IEC TR 62697-3

Edition 1.0 2018-02

TECHNICAL REPORT

Test methods for quantitative determination of corrosive sulfur compounds in unused and used insulating liquids –
Part 3: Test method for quantitative determination of elemental sulfur

colour inside

IEC TR 62697-3:2018-02(en)

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INTERNATIONAL
ELECTROTECHNICAL
COMMISSION

ICS 29.040.10

ISBN 978-2-8322-5361-8

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CONTENTS

INTERNATIONAL ELECTROTECHNICAL COMMISSION

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

Part 3: Test method for quantitative determination of elemental sulfur

FOREWORD

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IEC TR 62697-3, which is a Technical Report, has been prepared by IEC technical committee 10: Fluids for electrotechnical applications.

The text of this Technical Report is based on the following documents:

Draft TR	Report on voting
10/1014/DTR	10/1028/RVDTR

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

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

A list of all parts in the IEC 62697 series, published under the general title *Test methods for quantitative determination of corrosive sulfur compounds in unused and used insulating liquids*, can be found on the IEC website.

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

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- withdrawn,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

A bilingual version of this publication may be issued at a later date.

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

INTRODUCTION

During the IEC technical committee 10 plenary meeting in 2007, it was decided to set up a working group with the aim of developing a standard on "quantitative determination of corrosive sulfur compounds in insulating fluids".

TC 10 decided to divide the overall task into three parts:

- Part 1: Test method for quantitative determination of dibenzyl disulfide (DBDS);
- Part 2: Test method for quantitative determination of total corrosive sulfur (TCS);
- Part 3: Test method for quantitative determination of elemental sulfur.

Part 1 was published in 2012, however the work for the preparation of Part 2 and Part 3 took longer than anticipated. During the TC 10 plenary meeting in 2015, in order to finalize the important work achieved, a proposal was made to complete the work and publish Part 2 and Part 3 as Technical Reports.

Sulfur can be present in insulating liquids in various forms, including elemental sulfur, inorganic sulfur compounds and organic sulfur compounds. The number of diverse sulphur 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).

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, IEC 60296 states that corrosive sulfur compounds shall not be present in unused and used insulating liquids.

The serious detrimental impact of corrosive sulfur has also been linked to the presence of a specific highly corrosive sulfur compound, DBDS. This compound has been found in certain mineral insulating oils [1], [15], [16], [17][1]; 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]. It has been reported that elemental sulfur and other corrosive sulfur compounds such as mercaptans may be introduced during reclamation of mineral oil with adsorbents reactivated through a combustion process. A proposal for inclusion of a test method for quantification elemental sulfur in IEC 62697 was made by CIGRE WG A2.40. The proposal was approved by IEC TC 10 in 2013. Several methods for quantification of elemental sulfur in petroleum products and other matrices have been reported, however, methods do not directly deal with quantification of elemental sulfur in insulating oils.

However, current standard test methods for the detection of corrosive sulfur ([11] and [13]) and potentially corrosive sulfur in used and unused insulating oil [8] 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.

[1] Numbers in square brackets refer to the Bibliography.

Furthermore, methods for corrosive sulfur and potentially corrosive sulfur in insulating liquids ([8] and [11]) are applicable only for mineral insulating oils that do not contain a metal passivator additive, as these methods can otherwise 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, for example IEC 62535 specifies that if there are any doubts in the interpretation of the results of the inspection of paper, the composition of precipitate should be analysed by other methods (e.g. by SEM-EDX).

For this reason, a working group within IEC TC 10 was set up to prepare test methods for the unambiguous quantitative determination of corrosive sulfur compounds in unused and used insulating liquids.

WARNING – 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 this document 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 document 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 document involve the use of processes that could lead to a hazardous situation. Attention is drawn to the relevant standard for guidance.

WARNING – Environment

This document 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 3: Test method for quantitative determination of elemental sulfur

1 Scope

This part of IEC 62697 specifies a test method for the quantitative determination of elemental sulfur in used and unused insulating liquids over a 2 mg kg^{-1} to 400 mg kg^{-1} concentration range.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements 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 62697-1, *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 TR 62697-2, *Test methods for quantitative determination of corrosive sulfur compounds in unused and used insulating liquids – Part 2: Test method for quantitative determination of total corrosive sulfur (TCS)*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in IEC 62697-1 and IEC TR 62697-2 and the following apply.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

- IEC Electropedia: available at http://www.electropedia.org/
- ISO Online browsing platform: available at http://www.iso.org/obp

3.1
elemental sulfur
unbound form of the element with atomic number 16

Note 1 to entry: Under normal conditions, sulfur atoms occur in different forms (allotropes) of which the orthorhombic, cyclic octatomic form with chemical formula S_8 is the most abundant. This form is a bright yellow crystalline solid at room temperature.

3.2
allotropy
property of some chemical elements to exist in two or more different forms, in the same physical state

3.3
sulfur allotropes
sulfur which exists in a number of different allotropic forms

Note 1 to entry: These include the most abundant S_8 and sulfur rings comprised of 6, 7, 9, 15, 18 and 20 atoms. In addition to the allotropes, each allotrope often exists in polymorphs, delineated by Greek prefixes (α, β, etc.).

3.4
polymorphs
two or more minerals that have the same chemical composition for example S_8, but differ in their atomical arrangement and crystal structure

4 Sampling

Samples should be taken, following the procedure given in IEC 60475. A representative portion should 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

5.1.1 Determination with gas chromatography

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), a sulfur chemiluminescence detector (SCD), a flame photometric detector (FPD), an atomic emission detector (AED) or a mass spectrometer (MS).

Separation of oil constituents, elemental sulfur (if present) and IS is achieved with a suitable column such as a 15 m to 30 m × 0,25 mm (internal diameter) fused silica column with 5 % polyphenylsiloxane and 95 % methyl polysiloxane or other suitable stationary phase and helium or other suitable carrier gas. Separation is facilitated through temperature programming over a suitable temperature range. Elemental sulfur is monitored with the detector and quantified with the internal standard.

NOTE During the Round Robin Tests on the ECD, an FPD and an MS were used. Other suitable detectors such as sulfur chemiluminisence and atomic emission detector were not used.

5.1.2 Determination with differential pulse voltammetry

The test procedure is based on two standard additions. 10 ml of the base electrolyte is positioned in the test cell with the electrodes. 0,5 ml of the oil to be tested is added. The current density is recorded.

5.2 Significance and use

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

The most common form of elemental sulfur is the octacyclic form with formula S_8. If present, elemental sulfur 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).

Elemental sulfur is present in petroleum and may be present in insulating mineral oils at concentrations ranging between 1 mg kg^{-1} and 400 mg kg^{-1}, but it may be present at levels