INTERNATIONAL STANDARD

ISO 3012

Third edition
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Petroleum products — Determination of thiol (mercaptan) sulfur in light and middle distillate fuels — Potentiometric method

Produits pétroliers — Détermination de la teneur en soufre sous forme de thiols (mercaptans) dans les distillats légers et moyens — Méthode par potentiométrie

Reference number
ISO 3012:1999(E)

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 3.

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.

International Standard ISO 3012 was prepared by Technical Committee ISO/TC 28, *Petroleum products and lubricants*.

This third edition cancels and replaces the second edition (ISO 3012:1991), of which it constitutes a technical revision.

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Petroleum products — Determination of thiol (mercaptan) sulfur in light and middle distillate fuels — Potentiometric 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 thiol (mercaptan) sulfur in light distillates, such as gasolines and naphtha fractions, and middle distillate fuels, such as kerosines and gas oils, in the range of 0,000 3 % (*m/m*) to 0,010 0 % (*m/m*) (3 mg/kg to 100 mg/kg). Organic sulfur compounds such as sulfides, disulfides and thiophene do not interfere. Elemental sulfur does not interfere at contents less than 0,000 5 % (*m/m*). Hydrogen sulfide interferes, if not removed as described in 8.2.

NOTE 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 lates edition of the normative document referred to applies. Members of ISO and IEC maintain registers of currently valid International Standards.

ISO 385-1:1984, *Laboratory glassware – Burettes – Part 1: General requirements*.

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 3696:1987, *Water for analytical laboratory use – Specification and test methods*.

ISO 12185:1996, *Crude petroleum and petroleum products – Determination of density – Oscillating U-tube method*.

3 Principle

A hydrogen sulfide-free sample is dissolved in an alcoholic sodium acetate titration solvent and the solution obtained is titrated potentiometrically with silver nitrate standard alcoholic solution, using as an indicator the potential between a glass reference electrode and a silver/silver sulfide indicating electrode. Under these conditions, the mercaptan sulfur is precipitated as silver mercaptide, and the end-point of the titration is shown by an inflection point in the curve of titrated volume versus cell potential.

4 Reagents and materials

During the analysis, unless otherwise stated, use only reagents of recognized analytical grade. All references to water shall be understood to mean water conforming to grade 3 of ISO 3696.

4.1 Propan-2-ol, of 99 % minimum purity.

It is important that all propan-2-ol used in this analysis is free from peroxides. Either ensure that the alcohol is free from peroxides by analysis, or pass it through a column of activated alumina to remove peroxides that may have formed during storage.

4.2 Cadmium sulfate acid solution

For referee analysis, dissolve 150 g ± 1 g of cadmium sulfate ($3CdSO_4{\cdot}8H_2O$) in water, add 10 ml of approximately 16 % (*m/m*) sulfuric acid and dilute to 1 litre with water.

For routine analysis, use sodium hydrogen carbonate (4.2.1).

WARNING – Cadmium sulfate is toxic, and shall be disposed of as environmental toxic waste.

4.2.1 Sodium hydrogen carbonate solution

Dissolve 50 g ± 1 g of sodium hydrogen carbonate ($NaHCO_3$) in water, and make up to 1 litre. Since sodium sulfide is colourless, the removal of hydrogen sulfide shall be confirmed by the use of lead acetate paper (4.2.2).

4.2.2 Lead acetate paper

Soak strips of filter paper in a 5 % (*m/m*) solution of lead acetate [$(CH_3COO)_2Pb{\cdot}3H_2O$] in water, and allow to dry in a closed container.

4.3 Potassium iodide solution

Dissolve 17,0 g ± 0,5 g of potassium iodide (KI), weighed to the nearest 0,01 g, in 100 ml of water and dilute to 1 000 ml in a volumetric flask with propan-2-ol (4.1). Calculate the concentration in moles per litre.

4.4 Silver nitrate solutions

4.4.1 Preparation of 0,1 mol/l solution

Dissolve 17,0 g ± 0,5 g of silver nitrate ($AgNO_3$) in 100 ml of water and dilute to 1 litre with propan-2-ol (4.1). Store in a dark bottle and standardize at intervals frequent enough to detect a change of 0,000 5 mol/l or greater.

4.4.2 Standardization

Add 6 drops of concentrated nitric acid [HNO_3 = 35 % (*m/m*)] to 100 ml of water in a 300 ml tall-form beaker and boil for 5 min. Cool to ambient temperature and pipette 5 ml of potassium iodide solution (4.3) into the beaker. Titrate with the silver nitrate solution, choosing the end-point at the inflection of the titration curve.

