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AMERICAN SOCIETY FOR TESTING AND MATERIALS
100 Barr Harbor Dr., West Conshohocken, PA 19428
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Standard Test Method for Water in Fatty Nitrogen Compounds[1]

This standard is issued under the fixed designation D 2072; 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 test method was prepared jointly by ASTM and the American Oil Chemists' Society.

ε[1] NOTE—Former Footnote 4 was deleted editorially in May l998.

1. Scope

1.1 This test method covers the determination of water in fatty nitrogen compounds by titration with a water-methanol solution after addition of an excess of Karl Fischer reagent.

1.2 The procedures appear in the following order:

	Sections
Fatty Primary Amines, Diamines, and Amidoamines	4-8
Difatty Secondary Amines	9-12
Quaternary Ammonium Chlorides	13-16

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.* Specific hazard statements are given in 5.3, 6.1, and 11.2.

2. Referenced Documents

2.1 *ASTM Standards:*

D 1193 Specification for Reagent Water[2]

D 1364 Test Method for Water in Volatile Solvents (Fischer Reagent Titration Method)[3]

3. Summary of Test Method

3.1 An excess of Karl Fischer reagent is added to the specimen dissolved in the prescribed solvent. After reaction with the water in the specimen, the excess Karl Fischer reagent is back-titrated with water-methanol solution. The end point is best detected electrometrically, but with practice it may be satisfactorily determined visually.

FATTY PRIMARY AMINES, DIAMINES, AND AMIDOAMINES

4. Apparatus

4.1 *Buret and Bottle Assemblies* (or other convenient arrangement), protected with silica gel so as to maintain Karl Fischer reagent and water-methanol solutions free from contamination with moisture either through the atmosphere or otherwise (Note 1). The titration should be performed in a closed system to avoid the absorption of water. The electrode and buret shall be mounted through a close-fitting stopper, and provision made for mechanical stirring by means of a magnetic stirrer.

NOTE 1—It is essential that the Karl Fischer reagent, water-methanol solution, and anhydrous methanol be protected from atmospheric moisture at all times. In humid seasons or climates, the drying tubes used to protect the reagents against moisture in the air must be watched closely. The silica gel must be changed as soon as there is evidence of color change in it. Care also must be taken to minimize the exposure of the sample and solutions to atmospheric moisture during the determinations.

4.2 *Magnetic Stirrer*, that can be used with the closed titration beaker with inert plastic-coated stirring bar.

4.3 *Pipet*, automatic, 25-mL.

4.4 *Pipet*, weighing, or equivalent for weighing water, for standardization of reagent.

4.5 *Electrometric Titrator* of the "dead stop" type, equipped with platinum electrodes. On operation a small electrical potential is imposed across the electrodes. At the end point there is a change in the flow of current due to the change in polarization of the electrodes.

5. Reagents

5.1 *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.[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.

5.2 *Purity of Water*—Unless otherwise indicated, references

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[2] *Annual Book of ASTM Standards*, Vol 11.01.

[3] *Annual Book of ASTM Standards*, Vol 06.04.

[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.

to water shall be understood to mean reagent water conforming to Type II of Specification D 1193.

5.3 *Acetic Acid, Glacial* (CH_3COOH). **Warning**—(see 6.2).

5.4 *Karl Fischer Reagent*—Suitable reagent is available from most chemical supply houses or see Test Method D 1364.

5.5 *Methanol*, anhydrous, water content less than 0.05 %.

5.6 *Water-Methanol Solution*—Prepare by weighing approximately 10 g of water with the aid of a weighing pipet into a 2-L volumetric flask. Dilute to the mark with methanol and mix well. This solution will contain approximately 5 mg (weighed) of water per millilitre plus the amount of water normally present in the methanol. Standardize as described in Section 7.

6. Hazards

6.1 Fatty amines and diamines can sensitize and irritate. Wash from clothing and body surfaces immediately on contact.

6.2 **Warning**—Glacial acetic acid will cause burns of the skin and eyes. Use care in handling the acid. In case of contact, immediately flush skin or eyes with plenty of water.

