



Designation: E 104 – 85 (Reapproved 1996)

Standard Practice for Maintaining Constant Relative Humidity by Means of Aqueous Solutions¹

This standard is issued under the fixed designation E 104; 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 practice describes two methods for generating constant relative humidity (rh) environments in relatively small containers.

1.2 This practice is applicable for obtaining constant relative humidities ranging from dryness to near saturation at temperatures spanning from 0 to 50°C.

1.3 This practice is applicable for closed systems such as environmental conditioning containers and for the calibration of hygrometers.

1.4 This practice is not recommended for the generation of continuous (flowing) streams of constant humidity unless precautionary criteria are followed to ensure source stability. (See Section 9.)

1.5 **Caution**—Both saturated salt solutions and sulfuric acid-water solutions are extremely corrosive, and care should be taken in their preparation and handling. There is also the possibility of corrosive vapors in the atmospheres over the saturated salt solutions² and over the sulfuric acid solution.³

1.6 *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 more specific safety precautionary information see 1.5 and 10.1.

2. Referenced Documents

2.1 ASTM Standards:

D 1193 Specification for Reagent Water⁴

D 4023 Terminology Relating to Humidity Measurements⁵

¹ This practice is under the jurisdiction of ASTM Committee D-22 on Sampling and Analysis of Atmospheres and is the direct responsibility of Subcommittee D22.11 on Meteorology.

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² Opila, R., Jr., Weschler, C. J., and Schubert, R., "Acidic Vapors Above Saturated Salt Solutions Commonly Used for Control of Humidity," *IEEE Trans. Components, Hybrids and Manufacturing Technology*, Vol 12, No. 1, March 1989, pp. 114–120.

³ Kawasaki, K., and Kanou, K., "Control of Atmospheric Humidity for Aqueous Sulfuric Acid Solutions," Vol. III (A. Wexler, ed.), Reinhold Publishing Corporation, NY, 1964, pp. 531–534.

⁴ *Annual Book of ASTM Standards*, Vol 11.01.

⁵ *Annual Book of ASTM Standards*, Vol 11.03.

E 126 Test Method for Inspection and Verification of Hygrometers⁶

2.2 Other Document:

DIN50008 "Konstantklimate über waesserigen Loseungen" (Constant Climates Over Aqueous Solutions).

Part 1: Saturated Salt and Glycerol Solutions.

Part 2: Sulfuric Acid Solutions. (1981)⁷

3. Terminology

3.1 *non-hygroscopic material*—material which neither absorbs nor retains water vapor.

3.2 For definitions of other terms used in this practice refer to Terminology D 4023.

4. Summary of Practice

4.1 Standard value relative humidity environments are generated using selected aqueous saturated salt solutions or various strength sulfuric acid-water systems.

5. Significance and Use

5.1 Standard value relative humidity environments are important for conditioning materials in shelf-life studies or in the testing of mechanical properties such as dimensional stability and strength. Relative humidity is also an important operating variable for the calibration of many species of measuring instruments.

6. Interferences

6.1 Temperature regulation of any solution-head space environment to $\pm 0.1^\circ\text{C}$ is essential for realizing generated relative humidity values within $\pm 0.5\%$ (expected).

6.2 *Sulfuric Acid*—Water systems are strongly hygroscopic and can substantially change value by absorption and desorption if stored in an open container. Only freshly prepared solutions, or solutions which values have been independently tested for strength, should be used.

6.3 Some aqueous saturated salt solutions change composition following preparation by hydrolysis or by reaction with

⁶ *Annual Book of ASTM Standards*, Vol 14.03.

⁷ Published by Deutsches Institut für Normung, 4-10 Burggrafenstrasse Postfach 1107, D-1000 Berlin, Federal Republic of Germany. Also available from ANSI Publication Office, New York, NY.



environmental components (for example, carbon dioxide absorption by alkaline materials). These solutions should be freshly prepared on each occasion of use.

7. Apparatus

7.1 *Container*—The container, including a cover or lid which can be secured airtight, should be made of corrosion resistant, non-hygroscopic material such as glass. A metal or plastic container is acceptable if the solution is retained in a dish or tray made of appropriate material. Refer also to 9.2 for size restrictions.

