BRITISH STANDARD

BS 2000-156:
2005
IP 156:2005

Methods of test for petroleum and its products —

Part 156: Determination of hydrocarbon types in petroleum products — Fluorescent indicator adsorption method (Identical with IP 156:2005)

ICS 75.080

BSI
British Standards

National foreword

This British Standard reproduces verbatim IP 156:2005 and implements it as the UK national standard. It supersedes BS 2000-156:1997 which is withdrawn.

The UK participation in its preparation was entrusted to Technical Committee PT/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.

Energy Institute, under the brand of IP publishes and sells all parts of BS 2000, and all BS EN petroleum test methods that would be part of BS 2000, both in its annual publication "Standard methods for analysis and testing of petroleum and related products and British Standard 2000 parts" and individually.

Further information is available from:

Energy Institute, 61 New Cavendish Street, London W1G 7AR.
Tel: 020 7467 7110. Fax: 020 7255 1472.

Cross-references

The British Standards which implement international or European publications referred to in this document may be found in the *BSI Catalogue* under the section entitled "International Standards Correspondence Index", or by using the "Search" facility of the *BSI Electronic Catalogue* or of British Standards Online.

This publication does not purport to include all the necessary provisions of a contract. Users are responsible for its correct application.

Compliance with a British Standard does not of itself confer immunity from legal obligations.

Summary of pages

This document comprises a front cover, an inside front cover, pages 1 to 10, an inside back cover and a back cover.

The BSI copyright notice displayed in this document indicates when the document was last issued.

This British Standard was published under the authority of the Standards Policy and Strategy Committee on 18 November 2005

ISBN 0 580 46182 3

Amendments issued since publication

Amd. No.	Date	Comments

Determination of hydrocarbon types in petroleum products — Fluorescent indicator adsorption 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 describes a fluorescent indicator adsorption method for the determination of hydrocarbon types over the concentration ranges from 5 % (*V/V*) to 99 % (*V/V*) aromatic hydrocarbons, 0,3 % (*V/V*) to 55 % *(V/V)* olefins, and 1 % *(V/V)* to 95 % (*V/V*) saturated hydrocarbons in petroleum fractions that distill below 315 °C. This method may apply to concentrations outside these ranges, but the precision has not been determined.

When samples containing oxygenated blending components are analysed, the hydrocarbon type results can be reported on an oxygenate-free basis or, when the oxygenate content is known, the results can be corrected to a total-sample basis.

This test method is for use with full boiling range products. Cooperative data have established that the precision statement does not apply to petroleum fractions with narrow boiling ranges near the 315 °C limit. Such samples are not eluted properly, and results are erratic.

Samples containing dark-coloured components that interfere with reading the chromatographic bands cannot be analysed.

NOTE 1 - The precision of this test method has been determined with unleaded fuels that do not contain oxygenated blending components. It may or may not apply to fuels containing lead antiknock mixtures or oxygenated blending components or both. However the oxygenated blending components methanol, ethanol, *tert*-butyl methyl ether (MTBE), methyl *tert*-pentyl ether *(TAME)* and *tert*-butyl ethyl ether (ETBE) do not interfere with the determination of hydrocarbon types at concentrations normally found in commercial petroleum blends. These oxygenated compounds are not detected since they elute with the alcohol desorbent. The effects of other oxygenated compounds should be individually verified.

2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this Standard. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this Standard are encouraged to investigate the possibility of applying the most recent editions of the standards indicated below.

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

IP 408, *Determination of organic oxygenate compounds and total organically bound oxygen content by gas chromatography (O-FID).*
(≡EN 1601)

IP 466, *Determination of organic oxygenate compounds and total organically bound oxygen content by gas chromatography using column switching.*
(≡EN 13132)

IP 475, *Manual sampling*.
(≡EN ISO 3170)

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

3 Definitions

For the purposes of this Standard, the following definitions apply.

3.1
saturates
volume percent % (*V/V*) of alkanes plus cycloalkanes.

3.2
olefins
volume percent % (*V/V*) of alkenes plus cycloalkenes plus some alkadienes.

