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TECHNICAL REPORT

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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)

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

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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- withdrawn,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.

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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.

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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)

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.

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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.

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5.3.2 Interferences in turbidity measurements

Turbidity based determination of sulfate is affected by the presence of suspended non-transmitting particles or excessive organics that lead to turbid suspensions. Sulfate quantification can be readily carried out without interference as long as solutions are passed through 0,1 µm filters prior to precipitate formation.

5.3.3 Interferences in ion chromatography measurements

Ion chromatography measurements are generally free from interference, however the presence of organic ions may result in erroneous results. Use of particle free deionized water with a total anion concentration < 1,0 parts per billion is recommended.

5.4 Apparatus

5.4.1 Balance

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

5.4.2 Hot plate with stirrer

A hot plate capable of reaching 400 °C with a stirrer is recommended.

5.4.3 Heating block

An aluminium alloy block (10 cm x 8 cm x 5 cm) with bores for holding and heating 20 ml borosilicate vials.

5.4.4 Turbidity monitor

A laboratory turbid meter equipped with a halogen–tungsten lamp and a wavelength selector and an appropriate photodetector for monitoring intensity of radiation around 420 nm can be used. Laboratory UV/Vis spectrophotometers routinely used in chemical laboratories can be satisfactorily used.

5.4.5 Ion chromatograph

An ion chromatograph comprised of a fixed or variable volume injector, an anion exchange resin column, a background suppressor and a conductivity detector can be used for quantification of sulfate and appropriate internal standard ions.

5.4.6 Data system

A data system for control, monitoring, acquisition and storage of analytical data obtained from a turbidity monitor or ion chromatograph is recommended.

5.5 Reagents and materials

5.5.1 Purity of reagents

Analytical reagent grade chemicals should be used in all analysis performed with this document.

5.5.2 Gases

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.

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- Iso-octane can be used for resining copper powder after reaction.
- Pentane can be used for resining copper powder after reaction.
- Deionized water with anion concentration < 1 µg kg^{-1} will be used for solubilizing copper sulfate.

5.6 Standard materials

5.6.1 Dibenzyl disulfide (DBDS)

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

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

5.6.2 Blank oil

Insulating liquid that is free from corrosive sulfur compounds such as DBDS is used for the 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.

5.6.3 Copper powder

Copper powder particle size < 450 µm and purity > 99,5 %.

5.6.4 Potassium nitrate

Potassium nitrate purity > 99,0 %

5.6.5 Hydrochloric acid

12N hydrochloric acid.

5.6.6 Barium chloride

Barium chloride purity > 99,0 %

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 three months. The stock solution should be stored in amber glass bottles with polytetrafluoroethylene (PTFE) lined screw caps in a refrigerator at about 4 °C. The solution should be brought to room temperature (about 25 °C) prior to its use

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

5.7.2 Internal standard (IS) solution

Bromide solution obtained by dissolving crystalline sodium bromide (NaBr) purity > 99,0 % in anion free water can be used as internal standard during the determination of sulfate concentration with ion chromatography.

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6 Instrument set-up

6.1 Turbidity monitor

A simple turbidity monitor consisting of a radiation source such as the halogen–tungsten lamp sample holder and a photodetector can be used. A spectrophotometer with a radiation wavelength selector can also be used for monitoring turbidity. Differences between turbidity monitors and spectrophotometers from different manufacturers make it impractical to provide detailed operating conditions. Consult the manufacturer's instructions for operating the instrument to facilitate turbidity measurement.

6.2 Ion chromatograph

6.2.1 General

Ion chromatographs are offered commercially by at least two vendors. These chromatographs are comprised of a mobile phase reservoir, mobile phase delivery pumps, sample introduction systems, anion separation columns, a counter ion suppression system and a conductivity detector. Differences between ion chromatographs from different manufacturers make it impractical to provide detailed operating conditions. Consult the manufacturer's instructions for operating the ion chromatograph.