4.4.3 Preparation of 0,01 mol/l solution

Prepare daily by the dilution of 100 ml of 0,1 mol/l solution (4.4.1) to 1 000 ml with propan-2-ol (4.1) in a volumetric flask.

NOTE Commercial standard volumetric solutions are suitable.

4.5 Sodium sulfide solution

Prepare daily by dissolving 10 g of sodium sulfide (Na_2S) in water and diluting to 1 litre.

NOTE Anhydrous sodium sulfide is not widely available, and is expensive. An aqueous solution of hydrated sodium sulfide ($Na_2S{\cdot}9H_2O$) at 30,5 g/l is satisfactory.

4.6 Titration solvents

Mercaptans of low molecular mass, as usually found in light distillates, are readily lost from the titration solution if an acidic titration solvent is used. For the determination of mercaptans of higher molecular mass, as found in middle distillates, the acidic titration solvent is used to achieve more rapid equilibrium between successive additions of the titrant.

4.6.1 Alkaline titration solvent

Dissolve 2,7 g of sodium acetate trihydrate ($CH_3COONa{\cdot}3H_2O$) or 1,6 g of anhydrous sodium acetate (CH_3COONa) in 25 ml of oxygen-free water, and pour into 975 ml of propan-2-ol (4.1). Remove dissolved oxygen by purging the solution with a rapid stream of nitrogen for 10 min each day prior to use. Keep the solvent protected from the atmosphere.

4.6.2 Acidic titration solvent

Dissolve 2,7 g of sodium acetate trihydrate or 1,6 g of anhydrous sodium acetate in 20 ml of oxygen-free water, and pour into 975 ml of propan-2-ol (4.1) and add 4,6 ml of glacial acetic acid. Remove dissolved oxygen by purging the solution with a rapid stream of nitrogen for 10 min each day prior to use. Keep the solvent protected from the atmosphere.

5 Apparatus

Any automatic titration system that meets the precision requirements of this International Standard, and is capable of selecting the end-points specified in clause 8, is suitable. Subclauses 5.1 to 5.4 describe a manual system.

5.1 Titration burette, conforming to the requirements of ISO 385-1, of 10 ml capacity, graduated in 0,05 ml intervals, and with a tip that extends approximately 120 mm below the stopcock.

5.2 Cell system, consisting of a reference electrode and an indicating electrode.

The reference electrode shall be a sturdy, pencil-type glass electrode, having a shielded lead connected to earth (ground). The indicating electrode shall be made from a silver wire, 2 mm in diameter or larger, mounted in an insulated support.

NOTE A silver billet electrode is also suitable as an indicating electrode.

5.3 Electronic voltmeter, operating on an input of less than 9×10^{-12} A, and having a sensitivity of ± 2 mV over a range of at least ± 1 V.

The voltmeter shall be electrostatically shielded, and the shield shall be connected to earth (ground).

5.4 Titration stand, preferably built as an integral part of the meter housing and provided with supports for the electrodes and electrical stirrer, all connected to earth (ground).

No permanent change in the meter reading shall be noticeable upon connecting or disconnecting the stirrer motor.

5.5 Abrasive paper or cloth, having an average particle size of 18 µm (800 grit).

6 Samples and sampling

6.1 Unless otherwise specified, samples shall be obtained by the procedures given in ISO 3170 or ISO 3171.

6.2 Samples of light distillates shall be kept cold (< 4 °C) to avoid loss of volatile components containing thiols. When analysing light distillates with high thiol content, the titration solvent, and preferably the titration burette and pipette for measuring the test portion, shall also be cooled to a similar temperature, and the analysis shall be carried out as soon as possible after removal from the cooling chamber.

NOTE Light naphtha fractions of high thiol content (>100 mg/kg) boiling below 85 °C have been shown to be very sensitive to the titration temperature.

7 Preparation of apparatus

7.1 Glass electrodes

After each manual titration, or batch of titrations in the case of automatic titration systems, wipe the electrode with a soft clean tissue and rinse with water. Clean the electrode at frequent intervals (at least once per week) by stirring in strong oxidizing acid solution for 5 s to 10 s. When not in use, keep the lower half of the electrode immersed in water.

NOTE Chromosulfuric acid was historically the reference strong oxidizing acid cleaning solution, but users are recommended to use a non chromium-containing alternative to obtain equivalent cleanliness.

7.2 Silver/silver sulfide electrode

7.2.1 Prior to use, prepare a fresh silver sulfide coating on the electrode by the method given in 7.2.2 to 7.2.6.

7.2.2 Burnish with an abrasive paper or cloth (5.5) until a clean, polished surface shows.

7.2.3 Place the electrode in the operating position and immerse it in 100 ml of titration solvent (4.6) containing 8 ml of sodium sulfide solution (4.5).

