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ORIGINAL RESEARCH OR TREATMENT PAPER

Unveiling the Colours of Cellulose Nitrate Black and White Film-based Negatives in Colonial Photography

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ABSTRACT

Aiming at contributing to the preservation of black and white (b/w) film-based negatives held by Portuguese archives, four photographic collections from the first half of the twentieth century were selected for study. During the macro assessment of the collections the preservation condition and hues found in photographic negatives from the *Elmano Cunha e Costa* (ECC) were noticed, distinguishing this collection from the remaining ones. Additional attention was given considering that the ECC collection was formed in a colonial context in the 1930s, while the others were formed on the Portugal mainland. The ECC collection results from an ethnographic survey of Angolan tribes recorded with b/w film-based negatives. In this collection, sets of negatives with pink, lemon yellow, greenish, orange brownish, and red brownish hues were found. To identify the origin of such hues, the image layer was analysed by μ-energy dispersive X-ray fluorescence (μ-EDXRF) and scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDX). Additionally, to assess the base decay and its effect on the formation of hues, the plastic supports were characterized by μ-Fourier transform infrared spectroscopy (μ-FTIR). To complement the assessment of the film-base decay, pH was measured by using combined microelectrodes. The identification of mercury, iodine, chromium, and iron by μ-EDXRF allowed correlation of the hues found in the negatives with chemical corrective treatments performed to improve the image quality. SEM-EDX confirmed those results and proved that the elements found were in the photographic emulsion layer. The results obtained are relevant since the hues identified may now be used as markers to indicate the technical work performed on colonial photography. Additionally, the visual and molecular assessment of the negatives' supports (good to fair condition) allow proposing that the original storage conditions may have had a beneficial contribution to their present condition.

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Introduction

Photography was broadly used to document scientific, technological, anthropological, and social achievements, awarding it an unequivocal documental character. In the twentieth century, cellulose ester film-based negatives were significantly used by Portuguese photographers and researchers to document aspects of Portuguese culture not only on the Portugal mainland but also to record the Portugal colonizing presence in African countries (Vicente 2014; Matos 2016). To understand the present condition of black and white (b/w) cellulose ester film-based negatives resulting from the work carried out by Portuguese photographers and held by Portuguese archives, four photographic collections were selected for study. The selection of the collections relied on three main criteria: historical framework of the collection's production (dates, where they were carried out. technical issues, e.g. light, etc.); film characteristics (type of support, format, producers/brands); and preservation condition. Two of them, the San Payo and Silva Nogueira collections, are representative of studio portraits. The remaining two, the Direcção Geral de Edificios e Monumentos Nacionais (DGEMN) and the ECC collections, are representative of outdoor photography (Roldão 2018). Of the set of collections surveyed, only the ECC collection is representative of the practice of photography carried out during the Portuguese colonial period, being therefore situated in so-called colonial photography. The macro assessment of the collections allowed recognition of the unique specificities in the ECC collection, first the well-preserved condition of the specimens from the 1930s and secondly the diversity of hues detected that differs from what was observed in the three remaining collections that were made during the same period on the Portugal mainland.

Apart from the anthropological and ethnological studies published in the literature (Landau and Kaspin

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2002; Scherer 2010; Vicente 2014; Matos 2016), a lack of knowledge was found to exist regarding the photographic techniques and photographic materials used by the photographers in the colonial photography context. Thus, aiming at knowing more about the practice of colonial photography, and more specifically about the photographic techniques and materials used, the ECC collection was studied. Elmano Cunha e Costa was a Portuguese photographer with extensive work on colonial photography. The ECC collection resulted from an ethnographic survey of individuals, costumes, artefacts, artworks, and habitations from 58 Angolan tribes, carried out between 1935 and 1938. Besides a few silver gelatine developing-out-prints, the ECC collection is mainly composed of 8718 black and white (b/w) film-based negatives.

Despite what was expected for a collection made in the 1930s and carried out in a humid and hot climate of Angola, the visual assessment supported on a five-grade condition chart (Table A1 in the appendix) allowed to conclude that overall the ECC collection is in a Good to Fair condition. Additionally, during the observation a significant number of film-based negatives (864) with pink, yellow, greenish, brownish, and reddish tonalities were found (Figure 1). Additionally, negatives with red ink masks were also found (Figure 1).

