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TECHNICAL NOTE

Criminalistics

Non-destructive analysis in the study of historical photographs by pXRF and ATR-FTIR spectroscopies

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Abstract

Material characterization is essential to the provenance of graphic arts. Non-destructive analytical techniques are increasingly required in the authentication process of cultural heritage. This work presents a suite of portable, non-destructive, and complementary analytical techniques, energy dispersive x-ray fluorescence (EDXRF), Fourier transform infrared (FTIR) spectroscopies, and brightfield microscopy, applied to the analysis of historical photographs depicting São Paulo city architecture, whose registration date and process of fabrication are unknown. The EDXRF analysis emphasizes the use of typical POP (printing-out paper) photograph with baryta ($BaSO_4$) coated paper substrate while the FTIR and microscopy analyses confirm the presence of collodion and a gelatin-based baryta layer. This photographic process was widely employed by professional photographers from 1889 to 1930, when it was gradually abandoned in commercial use. This time interval (1889–1930) is consistent with the information surveyed on the photographic collection. In conclusion, employing complementary techniques (elemental and molecular spectroscopies and image magnification) is essential in identifying the manufacturing materials of cultural heritage material, which is the basis of contemporary authentication procedures. These data provide to curators and historians fundamental information for cataloging, adding subsidies for the correct storage and preservation ("heritage appreciation"). Still, for professional photographers, they present information on the manufacturing processes of historical photographs. The data from the present study also emphasize its perspective of use in graphic arts to aid connoisseurship in identifying forgeries during provenance and authentication studies.

KEYWORDS
art forensics, cultural heritage, non-destructive analytical techniques, provenance

1 | INTRODUCTION

Graphic arts such as photographs, prints, postcards, and stamps among others are of great interest for investigations of historical and artistic purposes. In recent years, these graphic arts have taken place of cultural relevance and have enabled the creation of private collections. Many of these objects need proper characterization, in order to situate the "object" within the context of its own time, in

addition to adding information that helps its conservation and preservation. Particularly for photographs, data about the development or printing processes, origin as well as the identification of copies or counterfeits, are relevant information for collectors, curators, and historians, as well as professional photographers. Nowadays, photographs are increasingly valuable to collectors. A single photograph can be auctioned by US$ 4,000,000 [1,2]. Therefore, photographical forgeries are a worrying subject to curators, art collectors and art dealers worldwide. Connoisseurship is a skill that helps dealing with obvious forgeries. Nevertheless, complex forgeries demand the aid of spectroscopic techniques to identify the physicochemical composition of art objects, confirming provenance information and authenticity of these objects [3].

Until the advent of digital photography and its inkjet printing process, photographic prints were produced by chromogenic dye formation from silver halides crystals in gelatin (emulsion). The combination of gelatins, different silver salts, and metal dopants (such as Au and Rh) are responsible for characteristics such as spectral sensitivity, speed, contrast, and graininess [4].

Photographic paper designates the photosensitive-coated paper employed in the production of photographic prints. This paper undergoes several chemical processes, such as fixation, washing, drying, and toning [5]. Therefore, it is always a multielemental material.

Historically, Thomas Wedgwood and Sir Humphry Davy were the first to fix images on paper and leather in 1802. Carl Wilhelm Scheele (1777) discovered the photochemical decomposition of AgCl, which was fundamental to the discovery of the permanent photograph by Joseph Niépce and Louis Jacques Daguerre in 1839. The daguerreotype was a silver-copper plate coated with silver iodine (photosensitive). Henry Fox Talbot (1840), using silver chlorine and silver nitrate, reduced exposure time creating the calotype process. This process was the first to use paper negatives and positives. Some years later (1848), Scott Archer introduced the collodion wet-plate process, also called collodion process, a solution of nitrocotton in a mixture of ether and ethanol. Its first use was on a glass plate, which was exposed wet inside the camera by pouring water, acetic acid and pyrogallic acid. Later, dry collodion was invented by adding preservatives. Dry collodion rendered daguerreotypes and calotypes obsolete. Nevertheless, modern photography only became viable with the invention of gelatin, where silver nitrate crystals were precipitated in collodion before coating the photographic paper [6]. Collodion chloride printing-out paper (POP) was introduced in 1886 and was composed of three-layer process with paper support, barium sulfate suspended in gelatin and photosensitive emulsion. POP process produced images with the direct action of sunlight without resorting to chemical development. Typically, POP processing consisted of a gold bath followed by fixing and washing. Figure 1 illustrates the schematic cross-section of a typical POP photograph, with baryta-coated paper substrate and the photosensitive collodion layer.

