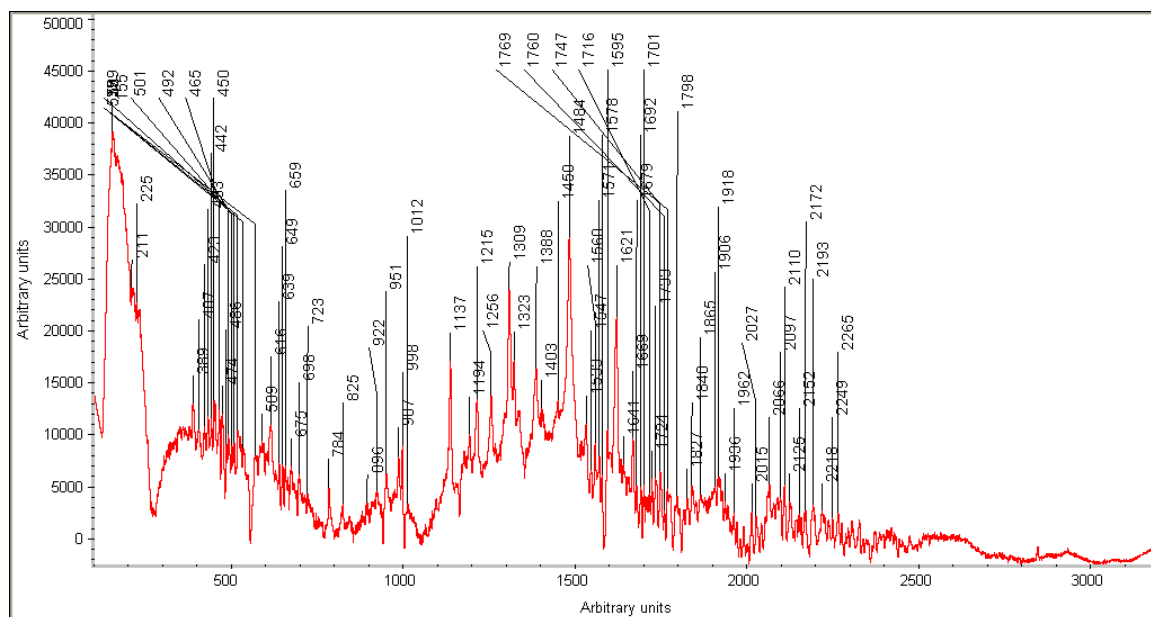
Figure 3.34: Raman Spectrum of the yellow paint on the ca. 1930 silver gelatin print, showing numerous peaks from Hansa red and Hansa yellow, as well as for barium sulfate.

3.3.3.3 Blue Tie

XRF Spectroscopy of the blue-painted tie revealed the expected presence of barium, sulfur, and strontium. A significant amount of iron was also found, which suggested the use of Prussian blue as a paint source. Some evidence of lead was also found, which suggested the use of flake white paint in the white areas around the tie. Raman spectroscopy confirmed the presence of Prussian blue in the area (**Figure 3.35**) with peaks at 2149 cm^{-1}, 2091 cm^{-1}, 531 cm^{-1}, and 276 cm^{-1}, which suggests this photograph may have been hand-colored with Marshall's Chinese Blue paint. It should also be noted that Prussian blue was observed in the sky area during Raman analysis of the brown telephone pole in **Chapter 3.3.3.9**.
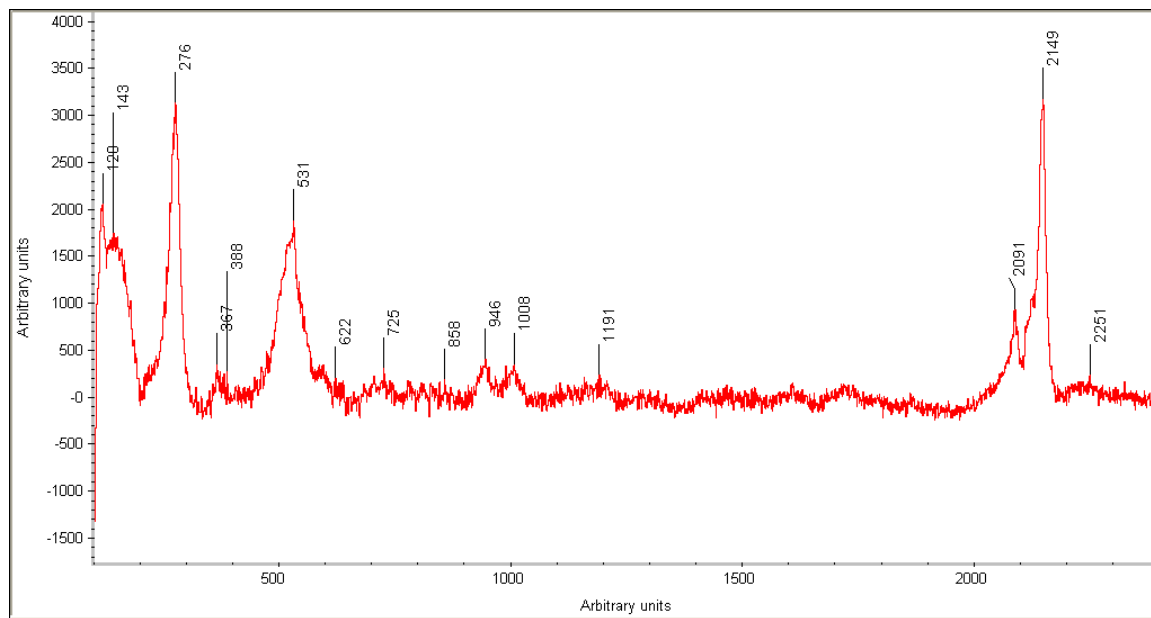
Figure 3.35: Raman spectrum of the painted blue tie. Note the strong peaks for Prussian blue.

