
**Plastics — Thermogravimetry (TG) of
polymers —**

Part 3:

**Determination of the activation
energy using the Ozawa-Friedman plot
and analysis of the reaction kinetics**

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Plastiques — Thermogravimétrie (TG) des polymères —

*Partie 3: Détermination de l'énergie d'activation à l'aide du
graphique d'Ozawa-Friedman et analyse cinétique de la réaction*

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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.

The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

For an explanation on the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the WTO principles in the Technical Barriers to Trade (TBT) see the following URL: Foreword - Supplementary information

The committee responsible for this document is ISO/TC 61, *Plastics*, Subcommittee SC 5, *Physical-chemical properties*.

ISO 11358 consists of the following parts, under the general title *Plastics — Thermogravimetry (TG) of polymers*:

- *Part 1: General principles*
- *Part 2: Determination of activation energy*
- *Part 3: Determination of the activation energy using the Ozawa-Friedman plot and the reaction kinetic analysis*

Introduction

Controlled rate thermogravimetry (CRTG) is used to study the decomposition of polymers. The Ozawa-Friedman method is typically applied to the analysis of data obtained by CRTG and also to that obtained by the combined use of isothermal thermogravimetry (iso-TG) with conventional linear heating rate thermogravimetry (LHTG), i.e. using a constant heating rate.

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Plastics — Thermogravimetry (TG) of polymers —

Part 3:

Determination of the activation energy using the Ozawa-Friedman plot and analysis of the reaction kinetics

1 Scope

This International Standard specifies an analysis method for determining the activation energy using the Ozawa-Friedman plot. It also specifies the preparation of master plots for verification of the reaction kinetics determined by thermogravimetry.

The Ozawa-Friedman plot (logarithm of the rate of mass loss versus the reciprocal of absolute temperature at a given mass loss) is a derivative method that can be applied to data obtained by any mode of temperature change in thermal analysis; e.g. isothermal, constant heating rate, sample-controlled thermal analysis, temperature jump, and repeated temperature scanning.

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 11358-1, *Plastics — Thermogravimetry (TG) of polymers — Part 1: General principles*

ISO 11358-2, *Plastics — Thermogravimetry (TG) of polymers — Part 2: Determination of activation energy*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 11358-1, ISO 11358-2 and the following apply.

3.1 conversion

$$C = (m_t - m_i) / (m_f - m_i)$$

where

m_i is the initial quantity, in mg;

m_t is the quantity at a particular time and temperature, in mg;

m_f is the final quantity, in mg.

See ISO 11358-1 and ISO 11358-2.

Note 1 to entry: It is also referred to as the mass loss fraction.

**3.2
generalized time**

$$t_{\text{gen}} = \int_0^t \exp\left(-\frac{E_a}{RT}\right) dt$$

where

- E_a is the activation energy, expressed in kJ/mol;
- R is the gas constant, expressed as 8.314 J/(mol K);
- T is the absolute temperature, expressed in Kelvin;
- t is time, expressed in minutes.

**3.3
generalized rate of conversion**

$$\frac{dC}{dt_{\text{gen}}} = \exp\left(\frac{E_a}{RT}\right) \frac{dC}{dt}$$

**3.4
master curve**

plot that can be used to evaluate the results and investigate the reaction kinetics models

Note 1 to entry: Examples of master curves are conversion versus the generalized time, conversion versus the generalized rate of conversion, generalized time versus the generalized rate of conversion.

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4 Principle

Test specimens are heated using any temperature profile and the change in mass is measured as a function of temperature and time. At a given conversion, the logarithm of the rate of conversion is plotted versus the reciprocal of the absolute temperature, and the activation energy is calculated from the slope of the straight line fit to the data thus obtained.

At least two of the master curves enable verification of the reaction kinetics analysis.

5 Apparatus

The apparatus shall be in accordance with ISO 11358-1.

6 Test specimens

Test specimens shall be in the form of powder, pellets, flakes, filaments, or film. The test specimens shall be prepared by cutting the material, as necessary, to a size appropriate for the apparatus (see ISO 11358-1).

