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TECHNICAL REPORT

colour
inside

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

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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

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ELECTROTECHNICAL
COMMISSION

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INTERNATIONAL ELECTROTECHNICAL COMMISSION

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- withdrawn,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.

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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. 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.

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[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 outside this range, in oils that have been blended, or oils in which elemental sulfur has been consumed through its reaction with the copper or other metals.

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

5.3 Interferences

5.3.1 Co-eluting compounds

Interferences experienced during quantitative determination of elemental sulfur will vary with the detector used for quantification of elemental sulfur 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, disulfides and elemental sulfur (S_6, S_7 and S_8). Presence of compounds with high affinity for thermal electrons especially polychlorinated biphenyls (PCBs) in insulating liquids can cause interference. In such cases an alternate detector should be used.

5.3.3 Flame photometric detector (FPD)

The FPD provides a selective signal for sulfur species including DBDS in the form of broad light emission centred around 393 nm. Emission is separated with an interference filter with a 20 nm band pass with peak transmission at 393 nm. The filter is mounted in front of a photomultiplier that provides electrical signal that is amplified and linearized. Sulfur containing organic compounds which elute with the same retention time can lead to interference; a column with different stationary phase can be used to eliminate or minimize interference.

5.3.4 Mass spectrometer (MS)

An 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 yield ions at m/z 256 and ions at m/z 218 will cause interference if such compounds elute from the GC column with retention times similar to those of the S_8 and DPDS (IS).

5.3.5 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.

An FPD response is selective for sulfur through S_2 emission. Other chemical species which emit radiation around the 393 nm can cause interference, however, such interference is generally low.

It is possible that certain insulating liquids contain molecules that yield ions at m/z 256 and m/z 218; such molecules can cause interferences with GC-MS.

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 recommended.

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 to 10 µl liquids into the column (an automated sampling injection device is preferred);
- a 30 m to 60 m x 0,25 mm (internal diameter) fused silica capillary column with 5 % phenyl polysiloxane and 95 % methyl polysiloxane or other suitable stationary phase;
- a column oven capable of operation over the 30 °C to 300 °C range with ramp rates of up to 20 °C min^{-1}.

5.4.2.2 Electron capture detector (ECD)

ECD with a ^{63}Ni foil detector capable of operating at a temperature of about 300 °C with a temperature stability of $\leq$ 0,5 °C.

5.4.2.3 Flame photometric detector (FPD)

FPD capable of detecting the broad S_2 emission around 393 nm.

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 $\leq$ 0,5°C.
- source temperature 200 °C or as recommended by the manufacturer.

5.4.2.5 Data system

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

5.4.3 Differential pulsed voltammetry

Electrodes are as follows:

Working electrode: MME (multi-mode electrode);
Auxiliary electrode: glassy carbon;
Reference electrode: Ag/AgCl/LiCl in ethanol (0,1 M);
Mode: differential pulse, standard additions.

5.5 Reagents and materials

5.5.1 Purity of reagents

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

5.5.2 Gases

The carrier gas (He or other suitable gas) 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 should be nitrogen or other gas specified by the instrument manufacturer.

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.

Methanol is used with toluene during preparation of standards for differential pulse voltammetry measurements. 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 Elemental sulfur

Elemental sulfur occurs as a mixture of allotropic forms, the most common form is the octacylic S_8 form, yellow crystals (vapor pressure 1 mmHg at 183,8 °C), its purity shall be ≥ 99 %.

Store elemental sulfur in an amber glass bottle with a screw cap in a secure cool place, away from a source of heat.

5.6.2 Diphenyl disulfide (DPDS)

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

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

5.6.3 Blank oil

Insulating liquid that is free from elemental sulfur and DPDS and 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.

5.7 Standard solutions

5.7.1 Stock solutions

5.7.1.1 Chromatography

Prepare a solution of elemental solution 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.

5.7.1.2 Differential pulse voltammetry

Base electrolyte

15 g ammonium acetate and 5,03 ml acetic acid (100 %) in a 1 l volumetric flask are filled with a toluene/methanol (1:1) mixture.

Sulfur standard stock solution (1 g/l) prepared from elemental S: 0,1 g elemental S (analytical precision) is dissolved in a 100 ml volumetric flask with base electrolyte.

Sulfur standard solution 10 mg kg^{-1}:1 ml of the sulfur standard solution are filled up with base electrolyte in a 100 ml volumetric flask.

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 be prepared every three months. The stock solution should be stored in amber glass bottles with 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.

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 elemental sulfur.

