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

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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 Water²
- D 1193 Specification for Reagent Water²
- D 2216 Test Method for Laboratory Determination of Water (Moisture) Content of Soil and Rock³
- D 3987 Test Method for Shake Extraction of Solid Waste with Water⁴
- D 4319 Test Method for Distribution Ratios by the Short-

Term Batch Method³

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

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.

³ *Annual Book of ASTM Standards*, Vol 04.08.

⁴ *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, 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_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 extractor⁵ 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 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.⁶ 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

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

⁶ *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.

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 geomeedia sample, corrected for moisture content:

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

$$A = M_s[1 + (M/100)] \quad (2)$$

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:

$$V = (M_s \times 20)/\rho \quad (3)$$

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 predetermined rate of rotation and time for the centrifugation equipment employed at constant temperature (the temperature recorded after 24 h):

$$t = 9/2 \left(\frac{\eta}{\omega^2 r_p^2 (\rho_p - \rho)} \right) \ln (R_b/R_t) \quad (4)$$

where:

$$\omega^2 = \frac{4\pi^2 (r/\text{min})^2}{60}$$

= angular velocity,

r_p = particle radius, cm,

η = viscosity of water, 8.95×10^{-3} g/s-cm at 25°C ,

ρ_p = particle density,

ρ = density of solution,

r/min = revolutions per minute,

R_t = distance from center of centrifuge rotor to top of solution in centrifuge tube, cm,

R_b = distance from center of centrifuge rotor to bottom of centrifuge tube, cm, and

t = time, min.

To remove particles $>0.1\text{-}\mu\text{m}$ radius and 2.65-g/cm^3 density from solution:

$$t = \left(\frac{3.71 \times 10^8}{(r/\text{min})^2} \right) \ln (R_b/R_t) \quad (5)$$

Note that if filtration is used, the affinity of the filtration membrane for the solute must be evaluated. Failure to do so, may lead to erroneous results.

9.14 After a clear solution has been obtained, place an aliquot in an appropriate container (see 7.3), and analyze or store in a refrigerator at $4 \pm 2^\circ\text{C}$ until analyzed.

9.15 Each geomeedia sample is to be subjected to the procedure in three or more replicates. The number of blanks (that is, solute solution without geomeedia) carried through all steps of the procedure should be a minimum of 5 % of the total number of geomeedia samples, but not less than three.

10. Calculation

10.1 Calculate the distribution ratio as follows:

$$R_d = \frac{(A - B)V}{(M_s)B} \quad (6)$$

where:

A = initial concentration of the solute defined as the mean concentration of the blanks, $\mu\text{g/mL}$,

B = final concentration of the solute after 24 h in contact with the geomeedia, $\mu\text{g/mL}$,

V = volume of solution used, mL,

M_s = mass of soil expressed on an oven-dried basis, g, and

R_d = distribution ratio, mL/g.

11. Report

11.1 The R_d value must be clearly marked as nonequilibrium 24-h distribution ratio.

11.2 Both the initial solute concentration (A in 10.1) and the final solute concentration (B in 10.1) must be reported.

11.3 The initial and final solute concentration for each blank (solution without geomeedia) must be reported.

11.4 The mass of the sorbent (M_s in 10.1), volume of solution (V in 10.1), and the room temperature at which the rotary extractor was operated must be reported.

11.5 Report the temperature of the solution and any changes noted in 9.11.

11.6 Note and report negative R_d values when and if they occur. Negative R_d values may occur if the geomeedia contains

the test solute prior to the application of the method.

11.7 It is suggested that the pH of the sorbent-solute mixture be determined prior to separating the sorbent from the liquid and reported where feasible.

12. Precision and Bias

12.1 An interlaboratory round-robin test was conducted at a soil-to-solution ratio of 1:20 using 70.0 g of soil. Intralaboratory testing using a 1:20 soil-to-solution ratio was carried out with no significant loss of precision for soil masses of 5.00, 10.0, and 70.0 g. Therefore, it is specified that the soil-to-solution ratio be 1:20 with the working mass of soil (on an oven-dried basis) between 5 and 70 g.

12.2 Precision:

12.2.1 The precision of this test method is limited by the ability to obtain a homogeneous sample of geomeedia, and the precision of the various methods used to carry out the procedure (that is, mass determinations, initial and 24-h concentration of constituents).

12.2.2 A comprehensive overall precision statement, covering all species, is not feasible. Interlaboratory testing of this procedure, using cadmium and arsenic as sorbates, with five independent laboratories, and single laboratory testing with PCBs indicated that a coefficient of variation of less than 10 % is obtainable.

12.2.3 For a summary of interlaboratory testing for the 24-h batch-type R_d determination see Table 1.

12.2.4 For a summary of single laboratory testing for an organic solute see Table 2.

TABLE 1 Summary of Interlaboratory Testing for the 24-h Batch-Type R_d Determination

Initial Concentration, $\mu\text{g/mL}$	Soil 1	Soil 1	Soil 2	Soil 3	Soil 4
	10	200	100	100	100
Cadmium Carbonate (as CdCO_3):					
$\bar{X} R_d$, mL/g	1568	96.3	69.50	69.74	28.94
Standard deviation, mL/g	± 156	± 6.32	± 7.73	± 7.87	± 2.64
Coefficient of variation, %	9.95	6.56	11.13	11.29	9.14
Number of replicates	12	12	10	12	9
Arsenic (as KH_2AsO_4):					
$\bar{X} R_d$, mL/g	15.42	2.75	4.95	3.25	2.99
Standard deviation, mL/g	± 0.92	± 0.85	± 0.27	± 0.26	± 0.20
Coefficient of variation, %	5.99	30.9	5.53	7.88	6.52
Number of replicates	12	12	12	12	12

12.3 *Bias*—A determination of the bias for this procedure is not possible since no standard soil or alternate technique exists.

TABLE 2 Summary of Single Laboratory for an Organic Solute

Initial Concentration, µg/mL	Soil 1 ^A 0.216 (0 % Ace- tone)	Soil 1 ^B 0.187 (20 % Acetone)	Soil 2 ^C 0.216 (0 % Ace- tone)	Soil 2 ^D 0.187 (20 % Acetone)
PCBs (as Aroclor 1242):				
\bar{X} R_{σ} , mL/g	798	78.62	23.83	2.28
Standard deviation, mL/g	±18.41	±3.45	±1.48	±0.11
Coefficient of variation, %	2.31	4.39	6.21	4.82
Number of replicates	4	4	4	4

^A Soil 1—Catlin silt loam.

^B Soil 2—Sangamon paleosol.

^C Soil 3—Kaolinite clay.

^D Soil 4—Vandalia till, unaltered phase.

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