# Standard Test Method for
# Measurements of Aqueous Solubility[1]

This standard is issued under the fixed designation E 1148; 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.

ε[1] NOTE—Section 10 was added editorially in April 1993.

## 1. Scope

1.1 This test method covers procedures for measurement of the solubility of organic compounds in water. Three procedures are described which will work over a variety of solubility ranges. These procedures are not appropriate for compounds that react with water or air at ambient conditions.

1.2 The procedure chosen will depend on the estimated solubility of the compound. This may be obtained from literature values (see Refs **1, 2, 3**)[2] by correlation with other parameters **(4)** or by analogy with the solubility of similar compounds.

1.3 *This standard does not purport to address all of the safety problems, 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:*
D 1193 Specification for Reagent Water[3]

## 3. Terminology Definition

3.1 *solubility in water*—the extent to which a substance mixes with pure water to form a molecular homogeneous system at a given temperature. For the case of a single pure substance, solubility in water is an equilibrium state **(5)**. The particular method used will define what one means by aqueous solubility.

## 4. Significance and Use

4.1 The solubility of organics is a basic physical parameter needed for the prediction of the fate of a chemical in the environment **(6)**.

4.1.1 The ionic strength and organic content of natural waters may cause an apparent decrease or increase from the value obtained in pure water. Data on this can be obtained in the laboratory by modifying the reagent water to simulate natural waters.

## 5. Reagents

5.1 Reagent grade or better chemicals shall be used in all procedures. It is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society,[4] where such specifications are available. Lower grades may be used provided it is first ascertained that the impurities do not interfere with the procedure.

5.2 *Purity of Water*—Reagent water shall conform to Specification D 1193 for Type II grade water.

## 6. Sampling

6.1 Take at least 3 samples at appropriate intervals and analyze to demonstrate that equilibrium has been reached. Equilibrium is defined as identical concentrations within the precision of the analytical method.

## 7. Procedure

7.1 Determine solubilities at 25°C[5] and any other temperature as appropriate. Measure those chemicals that reversibly ionize or protonate at a pH of pKa + 2 pH units and a pH of pKa − 2 pH units for pKa values which fall in the range of 5 to 9 **(7)**. Adjust the system with HCl or NaOH as appropriate. A weak buffer (for example, 0.001 *M*) may be useful to stabilize the pH, depending on the solubility of the test substance. Report the solubility as mg/L at the experimental temperature and pH. For lower solubilities it is suggested, in order to minimize losses due to adsorption, that all transfer apparatus should be prerinsed with portions of the solution.

7.1.1 The effect of ionic strength or organic matter or both may be studied by adding appropriate substances in the reagent water.

7.2 *Method A1—Solubilities of 1 mg/L or Greater*:

[1] This test method is under the jurisdiction of ASTM Committee E-47 on Biological Effects and Environmental Fate and is the direct responsibility of Subcommittee E47.06 on Environmental Fate of Chemical Substances.

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[2] The boldface numbers in parentheses refer to the list of references at the end of this test method.

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

[4] "Reagent Chemicals, American Chemical Society Specifications," Am. Chemical Soc., Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see "Reagent Chemicals and Standards," by Joseph Rosin, D. Van Nostrand Co., Inc., New York, NY, and the "United States Pharmacopeia."

[5] International Union of Pure and Applied Chemistry (IUPAC)," Commission on Thermodynamics and Thermochemistry," A Guide to Procedures for the Publication of Thermodynamic Data, *Pure and Applied Chemistry*, Vol 29, No. 397, 1972.