7 Mass and temperature calibration

7.1 Mass calibration

The procedure of mass calibration is given in ISO 11358-1.

7.2 Temperature calibration

The procedure of temperature calibration is given in ISO 11358-1.

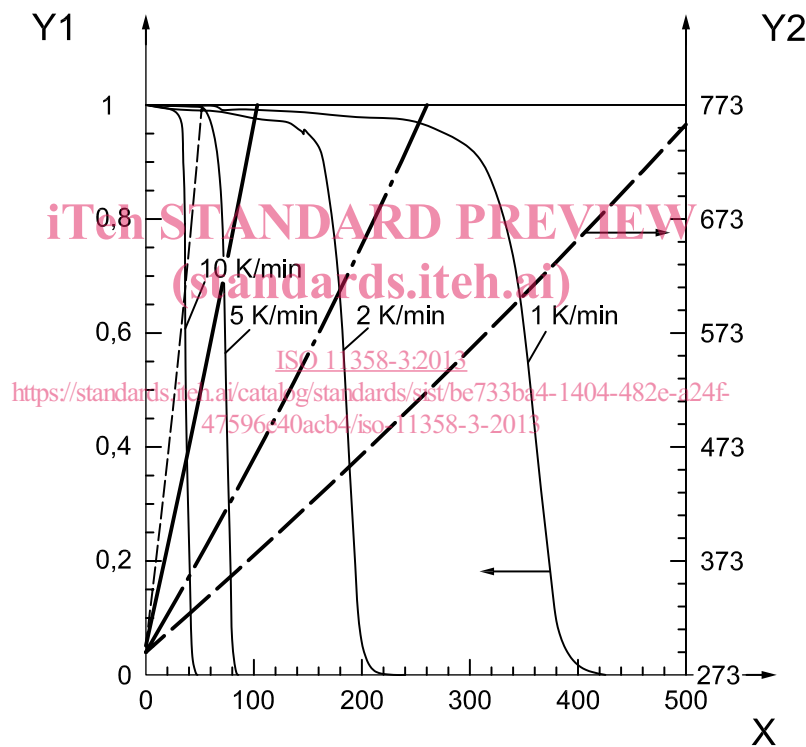
8 Procedure

8.1 General

The determination of the rate of conversion dC/dt is necessary for the analysis in this International Standard. The rate of conversion versus absolute temperature shall be determined.

See ISO 11358-1 and ISO 11358-2.

Perform tests using either an isothermal run, constant rate heating and cooling, sample mass controlled rate thermal analysis, temperature jump, repeated temperature scanning, or any combination of the above, using specimens of similar mass ($\pm 1\%$). For examples of linear heating rate thermogravimetry (LHTG) and sample mass controlled rate thermogravimetry (CRTG), see [Figures 1a](#) and [1b](#), respectively.