In general, b/w film-based negatives have neutral tones (Figure A1 in the appendix). The occurrence of hues or discolouration on b/w negatives is pointed out as a marker for film support decay (Nguyen, Lavédrine, and Flieder 1997; Lavédrine 2003; Valverde 2005), inadequate photographic processing (Eaton, Bard, and Lee William 1985), or chemical corrective treatments performed on the image (Mees 1942b; Neblette 1952a; Glafkidès 1987).

Regarding film decay, general yellowish and brown hues are usually correlated with cellulose nitrate base degradation (Valverde 2005), being the discolouration commonly observed in all the layers of the negative. Pink, blue (Reilly 1993), green, or magenta (Jamison 2003) hues might result from anti-halation dyes regeneration by acidic conditions resulting from film decay. In this case, this phenomenon occurs only on the back of the negative in the anti-curl layer (Figure A2 in the appendix).

Concerning incorrect processing, during ageing, residual processing solutions from pyrogallol developer (benzene-1,2,3-triol, $C_6H_3(OH)_3$) and fixing baths (sodium thiosulphate, argentic-thiosulphate salts) remaining in the image layer may result in overall yellow or brown staining (Crabtree, Eaton, and Muehler 1940; Johnsen 1994).

Moreover, the hues of b/w negatives may result from specific corrective chemical treatments performed on overexposed or underexposed negatives before printing. Wall (1924), Mees (1942a), Neblette (1952a), and Glafkidès (1987) presented some of the common chemical solutions used, which are conventionally gathered in two broad classes designated as intensification

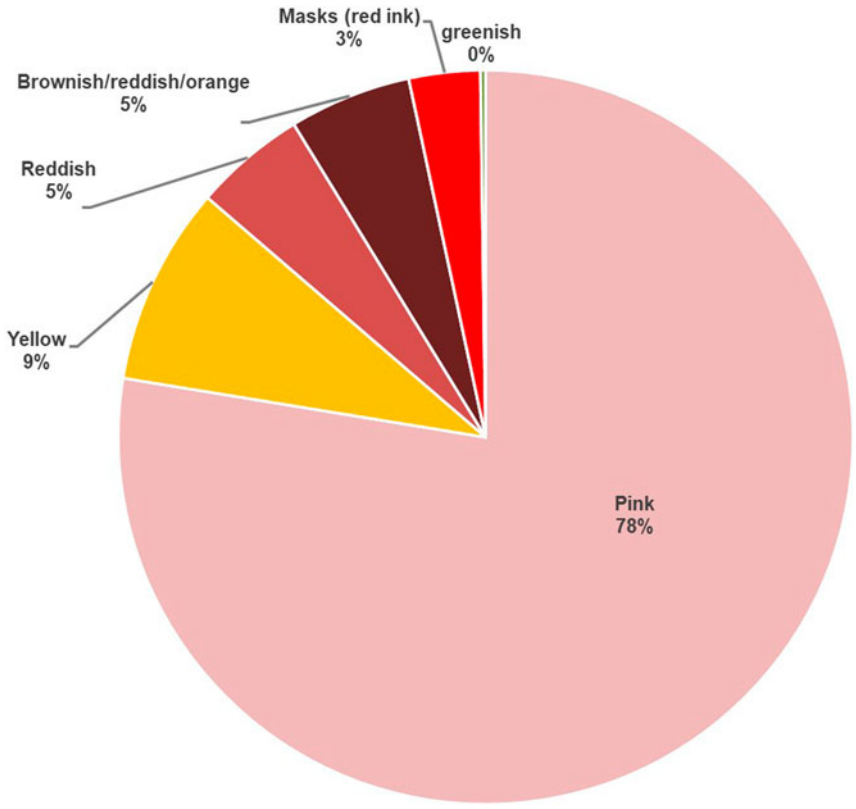


Figure 1. Percentage of negatives per hues and masks found on the image layer of film-based negatives from the ECC collection.

