BRITISH STANDARD

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IP 129:2003

Methods of test for petroleum and its products —

Part 129: Determination of bromine number — Colour indicator titration method (Identical with IP 129:2003)

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British Standards

National foreword

This British Standard reproduces verbatim IP 129:2003 and implements it as the UK national standard. It supersedes BS 2000-129:1993 which is withdrawn.

The UK participation in its preparation was entrusted to Technical Committee PTI/13, Petroleum testing and terminology, which has the responsibility to:

— aid enquirers to understand the text;

— present to the responsible international/European committee any enquiries on the interpretation, or proposals for change, and keep UK interests informed;

— monitor related international and European developments and promulgate them in the UK.

A list of organizations represented on this committee can be obtained on request to its secretary.

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Further information is available from:

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Cross-references

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Summary of pages

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Determination of bromine number — Colour indicator titration method

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 standard specifies a method for the determination of the bromine number of distillate liquid petroleum products which are substantially free from butanes and butenes. The precision applies to such products with 90 %(*V/V*) distillation recovery temperatures below 205 °C up to bromine numbers of 115, and to products with distillation recovery temperatures between 205 °C and 327 °C up to bromine numbers of 15. The distillation temperatures are those obtained by the procedures described in IP 123.

NOTE 1 - The bromine number does not correspond necessarily to a true content of unsaturates, since sulfur compounds and certain polycyclic aromatic hydrocarbons are reported to react with bromine.

NOTE 2 - Based on data given in the appendix to ASTM former method D 1158-59T, the reported behaviour of the main hydrocarbon types is as follows:

2 Normative references

The following normative documents contain provisions which, through reference in this text, constitute provisions of this standard. For dated references, subsequent amendments to, or revisions of, any of these publications do not apply. However, parties to agreements based on this standard are encouraged to investigate the possibility of applying the most recent editions of the normative documents indicated. For undated references, the latest edition of the normative document indicated applies.

IP 123, *Petroleum products — Determination of distillation characteristics at atmospheric pressure.* (≡ EN ISO 3405)

IP 160, *Crude petroleum and liquid petroleum products — Laboratory determination of density or relative density — Hydrometer method.* (≡ EN ISO 3675)

Hydrocarbon type	Bromine number of pure reference compound	Hydrocarbon type	Bromine number of pure reference compound
Paraffins	Zero	Conjugated dienes	Lower than theoretical
Straight chain olefins	Theoretical	Aromatics with unsaturated side chains	Not assessed
Branched chain olefins	Mostly higher than theoretical	Monocyclic aromatics	Zero
Cyclic olefins	Theoretical	Bicyclic aromatics	Zero
Non-conjugated dienes	Not assessed	Polycyclic aromatics	Mostly higher than theoretical
Non-conjugated cyclic dienes	Theoretical	Naphthenes	Zero

IP 365, *Crude petroleum and liquid petroleum products — Determination of density — Oscillating U-tube method.* (≡ EN ISO 12185)

IP 367, *Petroleum products — Determination and application of precision data in relation to methods of test.* (≡ EN ISO 4259)

IP 475, *Petroleum liquids — manual sampling.* (≡ EN ISO 3170)

IP 476, *Petroleum liquids — Automatic pipeline sampling.* (≡ EN ISO 3171)

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

3 Definition

For the purpose of this standard, the following definition applies:

3.1
bromine number
number of grams of bromine consumed by 100 g of sample when reacted under the conditions specified in this standard.

4 Principle

The test portion, dissolved in dichloromethane, is treated at room temperature with an excess of bromide-bromate solution in the presence of glacial acetic acid. The excess bromine is reduced with potassium iodide and the liberated iodine determined by titration with sodium thiosulfate solution.

5 Reagents and materials

5.1 Dichloromethane (CH_2Cl_2)

NOTE 3 - The previously specified 1,1,1-trichloroethane is an ozone depleting substance, and as such is banned by the Montreal Protocol from manufacture or importation. Comparative work has shown that its replacement by dichloromethane gives no discernible change in results, and thus the replacement of solvent has been made.

5.2 Acetic acid

Glacial, 99 % (*m/m*).

5.3 Water

Unless otherwise specified, water shall be that specified in grade 3 of EN ISO 3696.

