INTERNATIONAL STANDARD

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Petroleum products and hydrocarbon solvents — Detection of thiols and other sulfur species — Doctor test

Produits pétroliers et solvants hydrocarbonés — Détection des thiols (mercaptans) et autres espèces soufrées — Méthode au plombite de sodium («Doctor test»)

Reference number
ISO 5275:2003(E)

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Foreword

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International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. 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 document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO 5275 was prepared by Technical Committee ISO/TC 28, *Petroleum products and lubricants*.

This second edition cancels and replaces the first edition (ISO 5275:1979), which has been technically revised.

Petroleum products and hydrocarbon solvents — Detection of thiols and other sulfur species — Doctor test

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 procedure (Doctor test) for the detection of thiols (mercaptans), hydrogen sulfide and elemental sulfur in hydrocarbon solvents and distillate petroleum feedstocks and products. Preliminary procedures also detect the presence of peroxides and phenolic substances, which, when present in more than trace quantities, make the application of this International Standard inappropriate. Carbon disulfide, at relatively high concentrations [above 0,4 % (m/m) sulfur], also interferes with the interpretation of the test by causing darkening of the aqueous layer.

NOTE For the purposes of this International Standard, the term "% (m/m)" is used to represent the mass fraction of a material.

The test is a go/no-go procedure with a threshold value of thiol concentration dependent on the material under test. It is frequently used as a substitute for the quantitative determination of thiol content.

2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 1995:1981, *Aromatic hydrocarbons — Sampling*

ISO 3170:—[1], *Petroleum liquids — Manual sampling*

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

ISO 3696:1987, *Water for analytical laboratory use — Specification and test methods*

3 Principle

A test portion is shaken with sodium plumbite solution and the mixture observed. From its appearance, the presence or absence of thiols, hydrogen sulfide, elemental sulfur or peroxides may be deduced. The presence of thiols may be confirmed by the addition of sublimed sulfur, further shaking, and observation of the appearance of the final mixture.

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[1] To be published. (Revision of ISO 3170:1988)

4 Reagents and materials

4.1 General

Unless otherwise specified, the reagents specified in 4.2 to 4.11 shall be of analytical reagent grade, and water shall conform to the requirements of grade 3 of ISO 3696.

4.2 Lead acetate trihydrate [$(CH_3COO)_2Pb \cdot 3H_2O$], crystals.

4.3 Sodium hydroxide ($NaOH$), solid.

4.4 Sodium plumbite (Doctor) solution

Dissolve 25 g of lead acetate (4.2) in 200 ml of water, filter and add to a solution of 60 g of sodium hydroxide (4.3) in 100 ml of water. Heat the mixture in a boiling water bath for 30 min ± 5 min, cool and dilute to 1 000 ml with water.

Store the solution in a tightly closed stoppered bottle and filter before use if it is not clear.

4.5 Cadmium chloride ($CdCl_2$)

See the warning in 4.7.

4.6 Hydrochloric acid (HCl), concentrated, approximately 36 % (m/m) HCl (11 mol/l).

4.7 Cadmium chloride solution

Dissolve 100 g of cadmium chloride (4.5) in water, add 10 ml of hydrochloric acid (4.6) and dilute to 1 000 ml.

WARNING — Cadmium chloride is toxic, and shall be disposed of as environmental toxic waste.

For routine analysis, sodium hydrogen carbonate ($NaHCO_3$) solution at 50 g/l in water can be used, but since sodium sulfide is colourless, lead acetate paper is required to confirm the removal of hydrogen sulfide (see 7.3).

4.8 Sulfur, sublimed (“flowers of sulfur”), dry.

Store in a closed container.

4.9 Potassium iodide solution (KI)

Freshly prepare (daily) before use, a solution of 100 g/l of potassium iodide in water.

4.10 Acetic acid solution (CH_3COOH)

Freshly prepare (daily) before use, a solution of 100 g/l of glacial acetic acid in water.

4.11 Starch solution

Freshly prepare (daily) before use, a solution of 5 g/l of starch in water.

5 Apparatus

5.1 Mixing cylinders, made of glass, stoppered, of capacity 50 ml.

5.2 Measuring cylinders, made of glass, of capacity 5 ml and 10 ml.

5.3 Separating funnel, made of glass, stoppered, of capacity 50 ml.

6 Samples and sampling

6.1 Unless otherwise specified, obtain laboratory samples in accordance with the procedures described in ISO 1995, ISO 3170 or ISO 3171, appropriate to the type of material being analysed and the sample source.

