Designation: D5291 – 21

Standard Test Methods for Instrumental Determination of Carbon, Hydrogen, and Nitrogen in Petroleum Products and Lubricants[1]

This standard is issued under the fixed designation D5291; 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 These test methods cover the instrumental determination of carbon, hydrogen, and nitrogen in laboratory samples of petroleum products and lubricants. Values obtained represent the total carbon, the total hydrogen, and the total nitrogen.

1.2 These test methods are applicable to samples such as crude oils, fuel oils, additives, and residues for carbon and hydrogen and nitrogen analysis. These test methods were tested in the concentration range of at least 75 % to 87 % by mass for carbon, at least 9 % to 16 % by mass for hydrogen, and <0.1 % to 2 % by mass for nitrogen.

1.3 The nitrogen test method is not applicable to light materials or those containing <0.75 % by mass nitrogen, or both, such as gasoline, jet fuel, naphtha, diesel fuel, or chemical solvents.

1.3.1 However, using Test Method D levels of 0.1 % by mass nitrogen in lubricants could be determined.

1.4 These test methods are not recommended for the analysis of volatile materials such as gasoline, gasoline-oxygenate blends, or gasoline type aviation turbine fuels.

1.5 The results of these tests can be expressed as mass % carbon, hydrogen or nitrogen.

1.6 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.7 *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.*

1.8 *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]

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

D6299 Practice for Applying Statistical Quality Assurance and Control Charting Techniques to Evaluate Analytical Measurement System Performance

3. Terminology

3.1 For definitions of terms used in these test methods, refer to Terminology D4175.

4. Summary of Test Methods

4.1 In these test methods, carbon, hydrogen, and nitrogen are determined concurrently in a single instrumental procedure. With some systems, the procedure consists of simply weighing a portion of the sample, placing the portion in the instrument, and initiating the (subsequently automatic) analytical process. In other systems, the analytical process, to some degree, is manually controlled.

4.2 The actual process can vary substantially from instrument to instrument, since a variety of means can be utilized to effect the primary requirements of the test methods. All satisfactory processes provide for the following:

4.2.1 The conversion of the subject materials (in their entirety) to carbon dioxide, water vapor, and elemental nitrogen, respectively, and

4.2.2 The subsequent, quantitative determination of these gases in an appropriate gas stream.

[1] These test methods are under the jurisdiction of ASTM Committee D02 on Petroleum Products, Liquid Fuels, and Lubricants and are the direct responsibility of Subcommittee D02.03 on Elemental Analysis.

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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.

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

4.3 The conversion of the subject materials to their corresponding gases takes place largely during combustion of the sample at an elevated temperature in an atmosphere of purified oxygen. Here, a variety of gaseous materials are produced, including the following:

4.3.1 Carbon dioxide from the oxidation of organic and elemental carbon,

4.3.2 Hydrogen halides from organic halides (and organic hydrogen, as required),

4.3.3 Water vapor from the oxidation of (the remaining) organic hydrogen and the liberation of moisture,

4.3.4 Nitrogen and nitrogen oxides from the oxidation of organic nitrogen, and

4.3.5 Sulfur oxides from the oxidation of organic sulfur. In some systems, sulfurous and sulfuric acids can also be obtained from a combination of the sulfur oxides and the water vapor.

4.4 There are several accepted ways of isolating the desired gaseous products and quantitatively determining them. These are as follows:

4.4.1 *Test Method A*[3,4]—From the combustion product gas stream, oxides of sulfur are removed with calcium oxide in the secondary combustion zone. A portion of the remaining mixed gases is carried by helium gas over a hot copper train to remove oxygen, and reduce NO_x to N_2, over NaOH to remove CO_2, and over magnesium perchlorate to remove H_2O. The remaining elemental nitrogen is measured by the thermal conductivity cell. Simultaneously, but separately from the nitrogen measurement, the carbon and hydrogen selective infrared cells measure the CO_2 and H_2O levels.

4.4.2 *Test Method B*[4,5]—From the combustion product gas stream (which is cleaned from sulfur oxides, excess oxygen, etc. as in 4.4.1), the remaining CO_2, water vapor, and N_2 are flushed into a mixing chamber and are thoroughly homogenized at a precise volume, temperature, and pressure. After homogenization, the chamber is depressurized to allow the gases to pass through a heated column, where the gases separate as a function of selective retention times. The separation occurs in a stepwise steady-state manner for nitrogen, carbon dioxide, and water.

