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

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Bensin, fotogen och destillatbränslen – Bestämning av merkaptansvavel – Potentiometrisk metod

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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 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 latest 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 $150 \text{ g} \pm 1 \text{ g}$ of cadmium sulfate ($3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$) 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 $50 \text{ g} \pm 1 \text{ g}$ 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 [$(\text{CH}_3\text{COO})_2\text{Pb} \cdot 3\text{H}_2\text{O}$] in water, and allow to dry in a closed container.

4.3 Potassium iodide solution

Dissolve $17,0 \text{ g} \pm 0,5 \text{ g}$ 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 $17,0 \text{ g} \pm 0,5 \text{ g}$ 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 [$\text{HNO}_3 = 35 \text{ } (m/m)$] 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 ($\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$) 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 ($\text{CH}_3\text{COONa}\cdot 3\text{H}_2\text{O}$) 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 ($< 4\text{ °C}$) 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 ($>100\text{ mg/kg}$) 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.