Standard Test Method for
Total Moisture of Hazardous Waste Fuel by Karl Fischer Titrimetry[1]

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 and health practices and determine the applicability of regulatory limitations prior to use.*

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

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

3. Summary of Test Method

3.1 An amount of solvent (see 7.3) sufficient to immerse the electrode in the titration flask fully (see Note 1) is titrated to dryness as explained in 9.1, 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 5.3) 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 for each sample.

3.2 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.

4. Significance and Use

4.1 The determination of total moisture is important for assessing the quality of fuels. Water content will affect the heating value of fuels directly and can contribute to instability in the operation of an industrial furnace. Additionally, high water contents can present material handling and storage problems during winter months or in cold environments.

5. Interferences

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

5.2 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.

5.3 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.

6. Apparatus

6.1 *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.

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[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.

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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.

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.

6.2 *Syringe,* 100-µL capacity, with needle.

6.3 *Syringe,* 1 to 5-mL capacity, without needle.

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

7. Reagents and Materials

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.[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.

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

7.3 *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.

7.4 *Karl Fischer Reagent*—The reagent should have a standard titer value of 5 mg H_2O/mL reagent and be listed as being compatible with the solvent system.

8. Sample

8.1 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.

9. Calibration and Standardization

9.1 Determination of Karl Fischer reagent factor (*F*):

9.1.1 Determine the mg H_2O/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 3).

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

9.1.3 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.

9.1.4 Refill the burette with reagent.

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

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

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

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

9.1.9 *Calculation:*

9.1.9.1 Calculate *F* by the following formula:

$$F\ (\text{mg/mL}) = \text{water weight (mg)/reagent volume (mL)} \qquad (1)$$

9.1.9.2 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.

10. Procedure

10.1 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.

10.2 Refill the burette with reagent.

10.3 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 easily, it may be necessary to weigh the sample and introduce it using a laboratory spatula or suitable device.

10.4 Weigh the syringe with sample to the nearest 0.0001 g.

10.5 Add the sample to the titration vessel and allow sufficient time for the material to dissolve adequately. The suggested amount of sample based on the amount of expected water content is as given in Table 1.

NOTE 2—The information given in Table 1 is described in Test Method D4017.

10.6 Reweigh the syringe and record the sample mass added to the vessel to the nearest 0.0001 g.

10.7 If solid material is observed interfering with the sensing probe, or it is observed that the sample is not dissolved in the KF solvent sufficiently, extract the sample with solvent as follows:

TABLE 1 Specimen Guidelines

Expected water, %	Approximate Specimen Mass, g	Approximate Titrant Volume at 5 mg/mL titre, mL
0.5–1.0	5	5–10
1–3	2–5	10–20
3–10	1–2	10–20
10–30	0.4–1.0	15–25
>70	0.1	20

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[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.

10.7.1 Beginning again with a new sample, combine the sample and solvent gravimetrically at an approximate 1:1 ratio in a large test tube. Record the mass of both sample and solvent.

10.7.2 Cap the sample mixture and shake or mix on a vortex-type or orbital mixer for approximately 1 min.

10.7.3 Centrifuge the sample mixture to separate the undissolved/leached solids.

10.7.4 Analyze the supernatant beginning with 10.1.

10.7.5 In addition to the extracted sample, analyze a blank solution of virgin KF solvent beginning with 10.1. The KF solvent blank (mL of titrant used) is subtracted in 10.9.3.

10.8 Titrate with reagent until the endpoint is reached. Record the volume.

10.9 The final percentage of water should be based on the mean of a minimum of two determinations.

10.9.1 Calculation:

10.9.1.1 For unextracted samples, calculate the percentage water as follows:

$$(V)(F) = W$$
$$(W/S)\ 100 = \text{water, weight\%} \tag{2}$$

where:

V = reagent volume (mL),
F = Karl Fischer reagent factor (mg/mL),
W = mass of water contained in the sample (mg), and
S = sample mass (mg).

10.9.1.2 For extracted samples, calculate the percentage water as follows:

$$(V - \text{solvent blank})(F) = W$$
$$(W/S)(\text{dilution factor}) = \%\ \text{water} \tag{3}$$

where:

V = reagent volume (mL),
F = Karl Fischer reagent factor (mg/mL),
W = mass of water contained in the sample (mg),
S = sample mass (mg), and

$$\text{dilution factor} = \frac{\text{KF solvent (mg)} + \text{sample (mg)}}{\text{sample (mg)}}$$

11. Precision and Bias[4]

11.1 *Precision*—The precision estimates are based on an interlaboratory study in which operators in six different laboratories analyzed in duplicate, on separate days, five samples of hazardous waste fuel containing between 13 and 32 % water. The results were analyzed statistically in accordance with Practice E691.

11.1.1 *Repeatability (Within Laboratory)*—The coefficient of variation of results (each the average of duplicate determinations), obtained by the same analyst on different days, has been estimated to be 1.3 % relative at 30 degrees of freedom. Therefore, the results of two properly conducted tests, by the same operator on the same sample, should not differ by more than 3.6 % of their average.

11.1.2 *Reproducibility (Between Laboratories)*—The coefficient of variation of results (each the average of duplicate determinations), obtained by analysts in different laboratories, has been estimated to be 4.3 % relative at 5 degrees of freedom. Therefore, the results of properly conducted tests, on identical samples of the same material, by two different laboratories, should not differ from each other by more than 11.9 % of their average.

11.2 *Bias*—The bias of this test method has not been determined because there are no recognized reference standards.

12. Keywords

12.1 hazardous waste fuel; Karl Fischer titrimetry; percent water; total moisture

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[4] A copy of the research report used to develop the precision statement is available from ASTM headquarters. Request RR:D 34-1009.