treatments (for underexposed negatives) or reduction treatments (for overexposed negatives). To increase the image density, different chemical compounds were combined with the silver image by treatments including mercuric chloride ($HgCl_2$), potassium ferricyanide ($C_6N_6FeK_3$), copper sulphate ($CuSO_4$) solutions, sulphide (S^{2-}), etc. (Osterman and Romer 2007). These procedures were indicated as 'image recovery methods' which were recommended to photographers whenever there were difficulties adapting the practice of photography in different geographical contexts, e.g. African countries in which natural light is different from Europe (*Boletim Photographico* 1900). As described by Freeman (1992), several issues must be considered when photographing with natural light. For instance, the light characteristics (e.g. sun's position and height), as well as latitude, atmosphere (e.g. relative humidity, dust, haze) and surroundings in tropical countries challenge photographers, especially when considering outdoor photography carried out during an expedition. As Cunha e Costa reported the quality of the photographs taken under tropical conditions demanded 'patient work', emphasizing the need to properly understand the light in tropical countries in order to avoid 'bewildering shadows' that could damage the accuracy and detail of the subject photographed (Costa 1943).

Considering the ECC collection visual assessment, the hues visually perceived were mainly on the image layer, being mostly associated with density of the silver image (Figure 2). Additionally, in opposition to what was explained about the general incidence of discolouration of negatives showing signs of chemical decay, the lack of the hues on the transparent fringe of the negative emphasizes the possibility of corrective treatments. Additionally, the framework in which this collection was performed, the comments made by Cunha e Costa, and invoices found in historical documentation related with the ECC collection also support this proposal. Despite the straightfoward proposal of a correlation between pink and strong yellow hues and the occurrence of corrective treatment, doubts were raised regarding the yellowish, reddish-brownish, and orange tonalities visually perceived, since those are visually similar to the discolorations proposed in the literature for cellulose nitrate film decay. Therefore, and considering that the hues found on the ECC collection may also result from chemical decay of the film base and/or from specific corrective chemical treatments, it was decided to look for chemical markers that would allow identifying the origin of such hues and understanding the photographic technique used by the photographer (Figure 2).

According to the historical documentation, such as invoices, it was possible to know that the photographer used metol (developing agent), and thiosulphate and thiocyanate (fixing agent) in distilled water for processing the negatives' image. Moreover, references to the purchase of iodine and mercury chemical products were also found. Fourteen naturally aged b/w film-based negatives with different hues were selected for this study. The image forming materials were identified by μ-EDXRF analysis. However, minor differences in the intensity of the peaks led to the need to confirm the results obtained through SEM-EDX analysis.

This study will contribute to a better comprehension and assessment of the photographic practice during the so-called colonial photography period carried out in the beginning of the twentieth century.

Materials and methods

Description of the film-based negatives

In order to perform an accurate characterization, a total of 14 negatives were selected from the ECC collection, based on (i) representative colours visually perceived; (ii) the relative importance and quantities of the hues found in the collection (Figure 1); (iii) the homogeneity and intensity of hues and uniformity of the surface of the negatives. Additionally, the selection of areas for analysis also relied on visual lack of signs of contamination or changes cause by inadequate storage or handling. By establishing these criteria, a higher assurance and reliability of data was accomplished. All the film-based negatives selected have a medium format roll film, cut individually in 6 × 6 cm format. The negatives selected show different tonalities: yellow (2 negatives), pink (6 negatives), red-brownish (2 negatives), orange-brownish (3 negatives), and pale green (1 negative). The three remaining negatives had neutral hues. The samples were organized into six groups (from A to F, named grA, etc.) according to the tonality presented.

Instrumentation

To characterize the negatives colourimetry, X-ray fluorescence spectroscopy, scanning electronic microscopy, infrared spectroscopy, and pH measurements were used, detailed as follows.

Colourimetry

Colour measurements were carried out with a hand-held colourimeter Data Colour International® with a D65 Standard Illuminant and 10° Standard Observer, following the International Commission on Illuminant (CIE) colourimetry system. The CIE *L*a*b** colourimetric space is defined according to three coordinates: *L**, *a**, and *b**. *L** refers to the level of lightness (0 = black, 100 = white); *a** refers to the redness–greenness (red: *a**>0, green: a*<0); and *b** to the yellowness–blueness

