Designation: C1733 – 17

Standard Test Method for
Distribution Coefficients of Inorganic Species by the Batch Method[1]

INTRODUCTION

As an aqueous fluid migrates through geologic media or contacts an engineered material, certain reactions occur that are dependent upon the chemistry of the fluid itself and upon the chemistry and geochemistry of other fluids and solid phases with which it comes in contact. These chemical and geochemical interactions affect the relative rates at which chemical species in the migrating fluid (such as ions) travel with respect to the advancing front of water. Processes of potential importance in retarding the transport of chemical species in the migrating fluid (movement of species at velocities less than the ground-water velocity) include ion exchange, adsorption, complex formation, precipitation (or coprecipitation, for example Ba^{2+} and Ra^{2+} co-precipitating as a sulfate), redox reactions, and precipitate filtration. Partitioning may be caused by processes that include adsorption, precipitation, and coprecipitation that cannot be described easily by equations and, furthermore, these solute removal mechanisms may not instantaneously respond to changes in prevailing conditions and may not be entirely reversible.

An empirical ratio known as the *distribution coefficient (K_d)* is defined as:

$$K_d = \frac{\textit{Mass of solute on the solid phase per unit mass of solid phase}}{\textit{Mass of solute in solution per unit volume of the liquid phase}}$$

and has been used to quantify the collective effects of these processes for the purpose of modeling (usually, but not solely, applied to ionic species). K_d is used to assess the degree to which a chemical species will be removed from solution (permanently or temporarily) as the fluid migrates through the geologic medium or contacts a solid material; that is, K_d is used to calculate the retardation factor that quantifies how rapidly an ion can move relative to the rate of ground-water movement.

This test method is for the laboratory determination of the K_d, which may be used by qualified experts for estimating the retardation of contaminants for given underground geochemical conditions based on a knowledge and understanding of important site-specific factors. It is beyond the scope of this test method to define the expert qualifications required, or to justify the application of laboratory data for modeling or predictive purposes. Rather, this test method is considered as simply a measurement technique for determining the degree of partitioning between liquid and solid, under a certain set of conditions, for the species of interest.

Justification for the K_d concept is generally acknowledged to be based on expediency in modeling-averaging the effects of attenuation reactions. In reference to partitioning in soils, equilibrium is assumed although it is known that this may not be a valid assumption in many cases.

The K_d for a specific chemical species may be defined as the ratio of the mass sorbed per unit of solid phase to the mass remaining per unit of solution, as expressed in the above equation. The usual units of K_d are mL/g (obtained by dividing g solute/g solid by g solute/mL solution, using concentrations obtained in accordance with this test method).

Major difficulties exist in the interpretation, application, and meaning of laboratory-determined K_d values relative to a real system of aqueous fluid migrating through geologic media (1)[2]. The K_d concept is based on an equilibrium condition for given reactions, which may not be attained in the natural situation because of the time-dependence or kinetics of specific reactions involved. Also, migrating solutions always follow the more permeable paths of least resistance, such as joints and fractures, and larger sediment grain zones. This tends to allow less time for reactions to occur and less sediment surface exposure to the migrating solution, and may preclude the attainment of local chemical equilibrium.

Sorption phenomena also can be strongly dependent upon the concentration of the species of interest in solution. Therefore, experiments performed using only one concentration of a particular chemical species may not be representative of actual in situ conditions or of other conditions of primary interest. Similarly, experimental techniques should consider all ionic species anticipated to be present in a migrating solution, in order to address competing ion and ion complexation effects, which may

strongly influence the sorption of a particular species.

Sorption can be strongly controlled, by pH. Therefore, in situ pH, especially of groundwater, should be considered in determinations of K_d. Values of pH must be determined, preferably in the field when materials are sampled and must be carefully determined in the laboratory procedure. Other in situ conditions (for example, ionic strength, anoxic conditions, or temperature) could likewise have considerable effect on the K_d and need to be considered for each situation.

