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Petroleum products — Determination of total sulfur content of liquid petroleum products — Ultraviolet fluorescence method

Produits pétroliers — Détermination de la teneur en soufre total des produits pétroliers liquides — Méthode par fluorescence ultra-violette

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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.

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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.

Attention is drawn to the possibility that some of the elements of this International Standard may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

International Standard ISO 20846 was prepared by Technical Committee ISO/TC 28, *Petroleum products and lubricants*.

Introduction

Petroleum products — Determination of total sulfur content of liquid petroleum products — Ultraviolet fluorescence method

WARNING — The use of this International Standard may involve hazardous materials, 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 total sulfur content of liquid hydrocarbons boiling in the approximate range of 25 °C to 400 °C, and with viscosities in the approximate range of 0,2 mm²/s to 10 mm²/s at room temperature. This method is applicable to naphthas, automotive gasolines, including those containing oxygenated blend components, kerosenes and gas oils, containing 1 mg/kg to 500 mg/kg total sulfur. Halogens interfere with this detection technique at concentrations above approximately 3 500 mg/kg.

NOTE 1 Some process catalysts used in petroleum and chemical refining may be poisoned when trace amounts of sulfur bearing materials are contained in the feedstocks.

NOTE 2 This test method may be used to determine sulfur in process feeds and may also be used to control sulfur in finished products.

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 normative documents contain provisions which, through reference in this text, constitute provisions of this International Standard. For dated references, subsequent amendments to, or revisions of, any of these publications do not apply. However, parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent editions of the normative documents indicated below. For undated references, the latest edition of the normative document referred to applies. Members of ISO and IEC maintain registers of currently valid International Standards.

ISO 1042:1983, *Laboratory glassware — One-mark volumetric flasks.*

ISO 3170:1988, *Petroleum liquids — Manual sampling.*

ISO 3171:1988, *Petroleum liquids — Automatic pipeline sampling.*

ISO 3675:1998, *Crude petroleum and liquid petroleum products — Laboratory determination of density — Hydrometer method.*

ISO 12185:1996, *Crude petroleum and petroleum products — Determination of density — Oscillating Utube method.*

3 Principle

A hydrocarbon sample is directly injected. The sample enters into a high temperature combustion tube (1 000 °C to 1 100 °C), where the sulfur is oxidized to sulfur dioxide (SO₂) in an oxygen-rich atmosphere. Water produced during the sample combustion is removed and the sample combustion gases are next exposed to ultraviolet (UV) light. The SO₂ absorbs the energy from the UV light and is converted to excited sulfur dioxide (SO₂*). The fluorescence emitted from the excited SO₂* as it returns to a stable state SO₂ is detected by a photomultiplier tube and the resulting signal is a measure of the sulfur contained in the sample.

CAUTION — Exposure to excessive quantities of ultraviolet (UV) light is injurious to health. The operator must avoid exposing any part of their person, especially their eyes, to not only direct UV light but also to secondary or scattered radiation that may be present.

4 Reagents and materials

4.1 Inert gas, argon or helium, high purity grade with a minimum purity of 99,998 %.

4.2 Oxygen, high purity grade with a minimum purity of 99,75 %.

CAUTION — Vigorously accelerates combustion.

4.3 Solvent

4.3.1 General

Use either the solvent specified in 4.3.2 or 4.3.3 or a solvent similar to that occurring in the sample under analysis. Correction for sulfur contribution from solvents used in standard preparation and sample dilution is required. Alternatively, use of a solvent with non-detectable sulfur contamination relative to the unknown sample makes the blank correction unnecessary.

4.3.2 Toluene, reagent grade.

4.3.3 Isooctane, reagent grade.

CAUTION — Flammable solvents.

4.4 Sulfur compounds

4.4.1 Compounds of accurately known high purity with a minimum purity of 99 %. Examples are given in 4.4.1.1 to 4.4.1.3.

NOTE A correction for chemical impurity can be required.

Certified reference materials (CRMs) from accredited suppliers are suitable alternatives to the compounds listed in 4.4.1.1 to 4.4.1.3.

