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Imaging materials — Test method for Arrhenius-type predictions

Matériaux d'image — Méthode d'essai pour les prédictions de type Arrhenius

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Foreword

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International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO 18924 was prepared by Technical Committee ISO/TC 42, *Photography*.

This second edition cancels and replaces the first edition (ISO 18924:2000), of which it constitutes a minor revision with the following changes:

- Clause 2 has been removed;
- Annex A has been removed.

Imaging materials — Test method for Arrhenius-type predictions

1 Scope

This International Standard specifies a test method for the prediction of certain physical or chemical property changes of imaging materials.

This International Standard is applicable to the Arrhenius test portion of ISO 18901, ISO 18905, ISO 18909, ISO 18912, and ISO 18919.

This International Standard is applicable to the prediction of the optical-density (*D*) loss or gain of imaging materials. Photographic dye images may be produced by chromogenic processing, by formation of diazo dyes, or by non-chromogenic methods such as dye diffusion and silver dye-bleaching processing. This International Standard also covers density changes caused by

- residual coupler changes in dye images,
- excess residual processing chemicals in silver black-and-white materials,
- temperature effects on thermally processed silver images.

This International Standard is applicable to the prediction of support degradation. One such example is the generation of acetic acid by degradation of cellulose acetate film support. Another example is the change in tensile energy absorption of black-and-white paper support.

2 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

2.1
Arrhenius plot
plot of the logarithm of the time for a given change in a characteristic proportional to the reaction rate (dye loss, tensile strength change, D_{min} yellowing, etc.) versus the reciprocal of the temperature, in kelvins

Note 1 to entry: The Arrhenius plot may be used to predict behaviour at a temperature lower than those at which the tests are run.

2.2
glass transition
reversible change in an amorphous polymer from, or to, a viscous or rubbery condition to, or from, a hard and relatively brittle one

2.3
glass transition temperature
T_g
approximate mid-point of the temperature range over which glass transition takes place

Note 1 to entry: T_g can be determined readily only by observing the temperature at which a significant change takes place in a specific electrical, mechanical, or other physical property.[1]

Note 2 to entry: T_g can also be sensitive to the moisture content of the polymer (see 4.4, Annex A, and B.3 of Annex B for information).

Note 3 to entry: For imaging materials containing gelatin, T_g is very humidity dependent.

2.4
irrelevant physical or chemical reactions
chemical or physical reactions that take place only at high temperatures and/or humidities and do not take place at the temperatures at which the Arrhenius predictions are to be made

Note 1 to entry: Such reactions may nevertheless affect the quality of the image, binder, or support.

2.5
morphological changes
changes in the physical structure of the association of the molecules

2.6
thermodynamic temperature
temperature measured on the absolute scale which is based on absolute zero (–273,15 °C) and having an interval of measurement that is equivalent to degrees Celsius

Note 1 to entry: The temperature unit in the absolute scale is the kelvin.

3 Background and theory

3.1 Background

In the 1890s, Svante Arrhenius discovered that the rate of some chemical reactions is proportional to the reciprocal of the absolute temperature. This relationship has been used with phenomena related to a chemical change, such as the loss of a particular physical property or the change in the optical density of film. If a linear relationship exists between the logarithm of the time for a change of a particular property and the reciprocal of the temperature, then this plot can be extrapolated to lower temperatures than those used in laboratory studies. This allows the prediction of the time required for the change to happen at room temperature or lower.

This relationship was first used for the rates of chemical reactions[2] and was later applied to paper materials.[3,4] This theory became the basis for TAPPI Standard 453.[5] The approach was also applied to textiles[6] and to physical properties of photographic film supports.[7,8] More recently, it has been used to predict the fading of both chromogenic and non-chromogenic photographic dyes.[9-11]

Predictions based on the Arrhenius equation require the reactions to be run under a series of temperatures at either constant relative humidity (free-hanging) or constant moisture content inside the enclosure. The investigator shall determine which of the above conditions is more relevant to the system being tested.

There may also be cases where elevated temperatures cause different reaction pathways from those occurring at ambient or sub-ambient conditions. In these cases, the plot of the logarithm of time versus the reciprocal of the absolute temperature will be nonlinear and great caution shall be taken in drawing conclusions. Only the linear and lower temperature portion of the plot can be extrapolated to ambient conditions or below.

