

Article

Non-Invasive Investigation of 19th-Century Photographs: Enrico Van Lint's Historical Collection in Pisa

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Abstract: Enrico Van Lint (Pisa, 1808–1884) was a very prolific photographer, active in Pisa in the 19th century where he had a prominent photographic atelier. He was a meticulous experimenter, investigating the evolving photographic activity of his historical period. While his early works included calotypes using Fox Talbot's methods, he rapidly adopted the collodion processes, becoming one of the most important Italian photographers that used this technique. At the present time, a vast number of examples of the works from Van Lint's ateliers are preserved and archived in Pisa, under the supervision of the Italian Ministry of Culture in the Photographic Archive of the "Soprintendenza Archeologia, Belle Arti e Paesaggio per le provincie di Pisa e Livorno" (SABAP). This collection is composed of positive prints as well as glass plate negatives, from both Van Lint himself and his colleagues. To this day, Van Lint's collection has not been studied using analytical techniques, and the identification of the photographic processes involved in the preparation of the positive prints has relied exclusively on thorough observation by historians and conservators. This provides a unique occasion for a first study of Van Lint's collection, using multiple non-invasive and non-destructive techniques (multispectral imaging, XRF, and FTIR) that can identify the photographic process used to make the positives, as well as highlight significant differences or degradation phenomena. In this preliminary work, we investigated a selection of ten positive prints, attributed to both Van Lint himself and later reproductions from the original glass negatives. The selected samples include prints previously classified as albumen prints and gelatin prints, displaying slight differences in conservation status as well as in print finish. This analytical approach allowed for a proper characterization of these Van Lint's prints, improving the historical and conservation knowledge to implement the best preventive preservation actions in the near future.

Keywords: photography; Van Lint; FTIR; multispectral imaging; XRF



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1. Introduction

1.1. Characterization of Photographs: State of the Art

Photography is a relatively recent technique for the portrayal of images when compared to paintings. Nevertheless, literature is rich in works that describe its evolution, the introduction of new materials and methodologies, its spread, and its cultural impact [1–6].

Due to the wide range of photographic processes introduced since the first half of the 19th century, it is easy to imagine the large number of materials and techniques employed.

As such, the correct identification and characterization of each photograph becomes a non-trivial task. While sometimes it is possible to find identifying features (signatures, symbols, watermarks, etc.), more often, this is not the case. Traditionally, the study of photographs has always been performed by expert art historians, using visual inspection paired with archival research [7–9]. In recent years, this knowledge has been integrated with physical and chemical analyses [10]. According to published literature, the most common non-invasive analytical technique used for the characterization and study of photographic prints is Fourier-transform infrared (FTIR) spectroscopy, generally in the attenuated total reflection configuration [11–13]. This allows for the investigation of photographic prints, and in particular, the determination of the organic binder, with minimal sample manipulation and measurement time.

1.2. Enrico Van Lint's Activity and the Historical Collection

Enrico Van Lint (Pisa, 1808–1884), sculptor and photographer, was a key figure in the early history of photography in Italy [14]. He began practicing photography in 1849 and, in May 1850, started creating his first paper negatives, the calotypes, following the method developed by William Henry Fox Talbot in 1840. He experimented with various types of paper and processes, in particular those perfected by Louis-Désiré Blanquart-Évrard (1847) and Gustave Le Gray (1851), and after the documented visit of the photographer Eugène Piot to Van Lint's shop along the Arno on the 10th of October 1851 [15], he began to use waxed paper in 1852. Between 1851 and 1853, he created more than 300 calotypes, meticulously documenting key technical information for each photograph: he recorded essential technical details almost always on the margin or the back of the calotypes, as well as the photographic equipment used. Several of them are dedicated to the Lungarni and the Piazza del Duomo. Van Lint recognized the ongoing evolution of photographic techniques during his time. In 1854, he realized the first complete photographic view of the city of Pisa, a general panoramic view of the walled city captured from the top of the Guelfa Tower in the Citadel, spread across four sheets. Van Lint's key calotype works are preserved in three rare albums created by his son Leonardo in 1907. These albums demonstrate Van Lint's pioneering role in calotype in Italy and offer insight into his early photographic interests (1850–1855), which can be compared to the later, extensive use of collodion and gelatin photography. He experimented with printing processes using carbon paper, developed by Louis-Alphonse Poitevin (1855) and Joseph Wilson Swan (1864).

1.3. Van Lint's Collodion Process Period

In 1855, Van Lint began experimenting with the collodion process using glass plates. He was a celebrated presence at various esteemed exhibitions, including those in Florence (1861), London (1862), Paris (1867), and Pisa (1868). After Enrico's death, the commercial activity of the photographic studio continued for some time under the care of his heirs. The last local guide to specifically mention Van Lint's business activity is the 1893 Da Scorno guide. Many of Enrico's works were lovingly preserved and curated by his heirs and conserved in Genoa in the Van Lint family archive.

A significant number of photographic prints and collodion glass plates were acquired by the Superintendence of Galleries in Pisa in the early 20th century. The most common photographic printing techniques that are contemporary with Enrico Van Lint's work are essentially three: the albumen print process [7,14,16], the silver gelatin, and collodion printing-out prints [1,10]. These last two papers, collectively known as "Aristotypes", were developed alongside innovations like the baryta coating, which made prints more uniform and brighter by masking the paper fibers. The collodion that was used as a binder for photographic negatives began to be used on paper in the early 1850s, and in 1866, the first

commercial printing-out paper was commercialized. The popularity of this paper rose in the 1880s and decreased in the 1890s. Gelatin printing-out papers were invented by Sir William Abney in 1882 and were commercialized by several companies beginning in 1884.

Indeed, the gelatin process quickly became dominant shortly after its introduction due to its lower cost, ease of storage and manufacture, and higher-quality photographic results. Gelatin prints can be divided into two types: printing-out paper (POP) and developing-out paper (DOP). Although their internal chemical content is the same, POP uses direct exposure to light to create the image-forming silver crystals, while DOP employs a chemical development process to generate and fix the final image. Interestingly, DOP was initially less appreciated due to its grey color, in contrast with the rich brown tones of earlier papers [6].

