This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.

Designation: D7900 – 23

Standard Test Method for Determination of Light Hydrocarbons in Stabilized Crude Oils by Gas Chromatography[1]

This standard is issued under the fixed designation D7900; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope*

1.1 This test method specifies a method to determine the boiling range distribution of hydrocarbons in stabilized crude oil up to and including n-nonane. A stabilized crude oil is defined as having a Reid Vapor Pressure equivalent to or less than 82.7 kPa. The results of this test method can be combined with those from Test Method D7169 and IP 545 to give a full boiling point distribution of a crude oil (see Appendix X3).

1.2 The values stated in SI units are to be regarded as the standard. The values given in parentheses are provided for information purposes only.

1.3 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.4 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D323 Test Method for Vapor Pressure of Petroleum Products (Reid Method)

D4057 Practice for Manual Sampling of Petroleum and Petroleum Products

D4175 Terminology Relating to Petroleum Products, Liquid Fuels, and Lubricants

D4177 Practice for Automatic Sampling of Petroleum and Petroleum Products

D5134 Test Method for Detailed Analysis of Petroleum Naphthas through n-Nonane by Capillary Gas Chromatography

D6729 Test Method for Determination of Individual Components in Spark Ignition Engine Fuels by 100 Metre Capillary High Resolution Gas Chromatography

D6730 Test Method for Determination of Individual Components in Spark Ignition Engine Fuels by 100-Metre Capillary (with Precolumn) High-Resolution Gas Chromatography

D6733 Test Method for Determination of Individual Components in Spark Ignition Engine Fuels by 50-Metre Capillary High Resolution Gas Chromatography

D7169 Test Method for Boiling Point Distribution of Samples with Residues Such as Crude Oils and Atmospheric and Vacuum Residues by High Temperature Gas Chromatography

E355 Practice for Gas Chromatography Terms and Relationships

2.2 *Energy Institute Standards:*[3]

IP 475 Manual Sampling

IP 476 Automatic Pipeline Sampling

IP 545 Crude Petroleum and Petroleum Products—Determination of Boiling Range Distribution of Crude Oil

2.3 *ISO Standard:*[4]

ISO 4259 Petroleum Products—Determination and Application of Precision Data in Relation to Methods of Test

3. Terminology

3.1 *Definitions*—This test method makes reference to many common petroleum and gas chromatographic procedures terms and relationships. Detailed definitions can be found in Terminology D4175 and Practice E355.

4. Summary of Test Method

4.1 An amount of internal standard is quantitatively added to an aliquot of the stabilized crude oil. A portion of this mixture is injected into a pre-column in series via a splitter

[1] This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products, Liquid Fuels, and Lubricants and is the direct responsibility of Subcommittee D02.04.0L on Gas Chromatography Methods.

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[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

[3] Information on Energy Institute Standards can be obtained from the Energy Institute at www.energyinst.org.

[4] Available from American National Standards Institute (ANSI), 25 W. 43rd St., 4th Floor, New York, NY 10036, http://www.ansi.org.

*A Summary of Changes section appears at the end of this standard

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TABLE 1 Typical Chromatographic Conditions

	Pre-column A	Pre-column B	Analytical	Accelerated Analytical
Column Length—metres	1.0 m	0.075 m	50 or 100 m	40 m
Column Internal Diameter—mm	2 mm	2.5 mm	0.25 mm	0.10 mm
Phase Loading	5 %[A]	10 % OV-101 on Chromosorb 80-100 mesh		
Film Thickness			0.5 um	
Injection Volume			0.1 µL	0.1 µL
Injector Split Ratio			100 : 1	600 : 1
Injector Temperature	300 °C	100 °C		
Pre-column Temperature	200 °C	100 °C		
Injector Prog. Rate °C/min		50 °C/min		
Final Injector Temperature		300 °C		
Initial Oven Temperature			35 °C	35 °C
Hold Time			30 min	2.6 min
Oven Program Rate °C/min			2 °C/min	50 °C/min → 45 °C (hold time 3 min) 5 °C/min → 60 °C (hold time 3 min) 9.5 °C/min →
Final Oven Temperature			200 °C (hold time 20 min)	200 °C (hold time 1 min)
Flame Ionization Detector			300 °C	300 °C

[A]Phase type not reported except as indicated, assumed non-polar.

with a capillary analytical column. When the n-nonane has quantitatively passed to the analytical column, the pre-column is back-flushed to vent the higher boiling components. The individual components are identified by comparison with reference chromatograms and a database of hydrocarbon compounds (see Appendix X1). The boiling point distribution up to and including n-nonane (n-C9) is calculated.

