

**Hazen Research, Inc.**

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October 28, 2002

Mr. Gareth E. Van De Steeg
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Re: Determination of Distribution Coefficients (K_d) for Uranium in Soils
Hazen Project 9936

Dear Mr. Van De Steeg:

On September 20, 2002, Hazen Research, Inc. received two soil samples and one water sample from Cimarron Corporation (Cimarron). All samples were contained in 1-L, high-density polyethylene bottles packed in blue ice. The water was reported to contain about 5,000 pCi/L of uranium. Upon receipt, the samples were assigned Hazen numbers for internal identification and future reference as shown in Table 1. After logging in, samples were stored in a refrigerator at about 4°C. You requested that Hazen determine a distribution ratio (R_d) for uranium between each soil and the water following the procedure given in ASTM D 4319-93, Standard Test Method for Distribution Ratios by the Short-Term Batch Method (enclosed). The distribution ratios will be used by Cimarron to determine distribution coefficients (K_d) for the soils.

Table 1. Sample Identification

HRI	Cimarron Identification
50622-01	02W02-FA1563 Soil (2 Containers)
50622-02	02W08-FA1564 Soil (2 Containers)
50622-03	02W04-1606 Water (8 Containers)

The first soil (02W02-FA1563) appeared to be high in clay content, while the second soil (02W02-FA1564) appeared to be very sandy. Both soil samples had standing water on their surfaces when received. By mutual agreement, the soil samples were dried at about 60°C, resulting in a moisture loss of 25.3% for the clay sample and 15.8% for the sandy sample. The dried cakes were broken up, and test samples of about 25 g each were removed by riffle splitting. An additional sample from each dried soil was further dried at 105°C to obtain residual moisture,

which was 3.0% for the clay soil and 0.5% for the sandy soil. Overall moisture contents of the as-received soils were determined to be 27.5% for the clay soil and 16.2% for the sandy soil. At the request of Mr. Jim Crawford, the sandy soil was also wet screened at 200 mesh (75 μm) and was found to contain 28.3% minus 200-mesh material.

A head sample of the water was taken on September 25 for uranium analysis. Three head samples were taken on September 26: one corresponding for water used for the clay soil (Head), one for the sandy soil (Head A, 9/26), and one for the blanks (Head B, 9/26). The three samples taken on September 26 were analyzed for uranium, pH, specific conductivity, and Eh. Results are shown in Table 2. The uranium values were used in the distribution ratio calculations. The R_d tests were performed in triplicate for each sampling period (3, 6, 9, and 15 days), and a blank (B1, B2, B3, and B4) was included for each period.

Table 2. Compositions of Head and Blank Samples

Sample	U mg/L	pH	Sp. Cond. $\mu\text{mho/cm}$	Eh mV
Head, 9/25	3.9	--	--	--
Head, 9/26	4.1	8.40	1,310	550
Head A, 9/26	3.3	8.53	1,290	530
Head B, 9/26	3.5	8.69	1,310	530
Average	3.6	8.54	1,303	537
Blanks				
B1 (3 Days)	3.0	8.53	1,260	490
B2 (6 Days)	3.5	8.69	1,320	470
B3 (9 Days)	3.0	8.63	1,300	430
B4 (15 Days)	2.7	8.61	1,259	410

These results show that very little plating of uranium from solution onto container walls occurred during the course of the 15-day test. The uranium in the blanks, 2.7 to 3.5 mg/L, is only slightly less than the average in the heads, 3.6 mg/L.

About 25 g of soil (weighed to the nearest 0.1 g) for each sample were placed into a 250-mL, flat-bottomed, polypropylene centrifuge tube. Contaminated water was added in the amount of exactly four times the weight of soil, or about 100 mL, and the tube was sealed with a cap. The samples were gently shaken on a shaking table for 3 hr on Day 1 and 3 hr on Day 2 for each sampling period, then allowed to settle until sampling time. At sampling time, the appropriate

samples were centrifuged for about 20 min, which resulted in very clear solutions. The clear solutions were decanted and placed into high-density, polyethylene bottles with screw caps. The solution samples for uranium analysis were acidified to less than 2 pH with nitric acid; the remaining solutions were left as they were for analysis. Solids were not analyzed, but were retained for possible future characterization.