3.3
aromatics
volume percent % (*V/V*) of monocyclic and polycyclic aromatic hydrocarbons plus aromatic olefinic hydrocarbons, some dienes, compounds containing sulfur and nitrogen, or higher-boiling oxygenated compounds, excluding those listed in note 1.

4 Principle

Approximately 0,75 ml of sample is introduced into a special glass adsorption column packed with activated silica gel. A small layer of the silica gel contains a mixture of fluorescent dyes. When all the sample has been adsorbed onto the gel, alcohol is added to desorb the sample down the column. The hydrocarbons are separated, according to their adsorption affinities, into aromatics, olefins and saturates. The fluorescent dyes are also separated selectively with the hydrocarbon types, and render the boundaries of the aromatic, olefin and saturate zones visible under ultraviolet light. The volume percentage % (*V/V*) of each hydrocarbon type is calculated from the length of each zone in the column.

5 Apparatus

5.1 Adsorption column, with precision bore tubing conforming to the specification given in Table 1 and as shown in Figure 1, made of glass and consisting of a charger section with a capillary neck, a separator section, and an analyzer section.

NOTE 2 - For routine/non-specification compliance analysis adsorption columns with standard wall tubing conforming to the specification given in Annex A and as shown in Figure 1 may be used.

In addition the length of a thread of liquid approximately 100 mm long shall not vary in length by more than 0,3 mm in any part of the analyzer section.

Glass-sealing of the various sections to each other shall be done with long-taper connections rather than shouldered connections. The silica gel shall be supported with a small piece of glass wool located between the ball socket of the 12/2 spherical joint and covering the analyzer outlet. The column tip attached to the 12/2 socket shall be approximately 2 mm inside diameter. The ball and socket joints shall be clamped together to ensure that the tip does not tend to slide from a position in a direct line with the analyzer section during the packing and subsequent use of the column.

Table 1 - Precision bore column dimensions and tolerance limits

Precision bore column dimensions	
Charger section	
Inside diameter	12 mm ± 2 mm
Overall length	150 mm ± 5 mm
Neck section	
Inside diameter	2 mm ±0,5 mm
Overall length	50 mm ± 5 mm
Separator section	
Inside diameter	5 mm ± 0,5 mm
Overall length	190 mm ± 5 mm
Analyzer section	
Inside diameter	1,60 mm to 1,65 mm
Overall length	1200mm ± 30 mm
Tip	
Overall length	30 mm ± 5 mm

5.2 Zone-measuring-device

Either a metre rule mounted adjacent to the column, fitted with four movable metal index clips, for measuring the length of each zone, see Figure 1, or glass-writing pencils for marking zone boundaries and metre rule for measuring the length of each zone.

5.3 Ultraviolet light source, with radiation predominantly at wavelength 365 nm.

NOTE 3 - A convenient arrangement consists of one or two units 915 mm or 1 220 mm in length mounted vertically alongside the apparatus adjusted to give the best fluorescence.

