heritage

Tracked for Impact Factor

CITESCORE 1.8

Article

The Colors of the Butterfly Wings: Non-Invasive Microanalytical Studies of Hand-Coloring Materials in 19th-Century Daguerreotypes

Diego Quintero Balbas, Barbara Cattaneo, Andrea Cagnini, Paolo Belluzzo, Silvia Innocenti, Sandra Rossi, Raffaella Fontana and Jana Striova

Special Issue
Colour Photography and Film: Analysis, Preservation, and Conservation of Analogue and Digital Materials

Edited by
Dr. Marcello Picollo and Barbara Cattaneo

MDPI

https://doi.org/10.3390/heritage5040221

heritage

Article

The Colors of the Butterfly Wings: Non-Invasive Microanalytical Studies of Hand-Coloring Materials in 19th-Century Daguerreotypes

Diego Quintero Balbas [1], Barbara Cattaneo [2], Andrea Cagnini [3], Paolo Belluzzo [4], Silvia Innocenti [1], Sandra Rossi [2], Raffaella Fontana [1] and Jana Striova [1,*]

1 National Research Council—National Institute of Optics (CNR-INO), Largo E. Fermi 6, 50125 Florence, Italy
2 Laboratorio di Restauro Cartacei e Membranacei, Opificio delle Pietre Dure–MiC, Viale F. Strozzi, 1, 50129 Firenze, Italy
3 Laboratorio Scientifico, Opificio delle Pietre Dure–MiC, Viale F. Strozzi, 1, 50129 Firenze, Italy
4 Laboratorio di Restauro Oreficerie, Opificio delle Pietre Dure–MiC, Via degli Alfani 78, 50121 Firenze, Italy
* Correspondence: jana.striova@cnr.it

Abstract: The public expected color from the early photographic images, yet, daguerreotypes—the first commercially available photographic process—failed to register the natural colors. Daguerreotypists developed several coloring methods to solve this inconvenience after 1840. Scientific analyses of the hand-colored daguerreotypes are limited, and the primary information sources available are manuals and patents. This study aims to contribute to the knowledge of hand-coloring techniques, which impacts conservation practices, mainly the cleaning procedures and complements technical art history investigations. We studied nine colored daguerreotypes with a non-invasive methodology based on three spectroscopic techniques: X-ray fluorescence (XRF), micro-Raman spectroscopy (μ-Raman), and micro-Fourier-transform infrared spectroscopy in reflection mode (μ-rFTIR). The results revealed the different colorants and some of their mixtures employed by the colorist. It also adds information regarding the photographic production of three studios: Désiré François Millet, active in Paris between 1840 and 1868; Antoine Claudet (1797–1867), active in London; and the James E. McClees and Washington Lafayette Germon studio, operative between 1846 and 1855 in Philadelphia, USA. These technical details constitute a helpful comparison to future studies on Daguerreian studios and colored daguerreotypes.

Keywords: daguerreotypes; pigments; Raman spectroscopy; FTIR; XRF; photography; bismuth white; cochineal lake; Prussian blue; colorants

check for updates

Citation: Quintero Balbas, D.; Cattaneo, B.; Cagnini, A.; Belluzzo, P.; Innocenti, S.; Rossi, S.; Fontana, R.; Striova, J. The Colors of the Butterfly Wings: Non-Invasive Microanalytical Studies of Hand-Coloring Materials in 19th-Century Daguerreotypes. *Heritage* **2022**, *5*, 4306–4324. https://doi.org/10.3390/heritage5040221

Academic Editor: Vittoria Guglielmi

Received: 28 November 2022
Accepted: 16 December 2022
Published: 18 December 2022

1. Introduction

Daguerreotypes are the first commercially available photographic technique based on image reproduction over metallic support using a camera obscura. The process, invented by Nicéphore Niépce (1765–1833) together with Louis Daguerre (1787–1851), who later patented the process, was made public at the French Academy of Science in 1839 by François Arago (1789–1853). Daguerreotypes, which are complex polymateric objects, are both positive and negative images formed by silver-mercury amalgam nanoparticles over a copper-silver plate, generally covered by a layer of gold obtained by gilding. The image plate was typically enclosed or mounted in a housing system made of different materials, such as wood, textiles, paper, glass, and metals [1–4].

Arago compared the daguerreotypes to butterfly wings because of their fragility, iridescence, and precision; the only thing missing was color [5]. The public expected colored images from early photographs [6], and because of this, many scientific and technological efforts [7–9] tried to develop methods to register the natural colors, but very few succeeded. In this respect, the experiments were performed, for example, by

Edmond Becquerel (1820–1891) [6], Claude Niépce de Saint-Victor (1805–1870), and Gabriel Lippmann (1845–1921) [10,11]. However, those processes were not practical since fixing the colors was complicated, and preserving the plate required storage in the dark [9,11,12]. Consequently, photographers developed an alternative option: hand coloring.

As early as 1840—after the invention of the plate gilding by Hippolyte Fizeau (1819–1896)—methods for applying color to daguerreotypes were developed and patented. Antoine Claudet (1797–1867) was one of the earliest daguerreotypists to propose colored plates, and several manuals describe his method [9]. Between 1842 and 1856, different patents regarding the hand-coloring of daguerreotypes were registered in the USA, UK, and France (Figure 1) [2,8,13,14].

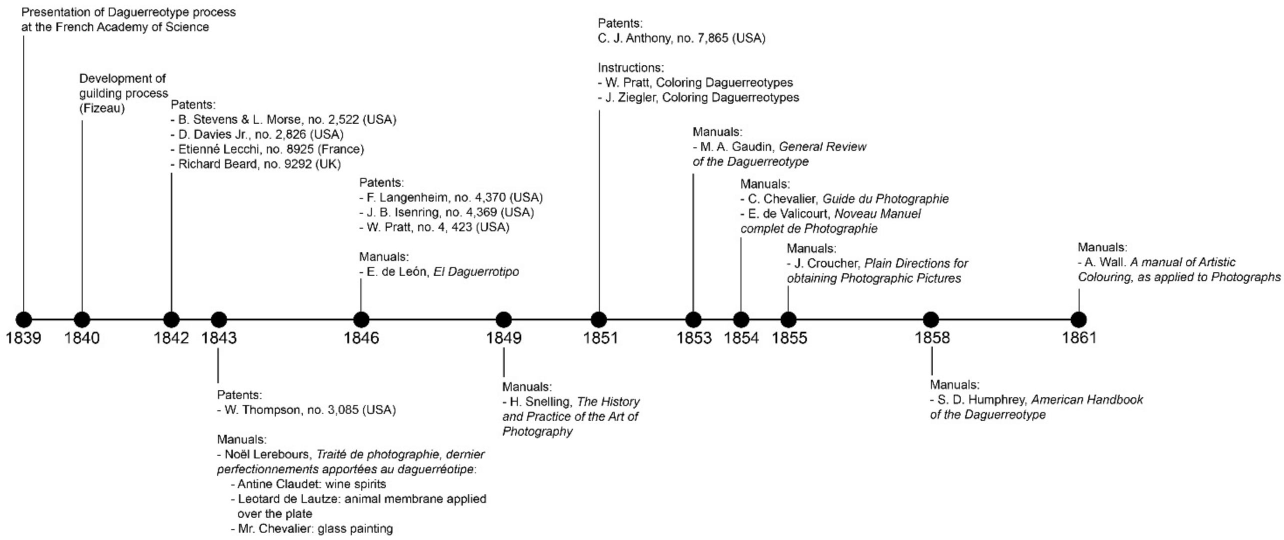


Figure 1. Timeline of different patents and manuals with information regarding coloring of daguerreotypes.

During the 19th century, miniatures were fashionable, yet daguerreotypes were more affordable and faster to obtain [15,16], gradually replacing miniature portraits. Despite the disagreement of many photographers and critics, coloring daguerreotypes became popular. It was a task that required some notions of painting. Because of it, hand coloring attracted many miniaturists who became colorists in studios that offered daguerreotypes and miniatures [7,9].

Colorists employed two types of techniques: (i) the indirect method of painting the cover glass, also known as Chevalier's method, based on the Phantasmagoria technology of projecting images using painted glasses, and (ii) the direct methods that included two variants, the hand-applied colorants (dry and wet), primarily employed in Europe, and the electrochemical, patented in the USA by Daniel Davis Jr. (1813–1887) in 1842 (no. 2826) and later improved by Montgomery P. Simons in 1843 (no. 3085) [2,8].

The complexity and poor control limited the application of the electrochemical technique [2]. The most commonly employed method was the dry hand-applied pigments (so-called Claudet's method by many manuals). Colorists prepared the colorants by grinding the dry powders, then adding the binder—generally gum Arabic—and letting dry the mixture before grinding it again. Some manuals recommended pouring the pigment powder into a solution of water with a low concentration of gum Arabic, later filtering with paper the mixed materials, and letting it dry before grinding. The so-obtained fine powders were applied to the plate with soft brushes, and their adhesion to the metallic surface was induced by breathing over it or slightly heating the plate [2,8,16–18].

As a consequence of the interest of 19th-century society, hand-coloring daguerreotypes became in vogue, and coloring boxes with ready-to-use materials in labeled glass bottles (e.g., "sky blue" or "ladies' flesh") [7] were available in the market. According to Snelling, the boxes generally contained eight colors, four brushes, and a gold cup [13]; the Gouin Couleurs packages consisted of 12 color bottles, gold and silver, and six brushes and were sold for 15 francs (approximately £50.12 (1850/2017 conversion) [19]) [9], while Newman's coloring kits also included manuals with the instructions for their handling [7]. Additionally, some boxes included the "blower"—a rubber bottle with an ivory spout to remove loose pigment particles from the plate [20].

Patents and manuals are the primary information sources regarding the daguerreotype coloring materials that are summarized in Table 1 [7,13,14,16,17]. From the column "Scientific literature" of Table 1, it is evident that very few analytical examinations report on the coloring materials. There are still some questions to be solved, for example, the correct identification of the binder and other organic materials employed. Gum Arabic seems to be the most popular, yet, manuals also mention wine spirit, poppy oil, copal resin, fish glue, gelatin, and mastic [13,14,18]. Moreover, historical sources record protective varnishes, animal membranes, or paper applied to the plate before or after coloring [14,16].

