BS EN 60666:2010

BSI Standards Publication

Detection and determination of specified additives in mineral insulating oils

raising standards worldwide™

National foreword

This British Standard is the UK implementation of EN 60666:2010. It is identical to IEC 60666:2010. It supersedes BS 5984:1980 which is withdrawn.

The UK participation in its preparation was entrusted to Technical Committee GEL/10, Fluids for electrotechnical applications.

A list of organizations represented on this committee can be obtained on request to its secretary.

This publication does not purport to include all the necessary provisions of a contract. Users are responsible for its correct application.

ISBN 978 0 580 58307 0

ICS 17.220.99; 29.040.10

Compliance with a British Standard cannot confer immunity from legal obligations.

This British Standard was published under the authority of the Standards Policy and Strategy Committee on 31 August 2010.

Amendments issued since publication

Amd. No.	Date	Text affected

EUROPEAN STANDARD

NORME EUROPÉENNE

EUROPÄISCHE NORM

EN 60666

July 2010

ICS 17.220.99; 29.040.10

Supersedes HD 415 S1:1981

English version

Detection and determination of specified additives in mineral insulating oils
(IEC 60666:2010)

Détection et dosage d'additifs spécifiques présents dans les huiles minérales isolantes
(CEI 60666:2010)

Nachweis und Bestimmung spezifizierter Additive in Isolierflüssigkeiten auf Mineralölbasis
(IEC 60666:2010)

This European Standard was approved by CENELEC on 2010-07-01. CENELEC members are bound to comply with the CEN/CENELEC Internal Regulations which stipulate the conditions for giving this European Standard the status of a national standard without any alteration.

Up-to-date lists and bibliographical references concerning such national standards may be obtained on application to the Central Secretariat or to any CENELEC member.

This European Standard exists in three official versions (English, French, German). A version in any other language made by translation under the responsibility of a CENELEC member into its own language and notified to the Central Secretariat has the same status as the official versions.

CENELEC members are the national electrotechnical committees of Austria, Belgium, Bulgaria, Croatia, Cyprus, the Czech Republic, Denmark, Estonia, Finland, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, the Netherlands, Norway, Poland, Portugal, Romania, Slovakia, Slovenia, Spain, Sweden, Switzerland and the United Kingdom.

CENELEC

European Committee for Electrotechnical Standardization
Comité Européen de Normalisation Electrotechnique
Europäisches Komitee für Elektrotechnische Normung

Management Centre: Avenue Marnix 17, B - 1000 Brussels

Ref. No. EN 60666:2010 E

Foreword

The text of document 10/803/FDIS, future edition 2 of IEC 60666, prepared by IEC TC 10, Fluids for electrotechnical applications, was submitted to the IEC-CENELEC parallel vote and was approved by CENELEC as EN 60666 on 2010-07-01.

This European Standard supersedes HD 415 S1:1981.

The main changes with respect to HD 415 S1:1981 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.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. CEN and CENELEC shall not be held responsible for identifying any or all such patent rights.

The following dates were fixed:

– latest date by which the EN has to be implemented at national level by publication of an identical national standard or by endorsement	(dop)	2011-04-01
– latest date by which the national standards conflicting with the EN have to be withdrawn	(dow)	2013-07-01

Annex ZA has been added by CENELEC.

Endorsement notice

The text of the International Standard IEC 60666:2010 was approved by CENELEC as a European Standard without any modification.

In the official version, for Bibliography, the following notes have to be added for the standards indicated:

[3] IEC 60422	NOTE Harmonized as EN 60422.
[5] IEC 61198	NOTE Harmonized as EN 61198.

Annex ZA
(normative)

Normative references to international publications with their corresponding European publications

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.

NOTE When an international publication has been modified by common modifications, indicated by (mod), the relevant EN/HD applies.

Publication	Year	Title	EN/HD	Year
IEC 60296	-	Fluids for electrotechnical applications - Unused mineral insulating oils for transformers and switchgear	EN 60296	-
IEC 60475	-	Method of sampling liquid dielectrics	-	-
ISO 5725	Series	Accuracy (trueness and precision) of measurement methods and results	-	-

CONTENTS

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 %.

3.4 Determination of phenolic inhibitors by gas chromatography – Mass spectrometry (GC-MS)

3.4.1 Summary of method

Solvent containing an internal standard (the dimethyl ester of phthalic acid) is added to the oil and to suitable calibration standards containing known amounts of 2,6-di-tert-butyl-phenol (DBP) and of 2,6-di-tert-butyl-para-cresol (DBPC). Samples and standards are injected on the GC (split injection) using mass spectrometric detection. Ion chromatograms of m/z = 191, 205 and 163 are used for the quantitation of DBP, DBPC and the internal standard, respectively.

This method is applicable to all mineral oils, including such used oils where the IR spectrophotometric methods may suffer from interferences. Because of the high sensitivity of this method it can also be used to ascertain the absence of inhibitor in uninhibited oils.

3.4.2 Example of instrument parameters

Split injection:	1 µl injected, with a split ratio of 200:1, at 275 °C
Carrier gas:	Helium
Column head pressure:	Constant flow mode, 1,2 ml/min
Column:	5 % phenyl- 95 % dimethyl-polysiloxane, 30 m, 0,25 mm, 0,25 µm or equivalent
GC temperature program:	Start at 120 °C, hold for 1 min, increase 10 ºC/min until DBPC has eluted, then increase at 50 °C/min to 300 °C. Hold at 300 °C until the baseline is restored.
MS settings:	EI+, 70 eV, trap temperature 150 °C, manifold temperature 80 °C, scan from m/z = 50 to 500, 3 scans per second to establish retention times and identities (3.4.7). Start scanning at 3 min, stop scanning at 7 min or later.

