INTERNATIONAL STANDARD

ISO 3837

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Liquid petroleum products — Determination of hydrocarbon types — Fluorescent indicator adsorption method

Produits pétroliers liquides — Détermination des groupes d'hydrocarbures — Méthode par adsorption en présence d'indicateurs fluorescents

Reference number
ISO 3837:1993(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 3837 was prepared by Technical Committee ISO/TC 28, *Petroleum products and lubricants*.

Annex A of this International Standard is for information only.

International Organization for Standardization
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Introduction

The determination of the total volume percent [% (*V/V*)] of saturates, olefins and aromatics in petroleum fractions is important in characterizing the quality of petroleum fractions as gasoline blending components and as feeds to catalytic reforming processes, and in characterizing petroleum fractions and products from catalytic reforming and from thermal and catalytic cracking as blending components for motor and aviation fuels. This information is also important as a measure of the quality of aviation turbine fuels.

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Liquid petroleum products — Determination of hydrocarbon types — Fluorescent indicator adsorption method

WARNING — This 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 consult and establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

1 Scope

This International Standard specifies 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.

Restrictions inherent in the method and the determination of precision may limit its application as noted.

NOTES

1 This method may apply to concentrations outside these ranges, but the precision has not been determined.

2 This test method is intended 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.

3 The applicability of this test method to products derived from fossil fuels other than petroleum, such as coal, shale or tar sands, has not been determined and the precision statement does not apply to such products.

4 The precision of this test method has not been determined with oxygenated fuels and thus does not apply to automotive gasolines containing lead anti-knock mixtures.

5 The oxygenated blending components methanol, ethanol, methyl *tert*–butyl ether, *tert*–amyl methyl ether and ethyl *tert*–butyl ether do not interface 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. Other oxygenated compounds must be individually verified. When samples containing oxygenated blending components are analyzed, 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.

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

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 756-1:1981, *Propan-2-ol for industrial use — Methods of test — Part 1: General.*

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

ASTM D 3663-84, *Test method for surface area of catalysts.*

ASTM D 4815-89, *Test method for analysis of* C_1 *to* C_4 *alcohols and MTBE in gasoline by gas chromotography.*

3 Definitions

For the purposes of this International 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 condensed 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 5).

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.

NOTE 7 Errors leading to high saturate values and low aromatic and low olefin values can result if the sample contains C_3 or lighter hydrocarbons, or more than 5 % C_4 hydrocarbons, or more than 10 % C_4 and C_5 hydrocarbons. Such samples should be depentanized as specified in ANSI/ASTM D2001 (see annex A).

5 Apparatus

5.1 Adsorption columns, either with precision bore tubing, as shown on the right in figure 1, made of glass and consisting of a charger section with a capillary neck, a separator section, and an analyzer section; or with standard wall tubing, as shown on the left in figure 1.

The inside diameter of the analyzer section for the precision bore tubing shall be 1,60 mm to 1,65 mm and an approximately 100 mm thread of mercury shall not vary by more than 0,3 mm in any part of the analyzer section. In glass-sealing the various sections to each other, long-taper connections shall be made instead of shouldered connections. Support the silica gel 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 have a 2 mm inside diameter. Clamp the ball and socket together and 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.

For convenience, adsorption columns with standard wall tubing, as shown on the left in figure 1, may be used. When using standard wall tubing for the analyzer section, it is necessary to select tubing of uniform bore and to provide a leakproof connection between the separator and the analyzer sections. Calibrations of standard wall tubing would be impractical; however, any variations of 0,5 mm or greater, as measured by ordinary calipers, in the outside diameter along the tube may be taken as an indication of irregularities in the inside diameter and such tubing should not be used. Draw out one end of the tubing selected for the analyzer section to a fine capillary to retain the gel. Connect the other end of the analyzer section to the separator section with a 30 mm length of polyvinyl tubing, making certain that the two glass sections touch. To ensure a leakproof glass-to-polyvinyl seal with the analyzer section, it is necessary to 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.

5.2 Zone-measuring-device.

The zones may be marked with glass-writing pencil and the distances measured with a metre rule, with the analyzer section lying horizontally. Alternatively, the metre rule may be fastened adjacent to the column. In this case, it is convenient to have each rule fitted with four movable metal index clips (figure 1) for marking zone boundaries and measuring the length of each zone.

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

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

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

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

Needles of No. 18, 20 or 22 gauge are satisfactory.

