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Céline Daher, Marie-Angélique Languille, Anne de Mondenard, Martin Becka, Chantal Garnier, et al.. Spectroscopic characterization of selected French paper negatives (1843-1856): how to see through many processes?. *Microchemical Journal*, 2019, 149, pp.104069. 10.1016/j.microc.2019.104069 . hal-02465696

HAL Id: hal-02465696

<https://hal.science/hal-02465696v1>

Submitted on 25 Oct 2021

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Spectroscopic characterization of selected French paper negatives (1843-1856): how to see through many processes?

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Abstract

Photographic negative images on paper are certainly the earliest types of photographs ever produced, giving access to multiple photographic prints using a unique matrix. As early as 1841 in France, many variants of the paper negatives processes have been developed by skilled chemists and photographers covering a wide spectrum of practical and aesthetic concerns. Nowadays, due to their inherent historical and esthetical values, those negatives are getting an increasing interest from the art and museum community. However, their materiality has been poorly studied despite a large variety of processes involving many different chemicals and organic coatings; limiting our possibilities of identification, attribution or even preservation. The aim of this work was to develop a methodology to better assess the way those images were produced based on physical and chemical characteristics. A non-invasive approach combining optical, vibrational and X-Ray spectroscopies was implemented on a collection of 138 historical images between 1841 and 1856 from French collections. A survey was carried out on these negatives to provide a series of relevant physical data (dimensions, thickness, weight, *etc.*). Non-invasive reflectance FTIR showed great potentiality in revealing the presence of organic sizing (gelatin) or impregnation (wax). Multivariate analysis was applied on XRF data to help clustering negatives that have similar elemental composition and highlight relationships between makers. Finally, the morphological, physical and chemical results were all combined to answer historical questioning on the paper negative process.

Keywords

19th century photography; Paper negative process; XRF; reflectance FTIR; Multiple Correspondence Analysis

Introduction

The paper negative process is the first photographic process that provides multiply photographic prints. William Henri Fox Talbot developed the calotype process in 1840, and patented it in 1841, limiting its outreach to France at first [1]. Practical reasons such as the complex implementation of the process and the lack of image details limit also its use until the improvements made by Blanquart-Évrard from Lille. The Blanquart-Évrard process, presented at the Académie des Sciences in December 1846 [2] and published in December 1847 [3], similar to Talbot's, brought a simplification of the preparation steps. It does not yet have the same light sensitivity and details rendering as the daguerreotype, but it is ideal for travelers, as it allows sensitized sheets to be prepared in advance for a one-day excursion. The Blanquart-Évrard process was readapted and simplified by Guillot-Saguez as soon as 1847 [4]. The negative on paper is widely practiced in France for about ten years before being gradually replaced by the negative on glass plate having a higher light sensitive layer made of collodion and silver iodide and allowing a better image quality. However, due to its light weight compared to glass, paper still has an advantage, especially for travel photography. Throughout the 1850's, many practitioners would continue to search for the most appropriate papers and improve the sensitivity and translucency of the negative. Gustave Le Gray, who widely published his work in France, stimulated the practice of paper negatives. He taught in his studio and published his first treatise in 1850 [5]. Three increased editions followed, in 1851, 1852 and 1854 [6–8]. This photographer is above all the author of a revolutionary invention, the dry waxed process, which he describes in the 1851 treatise [6] and which he has protected with a sealed envelope deposited at the Académie des Sciences on February 25, 1851. This process allows a good conservation of the photosensitized papers for several days, which enable the photographers to shoot during longer journeys. Another famous photographer, Edouard Baldus, developed and used his own recipe as early as 1852 [9]. He chose English papers sized with gelatin and resin. Baldus also used its own method of sensitization.

More than 4100 negatives have been recently located in public collections in France, produced by some 61 practitioners [10]. These paper negatives present visually significant differences. However, data on their production mode remains incomplete, which limits the precise identification of the process. This research aims at assessing the materiality of French paper negatives. If the chemical evolution of the paper negatives in UK and France has been well studied based on 19th century technical literature such as technical treaties and scientific papers [11], few scientific studies of these paper negatives have been published especially on French paper negatives. Most of the paper negatives that have been characterized were period negatives produced with the Talbot process or

were contemporary negatives especially produced for scientific examination [12]. Scottish paper negatives produced from 1841 to 1850 have been characterized by Eremin *et al.* with X-ray fluorescence spectroscopy (XRF) [13]. Thanks to elemental composition determination, the authors suggest most of the analyzed negatives were sensitized with silver iodide and fixed with potassium bromide (predominant), sodium thiosulphate or potassium iodide. Daffner *et al.* [14] focused their work on paper negatives coatings. In particular, they studied Flachéron paper negatives. They have found a high resin content in the eight negatives they have analyzed. By comparison of FTIR spectra with FTIR references spectra, they identified it as sandarac resin and one sample analyzed with gas-chromatography confirmed that the varnish was composed of sandarac mixed with pine resin and other components.

In this work, we have analyzed a large set of historical paper negatives from French collections and produced by 18 photographers. Infra-red and X-ray fluorescence spectroscopies (FTIR and XRF), physical characterization and colorimetry were performed. The results provide information on the paper characteristics and the preparation of the paper negatives. Statistical treatment of XRF data help to cluster identify (i) proximities between paper negatives in terms of their elementary composition and (ii) specific steps in the process (fixing, enhancement). Finally, those findings are discussed from a historical perspective of photographic practices.

Experimental methods

Historical negatives

138 negatives from 18 photographers (Fig. 1) were analyzed. They belong to the *Bibliothèque nationale de France* (53 negatives), the *Société française de photographie* (20 negatives), the *Institut national d'histoire de l'art* (4 negatives), the *Bibliothèque des Arts décoratifs* (3 negatives), the *Musée Carnavalet* (7 negatives), the *Médiathèque de l'architecture et du patrimoine* (20 negatives), the *Musée d'Orsay* (26 negatives), and the *Bibliothèque de l'Institut de France* (5 negatives). They were selected in order to meet several requirements: (i) they are all attributed to a known photographer, (ii) they are more or less precisely dated, and if not, they at least belong to the 1845-1858 period, (iii) they are of various dimensions (iv) they were done using different types of lenses represent (portraits, landscapes, still life, etc), and finally (v) they are all in good conditions in order to be manipulated without the risk of causing damages.

Within this corpus, 22 negatives (3 by Le Secq, 11 by Le Gray and Mestral, and 8 by Baldus) are part of what was later called the *Mission Héliographique*, for which five photographers have been commissioned in 1851 by the historical monuments commission from the department of *Beaux-Arts*

of the French Ministry of the Interior to travel around the country and shoot specific French monuments [15]. Among these, two of Baldus' negatives are part of a panoramic view of Arles's amphitheater in 1851. Finally, some negatives were selected because they were made in extreme conditions: Du Camp was in Egypt and Middle East between 1848 and 1850, Greene was in Egypt as well, but later, in 1854/1855 and Campigneulles even later, in 1858.

Le Gray's Patent

In addition to this large corpus, Le Gray's patent "*Un genre de papier préparé pour la photographie*" from 1851 [16] that is kept at the *Institut national de la propriété industrielle* was examined. Along with the text that describes his process, three samples were added by Le Gray. They are examples of three steps of the preparation of the paper and that he refers to in his text. Sample n°1 "*papier ciré*" is a waxed paper, sample n°2 "*papier ciré ioduré*" is a waxed paper soaked in a potassium iodide solution, and sample n°3 "*papier ciré ioduré et nitraté*" is waxed, soaked in a potassium iodide solution, then in a silver nitrate solution.

Analytical techniques

Physical characterization

The length and height, thickness and mass of the negatives have been measured. Their surface was calculated using the first two features. The negatives were placed on a foamboard support to be weighted on a common laboratory scale (Navigator N34120, Ohaus, capacity 410g, precision 0.01g). Three measurements have been performed for each negative and the mean values, after subtraction of the support, are presented here. The thickness (Fig. 2-a) has been determined by using a Mitutoyo Absolute electronic digital micrometer (reference number 227-221) with a disk shape contact surface of 14.3cm in diameter and a selected pressure of 1,5N. The measurements (3 replicas) were performed on a side of the negative that looks original, with no additional paper bands or mending and repairs.

Colorimetry

Color measurements (Fig. 2-b) were performed using a portable sphere spectrophotometer X-Rite SP64 with the following set-up parameters: 4mm measurement area (6.5mm target window), illuminant type D65, 10° standard observer angle and specular component included. The L^* , a^* , b^* colorimetric coordinates were calculated in the 1976 CIE space. The measurements were done on two different spots of the negatives, one in a low-density area and one in a high-density area. A

polyester sheet (Mylar®) was placed in between the negative and the bottom part of spectrophotometer to avoid any risk of abrasion.

FTIR spectroscopy

FTIR in reflectance mode was performed using a Bruker Alpha portable spectrometer with a reflectance sampling module for contactless analysis and an integrated video camera (Fig. 2-c). The background spectrum was acquired using a gold mirror placed at a working distance of 15mm. Spectra were recorded between 7500 and 375 cm^{-1} , at 4 cm^{-1} spectral resolution and 200 scans per spectrum. The negatives were placed horizontally on a table and the FTIR spectrometer was positioned above the negative using a tripod, a slider and a ball head. The collected spectra were converted to absorbance mode using the Kramers-Kronig transformation (KKT). When necessary, acquired spectra were pre-treated by a water vapor and carbon dioxide compensation, using Bruker's OPUS software 7.0. Two areas were analyzed for each negative on the front (recto) and the back (verso) in the exact same locations. The analytical spots are of 5mm approximately and were selected in low densities in order to maximize the reflection: a dark area would absorb most of the IR beam and the resulted spectrum would show a weak signal.

X-ray fluorescence spectroscopy

XRF analyses were carried out using the ELIO spectrometer (XGLab) that is equipped with a Rh target ($L_{\alpha 1}$ at 2.696keV, $L_{\alpha 2}$ at 2.692keV, $L_{\beta 1}$ at 2.834keV, $L_{\beta 2}$ at 3.001keV and $L_{\gamma 1}$ at 3.143keV) and 1 mm beam size (Fig. 2-d). An integrated CCD camera and two laser pointers allow precise focus on the region of interest. All analyses were performed in atmospheric conditions, at 40kV and 100 μA , with a collection time of 200s. Points have been selected in order to overlap with the FTIR and colorimetric measurements, leading to at least four measurements on each negative. Some elements that are believed to be related to the instrument were observed on most of the spectra: titanium ($K_{\alpha 1}$ at 4,512keV), chromium ($K_{\alpha 1}$ at 5,414keV), nickel ($K_{\alpha 1}$ at 7,480keV), and copper ($K_{\alpha 1}$ at 8.046keV). A cut out foamboard structure was built to keep the analyzed negative horizontal and away from the table in order to avoid any spurious signal (see Fig.2-d).