7.2 *Hydrometers*—One or more hydrometers may be used to test sulfuric acid solution specific gravities for the range of humidities concerned. The hydrometer(s) should have a minimum scale division of 0.001. (Refer to Test Method E 126.)

8. Reagents and Materials

8.1 *Purity of Reagents*—Reagent grade chemicals shall be used for preparation of all standard solutions. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.⁸ 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.

8.1.1 Saturated salt solutions may be prepared using either amorphous or hydrated reagents (that is, reagents containing water of crystallization). Hydrated reagents are often preferred to amorphous forms for their solvating characteristics.

8.2 *Purity of Water*—Reagent water produced by distillation, or by ion exchange, or reverse osmosis followed by distillation shall be used. See Specification D 1193.

9. Technical Precautions

9.1 Although a container capable of airtight closure is described in Section 7, it may be desirable to have a vent under certain conditions of test or with some kinds of containers (changes in pressure may produce undesirable cracks in some types of containers). The vent should be as small as practical to minimize loss of desired equilibrium conditions when in use.

9.2 The container should be small to minimize the influence of any temperature variations acting upon the container and contents. A maximum proportion of 25 cm³ volume/cm² of solution surface area is suggested, and overall container headspace volume should be no larger than necessary to confine a stored item.

9.3 Measurement accuracy is strongly dependent on the ability to achieve and maintain temperature stability during actual use of any solution system. Temperature instability of $\pm 0.1^\circ\text{C}$ can cause corresponding instabilities in generated values of relative humidity of $\pm 0.5\%$.

9.4 The compatibility of any constant relative humidity system used for instrument calibration testing should be confirmed by reference to the instrument manufacturer's instructions.

9.5 Important considerations leading to stability should include (but are not necessarily limited to) the following:

9.5.1 Elimination of leakage paths.

9.5.2 Elimination of heat sources or heat sinks, or both, for temperature stability.

9.5.3 Limiting flow rate to preclude source carry-over.

10. Preparations of Aqueous Solutions

10.1 **Caution**—Saturated salt-water systems and sulfuric acid solutions should be regarded as hazardous materials. Refer to 1.5 and 1.6 for guidelines.

10.2 *Saturated Salt-Water Systems:*

10.2.1 Select a salt of characteristic value from Annex A1.

The reference document by Greenspan⁹ contains information on many other saturated salt solutions which may be used. These additional systems, however, are less accurately or less completely defined in value. Also, some may only be used when freshly prepared (to limit the influence of chemical instability such as hydrolysis or acid gas absorption). The salts listed in Annex A1 can be used for a year or more.

10.2.2 Place a quantity of the selected salt in the bottom of a container or an insert tray to a depth of about 4 cm for low rh salts, or to a depth of about 1.5 cm for high rh salts.

10.2.3 Add water in about 2-mL increments, stirring well after each addition, until the salt can absorb no more water as evidenced by free liquid. Although a saturated solution system is defined when any excess quantity of undissolved solute is present, it is preferred to keep the excess liquid present to a minimum for ease in handling and for minimal impact on stability should temperature variations occur.

10.2.4 Close the container and allow 1 h for temperature stabilization.

10.2.5 The container may be used as a reservoir from which quantities of slush can be transferred for use, or the entire container may be used for conditioning tests.

10.3 *Sulfuric Acid-Water Solutions:*

10.3.1 Determine the acid concentration corresponding to the desired relative humidity value from Annex A2, interpolating as necessary.

10.3.2 Measure sufficient working quantities of sulfuric acid reagent and reagent water so that, when mixed in proper proportion, a sufficient depth of liquid is available for proper floatation of a test hydrometer. (See Section 9.)

10.3.3 Measure solution specific gravity after the sulfuric acid-water solution has cooled following mixing. Refer to Annex A2 for desired values.

10.3.4 Store the prepared mixture in a container with a tight-fitting lid. Check solution specific gravity before each occasion of use.

11. Precision and Bias

11.1 Under ideal conditions, the bias (accuracy) of the

⁸ *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. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

⁹ Greenspan, L., "Humidity Fixed Points of Binary Saturated Aqueous Solutions," *Journal of Research*, National Institute of Standards and Technology, Vol. 81A, 1977, pp. 89–96.