Non-Destructive Dating of Fiber Based Gelatin Silver Prints Using Near Infrared Spectroscopy and Multivariate Analysis

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Abstract

An innovative approach to date fiber based gelatin silver prints using Near Infrared Spectroscopy and Multivariate Analysis (NIR/MVA) is presented. NIR spectra were acquired for 152 film stills printed in the US between 1914 and 1986 and Partial Least Square (PLS) analysis was used to correlate the spectra with the year the photographs were printed. Principal Component Analysis (PCA) and spectral interpretation helped clarify the underlying correlation between the print date and the composition and ageing of the photographic papers. The method was successfully validated with an independent set of 66 film stills printed in the US and a prediction error (RMSEP) of 6 years was achieved. The method was also tested on films stills printed in Germany and Russia, as well as amateur prints and photographs in the collection of the Museum of Modern Art (MoMA). The prediction error was significantly larger, with the exception of the amateur prints, due to differences in the composition and/or properties of the papers depending on their geographical origin and purpose as confirmed by Discriminant Analysis (PLS-DA)

Keywords

Photographic Paper, Cultural Heritage, Dating method, Near infrared spectroscopy, Multivariate Analysis

Introduction

The date a photograph was printed can be fundamental to the understanding of the work, its historical context, and the artist's aesthetic at the time the print was made. It also carries implications for its conservation, treatment, display and storage. When the provenance of a gelatin silver print is unknown or in question, examination of the physical properties of the photograph is the first step in establishing a plausible date range. In addition, more objective information such as manufacturer back printing [1, 2], surface texture [3, 4], presence of optical brighteners [5], mineral content [6, 7], pulp type and fiber species [1, 8, 9] might corroborate and possibly narrow the time frame.

Even though the paper support is but one aspect of the complex and multilayer fiber based gelatin silver photograph, dating methodologies based on the composition of the paper are becoming increasingly valuable tools [10, 11]. Manufacturing processes and selection of raw materials have changed over the course of the last century, for pulp and paper in general [12, 13] as well as for photographic paper [14]. In addition, changes in the chemical composition and the physical properties of paper are brought by natural ageing [15]. These changes in the composition and properties of the paper could, thus, in principle, be the foundation of a dating methodology if a) suitable techniques are available to register and quantify these changes and b), a representative set of dated photographic papers can be used as a reference material to establish correlations between the measured properties and the print date.

Near-infrared spectroscopy is an exceptionally versatile and flexible non-destructive and non-invasive technique with numerous applications in a wide range of research fields and industrial sectors, including paper and pulp manufacturing [16-25]. It provides limited structural information when compared to other infrared regions, but when combined with multivariate analysis, methods can be developed to predict chemical composition, physical properties and attributes of a wide range of materials and products [26-28]. NIR is steadily making its way into the field of cultural heritage. Applications of this technique have been proposed to characterize and monitor the condition of textiles [29], historical papers [30,31], chromogenic color prints [32], iron gall inks [33,34], parchment [35] and archeological wood [36]. Quantitative chemical imaging applications have also recently been explored [37]. Additionally, portable instruments are increasingly available, which is important for heritage institutions.

In some of the cultural heritage applications cited above, NIR was used to develop indirect methods to date cultural heritage objects. In this work, we report on the development of a method to date fiber based gelatin silver prints using a similar approach. Reflectance spectra were acquired for more than two hundred gelatin silver photographs

printed in the US between 1914 and 1986. Partial Least Square (PLS) was used to model the known print date and develop a calibration. Principal Component Analysis (PCA) and analytical interpretation of spectra were used to clarify the correlation between the print date and the composition and properties of the paper. The method was also tested on film stills from Germany and Russia, as well as amateur prints and photographs in the Museum of Modern Art (MoMA) collection. Discriminant Analysis (PLS-DA) was used to compare the properties of the different types of paper.

Experimental Section

Photographic papers

The dating method was developed using a set of gelatin silver photographs from the MoMA Film Stills Archive, an extensive collection of photographs numbering in the millions that were originally made on the movie set during production and primarily served a promotional purpose. A evenly distributed set of 218 photographs printed in the US between 1914 and 1986 was used to develop and validate the dating method. The year each photograph was printed is given by the movie release date and confirmed by dated stamps, on the verso, for their publication or distribution. Small sets of film stills printed in Germany (37) and Russia (10), amateur prints from a personal collection (8) and photographs from the Museum of Modern Art collection (8) were used to evaluate the applicability of the dating method to papers with different geographical origin and quality.

