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Standard Test Method for Coulometric and Volumetric Determination of Moisture in Plastics Using the Karl Fischer Reaction (the Reaction of Iodine with Water)[1]

This standard is issued under the fixed designation D6869; 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 method uses the reaction of Iodine (I_2) with water (Karl Fischer Reaction) to determine the amount of moisture in a polymer sample.[2]

1.2 This test method is intended to be used for the determination of moisture in most plastics. Plastics containing volatile components such as residual monomers and plasticizers are capable of releasing components that will interfere with the I_2/water reaction.

1.3 This method is suitable for measuring moisture over the range of 0.005 to 100 %. Sample size shall be adjusted to obtain an accurate moisture measurement.

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

NOTE 1—This standard is technically equivalent to ISO 15512 Method B.

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.*

2. Referenced Documents

2.1 *ISO Document:*

ISO 15512 Plastics—Determination of Water Content[3]

3. Summary of Test Method[2]

3.1 Samples are heated to vaporize water that is transported by a nitrogen carrier gas to the titration cell. The moisture collected in the solution within the titration cell is determined using the reaction of water with I_2.

3.2 Endpoint detection is made by instrumented methods. Determination of the moisture present is made using the reaction of I_2 with water.

3.3 Coulometric instruments use Faraday's law to measure the moisture present with 10.71 Coulombs (C) of generating current corresponding to 1 mg of water ($2I^- \rightarrow I_2 + 2e^-$). Volumetric instruments measure the volume of solution containing I_2 that is required to keep the current constant.

4. Significance and Use

4.1 Moisture will affect the processability of some plastics. High moisture content causes surface imperfections (that is, splay or bubbling) or degradation by hydrolysis. Low moisture (with high temperature) causes polymerization.

4.2 The physical properties of some plastics are affected by the moisture content.

5. Interferences

5.1 Some compounds, such as aldehydes and ketones, interfere in the determination of moisture content using this method.

6. Apparatus

6.1 *Heating Unit,* consisting of an oven capable of heating the sample to approximately 300°C, a furnace tube, a temperature control unit, a carrier gas flow meter, and desiccating tubes for the carrier gas.

6.2 *Sample Pan (Boat),* normally a glass sample boat or boat manufactured of a suitable material to transfer the oven heat to the sample. It is permitted to use aluminum foil as a disposable liner for the sample pan.

6.3 *Titration Unit,* consisting of a control unit, titration cell with a solution cathode, platinum electrode, and solution stirring capability. This apparatus has the capability to generate or deliver iodine to react stoiciometrically with the moisture present in the titration cell. The current or volume required to generate the iodine converts to micrograms of water present.

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[1] This test method is under the jurisdiction of ASTM Committee D20 on Plastics and is the direct responsibility of Subcommittee D20.70 on Analytical Methods.

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[2] See Appendix X1, History of Reagents Associated With the Karl Fischer Reaction, for an explanation of coulometric and volumetric techniques as well as an explanation of the Karl Fischer Reaction and Karl Fischer Reagents.

[3] Available from American National Standards Institute (ANSI), 25 W. 43rd St., 4th Floor, New York, NY 10036, http://www.ansi.org.

The percent moisture in the sample is then calculated based on the sample weight used and is given as a direct digital readout.

6.4 *Analytical Balance,* capable of weighing 0.1 mg (four decimal place balance).

6.5 *Glass Capillary (Micropipette),* used to measure a known amount of water, typically 2 mg (2000 µg).

7. Reagents and Materials

7.1 *Anode (Generator) Solution,* per manufacturer's recommendation.

7.2 *Cathode Solution,* per manufacturer's recommendation.

NOTE 2—Hydranal or similar anode and cathode solutions are recommended. These reagents do not contain pyridine, are less toxic, and have no offensive odor.

7.3 *Silica Gel,* granules, approximately 2 mm, desiccant for drying tube of titration assembly (if applicable).

7.4 *Special Grease,* as supplied by manufacturer for ground glass joints.

7.5 *Molecular Sieve,* or suitable desiccant (for drying the nitrogen carrier gas stream).

7.6 *Nitrogen Gas* (N_2), containing less than 5 µg/g of water.

7.7 *Neutralization Solution,* or check solution (per manufacturer's recommendation).

8. Hazards

8.1 Due to the low quantities of water measured, maximum care shall be exercised at all times to avoid contaminating the sample with water from the sample container, the atmosphere or transfer equipment. Hygroscopic resin samples shall be protected from the atmosphere.

8.2 Due to the high temperatures and the chemicals involved in this test method, safe lab practices must be followed at all times.

9. Sampling, Test Specimens, and Test Units

9.1 Unless otherwise agreed upon by interested parties or described in a specification, the material shall be sampled statistically or the sample shall come from a process that is in statistical control.

