

Use of Design-of-Experiment principles to develop a dose-response function for colour photographs

Ann Fenech^{a,*}, Tom Fearn^b, Matija Strlic^a

^a Centre for Sustainable Heritage, University College London, The Bartlett School of Graduate Studies, Gower Street (Torrington Place site), London WC1E 6BT, UK

^b Department of Statistical Science, University College London, Gower Street, London WC1E 6BT, UK

ARTICLE INFO

Article history:

Received 12 December 2011

Accepted 9 January 2012

Available online 28 January 2012

Keywords:

Design-of-Experiments

Dose-response function

Accelerated degradation

Colour photographs

Archival environments

ABSTRACT

Colour photographs are very vulnerable to the environmental conditions they are stored in. Although ideal conditions of storage have been identified, these conditions are often not appropriate in archival collections. Therefore, it is essential to understand how these environmental conditions affect degradation in order to optimise material lifetime. Such information is typically obtained using accelerated degradation experiments following 'one-factor-at-a-time' methodologies. However, when planned using 'Design-of-Experiment' principles, such experiments provide more information with fewer experimental runs, while information is provided not only on factor effects but also on interactions between factors. This study employed a central composite experimental design plan to develop a dose-response function relating the rate of degradation of dyes in colour photographs to temperature (T), relative humidity (RH) and acetic acid concentrations ($c(AA)$), which had been identified as the environmental parameters of greatest concern for colour photographs in archival collections:

$$\ln\left(\frac{\Delta E_{RGB}}{t}\right) = 32 + 0.0002(c(AA)) + 0.01(RH) - 11\left(\frac{1000}{T}\right).$$

This function now allows managers to appraise various options of environmental management within their collections.

© 2012 Elsevier Ltd. All rights reserved.

1. Introduction

All materials eventually decay. However, the rate depends on the composition and condition of the material in question and, in addition, on the presence and magnitude of environmental deterioration factors (or agents). A thorough understanding of the effect of the environmental parameters on degradation processes is essential to optimise material lifetime.

This is equally of concern in the management of culturally significant material collections. In archives, photographic materials based on silver halides, such as chromogenic colour prints, are more sensitive to their environment than most other materials [1]. In fact, appropriate conditions quoted for chromogenic prints include cool (10–16 °C), cold (2–8 °C), or freezing (<0 °C) conditions for extended storage, and 30–40% RH [2,3]. This is colder and drier than the recommended 20 °C and 50% RH for other archival materials [4], which are the typical environmental conditions present in archival storage.

Data on the effect of deterioration agents on materials is often obtained through accelerated degradation experiments.

Accelerated degradation is thought to indicate "in a relatively short period of time what will happen to materials [...] over a period of years" [5]. The typical accelerated degradation experiments carried out to predict the lifetime of materials under specific environmental conditions follow the 'one-factor-at-a-time' method of experimentation [6]. In this method, factors are varied one at a time while the remaining factors are held constant.

Data on the degradation of imaging materials, including colour photographs [7,8] have typically been elucidated using such experimental methods and a limited number of samples. The latter may be an issue given the extreme variability of chromogenic colour prints. In addition, most deterioration agents do not operate independently of each other and changes in one will often influence the effect of another. Therefore, it is also appropriate to investigate the presence of any interactions between factors.

An efficient way of planning and optimising such experiments involves principles of Design-of-Experiments (DOE). The key property of DOE is that while several factors are varied simultaneously, each factor may then be evaluated independently. As Box, Hunter et al. [9] highlight, "if the factors do act additively, the DOE design does the job with much more precision than one-factor-at-a-time methods, and (2), if the factors do not act additively, the DOE, unlike the one-factor-at-a-time design, can detect and estimate interactions that measure this non-additivity".

* Corresponding author.

E-mail addresses: annmucc@gmail.com (A. Fenech), t.fearn@ucl.ac.uk (T. Fearn), m.strlic@ucl.ac.uk (M. Strlic).

