



Designation: D 5373 – 93 (Reapproved 1997)

# Standard Test Methods for Instrumental Determination of Carbon, Hydrogen, and Nitrogen in Laboratory Samples of Coal and Coke<sup>1</sup>

This standard is issued under the fixed designation D 5373; 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 ( $\epsilon$ ) 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 coal and coke prepared in accordance with Test Methods D 2013 and D 346.

1.2 Within the limitations outlined below, these test methods are applicable to either the air-dry or moisture-free laboratory sample, or both.

1.2.1 For instrumental systems in which the moisture and waters of hydration in the sample are liberated with (and only with) the oxidation products upon combustion, the analyses can be performed on a test specimen of the air-dry sample (Note 1). Concentrations determined on this air-dried basis represent the total carbon (including that present as carbonate), total hydrogen (including that present as water), and total nitrogen.

NOTE 1—These systems are also satisfactory for determining the subject materials in the moisture-free sample.

1.2.2 For systems in which the moisture and hydrates are otherwise liberated, the analysis shall be performed on the moisture-free sample. Values obtained on this basis represent the total carbon, organic hydrogen, and total nitrogen.

1.3 These test methods can be used to provide for the requirements specified in Practice D 3176 for the ultimate analysis.

1.4 The values stated in SI units shall be regarded as the standard.

1.5 *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 and health practices and determine the applicability of regulatory limitations prior to use.* Specific precautionary statements are given in 8.3.1.

## 2. Referenced Documents

### 2.1 ASTM Standards:

D 346 Test Method for Collection and Preparation of Coke Samples for Laboratory Analysis<sup>2</sup>

<sup>1</sup> These test methods are under the jurisdiction of ASTM Committee D-5 on Coal and Coke and are the direct responsibility of Subcommittee D05.21 on Methods of Analysis.

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<sup>2</sup> *Annual Book of ASTM Standards*, Vol 05.05.

D 2013 Test Method for Preparing Coal Samples for Analysis<sup>2</sup>

D 3173 Test Method for Moisture in the Analysis Sample of Coal and Coke<sup>2</sup>

D 3174 Test Method for Ash in the Analysis Sample of Coal and Coke from Coal<sup>2</sup>

D 3176 Practice for Ultimate Analysis of Coal and Coke<sup>2</sup>

D 3180 Practice for Calculating Coal and Coke Analyses from As-Determined to Different Bases<sup>2</sup>

D 4621 Guide for Accountability and Quality Control in the Coal Analysis Laboratory<sup>2</sup>

D 5142 Test Methods for the Proximate Analysis of the Analysis Sample of Coal and Coke by Instrumental Procedures<sup>2</sup>

## 3. Summary of Test Methods

3.1 Carbon, hydrogen, and nitrogen are determined concurrently in a single instrumental procedure. In some systems, the procedure consists of simply weighing a test specimen, placing the test portion into the instrument, and initiating the (subsequently automatic) analytical process. In other systems, the analytical process may be controlled manually to some degree.

3.2 The actual process can vary substantially from instrument to instrument because a variety of means can be used to effect the primary requirements of the test methods. These test methods provide for the following: (1) conversion of the subject materials in an oxygen stream in their entirety to carbon dioxide, water vapor, nitrogen oxides, and ash, respectively; and (2) subsequent, quantitative determination of the gases in an appropriate reference gas stream.

3.2.1 The conversion of the subject materials to their corresponding gases occurs largely during combustion of the sample at an elevated temperature in an atmosphere of purified oxygen. The gases that are produced include the following:

3.2.1.1 Carbon dioxide from the oxidation of organic and elemental carbon and the decomposition of carbonate minerals;

3.2.1.2 Hydrogen halides from organic halides (and organic hydrogen, as required);

3.2.1.3 Water vapor from the oxidation of (the remaining) organic hydrogen and the liberation of moisture and waters of hydration;

3.2.1.4 Nitrogen and nitrogen oxides from the oxidation of organic nitrogen and the decomposition of nitrates; and

3.2.1.5 Sulfur oxides from the oxidation of organic sulfur,

and the decomposition of sulfide and sulfate minerals.

(I) In some systems, sulfurous and sulfuric acids can also be obtained from a combination of the sulfur oxides and the water vapor.

3.2.2 For hydrogen and nitrogen, the required conversion is completed in a two-step process consisting of the following:

3.2.2.1 Removal of the halides and sulfur oxides and liberation of the associated hydrogen (as water), by conducting the combustion gases through a series of absorption traps containing appropriate absorbing materials.

