INTERNATIONAL STANDARD

ISO 3839

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Petroleum products — Determination of bromine number of distillates and aliphatic olefins — Electrometric method

Produits pétroliers — Détermination de l'indice de brome de distillats et d'oléfines aliphatiques — Méthode électrométrique

Reference number
ISO 3839:1996(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 3839 was prepared by Technical Committee ISO/TC 28, *Petroleum products and lubricants*.

This second edition cancels and replaces the first edition (ISO 3839:1978), which has been technically revised.

Annex A of this International Standard is for information only.

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Petroleum products — Determination of bromine number of distillates and aliphatic olefins — Electrometric 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 the bromine number of the following materials:

a) petroleum distillates that are substantially free of material lighter than 2-methylpropane, and that have 90 %(*V/V*) (i.e. volume fraction 90 %) distillation recovery temperatures under 327 °C. The method is generally applicable to gasolines (including leaded, unleaded and oxygenated fuels), kerosines and distillates in the gas oil range that fall within the following limits:

90 %(*V/V*) recovery distillation temperature (ISO 3405)	**Bromine number, max.** (see note 1)
Under 205 °C	175
205 °C to 327 °C	10

b) commercial olefins that are essentially mixtures of aliphatic monoolefins and that fall within the range of 95 to 165 bromine number (see note 1).

The method has been found suitable for such materials as commercial propene trimer and tetramer, butene dimer, and mixed nonenes, octenes and heptenes. The method is not suitable for normal alpha-olefins.

NOTES

1 These limits are imposed since the precision of the method has been determined only up to or within the range of these bromine numbers.

2 The value of the bromine number is an indication of the quantity of bromine-reactive constituents, not an identification of constituents. Annex A and table A.1 give information related to the use of this International Standard as a measure of olefinic unsaturation.

2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this International Standard. At the time of publication, the editions indicated were 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 editions of the standards indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 3405:1988, *Petroleum products — Determination of distillation characteristics.*

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

3 Definition

For the purposes of this International Standard, the following definition applies:

3.1 bromine number: Mass, in grams, of bromine which will combine with 100 g of the sample under standardized conditions.

4 Principle

A known mass of the test portion dissolved in a specified solvent maintained at 0 °C to 5 °C is titrated with standard volumetric bromide/bromate solution. The end-point is indicated by a sudden change in potential on an electrometric end-point titration apparatus due to the presence of free bromine.

5 Reagents and materials

During the analysis, use only reagents of recognized analytical grade, and water equivalent to grade 3 of ISO 3696.

5.1 1,1,1-Trichloroethane (CH_3CCl_3).

CAUTION — 1,1,1-trichloroethane is hazardous to the environment. A substitute is under active investigation.

5.2 Methanol (CH_3OH).

5.3 Potassium iodide solution, 150 g/l.

Dissolve 150 g of potassium iodide (KI) in water and dilute to 1 l.

5.4 Sulfuric acid, dilute solution (1:5).

Carefully mix 1 volume of concentrated sulfuric acid [H_2SO_4, 98 %(*m/m*) (i.e. mass fraction 98 %) min.] with 5 volumes of water.

5.5 Titration solvent.

Prepare 1 l of titration solvent by mixing the following volumes of materials: 714 ml of acetic acid (5.9), 134 ml of 1,1,1-trichloroethane (5.1), 134 ml of methanol (5.2) and 18 ml of sulfuric acid solution (5.4).

5.6 Bromide/bromate solution, [$c(Br_2)$ = 0,250 mol/l].

Dissolve 51,0 g ± 0,1 g of potassium bromide (KBr) and 13,92 g ± 0,01 g of potassium bromate ($KBrO_3$), both dried at 105 °C for 30 min, in water and dilute to 1 l.