3.4.3 GC accessories

Liner:	Split injection liner
Syringe:	5 µl or 10 µl
Washing solvent:	Toluene

3.4.4 Calibration standard solutions

Weigh about 0,28 g of DBPC and/or DBP into a 10 ml vial and record the weight to ± 0,001 g. Add about 8 g mineral oil complying with IEC 60296 containing no inhibitor and record the weight to ±0,01 g. Mix and stir with magnet until DBPC and DBP are dissolved, heating slightly if required. Prepare a series of calibration standard solutions containing 0,02 %, 0,04 %, 0,1 %, 0,2 % and 0,4 % by weight of the calibration standard solution above, using the same oil and mixing the solutions thoroughly.

The standards may be stored in darkness and cool conditions for maximum of 6 months.

3.4.5 Internal standard solutions

Solution 1: Weigh about 1,0 g dimethylphthalate into a 100 ml volumetric flask and record the weight to ±0,001 g.

Fill with toluene to 100 ml, record the weight and mix thoroughly.

Solution 2: Transfer 1 000 µl of internal standard solution 1 into a 100 ml volumetric flask, fill up with toluene to 100 ml and mix thoroughly.

Do not store solution 2; it must be prepared for each set of analyses.

3.4.6 Preparation of samples and calibration standards

Add 100 µl of the sample(s) and of each of the series of calibration standard solutions into separate vials, then add 1 000 µl of internal standard solution 2 and mix well. Analyse the sample(s) and the calibration standard solutions.

3.4.7 Analytical procedure

Set up and tune the MS according to the manufacturer's instructions.

Carry out a full scan for determination of the retention time and identification according to target ions of DBPC, DBP and dimethylphthalate and a SIM method (selective ion monitoring) for calibration and analysis.

NOTE For many mass spectrometers used as detectors, the ion chromatograms for quantitation can be extracted from chromatographic runs with full MS scans and with sufficient signal-to-noise ratio. In such cases, it is not necessary to run the MS in SIM mode. However, SIM might still be preferable in order to save on data storage capacity.

3.4.8 Calculation of results

Integrate and note the area for the target ions on DBPC, DBP and dimethylphthalate and calculate the RFx for each level of calibration standard:

$$\mathrm{RFx} = [A_{IS}/M_{IS}] \,/\, [A_C/M_C]$$

where

A_{IS} is the area of the internal standard;

M_{IS} is the mass of the internal standard;

A_C is the area of the compound;

M_C is the mass of the compound.

The RFx from calibration, internal standard areas and sample areas are used for calculation of the inhibitor content. Use of a spreadsheet program is recommended.

$$C_S = [A_S/\mathrm{RFx}] \,/\, [M_{IS}/A_{IS}] \times M_S$$

where

C_S is the content of the sample;

A_S is the area of the sample;

RFx is the reference factor from calibration;

M_{IS} is the mass of the internal standard;

A_{IS} is the area of the internal standard;

M_S is the mass of the sample.

NOTE The method could be modified to include other sufficiently volatile phenolic inhibitors and also amine inhibitors. Some diphenylamines have been used in the past in transformer oils and may possibly still be used by some producers. However, BTA may decompose at the temperatures used in this method.

3.4.9 Precision

This method is capable of detecting anti-oxidants at trace levels or confirmation of absence of these compounds and, while only a limited number of laboratories were involved in evaluation, the precision is dependent principally on the dilution stage which can be easily evaluated by each laboratory.

3.4.10 Report

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

Annex A
(informative)

Detection of anti-oxidant additives by thin layer chromatography (TLC)

NOTE This method may be used for screening or semi-quantitative purposes.

A.1 Summary of the method

The method described can be used to obtain a semi-quantitative estimation of DBPC when an IR spectrophotometer, an HPLC or a GC-MS are not available. It gives a semi-quantitative determination of the DBPC content, of new or used mineral oils in the range 0,01 % to 0,10 % by mass, with differentiation between increments of 0,02 % by mass. It can also be used for the range 0,10 % to 0,50 % by mass after suitable dilution of the oil.

A known amount of a mixture of oil and chloroform (1:1 volume) is applied into a silica gel coated TLC aluminium sheet (sheet A). After the solvent has evaporated, sheet A is covered with an identical sheet B, silica gel against silica gel.

Sheet A is then heated while sheet B, on which the inhibitor condenses, is simultaneously cooled. Sheet B is then treated with phosphomolybdic acid and ammonia. The area of the blue spot produced is proportional to the quantity of DBPC.

A.2 Reagents and solvents

The following reagents and solvents are used:

– phosphomolybdic acid 3,5 % in isopropanol, spray reagent for chromatography;
– chloroform, analytical grade;
– ammonia solution (25 % NH3, density at 20 °C: 0,91 g/cm^3);
– white oil or insulating oil, free of DBPC and other phenolic impurities according to the method of detection.

A.3 Equipment

The following equipment shall be used:

– TLC aluminium sheets, silica gel coated, layer thickness 0,25 mm;
– 10 µl syringe;
– heating plate able to maintain a temperature of 125 °C ± 5 °C;
– device for measuring the temperature of the heating plate;
– metal box, water-tight and with a flat bottom, approximate dimensions 6 cm × 6 cm, height 7 cm to 10 cm;
– glass container with a tight cover, as used in TLC, approximate size 20 cm × 7 cm, height 20 cm (a conventional desiccator may also be used).

A.4 Procedure

A.4.1 For DBPC concentrations of 0,01 % to 0,10 % by mass

Prepare standard solutions in white oil or in a DBPC-free insulating base oil, containing 0,01 %, 0,02 %, 0,05 % and 0,10 % by mass of DBPC.

Dilute the oil to be tested and the standard solutions with chloroform (one volume oil to one volume chloroform).

