# A STATISTICAL METHOD FOR THE SPECTROSCOPIC ANALYSIS
# OF PHOTOGRAPHIC COLOR PROCESSES

Giorgio Trumpy and Rudolf Gschwind - Digital Humanities Lab - Universität Basel

## Introduction

The 'mature age' of photography is an industrial history, which is to be narrated through the successes, vicissitudes and failures of numerous photographic companies, which competed for producing technologies attractive for a wider and wider public. The competition between these companies implied that formula, processes and recipes were often kept as trade secrets to protect their economic advantage over competitors.

For materials of recent production, the manufacturers often supplied datasheets containing some technical information of the product; conversely, for older materials it is difficult, or even impossible, to obtain technical information, as the manufacturer may no longer exist. A German film historian collected the technical data published by the photographic companies [1]; the book is the outcome of a comprehensive research and a valuable source of information, but its structure, however, denotes the disorganized and incomplete essence of the available material.

The 'digital revolution' is producing a sudden change in the technology of image production and 'classical photography' is disappearing. This demise is taking place in a precipitous and often ruinous way, causing the bankrupt of several memorable companies [2, 3]; the recipes of their products may become permanently irretrievable in a close future and many of them are already lost.

Today's information society needs efficient and economic solutions for the digitization of the photographic heritage; the effectiveness and the efficiency the processes determine the amount of photographs and motion pictures that can be digitized, restored and made available to the community.

The project is determined to configure a methodology for the estimation of the single dyes spectra (*analytical densities*) from the integral absorbance spectra of photographic films and papers. The knowledge of the analytical densities can be useful for (I) identification purposes and (II) for the optimization of the digitization workflows.

### Photograph identification and historical research

A spectral database of photographic color processes can be useful for historical research. The spectroscopic analysis in the near-infrared and visible ranges can be characterizing for the color photographic processes.

Other type of analysis can be adopted for making a photograph a reliable historical source. An expert direct observation of the object may already provide important informative elements, relying on its format, type, notches, imprintings and barcodes (paying attention to their location, font, color, etc.) [4].

In case a photographic relic is found devoid of these metadata, or in case the metadata are not sufficient, spectroscopy may allow to identify the product and its color process through a non-invasive analysis; to this purpose, becomes necessary to query a previously collected spectral database of photographic processes.

### Optimization of the digital imaging workflow

The choice of the illumination used for image acquisition massively determines the quality of the digital image data, thus affecting the image usability for its preservation and restoration purposes.

The dyes of common chromogenic processes are chemically rather unstable and color fading is a very diffuse problem; in such cases, the development of accurate technologies and advanced acquisition procedures becomes fundamental. The possibility of digital technologies to restore faded photographs is determined by the illumination used during image acquisition [5].