Table 1. List of pigments reported in historical records and scientific literature. N.D.: no data.

Pigment	Chemical Composition	Historical Records	Scientific Literature
Cochineal lake	Main component is carminic acid	Gaudin (1844), Snelling (1849), Vaillat (1850), Ziegler (1851), Croucher (1855), Baird (1855), Legros (1856), Humphrey (1858), Wall (1861)	Kozachuk, et al. [21], probably in a coloring box studied by Swan [17]
Red oxide	Fe_2O_3	Snelling (1849), Vaillat (1850), Baird (1855), Humphrey (1858)	Swan [17], Anglos et al. [22],
Vermillion/Cinnabar	HgS	Gaudin (1844), Vaillat (1850), Ziegler (1851)	N.D.
Chrome red	$Pb_2O(CrO_4)$	Ziegler (1851)	N.D.
Madder lake	Purpurin, alizarin, and other components.	Ziegler (1851), Legros (1856)	N.D.
Prussian blue	$Fe_4[Fe(CN)_6]_3$	Gaudin (1844), Snelling (1849), Vaillat (1850), Ziegler (1851), Legros (1856)	Swan [17], Anglos et al. [22], Golovlev, et al. [23]
Ultramarine	Na_{8-x} $[SiAlO_4]_6{\cdot}[S_2,S_3,SO_4,Cl]_{2-x}$	Ziegler (1851), Croucher (1855), Baird (1855), Humphrey (1858)	N.D.
Antwerp blue	$Fe_4[Fe_3(CN)_6]nH_2O + CoO{\cdot}Al_2O_3$	Snelling (1849)	N.D.
Indigo	Main component indigotin	Gaudin (1844), Snelling (1849), Ziegler (1851)	N.D.
Indigo carmine	5,5′-indigodisulfonic acid Na salt	Legros (1856)	N.D.
English smalt/Cobalt blue	$CoO{\cdot}Al_2O_3$	Ziegler (1851)	N.D.
Gamboge	Resin from *Garcinia* tree	Snelling (1849)	N.D.
Indian yellow	Magnesium euxanthate	Snelling (1849)	N.D.
Yellow ochre	FeO(OH) + Clay	Snelling (1849), Vaillat (1850), Ziegler (1851), Wall (1861)	N.D.
Cadmium yellow	CdS	Gaudin (1844), Ziegler (1851), Humphrey (1858)	N.D.
Chrome yellow	$PbCrO_4$	Snelling (1849), Ziegler (1851), Croucher (1855), Baird (1855)	Swan [17]
Chrome orange	$PbCrO_4{\cdot}PbO$	Ziegler (1851)	N.D.
Naples yellow	$Pb_3(SbO_4)_2$	Ziegler (1851), Wall (1861)	N.D.
Turbith (Turpeth mineral)	$Hg_3O_2SO_4$	Ziegler (1851)	N.D.
Shell gold	Au-Ag-Cu alloy	Croucher (1855), Baird (1855), Wall (1861)	Anglos, et al. [22]
Shell silver	Ag mixed with gum Arabic	Baird (1855), Wall (1861)	N.D.
Emerald green	$Cu(C_2H_3O_2)_2{\cdot}3Cu(AsO_2)_2$ could also refer to Viridian green ($Cr_2O_3{\cdot}2H_2O$)	Legros (1856)	N.D.
Burnt Sienna	Fe oxide	Snelling (1849), Vaillant (1850), Croucher (1855), Legros (1856), Humphrey (1858), Wall (1861)	N.D.
Burnt Umber	Fe oxide + Mn oxide	Snelling (1849), Baird (1855), Humphrey (1858)	N.D.
Bistre	Extract from tarry soot of burnt resinous wood	Gaudin (1844), Snelling (1849), Wall (1861)	N.D.
Tripoli/rotten-stone	Diatoms and weathered chert	Humphrey (1858)	N.D.

Table 1. *Cont.*

Pigment	Chemical Composition	Historical Records	Scientific Literature
Barium white	$BaSO_4$	N.D.	Anglos et al. [22], Golovlev et al. [23]
Lead white	$Pb(OH)_2{\cdot}PbCO_3$	Ziegler (1851), Legros (1856)	Anglos et al. [22]
Bismuth white	$4BiNO_3(OH)_2$-BiO(OH) or BiOCl	Ziegler (1851)	Swan [17] (variety not fully identified)
White clay	Kaolin	Ziegler (1851)	N.D.
Spanish white	$CaCO_3$	Ziegler (1851)	N.D.
Zinc white	ZnO	Ziegler (1851)	N.D.
Lamp black	Amorphous carbon (soot)	Snelling (1849), Baird (1855), Humphrey (1858)	N.D.

The composition of some mixtures included in the ready-to-use materials is another aspect that needs to be explored. For example, the flesh tone mixtures varied according to gender, age, and body part to be colored. The work by Swan [17] is, to the best of our knowledge, the sole study that reports on some mixture of colorants for coloring daguerreotypes contained in a coloring kit.

Early investigations with laser-induced breakdown spectroscopy (LIBS) report the presence of barium (Ba), associated with barium white (barite, $BaSO_4$), in white areas. Iron (Fe) was detected in blue regions, attributed to Prussian blue ($Fe_4[Fe_3(CN)_6]_nH_2O$), sometimes mixed with lead white (lead carbonate, $Pb(OH)_2{\cdot}PbCO_3$), and Mars red (iron oxide, Fe_2O_3) was identified in the red field [22,23]. In the shell gold employed to color the jewelry, a higher emission of Au and Cu confirmed the application of gold paint [22].

Kozachuk et al. [21] identified a cochineal lake in another daguerreotype with scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDX), FTIR, and Raman spectroscopy. The lake, constituted by cochineal dye precipitated into an Al-rich substrate, was used to color the cheeks of the portrayed woman. Alice Swan [17] analyzed seven colors present in a coloring box using spot tests and SEM-EDX. The box contained chrome yellow ($PbCrO_4$) mixed with barite, iron oxide, bismuth white (Swan hypothesized bismuth nitrate), Prussian blue, and two possible lakes: one red (most probably cochineal lake) and one purple not fully characterized.

Table 1 shows evidence that the information available is very fragmented and that the historical records still need to be corroborated by analytical investigations. Unfortunately, the scientific examination has disclosed no information regarding the binder or other organic materials (e.g., varnishes or animal tissue). Identifying the coloring materials in daguerreotypes is not only a matter of technical art history, but it may also impact conservation practices, particularly regarding the selection of cleaning procedures (e.g., wet or mechanic methods or laser cleaning).

In this work, we present the non-invasive contactless analyses of nine hand-colored daguerreotypes from two Italian collections, the Fondazione Alinari per la Fotografia (FAF) (Florence, Italy) [24] and the private collection Chiesa-Gosio (Brescia, Italy). We used three spectroscopic techniques, X-ray fluorescence (XRF), μ-Raman, micro-Fourier-transform infrared (μ-rFTIR) spectroscopy in reflection mode, and stereoscopic microscopy to investigate the colorants applied to the plates. This work aims to cover the literature gaps by providing scientific evidence of the coloring materials, including single pigment and their mixtures. Our results agree with previous investigations but expand the knowledge by unprecedently revealing some uncommon pigments and their mixtures employed in daguerreotypes. Moreover, the evidence of the later coloring restoration intervention is disclosed.

2. Materials and Methods

2.1. Daguerreotypes Analyzed

Nine daguerreotypes from two Italian collections were studied. Table 2 summarizes their characteristics.

Table 2. Summary of the daguerreotypes studied in this work. FAF: Fondazione Alinari per la Fotografia.

Collection	Code	Daguerreotypist	Date	Subject	Plate Size (cm)	Housing
FAF	DVQ-F-000535	Unknown	Before 1845	Portrait of a couple	7.6 × 6.4	Hinged case
	DVQ-F-000761	Unknown	After 1850	Portrait of a girl (crayon daguerreotype)	8.4 × 7.2	Hinged case
	DVQ-F-001667	Désiré François Millet (active 1840–1868, Paris, France)	1855 ca.	Portrait of a young woman	11.0 × 8.5	Colored glass
	DVQ-F-001829	Antoine Claudet (1797–1867), active in London	-	Portrait of a young woman	7.7 × 6.5	Stereoscopic case
	DVQ-F-002339	James E. McClees and Washington Lafayette Germon(actives 1846–1855,Philadelphia, USA)	1847–1860	Portrait of a seated man	14.0 × 10.7	Hinged case
	DVQ-F-002694	Unknown	After 1850	Portrait of a seated man with a cane	8.2 × 7.1	Passe-partout
	DVQ-F-000719/1	Unknown	-	Portrait of a young man	8.4 × 7.1	Hinged case
Chiesa-Gosio	Dag504-3	Unknown	-	Portrait of a young woman	8.0 × 9.4	Hinged case
	Dag534	Unknown	After 1844	Portrait of a woman in a bonnet	8.0 × 7.0	Unknown

2.2. Stereomicroscopy

The daguerreotypes were examined under a Leica M205C stereomicroscope with a camera Leica DFC 295 at 0.78× and 2.5× according to the areas investigated. White balance over a white surface was performed before capturing the images that were processed with LAS v4.6 software.

2.3. Raman Microspectroscopy

Raman microspectroscopy (μ-Raman) spectra were measured with a Renishaw inVia Raman confocal microscope equipped with a Leica DM2700 optical microscope and an excitation source at 785 nm. The measurements were performed in an extended spectral range of 100–3200 cm^{-1} using a grating of 1200 L/mm and a thermoelectrically cooled CCD detector (spectral range 400–1060 nm) with a spectral resolution of 1 cm^{-1} per CCD pixel (functional resolution of 3 cm^{-1}). The laser power on the daguerreotype surface was >1 mW, with typical 20 s integration times and 1–5 accumulations. The data spectra were collected with 50× (N PLAN NA = 0.5; theoretical spot size$_{785}$ = 0.95 μm) and 100× (HC PL FLUOTAR NA = 0.75; theoretical spot size$_{785}$ = 0.64 μm) long-distance objectives and processed with Wire5.5 and OriginPro8.5 software.