Cut two TLC sheets (A and B) of size 6 cm × 6 cm. Divide these into areas of 1 cm^2 by pencil marks. Areas within 1 cm of the edge shall not be used.

Using the syringe, apply 10 µl of the oil-chloroform solution into the middle of one of the 1 cm^2 areas on sheet A.

Proceed similarly with the standard solutions applying 10 µl in the middle of neighbouring areas on sheet A.

Evaporate the chloroform by exposing the sheet in air at ambient temperature (approximately 2 min).

NOTE 1 It is important to remove completely the solvent as ascertained by elimination of the smell of chloroform.

Place on sheet A the second sheet B, silica gel against silica gel.

NOTE 2 With oils of higher aromatic content and particularly when using TLC plates of poor consistency, it has been found that better differentiation at the 0,01 % by mass DBPC level is obtained if a small gap (0,8 mm) is left between plates.

Cool sheet B by putting on its upper surface the metal container filled with ice.

Place the system (sheets A and B and the cold box) on the heating device maintained at 125 °C ± 5 °C. The aluminium face of plate A should be in direct contact with the heating surface.

After 5 min, separate sheets A and B.

Spray sheet B with the phosphomolybdic reagent. Dry at ambient temperature, (the colour will appear more quickly if the plate is heated to approximately 90 °C for a few minutes) and expose the chromatographic plate to ammonia vapours. The DBPC spot is blue on a white background.

A.4.2 For DBPC concentrations of 0,10 % to 0,50 % by mass

Dilute the sample with white oil or with an insulating base oil in the ratio one volume of sample to three volumes of diluent.

NOTE The oil used as diluent must not contain DBPC.

Proceed with the diluted sample as described in A.4.1.

A.5 Results

Compare the colours developed with those obtained from the standard solutions. In the case of A.4.2, take account of the factor of dilution.

A.6 Precision

Not evaluated.

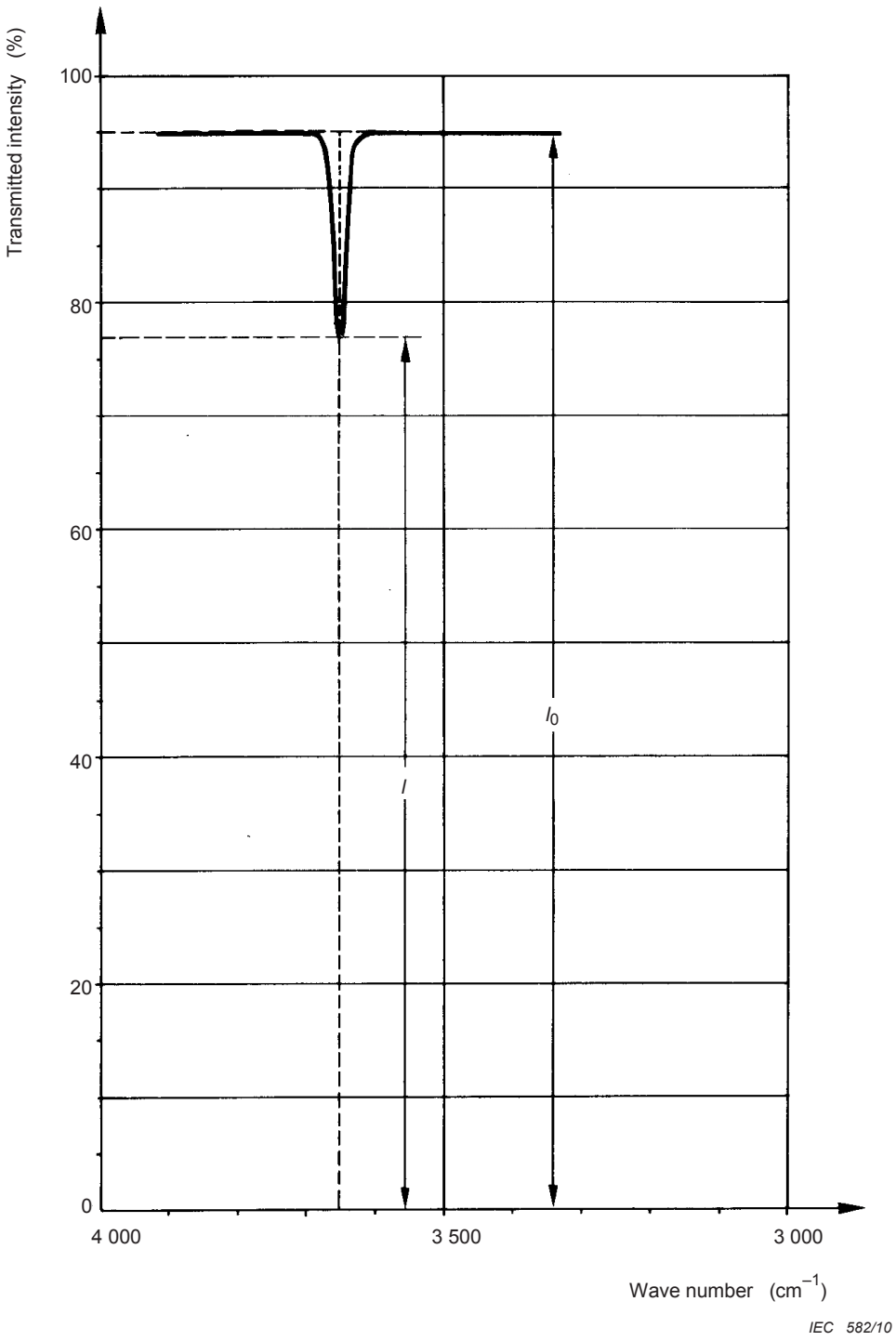
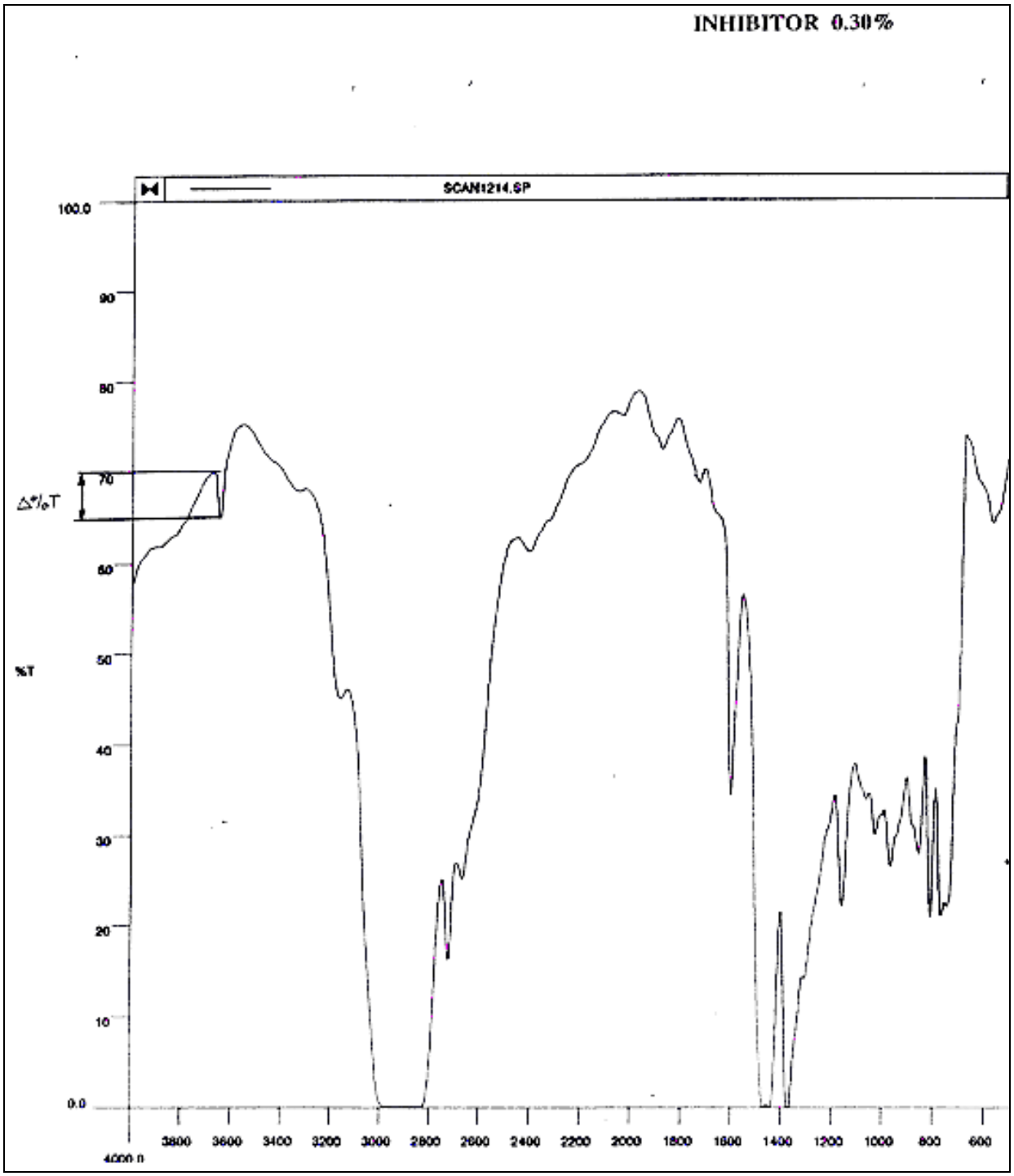