NOTE — If the bromine numbers of the reference olefins specified in clause 7 and determined using this solution do not conform to the limits specified, or if there is some uncertainty as to the quality of primary reagents, it is recommended that the concentration (mol/l) be determined (and used in subsequent calculations) by standardizing the solution. The standardization procedure shall be carried out as follows:

Place 50 ml of acetic acid (5.9) and 1 ml of concentrated hydrochloric acid (5.10) in a 500-ml iodine-number flask. Chill the solution in an ice bath for approximately 10 min, and with constant swirling of the contents of the flask, add from a 10-ml calibrated burette, 5,00 ml ± 0,01 ml of bromide/bromate solution being standardized at the rate of 1 drop/s or 2 drops/s. Stopper the flask immediately, shake the contents, place it again in the ice bath, and add 5 ml of potassium iodide solution (5.3) in the lip of the stoppered flask. After 5 min, remove the flask from the ice bath and allow the potassium iodide solution to flow into the flask by slowly removing the stopper. Shake vigorously, add 100 ml of water in such a manner as to rinse the stopper, lip and walls of the flask, and titrate promptly with sodium thiosulfate solution (5.7). Near the end of the titration, add 1 ml of starch solution (5.8) and titrate slowly to disappearance of the blue colour. Calculate the concentration $c_1(Br_2)$, expressed in moles per litre, of the bromide/bromate solution as follows:

$$c_1 = \frac{V_0 c_0}{2V_1}$$

where

V_0 is the volume of sodium thiosulfate solution required for titration of the bromide/bromate solution, in millilitres;

V_1 is the volume of bromide/bromate solution, in millilitres (nominally 5,00);

c_0 is the concentration of the sodium thiosulfate solution, in moles per litre;

2 is the number of electrons transferred during redox titration of bromide/bromate.

Repeat the standardization until two successive determinations do not differ from their mean value by more than 0,002 mol/l.

5.7 Sodium thiosulfate solution, 0,1 mol/l.

Dissolve 25,0 g ± 0,1 g of sodium thiosulfate pentahydrate ($Na_2S_2O_3 \cdot 5H_2O$) in water and add 0,01 g of sodium carbonate (Na_2CO_3) to stabilize the solution. Dilute to 1 l and mix thoroughly by shaking. Standardize by any accepted procedure that determines the concentration with an error not greater than ± 0,000 2 mol/l. Restandardize at intervals frequent enough to detect changes in concentration of ± 0,000 5 mol/l.

5.8 Starch solution.

Grind and mix thoroughly 5 g of starch and 5 mg to 10 mg of mercury(II) iodide (HgI_2) with 3 ml to 5 ml of water. Add the suspension to 2 l boiling water and boil for 5 min to 10 min. Allow to cool and decant the clear, supernatant liquid into bottles having ground-glass stoppers.

CAUTION — Mercury(II) iodide is toxic. A substitute is under active investigation.

5.9 Acetic acid, glacial, 99,0 % (*m/m*) (i.e. mass fraction 99,0 %) minimum purity.

5.10 Hydrochloric acid, concentrated, 35,4 % (*m/m*) (i.e. mass fraction 35,4 %) HCl.

5.11 Nitric acid, concentrated, 69,0 % (*m/m*) to 70,5 % (*m/m*) (i.e. mass fraction 69,0 % to 70,5 %).

6 Apparatus

6.1 Electrometric end-point titration apparatus.

Use any apparatus designed to perform titrations to pre-set end points in conjunction with a high-resistance polarizing current supply capable of maintaining approximately 0,8 V across two platinum electrodes, and with a sensitivity such that a voltage change of approximately 50 mV at these electrodes is sufficient to indicate the end-point.

NOTE — Other types of commercially available electronic titrimeters, including certain pH-meters, have also been found suitable.

6.2 Titration vessel.

A jacketed glass vessel approximately 120 mm high and 45 mm in internal diameter and of a form that can be conveniently maintained at 0 °C to 5 °C.

6.3 Stirrer.

Any magnetic stirrer system.