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 285 °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, 15 m to 30 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 elemental sulfur. 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 elemental sulfur 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
80	0	10	280	5

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

A carrier gas flow rate between 0,8 ml/min to1 ml/min is suitable (linear velocity 30 cm s^{-1} to 35 cm s^{-1}).

6.1.5 ECD detection

Set the ECD to a temperature of 300 °C (290 °C to 320 °C). Nitrogen or other suitable gas is used as the make-up gas. Follow the manufacturer’s recommendations for operation of the ECD. GC-ECD outputs for elemental sulfur fortified white mineral oil are shown in Figure A.1 and Figure A.2.

6.1.6 FPD detection

Set the FPD for detecting the S_2 molecular emission band at 393 nm (bandpass 10 nm). The FPD utilizes a “cool” hydrogen rich air flame, H_2 flow 75ml min^{-1}, air flow 100 ml min^{-1}. Normally the detector is operated at 280 °C. For optimal operating conditions follow the manufacturer’s recommendations.

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 be 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 instructions for setting up the instrument.

Table 2 – Mass spectrometer parameters

S_8 ions	**Dwell time** ms
256	100
258	100
DPDS ions	
218	100

6.2 Calibration

6.2.1 General

The response of elemental sulfur (S_8) 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 elemental sulfur 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. 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 500 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 FPD)

Add a known amount of IS solution by weight or using a calibrated syringe (with 50 mg kg^{-1} IS). See Figure A.1 and Figure A.2.

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

Calculate the response factor (k) as:

$$k = [A_{\mathrm{IS}} \times m_{\mathrm{S8}}] / [m_{\mathrm{IS}} \times A_{\mathrm{S8}}] \qquad (1)$$

where

A_{IS} is the area of the DPDS or other suitable IS peak;

A_{S8} is the area of the S_8 peak;

m_{S8} is the mass of S_8 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 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:

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

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_{S8} is the area of the molecular ion peak m/z 256 of the S_8;

M_{S8} is the known mass of S_8 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 iso-octane 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, FPD 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 a manual adjustment if and when required.

Record the area of S_8 peak as A_{S8} and the area of DPDS peak as A_{IS}; use these for calculating the S_8 concentration.

6.4 Calculations

6.4.1 ECD and FPD

Calculate the S_8 concentration in oil with Formula (3).

$$\text{mg kg}^{-1}\ [\mu\text{g g}^{-1}]\ \text{S}_8 = [k m_{\text{IS}} A_{\text{S}_8}]\ /\ [A_{\text{IS}} W_{\text{OIL}}] \tag{3}$$

where

A_{IS}	is the area of the peak of the DPDS;
A_{S8}	is the area of the peak of the S_8 (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:

$$\text{mg kg}^{-1}\ [\mu\text{g g}^{-1}]\ \text{S}_8 = [k\text{x}\ m_{\text{IS}}\text{x}\ A_{\text{S}_8\,(\text{m/z }256)}]\ /\ [A_{\text{IS }(\text{m/z }218)}\text{x}W_{\text{OIL}}] \tag{4}$$

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 should be monitored;
A_{S_8}	is the area of the extracted molecular ion peak m/z 256 of the S_8;
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 Differential pulse voltammetry measurements

The measurement is made according to the scheme outlined below (see Figure 1)

