BS EN 62697-1:2012

BSI Standards Publication

Test methods for quantitative determination of corrosive sulfur compounds in unused and used insulating liquids

Part 1: Test method for quantitative determination of dibenzyldisulfide (DBDS)

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National foreword

This British Standard is the UK implementation of EN 62697-1:2012. It is identical to IEC 62697-1:2012.

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.

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Test methods for quantitative determination of corrosive sulfur compounds in unused and used insulating liquids - Part 1: Test method for quantitative determination of dibenzyldisulfide (DBDS)

(IEC 62697-1:2012)

Méthodes d'essai pour la détermination quantitative des composés de soufre corrosif dans les liquides isolants usagés et neufs -
Partie 1: Méthode d'essai pour la détermination quantitative du disulfure de dibenzyle (DBDS)
(CEI 62697-1:2012)

Prüfverfahren zur quantitativen Bestimmung von Verbindungen korrosiven Schwefels in neuen und gebrauchten Isolierflüssigkeiten -
Teil 1: Prüfverfahren zur quantitativen Bestimmung von Dibenzyldisulfid (DBDS)
(IEC 62697-1:2012)

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

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Foreword

The text of document 10/887/FDIS, future edition 1 of IEC 62697-1, prepared by IEC/TC 10 "Fluids for electrotechnical applications" was submitted to the IEC-CENELEC parallel vote and approved by CENELEC as EN 62697-1:2012.

The following dates are fixed:

- latest date by which the document has to be implemented at national level by publication of an identical national standard or by endorsement (dop) 2013-06-28
- latest date by which the national standards conflicting with the document have to be withdrawn (dow) 2015-09-28

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Endorsement notice

The text of the International Standard IEC 62697-1:2012 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:

IEC 60296	NOTE	Harmonised as EN 60296.
IEC 60422	NOTE	Harmonised as EN 60422.
IEC 60567	NOTE	Harmonised as EN 60567.

Annex ZA
(normative)

Normative references to international publications with their corresponding European publications

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

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 60475	-	Method of sampling insulating liquids	EN 60475	-
IEC 62535	2008	Insulating liquids - Test method for detection of potentially corrosive sulphur in used and unused insulating oil	EN 62535	2009

CONTENTS

INTRODUCTION

Sulfur can be present in insulating liquids in various forms, including elemental sulfur, inorganic sulfur compounds and organic sulfur compounds. The number of diverse sulfur species comprised of different isomers and homologous can run into hundreds. The total sulfur(TS) concentration in insulating liquids depends on the origin of the liquid, refining processes and the degree of refining and formulation including addition of additives to the base oils. Base oils include mineral based paraffinic and naphthenic oils, synthetic iso-paraffins obtained through gas to liquid conversion process (GTL-Fischer-Tropsch), esters, poly alpha olefins, poly alkylene glycols, etc. Additives can be comprised of electrostatic discharge depressants, metal deactivators, metal passivators, phenolic and sulfur containing antioxidants such as the polysulfides, disulfides, dibenzyl disulfide (DBDS), etc.

Certain sulfur compounds present in the insulating liquids exhibit antioxidant and metal deactivating properties without being corrosive, whereas other sulfur compounds have been known to react with metal surfaces. Specifically, sulfur compounds such as mercaptans are very corrosive to metallic components of electrical devices. Presence of these corrosive sulfur species has been linked to failures of electrical equipment used in generation, transmission and distribution of electrical energy for several decades. Therefore, the IEC standard for mineral insulating oils states that corrosive sulfur compounds shall not be present in unused and used insulating liquids (see IEC 60296) [5][1].

Recently, the serious detrimental impact of corrosive sulfur has been linked to the presence of a specific highly corrosive sulfur compound, DBDS. This compound has been found in certain mineral insulating oils [1, 14, 15, 16]; presence of this compound has been shown to result in copper sulfide formation on the surfaces of copper conductors under normal operating conditions of transformers [2].

Current standard test methods for detection of corrosive sulfur (ASTM D1275, methods A and B, and DIN 51353) and potentially corrosive sulfur in used and unused insulating oil (IEC 62535) are empirical and qualitative. These methods rely on visual and subjective perception of colour profiles. The methods do not yield quantitative results in regard to the concentration of DBDS or other corrosive sulfur compounds present in insulating liquids.

Furthermore, methods for corrosive sulfur and potentially corrosive sulfur in insulating liquids (ASTM D1275, method B and IEC 62535) are applicable only to mineral insulating oils that do not contain a metal passivator additive, the methods otherwise can yield negative results even when corrosive sulfur compounds are present in the insulating liquids – thus providing a false negative test result. On the other hand, the test method when used with aged insulating oils (e.g. those with relative high acidity), may give ambiguous results and lead to a false positive test result. Further analysis of insulating liquids is stipulated, e.g. IEC 62535 specifies that if there are any doubts in the interpretation of the results of inspection of paper, the composition of precipitate should be analyzed by other methods (for example by SEM-EDX).

For this reason, IEC TC 10 WG 37 was set up to prepare test methods for the unambiguous quantitative determination of corrosive sulfur compounds in unused and used insulating liquids. Because of the complexity of such determinations, the test methods are divided into three parts:

Part 1 – Test method for quantitative determination of dibenzyldisulfide (DBDS).

Part 2 – Test methods for quantitative determination of total corrosive sulfur (TCS).

Part 3 – Test methods for quantitative determination of total mercaptans and disulfides (TMD) and other targeted corrosive sulfur species.

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[1] Figures in square brackets refer to the bibliography.

Health and safety

This part of IEC 62697 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 insulating liquids 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.

Environment

This standard involves mineral insulating oils, natural ester insulating liquids, 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 of chemicals used during the test into the environment.

TEST METHODS FOR QUANTITATIVE DETERMINATION OF CORROSIVE SULFUR COMPOUNDS IN UNUSED AND USED INSULATING LIQUIDS –

Part 1: Test method for quantitative determination of dibenzyldisulfide (DBDS)

1 Scope

This part of IEC 62697 specifies a test method for the quantitative determination of corrosive sulfur compounds-dibenzyl disulfide (DBDS) in used and unused insulating liquids over a 5 – 600 mg kg^{-1} concentration range.

2 Normative references

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

IEC 60475, *Method of sampling liquid dielectrics*

IEC 62535:2008, *Insulating liquids – Test method for detection of potentially corrosive sulfur in used and unused insulating oil*

3 Terms, definitions and abbreviations

For the purposes of this document, the following terms, definitions and abbreviations apply.

3.1 Terms and definitions

3.1.1
accuracy
closeness of agreement between test result and the accepted reference value

3.1.2
additive
a suitable chemical substance that is deliberately added to insulating liquid in order to improve certain characteristics

Note 1 to entry: Examples include antioxidants, pour-point depressants, electrostatic charging tendency depressant such as benzotriazol (BTA) metal passivator or deactivators, antifoam agent, refining process improver, etc.

3.1.3
atomic emission detector
AED
simultaneously monitors emissions of radiation resulting from atomic species excited in a microwave-induced plasma and permits quantitative determination of selected heteroatoms in compounds that elute from a GC column

Note 1 to entry: AED thus provides heteroatom profiles, i.e. “fingerprints” of complex samples such as insulating liquids.