The premise of characterizing art related materials, such as photographic paper, is the preservation of the object. Therefore, X-ray fluorescence (XRF) spectroscopy is a fundamental technique in the study of different types of the graphic arts and archeological objects [7–14]. This analytical technique offers characteristics as being non-destructive, non-invasive, multielemental, fast, and demanding no pre-treatment of the sample. The basis of the Energy dispersive X-ray fluorescence (EDXRF) technique is on electronic transitions between internal atomic orbitals induced by X-ray electromagnetic energy. These transitions result in the emission of X-rays of characteristic energies, which allow the identification of different chemical elements present in the same sample [15]. Portable systems have rendered the technique to be non-invasive.

Highlights

- The use of portable, non-destructive techniques is vital in the authentication process of cultural heritage.
- Collodion photographic process was identified in 48 historical photographs (1889–1930).
- The adopted methodology can be applied to classify other photographical processes.

This work presents the energy dispersive X-ray fluorescence (EDXRF), Fourier transform infrared (FTIR) and brightfield microscopic analyses of historical photographs related to São Paulo city architecture aiming information about age and process of production for conservation and provenance studies. This historical collection depictures “palacetes” (small palaces or palazzi) situated in São Paulo city, as shown in Figure 2.

Historically, they were built mid-XIX century by the coffee elite as the first residential neighborhoods, then stimulated by the recent construction of the railway (1867). The semi-rural residences were being slowly replaced by the architectural Neo-classicism and Eclecticism. To study the “palacetes” of this collection also means to study the urban development of São Paulo city, with its constructive techniques and materials and decorative language [16]. Nowadays, some of these "palacetes" still exist, but have undergone renovations that modified their architecture and, usually, house public service offices.

2 | MATERIALS AND METHODS

A group of 48 monochrome photographs from a private collection called “Palacetes da Cidade de São Paulo” (Palaces in the City of São Paulo) were analyzed by EDXRF, FTIR, and brightfield microscopy. All photographs are similar in size (22.5 × 16.5 cm), as the exemplary picture shown in Figure 3.

The EDXRF analysis aims at providing the identification of the chemical elements. These measurements were performed with a portable Amptek assemble of Si-drift XR-100SSD (25 mm^2 × 500 μm) detector, equipped with a 12.5 μm Be entrance window, preamplifier and digital pulse multichannel processor and Au target [17]. Analytical parameters were 5 μA and 30 kV for 120 s at 2 mm

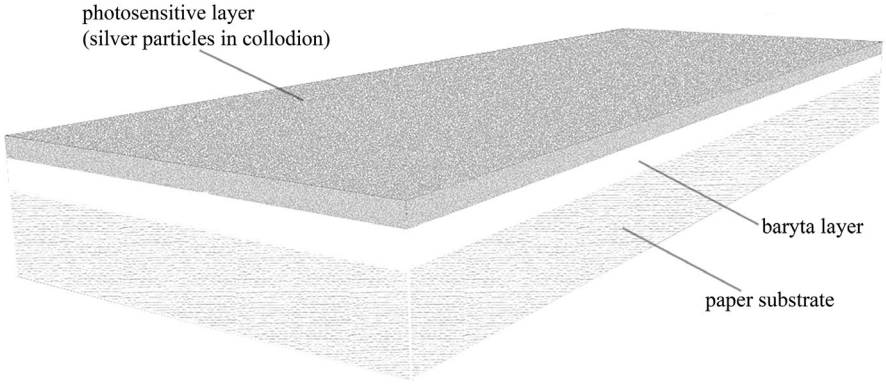

FIGURE 1 Illustrative scheme of the photograph paper

FIGURE 2 Photograph from "Palacetes da Cidade de São Paulo" collection

distance to the target. The WinQxas software was employed for spectral analyses [18]. At least four points distributed in black region and four points in the white region were analyzed on each photograph. X-rays can easily penetrate photographic paper providing information on photographic process.

Vibrational spectroscopy (FTIR) was also employed to characterize organic compounds. An Agilent 630 Cary model was used coupled with an attenuated total reflectance (ATR) module. Spectral range was 4000 to 650 cm^{-1}, with 32 scans at 4 cm^{-1} resolution.