5.4 Electric vibrator, for vibrating the individual columns or for vibrating the frame supporting multiple columns.

Dimensions in millimetres
unless otherwise indicated

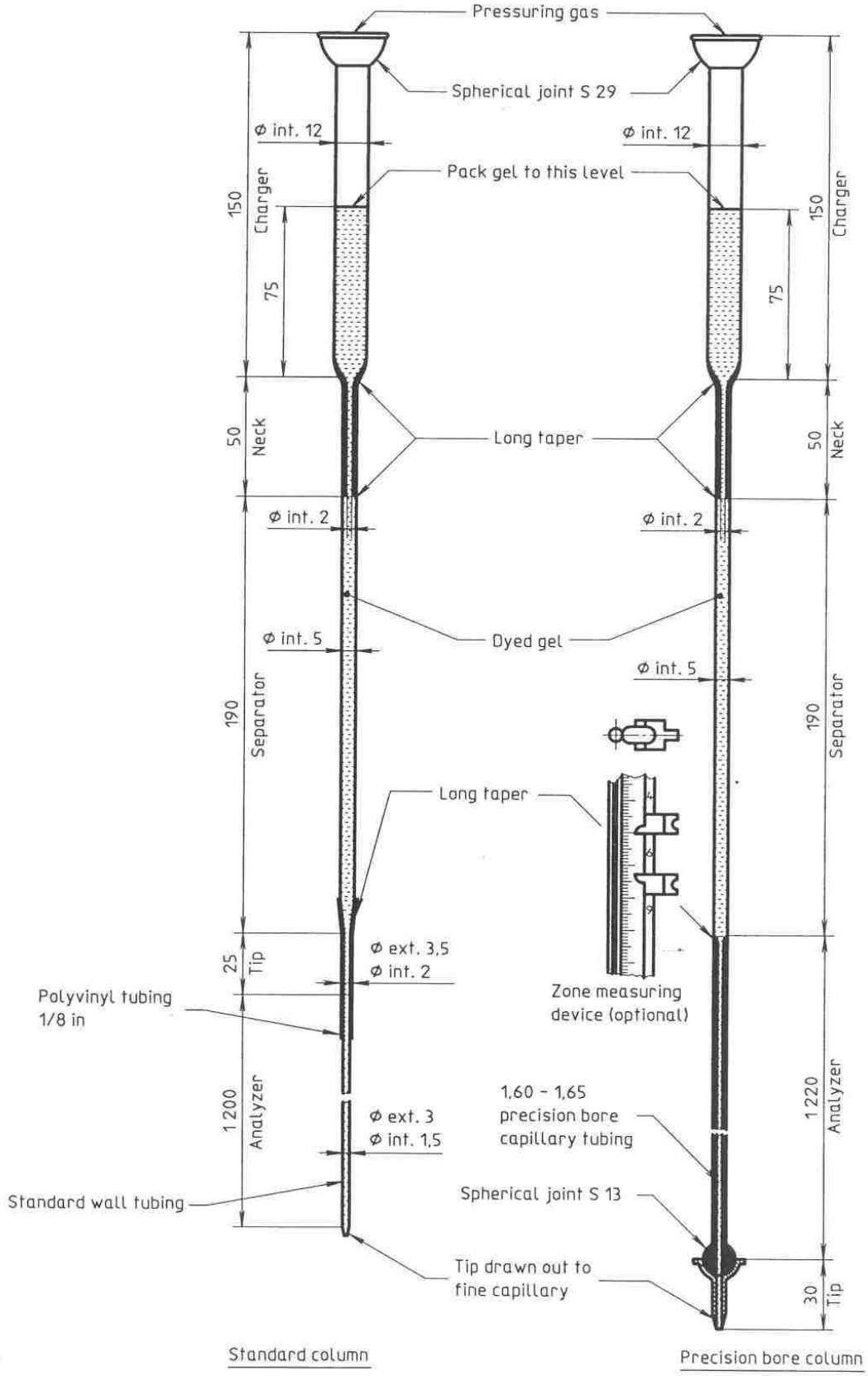

Figure 1 - Adsorption columns with standard wall (left) and precision bore (right) tubing in analyzer section

5.5 Hypodermic syringe, capacity 1 ml, graduated to 0,01 ml or 0,02 ml fitted with a needle 102 mm in length having an inside diameter of 0,7 mm to 1,2 mm.

NOTE 4 - Needles of No. 18, 20 or 22 gauge have been found to be satisfactory.

5.6 Glass funnel, with a stem of less than 10 mm external diameter

6 Chemicals and materials

During the analysis use only chemicals and reagents of recognised analytical grade and water conforming to grade 3 of ISO 3696.

6.1 Silica gel, manufactured to conform to the specifications given in annex B.

NOTE 5 - Grace Davison silica gel Grade 923 meets the requirements of this specification.

Before use, dry the gel in a shallow vessel at 176 °C for at least 3 h. Transfer the dried gel to an airtight container while still hot, and protect it from atmospheric moisture.

NOTE 6 - Some batches of silica gel that otherwise meet specifications have been found to produce olefin-boundary fading. The exact reason for this phenomenon is unknown but will affect accuracy and precision.