5.4 Sodium thiosulfate solution

Approximately 0,5 mol/l accurately standardized. Dissolve 25 g of sodium thiosulfate ($Na_2S_2O_3.5H_2O$) in water (5.3) and add 0,01 g of sodium carbonate (Na_2CO_3) to stabilize the solution. Dilute to 1 l in a volumetric flask (6.2) 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.

5.5 Potassium iodide solution

150 g KI per litre.

5.6 Starch solution

Mix approximately 1 g of soluble starch with 5 ml to 6 ml of boiling water (5.3), add to 1 l of water and boil for 3 min. Allow to cool and decant the clear supernatant liquid of 0,5 %(*m/m*) starch solution into a glass-stoppered bottle. Prepare fresh daily. Commercially available starch solutions (some containing salicylic acid as a preservative), may be used.

5.7 Potassium bromide-bromate solution

Prepare a standard solution of 0,5 mol/l Br by weighing out 51,0 g ± 0,1 g of potassium bromide and 13,92 g ± 0,01 g of potassium bromate. Dissolve in water (5.3) and dilute to 1 l in a volumetric flask (6.2).

6 Apparatus

6.1 Iodine number flasks

500 ml capacity, glass-stoppered.

6.2 Volumetric flasks

One-mark flasks of 50 ml and 1 000 ml capacity. Class A.

6.3 Pipettes

5 ml capacity. Class A. Graduated pipettes of between 2 ml and 25 ml as required by the test portion volume (see Table 1).

6.4 Burettes

Class A for bromide-bromate and thiosulfate solutions.

7 Procedure

7.1 Determine the density of the sample by the procedures described in IP 160 or IP 365.

7.2 Place 10 ml of dichloromethane in a 50 ml volumetric flask (6.2) and add by pipette (6.3) a volume of test portion equivalent to the mass indicated in Table 1 (see note 4). Fill the flask to the mark with dichloromethane and mix well. Pipette a 5 ml aliquot of the solution into an iodine flask (6.1) containing 50 ml acetic acid (5.2).

Table 1 - Test portion size

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	1 to 0,5

NOTE 4 - Frequently, the order of magnitude of the bromine number of the sample is unknown. In this case a trial test is recommended using a 2 g test portion in order to obtain the approximate bromine number. The value obtained can then be used to obtain the correct test portion mass from Table 1 for another determination.

NOTE 5 - The dilution of the test portion may be made with acetic acid in place of the dichloromethane if desired. If the dilution is made with acetic acid, the 5 ml aliquot should be added to the iodine number flask containing 45 ml acetic acid and 5 ml of dichloromethane.

7.3 Shield the flask from exposure to direct sunlight and keep it at a temperature of 20 °C ± 5 °C. Add bromide-bromate solution from a burette at a rate of 1 drop/s to 2 drop/s, swirling the contents of the flask constantly during the addition. Continue adding the reagent until the reaction mixture assumes a yellow colour (see note 6) that remains for at least 5 s. Add an additional 1 ml of the reagent as quickly as possible, stopper the flask, and continue swirling immediately for 40 s ± 5 s. At the end of this period, place 5 ml of potassium iodide solution (5.5) in the lip of the flask and lift the stopper, allowing the solution to flow slowly into the flask. Replace the stopper, shake vigorously, add 100 ml of water, and shake again for 60 s. Titrate promptly with thiosulfate solution (5.4). Near the end of the titration, add 1 ml of starch solution (5.6) and titrate slowly to disappearance of the blue colour. The final drop shall be that which removes the blue colour for not less than 30 s. Discard the test if the back-titration is less than 5 ml or greater than 10 ml of thiosulfate solution (see note 7).

NOTE 6 - The yellow colour produced should be equivalent to that obtained by adding 5 ml of bromide-bromate solution to 50 ml of acetic acid and 5 ml of dichloromethane in a similar flask.

NOTE 7 - In certain cases, notably high-boiling samples, it is impossible to meet the requirements of a 5 ml to 10 ml thiosulfate back-titration. In such cases, the results are indeterminate.

7.4 Make a blank determination on each batch of reagents by carrying out 7.2 and 7.3 using 5 ml of dichloromethane in place of the test portion (see note 8).

