INTERNATIONAL STANDARD

ISO 11409

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Plastics — Phenolic resins — Determination of heats and temperatures of reaction by differential scanning calorimetry

Plastiques — Résines phénoliques — Détermination des chaleurs et températures de réaction par calorimétrie différentielle à balayage

Reference number
ISO 11409:1993(E)

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.

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.

International Standard ISO 11409 was prepared by Technical Committee ISO/TC 61, *Plastics*, Sub-Committee SC 12, *Thermosetting materials*.

Later, this International Standard will become part of a general standard concerning differential scanning calorimetry.

Annex A of this International Standard is for information only.

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Plastics — Phenolic resins — Determination of heats and temperatures of reaction by differential scanning calorimetry

1 Scope

1.1 This International Standard specifies a method for the determination of heats and temperatures of reaction of phenolic resins by differential scanning calorimetry.

1.2 The method is applicable to phenolic resins with exothermic behaviour, such as resols or mixtures of novolaks with hexamethylenetetramine or other curing agents.

1.3 The method is useful for the characterization of products and for research.

2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this International Standard. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent editions of the standards indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 472:1988, *Plastics — Vocabulary.*

ISO 5725:1986, *Precision of test methods — Determination of repeatability and reproducibility for a standard test method by inter-laboratory tests.*

ISO 10082:1991, *Plastics — Phenolic resins — Definitions and test methods.*

3 Definitions

For the purposes of this International Standard, the following definitions apply.

3.1 differential scanning calorimetry (DSC): A technique whereby the difference in energy absorbed or released by a polymer and by a reference material is measured as a function of temperature and/or time while the polymer and the reference are subjected to the same temperature schedule.

3.2 phenolic resin: Generally, a class of resins made by polycondensation of phenol, its homologues and/or derivatives, with aldehydes or ketones. [ISO 472]

3.3 novolaks: Non-self-curing, soluble, fusible phenolic resins that remain stable when stored, the phenol nuclei of which are linked primarily by methylene bridges. Novolaks can be made to react further and crosslink by the addition of hardeners; heating is also usually necessary. [ISO 10082]

See also *novolak* in ISO 472.

3.4 resols: Soluble, fusible phenolic resins which, in contrast to novolaks, contain methylol groups and methylene-ether and sometimes also methylene-amine bridges. Resols are self-curing; they crosslink into insoluble products when heated and/or mixed with catalysts, without addition of further reaction components. Resols are perishable and can be stored for a limited time only. [ISO 10082]

See also *resol* in ISO 472.

NOTE 1 In this document, the term "heat" and "heat of reaction" used throughout the text are equivalent to the terms "enthalpy" and "enthalpy of reaction".

4 Test method

4.1 Principle

The heat flux (power) supplied to a test sample is measured as a function of time or temperature, while the test sample is subjected to a temperature schedule under a specified atmosphere.

In practice, what is measured is the difference between the heat flux supplied to a sample holder containing the test sample and the heat flux supplied to a reference holder.

A reaction is marked by the release of energy from the sample, resulting in an exothermic peak in the heating curve. Integration of the recorded peak area as a function of time gives a measure of the energy of the reaction. Observing the position of the reaction on the temperature axis provides the necessary temperature information.

4.2 Materials

4.2.1 Indium, for calibration of the apparatus (see 4.5.1).

4.3 Apparatus

4.3.1 Differential scanning calorimeter, having the following characteristics:

a) heating or cooling rate of up to 10 °C/min;

b) automatic recording of differential heat flow between the sample and reference material;

c) sensitivity for measurement of heat flux or energy difference such that a precision of ± 1 % is ensured;

d) time-base precision of ± 1 % over the time-base range from 0,1 min/cm to 2,0 min/cm (10,0 cm/min to 0,5 cm/min) on the chart;

e) temperature sensitivity such that the sample temperature is readable to at least ± 0,1 °C;

f) operating range preferably from 20 °C to 300 °C.

4.3.2 Area-measurement device, with an accuracy of ± 0,1 %.

4.3.3 Pressure-tight sample holders, inert to the test material, of high thermal conductivity, for example steel capsules, pressure-tight to at least 2 MPa[1] (see recommended design in figure 1).

NOTE 2 If a differential scanning calorimeter with a high-pressure calorimeter cell is used, normal sample holders should be used.

4.3.4 Analytical balance, preferably accurate to 0,01 mg.

4.4 Preparation of test samples

4.4.1 Since small quantities of materials are used, it is essential that test samples be representative of the material.

4.4.2 Prepare test samples of powdered or granular resins by removing portions from various parts of the batch. Mix these thoroughly to ensure a representative test sample for the determination. Grind coarse granular materials with a device that does not generate heat to reduce the grain size and give a more uniform mixture. If not already present in the resin, add the required amount of hexamethylenetetramine before grinding.

4.4.3 Unless otherwise specified, analyse samples as received. If the sample is heated prior to analysis, note this in the test report. Record any loss in mass as a result of the heat treatment.