3.3.3.4 Green Flower

XRF spectroscopy of a green painted flower in the foreground showed the presence of a large amount of barium, as well as sulfur and strontium. A significant amount of iron was also found, as was lead and chromium. This suggested that Marshall's Chrome Green may have been used to paint this area, as it was found to contain a mixture of the yellow lead chromate and Prussian blue to produce its green color. Raman confirmed this hypothesis, with peaks for Prussian blue at 2152 cm^{-1}, 2125 cm^{-1}, 2091 cm^{-1}, 532 cm^{-1}, and 274 cm^{-1}. The two strongest peaks of chrome yellow were observed at 362 cm^{-1} and 842 cm^{-1} Peaks for barium white were also observed at 987 cm^{-1} and 454 cm^{-1} (**Figure 3.36**).
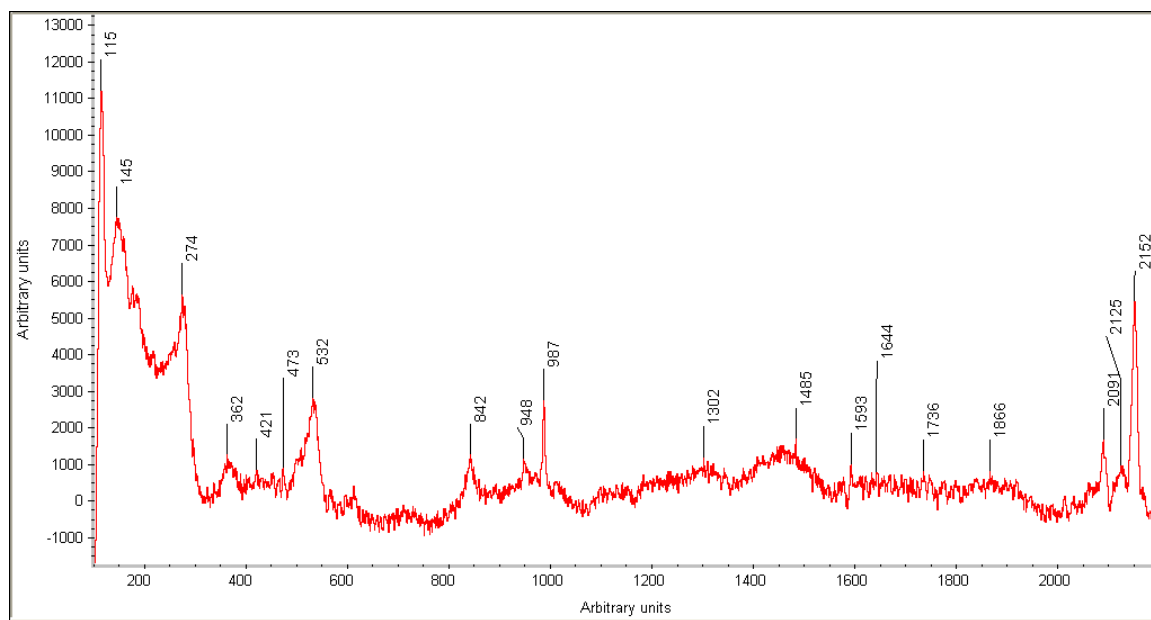
Figure 3.36: Raman spectrum of the green paint used on the ca. 1930 silver gelatin print.