5. Significance and Use

5.1 Knowledge of the boiling point distribution of stabilized crude oils is important for the marketing, scheduling, and processing of crude oil in the petroleum industry. Test Method D7169 and IP 545 purport to give such a distribution in crude oils, but are susceptible to significant errors in the light ends portion of the distribution as well as in the mass recovery of the whole crude oil due to the interference imposed by the diluent solvent. This test method allows for more accurate determination of the front end of the boiling point distribution curve, in addition to providing important C1 to C9 (nonane) component level information, and more accurate mass recovery at C9 (nonane).

6. Apparatus

6.1 *Gas Chromatograph,* with the operational characteristics given in Table 1.

6.2 *Inlet*—A temperature programmable vaporizing (PVT) or split/splitless inlet.

6.2.1 *Carrier Gas Pneumatic Control*—Constant carrier gas pressure or flow control is required.

6.3 *Column*—A fused silica-bonded polydimethylsiloxane coated capillary column and pre-column are employed. See Table 1 for suggested columns. The analytical column shall elute hydrocarbons in a boiling point order. The eluate from the injector passes through the pre-column before eluting onto the analytical column.

6.4 *Data System*—A computer-based chromatography data system capable of accurately and repeatedly measuring the retention time and areas of eluting peaks. The system shall be able to acquire data at a rate adequate to accurately measure 10 to 20 points around an individual peak. For the accelerated methods (see Table 1), a sampling rate of at least 20 Hz is recommended.

6.5 *Sample Introduction*—Sample introduction by means of an automatic injection is highly recommended.

6.6 *Flame Ionization Detector (FID),* with sufficient sensitivity to detect 0.01 % mass n-heptane with a signal to noise of greater than five. When operating at this sensitivity level, detector stability shall be such that a baseline drift of not more than 1 % per hour is obtained. The detector shall be connected to the column so as to avoid any cold spots. The detector shall be capable of operating at a temperature equivalent to the maximum column temperature used.

6.7 *Pre-Column Configurations:*

6.7.1 *Heated Valve Switching Box Configuration*—For the isothermal 1 m pre-column, a heated valve box is needed with its own temperature control. The box will contain an automated six-port valve, which is used to back-flush the pre-column. The six-port valve should be made out of material that will not be corroded by the sample (some crude oils contain high amounts of sulfur components). The valve shall be situated in a heated isothermal oven and be attached to the injector, pre-column, splitter, analytical column, and the detector without any cold spots. An example configuration is given in Fig. X2.1 in Appendix X2. Alternatively, a Dean Switch type back-flush of the petroleum may also be employed in place of a rotary valve.

6.7.2 *Injection Port Back-Flush Configuration*—A temperature programmable injection port capable of containing a 7.5 cm pre-column, and this injection port must be equipped with a back-flush option. This injector can be connected

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directly to the capillary column (Fig. X2.2, Appendix X2) or via a splitter (Fig. X2.3, Appendix X2).

6.8 *Analytical Balance,* capable of weighing with an accuracy of 0.1 mg.

7. Reagents and Materials

7.1 *Gas Chromatograph Gases*—All of the following gases shall have a purity of 99.995 % (V/V) or greater. (**Warning—** Gases are compressed. Some are flammable, and all gases are under high pressure.)

NOTE 1—These specifications can be obtained by proper use of filtering devices and meeting the FID specifications in 6.6.

7.1.1 *Carrier Gas*—Helium or hydrogen is required. Any oxygen present shall be removed, for example, by a suitable chemical filter. If hydrogen is employed as a carrier gas, the user is advised to follow all manufacturer's safety guidelines for its use. (**Warning—**Hydrogen is an extremely flammable gas under high pressure.)

