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INTERNATIONAL STANDARD

ISO 3012

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Gasoline, kerosine and distillate fuels — Determination of mercaptan sulfur — Potentiometric method

Essence, pétroles lampants et fuel-oils distillés — Dosage du soufre sous forme de mercaptans — Méthode potentiométrique

Reference number
ISO 3012:1991(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.

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 second edition cancels and replaces the first edition (ISO 3012:1974), of which it constitutes a technical revision. This revision includes the deletion of the amperometric method which previously formed part of the standard.

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Gasoline, kerosine and distillate fuels — Determination of mercaptan sulfur — Potentiometric method

WARNING — The use of this International Standard may involve hazardous materials, operations and equipment. This standard does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this 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 mercaptan sulfur in gasolines, kerosines and distillate fuels containing a mass fraction of from 0,000 3 % to 0,01 % of mercaptan sulfur. Organic sulfur compounds such as sulfides, disulfides and thiophene do not interfere. Elemental sulfur in amounts of a mass fraction at less than 0,000 5 % does not interfere. Hydrogen sulfide will interfere, if not removed as described in 7.2.

2 Normative reference

The following standard contains provisions which, through reference in this text, constitute provisions of this International Standard. At the time of publication, the edition indicated was valid. All standards are subject to revision, and parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent edition of the standard indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 3675:1976, *Crude petroleum and liquid petroleum products — Laboratory determination of density or relative density — Hydrometer method.*

3 Principle

The hydrogen-sulfide-free sample is dissolved in an alcoholic sodium acetate titration solvent and 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 a large change in cell potential.

4 Reagents

Reagent-grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to recognized standards for reagent chemicals. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

Unless otherwise indicated, reference to water shall be understood to mean distilled water or water of equivalent purity.

4.1 Cadmium sulfate, 150 g/l acid solution.

Dissolve 150 g of cadmium sulfate ($3CdSO_4.8H_2O$) in water. Add 10 ml of sulfuric acid (H_2SO_4) and dilute to 1 litre with water.

4.2 Sodium sulfide, 10 g/l solution.

Dissolve 10 g of sodium sulfide (Na_2S) in water and dilute to 1 litre with water. Prepare a fresh solution as needed.

4.3 Titration solvent.

Mercaptans of low relative molecular mass, as usually found in gasoline, are readily lost from the titration solution if an acidic titration solvent is used. For the determination of mercaptans of higher molecular mass as normally encountered in kerosines and distillate fuels, the acidic titration solvent is used to achieve more rapid equilibrium between successive additions of the titrant.

4.3.1 Alkaline titration solvent.

Dissolve 2,7 g of sodium acetate trihydrate ($CH_3COONa.3H_2O$) 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 (99 %) (see 4.5, second paragraph). Remove dissolved oxygen by purging the solution with a rapid stream of nitrogen for 10 min each day prior to use; keep protected from the atmosphere.

4.3.2 Acidic titration solvent.

Dissolve 2,7 g of sodium acetate trihydrate ($CH_3COONa.3H_2O$) or 1,6 g of anhydrous sodium acetate (CH_3COONa) in 20 ml of oxygen-free water and pour into 975 ml of propan-2-ol (99 %) 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 protected from the atmosphere.

4.4 Potassium iodide, 0,1 mol/l standard solution.

Dissolve approximately 17 g of potassium iodide (KI), weighed to the nearest 0,01 g, in 100 ml of water and dilute to 1 litre in a volumetric flask with water.

4.5 Silver nitrate, 0,1 mol/l standard alcoholic solution.

4.5.1 Preparation.

Dissolve 17 g of silver nitrate ($AgNO_3$) in 100 ml of water and dilute to 1 litre with propan-2-ol (99 %) (see following paragraph), store in a dark bottle and standardize weekly.

It is important to pass the propan 2-ol through a column of activated alumina to remove peroxides that may have formed on storage; failure to remove peroxides will lead to low results. It is not necessary to perform this step if the alcohol is tested and found free of peroxides.