Photographic paper is a complex material arranged in several layers of varying thickness (see image 1) [38-40]. The primary support is paper and it is mostly composed of cellulose fibers from various sources (hardwoods, softwoods, cotton, bast) and obtained through different pulping processes (generally soda, sulfite, kraft chemical processes), thus leading to a high variability within the raw material [1,41]. The paper also contains inorganic fillers, sizing, wet strength agents, optical brighteners, etc… [13]. An intermediate layer, also called baryta layer, consists of a mixture of barium sulfate and gelatin (optical brighteners and other additives may also be present) and is applied to modify the surface and reflective properties of the image layer. Directly over the baryta is the gelatin binder which contains the silver image material. Photographs may be treated with surface coatings but this is either applied by the artist or is an indication of the photograph's treatment history.

An independent survey conducted by Duverne et al. [39] on 550 photographic papers from 25 different manufacturers found that the thickness of the paper support varied between 0.066 and 0.465 mm, the baryta layer between 0.006 and 0.045mm, and the emulsion layer average thickness was 0.015 mm. Two major groups of papers were distinguishable, with 0.17 and 0.36 mm average thickness respectively, corresponding to "single weight" and "double weight" papers (designations amongst manufacturers may vary slightly). In the case of the film stills used in

this study, the same two categories of paper were clearly distinguished (< or > 0.23 mm) the majority being thinner (in average 0.17 mm) and around 10% of the papers being thicker (on average 0.31 mm). Both types of papers are distributed throughout the time period under analysis.
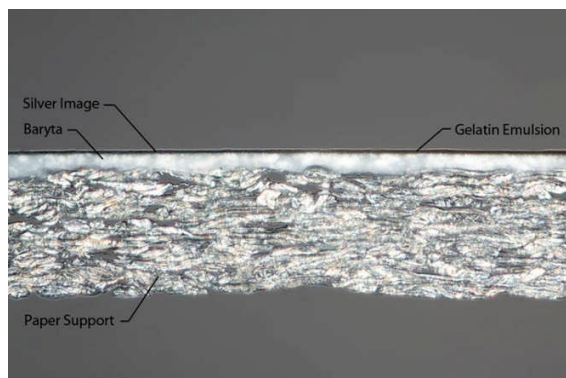
Image 1: Cross-section of a fiber-base gelatin silver print showing its layered structure (Courtesy Image Permanence Institute)

Spectroscopic analysis

Two different instruments were used to study the advantages and shortcomings of portable vs. benchtop instruments. The handheld instrument was a Thermo Fisher Scientific microPHAZIR RX, equipped with a Tungsten light source, single-element InGaAs detector, spectral range: 1600 – 2400 nm (6250 - 4100 cm^{-1}), and optical resolution 11 nm. The benchtop instrument was a Thermo Fisher Scientific Antaris II FT-NIR analyzer, with a quartz halogen light source, single element InGaAs detector, spectral range: 10,000 – 4,000 cm^{-1} and optical resolution: 8 cm^{-1}. Spectra were collected in diffuse reflectance mode in both cases with a gold-coated integrating sphere. The data are transformed and presented as absorbance.

Spectra were acquired from the verso only (64 scans with the Phazir and 100 scans with the Antaris). A Spectralon® Diffuse Reflectance Standard (SRS-02, 2% reflectance factor) was used as backing material. A special cardboard platform was designed for the Antaris instrument so that prints could be analyzed safely. The prints were sandwiched between 2 sheets of 0.008 mm clear Mylar® polyester film, each of them with a Ø1.5 cm punched hole for and over the sampling area.

The spectral variability introduced by sample positioning and heterogeneity of the paper was calculated as the average standard deviation for 16 randomly acquired spectra (4 measurements on 4 different locations) and was estimated to 0.002 absorbance unit corresponding to less than 1% of the average absorbance. No further investigation of the robustness with respect to these two factors was pursued at this stage. Three spectra were

acquired for each print when using the Antaris (on three different spots with medium image density on the recto side). The average spectra were computed using GRAMS AI Spectroscopy Software (Thermo Scientific). One single spectrum was acquired for each sample with the Phazir.