2.4. X-ray Fluorescence Spectroscopy

X-ray fluorescence analyses were performed with a portable XGLab ELIO spectrometer with an X-ray tube with an Rh anode coupled to a 1 mm collimator. The measurements were done using 50 kV and 5 mA. The instrument is equipped with a 25 mm^2, Peltier-cooled, Si Drift Detector (energy resolution < 135 eV on the Mn-kα line at 0.5 ms shaping time, a peak-to-background ratio of the order of 15,000, silicon thickness= 500 mm, Be window thickness= 12 μm). The focal distance from the detection head (90°/63.5° measurement/detection geometry) is 1.4 cm, and the spatial resolution of ~1.2 mm. The intensity, expressed in counts per second (cps), was calculated by dividing the area under the correspondent characteristic analytical line in the XRF spectra by the measuring time in seconds. The data was processed with Elio SW, PyMCA, and Origin Pro8.5 software.

2.5. Micro Reflection Fourier-Transform Infrared Spectroscopy

Micro reflection Fourier-transform infrared (μ-rFTIR) spectra were acquired in a contactless reflection mode with a Thermo Nicolet Continuum microscope equipped with a 15× objective (NA 0.58). The spectra were recorded in the 4000–400 cm^{-1} spectral range, with a spectral resolution of 4 cm^{-1} and the autogain mode activated. To maximize the signal-to-noise ratio, each measurement was performed with an aperture of 175 × 175 μm^2 and 256 scans. The background acquisition was performed with the same conditions over an Au-coated glass slide. The data was processed with Omnic 9.0 and Origin Pro 8.5 software.

3. Results

3.1. Single Pigments

Some daguerreotypes analyzed contained single red pigments applied mainly to the flesh tones. As recommended by several manuals, a higher amount of pigment was generally applied to the lips and cheeks of the portrayed person. The different hues were obtained by modulating the colorant amount.

The Raman spectra of the daguerreotypes DVQ-F-000761, DVQ-F-000719/1, and DVQ-F-001829 by Claudet (Figure 2a–c) show the characteristic Raman bands of red zones (Figure 2d–f) associated with cochineal lake (Figure 2g) [25–27]. Carmine or carmine lake, as it is named in the manuals, was widely employed for coloring daguerreotypes even though, in some cases, its application was discouraged because of its instability towards light exposure, information that was well-known by artists of the time [28]. Its presence is not surprising since the 19th-century red lakes were mainly based on natural dyestuffs [29]. Besides, the μ-Raman and μ-rFTIR spectra suggest that the same colorant was employed in the curtains (Raman spectrum in Figure A1) and the cushion (μ-rFTIR spectrum in Figure 2h) of the daguerreotype DVQ-F-001829. Thanks to the particular highly reflective properties of the plate surface that might give rise to the reflection-absorption phenomenon [30], the μ-rFTIR spectra are very informative, and it is possible to identify the characteristic bands of the lake (Table A1) [31,32], which is not always possible with FTIR spectroscopy.

On the hand, in the other two daguerreotypes (DVQ-F-001667 by Millet—Figure 3a and DVQ-F-002339 by McGlees & Germon), the flesh tones were obtained with iron oxide (Fe_2O_3, called light red in the manuals) as identified by Raman spectra (data from DVQ-F-001557 as an example reported in Figure 3b). This pigment was considered the best to represent flesh color, as mentioned by Snelling (1849) [13].

Additionally, the XRF results of the blueish-pinkish dress of the young woman portrayed in DVQ-F-001667 differ from the ones detected in the background of the plate due to a slight increase in the signal from Fe (2.5 cps vs. 1.3 cps for $Fe_{K\alpha}$). These results could lead to hypothesizing the presence of Prussian blue. However, no analytical evidence of the latter was found. Therefore, the blue tone derives most likely from the light scattering on the silver grains of the plate, a phenomenon called by daguerreotypists as "solarization." The blue hue of the dress appears when observing the plate at low angles from the vertical view (Figure 3c) [33]. However, under the microscope (Figure 3d), only red particles are visible in the dress area. Indeed, the Raman spectra (Figure 3b) and the increase of the iron signal detected with XRF evinced the presence of iron oxide, which might be responsible for the pinkish hue of the dress.

Besides, it has been found that shell gold was applied to the jewelry of three daguerreotypes (DVQ-F-001667, DVQ-F-001829 (Figure 4), and DVQ-F-002694). Table 3 reports the main XRF results of DVQ-F-001829, the increase in gold concentration in the golden area is clear. According to Anglos et al. [22], shell gold generally contains a ternary alloy (Au-Ag-Cu). However, the presence of silver (Ag) and copper (Cu) in the shell gold alloy employed here cannot be confirmed because of the possible influence of the underlying plate. Interestingly, the $Ag_{K\alpha}$ and $Ag_{L3\text{-shell}}$ lines' cps change in the golden area (Point 3) in comparison with other points of analysis (Table 3). It is known that the ratio between the $Ag_{K\alpha}$ and Ag $_{L3\text{-shell}}$ signal can give depth information, particularly in matrices containing copper, when compared to standard alloys since the $Ag_{K\alpha}$ line—which arises from deeper layers—tend to interact with the Cu present in the matrix. Therefore, its intensity is attenuated [34,35]. It is worth noting that the ratio is also modified in other areas due to the increase of the $Ag_{K\alpha}$

cps; thus, further investigations are required to establish if silver is also present in the shell gold employed for coloring the daguerreotype.

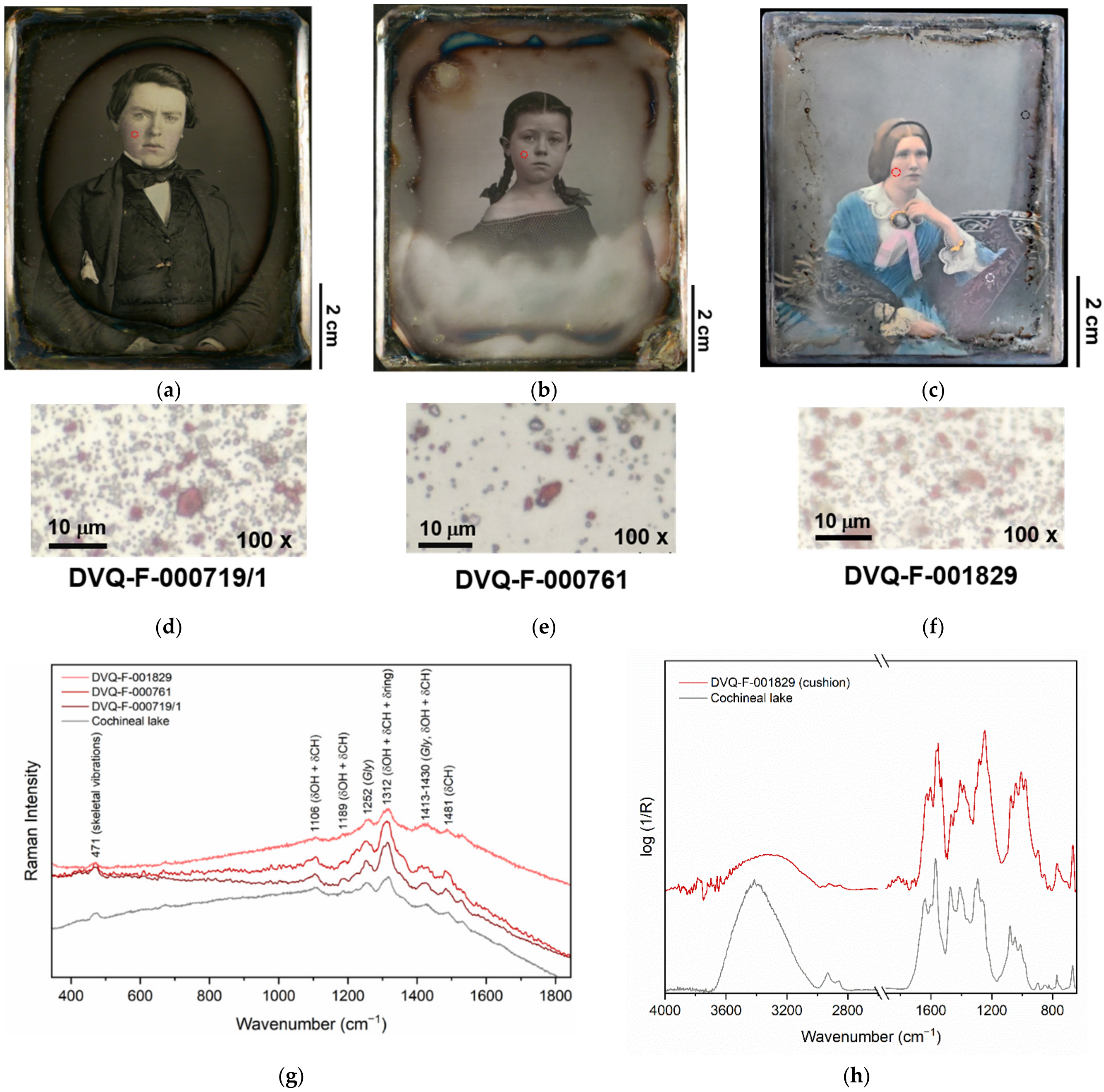


Figure 2. Positive photograph of daguerreotypes (**a**) DVQ-F000719/1, (**b**) DVQ-F000761, and (**c**) the left plate of the stereoscopic daguerreotype DVQ-F-001829 courtesy of Fondazione Alinari per la Fotografia. The analyzed areas of the flesh are marked with a red circle. The micro-photographies in (**d**–**f**) show the distribution of the lake particles deposited over the plate surface. (**g**) Raman spectra obtained from the red particles in (**d**–**f**) compared to a reference of cochineal lake. The characteristic bands with their assignment [26,27] are indicated. (**h**) the μ-rFTIR spectrum of cochineal lake detected in the cushion in DVQ-F-001829, the area analyzed is marked with a white circle in (**c**), compared to the reference of cochineal lake.