Multivariate analysis

Multiple Correspondence Analysis (MCA) was performed on the XRF data using R software and *FactmineR* package. The principle is the same as for the more commonly used Principal Component Analysis (PCA), but the variables are qualitative: it is the presence or the absence of the elements that are here used as variables. The variables values "YES" (for the presence) or "NO" (for the absence) are called modalities. Then the proximity between individuals is studied in a low

dimensional space: two negatives are close to each other if they have similar elemental composition. As for PCA, the projection of the variables in the new space can also bring information about their relationships.

Results and discussion

The paper dimensions

The paper negative practitioners give a crucial importance to the paper and most of historical publications have a chapter dedicated to this material. They discuss the color of the paper, its homogeneity, its thickness, its opacity, its fineness, and also its sizing (gelatin, resin, starch) [17]. Some paper makers are sometimes named such as Lacroix [6], Canson [6], Marion [18], Rives (by *Blanchet Frères et Kléber*) [6,9], Saxe, or Whatman [6]; even though very few of the commercial papers are especially produced for photographic use [6,9]. The authors often regret the important heterogeneity in the paper batch, where sometimes only few paper sheets are workable.

It was possible to identify the paper used for some historical negatives just by the presence of a watermark. However, only “*Whatman*” watermark was observed on some negatives (Fig. 3-a), and most of the negatives were free of any watermark. Indeed, since negatives are prone to be printed, the watermark may appear on the print and compromise the image.

The thickness of all negatives was measured. The data are presented in Figure 3-b and in Table 1 along with the surface of each negative. The thickness of the negatives goes from 40µm to 170µm (even thicker than the ones measured by Daffner [19] from 58 to 142µm) and with a majority of the papers around 90µm.

One would assume that the paper thickness can be related to the size of the camera: a thin paper that would go through several bathes and a lot of manipulation would be more suitable for small negatives than bigger ones. But it does not seem to be confirmed: one of Le Secq’s negatives (see Fig. 3, dotted grey circle) is the biggest negative that was analyzed (38cm x 50cm) but its thickness is less than 80µm.

Identification of organic substances

The paper preparation is a key step of this process. There are many ways of preparing the paper before its sensitization. The most common techniques are a) a direct iodination of the paper with specific solutions as mentioned by Blanquart-Evrard [3] or Guillot-Saguez [4]; b) an additional sizing

of the paper with a proteinaceous substance [4,5,9,20], or waxing it using beeswax as did Le Gray [6] before the iodination; and finally c) an additional sizing combined with the iodination step (see for example Baldus' treatise [9]).

Le Gray's paper samples attached to the patent were analyzed in order to confirm the presence of beeswax. Figure 4 shows the three samples (Fig. 4-a) along with the reflectance FTIR spectra that were obtained on each sample (Fig. 4-b). The reflectance spectra present few bands in derivative shapes that hamper the reading of the bands' positions. Therefore, the KKT was performed and spectra equivalent to absorbance spectra are also presented. The spectra are similar for all samples, with bands specific of the paper support (highlighted in yellow) at 1166, 1112, 1062, and 1035 cm^{-1} and related to the C-O stretching vibrations of cellulosic materials. In addition, characteristic bands of beeswax are observed: C=O stretching vibrations at 1732 cm^{-1} , sharp C-H stretching vibration bands at 2915 and 2847 cm^{-1} and sharp combination bands of CH stretching and bending of aliphatic chains at 4314 and 4343 cm^{-1} [21]. These results are in agreement with Le Gray's patent and his other publications [6–8,16].

For the negatives, three characteristic spectra were obtained regarding the organic coatings. The data are gathered in Figure 5 and in Table 1. A first characteristic spectrum (observed on 22 negatives) showed only bands related to the paper support as shown on the grey spectrum (EI_19_2 Humbert de Molard) in Figure 5-a. The second characteristic spectrum (observed on 102 negatives) presents, in addition to the paper bands, vibrations related to the presence of beeswax (Fig. 5-a, black spectrum, EI_2_17 Nègre). But unlike Le Gray's patent, supplementary twin bands are visible at 1470 and 1463 cm^{-1} and 727 and 718 cm^{-1} , and are assigned to $-\text{CH}_3$ and C-H bending vibrations, and CH_2 - rocking vibrations of aliphatic chains, respectively [22, 23, 24]. When wax was identified on a negative, it was always present on both sides. One would assume that thick papers would be waxed, to ensure a print of rather good quality. Nevertheless, two of Humbert de Molard negatives have the thickest paper analyzed in this study (around 160 μm , see Fig. 3-b, dashed circle), but are not waxed.

The third type of spectra (visible on 14 negatives) is represented on Figure 5-b. In addition to the paper and beeswax features, two bands are observed around 1656 and 1542 cm^{-1} , and are assigned to the stretching vibration of C=O of amide I and the bending vibration of N-H of amide II respectively, showing the presence of proteins [24]. For some negatives, these bands are observed on both sides of the paper as visible on one of Baldus' negatives EI-4-1 (Fig. 5-b, black spectra), but for some others, the amide bands are only present on the recto of the negative *i.e.* on the image side, for example negative EI-19-8 by Humbert de Molard (Fig. 5-b, grey spectra).

The presence of a protein on the negatives may correspond to three distinct sources. The first one is very likely the presence of gelatin, especially on Baldus' images, as he recommends the sizing of the paper with gelatin in his 1852 treatise [9]. Also, gelatin was also used by paper manufacturers to size the paper in that period [25], but the amounts might be too low to be detectable using reflectance FTIR. Since Humbert de Molard's images are prior to 1852, he has likely used another substance, for example albumin. Indeed, in 1847, Niépce de Saint Victor has developed a process published in the *Comptes rendus de l'Académie des Sciences* of December 1847 and involving a glass sheet covered with an albumin solution, which can be applied on paper too [4]. The use of albumin is also mentioned in Blanquart-Evrard's treatise from 1851, as he recommends using egg white for paper sizing as part of the paper negative process [20]. Finally, in Le Gray's treatise from 1850, there is a process where fish glue is used to prepare the paper during the iodination step [5]. It is however impossible to distinguish between these proteinaceous substances using reflectance FTIR. For a better identification of this material, separation techniques would be necessary, but would require sampling the negatives.

Identification of inorganic substances

Identifying the chemical elements that are present in the negatives constitute a way of documenting the process used by the maker. For that purpose, XRF analyses were performed on Le Gray's patent samples, and on all the negatives, on several spots.

Sample 1 of Le Gray's patent is a waxed paper that was not sensitized. So, the elements visible on the XRF spectrum in Figure 4-c are actually contained in the paper. Indeed, calcium and iron are commonly found in 19th century paper [26] and may be linked to the use of fillers, or when found at low counts, to the water used for manufacturing the paper.

Several elements were identified on the negatives, and typical spectra are presented on Figure 6. The presence and absence of each element is indicated in Table 1. Some negatives such as negative 473-130 by Regnault (Fig. 6, black spectrum) contain only silver (Ag), which is the image material, in addition to calcium (Ca) and iron (Fe) from the paper support. In some cases, silicon (Si), potassium (K), additional Fe, cobalt (Co), nickel (Ni), and arsenic (As) (sometimes associated to bismuth (Bi) [27]) were identified, see for example negative DO-1982-700 by Mestral and Le Gray (Fig. 6, dark grey spectrum). This indicates the presence of smalt [26, 28] a blue pigment that was added to the paper as a whitening agent [13]. The last two examples presented in Figure 6 (EI-19-4 by Humbert de Molard and EI-1-12 by Le Secq) show additional elements that are related to the process: bromine

(Br) and iodine (I). The presence of Br can be explained by the use of potassium bromide (KBr) that was for a time considered as a fixing agent [9,29], or as a stabilizing agent that can be used during a journey, before returning to the studio and fix the image with a thiosulfate solution [6]. Potassium iodide (KI) is generally used for sensitizing the paper along with silver nitrate. Humbert de Molard has used it in a slightly different way: a non-photosensitive mixture of silver iodide (AgI) with an excess of KI was first applied, then the paper was sensitized with silver nitrate. However, potassium iodide should normally be eliminated in solution during processing. If the washing steps are not sufficient, an excess of KI might remain in the paper. But once the paper is sensitized, iodine is normally present as AgI. In that case, residual iodine in the negative would mean that the fixing step was done too quickly, or even that the sodium thiosulfate solution is less efficient because of multiple uses [30, 31]. Finally, Eremin *et al.* suggested that KI might have been used as a “fixing agent” (*sic*) [13]. Two other elements were occasionally identified: zinc (Zn) and lead (Pb). The presence of Pb could be explained by the addition of lead acetate that can be used to reinforce the image development as stated by Le Gray [6] and by C. Laborde in a letter from December 1850 that is presented at the end of Aubrée’s treatise [32]. Zn is present on three negatives with pretty low counts and the origin of its presence is still not clear. C. Laborde, in Aubrée’s treatise, recommends the use of zinc nitrate during the sensitization step along with silver nitrate [32], to make the paper more sensitive and to preserve the whites. Le Gray in 1854 also mentions zinc nitrate, and explains that zinc oxide precipitate in the paper, making it whiter [8].

MCA was performed on the XRF data and the projections of variables and individuals on the first two dimensions (that display around 69% of the total variance) are presented in Figure 7-a and -b respectively. The data used are the presence/absence of the elements that are presented in Table 1, which means that Ca, Fe and Ag, since they are common to all negatives were not used for this multivariate analysis. Regarding the variables, it is interesting to note that the elements related to the smalt in the paper are all grouped around 0.9 on Dim.1 and 0.0 on Dim.2: they are clearly correlated. The same observation is made for I and Br, which are both related to the photographic process. The projection of individuals is presented along with the variables’ modalities: for example, the presence of Br is represented by the “Br_Y” modality and its absence by the “Br_N” modality. The individuals that are close to a modality are affiliated to that modality, and the negatives that are located in a same plot have all the same elemental composition. For example, the group of four Flachéron (EI-35-6, EI-35-10, EI-35-14 and EI-35-15) and one Humbert de Molard (EI-19-9), located at (0.25;1.0) are close to the Pb_Y modality which means they contain Pb. However, another Humbert de Molard (DO-1982-102) contains Pb (see Table 1) but is not in the same group: the absence of I and Br in that negative moves it towards the I_N and Br_N modalities.

Historical considerations

The combination of data presented in Table 1 and Figure 7 helps in drawing general conclusions about the makers' practice between 1843-1856.