6.2 Fluorescent indicator-dyed gel[1)]**,** a standard dyed gel, consisting of a mixture of recrystallized Petrol red AB4 and purified portions of olefin and aromatic dyes obtained by chromatographic adsorption following a definite, uniform procedure, and deposited on silica gel. Store the dyed gel in a dark place under an atmosphere of nitrogen.

NOTE 7 - When stored under these conditions, dyed gel can have a shelf life of at least five years. It is recommended that portions of the dyed gel be transferred as required to a smaller working vial from which the dyed gel is routinely taken for analyses.

6.3 Propan-2-ol, 99 %

6.4 3-methylbutan-1-ol, 99 % (optional)

6.5 Acetone, reagent grade

6.4 Pressurizing gas, air (or nitrogen) capable of being delivered to the top of the column at controllable pressures over the range from 0 kPa gauge to 103 kPa gauge,

7 Sampling

7.1 Unless otherwise specified obtain samples for analysis in accordance with IP 475, IP 476 or an equivalent National Standard.

7.2 Store the sample in the dark at a temperature of 2 °C to 4 °C until ready for analysis.

8 Apparatus preparation

8.1 Mount the apparatus assembly in a room or area darkened to facilitate observations of zone boundaries. For multiple determinations, assemble an apparatus that includes the ultraviolet source, a rack to hold the columns, and a gas manifold system with spherical joints to connect to the desired number of columns.

8.2 Freely suspend the column from a loose-fitting clamp placed immediately below the spherical joint of the charger section. Place the glass funnel (5.7) in the column. Using the vibrator (5.5) vibrate the column along its entire length and add small increments of silica gel (6.1) through the glass funnel into the charger section until the separator section is half full. Stop the vibrator and add a 3 mm to 5 mm layer of dyed gel (6.2). Re-start the vibrator and vibrate the column while adding silica gel until the tightly packed gel extends 75 mm ± 5 mm into the charger section. To aid packing by removing static electricity wipe the length of the column with a damp cloth while vibrating the column. Vibrate the column for about 4 min after filling is completed.

NOTE 8 - More than one column can be prepared simultaneously by mounting several on a frame or rack to which an electric vibrator is attached.

Attach the filled column to the apparatus assembly.

1) A list of suppliers is available from the IP.