The drawback to elimination of higher temperature data is that the experiment will then take longer because of the slow reaction rate at lower temperatures. Patience is the only solution for getting the correct answer when this happens. When incubations are limited to a few of the higher temperatures, this can lead to incorrect or misleading results and shall be done with extreme caution.

Confidence in the Arrhenius methodology is obtained when predictions for phenomena with reasonably short lifetimes correspond to the real-time results. Such data do exist for the fading of photographic dyes[12,13] and the stability of cellulose ester film supports.[8,14]

3.2 Theory

The basic relationship in the study of chemical reaction rates is the Arrhenius equation:

$$\log k = \frac{-E}{2{,}30\,RT} + C \tag{1}$$

where

k	is the rate of reaction (change per time);
E	is the energy of activation for a specific reaction;
R	is the gas constant;
T	is the temperature (in kelvins);
C	is a constant for the specific reaction.

By combining all the constant terms ($E/2{,}30\ R$) into a constant "a" and measuring the time for a given change, this equation can be rewritten as:

$$\log\,(\text{time}) = \frac{a}{T} + C \tag{2}$$

Consequently, when the logarithm of the time is plotted against the reciprocal of the absolute temperature, a straight line is produced. This relationship can be used to predict the time required for a given change to occur at lower temperatures where the reaction might require hundreds of years. This is done experimentally by determining the time required for a given change at a number of elevated temperatures (where the times required are reasonable), plotting these points, and extending the straight-line graph to the lower temperatures of interest. This "Arrhenius method" of predicting long-term ageing behaviour is widely used and accepted by experts in the photographic industry.

In the chemical literature, the equation has been widely applied to relatively simple, chemical reactions where both reactants and products have been identified. However, there may be circumstances in which the fit of the Arrhenius prediction line is less than perfect. In these cases, there may be more than one reaction occurring and this may result in nonlinear behaviour or two distinct linear portions to the prediction line. In other situations, physical properties are measured, although the changes are the result of chemical reactions. More details of these phenomena are given for information in Annex B. However, despite the complex reactions involved, this equation applies very well to many complicated reactions that occur with photographic materials.

3.3 Effects of relative humidity

The Arrhenius method is run at either constant relative humidity or constant moisture content in the enclosure. It should be noted that many of the responses evaluated by the Arrhenius method are humidity dependent and that rates can change quite drastically as a function of relative humidity.[15]

The effect of moisture may be determined by several separate experiments at multiple temperatures, with each experiment at a constant relative humidity or moisture content.

4 Experimental procedures

4.1 Outline of Arrhenius test

An Arrhenius test should have the following steps that are explained in more detail in several of the references.[16,17]

a) Prepare specimens; this may include exposing, processing, cutting, trimming, etc.

b) Take initial readings of the property of interest on the non-incubated specimens.

c) Incubate the specimens at a minimum of four temperatures, using either the free-hanging or the sealed-bag technique (see 4.3).

d) Measure the property of interest on the incubated specimens after different incubation times.

e) Determine the incubation time at each incubation temperature for the property of interest to reach a predetermined level.

f) Plot the log of the incubation time determined in e) against the reciprocal of the thermodynamic temperature to obtain an Arrhenius plot.

g) Predict the time for the property of interest to change the desired amount at the desired temperature by extrapolation of the Arrhenius plot.

h) Examples of Arrhenius plots are given in Annex C.

4.2 Requirements for a meaningful Arrhenius test

Although a straight line can be drawn between two points and an Arrhenius prediction may be made by plotting the results of two different incubation temperatures, there can be no evaluation of the statistical significance of this experiment unless three or more temperatures are used. Because a smaller number of data points is apt to lead to a strongly biased prediction, a minimum of four temperatures shall be run for each prediction.

If the effect of relative humidity needs to be considered, experiments at different relative humidities shall be studied. The relative humidities shall be at least 10 % RH apart and preferably should be 20 % RH apart. The tests shall be run at a humidity range representing the anticipated storage of the material.

4.3 Sealed-bag versus free-hanging testing

Two test methods, known as the “sealed-bag” and the “free-hanging” methods, are available for accelerated stability testing. These kinds of test conditions tend to give somewhat different results.

