IEC 60666

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INTERNATIONAL STANDARD

NORME INTERNATIONALE

colour inside

Detection and determination of specified additives in mineral insulating oils

Détection et dosage d'additifs spécifiques présents dans les huiles minérales isolantes

IEC 60666:2010

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Detection and determination of specified additives in mineral insulating oils

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INTERNATIONAL ELECTROTECHNICAL COMMISSION

DETECTION AND DETERMINATION OF SPECIFIED ADDITIVES IN MINERAL INSULATING OILS

FOREWORD

1) The International Electrotechnical Commission (IEC) is a worldwide organization for standardization comprising all national electrotechnical committees (IEC National Committees). The object of IEC is to promote international co-operation on all questions concerning standardization in the electrical and electronic fields. To this end and in addition to other activities, IEC publishes International Standards, Technical Specifications, Technical Reports, Publicly Available Specifications (PAS) and Guides (hereafter referred to as "IEC Publication(s)"). Their preparation is entrusted to technical committees; any IEC National Committee interested in the subject dealt with may participate in this preparatory work. International, governmental and non-governmental organizations liaising with the IEC also participate in this preparation. IEC collaborates closely with the International Organization for Standardization (ISO) in accordance with conditions determined by agreement between the two organizations.
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International Standard IEC 60666 has been prepared by IEC technical committee 10: Fluids for electrotechnical applications.

This second edition cancels and replaces the first edition, published in 1979, and constitutes a technical revision.

The main changes with respect to the previous edition are listed below:

– a change in the title from "Detection and determination of specified anti-oxidant additives in insulating oils" to "Detection and determination of specified additives in mineral insulating oils". The previous edition only addressed the detection and determination of anti-oxidant additives, with particular regard to the DBPC, phenolic inhibitors and anthranilic acid;
– more advanced methods for the determination of such anti-oxidant additives;
– new Annexes B and C which provide methods for the determination of two additives different from the anti-oxidants. In particular, Annex B contains a method for the determination of the concentration in used and unused insulating mineral oils of passivators of the family of derivatives of benzotriazole. Annex C contains a method

for the qualitative identification of pour point depressants used in some commercially available paraffinic oils to improve their low temperature properties.

The text of this standard is based on the following documents:

FDIS	Report on voting
10/803/FDIS	10/807/RVD

Full information on the voting for the approval of this standard can be found in the report on voting indicated in the above table.

This publication has been drafted in accordance with the ISO/IEC Directives, Part 2.

The committee has decided that the contents of this publication will remain unchanged until the stability date indicated on the IEC web site under "http://webstore.iec.ch" in the data related to the specific publication. At this date, the publication will be

- reconfirmed,
- withdrawn,
- replaced by a revised edition, or
- amended.

IMPORTANT – The 'colour inside' logo on the cover page of this publication indicates that it contains colours which are considered to be useful for the correct understanding of its contents. Users should therefore print this document using a colour printer.

INTRODUCTION

General caution, health, safety and environmental protection

This International Standard does not purport to address all the safety problems associated with its use. It is the responsibility of the user of the standard to establish appropriate health and safety practices and determine the applicability of regulatory limitations prior to use.

The mineral oils which are the subject of this standard should be handled with due regard to personal hygiene. Direct contact with eyes may cause slight irritation. In the case of eye contact, irrigation with copious quantities of clean running water should be carried out and medical advice sought.

Some of the tests specified in this standard involve the use of processes that could lead to a hazardous situation. Attention is drawn to the relevant standard for guidance.

This standard involves mineral oils, chemicals and used sample containers. The disposal of these items should be carried out in accordance with current national legislation with regard to the impact on the environment. Every precaution should be taken to prevent the release into the environment of mineral oil.

DETECTION AND DETERMINATION OF SPECIFIED ADDITIVES IN MINERAL INSULATING OILS

1 Scope

The methods described in this International Standard concern the detection and determination of specified additives in unused and used mineral insulating oils.

The detection methods may be applied to assess whether or not a mineral insulating oil contains an additive as specified by the supplier.

The determination methods are used for the quantitative determination of additives known to be present or previously detected by the appropriate detection method.

