Designation: D4646 – 16

Standard Test Method for 24-h Batch-Type Measurement of Contaminant Sorption by Soils and Sediments[1]

This standard is issued under the fixed designation D4646; 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 D3987 shake extraction method.

1.2 This test method is applicable in screening and providing relative rankings of a large number of geomedia samples for their sorption affinity in aqueous leachate/geomedia suspensions. This test method may not 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, hydrolysis, or sorption to material surfaces. This test method should not be used for volatile chemical constituents (see 6.1).

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]

E11 Specification for Woven Wire Test Sieve Cloth and Test Sieves
D5681 Terminology for Waste and Waste Management
D1193 Specification for Reagent Water
D2216 Test Methods for Laboratory Determination of Water (Moisture) Content of Soil and Rock by Mass
D3987 Practice for Shake Extraction of Solid Waste with Water
D4319 Test Method for Distribution Ratios by the Short-Term Batch Method (Withdrawn 2007)[3]
E2551 Test Method for Humidity Calibration (or Conformation) of Humidity Generators for Use with Thermogravimetric Analyzers

3. Terminology

3.1 *Definitions:*

3.1.1 For definition of terms used in this test method refer to Terminology D5681.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *distribution coefficient, K_d*—the ratio of the concentration of solute sorbed on the soil or other geomedia divided by its concentration in solution. A 24-h K_d is the analogous ratio evaluated after 24 h of contact of the solute with the geomedia.

3.2.1.1 *Discussion*—The dimensions of K_d reduce to units of volume per mass. It is convenient to express K_d in units of milliliters (or cubic centimeters) of solution per gram of geomedia. Dissimilar 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 geomedia (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 K_d values that are independent of the concentration of solute (that is, linear sorption curve).

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

3.2.3 *sorbate*—a chemical species retained by a sorbent.

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[1] This test method is under the jurisdiction of ASTM Committee D34 on Waste Management and is the direct responsibility of Subcommittee D34.01.04 on Waste Leaching Techniques.

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[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] The last approved version of this historical standard is referenced on www.astm.org.

3.2.4 *sorbent*—a solid medium (for example, soil, sediment, till, etc.) in or upon which solutes are collected by absorption or adsorption.

3.2.5 *sorption*—a physical and chemical process by which a sorbate is taken up or held (that is, sorbed) to a sorbent by a combination of adsorption and absorption.

3.2.6 *sorption affinity*—the relative degree of sorption that occurs between a solute and a sorbent.

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

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, after which equilibrium between the sorbent and solution phase is presumed to occur. The sorbent-to-solution ratio for this test is 1:20 on a mass basis. The concentration of solute remaining in solution is measured and the amount of solute adsorbed is calculated by difference with the known concentration in the initial solute. Given that the mass of solid phase is known, the distribution coefficient, K_d, 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 geomedia's sorption affinity for given solutes in environmental waters or leachates. A large number of samples may be run in parallel 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, light, or hydrolytic degradation which may be a problem in longer-timed procedures. While K_d values are directly applicable for screening and comparative ranking purposes, their use in predictive field applications generally requires the assumption that K_d be a fixed value.

5.2 While this test method may be useful in determining 24-h K_d values for nonvolatile organic constituents, interlaboratory testing has been carried out only for the nonvolatile inorganic species, arsenic and cadmium (see Section 12). 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 K_d; however, the calculated K_d value should be considered a non-equilibrium measurement unless steady-state has been determined. To report this determination as a steady-state K_d, 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. If a test duration of greater than 24 h is required, refer to Test Method D4319 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 (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.

6.2 Although efforts should be taken to find equipment made with contact surface materials compatible with the solute solution, solute losses may occur due to sorption to material surfaces. Thus, method blanks (that is, solutes carried through the process with sorbents) should be conducted.

6.3 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 method blank concentration of the solute (see 9.16). If this difference is greater than the expected precision of the method (10 %), then the K_d value generated may be unreliable and must be carefully evaluated.

7. Apparatus

7.1 *Agitation Equipment*—A device of any type that rotates about a central axis at a rate of 29 ± 2 revolutions per minute and mixes samples in an end-over-end fashion (see Test Method D3987).