Microscopic analyses were performed directly on the photographs using a Leica microscope DM LM model with up to 1500× magnification and dark-field observation, equipped with a digital camera model EC3 to capture images with Leica software.

3 | RESULTS AND DISCUSSION

A representative spectrum for P1 (black) and P2 (white) spots obtained by the EDXRF analysis (Figure 4) indicates the presence of S, Cl, K, Ca, Fe, Sr, Ba, and Ag. Related to the Au and Pt peaks, observable in all samples, they are caused by the Au target. Nevertheless, Au peaks are observed after blank samples' spectral subtraction (Figure 5). Therefore, gold is present on the photograph's surface.

The EDXRF spectrometry results indicate that the elemental composition is similar in black and white areas in all photographs. To illustrate this similarity, a comparative analysis by the radar charts of the spots P1 (black region) and P2 (white region), for each element, is shown in Figure 6.

The EDXRF measurements, in the black (P1) and white (P2) spots, have been performed in each photograph. The total number of counts, the standard deviation, minimum and maximum values (expressed by the mean values of the net area), for the identified elements in the spots analyzed in the 48 photographs, are presented in Table 1.

Figure 6 presents element radar charts with two series (P1 and P2) and 48 axes (one for each sample measurement). The values of each axis represent the total number of counts for the referred chemical element. The significant presence (largest radar coverage) of Ba and S in all photos is consistent with the process using baryta ($BaSO_4$) coated paper. Results also indicate that chloride-based fixatives ($CaCl_2$, $FeCl_3$ and $SrCl_2$) and borax-gold bath were employed. Furthermore, presence of K is consistent with the use of potassium metabisulphite (K_2S_2O), an antioxidant.

From the values of standard deviation (SD), we can also observe the distribution of the elements on the photographs' surface. Ba and S, from baryte, have the lowest SD (8%–13%) when compared with other elements that were more prone to variation, such as Ag (from collodion) or Cl (from washing).

Photographic papers coated with baryta layer were invented in 1866 and done by hand until the advent of the collodion emulsion machine in 1889 [19]. Therefore, collodion was employed as well. Collodion-silver chloride emulsion required the photographic paper to be coated with a baryta layer (barium sulfate dispersed in stiffened gelatin) to prevent absorption of solvents used in the emulsion by paper fibers. This process ended in the 1930 s [20]. These spectroscopic data emphasize that these photographs were produced

FIGURE 3 Photograph from the "Palacetes da Cidade de São Paulo," spots in black (P1) and white (P2)