6.4 Electrodes.

A platinum wire electrode pair with each wire approximately 12 mm long and 1 mm in diameter. The wires shall be located 5 mm apart and approximately 55 mm below the level of the titration solvent. Clean the electrode pair at regular intervals with nitric acid (5.11) and rinse with water before use.

6.5 Burette.

Any delivery system capable of measuring titrant in 0,05 ml or smaller graduations.

7 Check test

If there are reservations in applying the procedure to actual test portions, check the reagents and techniques by means of determinations on freshly purified cyclohexene or diisobutene. Proceed in accordance with clause 8, using a test portion of 0,6 g to 1,0 g of either cyclohexene or diisobutene (see table 1), or 6 g to 10 g of a 10 %(*m/m*) (i.e. mass fraction 10 %) solution of these materials in 1,1,1-trichloroethane (5.1). If the reagents and techniques are correct, values within the following ranges will be obtained:

Standard	Bromine number
Cyclohexene, purified (see notes 1, 2 and 3)	187 to 199 (see note 4)
Cyclohexene, 10 % solution	18 to 20
Diisobutene, purified (see notes 2 and 3)	136 to 144 (see note 4)
Diisobutene 10 % solution	13 to 15

NOTES

1 Purified test samples of cyclohexene and diisobutene may be prepared from cyclohexene concentrates with a boiling range of 81 °C to 83 °C and from diisobutene (1-pentene, 2,2,4-trimethyl isomer only) concentrates with a boiling range of 100 °C to 102 °C, by the following procedure:

Add 65 g of activated silica (75 µm to 150 µm particle size, manufactured to ensure minimum olefin polymerization) to a column of approximately 16 mm inside diameter and 760 mm length, that has a stopcock at the lower end and that contains a small plug of glass wool immediately above the latter. A 100-ml burette, or any column providing a height-to-diameter ratio of the silica gel of at least 30:1, is suitable. Tap the column during addition of the gel to ensure uniform packing.

To the column add 30 ml of the olefin to be purified. When the olefin disappears into the gel, fill the column with methanol (5.2). Discard the first 10 ml of percolate and collect the next 10 ml, which is the purified olefin ready for use in the procedure for determining bromine number. Determine and record the density and refractive index of the purified test samples at 20 °C. Discard the remaining percolate.

2 If distillation of these olefins is required as a prepurification step, a few pellets of potassium hydroxide (KOH) should be placed in the distillation flask and distillation should not be continued beyond 90 %(*V/V*) (i.e. volume fraction 90 %) recovery to minimize the hazards from decomposition of any peroxides that may be present.

3 The reference olefins yielding the above results are characterized by the properties given in table 1.

4 The theoretical bromine numbers of cyclohexene and diisobutene are 194,5 and 142,4 respectively.

Table 1 — Physical properties of purified olefins

Compound	Boiling point °C	Density at 20 °C kg/m³	Refractive index n_D^{20}
Cyclohexene	82,5 to 83,5	810,0	1,446 5
Diisobutene	101,0 to 102,5	717,5 ± 1,5	1,411 2

8 Procedure

8.1 Place 10 ml of 1,1,1-trichloroethane (5.1) in a 50-ml volumetric flask and, by means of a pipette, introduce a quantity of sample as indicated in table 2. Obtain the mass of sample introduced either by taking the difference between the mass (to the nearest 1 mg) of the flask before and after addition of sample or, if the density is known accurately, by calculating the mass from the measured volume. Fill the flask to the mark with 1,1,1-trichloroethane and mix well.

Table 2 — Recommended test portion mass

Bromine number	Test portion mass g
0 to 10	20 to 16
Over 10 to 20	10 to 8
Over 20 to 50	5 to 4
Over 50 to 100	2 to 1,5
Over 100 to 150	1,0 to 0,8
Over 150 to 200	0,8 to 0,6

NOTES

1 If the order of magnitude of the bromine number of a test portion is unknown, a trial test is recommended using a 2-g test portion in order to obtain the approximate magnitude of the bromine number, followed by another determination using the appropriate test portion mass as indicated in table 2. The mass of the test portion should also be such that the volume of bromide/bromate titrant used does not exceed 10 ml, and that no separation of the reaction mixture into two phases occurs during the titration.