Regarding the size of the negatives, it is noticeable that the smallest ones are mainly portraits. For example, Regnault's negatives that are portraits are not bigger than 20cm x 16cm, (see also Fig. 2, pink dots) whereas the only two negatives (473-167 and 473-170) that are slightly bigger (43cm x 36cm) represent landscapes. This is classic in 19th century photography: the frames sold for portraits are only of small dimensions as presented in Derogy's [33] catalog of photographic materials in 1860 (see Fig. 3-c). This is a consequence of the use of wide-angle lenses allowing a short time exposure more suitable for shooting portraits. The same observation can be made about Humbert de Molard's negatives, the two smallest are the one representing his daughter (PHO-1980-261) and a bearded man (EI-19-3). In ancient treatises, the thickness of the paper is discussed regarding the portrait/landscape representation, as Le Gray mentions in his 1851 treatise [6], he would choose a Whatman thin paper for portraits, and a thicker for landscapes: "*Pour opérer sans la préparation préliminaire, comme finesse de grain et solidité, je préfère à tous le papier Whatman légèrement glacé, dans les poids intermédiaires entre 6 et 12 kilogr. la rame, format coquille. Pour le portrait, le mince vaut mieux, et l'épais pour le paysage et les monuments.* [To operate without the preliminary preparation, for its fineness of grain and solidity, I prefer to all the slightly glossy Whatman paper, in intermediate weights between 6 and 12 kilograms the ream, [44cm x 56cm] format. For the portrait, the thin is better, and the thick for the landscape and the monuments]". However, no particular observation could be made regarding the relation between the paper and the subject, some very thick papers were used for portraits (see PHO-1981-2 by Nègre, 154µm) and pictures of landscapes were taken on rather thick papers (see MH-7480 by Mestral and Le Gray, 70µm).

The use of different papers can also be tracked by looking at their elemental composition, for example the presence of smalt in some negatives by Mestral and Le Gray during their journey for the *Mission Héliographique* in 1851. They started their travel in Blois then Chambord, and after several stops among them Carcassonne, they ended up in Le Puy, Brioude and Issoire [15]. The negatives that were taken at the beginning of their trip are free of smalt, but in Le Puy and Brioude, they contain smalt. Among the negatives representing Issoire, only one contains smalt. This shows that the makers have probably used different papers according to what was available on the multiple stages of their journey.

Baldus also used various papers, but in a panoramic view of Arles's amphitheater. Figure 8 outlines the four components of the view, two whole and two partial negatives (in Table 1, DO-1982-538 and DO-1982-539; and bp and bp2 respectively). Among these four parts, only the bottom band of paper (bp) is free of smalt. The two central negatives contain I and Br, and their color tends to more neutral colors as the a^* parameter is 0.89 for DO-1982-538 and 1.89 for DO-1982-539, whereas the two partial negatives are more reddish with the a^* parameter equal to 4.0 and 5.7 for bp and pb2 respectively. This correlation between the presence of halide and the redness of the negatives can be extended to the other images by Baldus: the a^* mean value is 1.6 for the ones that contain halides and 3.8 for the ones that do not (see Table 1). Also, by comparing Baldus negatives from 1851 with the ones from 1856, one can observe that most of the 1851 negatives contain halides while the 1856 negatives are exempted. This means that Baldus was somehow aware of the effect of halides on the image stability, and the fixing and washing steps were totally mastered in 1856.

Greene might have also been aware of the impact of I and Br on the image permanence. Indeed, among the negatives that were analyzed only the ones free of halides are waxed (see Table 1), Greene has likely post-waxed his stable negatives to print the images, in order to reduce the contrast for a better rendering of the details in the bright areas. However, it is not always easy to determine whether the wax was applied as a paper preparation step, or after the fixing of the negative, as a post-waxing step to print the positive image. Some makers are known for being Le Gray followers, for example Mestral, Le Secq, Le Dien or Nègre [34] they have likely pre-waxed their negatives, others did not wax their negatives, for example Bayard who was a pretty early maker.

Conclusion

In this study and for the first time, 138 negatives from French collections were analyzed using complementary techniques. The physical characterization (dimensions mass, and thickness) brought information about the chamber sizes and the kind of papers that were chosen by the makers. The FTIR analyses allowed the identification of the paper preparation (wax and/or proteins), and the obtained results helped to evaluate the sensitivity of the FTIR reflectance mode for detecting these substances in paper. XRF analyses completed the study with important results about several steps of the negative's process: from the sensitization to a final washing of even an optional reinforcement step. The multivariate analysis was clearly helpful to compare large amounts of data using a visual representation that groups negatives according to their elemental composition.

Within this 138 negatives corpus, our results show that the papers were in majority waxed with beeswax on both sides. The number of photographers that have re-sized the paper with a proteinaceous substance is smaller. As expected, this reflects, in particular, the early wide diffusion

of the Le Gray process whereas the Baldus process has been much less practiced. We were able to assign the origin of chemical elements to the paper itself or to the photographic process. The presence of bromine and/or iodine might have several origins that we have discussed: stabilization or fixing of the negatives. This study reveals very homogeneous productions of some makers as Nègre or Regnault (respectively 16 and 13 analyzed negatives) and, in contrast, evolutions in the practice of some makers, as Baldus who got rid of halides in his negatives over time.

The next step of this work is to focus on the stability of these negatives. Indeed, as discussed previously, many of the analyzed negatives still contain I or Br, two halides that if combined with Ag are light sensitive. Recent studies [35] show the importance of using micro-fading test to determine how sensitive is the negative, and that special care must be taken for exposing these negatives to avoid any degradation of the image. This is already an on-going study for a set of French paper negatives that were described in this paper.

Acknowledgements

The authors would like to thank all the people in French institutions who contributed to the success of this study: Patrick Lamotte and Philippe Bérard (*bibliothèque nationale de France*), Thomas Galifot, Fabrice Golec, and Odile Michel (*musée d'Orsay*), Paul-Louis Roubert (*société française de photographie*), Mathilde Falguière (*médiathèque de l'Architecture et du Patrimoine*), Catherine Tambrun (*musée Carnavalet*), Jérôme Delatour (*bibliothèque de l'institut national d'Histoire de l'art*), Béatrice Krikorian (*bibliothèque des Arts décoratifs*), Sylvain Besson (*musée Nicéphore Niépce*), Steeve Gallizia, Julie Randriambao, and Amandine Gabriac (*institut national de la propriété industrielle*). The authors would like to thank the colleagues who gave us access to some instruments: Xavier Gallet, and Olivier Tombret (*UMR 7194 CNRS - Histoire Naturelle de l'Homme Préhistorique*), François Mirambet and Eric Laval (*Centre de Recherche et de Restauration des Musées de France*). Clément Hado is thanked for his work on the historical background of the paper negative process. This study was based on a first collaboration with Sarah Freeman and Karen Hellman (J. Paul Getty Museum), and Art Kaplan (Getty Conservation Institute). This work was financially supported by *La fondation des Sciences du Patrimoine/LabEx PATRIMA* (ANR-10-LABX-0094-01).

References

- [1] S. Aubenas, P.-L. Roubert, M. Frizot, N. Le Guern, M. Durand, B. Racine, Primitifs De La Photographie : Le Calotype En France 1843-1860, Editions Gallimard, Paris, 2010.

- [2] « Procédés employés pour obtenir les épreuves de photographie sur papier », *Comptes Rendus hebdomadaire des séances de l'Académie des Sciences* (CR), 28 septembre 1846, t. XXIII, p. 639 ; id., 27 janvier 1847, t. XXIV, p. 117-123.
- [3] E. de Valicourt, *Nouveaux enseignements pratiques sur le procédé de photographie sur papier*, de M. Blanquart-Évrard, La librairie Encyclopédique de Roret, Paris, 1847.
- [4] *Comptes rendus hebdomadaires des séances de l'Académie des sciences*, Bachelier, Paris, 1847.
- [5] G. Le Gray, *Traité pratique de photographie sur papier et sur verre*, G. Baillièrre, Paris, 1850.
- [6] G. Le Gray, *Nouveau traité théorique et pratique de photographie sur papier et sur verre*, Lerebours et Secretan, Paris, 1851.
- [7] G. Le Gray, *Nouveau traité théorique et pratique de photographie sur papier et sur verre : contenant les publications antérieures et une nouvelle méthode pour opérer sur un papier sec restant sensible huit à dix jours*, Lerebours et Secretan, Paris, 1852. <http://www.e-rara.ch/doi/10.3931/e-rara-14789> (accessed February 19, 2019).
- [8] G. Le Gray, *Photographie. Traité nouveau des procédés et manipulations sur papier et sur verre*, Lerebours et Secretan, 1854.
- [9] E. Baldus, *Concours de photographie*, Victor Masson, Paris, 1852.
- [10] A. de Mondenard, *Calotype data : les collections publiques françaises comme sources*, (2017). <https://www.youtube.com/watch?v=kdeCP0rvmGo>.
- [11] R. Taylor, M. Ware, 'Pilgrims of the Sun' The chemical evolution of the calotype 1840–1852, *History of Photography*. 27 (2003) 308–319. doi:10.1080/03087298.2003.10441266.
- [12] K. Jennings, *Research into the conservation of nineteenth century paper negatives. A Research Project presented for the Andrew W. Mellon Fellowship The Advanced Residency Program in Photograph Conservation*, (2003).
- [13] K. Eremin, J. Tate, A. Morrison-Low, J. Berry, S. Stevenson, *Non-destructive analysis of Nineteenth century Scottish calotype negatives and salt prints*, *MRS Online Proceedings Library Archive*. 712 (2002). doi:10.1557/PROC-712-II10.2.
- [14] L.A. Daffner, "A transparent Atmosphere": The Paper Negatives of Frédéric Flachéron in the Harrison D. Horblit Collection, *Journal of the American Institute for Conservation*. 42 (2003) 425–439.
- [15] A. de Mondenard, *La Mission héliographique : Cinq photographes parcourent la France en 1851*, Monum, Éditions du patrimoine, Paris, 2002.
- [16] G. Le Gray, *Genre de papier préparé pour la photographie*, 12738, 1851.
- [17] M. Becka, *Le Gray en inventeur de la photographie : Sur les pas de ses découvertes. Le Gray as inventor of photography. following the path of his discoveries.*, Tours, 2002.
- [18] L.D. Blanquart-Evrard, *Des Papiers photographiques, procédés de M. Blanquart-Évrard et autres, avec notes de N. P. Lerebours.*, 1847.
- [19] L.A. Daffner, *Coatings on paper negatives*, in: *Coatings on Photographs Materials, Techniques, and Conservation*, American Institute for Conservation of Historic and Artistic Works, Constance McCabe, 2005.
- [20] L.D. Blanquart-Evrard, *Traité de photographie sur papier*, Librairie Encyclopédique de Roret, 1851.
- [21] C. Daher, K. Sutherland, H. Stratis, F. Casadio, *Paul Gauguin's Noa Noa prints: Multi-analytical characterization of the printmaking techniques and materials*, *Microchemical Journal*. 138 (2018) 348–359. doi.org/10.1016/j.microc.2017.12.014.
- [22] C. Miliani, F. Rosi, B.G. Brunetti, A. Sgamellotti, *In Situ Noninvasive Study of Artworks: The MOLAB Multitechnique Approach*, *Accounts of Chemical Research*. 43 (2010) 728–738. doi:10.1021/ar100010t.
- [23] T. Poli, O. Chiantore, M. Nervo, A. Piccirillo, *Mid-IR fiber-optic reflectance spectroscopy for identifying the finish on wooden furniture*, *Analytical and Bioanalytical Chemistry*. 400 (2011) 1161–1171. doi:10.1007/s00216-011-4834-5.