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 (for example, 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 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 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, 250, or 2000-mL bottles for sample sizes of 5, 10, or 70 g respectively). For nonvolatile organic constituents, 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 capacity of at least 70 g and a sensitivity of ±0.005 g shall be used.

7.5 *Mortar and Rubber-tipped Pestle*—Apparatus suitable for breaking up aggregations of air-dried soil particles with breaking individual particles.

7.6 *Sieve*—No. 10 (2 mm) brass or stainless steel wire mesh sieve that conforms to the requirements of Specification E11.

7.7 *Thermometer*—A gravity thermometer conforming to the requirements of Specification E2551.

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 reagent water meeting the criteria of Type IV in Specification D1193.

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 % over a 24-h period) is achieved. Do not oven dry the geomedia.

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. The mass fraction of irreducible material greater than 2-mm should be noted and removed from the geomedia sample.

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 D2216).

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:

$$A = M_s[1+(M/100)] \tag{1}$$

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 (see 7.3).

9.7 Add to the container an amount of solute solution necessary to yield a 1:20 sorbent-to-solution ratio on a mass basis using the oven-dried geomedia mass:
Determination of solution volume needed per sample for a sorbent-to-solution ratio of 1:20:

$$V = (M_s \times 20)/\rho \tag{2}$$

where:

ρ = density of solution, g/cm^3,
V = volume of solution per sample, cm^3, and
M_s = mass of geomedia to be used, g, (oven-dried basis).

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

9.9 Method blanks may be prepared by placing the same volume of solute solution into an empty container without geomedia. These blanks should be carried through the entire remainder of the procedure including agitation, filtration, or centrifugation and analysis.

9.10 Close the container and place it on the rotary extractor.

9.11 Agitate continuously for 24 ± 0.5 h at 29 ± 2 r/min at room temperature (22 ± 5°C).

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

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

9.14 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):

$$t = 9/2\left(\frac{\eta}{\omega^{2} r_{p}^{2}(\rho_p - \rho)}\right)\ln(R_b/R_t) \tag{3}$$

where:

ω^2 = $\frac{4_{\pi}^{2}(r/min)^2}{60}$ = 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-µm radius and 2.65-g/cm^3 density from solution:

$$t = \left(\frac{3.71 \times 10^{8}}{(\text{r/min})^{2}}\right)\ln(R_b/R_t) \tag{4}$$

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[4] *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.

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.

9.15 Place an aliquot of filtered or centrifuged liquid into an appropriate container (see 7.3), preserve in accordance with the intended analytical method, and analyze or store in a refrigerator at 4 ± 2°C until analyzed.

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

10. Calculation

10.1 Calculate the distribution as follows:

$$K_d = \frac{(A - B)V}{(M_s)B} \tag{5}$$

where:

A = initial concentration of the solute defined as the mean concentration of the blanks, µg/mL,
B = final concentration of the solute after 24 h in contact with the geomedia, µg/mL,
V = volume of solution used, mL,
M_s = mass of soil expressed on an oven-dried basis, g, and
K_d = distribution coefficient, mL/g.

11. Report

11.1 The K_d value must be clearly marked as non-equilibrium 24-h distribution coefficient.

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 geomedia) 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 9.12.

11.6 Note and report negative K_d values when and if they occur. Negative K_d values may occur if the geomedia 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 sorbent-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.

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

Initial Concentration, µg/mL	Soil 1	Soil 1	Soil 2	Soil 3	Soil 4
	10	200	100	100	100
Cadmium Carbonate (as $CdCO_3$):					
$\bar{X}$ K_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):					
$\bar{X}$ K_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

TABLE 2 Summary of Single Laboratory for an Organic Solute

Initial Concentration, µg/mL	Soil 1[A] 0.216 (0 % Acetone)	Soil 1[B] 0.187 (20 % Acetone)	Soil 2[C] 0.216 (0 % Acetone)	Soil 2[D] 0.187 (20 % Acetone)
PCBs (as Aroclor 1242):				
$\bar{X}$ K_d, 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.

12.2 *Precision:*

12.2.1 The precision of this test method is limited by the ability to obtain a homogeneous sample of geomedia, 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 K_d determination see Table 1.

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

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

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