To maximize the color information recorded, the ideal light source for the image acquisition of a color photograph consists of three narrow-band sources whose wavelengths maximize the absorbance variance of the three component dyes,
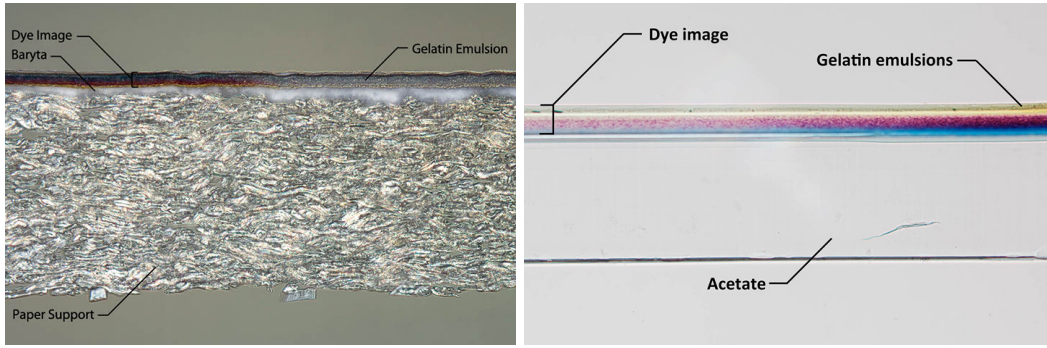
Figure 0.1: Microscope images of thin sections: on the left a chromogenic print (Kodacolor), on the right a chromogenic film (Ferraniacolor) - images taken from [7]
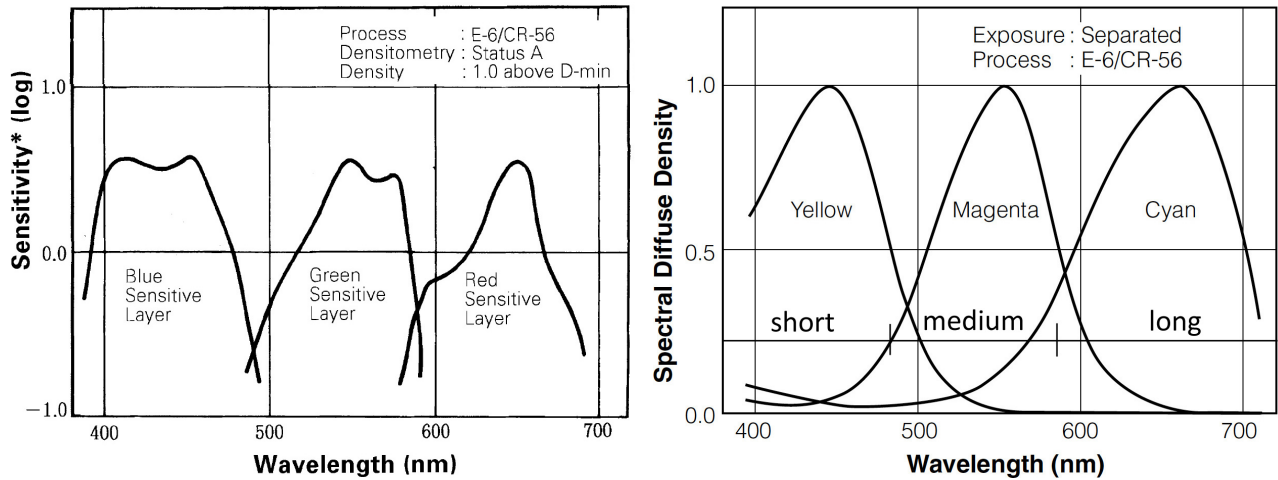


Figure 0.2: Spectral sensitivities (left) and spectral densities (right) of FUJICHROME Velvia 50 Professional [RVP50] - images taken from [8]

and at the same time minimize the influence of the *side absorptions*; this allows lowering the correlation between the signal recorded by the color channels of the sensor, and consequently, the acquired color information is increased.

In light of this, the knowledge of the analytical densities provides useful information to design the digitization workflows.

## Principles of color photography

Modern color photography is a triumph of applied chemistry; the present text focuses on the spectroscopic aspects, without examining in depth the chemical reactions involved in the processes.

As in the majority of color reproduction technologies, in photography color is reproduced with a tri-variant system. The basic step in subtractive color photography is the formation of cyan, magenta, and yellow dye-images; in an exposed and developed photograph the dye concentrations vary from point to point, and a dye concentration triad characterizes each point [6].

In modern subtractive processes of color photography, the three images are taken simultaneously on three emulsions coated one on top of the other (Fig. 0.1). During emulsion manufacturing, the three layers are made sensible to different parts of the visible electromagnetic range, with a process that is called *sensitization*. The plot in Figure 0.2 shows a typical distribution of the emulsion *sensitivities*, which express the efficiency of each exposing wavelength to produce the required effect (i.e. formation of dye).

After the exposure in camera, in each emulsion layer the developing process produces a dye; the quantity of produced dye is dependent on the spectral composition of the light to which the emulsion was exposed. The precognition of the
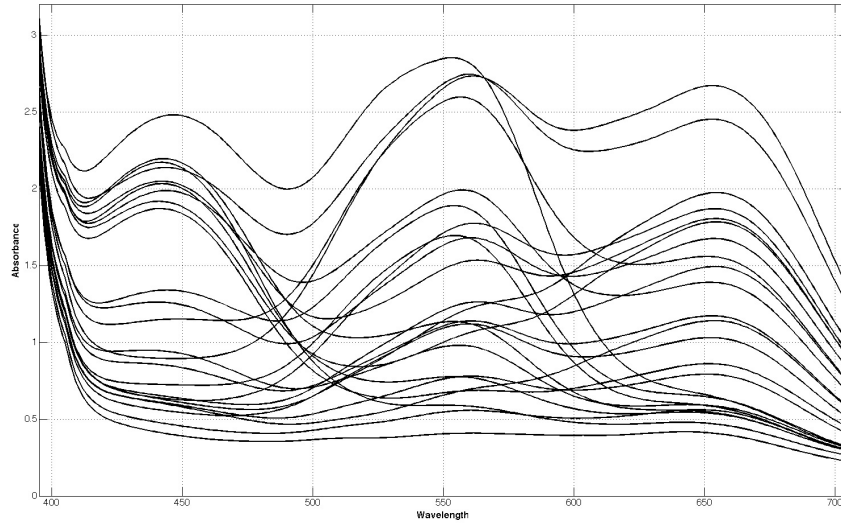
Figure 0.3: Spectral measurements on a FUJICHROME Provia 400X [RXP]