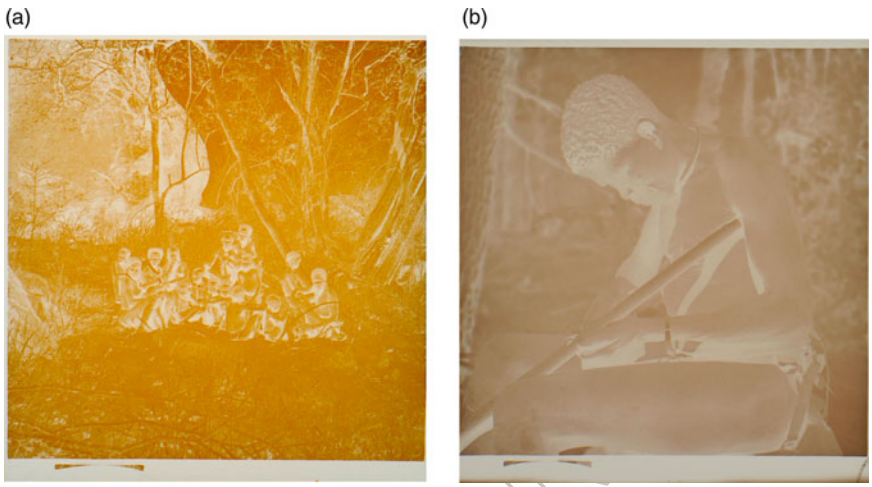


Figure 2. Black and white film based-negatives from the ECC collection presenting distinct colours; chemically treated with (a) intensification and (b) reduction solutions.

(yellow: $b^*>0$, blue$^*<0$). The negative's support was placed on top of seven sheets of Whatman#1 paper, using a transparent polyester sheet film template to position the colourimeter in the same spots for each measurement taken. The colour measurements were performed on areas of the image (matte surface) where the hues were homogeneous. The reported *L*a*b* values for each negative are thus the average and standard deviation of 6 measurements performed in 4 different areas, for a total of 24 measurements.

µ-EDXRF

Micro-energy dispersive X-ray fluorescence analyses were carried out using an *ArtTAX* spectrometer from Bruker, with a molybdenum (Mo) X-ray source, focusing polycapillary lens and electro-thermally cooled *xFlash* (Si drift) detector, with 170 eV resolution (Mn Kα). The accurate positioning system and polycapillary optics enable a small area of primary radiation (Ø~70 µm) at the sample. Elemental composition was obtained from the analysis of six independent spots (three transparent areas and three areas of the image), with a tube voltage of 40 kV and a current intensity of 600 µA and live time 100 s. Spectra are presented as acquired. To obtain accurate and comparable data, for the analysis, from each negative, three areas of higher density and homogeneity of the image were selected.

SEM-EDX

The morphology of the cross sections of four film based-negatives was characterized by SEM-FIB using a Carl Zeiss AURIGA Cross Beam workstation instrument equipped with an Oxford X-ray energy dispersive spectrometer. A small piece of the corner on the edge of the negative (transparent fringe) was cut for cross section evaluation. Samples were taken from areas that could be representative of all layers of the film negative. The samples were mounted on a holder and covered with a carbon coating. The experimental conditions of the image acquisition were 5 kV accelerating voltage, 20 µm of beam emission, and 4.8 working distance. Elemental composition was obtained from the analysis of six independent spots (two on the emulsion layer, two on the film support, two on the anti-curl layer (see a cross section of the film in the appendix, Figure A.1)).

µ-FTIR

Infrared spectra were acquired using a *Nicolet Nexus* spectrophotometer coupled to a Continuum microscope (15× objective) with a MCT-A detector cooled by liquid nitrogen. Samples were collected from the support of the negatives with a micro-tool (Roldão 2018) and placed into a thermo-diamond anvil compression cell. Spectra were collected in transmission mode from 4000 to 650 cm^{-1}, 128 co-scans, and 4 cm^{-1} spectral resolution. Spectral analysis was performed using Omnic E.S.P. and OriginPro 8 software and all spectra were baseline-corrected, normalized for the NO_2 vs at ≈ 1280 cm^{-1} (identified as the most stable absorption) and CO_2 (absorption at ca. 2300–2400 cm^{-1}) was removed.

pH determination

pH measurements were performed using a surface pH measurement method for paper, TAPPI 529 om-04 (TAPPI, 2009), using a pH/mV meter with pH-500 microelectrode, with 400–800 µm external diameter, and a glass reference electrode with a 10 µm external diameter, all manufactured by Unisense™ A/S. After testing it was established to use a drop of 0.02 mL Millipore water. The reported pH values for each negative are the average and standard deviation of 5 measurements.

Results and discussion

To gather and summarize the obtained results for each negative by the used techniques, Table 1 was designed, and its detailed discussion is presented in the following sections.