Figure A.1 – Typical infrared spectrum to determine DBPC content



IEC 583/10

Figure A.2 – Typical infrared spectrum with 0,3 % DBPC

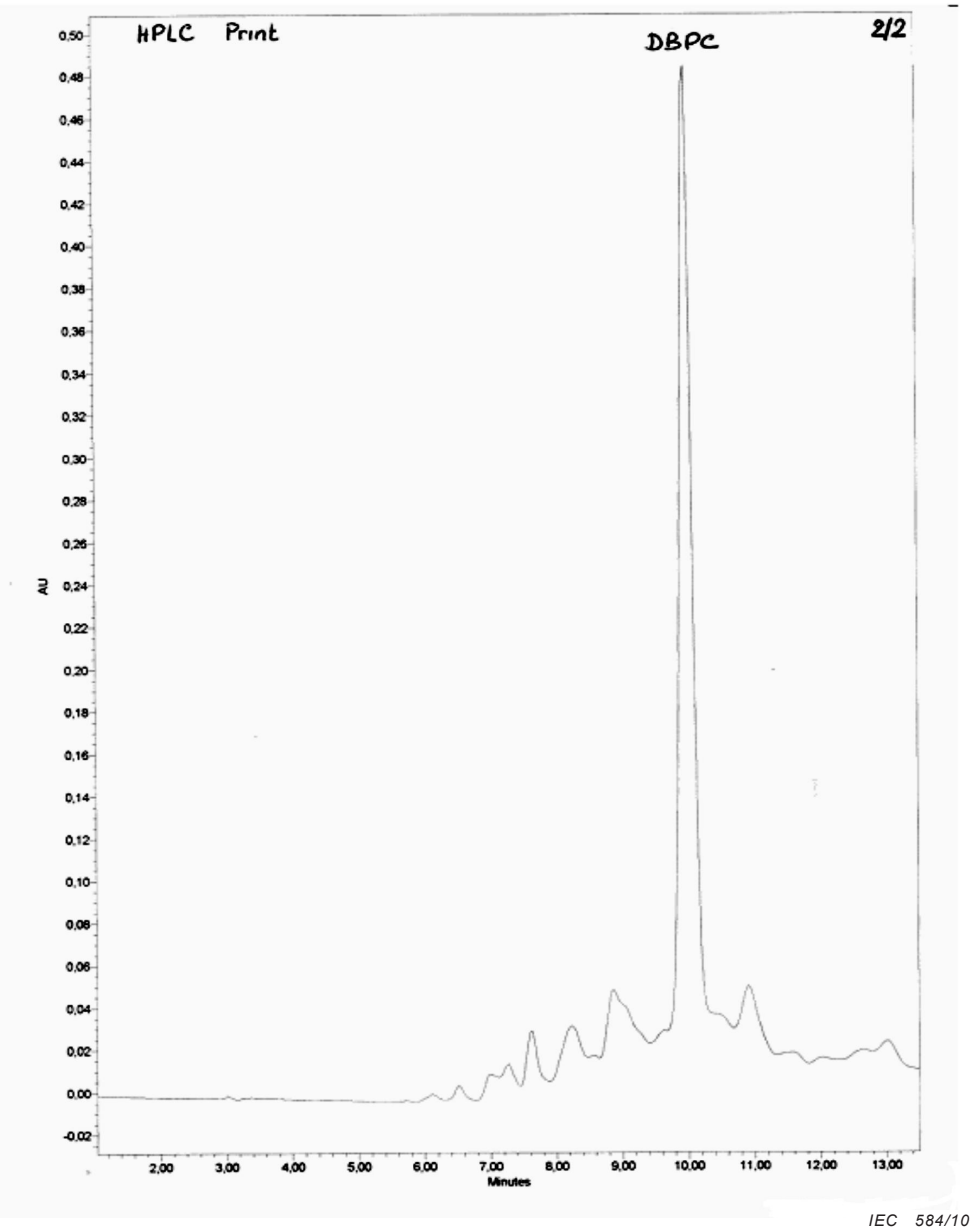


Figure A.3 – Typical HPLC chromatogram to determine DBPC content

Annex B
(informative)

Analysis method for determination of passivators in mineral oils by high performance liquid chromatography (HPLC)

B.1 Field of application

This test method covers the determination of passivators of the family of derivatives of benzotriazole such as: N-bis(2-ethylhexyl)-aminomethyl-tolutriazol (referred to as TTAA in this standard), benzotriazole (referred to as BTA in this standard) and 5-methyl-1H-benzotriazole (referred to as TTA in this standard) [1] in mineral oils by high performance liquid chromatography (HPLC) in used and unused insulating mineral oils.

NOTE This method is based on an existing method for determination of another passivator, BTA (Benzotriazole), which can be detected in the same chromatographic run of TTAA, as described.

This test method uses the commercial product of TTAA for calibration. Its inherent uncertainty is related to its degree of purity as supplied.

B.2 Principles

B.2.1 Summary

A weighed portion of the sample oil is diluted with pentane and passed under vacuum through a silica gel SPE cartridge, previously rinsed with methanol and pentane. The residue of non-polar oil constituents retained by the solid phase is then eluted with a further volume of pentane and discarded. The cartridge is then dried by flushing it with air under vacuum.

The analytes are eluted with a known volume of methanol and filtered through a 0,45 μm PTFE filter.

The solution is injected into a HPLC system equipped with a reverse-phase column, and TTAA detected with a UV detector at a wavelength of 260 – 270 nm.

B.2.2 Significance and use

This test method covers the determination of TTAA for routine analysis.

TTAA is an amine derivative of tolutriazole, liquid at room temperature, added in mineral insulating oils mainly as a metal passivator, for its capability to inhibit the corrosive reactions involving surfaces of copper (and other metals) and of metal-reactive compounds present in the oil. TTAA is usually added to mineral oils in concentrations 0,005 – 0,02 %.

Other triazole derivatives are used in insulating mineral oils such as BTA (benzotriazole) and TTA (tolutriazole) having a lower solubility in oil. BTA is more widely used then TTA, mainly to modify the electrical behaviour of copper surfaces.

TTAA is a mixture of 2 isomers: N,N-bis(2-ethylhexyl)-4-methyl-1H-benzotriazol-1-methylamine and N,N-bis (2-ethylhexyl)-5-methyl-1H-benzotriazol-1-methylamine. The two isomers are not usually separated in the conditions described in this method, but they may

---

[1] As examples, TTAA is commercially available as well in Ciba® Irgamet 39 (CAS Number 80584-90-3 + 80595-74-0 and as mixture in DSI® Sulfur Inhibitor). This information is given for the convenience of users of this standard and does not constitute an endorsement by IEC of these products.

give two partially overlapping peaks if a high efficiency column is used (C18, 250 mm); in this case the total area of two peaks shall be considered.

Heavily oxidized oils may partially affect the analysis, giving relevant interferences from UV-absorbing polar compounds. If in doubt, the standard addition method can be used for more accurate determinations.

This method can be used for monitoring TTAA content in passivated used and unused insulating mineral oils.

NOTE In order to obtain the optimal separation and detection condition with individual chromatographic systems, this method allows a large flexibility in choice of stationary phase and mobile phase separation.

B.2.3 Interferences

B.2.3.1 Co-eluting compounds

TTA was found to co-elute with TTAA in the conditions described in this method.

TTAA seems to decompose to TTA during some stage of the chromatographic run, the UV spectra of the two compounds (recorded from the chromatogram) being identical.

NOTE It is recommended that the effective co-elution of TTAA and TTA under the selected separation conditions is verified.

B.2.3.2 UV-adsorbing interfering compounds

Heavily oxidized oils may contain UV-adsorbing compounds showing retention times close to TTAA. For the same reason, background noise may be encountered.