- [24] C. Invernizzi, T. Rovetta, M. Licchelli, M. Malagodi, Mid and Near-Infrared Reflection Spectral Database of Natural Organic Materials in the Cultural Heritage Field, *International Journal of Analytical Chemistry*. 2018 (2018) 1–16. doi:10.1155/2018/7823248.
- [25] Lacroix, Gaury, Application du collage à la gélatine, au papier mécanique continu, au moyen d'une machine, sans qu'il soit besoin de le couper avant le collage, 1BA10157, 1842.
- [26] M. Manso, M. Costa, M.L. Carvalho, X-ray fluorescence spectrometry on paper characterization: A case study on XVIII and XIX century documents, *Spectrochimica Acta Part B: Atomic Spectroscopy*. 63 (2008) 1320–1323. doi:10.1016/j.sab.2008.07.001.
- [27] L. Robinet, M. Spring, S. Pagès-Camagna, D. Vantelon, N. Trcera, Investigation of the Discoloration of Smalt Pigment in Historic Paintings by Micro-X-ray Absorption Spectroscopy at the Co K-Edge, *Analytical Chemistry*. 83 (2011) 5145–5152. doi:10.1021/ac200184f.
- [28] S. Freeman, The art and science of the paper negatives, in: *Real/Ideal: Photography in Mid-Nineteenth-Century France*, J. Paul Getty Museum, Karen Hellman, 2016.
- [29] C. Chevalier, *Recueil de mémoires et de procédés nouveaux concernant la photographie sur plaques métalliques et sur papier*, Paris, 1847.
- [30] J.M. Reilly, *The albumen & salted paper book: the history and practice of photographic printing, 1840-1895*, Light Impressions Corp., Rochester, N.Y., 1980.
- [31] C. Sessa, L. Barro, S.A. Centeno, H. Bagán, F. Carò, J.F. García, Investigation of the possible origins of sulfur in 19th century salted paper photographs by x-ray fluorescence spectroscopy, *X-Ray Spectrom*. 45 (2016) 176–184. doi:10.1002/xrs.2684.
- [32] C. Aubrée, *Traité pratique de photographie sur papier, sur verre et sur plaques métalliques*, Paris, 1851.
- [33] Derogy, *Prix courant des objectifs, appareils complets, produits chimiques et en général de tous les articles relatifs à la photographie, brevetés S.G.D.G., (1860)*.
- [34] A. de Mondenard, M. Pagneux, *Modernisme ou modernité. Les photographes du cercle de Gustave Le Gray*, Actes Sud, Arles, 2012.
- [35] K. Hellman, S. Freeman, *Seeing the negative: Display techniques for French calotypes in "Real/Ideal: Photography in France, 1847-1860" at the J. Paul Getty Museum, (2017)*. <https://youtu.be/P8C7JzBohDw>.

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Figure 5: Characteristic FTIR spectra of the organic coatings a) beeswax and b) proteins. Yellow blocks refer to the bands assigned to the paper, pink blocks refer to the bands assigned to beeswax, and blue blocks refer to the bands assigned to proteins. Spectra are presented with an offset for more clarity.

Figure 6: Typical XRF spectra obtained on the negatives. The 1 to 5 keV range is presented in an insert for more clarity. The peaks with an * are assigned to elements related to the instrument (see experimental section). The presence and absence of the elements for each negative is indicated in Table 1. Spectra are presented with an offset for more clarity.

Figure 7: Results of the MCA analysis, with the projection of a) individuals along with the variables' modalities, and b) variables on the first two dimensions (that display around 69% of the total variance).

Figure 8: Baldus's panoramic view of Arles antique theater composed of 4 pieces. The elemental composition of each piece is specified and discussed in the text.

Table 1: Dimensions, surface area, thickness, colorimetric parameters (L^* , a^* , b^*), presence/absence of beeswax and protein, and presence/absence of several chemical elements for all the analyzed negatives sorted by photographers

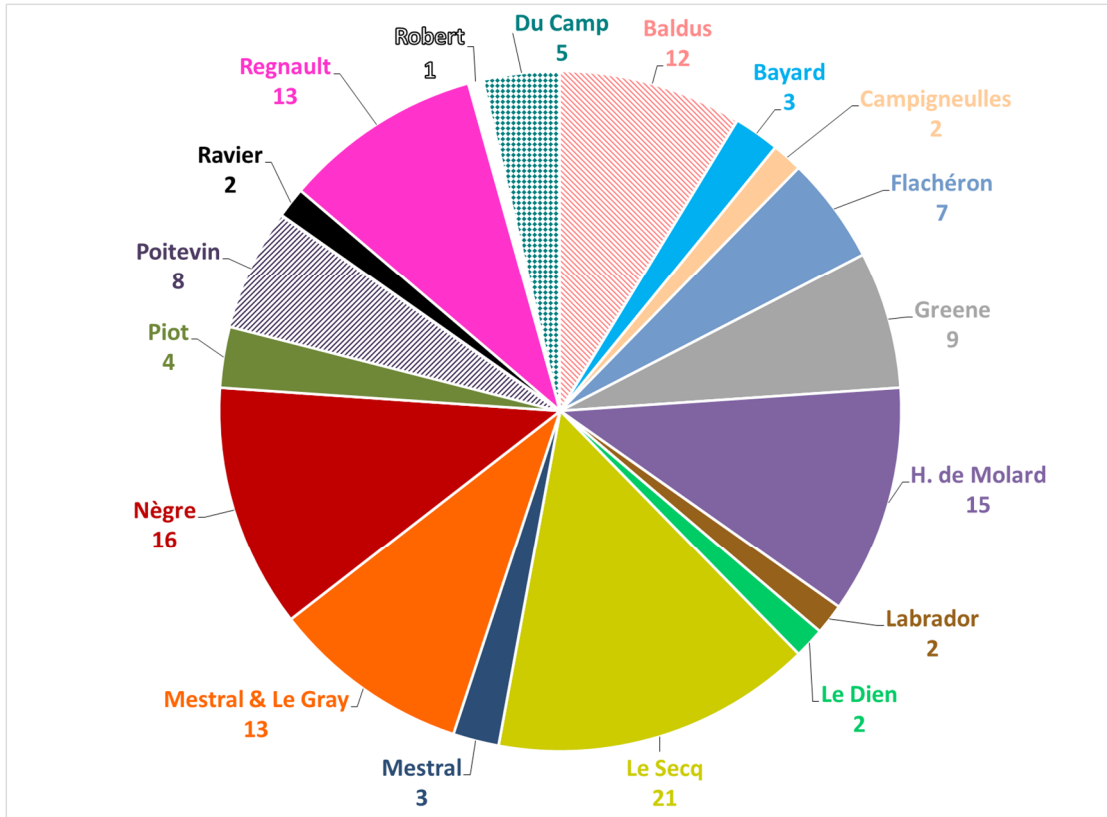


Figure 1: Number of analyzed negatives for each maker.

