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BSI Standards Publication

Petroleum products — Determination of sulfur content — Oxidative microcoulometry method (ISO 16591:2010)

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National foreword

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The UK participation in its preparation was entrusted to Technical Committee PTI/13, Petroleum Testing and Terminology.

A list of organizations represented on this committee can be obtained on request to its secretary.

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Produits pétroliers - Dosage du soufre - Méthode par microcoulométrie oxydante (ISO 16591:2010)

Mineralölerzeugnisse - Bestimmung des Schwefelgehaltes - Oxidatives mikrocoulometrisches Verfahren (ISO 16591:2010)

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EUROPEAN COMMITTEE FOR STANDARDIZATION
COMITÉ EUROPÉEN DE NORMALISATION
EUROPÄISCHES KOMITEE FÜR NORMUNG

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Foreword

This document (EN ISO 16591:2010) has been prepared by Technical Committee ISO/TC 28 “Petroleum products and lubricants” in collaboration with Technical Committee CEN/TC 19 “Gaseous and liquid fuels, lubricants and related products of petroleum, synthetic and biological origin” the secretariat of which is held by NEN.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by June 2011, and conflicting national standards shall be withdrawn at the latest by June 2011.

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Endorsement notice

The text of ISO 16591:2010 has been approved by CEN as a EN ISO 16591:2010 without any modification.

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

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ISO 16591 was prepared by Technical Committee ISO/TC 28, *Petroleum products and lubricants*.

INTERNATIONAL STANDARD **ISO 16591:2010(E)**

Petroleum products — Determination of sulfur content — Oxidative microcoulometry method

WARNING — The use of this International Standard may involve hazardous material, operations and equipment. This International Standard does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this International Standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

1 Scope

This International Standard specifies a method for the determination of the sulfur content by oxidative microcoulometry of petroleum light and middle distillates with a final boiling point not higher than 400 °C. It is applicable to materials with sulfur contents in the range of 1 mg/kg to 100 mg/kg. Products with sulfur contents above 100 mg/kg can be analysed after dilution with a suitable sulfur-free solvent. Products with sulfur contents below 1 mg/kg can also be analysed by a modified technique described in Annex A. The precision quoted only applies to measurements in the 1 mg/kg to 100 mg/kg range. Nitrogen interferes with the analysis at concentrations above 0,1 % (m/m), and chlorine interferes at concentrations above 1,0 % (m/m), but these interferences are overcome by the addition of sodium azide to the cell electrolyte. Bromine and organometallic compounds also interfere with the analysis at concentrations above approximately 500 mg/kg.

NOTE 1 The microcoulometric method is capable of analysing light liquid hydrocarbons boiling in the range from 26 °C to 274 °C (for example, naphtha and MS samples) that undergo pyrolysis at 900 °C to 1 200 °C. The combustion of high boiling components (for example, diesel) can result in the formation of carbonaceous deposits in the inlet portion of the combustion tube, which need to be removed frequently.

NOTE 2 The results obtained using this International Standard on light and light-middle distillates generally approximate to those obtained using ISO 4260.

NOTE 3 For the purposes of this International Standard, the term "% (m/m)" is used to represent the mass fraction of a material.

2 Normative references

The following referenced documents are indispensable for the application 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.

ISO 3170, *Petroleum liquids — Manual sampling*

ISO 3171, *Petroleum liquids — Automatic pipeline sampling*

ISO 3675, *Crude petroleum and liquid petroleum products — Laboratory determination of density — Hydrometer method*

ISO 3696, *Water for analytical laboratory use — Specification and test methods*

ISO 12185, *Crude petroleum and petroleum products — Determination of density — Oscillating U-tube method*

3 Principle

A test portion is burned in a combustion tube under a flowing stream of oxygen plus an inert gas. The combustion products are swept into a titration cell, where the sulfur dioxide reacts with tri-iodide ion present in the electrolyte. The tri-iodide ions that are consumed are coulometrically replaced, and the current required for replacement is a direct measure of the sulfur content of the sample. The reactions are:

$$I_3^- + SO_2 + H_2O \rightarrow SO_3 + 3I^- + 2H^+ \quad (1)$$

$$3I^- \rightarrow I_3^- + 2e^- \quad (2)$$

4 Reagents and materials

All reagents shall be of recognized analytical grade, and water shall conform to the requirements of Grade 3 of ISO 3696.

