Designation: D 1364 – 02

Standard Test Method for Water in Volatile Solvents (Karl Fischer Reagent Titration Method)[1]

This standard is issued under the fixed designation D 1364; 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 volatile solvents and chemical intermediates used in paint, varnish, lacquer, and related products.

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

1.3 For purposes of determining conformance of an observed or a calculated value using this test method to relevant specifications, test result(s) shall be rounded off "to the nearest unit" in the last right-hand digit used in expressing the specification limit, in accordance with the rounding-off method of Practice E 29.

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.*

1.5 For hazard information and guidance, see the supplier's Material Safety Data sheet.

2. Referenced Documents

2.1 *ASTM Standards:*

D 1500 Test Method for ASTM Color of Petroleum Products (ASTM Color Scale)[2]

E 29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications[3]

3. Terminology

3.1 *Definitions of Terms Specific to This Standard:*

3.1.1 *instrumental end point*—that point in the titration when two small platinum electrodes, upon which a potential of 20 to 50 mV has been impressed, are depolarized by the addition of 0.05 mL of Karl Fischer reagent (6 mg of H_2O per mL), causing a change of current flow of 10 to 20 μA that persists for at least 30 s.

NOTE 1—This end point is sometimes incorrectly called the "dead stop" which is the reverse of the above.

3.1.2 *color end point*—During the titration, the solution first turns yellow, then later deepens towards the end of the titration; the end point is indicated by the change from yellow to orange-red which is quite sharp and easily repeated. The orange-red color must persist for at least 30 s in order to indicate an end point.

NOTE 2—View the color by transmitted daylight or by transmitted light from an artificial daylight lamp, such as the one that complies with the specifications given in Test Method D 1500.

4. Summary of Test Method

4.1 This test method is based essentially upon the reduction of iodine by sulfur dioxide in the presence of water. This reaction can be used quantitatively only when pyridine and an alcohol are present to react with the sulfur trioxide and hydriodic acid produced according to the following reactions:

$$H_2O + I_2 + SO_2 + 3C_5H_5N \rightarrow 2C_5H_5N{\cdot}HI + C_5H_5N{\cdot}SO_3$$
$$C_5H_5N{\cdot}SO_3 + ROH \rightarrow C_5H_5N{\cdot}HSO_4R \quad (1)$$

4.2 To determine water, Karl Fischer reagent (a solution of iodine, pyridine, and sulfur dioxide, in the molar ratio of 1 + 10 + 3) dissolved in anhydrous 2-methoxyethanol is added to a solution of the sample in anhydrous pyridine-ethylene glycol (1 + 4) until all water present has been consumed. This is evidenced by the persistence of the orange-red end-point color; or alternatively by an indication on a galvanometer or similar current-indicating device which records the depolarization of a pair of noble-metal electrodes. The reagent is standardized by titration of water.

[1] This test method is under the jurisdiction of ASTM Committee D01 on Paint and Related Coatings, Materials, and Applications and is the direct responsibility of Subcommittee D01.35 on Solvents, Plasticizers, and Chemical Intermediates.

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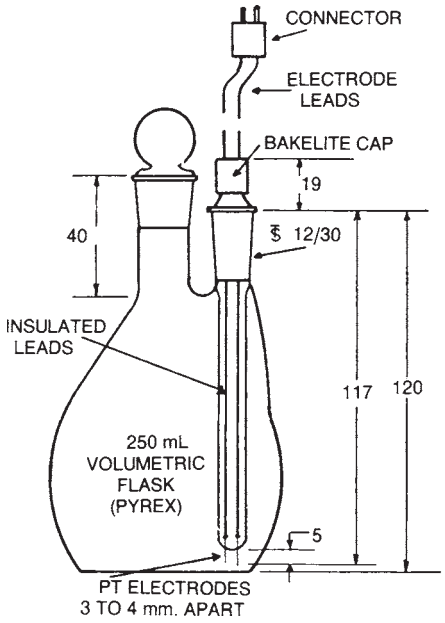
[2] *Annual Book of ASTM Standards*, Vol 05.01.

