
INTERNATIONAL STANDARD



3839

INTERNATIONAL ORGANIZATION FOR STANDARDIZATION • МЕЖДУНАРОДНАЯ ОРГАНИЗАЦИЯ ПО СТАНДАРТИЗАЦИИ • ORGANISATION INTERNATIONALE DE NORMALISATION

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

Distillats du pétrole et oléfines aliphatiques commerciales — Détermination de l'indice de brome — Méthode électrométrique

First edition — 1978-04-01

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[ISO 3839:1978](https://standards.iteh.ai/catalog/standards/sist/9bfdc24e-b1df-4c04-8895-d9e4d428eaae/iso-3839-1978)

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UDC 665.7-404 : 543.257

Ref. No. ISO 3839-1978 (E)

Descriptors : petroleum products, distillation, alkene compounds, chemical analysis, bromine number, electrometric analysis.

Price based on 12 pages

FOREWORD

ISO (the International Organization for Standardization) is a worldwide federation of national standards institutes (ISO member bodies). The work of developing International Standards is carried out through ISO technical committees. Every member body interested in a subject for which a technical committee has been set up 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.

Draft International Standards adopted by the technical committees are circulated to the member bodies for approval before their acceptance as International Standards by the ISO Council.

International Standard ISO 3839 was developed by Technical Committee ISO/TC 28, *Petroleum products*, and was circulated to the member bodies in August 1975.

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It has been approved by the member bodies of the following countries :

[ISO 3839:1978](#)

Australia	Germany	Poland
Austria	Hungary	Portugal
Belgium	India	Romania
Brazil	Iran	South Africa, Rep. of
Bulgaria	Israel	Spain
Canada	Italy	Sweden
Czechoslovakia	Japan	Turkey
Egypt, Arab Rep. of	Mexico	U.S.A.
France	Netherlands	U.S.S.R.

No member body expressed disapproval of the document.

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

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1 SCOPE AND FIELD OF APPLICATION

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 isobutane and that have 90 % distillation points under 330 °C. The method is generally applicable to gasoline (including leaded fuels), kerosine, and distillates in the gas oil range that fall in the following limits, but not when blending agents such as alcohols, ketones, ethers, or amines are present:

90 % Recovery distillation temperature ISO 3405	Bromine number, max. (see the note)
Under 205 °C	100
205 to 330 °C	10

- b) Commercial olefins that are essentially mixtures of aliphatic mono-olefins and that fall within the range of 95 to 165 bromine number (see the note). The method has been found suitable for such materials as commercial propylene trimer and tetramer, butene dimer, and mixed nonenes, octenes, and heptenes. The method is not satisfactory for normal alpha-olefins.

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

The value of the bromine number is an indication of the quantity of bromine-reactive constituents, not an identification of constituents; therefore, its use as a measure of olefinic unsaturation should not be made without a study of table 3 — Reported behaviour of compounds by the electrometric bromine number method (see annex).

2 REFERENCE

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

3 DEFINITION

bromine number: The mass, in grams, of bromine which will combine with 100 g of the sample under standardized conditions. It is used as an indication of the degree of unsaturation.

4 PRINCIPLE

A known mass of the test portion dissolved in a specified solvent maintained at 0 to 5 °C is titrated with standard volumetric bromide/bromate solution. The end point, indicated by a dead-stop electrometric titration apparatus, is reached when the presence of free bromine causes a sudden change in the electrical conductivity of the system.

5 REAGENTS

During the analysis, use only reagents of recognized analytical grade, and only distilled water or water of equivalent purity.

5.1 1,1,1-Trichloroethane (CH₃.CCl₃).

5.2 Potassium iodide solution, 150 g/l.

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

5.3 Sulphuric acid, dilute solution (1 + 5).

Carefully mix 1 volume of concentrated sulphuric acid (H₂SO₄, ρ 1,84 g/ml) with 5 volumes of water.

