Densitometry versus Colorimetry for Permanence Investigations

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Abstract

For many years, densitometry has been the measurement of choice for photographic permanence investigations. With the availability of affordable colorimeters, CIELab data are often used instead. To investigate if both types of measurement are applicable to permanence investigations, Status A densitometry, CIELab and full spectral readings were performed on samples in accelerated light stability, pollutant fading and thermal stability tests. The quality of the prediction between the two measurement methods is compared. For monochrome wedges and in images where primarily one colorant fades much faster than the others CIELab ΔE gave similar predictions as density. Even in gray wedges and when several colorants fade at similar rate, densitometry did not prove much superior to CIELab ΔE. Predictions based on CIELab a* and b* provided even better results than those based on ΔE. Contrary to CIELab data, densitometry measurements are suited to investigate fade mechanisms and distinguish between the contribution of the single colorants to overall fading. However, the full spectra available from spectral densitometers make those even more valuable tools in elucidating colorant reactions.

Introduction

Densitometry has been widely used to follow the change of imaging colorants which result after the impact of light, humidity, temperature and air pollutants. In the Arrhenuis test for example, data from experiments at high temperatures are extrapolated to predict life expectancy at room temperature. This requires certain assumptions about the reaction mechanism to be made. Densitometry was suitable to follow the reaction as it separates the three color channels and allows predictions for every colorant separately. Status A and T standards [1] unambiguously described the geometry and filters to be used for the three color channels. The filters are well adapted to the typical spectra of photographic imaging dyes [2]. The 0°/45° geometry is representative of the typical viewing conditions for glossy photos [3]. With the use of new colorants in digital hardcopy technologies like ink-jet, three channel densitometry may no longer be sufficient. Ink-jet printing allows the use of more than 3 colorants, varying substrates with surface textures between matt and glossy, fabrics and fine art papers. Colorimetry may be more applicable to the wider range of media used in ink-jet. However, the exact measurement conditions need to be defined for the spectral measurement as the inclusion/exclusion of UV and the measurement geometry (0°/45° or integrating sphere) are both available in commercial instruments. Also, CIELab data may be based on different light sources (D50, D65, A, C) and different observer viewing angles (10°, 2°).[4] ΔE is not directional and combines the effect of changes in the different colorants into one value, which may be of concern for permanence studies. In the following paper we have used both CIELab and densitometer measurements on light stability, thermal stability and pollutant stability data to compare the quality of the predictions as well as the insight into the fading mechanisms that could be achieved.

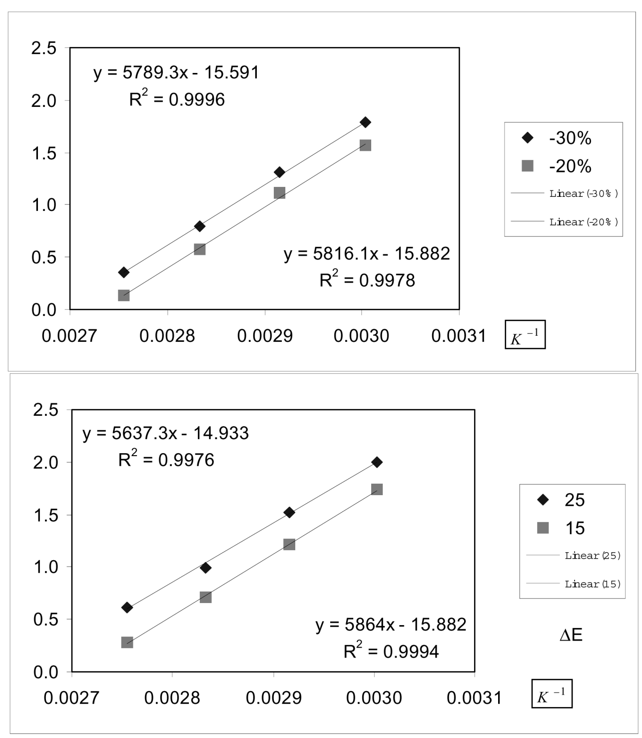

Figure 1. Arrhenius plot of cyan wedge media A, log(days) versus 1/T for (top) 20% and 30% density loss and (bottom) CIELab ΔE 15 and 25