6.2 Mix laboratory samples by thoroughly shaking before withdrawing the test portion. Take care to avoid pressure build-up in the container if the sample has a vapour pressure exceeding 30 kPa at the laboratory temperature. Release pressure frequently and safely as required.

7 Procedure

7.1 Preliminary tests

7.1.1 Phenolic substances

If the material under test is suspected of containing phenolic substances used as oxidation inhibitors, and which may interfere with the interpretation of test results (coloration of the aqueous layer), shake vigorously for 15 s in a mixing cylinder (5.1), a 10 ml test portion with 5 ml of 10 % (*m/m*) sodium hydroxide (4.3) in water solution. Observe the degree of coloration, and use this for comparison when assessing the results from 7.1.2. If the coloration is significant, the test shall be discontinued.

NOTE Any coloration beyond pale yellow is significant. If yellow is produced, the fourth assessment in Table 1 may need to be modified, dependent upon the intensity.

7.1.2 Sulfur species and peroxides

Place a 10 ml test portion of the sample and 5 ml of sodium plumbite solution (4.4) in a mixing cylinder (5.1) and shake vigorously for 15 s. Observe the appearance of the mixture and continue the procedure as indicated in Table 1.

Table 1 — Observations from preliminary test

Observation	Inference	Continue test as described in subclause
Black precipitate forms immediately	Hydrogen sulfide present	7.3
Brown precipitate forms slowly	Peroxides probably present	7.2
During the shaking period, the solution becomes opalescent and then darkens in colour	Thiols (mercaptans) and/or elemental sulfur present	7.4
No change occurs or a yellow colour is produced	Thiols may be present	7.4

7.2 Peroxides

Place a 10 ml test portion of the sample in a mixing cylinder (5.1) and add 2 ml of potassium iodide solution (4.9), a few drops of acetic acid solution (4.10) and a few drops of starch solution (4.11). Shake vigorously for 15 s and observe the aqueous layer after settling. A blue colour in the aqueous layer confirms the presence of peroxides in sufficient concentration to invalidate the test.

7.3 Hydrogen sulfide

If a black precipitate has formed when carrying out the procedure described in 7.1.2, place a fresh 20 ml test portion of the sample in the separating funnel (5.3), add 1 ml of cadmium chloride solution (4.7) and shake vigorously for 15 s. Allow the layers to settle, and then decant 10 ml of the non-aqueous layer into a mixing cylinder and repeat the procedure described in 7.1.2. If no black precipitate is formed after this first washing, continue the procedure described in 7.4 on the washed test portion together with the sodium plumbite solution. If a black precipitate is still formed, withdraw the aqueous layer from the separating funnel, add a fresh 0,5 ml of cadmium chloride solution, and repeat the washing and testing. If sodium hydrogen carbonate is used, see 4.7.

It is unlikely that a black precipitate will continue to form after two washings, but if it does, a washed test portion free of hydrogen sulfide should be obtained by successive washing and testing of a volume that ensures that a 10 ml test portion is available for final testing in accordance with 7.1.2 followed by 7.4.

7.4 Thiols

To the mixture of test portion and sodium plumbite obtained as specified in 7.1.2 or 7.3, add a small quantity of sublimed sulfur (4.8) that is not more than sufficient to cover the interface between the layers in the cylinder. Shake the cylinder vigorously for 15 s and allow to stand for 60 s ± 5 s. Observe the contents of the cylinder for the presence of a brown or black precipitate. If a precipitate is formed, thiols, above the threshold concentration of this International Standard, are present.

8 Expression of results

8.1 If the test could not be completed due to interfering substances, as determined in 7.1, report the result as “Test invalid — interfering substances present”.

8.2 If peroxides are present, as determined in 7.2, report the result as “Test invalid — peroxides present”.

8.3 If an immediate black precipitate is formed during shaking with the sodium plumbite solution as described in 7.1.2, report the result as “Doctor positive — hydrogen sulfide present”.

If after removal of hydrogen sulfide, a black or brown precipitate is formed after the addition of sulfur as described in 7.4, report the result as “Doctor positive — hydrogen sulfide and thiols present”.

8.4 If during shaking as described in 7.1.2, the solution becomes opalescent and then darkens in colour, report the result as “Doctor positive — thiols and/or elemental sulfur present”.

8.5 If an opalescent colour is produced during shaking with the sodium plumbite solution, and a brown or black precipitate is formed after addition of the sulfur as described in 7.4, report the result as “Doctor positive — thiols present”.

8.6 If after shaking as described in 7.1.2, no change occurs or only a pale yellow colour is produced, and no precipitate is formed after addition of the sulfur as described in 7.4, report the result as “Doctor negative”.