6.2.2 Column

Separation of sulfate from other anions such as bromide, chloride and nitrate which are likely to be present in the solution is achieved with a polymeric anion exchanger with covalently bound quaternary ammonium anion exchange sites. PEEK columns with an internal diameter of 2 mm to 4 mm, and length between 125 mm to 250 mm packed with the 6 µm anion exchange resin particles have been found to yield adequate resolution to permit unambitious quantification of sulfate ions in solutions. The column temperature should be maintained at 25 °C.

6.2.3 Mobile phase

A mixture of 2,2 mM sodium carbonate and 2,8 mM sodium bicarbonate in deionized water yields satisfactory separation of anions, with sulfate retention time of < 15 min. The mobile phase should be degassed and filtered through a membrane filter with pore size 0,2 µm prior to use in the ion chromatograph. The flow rate recommended for the column by the manufacturer should be used.

6.2.4 Injector

A PTFE loop injector with fixed or variable volume loop is used for introducing a known amount of sample into the anion exchange column. The injector parameters should be chosen taking into account the capacity of the column and the dilution of the sample may be required in cases when anion concentrations are high. The injector temperature should be maintained at 25 °C. An autosampler designed to operate with the ion chromatograph should be used when available.

6.2.5 Suppressor

Suppressors are an essential component of the ion chromatographic system and permit ion detection through conductivity measurement. Adherence to vendor specified use and maintenance procedures is essential for obtaining satisfactory quantitative results.

6.2.6 Conductivity detector

Sulfate and other ions separated with the anion exchange column are monitored and quantified with the conductivity detector. Detector response is expressed in conductivity units micro-siemens (µS cm^{-1}).

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6.3 Corrosive chemistry

6.3.1 Reaction of corrosive sulfur compounds with copper – formation of Cu_2S

Three grams (±0,01 g) of copper powder is added to a 20 ml borosilicate glass vial along with a small PTFE coated magnetic needle. The vial containing the copper powder and magnetic needle is then capped and tarred. A known volume (10 ml ± 0,5 ml) of oil is added to the tarred capped vial through the septum. The vial is weighed again to determine the weight of the oil. The vial is then purged with argon to remove air from the headspace. The vial is placed in a vial holder on a hot plate with a magnetic stirrer. The hot plate temperature is set at 150 °C. The stirring speed is set at about 800 r/min The oil and copper powder is allowed to interact for a selected time period (2 h or 12 h). The vial is removed from the holder after the selected reaction period and allowed to cool down to ambient temperature. The vial is opened with an appropriate tool and most of the oil is carefully pipetted out and discharged into a suitable container. Approximately 1 ml to1,5 ml of the oil is left over the copper to prevent accidental removal of copper from the vial.

10 ml of iso-octane is added to the vial and the vial is placed in the vial holder at ambient temperature. Contents of the vial are stirred at 800 r/min for 5 min, the vial is removed from the holder and copper powder is allowed to settle at the bottom for about 5 min. Solvent and oil are pipetted out from the vial. Pipetting is done very carefully to avoid removal of copper powder from the vial. The copper powder is rinsed twice with iso-octane and twice with pentane. The rinsed copper powder is dried for 60 min in the vial holder at 40 °C with constant stirring at about 350 r/min The vial is removed from the holder and allowed to cool down to ambient temperature, the magnetic bar is carefully removed with a magnetic stick.

6.3.2 Conversion of cuprous sulfide into cupric sulfate

6.3.2.1 Oxidation with potassium nitrate

Two grams of KNO_3 is added to the vial and mixed thoroughly with copper using a clean and dry stainless steel spatula. The vial is placed in the holder and its temperature is gradually raised to 350 °C. The reaction between Cu_2S and KNO_3 is allowed to occur for 2 h at 350 °C until the copper powder turns pitch black. The vial is removed from the holder and allowed to cool down to ambient temperature. 10 ml of deionized water is added to the vial and the vial is placed back in the vial holder and heated at 120 °C for 15 min to 20 min. The vial is removed from the vial holder and allowed to cool down to ambient temperature.