Colourimetry

Although the colours on the negatives are visually perceivable, it seemed appropriate to perform colour measurements to obtain quantitative data supporting the differentiation between warmer colours from groups C, E, and F. The *L*a*b** values presented in Table 1 are the result of 24 measurements for each negative. In order to obtain accurate values, it was decided to perform the colour measurements on areas of higher density of the image. In general, by comparing the *L*a*b** coordinates values obtained, group B presents the highest values. Concerning specifically the *L**coordinate values, the results confirm what is visually perceived, groups B and D are more transparent. However, and despite the hues visually perceived, the *L*a*b** coordinates values for most of the negatives from the remaining groups A, C, and F, are very similar. Therefore, the data obtained do not support the differentiation of negatives from groups C, E, and F (Table 1).

Overall, the standard deviation found for colour measurements shows a low variation of the *L**, *a**, and *b** values that results from heterogeneities on density and colour intensity of each negative.

μ-EDXRF results

The μ-EDXRF analysis was performed firstly for identification of the chemical elements in the image and secondly to correlate those results with the hues seen on the negatives. The indication of the elements as major and minor was made based on the relative intensity of the peaks characteristic of each element, being established that the major elements (proposed in Table 1) present at least twice the intensity compared with the correspondent peaks' intensities obtained for the remaining negatives.

The presence of calcium, chromium, silver, iron, zinc, sulphur, and chlorine was identified in all negatives (Figures A3 to A8, in the appendix). Additionally, mercury and Hg and iodine were identified in grB and grD, respectively (Figures A4 and A6, in the appendix). Visual assessment and μ-EDXRF data obtained point out a possible correlation between pink hue and mercury. Based on the literature (Mees 1942b; Neblette 1952b; Glafkidès 1987) and μ-EDXRF data it is proposed that negatives from grB have been treated with Eder's reduction treatment (Table 1). Regarding the yellow hue, visual assessment and μ-EDXRF data allow correlation of the hue with mercury iodide solution. In this case, the results obtained and the literature review (Lavédrine and Garnier 1989) allow to propose that a Mercuric Iodide intensification corrective treatment was carried out on negatives from grD.

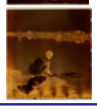
Concerning the presence of Ca, Cunha e Costa (1943) and Castelo and Mateus (2014) described that the negatives under study were stored in metal boxes filled with calcium carbonate to prevent the effects of moisture (and consequently of the high temperatures) of Angola. Similar recommendations were found on Portuguese photographic bulletins from the beginning of the twentieth century (*Boletim Photographico 1900*), showing the awareness of the effects of moisture on photographic materials. The storage boxes no longer exist; therefore, it was not possible to analyse them. However, the consistency of the results allows proposing that the presence of Ca results from the storage system used. The presence of Zn was questioned, with two hypotheses proposed: the presence of Zn in the composition of the metal boxes used by Cunha e Costa (Castelo and Mateus 2014) or the use of zinc hypochlorite solution (Flandreau's eliminator) to remove the fixing agent (sodium or ammonium thiosulphate) (Crabtree, Eaton, and Muehler 1940). More information was found highlighting the use of zinc 'boxes with reservoirs in the bottom filled with lime chloride' in the beginning of the twentieth century that may justify the presence of Zn (Santo 1907). However, the absence of the storing boxes used by *Cunha e Costa* does not allow achievement of a conclusion. Additionally, further work must be performed to assess the quantities of Zn left by treatments performed with the Flandreau's solution.

Regarding the presence of Cr, this may result also from *permanent* or *temporary hardening* of gelatine. Commonly, *temporary hardening* was performed by the photographers as a preventive action to avoid the gelatine swelling, peptization, and physical damage in '*hot seasons or tropical climates*' (Mees 1942a).

The identification of Fe in all negatives can probably be traced to residues left from the water used during photographic processing, due to films' industrial production or even due to permanent gelatine hardening (Mees 1942a; Neblette 1952a; Glafkidès 1987). However, the detection of peaks with twice the intensity for negatives from grE and the orange-brownish hue of those allows proposing that the negatives from grE have been treated with a corrective solution containing Fe.