Tables 3 and 4 show the analytical results and the calculated R_d values for the 02W02-FA1563 (clay) and 02W08-FA1564 (sandy) soils, respectively. The R_d values were calculated as follows:

1. The uranium concentration in the sampled solution was subtracted from the concentration in the starting solution. As an example and referring to Tables 2 and 3 and the average uranium analyses therein, the starting solution contained 3.6 mg/L, and the first sample contained 2.4 mg/L U, resulting in a difference of 1.2 mg/L U. This value is considered the amount of uranium absorbed by solids and possibly precipitated or plated on the container walls.
2. The uranium content of the blank was subtracted from the starting solution composition, which was considered to be loss due to plating only. Following the example above, the blank from the first sampling period contained 3.0 mg/L U. Subtracting this value from the starting solution content of 3.6 mg/L results in 0.6 mg/L U. The difference between Points 1 and 2 (0.6 mg/L) is considered to be the amount of uranium absorbed by solids.
3. The uranium content absorbed by solids was then converted to a uranium value in mg/kg. For example, 0.6 mg/L times 0.1 L (the amount of contaminated water added to 25 g of solids) is 0.06 mg of U that was absorbed onto 0.025 kg of solids, resulting in a calculated solids analysis of 2.4 mg/kg. A value for R_d was calculated by dividing the calculated solids content (mg/kg) by the solution content (mg/L), as shown in the following formula:

$$R_d = \frac{(\text{Mass of Solute in the Solid Phase per Unit Mass of Solid Phase})}{(\text{Mass of Solute in Solution per Unit Volume of the Liquid Phase})}$$

or

$$\frac{2.4 \text{ mg/kg (Calculated Uranium in the Solids)}}{2.4 \text{ mg/L (Solution Content)}} = 1.0 \text{ mL/g}$$

4. The next iterated step is calculated by using the solution analysis from the previous sampling period as the starting solution and using the analysis of the blank for that particular sampling period. As an example, for the 6-day period, the average starting

Table 3. Analytical Results and Distribution Ratios for Sample 02W02-FA1563 (Clay)

Sample	U mg/L	pH	Sp. Cond. μ mho/cm	Eh mV	U, R_d^1
3-day					
1,1	2.5	8.61	1,400	520	0.7
1,2	2.4	8.67	1,350	480	1.0
1,3	2.3	8.70	1,300	460	1.2
Average	2.4	8.66	1,350	487	1.0
6-day					
1,4	2.6	8.56	1,350	530	1.3
1,5	2.0	8.63	1,340	510	3.2
1,6	1.9	8.60	1,390	490	3.6
Average	2.1	8.60	1,360	510	2.7
9-day					
1,7	1.9	8.63	1,330	420	2.4
1,8	1.9	8.68	1,360	450	2.4
1,9	2.1	8.77	1,390	450	1.6
Average	2.0	8.69	1,360	440	2.2
15-day					
1,10	1.7	8.82	1,365	410	2.5
1,11	1.3	8.91	1,365	440	4.7
1,12	1.9	8.77	1,312	460	1.9
Average	1.6	8.83	1,347	437	3.0

¹ R_d determined by dividing the calculated solids analysis (mg/kg) by the solution analysis (mg/L).

Table 4. Analytical Results and Distribution Ratios for Sample 02W08-FA1564 (Sand)

Sample	U mg/L	pH	Sp. Cond. $\mu\text{mho/cm}$	Eh mV	U, R_d ¹
3-day					
2,1	2.5	8.67	1,360	470	0.8
2,2	2.3	8.81	1,340	480	1.2
2,3	2.5	8.73	1,370	480	0.8
Average	2.4	8.74	1,357	477	1.0
6-day					
2,4	1.8	8.51	1,370	500	3.8
2,5	2.2	8.61	1,390	520	2.3
2,6	2.3	8.61	1,330	480	2.1
Average	2.1	8.58	1,363	500	2.7
9-day					
2,7	2.0	8.81	1,340	440	2.1
2,8	1.9	8.81	1,340	440	2.4
2,9	1.9	8.81	1,380	430	2.4
Average	1.9	8.81	1,353	437	2.3
15-day					
2,10	1.4	8.98	1,291	440	3.5
2,11	1.4	8.82	1,280	400	4.0
2,12	2.0	8.65	1,312	400	1.6
Average	1.6	8.82	1,294	413	3.0

¹ R_d determined by dividing the calculated solids analysis (mg/kg) by the solution analysis (mg/L).

