Designation: D 3401 – 97

An American National Standard

Standard Test Methods for Water in Halogenated Organic Solvents and Their Admixtures[1]

This standard is issued under the fixed designation D 3401; 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 These test methods describe the use of the Karl Fischer (KF) titration for determination of water in halogenated organic solvents and mixtures thereof. Water concentrations from 2 to 1000 ppm can be determined in these solvents. Two test methods are covered as follows:

1.1.1 *Test Method A, Water Determination Using a Coulometric KF Titrator*—The coulometric test method is known for its high degree of sensitivity (typically < 10 µg H_2O) and should be the test method of choice if water concentrations are typically below 50 ppm or if only small amounts of sample are available for water determinations. This test method requires the use of equipment specifically designed for coulometric titrations.

1.1.2 *Test Method B, Water Determination Using a Volumetric KF Titrator*—The volumetric test method is a more traditional approach to KF water determinations. Although titrators are specifically designed for KF volumetric determinations, many automatic titrators on the market can be adapted to perform KF titrations.

1.2 Either of these test methods can be used to determine typical water concentrations (15 to 500 ppm) found in halogenated solvents.

1.3 These test methods recommend the use of commercially available Karl Fischer titrators and reagents.

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.* For specific precautionary statements, see Sections 11 and 15.

2. Referenced Documents

2.1 *ASTM Standards:*

E 203 Test Method for Water Using Karl Fischer Titration[2]

3. Summary of Test Methods

3.1 In the Karl Fischer reaction, water will react with iodine in the presence of sulfur dioxide, alcohol, and an organic base according to the following equation:

$$H_2O + I_2 + SO_2 + CH_3OH + 3RN \rightarrow (RNH)SO_4CH_3 + 2(RNH)I \quad (1)$$

where RN = organic base.

3.2 When the volumetric titration test method is used for this determination, the halogenated sample is added to a KF solvent that usually consists of sulfur dioxide and an amine dissolved in anhydrous methanol. This solution is titrated with an anhydrous solvent containing iodine. The iodine titrant is first standardized by titrating a known amount of water.

3.3 In the coulometric titration test method, the sample is injected into an electrolytic cell where the iodine required for the reaction with water is produced by anodic oxidation of iodide. With this technique, no standardization of reagents is required.

3.4 In both test methods, the end point is determined amperometrically with a platinum electrode that senses a sharp change in cell resistance when the iodine has reacted with all of the water in the sample.

4. Significance and Use

4.1 High water concentrations can have a detrimental effect on many uses of halogenated solvents.

4.1.1 Water can cause corrosion and spotting when solvents are used for metal cleaning.

4.1.2 Water can reduce the shelf life of aerosol formulations.

4.1.3 Water can inhibit desired reactions when solvents are used in formulations.

5. Interferences

5.1 Certain compounds or classes of compounds interfere with the accurate determination of water by the Karl Fischer test method. They include aldehydes, ketones, free halogens, ferric salts, and strong oxidizing and reducing agents.

5.2 Free halogens can oxidize the iodate in the KF reagents to form iodine; this causes erroneously low water values.

[1] These test methods are under the jurisdiction of ASTM Committee D-26 on Halogenated Organic Solvents and Fire Extinguishing Agents and are the direct responsibility of Subcommittee D26.04 on Test Methods.

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[2] *Annual Book of ASTM Standards*, Vol 15.05.

5.3 A more detailed discussion of KF interferences can be found in Test Method E 203 and other sources.[3,4]

6. Apparatus

6.1 *Coulometric Titrator*, [5] (for Test Method A only) consisting of a single or dual bath electrolytic cell, dual platinum electrode, magnetic stirrer, and control unit.

6.2 *Volumetric Titrator*, [5] (for Test Method B only) consisting of a titration cell, dual platinum electrode, magnetic stirrer, dispensing buret, and control unit.

6.3 *Syringes*, 2, 5, 10, or 20-mL sizes.

6.4 *Syringe*, 5-µL size.

6.5 *Silicon Rubber Blocks or Silicon Rubber Septa*.

6.6 *Drying Oven*, air circulating.

6.7 *Desiccator*.

6.8 *Analytical Balance*, capable of weighing to ±0.01 g.

7. Reagents

7.1 *Anode Reagent*, for dual bath titration (for Test Method A only), use reagent recommended by manufacturer of titrator.

7.2 *Cathode Reagent*, for dual bath titration (for Test Method A only), use reagent recommended by manufacturer of titrator.