To help in the interpretation of the NIR data for photographic papers, spectra were also acquired for some of the materials typically found in photographic papers, namely kaolin, barium sulfate, calcium carbonate, titanium white, and gelatin (from the MoMA Photo Conservation Lab reference collection) and 100% cotton paper (Whatman Qualitative Filter Paper 100% cotton fibers).

Multivariate Analysis

The analytical information contained in the typically broad and extensively overlapped bands of the NIR spectra is hardly selective and spectral differences between samples are generally difficult to distinguish. The relevant chemical or physical information can be enhanced by mathematical preprocessing of the spectra and extracted from the spectral background using multivariate classification methods (for qualitative analysis) or multivariate regression methods (for quantitative analysis). Principal Component Analysis (PCA), Discrimant Analysis (DA) and Partial least Square (PLS) are among the more extensively used variable reduction and regression methods to handle NIR spectra [17, 26, 27] and were used in this study. Several data preprocessing methods were used to linearize, average and smooth the data and correct for scattering. Different methods are available and discussed thoroughly in the literature [17,26-28]. Details for method development, optimization and evaluation are given in the results section.

Omnic™, TQ Analyst™ and Polychromix-MG analysis software (Thermo Scientific) were used for a pre-evaluation of the data acquired with the Antaris and Phazir instruments, respectively. The Unscrambler® (CAMO) was used for a more detailed multivariate and statistical analysis. OriginPro (OriginLab) was used for graphing.

Results

Spectral interpretation

The most prominent absorption bands occurring in the NIR region (780 – 2500 nm / 12820 - 4000 cm^{-1}) are related to the overtones and combination bands of the fundamental molecular vibrations of –CH, –NH, –OH and –SH functional groups observed in the mid-IR spectral region, although typically 10 to 100 times weaker, which allows for a higher degree of penetration into the sample [42]. For solid samples, information with respect to scattering, diffuse reflectance, specular reflectance, surface gloss, refractive index, and polarization of reflected light are all superimposed on the near infrared vibrational information.

NIR is not particularly suited for molecular structure elucidation, but some of the spectral features of the NIR spectra can be assigned to specific components of photographic paper. Fig. 1 shows the typical spectrum of a fiber based gelatin silver print examined from recto and verso. Also included are the spectra of clay, gelatin, and pure cotton paper.
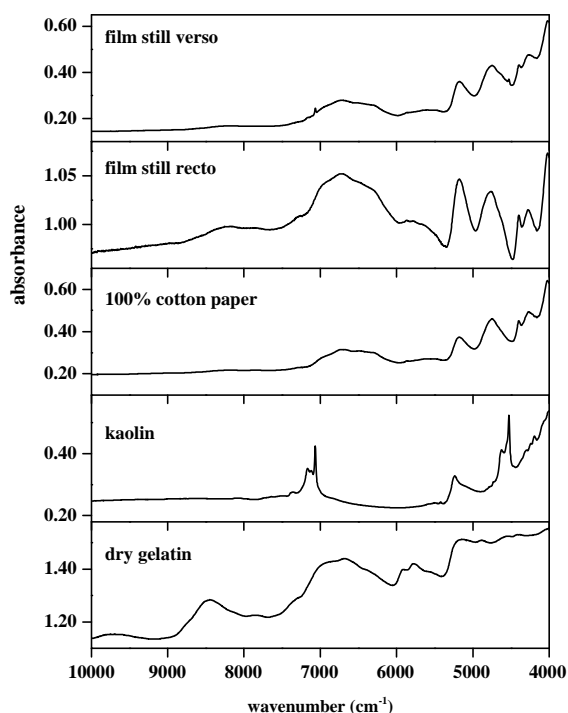
Figure 1: Typical NIR spectra for the film stills examined from the (a) verso, and (b) recto. NIR spectra for pure cotton paper (c) kaolin (d) and dry gelatin. All spectra were acquired with Antaris.