4.1 Electrolyte

Dissolve 0,5 g $\pm$ 0,01 g of potassium iodide (KI) and 0,6 g $\pm$ 0,01 g of sodium azide (NaN_3) in approximately 500 ml of water in a 1 000 ml volumetric flask. Add 5 ml of glacial acetic acid (CH_3COOH) and make up to the mark with water. Store in a dark glass bottle or in a dark place.

CAUTION — Sodium azide is highly toxic in contact with the skin. Wear protective clothing at all times when handling sodium azide. Crystalline sodium azide decomposes explosively under conditions of heat, shock, concussion and friction. Ensure adequate precautions are taken to prevent these conditions occurring.

NOTE The shelf life of bulk electrolyte has been found to be approximately three months.

4.2 Oxygen, of high-purity grade, minimum purity of 99,995 %.

4.3 Carrier gas, of high-purity grade argon, helium or nitrogen, with a minimum purity of 99,995 %. If nitrogen is used, it should be tested in the apparatus for baseline stability.

4.4 Iodine, resublimed.

4.5 Sulfur-free solvent, preferably a sulfur solvent which is essentially sulfur-free ($<$ 0,5 mg/kg) or has an accurately known low ($<$ 5 mg/kg) sulfur content, similar in characteristics to the sample being analysed. Alternatively, a high-purity grade of cyclohexane, 2,2,4-trimethylpentane, toluene or hexadecane is suitable, as appropriate.

4.6 Sulfur stock solution

4.6.1 General

A certified reference material (CRM), or a prepared stock solution with a sulfur content in the range 200 mg/kg to 500 mg/kg.

4.6.2 Preparation

Select a solvent-soluble sulfur compound (see the note in this subclause) of accurately known sulfur content, preferably appropriate to the boiling range and sulfur type expected to be present in the sample. Weigh, to the nearest 0,1 mg, a quantity of this compound into a weighed 100 ml volumetric flask. Add solvent (4.5), swirl to ensure dissolution, make up to the mark with solvent and reweigh to the nearest 0,1 mg. Calculate the exact sulfur content to the nearest 0,000 1 % (m/m) (1 mg/kg).

NOTE Suitable sulfur compounds include:

a) thiophene, of nominal sulfur content 38,103 % (m/m);

b) dibutyl sulfide (DBS), of nominal sulfur content 21,915 % (m/m);

c) dibenzothiophene (DBT), of nominal sulfur content 17,399 % (m/m);

d) thionaphthene (TNA), of nominal sulfur content 23,89 % (m/m).

4.7 Sulfur standard solutions

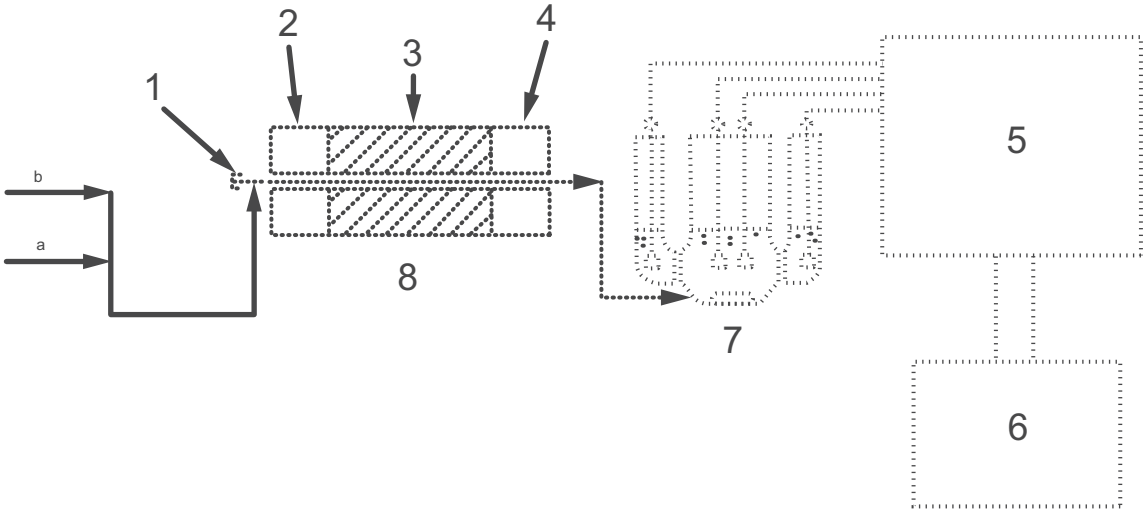
Prepare a range of sulfur standard solutions to cover the range of concentrations expected in the samples being analysed, by dilution of the stock solution (4.6) with solvent (4.5) calculated on the basis of mass fraction. At least three standard solutions are required for each concentration level, or a range of not less than five standard solutions to cover a set of sample analyses within the total scope of this International Standard.

