IEC TR 62697-2

Edition 1.0 2018-02

TECHNICAL REPORT

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)

IEC TR 62697-2:2018-02(en)

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INTERNATIONAL
ELECTROTECHNICAL
COMMISSION

ICS 29.040.10

ISBN 978-2-8322-5362-5

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CONTENTS

FOREWORD 4
INTRODUCTION 6
1 Scope 8
2 Normative references 8
3 Terms and definitions 8
4 Sampling 9
5 Procedure 9
5.1 Principle 9
5.2 Significance and use 9
5.3 Interferences 9
5.3.1 General 9
5.3.2 Interferences in turbidity measurements 10
5.3.3 Interferences in ion chromatography measurements 10
5.4 Apparatus 10
5.4.1 Balance 10
5.4.2 Hot plate with stirrer 10
5.4.3 Heating block 10
5.4.4 Turbidity monitor 10
5.4.5 Ion chromatograph 10
5.4.6 Data system 10
5.5 Reagents and materials 10
5.5.1 Purity of reagents 10
5.5.2 Gases 10
5.5.3 Solvents 10
5.6 Standard materials 11
5.6.1 Dibenzyl disulfide (DBDS) 11
5.6.2 Blank oil 11
5.6.3 Copper powder 11
5.6.4 Potassium nitrate 11
5.6.5 Hydrochloric acid 11
5.6.6 Barium chloride 11
5.7 Standard solutions 11
5.7.1 Stock solution 11
5.7.2 Internal standard (IS) solution 11
6 Instrument set-up 12
6.1 Turbidity monitor 12
6.2 Ion chromatograph 12
6.2.1 General 12
6.2.2 Column 12
6.2.3 Mobile phase 12
6.2.4 Injector 12
6.2.5 Suppressor 12
6.2.6 Conductivity detector 12
6.3 Corrosive chemistry 13
6.3.1 Reaction of corrosive sulfur compounds with copper – formation of Cu_2S 13

6.3.2 Conversion of cuprous sulfide into cupric sulfate 13
6.3.3 Quantification of cupric sulfate in solution 14
6.3.4 Turbidity measurement 14
6.3.5 Ion chromatography measurement 14
6.4 Calibration 14
6.4.1 General 14
6.4.2 Calibration procedure 14
6.4.3 Quantification of total corrosive sulfur (TCS) 15
6.4.4 Quantification of total corrosive sulfur and DBDS equivalents ($DBDS_{eq}$) 15
6.5 Results 15
7 Precision data 15
7.1 Detection limit 15
7.2 Repeatability 16
7.3 Reproducibility 16
8 Report 16
Annex A (informative) Figures with typical chromatograms and results 17
Annex B (informative) RRT results for quantitative determination of corrosive sulfur 18
Bibliography 18

Figure A.1 – Ion exchange chromatography detection DBDS as sulfate 17
Figure A.2 – Photograph of turbidity meter cuvette containing $BaSO_4$ suspension 17

Table 1 – Repeatability limit 16
Table 2 – Reproducibility limit 16
Table B.1 – Turbidity and ion chromatography 18
Table B.2 – RRT results for quantitative determination of DBDS (GC-ECD or GC-AED) – Sample number 1 to 7 19
Table B.3 – RRT results for potentially corrosive sulfur according to IEC 62535 – Sample number 1 to 7 19

INTERNATIONAL ELECTROTECHNICAL COMMISSION

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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)

FOREWORD

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IEC TR 62697-2, 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
10/1013/DTR	10/1027/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.

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. Hundreds of diverse sulfur species comprised of different isomers and homologous have been identified in petroleum products. To simplify quantification, sulfur species are expressed as the total sulfur (TS). Total sulfur concentration in insulating liquids depends on the origin of the base oils, 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 olefins, poly alkylene glycols, etc. To improve characteristics of insulating liquids, additives are sometimes added. Additives can be comprised of electrostatic discharge depressants, metal deactivators, metal passivators, phenolic and sulfur containing antioxidants.

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 and lead to the formation of metal sulfides. 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.

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]. A specific standard test method for quantitative determination of this corrosive compound has been developed (see IEC 62697-1).

However, current standard test methods for the detection of corrosive sulfur species ([11], and [13]) and potentially corrosive sulfur in used and unused insulating oil (IEC 62535) are empirical and yield qualitative results based on visual and subjective perception of colour profiles.