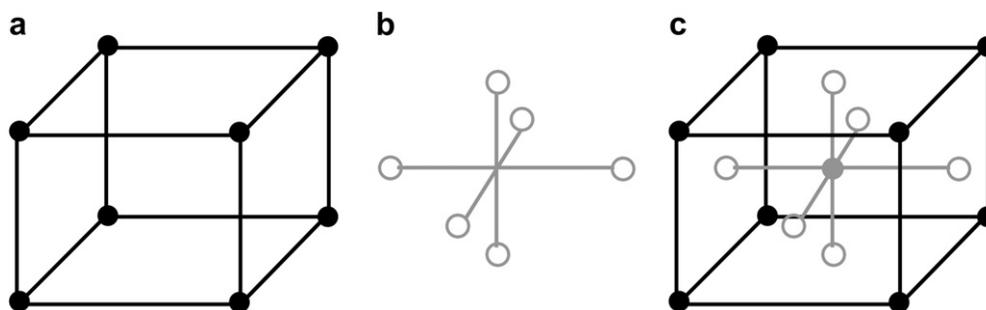


Fig. 1. Three-factor face-centred ($\alpha = 1$) central composite design. a) Points in the factorial portion of the design are coded to be -1 and $+1$; b) Points in axial (star) portion of the design are at $(+\alpha, 0)$, $(-\alpha, 0)$, $(0, +\alpha)$, $(0, -\alpha)$; c) the factorial and axial portions joined to give a CCD. The design centre is at $(0, 0)$.

Hence, an advantage of DOE is that it allows for the maximum amount of information to be extracted using the minimum number of experiments [10,11]. DOE is also useful as it allows for straightforward handling of experimental errors and that it allows for data extrapolation [11].

The simplest DOEs are often factorial experiments, where all factors are varied simultaneously at a limited number of factor levels [9]. More complex DOEs involve response surface designs. Central Composite Designs (CCD) are possibly the most popular types of response surface designs. They may be thought of as a combination of three components (Fig. 1), namely:

- a factorial DOE at two levels,
- axial points (star design),
- a centre point [12].

This paper investigates the effect of environmental factors on the rate of degradation of chromogenic colour prints. In this accelerated degradation experimental design, the effect of three factors – temperature (T), RH and acetic acid concentration ($c(\text{AA})$) – were investigated using a face-centred CCD. Since the degradation of dyes is a chemical reaction, T was expected to have a significant effect on the reaction rate. RH was also investigated as moisture generally accelerates the rate of degradation, although the exact mechanism is not necessarily understood [6,13].

The third factor investigated was the effect of pollutants. It was shown by Fenech et al. [14] that acetic acid is the most abundant pollutant in archival boxes and it was also identified as the pollutant most intensively promoting degradation [15]. Hence, acetic acid was selected as the pollutant of greatest interest for this study. The expected outcome of this study was a multiparametric dose–response function relating the effect of T , RH and $c(\text{AA})$ on chromogenic prints. Such a function can then be used to compare the effect of various environmental scenarios on an archival collection of such prints.

2. Methodology

2.1. Experimental design

A three factor, three-level face-centred CCD was used to determine the effect of environmental conditions on the rate of colour

Table 1
Uncoded and coded levels of the independent factors.

Factor	-1	0	1
$c(\text{AA})$ (ppb), x_1	0	500	1000
RH (%), x_2	20	40	60
T ($^{\circ}\text{C}$), x_3	50	65	80

change. Three independent factors, namely $c(\text{AA})$ (x_1), RH (x_2) and T (x_3) were considered relevant.

Each independent factor assumed three coded levels that were -1 , 0 , and $+1$ (Table 1). A value was then assigned to the -1 and $+1$ levels for each factor, with 0 being assigned to the middle value. The RH and $c(\text{AA})$ values were chosen to include the values typically encountered in archival collections [16]. The values for T were selected by considering the balance between accelerating the degradation processes so that the effect could be observed in a reasonable time and not moving too far from realistic storage conditions.

A total of 17 different degradation experiments (including three replicates of the centre point) were carried out according to a CCD configuration for three factors (Table 2). The CCD is smaller than a 3^3 factorial experiment, which would have 27 runs, and much more efficient than 3 one-factor-at-a-time experiments which would need 45 runs in total to give similar precision for the linear and quadratic coefficients of the fitted equations.

2.2. Samples and apparatus set-up

95 photographs were chosen at random from the research collection of chromogenic prints developed as part of the project. The selected sample set represented a range of manufacturers and dates of production. Sample preparation and apparatus set-up was as discussed in Fenech et al. [15]. Samples were flushed with the appropriate conditions and measured using an X-Rite 530 SpectroDensitometer (D50/2 $^{\circ}$ observation conditions, standard white background) at least three times a week for one month at 80°C , once a week for 4 months at 65°C and every two weeks for nine months at 50°C (average of 14 data points per sample).