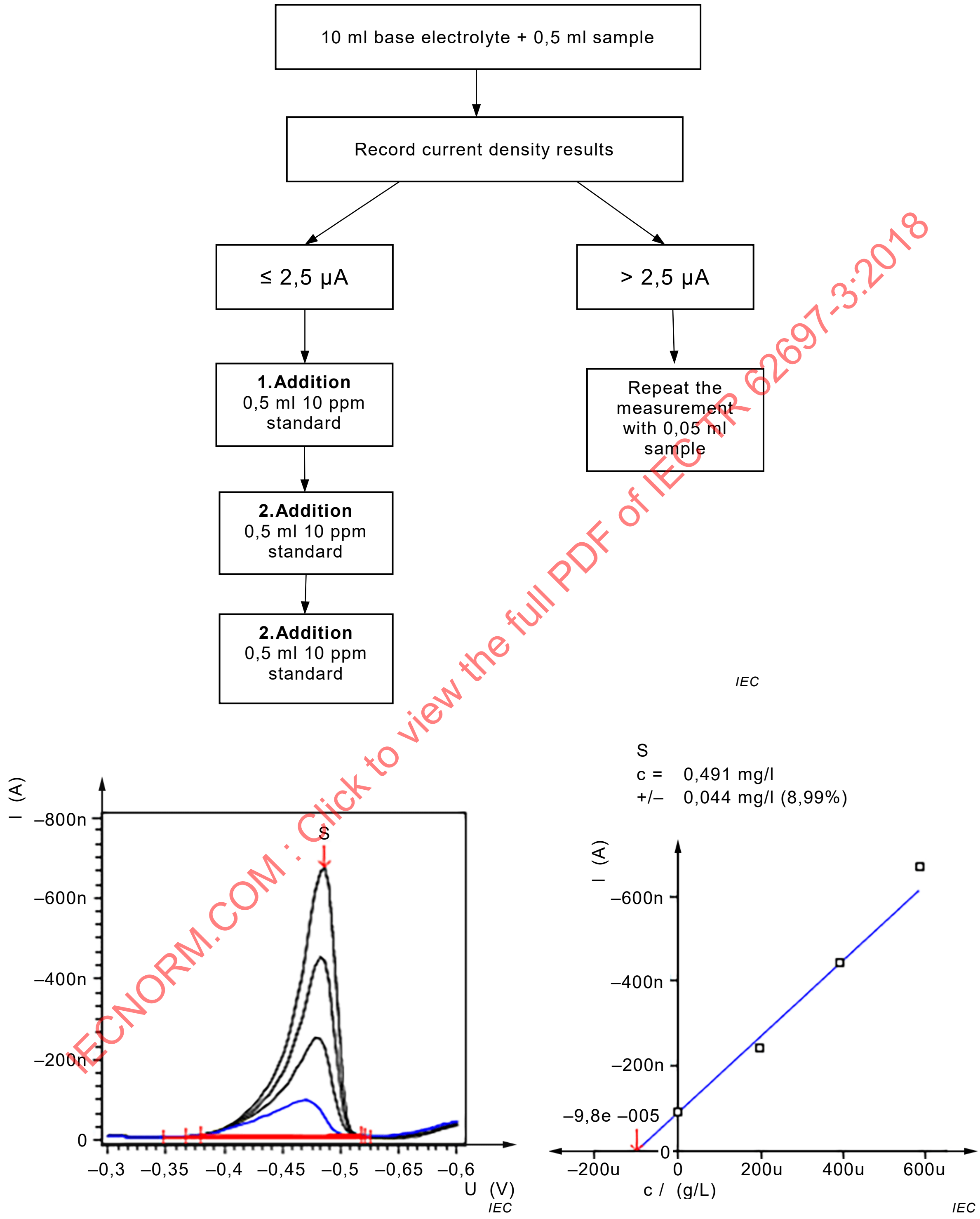

Figure 1 – Typical peak form and concentration calculation

6.5 Results

Report elemental sulfur (S_8) 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	***r*** **(repeatability)** %
3	24
10	2
45	1
100	1

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). See Annex B.

Table 4 – Reproducibility limit

Concentration mg/kg	***R*** **(Reproducibility) %**
10	13
35	11
100	6

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 62697-3;
- 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

Chromatograms of elemental sulfur standard and (IS) in white mineral oil and in mineral insulating oils obtained with GC-ECD are shown in Figure A.1 and Figure A.2.