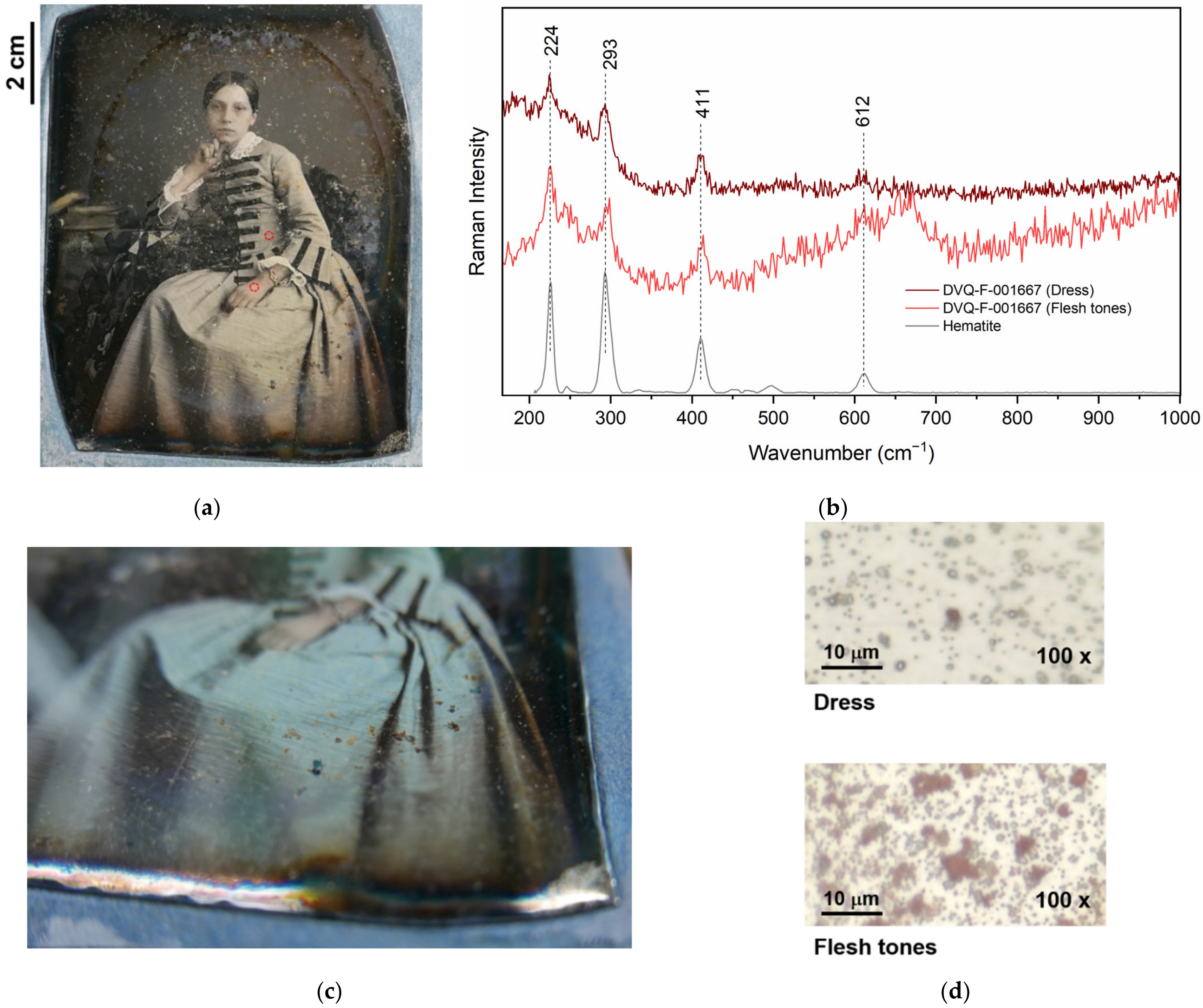
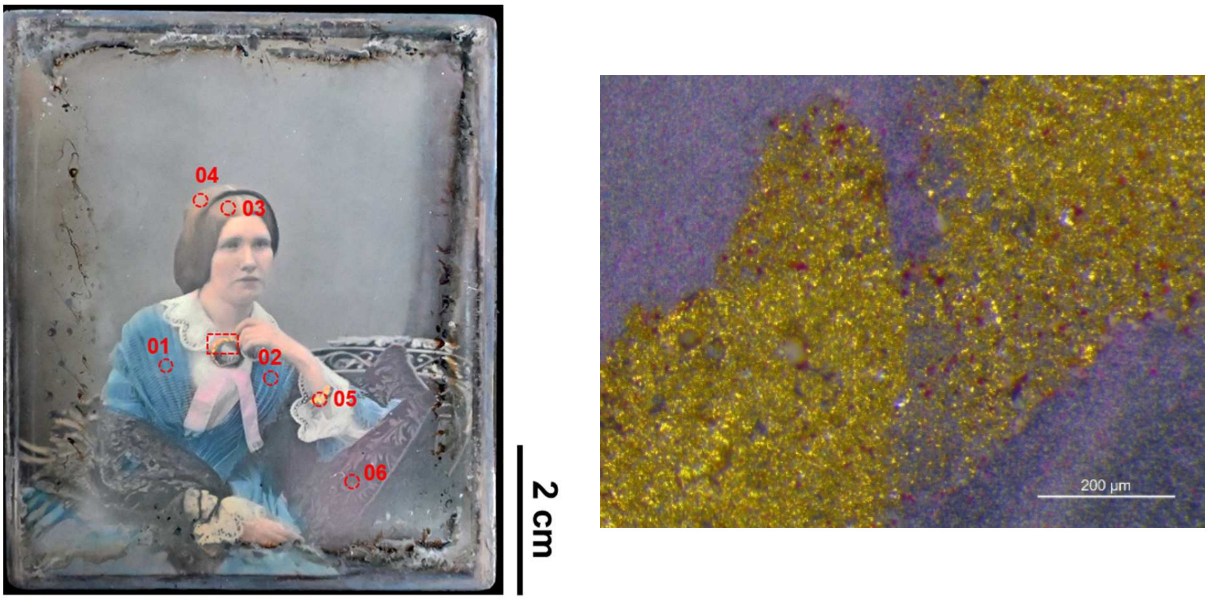


Figure 3. (**a**) Positive photograph of the daguerreotype DVQ-F-001667 by Millet (1855 ca.), courtesy of Fondazione Alinari per la Fotografia, observed at high angles from the frontal view. The red circles indicate the points of analysis. The pinkish color of the dress changes to a bluish hue when observed at lower angles (**b**) as a result of the "solarization" phenomenon produced by Ag particles. (**c**) Raman spectra obtained from the red particles in the flesh tones and the dress compared to the references of hematite (Fe_2O_3). (**d**) The micro-photographs show the pigment particles over the surface.



(**a**) (**b**)

Figure 4. (**a**) Positive image of the daguerreotype DVQ-F-001829 by Claudet courtesy of Fondazione Alinari per la Fotografia. The red dashed square indicates a detail of the shell gold observed in detail under the stereomicroscope in (**b**) at 2.5×. The red circles denote the points of XRF analyses.

Table 3. XRF results of the four main elements contained in the daguerreotype plate and shell gold measured in different points, indicated in Figure 4a, analyzed in the daguerreotype DVQ-F-001829.

Point of Analysis	XRF Results (cps)					Ratio
	$Cu_{K\alpha}$	$Ag_{L3\text{-shell}}$	$Ag_{K\alpha}$	$Hg_{L3\text{-shell}}$	$Au_{L3\text{-shell}}$	$Ag_{K\alpha}/Ag_{L3\text{-shell}}$
01	38.8	1603.1	7048.5	119.1	219.2	4.39
02	36.9	1523.5	10948.6	119.2	230.9	7.18 *
03	30.2	1414.2	7515.6	145.5	325.0	5.31
04	32.7	1439.7	7351.8	154.7	337.2	5.10
05—jewelry	36.5	**947.7**	7202.5	148.0	**879.4**	**7.59**
06	30.2	1757.7	7354.5	162.6	275.6	4.18

* Notice that the ratio in this point is the result of the cps increase of the $Ag_{K\alpha}$ line, which can suggest a lower interaction of the Kα (22.2 KeV) line with the copper (Cu) present in the matrix of the plate in that point [34].

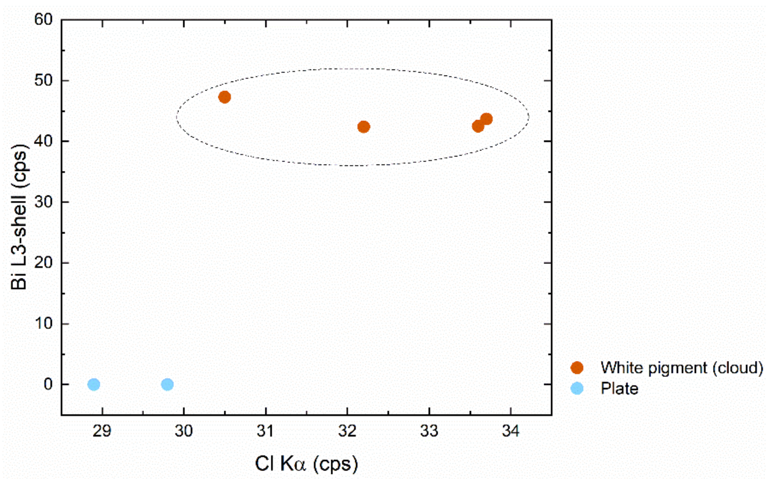
A less commonly employed pigment in daguerreotypes, vermillion (HgS), was identified in Dag534 from the Chiesa-Gosio collection, as confirmed by Raman spectroscopy (Figure A2a). The color in flesh tones in this daguerreotype is not very intense. Indeed, the manuals suggest avoiding the application of cinnabar or vermillion due to the possible damage that this pigment can induce to the plate [16]. In the same area where the particles of vermilion were identified, particles of a mixture of synthetic organic pigments (SOPs) were found. The Raman spectrum (Figure A2b) indicates the presence of a phthalocyanine pigment mixed with another SOP not fully identified. These colorants, commercially introduced in the 1930s [36], are anachronistic to the historical period when daguerreotypes were realized. Therefore, they can be associated with the re-application of color to recover the original decoration that was highly degraded. Finally, Prussian blue was identified in several of the daguerreotypes studied but only in the blue garment of the sitter of the daguerreotype DVQ-F-001829 was it applied alone.

