

Dimitrios STAMOVLASIS
University of Ioannina, Department of Chemistry

TEACHING CHEMOMETRICS WITH PHOTOGRAPHY EXPERIMENTS IN A UNIVERSITY COURSE ON EXPERIMENTAL DESIGN

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ABSTRACT: Stochastic methods have been proved to be very useful tools when we deal with multifactor chemical systems. On the other hand, chemometrics has been a necessary part of a curriculum in higher chemistry education and of a great and increasing interest as well. In this paper we propose an introduction to statistical methods dealing with multifactor chemical systems, by employing photography. The proposed experimental work concerns the determination of a photographic parameter, *the contrast*, also known as *gamma* γ , which is the slope of the characteristic curve of a photographic film. In practical sensitometry, the determination of γ has been based on the “single-factor-at-a-time” approach. Here we present a stochastic approach to development kinetics of a photographic emulsion. This application includes easy experiments and statistical treatment of the experimental data, and can be used as a tool for introducing chemometrics through photography and vice versa. In addition the obtained formulas can predict the slope γ of the characteristic curve of a photographic film and are useful to professional photographers or in the college photography lab. [*Chem. Educ. Res. Pract. Eur.*: 2000, 1, 393-399]

KEYWORDS: *chemometrics; photographic chemistry; silver halide reduction; photography; characteristic curve of a negative film*

BACKGROUND

The black and white (*B/W*) photographic image as perceived is created by variation in the absorption of light in the photosensitive *AgCl* emulsion, corresponding to the quantities of metallic silver *Ag* formed after exposure and development. When a photographic material is developed, the silver halide crystals, which have been exposed to light and bear a latent-image center (Keller 1993), are reduced to metallic silver *Ag* by a reducing agent:



where *Red* is the developing agent, and *Ox* is its oxidized form. The developing agent is an alkaline solution of hydroquinone, which is oxidized to quinone (Eaton 1957).

Photographic development is thus based on a kinetic effect. The amount of metallic silver formed on a developed transparent emulsion can be estimated by measuring its optical density, $D = -\log(I_0/I_t)$, where I_0 is the radiant flux incident on a developed transparent emulsion and I_t is the radiant transmitted after absorption. If the optical density D , which depends on the geometry of the measuring apparatus, is plotted versus the logarithm of exposure $H = E * t$ (in lux*sec), the characteristic curve is obtained (Figure 1).

This curve is known as the *Hurter & Driffield (H & D) curve* and it is described in terms of parameters that convey information about the photographic properties (Hurter, 1890; Keller, 1993). The more essential parameter is the *contrast*, the slope of the linear portion of the graph, called *gamma* γ :

$$\gamma = dD / d(\log H)$$

Gamma corresponds to the normally exposed region and it is a measure of how relative exposure differences are transformed into density differences or density contrasts.