Experimental Results

Permanence tests were run with photographic and ink-jet media. The images were color patches of monochrome cyan, magenta yellow and black as well as composite black with density levels around 0.5, 1.0 and 1.5. The color change was measured in status A density as well as in CIELab L*, a*, b* using the conditions D65, 2°, 0°/45° geometry on a Gretag Spektrolino spectral densitometer. In some of the experiments, an additional UV filter was used.

To determine end points, linear interpolation and extrapolation was used, as other types of trend curves tend to introduce artifacts.

Thermal Stability of Continuous Tone Images

In thermal stability tests of hardcopy media as ink-jet or dye-sublimation prints, humidity effects often override thermal effects. Color changes result from the diffusion of dots into neighboring white areas and make meaningful Arrhenius extrapolations difficult. That's why we choose two photographic papers for our colorimetric investigation. The papers were incubated and measured according to ANSI IT-9.3 at 4 different temperatures (60°, 70°. 80°, 90°C) and their color changes were followed after 7, 14, 28, 56 and up to 448 days. The Arrhenius plot was done for a density loss of 30% and 20% in one case and 10% and 5% in a second case. The standard requires that color changes be followed on monochrome as well as gray wedges to reveal possible dye interactions.

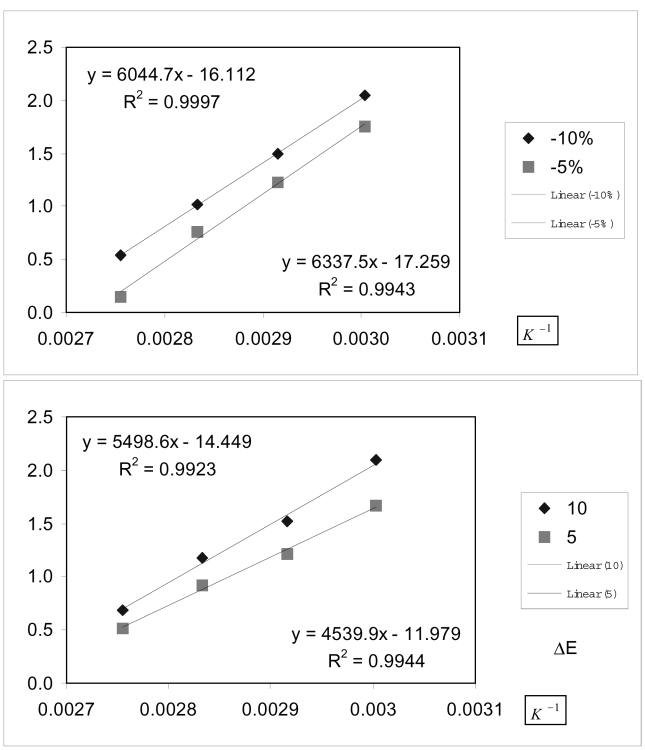

Figure 2a. Arrhenius plot of grey wedge media B, log(days) versus 1/T for (top) 10% and 5% cyan density loss and (bottom) CIELab ΔE 10 and 5

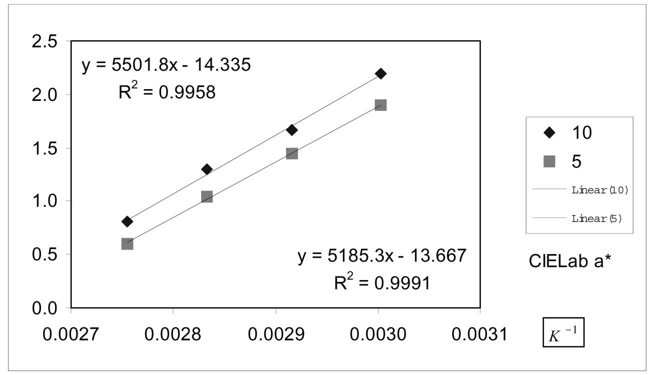

Figure 2b. Arrhenius plot of grey wedge media B, log(days) versus 1/T for CIELab a change of 5 and 10*

