Designation: D890 – 12 (Reapproved 2016)

Standard Test Method for Water in Liquid Pine Chemicals[1]

This standard is issued under the fixed designation D890; 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 These test methods cover the quantitative determination of dissolved or occluded water present in any proportion in liquid pine chemicals, such as turpentine, pinene, dipentene, pine oil, tall oil, and tall oil fatty acids. Three methods of moisture testing are included. The Karl Fisher titration method is the preferred method for testing tall oil, Test Methods D803.

1.1.1 The Karl Fischer Titration method is based on the reaction between water and a complex reagent[2] consisting of iodine, sulfur dioxide, pyridine, and methanol, whereby the iodine is converted to a colorless compound. The appearance of a persistent iodine color in the reaction mixture indicates the complete removal of free water by reaction with the reagent, and the endpoint may be measured colorimetrically. Automatic titrators find this endpoint by the restoration of a current strength when the resistance provided by the presence of water is eliminated. Amperometric automatic titrators find this endpoint by detecting the current flow that occurs once water is eliminated.

1.1.2 The coulometric titration method determines water content by electronic integration of a current sufficient to generate the precise amount of iodine from the required reagent to react with the water in the sample.

1.1.3 The azeotropic method utilizes the relatively low boiling point of water, as compared with other sample constituents, in a toluene or xylene matrix so that water is collected in a trap and measured.

1.2 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

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.*

2. Referenced Documents

2.1 *ASTM Standards:*[3]

D803 Test Methods for Testing Tall Oil

D1364 Test Method for Water in Volatile Solvents (Karl Fischer Reagent Titration Method)

3. Significance and Use

3.1 Many pine chemical products contain water as a result of the processes used for their production. Typically refined products such as terpenes, pine oil, tall oil fatty acids, and distilled tall oil contain only traces of water, but crude tall oil might contain 0.5 to 2.5 % of water. Although the Karl Fischer and coulometric methods are most applicable to low levels of moisture, these can be and are used at higher levels. The azeotropic distillation method is generally used at higher levels.

Moisture By Karl Fischer Titration (Preferred method)

4. Apparatus

4.1 *Titration Vessel,* preferably closed, with stirring capabilities,

4.2 *Buret,* capable of being read at 0.1 mL divisions, or automatic buret, or

4.3 *Automatic Karl Fischer titrator.*

4.4 *Balance,* capable of weighing to the nearest 0.0001 g.

5. Reagents

5.1 *Karl Fischer Reagent, or Other Suitable Reagent, such as Pyridine-free Adaptations of Karl Fischer Reagent.* Reagents vary in strength (titer). This test method is written

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[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 D01.34 on Pine Chemicals and Hydrocarbon Resins.

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[2] This procedure has been adapted from the method of Karl Fischer published in *Zeitschrift für Angewandte Chemie*, Vol 48, 1935, p. 395; *Chemical Abstracts*, Vol 29, 1935 p. 6532; as modified by Smith, Bryant, and Mitchell, *Journal*, Am. Chemical Soc., Vol 61, 1939, p. 2407; and further modified by Axel Johansson, *Svensk Papperstidning*, Vol 50, No. 11B, 1947, p. 124; see also *Publication 19* of the Swedish Wood Research Institute, Wood Chemistry and Paper Technique (Stockholm) (1947). Karl Fischer reagent is available from various laboratory supplies. Pyridine-free adaptations of the Karl Fischer reagent are available commercially.

[3] 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.

assuming a titer of 5 mg water/mL reagent. Recommended additions of water in this test method may need to be adjusted depending on the titer of the reagent.

5.2 *Methanol*—ACS grade.

6. Standardization of Iodine Reagent

6.1 Add methanol to the titration vessel, and titrate with reagent until the lemon-yellow color just changes to a red-brown color, or, if an automatic titrator is used, until the readings indicate no free water present. The titration vessel is now ready for titrating, and is considered conditioned.

6.2 Add a drop of water, weighed to the nearest 0.0001 g, to the titration vessel by use of a transfer pipet, or a weighing pipet, weighing the pipet before and after the addition. Each drop will weigh approximately 0.03 g and will require roughly 6 mL of titrant having a titer of 5 mg/mL. Alternatively, a 25-µL, or other volume syringe may be used to introduce exact volumes.

6.3 Titrate with reagent until the lemon-yellow color just changes to a red-brown color, or, if an automatic titrator is used, until the readings indicate no free water present. Record the mL of titrant used.

6.4 Calculate the water equivalent of the iodine reagent, in milligrams of water per millilitre of reagent, as follows:

$$T = \frac{W \times 1000}{V} \tag{1}$$

where:

T = water equivalent of the iodine reagent, mg/mL,
W = weighed water added, in g, and
V = iodine reagent, mL.

7. Procedure

7.1 Condition the titration vessel, as described in 6.1.

7.2 Add an amount of sample which will contain 50 mg or less water to the titration vessel.

7.3 Titrate to a red-brown color end point, as with previous titrations, or, if an automatic titrator is used, titrate according to the instrument's operating instructions.

8. Calculation

8.1 Calculate the percentage of water as follows:

$$\text{Water, \%} = \frac{V \times T}{W \times 10} \tag{2}$$

where:

V = iodine reagent required for the titration of the sample, in mL,
T = (titer), water equivalent of the iodine reagent, and
W = sample used, g.