4.4.1.1 Dibenzothiophene (DBT), FW 184,26 with a nominal sulfur content of 17,399 % (*m/m*).

4.4.1.2 Dibutyl sulfide (DBS), FW 146,29 with a nominal sulfur content of 21,915 % (*m/m*).

4.4.1.3 Thionaphthene (Benzothiophene) (TNA), FW 134,20 with a nominal sulfur content of 23,890 % (*m/m*).

4.5 Sulfur stock solution

Prepare a stock solution of approximately 1 000 mg/l sulfur content by weighing accurately the appropriate quantity of sulfur compound (4.4). Ensure complete dissolution. Calculate the exact concentration of sulfur, to the nearest 1 mg/l in the stock solution. This stock solution is used for the preparation of calibration standards.

NOTE 1 The appropriate mass of sulfur compound described in 4.4.1.1 to 4.4.1.3 to add to the 100 ml flask is 0,574 8 g (DBT), 0,456 3 g (DBS) and 0,418 6 g (TNA).

NOTE 2 A sulfur stock solution of approximately 1 000 mg/kg could either be prepared by weighing accurately the appropriate quantity of sulfur compound and the final quantity after the solvent addition. Take precautions to ensure that evaporation of the solvent and/or sulfur compounds is not causing weighing errors.

NOTE 3 When stored at low temperature, typically in a refrigerator, the shelf life of the stock solution is approximately three months.

4.6 Calibration standards

Prepare the calibration standards by volumetric (milligrams per litre) or weighing (milligrams per kilogram) dilutions of the stock solution (4.5) with the selected solvent (4.3).

Calculate the exact sulfur content of each calibration standard.

NOTE Calibration standards should be remixed on a regular basis depending upon frequency of use and age. When stored at low temperature, typically in a refrigerator, the calibration standards, with a sulfur content above 30 mg/kg (or mg/l) have a useful life up to one month. Below this sulfur content (30 mg/kg), the shelf life should be reduced.

4.7 Quality control samples

These are stable samples representative of the materials being analyzed, that have a sulfur content that is known by this test method over a substantial period of time, or is supplied commercially with a certified value. Ensure before use, that the material is within its shelf life.

4.8 Quartz wool

5 Apparatus

5.1 Furnace, comprising an electric device, capable of maintaining a temperature sufficient to pyrolyse all of the sample and oxidize all sulfur to sulfur dioxide (SO₂). It can be set either in a horizontal or vertical position.

5.2 Combustion tube, of quartz, constructed to allow the direct injection of the sample into the heated oxidation zone of the furnace (5.1). The combustion tube shall have side arms for the introduction of oxygen and carrier gas. The oxidation section shall be large enough to ensure complete combustion of the sample. It can be set either in a horizontal or vertical position.

5.3 Flow controllers, capable of maintaining a constant supply of oxygen and carrier gas.

5.4 Vapour drier, capable of removing water vapour formed during combustion prior to measurement by the detector (5.5).

5.5 UV fluorescence detector, a qualitative and quantitative detector capable of measuring light emitted from the fluorescence of sulfur dioxide by UV light.

5.6 Microlitre syringe, capable of accurately delivering between 5 μ l to 50 μ l quantities. Follow the manufacturer's instructions for determining the length of the needle required.

5.7 Sample inlet system, either vertical or horizontal. It shall consist of a direct injection inlet system capable of allowing the quantitative delivery of the material to be analyzed into an inlet carrier stream which directs the sample into the oxidation zone at a controlled and repeatable rate. A syringe drive mechanism which discharges the sample from the microlitre syringe at a constant rate of approximately 1 µl/s maximum is required.

5.8 Balance, capable of weighing with an accuracy of at least 0,1 mg.

5.9 Volumetric flasks, Class A one-mark volumetric flasks, according to ISO 1042, of appropriate capacities, including 100 ml, for the preparation of sulfur stock solution (4.5) and calibration standards (4.6).