NOTE 8 - In routine work, no correction need be applied as long as the blank does not exceed 0,02 mmol bromine. For work of highest accuracy, a correction should be applied if the blank exceeds 0,01 mmol Br. The correction should be made by subtracting from the term (VM - V_1M_1) in clause 8 the millimoles of bromine consumed by the volume of dichloromethane actually present in the 5 ml aliquot of test portion solution used in the analysis. This volume may vary from 2,5 ml to 4,9 ml depending on the mass of test portion used.

8 Calculation

Calculate the bromine number, N, of the sample by means of the following equation:

$$N = 7{,}99\ (VM - V_1M_1) / m$$

where

V is the volume of bromide-bromate solution added to the test portion, ml;

M is the concentration of bromine in the bromide-bromate solution, mol/l;

V_1 is the volume of thiosulfate solution used for the back-titration, ml;

M_1 is the concentration of thiosulfate solution, mol/l;

m is the mass of the test portion in the aliquot used, g.

9 Expression of results

Report the bromine number, to the nearest 0,1.

NOTE 9 - The approximate relationship between the bromine numbers (*N*129) of straight-run gasolines, kerosines and light gas oils determined by this standard, and those determined by the electrometric method, IP 130 (*N*130), is given by the equation:

$$(N129)^{1/3} = 1{,}012\ (N130)^{1/3} + 0{,}135$$

10 Precision

10.1 General

The precision given in 10.2 and 10.3 and illustrated in Figures 1 and 2, was derived from statistical examination of interlaboratory test results by IP 367. The precision was first published in 1961, and is based on the use of 1,1,1-trichloroethane as the solvent (see note 3).

Table 2 - Precision values

90 %(*V/V*) recovery temperature, °C	Range of bromine number	Repeatability, *r*	Reproducibility, *R*
Less than 205	0 to 115	$0{,}15x^{2/3}$	$0{,}31x^{2/3}$
205 to 327	0 to 15	$0{,}18x^{2/3}$	0,51 [1)]

where *x* is the mean of the results being compared.

1) Provisional result based on a limited amount of data.

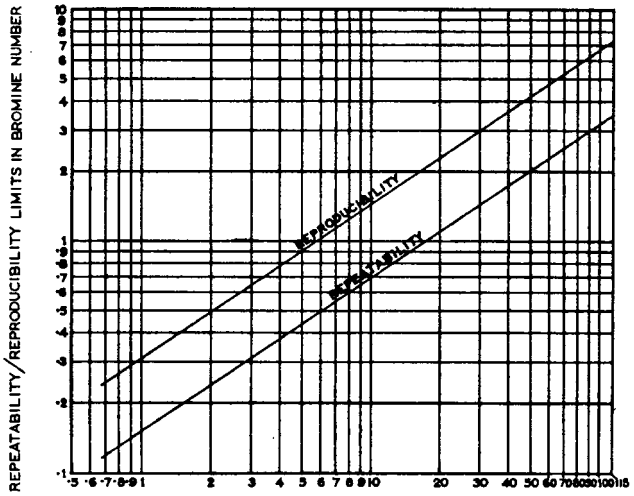

Figure 1 - Precision values for high volatility samples

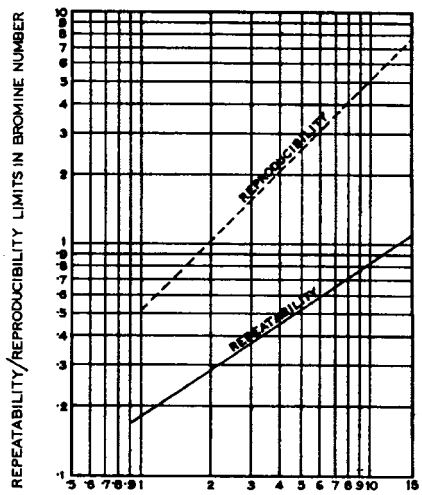

Figure 2 - Precision values for lower volatility samples

10.2 Repeatability, *r*

The difference between successive 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 values given in Table 2 only in one case in 20.

10.3 Reproducibility, *R*

The difference between two test results independently obtained by different operators operating in different laboratories on nominally identical test material would, in the normal and correct operation of the test method, exceed the values given in Table 2 only in one case in 20.

11 Test report

The test report shall contain at least the following information:

a) a reference to this standard;

b) the type and complete identification of the product tested;

c) the result of the test (see clause 9);

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

e) the date of the test.

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