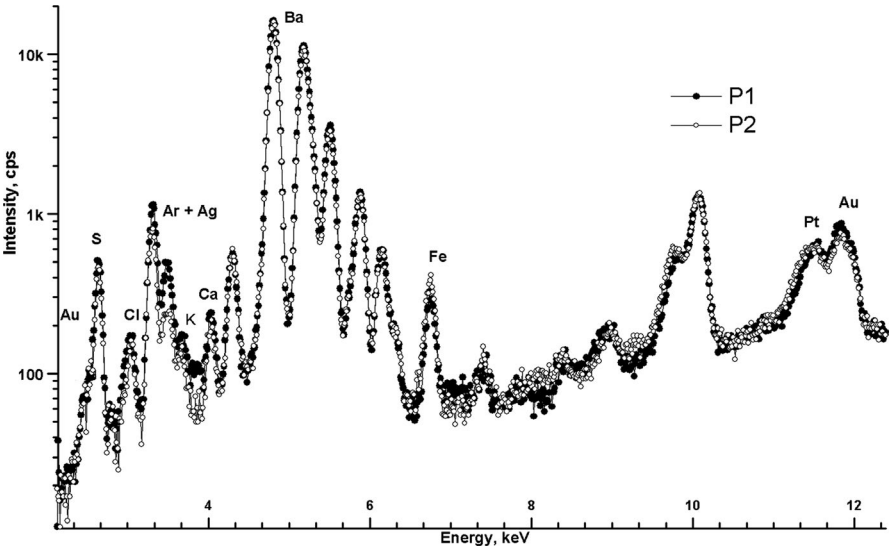

FIGURE 4 EDXRF photo spectrum at black (P1) and white (P2) spots

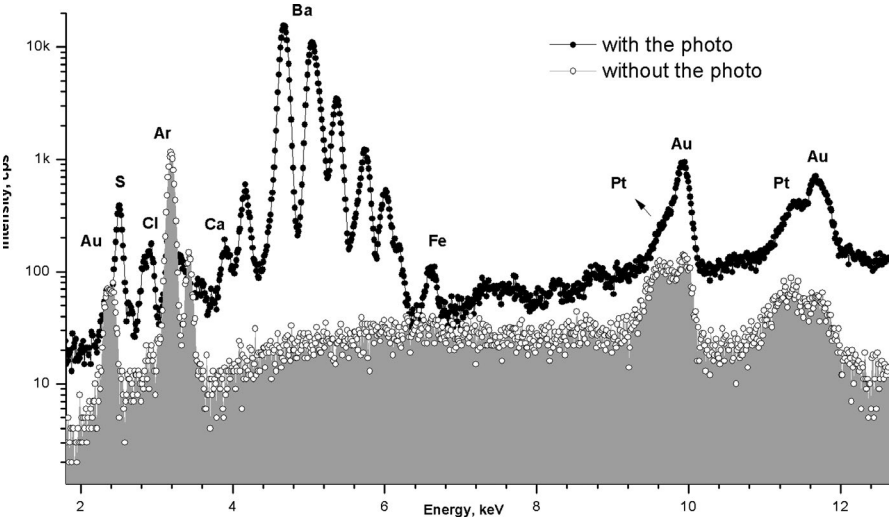

FIGURE 5 EDXRF spectra comparison with photograph (•) and without the photograph (○)