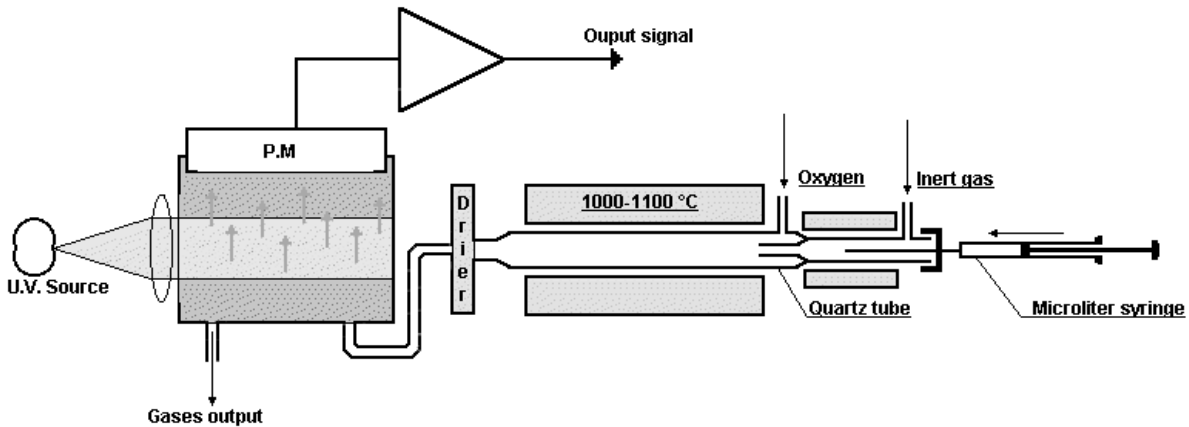


Figure 1 — Synopsis of the apparatus

6 Sampling

6.1 Unless otherwise specified, obtain the laboratory sample by the procedures describes in ISO 3170 or ISO 3171. To preserve volatile components which are in some samples, keep samples at as low temperature as is practicable and do not uncover samples any longer than necessary.

Samples should be analyzed as soon as possible after taking from bulk supplies to prevent loss of sulfur or contamination due to exposure or contact with the sample container.

CAUTION — Samples that are collected at temperatures below room temperature can undergo expansion and rupture the container. For such samples, do not fill the container to the top; leave sufficient air space above the sample to allow room for expansion.

6.2 If the sample is not used immediately, then thoroughly mix in its container prior to taking a test portion.

7 Apparatus preparation

7.1 Assemble the apparatus and check for leaks according to the manufacturer's instructions.

7.2 Adjust the inlet pressure and flow rate of each gas according to the manufacturer's instructions.

7.3 Refer to the manufacturer's instructions to set the temperature of the furnace (5.1) high enough to ensure all sulfur pyrolysis and oxidation, typically 1100 °C in the case of a one temperature zone furnace or 750 °C for pyrolysis, and 1 000 °C to 1 100 °C for oxidation in the case of a two zone temperature furnace.

7.4 Adjust the instrument sensitivity and baseline stability, and perform instrument blanking procedures following the manufacturer's guidelines. Ensure that the UV light is stable before measurement.

NOTE For the UV light, a warm up time of at least 30 min is usually required.

8 Apparatus calibration and verification

8.1 Multi-points calibration

8.1.1 Select one of the suggested curves outlined in Table 1. Prepare a series of calibration standards (4.6) by carrying out dilutions of the stock solution (4.5) to cover the range of operation. The number of calibration standards used in construction of the calibration curve can vary but it should not be less than four.

Table 1 — Calibration standards

Curve I	Curve II	Curve III
Sulfur mg/l or mg/kg	Sulfur mg/l or mg/kg	Sulfur mg/l or mg/kg
0,5	5	50
2	25	150
5	50	350
10	100	500

8.1.2 Flush the microlitre syringe (5.6) several times with the solution to be analyzed and ensure that the final liquid column in the syringe contains no bubbles.

8.1.3 An appropriate sample size, given by the manufacturer's instructions, shall be quantitatively measured prior to injection into the combustion tube for analysis, by one of the techniques described in 8.1.3.1 or 8.1.3.2.

NOTE Injection of a constant or similar sample size for all materials analyzed in a selected operating range promotes consistent combustion conditions.

8.1.3.1 For volumetric measurement, fill the syringe to the selected level and retract the plunger so that air is aspirated and the lower liquid meniscus falls on the 10 % scale mark. Record the volume of liquid in the syringe. After injection, again retract the plunger so that the lower liquid meniscus falls on the 10 % scale mark and record the volume of liquid in the syringe. The difference between the two volume readings is the volume of sample injected.

NOTE An automatic sampling and injection device can be used in place of the described manual injection procedure.

8.1.3.2 For mass measurement, weigh the syringe complete with a filled needle before, and the syringe and needle after injection, to determine the mass of the test portion injected.