Table 2
The central composite design (CCD) with three independent variables (coded variables) showing the experimental runs (degradation experiments) carried out.

Run	x_1	x_2	x_3	Point
1	-1	-1	-1	Factorial
2	1	-1	-1	Factorial
3	-1	1	-1	Factorial
4	1	1	-1	Factorial
5	-1	-1	1	Factorial
6	1	-1	1	Factorial
7	-1	1	1	Factorial
8	1	1	1	Factorial
9	-1	0	0	Axial
10	1	0	0	Axial
11	0	-1	0	Axial
12	0	1	0	Axial
13	0	0	-1	Axial
14	0	0	1	Axial
15	0	0	0	Centre
16	0	0	0	Centre
17	0	0	0	Centre

2.3. Data analysis

sRGB has been identified as an appropriate colour space for monitoring dye concentrations in chromogenic colour prints [15]. Therefore, sRGB values were calculated from reflectance spectra. The overall colour change was calculated as ΔE_{RGB} of normalised RGB values:

$$\Delta E_{RGB} = \sqrt{\left(1 - \frac{R_t}{R_0}\right)^2 + \left(1 - \frac{G_t}{G_0}\right)^2 + \left(1 - \frac{B_t}{B_0}\right)^2}$$

Where ΔE_{RGB} is total colour change in terms of RGB, R_0 , G_0 and B_0 are RGB values prior to accelerated degradation, and R_t , G_t and B_t are RGB values at time t .

The rate of change was calculated as the slope of a graph of ΔE_{RGB} against time (in years). The colour change per year was defined as the normalised annual colour change of the image, ΔE_T .

The ΔE_T of the collection of samples used in the experiment was then calculated by averaging the values for all the 95 samples degraded under each of the environmental conditions of interest.

2.4. DOE analysis

Statistical analysis of DOE data was carried out using Minitab 15.1.30.0 (Minitab Inc.) software package.

To fit the model, the rate of degradation, ΔE_T , was converted to its natural logarithm, and the temperature was converted to $1000/T$ (in K) to allow for the dose-response function to follow the Arrhenius equation.

3. Results and discussion

The objective of this study was to develop a multiparametric dose-response function that quantifies the effect of three environmental factors - T , RH and $c(\text{AA})$ - on the rate of image degradation in chromogenic prints using a DOE approach to accelerated degradation experiments. These were planned following a face-centred CCD.

To understand the characteristics of the collection, a frequency plot of ΔE_T for the 95 individual samples was examined for each of the experimental runs. In all cases, the results of a Kolmogorov–Smirnov test showed that normal distribution may be reasonably assumed (Fig. 2), $Z = 0.836$ – 1.259 , $p > 0.05$. This indicated that the photographs can be considered as a single set in the DOE analysis and that the mean ΔE_T for the set is an appropriate summary. This would not have been the case had, e.g., a bimodal distribution been identified.

Degradation was accelerated by carrying out the experiments at higher temperatures than encountered in a typical archival repository. The obtained results thus had to be extrapolated to the temperatures expected in archival collections. Previous investigations within the photographic industry had shown good correlations between Arrhenius test predictions and trade experience and this is a widely used methodology in photographic companies, including Kodak [17–19]. Therefore, it was assumed that extrapolations would assume the form of an exponential function. To enable this, natural logarithm of the rate of reaction and inverse temperature should be used in calculations [19]. For this reason, T was converted to $1/T$ and the normalised annual colour change, ΔE_T , was converted into its natural logarithm. Due to the significant differences in magnitude between the resulting T , RH and $c(\text{AA})$ coefficients, the temperature parameter was multiplied by 1000.