1.4. “Fondo Storico” of the Soprintendenza Archeologia, Belle Arti e Paesaggio per le Provincie di Pisa e Livorno

The Historical Photographic Archive of the “Soprintendenza Archeologia, Belle Arti e Paesaggio per le provincie di Pisa e Livorno” (SABAP) houses a rich and valuable collection of documentation related to the cultural heritage of northwestern Tuscany (the provinces of Pisa, Livorno, Lucca, and Massa Carrara) and the national museums of Pisa (San Matteo and Palazzo Reale), Calci (Monumental Certosa), Portoferraio (Museum of Napoleon’s Residences on Elba), and Lucca (Palazzo Mansi and Villa Guinigi). The initial inventory of the collected materials dates back to 1943, but the collection includes historical collections and funds from previous institutions. Part of this historical collection has been digitized and is accessible, but no scientific studies have ever been conducted. In the early 1990s, a restoration campaign began, alongside a cataloging and historical study of this still unknown photographic heritage. The first group of 91 photographic prints, all attributed to Enrico Van Lint, was restored by the paper conservator Piero Ungheretti from Livorno. The photographic prints showed typical alterations due to storage in unsuitable environments and materials: numerous insect infestations and yellowing on the surface of the paper. Yellowing and stains are often found, which can be attributed to the manufacturing and development stages: improper handling processes, such as residues from chemicals (fixing bath due to insufficient washing or exhausted fixer), can cause lightening or loss of detail in the image. The prints were glued with a plant-based adhesive onto acidic cardboard, which had to be removed. The prints were cleaned and placed in acid-free matting and durable cardboard folders for preservation.

1.5. Scope of the Work

In this paper, we present the results we obtained from the study and characterization of ten photographic reproductions from Enrico Van Lint’s historical collection in Pisa. We present the results of the multispectral imaging investigation of the photographs, coupled with a blind source separation (BSS) approach for feature enhancement, used for the first time to investigate this type of material. This allows for the identification of features of interest not visible to the naked eye, and that might be useful from a conservation point of view. Additionally, we performed spectroscopic analyses using Fourier-transform infrared (ATR-FTIR) and X-ray fluorescence (XRF) [17–20] that allowed us to characterize the materials used in the photographic prints, aiding in a correct classification of the photographic process used.

2. Materials and Methods

2.1. Selected Samples

In this study, we selected ten photographic prints from the first 91 restored prints of Enrico Van Lint's historical collection, under the supervision of the Ministry of Culture SABAP Pisa. The selection of the prints was made on the basis of two criteria: firstly, the presence of stamps which, together with the historical information found in the inventories of the Photographic Archive, attest to the certainty of their attribution to Enrico Van Lint; secondly, the assessment of the state of conservation of the prints after the restoration carried out in the 1990s.

In Figure 1, we present one of the selected photographic prints (h 23 cm × w 29.3 cm), named Photograph 5. It shows a panoramic view of Pisa with the Aqueduct of the Medici family. The main characteristics of the collotype printing are evident, such as the soft gradations of tone and the presence of rich and velvety blacks.

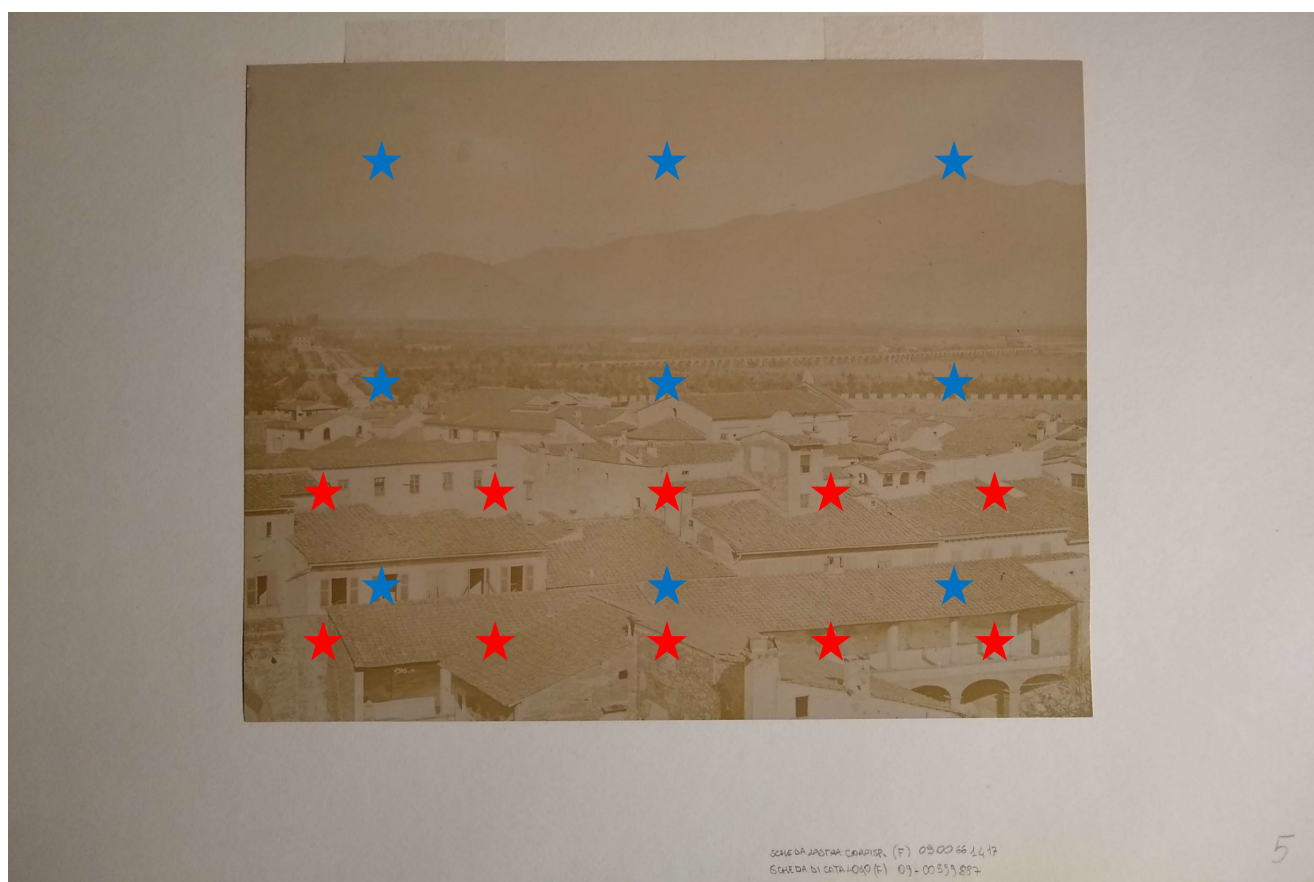


Figure 1. Photo 5 mounted on its support. The red stars mark the ATR-FTIR analysis spots, and the blue stars mark the XRF analysis spots.

Figure 1 also highlights the XRF and ATR-FTIR analysis spots in blue and red, respectively.

