
Imaging materials — Test method for Arrhenius-type predictions

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

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ISO copyright office
Case postale 56 • CH-1211 Geneva 20
Tel. + 41 22 749 01 11
Fax + 41 22 749 09 47
E-mail copyright@iso.org
Web www.iso.org

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

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.

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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 ($-273,15\text{ }^{\circ}\text{C}$) 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:

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

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:

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

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.