6.3.2.2 Oxidation with hydrogen peroxide

Solvent rinsed dry copper powder is transferred to a clean long neck digestion flask and 10 ml of 35 % H_2O_2 is added to the flask and allowed to react with the copper powder for one hour at ambient temperature. After the one hour interaction period approximately 10 to 15 drops of 30 % NH_4OH solution is added to the flask. The contents of the flask are gently shaken for 20 min. Interactions between Cu_2S coated copper powder and reagents are exothermic and quite vigorous, therefore care should be exercised in handling the reaction flasks. No more than five drops of 30 % NH_4OH solution should be added at one time. Once the intensity of the reaction had subsided, 4 ml of 30 % NH_4OH is added to the flask and the contents heated until a clear solution is obtained. The clear solution is gently swirled until the blue gel which appears during the reaction is completely dissolved. The liquid is carefully decanted through a filter paper into a volumetric flask leaving the black residue (CuO) behind. 10 ml of 35 % H_2O_2 is added to the black residue in the flask and the contents are allowed to stand for 30 min. Approximately 20 drops of 30 % NH_4OH are added to the flask and the flask is carefully swirled until reaction ceases. The flask is heated on a hot plate at 100 °C until all of the blue precipitates dissolve and a clear solution is obtained. The digests are transferred to the volumetric flask. The volume of liquid in the flask is brought to the mark with deionized water. Further dilutions may be performed if required with deionized water. A known amount of chloride is then added as the internal standard. The sulfate (SO_4^{2-}) ions obtained through oxidation of Cu_2S are separated and their concentrations in the solutions are determined with a calibrated IC system.

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6.3.3 Quantification of cupric sulfate in solution

The contents of the vial including the solid at the bottom are mixed with a spatula. The entire contents of the vial are transferred to a clean weighed bottle. The vial is rinsed twice with 2 ml of demineralized water and rinses are added to the bottle. Deionized water is added to bring the volume to the 20 ml mark on the bottle. The bottle is weighed and the net weight of the solution is recorded. The cupric sulfate in solution is quantitatively determined either through turbidity measurement after formation of barium sulfate precipitate or through ion chromatography.

6.3.4 Turbidity measurement

A 10 ml aliquot of the well mixed solution is drawn with a syringe, and filtered through a 0,45 µm filter to remove particulate matter. The filtered aliquot is transferred to a clean cuvette of a turbidity detector. Two drops of 12N HCl acid are added to the cuvette. The cuvette is closed with a screw cap and weighed. The screw cap is removed and the sulfate reagent is added to the cuvette. Contents are shaken and allowed to settle for several minutes. The cuvette is placed in the turbidity detector and the turbidity reading of the solution is noted. A second turbidity reading is taken to ensure that the reaction has come to completion. The reaction completion is indicated by constant turbidity readings. The response of the turbidity detector is calibrated with oils containing a known concentration of DBDS as the model corrosive sulfur compound. See Figure A.1 and Figure A.2.

6.3.5 Ion chromatography measurement

An appropriate volume of the solution filtered through a 0,2 µm filter is introduced into the IC column through a fixed volume loop injector. Separations of anions including SO_4^{2-} are achieved with an anion exchange column under isocratic conditions with a mobile phase comprised of 2,2 mM sodium carbonate and 2,8 mM sodium bicarbonate in deionized water. The mobile phase flow rate is maintained at 1,8 ml min^{-1}. Anions separated with the anion exchange column were quantified with a conductivity detector after their passage through a membrane suppressor. The IC response was calibrated for SO_4^{2-} over the 5 ppm to 150 ppm range (20 ppm to 575 ppm DBDS). See Figure A.1 and Figure A.2.