Each photograph was mounted with two strips of Japanese paper and methylcellulose on an acid-free cardboard passe-partout onto which the relevant archival data were written. Each print was protected using a plastic transparent sheet. The list of the selected prints is reported in Table 1. For a comprehensive description of the selected prints, see Supplementary Information.

Table 1. List of the selected photographic prints. The Process ID 2007 column shows the presumed photographic process identification carried out in 2007 in the National Catalog of the Italian Ministry of Culture, and the Literature 2004 column shows the identification of Giovanni Fanelli's works about Van Lint.

Name	Subject	Archive No.	Process ID 2007	Literature 2004
Photograph 5	Panoramic view	n/a	silver bromide gelatin/paper	albumen print
Photograph 7	Piazza dei Miracoli	00599935	silver bromide gelatin/paper	/
Photograph 11	Battistero	00600006	silver bromide gelatin/paper	/
Photograph 23	Sta. Caterina Church	00599891	silver bromide gelatin/paper	/
Photograph 26	Sta. Maria Church	0900599892	silver chloride gelatin/paper	albumen print
Photograph 29	Sta. Maria Church	0900600012	silver chloride gelatin/paper	albumen print
Photograph 39	Lungarno Pacinotti	0900599903	silver chloride gelatin/paper	/
Photograph 131	Palazzo dell'Orologio	0900601770	silver bromide gelatin/paper	/
Photograph 134	Schiff Palace	0059932	gelatin/paper	/
Photograph 135	Schiff Palace and Lungarno	00599933	gelatin/paper	/

2.2. Instrumentation

FTIR measurements were performed using a Frontier FTIR spectrometer (Perkin Elmer, Springfield, MA, USA) in ATR mode (resolutions 1 cm^{-1} , measurement area approx. 12 mm^2). Ten different measurement points were investigated on each print and, for each point, 32 scans were registered over the spectral range $4000\text{--}600\text{ cm}^{-1}$, subtracting the air spectra as background. The IR spectra were elaborated using the Spectragryph optical spectroscopy software v1.2.

XRF analyses were performed using an Elio portable XRF spectrometer (Bruker, Berlin, Germany) equipped with a $10\text{--}40\text{ keV}/5\text{--}200\text{ }\mu\text{A}$ X-ray tube (Rh anode, 1 mm collimated beam on the sample) and a large-area energy dispersive Si-drift detector (130 eV FWHM at Mn K). For each print, nine points were investigated, both in white and dark areas of the image. The measurement conditions were as follows: 60 s acquisitions at 40 keV and $80\text{ }\mu\text{A}$. The spectra were elaborated using OriginPro 2018 (OriginLab, Northampton, MA, USA) and the proprietary software XRF++, developed at CNR.

The multispectral imaging camera was a high-resolution Moravian G2-8300 (Tecnosky, Alessandria, Italy) (KAF-8300 CCD detector, imaging area $18.1 \times 13.7\text{ mm}$, pixel size $5.4 \times 5.4\text{ }\mu\text{m}$) with high dynamic range (16 bits). To reduce the electronic noise during image acquisition, the sensor was actively cooled. The camera was equipped with interferential filters, arranged in an automatic rotary wheel, with $\pm 25\text{ nm}$ pass-bands around the central wavelengths: $450, 500, 550, 600, 650\text{ nm}$ in the visible range and $850, 950, 1050\text{ nm}$ in the near-infrared. During the study, the photographs were illuminated using a halogen lamp emitting both in the visible and IR spectral range, positioned side

by side to the camera, and oriented to have a diffused and uniform illumination of the photographic prints.

The multispectral set of 9 images for each photographic print was registered, and the resulting stack was elaborated using advanced statistical methods such as the chromatic derivative imaging (ChromaDI) method [21,22], which operates on the three RGB images in the visible range and the IR image taken at 1050 nm to obtain a color image built from the differences of the original images according to the scheme:

$$\begin{cases} R' = IR - R \\ G' = R - G \\ B' = G - B \end{cases}$$

Other blind source separation (BSS) techniques were also applied [21,23,24], including the new interesting features finder (IFF) method [25], which has recently been introduced by our group for the analysis of multispectral image sets. This method is based on the determination of the extreme hyper-colors in the multispectral set (i.e., the ones that cannot be represented as linear combinations of other hyper-colors). The corresponding hyper-vectors can thus be considered as viable independent components for representing a new set of images, obtained by projecting the hyper-colors along these axes.

For image segmentation, the K-means method [26,27] was also used, dividing the image set into six clusters. The $K = 6$ parameter was empirically determined for obtaining meaningful clustering. When appropriate, the above-described statistical methods were applied using both conventional Euclidean metrics and spectral angle metrics. Spectral angle metrics is insensitive to luminance variations and in some cases can be preferable, being less sensitive to residual illumination irregularities.

3. Results and Discussion

3.1. Multispectral Imaging Analysis

The investigation of photographic material using multispectral imaging, paired with clustering and machine learning algorithms, is of particular interest from a conservation point of view. In fact, it can highlight existing damage or retouched areas that are invisible to the naked eye or by microscopic investigation. Moreover, using advanced statistical methods [28] can, in some cases, bring to light some hidden features (writing, stamps, watermarks, etc.) which can help with a correct and thorough historical collocation of the artifacts [29–32].

In this section, we will present a selection of images obtained during this study, which were deemed particularly interesting, while a more complete collection can be found in the Supplementary Information. Indeed, the complete elaboration of the collected multispectral images gave an output of around 100 new images for each photograph. However, only a few contained significantly valuable insights on the studied photographs.

The normalized orthogonalization of Photograph 7 acquisitions (Figure 2) shows a view of Piazza dei Miracoli in Pisa, with the Baptistery in the foreground and the Cathedral in the background. On the top right, the presence of what appears to be partial writing is detectable, which is not visible to the naked eye (see Figure S2). These are most likely numbers from a stamp on another support above, which have shifted over time and could cause conservation problems.