7.2.4 Add slowly from a burette, while stirring, 10 ml of 0,1 mol/l silver nitrate solution (4.4.1) over a period of 10 min to 15 min.

7.2.5 Remove the electrode from the solution, wash with water, and wipe with a soft, clean tissue.

7.2.6 Between manual titrations, or batches of titrations in the case of automatic titration systems, store the electrode for at least 5 min in 100 ml of titration solvent (4.6) containing 0,5 ml of 0,1 mol/l silver nitrate solution (4.4.1).

8 Procedure

8.1 Determination of density

If the sample is to be measured volumetrically, determine the density in accordance with ISO 3675 or ISO 12185 at the temperature at which the test portion will be taken.

NOTE The density may be calculated from determined density at a reference temperature by use of the Petroleum Measurement Tables (ISO 91-1 or ISO 91-2).

8.2 Removal of hydrogen sulfide

Test the sample qualitatively for hydrogen sulfide by shaking 5 ml of the sample with 5 ml of the cadmium sulfate acid solution (4.2), or by immersion of a small strip of lead acetate paper (4.2.2). If no precipitate appears with the cadmium sulfate acid solution, or the colour of the lead acetate paper does not change to brown or black, proceed as described in 8.3. If a yellow precipitate appears with cadmium sulfate, or the lead acetate paper changes colour, remove the hydrogen sulfide as described in 8.2.1 or 8.2.2.

8.2.1 Cadmium sulfate acid solution method

8.2.1.1 Place a quantity of the sample (three to four times that required for the analysis) in a separating funnel containing a volume of the cadmium sulfate acid solution (4.2) equal to one-half that of the sample, and shake vigorously.

8.2.1.2 Draw off and discard the aqueous phase containing the yellow precipitate. Repeat the extraction with a fresh portion of cadmium sulfate acid solution, discarding the aqueous phase. Wash the sample with three 25 ml to 30 ml portions of water, discarding the aqueous phase after each washing.

8.2.1.3 Filter the washed sample through a qualitative filter paper, and test a small portion of the washed and filtered sample with an approximately equal volume of the cadmium sulfate acid solution.

8.2.1.4 If no further precipitate is formed, proceed as described in 8.3.

8.2.1.5 If a precipitate appears, repeat the extraction and filtration described in 8.2.1.1 to 8.2.1.3 until all of the hydrogen sulfide has been removed.

8.2.2 Sodium hydrogen carbonate solution method

8.2.2.1 Place a quantity of the sample (three to four times that required for analysis) in a separating funnel containing a volume of the sodium hydrogen carbonate solution (4.2.1) equal to one-half that of the sample, and shake vigorously.

8.2.2.2 Draw off and discard the aqueous phase, and check for the existence of hydrogen sulfide in the sample phase with lead acetate paper as described in 8.2.

8.2.2.3 If hydrogen sulfide is still present in the sample phase, repeat the washing with successive portions of sodium hydrogen carbonate solution until no hydrogen sulfide is detected.

8.2.2.4 Wash the sample phase with 30 ml to 50 ml of water, shaking vigorously, and discard the aqueous phase.

8.3 Analysis of sample

8.3.1 Either measure with a pipette, or weigh, 20 ml to 50 ml of the original or treated sample into a 300 ml beaker containing 100 ml of the appropriate titration solvent (4.6). Place the beaker on the titration stand (5.4) or on the autosampler carousel of an automatic titration system. Adjust the position of the titration stand so that the electrodes are about half-immersed. Fill the burette (5.1) with 0,01 mol/l silver nitrate solution (4.4.3), and position it in the titration assembly so that the tip extends approximately 25 mm below the surface of the liquid in the beaker. Adjust the speed of the stirrer to give vigorous stirring without spattering.

NOTE 1 Samples with a thiol content above 0,010 0 % (*m/m*) (100 mg/kg) may be analysed by an appropriate reduction in test portion mass, ensuring that the minimum volume of titration solvent plus test portion exceeds 120 ml. If additional titration solvent is used to maintain this requirement, a similar volume should be used for the blank titration (8.4). No precision has been determined for thiol contents above 0,010 0 % (*m/m*) (100 mg/kg).

NOTE 2 If an automatic titration system is used, appropriate modifications to 8.3.1 to 8.3.4, in line with the manufacturer's instructions, may be made.

8.3.2 Record the initial burette and cell-potential readings. Add suitable small portions of the silver nitrate solution and, after waiting until a constant potential has been established, record the burette and voltmeter readings.

