



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

This standard is issued under the fixed designation D 5285; 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, for example, soils, fluvial sediments, sedimentary deposits, or any other accumulations of unconsolidated solid particles (for a companion method, for metal solute, see Test Method D 4319). The waste solute may be derived from a variety of sources such as wells, underdrain systems, or laboratory solutions like those produced by waste extraction tests (for example, Test Method D 3987).

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

1.3 While this test method is intended to be applicable for all soluble organic constituents, care must be taken with respect to the stability of the particular constituents and their possible losses from solution by such processes as volatilization or degradation by microbes, light, or hydrolysis.

1.4 The values stated in SI units are to be regarded as the 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:<sup>2</sup>

D 653 Terminology Relating to Soil, Rock, and Contained Fluids

D 1129 Terminology Relating to Water

D 1193 Specification for Reagent Water

D 2216 Test Method for Laboratory Determination of Water (Moisture) Content of Soil and Rock

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

D 4410 Terminology of Fluvial Sediment

## 3. Terminology

3.1 Definitions—For definitions of terms used in this test method, refer to Terminology D 1129. For additional definitions of terms pertaining to soils and fluvial sediments, refer to Terminologies D 653 and D 4410.

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

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

3.1.3 *sorbent*—a solid 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 *unconsolidated geologic material (geomedia)*—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,  $K_d$* —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*—Dissimilar  $K_d$  values may be obtained for the same solute 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. It is absent when 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 *octanol water partition coefficient,  $K_{ow}$* —the distribution coefficient of an organic compound between *n*-octanol and water. It has been found to be useful in predicting other

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<sup>2</sup> For referenced ASTM standards, visit the ASTM website, [www.astm.org](http://www.astm.org), or contact ASTM Customer Service at [service@astm.org](mailto:service@astm.org). For Annual Book of ASTM Standards volume information, refer to the standard's Document Summary page on the ASTM website.

constants that describe the distribution of organics between organic carbon-containing media and water and is usually easy to measure experimentally.

3.2.3 *sorption affinity*—the relative degree of sorption that occurs by a geomedia.

3.2.4 *test compound constant*,  $K_{oc}$ — the distribution coefficient between water and a hypothetical geomedia that is 100 % organic carbon. As such, it is used to convert distribution coefficients measured for one geomedia to another geomedia with a different organic carbon content.

#### 4. Summary of Test Method

4.1 Distilled water, natural water, waste leachate, or any aqueous solution containing a known concentration of solute is mixed with a known amount of unconsolidated geologic material (geomedia) 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. The remainder is presumed to be adsorbed onto the solid phase. Given that the mass of solid phase has previously been determined, the distribution coefficient for the specified experimental conditions can then be calculated.

#### 5. Significance and Use

5.1 This test method is intended to allow for a rapid (24-h) index  $K_d$  of a geomedia's sorption affinity for given chemicals or leachate constituents. A large number of samples may be analyzed using this test method to determine a comparative ranking of those samples, based on the amount of solute sorbed by the geomedia, or by various geomedia or leachate constituents. The 24-h time period is used to make the test convenient as well as to minimize microbial degradation, which may be a problem in longer 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 The 24-h time limit may be sufficient to reach a steady-state  $K_d$ . However, to report this determination as a steady-state  $K_d$ , this test method should be conducted for intermediate times (for example, 12, 18, 22 h) to ensure that solute concentrations in the solution phase have reached a steady state by 24 h.

#### 6. Interferences

6.1 When solutes of unknown stability are dealt with, when they are either in contact with the geomedia or used as blanks, care must be taken to ensure that volatilization, hydrolysis, photodegradation, microbial degradation, oxidation-reduction, or other physicochemical processes are not 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 test method and the solute of interest may be assessed by determining the differences between the initial solute concentration (see 9.3.3) and the silica sand blank concentration of the solute (see 9.3.7). If this difference is significant compared to the expected precision of the test method, the  $K_d$  value generated may be unreliable and thus must be evaluated carefully.