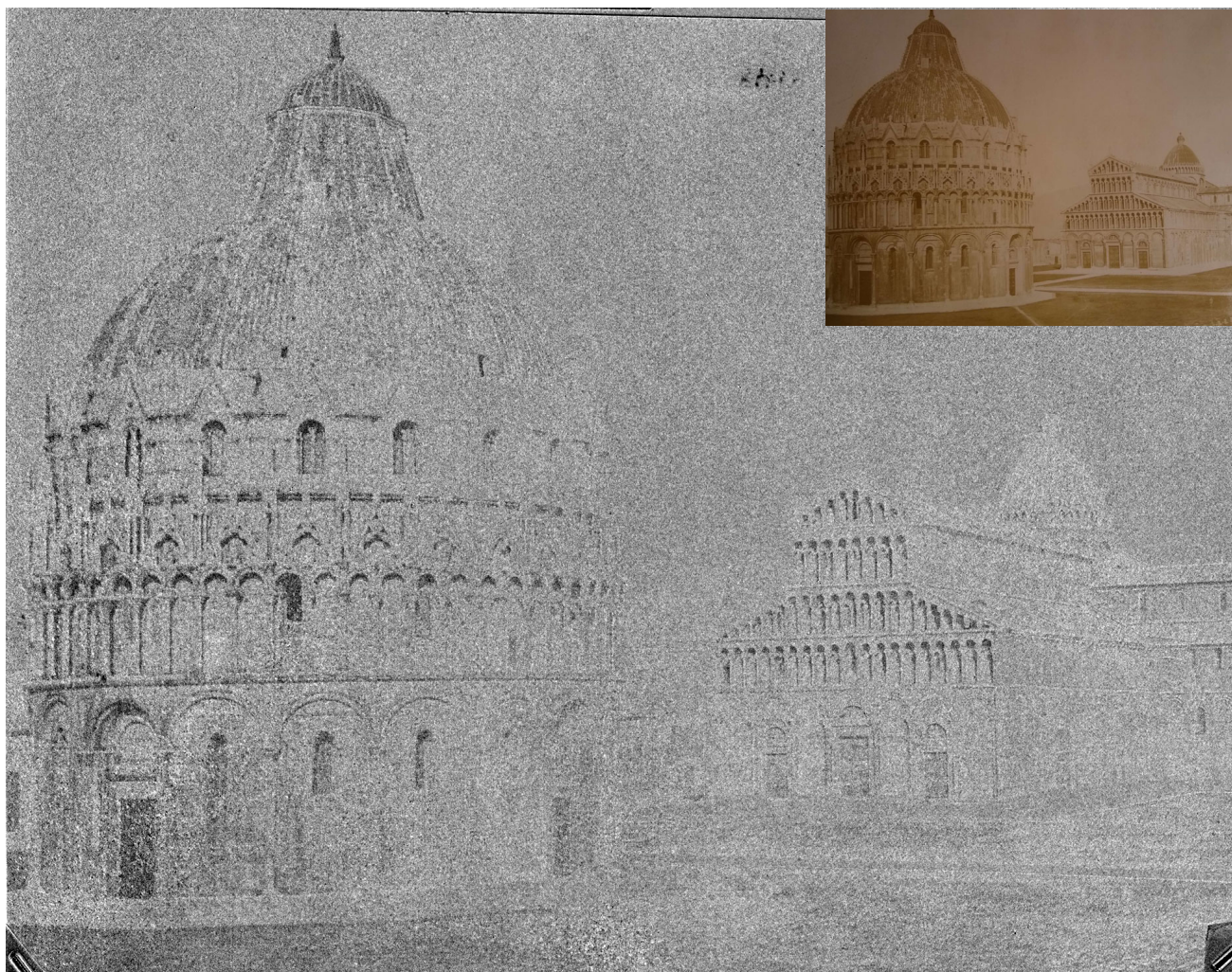


Figure 2. Normalized orthogonalization of Photograph 7 showing the partial writing in the top center-right.

In Figure 3, the principal component analysis (PCA) of Photograph 11 (Figure S1) acquisitions highlights the presence of a retouched area in the bottom right corner, characterized by a bright white response in the elaborated image. Additionally, some of the cracks of the negative plate are highlighted as well, while being relatively invisible in the original print.

One of the PCA images obtained for Photograph 29 (see Figure S5 for the original print) gives a particularly interesting image (Figure 4).

Here, we can observe pencil writings from the back of the print (which are highly visible in the IR band), as well as the presence of discolored spots in the top portion of the photograph, which can be correlated with the degradation of the surface layer as well as with the effects of an ink stamp (top left corner), which was left in contact with the print itself for some time.

A similar effect can be observed in Figure 5, showing one of the FI elaborations of Photograph 39 (Figure S6), where the transferred effects of a stamp can be clearly seen in the bottom left and center-right areas of the print.

Figure 6 shows the normalized IFF of Photograph 23 (Figure S3), where the presence of a probable masking effect due to an incorrect development of the negative is evident. The effect is called “ghosting,” and was used extensively by artists, including Van Lint, to

create shadows in prints by playing with the overlap of the cardboard during the printing process to accentuate the shadows.



Figure 3. Normalized PCA of Photograph 11 highlighting the retouched area in the bottom right.