5.4 Titration solvent.

Prepare 1 litre of titration solvent by mixing the following volumes of materials: 714 ml of glacial acetic acid, 134 ml of 1,1,1-trichloroethane (5.1), 134 ml of methanol (CH₃OH) and 18 ml of sulphuric acid solution (5.3).

5.5 Bromide/bromate, 0,500 N standard volumetric solution.

Dissolve 51,0 g of potassium bromide (KBr) and 13,92 g of potassium bromate (KBrO₃), both dried at 105 °C for 30 min, in water and dilute to 1 litre.

NOTE — If the bromine numbers of the reference olefins specified in clause 7 determined using this solution do not conform to the prescribed limits, or if for reasons of uncertainty in the quality of primary reagents it is considered desirable to determine the normality of the solution, the solution shall be standardized and the normality thus determined shall be used in subsequent calculations. The standardization procedure shall be as follows:

To standardize, place 50 ml of glacial acetic acid and 1 ml of concentrated hydrochloric acid (HCl, ρ 1,19 g/ml) 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 ± 0,01 ml of bromide/bromate solution at the rate of 1 or 2 drops per second. Stopper the flask immediately, shake the contents, place it again in the ice bath, and add 5 ml of potassium iodide solution (5.2) in the lip of the 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 thiosulphate solution (5.6). Near the end of the titration, add 1 ml of starch solution (5.7)

and titrate slowly to disappearance of the blue colour. Calculate the normality T_1 of the bromide/bromate solution as follows:

$$T_1 = \frac{V_0 T_0}{5}$$

where

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

T_0 is the normality of the sodium thiosulphate solution.

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

5.6 Sodium thiosulphate, 0,1 N standard volumetric solution.

Dissolve 25 g of sodium thiosulphate pentahydrate (Na₂S₂O₃.5H₂O) in water and add 0,01 g of sodium carbonate (Na₂CO₃) to stabilize the solution. Dilute to 1 litre and mix thoroughly by shaking. Standardize by any accepted procedure that determines the normality with an error not greater than ± 0,000 2 N. Restandardize at intervals frequent enough to detect changes of 0,000 5 N in normality.

5.7 Starch solution.

Triturate 5 g of starch and 5 to 10 mg of mercury(II) iodide (Hg₂I₂) with 3 to 5 ml of water. Add the suspension to 2 litres of boiling water and boil for 5 to 10 min. Allow to cool and decant the clear, supernatant liquid into bottles having ground glass stoppers.

6 APPARATUS

6.1 Dead-stop electrometric titration apparatus.

Any dead-stop apparatus may be used provided that it incorporates a high-resistance polarizing current supply capable of maintaining approximately 0,8 V across two platinum electrodes and has a sensitivity such that a voltage change of approximately 50 mV at these electrodes is sufficient to indicate the end point. The procedure described is based on the transistorized circuit shown in figure 1, which has been found satisfactory in operation. Other types of commercially available electric titrimeters, including certain pH meters, have also been found suitable.

6.2 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 65 % nitric acid and rinse with water before use.

6.3 Titration vessel.

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



Published 1979-11-15

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**Petroleum distillates and commercial aliphatic olefins — Determination of bromine number —
Electrometric method****ERRATUM***Page 3*

Replace the key under the figure by the following :

R1 — 10 k Ω	R12 — 180 k Ω (100 k Ω if a 100 μ A meter is used)	I — AD 741K
R2 — 560 Ω	R13 — 10 k Ω	II — SN 741P
R3 — 100 k Ω	R14 — 560 Ω	D1 — 15920 or 1N4001
R4 — 1 k Ω	R15 — 180 Ω	D2 — LED, Type A
R5 — 100 k Ω	R16 — 1 M Ω	D3 — LED, RL21
R6 — 6,8 k	R17 — 10 k Ω	V1 — BC 182LB or 2N3302, 2N4953, 2N5376, 2N5377, SK3122
R7 — 3,3 k	R18 — 6,9 k	V2 — BC 212LB or 2N2907, 2N3251, 2N3486, 2N3505, 2N3672, 2N3673, 2N4143, 2N4228, SK3114
R8 — 2,7 k	R19 — 1,2 k	F — Fuse, 100 μ A
R9 — 330 k Ω	R20 — 1,2 k	M — Meter, 50 or 100 μ A
R10 — 47 k Ω	All resistors 0,5 W thin film	S — Switch, SPST
R11 — 4,7 k	R10 may be varied to suit measurement conditions	L — Pilot light, NE 51
VR1 — 10 k Ω	C1 — 0,2 μ F	
VR2 — 470 Ω 10-turn	C2 — 10 μ F	
VR3 — 10 k Ω	C3 — 0,1 μ F	
VR4 — 1 k Ω	C4 — 0,1 μ F	

