IEC 62697-1

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INTERNATIONAL STANDARD

NORME INTERNATIONALE

colour inside

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)

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)

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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)

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

FDIS	Report on voting
10/887/FDIS	10/891/RVD

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

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

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

- reconfirmed,
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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