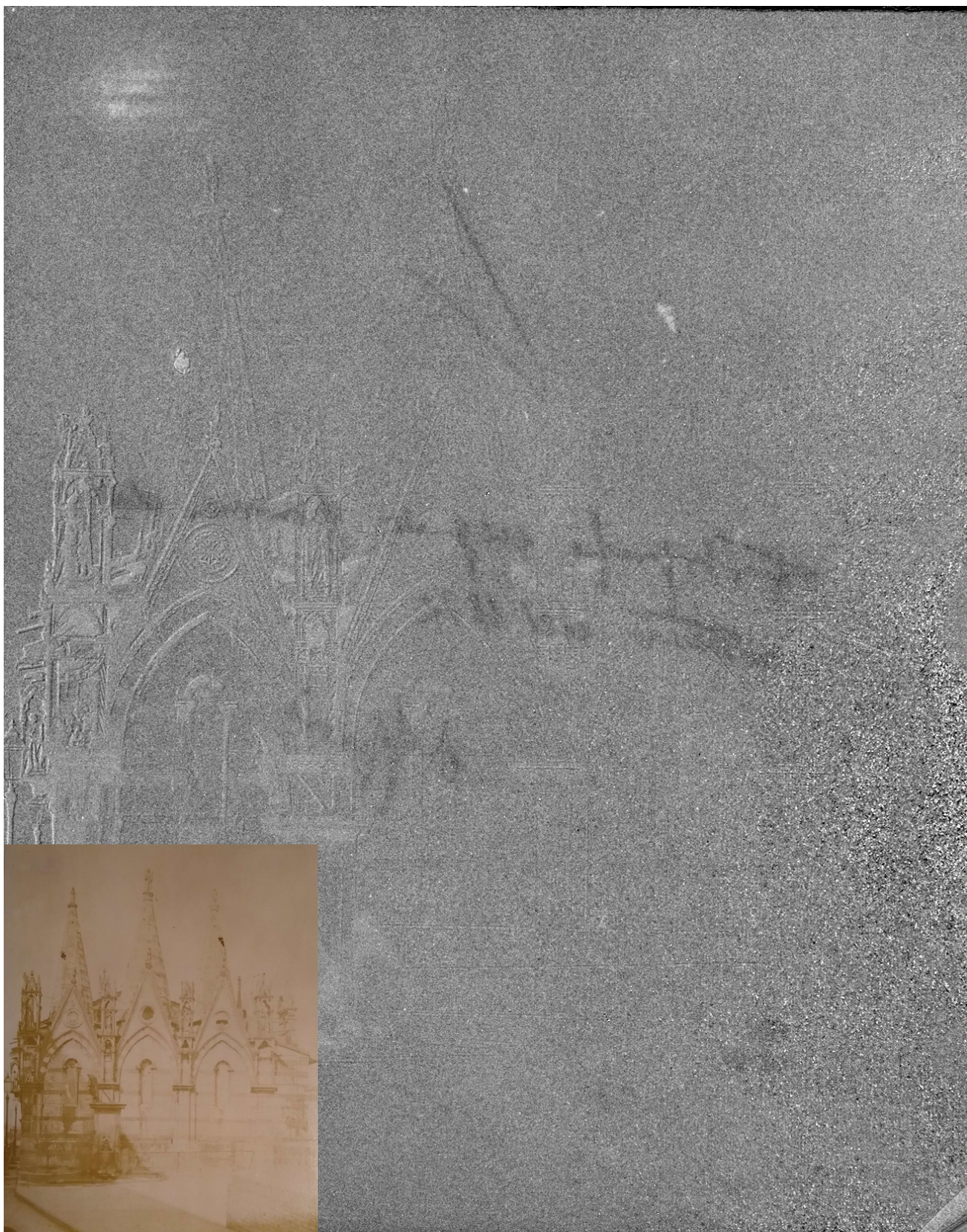


Figure 4. PCA of Photograph 29.

Lastly, in Figure 7, we present an interesting discovery from one of the FIs of Photograph 131 (Figure S7).

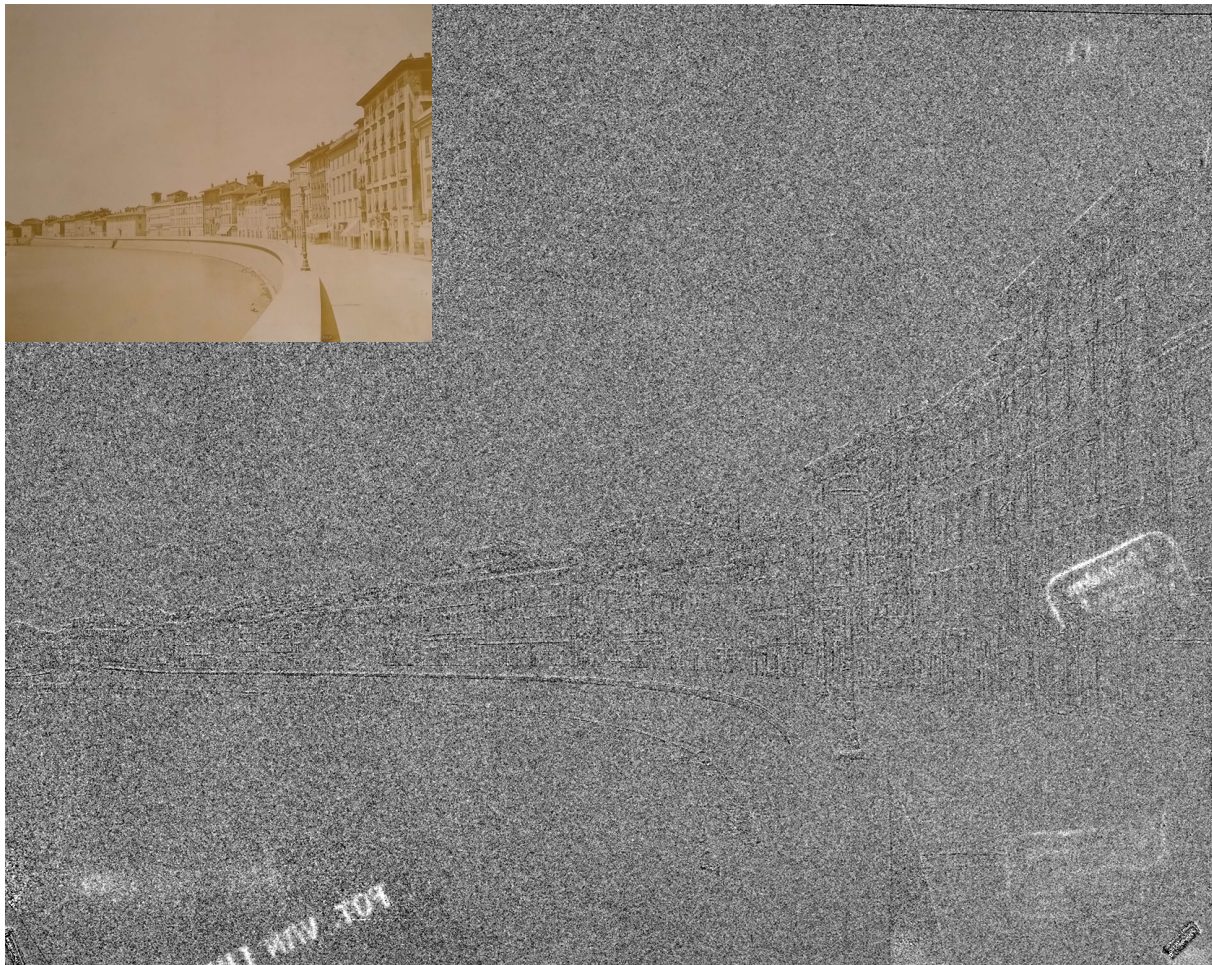


Figure 5. Normalized FI of Photograph 39 highlighting the transferred stamps.

In this image, we can clearly observe the presence of several straight lines, seemingly drawn across the photograph in a regular pattern. Indeed, these were identified as the traces left from pencil marks, which have now been erased. This suggests that this particular print was used at some point in the past as a reference for the making of possibly an architectural study or drawing of the Clock's Building located in Piazza dei Cavalieri in Pisa, which is the subject of this photograph. It should also be noted that one of Enrico Van Lint's original ateliers was located in the same building and can be seen in the bottom left corner of the structure.