Page 5

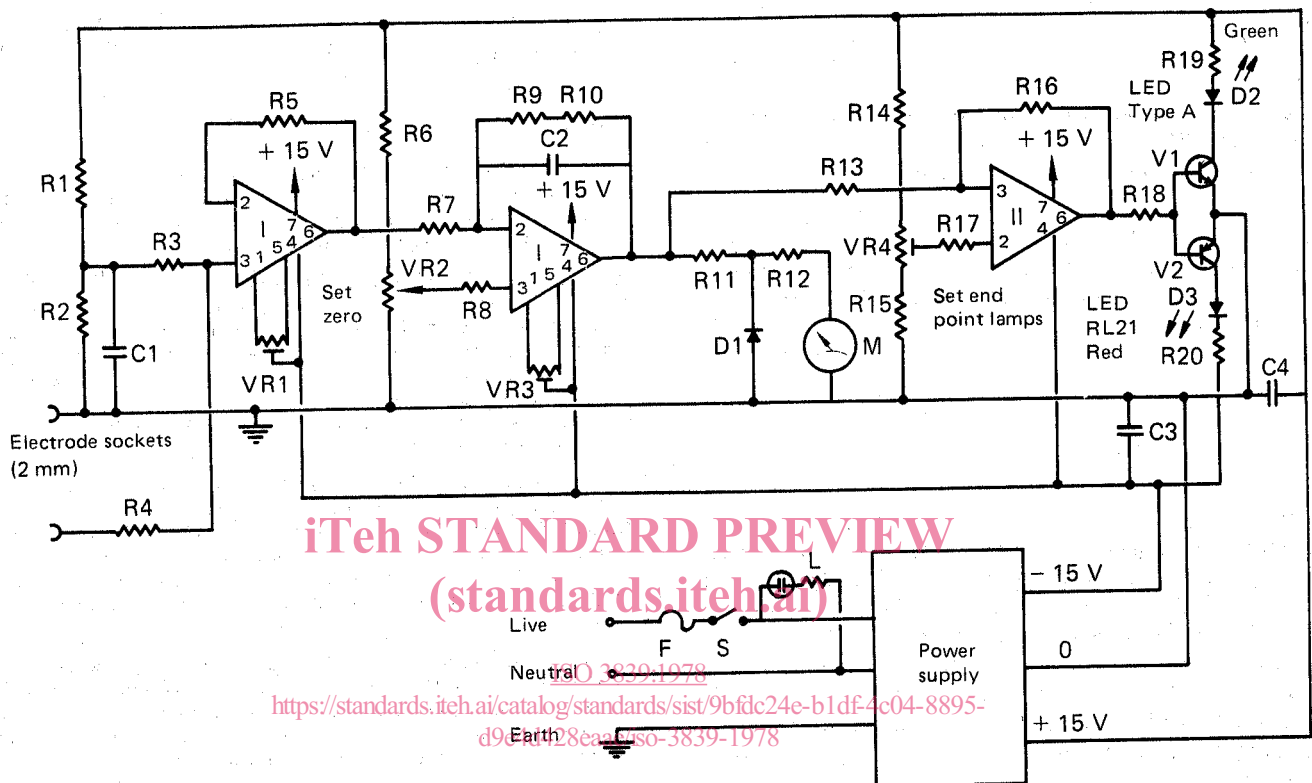
Replace the footnote by the following :