4.4.3 *Test Method C*[4,6]—The combustion product gas stream, after full oxidation of component gases, is passed over heated copper to remove excess oxygen and reduce NO_x to N_2 gas. The gases are then passed through a heated chromatographic column to separate and elute N_2, CO_2, and H_2O in that order. The individual eluted gases are measured by a thermal conductivity detector.

4.4.4 *Test Method D*[4,7]—The organic samples are packed into lightweight containers of oxidizable metal and dropped at preset times into a vertical quartz, inconel, or stainless steel reactor, heated at about 1050 °C, through which a constant flow of helium is maintained. When the samples are introduced, the helium stream is temporarily enriched with pure oxygen. Flash combustion takes place primed by the oxidation of the container. Quantitative combustion is then achieved by passing the gases over chromium trioxide and cupric oxide. The mixture of the combustion gases is transferred over copper at about 640 °C (840 °C in a steel reactor) to eliminate the excess of oxygen; then without stopping, it is introduced into the chromatographic column heated to about 120 °C (50 °C for Flash EA 1112 units). The individual components are then separated by elution in the order nitrogen, carbon dioxide, and water by a dedicated Poropak column (active carbon column for Flash EA 1112 units for nitrogen determination) and measured by a thermal conductivity detector. With dedicated software the percentage of elements present in the sample are calculated. The instrument is calibrated with standard pure organic compounds. K-factors or linear regression can be used for instrument calibration. The typical operator analysis time for a single sample is about 4 min, and the total elapsed time is 8 min.

NOTE 1—None of the four test methods is preferred as a referee test method.

NOTE 2—Other instrument models in addition to the four included here are available in the marketplace; however, no precision statements have been generated for them.

4.5 In all cases, the concentrations of carbon, hydrogen and nitrogen are calculated as functions of the following:

4.5.1 The measured instrumental responses,

4.5.2 The values for response per unit mass for the elements (established via instrument calibration), and

4.5.3 The mass of the sample.

4.6 A capability for performing these computations automatically can be included in the instrumentation utilized for these test methods.

5. Significance and Use

5.1 This is the first ASTM standard covering the simultaneous determination of carbon, hydrogen, and nitrogen in petroleum products and lubricants.

5.2 Carbon, hydrogen, and particularly nitrogen analyses are useful in determining the complex nature of sample types covered by this test method. The CHN results can be used to estimate the processing and refining potentials and yields in the petrochemical industry.

5.3 The concentration of nitrogen is a measure of the presence of nitrogen containing additives. Knowledge of its concentration can be used to predict performance. Some petroleum products also contain naturally occurring nitrogen. Knowledge of hydrogen content in samples is helpful in

[3] The sole source of supply of the Leco CHN-600 instrument known to the committee at this time is Leco Corporation, 3000 Lakeview Ave., St. Joseph, MI 49085.

[4] If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee [1], which you may attend.

[5] The sole source of supply of the Perkin Elmer 240C, 2400 series and CEC 240XA and 440 instruments known to the committee at this time is Perkin Elmer Corporation, Main Ave., Norwalk, CT 06856.

[6] The sole source of supply of the Carlo Erba 1106, 1108, and 1500 instruments known to the committee at this time is Carlo Erba Strumentazione, Strada Rivoltana, 20090 Rodano, Milan, Italy.

[7] The sole source of supply of the Flash EA instruments known to the committee at this time is Thermo Fisher Scientific, Strada Rivoltana, 20090 Milano, Italy.

addressing their performance characteristics. Hydrogen to carbon ratio is useful to assess the performance of upgrading processes.

6. Apparatus

6.1 Since a variety of instrumental components and configurations can be satisfactorily utilized for these test methods, no specifications are given here with respect to overall system design.

6.2 Functionally, however, the following are specified for all instruments:

6.2.1 The conditions for combustion of the sample must be such that (for the full range of applicable samples) the subject components are completely converted to carbon dioxide, water vapor (except for hydrogen associated with volatile halides and sulfur oxides), and nitrogen or nitrogen oxides. Generally, instrumental conditions that affect complete combustion include availability of the oxidant, temperature, and time.

