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Experimental Measurement: Interpreting Extrapolation and Prediction by Accelerated Aging

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The present is the intersection of the past and the future. Correspondingly, the past influences the future as one of several possible actions is selected to be realized at present. The restorer preserves the witnesses of the past to become a source of innovation in the future.

Restoration itself, however, has its own past. The art of restoration of former times affects the future. In restoration decisions are made today that will be of importance when future generations of restorers handle the objects restored. New techniques are applied (or not applied) in restoration and we attempt to predict their usefulness using accelerated aging.

PIECES OF ART AS COMPLEX SYSTEMS

Berger & Zeliger¹ address restorers of oil paintings, but many points are of interest to restorers in general. Berger & Zeliger consider an art masterpiece to be a complex entity. Correspondingly, they do not just examine the aging behaviour of linen itself but also the aging behaviour of linen coated with adhesive. They find that beeswax under aging conditions of 54°C for 1 year protects the texture and that 94°C for 5 d destroys the texture. Coating the linen with a high-melt adhesive (Thermogrip) produces the opposite result: protection at 94°C for 5 d and destruction at 54°C for 1 year. Baer et al.² have done similar work on the system of paper and adhesive.

The aging behaviour of the complex system of paper (or linen) and adhesive not only depends on temperature but also on the structure of the fabric, the composition of the surrounding atmosphere, the history of the system, and so on. Applied engineering in manufacturing industry examines such complex coupled systems by using statistical methods of planning and interpreting experiments (factorial design). The precondition for applying statistics is the existence of a quantitative measure for each variable. This precondition has not been fulfilled at present for examination of pieces of art. Correspondingly, Berger & Zeliger¹ question whether standardized industrial tests should be applied to restoration research. Industrial tests try to simulate rapid changes, whereas research in restoration examines extremely slow processes. Tests for restoration require high performance and resolution in a different range of measurement than industrial tests.

Even the base materials themselves, linen or paper, have a complex structure characterized by a fractal geometry³. Besides cellulose, paper contains sizing agents, fillers, additives and impurities. The main cause of destruction is acid-catalyzed hydrolysis of cellulose. The acid originates from atmospheric pollution, the amount of alum and the decomposition products of lignin. Oxidative processes are important, too. The experimenter attempts to observe the changes in this complex system, comparable to a time-lapse camera in an oven at elevated temperature. The results are then interpreted using a simple model such as the Arrhenius equation. By extrapolation over several decimal powers of time the researcher tries to predict the state of the system in the distant future.

LIMITS OF THE KINETIC APPROACH^{4,5}

The kinetic model for describing the decay of paper

In general, the destruction of paper is described by a law of first-order kinetics.

This description is a model of reality:

decay rate (cellulose/time)=
constant (1/time) x content of cellulose
or

$\ln(\text{cellulose}/\text{cellulose}_0) = -\text{constant} \times t$

where cellulose is the content of cellulose at time t of the experiment and cellulose₀ is the content, at the beginning of the experiment ($t=0$).

$\ln(\text{cellulose}/\text{cellulose}_0)$ is set proportional to the logarithm of a characteristic variable $\ln(\text{variable})$, which can be measured quantitatively. The variable can be tensile strength, stretch at break, tear resistance or any other macroscopic measure of the mechanical stability of the paper. The natural logarithm of the measured values is plotted against time (t) of the experiment. If the model is valid, a straight line is achieved. The slope of the line is the constant in the equation above.

The constant includes the influence of pollution, the history of the paper, the water content of the atmosphere, temperature etc.

According to Arrhenius, the constant is exponentially dependent on temperature:

constant (1/time) = $A(1/time) \times \exp(-EA/RxT)$

or

$\ln(\text{constant}) = \ln A - (EA/R) \times 1/T$

If the Arrhenius model is valid, a straight line can again be obtained by plotting the logarithm of the values of the constant, determined at different temperatures, against the reciprocal of these temperatures. In this case the slope gives the energy of activation (EA) divided by the universal constant $R=8.314 \text{ J/Kxmol}$.