6.2 It is essential that the geomedia used for measuring distribution coefficients be free of any chemical species for which the distribution coefficient is to be measured. If it is suspected that the geomedia is contaminated, a procedure identical to that described in 9.3.1-9.3.7 should be followed, with Type IV water substituted for the test solution. If the concentration of a chemical in the water after equilibrating for 24 h, compared to the concentration of that chemical in the solution to be tested, is significant compared to the expected precision of the test method ( $\pm 8\%$ ), a different geomedia should be used. Correcting the measured  $K_d$  for contaminated soil is not recommended since the preexisting contamination may not be adsorbed such that it can equilibrate readily with water.

#### 7. Apparatus

7.1 *Agitation Equipment*—The Rotary Solid Waste Extractor<sup>3</sup> specified in Test Method D 3987.

7.2 *Containers*—Round, wide-mouth glass bottles that can be fitted with standard volatile organics analysis (VOA) caps and are compatible with the rotary extractor.

7.3 *Balance*, having a minimum capacity of 500 g and a sensitivity of  $\pm 0.05$  g, to be used for weighing the geomedia and solute solution. A more sensitive balance may be required for preparing analytical standards.

#### 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 Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.<sup>4</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 conforming to Specification D 1193.

8.3 *Silica Sand*— 20/40 grit sand blasting pure silica sand, to be used for the silica sand blank.

8.4 *Preparation of Analytical Standard Solutions:*

8.4.1 *Standard Stock Solutions*—Place approximately 9 to 9.8 mL of methanol into a 10-mL ground-glass, stoppered volumetric flask, and then allow the flask to stand unstoppered for a few minutes or until all methanol-wetted surfaces have dried. Weight the flask to the nearest 0.1 mg and immediately add a few drops of the test organic to the flask by using a 100- $\mu$ L syringe, and then reweigh. Be sure that the drops fall directly into the methanol without contacting the neck of the flask. Finally, dilute to volume, stopper, and mix by inverting the flask several times.

<sup>3</sup> Diamondstone, B. T., Burke, R. W., and Gardner, E. L., "Improved Leach Measurements on Solid Wastes," *Standardization News*, Vol 10, No. 6, June 1982, pp. 28-33.

<sup>4</sup> "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 "Analar Standards for Laboratory U.K. Chemicals," BDH Ltd., Poole, Dorset, and the "United States Pharmacopeia."

8.4.2 Transfer the stock solution into a polytetrafluoroethylene-sealed screw-cap vial. Store, with minimal headspace, at approximately 4°C.

8.4.3 All standard stock solutions must be replaced after one month, or sooner, if a comparison with check standards indicates a change of concentration greater than 5 %.

8.4.4 When ready to prepare secondary standard solutions, stabilize the temperature of the vial containing the standard stock solutions. When the temperatures of the stock solutions and containers have been stabilized, transfer into a known amount of pure water using a 25- $\mu$ L syringe. Keep the headspace as small as possible.

8.4.5 Aqueous standards and solutions stored with headspace are not stable and should be discarded after 1 h.

#### 8.5 Preparation of Test Solutions for Sorption Studies:

8.5.1 Solutions used as the test fluid for sorption studies may be actual environmental samples, laboratory or field leachates, or laboratory-prepared solutions. The following procedure is recommended if laboratory-prepared solutions are used as the test fluid.

8.5.2 Place 990 mL of Type IV water into a 1000-mL clean amber glass bottle, and then seal with an open-top screw-cap with polytetrafluoroethylene-lined septum. Inject known amounts of the pure test components into each bottle using a 100- $\mu$ L syringe. (Prepare at least two different concentration levels.) Then mix by inverting the bottle several times. The actual test concentration should be determined by gas chromatographic analysis.

8.5.3 When the sorption coefficients for weakly adsorbing organics are to be measured, the best results are obtained using test fluids that are as concentrated as possible. However, experience has shown that it is very difficult to dissolve many nonpolar organics at concentrations approaching their published solubilities. Concentrations that are approximately one-half of the published solubilities seem to be a reasonable compromise between the need for concentrated solutions and the practicality of preparing them.