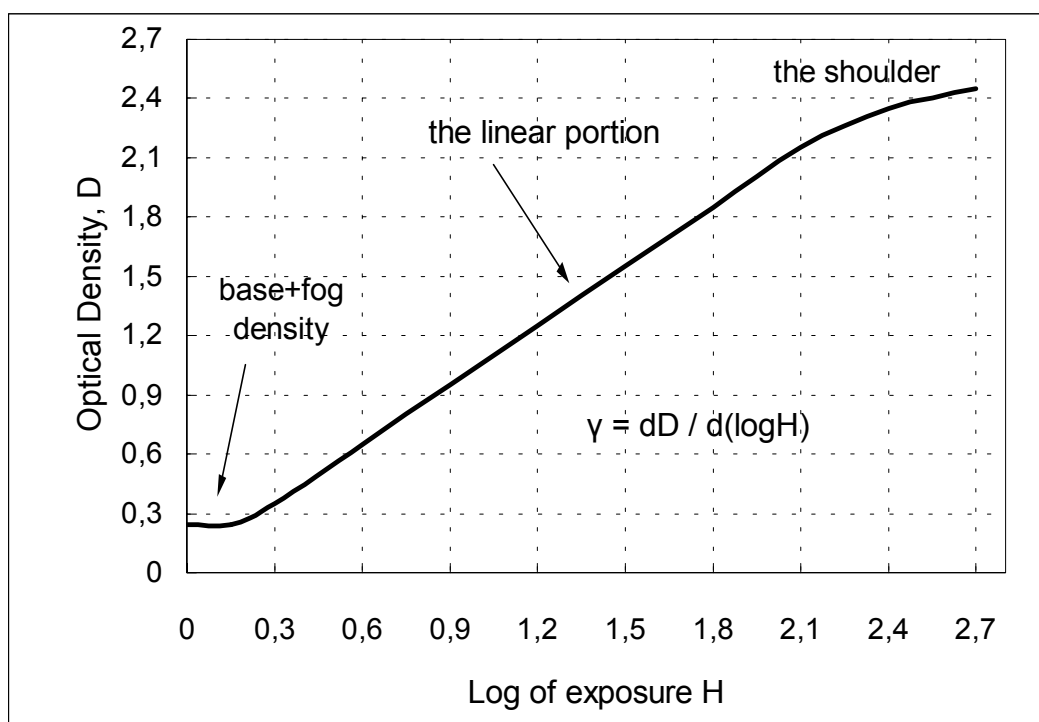


FIGURE 1. *The characteristic curve of a photographic film.*

From the photographic standpoint, the development rate of an emulsion is defined (Keller 1993) either as the growth rate of optical density D or as the rate of increase of gradation γ . The principal factors affecting the development kinetics of emulsion are:

- 1) the size and the nature of the emulsion [grain size, packing density, contents of the photosensitive material (AgX)];
- 2) the concentration and the nature of the developing agent;
- 3) the pH of the developing solution;
- 4) the concentration and the nature of special compounds in the developing solution (accelerators, restrainers, sulfide, halide, developer oxidation products);
- 5) the exposure conditions (intensity of light);
- 6) the development temperature.

In practical sensitometry the kinetics of the development is described by the parameter *gamma* γ , which always is the quantity to be determined for a given exposed photographic

emulsion, in order to control the quality of the final image. For a given emulsion and a given developing solution, the factors controlling the levels of gamma γ are:

- *the length of a the film strip*, (which in kinetic terms represents the contact area);
- *the concentration of the developing (reducing) agent*,
- *the development time*,
- *the development temperature*.

In the experimental section which follows, we describe how one can obtain sensitometric data for statistical treatment.

EXPERIMENTAL PROCEDURE

SAFETY NOTE: *Chemicals used for photographic development are in general harmless. Only hydroquinone, which is the developing agent, is moderately toxic. The stop bath solution (acetic acid) and the fixing solution (sodium thiosulfate with acetic acid) are weak acids with pH about 4.5 and should be handled carefully preventing hazardous spills. In case of contact with either chemical, immediately wash of the affected part with large quantities of water. Since the developing procedure is carried out in the developing tank, safety goggles are recommended.*

The experimental procedure could be divided into three steps: The exposure, the development and the optical density measures.

The film-exposure. A negative B/W photographic film is placed in a camera facing a light source of colour temperature of 5000 degrees of Kelvin. Alternatively one could use a tungsten lamp of 3200° K and add a conversion filter in front of the lens of the camera.

- Colour temperature is a way of expressing the colour content of a light source. The colour temperature of a white light source is the temperature in Kelvin degrees (K) of the radiating “black body” when emitting light matching the source under test. (Keller 1993).
- Conversion filters are used to change the colour balance of a source to a desired proportion of red, green and blue.

Let the photometer indication be $V = 16$ relative units of exposure. This is the normal exposure. Then eleven exposures are taken from 0.5 to 256 relative units. In photographic language, this corresponds to from -5 stops below to +5 stops above the normal exposure. Table 1 shows the relative exposure units, which are used in constructing the characteristic curve.

The film-development. One can use a procedure of film developing suggested by any film manufacturer. In the present work the method described by Kodak Workshop Series (1988) was used. The negative B/W films used were Kodak TMX100, treated with TMX-developer and fixed with Kodak T-fixer for 10 min. The films were developed under the chosen conditions of temperature, developing time and concentration of developer with the tank method. Note that agitation during development is important and should always be the same in order that

TABLE 1. *Relative units of exposure. V is the normal exposure (photometer indicator).*

Exposure, H	0.5	1	2	4	8	V 16	32	64	128	512	256
Log of Exposure Log (H)	-0.3	0	0.3	0.6	0.9	1.2	1.5	1.8	2.1	2.3	2.6
Stop difference from V	-5	-4	-3	-2	-1	0	+1	+2	+3	+4	+5

reproducible results are obtained. In addition, a temperature-control unit for solution temperature regulation is necessary. After the films had been washed and dried, the optical densities of the different exposures were measured.

Optical-density measurement. The optical density is measured by a densitometer. The measured densities, the corresponding exposure units, and the development conditions of agent concentration, development time and temperature are the data to be used for statistical treatment.