Dimensions in millimetres
unless otherwise indicated

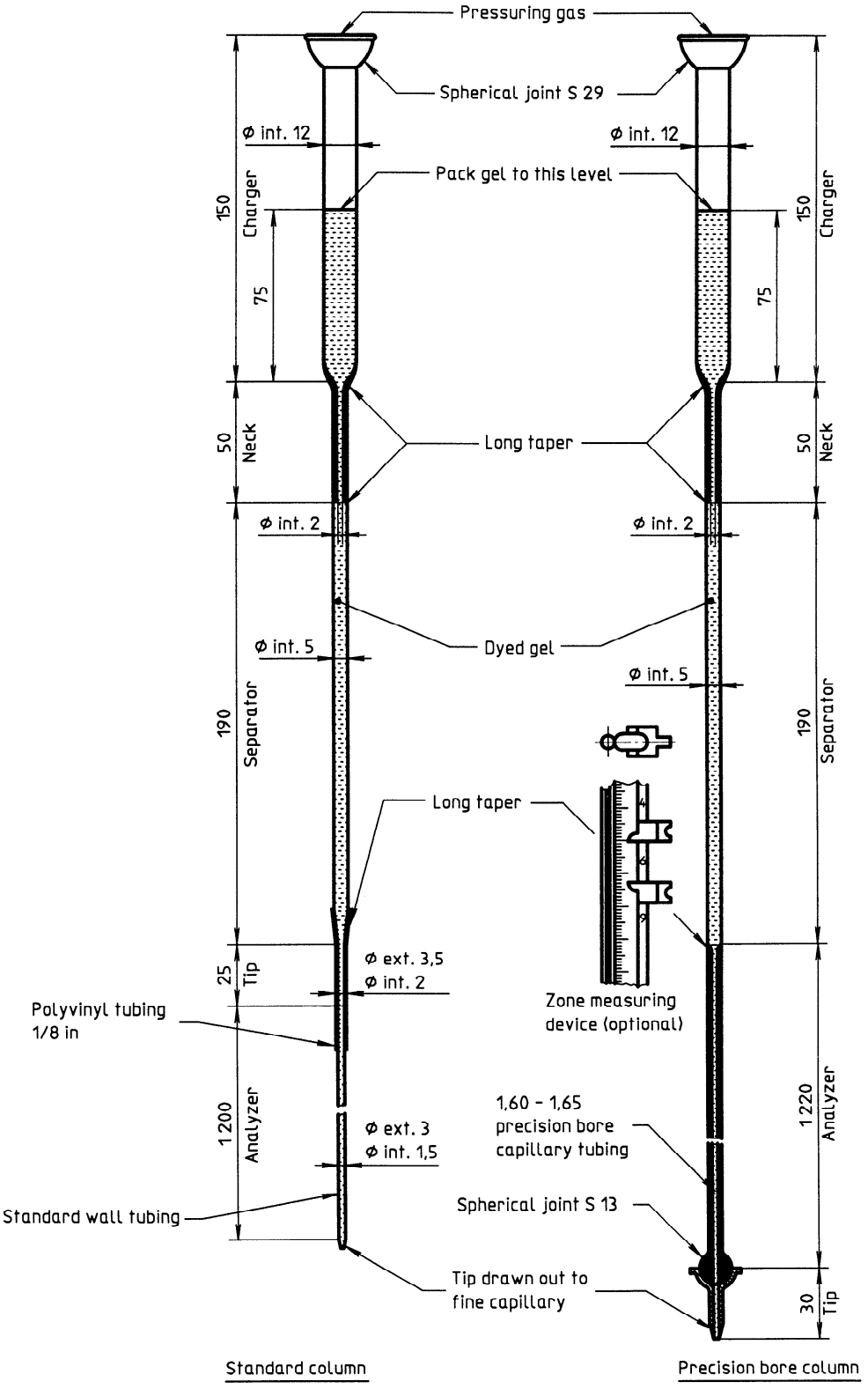

Figure 1 — Adsorption columns with standard wall (left) and precision bore (right) tubing in analyzer section

6 Reagents

6.1 Silica gel[1], manufactured to conform to the specifications shown in table 1. The surface area of the gel is determined in accordance with ASTM D 3663. Determine the pH of the silica gel by placing 5 g of the gel sample in a 250 ml beaker. Add 100 ml of water and a stirring bar. Standardize the pH meter with standards of pH 4 and pH 7. Stir the slurry with the magnetic stirrer for 20 min and then determine the pH. Before use, dry the gel in a shallow vessel at 176 °C for 3 h. Transfer the dried gel to an airtight container while still hot, and protect it from atmospheric moisture.

NOTE 8 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.

Table 1 — Silica gel specifications

Surface area: 430 to 530 m^2/g		
pH of 5 % water slurry: 5,5 to 7,0		
Loss on ignition at 955 °C: 4,5 to 10,0 mass %		
Iron as Fe_2O_3, dry basis: 50 max. mass ppm		
Particle size distribution		
µm	Sieve number	Mass %
250	on 60	
180	on 80	100
150	on 100	95 min.
75	through 200	15 max.

6.2 Fluorescent indicator-dyed gel[2], 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. The dyed gel must be stored in a dark place under an atmosphere of nitrogen. 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 % pure, as specified in ISO 756-1.

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

7 Sampling

Obtain a representative sample in accordance with sampling procedures given in ISO 3171. Store the sample at 2 °C to 4 °C until ready for analysis.

8 Test procedure

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. While vibrating the column along its entire length, add small increments of silica gel through a 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. Start the vibrator and vibrate the column while adding additional silica gel. Continue to add silica gel until the tightly packed gel extends 75 mm into the charger section. Wipe the length of the column with a damp cloth while vibrating the column. This aids in packing the column by removing static electricity. Vibrate the column for about 4 min after filling is completed.