2 Difficulty may be experienced in dissolving test portions of the high-boiling range products in the titration solvent; this difficulty can be prevented by the addition of a small quantity of toluene.

8.2 Cool the titration vessel (6.2) to between 0 °C and 5 °C and maintain at this temperature throughout the titration. Switch on the titrimeter (6.1) and allow the electrical circuit to stabilize.

8.3 Introduce 110 ml of titration solvent (5.5) into the vessel and pipette in a 5-ml aliquot of the sample solution (8.1) from the 50-ml volumetric flask. Switch on the stirrer (6.3) and adjust to a rapid stirring rate, but avoid any tendency for air bubbles to be drawn down into the solution.

8.4 Set the end-point potential. With each instrument, follow the manufacturer's instructions for end-point setting and to achieve the sensitivity in the platinum electrode circuit specified in 6.1.

8.5 Depending on the titrator apparatus, add the bromide/bromate solution (5.6) manually or by microprocessor control in small increments from the burette (6.5).

With commercial titrimeters, a sudden change in potential is indicated on the meter or recorder of the instrument as the end point is approached. The end-point of the titration has been reached when the change in potential persists for 30 s.

8.6 Carry out a blank titration of each batch of titration solvent and reagents by repeating the entire procedure, using 5 ml of 1,1,1-trichloroethane in place of the sample aliquot. If more than 0,1 ml of bromide/bromate solution is required to reach the end-point, disregard the analysis, prepare fresh titration solvent and fresh reagents and repeat the analysis.

9 Calculation

Calculate the bromine number, Br No., as follows:

$$\text{Br No.} = \frac{(V_1 - V_2)\, c_1 \times 15{,}98}{m}$$

where

V_1 is the volume of bromide/bromate solution required for titration of the test solution aliquot, in millilitres;

V_2 is the volume of bromide/bromate solution required for titration of the blank, in millilitres;

c_1 is the concentration of the bromide/bromate solution, expressed as moles bromine per litre of solution;

15,98 is the factor for converting grams of bromine per 100 g of sample and incorporating molecular mass of bromine (as Br_2) and converting millilitres to litres;

m is the mass of sample in the aliquot used, in grams.

10 Expression of results

Report the result, rounded to the nearest 0,1 for bromine numbers below 10,0, and to the nearest whole number for those above.

11 Precision

The precision of the method, as obtained by statistical examination of interlaboratory test results, is as follows.

11.1 Repeatability, r

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 normal and correct operation of the test method, exceed the following values only in one case in 20.

Petroleum distillates:

a) 90 % (V/V) distillation recovery under 205 °C

$$r = 0{,}11\left(X^{0{,}70}\right)$$

b) 90 % (V/V) distillation recovery 205 °C to 327 °C

$$r = 0{,}11\left(X^{0{,}67}\right)$$

where X is the average value of the samples being tested.

Commercial olefins:

$r = 3$

11.2 Reproducibility, R

The difference between two single and independent results obtained by different operators working in different laboratories on nominally identical test material would, in the normal and correct operation of the test method, exceed the following value only in one case in 20.

Petroleum distillates:

a) 90 % (*V/V*) distillation recovery under 205 °C

$$R = 0{,}72\left(X^{0{,}70}\right)$$

b) 90 % (*V/V*) distillation recovery 205 °C to 327 °C

$$R = 0{,}78\left(X^{0{,}67}\right)$$

where X is the average value of the samples being tested.

Commercial olefins:

$R = 12$*)

12 Test report

The test report shall contain at least the following information:

a) a reference to this International Standard;

b) the type and identification of the product tested;

c) the result of the test (see clause 10);

d) any deviation, by agreement or otherwise, from the procedure specified;

e) the date of the test.

*) Provisional value obtained from a limited amount of data.