4.5 Procedure

Resins release volatile matter on heating. Therefore phenolic resins must be analysed in hermetically sealed pressure-tight sample holders.

4.5.1 Calibration

Carry out the calibration of the apparatus with respect to heat flux or energy difference, time base and heat axis following the apparatus manufacturer's instructions, using either an electrical method or a reference material, on each side of the reaction temperature.

Reference material	Melting point (°C)	Heat of fusion (J/g)
Indium	156,6	28,42 ± 0,36

See annex A, references [1] and [2].

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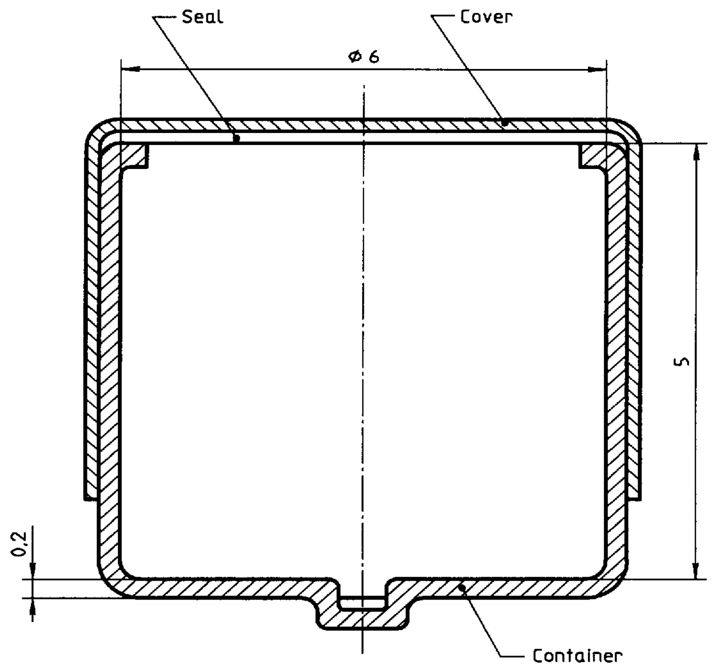
[1] 2 MPa = 20 bar

Dimensions in millimetres



Sample container made of steel

- — useful sample volume 140 µl
- — max. internal pressure 2 MPa
- — suitable seal
- — seal with pressure tools
- — sample container not to be re-used

Figure 1 — Recommended design of sample holder

4.5.2 Determination

4.5.2.1 Select the appropriate heat-flow-axis sensitivity on the recorder to yield a 25 % to 95 % deflection on the recorder.

NOTE 3 A preliminary run using a similar specimen may be made to provide this information.

4.5.2.2 If a recorder is used, select the appropriate scales for time and temperature on the recorder to yield an area of 30 cm^2 to 60 cm^2.

4.5.2.3 Start at a temperature at least 30 °C below the beginning of the reaction.

4.5.2.4 Into a clean sample holder (4.3.3), weigh 10 mg ± 2 mg of sample to an accuracy of 0,05 mg using the balance (4.3.4).

4.5.2.5 Seal the sample holder so that it is pressure-tight.

4.5.2.6 Place the sample holder in the calorimeter (4.3.1). If specified by the manufacturer of the instrument, purge both chambers with purge gas at the rate recommended. Typical rates are in the range 10 ml/min to 50 ml/min.

4.5.2.7 Heat the test sample preferably at 5 °C ± 1 °C per minute. Other heating rates may be used, but shall be noted in the test report. Record the thermal curve which results. Reweigh the test sample on completion of scanning. Discard the results if the mass loss exceeds 10 % of the original mass of the test sample (see 4.5.2.4).