3.2. Mixtures of Pigments

Very few examples have been reported in the literature on pigment mixtures [17,22], so their investigation is particularly interesting. In this respect, a crayon daguerreotype (DVQ-F-000761) (Figure 5a) was examined. Crayon daguerreotypes, patented in 1849 by Whipple in the USA, imitate crayonist portraits by restricting the image to the head of the sitter thanks to the white areas obtained by positioning, in front of the camera, screens with an aperture in the center and moving them during the sitting session. However, in some cases, as for the daguerreotype DVQ-F-000761, the same effect was imitated by applying white pigments.

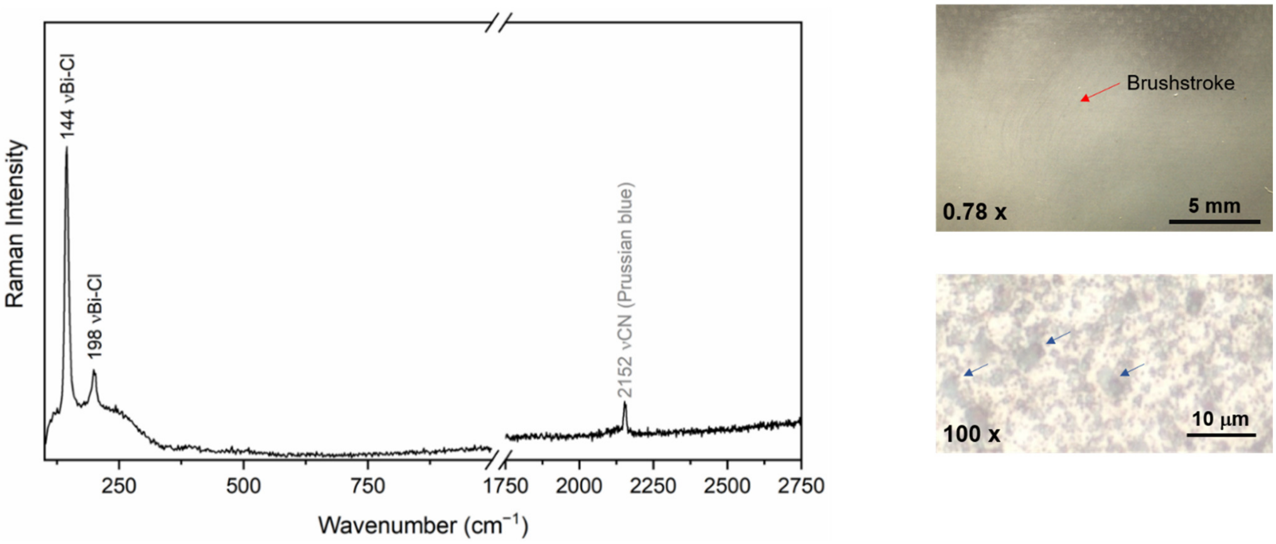
The XRF and Raman analytical evidence suggest that Prussian blue was mixed with shell gold (data not shown) and bismuth white. For the latter, the XRF data show a correlation between the presence of bismuth (Bi L3-shell) and an increase in the concentration of chlorine (Cl Kα) (Figure 5b) in the whitish cloud in the bottom portion of the daguerreotype. Raman spectra (Figure 5c) confirmed the presence of bismuth oxychloride (BiOCl) and Prussian blue. There are two varieties of bismuth white pigment, bismuth oxynitrate ($4BiNO_3(OH)_2$-BiO(OH)) and bismuth oxychloride. Both have a pearlescent appearance and are commonly used in beauty products, plastic objects, and paints. In artwork, their application was reduced, generally to imitate nacreous/pearl luster. Bismuth white, a non-toxic option to lead-based pigments, had a wider application during the 20th century [37]. Swan [17] identified bismuth white in a coloring box, but the variant of this pigment was not disclosed due to instrumental limitations, yet the author hypothesized the presence of bismuth oxynitrate.

(a)



(b)

Figure 5. *Cont.*

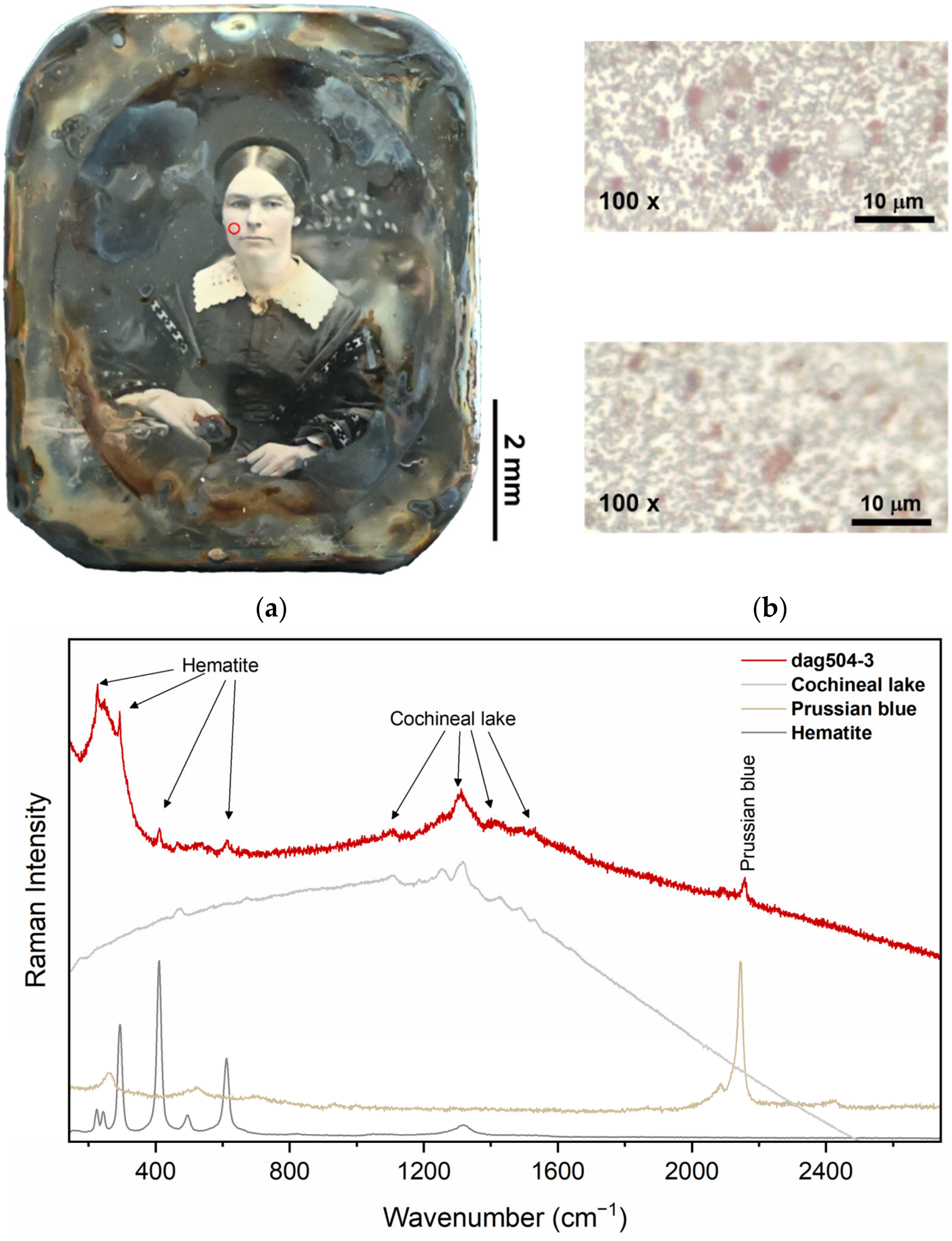


(**c**) (**d**)

Figure 5. (**a**) Positive image of the "crayon daguerreotype" (DVQ-F-000761) courtesy of Fondazione Alinari per la Fotografia; the orange and light blue circles indicate the analyzed XRF points, respectively, on the white cloud and plate. The scatter plot (**b**) shows the correlation between the higher concentration of chlorine (Cl) and the presence of bismuth (Bi). (**c**) Raman spectrum obtained from the cloud area that shows the main peaks of Bi white (bismuth oxychloride, BiOCl) and Prussian blue. (**d**) Micro-photography under a stereomicroscope (0.78×), where a possible brushstroke of the pigment application is evident, and optical microscope (100×), showing particles of Prussian blue (blue arrows).

More complex mixtures were identified in the flesh tones of the young woman portrayed in dag504-3 (Figure 6), where iron oxide, cochineal lake, and Prussian blue (Raman spectrum in Figure 6c) were applied to the cheeks. The first two pigments are listed in the manual as the adequate colors for the flesh tints, while blue pigments are suggested to modulate the hues according to the area to be colored. For example, Wall (1861) suggests applying blue in the areas where the skin is thin, and the veins add their bluish color.