In the sealed-bag method, the photographic material is stored in a sealed container with very little air. Pre-equilibration of the samples to a constant relative humidity is necessary before they are sealed. This test simulates real-life storage conditions in which substances released by the photographic material are trapped inside the container and can interact with the image or support layers. For example, with cellulose-acetate-base motion picture films stored in sealed bags or closed metal or plastic cans, the fading of the dye images may be accelerated by the presence of acetic acid generated by the degradation of the acetate film base.

In the free-hanging method, the specimens are suspended in a relatively large humidity-controlled test chamber at a sufficient distance from each other to ensure free access of circulating air to all surfaces. This test would be appropriate to simulate storage conditions in which photographic materials are stored in vented containers and circulating air is used to remove any released substances.

The advantages and disadvantages of each method are discussed in informative Annex A.

4.4 Effect of heating on sealed bags containing photographic film or paper

If photographic paper or film containing significant amounts of gelatin is incubated in a sealed foil bag, the relative humidity (RH) of the environment will increase with increasing temperature, even though the moisture content of the overall system remains constant. In some systems, this increase of humidity can also cause physical changes such as the transformation of the gelatin conformation to the above T_g state (see 2.3).

Experimental evidence has shown that this increase of relative humidity results in more staining on paper and, in some cases, more dye fading in colour photographs. For example, if a processed black-and-white paper is incubated in the free-hanging mode, thermal yellowing will be considerably less than if it is incubated in a sealed foil bag. Thus, in order to establish the same environmental conditions for both the sealed bag and free-hanging test methods, one shall choose pre-equilibration RH levels for the bagged samples which compensate for the RH increase that occurs at the elevated test temperature.

The amount of RH compensation required may be sample dependent, since different materials can have different moisture-sinking properties.[15] From a practical standpoint, the determination of correct RH values for sealed-bag incubations may require a few trial runs where RH measurements are taken inside bags containing representative materials prior to commencement of the actual tests.

4.5 Determination of test increments

If the free-hanging method is used, time increments of treatment can be accumulated upon the same samples and they can be returned to the oven until the failure point has been reached. However, foil-bag testing requires that the increments be determined in advance, since all the bags are pre-equilibrated and prepared at the same time.

It is strongly recommended that the initial increments for foil-bag testing be somewhat conservative so as not to overshoot the failure point, and that subsequent increments be adjusted once data have been obtained on the first few increments. Adjusting the schedule in this way increases the probability that the failure point is neither underreached nor overreached.

5 Calculations

Figure 1 illustrates the dye density loss of a generic yellow dye, at a starting optical density of 1,0, incubated at 40 % RH. The top plot shows the rate of fade curves for each incubation temperature. The time at which a 10 % loss of density occurs is translated down to the lower plot where the log of this time is plotted versus the reciprocal of the temperature for that particular incubation. The prediction line connecting these latter data points is then extrapolated to the desired keeping temperature to determine the length of time required for the 10 % blue density loss to occur. In this example, it is approximately 30 years at 24 °C.[9]

6 Test report

The following shall be reported:

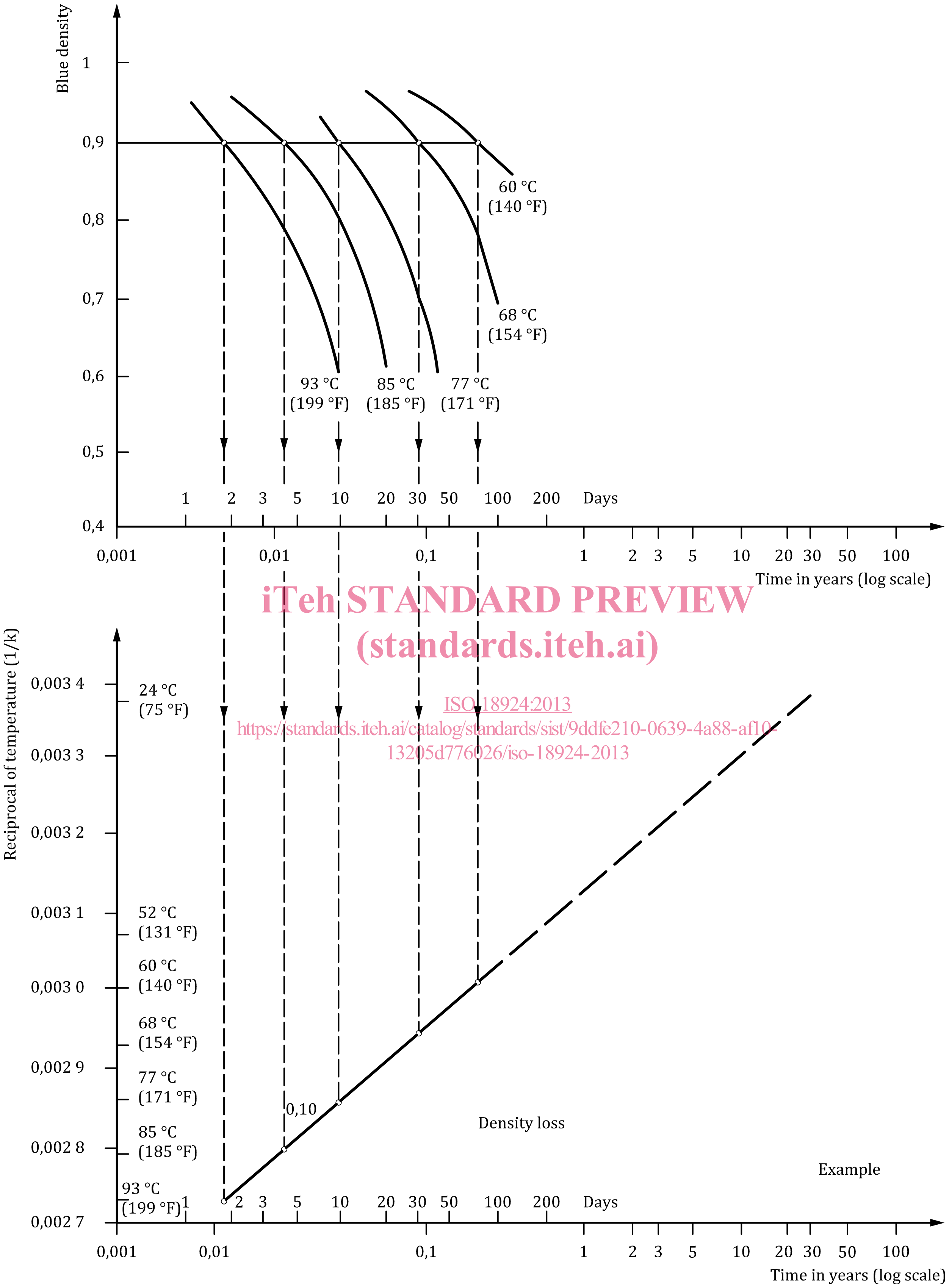
a) property being measured, along with its starting value (e.g. colour of the patch, dye density loss, density 1,0 above $D_{\min}$, etc.);

b) percent of property change which determines the end-point;

c) whether the incubation was free hanging or was in a sealed container (foil bag, film can, etc.);

d) range of temperatures and the specific RHs at which the test was run;

e) extrapolated time for the end-point to occur at a specified temperature and relative humidity.


Blue density
1
0,9
0,8
0,7
0,6
0,5
0,4
60 °C
(140 °F)
68 °C
(154 °F)
93 °C
(199 °F)
85 °C
(185 °F)
77 °C
(171 °F)
1
2
3
5
10
20
30
50
100
200
Days
0,001
0,01
0,1
1
2
3
5
10
20
30
50
100
Time in years (log scale)
Reciprocal of temperature (1/k)
0,003 4
0,003 3
0,003 2
0,003 1
0,003 0
0,002 9
0,002 8
0,002 7
24 °C
(75 °F)
52 °C
(131 °F)
60 °C
(140 °F)
68 °C
(154 °F)
77 °C
(171 °F)
85 °C
(185 °F)
93 °C
(199 °F)
0,10
Density loss
Example
1
2
3
5
10
20
30
50
100
200
Days
0,001
0,01
0,1
1
2
3
5
10
20
30
50
100
Time in years (log scale)

X time, in years (log scale)

Y blue density

Y′ reciprocal of temperature (1/k)

NOTE See Reference[9].

Figure 1 — Illustration of a prediction method (blue density change for 1,0 yellow dye)