7.1.2 *Detector Combustion Gases,* Air, Hydrogen, and Make-up Gas (Helium or Nitrogen). (**Warning—**Hydrogen is an extremely flammable gas under high pressure.) (**Warning—** Compressed air is a gas under high pressure and supports combustion.)

7.2 *Internal Standard*—The internal standard shall have baseline resolution from any adjacent eluting peaks. Hexene-1 or 3,3–dimethylbutene-1 (99 % pure) have been found to be suitable.

7.3 *Valve Timing Mixture/Splitter Linearity Mix*—A quantitative mixture of approximately 1 % mass of each normal alkane from pentane to decane in hexadecane (99+ % purity). Accurately record the mass (g) of each normal alkane as well as the hexadecane solvent and calculate the actual mass percent of each alkane in the mixture.

7.4 *Viscosity Agent,* Carbon disulfide, 99+ % pure, (**Warning—**Extremely flammable and toxic liquid.) is used as a viscosity reduction agent in the preparation of samples.

8. Sampling

8.1 Samples to be analyzed by this test method must be obtained using the procedures outlined in Practice D4057 or Practice D4177 (IP 475 and IP 476, respectively).

8.2 The test specimen to be analyzed must be homogeneous and free of dust or undissolved material.

9. Preparation of Apparatus

9.1 *Chromatograph*—Place in service according to manufacturer's instructions. Typical operating conditions are given in Table 1.

9.2 *Column Preparation*—Condition analytical columns in accordance with manufacturer's instructions.

9.3 *System Performance Specification:*

9.3.1 *Skewness*—Determine the skew of the n-hexane peak by measuring the width of the leading part of the peak at 5 % peak height (A) and the width of the following part of the peak at 5 % peak height (B). The ratio (B)/(A) shall be not less than 1 or more than 4 (see Fig. 1).

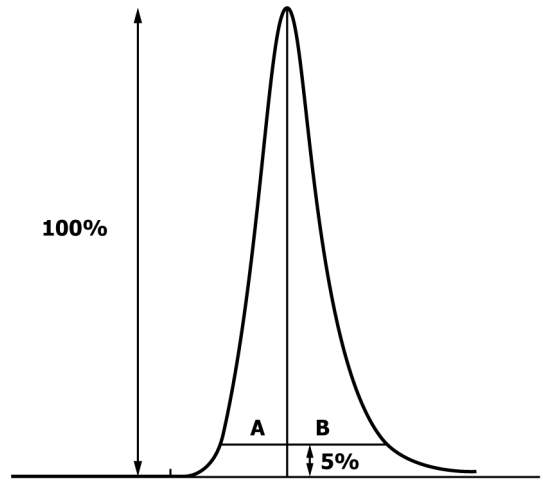

FIG. 1 Calculation of Peak Skewness (see 9.3.1)

9.3.2 *Column Resolution*—Determine the resolution between the internal standard and the nearest n-paraffin peak.

$$R = 2 \times (t2 - t1) / 1.699(w1 + w2) \quad (1)$$

where:

R = the column resolution,
$t1$ = the retention time of the first peak (peak 1),
$t2$ = the retention time of the second peak (peak 2),
$w1$ = the peak width at half height of peak 1, and
$w2$ = the peak width at half height of peak 2.

For example, if Hexene-1 is used as the internal standard, the resolution is determined between Hexene-1 and n-hexane. The resolution shall be at least 2.0.

9.3.3 *Detector Response Factor Calculations*—Calculate the flame ionization detector response factor relative to methane, which is considered to have a response factor of unity (1), for each hydrocarbon group type of a particular carbon number using Eq 2.

$$RRf = \frac{[(C_{aw} \times C_n) + (H_{aw} \times H_n)] \times 0.7487}{(C_{aw} \times C_n)} \quad (2)$$

where:

RRf = relative response factor for a hydrocarbon type group of a particular carbon number,
C_{aw} = atomic mass of carbon, 12.011,
C_n = number of carbon atoms in the hydrocarbon type group, of a particular carbon number,
H_{aw} = atomic mass of hydrogen, 1.008,
H_n = number of hydrogen atoms in the hydrocarbon type group of a particular carbon number, and
0.7487 = factor to normalize the result to a methane response of unity, (1).