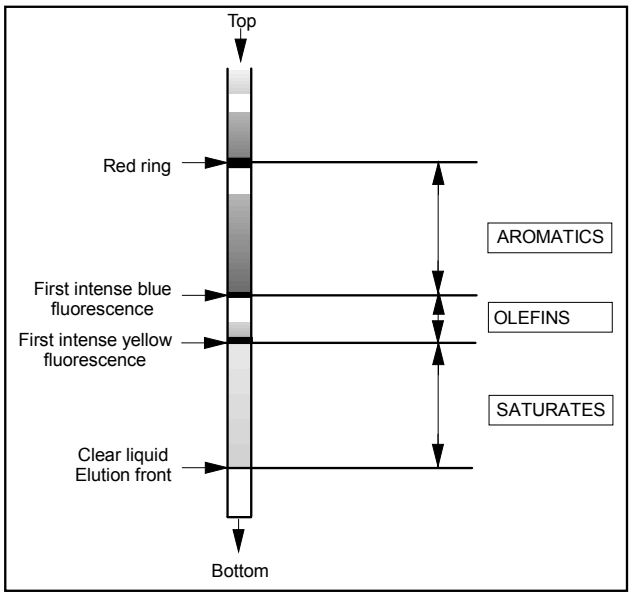

Figure 2 - Pictorial Aid for Identification of Chromatographic Boundaries

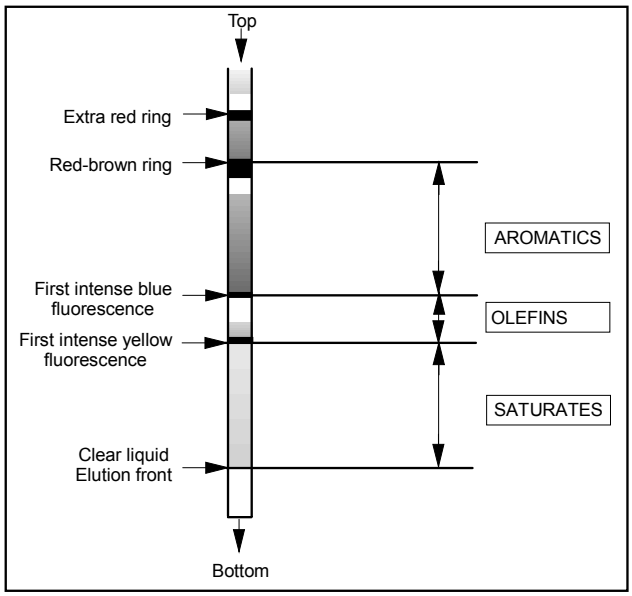

Figure 3 - Pictorial Aid for Identification of Chromatographic Boundaries of Oxygenate Blended Fuel Samples

9 Procedure

9.1 Bring the sample and a hypodermic syringe (5.5) to a temperature of 2 °C to 4 °C. Draw a 0,75 ml ± 0,05 ml test portion into the syringe and inject it approximatley 30 mm below the surface of the gel in the charger section.

9.2 Fill the charger section to the spherical joint with propan-2-ol (6.3), see note 9. Connect the column to the gas manifold (6.4) and supply 14 kPa ± 2kPa gauge gas pressure for 2,5 min ± 0,5 min to move the liquid front down the column. Increase the pressure to 34 kPa ± 2kPa gauge for another 2,5 min ± 0,5 min and then adjust the pressure required to give a column transit time of about 1 h, see note 10. A transit time of 1 h is optimum; however, high-molecular mass samples may require longer transit times.

NOTE 9 - For samples containing substantial amounts of material boiling above 205 °C, the use of 3-methylbutan-l-ol (6.4) instead of propan-2-ol may improve elution.

NOTE 10 - Usually 28 kPa to 69 kPa gauge gas pressure is needed for gasoline type material and 69 kPa to 103 kPa gauge gas pressure for kerosine and aviation turbine fuel. The pressure required will depend on the tightness of packing of the gel and the molecular mass of the sample.

9.3 After the red, alcohol/aromatic boundary has advanced approximately 350 mm into the analyzer section, make a set of readings in ultraviolet light by either quickly marking the boundary of each hydrocarbon type zone observed with the glass-writing pencil or if using the metre rule with the index clips (5.2) mark the boundaries, in the sequence given below. Avoid touching the column with the hands during this operation. Figure 2 gives a pictorial aid for the identification of the chromatographic boundaries.

Caution: Direct exposure to ultraviolet light can be harmful, particularly to the eyes. Operators must avoid such exposure as much as possible and wear UV adsorbent goggles or glasses.

For the non-fluorescent saturate zone, mark the front of the charge and the point where the yellow fluorescence first reaches its maximum intensity; for the upper end of the second, olefin zone, mark the point where the first intense blue fluorescence occurs; finally, for the upper end of the third, aromatic zone, mark the upper end of a reddish or brown zone. With colourless distillates, the alcohol-aromatic boundary is clearly defined by a red ring of dye. However, impurities in cracked fuels often obscure this red ring and give a brown coloration, which can vary in length. This shall be included as a part of the aromatic zone, except when no blue

fluorescence is present, in this case the brown or reddish ring shall be considered as part of the next distinguishable zone below it in the column.

9.4 With some oxygenate blended fuels another red band may appear several centimetres above the reddish or brown alcohol/aromatic boundary and this shall be ignored. Figure 3 gives a pictorial aid for the identification of the chromatographic boundaries for fuels containing oxygenated blending components.

9.5 If the boundaries have been marked off with index clips, record the measurements.

9.6 When the sample has advanced approximately 50 mm further down the column, make a second set of readings in reverse order to those made in 9.3 so as to minimize errors due to the advancement of boundary positions during readings. See note 11. Avoid touching the column with the hands during this operation. If the boundaries have been marked off with index clips, record the measurements.

