



Designation: D 1364 – 95 (Reapproved 1999)

## Standard Test Method for Water in Volatile Solvents (Karl Fischer Reagent Titration Method)<sup>1</sup>

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 ( $\epsilon$ ) 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 *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.*

1.4 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)<sup>2</sup>

### 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<sub>2</sub>O per mL), causing a change of current flow of 10 to 20  $\mu$ A 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.

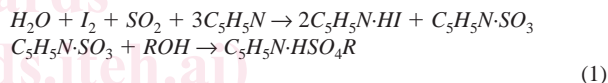
3.1.2 *color end point*—During the titration, the solution first turns yellow, then later deepens towards the end of the titration; the end point is indicated by the change from yellow to orange-red which is quite sharp and easily repeated. The

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:



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.

### 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

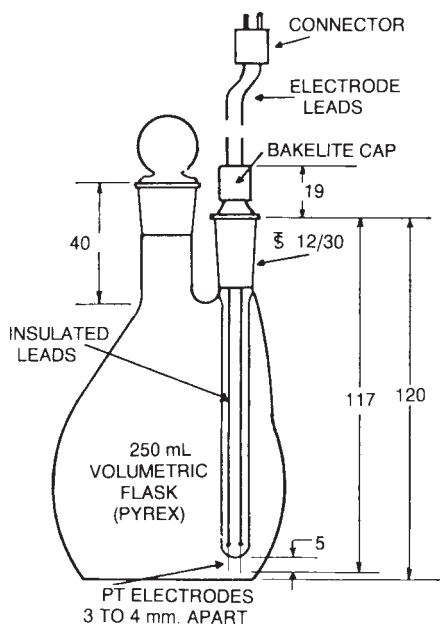
6.1 *Titration Vessel*—For color end point titrations, use a 100 or 250-mL volumetric flask, which need not be calibrated; a 250-mL flask fitted with interchangeable electrodes (Fig. 1)<sup>3</sup>

<sup>1</sup> This test method is under the jurisdiction of ASTM Committee D-1 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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<sup>2</sup> *Annual Book of ASTM Standards*, Vol 05.01.

<sup>3</sup> 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 Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,<sup>1</sup> which you may attend.



NOTE 1—All dimensions in millimetres.

FIG. 1 Titration Flask Assembly

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  $\Omega$  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  $\mu$ A by means of a galvanometer or radiotuning eye circuit.<sup>4</sup>

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<sup>5</sup> 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 con-

taining 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.<sup>6</sup> 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<sub>2</sub>O per mL)*<sup>7</sup>—For each liter of solution, dissolve  $133 \pm 1$  g of I<sub>2</sub> in  $425 \pm 2$  mL of anhydrous (less than 0.1 % H<sub>2</sub>O) pyridine in a dry glass-stoppered bottle. Add  $425 \pm 2$  mL of anhydrous (less than 0.1 % H<sub>2</sub>O) 2-methoxyethanol. Cool to below 4°C in an ice bath and add gaseous SO<sub>2</sub>, dried by bubbling through concentrated H<sub>2</sub>SO<sub>4</sub>(sp gr 1.84); determine the amount of SO<sub>2</sub> added by measuring the change in weight of the SO<sub>2</sub> cylinder ( $102 \pm 1$  g) or the increase in volume ( $70 \pm 1$  mL) of the reagent mixture. Alternatively, add 70 mL of freshly drawn liquid SO<sub>2</sub> in small increments.

7.1.2 *Solvent Mixture*—Mix 1 volume of anhydrous (less than 0.1 % H<sub>2</sub>O) pyridine with 4 volumes of anhydrous (less than 0.1 % H<sub>2</sub>O) ethylene glycol.

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

NOTE 4—If adequately dry reagents cannot be procured, they can each be dried by distillation through a multiple-plate column, discarding the first 5 % of material distilling overhead and using the 95 % remaining. Drying may also be accomplished by the addition of 1 volume of toluene or cyclohexane to 19 volumes of the pyridine-glycol, or of the pyridine ethylene glycol monomethyl ether mixture, followed by distillation; the first 5 % distilled is discarded and the residual 95 % is used.

## 8. Sampling

8.1 *Hygroscopic Solvents*, including for example, ketones, acetates, alcohols, and glycol ethers, absorb ambient moisture. It is essential to avoid changes in the water content of these materials during sampling operations. Errors from this source are particularly significant in the analysis of materials having low water content. When analyzing materials that absorb ambient water readily, limit as much as possible contact with air in transferring the specimen into the titration vessel. Avoid intermediate sample containers, if possible.

<sup>4</sup> 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 Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,<sup>1</sup> which you may attend.

<sup>5</sup> 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 Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,<sup>1</sup> which you may attend. These specifically designed burets present the minimum contact of reagent with stopcock lubricant.

<sup>6</sup> *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 Pharmacopoeia and National Formulary*, U.S. Pharmacopoeial Convention, Inc. (USPC), Rockville, MD.

<sup>7</sup> 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 Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,<sup>1</sup> which you may attend.