Site-specific materials must be used in the measurement of K_d. This is because the determined K_d values are dependent upon rock and soil properties such as the mineralogy (surface charge and energy), particle size distribution (surface area), and biological conditions (for example, bacterial growth and organic matter). Special precautions may be necessary to assure that the site-specific materials are not significantly changed prior to laboratory testing. This may require refrigeration or freezing of both soil and water samples. Chemical means of preservation (such as addition of acid to groundwater) will cause changes in sample chemistry and must be avoided.

The choice of fluid composition for the test may be difficult for certain contaminant transport studies. In field situations, the contaminant solution moves from the source through the porous medium. As it moves, it displaces the original ground water, with some mixing caused by dispersion. If the contaminant of interest has a K_d of any significant magnitude, the front of the zone containing this contaminant will be considerably retarded. This means that the granular medium encountered by the contaminant has had many pore volumes of the contaminant source water pass through it. The exchange sites achieve a different population status and this new population status can control the partitioning that occurs when the retarded contaminant reaches the point of interest. It is recommended that ground water representative of the test zone (but containing added tracers) be used as contact liquid in this test, or a carefully prepared simulated (site-specific) groundwater; concentrations of potential contaminants of interest used in the contact liquid should be judiciously chosen. For studies of interactions with intrusion waters, the site-specific ground water may be substituted by liquids of other compositions.

The K_d for a given chemical species generally assumes a different value when conditions are altered. Clearly, a very thorough understanding of the site-specific conditions that determine their values is required if one is to confidently apply the K_d concept to migration evaluation and prediction.

The most convenient method of determining K_d is probably the batch method (this test method), in which concentrations of the chemical species in solid and liquid phases, which are in contact with one another, are measured. Other methods include dynamic column flow-through methods using continuous input of tracer or pulsed input. In the field, a dual tracer test can be conducted using a conservative (non-sorbing) tracer and one that does sorb; from the difference in travel times of the two tracers, K_d can be calculated.

In summary, the distribution coefficient, K_d, is affected by many variables, some of which may not be adequately controlled or measured by the batch method determination. The application of experimentally determined K_d values for predictive purposes must be done judiciously by qualified experts with a knowledge and understanding of the important site-specific factors. However, when properly combined with knowledge of the behavior of chemical species under varying physicochemical conditions of the solid surface (or geomedia) and the migrating fluid, K_d can be used for assessing the rate of migration of chemical species through a saturated geomedium.

---

1. Scope

1.1 This test method covers the determination of distribution coefficients, K_d, of chemical species to quantify uptake onto solid materials by a batch sorption technique. It is a laboratory method primarily intended to assess sorption of dissolved ionic species subject to migration through pores and interstices of site specific geomedia, or other solid material. It may also be applied to other materials such as manufactured adsorption media and construction materials. Application of the results to long-term field behavior is not addressed in this method. K_d for radionuclides in selected geomedia or other solid materials are commonly determined for the purpose of assessing potential migratory behavior of contaminants in the subsurface of contaminated sites and out of a waste form and in the surface of waste disposal facilities. This test method is also applicable to studies for parametric studies of the variables and mechanisms which contribute to the measured K_d.

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

1.3 *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, health and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.4 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the*

Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.

2. Referenced Documents

2.1 *ASTM Standards:*[3]

D422 Test Method for Particle-Size Analysis of Soils (Withdrawn 2016)[4]

D1293 Test Methods for pH of Water

D2216 Test Methods for Laboratory Determination of Water (Moisture) Content of Soil and Rock by Mass

D2217 Practice for Wet Preparation of Soil Samples for Particle-Size Analysis and Determination of Soil Constants

D2488 Practice for Description and Identification of Soils (Visual-Manual Procedures)

D3370 Practices for Sampling Water from Closed Conduits

D4319 Test Method for Distribution Ratios by the Short-Term Batch Method (Withdrawn 2007)[4]