6.3 **Warning**—The U. S. Food and Drug Administration has declared that chloroform is injurious to health. Care should be used in handling chloroform as it can be absorbed through the skin.

7. Standardization of Reagents

7.1 Deliver from a buret 25 mL of Karl Fischer reagent in a dry, 300-mL Berzelius beaker. Titrate (see 4.1) with the water-methanol solution, adding it slowly but steadily, so that it is thoroughly dispersed by the stirrer until the end point is approached. Add dropwise when nearing the end point which is indicated by the change in color from dark reddish-brown to golden yellow. Titrate to completion electrometrically.

NOTE 2—Test Method D 1364 describes the visual endpoint, but in that method the titration is direct, not a back-titration.

7.2 Deliver from a buret 25 mL of Karl Fischer reagent into a dry, 300-mL beaker. Pipet 25 mL of methanol into the beaker. Repeat the titration as described in 7.1.

7.3 Calculate the water factor, *F*, as follows:

$$F = \frac{N(L - M)}{25 + M - L} + N \quad (1)$$

where:

- F = water per millilitre of water-methanol solution, mg,
- L = water-methanol solution required for titration of 25 mL of Karl Fischer reagent, mL,
- M = water-methanol solution required for titration of 25 mL of Karl Fischer reagent plus 25 mL of absolute methanol, mL, and
- N = water added per millilitre to the water-methanol solution described in 5.6, mg.

8. Procedure

8.1 Melt the sample, if it is not already liquid, in a water bath. Mix thoroughly and weigh into a dry beaker 10 g of sample or enough to give 5 to 25 mg of water.

8.2 Pipet 25 mL of glacial acetic acid and stir to dissolve.

8.3 Deliver from a buret 25 mL of Karl Fischer reagent. Back-titrate with water-methanol solution slowly but steadily, stirring so that it is thoroughly dispersed by the stirrer until the end point is approached. Add dropwise when nearing the end point which is indicated by the change in color from dark reddish-brown to golden yellow. Titrate to the same end point used in standardization.

8.4 Prepare a blank using 25 mL of Karl Fischer reagent and 25 mL of glacial acetic acid. Carry through the procedure separately and in an identical manner as for the specimen.

9. Calculation

9.1 Calculate the percent of water as follows:

$$\text{Water, \%} = [(B - V) \times F]/(S \times 10) \quad (2)$$

where:

- B = water-methanol solution required for titration of the blank, mL,
- V = water-methanol solution required for titration of the specimen, mL,
- F = water factor determined in accordance with Section 7, and
- S = specimen weight used, g.

DIFATTY SECONDARY AMINES

10. Apparatus

10.1 See Section 4.

11. Reagents

11.1 The reagents used in this procedure are the same as those listed in 5.1, 5.2, 5.4, 5.5, 5.6, and 11.2.

11.2 *Chloroform* ($CHCl_3$). **Warning**—See 6.3.

12. Procedure

12.1 Proceed in accordance with Section 8, except in 8.2 use 25 mL of $CHCl_3$ heated to not over 30°C instead of acetic acid. Also, in 8.4 substitute $CHCl_3$ for acetic acid when preparing the blank.

13. Calculation

13.1 See Section 9.

QUATERNARY AMMONIUM CHLORIDES

14. Apparatus

14.1 See Section 4.

15. Reagents

15.1 The reagents used in this procedure are the same as those listed in 5.1, 5.2, 5.4, 5.5, and 5.6.

16. Procedure

16.1 Proceed in accordance with Section 8 except to omit 8.2. In 8.3, stir to dissolve after addition of the Karl Fischer reagent. In 8.4 omit the acetic acid when preparing the blank.

17. Calculation

17.1 See Section 9.

18. Precision and Bias

18.1 Precision and bias were not established at the time this

method was written. An effort is being made to obtain the precision and, if obtainable, it will be published in future revisions. This test method has been in use for many years, and its usefulness has been well established.

19. Keywords

19.1 fatty nitrogen compounds; Karl Fischer reagent; water