5 Apparatus

5.1 Microcoulometric apparatus

5.1.1 General

The microcoulometer and associated apparatus are described in 5.1.2 to 5.1.7, and the general arrangement is shown in Figure 1.



Key

1 sample injection septum
2 inlet zone
3 oxidizing combustion zone
4 outlet zone
5 mirocoulometer
6 potentiometric recorder
7 titration cell
8 pyrolysis furnace

[a] Oxygen, O_2.

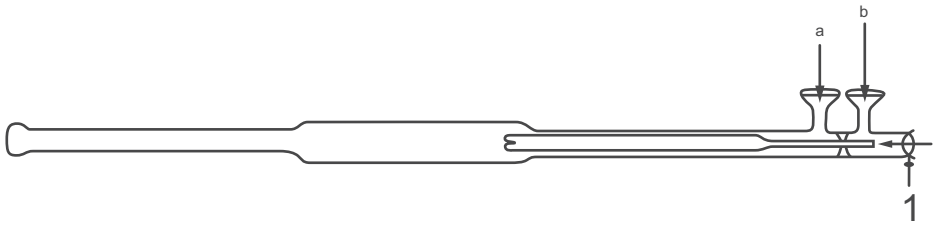
[b] Carrier gas.

Figure 1 — General arrangement of microcoulometric apparatus

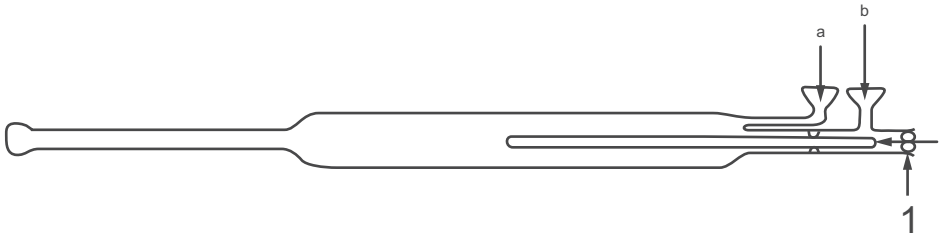
5.1.2 Pyrolysis furnace, electrically powered, consisting of two or three independently controlled temperature zones. The first, or inlet, zone shall maintain a temperature sufficient to volatilize the entire organic sample. The second zone, or oxidizing combustion zone, shall maintain a temperature sufficient to pyrolize the organic matrix and oxidize all the organically bound sulfur. The third, or outlet, zone for further pyrolysis, is optional. The manufacturer's instructions should be consulted for optimum temperatures.

5.1.3 Pyrolysis tube, of quartz, constructed in such a way that the test portion is completely vaporized in an inert gas atmosphere in the inlet section and swept into the oxidation zone, where it mixes with oxygen and is burned. The inlet end of the tube shall hold a septum for syringe introduction of the test portion, and side arms for the admission of oxygen and carrier gas. The oxidizing combustion zone(s) shall be of sufficient volume to ensure complete pyrolysis of the test portion. The outlet section of the tube may be closed by a 20 mm length of quartz-wool if desired. Typical designs of pyrolysis tube are shown in Figure 2. Some manufacturers recommend the use of a chemical scrubber in line between the pyrolysis furnace and the titration cell. This scrubber is used for the removal of soot, water and heavy metals, and aids the stability of the titration cell.

For the analysis of products with a substantial portion boiling above 230 °C, a boat inlet system may give better recovery.



a) TOT tube



b) COT tube

Key

1 septum

a Oxygen, O_2.

b Ar, He or N_2.

Figure 2 — Typical designs of pyrolysis tube

5.1.4 Boat inlet system, sealed to the combustion tube, with boats made from platinum or quartz, and with a drive mechanism that advances and withdraws the boat at a controlled and repeatable rate.