The spectrum for the photographic paper is clearly dominated by features characteristic of cellulose fibers (the matching correlation coefficient between the average spectrum for all the film stills taken from the verso and the spectrum for pure cotton paper = 0.997) and free/bridging water. Bands can be assigned to the 2nd overtone of the C-H stretching (8800-7700cm^{-1}), the first overtone of the hydroxyl groups (7000-6200cm^{-1}), the first overtone of the C-H stretching and O-H vibrations combination bands (6000-5400cm^{-1}), the combination bands of OH (5300-4500cm^{-1}), and combinations of C-H, C-C, O-H and C-O vibrations (4500-4000cm^{1}) [43-45]. The pronounced broad band at 5175 cm^{-1} can be assigned to the O-H stretching and oscillation vibrations in adsorbed free water [42].

Hydroxyl and water in minerals and inorganic compounds have a band with an average position around 4200cm^{-1} due to M-OH motions, a second band assigned to H_2O combination mode (bend + stretch) at 5200cm^{-1} for hydrated minerals and around 4600cm^{-1} for inner hydroxyls, and a third average band around 7100cm^{-1} corresponding to the

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first OH stretch overtone [46,47]. Clay is one of the most widely used fillers in paper [13] and the NIR spectrum of kaolinites shows bands at the exact same position as the sharper small bands observed for the photographic paper (7065 cm^{-1} and 4525 cm^{-1}) [47,48].

Other minerals may be expected in the paper, such as alum, used as a precipitating agent for both gelatin and rosin sizes, but previous studies could not establish a satisfactory correlation between aluminum content and NIR spectra for historical papers [30]. Calcium carbonate might also be present as a filler [6,13] but has no significant contribution in NIR (the major carbonate bands around 4000cm^{-1} and 4300 cm^{-1} were not to be detected [49]), and so does barium sulfate present in the baryta layer (barium sulfate based coatings are used as reflectance standards in the UV-VIS-NIR spectroscopy). Alternative techniques such as mid infrared spectroscopy, Raman and X-Ray fluorescence spectroscopy are better suited and are being used to confirm the presence of these compounds.

In terms of other organic constituents besides cellulose, previous studies have established correlations between NIR spectra and the concentration of rosin [50] and gelatin sizing [31] in historical papers. A small band is observed at 4620cm^{-1} (shoulder), not common to the 100% cotton paper. In this region, combination bands of the N-H stretching mode are usually observed [42], suggesting that this band, also observed from the recto side (gelatin image layer) might be related to the presence of gelatin [31, 51].

1425 (s, b) 870 710	ν_3 (CO3) asymmetric stretching ν_2(CO$_3$) out of phase CO3 bending vibration ν_4(CO$_3$) in plane CO2 bending	CaCO3
1160 (s)	vas(C-O-C)	cellulose
1104 (s)	ν(C-O)	
1028(vs)/1051 /1002/985 (sh)	ν(C-O)	
897 (m)	C1-H bending	

b1 (C=O)
$\nu 3$(CO3)
vac(C-O)
b2 (C1-H bending)
ν(C-O)
C1-H bending
ν_2(CO$_3$)
b3 (C-H out-of-plane bending)
ν_4(CO$_3$)
b4 (C-H out-of-plane bending)

Exploratory data analysis

It has already been established, in the case of books, that NIR is sensitive to changes in the composition of paper as a result of ageing and different manufacturing processes, and that an indirect correlation between NIR spectra and a paper's age or manufacturing date can be derived [31]. A similar correlation is the main objective of this study.