8.2 Report to the nearest 0.01 %.

9. Precision and Bias

9.1 The precision and bias of this test method for measuring water content of the most highly refined pine chemical products are essentially as specified in Test Method D1364. It is not practical to measure the precision for moisture content of pine chemical products, since these test methods are applicable to many of these products that vary widely in purity, and the precision would vary with the purity of each product.

Moisture By Coulometric Titration

10. Apparatus

10.1 *Coulometric Karl Fischer Titrator.*

10.2 *Sample Vials,* 8-mL or 4-dram.

10.3 *Medicine Dropper.*

10.4 *Disposable Plastic Syringes,* 1-cc with 16, 18 or 20 gage needles.

10.5 *Syringe,* 10 µL.

11. Reagents

11.1 See 5.1.

12. Instrument Preparation

12.1 Prepare and calibrate the instrument according to the manufacturer's operating instructions. This generally includes:

12.1.1 Clean and assemble the titration chamber.

12.1.2 Pour titration solution into the chamber.

12.1.3 Add the iodine generator solution to the generator assembly.

12.1.4 Put the instrument in the STANDBY position.

12.1.5 Slowly add water, or a solution containing water, (normally by injection with a syringe).

12.1.6 Continue the addition until the instrument indicates that excess water is present, usually by a light or liquid crystal display (LCD) reading.

12.1.7 Stop the addition of water.

12.1.8 Let the instrument stabilize for 1 h in the STANDBY position.

12.2 Verify the instrument by injecting a known amount of water, usually 1 µL to 5 µL, below the surface of the titration solution.

12.3 Put the instrument in the TITRATE or RUN position and record the reading when the END light comes on or a message appears that the titration is complete.

12.4 Record the reading. This reading is usually in micrograms or milligrams of water and should be within ±5 % of the amount of water added. Example: for 5 µL of water the reading should be 5000 µg ± 250 µg.

13. Procedure

13.1 Some coulometric titrators require that the sample be injected through a septum. If this is the case proceed as follows (for instruments that do not require through-septum injections, go to 13.2):

13.1.1 Draw approximately 0.5 mL of sample into a 1-cc disposable syringe. Wipe the needle clean with a dry paper towel.

13.1.2 Weigh the syringe with the sample to the nearest 0.0001 g. Record this weight.

13.1.3 Inject about 0.1 to 0.2 mL of the sample into the titrator. Withdraw the syringe.

13.1.4 Weigh the syringe to the nearest 0.0001 g and record this weight.

13.1.5 Proceed to 13.6.

13.2 Add approximately 4 mL of sample in a small sample vial. Do not allow the sample to touch the outside of the vial.

13.3 Put a medicine dropper into the vial, and weigh the vial, sample, and medicine dropper together on an analytical balance to the nearest 0.0001 g. Record this weight.

13.4 Using the medicine dropper, introduce one to two drops of sample into the coulometric titrator.

13.5 Put the medicine dropper back in the vial, and weigh to the nearest 0.0001 g. Record this weight.

13.6 Begin the titration.

14. Calculation

14.1 Calculate the percentage of water as follows:

$$\text{Water, \%} = \frac{\text{Water, } \mu\text{ g}}{\text{Sample Weight, g} \times 10\,000} \quad (3)$$

14.2 Report to the nearest 0.01 %.

15. Precision and Bias

15.1 It is not possible to specify the precision of this coulometric titration procedure for measuring the water content of pine chemical products because the procedure is not widely used and insufficient data could be generated to develop a meaningful precision and bias statement.

Moisture By Azeotropic Distillation

16. Apparatus

16.1 *Flask,* 1-L, short-neck, round-bottom glass flask or Erlenmeyer flask. Use of smaller flasks should be accompanied by reductions in sample size and solvent.

16.2 *Electric Mantle,* with variable-resistance controller.

16.3 *Condenser,* connected to the flask and discharging into a trap.

16.4 *Trap,* 5-mL, subdivided into 0.1 mL divisions, with each 1 mL line numbered.

17. Reagents

17.1 *Toluene or Xylene*—Reagent grade, moisture free.

18. Procedure

18.1 Weigh 100 g of sample into the flask. Add a few boiling stones. Fit the flask with a moisture trap and a reflux condenser.

18.2 Add 150 mL of toluene or xylene to the flask and fill the moisture trap with the solvent.

18.3 Heat gently until the solvent begins to reflux. Continue vigorous refluxing for 2 h. Wash the condenser down with 5-mL portions of solvent from time to time during the reflux period, and with four 5-mL portions of solvent at the end. A drop of water on the condenser may be dislodged with a fine wire or a stirring rod wet with methanol.

18.4 Record the volume of water in the trap.

19. Calculation

19.1 Calculate the percentage of water as follows:

$$\text{Water, \%} = \frac{V}{W} \times 100 \quad (4)$$

where:

V = volume of water, mL
W = weight of sample, g.

19.2 Report to the nearest 0.1 %.

20. Precision and Bias

20.1 It is not possible to specify the precision of this azeotropic distillation procedure for measuring the water content of pine chemical products because this procedure is no longer widely used and insufficient data could be generated to develop a meaningful precision and bias statement.

21. Keywords

21.1 azeotropic; coulometric, Karl Fischer; moisture; naval stores; pine chemicals; pine oil; tall oil; terpenes; turpentine; water