3.1.4
contaminants
foreign substances or materials in an insulating liquid or gas which usually has a deleterious effect on one or more properties

[SOURCE: IEC 60050-212:2010, 212-17-27, modified]

3.1.5
corrosion
disintegration of a metal due to chemical reactions with sulfur and other chemical species in insulating liquids

3.1.6
corrosive sulfur
free sulfur and corrosive sulfur compounds detected by subjecting metals such as copper to contact with an insulating liquid under standardized conditions

[SOURCE: IEC 60050-212:2010, 212-18-20]

3.1.7
dibenzyl disulfide
DBDS
aromatic disulfide containing two benzyl functionalities with a molecular formula $C_{14}H_{14}S_2$, nominal molecular mass of 246 and a melting point of 71 – 72 °C

3.1.8
diphenyl disulfide
DPDS
aromatic disulfide with two phenyl functionalities with a molecular formula $C_{12}H_{10}S_2$, nominal molecular mass of 218 and a melting point of 61 °C – 62 °C

3.1.9
electron capture detector
ECD
device used for quantification of compounds with high electron affinity such as polychlorinated aromatics, nitroaromatics and aromatic disulfides present in gas chromatography effluent at very low concentrations

Note 1 to entry: ECD can have a radioactive internal ionization source (e.g. ^{63}Ni) or thermal electron produced through photo-induced ionization (e.g. helium discharge – HD or photoionization – PID).

3.1.10
flame photometric detector
FPD
detector that uses the chemiluminescent reaction of sulfur-containing compounds in a cool hydrogen/air flame that result in the formation of excited S_2^* species, which decays with broad radiant out around 394 nm that is monitored with an interference filter and a photomultiplier

3.1.11
homologue
compound belonging to a series of compounds that differ in the number of repeating groups

3.1.12
internal standard
IS
substance which is similar in the chemical behaviour (chemical structure – polarity) and analytical response to a certain target analyte

Note 1 to entry: A defined volume of the internal standard solution is added to both the sample and calibration solutions such that they both contain an identical concentration.

3.1.13
isomer
compounds that have the same molecular formula but different structural formula

3.1.14
gas chromatograph
device used for separating volatile and semi-volatile compounds in mixtures that can be vaporized without decomposition through differential migration with a carrier gas through a column

3.1.15
mass spectrometer
MS
instrument used for ionizing neutral chemical species and separating ions according to their mass to charge ratio

Note 1 to entry: It permits determining concentrations of target compounds in complex mixtures such as insulating liquids.

3.1.16
mercaptans (thiols) and disulfides
corrosive organic compounds that contain the functional group composed of a sulfur-hydrogen bond (-SH); disulfides are corrosive compounds that contain a linked pair of sulfur atoms (S-S, disulfide bond)

3.1.17
precision
closeness of agreement between independent test results obtained under stipulated conditions (repeatability conditions or reproducibility conditions)

3.1.18
potentially corrosive sulfur
organo-sulfur compounds present in transformer oils that may cause copper sulfide formation

Note 1 to entry: Some of these compounds may be initially corrosive, or become corrosive under certain operating conditions.

[SOURCE: IEC 62535:2008, 3.1]

3.1.19
qualitative analysis
analysis that establishes the presence or the absence of a compound in a sample

3.1.20
quantitative analysis
analysis that establishes the amount or concentration of a compound in a sample

3.1.21
repeatability conditions
conditions where independent test results are obtained with the same method on identical test items in the same laboratory

3.1.22
repeatability limits
r
value less than or equal to which the absolute difference between two test results obtained under repeatability conditions may be expected to be with a probability of 95 %

3.1.23
reproducibility conditions
conditions where independent test results are obtained with the same method on identical test items in different laboratories with different operators using different equipment

3.1.24
reproducibility limits
R
value less than or equal to which the absolute difference between two test results obtained under reproducible conditions may be expected to be with a probability of 95 %

3.1.25
sulfur chemiluminescence detector
SCD
detector that makes use of a dual plasma burner to combust sulfur-containing compounds to yield sulfur monoxide (SO)

Note 1 to entry: A photomultiplier tube detects the light produced by the chemiluminescent reaction of SO with ozone. This results in a linear and equimolar response to the sulfur compounds without interference from most sample matrices.

3.1.26
tandem mass spectrometer
MS/MS
system that permits selection of specific precursor ion/s and dissociation of these ions to produce characteristic fragment ion/s

Note 1 to entry: Monitoring of fragment ions permits matrix interference-free quantification of targeted compounds in complex samples.

3.1.27
total corrosive sulfur
TCS
sum of all free and chemically bound sulfur in an insulating liquid that reacts with metals such as copper under certain operating conditions

3.1.28
total sulfur
TS
sum of all free sulfur and chemically bound sulfur present in an insulating liquid

3.1.29
trueness
closeness of agreement between the average value obtained from large series of test results and an accepted reference value

3.1.30
unused mineral insulating oil
mineral insulating oil as delivered by the supplier

Note 1 to entry: Such oil should not have been used in, nor been in contact with, electrical equipment not required for manufacture, storage or transportation.

Note 2 to entry: The manufacturer and supplier of unused oil will have taken all reasonable precautions to ensure that there is no contamination with polychlorinated biphenyls or terphenyls (PCBs, PCTs), used, reclaimed or dechlorinated oil or other contaminants

[SOURCE: IEC 60296:2012, definition 3.9, modified]

3.2 Abbreviations

Abbreviation	Term
AED	atomic emission detection
DBDS	dibenzyl disulfide
DPDS	diphenyl disulfide
ECD	electron capture detector
EI	electron ionization
FPD	flame photometric detector
GC	gas chromatography
IS	internal standard
MS	mass spectrometer
SCD	sulfur chemiluninescence detector
MS/MS	tandem mass spectrometer
TCS	total corrosive sulfur
TS	total sulfur

4 Sampling

Samples shall be taken, following the procedure given in IEC 60475. A representative portion shall be taken after thorough mixing. The specific sampling technique can affect the accuracy of this test method.

Precautions should be taken to prevent cross-contamination during sampling.

5 Procedure

5.1 Principle

The oil sample is diluted approximately 1:20 with a suitable solvent, fortified with a known amount of an internal standard (IS) such as DPDS, and injected into the split/splitless injector of a gas chromatograph equipped with a suitable detector including an electron capture detector (ECD), an atomic emission detector (AED), a sulfur chemiluminescence detector (SCD), a flame photometric detector (FPD), a mass spectrometer (MS) or a tandem mass spectrometer (MS/MS).

Separation of oil constituents, DBDS (if present) and DPDS is achieved with a suitable column such as a 30 m to 60 m × 0,25 mm (internal diameter) fused silica column with 5 % polyphenylsiloxane and 95 % methylpolysiloxane or other suitable stationary phase and helium or other suitable carrier gas. Separation is facilitated through temperature programming over a suitable temperature range. DBDS is monitored with the detector and quantified with the internal standard.

NOTE Other suitable detectors such as sulfur chemiluminisence detector or flame photometric detector can be used. However, these detectors were not used during the Round Robin Tests.

5.2 Significance and use

This test method describes the determination of DBDS in insulating liquids for analysis.

DBDS is an aromatic organosulfur compound, which may be present in insulating liquids and impart oxidation stability to the liquids. However, DBDS can react with copper and other metal conductors in transformers, reactors and other similar devices to form copper and other metal sulfides. Therefore, this compound is classified as potentially corrosive sulfur (see IEC 62535).

DBDS has been found in insulating mineral oils at concentrations ranging between 5 mg kg^{-1} and 600 mg kg^{-1}, but it may be present at levels outside this range, in oils that have been blended, or oils in which DBDS have been consumed through its reaction with the copper or other metals.

This method can be used for detecting and quantifying DBDS content in used and unused insulating liquids.

5.3 Interferences

5.3.1 Co-eluting compounds

Interferences experienced during quantitative determination of DBDS will vary with the detector used for quantification of DBDS separated with the gas chromatographic column.

5.3.2 Electron capture detector (ECD)

An ECD is a very sensitive and selective detector that responds to volatile/semi-volatile compounds with high electron affinity. It has gained wide acceptance and use due to its very high sensitivity and selectivity for certain classes of compounds, including halogenated hydrocarbons, organometallic compounds, nitriles, or nitro compounds and disulfides. Presence of such compounds especially polychlorinated biphenyls (PCBs) in insulating liquids can cause interference. In such cases an alternate detector should be used.