NOTE 9 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 in the darkened room or area. If a permanently mounted metre rule is used, fasten the lower end of the column to the fixed rule with a rubber band.

8.3 Chill the sample and a hypodermic syringe to 2 °C to 4 °C. Draw 0,75 ml ± 0,03 ml of sample petroleum fraction into the syringe and inject the sample 30 mm below the surface of the gel in the charger section.

1) Available from W.R. Grace Co., Davison Chemical Division, Baltimore, MD 21203, USA by specifying Code 923. This is an example of a suitable product available commercially. This information is given for the convenience of users of this International Standard and does not constitute an endorsement by ISO of this product.

2) Available from UOP Organics Dept., 25 E. Algonquin Rd., Des Plaines, IL 60017-5017, USA by requesting "FIA Standard Dyed Gel", UOP Product No. 675. This is an example of a suitable product available commercially. This information is given for the convenience of users of this International Standard and does not constitute an endorsement by ISO of this product.

8.4 Fill the charger section to the spherical joint with propan-2-ol. Connect the column to the gas manifold and supply 14 kPa gauge gas pressure for 2,5 min to move the liquid front down the column. Increase the pressure to 34 kPa gauge for another 2,5 min and then adjust the pressure required to give a column transit time of about 1 h. Usually 28 kPa to 69 kPa gauge gas pressure is needed for gasoline-type samples and 69 kPa to 103 kPa gauge gas pressure for jet propulsion fuels. The pressure required will depend on the tightness of packing of the gel and the molecular mass of the sample. A transit time of 1 h is optimum; however, high-molecular mass samples may require longer transit times.

8.5 After the red, alcohol–aromatic boundary has advanced 350 mm into the analyzer section, make a set of readings by quickly marking the boundary of each hydrocarbon-type zone observed in ultraviolet light in the sequence given below. Avoid touching the column with the hands during this operation.

WARNING — Direct exposure to ultraviolet light can be harmful, particularly to the eyes. Operators should avoid such exposure as much as possible.

For the nonfluorescent 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, or olefin zone, mark the point where the first intense blue fluorescence occurs; finally, for the upper end of the third, or 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 varies in length, but which shall be counted as a part of the aromatic zone, except that when no blue fluorescence is present, the brown or reddish ring shall be considered as part of the next distinguishable zone below it in the column. If the boundaries have been marked off with index clips, record the measurements.

When the sample has advanced another 50 mm down the column, make a second set of readings by marking the zones in the reverse order to that described above so as to minimize errors due to the advancement of boundary positions during readings. If the marking has been made with a glass-writing pencil, two colours can be used to mark off each set of measurements and the distances measured at the end of the test with the analyzer section lying horizontally on the bench top. If the boundaries have been marked off with index clips, record the measurements.

NOTE 10 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, which must be at least 500 mm for a satisfactory analysis. With standard wall tubing, this criterion of total sample length is not strictly applicable because the inside diameter of the analyzer section is not the same in all columns. For samples containing substantial amounts of material boiling above 205 °C, the use of 2-methylbutan-1-ol instead of propan-2-ol may improve elution.

8.6 Release the gas pressure and disconnect the column. To remove used gel from the precision bore column, invert it above a sink and insert through the wide end a long piece of hypodermic tubing of 1 mm to 1,5 mm nominal external diameter with a 45° angle tip. By means of 6 mm copper tubing at the opposite end, attach a rubber tube, connect to a water tap and flush with a rapid stream of water. Rinse with residue-free acetone and dry by evacuation.

9 Calculation

9.1 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 millimetres;

L_o is the length of the olefin zone, in millimetres;

L_s is the length of the saturate zone, in millimetres;

L is the sum of $L_a + L_o + L_s$, in millimetres.

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 %.

9.2 The equations given in 9.1 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 5), the above results can be corrected 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 ASTM D 4815, or equivalent.

10 Expression of results

10.1 Report the average values as volume percent [% (*V/V*)] for each hydrocarbon type to the nearest 0,1 % (*V/V*) in the sample as analyzed.

10.2 Results from samples that have been depentanized shall be identified as being for the C_6 and heavier portion of the sample. Alternatively, the C_5 and lighter portion of the sample can be analyzed for olefins and saturates in accordance with ANSI/ASTM D 2427 (see annex A). Using these values and the percentage of overhead and bottoms, the hydrocarbon type distribution in the total sample can be calculated.

11 Precision

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

11.1 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 2 in only one case in twenty.

11.2 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 2 in only one case in twenty.

12 Test report

The test report shall contain at least the following information:

a) a reference to this International 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 2 — Reproducibility and repeatability
% (*V/V*)

	Level of result (%)	Repeatability	Reproducibility
Aromatics	5	0,7	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
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	1,7	5,3
	75	1,5	4,8
	85	1,2	4,6
	95	0,3	2,4

Annex A
(informative)

Bibliography

[1] ANSI/ASTM D 2001-86 *Test method for dependanization of gasolines and naphthas.*

[2] ANSI/ASTM D 2427-87 *Method for determination of C_2 through C_5 hydrocarbons in gasolines by gas chromatography.*

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