Concerning colours visually perceived on negatives from groups C and F, a clear correlation was not found between μ-EDXRF and colour. However, and according to literature, the colour can be a consequence of thiosulphate residues or due to *toning intensification* performed to increase the opacity and the

Table 1. Results from colourimetry, molecular analysis by µ-EDXRF (major and (minor) chemical elements), µ-FTIR analysis (peak ratios vs NO_2 $_{1655\ cm\text{-}1}$/δCH $_{1374cm\text{-}1}$ [(a)]), pH, and proposal of chemical treatments performed on b/w film-based negatives of ECC collection.

(gr)	Ref.		L^* $a^{*(1)}$ $b^{*(2)}$	µ-EDXRF	µ-FTIR	pH	Conclusion
A	ECC 1256		31 ± 2 0.4 ± 0 1 ± 0.5	Ca, Cr, Ag, Fe, Zn, S, Cl	13.6	–	No chemical elements linked to corrective treatments
	ECC 2413		30 ± 0.7 0.4 ± 0.1 0.9 ± 0.2	Ca, Fe, Ag, S, Cl	6.4	4 ± 0.4	No chemical elements linked to corrective treatments
	ECC 2518		33 ± 0.2 0.5 ± 0 2 ± 0.1	Ca, Cr, Fe, Ag, S, Cl	6.9	5.4 ± 0.2	No chemical elements linked to corrective treatments
B	ECC 981		74 ± 0.8 10 ± 0.5 15 ± 0.5	Hg, Cr, (Ca, Ag, Cl)	14	5.3 ± 0.1	*Subtractive reduction* Mercury and cyanide[(a)] (Eder's solution)
	ECC 1616		61 ± 3 9 ± 0.2 15 ± 0.7	Hg, Cr, (Ca, Cl, Ag)	10.2	4.3 ± 0.4	*Subtractive reduction* Mercury and cyanide[(a)] (Eder's solution)
	ECC 1228		59 ± 0.6 7 ± 0.6 14 ± 0.7	Hg, Cr, Fe, (Ca, Cl, Ag)	6.5	5.5 ± 0.1	*Subtractive reduction* Mercury and cyanide[(a)] (Eder's solution)
C	ECC 286		30 ± 0.3 2 ± 0.3 3 ± 0.5	Cr, (Ag, Fe, Zn, S, Cl)	10.4	3.6 ± 0.1	–
	ECC 631		28 ± 0 0.5 ± 0 0 ± 0	Cr, (Ag, Fe, Zn, S, Cl)	11.3	3.7 ± 0.2	
D	ECC 2641		44 ± 2 1 ± 0.3 10 ± 1	Cr, Hg, I, (Ca, Zn, Ag, Cl)	7.3	5.5 ± 0.3	*Subproportional Intensification* Mercuric Iodide
	ECC 879		63 ± 2 13 ± 0.5 47 ± 2	Cr, Hg, I, (Ca, Zn, Ag, Cl)	10.6	5.8 ± 0.1	*Subproportional Intensification* Mercuric Iodide
	ECC 2799		81 ± 2 1 ± 1 46 ± 3	Hg, I, (Ca, Zn, Ag, Cl)	8.8	5.4 ± 0.1	*Subproportional Intensification* Mercuric Iodide
E	ECC 2203		29 ± 0 1 ± 0 1 ± 0	Fe, (Ca, Cr, Ag, Zn Cl)	4.1	4.2 ± 0.3	–
	ECC 2282		30 ± 0 1 ± 0 2 ± 0	Fe, (Ca, Cr, Ag, Zn Hg, Cl)	7.9	4.5 ± 0.3	
F	ECC 5142		31 ± 0 3 ± 0 4 ± 0	Cr, Ag, Fe, Zn, S, Cl	10	3.4 ± 0.1	–

(a) v_s: very strong, δ: scissoring. (1) (2) The reddish and yellow colours indicated for some a* and b* values, respectively, mean that the samples showed a clear tendency to those colours.

contrast of the image through the formation of yellow to brown hues (Mees 1942a). These hues will act as 'filters' absorbing blue light (Mees 1942b). Identical characteristics were visually perceived in negatives from groups C and F. By crossing this data with the colourimetry results (L^* values) (Table 1), the proposal of the use of a toning intensification corrective treatment is reinforced.

In sum, all types of intensification methods promote the formation of colours. According to µ-EDXRF results and colour measurement results, it is possible to suggest a correlation between colour and chemical elements used to perform corrective treatments of the image (Table 1).