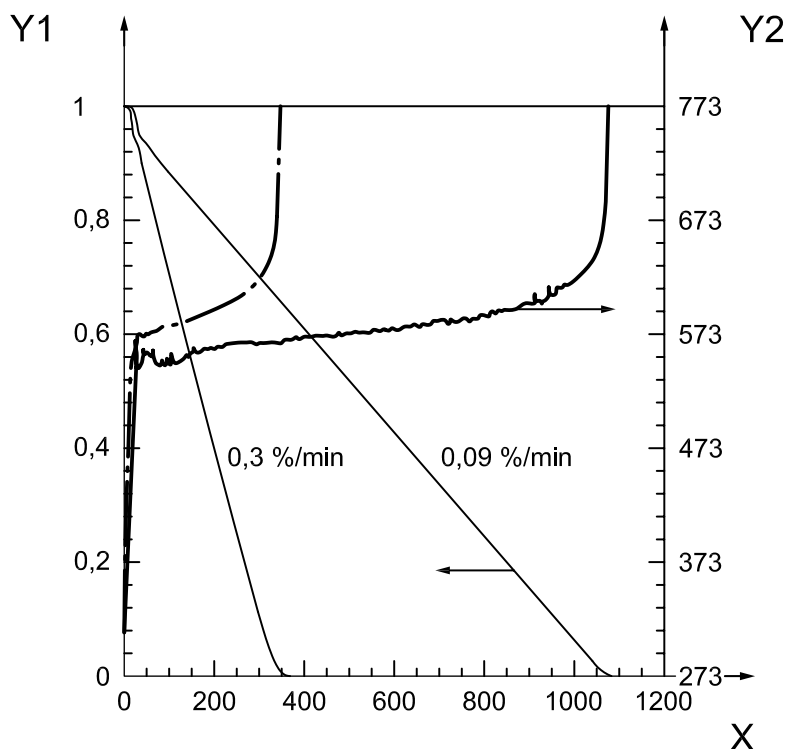
Key

X t/min

Y1 $(1 - C)$

Y2 T/K

Figure 1a — Example of linear heating rate thermogravimetry (LHTG) measurements of PMMA



Key
 X t/min
 Y1 $(1 - C)$
 Y2 T/K

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NOTE The units of %/min indicate the percentage weight loss per minute of the mass controlled rate.

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Figure 1b — Example of sample mass controlled rate thermogravimetry (CRTG) measurements of PMMA

Preferably, the specimen mass should be between 1 mg and 10 mg and the temperature scanning rate between 2 K min^{-1} and 10 K min^{-1} .

Determine the rate of conversion (or rate of change of mass loss fraction with time) at a given conversion (or given mass loss fraction).

8.2 Non-oxidative reactions

The procedure of non-oxidative reactions is given in ISO 11358-2.

8.3 Oxidative reactions

The procedure of oxidative reactions is given in ISO 11358-2.

9 Expression of results

9.1 Graphical presentation

For a given conversion (or mass loss fraction), present the thermogravimetry data in the form of a plot of the logarithm of the rate of conversion (or rate of change of mass loss fraction with time) versus the reciprocal of the absolute temperature, i.e. the Ozawa-Friedman plot, see [Figure 2](#).

9.2 Determination of activation energy

The conversion (or the mass loss fraction) is not directly related to the quantity of reacted pieces, for example as in the random scission of the main chain of polymers. Generally, the rate formulae are as follows:

$$C = f(\alpha) \quad (1)$$

and

$$\frac{d\alpha}{dt} = A \exp\left(\frac{-E_a}{RT}\right) g(\alpha) \quad (2)$$

where

α is the reacted fraction at time t ;

$f(\alpha)$ is an arbitrary function;

A is the pre-exponential factor;

$g(\alpha)$ is a function describing the reaction mechanism.

By taking the logarithm of both sides of Formula (2) then

$$\ln\left(\frac{d\alpha}{dt}\right) = \ln\{Ag(\alpha)\} - \frac{E_a}{RT} \quad (3)$$

When plotted for fixed values of α , with various conversion rate values determined for different experimental temperature control profiles, the slope of the plot of $\ln\left(\frac{d\alpha}{dt}\right)$ versus $\frac{1}{T}$ has the value $-E_a/R$ and is used to determine the activation energy E_a , as the first term in the right side of Formula (3) is constant.

As an example, the experimental data presented in [Figures 1a](#) and [1b](#) have been analysed, assuming an n^{th} order type reaction and thus $C = f(\alpha) = \alpha$ ([Annex A](#)), the results of which are presented in [Table 1](#) and [Figure 2](#).

Table 1 — The rate of conversion dC/dt and the estimated activation energy E_a at different conversion levels, determined from the controlled rate thermogravimetry (CRTG) data presented in [Figure 1b](#)

	1000/T (K ⁻¹)	ln(dC/dt (% min ⁻¹)) at C = 0,2	1000/T (K ⁻¹)	ln(dC/dt (% min ⁻¹)) at C = 0,5	1000/T (K ⁻¹)	ln(dC/dt (% min ⁻¹)) at C = 0,8
CRTG, 0,09 %/min	1,779	-2,425	1,735	-2,411	1,677	-2,448
CRTG, 0,3 %/min	1,731	-1,161	1,693	-1,183	1,641	-1,288
Activation Energy (kJmol ⁻¹)						
Ozawa-Friedman plot		207,3	232,8		261,9	