5.3.3 Atomic emission detector (AED)

An AED responds to volatile and semi-volatile compounds separated with a gas chromatograph that contains carbon and selected heteroatoms, including sulfur, nitrogen, oxygen and halogens (fluorine, chlorine, bromine and iodine). AED can thus provide a carbon and heteroatom fingerprint of complex mixtures such as insulating liquids. It can be used for quantification of selected additives and their homologues with minimum interferences. It can also be used for determination of origin and formulation through pattern recognition. Interferences can arise from co-eluting sulfur compounds.

5.3.4 Mass spectrometer (MS)

MS is a very sensitive and selective detector that responds to the volatile and semi-volatile compounds. It has gained wide acceptance and use due to its very high sensitivity and selectivity for a broad class of compounds. Compounds present in the GC effluent that give yield ions at m/z 246 or m/z 218 will cause interference if such compounds elute from the GC column with retention times similar to those of the DBDS and DPDS (IS).

5.3.5 MS/MS

MS/MS is a highly sensitive detector that can yield greater specificity for targeted volatile and semi-volatile compounds separated with a gas chromatograph. It minimizes background interferences arising from complex matrices and enhances certainty in quantitative determination of DBDS, other compounds, their isomers (compounds with the same elemental composition but different connectivity) and their homologues (compounds with the same functional group(s) but a different carbon chain) in insulating liquids. This detector provides a largely interference-free response.

5.3.6 Interference from the matrix

The insulating liquid matrix is comprised of hydrocarbons that do not respond well in the ECD; therefore, matrix interference should be low with GC-ECD.

AED response is selective for heteratoms present in an organic compound; therefore, matrix interference should not be encountered.

It is possible that certain insulating liquids can contain molecules that yield ions at m/z 246 and m/z 218. Such molecules can cause interferences with GC-MS.

MS/MS response is highly specific for target compound; therefore, matrix interference should not be present.

5.4 Apparatus

5.4.1 Balance

A balance with a capability for automatic tare, accuracy down to 0,001 g, and a maximum weight range of ≥ 100 g is required.

5.4.2 Gas chromatography system

5.4.2.1 General

Gas chromatograph equipped with:

- a split/splitless injector with temperature stability of better than 0,5 °C and maximum operating temperature above 300 °C;
- an injection device suitable for introducing 1 µl – 10 µl liquids into the column (an automated sampling injection device is preferred);
- a 30 m à 60 m × 0,25 mm (internal diameter) fused silica capillary column with 5 % phenyl polysiloxane and 95 % methylpolysiloxane or other suitable stationary phase;
- a column oven capable of operation over the 30 °C – 300 °C range with ramp rates of up to 20 °C min^{-1}.

5.4.2.2 ECD

ECD with a ^{63}Ni foil detector capable of operating at temperature ~ 300 °C with temperature stability of ≤ 0,5 °C.

5.4.2.3 Atomic emission detector(AED)

AED capable of detecting the sulfur emission line at 181 nm (or other suitable sulfur emission line).

5.4.2.4 Mass spectrometer (MS)

- quadrupole or other suitable MS with an electron ionization (EI) source, operated in positive ion selected ion monitoring (SIM) mode;
- electron energy 70 eV;
- GC – MS interface temperature 270 °C with temperature stability of ≤ 0,5 °C;
- source temperature 200 °C or as recommended by the manufacturer.

5.4.2.5 MS/MS

- triple quadrupole or other suitable MS with an (EI) source, operated in positive ion SIM mode;
- electron energy 70 eV;
- GC – MS interface temperature 270 °C with temperature stability of ≤ 0,5 °C;
- source temperature 200 °C or as recommended by the manufacturer;

– system shall permit selection of precursor ions, dissociation of precursor ion into characteristic fragment ions and quantification of the fragment ions.

5.4.3 Data system

For control, monitoring, acquisition and storage of analytical data.

5.5 Reagents and materials

5.5.1 Purity of reagents

Analytical reagent grade chemicals shall be used in all analysis performed with this method.

5.5.2 Gases

The carrier gas (He or other suitable gases) shall have purity equal to or better than 99,999 % (grade 5). Refer to the specifications provided by the manufacturer of the GC system to verify the purity requirements.

Make up gas for the ECD shall be nitrogen or other gas specified by the instrument manufacturer.

Collision gas for the MS/MS system shall be argon with purity equal to or better than 99,999 %.

5.5.3 Solvents

Toluene may be used for the preparation of the stock solution.

Iso-octane or other suitable solvents should be used for dilution.

Low-boiling solvents such as hexane should not be used because their volatility can cause problems during weighing.

5.6 Standard materials

5.6.1 Dibenzyl disulfide (DBDS)

DBDS is solid at ambient temperature (melting point 71 °C – 72 °C); its purity shall be ≥ 97 %.

Store DBDS in an amber glass bottle with screw cap in a secure place. Keep the bottle away from a source of heat.

5.6.2 Diphenyl disulfide (DPDS)

DPDS is solid at ambient temperature (melting point 61 °C – 62 °C); its purity shall be ≥ 97 %.

Store DPDS in an amber glass bottle with screw cap in a secure place. Keep the bottle away from any heat source.

5.6.3 Blank oil

Insulating liquid that is free from DBDS and DPDS is used for preparation of standard solutions and blank samples.

NOTE White mineral oil with viscosity in the same range as the insulating mineral oil samples is suitable for this purpose.

5.7 Standard solutions

5.7.1 Stock solution

Prepare a solution of DBDS in toluene with known concentration. It is recommended that a fresh stock solution should be prepared every 3 months. The stock solution should be stored in amber glass bottles with polytetrafluoroethylene (PTFE) lined screw caps in refrigerator at ~4 °C. The solution shall be brought to room temperature (~25 °C) prior to its use.

1 000 mg kg^{-1}stock solutions have been found to be stable for at least 3 months. Stability of stock solution should be checked with a fresh standard solution for periods longer than three months.

5.7.2 Internal standard (IS) solution

Diphenyl disulfide (DPDS) is recommended as the internal standard. A stock solution of DPDS should be prepared in toluene at 500 mg kg^{-1} concentration. It is recommended that a fresh IS stock solution should be prepared every 3 months. The stock solution should be stored in amber glass bottles with PTFE lined screw caps in a refrigerator at ~4 °C. The solution shall be brought to room temperature (~25 °C) prior to its use.

6 Instrument set-up

6.1 Gas chromatograph

6.1.1 General

Differences between gas chromatographs and detectors from different manufacturers make it impractical to provide detailed operating conditions. Consult the manufacturer’s instructions for operating the instrument to facilitate separation and detection of DBDS.

6.1.2 Carrier gas

Helium or other suitable gas with purity higher than 99,999 % is recommended as the carrier gas.

6.1.3 Injector

A split/splitless injector is used to introduce a known amount of sample into the gas chromatographic column. The split/splitless injector parameters should be chosen taking into account the capability of the column and the dilution of the sample.

For samples that have been diluted 20 fold, the split mode is appropriate.

The injector temperature should be maintained at 275 °C to avoid condensation of the oil. A borosilicate glass liner with glass-wool is recommended to increase the vaporization rate of the injected sample.

6.1.4 Separation parameters

Capillary columns, 30 m to 60 m, with 0,25 mm internal diameter and 0,32 µm 5 % phenyl 95 % methyl polysiloxane stationary phase thickness, have been found to be suitable for chromatographic separation of DBDS. Good chromatographic separation can also be achieved with columns with other suitable stationary phases (e.g. methyl polysiloxane). When using columns with other stationary phases, chromatographic separation of organo-sulfur compounds should be checked to ensure adequacy of separation prior to the use of columns for DBDS analysis.

Column oven temperature programming parameters given in Table 1 have been found to give satisfactory separation; however, other parameters may be used with other columns.

Table 1 – Column oven temperature programming parameters

Initial temperature °C	**Initial hold** min.	**Ramp rate** °C	**Final temperature** °C	**Final hold** min.
90	0	10	275	10

The temperature ramp may be adjusted to optimize separation and elution time.