An example of detectable changes in the composition of photographic papers over the time period under study is evidenced in figure 2. The sharp band at 7070-7030cm^{-1}, attributed to kaolin (until further confirmation with another technique) is observed in papers manufactured until the mid 1930s. Independent studies on a reference collection of photographic papers manufactured in the US [52] had already evidenced that the abundance of Si, Fe, K (consistent with clay) is significant for that time period [7]. A similar trend is observed for the other bands assigned to clay around 7200-7100 cm^{-1} and 4520cm^{-1} (not shown).
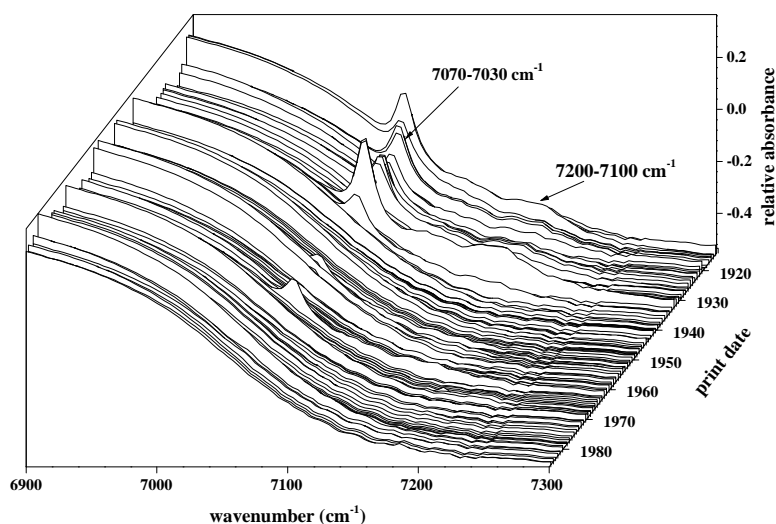
Figure 2: Segment of the NIR spectra obtained for the film stills over the time period under study.

The NIR data was further examined using Principal Component Analysis (PCA) to better reinforce and clarify the variation between samples and visualize the region of the spectrum where variation occurs. The first three principal components account for 99% of the spectral variation (PC1: 79%, PC2: 19%, PC3: 1%). The corresponding loadings plots (figure 3) suggests that the variation in the samples spectra is related to paper ageing (PC1), paper thickness (PC2) and presence of clay (PC3).
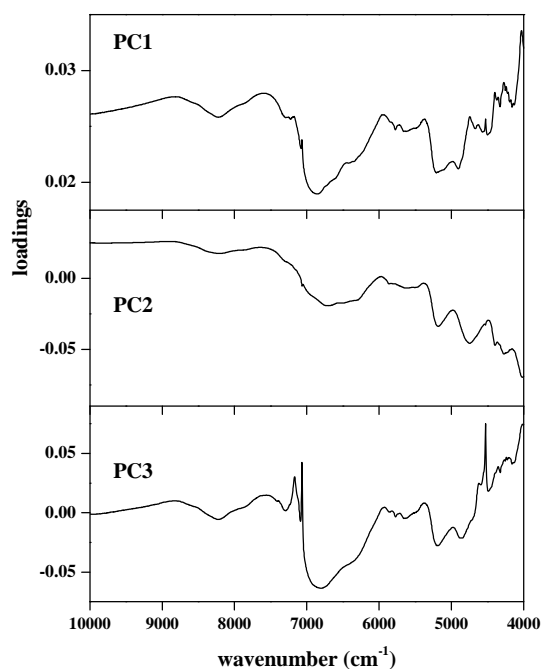
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Figure 3: PCs loadings plot from the PCA on the raw spectra for the 218 film stills.

The first component accounts for the variation observed in the regions of the spectrum associated with C-H bands and in an inverted proportion with O-H bands indicative of hydrolysis as a major component of a paper's aging. The apparent systematic variation of the PC1 scores vs. the print date (figure 4) reflects an increase of the abundance of C-H groups and decrease for the O-H groups as expected when paper ages [15, 31].
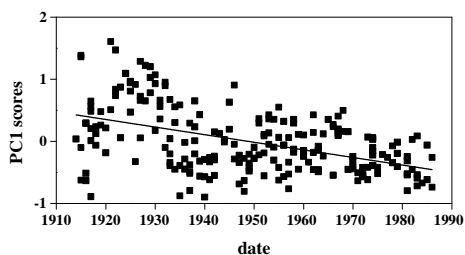

Figure 4: PC1 scores vs print date for the 218 film stills.