In these cases, when the integration of the peak is difficult, or an overlapping peak appears, the standard addition method should be used for quantification.

B.3 Equipment

B.3.1 Apparatus

- Balance:
  Top loading, with automatic tare, capable of weighing to 0,001 g, capacity of 100 g minimum.
- Vacuum manifold for SPE:
  For vacuum elution of silica cartridges.
- Silica SPE cartridges:
  Sorbent substrate: silica; sorbent weight: 500 mg to 1 000 mg; pH range: 2 – 8; particle size: 20 μm – 200 μm.

NOTE 1 The choice of the sorbent weight should be carefully correlated with the weight of sample analysed and to the load capacity of the cartridge. While optimizing the method a check for analyse recovery is recommended.

- PFTE filters:
  0,45 μm, fitting Luer plug.
- HPLC system:
  Equipped with
  – a pumping device suitable for at least two solvents;
  – an injection device suitable for injection of 10 – 100 μl (automatic injection is preferable);
  – RP column, C8 or C18, end-capped, suitable for mobile phase with pH 2 – 8.

NOTE 2 The choice of the length of the column and particle diameter may vary and it is the responsibility of the laboratory applying this method. Good analytical results were obtained with 150 mm to 250 mm columns, particles Ø 3,5 μm to 5 μm, column diameter 4,6 mm.

- RP pre-column, with the same stationary phase
- UV detector (a diode array detector is preferable, to record UV spectra)
- Data acquisition device

B.3.2 Reagents and materials

B.3.2.1 Purity of reagents

Reagent grade chemicals shall be used in all tests.

All solvents used for chromatographic elution shall be HPLC grade.

B.3.2.2 Required reagents

- Methanol, HPLC grade
- Water, HPLC grade
- n pentane, HPLC grade
- Toluene

B.3.2.3 Standard materials

- TTAA and BTA:

  The commercially available product of BTA and equivalent to TTAA shall be used as standard for calibration.

NOTE 1 Commercially available products, obtained by dilution of TTAA in mineral oil or other suitable solvents, should not be used for calibration, even if the TTAA content is known.

- TTA:
  TTA of analytical grade.
- BTA:

  BTA of analytical grade.
- Blank oil:
  A mineral insulating oil, free from BTA and TTAA, for dilution.

NOTE 2 For the reasons reported in B.2.3.1, the blank oil for dilution should also be TTA and BTA free.

B.3.2.4 Standard solutions

B.3.2.4.1 Stock solution

This is a concentrated solution of TTAA and BTA in toluene. It is recommended that a fresh stock solution is prepared each 3 months, and stored in dark bottles at room temperature.

NOTE 1 000 mg/kg stock solutions were found to be stable for at least 3 months. If a longer duration is desired, the stability shoud be checked by comparison with a fresh solution.

B.3.2.4.2 Standard solutions

From the stock solution, at least 5 diluted solutions should be prepared for calibration.

The solutions are prepared freshly for each calibration stage, by diluting the stock solution with blank oil.

The standard solutions should cover the range of 5 – 500 mg/kg.

B.4 Sampling

The objective of sampling is to obtain a representative test specimen. Thus, take laboratory samples in accordance with IEC 60475. The specific sampling technique can affect the accuracy of this test method.

B.5 Analytical procedure

B.5.1 Preparation of apparatus

B.5.1.1 Instrument

Design differences between instruments, columns and detectors make it impractical to detail the operating conditions. Consult the manufacturer's instructions for operating the instrument, according to the selected separation and detection conditions.

B.5.1.2 Separation conditions

Both C8 and C18 end-capped RP columns were found suitable for separation of TTAA. Good separation can be carried out either with isocratic or gradient elutions, with mobile phase water/methanol; the solvent ratio may be 50 % / 50 % (with C8 columns) to 20 % water / 80 % methanol (with C18 columns).

A flow rate of 0,5 ml/min to 1 ml/min is suitable.

Table B.1 reports some experimental conditions as a guide, but each laboratory should optimize its own separation parameters.

A good separation is obtained if a sharp, shoulder-less peak is obtained, with no overlapping with a BTA peak.

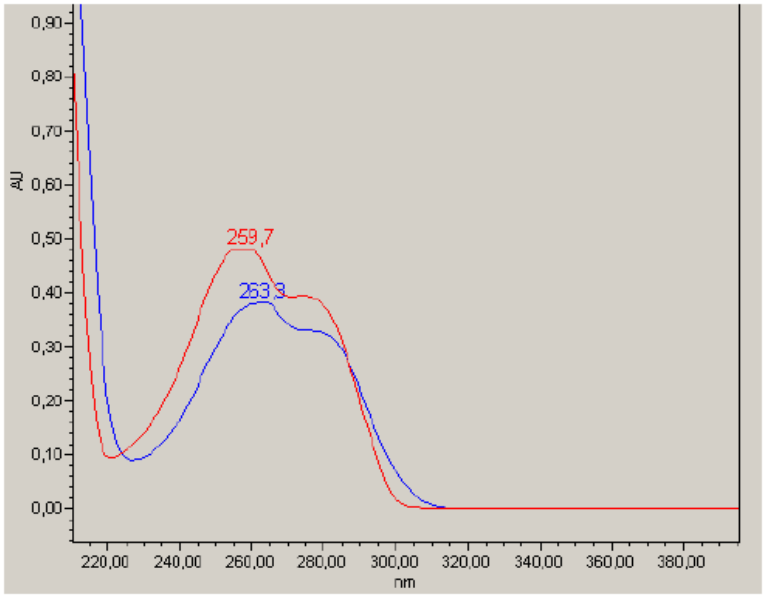
NOTE In some cases, to have a better separation and to avoid peak tailing, it is preferable to use a buffer instead of pure water in the mobile phase. Acetic buffers were used at pH 3 (concentration between 50 mM and 80 mM), increasing the quality of the separation. When using buffers, check for absorbance spectrum of TTAA since it may vary with pH.