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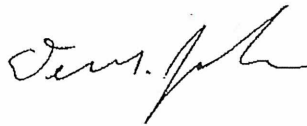
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solution analysis, as shown in Table 3, is 2.4 mg/L U, and the blank analysis (B2) is 3.5 mg/L U. The blank analysis appears to be anomalously high, which resulted in an anomalously higher R_d of 2.7 mL/g.

As shown in Tables 3 and 4, the R_d values for both the soil samples are similar, with averages ranging from 1.0 to 3.0. The results show that some absorption appears to occur during the first 3-day period, after which the absorption slows or stops. Plating also appears to have slowed or stopped after the first 3-day period.

We hope the data presented here prove beneficial to you. Should you have any questions concerning the test work or results, please call either Rick Kenney or me. We look forward to hearing from you again soon.

Yours very truly,



Dennis M. Johnson
Consultant

DMJ:wlk

Enclosure

xc: Jerry Downey, Hazen
Rick Kenney, Hazen



Standard Test Method for Distribution Ratios by the Short-Term Batch Method¹

This standard is issued under the fixed designation D 4319; 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.

INTRODUCTION

As an aqueous fluid migrates through geologic media, 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 geochemical interactions determine 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 flow 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^{++} and Ra^{++} co-precipitating as the sulfate), oxidation-reduction reactions, and precipitate filtration. This test method applies to situations in which only sorptive processes (adsorption and ion exchange) are operable for the species of interest, however, and is restricted to granular porous media.

It is difficult to derive generalized equations to depict ion exchange-adsorption reactions in the geological environment. Instead, a parameter known as the *distribution coefficient* (K_d) has been used to quantify certain of these sorption reactions for the purpose of modeling (usually, but not solely, applied to ionic species). The distribution coefficient is used to assess the degree to which a chemical species will be removed from solution as the fluid migrates through the geologic media; that is, the distribution coefficient provides an indication of how rapidly an ion can move relative to the rate of ground-water movement under the geochemical conditions tested.

This test method is for the laboratory determination of the *distribution ratio* (R_d), which may be used by qualified experts for estimating the value of the distribution coefficient 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 distribution ratio or degree of partitioning between liquid and solid, under a certain set of laboratory conditions, for the species of interest.

Justification for the distribution coefficient 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. Equilibrium implies that (1) a reaction can be described by an equation and the free energy change of the reaction, within a specific system, is zero, and (2) any change in the equilibrium conditions (T , P , concentration, etc.) will result in immediate reaction toward equilibrium (the concept is based upon reversibility of reactions). Measured partitioning factors may include adsorption, coprecipitation, and filtration processes that cannot be described easily by equations and, furthermore, these solute removal mechanisms may not instantaneously respond to changes in prevailing conditions. Validity of the distribution coefficient concept for a given set of geochemical conditions should not be assumed initially, but rather should be determined for each situation.

This is a short-term test and the attainment of equilibrium in this laboratory test is not presumed, although this may be so for certain systems (for example, strictly interlayer ion exchange reactions of clays). Consistent with general usage, the result of this test could be referred to as "distribution coefficient" or as "distribution ratio;" in the strictest sense, however, the term "distribution ratio" is preferable in that the attainment of equilibrium is not implied.

The distribution ratio (R_d) for a specific chemical species may be defined as the ratio of the mass sorbed onto a solid phase to the mass remaining in solution, which can be expressed as:

$$R_d = \frac{(\text{mass of solute on the solid phase per unit mass of solid phase})}{(\text{mass of solute in solution per unit volume of the liquid phase})} \quad (1)$$

The usual units of R_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 distribution ratio values relative to a real system of aqueous fluid migrating through geologic media.² Typically, only reactions between migrating solutions and solid phases are quantified. In general, geochemical reactions that can result from interaction of the migrating fluid with another aqueous phase of a differing chemistry have not been adequately considered (interactions with other liquids can profoundly change the solution chemistry). Additionally, as noted above, the distribution coefficient or K_d concept implies an equilibrium condition for given reactions, which may not realistically apply 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. Thus, the distribution coefficient or K_d concept is only directly applicable to problems involving contaminant migration in granular porous material.