7.2.1 Obtain equilibrium by gently shaking or stirring an excess of the compound in a flask of reagent water. Equilibrium times will depend upon the physical properties of the compound. Obtain the solubility by periodically determining the concentration of the solute over a length of time, at least 2 h between determinations. The solute concentration will assume a constant value, within experimental error, as equilibrium is attained. Before analysis, centrifuge the solution at the test temperature to ensure the removal of any suspended solute. Use a constant temperature centrifuge and run at about 12 000 g for at least 20 min[6] (8). Take care to maintain a constant temperature throughout the procedure.

$$t \ = 9/2 \ \eta/\omega^2 r_p{}^2 (\rho_p - \rho_w \ln R_b/R_t) \qquad (1)$$

where:
$\omega^2 \ = \dfrac{4 \ \pi^2 \ (r/min)^2}{3600}$
$t \ =$ time in seconds,
$r/min \ =$ revolutions per minute,
$R_t \ =$ distance in centimetres from center of centrifuge rotor to top of solution in centrifuge tube, and
$R_b \ =$ distance in centimetres from center of centrifuge rotor to bottom of centrifuge tube.

Taking the following values as typical:

$r_p \ =$ particle radius $= 0.1 \ \mu m$
$\eta \ =$ viscosity of water $= 0.8904 \times 10^{-2}$ g/s cm at 25°C,
$\rho_p \ =$ particle density $= 1.20$ g/cm$^3$(for this example),
$\rho_w \ =$ density of water $= 0.997$ g/cm$^3$ at 25°C, and
$t \ = \dfrac{1.83 \times 10^{11}}{(r/min)^2} \ln R_b/R_t.$

In general practice, double the calculated centrifuge times to assure complete separation.

7.2.2 This technique is suitable only if particles may be removed by centrifugation. Filtration may be used if it is demonstrated that no soluble material is lost by adsorption and that filtration removes insoluble material (9). If a stable suspension is formed, use 7.3

7.3 *Method A2—Solubilities of 1 mg/L or Greater*:

7.3.1 The nephelometric technique involves making several serial dilutions of a stable suspension of known concentrations. Alternatively, suspensions of various concentrations can be produced by mixing (10 s sonication is often effective) aliquots of a water miscible solvent solution of the test substance. A plot of total concentration versus turbidity (measured with any of a variety of turbidimeters) should yield a straight line (10, 11, 12). Use standard techniques of linear regression to estimate the concentration at zero turbidity or the turbidity of solvent controls, the value of which represents solubility. The sensitivity of the procedure to mixing time, equilibration time, and other aspects will vary with the equipment used and should be documented in each laboratory. This procedure is not chemical specific and it can be valuable for mixtures or difficult analyses. Errors may be introduced by a cosolvent, incomplete

suspension of the test substance, or a less soluble impurity.

7.4 *Method B—Solubilities less than 1 mg/L*:

7.4.1 The basic problem presented by solubility measurements of these compounds is the time required to reach equilibrium and adsorption of compounds on the surfaces of equipment. At very low concentrations, less than 1 μg/L, the definition of water solubility may become ill-defined because of the presence of dimers and molecular clusters. The generator column method of May, Wasik, and Freeman is preferable for compounds of low-water solubility in many cases (13). A separate ASTM test method using a generator column is under development. The U.S. EPA has also published this method in the Toxic Substances Control Act Test Guidelines (5). The following procedure is a modification of the method of Haque and Schmedding (14).

7.4.2 Dissolve a sample of the compound in an appropriate volatile solvent. Swirl this onto the walls of a well-cleaned glass carboy. Insure that excess compound is present. Do not allow the mixture to reach the bottom of the carboy. Residual solvent is evaporated using a nitrogen stream leaving a thin film of the compound on the carboy walls. Reagent water is slowly added along with a magnetic stirring bar and the carboy sealed airtight. Isolate each carboy from the magnetic stirrer by a ½-in. thick sheet of insulating material to minimize temperature gradients.

7.4.3 Stir solutions at about 250 r/min and take samples periodically through the air tight seal (at least once per week) until equilibrium is reached. In order to minimize losses due to adsorption, design the experiment to minimize transfers and prerinse all transfer apparatus with portions of the solution. Stop stirring for 24 h before taking samples. Take and analyze samples as appropriate. After the equilibrium point is reached, cease stirring and continue sampling until a new equilibrium, representing solubility, is reached. Centrifuge all samples to remove excess undissolved compound before analysis (see 7.2.1 for details).