Table B.1 – Examples of separation conditions

Column	Separation conditions	Timetable			TTAA RT min	(BTA RT) min	Notes
		Time min	% H_2O	% Met			
C18, 250 mm	Isocratic, 1 ml/min	0:00	30	70	3,5 – 4,5	2,5 – 3	
		20:00	30	70			
C18, 250 mm	Gradient, 1 ml/min	0:00	30	70	3,5 – 4,5	2,5 – 3	The step with 100 % methanol provides column clean up
		4:00	30	70			
		6:00	0	100			
		10:00	0	100			
		14:00	30	70			
C18, 150 mm	Gradient, 0,5 ml/min	0:00	50	50	8 – 9	5 – 6	
		15:00	50	50			
		20:00	0	100			
		45:00	0	100			
		50:00	0	100			
C18, 150 mm	Gradient, 1 ml/min	0:00	20	80	6 – 7	5 – 6	
		7:30	0	100			
		14:00	50	50			
		18:00	20	80			
C8, 150 mm	Isocratic, 0,5 ml/min	0:00	50	50	3,5 – 4,5	2,5 – 3	
		20:00	50	50			
C8, 250 mm	Isocratic, 1 ml/min	0:00	30	70	3,5 – 4,5		
		10:00	30	70			

B.5.1.3 UV detection

UV detection of TTAA can be at a wavelengths of 264 nm, corresponding to the maximum absorbance (see Figure B.1).



IEC 581/10

Figure B.1 – UV spectra of TTAA (in blue) and BTA (in red)

B.5.2 Calibration

B.5.2.1 The linear range shall be established for the particular instrument being used and the selected separation procedure. The method should show a linear response in a concentration range 5 – 500 mg/kg.

B.5.2.2 Calibration procedure

Prepare at least 5 standard solutions by diluting the stock solution of B.3.2.4.1 with blank mineral oil. The standard solution shall be prepared fresh for each calibration.

Extract the blank oil and each standard solution following the procedure in B.5.3.1. Run in triplicate at least the two external points (the minimum and the maximum).

Plot the peak area against the concentration and calculate the best calibration curve to fit the experimental points using regression model ($y = bx + m$) as calibration curve. A correlation factor higher than 0,99 may be considered acceptable. The intercept, m, should be very close to the origin; verify that $|m/b| < 1$.

Recalibration each 6 months is recommended. The control sample of known concentration should be tested periodically to verify the method's stability.

B.5.3 Analysis

B.5.3.1 Sample pre-treatment by SPE

Using a vacuum manifold, slowly rinse a SPE Silica cartridge with ~5 ml of methanol, then condition it by passing ~10 ml of pentane.

Weigh to the nearest 0,01 g a sample portion of 0,5 – 2 g.

NOTE 1 The weight of the sample should be optimized in connection to the sorbent material mass in the cartridge. An excessive weight of sample may overload the sorbent and affect the linearity of the method, underestimating the highest concentrations.

Dilute it with 10 ml pentane and pass the solution through the pre-conditioned cartridge at a maximum rate of 3 ml/min. Discard the eluate.

Rinse the cartridge with 20 ml fresh pentane at a maximum rate of 3 ml/min, to remove the non-polar oil constituents adsorbed by the silica. Discard the eluate.

Dry the sorbent material by flushing it under vacuum for 5–10 min.

Slowly elute the cartridge (in the same vacuum manifold or manually, with a syringe) with methanol, collecting the first 5,00 ml into a volumetric flask.

NOTE 2 The sample may be eluted with a different solvent, e.g. with the chromatographic mobile phase. Check for the solubility of TTAA if an alternative solvent is used.

NOTE 3 A different volume of solvent can be used to satisfy the requirements of analytic recovery (see Clause B.6).

B.5.3.2 HPLC analysis

With a precision syringe inject into the HPLC a portion of the last eluate collected into the 5 ml flask. The injection volume depends on the sensitivity of the instrument and on the weight of oil analysed: usually 10 µl to 100 µl loops are suitable.

Run the chromatogram and record the area of the peak corresponding to TTAA retention time.

B.5.4 Calculations

Being y = bx + m the model obtained during calibration, calculate the result as:

$$\text{mg/kg (TTAA)} = [(\text{peak area}) - m] / b$$

B.5.5 Report

Report the concentration of TTAA in mg/kg to three significant figures.

B.6 Analytic recovery yield

B.6.1 Adsorption yield

Verify the adsorption yield of the silica SPE cartridges as follows:

- put 2 cartridges in series in the vacuum manifold;
- pass a standard sample (200 mg/kg) through both cartridges as described in B.5.3.1, then separate the two cartridges and elute them separately with 5 ml methanol each one;
- analyse the two samples, and record the results as x_1 (concentration found in the upper cartridge) and x_2 (concentration found in the lower cartridge);
- check that $x_1/(x_1 + x_2) \geq 0{,}98$.

B.6.2 Elution yield

Verify the elution yield from the silica SPE cartridges as follows:

- pass a standard sample (200 mg/kg) through a cartridge as described in B.5.3.1;
- elute the cartridge firstly with 5 ml methanol, then elute it again with a second aliquot of 5 ml methanol;
- analyse the two samples separately, and record the results as x_1 (concentration found in the first elution) and x_2 (concentration found in the second elution);
- check that $x_1/(x_1 + x_2) \geq 0{,}98$.

B.7 Precision data

B.7.1 Detection limit

In the condition prescribed in this method, a detection limit of <5 mg/kg is expected. Each laboratory shall estimate its own detection limit.