Sorption phenomena are also strongly dependent upon the thermodynamic activity of the species of interest in solution (chemical potential). Therefore, experiments performed using only one activity or concentration of a particular chemical species may not be representative of actual in situ conditions or of other conditions of primary interest. Similarly, unless experimental techniques consider all ionic species anticipated to be present in a migrating solution, adequate attention is not directed to competing ion and ion complexation effects, which may strongly influence the R_d for a particular species.

Many "sorption" ion complexation effects are strongly influenced, if not controlled, by conditions of pH and Eh. Therefore, in situ conditions of pH and redox potential should be considered in determinations of R_d . To the extent possible, these pH and Eh conditions should be determined for field locations and must be approximated (for transition elements) in the laboratory procedure.

Other in situ conditions (for example, ionic strength, anoxic conditions, or temperature) could likewise have considerable effect on the R_d and need to be considered for each situation. Additionally, site-specific materials must be used in the measurement of R_d . This is because the determined R_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.

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 an R_d of any significant magnitude, the front of the zone containing this containment will be considerably retarded. This means that the porous 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 be used as contact liquid in this test; 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 distribution ratio for a given chemical species generally assumes a different value when any of the above conditions are altered. Clearly, a very thorough understanding of distribution coefficients and the site-specific conditions that determine their values is required if one is to confidently apply the K_d concept (and the measured R_d values) to migration evaluation and prediction.

The adoption of a standard method for determining distribution ratios, R_d , especially applicable for ionic species, is important in that it will provide a common basis for comparison of experimental results (particularly for near-similar conditions).

The most convenient method of determining R_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 with time. Other methods include the dynamic test or column flow-through method using (1) continuous input and (2) pulsed input, the in situ dual tracer test, and the thin-layer chromatography (TLC) test.

In summary, this distribution ratio, R_d , is affected by many variables, all of which may not be adequately controlled or measured by the batch method determination. The application of experimentally determined R_d values for predictive purposes (assuming a functional relationship such as $R_d = K_d$) 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 geomedia and the migrating fluid, distribution coefficients (ratios) 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 ratios of chemical species for site-specific geological media by a batch sorption technique. It is a short-term laboratory method primarily intended for ionic species subject to migration in granular porous material, and the application of the results to long-term field behavior is not known. Distribution ratios for radionuclides in selected geomedia are commonly determined for the purpose of assessing potential migratory behavior at waste repositories. This test method is also applicable to studies of intrusion waters and for parametric studies of the effects of variables and of mechanisms which determine the measured distribution ratios.

1.2 The values stated in acceptable metric units are to be regarded as the standard.

1.3 *This standard does not purport to address all of the safety problems, 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 422 Test Method for Particle-Size Analysis of Soils¹
- D 2217 Practice for Wet Preparation of Soil Samples for Particle-Size Analysis and Determination of Soil Constants¹
- D 2488 Practice for Description and Identification of Soils (Visual-Manual Procedure)¹
- D 3370 Practices for Sampling Water²

3. Terminology

3.1 Definitions of Terms Specific to This Standard:

3.1.1 *distribution coefficient, K_d* —is identically defined as R_d for equilibrium conditions and for ion exchange-adsorption reactions only. To apply R_d values to field situations, an assumption such that $R_d = K_d$ is necessary. The validity of such

an assumption can only be determined by informed experts making a judgment (albeit uncertain) based on a detailed study of the specific site.

3.1.2 *distribution ratio, R_d* —the ratio of the concentration of the species sorbed on the soil or other geomedia, divided by its concentration in solution under steady-state conditions, as follows:

$$R_d = \frac{(\text{mass of solute on the solid phase per unit mass of solid phase})}{(\text{mass of solute in solution per unit volume of the liquid phase})} \quad (2)$$

by steady-state conditions it is meant that the R_d values obtained for three different samples exposed to the contact liquid for periods ranging from 3 to at least 14 days, other conditions remaining constant, shall differ by not more than the expected precision for this test method.

The dimensions of the expression for R_d reduce to cubic length per mass (L^3/M). It is convenient to express R_d in units of millilitres (or cubic centimetres) of solution per gram of geomedia.