The daguerreotype DVQ-F-001829 by Antoine Claudet exhibits the most complex coloration of all the examples studied (Figure 7). Indeed, his colored daguerreotypes received particular attention due to their high quality [16]. In addition to the single application of Prussian blue to the woman's dress, the colorist applied to the pinkish collar band (Figure 7a) a mixture of cochineal lake and barite, a mixture called "crimson" by Snelling (1849) (Raman spectrum in Figure 7b). Prussian blue characteristic bands in the Raman spectra were also identified in this area (Figures 7c and A3). Yet, it is not possible to determine whether it was originally part of the mixture or if it was contamination from the application of the blue color of the dress. Additionally, Cochineal lake and Prussian blue were identified in the curtain area (Figure A1); the mixture of Carmine and Prussian blue is recommended by Snelling (1849) [13] to obtain the richest purple color.



(c)

Figure 6. (**a**) Positive image of daguerreotype dag504-3 courtesy of the Chiesa-Gosio collection. The red circle indicates the area analyzed, shown under the optical microscope in (**b**). The Raman spectrum reported in (**c**) reports the mixture used for coloring the flesh tones of the portrayed woman compared to the references of cochineal lake, Prussian blue, and hematite.

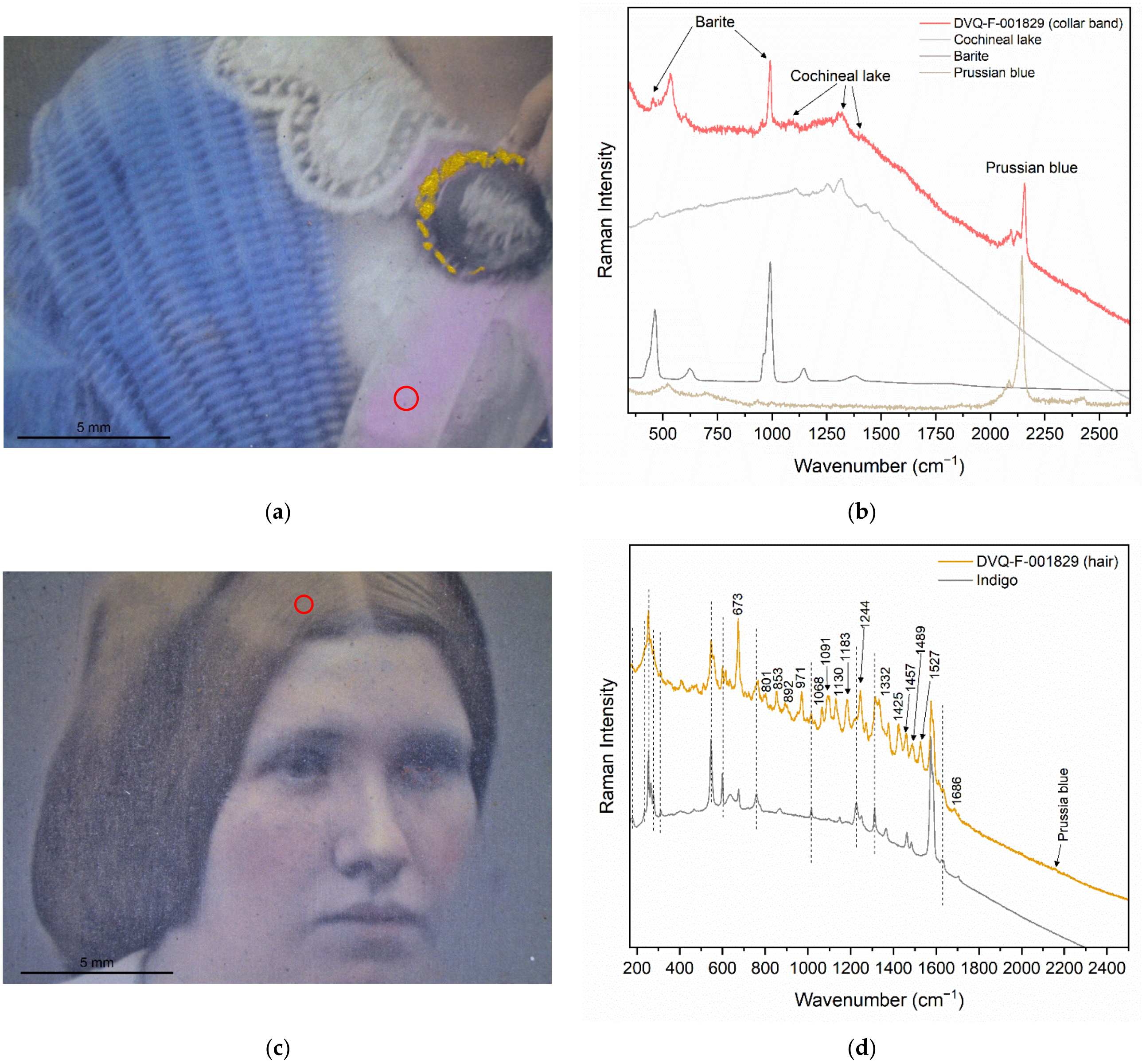


Figure 7. Micro-photographs of the daguerreotype DVQ-F-001829 by Claudet at 0.78× of the (**a**) pink collar and (**c**) head. The red circle indicates the area analyzed where the Raman spectrum reported in (**b**,**d**) shows the mixtures used for coloring the pink collar (i.e., cochineal lake, barite, and Prussian blue?) and the hair (i.e., indigo, Prussian blue, and an organic yellow pigment).

Moreover, the hair color was achieved by mixing indigo and another organic yellow pigment not fully identified (Figure 7c,d). Moreover, a weak signal from Prussian blue was identified (Figure 7d) and confirmed by analyzing in detail a blue particle (Figure A3). Snelling [13], in his manual, suggests the addition of blue pigments in the root of the hair and forehead of women with light or auburn hair, as is the case of the woman portrayed in the daguerreotype analyzed.

4. Discussion

Table 4 summarizes the results obtained in this work compared to the historical records and the scientific literature.

Table 4. Summary of the colorants identified in this work correlated to the historical records and compared to the scientific literature available.

This Work	Other Names in the Historical Records	Daguerreotype	Area	Scientific Lit.
Cochineal lake	Carmine, carmine lake	DVQ-F-001829 by Claudet, DVQ-F-000761, DVQ-F000719/1	Flesh tones, cushion	[17,21]
Iron oxide	Light red	DVQ-F-001667 by Millet, DVQ-F-002339 by McClees & Germon	Flesh tones, dress	[17,23]
Prussian blue	-	DVQ-F-001829 by Claudet	Dress, flesh tones, hair	[17,22,23]
Barite	Not mentioned (white?)	DVQ-F-001829 by Claudet	Dress	[17,22,23]
Vermilion	-	Dag534	Flesh tones	-
Shell gold (in one case mixed with Prussian blue)	-	DVQ-F-001829 by Claudet, DVQ-F-000535	Jewelry	[22]
Bi white (Bi oxychloride) + Prussian blue	-	DVQ-F-000761	Crayon effect	[17]
Cochineal lake and Barite	Crimson	DVQ-F-001829 by Claudet	Dress (collar)	-
Cochineal and Prussian blue	The mixture suggested to obtain the richest purple color	DVQ-F-001829 by Claudet	Curtain	-
Iron oxide + Cochineal lake + Prussian blue	The mixture of light red and carmine is called "scarlet."	Dag504-3	Flesh tones	-
Indigo + Prussian blue + natural yellow pigment	-	DVQ-F-001829 by Claudet	Hair	-
Phthalocyanine and red SOP	Anachronistic, possible modification	Dag534	Flesh tones	-

Identifying the pigments present in the daguerreotypes is of paramount importance for their adequate conservation. Some pigments are particularly prone to damage upon electromagnetic radiation. For example, Prussian blue tends to fade or change its color to green as a result of light exposure [38], and its degradation might be induced by irradiation with a laser [39] during cleaning procedures. Similar phenomena may occur in cochineal lake, which tends to be less photostable when complexed to aluminum or tin mordants [28,40]. Light exposure may also induce changes to vermillion pigment (HgS) when in the presence of chlorine (Cl), an element that can be present in traces in daguerreotype plates as a result of the production process [41]. Additionally, the sulfur contained in vermillion can contribute to the plate's corrosion due to its sulfur content. Thus, when exhibiting or storing those daguerreotypes, constant monitoring is required.

Particular attention must be paid to the presence of bismuth white in his oxychloride variant. Its chlorine (Cl) content can induce alterations to the Ag plate. Moreover, bismuth oxychloride is known for its photocatalytic properties, yet, it only absorbs UV light; thus, limiting exposure to it avoids its photocatalytic activity [42].

The characterization of the binding media employed in colored daguerreotypes remains a particularly challenging issue to be addressed because (i) the pigments contained a very low concentration of binder and (ii) the fragility of the plate surface excludes any analytical technique that requires contact (e.g., FTIR-ATR). The development of adequate methodologies for identifying binders in hand-colored daguerreotypes is a line for future research.

5. Conclusions

In this work, nine hand-colored daguerreotypes were studied non-invasively with three spectroscopic techniques, XRF, μ-Raman, and μ-rFTIR. Their main advantage is the possibility to investigate the surface from the elemental and molecular point of view and when properly used without inducing any mechanical or photochemical damage in the highly fragile artworks.

The results reveal seven different colorants (i.e., Prussian blue, cochineal lake, barite, indigo, vermillion, iron oxide, shell gold) and their mixtures; some of them were not identified analytically before. Moreover, synthetic organic pigments (SOPs) were identified in one case, probably applied to restore the damaged colored surface of the daguerreotype. Additionally, we have enriched the previous knowledge by identifying the type of bismuth white pigment (Bi oxychloride) employed in one daguerreotype.

Our results complement the state-of-art knowledge of colored daguerreotypes and increase the number of colorants mentioned in the historical records identified in actual daguerreotypes. Up to now, very few mixtures of pigments have been reported in the scientific literature, and it is the first time that some of the colorants (i.e., indigo and vermilion) are identified in daguerreotypes. This study also expands the knowledge about the photographic production of three photographic studios: Désiré François Millet, active in Paris between 1840–1868; Antoine Claudet (1797–1867) active in London, the James E. McClees and Washington Lafayette Germon studio active between 1846–1855 in Philadelphia.