The pre-exponential factor A now contains the influence of pollution, the history of the paper and the water content. The value of the energy of activation determines how much a change in temperature influences the value of the constant and thus the degradation of cellulose. Energy of activation has the units kJ/mol. Temperature is given as the unit Kelvin in the absolute temperature scale. By this the expression $(-EA/R \times T)$ is dimensionless.

Arrhenius' law can be derived from statistical thermodynamics for elementary reaction only: two well defined molecules collide and react. In other cases its application is based on empirical experience and practical success. Many complex systems do not strictly follow Arrhenius' law. Paper is one of these complex systems.

The following assumptions have been made for further interpreting the results of measurement:

- The kinetics of aging conforms to a first-order reaction model and Arrhenius' law is valid.
- The degradation of paper and of the cellulose backbone can be described by an easily measured macroscopic variable. We even assume proportionality between degradation and the macroscopic variable.

Critical review of the literature and experience

Browning & Wink⁶ examined the aging of paper by observing changes in folding endurance. For diverse papers they found an energy of activation between 112 and 138 kJ/mol. For most of the papers examined, plotting of the logarithm of folding endurance against time of aging generates a weakly or even strongly convex line. The line is not straight. Nevertheless, by using regression analysis, Browning & Wink derived the optimal straight line for each group of measuring points. From the slope of the line they derived the values of the constants and from these the value of Arrhenius energy of activation.

Browning & Wink have also found skewed Arrhenius plots. They did not get a straight line by plotting the logarithm of the constants against the reciprocal of temperature. In these cases the simple model of Arrhenius' law obviously does not describe the dependence of aging on temperature for this complex system of paper.

The energy of activation range found by Browning & Wink is 125 +/-13 kJ/mol. Extrapolation then leads to strongly diverging results. At room temperature, paper ages 43,000 times faster at an energy of activation of 112 kJ/mol than at 138 kJ/mol. At 60°C (333 K) and energy of activation of 112 kJ/mol, aging is accelerated 12,000 times compared with 138 kJ/mol. One, 12,000 or 43,000 years makes a vast difference. Paper was invented just 2000 years ago!

The energy of activation has to be determined much more precisely to predict the aging behaviour of paper in a way that makes sense. Usually the restorer thinks in terms of centuries. For 100 years, 1 year of uncertainty in aging behaviour is tolerable. This precision requires the energy of activation to be known within 0.025 kJ/mol. By measuring such macroscopic variables as folding endurance or tear resistance, one should have no problem meeting this requirement. Measuring the macroscopic variable tear resistance with a 2% margin of error results in a range of energy of activation by Arrhenius' model of approximately +/-0.010 kJ/mol.

The techniques of measurement allow the energy of activation to be quite precisely determined. Unfortunately, Arrhenius' model dose not describe papers precisely enough, and these assumptions are only approximative.

A general rule says that increasing temperature by 10°C doubles the rate of a given aging process. This rule originates from the organic chemistry of homogeneous liquid-phase reactions. In everyday use by restorers it has proved useful for describing aging empirically. It corresponds to an average energy of activation of about 50 kJ/mol. This energy of activation is far from the margin of error of 125 +/-13 kJ/mol found by Browning & Wing6 for aging of solid paper.

Finally, there are two possible pitfalls in interpreting aging measurements over a large temperature range.