5.1.5 Titration cell, containing a sensor-reference pair of electrodes to detect changes in tri-iodide ion concentration, and a generator anode-cathode pair of electrodes to maintain constant tri-iodide ion concentration in the cell electrolyte. For the description of the sensor electrodes used, consult the manufacturer's operating manual.

Shielding of the cell from electrical interferences by means of an earthed (grounded) Faraday cage is recommended by some manufacturers and should be described in the manufacturer's operating manual, particularly in the determination of very low milligram per kilogram levels of sulfur.

The cell shall be provided with a suitable inlet for the combustion gases from the pyrolysis tube, and supplied with appropriate stirring. If a magnetic stirrer is used, the stirring rate should not be excessive, to ensure that the stirring bar does not rise in the cell and damage the electrodes. The creation of a slight vortex is adequate. Some instruments rely on the agitation caused by gas bubbling through the solution.

5.1.6 Microcoulometer, supplied with variable or automatic attenuation and gain control, and capable of measuring the potential of the sensor-reference electrode pair, and comparing this potential with a bias potential, amplifying this difference in potential, and applying the equivalent current to the amplified difference to the generator electrode pair so as to generate a titrant. The microcoulometer output voltage shall be proportional to the generating current.

5.1.7 Recorder/integrator, having a sensitivity of at least 0,1 mV/25 mm, with speeds of 10 mm/min to 20 mm/min. A mechanical or electronic integrator is recommended for peak area measurement. Modern systems normally have an integrated or separate PC/printer for recording and printing of data.

5.1.8 Heating tape, electrically powered, of capacity 30 W to 60 W, wound around the cell gas inlet tube, required to maintain a temperature of approximately 90 °C to 300 °C to prevent condensation of water (consult the manufacturer's operating manual).

5.2 Sampling (micro)syringes, of appropriate capacity, fitted with needles of sufficient length to reach the inlet zone of the pyrolysis furnace (used according to the manufacturer's instructions).

Means should be provided to control the test portion injection rate to ensure that the pyrolysis capacity of the tube is not exceeded. Consult the manufacturer's recommendations for the appropriate injection rate. Automatic injection devices are available and are recommended as a means to control the rate of injection.

5.3 Gas regulators, comprising two-stage regulators for the oxygen (4.2) and carrier gas (4.3), to provide the specified flow rates at the outlet.

5.4 Analytical balance, single-pan or two-pan, capable of weighing with an accuracy of 0,1 mg.

5.5 Volumetric flasks, one-mark, of capacities between 100 ml and 1 000 ml for the preparation of electrolyte, stock and sample solutions.

6 Samples and sampling

6.1 Unless otherwise specified, laboratory samples shall be obtained in accordance with ISO 3170 or ISO 3171.

6.2 Samples that are clear and bright at the laboratory ambient temperature can have subsamples or test portions removed directly from the container. For some heavier middle distillates, gentle warming to a temperature at least 15 °C above the cloud point is necessary to ensure homogeneity prior to subsampling, although the sample temperature shall not exceed 70 °C.

7 Apparatus preparation

7.1 Titration cell

7.1.1 Ensure that the generator electrodes and the sensor electrode are perfectly clean. If in doubt, wash with water followed by acetone, dry, and then carefully heat to a bright orange colour in a gas flame. Allow to cool before insertion in the electrolyte. Consult the manufacturer's instructions for the cleaning procedures for their particular electrode types.

7.1.2 Prepare the reference electrode using approximately 2 g of coarsely ground iodine (4.4), covered with electrolyte (4.1). Fill the cell with electrolyte to a height of approximately 50 mm and transfer the ground iodine in small portions to the reference side arm, making sure that no air bubbles are trapped between the iodine granules. Carefully insert the platinum electrode into the iodine granules with the ground-glass joint very lightly greased to give a gas-tight seal. Ensure that no air bubbles are trapped in the electrolyte above the iodine.

7.1.3 Flush the cell with several volumes of electrolyte, ensuring that no air bubbles are trapped in the cell, particularly the generator and reference electrode side arms. Adjust the electrolyte level to between 5 mm and 8 mm above the electrodes.