A carrier gas flow rate between 0,8 ml/min to 1,5 ml/min is suitable.

6.1.5 ECD detection

Set the ECD detector to a temperature of 280 °C to 340 °C. Nitrogen or other suitable gas is used as the make-up gas. Follow the manufacturer’s recommendation for operation of the ECD.

6.1.6 AED detection

Set the AED detector for detecting the sulfur emission line at 181 nm (or other suitable wavelength). Hydrogen and oxygen are normally used as the reagent gases in the discharge tube of the AED emission source.

An automatic correction of background is recommended, due to the interferences of carbon at 179 nm. Follow the manufacturer’s recommendation for operation of the AED.

6.1.7 MS detection

Operate the MS with an EI source in positive ion mode and set the electron energy at 70 eV.GC-MS interphase and source temperature should to set at 270 °C and 200 °C, respectively. Set the MS in SIM mode for detection and quantification of selected DBDS and DPDS ions given in Table 2. Follow the manufacturer’s instruction for setting up the instrument.

Table 2 – Mass spectrometer parameters

DBDS ions	**Dwell time** ms
246	100
DPDS ions	
218	100

6.1.8 MS/MS detection

Operate the tandem MS with an electron ionization (EI) source in positive ion mode, set electron energy at 70 eV. Detection is carried out with a triple quadrupole mass spectrometer operated with an EI source in the positive ion mode. GC-MS interphase and source temperatures should be set at 270 °C and 200 °C, respectively. In a triple quadrupole system the first quadrupole (Q1) mass filter shall be set to transmit ions with m/z 218 and m/z 246 for DPDS and DBDS. Ion energy should be set at 15 eV. The second quadrupole (Q2) shall be operated as the collision chamber in which collisions of selected precursor ion with argon atoms (Ar) lead to fragment ion through collision induced dissociation (CID). The collision gas pressure shall be set at 0,2 mtorr. The third quadrupole (Q3) shall be set to transmit product ion with m/z 91 and m/z 109 [3]. Follow manufacturer’s instructions for setting up of the instrument.

6.2 Calibration

6.2.1 General

The response of DBDS is compared with the response of a known amount of DPDS (IS).

6.2.2 Calibration procedure

Prepare the calibration standard solutions by introducing known volumes of the stock solution (see 5.7.1) in DBDS free mineral oil. Weigh out 0,25 g aliquots of the fortified oil samples to the nearest 0,001 g and dilute with 5ml of isooctane or other suitable solvent. Add a known amount of the IS solution (see 5.7.2) to the calibration standard.

Calibration standard solutions should be prepared fresh each month. If the standard solutions are kept for longer periods, these should be compared with fresh solutions. Calibration standards should cover the 5 mg kg^{-1} to 600 mg kg^{-1} concentration range, an IS concentration of 50 mg kg^{-1} has been found to be satisfactory.

6.2.3 Response factor determination (ECD and AED)

Add a known amount of IS solution (see 5.7.2) by weight or using a calibrated syringe (with 50 mg kg^{-1} IS).

Analyse the fortified oil samples following the same procedure used for the samples. Run the analysis in triplicate.

Calculate the response factor (k) as:

$$k = [A_{\text{IS}} \times m_{\text{DBDS}}] / [m_{\text{IS}} \times A_{\text{DBDS}}] \qquad (1)$$

where

A_{IS} is the area of the DPDS or other suitable IS peak;
A_{DBDS} is the area of the DBDS peak;
m_{DBDS} is the mass of DBDS added to the oil in mg;
m_{IS} is the mass of DPDS or other suitable IS added to the oil in mg.

6.2.4 Response factor determination (MS)

Add a known amount of IS solution (see 5.7.2) by weight or using a calibrated syringe (with 50 mg kg^{-1} IS).

Analyse the fortified oil samples following the same procedure used for the samples. Run the analysis in triplicate.

Calculate the constant RF (k) as:

$$k = [A_{\text{IS}} \times m_{\text{DBDS}}] / [m_{\text{IS}} \times A_{\text{DBDS}}] \qquad (2)$$

where

A_{IS} is the area of the molecular ion peak m/z 218 of the DPDS (IS); a suitable ion shall be monitored in case a different IS is used;
A_{DBDS} is the area of the molecular ion peak m/z 246 of the DBDS;
m_{DBDS} is the known mass of DBDS added to the oil in mg;
m_{IS} is the known mass of DPDS or other suitable IS added to the oil in mg.

6.2.5 Response factor determination (MS/MS)

Add a known amount of IS solution (see 5.7.2) by weight or using a calibrated syringe (with 50 mg kg^{-1} IS).

Analyse the fortified oil samples following the same procedure used for samples. Run the analysis in triplicate.

Calculate the constant RF (k) as:

$$k = [A_{\text{IS}} \times m_{\text{DBDS}}\ / [m_{\text{IS}} \times A_{\text{DBDS}}] \tag{3}$$

where

A_{IS}	is the area of the fragment ion peak m/z 109 resulting from collision-induced dissociation (CID) of molecular ion m/z 218 of the DPDS; another suitable ion shall be selected when a different IS is used;
A_{DBDS}	is the area of the fragment ion peak m/z 91 resulting from CID of molecular ion m/z 246 of the DBDS;
m_{DBDS}	is the known mass of DBDS added to the oil in mg;
m_{IS}	is the known mass of DPDS or other suitable IS added to the oil in mg.

6.3 Analysis

6.3.1 Sample pre-treatment

Weigh out a 0,25 g aliquot of homogenized oil sample into a glass container to the nearest 0,001 g. Record the weight of sample as W_{OIL}.

Dilute to 5 ml with isooctane or other suitable solvent.

Add (by weight or volume) a known amount of DPDS; the recommended amount is 50 µg.

Mix the solution obtained by shaking it briefly by hand, and take an aliquot for the analysis.

6.3.2 Sample injection

Inject 1 µl of sample solution into the gas chromatographic system by means of a micro syringe. The use of an automated sampler is preferred.

If a split technique is used, set the appropriate split ratio and the injected volume.

6.3.3 Chromatographic run

Run the established temperature ramp, acquire and store the detector (ECD, AED or other suitable detector) signal with suitable chromatographic data system.

6.3.4 Peak integration

The data systems are equipped with peak integration capability. Verify the proper integration and, in case of error, make manual adjustment if and when required.

Record the area of DBDS peak as ADBDS and the area of DPDS peak as AIS; use these for calculating DBDS concentration.

6.4 Calculations

6.4.1 ECD and AED

Calculate the DBDS concentration in oil with Equation (4):

$$\text{mg kg}^{-1}\ [\mu\text{g g}^{-1}]\ \text{DBDS} = [k \times m_{\text{IS}} \times A_{\text{DBDS}}] / [A_{\text{IS}} \times W_{\text{OIL}}] \tag{4}$$

where

A_{IS} is the area of the peak of the DPDS;

A_{DBDS} is the area of the peak of the DBDS (if detected);

m_{IS} is the mass of DPDS added into the sample oil;

W_{OIL} is the amount of oil weighted for the analysis.

6.4.2 Mass spectrometer (MS)

Calculate the result as:

$$\text{mg kg}^{-1}\ [\mu\text{g g}^{-1}]\ \text{DBDS} = [k \times m_{\text{IS}} \times A_{\text{DBDS (m/z 246)}}] / [A_{\text{IS (m/z 218)}} \times W_{\text{OIL}}] \tag{5}$$

where

A_{IS} is the area of the extracted molecular ion peak m/z 218 of the DPDS, when a different IS is used, another suitable ion peak shall be monitored;

A_{DBDS} is the area of the extracted molecular ion peak m/z 246 of the DBDS;

m_{IS} is the mass, in mg, of DPDS or other suitable IS added to the sample oil;

W_{OIL} is the weight of the oil sample used for the analysis.