4.5.2.8 Carry out determinations on at least two test

4.5.3.1.2 Measure the area under the curve three

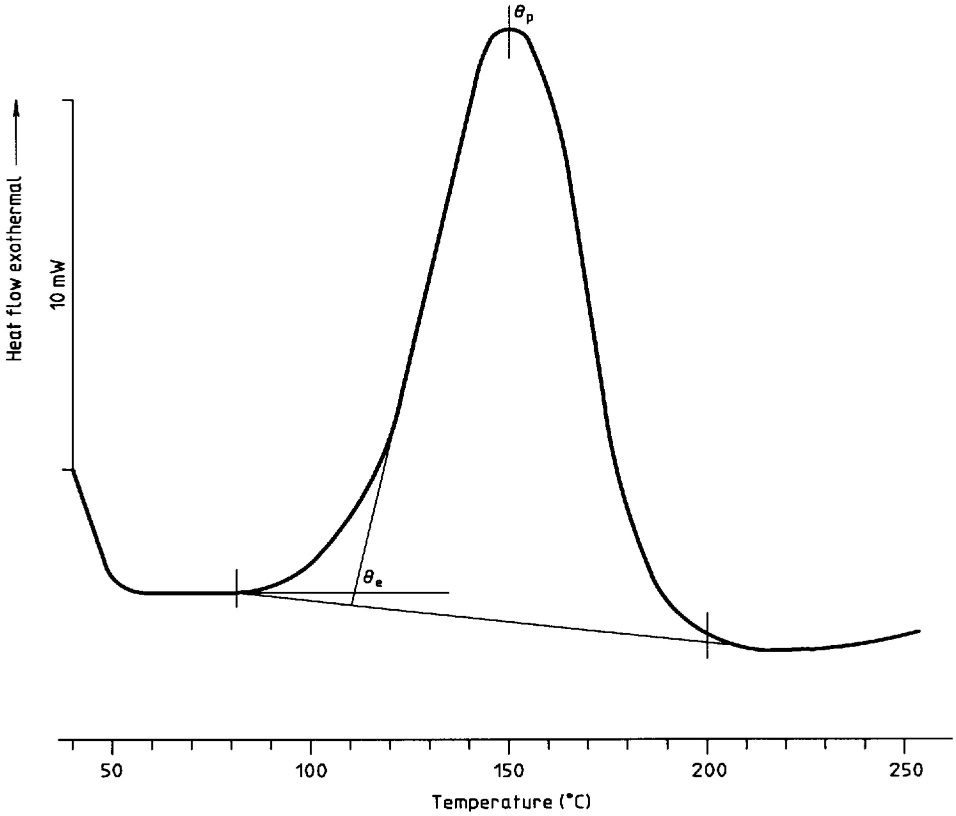


Figure 3 — Baseline construction and reaction temperatures for a phenolic resol

4.5.3.1.3 Calculate the heat of reaction (enthalpy of curing) Δh_R, expressed in joules per gram, using the equation

$$\Delta h_R = \frac{AB\phi}{m} \times \frac{\Delta h_S m_S}{A_S B_S \phi_S}$$

where

Δh_S is the heat of fusion (or crystallization) of the reference material, in joules per gram;

A is the peak area under the sample curve, in square centimetres;

A_S is the peak area under the reference-material curve, in square centimetres;

B is the time scale used for the sample, in minutes per centimetre;

B_S is the time scale used for the reference material, in minutes per centimetre;

m is the mass of the test sample, in milligrams;

m_S is the mass of reference material used to calibrate the calorimeter;

ϕ is the heat-flow-axis sensitivity used for the sample, in milliwatts per centimetre;

ϕ_S is the heat-flow-axis sensitivity used for the reference material, in milliwatts per centimetre.

4.5.3.2 Calculation of transition temperatures

From the temperature-based curve, calculate the transition temperatures θ_e, θ_p (see figures 2 and 3)

where

θ_e is the temperature, obtained by extrapolation, of the onset of fusion or reaction, in degrees Celsius;

θ_p is the peak fusion or reaction temperature, in degrees Celsius.

Report two values of θ_p if observed.

NOTE 4 The actual temperature on the temperature axis will differ depending upon instrument type. It may, for example, be the sample temperature, the programmed temperature or the average of the sample temperature and the programmed temperature.

Follow the manufacturer's instructions for the particular instrument used to obtain the sample temperature at the point of interest.

4.5.3.3 Average values

Report results as average values obtained on at least two test samples.

4.5.3.4 Precision for determination of Δh_R (ISO 5725:1986, subclause 14.10)

Round-robin test involving 10 laboratories:

a) novolak + hexamethylenetetramine

  repeatability: ± 5 %

  reproducibility: ± 10 %

b) liquid resol

  repeatability: ± 5 %

  reproducibility: ± 15 %

4.5.4 Test report

The test report shall include the following information:

a) a reference to this International Standard;

b) all details necessary for the identification of the resin;

c) a description of the instrument used for the test;

d) the dimensions and design of the sample holder, if other than specified in figure 1, and the material of which it is made;

e) the heating rate, if other than 5 °C/min;

f) a description of the temperature-calibration and heat-calibration procedure;

g) the form of the sample, the method of preparation and any pretreatment carried out;

h) the method used to integrate the area under each curve;

i) the heats of reaction Δh_R, in joules per gram;

j) the temperatures θ_e and θ_p, or any other parameters relating to the shape of the curve, as appropriate.

k) the percentage loss in mass of the sample;

l) a copy of the thermogram obtained;

m) the date of the test.

Annex A
(informative)

Bibliography

[1] ROSSINI, F.D., *Pure and Applied Chemistry,* Volume 22, 1970, page 557.

[2] HULTGREEN, R.R. *et al., Selected Values of Thermodynamic Properties of the Elements,* John Wiley & Sons, New York, 1973.

[3] IEC 1074:1991, *Determination of heats and temperatures of melting and crystallization of electric insulating materials by differential scanning calorimetry.*

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Descriptors: plastics, thermosetting resins, phenoplasts, chemical reactions, tests, determination, heat, temperature, calorimetry.

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