

Guidelines for application of analytical test methods for thermal endurance testing of electrical insulating materials

Committees responsible for this British Standard

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National foreword

This British Standard has been prepared by Technical Committee GEL/15. It is identical with IEC 1026:1991, *Guidelines for application of analytical test methods for thermal endurance testing of electrical insulating materials*, published by the International Electrotechnical Commission (IEC).

Cross-references

Publication referred to	Corresponding British Standard
IEC 216 (series)	BS 5691 (series) <i>Guide for the determination of thermal endurance properties of electrical insulating materials</i>

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Summary of pages

This document comprises a front cover, an inside front cover, pages i and ii, pages 1 to 22, an inside back cover and a back cover.

This standard has been updated (see copyright date) and may have had amendments incorporated. This will be indicated in the amendment table on the inside front cover.

Introduction

Analytical methods have been applied to investigations of ageing processes in electrical insulating materials and to the measurement of ageing reaction rates for more than 25 years. The reference list attached to this report is limited to investigations where sensitive analytical methods have been applied for reaction rate measurements down to the application temperature range of materials.

The first investigators [1,2]¹⁾ used gas chromatography or mass spectrometry as analytical methods in a way from which procedure A of this report could be developed, together with several later published results [5, 7, 10, 11].

Later investigators used a new analytical instrument, the isothermal differential calorimeter [4], which, together with theoretical developments [9] and other publications [6, 12, 13, 14] is the basis of procedures B and C of this report.

Other investigators have concentrated on the use of rapid analytical techniques (such as thermogravimetric analysis TGA and differential thermoanalysis DTA), and on the derivation of an estimate of thermal endurance solely on the basis of these measurements. While these methods may be valuable tools when developing new polymers or selecting materials for long-term thermal endurance testing, they do not belong to the scope of this report, since these methods lead to extrapolation of test results over a large temperature span, which may lead to erroneous conclusions.

There is thus sufficient knowledge gathered in this field to prepare detailed procedures to be published as an IEC Report, in order to pave the way for the later standardization of the method. This report is also intended to stimulate further work on the application of analytical methods for thermal endurance testing of insulating materials.

This report is based on the following principles:

- 1) The analytical methods used must be sensitive enough to enable measurements of ageing reaction rates down to the application temperatures of the materials.
- 2) Several analytical methods have been shown to be suitable for reaction rate measurements and to produce similar information about reaction rates. Therefore, the test procedures allow the use of several analytical methods.
- 3) Measurements of the ageing reaction rates serve the purpose of determining the rate of the ageing process (or of separate reactions), producing information e.g. about the slope of the thermal endurance graph.
- 4) Reaction rate values alone cannot be used to totally describe the thermal endurance of materials. They must be combined with ageing tests of the conventional type to produce actual thermal endurance values in the same form as IEC Publication 216.
- 5) The goal of analytical reaction rate measurements is to ensure the same physicochemical ageing mechanism in the conventional ageing tests as at application temperatures, but at a much higher rate.
- 6) There are materials with ageing processes of different complexity. The test procedures should be either universal (applicable to any material) or also of different complexity.

When test procedures which are described in this report are compared with the presently standardized conventional thermal endurance test methods specified in IEC Publication 216, the following differences may be revealed:

- test procedures in this report produce experimental data down to the application temperature range of materials, eliminating the need for extrapolation;
- the total testing time will be shorter since fewer conventional ageing tests with a shorter duration are needed, and the analytical procedures themselves require little time;
- actual service conditions can be accurately simulated, especially regarding the ageing due to atmospheric humidity and oxidation.

Following the principles 1) to 6) described above, three test procedures of increasing complexity are described in this report. These procedures may be found extremely useful in establishing some basic parameters of materials, additional to those obtained through using IEC Publication 216.

Throughout this report the terminology and concepts presented in IEC Publication 216 are used.

¹⁾ Numbers in square brackets refer to Appendix B — References.