6.4.3 MS/MS

Calculate the result as:

$$\text{mg kg}^{-1}\ [\mu\text{g g}^{-1}]\ \text{DBDS} = [k \times m_{\text{IS}} \times A_{\text{DBDS (m/z 91)}}] / [A_{\text{IS(DPDS m/z 109)}} \times W_{\text{OIL}}] \tag{6}$$

where

A_{IS} is the area of the fragment ion peak m/z 109 resulting from CID of molecular ion m/z 218 of the DPDS; another suitable ion shall be selected when a different IS is used;

A_{DBDS} is the area of the extracted ion peak of the DBDS at m/z 91 (if detected);

m_{IS} is the mass of DPDS added into the sample oil (in µg);

W_{OIL} is the amount of oil weighted for the analysis (in g).

6.5 Results

Report DBDS concentrations in mg kg^{-1} to two significant figures.

7 Precision data

7.1 Detection limit

Detection limit for the procedure outlined above is expected to be ≤ 5 mg kg^{-1}. Each laboratory should determine its own detection limit.

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 3 (expressed as a percentage of the average value).

Table 3 – Repeatability limit

Concentration mg/kg	**Repeatability, *r*** %
17	15
150	10
350	10
430	10

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 4 (expressed in percentage of the average value).

Table 4 – Reproducibility limit

Concentration mg/kg	**Reproducibility, *R*** **%**
17	20
150	15
350	15
430	15

8 Report

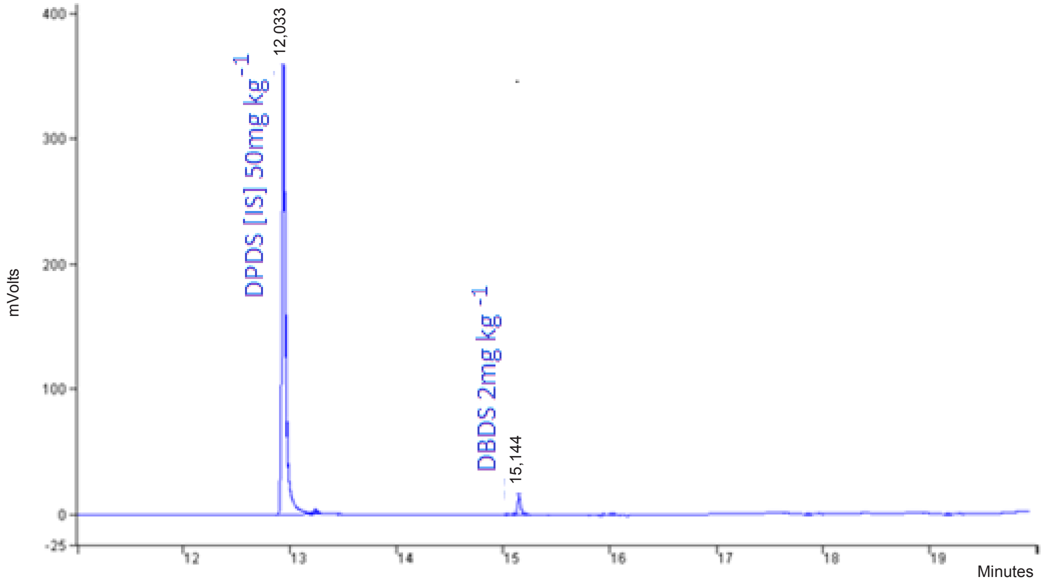
The test report shall contain at least the following information:

- the name of testing laboratory;
- the type and identification of the product tested;
- a reference to this standard, IEC 62697-1.
- the result of the test (see 6.5).
- the procedure used, including the type of detector.
- any deviation, by agreement or otherwise, from the procedure specified.
- the date of the test.

Annex A
(informative)

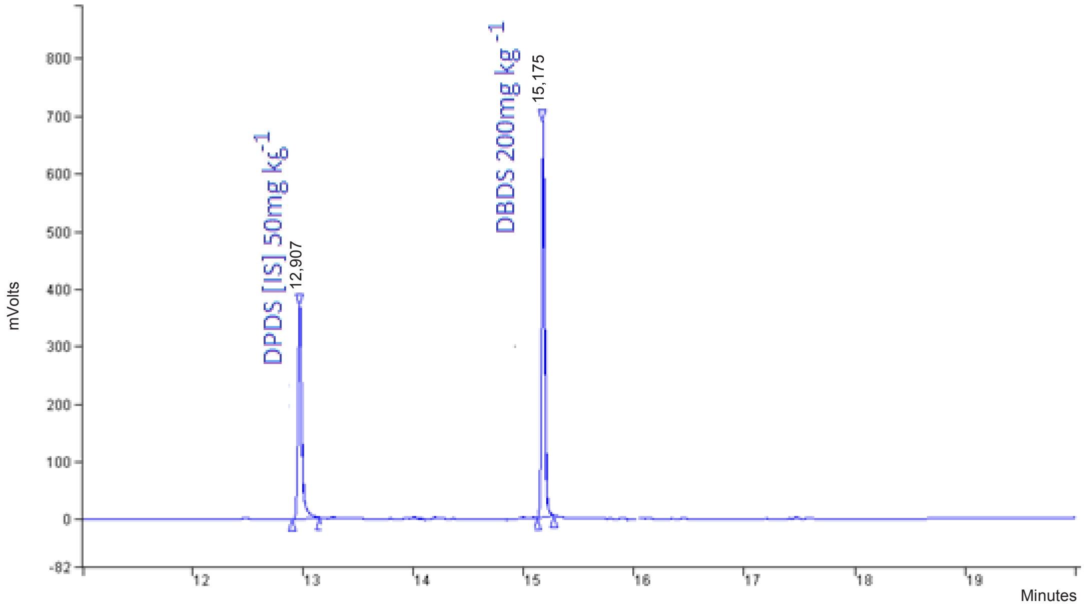
Figures with typical chromatograms and results

A.1 Chromatograms of DBDS standard and DPDS (IS) in white mineral oil and in mineral insulating oils obtained with GC-ECD



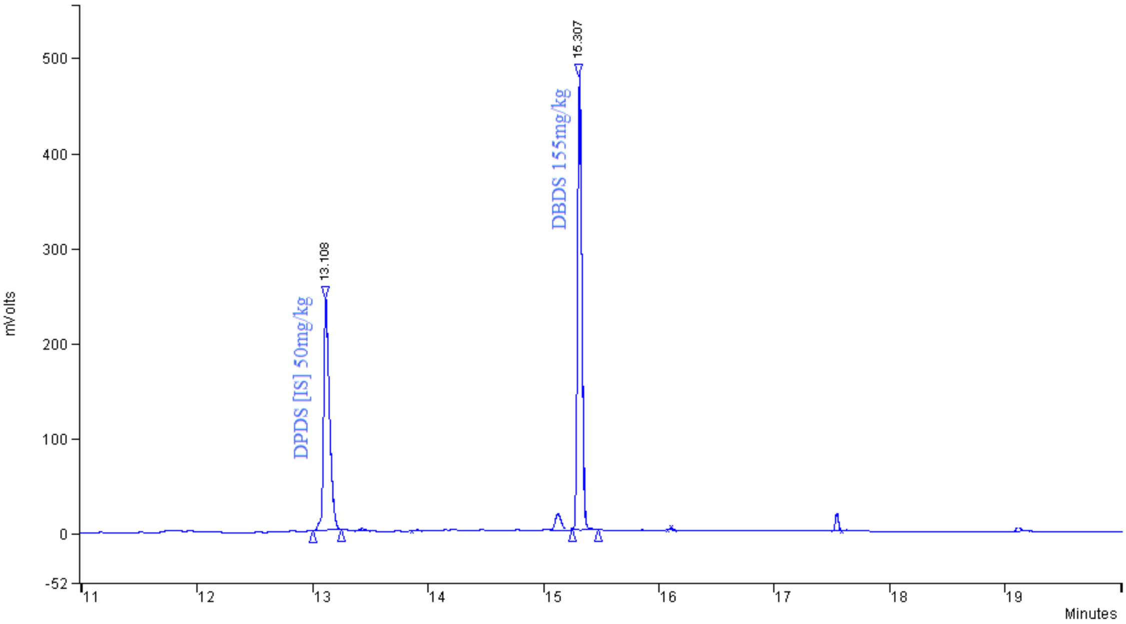
IEC 1603/12

Figure A.1 – GC-ECD chromatogram of 2 mg kg^{-1} DBDS and DPDS (IS) in white mineral oil