Author Contributions: Conceptualization, D.Q.B. and J.S.; methodology, D.Q.B., B.C., and J.S.; formal analysis, D.Q.B., S.I., and A.C.; investigation, D.Q.B., B.C., A.C., and P.B.; resources, R.F. and J.S.; data curation, D.Q.B., A.C., S.I., and J.S.; writing—original draft preparation, D.Q.B.; writing—review and editing, D.Q.B., P.B., B.C., A.C., S.I., S.R., R.F. and J.S.; supervision, B.C., A.C., S.R., R.F., and J.S.; project administration, J.S.; funding acquisition, J.S. All authors have read and agreed to the published version of the manuscript.

Funding: This research is part of the Diagnostica Non invaSiva e conservazione di daghErrotipi e altri materiali fotografici (DIAGNOSE) project co-funded by Tuscany Region, POR FSC 2014–2020-Axis Employment GiovaniSì (Grant No. CUP B53D21008070008), Museo Galileo, El.En. group, and the National Institute of Optics from the National Council of Research (CNR-INO), in collaboration with the Opificio delle Pietre Dure (OPD).

Data Availability Statement: Data available on reasonable request to the corresponding author.

Acknowledgments: The authors are very grateful to the Fondazione Alinari per la Fotografia (FAF) and Gabriele Chiesa and Giampaolo Gosio (Chiesa-Gosio collection) for access to the daguerreotypes studied. We would also like to acknowledge Grant Romer for the generous and valuable information regarding the Crayon daguerreotype. We also wish to thank Edoardo Tartaglia and Alessandra Santagostino Barbone from the Scientific Laboratory of the Opificio delle Pietre Dure for their support during the XRF and μ-rFTIR analysis.

Conflicts of Interest: The authors declare no conflict of interest.

Appendix A

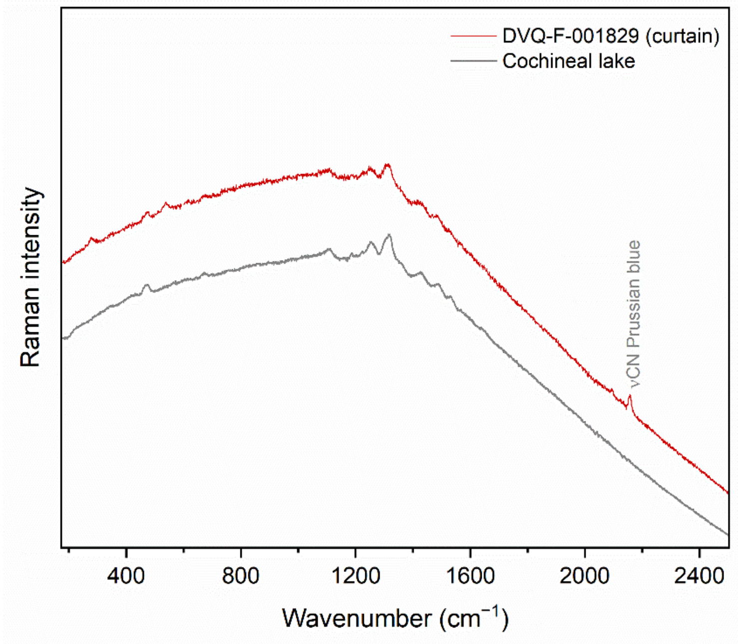


Figure A1. µ-Raman spectrum of the purple hue obtained by mixing cochineal lake and Prussian blue applied to the curtain in the daguerreotype DVQ-F-001829 by Claudet. According to Snelling (1849), the mixture of these two colorants produced the richest purple hue. The spectra are compared to the cochineal lake reference. The point of analysis is marked with a black dashed circle in in Figure 2c.

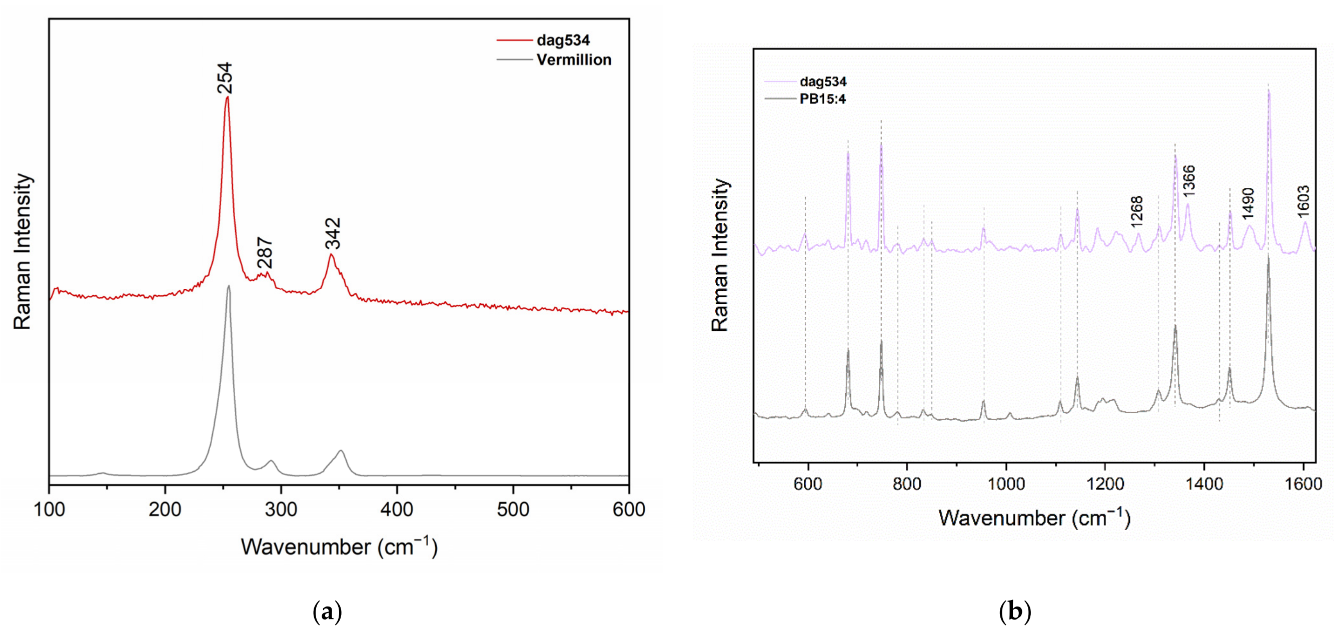


Figure A2. Raman spectra of (**a**) vermillion and (**b**) a mixture of SOPs (i.e., phthalocyanine blue and a red component) identified in the flesh tones of the daguerreotype 534. The spectra are compared to the corresponding reference material.

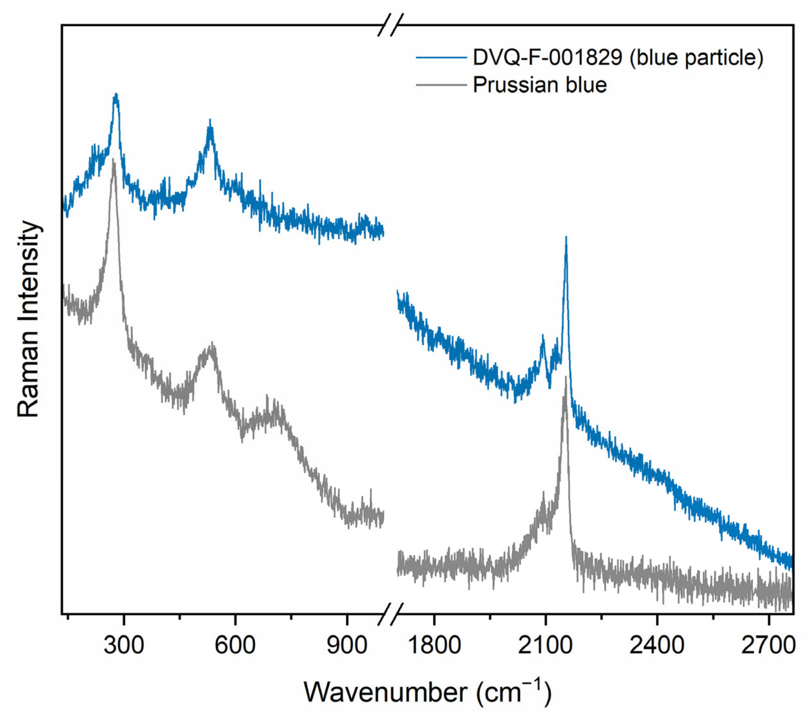


Figure A3. Raman spectra from a blue particle, compared to the reference of Prussian blue, in the hair of the portrayed woman in the daguerreotype DVQ-F-001829 by Claudet.

Appendix B

Table A1. Band assignment of the μ-rFTIR spectrum obtained from DVQ-F-001289.