Figure 1 shows the Arrhenius plot for media A, which under our test exhibits only degradation of cyan. For such a single dye degradation mechanism, ΔE and density plots are linear (correlation coefficient >0.99) and curves for different end points are parallel using either the cyan wedge or the gray wedge for evaluation. Both extrapolations to archival life expectancy at 25°C lead to a similar prediction of 17 to 20 years. In the case of photographic media B, there is thermal degradation of cyan as well as yellow. The Arrhenius plots established on monochrome wedges of cyan and yellow each are linear and parallel both for densities and ΔE. The density measurements applied to the gray wedge provided parallel curves for the two end points of 5% and 10% dye loss in Figure 2a. ΔE curves were slightly less parallel, but the deviation in parallelism was in the range of normal experimental variation of such curves.

For archival stability at 25°, the extrapolation for first visible change at ΔE 10 leads to predictions of 27 years compared to 43 years in the case of a density loss of 10%. Slightly adapting the two thresholds may improve the agreement. Using CIELab a* and b* instead of ΔE generated even more parallel curves (Figure 2b) and an extrapolated life expectancy of 34 years. However, ΔE does not allow independent predictions for the yellow and the cyan degradation.

Light Stability Predictions for Pigment Prints on Fine Art Paper

Pigment prints on fine art paper were exposed to an Atlas weatherometer using direct daylight conditions. Pigments are less prone to changes in humidity and to gas fading. Their fading curves are expected to be the results of light fading with less interference of other factors and often show fewer anomalies. The degradation of the colorants was followed in density and CIELab. Full spectral measurements were performed in parallel. For the monochrome wedges Y, M, C the linear extrapolation to a change of density of –35% for yellow, -30% for cyan and -20% in magenta in the pure wedges provided a similar life expectancy as the CIELab ΔE extrapolation to ΔE=17, (Figure 3). A ΔE of about 15 may be an approximation of an end point that corresponds to the end point criteria suggested in the ANSI standard IT9.9-1996.[5] The different thresholds for Y, M, C and neutral result from the different sensitivity of the human observer for the color channels. This adaptation is included by using colorimetric units as end point criteria.

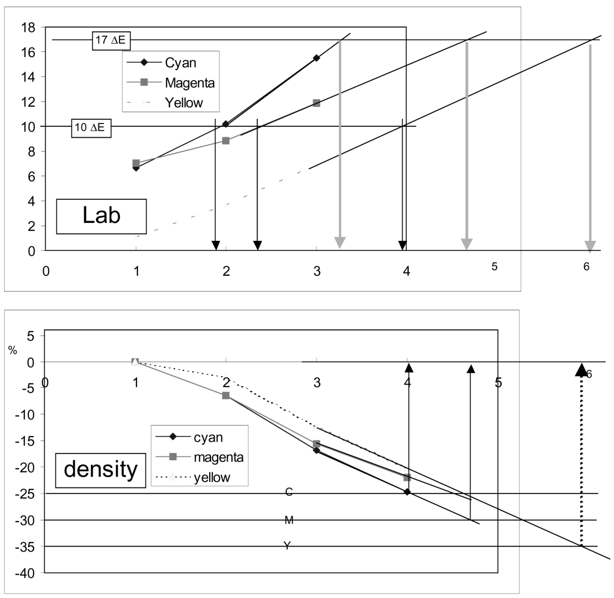

Figure 3. Light stability of y,m,c pigments on fine art paper in steps of 240 hours of exposure. Extrapolation to a limit of acceptability in CIELab (top), density changes according to [5] (bottom)

Not surprisingly, the density changes in the light fastness test seem to correspond a little better to the actual colorant changes as revealed by the difference of the spectral absorption curves. The spectral curves show yellow and cyan to be slightly more stable than magenta as it shows in the density plots, but not in the ΔE plot, where yellow is better than magenta and cyan. This results in a better approximation of the visual appearance.