6.2.2 Representative aliquots of the combustion gases must then be treated:

6.2.2.1 To liberate (as water vapor) hydrogen present as hydrogen halides and sulfur oxyacids, and

6.2.2.2 To reduce (to the element) nitrogen present as nitrogen oxides.

6.2.3 The water vapor and nitrogen so obtained must be included with the materials originally present in these aliquots.

6.2.4 Additional treatment of the aliquots (prior to detection) depends on the detection scheme utilized for the instrument (see Note 3).

NOTE 3—These additional treatments can be provided by the instrumental components utilized to satisfy 6.2.2.

6.2.5 The detection system (in its full scope) must determine the analytical gases individually and without interference. Additionally, for each analyte, either:

6.2.5.1 The detectors must provide linear responses with respect to concentration over the full range of possible concentrations from the applicable samples, or

6.2.5.2 The system must include provisions for appropriately evaluating nonlinear responses so that they can be accurately correlated with these concentrations.

6.2.6 Such provisions can be integral to the instrumentation, or they can be provided by (auxiliary) computation schemes.

6.2.7 Lastly, except for those systems where the concentration data are output directly, the instrument must include an appropriate readout device for the detector responses.

6.3 Additionally consumables needed for the analyses include:

6.3.1 *Tin Capsules,* large and small,

6.3.2 *Ceramic Crucibles,*

6.3.3 *Copper Capsules,*

6.3.4 *Tin Plugs,*

6.3.5 *Tin Boats,*

6.3.6 *Copper Plugs,*

6.3.7 *Aluminum Capsules,*

6.3.8 *Combustion Tubes,*

6.3.9 *Adsorption Tubes,*

6.3.10 *Nickel Capsules,* and

6.3.11 *Reduction Tubes.*

6.4 *Analytical Balance*, capable of weighing to the nearest 0.00001 g.

6.5 *Syringes or Pipettes*, to transfer the test specimens to capsules.

TABLE 1 Calibration Standards for CHN Instrumental Analysis[A,B]

Compound	Molecular Formula	Carbon, Mass%	Hydrogen Mass %	Nitrogen Mass %
Acetanilide	C_8H_9NO	71.09	6.71	10.36
Atropine	$C_{17}H_{23}NO_3$	70.56	8.01	4.84
Benzoic acid	$C_7H_6O_2$	68.84	4.95	. . .
Cyclohexanone-2,4-dinitrophenylhydrazone	$C_{12}H_{14}N_4O_4$	51.79	5.07	20.14
Cystine	$C_6H_{12}N_2O_4S_2$	29.99	5.03	11.66
Diphenyl	$C_{12}H_{10}$	93.46	6.54	. .
EDTA	$C_{10}H_{16}N_2O_8$	41.10	5.52	9.59
Imidazol	$C_3H_4N_2$	52.92	5.92	41.15
Nicotinic acid	$C_6H_5NO_2$	58.53	4.09	11.38
Stearic acid	$C_{18}H_{36}O_2$	75.99	12.76	. .
Succinamide	$C_4H_8N_2O_2$	41.37	6.94	24.13
Sucrose	$C_{12}H_{22}O_{11}$	42.10	6.48	. .
Sulphanilamide	$C_6H_8N_2O_2S$	41.84	4.68	16.27
Triethanol amine	$C_6H_{15}NO_3$	48.30	10.13	9.39

[A] The Merck Index, 10th Edition, Merck and Company, Inc., Rahway, New Jersey, 1983.

[B] Many of these compounds can be obtained from commercial chemical manufacturers. See 7.1 for the purity of these reagents.

7. Reagents

7.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.[8] Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.2 *Calibration Standards*—Table 1 lists the pure organic compounds most commonly used to calibrate the instruments operated according to 4.4.1 – 4.4.3; other suitable pure compounds can also be used.

7.3 *Carrier and Combustion Gases:*

7.3.1 *Oxygen,* high purity (99.998 %),

7.3.2 *Helium,* high purity (99.995 %),

7.3.3 *Compressed Air, Nitrogen*, *or Argon*, for operating pneumatic valves, if needed, and

7.3.4 *Carbon Dioxide.*

7.4 *Additional Reagents (as Specified by the Instrument Manufacturer)*—This specification covers the reagents utilized to provide for the functional requirements cited in 6.2.2 and 6.2.3. These reagents can vary substantially for different

[8] *ACS Reagent Chemicals, Specifications and Procedures for Reagents and Standard-Grade Reference Materials*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.