3.3.3.5 Red Lips

The red lips of Christian Bader were analyzed using XRF spectroscopy. This technique revealed a large concentration of barium, as well as some sulfur and strontium. Small amounts of iron and calcium were also found, as well as a trace amount of silver. The color of the sample area suggested that as in the flower studied in the previous section, it too contained Marshall's Carmine. Raman spectroscopy showed the presence of alizarin crimson, with peaks of the pigment observed at 1189 cm^{-1}, 1289 cm^{-1}, 1324 cm^{-1}, 1479 cm^{-1}, and 1634 cm^{-1},suggesting that the photograph was hand-colored with Marshall's Carmine. Peaks for barium white were also observed at 458 cm^{-1} and 987 cm^{-1} (**Figure 3.37**).
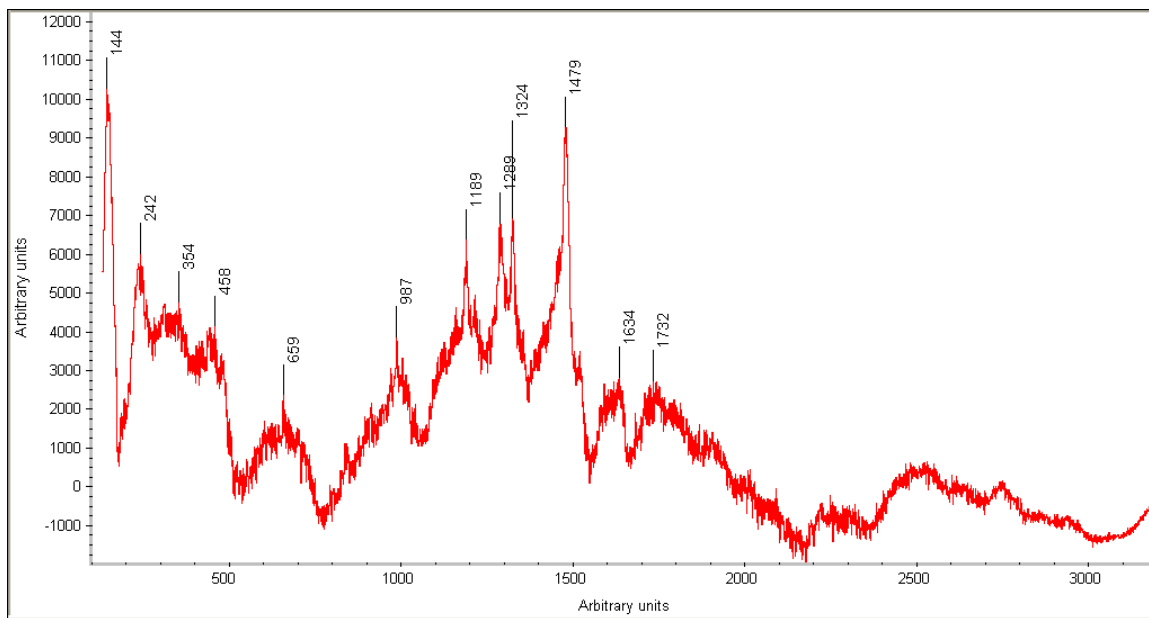
Figure 3.37: Raman spectrum of the red painted lips, showing presence of alizarin crimson.

3.3.3.6 Pink Dress

The color of Anna Bader's pink dress suggested it was painted with a Marshall's Flesh color. XRF analysis of a pigment particle in the dress showed a large amount of barium, as well as a large amount of iron. Some strontium, sulfur, and potassium were also observed. Raman spectroscopy was forgone in this case, as it seemed to be very similar to the flesh color of the faces.

3.3.3.7 Flesh

An area of flesh on Christian Bader's forehead was analyzed using XRF spectroscopy, which found an abundance of barium, sulfur, and strontium from the baryta layer. Also found was iron, as well as a trace amount of silver. Raman spectroscopy showed the possible presence of hematite, though that observation was inconclusive. Barium sulfate was also observed with a strong peak at 986 cm^{-1}.

3.3.3.8 Brown Suit

Christian Bader's brown suit appeared to be colored with a shade of brown, perhaps with Marshall's Sepia (refer to **Figure 1.4**). XRF analysis of a concentrated area of pigment showed the present of barium, sulfur, and strontium, as expected, as well as a small amount of iron, calcium and silver. Raman spectroscopy showed two very strong, broad peaks centered around 1324 cm^{-1} and 1592 cm^{-1}, which is similar to the given reference values for the pigment lamp black. Though evidence of an iron-based pigment was not found with Raman, it seems likely that a mixture of an iron-based pigment, such as Marshall's Verona Brown, with a carbon black pigment, such as Marshall's Ivory Black, or even a premade mixture of the two, such as Marshall's Sepia, may very well be present (refer to **Figure 3.38**). This conjecture is supported by the presence of a spot on an area of the suit where a drop of liquid appears to have caused the black portion of the