NOTE Mass measurement may be more accurate than the volume measurement for less volatile samples, if a balance with an accuracy of at least 0,01 mg is used.

8.1.4 Once the appropriate sample size has been measured into the microlitre syringe, promptly and quantitatively deliver the sample into the apparatus.

For direct injection, carefully insert the syringe into the inlet of the combustion tube (5.2) and the syringe drive. Allow time for sample residues to be burned from the needle (needle blank). Once a stable baseline has re-established, promptly start the analysis. Remove the syringe once the apparatus has returned to a stable baseline.

8.1.5 Construct each calibration curve by one of the techniques described in 8.1.5.1 to 8.1.5.2.

8.1.5.1 For manual construction, perform measurements for the calibration standards and the blank using the procedure described in 8.1.2 to 8.1.4. Measure the calibration standards and the blank three times. Subtract the average blank response from each standard measurement before determining the average integrated response. Construct a curve plotting average integrated detector response (y-axis) versus quantity (in nanograms) of sulfur injected (x-axis). This curve should be linear with a correlation factor of at least 0,995 min.

8.1.5.2 If the apparatus features an internal calibration routine, measure the calibration standards and the blank three times using the procedure described in 8.1.2 to 8.1.4. If blank correction is required and is not available (see 4.3), correct the analyzer responses using the average response for each standard versus quantity (in nanograms) of sulfur, as obtained in 8.1.5.1. This curve should be linear with a correlation factor of at least 0,995 min.

NOTE For curve III (Table 1), the blank correction may be omitted.

8.1.6 The analyzer calibration can be performed using a different calibration curve to those listed in Table 1. A good practice consists of constructing a calibration curve in such a way that the sulfur content of the sample to be analyzed is in the middle of the calibration curve.

8.2 One-point calibration

8.2.1 Prepare a calibration standard (4.6) with a sulfur content close to that of the sample to be analyzed (? 20 % maximum), by carrying out dilutions of the stock solution (4.5).

If necessary, the sulfur content of the calibration standard should be corrected by the sulfur content of the selected solvent (4.3).

NOTE In order to measure the sulfur content of the selected solvent, the method of standard additions on the solvent gives satisfactory results.

8.2.2 Measure a minimum of three times the appropriate sample size of the calibration standard, according to the manufacturer's instructions, using the procedure described in 8.1.2 to 8.1.4.

8.2.3 Calculate a calibration factor, K , in counts number per nanogram of sulfur (counts/ng S) as follows:

$$K = \frac{A_c}{M_c \cdot S_{cg}}$$

or

$$K = \frac{A_c}{V_c \cdot S_{cv}}$$

where

A_c is the integrated detector response for calibration standard, in counts number;

M_c is the mass of calibration standard injected, expressed in milligrams, either measured directly or calculated from the measured volume injected and the density as follows:

$$M = V \cdot D_c$$

D_c is the density of the calibration standard at measurement temperature, expressed in grams per millilitre;

V_c is the volume of calibration standard injected, expressed in microlitres;

S_{cg} is the sulfur content of the calibration standard, expressed in milligrams per kilogram;

S_{cv} is the sulfur content of the calibration standard, expressed in milligrams per litre.

Calculate the average of the calibration factor and check that the standard deviation is within the tolerance accepted.

This calibration factor shall be established every day.

8.3 Verification

8.3.1 Check the calibration validity with a quality control sample, having a known sulfur content, at the beginning of a series of analysis and each time it is necessary during a long series of analysis.

8.3.2 Compare the results to the known values and associated uncertainties. The out of limit results shall be investigated for root cause(s).

9 Procedure

9.1 Determine the density of the sample at laboratory ambient temperature 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.

9.2 Estimate the sulfur content of the sample, and prepare a test portion that contains a quantity of sulfur within the range of the calibration curve selected, if the multi-points calibration is chosen; or close to the sulfur content of the calibration standard (± 20 % maximum), if one-point calibration is chosen. If the expected sulfur content is above the concentration of the calibration standards, prepare either a volumetric or mass diluted solution with a selected solvent (4.3).

9.3 Measure three times, the appropriate sample size of the test portion, according to the manufacturer's instructions, using the procedure described in 8.1.2 to 8.1.4.