## 9. Procedure

### 9.1 Preparation of Materials to be Used as Sorbents:

9.1.1 Samples of sorbents such as soils, clays, or sediments 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 of less than 5 % per 24-h period) is achieved. Do *not* oven dry the samples.

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

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

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

9.1.5 Determine the mass of the geomeedia sample, corrected for moisture content. Determination of the air-dry soil mass equivalent to the desired mass of oven-dried soil is made as follows:

$$A = Mm \frac{100}{100 - W} \quad (1)$$

where:

$A$  = air-dry geomeedia mass,

$Mm$  = mass of oven-dried geomeedia desired, and

$W$  = moisture percent in air-dried geomeedia.

### 9.2 Selection of a Geomeedia: Solution Ratio:

9.2.1 The geomeedia to solution ratios used for sorption studies will depend on the distribution coefficient ( $K_d$ ) and the relative degree of sorption desired. The first step in selection of a geomeedia to solution ratio for a test solute is to estimate the value of the test compound constant ( $K_{oc}$ ) from the water solubility ( $S$ , ppm) of the test compound, or from the value of its *n*-octanol/water partition coefficient ( $K_{ow}$ ). The relationship between the  $K_{oc}$  and  $S$  or  $K_{oc}$  and  $K_{ow}$  for various hydrophobic compounds has been reported by Hassett, et al.<sup>5</sup>

$$\log K_{oc} = 3.95 - 0.62 \log S \text{ (ppm)} \quad (2)$$

$$\log K_{oc} = 0.088 + 0.909 \log K_{ow} \quad (3)$$

9.2.2 Sorption constant values ( $K_{oc}$ ) can be adjusted for the organic carbon content of the geomeedia by using the percent organic carbon to predict the geomeedia  $K_d$ . Therefore, the individual values of the  $K_d$  can be calculated if the respective percent organic carbon content of the geomeedia is known:

$$K_d = \frac{K_{oc} \times \% OC}{100} \quad (4)$$

9.2.3 The selection of an appropriate ratio can be based on a plot of  $1/R$  (where  $R = \text{g soil/g water}$ ) versus  $K_d$  (estimated) for fixed percents of solute desired to be sorbed:

$$\frac{1}{R} = \left[ \left( \frac{W_{s^o}}{W_s} \right) - 1 \right] \times K_d \quad (5)$$

where:

$W_{s^o}$  = weight of total solute initially in the aqueous solution, and

$W_s$  = weight of solute adsorbed.

Examples of ranges of  $K_d$  (up to 25) and water/geomeedia ratios (up to 30) are shown in Fig. 1. For detailed procedures, refer to "Batch-Type Adsorption Studies: Conceptual Guidelines and Experimental Procedures" (Roy, et al.).<sup>6</sup>

9.2.4 In theory, sorption studies can be performed at any geomeedia/water ratio, but in practice it is recommended that the geomeedia/water ratio selected fall within the range of 20 to 80 % sorption of the compound.

9.2.5 Many of the volatile organic-soil combinations of interest result in an  $K_d$  value so low that Fig. 1 is not particularly useful. In this case, it is recommended that a water to geomeedia ratio ( $1/R$ ) of 2 be used as a practical lower limit.

<sup>5</sup> Hassett, J. J., Banwart, W. L., and Griffin, R. A., "Correlation of Compound Properties with Sorption Characteristics of Non-Polar Organic Compounds by Soils and Sediments," *Concepts and Limitations, Environment and Solid Waste; Characterization Treatment and Disposal*, Chapter 15, Eds. C. W. Francis and S. I. Auerbach, Butterworth Publishers, Woburn, MA, 1983, pp. 161-178.

<sup>6</sup> Roy, W. R., Krapac, I. G., Chou, S. F. J., and Griffin, R. A., "Batch Type Adsorption Procedures for Estimating Soil Attenuation of Chemicals," *Technical Resource Document*, EPA/530-SW-87-006 (NTIS No. PB87146-155), Washington, DC, 1986.