"1 min⁻¹ corresponds to 1 r/min"

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- | | | |
|---------------------|--------------------------------------------------|--------------------------------------------------------------------------------------------------|
| R1 – 10 kΩ | R12 – 180 kΩ (100 kΩ if a 100 μA meter is used) | I – AD 741K |
| R2 – 560 Ω | R13 – 10 kΩ | II – SN 741P |
| R3 – 100 kΩ | R14 – 560 Ω | D1 – 15920 or 1N4001 |
| R4 – 1 kΩ | R15 – 180 Ω | D2 – LED, Type A |
| R5 – 100 kΩ | R16 – 1 MΩ | D3 – LED, RL21 |
| R6 – 6k 8 | R17 – 10 kΩ | V1 – BC 182LB or 2N3302, 2N4953,
2N5376, 2N5377, SK3122 |
| R7 – 3k 3 | R18 – 6k 8 | V2 – BC 212LB or 2N2907, 2N3251,
2N3486, 2N3505, 2N3672,
2N3673, 2N4143, 2N4228,
SK3114 |
| R8 – 2k 7 | R19 – 1k 2 | F – Fuse, 100 μA |
| R9 – 330 kΩ | R20 – 1k 2 | M – Meter, 50 or 100 μA |
| R10 – 47 kΩ | All resistors 0,5 W thin film | S – Switch, SPST |
| R11 – 4k 7 | R10 may be varied to suit measurement conditions | L – Pilot light, NE 51 |
| VR1 – 10 kΩ | C1 – 0,2 μF | |
| VR2 – 470 Ω 10-turn | C2 – 10 μF | |
| VR3 – 10 kΩ | C3 – 0,1 μF | |
| VR4 – 1 kΩ | C4 – 0,1 μF | |

FIGURE 1 – Transistorized electrometric titrimeter circuit¹⁾

1) Names and addresses of manufacturers of suitable components are available from the ISO Central Secretariat or from the Secretariat of ISO/TC 28.

6.4 Stirrer (figure 2).

A suitable design consists of a glass rod 6 mm in diameter and approximately 150 mm in length with three sets of paddles located at the bottom, at 30 mm up, and at 50 mm up from the bottom. Each set of paddles shall consist of two round glass plates 1,5 mm thick and 7 mm in diameter fused at an angle of 45° to the rod and 90° to each other. The sets of paddles shall be offset 22° from each other around the circumference of the rod. The stirrer shall be located approximately 5 mm from the bottom of the titration cell and shall be driven mechanically or electrically. When in operation, each set of paddles shall direct the titration solvent towards the surface.

6.5 Burette, 10 ml graduated at 0,05 ml or smaller intervals. To avoid vibration, mount the burette separately from the stirrer.

7 CHECK TEST

In case of doubt in applying the procedure to actual test portions, the reagents and techniques should be checked by means of determinations on freshly purified cyclohexene and diisobutene. Proceed in accordance with clause 8, using as a test portion either 0,6 to 1 g of freshly purified cyclohexene or diisobutene (see table 1), or 6 to 10 g of a 10 % (m/m) solution of these materials in 1,1,1-trichloroethane (5.1). If the reagents and techniques are correct, values within the following ranges should 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 to 83 °C and from diisobutene concentrates with a boiling range of 100 to 102 °C, by the following procedure :

Add 65 g of activated silica (75 to 150 μm particle size, manufactured to ensure minimum olefin polymerization)¹⁾ to a column approximately 16 mm in inside diameter and 760 mm in 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 the adding 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. Discard the first 10 ml of percolate and collect the next 10 ml, which is the purified olefin for test of the bromine number procedure. Determine and record the density and refractive index of the purified test samples at 20 °C. Discard the remaining percolate.

2 CAUTION : If distillation of these olefins is required as a pre-purification step, a few pellets of potassium hydroxide should be placed in the distillation flask and distillation should not be continued beyond 90 % recovery to minimize the hazards from decomposition of any peroxides that may be present.