9.2 Samples that will determine the moisture of a larger lot of material must be taken in such a manner that the moisture content will not change from the original material. Sample containers must be adequately dried and the environment in which sampling is performed must not add additional moisture to the sample. Most normal plant or lab operating conditions are adequate for sampling. The sample container shall be properly sealed to prevent moisture pick-up before testing.

9.3 Samples in many forms, such as molded powder, molded shapes, or re-grind are permitted. It is recommended that molded specimens be cut into smaller parts prior to testing (recommended maximum size 4 by 4 by 3 mm)

9.4 Transfer samples quickly from sealed container to balance to instrument to prevent moisture pick-up.

10. Preparation of Apparatus

10.1 Assemble the apparatus according to the manufacturer's instructions. Molecular sieve or suitable desiccant must be used in the drying tubes for the nitrogen carrier gas.

10.2 Pour approximately 200 mL (or an amount specified by the manufacturer) of generator (anode) solution into the titration cell.

10.3 Add 10 mL of cathode solution to the cathode cell.

NOTE 3—The condition of both anode and cathode solutions are determined by the appearance of the fluids. The solutions must be light amber in color. As solutions age, viscosity will increase and solution color will turn dark. The instrument will indicate solution integrity by the "background" value titration rate. Do not analyze samples containing low moisture content if the "background" value is greater than 0.10 µg/s.

10.4 Turn the cell power switch on. If the cell potential shows a negative value, indicating that the anode solution contains excess iodine, add approximately 50 to 200 µL of neutralization solution or check solution.

10.5 Disconnect the tube connecting the vaporizer unit to the titration cell. Set nitrogen flow rate to achieve steady bubbling of nitrogen to the titration cell. (A flow rate of 200 to 300 mL/min is recommended.)

10.6 Lift the titration cell and agitate the solution by gently swirling the cell to remove any residual water from the walls. Stir the solution for a minute in the Titration Mode to dry and stabilize the inner atmosphere.

10.7 Reconnect the tube from the vaporizer unit to the titration cell. Keep the carrier gas flow on during the whole titration. The instrument is now ready for sample analysis.

10.8 Set the oven and furnace tube temperature as required to obtain accurate results for the plastic to be tested. The temperature is set so that the analysis is completed in a short time period, yet eliminating the generation of water from thermal degradation of the sample. Selection of Optimum Heating Temperature is discussed below.

10.9 *Selection of Optimum Heating Temperature:*

10.9.1 Select optimum heating temperature for material to be tested by carrying out tests in several different temperatures to make a curve as shown in Fig. 1.

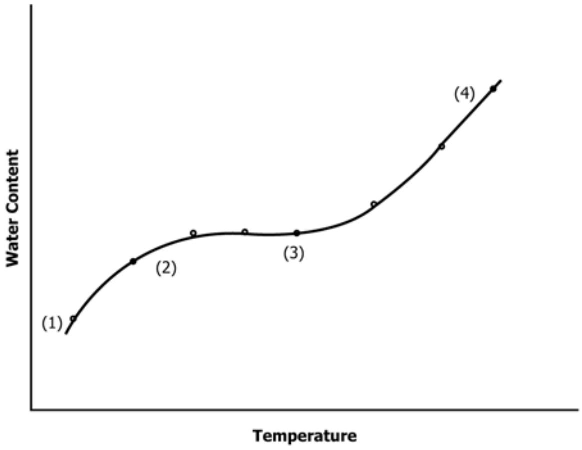

FIG. 1 Optimum Heating Temperature Selection for Material

10.9.1.1 In the range from 1 to 2, the water in the sample is not vaporized sufficiently so that the water content indicated increases in proportion to the temperature.

10.9.1.2 Between 2 and 3, the water content measured appears nearly constant and is considered the optimum heating temperature range for determining moisture content.

10.9.1.3 Water content appears to increase between 3 and 4. This is probably caused by the generation of water due to thermal decomposition or solid phase polymerization of the sample.

10.9.1.4 Measurement time is also a consideration in selection of the optimum heating temperature.

11. Calibration and Standardization

11.1 The apparatus is verified for proper operation by either analysis of a known quantity of water or analysis of a hydrate sample that will release moisture upon heating. Two methods of checking the instrument are listed here, a micro-capillary method and a sodium citrate method.

11.2 *Micro-capillary Method:*

11.2.1 A glass capillary (micropipette) is used to measure a known amount of water, typically 2 mg (2000 µg). Prepare the instrument as detailed in Section 12.

11.2.2 Fill the micropipette by holding it at its midpoint with a pair of tweezers and dipping the tip into distilled or demineralized water. Take care not to get excess moisture on the outside surface of the capillary.

11.2.3 Place the capillary in the sample boat through the furnace tube port. An oven temperature of 150°C or greater shall be used.

11.3 *Sodium Citrate Method:*

11.3.1 This method uses sodium citrate dihydrate ($C_6H_5Na_3O_7 \cdot 2H_2O$) with theoretical water content of 12.24 %.