Section 1. General aspects

1 Scope and object

This report describes test procedures for evaluation of the thermal endurance of electrical insulating materials, based on the combined use of sensitive analytical methods for the determination of test acceleration and of conventional ageing tests. It describes the conditions to be observed in the test procedures and shows how characteristics corresponding to temperature index (TI) and halving interval (HIC) of IEC Publication 216 are derived from the test results.

2 General principles

2.1 Description of test procedures

Thermal ageing of insulating materials is mainly composed of chemical reactions, which progressively cause changes in the physical properties of the material and in the end affect its functionality. The chemical composition (as a result of deterioration due to the thermal ageing reactions) and the value of any physical property of the material are therefore closely correlated.

It is thus possible to provide means of estimating the long term performance of materials through suitable measurements of ageing reaction rates (which describe the speed of degradation) combined with ageing tests of conventional type.

Since the correlation given above may be of variable complexity, three test procedures (A, B and C) are presented in this guide, taking into account the increasing complexity of the ageing process.

In procedure A, the thermal ageing process is treated as one reaction, assuming that one ageing reaction dominates the ageing process. In this case the time to end-point in a conventional ageing test is inversely proportional to the ageing reaction rate at the ageing temperature. The inverse values of reaction rates as function of temperature can therefore be used to describe the thermal endurance graph, if the curve is fixed so that it contains a point determined from an actual conventional ageing test result. Based on this constructed thermal endurance graph, values of the thermal endurance characteristics corresponding to temperature index TI and halving interval HIC (see IEC Publication 216) can be obtained.

In procedures B and C, three ageing reactions are assumed to be important: thermal degradation proceeding in an inert atmosphere, oxidation and hydrolysis (or at least two of these reactions). It is assumed that if there is more than one reaction of the same kind (e.g. several oxidative reactions), then one reaction dominates that reaction group (e.g. one oxidative reaction dominates the oxidative reactions). The main principle is to select the ageing conditions so as to accelerate all the three principal reactions by equal amounts, in order to simulate the real ageing process occurring at a lower temperature as closely as possible. This is accomplished in two steps.

Firstly, through reaction rate measurements the acceleration of each of the three reactions is determined (at constant conditions). Secondly, conventional ageing tests are performed using such concentrations of oxygen and water vapour that the equalizing of the process is achieved. This method of testing is also known as the EAP method (equalized ageing process). In procedure B, all the ageing reactions are assumed to be essentially independent and homogeneous (i.e. to proceed identically everywhere in the test material). From the test results the thermal endurance characteristics as in procedure A can be calculated.

If one of the ageing reactions is diffusion-controlled, it can no longer be treated as being independent of the dimensions of the material (mainly thickness). Procedure C gives instructions for handling such a case.

2.2 Selection of test procedures

Depending on the degree of complexity of the material to be tested and the instrumentation at hand, an appropriate test procedure and analytical method should be selected. The basic assumptions presented for each procedure (Sub-clauses 4.1, 9.1 and 15.1) have to be fulfilled.

3 Analytical methods for reaction rate measurements

3.1 General requirements

In this publication, only such features of analytical methods which are important for the reaction rate measurements are dealt with. The precise nature of the instrumentation that is required is dependent on the analytical methods that are chosen.

There are numerous methods suitable for measurements of ageing reaction rates of electrical insulating materials. Most important requirements for an analytical method are as follows:

- *sensitivity* of the method shall be high enough to enable reproducible measurements to be made at the application temperature range of the material or at the expected TI temperature. Different methods may be applied for different reactions, when appropriate;

- *selectivity* required of the method depends on the procedure used. In procedure A, either the “total” reaction rate or the rate of the strongest reaction is measured, so the selectivity is not very critical.

In procedures B and C, a clear differentiation between the three principal reactions shall be made. With regard to the thermal degradation reaction, this separation may not be directly possible. In such case, a suitable differential technique can be applied (see e.g. Sub-clause 3.5);

- *duration of the measurements* shall be short enough for the results to be obtained in a reasonable time. It is recognized that due to the high sensitivity required the time needed may be in the order of weeks, at the lowest temperature even up to 1 000 h.

It is essential that thermal ageing of the test material be as small as possible during the measurements. See Sub-clause 10.3;

- *stabilized output*. The measurement or sample collection time at each test temperature shall be long enough to allow the reaction rate being measured to stabilize. The stabilization time may depend on the thickness and material of the test specimens.