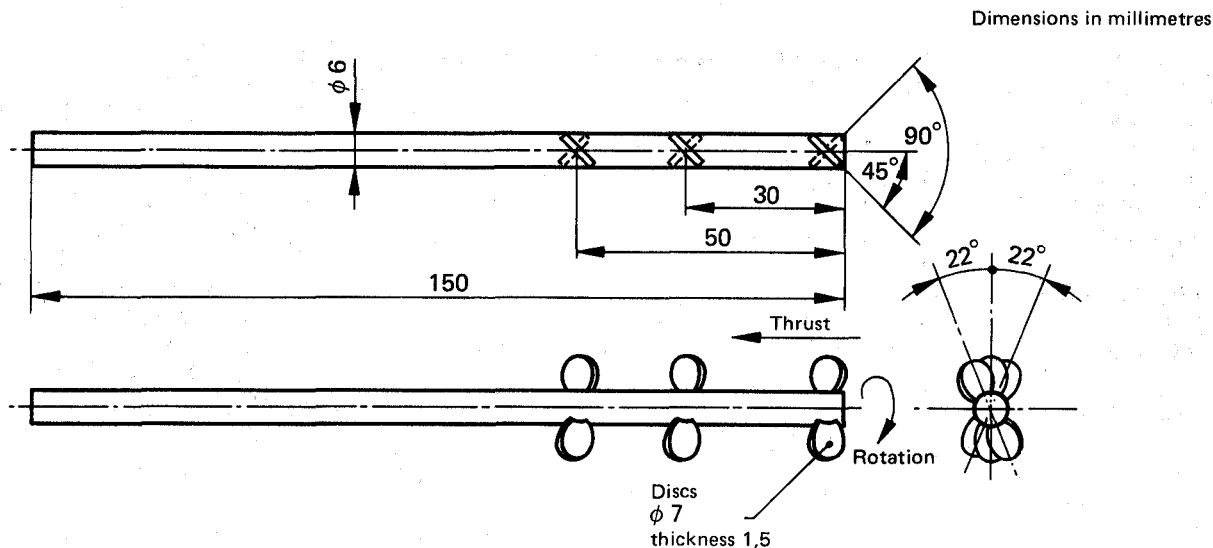


FIGURE 2 – Glass stirrer

1) The name and address of the manufacturer of a suitable product are available from the ISO Central Secretariat or from the Secretariat of ISO/TC 28.

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

TABLE 1 — Physical properties of purified olefins

Compound	Boiling point °C	Density at 20 °C g/ml	Refractive index n_D^{20}
Cyclohexene	82,5 to 83,5	0,810 0	1,446 5
Diisobutene	101 to 102,5	0,717 5 ± 0,001 5	1,411 2

4 The theoretical bromine numbers of cyclohexene and diisobutene are 194,6 and 142,4, respectively.

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 test portion having a mass as indicated in table 2 (see notes 1 and 2). Either obtain the mass of the test portion introduced by difference between the mass (to the nearest 1 mg) of the flask before and after addition of the test portion or, if the density is known accurately, calculate the mass from the measured volume. Fill the flask to the mark with 1,1,1-trichloroethane and mix well.

TABLE 2 — 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 Frequently, the order of magnitude of bromine number of a test portion is unknown. In this case, a trial test is recommended using a 2 g test portion in order to obtain the approximate magnitude of the bromine number. This exploratory test shall be followed with another determination using the appropriate test portion mass as indicated in table 2.

2 The mass of the test portion shall also be such that the volume of bromide/bromate titrant used will not exceed 10 ml and that no separation of the reaction mixture into two phases will occur during the titration. Difficulty may be experienced in dissolving test portions of the high boiling ranges in the titration solvent; this difficulty can be prevented by the addition of a small quantity of benzene.

8.2 Cool the titration vessel (6.3) to 0 to 5 °C and maintain the contents at this temperature throughout the titration. Switch on the titrimeter (6.1), and allow the electrical circuit to become stabilized.