D4448 Guide for Sampling Ground-Water Monitoring Wells

D5730 Guide for Site Characterization for Environmental Purposes With Emphasis on Soil, Rock, the Vadose Zone and Groundwater (Withdrawn 2013)[4]

3. Terminology

3.1 *Definitions of Terms Specific to This Standard:*

3.1.1 *distribution coefficient, K_d, n*—the concentration of a species sorbed on a solid material, divided by its concentration in solution in contact with the solid material, under constant concentration conditions, as follows:

$$K_d = \frac{Mass\ of\ solute\ on\ the\ solid\ phase\ per\ unit\ mass\ of\ solid\ phase}{Mass\ of\ solute\ in\ solution\ per\ unit\ volume\ of\ the\ liquid\ phase}$$

(1)

3.1.1.1 *Discussion*—By constant concentration conditions, it is meant that the K_d values obtained for samples exposed to the contact liquid for two different time periods (at least one day apart), other conditions remaining constant, shall differ by not more than the expected precision for this test method. It is convenient to express K_d in units of mL (or cm^3) of solution per gram of solid material.

3.1.2 *species, n*—specific form of an element defined as to isotopic composition, electronic or oxidation state, complex or molecular structure, or combinations thereof (**2**).

3.1.3 *tracer, n*—an identifiable substance, such as a dye or radioactive isotope, that can be followed through the course of a mechanical, chemical, or biological process.

4. Significance and Use

4.1 The distribution coefficient, K_d, is an experimentally determined ratio quantifying the distribution of a chemical species between a given fluid and solid material sample under certain conditions, including the attainment of constant aqueous concentrations of the species of interest. The K_d concept is used in mass transport modeling, for example, to assess the degree to which the movement of a species will be delayed by interactions with the local geomedium as the solution migrates through the geosphere under a given set of underground geochemical conditions (pH, temperature, ionic strength, etc.). The retardation factor (R_f) is the ratio of the velocity of the groundwater divided by the velocity of the contaminant, which can be expressed as:

$$R_f = 1 + (\rho_b/\eta_e)\ K_d$$

(2)

where:

ρ_b = bulk density of the porous medium (mass/length^3) and

η_e = effective porosity of the medium (unitless) expressed as a decimal.

4.2 Because of the sensitivity of K_d to site specific conditions and materials, the use of literature derived K_d values is strongly discouraged. For applications other than transport modeling, batch K_d measurements also may be used, for example, for parametric studies of the effects of changing chemical conditions and of mechanisms related to the interactions of fluids with solid material.

5. Apparatus

5.1 *Laboratory Ware,* (plastic bottles, centrifuge tubes, open dishes, pipettes) cleaned in a manner consistent with the analyses to be performed and the required precision. Where plateout may have significant effect on the measurement, certain porous plastics should be avoided and the use of fluorinated ethylene propylene (FEP) or tetrafluoroethylene (TFE) containers is recommended.

5.2 *Centrifuge,* capable of attaining 1400 g, or filtering apparatus.

5.3 *Filters,* filtration apparatus, including syringe filters, capable of removing particles of ≥0.45 micrometers. Filter media should be selected to not sorb species of interest under the experiment conditions. Sorption has been observed on filter media composed of certain materials (**3**).

5.4 *Laboratory Shaker/Rotator,* ultrasonic cleaner (optional).

5.5 *Environmental Monitoring Instruments,* a pH meter, conductance meter, and thermometer.

5.6 *Analytical Balance* capable of measuring to 0.01 g.

5.7 *Appropriate Equipment,* necessary to replicate in situ conditions within the laboratory apparatus.

5.8 *Analytical Instrumentation,* appropriate for determination of the concentration of major constituents (cations and anions) and of the species of interest (for which K_d is being determined) in the contact solutions (and, optionally, in the solid material samples).

6. Sampling

6.1 The solid samples of soil, rock, sediment, or other materials shall be considered to be representative of the stratum

---