7.1.4 If a magnetic stirrer is used, slide in the stirring bar and place the cell cap in position, such that the sensor electrode is adjacent to the reference side arm. With the magnetic stirrer switched off, place the cell centrally on the stirrer and connect the gas inlet to the combustion tube.

7.1.5 Connect the electrodes to the microcoulometer via the appropriate connecting plugs.

7.2 Microcoulometer and recorder

Assemble and connect the microcoulometer and recorder (and/or integrator) in accordance with the manufacturer's instructions, and in the general arrangement shown in Figure 1.

CAUTION — For certain instruments, it is recommended that the microcoulometer unit not be placed on top of the furnace without a heat-resistant layer between the two units (see the manufacturer's instructions).

7.3 Heating tape

For certain instruments, it is necessary to independently turn on the heating tape (5.1.8).

7.4 Typical operating conditions

Adjust the flow of gases, the pyrolysis furnace temperatures, titration cell and microcoulometer to the desired operating conditions. See the manufacturer's operating conditions for the correct setting for the instrument.

8 Apparatus verification and calibration curve construction

8.1 Select sulfur standard solutions (4.7) to cover the range of sulfur contents expected. Perform at least three measurements on each standard solution.

8.2 Adjust the operational parameters according to the manufacturer's recommendations, and select the appropriate test portion sizes.

8.3 Inject the test portion, and record the volume and/or mass injected. If the density of the sulfur standard solution is known, or has been determined, the mass can be calculated from the volume injected. Alternatively, weigh, to the nearest 0,1 mg or better, the syringe containing the sulfur standard solution before and after injection, and determine the difference between the two masses to obtain the mass injected. An even injection rate of the solution within the range of 0,1 µl/s to 1,0 µl/s is recommended.

For volumetric injection, it is important to be aware of the sample present in the needle of the syringe — the “needle blank”. Thus, the volume injected should be obtained by withdrawal of the plunger to a suitable graduation on the syringe barrel prior to injection and the volume noted. The needle is then placed through the septum, allowing the remaining sample in the needle to evaporate. Once the base-line returns to a stable position, the analyser is then started.

8.4 Check the shape of the sulfur peak.

8.4.1 The sulfur peak shall be of the correct shape [see Figure 3 b)].

8.4.2 If the peak is tailing [see Figure 3 a)], increase the gain and/or bias control in small increments until the peak has the correct shape.

8.4.3 If the peak is overshooting [see Figure 3 c)], reduce the gain and/or bias control in small increments until the peak has the correct shape.

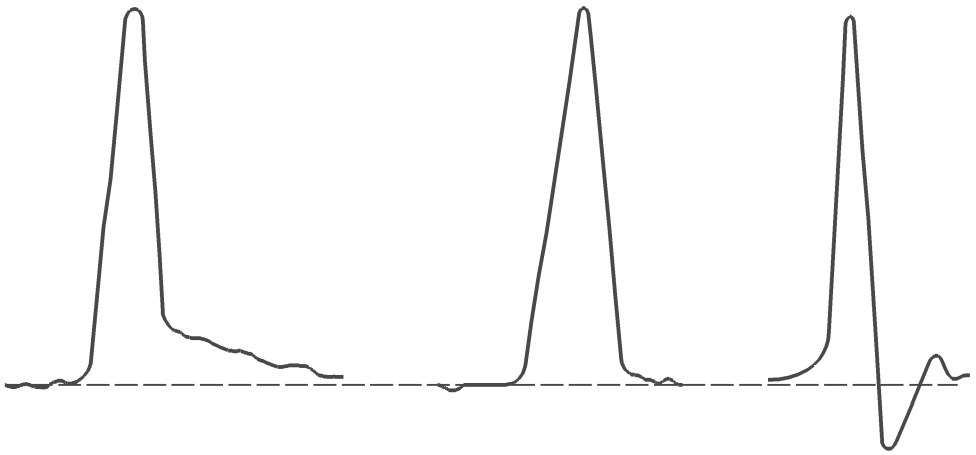
8.5 Record the peak area, either manually or by means of an integrator (5.1.7) or the system data station. With manual instruments, select the attenuation to give a peak size of approximately half the chart width.

8.6 Plot the average peak area for each standard against mass of sulfur, in micrograms (µg), for each series of sulfur standard solutions.

