Designation: E3146 – 20

# Standard Test Method for Determination of Carbonyls in Pyrolysis Bio-Oils by Potentiometric Titration[1]

This standard is issued under the fixed designation E3146; 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 covers the determination of the carbonyl content of bio-oils derived from thermochemical decomposition of lignocellulosic biomass and their deoxygenated products. This method is used for determination of carbonyls between 0.5 and 8 mol/kg.

1.2 Review the current and appropriate Safety Data Sheets (SDS) for detailed information concerning toxicity, first aid procedures, and safety precautions and proper personal protective equipment.

1.3 *Units*—The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.4 *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.*

1.5 *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]

D664 Test Method for Acid Number of Petroleum Products by Potentiometric Titration

D1193 Specification for Reagent Water

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

D6300 Practice for Determination of Precision and Bias Data for Use in Test Methods for Petroleum Products, Liquid Fuels, and Lubricants

2.2 *Other Standards*

CEN/TR 17103:2017 Petroleum and Related Products - Fast Pyrolysis Bio-oils for Stationary Internal Combustion Engines - Quality Determination[3]

EN 16900:2017 Fast Pyrolysis Bio-oils for Industrial Boilers—Requirement and Test Methods[4]

## 3. Terminology

3.1 *Definitions:*

3.1.1 *bio-oil, n*—the crude liquid product of converting solid biomass into a liquid via fast pyrolysis or other thermochemical conversion process.

3.1.2 *carbonyl, n*—the chemical functional group consisting of a carbon-oxygen double bond, C=O.

3.1.2.1 *Discussion*—For this method, this includes all aldehydes and ketones; carboxylic acids, esters, and lactone groups are not measured by this method.

3.1.3 *fast pyrolysis, n*—pyrolysis conducted with rapid heating and short residence time; typically less than 10 s.

3.1.3.1 *Discussion*—Other definitions for fast pyrolysis state residence times of typically less than 10 s (**1, 2**),[5] 5 s (CEN/TR 17103:2017, EN 16900:2017), and 1 s (**3, 4**).

3.1.4 *pyrolysis, n*—chemical decomposition of organic materials by heating in the absence of oxygen.

3.1.5 *oxime, n*—a group of compounds containing the chemical functional group >C=NOH, produced by the condensation of ketones or aldehydes with hydroxylamine.

3.1.6 *oximation reaction, n*—reaction with or conversion into an oxime.

[1] This test method is under the jurisdiction of ASTM Committee E48 on Bioenergy and Industrial Chemicals from Biomass and is the direct responsibility of Subcommittee E48.05 on Biomass Conversion.

Current edition approved May 1, 2020. Published June 2020. Originally approved in 2018. Last previous edition approved in 2018 as E3146 – 18a. DOI: 10.1520/E3146-20.

[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] Available from European Committee for Standardization (CEN), Avenue Marnix 17, B-1000, Brussels, Belgium, http://www.cen.eu.

[4] Available from British Standards Institution (BSI), 389 Chiswick High Rd., London W4 4AL, U.K., http://www.bsigroup.com.

[5] The boldface numbers in parentheses refer to the list of references at the end of this standard.

## 4. Summary of Test Method

4.1 A bio-oil sample is dissolved in dimethylsulfoxide (DMSO) and solutions are added containing hydroxylamine hydrochloride ($NH_2OH{\cdot}HCl$) and triethanolamine (TEA). The mixture is sealed, stirred, and heated to 80 °C for 2 h. Carbonyl compounds (aldehydes and ketones) react with $NH_2OH{\cdot}HCl$ forming the corresponding oxime and liberating HCl. Liberated HCl is consumed by TEA, which drives the reaction forward. After the reaction, unconsumed TEA is titrated with a standardized HCl titrant to determine the molar concentration of carbonyls in the sample.

## 5. Significance and Use

5.1 While pyrolysis bio-oils are comprised of a large variety of compounds and chemical functional groups, quantification of carbonyl groups is especially important. Carbonyls are known to be responsible for the instability of bio-oil during both storage and processing. This method can be used to quantify the total carbonyl content of bio-oils.

## 6. Interferences

6.1 The selectivity of the method was tested by using 1-butanol, 1-pentanol, tertiary-butanol, 2-propanol, ethyl acetate, acetic acid, xylose, and glucose as model compounds, representing alcohol, ester, carboxylic acid, and carbohydrates in the bio-oil. No interferences were seen for ethyl acetate or acetic acid. Monosaccharides are measured using this method. Addition of alcohols causes interferences, but it is dependent on chain length. The reason is as yet undetermined but may be related to solvent properties of the alcohol rather than reaction with $NH_2OH{\cdot}HCl$ or TEA. Tests with primary, secondary, and tertiary butanol have shown the same effect.

## 7. Apparatus

7.1 *Analytical Balance,* accurate to 0.0001 g.