NOTE 1 The usual voltmeter readings for mercaptan presence are in the range –250 mV to –350 mV.

NOTE 2 If potential readings obtained with freshly prepared electrodes are erratic, it is possible that the electrodes are not properly conditioned. This difficulty usually disappears in succeeding titrations.

NOTE 3 A cell potential is considered constant if it changes by less than 6 mV/min.

NOTE 4 With certain instruments, the algebraic sign of the potential may appear reversed.

8.3.3 When the change of potential is small for each increment of silver nitrate solution, add volumes as large as 0,5 ml. When the change of potential becomes greater than 6 mV per 0,1 ml, use 0,05 ml increments of silver nitrate solution. Near the end-point of the titration, 5 min or 10 min may elapse before a constant potential is obtained. Nevertheless, it is important that the duration of the titration be as short as possible in order to avoid oxidation of the sulfur compounds by atmospheric oxygen. Once started, a titration shall never be interrupted and resumed later.

8.3.4 Continue the titration until the meter reading change of the cell potential per 0,1 ml of silver nitrate solution has become relatively constant (see note 1 in 8.3.1). Remove the titrated solution, rinse the electrodes well with propan-2-ol (4.1), and wipe them with a clean, dry tissue. If an automatic titration system is used, rinse the electrodes well with propan-2-ol, allow the excess to drain off the electrodes, and then proceed with the next sample. Between successive determinations (or batches of determinations in the case of an automatic titration system) on the same day, store electrodes as described in 7.1 and 7.2.5.

8.4 Blank determination

Carry out the procedures described in 8.3.1 to 8.3.4 on 100 ml (see note 1 in 8.3.1) of the appropriate titration solvent, omitting the test portion addition. Record the volume of 0,01 mol/l silver nitrate solution used to reach the end-point.

9 Interpretation of results

9.1 Treatment of data

Plot the cumulative volumes of 0,01 mol/l silver nitrate solution (4.4.3) added against the corresponding cell potentials. Select the end-point at the most positive value of the steepest portion of each “break” in the titration curve, as shown in Figure 1. The shape of the titration curve may change with different instruments. However, the above interpretation of end-point shall be followed.

9.2 Thiols (mercaptans) only

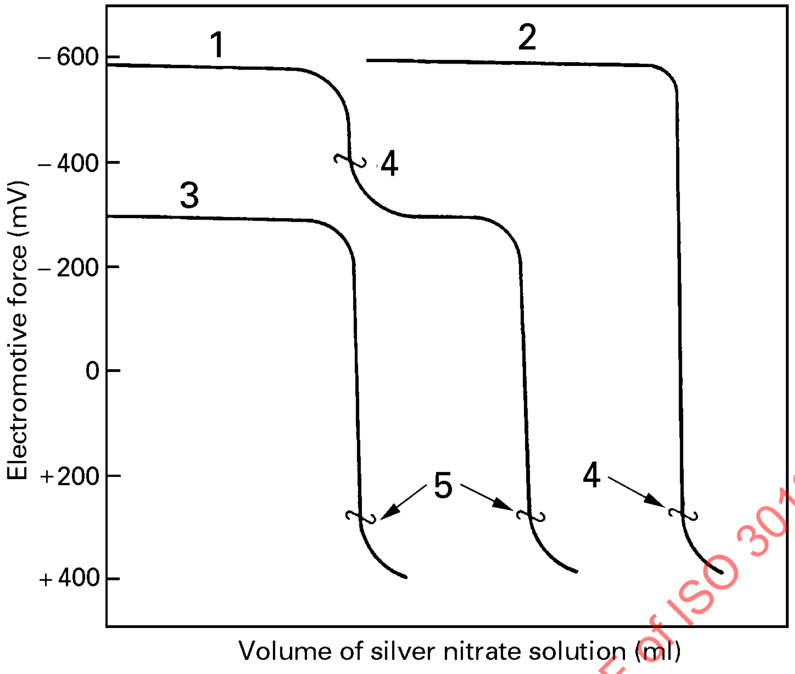
If mercaptans alone are present in the sample, the titration produces a curve of the first type shown in Figure 1, having a plateau in the vicinity of –300 mV to –350 mV and an end-point at approximately +300 mV.

9.3 Mercaptans and elemental sulfur

9.3.1 When elemental sulfur and mercaptans are both present in the sample, a chemical interaction occurs which, in the titration solvent used, precipitates silver sulfide during the titration.

9.3.2 When mercaptans are present in excess, the end of the silver sulfide precipitation occurs at approximately –500 mV, and is followed by the precipitation of the silver mercaptide at the +300 mV end-point. This situation is shown by the middle curve of Figure 1. Since all of the silver sulfide originates from an original amount of mercaptan, the total titration to the mercaptide end-point shall be used to calculate the amount of mercaptan sulfur.