3.2 Gas chromatography and mass spectrometry

The use of gas chromatography (GC) or mass spectrometry (MS) is based on the fact that, as a consequence of thermal ageing reactions, gaseous reaction products are evolved. In numerous published investigations [10, etc.] the term “Evolved Gas Analysis” (EGA) has been used in this connection. Through appropriate means the reaction products are collected and quantitatively analysed.

In both methods the reaction rate is measured as the rate of evolution of some gaseous reaction product (often CO and CO₂).

Two different procedures are possible: periodical and continuous.

Periodical procedure

During a short heat exposure at the test temperature the test specimen is kept in a hermetically closed container. After this period a sample of the gas atmosphere from this container is analyzed, using GC or MS or a combination thereof.

Continuous procedure

During a short heat exposure a slow gas flow is fed through the specimen container. From time to time, samples collected at the outlet of the container are analyzed, using GC or MS or a combination thereof.

For application of procedure B or C, the different reaction rates may be measured either simultaneously or separately.

Simultaneous measurement is only possible if a characteristic reaction product for each reaction in question can be found. Separate measurements are made by performing short exposures to heat in different gas compositions: inert atmosphere for thermal degradation reaction, oxygen-containing atmosphere for oxidation and water-vapour-containing atmosphere for hydrolysis. For the latter two, the respective evolution rates in inert gas have to be subtracted from the measured values to obtain the reaction rate in question. See also Sub-clause 3.5.

NOTE Gas chromatography (GC) or mass spectrometry (MS) have mostly been used in published investigations on which procedure A is based [1, 2, 5, 7, 10, 11 and 14].

3.3 Isothermal differential calorimetry

Isothermal differential calorimetry (IDC) is based on sensitive heat flow measurements, utilizing the proportionality between reaction rate and reaction heat flow from the test specimen in isothermal conditions [4]. The unit for reaction rate is thus microwatts per gram of test material (μW/g). Sensitivity of 0.01 μW/g enables reaction rate measurements of most materials down to TI temperatures. A large test specimen with a mass of 5 g to 100 g is needed, to achieve the high sensitivity, if the heat flow measuring sensitivity is in the order of 1 μW. In the present situation, the commercial DSC instruments (differential scanning calorimeter) and alike, while measuring the same entities, do not have the sensitivity needed.

In IDC, the total reaction heat flow from the specimen is always measured, which can directly be used in procedure A. For procedures B and C, the separation of different reaction rates is possible using the differential techniques described in Sub-clause 3.5.

NOTE IDC has mostly been used in published investigations on which procedures B and C are based [4, 6, 9, 12, 14].

3.4 Other methods

Procedures A, B and C may be applied using any analytical method which fulfils the basic requirements given in Sub-clause 3.1.

Isothermal thermogravimetry [14] or liquid chromatography [8] have been applied. However, experience at the present time is limited.

3.5 Separation of reactions by the difference method

Often two thermal ageing reactions cannot be distinguished using a direct measurement. This happens with GC or MS, when a characteristic reaction product for every important reaction cannot be found. When IDC is used, the thermal degradation reaction (see Sub-clause 2.1) is always present when the rates of oxidation or hydrolysis are to be determined.

One of the following difference methods may be useful when determining the individual reaction rates. The rate of the thermal degradation reaction is denoted R_{inert} and the rate of a reaction produced by an active gas is denoted R_{act} .

I. Two sufficiently strong reactions

Measure the reaction rate R_1 in a suitable inert gas. Change the atmosphere to the gas mixture containing the prescribed concentration of the active gas and read the reaction rate R_2 . Then

$$R_{\text{inert}} = R_1$$

$$R_{\text{act}} = R_2 - R_1$$

II. Weak reaction due to the active gas

Let temperature and reaction rate stabilize first using inert gas flow and read off the reaction rate (R_1). Change the gas flow to contain a known amount of active gas, then let the output stabilize again and take the reading (R_2). Change the gas flow back to the inert gas and take the reading (R_3) after stabilization of the output. The readings R_1 and R_3 should be near to each other. Calculate the reaction rates:

$$R_{\text{inert}} = (R_1 + R_3)/2$$

$$R_{\text{act}} = R_2 - R_{\text{inert}}$$

NOTE When changing to the active gas, often a strong peak in the heat flow (when IDC is used) appears before stabilization to a lower level. By hydrolysis reaction it is caused by the condensation heat of water entering the material during stabilization.