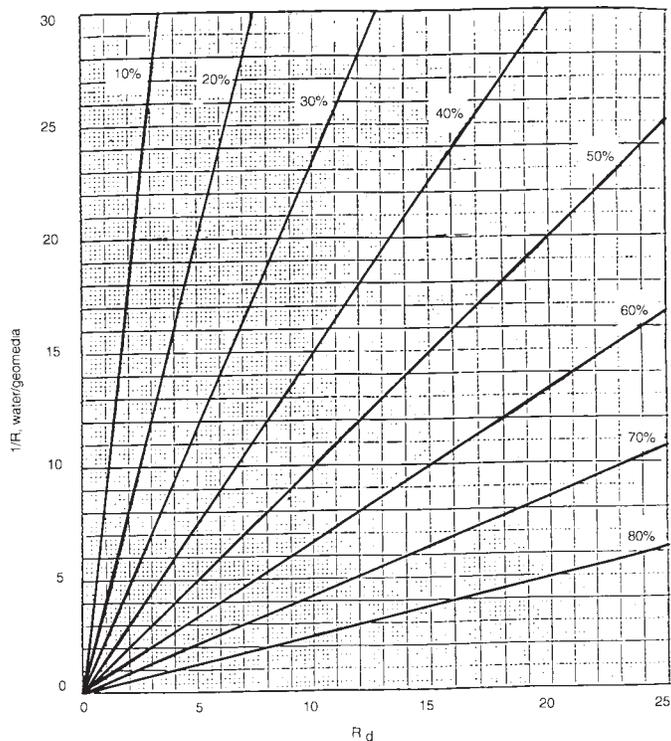


FIG. 1 Relationship Between the Water/Geomedia Ratios and  $K_d$  at Various Percents of Solute Adsorbed

9.3 Reaction Container Filling:

9.3.1 Pre-weigh a reaction container (such as a 125-mL amber glass serum bottle), a polytetrafluoroethylene-faced septum and aluminum seal, and then place an appropriate amount of air-dried geomedia into the reaction container. Weigh the geomedia, bottle, polytetrafluoroethylene-faced septum, and aluminum seal combination, and calculate the weight of geomedia (oven-dried basis) to the nearest 0.1 g. The amount of geomedia used depends on the geomedia/solution ratio estimated previously.

9.3.2 Fill the container with the solute solution. The filling procedure may require shaking the geomedia/solution sample gently, to drive trapped air from the geomedia, and refilling with solution to minimize headspace. Place the polytetrafluoroethylene-faced septum and aluminum seal or the VOA cap on the container and invert to ensure that no air bubbles are present. Weigh the filled bottle and calculate the weight of solution to the nearest 0.1 g.

9.3.3 Retain a separate reaction container of the initial solute solution after filling each set of containers to determine the initial solute concentration. If the work is completed quickly and carefully, solute losses from the filling are negligible.

9.3.4 Place the filled reaction container from 9.3.2 on a rotating tumbler and rotate continuously at  $29 \pm 2$  r/min for 24 h. Maintain the temperature at  $22 \pm 5^\circ\text{C}$ .

9.3.5 After 24 h of tumbling, allow the solutions in the reaction containers to settle for a minimum of 1 h. If the water in the neck of the bottle is too turbid to sample with a syringe, centrifuge for a minimum of 1 h at 3000 r/min. Analyze

directly from the container by removing the samples through the septum with a syringe.

9.3.6 Analyze the aqueous supernatant for the volatile organic constituents of interest. Consult U.S. EPA Test Methods 8010, 8020, and 8240 for detailed analysis procedures for volatile solutes.<sup>7</sup>

9.3.7 Each geomedia sample is to be subjected to the procedure in three or more replicates of at least two different concentrations. Blanks handled exactly as described above (steps given in 9.3.1-9.3.6), except that silica sand is used in place of the geomedia, are required for each solute solution, or dilution thereof, each time a series of geomedia is analyzed.