9.3.4 *Determination of Back-Flush Time*—With the pre-column and analytical column in series, inject an aliquot of the pre-column switch test mixture (7.3) and determine the ratio of the alkanes.

9.3.4.1 *Non-Accelerated Analytical Column*—Set the switching time to one minute and repeat the analysis. Increase or decrease the valve time to ensure the complete recovery of the highest alkane required (for example, n-nonane) and partial

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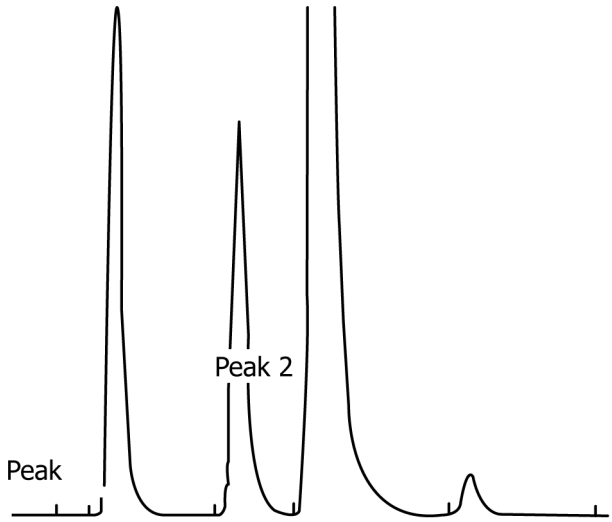

FIG. 2 Determination of Resolution (see 9.3.2)

recovery of the next alkane (for example, decane). (See example chromatogram (Fig. 3).)

9.3.4.2 *Accelerated Analytical Column*—Set the switching time to 30 s and repeat the analysis. Increase or decrease the valve time to ensure the recovery of the highest alkane required (for example, n-nonane) and partial recovery of the next alkane (for example, n-decane). (See example chromatogram (Fig. 3).)

9.3.5 *Split Injection Linearity*—For systems utilizing split injection, injector linearity must be established to determine proper quantitative parameters and limits.

9.3.5.1 Set the injector temperature and split ratio to the operating values as indicated in Table 1 for split inlets.

9.3.5.2 Inject 0.1 µL of the splitter linearity mixture (7.3) into the system.

9.3.5.3 Calculate the normalized area % of the n-C5 through n-C9 paraffins using Eq 3:

$$\text{Corrected Normalized Area } \%C_n$$
$$100 \times \left[\left(\text{Area } C_n \times \text{RRf } C_n \right) / \text{TA} \right] \quad (3)$$

where:

Area C_n = integrated peak area of normal alkane C_n,
RRf C_n = theoretical relative response factor for C_n (Eq 2), and
TA = sum of RRf corrected peak areas from C_5 to C_9.

9.3.5.4 The corrected normalized area percent of each normal alkane must agree within 10 % or better from their gravimetric values after the back-flush time is optimized. Values outside of this range may indicate possible mass discrimination, possibly due to liner issues, blockage of the split vent, an inlet leak, incorrect detector Air/H2 ratio, weathering of the gravimetric mixture, or premature back-flush time. Correct any issues and perform the linearity check until it passes the specification.

10. Procedure

10.1 Set the operating conditions of the gas chromatograph as shown in Table 1.

10.2 Obtain a representative sample following the guidelines of Practice D4057 and any other applicable guidelines. Take precautions to minimize the loss of light ends from volatile samples.

NOTE 2—To minimize losses of light hydrocarbons, it is recommended in the field to use septum sealed sampling containers such as DOPAK or equivalent.

10.3 *Sample Preparation*—Weigh to the nearest 0.1 mg, approximately 5 g ± 0.2 g of sample into a tared, screw capped vial. Add approximately 0.15 g ± 0.02 g of internal standard and reweigh to the nearest 0.1 mg. Where the mass of available sample is less than 5 g, the internal standard shall be added to create the equivalent of a 3 % concentration. Gently mix the two liquids without causing the sample to degas. Carbon disulfide can be added to improve the viscosity of the sample. Fill the sample into GC vials with a minimum amount of headspace. Store the vials in a sub ambient cupboard until use.