2 Normative references

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

IEC 60296, *Fluids for electrotechnical applications – Unused mineral insulating oils for transformers and switchgear*

IEC 60475, *Method of sampling liquid dielectrics*

ISO 5725 (all parts), *Accuracy (trueness and precision) of measurement methods and results*

3 Methods for the determination of anti-oxidant additives

3.1 Determination of phenolic and amine-based antioxidants by infrared (IR) spectrophotometry – Method A

3.1.1 Introductory remark

This method determines the amount of 2,6-di-tert-butyl-para-cresol (DBPC) in unused and used mineral oils by measurement of the infrared absorption at the (O–H) stretching frequency of hindered phenols. It can also be used to determine the amount of 2,6-di-tert-butyl-phenol (DBP), but does not discriminate between them.

The previous test method in the first edition of IEC 60666 described a procedure for the determination of specific antioxidants using IR techniques. This test method was satisfactory with new oils, where no oxidation by-products interfere with the antioxidant. However, this method was less satisfactory for used oils because oxidation by-products may modify the IR baseline, making the detection and quantification of the antioxidants difficult. To overcome this problem, a procedure for preparing a reference oil to be used as a baseline was described. Unfortunately, this procedure was difficult to perform, was time-consuming and did not ensure that the new baseline matched adequately that of the oil to be analysed, because the content of some components of the baseline oil and the analysed oil could be quite different.

This new method describes a procedure for preparing reference, antioxidant-free oils by solid phase extraction (SPE) using silica gel.

3.1.2 Equipment, materials and solvents

The following materials and reagents are used:

– FT-IR or double-beam IR spectrometer having matched 1 mm sodium chloride cells (other materials are accepted provided they do not absorb IR radiation in the range 3 000 cm^{-1} to 3 800 cm^{-1});
– 5 ml or 10 ml round-bottom flasks;
– 5 ml or 10 ml beakers;
– rotary evaporator;
– silica gel cartridges (1 g or 2 g size is satisfactory);
– n-pentane, analytical grade.

3.1.3 Sample preparation

Into a beaker pour 1 g of the oil to be analysed for antioxidants, add 2 ml of analytical grade n-pentane and mix thoroughly.

Filter the solution through a silica gel cartridge and recover the eluate in a round-bottom flask. Evaporate the n-pentane in the rotary evaporator.

Take a portion large enough to completely fill one IR cell of the oil that remains in the flask, fill one IR cell and put it on the reference beam of the spectrometer.

Fill a second IR cell with the oil to be analysed, which has not been submitted to the filtration process, and insert it on the analytical beam of the spectrometer.

Record the IR spectrum as described in 3.1.5.

3.1.4 Calibration

Prepare standard calibration solutions by dissolving weighed amounts of DBP or DBPC inhibitor in weighed amounts of antioxidant-free oil, prepared if necessary from the oil sample under test using the procedure in 3.1.3 (larger cartridges and amounts of oil will be necessary).

The maximum life of the standard solution shall be six months.

NOTE The calibration solutions may be prepared using an unused, inhibitor-free oil, provided the base oil is known to be the same as that under test. The oil should be tested by this procedure to ensure that no inhibitor is detectable. This alternative should not be used where the oil under test is heavily aged.

Prepare at least five calibration solutions, covering the range 0,02 % to 0,50 % inhibitor by mass.

Intermediate standards may be prepared if necessary when the approximate concentration of inhibitor in the sample is known.

The absorbance (at 3 650 cm^{-1} for DBPC) of the calibration solutions is recorded as described in 3.1.5 and a calibration curve of absorbance against per cent inhibitor content produced. The calibration should be a straight line passing through the origin, according to the Beer-Lambert law of absorption:

$$A = \log_{10} \frac{I_o}{I} = KCD$$

where

A is the absorbance;

I_o is the intensity of incident radiation;

I is the intensity of transmitted radiation;

K is the extinction coefficient (constant for (O-H) of DBPC);

C is the concentration of DBPC in percentage by mass;

D is the cell path-length.

Since K and D are constant for this determination, A is directly proportional to C.

3.1.5 Analysis

1. FT-IR instrument

Check the equipment. The quality tests should be performed according to the manufacturer's recommendations.

2. Double-beam IR spectrophotometer

Prepare two matched liquid cells with path-lengths of 1 mm and sodium chloride windows. Fill both cells with the base oil and, with one cell in the sample beam and the other in the reference beam of the spectrometer and check that the IR spectrum between 3 800 cm^{-1} and 3 400 cm^{-1} is a straight line. Record the percentage transmittance (95 % – 100 %).

Exchange the cells, i.e. transfer the cell in the sample beam to the reference beam and the cell in the reference beam to the sample beam. Repeat the spectrum acquisition and again ensure a straight line of approximately 95 % to 100 % transmittance is obtained.

If the above conditions are not obtained, clean and polish or reject windows that have an absorbance in this region, and repeat the process until a matched pair of cells is obtained. These are then used for all the determinations.