mixture to migrate to the outer area, leaving a red-brown spot surrounded by a black ring (**Figure 3.39**).
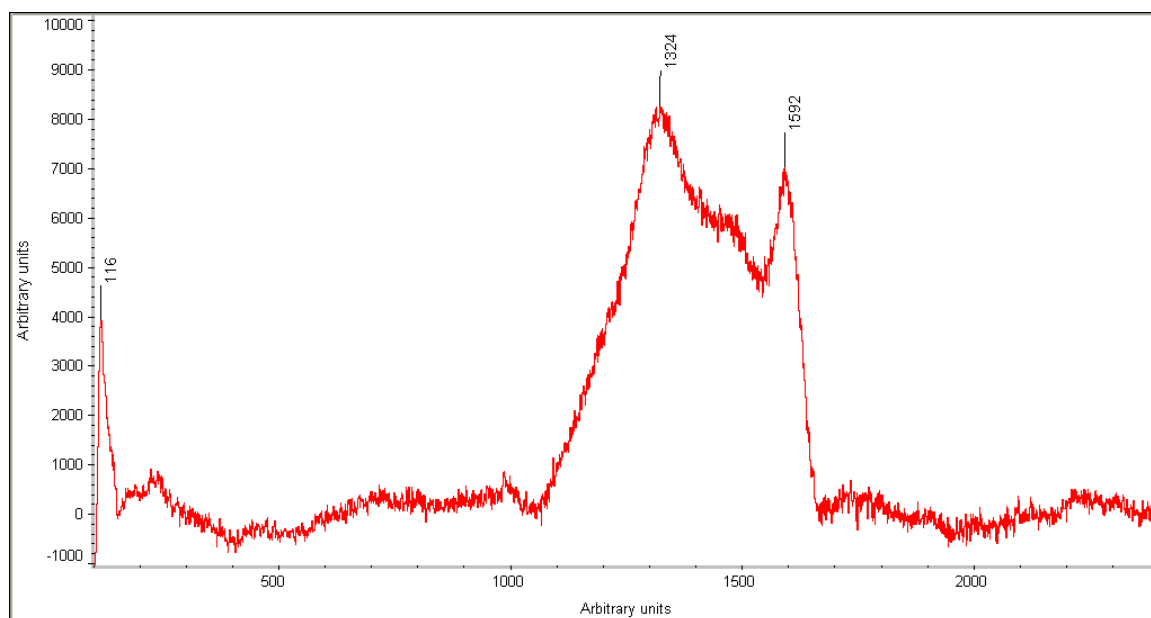
Figure 3.38: Raman spectrum of the brown-painted suit.
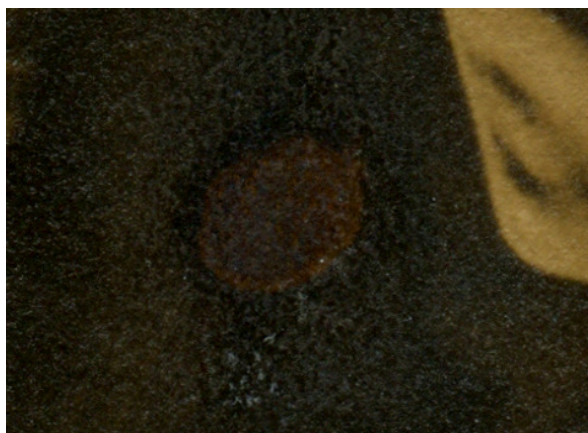
Figure 3.39: Spot of apparent liquid spill that has separated the paint into brown and black areas.

3.3.3.9 Red-Brown Telephone Pole and Eyes

XRF spectroscopy of the red-brown painted telephone pole showed a large amount of iron present, in addition to the anticipated barium, strontium, and sulfur. Trace amounts of silver and calcium were also found. Raman spectroscopy of the pole's crossarm indicated the presence of Mars red, with distinct peaks at 224 cm^{-1}, 288 cm^{-1}, 406 cm^{-1}, and 617 cm^{-1}. Surprisingly, Prussian blue was also found, with a peak near 282 cm^{-1}, a peak at 536 cm^{-1}, 2902 cm^{-1}, and a very strong peak at 2152 cm^{-1}. This is most likely due to the blue-colored sky, which probably was colored with Marshall's Chinese Blue first and may very well have mixed in with the brown-red paint used to color the pole. Barium sulfate was also noted, with a peak at 986 cm^{-1} (**Figure 3.40**).