9.3.3 When elemental sulfur is present in excess, the end of the silver sulfide precipitation is taken in the same region (+300 mV) as in the case of silver mercaptide, and the elemental sulfur is calculated as mercaptan sulfur.



Key

1 Elemental sulfur + excess mercaptans
2 Mercaptans + excess sulfur
3 Mercaptans alone
4 Silver sulfide
5 Silver mercaptide

Figure 1 — Examples of potentiometric titration curves

10 Calculation

Calculate the thiol (mercaptan) sulfur content of the sample, w_S, as a percentage by mass [% (*m/m*)], using the following equation.

$$w_S = \frac{(V_1 - V_0) \times c \times 3{,}206}{m}$$

where

V_1 is the volume, in millilitres, of titrant required to titrate the sample to the end-point;

V_0 is the volume, in millilitres, of titrant required to titrate the blank to the end-point;

c is the concentration of the silver nitrate solution, in moles per litre;

m is the mass, in grams, of the test portion;

3,206 is 100 times the relative millimolar mass of sulfur in mercaptan.

NOTE If measured volumetrically, the mass of test portion mass is equal to the volume times the density at the temperature of measurement (see 8.1).

11 Expression of results

Report the result to the nearest 0,000 1 % (*m/m*) or to the nearest 1 mg/kg.

12 Precision

12.1 General

The precision, as determined by statistical examination of interlaboratory test results, is given in 12.2 and 12.3, and is illustrated in Figure 2.

12.2 Repeatability

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.

$$r = 0{,}000\,07 + 0{,}027\,\overline{X}$$

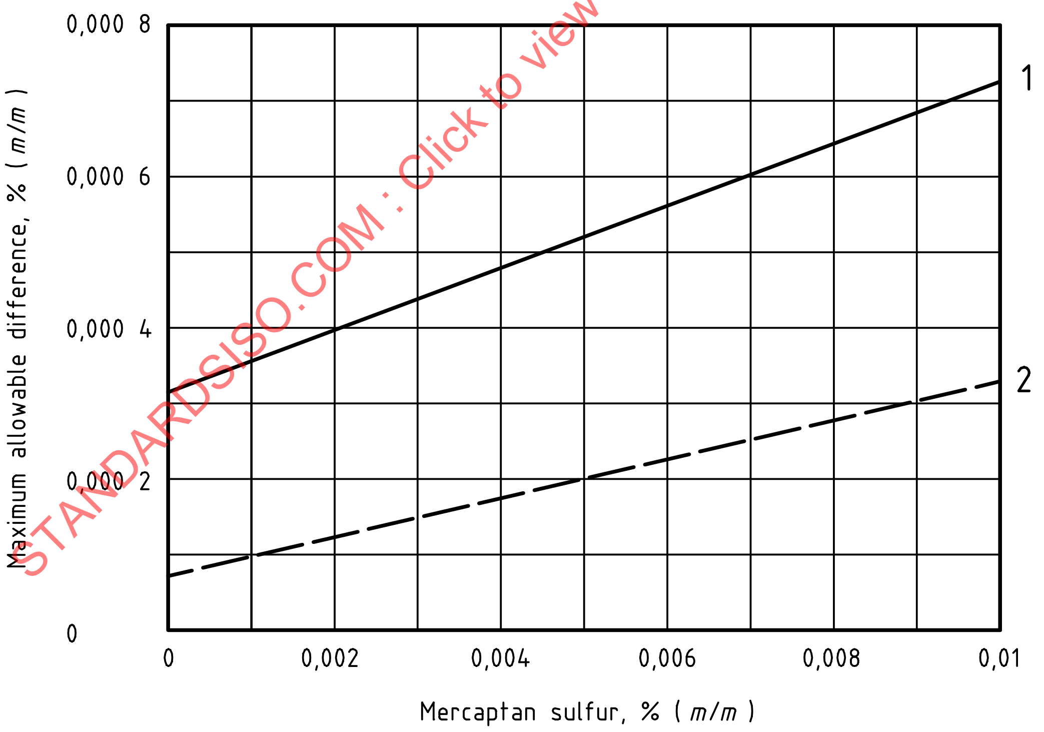
where $\overline{X}$ is the average of the values being compared.

12.3 Reproducibility

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.

$$R = 0{,}000\,31 + 0{,}042\,\overline{X}$$

where $\overline{X}$ is the average of the values being compared.



Key

1 Reproducibility
2 Repeatability

Figure 2 — Precision curves

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.