NOTE 3—For laboratory sample preparations, septum sealed vials and gas tight syringes for sample transfers are recommended. If smaller sample quantities are shipped among laboratories, septum sealed vials are also recommended. The use of septum sealed vials has been found to minimize sample losses and to produce better result agreement among laboratories testing identical samples.

NOTE 4—The amount of sample and internal standard taken can vary according to the level of C1 to C6 components in the sample and the amount of the sample available.

10.4 *Sample Analysis*—Inject a suitable aliquot of the sample and internal standard onto the inlet of the pre-column, which is in series with the analytical column. At the time determined above (9.3.4) switch the valve and back-flush the high boilers to vent.

NOTE 5—The valve time reflects the highest carbon number required. As a general rule, if C(z) is required, then C(z + 1) should be eluted.

11. Calculation

11.1 Calculate the individual hydrocarbons up to and including nonane using:

$$\%\ \text{m/m component Q} = \frac{(\text{Area component Q}) \times (\text{RRFQ})}{(\text{Area IS}) \times (\text{RRF IS})} \times (\%\ \text{m/m IS}) \quad (4)$$

where RRF Q and RRF IS are the relative response factors relative to methane respectively for component Q and the internal standard IS as calculated in 9.3.3. The generic response factors for the components can be transformed to a specific factor belonging to this internal standard, by dividing the generic response factors by the relative response factor of the internal standard (in this case a C_6 olefin for which the response relative to methane is 0.874).

11.2 By summation of all the % m/m per peak up to and including nonane, the % m/m recovery of this fraction can be calculated.

NOTE 6—Test Methods D6729, D6730, and D6733 contain information that can be used to help with the identification of individual components.

11.3 Calculation of boiling point distribution of fraction up to and including nonane.

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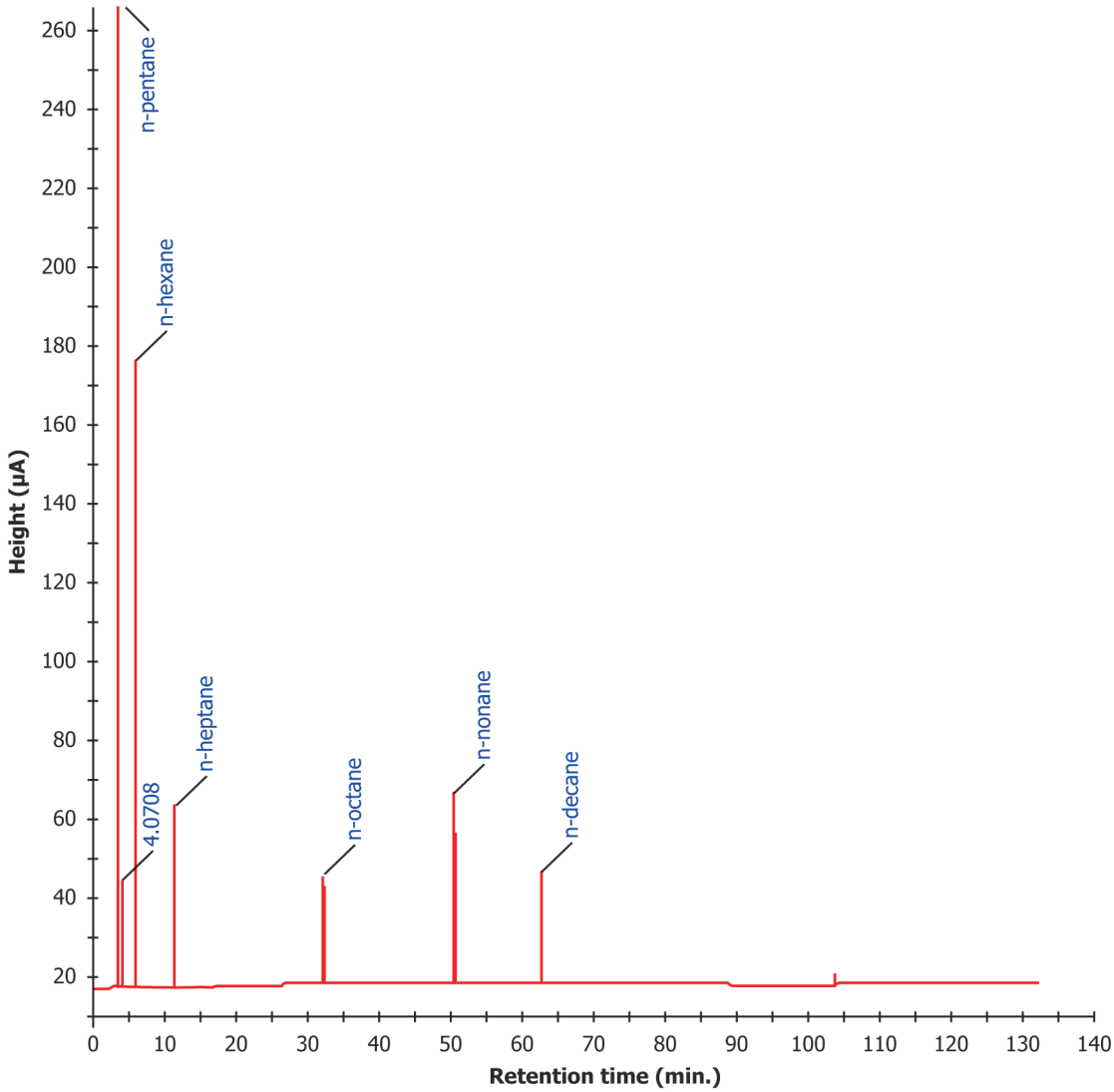