STATISTICAL TREATMENT

The slope γ of the characteristic curve was calculated from optical densities and the logarithms of the exposure by using the least-squares method. The calculated gammas were introduced in the factorial design shown in Table 2. To carry out a factorial design, we select a certain number of levels for each factor (variable) and then run the experiment with all possible combination of the factors. The total number of runs can be obtained by multiplication of the levels for each factor. In our case, a two level-four factor design requires $2^4 = 16$ runs. The factor levels for the 2^4 factorial design are given in Table 2.

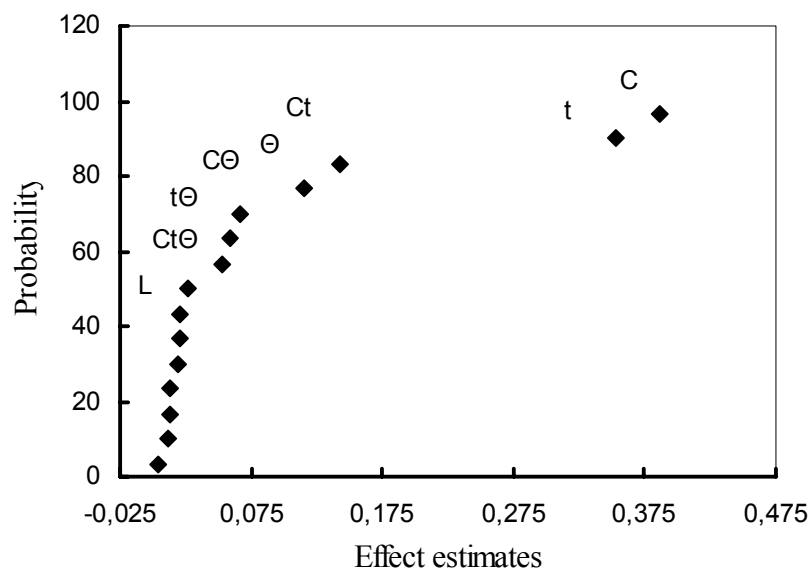
To calculate the effects in this experimental design, the Yates's algorithm was employed (Morgan, 1995). The calculations were easily carried out on a spreadsheet. The results are shown in Table 3. Normal probability plot of effects is used to reveal the significant effects. All of the effects that lie along the line are negligible, whereas the large effects are far from the line. The important effects that emerge from the analysis are the main effects from C, t, Θ and the Ct, C Θ , t Θ , and Ct Θ interactions (Figure 2).

TABLE 2. 2^4 factorial design.

Levels Factor	Symbol	units	-I	+I
Length of the film	L	m	0.50	1.50
Concentration of the reductant	C	%vol	6	20
Development temperature	Θ	$^{\circ}$ C	20	26
Development time	T	Min	3	10

TABLE 3. Calculated Effects on gamma by Yates' algorithm.

Run number	Treatment code	Design matrix variables				Response gamma		Estimate of effect
		L	C	t	Θ	γ	esd	
1	(1)	-	-	-	-	0.118	0.006	0.430
2	L	+	-	-	-	0.113	0.005	0.021
3	C	-	+	-	-	0.339	0.016	0.386
4	LC	+	+	-	-	0.341	0.014	0.027
5	t	-	-	+	-	0.311	0.009	0.353
6	Lt	+	-	+	-	0.318	0.009	0.013
7	Ct	-	+	+	-	0.716	0.027	0.142
8	LCt	+	+	+	-	0.730	0.028	0.011
9	Θ	-	-	-	+	0.153	0.006	0.116
10	L Θ	+	-	-	+	0.152	0.005	0.019
11	C Θ	-	+	-	+	0.387	0.011	0.067
12	LC Θ	+	+	-	+	0.435	0.008	0.021
13	t Θ	-	-	+	+	0.376	0.020	0.059
14	Lt Θ	+	-	+	+	0.362	0.012	0.004
15	Ct Θ	-	+	+	+	0.953	0.044	0.053
16	LCt Θ	+	+	+	+	1.083	0.043	0.013

**FIGURE 2.** Normal probability plot of effects.

The statistical treatment led to a model that predicts *gamma* within certain limits. These limits (by design) correspond to the usual working conditions. The resulting linear model contains an offset term β_0 , first order effects β_1 , β_2 , β_3 , and interaction effects β_{12} , β_{13} , β_{23} and β_{123} . The effect of the length (L) of the photographic film and the interaction effect of length-concentration (LC) are statistically insignificant. However, since these effects represent the contact area of the solid reactants, they could be kept in the model. The adequacy of the produced model was tested by ANOVA is shown in Table 4.