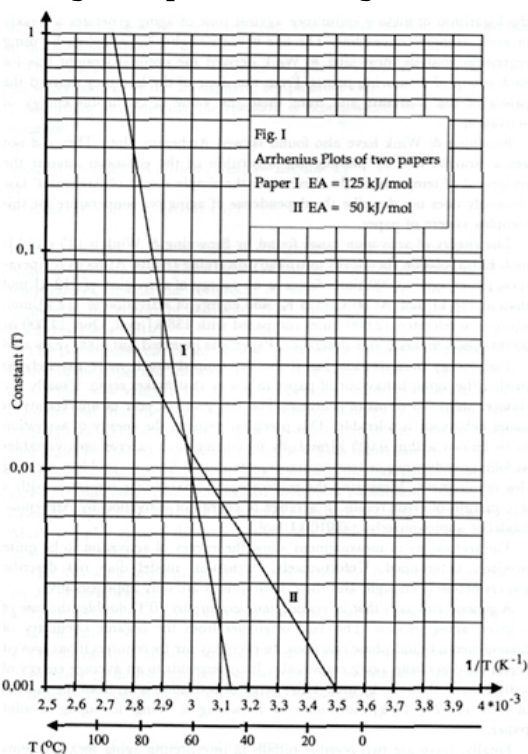


Fig. 1.

We have learnt to distrust absolute predictions of aging behaviour over time by Arrhenius' model. Nevertheless, even conclusions drawn from relative results

obtained by comparing the aging of two papers have to be handled with care. Fig. 1 shows the Arrhenius plots of two papers (logarithm of the constants versus reciprocal of temperature). Papers I and II have different energies of activation for their aging processes, which results in different slopes for the straight lines. The preexponential factors are also different. At 80°C the constant for paper I is larger than the constant for paper II, which means that paper I ages faster than paper II at 80°C. At 20°C it is just the opposite: paper II ages faster than paper I. A series of measurements that determine the relative aging behaviour of the papers at 80°C says nothing about the relative aging behaviour at 20°C.

Various authors warn that aging experiments should not be performed at temperatures above 55°C⁷. Calvani et al.⁸ follow the recommendation of Graminski et al.⁹; in their studies on the effectiveness of paper deacidification they never exceeded 70°C. It is assumed that the mechanisms of degradation are different above and below that temperature. If the mechanisms are different, different kinetic laws are valid and the energies of activation are also different. The paper behaves, in fact, like two different papers I and II (Fig. 1): the results of high-temperature aging do not allow prediction of aging at room temperature. Extrapolation is not allowed!

Table 1

Paper	Tear resistance (mN) in machine direction after accelerated aging of				
	0 days	3 days	6 days	12 days	24 days
1881	177	150	151	118	107
S26	341	327	346	292	278
S31	468	433	410	368	331
S71	371	334	311	278	244
1879	288	252	247	202	162
S67	458	419	394	350	307
S68	436	410	403	364	315
S73	433	334	298	245	172
1935	147	133	132	110	98
S28	242	228	240	216	190
S38	221	221	211	202	177
S44	230	222	207	185	176
S67	458	419	394	350	307
S68	436	410	403	364	315
S72	253	230	233	210	171

Vovelle et al.¹⁰ examined high-temperature thermal degradation of cellulose and found energies of activation between 80 and 250 kJ/mol. *Degradation of cellulose and its derivatives*¹¹ discusses the different mechanisms of degradation of cellulose. The origin of all this work is on industrial application. The authors mainly intended to accelerate the degradation of cellulose. This goal is exactly contrary to that of restorers. Correspondingly, degradation was examined under temperature conditions completely different from those of interest to the restorers. Industrial and restoration tests have different goals.

FURTHER APPROACHES TO DETERMINING THE AGING OF PAPER

Statistical planning of experiments^{12,13}

In industry the properties of textiles and paper are determined by methods of statistical factorial design. The influence of parameters such as temperature and humidity on a target variable (such as tear resistance) is examined. The relationships can be quite complex. The method has the advantage that it can reveal the interactions and correlations between the different parameters. Finally, a mathematical relation is achieved between the target variable and parameters that is not based on an underlying physical model and is therefore not comprehensible. Extrapolations beyond the region examined are not allowed either. Further, this method has the disadvantage that it requires:

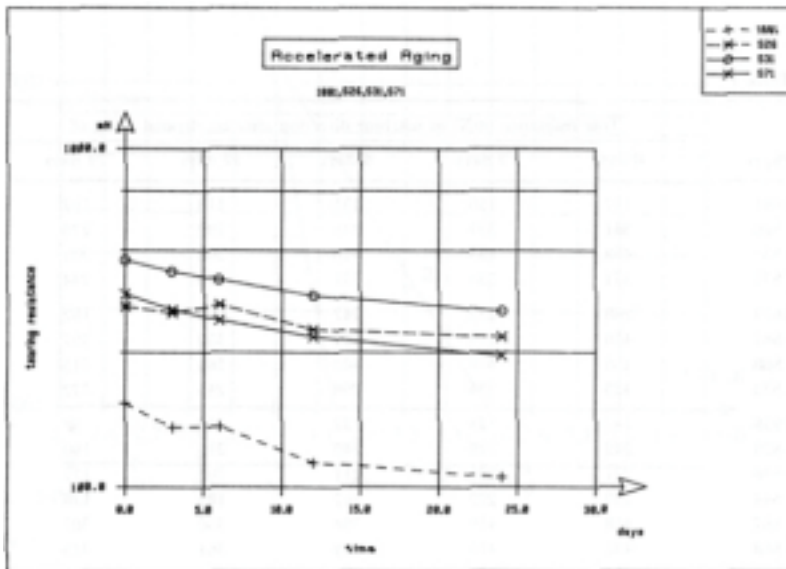


Fig. 2

- extensive computer software to design the tests;
- a well-prepared, reproducible, quantitative analytical test method;
- substantial working capacity to execute tens or hundreds of tests, and therefore:
- a partially automated workplace;
- capacity for a large number of samples; and
- extensive computer software to interpret data and a broad knowledge of statistics and regression.

All this is not available in restoration laboratories at present. It must also be emphasized again that extrapolations beyond the region examined are not permitted in this case either and that we still assume that the molecular mechanism of the decay of paper can be comprehended by a macroscopic variable such as tear resistance or folding endurance.

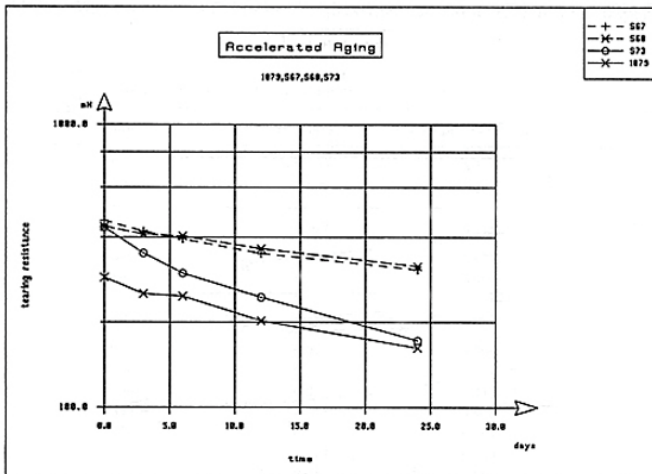


Fig. 3.

Comparison of aging behaviour of historical and new papers

In the following we examine the problem of meaningful extrapolation from a different point of view. Historical papers and comparable new papers are both aged artificially under identical conditions and the aging behaviour of historical and new papers is compared.

Rasch & Scribner¹⁴ did not examine historical papers but only papers stored under natural conditions for four years. They compared the folding endurance and chemical properties of these naturally aged papers with those of artificially

aged new ones. Wilson & Parks¹⁴ checked all literature up to 1980 and found statistical correlations between paper aged naturally for 36 years and paper aged artificially in 1937. Bansa & Hofer¹⁶ continued this work for historical paper.