3.1.3 *species*—a distinct chemical entity (such as an ion) in which the constituent atoms are in specified oxidation states.

4. Significance and Use

4.1 The distribution ratio, R_d , is an experimentally determined parameter representing the distribution of a chemical species between a given fluid and a geomedium sample under certain conditions, including the attainment of a steady state. Based on a knowledge and understanding of the important site-specific factors, R_d values may be used by qualified experts for estimating the value of the distribution coefficient, K_d , for a given set of underground geochemical conditions. The K_d concept is used in mass transport modeling, for example, to assess the degree to which an ionic species will be removed from solution as the solution migrates through the geosphere. For applications other than transport modeling, batch R_d measurements also may be used, for example, for parametric studies of the effects of variables and of mechanisms related to the interactions of fluids with geomedia.

5. Apparatus

5.1 *Laboratory Ware* (plastic bottles, centrifuge tubes, open dishes, pipets, graduates), 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 FEP TFE-fluorocarbon containers is recommended.

¹ This test method is under the jurisdiction of ASTM Committee D18 on Soil and Rock and is the direct responsibility of Subcommittee D18.14 on Geotechnics of Waste Management.

Current edition approved April 15, 1993. Published August 1993.

² Coles, D. G., and Ramspeck, L. D., "Migration of Ruthenium-106 in a Nevada Test Site Aquifer: Discrepancy Between Field and Laboratory Results," *Science*, Vol. 215, pp. 1235-1237, March 5, 1982.

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

⁴ *Annual Book of ASTM Standards*, Vol. 11.01.



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

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

5.4 *Environmental Monitoring Instruments*, a pH meter, electrometer and electrodes for Eh determination, conductance apparatus, and thermometer.

5.5 *Analytical Balance*.

5.6 *Appropriate Equipment*, necessary to maintain in situ conditions within the laboratory.

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

6. Sampling

6.1 The samples of soil, rock, or sediment shall be considered to be representative of the stratum from which it was obtained by an appropriately accepted or standard procedure and based on expert judgment.

6.2 The sample shall be carefully identified as to origin in accordance with Practice D 2488.

6.3 A geological description shall be given of the core material used for the distribution ratio measurement, including particle-size analysis (Method D 422) for unconsolidated material, depth of sample, and boring location.

6.4 Sampling of representative ground water in the test zone for use as the contact liquid in this test method shall be accomplished in accordance with Practices D 3370, using sampling devices that will not change the quality or environmental conditions of the waters to be tested. Recommended methods include the use of Kemmerer samplers or inert gas pressure lifts (provided this does not alter the ground-water sample by stripping out carbon dioxide and raising the pH, for example) or submersible diaphragm-type pumps. Proper precautions should be taken to preserve the integrity of in situ conditions of the sampled water, and in particular to protect against oxidation-reduction, exposure to light for extended periods, and temperature variation.

NOTE 1—It is recognized that sampling is likely to be a major problem. Materials (or fractures) that the contaminants pass through are likely to be the most difficult part of the geologic section to sample. In addition, proper sampling entails determining the path of ground-water flow so that the critical materials can be sampled. This determination is seldom accomplished in sufficient detail in normal geologic site exploration programs, and, if it is attempted in some cases, the exploration program may become unacceptably expensive. Specific guidelines are beyond the scope of this test method, however, it is recommended that geologic and water sampling procedures be carefully considered by the personnel involved in the site examination.

7. Procedure

7.1 This test method can be applied directly to consolidated core material samples or to disaggregated portions of the core material samples. For the applications intended for this test method, however, disaggregation of the samples is the recommended procedure. Disaggregate the sampled soil and friable core materials (this may be done by ultrasonic method although should be noted that the effect of ultrasonics on the

microstructure of geological material may lead to higher sorption values in certain cases). If a sufficiently large-sized sample is available, separate 200-g portions through a "non-bias" riffle splitter. Crush competent sedimentary rock materials to a desired particle size or equivalent soil texture anticipated to result from natural weathering processes (this is because surface area is controlled by sample particle size).