spectral sensitivity of the emulsion layer allows predicting how much dye will be formed for a specified exposure of a specified spectral distribution.

The *absorption* (or *optical density*) due to the dye of a developed photograph 'subtracts' light from the illumination and put the subtractive color reproduction into effect.

In a simplistic description of the subtractive process, the visible spectrum (400-700nm) is divided in three regions: short (400-480nm), medium (480-580nm), and long (580-700nm) wavelengths. A dye absorbs the long (red) wavelengths and transmits the short (blue) and medium (green) wavelengths: the visual result is cyan. Another dye absorbs the medium (green) wavelengths and transmits the short (blue) and long (red) wavelengths: the visual result is magenta. The last dye absorbs the short (blue) wavelengths and transmits the medium (green) and long (red) wavelengths: the visual result is yellow. The effects of the three dyes combine according to their concentrations, leading to a multitude of final visual results.

For a more precise description of the process the *spectral densities* have to be considered; the typical spectral densities (normalized to 1) of the cyan, magenta, and yellow image-forming dyes are reported in Figure 0.2-right for the visible range.

In principle, there is not direct relation between the spectral sensitivity of a layer (Fig. 0.2-left) and the optical density of the dye produced by that layer with the development (Fig.0.2-right); in fact, sensitization and development are two distinct processes. However, the success of the color reproduction requires that the final image is judged satisfactorily by an observer; this satisfaction is connected to the relation between the spectral sensitivities and the optical densities of the final image: in case of the negative-positive system the final image is that of the print, whereas in a reversal film it is the image formed directly on the film with processing.

In color films, the absorbances of the single dyes compose together respecting two assumptions: the *Beer's law* is valid, and therefore, at any wavelength the optical density of each dye is proportional to the dye concentration in the layer; at any wavelength the final optical density of the composite image is equal to the sum of the optical densities of the single layers. In Figure 0.3 a set of spot measurements on differently colored points of a film is reported: the spectra subtend the tri-variant nature of the color information recorded.

Every photographic company tuned their own processes, adopting different *sensitizers* (which are also dyes) and different image-forming dyes; the majority of practical sensitizers are *cyanine* and *merocyanine*, while the image-forming dyes generally belong to the families of the *indoanilines* and the *azomethines*. These subtractive colorants should ideally modulate only the light of a single portion of the spectrum; in reality, the cyan dye, beside the long wavelengths, modulates also some short and medium wavelengths (see Fig. 0.2-right), and the same applies to the magenta and the yellow dyes. Actually, all real dyes have some unwanted absorptions: these are called *side absorptions*.
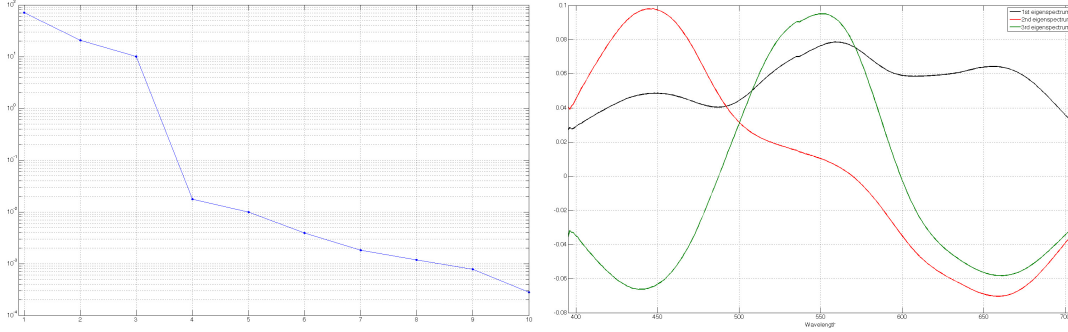
Figure 0.4: The first ten eigenvalues (left) and the three eigenspectra with the highest eigenvalues (right)