Since not all of the sulfur is converted in the strongly oxidative conditions of the furnace to sulfur dioxide (SO_2), and some is converted to sulfur trioxide (SO_3) which does not react with the titrant, more than one series of sulfur standard solutions may be required to cover the different conversion rates related to sample and sulfur compound type (see 4.5 to 4.7). Recoveries of less than 75 % are suspect, and the operator should check the instrument parameters, the coulometric system and his/her operating techniques. Recoveries of between 75 % and 90 % are to be expected. Annex B gives information on possible faults and corrective actions. Further information should be available from the manufacturer of the instrument.

8.7 Repeat points on the calibration curves frequently to ensure consistency of operating conditions.

8.8 It is recommended that daily, or every 10 determinations, a sulfur solution close in characteristics to the last sample analysed be run, and the results examined for compliance within the repeatability of this International Standard. This may be done by a standard solution (4.7), but not by one that has been used to construct the calibration curve (see 8.1).



a) Tailing **b) Correct shape** **c) Overshooting**

Figure 3 — Sulfur peak shapes

9 Procedure

9.1 Determine the density of the sample at laboratory ambient temperature, to the nearest 0,1 kg/m^3, in accordance with ISO 3675 or ISO 12185.

If the temperature of sample injection is more than 3 °C from the temperature of determination, or if the density used is at a reference temperature, ISO 91-1 may be used to calculate the density at the injection temperature.

9.1.1 Syringe inlet system

Using a clean syringe (5.2), carry out the operations described in 8.3 to 8.5, and record the peak area. Perform a minimum of three measurements on the sample and calculate the mean value.

9.1.2 Boat inlet system

The boat inlet system shall be assembled consistent with the manufacturer's instructions. Perform a minimum of three measurements on the sample and calculate the mean value.

9.2 From the appropriate calibration curve (8.6), read off the mass of sulfur in the test portion.

10 Calculation

10.1 Calculate the sulfur content, w_S, in milligrams per kilogram (mg/kg), using Equation (3):

$$w_S = \frac{m_{S,t}}{m_{test}} \tag{3}$$

where

$m_{S,t}$ is the mass of sulfur in the test portion, obtained from the calibration curve, expressed in micrograms (µg);

m_{test} is the mass of the test portion [or the volume (in µl) × the density (in kg/m^3) × 10^{-6}], expressed in grams (g).

10.2 If the sample was diluted to produce the test portion, calculate the sulfur content using Equation (4):

$$w_S = m_{S,t} \times \frac{m_{test}}{m_{test1}} \tag{4}$$

where m_{test1} is the mass of sample in the mass of test portion, m_{test}, expressed in grams (g).

10.3 The sulfur content can be calculated from the electrochemical data and peak area measurements, as described in Annex C. Values calculated directly in this manner give information on sulfur (SO_2) recovery, necessary for apparatus set-up parameters.

11 Expression of results

Report the sulfur content to the nearest 0,1 mg/kg for values below 10 mg/kg, and to the nearest 1 mg/kg for values of 10 mg/kg to 100 mg/kg.

12 Precision

12.1 General

The precision, as determined by statistical examination according to ISO 4259, of interlaboratory test results on a matrix of samples with sulfur contents in the range of 1 mg/kg to 110 mg/kg is given in 12.2 and 12.3.

12.2 Repeatability, r

The difference between two test results obtained by the same operator with the same apparatus under constant operating conditions on identical test material would in the long run, in the normal and correct operation of the test method, exceed the following value in only one case in twenty.

$$r = 0{,}063X$$

where X is the average of the test results being compared.

12.3 Reproducibility, R

The difference between two single and independent test results obtained by different operators working in different laboratories on identical test material would in the long run, in the normal and correct operation of the test method, exceed the following value in only one case in twenty.

$$R = 0{,}147X$$

where X is the average of the test results being compared.

13 Test report

The test report shall contain at least the following information:

a) a reference to this International Standard, i.e. ISO 16591;

b) the type and complete identification of the product tested;

c) the result of the test (see Clause 11);

d) any deviation, by agreement or otherwise, from the procedure specified;

e) the date of the test.

Annex A
(informative)

Determination of sulfur contents below 1 mg/kg — Standby technique

A.1 General

At sulfur levels below 1 mg/kg, the standby technique is recommended by certain manufacturers as, apart from the larger test portion employed, the titration of the SO_2 formed is delayed until interfering phenomena in the titration cell have ceased and equilibrium is re-established. Some manufacturers offer a special titration cell for use with determinations below 1 mg/kg.