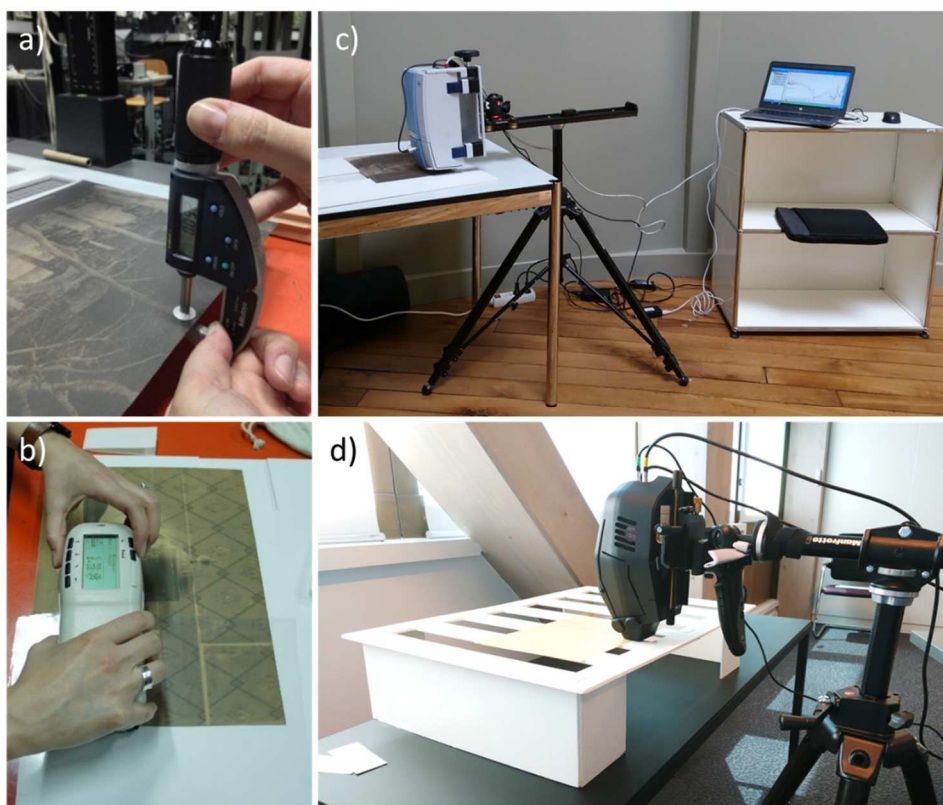


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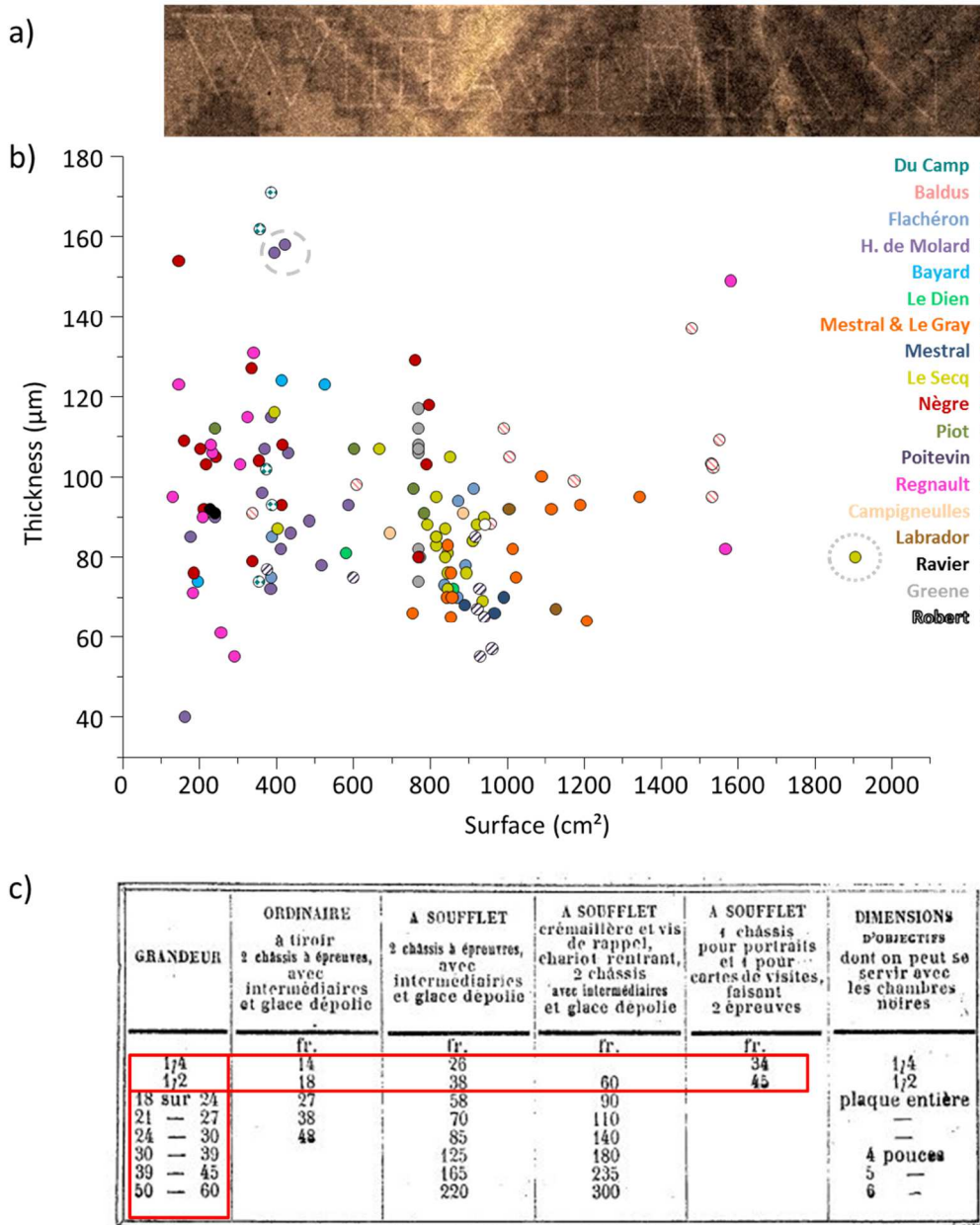


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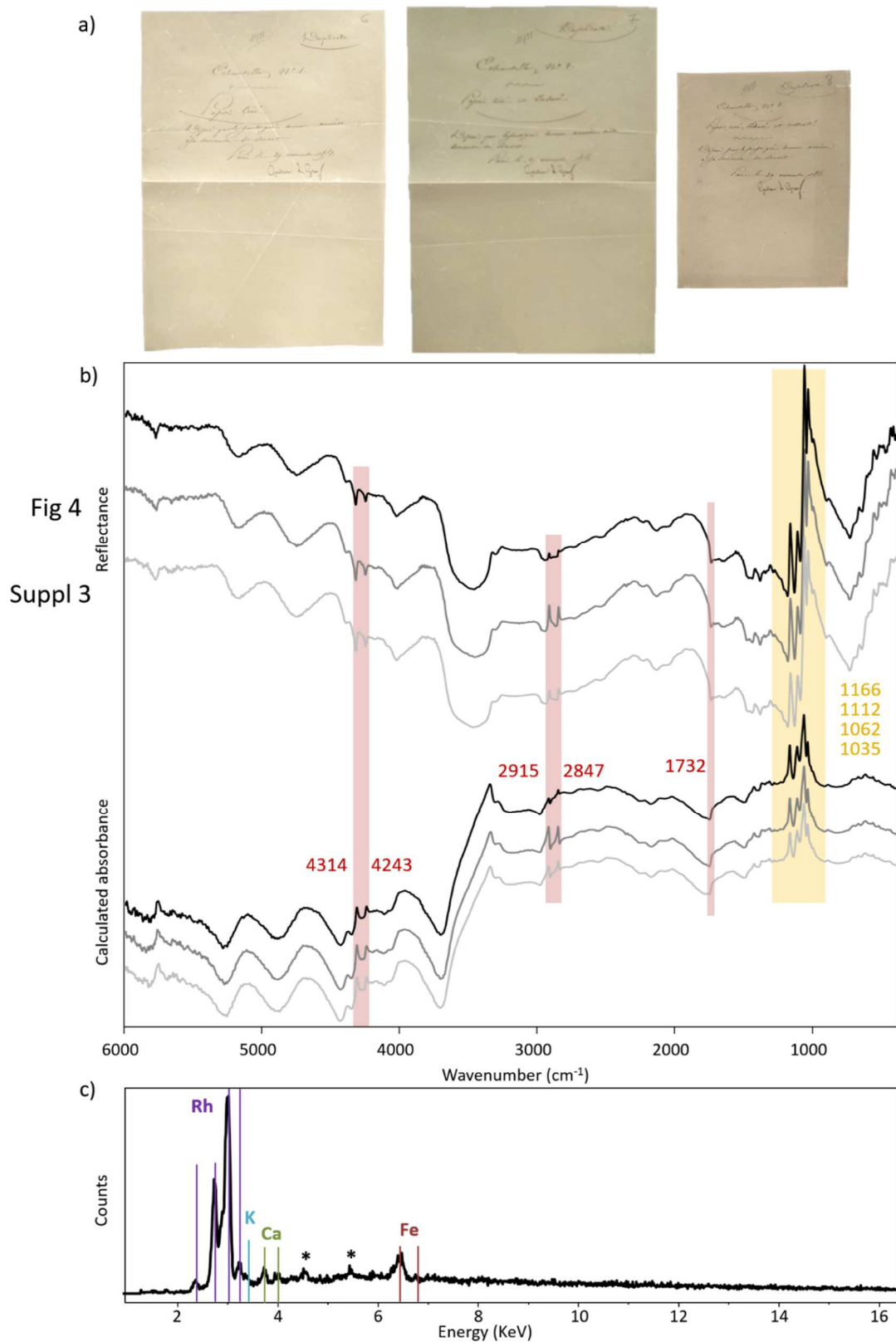


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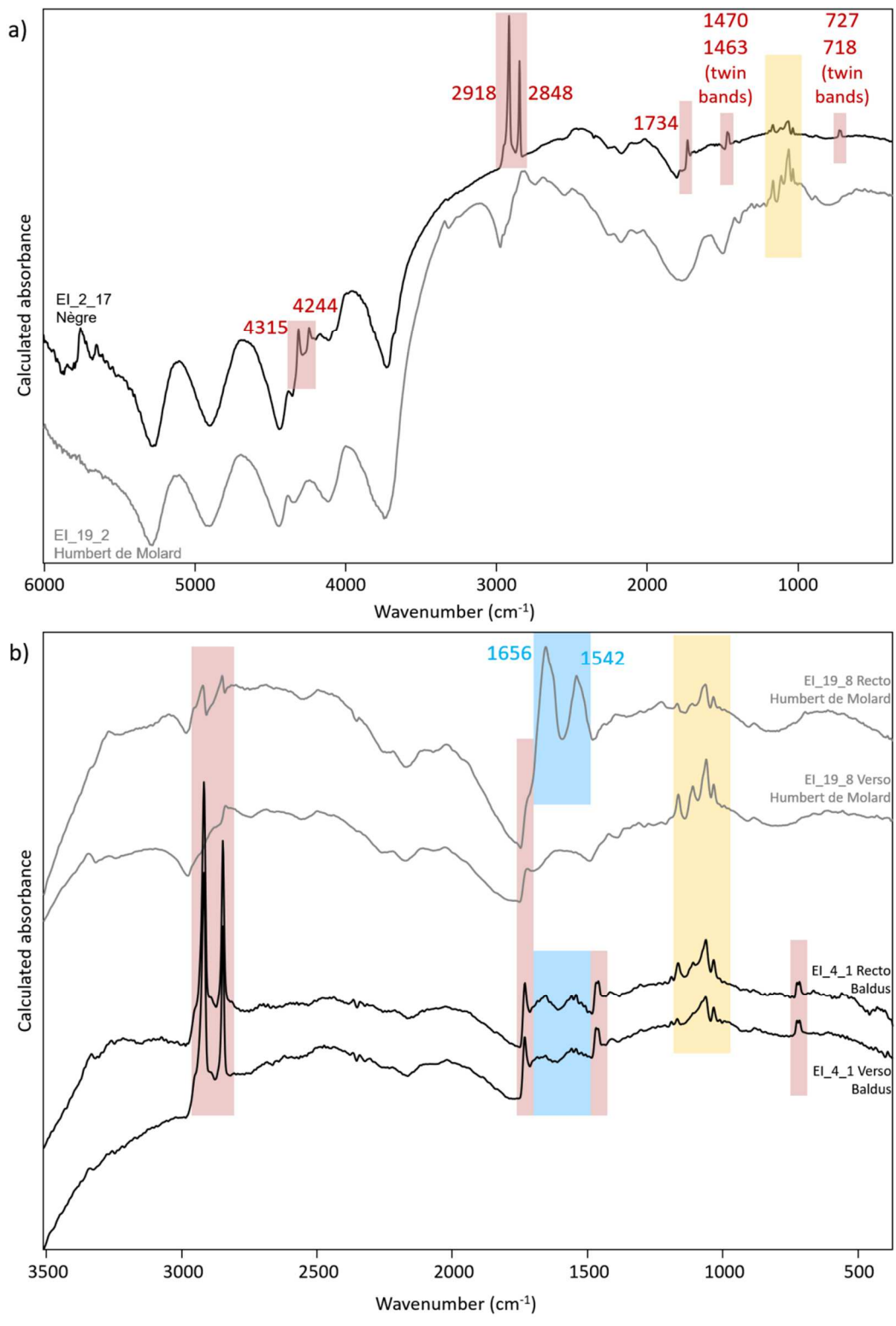