3.6 Stabilization of test specimens

Test specimens for reaction rate measurements should be stabilized before the measurements.

Stabilization is made by a suitable heat treatment, to drive off volatiles, to complete the post hardening reactions, etc. Often, 48 h at the expected TI temperature is sufficient.

Section 2. Test procedure A, Single reaction case

4 Range of application for procedure A

4.1 Basic assumptions

Procedure A can be used in thermal endurance testing, if the following two conditions are fulfilled:

- 1) One ageing reaction is known to be dominant in the ageing process in the temperature range in question (from the TI temperature to the highest conventional ageing test temperature). This knowledge may be based on previous ageing and reaction rate tests (e.g. on closely similar materials), or on known degradation mechanism of the material.
- 2) The dominant reaction is not diffusion-controlled, or the material tested is thin enough that the reaction can be taken to be homogeneous.

4.2 Range of application

The reaction rate curve should be essentially linear in the temperature range of interest. A bend in the reaction rate curve may indicate a change of dominant reaction or a change-over to a diffusion-controlled reaction. In such cases, conventional ageing tests of procedure A should be performed at temperatures below the bend, or procedure B or C should be invoked.

NOTE 1 A bend in the reaction rate curve does not necessarily coincide with the change in the relative importance of such ageing reactions, which determine the degradation of physical properties. However, it can be taken to be near such a change.

NOTE 2 With some materials the test procedures according to IEC Publication 216 produce different slopes of the thermal endurance characteristic when different properties or end-point values are used. These materials should be tested according to procedure B or C.

5 Reaction rate measurements in procedure A

5.1 General aspects of reaction rate measurements

The analytical method selected should be suitable for measurements of the rate of the dominant reaction at the expected TI temperature of the material.

Quite often oxidation seems to be the dominant reaction, especially with materials with low thermal endurance ($TI < 130$). In such cases the rate of the total oxidation or sum of evolution rates of CO and CO₂ are valid measures of reaction rate.

With materials of higher thermal endurance care should be taken in the search of the dominant reaction, since, for example, oxidation may take over at high temperatures only.

All the methods described in Clause 3 are in principle suitable for reaction rate measurements for procedure A.

5.2 Test temperatures for reaction rate measurements

Test temperatures for reaction rate measurements should be selected to cover the range from below the expected TI temperature to the highest possible conventional ageing test temperature plus 20 K, to reveal possible non-linearity even at that temperature.

The measurements should be performed at four test temperatures or more.

5.3 Test sequence

There are two possible test strategies in the reaction rate measurements: either fresh specimens are used at each test temperature, or the same specimens are used successively at all test temperatures. It is required that all specimens are as similar as possible (preferably identical) and that the extent of thermal ageing during the high temperature exposure periods required in the tests be as small as possible.

5.4 Acceleration factor

In procedure A, one reaction is assumed to dominate the ageing process. Consequently, the reaction rate is inversely proportional to the time to end-point in a conventional ageing test.

The acceleration factor from a lower temperature to the ageing temperature is calculated as the inverse quotient of the respective reaction rates.

6 Conventional ageing tests in procedure A

6.1 Ageing test temperature

One ageing test temperature is selected for the conventional ageing tests.

It is advisable to select the temperature of the conventional ageing tests to produce a median time to end-point of approximately 1 000 h. Table 1 of IEC Publication 216-1 may be used when selecting it.

If there is a bend in the reaction rate curve, then the ageing temperature should be selected below that bend.

6.2 Procedure

In the conventional ageing tests, IEC Publication 216 and relevant IEC material specifications should be followed regarding the test specimens, properties measured, end-points and the performance of the conventional ageing test.