FIG. 3 Example Chromatogram Showing Elution on n-Nonane and n-Decane for Determining Back-Flush Time (see 9.3.4)

11.4 Plot for all peaks (beginning with the lowest boiling point) the cumulative % m/m versus the boiling point up to the last peak of interest, for example, n-nonane. See Test Method D7169 (IP 545) for merging of the results to give a full crude analysis.

12. Report

12.1 Report the cumulative mass percent versus boiling point results to the nearest 0.01 % m/m, and 0.5 °C (1 °F) respectively, up to the last peak of interest, for example n-nonane.

13. Precision and Bias

13.1 *Precision*—The precision of this test method was determined by statistical evaluation of the interlaboratory test results consisting of 14 labs (ten from Europe and four from the U.S.) analyzing eight crude oil samples in duplicate. The repeatability and reproducibility were calculated following the procdures of ISO 4259. The recovery up to n-nonane results in this precision study ranged from 7.48 to 25.36 % m/m.[5]

13.1.1 *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 following values only in one case in 20 (see Table 2).

13.1.2 *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, exceed the following values only in one case in 20 (see Table 2).

NOTE 7—The degrees of freedom associated with the reproducibility

[5] Supporting data have been filed at the Energy Institute Headquarters and may be obtained by requesting EI Research Report for method IP PM DL: Determination of Light Hydrocarbons in Stabilized Crude Oil—Gas Chromatography Method.

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TABLE 2 Precision Values

	Recovery (% m/m)
Repeatability, r	0.01982(x + 8)[A]
Reproducibility, R	0.1267(x + 8)[A]

[A]Where x = % m/m recovered.

estimate from this round robin study was 29. Since the minimum requirement of 30 (in accordance with ASTM requirements) is not met, users are cautioned that the actual reproducibility may be significantly different than these estimates.

13.2 *Bias*—The procedure in this test method for determining the boiling range distribution of stabilized crude oils to n-nonane by gas chromatography has no bias because the boiling range distribution can only be defined in terms of a test method.

13.2.1 A rigorous, theoretical definition of the boiling range distribution of stabilized crude oils to n-nonane is not possible due to the complexity of the mixture as well as the unquantifiable interactions among the components (for example, azeotropic behavior). Any other means used to define the distribution would require the use of a physical process such as a conventional distillation of further gas chromatographic characterization. This would therefore result in a method-dependent definition and would not constitute a true value from which bias can be calculated.

14. Keywords

14.1 boiling range distributions; crude oils; distillations; gas chromatography; petroleums; simulated distillations

APPENDIXES

(Nonmandatory Information)

X1. RETENTION INDEX DATA FOR IDENTIFYING INDIVIDUAL COMPONENTS

X1.1 See Table X1.1 and Figs. X1.1-X1.6.

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