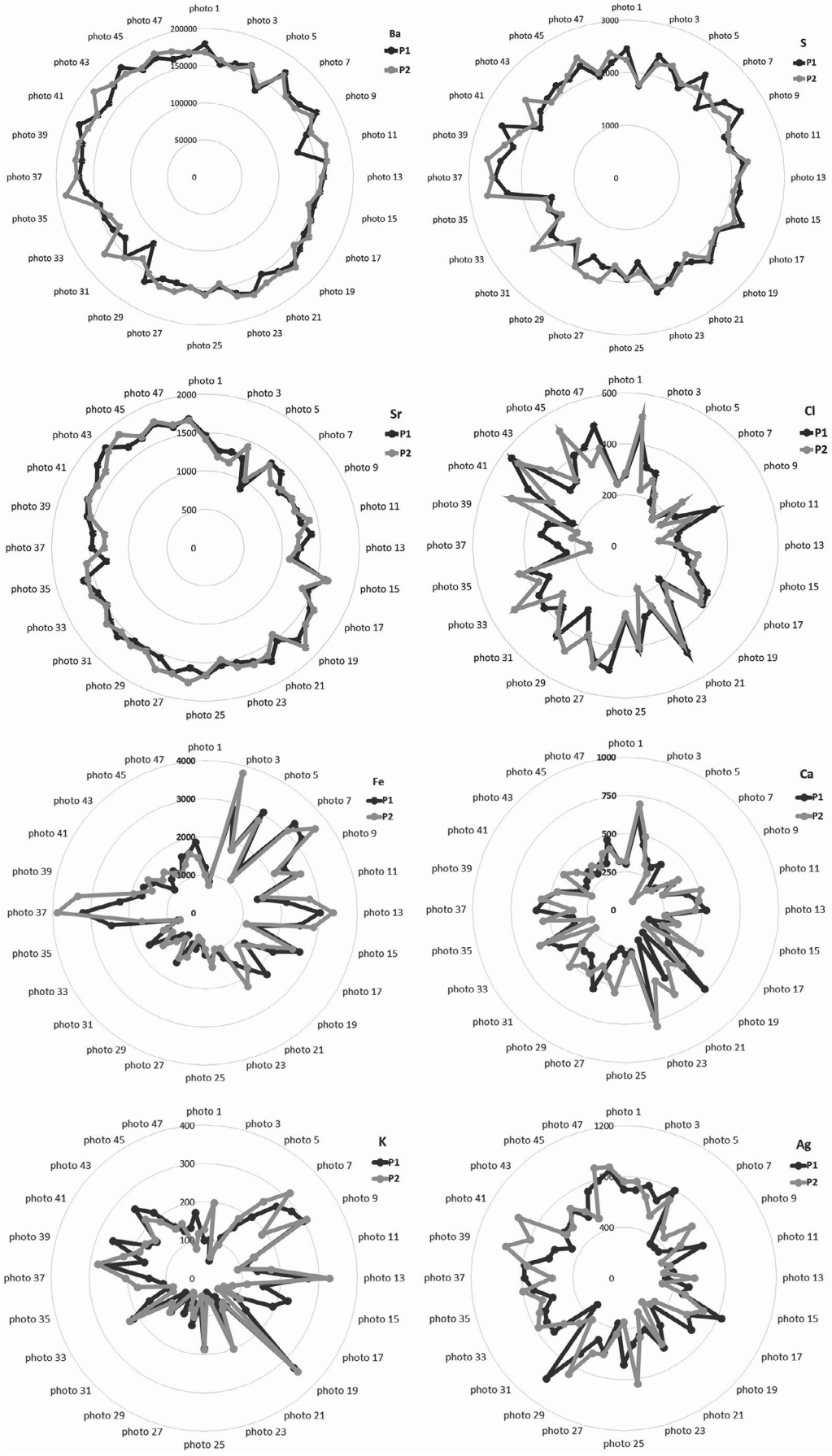

FIGURE 6 Radar charts based on XRF elemental results

TABLE 1 The total number of counts (mean value), minimum, and maximum values, for the identified elements in the spots P1 and P2 in the photographs

Elements spots	MV Net area	Min	Max
Ba			
P1	158,425	113,301	185,393
P2	161,737	133,027	188,942
S			
P1	2064	2092	2564
P2	1471	1422	2669
Sr			
P1	1502	989	1031
P2	1503	1843	1856
Fe			
P1	1721	722	3313
P2	1748	670	3880
Ag			
P1	461	100	999
P2	431	92	960
Cl			
P1	324	151	563
P2	316	143	532
Ca			
P1	351	151	917
P2	363	74	789
K			
P1	127	33	431
P2	138	41	439

MV, mean value; Min, minimum; Max, maximum.

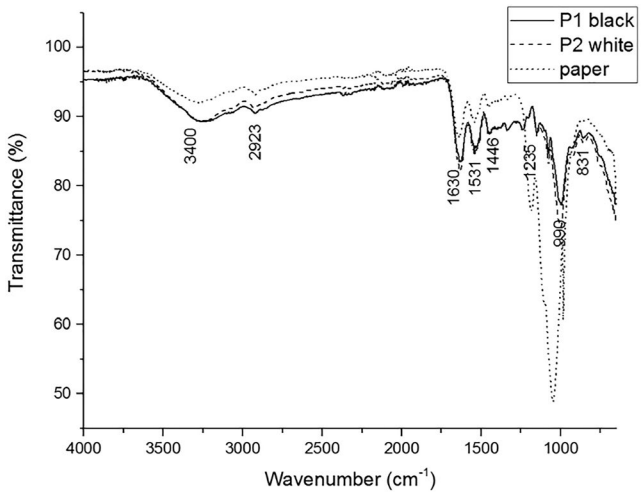

FIGURE 7 ATR-FTIR spectra comparison of P1, P2, and paper

TABLE 2 Characteristic peaks for FTIR spectra of photographs

Chemical compound	Wavenumber (cm^{-1})
Collodion	1630, 1235, 831
Gelatin	1531, 1446
Cellulose	3400, 990

between 1889 and 1930 on baryte paper, in agreement with the architectural esthetics of the time, according to São Paulo City Hall Demographic History websites [21,22].

The Fourier transform infrared spectroscopy (FTIR) was employed to characterize organic compounds and confirm the presence of collodion and a gelatin-based baryta layer. Based on the XRF methodology, P1 and P2 points were analyzed. The paper was also analyzed using the back of the sample (Figure 7). In the FTIR spectra, the following peaks can be identified: collodion (1630, 1235 and 831 cm^{-1}), 2923 cm^{-1} for νCH and 1531 and 1446 cm^{-1} for νNH amide (gelatin layer) [19]. Paper (cellulose) contributes with 3400 cm^{-1} νOH and 990 cm^{-1} νCO [23]. Table 2 summarizes the peak interpretation.

A visual examination indicates a semi-glossy finish and a tendency to curl, so that the photographs were commonly mounted on a solid board. The micrographs are presented on Figure 8, under 10× and 20× magnification. Collodion micrographs are often identified by absence of typical patterns of other photographic processes, such as carbon dots for carbon prints, gravure for photogravure, wormlike for collotype, and symmetrical dots for halftone prints (Figure 9) [19].