## Spectral measurements and estimation of the analytical densities

The arrangement of spectroscopic measurements for photographs is completely different depending on whether the support is paper or film. In case of paper prints *reflection measurements* have to be performed while, on the other hand, *transmission measurements* have to be performed in case of films; however, some basic principles of spectroscopy are equivalent in both cases [6].

Let $J_o(\lambda)$ and $J_1(\lambda)$ be the spectral radiant flux of the incident and emergent (reflected or transmitted) beams. The spectral absorbance $D(\lambda)$ is defined as:

$$D(\lambda) = \log {}^{J_0(\lambda)}\!/_{J_1(\lambda)}$$

The potentiality of spectroscopy relies in the possibility to measure the single absorption spectrum of each layer and to determine its absorption coefficient, irrespective to the specific local concentration. It has to be considered that (I) it is not feasible to mechanically separate the emulsion layers, (II) it is rather impossible to find points where only one dye was formed during the processing and (III) the principal absorptions of the three dyes are different but their spectra considerably overlay (Fig. 0.2-right).

For the above reasons, an absorbance measurement always involves and adds together the contributions of all the layers; therefore, it is necessary to find a procedure to infer the absorbance spectra of the single dyes (*analytical densities*) from the absorbance spectra of their mixtures (*integral density*). Principal Component Analysis (PCA) is a statistical technique that provides the possibility to estimate the absorbance spectra of the single dyes from their mixtures [9].

We measured a set of twenty-four points of a photographic film with a bench spectrophotometer (Shimadzu UV-1800); the spectra are reported in Figure 0.3. We applied the PCA on the spectra measured, considering the absorbance values of the various wavelengths as *attributes* of each observed point of the photograph. It can be seen from Figure 0.4-left that there is a prominent difference between the third and the fourth eigenvalues; we can therefore estimate with considerable objectivity that the number of independently variable components must be three. The three eigenspectra with the highest eigenvalues are reported in Figure 0.4-right.

The three *principal eigenspectra* are linear combinations of the real spectra of the constituent dyes. By supposing reasonable assumptions (e.g. spectral absorptions and concentrations of the dyes are always non-negative) and considering other information on plausible spectral characteristics, we can restrict the possible linear combinations of the eigenspectra into a narrower range and positively estimate the spectra of the constituent dyes [9].

In order to have an approximation of the real spectra of the dyes, and at the same time, reaching a single solution for every film treated with our procedure, we performed a minimization with a linear least-squares method to the *block dyes*; these are the ideal dyes that absorb uniformly in a specific spectral region of the visible range (short, medium or long wavelengths) and completely transmit in the other regions. By performing the minimization to these ideal dyes, we obtain a result that is unbiased.

The same procedure was applied on different film brands, and some differences between the calculated spectra emerged. Figure 0.5 reports the calculated spectra of a Fuji Provia 400X and a Kodak Ekta 100VS; the peaks of the yellow and the magenta dyes of the two films are found to be in a slightly different position; the cyan dye of the Kodak film has broader absorption and starts to absorb again towards 400nm; the magenta dye of the Kodak film has a noticeable side absorption at 440nm.
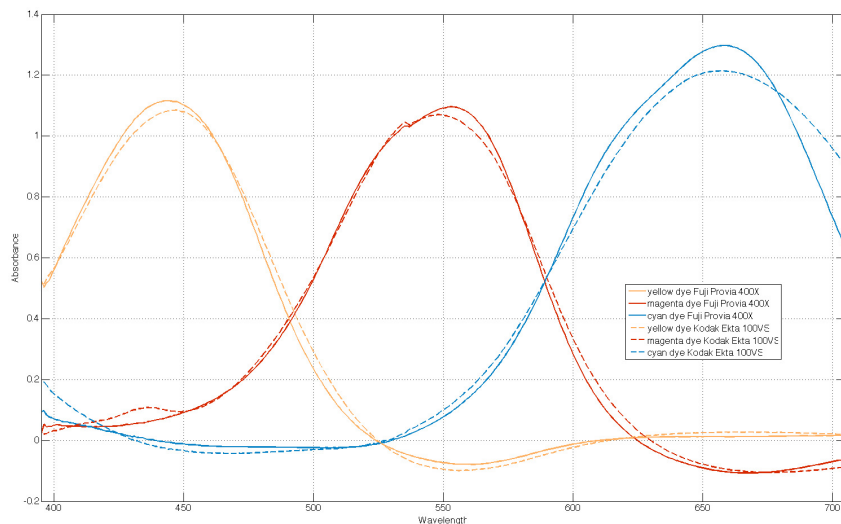
Figure 0.5: The calculated dye spectra of a Fuji Provia 400x and of a Kodak Ekta 100VS