7.2 *Micro Reaction Vial,* borosilicate glass, cone shaped inside with at least 5 mL capacity and PTFE lined caps. See Fig. 1.

7.3 *Triangular Magnetic Stirring Bar,* PTFE lined and suitable size for use with micro reaction vessels.

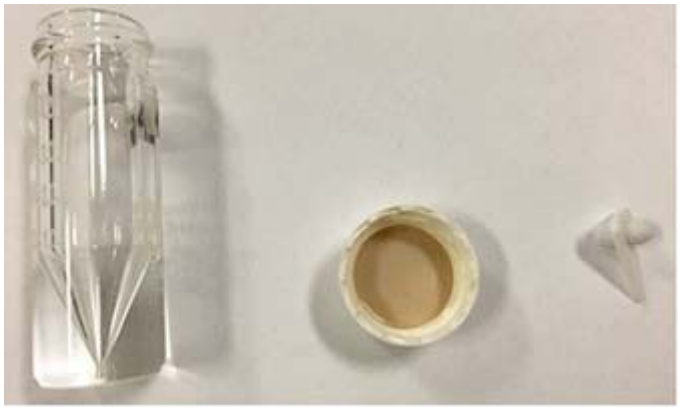

**FIG. 1 Micro Reaction Vial with PTFE Lined Cap and Triangular Magnetic Stirring Bar**

7.4 *Dry Block Heater with Magnetic Stirrer,* capable of maintaining a temperature of 80 °C, for use with micro reaction vials. See Fig. 2.

7.4.1 A hot water bath with flat circular magnetic stirrer is also acceptable.

7.5 *Potentiometric Titrator*—Automatic titration systems capable of adding fixed increments of titrant at fixed time intervals (monotonic) or variable titrant increments with electrode stability between increment additions (dynamic) with endpoint seeking capabilities as prescribed in the method. At the very least, the automatic titration system shall meet the performance and specification requirements as warranted by the manufacturer.

7.5.1 A monotonic or dynamic mode of titrant addition shall be used. During the titration, the speed and volume of the addition may vary depending on the rate of change of the system. The recommended minimum volume increment is 0.05 mL, and the recommended maximum volume increment is 0.1 mL. A signal drift of 10 mV/min and endpoint recognition set to last is recommended to ensure endpoint detection. When using a monotonic titrant addition, the waiting time between increment additions shall be sufficient to allow for mixing and a stable electrode response. Wait at least 10 s between additions.

7.6 *Buret,* capable of delivering titrant in 0.02 mL or larger increments. The buret tip shall deliver titrant directly into the titration vessel (immersed about 25 mm in liquid) without exposure to the surrounding air.

7.7 *Titration Stand,* suitable for supporting the electrode, stirrer, and buret.

7.8 *Sensing Electrode,* standard pH, suitable for non-aqueous titrations.

7.9 *Reference Electrode*—Silver/Silver Chloride (Ag/AgCl) Reference Electrode, filled with 1M-3M LiCl in ethanol.

7.10 *Combination pH Electrodes*—Sensing electrodes may have the Ag/AgCl reference electrode built into the same electrode body, which offers the convenience of working with and maintaining only one electrode. A combination pH electrode designed for non-aqueous titrations of organic solvents is needed for titration of bio-oils. The combination pH electrode shall have a sleeve junction on the reference compartment and shall use an inert ethanol electrolyte, 1 to 3 mol/L (M) LiCl in

**FIG. 2 Dry Block Heater**

ethanol. Combination pH electrodes shall have the same or better response than a dual electrode system. They shall have a movable sleeve for easy rinsing and addition of electrolyte.

7.11 *Titration Beaker,* borosilicate glass or plastic beaker of suitable size for the titration.

7.12 *Variable-Speed Mechanical Stirrer,* a suitable type, equipped with either magnetic stirrer and stirring bars or propeller-type stirring paddle. The rate of stirring shall be sufficient to produce vigorous agitation without spattering and without stirring air into the solution.

7.12.1 If an electrical stirring apparatus is used, it shall be electrically correct and grounded so that connecting or disconnecting the power to the motor will not produce a permanent change in the instrument reading during the course of the titration.

## 8. Reagents and Materials

8.1 *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.[6]

8.2 *Purity of Water*—Unless otherwise indicated, reference to water shall be understood to mean reagent water that meets the requirements of either Type I, II, or III of Specification D1193.

8.3 *Ethanol,* reagent grade (**Warning—**Flammable and toxic).

NOTE 1—Do not use ethanol containing 2-butanone or other ketone denaturant as this will interfere with this method.

8.4 *Lithium Chloride,* LiCl.

8.5 *Lithium Chloride Electrolyte*—Prepare a 1M–3M solution of lithium chloride (LiCl) in ethanol.

