



Designation: D 4646 – 87 (Reapproved 2001)

## Standard Test Method for 24-h Batch-Type Measurement of Contaminant Sorption by Soils and Sediments<sup>1</sup>

This standard is issued under the fixed designation D 4646; 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 ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

### 1. Scope

1.1 This test method describes a procedure for determining the sorption affinity of waste solutes by unconsolidated geologic material in aqueous suspension. The waste solute may be derived from a variety of sources such as wells, underdrain systems, or laboratory solutions such as those produced by waste extraction tests like the Method D 3987 shake extraction method.

1.2 This test method is applicable in screening and providing relative rankings of a large number of geomeedia samples for their sorption affinity in aqueous leachate/geomeedia suspensions. This test method may not exactly simulate sorption characteristics that would occur in unperturbed geologic settings.

1.3 While this procedure may be applicable to both organic and inorganic constituents, care must be taken with respect to the stability of the particular constituents and their possible losses from solution by such processes as degradation by microbes, light, or hydrolysis. This test method should not be used for volatile chemical constituents (see 6.1).

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.*

### 2. Referenced Documents

#### 2.1 ASTM Standards:

- D 1129 Terminology Relating to Water<sup>2</sup>
- D 1193 Specification for Reagent Water<sup>2</sup>
- D 2216 Test Method for Laboratory Determination of Water (Moisture) Content of Soil and Rock<sup>3</sup>
- D 3987 Test Method for Shake Extraction of Solid Waste with Water<sup>4</sup>
- D 4319 Test Method for Distribution Ratios by the Short-

Term Batch Method<sup>3</sup>

### 3. Terminology

3.1 *Definitions*—For definition of terms used in this test method refer to Terminology D 1129.

3.1.1 *solute*—chemical species (for example, ion, molecule, etc.) in solution.

3.1.2 *sorbate*—chemical species sorbed by a sorbent.

3.1.3 *sorbent*—a substance that sorbs the solute from solution (for example, soil, sediment, till, etc.).

3.1.4 *sorption*—depletion of an amount of solute initially present in solution by a sorbent.

3.1.5 *sorption affinity*—the relative degree of sorption that occurs by a geomeedia.

3.1.6 *unconsolidated geologic material (geomeedia)*—a loosely aggregated solid natural material of geologic origin (for example, soil, sediment, till, etc.).

#### 3.2 Definitions of Terms Specific to This Standard:

3.2.1 *distribution coefficient,  $K_d$* —is defined identically to  $R_d$ , except it is considered to be an equilibrium value and independent of the concentration of solute (that is, linear sorption curve).

3.2.2 *distribution ratio ( $R_d$ )*—the ratio of the concentration of solute sorbed on the soil or other geomeedia divided by its concentration in solution. A 24-h  $R_d$  is the analogous ratio evaluated after 24 h of contact of the solute with the geomeedia. The  $R_d$  value is calculated as follows:

$$\begin{aligned} R_d &= \frac{(\text{mass of solute sorbed per unit mass of geomeedia})}{(\text{mass of solute in solution per unit volume of solution})} \\ &= \frac{\mu\text{g/g}}{\mu\text{g/mL}} \\ &= \frac{\text{mL}}{\text{g}} \end{aligned} \quad (1)$$

The dimensions of  $R_d$  reduce to units of volume per mass. It is convenient to express  $R_d$  in units of millilitres (or cubic centimetres) of solution per gram of geomeedia. Dissimilar  $R_d$  values may be obtained if different initial solute concentrations are used, depending on the sorption behavior of the solute and the properties of the geomeedia (that is, nonlinear sorption curve). This concentration dependency may be absent where the solute concentrations are sufficiently low or the characteristics of the particular solute-sorbent combination yield  $R_d$  values that are independent of the concentration of solute (that

<sup>1</sup> This test method is under the jurisdiction of ASTM Committee D34 on Waste Management and is the direct responsibility of Subcommittee D34.01.06 on Analytical Methods.

Current edition approved March 3, 1987. Published April 1987. Originally published as ES 10 – 85. Last previous edition ES 10 – 85.

<sup>2</sup> *Annual Book of ASTM Standards*, Vol 11.01.

<sup>3</sup> *Annual Book of ASTM Standards*, Vol 04.08.

<sup>4</sup> *Annual Book of ASTM Standards*, Vol 11.04.

is, linear sorption curve).

#### 4. Summary of Test Method

4.1 Distilled water, natural water, waste leachate, or other aqueous solution containing a known concentration of a solute is mixed with a known amount of unconsolidated geologic material (geomedia) for 24 h. Changes in solute concentrations are used to calculate a distribution ratio ( $R_d$ ).