4.5.2 Standardization.

To standardize, add 6 drops of concentrated nitric acid (HNO_3) (ρ = 1,42 g/ml) to 100 ml of water in a 300 ml tall-form beaker, and remove the oxides of nitrogen by boiling for 5 min. Cool to ambient temperature. Pipette 5 ml of potassium iodide solution (4.4) into the beaker, and titrate with the silver nitrate solution prepared in 4.5.1, choosing the end point at the inflection of the titration curve.

4.6 Silver nitrate, 0,01 mol/l standard alcoholic solution.

Prepare daily by dilution of 100 ml of silver nitrate alcoholic solution (4.5) to 1 litre with propan-2-ol (99 %) in a volumetric flask.

5 Apparatus

5.1 Burette, capacity 10 ml, graduated in 0,05 ml intervals, with a tip that extends approximately 120 mm below the stopcock.

NOTE 1 Burettes of 10 ml capacity conforming to the requirements of ISO 385-1[1], class B, are suitable.

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

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

5.3 Meter, meeting the following minimum requirements:

range ± 1 V;

sensitivity ± 2 mV over entire range at a maximum input current of less than 9×10^{-12} A.

NOTE 2 Any apparatus that will give equal or better precision is acceptable.

5.4 Titration stand, preferably built as an integral part of the meter housing and provided with supports for the electrodes and an electrical stirrer, all connected to ground. No permanent change in meter reading shall be noticeable upon connecting or disconnecting the stirrer motor.

5.5 Abrasive cloth or paper, having an average particle size of 18 µm.

6 Preparation of apparatus

6.1 Glass electrode

Before and after each titration, wipe the electrode with a soft, clean tissue and rinse with water. Clean the electrode at frequent intervals (at least once every week during continual use) by stirring in cold chromic acid cleaning solution for a few seconds (10 s max.). When not in use, keep the lower half of the electrode immersed in water.

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[1] ISO 385-1:1984, *Laboratory glassware — Burettes — Part 1: General requirements.*

6.2 Silver/silver sulfide electrode

6.2.1 Each day, prior to use, prepare a fresh silver sulfide coating on the electrode in the following manner:

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

Place the electrode in the operating position and immerse it in 100 ml of titration solvent (4.3) containing 8 ml of sodium sulfide solution (4.2).

Add slowly from a burette, with stirring, 10 ml of 0,1 mol/l silver nitrate solution (4.5) over a period of 10 min to 15 min.

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

6.2.2 Between titrations, store the electrode for at least 5 min in 100 ml of titration solvent (4.3) containing 0,5 ml of 0,1 mol/l silver nitrate solution (4.5).

7 Procedure

7.1 Determination of density

If the test portion is to be measured out volumetrically, first measure the density of the sample directly at the temperature at which the test portion is to be taken. The determination shall be carried out in accordance with ISO 3675.

7.2 Removal of hydrogen sulfide

Test the sample qualitatively for hydrogen sulfide by shaking 5 ml of the sample with 5 ml of the acid cadmium sulfate solution (4.1). If no precipitate appears, proceed with the analysis of the sample as described in 7.3.

If a yellow precipitate appears, remove the H_2S in the following manner:

7.2.1 Place a quantity of the sample (three to four times that required for the analysis) in a separating funnel containing a volume of the acid $CdSO_4$ solution (4.1) equal to one-half that of the sample and shake vigorously.

7.2.2 Draw off and discard the aqueous phase containing the yellow precipitate. Repeat the extraction with another portion of the $CdSO_4$ solution. Again draw off the aqueous phase, and wash the sample with three 25 ml to 30 ml portions of water, drawing off the water after each washing.

7.2.3 Filter the washed sample through a qualitative filter paper. Test a small portion of the washed sample in a test tube with a few millilitres of the $CdSO_4$ solution.