3.2.2.2 Reduction of the nitrogen oxides to elemental nitrogen (see Note 2) by passing the resultant gases over copper at an elevated temperature. The carbon dioxide, water vapor, and nitrogen may then be determined via one of several satisfactory detection schemes.

NOTE 2—In this process, residual oxygen is also removed.

3.2.3 In one configuration, the gases are conducted through a series of thermal conductivity detectors and gas absorbers aligned so that, at the water vapor detector level, the gases pass through the sample side of the detector, a water vapor absorber, and the reference side of the detector. At the carbon dioxide detector level, the gases are then conducted through the sample side of the detector, a carbon dioxide absorber, and the reference side of the detector. Finally, the resultant gases, which contain only nitrogen and the carrier gas, pass through the sample side of the nitrogen detector and are vented. At this detector level, high-purity carrier gas is used as the reference gas. In these ways, the detectors determine the thermal conductivities solely of the specified components.

3.2.4 In a second configuration, the carbon dioxide and water vapor are determined by infrared detection, using an aliquot of the combustion gases from which only the halides and sulfur oxides have been removed. These detectors determine the infrared absorption of the pertinent gases at precise wavelength windows so that the absorbances result from only the specified components. In these systems, nitrogen is determined by thermal conductivity, using a second aliquot of the gases, additionally treated to also reduce the nitrogen oxides to nitrogen and to remove the residual oxygen, carbon dioxide, and water vapor.

3.2.5 In a third configuration, which is essentially a modified gas chromatographic system, the nitrogen, carbon dioxide, and water vapor in the treated combustion gases are eluted from a chromatographic column and determined (at appropriate retention times) by thermal conductivity detection.

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

3.3.1 Measured instrumental responses,

3.3.2 Values for response per unit mass for the elements (established via instrument calibration), and

3.3.3 Mass of the sample.

3.4 Or to the following: the instrument response is proportional to the gas density, which has been calibrated against a gas density of known concentration.

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

## 4. Significance and Use

4.1 Carbon and hydrogen values are used to determine the amount of oxygen (air) required in combustion processes and for the calculations of efficiency of combustion processes.

4.2 Carbon and hydrogen determinations are used in material balance calculations on coal conversion processes; also, one or the other is used frequently in correlations of chemical and physical properties, such as yields of products in liquefaction reactivity in gasification and the density and porosity of coal.

4.3 Nitrogen data are required to fulfill the requirements of the ultimate analysis, Practice D 3176. Also, the data obtained can be used to evaluate the potential formation of nitrogen oxides as a source of atmospheric pollution.

4.4 Nitrogen data are used for comparing coals and in research. If the oxygen content of coal is estimated by difference, it is necessary to make a nitrogen determination.

## 5. Apparatus

5.1 Because a variety of instrumental components and configurations can be used satisfactorily for these test methods, no specifications are presented here with respect to overall system design.

5.2 Functionally, however, the following requirements are specified for all approved instruments (Note 3):

NOTE 3—The approval of an instrument with respect to these functions is paramount to these test methods, since such approval tacitly provides approval of both the materials and the procedures used with the system to provide for these functions.

5.2.1 The conditions for combustion of the sample shall be such that (for the full range of applicable samples) the subject components shall be converted completely to carbon dioxide, water vapor (except for hydrogen associated with volatile halides), and nitrogen or nitrogen oxides. Generally, instrumental conditions that effect complete combustion include (1) availability of the oxidant, (2) temperature, and (3) time.

5.2.2 Representative aliquots of the combustion gases shall then be treated for the following reasons:

5.2.2.1 To liberate (as water vapor) hydrogen present as hydrogen halides and sulfur oxyacids; and

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

(I) The water vapor and nitrogen so obtained shall be included with the materials originally present in these aliquots.

5.2.3 Additional treatment of the test specimens (prior to detection) depends on the detection scheme used for the instrument (Note 4).

NOTE 4—The additional treatments can be provided by the instrumental components used to satisfy 5.2.2.

5.2.3.1 For the configuration described in 3.2.3, the halides proper, sulfur oxides, and residual oxygen shall be removed from the single test specimen in which the water vapor, carbon dioxide, and nitrogen are determined sequentially.

5.2.3.2 For the configuration described in 3.2.4, the test specimen in which the water vapor and carbon dioxide are determined, only the halides and sulfur oxides shall be removed from the gas stream in which the water vapor and carbon dioxide are determined. For combusted gases in which