The red-brown-painted eyes of the figures, which were examined with Raman spectroscopy as it was assumed the concentration of the paint would be higher in them than on the telephone pole. Two Raman spectra of one of the eyes were collected; the first (**Figure 3.41**) showed the possible presence of Mars red, with weak peaks at 222 cm^{-1}, 285 cm^{-1}, 403 cm^{-1}, and 611 cm^{-1}. Barium sulfate was observed as well, with a weak peak at 988 cm^{-1}. Also observed were two large, broad peaks at 1174 cm^{-1} and 1243 cm^{-1} that could not be correlated with any reference material. The second spectrum collected (**Figure 3.42**) did not show the presence of any iron pigment, only two similar large, broad peaks at 1171 cm^{-1} and 1252 cm^{-1}. Nevertheless, these results suggest that both areas were colored with a mixture of iron oxide-containing paints, such as Marshall's Verona Brown, Raw Sienna, or Flesh.
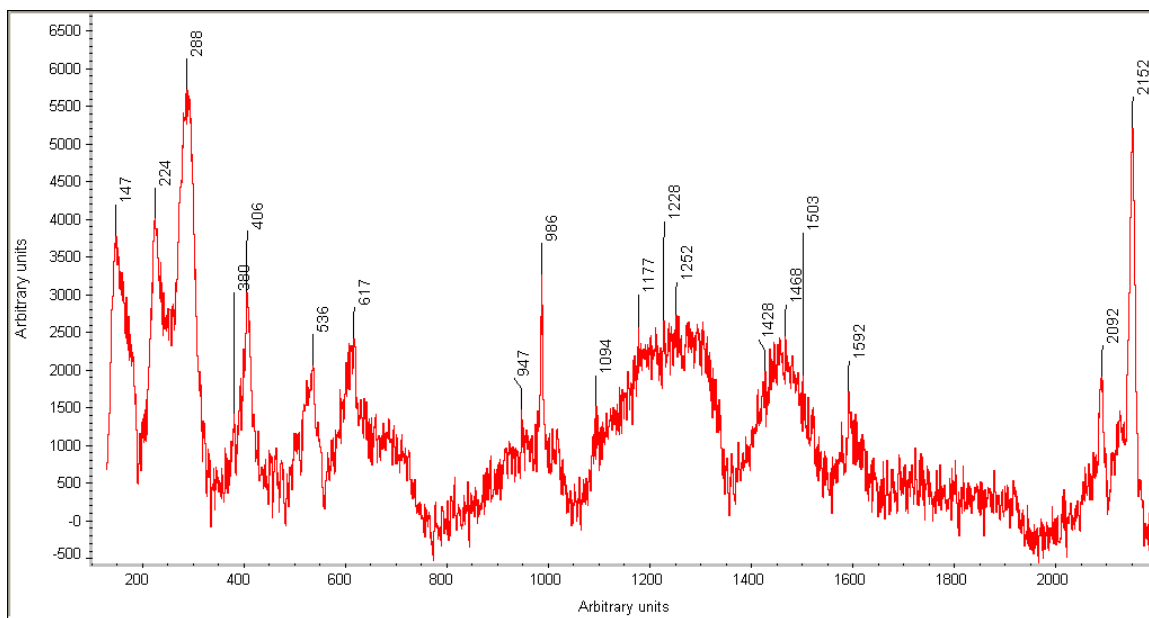
Figure 3.40: Raman spectrum of the red-brown painted telephone pole.
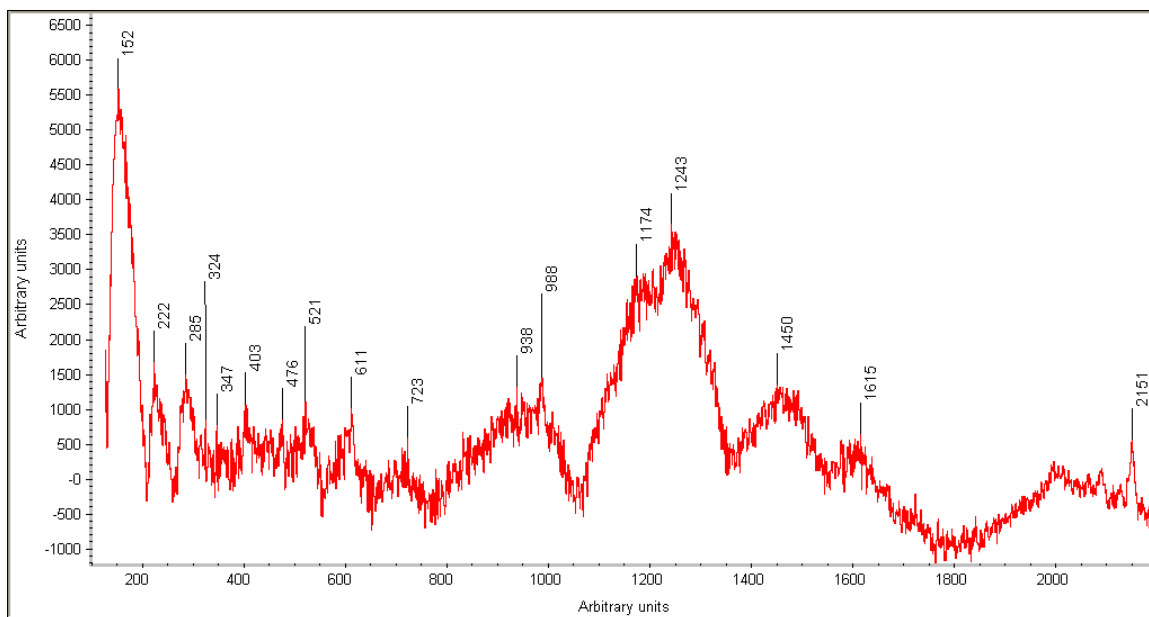
Figure 3.41: First collected Raman spectrum of a red-brown painted eye.

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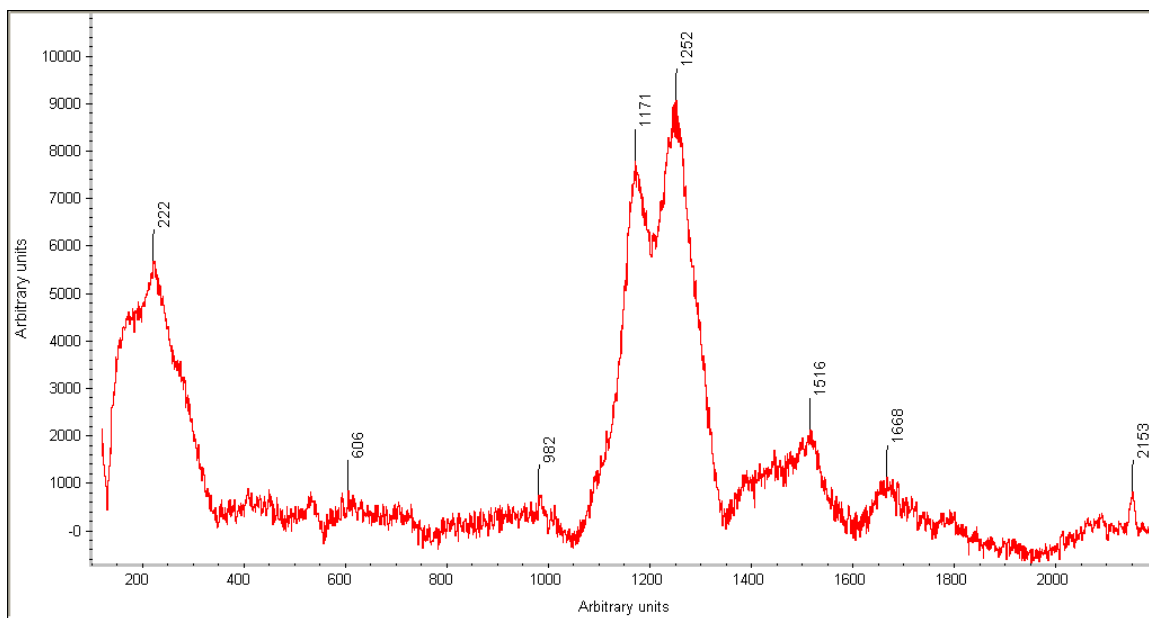
Figure 3.42: Second collected Raman spectrum of a red-brown painted eye, showing two similar large, broad peaks as found in the first collected spectrum.