## Analytical densities for a spectral database

The procedure for the estimation of the *analytical densities*, even though it requires a complex elaboration, can be made clear and simple to execute. The clearness and simplicity of the method is fundamental for a successful cooperation with other institutions; collectors, archives, museums that own catalogued photo collections, can be able to contribute to the construction of the database, initializing the data-gathering (Fig. 0.6). A collaborative web-platform would be ideal for this purpose.

The flow-chart in Figure 0.6 describes the process of data-gathering. The constituent dyes spectra are calculated for photographs of known provenance (reliable sources). In light of historical researches on the evolution of the photographic companies and their products [10, 11, 12, 13, 14], important information (brand, model, time period of production, geographic commercial distribution of the product, etc.) can be linked to the eigenspectra found. The entirety of these links constitutes the database.

Once a consistent amount of data will be gathered, the global community will have the possibility to query the database for the achievement of historical information of their unknown photographic samples and finds. The flow-chart in Figure 0.7 describes the use of the database. The defined method is executed on a photograph devoid of edge data or historical data (photographic relic); the set of eigenspectra found is used to query the database; the query consists in finding in the database the spectral set that shows the highest correlation with the set of eigenspectra of the relic; the correlated information (the answer of the query) can now be linked to the photographic relic. The identification is therefore accomplished.

## Analytical densities for digitization

As it was already explained in the introduction, the knowledge of the analytical densities of a photograph allows choosing the best light sources to be used during the digital image acquisition. In particular, to maximize the color information recorded, the ideal light source for the image acquisition of a 3-layer photographic photograph consists of three monochromatic lights whose wavelengths correspond to the absorption peaks of the three dyes [5].

The measurement of the integral density of a photograph already gives a hint for the identification of the absorption maxima of the component dyes; however, significant shifts may occur. In fact, the spectral positions of the absorption peaks can be influenced by the concentration ratios between the dyes. In the example of Figure 0.8, the analytical density of the magenta dye, which was estimated with the proposed procedure, shows a maximum at 553nm; the integral density may have the same peak position, as 'measurement-2' of the example, or instead, it may exhibit significant wavelength shift: e.g. the peak of absorption for 'measurement-1' falls at 563nm.