Test solutions

1. FT-IR instrument

Fill the cell with the oil to be analysed and record the IR spectrum (A) at the appropriate wavelength. Repeat using the inhibitor-free reference oil and subtract this result from spectrum A to produce a spectrum with a linear baseline.

2. Double-beam IR spectrophotometer.

Take a portion of the inhibitor-free reference oil in the flask, completely fill an IR cell and place it in the path of the reference beam of the spectrometer. Completely fill a second IR cell with the oil to be analysed and place it in the analytical beam of the spectrometer. Record the IR spectrum at the appropriate wavelength (in the range 3 500 cm^{-1} to 3700 cm^{-1} for DBPC).

3.1.6 Calculation

Measurement of absorbance

1. FT-IR instrument

Record the absorbance at the position of maximum peak height for the sample and for the inhibitor-free reference oil.

Subtract the reference oil spectrum from the sample oil spectrum and quantify the result by reference to calibration curves.

2. Double-beam IR spectrophotometer (see Figure A.1)

Draw a base line as nearly as possible between 3 610 cm^{-1} and 3 680 cm^{-1} and record the percentage transmittance (I_o) at which the base line crosses the 3 650 cm^{-1} line.

Record the percentage transmittance at the tip of the peak at 3 650 cm^{-1} (I), then:

$$A_{3\,650} = \log_{10} \frac{I_o}{I}$$

The percentage DBPC equivalent to $A_{3\,650}$ is read from the calibration graph.

Alternatively, automatic determination by the spectrometer may be used.

3.1.7 Precision

The repeatability and reproducibility limits were established in accordance with the ISO 5725 series.

3.1.8 Repeatability

The difference between successive test results obtained by the same operator with the same apparatus under constant operating conditions on identical test material would, in the long run, in the normal and correct operation of the test method, exceed the values shown below by only 1 case in 20:

– unused and used oils – 15 %, which can be calculated as $(x_1+x_2)/2 \times 0{,}15$, where x_1 and x_2 are the results of the two replicates.

NOTE The repeatability values for oils only apply where the result is above 0,05 % DBPC in oil.

3.1.9 Reproducibility

The difference between two single and independent results obtained by different operators working in different laboratories on identical test material would, in the long run, in the normal and correct operation of the test method, exceed the values shown below by only 1 case in 20:

– unused oils: for DBPC concentrations ≤ 0,1 %, the reproducibility is 0,02 % – absolute value;

– unused oils: for DBPC concentrations > 0,1 %, the reproducibility is 45 %, which can be calculated as $(x_1+x_2)/2 \times 0{,}45$, where x_1 and x_2 are the results of the two replicates;

– used oils – 45 %, which can be calculated as $(x_1+x_2)/2 \times 0{,}45$, where x_1 and x_2 are the results of the two replicates.

NOTE The reproducibility values for used oils only apply where the result is above 0,05 % DBPC in oil.

3.1.10 Report

Report the concentration of phenolic and amine-based antioxidants in % to the nearest 0,01 %.

3.2 Determination of 2,6-di-tert-butyl-para-cresol by IR spectrophotometry – Method B

For routine analysis of oils in service, a procedure, modifying 3.1 by the following changes, may be used.

3.2.1 Calibration

Prepare one liquid cell with a path length of 0,2 mm and equipped with sodium chloride windows.

Fill the cell with a mineral transformer oil without inhibitor (0 % inhibitor calibration solution) and measure the IR spectrum.

Prepare at least 3 calibration solutions by adding DBPC inhibitor to achieve concentrations between 0,1 % and 0,4 %.

Measure the IR spectrum of each calibration solution.

Measure the heights of the inhibitor characteristic peaks at approximately 3 650 cm^{-1} (see Figure A.2).

Construct the calibration line: height of the peak as a percentage of transmission ~ concentration of DBPC as mass per cent in oil.

3.2.2 Sample test – New or used oil

Fill and drain the calibrated cell with the test oil 3 times.

Fill the cell and measure the IR spectrum.

Measure the height of the inhibitor characteristic peak as a percentage of transmission by visual examination, in the same way as during the calibration procedure (see Figure A.2).

From the peak height, read the mass per cent of inhibitor in the oil sample under test using the calibration line.

3.2.3 Precision

The repeatability and reproducibility limits for method B have been established to be the same as for Method A.