3.2. XRF Analysis

The analysis of the photographic prints using XRF spectroscopy aimed at identifying the elemental content of each sample, as well as the possible presence of metallic trace impurities that might be of interest from a conservation and classification point of view.

A preliminary test was performed on Photograph 5 by using a 9-point grid along the entire surface of the photograph. The goal was to verify the homogeneity of the samples while performing XRF. A scheme of the selected points is reported in Figure 1.

Figure 8 demonstrates how the XRF spectra, taken at different points of the photograph's surface, show no significant difference between them, proving that the sample can be considered homogeneous for its elemental makeup.



Figure 6. Normalized IFF of Photograph 23; the orange lines highlight the presence of a probable masking effect due to an incorrect development of the negative.

Subsequently, for each print, two measurement spots were selected: one in a white/light area of the photograph and one in a black/dark area. A preliminary screening showed that the XRF spectra of the prints are very homogeneous regardless of the investigated area. For this reason, we deemed it sufficient, for this study, to select just two points for each sample. An example spectrum for Photograph 5 is reported in Figure 9.

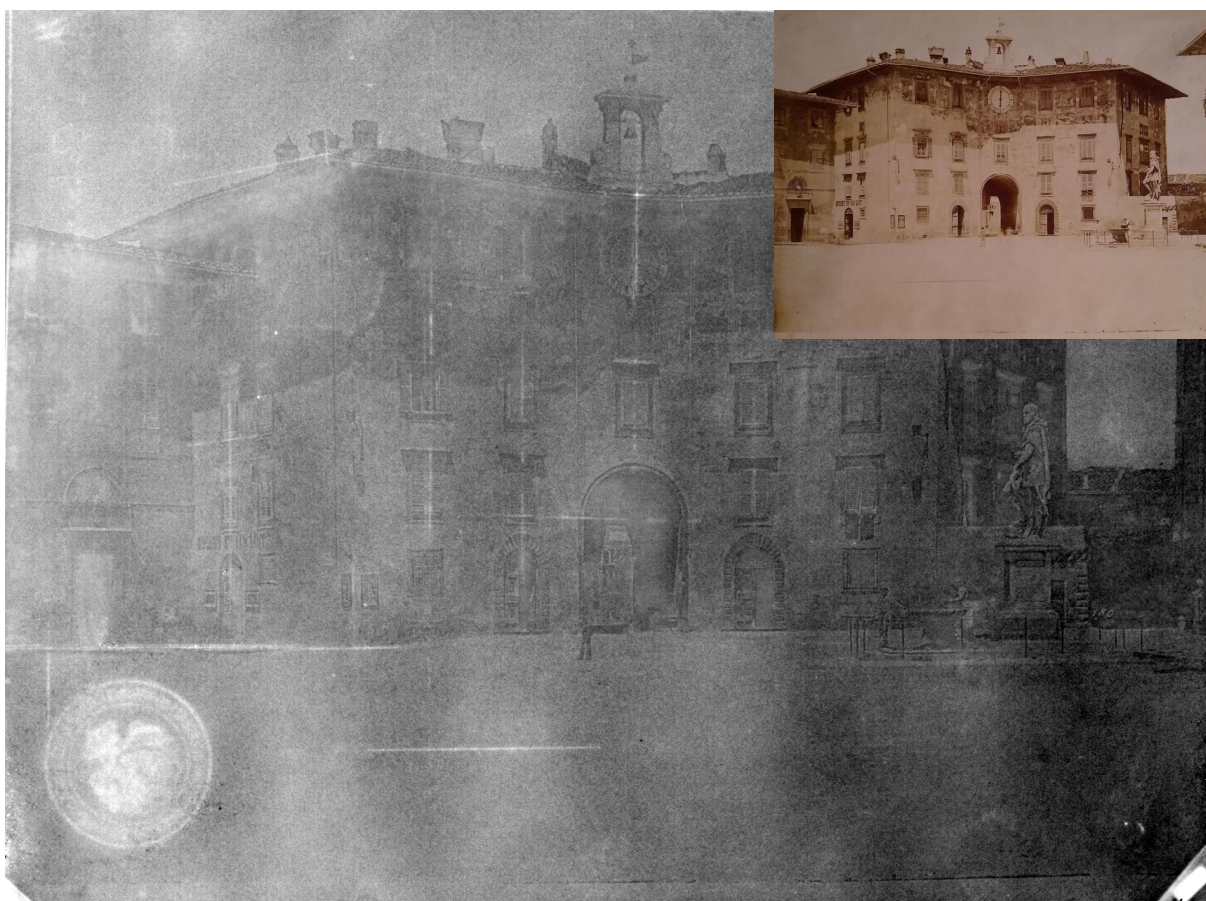


Figure 7. FI of Photograph 131.

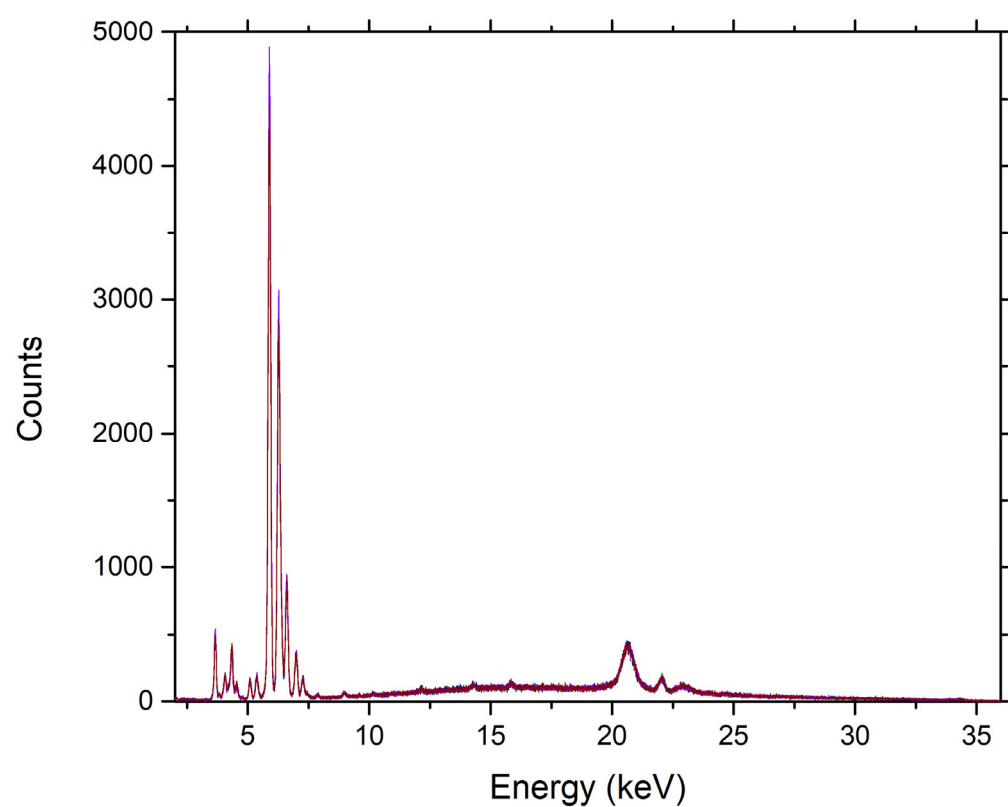


Figure 8. XRF spectra of Photograph 5 over the entire sample surface.