6.4 Calibration

6.4.1 General

Turbidity was measured as attenuation (reduction) in intensity of transmitted radiation during its passage through the solution/suspension. It is generally expressed as turbidance S, which is defined in analogous terms to absorption (see Formula (3)):

$$S = -\log I / I_0 \quad (3)$$

where

I is the intensity of transmitted radiation

I_0 is the intensity of the incident radiation

At low precipitate (S = 0,05) concentrations, nehpelometry is the preferred method of measurement. However, in the present case, turbidimetry is preferred. The transmission response obtained by introducing a known amount of corrosive sulfur compound (DBDS) is compared with the response of a known amount of sulfur.

6.4.2 Calibration procedure

Prepare the calibration standard solutions by introducing known volumes of the stock solution (see 5.6.1) 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 5 ml of iso-octane or other suitable solvent.

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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 20 mg kg^{-1} to 575 mg kg^{-1} concentration range.

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

6.4.3 Quantification of total corrosive sulfur (TCS)

TCS in oil samples can be quantified either through turbidity measurement or ion chromatography. Cu_2S formed through the interaction of corrosive sulfur in insulating liquid is quantitatively oxidized to $CuSO_4^{2-}$ over more than two orders of magnitude and quantified concentration range. Ion chromatographic analysis and turbidity measurements of sulfate obtained after oxidation of Cu_2S to $CuSO_4^{2-}$ proved to be sensitive; the minimum quantifiable limit for sulfate with both techniques was found to be 0,5 mg SO_4^{2-} in solution. When DBDS is used as a model corrosive sulfur compound its overall conversion to SO_4^{2-} was found to be 95 %.

6.4.4 Quantification of total corrosive sulfur and DBDS equivalents ($DBDS_{eq}$)

The sulfate concentration obtained through turbidity or ion chromatography measurements can be used for calculating the total corrosive sulfur (TCS) concentration expressed as milligram of total corrosive sulfur per gram of oil through the expression given in Formula (4).

$$TCS = [(C_{sulfate} \times W / 96{,}06) \times 32{,}07] / \text{oil weight} \quad (4)$$

where:

$C_{sulfate}$ is the sulfate concentration in mg l^{-1} in the solution;

W is the net weight of the sulfate solution;

96,06 is the molecular weight of sulfate;

32,06 is the atomic weight of sulfur;

oil weight is the weight of the oil loaded on vial A and B, in kg.

The TCS value can be converted into DBDS equivalents ($DBDS_{eq}$), through the expression given in Formula (5).

$$DBDS_{eq} = (TCS \times 246{,}39)/(2 \times 32{,}07) \quad (5)$$

where:

32,06 is the atomic weight of sulfur;

246 is the molecular weight of DBDS;

2 is the number of sulfur atoms in a DBDS molecule.

6.5 Results

Report TCS concentrations in mg kg^{-1} to two significant figures or in $DBDS_{eq}$ in mg kg^{-1}.

7 Precision data

7.1 Detection limit

Detection limit for DBDS as a representative corrosive sulfur compound through the procedure outlined above is expected to be ≤ 10 mg kg^{-1}. Each laboratory should determine its own detection limit.

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

Table 1 – Repeatability limit

Concentration mg/kg	*r* (repeatability) %
15	15
50	10
150	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 2 (expressed in percentage of the average value). See Annex B.

Table 2 – Reproducibility limit

Concentration mg/kg	*R* (reproducibility) %
15	20
50	15
150	15

8 Report

The test report should contain at least the following information:

- testing laboratory;
- the type and identification of the product tested;
- a reference to this document, IEC TR 62697-2;
- 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.