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The second component accounts for the variation in the scattering contribution (10000 – 7000cm^{-1} region). The PC1 vs. PC2 scores plot (figure 5) evidences that the scattering is more pronounced for the thinner papers as expected if related to the presence of the baryta layer (previous studies have shown that effective path length in the case of paper is ~0.5 mm [31], which is more than the thickest photographic paper in the sample set).
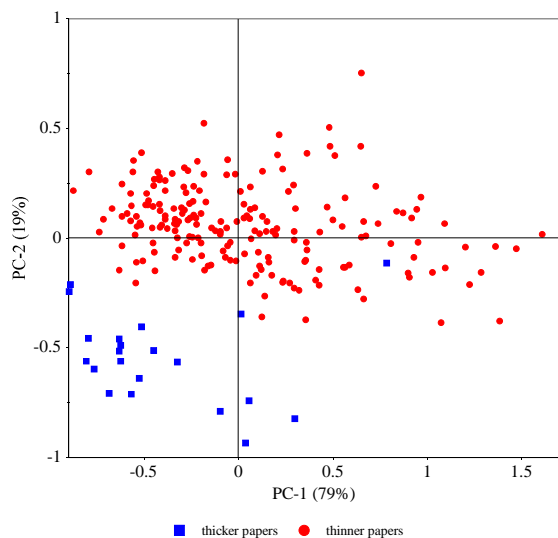
Figure 5: PCA scatter plot for the 218 film stills printed. Grouping by paper thickness is evident (thickness > 0.23 mm for thicker papers).

The loadings plot for the third component confirms that some of the variation in the spectra is related to the presence of kaolin as already evidenced above.

Development of the calibration method

Partial Least Square (PLS) was used to establish a correlation between NIR spectra and the year the prints were made and to develop a predictive model to date photographs.

Ideally a calibration model needs to be validated with a set of independent samples in order to check how well the model will perform when used on unknowns. Validation can be done by testing the model on a subset of the available sample set, which is not used in calibration. The test set should contain 20-40% of all available samples the calibration and test set should in principle cover the same variability of samples. Sample set splitting into calibration and independent validation set can be performed manually, or resorting to mathematical approaches to select/divide/optimize the calibration and validation test sets. In this particular study, stratified sampling (per

decade) was the approach chosen to divide the original sample set in two uniformly distributed sets, 152 samples for the calibration, and 66 for the validation.

Signal pre-processing generally improves model accuracy by reducing the impact of sources of variability and increasing signal to noise level. There are several standard mathematical treatments available to compensate for scatter-induced baseline offsets, including multiplicative scatter correction (MSC) and standard normal variate (SNV). Baseline shifts and intensity differences resulting from variable positioning or path length variations may be reduced or eliminated by normalization algorithms. Derivatives can be applied to improve the resolution of overlapping bands and in addition, they also reduce baseline offsets. Since spectral noise is, however, amplified by derivation, derivatives are usually combined with smoothing algorithms such as Taylor or Savitzky Golay (SG). Detailed description of spectra preprocessing is provided in the literature [17, 19, 21, 26, 53]. The algorithms are frequently combined to improve the model (see table 1 for a partial list of the preprocessing methods tested in this study), and the quality of the fit can be evaluated through the statistics of the regression: correlation coefficient for the regression (R^2), the root mean square error of cross-validation (RMSECV), the root mean square error of prediction for independent sets (RMSEP) and number of required PLS factors to model the data.

The PLS analysis was performed using the entire wavelength range. There are several mathematical methods available to determine and select the most relevant variables or spectral regions to improve the accuracy and performance of the model [37,54-56]), but the results of the calibration using the whole spectra were considered satisfactory at this stage.

The optimal combination of preprocessing operations (levels of significant difference between treatments were not calculated) was standard normal variate (SNV) followed by Savitsky-Golay first derivative (second order polynomial and smoothing over 7 points window width). The highest correlation coefficient was obtained for a model with 8 latent variables, an error of cross calibration (RMSECV) of 7.1 years and an error of prediction (RMSEP) of 6.1 years. The corresponding calibration and validation plots are shown in figure 6. PCA analysis was performed on the pre-processed data to ensure that the influence of the paper thickness had been suppressed.