NOTE 11 - If the marking has been made with a glass-writing pencil, two colours can be used one for each set of readings.

9.7 The combined lengths of the various zones shall be at least 500 mm, see note 12.

NOTE 12 - Erroneous results can be caused by improper packing of the gel or incomplete elution of hydrocarbons by the alcohol. With precision bore columns, incomplete elution can be detected from the total length of the several zones. With standard wall tubing, this criterion of total test portion length is not strictly applicable as the inside diameter of the analyzer section is not the same in all columns.

9.8 Release the gas pressure and disconnect the column.

9.9 If applicable place the analyser section horizontally on a bench and using the metre rule measure the lengths of the zones. Record these measurements.

9.10 Remove the used silica gel from the column by inverting it above a sink and inserting, through the wide end, a long piece of hypodermic tubing, 1,0 mm to 1,5 mm nominal external diameter with a 45° angle tip, connected to the laboratory water supply. Turn on the water and flush with a rapid stream of water. After removal of the silica gel using the same piece of hypodermic tubing rinse the tube with water conforming to grade 3 of ISO 3696 grade. Drain and rinse with acetone (6.5). Dry the tube by evacuation.

10 Calculation

10.1 For each set of observations, calculate the hydrocarbon types to the nearest 0,1 % (*V/V*) as follows:

aromatics, % (*V/V*) = $(L_a/L) \times 100$
olefins, % (*V/V*) = $(L_o/L) \times 100$
saturates, % (*V/V*) = $(L_s/L) \times 100$

where

L_a is the length of the aromatic zone, in mm;
L_o is the length of the olefin zone, in mm;
L_s is the length of the saturate zone, in mm;
L is the sum of $L_a + L_o + L_s$, in mm.

Calculate the mean of the respective values for each type and include it in the test report. If necessary, adjust the result for the largest component so that the sum of the means of the components is 100 %.

10.2 The equations given in 10.1 calculate concentrations on an oxygenate-free basis and are correct only for samples that are composed exclusively of hydrocarbons. For samples that contain oxygenated blending components (see note 1), correct the results from 10.1 to a total sample basis as follows:

$$C' = C \times \frac{100 - B}{100}$$

where

C' is the concentration of hydrocarbon type % (*V/V*) on a total sample basis;
C is the concentration hydrocarbon type % (*V/V*) on an oxygenate-free basis;
B is the concentration of total oxygenate blending components % (*V/V*) in the sample as determined in accordance with IP 408 or IP 466 or an equivalent test method.

11 Expression of results

Report the average values for each hydrocarbon type (corrected to a total sample basis if oxygenates are present) as volume percent % (*V/V*) to the nearest 0,1 % (*V/V*) and the total volume percent % (*V/V*) oxygenates in the sample as calculated.

12 Precision

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

12.1 Repeatability, 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 long run, in the normal and correct operation of the test method, exceed the values in Table 4 or Table 5 in only one case in twenty.

12.2 Reproducibility, the difference between two single and independent results obtained by different operators working in laboratories on identical test material, would in the long run, in the normal and correct operation of the test method, exceed the values in Table 4 or Table 5 in only one case in twenty.

13 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;

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

e) the date of the test.

Table 4 - Reproducibility and repeatability for oxygenate free samples, % (*V/V*)

	Level of result	Repeatability	Reproducibility
Aromatics	5	7	1,5
	15	1,2	2,5
	25	1,4	3,0
	35	1,5	3,3
	45	1,6	3,5
	50	1,6	3,5
	55	1,6	3,5
	65	1,5	3,3
	75	1,4	3,0
	85	1,2	2,5
	96	0,7	1,5
	99	0,3	0,7
Olefins	1	0,4	1,7
	3	0,7	2,9
	5	0,9	3,7
	10	1,2	5,1
	15	1,5	6,1
	20	1,6	6,8
	25	1,8	7,4
	30	1,9	7,8
	35	2,0	8,2
	40	2,0	8,4
	45	2,0	8,5
	50	2,1	8,6
	55	2,0	8,5