This Work (cm^{-1})	Literature (cm^{-1}) [31,32,43]	Assignment
1627	1633	νC-C
1604	1615	-
1552	1565	ν_IC-C
1467	1466	$\nu_{I–II}$C-C
1407	1409	δCH + δOH
1384	1379	-
1282	1285	δOH
1246	1252–1255	νC-O catechol functions
1072	1070–1080	ρCH_3
1041	1046	ν-CC in a glucose unit
1006	1005	ρCH_3
977	983	-
895	885–890	ωCH2 + δOH
768	750	-
664	667	δCH

References

1. Cattaneo, B. (Ed.) Elvira Tonelli I Dagherrotipi. In *Il Restauro Della Fotografia. Materiali Fotografici e Cinematografici, Analogici e Digitali*; Nardini Editore: Florence, Italy, 2012; pp. 63–78.
2. Barger, M.S.; White, W.B. *The Daguerreotype: Nineteenth-Century Technology and Modern Science*; Johns Hopkins, pbk., Ed.; Johns Hopkins University Press: Baltimore, MD, USA, 2000; ISBN 978-0-8018-6458-2.
3. Barger, M.S. Daguerreotype Research at the Materials Research Laboratory, The Pennsylvania State University: 1979–1984. *Top. Photogr. Preserv.* **2009**, *13*, 137–146.
4. Ravines, P.; Li, L.; McElroy, R. An Electron Microscopy Study of the Image Making Process of the Daguerreotype, the 19th Century's First Commercially Viable Photographic Process. *J. Imaging Sci. Technol.* **2016**, *60*, 30504-1. [CrossRef]
5. Lehmann, A.-S. The Transparency of Color: Aesthetics, Materials, and Practices of Hand Coloring Photographs between Rochester and Yokohama. *Getty Res. J.* **2015**, *7*, 81–96. [CrossRef]

6. de Seauve, V.; Languille, M.-A.; Vanpeene, S.; Andraud, C.; Garnier, C.; Lavédrine, B. Replication and Study of the Colouration of Edmond Becquerel's Photochromatic Images. *J. Cult. Herit.* **2020**, *45*, 114–121. [CrossRef]
7. Smith, L. *Color and Victorian Photography*; Bloomsbury Visual Arts: London, UK, 2020; ISBN 978-1-00-308497-6.
8. Jacob, M.G. *Il Dagherrotipo a Colori. Tecniche e Conservazione*; Nardini Editore: Florence, Italy, 1992.
9. Buerger, J.E. *French Daguerreotypes*; University of Chicago Press: London, UK, 1989.
10. Nareid, H. A Review of the Lippmann Colour Process. *J. Photogr. Sci.* **1988**, *36*, 140–147. [CrossRef]
11. Seauve, V.; Languille, M.; Kociak, M.; Belin, S.; Ablett, J.; Andraud, C.; Stéphan, O.; Rueff, J.; Fonda, E.; Lavédrine, B. Spectroscopies and Electron Microscopies Unravel the Origin of the First Colour Photographs. *Angew. Chem. Int. Ed.* **2020**, *59*, 9113–9119. [CrossRef]
12. Romer, G.; Delamoir, J. The First Color Photographs. *Sci. Am.* **1989**, *261*, 88–99. [CrossRef]
13. Snelling, H.H. *The History and Practice of the Art of Photography*; Books on Demand: Norderstedt, Germany, 1849; ISBN 978-3-7481-8239-9.
14. Jacob, M.G. Colour and the Daguerreotype. *Daguerreotype J.* **2014**, *1*, 12–19.
15. Ruggles, M. Paintings on a Photographic Base. *J. Am. Inst. Conserv.* **1985**, *24*, 92–103. [CrossRef]
16. Ferguson, S.H. In Living Color: Process and Materials of the Hand Colored Daguerreotype. *Daguerreian Annu.* **2008**, 13–18.
17. Swan, A. Appendix II. Coloriage Des Epreuves: French Methods and Materials for Coloring Daguerreotypes. In *French Daguerreotypes*; University of Chicago Press: London, UK, 1989; pp. 150–163.
18. Ogayar Oroz, P. To Colour a Mirror. Identification of Hand-Colouring Techniques in Daguerreotypes by Studying and Reconstructing. Master's Thesis, University of Amsterdam, Amsterdam, The Netherlands, 2022.
19. Archives, T.N. The National Archives-Currency Converter: 1270–2017. Available online: https://www.nationalarchives.gov.uk/currency-converter/ (accessed on 18 August 2022).
20. Wall, A.H. A Manual of Artistic Colouring, as Applied to Photographs. In *Color and Victorian Photography*; Smith, L., Ed.; Routledge: London, UK, 2020; ISBN 978-1-4742-6420-4.
21. Kozachuk, M.S.; Avilés, M.O.; Martin, R.R.; Potts, B.; Sham, T.-K.; Lagugné-Labarthet, F. Imaging the Surface of a Hand-Colored 19th Century Daguerreotype. *Appl. Spectrosc.* **2018**, *72*, 1215–1224. [CrossRef] [PubMed]
22. Anglos, D.; Melesanaki, K.; Zafiropulos, V.; Gresalfi, M.J.; Miller, J.C. Laser-Induced Breakdown Spectroscopy for the Analysis of 150-Year-Old Daguerreotypes. *Appl. Spectrosc.* **2002**, *56*, 423–432. [CrossRef]
23. Golovlev, V.V.; Gresalfi, M.J.; Miller, J.C.; Anglos, D.; Melesanaki, K.; Zafiropulos, V.; Romer, G.; Messier, P. Laser Characterization and Cleaning of 19th Century Daguerreotypes II. *J. Cult. Herit.* **2003**, *4*, 134–139. [CrossRef]
24. Catalogo Immagini Archivio Fotografico-FAF Toscana. Available online: https://www.alinari.it/en/explore-unicum-objects (accessed on 24 October 2022).
25. Pozzi, F.; Lombardi, J.R.; Leona, M. Winsor & Newton Original Handbooks: A Surface-Enhanced Raman Scattering (SERS) and Raman Spectral Database of Dyes from Modern Watercolor Pigments. *Herit Sci* **2013**, *1*, 23. [CrossRef]
26. Osticioli, I.; Pagliai, M.; Comelli, D.; Schettino, V.; Nevin, A. Red Lakes from Leonardo's Last Supper and Other Old Master Paintings: Micro-Raman Spectroscopy of Anthraquinone Pigments in Paint Cross-Sections. *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.* **2019**, *222*, 117273. [CrossRef]
27. Innocenti, S.; Ricci, M.; Lanterna, G.; Fontana, R.; Striova, J.; Becucci, M. Direct Microextraction for Red Lakes Detection in Painting Layers by Raman Spectroscopy. *Eur. Phys. J. Plus* **2021**, *136*, 1081. [CrossRef]
28. Berrie, B.H.; Strumfels, Y. Change Is Permanent: Thoughts on the Fading of Cochineal-Based Watercolor Pigments. *Herit. Sci.* **2017**, *5*, 30. [CrossRef]
29. Kirby, J. The Reconstruction of Late 19th-Century French Red Lake Pigments. In Proceedings of the Art of the Past. Sources and Reconstructions; Clarke, M., Townsend, J.H., Stijnman, A., Eds.; Archetype: London, UK, 2005; pp. 69–77.
30. Trenary, M. Reflection Absorption Infrared Spectroscopy and the Structure of Molecular Adsorbates on Metal Surfaces. *Annu. Rev. Phys. Chem.* **2000**, *51*, 381–403. [CrossRef]
31. Pagliai, M.; Osticioli, I.; Nevin, A.; Siano, S.; Cardini, G.; Schettino, V. DFT Calculations of the IR and Raman Spectra of Anthraquinone Dyes and Lakes. *J. Raman Spectrosc.* **2018**, *49*, 668–683. [CrossRef]
32. Harris, M.; Stein, B.K.; Tyman, J.H.P.; Williams, C.M. The Structure of the Colourant/Pigment, Carmine Derived from Carminic Acid. *J. Chem. Res.* **2009**, *2009*, 407–409. [CrossRef]
33. Schlather, A.E.; Gieri, P.; Robison, M.; Centeno, S.A.; Manjavacas, A. Nineteenth-Century Nanotechnology: The Plasmonic Properties of Daguerreotypes. *Proc. Natl. Acad. Sci. USA* **2019**, *116*, 13791–13798. [CrossRef] [PubMed]
34. Hrnjić, M.; Hagen-Peter, G.A.; Birch, T.; Barfod, G.H.; Sindbæk, S.M.; Lesher, C.E. Non-Destructive Identification of Surface Enrichment and Trace Element Fractionation in Ancient Silver Coins. *Nucl. Instrum. Methods Phys. Res. Sect. B Beam Interact. Mater. At.* **2020**, *478*, 11–20. [CrossRef]
35. Brocchieri, J.; Scialla, E.; Sabbarese, C. Estimation of Ag Coating Thickness by Different Methods Using a Handheld XRF Instrument. *Nucl. Instrum. Methods Phys. Res. Sect. B Beam Interact. Mater. At.* **2021**, *486*, 73–84. [CrossRef]
36. Lomax, S.Q. Phthalocyanine and Quinacridone Pigments: Their History, Properties and Use. *Stud. Conserv.* **2005**, *50*, 19–29. [CrossRef]
37. Angelin, E.M.; Babo, S.; Ferreira, J.L.; Melo, M.J. Raman Microscopy for the Identification of Pearlescent Pigments in Acrylic Works of Art. *J. Raman Spectrosc.* **2019**, *50*, 232–241. [CrossRef]

38. Samain, L.; Gilbert, B.; Grandjean, F.; Long, G.J.; Strivay, D. Redox Reactions in Prussian Blue Containing Paint Layers as a Result of Light Exposure. *J. Anal. At. Spectrom.* **2013**, *28*, 524. [CrossRef]
39. Moretti, G.; Gervais, C. Raman Spectroscopy of the Photosensitive Pigment Prussian Blue. *J. Raman Spectrosc.* **2018**, *49*, 1198–1204. [CrossRef]
40. Saunders, D.; Kirby, J. Light-Induced Colour Changes in Red and Yellow Lake Pigments. *Natl. Gallery Tech. Bull.* **1994**, *15*, 79–97.
41. Radepont, M.; Coquinot, Y.; Janssens, K.; Ezrati, J.-J.; de Nolf, W.; Cotte, M. Thermodynamic and Experimental Study of the Degradation of the Red Pigment Mercury Sulfide. *J. Anal. At. Spectrom.* **2015**, *30*, 599–612. [CrossRef]
42. Kang, S.; Pawar, R.C.; Pyo, Y.; Khare, V.; Lee, C.S. Size-Controlled BiOCl–RGO Composites Having Enhanced Photodegradative Properties. *J. Exp. Nanosci.* **2016**, *11*, 259–275. [CrossRef]
43. Haberová, K.; Jančovičová, V.; Veselá, D.; Machatová, Z.; Oravec, M. Impact of Organic Binders on the Carminic-Colorants Stability Studied by: ATR-FTIR, VIS and Colorimetry. *Dye. Pigment.* **2021**, *186*, 108971. [CrossRef]