Instrument	Spectral range (cm⁻¹)	N	Preprocessing method	calibration			validation	
				# PLS factors	R^2	RMSECV (years)	R^2	RMSEP (years)
Antaris	12000-4000	3	raw spectra	11	0.86	7.9	0.84	7.9
			MSC	9	0.85	8.0	0.82	8.2
			SNV	9	0.85	8.0	0.82	8.2
			normalization	10	0.86	7.9	0.83	8.0

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			baseline offset	10	0.85	8.0	0.83	8.1
			1rst derivative SG	11	0.91	6.3	0.89	6.4
			2nd derivative SG	8	0.89	7.0	0.89	6.7
			normalization + SNV	9	0.85	8.0	0.82	8.2
			SNV + 1st derivative SG	**7**	**0.86**	**7.1**	**0.90**	**6.1**
			SNV + 2nd derivative SG	8	0.90	6.6	0.89	6.5
			SNV + 1st derivative SG + normalization	8	0.87	7.4	0.90	6.1
Phazir	6250-4100	1	**MSC + 1st derivative SG**	**6**	**0.86**	**8.2**	**0.82**	**9.9**

Table 1: Summary of the parameters of PLS calibration and validation for different preprocessing methods (R^2: correlation coefficients for the cross validation and the validation, RMSECV: root mean square error of cross validation, RMSEP: root mean square error of prediction, N: number of spectra averaged for each sample).

Results of PLS analysis for the data acquired with the Phazir handheld instrument are also included in Table 1. The loss of accuracy is most probably related to the sampling variance.
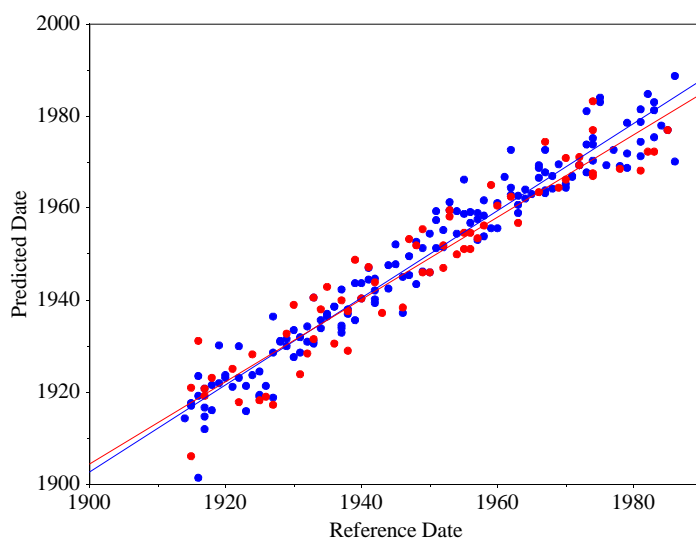
Figure 6: Year a photograph was printed as predicted by the optimized PLS model versus the reference value; (in blue) values predicted for calibration and (in red) for the validation set.

The quality of the model is similar to the quality of other dating models for chromogenic color prints (RMSECV = 5.4 years / 1942-2008 period) [32], and paper produced post-1850 (RMSEP = 9 years / 1850–1990 period) [31], and better than obtained for parchment (RMSECV = 72 years / 1200-1800 period) [35].

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While the error of prediction (RMSEP) is acceptable, it is worth examining the uncertainty in the reference dates for the film stills. Considering the dating method does in fact reflect the nature and concentration of the paper constituents as they changed over the 20th century, and possibly to a lesser extent the accumulation of degradation products over time, the correlation should be established *vis a vis* the manufacturing date and not the printing date. The time elapsed between paper manufacturing and printing can be up to 3 years and even more if the shelf life of the photographic paper is extended beyond its expiration date [1]. Moreover, photographic paper manufacturing entails different steps performed over a period of time, from pulp production, preparation and application of the baryta coating, and finally coating with the emulsion [14]. Another conceivable contribution to the prediction error is the history of each photograph, hence its ageing, prior its arrival in the museum archive.

Testing the scope of the dating method

The calibration model was developed and validated for film stills produced in the US. Ultimately, the objective is to widen the scope of application of the dating method to other types of photographs. Consequently the method must be validated accordingly and if not suitable, a new method must be developed specifically for each type of photograph or by including them in the calibration set.

The dating method was used to predict the printing date of film stills printed in Germany (37 samples) and Russia (10 samples), and of photographs other than film stills, namely amateur photographs from a private collection (8 photographs) and photographs in the MoMA collection (8 photographs). Results are summarized in table 2 and show that the error of prediction is generally larger than the error obtained for the film stills printed in the US, and that bias in the dating is also observed.