8.3 Introduce 110 ml of titration solvent (5.4) into the vessel, switch on the stirrer (6.4) and adjust to a rapid stirring rate, but avoid any tendency for air bubbles to be drawn into the solution. A rotational frequency of approximately 1 200 min⁻¹* is generally satisfactory for the stirrer described in 6.4.

8.4 Adjust the titrimeter until the meter reads zero. Add one or two drops of bromide/bromate solution (5.5) until the meter reaches the set end point and remains there for at least 30 s. Pipette into the titration vessel a 5 ml aliquot of the test solution from the 50 ml volumetric flask.

8.5 Add bromide/bromate solution (5.5) in small increments from the burette until the meter starts to register. Continue adding the reagent, 2 drops at the time, until the meter registers the set end point and continues to register this indication for a period of not less than 30 s. This is the end point.

NOTE — With commercial titrimeters, a sudden change in potential is indicated on the meter or dial of the instrument as the end point is approached. When this change persists for 30 s, it marks the end point of the titration.

With each instrument, the manufacturer's instructions should be followed to achieve the sensitivity in the platinum electrode circuit specified in 6.1.

8.6 Make duplicate blank titrations on each batch of titration solvent and reagents by repeating the entire procedure, using 5 ml of 1,1,1-trichloroethane in place of the test solution aliquot. Less than 0,1 ml of bromide/bromate solution should be required.

9 EXPRESSION OF RESULTS

Calculate the bromine number (Br No.) as follows :

$$\text{Br No.} = \frac{(V_1 - V_2) T_1 \times 7,99}{m}$$

where

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

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

T_1 is the normality of the bromide/bromate solution;

m is the mass, in grams, of test portion in the aliquot.

10 PRECISION

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

10.1 Repeatability

The difference between two test results, obtained by the same operator with the same apparatus under constant

* 1 min⁻¹ corresponds to 1 rev/min

operating conditions on identical test material, would in the long run, in the normal and correct operation of the test method, exceed the values shown in figures 3 and 4 only in one case in twenty, in the case of petroleum distillates.

The corresponding difference for commercial aliphatic olefins is 3.

10.2 Reproducibility

The difference between two single and independent results obtained by different operators working in different

laboratories on identical test material, would in the long run, in the normal and correct operation of the test method, exceed the values shown in figures 3 and 4 only in one case in twenty, in the case of petroleum distillates.

The corresponding difference for commercial aliphatic olefins is 12.¹⁾

11 TEST REPORT

Report the bromine number as calculated in clause 9 and make reference to this International Standard.