NOTE 2—A significant source of error may be introduced by disaggregating the sample in a batch test in that (a) disaggregation can mask a preferred flow path (either horizontal or vertical), (b) disaggregation can destroy the effect of preferred flow paths caused by fractures or perhaps thin sand stringers, and (c) disaggregation will tend to increase the available surface area of the geologic materials. It is for the purpose of achieving uniformity of application, however, that disaggregation is recommended for this test method. It should be realized by persons applying results from this method that inclusion of the disaggregating operations may for these reasons tend to maximize the values of the distribution coefficients (ratios) obtained from this test method.

7.2 In some cases, it may be desirable to remove organic material from the geomedium (soil specimen) for comparative purposes. If this is so indicated, remove the organic material from the composite sample mixtures for selected samples by treatment with concentrated hydrogen peroxide (30 % H_2O_2), using the procedure given in "Soil Chemical Analysis."⁵ In such a case, make duplicate runs using samples both with and without pretreatment to remove organics. It should be noted, however, that treatment with concentrated hydrogen peroxide could cause other changes in the geomedium, for example, dissolution of hydrous metal oxides that may be important adsorbents.

7.3 Using standard analytical procedures, characterize the geologic specimen (without pretreatment and, if so done, with the pretreatment to eliminate organics) as considered appropriate. The analyses may include percent chemical composition of anhydrous oxides (for example, SiO_2 , FeO , MnO , CaO , Na_2O , etc.), hydrous oxides (for example, Fe , Mn , and Al hydrous oxides), and minerals that are present, and carbonate content, surface area (m^2/g), and cation and anion exchange capacity (at specified pHs). Similarly, characterize the contact liquid obtained from the test zone as appropriate for interpreting the results. Chemical analysis of the liquid should include macro constituents (for example, Na^+ , Ca^{++} , K^+ , Mg^{++} , Cl^- , HCO_3^-/CO_3^{--} , SiO_2 , etc.) and redox-active and hydrolyzable species such as Fe and Mn ions. Likewise, determine the pH and Eh of the contact liquid, as well as the concentration (if present) of the chemical species of interest. Specific instructions for the Eh determination are not part of this test method, however, use of a referenced technique is advised (such as a platinum versus standard calomel electrode measurement). If the species of interest may exist in the contact liquid in a variety of valence or chemical states (for example, with studies of actinides), a method of determining speciation should be applied.

7.4 Pass each of the soil and rock (core sediments) fractions again through a "nonbias" riffle splitter and place four 5- to 25-g portions (record weight to nearest 0.1 g) in centrifuge tubes or bottles.

⁵ Jackson, M., *Soil Chemical Analysis*, Prentice Hall, Englewood Cliffs, NJ, 1954.

NOTE 3—Unless it is decided that the samples may be allowed to dry by exposure to the open air, record a moisture weight (for comparative purposes, a moisture content determination should be done with a separate sample). Some soils never dry in nature, and characteristics may be greatly altered when dried. This is especially true for originally anoxic sediments. If the samples are not to be allowed to dry before testing, follow Practice D 2217 (Procedure B) for maintaining a moisture content equal to or greater than the natural moisture content. In all cases, the contact liquid used in this test is the sampled ground water from the site test zone.

7.5 If a radiotracer or spiked stable tracer determination of the distribution ratio is desired, pretreat the composite samples with exact solution (contact liquid) used in the determination but without the tracer present. This solution will be either the site-specific ground water or a selected intrusion water. Wash the composite soil and rock samples four times with the pretreatment solution. For the first three washes, stir the mixtures of soil and rock and pretreatment solution several times over a 15-min period, allow to settle, centrifuge at 1000 g or more for 5 min, and decant off the wash. Apply the fourth wash for at least 24 h with occasional stirring, and again separate the wash from the composite sample by centrifugation and decantation as before.