In addition to the exact position of the absorption peak, the estimation of the analytical densities provides information
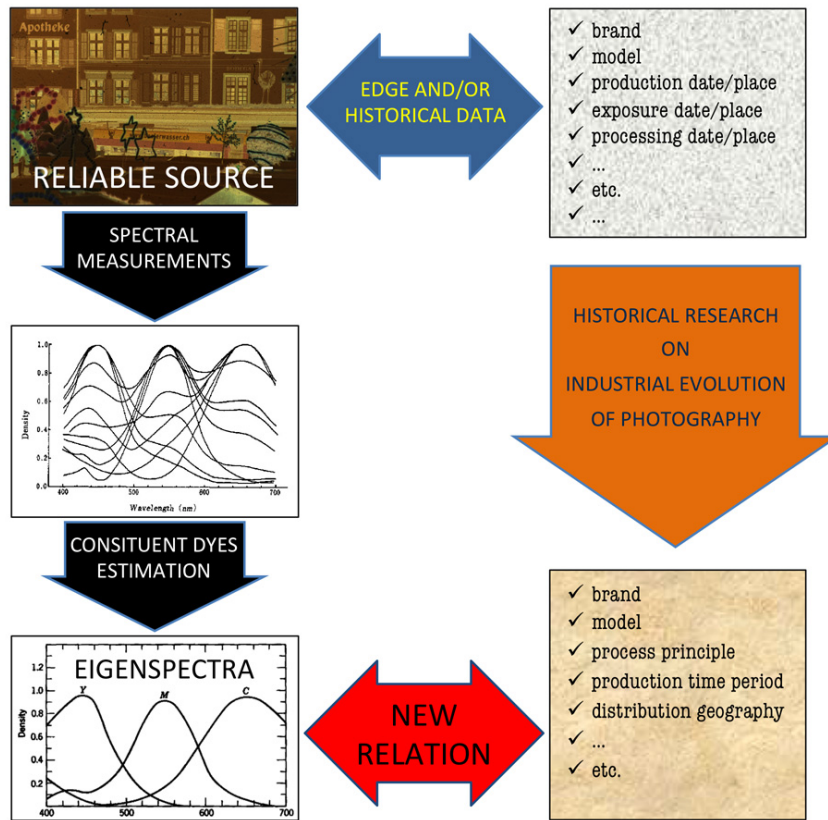
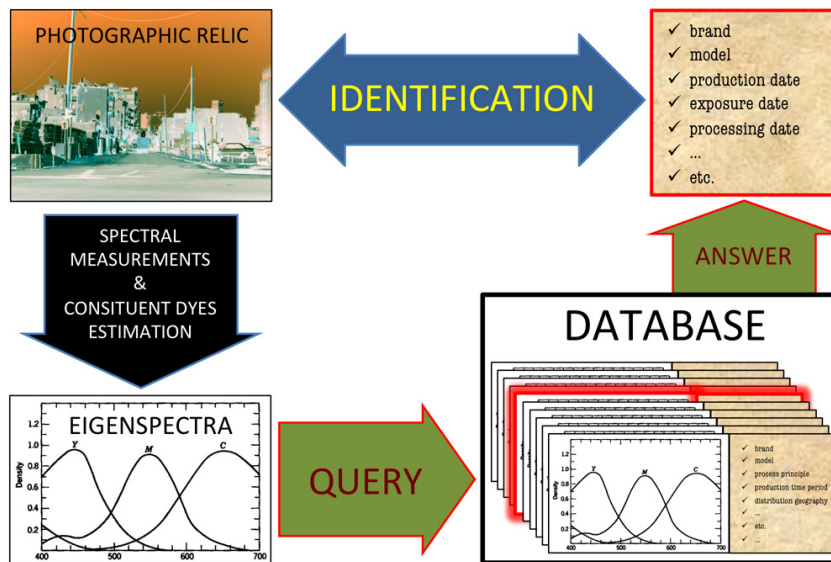Figure 0.6: Data-gathering
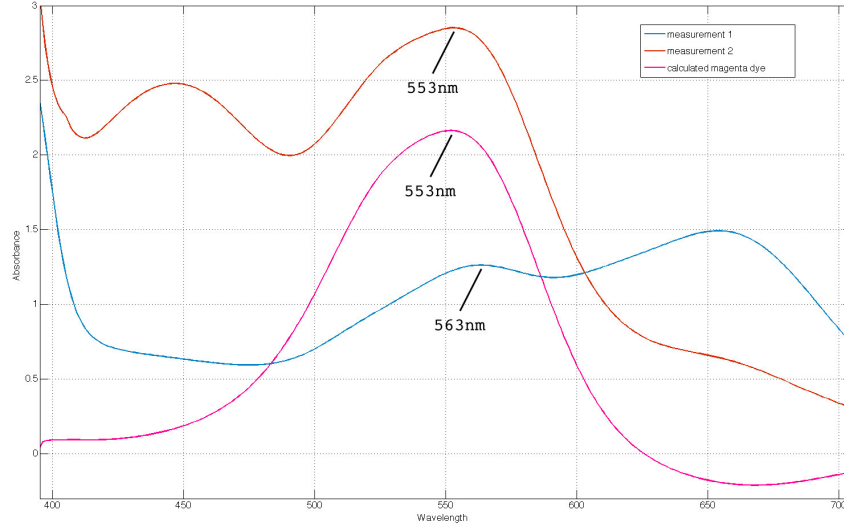


Figure 0.7: Use of the database

Figure 0.8: Measured integral densities of two points of a film and its calculated magenta dye spectrum

on the side absorption of the dyes, which is another important element to be considered in the choice of the light sources for digitization. To extract the maximum of color information of a photograph, it is opportune to choose a set of light sources that highlight the variance of the dye concentrations on the image, and at the same, time minimize the negative effects due to the side absorptions. For example, in case of the magenta dye of the Kodak Ekta 100VS (Fig. 0.5), we found a quite strong side absorption at 440nm, and we may prefer to avoid this wavelength for the light sources to be used for its digitization.