A.2 Procedure

A.2.1 Ensure that the titration cell is scrupulously clean, and adjust the operating conditions of the microcoulometer according to the manufacturer's recommendations.

A.2.2 Withdraw 10 µl of sample into a 25 µl microsyringe barrel. With the function switch on the microcoulometer in the “operate” position, insert the needle through the septum into the inlet portion of the combustion tube and allow the needle peak to appear on the recorder. (Some instruments have this facility or a similar system; see the manufacturer's instructions to operate this technique.)

A.2.3 Switch the function switch on the microcoulometer to “standby”, start a timing device, and inject a test portion of 10 µl at a rate not exceeding 0,3 µl/s. The use of a cranking device is recommended.

A.2.4 Allow the cell to equilibrate for 30 s to 60 s. After a total combustion period of 1 min to 2 min, measured accurately, switch the function switch back to “operate”.

NOTE This causes the appearance of a sharp peak.

A.2.5 Repeat the procedure given in A.2.2 to A.2.4 with an appropriate sulfur standard solution (4.7), and then with the solvent used in that standard solution (4.5). Use the same duration of the combustion period (time on “standby”) as for the test portion.

A.2.6 Plot the peak areas for the determinations, and calculate the sulfur content of the sample from a linear plot of the concentrations of sulfur standard solution and solvent.

Annex B
(informative)

Troubleshooting

B.1 Noisy baseline and/or low response

B.1.1 Gas bubbles

Gas bubbles can accumulate in the reference and/or generator cathode side arms, which can be removed by flushing with electrolyte. In the case of the reference side arm, lift the electrode and allow the electrolyte to overflow from the vertical section. Re-insert the electrode.

B.1.2 Contaminated sensor and generator anode

Consult the manufacturer's instructions for the best advice on cleaning the electrodes.

B.1.3 Gas regulation

Replace regulators, particularly second-stage regulators, which give poor regulation of pressure and/or flow.

B.1.4 Combustion tube deposits

NOTE Each manufacturer has his/her own procedures for the cleaning and rejuvenation of the glassware.

Carbonaceous deposits or “active spots” can occur in the combustion tube. Carbonaceous deposits in the inlet portion develop when the inlet temperature is too high and/or samples of excessive final boiling point (FBP) are combusted. Burn off the carbon deposits in a stream of air, removing the tube, if necessary. Carbonaceous deposits in the cold portion of the tube outlet are a result of oversize test portions or insufficient oxygen (flow rate too low). Burn off in a stream of air.

If the above-mentioned does not restore a satisfactory baseline, “active spots”, due to local devitrification of the tube, might have developed. Treatment of the tube with 50:50 (by volume) hydrofluoric acid (HF) may restore the tube. If it does not, discard the tube.

CAUTION — Hydrofluoric acid is highly corrosive and aggressive to any contact with skin and nails. It is particularly aggressive to glass. Wear appropriate gloves and full-face shield when handling.

If carbonaceous deposits have formed on the combustion tube outlet, it is possible that they have also formed in the cell gas inlet capillary. In that case, drain the electrolyte from the cell through the generator cathode side arm, leaving the electrolyte in the reference side arm, and remove the cell cap. Add a small quantity of concentrated HF (see the caution given in this subclause) into the cell body, tilt the cell, and allow the acid to drain through the gas capillary. As soon as the carbon deposits are loosened, flush the cell very thoroughly with water, not disturbing the electrolyte in the reference side arm. Finally, flush the cell through both arms with fresh electrolyte. Do not allow the HF to be in contact with the cell for more than 1 min, to prevent severe attack by the acid.

B.1.5 Static interference

At high sensitivity settings, instability of the baseline can occur if a static field exists in the area of the titration cell. The effect can be reduced by earthing (grounding) the stirrer motor, and using a Faraday cage [also earthed (grounded)] around the cell (see 5.1.5, second paragraph). Consult the manufacturer's instructions.

B.1.6 Suspected faulty amplifier

Consult the manufacturer's instructions or contact the supplier.

B.1.7 Recorder (if applicable)

If the recorder gain is too high, it can give a noisy baseline.