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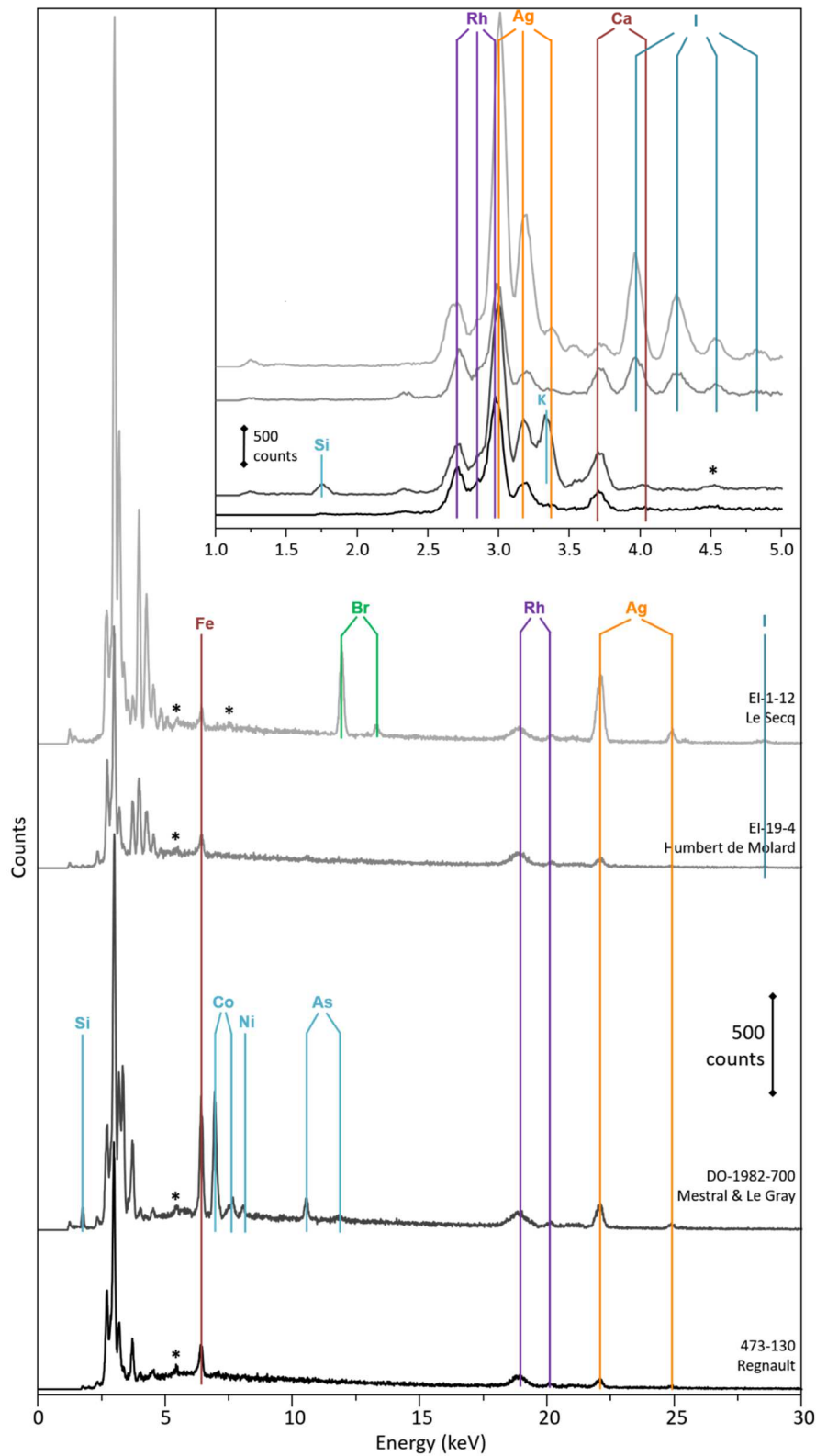


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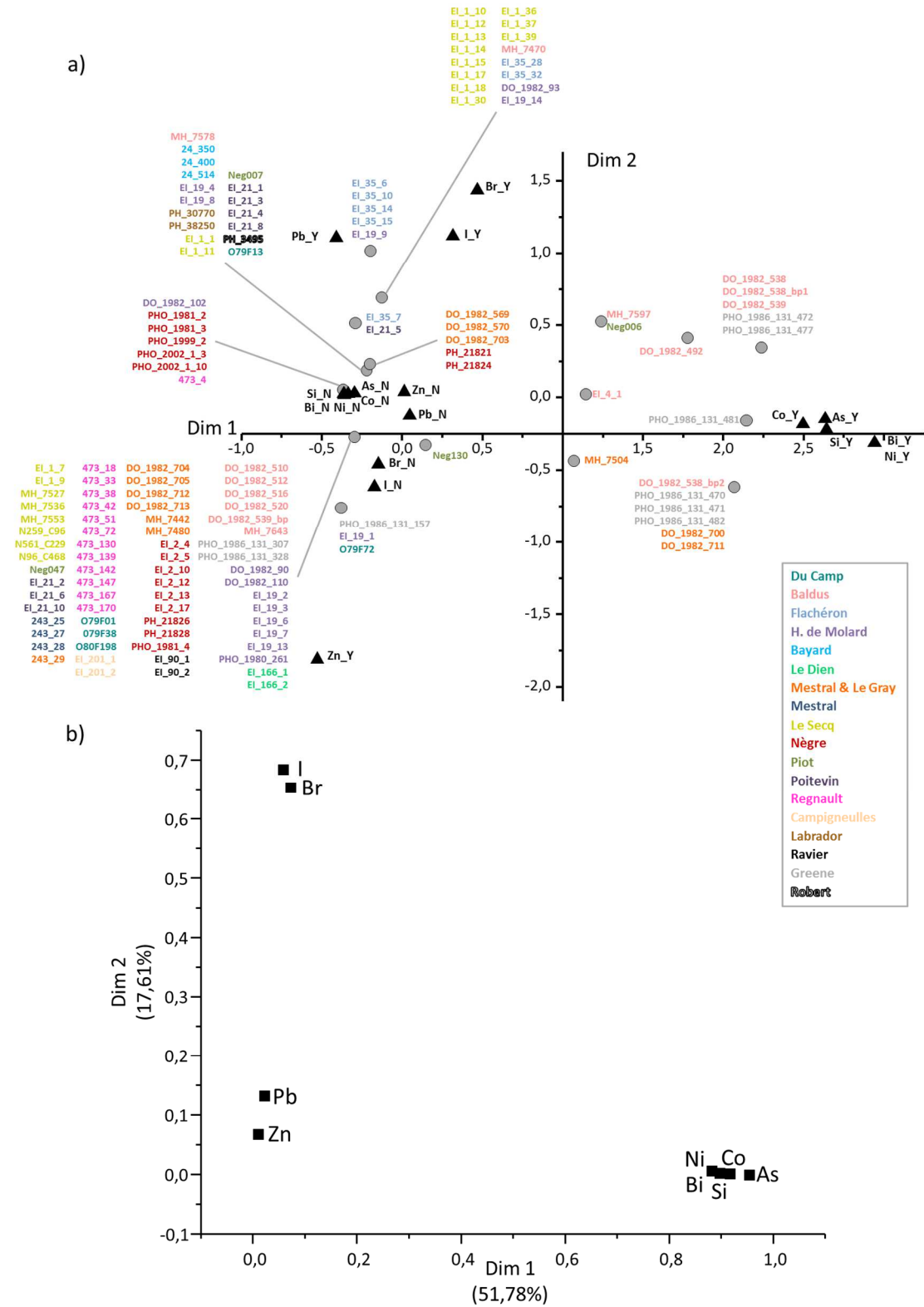


Figure 7: Results of the MCA analysis, with the projection of a) individuals along with the variables' modalities, and b) variables on the first two dimensions (that display around 69% of the total variance).

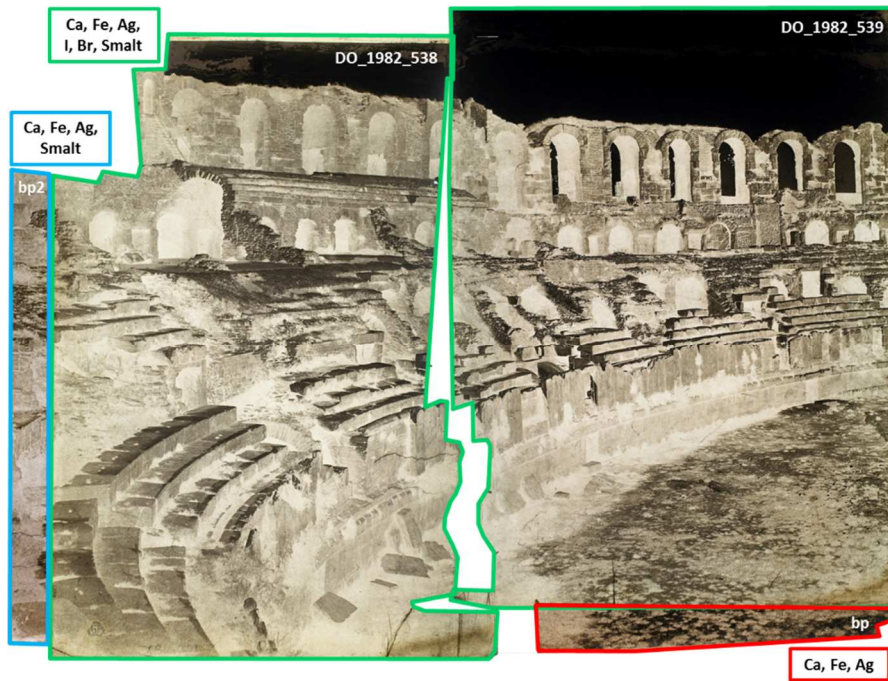


Figure 8: Baldus's panoramic view of Arles antique theater composed of 4 pieces. The elemental composition of each piece is specified and discussed in the text.