When digitizing a photographic film, the color information acquired by the imaging device can be further maximized with a particular procedure. Three separate monochromatic images are acquired using the three chosen light sources; the color image is obtained by merging those monochromatic images in a new "artificial" RGB image [15].

$$\begin{bmatrix} R \\ G \\ B \end{bmatrix} = \begin{bmatrix} C_{RC} & C_{RM} & C_{RY} \\ C_{GC} & C_{GM} & C_{GY} \\ C_{BC} & C_{BM} & C_{BY} \end{bmatrix} \times \begin{bmatrix} I_C \\ I_M \\ I_Y \end{bmatrix}$$

The 3x3 matrix $C$ describes the method in which the acquired monochromatic images ($I_C$, $I_M$, $I_Y$) can be merged in the final RGB color image. The simplest method is represented by the identity matrix. However, more complex method can be developed to balance out the side absorptions and maximize the acquired color information. The knowledge of the analytical densities of the film digitized with a certain triad of light sources provides the information necessary to determine the suitable matrix $C$.

# References

[1] G. Koshofer, *Das fimdaten buch - Grundwissen Filmeigenschaften Marktübersicht*. Gilching (D): Verlag für Foto, Film und Video, 1993.

[2] 20 minutes. (2013, July) Ilford serait sur le point de déposer le bilan. [Online]. Available: http://www.20min.ch/ro/news/romandie/story/Ilford-serait-sur-le-point-de-d-poser-le-bilan-15906337

[3] M. J. de La Merced. (2012, January) Eastman kodak files for bankruptcy. [Online]. Available: http://dealbook.nytimes.com/2012/01/19/eastman-kodak-files-for-bankruptcy/?_r=0

[4] D. G. Horvath, "The acetate negative survey," University of Louisville, Louisville (KY-USA), final report, February 1987.

[5] R. Gschwind and F. Frey, "Digital reconstruction of faded color photographs," *Revue Informatique et Statistique dans les Sciences Humaines*, vol. 33, no. 1, pp. 235–274, 1997.

[6] P. Kowaliski, *The Theory of the Photographic Process*, 4th ed.  New York, NY-USA: Macmillan Publishing Co., Inc, 1977, no. 18, ch. Sensitometry of Color Films and Papers, pp. 517–535.

[7] Image Permanence Institute. (2013) Graphics atlas. [Online]. Available: http://www.graphicsatlas.org/

[8] "Fujichrome velvia 50 professional [rvp50]," Fujifilm, FUJIFILM PRODUCT INFORMATION BULLETIN AF3-0221E2.

[9] N. Ohta, "Estimating absorption bands of component dyes by means of principal component analysis," *Anal. Chem.*, vol. 45, no. 3, pp. 553–557, March 1973.

[10] R. T. Ryan, *A History of Motion Picture Color Technology*.  London (UK): Focal Press, January 1977.

[11] A. Cornwell-Clyne, *Colour cinematography*.  Vancouver (WA-USA): Chapman and Hall, 1951.

[12] B. Lavédrine, *Photographs of the Past: Process and Preservation*.  Los Angeles, CA-USA: J. Paul Getty Trust, 2009.

[13] B. Flückiger. (2013, August) Timeline of historical film colors. [Online]. Available: http://zauberklang.ch/filmcolors/

[14] M. Osterman, *The Focal Encyclopedia of Photography*, 4th ed.  Elsevier Inc., 2007, ch. History and evolution of Photography, pp. 23–176.

[15] G. Trumpy and M. Selva, "Digitization of color negative films with LEDs lighting systems and DSLR cameras: a signal processing analysis," in *Colour and Colorimetry - Multidisciplinary Contributions*, ser. Optics and Photonics Series Notebooks, M. Rossi, Ed., vol. VII B, no. 21, Gruppo del Colore.  Santarcangelo di Romagna (I): Maggioli Editore, July 2011.