Several field examinations of transformers and other electrical equipment filled with insulating liquids have shown that copper sulfide formation is related to corrosive sulfur compounds. Stability and the reactivity of different classes of sulfur species (elemental sulfur, aliphatic and aromatic mercaptans, sulfides, disulfides, thiophens) which could be present in the insulating liquids have been examined. Corrosivity of nine compounds sulfur containing organic

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1 Numbers in square brackets refer to the Bibliography.

compounds including dodecylmercaptan, hexadecylmercaptan, benzylmercaptan, butyldisulfide dibenzylsulfide, phenylvinylsulfur, phenyldisulfide, dibenzyldisulfide, and dibenzothiophene, was evaluated under conditions which simulated hermetically sealed or free breathing type transformers. Corrosivity was assessed quantitatively through conversion of copper sulfide to copper sulfate which was determined through turbidity measurement. The data obtained was used for the ranking of compounds according to their corrosivity towards copper. Corrosivity was found to vary with temperature, for example at temperatures between 80 °C to 120 °C, mercaptans were found to be the most corrosive compounds, while at temperatures between 150 °C to 180 °C, the highest corrosivity was exhibited by disulfides [18].

Furthermore, methods for corrosive sulfur and potentially corrosive sulfur in insulating liquids ([8] and [11]) can be used only for mineral insulating oils that do not contain metal passivator additives. In the presence of such additives, methods can yield negative results even when corrosive sulfur compounds are present in the insulating liquids – thus providing a false negative test result [11]. 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 corrosive sulfur test result. In such cases, further analysis of insulating liquids is stipulated, for example IEC 62535 specifies that if there are doubts in the interpretation of the results from the inspection of paper, the composition of precipitate should be analysed by other methods (e.g. by SEM-EDX).

To overcome limitations of standard test methods for corrosive sulfur, a working group within IEC TC 10 was set up to prepare test methods which will yield the unambiguous quantitative results for corrosive sulfur compounds in unused and used insulating liquids. This test method is described in this part of IEC 62697.

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 2: Test method for quantitative determination of total corrosive sulfur (TCS)

1 Scope

This part of IEC 62697 specifies a test method for the quantitative determination of total corrosive sulfur (TCS) in unused and used insulating liquids and solid matrices through the conversion of corrosive sulfur species to metal (copper, silver etc.) sulfides. The sulfides formed are quantitatively converted to sulfates; sulfates are determined through turbidity measurement or with ion chromatography. The method is applicable with the following matrices:

a) Unused and used insulating liquids, for example mineral insulating oils and natural esters, which allow the determination of corrosive sulfur compounds over concentrations ranging between 2,5 mg kg^{-1} to 80 mg kg^{-1} TCS.

b) Solid matrices that come in contact with the insulating liquid, for example insulating papers in electrical equipment. The quantification limits for these matrices depend on the amount of matrix used during the determination. The method can be used for the quantitative or semi-quantitative determination of copper sulfide on paper after the test according to IEC 62535. The method can provide unambiguous quantitative assessment of copper sulfide present on paper rather than qualitative results obtained with the SEM-EDX examination stipulated in case of doubts in the interpretation of results obtained from the inspection of paper according to IEC 62535:2008, 6.3.

c) Paper and other solid insulating material/s obtained from failed transformers, reactors and other electrical equipment to assist in failure diagnostics.

d) Metal deactivator or passivators additives present in insulating liquids (qualitative assessment).

However, the method is not applicable for assessing corrosion phenomena for example the dissolution of copper in insulating liquids and deposition on solid matrices, which do not lead to sulfide formation.

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)*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in IEC 62697-1 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
ion chromatography
chromatography technique that separates ions based on their affinity for the immobilized ion exchange sites on the ion exchanger followed by quantitation of ions through conductivity measurement

3.2
turbidity measurement
measurement that involves monitoring of transmitted light intensity through a liquid due to the presence of non-transparent particles in the liquid

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

The TCS test involves the conversion of corrosive sulfur in insulating liquid, into metal sulfide for example copper sulfide (Cu_2S) (see Equation 1). The reaction between copper and oil is accomplished preferably in vials with argon headspace, to prevent oxidation of copper with air. This reaction is accomplished at 150 °C.

Cu + Corrosive sulfur → Cu_2S (1)

Cu_2S is then oxidized to cupric sulfate ($CuSO_4$) (2)

Cu_2S + Oxidizer → $CuSO_4$ (2)

Sulfate thus obtained is dissolved in particle free deionized water and quantified through turbidity measurement after addition of a precipitating agent. The sulfate concentration in solution can also be determined with ion chromatography.

5.2 Significance and use

This test method describes the determination of TCS in insulating liquids.

TCS is the sum of all elemental and chemically bound sulfur in an insulating liquid that reacts with metals such as copper under certain conditions to form sulfides. The method provides quantitative measure for total corrosive sulfur in insulating liquids rather than qualitative results obtained through current standard test methods for corrosive or potentially corrosive sulfur in insulating liquids.

5.3 Interferences

5.3.1 General

Interferences experienced during the quantitative determination of TCS will vary with the instrumentation used for the quantification of sulfate obtained through the oxidation of sulfides.