Standard Test Method for Water in Phenol and Related Materials by the Iodine Reagent Method[1]

This standard is issued under the fixed designation D1631; 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.

This standard has been approved for use by agencies of the Department of Defense.

1. Scope*

1.1 This test method covers the determination of water in phenol and related materials such as cresols, xylenols, naphthalene, pyridine, and quinoline.

1.2 This test method has been found applicable to a variety of materials varying in water content from 100 mg/kg to solutions containing a relatively high percent of water.

1.3 In determining the conformance of the test results using this method to applicable specifications, results shall be rounded off in accordance with the rounding-off method of Practice E29.

1.4 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this 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.* For specific hazard statements, see Section 9.

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D1364 Test Method for Water in Volatile Solvents (Karl Fischer Reagent Titration Method)
D3437 Practice for Sampling and Handling Liquid Cyclic Products
D3852 Practice for Sampling and Handling Phenol, Cresols, and Cresylic Acid
D4790 Terminology of Aromatic Hydrocarbons and Related Chemicals
D6809 Guide for Quality Control and Quality Assurance Procedures for Aromatic Hydrocarbons and Related Materials
E29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications

2.2 *Other Document:*[3]

OSHA Regulations, 29 CFR paragraphs 1910.1000 and 1910.1200

3. Terminology

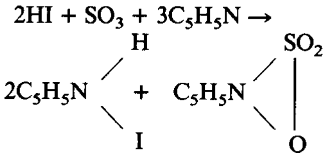
3.1 See Terminology D4790 for definition of terms used in this test method.

4. Summary of Test Method

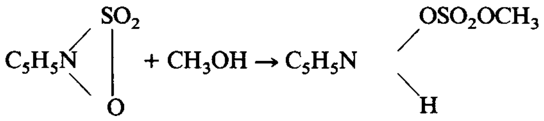
4.1 When solutions of iodine in methanol and of sulfur dioxide in pyridine are mixed in the presence of water, the following reaction occurs:

$$I_2 + SO_2 + H_2O \rightleftarrows 2HI + SO_3 \quad (1)$$

4.1.1 Sufficient pyridine is present in the reagent to consume the hydriodic acid and sulfur trioxide:



4.1.2 The pyridine sulfur trioxide salt reacts with the methanol, this preventing a second mole of water from being consumed:



4.2 When the pyridine solution contains water and the sulfur dioxide is titrated with iodine in methanol solution, the

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[1] This test method is under the jurisdiction of ASTM Committee D16 on Aromatic Hydrocarbons and Related Chemicals and is the direct responsibility of Subcommittee D16.02 on Oxygenated Aromatics.

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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.

[3] Available from U.S. Government Printing Office Superintendent of Documents, 732 N. Capitol St., NW, Mail Stop: SDE, Washington, DC 20401.

***A Summary of Changes section appears at the end of this standard**

platinum electrodes remain polarized until all the water reacts. A slight excess of iodine depolarizes the electrodes, allowing current to flow through the microammeter which indicates the end point.

5. Significance and Use

5.1 This test method is particularly useful for determining small amounts of water in hygroscopic materials. This test method is suitable for setting specifications on materials referenced in the scope. It may also be used as an internal quality control tool and in development or research work.

6. Interferences

6.1 This test method is not applicable in the presence of mercaptans, peroxides, or appreciable quantities of aldehydes or amines.

6.2 If ketones are present in the sample, interference from them can be avoided by employing the glycol-pyridine sample solvent specified in Test Method D1364.

7. Apparatus

7.1 The apparatus shall be assembled as shown in Fig. 1. Any suitable modification permitting equal facility and accuracy may be used. Automatic titration equipment is commercially available and may be used.

8. Reagents

8.1 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.[4] 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.