#### 5. Significance and Use

5.1 This test method is meant to allow for a rapid (24 h) index of a geomedia's sorption affinity for given chemicals or leachate constituents. A large number of samples may be run using this test method to determine a comparative ranking of those samples, based upon the amount of solute sorbed by the geomedia, or by various geomedia or leachate constituents. The 24-h time is used to make the test convenient and also to minimize microbial degradation which may be a problem in longer-timed procedures. Due to this time constraint, the final (24-h) concentration should not be confused with that of an equilibrium or steady-state concentration. While  $R_d$  values are directly applicable for screening and comparative ranking purposes, their use in predictive field applications generally requires the assumption that  $R_d = K_d$ ; the validity of this assumption must be carefully evaluated by qualified personnel.

5.2 While this test method may be useful in determining 24-h  $R_d$  values for nonvolatile organic constituents, interlaboratory testing has been carried out only for the nonvolatile inorganic species, arsenic and cadmium. However, the procedure has been tested for single laboratory precision with polychlorinated biphenyls (PCBs) and is believed to be useful for all stable and nonvolatile inorganic, and organic constituents. This test method is not considered appropriate for volatile constituents.

5.3 The 24-h time limit may be sufficient to reach a steady-state  $R_d$ . However, to report this determination as a steady-state  $R_d$  (that is,  $R_d = K_d$ ), the relevant time studies must be carried out to document the development of steady-state conditions within the 24-h time period. Tests exceeding the 24-h time period are beyond the scope of this test method. Refer to Test Method D 4319, for an alternate procedure of longer duration.

#### 6. Interferences

6.1 When dealing with solutes of unknown stability either in contact with the geomedia or when used as blanks, care must be taken to determine if volatilization, hydrolysis, photodegradation, microbial degradation, oxidation-reduction (that is,  $\text{Cr}^{3+}$  to  $\text{Cr}^{6+}$ ) or other physicochemical processes are operating at a significant rate within the time frame of the procedure. The stability and hence loss from solution may affect the outcome of this procedure if the aforementioned reactions are significant. The compatibility of the method and the solute of interest may be assessed by determining the differences between the initial solute concentration (see 9.8) and the final blank concentration of the solute (see 9.15). If this difference is greater than the expected precision of the method (10 %), then the  $R_d$  value generated may be unreliable and must be carefully evaluated.

#### 7. Apparatus

7.1 *Agitation Equipment*—The agitation equipment to be used is the rotary solid waste extractor<sup>5</sup> specified in Test Method D 3987.

7.2 *Phase Separation Equipment*—A filtration apparatus made of materials compatible with the solutions being filtered and equipped with a 0.45- $\mu\text{m}$  pore size membrane filter, or a constant temperature centrifuge capable of separating particles with diameters greater than 0.1  $\mu\text{m}$  (see Section 9). If organic compounds are being measured, the filtration apparatus, centrifuge tubes etc., should be compatible with the compounds being measured (that is, glass or stainless steel). Sorption of solute onto the filtration membrane may be significant for some solutes, and must be evaluated by the use of blanks through all steps of the procedure.

7.3 *Containers*—Round, wide-mouth bottles compatible with the rotary extractor (Test Method D 3987) and of composition suitable to the nature of the solute(s) under investigation and the analysis to be performed will be used. For nonvolatile inorganic constituents, high-density, linear polyethylene bottles should be used with the size of the bottle dictated by sample size, and the need for the solution to occupy 70 to 80 % of the container volume (that is, 125 mL, 250 mL, or 2-L bottles for sample sizes of 5, 10, or 70 g respectively). For nonvolatile organic constituents, TFE-fluorocarbon, glass bottles, or stainless steel containers with water-tight closures made of chemically inert materials should be used with size requirements being the same as for nonvolatile inorganics. Containers should be cleaned in a manner consistent with the analyses to be performed. Samples of the solutions to be analyzed should be stored in similar chemically compatible bottles.

7.4 *Balance*, having a minimum capacity of 70 g and a sensitivity of  $\pm 0.005$  g shall be used.

#### 8. Reagents

8.1 *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 American Chemical Society, where such specifications are available.<sup>6</sup> 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.

8.2 *Purity of Water*— Unless otherwise indicated, references to water shall be understood to mean Type IV reagent water of Specification D 1193.

#### 9. Procedure

9.1 Geomedia samples are spread out on a flat surface, no more than 2 to 3 cm deep, and allowed to air dry for 7 days or

<sup>5</sup> Diamondstone, B. T., Burke, R. W., and Garner, E. L., "Improved Leach Measurements on Solid Wastes," *ASTM Standardization News*, June 1982, pp. 28–33.

<sup>6</sup> *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.