8.6 *Commercial Aqueous pH 4 and pH 7 Buffer Solutions*—These solutions shall be replaced at regular intervals consistent with their stability or when contamination is suspected. Information relating to their stability is provided by the manufacturer.

8.7 *Hydroxylamine Hydrochloride ($NH_2OH·HCl$),* ≥ 99 % purity.

8.8 *Hydroxylamine Hydrochloride Solution (Solution A)*—Add 7.7 g of hydroxylamine hydrochloride and 50 mL of water to a 250 mL volumetric flask. Swirl until all solids are dissolved, then dilute up to the mark with ethanol.

8.9 *Sodium Carbonate (Primary Standard, $Na_2CO_3$),* ≥ 99 % purity.

8.10 *Triethanolamine (TEA),* ≥ 99 % purity.

8.11 *Triethanolamine Solution (Solution B)*—Add 17.4 mL of triethanolamine to a 250 mL volumetric flask, then dilute up to the mark with ethanol.

8.12 *Hydrochloric Acid (HCl),* concentrated (**Warning—** Toxic and corrosive).

8.13 *Hydrochloric Acid Solution*—Prepare 0.1N solution by adding 10 ml concentrated HCl and 1 L water.

8.14 *Carbonyl Validation Sample*—4-(Benzyloxy)benzaldehyde (4-BBA), ≥ 99 % purity.

8.15 Commercially available solutions may be used in place of laboratory preparations, provided the solutions have been certified as being equivalent.

8.16 Alternate volumes of the solutions may be prepared, provided the final solution concentration is equivalent.

## 9. Sampling, Test Specimens, and Test Units

9.1 Make sure the oil sample is at room temperature prior to withdrawing an aliquot for analysis. Bio-oil shall be thoroughly homogenized to obtain a representative sample. Mix by shaking vigorously for at least 1 min, and visually inspect the sample to ensure it is homogenous. Some bio-oils may require longer shaking times.

9.2 Exposure to oxygen and heat shall be minimized to prevent sample degradation prior to analysis.

## 10. Preparation of Apparatus

10.1 Prepare the titrator in accordance with the manufacturer's instructions. Any visible air bubbles in the buret tip shall be eliminated prior to titration since this can lead to errors.

10.2 *Preparation of Electrodes*—When the combination pH electrode contains Ag/AgCl reference with an electrolyte, which is not 1 to 3 mol/L (M) LiCl in ethanol, the electrolyte shall be replaced. Drain the electrolyte from the electrode (vacuum suction), wash away all the salt (if present) with water, and then rinse with ethanol. Rinse several times with LiCl electrolyte solution. Finally, replace the sleeve and fill the electrode with the LiCl electrolyte to the filling hole. When refitting the sleeve, ensure that there will be a free flow of electrolyte into the system.

10.3 *Maintenance and Storage of Electrodes:*

10.3.1 Follow the manufacturer's instructions for storage and use of the electrode.

10.3.2 Prior to each titration, the glass membrane needs to be rehydrated by soaking the prepared electrode in water for at least 2 min. Rinse the electrode with water immediately prior to use.

10.3.3 When not in use, immerse the lower half of the combination electrode in LiCl electrolyte. Do not allow electrodes to remain immersed in a titrated sample solution for any longer than it is necessary. While the electrodes are not extremely fragile, handle them carefully at all times.

## 11. Calibration and Standardization

11.1 *Calibration of Electrode:*

11.1.1 Verify that the electrode is filled with 1 to 3 mol/L (M) LiCl in ethanol solution (see 10.2).

[6] Reagent Chemicals, American Chemical Society Specifications, 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.

11.1.2 Prepare the two buffer solutions, pH 7.0 and pH 4.0 by placing approximately 50 mL of each solution in individual beakers.

11.1.3 Calibrate the electrode using the two buffer solutions according to the manufacturer's instructions. Immerse the electrode in each buffer solution, adjust the stirring speed so that adequate mixing occurs without forming a vortex, and wait for the instrument reading. When the reading is complete, rinse the electrode in high purity water, wipe gently, and repeat the measurements with the other buffer solution. Record the pH value with an accuracy of 0.01 and the temperature with an accuracy of 0.1 °C. The measured pH values should be within ±0.05 pH units of the buffer's certified value.

11.1.3.1 Verify that the calibration slope is between 0.95 and 1.02. An ideal pH glass electrode has a slope of 1.00 (100 % of the Nernst slope) and an electrode zero point of 0 mV for pH 7 at 25 °C. In practice, the electrode zero point potential shall be within ±15 mV (corresponding to pH 6.75 to 7.25) and the slope shall be >0.95 (>56.2 mV per pH at 25 °C). The electrode zero point and the electrode slope may change as a result of the aging of the glass membrane or contamination of the diaphragm. If the electrode slope falls below 0.95, follow the electrode manufacturer's instructions for electrode maintenance or replace the electrode. The pH electrode shall be calibrated at regular intervals using (per manufacturer's instructions) fresh buffer solutions.