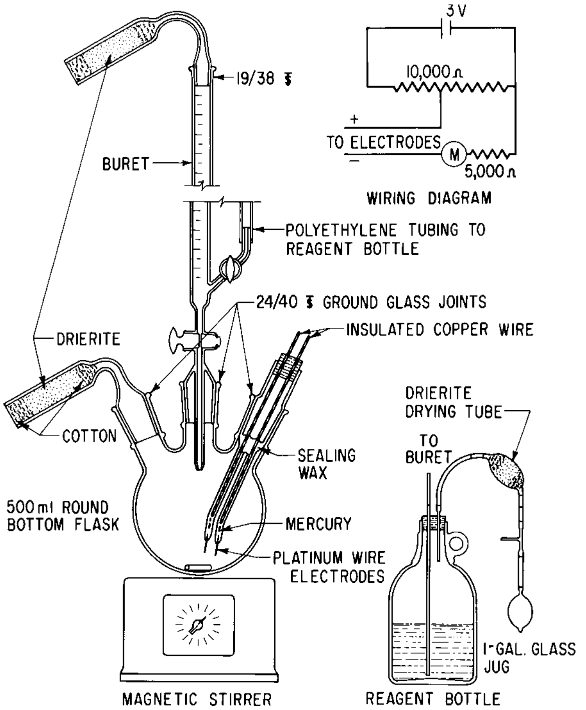

FIG. 1 Titration Assembly

8.2 *Iodine Solution*—Dissolve 150 g of iodine (I_2) crystals in 3 L of anhydrous methanol. Place the solution in the reagent bottle connected to the buret as shown in Fig. 1.

8.3 *Methanol,* anhydrous, containing less than 0.05 % water.

8.4 *Pyridine Solution*—Place 4000 mL of refined grade pyridine in a 5000-mL distilling flask. Distill over and discard 400 mL of forecut at atmospheric pressure. Distill off 3400 mL of center cut and transfer to a suitable glass bottle fitted with a two-hole stopper. Through one hole of the stopper insert a piece of glass tubing that extends almost to the bottom of the bottle; through the other hole insert a short piece of glass tubing to serve as a vent. Through the long tube add 400 g of refrigerant-grade sulfur dioxide (SO_2) dried through concentrated sulfuric acid (H_2SO_4 sp gr 1.84), and allow the solution to cool. Fit the vent tube with a drying tube and an aspirator bulb; connect the long tube with an adapter suitable for introducing the reagent into the titration flask. For convenience in measuring, a suitable reservoir may be placed in the system.

NOTE 1—In place of the divided reagents described in 8.2, 8.3, and 8.4 it is permissible to employ the single solution reagent specified in Test Method D1364 or commercial Karl Fischer reagents. Pyridine-free reagents are available from various laboratory suppliers and may be used if suitable for the material being tested.

8.5 When handling Karl Fischer reagent refer to Practice D3437.

9. Hazards

9.1 Consult current OSHA regulations supplier's Material Safety Data Sheets and local regulations for all materials used in this test method.

9.2 Phenol, pyridine, and related materials are extremely toxic when ingested and corrosive to the skin. Appropriate precaution must be exercised when handling them.

10. Sampling

10.1 Sample in accordance with Practice D3852 for proper sampling and handling of phenol and related materials analyzed by this test method (see 9.1 and 9.2.).

10.2 Precautions must be taken in sampling to preclude any possibility of contamination with atmospheric moisture adhering to the walls of the pipet.

10.3 The sample size recommended, on the basis of water content expected is as follows:

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[4] *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.

Expected Water Content, %	Size of Specimen, g
0.01 to 0.03	50
0.03 to 0.3	25
0.3 to 0.6	10
0.6 to 1.0	5
1.0 to 5.0	2
5.0 to 10.0	1
10.0 to 20.0	0.5

11. Standardization of Sulfur Dioxide–Iodine Reagent

11.1 By means of pressure from the aspirator bulb, transfer sufficient pyridine solution (**Warning**—see 9.2) to the titration flask to cover the electrodes. If an automatic titration apparatus is used, a small amount of methanol may be added to the pyridine to improve the response of the titrator. Turn on the magnetic stirrer and turn the "zero-set" knob until a reading of 70 µA is obtained on the ammeter. Add the iodine solution dropwise from the buret until the ammeter reads a maximum value, about 130 µA. Remove the drying tube from the sidearm and quickly introduce an amount of distilled water, or water of equivalent purity, at least equal to that to be determined, weighed to the nearest 0.1 mg by means of a suitable weighing pipet. Immediately replace the drying tube.