Having specified the factors, a response surface model could be fitted. As is typical, a linear (first-order) function was investigated first. The regression coefficients for this linear model and results for

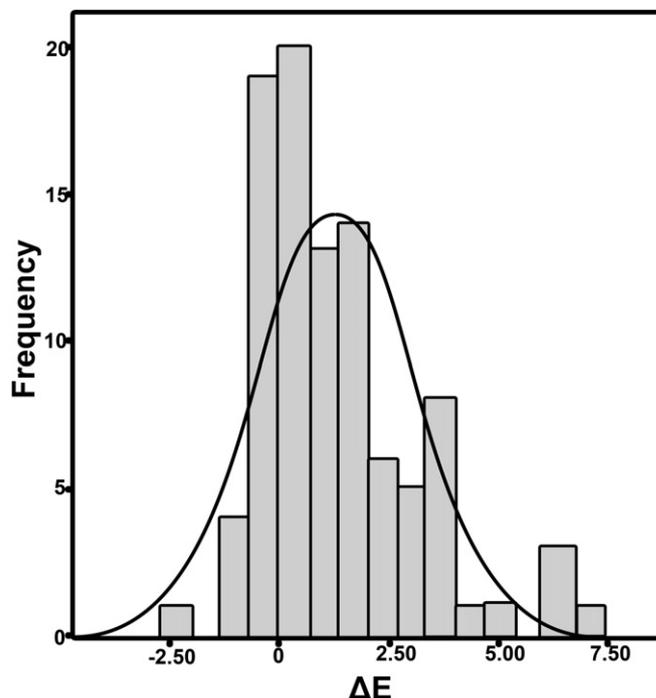


Fig. 2. Frequency plot of ΔE_T for samples exposed to 80 °C, 20% RH and 0 ppb acetic acid. The samples exhibit a distribution not significantly different from a normal distribution, $p > 0.05$.

the linear term are presented in Table 3. The results for uncoded variables are provided, to provide an idea of the relationship between the effects of 1 unit of temperature, RH and acetic acid concentration.

Having developed the DOE function, it was necessary to confirm the adequacy of the fitted function, as an incorrect or under-specified model can lead to misleading conclusions. The statistical analysis indicates that the fitted function was adequate, possessing no significant lack of fit ($p > 0.05$) and with a very satisfactory R^2 (98.2%).

The residuals of the fitted function were also analysed to examine the goodness of model fit. If normal distribution of residuals is to be assumed, the points on the normal probability plot should lie close to a straight line, though these plots typically exhibit noise in the tails. The Anderson–Darling statistics determines how well a data set follows a specific distribution (normal in this case). Randomness of residuals is then assessed using the residuals versus fit plot. This demonstrates a random pattern of residuals on both sides of 0. Also, there should not be any recognisable patterns in the residual plot. Another important way to assess the goodness of fit is to add quadratic terms and interactions

Table 3

Regression coefficients for the first order equation and results for the linear term. The regression coefficients are the coefficients used to build the function relating the effect of the factors on the rate of colour change. The t - and p - values are the results for the significance of these linear terms, S is the residual standard deviation and R^2 the coefficient of determination for the fitted equation.

Term	Coefficient	SE Coefficient	t -value	p -value
Constant	31.79	1.27	25.04	0.00
$c(\text{AA})$ (ppb)	0.0002	0.0001	1.35	0.20
RH (%)	0.0101	0.0028	3.62	0.00
1000/ T (K)	-11.09	0.43	-26.05	0.00

$S = 0.18$; $R^2 = 98.2\%$.