Pollutant Fading

Nanoporous media[6] show color degradation in the dark due to attack of air pollutants. Printed samples of pollutant sensitive media were exposed to forced air flow (4m/s) in an atmosphere of ambient air in total darkness. The samples, contained patches of 10%, 40% and 70% dot percent in pure cyan, pure magenta, pure yellow and composite black (3K) and were measured after exposure to air of 1 up to 7 days. Figure 4a shows the ΔE change for the pollutant fading of a nanoporous print measured for seven days on the three patches for cyan, yellow and on composite black. Figure 4b shows the same patches measured in red density for cyan, blue density for yellow and visual density for black.

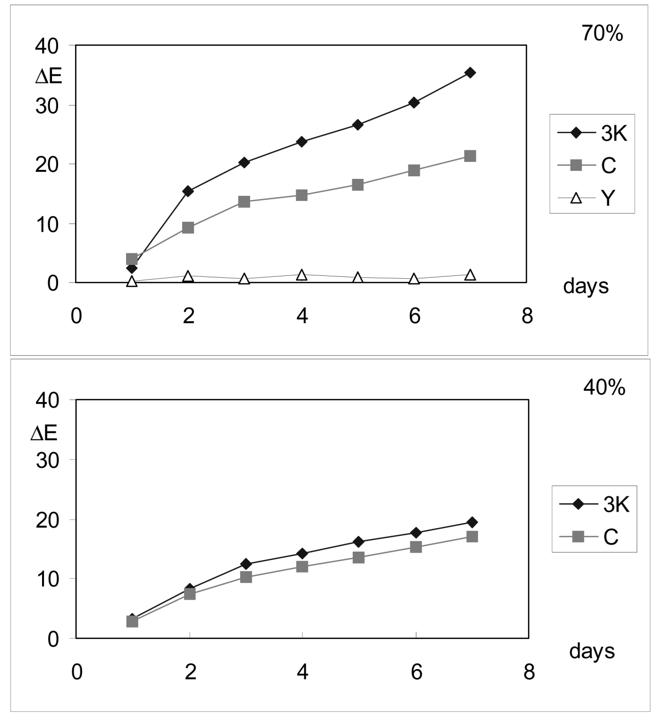

Figure 4a. 7 day pollutant fading on nanoporous media: ΔE of 3K, cyan and yellow wedge for two levels of dot coverage (top) 70%, (bottom) 40%.

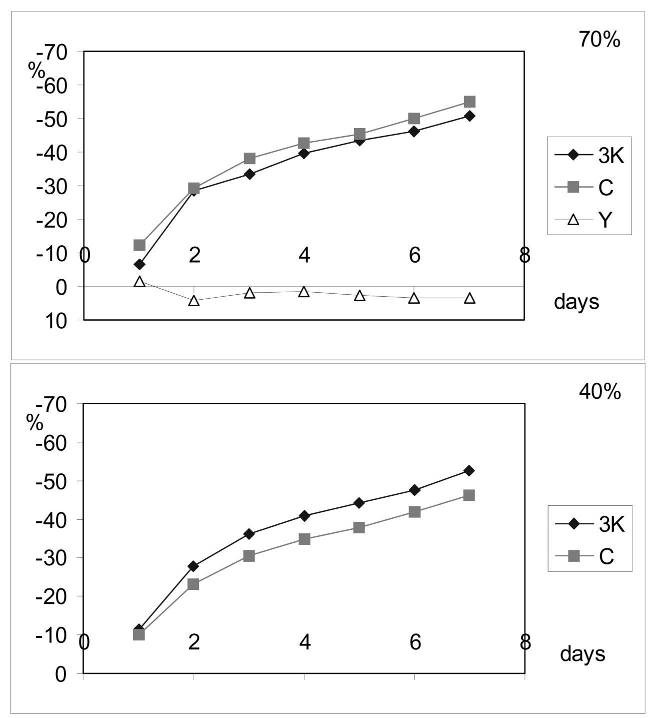

Figure 4b. 7 day pollutant fading on nanoporous media:density change on 3K, cyan and yellow wedge for two levels of dot coverage (top) 70%, (bottom) 40%