7.3 *Single Bath Reagent*, (for Test Method A only), use reagent recommended by manufacturer of titrator.

7.4 *Karl Fischer Volumetric Titrant*, [4] (for Test Method B only) typically consists of a mixture of an organic amine, sulfur dioxide, and iodine dissolved in a non-hydroscopic solvent(s). Reagents with titers of 1.00, 2.00, and 5.00 mg of H_2O/mL can be commercially obtained.

7.5 *Karl Fischer Solvent*, [4] (for Test Method B only) typically consists of a mixture of an organic amine and sulfur dioxide dissolved in anhydrous methanol.

NOTE 1—Pyridine was the organic amine that was traditionally used in Karl Fisher reagents, however, pyridine-free formulations are now available and preferred by most KF instrument manufacturers for use with their equipment. Pyridine-free reagents are said to be less toxic, less odorous, and more stable than pyridine types.

8. Sampling

8.1 Since halogenated solvents normally contain low concentrations of water, care must be taken to eliminate the introduction of water from sampling equipment and atmospheric moisture.

8.2 Without taking the proper sampling precautions, more error is typically introduced into the determination of water through sampling techniques than in the titration process itself.

8.3 Dry sample bottles and closures in an oven at 110°C for several hours. Place caps on the bottles immediately after removing from the oven.

8.4 Transfer solvent to the bottles as quickly as possible. Adjust the liquid level to come within 1 in. of the top of the bottle. Immediately place the cap on the bottle and tighten.

8.5 When removing a portion of sample from the bottle for KF analysis, use pipets or syringes that have been thoroughly dried. Replace the cap on the bottle immediately.

8.6 If more than one portion of sample is to be taken from the bottle or if the sample is to be retained for further water analysis, it is a good practice to blanket the top of the bottle with dry nitrogen when removing the sample. If septum cap closures are being used, dry nitrogen can be introduced with a syringe at the same time a portion of the sample is being removed with a second syringe.

TEST METHOD A—WATER DETERMINATION USING A COULOMETRIC KF TITRATOR

9. Summary of Test Method

9.1 The dual bath coulometric titration cell consists of a sealed vessel containing both an anode and cathode compartment. The anodic compartment usually contains a solution consisting of sulfur dioxide, iodide, and an amine in a methanol/chloroform solvent. The cathodic compartment contains similar reagents optimized for cathodic reduction.

9.2 When a sample containing water is injected into the anode compartment, the electrolytic cell generates its own supply of iodine from the iodide present. The iodine reacts stoichiometrically with the water and the completion of the reaction is detected with a platinum sensing electrode. The coulombs of electricity required to generate the necessary amount of iodine is then translated by the microprocessor in the control unit into the amount of water that was present in the sample.

9.3 The single bath coulometric titration cell consists of a sealed vessel filled with single bath reagent and dual platinum electrodes. When a sample containing water is injected into the vessel, the electrolytic cell generates its own supply of iodine from the iodide present in the single bath reagent. The iodine reacts stoichiometrically with the water and the completion of the reaction is detected by a platinum sensing electrode. The coulombs of electricity required to generate the necessary amounts of iodine is then translated by the microprocessor in the control unit into the amount of water that was present in the sample.

10. Verification of Instrument Accuracy

10.1 Coulometric titrators do not have a titrant that needs to be standardized since the iodine is being generated on demand by the titration cell. However, occasional checks of the instrument accuracy are recommended. This can be done by titrating a known amount of water and comparing this amount with the amount of water reported by the titrator.

10.2 Use a 5-µL syringe to inject exactly 3.0 µL of water into the titration cell. Once the titration is complete, the titrator should report a value of 3000 µg (3.0 mg) H_2O. The deviation from this value should not be larger than 10 %. If the value is larger than 10 %, consult the instrument manual or manufacturer to determine the cause.

10.3 Alternatively, standard solutions containing known

[3] Mitchell, J., Jr. and Smith, D. M., *Aquametry—A Treatise on Methods for the Determination of Water, Part III—The Karl Fischer Reagent*, 2nd ed., J. Wiley and Sons, Inc., New York, NY, 1977.

[4] *Hydranal—Eugen Scholz Reagents for Karl Fischer Titration*, 4th ed., by Riedel-deHaen Aktiengesellschaft (US Distributor—Cresent Chemical Co., Inc.).

[5] Automatic coulometric and volumetric titrators are manufactured by many different companies. Models that have been found satisfactory for this purpose are available from Fisher Scientific, EM Science, Metrohm, Mettler, Photovolt, Mitsubishi, and others.