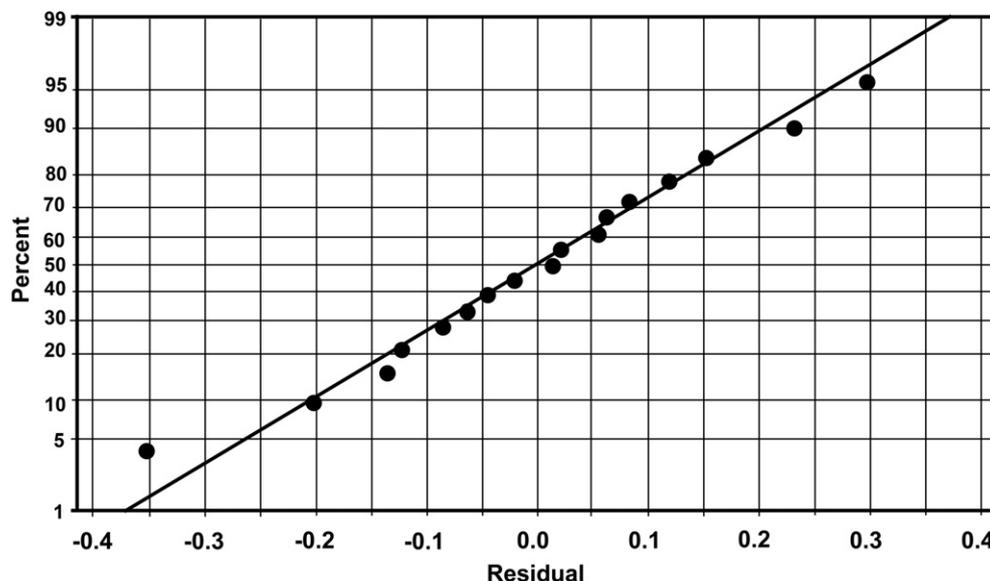


Fig. 3. Normal probability plot of residuals. The straight line indicates that the residuals are normally distributed, meaning that the DOE function is a good fit.

to the fit and see if they are significant. In this case they were not and has the linear model was used.

In our case, both the normal probability plot (Fig. 3) and the Anderson-Darling statistical analysis ($AD = 0.12$, $p > 0.05$) indicated that the residuals were normally distributed. The residuals-versus-fit plot (not shown) demonstrates that the residuals are randomly distributed as no recognisable pattern can be observed. These observations indicated that the function fits the empirical data well.

Once the fitness of the DOE function is confirmed, the coefficients (Table 3) can be investigated. It is immediately apparent from the t -value that temperature has by far the most significant effect on the rate of change. However, some sources have stated that RH is the most important factor in the degradation of photographic materials [1].

Although this is possibly true for gelatine itself, with respect to the dyes the effect of moisture depends largely on the way the dyes are incorporated into the gelatine layer [20]. Dyes are generally more resistant if incorporation is carried out by suspending the dye couplers in microscopically small droplets of an oily substance, providing a hydrophobic environment (typical of the Kodacolor principle), than if in a hydrophilic environment as occurs when the dyes are made immobile by adding long-chain molecules to the couplers (typical of the Agfacolor principle) [1]. It is, therefore, worth mentioning that the Kodacolor principle is the main coupler system used [1,21–23].

The value of the RH coefficient was, nevertheless, around 50 times that of the acetic acid coefficient (in ppb). The results also indicate that while the effect of RH and T are statistically significant ($p < 0.05$), the effect of acetic acid is not significant based on the data collected ($p > 0.05$). In relation to the latter, it is important to

note that although acetic acid concentration was found not to have a significant effect on the rate of chromogenic prints on average, this does not mean that it has no effect on individual photos, and that acetic acid can thus be allowed to accumulate. The analysis of multiparametric dose–response functions for individual samples, such as the example shown in Table 4, confirms this. Statistical analysis indicates that this particular fitted function is also adequate, possessing no significant lack of fit ($p > 0.05$), with a very satisfactory R^2 (99.2%) and normally distributed residuals. The reason for such differences is that individual dyes and, hence, individual photographs, may be much more sensitive to the effects of acetic acid than others, as has already been identified in previous work [15].

3.1. Isoperms

The effect of environmental factors on the anticipated permanence of materials is often presented in the form of isoperm diagrams [24]. These diagrams provide a straightforward way of appraising the effect of degradation factors on the material by plotting curves describing ‘constant permanence’ [6].

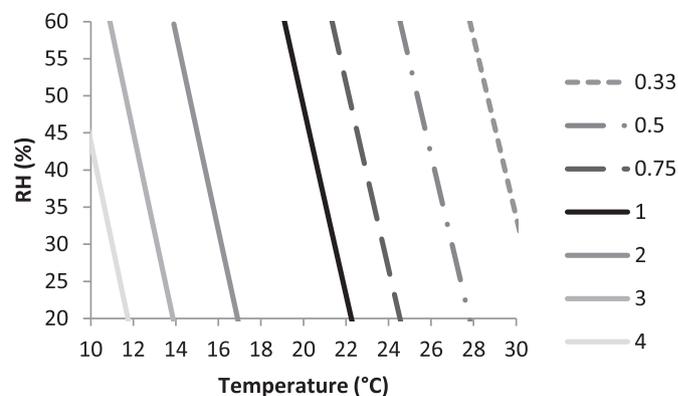


Fig. 4. RH (%) vs. T isoperm diagram showing curves of equal permanence. As in the case of the Sebera isoperms [24], permanence at 20 °C and 50% RH (and 0 ppb acetic acid) is used to represent a permanence of 1.

Table 4
Regression coefficients for the first order polynomial equation and results for the linear term for one individual sample (1989, Konica).