11.2 Titrate with the iodine solution, approaching the end point dropwise until the maximum value, about 130 µA, is obtained on the ammeter. The standardization should be repeated daily. If desired, a suitable accurately weighed amount of sodium tartrate dihydrate reagent may be used in place of water as follows: Accurately weigh a small aluminum weighing dish containing about 0.20 to 0.22 g of powdered sodium tartrate dihydrate ($Na_2C_4H_4O_6 \cdot 2H_2O$) to the nearest 0.1 mg. Remove the stopper from the titration flask and introduce the tartrate by inserting the spout into the opening and gently tapping so that the powder falls freely into the liquid without contacting the side walls. Do not brush out the dish: accurately reweigh it and calculate the weight of tartrate used by difference. Quickly reseal the flask, turn on the stirrer, and titrate to the end point. Record the volume of reagent and weight of tartrate used.

11.3 Calculate the water equivalent of the sulfur dioxide-iodine reagent as follows:

$$F = 100A/B \tag{2}$$

where:

F = water equivalent of the reagent, g/100 mL
A = water added, g
B = volume of reagent used for the titration, mL

If sodium tartrate dihydrate is used in place of water for standardizing:

$$F = 15.66S/B \tag{3}$$

where S = tartrate used, g.

12. Procedure

12.1 Repeat the procedure described in Section 11 adding, instead of water, an amount of specimen selected according to Section 10. Record all weighings to the nearest 0.1 mg. As long as an excess of pyridine remains in the titration flask, further additions of specimen and titration may be made. (**Warning**—See 9.2.)

NOTE 2—The titration flask may be removed and cleaned between specimens. Washing should be followed by an alcohol or acetone rinse and drying in a ventilated oven at 100 to 130°C for several hours. The clean flask may be cooled in a desiccator or attached to the buret to cool with the openings closed with drying tubes. If a series of specimens is to be tested, it is preferable to continue additions of specimens and titration (and addition of pyridine if necessary) until the volume of liquid in the flask is too great for further titration.

NOTE 3—Visual observation of the end point may be used in place of the more precise electrometric method described if the solution is very lightcolored. During the titration the solution turns yellow after the addition of the first few millilitres of the reagent. This color change must not be confused with the true end point, which is brown. The transition from yellow to brown is quite sharp and easily reproducible.

13. Calculation

13.1 Calculate the amount of water in the specimen as follows:

$$\text{Water, weight\%} = CF/D \tag{4}$$

where:

C = sulfur dioxide-iodine reagent required for titration of the specimen, mL
D = weight of specimen used, g

14. Precision and Bias

14.1 *Intermediate Precision (formerly called Repeatability)*—Duplicate results should be considered suspect if they differ by more than the following:

Range, %	Intermediate Precision (By Same Operator)	Reproducibility (By Two Different Laboratories)
0.01 to 0.12	0.0035	0.021

14.1.1 Data on which these precision values are based are given in the 1959 Report of Committee D16, *Proceedings* , ASTM, Vol 59, 1959.

14.2 *Bias*—Since there is no accepted reference material suitable for determining the bias in this test method, bias has not been determined.

15. Quality Guidelines

15.1 Laboratories shall have a quality control system in place.

15.1.1 Confirm the performance of the test instrument or test method by analyzing a quality control sample following the guidelines of standard statistical quality control practices.

15.1.2 A quality control sample is a stable material isolated from the production process and representative of the sample being analyzed.

15.1.3 When QA/QC protocols are already established in the testing facility, these protocols are acceptable when they confirm the validity of test results.

15.1.4 When there are not QA/QC protocols established in the testing facility, use the guidelines described in Guide D6809 or similar statistical quality control practices.

16. Keywords

16.1 cresols; iodine; Karl Fischer method; naphthalene; phenol; pyridine; quinoline; water; xylenols

SUMMARY OF CHANGES

Committee D16 has identified the location of selected changes to this standard since the last issue (D1631 - 99 (2004)) that may impact the use of this standard. (Approved January 1, 2010.)

(1) Added Quality Guidelines — Section 15.
(2) Added a metric statement — section 1.4.
(3) Added Guide D6809 to list of Referenced Documents — section 2.1.

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