3.3.3.10 White Shirt

While it was at one time thought the white shirt area could be painted with flake white (lead white) paint, XRF analysis dispelled this notion, showing the presence of barium, sulfur, strontium, calcium, and silver only. No lead was observed. Raman analysis showed only the presence of barium white, indicating that if a paint was used, it was composed of this white pigment, or that no paint was present.

REFERENCES

[1]   Rutherford J. Gettens and George L. Stout, *Painting Materials: A Short Encyclopedia* (New York: Dover Publications, 1966), 167-168.

[2]   Ibid., 156.

[3]   Ibid., 105.

[4]   Ibid.

Chapter 4

CONCLUSIONS

The analyses of the materials in the Marshall's kits demonstrated that spectroscopic methods, when used in conjunction with one another, could identify most of the primary components of the photo-oils and P.M. Solution. While all of the techniques provided valuable information about the compositions of the materials, X-ray fluorescence spectroscopy and Raman spectroscopy yielded the most practical information about the pigment components; on the basis of XRF, it was determined whether the primary coloring agents were organic or inorganic, and from that basis, a guess could be formulated about a possible composition. By supplementing this information with Raman spectroscopy, the identification of the pigment components could be determined conclusively in most cases. That is not to say that the other techniques were not valuable: without use of FT-IR spectroscopy and SEM-EDS, the nature of the organic components and the filler would not have been well understood. Nevertheless, XRF and Raman stood out immediately for their utility, as well as for their potential for nondestructive sampling.

Analysis of the kit materials also verified much of what Marshall printed in *Photo-Oil Coloring for Fun or Profit* regarding the paints themselves. The paints were found to have differing compositions than their trade names suggested, and, for example, that the paint Carmine was really alizarin crimson, and that Verona Brown did appear to be burnt umber, as noted in that publication.[1] Identifications of the primary components of the materials in the kits are presented in **Table 4.1**.

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Table 4.1: Primary Components of Materials in Marshall's Kits

Material Name	Composition
Paint "Viridian"	Phthalocyanine green (PG 7)
Paint "Raw Sienna"	Goethite (raw umber)
Paint "Verona Brown"	Hematite, with manganese dioxide (burnt umber)
Paint "Flesh"	Hematite
Paint "Chinese Blue"	Prussian blue (PB 27)
Paint "Cadmium Yellow"	Lead chromate (chrome yellow) (PY 34)
Paint "Cheek"	Toluidine red (Hansa red) (PR 3)
Paint "Extender"	Linseed oil medium with clay filler
Paint "Flesh No. 2"	Hematite
Paint "Oxide Green"	Mixture of lead chromate and Prussian blue (chrome green) (PG 15)
Paint "Carmine"	Alizarin crimson (PR 83)
Paint medium	Linseed oil
Paint filler	Clay material similar to montmorillonite
P.M. Solution	Linseed oil and turpentine

While other photographic kits, such as DeVoe Photo-Oil-Colors, Japanese Peerless Permanent Photo Oil-Colors, Brady Photo Colors, and Roehig's Transparent Oil Photo-Colors were not a part of this study, further research into the composition of their paints would be most prudent, not only to add to the knowledge base of hand-coloring materials, but also to elucidate the differences between these and Marshall's Photo-Oils. Also worthy of future study are the other paints produced by the Marshall Company not analyzed in this study, such as those illustrated in **Figure 1.4**, as well as other Marshall's products, such as the Duolac varnish, the marlene solution, and Marshall's Photo-Pencils and Marshall's Retouching Colors.