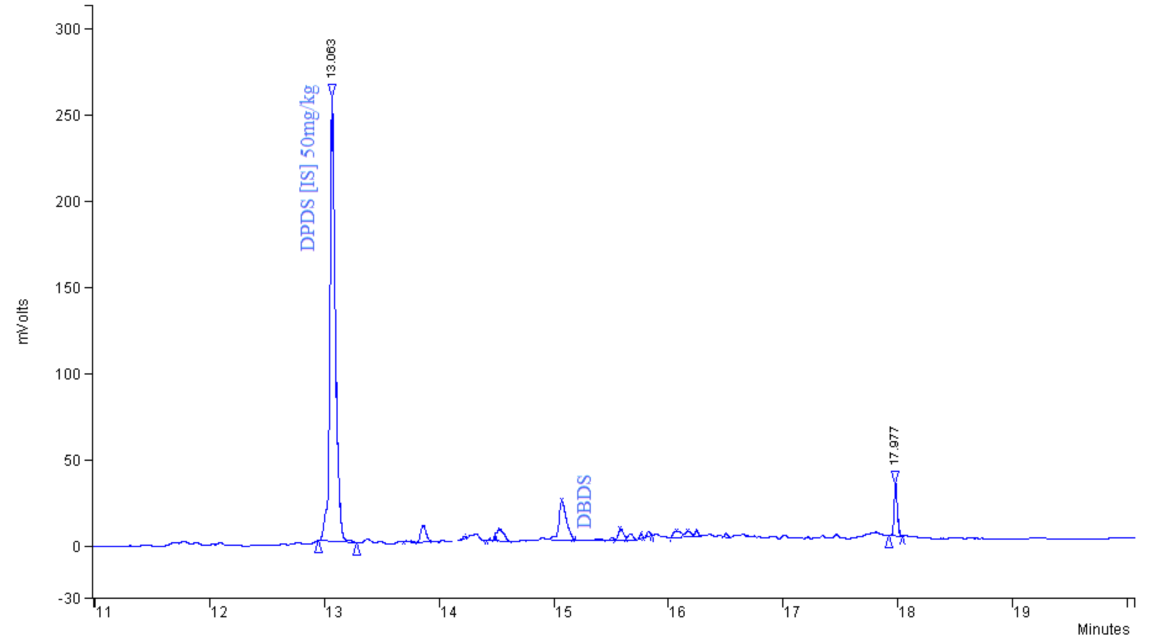
IEC 1604/12

Figure A.2 – GC-ECD chromatogram of 200 mg kg^{-1} DBDS and DPDS (IS) in white mineral oil



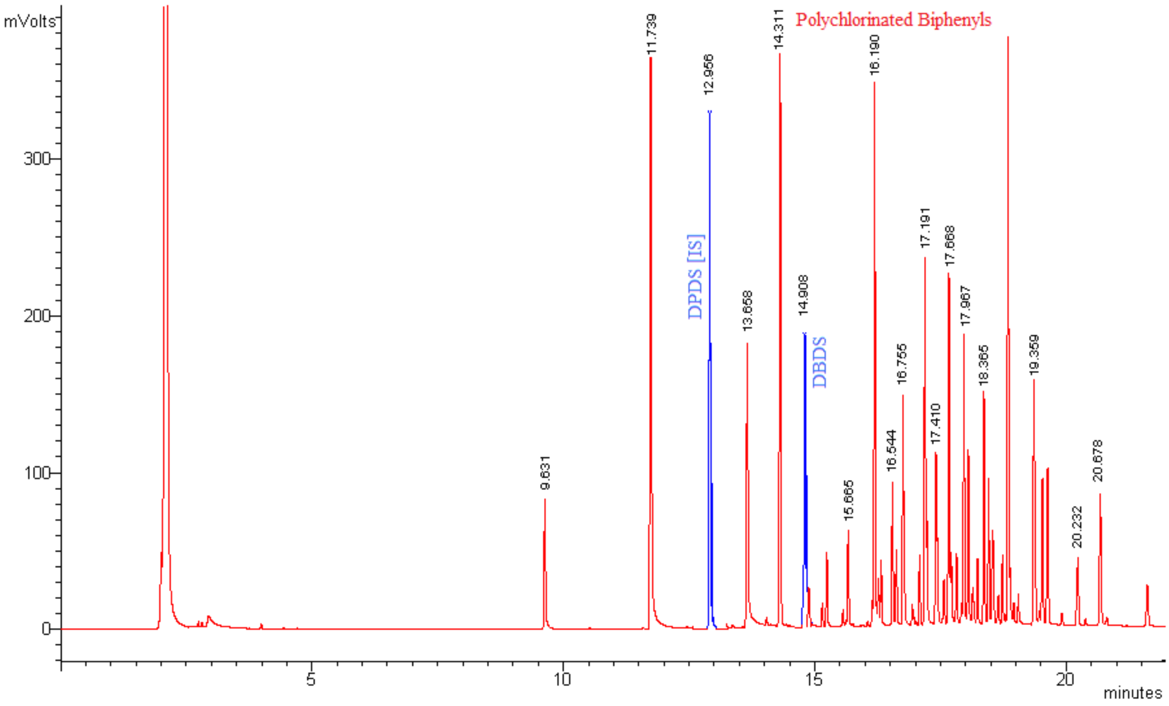
IEC 1605/12

Figure A.3 – GC-ECD chromatogram of commercial mineral insulating oil with a known DBDS contamination



IEC 1606/12

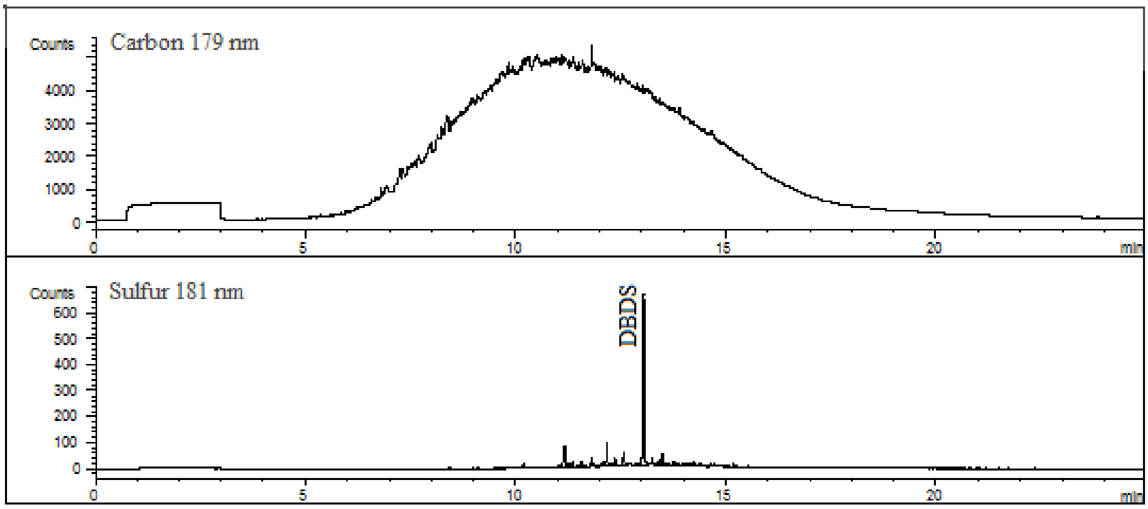
Figure A.4 – GC-ECD chromatogram of commercial mineral insulating oil with no known DBDS contamination