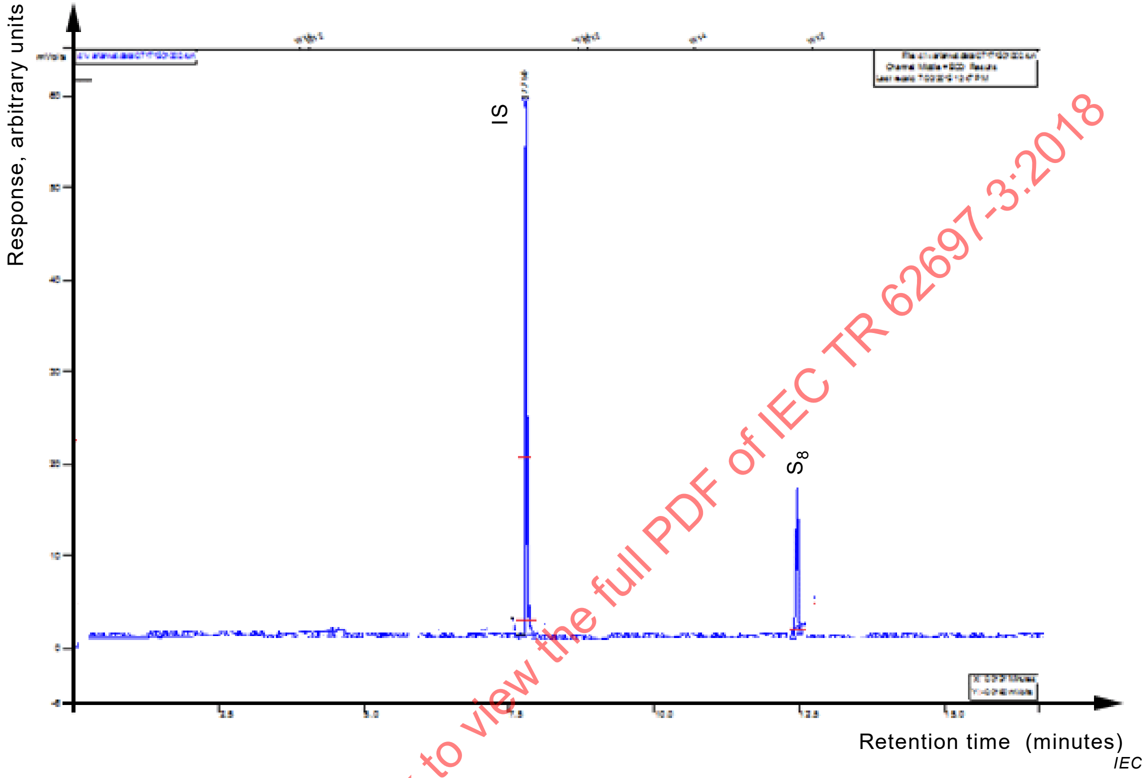

Figure A.1 – GC-ECD chromatogram of 5 mg kg^{-1} elemental sulfur and (IS) in white mineral oil

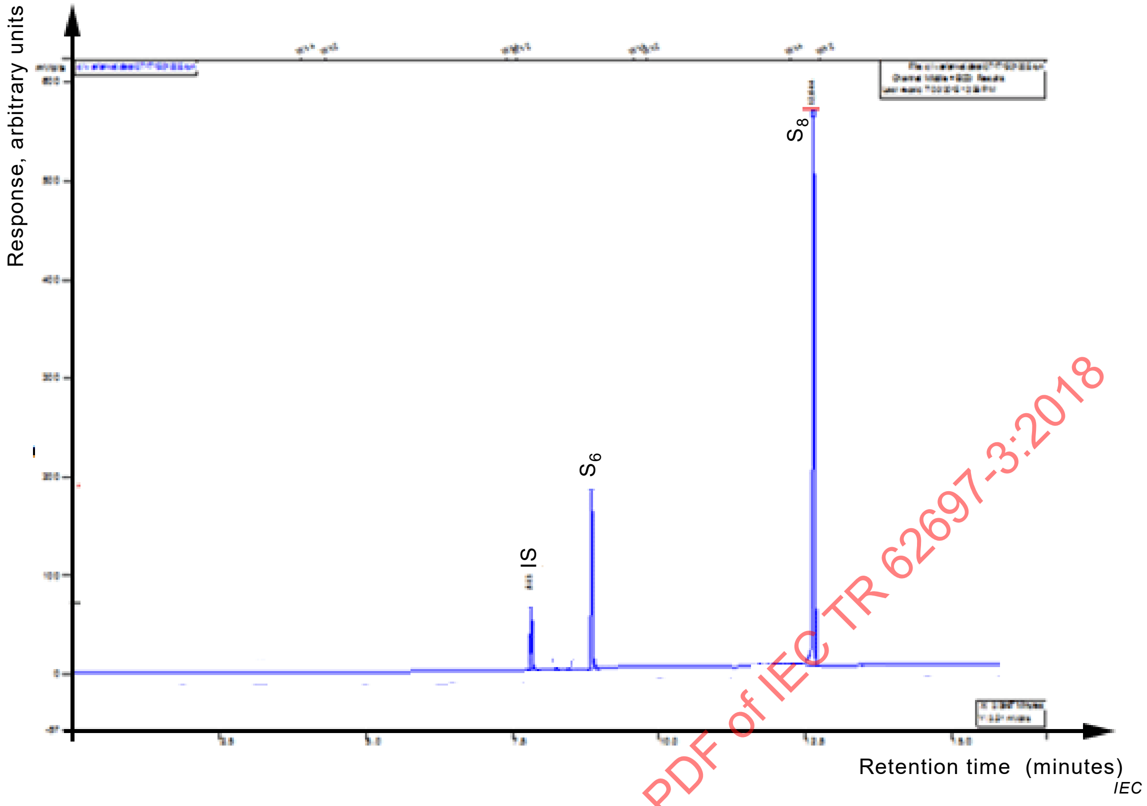

Figure A.2 – GC-ECD chromatogram of 100 mg kg^{-1} elemental sulfur and (IS) in white mineral oil