



Designation: D5530 – 22

Standard Test Method for Total Moisture of Hazardous Waste Fuel by Karl Fischer Titrimetry¹

This standard is issued under the fixed designation D5530; 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 by Karl Fischer (KF) titrimetry of total moisture in solid or liquid hazardous waste fuels used by industrial furnaces.

1.2 This test method has been used successfully on numerous samples of hazardous waste fuel composed of solvents, spent oils, inks, paints, and pigments. The range of applicability for this test method is between 1.0 and 100 %; however, this evaluation was limited to samples containing approximately 5 to 50 % water.

1.3 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

D1193 Specification for Reagent Water

D4017 Test Method for Water in Paints and Paint Materials
by Karl Fischer Method

D5681 Terminology for Waste and Waste Management

¹ This test method is under the jurisdiction of ASTM Committee D34 on Waste Management and is the direct responsibility of Subcommittee D34.01.06 on Analytical Methods.

Current edition approved Oct. 1, 2022. Published October 2022. Originally approved in 1994. Last previous edition approved in 2015 as D5530 – 15. DOI: 10.1520/D5530-22.

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.

E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

3. Terminology

3.1 For definitions of terms used in this test method, refer to Terminology D5681.

4. Summary of Test Method

4.1 Karl Fischer reagent contains iodine, sulfur dioxide in pyridine (nonpyridine-containing reagents are currently available). The iodine in the presence of water is reduced to colorless hydrogen iodide, with the endpoint being the presence of free I₂. The basic reaction of the KF reagent with water is:



4.1.1 The methanol in the solution drives the equation to the right, removing sulfur trioxide.

4.2 An amount of solvent (see 8.3) sufficient to immerse the electrode fully in the titration flask (see Note 1) is titrated to dryness as explained in 10.1, and the Karl Fischer reagent factor is determined by titration of measured amounts of water. A weighed portion of the sample is dissolved in KF solvent and titrated with reagent to dryness. If solid material interferes (see 6.3) with the electrode or does not dissolve sufficiently, an extraction using KF solvent is performed prior to introduction into the titration flask. The total moisture in the sample is then determined. The final total moisture percent is an average of two trials meeting the repeatability as stated in 12.1.1 or repeatability criteria agreed upon between involved parties for each sample. The measurement can be repeated to obtain results that meet repeatability criteria.

4.3 The contents of the titration flask may be retained and used for additional analyses. The contents of the titration flask will need to be emptied and replaced with new solvent when the capacity of the flask is nearly exhausted or when solid material affects the sensing by the electrode.

5. Significance and Use

5.1 The determination of total moisture is important for assessing the fuel quality. Water content will affect the heating

value of fuels directly and can contribute to instability in the operation of an industrial furnace or adversely impact performance in other applications. Additionally, high water content can present material handling and storage problems during winter months or in cold environments.

6. Interferences

6.1 A small number of oxidants such as ferric and chromate salts can oxidize iodide and may produce artificially low results.

6.2 Certain reductants oxidized by iodine such as mercaptans, thioacetate, thiosulfate, stannous chloride, sulfides, hydroquinone, and phenylenediamines can consume iodine and may cause artificially high results. Basic materials such as hydroxides, oxides, and inorganic carbonates may cause artificially high results by water-forming reactions.

6.3 Some types of solid material found in waste-derived fuel may interfere with the electrode by blocking its contact with the solvent. Depending on the nature of the solid material, artificially high or low results can occur.

7. Apparatus

7.1 *Karl Fischer Potentiometric Titration Unit*, automated or semi-automated, equipped with a magnetic vessel stirrer. The user must follow the manufacturer's instructions for installation and use.

NOTE 1—The Karl Fischer unit used for developing this test method was equipped with a twin platinum electrode, 25 to 80 mL capacity titration flask, magnetic stirrer, electronic piston burette, adjustable delay interval, LED display, visual and audible endpoint notification.

7.2 *Syringe*, 100 μL capacity, with needle.

7.3 *Syringe*, 1 to 5 mL capacity, without needle.

7.4 *Analytical Balance*, with minimum capacity of 160 g and capable of weighing to 0.0001 g.

8. Reagents and Materials

8.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.³ 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.

8.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water as defined by Type II of Specification D1193.

8.3 *Karl Fischer Solvent*—The solvent system must be a non-methanol formulation for the analysis of aldehydes and ketones and for general usage. The use of a strictly general

purpose solvent is not acceptable because of the potential of obtaining artificially high results from water-forming reactions by chemicals with active carbonyl groups.

8.4 *Karl Fischer Reagent*—The reagent should have a standard titer value of 5 mg $\text{H}_2\text{O}/\text{mL}$ reagent and be listed as being compatible with the solvent system.

9. Sample

9.1 Because stratification or layering of liquid samples is possible, the laboratory sample should be mixed thoroughly by shaking prior to withdrawing a portion for testing. Strongly multi-phasic samples should have each layer analyzed separately and the total moisture percent of the sample calculated as a weighted average. Solid samples should be mixed thoroughly by shaking or stirring, depending on the physical characteristics of the sample.

10. Calibration and Standardization

10.1 Determination of Karl Fischer reagent factor (F):

10.1.1 Determine the mg $\text{H}_2\text{O}/\text{mL}$ reagent (F) for each new procurement of KF solvent and at a minimum of daily on a solvent retained for further titrations (see Section 4).

10.1.2 Add a sufficient quantity of solvent to cover the electrode tip, set the delay interval to 30 s, and engage the magnetic stirrer.

10.1.3 Bring the KF solvent to dryness by titrating with reagent to the endpoint. The endpoint is typically indicated by a visual or audible alarm, or both, depending on the equipment manufacturer.

10.1.4 Refill the burette with reagent.

10.1.5 Fill the 100 μL syringe with approximately 10 μL of water and weigh to the nearest 0.0001 g.

10.1.6 Dispense the syringe contents into the titration vessel and replace the sample port stopper immediately. Reweigh the syringe and record the water mass.

10.1.7 Titrate with reagent until the endpoint is reached. Record the titrant volume used.

10.1.8 The final value for F should be based on the mean of a minimum of three replicates.

10.1.9 *Calculation*:

10.1.9.1 Calculate F by the following formula:

$$F (\text{mg/mL}) = \text{water weight (mg)} / \text{reagent volume (mL)} \quad (3)$$

10.1.9.2 The replicate values for F should have a relative standard deviation of not greater than 5 %. The standardization should be repeated if a greater variance is determined.

11. Procedure

11.1 Bring the KF solvent to dryness by titrating with reagent to the endpoint. The endpoint is typically indicated visually or by an audible alarm, or both, depending on the equipment manufacturer.

11.2 Refill the burette with reagent.

11.3 Draw a portion of the sample into the 1 to 5 mL syringe, and clean any residual sample material from the syringe tip. If the sample contains a large amount of solids or its viscosity is such that it cannot be drawn into the syringe

³ *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.