3.2.4 Repeatability

The difference between successive test results obtained by the same operator with the same apparatus under constant operating conditions on identical test material would, in the long run, under normal and correct operation of the test method, exceed the values shown below by only 1 case in 20:

– unused and used oils – 15 %.

NOTE The repeatability values for oils only apply where the result is above 0,05 % DBPC in oil.

3.2.5 Reproducibility

The difference between two single and independent results obtained by different operators working in different laboratories on identical test material would, in the long run, in the normal and correct operation of the test method, exceed the values shown below by only 1 case in 20:

– unused oils: for DBPC concentrations ≤ 0,1 %, the reproducibility is 0,02 % – absolute value;
– unused oils: for DBPC concentrations > 0,1 %, the reproducibility is 45 %;
– used oils – 45 %.

NOTE The reproducibility values for used oils only apply where the result is above 0,05 % DBPC in oil.

3.2.6 Report

Report the concentration of 2,6-di-tert-butyl-para-cresol (DBPC) in % to the nearest 0,01 %.

3.3 Determination of 2,6-di-tert-butyl-para-cresol (DBPC) by high performance liquid chromatography (HPLC)

3.3.1 Introductory remark

This method determines the amount of 2,6-di-tert-butyl-para-cresol (DBPC) in unused and used mineral oils by using high-performance liquid chromatography after sample preparation using solid phase extraction technique.

3.3.2 Materials and equipment

The following materials and equipment are used:

– HPLC with a UV or a diode array UV detector;

– column – an example of column found satisfactory is C_{18}, 3,9 mm × 300 mm with 5 µm coating thickness;

– pre-column – C_{18}, 5 µm;

– cartridges – 0,6 g to 1 g of silica;

– syringe filter – PTFE, maximum pore-size 0,5 µm (optional).

3.3.3 Reagents and solvents

Reagents shall comprise:

– methanol, HPLC grade;

– water, HPLC grade;

– n-pentane, HPLC grade.

3.3.4 Solid-liquid extraction

Weigh between 0,25 g and 0,5 g of oil sample to an accuracy of 0,01 g and dissolve it in 2,5 ml of n-pentane.

Rinse a new silica cartridge with 3 ml of n-pentane and discard the eluate. While the silica is still wet, immediately pass the sample solution through the cartridge under a slight vacuum at a maximum flow of 3 ml/min. Discard eluate.

Dry the cartridge by suction maintaining the vacuum for at least 10 min.

Stop the vacuum and elute the absorbed material with the same eluent to be used in the chromatographic analysis.

Collect the first 5 ml in a 5 ml volumetric flask.

It may be advantageous to filter this solution through a syringe filter when transferring it to a vial.

Transfer the eluate to a suitable vial for analysis by HPLC.

3.3.5 Analysis of the extract

The following conditions have been used:

Mobile phase:	Isocratic conditions
Eluent:	Levels between 100 % methanol and methanol containing up to 40 % of water (volume/volume) have been used.
Injection volume:	10 µl to 20 µl
Flow rate:	1 ml/min
Temperature:	Isothermal at a temperature between 30 °C and 40 °C
Peak detection:	About 276 nm to 278 nm with a retention time from about 3 min to 10 min depending on elution conditions.

See Figure A.3 for an example of the chromatogram.

3.3.6 Calculation

Peak areas or peak heights of the sample are compared with calibration standards prepared as in 3.1.4.

Plot a calibration curve of peak heights or peak areas against per cent inhibitor content. Read on the calibration curve the percentage of DBPC in the sample.

3.3.7 Precision

The repeatability and reproducibility limits were established in accordance with the ISO 5725 series.

3.3.8 Repeatability

The difference between successive test results obtained by the same operator with the same apparatus under constant operating conditions on identical test material would, in the long run, under normal and correct operation of the test method, exceed the values shown below by only 1 case in 20:

– unused and used oils – 15 %.

NOTE The repeatability values for oils only apply where the result is above 0,05 % DBPC in oil.

3.3.9 Reproducibility

The difference between two single and independent results obtained by different operators working in different laboratories on identical test material would, in the long run, under normal and correct operation of the test method, exceed the values shown below by only 1 case in 20:

– unused oils: for DBPC concentrations ≤ 0,1 %, the reproducibility is 0,02 % – absolute value;

– unused oils: for DBPC concentrations > 0,1 %, the reproducibility is 45 %;

– used oils – 45 %.

NOTE The reproducibility values for used oils only apply where the result is above 0,05 % DBPC in oil.

3.3.10 Report

Report the concentration of 2,6-di-tert-butyl-para-cresol (DBPC) in % to the nearest 0,01 %.