7.6 It may be advisable to pre-equilibrate the treatment solution (contact liquid) with the geomedium prior to the start of this test method. Proceed as in 7.5, using the fourth wash after centrifugation and decantation as the treatment solution. Unless otherwise noted, add 20 to 100 mL (exact value should be equal to four times the weight in g of the geomedium) to each 100 to 250 mL centrifuge tube or bottle, and thoroughly mix the contents by stirring action. Prior to contact, the treatment solution should contain the species of interest at a known concentration prepared by the addition of chemically pure reagents to the site-specific ground-water sample. (The species of interest may be at trace concentration; if it is a radioactive or stable tracer added to the treatment solution, the elemental concentration as well as the isotopic concentration must be known.) If tracers are used, first equilibrate the tracer with the ground-water (or intrusion-water) sample by allowing to stand overnight and then filter using a $\leq 0.45 \mu\text{m}$ pore size membrane filter. Following this step, analyze the contact solution and add to the soil and rock composite samples as indicated above. Measure the pH of the soil/rock-solution system; if the pH has changed or if other than the natural pH is desired, adjust by addition of *N* NaOH solution or HCl, or by an appropriate buffer. The in situ Eh should be maintained, if necessary, under an inert atmosphere.

NOTE 4—Experiments have shown that R_d will vary depending on the solution-to-geomedium ratio used in the test. If other ratios are indicated (which would more closely approximate the normal field situation), duplicate runs should be made, however, the ratio prescribed here should also be run as the reference case. Because R_d varies with the solution/medium ratio, it is strongly recommended that this measurement include determination of the isotherm by making several runs with different ratios of solution-to-geomedium than specified above.

NOTE 5—Some analytical techniques may require larger volumes of sample fluid. Increased volume can be obtained by compositing samples or by scale-up using larger centrifuge tubes.

7.7 Determine the specific conductance of each solution and report in units of micromhos per centimetre at 20°C.

7.8 Run each set of samples at least in triplicate to demon-

strate that steady state is attained in this short-term test. Stir the contents of each contact tube, then gently shake all of the soil/rock solution mixtures on a laboratory shaker/rotator for a minimum of 6 h for every 3-day portion of the contact period. The contact periods shall be for a minimum of 3 days, and the longest shall extend to 14 days or longer. The contact periods shall differ by at least a 3-day period. During the latter 1 or 2 days of the contact period, allow all mixtures to stand and settle. If the variation of R_d with exposure time for these three or more contact periods is greater than the precision expected for this experiment, then the determination should be repeated for longer times until such a consistency is obtained. This is taken to be an indication that steady state has been established. In cases where the steady-state situation is not achieved, the extension of R_d values to the prediction of migratory behavior becomes of dubious value and requires clear reference to the inexactness of the application.

7.9 Measure and report the pH and Eh of all mixtures (in many investigations, pH and Eh will not vary greatly, so it might not be necessary to measure them on all samples).

7.10 Centrifuge each mixture for 20 min at a minimum setting of 1400 g. Controlled temperature centrifugation may be advised, particularly in the case of experiments run below ambient temperature. Carefully separate the phases. For the supernatant, the concentration of the species of interest can be directly determined using the appropriate standard analytical method.

7.11 If filtering is necessary or if desired for comparative purposes, use polycarbonate member filters (0.002 to 0.02 μm pore size), or the equivalent. Pretreat the filter disc by passing through it approximately 50 mL of 1.0 *N* HCl, followed by 50 mL of distilled water, by gravity flow or suction to near dryness. Check the possibility of sorption of tracers onto the filter by a standard "double filter" technique using the original contact solution.

7.12 Filter the supernate from each soil/rock-solution mixture by gravity flow or suction to near dryness. Determine the concentration and speciation (chemical state), if it is variable, of the species of interest in this solution by the appropriate standard analytical method. Make a blank determination using the equivalent procedure outlined here (7.6 through 7.12, except do not add the soil/rock sample) with treatment solution only. The use of tracers involves particular attention to corrections for blanks and potential plateout of the tracer on container walls, filters, and other surfaces as well as other losses. For example, it should be ascertained that loss of tracer to the blank vial walls is the same as for the walls of the sample vial, etc.

7.13 If necessary or if desired for comparative purposes or for a mass-balance determination, determine the concentration of the species of interest for each filtered solid residue. In this case, note the necessity of removing the residual solution from the solid phase, or correcting for it, particularly for solids with low R_d values. If this determination is made, a correction is required for the amount (if any) of the species of interest to be found naturally present in the soil/rock sample. Provided a satisfactory analysis is accomplished for the species concentration in the soil/rock residue, calculate R_d by dividing this value (g solute per g solid residue) by the final concentration in

the contact solution (g solute per mL solution), assuming the tracer did not remove tracer from the solution. An alternative method is to compute R_d as shown on the Example Calculation Sheet (Table 1).