[3] *Annual Book of ASTM Standards*, Vol 14.02.

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



NOTE 1—All dimensions in millimetres.

FIG. 1 Titration Flask Assembly

5. Significance and Use

5.1 Volatile solvents are used in a variety of chemical processes which may be affected by water. Therefore, this test method provides a test procedure for assessing compliance with a specification.

6. Apparatus

6.1 *Titration Vessel*—For color end point titrations, use a 100 or 250-mL volumetric flask, which need not be calibrated; a 250-mL flask fitted with interchangeable electrodes (Fig. 1)[4] may also be used for the instrumental end point and is particularly suitable for titrations at ice temperatures. For permanently mounted assemblies, the vessel should have a capacity about equal to that of a 300-mL tall-form beaker; and be provided with a tight-fitting closure to protect the sample and reagent from atmospheric moisture, a stirrer, and a means of adding sample and reagents and removing spent reaction mixture. It is desirable to have a means for cooling the titration vessel to ice temperature.

6.2 *Instrument Electrodes*—Platinum with a surface equivalent to two No. 26 wires 5 mm long. The wires should be 3 to 8 mm apart and so inserted in the vessel that 25 mL of liquid will cover them.

6.3 *Instrument Depolarization Indicator*, having an internal resistance of less than 5000 Ω and consisting of a means of impressing and showing a voltage of 20 to 50 mV across the electrodes and capable of indicating a current flow of 10 to 20 μA by means of a galvanometer or radiotuning eye circuit.[5]

6.4 *Buret Assembly* for Karl Fischer reagent, consisting of a 25 or 50-mL buret connected by means of glass (not rubber) connectors to a source of reagent; several types of automatic dispensing burets[6] may be used. Since the reagent loses strength when exposed to moist air, all vents must be protected against atmospheric moisture by adequate drying tubes containing indicating calcium sulfate drying agent. All stopcocks and joints should be lubricated with a lubricant not particularly reactive with the reagent.

6.5 *Weighing Bottle*, of the Lunge or Grethen Type, or equivalent.

7. Reagents

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.[7] Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without decreasing the accuracy of the determination.

7.1.1 *Karl Fischer Reagent (equivalent to 6 mg of H_2O per mL)*[8]—For each liter of solution, dissolve 133 ± 1 g of I_2 in 425± 2 mL of anhydrous (less than 0.1 % H_2O) pyridine in a dry glass-stoppered bottle. Add 425 ± 2 mL of anhydrous (less than 0.1 % H_2O) 2-methoxyethanol. Cool to below 4°C in an ice bath and add gaseous SO_2, dried by bubbling through concentrated H_2SO_4(sp gr 1.84); determine the amount of SO_2 added by measuring the change in weight of the SO_2 cylinder (102 ± 1 g) or the increase in volume (70 ± 1 mL) of the reagent mixture. Alternatively, add 70 mL of freshly drawn liquid SO_2 in small increments.

7.1.2 *Solvent Mixture*—Mix 1 volume of anhydrous (less than 0.1 % H_2O) pyridine with 4 volumes of anhydrous (less than 0.1 % H_2O) ethylene glycol.

NOTE 3—Pyridine, ethylene glycol, and 2-methoxyethanol, each containing less than 0.1 % water, are available and should be used.

[4] The sole source of supply of flasks known to the committee at this time is the Rankin Glass Blowing Co., 3920 Franklin Canyon Road, Martinez, CA. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,[1] which you may attend.

[5] The sole source of supply of instrument depolarization indicator known to the committee at this time is Fisher Scientific Co. (need address). If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,[1] which you may attend.

[6] The sole source of supply of automatic dispensing burets, No. J-821, known to the committee at this time is Scientific glass Apparatus Co., Bloomfield NJ. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,[1] which you may attend. These specifically designed burets present the minimum contact of reagent with stopcock lubricant.

[7] *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.

[8] Karl Fischer Reagent is available from various laboratory suppliers. Pyridine-free adaptations are available and may be used if precision can be established. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,[1] which you may attend.