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Annex A
(informative)

Figures with typical chromatograms and results

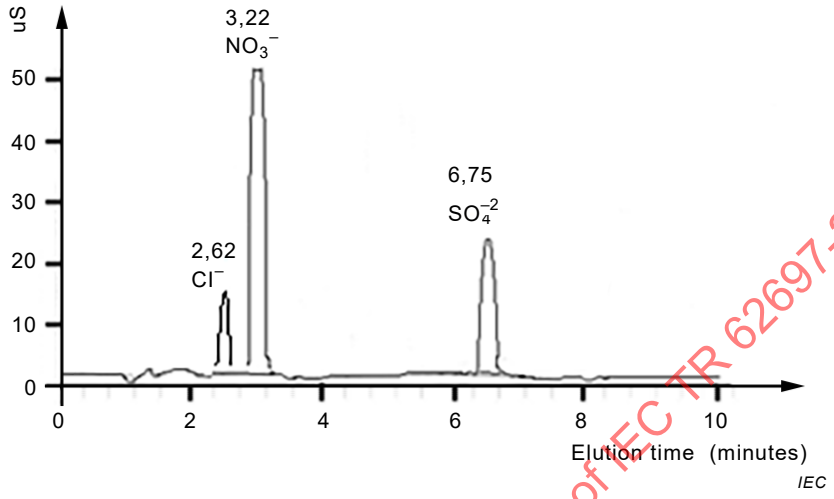

Figure A.1 – Ion exchange chromatography detection DBDS as sulfate

Figure A.2 – Photograph of turbidity meter cuvette containing $BaSO_4$ suspension

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Annex B
(informative)

RRT results for quantitative determination of corrosive sulfur

Results for the quantitative determination of corrosive sulfur are given in Tables B.1, B.2 and B.3.

Table B.1 – Turbidity and ion chromatography

Sample number	Lab. B		Lab. C		Lab. D		Lab. E				Lab. F		Lab. G		Average		Standard deviation		Relative percent deviation	
	TCS	$DBDS_{eq}$	TCS	$DBDS_{eq}$	TCS	$DBDS_{eq}$	TCS		$DBDS_{eq}$		TCS	$DBDS_{eq}$	TCS	$DBDS_{eq}$	TCS	$DBDS_{eq}$	TCS	$DBDS_{eq}$	TCS	$DBDS_{eq}$
							Turb.	IC	Turb.	IC										
1	29	110	28	108	28	108	24	19	91	71	30	113			26,0	98,6	5,2	14,4	**14,2**	**14,6**
	30	114	58	223	30	119	31	24	119	92	30	116	55,6	213,5	29,0	112,	1,4	9,3	**8,0**	**8,3**
2	17	64	48	184	22	85	13	10	49	40	16	63			15,6	60,2	1,7	14,0	**23,6**	**23,2**
	32	121	55	211	22	85	27	22	103	84	15	57	33,6	129,1	23,6	90,0	1,6	19,5	**22,0**	**21,7**
3	14	53	0	<	14	54	12	10	44	37	12	47			12,4	47,0	2,4	5,7	**11,0**	**12,1**
	14	53	9	35	15	58	10	15	40	58	14	52	35,0	134	13,6	52,2	2,1	6,0	**12,4**	**11,5**
4	<	<	0	0	<	<	<2	4	<8	15	0	0			2,0	-	-	-	-	-
	<	<	3	12	<	<	<2	6	<8	22	0	0	3,1	11,9	3,0	-	-	-	-	-
5	<	<	4	15	2,5	9	<2	6	<8	22	0	0			2,8	-	-	-	-	-
	3	11,4	7	27	5	19	<2	10	<8	37	0	0	7,1	27,2	4,5	-	-	-	-	-
6	3	11,4	3	12	10	38	<2	5	<8	20	0	0			4,5	17,4	4,4	12,4		71,5
	7	26,5	8	31	11	42	<2	9	<8	33	0	0	8,9	34,1	6,8	25,4	5,2	14,0		55,2
7	14	53	13	50	25	96	11	9	43	33	22	83			16,2	61,6	1,4	21,9	35,2	35,6
	22	83	34	131	30	115	19	18	73	69	28	106	44,4	170,4	23,4	89,2	1,7	16,6	18,7	18,6

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