SEM-EDX results

To clarify the presence of the chemical elements identified by µ-EDXRF, SEM-EDX analysis of the cross section of four negatives was carried out: ECC 2518, ECC1228,

ECC 879, and ECC5142, each one representative of the groups A, B, D, and E, respectively. The analysis of support, photographic emulsion, and anti-curling layers gave insightful information concerning the presence and origin of chemical elements identified by μ-EDXRF analysis. The predominant percentages found are attributed to carbon and oxygen (above 90 at. %, atomic percentage), which are associated with gelatine layers (photographic emulsion and anti-curling layer) and CN support. No chemical elements were detected on the support and anti-curling layer. Therefore, all elements were on photographic emulsion supporting the theory that with the exception of negative ECC 2518 a corrective treatment of the image with different solutions was performed.

Vestigial percentages of Si (0.1–1.5 at. %), Cl (0.2–6.3 at. %), and Ca (0.03–0.9 at. %) were detected. The presence of Cl and Si was not clarified in this study, demanding further work. The vestigial presence of Ca may be correlated with storage or with photographic processing. By SEM-EDX analysis the presence of Al on negatives ECC 5142 (grA) and ECC 879 (grD) in percentages ranging from 0.5–1.6% (at. %) was identified. Additionally, Cr, Fe, and Cu were also identified. Al^{3+}, Cr^{3+}, Cu^{3+}, and Fe^{3+} were used as gelatine hardeners (Mees 1942b). Based on at. % obtained for Cr (10–21% at. %) and μ-EDXRF data it is possible to propose that Cunha e Costa consistently used Cr as a temporary hardening agent rather than as a corrective treatment. Additionally, in order to prevent the loss and damage of the gelatine in hot climates, the addition of chromium salts to the developer was also recommended (*Boletim Photographico 1906*). The low percentage of Fe (0.3 at. %) detected in negatives ECC 2518 and ECC 1228 allows the suggestion that its presence results from residues left on the image during processing. Unique assignments for Cu and Zn were identified for negative ECC 5142 (grF). Therefore, there is no clear justification for the presence of those elements. Furthermore, Ag, Hg, and I (2.4%, 2.8%, and 0.09% at.%, respectively) were identified for negative ECC 879 (grD).

Unlike μ-EDXRF results, Zn was only confirmed for negative ECC 5142 (grF), demanding further research to understand the presence of this element. Apart from negative ECC 1228 (grB) for which Hg was not detected as expected, the SEM-EDX results support the μ-EDXRF results. Additionally, SEM-EDX results confirmed that the chemical elements were present on the photographic emulsion, rather than on the film base or on the anti-curling layer.

Considering that transition metals may induce the degradation of cellulose ester films (Edge et al. 1989, 1990; Shashoua 2008), the SEM-EDX and μ-EDXRF results are relevant for the preservation of film collections. Given that gelatine is permeable, the risk of penetration of these transition metals into the film base and its contribution to film decay must be considered a priority for the preservation strategies of photographic collections.

Film support identification and assessment by μ-FTIR

Based on the identification of the main infrared characteristic peaks (Shashoua 2008; Quye et al. 2011), the film base of the 14 negatives was identified as cellulose nitrate (Figure 3). The chemical decay of the CN base was assessed by μ-FTIR analysis from the intensities ratio $\nu_s NO_2$ $_{1655cm\text{-}1}/\delta CH_{1374cm\text{-}1}$ since the decrease of the ratio reveals the denitration of the cellulosic polymer.

By comparing the spectra of the negatives under study with the spectra of two negatives in Poor and Severe condition (Figure A9, appendix), it is possible to propose that besides negative ECC 2203 the remaining negatives selected are well preserved, possibly being in an early stage of degradation. In part, the preservation condition may be related with the storage system used by the photographer. Furthermore, according to the μ-FTIR, apart from negative ECC 2203, no correlation between film decay and colour was found suggesting that the slight yellowing and brownish hues result from corrective treatments. Therefore, by correlating the colourimetric and μ-FTIR results it was concluded that the yellowish, reddish-brownish, and orange tonalities result from chemical treatments rather than chemical decay of the negative's base.

pH measurements

Aside from the negative ECC 1256, pH measurements were recorded for all negatives, ranging from 5.8 (maximum) to 3.4 (minimum). The pH measurements do not allow assessment of the film supports' condition since those measurements were performed on the