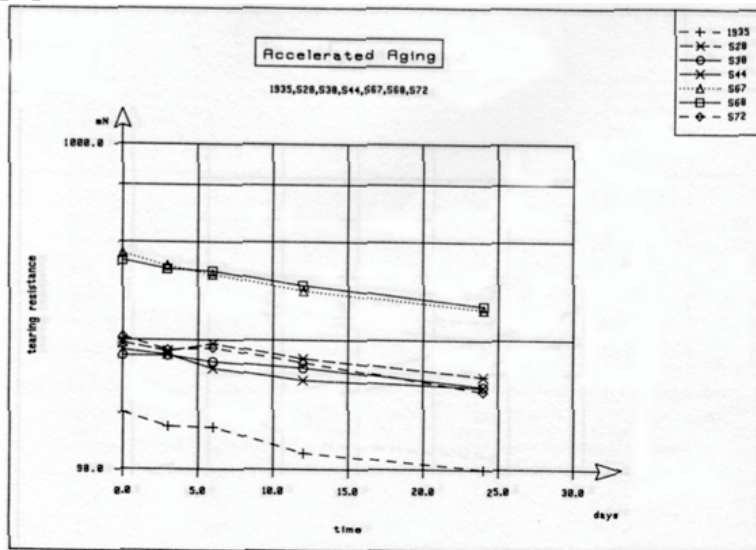


Fig. 4.

In our test series, however, we aged artificially the new and the old papers under identical conditions: 80°C and 65% relative humidity (ISO Standard 5630/3). We had at our disposal three old papers from 1935 (68 g/m², 1879 (70-74 g/m²) and 1881 (77-80 g/m²). To each of those we selected a group of papers from current production that had similar weights per area and for which we expected similar aging behaviour. The aging behaviour of the new papers was estimated from a large number of tests according to DIN Npa21 Nr. 36-89.¹⁷ We only selected the new papers that showed a strong change in the tear resistance in the direction of the machine after accelerated aging. This is not true in general for all papers. Other variables measured by DIN Npa21 Nr. 36-89¹⁷ (such as stretch at break or tensile strength) only display small changes after accelerated aging. The selection criterion mentioned above leads to the peculiar result that only new papers of low quality were selected for comparison with the historical ones. Nevertheless, the accelerated aging experiments according to DIN Npa-21 No. 36-89 17 lead to the even more interesting result that the stability of only one of these new low-quality papers decreased after 24 d of accelerated aging below the stability of the original naturally aged historical papers (S73 and 1879) (Table 1). This reflects the difficulty in bringing a new paper into the state of a historical one by accelerated aging. Libraries and archives have a lot of 100-year-old paper in a state so fragile that it cannot be simulated by accelerated aging in realistic periods of time (3, 6, 24 or 30 d).

According to DIN Npa21 Nr. 36-89 we aged for 3, 6 12 and 24 d and measured the variable tear resistance in the direction of the machine. Other variables such as stretch at break and tensile strength did not give interpretable results. The experimental results are presented in Table 1. The new papers are characterized by sample numbers: S(ample) 26, 28, etc. The historical paper are characterized by the year of manufacture: 1935, 1879 or 1881.

Table 2. Regression lines $\ln(\text{value of tear resistance}) = \text{slope} \times (\text{time } t) + \text{intercept}$

Paper	Slope (days ⁻¹)	Intercept (no dimensions)
1881	-0.020	5.112
S26	-0.009	5.837
S31	-0.014	6.115
S71	-0.017	5.868
1879	-0.023	5.630
S67	-0.016	6.091
S68	-0.013	6.069
S73	-0.038	5.992
1935	-0.017	4.960
S28	-0.010	5.494
S38	-0.010	5.413
S44	-0.011	5.408
S67	-0.016	6.091
S68	-0.013	6.069
S72	-0.016	5.522

Interpreting these experiments was straightforward according to first-order kinetics: plots of the natural logarithm of the tear resistance against time (Figs. 2-4). Analogous to the results of Browning & Wink⁶, most lines show a convex curving. As the accelerated aging process proceeds, aging is increasingly inhibited, and the process of degradation slows down. This is an example of negative feedback: the history of the paper results in slower decay in the future.

The optimal straight line found by regression analysis results in the slopes and intercepts given in Table 2. Regression analysis was performed using a pocket calculator.

