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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 $\pm$ 1 V;

sensitivity $\pm$ 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.

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