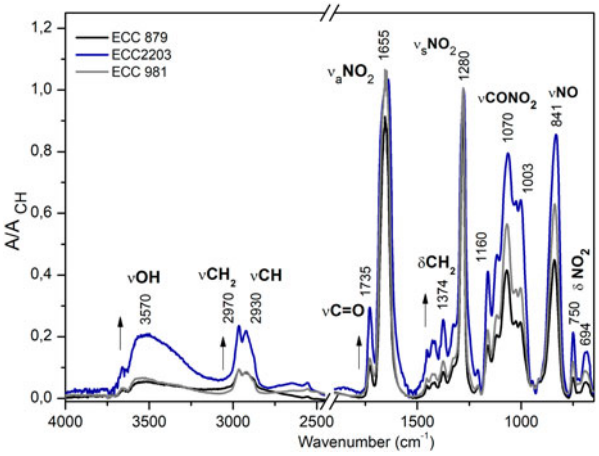


Figure 3. μ-FTIR spectra for three CN film-based negatives from the ECC collection representative of the different intensities found for the overall sample set.

surface of the gelatine anti-curling layer, and by crossing μ-FTIR and pH results there was effectively no correlation. However, the data obtained for negatives from groups B to E indicate a possible correlation between the pH and the image corrective treatments. This fact is particularly evident for negatives from groups C and F for which μ-EDXRF analysis confirmed that Cr is the main element present in the image and lower pH values were recorded.

Further work on a larger set of negatives must be performed to confirm this possibility.

Conclusions

This work allowed gathering of insightfull information about materials and photographic techniques used in 'colonial photography'. Documentary sources indicated the storage conditions and the possible photographic techniques used by the photographer to correct the image density. The results obtained in this work confirmed the use of chemical treatments to correct the image and also allowed to distinguish and propose which intensification and reduction solutions were used. It was shown that several hues result from those intensification and reduction treatments and a clear association between hues and treatments was suggested. Considering the framework of this study, μ-EDXRF and SEM-EDX analysis gave an insightful comprehension of *Elmano Cunha e Costa* work and launch new perspectives about the practice of colonial photography that might be transversal to other collections performed in the same context. According to the results it was concluded that from the total set of negatives selected for this study, 11 have been submitted to intensification and reduction corrective treatments, being representative of the macro assessment performed. Moreover, apart from two groups of negatives, the chemical elements found allowed correlation of the colours with the type of intensification and reduction corrective treatments used.

Moreover, the results obtained in this study suggest that chromium salts were used for hardening the gelatine layer as a preventive action in hot climates. Thus, considering the correlation between low pH and Cr found, new preservation priorities may be launched since this chemical element has a detrimental effect on polymers and may catalyse the degradation of the object. Additionally, the SEM-EDX results confirmed the presence of the transition metals identified by μ-EDXRF localized in the emulsion layer, reinforcing the need for establishing these negatives as a priority for the preservation strategy.

The preservation strategies for the ECC collection as well as other collections resulting from colonial photography may be reviewed and tailored measures may be implemented on the basis of the results presented in this work.

Taking that into consideration, further research on photographic negatives with the same types of hues and resulting from colonial photography must be carried out. Additionally, further work must be done to assess the effects of different intensification and reduction chemical treatments on the gelatine layer and CN supports with the aim to predict their impact on the lifetime of those negatives. The presence of Zn should also be investigated since the presence of this metal was not clarified. Additionally, by correlating the colourimetric and μ-FTIR results it was concluded that in this collection the yellowish, reddish-brownish, and orange tonalities result from chemical treatments rather than chemical decay of the negative's support. Additionally, the visual and molecular assessment of the negatives' supports (good to fair condition) allow proposing that the original storage conditions may have had a beneficial contribution for their present condition.

These results are relevant for the conservation and preservation of photographic negative collections since the hues may be used as markers for identification of the elements forming the image of historical film-based negative collections produced in a colonial context. Identifying the origin of the hues will also help to better assess the history of the collection.

To our knowledge, this is the first research focused on the analytical study of photographic materials and photographic techniques carried out in a 'colonial photography' context. Furthermore, based on the analytical results obtained new perspectives on the practice of colonial photography are launched by introducing an innovative contribution about the image corrective treatments and possible contributions of the storage systems used for the present preservation of film collections.

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