11.3.2 Weigh 0.0100 to 0.0200 g of sodium citrate to the nearest 0.0001 g. Record the sample weight.

11.3.3 Analyze the moisture content using an oven temperature of 225°C or greater.

NOTE 4—Another permissible method, which uses a micro syringe, is described in section 4.5.3.1 of ISO 15512. It is permissible to use similar hydrates to check instrument performance.

12. Procedure

12.1 If the oven is at the selected operating temperature before the analysis begins, pre-heat the sample boat to eliminate any moisture present. Heat the boat in the oven for 2 min, and then allow the boat to cool for 2 min prior to the introduction of samples.

12.2 Weigh the sample to be tested and record the weight to the nearest 0.1 mg. Sample weight to be used is dependent on the amount of moisture expected in the sample. The following table lists recommended sample weights for various moisture ranges:

Expected Moisture Content (w)	Sample Weight (m)
w > 1 %	0.2 g > m ≥ 0.1 g
1 % ≥ w > 0.5 %	0.4 g > m ≥ 0.2 g
0.5 % ≥ w > 0.1 %	1 g > m ≥ 0.4 g
0.1 % ≥ w	m ≥ 1 g

12.3 Place the sample in the sample boat through the furnace tube port. Move the sample boat into the oven and begin analysis.

12.4 At completion of the sample analysis, the instrument will automatically report the result or display µg of moisture titrated.

12.5 Remove the sample boat and empty the contents, then prepare the sample boat for next analysis. Removal of the previous sample will provide more accurate results.

13. Calculation or Interpretation of Results

13.1 Most commercial coulometric instruments will perform calculations automatically based on the micrograms of water detected.

13.2 If the moisture is not calculated automatically, calculate the water content in the test portion (expressed as a percentage by mass) as follows:

$$\%\ \text{moisture} = \frac{\text{micrograms of water}}{\text{grams of water}} \times 10^{-4}$$

$$\%\ \text{moisture} = \frac{\text{grams of water}}{\text{grams of sample}} \times 100$$

14. Report

14.1 Report the sample type, oven temperature, sample weight, and % moisture.

15. Precision and Bias

15.1 The precision of this test method is not known because inter-laboratory data are not available. If and when inter-laboratory data are obtained, a precision statement will be added at a subsequent revision.

15.2 A "ruggedness" test was run at three labs using nylon 6,6 with the following results:

Lab Number	Day	Analysis Temp. (°C)	First Analysis	Second Analysis
1	1	190	0.2323	0.2298
1	2	190	0.2047	0.2323
1	1	200	0.2491	0.2250
1	2	200	0.1842	0.1927
2	1	240	0.308	0.316
2	2	240	0.314	0.304
2	1	200	0.264	0.263
2	2	200	0.285	0.297
3	1	220	0.25	0.24
3	2	220	0.24	0.23
3	1	200	0.23	0.24
3	2	200	0.25	0.24

16. Keywords

16.1 moisture content; moisture determination; plastics

APPENDIX

(Nonmandatory Information)

X1.

X1.1 History of Reagents Associated with the Karl Fischer Reaction

X1.1.1 The Karl Fischer chemical reaction is:

$$I_2 + 2H_2O + SO_2 \rightarrow 2HI + H_2SO_4$$

X1.1.2 This reaction takes place in the presence of a base and a solvent. Karl Fischer's original combination of reagents, which contained pyridine, was first used in 1935. It was not widely used because of the objectionable odor of pyridine.

X1.1.3 Wider use of the Karl Fischer reaction did not take place until the early 1980's when reagents were offered where pyridine was replaced with methanol. This eliminated the odor problem associated with pyridine. Halogenated alcohols (especially trifluoroethanol) were used in place of methanol in some cases to overcome side reactions caused by a large group of samples.

X1.1.4 Because of the safety and environmental concerns associated with methanol and halogenated compounds, new generations of reagents that use the Karl Fischer reaction are being offered that are based on long-chain ethers or ethanol/ salts combinations.

X1.1.5 Reagents using the Karl Fischer chemical reaction include those sold under the trade names of Hydranal, Watermark, Hydra-Point, Aquastar, and Aqualine from Riedel de Haen, GFS Chemicals, Mallinckrodt, EM Science, and Fischer Scientific, respectively.

X1.2 Coulometric Titration

X1.2.1 Coulometric titration instruments determine the amount of water present by measuring the amount of current generated during the titration. Faraday's law is used to calculate the moisture present, with 10.71 C (Coulombs) of generating current corresponding to 1 mg of water ($2I^- \rightarrow I_2 + 2e^-$).

X1.3 Volumetric Titration

X1.3.1 Volumetric titration instruments measure the volume of iodine-containing reagent needed to react with the moisture in a sample. Their electrode detects the current generated during the titration. A volumetric burette adds iodine-containing reagent to the titration cell until no more current is generated. The volume of reagent that is added during the titration is measured and used to calculate the amount of moisture in the sample.