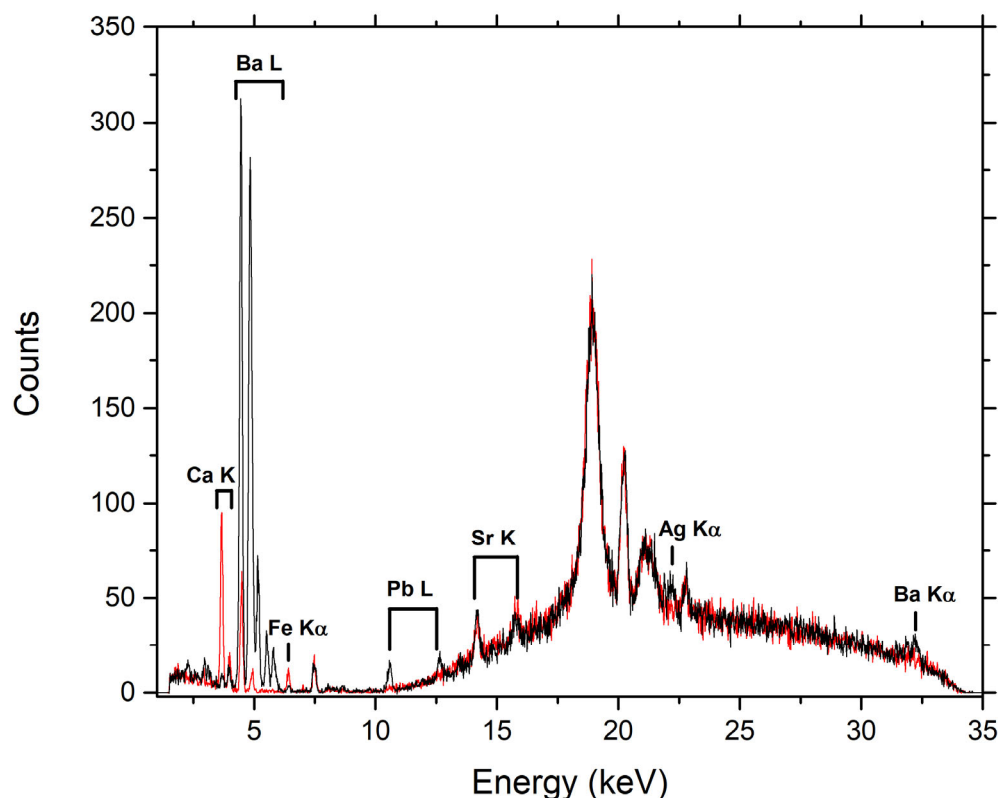


Figure 9. XRF spectra of Photograph 5 from the backing cardboard (red) and a dark area on the photograph (black).

In the XRF spectrum, several signals can be observed. Multiple lines were associated with the presence of Ba (Ba L 4.46 eV, Ba K α 32.19 eV) and Sr (Sr K α 14.16 eV, Sr K β 15.83 eV). These are associated with the presence of a baryta layer in the photographic paper, which was generally used to improve the visual quality of the prints and the toughness of the paper support. We can also identify smaller Ag signals for both the Ag K α and Ag K β around 22 eV. Signals relative to Pb (10.5 eV, 12.5 eV) are also present in some of the samples, which is commonly found in some types of early photographic prints [10].

Additionally, signals relative to Ca (3.5–4 eV) and Fe (6.4 eV) were also visible in a few of the analyzed prints. However, a series of measurements on the backing cardboard that serves as a mounting support for the photographs showed that a large concentration of these elements is contained in such material. The presence of these signals in the spectra recorded for the photographs was then correlated to the penetration power of X-ray photons, which results in spectra which contain a small contribution of the underlying layers of material.

Overall, XRF measurements suggest the presence of a baryta layer, which can be found in both gelatin DOP and POP and in collodion POP, but also in albumen papers from the late 1800s. Due to the presence of Ag signals, we can hypothesize that the analyzed samples are a class of silver salt-based printing-out paper (POP) with a baryta layer, which is consistent with the time period of Van Lint's atelier activity (second half of the 19th century) and the techniques used.

3.3. FTIR Analysis

The identification of the type of binder used in the preparation of the photographic paper is crucial from a conservation and historical point of view. Indeed, this is generally difficult, if not impossible, to identify just from the observation of the print's features. Theoretically, albumen prints appear less glossy and with less defined image edges than

gelatin or collodion prints. However, the degradation, preservation conditions, or post-developing treatments can alter the optical properties of a photograph. By using ATR-FTIR spectroscopy, we can easily determine the presence of one or more binders and coatings, with a non-destructive and minimally invasive analysis.

As for the XRF analysis, we noticed an extremely high consistency both between different measurement points on the same sample (Figure 10) and between different photographs (Figure 11). This indicates that all of the selected photographs were produced using the same type of photographic process.

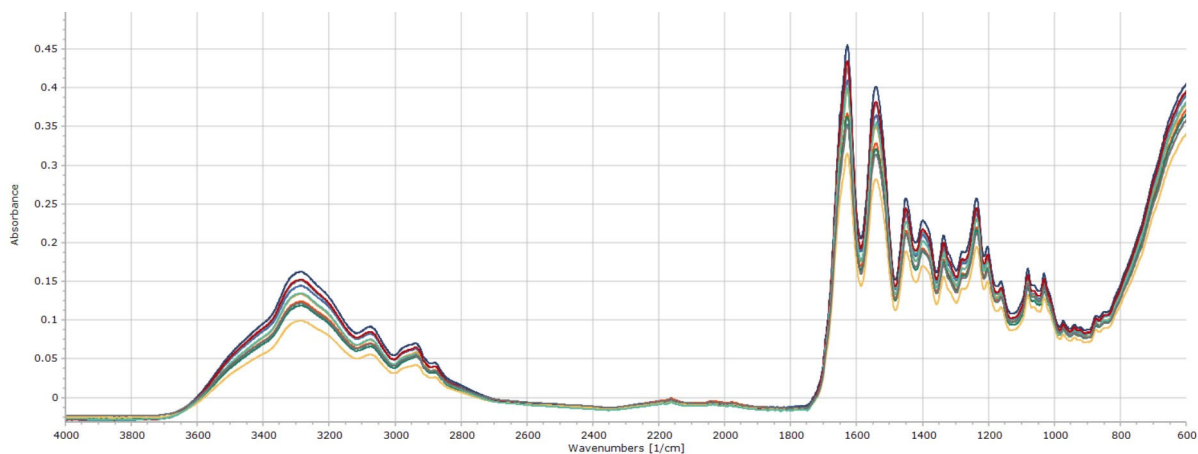


Figure 10. Comparison of the ATR-FTIR spectra from 10 different points on Photograph 5. The different colors are related to the different analysed points.