TABLE 1 Example Calculation Sheet

The distribution ratio is given by:

$$R_d = \frac{(F_m)(V_s)}{(F_s)(W_m)}$$

where:

- R_d = distribution ratio, mL/g,
 F_s = fraction of total activity in solution, which equals the total concentration in solution, assuming the activity coefficients of a given ion were the same before and after steady state was attained in contact of the solution with the soil/rock materials (that is, the ionic strength is unchanged). Making this assumption, F_s is found by dividing the concentration of the ion after the solution has come to "equilibrium" (reaches steady state) with the soil/rock fraction by the concentration (of same units) of the ion before the solution was allowed to come to equilibrium with the soil fraction,
 F_m = fraction of activity sorbed onto the mineral or solid residue (correcting for the natural content of the species of interest initially present), or, making the same assumption as to activity coefficients,

$$F_m = 1 - F_s$$

V_s = volume of solution "equilibrated" with W_m mL, and

W_m = weight of mineral or solid residue, g.

In the case of a radioactive species of interest, where the radioactivities of the solution and solid residue are determined, the distribution coefficient is given by:

$$R_d = \frac{(A_m)(V_s)}{(A_s)(W_m)}$$

where:

- = activity of the mineral or solid residue, mCi, and
 = activity of the solution "equilibrated" with W_m mCi.

8. Precision and Bias

8.1 The accuracy of this test is operator-dependent and is a function of the care exercised in performing the steps and systematic repetition of the procedures used. Subcommittee D18.14 is seeking pertinent data from users of this test method on precision and bias.

8.2 *Within Laboratory Precision*—Precision results (repeatability) for distribution ratios by short-term batch method for Cd, Hg, Se, and Sr have been reported by Del Debbie and Thomas⁶, and are found to be in the range of 1 % to 7 %. Fuhrman⁷, et al. reported R_d values for Cs with a precision (repeatability) of 4 %.

8.3 *Multi-Laboratory Precision*—Precision of distribution ratio by short-term batch method between different laboratories has not been determined yet. Subcommittee D18.14 is seeking pertinent data from users of this test method on reproducibility conditions.

8.4 *Bias*—Since there is no accepted reference material suitable for determining the bias for the procedure in Test Method D 4319, Distribution Ratios by the Short-Term Batch Method, bias has not been determined.

9. Keywords

9.1 adsorption; attenuation; batch sorption; distribution ratio; geochemical; ground water; ion exchange capacity; liquid migration; modeling; short-term batch

⁶ Del Debbie, J.A., and Thomas, T.R., *Hazardous Properties of Radionuclides and Hazardous Chemical Species in Soils at the Idaho Processing Plant*, WICNO-1068, Westinghouse Idaho Nuclear Company, Inc., Idaho Falls, ID, October, 1989.

⁷ Fuhrman, M., Pietrzak, R., and Colombo, P., "Distribution Ratios of Cs-137 in Sediments from the Black Sea," *Draft Report, Department of Nuclear Energy*, Brookhaven National Laboratory, Upton, NY, December, 1990.



Tabulated Results for Distribution Ratio Determination of Sample Number _____:

Contact liquid: Site-Specific Ground Water _____ Other (intrusion) Water _____ initial pH _____ initial Eh _____; method of determining Eh _____
final pH _____ final Eh _____ temperature _____°C specific conductance _____ $\mu\text{mhos/cm}$ solid-to-liquid ratio _____ g/mL
contact time _____ da equilibrating atmosphere _____ air _____ other (specify) _____ contact solution filtered after centrifugation? _____ yes
_____ no disaggregated? _____ yes _____ no particle size _____ mm H_2O_2 treatment to remove organics? _____ yes
_____ no calculated dry weight of solid _____ g volume of contact liquid _____ mL species of interest _____ method of analyzing for species
of interest _____

(use separate sheet if necessary)

Site description, sampling methodology and core material description, analysis of core materials and of site-specific ground water or other contact liquid:

ATTACH SHEET

Species (Ion) of Interest	Initial Conc. in Solid (units)	Initial Conc. in Solution (units)	$F_s F_m R_{\text{eff}}$	(mL/g)

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