Analysis of the photographs painted with the materials from the Marshall's kits ("Ed" and "Alice") demonstrated that the most effective of the spectroscopic techniques evaluated were X-ray fluorescence and Raman spectroscopy. The best results

for both techniques were achieved by focusing on the most visually concentrated areas of pigment and on pigment particles, as these areas generally had greater amounts of pigment present. Such microscopically concentrated areas were found on both photographs, even in areas that appeared to be uniformly or very lightly painted, owing to slight variations in the method of application and in the surface of the photographic prints. The combination XRF-Raman method revealed the presence of most of the paints used to hand-color the photographs, and where one was ineffective, the other generally revealed enough information that a determination could be made, e.g. XRF finding high amounts of iron in areas painted with the iron oxide-based flesh areas, with Raman being able to identify organic pigments.

Analysis of the unmixed paints on "Alice" generally yielded more complete identifications than the mixed and blended paints on "Ed". The reasons for this discrepancy can only be speculated; it could be due to the differing methods of application, it may be owed to a smaller amount of the paints being used on "Ed", it may even be due to not finding the right areas to gather spectra in. Regardless of the cause, the mixed success with "Ed" demonstrated that the techniques were likely to meet with varying levels of success based upon the nature of application and pigments used. Though their presence was indicated quite strongly in the XRF spectra, the iron oxide-based pigments in particular were observed to have limited Raman scattering, rendering a more thorough identification quite difficult with Raman spectroscopy.

Reflectance FT-IR spectroscopy of these photographs showed only limited success. While some materials, such as the Prussian blue pigment on "Alice", could be readily observed, most proved to have reflect only minimally; as a result, most components would likely not be identified in the IR spectra unless one was looking for them specifically. Furthermore, the Kramers-Kronig Transformation made identification

of even large peaks in the IR spectrum that were known to be present challenging, while many peaks that may have been present were likely not found at all. Because of these limitations, the technique was not used further for these practical investigations. However, more research is needed in this area to gauge the true effectiveness of the techniques for use in hand-colored photographs. One technique that may warrant further investigation is Attenuated Total Reflectance FT-IR (ATR-FT-IR), which could, in theory, produce clearer spectra without the need for sampling. However, the possibility of impressing a permanent dimple in the photograph may limit the use of this technique.

Spectroscopic analysis of the two late 19th-centruy albumen prints demonstrated the limitations of the spectroscopic techniques for hand-colored photographs. Despite taking spectra in the most concentrated areas, no identification of the coloring agents could be made. The likely cause seems to be the probable use of more modern coloring agents, perhaps from a colored marking pen, that are not contained in the reference libraries used to analyze the spectra. Whatever the cause, these two photographs demonstrated that it is not possible to use these spectroscopic techniques to identify every coloring agent on hand-colored photographs.

Identification of the coloring agents on the ca. 1930 silver gelatin print was much more successful. Both XRF and Raman spectroscopy yielded useful information that enabled most of the pigments to be identified fully or partially. Those results can be found in **Table 4.2**. As was noticed with "Ed" and "Alice", even though the presence of iron-oxide based pigments in certain sample areas was indicated quite strongly in the XRF spectra, the small amounts present and the limited Raman scattering produced by the iron oxides did not usually produce identifiable peaks in the collected Raman spectra. This is likely an unavoidable limitation of Raman spectroscopy, and other spectroscopic

techniques will likely be needed if a fuller identification of the iron oxide in the pigment is required.

Table 4.2: Identification of Pigments Found on ca. 1930 Silver gelatin Print

Paint Color/Location	Pigment(s) Found	Notes
Yellow Flower	Hansa red (PR 3), Hansa yellow (PY 3)	Possibly Marshall's Cadmium Yellow Deep
Blue Tie, Blue Sky	Prussian blue (PB 27)	Possibly Marshall's Chinese Blue
Green Flower	Lead chromate, Prussian blue (PG 15)	Possibly Marshall's Oxide Green
Red Lips, Red Flower	Alizarin crimson (PR 83)	Possibly Marshall's Carmine
Flesh; Pink Dress	Iron-based pigment	Possibly Marshall's Flesh
Brown Suit	Mixture of iron-oxide pigment with carbon black	Possibly Marshall's Sepia, or mixture of Marshall's Verona Brown with Ivory Black
Red-Brown Telephone Pole, Brown Eyes	Iron oxide-based pigment	Possibly Marshall's Verona Brown, Raw Sienna, Flesh, etc.

Though the pigments used in hand-coloring of the ca. 1930 silver gelatin print were mostly identified, further research is needed to truly gauge the effectiveness of spectroscopic techniques in identifying coloring agents on photographs. This study would have liked to have included more tests with FT-IR spectroscopy, but owing to time constraints this method had to be abandoned in order to gather spectra with the more-promising Raman spectroscopy. One technique that may hold potential for hand-colored photographs is Attenuated Total Reflectance FT-IR (ATR FT-IR) spectroscopy, a spectroscopic method that has been effectively used to identify components on the surfaces of materials. Because many hand-coloring agents sit on the surface of the

photographic base to which they are applied, ATR-FT-IR could be used to examine the coloring agents without interference from other components in the photograph.

When analyzing the hand-colored photographs in this study, it was found that generally, the best results were obtained by focusing on areas of paints that appeared to be the most visually concentrated, or by focusing on pigment particles if they are present. However, no two photographs were alike; thus, no specific recommendations can be made in selecting sample sites for study. To be most effective, though, multiple areas of each paint color on the photograph should be analyzed if possible to obtain multiple spectra to search for all pigments present.