11.1.3.2 The slope is automatically stored in the titrator.

11.1.3.3 The slope is not used for sample analysis, but rather, it provides information on the responsiveness of the electrode. An electrode not meeting the stated criteria in 11.1.3.1 is not suitable to perform this method.

11.2 *Standardization of HCl Titrant:*

11.2.1 Weigh 0.10 to 0.15 g of sodium carbonate into titration beaker and record weight.

11.2.2 Add magnetic stir bar and 25 mL of water.

11.2.3 Titrate with HCl titrant using automatic titrator and record endpoint.

11.2.4 Prepare two additional sodium carbonate solutions to standardize the titrant a total of three times.

11.2.5 Determine HCl molarity from each sodium carbonate titration using the calculation in 13.1. If the range of the three determinations (maximum-minimum) is ≤ 0.003, calculate the average mol/L. If the range is > 0.003, the source of imprecision shall be investigated and corrected.

## 12. Procedure

12.1 *Preparation of Titration Blanks:*

12.1.1 *Blank A:*

12.1.1.1 Prepare Blank A in duplicate (two separate vials).

12.1.1.2 Add 0.5 mL DMSO to a 5 mL reaction vial and add triangular stir bar.

12.1.1.3 Add 2 mL of Solution A and 2 mL Solution B.

12.1.1.4 Cap tightly, place in preheated (80 °C) heater block or water bath, and stir for 2 h.

12.2 *Preparation of Carbonyl Validation Sample (4-BBA):*

12.2.1 Prepare validation sample in duplicate.

12.2.2 Weigh 0.1 g to 0.15 g of 4-BBA into a 5 mL reaction vial. Record weight and add 0.5 mL DMSO and triangular stir bar.

12.2.3 Add 2 mL of Solution A and dissolve sample.

12.2.4 Add 2 mL of Solution B.

12.2.5 Cap tightly, place in preheated (80 °C) heater block or water bath, and stir for 2 h.

12.3 *Sample Preparation:*

12.3.1 Prepare each sample in duplicate.

12.3.2 Weight 0.1 g to 0.15 g of bio-oil sample into a 5 mL reaction vial. Record weight and add 0.5 mL DMSO and triangular stir bar.

12.3.3 Add 2 mL of Solution A and dissolve sample.

12.3.4 Add 2 mL of Solution B.

12.3.5 Cap tightly, place in preheated (80 °C) heater block or water bath, and stir for 2 h.

12.4 For blanks, samples, and validation sample, the volume of DMSO added can be increased to 1 mL to improve sample dissolution if necessary. It is recommend that the reaction vial volume be increased to 8 mL if DMSO volume is increased.

12.5 *Titration Procedure for Blanks, Carbonyl Validation Sample, and Bio-oil Samples:*

12.5.1 After 2 h of heating at 80 °C, remove blanks and samples from heat and allow to cool to room temperature.

NOTE 2—Titration of blanks and samples following oximation reaction should be done within 2 to 8 h. Triethanolamine can form triethanolamine-•HCl which will result in an error in the measurement.

12.5.2 Quantitatively transfer the reacted solution to a titration beaker by rinsing 4 times with 5 mL aliquots of ethanol (total of 20 mL ethanol) and complete the transfer by rinsing one time with 5 mL of water.

NOTE 3—The final titration solution will be 25 mL of 80 % ethanol.

12.5.3 Titrate with automatic titrator and record end point. An example titration curve of a sample and a blank are provided in Fig. 3.

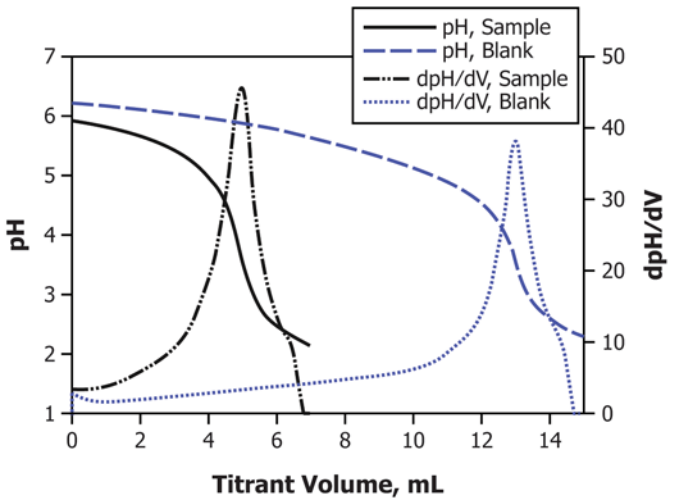


**FIG. 3 Example Titration Curves of Pyrolysis Oil and a Blank Titration**