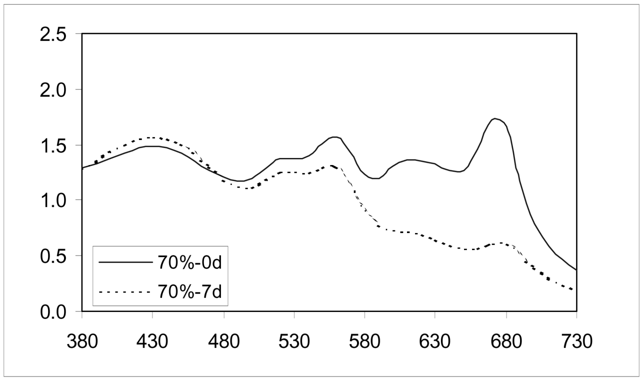

Figure 4c. Pollutant fading on nanoporous media: Spectra of 70% dot 3K sample at 0 days and at 7 days

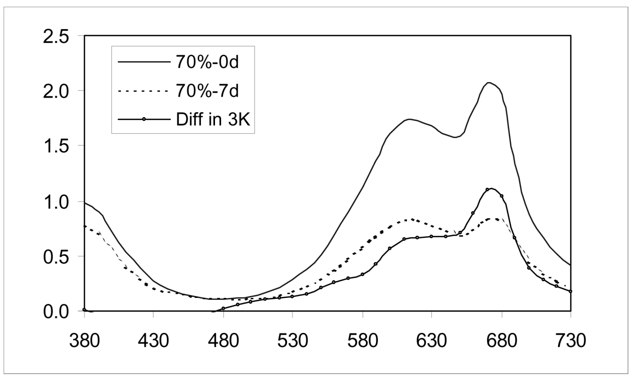

Figure 4d. Pollutant fading on nanoporous media: spectra of 70% dot Cyan sample at 0 days and at 7 days compared to difference of 3K spectra in 4c

Figure 4c shows the full spectra measured for the 40% and the 70% level as well as the difference spectra between faded and not faded. The patches measured in density show a similar percentage loss on the three density levels printed. ΔE is an absolute number. Similar spectral changes in light colors result in smaller ΔE changes than on darker patches, which is a better approximation to the visual appearance. The interpolation to ΔE=15 would again provide a good endpoint for an objectionable print. However ΔE is not a good measure for the actual colorant changes. Analyzing the full spectra in figure 4c and d, shows that in the composite black patches, it is mainly the cyan colorant that is degraded. This is also obvious by comparing the cyan density and composite density curves. The ΔE curves of cyan and 3K do not show the same parallel behavior. In a case like figure 4c, where a loss of cyan is accompanied by a gain in yellow, the density measurements reveal this mechanism well, ΔE does not.

Conclusion

Colorimetry can be used for permanence investigations. The interpolation and extrapolation of ΔE delivered similar predictions as the same samples measured in Status A density. However, ΔE is not suitable for mechanistic investigations, as it does not differentiate between the color channels and does not show the direction of change. Using L*, a*, b* instead of ΔE would provide more insight into mechanisms.

References

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Biography

R. Hofmann has a degree in physical chemistry from the University of Goettingen. After postdoctoral studies in atmospheric sciences at the University of Colorado, she worked at Ciba-Geigy central research in the field of analytical chemistry and laser applications. Since she joined ILFORD in 1985 she has been involved in research and applications for digital photography, photographic color science and image evaluation of hardcopy technologies. She is currently head of R&D for ILFORD and focuses on the development of tests methods for ink-jet media.