7.2.4 If no further precipitate is formed, proceed as directed in 7.3.

7.2.5 If a precipitate appears, repeat the extraction with the $CdSO_4$ solution until all of the H_2S has been removed.

7.3 Analysis of sample

7.3.1 Measure, with a pipette, 20 ml to 50 ml of the original or treated sample into a 300 ml tared titration beaker and determine the mass of the test portion. Add 100 ml of titration solvent (4.3). Immediately place the beaker on the titration stand (5.4) and adjust its position so that the electrodes of the cell system (5.2) are about half-immersed. Fill the burette (5.1) with 0,01 mol/l alcoholic silver nitrate solution (4.6) and place the burette in position 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.

7.3.2 Record the initial burette and cell-potential readings. Add suitable small portions of 0,01 mol/l silver nitrate solution (4.6) and, after waiting until a constant potential has been established, record the burette and meter readings. Consider the potential constant if it changes less than 6 mV per minute.

7.3.3 When the potential change 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.

NOTE 3 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.

7.3.4 Continue the titration until the meter reading has passed +350 mV (see note 4) and the change of cell potential per 0,1 ml of silver nitrate solution has become relatively constant. Remove the titrated solution, rinse the electrodes well, first with alcohol and then with water, and wipe them with a dry tissue. Burnish the silver electrode lightly with abrasive cloth or paper (5.5). Between successive determinations on the same day, immerse the electrodes in 100 ml of titration solvent containing approximately 0,5 ml of 0,1 mol/l silver nitrate solution (4.5).

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

8 Expression of results

8.1 Treatment of data

Plot the cumulative volumes of 0,01 mol/l silver nitrate solution (4.6) 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 (see note to 7.3.4). The shape of the titration curve may change with different instruments. However, the above interpretation of end point shall be followed.

8.1.1 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 about +300 mV.

8.1.2 Mercaptans and elemental sulfur

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.

8.1.2.1 When mercaptans are present in excess, the end of the silver sulfide precipitation occurs at about −500 mV to −350 mV, and is followed by precipitation of the silver mercaptide to the +300 mV end point. This situation is shown in the middle curve of figure 1. Since all of the silver sulfide originates from an equivalent amount of mercaptan, the total titration to the mercaptide end point shall be used to calculate the amount of mercaptan sulfur.

8.1.2.2 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.

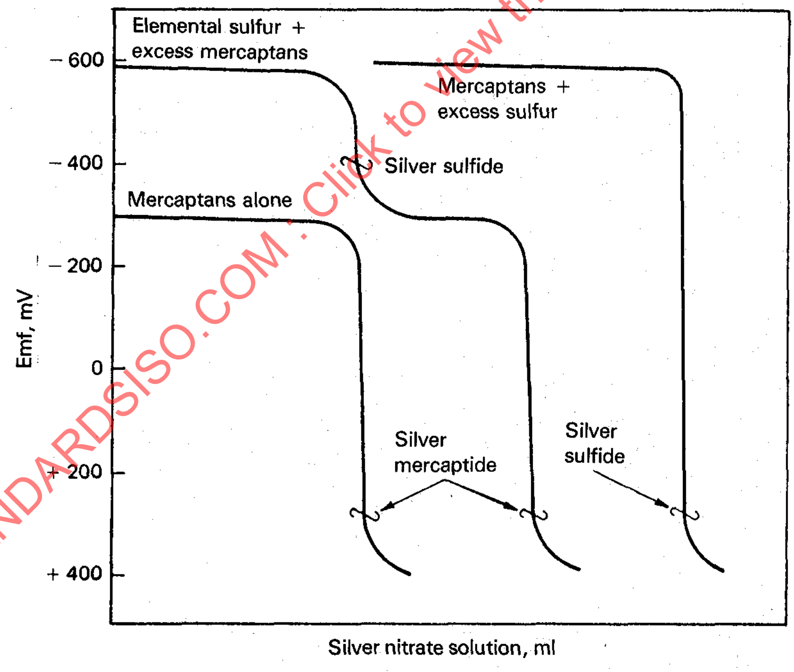

Figure 1 — Illustrative potentiometric titration curves