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Standard Test Method for 24-h Batch-Type Measurement of Contaminant Sorption by Soils and Sediments¹

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 (ϵ) 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 Test 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

1.4 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.5 *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:*²

D 1129 Terminology Relating to Water

D 1193 Specification for Reagent Water

D 2216 Test Methods for Laboratory Determination of Water (Moisture) Content of Soil and Rock by Mass

D 3987 Test Method for Shake Extraction of Solid Waste with Water

D 4319 Test Method for Distribution Ratios by the Short-Term Batch Method

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_{K_d} is the analogous ratio evaluated after 24 h of contact of the solute with the geomeedia.

¹ 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.

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² Annual Book of ASTM Standards, Vol 11.01.

² For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For Annual Book of ASTM Standards volume information, refer to the standard's Document Summary page on the ASTM website.

3.2.1.1 *Discussion*—The dimensions of R_{K_d} value is calculated as follows:

$$R_{K_d} = \frac{(\text{mass of solute sorbed per unit mass of geomeia})}{(\text{mass of solute in solution per unit volume of solution})} = \frac{\mu\text{g/g}}{\mu\text{g/mL}} = \frac{\text{mL}}{\text{g}} \quad (1)$$

The dimensions of R_{K_d} reduce to units of volume per mass. It is convenient to express R_{K_d} in units of millilitres (or cubic centimetres) of solution per gram of geomeia. Dissimilar R_{K_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 geomeia (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_{K_d} values that are independent of the concentration of solute (that 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 (geomeia) for 24 h. Changes in solute concentrations are used to calculate a distribution ratio (R_d).

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 (geomeia) for 24 h. After 24 h, equilibrium between the solid and solution phase is presumed to occur. The concentration of solute remaining in solution is measured and the amount of solute adsorbed is calculated. Given that the mass of solid phase is known, the distribution coefficient for the specified experimental conditions can then be calculated.

5. Significance and Use

5.1 This test method is meant to allow for a rapid (24 h) index of a geomeia'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 geomeia, or by various geomeia 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_{K_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. be a fixed value.

5.2 While this test method may be useful in determining 24-h R_{K_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_{K_d} . However, to report this determination as a steady-state R_{K_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 D4319; for an alternate procedure of longer duration, this test method should be conducted for intermediate times (for example, 12, 18 and 22 h) to ensure that the soluble concentrations in the solution have reached a steady state by 24 h. 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 geomeia or when used as blanks, care must be taken to determine if volatilization, hydrolysis, photodegradation, microbial degradation, oxidation-reduction (that is, for example, Cr^{3+} to 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_{K_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 extractor³ 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- μm pore size membrane filter, or a constant temperature centrifuge capable of separating particles with diameters greater than 0.1 μm (see Section 9). If organic compounds are being measured, the filtration apparatus, centrifuge tubes

³ Annual Book of ASTM Standards, Vol 04.08.

³ Diamondstone, B. T., Burke, R. W., and Garner, E. L., "Improved Leach Measurements on Solid Wastes," *ASTM Standardization News*, June 1982, pp. 28–33.

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 ± 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.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.

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 until constant weight (a change that is less than 5 %/24-h period) is achieved (do *not* oven dry).

9.2 After the sample has air dried, it is passed through a 2-mm screen sieve. Large aggregates are to be crushed, without grinding, using a clean mortar and a rubber-tipped pestle.

9.3 Mix the sieved material until the sample is homogeneous. Use a riffle splitter, or other unbiased splitting procedure, to obtain subsamples of appropriate size.

9.4 Remove subsamples and determine the moisture content of the air-dried sample (refer to Test Method D 2216).

9.5 Determine the mass of geomedia sample, corrected for moisture content:

Determination of air-dried soil mass equivalent to the desired mass of oven-dried soil:

$$A = M_s[1 + (M/100)] \quad (1)$$

where:

A = air dry soil mass

M_s = mass of oven-dried soil desired, and

M = moisture, %.

9.6 Place between 5 and 70 g (oven-dried basis) of the weighed air-dried sample into the appropriate container. The samples should be weighed to a minimum of three significant figures.

9.7 Add to the container an amount of solute solution necessary to yield a 1:20 soil-to-solution ratio. This is determined on the oven-dried basis:

Determination of solution volume needed per sample for a soil-to-solution ratio of 1:20: $V = (M_s \times 20) / \rho$

$$V = (M_s \times 20) / \rho \quad (2)$$

where:

ρ = density of solution, g/cm³,

V = volume of solution per sample, cm³, and

M_s = mass of soil to be used, g, (oven-dried basis).

9.8 Retain a separate, appropriately preserved aliquot of the initial solute solution for analysis.

9.9 Close the container and place it on the rotary extractor (Test Method D 3987).

9.10 Agitate continuously for 24 ± 0.5 h at 29 ± 2 r/min at room temperature ($22 \pm 5^\circ\text{C}$).

9.11 Open the container. Note the temperature of the solution and any changes in the sample or solution (that is, color, odor, etc.).

9.12 Separate the solution phase from the majority of the solid phase by decantation.

9.13 Filter the solution phase through a 0.45- μm pore size membrane filter (see 7.2), or centrifuge a subsample at the

⁴ *Annual Book of ASTM Standards*, Vol 11.04-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.