B.2 Baseline shifts

If the baseline shifts significantly with increasing attenuation, it is likely to be due to impurities in the gas supplies. Insert an adsorber, packed with 5A activated molecular sieve, into the appropriate line.

B.3 Explosion on injection

If a small explosion occurs when injecting the test portion, this is due to a leaky septum, which shall be replaced. A sign of a worn septum is little pieces of rubber in the inlet tube just behind the septum. Carefully remove these pieces when replacing the septum as introduction into the combustion tube can cause carbonizing.

B.4 Poor precision

Poor precision can be due to a worn, or a poor-quality microsyringe, worn septum or contamination by the sample container's seals.

B.5 Peak overshoot

B.5.1 If the peak overshoots, and the baseline drifts downscale, this can be due to diffusion of iodine solution from the reference electrode into the side arm. The cell has not yet reached equilibrium, or the ground-glass joint is not sealed properly. Lightly grease the joint and re-insert. Consult the manufacturer's instructions.

B.5.2 If the peak overshoots, and this is not corrected by lowering the bias, the centre electrodes are contaminated and/or the electrolyte is exhausted. Clean the electrodes, as described in the manufacturer's operating instructions, and prepare fresh electrolyte.

Annex C
(informative)

Calculation of sulfur content from electrochemical data

C.1 Derivation of equations

C.1.1 The derivation of the equations is based on the coulometric replacement of the tri-iodide (iodine) ions consumed in the microcoulometer titration cell reaction [see Equation (2)]. The quantity of the reactant formed (tri-iodide ions) between the beginning and the interruption of current at the end of the titration is directly proportional to the net charge transferred, Q.

C.1.2 In most applications, a constant current is used such that the product of current, i, in amperes (coulombs per second), multiplied by the time, T, in seconds, required to reach the end point provides a measure of the charge, Q, in coulombs, necessary to generate the iodine equivalent of the reactant; that is $Q = iT$. Therefore, the number of equivalents of reactant is equal to Q/F, where F is the Faraday constant at 96 500 C per equivalent (C/eq).

C.1.3 Therefore, the expression that should be solved to find the sulfur content is:

$$w_S = \frac{m_{S,t}}{m_{test}} = \frac{\left[Q(C)/F(C/eq)\right] \times 16\ g/eq}{m_{test}} \quad (C.1)$$

where

w_S is the concentration of sulfur in the test portion;

$m_{S,t}$ is the mass of sulfur in the test portion;

m_{test} is the mass of the test portion.

The mass of sulfur in the test portion, $m_{S,t}$, is given, in micrograms (µg), by Equation (C.2):

$$m_{S,t} = A \times \frac{U \times V \times 60 \times 10^{-3} \times 16 \times 10^{6}}{R \times 96\,500 \times (A \cdot s/C) \times f} \quad (C.2)$$

where

A is the peak area, expressed in square units of length;

U is the millivolt span of upscale recorder deflection, expressed in millivolts per same length scale as A;

V is the chart speed, expressed in the same length scale as A per minute;

60 is seconds per minute;

10^{-3} is volts per millivolt;

16 is the gram-equivalent of sulfur;

10^6 is micrograms per gram;

R is the microcoulometer range switch setting, expressed in ohms;

A·s/C is the conversion of coulombs to ampere-seconds;

f is the recovery factor (ratio of determined:known sulfur content of standard solutions).

Since $V/R = I$ (amps)

$$Q = \frac{A \times U \times V \times 60 \times 10^{-3}}{R} \tag{C.3}$$

Therefore

$$m_{S,t} = \frac{A \times U \times V \times 60 \times 10^{-3} \times 16 \times 10^{6}}{R \times 96\,500 \times f} \tag{C.4}$$

and the sulfur content, w_S, expressed in milligrams per kilogram, mg/kg, becomes:

$$w_S = \frac{A \times U \times V \times 9{,}948}{R \times f \times m_{test}} \tag{C.5}$$

where m_{test} is the mass of the test portion, expressed in grams.

Bibliography

[1] ISO 91-1, *Petroleum measurement tables — Part 1: Tables based on reference temperatures of 15 °C and 60 °F*

[2] ISO 4259, *Petroleum products — Determination and application of precision data in relation to methods of test*

[3] ISO 4260, *Petroleum products and hydrocarbons — Determination of sulfur content — Wickbold combustion method*

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