Author	Negative	Title	Date	Dimension (cm x cm)	Surface (cm ²)	Thickness (µm)	L*	a*	b*	Beeswax	Protein	Si	Co	As	Ni	Bi	I	Br	Pb	Zn
Baldus	DO_1982_492	Avignon (Vaucluse) - Vue générale	1851	26.4 x 36.3	958.3	87.7	44.74	2.07	11.44	✓	✓		✓	✓	✓	✓	✓			
	DO_1982_510	Lyon, les Brotteaux, inondations du Rhône	1856	34.3 x 44.6	1529.7	103.3	69.48	4.74	27.45	✓										
	DO_1982_512	Inondations du Rhône en 1856, Lyon	1856	34.5 x 45	1552.5	109.3	54.87	4.56	22.39	✓										
	DO_1982_516	Inondations du Rhône en 1856, Avignon	1856	34.3 x 44.8	1536.6	102.3	50.48	2.91	17.42	✓										
	DO_1982_520	Inondations du Rhône en 1856, à Avignon	1856	34.4 x 44.6	1534.2	95.0	42.63	2.64	11.36	✓										
	DO_1982_538	Arlés (Bouches-du-Rhône) - Amphithéâtre, vue intérieure	1851	38.9 x 25.5	991.9	112.3	65.59	0.89	21.99	✓	✓	✓	✓	✓	✓	✓	✓	✓		
	DO_1982_538_bp2	(additional band of paper #2) (see Fig. 8)				93.3	48.19	5.73	12.20	✓	✓	✓	✓	✓	✓	✓	✓			
	DO_1982_539	Arlés (Bouches-du-Rhône) - Amphithéâtre, vue intérieure	1851	32 x 36.7	1174.4	99.3	50.48	1.89	8.35	✓	✓	✓	✓	✓	✓	✓	✓	✓		
	DO_1982_539_bp	(additional band of paper) (see Fig. 8)				110.0	41.94	4.00	9.69	✓	✓									
	EI_4_1	Théâtre d'Arlés	possibly 1853	43.4 x 34.1	1479.9	137.3	58.76	3.14	22.89	✓	✓	✓	✓				✓			
	MH_7470	Nîmes : temple de Diane	1851	21 x 29	609.0	98.3	50.01	2.86	12.84	✓							✓	✓		
	MH_7578	Château de Fontainebleau	1851	19.6 x 17.2	337.1	91.0	62.38	2.24	18.30	✓							✓			
MH_7597	Orange : théâtre antique	1851	36.2 x 27.8	1006.3	105.0	50.58	0.29	9.16	✓	✓	✓	✓				✓	✓			
MH_7643	Inondations du Rhône : Villeneuve	1856	34.4 x 44.6	1534.2	103.0	54.03	3.76	18.75	✓											
Bayard	24_350	Fontaine des Evêques place St Sulpice	~ 1847	26 x 20.3	527.8	123.3	77.21	-0.03	25.28								✓			
	24_400	Vue des Batignolles	~ 1847	17.7 x 23.4	414.1	124.3	89.56	-1.57	21.20								✓			
	24_514	Trois personnages dans un jardin	~ 1845	12.6 x 15.6	196.5	74.0	82.02	-0.97	15.64								✓			
Campigneulles	EI_201_1	Vue générale des ruines avec maisons françaises, Louxor, Haute-Egypte	1858	21.2 x 32.8	695.3	86.0	48.93	2.48	8.85	✓										
	EI_201_2	Temple hypaetrale, Philae, Nubie	1858	32.6 x 27.15	885.0	91.0	51.29	2.69	9.51	✓										
Du Camp	O79F01	Alexandrie, Interieur du khan de l'hôtel d'Orient	November 17, 1849	22.7 x 15.8	355.5	74.3	55.18	7.58	24.22	✓										
	O79F13	Le Caire, jardin de l'hôtel du Nil	1848/1850	17 x 22.7	385.9	171.3	60.38	10.15	32.38	✓	✓						✓			
	O79F38	Le Sphyx	December 9, 1849	16.2 x 22	356.4	162.3	60.93	9.87	31.47	✓	✓									
	O79F72	Thèbes, Palais de Karnac Entrée septentrionale de salle hypostyle	May 5, 1850	17 x 22	374.0	102.0	55.71	4.24	20.81	✓	✓									✓
	O80F198	Palestine, coiffure des femmes mariées de Bethléem	August 14, 1850	22.4 x 17.4	389.7	93.3	71.45	4.21	26.03	✓	✓									
Flachéron	EI_35_6	Rome. L'arc de Titus	1850	25.7 x 34	873.8	94.0	51.11	6.58	21.72	✓							✓	✓	✓	
	EI_35_7	Rome. Socle de la colonne Trajane	1850	34 x 25.6	870.4	69.7	63.80	3.19	22.32	✓							✓		✓	
	EI_35_10	Rome, Capitole. Statues des Dioscures et église Santa Maria d'Aracoeli	1850	35 x 25.5	892.5	78.0	59.41	8.76	26.42	✓							✓	✓	✓	
	EI_35_14	Rome. Ponte Rotto et île Tibérine	1850	26.5 x 34.5	914.2	97.3	58.72	7.49	26.15	✓							✓	✓	✓	
	EI_35_15	Rome. Château Saint-Ange	1849	25 x 33.5	837.5	73.3	41.37	4.77	11.08	✓							✓	✓	✓	
	EI_35_28	Forum romain, vu vers le Capitole	1848	17.8 x 21.7	386.2	75.0	53.37	5.79	20.90	✓							✓	✓		
	EI_35_32	Basilique de Maxence	1849	17.7 x 22	389.4	84.7	52.24	4.68	18.67	✓							✓	✓		
Greene	PHO_1986_131_157	Le Caire, madrasa du Sultan Barkouk et tombeau	1854	24 x 32	768.0	80.0	48.89	3.82	10.98	✓										✓
	PHO_1986_131_307	Rue du Caire	1854	24 x 32	768.0	73.7	43.25	1.76	6.92	✓										
	PHO_1986_131_328	Sphinx de Giseh	1854	24 x 32	768.0	82.3	44.55	3.59	7.97	✓										

Author	Negative	Title	Date	Dimension (cm x cm)	Surface (cm²)	Thickness (µm)	L*	a*	b*	Beeswax	Protein	Si	Co	As	Ni	Bi	I	Br	Pb	Zn	
Greene (continued)	PHO_1986_131_470	Médinet-Habou, colosse de Ramsès III	1855	24 x 32	768.0	112.0	44.90	10.03	13.55	✓		✓	✓	✓	✓	✓					
	PHO_1986_131_471	Médinet-Habou, colosse de Ramsès III	1855	24 x 32	768.0	107.0	44.24	7.95	12.79	✓		✓	✓	✓	✓	✓					
	PHO_1986_131_472	Médinet-Habou, colosse de Ramsès III	1855	24 x 32	768.0	106.0	46.20	5.34	9.66			✓	✓	✓	✓	✓	✓	✓			
	PHO_1986_131_477	Colosses de Memnon	1854/1855	24 x 32	768.0	108.0	41.68	4.92	9.39			✓	✓	✓	✓	✓	✓	✓			
	PHO_1986_131_481	Colosses de Memnon	1854/1855	24 x 32	768.0	107.3	44.27	9.41	16.36	✓		✓	✓	✓	✓	✓	✓				
	PHO_1986_131_482	Colosses de Memnon	1854/1855	24 x 32	768.0	117.0	47.00	6.41	9.84			✓	✓	✓	✓	✓					
Humbert de Molard	DO_1982_90	Groupe d'arbres avec deux carrioles en premier plan	1847	23.3 x 17.7	412.4	82.0	53.34	4.49	17.21	✓											
	DO_1982_93	Jardin des Batignolles	1847	17.2 x 22.5	387.0	114.7	60.54	2.93	16.88	✓							✓	✓			
	DO_1982_102	Le Château de Falaise, vu de la vallée	1847	23.3 x 18.5	431.0	106.0	59.17	4.38	21.76	✓	✓								✓		
	DO_1982_110	Coin du jardin à Argenteuil	1847	23.8 x 21.8	518.8	78.3	43.81	1.51	9.21	✓	✓										
	EI_19_1	Femme assise	1845/1855	21.6 x 16.8	362.8	96.0	77.17	2.40	23.05	✓										✓	
	EI_19_2	Vieille paysanne assise	1845/1853	17.5 x 13.8	241.5	90.3	73.67	2.30	15.94												
	EI_19_3	Homme barbu assis sur un perron	1845/1855	11 x 16.1	177.1	85.0	42.75	0.95	8.11	✓	✓										
	EI_19_4	Vue d'Alger	1845/1855	26.7 x 22	587.4	92.7	88.09	1.46	14.39									✓			
	EI_19_6	Cultures et usine dans une vallée	1845/1855	19.2 x 19.3	370.5	106.7	65.25	10.35	32.01	✓											
	EI_19_7	Lagny	1845/1853	18.2 x 23.2	422.2	158.3	81.01	2.12	18.88												
	EI_19_8	Falaise	1845/1853	25 x 19.4	485.0	89.3	53.10	3.92	14.76	✓	✓							✓			
	EI_19_9	Maisons et arrière-cours	1845/1855	17.2 x 22.4	385.2	72.0	67.36	2.45	24.17									✓	✓	✓	
	EI_19_13	Deux charrues devant une barrière	1845/1853	22 x 18	396.0	156.3	81.62	2.05	19.38												
	EI_19_14	Paysan et cheval devant une barrière	1845/1853	18 x 24.3	437.4	86.3	60.45	-1.74	9.82	✓								✓	✓		
PHO_1980_261	Portrait de Julie, fille du photographe	1850	11.8 x 13.8	162.8	40.0	64.73	6.02	31.10													
Labrador	PH_30770	Passage de l'Elysée des Beaux-Arts, 18ème Paris		27.6 x 40.8	1126.0	66.7	53.58	5.14	21.98	✓											
	PH_38250	Barrière de Montmartre, place Pigalle, 9ème Paris		24.8 x 40.5	1004.4	92.3	51.54	5.29	20.44	✓											
Le Dien	EI_166_1	Chemin creux aux portes de Rome	1852/1853	25.4 x 22.9	581.6	80.7	65.18	6.00	24.70	✓											
	EI_166_2	Rome, vue de l'esplanade	1852/1853	25.4 x 33.9	861.0	72.0	57.71	7.17	20.47	✓											
Le Secq	EI_1_1	Port de Dieppe à marée basse	1851/1860	24.5 x 34.5	845.2	72.0	69.49	2.64	24.54	✓											
	EI_1_7	Falaises près de Dieppe	1851/1860	24 x 35.5	852.0	104.7	44.49	6.30	11.78	✓											
	EI_1_9	Dieppe, la tour Saint-Rémy du château	1851/1860	34.5 x 24.5	845.2	76.0	59.20	3.69	13.81	✓											
	EI_1_10	Dieppe, proue et mats	1851/1860	24 x 34	816.0	94.7	53.76	3.06	11.35								✓	✓			
	EI_1_11	Falaises près de Dieppe	1851/1860	34.5 x 24.5	845.2	80.7	54.59	3.92	16.98	✓											
	EI_1_12	Deux bateaux de pêche au sec dans le port de Dieppe	1851/1860	24 x 34	816.0	83.3	46.83	4.35	7.99									✓	✓		
	EI_1_13	Bateaux dans le port de Dieppe	1851/1860	24 x 35	840.0	79.7	47.69	3.93	10.87	✓									✓	✓	
	EI_1_14	Dieppe. Les jetées à l'entrée du port et la falaise	1851/1860	24 x 34	816.0	85.3	51.27	2.53	9.87											✓	✓
	EI_1_15	Bateau à quai dans le port de Dieppe	1851/1860	24 x 34	816.0	85.3	55.99	1.81	15.09											✓	✓
	EI_1_17	Harengs	1851/1860	35 x 24	840.0	87.3	56.12	6.26	18.34	✓										✓	✓
EI_1_18	Poires et raisins	1851/1860	26 x 35.5	923.0	88.0	44.04	7.39	14.75	✓										✓	✓	