B.7.2 Repeatability

Duplicate determinations carried out by one laboratory should be considered suspect at the 95 % confidence level if they differ by more than the value reported in Table B.2 (expressed in percentage of the average value).

Table B.2 – Repeatability

Concentration of TTAA mg/kg	**Repeatability** r %
≤ 50	10
> 50	5

B.7.3 Reproducibility

Duplicate determinations carried out by different laboratories should be considered suspect at the 95 % confidence level if they differ by more than the value reported in Table B.3 (expressed in percentage of the average value).

Table B.3 – Reproducibility

Concentration of TTAA mg/kg	**Reproducibility** R %
≤ 50 mg/kg	15
> 50 mg/kg	8

Annex C
(informative)

Determination of pour point depressants by gel permeation chromatography

C.1 Introductory remark

Several commercially available paraffinic oils contain pour point depressants to improve their low temperature properties. This method describes a procedure for the qualitative identification of these compounds.

C.2 Description of the procedure

Pour point depressants are relatively high molecular weight polymers. From a chemical point of view, they can be divided into two general groups: polymethacrylates and polynaphthalenes.

The technique chosen, gel permeation chromatography (GPC) is a high performance liquid chromatography (HPLC) technique in which the typical columns of HPLC, based on the absorption properties of the compounds to be analysed to a specific support, are replaced by other columns packed with spherical polymers which have very precisely defined pore sizes. When a mixture of compounds having different molecular sizes are filtered through such columns, smaller molecules can pass through a large number of channel-like pores, thus eluting after the largest molecules which, if their size is large enough, then they should only be able to pass through the spaces between the polymer spheres.

In the case of detection of pour point depressants in mineral insulating oils, the additives are the first ones to be eluted, well separated from the oil components.

C.3 Materials and reagents

The following materials and reagents are used:

– high performance liquid chromatograph;
– ultraviolet (UV) and refractive index (RI) detectors;
– gel permeation chromatography (GPC) column;
– laboratory glassware;
– tetrahydrofuran (THF).

C.4 Procedure

To a suitable amount of oil in a beaker, e.g. 100 mg, add 10 ml of dry tetrahydrofuran (THF) and mix thoroughly.

Stabilize the HPLC system according to manufacturer's recommendations, especially when working with the RI detector, which is highly influenced by small variations on room temperature.

With a suitable syringe, inject the THF solution into the HPLC, completely filling the injection loop (5 ml) and register the chromatogram.

Polymethacrylates shall be analysed using the RI detector, whereas the UV detector is better for the determination of polynaphthalenes.

C.5 Precision

Not evaluated.

Bibliography

[1] LAMARRE, DUVAL and GAUTHIER, *Analysis of DBPC by HPLC in new and used transformer oils*, J. Chrom., 213, 481-490 (1981)

[2] DUVAL, LAMOTHE, LAMARRE and GIGUÈRE, *Determination of flow improver additives in new and aged insulating oils by gel permeation chromatography*, J.Chrom., 244 (1), 169-173 (1982)

[3] IEC 60422, *Mineral insulating oils in electrical equipment – Supervision and maintenance guidance*

[4] IEC 60590, *Determination of the aromatic hydrocarbon content of new mineral insulating oils*

[5] IEC 61198, *Mineral insulating oils – Methods for the determination of 2-furfural and related compounds*

_____

This page deliberately left blank

British Standards Institution (BSI)

BSI is the independent national body responsible for preparing British Standards and other standards-related publications, information and services.
It presents the UK view on standards in Europe and at the international level.

It is incorporated by Royal Charter.

Revisions

British Standards are updated by amendment or revision. Users of British Standards should make sure that they possess the latest amendments or editions.

It is the constant aim of BSI to improve the quality of our products and services. We would be grateful if anyone finding an inaccuracy or ambiguity while using this British Standard would inform the Secretary of the technical committee responsible, the identity of which can be found on the inside front cover.

Tel: +44 (0)20 8996 9001 Fax: +44 (0)20 8996 7001

BSI offers Members an individual updating service called PLUS which ensures that subscribers automatically receive the latest editions of standards.

Tel: +44 (0)20 8996 7669 Fax: +44 (0)20 8996 7001
Email: plus@bsigroup.com

Buying standards

You may buy PDF and hard copy versions of standards directly using a credit card from the BSI Shop on the website **www.bsigroup.com/shop.** In addition all orders for BSI, international and foreign standards publications can be addressed to BSI Customer Services.

Tel: +44 (0)20 8996 9001 Fax: +44 (0)20 8996 7001
Email: orders@bsigroup.com

In response to orders for international standards, it is BSI policy to supply the BSI implementation of those that have been published as British Standards, unless otherwise requested.

Information on standards

BSI provides a wide range of information on national, European and international standards through its Knowledge Centre.

Tel: +44 (0)20 8996 7004 Fax: +44 (0)20 8996 7005
Email: knowledgecentre@bsigroup.com

Various BSI electronic information services are also available which give details on all its products and services.

Tel: +44 (0)20 8996 7111 Fax: +44 (0)20 8996 7048
Email: info@bsigroup.com

BSI Subscribing Members are kept up to date with standards developments and receive substantial discounts on the purchase price of standards. For details of these and other benefits contact Membership Administration.

Tel: +44 (0)20 8996 7002 Fax: +44 (0)20 8996 7001
Email: membership@bsigroup.com

Information regarding online access to British Standards via British Standards Online can be found at **www.bsigroup.com/BSOL**

Further information about BSI is available on the BSI website at **www.bsigroup.com/standards**

Copyright

BSI Group Headquarters

389 Chiswick High Road London W4 4AL UK

Tel +44 (0)20 8996 9001
Fax +44 (0)20 8996 7001
www.bsigroup.com/standards

raising standards worldwide™