Term	Coefficient	SE Coefficient	t -value	p -value
Constant	30.83	0.028	−34.84	0.00
$c(\text{AA})$ (ppb)	0.0003	0.00009	3.41	0.01
RH (%)	0.0150	0.0019	7.78	0.00
$10000/T$ (K)	−1.090	0.003	−36.62	0.00

$S = 0.11$; $R^2 = 99.2\%$.

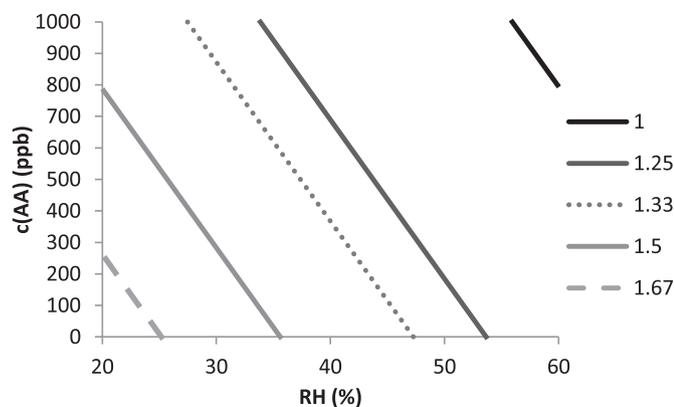


Fig. 5. $c(\text{AA})$ (ppb) vs. RH isoperm diagram showing curves of equal permanence at 20 °C.

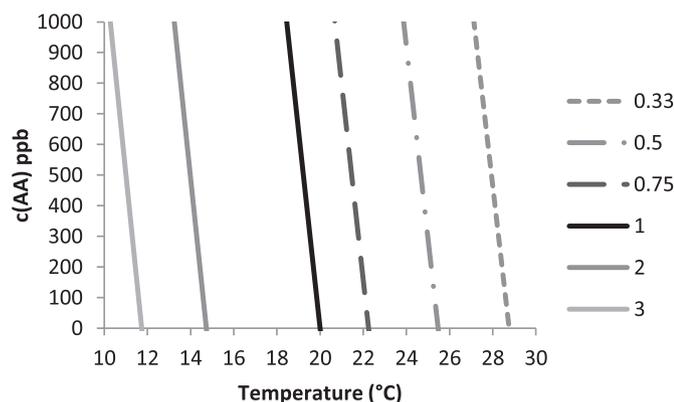


Fig. 6. $c(\text{AA})$ (ppb) versus T isoperm diagram showing curves of equal permanence at 50% RH.

Having developed a multiparametric dose–response function comparing the effect of three environmental conditions, two-dimensional diagrams can only be calculated by keeping one parameter constant (Figs. 4–6). As was used by Sebera [24], the temperature of 20 °C and relative humidity of 50% were used to represent a permanence of 1. As no pollutant concentration has been specified for other isoperms, 0 ppb acetic acid was used to represent a permanence of 1.

From the isoperms it is clear that a decrease in temperature of 1 °C has an equal effect to a 13% increase in RH, and 1% RH equals 50 ppb acetic acid and, hence, 1 °C equals around 650 ppb acetic acid. Such information allows collection managers to make preservation decisions, including on resource allocation, in terms of the required environmental conditions during storage.

4. Conclusions

This paper set out to identify the effect the principal degradation factors in the storage environment have upon the lifetime of chromogenic prints during storage in darkness. Having identified that the three factors of greatest concern for prints stored within mixed archival collections are temperature, RH and acetic acid, an experimental plan for investigating their effect was designed. A DOE approach using a central composite design was implemented to develop this knowledge due to its ability to provide information on factor interactions, besides on the effect of individual factors.

Data was collected during accelerated degradation experiments and a model was built and confirmed as adequate. The DOE analysis resulted in the development of the following multiparametric

function relating the rate of reaction to temperature (T , in K), RH (in %) and acetic acid concentration ($c(\text{AA})$, in ppb):

$$\ln\left(\frac{\Delta E_{\text{RGB}}}{t}\right) = 32 + 0.0002(c(\text{AA})) + 0.01(\text{RH}) - 11\left(\frac{1000}{T}\right)$$

Although the effect of acetic acid in this equation is not statistically significant, the term is retained to indicate that acetic acid does have an effect on chromogenic prints during dark storage and that in individual cases it can be significant.