## 8. Report

8.1 Include in the report the following information:

8.1.1 Procedure used and any modifications, the specific analytical technique used, pH, and temperature.

8.1.2 Time to reach equilibrium if applicable. This may be done by plotting solubility versus time.

8.1.3 If Method A 2 is used, include the concentration versus turbidity plot.

8.1.4 Report values as mean plus or minus one standard deviation and the number of measurements used to calculate the mean.

## 9. Precision and Bias

9.1 Precision and bias will depend upon the specific method chosen for the determination, upon the method used for detection and analysis, and upon the solubility of the material itself. No interlaboratory test for the evaluation of precision and bias has been conducted at this time.

## 10. Keywords

10.1 aqueous solubility; solubility of organic compounds in water

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[6] Centrifuge time to remove particles from suspension can be calculated assuming spherical particles.

# REFERENCES

(**1**) Gunther, F. A., Westlake, W. E., and Jaglan, W. E.," Reported Solubilities of 728 Pesticide Chemicals in Water," *Residue Reviews*, Vol 20, 1968, p. 1.

(**2**) Seidell, A., *Solubility of Inorganic, Metalorganics and Organic Compounds*, 3rd ed., D. Van Nostrand Co., New York, 1940.

(**3**) Stephen, J., and Stephen, T., *Solubility of Inorganic and Organic Compounds*, Vol 1, Binary Systems, Part 1, The Macmillan Co., New York. 1963.

(**4**) Kenaga, E. E., and Goring, C. A. I., "Relationship Between Water Solubility, Soil-Sorption, Octanol-Water Partitioning and Bioconcentration of Chemicals in Biota," in ASTM 3rd Aquatic Toxicology Symposium, Oct. 17–18, 1978, *ASTM STP 707*, 1980.

(**5**) U. S. Environmental Protection Agency, "Chemical Fate Testing Guidelines, Subpart B-Physical and Chemical Properties, Section 796.1840 Water Solubility (Generator Column Method)," *Federal Register*, Vol 50, No. 188, 1985, pp. 39265–39270.

(**6**) Metcalf, R. L., "Model Ecosystem Approach to Insecticide Degradation: A Critique," *Annual Reviews of Entomology*, Vol 22, 1977, p 241.

(**7**) Cheung, M. W., and Bigger, J. W., "Solubility and Molecular Structure of 4-amino-3,5,6-trichloropicolinic Acid in Relation to pH and Temperature," *Journal of Agricultural and Food Chemistry*, Vol 22, No. 2, 1974, pp. 202–206.

(**8**) Hoermann, W. D., and Eberle, D. O., "The Aqueous Solubility of 2-chloro-4-ethylamino-6-isopropylamino-1,3,5 triazine (Atrazine) Obtained by an Improved Analytical Method," *Weed Research*, Vol 12, 1972, p. 199.

(**9**) Hashimoto, Y., et al.," A Comparison of Water Solubilities by the Flask and Micro Column Methods," *Chemosphere*, Vol 11, 1982, pp. 991–1001.

(**10**) Davis, W. and Parke, T., "A Nephelometric Method for Determination of Solubilities of Extremely Low Order," *Journal of the American Chemical Society*, Vol 64, 1942, pp. 101–107.

(**11**) Furer, R. and Geiger, M. "A Simple Method of Determining the Aqueous Solubility of Organic Substances," *Pesticide Science*, Vol 8, 1977, p. 337.

(**12**) Hollifield, H. C.," Rapid Nephelometric Estimate of Water Solubility of Highly Insoluble Organic Chemicals of Environmental Interest," *Bulletin of Environmental Contamination and Toxicology*, Vol 23, 1979, p. 579.

(**13**) May, W. E., Wasik, S. P., and Freeman, D. H." Determinations of the Aqueous Solubility of Polynuclear Aromatic Hydrocarbons by a Coupled Column Liquid Chromatographic Technique," *Analytical Chemistry*, Vol 50, 1978, p. 175.

(**14**) Haque, R. and Schmedding, D., "A Method of Measuring the Water Solubility of Hydrophobic Chemicals," *Bulletin of Environmental Contamination and Toxicology*, Vol 14, No. 1, 1975, p. 13.