IEC 1607/12

Figure A.5 – GC-ECD chromatogram of commercial mineral insulating oil with known DBDS contamination fortified with acommercial polychlorinated biphenyls (PCBs) formulation

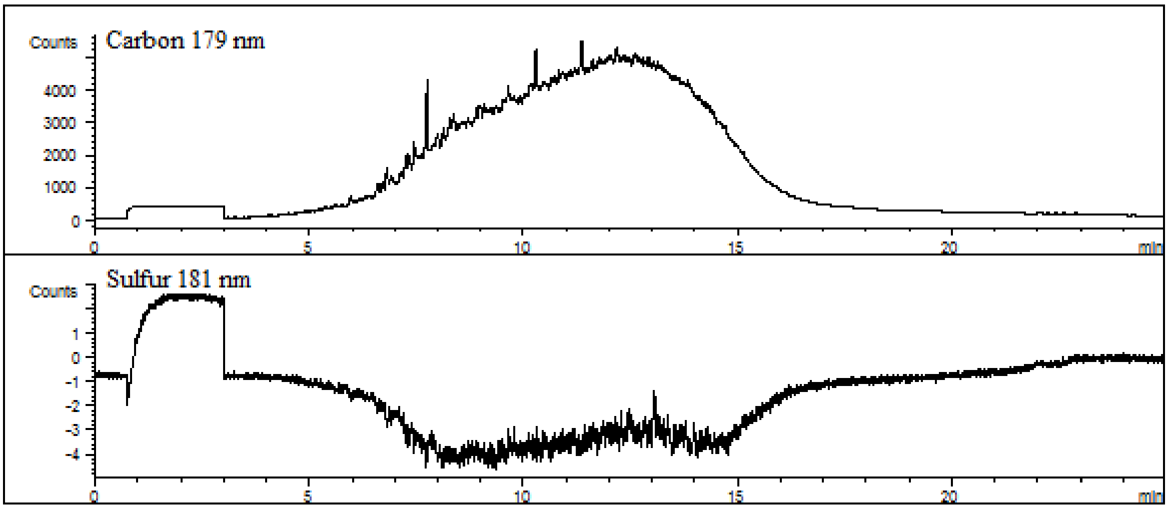
A.2 Chromatograms of DBDS in mineral insulating oils obtained with GC-AED



IEC 1608/12

NOTE The upper trace represents carbon emission monitored at λ 179 nm while the bottom trace represents sulfur emission monitored at 181 nm.

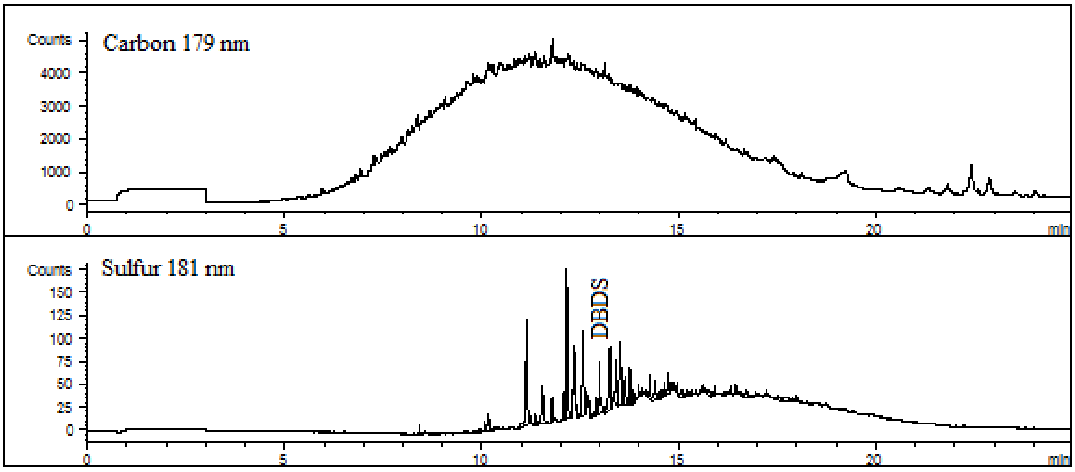
Figure A.6 – Carbon and sulfur (C-S) oil finger prints of a commercial mineral insulating oil with known DBDS contamination obtained with GC-AED



IEC 1609/12

NOTE The upper trace represents carbon emission monitored at λ 179 nm while the bottom trace represents sulfur emission monitored at 181 nm.

Figure A.7 – C-S oil fingerprints of a commercial mineral insulating oil with no known DBDS contamination obtained with GC-AED

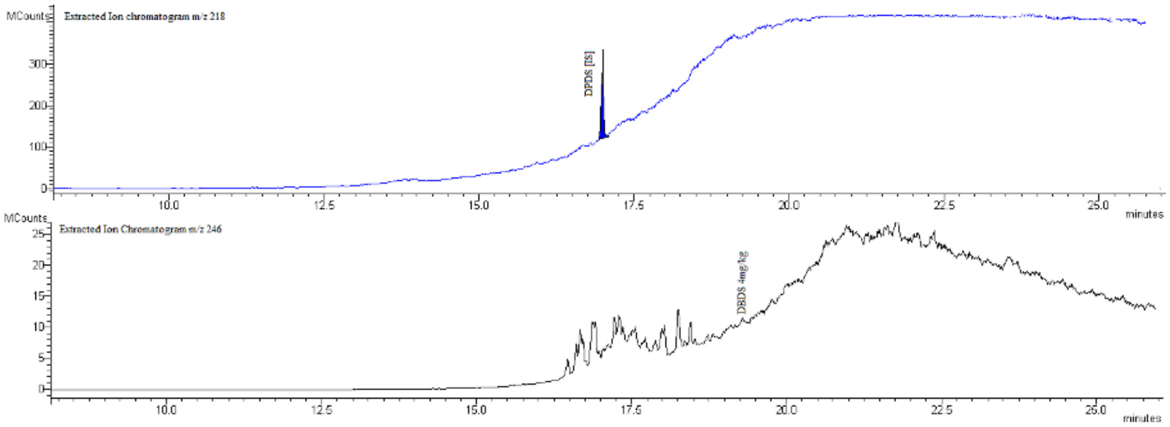


IEC 1610/12

NOTE Observe the presence of other sulfur species (corrosive and non-corrosive sulfur compounds) in the oil.

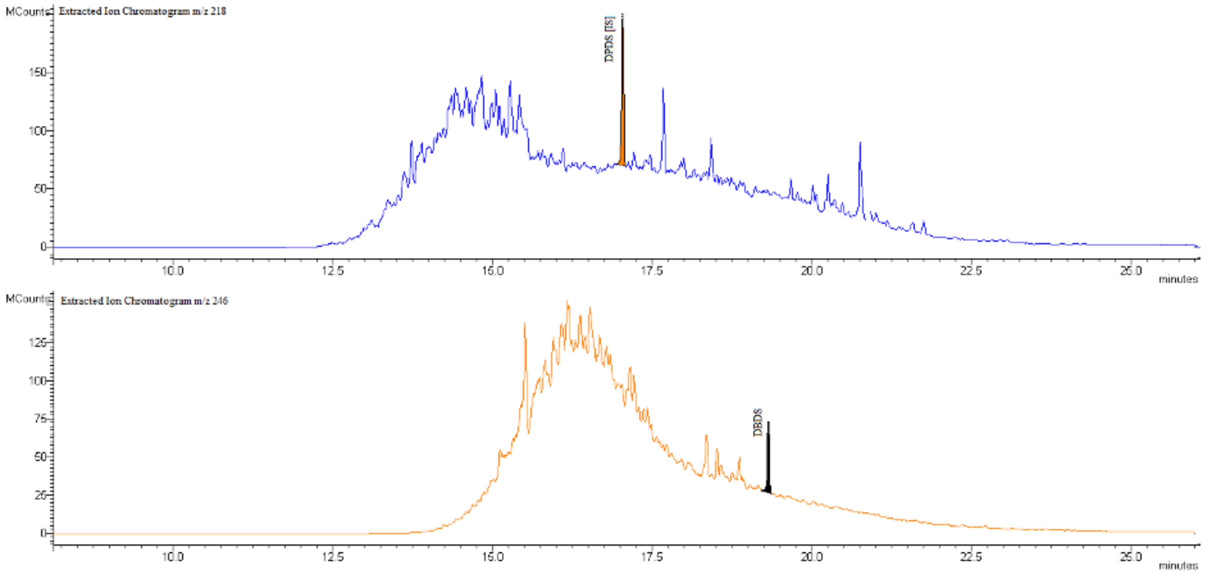
Figure A.8 – C-S oil fingerprints of a commercial mineral insulating oil with known DBDS contamination obtained with GC-AED