This research efficiently demonstrates the potential of DOE principles in the investigations of material stability. The developed function now allows managers to appraise various options of environmental management.

Acknowledgments

The authors gratefully acknowledge the financial support of the UK AHRC/EPSRC Science and Heritage Programme (project CDA 08/412, additionally supported by The National Archives, UK).

References

- [1] Hendriks KB. The preservation and restoration of photographic materials in archives and libraries: a RAMP study with guidelines. Paris: UNESCO; 1984. p. 128.
- [2] Keefe LE, Inch D. The life of a photograph: archival processing, matting, framing, storage. 2nd ed. Boston: Focal Press; 1990.
- [3] Roosa M. Information Leaflet on the care, handling, and storage of photographs. Library of Congress; 2006.
- [4] Peters D. Climates and Microclimates: a new attitude to the storage of archival materials; 1996.
- [5] Roberts M, Etherington D. Bookbinding and the conservation of books. In: Henry W, editor. A dictionary of descriptive terminology; 1994. electronic ed.
- [6] Feller R. Accelerated aging: photochemical and thermal aspects. Marina del Rey, CA: Getty Conservation Institute; 1994.
- [7] Wilhelm H, Brower C. The permanence and care of color photographs: traditional and digital color prints, color negatives, slides and motion pictures. Grinnell: Iowa; 1993. Preservation.
- [8] Reilly JM. Storage Guide for Color photographic materials. New York: University of the State of New York; 1998.
- [9] Box GEP, Hunter JS, Hunter WG. In: Hoboken NJ, editor. Statistics for experimenters: design, innovation, and discovery. 2nd ed. Wiley; 2005.
- [10] Yamini Y, Saleh A, Khajeh M. Orthogonal array design for the optimization of supercritical carbon dioxide extraction of platinum(IV) and rhenium(VII) from a solid matrix using cyanex 301. Separation and Purification Technology 2008;61:109–14.
- [11] Vanaja K, Shobha Rani RH. Design of experiments: Concept and Applications of Plackett Burman design. Clinical Research and Regulatory Affairs 2007;24:1–23.
- [12] Massart DL, Vandeginste BGM, Deming SN, Michotte Y, Kaufman L. Chemometrics: a textbook. Amsterdam. Oxford: Elsevier; 1988.
- [13] Lemaire J, Arnaud R, Gardette J-L. Low temperature Thermo-Oxidation of Thermoplastics in the solid State. Polymer Degradation and Stability 1991;33: 277–94.
- [14] Fenech A, Strlič M, Cigić IK, Levart A, Gibson LT, de Bruin G, et al. Volatile Aldehydes in Libraries and archives. Atmospheric Environment 2010;44: 2067–73.
- [15] Fenech A, Strlič M, Degano I, Cassar M. Stability of chromogenic colour prints in Polluted Indoor environments. Polymer Degradation and Stability 2010;95: 2481–5.
- [16] Ntanos K, Bell N. A holistic appraisal of environmental conditions in The National Archives, UK. In: Padfield T, Borchersen K, editors. Museum Microclimates. Copenhagen, Denmark: National Museum; 2007. p. 91–7.
- [17] Anderson S, Ellison R. Natural aging of photographs. Journal of the American Institute for Conservation 1992;31:213–23.
- [18] Adelstein PZ, Bigourdan JL, Reilly JM. Moisture relationships of photographic film. Journal of the American Institute for Conservation 1997;36:193–206.
- [19] Bard CC, Larson GW, Hammond H, Packard C. Predicting long-term dark storage dye Stability characteristics of Color photographic Products from short-term tests. Journal of Applied Photographic Engineering; 1980:6.
- [20] Andersen S. Our photographic heritage - The history, art and science of conservation. Copenhagen: Eastman Kodak Company; 1999.
- [21] Hunt RWG. The reproduction of colour. 6th ed. Chichester, West Sussex, England; Hoboken, NJ: John Wiley & Sons; 2004.
- [22] Sturge JM, Walworth V, Shepp A, Neblette CB. Imaging processes and materials. Neblette's 8th ed. New York: Van Nostrand Reinhold; 1989.
- [23] James TH, Mees CEK. The Theory of the photographic process. 3d ed. New York: Macmillan; 1966.
- [24] Sebera D. Isoperms - An environmental management Tool. CLIR; 1994.