10. Calculation

10.1 Calculate the distribution coefficient as follows:

$$K_d = \frac{(A - B)M_s}{(M_m)B} \tag{6}$$

where:

- A = initial concentration of the solute defined as the final concentration in the retained sample (9.3.3) in g/mL,
- B = final concentration of the solute after 24 h in contact with the geomedia in g/mL,
- $M_s$  = mass of solute solution in g,
- $M_m$  = mass of geomedia expressed on an oven-dried basis in g, and
- $K_d$  = distribution coefficient.

11. Report

11.1 Mark the  $K_d$  value clearly as a nonequilibrium 24-h distribution coefficient.

11.2 Report both the initial solute concentration (A in 10.1) and the final solute concentration (B in 10.1).

11.3 Report the final solute concentration for each blank. If a blank differs from the concentration of the retained solution by more than 10 %, repeat the procedure.

11.4 Report the mass of geomedia ( $M_m$  in 10.1), mass of solution ( $M_s$  in 10.1), and room temperature at which the extraction was conducted.

11.5 Note and report negative  $K_d$  values when and if they occur. Substantial negative  $K_d$  values may occur if the geomedia contains the test solute prior to application of the method. If this is suspected, test the geomedia with pure water extractions (see 6.2).

11.6 Where feasible, determine and report the pH of the solute solution and sorbent-solute mixture.

12. Precision and Bias <sup>8</sup>

12.1 Four laboratories participated in a collaborative study of this test method. Each laboratory was provided with two soil samples: (1) the A horizon of a Catlin silt loam to be used as the test geomedia and (2) a sample of Ottawa sand to be used

<sup>7</sup> "Test Methods for Evaluating Solid Waste," EPA/SW-846, Washington, DC, November 1986.

<sup>8</sup> Supporting data have been filed at ASTM Headquarters/Customer Service and may be obtained by requesting: RR:PCN:33-000004-56.

**TABLE 1 Volatile Organics Distribution Coefficients ( $K_d$ ); Four Laboratory Tests<sup>A</sup>**

Laboratory	Compound	High Concentration	Low Concentration
	1,1,1-Trichloroethane		
1		0.21	0.21
1		0.59	0.98
2		0.50	0.48
3		0.77	...
3		0.75	...
3		0.73	...
4		0.52	1.28
4		1.00	1.02
4		1.00	1.07
		$0.67 \pm 0.25$	$0.84 \pm 0.41$
	Toluene		
1		0.55	1.11
1		0.65	1.09
2		0.75	0.93
3		1.57	1.73
3		1.41	1.88
3		1.50	2.09
4		1.09	1.17
4		1.19	1.07
4		1.36	1.12
		$1.12 \pm 0.38$	$1.35 \pm 0.43$
	Ethyl Benzene		
1		1.29	1.57
1		0.67	1.53
2		1.69	1.56
3		3.15	3.80
3		4.00	3.95
3		4.10	3.88
4		1.69	2.65
4		2.60	2.34
4		2.29	2.36
		$2.39 \pm 1.19$	$2.62 \pm 1.02$

<sup>A</sup> The uncertainty shown is one standard deviation

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as a blank. Sorption coefficients were measured for 1,1,1-trichloroethane, toluene, and ethyl benzene. Each laboratory prepared two test solutions containing all three chemicals at approximately one-half and one-fourth of their published solubilities. The results indicating the precision of the test method are given in Table 1. Since no acceptable reference material exists that is suitable for determining the bias of this procedure for measuring sorption coefficients, no statement on bias is being made.

12.2 Two laboratories performed the experiments in triplicate, one conducted it in duplicate, and one performed only a single measurement of each sorption coefficient at each concentration. The standard deviation for a single operator, based on the two laboratories that performed the experiment in triplicate, averaged 13.9 % for all compounds at both concentrations.

12.3 The average standard deviation for all measurements from all laboratories was 38 %. This test method should be more precise when applied to less volatile, more strongly adsorbing compounds. It should also be noted that Table 1 displays a case of nonlinear sorption (see 4.2.1).