A.3 Extracted ion chromatograms of DBDS in mineral insulating oils obtained with GC-MS



IEC 1611/12

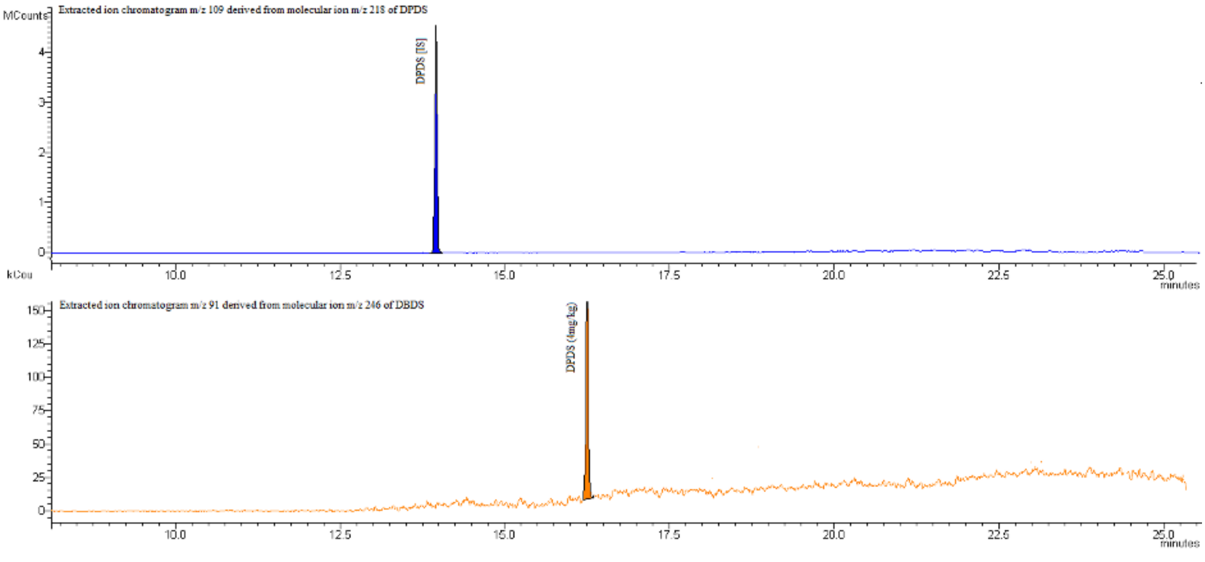
Figure A.9 – Extracted ion chromatograms of DPDS (IS) molecular ion m/z 218 and DBDS molecular ion m/z 246 in white mineral fortified with DBDS, concentration 4 mg kg^{-1}



IEC 1612/12

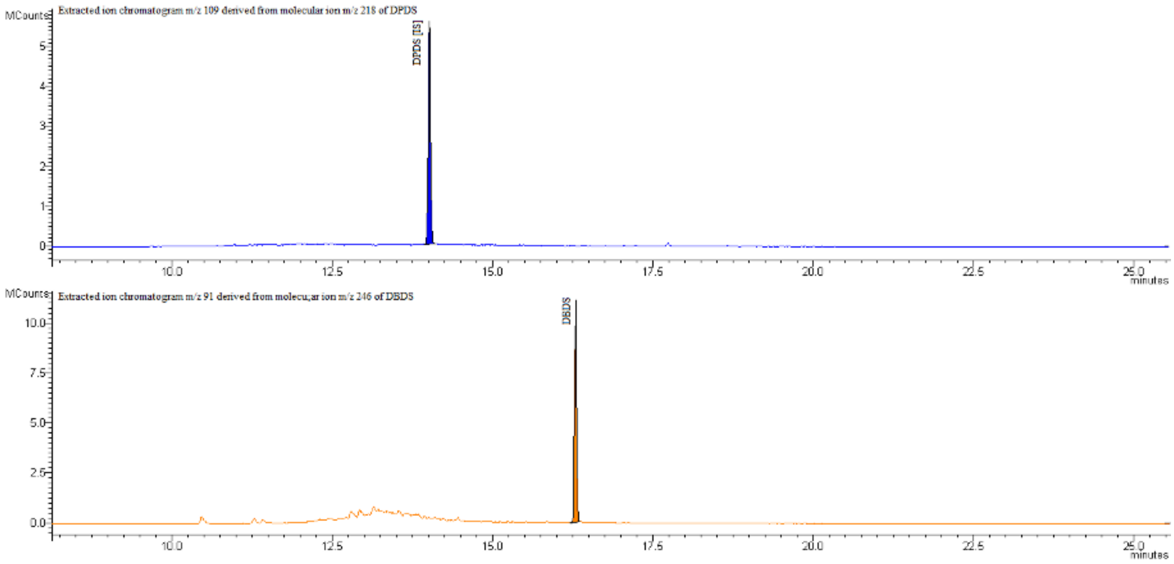
Figure A.10 – Extracted ion chromatograms DPDS (IS) molecular ion m/z 218 and DBDS molecular ion m/z 246 in commercial mineral insulating oil with known DBDS contamination

A.4 Extracted ion chromatograms of DBDS in mineral insulating oils obtained with GC-MS/MS



IEC 1613/12

Figure A.11 – Extracted ion chromatograms m/z 109 derived from CID of DPDS (IS) molecular ion m/z 218 and m/z 91 derived from CID of DBDS molecular ion m/z 246 in white mineral fortified with DBDS (4 mg/kg)



IEC 1614/12

Figure A.12 – Extracted ion chromatograms m/z 109 derived from CID of DPDS (IS) molecular ion m/z 218 and m/z 91 derived from CID of DBDS molecular ion m/z 246 in a commercial mineral oil with known DBDS contamination

Annex B
(informative)

Operating parameters for other suitable detectors

B.1 Flame photometric detector (FPD)

The FPD detector provides a selective signal for sulfur species including DBDS in the form of a broad light emission centred around 393 nm. The emission is separated with an interference filter with a 20 nm bandpass with a peak transmission at 393 nm. The filter is mounted in front of a photomultiplier that provides an electrical signal that is amplified and linearized. Typical detector operating conditions are as follows:

a) temperature 250 °C;

b) H_2 flow 75 mL min^{-1};

c) air flow 100 mL min^{-1}.

For optimal operating conditions, follow the manufacturer's recommendations.

B.2 Photonization detector (PID)

PID provides a selective ionization signal for chemical species depending on the ionization energy of the chemical species and the energy of incident photons. Ionization of chemical species occurs when the ionization energy of chemical species is less than the energy of photons. The detector can be used for selective determination of aromatic molecules with lower ionization in the presence of a hydrocarbon background with higher ionization energy. The detector is operated at 250 °C. Photoionization lamps with energy output at 10 eV are suitable for DBDS determination. For optimal operating conditions, follow the manufacturer's recommendations.

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