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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.~~4~~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

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[1] This test method is under the jurisdiction of ASTM Committee ~~D-1~~ 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] The sole source~~

[3] *Annual Book* 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 suuppliers, please provide this information to*~~ ASTM ~~Headquarters. Your comments will receive careful consideration at a meeting of the responsibile technical committee,[1] which you may attend.~~ *Standards*, Vol 14.02.

produced according to the following reactions:

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

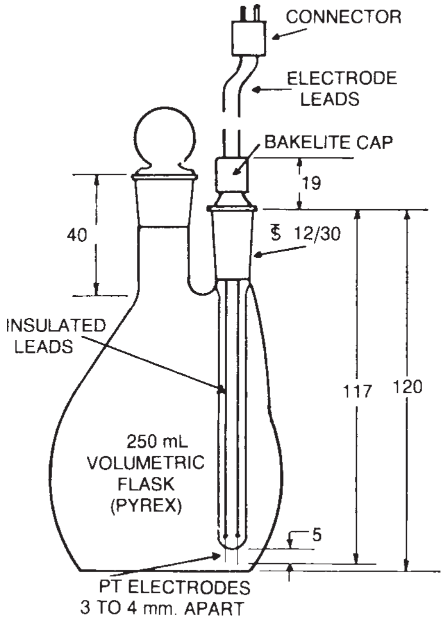
4.2 To determine water, Karl Fischer reagent (a solution of iodine, pyridine, and sulfur dioxide, in the molar ratio of 1 + 10 + 3) dissolved in anhydrous 2-methoxyethanol is added to a solution of the sample in anhydrous pyridine-ethylene glycol (1 + 4) until all water present has been consumed. This 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.

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.



NOTE 1—All dimensions in millimetres.

FIG. 1 Titration Flask Assembly

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]

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[4] The sole source of supply of ~~instrument depolarization indicator~~ flasks known to the committee at this time is ~~Fisher Scientific Co. (need address).~~ the Rankin Glass Blowing Co., 3920 Franklin Canyon Road, Martinez, CA. If you are aware of alternative su~~u~~ppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsib~~i~~ile technical committee,[1] which you may attend.

[5] The sole source of supply of ~~automatice dispensing burets, No. J-821,~~ instrument depolarization indicator known to the committee at this time is ~~Scientifice glass Apparatus Co., Bloomfield NJ.~~ Fisher Scientific Co. (need address). If you are aware of alternative su~~u~~ppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsib~~i~~ile technical committee,[1] which you may ~~attend. These specifically designed burets present the minimum contact of reagent with stopcock lubricant.~~ attend.

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.

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.

9. Standardization of Reagent

9.1 Standardize the Karl Fischer reagent each day used by either the color or instrument end point (Section 3) method using the same procedure as used for titrating the sample.

9.1.1 Add to each flask 25 mL of ethylene glycol-pyridene mixture, and titrate this as described in Section 10. Add to the solvent thus titrated, in place of the sample, 0.15 to 0.18 g of water from a weighing bottle or weighing pipet, weighed to the nearest 0.1 mg. Complete titration with Karl Fischer reagent as described in Section 10.

9.1.2 Calculate the equivalency factor, W, of the reagent in terms of water content per millilitre by means of the following equation:

$$W = A/V \tag{2}$$

~~*Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on~~

[6] The sole source of supply of automatic dispensing burets, No. J-821, known to the committee at this time is Scientifice glass Apparatus Co., Bloomfield NJ. If you are aware of ~~reagents not listed by~~ alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the ~~American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and~~ responsible technical committee,[1] which you may attend. These specifically designed burets present the ~~*United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.~~ minimum contact of reagent with stopcock lubricant.

~~[7] 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~~

[7] *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of ~~alternative suppliers, please provide this information to ASTM Headquarters. Your comments will receive careful consideration at a meeting of~~ reagents not listed by the ~~responsibile technical committee,[1] which you may attend.~~ 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] Supporting data~~

[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. ~~Request RR: D01 – 1049.~~ Your comments will receive careful consideration at a meeting of the responsible technical committee,[1] which you may attend.

where:
W = equivalency factor, mg of water per mL,
A = weight of water used in the standardization, mg, and
V = volume of Karl Fischer reagent required, mL.

10. Procedure

10.1 Introduce 10 to 25 mL of the anhydrous solvent mixture (pyridine-glycol, 1 + 4) into the titration vessel, making sure, if an instrument end point apparatus is used, that the electrodes are covered by this amount of solvent. If the color end point is to be determined, make up a second flask as well.

10.2 Adjust the stirrer, if any, to provide adequate mixing without splashing. Titrate the mixture to the instrumental end point (see 3.1), or the color end point (see ~~section 3.2~~ 3.1.2), with Karl Fischer reagent. If the color end point is to be observed, titrate one flask to the orange-red end point and the second to match the first. Set aside the first flask as a comparison standard for titrating the specimen.