The greatest need for further research is in testing other hand-colored photographs with the spectroscopic techniques, as this study has shown that the results are mixed. Several other hand-colored photographs were considered for analysis, but had to be abandoned due to time constraints. In addition, photographs colored with non-Marshall's paints should be further studied, as such photographs in this study could not have their coloring agents identified. Hand-colored photographs on different bases—such as daguerreotypes, ambrotypes, and tintypes—are also in need of exploration using these techniques. Nevertheless, the results of the analysis of the unknown photographs found in this study, though mixed, offer promise that nondestructive spectroscopic methods can be used to successfully identify many of the colorants on hand-colored photographs.

REFERENCES

[1]   Marshall, op. cit., 9.

Table A.1: Major Elements Identified by XRF Spectroscopy

Paint Name	Non-Trace Elements Identified by XRF											
	Cl	Cu	Fe	Mn	Pb	Cr	P	Ca	Ba	Sr	Ag	S
Marshall's Kits												
Viridian	X	X			X							
Raw Sienna			X									
Verona Brown			X	X				X				
Flesh			X									
Chinese Blue			X		X							
Cadmium Yellow					X	X						
Cheek					X							
Extender			X				X					
Flesh No. 2			X									
Oxide Green			X		X	X						
Carmine		X	X					X				
"Alice"												
Background (Unpainted)									X	X		X
Brown Hair (Verona Brown)			X						X	X	X	X
Green (Viridian)		X							X	X		X
Red Lips (Carmine)									X	X		X
Blue (Chinese Blue)			X						X	X		X
Skin (Flesh)			X						X	X		X
"Ed"												
Background (Unpainted)									X	X		X
Tan Tie (Cadmium Yellow, Flesh, Raw Sienna, and Verona Brown)			X						X	X		X
Skin (Flesh)			X						X	X		X
Lips (Carmine)			X						X	X	X	X

Table A.1: Major Elements Identified by XRF Spectroscopy – Continued

	Cl	Cu	Fe	Mn	Pb	Cr	P	Ca	Ba	Sr	Ag	S
Hat Strap (Verona Brown)			X						X	X	X	X
Green Uniform (Oxide Green, Viridian, and Verona Brown)			X		X				X	X		X
Brass Button (Cadmium Yellow and Raw Sienna)			X		X				X	X		X
Ca. 1930 Silver Gelatin DOP												
Background (Unpainted)									X	X		X
Red Lips			X						X	X		X
Red Flower			X					X	X	X		X
Pink Dress			X						X	X		X
Brown Suit			X						X	X	X	X
Flesh			X						X	X		X
Brown Telephone Pole			X						X	X	X	X
Yellow									X	X		X
Blue Tie			X						X	X		X
Green Plant			X		X	X			X	X	X	X

Table A.2: Major Materials Identified by Raman Spectroscopy

Paint Name	Materials Identified by Raman
Marshall's Kits	
Viridian	Phthalocyanine green
Raw Sienna	Goethite
Verona Brown	Hematite; possibly manganese dioxide; another unidentified material
Flesh	Hematite
Chinese Blue	Prussian blue
Cadmium Yellow	Lead chromate
Cheek	Hansa red (PR 3)
Extender	Linseed oil
Flesh No. 2	Hematite
Oxide Green	Lead chromate; Prussian blue
Carmine	Alizarin crimson
"Alice"	
Background (Unpainted)	Barium Sulfate
Brown Hair (Verona Brown)	Barium sulfate
Green (Viridian)	Phthalocyanine green; barium sulfate
Red Lips (Carmine)	Barium sulfate
Blue (Chinese Blue)	Prussian blue; barium sulfate
Skin (Flesh)	Barium sulfate
"Ed"	
Background (Unpainted)	Barium sulfate
Tan Tie (Cadmium Yellow, Flesh, Raw Sienna, and Verona Brown)	Barium sulfate; another unidentified material with similar spectrum to that of unidentified material in Verona Brown
Red Unit Patch (Carmine)	Alizarin crimson; calcium sulfate
Blue Unit Patch (Chinese Blue)	Prussian blue; barium sulfate, calcium sulfate
Hat Strap (Verona Brown)	Barium sulfate; another unidentified material
Green Uniform (Oxide Green, Viridian, and Verona Brown)	Barium sulfate
Brass Button (Cadmium Yellow and Raw Sienna)	Barium sulfate; possibly lead chromate

Table A.2: Major Materials Identified by Raman Spectroscopy – Continued

Ca. 1930 Silver Gelatin DOP	
Background (Unpainted)	Barium sulfate
Red Lips	Alizarin crimson
Brown eye	Possible hematite; barium sulfate; unidentified material with similar spectrum to that of unidentified material in Verona Brown
White shirt	Barium sulfate
Brown Suit	Lamp black (carbon black)
Flesh	Possible hematite; barium sulfate
Brown Telephone Pole	Hematite; Prussian blue (from neighboring blue-painted sky area); barium sulfate
Yellow	Hansa red (PR 3); Hansa yellow; barium sulfate
Blue Tie	Prussian blue
Green Plant	Lead chromate; Prussian blue; barium sulfate