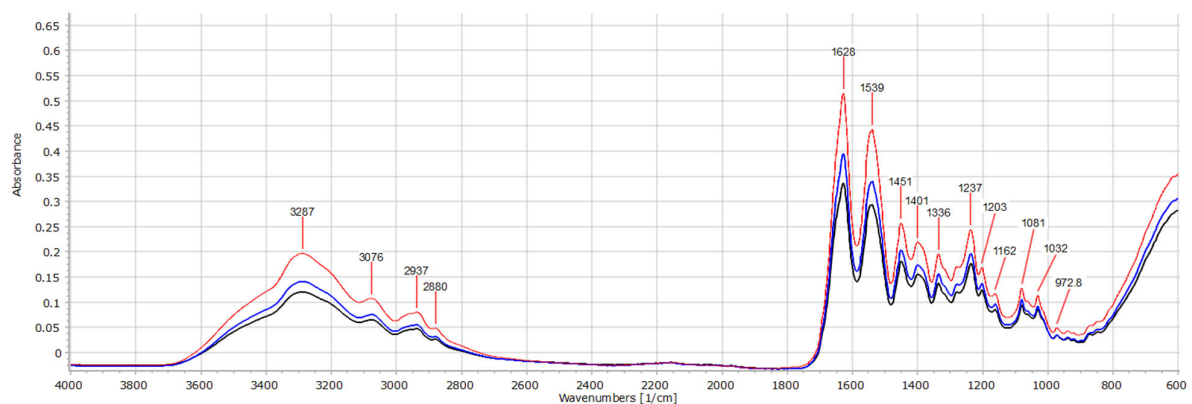


Figure 11. FTIR-ATR spectra of Photograph 5 (black), Photograph 26 (blue), and Photograph 39 (red).

By examining the spectral region between 1800 cm^{-1} and 850 cm^{-1} , a “fingerprint” region for the identification of binder materials in photographic material, and comparing it with spectral databases available in literature, we can determine the presence of a gelatin binder. This is evidenced by the different intensity ratio of the bands at 1451 cm^{-1} and 1399 cm^{-1} , which is typical of the gelatin spectrum [10], while they should be roughly the same intensity in the case of albumen photographic prints. Additionally, we can rule out the possibility of the selected samples being collodion prints coated with gelatin due to the absence of the FTIR bands characteristic of collodion.

Based on this evidence, we can confidently say that the selected photographic prints consist of gelatin-based print-out papers (POP).

4. Conclusions

In this work, we presented a case study from Enrico Van Lint's collection of photographic prints from the archives of SABAP in Pisa. We investigated 10 prints using a variety of non-invasive and non-destructive techniques, namely multispectral imaging coupled with mathematical methods for image analysis, X-ray fluorescence spectroscopy, and ATR-FTIR spectroscopy.

We showed how all of the selected prints are remarkably similar from a chemical point of view, indicating that they were all produced using the same photographic process and very similar stock materials. XRF analyses shown the presence of a baryta layer in all of the prints, which is consistent with the photographic papers of the last quarter of the 19th century (1855–1893), as well as the presence of traces of lead in the paper, which is coherent with the literature. Additionally, it was shown that the cardboard supports where the prints are mounted contain some traces of iron, which can be interesting from a conservation point of view.

The ATR-FTIR analyses confirmed the previously hypothesized photographic process of silver gelatin prints. Indeed, if XRF showed the presence of silver in the prints, the IR spectra clearly demonstrated the presence of a strong gelatin signal, which is compatible with the reference spectra found in the literature.

These observations can confidently suggest that the studied prints, as well as the ones preserved in the archives which are part of the same lot, are silver salt-based printing-out paper (POP) photographs with a baryta layer, which is a process that was widely popular during the time of Van Lint's ateliers.

Perhaps one of the more interesting results, from a historical and conservation point of view, was observed in the study of the multispectral images and their elaboration.

Indeed, it was observed how some prints showed signs of localized wear and degradation, as well as some imperfections and inhomogeneity in the gelatin coating. Some features visible in the original prints were highlighted and sharpened in the elaborated images, such as the presence of cracks, dark spots, and previous restoration attempts. Moreover, some conservation criticalities were also highlighted, such as the presence of markings and stains coming from the contact with other ink stamps, traces of erased pencil marks, and partial writings that are not visible in the original print.

Overall, this study allowed for a more detailed investigation of some of Van Lint's atelier works, which were never the object of a scientific study. Indeed, we believe that the information obtained during this measurement campaign can be of interest for the future conservation and cataloguing of the prints, and a starting point for further studies on other prints of interest in the SABAP archival collections.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/heritage8020059/s1>, Figure S1—Photograph 7; Figure S2—Photograph 11; Figure S3—Photograph 23; Figure S4—Photograph 26; Figure S5—Photograph 29; Figure S6—Photograph 39; Figure S7—Photograph 131; Figure S8—Photograph 134; Figure S9—Photograph 135; Figure S10—Normalized IFF of Photograph 23, showing the presence of a probable masking effect due to an incorrect development of the negative; Figure S11—Normalized orthogonalization of Photograph 26, showing the formation of a darker spot in the top right of the print; Figure S12—IFF of Photograph 134, highlighting darker spots in the top of the print; Figure S13—Normalized orthogonalization of Photograph 134, showing the uneven surface of the gelatin coating; Figure S14—Normalized PCA of Photograph 135, highlighting the defects of the negative plate; Figure S15—Normalized orthogonalization of Photograph 135, showing a diffuse modification (white spots in the lower part) of the print's surface which is not visible in the original.

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Data Availability Statement: The data are available upon reasonable request.

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

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