10.3 To the titration mixture thus prepared, add an amount of specimen as indicated in Table 1. Exercise care when the specimen is transferred so that water is not absorbed from the air, particularly under conditions of high humidity. Again, titrate the mixture with Karl Fischer reagent to the same instrumental or color end point previously employed. Record the amount of reagent used to titrate the water in the specimen.

NOTE 5—(*a*) *Ketones*—In titrating ketones when greatest precision is required, cool the reaction mixture in ice water during the addition of Karl Fischer reagent.

(*b*) Organic Acids—Cool the reaction mixture in ice water prior to the addition of Karl Fischer reagent.

NOTE 6—When using the volumetric flask type titration vessel in humid climates, place a piece of thin sheet rubber over the mouth of the vessel; provide a small hole for introducing the buret tip. In less humid climates it is sufficient to lower the tip of the buret deeply into the long neck of the titration flask.

NOTE 7—In titrating with the volumetric flask type titration vessel, avoid wetting the stopper and upper end of the flask with either the reagent or the sample solvent. Each time the titration is interrupted, touch the buret tip to the neck of the flask to remove droplets which, if not removed, would absorb moisture from the atmosphere. When the flask is removed from under the buret tip, wipe the tip with a clean dry cloth in a downward motion.

11. Calculation

11.1 Calculate the water content of the specimen as follows:

$$\text{Water, \%, by weight} = (V \times W)/(10 \times S) \tag{3}$$

where:
V = volume of Karl Fischer reagent required for titrating by the specimen, mL,
W = equivalency factor for Karl Fischer reagent, water per millilitre of reagent, mg, and
S = specimen weight used, g.

NOTE 8—If specimen was added volumetrically by means of a calibrated volumetric pipet, then S = volume of specimen × density of specimen, g.

12. Report

12.1 For water concentrations below 0.5 %, report all results to 0.001 %. Two determinations which agree within 0.008 %, absolute, are acceptable for averaging (95 % confidence level).

13. Precision and Bias

13.1 *Precision for Water 0.100 to 0.500 % by Weight*—On the basis of an interlaboratory study in which one operator made duplicate determinations in each of eight different laboratories, on two days, on samples of acetone containing 0.118 and 0.406 % water and of methyl ethyl ketone containing 0.050 and 0.176 % water, the following criteria should be used for judging at the 95 % confidence level the acceptability of results on samples containing less than 0.5 % water:

NOTE 9—Supporting documentation for this interlaboratory study is not available from ASTM Headquarters.

13.1.1 *Repeatability*—Two results, each the mean of duplicate determinations, obtained by the same operator should be considered suspect if they differ by more than 0.015 % absolute.

13.1.2 *Reproducibility*—Two results, each the mean of duplicate determinations, obtained by operator in different laboratories should be considered suspect if they differ by more than 0.027 % absolute.

TABLE 1 Recommended Specimen Sizes

Water Content, %	Specimen Size	Manner Specimen Taken
2.5 to 10	weight containing 0.15 to 0.18 g of H_2O	weighing pipet
0.5 to 2.5	10 mL	calibrated volumetric pipet
Below 0.5	25 mL	same as for 0.5 to 2.5

13.2 *Precision for Water 0.010 to 0.100 % by Weight*[9]—In another interlaboratory study, one operator in each of seven different laboratories, on two different days, made duplicate determinations on five randomly coded samples of hexyl acetate containing 0.015, 0.034, 0.052, 0.071, and 0.098 % water. One of the seven laboratories used three different equipment or procedural variations, or both, thereby making this, in effect, a nine interlaboratory study. The statistically designed study covered a variety of equipment, analytical methods, and reagents using the Karl Fischer chemistry.

13.2.1 *Repeatability*—Two results, each the mean of duplicate determinations, obtained by the same analyst should be considered suspect if they differ by more than 0.030 $\sqrt{\bar{x}}$ % absolute, where $\bar{x}$ is the average of two determininations.

13.2.2 *Reproducibility*—Two results, each the mean of duplicate determinations, obtained by analysts in different laboratories should be considered suspect if they differ by more than 0.060 $\sqrt{\bar{x}}$ % absolute, where $\bar{x}$ is the average of two determinations.

13.3 *Bias*—Bias cannot be determined for this test method because there is no available material having an accepted reference value. Refer to 8.1 and Note 5, Note 6, and Note 7 for factors that might influence test bias.

14. Keywords

14.1 Karl Fisher method; solvents; water content

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[9] Supporting data is available from ASTM International Headquarters. Request RR: D01–1049.

SUMMARY OF CHANGES

Committee D01.35 has identified the location of selected changes to this standard since the last issue (D 1364 - 95 (1999)) that may impact the use of this standard.

(1) Added reference to Practice E 29 in Section 1.3 of the Scope.
(2) Added Practice E 29 to Referenced Documents section.

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