TABLE 4. *Analysis of variance.*

Source of variation	Degrees of freedom, d.f.	Sum of squares (SS)	MS= SS / d.f.	Variation ratio, F
C	1	0.5971	0.5971	480.7
t	1	0.4974	0.4974	400.4
Ct	1	0.0811	0.0811	65.3
Θ	1	0.0535	0.0535	43.1
C Θ	1	0.0182	0.0182	14.6
t Θ	1	0.0140	0.0140	11.2
Ct Θ	1	0.0112	0.0112	9.5
LC	1	0.0029	0.0012	
L	1	0.0018		
LC Θ	1	0.0018		
L Θ	1	0.0015		
LCt Θ	1	0.0007		
Lt	1	0.0007		
LCt	1	0.0005		
Lt Θ	1	0.0001		
	8			

The theoretical value of F-ratio for d.f. one and eight is 5.32 at $p = 0.05$

The model can provide three-dimensional graphs or useful contours, such as one shown in Figure 3. Using these contours, a student can decide about the development time in a given temperature, in order to achieve a certain gamma, keeping the concentration of the developer constant. These contours for predicting *gamma* of a photographic film can be easily obtained with eight experiments and are very useful to a professional artist photographer and to the college photography laboratory, if available.

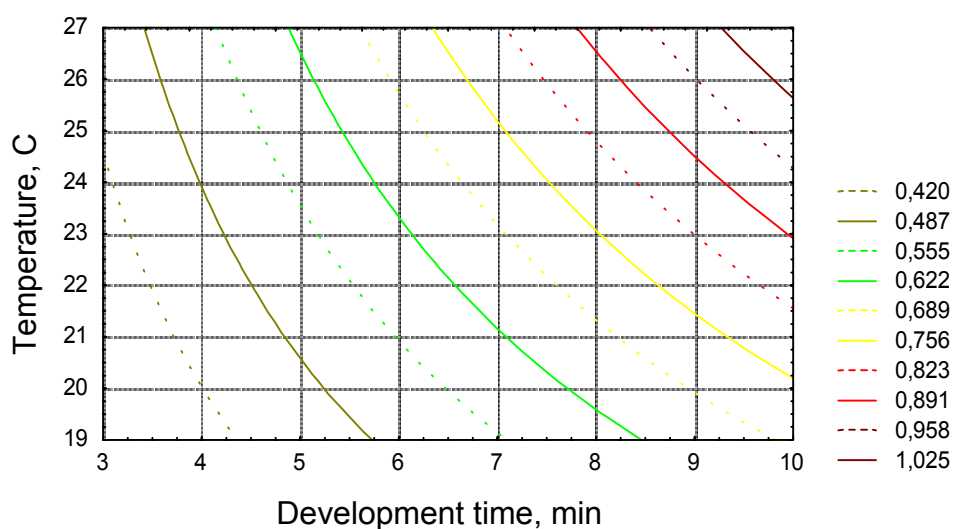


FIGURE 3. *Gamma as a function of development time and temperature (20% dilution of the reducing agent). The curves correspond to values of gamma from 0.420 (bottom left) to 1.025 (top right).*

DISCUSSION - TEACHING ASPECTS

In this paper we have described easy experiments with a multifactor chemical system. The experiments provide data to be analyzed by advanced statistical methods in order to describe the behaviour of that system. This work has actually two parts which require different working environments. The first part is the data collection, which needs a chemistry lab; the second part is the statistical analysis, which requires a classroom or a computer-room. Since the eight experiments are time consuming, a successful approach is to assign one run for 2-3 students and then have them bring together and discuss their results. The cooperative learning strategy would be appropriate for the case. Even though the primary goal is for students to become familiar with experimental design, the instructor has the opportunity to introduce sensitometry and photographic chemistry. An interesting approach is to employ an interplay between chemometrics and photography, such as the connection between kinetics of the chemical reaction taking place, and the appearance of the final photographic image.

Photography is very popular among students and sparks their interest to be involved in such experiments. The interdisciplinary nature of photography (scientific, technological, and social dimension) supports the proposed idea within the frame of a science-technology-environment-society (STES) oriented curriculum. The STES-oriented chemical education requires inter-/trans-disciplinarity as a core-element in chemistry teaching (Zoller, 2000) and that requirement is met by the above experiments.

ADDRESS FOR CORRESPONDENCE: Dimitrios STAMOVLASIS, *Department of Chemistry, University of Ioannina, GR-451 10 Ioannina, Greece; fax: +30 651 44989; e-mail: me00550@cc.uoi.gr*

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