With one exception (S73), the values of the slopes for the historical papers are larger than those for the new papers. The historical papers (1881, 1879 and 1935) degrade faster by accelerated aging than the new ones, although the new papers were selected for their low quality.

This leads to an important result. The history of the old papers influences accelerated aging by accelerating the aging process. There is positive feedback between the history of the historical papers and the accelerated aging process. From a philosophical point of view, the past influences the future. Each paper has its individual history. Accordingly, the slopes of the regression lines are different for all historical papers.

Nevertheless, something can be concluded by comparing the papers 1935 and S67 and S72, which display similar slopes. The difference of the intercepts must correspond to the 55 years of natural aging of paper 1935:

$$(6.091 - 4.96)/0.017 = 66 \text{ days}$$

$$(5.522 - 4.96)/0.017 = 33 \text{ days}$$

The 55 individual years of historical experience of paper 1935 correspond to 33-66 d of accelerated aging under our aging conditions.

Similarly, comparing the papers 1881 and S71 shows that the 109 years of paper 1881 correspond to 35-45 d of accelerated aging in our oven.

These findings do not contradict the results of Rasch & Scribner¹⁴, Wilson & Parks¹⁵ or Bansa & Hofer¹⁶. Aging is not a deterministic process. Paper ages faster in an oven at elevated temperatures than in a natural environment; pH value and humidity strongly influence aging, too. Nevertheless, deriving universal quantitative rules from accelerated aging violates experimental results.

CONCLUSION

The influence of the past on the future is an everyday experience in human life. Examples in science are hysteresis, material fatigue and evolution processes. Correspondingly, each sheet of paper is characterized by individual history that influences its aging behaviour in the future. Macroscopic variables and classical methods of aging do not reveal this history and the resulting possibilities of future behaviour.

SUMMARIES

Experimental Measurement: Interpreting Extrapolation and Prediction by Accelerated Aging

Accelerated aging (several days of storage in oven at elevated temperature, used in conservation research) is examined in the light of chemical kinetics. The result is quite sobering: the only effect of accelerated aging is an acceleration, but its rate is not known. Even relative conclusions are not always possible. Object A may age more quickly than object B at higher temperature, but more slowly at a lower temperature. In addition, the future of any single object is influenced by its specific history. History can only happen; it cannot be simulated in advance.

Mesures Expérimentales et Interprétation des Résultats: Extrapolation et Prédiction par Vieillissement Accéléré

Une technique utilisée en recherche sur la conservation des objets d'art, le vieillissement accéléré par exposition de l'objet à température élevée, est examinée sous l'angle de cinétique chimique. Le résultat est décevant: le seul effet du vieillissement accéléré est une accélération, mais sa vitesse est absolument inconnue. On ne peut en tirer aucune conclusion, même d'une façon relative. Il peut arriver que l'objet A viellisse plus vite que l'objet B à une température donnée, mais plus lentement à une autre température. De plus, l'évolution future de chaque objet est influencée d'une façon spécifique par le passé de cet objet. Ce passé ne peut être simulé à l'avance.

Messmethoden, Messergebnisse und ihre Interpretation: Extrapolation und Vorhersagen an Hand künstlicher Alterungsexperimente

Die in der restaurierungskundlichen Forschung übliche Methode der beschleunigten Alterung im Ofen bei erhöhter Temperatur wird einer kritischen Prüfung im Lichte der einschlägigen Gesetze chemischer Kinetik unterworfen: mit dem recht ernüchternden Ergebnis, dass außer der Tatsache, dass die Alterung im Ofen schneller abläuft als in natürlicher Umgebung, aus entsprechenden Experimenten nichts Sicheres abgelesen werden kann. Nicht einmal rein relative Aussagen sind zuverlässig möglich: es ist denkbar, dass Objekt A bei hoher Temperatur schneller altert als Objekt B, bei niedriger aber langsamer. Und noch mehr: die Zukunft eines jeden Objekts ist durch seine Geschichte bestimmt; Geschichte kann nur "geschehen"; lässt sich in keiner Weise simulieren.

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