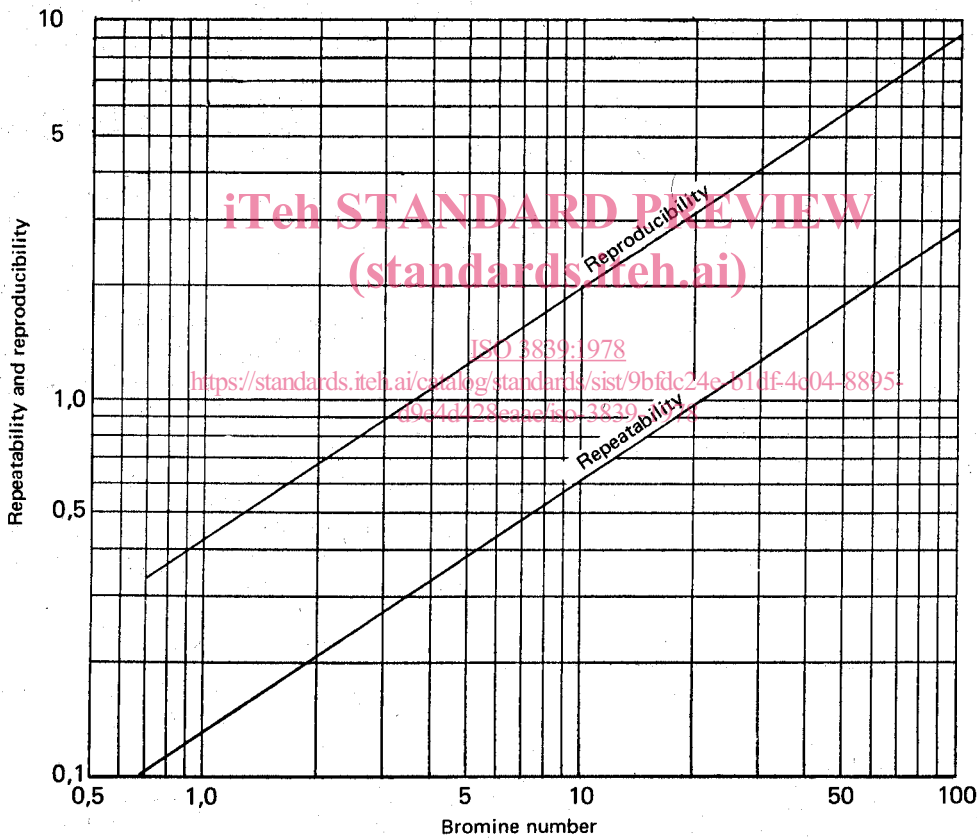


FIGURE 3 – Distillates with 90 % distillation point under 205 °C

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

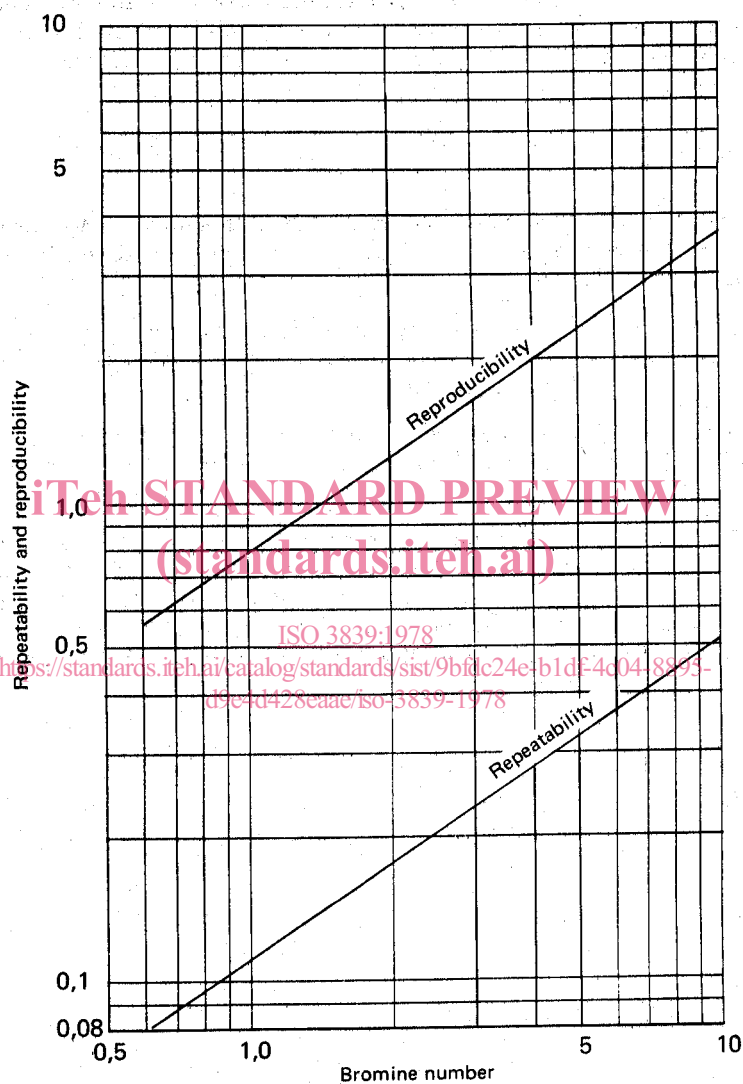


FIGURE 4 – Distillates with 90 % distillation point between 205 and 330 °C