9.4 Inspect the combustion tube and other flow path components to verify complete oxidation of the test portion. If deposits are noted, follow the procedures given in 9.4.1 and 9.4.2.

9.4.1 If coke or soot is observed, clean any parts in accordance with the manufacturer's instructions. After cleaning and/or adjustment, assemble the apparatus and check for leaks. Carry out a check on the calibration quality prior to re-analysis.

9.4.2 Use a reduced sample size or a reduction of injection rate, or both.

10 Calculation

10.1 Using multi-points calibration

For analyzers calibrated using a standard curve, calculate the sulfur content, S , of the sample, in milligrams per kilogram (mg/kg), using the following equation:

$$S = \frac{A - Y}{M \cdot S_s \cdot F_g}$$

or

$$S = \frac{A - Y}{V \cdot S_s \cdot F_v}$$

where

M is the mass of test portion solution injected, expressed in milligrams, either measured directly or calculated from the measured volume injected and density as follows;

$$M = V \cdot D$$

D is the density of test portion solution at measurement temperature, expressed in grams per millilitre;

V is the volume of the test portion solution injected, expressed in microlitres;

A is the integrated detector response for the sample, expressed in counts number;

S_s is the slope of the standard curve, expressed in counts per nanogram of sulfur;

Y is the y-intercept of the standard curve, expressed in counts number;

F_g is the gravimetric dilution factor, mass of test portion/mass of test portion and solvent, expressed in grams per gram;

F_v is the volumetric dilution factor, mass of test portion/volume of test portion and solvent, expressed in grams per millilitre.

10.2 Using one-point calibration

Calculate the sulfur content, *S*, of the sample, in milligrams per kilogram (mg/kg), using the following equation:

$$S = \frac{A}{M \cdot K \cdot F_g}$$

or

$$S = \frac{A}{V \cdot K \cdot F_v}$$

where

K is the calibration factor, expressed in counts per nanogram of sulfur;

M is the mass of test portion solution injected, expressed in milligrams, either measured directly or calculated from the measured volume injected and density as follows:

$$M = V \cdot D$$

D is the density of test portion solution at measurement temperature, expressed in grams per millilitre;

V is the volume of the test portion solution injected, expressed in microlitres;

A is the integrated detector response for the sample, expressed in counts number;

F_g is the gravimetric dilution factor, mass of test portion/mass of test portion and solvent, expressed in grams per gram;

F_v is the volumetric dilution factor, mass of test portion/volume of test portion and solvent, expressed in grams per millilitre.

If there is a dilution in low sulfur content, the calculation shall take into account the correction with the sulfur content of the solvent.

10.3 Calculate the average sulfur content of the sample from three measurements.

11 Expression of results

Report the sulfur content of the sample, in milligrams per kilogram (mg/kg), to the nearest 1 mg/kg above 10 mg/kg and to the nearest 0,1 mg/kg below 10 mg/kg.

12 Precision

12.1 General

The precision as determined by statistical examination in accordance with ISO 4259 [1, 2] of interlaboratory test results on 15 samples (8 gasolines and 7 gas oils) with sulfur contents in the range 5 mg/kg to 500 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 values in only one case in twenty.

For gasolines, $r \approx 0,0417 \cdot X \cdot 1$

For gas oils, $r \approx 0,0285 \cdot X \cdot 2$

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 material would, in the long run, in the normal and correct operation of the test method, exceed the following values in only one case in twenty.

For gasolines, $R \approx 0,1573 \cdot X \cdot 2$

For gas oils, $R \approx 0,1088 \cdot X \cdot 2$

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

Examples of the above precision estimates are given in Table 2.

Table 2 — Repeatability (*r*) and reproducibility (*R*)

Concentration mg/kg	Repeatability		Reproducibility	
	Gasoline	Gas oil	Gasoline	Gas oil
10	1	2	4	3
30	2	3	7	5
50	3	3	10	7
100	5	5	18	13
350	16	12	57	40
500	22	16	81	56

13 Test report

The test report shall contain at least the following information :

- a) a reference to this International Standard;
- 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.

Bibliography

- [1] ISO 4259:1992, *Petroleum products — Determination and application of precision data in relation to methods of test*.
- [2] ISO 4259:1992, Technical Corrigendum 1:1993 (English only).