Sample set	# of samples	BIAS (years)	RMSEP (years)	correlation
American film stills (validation set)	66	-0.8	6.1	0.95
Russian film stills	10	+ 3.8	16.4	0.50
German film stills	37	+ 5.6	19.3	0.27
Amateur prints	8	+ 7.2	7.8	0.90
Collection print	8	+ 10	16.0	0.60

Table 2: Summary of prediction statistics obtained for papers of different geographical origin, quality and purpose and using the model developed with the film stills printed in the US.

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This indicates that the calibration might not be suited to date photographs other than film stills printed in the US and that specific calibrations are required for the different types of photographs. The results might have been affected also by experimental conditions: the film stills printed in Germany, Russia, as well as the collection prints had been stored and were analyzed in a different laboratory (instrument transport) with slightly different environmental conditions (21 $^{\circ}$C / 50% RH and 25 $^{\circ}$C / 45% RH). Further robustness studies are required to examine the impact of these experimental parameters.

PLS Discriminant Analysis (PLS-DA) confirms that papers differ in their composition and properties. Figure 7 shows some selected scores plots for the PLS-DA of (a) films with different geographical origin (US, Russia and Germany) and (b) photographs intended for different purposes (film stills, collection prints and amateur photographs) that evidences those differences. Examining the PLS loadings to interpret the difference between the papers is rather complex as spectra were pre-processed. Complimentary analysis with other analytical techniques is required to determine the composition of the papers and to corroborate and explain the discrimination observed by PLS-DA.
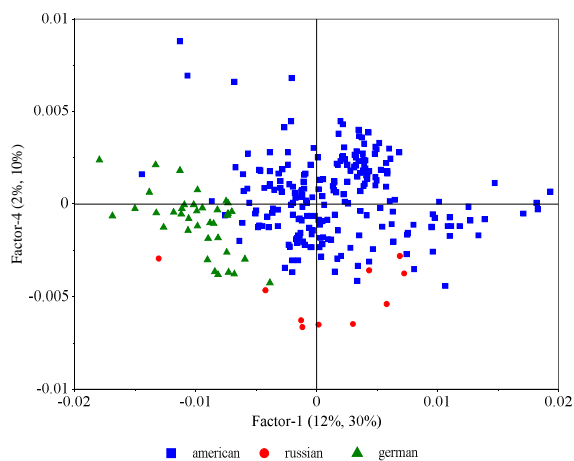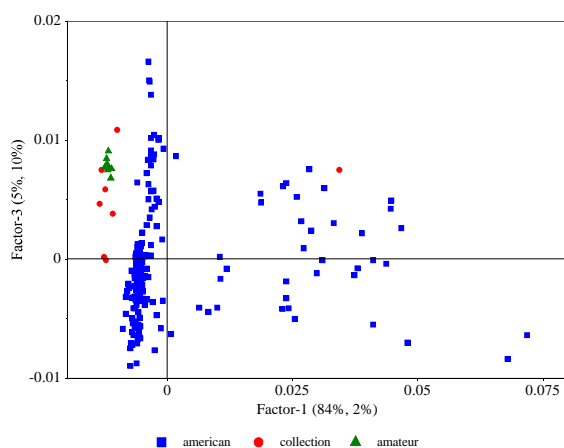
Figure 7: PLS-DA scores plot for (a) film stills printed in the US, Germany and Russia (8 factors / 97% of the variance) and b) film stills printed in the US, amateur prints and photographs in the MoMA collection (11 factors / 95% of the variance). Spectra were pre-processed (SNV + 1st derivative SG).

Conclusions

A scientific method was successfully developed to date fiber based gelatin silver photographic papers that relies on a correlation established by multivariate analysis between the year a photograph was printed and its NIR spectrum. The method is non-destructive and non-invasive and could thus be useful as an auxiliary tool for scholarly purpose and preventive conservation of photographs.

The calibration was developed using PLS analysis on the NIR spectra for a reference set of dated film stills printed in the US between 1914 and 1986. Spectral interpretation, PCA and PLS-DA revealed that discrimination of the papers is related to both their composition in terms of raw materials and ageing, and that significant differences may be observed depending on the geographical origin or purpose and intent. The validation of the model led to a prediction error of 6 years for film stills produced in the US. Specifically tailored calibrations are required for other types of photographs.

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