	Level of result	Repeatability	Reproducibility
Saturates	1	0,3	1,1
	5	0,8	2,4
	15	1,2	4,0
	25	1,5	4,8
	35	1,7	5,3
	45	1,7	5,6
	50	1,7	5,6
	55	1,7	5,6
	65	17	5,3
	75	1,5	4,8
	85	1,2	4,6
	95	0,3	2,4

Table 5 - Repeatability and reproducibility for sample containing oxygenates

Component	**Range** % *V/V*	**Repeatability** % *V/V*	**Reproducibility** % *V/V*
Aromatics	13 - 40	1,3	3,7
Olefins	4 - 33	$0,2578\ X^{0,6}$	$0,8185\ X^{0,6}$
Saturates	45 - 68	1,5	4,2
where X is the % *V/V* of the olefins			

Annex A
(Informative)

Standard adsorption column

A.1 Adsorption column, made of glass conforming to the dimensions and tolerances limits as given in Table A.1.

Table A.1

Standard column dimensions	
Charger section	
Inside diameter	12 mm ± 2 mm
Overall length	150 mm ± 5 mm
Neck section	
Inside diameter	2 mm ±0,5 mm
Overall length	50 mm ± 5 mm
Separator section	
Inside diameter	5 mm ± 0,5 mm
Overall length	190 mm ± 5 mm
Long taper section below separator	
Tip outside diameter	3,5 mm ± 0,5 mm
Tip inside diameter	2 mm ± 0,05 mm
Overall length	25 mm ± 2 mm
Analyzer section	
Internal diameter	1,5 mm ±0,5 mm, see A 2
Overall length	1200mm ± 30 mm

A.2 Analyser section checking

It would be impractical to calibrate the standard wall tubing for the analyzer. The conformity of the internal diameter of the section of the tube to be used as the analyser may be inferred by measuring the outside diameter of the tubing.

Using outside diameter measuring calipers measure the outside diameter of the analyser section of the absorption tube. Tubing that shows any variations in the outside diameter of 0,5 mm or greater along the tube may be taken as an indication of irregularities in the inside diameter and such tubing should not be used.

A.3 Column assembly

One end of the tubing selected for the analyzer section should be drawn out to a fine capillary to retain the gel. The other end of the analyzer section is connected to the separator section with a 30 mm length of polyvinyl tubing, with the two glass sections touching. To ensure a leakproof glass-to-polyvinyl seal with the analyzer section heat the upper end of the analyzer section until it is just hot enough to melt the polyvinyl, then insert the upper end of the analyzer section into the polyvinyl sleeve. Alternatively, this seal can be made by securing the polyvinyl sleeve to the analyzer section by wrapping it tightly with soft wire.

Annex B
(normative)

Specification for Silica Gel

B.1 Silica gel conforming to the following specification:

Surface area 430 m^2/g to 530 m^2/g

pH of a water slurry, 5,5 to 7,0

Loss on heating at 955 °C 4,5 % *m/m* to 10,0 % *m/m*

Iron content as Fe_2O_3, dry basis, 50 mg/Kg maximum

Particle size distribution as given in Table B.1.

Table B.1

Particle size distribution		
µm	Sieve number	Mass %
250	on 60	0,0 max
180	on 80	1,2 max
150	on 100	5,0 max
75	through 200	15,0 max

blank

BS 2000 Series

Energy Institute

61. New Cavendish Street
London
W1G 7AR

Tel: +44 (0)20 7467 7100
Fax: +44 (0)20 7255 1472
www.energyinst.org.uk

Buying Parts of BS 2000

Orders for BS 2000 publications should be addressed to:

The Library at the Energy Institute

British Standards Institution — Customer services
389 Chiswick High Road
London
W4 4AL

Tel: +44 (0)20 8996 9001
Fax: +44 (0)20 8996 7001
www.bsi-global.com

Order hard copy standards securely via:
www.bsi-global.com/bsonline

Copyright

IP

THE INSTITUTE
OF PETROLEUM

PTI/13