4 | CONCLUSION

The elemental profile by EDXRF and complementary ATR-FTIR and microscopy analyses indicates that the 48 historical photographs of São Paulo city architecture were produced between 1889 and 1930 using baryta paper. These analytical methodologies were capable of determining the photographic process and, consequently, the age of photographic papers, being a useful tool in provenance and authentication studies. This methodology can be applied to classify other photographical processes, helping to identify forgeries in graphical arts. Related to the use of portable instrumental for EDXRF analysis, they present relatively low cost as compared to large-scale facility for elemental analysis such as ion beam accelerators.

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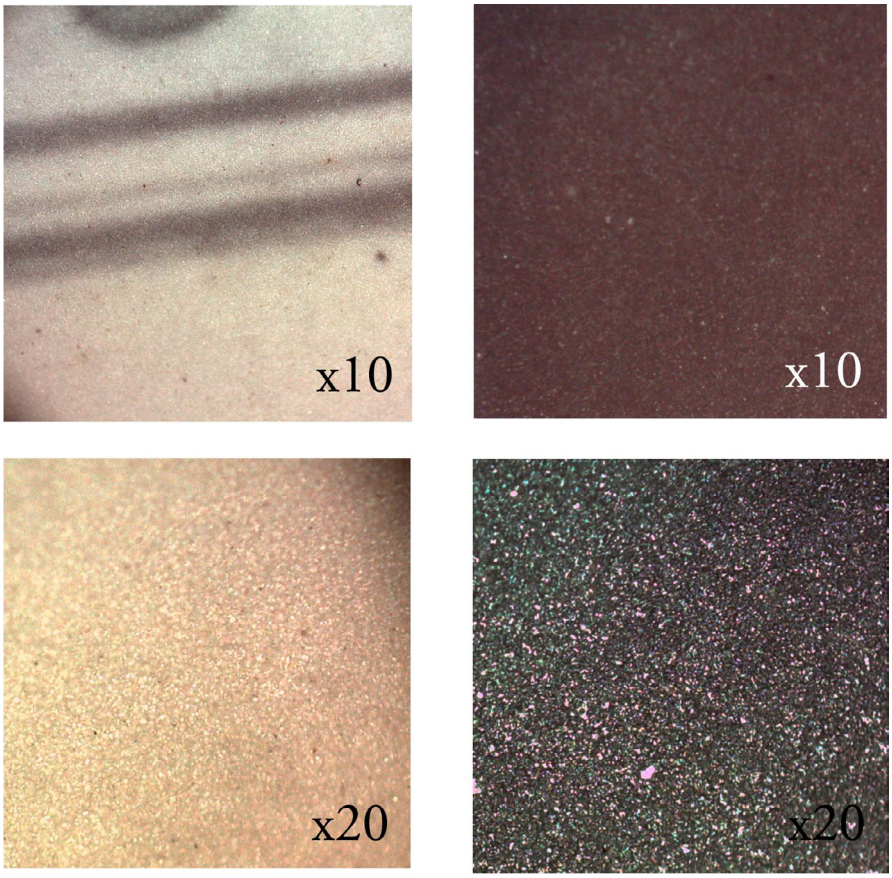

FIGURE 8 Brightfield micrograph of P1 (right) and P2 (left) areas [Color figure can be viewed at wileyonlinelibrary.com]

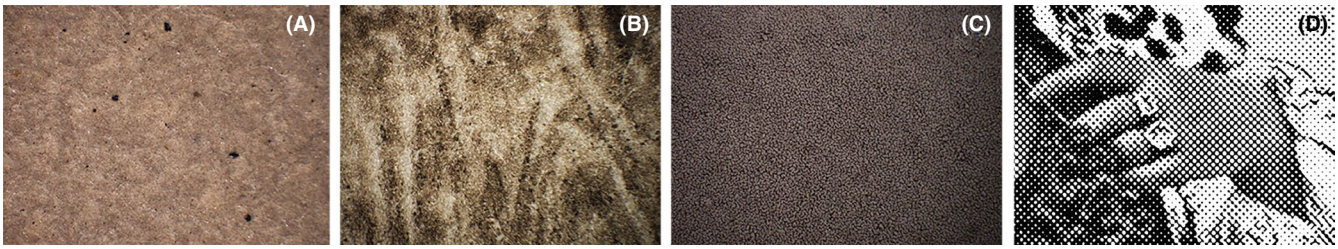

FIGURE 9 Micrographs of several photographic processes from reference [19]: (A) carbon, (B) photogravure, (C) collotype, and (D) halftone [Color figure can be viewed at wileyonlinelibrary.com]

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