Author	Negative	Title	Date	Dimension (cm x cm)	Surface (cm²)	Thickness (µm)	L*	a*	b*	Beeswax	Protein	Si	Co	As	Ni	Bi	I	Br	Pb	Zn	
	EI_1_30	Verre, pichet, pêche et raisins	1851/1860	26 x 35	910.0	84.0	39.06	4.97	7.87	✓							✓	✓			
Le Secq (continued)	EI_1_36	Hanap, chope et pipe	1851/1860	36 x 26	936.0	69.3	71.88	6.15	29.83	✓							✓	✓			
	EI_1_37	Pichet et verre de vin	1851/1860	35 x 26	910.0	84.3	35.32	3.93	11.79	✓	✓						✓	✓			
	EI_1_39	Nature morte : Pipe, hanap et chope	1851/1860	26.5 x 35.5	940.7	89.7	66.95	5.67	27.54	✓							✓	✓			
	MH_7527	Reims : transept nord	1851	31.9 x 20.9	666.7	107.3	58.91	4.24	17.64	✓											
	MH_7536	Reims : portail sud façade ouest	1851	22.2 x 18.2	404.0	87.0	57.81	5.89	21.03	✓											
	MH_7553	Saint-Leu d'Esserent	1851	23.8 x 33.3	792.5	87.7	59.39	2.48	16.47	✓											
	N259_C96	Reims : transept nord	1853	35.2 x 25.4	894.0	76.0	45.13	4.72	12.11	✓											
	N561_C229	Amiens cathédrale	1850/1851	17.7 x 22.3	394.7	116.3	46.97	5.14	18.69	✓	✓										
	N96_C468	Ruisseau en forêt : détail	~ 1855	38.1 x 50	1905.0	79.7	43.79	1.77	9.25	✓											
Mestral	243_25	Pencran	1852	35.5 x 27.9	990.4	69.7	57.47	5.21	18.67	✓											
	243_27	Bayeux	1852	27.9 x 31.9	890.0	67.7	59.60	6.14	20.41	✓											
	243_28	Lisieux : vieilles maisons	1852	35.3 x 27.4	967.2	65.7	57.11	5.75	17.38	✓											
Mestral & Le Gray	243_29	Blois : escalier	1851	37.6 x 32.1	1206.9	64.0	69.88	5.05	25.58	✓											
	DO_1982_569	Chambord (Loir-et-Cher) - Château, façade sud est	1851	26.9 x 38	1022.2	74.7	44.12	5.96	12.35	✓									✓		
	DO_1982_570	Chambord (Loir-et-Cher) - Château, façade nord-ouest	1851	22.6 x 33.4	754.8	66.0	49.81	4.81	12.22	✓									✓		
	DO_1982_700	Brioude (Haute-Loire) - Ensemble est, église Saint-Julien	1851	39 x 34.5	1345.5	95.3	55.08	4.18	19.04	✓		✓	✓	✓	✓	✓					
	DO_1982_703	Le Puy (Haute-Loire) - Vue d'ensemble du cloître, cathédrale Notre-Dame	1851	30.6 x 38.9	1190.3	92.7	62.16	4.38	20.55	✓									✓		
	DO_1982_704	Le Puy (Haute-Loire) - Détail d'une travée du cloître, cathédrale Notre-Dame	1851	34.6 x 24.7	854.6	64.7	65.27	5.90	22.04	✓											
	DO_1982_705	Le Puy (Haute-Loire) - Angle du cloître, cathédrale Notre-Dame	1851	34.2 x 24.7	844.7	82.7	60.83	6.10	21.58	✓											
	DO_1982_711	Issoire (Puy-de-Dôme) - Chevet, église Sainte-Austremoine	1851	38.7 x 26.2	1013.9	82.0	62.16	2.69	18.59	✓		✓	✓	✓	✓	✓					
	DO_1982_712	Issoire (Puy-de-Dôme) - Transept nord, église Sainte-Austremoine	1851	34.6 x 24.7	854.6	75.7	53.16	5.87	17.22	✓											
	DO_1982_713	Issoire (Puy-de-Dôme) - Façade nord, église Sainte-Austremoine	1851	28.6 x 39	1115.4	91.7	63.09	6.52	22.78	✓											
	MH_7442	Carcassonne : église Saint-Nazaire	1851	34 x 24.8	843.2	70.3	60.72	5.96	17.85	✓											
	MH_7480	Chenonceaux	1851	25 x 34.3	857.5	70.0	62.80	5.54	19.75	✓											
	MH_7504	Le Puy : porte Papale	1851	38.5 x 28.3	1089.5	100.3	67.92	-0.26	18.36	✓		✓	✓	✓							
Nègre	EI_2_4	Homme Barbu	1850/1855	23.6 x 17.5	413.0	93.0	32.75	9.84	6.98												
	EI_2_5	Homme Barbu	1850/1855	23.5 x 17.7	415.9	108.0	83.19	1.13	16.63												
	EI_2_10	Groupe sur une terrasse : deux hommes et une femme	1852	20.9 x 16.2	338.5	79.3	74.41	7.03	27.67	✓											
	EI_2_12	Nu	1850	17.7 x 13.7	242.4	105.3	41.88	1.43	8.29	✓											
	EI_2_13	Montmajour	1852	23.9 x 33.3	795.8	118.3	44.40	3.54	10.52	✓											
	EI_2_17	Reproduction de deux dessins de Meissonnier	1850/1855	23.9 x 32.4	774.3	79.7	54.16	11.64	29.33	✓											
	PH_21821	Ile Saint-Louis, travaux quai d'Orléans, 4ème arrondissement, Paris	1851	16.6 x 13.1	217.4	103.0	44.43	2.04	9.75	✓											
	PH_21824	Ile de la Cité, quais de la Seine, port de l'Hôtel de Ville, 4ème Paris	1851	10.1 x 15.8	159.5	109.0	53.92	3.90	16.11	✓											
	PH_21826	Ile de la Cité, quais de la Seine, 4ème arrondissement, Paris	1851	11.2 x 16.5	184.8	75.7	46.66	2.43	10.52	✓											
	PH_21828	Eglise Saint Germain l'Auxerrois, vers 1853, 1er arrondissement, Paris	1853	22.7 x 33.5	760.4	129.3	55.59	3.55	17.39	✓											

Author	Negative	Title	Date	Dimension (cm x cm)	Surface (cm ²)	Thickness (µm)	L*	a*	b*	Beeswax	Protein	Si	Co	As	Ni	Bi	I	Br	Pb	Zn	
Nègre (continued)	PHO_1981_2	Le petit chiffonnier appuyé contre une borne devant le 21 quai Bourbon à Paris	~ 1850	14 x 10.4	145.6	154.0	41.13	3.52	12.03	✓										✓	
	PHO_1981_3	Trois ramoneurs au repos quai Bourbon	~ 1851	16.8 x 20	336.0	127.3	38.78	3.14	8.32	✓										✓	
	PHO_1981_4	Etude d'après nature : nu allongé sur un lit dans l'atelier de l'artiste	~ 1850	11.3 x 18.7	211.3	92.3	55.98	3.62	17.50	✓											
	PHO_1999_2	Henri Le Secq et une petite fille faisant l'aumône au joueur d'orgue de barbarie	before 1853	16.5 x 21.5	354.7	104.0	68.23	3.66	18.75	✓											✓
	PHO_2002_1_3	Le Stryge	~ 1853	33.5 x 23.6	790.6	103.3	52.55	9.31	24.89	✓											✓
	PHO_2002_1_10	Cathédrale de Chartres, le portail nord	1851	16.8 x 12.1	203.2	106.7	64.87	7.05	30.14	✓											✓
Piot	Neg006	Saint-Remy de Provence	1852	33.5 x 23.4	783.9	91.0	79.81	-1.49	9.99			✓	✓	✓			✓	✓			
	Neg007	Vue de Florence	1850/1855	29 x 20.8	603.2	107.0	69.30	5.27	26.69	✓							✓				
	Neg047	Autoportrait		18.7 x 12.8	239.3	112.3	64.67	1.87	19.87	✓											
	Neg130	Fontaine à Rome	1850/1855	32.9 x 23	756.7	97.3	69.71	4.69	15.32				✓								
Poitevin	EI_21_1	Vue générale des salines de Gouhenans	1850/1855	26.4 x 35.6	939.8	65.3	47.19	3.50	15.09	✓							✓				
	EI_21_2	Salines de Gouhenans	~ 1850	26.8 x 34.7	929.9	55.3	47.20	3.50	12.58	✓											
	EI_21_3	Le presbytère de Conflans	1844/1855	27.7 x 34.7	961.1	56.7	58.55	5.30	20.99	✓							✓				
	EI_21_4	Donjon du château de Mondoubleau	1844/1855	33.8 x 27.3	922.7	67.0	47.73	1.29	10.79	✓							✓				
	EI_21_5	Satyre et Bacchante, terre cuite de Clodion	1844/1855	27.8 x 21.6	600.4	75.3	50.28	4.04	15.71	✓							✓		✓		
	EI_21_6	Cour de ferme à Conflans	1844/1855	26.6 x 34.5	917.7	85.3	40.78	4.66	10.48	✓											
	EI_21_8	Maisons le long d'un chemin (à Gouhenans ?)	1844/1855	28 x 33.2	929.6	71.7	49.23	3.58	13.90	✓							✓				
	EI_21_10	Église de Valréas	1844/1855	16.9 x 22.2	375.1	77.0	49.90	3.66	14.78	✓											
Ravier	EI_90_1	La rue du Marché-Vieux à Crémieu	1849/1850	17.7 x 12.9	228.3	92.3	64.94	5.48	12.08												
	EI_90_2	Bouquet d'arbres et chaumière derrière un mur	1849/1850	13.7 x 17.6	241.1	91.3	45.42	4.87	11.06	✓											
Regnault	473_4	Madame Regnault et enfants	1852	20.4 x 15.9	324.3	115.0	56.52	3.66	17.19	✓										✓	
	473_18	Madame Regnault et enfants	1852	12.1 x 10.8	130.6	94.7	76.97	1.88	25.29	✓											
	473_33	Madame Regnault et enfants	1853	16.1 x 14.6	235.0	106.3	59.11	5.41	22.85	✓											
	473_38	Autoportrait	possibly 1847	16.8 x 13.7	230.1	108.3	81.83	2.66	29.58	✓											
	473_42	Autoportrait	1844/1855	19.4 x 15	291.0	55.3	79.11	2.05	23.54	✓											
	473_51	Portrait d'Auguste Bavrais, Institut	possibly 1851	16.2 x 12.9	208.9	90.0	75.01	4.89	30.27	✓											
	473_72	Portrait Biot	1851	19.5 x 15.7	306.1	102.7	65.03	4.61	22.27	✓											
	473_130	Portrait	1850	15.1 x 12.1	182.7	70.7	63.74	4.48	22.00	✓											
	473_139	Portrait d'une servante	1852?	20.7 x 16.5	341.5	131.3	64.80	7.74	29.06	✓											
	473_142	Portrait	1850	19 x 13.5	256.5	61.0	76.65	2.12	19.53	✓											
	473_147	Portrait	1850	14.3 x 10.2	145.8	123.0	69.22	3.83	28.03	✓											
	473_167	Arbre	1850/1855	43.2 x 36.6	1581.1	148.7	68.87	5.57	19.82												
	473_170	Bords de Seine	1850/1855	43.3 x 36.2	1567.4	81.7	62.57	6.87	27.85	✓											
Robert	PH_3495	Le jardin de l'école des ponts et chaussées, 28 rue des Saints-Pères, 6ème Paris	~ 1850	29.0 x 32.5	942.5	88.0	65.92	1.78	19.09	✓		✓					✓				

Table 1: Dimensions, surface area, thickness, colorimetric parameters (L^* , a^* , b^*), presence/absence of beeswax and protein, and presence/absence of several chemical elements for all the analyzed negatives sorted by photographers